

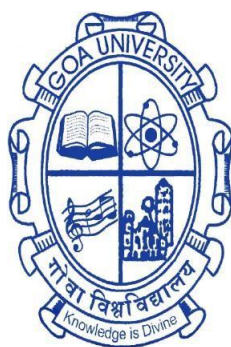
SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF COORDINATION POLYMERS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE DEGREE
OF

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN THE SCHOOL OF CHEMICAL SCIENCES
GOA UNIVERSITY



By

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OCT 2025

DECLARATION

I, Ms. Nikita Nonu Harmalkar, hereby declare that this thesis represents the work which has been carried out by me and that it has not been submitted, either in part or in full, to any other University or Institution for the award of any research degree.

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CERTIFICATE

I hereby certify that the above Declaration of the candidate, the name of the candidate, is true, and the work was carried out under my supervision

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ACKNOWLEDGEMENT

I am deeply grateful to my supervisor, **Prof. Sunder N. Dhuri**, School of Chemical Sciences (SCS), Goa University, for giving me the opportunity to conduct research under his guidance. His constant support and timely suggestions enhanced my research skills and helped me publish quality papers. I sincerely acknowledge **Prof. B. R. Srinivasan** for his valuable guidance in crystallographic studies. I also extend my heartfelt gratitude to my subject experts, **Prof. V. M. S. Verenkar** (Dean) and **Dr. Sandesh T. Bugde**, for their supervision and insightful comments throughout my Ph.D. tenure. Their encouragement motivated me to strive for excellence in my research. I am grateful to the School of Chemical Sciences for providing the necessary facilities and laboratory resources, which contributed to the completion of my research. I also thank the Honorable Vice Chancellor and the Registrar of Goa University for their support.

I acknowledge the help extended by former and present teaching faculty of SCS whenever needed. I thank Prof. S. G. Tilve, Prof. R. N. Shirsat, Prof. V. S. Nadkarni, Dr. Digamber G. Porob (Vice-Dean Academic), Dr. Rupesh E. Patre (Vice-Dean Research), Dr. Bidhan A. Shinkre, Vishnu R. Chari, Dr. Delicia A. Barretto, Dr. Kanchanmala B. Deshpande, Dr. Kiran T. Dhavaskar, Dr. Hari K. Kadam, Dr. Deepika Karmalkar, Dr. Savita A. Kundaikar, Dr. Rohan K. Kunkalekar, Siddhali V. Girkar, Dr. Rupesh A. Kunkalkar, Dr. Vinod K. Mandrekar, Dr. Pranay P. Morajkar, Dr. Anjani P. Nagvenkar, Dr. Diptesh G. Naik, Dr. Shrikant R. Naik, Dr. Kedar U. Narvekar, Dr. Prachi S. Torney, Dr. Prajesh S. Volvoikar, and Dr. Amrita N. Kharangate. I am thankful to Dr. Sandeep Dey and Dr. Prem Lama (Former DST faculty) for their help. I am equally thankful to the past and present non-teaching staff of SCS for their constant cooperation whenever needed.

I am grateful to all collaborators who worked with our research group and offered help when needed. I thank Prof. Beena Vernekar (Khandola College), Dr. Venkatesha Hathwar (SPAS, Goa University) and Dr. Jhuma Sannigrahi (School of Physical Sciences, IIT Goa) for their support. I thank Dr. K. Sundaravel (Asst. Professor, Bharathiar University) for TG-DTA analysis, BITS Pilani, Goa (CIF) for powder diffraction analysis and USIC, Goa University for the SEM Facility. We are grateful to Dr. Sanket Gaonkar and Dr. Delicia A. Barretto for their contributions to antimicrobial studies. I thank the dissertation students for creating a pleasant and motivating research environment.

I am indebted to the Goa University Research Studentship (GU/Acad-PG/Ph.D./Res.Stud/2020-21/881,27/01/21) for financial assistance for two years, and to the Savitribai Jyotirao Phule single girl child fellowship (UGCES-22-OB-GOA-F-SJSGC-6907) for support from April 2022 until the thesis submission. I thank the Librarian and supporting staff for providing the learning resources. I also extend my gratitude to the administrative staff (AR-PG) of Goa University for their timely assistance with all formalities regarding the DRC and fellowship claim.

My heartfelt gratitude goes to my labmates: Dr. Dattaparsad Narulkar, Dr. Sarvesh Harmalkar, Dr. Luann R. D'Souza, Dinesh Harmalkar and Dr. Jeffrey Viegas, Milagrina D'Souza, Disha Gauns, V. Swapna, and Medha Gaude. Their support and companionship have been unwavering. I am grateful to our interns, Kritika Gaur and Jocelyn N. Kaute, for their assistance and contributions during their time in the lab. A special mention goes to Dr. Luann and Dr. Mangala for their invaluable support during the early days of my Ph.D. I cherish moments we shared, especially when everything felt new and overwhelming. I also thank all the SCS research students (past and present) for their support and for creating wonderful memories along the way. Special mention to my seniors Dr. Pratik, Dr. Prajyoti, Dr. Seneca, Dr. Pooja, Dr. Neha, Dr. Sudesh, Dr. Megha, Dr. Rita, Dr. Rahul, Dr. Chandan, Dr. Abhijeet, Dr. Ketan, Dr. Shashank, Dr. Dinesh, Dr. Kerba, Dr. Geeta, Dr. Ratan, Dr. Lima and Anuja Vipul Ghare for sharing their experiences and guidance. I also thank, Pooja, Vilas, Apeksha, Sonali, Raneet, Pritesh, Leo, Vignesh, Pooja, Namrata, Shefali, Sanjali, Sonam, Pranav, Samantha, Sarvesha, Samidha, Crecia, Ria, Deepti and Asmita for all the help.

I owe my deepest thanks to ***Siddhi Salgaonkar, Dr. Shravni Korgaonkar, Nitesh Venji,*** and ***Pavan Patil***. Their friendship made this journey happier and more meaningful. I am profoundly grateful to my husband, ***Sahil N. Govekar***, whose love, patience, and constant encouragement made this journey possible. I am fortunate to have families who believed in me and supported me in every way possible. Last but not least, I thank the ***Universe*** for blessing me with more than I could have ever asked for. I remain forever thankful.

... ***Nikita N. Harmalkar***

DEDICATED TO

My Grandparents

LATE PRABHAVATHI JAGANNATH MANDREKAR

And

LATE PREMA SHRIPAD HARMALKAR

“The quiet architects of my life”



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LIST OF ABBREVIATIONS

MOF	: Metal-Organic Framework	CN	: Cyanide
CP	: Coordination polymers	C₆H₆	: Benzene
PCP	: Porous coordination polymers	NH₃	: Ammonia
SBU	: Secondary building units	Bz	: Benzoate
SE	: slow evaporation method	MeBz	: <i>o</i> -methylbenzoate
HT	: hydrothermal method	MeOBz	: <i>o</i> -methoxybenzoate
ST	: Solvothermal method	OHBz	: <i>o</i> -hydroxybenzoate
IR	: Infrared	NO₂Bz	: <i>o</i> -nitrobenzoate
EPR	: Electron Paramagnetic Resonance	ClBz	: <i>o</i> -chlorobenzoate
NMR	: Nuclear Magnetic Resonance	SMeBz	: <i>o</i> -(methylthio)benzoate
XPS	: X-Ray Photoelectron spectroscopy	NH₂Bz	: <i>o</i> -aminobenzoate
SCXRD	: Single crystal X-ray diffraction	fum	: Fumarate
CIF	: Crystallographic information file	suc	: Succinate
PXRD	: Powder X-ray diffraction	ida	: Iminodiacetate
TGA	: Thermogravimetric analysis	pyz	: Pyrazine
DTG	: Derivative Thermogravimetry	terpy	: 2,2':6',2''-terpyridine
DTA	: Differential Thermal Analysis	KBr	: Potassium bromide
SEM	: Scanning Electron Microscopy	BaSO₄	: Barium sulphate
UV-Vis	: Ultraviolet visible	3,5-DTBC	: 3,5-di- <i>tert</i> -butyl catechol
SQUID	: Superconducting Quantum Interference Device	3,5-DTBQ	: 3,5-di- <i>tert</i> -butyl quinone
TLC	: Thin Layer Chromatography	DCM	: Dichloromethane
HS	: Hirshfeld surface	EtOAc	: Ethyl acetate
ATCC	: American Type Culture Collection	PET	: Petroleum ether
DMSO	: Dimethyl sulfoxide	NiO	: Nickel oxide
THF	: Tetrahydrofuran	DMF	: Dimethylformamide

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- Figure 31.** The ^1H -NMR spectrum of condensed product (**2a**) (400 MHz, CDCl_3 , IIT-Goa); (a) δ 7.82 (2H, d, ArH), (b) δ 7.72 (1H, s, =CH), (c) δ 7.35 (2H, d, ArH) and (d) δ 2.46 (3H, s, CH_3).
- Figure 32.** ^1H -NMR data for (**3a**) (400 MHz, CDCl_3 , IIT-Goa); (a) δ 8.4 (2H, d, ArH), (b) δ 8.09 (2H, d, ArH), (c) δ 7.89 (1H, s, =CH)
- Figure 33.** ^1H -NMR data for (**4a**) (400 MHz, CDCl_3 , IIT-Goa); (a) δ 7.92 (2H, d, ArH), (b) δ 7.66 (1H, s, =CH), (c) δ 7.03 (2H, d, ArH) and (d) δ 3.92 (3H, s, OCH_3).

Figure 34. ^1H -NMR spectrum for **(5a)** (400 MHz, DMSO- d_6 , IIT-Goa)

CHAPTER 5: SECTION I

- Figure 1.** Overlaid infrared spectra of the compound obtained *via* the slow evaporation method (**12-SE**), the Hydrothermal method (**12-HT**), and fumaric acid.
- Figure 2.** Overlaid infrared spectra of compound **13** and succinic acid.
- Figure 3.** The IR spectra of compounds **14** and **15** overlaid with the IR spectrum of iminodiacetic acid.
- Figure 4.** **a)** Solid state UV-Vis spectra of compound **12** (**Left**), with an inset showing an enlarged region from 500 to 750 nm. **b)** Solid state UV-Vis of **13** (**Right**).
- Figure 5.** The TG-DTA plot of compound **12**.
- Figure 6.** The overlaid TG curves of compounds **12** (blue) and **13** (black).
- Figure 7.** The TG-DTA plot of compound **14**.
- Figure 8.** The TG-DTA plot of compound **15**.
- Figure 9.** The crystal structure of $[\text{Ni}(\text{H}_2\text{O})_2(\text{pyz})(\text{fum})]$ (**12**). Thermal ellipsoids drawn at a 30 % probability level for all the non-hydrogen atoms. The hydrogen atoms are depicted as spheres of arbitrary radii. (*Symmetry code* (i) $-x+1, -y+1, -z+1$ (ii) $-x+2, -y+1, -z+1$ (iii) $-x+1, -y, -z+1$)
- Figure 10.** A portion of a 2D grid viewed along the *c* direction displaying rectangular channels.
- Figure 11.** Inter-chain hydrogen bonding between the uncoordinated oxygen atom of fumarate and the coordinated water molecules observed along *a* direction.
- Figure 12.** The crystal structure of $[\text{Ni}(\text{H}_2\text{O})_2(\text{pyz})(\text{suc})]$ (**13**). Thermal ellipsoids drawn at a 30 % probability level for all the non-hydrogen atoms. The hydrogen atoms are depicted as spheres of arbitrary radii. (*Symmetry code* (i) $-x+3/2, -y+1/2, -z+1$)
- Figure 13.** The twisting of the succinate ligand over the C-C bond.
- Figure 14.** 2D packing along the *bc* plane, displaying wavy sheets
- Figure 15.** 2D packing along the *ac* plane, displaying 2D wavy sheets connected with pyrazine linkers to form an interpenetrating 3D structure. The atoms of the pyrazine linkers are marked in yellow for a clear view.

- Figure 16.** The crystal structure of $[\text{Ni}(\text{H}_2\text{O})_2(\text{pyz})(\text{ida})]$ (**14**). Thermal ellipsoids drawn at a 30 % probability level for all the non-hydrogen atoms. The hydrogen atoms are depicted as spheres of arbitrary radii. *Symmetry code (i) $x, 0.5-y, z$*
- Figure 17.** The crystal structure of $[\text{Ni}(\text{pyz})(\text{ida})]\cdot 2\text{H}_2\text{O}$ (**15**). Thermal ellipsoids drawn at a 30 % probability level for all the non-hydrogen atoms. The hydrogen atoms are depicted as spheres of arbitrary radii. (*Symmetry code (i) $-x+1/2, y+1/2, -z+3/2$ (ii) $-x, y+2, -z+1$ (iii) $-x+1, y+2, -z+1$.*) The intramolecular hydrogen bonds are shown in green dotted lines.
- Figure 18.** Schematic representation of the coordination modes of ida^{2-} anion with metal ions.
- Figure 19.** One-dimensional supramolecular chain formed via $\text{O1W-H4}\cdots\text{O1}$ running along the *c*-axis. (*Symmetry code $x, -y+1/2, z-1$*)
- Figure 20.** Molecular packing diagram of compound **14** viewed along the *ab* plane.
- Figure 21.** **a)** one-dimensional zig-zag chain structure, formed due to the bridging chelating mode of the ida ligand. **b)** The 2D rectangular sheet formed by interconnecting the 1D ida chains with alternating pyrazine linkers, adopting the bridging coordination mode.
- Figure 22.** Molecular packing diagram of compound **15** viewed along the *ac* plane.
- Figure 23.** Hydrogen bonding situation in compound **15**, between the lattice aqua molecules and the coordinated oxygen atoms, and the coordinated N atom of the ida linker.
- Figure 24.** Experimental PXRD pattern of **12-15** overlaid with simulated pattern
- Figure 25.** Comparison between the experimental powder patterns of the composite material, derived from the CPs after heating at 400 °C. The red star denotes the Nickel phase.
- Figure 26.** The SEM images (**a**), (**c**), (**e**) of the compounds **12**, **13** and **15**, respectively on (**Left**) and their corresponding Ni/NiO composite (**b**), (**d**) and (**f**) (**Right**)

CHAPTER 5: SECTION II

- Figure 1.** Experimental (Blue) and calculated (red) powder patterns of **16**.
- Figure 2.** X-band ESR spectrum of a polycrystalline sample of **16**
- Figure 3.** Infrared spectrum of $[(\text{VO}(\text{terpy})_4(\text{MoO}_4)_2(\text{Mo}_8\text{O}_{26}))\cdot 2\text{H}_2\text{O}]$

- Figure 4.** Raman spectrum of compound **16**
- Figure 5.** The TG-DTA curve of compound **16** in air. Heating rate (5°C/min)
- Figure 6.** The asymmetric unit of **16** showing six-fold coordination around V1 and V2. Displacement ellipsoids are drawn at 30% probability level for all the non-hydrogen atoms. Intramolecular H-bonding is shown as broken lines. For clarity symmetry generated atoms are labelled in blue. (*Symmetry code: (i) -x, -y+1, -z+1 (ii) -x+1, -y+2, -z+2*)
- Figure 7.** The Mo-O(terminal) and Mo-O(bridging) ligands in the centrosymmetric γ -(Mo₈O₂₆)⁴⁻ unit in **16**. Mo-O_t bonds in pink are for terminal O atoms; Mo-O bonds in green are μ_2 -bridging O atoms viz. O9, O10 and O17; Mo-O bonds in blue are μ_3 -bridging O atoms namely O13 and O14; Mo-O bonds of μ_4 -bridging O11 are in black
- Figure 8.** The μ_2 -bridging bidentate binding mode of the centrosymmetric (Mo₈O₂₆)⁴⁻ (**Left**) and the μ_3 -bridging tridentate binding mode of (MoO₄)²⁻ (**Right**) in **16**. (*Symmetry code i) -x, -y+1, -z+1*)
- Figure 9.** The {V₄Mo₂O₁₂}⁴⁺ cationic unit is made up of an eight-membered heterometallic {Mo₂V₂O₄} ring with protruding oxidovanadium handles. The terpy ligands around V1 and V2 are not shown. (*Symmetry code i) -x, -y+1, -z+1*).
- Figure 10.** A portion of an infinite chain showing alternating (Mo₈O₂₆)⁴⁻ anions and {V₄Mo₂O₁₂}⁴⁺ cations. The tridentate terpy ligands on the unique V atoms are not shown.
- Figure 11.** The same arrangement is observed after the inclusion of the terpy ligands. The {VO₃N₃} octahedra and (MoO₄)²⁻ tetrahedra are shown in polyhedral format.

SYNOPSIS

SYNTHESIS, CHARACTERIZATION AND APPLICATION OF COORDINATION POLYMERS

The thesis “Synthesis, characterization, and application of coordination polymers” involves synthesizing transition metal-based coordination compounds using a mixed ligand approach. Several instrumental techniques were employed to investigate the structural and chemical properties of the compounds. The current work mainly aims to grow single crystals of the compound study the structural arrangement of the molecules within the crystal with the help of the single-crystal X-ray diffraction technique. Additionally, we evaluated the compounds for their potential applications in catalysis.

The following five chapters make up the structure of the thesis:

Chapter 1	Literature review on mixed ligand coordination compounds and coordination polymers ➤ Section I: <i>Overview of metal cyclam-based mixed ligand compounds</i> ➤ Section II: <i>The O-donor carboxylate ligand and N-donor macrocyclic ligand are employed to prepare metal compounds.</i>
Chapter 2	Materials and synthetic methodology
Chapter 3	Mn(II), Co(III), and Ni(II) cyclam compounds appended with benzoate and its derivatives: Synthesis, characterization, and application
Chapter 4	Structural variation induced by <i>ortho</i> -substituted carboxylate ligands in Zn (II) cyclam compounds and their application in Knoevenagel condensation reaction
Chapter 5	Tailoring coordination compounds with rigid nitrogen donor linkers ➤ Section I: <i>Design of pyrazine-bridged nickel coordination polymers, structural description, and use as precursors for Ni/NiO Composite Material</i> ➤ Section II: <i>Synthesis, structure determination of new oxidovanadium CP containing terpyridine</i>

CHAPTER 1: LITERATURE REVIEW ON MIXED LIGAND COORDINATION COMPOUNDS AND COORDINATION POLYMERS

Introduction:

The ongoing advancements in material science and crystal engineering have considerably promoted the investigation of discrete coordination complexes and extended polymeric structures such as coordination polymers (**CPs**) and Metal-organic frameworks (**MOFs**). These materials continue to attract research interest due to their functional roles in catalysis, magnetism, storage, and biomedical applications [1,2]. For the rational design of such molecular and polymeric materials, judicious choice of metal centers and organic linkers is paramount [3]. In particular, intensive research in mixed ligand molecular compounds and **CPs** identifies the use of rigid N-donor ligands, which aid in providing basic sites, and also promote predictable network geometries and O-donor carboxylates, as they tend to offer flexible coordination modes contributing towards structural diversity. The crystalline nature of materials further enables their characterization by X-ray diffraction techniques, which helps establish the structure-property relationship and thereby allows their application across various domains [4]. Chapter 1 comprises two sections (I) and (II).

Section I: Overview of metal cyclam-based mixed ligand compounds

Historically, researchers have employed macrocyclic polyamine compounds in the synthesis of metal compounds since the early 20th century. Extensive work in the field of coordination compounds comprising cyclam-based ligands has been carried out, owing to the pronounced ability of macrocyclic ligands to accommodate a wide range of metal ions, aiding in stabilizing the unusual oxidation states [5]. Among these macrocyclic ligands, the most commonly used linker is a 14-membered cyclic ligand known as 1,4,8,11-tetraazacyclotetradecane (cyclam). The metal-cyclam compounds exhibit higher thermodynamic stability and kinetic inertness, making them a suitable candidate for use as a synthetic model in bioinorganic chemistry to understand and mimic metalloenzyme functions [6]. In coordination with the metal ion, the cyclam can adopt six configurational isomers influenced by the spatial arrangement of the nitrogen atoms. Among these, five *trans* configurational isomers are *trans*-I (RSRS), *trans*-II (RSRR), *trans*-III (RRSS), *trans*-IV (RSSR), and *trans*-V (RRRR), and one folded structure, *cis* isomer [5,7]. Understanding these configurational preferences is essential for designing compounds with the desired structure and functional properties. Hence, in recent years, researchers have been working on exploiting novel mixed ligand metal-cyclam cores with

auxiliary linkers to fine-tune the coordination environment and functional properties, opening new pathways for developing multifunctional compounds, with a greater tendency for structural variation [8-10].

Carboxylate linkers are often employed as auxiliary linkers to study the interaction with the metal cyclam core. Studies on metal cyclam compounds have indicated that the carboxylates can exert a strong influence over the configurational selectivity [11]. In this context, the present study aims to explore the synthesis and characterization of novel metal-cyclam-based compounds incorporating monobasic carboxylate linkers as auxiliary ligands, emphasizing understanding the configuration preferences and variation in the crystal lattices. Additionally, the study aims to evaluate their catalytic and biological applications. **Figure 1** illustrates the linkers employed in the present study.

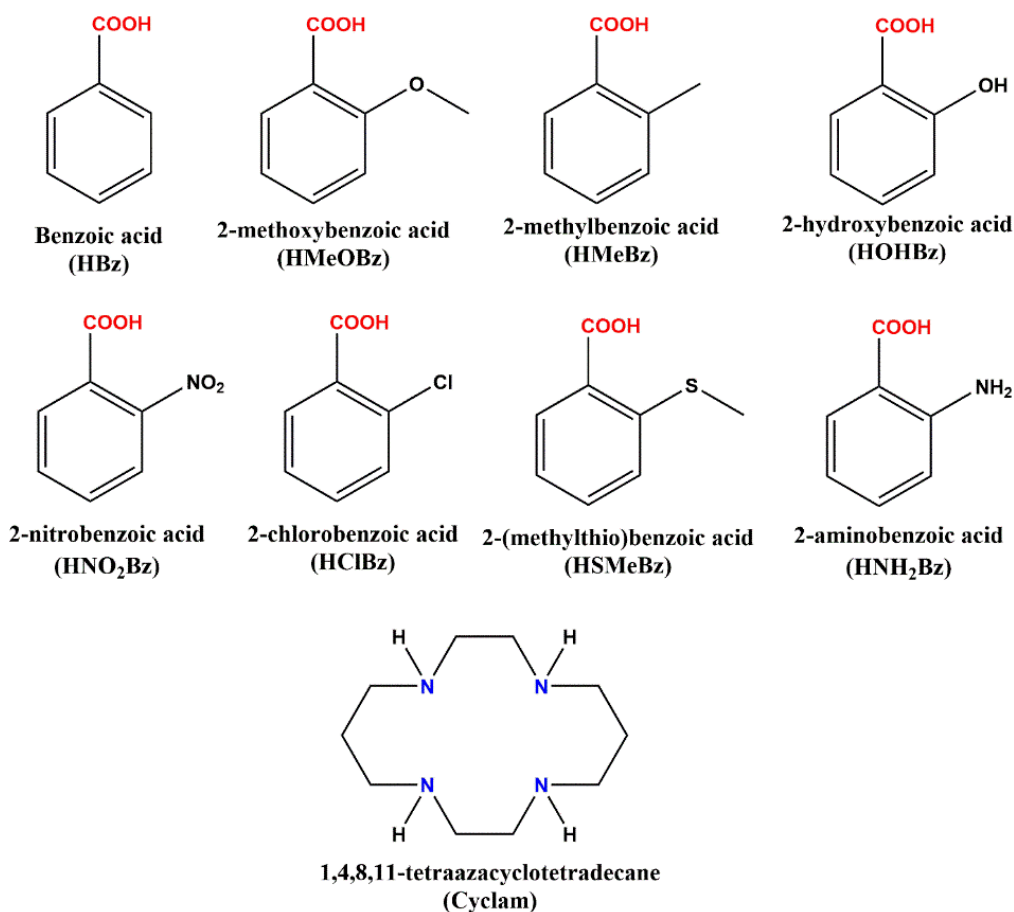


Figure 1. Benzoate and its derivatives with ortho substituents as the O-donors and cyclam as the N-donor ligand.

Section II: General overview of coordination polymers employing mixed ligand and mixed metal synthetic strategy.

In crystal engineering, the crystalline solids are designed with targeted structures by choosing suitable molecules or building units as the raw materials. One such class of crystalline solids includes the polymeric compounds named coordination polymers (CPs)¹². These materials are an intriguing class of hybrid materials known to exist as infinite crystalline lattices extended from the inorganic components, such as metal ions or metal clusters, and organic linkers via coordination interactions. The hydrogen bonds and other non-covalent interactions stabilize the crystalline lattice^[13-15].

Over the past few years, significant progress has been made in synthesizing various porous coordination polymers (PCPs), also commonly referred to as metal-organic frameworks (MOFs)^[16]. These materials offer various applications, such as storage, exchange, optical properties, and are also utilized in catalysis and magnetic investigations^[17-22]. The CPs, PCPs, and MOFs demonstrate remarkable structural versatility compared to the molecular materials, as the frameworks can be designed and tailored for desired applications^[23,24]. Ultimately, the properties of the polymeric crystalline materials are primarily governed by the nature and type of the organic building blocks and the type of metal ions or clusters used in the synthesis, along with other factors such as pH, solvent, and temperature^[25,26].

A prerequisite for obtaining extended structures is that the linkers must have two or more donor atoms. The carboxylate ligands with a rigid carbon backbone were the choice of many researchers due to their structural rigidity and thermal stability. On the contrary, the flexible O-donor molecules were identified to increase the complexity of the final network, and predicting the final composition was difficult due to the flexible carbon backbone, which enables them to adopt various conformations, leading to distinct crystal lattices. However, this property has been realized to be an advantage, as conformational mobility brings structural diversity. Some compounds with flexible ligands also allow breathing ability and adaptive recognition properties as a function of the guest molecules^[27,28].

Among the flexible ligands, aliphatic multitopic linkers are less explored. In this context, our study includes four carbon-chain aliphatic ligands to prepare CPs. Due to the energetically facile rotation of the central carbon chains during crystallization with the metal ions, various geometries and coordination modes can be generated^[29]. The mixed ligand synthetic strategy is most commonly employed to facilitate self-complementary reactions, such as those

involving pH or solubility of the components. In addition, the stability of the resulting CP is improved by reducing the likelihood that the solvent or counter anions will coordinate with the metal ions. Most common mixed ligand syntheses include the reaction between acid (O-donor) and base (N-donor) molecules^[4,30]. The rigid and flexible oxygen donor linkers utilized in the present study are shown in **Figure 2**.

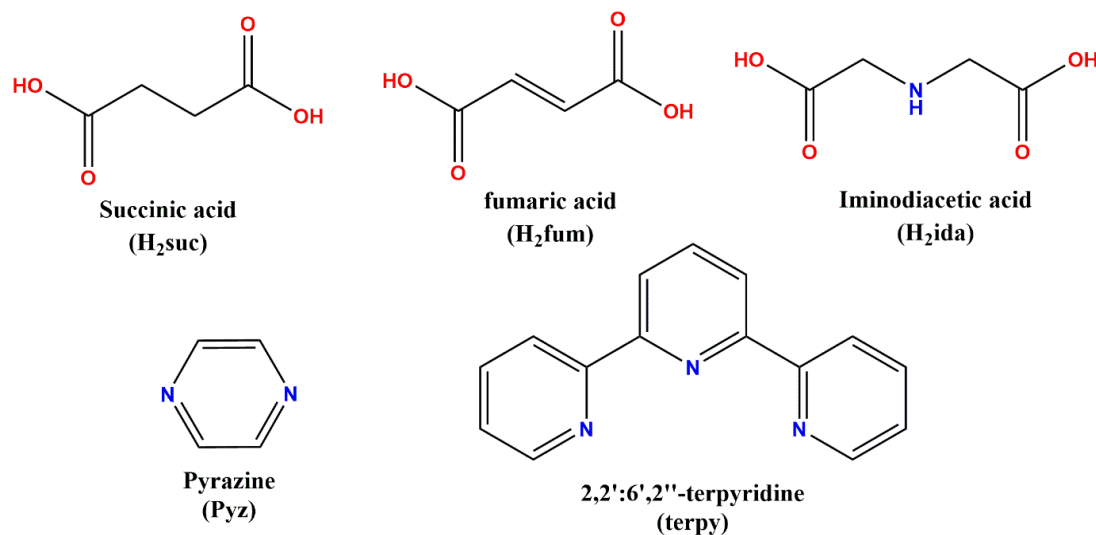


Figure 2. The O-donor and N-donor linkers employed in the preparation of coordination polymers.

Table 1: List of compounds included in this study

Sr. No.	Compound	Synthetic Method	Dimensionality
1	[Co(cyclam)(Bz) ₂](Bz)·H ₂ O	SE	0D
2	[Mn(cyclam)](Bz) ₂ ·2H ₂ O	SE	0D
3	[Ni (H ₂ O) ₂ (cyclam)](MeOBz) ₂ ·2H ₂ O	SE	0D
4	[Zn(H ₂ O) ₂ (cyclam)](Bz) ₂	SE	0D
5	[Zn ₂ (μ-H ₂ O) ₂ (cyclam)(MeBz) ₄]	SE	1D
6	[Zn ₂ (μ-H ₂ O) ₂ (cyclam)(MeOBz) ₄]	SE	1D
7	[Zn(cyclam)(OHBz) ₂]	SE	0D
8	[Zn(cyclam)(NO ₂ Bz) ₂]	SE	0D
9	[Zn(H ₂ O) ₂ (cyclam)](ClBz) ₂	SE	0D
10	[Zn(H ₂ O) ₂ (cyclam)](MeSBz) ₂ ·4H ₂ O	SE	0D
11	[Zn(H ₂ O) ₂ (cyclam)](NH ₂ Bz) ₂	SE	0D
12	[Ni(H ₂ O) ₂ (μ-pyz)(μ-fum)]	HT	1D
13	[Ni(H ₂ O) ₂ (μ-pyz)(μ-suc)]	HT	1D
14	[Ni(H ₂ O) ₂ (pyz)(ida)]	SE	0D
15	[Ni(μ-pyz)(μ-ida)]·2H ₂ O	Hydrothermal	3D
16	[(VO(terpy)) ₄ (MoO ₄) ₂ (Mo ₈ O ₂₆)]·2H ₂ O	Hydrothermal	1D

CHAPTER 2: MATERIALS AND SYNTHETIC METHODS

Chapter 2 highlights the materials and methods employed to prepare the compounds. **Figure 3** shows the detailed synthetic procedures adopted for the synthesis of compounds. Additionally, Chapter 2 presents the instrumentation and technical specifications of the equipment employed to characterize the synthesized compounds.

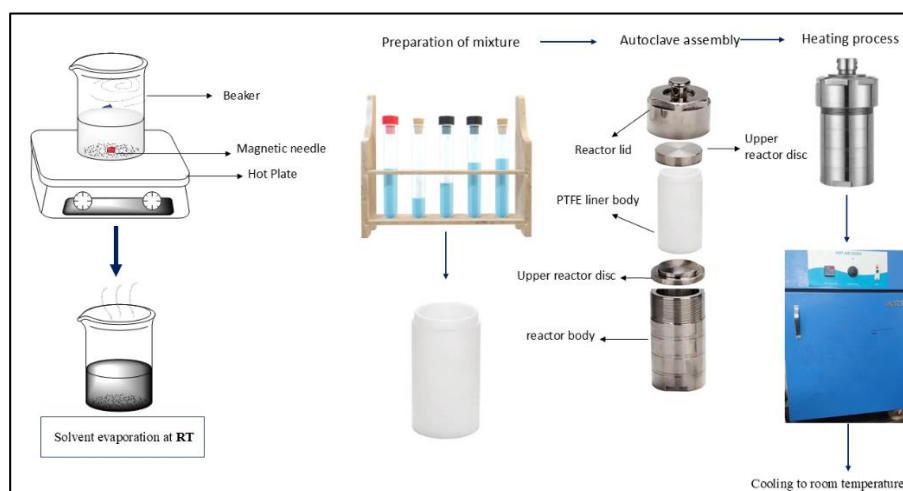
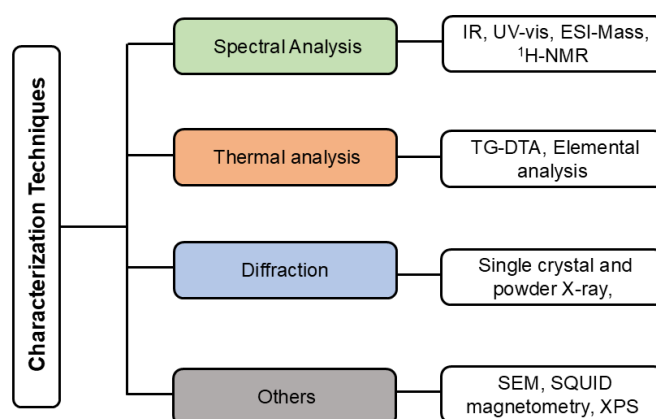


Figure 3. Depiction of the synthesis process for the compounds under room temperature conditions (**Left**) and the hydro/solvothermal setup for synthesizing the compounds at elevated temperatures in a programmable oven (**Right**)

An outline of the techniques employed for characterizing the prepared compounds is shown in **Scheme 1**.

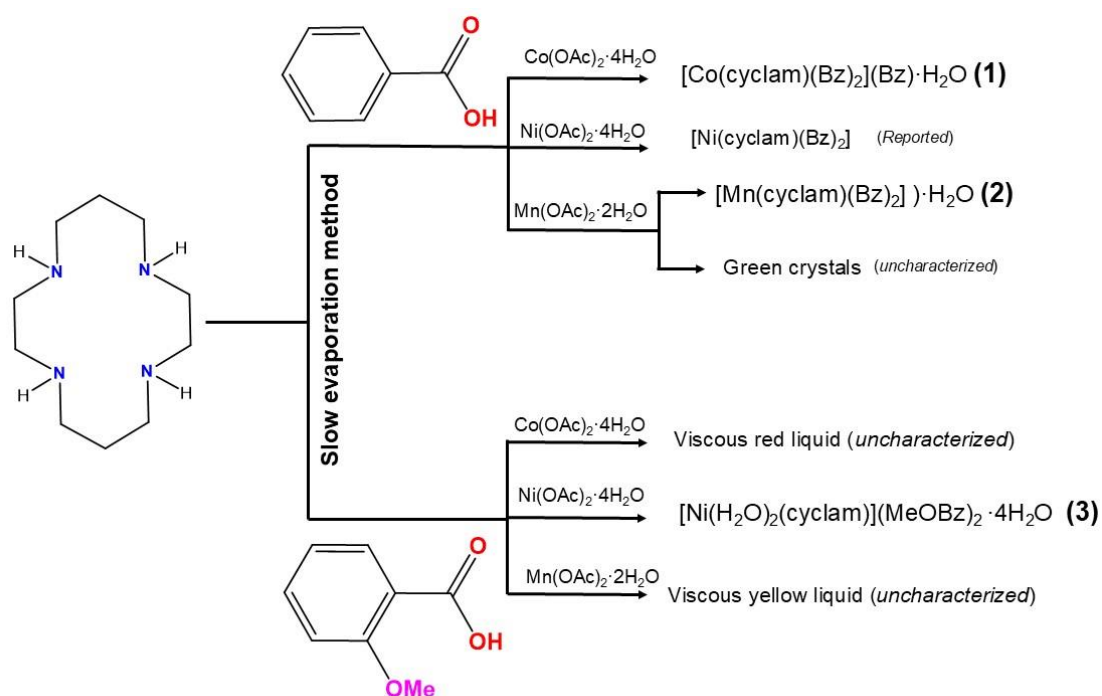


Scheme 1. Depicting the characterization techniques for prepared compounds.

CHAPTER 3: MN(II), CO(III), AND NI(II) CYCLAM COMPOUNDS APPENDED WITH BENZOATE AND ITS DERIVATIVES: SYNTHESIS, STRUCTURAL FEATURES, CATECHOLASE ACTIVITY, AND ANTIMICROBIAL PROPERTIES

Chapter 3 focuses on the study of the interaction between transition metal-based macrocyclic compounds and carboxylate, highlighting the influence of the aromatic carboxylate anion on the configuration of the macrocyclic unit, resulting in variation in the supramolecular arrangements. The mixed ligand compounds in the present study were prepared via the slow evaporation method in an aqueous medium, utilizing transition metal acetates as the source of metal ions, 1,4,8,11-tetraazacyclotetradecane (cyclam) as the nitrogen donor ligand, and monobasic benzoic and *o*-methoxy benzoic acid as the source of *o*-donor ligands (**Scheme 2**). This process resulted in the formation of single crystals $[\text{Co}(\text{cyclam})(\text{Bz})_2](\text{Bz})\cdot\text{H}_2\text{O}$ (**1**), $[\text{Mn}(\text{cyclam})(\text{Bz})_2]\cdot\text{H}_2\text{O}$ (**2**), and $[\text{Ni}(\text{H}_2\text{O})_2(\text{cyclam})](\text{MeOBz})_2$ (**3**).

The crystals of compounds **1** and **3** were isolated from the reaction mixtures and were further characterized by IR, UV-Vis, CHNS, and TG-DTA. The solution state was analyzed by ESI-mass spectrometry, and phase purity was determined by the PXRD technique.



Scheme 2: Preparation of mixed ligand coordination compounds (**1-3**)

The structural analysis of compounds **1-3** revealed that zero-dimensional compounds were obtained as the carboxylate ligands adopted the monodentate coordination mode. Compounds

1 and **3** crystallized in a monoclinic crystal system with a $P2_1/c$ and $P2_1/n$ space group, respectively. The central metal atom coordinated two carboxylates and one cyclam ligand, adopting octahedral geometry. Interestingly, the cobalt atom oxidized during the synthetic process, resulting in the crystal lattice consisting of one uncoordinated benzoate anion and one aqua molecule. The benzoate coordination allowed the cyclam to adopt the *cis-V* configuration. Compound **2** was isolated in small proportions from a mixture of compounds obtained from a single mother liquor and was solely characterized by a single-crystal X-ray diffraction method. The crystal data suggested that the compound crystallized in a triclinic crystal system with $P\bar{1}$ Space group. The coordination environment is similar to compound **1**; however, the manganese did not oxidize and retains its oxidation state. Compound **3** was prepared using an *o*-methoxy benzoate ligand, which does not coordinate with the central Ni (II) ion; instead, it is found in the crystal lattice and aqua molecules involved in extensive hydrogen bonding. The cyclam in this compound adopts the *trans-III* type configuration. The crystal structure of compounds **1-3** is shown in **Figure 4**. Compounds **1-3** were subjected to Hirshfeld surface analysis to assess the non-covalent interactions contributing to the stability of the supramolecular architecture.

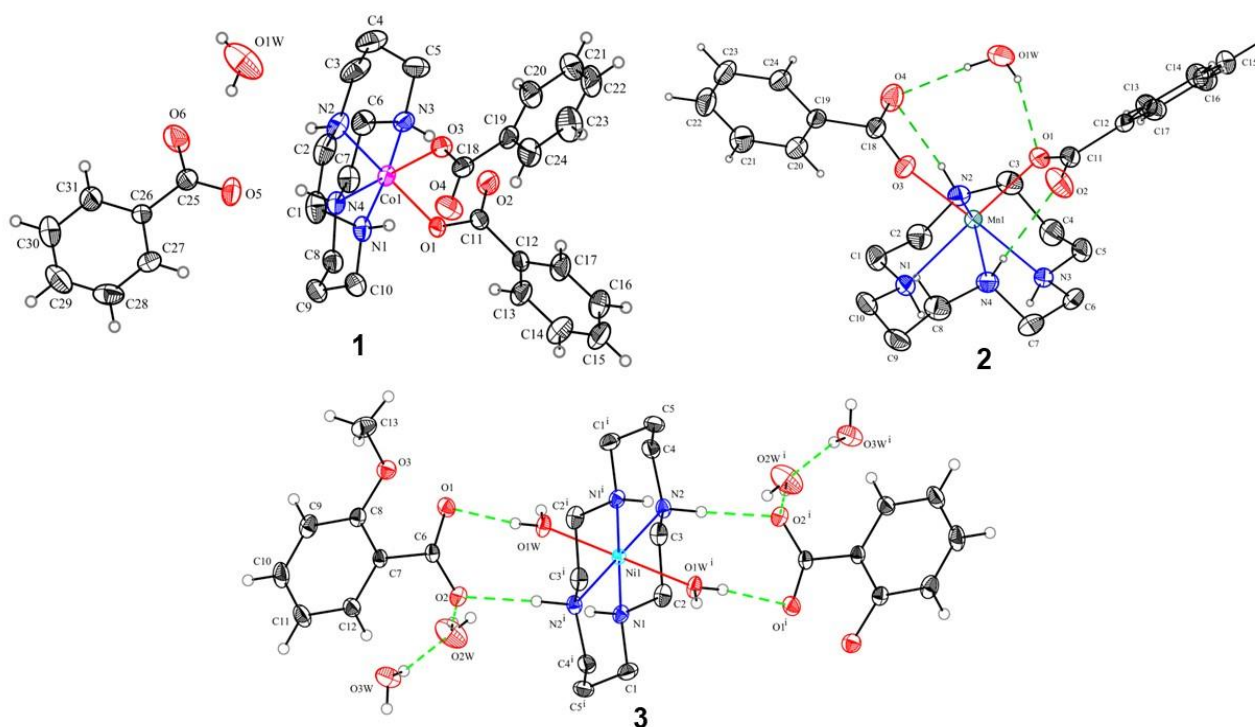


Figure 4. The crystal structure of compounds **1-3**. The hydrogen on the cyclam carbon backbone is removed for clarity purposes. The green dotted lines depict the intramolecular hydrogen bonds in the compounds. *Symmetry code for (3) i) 1-x, -y, 1-z*

The potential of compounds **1** and **2** in catalyzing the oxidation of catechol was investigated using 3,5-di-*tert*-butyl catechol as the model substrate. The results showed that the *trans*-nickel catalyst (**3**) was highly inefficient in catalyzing the oxidation process compared to compound **1**. Kinetic parameters were determined using compound **1** as the catalyst source to compare the results further with the literature reports (Figure 5). The higher catalyst loading and relatively low to moderate catalytic activity ($K(\text{cat}) = 18.9 \text{ (h}^{-1}\text{)}$), compared to similar compounds reported in the literature, suggest that the carboxylate incorporation into the metal cyclam system significantly affects the catalytic performance. The lower catalytic activity of **1** and **3** is likely due to competitive coordination between the carboxylate and the substrate, reducing catalytic efficiency.

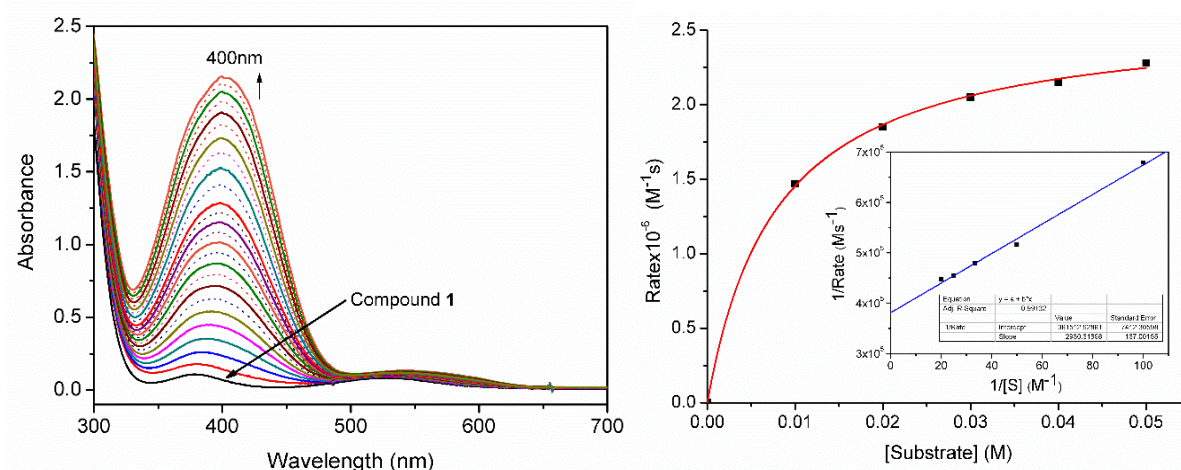
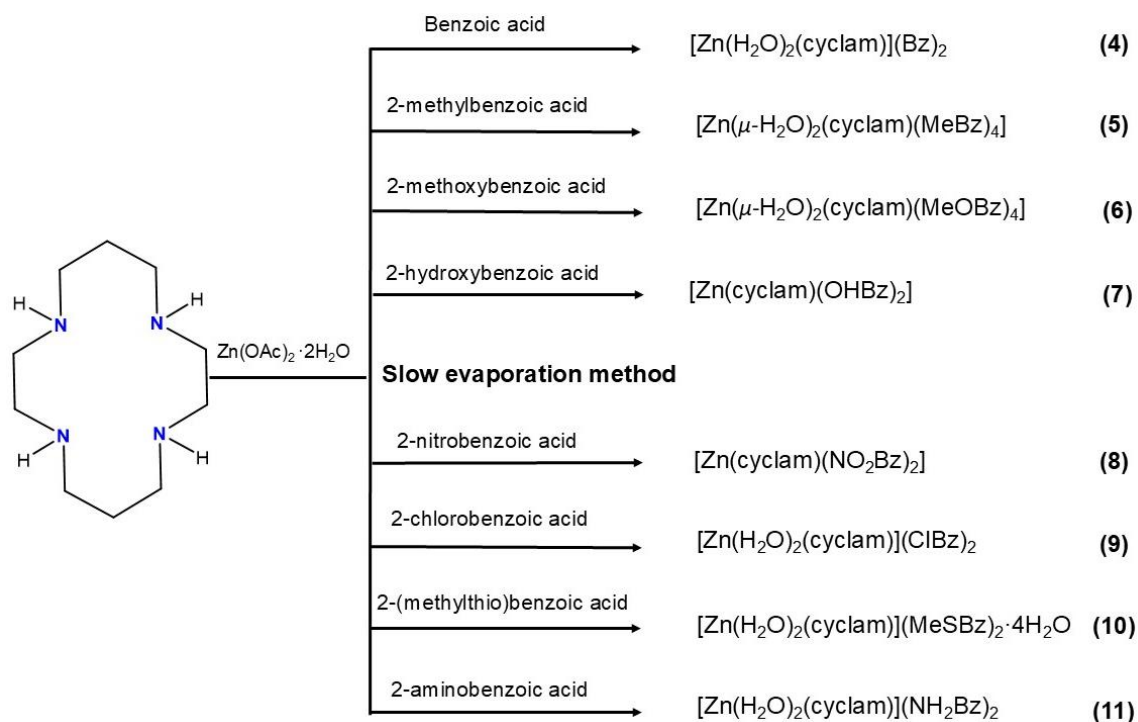


Figure 5. Increment in the absorbance at 400 nm upon addition of 100 eq. of 3,5-DTBC to 0.5 mM solution of compound **1** in ACN solvent (**Left**). The plot of initial rates versus substrate concentration with an inset showing the Lineweaver-Burk plot (**Right**).

The antibacterial properties of compounds **1** and **3** and their starting components, such as metal acetates, benzoic acid, and cyclam, were tested using the agar well diffusion method. The bacterial cultures used in this study were Gram-negative *E. coli* (ATCC 25922) and *S. aureus* (ATCC 25923). Among the different concentrations of 10 to 1000 $\mu\text{g/mL}$ of compound **1**, 90 $\mu\text{g/mL}$ was the lowest concentration identified to inhibit the growth of *E. coli* and *S. aureus*. On the other hand, compound **3** and the starting components showed negligible to no activity even at 1000 $\mu\text{g/mL}$ concentration. These results suggested that compound **1** has more potential to act as an antibacterial agent than compound **3** and its starting components.

CHAPTER 4: STRUCTURAL VARIATION INDUCED BY *ORTHO*-SUBSTITUTED CARBOXYLATE LIGANDS IN ZN(II) CYCLAM COMPOUNDS AND THEIR APPLICATION IN KNOEVENAGEL CONDENSATION REACTION

Chapter 4 discusses the synthesis of eight zinc cyclam-based compounds and their structural variation in supramolecular arrangement induced by the *ortho*-substituted carboxylate ligands. The compounds were further investigated for their efficiency in catalyzing the Knoevenagel condensation reaction. The synthetic route (**Scheme 3**) adopted for the preparation of the eight compounds was a simple, slow evaporation method, wherein water was used as the reaction medium, cyclam was employed as the nitrogen donor linker and monobasic benzoic acid (**4**) and its derivatives with *ortho* substituents such as Methyl- (**5**), Methoxy- (**6**), Hydroxy- (**7**), Nitro- (**8**), Chloro- (**9**), (Methylthio)- (**10**) and Amino-(**11**). All the compounds were characterized using IR, CHNS, TG-DTA, and diffraction techniques. The similarity of the unit cell parameters among related compounds **4-11** further led to investigating the extent of isostructurality in the associated compounds. Hirshfeld surface analysis was performed to study the non-covalent interactions in related compounds.



Scheme 3: Synthesis of zinc-based mixed ligand coordination compounds (**4-11**)

Preliminary infrared spectroscopic analysis of compounds **4-11** revealed sharp bands in the 1700-1400 cm^{-1} region, suggesting the incorporation of the carboxylate moieties in the zinc

cyclam compound. The TG-DTA analysis indicated the presence of aqua molecules in compounds **4** and **5**. However, a notable difference in dehydration steps was observed. Compared to **4**, the aqua molecules in compound **5** were lost at a slightly higher temperature in the 90-150°C range. This particular thermal behavior was better understood through the structural characterization of these compounds. The single-crystal X-ray diffraction studies showed that all eight zinc compounds adopt the *trans*-III configuration regardless of the variation in the carboxylate component. A closer look at the crystal structures of **4** and **5** revealed that the aqua molecules adopted different coordination modes adopted by the aqua molecules. In compound **4**, the aqua molecules adopt the monodentate coordination mode. In contrast, in **5**, it exhibits a bridging mode, where the oxygen atom acts as a bridge between the cationic and the anionic unit to form a one-dimensional chain structure. The difference in the coordination mode of the aqua molecule is likely responsible for the distinct thermal stability observed between the two compounds.

The variation in the ortho-substituted carboxylate groups led to the formation of isomorphous compounds. In crystallography, isomorphism refers to a phenomenon where two or more compounds tend to crystallize in the same or very similar crystal structures, even though they may differ in their chemical composition [31]. The similarity in the unit cell parameters of the related compounds signifies that the two compounds are isomorphous. While isomorphous compounds are often assumed to be isostructural, this is not always true. The isostructurality refers to the similarity of the internal arrangement of atoms or molecules. However, there are cases where compounds are identified to be non-isostructural due to slight differences in internal atomic arrangements or local coordination environment [32]. This raises an important question about the extent to which the related compounds are truly isostructural. To address this issue, Bombicz and coworkers have highlighted various methods to identify isostructurality in associated compounds, such as using numerical descriptors, which help investigate the extent of isostructurality in compounds. These numerical descriptors include the cell similarity index, the isostructurality index, and the molecular isometricity indices.

Interestingly, the synthesized metal cyclam compounds **4-11** also exhibited isomorphism as pairs or within groups. Therefore, compounds **4-11** were classified into three groups depending upon the similarity in unit cell parameters and further examined for isostructurality based on the numerical descriptors. Compounds **5** and **6** were placed in group I as they crystallized in the monoclinic space group with the *C2/m* space group. The crystal structure of both compounds exhibited a one-dimensional zig-zag chain structure composed of a cationic core

$[\text{Zn}(\text{cyclam})]^{2+}$ linked through a bridging aqua molecule to the anionic core in an alternating fashion (**Figure 6**). The cell similarity index of the molecular pair was identified to be 0.037, which is close to zero and indicates isomorphism. In contrast, the isostructurality index value was only 37%, suggesting variation in the internal arrangements of the crystal lattice. Furthermore, Mercury software was used to overlay the asymmetric unit of the related molecules to obtain the rmsD and maxD (3.7119 Å) values. The larger deviation from zero indicated a slight difference in how the substituents are oriented in the crystal lattice.

Hirshfeld surface analysis was employed to support this observation and to understand the contribution of the noncovalent interactions. The slight variation in the interaction between different noncovalent interactions is attributed to introducing a methoxy substituent (**6**) instead of a methyl group, disrupting the isostructurality in the two compounds (**Figure 7**)

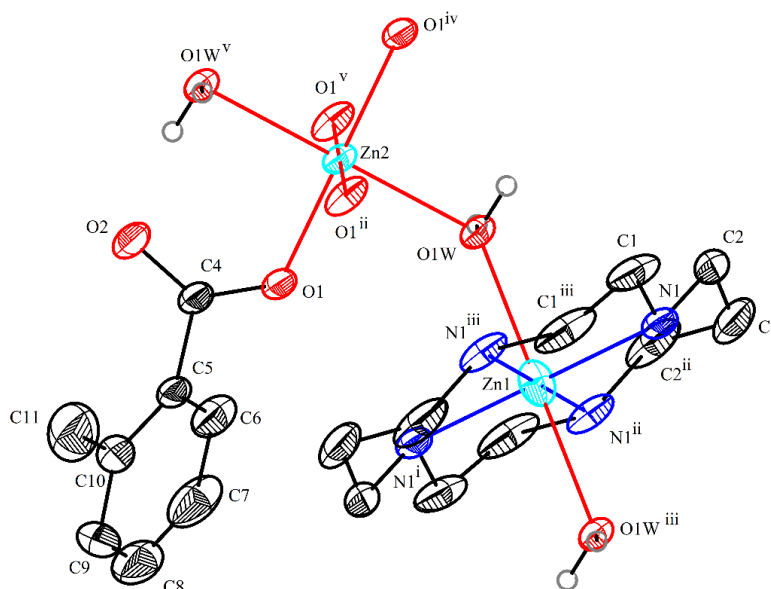


Figure 6. The crystal structure of compound **5** shows a portion of the one-dimensional chain. The thermal ellipsoids are drawn at 30 % probability except for the hydrogen atoms. The hydrogen atoms on the cyclam backbone are omitted for a clear view of the cyclam ligand.

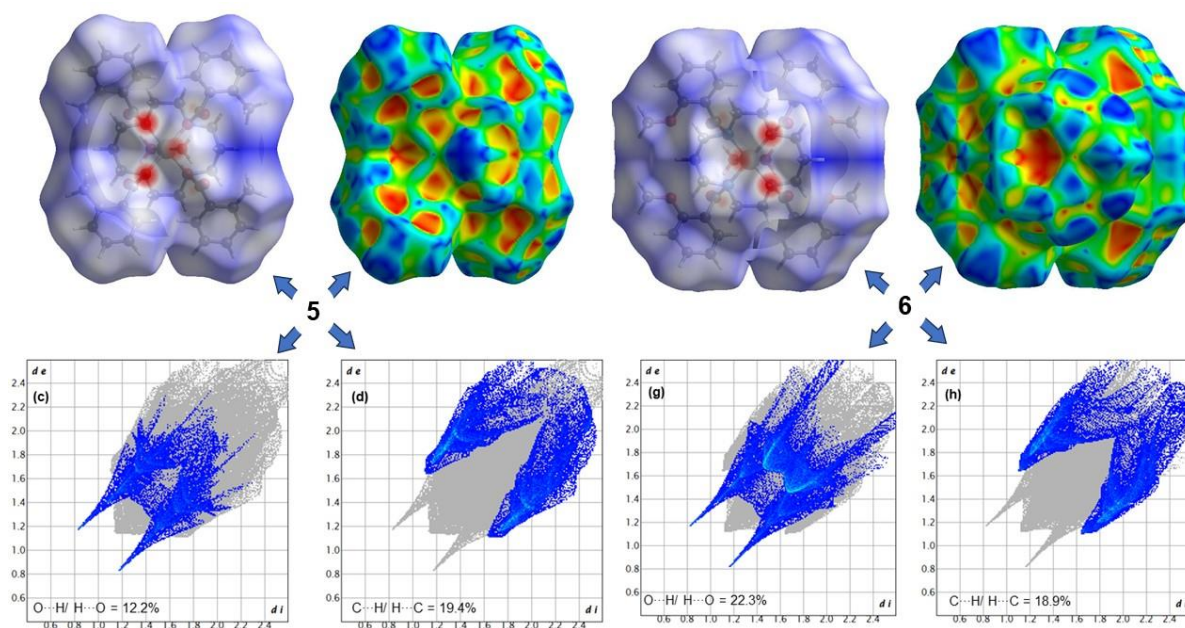


Figure 7. Illustrates the difference between the Hirshfeld surface, shape index plots viewed along the a-axis, and 2D fingerprint of compounds **5** (Left) and **6** (Right)

Similar observations were made for compounds **7** and **8**, which crystallized in the orthorhombic crystal system with the *Pbca* space group. The crystal structure comprises a centrally located zinc ion coordinated to a cyclam ligand, and the oxygen atoms occupy the axial positions contributed by carboxylate anions. Compounds showed isomorphism, reflected in a cell similarity index value of 0.0192. However, the two compounds were identified to be non-isosteric as the isostructurality index value was found to be 0 %, suggesting a significant difference in the crystal lattice. The diversion is attributed to the nature of substituents; in compound **7**, a hydroxy group forms intramolecular hydrogen bonding with the coordinating carboxylate group. In contrast, in compound **8**, a bulkier nitro group is tilted away from the carboxylate group, likely to minimize the steric hindrance. As a result, there is variation in the supramolecular arrangement, thereby breaking isostructurality among the two compounds. These results are further supported by Hirshfeld surface analysis.

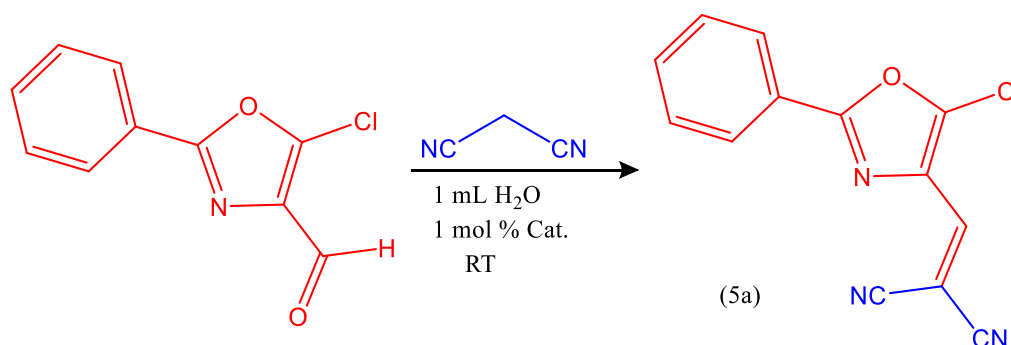
The compounds in group III (**4**, **9**, and **10**) also exhibited isomorphism. The compounds crystallized in the monoclinic *P2₁/n* space group. The crystal structure consists of a centrally located zinc ion in a special position. The zinc is coordinated to the cyclam ligand, and two aqua molecules are coordinated axially, thereby adopting octahedral geometry. Compound **10** also showed the presence of lattice aqua molecules involved in hydrogen bonding with the uncoordinated carboxylate anions present in the crystal lattice, unlike in compounds **4** and **9**.

The isostructurality indices obtained for pairs **4/9** and **4/10** were 0 %, suggesting they are purely isomorphous and show significant variation in their internal arrangement. The same was reflected in the Hirshfeld surface area analysis, which revealed new types of interactions such as Cl $\cdots$ H/ H $\cdots$ Cl and S $\cdots$ H/ H $\cdots$ S type in compounds **9** and **10**, respectively as a result of which the non-covalent interactions are pretty distinct from each other, thereby breaking isostructurality in the compounds.

Compounds **5** and **6** were assessed for their catalytic potential in the Knoevenagel condensation reaction, which was monitored for 2 hours. At first, the reactions were performed in 1 mL of tetrahydrofuran (THF) solvent using benzaldehyde and malononitrile as the starting reactants, with 1 mol% catalyst loading. It was observed that, as compared to the zinc acetate tetrahydrate, compounds **5** and **6** showed improved yields of the condensed product 2-benzylidene malononitrile (**1a**). Meanwhile, the blank reaction without a catalyst gave trace amounts of product **1a**. Suggesting that the catalyst can catalyze the known conventional condensation reaction. Further, we studied the effect of catalyst concentration. The studies indicate that as the catalyst concentration was increased, the yield also improved with small increments in yield beyond 5 mol% %, and the catalyst remained suspended in the medium. The pure product (**1a**) was isolated by column chromatography and identified by ^1H -NMR spectroscopy. We then tested the catalytic potential of compound **5** in aqueous medium, with 1 mol% catalyst loading, to compare the activity of the catalyst with that of a non-polar solvent using benzaldehyde and malononitrile as the reactants. The results indicated that 92 % of the product was obtained within 30 minutes of the reaction in the presence of 1 mol% catalyst in an aqueous medium. The reduced time interval and the use of aqueous medium improve the catalytic potential of compound **5** even at a much lower loading of 1 mol%. We then changed the aldehyde components to check the efficacy of the catalyst in the presence of different substituted aldehydes. The experimental results were compared to the observations published by Kolagkis and coworkers, who performed the reactions in a catalyst-free environment. In order to compare the noncatalytic reaction with our catalytic reactions, we have tried to keep all the parameters similar to the reported experiment. The comparison showed that higher yields were observed within 30 minutes when our zinc catalyst was employed as the catalyst source.

We also attempted the synthesis of novel condensed product 2-((5-chloro-2-phenyloxazole-4-yl)methylene)malonitrile (**Scheme 4**). 5-chloro-2-phenyloxazole-4-carboxyaldehyde was the starting material and reacted with malononitrile in aqueous medium with 1 mol% % catalyst loading. The reaction was sluggish; this slower response rate can be attributed to the aldehyde's

lower solubility and the condensed product's immediate precipitation. The reaction medium was monitored for 8 hours. After this, the product was isolated and purified to remove unreacted aldehyde. A yield of 64 % was obtained. On the other hand, the catalyst-free reaction, even after 24 hours of reaction, could give us only 23 % of the yield of the final product. We have successfully prepared a novel organic molecule while attempting to employ our zinc catalyst in a new reaction. However, efforts are ongoing to optimize the conditions to improve the yield in a shorter time.



Scheme 4. Synthesis of 2-((5-chloro-2-phenyloxazole-4-yl)methylene)malonitrile

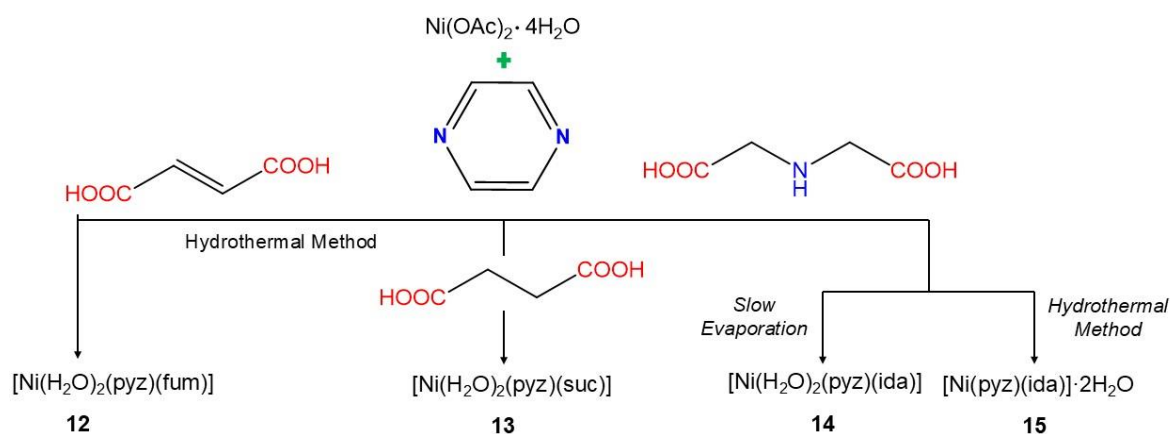
CHAPTER 5: TAILORING COORDINATION COMPOUNDS WITH RIGID NITROGEN DONOR LINKERS

Chapter 5 is divided into sections (I) and (II).

Section I: Design of pyrazine-bridged nickel coordination polymers, structural description, and use as precursors for Ni/NiO Composite Material.

Section I of Chapter 5 deals with preparing coordination polymers comprising a pyrazine-bridged rigid N-donor linker. Two methods were adopted for the synthesis purpose: i) conventional slow evaporation method (**SE**) and ii) Hydro(solvo)thermal (**HT/ST**) method to evaluate the effect of the reaction condition on the final architecture (**Scheme 5**). To study the effect of the solvent system on the final network, we have employed four solvents: water, methanol, N, N'-dimethylformamide (DMF), and N, N'-dimethylsulfoxide (DMSO). The compounds were further characterized by various spectroscopic, thermal, and X-ray diffraction techniques to study the effect. The detailed structural analysis revealed the dimensionality and underlying network topology (**2D, SQL**) (**3D, CDS**) and (**3D, Dia**) for **12**, **13**, and **15**, respectively.

The compounds 12-15 were further characterized by infrared, solid state UV-Vis spectroscopy, and Thermogravimetric analysis to gain insights into thermal stability. The compounds were also subjected to magnetic analysis, indicating that compounds **12**, **13**, and **15** showed paramagnetic behavior.



Scheme 5. Synthetic approach for the preparation of mixed ligand coordination polymers.

Crystallized compounds **12** and **13** were synthesized using the hydrothermal method. The structural analysis revealed crystallization in the monoclinic crystal system with the $P2_1/n$ space group. The nickel ion occupies an octahedral geometry (**Figure 8, Left**). The pyrazine ligand aids in forming 1 one-dimensional chain structure along the **a**-axis, while the fumarate ligand extends the chain along the **b**-axis. This arrangement leads to the formation of a 2D rectangular layered structure. When the carboxylic acid source was changed to succinic acid, a 3D microporous arrangement was observed in compound **13**, which was identified to crystallize in the monoclinic $C2/c$ space group. The nickel center adopts the distorted octahedral geometry, wherein the pyrazine bridges the nickel centers. The dynamic nature of the carbon backbone allows the succinate to adopt the Gauche conformation, leading to the formation of a zig-zag 2D layered structure (**Figure 8, Right**)

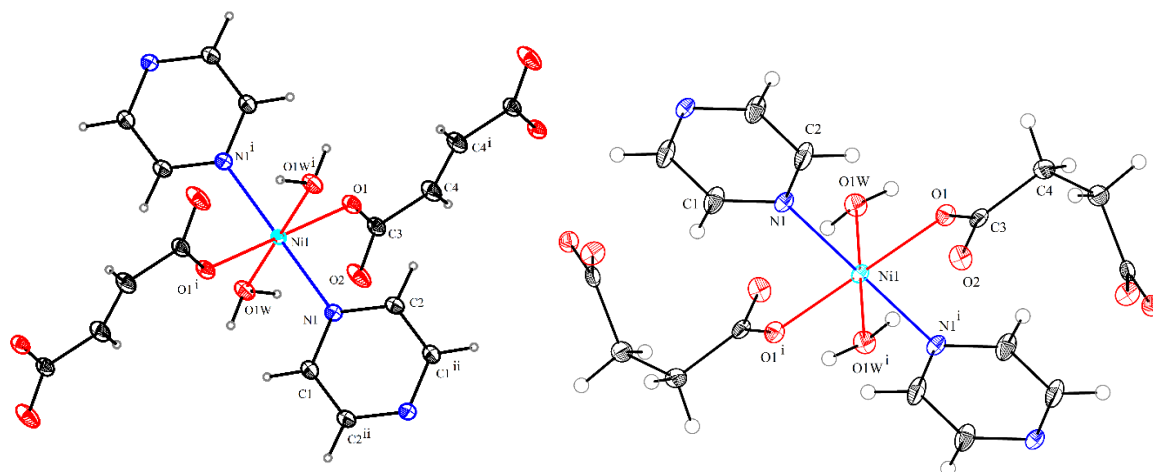


Figure 8. The portion of 2D and 3D networks showing octahedral coordination in compounds **12** (Left) symmetry code i) $1-x, 1-y, 1-z$, ii) $2-x, 1-y, 1-z$, and **13** (Right) symmetry code i) $1-x, 1-y, 1-z$

The crystals of compound **14** were isolated from the reaction kept at room temperature, while the same solution, when subjected to hydrothermal conditions, yielded colored block-shaped crystals **15**. The structural analysis of both compounds suggested that they shared the same chemical composition. However, there was a significant distinction between the structural arrangements of the two. Compound **14** crystallized in the orthorhombic *Pnma* space group. The central nickel ion adopted the distorted octahedral geometry, with two aqua molecules coordinated *cis* to each other. The iminodiacetate ligand adopted the chelating coordination mode, while the pyrazine ligand adopted the monodentate coordination mode. As a result, we could get a discrete molecular compound. The hydrogen bonding between the coordinated aqua molecules and oxygen atoms of the carboxylate ligand helps navigate the structure to form a one-dimensional supramolecular chain structure (**Figure 9, Left**). On the contrary, compound **15** was identified as a three-dimensional structure, with a centrally located nickel coordinating to the iminodiacetate ligand in chelate mode. The ida²⁻ ligand propagates the structure along the *ab* plane, forming a 2D layer. The bridging pyrazine ligand further connects the 2D layers to form a 3D network. Interestingly, the aqua molecules are present in the crystal lattice and are involved in extensive hydrogen bonding (**Figure 9, Right**). Based on these findings, it was inferred that the two compounds show hydrate isomerism. The compounds **12-15** showcase the effect of the nature of the carboxylate and its flexibility on the final architecture. The phase purity of all the compounds was evaluated by performing the powder X-ray diffraction studies.

The experimental powder patterns were in good agreement with the simulated pattern derived from the single crystal data.

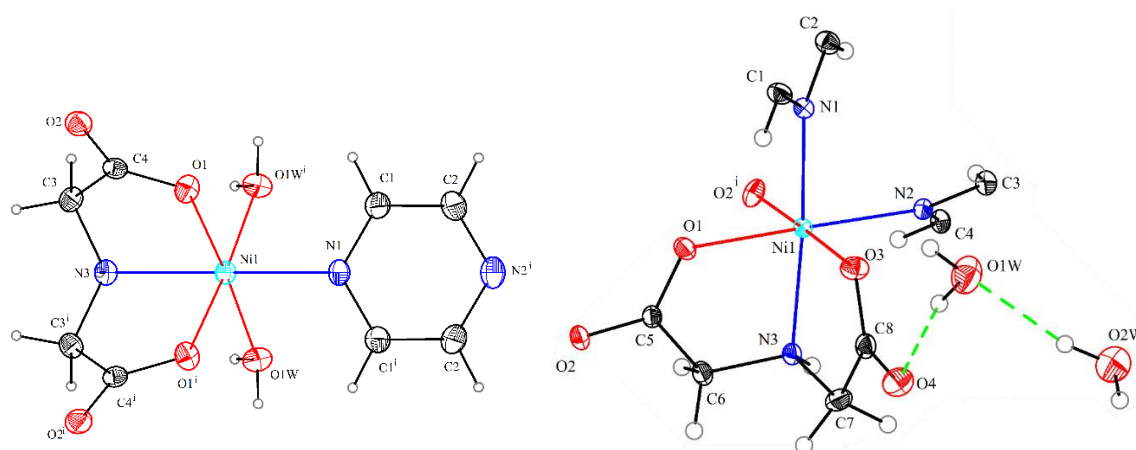


Figure 9. The portion of 0D and 3D structures showing octahedral coordination in hydrate isomers **14** (Left), symmetry code, and **15** (Right)

The nickel-based CPs **12**, **13**, and **15** were further employed as precursors to obtain the nickel oxide material to study the effect of the variation of the carboxylate on the crystalline phase formation and morphology of the final oxide material. The finally grounded CPs were heated in a furnace at 400 °C for 2 hours. After cooling to room temperature, the oxide material was ground into fine powder for 30 minutes. The resulting greyish solid was characterized by the IR and PXRD techniques. The recorded powder pattern was compared with the reference pattern for pure NiO (JCPDS card no #22-1189). The extra peaks in the pattern at 2θ values of 44.4° and 52.0° suggested the presence of impurity, which was identified as reduced nickel (JCPDS card no #01-078-0533) in the nickel oxide matrix (**Figure 10**). The formation of the composite material is attributed to the presence of nitrogen-rich compound pyrazine, which, upon decomposition, reduces the nickel oxide nanoparticles to nickel. The same composite material was subjected to scanning electron microscopy to display the morphology of the material.

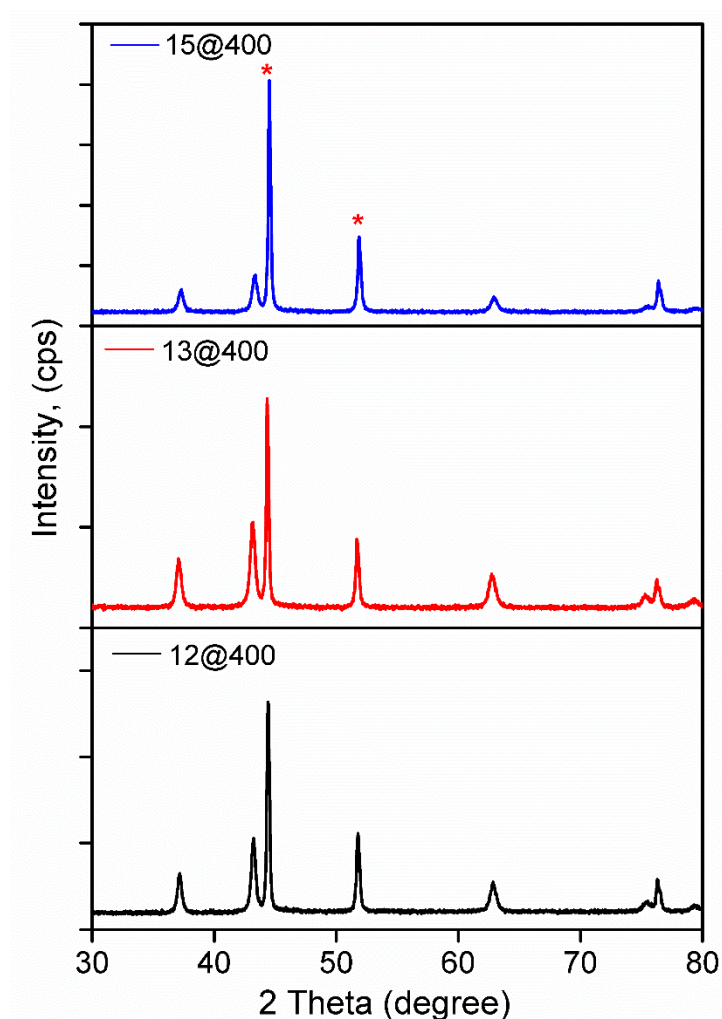


Figure 10. Comparison between the experimental powder patterns of the composite material, derived from the CPs after heating at 400 °C. The red star denotes the Nickel (0) phase.

Section II Synthesis, structure determination of new oxidovanadium CP containing terpyridine

Section II of Chapter V investigates novel heterometallic coordination polymers prepared from the hydrothermal technique. 2,2';6',2''-terpyridine (terpy) was employed as the source of the N-donor linker. Molybdic acid was used as the source of the Mo oxo anions, and Sodium metavanadate was used to generate in situ VO^{2+} ions by altering the pH of the solution to 3. The compound $[\text{VO}(\text{terpy})_4(\text{MoO}_4)_2(\text{Mo}_8\text{O}_{26})] \cdot 2\text{H}_2\text{O}$ **16** was characterized by IR, Raman, elemental analysis, TG-DTA, and X-ray diffraction techniques. The study of the dark green crystals obtained from the hydrothermal conditions suggested crystallization in the Triclinic $P\bar{1}$ space group. The asymmetric unit shown in **Figure 11** consisted of a crystallographically unique $\gamma\text{-(Mo}_8\text{O}_{26})^{4-}$ anion, indicated by an intense Raman signal at 968 cm^{-1} . A crystallographically independent tetratoxidomolybdate $(\text{MoO}_4)^{2-}$ anion exhibiting μ_3 -bridging

mode. As a result, the $\{\text{V}_4\text{Mo}_2\text{O}_{12}\}^{4+}$ cationic unit is generated, comprising an eight-membered heterometallic $\{\text{Mo}_2\text{V}_2\text{O}_4\}$ ring. A pair of $\{\text{V}_4\text{Mo}_2\text{O}_{12}\}^{4+}$ cationic units is bridged by the γ -(Mo_8O_{26})⁴⁻, resulting in the formation of a one-dimensional coordination polymer.

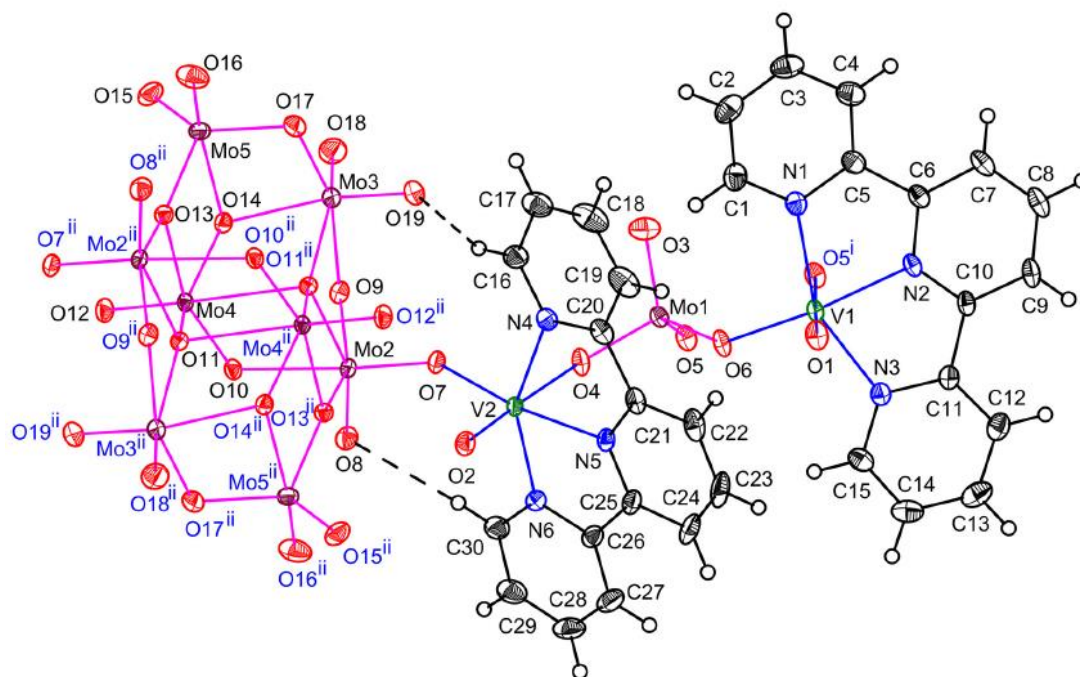


Figure 11. The asymmetric unit of compound **16**. The thermal ellipsoids are drawn at a 30% probability level for all non-hydrogen atoms except for the hydrogen atoms. *Symmetry code:* i) $-x, -y+1, -z+1$ ii) $-x, -y+2, -z+2$.

The phase purity of the crystalline compound was analyzed by recording the powder pattern, which was in good agreement with the powder pattern obtained from single-crystal data. Upon confirming the phase purity, the polycrystalline compound was subjected to Electron spin resonance (ESR) studies. The results indicated the presence of the V^{4+} ions in the compound from the characteristic ESR signal centered at $g = 1.987$. This is attributed to the presence of a terpyridine ligand, which acts as both a structure-directing agent and a reducing agent.

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CONFERENCES/SEMINARS AND WORKSHOPS ATTENDED

- 1] Participated in a Two-days **workshop on Material Science between the University of Porto, University of Coimbra, and Goa University**, organized by the Directorate of International Cooperation and Exchange (DICE) and Directorate of Research, Development and Resource Mobilization (DRDRM) on 18th and 19th November **2019** at Goa University.
- 2] Participated in the **virtual conference on Metal-Organic Frameworks and Open Frameworks compounds (MOF2020web)** organized by DECHEMA e. V. from 21st to 24th September **2020**.
- 3] Attended a virtual **international conference on Porous Materials for Energy and Environment** organized by the Government College of Arts, Science and Commerce, Khandola – Goa held on 12th and 13th March **2021**.
- 4] Two-day Industry-Academia International Symposium (Virtual) on “**Fuels for Environmental Sustainability**” organized by the Cluster Research Centre, PG and UG Department of Chemistry in association with IQAD, Government College of Arts, Science and Commerce, Khandola, Marcela-Goa and Vedanta Sesa Goa Ltd. on 8th and 9th October **2021**.
- 5] Volunteered in "7 Days training workshop under **Synergistic Training Program Utilizing the Scientific and Technological Infrastructure (STUTI)** on Operation of (NMR), (SCXRD), (AES), (HPLC) & (PL)“organized by the School of Chemical Sciences (SCS) in association with Sophisticated Analytical Instrumentation Facility (SAIF), Panjab University, Chandigarh funded by Department of Science & Technology (DST) held from 2nd to 9th January **2022**
- 6] Participated in the three-day workshop “**X-ray Crystallography**” organized by the School of Chemical Sciences and the School of Physical & Applied Sciences, Goa University, Goa held on 21st to 23rd July **2022**.
- 7] Participated in a **Synergistic Training Program utilizing the Scientific and Technological Infrastructure (STUTI)** at BITs Pilani Goa campus in association with the Department of Science & Technology, Government of India (DST) from 26th September to 2nd October **2022**.
- 8] Participated in a one-day **national seminar on “Recent Trends In Applied Organic Synthesis**” organized by Goa University, School of Chemical Sciences (SCS), in association

with Chemistry Department Faculty & Alumni Association (CDFAA) & Syngenta Biosciences Pvt. Ltd., Goa on 26th November **2022**.

9] Presented poster at the **international conference on Advanced Materials: Properties and Applications** organized by Goa University from 20th to 24th February **2023**.

10] Participated in the **international webinar on “Innovations and Applications in Material Chemistry”** organized by the Department of Chemistry -DCT's Dhempe College of Arts & Science, Miramar-Goa. In association with Meijo University Japan & BITS, Piani, K. K. Birla Goa campus, India on 21st March **2023**.

11] Participated in the **CCDC Virtual Workshop: Exploring and Leveraging Metal-Organic Structures for Multiple Applications** held on 27th April **2023**.

12] Participated in a five-day online **interactive workshop on “Introduction to ChemDraw”** organized by Goa University from the 10th to 14th of September **2023**.

13] Participated in **ICDD workshop on “Materials Characterization using powder X-ray Diffraction (GUCW-I)”** organized by Goa University held on 07th and 8th December **2023**.

14] Presented poster at the **international conference on “Modern trends in Inorganic Chemistry”** organized by Division of Chemical Sciences, Indian Institute of Science, Bangalore, India from 14th to 17th December **2023**.

15] Presented poster at the **national conference on “Advances in Material Science”** organized by the Department of Chemistry -& cluster Research Centre of Government College of Arts, Science, and Commerce, Khandola in collaboration with the Directorate of Higher Education and Under the aegis of DBT Star College Scheme & Vedanta Sesa Goa Ltd. On February 9th and 10th, **2024. (Awarded 1st place in poster category)**

PUBLICATIONS

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Chapter 1: From coordination compounds to coordination polymers: pathway towards extended framework materials

1.1 Historical background

The concept of chemical bonding in inorganic coordination compounds was first clearly understood through the pioneering work of Alfred Werner, a renowned scientist whose studies on the spatial arrangement of ligands around the metal centres revolutionized coordination compounds. His groundbreaking contributions has earned him the Nobel prize in 1913 and laid the foundation for exploring a wide range of molecular complexes [1]. One of the early milestones in this field was the structural elucidation of ferrocene (1952), which marked the birth of organometallic chemistry, that bridged the inorganic and organic chemistry fields [2]. By the early 1970s, another important area known bioinorganic chemistry, began to flourish. Researchers started designing synthetic model compounds to mimic metalloenzymes and study their intermediates or catalytic properties [3]. Around 1979, scientists began replacing neutral ligands with organic carboxylates, leading to the development of metal clusters and polyoxometalates [4]. These compounds gained importance for their potential applications in the petrochemical industry as molecular analogues of the extended metal oxides.

The origins of extended structures can be traced back to the Hofmann clathrates, discovered in 1972. Slow diffusion of benzene into ammonia solution of $\text{Ni}(\text{CN})_2$ yielded a crystalline material of general formula $[\text{Ni}(\text{CN})_2(\text{NH}_3)](\text{C}_6\text{H}_6)$ which was termed as the Hofmann clathrate. The terminal ammonia ligands on the octahedral nickel centres pointing towards adjacent layers facilitate the formation of cavities, rendering the compound capable of encapsulating benzene as guests, but structural collapse was observed on removal of the guest molecules. Furthermore, Iwamoto et al. focused on a more systematic approach for the synthesis of Hofmann-type compounds and discovered that in general this type of materials is built from two different units namely, $[\text{M}_a^{2+}(\text{CN})_4]^{2-}$ and $[\text{M}_b^{2+}(\text{NH}_3)_2]^{2+}$ (where a and b indicate different divalent metals). They demonstrated that the terminal ammonia ligands can be replaced with α, ω diamino alkanes which act as linkers between adjacent layers and thereby create space for encapsulation of guest molecules [1,5]. During the 90s numerous reports emerged describing coordination networks from metal ions and various neutral linkers [6-8]. Although some of these networks displayed porosity, clear experimental proof of permanent porosity was lacking. Their structures were frail and lacked architectural stability, due to weak

non-directional bonds linking their constituents and flexibility around the single metal node [1].

A major turning point arrived in 1995, when Prof. Omar Yaghi and his team at Arizona State University synthesized the first coordination network based on trimesic acid (H_3BTC). The metal carboxylate assembly resulted in formation of a two-dimensional sheet structure in which a single metal node was interconnected by spacer linkers. The thermogravimetric investigation revealed that the compound was able to release the pyridine guest molecules from its pores at 190°C , yet the overall crystallinity of host structure was retained even up to 350°C , also supported by the X-ray powder diffraction analysis and examination of crystals by optical microscope [9,10]. Following this breakthrough, the development of highly porous and thermally stable materials such as MOF-5 (1999) marked the beginning of an explosive era in MOF research [11,12]. These discoveries have since inspired scientist worldwide to explore similar frameworks for gas storage, catalysis and sensing applications. Recognizing their profound impact on modern materials science, the 2025 Nobel Prize in Chemistry was awarded to Prof. Susumu Kitagawa, Richard Robson and Prof. Omar Yaghi for their pioneering contributions to the development of metal-organic frameworks.

The ongoing advancements in material science and crystal engineering have considerably promoted the investigation of discrete coordination complexes and extended polymeric structures such as coordination polymers (CPs) and Metal-organic frameworks (MOFs) [13-15]. These materials continue to attract research interest due to their functional roles in catalysis, magnetism, storage, and biomedical applications [16,17]. For the rational design of such molecular and polymeric materials, judicious choice of metal centers and organic linkers is paramount [18]. In particular, intensive research in mixed ligand molecular compounds and CPs identifies the use of rigid N-donor ligands, which aid in providing basic sites, and also promote predictable network geometries and O-donor carboxylates, as they tend to offer flexible coordination modes contributing towards structural diversity. The crystalline nature of materials further enables their characterization by X-ray diffraction techniques, which helps establish the structure-property relationship and thereby allows their application across various domains [19].

1.2 Overview of metal cyclam-based mixed ligand compounds

Historically, researchers have employed macrocyclic polyamine compounds in the synthesis of metal compounds since the early 20th century. Extensive work in the field of coordination compounds comprising cyclam-based ligands has been carried out, owing to the pronounced ability of macrocyclic ligands to accommodate a wide range of metal ions, aiding in stabilizing the unusual oxidation states [20]. Among these macrocyclic ligands, the most commonly used linker is a 14-membered cyclic ligand known as 1,4,8,11-tetraazacyclotetradecane (cyclam). The metal-cyclam compounds exhibit higher thermodynamic stability and kinetic inertness, making them a suitable candidate for use as a synthetic model in bioinorganic chemistry to understand and mimic metalloenzyme functions [21]. In coordination with the metal ion, the cyclam can adopt six configurational isomers influenced by the spatial arrangement of the nitrogen atoms. Among these, five trans configurational isomers are *trans*-I (RSRS), *trans*-II (RSRR), *trans*-III (SSRR), *trans*-IV (RSSR), and *trans*-V (RRRR), and one folded structure, *cis* isomer [20,22] as shown in **Figure 1**. Understanding these configurational preferences is essential for designing compounds with the desired structure and functional properties. Hence, in recent years, researchers have been working on exploiting novel mixed ligand metal-cyclam cores with auxiliary linkers to fine-tune the coordination environment and functional properties, opening new pathways for developing multifunctional compounds, with a greater tendency for structural variation [23-25].

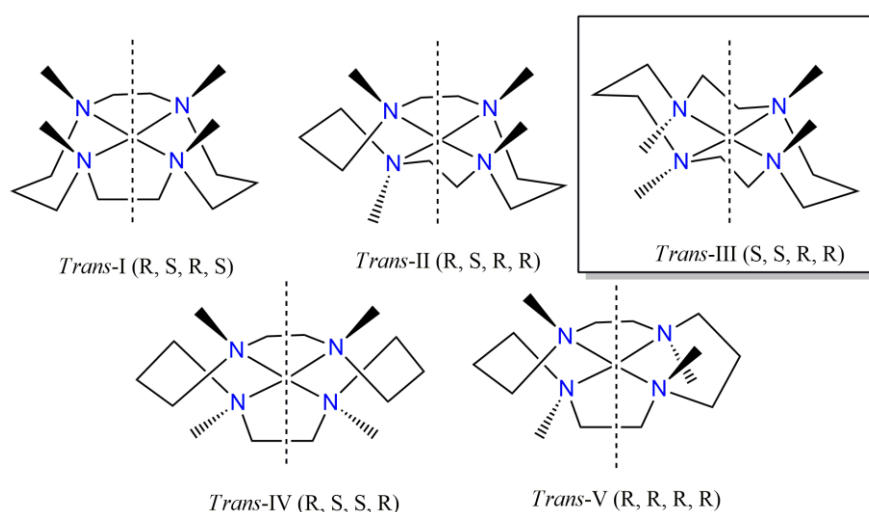


Figure 1. Shows the *trans* conformers of the cyclam ligand

Carboxylate linkers are often employed as auxiliary linkers to study the interaction with the metal cyclam core. Studies on metal cyclam compounds have indicated that the carboxylates can exert a strong influence over the configurational selectivity [26]. In this context, the present study aims to explore the synthesis and characterization of novel metal-cyclam compounds incorporating monobasic carboxylate linkers, emphasizing understanding the configuration preferences and variation in the crystal lattices. Additionally, the study aims to evaluate their catalytic and biological applications.

1.3 General overview of coordination polymers

In crystal engineering, the crystalline solids are designed with targeted structures by choosing suitable molecules or building units as the raw materials. One such class of crystalline solids includes the polymeric compounds named coordination polymers (CPs) [27]. These materials are an intriguing class of hybrid materials known to exist as infinite crystalline lattices extended from the inorganic components, such as metal ions or metal clusters, and organic linkers via coordination interactions. The hydrogen bonds and other non-covalent interactions stabilize the crystalline lattice [28-30].

Over the past few years, significant progress has been made in synthesizing various porous coordination polymers (PCPs), also commonly referred to as metal-organic frameworks (MOFs) [31]. These materials offer various applications, such as storage, exchange, optical properties, and are also utilized in catalysis and magnetic investigations [32-37]. The CPs, PCPs, and MOFs demonstrate remarkable structural versatility compared to the molecular materials, as the frameworks can be designed and tailored for desired applications [38,39]. Ultimately, the properties of the polymeric crystalline materials are primarily governed by the nature and type of the organic building blocks and the type of metal ions or clusters used in the synthesis, along with other factors such as pH, solvent, and temperature [40,41].

A prerequisite for obtaining extended structures is that the linkers must have two or more donor atoms. The carboxylate ligands with a rigid carbon backbone were the choice of many researchers due to their structural rigidity and thermal stability. On the contrary, the flexible O-donor molecules were identified to increase the complexity and difficulty in predicting the final architecture due to the ability of flexible carboxylate to adopt different conformation, which enables formation of diverse crystal structures. However, this property has been realized to be advantageous, as conformational mobility brings structural diversity. Some compounds with

flexible ligands also allow breathing ability and adaptive recognition properties as a function of the guest molecules [42,43].

1.3.1 Factors affecting the self-assembly process of Coordination polymers

The final structure depends upon various factors like the nature and coordination of metal nodes/ metal clusters, nature and type organic linkers rigid or flexible, solvent, temperature and pressure conditions, pH of the reaction mixture, concentration, crystallization techniques etc.

Metal nodes/SBUs: The metal centres are also called as nodes or hubs and show bonding at well-defined angles to a specific number of ligands. The alkali, alkaline earth, transition and lanthanides metal ions have been explored in synthesis of CPs. The transition metals are mostly used because they exhibit variability oxidation state and coordination geometries and are expected to form multi-dimensional networks of interesting topologies. Literature reports indicate that when the interaction energy between the metal ions and linkers is relatively weak, the resulting system become more sensitive to external factors such as counter ions and solvent molecules. To address this issue, researchers have introduced polynuclear cluster nodes, known as secondary building units (SBUs), which help stabilize the overall framework. These SBUs were found to provide (i) Thermodynamic stability, because the framework is entirely composed of strong M-O bonds and (ii) Chemical stability iii) structural diversity is observe due to metal ions tend to form oxo-centered SBUs [44,45]

Organic linkers: The organic struts or linkers play a dual role in the construction of the solid crystalline materials. Firstly, multitopic linkers help in linking the metal ions into higher dimensionalities with a myriad of different structural morphologies. Second, they provide charge balance necessary to avoid any inclusion of small molecules (anions). Furthermore, they can be modified with different functional groups, and also on varying the chain length results into different materials with different pore size and structures these can be very much useful in the gas storage and gas separation application as shown by Prof. Yaghi and coworkers in 2002 were they prepared series of IRMOFs based on MOF-5 using different organic ligands [46]. Most widely used ligands in the synthesis of CPs /MOFs are i) polytopic pyridine-based ligands ii) carboxylate-based ligands iii) hetero-functional ligands. Cationic organic ligands are comparatively less used, because of their low affinities for cationic metal ions, such ligands can be used as auxillary ligands, and hence the cationic sites on the organic sites on the organic ligands can detect toxic anions.

Solvents: It has been observed that the solvent greatly modulate the structural and chemical properties of CPs. As seen in the case of Silver-based CPs reported by Huang and coworkers. On switching the solvents from ethanol to 1,4-dioxane a series of Ag-based CPs were obtained [Ag₄(TTB)(H₂O)] (**1**), Ag₄(TTB)(H₂O)₃ (**2**) and Ag₄(TTB)(H₂O)₄ (**3**). The different sizes, shape and polarities of the solvent molecules even though not present in the final framework, served as the structure directing agent and regulated the coordination trend of the metal ions to form metal-metal bonds during the growth processes [47]. Our group has also worked on studying the influence of solvent on the final framework using cobalt succinate and pyrazine system [41]. By simply varying the solvent system, distinct architectures ranging from one-dimensional chains to three dimensional frameworks were obtained. The solvent influences the coordination environment, hydrogen-bonding interactions and overall, dimensionality of the resulting CPs by affecting the solubility and diffusion of the metal ions and organic linkers during crystallization. Thus, the choice of solvent acts as a key parameter in controlling the final structure and properties of the synthesized compounds.

Despite extensive progress in the synthesis of CPs or MOFs, using rigid and flexible organic linkers, there remains significant potential in exploring diverse combination of metal ions and organic linkers to better understand how mixed systems such as O- and N-donor functionalities influence the overall structure dimensionality, topology and functional behaviours of the resulting framework [48]. Most of the studies focus on rigid carboxylate-based MOFs or rigid pyridine-type CPs, whereas systematic investigations integrating macrocyclic amines such as cyclam with aliphatic or aromatic carboxylate are relatively scarce. Addressing these gaps is essential for advancing crystal engineering strategies towards the rational design of multifunctional materials. In this context, the present work focuses on employing simple N-donor linkers together with aromatic and aliphatic systems illustrated in **Figures 2** and **3**. The list of compounds prepared in this study are presented in **Table 1**.

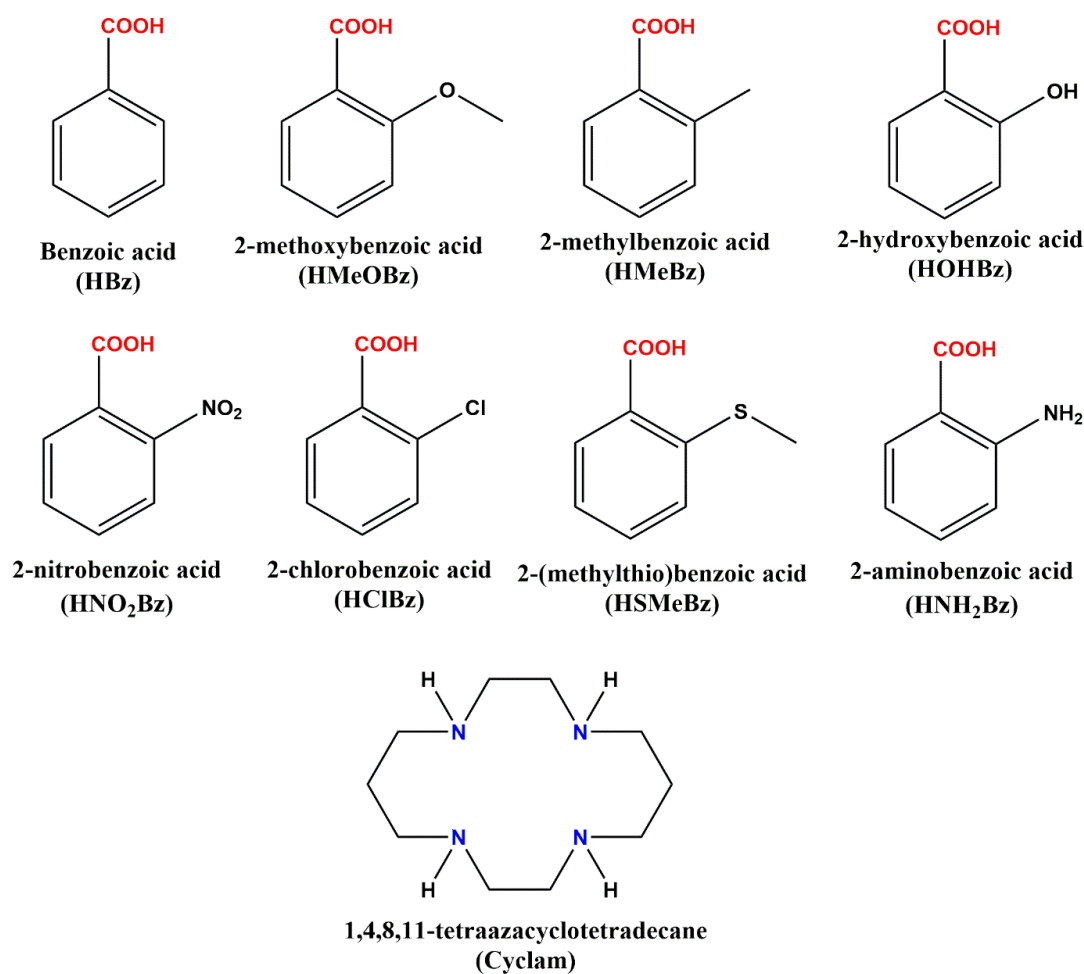


Figure 2. Benzoate and its derivatives with *ortho* substituents as the O-donors and cyclam as the N-donor ligand.

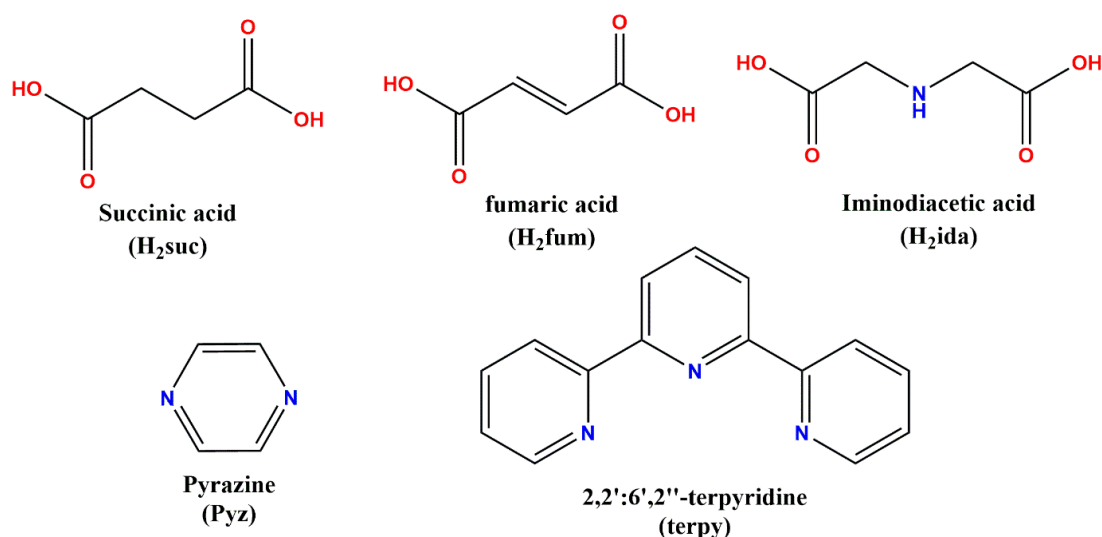


Figure 3. The O-donor and N-donor linkers employed in the preparation of coordination polymers.

Table 1. List of compounds included in this thesis

Code	Compound	Synthetic Method	Dimensionality
1	[Co(cyclam)(Bz) ₂](Bz)·H ₂ O	SE	0D
2	[Ni (H ₂ O) ₂ (cyclam)](MeOBz) ₂ ·2H ₂ O	SE	0D
3	[Mn(cyclam)](Bz) ₂ ·2H ₂ O	SE	0D
3a	[Mn(cyclam)](Bz) ₂ ·(Bz·HBz)·2HBz	SE	0D
4	[Zn(H ₂ O) ₂ (cyclam)](Bz) ₂	SE	0D
5	[Zn ₂ (μ-H ₂ O) ₂ (cyclam)(MeBz) ₄]	SE	1D
6	[Zn ₂ (μ-H ₂ O) ₂ (cyclam)(MeOBz) ₄]	SE	1D
7	[Zn(cyclam)(OHBz) ₂]	SE	0D
8	[Zn(cyclam)(NO ₂ Bz) ₂]	SE	0D
9	[Zn(H ₂ O) ₂ (cyclam)](ClBz) ₂	SE	0D
10	[Zn(H ₂ O) ₂ (cyclam)](MeSBz) ₂ ·4H ₂ O	SE	0D
11	[Zn(H ₂ O) ₂ (cyclam)](NH ₂ Bz) ₂	SE	0D
12	[Ni(H ₂ O) ₂ (μ-pyz)(μ-fum)]	HT	2D
13	[Ni(H ₂ O) ₂ (μ-pyz)(μ-suc)]	HT	3D
14	[Ni(H ₂ O) ₂ (pyz)(ida)]	SE	0D
15	[Ni(μ-pyz)(μ-ida)]·2H ₂ O	HT	3D
16	[(VO(terpy)) ₄ (MoO ₄) ₂ (Mo ₈ O ₂₆)]·2H ₂ O	HT	1D

Abbreviation: SE = slow evaporation, HT = Hydrothermal method

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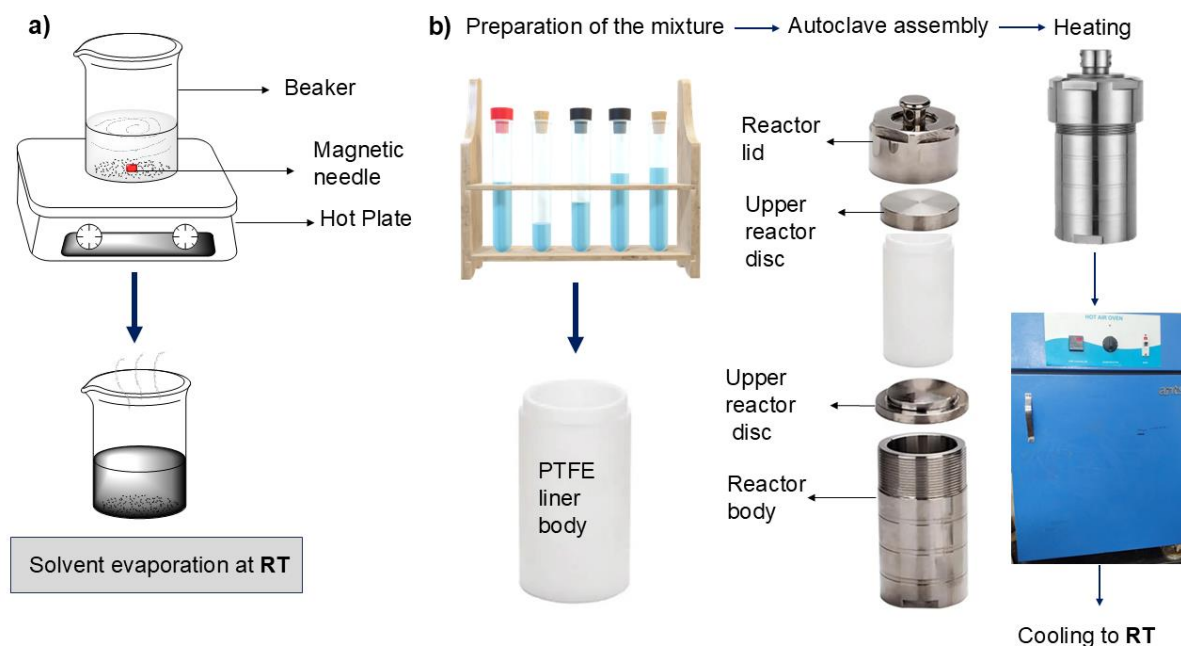
Chapter 2: Experimental Procedures and Instrumentation Techniques

2.1 Chapter abstract

This chapter outlines the experimental procedures for synthesis of compounds and computational methods employed in this thesis. Firstly, Section 2.2 discusses the methods utilized to synthesize metal compounds. Next, Section 2.3 provides a brief explanation of the analytical techniques used to characterize the metal compounds. These are i) Infrared and Raman spectroscopy, ii) UV-Vis spectroscopy, iii) Magnetic resonance spectroscopy, iv) Electron spray Ionization mass spectroscopy, v) X-Ray photoelectron spectroscopy, vi) CHNS elemental analysis, vii) X-Ray diffraction, viii) Thermal analysis, xi) Scanning electron microscopy, and x) Superconducting quantum Interference device. Sections 2.4 and 2.5 review the experimental procedure for the catalytic activity. Section 2.6 discusses the experimental procedure for antimicrobial activity using compounds **1** and **2**. Sections 2.7 and 2.8 establish a theoretical background for Hirshfeld surface analysis and Isostructurality determination, respectively. Section 2.9 outlines the experimental procedure for preparing compounds **1-16**.

2.2 The conventional slow evaporation method *versus* the Hydro/Solvothermal method

A systematic representation of the methods used for the self-assembly process is illustrated in **Scheme 1**. The chemicals used for the synthesis and catalysis purposes were obtained from commercial sources and were used without further purification. One of the key motives of the researchers working in coordination polymers is to get good-quality single crystals to acquire a deeper understanding of the structural aspects and, based on the findings, establish a structure-property relation towards specific applications. Single crystals can be grown using various synthetic methods, such as diffusion, slow evaporation, reflux, hydrothermal/solvothermal, microwave, and ultrasonication. Among these, the most commonly adopted strategies for synthesizing polymeric metal complexes are the conventional slow evaporation and Hydrothermal/ Solvothermal methods. The slow evaporation technique is the most straightforward technique used to grow high-quality crystals at room temperature, without requiring any special equipment or external energy source. This makes it a suitable method for synthesizing polymeric metal complexes under mild conditions [1,2].



Scheme 1. Systematic representation of the synthetic process: **a)** Slow evaporation method (**Left**) and **b)** the Hydro/solvothermal reaction setup (**Right**).

The choice of the solvents plays a crucial role in the crystallization process. The quality of the crystals and the speed of nucleation are depending on the rate of evaporation of the solvents. The low-boiling solvents evaporate more quickly, thus concentrating the solution much faster as a result microcrystalline powders or mixed phases are observed. The process can be slowed by choosing a different solvent or mixtures of high-boiling solvents, such as DMF and DMSO, in combination with the low-boiling solvents (MeOH and ACN) to obtain single crystals suitable for diffraction purposes. Even though it is a more conventional synthesis method, it is often considered a time-consuming process compared to the other synthetic methods available for coordination polymers. Furthermore, this method may be inadequate when the starting materials have lower solubility at room temperature, thus limiting its use to reactions where the solubility of the starting components is not a concern [3,4].

In the Hydrothermal/Solvothermal techniques, the metal salts and the organic linkers are dissolved in a suitable solvent and heated in glass vials for low-temperature reactions, or a Teflon-lined autoclave reactor for reactions heated at high temperatures in a temperature-programmable oven. Solvothermal reactions involve the use of solvents (high-boiling) at elevated temperatures in a sealed system while for hydrothermal setup only water is used as the medium. When solvents are under subcritical and supercritical conditions, they may

experience dramatic changes in their properties, consequently enhancing the reactivity of the chemical species and taking care of the solubility issues with particular chemical species due to increased diffusion during the heating process. These methods are explored much more in synthesizing CPs or MOFs, as they often produce high-quality single crystals essential for diffraction analysis. In addition, the reaction conditions in the hydrothermal/solvothermal setup are usually non-equilibrium. They may give rise to metastable products, which may not be possible to grow using the traditional crystallization methods [5].

A successful synthesis of a targeted CP largely depends on the experimental conditions, such as the solubility of the components, solvents, pH, reaction time, temperature, and pressure. Consequently, achieving complete control over the final product is still challenging when preparing such crystalline materials. Overall, the slow evaporation technique offers simplicity compared to the Hydrothermal/Solvothermal methods. Still, the latter is known to have a distinct advantage in preparing compounds with high-quality single crystals and may lead to the synthesis of metastable products that are inaccessible by conventional means.

2.3 Analytical tools for the characterization

2.3.1 Infrared (IR) and Raman spectroscopy

Vibrational spectroscopy provides valuable information regarding the nature of the bonds and the symmetry of the moiety under investigation, making it a valuable technique for the characterization of CPs and coordination compounds. The assignment of the observed vibrational bands is based on the position of certain functional groups exhibiting stretching or bending vibrational modes in a narrow spectral region. Vibrational spectroscopy encompasses two fundamental techniques, IR and Raman spectroscopy.

The IR spectroscopic method is based on the principle of absorption of infrared light, which causes the transition between the vibrational energy levels of the molecules. The vibrations are IR active when there is a change in the dipole moment. The IR region is divided into three subregions. The fundamental vibrations are observed in the mid-infrared ($4000\text{--}400\text{ cm}^{-1}$). The overtone and combination modes are detected near IR ($14000\text{--}4000\text{ cm}^{-1}$). The intermolecular vibrations can be observed in the far-IR region ($400\text{--}10\text{ cm}^{-1}$).

The Raman spectroscopic technique is based on the inelastic scattering of photons. The bands appear only when there is a change in polarizability. The molecular symmetry influences the appearance of the IR and Raman bands. For a molecule having a centre of symmetry, the IR

active vibrations are Raman inactive. Meanwhile, for a non-symmetric molecule, some of the bands could be both IR and Raman active. Both these techniques have been exploited in the analysis of CPs/MOFs as the spectra contain features arising from the organic linkers and inorganic moieties, and they have also been used to determine the host-guest interactions [6].

Instrument specification: *The samples were ground with KBr using a mortar and pestle. The fine powder was loaded in the sample holder. The data were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer. b) Alpha II-Transmittance FT-IR spectrometer in the range 4000 – 350 cm^{-1} with a resolution of 4 cm^{-1} . The Raman spectra were obtained from LabRAM HR Evolution Raman spectrometer (HORIBA Scientific). (SCS, Goa University)*

2.3.2 Ultraviolet-Visible (UV-Vis) spectroscopy

UV-Vis spectroscopy is a versatile method for analysing various complexes in the liquid phase and the solid state (diffuse reflectance mode). It typically measures the wavelengths between 200 and 400 nm (UV region) and 400 and 800 nm (visible region). When a beam of light is passed through the solution, the analyte absorbs a specific wavelength due to electronic transitions within the molecules. This includes π - π^* and n - π^* transitions commonly encountered in organic molecules. The Beer-Lambert law describes a relationship between the absorbance and the concentration in a solution. It is expressed as $A = \log_{10}(I_0/I) = \epsilon cl$ (where A = absorbance, I_0 = Intensity of incident light, I = Intensity of transmitted light, ϵ = Molar absorptivity, c = Concentration of analyte in the solution, l = path length). This technique is used to detect impurities, for the structural elucidation of organic compounds, and quantitative and qualitative analysis of the compounds [8].

Instrument specification: *The UV-Vis spectra of metal complexes were recorded on Agilent 8453 UV-Vis spectrophotometer, using Quartz cuvette. The solid-state Diffuse-reflectance spectra were recorded on a Shimadzu UV-2450 double-beam spectrophotometer using BaSO_4 as a reference. (SCS, Goa University)*

2.3.3 Magnetic resonance spectroscopy: EPR versus NMR

The Electron Paramagnetic Resonance (EPR) and Nuclear Magnetic Resonance (NMR) spectroscopic techniques involve the interaction of magnetic dipoles with an external magnetic field, using electromagnetic radiation of a suitable wavelength. NMR deals with splitting the nuclear spin states in a magnetic field, while EPR is concerned with splitting electronic spin states. The electron magnetic dipole in EPR arises from one or more unpaired electrons. The

EPR technique (Microwaves) requires a higher frequency of electromagnetic radiation than the NMR (radio waves). The most common ‘X-band’ EPR uses a 9.5 GHz microwave frequency and an applied field of 0.3 T. To overcome the much faster relaxation time in the EPR technique, unlike in NMR, the sample has to be frozen to observe the spectrum, and often the lines in the EPR spectra are much broader [9].

Instrument specification: The ^1H NMR and ^{13}C NMR spectra were recorded on a) Bruker Avance III 400 MHz NMR spectrometer (SCS, Goa University), b) Bruker Avance Neo 400 MHz (IIT Goa). The EPR spectrum is recorded on Jeol model JES FA200 spectrometer at a microwave field frequency of 9.5GHz and a modulation frequency of 100 kHz (IIT, Madras)

2.3.4 Electron Spray Ionization Mass (ESI-MS) spectroscopy

ESI-MS has become an important characterization tool in biochemistry, pharmaceuticals, and catalysis. This technique is used to analyse polar analytes such as low molecular weight amino acids, macromolecules, synthetic and natural polymers, which are ionizable using ESI. Applying high voltage through a liquid passing through a capillary and the high electric field generated atomizes the liquid into a fine spray of charged droplets. As the droplets evaporate, polar molecules dissolved in the liquid are ionized and brought into the gas phase, a phenomenon known as electrospray ionization (ESI). The gaseous ions are then analysed by mass spectrometry to determine their molecular mass and chemical structures. This technique can probe the solution-phase stability of catalytic species, intermediates, and compounds under near-real conditions in homogeneous catalysis [10].

Instrument specification: The stability of compounds **1** and **2** in acetonitrile was determined for catalytic purposes using an Xevo G2-XS QT instrument (IIT Ropar)

2.3.5 X-Ray Photoelectron spectroscopy (XPS)

XPS enables the study of surface reactions under vacuum conditions. It offers information regarding the chemical composition of material surfaces within 10 nm, along with the nature of elements, with detection sensitivity of 0.1-1 at% for all elements except for H and He, making it a suitable tool for surface characterization and corrosion evaluation. The X-rays are irradiated onto the surface of the material, after which the kinetic energy of the photoelectrons emitted from the sample is measured under an ultra-high vacuum. Using the KE, the binding energy (BE) is calculated using the following equation;

$$BE = h\nu - KE - \phi \dots\dots\dots(1)$$

($h\nu$ = Photon energy, ϕ = work function of the spectrometer)

This technique was employed to determine the oxidation state of cobalt in compound **1**. As the oxidation state of the metal increases, the core electrons experience a higher effective nuclear charge; consequently, the core electrons are held more tightly, thus increasing the binding energy [11].

Instrument specification: The XPS spectrum for the compound **1** was recorded on PHI 5000 Versa Probe II instrument (ACMS, IIT Kanpur)

2.3.6 CHNS Elemental analyses

The CHNS elemental analysis determines the percentage of Hydrogen, Carbon, Nitrogen, and Sulphur in the materials. It is based on the classical Pregl-Dumas method. The combustion process occurs in an oxygen-rich environment (Furnace 1150 °C) and proceeds with the conversion of carbon to CO₂, hydrogen to H₂O, nitrogen to N₂ gas/oxides of nitrogen (NO_x), and sulphur to SO₂. The combustion products are carried to the combustion chamber using inert carrier gas, such as helium, which consists of high-purity copper. The function of the copper is to eliminate unused oxygen in initial combustion and to convert any oxides of nitrogen to N₂. The gases are then passed through absorbent traps. The gases are quantified using thermal conductivity detectors (TCD). The calibration for each element is performed by using high-purity compounds such as sulphanilamide and benzoic acid [12].

Instrument specification: The chemical composition of the samples was studied using a Variomicro CHNS cube elemental analyser. (SCS, Goa University)

2.3.7 X-Ray diffraction techniques (XRD)

X-Ray diffraction is a robust tool for determining the structure of crystalline materials. The two commonly used diffraction techniques in elucidating the molecular structure are Single-crystal X-ray Diffraction and Powder diffraction techniques.

a) Single crystal X-ray diffraction technique (SCXRD)

The key requirement for structural analysis is obtaining a suitable single crystal. Ideally, the selected crystals should be small, transparent, and have well-defined and sharp edges. Furthermore, a polarizing microscope helps to distinguish single crystals from macroscopically twinned ones. Upon selection of the crystal, it is mounted on the goniometer, which can be rotated to change the orientation of the crystal concerning the beam of X-rays. The X-rays

generated (Sealed tube) are filtered to produce monochromatic radiation, collimated to concentrate, and subjected to the sample. The X-ray falls on different Bragg's planes having a spacing d and making different angles with the incident direction of X-rays. The constructive interference occurs for some value of d , λ , and θ , which satisfy Bragg's condition, $2d \sin\theta = n\lambda$. This causes the intensity to increase in a particular direction, producing a diffraction pattern [13].

Instrument and software specification: The X-ray intensity data were collected by using Bruker D8 Quest Eco at room temperature (296 K) using a graphite monochromated Mo- α radiation ($\lambda = 0.71073$), at the School of Chemical Sciences, Goa University, for compounds **1-16**. The program suite APEX 3 (version 2019.1) and 4 (version 2021.10.0) structures were solved with the SHELXT programme, and subsequent refinement was performed using full-matrix least-squares on F^2 with SHELXL [14,15]. The anisotropic thermal parameters were used for all non-hydrogen atoms. The H-atoms attached to the aromatic rings were introduced in calculated positions and included in the refinement by riding on their respective parent C-atoms. The hydrogen bonding parameters were obtained from the WinGX suite (version 2021.3) [16]. The crystal structure visualization software, such as Dimond (version 2.1e) and Mercury (version 2024.3.1), was used to visualize and draw molecular pictures [17,18]. The detailed structure protocols and their check CIF/PLATON reports are given in Appendix III.

b) Powder X-ray diffraction technique (PXRD)

Analysis of the powdered sample provides important information regarding phase identification, sample purity, crystallite size, and, in some cases, morphology. One of the most valuable applications of PXRD in coordination polymers is phase identification, which is achieved by comparing the experimental pattern with a reference pattern that is either simulated or obtained from the database. An unambiguous and complete match between the simulated and experimental data confirms the formation of a pure bulk phase [19]. The XRD patterns can be simulated directly from the crystallographic data using software programs such as Mercury, which also accounts for preferred orientation. The powder pattern of the compounds **1-16** is simulated using the crystallographic information files in Mercury software.

Instrument specification: The experimental data are collected on a RIGAKU SMARTLAB powder diffractometer equipped with Cu- α radiation ($1.5418 \text{ \AA}$) with a Ni filter at the Material Characterization laboratory, Goa University. The data for compounds **12** and **13**

were recorded using RIGAKU ULTIMA IV diffractometer equipped with Cu-K α radiation (1.5418 Å) with a Ni filter (BITS PILANI GOA CAMPUS, Goa).

2.3.8 Thermal Analysis (TA)

Thermal analysis is a group of techniques that monitor changes in a samples physical or chemical properties over time, as it is subjected to a temperature program. These techniques include Thermogravimetric analysis (TGA), Differential thermal analysis (DTA), and Differential scanning calorimetry (DSC) [20].

a) The Thermogravimetric Analysis (TGA): It measures the mass of the sample over time and temperature. The analyzer comprises a precise micro balance connected to a sample pan inside a furnace with a temperature programmer and controller-thermo-balance. A thermocouple is placed near the sample pan to monitor the sample temperature. A dynamic purge gas is passed over the sample to create a controlled atmosphere around the sample during decomposition. Additionally, the capillary gas is supplied in the chamber depending upon the experiment type, and may be oxidizing, inert, or reducing in nature. An oxidizing atmosphere (air, oxygen) enables the study of oxidative degradation or combustion behaviour of the organic matter and oxidizing metals. An inert atmosphere (nitrogen, argon) is used to study the pyrolysis and thermal stability of the compounds. Reducing gases like hydrogen or carbon monoxide generally stimulates a reduced environment.

b) Derivative Thermogravimetry (DTG): The first derivative of the weight loss profile. The peaks of the DTG correspond to the inflection points. The point at which the rate of mass loss (dW/dT) changes most rapidly. This technique is employed to get clearer insights into multi-step decomposition and to resolve closely overlapping thermal events.

c) Differential Thermal Analysis (DTA): It analyzes the temperature difference between a sample and an inert reference material as they are heated simultaneously under identical thermal conditions. Any thermal event in the sample, such as decomposition, crystallization, melting, or phase transition, results in either the release or absorption of heat, consequently leading to a temperature difference. This temperature difference is plotted against the temperature over time.

Instrument specification: The TGA and DTA were simultaneously determined using a Netzsch STA 409 analyzer in the RT to 800 °C temperature range.

2.3.9 Scanning Electron Microscopy (SEM)

It is a high-resolution imaging technique that uses a focused beam of high-energy electrons generated by an electron gun to scan the surface of a sample, producing detailed 3D-like images of its surface morphology, topography, and composition. When the electrons hit the surface of the material, they lead to the generation of secondary electrons, which are used to generate high-resolution surface images. The backscattered electrons give the atomic number contrast. Additionally, the X-Rays generated are used for elemental analysis *via* (EDX) energy-dispersive X-Ray spectroscopy.

Instrument specification: The SEM images were collected from a Carls-Zeiss Evo Scanning Electron Microscope operating at 20 kV (Goa University).

2.3.10 Magnetometry techniques

Superconducting Quantum Interference Device (SQUID) is used to determine the magnetic moment of a sample with significantly high sensitivity. It comprises two superconductors separated by thin insulating layers to form parallel Josephson junctions. The basic idea behind this technique comes from the Josephson effect. Brian Josephson, in 1962, discovered that a small current can pass between two superconductors even if a weak barrier exists between them. This phenomenon depends on the Phase difference between the superconducting wave functions. If there is a phase change with time, it generates a voltage. In a SQUID, the phase change is affected by the magnetic flux through the superconducting ring, produced when the sample is moved up and down. Therefore, such a structure can convert magnetic flux into an electrical voltage. This voltage is amplified and read out by the magnetometer's electronics, allowing precise measurement of weak magnetic signals.

SQUID is employed to determine the magnetic susceptibility (χ), which is a quantity related to magnetization (M) in a material under an applied magnetic field (H). Diamagnetism occurs in all materials and contributes very weakly to the susceptibility (10^{-6} to 10^{-5}); hence, it is ignored. Unlike the diamagnetic response in the magnetic field, paramagnetic materials may undergo a symmetry-breaking transition to a magnetically ordered state. However, at relatively higher temperatures, due to thermal fluctuations, the material exists in a magnetically disordered state. This behaviour is described by the Curie-Weiss law [21].

$$\chi = \frac{C}{T - \theta_{cw}} \dots\dots\dots(2)$$

Where C = Curie constant and θ_{cw} = Curie-Weiss temperature.

Instrument specification: Zero Field Cooling (ZFC) and Field Cooling (FC) were performed on a Quantum Design, MPMS-3-SQUID -VSM magnetometer in the temperature range of 10-300 K under an applied field of 1000 Oe (IISER Bhopal)

2.4 Experimental procedure for catalytic transformation of 3,5-DTBC substrate.

The catecholase-like activity of compounds **1** and **2** bearing monodentate benzoate ligands in *cis* and *trans* conformation, respectively, was evaluated utilizing 3,5-di-*tert*-butyl catechol (3,5-DTBC) as the model substrate in dioxygen-saturated acetonitrile solution. The oxidation process was monitored using a UV-Vis spectrophotometer for 30 minutes, and an increase in band intensity, attributed to quinone formation at 400 nm [22], was observed. In a typical experiment, 100 equivalents of 3,5-DTBC substrate in acetonitrile solution were added to a 0.5 mM solution of compounds **1** and **2**. Kinetic evidence was collected to analyse the dependence of the rates on the substrate concentration. The experiment involved the addition of a 0.5 mM solution of compound **1** to varying substrate concentrations, ranging from 20 to 100 equivalents, in acetonitrile under aerobic conditions at room temperature. The kinetic data were treated with the Michaelis-Menten model. The kinetic parameters, such as (V_{max}), binding constant (K_m), and turnover number (K_{cat}), were extracted from the Lineweaver-Burk plot.

2.5 General experimental procedure for catalytic activity of zinc-based CPs

Coordination polymers have emerged as promising heterogeneous catalysts for the Knoevenagel condensation. The properties of CPs have been explored in such reactions due to their high activity, selectivity, and facile recovery. Knoevenagel condensation is a C-C bond-forming reaction that includes condensation between an aldehyde/ketone and an active methylene compound and is usually catalysed by bases or acids. CPs offer a bifunctional catalytic site consisting of both Lewis acid and Lewis base in a single material, thus playing a critical role in activating the reagents, leading to more diversified substrate interactions and driving towards a more efficient reaction [23].

In this thesis, we have employed two zinc catalysts for the Knoevenagel condensation reaction compounds **5** and **6**. In a typical catalytic reaction, a mixture of aldehyde and malononitrile, and the zinc catalyst was placed in a 5 mL glass vial. To the resultant mixture, 1 mL of THF solvent was added and stirred for 2 hours at room temperature. The reaction was monitored every 5 minutes using TLC to track the consumption of the benzaldehyde. The solution was quenched after 30 minutes by adding 2 mL of DCM solvent. The solution was evaporated under vacuum to give the crude product 2-(phenylmethylene)malononitrile using the rotary evaporator. Using column chromatography, the crude compound was purified using a 10% EtOAc/PET solvent system. The purified products obtained were analysed using ¹H-NMR spectroscopy. At room temperature, the same reactions were carried out in 1 mL of distilled water instead of THF solvent. The solid product was thrown out of the water as the compounds are insoluble in aqueous conditions. The solid was filtered and air-dried.

Compound **5** was also tested for its catalytic activity in condensing a novel aldehyde, 5-Chloro-2-phenyloxazole-4-carboxyaldehyde, with malononitrile in an aqueous medium. The aldehyde under investigation was prepared by *Mr. Nitesh Venji*, PhD student of *Dr. Vinod Mandrekar* (SCS, Goa University). The pure product obtained after purifying on a column was analysed using ¹H-NMR spectroscopy and the single-crystal X-ray diffraction technique.

2.6 Description of the antibacterial activity

The antibacterial property of compound **1** was determined using Gram-positive *S. aureus* ATCC 25923 and Gram-negative *E. coli* ATCC 25922. The *E. coli* and *S. aureus* were inoculated in two separate flasks containing 25 mL of nutrient broth. After allowing 24 h of incubation, 100 µL of inoculum was spread plated on nutrient agar plates in triplicate and allowed for adsorption for 30 min. The stock solutions of prepared compound **1** (1 mg/mL) were prepared in a DMSO and water solvent mixture (1:1). The minimal amount of limiting the pathogens was determined by preparing different concentrations of **1** (10-1000 µg/mL). Nalidixic acid (10 µg/mL) (Positive control) and DMSO: H₂O (negative controls). The cyclam, Co(OAc)₂·4H₂O, benzoic acid, compound **2**, and Ni(OAc)₂·4H₂O were evaluated for antibacterial activity at 1 mg/mL concentration. Each concentration was added to 6 mm wells bored on nutrient agar plates marked appropriately. The plates were kept in the BOD incubator at 37°C. After 24 h, each plate was monitored for zones of growth inhibition in mm or no growth around the wells. The results were expressed as mean ± standard error for all experiments.

2.7 Description of the isostructurality studies

The structural similarity of related compounds can be evaluated by looking at the unit cell parameters. For two compounds to exhibit isostructurality, they must exhibit similar crystal structure, which is also reflected in their unit cell parameters, but may differ slightly in their chemical composition. Often, it is mistakenly assumed that two crystals showing similar unit cell parameters can be classified as isostructural compounds. However, this is not always true for all related compounds, as various factors influence their structural features. Therefore, studying the extent of isostructurality among related compounds is essential. This can be achieved using numerical descriptors, such as the unit cell similarity index and the isostructurality index, and by performing the isometricities studied. The ISOS program[24] is a reliable tool employed in crystallography to examine the isostructurality between related crystal structures by comparing their atomic coordinates and unit cell parameters. It provides a quantitative index to help assess the extent to which the structures are similar, allowing researchers to evaluate subtle packing differences and structural distortions. However, its validity depends on careful selection of the atom and interpretation, as it strictly accounts for symmetry differences, conformational changes, or variations in the intermolecular interactions[25,26].

Unit cell similarity index (π) is a quantitative measure used to evaluate the extent of similarity between two unit cell parameters.

$$\Pi = \left| \frac{a+b+c}{a'+b'+c'} - 1 \right| \dots\dots\dots(3)$$

where a , b , and c , and α , β , and γ are lattice parameters of two related crystals. In cases where the crystals show great similarity in the lattice parameters, the π value attains a value close to zero.

The isostructurality index (I_s) of compared crystals can be determined using the formula.

$$I_s(n) = \left| \left[\frac{\sum (\Delta R_i)^2}{n} \right]^{1/2} - 1 \right| \times 100 \dots\dots\dots(4)$$

ΔR_i is the distance difference between their atomic coordinates, and n is the number of related non-hydrogen atoms. The larger percentage signifies higher isostructurality for the pair of associated crystals. The isometricities of the compared molecular moieties were evaluated using Mercury software by superimposing the structures and determining the root mean square of the distance difference of the related atoms (rmsD) and the largest distance difference(maxD) between them. [25-28]

2.8 Description of the Hirshfeld surface analysis studies

The Hirshfeld surface method has proven to be a powerful tool for understanding the intermolecular interactions in molecules in a crystal lattice. These surfaces can be calculated using *CrystalExplorer* software, which primarily visualizes and investigates molecular crystal structure [29]. Five functions of curvature and distance can be used to map Hirshfeld surfaces, which include d_i representing distance from the surface to the nearest atom interior to the surface, d_e representing the distance from the surface to the nearest atom exterior to the surface, d_{norm} , shape index, and curvedness. The d_{norm} combines d_e and d_i for specific atoms in close contact with the surface. Equation 5 normalizes each of the contacts by the Van der Waals (vdW) radius (r_i^{vdw} , r_e^{vdw}) representing the *vdW* radii of the atoms closest to the points inside and outside the surface. *CrystalExplorer* can interactively generate the 2D fingerprint plots, which are used to identify the key contributors to these intermolecular interactions. The interactions between the molecules can be quantitatively studied based on the color-mapping of functions of the Hirshfeld surface (HS). The red and blue spots represent distances indicating shorter and longer contacts. At the same time, the white color denotes contacts with distances equal to the sum of van der Waals radii of the atoms [30].

$$d_{norm} = \frac{d_i - r_i^{vdw}}{r_i^{vdw}} + \frac{d_e - r_e^{vdw}}{r_e^{vdw}} \dots \dots \dots (5)$$

where r_i^{vdw} and r_e^{vdw} are the van der Waals radii of the atoms.

2.9 Synthetic procedures for metal compounds 1-16

a) Synthesis of *cis*-[Co(cyclam)(Bz)₂](Bz)·H₂O (1)

(2 mmol, 0.24 g) of benzoic acid was added to 25 mL of hot distilled water, and stirred until a clear solution was obtained. To this solution, (1 mmol, 0.25 g) of Co(OAc)₂·4H₂O was added and stirred for 30 minutes until the solution turned pink. To the resultant mixture, (1 mmol, 0.20 g) of 1,4,8,11-tetraazacyclotetradecane (cyclam) was added. This reaction mixture was further allowed to stir for another 30 minutes at 80 °C. After adding cyclam, the solution slowly turned from pink to reddish brown, and finally turned purple upon stirring for 30 minutes. The purple solution was kept at room temperature for crystallization. After a week, purple plate-shaped crystals were seen growing on the walls of the beaker. These crystals were isolated, washed with cold distilled water, and air dried. Yield: 36 % (0.23 g)

b) Synthesis of *trans*-[Ni(H₂O)₂(cyclam)](OMeBz)₂·2H₂O (2**)**

(2 mmol, 0.3 g) of *o*-methoxybenzoic acid was added to 25 mL of hot distilled water, and stirred until a clear solution was obtained. To this solution, (1 mmol, 0.249 g) of Ni(OAc)₂·4H₂O was added and stirred for 30 minutes until the solution turned green. To the resultant mixture, (1 mmol, 0.20 g) of cyclam was added. This reaction mixture was further allowed to stir for another 30 minutes at 80 °C. The solution slowly turned from green to purple upon stirring for 30 minutes. The purple solution was kept at room temperature for crystallization. After a week, purple plate-shaped crystals were isolated from the solution, washed in cold distilled water, and air dried. Yield: 61 % (0.36 g).

c) Synthesis of *cis*-[Mn(cyclam)(Bz)₂]·H₂O (3**) and *trans*-[Mn(cyclam)(Bz)₂]·(Bz·HBz) (2HBz) (**3a**)**

(2 mmol, 0.24 g) of benzoic acid was added to 25 mL of hot distilled water, and stirred until a clear solution was obtained. To this solution, (1 mmol, 0.24 g) of Mn(OAc)₂·4H₂O was added and stirred for 30 minutes. To the resultant mixture, (1 mmol, 0.20 g) of cyclam was added. This reaction mixture was further allowed to stir for another 30 minutes at 80 °C. The solution slowly turned from colourless to lemon green after adding cyclam. The solution was kept at room temperature for crystallization. After a few weeks, two different coloured crystals, colourless block-shaped crystals (**3**) and green plate-shaped crystals (**3a**), were seen isolated from a yellowish viscous liquid. The colourless crystals were isolated from the mixture, washed with distilled water and ethanol, and air dried.

d) Synthesis of *trans*-[Zn(H₂O)₂(cyclam)](Bz)₂ (4**), [Zn₂(μ-H₂O)₂(cyclam)(MeBz)₄] (**5**) and [Zn₂(μ-H₂O)₂(cyclam)(MeOBz)₄] (**6**)**

To three separate beakers containing 25 ml of distilled water, were added (2 mmol, 0.24 g) of benzoic acid (**4**), (2 mmol, 0.27 g) of *o*-methyl benzoic acid (**5**), and (2 mmol, 0.3 g) of *o*-methoxy benzoic acid (**6**). The solutions were stirred for 30 minutes until a clear solution was obtained. (1 mmole, 0.22 g) zinc acetate dihydrate was added to each beaker and stirred for another 15 mins. Cyclam was then added to the resultant mixtures (1 mmole, 0.2 g) and allowed to react for 30 mins. The temperature was kept at 80°C throughout the reaction process. Fine crystalline powder was initially formed in the case of solutions **5** and **6**, which was later dissolved by adding 1 ml of DMF solvent. After a few days, block-shaped colorless crystals were obtained from solution **4**, and fine needle-shaped colorless crystals were isolated from

reactions **5** and **6**. The crystals were isolated and washed in cold distilled water and later air-dried. The yield of compounds **4** = 0.28 g (52%), **5** = 0.15g (36 %), and **6** = 0.18g (41 %).

e) Synthesis of *trans*-[Zn(cyclam)](OHBz)₂ (7**) and *trans*-[Zn(cyclam)](NO₂Bz)₄ (**8**)**

Compounds **7** and **8** were obtained using a method employed to prepare **4**. The only difference lies in the source of acid, (2 mmole, 0.28 g) *o*-hydroxybenzoic acid and (2 mmole, 0.33 g) *o*-nitrobenzoic acid, were used in the preparation of compounds **7** and **8**, respectively. After a week, colourless block-shaped **7** and pale-yellow plate-shaped crystals of **8** were isolated from the reaction mixture. Later, the crystals were washed with cold distilled water and air-dried. The yield of compound **7** = 0.35 g (65 %) and **8** = 0.24 g (40 %).

f) *trans*-[Zn(H₂O)₂(cyclam)](ClBz)₂ (9**), *trans*-[Zn(H₂O)₂(cyclam)](MeSBz)₂·4H₂O (**10**), and *trans*-[Zn(H₂O)₂(cyclam)](NH₂Bz)₂ (**11**)**

A similar synthetic procedure was applied in preparing 9-11, as used in synthesizing compound **5**. The acids used herein were (2 mmole, 0.34 g) *o*-chlorobenzoic acid (**9**), (2 mmole, 0.34 g) *o*-methy(thio) benzoic acid (**10**), and (2 mmole, 0.27 g) *o*-amino benzoic acid (**11**), respectively. After a few weeks, colorless block-shaped crystals were isolated from the solutions of **9** and **10**, while dark brown-red crystals were isolated from the solution using *o*-aminobenzoic acid as a reactant. The crystals were washed with cold distilled water and air-dried. The yield of compounds **9** = 0.30 g (49 %), **10** = 0.42 g (59 %), and **11** = 0.21 g (37 %).

g) Synthesis of [Ni(H₂O)₂(μ-pyz)(μ-fum)] (12**)**

A 20 mL solvent containing (2 mmole, 0.48g) nickel acetate tetrahydrate was added (2 mmole, 0.23g) fumaric acid. The reaction was heated at 80 °C and stirred for 30 minutes to form a homogeneous solution. The solution was then cooled to room temperature, and pyrazine (4 mmole, 0.32g) was added. The clear blue solution obtained after the addition was divided into two sections. 10 mL of the solvent was kept at room temperature for slow evaporation, while the other 10 mL of the mixture was transferred into a Teflon cup (25 mL capacity), which was packed in a stainless-steel autoclave reactor and subjected to heating in a temperature programmable oven at 100 °C for 24 hours. The cooling rate of the oven was 10 °C/hour. The same procedure was used in the presence of different solvent systems for the optimization process. Blue rod-shaped crystals were obtained from the solution kept at room temperature, and the hydrothermal setup comprised water as the solvent. The crystals were isolated, washed

with distilled water, and air dried. Yield of **12** obtained *via* the slow evaporation method 0.09 g (41%) and *via* Hydrothermal method = 0.07 g (33 %)

h) Synthesis of $[\text{Ni}(\text{H}_2\text{O})_2(\mu\text{-pyz})(\mu\text{-suc})]$ (13**)**

A procedure similar to **12** was adopted to synthesize compound **13**. Only the acid reactant was switched to (2 mmole, 0.23g) succinic acid. The clear blue solution obtained after the addition was divided into two sections. 10 mL of the solvent was kept at room temperature for slow evaporation, while the other 10 mL of the mixture was transferred into a Teflon cup (25 mL capacity), which was packed in a stainless-steel autoclave reactor and subjected to heating in a temperature programmable oven at 100 °C for 24 hours. The cooling rate of the oven was 10 °C/hour. The different solvent systems for the optimization process. Blue block-shaped crystals were obtained from the solution subjected to a hydrothermal setup. The crystals were isolated, washed with distilled water, and air dried. Yield of **13** = 0.07g (32 %)

i) Synthesis of $[\text{Ni}(\text{H}_2\text{O})_2(\text{pyz})(\text{ida})]$ (14**) and $[\text{Ni}(\mu\text{-pyz})(\mu\text{-ida})]\cdot 2\text{H}_2\text{O}$ (**15**)**

A procedure similar to **12** was adopted to synthesize compounds **14** and **15**. The acid component was switched to (2 mmole, 0.26g) iminodiacetic acid. The clear blue solution obtained after the addition was divided into two sections. 10 mL of the solvent was kept at room temperature for slow evaporation, while the other 10 mL of the mixture was transferred into a Teflon cup (25 mL capacity), which was packed in a stainless-steel autoclave reactor and subjected to heating in a temperature programmable oven at 100 °C for 24 hours. The cooling rate of the oven was 10 °C/hour. The different solvent systems for the optimization process. The slow evaporation method resulted in the formation of blue plate-shaped crystals (**14**) (yield = 0.15g (65%)), whereas the solution, subjected to a hydrothermal setup, gave green needle-shaped crystals (**15**) (Yield = 0.068g (30%). The crystals were isolated, washed with distilled water, and air-dried before recording the yield.

Caution: The autoclave reactors must be opened only after they have attained room temperature.

j) Synthesis of $[(\text{VO}(\text{Terpy}))_4(\text{MoO}_4)_2(\text{Mo}_8\text{O}_{26})]$ **16**

Sodium metavanadate (0.046 g, 0.38 mM) and terpyridine (0.116 g, 0.497 mM) were taken in a beaker and added to 10 mL of distilled water. The pH of the mixture was adjusted to ~3 by adding a solution containing 6 mL of acetic acid and Molybdic acid (0.094 g, 0.58 mM). The contents of the beaker were transferred into a 25 mL Teflon cup. The Teflon reactor vessel was

fitted inside a stainless-steel autoclave and tightly closed. The autoclave was kept in a temperature-programmed oven, which was slowly heated to attain 200 °C for 67.5 h. The Teflon vial was carefully removed from the autoclave, and its contents were filtered to obtain (0.092 g) dark green blocks of **16**.

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Chapter 3: Cobalt (III), Nickel (II), and Manganese (II)/(III) cyclam compounds appended with carboxylate molecules: Synthesis, Characterization, and Applications

3.1 Chapter overview

Chapter 3 presents the synthesis and characterization of three mononuclear compounds, namely, *cis*-dibenzoato(1,4,8,11-tetraazacyclotetradecane)cobalt(III)benzoate monohydrate, *cis*-[Co(cyclam)(Bz)₂](Bz)·H₂O (**1**), *trans*-diaqua(1,4,8,11-tetraazacyclotetradecane)nickel(II) methoxybenzoate tetrahydrate *trans*-[Ni(cyclam)(H₂O)₂](MeOBz)₂·4H₂O (**2**), *cis*-dibenzoato(1,4,8,11-tetraazacyclotetradecane)manganese(II) hydrate, *cis*-[Mn(cyclam)(Bz)₂]·H₂O (**3**), and *trans*-dibenzoato(1,4,8,11-tetraazacyclotetradecane)manganese(III) (benzoate) (benzoic acid), *trans*-[Mn(cyclam)(Bz)₂](Bz·HBz)·2(HBz) (**3a**) Section 3.2 reviews literature on the mixed ligand transition metal compounds that feature compounds comprising N-donor macrocyclic ligands with various O-, N-donor auxiliary ligands. It also discusses the influence of the auxiliary ligands on the structural properties of the mixed metal compounds. Section 3.3 discusses the synthesis aspects and the analytical techniques used to study the compounds, which include elemental analyses and various spectroscopic techniques (IR, UV-Vis, NMR, ESI-mass), X-ray diffraction techniques, and thermogravimetric analysis. Section 3.4 Insights into the non-covalent interactions in **1** and **2** using Hirshfeld surface analysis. Section 3.5 evaluates compounds **1** and **2** for their ability to mimic catechol oxidase activity using 3,5-di-*tert*-butyl catechol (3,5-DTBC) as the model substrate. Section 3.6 presents the findings on the antibacterial properties of compounds **1** and **2**, assessed against the Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli* bacterial strains.

3.2 Literature survey on mixed ligand compounds comprising N-donor macrocyclic linkers

The architectural and functional attributes of the transition metal-based supramolecular compounds, comprising macrocyclic linkers, have attracted immense attention in bioinorganic chemistry. These compounds are explored for their roles in catalysis, such as hydroamination [1], electrochemical conversion of CO₂ to CO [2], C-H bond activation *via* dioxygen activation [3], as molecular sensors for the detection of small molecules, ions and gases [4-7], molecular magnetic materials [8,9], and biological applications [10]. Compared to the open-chain analogs, the macrocyclic ligands coordinate *via* a chelating coordination mode to offer

outstanding thermodynamic and kinetic stability to the metal complex [11]. Among the wide variety of macrocyclic ligands, saturated cyclam linkers are particularly notable for their frequent use in preparing metal complexes, with diverse functional properties [12,13]. This interest is reflected in a survey of the Cambridge Structural Database (CSD, version 5.46), which reveals about 120 unique entries of crystal structure of mixed ligand compounds that include a metal cyclam core and carboxylate molecules as co-ligands. The co-ligands in mixed ligand compounds are often known to influence the conformation of macrocyclic ligands around the metal ion [14].

Studies of similar compounds show that the cyclam can adopt six conformations, with the *trans*-III (S,S,R,R) conformation being the most stable in the solid state [15,16]. The interaction of the co-ligand with the metal and the cyclam significantly influences the conformation of the macrocyclic ligand. As a result, metallocyclams can serve as effective recognition probes for proteins and small anions. The two key contributing factors are i) kinetic inertness of the metal-cyclam core, which tends to resist demetallation, and ii) the availability of unsaturated sites that allow the binding of the anions without any steric constraints [17]. For instance, Liang and coworkers showed that the anions play a decisive role in the conformational preference of Zn(II)-cyclam complexes. It was found that the acetate stabilized the *cis*-V conformation in aqueous medium more effectively than the chloride or perchlorate anions, thus highlighting the importance of the choice of anions leading to the rich structural diversity [18]. Similarly, Cook and coworkers investigated how the minor structural changes in the cyclam backbone can affect the catalytic activity of nickel cyclam compounds. A series of Ni(II) cyclam compounds comprising substituted cyclam ligands was investigated for electrocatalytic CO₂ and H⁺ reduction in an aqueous organic medium. It was inferred that the phenyl-substituted cyclam adopted a *trans*-I conformation, which resulted in poor axial ligand coordination in the solid state. In contrast, the unsubstituted cyclam adopts the typical *trans*-III conformation, which readily favors the axial ligands. This shift in conformation affected the accessibility of the Ni redox state and altered the strength of substrate interactions at the axial sites, ultimately enhancing the catalytic activity [19].

As auxiliary ligands, carboxylates are particularly interesting because they adopt versatile coordination modes, resulting in rich structural diversity [20]. Using carboxylate ligands as co-ligands for fine-tuning the geometry of the metal and macrocyclic conformation can be useful

in designing novel biomimetic catalysts. Catechol oxidase is a well-known enzyme that catalyzes the oxidation of *o*-diphenols to the corresponding *o*-quinones. The enzyme's metal active site features a hydroxo-bridged dicopper (II) core, with each copper ion coordinated to three histidine residues in a trigonal pyramidal geometry. Inspired by the active site of the catechol oxidase enzyme, numerous synthetic models are investigated to mimic the catecholase-like activity, including those of manganese, iron, cobalt, nickel, and zinc, under standard laboratory conditions [20,21].

In addition to catalytic activity, cyclam compounds have been explored as antimicrobial agents. The growing concern about antimicrobial resistance has driven interest in exploring new metallodrugs with distinct actions from organic antibiotics, and strategies to boost the effectiveness of present antibiotics by incorporating transition metal ions are a key strategy against resistant infections [22,23]. The active roles of the metal compounds for antibacterial [24,25] and antifungal [26,27] activities are well known. One of the most promising drugs containing Co(III) includes CTC-96, a potent inhibitor of herpes simplex virus type 1 (HSV-1) comprising N and O-donor ligands [28]. Recently, Fang and coworkers reported the cytotoxic and immunogenic-activating properties of cobalt(III)-cyclam complex decorated with flufenamic acid on breast cancer stem cells (CSCs). According to mechanistic studies, the compound induces DNA damage, inhibits cyclooxygenase-2 expression, and promotes caspase-dependent apoptosis in breast CSCs [29]. In this study, we synthesized three metal cyclam-based compounds, *cis*-[Co(cyclam)(Bz)₂](Bz)·H₂O (**1**), *trans*-[Ni(cyclam)(H₂O)₂](MeOBz)₂·4H₂O (**2**), *cis*-[Mn(cyclam)(Bz)₂]·H₂O (**3**), and *trans*-[Mn(cyclam)(Bz)₂](Bz·HBz)·2(HBz) (**3a**). The Hirshfeld surface analysis was carried out to investigate the contribution from the non-covalent interaction. Compounds **1** and **2** were further analyzed to mimic catechol oxidase enzyme and assess their potential to act as antibacterial agents.

3. 3 Results and discussion

3.3.1 Synthetic aspects of compounds

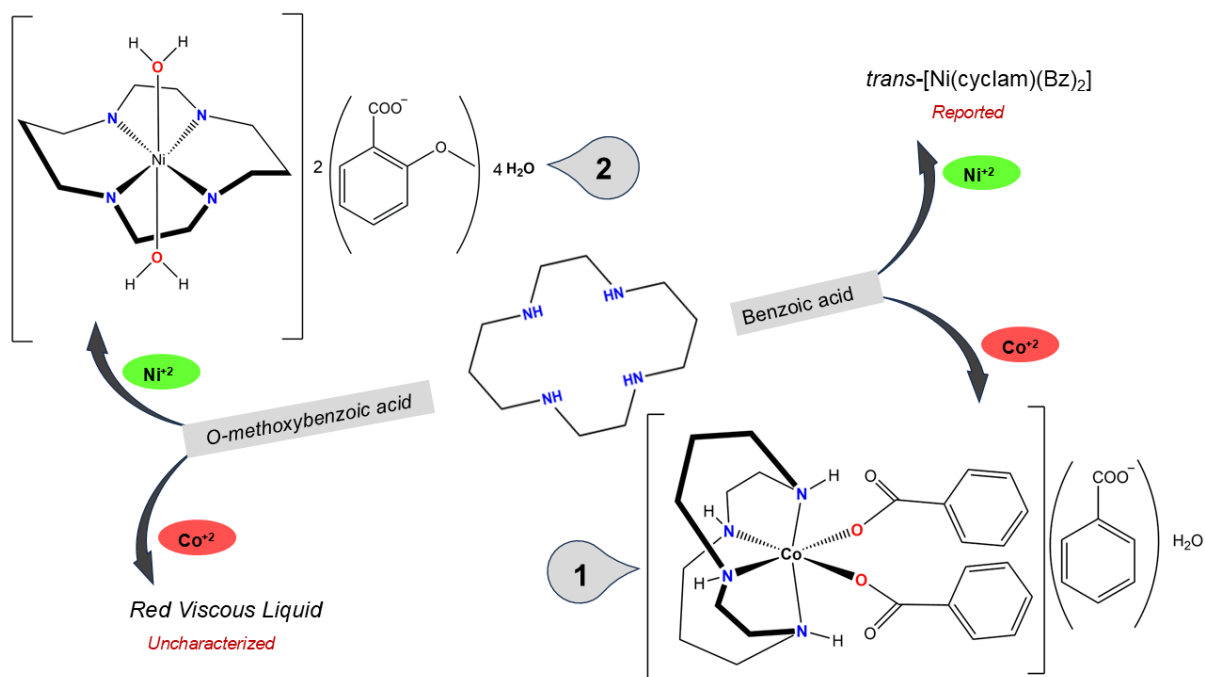
The crystalline compound **1** was synthesized by reacting benzoic acid and cobalt acetate tetrahydrate in a (2:1) ratio (Scheme 1), so as to generate cobalt benzoate salt in situ in the aqueous medium. N-donor linker cyclam was added to the resulting solution, and heated at

80°C on a hot plate to achieve a homogeneous solution. When left undisturbed at room temperature, the solvent evaporated with time yielding purple plate-shaped crystals. Suitable single crystals were chosen for structural analysis. Hasnan and coworkers reported a similar compound using a slightly different synthetic procedure. A dark brown semi-solid compound was reported to form upon reacting $[\text{Co}_2(\text{C}_6\text{H}_5\text{COO})_3\text{Cl}] \cdot \text{H}_2\text{O}$ with cyclam linker. However, no specific structural or spectroscopic aspects of this viscous compound was studied in the article. The viscous product was further reacted with pyridine-based ligands to obtain their desired material, which was later structurally characterized [30,31]. Hence our target was to grow the single crystal of cobalt benzoate and cyclam components and perform its structural analysis.

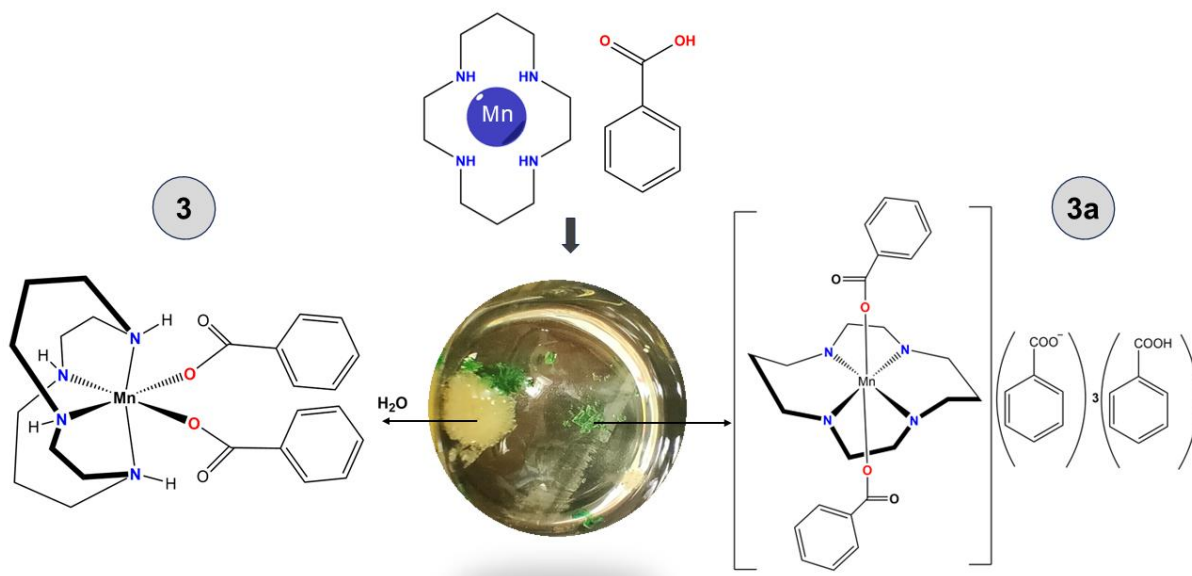
We also attempted the synthesis of a related cobalt compound by switching the benzoic acid with *o*-methoxybenzoic acid, using a similar procedure to compound **1**. Unfortunately, here, we could not observe any growth of the crystals even after the solution was kept for a month. On complete evaporation of the solvent, a red viscous mass was left in the beaker. Since no crystalline material was obtained, the viscous liquid was not investigated further.

The same reactions were carried out using nickel salt in place of cobalt. When nickel was reacted with benzoic acid in presence of cyclam block-shaped purple crystals were obtained. The structural analysis revealed that the crystal data had already been reported *trans*- $[\text{Ni}(\text{cyclam})(\text{Bz})_2]$ (CCDC number = 188536). When *o*-methoxybenzoic acid was used, purple crystals (**2**) were isolated. These single crystals were examined by X-ray diffraction, and the bulk product was characterized using various spectroscopic and thermal techniques.

Finally, we explored manganese salt instead of cobalt as illustrated in Scheme 2. Interestingly, two different crystals were obtained from the same solution during crystallization when benzoic acid was used as the O-donor. The colourless (**3**) and green crystals (**3a**) were carefully isolated from the solution and separated under the microscope to obtain samples for single-crystal X-ray diffraction studies. Of these, only compound **3a** could be examined in preliminary details, as the product often suffered from reproducibility issues, typically yielding a yellow viscous liquid instead of the crystals. Bulk studies of both have been carried out, and further efforts are ongoing to obtain independent crystal phase for detailed investigation. When *o*-methoxybenzoic acid was used, we did not observe growth of any crystalline product.



Scheme 1. Synthetic route for compounds **1** and **2** in aqueous medium using the slow evaporation method.



Scheme 2. Synthesis of **3** and **3a** in aqueous medium using the slow evaporation method.

3.3.2 Elemental analysis

The calculated percentage of carbon, hydrogen, and nitrogen in compounds **1**, **2**, and **3a** agreed with their experimental values, as depicted in [Table 1](#).

Table 1. Elemental analysis data for the synthesized compounds.

Sr. No.	Molecular formula	Molecular Weight	Calculated %	Experimental %
1	CoC ₃₁ H ₄₁ N ₄ O ₇ (1)	640.69	C = 58.11 H = 6.46 N = 8.75	C = 58.45 H = 6.71 N = 9.01
2	NiC ₂₆ H ₅₀ N ₄ O ₁₂ (2)	669.49	C = 46.65 H = 7.54 N = 8.37	C = 46.95 H = 7.85 N = 8.56
3	MnC ₅₂ H ₅₇ N ₄ O ₁₂ (3a)	985.07	C = 63.40 H = 5.84 N = 5.69	C = 62.89 H = 5.78 N = 5.85

3.3.3 Infrared (IR) analysis

The spectra of compounds **1**, **2**, and **3a** were compared with those of the corresponding free acids, benzoic acid and *o*-methoxy benzoic acid, as shown in [Figures 1-3](#), respectively. The absorption bands observed in the IR spectra of all the compounds are listed in ([Table 2](#)). Compound **1** exhibits a broad band at 3415 cm⁻¹, attributed to the O-H stretching vibration in the water molecules. The broadness suggests extensive hydrogen bonding within the crystal lattice. In contrast to the free acid, which shows a carbonyl stretching vibration band at 1690 cm⁻¹, compound **1** showed two sharp bands at a lower frequency. These characteristic features of the carboxylate functional group confirm the deprotonation and coordination of carboxylate moieties. The asymmetric $\nu_{\text{asym}}(\text{COO}^-)$ and symmetric $\nu_{\text{sym}}(\text{COO}^-)$ stretching vibrations of the carboxylate anion in compound **1** arise at 1598-1560 and 1379-1355 cm⁻¹, respectively. Similarly, compound **2** exhibited a broad band between 3585 to 3433 cm⁻¹, again arising from water molecules. Strong absorption between 1652-1537 and 1462-1377 cm⁻¹ corresponds to the stretching vibration of coordinated carboxylate molecules (asymmetric and symmetric), thus confirming the presence of the *o*-methoxybenzoate in the final product. The IR spectrum of compound **3a** shows a broad absorption band around 3275 – 2872 cm⁻¹, typically related to the O-H stretching vibration of acid functionality in the compounds. Also, the presence of a sharp band around 1712 cm⁻¹ suggests the presence of an acid component in the compound. Notably, the (C=O) stretching vibration band appears slightly blue-shifted compared to that of benzoic

acid. This shift arises because the carbonyl group is not involved in the hydrogen bonding, thereby retaining its double bond character, leading to absorption at a higher frequency. Such behaviour has also been reported in the salt cocrystal of benzoate and benzoic acid [32]. Furthermore, the presence of a distinct sharp band around 1537 and 1392 cm^{-1} suggests the incorporation of the deprotonated carboxylate molecules in the compound. These bands are associated with the asymmetric and symmetric stretching vibration of coordinated carboxylate functional groups.

Table 2: The IR absorption bands in synthesized compounds.

Compound	IR data (cm^{-1})
1	3441 (br), 3076 (br), 2872 (br), 1598(s), 1562 (s), 1379 (s), 1355 (s), 1220 (m), 1172(m), 1068 (m), 1024(m), 839 (m), 719 (s), 684 (m) 449 (m).
2	3460 (br), 3255 (m), 2931 (m), 1654 (m), 1537 (s), 1377 (s), 1247 (m), 1101 (s), 989 (m), 769 (s), 655 (m), 567 (m)
3a	3101 (br), 2943 (br), 2887 (br), 1712 (s), 1537 (s), 1454 (m), 1392(s), 1260 (s), 1178 (m), 1097 (m), 1028 (m), 893 (m), 779 (w), 653 (m), 489(m)

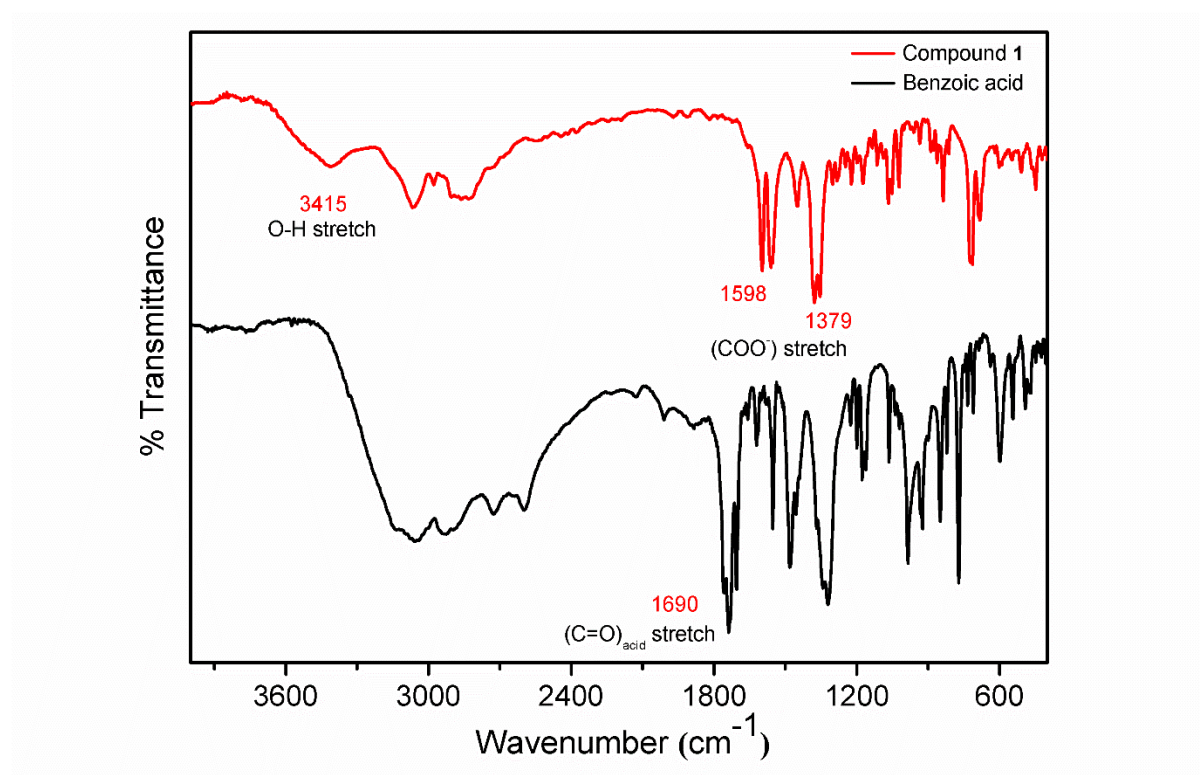


Figure 1 The infrared spectra of compound 1 overlaid with that of benzoic acid.

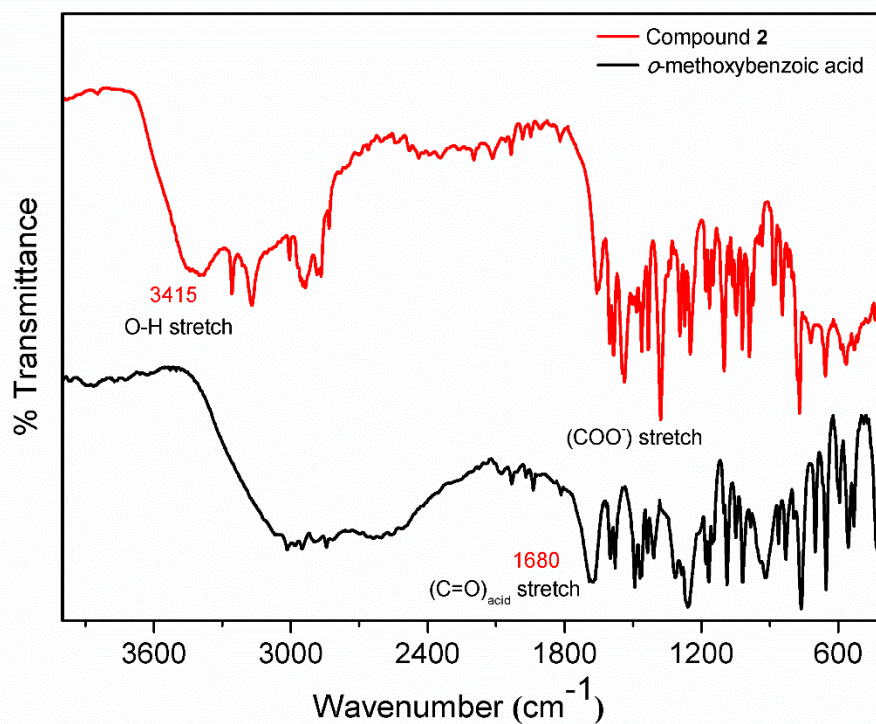


Figure 2 The infrared spectra of compound **2** overlaid with *o*-methoxybenzoic acid.

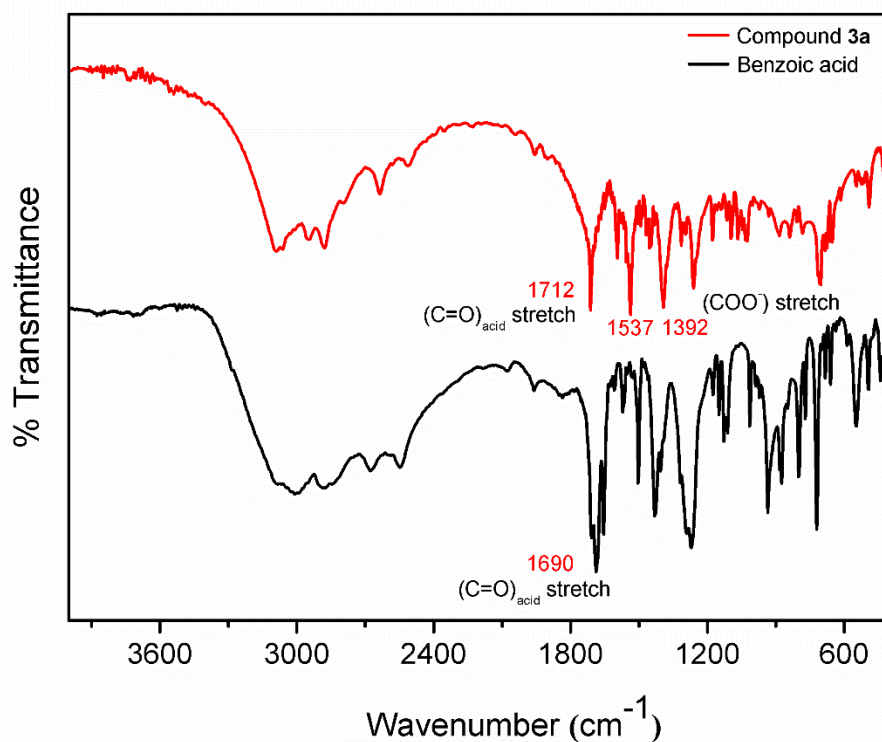


Figure 3 The infrared spectra of compound **3a** overlaid with that of benzoic acid.

3.3.4 Electronic absorption and ESI-MS spectral analysis

At room temperature, the UV-Vis spectra of compounds **1**, **2**, and **3a** (Figure 4) were measured using a 2×10^{-3} M acetonitrile solution. The intra-ligand transitions below 300 nm was attributed to the $\pi\text{-}\pi^*$ or $n\text{-}\pi^*$ transitions originating from the organic moieties. The absorption band in compound **1** appears at 378 nm and 530 nm, assigned to the spin-allowed $d\text{-}d$ transitions ($^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$, respectively) of the octahedral geometry in the diamagnetic spin state, indicating the presence of a low-spin compound [33,34]. In contrast, compound **2** at the same concentration exhibits a very weak shoulder band at around 340 nm and another broad band at 520 nm due to $^3A_{2g}(\text{F}) \rightarrow ^1T_{1g}(\text{F})$ (inset (a) of Figure 4). The $d\text{-}d$ band appearing at 520 nm suggested the presence of a high-spin octahedral Ni(II) ion and is in good agreement with the values reported for similar Ni(II) ions [19,35]. The absorption spectrum of **3a** shows a weak maximum at 354 nm, which is attributed to the ligand-to-metal charge transfer transition. A very weak $d\text{-}d$ absorption band (inset (b) of Figure 4), which is relatively very broad, is observed in the region of 550 to 900 nm characteristic of manganese (III) complexes in the high-spin state [36]. The ESI-MS technique was used to further confirm the solution state stability of the ionic cores of the compound in acetonitrile solvent. A prominent parent peak was observed at $m/z = 501.1717$ (**1**) and 257.1198 (**2**), assigned to $[\text{Co}(\text{cyclam})(\text{Bz})_2]^+$ and $[\text{Ni}(\text{cyclam})]^+$ species in the solution, respectively.

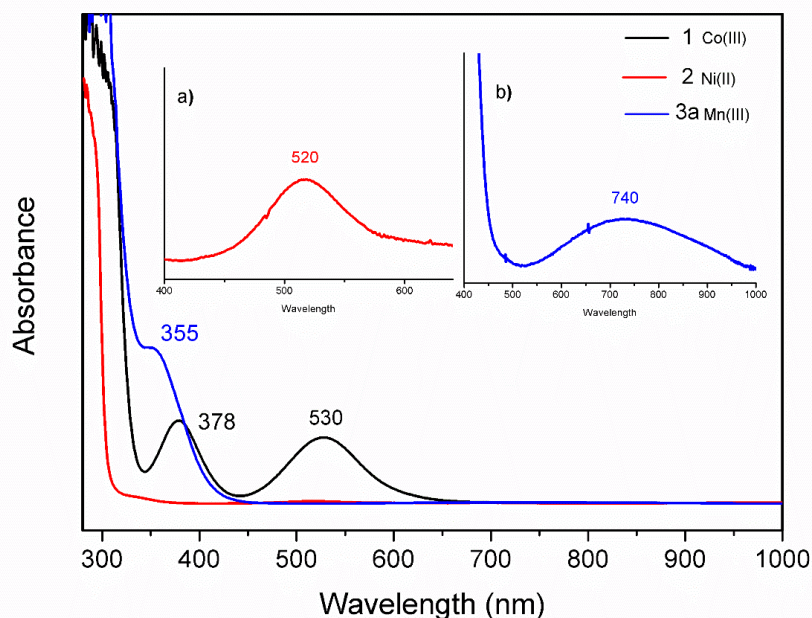


Figure 4. The UV-Vis spectra of a 2 mM ACN solution of compounds **1** (black curve), **2** (red curve), and **3a** (blue curve) were recorded at ambient temperature. The inset (a) and (b) show an enlarged view of the visible region of spectra of compounds **2** and **3a**, respectively.

3.3.5 X-ray photoelectron spectroscopy

The XPS technique was utilized to elucidate the core-level electronic structure and binding energy of the elements present in the cobalt compound. The high-resolution XPS spectrum of Co2p, (**Figure 5**) was plotted and deconvoluted using the peak fitting software. The spectrum featured two dominant peaks and two weak satellite signals. The Co2p peaks corresponding to spin-orbit components Co2p_(3/2) and Co2p_(1/2) exhibited binding energies of 780.808 eV and 795.876 eV, respectively. Typically, the energy separation is ~16 eV for high-spin Co(II) and approximately 15eV for low-spin Co(III) [37]. The measured binding energy separation of 15.068 eV was consistent with Co(III), accompanied by two satellite peaks near the spin-orbit doublets at 787.330 and 801.727 eV. Consequently, the XPS analysis suggests that cobalt exists in the low-spin state, corroborating the findings from UV-Vis spectroscopy.

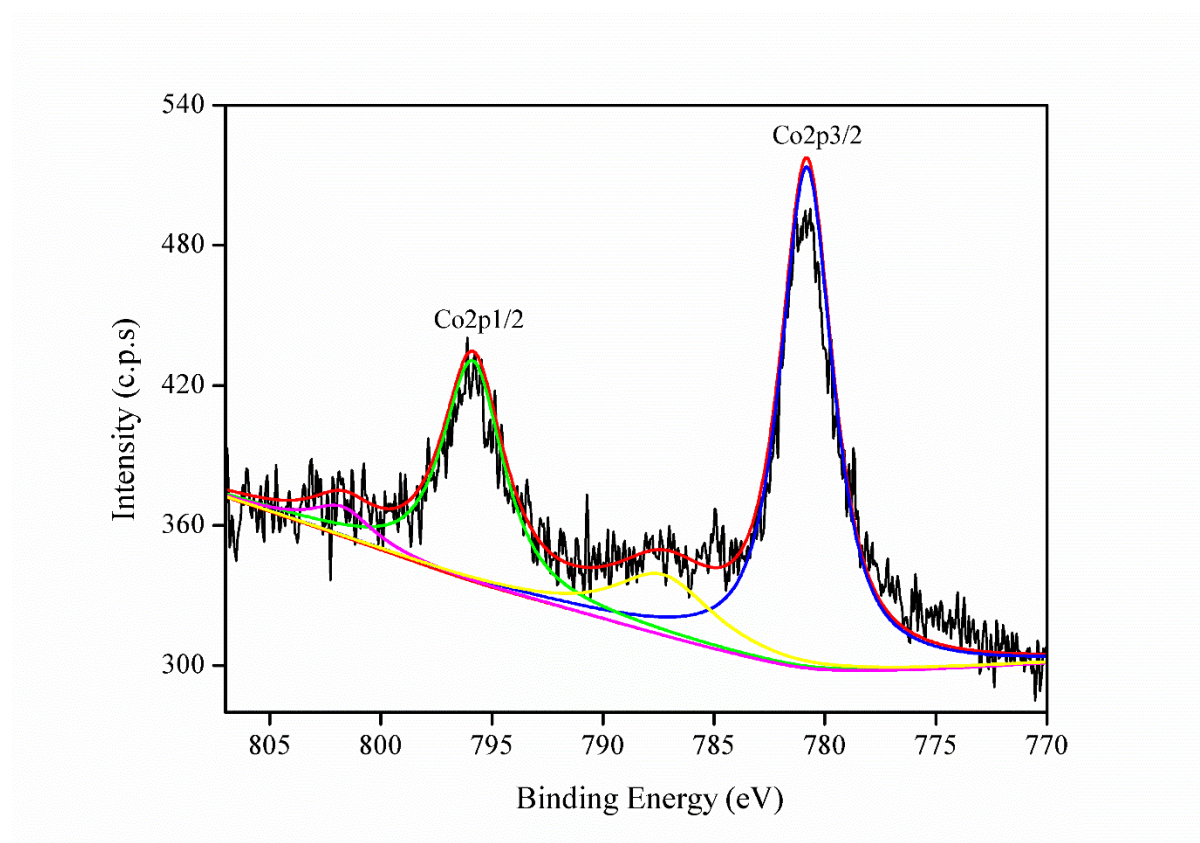


Figure 5. The XPS spectrum of compound 1.

3.3.6 The structure description of synthesized compounds

The crystal structure data of the compounds have been collected at room temperature. The technical details of data acquisition and selected refinement parameters are shown in [Table 3](#)

***cis*-[Co(cyclam)(Bz)₂](Bz)·H₂O (1)** The structural analysis of compound **1** reveals crystallization in centrosymmetric monoclinic crystal systems with the *P*2₁/*c* space group. The asymmetric unit comprises a cationic core, [Co(cyclam)(Bz)₂]⁺, featuring a centrally located cobalt ion as shown in [Figure 6](#). The cobalt ion adopts an octahedral geometry, which exhibits distortion due to the slight variation in the axial and equatorial bonds. The coordination sphere includes two crystallographically independent benzoate anions lying adjacent to one another. Both the benzoate ligands coordinate to the central metal *via* the oxygen atoms (O1 & O3) in a monodentate fashion. The other positions of the octahedron are occupied by the four nitrogen atoms (N1-N4) of the cyclam ligand, thus forming the {CoN₄O₂} chromophore. The coordination of the benzoate ligands induces a diagonal folding of the cyclam ligand at N2 and N4 atoms, resulting in a *cis*-V conformation. The five-membered chelate rings of cyclam adopt the *gauche* conformation with average fold angles around the Co atom of 86.16(15)°, which is less than the fold of the six-membered rings, with chair conformation. Distortion from the ideal octahedral geometry around the Co atom is evident from the Co-O and Co-N bond distances. For instance, the Co-O(coordinated) bond lengths are 1.923(2) Å (Co1-O1), 1.947(2) Å (Co1-O3), and are slightly shorter as compared to the Co-N bond lengths that range from 1.971(3) to 1.979(3) Å. The *trans* and *cis* bond angles also indicate the distortion with (O-Co-O, O-Co-N, N-Co-N) falling in the range of 171.57(14) to 174.48(15)° and 85.96(14) to 95.96(14)° respectively. The nominated bond lengths and bond angles are given in [Table 3.1](#). Additionally, the bond distances of Co-O and Co-N bond align closely with those observed for Co(III) compounds, thus further supporting the cobalt in a higher oxidation state, as summarized in [Table 3.2](#)

Table 3.2 Comparative study of structural features of cobalt(III) compounds

Compound	C.S	CCDC no	Reference
[Co(cyclam)(flufenamic acid) ₂](PF ₆)	{CoN ₄ O ₂ }	DODKEQ	29
[Co(L3)(8-quinolinato)](ClO ₄) ₂	{CoN ₅ O}	WINTIY	38
[Co(cyclam)(naproxen) ₂](PF ₆)	{CoN ₄ O ₂ }	TEMKUU	39

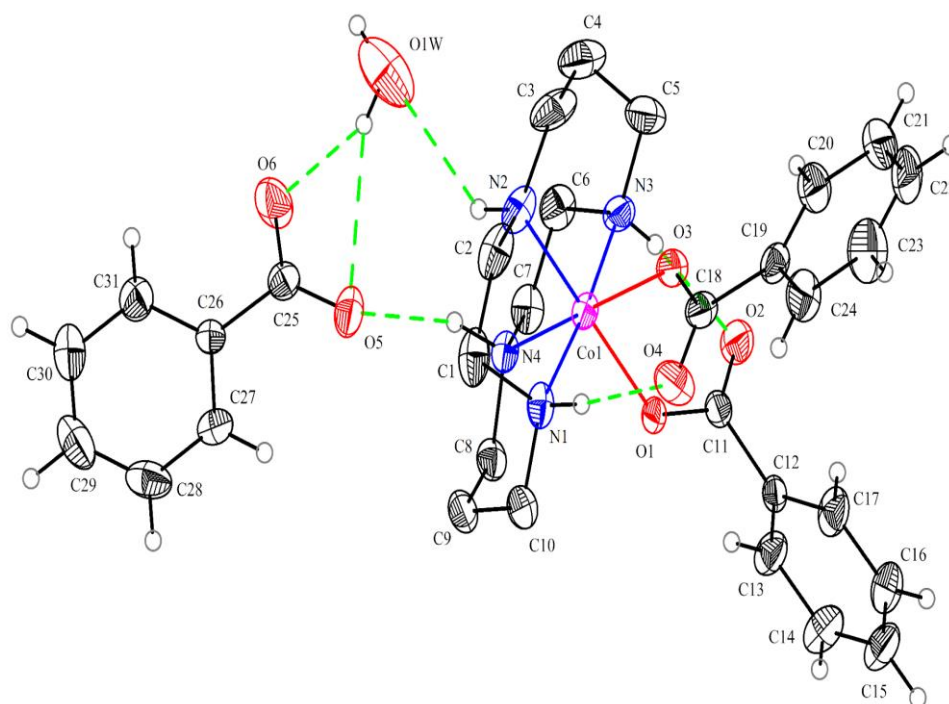


Figure 6. The asymmetric unit of **1** with the atom labelling scheme. The hydrogens on the cyclam carbon skeleton are excluded for clarity. Thermal ellipsoids represent the atom position with 30% probability. The intramolecular hydrogen bonds are represented in green dotted lines.

The cationic core is balanced by one uncoordinated benzoate moiety in the crystal lattice, which, along with the lattice aqua molecule, is involved in forming an intense hydrogen bonding network contributing to the stability of the supramolecular assembly. The non-covalent interactions in compound **1** include the $\text{N-H}\cdots\text{O}$ and $\text{C-H}\cdots\text{O}$ originating from the organic components of the compound and $\text{O-H}\cdots\text{O}$ type from the aqua molecules. The hydrogen bonding parameters are outlined in [Table 3.3](#). The structure, when viewed along the *ab* plane, reveals that the adjacent molecules are interconnected *via* the intermolecular hydrogen bond ($\text{C6-H6A}\cdots\text{O6}$), which involves the oxygen atom (O6) of the uncoordinated benzoate and the carbon atom (C6) of the cyclam ligand. This arrangement results in the formation of a one-dimensional supramolecular chain structure. On the other hand, the aqua molecules form an intermolecular hydrogen bond with the carbon of the cyclam ($\text{C1-H1A}\cdots\text{O1W}$) and create a bridge between the adjacent one-dimensional chains running along *a* axis to each other, thus giving an appearance of the three-dimensional twisted ladder-shaped structure as shown in [Figure 7](#).

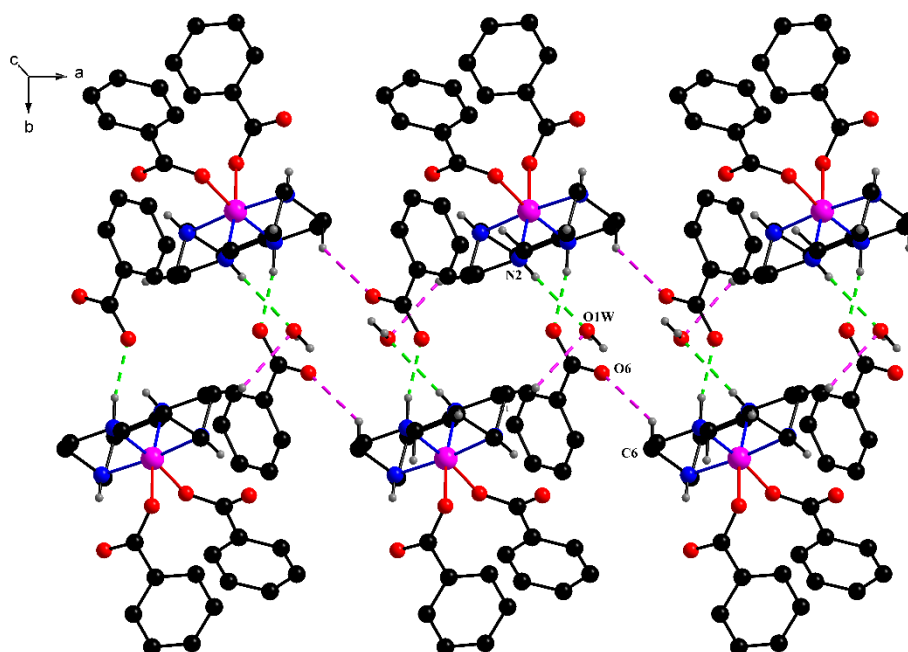


Figure 7. The packing diagram of **1** shows a three-dimensional Zig-Zag ladder-shaped packing due to the intermolecular hydrogen bonds (purple dotted lines), such as C1-H1A $\cdots$ O1Wⁱ and C6-H6A $\cdots$ O6ⁱ, (symmetry code $i = -x, -y+1, -z+2$)

***trans*-[Ni(cyclam)(H₂O)₂](MeOBz)₂·4H₂O (**2**)** crystallizes in centrosymmetric monoclinic space group with $P2_1/n$ space group. The crystal structure comprises a cationic unit [Ni(cyclam)(H₂O)₂]²⁺, which includes a centrally located Ni(II) ion in a special position (inversion centre), half of the molecule is symmetry-generated. The Ni ion adopts the octahedral geometry, wherein the axial sites are occupied by two terminal aqua molecules *via* (O1W and O1Wⁱ). Whereas, the cyclam ligand coordinates to the metal *via* four nitrogen atoms at the equatorial positions (N1, N1ⁱ, N2, and N2ⁱ), thus forming a {NiO₂N₄} chromophore (**Figure 8**). The cyclam ligand in compound **2** adapts the *trans*-III conformation, which is the most thermodynamically stable isomer. The cationic unit is charge-balanced by two uncoordinated *o*-methoxy benzoate anions. These are further engaged in extensive hydrogen bonding interactions with the lattice aqua molecules. These non-covalent interactions stabilize the three-dimensional supramolecular assembly.

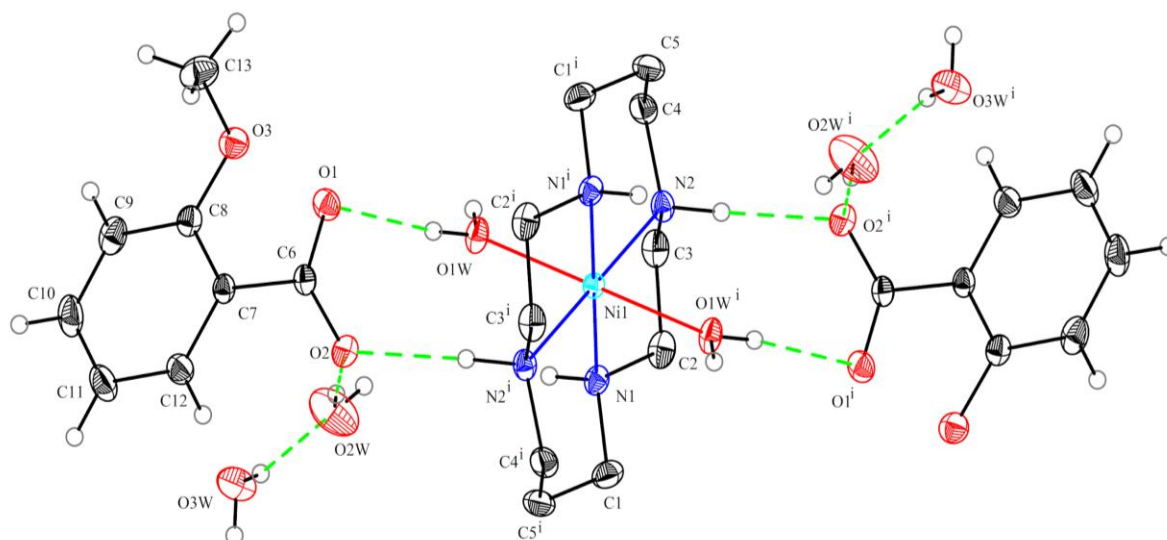


Figure 8. The crystal structure of compound **2** with an atom labelling scheme. The thermal ellipsoids are drawn at 30% probability level except for the H atoms, which are shown as spheres of arbitrary radius. The hydrogen atoms on the cyclam carbon skeleton are omitted for clarity. The intramolecular hydrogen bonds are shown as green dotted lines.

Compound **2** displays a slight tetragonal distortion, as evidenced by the axial Ni-O bonds (2.1666 Å) from the aqua ligands being marginally more extended than the average Ni-N bond length (average 2.0653). The values are in good agreement with similar nickel compounds bearing $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2]^{2+}$ core listed in [Table 3.4](#). The selected bond distances and bond angles are listed in [Table 3.1](#). Analysis of the hydrogen bonding situation in **2** revealed that the uncoordinated carboxylate molecules form intramolecular hydrogen bonds with the cyclam and aqua molecules. The oxygen atom of carboxylate (O1) acts as the acceptor, and the nitrogen atom of the cyclam N2 acts as the donor atom (N2-H $\cdots$ O2). Among the ten hydrogen bonds identified in compound **2** ([Table 3.3](#)), five are involved in intermolecular interaction, which are responsible for extending and stabilizing the 3D supramolecular network. The packing diagram of compound **2** and the hydrogen bonding network extending along the *ab* plane are illustrated in [Figure 9](#).

Table 3.4 The influence of anions on the configuration of cyclam in nickel compounds

Sr. No	Compound	Configurational isomer	Ref.
1	$[\text{Ni}(\text{cyclam})(\text{MeSCoM})_2]$	<i>trans</i> -III (SSRR)	40
2	$[\text{Ni}(\text{cyclam})(\text{NO}_3)_2](\text{NO}_3)$	<i>trans</i> -III (SSRR)	41
3	$[\text{Ni}(\text{cyclam})\text{I}]\cdot\text{H}_2\text{O}$	<i>trans</i> -III (SSRR)	42

Abbreviation: MeSCoM = methyl coenzyme M

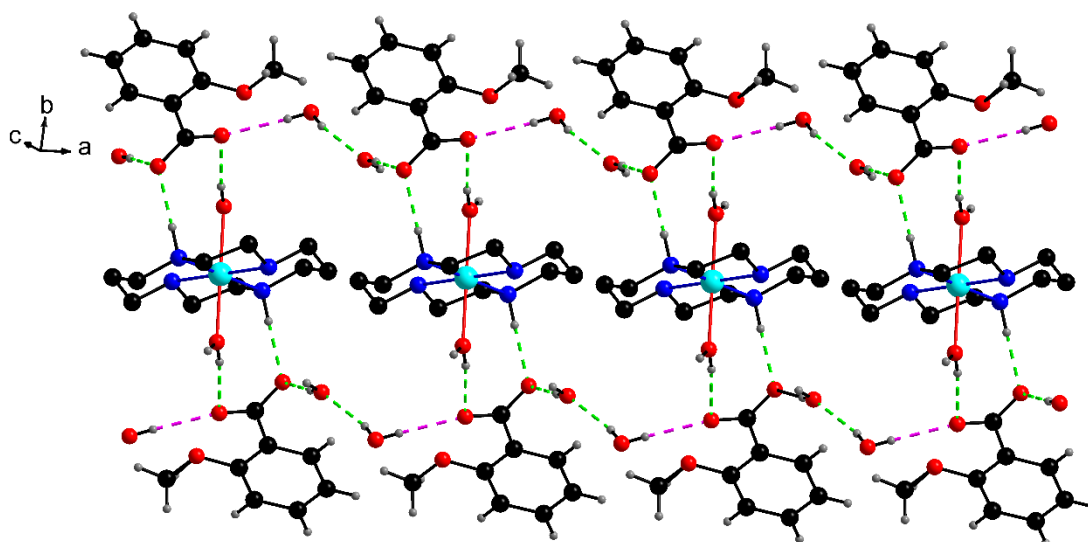


Figure 9. The hydrogen bonding pattern in compound **2**. The individual $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2](\text{MeOBz})_2 \cdot 4\text{H}_2\text{O}$ molecules are extended with intermolecular (purple dotted line) hydrogen bonds forming a 1D chain structure.

***cis*-[Mn(cyclam)(Bz)₂]·H₂O (**3**)** The title manganese compound crystallizes in the centrosymmetric triclinic $P\bar{1}$ space group. The Mn (II) ion is coordinated by two oxygen atoms from the independent benzoate molecules in *cis* arrangement, while the remaining sites are occupied by the four nitrogen donors of the cyclam entity that adopts the *cis*-V conformation. The neutral compound also consists of aqua molecules in the crystal lattice held by the intramolecular hydrogen bonding through the oxygen atoms of the coordinated benzoate molecules, as depicted in **Figure 10**. In the neutral mononuclear compound, the Mn-O bond distances, (Mn1-O1) 2.1511(11) and (Mn1-O3) 2.1399(11), are comparatively shorter than the Mn-N bond distances, ranging from (2.2618(15) to 2.3161(14) Å) (**Table 3.1**). The reports on containing Mn (II) species compared to the compounds comprising Mn(III) species with cyclam in the *cis* conformation are very scanty. A very closely related Mn(II) compound reported by Mathonière and coworkers [43] was used to correlate the Mn-O/N bond lengths, it was observed that the bond lengths reported for heterodinuclear compound with formula $[\text{Mn}(\text{Me}_6\text{-[14]ane-N}_4)\text{Cu}(\text{oxpn})](\text{CF}_3\text{CO}_3)_2$ (where $\text{Me}_6\text{-[14]ane-N}_4 = 5,7,7,12,14,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradecane}$ and $\text{oxpn} = \text{N,N'-bis(3-aminopropyl)oxamide}$) align well with that of bond lengths reported for compound **3** in our work. The bond angles (**2**) deviate from the ideal values of 90° (77.01(5) to 102.71(5) $^\circ$) and 180° (153.61(6) to 177.11(5)), indicating a distortion of the $\{\text{MnN}_4\text{O}_2\}$ octahedra. The constituents in the crystal structure of

3, viz. the core $[\text{Mn}(\text{cyclam})(\text{Bz})_2]$ and the water molecules, are interlinked with $(\text{N}-\text{H}\cdots\text{O1W})$ type of intermolecular hydrogen bonding interactions, which results in extension of the structure in one one-dimensional chain along the axes (**Figure 11**).

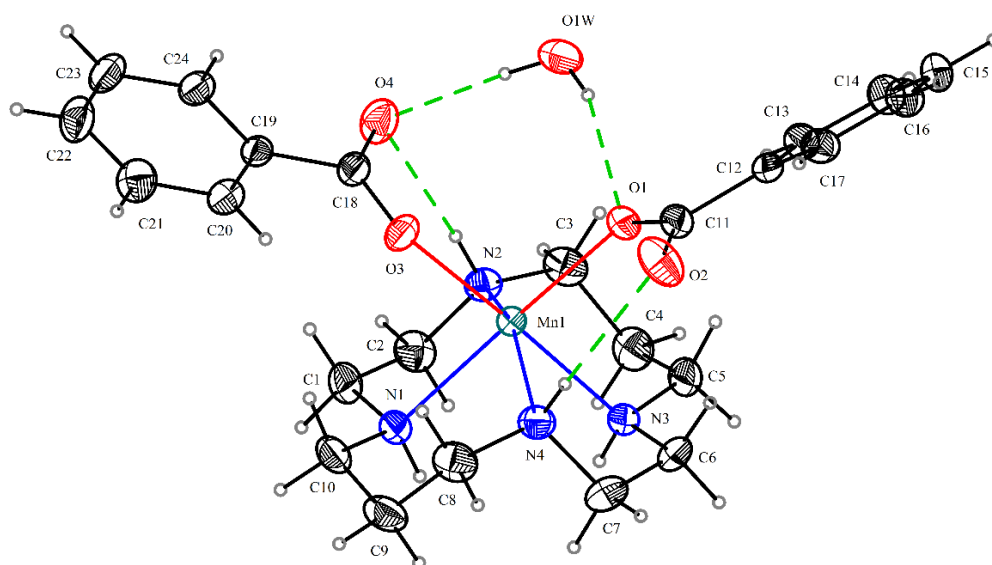


Figure 10. The asymmetric unit of **3** shows octahedral coordination around the Mn(II) ion. Displacement ellipsoids are drawn at a 30 % probability level for non-hydrogen bonds. The intramolecular hydrogen bonding is shown by broken lines.

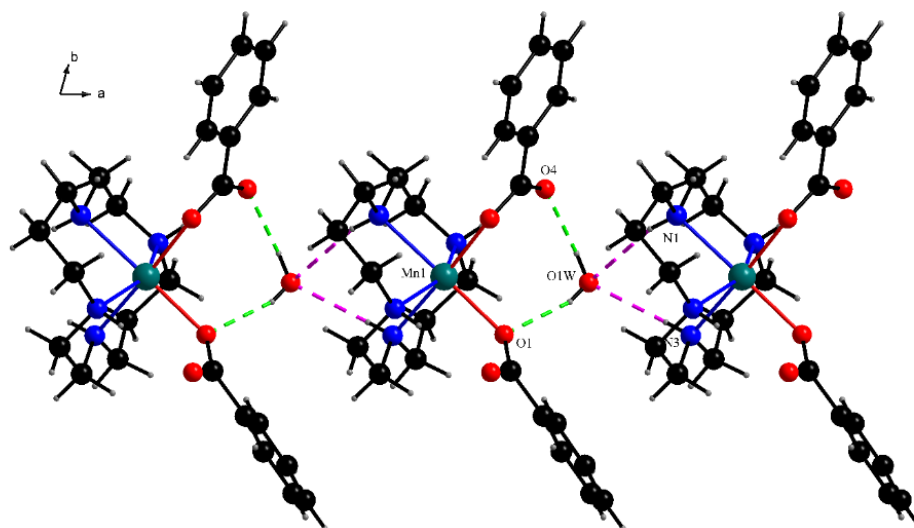


Figure 11. View of the chain arrangement of **3** with the aqua molecule links the adjacent molecules *via* the intermolecular hydrogen bond $(\text{N}-\text{H}\cdots\text{O})$ as shown by purple dotted line.

trans-[Mn(cyclam)(Bz)₂](Bz·HBz)·3(HBz) (**3a**) crystallizes in a centrosymmetric monoclinic $P2_1/n$ space group. X-ray analysis indicates that the asymmetric unit of **3a** contains a Mn(III) atom located on the inversion centre, leaving half of the molecule symmetry-generated (**Figure 12**). The Mn is hexa-coordinated with a highly distorted [N₄O₂] octahedral environment as expected for the d⁴ high-spin Mn(III) configuration. Two oxygen atoms (O1 and O3) are contributed by two crystallographically independent benzoate binding in monodentate coordination fashion and occupy the axial positions of the octahedron. While all the equatorial positions are occupied by the nitrogen donor atoms of the cyclam, adopting the *trans*-III conformation. Bond distances are arranged in the following order: (Mn1-O1) 2.1452(12), (Mn1-N2) 2.0376(16), and (Mn1-N1) 2.0345(15).

The distortion in the octahedron is also evident from the bond angles, as the N-Mn-O bond angle deviates from 90° in the range of 87.64(6)° – 92.36(6)°. A comparable distortion of octahedral geometry has also been observed in other *trans* Mn(III) cyclam compounds, such as H[Mn(cyclam)(pyridine-2,6-dicarboxylate)₂]·H₂O [44], *trans*-[Mn(cyclam)(H₂O)₂](CF₃SO₃)₃·H₂O, *trans*-[Mn(cyclam)(ONO)₂](ClO₄) [45], *trans*-[Mn(CN)₂(cyclam)](ClO₄) [46], *trans*-[Mn(cyclam)(Cl)₂](BF₄) [47]. The compound is stabilized by intermolecular hydrogen bonds involving O-H···O, N-H···O, and C-H···O types (**Table 3.3**). The Mn(III) compound is organized in a one-dimensional chain by means of remarkably strong and short symmetric H-bonds between non-coordinating benzoate and benzoic acid (**Figure 13**). The H atom lies in a crystal inversion centre; thus, both the O-H distances are equivalent 1.224 (15) Å. The distance between the donor atom and acceptor atom in the dimer is found to be 2.448, which is in good agreement with those reported in the literature [37, 43, 48-50]

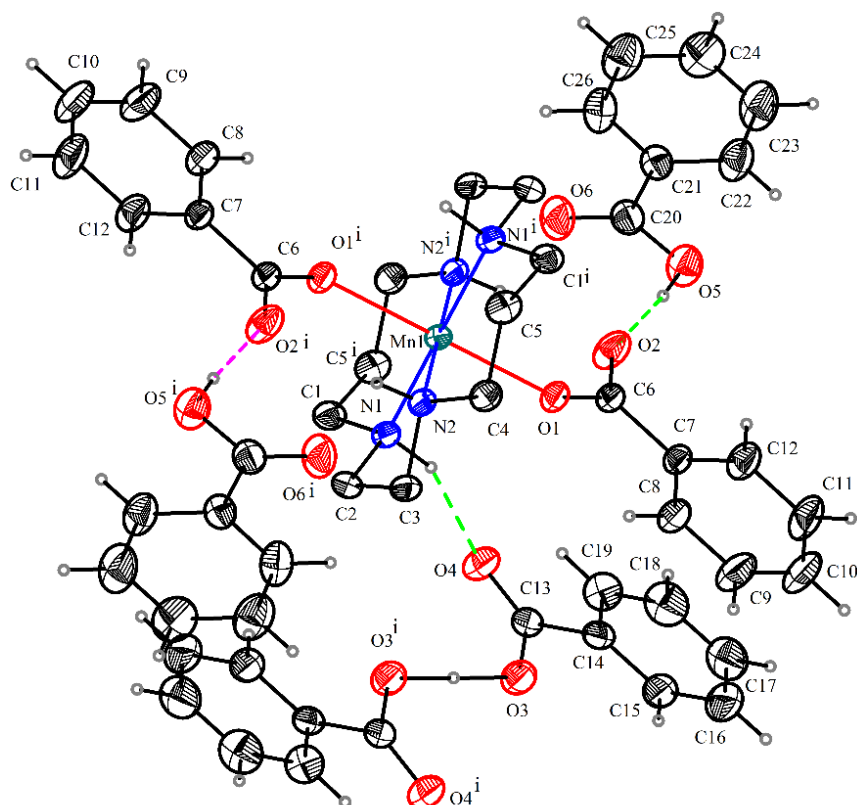


Figure 12. The asymmetric unit of **3a**. Displacement ellipsoids are drawn at a 30 % probability level for non-hydrogen bonds. The hydrogen atoms on the cyclam carbon backbone are omitted for clarity. The intramolecular hydrogen bonding is shown by broken lines.

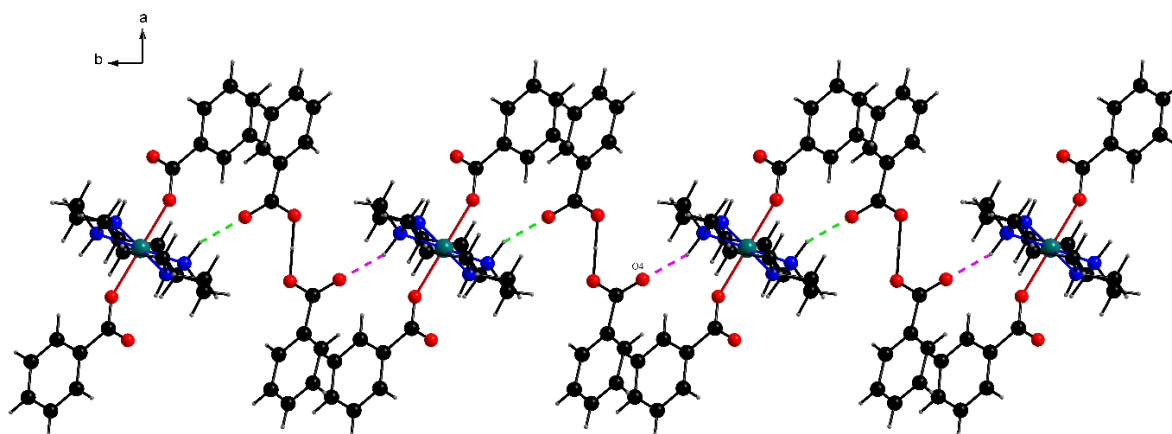


Figure 13. The view of the supramolecular chain of **3a** due to the strong symmetric H-bond between the benzoate-benzoic acid dimer, extending through the *b* axis

Table 3. The crystal data and structure refinement parameters for compounds.

Compound	1	2	3	3a
Empirical formula	C ₃₁ H ₄₁ CoN ₄ O ₇	C ₂₆ H ₅₀ NiN ₄ O ₁₂	C ₂₄ H ₃₆ MnN ₄ O ₅	C ₅₂ H ₅₇ MnN ₄ O ₁₂
Temperature/K	296(2)	296(2)	296(2)	296(2)
Formula weight	640.69	669.49	515.58	985.07
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	9.2901(3)	8.6697(2)	7.7263(2)	15.4671(4)
<i>b</i> / Å	35.1546(11)	7.8613(2)	12.2863(3)	11.155(3)
<i>c</i> / Å	9.6023(3)	23.0083(6)	13.8902(4)	14.2638(4)
α / °	90	90	88.363(10)	90
β / °	103.024(1)	91.6860(10)	84.391(10)	90.884(10)
γ / °	90	90	74.148(10)	90
Volume / Å ³	3055.34(17)	1567.45(7)	1262.34(6)	2460.72(11)
Z	4	2	2	2
D _{calc.} [Mg cm ⁻³]	1.393	1.418	1.356	1.329
μ / mm ⁻¹	0.615	0.685	0.564	0.335
F(000)	1352	716	546	1036
Radiation	MoK α (λ =0.71073)	MoK α (λ =0.71073)	MoK α (λ =0.71073)	MoK α (λ =0.71073)
Crystal size/mm	0.29 x 0.16 x 0.05	0.21 x 0.14 x 0.09	0.29 x 0.14 x 0.07	0.4 x 0.3 x 0.21
θ range for data collection (°)	2.53 to 28.28	2.54 to 28.31	2.75 to 28.27	2.634 to 25.65
Index ranges	-12 $\leq h \leq$ 11, -46 $\leq k \leq$ 46, -12 $\leq l \leq$ 12	-11 $\leq h \leq$ 11, -10 $\leq k \leq$ 10, -30 $\leq l \leq$ 30	-10 $\leq h \leq$ 10, -16 $\leq k \leq$ 16, -18 $\leq l \leq$ 18	-18 $\leq h \leq$ 18, -13 $\leq k \leq$ 13, -17 $\leq l \leq$ 17
Reflections collected	30131	21437	23521	17731
Independent reflections	7590 [R(int) = 0.0756]	3905 [R(int) = 0.0279]	6265 [R(int) = 0.0277]	4647 [R(int) = 0.034]
Completeness to $\theta = 25.242$ (%)	99.9	99.9	99.8	99.8
SGoodness-of-fit on F ²	1.095	1.048	1.035	1.022
Final R indexes [I > 2 σ (I)]	R1 = 0.0754, wR2 = 0.1294	R1 = 0.0307, wR2 = 0.0709	R1 = 0.0346, wR2 = 0.0795	R1 = 0.0373, wR2 = 0.0812
Final R indexes [all data]	R1 = 0.1338, wR2 = 0.1492	R1 = 0.0363, wR2 = 0.0733	R1 = 0.0795, wR2 = 0.0882	R1 = 0.0572, wR2 = 0.092
Largest diff. peak/hole/eÅ ⁻³	0.39 and -0.45	0.38 and -1.26	0.326 and -0.29	0.156 and -0.24
CCDC No	2206672	2284051	2285724	

Table 3.1. Selected bond lengths (Å) and angles (°) of compounds

Compound 1					
<i>Bond distance</i>		<i>Bond angle</i>			
Co1-O1	1.923(2)	O1-Co1-O3	86.74(11)	N1-Co1-O1	87.79(12)
Co1-O3	1.947(2)	O3-Co1-N2	87.78(13)	N1-Co1-O3	95.50(13)
Co1-N1	1.979(3)	N2-Co1-N4	95.96(14)	N1-Co1-N2	86.37(16)
Co1-N2	1.978(3)	N4-Co1-O1	90.10(12)	N1-Co1-N4	89.98(14)
Co1-N3	1.971(4)	N3-Co1-O1	95.96(13)	N1-Co1-N3	174.48(15)
Co1-N4	1.971(3)	N3-Co1-O3	88.78(13)	O1-Co1-N2	171.57(14)
		N3-Co1-N2	90.32(16)	O3-Co1-N4	173.56(12)
		N3-Co1-N4	85.96(14)		
Compound 2					
Ni1-N1	2.0705(12)	N1-Ni1-N2	85.39(5)		
Ni1-N2	2.0602(12)	N2-Ni1-N1 ⁱ	94.61(5)		
Ni1-O1W	2.1666(10)	N2 ⁱ -Ni1-N1 ⁱ	85.39(5)		
		N2 ⁱ -Ni1-N1	94.61(5)		
		O1W-Ni1-O1W ⁱ	180.00(7)		
Compound 3					
Mn1-O1	2.1511(11)	O1-Mn1-O3	95.73(5)	N1-Mn1-N2	77.01(5)
Mn1-O3	2.1399(11)	O3-Mn1-N4	102.71(5)	N1-Mn1-N3	89.79(5)
Mn1-N1	2.3161(14)	O3-Mn1-N2	94.57(5)	N1-Mn1-N4	83.88(6)
Mn1-N2	2.2716(15)	O3-Mn1-N3	90.10(12)	N2-Mn1-N3	83.71(6)
Mn1-N3	2.3007(14)	O3-Mn1-N1	87.55(5)	N3-Mn1-N4	78.13(6)
Mn1-N4	2.2618(15)	O1-Mn1-N4	99.72(5)	N4-Mn1-N2	153.61(6)
		O1-Mn1-N2	98.21(5)	O3-Mn1-N3	177.11(5)
		O1-Mn1-N3	86.83(5)	O1-Mn1-N1	174.44(5)
Compound 3a					
Mn1-N1	2.0345(15)	N1-Mn1-N2	85.77(6)	N2-Mn1-O1	87.64(6)
Mn1-N2	2.0376(16)	N1 ⁱ -Mn1-N2	94.23(6)	N1-Mn1-N1 ⁱ	180
Mn1-O1	2.1452(12)	N1-Mn1-O1 ⁱ	91.55(6)	N2-Mn1-N2 ⁱ	180(6)
		N2-Mn1-O1 ⁱ	92.36(6)	O1 ⁱ -Mn1-O1	180(6)
		N1-Mn1-O1	88.45(6)		

Symmetry code ($i = 1-x, 1-y, 1-z$)

Table 3.3 Hydrogen bonding parameters (Å, °) for **1-3** and **3a**

<i>D-H...A</i>	<i>d(D-H)</i>	<i>d(H...A)</i>	<i><DHA</i>	<i>d(D...A)</i>	<i>Symmetry code</i>
<i>cis</i> -[Co(cyclam)(Bz) ₂](Bz)·H ₂ O (1)					
N1-H1...O4	0.895	1.815	167.2	2.695	
N2-H2...O1W	0.818	2.609	135.18	3.241	
N3-H3...O2	0.794	1.955	167.52	2.736	
N4-H4...O5	0.980	1.919	159.41	2.857	
C1-H1A...O1W	0.970	2.643	130.55	3.355	[1-x, 1-y, 2-z]
C6-H6A...O6	0.970	2.590	139.67	3.388	[-x, 1-y, 2-z]
O1W-H1W...O5	0.85	2.592	142.62	3.308	
O1W-H1W...O6	0.85	1.938	154.03	2.728	
<i>trans</i> -[Ni(cyclam)(H ₂ O) ₂](MeOBz) ₂ ·4H ₂ O (2)					
N1-H1...O3W	0.871	2.498	160.48	3.331	[-x, -y+1, -z+1]
N2-H2...O2	0.98	1.945	167.86	2.91	[-x+1, -y, -z+1]
O2W-H6...O3W	0.739	2.086	166.26	2.809	[-x, -y+1, -z+1]
O1W-H3...O1	0.795	2.061	172.49	2.851	[-x+1, -y+1, -z+1]
O3W-H8...O1	0.773	2.147	158.34	2.879	[1-x, y, z]
O3W-H8...O3	0.773	2.531	124.73	3.039	[1-x, y, z]
O1W-H4...O1	0.833	1.995	172.45	2.823	
O1W-H4...O2	0.833	2.59	131.33	3.201	
O2W-H5...O2	0.736	2.111	176.4	2.846	
O3W-H7...O2W	0.806	2.027	161.29	2.809	
<i>cis</i> -[Mn(cyclam)(Bz) ₂](Bz)·H ₂ O (3)					
N1-H1...O1W	0.832	2.559	162.93	3.364	[x-1,y,z]
N3-H3...O1W	0.767	2.315	176.15	3.08	[x-1,y,z]
N2-H2...O4	0.799	2.356	153.50	3.092	
N4-H4...O2	0.845	2.222	149.44	2.981	
O1W-H5...O4	0.828	1.912	173.90	2.737	
O1W-H6...O1	0.738	2.087	161.75	2.797	
<i>trans</i> -[Mn(cyclam)(Bz) ₂](Bz)·3(HBz) (3a)					
N1-H1...O4	0.980	1.911	155.79	2.833	
O5-H5...O2	0.887	1.782	174.35	2.666	
N2-H2...O2	0.867	2.065	157.79	2.886	[1-x, 1-y, 1-z]
N2-H2...O6	0.867	2.580	116.66	3.069	[1-x, 1-y, 1-z]
O3-H3...O3	1.224	1.224	179.97	2.4480	[1-x, 1-y, 1-z]
O3-H3...O4	1.224	2.545	119.00	3.316	[1-x, 1-y, 1-z]
C2-H2A...O4	0.97	2.456	136.27	3.228	[1-x, 1-y, 1-z]
C3-H3A...O4	0.97	2.551	125.18	3.209	[1-x, 1-y, 1-z]
C4-H4A...O6	0.97	2.542	124.90	3.198	[1-x, 1-y, 1-z]

3.3.7 Powder X-ray diffraction analysis

The compounds **1** and **2** were further investigated for bulk purity using X-ray powder diffraction. The experimentally obtained pattern of the powdered samples was matched with the stimulated pattern generated using the single crystal data *via* Mercury software. An overlaid experimental and simulated pattern of compounds **1** and **2** is shown in **Figures 14 a)** and **14 b)**, respectively. The near-perfect alignment of the experimental and the simulated patterns verified the bulk purity of compounds **1** and **2**. With the confirmed solid-state structure and bulk purity by diffraction techniques, the powdered samples were subsequently utilized for catecholase and antimicrobial activities.

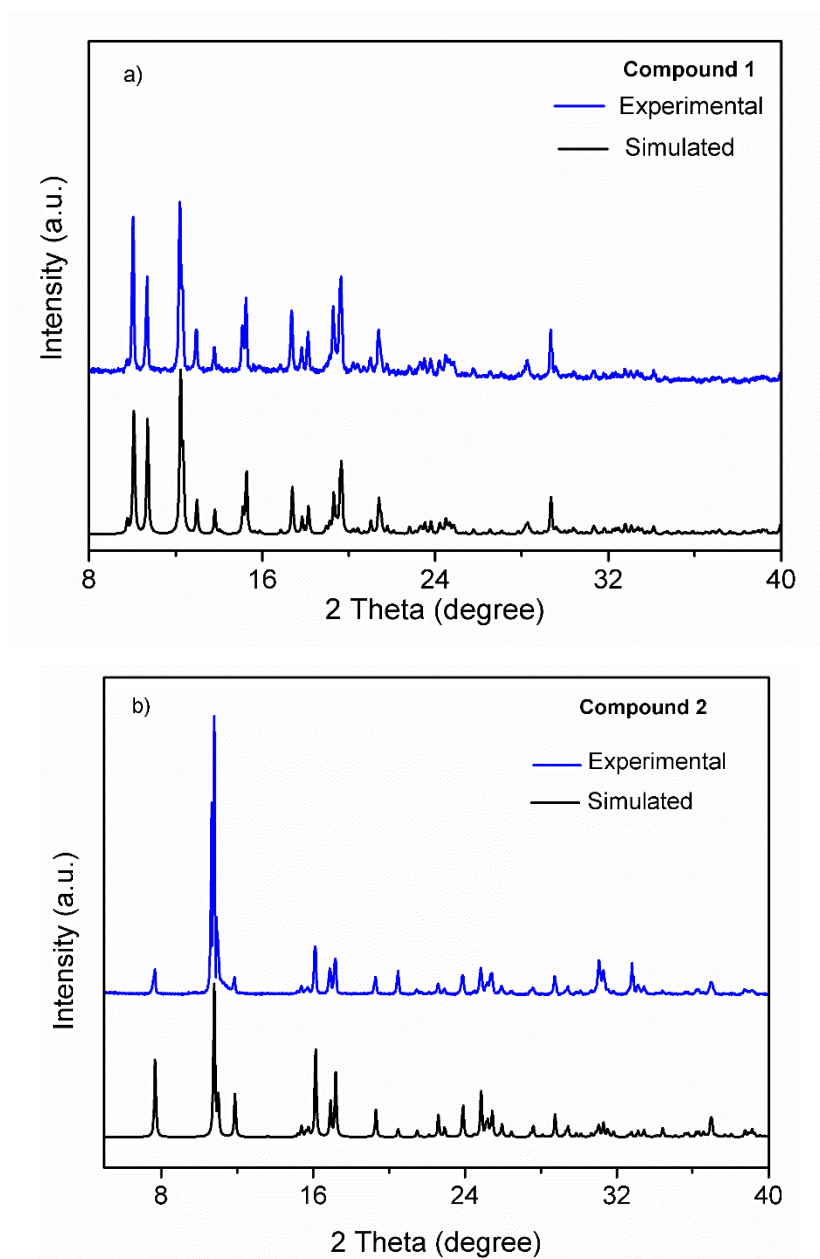


Figure 14. The experimental and simulated powder patterns of compounds **a) 1** and **b) 2**.

3.3.8 Thermogravimetric analysis

The TG-DTA analysis was carried out to investigate the thermal stability and decomposition patterns of compounds **1** and **2**, depicted in **Figures 15** and **16**, respectively. The TG data, collected under a nitrogen atmosphere, indicate that both compounds are stable below 200°C upon elimination of the lattice and coordinated water molecules. For compound **1**, the initial decomposition event, marked by an endothermic peak in the DTA, occurs at ~100 °C, corresponding to 2.63% mass loss (calcd. 2.81%), signifying complete dehydration. A further mass loss of 48.62% (*Calcd.* 50.17%) was observed, associated with the thermal decomposition of cyclam and benzoate, with exothermic and endothermic peaks at 180°C and 261°C, respectively, in the DTA plot. Above 300°C, a mass loss of 34.09 % (*Calcd.* 34.06 %) is attributed to the loss of two benzoate ligands, with a sharp endotherm at 350°C. The final residue is 14.66 %, close to the calculated 14.19%, for Co₃O₄ oxide, with no further weight loss observed beyond 400°C. The TG-plot of **2** revealed two successive mass losses. Firstly, the mass loss of 16.06% (*Calcd.* 16.15%) was related to the loss of six water molecules between ~50-100°C. Followed by a mass loss of 72.12% (*Calcd.* 72.7%) between 210 - 380°C due to the decomposition of cyclam and two moles of o-methoxy benzoate, with two DTA peaks centered at 222°C and 340°C. Above 380 °C, there is no mass loss, and the final residue of 11.77 % corresponds to the formation of nickel oxide (*Calcd.* 11.16%).

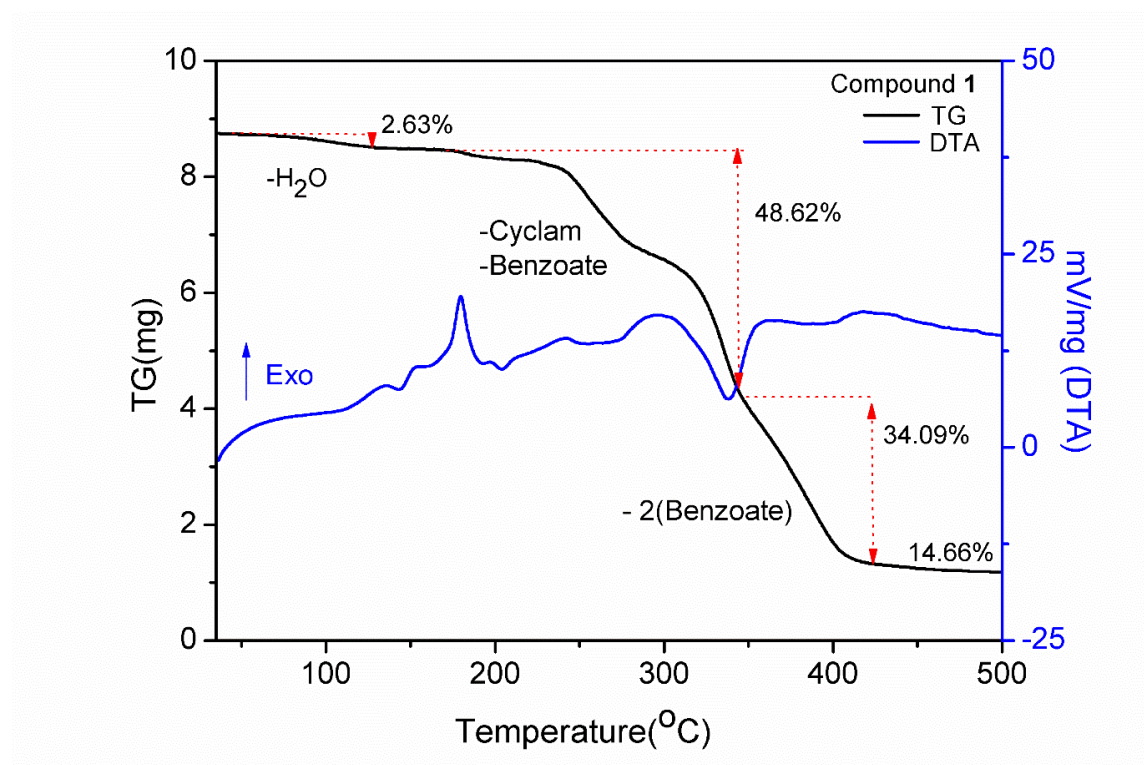


Figure 15 The TG-DTA plot of *cis*-[Co(cyclam)(Bz)₂](Bz)·H₂O in N₂ atmosphere.

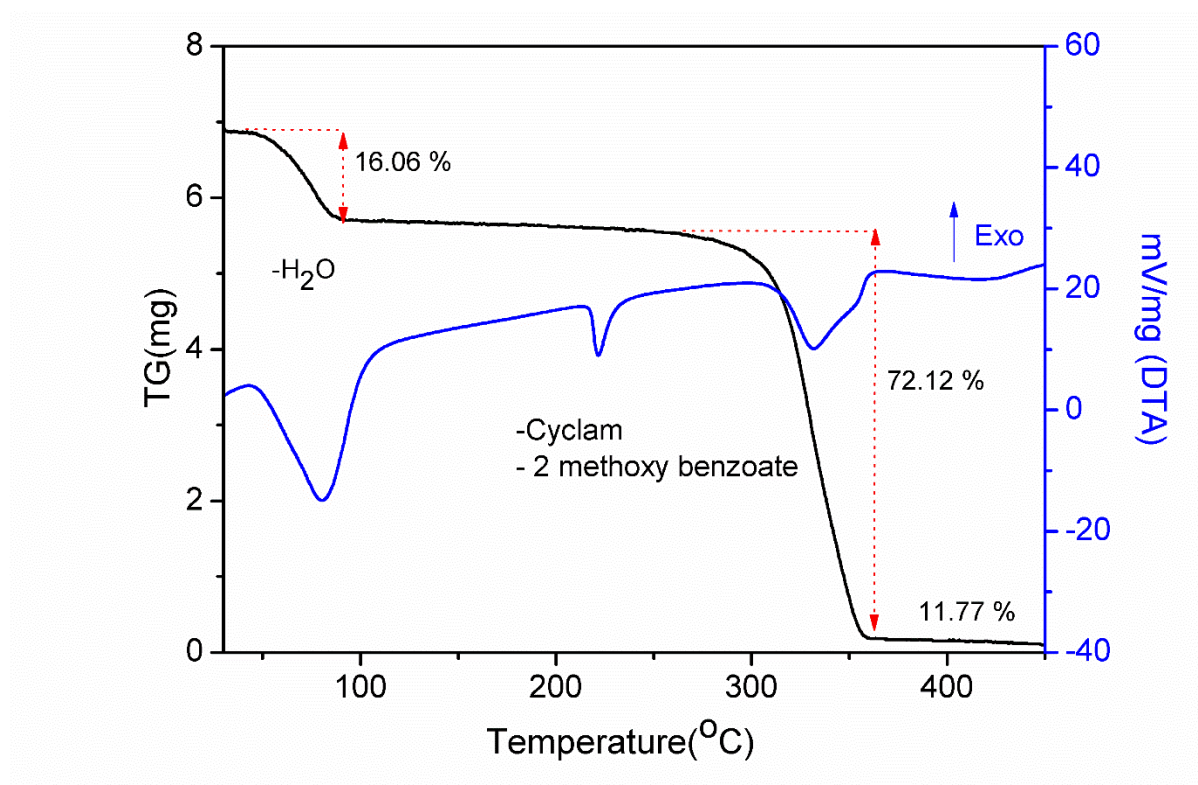


Figure 16 The TG-DTA plot of *trans*-[Ni(cyclam)(H₂O)₂](MeOBz)₂·4H₂O in N₂ atmosphere.

3.4 Molecular Hirshfeld surface analysis

The structures of compounds **1** and **2** were analyzed using Hirshfeld surface studies to gain in-depth visualization of the 3D intermolecular interactions responsible for crystal packing in the lattice. The 2D fingerprint plots identified the key contributors to these intermolecular interactions. The interactions between the molecules can be quantitatively studied based on the color-mapping of functions of the Hirshfeld surface (HS). The red and blue spots represent distances indicating shorter and longer contacts, while the white color denotes contacts with distances equal to the sum of van der Waals radii of the atoms [51]. The Hirshfeld surface plots for compounds **1** and **2** are displayed in **Figures 17a** and **18a**, respectively.

The d_{norm} surfaces of **1** and **2**, with short contacts, are defined by the red regions, which arise primarily from donor O-H and acceptor O atoms. Other significant interactions and characteristics of close-contact environments can be visualized using a 2D fingerprint plot. The 2D fingerprint plots and the relative contributions of various interactions for **1** and **2** are illustrated in **Figures 17b** and **18b**, respectively. The fingerprint plot can be further segmented into individual close contacts, each detailing their specific share of the total intermolecular interactions, quantified as percentages. The molecular packing in the crystal structure is

predominantly driven by $\text{H}\cdots\text{H}$, $\text{H}\cdots\text{O}$, and $\text{H}\cdots\text{C}$ interactions. The 2D fingerprint plots indicate that the principal contributors to the supramolecular assembly are the $\text{H}\cdots\text{H}$ interaction, accounting for 61.3% in **1** and 62.1 % in compound **2**. In addition to the $\text{H}\cdots\text{H}$ interactions, compound **2** displays a more significant percentage of O-H interactions compared to compound **1**, attributed to the increased water content and the substitution of the carboxylate group from benzoate to o-methoxy benzoate.

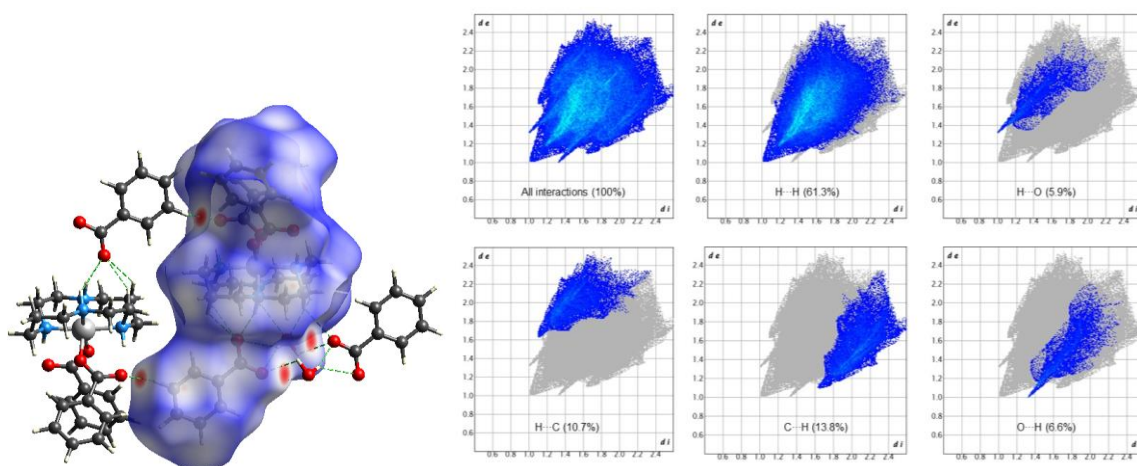


Figure 17 a) HS mapped with the d_{norm} function for **1**, showing the intermolecular interactions. b) 2D fingerprint plots with the relative contribution in % of interaction to the HS area.

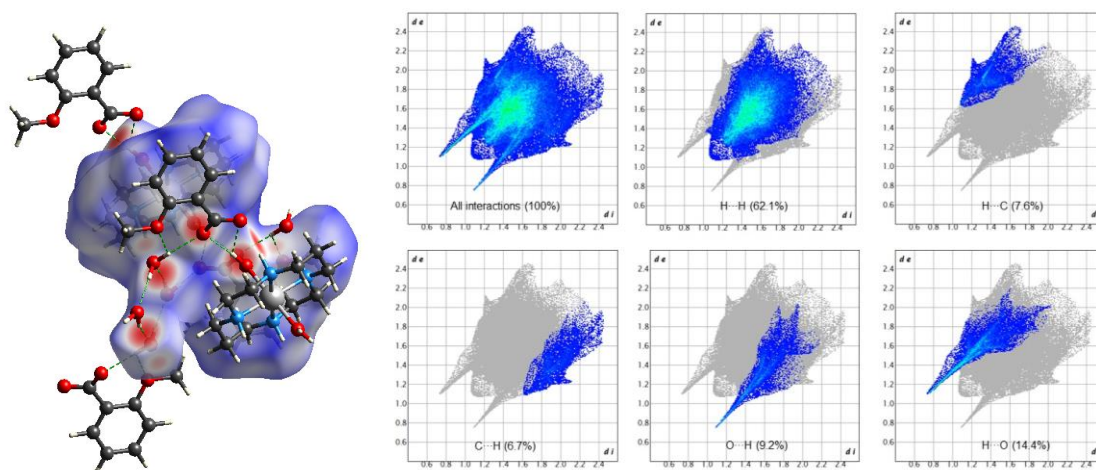


Figure 18 a) HS mapped with the d_{norm} function for **2**, showing the intermolecular interactions. b) 2D fingerprint plots with the relative contribution in % of interaction to the HS area

3.5 Catecholase-like activity of **1** and **2**

Several mononuclear and dinuclear cobalt and nickel complexes have been examined for their catalytic efficacy in oxidizing 3,5-di-*tert*-butyl catechol (3,5-DTBC) [52-54]. However, the literature needs to include specific findings on the oxidation of catechol by carboxylate-supported cobalt and nickel cyclam coordination complexes. Consequently, the impact of carboxylate binding in compounds **1** and **2** on the catecholase activity was explored by employing 3,5-DTBC as a model substrate. Due to the quinone-catechol pair's lower reduction potential, 3,5-DTBC is commonly utilized in catechol oxidation studies [55]. The reaction kinetics were evaluated by monitoring the time-dependent change in absorbance at 400 nm during the oxidation process, as shown in **Figures 19** and **20** for compounds **1** and **2**, respectively, in acetonitrile solvent.

The initial rate method was utilized to elucidate the kinetics of the oxidation of 3,5-DTBC to 3,5-DTBQ at room temperature. The change in absorbance (ΔA) at 400 nm was plotted against time to determine the initial rate of the reaction. The Ni(II) based catalyst **2** exhibited less activity towards the oxidation of 3,5-DTBC than compound **1**. To determine the kinetic parameters of the reaction catalyzed by compound **1**, a 0.5 mM solution of the catalyst was reacted with varying substrate concentrations (20-100 equivalents). The rate for each substrate concentration was ascertained using the initial rate method. The rate versus substrate concentration plot was analyzed using the Michaelis-Menten model to derive the Lineweaver-Burk plot (**Figure 21**). Additionally, the kinetic parameters are summarized in **Table 4** for compound **1**. The product was identified by ^1H -NMR spectroscopy.

The higher catalyst concentration required for the conversion of substrate to the product, compared to those reported in the literature using catalysts in the range of 10^{-4} to 10^{-5} M [56,57] suggests that this catalyst exhibits moderate to low activity towards the oxidation of the 3, 5-DTBC. This may be due to competitive carboxylate ligands, which render the compound less effective in the oxidation process at lower concentrations.

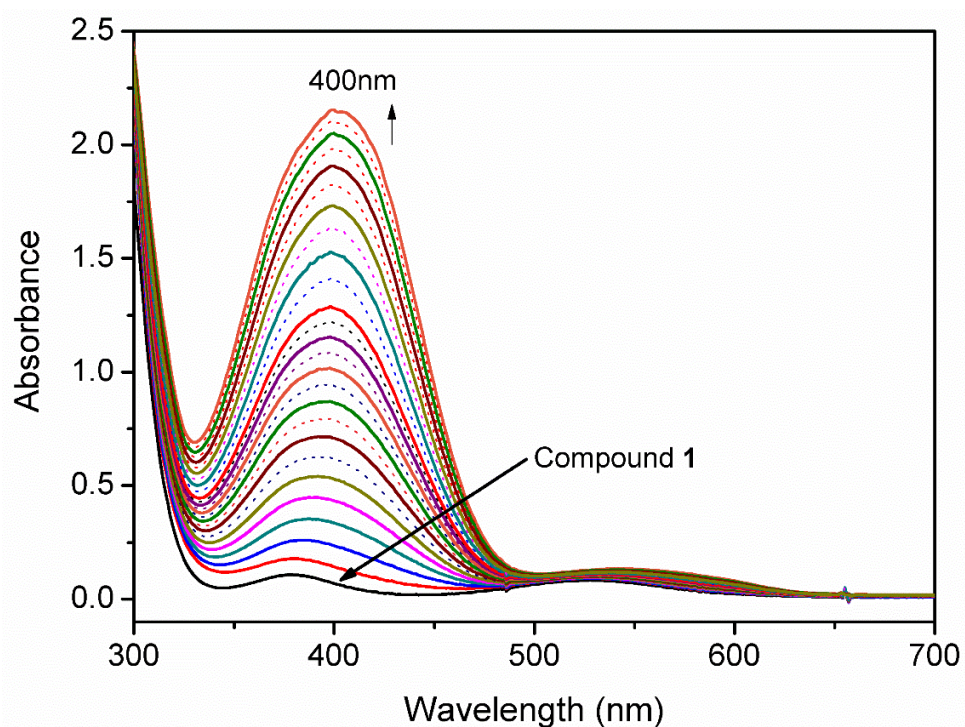


Figure 19. Escalated absorbance around 400 nm after adding 100 equivalents of 3,5-DTBC to a 0.5 mM solution of compound **1** in acetonitrile.

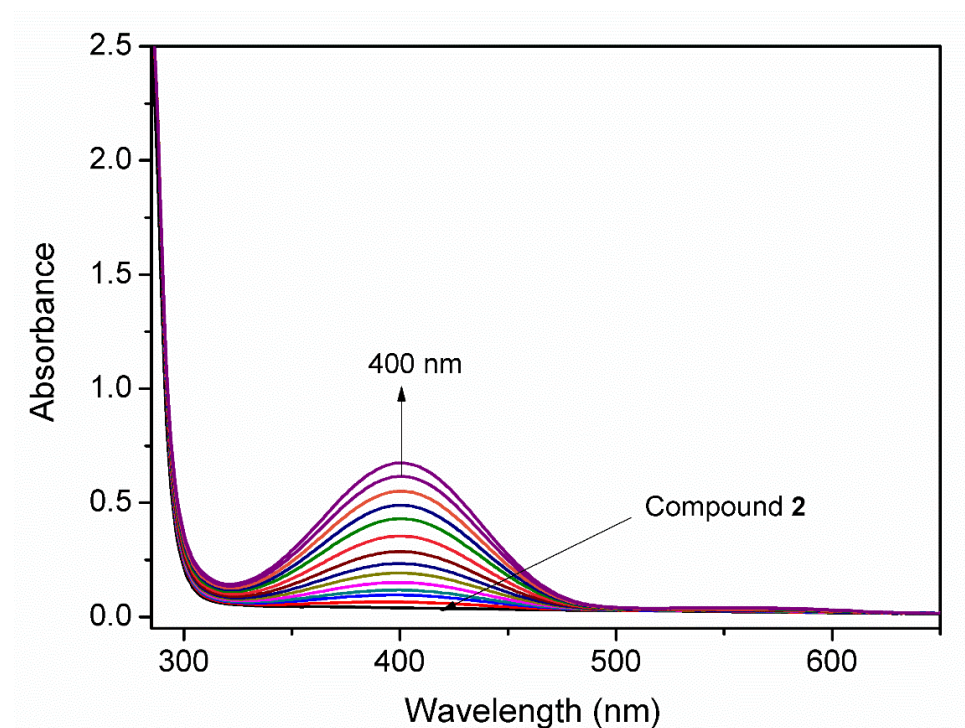


Figure 20 Escalated absorbance around 400 nm after adding 100 equivalents of 3,5-DTBC to a 0.5 mM solution of compound **2** in acetonitrile.

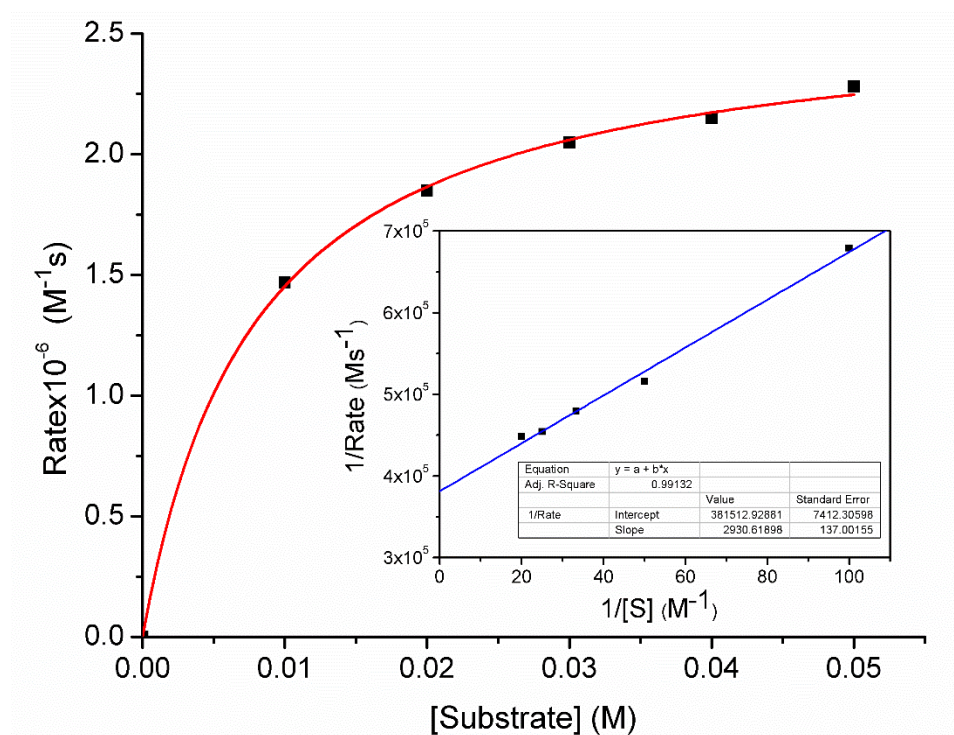


Figure 21 The plot of the initial rates versus substrate concentration. The inset shows the Lineweaver-Burk plot.

Table 4. Kinetic parameters for the oxidation of 3,5-DTBC

Compound	$V_{\max}(\text{M s}^{-1})$	$K_M (\text{M})$	$K_{\text{cat}} (\text{h}^{-1})$
1	2.62×10^{-6}	7.68×10^{-2}	18.9

Note: Standard error for $V_{\max} (\text{M min}^{-1}) = 0.0353 \times 10^{-6}$ and $K_M = 4.5288 \times 10^{-4}$

3.6 Antibacterial activity

The antimicrobial activity of metal-cyclam complexes and their derivatives against *Mycobacterium tuberculosis*, which causes tuberculosis, was the principal focus initiated by researchers [58]. Interestingly, research has progressed towards evaluating the antimicrobial properties of cyclam salt derivatives against bacterial (*E. coli*, *Pseudomonas aeruginosa*, *S. aureus*) and fungal (*Candida* sp.) pathogens [59]. Although various studies are being carried out to evaluate the antimicrobial performance of cyclam-based metal complexes, there are scarce reports on carboxylate-supported metal cyclam complexes for biological activity [60].

Considering this, the antibacterial properties of newly synthesized **1**, **2**, along with cyclam, $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, and benzoic acid against *E. coli* ATCC 25922 and *S. aureus* ATCC 25923 were evaluated using the agar well diffusion method. Among different concentrations of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 300, 500, 700, 900, and 1000 $\mu\text{g}/\text{ml}$ of **1**, 90 $\mu\text{g}/\text{ml}$ was the lowest concentration found to be effective against both *E. coli* and *S. aureus*. Moreover, as seen in **Figure 22**, the antibacterial activity of **1** against *E. coli* and *S. aureus* varied in a dose-dependent manner, ranging from 11.0–27.3 mm and 9.33–26.0 mm, respectively, for concentrations 100, 300, 500, 700, 900, and 1000 $\mu\text{g}/\text{mL}$. However, compound **1** was more effective against Gram-negative *E. coli* than *S. aureus*. Alves et al. [61] reported the minimum inhibitory concentration (MIC) of 9, 261, and 15 $\mu\text{g}/\text{mL}$ for $\text{H}_2\{\text{H}_2(^4\text{-CF}_3\text{PhCH}_2)_2\text{Cyclam}\}[(\text{CH}_3\text{COO})_2 \cdot (\text{CH}_3\text{COOH})_2]$ against *E. coli*, *P. aeruginosa*, and *S. aureus* strains, respectively, by the broth dilution method. Furthermore, protonated cyclam $[\text{H}_4(\text{H}_4\text{Cyclam})\text{Cl}_4]$ showed MIC of $> 512 \mu\text{g}/\text{mL}$ for *E. coli* ATCC 25922 and *S. aureus* strains, respectively [59]. Nikolića and co-workers [60] examined Cu and Co-based substituted cyclam derivatives for antimicrobial activity. Their results revealed significant antimicrobial activity of $\text{Co}_4(\text{pm})(\text{topic})_2[(\text{ClO}_4)_4 \cdot 6\text{H}_2\text{O}]$ against *Bacillus subtilis*, *Klebsiella pneumonia*, and *S. aureus* strains with a MIC of 53 $\mu\text{g}/\text{mL}$, whereas the MIC was 212 $\mu\text{g}/\text{mL}$ for *E. coli* and *Enterococcus faecalis*. In contrast, $[\text{Cu}_2(\text{pma})(\text{tpmc})] \cdot 8\text{H}_2\text{O}$ failed to exhibit activity against the pathogenic strains. It is important to note that cyclam, $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, and benzoic acid at 1000 $\mu\text{g}/\text{ml}$ did not exhibit antibacterial activity. Similarly, compound **2** and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ failed to inhibit the growth of *E. coli*, and *S. aureus* at 1000 $\mu\text{g}/\text{ml}$. In contrast, Sreedaran et al. [62] reported antimicrobial activity of cyclam-based nickel (II) complexes at 100 $\mu\text{g}/\text{mL}$ against *E. coli* ATCC 11775, *P. aeruginosa* ATCC 10145, *K. pneumonia* ATCC 13883, *B. subtilis* ATCC 6633, and *S. aureus* ATCC 12600. The lack of activity by individual components suggests that they do not contribute effectively at 1 mg/mL against the tested pathogens, implying a synergistic effect of these components in **1** that could be responsible for antibacterial activity. Furthermore, the differences in the antibacterial activity in terms of zone of growth inhibition could be attributed to the morphological and structural differences between *E. coli* and *S. aureus*. Additionally, the presence of lipopolysaccharide in *E. coli* may account for the pathogen's sensitivity to antimicrobial agents. In conclusion, the current investigations have revealed the antimicrobial performance of **1**, which could be explored as a potent antimicrobial agent in the future.

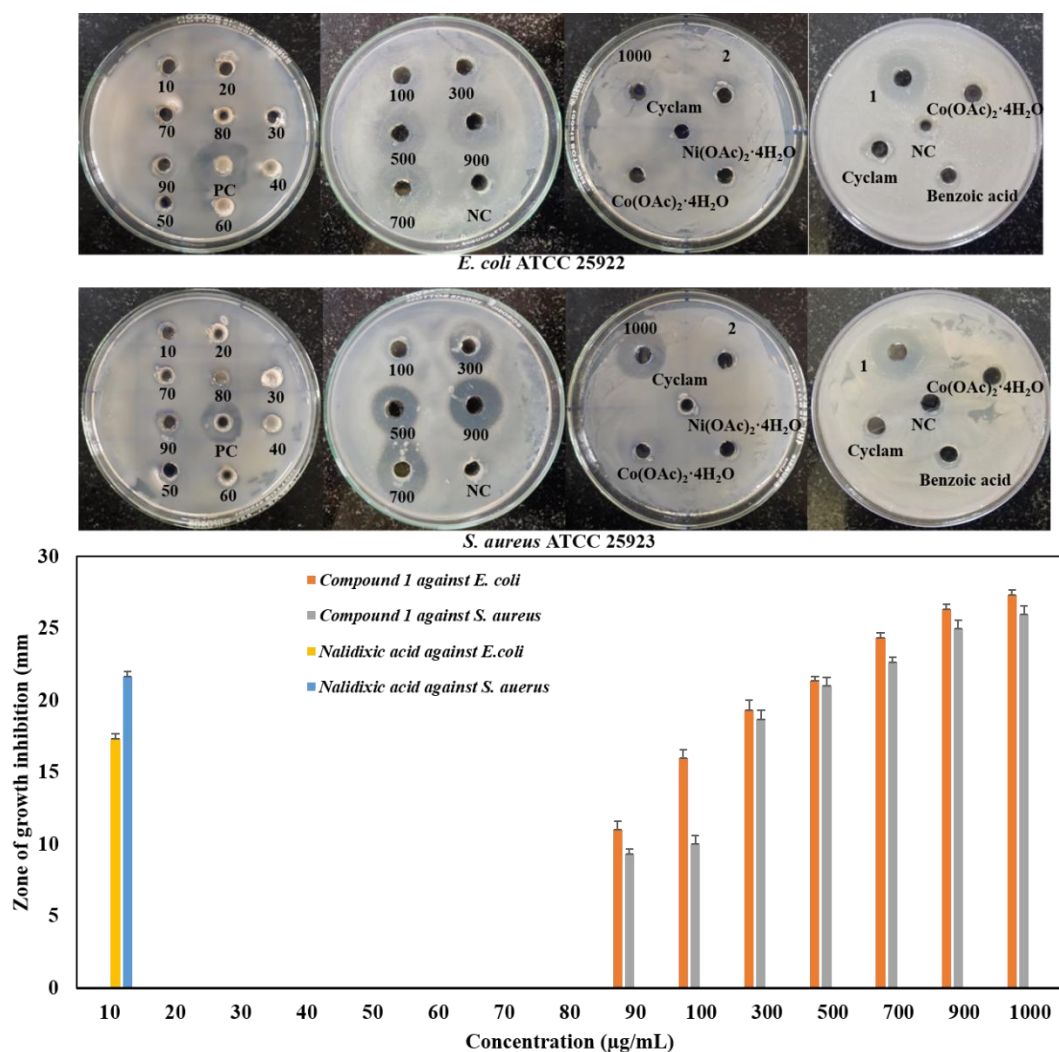


Figure 22 Antibacterial activity of **1** at different concentrations (10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 300, 500, 700, 900 and 1000 μg/ml); NC, negative control (DMSO: H₂O); PC, positive control (Nalidixic acid, 10 μg/ml); **2**, [Ni(cyclam)(H₂O)₂](MeOBz)₂·4H₂O.

3.7 Conclusions

In this work, four mononuclear compounds [Co(cyclam)(Bz)₂](Bz)H₂O (**1**) *trans*-[Ni(cyclam)(H₂O)₂](MeOBz)₂·4H₂O (**2**), *cis*-[Mn(cyclam)(Bz)₂]·H₂O (**3**), and *trans*-[Mn(cyclam)(Bz)₂]·(Bz·HBz)·2(HBz) (**3a**) were synthesized and structurally characterized. The study revealed distinct conformations of the cyclam linker depending on the metal centre and co-ligands, emphasizing the role of carboxylates in shaping supramolecular architecture. Beyond structural aspects, the cobalt compound exhibited moderate to low catecholase-like activity and a clear antibacterial effect, particularly against the *E. coli* species, highlighting its dual catalytic and biological potential as compared to the nickel compound (**2**). These findings

demonstrate that subtle changes in the ligand environment and conformation can strongly influence both the reactivity and biological properties of the metal compounds.

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Chapter 4: Structural variation induced by *ortho*-substituted carboxylate ligands in Zn (II) cyclam compounds and application in Knoevenagel condensation reactions

4.1 Chapter overview

This chapter deals with the preparation and detailed structural characterization of eight zinc coordination compounds featuring benzoate and *ortho*-substituted benzoate derivatives as co-ligands. *trans*-[Zn(cyclam)(H₂O)₂](Bz)₂ (**4**), [Zn₂(μ-H₂O)₂(cyclam)(MeBz)₄] (**5**), [Zn₂(μ-H₂O)₂(cyclam)(MeOBz)₄] (**6**), *trans*-[Zn(cyclam)(OHBz)₂] (**7**), *trans*-[Zn(cyclam)(NO₂Bz)₂] (**8**), *trans*-[Zn(cyclam)(H₂O)₂](ClBz)₂ (**9**), *trans*-[Zn(cyclam)(H₂O)₂](MeSBz)₂·4H₂O (**10**), *trans*-[Zn(cyclam)(H₂O)₂](NH₂Bz)₂ (**11**). Section 4.2 provides a literature survey on zinc cyclam compounds synthesized using a mixed ligand strategy. Section 4.3 focuses on the synthetic aspect, as well as the spectrochemical, structural, and thermal analysis of the compounds. Section 4.4 presents the structural relationship between the isomorphous compounds by analysing the isometricity parameters and describing the non-covalent interactions contributing to the supramolecular structure variation. Sections 4.5 and 4.6 evaluate the catalytic potential of selected compounds as a catalyst for Knoevenagel condensation reactions.

4.2 Literature survey on zinc cyclam-based coordination compounds.

Cyclam and its derivatives have been widely employed in synthesizing metal compounds owing to their property to stabilize the metal center through strong coordination and exhibit remarkable conformational flexibility [1-3]. Various cyclam and its derivatives-based metal compounds have been reported, most notably with cobalt, nickel, copper, and zinc. Depending upon the nature of the compounds, they are then explored for diverse purposes, such as in catalysis [4,5], sensing [6], and medicinal applications [7,8]. Zinc cyclam compounds, in particular, have gained considerable attention because the structural features of some zinc-cyclam derivatives are biologically significant, with some showing potent activity as CXCR4 antagonists, which is valuable in HIV treatment and controlling cancer metastasis [9]. CXCR4 is a chemokine receptor that is implicated in multiple diseases such as cancer, HIV/AIDs, and inflammatory disorders. The Xylyl-bicyclam (AMD3100 (PlerixaforTM)) is the most notable cyclam derivative effective as a CXCR4 antagonist; however, it has not been that effective in cancer treatment as an individual agent. Coordination of such potent ligands with a transition metal can bring about configurational restriction, which may increase the receptor binding affinity and residence time [10]. The carboxylate group of the aspartate residue in CXCR4

likely forms non-covalent interactions with the cyclam ligand, contributing to its binding affinity [11]. The development of new anti-HIV drugs using cyclam-based compounds has thus become a pressing need. Achieving this requires a clear understanding of the different conformations that N-donor ligands can adopt and how the carboxylate groups interact with the zinc (II) cyclam units [12]. In this context, several studies have investigated the carboxylate moiety on the metal cyclam core and its therapeutic potential. For instance, Ligan and coworkers studied the zinc complex of xylyl-bicyclam in both solution and solid states. Detailed NMR studies showed that the compound mainly adopts *trans* I configuration along with a *trans* III conformation, while in the solid state, acetate binds in a bidentate fashion, stabilizing the ligand in *cis* V conformation. Molecular modelling further showed that the flexibility of the ligand allows it to switch between different geometries, enabling favorable interactions with the CXCR4 receptor, which is essential for its potential as an anti-HIV therapeutic [9]. Likewise, Liang and coworkers reported zinc(II) cyclam compounds with different counter anions, such as acetate, phthalate, perchlorate, and chloride ions. Their advanced NMR studies revealed that carboxylates induced a higher proportion of the *cis*-V configuration and a slight increase in *trans*-I at the expense of *trans*-III, which is generally considered the most stable configuration. These findings suggest that carboxylates exert a strong influence over the configurational preference of zinc cyclam compounds, and strong hydrogen bonding may play an important role in the anti-HIV activity of these compounds [11].

The carboxylate interactions with zinc-cyclam compounds have been explored for their role in controlling structure, stability, and reactivity. In 2005, Jo and coworkers, investigated compounds such as $[\text{Zn}(\text{L})(\text{tp})] \cdot \text{H}_2\text{O}$, $[\text{Zn}(\text{L})(\text{H}_2\text{bta})] \cdot 2\text{H}_2\text{O}$, $[\text{Zn}_2(\text{L})_2(\text{ox})]_2\text{ClO}_4 \cdot 2\text{DMF}$ and $[\text{Zn}(\text{L})(\text{H}_2\text{bta})] \cdot 2\text{H}_2\text{O}$ where **L** = cyclam, tp = 1,4-benzenedicarboxylate, H₂bta = 1,2,4,5-benzenetetracarboxylate, ox = oxalate and H₂btc = 1,3,5-benzenetricarboxylate. Their structural analysis revealed strong coordination between the carboxylate anions and the $[\text{Zn}(\text{cyclam})]^{2+}$ core. In the case of the oxalate ligand, a dinuclear compound was formed containing $[\text{Zn}_2(\text{L})_2(\text{Ox})]^{2+}$ cationic units, with the oxalate adopting a bis-bidentate coordination mode. As a result, the cyclam in $[\text{Zn}_2(\text{L})_2(\text{ox})]_2\text{ClO}_4 \cdot 2\text{DMF}$ adopts the *cis*-V configuration. In contrast, aromatic carboxylate ligands such as 1,4-benzenedicarboxylate and 1,2,4,5-benzenetetracarboxylate promoted the formation of 1D coordination polymers [13]. A CSD search further revealed many analogous compounds, where extension into 1D is assisted by various linear or bent ditopic or polytopic carboxylate linkers [14-16]. In 2006, Kim and

coworkers studied two zinc-cyclam compounds, $[\text{Zn}(\text{L})(\text{maleate})]\cdot\text{H}_2\text{O}$, $[\text{Zn}(\text{L})(\text{H}_2\text{O})_2](\text{fumarate})\cdot 4\text{H}_2\text{O}$ where L = cyclam. In the presence of maleate ligand, a 1D coordination polymer was obtained by bridging two $[\text{Zn}(\text{cyclam})]^{2+}$ cores. However, the fumarate ligand did not coordinate to the metal ion. The difference arises from the conformations of the maleate and fumarate. In the case of maleate, the *cis* orientation of the carboxylate groups enables strong coordination and hydrogen bonding, while in fumarate, the *trans* orientation prevents such interactions [17]. In the same year, Kim and coworkers also reported a nickel-cyclam compound with maleate, $[\text{Ni}(\text{L})(\text{maleate})]\cdot\text{H}_2\text{O}$, which formed a 1D coordination polymer analogous to $[\text{Zn}(\text{L})(\text{maleate})]\cdot\text{H}_2\text{O}$ [18]. These examples clearly show that crystal packing and overall structure arrangements in metal-cyclam compounds can be tuned by varying the carboxylate linkers or modifying the substituents on the macrocycle.

In a multi-component system, the molecular nature and positioning within the lattice play a crucial role in determining crystal packing. In some cases, small variations can significantly disrupt the overall packing, as observed for $[\text{Zn}(\text{L})(\text{maleate})]\cdot\text{H}_2\text{O}$ and $[\text{Zn}(\text{L})(\text{H}_2\text{O})_2](\text{fumarate})\cdot 4\text{H}_2\text{O}$ discussed earlier. Whereas in some cases, slight variations in the molecules do not disrupt the overall packing, leading to the formation of analogous compounds. Such compounds can be described as isostructural when they share similar chemical composition, molecular conformation, and most importantly, a closely related supramolecular arrangement in the same space group [19-22]. Bombicz and co-workers highlighted various methods to recognize isostructurality in related compounds. These methods include numerical descriptors such as cell similarity (π), isostructurality index (I_s), and molecular isometricity indices. Statistical approaches help investigate the extent of isostructurality exhibited by related compounds with the same space group and Z [19]. In the present work, we build on this foundation by investigating zinc-cyclam-based compounds incorporating *ortho*-substituted carboxylates, with a focus on understanding how carboxylate anions interact with the zinc-cyclam core and influence the resulting supramolecular arrangement.

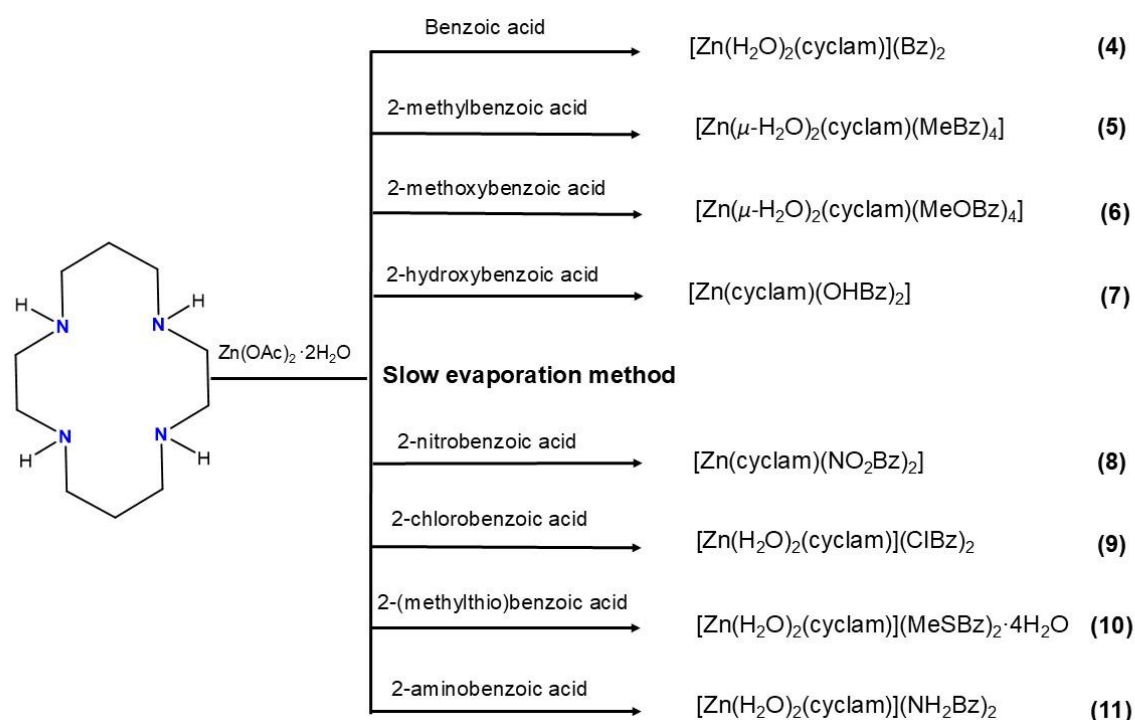
Beyond their structural diversity and supramolecular features, transition metal-cyclam compounds are increasingly valued for their catalytic potential. Zinc compounds with N-donor ligands, in particular, have been explored in reactions including electrochemical reduction of CO_2 [23,24], ester hydrolysis [25], and hydroamination reactions [26]. The environmentally benign nature, natural abundance, and low toxicity of zinc make it an attractive candidate for

catalyzing the synthesis of heterocyclic compounds [27]. Moreover, the redox-inactive nature of zinc allows it to form stable complexes with N- O- and S-donor linkers [28]. In this context, our work focuses on exploring the catalytic potential of the newly synthesized zinc coordination polymers for preparing biologically relevant heterocyclic compounds.

4.3 Results and discussion

4.3.1 Synthetic aspects of compounds 4-11

The zinc compounds **4-11** were synthesized *via* the slow evaporation method at room temperature, wherein aqueous $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ solution was initially mixed with the corresponding carboxylic acid and stirred at 80°C until a clear solution was obtained. The resulting solution was then reacted with the cyclam ligand for 1 hour. Upon standing at room temperature, this reaction mixture afforded suitable single crystals of compounds **4-11**, which were then washed using cold distilled water and used for further analysis. A general scheme showing the synthetic route for **4-11** is shown in **Scheme 1**.



Scheme 1. Schematic representation of the synthesis of zinc-cyclam compounds with incorporated carboxylate ligands.

4.3.2 Elemental analysis of compounds 4-11

The Elemental data of the synthesized compounds are shown in **Table 1**. The calculated percentage of carbon, hydrogen, and nitrogen in compounds **4-11** is in good agreement with their experimental values.

Table 1. Elemental analysis data

Sr. No.	Molecular formula	Molecular Weight	Calculated %	Experimental %
1	ZnC ₂₄ H ₃₈ N ₄ O ₆ (4)	543.97	C = 52.98 H = 7.05 N = 10.3	C = 52.9 H = 6.98 N = 10.15
2	ZnC ₄₂ H ₅₆ N ₄ O ₁₀ (5)	907.68	C = 55.57 H = 6.23 N = 6.17	C = 55.97 H = 6.32 N = 6.48
3	ZnC ₄₂ H ₅₆ N ₄ O ₁₄ (6)	971.68	C = 51.91 H = 5.82 N = 5.77	C = 51.9 H = 5.86 N = 5.67
4	ZnC ₂₄ H ₃₄ N ₄ O ₆ (7)	539.94	C = 53.38 H = 6.36 N = 10.38	C = 53.5 H = 6.48 N = 10.69
5	ZnC ₂₄ H ₃₂ N ₆ O ₈ (8)	597.95	C = 48.2 H = 5.4 N = 14.06	C = 48.5 H = 5.65 N = 14.2
6	ZnC ₂₄ H ₃₆ N ₄ O ₆ Cl ₂ (9)	612.86	C = 47.08 H = 5.93 N = 9.14	C = 48.02 H = 6.02 N = 9.58
7	ZnC ₂₆ H ₅₀ N ₄ O ₁₀ S ₂ (10)	708.21	C = 44.09 H = 7.13 N = 7.91	C = 43.97 H = 7.02 N = 7.85
8	ZnC ₂₄ H ₄₀ N ₆ O ₆ (11)	574.01	C = 50.21 H = 7.04 N = 14.64	C = 50.4 H = 7.15 N = 14.8

4.3.3 Infrared (IR) analysis

The IR spectral analysis showed sharp absorption bands in the range of ~1670 and 1300 cm⁻¹, corresponding to the characteristic asymmetric and symmetric stretching vibration of the carboxylate (COO⁻) group. This confirms the incorporation of the carboxylate moieties in the synthesized compounds. The bands observed in the IR spectra of compounds **4-11** are shown in **Table 2**. The IR spectrum of compound **4** (**Figure 1**) shows two distinct bands at 1579 and 1379 cm⁻¹, which can be assigned to the vibrations of the deprotonated carboxylate groups. The

spectra of compounds **5** and **6** are presented in **Figure 2**, while those of compounds **7-11** are shown in **Figure 3**. Broad absorption bands appearing approximately below 3500 cm^{-1} in compounds **4-6** and **9-11** are attributed to the O-H stretching vibrations of the aqua molecules [29]. In addition, medium to weak bands in the region of $3100\text{ -}2800\text{ cm}^{-1}$ correspond to C-H and N-H vibrations of the organic moieties. In the spectral analysis of compound **11**, we identified an asymmetric stretching vibration ν_{as} (N-H), of the amino group in the range of $3494\text{--}3463\text{ cm}^{-1}$ and a symmetric stretching vibration ν_{s} (N-H), in the range of $3388\text{--}3360\text{ cm}^{-1}$. The N-H peaks in the compound are comparatively broader than in the free acid, which indicates involvement of the primary amino group in extensive hydrogen bonding with the carboxylate groups [30].

Table 2. The IR absorption bands in synthesized compounds **4-11**

Compound	IR data (cm^{-1})
4	3423-2864 (br), 1579(sh), 1554(sh), 1382(sh), 1095(m), 1041(m), 954(m), 727(sh), 673(m), 526(m), 418(m)
5	3402-3289(br), 3272(m), 3145-2854(br), 1678(w), 1565(sh), 1383(sh), 1092(m), 950(m), 844 (m), 752(sh), 661(m), 471(m)
6	3442-2814(br), 1610(m), 1543(sh), 1462(m), 1377(sh), 1249(m), 1099(m), 1022(m), 966(m), 879(m), 769(m), 655(m) 566(m)
7	3302-2816(br), 3224(m), 3142(m), 1570(m), 1523(sh), 1427(sh), 1334(sh), 1298(m), 1053 (m), 904(m), 719(sh), 613(m), 487(m)
8	3392-2870(br), 1614(sh), 1568(m), 1527(sh), 1375(sh), 1284(m), 1095(m), 989(m), 939(m), 825(m), 788(s), 694(m) 648(m), 432(m)
9	3537-3309(br), 3277(m), 3149-2852(br), 1665(w), 1586(sh), 1469(m), 1388(sh), 1095(m), 1041(m), 954(m), 760(sh), 649(sh)
10	3516-3313(br), 3246-2816(br), 1660(w), 1586(m), 1569(m), 1545(m), 1381(s), 1094(m), 967(m), 756(sh), 651(m), 459(m).
11	3512-3387(br), 3296-2868(br), 1662(w), 1614(sh), 1535(sh), 1487(m), 1355(sh), 1265(m), 1095(m), 748(sh), 663(m), 526(m).

Note: **br**(broad), **sh**(sharp), **w**(weak), **m**(medium)

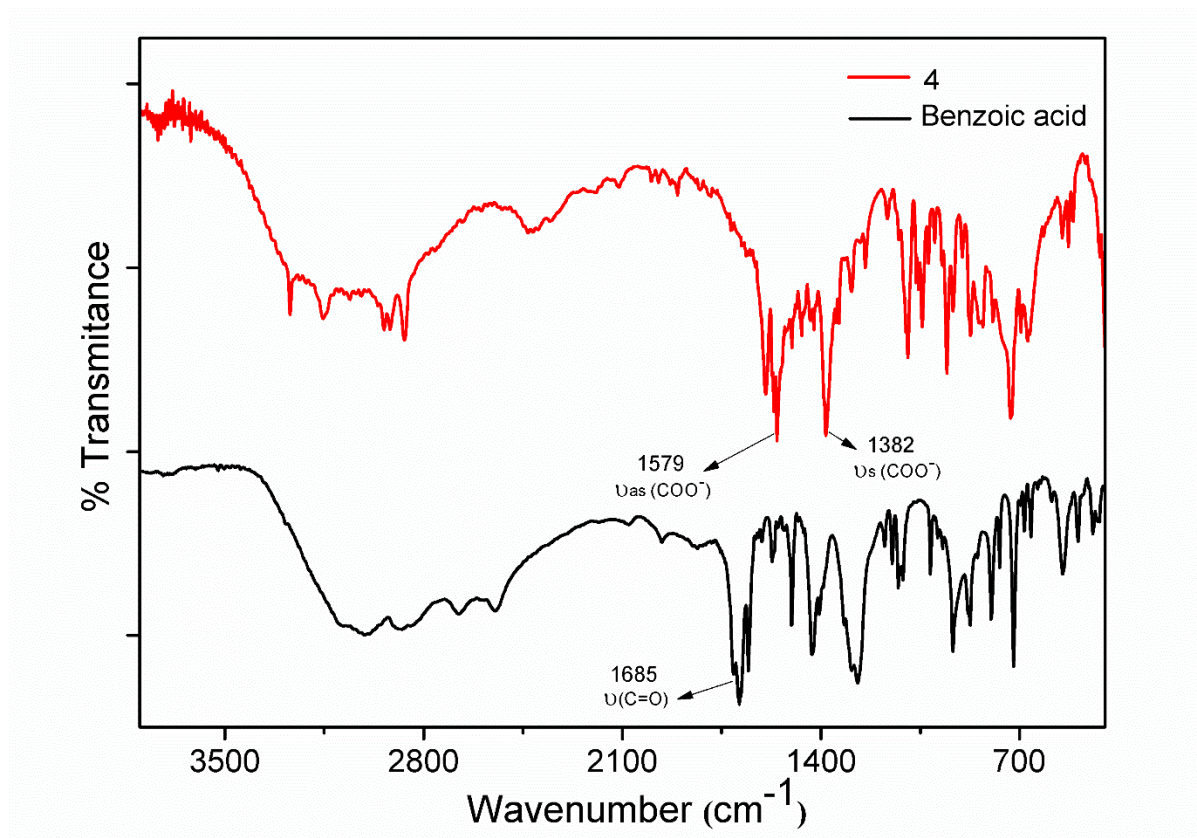


Figure 1. The IR spectra of compound **4** overlaid with that of benzoic acid.

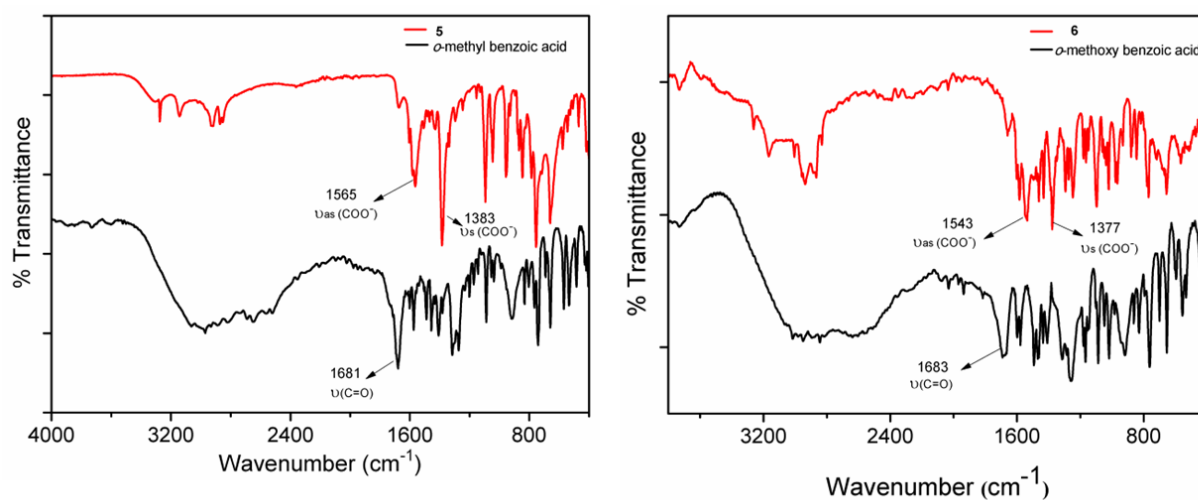


Figure 2. a) The IR spectrum of **5** overlaid with *o*-methylbenzoic acid (Left) and b) The IR spectrum of **6** overlaid with *o*-methoxybenzoic acid (Right)

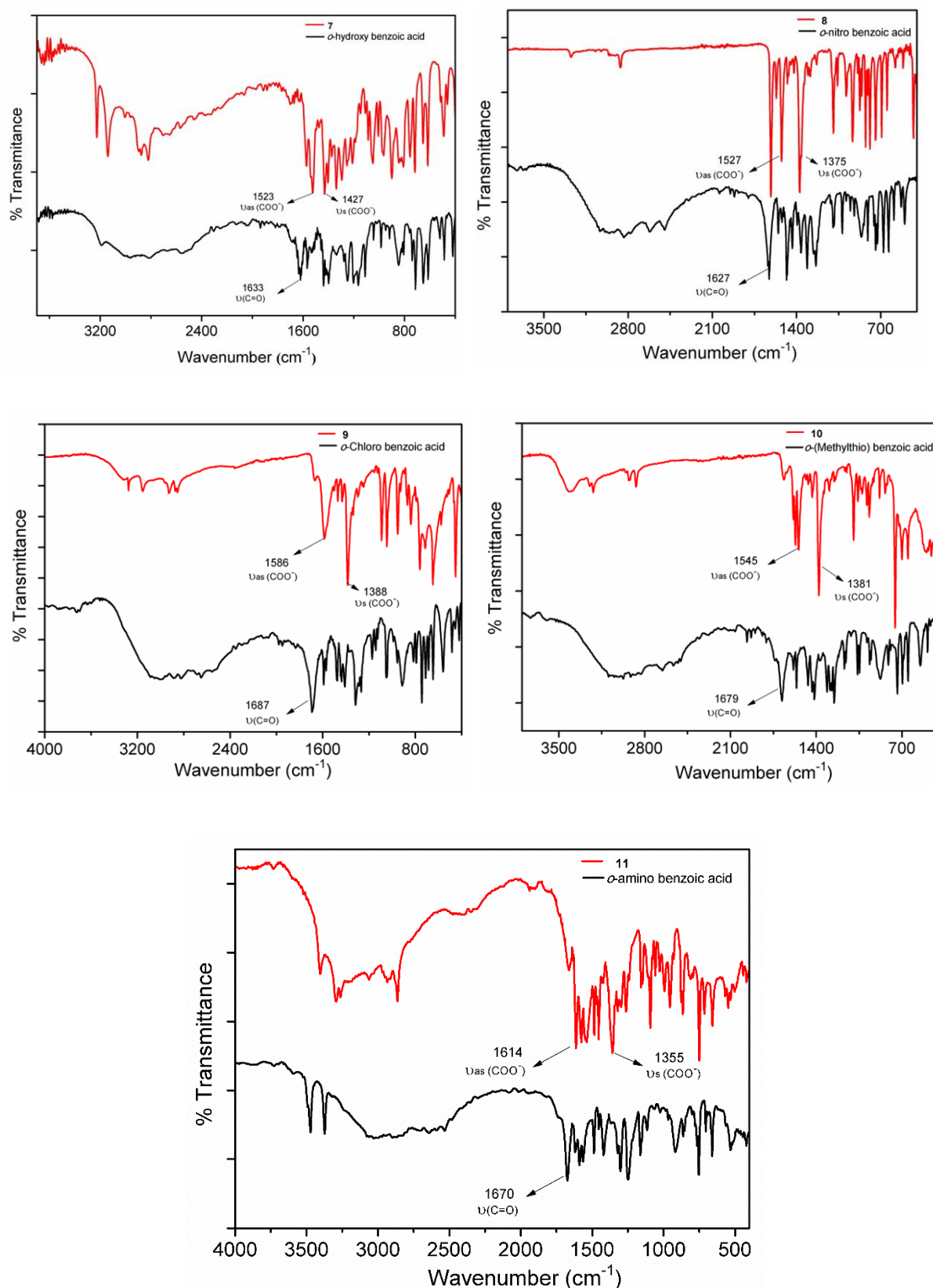


Figure 3. The IR spectra of compounds 7-11 overlaid with their corresponding carboxylic acids.

4.3.4 Thermal data analysis

The thermal decomposition behaviour of compound **4**, comprising the parent benzoate ligand, was compared with that of **5**. The thermal profiles of **4** and **5** are shown in **Figures 4** and **5**, respectively. In both compounds, the initial mass loss corresponds to the removal of coordinated water molecules. For compound **5**, this loss occurs 90-150°C, amounting to 3.91 % (Calcd. 3.97%), and is attributed to the release of bridging aqua molecules. This process is accompanied by two endothermic peaks in the DTA curve, centered at 118 and 145°C. In contrast, compound **4** loses its aqua ligands in a much lower temperature range of 80°C and 125°C, due to their monodentate coordination as reflected by an endothermic signal at 87°C in the DTA trace. This suggests that compound **5** is thermally more stable than **4**, as it can retain the coordinated water up to slightly higher temperatures.

The next stage of decomposition involves the cyclam ligand. In compound **5**, a mass loss of 22.72 % (Calcd. 22.07 %) is observed, while in **4**, it shows 36.92 % (Calcd. 37 %) in the range of 250 -350°C. After dehydration and the breakdown of the cyclam, further heating up to 700°C results in the decomposition of the carboxylate moieties. In compound **5**, a mass loss of 56.15 % (Calcd. 56.05 %) was observed due to the elimination of *o*-methylbenzoate groups, whereas in **4**, due to the decomposition of the benzoate ligand, a mass loss of 39.28% (Calcd. 41.6 %) was observed. The final residue left after complete decomposition is 17.22 in **5**, which is in close agreement with the calculated value for ZnO (17.91%). In the case of compound **4**, the residue is slightly higher at 17.7 % compared with the calculated value of 15 % for (ZnO).

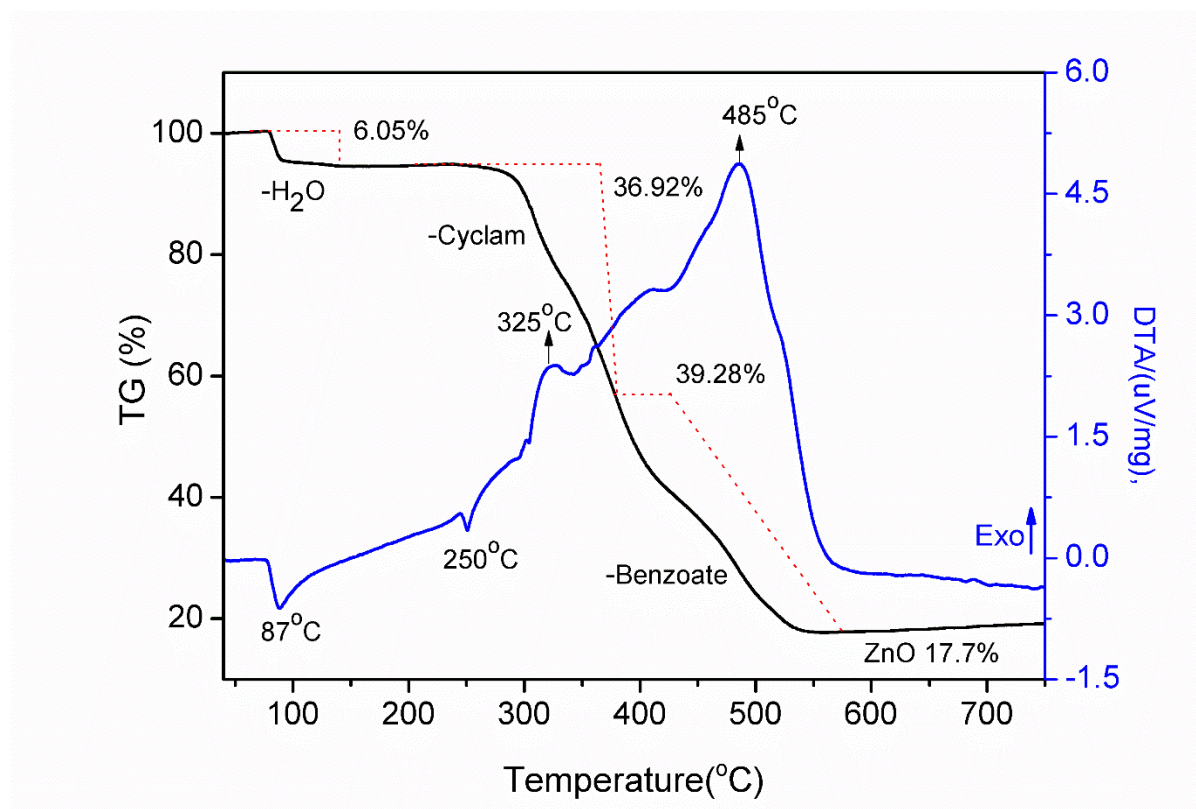


Figure 4. The TG-DTA plot of **4** recorded at a heating rate of 10 °C min⁻¹ in N₂ atmosphere

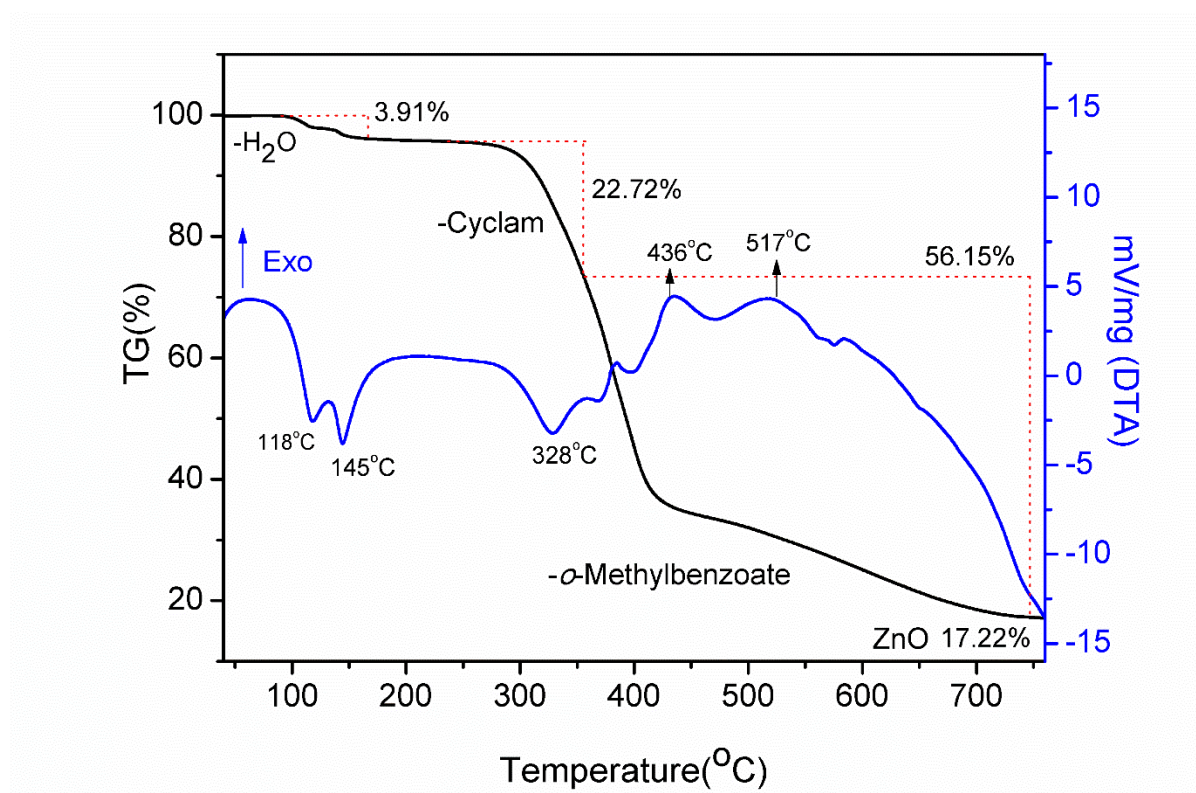


Figure 5. The TG-DTA plot of **5** recorded at a heating rate of 10 °C min⁻¹ in N₂ atmosphere

4.4 Single-crystal X-ray diffraction studies and comparative analysis of synthesized compounds

The structural analysis of the eight zinc compounds (**4-11**) showed that the cyclam ligand consistently adopts the *trans*-III configuration regardless of the carboxylate anion. This shows that any structural variations within the series primarily arise because of the interactions between the zinc cyclam core and the carboxylate anions bearing *ortho* substituents. By comparing the structures across the series, the extent to which these substituents influence the overall crystal packing can be better understood. To explore the influence of the carboxylates on the crystal packing, the compounds were first classified according to their unit cell parameters and subsequently evaluated for isostructurality parameters. The technical details of data acquisition and selected refinement parameters are shown in [Table 3](#). The zinc series was divided into three groups as follows, **Group I:** Includes compounds **5** and **6**, as both crystallize in the monoclinic system with the *C2/m* space group. **Group II:** Includes **7** and **8** as they crystallize in the orthorhombic system with *Pbca* space group. **Group III:** includes **4**, **9**, and **10** as these compounds crystallize in the monoclinic *P2₁/n* space group. Compound **11** could not be included in any of these groups, as it crystallized in the monoclinic crystal system with the *C2/c* space group.

4.4.1 Single crystal analysis of compounds **5** and **6**

The crystal structure of compounds belonging to Group I exhibits a one-dimensional *zig-zag* chain structure due to bridging aqua molecules located on a two-fold crystallographic axis that binds to the $[\text{Zn}(\text{cyclam})]^{2+}$ cationic and the anionic units $[\text{Zn}(\text{L})_4]^{2-}$. The crystal structure of compound **5**, depicted in [Figure 6](#), comprises two crystallographically independent Zn^{+2} ions occupying the special positions (Zn1 and Zn2), each adopting a distorted octahedral geometry. The $\text{Zn}\cdots\text{Zn}$ separation in the coordination polymer (CP) was observed to be 4.318 Å. The Zn1 ion coordinates with the cyclam ligand *via* four nitrogen atoms (N1, N1ⁱ, N1ⁱⁱ, N1ⁱⁱⁱ) on the equatorial plane (*symmetry code* *i* = -*x*, 1-*y*, 1-*z*, *ii* = *x*, -*y*+1, *z*, *iii* = -*x*, *y*, 1-*z*). The axial positions are occupied by the oxygen atom (O1W and O1Wⁱⁱⁱ) from the bridging aqua molecules, thus forming {ZnN4O2} coordination sphere. On the other hand, the Zn2 ion coordinates to six oxygen atoms forming the {ZnO6} core, wherein the four oxygen atoms are contributed from the carboxylate group of *o*-methyl benzoate ligands as depicted in [Figure 7](#). The O-donor ligand adopts a monodentate coordination mode, and axial oxygen atoms are contributed by the bridging aqua molecules. The coordination environment in compound **6** also

shows a similar coordination environment to that seen in **5**. Here, the two zinc ions also adopt an octahedral geometry, with Zn1 ion forming {ZnN₄O₂} and Zn2 forming {ZnO₆} coordination sphere depicted in **Figure 8**.

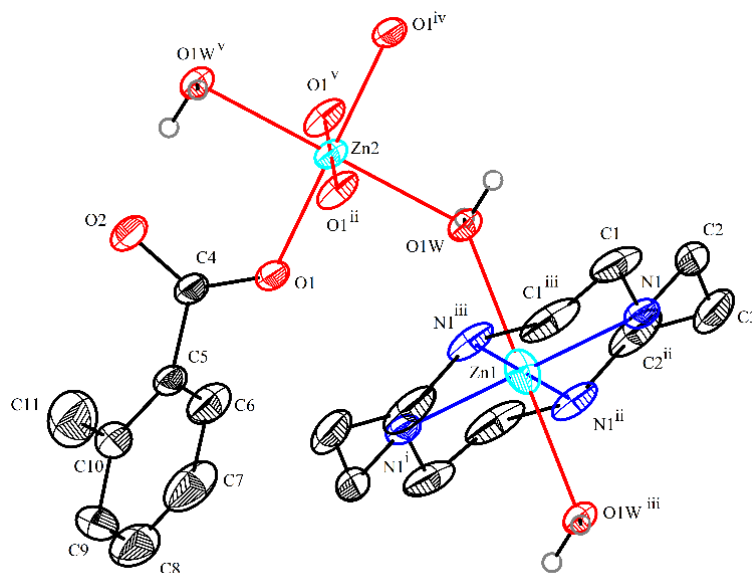


Figure 6. The ORTEP diagram **5** exhibits a portion of the chain with an atom labelling scheme. Thermal ellipsoids are drawn at 30 % probability except for the hydrogen atoms. For clarity, the hydrogen atoms on the cyclam and the carboxylate ligand have been omitted. *Symmetry codes i) -x, 1-y, 1-z, ii) x, 1-y, z, iii) -x, y, 1-z, iv) 1-x, 1-y, 1-z and v) 1-x, y, 1-z*

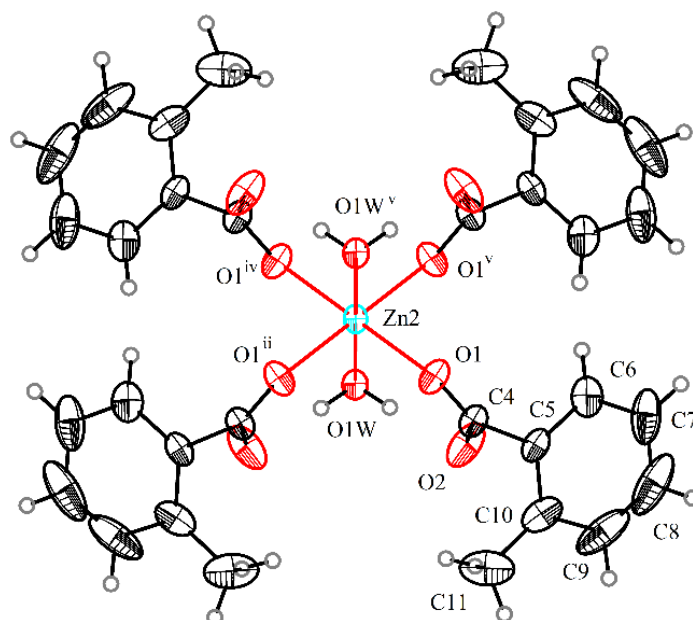


Figure 7. Shows the monodentate coordination mode adopted by *o*-methylbenzoate anions around the Zn2 ion in **5**.

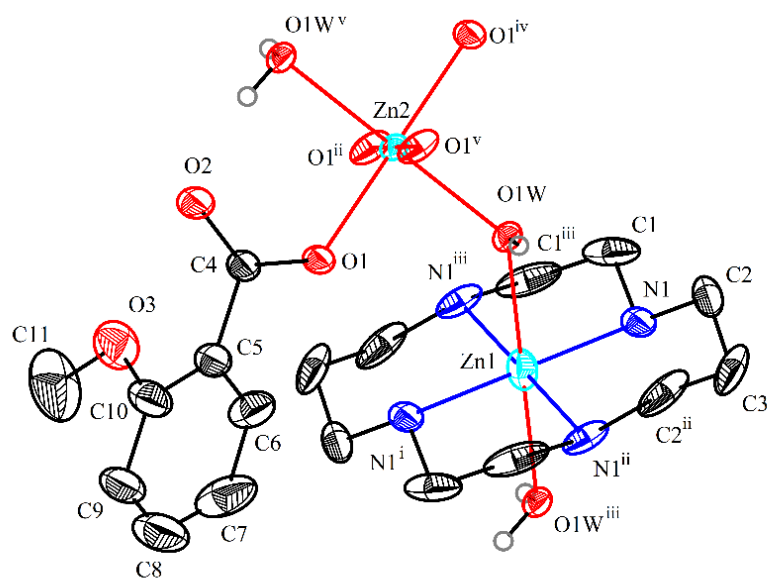


Figure 8. A portion of a 1D chain of **6**, along with an atom labelling scheme. The thermal ellipsoids were drawn at 30 % probability except for the hydrogen atoms. For clarity, the hydrogens on the cyclam and *o*-methoxybenzoate have been omitted. (Symmetry codes *i*) 2-*x*, 1-*y*, 1-*z*, *ii*) *x*, 1-*y*, *z*, *iii*) 2-*x*, *y*, 1-*z*, *iv*) 1-*x*, 1-*y*, 1-*z* and *v*) 1-*x*, *y*, 1-*z*)

In both compounds, the octahedral geometry shows noticeable distortion, primarily due to elongation of the axial bonds caused by the bridging aqua molecules. The Zn-O1W_(aqua bridged) bond (**5**) 2.448(17) and (**6**) 2.463(4) Å is comparatively longer than the Zn-O1W_(aqua monodentate) reported for [Zn(cyclam)(H₂O)₂](OAc)₂ [11], [Zn(cyclam)(H₂O)₂](fumarate)·4H₂O [17], [Zn(L)(H₂O)₂]Cl₂ (where L = 2,5,9,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane) [31], Despite the presence of different acid counterparts, the Zn1-O1W-Zn2 bond angles in both compounds are very similar to one another, measured at **5** 133.23° (19) and **6** 132.49 (17)° and are in good agreement with the bond angle observed in compounds containing Zn-O_(aqua)-Zn type bridges observed in [Zn(μ²-H₂O)_{0.5}(5N₃-IPA)(2,2'-bpe)] and [Zn(μ²-H₂O)_{0.5}(5N₃-IPA)(1-10-Phen)], (where 5N₃-IPA = 5-azidoisophthalate, 2,2'-bpe = 2,2'-bipyridine and 1,10-Phen = 1,10-phenanthroline)[32]. The Zn-N and Zn-O bond length in compounds **5** (2.078(17) Å) and **6** (2.056(13) Å) lies in accordance with the bond lengths reported for zinc compounds exhibiting tetragonal elongation in their structures [33,34]. The selected bond distances and angles for **5** and **6** are summarized in Table 4.

The CSD search on the aqua bridged compound with cyclam as the N-donor linker, showed only one entry [CCDC no = 1985181]. Dissem *et al* synthesized a similar mixed ligand CP,

$[\text{Cu}(\text{H}_2\text{btca})_2(\text{H}_2\text{O})_2\text{Cu}(\text{cyclam})]\cdot\text{H}_2\text{O}$ here (H_2btca = 1,2,4,5-benzene tetracarboxylic dianion) in methanol at room temperature. Some of the structural features of the title compound are akin to those of compounds **5** and **6**. The asymmetric unit contains two crystallographically independent Cu(II) ions located in a special position; one of the ions is coordinated with the cyclam molecule, forming the $[\text{Cu}(\text{cyclam})]^{2+}$ cationic core, which is further bridged by aqua molecule present in a special position with site occupancy of 0.5 as seen in cases of **5** and **6**. However, due to the extending nature of the H_2btca linker, it adopts the μ_2 -bidentate coordination mode, with two of the $-\text{COOH}$ groups remaining protonated, resulting in a three-dimensional CP. The macrocyclic unit $[\text{Cu}(\text{cyclam})]^{2+}$ exhibits tetragonal distortion due to the bridging aqua molecules with an average Cu-O(aqua bridged) distance of 2.52 Å. Compared to the bonds of zinc compounds **5** and **6**, the bonds are slightly longer and can be attributed to the Jahn-Teller distortion in copper compounds [35].

A better understanding of the non-covalent interactions, such as $\text{N-H}\cdots\text{O}$, $\text{O-H}\cdots\text{O}$, and $\text{C-H}\cdots\text{O}$, along with π - π stacking interactions between aromatic benzene rings of the acid component, can be achieved through structural analysis. These interactions contribute to stabilizing the crystal lattice. In compound **5**, Each cationic unit interacts with an anionic unit with the help of $\text{N1-H1}_{(\text{cyclam})}\cdots\text{O1}_{(\text{carboxylate})}$ with a donor-acceptor distance of 3.012 Å (**Table 5**). Additionally, the hydrogen atoms of the bridging aqua ligand are also involved in hydrogen bonding with the uncoordinated oxygen atoms of the carboxylate ligand $\text{O1W-H1W}_{(\text{aqua})}\cdots\text{O2}_{(\text{carboxylate})}$ with a donor-acceptor distance of 2.62 Å, thus playing significant roles in the stabilization of the structure. The formation of a 1D CP *via* intermolecular hydrogen bonds is shown in **Figure 9**. Moreover, the 1D chain is also supported through $\text{C-H}\cdots\text{O}$ and π - π interactions. Each adjacent aromatic ring of the carboxylate interacts with a weak π - π stacking interaction (centroid distance of 4.82 Å) in **5**, as shown in **Figure 10**. These weaker interactions extend the 1D chain into a 3D supramolecular network and stabilize the crystal structure.

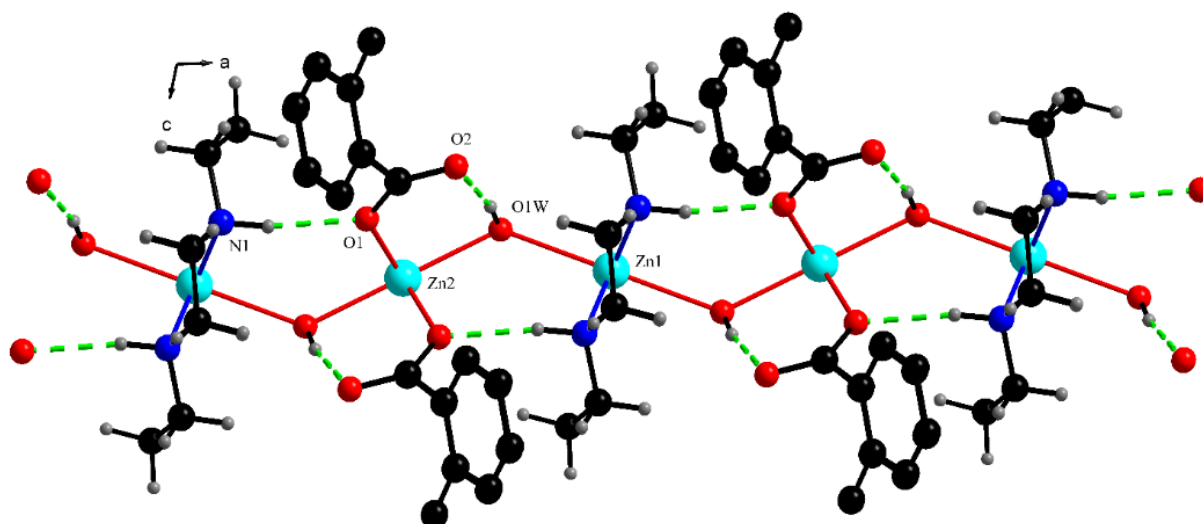


Figure 9. 1D chain structure of **5** due to bridging aqua molecules running along *a* axis. Green dotted lines show the intermolecular hydrogen bonds.

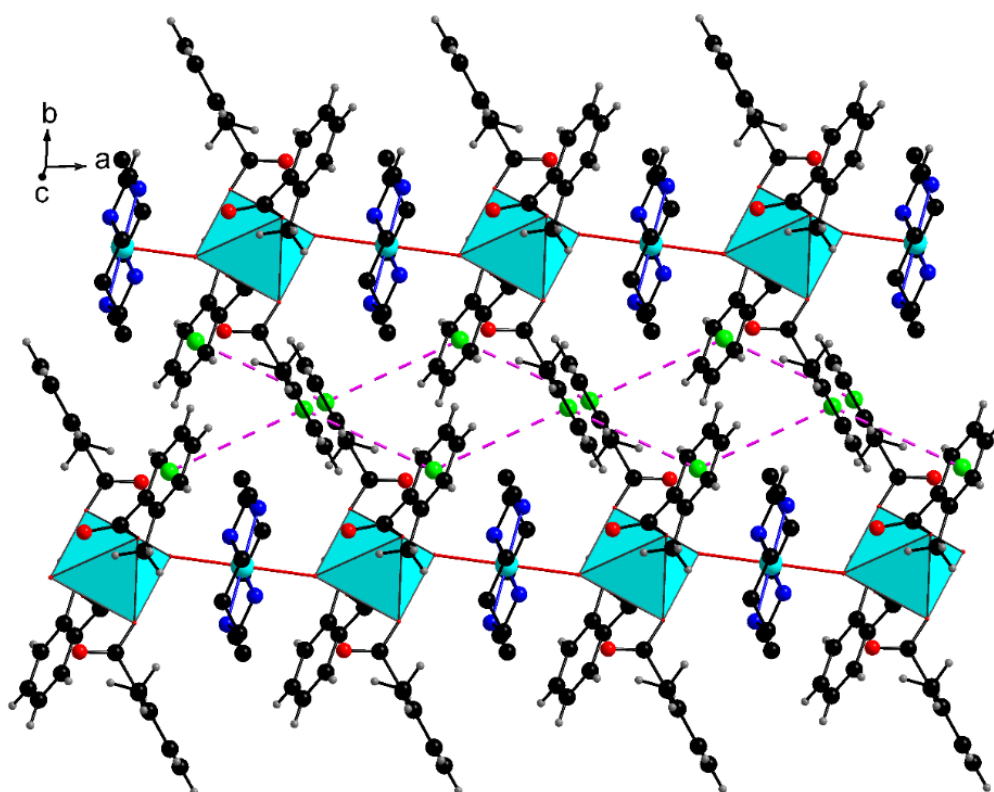


Figure 10. The weak π - π interactions between the aromatic rings of the adjacent chains, in **5** with a centroid distance of 4.82 Å

Table 3. The crystallographic data and structure refinement parameters for **4-11**.

Compound	5	6	7	8	4	9	10	11
Empirical formula	C ₄₂ H ₅₆ N ₄ O ₁ 0Zn ₂	C ₄₂ H ₅₆ N ₄ O ₁ 4Zn ₂	C ₂₄ H ₃₄ N ₄ O ₆ Zn	C ₂₄ H ₃₂ N ₆ O ₈ Z n	C ₂₄ H ₃₈ N ₄ O ₆ Zn	C ₂₄ H ₃₆ Cl ₂ N ₄ O ₆ Zn	C ₂₆ H ₅₀ N ₄ O ₁ 0S ₂ Zn	C ₂₄ H ₄₀ N ₆ O ₆ Zn
Formula Weight (g)	907.68	971.68	539.94	597.95	543.97	612.86	708.21	574.01
T (K)	296 (2)	296 (2)	296 (2)	296 (2)	296 (2)	296 (2)	296 (2)	296 (2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C</i> 2/ <i>m</i>	<i>C</i> 2/ <i>m</i>	<i>P</i> <i>b</i> <i>c</i> <i>a</i>	<i>P</i> <i>b</i> <i>c</i> <i>a</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
Unit cell dimensions (Å/°)	a= 8.6359(7)	a= 8.5789(8)	a= 13.2057(6)	a= 13.3732(5)	a= 8.6104(2)	a= 8.6444(2)	a= 9.012 (11)	a= 16.7589 (9)
	b = 22.2604(16)	b = 22.352(2)	b = 10.6115(5)	b = 11.096(4)	b = 10.7391(3)	b = 12.0356(3)	b = 8.3398(6)	b = 12.6958(7)
	c = 11.6583(9)	c = 11.6195(10)	c = 17.6741(8)	c = 17.8362(7)	c = 14.157(3)	c = 14.1167(3)	c = 22.593(2)	c = 13.9540(8)
	β = 103.563(3)	β = 97.157(3)	β = 90	β = 90	β = 104.43(10)	β = 106.761(1)	β = 92.04(4)	β = 118.206(2)
Volume (Å ³)	2178.7(3)	2210.8(3)	2476.7(2)	2646.70(17)	1267.77(5)	1406.31(6)	1697.0(3)	2616.4(3)
Z	4	4	4	4	2	2	2	4
ρ (calcd.) (Mg/m ³)	1.384	1.46	1.448	1.501	1.425	1.447	1.386	1.457
Absorption coefficient (mm ⁻¹)	1.16	1.155	1.039	0.987	1.015	1.108	0.902	0.99
F(000)	952	1016	1136	1248	576	640	752	1216
Crystal size (mm ³)	0.30x 0.11 x 0.09	0.31x 0.25 x 0.15	0.42x 0.31 x 0.15	0.43x 0.27 x 0.12	0.21x 0.12 x 0.09	0.12 x 0.09 x 0.08	0.47 x 0.30 x 0.14	0.41 x 0.35 x 0.25
θ range (°)	2.593 to 28.325	2.538 to 28.358	2.719 to 28.294	2.745 to 28.284	2.971 to 28.303	2.266 to 28.381	2.604 to 28.286	2.115 to 28.402
Index ranges	-11 $\leq$ h $\leq$ 11, -29 $\leq$ k $\leq$ 29, -15 $\leq$ l $\leq$ 15	-11 $\leq$ h $\leq$ 11, -29 $\leq$ k $\leq$ 29, -15 $\leq$ l $\leq$ 15	-17 $\leq$ h $\leq$ 17, -14 $\leq$ k $\leq$ 14, -23 $\leq$ l $\leq$ 23	-17 $\leq$ h $\leq$ 17, -14 $\leq$ k $\leq$ 14, -23 $\leq$ l $\leq$ 23	-11 $\leq$ h $\leq$ 11, -14 $\leq$ k $\leq$ 14, -18 $\leq$ l $\leq$ 18	-11 $\leq$ h $\leq$ 11, -16 $\leq$ k $\leq$ 16, -18 $\leq$ l $\leq$ 18	-12 $\leq$ h $\leq$ 12, -11 $\leq$ k $\leq$ 11, -30 $\leq$ l $\leq$ 30	-18 $\leq$ h $\leq$ 22, -14 $\leq$ k $\leq$ 16, -17 $\leq$ l $\leq$ 18
Reflections collected	32271	25506	69830	85827	42805	32990	33021	12188
Independent reflections	2781 [R(int) = 0.0335]	2830 [R(int) = 0.0713]	3078[R(int) = 0.0547]	3279 [R(int) = 0.0379]	3158 [R(int) = 0.0392]	3512 [R(int) = 0.0327]	4190 [R(int) = 0.0266]	3255 [R(int) = 0.0378]
Completeness to θ = 25.242° (%)	99.8	99.9	100	99.8	99.7	99.8	99.8	99.2
Data/restraints/parameters	2781 / 0 / 142	2830 / 120 / 156	3078 / 0 / 172	3279 / 0 / 186	3158 / 0 / 172	3521 / 0 / 178	4190 / 0 / 218	3255 / 0 / 180
Goodness-of-fit on F ²	1.018	1.149	1.15	1.075	1.057	1.051	1.05	1.022
Final R indices [I $\geq$ 2 σ (I)]	R1=0.0335, wR2=0.084	R1=0.0577, wR2=0.148	R1=0.0343, wR2=0.085	R1=0.0315, wR2=0.080	R1=0.027, wR2=0.07	R1=0.041, wR2=0.112	R1=0.026, wR2=0.067	R1=0.05, wR2=0.118
R indices (all data)	R1=0.0437, wR2=0.089	R1=0.0799, wR2=0.163	R1=0.0604, wR2=0.113	R1=0.041, wR2=0.092	R1=0.031, wR2=0.076	R1 =0.051, wR2=0.119	R1=0.031 wR2=0.069	R1=0.0762, wR2=0.133
Largest diff. peak and hole (e.Å ⁻³)	0.266 and - 0.888	0.788 and - 1.045	0.294 and - 0.524	0.472 and - 0.405	0.368 and - 0.399	0.771 and - 0.741	0.339 and - 0.368	0.670 and - 0.414
CCDC No	2376524	2376525	2376526	2376527	2376528	2376529	2376530	2376531

Table 4. Selected bond distances and bond angles for **5** and **6**

5					
<i>Bond distance</i>		<i>Bond angle</i>			
Zn1-N1	2.078(17)	N1-Zn1-O1W	91.89(5)	O1W-Zn2-O1	86.41(5)
Zn1-N1 ⁱ	2.078(17)	N1 ⁱⁱ -Zn1-O1W	88.1(5)	O1W-Zn2-O1 ⁱⁱ	86.41(5)
Zn1-N ⁱⁱ	2.078(17)	N1 ⁱ -Zn1-O1W	91.9(5)	O1W-Zn2-O1 ^{iv}	93.59(5)
Zn1-N ⁱⁱⁱ	2.078(17)	N1 ⁱⁱⁱ -Zn1-O1W	91.9(5)	O1W-Zn2-O1 ^v	93.59(5)
Zn1-O1W ⁱⁱⁱ	2.448(17)	N1-Zn1-N1 ⁱⁱ	94.34(12)	O1-Zn2-O1 ⁱⁱ	91.73(9)
Zn1-O1W	2.448(17)	N1 ⁱ -Zn1-N1 ⁱⁱ	85.66(12)	O1 ⁱⁱ -Zn2-O1 ^{iv}	88.27(9)
Zn2-O1 ^{iv}	2.056(13)	N1 ⁱ -Zn1-N1 ⁱⁱⁱ	94.34(12)	O1 ^{iv} -Zn2-O1 ^v	91.73(9)
Zn2-O1 ⁱⁱ	2.056(13)	N1-Zn1-N1 ⁱⁱⁱ	85.66(12)	O1 ^v -Zn2-O1	88.27(9)
Zn2-O1 ^v	2.056(13)	N1 ⁱⁱⁱ -Zn1-N1 ⁱⁱ	180(7)	O1W-Zn2-O1W ^v	180
Zn2-O1	2.056(13)	N1 ⁱ -Zn1-N1	180(7)	O1-Zn2-O1 ^{iv}	180
Zn2-O1W	2.255(17)	O1W-Zn1-O1W ⁱⁱⁱ	180(7)	O1 ⁱⁱ -Zn2-O1 ^v	180
Zn2-O1W ^v	2.255(17)				
6					
<i>Bond distance</i>		<i>Bond angle</i>			
Zn1-N1	2.074(3)	N1-Zn1-O1W	91.53(11)	O1W-Zn2-O1	86.99(1)
Zn1-N1 ⁱ	2.074(3)	N1 ⁱⁱ -Zn1-O1W	91.53(11)	O1W-Zn2-O1 ⁱⁱ	86.99(1)
Zn1-N ⁱⁱ	2.074(3)	N1 ⁱ -Zn1-O1W	88.47(11)	O1W-Zn2-O1 ^{iv}	93.01(1)
Zn1-N ⁱⁱⁱ	2.074(3)	N1 ⁱⁱⁱ -Zn1-O1W	88.47(11)	O1W-Zn2-O1 ^v	93.01(1)
Zn1-O1W ⁱⁱⁱ	2.463(4)	N1-Zn1-N1 ⁱⁱ	94.4(3)	O1-Zn2-O1 ⁱⁱ	91.12(18)
Zn1-O1W	2.463(4)	N1 ⁱ -Zn1-N1 ⁱⁱ	85.6(3)	O1 ⁱⁱ -Zn2-O1 ^{iv}	88.88(18)
Zn2-O1 ^{iv}	2.065(3)	N1 ⁱ -Zn1-N1 ⁱⁱⁱ	94.4(3)	O1 ^{iv} -Zn2-O1 ^v	91.12(18)
Zn2-O1 ⁱⁱ	2.065(3)	N1-Zn1-N1 ⁱⁱⁱ	85.6(3)	O1 ^v -Zn2-O1	88.88(18)
Zn2-O1 ^v	2.065(3)	N1 ⁱⁱⁱ -Zn1-N1 ⁱⁱ	180(15)	O1W-Zn2-O1W ^v	180
Zn2-O1	2.065(3)	N1 ⁱ -Zn1-N1	180	O1-Zn2-O1 ^{iv}	180
Zn2-O1W	2.222(3)	O1W-Zn1-O1W ⁱⁱⁱ	180	O1 ⁱⁱ -Zn2-O1 ^v	180

Note: Symmetry code (5): $i = -x, l-y, l-z$, $ii = x, l-y, z$, $iii = -x, y, l-z$, $iv = l-x, l-y, l-z$, $v = l-x, y, l-z$,

(6) $i = 2-x, l-y, l-z$, $ii = x, l-y, z$, $iii = 2-x, y, l-z$, $iv = l-x, l-y, l-z$, $v = l-x, y, l-z$

Table 5. Selected hydrogen bond parameters for **4-11**

D-H...A	d(D-H)	d(H...A)	<DHA	d(D...A)	Symmetry code
4					
O1W-H1W...O1	0.796	1.887	176.47	2.682	
O1W-H2W...O2	0.765	1.98	159.77	2.711	1-x, 1-y, 1-z
N1-H1...O2	0.98	1.972	169.18	2.94	1-x, y, z
5					
O1-H1W...O2	0.83	1.8	169.17	2.62	1-x, 1-y, 1-z
N1-H1...O1	0.98	2.052	165.8	3.012	-x, 1-y, 1-z
C1-H1A...O2	0.97	2.594	158.56	3.515	1-x, 1-y, 1-z
6					
O1W-H1W...O2	0.804	1.852	165.46	2.638	1-x, y, 1-z
N1-H1...O1	0.764	2.235	170.99	2.992	2-x, 1-y, 1-z
C1-H1A...O2	0.97	2.545	159.48	3.47	1-x, 1-y, 1-z
7					
O3-H1...O2	0.92	1.661	154.67	2.523	
N2-H2...O2	0.834	2.153	162.57	2.959	1-x, 1-y, 1-z
C9-H9A...O2	0.97	2.531	139	3.325	1/2-x, 1/2-y, 1-z
8					
N1-H1...O2	0.852	2.498	141.79	3.211	
C4-H4A...O1	0.97	2.608	113.82	3.129	
C1-H1A...O1	0.97	2.543	116.35	3.098	1-x, 1-y, 1-z
9					
O1W-H1W...O2	0.77	1.892	171.29	2.656	
O1W-H2W...O1	0.795	1.921	157.34	2.673	1-x, 1-y, 1-z
N1-H1...O1	0.98	1.946	168.94	2.914	1+x, y, z
10					
O3W-H1E...O2	0.757	2.131	169.93	2.879	
O3W-H2E...O2W	0.821	2.006	174.46	2.825	
O1W-H2C...O2	0.822	1.923	175.52	2.744	
O1W-H1C...O1	0.829	1.964	169.46	2.783	1-x, 1-y, 1-z
O2W-H1D...O1	0.833	2.037	169.27	2.859	1-x, 1-y, 1-z
11					
N3-H3...O1	0.86	2.075	128.36	2.695	
O1W-H1W...O1	0.707	2.097	173.68	2.801	
O1W-H2W...O1	0.691	2.175	159.74	2.833	x+3/2, 1/2-y, 1-z
O1W-H2W...O2	0.691	2.611	147.49	3.215	x+3/2, 1/2-y, 1-z
N3-H3A...O2	0.86	2.041	167.39	2.887	x, 1-y, 1/2-z

4.4.2 Cell similarity, isostructurality, and molecular isometricity and Hirshfeld surface area studies of **5** and **6**

The isostructurality index offers a strict criterion for structural similarity, accounting for the geometrical and positional differences caused by rotation and translation [19,36]. The cell similarity index obtained for the molecular pair **5** and **6** was 0.037, close to zero, suggesting similar unit cell parameters. However, the lower isostructurality index of 37% indicates a considerable difference in the close packing of the two compounds. Furthermore, the Mercury software was used to overlay the asymmetric unit of the related molecules, as depicted in **Figure 11a**, to obtain the rmsD and max D values. A higher deviation of the max D (3.7119 Å) from zero can be attributed to varying orientations of the substituents, which assume almost opposite directions. Analysis of the geometrical parameters of the carboxylate anion highlights how substituents disrupt the isostructurality in compounds **5** and **6**. Due to the ortho effect, the carboxylate group exhibits a slight bend around the ring in both compounds. The dihedral angles between the ring carrying the substituent (C5-C6-C7-C8-C9-C10) and the plane defined by (O1-C4-O2) are 64.93° in (**5**), as shown in **Figure 11b**, and 73.82° in compound **6**. Additionally, the torsion angle in compound **5** is 115.73° and -106.81° in compound **6**. These variations suggest that substituents might greatly induce conformational changes, leading to a loss of isostructurality between the related compounds.

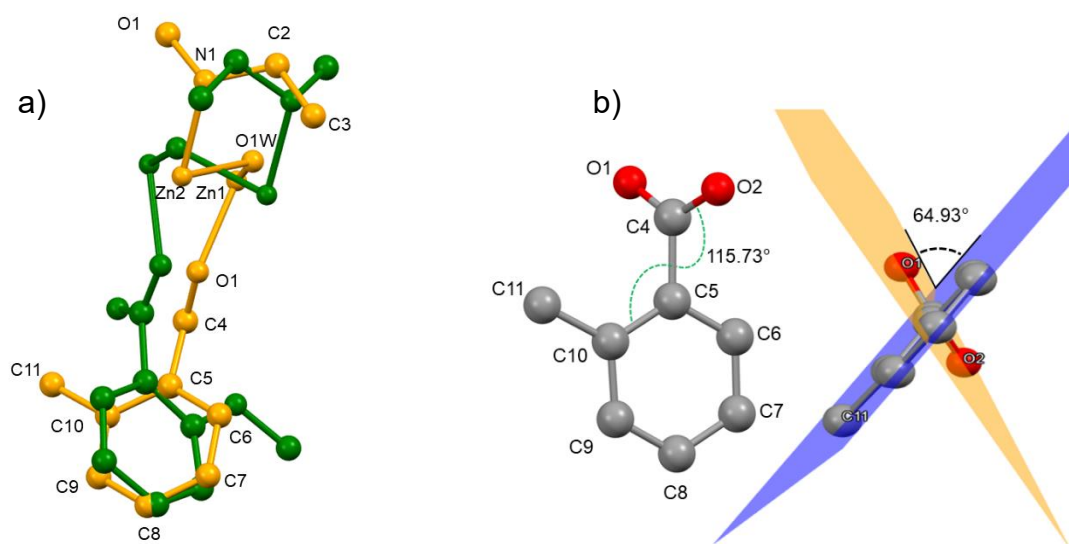


Figure 11 a). Overlay diagram of the asymmetric units of **5** (yellow) and **6** (green) compounds with rmsD = 1.9347 and max = 3.711 Å. **b).** View along the carboxylate anion, highlighting the orientation of the substituents (**left**) and dihedral angle between the mean plane through the benzene ring (C5-C6-C7-C8-C9-C10) and (O1-C4-O2) (**right**)

Further investigation of HS effectively quantifies the intermolecular interaction in the crystals. The d_{norm} surfaces with short contacts, where the distance between the atoms is shorter than the sum of their van der Waals radii, are indicated in red. The d_{norm} mapping reveals strong hydrogen bonds such as N-H $\cdots$ O contacts between the N atoms of the cyclam in the cationic unit and oxygen of the neighbouring carboxylate ligand as a bright red area in the surface, as shown in **Figure 12a** and **12e** for compounds **5** and **6**, respectively. In both compounds, the predominant interactions are of the H $\cdots$ H type, accounting for up to 67 % in compound **5**, which consists of methyl benzoate anion as the anion. However, with the introduction of methoxy benzoate in the structure of compound **6**, the H $\cdots$ H type interaction reduces by 9.4 %. Other significant interactions include C $\cdots$ H/ H $\cdots$ C and O $\cdots$ H/ H $\cdots$ O type seen in both the compounds. Given the change as mentioned earlier in the anion source, an increment of 10% is observed in the contribution from the O $\cdots$ H/ H $\cdots$ O type of interaction in compound **6**, with compound **5** accounting for 12.2%. The intermolecular interactions arising due to C $\cdots$ H/ H $\cdots$ C are nearly the same in both compounds, contributing 19.4% and 18.9 % in **5** and **6**, respectively. The 2D fingerprint plots are illustrated in **Figure 12b-d** and **12f-h** for compounds **5** and **6**, respectively.

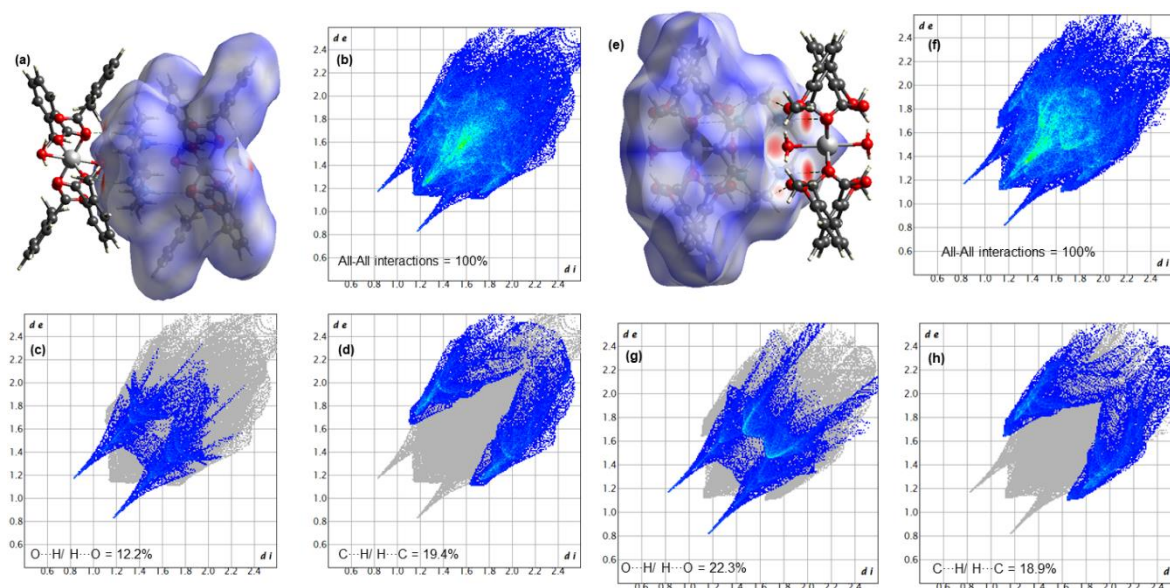


Figure 12 a) Intermolecular N-H $\cdots$ O interactions in **5** and e) interactions in **6**. b-d) 2D Fingerprint showing full, O $\cdots$ H/H $\cdots$ O and C $\cdots$ H/H $\cdots$ C type interactions with the percentage of contribution to the total Hirshfeld surface area in **5**, and figures f-h) show percentage contributions for compound **6**

Additionally, the Hirshfeld surfaces of **5** and **6** have been mapped with shape index and curvedness to identify the characteristic way the adjacent molecules interact. The effect of the substituents can be easily seen from the HS of **5** and **6**, which are distinct, suggesting that the two molecules possibly show variation in the close packing arrangements. **Figure 13** illustrates the front view of the HS of **5**, along with the shape index and curvedness plots. Curvature is an intrinsic property of any surface and shows large regions marked in green, representing a flatter surface, indicating stacking interaction [37,38]. In **5**, the curvedness plot shows similar flat surface patches above the aromatic ring, thereby supporting the presence of $\pi\cdots\pi$ interactions. Furthermore, a more distinctive feature is the red concave region on the surface around the acceptor atom and the blue region around the donor atom, further supporting the inclusion of π - π interactions between the aromatic rings, more prominent in **5** than in **6**.

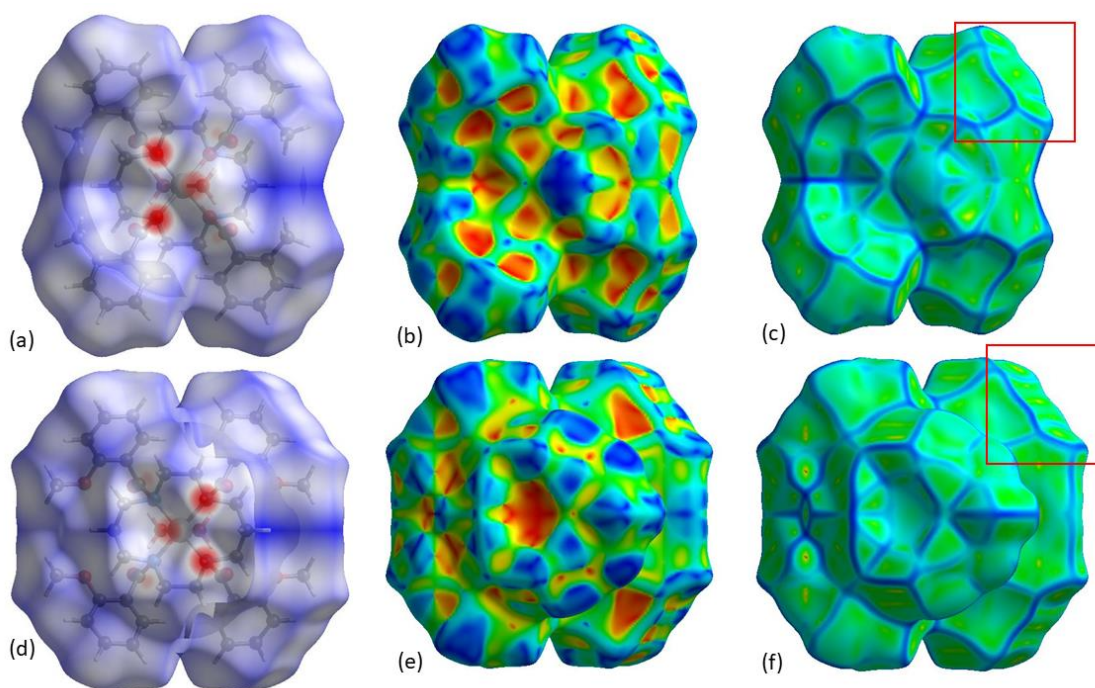


Figure 13 Hirshfeld surface mapped with (a) d_{norm} ranging from $-0.40 \text{ \AA}$ (red) to $2.04 \text{ \AA}$ (blue) $\text{\AA}$ (b) shape index, (c) curvedness of **5**, and (d) d_{norm} ranging from $-0.47 \text{ \AA}$ to $1.74 \text{ \AA}$ (e) shape index, (f) curvedness of **6** (View along *a*-axis)

4.4.3 Single crystal analysis of compounds **7** and **8**

Interestingly, the 1D chain structure observed in compound **6** was preserved when the methyl substituent was replaced with the methoxy group. This prompted further exploration with other simple substituents. Compound **7** was synthesized using *o*-hydroxybenzoic acid, and its structural analysis revealed a discrete 0D assembly rather than a polymeric chain. In the crystal structure of **7**, the zinc ion is located on an inversion center, thereby generating half of the molecule through symmetry operations. The zinc adopts an octahedral geometry coordinated equatorially to four nitrogen atoms of the cyclam ligand (N1, N1ⁱ, N2, N2ⁱ), while the axial positions were occupied by the oxygen atoms (O1 and O1ⁱ) from the carboxylate anion, in monodentate fashion (**Figure 14a**).

A comparable structural feature was observed for compound **8** in the series, obtained from *o*-nitrobenzoic acid. The crystal structure of **8** is depicted in **Figure 14b**. Both compounds display distorted octahedral environments as reflected by the slightly elongated Zn-O (2.255(15) Å in (**7**) and (2.187(12) Å) in (**8**) as compared to the average Zn-N (2.091 Å) (**7**) and (2.103 Å) in **8**. The selected bond lengths and angles of compounds **7** and **8** are listed in **Table 6**.

The crystal packing is stabilized by a combination of non-covalent interactions, including N-H $\cdots$ O, O-H $\cdots$ O, and C-H $\cdots$ O hydrogen bonds. The hydrogen bonding situation in **7**, reveals that the oxygen atom of the hydroxy group (O3) forms intramolecular hydrogen bonding with the uncoordinated oxygen atom (O2) of the carboxylate group. While the C9 (donor atom) of the cyclam ligand is involved in the formation of an intermolecular hydrogen bond with the adjacent molecule through the uncoordinated oxygen atom O2 (acceptor atom) with a D $\cdots$ A distance of 3.325 Å. These interactions give rise to an extended supramolecular network. A view of the supramolecular assembly of **7** is shown in **Figure 15**. The hydrogen bonding parameters are summarized in **Table 5**.

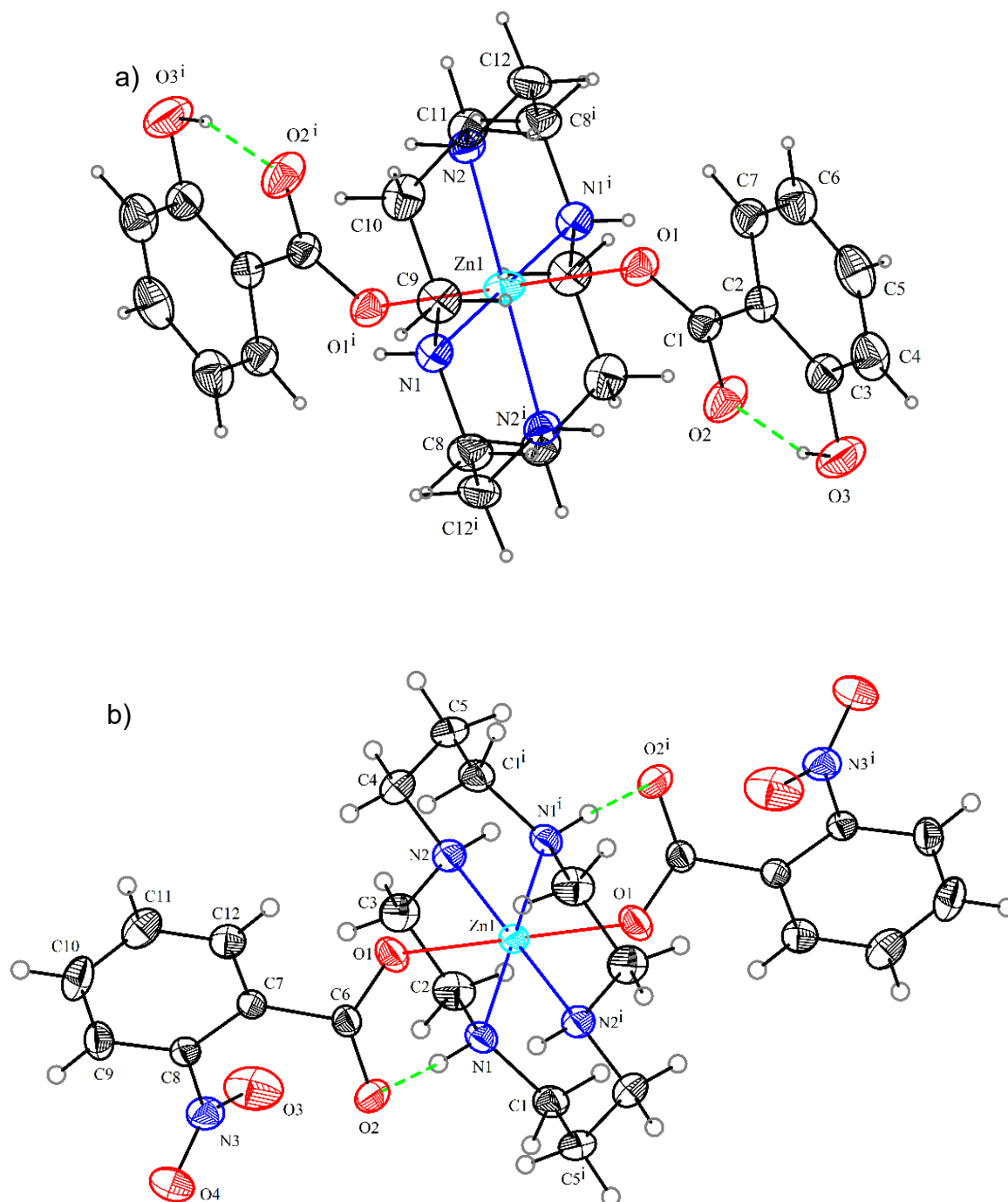


Figure 14. The thermal ellipsoid plot of compounds **7** (a) and **8** (b) with the atomic numbering scheme.

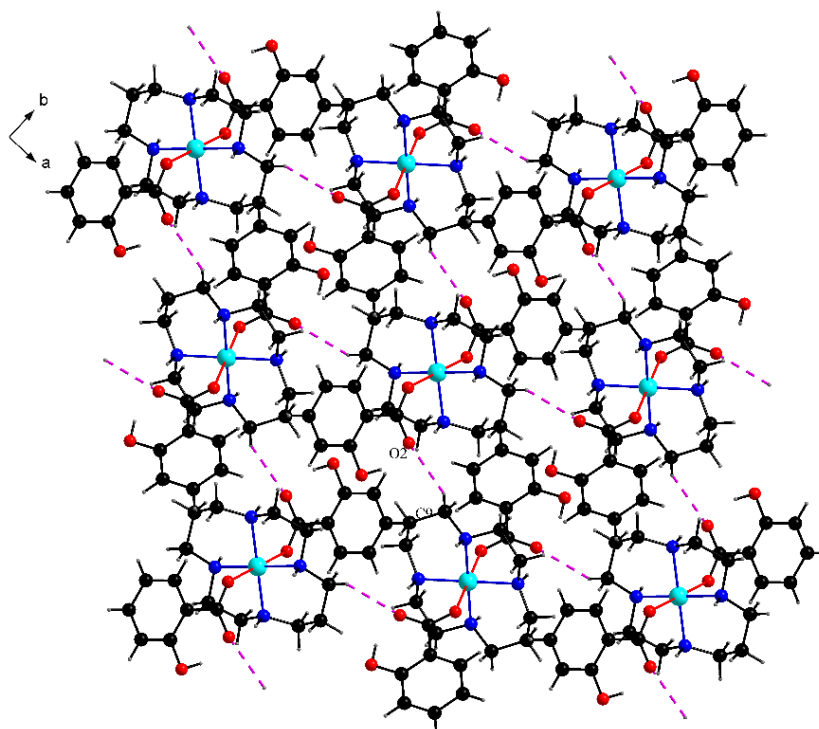


Figure 15. The C-H $\cdots$ O intermolecular hydrogen bonding situation. A view of the supramolecular network in **7**.

Table 6. Selected hydrogen bond distances and bond angles for **7** and **8**

7					
<i>Bond distance</i>		<i>Bond angle</i>			
Zn1-N1 ⁱ	2.084(18)	N1 ⁱ -Zn1-N2 ⁱ	95.08(7)	N1 ⁱ -Zn1-O1	88.14(7)
Zn1-N1	2.084(17)	N1-Zn1-N2 ⁱ	84.92(7)	N1-Zn1-O1	91.85(7)
Zn1-N2 ⁱ	2.099(17)	N1-Zn1-N2	95.08(7)	N2 ⁱ -Zn1-O1	93.08(7)
Zn1-N2	2.099(17)	N1 ⁱ -Zn1-O1 ⁱ	91.85(7)	N1 ⁱ -Zn1-N1	180
Zn1-O1 ⁱ	2.255(15)	N1-Zn1-O1 ⁱ	88.15(7)	N2 ⁱ -Zn1-N2	180
Zn1-O1	2.255(15)	N2 ⁱ -Zn1-O1 ⁱ	86.92(7)	O1 ⁱ -Zn1-O1	180
8					
Zn1-N2	2.092(14)	N2-Zn1-N1 ⁱ	94.73(6)	N2-Zn1-O1 ⁱ	91.81(6)
Zn1-N2 ⁱ	2.092(14)	N2 ⁱ -Zn1-N1 ⁱ	85.27(6)	N1 ⁱ -Zn1-O1 ⁱ	92.13(5)
Zn1-N1 ⁱ	2.115(13)	N2-Zn1-N1	85.27(6)	N1-Zn1-O1 ⁱ	87.87(5)
Zn1-N1	2.115(13)	N2 ⁱ -Zn1-N1	94.73(6)	N2-Zn1-N2 ⁱ	180
Zn1-O1	2.187(12)	N2-Zn1-O1	88.19(6)	N1 ⁱ -Zn1-N1	180
Zn1-O1 ⁱ	2.187(12)	N2 ⁱ -Zn1-O1	91.81(6)	O1-Zn1-O1 ⁱ	180

Note: Symmetry code $i = 1-x, 1-y, 1-z$

4.4.4 Cell similarity, isostructurality, and molecular isometricity and Hirshfeld surface area studies of **7** and **8**

Compounds **7** and **8** were found to be isomorphous, as indicated by the cell similarity index (π) of 0.0192, a value very close to zero, suggesting strong resemblance in the unit cell parameters. However, despite these similarities, the two compounds are not isostructural. To investigate further, the asymmetric units were overlaid, and the resulting rmsD and max D values indicated a higher deviation of the max D value, 3.5487, from zero, revealing a considerable difference in the crystal structure packing of the two compounds, which can be attributed to the influence of the different substituents. Unlike the methyl or methoxy substituent, the hydroxy substituent is involved in intramolecular hydrogen bonding with the carboxylate group through the uncoordinated oxygen atom (O2), which does not allow the carboxylate group to bend to a greater extent (**Figure 16a**). The dihedral angle between the aromatic ring (C2-C3-C4-C5-C6-C7) carrying the substituent and the plane defined by (O1-C1-O2) is 10° in (**7**). On the contrary, the dihedral angle observed in **8** is 44.25° between the plane defined by (C7-C8-C9-C10-C11-C12) and (O1-C6-O2) shown in **Figure 16b**.

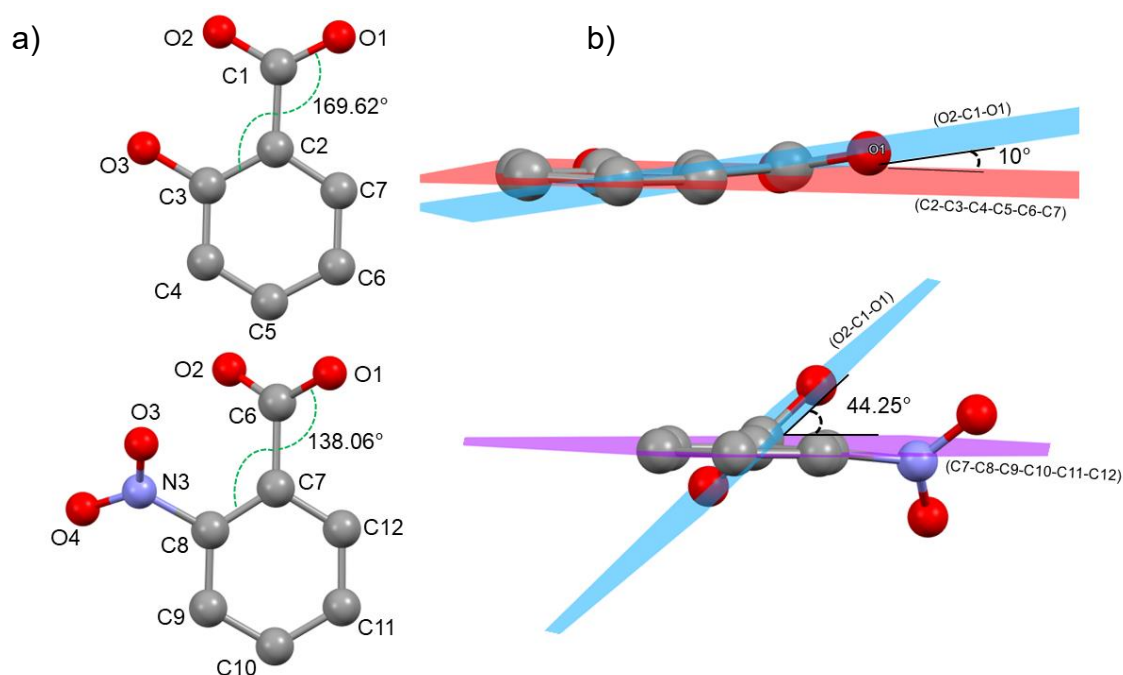


Figure 16 a) View along the carboxylate anion in **7** and **8**, highlighting the orientation of the substituents (left) and b) dihedral angle between the mean plane through the benzene ring (C2-C3-C4-C5-C6-C7) and (O2-C1-O1) (**7**) and (C7-C8-C9-C10-C11-C12) and (O2-C6-O1) (**8**) (right)

Additionally, we conducted HS analysis on the compounds to gain more insights into the supramolecular non-covalent interactions. The HSs for **7** and **8** were mapped over the d_{norm} range (-0.17 Å to 1.78 Å) and (-0.22 to 1.34), respectively. The d_{norm} surfaces indicated short contacts such as N-H $\cdots$ C formed between the cyclam ligand and the carbon atom of the carboxylate ligand of the neighboring molecule, seen as bright red area in the Hirshfeld surfaces (Figure 17a). In the case of **8**, short contacts C-H $\cdots$ O were observed between the carbon atoms of the coordinated carboxylate and the oxygen atoms of the nitro group, also with the uncoordinated oxygen atom of the carboxylate group of neighboring molecules (Figure 17 b).

Comparatively, more O $\cdots$ H/H $\cdots$ O type interactions are witnessed in **8** with 32.2 % than in **7**, as depicted in the 2D figure print plot Figure 17(c and d) (**7**) and (e and f) (**8**). This pronounced difference in orientation is likely the key factor disrupting the isostructurality despite the overall isomorphism of the two compounds. The shape indices of **7** and **8** exhibit red triangles above the aromatic ring and a relatively flatter region in the crudeness plot, indicating the presence of π - π stacking interactions illustrated in Figure 18.

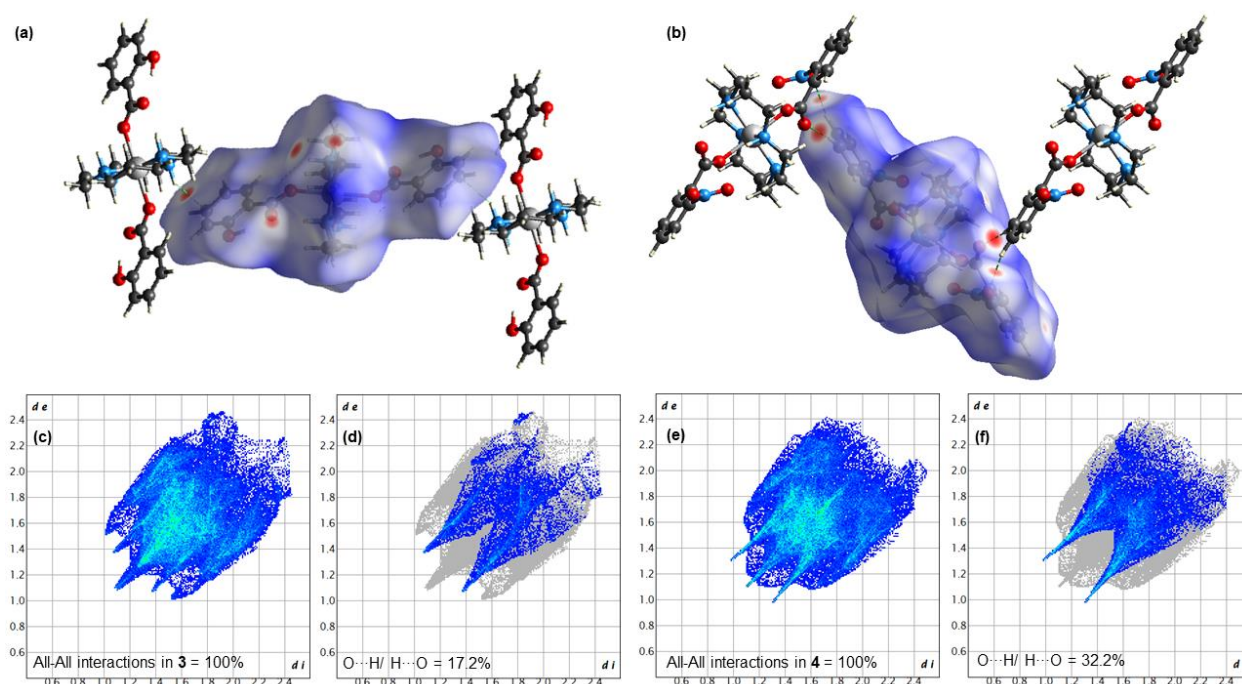


Figure 17 a) Intermolecular N-H $\cdots$ C interactions in **7** and b) C-H $\cdots$ O in **8**. c-f) 2D Fingerprint showing full and O $\cdots$ H/H $\cdots$ O type interactions with the percentage of contribution to the total Hirshfeld surface area in **7** and **8**.

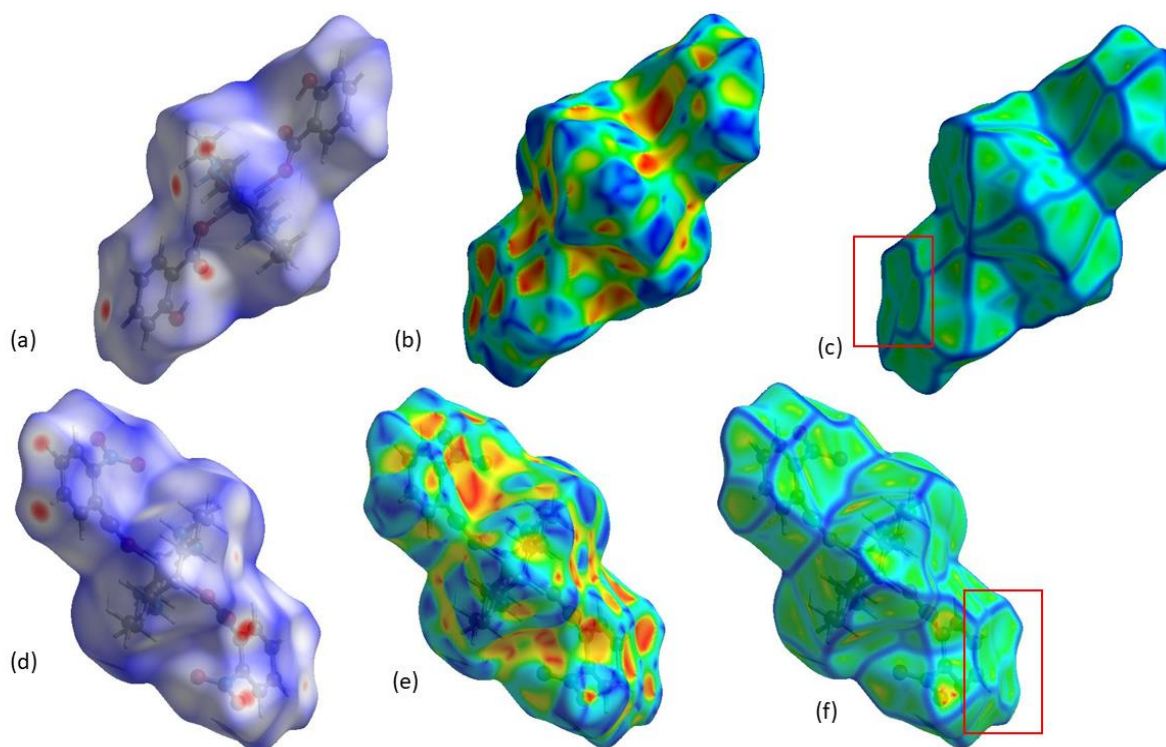


Figure 18. **(a)** Hirshfeld surface mapped with d_{norm} ranging from $-0.17 \text{ \AA}$ (red) to $1.78 \text{ \AA}$ (blue) **(b)** shape index, **(c)** curvedness for **3**, and **(d)** d_{norm} ranging from $-0.22 \text{ \AA}$ to $1.34 \text{ \AA}$, **(e)** shape index, and **(f)** curvedness for **4** (View along *b*-axis).

4.4.5 Single crystal analysis of compounds 4 and 9-11

Compounds **4** synthesized using simple benzoic acid as parent ligand shows close structural resemblance to compounds **9-11**, which were prepared using a derivative of benzoate bearing ortho substituents such as chloro, methyl(thio), and an amino group, respectively. The structural analysis revealed that, except for **11**(Figure 20), are isomorphous and therefore were grouped together as Group III to establish their structural relationship.

The asymmetric unit of all four compounds, **4** and **9-11**, showed common structural features. In each case, the Zn(II) ion is situated on an inversion center, coordinated by four nitrogen atoms of the cyclam ligand (N1, N2, N1i, and N2i) (where $i = -x, -y, -z$) on the equatorial plane. The axial positions were occupied by the oxygen atoms from the coordinated aqua molecules, thus forming a $[\text{ZnN}_4\text{O}_2]$ coordination environment. The bond length of the metal to nitrogen of the cyclam $\text{Zn1-N1} = 2.105(1) \text{ \AA}$, slightly shorter than the Zn-O(coordinated aqua) with a bond distance of $2.245(1) \text{ \AA}$ in compound **4**. Similar observations were also seen in compounds **9**, **10**, and **11**. The selected bond angles and bond distances are summarized in

Table 7. These bond distances and angles are consistent with the similarly reported compound having $[\text{Zn}(\text{cyclam})]^{2+}$ cationic core [39,40]. The cationic unit in all four compounds is stabilized through intramolecular hydrogen bonding, where the O-H groups of the coordinated aqua molecules interact with the uncoordinated oxygen atom of the carboxylate group acting as the hydrogen bond acceptor. This results in the formation of a zero-dimensional mononuclear compound. Notably, compound **10** exhibits structural variation due to the incorporation of additional lattice water molecules, which generate an extended hydrogen-bonding network. The crystal structures of compounds **4**, **9**, and **10** are shown in **Figure 19 (a-c)**.

Table 7. Selected hydrogen bond distances and bond angles for **4** and **9-11**

<i>Bond distance</i>		<i>Bond angle</i>			
4					
Zn1-N2	2.102(11)	N2-Zn1-N1 ⁱ	94.87(4)	N1i-Zn1-O1W	88.42(4)
Zn1-N1	2.104(10)	N2-Zn1-N1	85.13(4)	N1-Zn1-O1W	91.58(4)
Zn1-O1W	2.245(10)	N2-Zn1-O1W	88.05(4)	N2i-Zn1-N2	180
		N2-Zn1-O1Wi	91.95(4)	N1i-Zn1-N1	180
9					
Zn1-N1	2.099(17)	N1-Zn1-N2 ⁱ	94.70(7)	N2-Zn1-O1W ⁱ	91.84(7)
Zn1-N2	2.101(2)	N1-Zn1-N2	85.30(7)	N2-Zn1-O1W	88.16(7)
Zn1-O1W	2.250(16)	N1iZn1-O1W	90.77(6)	N1 ⁱ -Zn1-N1	180
		N1-Zn1-O1W ⁱ	89.22(6)	N2 ⁱ -Zn1-N2	180
10					
Zn1-N1	2.087(11)	N1-Zn1-N2	84.96(4)	N2-Zn1-O1W ⁱ	87.76(4)
Zn1-N2	2.109(11)	N1 ⁱ -Zn1-N2	95.05(4)	N2-Zn1-O1W	92.24(4)
Zn1-O1W	2.267(10)	N1-Zn1-O1W ⁱ	91.24(4)	N1-Zn1-N1 ⁱ	180
		N1-Zn1-O1W	88.76(4)	N2-Zn1-N2 ⁱ	180
11					
Zn1-N2	2.094(2)	N2 ⁱ -Zn1-N2	85.02(15)	N1 ⁱ -Zn1-O1W	91.21(9)
Zn1-N1	2.105(2)	N2-Zn1-N1	94.95(10)	N1-Zn1-O1W	88.11(8)
Zn1-O1W	2.266(2)	N1i-Zn1-N1	85.09(12)	N2-Zn1-N1 ⁱ	179.95(9)
		N2i-Zn1-O1W	91.85(9)	N2 ⁱ -Zn1-N1	179.95(9)

Note: Symmetry code $i = 1-x, 1-y, 1-z$ (**4**), $i = 2-x, 1-y, 1-z$ (**9**), $i = 1-x, 2-y, 1-z$ (**10**), $i = 1-x, y, 1/2-z$ (**11**),

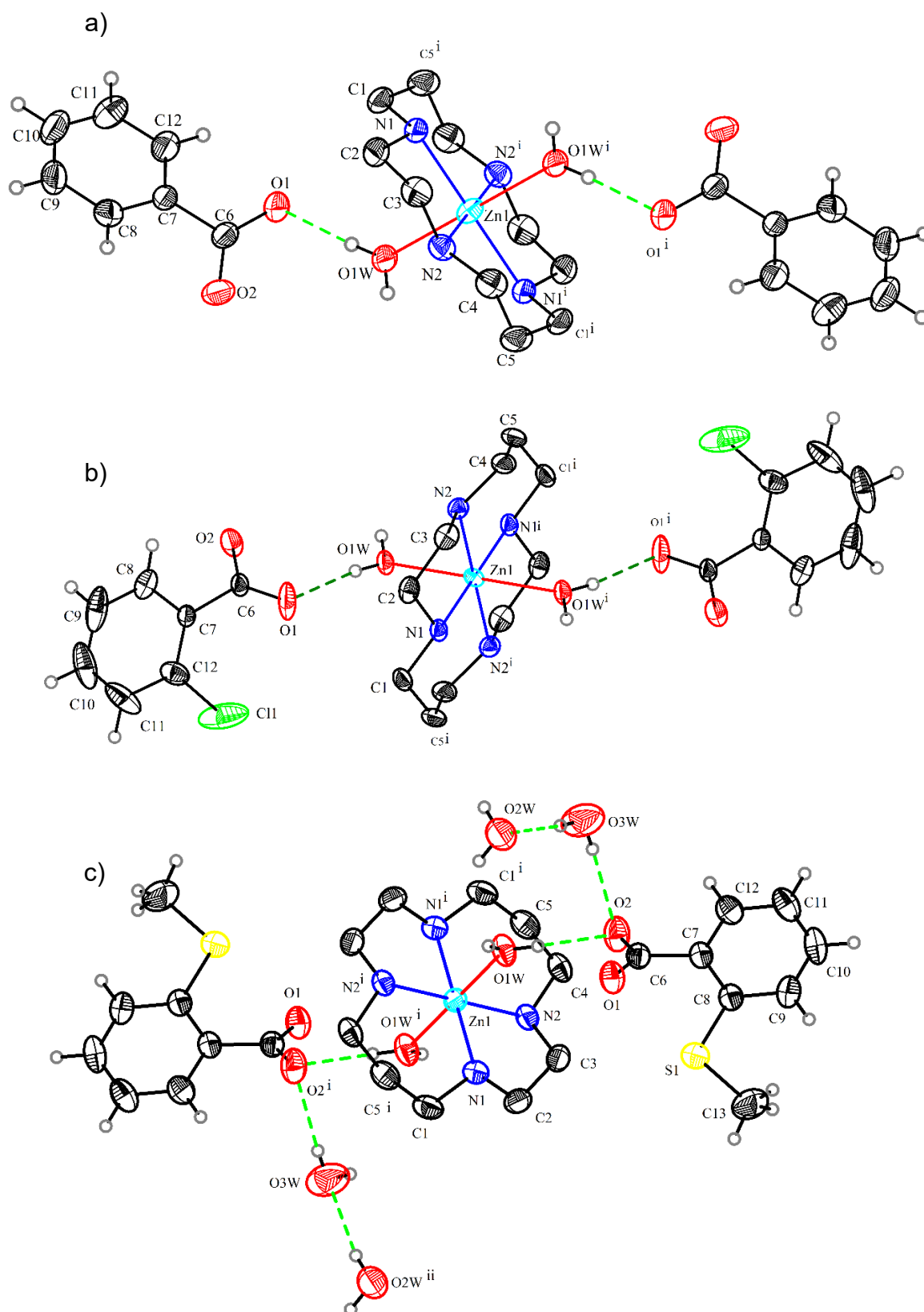


Figure 19 a-c) The thermal ellipsoid plot of compounds **4**, **9**, and **10**, respectively, with an atom labelling scheme. H-atoms are removed for clarity purposes.

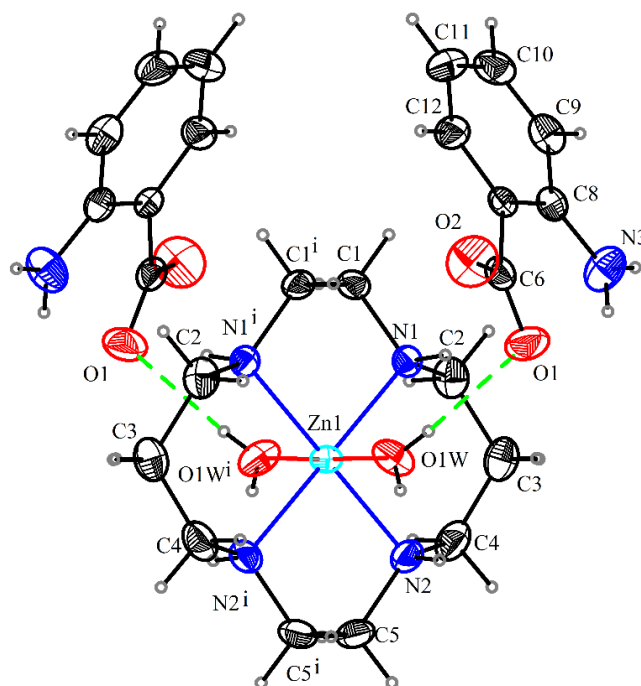


Figure 20. Crystal structure of **11** with atom labelling scheme. The thermal ellipsoids are drawn at 30 % probability. For clarity, the hydrogens on cyclam are omitted. ($i = 1-x, y, \frac{1}{2}-z$)

Compounds **4** and **9** both exhibit a total of four hydrogen bonds, among which two are intermolecular N-H $\cdots$ O and O-H $\cdots$ O type hydrogen bonds responsible for the extension of the discrete unit in a one-dimensional supramolecular chain along the axes depicted in **Figure 21**. Further, the ligated aqua molecules were involved in hydrogen bonding with the oxygen of the carboxylate group O1W-H1W $\cdots$ O1_(intra) and O1W-H2W $\cdots$ O2_(inter), resulting in the formation of edge-fused R_2^2 (8) ring along the *ac* plane with H $\cdots$ A distances of 1.887 and 1.980 Å, accompanied by the D-H $\cdots$ A of 176.47 and 159.77° respectively in **4**. A similar arrangement was observed in compound **9**. On the other hand, compound **10** exhibits extensive hydrogen bonding interactions due to non-ligated water molecules in its structure. Compound **10** exhibits eleven hydrogen bonds, four intramolecular and seven intermolecular hydrogen bonds. The cationic unit interacts with the charge-balancing carboxylate anion via intramolecular hydrogen bond interaction (O1W-H2C $\cdots$ O2), where O1W atoms act as the donor and O2 acts as the acceptor atom with H $\cdots$ A distance of 1.923 Å. The other hydrogen of the O1W is involved in interlinking the adjacent units via (O1W-H1C $\cdots$ O1ⁱⁱ) interaction, where ($ii = (1-x, 1-y, 1-z)$), thus forming a similar eight-membered ring structure as seen in **4** and **9**, resulting in a one-dimensional supramolecular chain structure along the *b* axes (**Figure 22**). The non-ligated ligand aids in interlinking the individual chain structure by forming a four-membered water

cluster, which extends along the *ac* plane, thereby rendering a 2D layered supramolecular network in compound **10**, as depicted **Figure 23**. A view of the supramolecular assembly of **11** is exhibited in **Figure 24** shows crystal packing stabilized by N-H $\cdots$ O and O-H $\cdots$ O type of interactions (**Table 5**) with H $\cdots$ O distance in the range of 2.041 to 2.611 Å. Compound **11** exhibits two intra- and four intermolecular hydrogen bonding interactions responsible for stabilizing the crystal structure. The amino group, unlike other substituents, participates in hydrogen bonding with the unbounded carboxylate oxygen (O2), resulting in the formation of a chain-like structure, interlinking the cationic units, thus resulting in the formation of a 1D ladder-shaped supramolecular layer.

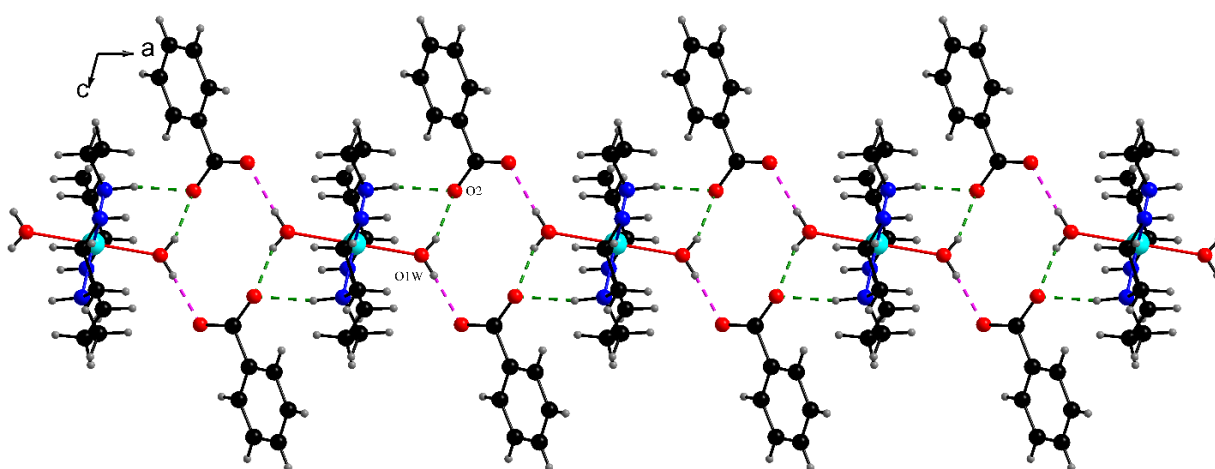


Figure 21. Formation of 1D supramolecular chain through N1-H1 $\cdots$ O2 and O1W-H $\cdots$ O2 shown in purple dotted lines in **4**.

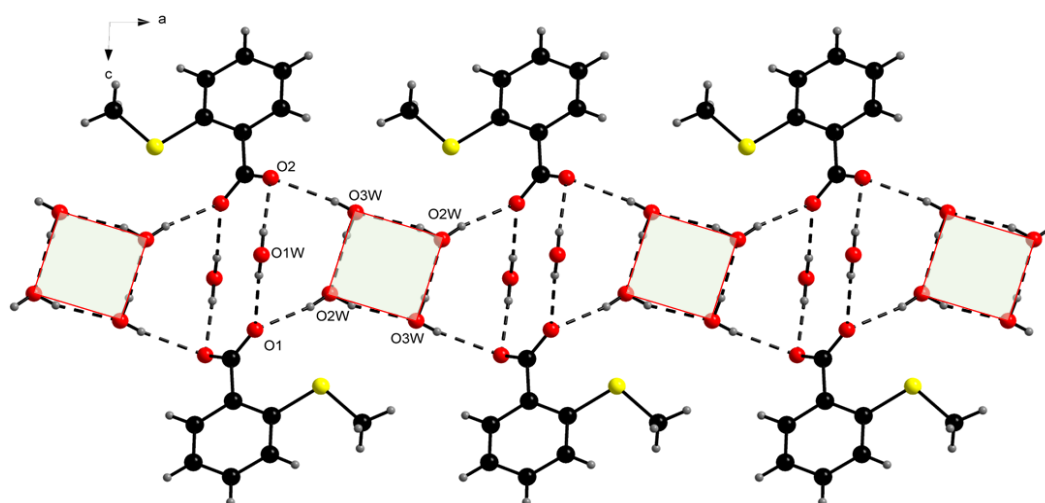


Figure 22. Hydrogen bonding viewed along an *b*-axis showing water clusters running along *a*-axis in **10**.

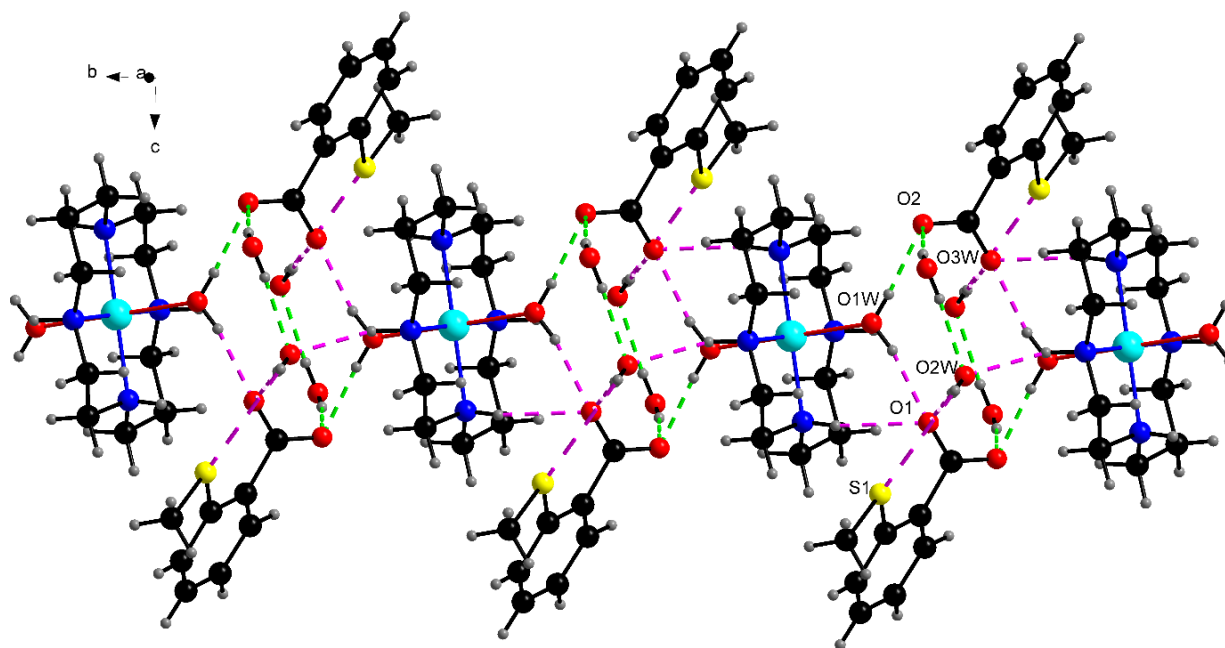


Figure 23. Formation of 1D supramolecular chain structure via N-H $\cdots$ O, O-H $\cdots$ O and O-H $\cdots$ S type of intermolecular interactions shown in purple dotted lines in **10**.

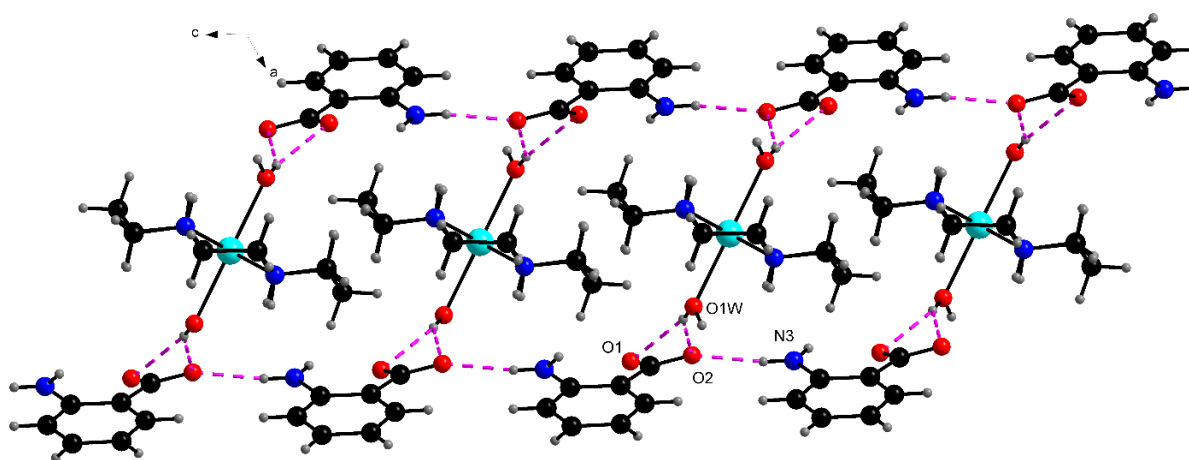


Figure 24. Formation of 1D supramolecular double chain structure via N-H $\cdots$ O and O-H $\cdots$ O interactions shown in purple dotted lines in **11**.

4.4.6 Cell similarity, isostructurality, and molecular isometricity and Hirshfeld surface area studies of Group III compounds.

It is evident that compounds **4**, **9**, and **10** lack isostructurality due to significant variations in the hydrogen bonding situation in the crystal structure upon including different substituents. The cell similarity index π value for the molecular pair **4/9** is 0.0197, whereas for **4/10**, it increases up to 0.2452. The highest deviation of the cell similarity index from zero is seen in the case of a **4/10** pair among the three groups. It is attributed to the intense hydrogen bonding situation in compound **10**, which comprises lattice water molecules.

The Hirshfeld surface is mapped over d_{norm} range (-0.7068 to 1.4553) in **4**, (-0.72 to 1.3264) in **9**, and (-0.6574 to 1.6115) in **10**. The red spots on the surface indicate the dominant interactions. The HS analysis indicates strong hydrogen bond interactions such as O-H $\cdots$ O and N-H $\cdots$ O co-exist between the cationic and the anionic unit in **4**, **9**, and **10**, shown in **Figure 25a-c**, respectively. The 2D fingerprint plots exhibit the crucial contributors to crystal packing for compounds **4**, **9**, and **10**, as summarized in the pie chart shown in **Figure 25d-f**. The majority of the contribution in all isomorphous compounds arises from the H $\cdots$ H type in the order of **4** > **10** > **9**. Compared to the parent compound **4**, **9** and **10** exhibit H $\cdots$ Cl with 13.4 % contribution and H $\cdots$ S type with 6.7 % contribution in the respective compounds. Consequently, the additional interactions seen in **9** and **10** alter the crystal packing, thereby preventing the attainment of isostructurality. Aromatic rings in the crystal structure enable close molecular packing through π - π stacking interactions. These interactions are illustrated by red triangles above the aromatic rings in the shape index plot and flatter regions in the curvedness plot of compounds **4**, **9**, and **10** depicted in **Figure 26**. This observation underscores the role these interactions play in stabilizing the overall structure.

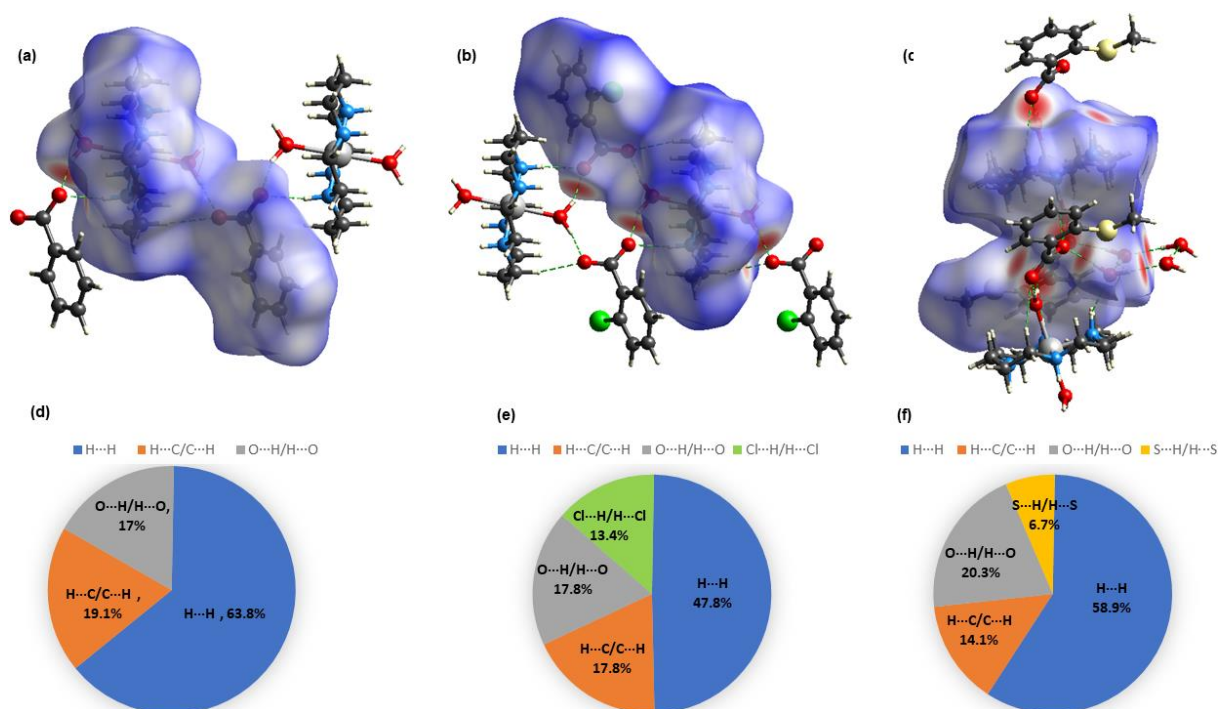


Figure 25 a-c) Intermolecular O-H...O and N-H...O type non-covalent interactions in **4**, **9**, and **10**, respectively.

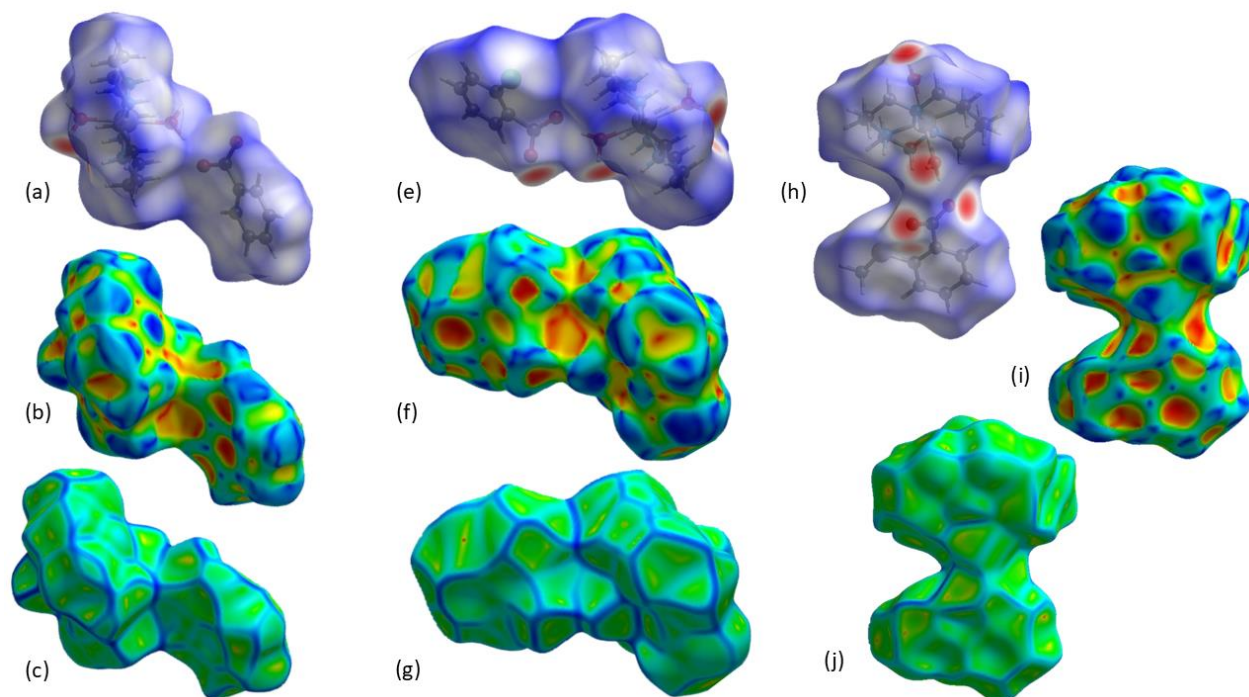


Figure 26 Hirshfeld surface mapped with (a) d_{norm} ranging from -0.71 Å (red) to 1.45 (blue) Å (b) shape index, and (c) curvedness for **4**, (d) d_{norm} ranging from -0.72 Å to 1.33 Å (e) shape index, and (f) curvedness for **9** (View along *b*-axis) and (h) d_{norm} ranging from -0.65 Å to 1.58 Å (i) shape index, and (j) curvedness for **10**

To estimate the effect of substituents on the final architecture, we calculated the void spaces generated during molecular packing. The presence and distribution of these voids are generally studied to understand the response of molecular crystals to external pressures [38,41].

The quantitative measures, such as Volume (VH), Surface area (SH), globularity (G), and asphericity, were computed from the HSs of compounds **4-10** and summarized in **Table 8**. The void volume of Group I compounds illustrated in **Figure 27** shows that compound **6** has a void volume of 281.16 Å³ (void percentage of 12.7%), which is relatively less than that of compound **5**, 329.16 Å³ (void percentage of 15%). The small difference in the void volume may be attributed to the variation in the ortho substituents. The globularity in all the compounds is found to be <1, which indicates that the molecular surfaces are more structured. The asphericity is the measure of anisotropy and follows the order of Group III (**10**) > Group I (**5**) ≈ (**6**) > Group III (**4**) ≈ (**9**) > Group II (**7**) ≈ (**8**). From the computed values, it can also be learned that the molecules have occupied the major space in the crystal. Thus, the compounds can bear considerable pressure before undergoing any permanent change in their shape.

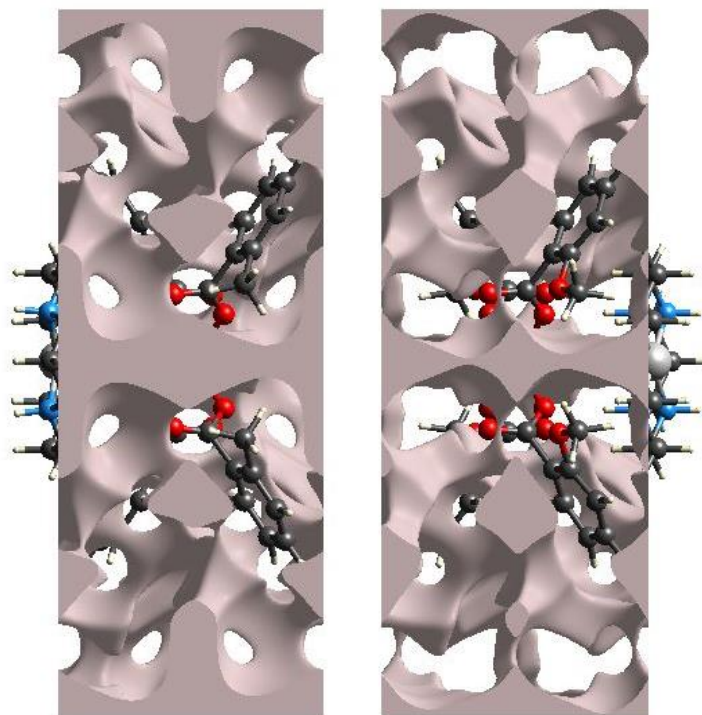


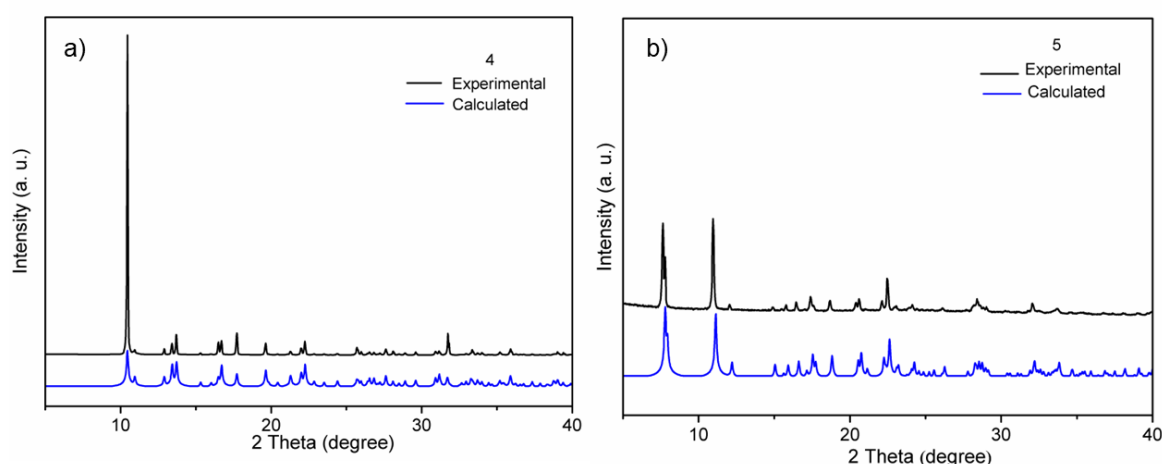
Figure 27 Crystal structure of compounds **5** and **6** with 0.002 au void surface, viewed along the *c*-axis

Table 8. Quantitative measurements taken from crystal void analysis using Crystal Explorer software.

Compound	Void Volume (V _H) Å ³	Surface area (S _H) Å ²	Globularity(G)	Asphericity
5	329	861.5	0.27	0.24
6	276	846.2	0.24	0.25
7	274	894.9	0.23	0.08
8	298	1042.5	0.21	0.07
4	121	428.9	0.28	0.11
9	188	559.1	0.28	0.10
10	201	670.8	0.25	0.40

4.5. X-ray powder analysis.

Powder X-ray diffraction (PXRD) patterns were recorded to investigate the phase purity of the bulk materials. Simulated data for all the compounds were obtained from the Mercury 4.0 software. The diffractograms for compounds **4-11** are shown in **Figure 28a-h**. The diffraction peaks in the simulated pattern showed an excellent match with the experimental data collected at room temperature, suggesting that the single crystal model represents the bulk crystalline material. Powder diffractograms can be a suitable technique for identifying isostructurality in related compounds, as they show unique fingerprints of the solid compounds. Upon comparing the powder patterns of the related compounds, of individual groups, it was observed that the powder patterns slightly varied, again suggesting that the related compounds sharing similar unit cell parameters are not isostructural.



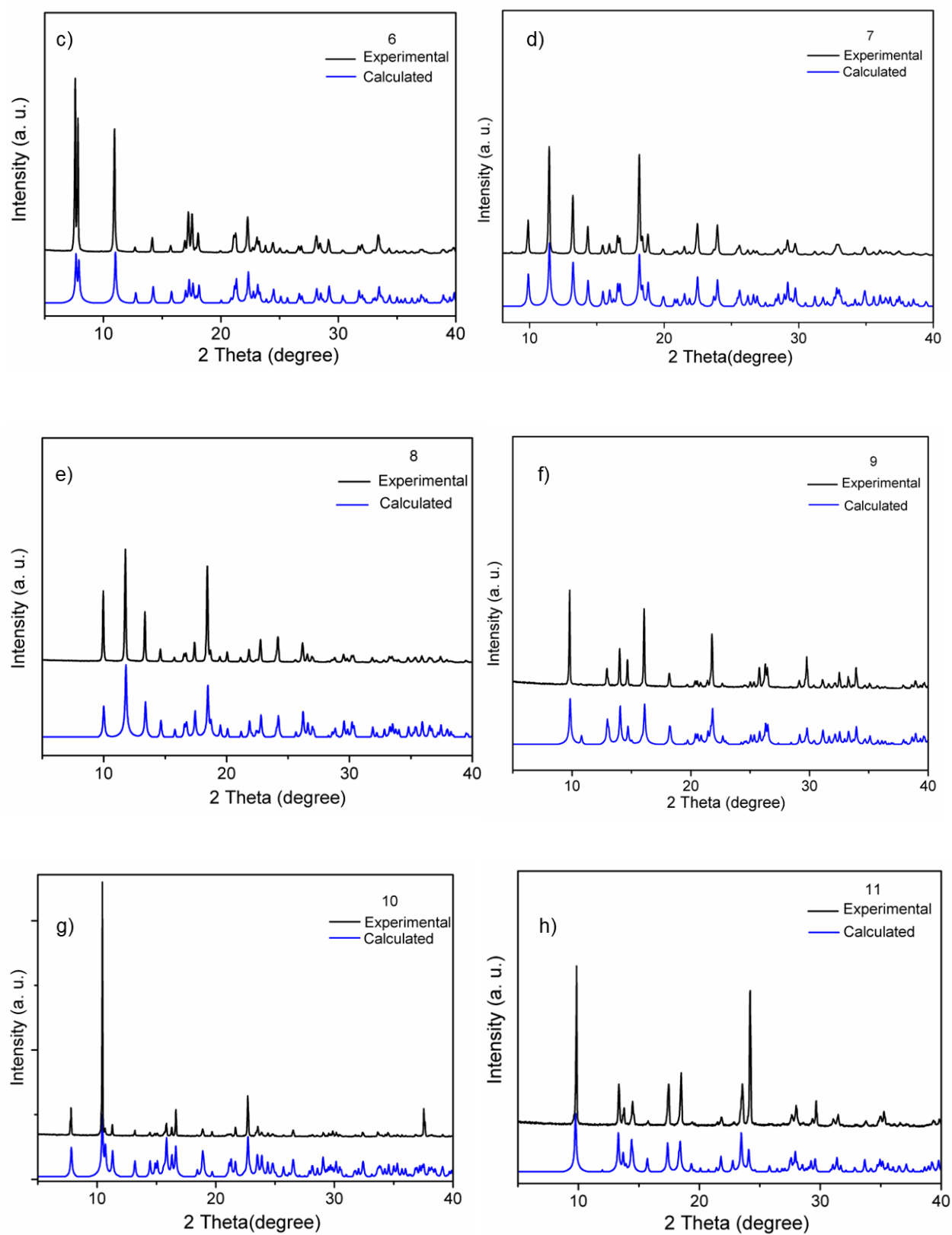
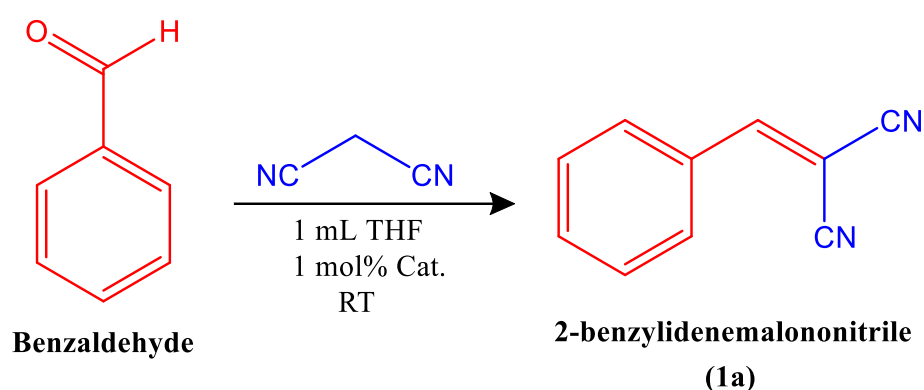


Figure 28 a-h) the experimental powder pattern overlaid with calculated pattern obtained from the crystal data.

4.6. Evaluation of catalytic activity of zinc compounds

4.6.1. One-dimensional coordination polymers as catalyst for model Knoevenagel condensation reactions.

The Knoevenagel condensation process involves a reaction between an aldehyde and an active methylene compound to give an α , β -unsaturated compound. To uncover the potential of the zinc catalyst, we used a model reaction that uses benzaldehyde and malononitrile as the starting materials, shown in **Scheme 2**.



Scheme 2. Depicting the model reaction employed in a catalytic reaction

To begin with, 0.5 mmole of benzaldehyde was reacted with 1 mmole of malononitrile in 1 mL of dry THF (tetrahydrofuran) solvent in the presence of 1 mol% of zinc catalyst. The same reaction was carried out without the catalyst as a blank reaction and one with 1 mol% $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ as a catalyst for reference purposes. All the reactions were monitored for two hours using the TLC technique. After two hours, the reactions were quenched by adding DCM (1 mL) and purified using column chromatography. The product (**1a**) was analysed by ^1H -NMR spectroscopy (**Figure 30**). The observations are summarized in **Table 9**. The results indicate that the newly prepared zinc coordination polymers (**5** and **6**) could catalyze the model reaction with improved yields compared to $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$. Meanwhile, the reaction without the catalyst (Blank reaction) showed a trace amount of the condensed product. The product 2-benzylidenemalononitrile obtained higher yields, up to 48 %, when **5** was employed as the catalyst (**Entry 2**).

We then used compound **5** to evaluate further the effect of catalyst concentration on the yield of the final product. During this experiment, the reaction conditions were nearly the same as those used in the model reaction between benzaldehyde and malononitrile. Still, only the

catalyst concentration varied from 2-5 mol%. The results of the experiment are summarized in **Table 9**. The results revealed that as the catalyst concentration was increased gradually, the product yield also improved with small increments up to 3 mol% catalyst loading. There was not much improvement in the yield of the product beyond 5 %, which was attributed to the solubility issue of the zinc catalyst in 1 mL of the THF solvent.

Table 9. The catalytic activity of zinc compounds in THF

Entry	Catalyst	Yield ^a (%)
1	Zn(OAc) ₂ ·2H ₂ O	25
2	5 (1 mole %)	48
3	6	35
4	Blank	Trace
Effect of catalyst concentration		
5	5 (2 mole %)	61
6	5 (3 mole %)	80
7	5 (4 mole %)	82
8	5 (5 mole %)	87

Note: Reaction condition: 0.5 mmole Benzaldehyde, 1 mmole Malononitrile, 1 mL dry THF, Reaction time = 2h, RT, **a** = isolated yield by column chromatography (10% EtOAc:PET)

While reviewing the literature on the effect of solvents in the Knoevenagel condensation reaction, we encountered a recent publication by Kolagkis and coworkers. This study suggests that a water-mediated protocol is an effective and greener alternative for condensing benzaldehyde and malononitrile, eliminating the need for metal or non-metal catalysts. The research indicates that water molecules act as Brønsted bases, catalyzing the reaction [42]. Their finding demonstrated a 90 % yield of (**1a**) obtained in 4 hours when 1 mL of double-distilled water was used as the solvent. Motivated by this finding, we adopted water as the solvent system to compare the catalytic potential of the zinc compound directly.

In a typical reaction, a mixture of 0.5 moles of benzaldehyde and 1 mmole of malononitrile was added to a glass vial along with 1 mL of distilled water. This reaction mixture was charged with 1 mol % of zinc catalyst (**5**) and stirred until the aldehyde was consumed entirely. It was observed from this reaction that aldehyde consumption only takes around 30 minutes, with the product immediately precipitating out of the aqueous medium, due to poor solubility. The condensed product (**1a**) was directly purified using a simple filtration technique and further purified using column chromatography to avoid any traces of the catalyst in the final product. The condensed product was characterized using the ¹H-NMR spectroscopic technique. We also

extended this strategy to prepare other benzylidene derivatives to determine the substrate scope by monitoring the reaction for 30 minutes for better comparison. The introduction of just 1 mol% zinc catalyst markedly reduced the reaction time for the condensation of benzaldehyde, nitrobenzaldehyde, and anisaldehyde compared with the results reported by Kolagkis and coworkers (**Figure 29**). This improved activity can be attributed to the coexistence of the Lewis acid and the Lewis base sites, which tend to activate the electrophile and nucleophiles simultaneously, acting as a bifunctional catalyst, thus speeding up the process. The products labelled **(2a)**, **(3a)**, and **(4a)** were purified by recrystallization in ethanol and further characterized by ^1H NMR as shown in **Figure 31-33** respectively. The effect of catalyst concentration was also studied by varying the catalyst loading from 1-5 mol%; however, there were no drastic changes in the reaction time observed. It was also interesting to note that the **5** behaved as a heterogeneous catalyst in aqueous medium due to its lower solubility compared to the THF solvent, and catalyst recovery studies are underway.

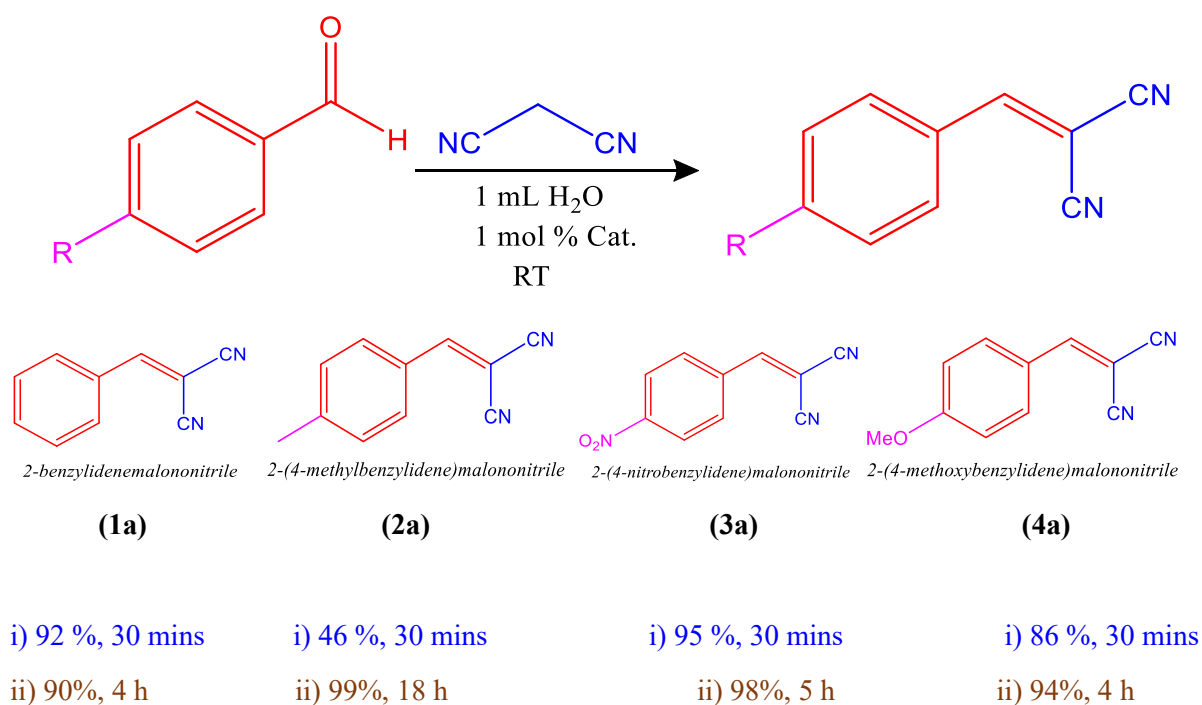


Figure 29 Reaction of different aldehyde substrates with malononitrile in the presence of 1 mol% compound **5** in aqueous medium. Comparison of our protocol (i) (blue) with Kolagkis protocol (ii) (brown).

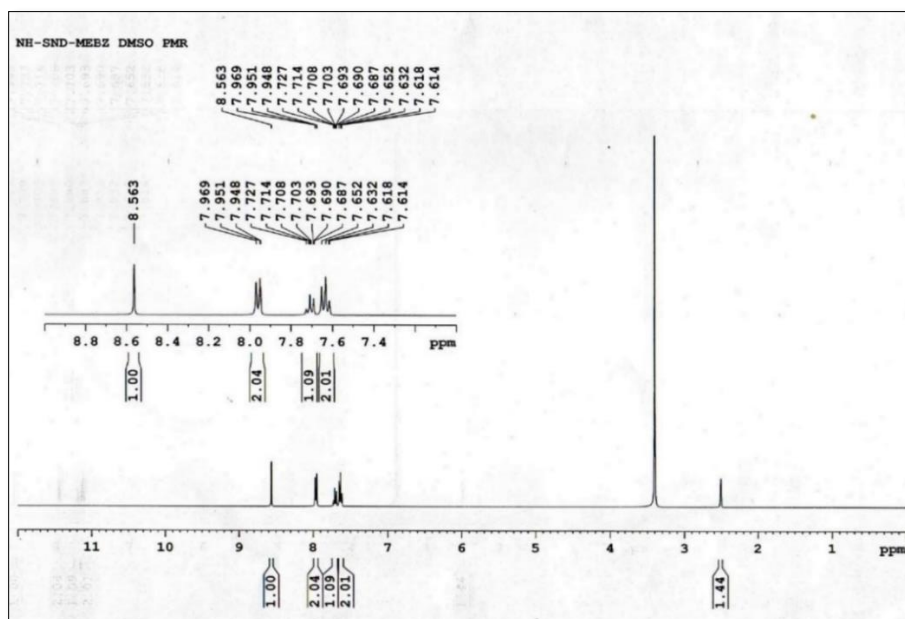


Figure 30. ^1H -NMR of the purified product 2-benzylidenemalononitrile (**1a**) in DMSO-d_6 solvent

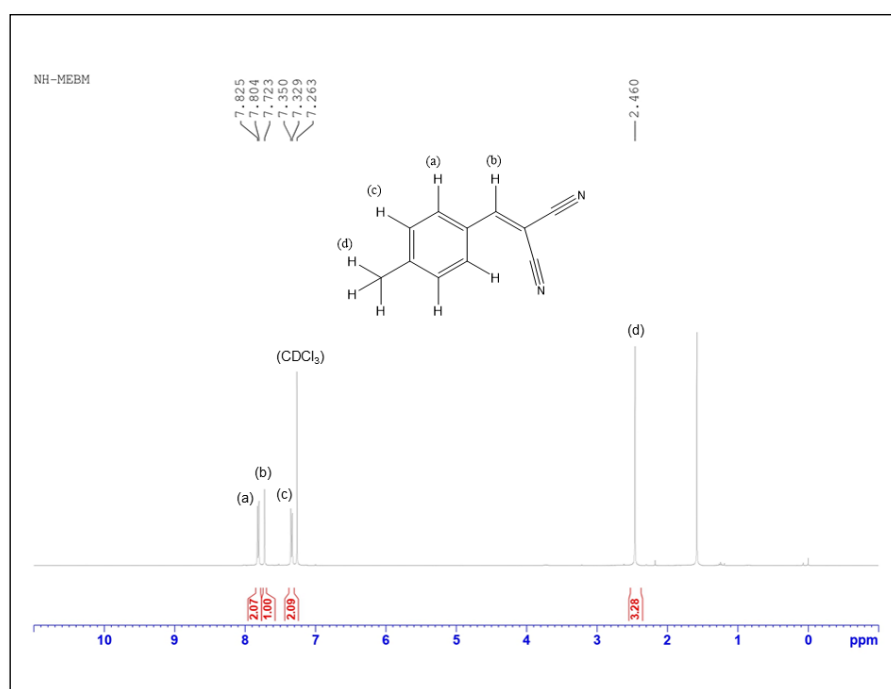


Figure 31 The ^1H -NMR spectrum of condensed product (**2a**) (400 MHz, CDCl_3 , IIT-Goa); (a) δ 7.82 (2H, d, ArH), (b) δ 7.72 (1H, s, =CH), (c) δ 7.35 (2H, d, ArH) and (d) δ 2.46 (3H, s, CH_3).

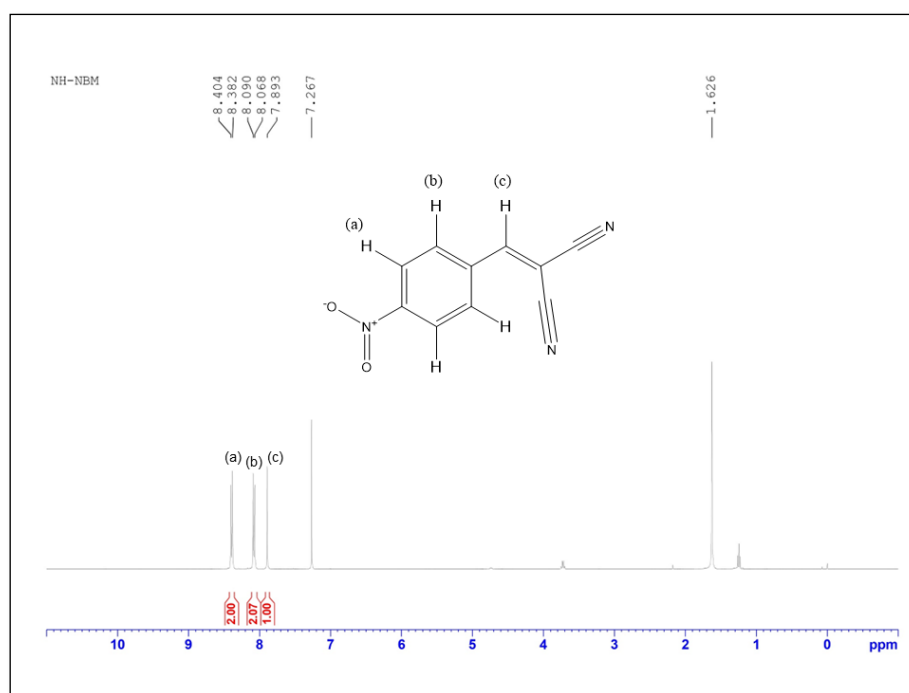


Figure 32. ¹H-NMR data for **(3a)** (400 MHz, CDCl₃, IIT-Goa); (a) δ 8.4 (2H, d, ArH), (b) δ 8.09 (2H, d, ArH), (c) δ 7.89 (1H, s, =CH)

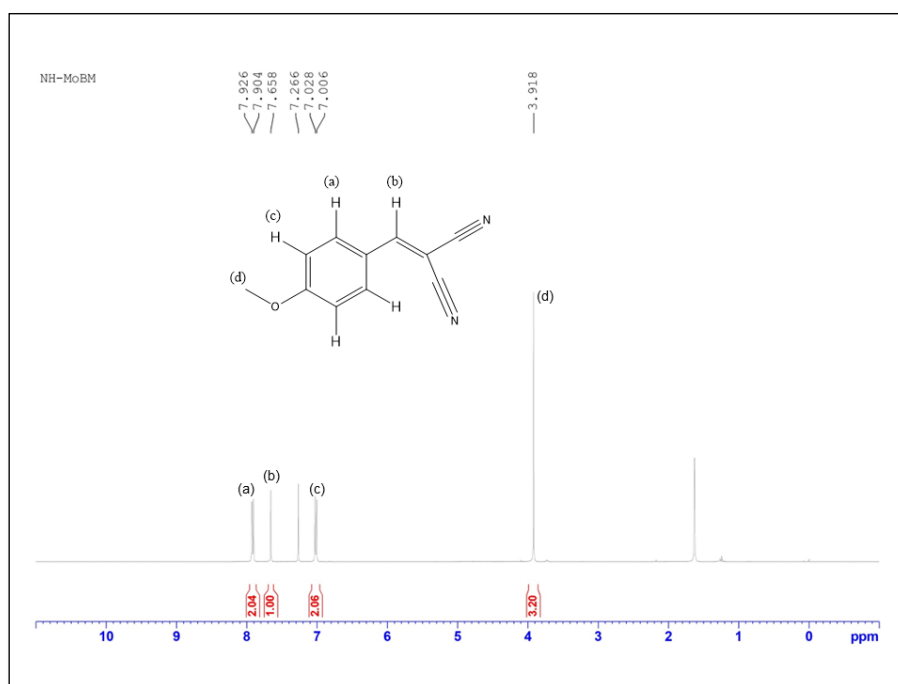
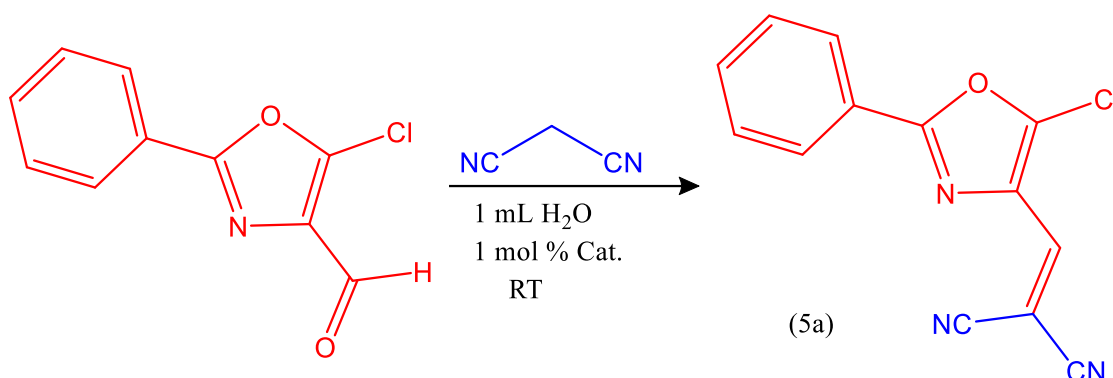


Figure 33. ¹H-NMR data for **(4a)** (400 MHz, CDCl₃, IIT-Goa); (a) δ 7.92 (2H, d, ArH), (b) δ 7.66 (1H, s, =CH), (c) δ 7.03 (2H, d, ArH) and (d) δ 3.92 (3H, s, OCH₃).

4.6.2. Synthesis of 2-((5-chloro-2-phenyloxazole-4-yl)methylene)malonitrile using compound **5** as catalyst.

We further extended our investigation on the effectiveness of our catalytic system on synthesizing a novel compound, namely, 2-((5-chloro-2-phenyloxazole-4-yl)methylene)malonitrile (**5a**). In a typical reaction, we used 5-chloro-2-phenyloxazole-4-carbaldehyde, a substrate prepared by Mr. Nitesh Venji (SCS), to explore the substrate scope on oxazole-type compounds, as depicted in **Scheme 3**.



Scheme 3. Knoevenagel condensation reaction of 5-chloro-2-phenyloxazole-4-carbaldehyde with malononitrile

Here we employed 0.5 mmole of 5-chloro-2-phenyloxazole-4-carbaldehyde, a water-insoluble substrate, which was reacted with 1 mmole of malononitrile in 1 mL of a distilled water: ethanol mixture and charged with 1 mol % **5** catalyst. The reaction was monitored using TLC. A new spot was observed on the TLC, however, it was noticed that the aldehyde was present even after 1 hour of the reaction. The reaction was sluggish; hence, it was monitored for 8 hours, but even then, the aldehyde was not consumed entirely. The solid product was filtered out of the aqueous medium, and the crude product was further purified to remove any impurity due to unreacted aldehyde or the catalyst and recrystallized several times with ethanol. Product **5a** was obtained in 64 % yield, and was characterized by ¹H-NMR spectroscopy (**Figure 34**).

In contrast to the catalyst-based reaction, the blank reaction was carried out under identical conditions, resulting in only 23 % yield after 24 hours, with a strong spot of unreacted aldehyde still visible on the TLC plate. These observations indicate that the zinc catalyst significantly accelerates the transformation and improves product yield compared to the non-catalyzed system. Our preliminary results highlight the potential of the 1D zinc catalyst in accelerating the product formation; however, further optimization of the reaction conditions is underway to enhance both the yield and the reaction time.

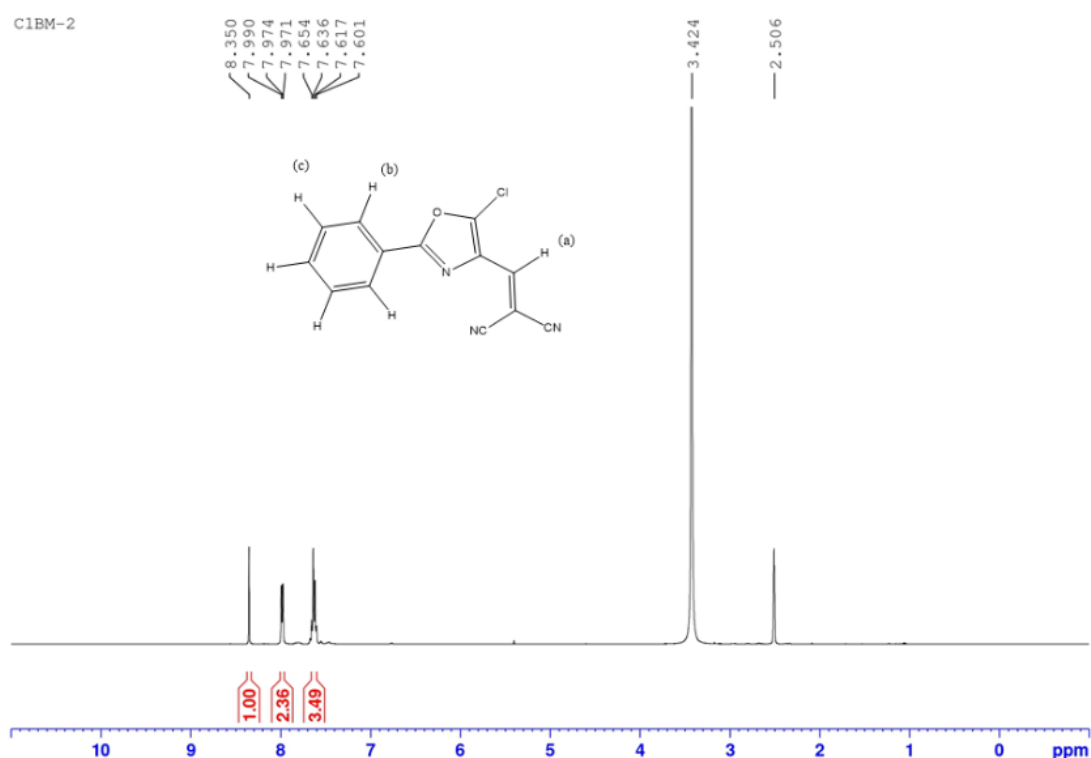


Figure 34. ¹H-NMR spectrum for (**5a**) (400 MHz, DMSO-d₆, IIT-Goa)

4.7 Conclusion

Chapter 4 demonstrates the subtle variations in ortho-substituents on benzoate ligands can profoundly alter the structural organization of zinc-cyclam compounds. While the cyclam consistently adopts the trans-III conformation, the supramolecular arrangement is dictated by the substituent-dependent hydrogen-bonding patterns, π - π stacking interaction, and aqua bridging modes. The isomorphism observed in some cases does not necessarily translate to isostructurality, highlighting a sensitive balance of non-covalent interactions in crystal packing. The Hirshfeld surface area and void analyses provided a quantitative understanding of the differences. Beyond their structural diversity, the coordination polymers also showed catalytic activity in the Knoevenagel condensation. Collectively, these findings underline the dual significance of zinc-cyclam compounds as model systems for probing supramolecular chemistry and as potential candidates for catalytic applications.

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Chapter 5: Section I: *Aliphatic carboxylate anion-driven self-assembly of Nickel pyrazine coordination polymers: precursors for Ni/NiO composite materials***5.1 Chapter overview**

Chapter 5, Section I, focuses on preparing and characterizing nickel pyrazine coordination polymers decorated with aliphatic carboxylate ligands. The compounds described include $[\text{Ni}(\text{H}_2\text{O})_2(\text{pyz})(\text{fum})]$ (**12**), $[\text{Ni}(\text{H}_2\text{O})_2(\text{pyz})(\text{suc})]$ (**13**), $[\text{Ni}(\text{H}_2\text{O})_2(\text{pyz})(\text{ida})]$ (**14**), and $[\text{Ni}(\text{pyz})(\text{ida})]\cdot 2\text{H}_2\text{O}$ (**15**). Section 5.2 provides a literature survey on coordination polymers featuring O- and N-donor linkers. Section 5.3. Give detailed synthetic strategies and optimization of the reaction conditions to obtain suitable single crystals for diffraction purposes, and perform subsequent spectral, structural, and thermal analyses of the synthesized compounds. Section 5.4 highlights their potential as precursors for preparing Ni/NiO composite materials.

5.2 Literature survey on coordination polymers featuring O-donor and N-donor linkers.

Coordination polymers (CPs) are hybrid materials that exist as infinite crystalline structures extended from the inorganic vertices (metal ions or clusters) and organic spacers [1]. A subset of CPs is the Metal-organic frameworks (MOFs), which are polymeric materials that endorse high porosity, high thermal and chemical stability [2]. These unique physicochemical properties of extended compounds make CPs/MOFs attractive and have become increasingly important in Inorganic chemistry due to their potential applications in gas storage, gas separation [3-5], molecular sensing [6-8], catalysis [9,10], and magnetism [11,12]. The overall architecture of CPs/MOFs is largely determined by several key factors, including the nature and coordination behaviour of the metal nodes, the type of organic linkers, and experimental conditions such as reaction temperature, pH, solvent, and concentration of the starting materials. The building blocks provide control in the construction of frameworks owing to the well-defined structure and geometry of the metal and the organic counterparts. Coordinate bonds impart thermal and chemical stability, long-range ordering in the crystalline material ensures their structural characterization by the single crystal X-ray diffraction technique, and may also exhibit host-guest interactions in those featuring high porosity and network stability [13,14].

Many of the first-row divalent transition metal ions (Zn^{+2} , Co^{+2} , Ni^{+2} , and Cu^{+2}) are widely used to construct stable crystalline mixed ligand CPs/MOFs. In particular, Ni(II) is

considered an attractive choice because it is relatively abundant, non-toxic, and possesses a comparatively large ionic radius, which favours the formation of robust CPs [15]. For example, in the chiral CP [Ni(SDB)(BIX)], the Ni(II) ions serve as the central scaffold. Its flexible coordination geometry and strong bonding interactions enable the achiral ligands to organize into a stable, extended network, which ultimately gives rise to chirality in the CP, through spontaneous resolution [16]. In another example, a comparison of different M-MOF-74 materials (M = Ni, Co, Mg, and Zn) for H₂-metal interaction strength through experimental and electronic structure calculations revealed that Ni-MOF-74 exhibited the strongest H₂-metal interaction. This was attributed to the strong binding between the H₂ molecules and the nickel sites and the relatively higher induced dipoles on the metal-sorbed H₂ molecules [17].

Aromatic carboxylates are widely used in the construction of CPs or MOFs, as their rigid O-donor linkers provide strong structural stability to the frameworks. In contrast, aliphatic or acyclic linkers have received far less attention because of their flexibility, which makes the resulting architectures harder to predict. Interestingly, this same flexibility can be turned into an advantage, allowing the design of unusual conformations and breathing frameworks that behave like sponges for selective separation and a storage house for gas molecules [18]. Moreover, CPs built from aliphatic carboxylates have shown promising features such as optical properties and, in some cases, good thermal stability [19]. Since many of these linkers can be derived from renewable sources, they represent an attractive option for sustainable CP synthesis. Our group had prepared series of cobalt-based coordination polymers using succinate anions in combination with pyrazine, and we investigated their potential for sensing nitroaromatic compounds (NACs). The study revealed that the conformation of the succinate ligand plays a key role in producing structural variations within the framework, particularly when different solvent systems were employed [20]. Building upon our earlier findings, we shifted the focus from cobalt with nickel ions in order to examine how the change in metal centre influences the structural features of the resulting CPs. Alongside this, different carboxylate ligands were introduced systematically to evaluate their influence on the final architecture. Through this approach, we could explore the combined role of the metal ion and the carboxylate linker in framework construction, which offered a deeper understanding of the structural properties of the synthesized materials.

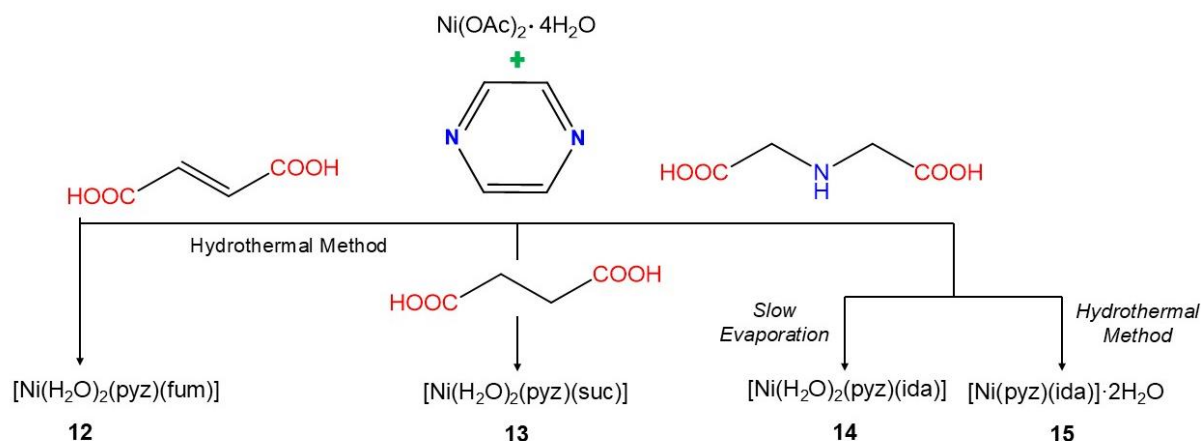
5.3 Results and discussion

5.3.1 Synthesis and solvent optimization of compounds 12-15.

The synthesis of the CPs was carried out by separately dissolving 2 mM of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in 10 ml of the solvent, together with 2 mM acid and 4 mM pyrazine. The reaction mixture was stirred for 30 minutes until a clear solution was obtained. The resultant mixture was then divided into two parts. In the first approach, 5 mL of the solution was added to a clean beaker and kept aside at room temperature for slow evaporation of the solvent. The remaining 5 mL of the solution was transferred into a 25 mL autoclave and subjected to heating in the oven at 80°C for 24 h. After heating, the autoclave was allowed to cool to room temperature. The outcomes obtained with different solvents using both the slow evaporation method and hydro(Solvo)thermal methods are summarized in **Table 1** for fumarate-based, succinate- and iminodiacetate-based CPs. The synthesized nickel CPs are summarized in **Scheme 1**.

Table 1. Results for aliphatic carboxylate-based CPs.

Serial No	Solvent (5 mL)	Method of synthesis Slow Evaporation (SE) RT	Hydro (Solvo)thermal (HT/ST) Δ 80°C, 24 h
<i>Fumarate-based CPs</i>			
1	H ₂ O	Blue rod-shaped crystals	Blue rod-shaped crystals (12)
2	H ₂ O/MeOH	Blue powder	Blue powder
3	H ₂ O/DMF	Clear blue solution	Clear Blue solution
4	H ₂ O/DMSO	Clear blue solution	Clear Blue solution
<i>Succinate-based CPs</i>			
5	H ₂ O	Clear blue solution	Blue block-shaped crystals (13)
6	H ₂ O/MeOH	Blue powder	Blue powder
7	H ₂ O/DMF	Clear blue solution	Blue powder
8	H ₂ O/DMSO	Clear blue solution	Blue powder
<i>Iminodiacetate-based CPs</i>			
9	H ₂ O	Blue plate-shaped crystals (14)	Green needles (15)
10	H ₂ O/MeOH	Clear blue solution	Green+Blue crystals (Mix)
11	H ₂ O/DMF	Clear blue solution	Green powder
12	H ₂ O/DMSO	Clear blue solution	Blue powder



Scheme 1. The synthesis of nickel coordination polymers using aliphatic carboxylate and pyrazine linkers.

The reaction between nickel, fumaric acid, and pyrazine in aqueous medium resulted in the formation of blue rod-shaped crystalline material, in the SE method as well as in the HT method. However, there was a considerable difference between the crystallinity of the materials. The SE method yielded microcrystalline solids, whereas high-quality single crystals were grown under autoclave conditions. Hence, the crystals obtained from the HT method were used for further analysis. It is worth noting that the compounds obtained from both methods were analysed using powder diffraction, which showed complete overlap of the patterns, indicating the absence of any phase difference. All the compounds **12-15** were crystallized from the aqueous solution, and other solvents did not appear to play any specific role in obtaining suitable single crystals.

5.3.2 Infrared spectroscopic analysis of the synthesized compounds.

The spectra of the CPs were compared with their corresponding acid components (**Figures 1-3**). The spectrum of compounds **12-15** exhibits a broad absorption band over a much wider range corresponding to $\nu(\text{O-H})$ stretching vibration of the water molecules and $\nu(\text{C-H})$ stretching vibration of the organic ligands. The broadening of the band indicates the presence of extensive hydrogen bonding [21]. The characteristic sharp bands due to $\nu_{\text{as}}(\text{COO})/\nu_{\text{s}}(\text{COO})$ vibrations of the carboxylate group were observed around (1552 and 1390 cm^{-1}) **12**, (1543 and 1409 cm^{-1}) **13**, (1614 and 1404 cm^{-1}) **14**, and (1595 and 1409 cm^{-1}) **15**, respectively shown in **Table 2**. Thus, indicating incorporation of the deprotonated carboxylate moieties in all the compounds. Spectral analysis of compounds **12-15** confirms the presence of the pyrazine linker, as evidenced by the band appearing in the range of 1200

to 600 cm^{-1} , which corresponds to the C-N, C-C, and C-H vibrations of the pyrazine molecules [22,23]. Furthermore, the bands observed around $470\text{--}485\text{ cm}^{-1}$ in compounds **12**, **13**, and **15** indicate that the pyrazine adopted the bridging bidentate coordination mode. In contrast, compound **14** exhibits a band at 408 cm^{-1} , which closely matches the band at 417 cm^{-1} observed in the spectrum of free pyrazine, indicating a distinct coordination environment.

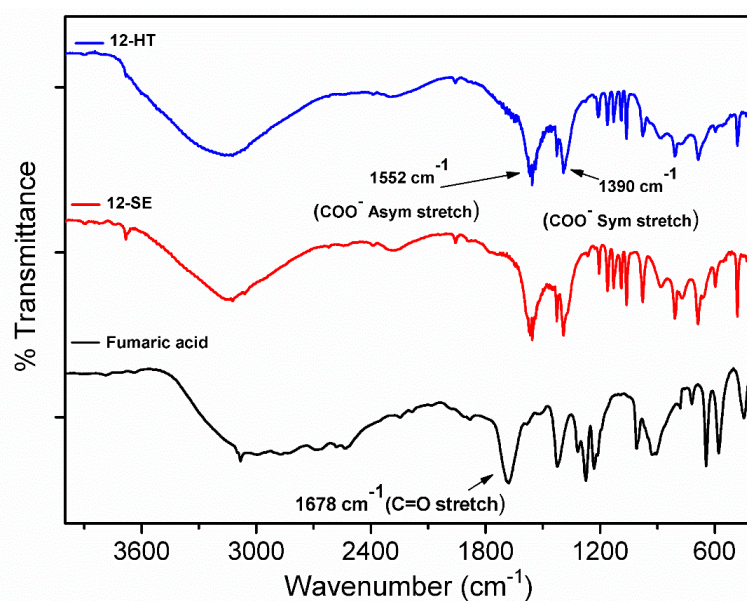


Figure 1. Overlaid infrared spectra of the compound obtained *via* the slow evaporation method (**12-SE**), the Hydrothermal method (**12-HT**), and fumaric acid.

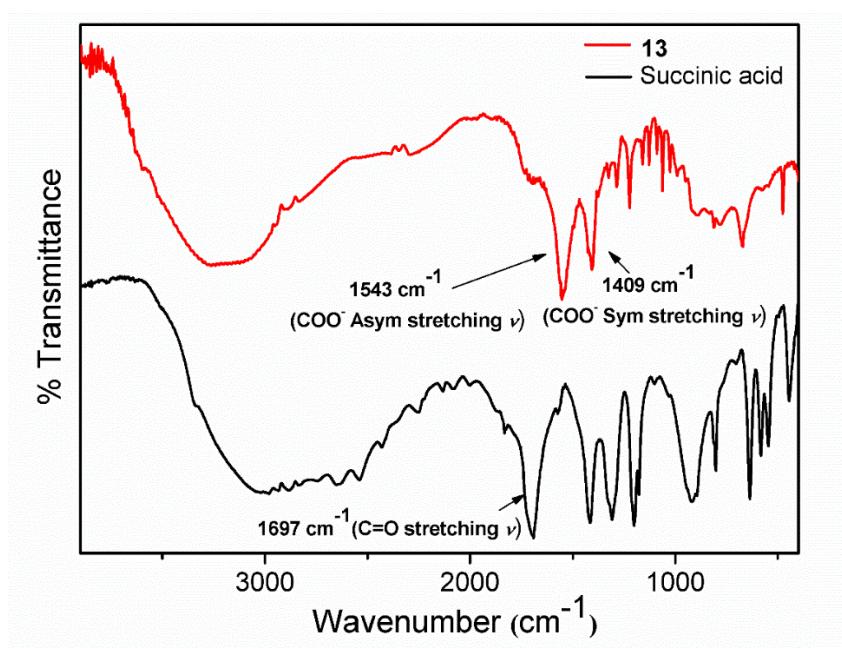


Figure 2. Overlaid infrared spectra of compound **13** and succinic acid.

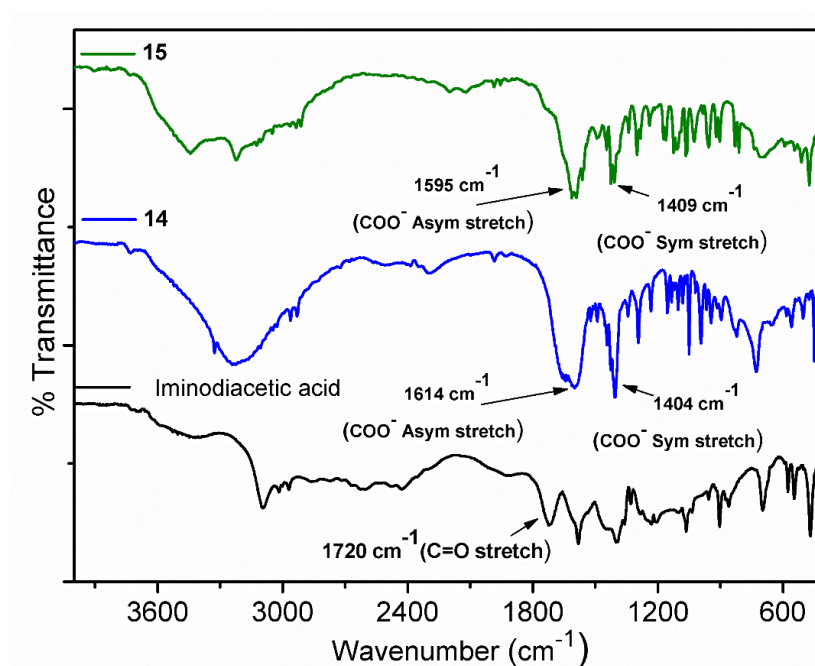


Figure 3. The IR spectra of compounds **14** and **15** overlaid with the IR spectrum of iminodiacetic acid.

Table 2. The IR absorption bands

Compound	IR data (cm ⁻¹)
12	3564-2902 (br), 1552 (sh), 1390 (sh), 1211(m), 1161 (m), 1130 (m), 1089 (m), 1062 (m), 977(m), 881 (br), 810(m), 688 (m), 482 (m)
13	3589-2953 (br), 1543 (sh), 1409 (sh), 1284 (m), 1222 (m), 1159 (m), 1128 (m), 1089 (m), 1062 (m), 1026 (m), 889 (br), 781 (m), 675 (m), 476 (m)
14	3525-3022 (br), 3327(m), 1614 (sh), 1404 (sh), 1294 (m), 1232 (m), 1153 (m), 1103 (m), 1080 (m), 1051 (m), 993 (m), 947 (m), 894 (m), 823 (m), 729 (m), 559 (m), 503 (m), 451 (m), 408(m)
15	3612-3358 (br), 3215 (m), 1595 (sh), 1425-1409 (sh), 1300 (m), 1161 (m), 1124 (m), 1105 (m), 1066 (m), 1026 (m), 956 (m), 920 (m), 902 (m), 831 (m), 812 (m), 698 (br), 513 (m), 474 (m)

Note: br (broad), sh (sharp), w (weak), m (medium)

5.3.3 Absorption spectral analysis of compounds **12** and **13**

The solid-state UV-Vis spectra of compounds **12** and **13**, shown in **Figure 4a** and **4b**, exhibit two *d-d* transition bands. This band arises from the electronic transition from the $3A_{2g}$ ground term to the excited triplet terms, namely $3T_{2g}$ (P) and $3T_{1g}$ (F), at (370 and 600 nm) in compound **12** and (357 nm and 648 nm) in **13**, corresponding to the first and second

transitions. The third transition is expected to occur approximately at 1082 due to the transition from $3A_{2g}$ to $3T_{2g}(F)$, which is masked by noise and has been omitted. The transitions in both compounds suggest that the nickel ions adopt an octahedral geometry [24].

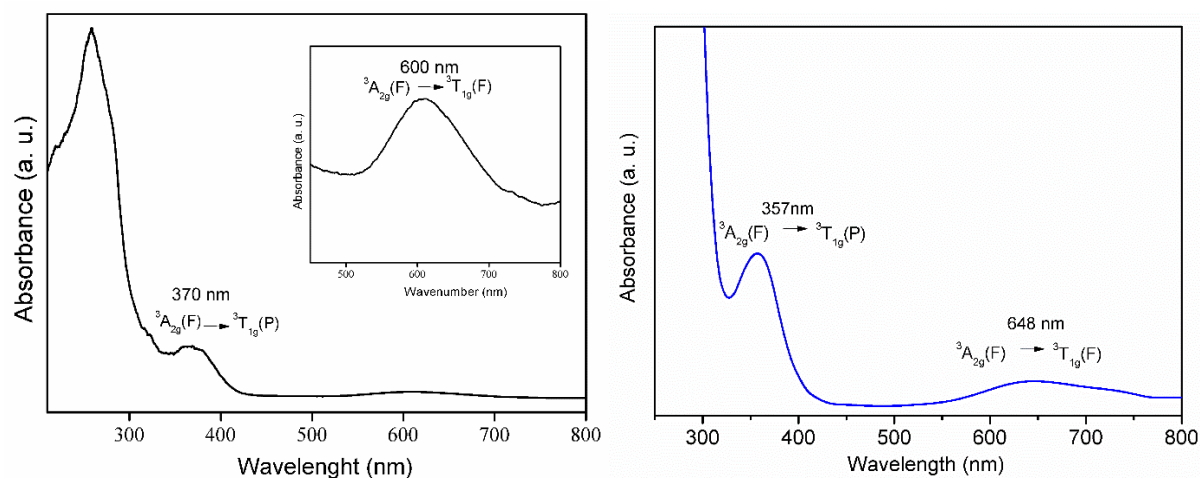


Figure 4. a) Solid state UV-Vis spectra of compound **12** (Left), with an inset showing an enlarged region from 500 to 750 nm. b) Solid state UV-Vis of **13** (Right).

5.3.4 Thermal analysis of compounds **12-15**

The thermal curve in compound **12** exhibits two initial decomposition steps occurring between 70 and 330 °C (**Figure 5**). The first decomposition step involves the release of water molecules, while the second is attributed to the decomposition of the N-donor molecules, resulting in a weight loss of 32% (the calculated value is 34%, corresponding to an endothermic peak at 118 °C). The next stage of weight loss, which occurs in the temperature range of 330 to 700 °C, is attributed to the decomposition of the fumarate moieties. Here, the experimental weight loss is approximately 39.6% (the calculated value is 40%), with the corresponding endothermic peak appearing at 424 °C. At temperatures above 400 °C, the decomposition ultimately yields a stable residue identified as NiO, with a remaining mass of 28.4%, and is in good agreement with the calculated value of 26%. To further evaluate the thermal stability of the compounds, the decomposition behaviour of compound **12** was compared with that of compound **13**, as shown in **Figure 6**. Both compounds follow a similar decomposition sequence, beginning with the release of water molecules, followed by the breakdown of the pyrazine ligands and the respective dicarboxylate linkers. In compound **13**, however, the dehydration occurs at slightly higher temperatures, suggesting that replacing the fumarate linker with succinate influences the overall thermal stability of the compound.

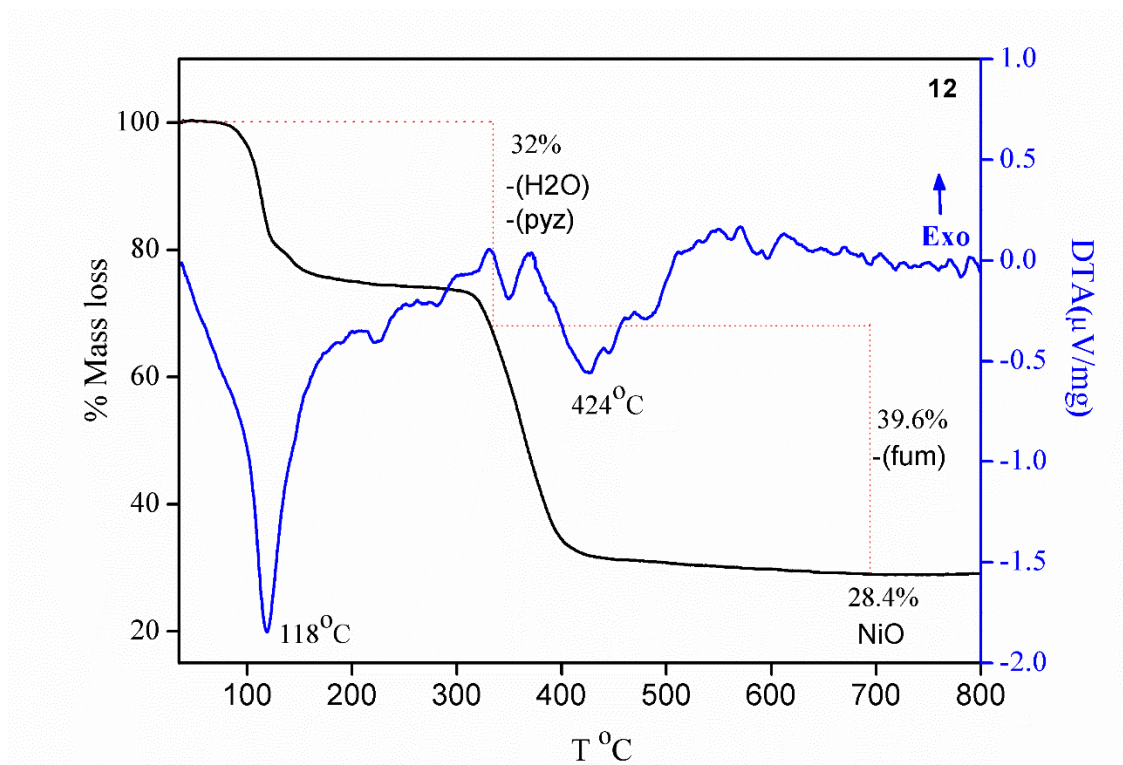


Figure 5. The TG-DTA plot of compound 12.

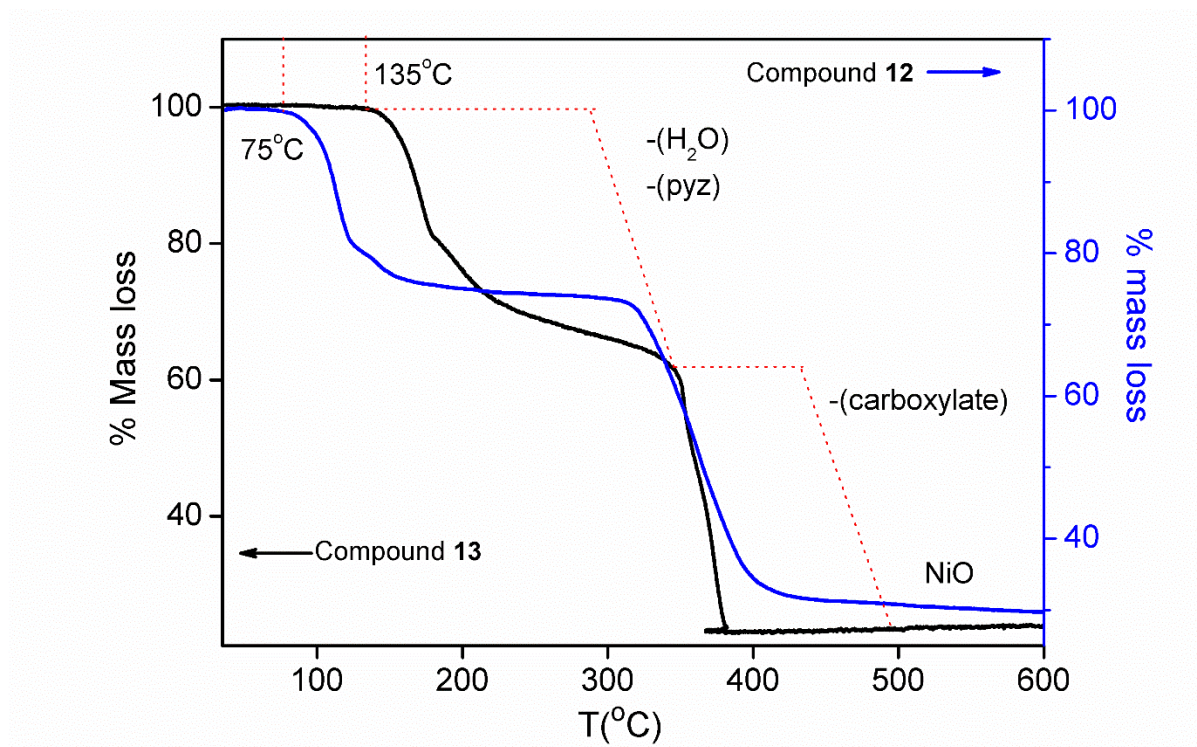


Figure 6. The overlaid TG curves of compounds 12 (blue) and 13 (black).

The thermal analysis of compounds **14** and **15** reveals slight differences in their decomposition behavior, as illustrated in **Figure 7**. The TG plot of compound **14** exhibits distinct decomposition steps, where the first mass loss of 12.44%, attributed to the release of two water molecules (Calcd: 11.74%) over the temperature range of 80 to 190°C. Following the dehydration step, the pyrazine molecules are broken down, resulting in a mass loss of 25.73%, which is in good agreement with the calculated value of 26.07%. The third distinct mass loss of 38.24 % (Calcd. 37.8 %) beyond 320°C is attributed to the loss of one ida moiety from the compound. The final residue remaining in the crucible is approximately 23.59% and was identified as NiO (Calcd. 24.4%). Compound **15** (**Figure 8**) plot shows a combined first and second mass loss of 36.70 % (Calcd 37.98 %) between 100 to 290°C, corresponding to the concurrent loss of two water molecules (11.8 %) and one pyrazine (26.18 %) entity from the compounds. The third step, a mass loss of 38.23 % (Calcd. 37.62 %) between 290 and 400°C, was assigned to the loss of one ida moiety from the compound. The final residue of about 25.07 % (Calcd. 24.4%) is identified to be NiO. Notably, the final residues obtained after decomposition of both compounds are nearly identical and in close agreement with their calculated NiO content, underscoring a marked similarity in the overall composition and thermal stability of compounds **14** and **15**.

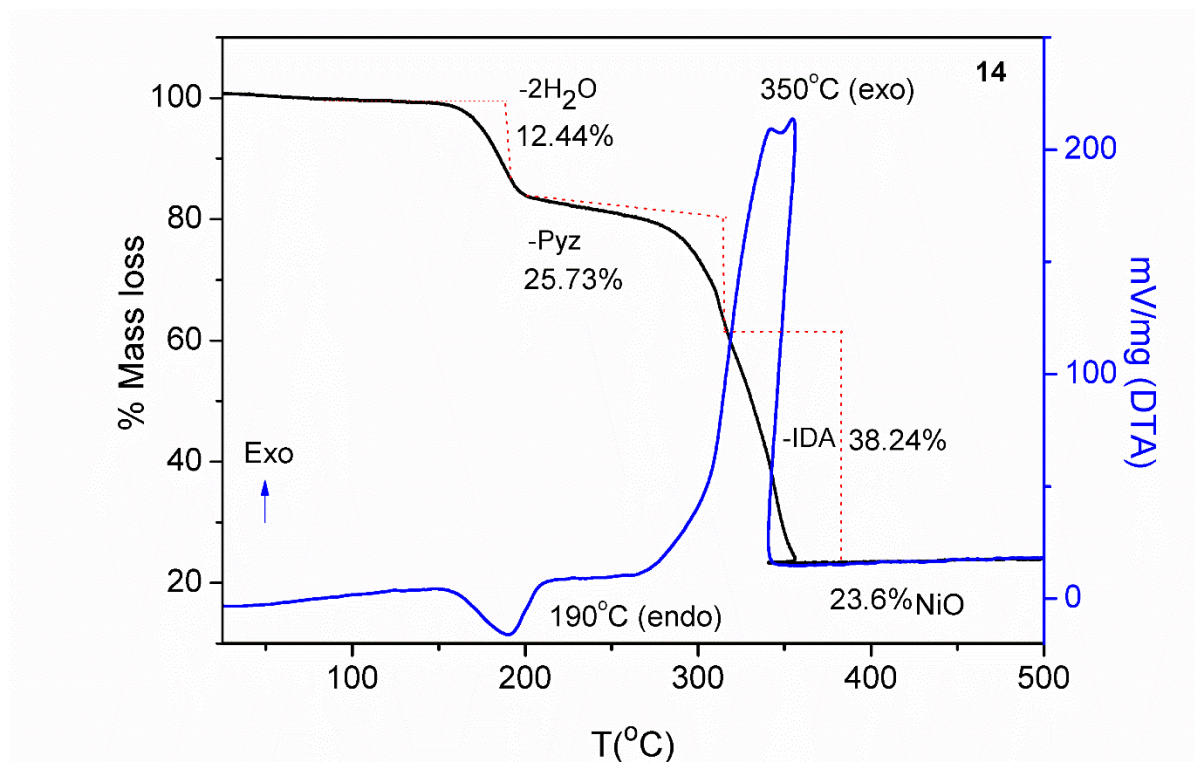


Figure 7. The TG-DTA plot of compound **14**.

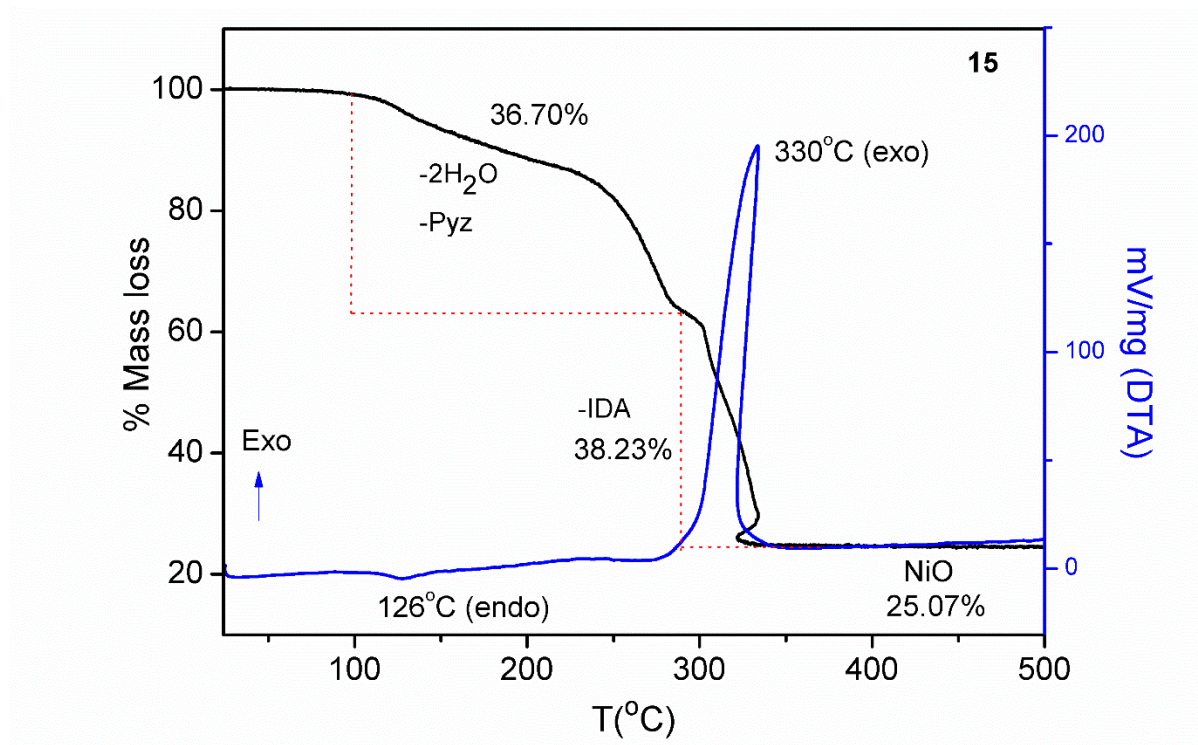


Figure 8. The TG-DTA plot of compound **15**.

5.3.5 Structural description of synthesized compounds.

The crystal data were collected at room temperature, and the technical details of the data acquisition and selected refinement parameters are presented in [Table 3](#).

[Ni(H₂O)₂(pyz)(fum)] (**12**) Structural analysis of **12** revealed it crystallized in the monoclinic crystal system, $P2_1/n$ space group. The crystal structure comprises one Ni(II) ion, one crystallographically independent pyrazine linker, one fumarate ligand, and two coordinated water molecules, as shown in [Figure 9](#). The nickel ion is present at the inversion centre; hence, half of the molecule is symmetry-generated and adopts an octahedral geometry, with a [NiO₄N₂] coordination environment. The topological study of compound **12** revealed a 4-connected underlying *sql* net, which is the simplest and the most commonly observed topology in microporous CPs and MOFs. The *sql* nets are further classified into Type I and Type II depending on the type and number of ligands used in the synthesis. The single linker variants include N-donor-only, dicarboxylate, or N-donor-carboxylate linkers (e.g. isonicotinate anion), which tend to adopt the Type-I *sql* nets. Whereas, six families of mixed linker nets can be achieved by either mixing only N-donor ligands (Type-II-a), only carboxylates (Type-II-b), N-donor-carboxylates only (Type-II-c), N-donor and dicarboxylate linkers (Type-II-ab), N-donor and (N-donor-carboxylate) (Type-II-ac), and dicarboxylate and

(N-donor-carboxylate) (Type-II-bc) [25]. In $[\text{Ni}(\text{H}_2\text{O})_2(\text{pyz})(\text{fum})]$ the pyrazine ligates adjacent nickel centres *via* a $\kappa\text{-N}$ mode and extends the polymeric structure along the *a*-axis. While the fumarate linker adopts an *anti-anti* conformation and extends the polymeric structure along the *b*-axis, it adopts a monodentate coordination mode. This arrangement yields a two-dimensional grid structure, as illustrated in Figure 10, and reveals a Type-II-ab *sql* network.

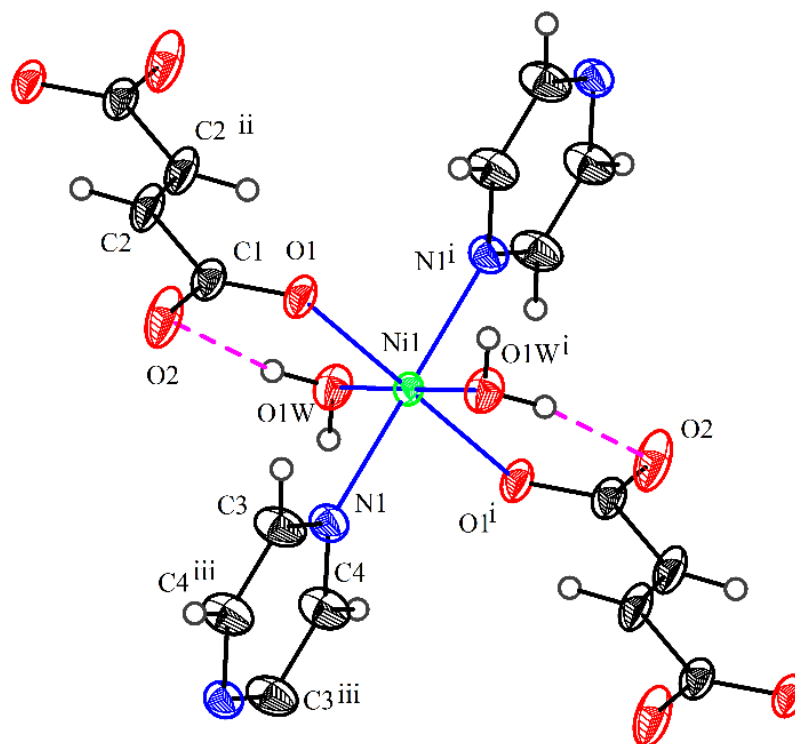


Figure 9 The crystal structure of $[\text{Ni}(\text{H}_2\text{O})_2(\text{pyz})(\text{fum})]$ (**12**). Thermal ellipsoids drawn at a 30 % probability level for all the non-hydrogen atoms. The hydrogen atoms are depicted as spheres of arbitrary radii. (Symmetry code (i) $-x+1, -y+1, -z+1$ (ii) $-x+2, -y+1, -z+1$ (iii) $-x+1, -y, -z+1$)

The $\text{Ni}\cdots\text{Ni}$ separation between the fumarate-linked ions was determined to be 9.019 Å, while those connected by pyrazine were at a distance of 7 Å. The typical Ni-O, Ni-N, and Ni- $\text{O}_{(\text{aqua})}$ bond distances were measured to be 2.0465(11), 2.1585(12), and 2.0714(12), respectively (Table 4), and are in accordance with the values reported for Ni(II) mixed ligand CPs containing fumarate [24,26,27] and pyrazine linkers [28-30]. Extensive intermolecular hydrogen bonding interactions (Table 5) are observed between the uncoordinated oxygen Atoms (O2) of the fumarate and the coordinated water molecules, resulting in a 3D supramolecular architecture illustrated in Figure 11.

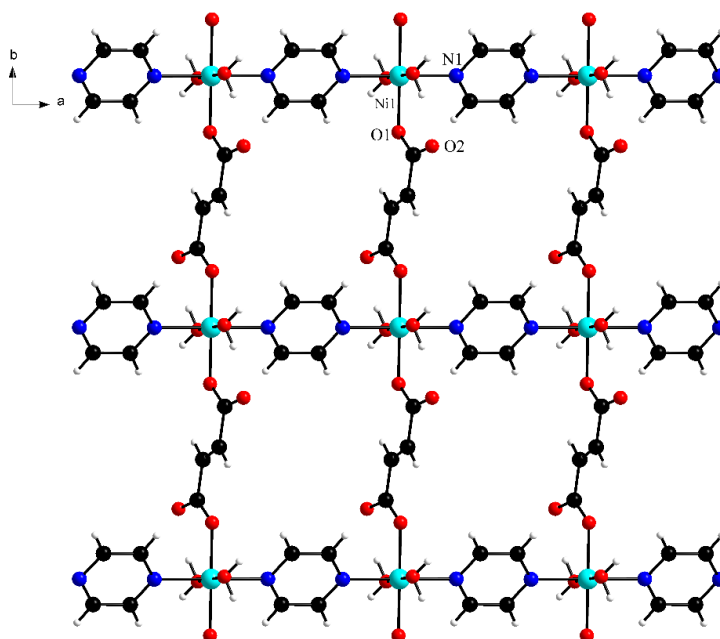


Figure 10. A portion of a 2D grid viewed along the *c* direction displaying rectangular channels.

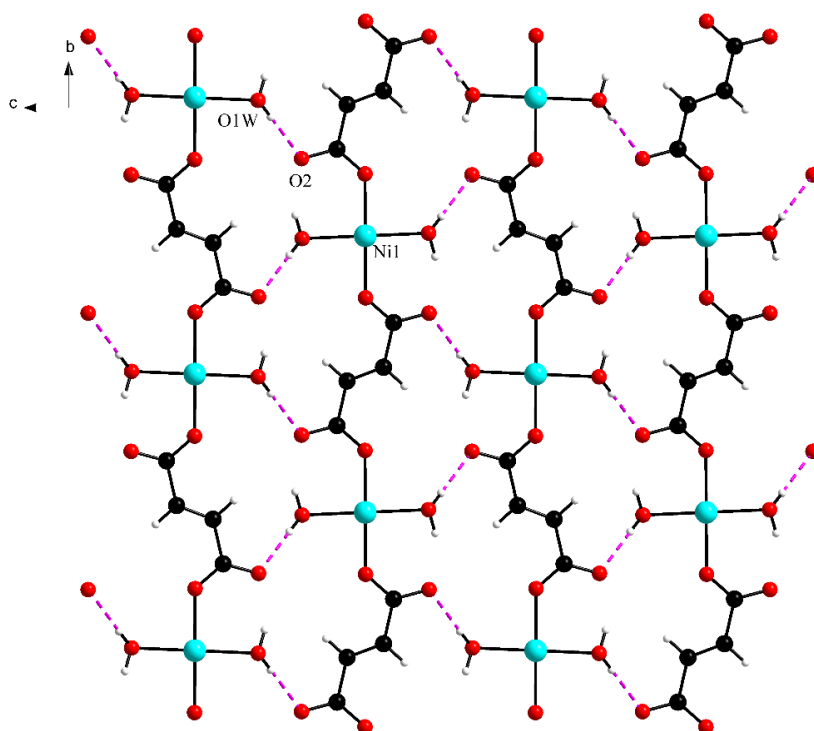


Figure 11. Inter-chain hydrogen bonding between the uncoordinated oxygen atom of fumarate and the coordinated water molecules observed along *a* direction.

[Ni(H₂O)₂(pyz)(suc)] (**13**) Upon replacing the fumarate source with the succinate source, sky blue crystals were obtained. The crystal structure analysis revealed that it crystallized in the

monoclinic $C2/c$ space group. This compound was found to be analogous to the cobalt compound $[\text{Co}(\text{H}_2\text{O})(\text{pyz})(\text{suc})]$ reported by Luann and coworkers [19], which was synthesized under hydrothermal conditions. In the crystal structure, the Ni(II) centre adopts a slightly distorted octahedral geometry, coordinated by two nitrogen atoms from the pyrazine position on a two-fold axis, two oxygen atoms contributed by the carboxylate group of the succinate ligand, and two coordinated water molecules, as depicted in **Figure 12**. This arrangement forms a $[\text{NiN}_2\text{O}_4]$ coordination environment similar to that observed in compound **12**. Despite a similar coordination environment and similar molecules, compounds **12** and **13** exhibit distinct structural features in terms of dimensionality. While compound **12** forms a 2D framework with *sql* topology, the flexibility of the carbon backbone in the succinate linker allows compound **13** to extend into a 3D architecture.

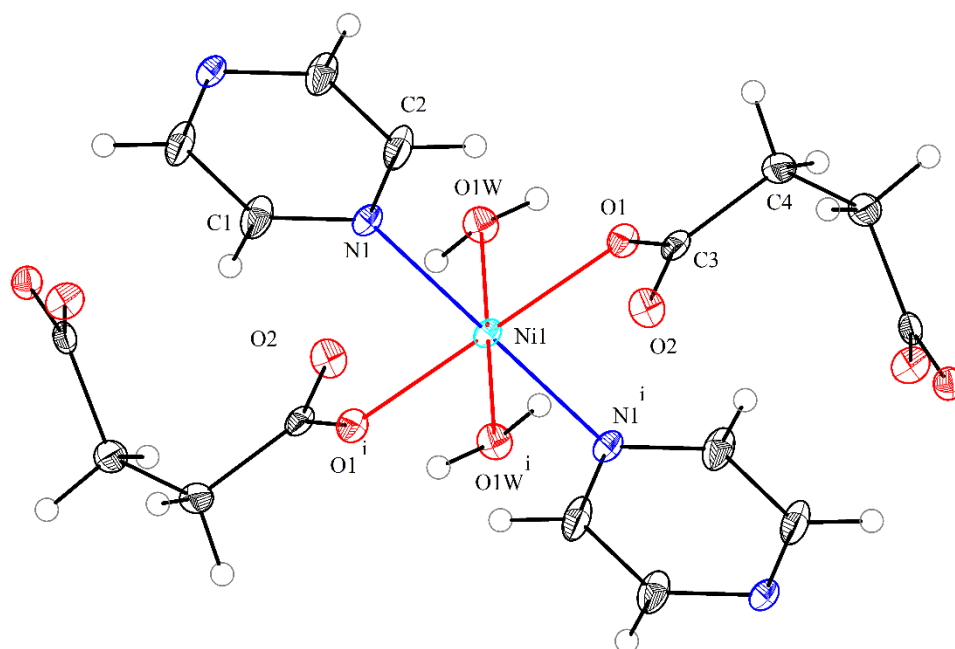


Figure 12 The crystal structure of $[\text{Ni}(\text{H}_2\text{O})_2(\text{pyz})(\text{suc})]$ (**13**). Thermal ellipsoids drawn at a 30 % probability level for all the non-hydrogen atoms. The hydrogen atoms are depicted as spheres of arbitrary radii. (Symmetry code (i) $-x+3/2, -y+1/2, -z+1$)

The succinate linker adopts a monodentate coordination mode. The orientation of the succinate ligand is shown in **Figure 13**, where the linker bridges two nickel ions through the carboxylate oxygen atoms, and two distinct planes are shown in red and green. These planes correspond to the two carboxylate groups of the succinate, which are twisted relative to each other by approximately 72.4° , illustrating the flexibility of the succinate backbone. The

rotation around the C-C single bond allows succinate to adopt the *gauche* conformation with a torsion angle, $[C3, C4, C4^{iii}, C3^{iii}] = 58.11^\circ$. This twisting facilitates the formation of a three-dimensional framework, in contrast to the planar arrangement observed in the fumarate-based analogues. This twisting also influences the Ni $\cdots$ Ni separation between the succinate-linked ions and was determined to be slightly shorter, 7.65 Å, than that observed between the fumarate-linked nickel centers.

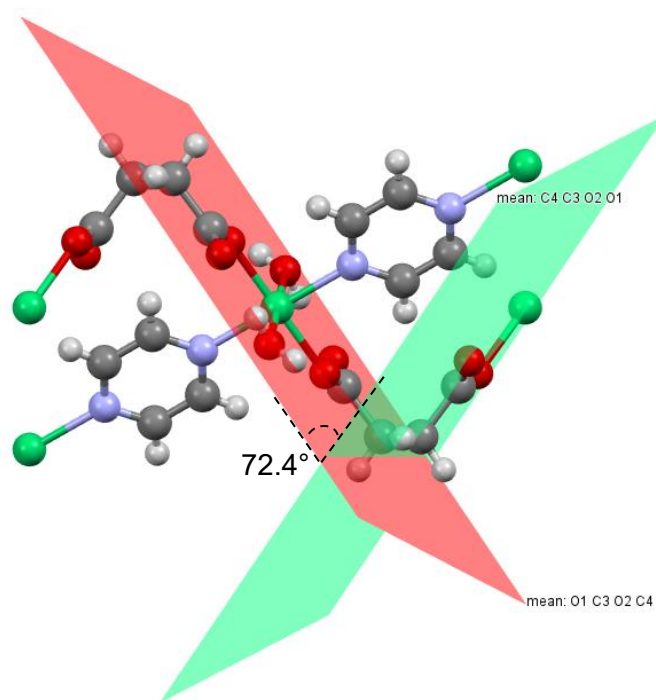


Figure 13. The twisting of the succinate ligand over the C-C bond.

The Ni-N, Ni-O, and Ni-O_(aqua) bond lengths were found to be 2.1082(15), 2.0216(12), and 2.0679 (13), respectively (Table 4). These values were in good agreement with those reported for similar nickel compounds containing succinate linkers in the literature [31-33].

The topological approach revealed that the compound **13** adopts a *cds* topology as seen in the 3D cadmium sulfate compound [34]. The fundamental building block of this three-dimensional network is a 1D chain comprising nickel bridged by a pyrazine linker; the adjacent chains are linked together with the aid of the succinate linkers, forming a 2D wavy sheet (Figure 14) along the *bc* plane. These 2D sheets are further interlinked to form the 3D interpenetrating architecture with the aid of pyrazine ligands moving in between the *ac* plane, as shown in Figure 15.

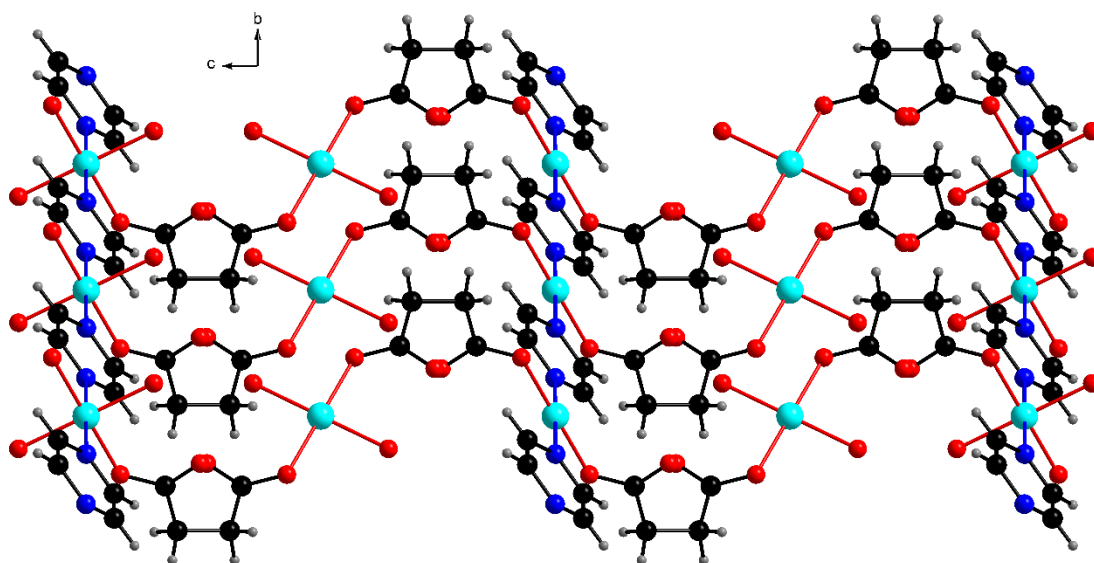


Figure 14. 2D packing along the *bc* plane, displaying wavy sheets.

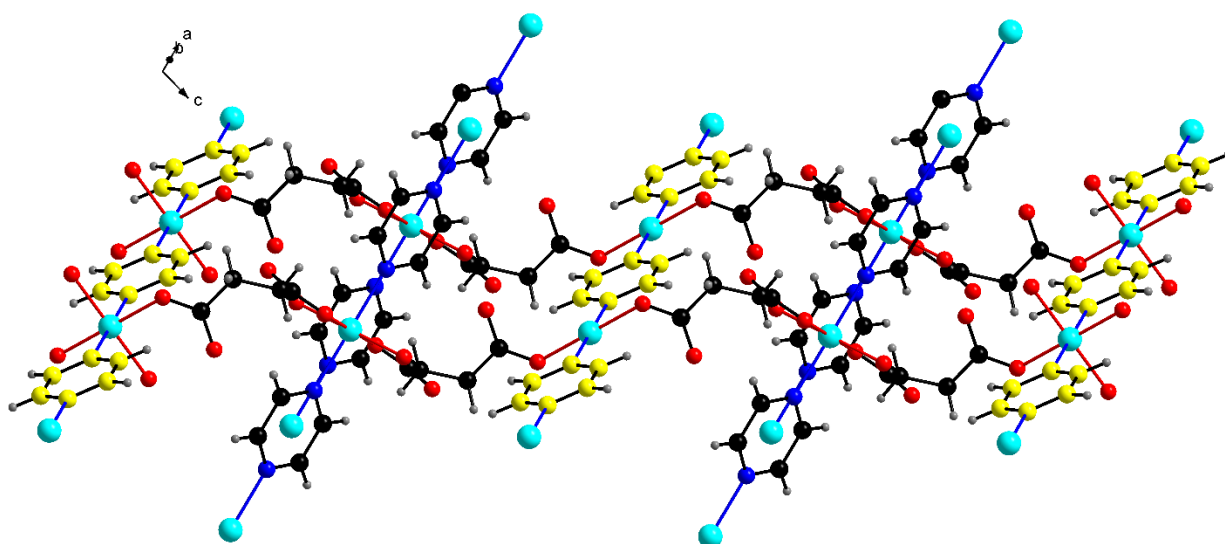


Figure 15. 2D packing along the *ac* plane, displaying 2D wavy sheets connected with pyrazine linkers to form an interpenetrating 3D structure. The atoms of the pyrazine linkers are marked in yellow for a clear view.

Compound **13** shows similar structural characteristics to those of the analogous cobalt compound [Co(H₂O)(pyz)(suc)]. To evaluate the degree of isostructurality between these two compounds, their respective .res files were examined using ISOS program [35,36]. The calculated cell similarity (π) of 0.0061 is nearly zero, confirming that both compounds are isomorphous. Furthermore, the isostructurality index ($I(s)$) of 85.5% reflects a strong

resemblance in the crystal lattice of the two compounds. The reason for not achieving a 100% score may be due to variations in the metallic radii. Consequently, the physicochemical properties of these materials may differ based on the type of metal ion present, even when their overall apical arrangements are nearly identical [37].

[Ni(H₂O)₂(pyz)(ida)] (**14**), and [Ni(pyz)(ida)]·2H₂O (**15**). It was interesting to note that when iminodiacetic acid was employed as a carboxylate source and water was used as the solvent, two hydrate isomers were obtained from the same reaction mixture. Upon subjecting the reaction mixture to slow evaporation conditions, we were able to isolate compound **14** as blue, plate-shaped crystals. However, carrying out the same reaction in hydrothermal conditions yielded us green needle-shaped crystals of compound **15**.

Compound **14** crystallizes in the orthorhombic crystal system, *P n m a* space group. The crystal structure features a Ni(II) centre that adopts a slightly distorted octahedral geometry. Two aqua molecules coordinate to the Ni(II) ion at the *cis* positions of the equatorial site, while the other two equatorial sites are occupied by the oxygen atoms of the iminodiacetate anion. One of the axial sites of the octahedron is occupied by the pyrazine molecule, which this time acts as a monodentate ligand, whereas the other axial position is occupied by the nitrogen atom of the chelating ida²⁻linker; thus, the compound shows a [NiN₂O₄] coordination environment, as shown in **Figure 16**. Compound **15**, on the other hand, crystallizes in the monoclinic crystal system, *P2₁/n* space group. The crystal structure comprises a Ni(II) centre, which again adopts an octahedral geometry with slight distortion. The equatorial sites are occupied by two oxygen atoms, one is contributed by a chelating ida²⁻ molecule (O3), while the other oxygen (O2ⁱ) is contributed from the neighbouring ida²⁻ ligand. While the remaining equatorial sites were occupied by the nitrogen atoms, one from the bridging pyrazine linker, while the other comes from the chelating ida²⁻ anion. One of the axial positions was occupied by the oxygen atom (O1) of the chelating ida²⁻linker, while the other axial position was occupied by the nitrogen atom of another pyrazine molecule involved in bridging. Thus, a [NiN₃O₃] coordination environment is formed (**Figure 17**). Apart from this, the crystal structure of **15** also contains lattice aqua molecules, which are held together by intramolecular hydrogen bonds.

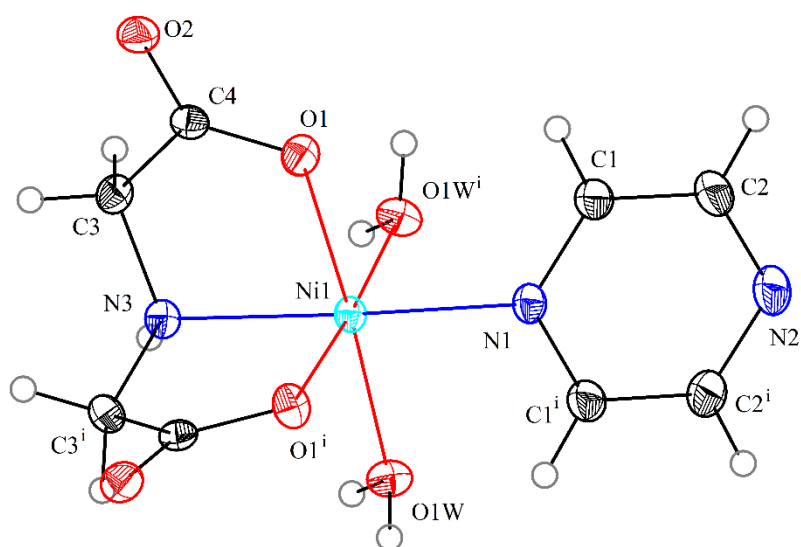


Figure 16 The crystal structure of $[\text{Ni}(\text{H}_2\text{O})_2(\text{pyz})(\text{ida})]$ (**14**). Thermal ellipsoids drawn at a 30 % probability level for all the non-hydrogen atoms. The hydrogen atoms are depicted as spheres of arbitrary radii. (Symmetry code (i) $x, 0.5-y, z$)

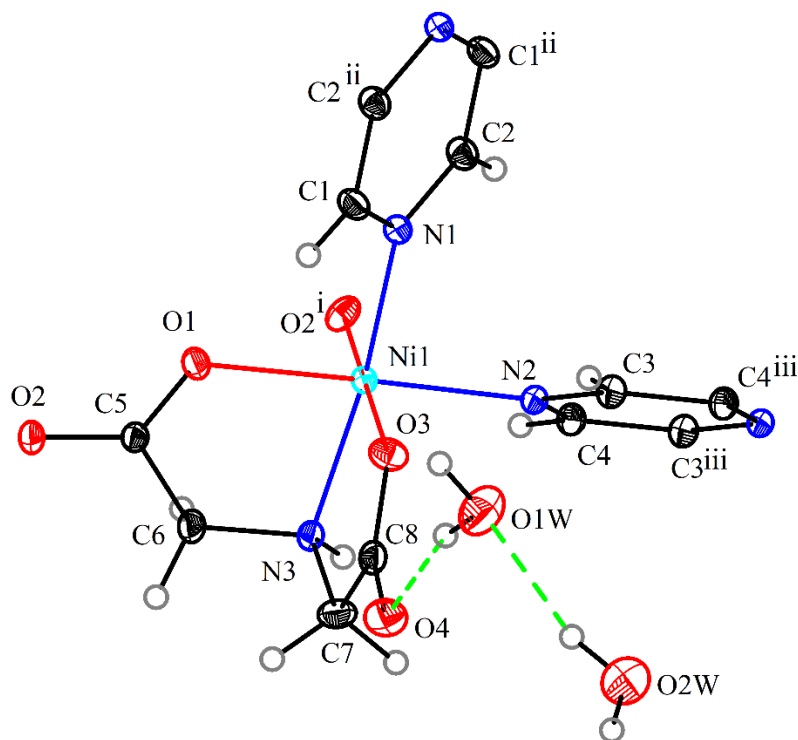


Figure 17 The crystal structure of $[\text{Ni}(\text{pyz})(\text{ida})]\cdot 2\text{H}_2\text{O}$ (**15**). Thermal ellipsoids drawn at a 30 % probability level for all the non-hydrogen atoms. The hydrogen atoms are depicted as spheres of arbitrary radii. (Symmetry code (i) $-x+1/2, y+1/2, -z+3/2$ (ii) $-x, y+2, -z+1$ (iii) $-x+1, y+2, -z+1$). The intramolecular hydrogen bonds are shown in green dotted lines.

The pyrazine ligand in compound **14** adopts the monodentate coordination mode, while the ida^{2-} anion adopts the chelating coordination mode with the nickel center. As a consequence, it forms a zero-dimensional molecular compound. The Ni-N bond lengths (2.0813(15) (Ni-N1) and 2.0958(15) (Ni-N3)) (**Table 4**) were found to be in the normal range with those reported in the literature for nickel compounds [38,39]. Expectedly, the internal ring angles at C1-N1-C1ⁱ and C2-N2-C2ⁱ of the pyrazine molecule were found to be slightly different, that is, 116.52(16) and 115.86(18) respectively, and larger for the N1 sites as it is coordinated to the nickel centre [40].

Morel and coworkers studied a similar monomeric zinc compound $[\text{Zn}(\text{IDA})(\text{AdeH})(\text{H}_2\text{O})_2]$, which crystallized in the triclinic crystal system, $P\bar{1}$ space group. In this compound, the iminodiacetate linker adopts a *fac*-tridentate conformation, with an average Zn-O(carboxy) bond distance of 2.118(2) Å and an average Zn-O(aqua) bond distance of 2.162(2) Å [41]. A similar conformation was adopted by the ida^{2-} anion in another zinc compound $[\text{Zn}(\text{ida})(\text{phen})(\text{H}_2\text{O})]$ reported by Zhou and group [42]. Compound **14** also exhibits a similar conformation of the anion; however, the observed bond distances in compound **14** were much shorter, Ni-O (2.0569(9)) and Ni-O1W (2.0669(10)), than those in the zinc compounds, due to the difference in ionic radii.

On the other hand, the pyrazine ligand in compound **15** adopted a more common bridging coordination mode, whereas the ida^{2-} anion adopted a μ_2 bridging chelating coordination mode. As a consequence, a 3D coordination polymer was obtained under hydrothermal conditions. The ida^{2-} anion adopts different coordination modes, such as a bridging mode observed in the compound $(\text{NH}_4)_n [\text{Zn}(\text{Hida})\text{Cl}_2]$ [42], tridentate coordination [N,O,O] coordination mode, seen in compounds $[\text{Zn}(\text{Phen})(\text{ida})(\text{H}_2\text{O})]$ [42], tetradentate bridging coordination mode observed in $[\text{Co}_2(\text{ida})_2(\text{H}_2\text{O})_2]$ and pentadentate bridging coordination mode observed in a coordination polymer $[\text{Na}_2\text{Co}_2(\text{ida})_4(\text{H}_2\text{O})_4] \cdot 2n\text{H}_2\text{O}$ [43] representative structure for each type is shown in **Figure 18**. The bond distances reveal a distinct difference between the equatorial and axial coordination sites of the metal ion. In the case of the pyrazine ligand, the equatorial Ni-N1 = 2.0587 Å is much shorter compared to the axial Ni-N2 (2.1252(12) Å). A similar trend was observed for the ida^{2-} linker, where the equatorial Ni-O3 (2.0198(11) Å), was found to be shorter than the axial Ni-O1 (2.0899(11) Å). These variations in bond lengths indicate a slight axial elongation and equatorial compression, suggesting that the nickel center adopts a distorted octahedral geometry. The bond distances and angles are in the normal range, listed in **Table 4**.

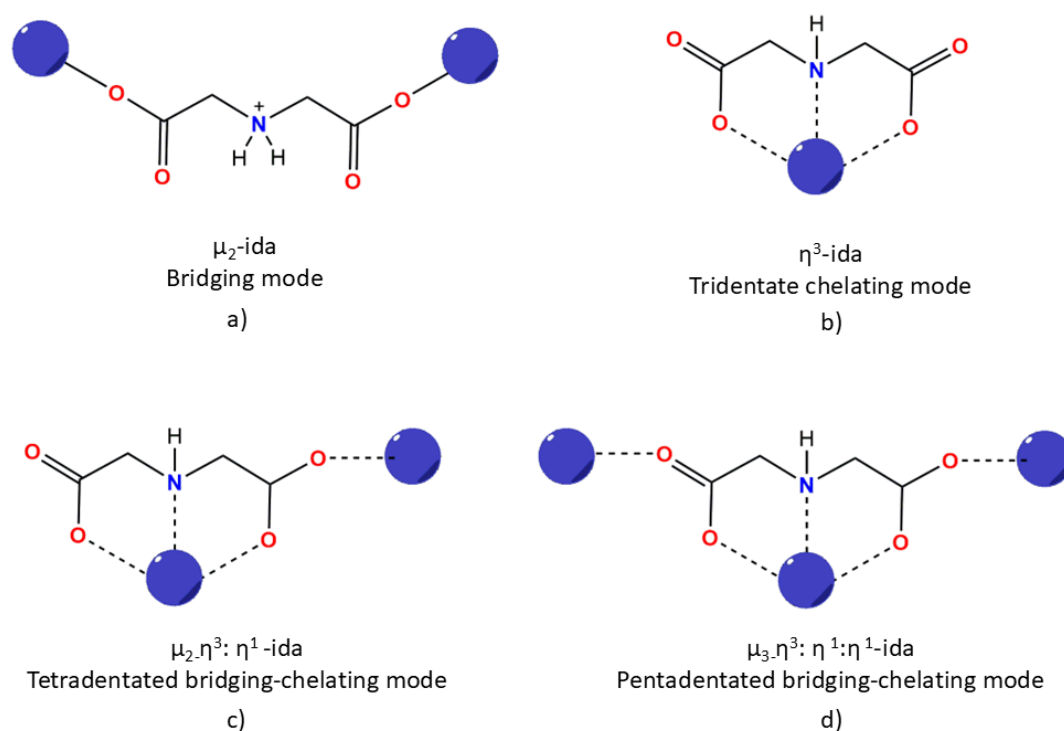


Figure 18. Schematic representation of the coordination modes of ida^{2-} anion with metal ions.

The molecular packing of compound **14** reveals the formation of a 3D supramolecular network. The 0D monomeric units of $[\text{Ni}(\text{H}_2\text{O})_2(\text{pyz})(\text{ida})]$ interact with each other with the help of intermolecular hydrogen bonds originating from coordinated aqua molecules and the uncoordinated (O1) and coordinated (O2) oxygen atoms of neighbouring molecules. The O1W acts as the donor atom and forms a hydrogen bond with the coordinated O1 atom of the ida^{2-} linker, along the *c*-axis with the D-A distance of 2.704 Å, thus forming a 1D chain of the molecules (**Figure 19**). This chain is further interlinked along the *b*-axis via the hydrogen bond between the O1W (donor atom) and the uncoordinated O2 atom of the carboxylate linker (**Table 5**) as a result, a 2D supramolecular network is formed. These 2D sheets are then connected through weaker $\text{C-H}\cdots\text{O}$ interactions originating from the carbon atoms of the monotopic pyrazine linker along the *a*-axis, resulting in the formation of a 3D supramolecular framework shown in **Figure 20**.

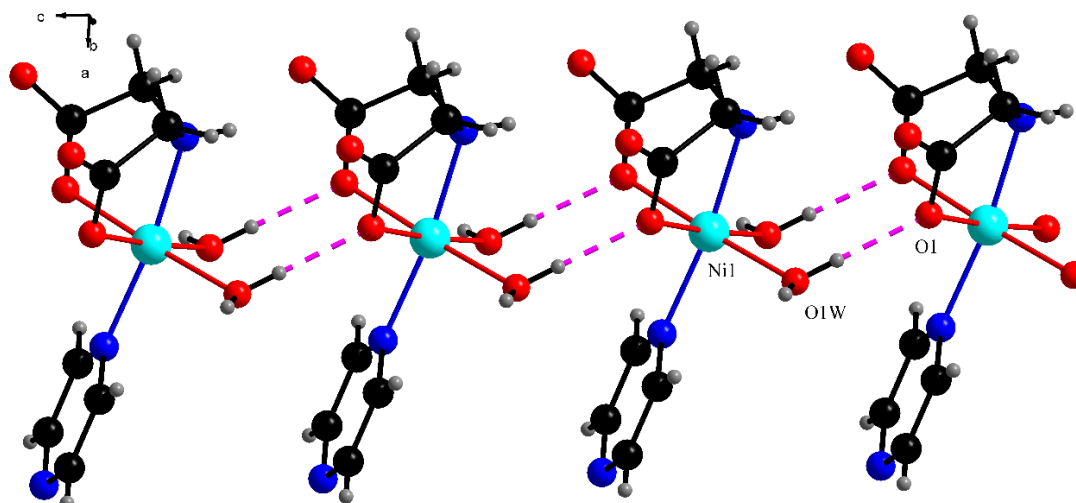


Figure 19. One-dimensional supramolecular chain formed via O1W-H4 $\cdots$ O1 running along the *c*-axis. (Symmetry code $x, -y+1/2, z-1$)

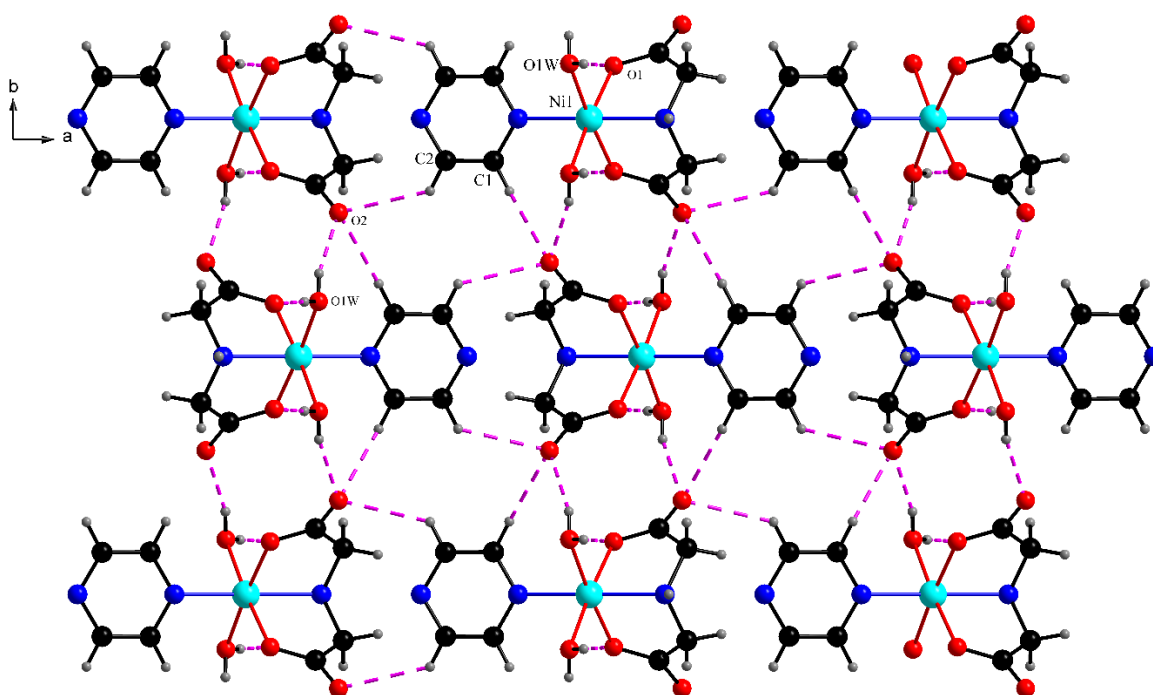


Figure 20. Molecular packing diagram of compound **14** viewed along the *ab* plane.

The construction of the 3D network of compound **15** is depicted in **Figures 21-23**. In this compound, both pyrazine and the ida²⁻ anions adopt bridging coordination modes. The ida²⁻ linker is involved in sewing the nickel ions into a zig-zag chain running along the *b* axis as depicted in **Figure 21a**. These individual chains are then connected on either side with the aid of the pyrazine linkers, forming a 2D rectangular grid (**Figure 21b**). These rectangular grids

are further interconnected to form a 3D structure, utilizing another crystallographically unique pyrazine linker, as shown in **Figure 22**.

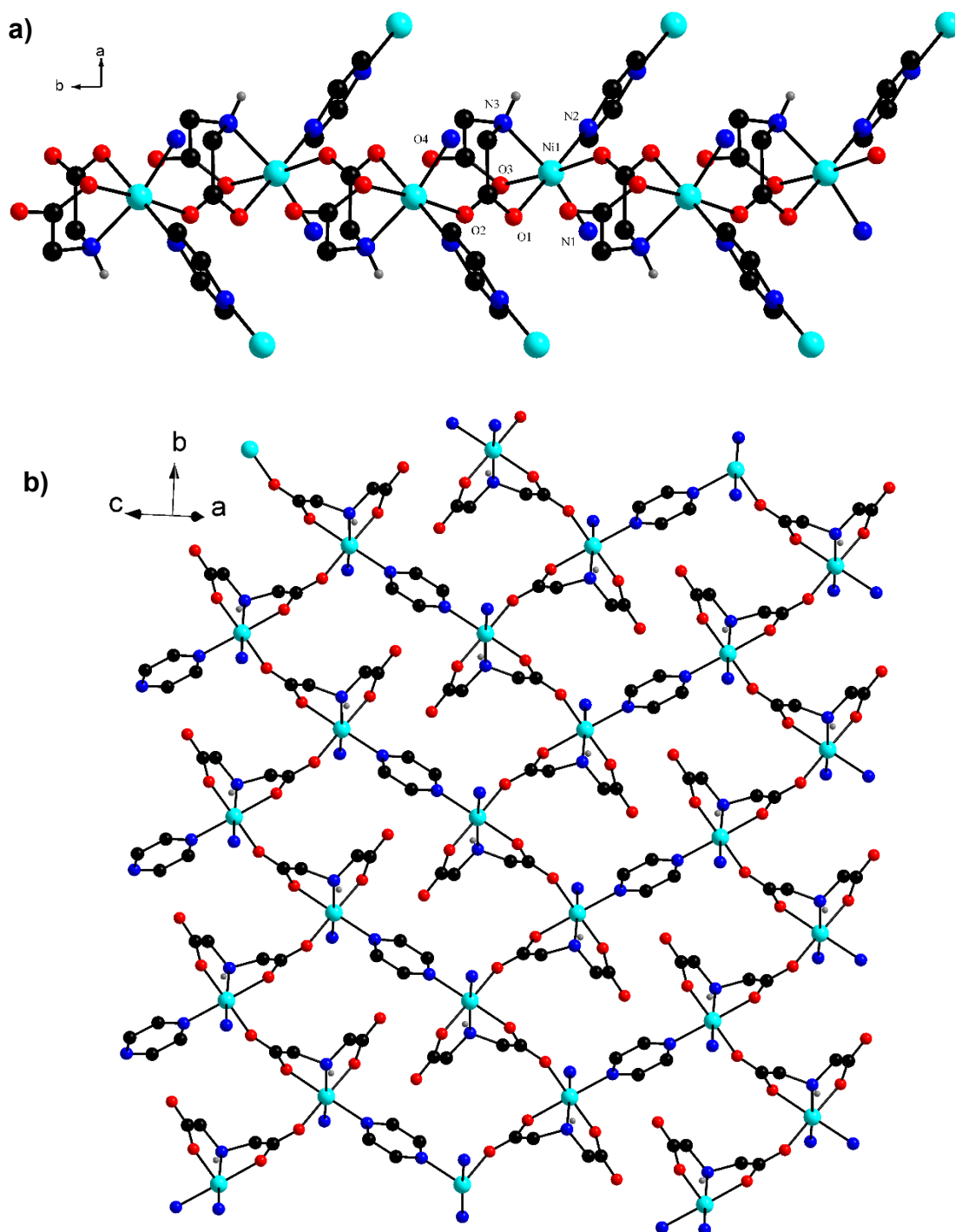


Figure 21 a) one-dimensional zig-zag chain structure, formed due to the bridging chelating mode of the ida ligand. b) The 2D rectangular sheet formed by interconnecting the 1D ida chains with alternating pyrazine linkers, adopting the bridging coordination mode.

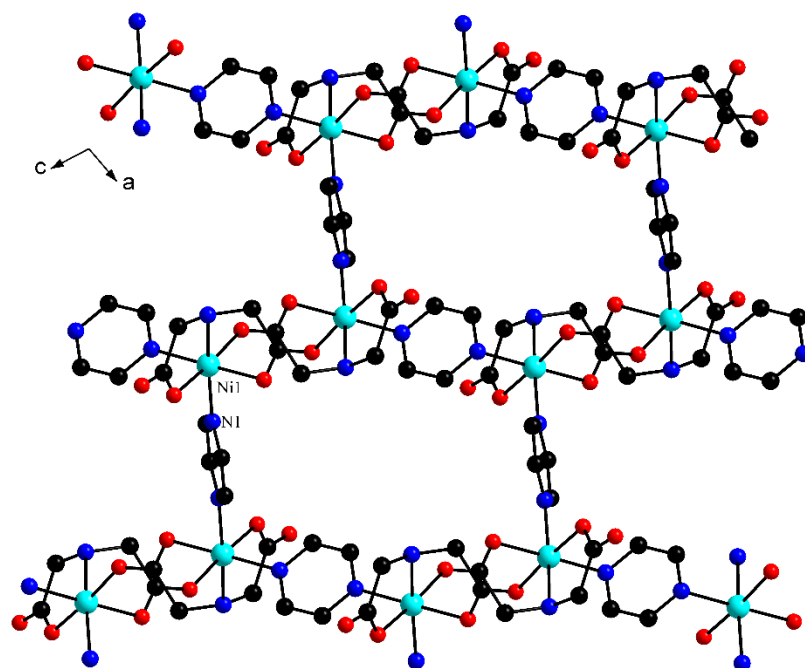


Figure 22. Molecular packing diagram of compound **15** viewed along the *ac* plane.

The H-atoms attached to the nitrogen atom of the ida linker and oxygen atoms of the lattice waters act as a hydrogen donor, resulting in an intermolecular hydrogen bond of type N-H $\cdots$ O and O-H $\cdots$ O type, filling the empty spaces in the 3D architecture of compound **15** as shown in a small portion in [Figure 23](#). The hydrogen bonding parameters of compound **15** are listed in [Table 5](#).

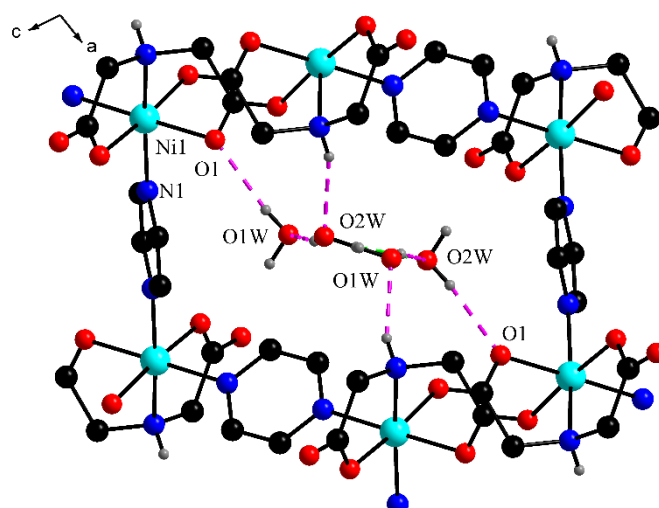


Figure 23. Hydrogen bonding situation in compound **15**, between the lattice aqua molecules and the coordinated oxygen atoms, and the coordinated N atom of the ida linker

Table 3. The crystallographic data and structures refinement parameters **12-15**

Compound	12	13	14	15
Empirical formula	C ₈ H ₁₀ N ₂ O ₆ Ni	C ₈ H ₁₂ N ₂ O ₆ Ni	C ₈ H ₁₃ N ₃ NiO ₆	C ₈ H ₁₃ N ₃ NiO ₆
Temperature/K	296(2)	296(2)	296(2)	296(2)
Formula weight	288.87	290.89	305.9	305.9
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> <i>n</i> <i>m</i> <i>a</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	7.002(4)Å	12.509(5)	18.399(2)	9.8615(4)
<i>b</i> / Å	9.021(5)Å	6.832(3)	12.7345(13)	7.7100(3)
<i>c</i> / Å	11.544(7)Å	13.319(6)	5.1379(5)	15.8643(6)
α / °	90°	90	90	90
β / °	105.49(2)°	107.423(10)	90	102.692(10)
γ / °	90°	90	90	90
Volume / Å ³	702.51(7)	1086.18(8)	1203.8(2)	1176.72(8)
<i>Z</i>	2	4	4	4
D _{calc.} [Mg m ⁻³]	1.366	1.779	1.688	1.727
μ / mm ⁻¹	1.396	1.806	1.636	1.674
F(000)	296	600	632	632
Radiation	MoK α (λ =0.71073)	MoK α (λ =0.71073)	MoK α (λ =0.71073)	MoK α (λ =0.71073)
Crystal size/mm	0.25 × 0.14 × 0.08	0.14 × 0.12 × 0.1	0.35 x 0.21 x 0.09	0.20 x 0.17 x 0.11
θ range for data collection (°)	2.908 to 28.26	3.206 to 28.355	2.731 to 28.275	2.632 to 28.274
Index ranges	-9≤ <i>h</i> ≤9, -12≤ <i>k</i> ≤12, -15≤ <i>l</i> ≤15	-16≤ <i>h</i> ≤ 15, -6≤ <i>k</i> ≤ 9 -17≤ <i>l</i> ≤ 17	-20≤ <i>h</i> ≤24, -16≤ <i>k</i> ≤16, -6≤ <i>l</i> ≤6	-13≤ <i>h</i> ≤13, -10≤ <i>k</i> ≤10, -21≤ <i>l</i> ≤21
Reflections collected	12322	7366	14109	25654
Independent reflections	1734 [R(int) = 0.0272]	1339 [R(int) = 0.0227]	1555 [R(int) = 0.0352]	2927 [R(int) = 0.0294]
Completeness to θ = 25.242 (%)	99.8	98.5	99.7	99.8
Data/restraints/parameters	1734/0/87	1339/0/85	1555/0/96	2927/0/178
Goodness-of-fit on F ²	1.091	1.117	1.071	1.119
Final R indexes [<i>I</i> > 2 σ (<i>I</i>)]	R1 = 0.0271, wR2 = 0.061	R1 = 0.0217, wR2 = 0.057	R1 = 0.0214, wR2 = 0.054	R1 = 0.0232, wR2 = 0.0522
Final R indexes [all data]	R1 = 0.0341, wR2 = 0.0650	R1 = 0.0252, wR2 = 0.0585	R1 = 0.0234, wR2 = 0.055	R1 = 0.0267, wR2 = 0.0538
Largest diff. peak/hole/eÅ ⁻³	0.602 and - 0.368	0.277 and - 0.324	0.302 and -0.33	0.345 and - 0.219

Note: Absorption correction: semi-empirical from equivalents, Refinement method: Full-matrix least-square on F²

Table 4. Selected bond distances and bond angles

<i>Bond distance</i>		<i>Bond angle</i>			
12					
Ni1-O1	2.0216(12)	O1-Ni1-O1W ⁱ	87.86(6)	O1-Ni1-N1 ⁱ	88.68(6)
Ni1-O1 ⁱ	2.0216(12)	O1 ⁱ -Ni1-O1W ⁱ	92.14(6)	O1W ⁱ -Ni1-N1 ⁱ	91.98(6)
Ni1-O1W	2.068(13)	O1-Ni1-N1	91.32(6)	O1W-Ni2-N1 ⁱ	88.02(6)
Ni1-O1W ⁱ	2.068(13)	O1 ⁱ -Ni1-N1	88.68(6)	O1-Ni1-O1 ⁱ	180
Ni1-N1	2.1082(15)	O1W ⁱ -Ni1-N1	88.02(6)	N1 ⁱ -Ni1-N1	180
Ni1-N1 ⁱ	2.1082(15)	O1W-Ni1-N1	91.98(6)	O1W ⁱ -Ni1-O1W	180
13					
Ni1-O1	2.0465(11)	O1 ⁱ -Ni1-O1W	90.84(5)	O1-Ni1-N1 ⁱ	88.81(5)
Ni1-O1 ⁱ	2.0465(11)	O1-Ni1-O1W	89.16(5)	O1 ⁱ -Ni1-N1 ⁱ	91.19(5)
Ni1-O1W	2.074(12)	O1-Ni1-N1	91.19(5)	O1W ⁱ -Ni1-N1 ⁱ	87.48(5)
Ni1-O1W ⁱ	2.074(12)	O1 ⁱ -Ni1-N1	88.81(5)	O1W-Ni1-N1 ⁱ	92.52(5)
Ni1-N1	2.158(12)	O1W ⁱ -Ni1-N1	92.52(5)	O1-Ni1-O1 ⁱ	180
Ni1-N1 ⁱ	2.158(12)	O1W-Ni1-N1	87.48(5)	N1 ⁱ -Ni1-N1	180
				O1W ⁱ -Ni1-O1W	180
14					
Ni1-O1	2.0569(9)	O1 ⁱ -Ni1-O1W	86.64(6)	O1-Ni1-N3	82.52(4)
Ni1-O1 ⁱ	2.0569(9)	O1-Ni1-O1W ⁱ	91.22(4)	O1W-Ni1-N3	94.36(4)
Ni1-O1W	2.0669(10)	O1-Ni1-O1W	176.42(4)	N1 ⁱ -Ni1-N1	172.5(6)
Ni1-O1W ⁱ	2.0669(10)	O1-Ni1-N1	92.04(4)	O1W-Ni1-O1W	90.77(6)
Ni1-N1	2.0813(15)	O1W-Ni1-N1	90.90(4)		
Ni1-N3	2.0958(15)				
15					
Ni1-O3	2.0198(11)	O3-Ni1-N1	89.09(5)	N1-Ni1-O2 ⁱ	94.50(5)
Ni1-N1	2.0587(12)	O3-Ni1-N3	83.78(5)	N3-Ni1-O2 ⁱ	92.95(5)
Ni1-N3	2.073(13)	O3-Ni1-O2 ⁱ	175.85(5)	N1-Ni1-O1	90.68(5)
Ni1-O2 ⁱ	2.0796(11)	O3-Ni1-O1	89.17(5)	N3-Ni1-O1	81.24(5)
Ni1-O1	2.0899(11)	O2 ⁱ -Ni1-O1	92.86(4)	O3-Ni1-N2	90.50(5)
Ni1-N2	2.1252(12)	N1-Ni1-N3	169.28(5)	O2 ⁱ -Ni1-N2	87.41(4)
		N1-Ni1-N2	90.29(5)	O1-Ni1-N2	178.96(4)
		N3-Ni1-N2	97.75(5)		

Symmetry code (12): $i = -x+1, -y+1, -z+1$, *(13):* $i = -x+3/2, -y+1/2, -z+1$, *(14):* $i = x, -y+1/2, z$, *(15):*

$i = -x+1/2, y+1/2, -z+3/2$

Table 5. Selected hydrogen bond parameters for **12-15**

D-H...A	d(D-H)	d(H...A)	<DHA	d(D...A)	Symmetry code
12					
O1W-H1W...O2	0.812	1.948	176.21	2.759	-x+3/2, y+1/2, -z+3/2
O1W-H2W...O2	0.838	1.907	158.11	2.703	
13					
O1W-H1W...O2	0.844	1.815	163.59	2.635	-x+3/2, y+1/2, -z+1
O1W-H2W...O2	0.847	1.993	159.74	2.803	x, -y+1, z-1/2
14					
O1W-H4...O1	0.848	1.867	178.63	2.714	x, -y+1/2, z-1
O1W-H5...O2	0.809	1.916	164.37	2.704	-x+1, y-1/2, -z+1
C1-H1...O2	0.93	2.445	163.21	3.346	-x+1, -y+1, -z+1
C2-H2...O2	0.93	2.591	131.64	3.283	x+1/2, y, -z+3/2
C3-H3B...O2	0.97	2.53	148.83	3.397	x, y, z-1
15					
O1W-H1W...O4	0.858	1.954	168.13	2.799	
O1W-H1W...O4	0.829	2.138	171.58	2.96	-x, -y+1, -z+1
O2W-H3W...O1W	0.841	2.005	158.00	2.803	
O2W-H4W...O1W	0.837	2.102	167.98	2.926	-x+1/2, y-1/2, -z+1/2
N3-H5...O2W	0.849	2.13	160.26	2.943	-x+1, -y+1, -z+1

5.3.6 Powder X-ray diffraction analysis

The powdered samples of **12-15** were analyzed for their bulk purity using the X-ray diffraction technique. The simulated powder patterns generated from the single crystal data were used for comparison purposes. The high-intensity peaks observed in the experimental data closely matched those in the simulated data set. This ensures that the single-crystal model accurately represents the bulk phase of the microcrystalline samples. The overlaid powder patterns are shown in **Figure 24** for compounds **12-15**, respectively.

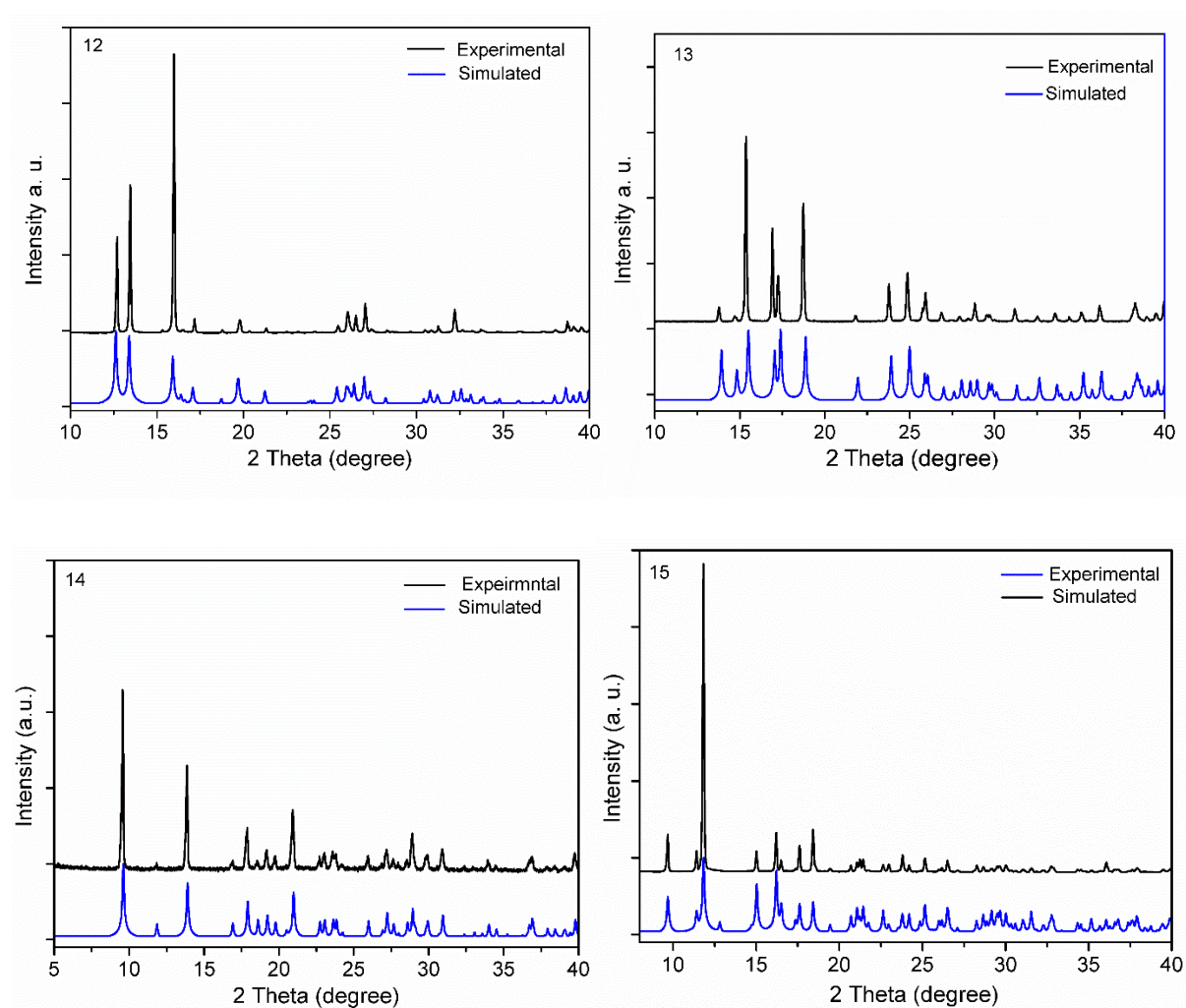


Figure 24. Experimental PXRD pattern of **12-15** overlaid with simulated pattern

5.4. Preparation and characterization of NiO composite using Ni-CPs.

In recent years, CP-derived NiO materials have garnered considerable attention for various applications, including electrochemical glucose sensing, supercapacitor applications, gas sensing, and heterogeneous catalysis, with the added advantage of being low-cost and environmentally friendly [44-47]. Especially in supercapacitor applications, because the performance of the supercapacitor depends on morphologies, surface area, particle size, and porosity. MOFs or CPs provide an excellent platform for generating oxide materials that exhibit such properties mentioned earlier, compared to traditional nickel hydroxide calcination [48]. The higher carbon content in the CPs or MOFs tends to emit more gases during the decomposition process, which may result in a more porous final material. So also, the morphology, size and the elemental composition of the metal oxides can be finely tuned by varying the components of the CPs/MOF materials. The long-term ordering in the crystalline CPs ensures uniformity in particle size. Different morphologies of 2D and 3D NiO have been reported in the literature, including 2D NiO nanosheets, nanoplates, and nanoflakes, as well as 3D NiO microspheres, flowers, and nanorods. Carbon-based nanomaterial composites have also been on the rise, as the high surface area of carbon materials is thought to increase the active sites of NiO/carbon nanomaterials and may also improve their conductivity and mechanical strength [49,50]. In this context, we used our synthesized Ni-CPs (**12**, **13**, and **15**) as precursors for the preparation of metal oxides and investigate their properties. Furthermore, the effect of varying the carboxylate on the crystalline phase formation and morphology of the final oxide material was also of interest to us.

5.4.1 Synthesis of Ni-CP derived nanomaterials, phase identification and SEM analysis

The finally grounded CPs were heated in a furnace at 400 °C for 2 hours. After cooling to room temperature, the oxide material was ground into fine powder for 30 minutes. The resulting greyish solid was characterized by the PXRD techniques shown in **Figure 25**. The formation of the composite material is attributed to the presence of nitrogen-rich compound pyrazine, which, upon decomposition, reduces the nickel oxide nanoparticles to nickel. The same composite material was subjected to scanning electron microscopy to visualize its morphology.

The phase information of the composites was verified by PXRD technique. The recorded powder pattern was compared with the reference pattern for pure NiO (JCPDS card no. 22-1189). The sharp peaks located at 44.5, 51.9 and 76.3° corresponds to the (111), (200) and

(220) planes of the cubic Ni phase, While the peaks at 2θ values of 37.3° , 43.4° , 63.0° and 79.2° are well assigned to the typical (003), (012), (104) and (006) planes of the rhombohedral NiO phase (JCPDS card no 01-078-0533) [45].

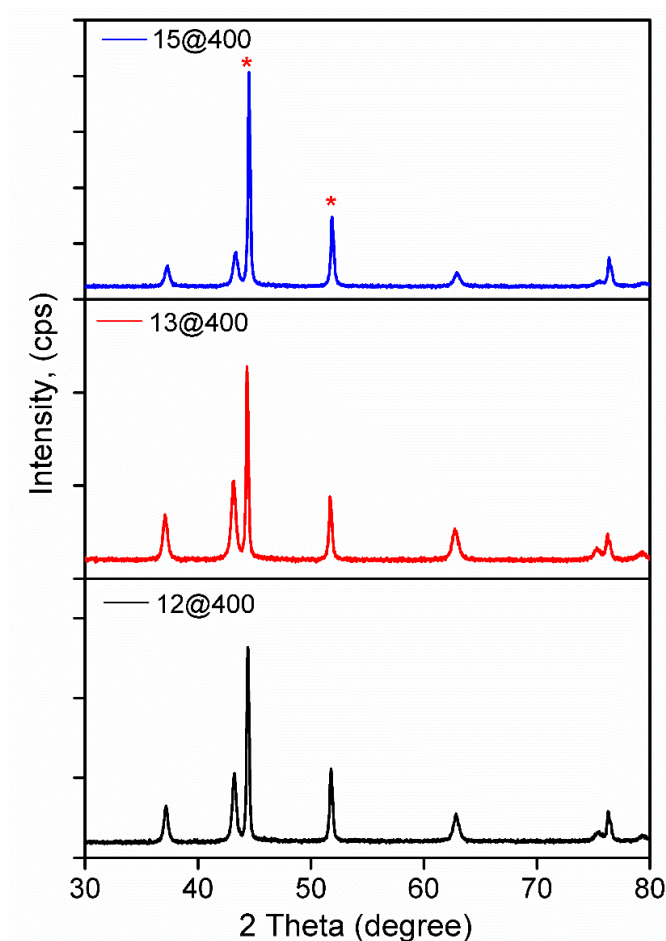


Figure 25. Comparison between the experimental powder patterns of the composite material, derived from the CPs after heating at 400°C . The red star denotes the Nickel phase.

The surface morphology was inspected using scanning electron microscopy technique (SEM). The SEM images for powdered CPs were obtained at 20kV with magnification up to 50 KX shown in **Figure 26**. The morphological examination of the powder samples of **12**, **13** and **15** (**Figure 26, Left**) shows significant variation in the particles shape, where compound **12** exhibits rod-like crystalline particles, which are tightly packed forming a more compact microcrystalline structure. The surfaces of these crystals are relatively smooth and the edges are well- developed indicating high degree of crystallinity and uniform crystal growth. Compound **12** exhibits a irregular globular shaped crystals stacked on each other with smooth surfaces, while compound **15** shows a mix of plate shaped and irregular globular particles

with clear edges suggesting high crystallinity. On apply thermal treatment to these materials, a distinct change in the morphology was observed, wherein the SEM images of the oxide material showed densely packed, spherical microcrystals, with uniform thickness. A deeper understanding of the composite materials is still needed, especially regarding their surface features, shape and internal structures. Further studies are also required to determine their exact elemental composition and porosity. Work is currently in progress to explore theses aspects in detail.

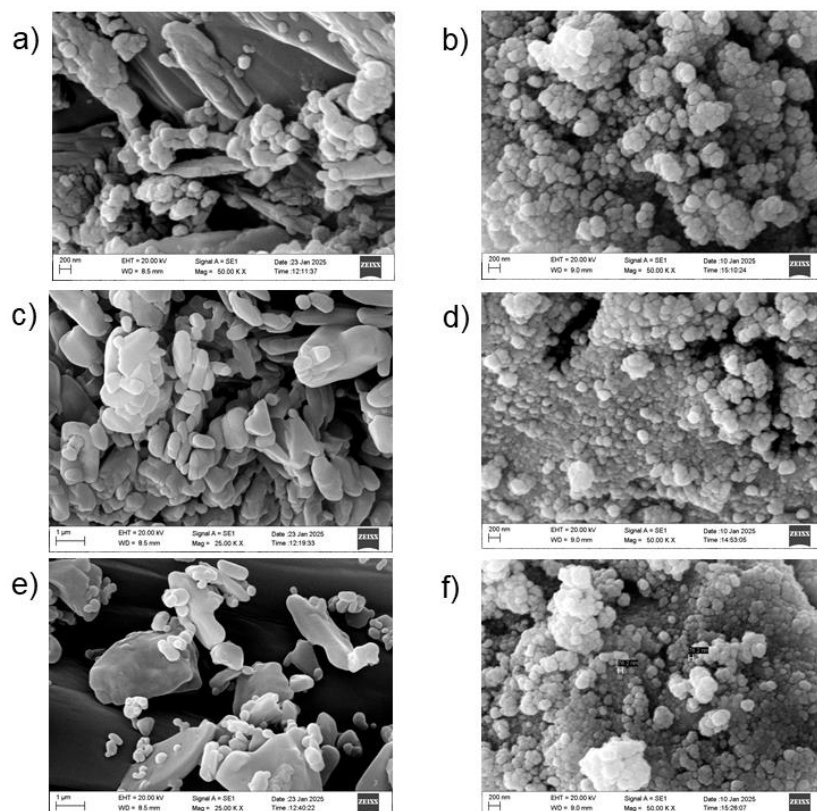


Figure 26 The SEM images (a), (c), (e) of the compounds **12**, **13** and **15** respectively on (Left) and their corresponding Ni/NiO composite (b), (d) and (f) (Right)

5.5 Conclusion

We studied three nickel coordination polymers by varying simple aliphatic carboxylate ligands, moving from rigid fumaric acid to more flexible iminodiacetic acid. Crystals were grown using hydrothermal methods using water as the solvent, offering a more sustainable approach to prepared CPs. A significant difference in the dimensionality was observed when reactions involving nickel pyrazine and iminodiacetic acid was subjected to slow evaporation method and hydrothermal conditions. The slow evaporation method yielded a zero-dimensional compound **14**, which exhibited hydrate isomerism with **15** obtained from

hydrothermal condition. Upon heating these compounds to 400 °C, nickel/nickel oxide composite were formed, as the nitrogen facilitated the reducing the Ni⁺² ions to nickel species at 400°C. SEM analysis revealed that the nickel/nickel oxide composite had a uniform spherical shape, independent of the original crystal shapes.

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Chapter 5: Section II: Synthesis, structure determination of a new oxidovanadium coordination polymer containing terpyridine**5.6 Chapter overview**

Chapter 5, Section II, focuses on preparing and characterizing a hydrothermally synthesized, new heterometallic coordination polymer $[(VO(terpy))_4(MoO_4)_2(Mo_8O_{26})] \cdot 2H_2O$ **16** (terpy = 2,2';6',2''-terpyridine). Section 5.6 provides a literature review on the polyoxometalate-based coordination polymers featuring rigid N-donor linkers. Section 5.7. Provides detailed synthetic strategies and subsequent spectral, thermal, and structural characterization of the prepared compound.

5.7 literature review on the polyoxometalate-based coordination polymers

Polyoxometalates (POMs) are discrete anionic transition metal clusters having unique topologies, nuclearities, and electronic versatilities. The isopoly- and heteropolyanion clusters usually contain symmetrical core assemblies of metal-oxido motifs ($M = V, Mo, W$) and often adopt quasi-spherical structures of considerable topological interest [1, 2]. POMs are formed through the condensation processes of simple anions in solution under various temperature and pH (mainly acidic) conditions [3, 4]. Due to their promising biological applications [5, 6] POMs are actively used as metallodrugs. In recent years, they have gained importance for their antitumor, antiviral, antibacterial, and anticancer activities [6]. In addition, these compounds exhibit remarkable redox properties and thus find potential applications in several areas *viz.* catalysis, medicine, electrochemistry, magnetic materials etc. [7-12]. The concept of hybrid polyoxometalates has emerged in recent years. These post-functionalizable hybrid-POMs serve as building blocks due to their structural diversity, allowing the coupling of properties of POMs with different organic and inorganic metal cation functionalities. This makes them useful in (photo) catalysis, bioinorganic chemistry, and materials science [13, 14]. The structural, electronic, and magnetic properties of well-known polyoxovanadates (POVs), such as the robust $[V^{IV}_{18}O_{42}]^{12-}$ polyoxoanion, can be altered by infusion of elements like Si-, Ge-, As-, or Sb to form decorated heteroPOVs. The four general families of POVs are: fully-oxidised (V^V), mixed-valent (V^V/V^{IV} or V^{IV}/V^{III}), “fully-reduced” (V^{IV}), and “highly-reduced” (V^{III}) species [15-17].

The chemistry of POV is dominated by the decavanadate anion $[V_{10}O_{28}]^{6-}$ containing the fully oxidised V^V ion [18-20], and several examples of structurally characterized decavanadates charge-balanced by a variety of counter cations are listed in the Cambridge Structural Database [21]. As in the case of other early transition metals like Mo and W [22, 23], decavanadates can be readily obtained by treatment of V_2O_5 with a limited amount of base [24] or by acidification of tetraoxido vanadate / metavanadate solution in the presence of appropriate counter cations [25-28]. Unlike decavanadates, the fully reduced POVs containing V^{IV} are air-sensitive as evidenced by the report on the Na^+ or K^+ salt of $[V^{IV}_{18}O_{42}]^{12-}$ [29]. In this spherical polyoxoanion, each of the eighteen V^{+4} atoms is coordinated by five oxygens, one of which is unshared, which is a typical structural feature in the chemistry of the vanadyl $\{VO\}^{2+}$ moiety. The stringent air-free conditions required to access V^{+4} species in aqueous chemistry can be overcome in hydrothermal reactions by use of a N-donor ligand as structure directing agent as evidenced by the synthesis of the heterometallic compounds $[VO(tren)(MoO_4)]$ (tren = tris-2-aminoethylamine; M = Mo or W), $[VO(bpy)(MoO_4)]$ (bpy = 2,2'-bipyridine) etc. [30-32]. During the course of our investigations aimed at the synthesis of mixed metal hybrid organic compounds, we obtained a new heterometallic coordination polymer $[(VO(terpy))_4(MoO_4)_2(Mo_8O_{26})] \cdot 2H_2O$ **1**, (terpy = 2,2';6',2''-terpyridine) containing bridging γ -octamolybdate $(Mo_8O_{26})^{4-}$ and tetraoxido molybdate $(MoO_4)^{2-}$ ligands.

5.8 Results and Discussion

5.8.1 Synthetic aspects, powder diffraction analysis, and ESR measurements.

The oxido vanadium(IV) containing compound **16** was prepared by a hydrothermal reaction of molybdic acid, sodium metavanadate, and 2,2':6',2''-terpyridine as dark green crystalline blocks. A comparison of the experimental powder pattern of a bulk sample of **16** with that of the theoretical pattern obtained using the crystal data (**Figure 1**) reveals the formation of a phase-pure product. In this reaction, the N-donor serves as both a structure-directing ligand and a reducing agent. The formation of $\{VO\}^{2+}$ containing compounds, starting from V^{+5} reactants, in the presence of N-donor ligands under hydrothermal conditions is a well-established synthetic methodology in the literature [30-32]. The presence of V^{+4} is confirmed by the characteristic ESR signal centred at $g = 1.987$ of a polycrystalline sample of **16** (**Figure 2**).

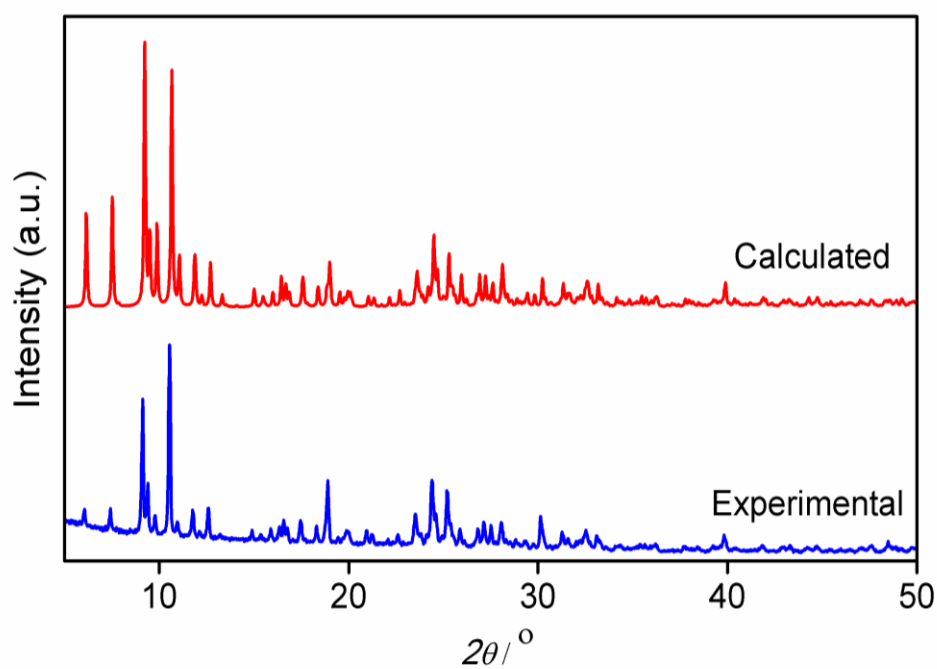


Figure 1. Experimental (Blue) and calculated (red) powder patterns of **16**.

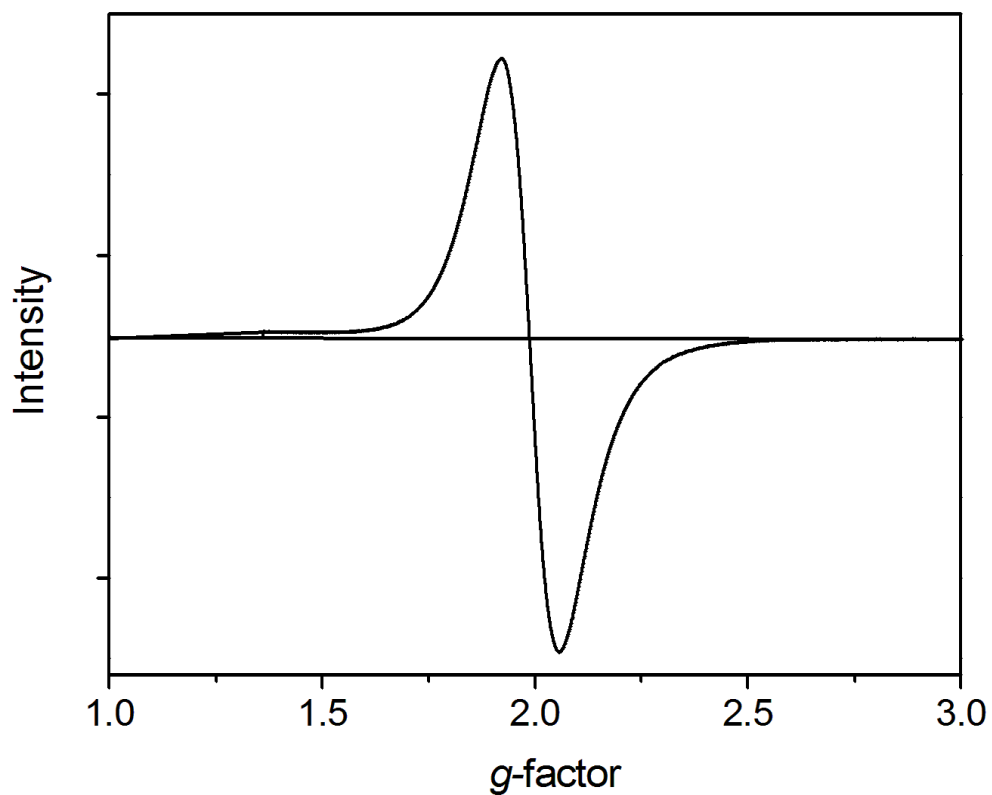


Figure 2. X-band ESR spectrum of a polycrystalline sample of **16**

5.8.2 Infrared, Raman spectroscopic analysis and thermal analysis of compound 16

The infrared (IR) and Raman spectra (Figure 3, 4) of **16** exhibit several characteristic bands. The broad IR band centred at around 3410 cm^{-1} can be attributed to the O-H stretching vibration of the lattice water. The IR spectrum also consists of peaks arising due to V-O (terminal) and various Mo-O stretching vibrations at 946, 893, 796, 725, 672, 543, 452 cm^{-1} . The intense Raman signal at 968 cm^{-1} can be assigned for a vibration of the $\gamma\text{-[Mo}_8\text{O}_{26}]^{4-}$ unit [33]. The TG-DTA curves of **1** exhibit an initial mass loss of 1.2 % (Calcd: 1.3 %) accompanied by a weak endothermic signal at 92°C assignable for the loss of lattice water (Figure 5). This is followed by an exothermic event at 440°C corresponding to a large mass loss of 34.5 %. This value is in close agreement with the calculated value of 34.0 % for loss of the organic ligand. The residual mass of 64.3 % (Calcd. 65.8 %) can be assigned for the formation of a phase having composition $\text{V}_2\text{Mo}_5\text{O}_{20}$.

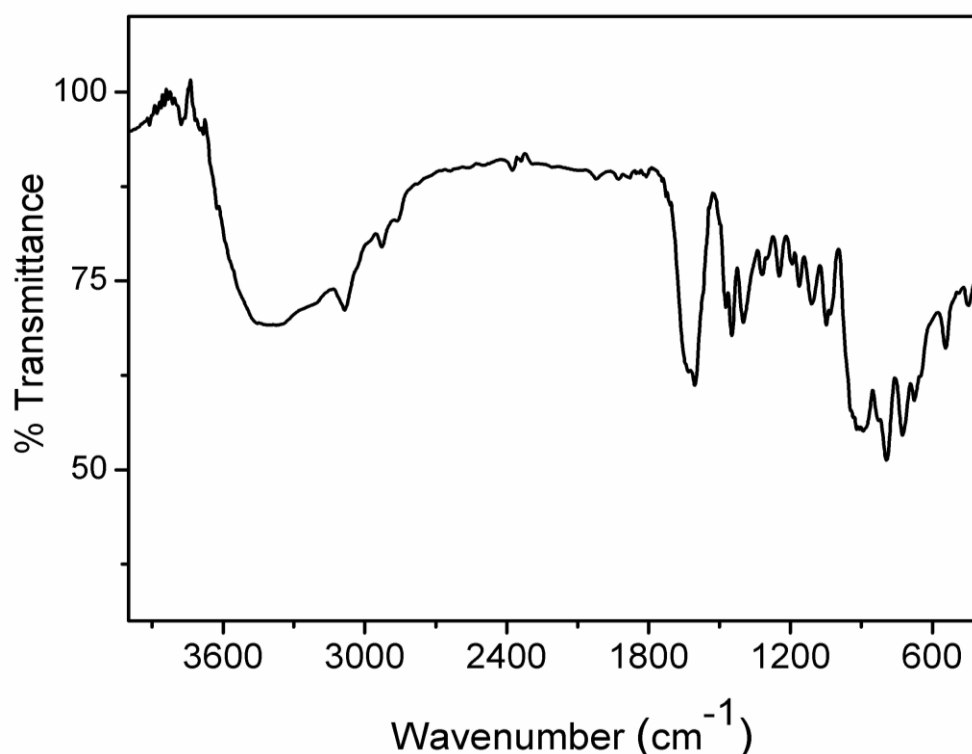


Figure 3. Infrared spectrum of $[(\text{VO}(\text{terpy})_4(\text{MoO}_4)_2(\text{Mo}_8\text{O}_{26})) \cdot 2\text{H}_2\text{O}]$

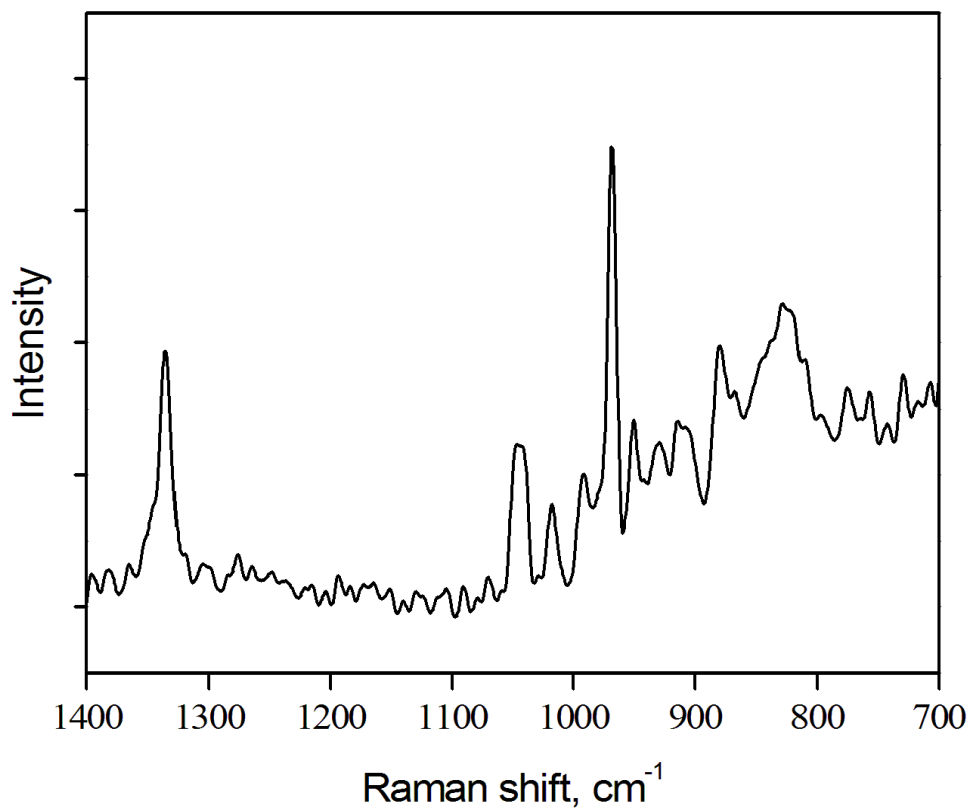


Figure 4. Raman spectrum of compound **16**

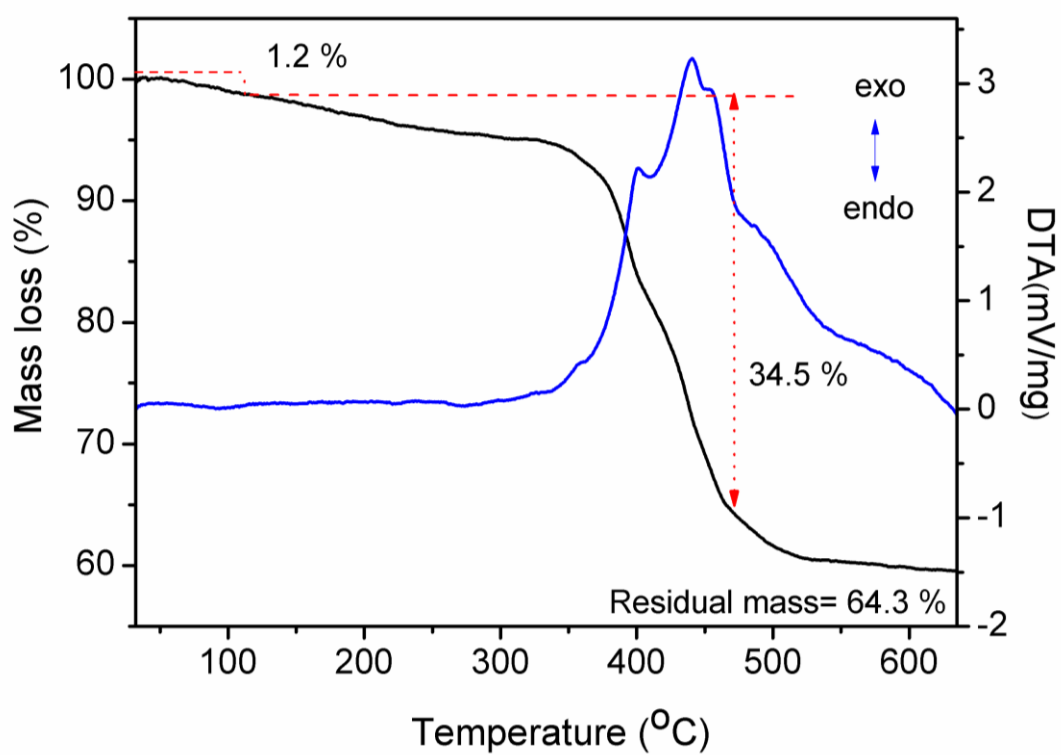


Figure 5. The TG-DTA curve of compound **16** in air. Heating rate (5°C/min)

5.8.3 description of the crystal structure of 16

The title coordination polymer **16** $[(VO(terpy))_4(MoO_4)_2(Mo_8O_{26})] \cdot 2H_2O$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$. Its structure consists of a crystallographically unique $\gamma-(Mo_8O_{26})^{4-}$ located on an inversion centre, an independent tetraoxidomolybdate $(MoO_4)^{2-}$ dianion, two crystallographically unique $(VO(terpy))^{+2}$ moieties, and a lattice water (**Figure 6**). Both the unique vanadium V1 and V2 are bonded to a terminal oxido ligand O1 and O2 respectively and are further coordinated to a terpy ligand, whose three N atoms span the meridional sites of a $\{VN_3O_3\}$ octahedron. The geometric parameters of the two crystallographically unique terpyridine ligands bonded to V1 and V2 are in the normal range. The technical data acquisition and selected refinement parameters of compound 16 are given in **Table 1**

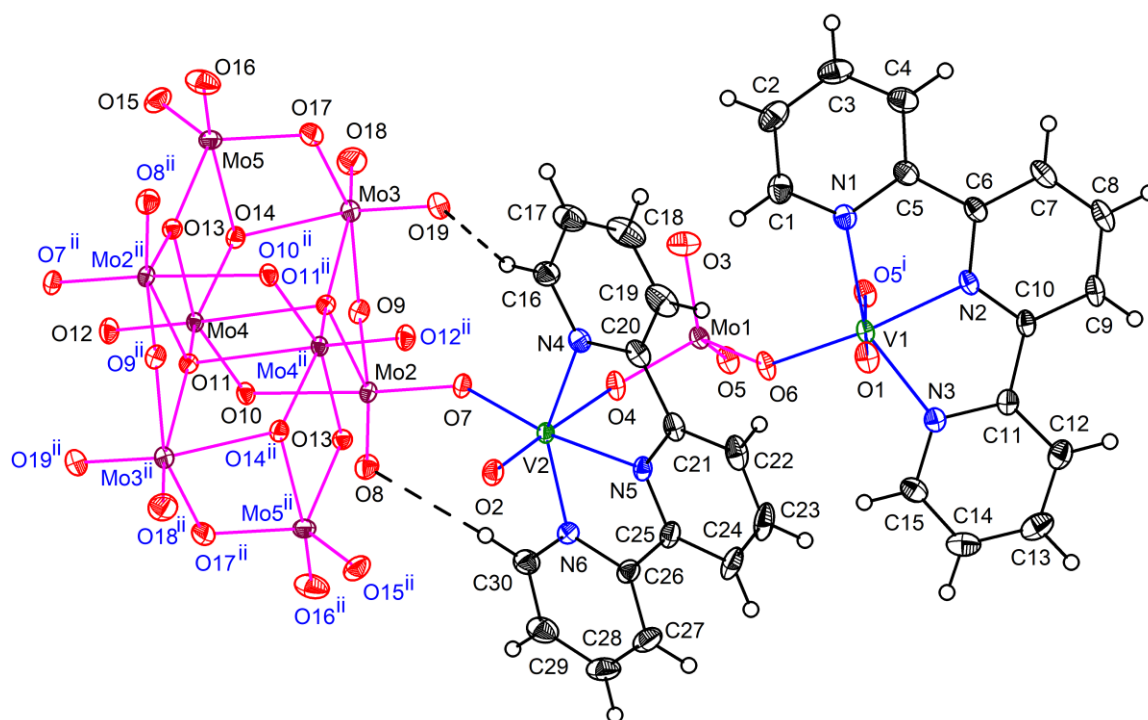


Figure 6. The asymmetric unit of **16** showing six-fold coordination around V1 and V2. Displacement ellipsoids are drawn at 30% probability level for all the non-hydrogen atoms. Intramolecular H-bonding is shown as broken lines. For clarity symmetry generated atoms are labelled in blue. Symmetry code: (i) $-x, -y+1, -z+1$ (ii) $-x+1, -y+2, -z+2$

Table 1. Selected refinement results for [(VO(terpy))₄(MoO₄)₂(Mo₈O₂₆)]·2H₂O

Refinement result	Compound 16
Empirical formula	C ₃₀ H ₂₄ Mo ₅ N ₆ O ₂₀ V ₂
Formula weight (g mol ⁻¹)	1370.14
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell dimensions	
<i>a</i> (Å)	11.4507(16)
<i>b</i> (Å)	11.8541(17)
<i>c</i> (Å)	14.675(2)
α (°)	92.023(4)
β (°)	98.321(4)
γ (°)	91.804(4)
Volume (Å ³)	1968.4(5)
<i>Z</i>	2
<i>D</i> _{calc} (g/cm ³)	2.308
Absorption coefficient (mm ⁻¹)	2.086
<i>F</i> (000)	1320
Crystal size (mm ³)	0.24 x 0.16 x 0.14
θ range for data collection (°)	2.53 to 28.31
Limiting indices	$-15 \leq h \leq 15$ $-15 \leq k \leq 15$ $-19 \leq l \leq 19$
Reflections collected / unique	66874 / 9787 [<i>R</i> (int) = 0.0290]
Completeness $\theta = 25.242^\circ$	99.9
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	9787 / 0 / 568
Goodness of fit on <i>F</i> ²	1.104
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0198 w <i>R</i> 2 = 0.0480
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0238 w <i>R</i> 2 = 0.0507
Largest diff. peak and hole (e Å ⁻³)	0.673 and -0.725
Bond valence sum	V1 = 3.77; V2 = 3.81
CCDC Deposition No	2131584

The first unique V^{+4} (V1) is further bonded to two oxygen atoms (O5 and O6) of $(MoO_4)^{2-}$ while the second independent V namely V2 is bonded to O4 of $(MoO_4)^{2-}$ and O7 of $(Mo_8O_{26})^{4-}$ completing the $\{VN_3O_3\}$ octahedron. The terminal oxido ligands O1 and O2 make the shortest V-O bonds (**Table 2**). Unlike the V-O distances which range from 1.5940(17) to 2.1833(16) Å for V1 (1.5998(16) to 2.1198(16) for V2), the V-N bond distances scatter in a narrow range between 2.0643(18) and 2.149(2) Å for V1 (2.0452(18) and 2.131(2) for V2). Bond valence sum of the V-N and V-O bonds for V1 and V2 were determined using the VaList program [34]. The values of 3.77 and 3.81 for V1 and V2 reveal that the unique vanadiums can be formulated as V(IV). The *cis*- as well as the *trans*- O-V-N or N-V-N angles deviate from ideal values and cover a wide range (76.36(8) to 101.97(7) and 152.35(8) to 178.54(8)° for V1; 76.83(8) to 104.11(7)° and 151.79(8) to 177.15(9)° for V2) indicating a distortion of the $\{VN_3O_3\}$ octahedron. The Mo-O bond lengths of the tetrahedral $(MoO_4)^{2-}$ range from the shortest Mo-O3 bond of 1.7159(19) to 1.8042(16) Å for Mo-O6. The binding of O6 with V1 can explain the elongation of the Mo-O6 bond. The O-Mo-O bond angles range from 107.79(7) to 112.53(8)° indicating a slight distortion of the $\{MoO_4\}$ tetrahedron.

Table 2. Selected geometric parameters for **16**

Bond lengths and angles (Å, °) of $\{VN_3O_3\}$, $(MoO_4)^{2-}$ and $(Mo_8O_{26})^{4-}$ moieties in 16					
V1-O1	1.5940(17)	Mo1-O4	1.7637(16)	Mo3-O18	1.6892(19)
V1-O5 ⁱ	2.1833(16)	Mo1-O5	1.7750(16)	Mo3-O19	1.7029(18)
V1-O6	1.9674(15)	Mo1-O6	1.8042(16)	Mo4-O10	1.7648(15)
V1-N1	2.142(2)	Mo2-O7	1.7605(15)	Mo4-O11	1.8973(14)
V1-N2	2.0643(18)	Mo2-O8	1.6884(16)	Mo4-O11 ⁱⁱ	2.5049(14)
V1-N3	2.1490(2)	Mo2-O9	1.8539(15)	Mo4-O12	1.6886(15)
V2-O2	1.5998(16)	Mo2-O10	2.2146(15)	Mo4-O14	1.8995(15)
V2-O4	2.1198(16)	Mo2-O11 ⁱⁱ	2.2450(14)	Mo4-O13	2.2101(15)
V2-O7	2.0096(15)	Mo2-O13 ⁱⁱⁱ	2.0192(14)	Mo5-O13	1.9076(15)
V2-N4	2.1231(19)	Mo3-O9	1.9724(16)	Mo5-O14	2.3318(15)
V2-N5	2.0452(18)	Mo3-O11 ⁱⁱ	2.4960(15)	Mo5-O15	1.7032(18)
V2-N6	2.131(2)	Mo3-O14	2.1297(15)	Mo5-O16	1.6949(19)
Mo1-O3	1.7159(19)	Mo3-O17	1.9819(18)	Mo5-O17	1.8579(18)

O1-V1-O6	100.44(8)	O8-Mo2-O9	104.32(8)	O11-Mo4-O13	73.39(6)
O1-V1-N2	100.17(8)	O7-Mo2-O9	101.46(7)	O14-Mo4-O13	75.28(6)
O6-V1-N2	159.39(7)	O8-Mo2-O13 ⁱⁱ	101.14(7)	O12-Mo4-O11 ⁱⁱ	175.01(7)
O1-V1-N1	94.12(9)	O7-Mo2-O13 ⁱⁱ	90.94(6)	O10-Mo4-O11 ⁱⁱ	75.15(6)
O6-V1-N1	101.90(8)	O9-Mo2-O13 ⁱⁱ	148.10(6)	O11-Mo4-O11 ⁱⁱ	79.50(6)
N2-V1-N1	76.37(8)	O8-Mo2-O10	85.89(7)	O14-Mo4-O11 ⁱⁱ	71.37(5)
O1-V1-N3	95.08(9)	O7-Mo2-O10	168.50(6)	O13-Mo4-O11 ⁱⁱ	83.38(5)
O6-V1-N3	101.97(7)	O9-Mo2-O10	82.54(6)	O16-Mo5-O15	105.15(10)
N2-V1-N3	76.36(8)	O13 ⁱⁱ -Mo2-O10	80.42(6)	O16-Mo5-O17	101.46(9)
N1-V1-N3	152.35(8)	O8-Mo2-O11 ⁱⁱ	158.66(7)	O15-Mo5-O17	112.62(9)
O1-V1-O5 ⁱ	178.54(8)	O7-Mo2-O11 ⁱⁱ	96.52(6)	O16-Mo5-O13	99.59(8)
O6-V1-O5 ⁱ	80.88(6)	O9-Mo2-O11 ⁱⁱ	78.91(6)	O15-Mo5-O13	116.32(8)
N2-V1-O5 ⁱ	78.51(7)	O13 ⁱⁱ -Mo2-O11 ⁱⁱ	70.48(6)	O17-Mo5-O13	118.38(7)
N1-V1-O5 ⁱ	84.99(7)	O10-Mo2-O11 ⁱⁱ	73.51(5)	O16-Mo5-O14	166.35(9)
N3-V1-O5 ⁱ	85.21(7)	O18-Mo3-O19	105.13(10)	O15-Mo5-O14	88.39(8)
O2-V2-O7	95.20(7)	O18-Mo3-O9	98.92(9)	O17-Mo5-O14	74.17(6)
O2-V2-N5	95.15(8)	O19-Mo3-O9	96.60(8)	O13-Mo5-O14	72.22(6)
O7-V2-N5	169.48(7)	O18-Mo3-O17	99.81(9)	Mo1-O4-V2	146.34(9)
O2-V2-O4	177.15(9)	O19-Mo3-O17	93.97(9)	Mo1-O5-V1 ⁱ	144.17(10)
O7-V2-O4	85.34(6)	O9-Mo3-O17	155.26(7)	Mo1-O6-V1	134.78(9)
N5-V2-O4	84.42(7)	O18-Mo3-O14	100.75(8)	Mo2-O7-V2	145.82(9)
O2-V2-N4	98.67(9)	O19-Mo3-O14	153.66(8)	Mo2-O9-Mo3	119.09(8)
O7-V2-N4	99.70(7)	O9-Mo3-O14	84.02(6)	Mo4-O10-Mo2	118.35(7)
N5-V2-N4	76.83(8)	O17-Mo3-O14	76.72(6)	Mo4-O11-Mo2 ⁱⁱ	108.74(6)
O4-V2-N4	83.98(7)	O18-Mo3-O11 ⁱⁱ	165.24(8)	Mo4-O11-Mo3 ⁱⁱ	158.74(7)
O2-V2-N6	94.07(9)	O19-Mo3-O11 ⁱⁱ	86.91(8)	Mo2 ⁱⁱ -O11-Mo3 ⁱⁱ	88.02(5)
O7-V2-N6	104.11(7)	O9-Mo3-O11 ⁱⁱ	70.76(5)	Mo4-O11-Mo4 ⁱⁱ	100.50(6)
N5-V2-N6	77.03(8)	O17-Mo3-O11 ⁱⁱ	87.60(6)	Mo2 ⁱⁱ -O11-Mo4 ⁱⁱ	92.12(5)
O4-V2-N6	83.09(7)	O14-Mo3-O11 ⁱⁱ	68.34(5)	Mo3 ⁱⁱ -O11-Mo4 ⁱⁱ	91.60(5)
N4-V2-N6	151.79(8)	O12-Mo4-O10	103.48(7)	Mo5-O13-Mo2 ⁱⁱ	142.53(8)
O3-Mo1-O4	109.17(10)	O12-Mo4-O11	105.48(7)	Mo5-O13-Mo4	108.46(6)
O3-Mo1-O5	109.80(9)	O10-Mo4-O11	99.25(7)	Mo2 ⁱⁱ -O13-Mo4	105.69(6)

O4-Mo1-O5	107.93(8)	O12-Mo4-O14	104.37(7)	Mo4-O14-Mo3	125.60(7)
O3-Mo1-O6	109.54(9)	O10-Mo4-O14	100.23(7)	Mo4-O14-Mo5	104.03(6)
O4-Mo1-O6	107.79(7)	O11-Mo4-O14	139.13(6)	Mo3-O14-Mo5	93.44(6)
O5-Mo1-O6	112.53(8)	O12-Mo4-O13	98.19(7)	Mo5-O17-Mo3	115.67(8)
O8-Mo2-O7	103.33(8)	O10-Mo4-O13	158.30(6)		

Symmetry transformations used to generate equivalent atoms: *Symmetry code*: i) $-x, -y+1, -z+1$; ii) $-x+1, -y+2, -z+2$

The tetraanionic octamolybdate ($\text{Mo}_8\text{O}_{26}^{4-}$) is well-known to exhibit polymorphism, and several polymorphic modifications of ($\text{Mo}_8\text{O}_{26}^{4-}$) are well-documented in the literature [35-44]. Although the α - and β -modifications are more often encountered, other polymorphic forms like γ , δ , ϵ etc are also known [Table 3]. The centrosymmetric ($\text{Mo}_8\text{O}_{26}^{4-}$) unit in **16** which consists of three unique octahedral Mo atoms (Mo2, Mo3 and Mo4) and a penta-coordinated Mo5 (Figure 7) is a γ -modification of ($\text{Mo}_8\text{O}_{26}^{4-}$) and the thirteen unique O atoms can be classified under four types viz i) the terminal oxido (O_t) ligands O7, O8, O12, O15, O16, O18 and O19, ii) μ_2 -bridging oxido ligands O9, O10, O17 iii) μ_3 -bridging O13 and O14 iv) μ_4 -bridging O11. The terminal Mo- O_t bond distances range from 1.6884(16) to 1.7605(15) Å. O7 which makes the longest Mo2-O7 distance of 1.7605(15) Å is also coordinated to V2, which can explain its elongation.

Unlike the terminal oxygens, the bridging oxido ligands exhibit longer Mo-O distances which scatter in a wider range viz. 1.7648(15) to 2.2146(15) for μ_2 -bridging ligands, and 1.8995(15)-2.3318(15) Å and 1.8973(14)-2.5049(14) for μ_3 - and μ_4 -bridging ligands respectively. Oxidovanadium(IV) compounds containing a coordinated (MoO_4) $^{2-}$ unit are well-documented in the literature [30-32]. However, compound **16** is as it contains two bridging ligands viz. (MoO_4) $^{2-}$ and ($\text{Mo}_8\text{O}_{26}^{4-}$). To the best of our knowledge, no V^{+4} compound other than **16** is known containing coordinated (MoO_4) $^{2-}$ and ($\text{Mo}_8\text{O}_{26}^{4-}$) ligands. However, one example of a three-dimensional Cu(II) compound [$\{\text{Cu}_2(\text{L}_4)\}_2\{\gamma\text{-Mo}_8\text{O}_{26}\}\{\text{MoO}_4\}_2\} \cdot 2\text{H}_2\text{O}$ containing both ligands was reported by the Zubieta group [37].

Table 3. Polyhedral components of octamolybdate isomers.

Compound formula		Polyhedra	Types of oxo ligands					Ref.
form			O _t	μ ₂	μ ₃	μ ₄	μ ₅	
α	[{Cu(py) ₃ } ₂ {Cu(py) ₂ } ₂ (α-Mo ₈ O ₂₆)]	6(MoO ₆), 2(MoO ₄)	14	6	6	-	-	35
β	{Cu ₂ (OH)(Ptep) ₂ [H(β-Mo ₈ O ₂₆)]} · 2H ₂ O	8(MoO ₆)	14	6	4	-	2	36
γ	[(VO(terpy)) ₄ (MoO ₄) ₂ (γ-Mo ₈ O ₂₆)] · 2H ₂ O	6(MoO ₆), 2(MoO ₅)	14	6	4	2	-	This work
γ	[{Cu ₂ (L ₄)} ₂ {γ-Mo ₈ O ₂₆ } {MoO ₄ } ₂] · 2H ₂ O	6(MoO ₆), 2(MoO ₅)	14	6	4	2	-	37
δ	[Cu ^I (bix)][Cu ^I (bix)(δ-Mo ₈ O ₂₆) _{0.5}]	4(MoO ₆), 4(MoO ₄)	14	10	2	-	-	38
ε	[{Ni(H ₂ O) ₂ (4,4'-bpy) ₂ } ₂ Mo ₈ O ₂₆]	2(MoO ₆), 6(MoO ₅)	16	4	6	-	-	39
ζ	[{Cu ₂ (tpyrpyz)} ₂ {ζ-Mo ₈ O ₂₆ }] · 7H ₂ O	4(MoO ₆), 4(MoO ₅)	14	6	6	-	-	40
η	[Cu(<i>t</i> -Bu ₂ bpy) Mo ₄ O ₁₃]	6(MoO ₆), 2(MoO ₅)	14	4	8	-	-	41
θ	[Cu(bbi)][Cu(bbi)(θ-Mo ₈ O ₂₆) _{0.5}]	4(MoO ₆), 2(MoO ₅), 2(MoO ₄)	14	8	4	-	-	42
ι	[TbI ₁] ₂ (β-Mo ₈ O ₂₆) _{0.5} (ι-Mo ₈ O ₂₆)]	5(MoO ₆), 3(MoO ₄)	14	8	4	-	-	43

Abbreviations: Terminal oxygen atoms (O_t); μ₂-bridged (μ₂); μ₃-bridged (μ₃); μ₄-bridged (μ₄); μ₅-bridged (μ₅) oxygen atoms; Py = pyridine; Ptep = 1-[2-(3-pyridin-4-yl-[1,2,4]triazol-4-yl)-ethyl]-piperazine; terpy = 2,2':6',2''-terpyridine; L₄ = N¹, N¹, N⁴, N⁴-tetrakis(pyridin-2-ylmethyl)butane-1,4-diamine; bix = 1,4-bis(imidazole-1-ylmethyl)benzene; 4, 4'-bpy = 4, 4'-bipyridyl; tpyrpyz = tetra-2-pyridylpyrazine; *t*-Bu₂bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine; bbi = 1,1'-(1,4-butanediyl)bis(imidazole) TbI₁ = 1,3,5-tris[(3-methylimidazol-3-iumyl)methyl]benzene tribromide.

The μ_3 -bridging $(\text{MoO}_4)^{2-}$ dianion binds to two symmetry-related V1 atoms via O5 and O6 and a V2 through O4, while the centrosymmetric $(\text{Mo}_8\text{O}_{26})^{4-}$ binds to V2 via O7 (**Figure 8**). The μ_3 -bridging tridentate binding of $(\text{MoO}_4)^{2-}$ results in the formation of a $\{\text{V}_4\text{Mo}_2\text{O}_{12}\}^{4+}$ cationic unit which is composed of an eight-membered heterometallic $\{\text{Mo}_2\text{V}_2\text{O}_4\}$ ring containing one of the unique V (V1 in the ring) with the other unique V (V2) protruding as handles (**Figure 9**).

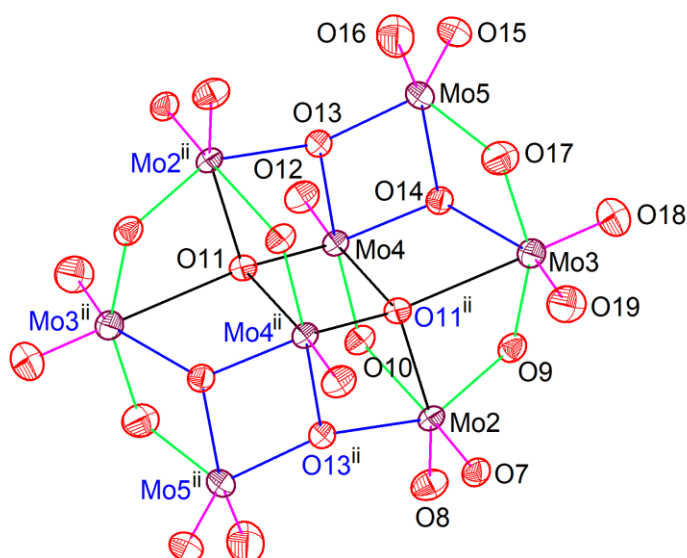


Figure 7. The Mo-O(terminal) and Mo-O(bridging) ligands in the centrosymmetric γ - $(\text{Mo}_8\text{O}_{26})^{4-}$ unit in **16**. Mo-O_t bonds in pink are for terminal O atoms; Mo-O bonds in green are μ_2 -bridging O atoms viz. O9, O10 and O17; Mo-O bonds in blue are μ_3 -bridging O atoms namely O13 and O14; Mo-O bonds of μ_4 -bridging O11 are in black

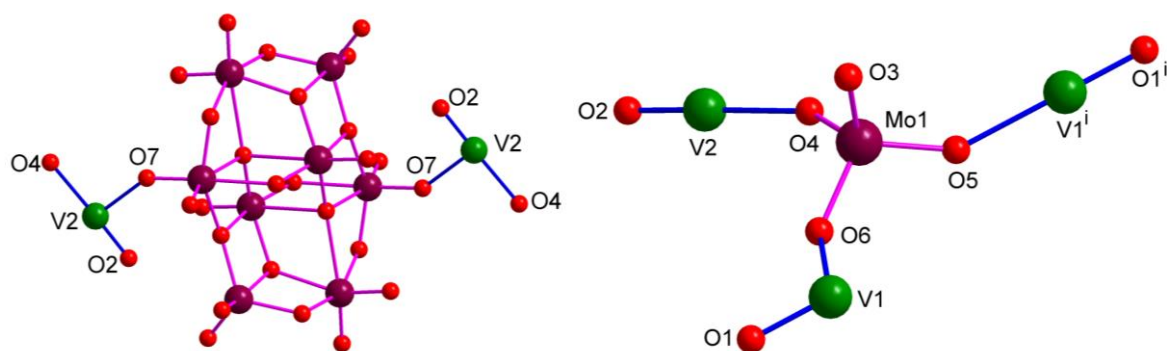


Figure 8. The μ_2 -bridging bidentate binding mode of the centrosymmetric $(\text{Mo}_8\text{O}_{26})^{4-}$ (**Left**) and the μ_3 -bridging tridentate binding mode of $(\text{MoO}_4)^{2-}$ (**Right**) in **16**. Symmetry code *i*) $-x, -y+1, -z+1$

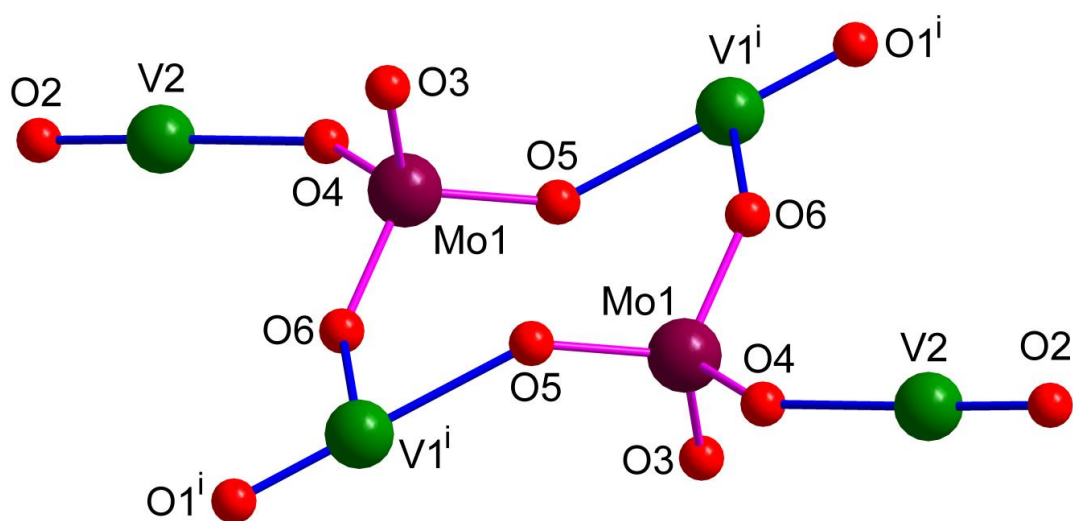


Figure 9. The $\{V_4Mo_2O_{12}\}^{4+}$ cationic unit is made up of an eight-membered heterometallic $\{Mo_2V_2O_4\}$ ring with protruding oxidovanadium handles. The terpy ligands around V1 and V2 are not shown. *Symmetry code i) $-x, -y+1, -z+1$.*

A pair of $\{V_4Mo_2O_{12}\}^{4+}$ units is bridged by a $(Mo_8O_{26})^{4-}$ ligand, resulting in the formation of a polymeric chain consisting of alternating $\{V_4Mo_2O_{12}\}^{4+}$ cations and $(Mo_8O_{26})^{4-}$ anions (**Figure 10** and **11**). The H atoms attached to the carbon atoms C4, C7, C9, C14, C16, C19, C24, C27, C29, and C30 of the unique terpy ligands function as hydrogen donors while the O atoms O1 and O2 attached to V1 and V2, and the O atoms of the γ - $(Mo_8O_{26})^{4-}$ viz. O8, O9, O10, O14, O15, O17, and O19 function as hydrogen acceptors, resulting in a total of eleven C-H $\cdots$ O bonds (**Table 3**) of which two are intramolecular. The intermolecular C-H $\cdots$ O bonds serve to link parallel polymeric chains. The difficulty in locating the H atoms attached to the lattice water precludes a description of the O-H $\cdots$ O interactions.

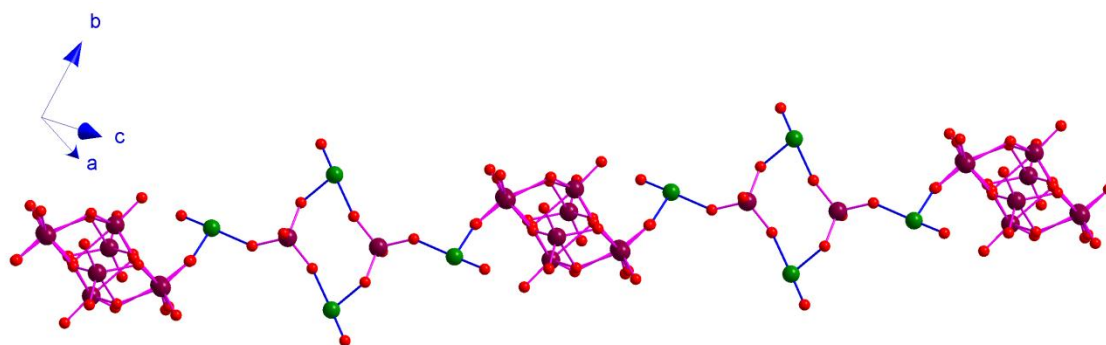


Figure 10 A portion of an infinite chain showing alternating $(\text{Mo}_8\text{O}_{26})^{4-}$ anions and $\{\text{V}_4\text{Mo}_2\text{O}_{12}\}^{4+}$ cations. The tridentate terpy ligands on the unique V atoms are not shown.

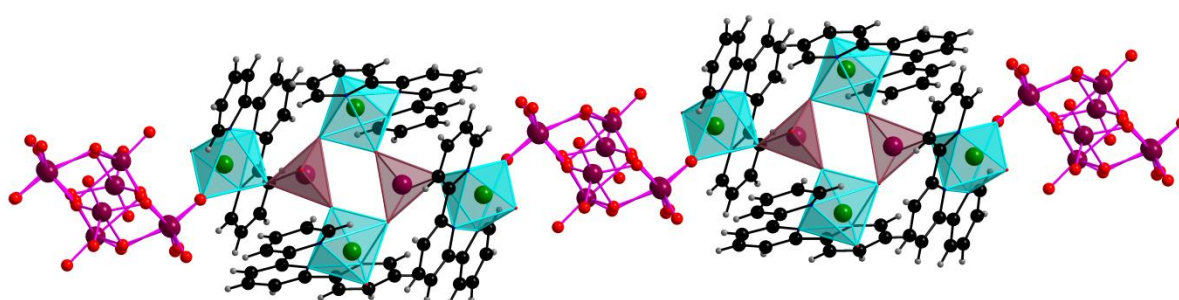


Figure 11 The same arrangement is observed after the inclusion of the terpy ligands. The $\{\text{VO}_3\text{N}_3\}$ octahedra and $(\text{MoO}_4)^{2-}$ tetrahedra are shown in polyhedral format.

Table 4. C-H $\cdots$ O hydrogen bonding parameters ($\text{\AA}$, $^\circ$) for **16**.

D-H	d(D-H)	d(H $\cdots$ A)	$\angle$ D-H $\cdots$ A	d(D $\cdots$ A)	Symmetry code
C4-H4 $\cdots$ O19	0.930	2.469	130.22	3.151	1-x, 1-y, 1-z
C7-H7 $\cdots$ O17	0.930	2.420	153.48	3.279	1-x, 1-y, 1-z
C9-H9 $\cdots$ O1	0.930	2.510	120.27	3.085	-x, -y, 1-z
C9-H9 $\cdots$ O9	0.930	2.524	150.18	3.363	-x, 1-y, 1-z
C14-H14 $\cdots$ O15	0.930	2.553	128.22	3.213	1-x, 1-y, z
C16-H16 $\cdots$ O19	0.930	2.491	157.62	3.370	x, y, z
C19-H19 $\cdots$ O14	0.930	2.365	144.53	3.169	x, 1-y, z
C24-H24 $\cdots$ O15	0.930	2.406	143.22	3.200	1-x, 1-y, z
C27-H27 $\cdots$ O2	0.930	2.590	136.66	3.328	-x, 1-y, 2-z
C29-H29 $\cdots$ O10	0.930	2.539	133.53	3.250	-x, 2-y, 2-z
C30-H30 $\cdots$ O8	0.930	2.476	165.28	3.384	x, y, z

5.9 Conclusions

A new heterometallic CP $[(VO(terpy))_4(MoO_4)_2(Mo_8O_{26})] \cdot 2H_2O$, **16** has been synthesized under hydrothermal condition. The compound features alternating $\{V_4Mo_2O_{12}\}^{4+}$ cations and $(Mo_8O_{26})^{4-}$ anions giving rise to one dimensional chain structure. Structural analysis reveal that the compound contains two crystallographically unique Vanadium (IV) atoms, each bonded to a terminal oxido ligand and coordinated to a terpyridine ligand. The presence of V^{+4} was confirmed by the ESR. The three nitrogen atoms of terpyridine ligand occupy the meridional sites of a distorted VN_3O_3 octahedron. μ_3 -bridging tridentate binding of $(MoO_4)^{2-}$ leads to the forming of a $(V_4Mo_2O_{12})^{4+}$ cationic unit consisting of an eight-membered heterometallic ring with protruding oxovanadium handles. A pair of $(V_4Mo_2O_{12})^{4+}$ cationic units are bridged by the centrosymmetric $(Mo_8O_{26})^{4-}$ ligand, resulting in an infinite chain structure. The formation of this unique structure demonstrates the ability of Vanadium (IV) and molybdate ligands to form complex heterometallic CP with diverse structural features.

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APPENDIX I

LIST OF PUBLICATIONS APPENDED TO THE THESIS

- [1] **Harmalkar, N. N.**; Srinivasan, B. R.; Dhuri, S. N. Synthesis, Structure Characterization and Properties of a New Oxidovanadium(IV) Coordination Polymer Incorporating Bridging $(\text{MoO}_4)^{2-}$ and $(\text{Mo}_8\text{O}_{26})^{4-}$ Ligands. *Z. Naturforsch. B* **2022**, 77, 245–252. <https://doi.org/10.1515/znbn-2022-0005>
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- [5] **Harmalkar, N. N.**; Gaonkar, S.; Barretto, D. A.; Dhuri, S. N. Structural Characterization of Benzoate Anion-Supported Supramolecular Assemblages of Co(III) and Ni(II) Cyclam Compounds with Catecholase-like and Antibacterial Activities. *Inorg. Chim. Acta* **2024**, 569, 122139-122150. <https://doi.org/10.1016/j.ica.2024.122139>
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- [7] **Harmalkar, N.**; Dhuri, S. N. Variation in Structural Features Induced by *Ortho*-Substituted Benzoate Ligands in Zinc Cyclam-Based Compounds: Synthesis, Characterization, and Hirshfeld Studies. *ChemistrySelect* **2025**, 10, e202404167. <https://doi.org/10.1002/slct.202404167>
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Manuscripts under preparation

- 1) Structural variation induced by aliphatic carboxylate molecules in nickel pyrazine frameworks; synthesis, characterization and applications

APPENDIX II

PAPERS PRESENTED AT THE CONFERENCES

- 1) Presented poster at the **international conference on Advanced Materials: Properties and Applications** organized by Goa University from 20th to 24th February **2023**.
- 2) Presented poster at the **international conference on Advanced Materials: Properties and Applications** organized by Goa University from 20th to 24th February **2023**.
- 3) Presented poster at the **international conference on “Modern trends in Inorganic Chemistry”** organized by Division of Chemical Sciences, Indian Institute of Science, Bangalore, India from 14th to 17th December **2023**.
- 4) Presented poster at the **national conference on “Advances in Material Science”** organized by the Department of Chemistry -& cluster Research Centre of Government College of Arts, Science, and Commerce, Khandola in collaboration with the Directorate of Higher Education and Under the aegis of DBT Star College Scheme & Vedanta Sesa Goa Ltd. On February 9th and 10th, **2024. (Awarded 1st place in poster category)**

CONFERENCES, SEMINARS AND WORKSHOP ATTENDED

- 1) Participated in a Two-days **workshop on Material Science between the University of Porto, University of Coimbra, and Goa University**, organized by the Directorate of International Cooperation and Exchange (DICE) and Directorate of Research, Development and Resource Mobilization (DRDRM) on 18th and 19th November **2019** at Goa University.
- 2) Participated in the **virtual conference on Metal-Organic Frameworks and Open Frameworks compounds (MOF2020web)** organized by DECHEMA e. V. from 21st to 24th September **2020**.
- 3) Attended a virtual **international conference on Porous Materials for Energy and Environment** organized by the Government College of Arts, Science and Commerce, Khandola – Goa held on 12th and 13th March **2021**.
- 4) Two-day Industry-Academia International Symposium (Virtual) on **“Fuels for Environmental Sustainability”** organized by the Cluster Research Centre, PG and UG Department of Chemistry in association with IQAD, Government College of Arts, Science and Commerce, Khandola, Marcela-Goa and Vedanta Sesa Goa Ltd. on 8th and 9th October **2021**.
- 5) Volunteered in "7 Days training workshop under **Synergistic Training Program Utilizing**

the Scientific and Technological Infrastructure (STUTI) on Operation of (NMR), (SCXRD), (AES), (HPLC) & (PL)“organized by the School of Chemical Sciences (SCS) in association with Sophisticated Analytical Instrumentation Facility (SAIF), Panjab University, Chandigarh funded by Department of Science & Technology (DST) held from 2nd to 9th January **2022**

6) Participated in the three-day workshop “**X-ray Crystallography**” organized by the School of Chemical Sciences and the School of Physical & Applied Sciences, Goa University, Goa held on 21st to 23rd July **2022**.

7) Participated in a **Synergistic Training Program utilizing the Scientific and Technological Infrastructure (STUTI)** at BITS Pilani Goa campus in association with the Department of Science & Technology, Government of India (DST) from 26th September to 2nd October **2022**.

8) Participated in a one-day **national seminar** on “**Recent Trends In Applied Organic Synthesis**” organized by Goa University, School of Chemical Sciences (SCS), in association with Chemistry Department Faculty & Alumni Association (CDFAA) & Syngenta Biosciences Pvt. Ltd., Goa on 26th November **2022**.

9) Participated in the **international webinar** on “**Innovations and Applications in Material Chemistry**” organized by the Department of Chemistry -DCT’s Dhempe College of Arts & Science, Miramar-Goa. In association with Meijo University Japan & BITS, Piani, K. K. Birla Goa campus, India on 21st March **2023**.

10) Participated in the **CCDC Virtual Workshop: Exploring and Leveraging Metal-Organic Structures for Multiple Applications** held on 27th April **2023**.

11) Participated in a five-day online **interactive workshop** on “**Introduction to ChemDraw**” organized by Goa University from the 10th to 14th of September **2023**.

12) Participated in **ICDD workshop** on “**Materials Characterization using powder X-ray Diffraction (GUCW-I)**” organized by Goa University held on 07th and 8th December **2023**.

Nikita N. Harmalkar, Bikshandarkoil R. Srinivasan and Sunder N. Dhuri*

Synthesis, structure characterization and properties of a new oxidovanadium(IV) coordination polymer incorporating bridging $(\text{MoO}_4)^{2-}$ and $(\text{Mo}_8\text{O}_{26})^{4-}$ ligands

<https://doi.org/10.1515/znb-2022-0005>

Received January 13, 2022; accepted January 20, 2022;

published online February 4, 2022

Abstract: Hydrothermal synthesis, crystal structure and properties of a new heterometallic coordination polymer $[(\text{VO}(\text{terpy}))_4(\text{MoO}_4)_2(\text{Mo}_8\text{O}_{26})] \cdot 2\text{H}_2\text{O}$ (**1**) (terpy = 2,2',6',2''-terpyridine) are reported. Compound **1** contains two crystallographically unique vanadium(IV) atoms, bonded to a terminal oxido ligand and further coordinated to a terpy ligand. The three N atoms of terpy occupy the meridional sites of a distorted $\{\text{VN}_3\text{O}_3\}$ octahedron. A γ -octamolybdate $(\text{Mo}_8\text{O}_{26})^{4-}$ located on an inversion centre and a tetraoxido-molybdate $(\text{MoO}_4)^{2-}$ function as bridging ligands. The μ_3 -bridging tridentate binding of $(\text{MoO}_4)^{2-}$ leads to the formation of a $\{\text{V}_4\text{Mo}_2\text{O}_{12}\}^{4+}$ cationic unit consisting of an eight-membered heterometallic $\{\text{Mo}_2\text{V}_2\text{O}_4\}$ ring with protruding oxido-vanadium handles. A pair of $\{\text{V}_4\text{Mo}_2\text{O}_{12}\}^{4+}$ units are bridged by the centrosymmetric $(\text{Mo}_8\text{O}_{26})^{4-}$ ligand, resulting in the formation of an infinite chain of alternating $\{\text{V}_4\text{Mo}_2\text{O}_{12}\}^{4+}$ cations and $(\text{Mo}_8\text{O}_{26})^{4-}$ anions.

Keywords: γ -octamolybdate; bridging ligand; coordination polymer; tetraoxido-molybdate; vanadium.

Dedicated to Professor Christian Näther on the occasion of his 60th birthday.

1 Introduction

Polyoxometalates (POMs) are discrete anionic transition metal clusters having unique topologies, nuclearities and electronic versatilities. The isopoly- and heteropolyanion

clusters usually contain symmetrical core assemblies of metal-oxido motifs ($M = \text{V}, \text{Mo}, \text{W}$) and often adopt quasi-spherical structures of considerable topological interest [1, 2]. POMs are formed in condensation processes of simple anions in solution under different temperature and pH (mainly acidic) conditions [3, 4]. Due to their promising biological applications [5, 6] POMs are actively used as metallodrugs. In recent years, they are gaining importance for their antitumor, antiviral, antibacterial, anticancer activities [6]. In addition, these compounds exhibit remarkable redox properties and thus find potential applications in several areas viz. catalysis, medicine, electrochemistry, magnetic materials etc. [7–12]. The concept of hybrid polyoxometalates has emerged in recent years. These post-functionalizable hybrid-POMs serve as building blocks due to structural diversity in such a way that they allow coupling of properties of POMs with different organic and inorganic metal cation functionalities making them useful in (photo) catalysis, bioinorganic chemistry and material science [13, 14]. The structural, electronic and magnetic properties of well-known polyoxovanadates (POVs), such as the robust $[\text{V}^{\text{IV}}_{18}\text{O}_{42}]^{12-}$ polyoxoanion can be altered by replacement of V by elements like Si-, Ge-, As- or Sb to form decorated heteroPOVs. The four general families of POVs are: fully-oxidised (V^{V}), mixed-valent ($\text{V}^{\text{V}}/\text{V}^{\text{IV}}$ or $\text{V}^{\text{IV}}/\text{V}^{\text{III}}$), “fully-reduced” (V^{IV}) and “highly-reduced” (V^{III}) species [15–17].

The chemistry of POVs is dominated by the decavanadate anion $[\text{V}_{10}\text{O}_{28}]^{6-}$ containing the fully oxidised V^{V} ion [18–20] and several examples of structurally characterized decavanadates charge balanced by a variety of counter cations are listed in the Cambridge Structural Database [21]. As in the case of other early transition metals like Mo and W [22, 23], decavanadates can be readily obtained by treatment of V_2O_5 with a limited amount of base [24] or by acidification of tetraoxido-vanadate/meta-vanadate solution in the presence of appropriate counter cations [25–28]. Unlike decavanadates, the fully reduced POVs containing V^{IV} are air-sensitive as evidenced by the report on the Na^+ or K^+ salt of $[\text{V}^{\text{IV}}_{18}\text{O}_{42}]^{12-}$ [29]. In this spherical polyoxoanion each of the eighteen V^{4+} cations is coordinated by five oxygen atoms, one of which is unshared

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pointing outwards of the cluster shell, which is a typical structural feature in the chemistry of the vanadyl $[\text{VO}]^{2+}$ moiety. The stringent air-free conditions required to access V^{4+} species in aqueous chemistry can be overcome in hydrothermal reactions by use of a N-donor ligand as structure directing agent as evidenced by the synthesis of the heterometallic compounds $[\text{VO}(\eta^1\text{-MoO}_4)(\text{tren})]\cdot\text{H}_2\text{O}$ (tren = tris-2-aminoethylamine), $[\text{VO}(\mu_3\text{-MoO}_4)(\text{bpy})]$ (bpy = 2,2'-bipyridine) etc. [30–32]. During the course of our investigations aimed at the synthesis of mixed metal hybrid organic compounds, we obtained a new heterometallic coordination polymer $[(\text{VO}(\text{terpy}))_4(\text{MoO}_4)_2(\text{Mo}_8\text{O}_{26})]\cdot 2\text{H}_2\text{O}$ (**1**), (terpy = 2,2';6',2''-terpyridine) containing bridging γ -octamolybdate $(\text{Mo}_8\text{O}_{26})^{4-}$ and tetraoxido molybdate $(\text{MoO}_4)^{2-}$ ligands. Details of the hydrothermal synthesis, spectral characterization and structure of **1** are described in this report.

2 Results and discussion

2.1 Synthetic aspects, spectral and thermal studies

The oxido vanadium(IV) containing compound **1** was prepared by a hydrothermal reaction of molybdic acid, sodium metavanadate and 2,2':6',2''-terpyridine as dark green crystalline blocks. A comparison of the experimental powder pattern of a bulk sample of **1** with that of the calculated pattern (Figure S1) reveals the formation of a phase pure product. In this reaction the N-donor serves as a structure directing ligand as well as a reducing agent. The formation of a $[\text{VO}]^{2+}$ containing compounds starting from V^{5+} reactants in the presence of N-donor ligands under hydrothermal conditions is a well-known synthetic methodology in the literature [30, 32]. The presence of V^{4+} is confirmed by the characteristic ESR signal centred at $g = 1.987$ of a polycrystalline sample of **1** (Figure S2). The infrared (IR) and Raman spectra (Figures S3 and S4) of **1** exhibit several characteristic bands. The broad IR band centred at around 3410 cm^{-1} and the signal at 1609 cm^{-1} can be attributed to the stretching and bending vibrations respectively of the $-\text{OH}$ moiety of lattice water. The IR spectrum also consists of peaks arising due to V–O (terminal) and various Mo–O stretching vibrations at 946, 893, 796, 725, 672, 543, 452 cm^{-1} . The intense Raman signal at 968 cm^{-1} can be assigned for a vibration of the γ - $[\text{Mo}_8\text{O}_{26}]^{4-}$ unit [33]. The TG-DTA curves of **1** exhibit an initial mass loss of 1.2% (Calcd: 1.3%) accompanied by a weak endothermic signal centered at 92°C assignable for the loss of coordinated water (Figure S5). This is followed by an exothermic

peak at 440°C corresponding to a large mass loss of 34.5%. This value is in close agreement with the calculated value of 34.0% for loss of the organic ligand. The residual mass of 64.3% (Calcd. 65.8%) can be assigned for the formation of a phase of composition $\text{V}_2\text{Mo}_5\text{O}_{20}$.

2.2 Description of the crystal structure of **1**

The title coordination polymer **1** $[(\text{VO}(\text{terpy}))_4(\text{MoO}_4)_2(\text{Mo}_8\text{O}_{26})]\cdot 2\text{H}_2\text{O}$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$. Its structure consists of a crystallographically unique γ - $(\text{Mo}_8\text{O}_{26})^{4-}$ anion located on an inversion centre, an independent tetraoxido molybdate $(\text{MoO}_4)^{2-}$ dianion, two crystallographically unique $(\text{VO}(\text{terpy}))^{2+}$ moieties and a lattice water molecule (Figure 1). Both the unique vanadium V1 and V2 species are bonded to a terminal oxido ligand O1 and O2, respectively, and are further coordinated to a terpy ligand, whose three N atoms span the meridional sites of a $\{\text{VN}_3\text{O}_3\}$ octahedron. The geometric parameters of the two crystallographically unique terpyridine ligands bonded to V1 and V2 are in normal range (Table S1).

The first unique V^{4+} (V1) is further bonded to two oxygen atoms (O5 and O6) of $(\text{MoO}_4)^{2-}$ while the second independent V (V2) is bonded to O4 of $(\text{MoO}_4)^{2-}$ and O7 of $(\text{Mo}_8\text{O}_{26})^{4-}$ completing the $\{\text{VN}_3\text{O}_3\}$ octahedron. The terminal oxido ligands O1 and O2 make the shortest V–O bonds (Table 1). Unlike the V–O distances which range from $1.5940(17)$ to $2.1833(16)\text{ \AA}$ for V1 ($1.5998(16)$ to $2.1198(16)$ for V2), the V–N bond distances scatter in a narrow range between $2.0643(18)$ and $2.149(2)\text{ \AA}$ for V1 ($2.0452(18)$ and $2.131(2)$ for V2). Bond valence sum of the V–N and V–O bonds for V1 and V2 were determined using the VALIST program [34]. The values of 3.77 and 3.81 for V1 and V2 reveal that the unique vanadium atoms can be formulated as V(IV). The *cis*- as well as the *trans*- O–V–N or N–V–N angles deviate from ideal values and cover a wide range ($76.36(8)$ to $101.97(7)$ and $152.35(8)^\circ$ to $178.54(8)^\circ$ for V1; $76.83(8)^\circ$ to $104.11(7)^\circ$ and $151.79(8)^\circ$ to $177.15(9)^\circ$ for V2) indicating a distortion of the $\{\text{VN}_3\text{O}_3\}$ octahedron. The Mo–O bond lengths of the tetrahedral $(\text{MoO}_4)^{2-}$ anion range from the shortest Mo–O3 bond of $1.7159(19)$ to $1.8042(16)\text{ \AA}$ for Mo–O6. The binding of O6 with V1 can explain the elongation of the Mo–O6 bond. The O–Mo–O bond angles range from $107.79(7)^\circ$ to $112.53(8)^\circ$ indicating a slight distortion of the $\{\text{MoO}_4\}$ tetrahedron.

The tetraanionic octamolybdate $(\text{Mo}_8\text{O}_{26})^{4-}$ is well-known to exhibit polymorphism and several polymorphic modifications are well documented in the literature [35–44]. Although the α - and β -modifications are more often encountered, other polymorphic forms like γ , δ , ϵ etc.

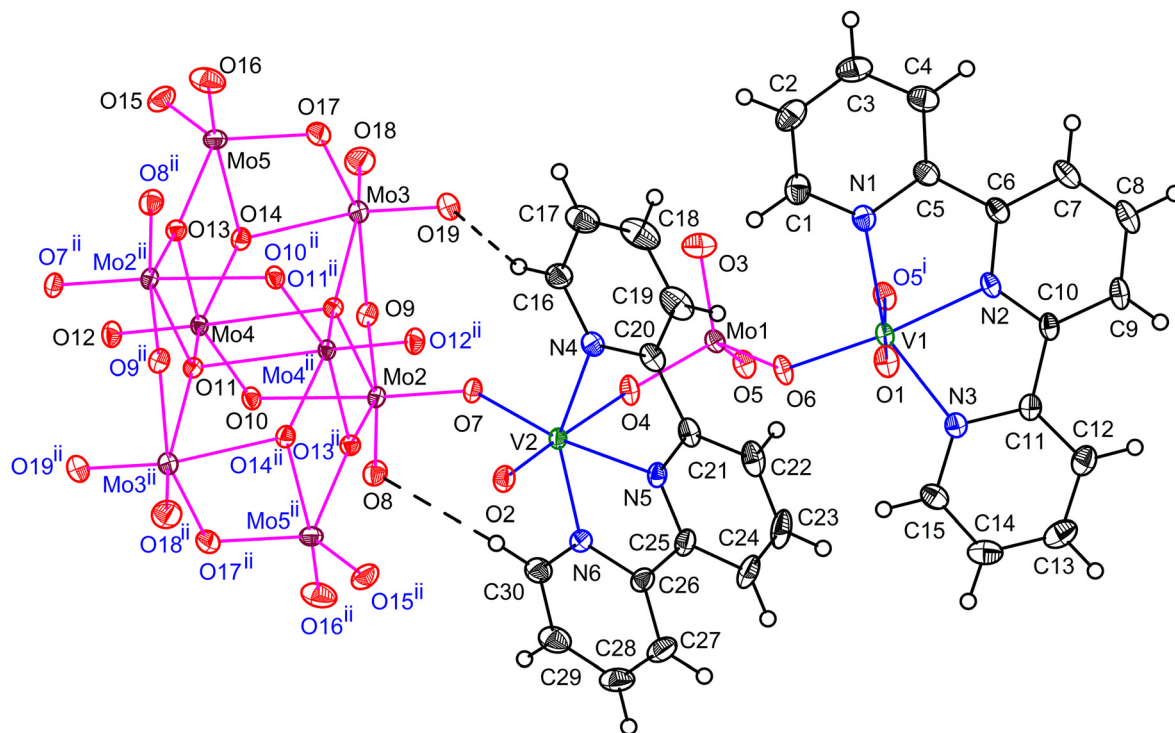


Figure 1: The asymmetric unit of **1** showing sixfold coordination around V1 and V2. Displacement ellipsoids are drawn at 30% probability level for all the non-hydrogen atoms. Intramolecular H-bonding is shown as broken lines. For clarity, symmetry generated atoms are labelled in blue. Symmetry code: (i) $-x, -y + 1, -z + 1$ (ii) $-x + 1, -y + 2, -z + 2$.

are also known (Table S2). The centrosymmetric $(\text{Mo}_8\text{O}_{26})^{4-}$ unit in **1** which consists of three unique octahedrally surrounded Mo atoms (Mo2, Mo3 and Mo4) and the penta-coordinated Mo5 atom (Figure S6) is a γ -modification of $(\text{Mo}_8\text{O}_{26})^{4-}$ and the 13 unique O atoms can be classified under four types viz. i) the terminal oxido (O_t) ligands O7, O8, O12, O15, O16, O18 and O19, ii) μ_2 -bridging oxido ligands O9, O10, O17 iii) μ_3 -bridging O13 and O14 iv) μ_4 -bridging O11. The terminal Mo– O_t bond distances range from 1.6884(16) to 1.7605(15) Å. O7 which makes the longest Mo2–O7 distance of 1.7605(15) Å has also a bond to V2, which can explain its elongation. Unlike the terminal oxygen atoms, the bridging oxido ligands exhibit longer Mo–O distances which scatter in a wider range viz. 1.7648(15)–2.2146(15) Å for μ_2 -bridging ligands, and 1.8995(15)–2.3318(15) Å and 1.8973(14)–2.5049(14) Å for μ_3 - and μ_4 -bridging ligands respectively.

Oxidovanadium(IV) compounds containing monodentate and bridging $(\text{MoO}_4)^{2-}$ ligand are well documented in the literature [30, 32]. Compound **1** is unique due to the presence of two different Mo-based ligands viz. $(\text{MoO}_4)^{2-}$ and $(\text{Mo}_8\text{O}_{26})^{4-}$. To the best of our knowledge no

other V^{4+} compound is known containing coordinated $(\text{MoO}_4)^{2-}$ and $(\text{Mo}_8\text{O}_{26})^{4-}$ ligands. Zubietta and coworkers reported an example of a three-dimensional Cu(II) compound $[\{\text{Cu}_2(\text{L}_4)\}_2\{\gamma\text{-Mo}_8\text{O}_{26}\}\{\text{MoO}_4\}_2]\cdot 2\text{H}_2\text{O}$ (entry 4 in Table S2) containing two differing molybdate ligands [37].

The μ_3 -bridging $(\text{MoO}_4)^{2-}$ dianion binds to two symmetry related V1 atoms via O5 and O6 and a V2 through O4 while the centrosymmetric $(\text{Mo}_8\text{O}_{26})^{4-}$ binds to V2 via O7 (Figure S7). The μ_3 -bridging tridentate binding of $(\text{MoO}_4)^{2-}$ results in the formation of a $\{\text{V}_4\text{Mo}_2\text{O}_{12}\}^{4+}$ cationic unit which is composed of an eight membered heterometallic $\{\text{Mo}_2\text{V}_2\text{O}_4\}$ ring containing one of the unique V atoms (V1 in the ring) with the other unique V atom (V2) protruding as handles (Figure 2).

A pair of $\{\text{V}_4\text{Mo}_2\text{O}_{12}\}^{4+}$ units are bridged by a $(\text{Mo}_8\text{O}_{26})^{4-}$ ligand resulting in the formation of a polymeric chain which consists of alternating $\{\text{V}_4\text{Mo}_2\text{O}_{12}\}^{4+}$ cations and $(\text{Mo}_8\text{O}_{26})^{4-}$ anions (Figure 3). The H atoms attached to the carbon atoms C4, C7, C9, C14, C16, C19, C24, C27, C29 and C30 of the unique terpy ligands function as hydrogen donors while the O atoms O1 and O2 attached to V1 and V2 and the O atoms of the γ - $(\text{Mo}_8\text{O}_{26})^{4-}$ unit, viz. O8, O9, O10, O14,

Table 1: Bond lengths and angles (Å, °) of {VN₃O₃}, (MoO₄)²⁻ and (Mo₈O₂₆)⁴⁻ moieties in 1.

V1–O1	1.5940(17)	Mo1–O4	1.7637(16)	Mo3–O18	1.6892(19)
V1–O5 ⁱ	2.1833(16)	Mo1–O5	1.7750(16)	Mo3–O19	1.7029(18)
V1–O6	1.9674(15)	Mo1–O6	1.8042(16)	Mo4–O10	1.7648(15)
V1–N1	2.142(2)	Mo2–O7	1.7605(15)	Mo4–O11	1.8973(14)
V1–N2	2.0643(18)	Mo2–O8	1.6884(16)	Mo4–O11 ⁱⁱ	2.5049(14)
V1–N3	2.1490(2)	Mo2–O9	1.8539(15)	Mo4–O12	1.6886(15)
V2–O2	1.5998(16)	Mo2–O10	2.2146(15)	Mo4–O14	1.8995(15)
V2–O4	2.1198(16)	Mo2–O11 ⁱⁱ	2.2450(14)	Mo4–O13	2.2101(15)
V2–O7	2.0096(15)	Mo2–O13 ⁱⁱ	2.0192(14)	Mo5–O13	1.9076(15)
V2–N4	2.1231(19)	Mo3–O9	1.9724(16)	Mo5–O14	2.3318(15)
V2–N5	2.0452(18)	Mo3–O11 ⁱⁱ	2.4960(15)	Mo5–O15	1.7032(18)
V2–N6	2.131(2)	Mo3–O14	2.1297(15)	Mo5–O16	1.6949(19)
Mo1–O3	1.7159(19)	Mo3–O17	1.9819(18)	Mo5–O17	1.8579(18)
O1–V1–O6	100.44(8)	O8–Mo2–O9	104.32(8)	O11–Mo4–O13	73.39(6)
O1–V1–N2	100.17(8)	O7–Mo2–O9	101.46(7)	O14–Mo4–O13	75.28(6)
O6–V1–N2	159.39(7)	O8–Mo2–O13 ⁱⁱ	101.14(7)	O12–Mo4–O11 ⁱⁱ	175.01(7)
O1–V1–N1	94.12(9)	O7–Mo2–O13 ⁱⁱ	90.94(6)	O10–Mo4–O11 ⁱⁱ	75.15(6)
O6–V1–N1	101.90(8)	O9–Mo2–O13 ⁱⁱ	148.10(6)	O11–Mo4–O11 ⁱⁱ	79.50(6)
N2–V1–N1	76.37(8)	O8–Mo2–O10	85.89(7)	O14–Mo4–O11 ⁱⁱ	71.37(5)
O1–V1–N3	95.08(9)	O7–Mo2–O10	168.50(6)	O13–Mo4–O11 ⁱⁱ	83.38(5)
O6–V1–N3	101.97(7)	O9–Mo2–O10	82.54(6)	O16–Mo5–O15	105.15(10)
N2–V1–N3	76.36(8)	O13 ⁱⁱ –Mo2–O10	80.42(6)	O16–Mo5–O17	101.46(9)
N1–V1–N3	152.35(8)	O8–Mo2–O11 ⁱⁱ	158.66(7)	O15–Mo5–O17	112.62(9)
O1–V1–O5 ⁱ	178.54(8)	O7–Mo2–O11 ⁱⁱ	96.52(6)	O16–Mo5–O13	99.59(8)
O6–V1–O5 ⁱ	80.88(6)	O9–Mo2–O11 ⁱⁱ	78.91(6)	O15–Mo5–O13	116.32(8)
N2–V1–O5 ⁱ	78.51(7)	O13 ⁱⁱ –Mo2–O11 ⁱⁱ	70.48(6)	O17–Mo5–O13	118.38(7)
N1–V1–O5 ⁱ	84.99(7)	O10–Mo2–O11 ⁱⁱ	73.51(5)	O16–Mo5–O14	166.35(9)
N3–V1–O5 ⁱ	85.21(7)	O18–Mo3–O19	105.13(10)	O15–Mo5–O14	88.39(8)
O2–V2–O7	95.20(7)	O18–Mo3–O9	98.92(9)	O17–Mo5–O14	74.17(6)
O2–V2–N5	95.15(8)	O19–Mo3–O9	96.60(8)	O13–Mo5–O14	72.22(6)
O7–V2–N5	169.48(7)	O18–Mo3–O17	99.81(9)	Mo1–O4–V2	146.34(9)
O2–V2–O4	177.15(9)	O19–Mo3–O17	93.97(9)	Mo1–O5–V1 ⁱ	144.17(10)
O7–V2–O4	85.34(6)	O9–Mo3–O17	155.26(7)	Mo1–O6–V1	134.78(9)
N5–V2–O4	84.42(7)	O18–Mo3–O14	100.75(8)	Mo2–O7–V2	145.82(9)
O2–V2–N4	98.67(9)	O19–Mo3–O14	153.66(8)	Mo2–O9–Mo3	119.09(8)
O7–V2–N4	99.70(7)	O9–Mo3–O14	84.02(6)	Mo4–O10–Mo2	118.35(7)
N5–V2–N4	76.83(8)	O17–Mo3–O14	76.72(6)	Mo4–O11–Mo2 ⁱⁱ	108.74(6)
O4–V2–N4	83.98(7)	O18–Mo3–O11 ⁱⁱ	165.24(8)	Mo4–O11–Mo3 ⁱⁱ	158.74(7)
O2–V2–N6	94.07(9)	O19–Mo3–O11 ⁱⁱ	86.91(8)	Mo2 ⁱⁱ –O11–Mo3 ⁱⁱ	88.02(5)
O7–V2–N6	104.11(7)	O9–Mo3–O11 ⁱⁱ	70.76(5)	Mo4–O11–Mo4 ⁱⁱ	100.50(6)
N5–V2–N6	77.03(8)	O17–Mo3–O11 ⁱⁱ	87.60(6)	Mo2 ⁱⁱ –O11–Mo4 ⁱⁱ	92.12(5)
O4–V2–N6	83.09(7)	O14–Mo3–O11 ⁱⁱ	68.34(5)	Mo3 ⁱⁱ –O11–Mo4 ⁱⁱ	91.60(5)
N4–V2–N6	151.79(8)	O12–Mo4–O10	103.48(7)	Mo5–O13–Mo2 ⁱⁱ	142.53(8)
O3–Mo1–O4	109.17(10)	O12–Mo4–O11	105.48(7)	Mo5–O13–Mo4	108.46(6)
O3–Mo1–O5	109.80(9)	O10–Mo4–O11	99.25(7)	Mo2 ⁱⁱ –O13–Mo4	105.69(6)
O4–Mo1–O5	107.93(8)	O12–Mo4–O14	104.37(7)	Mo4–O14–Mo3	125.60(7)
O3–Mo1–O6	109.54(9)	O10–Mo4–O14	100.23(7)	Mo4–O14–Mo5	104.03(6)
O4–Mo1–O6	107.79(7)	O11–Mo4–O14	139.13(6)	Mo3–O14–Mo5	93.44(6)
O5–Mo1–O6	112.53(8)	O12–Mo4–O13	98.19(7)	Mo5–O17–Mo3	115.67(8)
O8–Mo2–O7	103.33(8)	O10–Mo4–O13	158.30(6)		

Symmetry transformations used to generate equivalent atoms: Symmetry code: i) $-x, -y + 1, -z + 1$; ii) $-x + 1, -y + 2, -z + 2$.

O15, O17 and O19 function as hydrogen acceptors resulting in a total of eleven C–H···O bonds (Table S3) of which two are intramolecular. The intermolecular C–H···O bonds

serve to link parallel polymeric chains. The difficulty to locate the H atoms attached to the lattice water precludes a description of the O–H···O interactions.

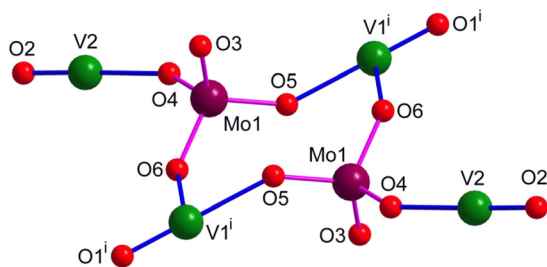


Figure 2: The $\{V_4Mo_2O_{12}\}^{4+}$ cationic unit made up of an eight-membered heterometallic $\{Mo_2V_2O_4\}$ ring with protruding oxidovanadium handles. The terpy ligands around V1 and V2 are not shown. Symmetry code i) $-x, -y + 1, -z + 1$.

3 Experimental

3.1 Materials and methods

All chemicals were used as received from commercial sources without any further purification. Infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer in the range $4000\text{--}400\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} . The Raman spectrum was recorded using a Labram HR Evolution Raman Spectrometer HORIBA Scientific at 785 nm laser radiation for excitation and laser power set to 5%. An ESR spectrum was recorded in a Jeol (JES, FA200) spectrometer using a microwave frequency of 9.5 GHz and modulation frequency of 100 kHz at Sophisticated Analytical

Instruments Facility (SAIF), IIT-Madras. The elemental analysis (C, H and N) was performed on an Elementar Variomicro Cube CHNS Analyser. TG-DTA experiment was performed in air at the heating rate of 5 K/min in the temperature range of $30\text{--}700\text{ }^\circ\text{C}$ on STA-409 PC simultaneous thermal analyser from Netzsch in an alumina crucible. Powder X-ray diffraction (PXRD) pattern was recorded on a Rigaku Smartlab powder diffractometer using $\text{Cu-K}\alpha$ radiation. For single crystal structure determination, X-ray intensity data was collected on a BRUKER D8 Quest Eco X-ray diffractometer, using graphite-monochromated $\text{Mo-K}\alpha$ radiation. The structure was solved with Direct Methods using SHELXS-97 [45] and refinement was carried out against F^2 using SHELXL-2016 [45]. All non-hydrogen atoms were refined anisotropically. The H atoms bonded to the aromatic carbons were located in difference Fourier maps but were positioned with idealized geometry and refined isotropically with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ using a riding model. The hydrogen atoms attached to the lattice water O1W could not be located. Technical details of data acquisition and selected refinement results for **1** are given in Table 2.

4 Synthesis of $[(VO(\text{terpy}))_4(\text{MoO}_4)_2(\text{Mo}_8\text{O}_{26})] \text{ 1}$

Compound **1** was synthesized under hydrothermal conditions in a steel autoclave with Teflon container (volume 25 mL). Sodium metavanadate (0.046 g , 0.38 mmol), 2,2':6',6''-terpyridine (0.116 g , 0.497 mmol) and molybdc

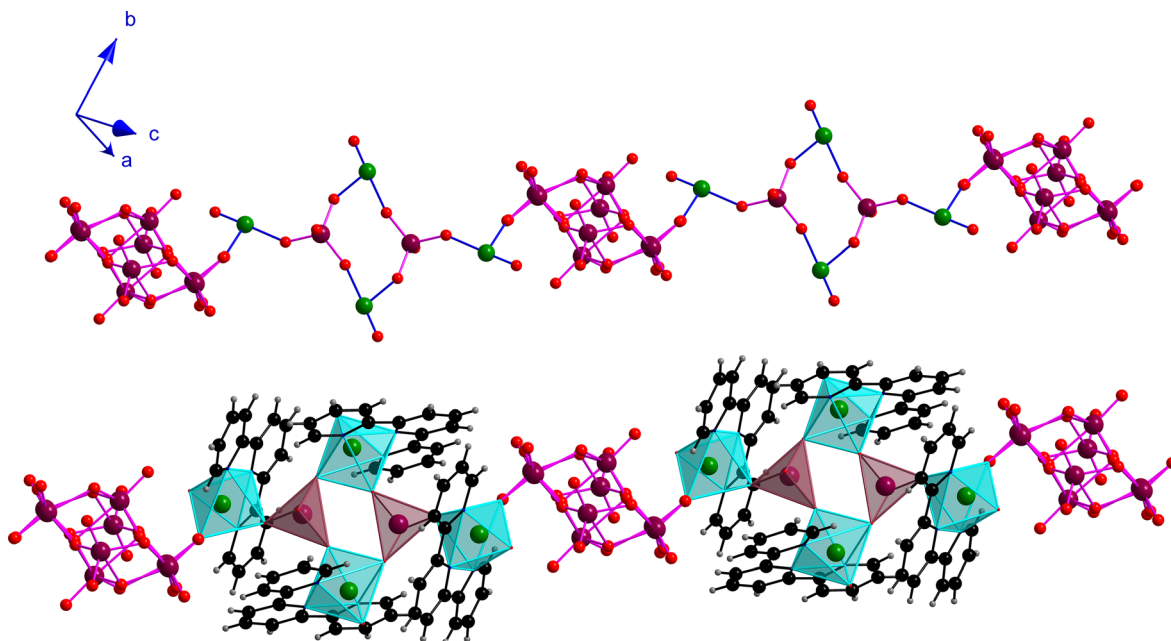


Figure 3: A portion of an infinite chain showing alternating $(\text{Mo}_8\text{O}_{26})^{4-}$ anions and $\{V_4Mo_2O_{12}\}^{4+}$ cations. The tridentate terpy ligands on the unique V atoms are not shown (**top**). Same arrangement after inclusion of the terpy ligands. The $\{VO_3N_3\}$ octahedra and $(\text{MoO}_4)^{2-}$ tetrahedra are shown in polyhedral format (**bottom**).

Table 2: Selected refinement results for $[(VO(terpy))_4(MoO_4)_2(Mo_8O_{26})] \cdot 2H_2O$ **1**.

Refinement result	Compound 1
Empirical formula	$C_{30}H_{24}Mo_5N_6O_{20}V_2$
Formula weight ($g\ mol^{-1}$)	1370.14
Temperature (K)	296(2)
Wavelength ($\text{\AA}$)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a ($\text{\AA}$)	11.4507(16)
b ($\text{\AA}$)	11.8541(17)
c ($\text{\AA}$)	14.675(2)
α ($^\circ$)	92.023(4)
β ($^\circ$)	98.321(4)
γ ($^\circ$)	91.804(4)
Volume ($\text{\AA}^3$)	1968.4(5)
Z	2
D_{calc} ($g\ cm^{-3}$)	2.31
Absorption coefficient (mm^{-1})	2.1
$F(000)$	1320
Crystal size (mm^3)	$0.24 \times 0.16 \times 0.14$
θ range for data collection ($^\circ$)	2.53–28.31
Limiting indices	$-15 \leq h \leq 15$ $-15 \leq k \leq 15$ $-19 \leq l \leq 19$
Reflections collected/unique	66,874/9787 [$R(int) = 0.0290$]
Completeness $\theta = 25.242^\circ$	99.9
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9787/0/568
Goodness of fit on F^2	1.104
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0198$ $wR2 = 0.0480$
R indices (all data)	$R1 = 0.0238$ $wR2 = 0.0507$
Largest diff. peak and hole ($e\ \text{\AA}^{-3}$)	0.67 and -0.73
Bond valence sum	$V1 = 3.77$; $V2 = 3.81$
CCDC Deposition No	2131584

acid (0.094 g, 0.58 mmol) were taken in water (~8 mL) and acetic acid (99.0%) was added to make the pH ~ 3 and the reaction mixture was heated at 200 °C for 68 h. The green reaction mixture was filtered and washed with water to obtain dark green crystalline blocks of **1** (Yield = 0.092 g, 35%).

Analytical data (%) Calcd.: C, 26.29; N, 6.13; H, 1.77. Found: C, 26.97; N, 6.31; H, 1.83.

IR data (KBr, cm^{-1}): 3410(br), 3084–2928(m), 1609(s), 1446(s), 1400(m), 1322(m), 1244(m), 1166(m), 1108(m), 1050(m), 946(s), 893(vs), 796(s), 725(s), 672(s), 543(m), 452(m).

Raman data (cm^{-1}): 1047, 968(vs), 881, 825.

5 Supporting information

Deposition number CCDC 2131584 (**1**), contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures. Supplementary Data (Figs. S1–S7) and Tables S1–S3 associated with this article are available in electronic form.

Acknowledgments: The authors thank the Department of Science and Technology (DST), New Delhi, for the sanction of a BRUKER Eco D8 Quest instrument under the FIST program. Miss Nikita N. Harmalkar acknowledges Research Studentship from Goa University.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: SND thanks Council of Scientific and Industrial Research (CSIR), New Delhi, India (No. 01(2923)/18/EMR-II) for funding.

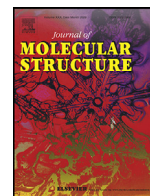
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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Syntheses, spectroscopic, structural characterization of Co(III) and Co(II) carboxylates and electron transfer reactions with ferrocene derivatives

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ARTICLE INFO

Article history:

Received 7 August 2021

Revised 27 November 2021

Accepted 3 February 2022

Available online 5 February 2022

Keywords:

Cobalt(III)

Bipyridine

5-nitroisophthalate

4-nitrobenzoate

Ferrocene

ABSTRACT

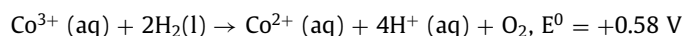
Herein we report five cobalt compounds; three compounds containing 5-nitroisophthalate viz. Bis[bis(2,2'-bipyridine- κ^2 -N,N') (carbonato- κ^2 -O,O')cobalt(III)]5-nitroisophthalate undeca-hydrate, [Co(bpy)₂(CO₃)]₂(5-nip)·11H₂O **1** synthesized by conventional steam bath reaction, while [Co(H₂O)₃(bpy)(5-nip)]·H₂O **2** and polymeric [Co(5-nip)(bpy)(H₂O)] **3** prepared under autoclave conditions. The two compounds of 4-nitrobenzoic acid viz. Bis(2,2'-bipyridine- κ^2 -N,N') (carbonato- κ^2 -O,O')cobalt(III)] 4-nitrobenzoate pentahydrate, [Co(bpy)₂(CO₃)](4-nba)·5H₂O **4** and [Co₂(4-nba)₂(bpy)₂(H₂O)₄](4-nba)₂ **5** were also obtained by steam bath and autoclave reactions. These compounds were characterized by single crystal X-ray diffractometry, elemental, spectroscopic, magnetic and thermal methods. Compounds **1** and **4** were studied by XPS, NMR, CV and VSM, revealing +3 oxidation state of Co. **1** showed eleven lattice waters while five waters were observed in **4** due to the change in carboxylate ligand. A large number of O-H...O and C-H...O interactions leading to extended networks were observed in their crystal structures. The thermal behavior of **1–5** was investigated using TG-DTA techniques. Both carbonato Co(III) compounds **1** and **4** were investigated for their oxidizing properties with ferrocene derivatives and the results of these electron transfer reactions are reported.

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1. Introduction

It is inevitable to recall the incredible contribution of Sir Alfred Werner to the coordination compounds of transition metal cobalt, which presently has a significant impact on inorganic and biological chemistry research [1]. The cobaltous (II) and cobaltic (III) states of cobalt metal have long been known, where Co(II/III) ion coordinate octahedrally to the nitrogen / oxygen donor ligands [2]. The Co(III) compounds are generally prepared by oxidizing Co(II) ions in the presence of N-donor ligand (inert to oxidation and strong coordination ability). The alkaline conditions of the reaction media lead to oxidation of cobalt(II) and also absorption of CO₂ in the solution. However, when the ligands are sensitive to oxidation, this method fails. In such cases, another method involves the use of hydrogen peroxide for the oxidation of Co(II) to Co(III) in the presence of excess sodium bicarbonate [3]. The Co(II) salts

and their aqua compounds are very stable in aqueous medium, but the addition of ligands (amines) in the presence of oxidizing atmosphere leads to a facile conversion to Co(III) [2,4]. Thus, Co(III) compounds in water are strong oxidizing agents and are reported to oxidize water in acidic medium [4] as shown below;



Many carbonato chelated Co(III) compounds such as Na₃[Co(CO₃)₃]·3H₂O [3], [Co(NH₃)_x(CO₃)](NO₃) (x = 4, 5) [5], [Co(CO₃)(en)₂]Cl; (en is ethylenediamine) [6], [Co(CO₃)(tn)₂]Cl; (tn is trimethylenediamine) [7] are well documented in the literature. Similarly, the cobalt(III) compounds wherein carbonato is coordinated to Co(III) along with polypyridyl ligands like 1,10-phenanthroline (phen) are known. In these compounds, cis-[Co(phen)₂(CO₃)]⁺ cation are stabilized by bromide [8], perchlorate [9], nitrophenolates [10]. The [Co(phen)₂(CO₃)]⁺ behaving as an anion receptor for derivatives of benzoates and nitrobenzoates is also well reported [11–15]. The carbonato cobalt(III) compounds containing tripodal tetraamine pyridyl / non-pyridyl based ligands [16–19], bulky tetraamines [20], histamine [21] and triaza

* Corresponding author: Dedicated to Professor Jayant S. Budkuley on the occasion of his 75th birthday

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macrocycles [22] are added to this library. Like phen-Co(III) compounds, the bpy ligand coordinated cobalt(III) carbonate cationic core, $[\text{Co}(\text{bpy})_2(\text{CO}_3)]^+$ has been utilized as a receptor for various anions such as nitrate [8], perchlorate [9], chloride [23], hydrogencarbonate [24], *o*-nitrophenolate [25], *p*-nitrophenolate [26], trifluoromethanesulfonate [27], iodide [28] and 2-[4-[(carboxylatomethyl)carbamoyl]benzamido]acetate [29]. Herein, we have unraveled the chemistry of $[\text{Co}(\text{bpy})_2(\text{CO}_3)]^+$, serving as a receptor for 5-nitroisophthalate (5-nip)²⁻ and 4-nitrobenzoate (4-nba)⁻ forming $[\text{Co}(\text{bpy})_2(\text{CO}_3)]_2(5\text{-nip})\cdot 11\text{H}_2\text{O}$ **1** and $[\text{Co}(\text{bpy})_2(\text{CO}_3)](4\text{-nba})\cdot 5\text{H}_2\text{O}$ **4** under heating. On using solvothermal conditions, three cobalt(II) compounds; $[\text{Co}(\text{H}_2\text{O})_3(\text{bpy})(5\text{-nip})]\cdot \text{H}_2\text{O}$ (**2**), $[\text{Co}(5\text{-nip})(\text{bpy})(\text{H}_2\text{O})]$ (**3**) and $[\text{Co}_2(4\text{-nba})_2(\text{bpy})_2(\text{H}_2\text{O})_4](4\text{-nba})$ (**5**) were obtained.

The electron transfer (ET) reactions serve as primary events in chemistry and biology, accompanied by proton or hydrogen atom transfers [30–32]. These ET reactions unambiguously follow the outer-sphere mechanism in accordance with Marcus theory [33]. The electron transfer reaction between ferrocene and CoL_3^{3+} compounds (*L* = 2,2'-bipyridine, 5-methyl-1,10-phenanthroline, and 5,6-dimethyl-1,10-phenanthroline) have been known and connected with redox behaviors of metalloproteins [34]. Baker and co-workers have studied the rates of electron transfer reaction between tris(phen)-Co(II)-tris(phen)-Co(III) systems and related bpy/triptyridine analogues, which followed the barrier tunneling model for electron transfer [35]. Zwickel and Taube, investigated an electron transfer process between $[\text{Co}(\text{L})_5]^+$ (*L* = NH_3 , OH_2 and Cl^-) and V^{2+} (aq) ion [36]. The reaction of $[\text{Co}(\text{ox})_3]^{3-}$ (ox = oxalate) with cytochrome *c* which follow an irreversible outer-sphere electron transfer mechanism is reported [37]. Apart from this, a great deal of work is devoted to the kinetics and mechanism of electron transfer reactions of tris-(polypyridine)cobalt(III) compounds with verdazyl radicals [33]. The concept and utility of electron transfer reactions using laboratory mimicked high valent metal-oxo intermediates is gaining attention in recent years [38,39]. In the context of importance of understanding electron transfer reactions with high valent metal ion species, herein we investigated the utility of Co(III)-carbonato compounds **1** and **4** with ferrocene derivatives which are versatile electron donors probed in biomimetic reactions.

2. Experimental section

2.1. Materials

Analytical grade chemicals and solvents obtained from chemical suppliers were directly used without any purification. Sodium salts of 5-nitroisophthalic acid (5-nipH₂) and 4-nitrobenzoic acid (4-nbaH) were prepared by the slow addition of NaHCO₃ to the hot aqueous solution of the respective carboxylic acid (2:1). Compositions of the sodium salts were confirmed by IR spectroscopy and elemental analyses (C, H, & N). For Na₂(5-nip), *Found*: C, 36.65; H, 1.09, N, 5.22%. *Calcd*: C, 37.67; H, 1.19; N, 5.49%. IR-data (KBr, cm⁻¹): 3309(br), 3105(s), 1650(s), 1530(m), 1460(m), 1370(s), 1325(w), 1190(m), 1090(m), 930(s), 781(s), 721(s), 534(m), 433(m). For Na(4-nba), *Found*: C, 43.96; H, 2.01; N, 6.98%. *Calcd*: C, 44.46; H, 2.13; N, 7.41%. IR-data (KBr, cm⁻¹): 3200(br), 2905(s), 1670(s), 1538(m), 1442(m), 1370(s), 1330(w), 1210(m), 1067(m), 945(s), 784(s), 715(s), 530(m), 429(m).

The preparation of **1** and **4** were performed under ambient atmospheric conditions, devoid of any attempts to keep out oxygen or water, while solvothermal synthesis of **2**, **3** and **5** were carried out using Teflon-lined stainless steel autoclaves heated in a temperature controlled oven (ANTS make). All necessary precautions were taken while performing the experiments using steel autoclaves.

2.2. Physical measurements

Infrared (IR) spectra of the powdered samples were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer in the region 4000–400 cm⁻¹. UV-Vis spectra were measured on Agilent UV-Vis Spectrophotometer (Model 8453). Elemental analyses (C, H and N) were carried using Elementar Variomicro Cube CHNS Analyzer. Thermogravimetry and differential thermal analysis (TG-DTA) were achieved on a Netzsch STA 409 analyzer under air atmosphere. The samples were heated from room temperature to 650 °C at a heating rate of 10 °C min⁻¹. The ¹H NMR spectra of **1** and **4** were measured in CD₃OD solvent on a Bruker 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. Cyclic voltammetry (CV) experiments were performed using an Electrochemical Workstation-CH Instrument, Inc. CHI6107. In these experiments, the compounds **1** and **4** were dissolved in water and transferred into a glass vessel equipped with a Pt-disc (working electrode), Pt-wire (counter electrode) and reference electrode Ag/AgCl (saturated with KCl, E⁰ = 0.197 V) and supporting electrolyte, KCl (0.1 M). The analyte solutions were then purged with N₂ gas for ~ 30 min. The oxidation states of elements in **1** were determined by using X-ray photoelectron spectroscopy (XPS) performed on PHI 5000 Versa Probe II (FEI Inc.). The field-dependent magnetization studies viz. Zero-Field Cooling (ZFC) and Field Cooling (FC) were performed between 60 and 310 K under an applied field of 100 Oe (M-T). The phase purity of powdered samples of **1–5** was confirmed using powder X-ray diffraction (PXRD) measurements carried out on a RIGAKU ULTIMA IV Diffractometer using Cu-Kα (λ = 1.5418 Å) with Ni filter.

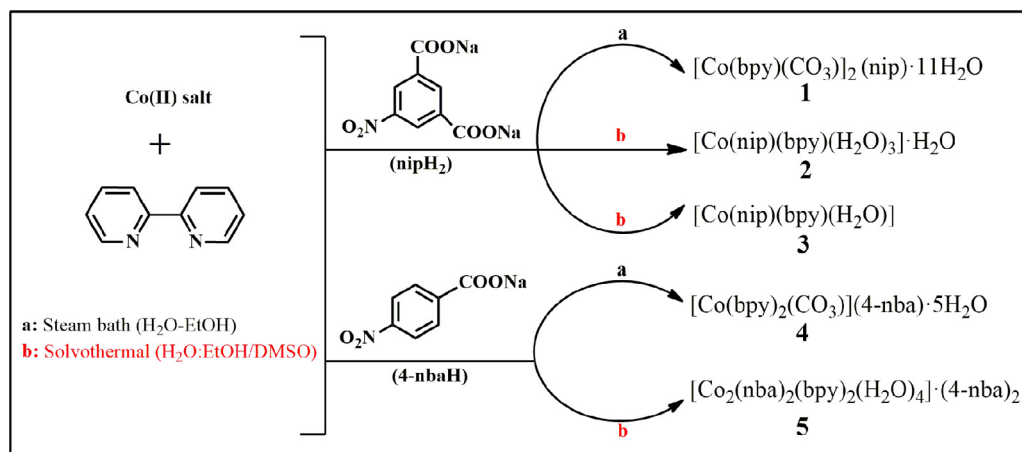
2.3. Single crystal X-ray diffraction studies

The single crystals of **1** was mounted on a Bruker APEX-II CCD diffractometer while that of compounds **2–5** were mounted on Bruker D8 Quest Eco X-ray diffractometer equipped with Mo-Kα = 0.71073 Å radiation and the data were collected. The CCD data were integrated and scaled using Bruker-SAINT software package in case of **1** while for compounds **2–5**, the program suite APEX3 (Version 2018.1) was used to integrate the frames, perform absorption correction and determine the unit cell. The structures were solved with SHELXS and subsequent refinements were performed with SHELXL7 [40]. The non-hydrogen atoms were refined with the anisotropic displacement parameters while the hydrogen atoms were located at the calculated positions.

2.4. Syntheses of compounds (1–5)

(i) *Synthesis of* $[\text{Co}(\text{bpy})_2(\text{CO}_3)]_2(5\text{-nip})\cdot 11\text{H}_2\text{O}$ (**1**) and $[\text{Co}(\text{H}_2\text{O})_3(\text{bpy})(5\text{-nip})]\cdot \text{H}_2\text{O}$ (**2**)

Sodium bicarbonate (20 mmol, 1.68 g) was added to a hot aqueous solution of 5-nipH₂ (10 mmol, 2.10 g) on steam bath with continuous stirring. On complete dissolution of acid 5-nipH₂, a pale yellow color solution was obtained, to which an aqueous solution (10 mL) of Co(OAc)₂·4H₂O (10 mmol, 2.49 g) was added slowly. To this mixture, then 2,2'-bipyridine (10 mmol, 1.56 g) dissolved in 2 mL of ethanol was added slowly with continuous stirring for ~ 2 h. A pale orange solid (**1a**) formed at pH ~ 8.3. It was separated by filtration and the dark orange mother liquor was left undisturbed at room temperature for formation of crystals. After 72 h, the rectangular shaped air stable maroon color crystals of **1** were obtained. Compound **1** is freely soluble in water and alcohol solvents. Yield of **1** was 3.3 g (42%). *Anal. Calc.* for **1** C₅₀H₅₇N₉O₂₃Co₂ (%): C, 47.29; H, 4.52; N, 9.93. *Found*: C, 47.14; H, 4.43; N, 9.55. IR (KBr, cm⁻¹): 3402 (br), 2980 (br), 2615 (w), 2395 (w), 2327 (w), 2130 (m), 1973 (w), 1823 (w), 1624 (s), 1610 (s), 1583 (m), 1512 (m), 1480 (m), 1447 (m), 1403 (s), 1313 (s), 1261 (w), 1230 (w), 1180



Scheme 1. Schematic representation of the syntheses of 1–5.

(m), 1150 (m), 1107 (w), 1055 (w), 1024 (w), 983 (w), 921 (w), 850 (w), 766 (w), 715 (m), 673 (m), 607 (w), 463 (w), 422 (w), 391 (w), 370 (w). UV-Vis data (H_2O , λ_{max} , nm, ϵ): 199 (74,000), 216 (68,667), 252 sh (36,667), 304 (28,667), 504 (180). *Anal. Calc.* for **1a** $[\text{Co}(5\text{-nip})(\text{bpy})(\text{H}_2\text{O})_2]$: $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_8\text{Co}$ (%): C, 46.97; H, 3.28; N, 9.13. *Found*: C, 45.5; H, 3.62; N, 9.32.

$[\text{Co}(\text{H}_2\text{O})_3(\text{bpy})(5\text{-nip})]\cdot\text{H}_2\text{O}$ (**2**) was obtained by solvothermal method. An aqueous solution (2 mL) of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.2 mM, 0.058 g) was added dropwise to an aqueous solution (3 mL) of $\text{Na}_2(5\text{-nip})$ (0.2 mM, 0.051 g) followed by addition of 2 mL ethanolic solution of 2,2'-bipyridine (0.2 mM, 0.0312 g). The reaction scale at 0.2 mM ensured no precipitate formation on mixing the reactants in water. The clear orange solution was transferred into a 25 mL Teflon-lined stainless steel vessel heated at 105 °C for 2 days. On cooling, the orange crystalline blocks of compound **2** were isolated by filtration and vacuum dried. Yield of the product was 0.042 g (30%). *Anal. Calc.* for **2** $\text{C}_{18}\text{H}_{19}\text{N}_3\text{CoO}_{10}$ (%): C, 43.56; H, 3.86; N, 8.47. *Found*: C, 42.98; H, 3.62; N, 8.31. IR (KBr, cm^{-1}): 3403 (br), 3060 (br), 2273 (m), 1966 (w), 1852 (w), 1660 (w), 1610 (s), 1568 (s), 1530 (m), 1466 (m), 1445 (m), 1366 (s), 1345 (s), 1246 (w), 1160 (m), 1098 (m), 1014 (m), 911 (m), 767 (s), 726 (s), 640 (w), 537 (w), 454 (w), 412 (s), 376 (m). UV-Vis data (H_2O , λ_{max} , nm, ϵ): 250 (7714), 295 (6430), 473 (20).

(ii) Synthesis of $[\text{Co}(5\text{-nip})(\text{bpy})(\text{H}_2\text{O})]$ (**3**)

On carrying out above autoclave reaction using a mixture of equal volumes of water and DMSO (1:1), compound **3** was obtained as maroon crystalline flakes. The yield of the crystalline product was 70%. This compound was insoluble in water and organic solvents at room temperature. *Anal. Calc.* for **3** $\text{C}_{18}\text{H}_{13}\text{N}_3\text{CoO}_7$ (%): C, 48.89; H, 2.96; N, 9.50. *Found*: C, 48.24; H, 2.88; N, 9.18. IR (KBr, cm^{-1}): 3250 (br), 2874 (m), 2548 (m), 2256 (m), 1852 (m), 1705 (w), 1630 (m), 1586 (m), 1555 (m), 1510 (m), 1465 (m), 1356 (s), 1246 (w), 1170 (w), 1092 (m), 1015 (m), 927 (m), 785 (s), 730 (s), 653 (w), 532 (w), 422 (w), 390 (w).

(iii) Synthesis of $[\text{Co}(\text{bpy})_2(\text{CO}_3)](4\text{-nba})\cdot 5\text{H}_2\text{O}$ (**4**) and $[\text{Co}_2(4\text{-nba})_2(\text{bpy})_2(\text{H}_2\text{O})_4](4\text{-nba})_2$ (**5**)

The synthetic method adopted for preparation of compound **4** was similar to that used in **1** except that 4-nbaH (10 mmol, 1.67 g) acid was used instead of 5-nipH₂. In this reaction, a light-brown powdery solid compound (**4a**) along with red block crystals of **4** was obtained after 3 days. The crystals were isolated, washed with ethanol and vacuum dried. Yield of **4** was 5.6 g (76%). *Anal. Calc.* for **4** $\text{C}_{28}\text{H}_{30}\text{N}_6\text{O}_{12}\text{Co}$ (%): C, 48.92; H, 4.4; N, 10.19. *Found*: C, 47.47; H, 4.02; N, 9.93. IR (KBr, cm^{-1}): 3440 (br), 3062 (br), 2433 (m), 2203 (m), 1996 (w), 1877 (w), 1940 (w), 1670 (m), 1574 (s), 1495 (s), 1447 (m), 1376 (m), 1335 (s), 1241 (m), 1167 (m), 1067 (m), 1025

(m), 953 (w), 882 (w), 826 (w), 776 (m), 731 (m), 660 (w), 500 (m), 445 (w).

UV-Vis data (H_2O , λ_{max} , nm, ϵ): 241 (3000), 284 (2860), 500 (103). *Anal. Calc.* for **4a** $[\text{Co}(4\text{-nba})_2(\text{bpy})_2(\text{H}_2\text{O})_6]$: $\text{C}_{34}\text{H}_{36}\text{N}_6\text{O}_{14}\text{Co}$ (%): C, 50.31; H, 4.47; N, 10.35. *Found*: C, 49.02; H, 4.39; N, 9.89.

Compound **5** was prepared as follows; $\text{Na}(4\text{-nba})$ (3 mmol, 0.41 g) was dissolved in H_2O / DMSO mixture (1:1 v/v, 5 mL) and then added to bpy solution (1.5 mmol, 0.23 g in 5 mL DMSO), followed by dropwise addition of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ solution (1.5 mmol, 0.437 g in 5 mL DMSO). The resultant brown mixture was transferred to a 25 mL Teflon-lined stainless steel autoclave and heated at 110 °C for 3 days. On cooling, the dark brown cube shaped crystals deposited along the walls of the Teflon cup were separated. The yield of the crystalline product was 0.432 g (40%). *Anal. Calc.* for **5** $\text{C}_{48}\text{H}_{40}\text{Co}_2\text{N}_8\text{O}_{20}$: C, 49.41; H, 3.46; N, 9.6. *Found*: C, 49.7; H, 3.8; N, 9.33. IR (KBr, cm^{-1}): 3469 (br), 3111 (br), 3058 (br), 2858 (m), 2430 (m), 2335 (m), 1994 (m), 1653 (m), 1580 (s), 1506 (s), 1464 (s), 1401 (s), 1350 (s), 1158 (m), 1106 (m), 1064 (m), 1011 (m), 958 (w), 895 (w), 874 (m), 811 (m), 717 (m), 651 (m), 566 (m), 514 (m), 421 (m). UV-Vis in DMSO (λ_{max} nm, ϵ): 252 (1530), 282 (1330), 523 (170).

3. Results and discussions

3.1. Synthetic aspects and methodology

The synthetic strategy used to obtain **1–5** are shown in Scheme 1. The stoichiometric mixing (1:1:1) of reagents under steam bath conditions afforded, carbonate compounds **1** and **4**. Under normal conditions, the Co(II) ions were oxidised to Co(III) by oxygen present in air along with bpy. The compositional changes were caused by the fixation of atmospheric CO_2 by the basic aqueous solution of bpy, resulting in the formation of a very small amount of carbonate ion which was sufficient to bind to Co(II), which ultimately got slowly oxidised to Co(III). Hence, basic conditions, enhanced sensitivity of the ligand towards oxidation thereby facilitating CO_2 absorption by the ligand [8,22]. Under solvothermal conditions, **2**, **3** and **5** were formed where Co(II) ions were coordinated to carboxylate, as reported in literature [63–66]. It is worth mentioning that, solvothermal synthesis was designed at a low reaction scale using Co(II) nitrate salt as the source when compared to steam heating reactions. A number of parameters influence crystallization under solvothermal conditions, they include; compositional parameters (solvent, pH of reaction mixture, molar ratio of reactants, concentration, counter ions) and process parameters (pressure, temperature, time). These have a profound ef-

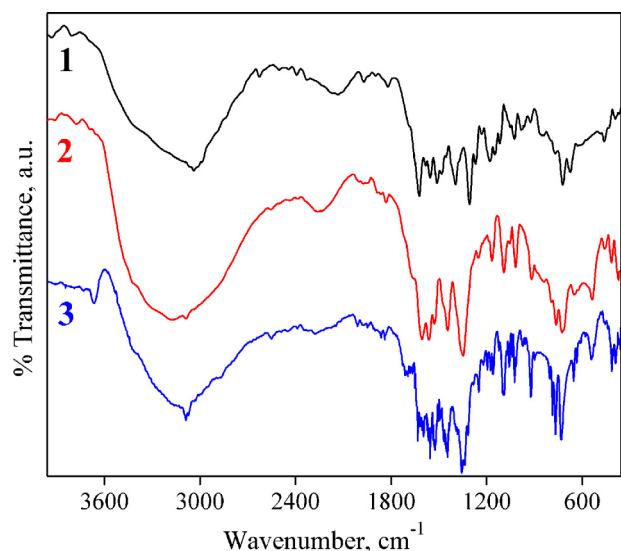


Fig. 1. Comparative Infrared spectra of compounds **1–3** between the region 4000 and 400 cm^{-1} .

fect on the structural chemistry and assembly of the ligands with the metal center. The solvothermal method is operated in a closed system above 100 °C under autogeneous pressure, which renders high solubility of the reactants with the formation of good quality crystals suitable for structural characterization. Hence, it was quite an efficient approach keeping in mind with these parameters to get the desired products. Also, the solvothermal method affected the number of water molecules in the compounds, which showed a progressive decrease. In case of **1**, eleven water molecules decreased from four to one in **2** and **3** respectively on autoclaving [67]. A similar trend is seen, with five waters (in **4**) gradually decreasing to four waters (in **5**) on autoclaving. Compound **5** was earlier reported by simple mixing of the reactants under room temperature [69]. The insoluble powders **1a** and **4a** obtained during the synthesis of **1** and **4**, respectively, were also characterized by different methods to prove that they were altogether different in composition.

3.2. Spectroscopic characterization

All the compounds were characterized by IR and UV-Vis spectroscopy. IR spectra of **1–5** were recorded in the region 4000–400 cm^{-1} , to trace incorporation of ligands and other moieties like water. Fig. 1 depicts the combined IR spectra of **1–3** containing $(5\text{-nip})^{2-}$. A broad band in the range from ~ 3430 to 2980 cm^{-1} is indicative of water molecules. The absence of absorption band at $\sim 1700 \text{ cm}^{-1}$, infers deprotonation of 5-nipH_2 in all the compounds. The bands between 3160 and 2895 cm^{-1} , 1650 – 1620 cm^{-1} and 461 – 453 cm^{-1} are attributed to the aromatic C–H, C=C and C=N moieties of $(5\text{-nip})^{2-}$ and bpy ligands, respectively. A markedly strong absorption at $\sim 1627 \text{ cm}^{-1}$ in **1** is assigned to the C–O vibration of coordinated carbonato ligand, which is absent in **2** and **3**. Symmetric and anti-symmetric vibrations of carboxylate ligand flank at ~ 1560 and 1450 cm^{-1} for **1–3**. The vibrations between ~ 1520 – 1510 cm^{-1} and ~ 1340 – 1310 cm^{-1} are assigned to anti-symmetric and symmetric stretching vibrations of the nitro group present in the carboxylic acid [10–15,25–28,41–43]. The solid product **1a**, obtained during synthesis was also characterised. On comparing the IR spectra of **1** and **1a** (Fig. S1a), we noticed a striking resemblance in the vibrations with absence of the characteristic absorption band at 1625 cm^{-1} in **1a**, suggesting no carbonato ligand in **1a**.

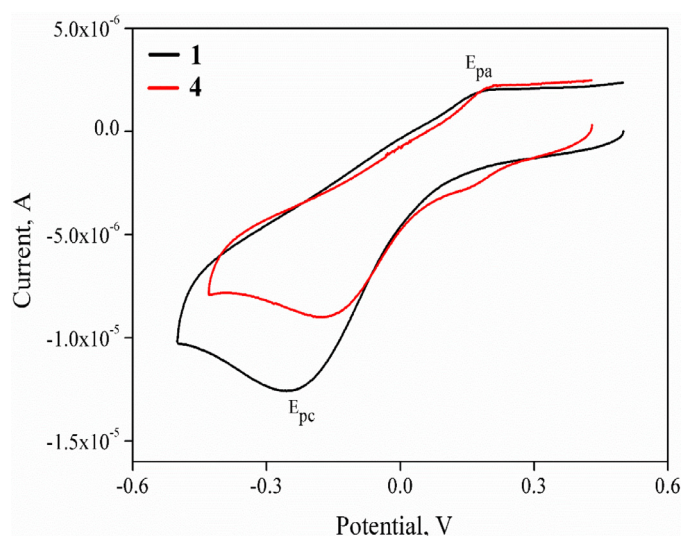


Fig. 2. The CV plots of **1** and **4** recorded in water containing 0.1M KCl as supporting electrolyte against Ag/AgCl (saturated) reference electrode at scan rate of 100 mVs^{-1} .

On inspecting the IR spectra of $(4\text{-nba})^-$ containing compounds **4** and **5** (Fig. S2), we observed a broad band at ~ 3570 – 3100 cm^{-1} due to water. No band at around 1700 cm^{-1} indicates deprotonation of 4-nbaH in **4** and **5**. The symmetric and asymmetric vibrations of COO^- of $(4\text{-nba})^-$ appear at 1570 and 1450 cm^{-1} for both the compounds while the symmetric and asymmetric vibrations of the nitro group in the acid appear at 1515 – 1500 and 1330 – 1315 cm^{-1} respectively. IR spectrum of solid product **4a** obtained during synthesis of **4** showed absence of carbonato ligand which was seen in **4**. (Fig. S1b).

The crystalline compounds **1**, **2**, **4** and **5** were readily soluble in water while **3** was insoluble in aqueous and non-aqueous solvents. For compound **1**, two bands corresponding to electronic transitions namely $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ were observed at $\sim 504 \text{ nm}$ and 304 nm , respectively, typical of octahedral low spin cobalt(III) ion (Fig. S3a). While the UV bands appearing at 199 , 216 and 252 nm are assigned to $\pi \rightarrow \pi^*$ transitions of bpy coordinated to cobalt(III). UV-Vis spectrum of **2** showed intense absorptions centered at 250 and 295 nm , assigned to $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions originating from bpy and $(5\text{-nip})^{2-}$ ligands (Fig. S3b). In the visible region, three characteristic peaks are expected for a high spin octahedral cobalt(II). A weak and broad absorption in the region $\sim 470 \text{ nm}$ is observed due to $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$ while other two bands appear at relatively low intensity. UV-Vis spectrum of **4** was similar to that of **1** suggesting that there is no much influence of anion on the electronic transitions (Fig. S3c). In the case of **5** (Fig. S3d), a strong absorption band at $\sim 252 \text{ nm}$ is assigned to the intramolecular charge transfer transitions of $(4\text{-nba})^-$ while that at 282 nm is indicative of $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions originating from bpy. A weak and broad absorption in the visible region at 523 nm is due to $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$ transition, characteristic of high spin octahedral Co(II) compounds [8,10–14,16–19,25,26,41,44]

3.3. Cyclic voltametric and magnetic property investigations

We investigated the redox behavior of Co(III) compounds **1** and **4** by cyclic voltammetry (CV). In the presence of supporting electrolyte, **2**, **3** and **5** were less soluble in both water and organic solvents. Hence, we have not recorded their cyclic voltammograms. The CV plot of **1** recorded in water is shown in Fig. 2. On sweeping from positive to the negative potential, a cathodic $E_{pc} = -0.25 \text{ V}$ and anodic $E_{pa} = 0.19 \text{ V}$ peaks were observed. The $E^{1/2}$ for the

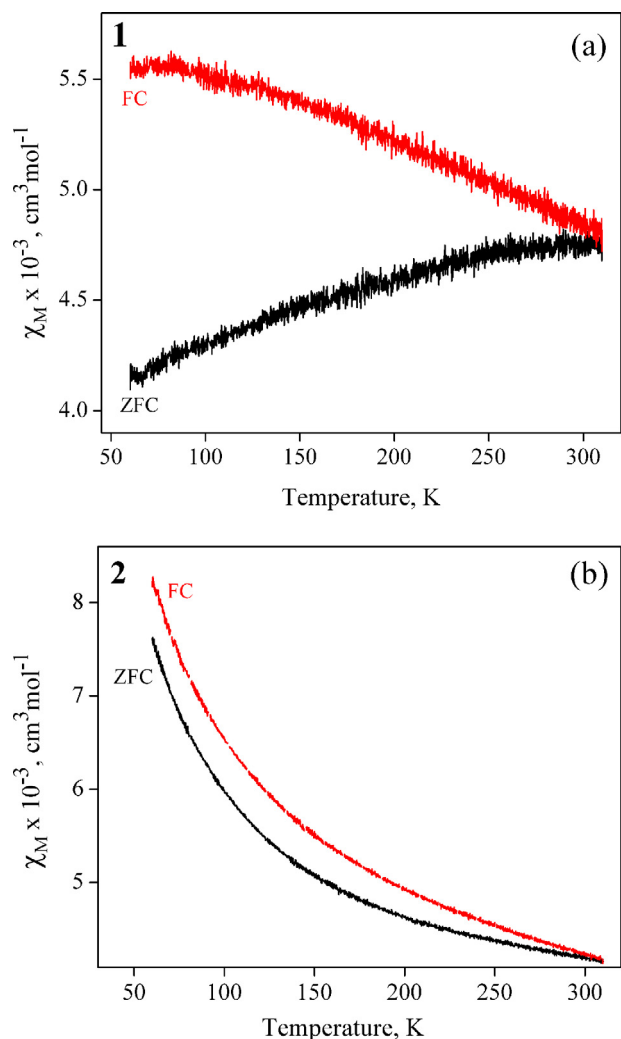


Fig. 3. Plot of Zero Field Cooled (ZFC)- Field Cooled (FC) magnetic susceptibility values as a function of temperature for (a) **1** and (b) **2** under an applied field of 100 Oe between 60 and 310 K.

reaction was found to be -0.06 V with redox potential (E^0) for Co(III)/Co(II) of -0.243 V vs Ag/AgCl reference electrode. Similarly, in case of **4** (Fig. 2), the E_{pc} and E_{pa} values appear slightly shifted to 0.209 V and -0.16 V, respectively, with potential peak difference (ΔE) of 0.37 V and $E_{1/2} = 0.0245$ V. The redox potential (E^0) for Co(III)/Co(II) system vs Ag/AgCl reference electrode was found to be -0.173 V [45–48].

We further resorted to study the magnetic properties with temperature dependent magnetic susceptibility (χ_M) measurements on finely powdered samples under an applied magnetic field of 100 Oe in the temperature range of 60–310 K. The plot of χ_M vs T showed the influence of temperature on the Zero Field Cooled-Field Cooled (ZFC-FC) curves. In case of **1** (Fig. 3a), during FC situation, magnetic susceptibility at 60 K of $5.55 \text{ cm}^3 \text{mol}^{-1}$ decreased to $4.81 \text{ cm}^3 \text{mol}^{-1}$ at 298 K. Similarly, **4** showed a slight drop of χ_M value from 2.6 at 60 K to $2.2 \text{ cm}^3 \text{mol}^{-1}$ at room temperature, such minimal values of χ_M suggested the diamagnetic behavior prevailing in **1** and **4**, thereby showing hardly any effect of temperature onto χ_M values (Fig. S4a). The FC-ZFC curves for **1** and **4** also presented a very large extent of bifurcation. In case of **2** (Fig. 3b) and **5** (Fig. S4b), during the ZFC measurement, sample was cooled to 60 K in the absence of applied magnetic field and thereafter studied with simultaneous heating up to 310 K in the presence of applied field. It was observed that the magnetic susceptibility val-

ues were high at 60 K and on approaching room temperature, the values were found to decrease. The ZFC-FC curves for **2** and **5** displayed an appreciable extent of bifurcation, higher χ_M values for FC measurements may be attributed to the spin alignment of the unpaired electrons with respect to the applied field (100 Oe) while in case of ZFC, the lower observed χ_M values may be furnished to randomization of unpaired electron spins in the absence of applied field. The effective magnetic moment (μ_{eff}) at room temperature (298 K) was calculated from the plot of χ_M vs T which was calculated to be ~ 3.85 BM. The observed magnetic moment was in good agreement with the calculated spin only magnetic moment ($\mu_s = 3.87$ BM) for high spin Co(II) $3d^7$ system with $S = 3/2$ [49–56]. As confirmed from the chemical composition and formula, the polymeric compound **3** was also paramagnetic in nature.

3.4. $^1\text{H-NMR}$ spectral analysis of compounds **1** and **4**

$^1\text{H-NMR}$ spectra of compounds **1** and **4** were measured in solvent CD_3OD . On account of C_2 symmetry (*vide infra*) in **1** and **4**, both the bpy ligands in each Co(III) core are magnetically equivalent, but the two pyridine rings (α and β) of each bpy are not equivalent (Figs. 4 and S5). The peak assignments for all the sixteen hydrogen atoms of bpy ligands and two protons of $(5\text{-nip})^{2-}$ are apparent as shown in Fig. 4 for **1**. The signals corresponding to the protons (α and β rings) of bpy coordinated to Co(III) appear at δ 8.97 (d, 4H, $J = 7.6$ Hz, H^a), δ 8.90 (d, 4H, $J = 7.6$ Hz, H^d), δ 8.86 (d, 4H, $J = 5.2$ Hz, H^d), δ 8.65 (t, 4H, $J = 7.6$ Hz, H^c), δ 8.65 (s, 2H, H^e), δ 8.56 (s, 1H, H^f), δ 8.37 (t, 4H, $J = 7.6$ Hz, H^c), δ 8.15 (t, 4H, $J = 6.8$ Hz, H^b), δ 7.62–7.57 (m, 8H, H^a and H^b). The H^a and H^b protons of bpy (β rings) are seen as multiplets in the region δ 7.62–7.57 ppm. While the proton signals for $(5\text{-nip})^{2-}$ appear as singlets at δ 8.65 and δ 8.56 for H^e and H^f , respectively. In a similar manner, the $^1\text{H-NMR}$ spectrum for **4** was consistent for the equivalent protons present in $(4\text{-nba})^-$ and bpy (Fig. S5). $^1\text{H-NMR}$ data thus, confirms the diamagnetic nature and presence of Co(III) ion in compounds **1** and **4**. The observed chemical shifts as shown in Figs. 4 and S5 lie in accordance with the literature values [11,57].

3.5. X-ray photoelectron spectroscopy (XPS)

Based on elemental analyses and IR studies, we confirmed that **1** contains two carbonato ligands in addition to one $(5\text{-nip})^{2-}$ ligand which led to an overall negative charge of 6-. The C, H, N analysis along with the determination of cobalt by volumetric method revealed that **1** contains two cobalt atoms. To neutralize the 6-charge, we assumed that in **1**, each cobalt is in 3+ oxidation state thus neutralizing the negative charge of two carbonato and one dianionic carboxylate, $(5\text{-nip})^{2-}$. Our preliminary fixing of 3+ oxidation state to cobalt is further supported by the evidence from CV, magnetic and $^1\text{H-NMR}$ studies on **1** (*vide supra*). To clear the unambiguity of oxidation state of cobalt, we then determined the core level electronic structure and binding energies of the constituent elements present in **1** by X-ray photoelectron spectroscopy. Initially a wide survey scan was recorded followed by a detailed analysis of the constituting elements viz. Co2p and O1s. Charging correction for carbon C1s was carried out for all the spectral data. The full scan spectrum along with the high-resolution XPS spectra of Co2p and O1s are plotted and deconvoluted using the peak fitting software. The usual survey of the XPS (Fig. S6) exhibits photoelectron peaks of Co2p, O1s and C1s, which indicates the presence of cobalt and oxygen in **1**. After deconvolution, the Co2p peak displayed two spin-orbit components corresponding to $\text{Co}2p_{3/2}$ and $\text{Co}2p_{1/2}$ peaks. The core level binding energy spectra of $\text{Co}2p_{1/2}$ and $\text{Co}2p_{3/2}$ peaks are shown in Fig. 5a. The Co(II) and Co(III) sites have almost close 2p binding energies but are differentiated on

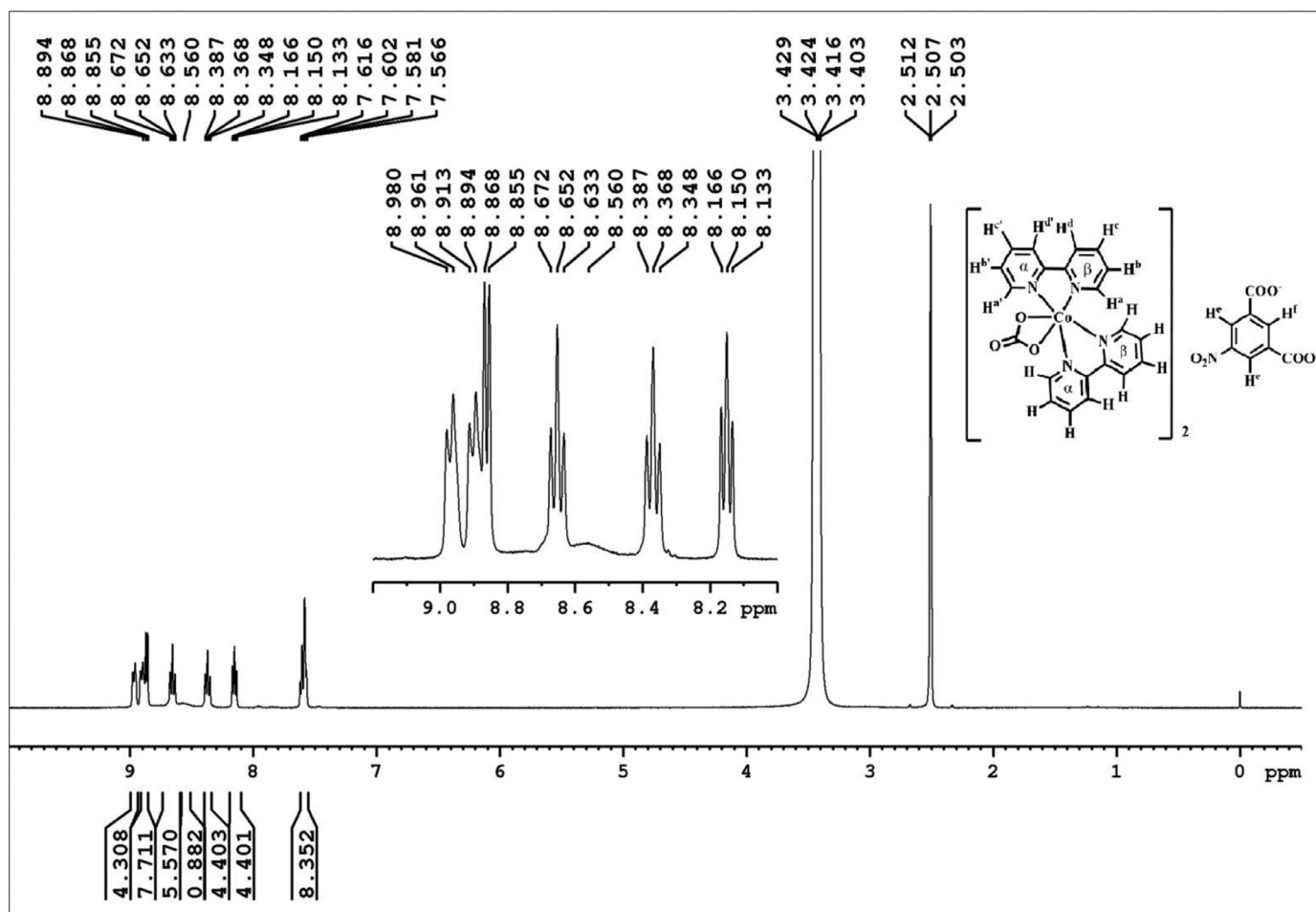


Fig. 4. ¹H-NMR spectrum of [Co(bpy)₂(CO₃)]₂(nip)·11H₂O (**1**) recorded in solvent CD₃OD.

the basis of the Co 2p_(1/2)-2p_(3/2) spin-orbit level energy spacing. The separation is usually ~16 eV for high-spin Co(II) and ~15 eV for low-spin Co(III). The observed binding energy values for cobalt were found to be 796.5 eV for Co2p_(1/2) and 781.34 eV for Co2p_(3/2) with an energy separation of 15.16 eV consistent with Co(III). The XPS core-level effects of O1s after curve fitting are displayed in Fig. 5b showing the existence of two different carbon-oxygen functional groups. The peak at 531.2 eV may be indexed to the C=O group while that at a higher binding energy of 532.23 eV may be designated to water, carbonate species (CO₃)²⁻ or C-O bonds [45,55,58–61]. Thus, XPS analysis evidently reveals the identity of cobalt present in **1** in 3+ oxidation state with two different types of oxygen atoms coordinated to it (*vide infra*).

3.6. Crystal structure description of 1–5

All the five compounds (**1**–**5**) gave single crystals suitable for X-ray analysis. Compound **1**, revealed its crystallization in the triclinic *P* $\bar{1}$ space group (Table 1). The asymmetric unit consists of two cationic cores of [Co(bpy)(CO₃)]⁺ which are charged balanced by an (5-nip)²⁻ anion beside eleven water molecules occupying the crystal lattice (Fig. 6). Co(III) ion present in the cationic core, deviates from the true octahedral geometry as evident from the bite angle of carbonate ligand differing to an extent of 20.4° from the ideal value of 90°. The pyridyl rings of each bpy attached to Co has an average N–N bite distance of 2.571 Å while the O–O bite of the carbonate ligand is 2.165 Å. These distortions are rationalized taking into consideration the restrictions imposed by the bpy ligands.

The bpy moieties of the two cationic cores are not perfectly planar as evidenced from their torsional angles; 3.07° (N1A–C5A–C6A–N2A) and -6.97° (N4A–C16A–C15A–N3A) for Co1 while -2.14° (N1B–C5B–C6B–N2B) and -2.9° (N3B–C15B–C16B–N4B) for Co2. The average Co1–O and Co1–N distances of 1.893(40) and 1.940(50) Å, respectively and those for Co2–O and Co2–N are 1.9(40) and 1.928(50) Å, respectively (Table 2) and lie in close agreement with related Co(III) compounds (Table S1) [8,23–29].

The crystal lattice of **1** is stabilized by an interplay of a number of non-covalent interactions such as O–H...O (water/water), C–H...O (water), C–H...O (carbonate) type hydrogen bonding interactions and π - π stacking interactions originating from pyridyl rings of the adjacent bpy. The hydrogen bonding parameters for **1** are summarized in Table 3, which give rise to extensive H-bonding interactions of the lattice waters with the cationic and anionic units (Figs. 7 & 8). The interplanar distance of 3.631 Å indicates a very weak intercationic π - π stacking interaction between the neighbouring bpy planes (Fig. 9). Moreover, **1** attains structural stability on account of the existing π - π stacking interactions along with the H-bonds which are interlinked to give a three dimensional network (Fig. S7). This is the first water-rich compound of Co(III) reported by us, while we have already published our work on the water rich Co(II) compound [Co(phen)₃](ppda)·14H₂O [56].

Compound [Co(C₈H₃NO₆)(C₁₀H₈N₂)(H₂O)₃].H₂O (**2**) crystallizes in the centrosymmetric triclinic *P* $\bar{1}$ space group and isostructural to zinc and nickel analogues [62,63]. The detailed crystallographic data and structural refinement parameters for **2** are summarized in Table 1. The asymmetric unit consists of a Co^{II} atom hexacoordi-

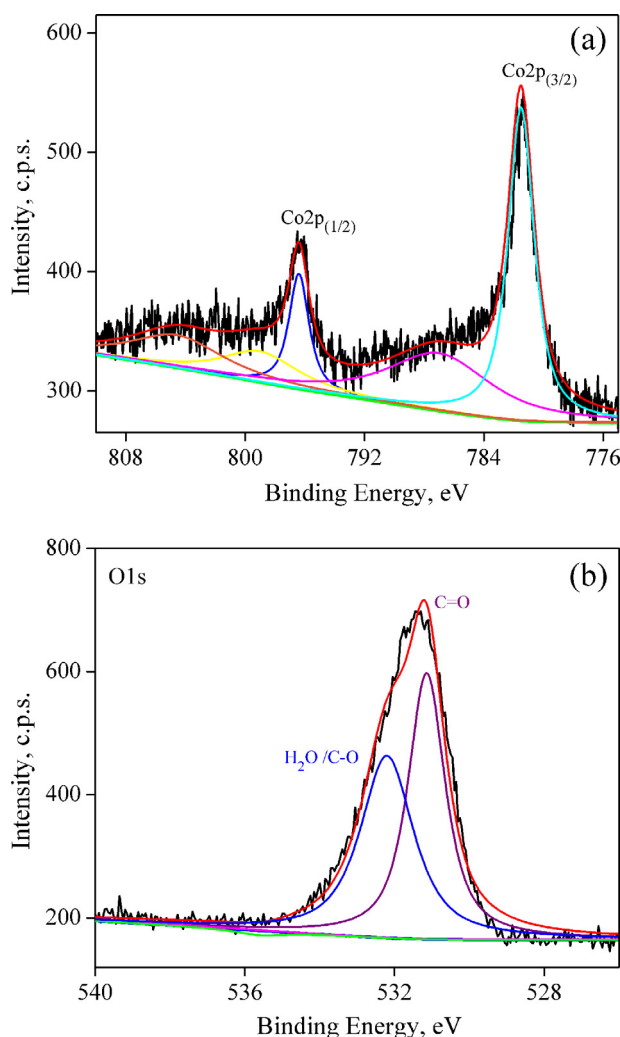


Fig. 5. (a & b). The high resolution XPS spectra of Co2p and O1s cores of **1**.

nated to one bpy in a *cis* fashion, monodentate binding of (5-nip)²⁻ dianion and three water molecules (Fig. 10). The Co-O1 (nip)²⁻ bond distance is 2.073(2) Å while Co-O (water) bond distances range between 2.083(3) and 2.153(3) Å while the average Co-N (bpy) distance is 2.115(3) Å (Table 2). This suggests that **2** shows distortion from true octahedral geometry. As in compound **2**, the coordination of (5-nip)²⁻ and bpy is reported in many other compounds and the M-O and M-N bond distances lie in close agreement with those of **2** (Table S2) [64–66]. The prevailing H-bonding interactions between O-H...O (water) and C-H...O (5-nip²⁻) render additional stability to **2** (Table 3, Fig. 11). The molecular packing of cations, anions and lattice water in **2** viewed along the *b* axis is shown in Fig. S8.

Compound **3** was earlier reported by Liu and co-workers; via the solvothermal reaction (H₂O: EtOH) of cobalt dichloride, bpy and 5-nipH₂ at 140 °C for 3 days. As a result of wrong atom labelling assignments in structure solving, the work was retracted [64]. We performed the reaction with minor modifications and obtained compound **3** whose structure is discussed below. Compound **3** crystallizes in the monoclinic *P*2₁/*n* space group, the crystallographic details and refinement parameters are shown in Table 1. The crystal structure is composed of the asymmetric unit consisting of two Co(II) atoms, two bpy ligands, two (5-nip)²⁻ ligands and two coordinated water molecules (Fig. 12). On account of non-crystallographic inversion symmetry, there are two symmetry-

independent one-dimensional coordination polymers. Each zigzag chain is composed of one Co(II) ion, one monodentate (5-nip)²⁻ dianion, one bidentate bpy ligand and a water molecule (Fig. 13). The symmetry-generated *O,O'*-bidentate (5-nip)²⁻ dianion completes the Co(II) coordination environment, with a distorted *cis*-CoN₂O₄ octahedra. Hence, (5-nip)²⁻ is found to exhibit two different coordination modes, bidentate and monodentate. Thus, the bridging (5-nip)²⁻ ligands form chains running parallel along the *a* direction. Table 2 gives an insight into the details of the Co-O and Co-N bond distances of **3** compared with those reported in literature (Table S2) [64–66].

Compound **4** crystallizes in the monoclinic *P*2₁/*c* space group, the crystallographic details and refinement parameters are shown in Table 4. The crystal structure of **4** consists of Co(III) complex cation, (4-nba)⁻ counteranion and five lattice water molecules, as shown in Fig. 14, and is isotopic to the structure of **1**. In the cation, the central Co(III) ion is six-coordinated with slightly distorted octahedral geometry. The equatorial plane is defined by two nitrogen atoms of two bpy ligands and two chelated oxygen atoms of the carbonate ligand while the other two nitrogen atoms of the two bpy ligands occupy the axial positions. The average Co-O and Co-N distances of 1.895(15) and 1.930(18) Å, respectively for **4** (Table 5) lie in close agreement for related known compounds [8,23–29]. The H-bonding interactions between O-H...O (water) and C-H...O (4-nba⁻) render additional stability to **4** (Table 6 and Fig. 15).

We have lately reported the preparation of compound **5** by reacting [Co(H₂O)₂(DMSO)₂(4-nba)](4-nba) [68] and bpy in DMSO at room temperature. Only the crystal structure of **5** is reported in IUCr data [69]. On the other hand, here we have carried out the reaction with Co(NO₃)₂·6H₂O as the source by the solvothermal method as described in Section 2.4 (iii).

Compound **5** i.e. Di- μ -aqua-bis[aqua(2,2'-bipyridine)](4-nitrobenzoato)cobalt(II)]bis(4-nitrobenzoate) crystallizes in triclinic *P*1 space group (Table 4). The crystallographic features of **5** have been already discussed in detail in our reported work [69]. It consists of a crystallographically unique Co(II) ion and a 2,2'-bipyridine molecule, two crystallographically independent (4-nba)⁻ anions and two unique aqua ligands (one terminal, one bridging). The Co(II) ion, one 4-nitrobenzoate ion, one 2,2'-bipyridine molecule and each of a terminal and bridging water molecule build up one half of a dimeric dicationic species [Co₂(H₂O)₂(C₁₀H₈N₂)₂(C₇H₄NO₄)₂(μ -H₂O)₂]²⁺, and the other half is symmetry generated (Fig. 16). A charge balancing (4-nba)⁻ completes the structure. The geometric parameters of **5** are in their normal ranges and are in agreement with reported data (Tables 5 and 6) [69]. Compound **5** forms a three-dimensional supramolecular network as depicted in Fig. S9.

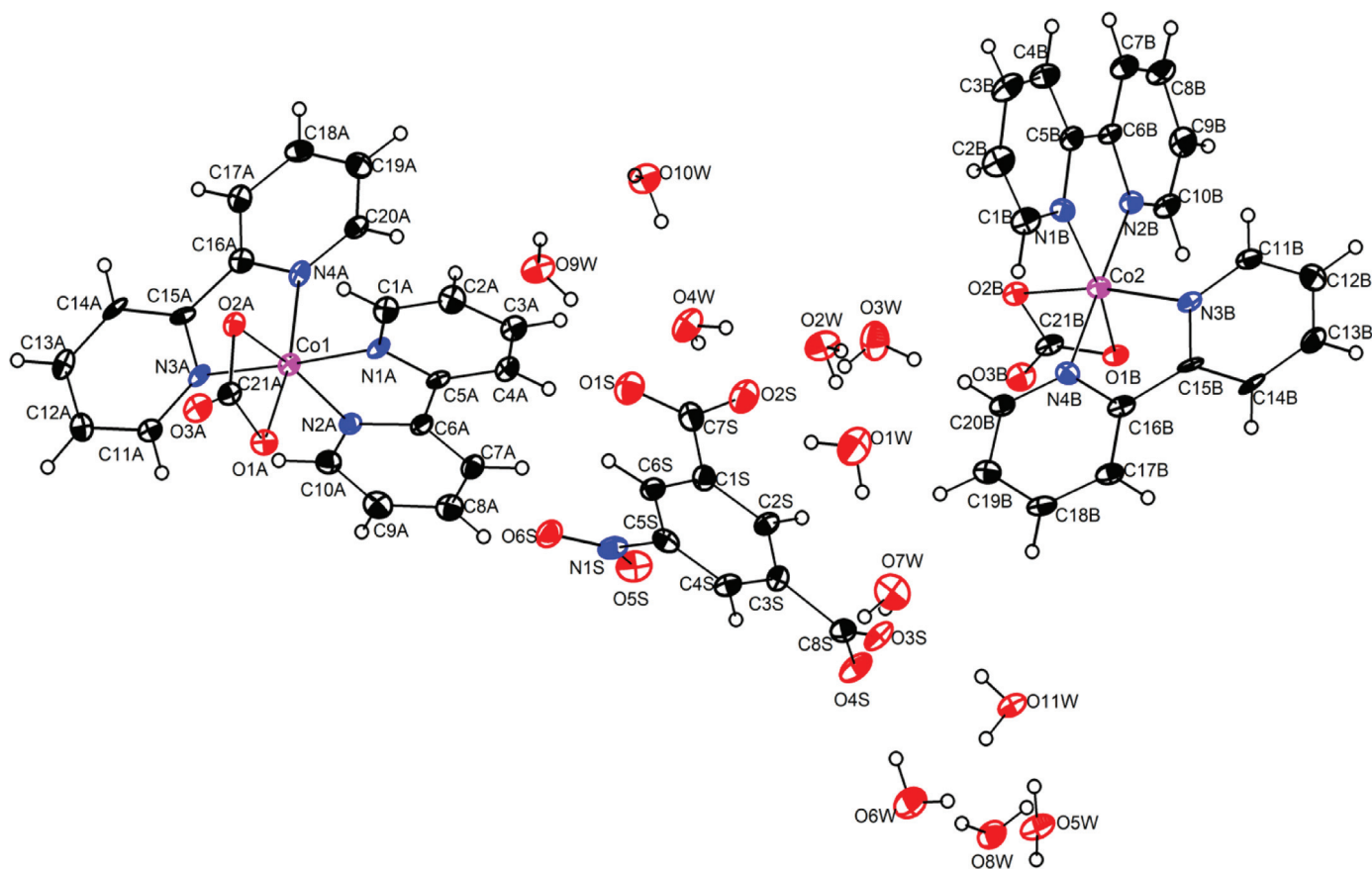
3.7. Powder diffraction and thermal decomposition studies

In order to confirm the phase purity of the crystalline compounds with that of the bulk, we recorded the powder X-ray diffraction patterns of **1–5**. From Figs. 17 and S10, it can be seen that the experimental powder patterns obtained for **1–5** resembled to their respective simulated patterns, thereby confirming the phase purity. We also recorded PXRD pattern for solid powder **1a** and compared with PXRD of the crystalline counterpart **1**. Their PXRD patterns were completely different indicating phase difference. Similarly, the PXRD patterns of **4a** varied from that of **4** suggesting different compositions (*vide supra*) (Fig. S11).

Crystal structure analyses of **1–5** revealed the existence of water molecules either in the lattice or coordinated to the metal. Hence, in order to get an insight into the structural aspects, we sort to record the thermal stability and understand the nature of comparative decomposition patterns of **1–5**. TG-DTA measurements were performed between 30 and 600 °C at a flow rate of

Table 1
Crystal data, data collection and refinement details for **1–3**.

Empirical formula	C ₅₀ H ₅₇ Co ₂ N ₉ O ₂₃ 1	C ₁₈ H ₁₉ Co N ₃ O ₁₀ 2	C ₁₈ H ₁₃ Co N ₃ O ₇ 3
Formula weight (g mol ⁻¹)	1269.90	496.29	442.24
Temperature (K)	100(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	7.2336(4)	7.512(5)	10.028(10)
<i>b</i> (Å)	14.7287(8)	10.839(8)	23.38(3)
<i>c</i> (Å)	25.1600(16)	12.852(8)	15.345(16)
α (°)	89.879(4)	89.82(3)	90
β (°)	89.449(4)	87.73(2)	96.41(3)
γ (°)	86.727(4)	74.51(2)	90
Volume (Å ³)	2676.1(3)	1007.6(12)	3601.5(3)
<i>Z</i>	2	2	8
Density (calc.) (mg/m ³)	1.576	1.636	1.631
Absorption coefficient (mm ⁻¹)	0.714	0.916	1.002
<i>F</i> (000)	1316	510	1800
Diffractionmeter	Bruker APEX-II CCD	Bruker D8 Quest eco	Bruker D8 Quest eco
Theta range for data collection (°)	1.385 to 28.441	2.816 to 28.379	2.708 to 28.375
Completeness to theta	99.5%	99.9%	99.7%
Index ranges	$-9 \leq h \leq 9, -19 \leq k \leq 19, -33 \leq l \leq 25$	$-10 \leq h \leq 10, -14 \leq k \leq 14, -17 \leq l \leq 17$	$-12 \leq h \leq 12, -31 \leq k \leq 31, -20 \leq l \leq 18$
Reflections collected	39,988	14,383	28,048
Independent reflections	13,336 [R(int) = 0.0634]	4996 [R(int) = 0.0608]	8926 [R(int) = 0.0712]
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Data / restraints / parameters	13,336/322/824	4996/1/318	8926/0/539
Goodness-of-fit on <i>F</i> ²	1.113	1.296	1.020
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1=0.0875, <i>wR</i> 2= 0.1882	<i>R</i> 1 = 0.0674, <i>wR</i> 2 = 0.1024	<i>R</i> 1 = 0.0507, <i>wR</i> 2 = 0.1187
<i>R</i> indices (all data)	<i>R</i> 1=0.1023, <i>wR</i> 2= 0.1962	<i>R</i> 1 = 0.0934, <i>wR</i> 2 = 0.1113	<i>R</i> 1 = 0.0949, <i>wR</i> 2 = 0.1434
Largest diff. peak and hole (e.Å ⁻³)	1.222 and -1.292	0.982 and -0.873	1.343 and -0.576

**Fig. 6.** Crystal structure of $[\text{Co}(\text{bpy})_2(\text{CO}_3)]_2(\text{nip}) \cdot 11\text{H}_2\text{O}$ **1**, showing the thermal ellipsoids drawn at the 50% probability level for all of the atoms except for the H atoms that are shown as spheres of arbitrary radii.

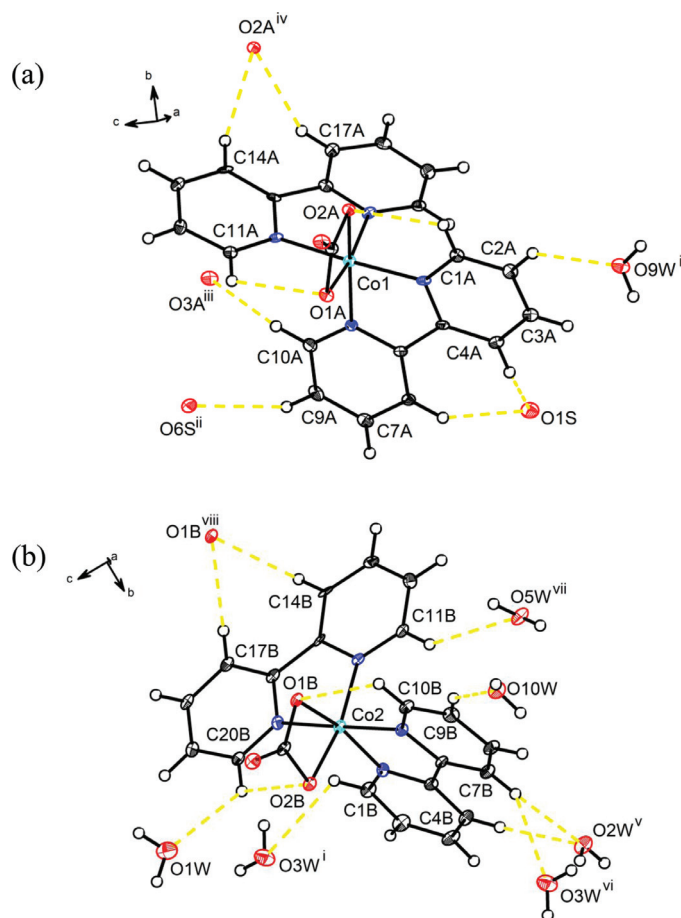


Fig. 7. (a & b). The hexa coordination around the unique Cobalt Co1 and Co2 in the crystal structure of **1**. Thermal ellipsoids drawn at the 50% probability level for all of the atoms except for the H atoms that are shown as spheres of arbitrary radii. Intramolecular H-bonding is shown in broken lines (yellow). Symmetry code: (i) $x + 1, y, z$ (ii) $-x, -y + 1, -z + 2$ (iii) $x - 1, y, z$ (iv) $-x + 1, -y + 2, -z + 2$ (v) $-x + 2, -y + 1, -z + 1$ (vi) $-x + 1, -y + 1, -z + 1$ (vii) $-x + 1, -y, -z + 1$ (viii) $-x + 2, -y, -z + 1$ (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1–3**.

1					
Co(1)–O(1A)	1.892(40)	O(1A)–Co(1)–O(2A)	69.78(18)	N(1A)–Co(1)–N(2A)	83.80(20)
Co(1)–O(2A)	1.894(40)	O(1A)–Co(1)–N(1A)	89.90(20)	N(3A)–Co(1)–N(2A)	97.60(20)
Co(1)–N(1A)	1.921(50)	O(2A)–Co(1)–N(1A)	91.30(20)	O(1A)–Co(1)–N(4A)	169.20(20)
Co(1)–N(3A)	1.933(50)	O(1A)–Co(1)–N(3A)	92.50(20)	O(2A)–Co(1)–N(4A)	100.12(19)
Co(1)–N(2A)	1.944(50)	O(2A)–Co(1)–N(3A)	87.90(19)	N(1A)–Co(1)–N(4A)	94.30(20)
Co(1)–N(4A)	1.961(50)	N(1A)–Co(1)–N(3A)	177.10(20)	N(3A)–Co(1)–N(4A)	83.10(20)
		O(1A)–Co(1)–N(2A)	98.30(20)	N(2A)–Co(1)–N(4A)	92.00(20)
Co(2)–O(1B)	1.899(40)	O(2A)–Co(1)–N(2A)	167.20(20)	O(2A)–Co(1)–N(4A)	100.12(19)
Co(2)–O(2B)	1.902(40)	O(1B)–Co(2)–O(2B)	69.42(18)	O(2B)–Co(2)–N(1B)	97.10(20)
Co(2)–N(2B)	1.914(50)	O(1B)–Co(2)–N(2B)	92.20(2)	N(4B)–Co(2)–N(1B)	97.10(20)
Co(2)–N(4B)	1.918(50)	O(2B)–Co(2)–N(2B)	89.00(20)	O(1B)–Co(2)–N(3B)	99.10(20)
Co(2)–N(1B)	1.930(50)	O(1B)–Co(2)–N(4B)	87.80(20)	O(2B)–Co(2)–N(3B)	167.85(19)
Co(2)–N(3B)	1.949(50)	O(1B)–Co(2)–O(2B)	69.42(18)	N(2B)–Co(2)–N(3B)	95.70(20)
		O(1B)–Co(2)–N(2B)	92.20(20)	N(4B)–Co(2)–N(3B)	83.50(20)
		O(2B)–Co(2)–N(4B)	91.80(20)	N(1B)–Co(2)–N(3B)	94.60(20)
		N(2B)–Co(2)–N(4B)	179.20(20)	N(4B)–Co(2)–N(1B)	97.10(20)
		O(1B)–Co(2)–N(1B)	165.90(20)	O(1B)–Co(2)–N(3B)	99.10(20)
		O(2B)–Co(2)–N(1B)	97.10(20)	O(2B)–Co(2)–N(1B)	97.10(20)
		N(2B)–Co(2)–N(1B)	83.00(20)	N(4B)–Co(2)–N(1B)	97.10(20)
2					
Co(1)–O(1)	2.073(20)	O(1)–Co(1)–O(90)	88.15(10)	O(7)–Co(1)–N(10)	93.80(11)
Co(1)–O(9)	2.083(30)	O(1)–Co(1)–O(70)	89.43(10)	N(2)–Co(1)–N(10)	77.05(10)
Co(1)–O(7)	2.097(30)	O(9)–Co(1)–O(70)	174.03(11)	O(1)–Co(1)–O(80)	93.23(11)
Co(1)–N(2)	2.108(30)	O(1)–Co(1)–N(20)	94.27(10)	O(9)–Co(1)–O(80)	88.18(12)
Co(1)–N(1)	2.122(30)	O(9)–Co(1)–N(20)	89.72(11)	O(7)–Co(1)–O(80)	86.51(12)
Co(1)–O(8)	2.153(30)	O(7)–Co(1)–N(20)	95.91(11)	N(2)–Co(1)–O(80)	172.14(11)
		O(1)–Co(1)–N(10)	171.00(9)	N(1)–Co(1)–O(80)	95.35(11)
		O(9)–Co(1)–N(10)	89.40(10)		
3					
Co(1)–O(2)	2.051(0)	N(2)–Co(1)–O(3)	94.7(0)	N(4)–Co(2)–O(8)	125.57(0)
Co(1)–O(3)	2.195(0)	N(1)–Co(1)–O(3)	88.6(0)	O(10)–Co(2)–N(3)	94.81(0)
Co(1)–O(4)	2.286(1)	N(1)–Co(1)–O(7)	93.4(0)	O(10)–Co(2)–O(8)	145.91(0)
Co(1)–O(7)	2.137(0)	N(1)–Co(1)–O(4)	146.46(0)	O(10)–Co(2)–O(13)	58.12(0)
Co(1)–N(1)	2.073(0)	N(1)–Co(1)–O(2)	126.31(0)	O(10)–Co(2)–O(14)	90.56(0)
Co(1)–N(2)	2.112(0)	O(3)–Co(1)–O(2)	145.06(0)	O(14)–Co(2)–O(13)	91.94(0)
Co(2)–O(8)	2.043(0)	O(3)–Co(1)–O(4)	58.16(0)	O(14)–Co(2)–O(8)	88.5(0)
Co(2)–O(10)	2.173(0)	O(4)–Co(1)–O(2)	86.93(0)	O(14)–Co(2)–N(3)	170.76(0)
Co(2)–O(13)	2.312(1)	O(2)–Co(1)–O(7)	88.86(0)	O(13)–Co(2)–O(8)	87.85(0)
Co(2)–O(14)	2.115(0)	O(3)–Co(1)–O(7)	90.56(0)	O(13)–Co(2)–N(3)	97.28(0)
Co(2)–N(3)	2.112(0)	O(4)–Co(1)–O(7)	91.4(0)	O(8)–Co(2)–N(3)	91.23(0)
Co(2)–N(4)	2.083(0)	N(3)–Co(2)–N(4)	77.56(0)		
N(2)–Co(1)–N(1)	77.85(0)	N(4)–Co(2)–O(10)	88.46(0)		
N(2)–Co(1)–O(2)	91.9(0)	N(4)–Co(2)–O(14)	95.1(0)		
N(2)–Co(1)–O(4)	98.95(0)	N(4)–Co(2)–O(13)	145.92(0)		

Note: The values in parenthesis indicate estimated standard deviations.

10 °C min^{−1} in air. TG of **1**, displayed a mass loss of 15.1% (*Calc.* 15.6%) due to eleven water molecules up to 135 °C, as evidenced by a small endothermic event at 150 °C in the DTA (Fig. 18a). A further mass loss of 74.3% (*Calc.* 75%) up to 380 °C is attributed to the concomitant decomposition of bpy, (5-nip)^{2−} and carbonate ligands which is supported by a sharp exo peak at 385 °C in the DTA. A residue of 10.8% after complete decomposition of **1** is of cobaltous(II) oxide, CoO. From the TG curve of **2**, the first decomposition step occurs with a weight loss of 14.47% corresponding to complete dehydration of the coordinated and lattice water molecules (*Calc.* 14.5%) (Fig. 18b). The weight loss of water molecules is accompanied by a small endotherm at ~150 °C in the DTA curve alongside the second thermal event upto 480 °C with the concomitant decomposition of bpy and (5-nip)^{2−} to give a mass loss of 70.51% (*Calc.* 73.5%) witnessed by a sharp exo peak at 410 °C in the DTA curve. The final residue of 15.04% obtained after complete decomposition of **2** is probably CoO. From the TG curve of **3**, we infer a mass loss of 3.95% (*Calc.* 4.07%) from room temperature to 80 °C due to the loss of water indicated by a sharp endo at 111 °C in the DTA (Fig. S12a). Furthermore, the collective mass loss step of 80.12% (*Calc.* 82.5%) till 400 °C for the decomposition of the con-

stituent ligands is evident by a sharp exo at 400 °C in the DTA. The final residue of 16.7% is due to CoO. As can be seen from the TG plot of **4**, a mass loss of 13.15% (*Calc.* 13.09%) from room temperature to 120 °C is accredited to the lattice water molecules as evident by a broad endo at 122 °C in the DTA curve (Fig. S12b). This was then followed by a continuous decomposition with a mass loss of 78.02% (*Calc.* 78.25%) due to the constituent ligands, witnessed by a sharp exo at 388 °C in the DTA. The final residue of 8.4% obtained after 400 °C is of CoO. The TG curve of **5**, displays a mass loss of 6.03% (*Calc.* 6.12%) from room temperature to 110 °C attributed to the escape of water molecules (Fig. S12c). The dehydrated compound then undergoes ligand decomposition to give a mass loss of 84.84% (*Calc.* 83.65%) evidenced by a sharp exo at 426 °C in the DTA. The residue of 5.53% formed after 450 °C could be cobaltic oxide. Similarly, we compared the decomposition patterns of **1** and **4** with the powder samples **1a** and **4a**, respectively. In case of **1a**, a mass loss of 10.91% (*Calc.* 11.3%) upto 100 °C was due to three water molecules followed by decomposition of ligands to 74.12% (*Calc.* 76.36%) with CoO residue of 15.55%. In case of **4a**, the mass loss of 13.02% (*Calc.* 13.3%) till 110 °C was attributed to

Table 3
Hydrogen bonding parameters (Å, °) for 1–3.

1				
D-H...A	d(D-H)	d(H...A)	<DHA	d(D...A)
C(1A)-H(1AA)...O(2A)	0.95	2.37	2.883(8)	113.5
C(4A)-H(4AA)...O(1S)	0.95	2.56	3.399(8)	147.2
C(7A)-H(7AA)...O(1S)	0.95	2.46	3.202(8)	135.4
C(10A)-H(10A)...N(3A)	0.95	2.61	3.113(8)	113.2
C(11A)-H(11A)...O(1A)	0.95	2.46	2.931(8)	110.4
C(20A)-H(20A)...N(1A)	0.95	2.51	3.022(8)	113.7
C(1B)-H(1BA)...N(4B)	0.95	2.57	3.080(8)	113.8
C(10B)-H(10B)...O(1B)	0.95	2.40	2.891(8)	111.5
C(11B)-H(11B)...N(2B)	0.95	2.55	3.049(8)	113.2
C(20B)-H(20B)...O(2B)	0.95	2.42	2.901(8)	110.8
C(20B)-H(20B)...O(1 W)	0.95	2.49	3.148(9)	126.0
O(1 W)-H(1W1)...O(7 W)	0.83(2)	1.90(3)	2.723(8)	170(10)
O(1 W)-H(1W2)...O(2S)	0.83(2)	1.97(5)	2.682(8)	144(9)
O(2 W)-H(2W1)...O(1 W)	0.81(2)	1.94(3)	2.715(7)	160(7)
O(3 W)-H(3W1)...O(2S)	0.82(2)	2.10(3)	2.884(8)	159(8)
O(3 W)-H(3W2)...O(3B)	0.82(2)	1.99(3)	2.783(7)	161(8)
O(4 W)-H(4W1)...O(2 W)	0.83(2)	1.96(3)	2.780(7)	170(7)
O(4 W)-H(4W2)...O(2S)	0.82(2)	2.00(3)	2.809(7)	167(7)
O(5 W)-H(5W2)...O(11 W)	0.804(19)	2.03(3)	2.802(7)	162(6)
O(6 W)-H(6W1)...O(4S)	0.82(2)	1.96(5)	2.715(7)	152(9)
O(6 W)-H(6W2)...O(5 W)	0.820(19)	1.97(3)	2.772(8)	164(7)
O(7 W)-H(7W1)...O(3S)	0.82(2)	1.96(2)	2.773(7)	172(8)
O(8 W)-H(8W2)...O(6 W)	0.82(2)	1.92(3)	2.720(7)	166(8)
O(9 W)-H(9W1)...O(1S)	0.82(2)	1.90(3)	2.701(7)	164(7)
O(10 W)-H(101)...O(4 W)	0.82(2)	1.90(3)	2.705(7)	170(8)
O(11 W)-H(111)...O(3S)	0.83(2)	2.02(4)	2.751(6)	146(6)
C(2A)-H(2AA)...O(9 W) ⁱ	0.95	2.50	3.284(8)	140.0
C(1B)-H(1BA)...O(3B) ⁱ	0.95	2.35	3.202(8)	148.4
O(2 W)-H(2W2)...O(3 W) ^j	0.82(2)	1.94(3)	2.726(8)	159(7)
O(7 W)-H(7W2)...O(4S) ^j	0.82(2)	2.08(6)	2.741(7)	137(8)
O(11 W)-H(112)...O(8 W) ⁱ	0.83(2)	2.09(4)	2.742(7)	135(5)
C(9A)-H(9AA)...O(6S) ⁱⁱⁱ	0.95	2.51	3.135(8)	123.1
C(10A)-H(10A)...O(3A) ⁱⁱⁱ	0.95	2.40	3.239(8)	146.8
O(8 W)-H(8W1)...O(11 W) ⁱⁱⁱ	0.81(2)	2.54(5)	2.742(7)	96(4)
C(14A)-H(14A)...O(2A) ^{iv}	0.95	2.50	3.367(7)	151.2
C(17A)-H(17A)...O(2A) ^{iv}	0.95	2.39	3.156(8)	138.1
C(4B)-H(4BA)...O(2 W) ^v	0.95	2.31	3.257(9)	176.8
C(7B)-H(7BA)...O(2 W) ^v	0.95	2.43	3.375(8)	170.8
C(7B)-H(7BA)...O(3 W) ^{vi}	0.95	2.65	3.280(8)	124.0
C(9B)-H(9BA)...O(10 W) ^{vi}	0.95	2.37	3.222(8)	149.4
C(11B)-H(11B)...O(5 W) ^{vii}	0.95	2.65	3.450(8)	141.8
C(14B)-H(14B)...O(1B) ^{viii}	0.95	2.43	3.203(7)	137.8
C(17B)-H(17B)...O(1B) ^{viii}	0.95	2.40	3.234(8)	147.0
O(5 W)-H(5W1)...O(9 W) ^{ix}	0.810(19)	1.90(3)	2.701(7)	170(9)
O(9 W)-H(9W2)...O(8 W) ^x	0.82(2)	2.00(3)	2.788(7)	159(6)
Note: The values in parenthesis indicate estimated standard deviations.				
Symmetry code: (i) x + 1, y, z (ii) -x, -y + 1, -z + 2 (iii) x - 1, y, z (iv) -x + 1, -y + 2, -z + 2 (v) -x + 2, -y + 1, -z + 1 (vi) -x + 1, -y + 1, -z + 1 (vii) -x + 1, -y, -z + 1 (viii) -x + 2, -y, -z + 1 (ix) x, y - 1, z (x) x + 1, y + 1, z.				
2				
D-H...A	d(D-H)	d(H...A)	<DHA	d(D...A)
O(1 W)-H(1A)...O(2)	0.680	2.046	161.99	2.701
O(7)-H(7B)...O(2)	0.856	1.940	158.19	2.754
O(8)-H(8A)...O(1 w) ⁱ	0.980	2.319	148.11	3.193
C(9)-H(9)...O(3) ^j	0.930	2.463	148.68	3.293
O(8)-H(8B)...O(4) ⁱⁱ	0.712	2.088	158.81	2.763
O(7)-H(7A)...O(4) ⁱⁱⁱ	0.696	2.097	154.73	2.743
O(1 W)-H(1B)...O(3) ^{iv}	0.767	1.882	171.04	2.643
C(7)-H(7)...O(6) ^v	0.930	2.540	158.01	3.420
O(9)-H(9A)...O(1 w) ^{vi}	0.771	1.891	168.67	2.651
O(9)-H(9B)...O(4) ^{vii}	0.845	1.946	168.82	2.780
Symmetry code: (i) -x + 1, -y + 1, -z + 1 (ii) -x + 1, -y, -z + 1 (iii) x, y + 1, z (iv) -x + 2, -y, -z + 1, (v) -x, -y + 1, -z + 2 (vi) x - 1, y, z (vii) x - 1, y + 1, z.				
3				
D-H...A	d(D-H)	d(H...A)	<DHA	d(D...A)
C(1)-H(1)...O(1)	0.930	2.567	120.43	3.142
O(1)-H(6)...O(9)	0.654	2.139	157.20	2.753
O(8)-H(8A)...O(2)	0.823	1.916	166.01	2.722
C(19)-H(19)...O(8)	0.930	2.613	120.43	3.187
C(1)-H(1)...O(7) ⁱ	0.930	2.596	136.56	3.333
O(1)-H(1A)...O(12) ⁱⁱ	0.922	1.933	145.60	2.744
C(4)-H(4)...O(6) ⁱⁱⁱ	0.930	2.487	143.00	3.278
C(4)-H(4)...O(13) ^{iv}	0.930	2.568	132.48	3.269
O(8)-H(5)...O(5) ^v	0.886	2.016	141.96	2.769
C(9)-H(9)...O(10) ^{vi}	0.930	2.606	160.60	3.497
C(19)-H(19)...O(14) ^{vi}	0.930	2.524	155.47	3.392
C(25)-H(25)...O(11) ^{vii}	0.930	2.451	150.89	3.295
C(27)-H(27)...O(3) ^{viii}	0.930	2.535	160.73	3.427
Symmetry code: (i) x - 1/2, -y + 3/2, z - 1/2 (ii) x + 1, y, z (iii) -x + 3/2, y + 1/2, -z + 3/2, (iv) -x, -y + 2, -z + 1 (v) x - 1, y, z (vi) x + 1/2, -y + 3/2, z + 1/2 (vii) -x, -y + 1, -z + 1 (viii) x - 1/2, -y + 3/2, z - 1/2.				

Table 4
Crystal data, data collection and refinement details for **4** and **5**.

Empirical formula	C ₂₈ H ₃₀ Co N ₅ O ₁₂ 4	C ₄₈ H ₄₀ Co ₂ N ₈ O ₂₀ 5
Formula weight (g mol ⁻¹)	687.50	1166.74
Temperature (K)	296(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> <i>1</i>
<i>a</i> (Å)	13.9484(3)	7.2759(5)
<i>b</i> (Å)	13.2538(4)	10.4949(8)
<i>c</i> (Å)	16.6920(4)	16.3600(12)
α (°)	90	97.740(2)
β (°)	103.575(1)	102.839(2)
γ (°)	90	102.604(2)
Volume (Å ³)	2999.63(13)	1166.43(15)
<i>Z</i>	4	1
Density (calc.) (mg/m ³)	1.522	1.661
Absorption coefficient (mm ⁻¹)	0.645	0.806
<i>F</i> (000)	1424	598
Diffractionmeter	Bruker D8 Quest eco	Bruker D8 Quest eco
Theta range for data collection (°)	2.606 to 28.329	2.611 to 28.273
Completeness to theta	99.2%	99.8%
Index ranges	- 14 ≤ <i>h</i> ≤ 18, - 17 ≤ <i>k</i> ≤ 17, - 19 ≤ <i>l</i> ≤ 22	- 9 ≤ <i>h</i> ≤ 9, - 13 ≤ <i>k</i> ≤ 13, - 21 ≤ <i>l</i> ≤ 21
Reflections collected	29,716	26,823
Independent reflections	7425 [R(int) = 0.0431]	5770 [R(int) = 0.0252]
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Data / restraints / parameters	7425 / 3 / 455	5770 / 0 / 368
Goodness-of-fit on <i>F</i> ²	1.023	1.023
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0410, <i>wR</i> 2 = 0.0780	<i>R</i> 1 = 0.0254, <i>wR</i> 2 = 0.0665
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0764, <i>wR</i> 2 = 0.0966	<i>R</i> 1 = 0.0293, <i>wR</i> 2 = 0.0706
Largest diff. peak and hole (e.Å ⁻³)	0.400 and -0.379	0.386 and -0.294

Table 5
Selected bond lengths (Å) and angles (°) for compounds **4** and **5**.

4					
Co(1)-O(2)	1.8878(15)	O(1)-Co(1)-N(3)	92.39(70)	N(5)-Co(1)-N(1)	83.15(80)
Co(1)-O(1)	1.9015(15)	N(5)-Co(1)-N(3)	178.41(80)	N(3)-Co(1)-N(1)	97.80(80)
Co(1)-N(5)	1.9188(18)	O(2)-Co(1)-N(2)	98.46(70)	N(2)-Co(1)-N(1)	91.49(80)
Co(1)-N(3)	1.9252(17)	O(1)-Co(1)-N(2)	167.49(70)		
Co(1)-N(2)	1.9330(18)	N(5)-Co(1)-N(2)	95.64(80)		
Co(1)-N(1)	1.9420(19)	N(3)-Co(1)-N(2)	83.08(70)		
O(2)-Co(1)-O(1)	69.59(70)	O(2)-Co(1)-N(1)	169.42(70)		
O(2)-Co(1)-N(5)	92.23(70)	O(1)-Co(1)-N(1)	100.70(70)		
O(1)-Co(1)-N(5)	88.67(70)				
O(2)-Co(1)-N(3)	87.04(70)				
5					
Co(1)-O(4)	2.0500(90)	O(4)-Co(1)-O(10 w)	88.81(40)	O(10 w)-Co(1)-O(9 w)	93.75(40)
Co(1)-O(10 w)	2.0755(10)	O(4)-Co(1)-N(2)	95.05(40)	N(2)-Co(1)-O(9 w)	167.84(40)
Co(1)-O(9 w)	2.1400(10)	O(10 w)-Co(1)-N(2)	98.23(40)	N(1)-Co(1)-O(9 w)	100.04(40)
Co(1)-O(9 w) ⁱ	2.1625(10)	O(4)-Co(1)-N(1)	172.65(40)	O(4)-Co(1)-O(9 w) ⁱ	91.60(40)
Co(1)-N(2)	2.1040(11)	O(10 w)-Co(1)-N(1)	89.89(40)	O(10 w)-Co(1)-O(9 w) ⁱ	172.45(40)
Co(1)-N(1)	2.1044(11)	N(2)-Co(1)-N(1)	77.98(40)	N(2)-Co(1)-O(9 w) ⁱ	89.25(40)
		O(4)-Co(1)-O(9 w)	87.27(40)	N(1)-Co(1)-O(9 w) ⁱ	90.64(40)
				O(9 w)-Co(1)-O(9 w) ⁱ	78.74(40)

Note: The values in parenthesis indicate estimated standard deviations.

Symmetry code: (i) -*x* + 1, -*y* + 1, -*z* + 1.

Table 6
Hydrogen bonding parameters (Å, °) for **4** and **5**.

4				
D-H...A	d(D-H)	d(H...A)	<DHA	d(D...A)
C(17)-H(17)...O(4 W)	0.930	2.414	168.85	3.331
O(1 W)-H(6)...O(3)	0.927	2.213	140.91	2.990
O(3 W)-H(21)...O(5 W)	0.913	1.787	174.04	2.697
O(1 W)-H(5)...O(5)	0.920	1.756	166.44	2.659
C(1)-H(1)...O(2)	0.930	2.404	112.38	2.889
C(14)-H(14)...O(4 W)	0.930	2.600	172.40	3.524
C(10)-H(10)...N(3)	0.930	2.643	113.50	3.133
C(11)-H(11)...N(5)	0.930	2.577	112.52	3.056
C(27)-H(27)...O(2) ⁱ	0.930	2.513	139.85	3.280
O(2 W)-H(15)...O(4 W) ⁱ	0.909	1.862	176.07	2.770
O(2 W)-H(16)...O(3 W) ⁱⁱ	0.943	1.748	179.21	2.691
O(3 W)-H(22)...O(4) ⁱⁱⁱ	0.884	1.844	174.45	2.725
O(4 W)-H(30)...O(4) ⁱⁱⁱ	0.917	1.800	173.59	2.714
O(4 W)-H(29)...O(1 W) ^{iv}	0.878	1.963	171.45	2.835
O(5 W)-H(26)...O(1 W) ^{iv}	0.834	2.162	155.67	2.942
O(5 W)-H(23)...O(2 W) ^v	0.955	1.795	165.13	2.729
C(7)-H(7)...O(2 W) ^{vi}	0.930	2.483	146.02	3.296
C(11)-H(11)...O(3) ^{vi}	0.930	2.495	139.61	3.260
C(2)-H(2)...O(7) ^{vii}	0.930	2.654	134.96	3.376
Symmetry code: (i) $-x + 1, y - 1/2, -z + 1/2$, (ii) $x, y - 1, z$, (iii) $x, y + 1, z$, (iv) $-x + 1, y + 1/2, -z + 1/2$, (v) $-x + 1, -y + 1, -z$, (vi) $-x + 2, y + 1/2, -z + 1/2$, (vii) $x + 1, -y + 1/2, z - 1/2$.				
5				
D-H...A	d(D-H)	d(H...A)	<DHA	d(D...A)
O(9 w)-H(1 w)...O(6)	0.841	1.674	172.73	2.511
O(9 w)-H(2 w)...O(3)	0.806	1.868	162.92	2.648
C(17)-H(17)...O(6)	0.930	2.245	171.88	3.168
O(10 w)-H(5 w)...O(3) ⁱ	0.825	2.026	174.12	2.847
O(10 w)-H(12 w)...O(5) ⁱ	0.801	1.886	171.02	2.681
C(9)-H(9)...O(8) ⁱⁱ	0.930	2.643	164.27	3.547
C(14)-H(14)...O(5) ⁱⁱⁱ	0.930	2.411	163.51	3.313
C(16)-H(16)...O(1) ^{iv}	0.930	2.575	160.45	3.465
C(23)-H(23)...O(1) ^{iv}	0.930	2.484	136.47	3.222

Symmetry code: (i) $-x, -y + 1, -z + 1$, (ii) $x + 1, y + 1, z + 1$, (iii) $x + 1, y + 1, z, -z + 1/2$, (iv) $x, y, z - 1$.

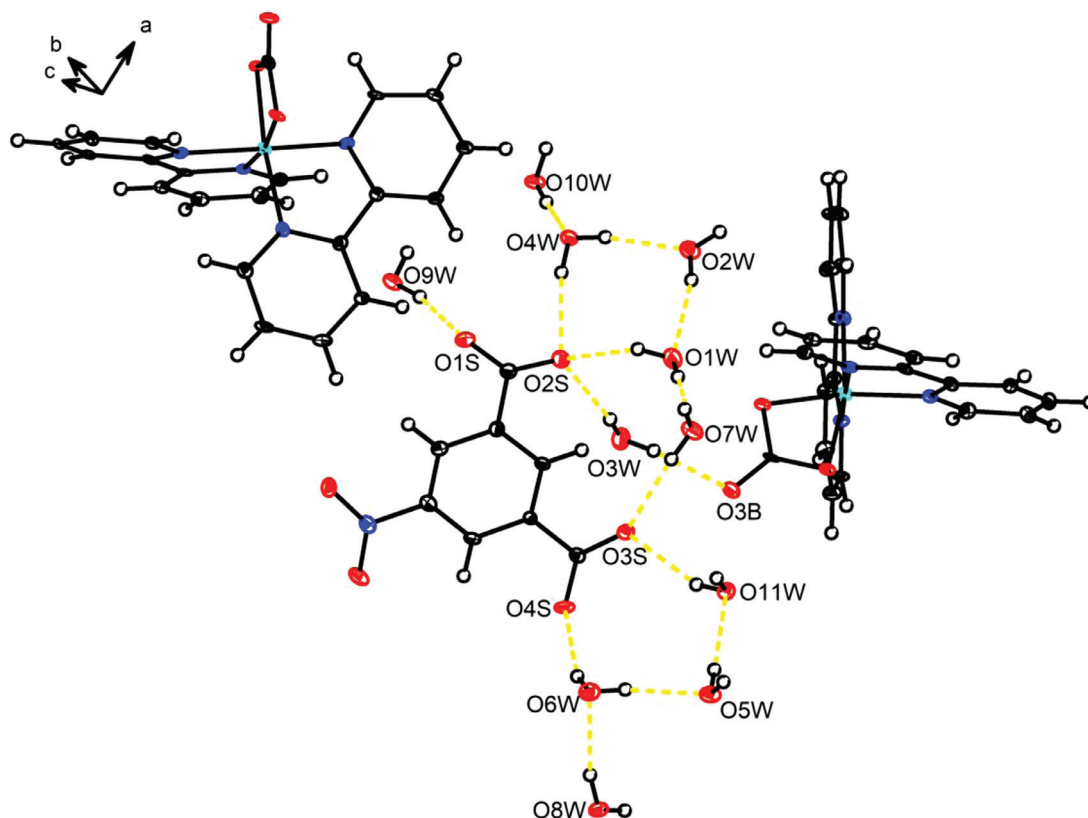


Fig. 8. The overall hydrogen bonding situation in **1** between the cationic, anionic units and lattice water molecules.

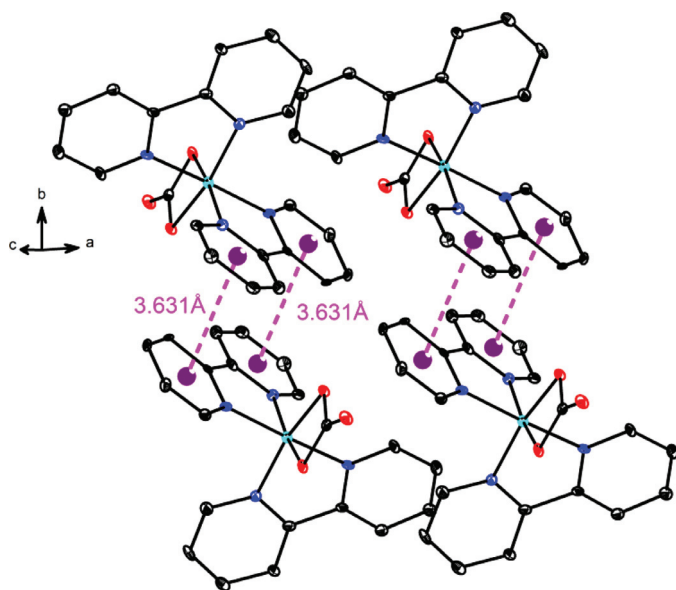


Fig. 9. The π - π stacking interactions in **1** between bpy rings of the adjacent cationic cores.

six water molecules. This was followed by ligand decomposition at 79.11% (Calc. 79.31%) with a residue of 8.2% of CoO (Fig. S13 a & b).

3.8. Reactivity of $[\text{Co}^{\text{III}}(\text{bpy})_2(\text{CO}_3)]_2(5\text{-nip})\cdot 11\text{H}_2\text{O}$ (**1**) $[\text{Co}^{\text{III}}(\text{bpy})_2(\text{CO}_3)](4\text{-nba})\cdot 5\text{H}_2\text{O}$ (**4**)

After neat characterization of Co(III) and Co(II) compounds **1–5**. We investigated the oxidizing strengths of **1** and **4** in the absence

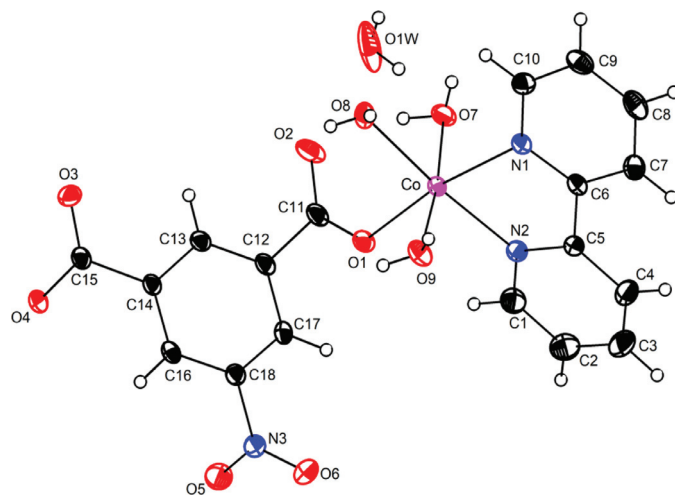


Fig. 10. Crystal structure of $[\text{Co}(\text{H}_2\text{O})_3(\text{bpy})(\text{nip})]\cdot\text{H}_2\text{O}$ **2** showing the thermal ellipsoids drawn at the 50% probability level for all of the atoms except for the H atoms that are shown as spheres of arbitrary radii.

and presence of acid as in both cobalt is in +3 oxidation state. It is well documented in literature that, Co(III) compounds are inert and show remarkable stability in acidic medium [4,17,18,44]. On performing acid hydrolysis on the Co(III) analogues **1** and **4** in concentrated hydrochloric acid (11.6 M), as expected there was a very slow and negligible decay of the $d-d$ band. Both the compounds reacted with a minimum absorbance decrease at λ_{max} over a period of ~ 3 h. Although the endo oxygen atoms of carbonato ligand is free of steric encumbrances, the chelating bpy ligands pose

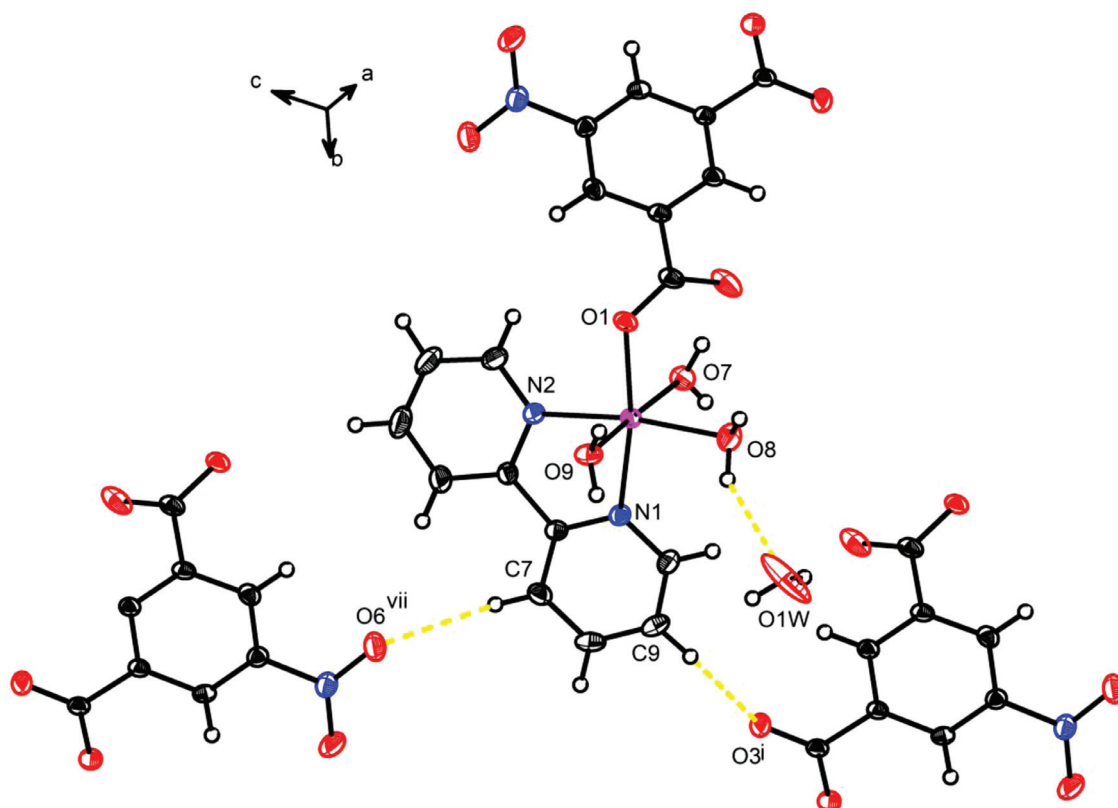


Fig. 11. The intramolecular H-bonding between O-H...O and C-H...O in **2** shown as broken lines (Yellow). Symmetry code: (i) $-x + 1, -y + 1, -z + 1$ (vii) $x - 1, y + 1, z$ (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

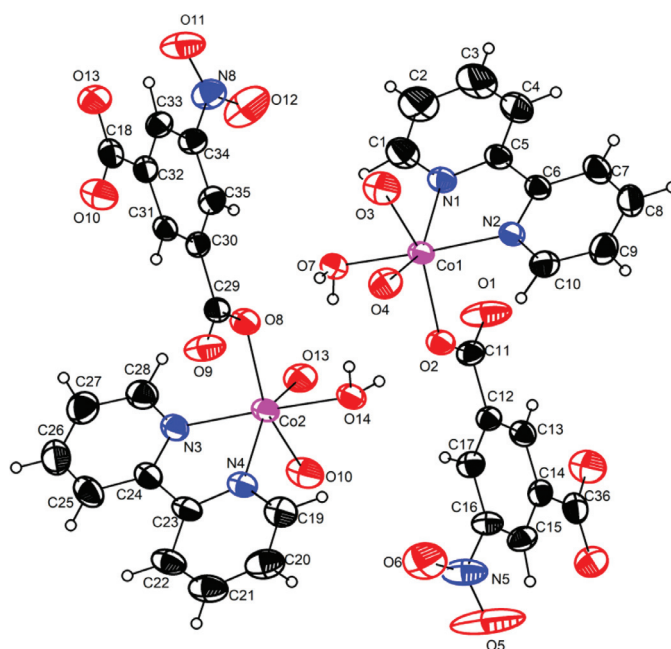


Fig. 12. Crystal structure of $[\text{Co}(\text{H}_2\text{O})(\text{bpy})(\text{nip})]$ **3** showing the thermal ellipsoids drawn at the 50% probability level for all of the atoms except for the H atoms that are shown as spheres of arbitrary radii.

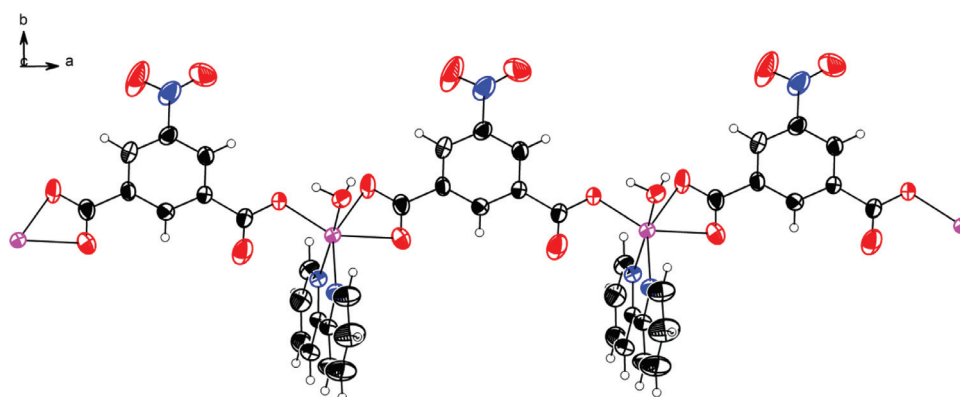


Fig. 13. A view along *c* axis showing the one- dimensional (1-D) polymeric chains of **3**.

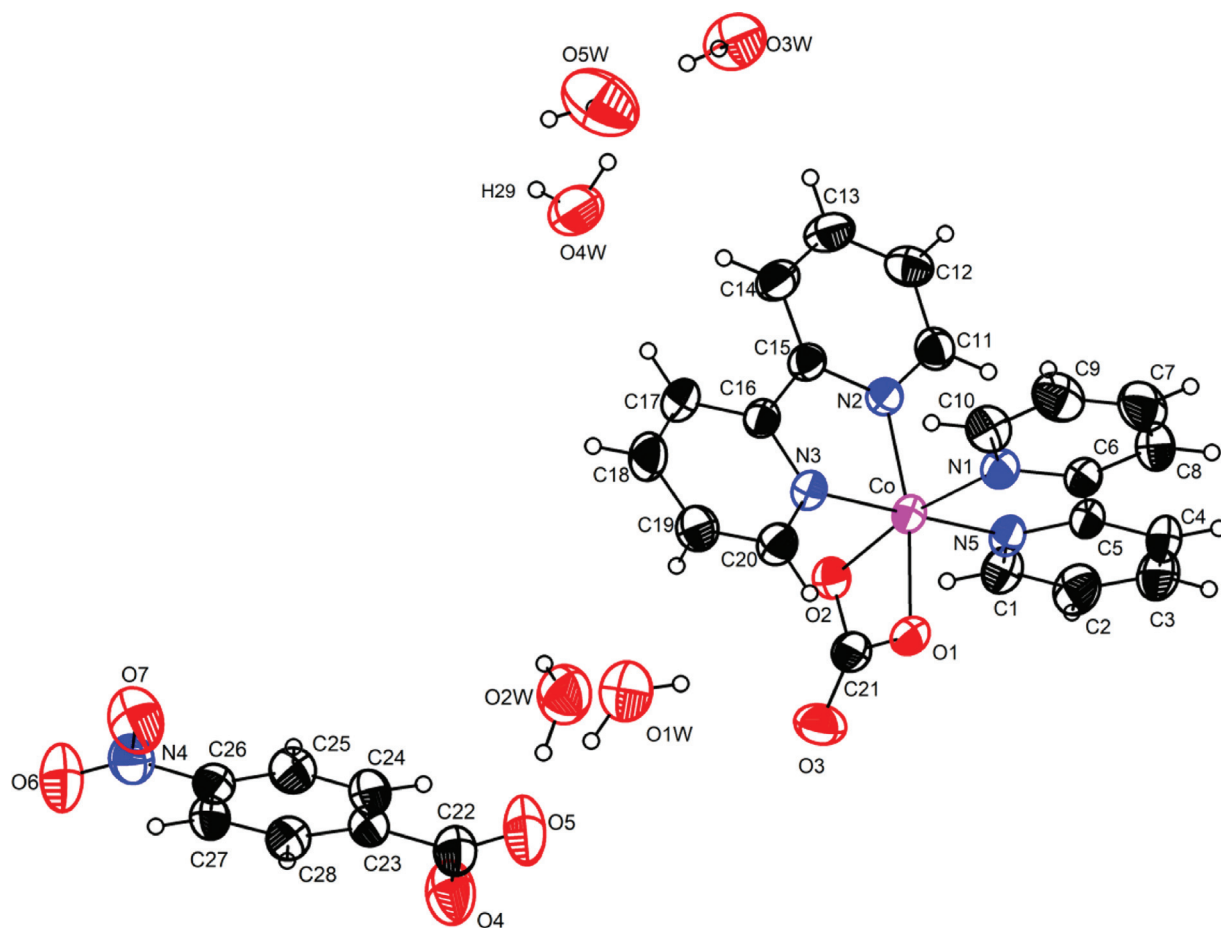


Fig. 14. Crystal structure of $[\text{Co}(\text{bpy})_2(\text{CO}_3)](4\text{-nba})\cdot 5\text{H}_2\text{O}$ **4** showing the thermal ellipsoids drawn at the 50% probability level for all of the atoms except for the H atoms that are shown as spheres of arbitrary radii.

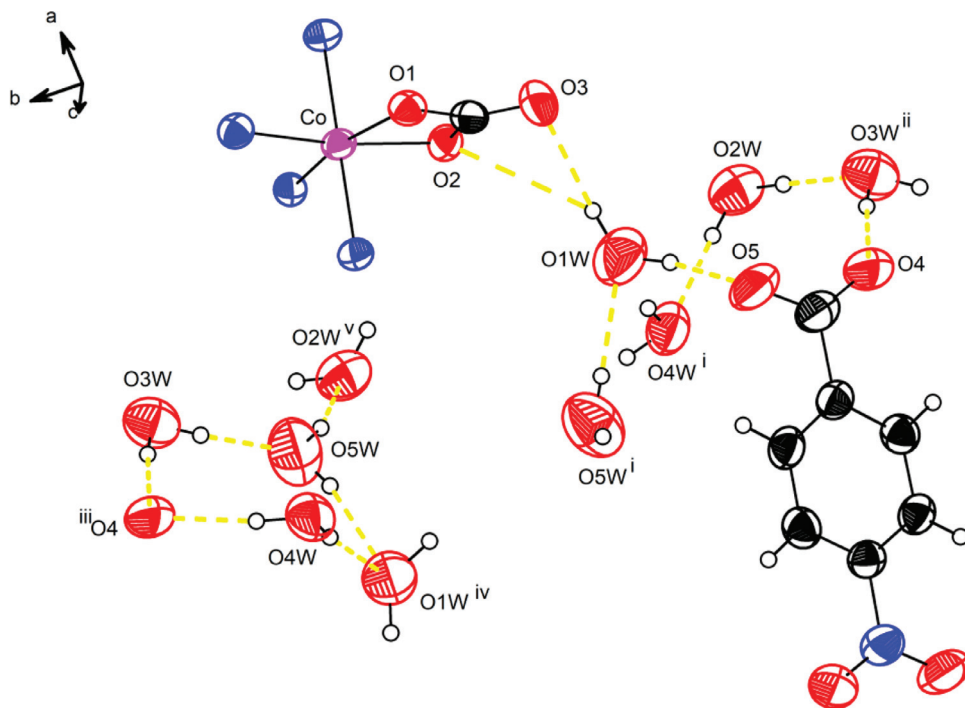


Fig. 15. Intramolecular H- bonding between carbonate of Co(III) core, 4-nitrobenzoate anion and lattice water molecules of **4** shown as broken lines (Yellow). Thermal ellipsoids drawn at the 50% probability level for all of the atoms except for the H atoms that are shown as spheres of arbitrary radii. Symmetry code: (i) $-x + 1, y - 1/2, -z + 1/2$, (ii) $x, y - 1, z$, (iii) $x, y + 1, z$, (iv) $-x + 1, y + 1/2, -z + 1/2$, (v) $-x + 1, -y + 1, -z$, (vi) $-x + 2, y + 1/2, -z + 1/2$, (vii) $x + 1, -y + 1/2, z - 1/2$ (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

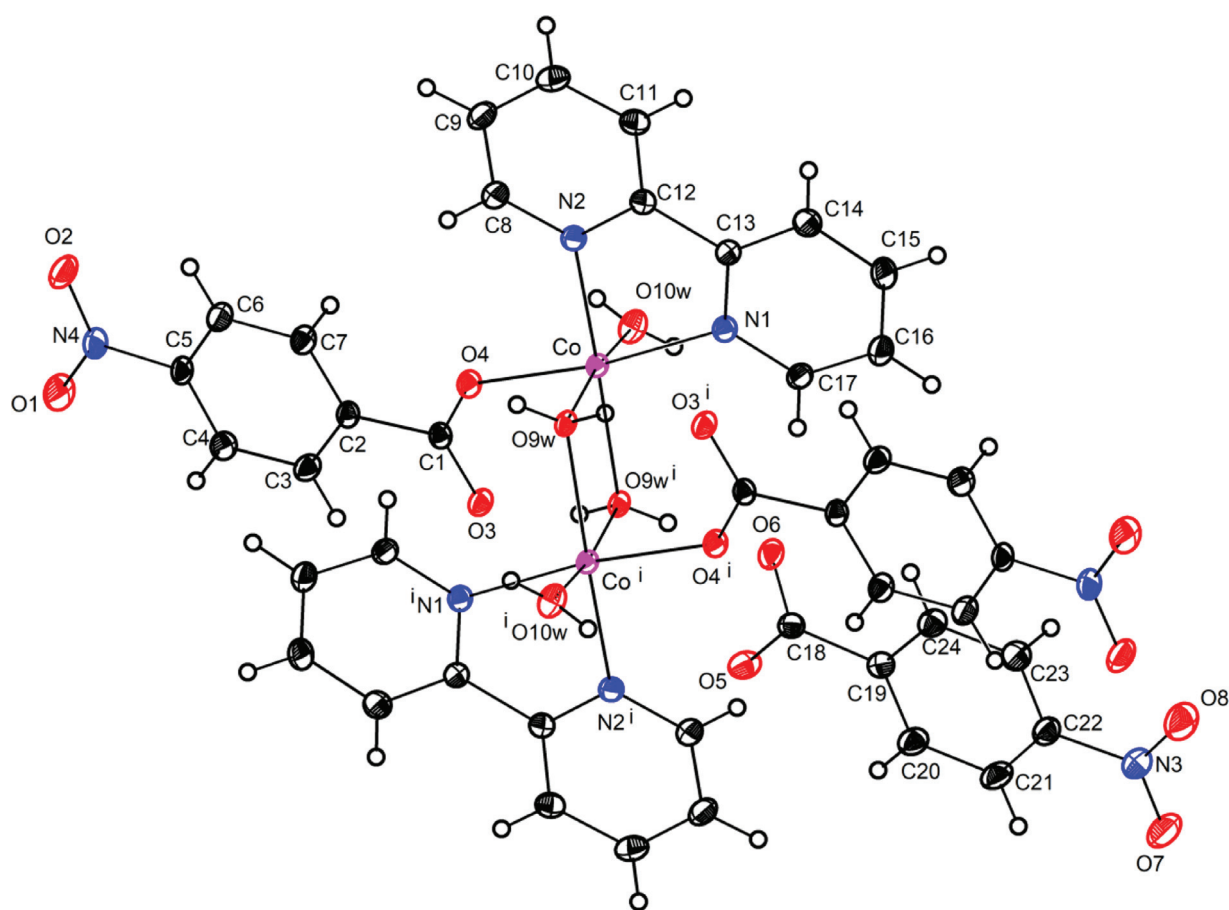


Fig. 16. Crystal structure of **5** showing the thermal ellipsoids drawn at the 50% probability level for all of the atoms except for the H atoms that are shown as spheres of arbitrary radii. Symmetry code: (i) 1-x, 1-y, 1-z.

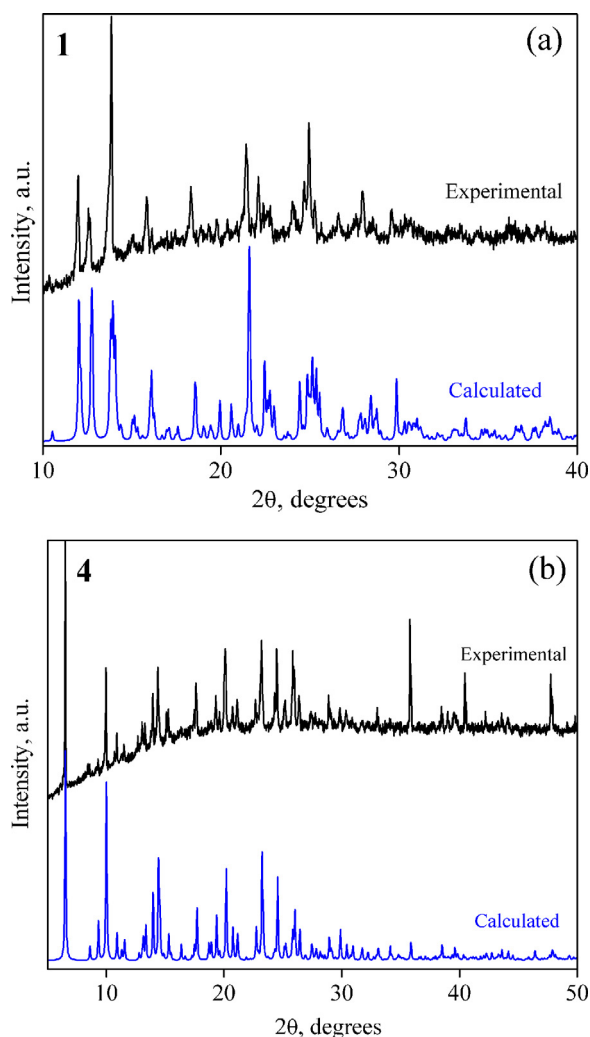


Fig. 17. Calculated and experimental powder X-ray diffraction patterns for (a) **1** and (b) **4**.

a significant retarding effect on the rate of hydrolysis of **1** and **4** [70–72].

Comparative CV in acid and without acid were recorded for both **1** and **4** to check their stabilities. In a typical experiment, about 30 equivalents of 1 mM of HCl was added to the aqueous Co(III) solutions of **1** and **4**. CV plots display, a shift in potential values in **1** with E_{pc} and E_{pa} at -0.405 V and -0.30 V, respectively (Fig. 19). On the other hand, **4** showed these peaks at -0.402 V and -0.256 V (Fig. S14). The $E^{1/2}$ values for both the compounds in acidic medium were found to lie in the range of -0.33 to -0.35 V corresponding to the Co(III)/Co(II) electron transfer process. This result suggests that the Co(III) core in **1** and **4** remained intact suggesting its remarkable stability in acidic medium, however enhancing the oxidizing potential of **1** and **4**. Owing to this fact, we then investigated the reactions of **1** and **4** with electron donating substituents like ferrocene, dimethylferrocene and octamethylferrocene. To the methanolic solution of **1** was added 2 equivalents of ferrocene (Fc) and 30 equivalents of HCl which immediately resulted in the formation of a new UV-Vis band at 619 nm (Fig. 20). A new peak formed at 619 nm is assigned to the formation of ferrocenium (Fc^+) ion caused by the oxidation of Fc. This was substantiated visually by the bluish green color of the solution [73–78]. On carrying out a blank reaction of Fc with acid solution, we observed negligible rise in Fc^+ peak at 619 nm (Fig. S15). In the absence of acid, there was no reaction of ferrocene with **1** and **4**. We

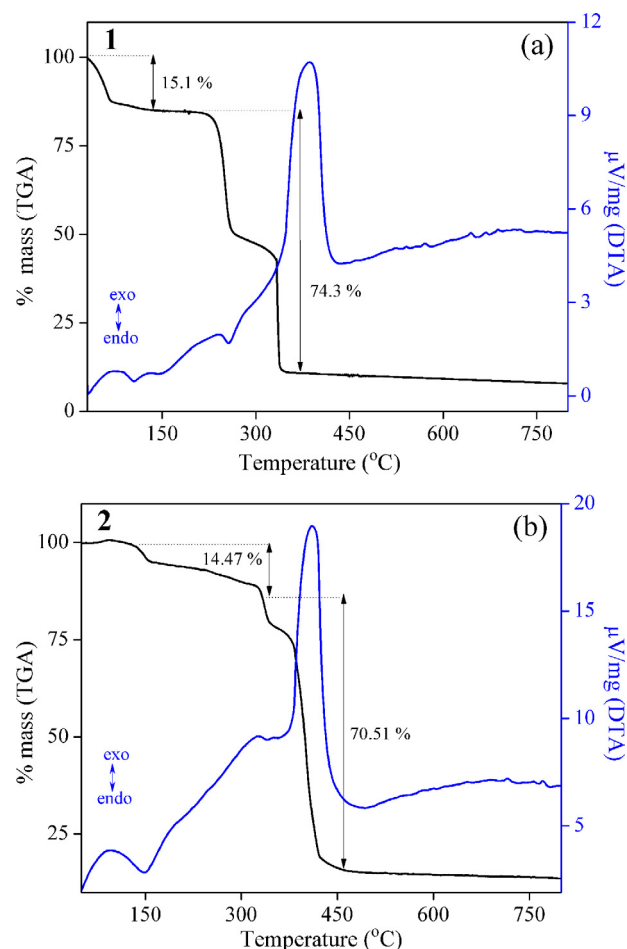


Fig. 18. TG-DTA plots for (a) **1** and (b) **2** recorded in air at a heating rate of $10^\circ\text{C}/\text{min}$.

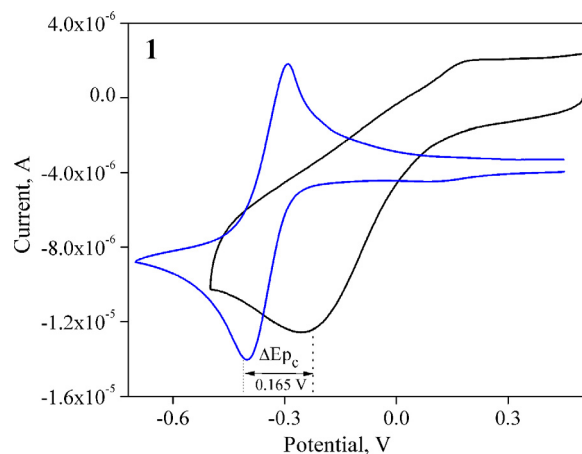


Fig. 19. CV of **1** without (blue) and with (black) acid (30 equivalents of 1 mmole HCl) recorded in aqueous medium containing 0.1 M KCl as supporting electrolyte and Ag/AgCl (saturated) as reference electrode at scan rate of 100 mVs^{-1} (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

then compared the reactivity of bench prepared Co(III) hexaammine compound, $[\text{Co}(\text{NH}_3)_6]^{3+}$ with Fc in the absence and presence of acid, however, no reaction was observed indicating compounds **1** and **4** containing bpy and carbonato ligands are better oxidisers than Co-ammine complex (Fig. S16). On performing the reaction of **1** with dimethylferrocene, we observed the formation

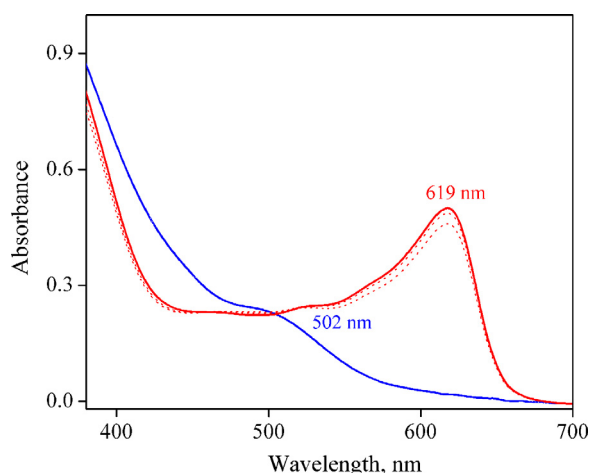


Fig. 20. UV-Visible spectral changes observed in the reaction of **1** with 2 equivalents of ferrocene in methanol at room temperature in the presence of 30 equivalents of HCl. The spectrum in blue shows **1** in methanol while the one in red depicts formation of ferrocenium cation (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

of a new peak at 654 nm while the reaction with octamethylferrocene showed a peak at 753 nm (Fig. S17 a & b). The formation of the respective ferrocenium ions was evidenced by the appearance of blue-green color to the resulting solutions. On similar lines, we carried out the reaction of **4** with ferrocene and its derivatives in methanolic medium. Figs. S18 and S19 a & b, shows new peak formation on reaction with ferrocene, dimethylferrocene and octamethylferrocene [77].

4. Conclusions

We have reported syntheses of Co(III) compounds **1** and **4** by steam bath heating and Co(II) compounds **2**, **3** and **5** under solvothermal conditions. All compounds were well-characterized by different spectroscopic methods. The crystal structures were determined by Single crystal X-ray diffractometry. The oxidation state of +3 in **1** and **4** were confirmed by various methods including XPS, ¹H-NMR and magnetic moment studies. The oxidizing reactivity of Co(III) compounds **1** and **4** with ferrocene derivatives was studied. Both **1** and **4** showed good oxidizing power in acidic medium.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

Authors thank the Council of Scientific and Industrial Research, New Delhi (No. 01(2923)/18/EMR-II) for financial support. LRD acknowledges the support in terms of Senior Research Fellowship from the same CSIR project. Authors also thank Department of Science and Technology for providing us single crystal X-ray diffractometer to the School of Chemical Sciences, Goa University.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2022.132572.

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Structural, Spectroscopic Characterization and Application of a Co(II) Coordination Polymer [Co(suc)(bpm)] · 2H₂O

Luann R. D'souza, Nikita N. Harmalkar, and Sunder N. Dhuri^{*[a]}

A Co(II) coordination polymer [Co(suc)(bpm)] · 2H₂O (**1**) built from succinate (suc) and bipyrimidine (bpm) is synthesized hydrothermally and characterized by different methods. It crystallizes in a monoclinic space group *P2₁/n* with an intriguing 3D polymeric architecture. The weak antiferromagnetic (AF) exchange interactions were evinced by Curie Constant (*C*) = 1.803 cm³mol^{−1}K and a negative Weiss constant

(*q*) = −30.163 K. Type VI adsorption isotherm behavior of **1** at 77 K revealed its non-porous property. Compound **1** was investigated and successfully utilized as an additive in lowering the decomposition temperature of ammonium nitrate (AN) based fuels as demonstrated from TG and DSC experiments performed in nitrogen atmosphere.

Introduction

The metal-organic coordination compounds incorporate the features of inorganic metal ions and organic ligands leading to the construction of intriguing structural topologies with potential applications in areas such as magnetism, catalysis, luminescence, chemical sensing, and more. The selection of suitable organic ligands is crucial for generating robust extended high-dimensional coordination frameworks, for instance zeolitic imidazolate frameworks (ZIFs) represent a class of polymeric compounds containing transition metal ions (Fe, Co, Cu, Zn) linked by only imidazolate ligands serving potential applications. Hence, a combination of flexible aliphatic or aromatic carboxylic acids along with nitrogen-containing auxiliary ligands serve as ideal candidates for the rational design of polymeric coordination compounds with merits.^[1–15] The carboxylate and nitrogen-based ligands usually mediate significant antiferromagnetic (AF) interactions between the paramagnetic metal ions they bridge, thereby generating interesting magnetic systems. Co(II) is deemed to have a rich diversity in magnetic properties like ferromagnetism, antiferromagnetism (AF), canted-spin ferromagnetism, canted-spin antiferromagnetism, spin crossover and long-range ordering.^[16] Taking into consideration these aspects, we have employed succinic acid (H₂suc): a flexible aliphatic dicarboxylate containing two carboxylate groups in 1,4 -positions adopting monodentate and bridging coordination modes and 2,2'-bipyrimidine (bpm): a α -diimine tetradentate ligand.^[16] Succinic acid portrays a range of conformational possibilities owing to the torsional flexibility of the carbon chain and the C–O bonds.^[17] Lately, we have explored the rich structural diversity of Co(II) succinate coordination polymers appended by pyrazine where-

in succinate adopted monodentate as well as bis-monodentate coordination modes to Co(II).^[18] Bpm is known to behave as a terminal bidentate ligand bonding with a transition metal in *cis*-fashion or as a bis-bidentate bridging ligand connecting two metal ions, depending upon the M: bpm molar ratios.^[19–21] These pre-requisites along with solvothermal reaction conditions foster the transmission of electronic interactions between the metals bridged by these ligands.^[18,22–25] There has been a great deal of work committed to the first-row transition metals (Fe, Co, Ni, Zn) bridged by bpm, the M...M separation is usually greater than 5.5 Å making it favourable for AF exchange interactions.^[1,2,18,22,23,26–31] With the surge in employing solid propellants for use in space and military operations, the propellants comprise the oxidizer (perchlorates or nitrates) and polymeric fuels. The propellants based on ammonium perchlorate (AP) release halogenated emissions which are threatening to life and the environment. Hence, ammonium nitrate (AN) is a potential halogen-free replacement that on blending with metal salts or acids was efficient in lowering the temperature and accelerating the decomposition of AN.^[32–38] Hence, our work emphasizes on designing a cobalt(II) coordination polymer by exploiting the excellent coordination abilities of succinic acid and bpm as ligands to yield [Co(suc)(bpm)] · 2H₂O (**1**). A thorough characterization of **1** including X-ray crystal structure determination revealed its intriguing polymeric architecture. In addition to this, the magnetic exchange interactions and the role of **1** in inducing the decomposition of AN were also investigated in this paper.

Results and discussion

Synthesis of [Co(suc)(bpm)] · 2H₂O (**1**)

The synthesis was carried out under hydrothermal conditions in a closed vessel under autogenous pressure. The compositional (solvent, pH of reaction mixture, molar ratio of reactants, concentration, counter ions) and process parameters (pressure, temperature, time) possess a profound effect on the assembly of the ligands with the metal centre to generate the overall

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/slct.202203016>

Table 1. Crystal data and structure refinement for 1.

Empirical formula	C ₁₂ H ₁₄ CoN ₄ O ₆
Formula weight (g mol ⁻¹)	369.19
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /n
a (Å)	10.0230(6)
b (Å)	14.1117(9)
c (Å)	10.1074(6)
α (°)	90
β (°)	96.047(2)
γ (°)	90
Volume (Å ³)	1421.65(15)
Z	4
Calc. Density (mg/m ³)	1.725
Absorption coefficient (mm ⁻¹)	1.246
F(000)	756
Theta range for data collection (°)	2.722 to 28.286
Completeness to theta	99.8
Index ranges	−12 ≤ h ≤ 13, −18 ≤ k ≤ 18, −13 ≤ l ≤ 13
Reflections collected	12691
Independent reflections	3512 (R _{int} = 0.0297)
Refinement method	Full-matrix least-squares on F ²
Absorption correction	None
Data/restraints/parameters	3512/0/224
Goodness-of-fit on F ²	0.952
Final R indices [I > 2σ(I)]	R ₁ = 0.0281, wR ₂ = 0.0654
R indices (all data)	R ₁ = 0.0340, wR ₂ = 0.0688
Largest diff. peak & hole (e.Å ⁻³)	0.607, −0.407
CCDC Number	2179421

structure.^[25] Thus, hydrothermal conditions enhance the solubility of reactants yielding crystals suitable for structural characterization. Hence, it was quite an efficient approach keeping in mind these parameters to get the desired product as already reported in our previous work on synthesizing Co(II)-phenylenediacrylates, succinates and nitro-isophthalates appended by N-donor ligands.^[18,39,40]

Structure Determination of 1

Compound 1 crystallized in the monoclinic P2₁/n space group (Table 1). The asymmetric unit is built from one independent Co(II) ion, two bpm ligands, two suc²⁻ ligands and two crystallization water molecules (Figure 1). Each Co(II) ion coordinates to four nitrogen atoms (N1, N2, N3, N4ⁱⁱ) from two bpm ligands, two oxygen atoms (O1, O4ⁱⁱⁱ) from two suc²⁻ completing the CoN₄O₂ distorted octahedral geometry along with two crystallization water molecules (O1w, O2w). The typical Co–N and Co–O bond lengths lie at 2.1512(14) Å and 2.0299(12) Å respectively as shown in Table S1. This is a consequence of the reduced bite angle of the bpm ligand (76.83° for N1–Co1–N2ⁱ and 77.89° for N3–Co1–N4ⁱⁱ) with bpm adopting the bidentate mode (*Mode I*) when linking a single cobalt atom and the bis-bidentate coordination mode (*Mode II*) linking two cobalt atoms through its nitrogen atoms (Co1–N1 and Co1–N2ⁱ). The aforementioned binding modes adopted by bpm in 1 are depicted in Figure 2.^[1,2,20–23,27,29–31] Both succinate and bpm act as bridging ligands to Co(II) centres with succinate adopting monodentate bridging coordination to Co(II)^[18] and bpm exhibiting the bis-bidentate bridging mode, thus forming an array of chains (Figure 3). On account of the bis-bidentate

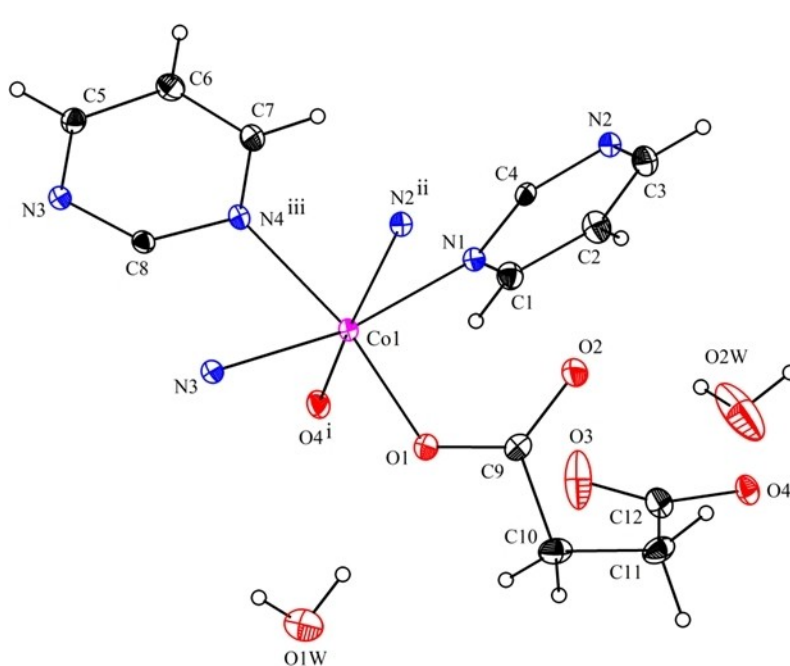


Figure 1. Crystal structure of [Co(suc)(bpm)] · 2H₂O(1) shows the thermal ellipsoids drawn at the 50% probability level for all of the atoms except for the H atoms that are shown as spheres of arbitrary radii. Symmetry codes: (i) $x-1/2, -y+3/2, z+1/2$ (ii) $-x+1, -y+1, -z+1$ (iii) $-x+1, -y+1, -z+2$.

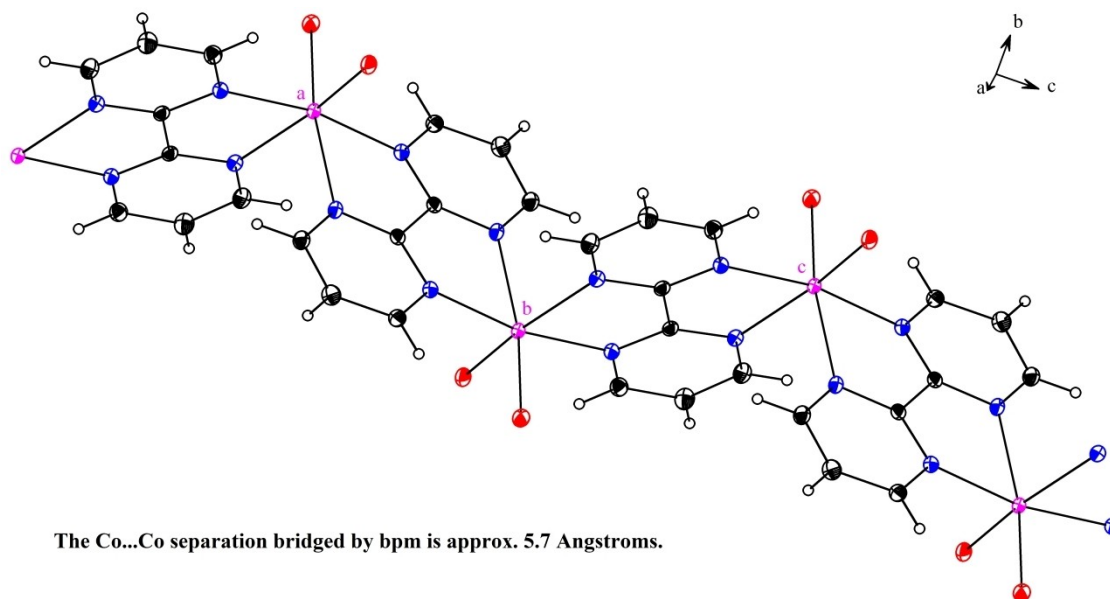


Figure 2. The view of **1** along *a* axis showing the extension of cobalt units through bpm with Co(a)⋯Co(b) separation of 5.703(2) Å [$-x+1, -y+1, -z+1$] and Co(b)⋯Co(c) separation of 5.720(2) Å [$-x+1, -y+1, -z+2$].

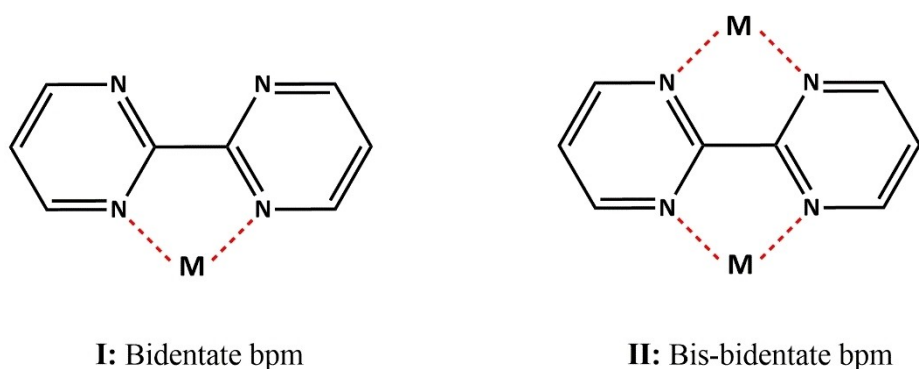


Figure 3. The observed binding modes of bpm in **1**.

chelation mode of bpm, the interchain Co⋯Co separation across bpm is found to be 5.720(3) Å while that for the succinate bridging the Co(II) centres it is 8.792(6) Å, as can be depicted by Figure 4 and Figure S1, lying in accordance with bridging bpmCo(II) compounds reported in the literature (Table S2).^[2,19,20–23,26–30,36] The bpm bridges the Co(II) centres extending along one dimension and thereby extending through the other dimension *via* the succinate ligand to generate a 3D network arrangement with the crystallization water molecules occupying the interstices (Figure S2). On the other hand, an important aspect concerning the succinate ligand bridging the Co(II) centres is the conformational change of *E* and *Z*-forms observed for succinate as shown in Figure S3. The perspective view of **1** along the *c*-axis gives rise to a flower-like supramolecular architecture and the crystallization water molecules present in the interstices give rise to hydrogen

bonding interactions with the succinate (Figure S4–S6, Table S3).

Infrared (IR) spectroscopy

The IR spectroscopy is a versatile tool for detection of functional groups. IR was employed to understand the carboxylate and hydrate binding features along with the rigid bpm linker. The IR spectrum of **1** compared with that of succinic acid and bpm shows features attributed to the composition of the coordination polymer. The strong and broad absorptions centred at 3300 cm^{−1} (O–H stretching vibrations) is due to the lattice water molecules. Medium-to-weak absorptions observed between 2890–3040 cm^{−1} are characteristic of C–H stretching vibrations of the organic ligands. The occurrence of strong absorption at 1550 cm^{−1} (ring stretching modes of bpm) is diagnostic of the *bis*-chelating coordination

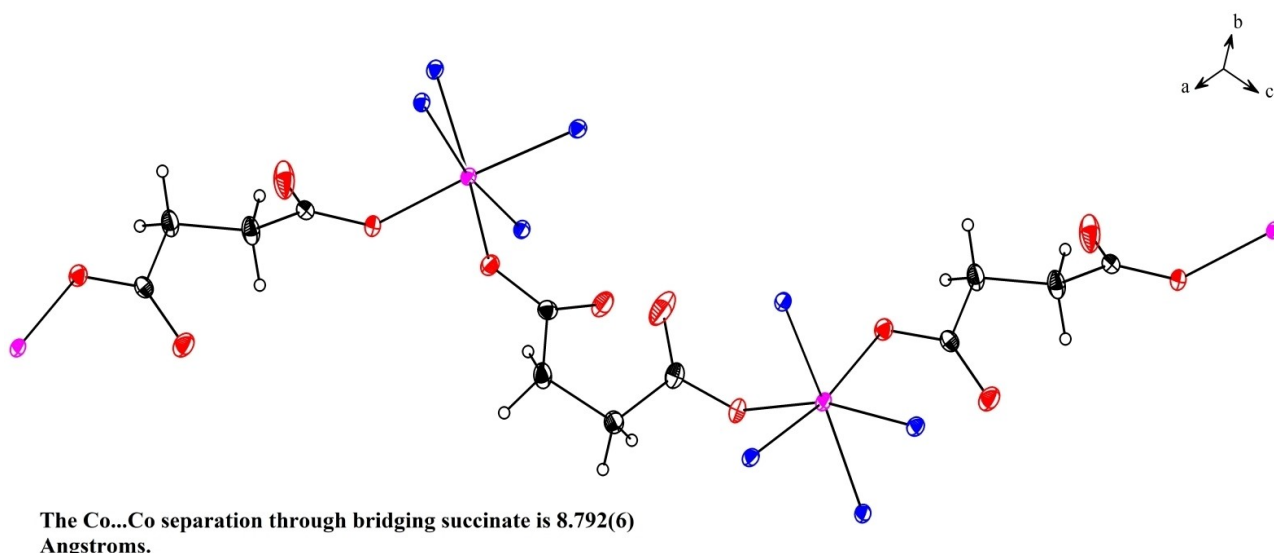


Figure 4. The view of **1** along the *ac* plane shows the extension of cobalt units through succinate with Co1...Co1 separation of 8.792(6) Å [$x + 1/2$, $-y + 3/2$, $z - 1/2$].

mode of bpm which is in agreement with the crystal structure data (*vide supra*). The strong-to-medium absorptions between 1460–1400 cm^{-1} are attributed to the stretching vibrations of succinate (Figure S7).^[2,19,23,26,31]

Thermal Investigation of **1**

The thermal profile of **1** is depicted with thermogravimetric (TG), differential thermal analysis (DTA) and derivative thermogravimetric (DTG) measurements performed between 30–650 °C under air atmosphere. The first weight loss step in the TG lies between 35–115 °C accounting for 10.01% (*calcd.* 9.75%) attributed to two lattice water molecules. This process is evidenced by a small endotherm at 106 °C and 91 °C in the DTA and DTG patterns respectively. Upon dehydration, further heating till 450 °C results in mass loss of 73% (*calcd.* 74.3%) due to ligand decomposition evinced by a sharp exo at 428 °C (DTA) and sharp endo at 403 °C (DTG) (Figure 5). The residue of 16.6% was obtained due to the formation of CoO.

Gas adsorption property

The thermal analysis of **1** revealed loss of two crystallization water molecules at 115 °C followed by robust stability of the dehydrated form up to 310 °C. Moreover, the crystal structural analysis revealed the presence of minute pores as visualised from Mercury 4.2 software (*vide infra*). Hence, this could be the basis for the robust architecture of **1** serving as a trap for selective gas adsorption. In order to calculate the solvent accessible void in **1**, we used the PLATON software to squeeze the two lattice water molecules. The total potential solvent area volume was calculated to be 136.8 Å³ which accounted for 9.6% of the unit cell volume of **1**. Hence, we investigated the nitrogen adsorption property of **1** which was degassed at

100 °C for 2 h to ensure removal of adsorbed moisture. The reversible N₂ sorption profile for **1** at 77 K (Figure 6) demonstrated a type VI adsorption isotherm behaviour which describes the typical layer-by-layer adsorption on a uniform non-porous surface with negligible gas uptake and surface area of 0.946 m² g⁻¹.^[41–47]

X-ray powder diffraction pattern of **1**

On account of the crystal structure of **1** showing the bpm bridging the Co(II) centres extending along one dimension and thereby extending through the other dimension *via* the succinate ligand to generate a 3D network arrangement with the crystallization water molecules occupying the interstices. To investigate the magnetic behaviour of **1** and employ it as an additive in ammonium nitrate-based fuels, we determined the phase purity of **1** by recording its X-ray powder pattern and compared it with the simulated X-ray powder pattern obtained from the crystal structure (Figure S8).^[3]

Field Emission Scanning Electron Microscopy (FESEM) imaging of **1**

We evaluated the morphology of **1** by FESEM imaging at different magnifications. The images were found to display cylindrical rods with agglomeration as depicted in Figure 7.

Magnetic property of **1**

We investigated the magnetic property of the powdered sample of **1** by temperature-dependent magnetic susceptibility (χ_M) measurements under an applied magnetic field of 1000 G between 10–300 K. From the plot of χ_M vs *T* depicting the Zero Field Cooled-Field Cooled (ZFC-FC) curves, the χ_M values were

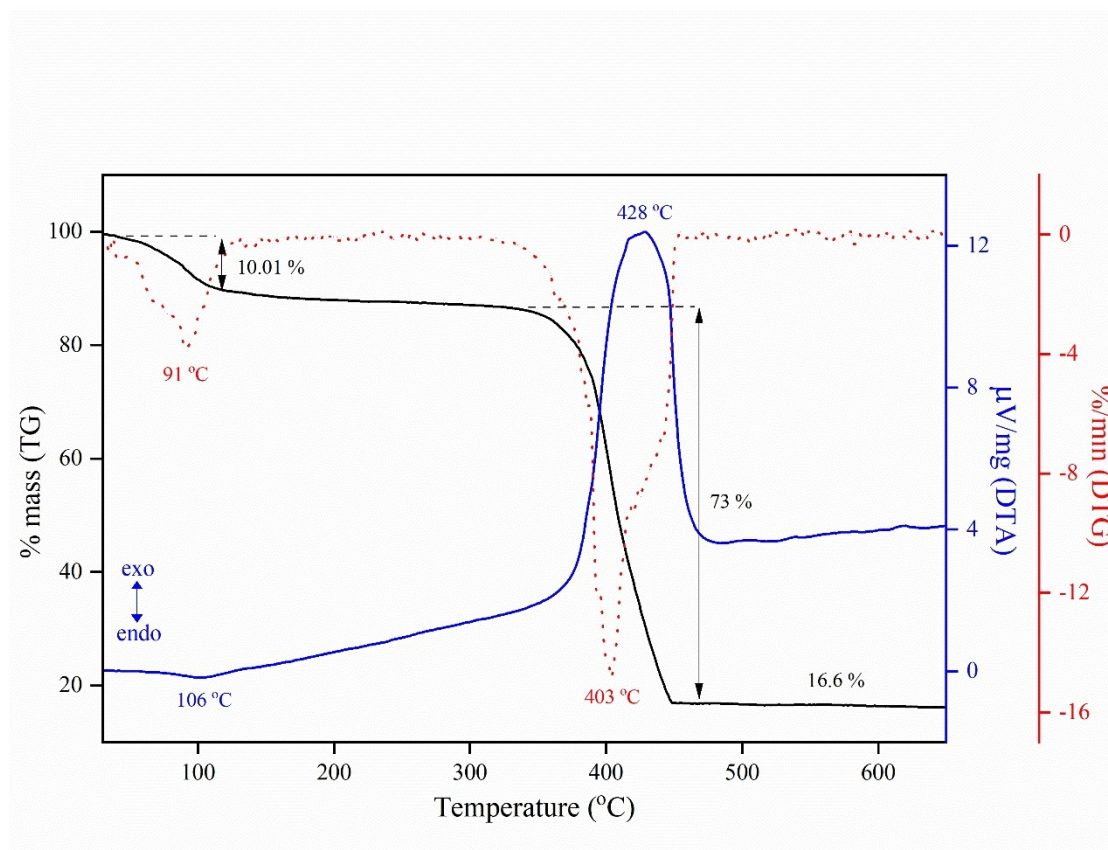


Figure 5. The thermal profile of 1 was depicted by the TG-DTA-DTG plots recorded in the air between 30–650 °C at a heating rate of 10 °C min⁻¹.

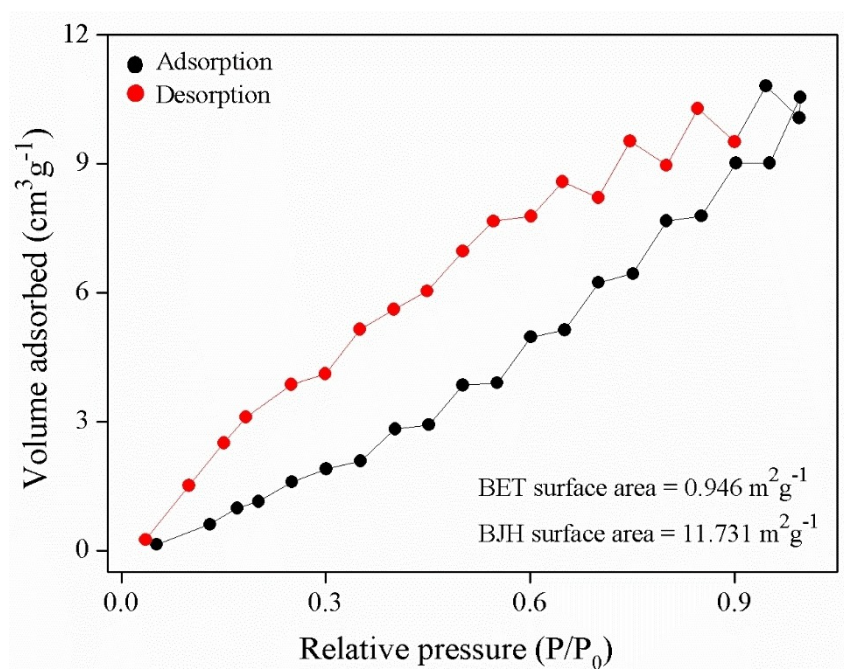


Figure 6. Nitrogen adsorption/desorption isotherms at 77 K for 1; black spheres, adsorption; red spheres, desorption.

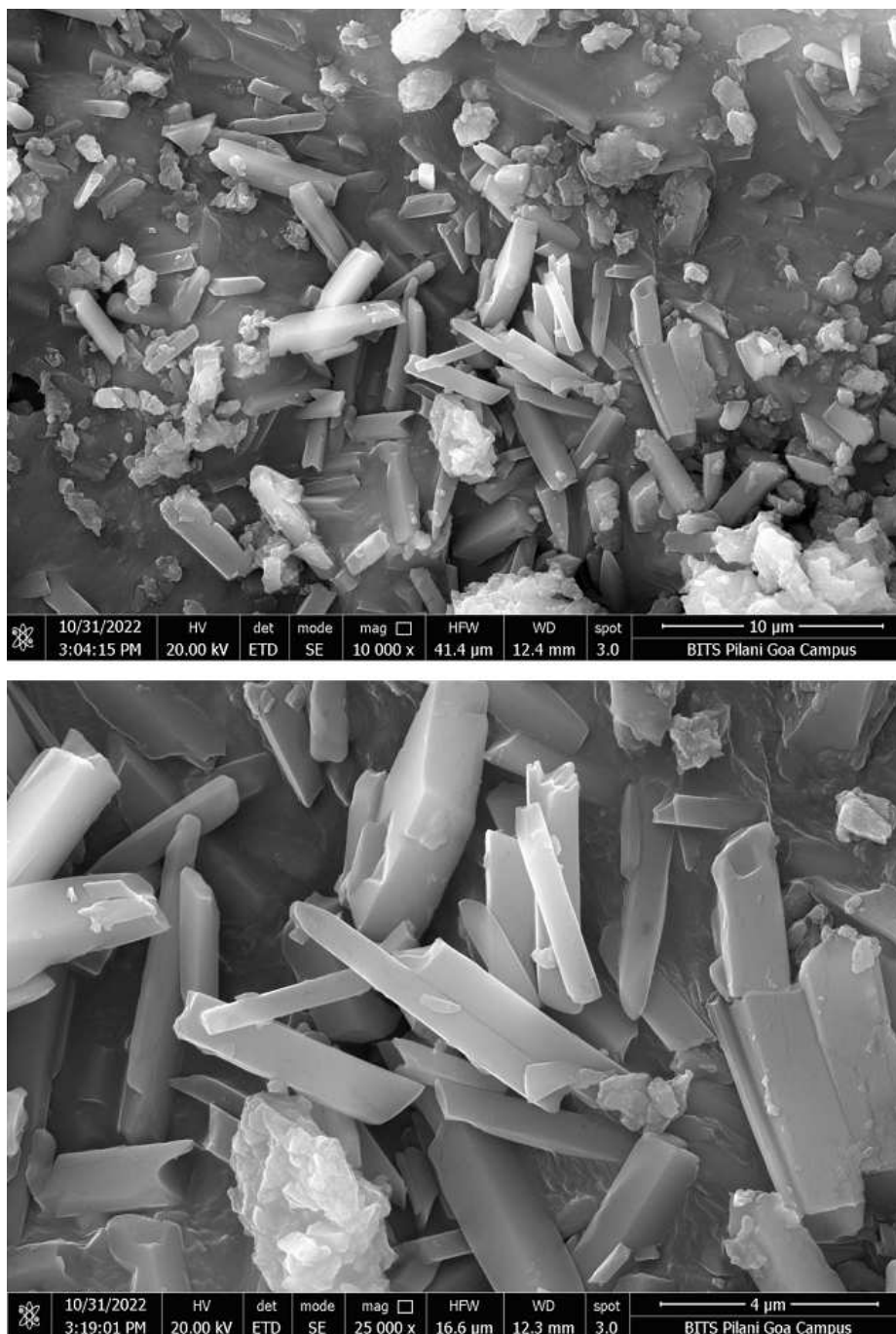


Figure 7. The FESEM images of **1** recorded at magnification scales of 10000X (top) and 25000X (bottom).

found to increase on lowering the temperature with the curves showing minimum bifurcation suggestive of magnetic ordering. The effective magnetic moment was 4.017 BM calculated using $\mu_{\text{eff}} = 2.82(\chi_{\text{M}}T)^{1/2}$, which was slightly higher compared to the calculated spin-only magnetic moment ($\mu_{\text{so}} = 3.873$ BM) for high spin Co(II) $3d^7$ system with $S = 3/2$ due to spin-orbit coupling (Figure 8a).^[16,18,39] Moreover, $\chi_{\text{M}}T$ vs T presented a continuous decrease of $\chi_{\text{M}}T$ values upon cooling to 10 K (Figure 8b). This feature is present in Co(II) compounds showing antiferromagnetic interactions among the Co(II) centres medi-

ated through bridging ligands. The crystal structure analysis (*vide infra*) of **1** shows Co(II) centres with average Co...Co distances of 5.720 Å and 8.792 Å flanked by bridging bpm and succinate respectively, sufficiently good for magnetic interactions to occur. These arise from the fact that single-ion anisotropy and antiferromagnetic (AF) interactions are mediated through ligands bridging the Co(II) centres. The plot of $1/\chi_{\text{M}}$ vs T showed linearity over the entire temperature range obeying the Curie-Weiss law given as; $\chi_{\text{M}} = \frac{C}{T - \phi}$ where χ_{M} is the magnetic susceptibility in $\text{cm}^3 \text{mol}^{-1}$, C is the Curie constant in

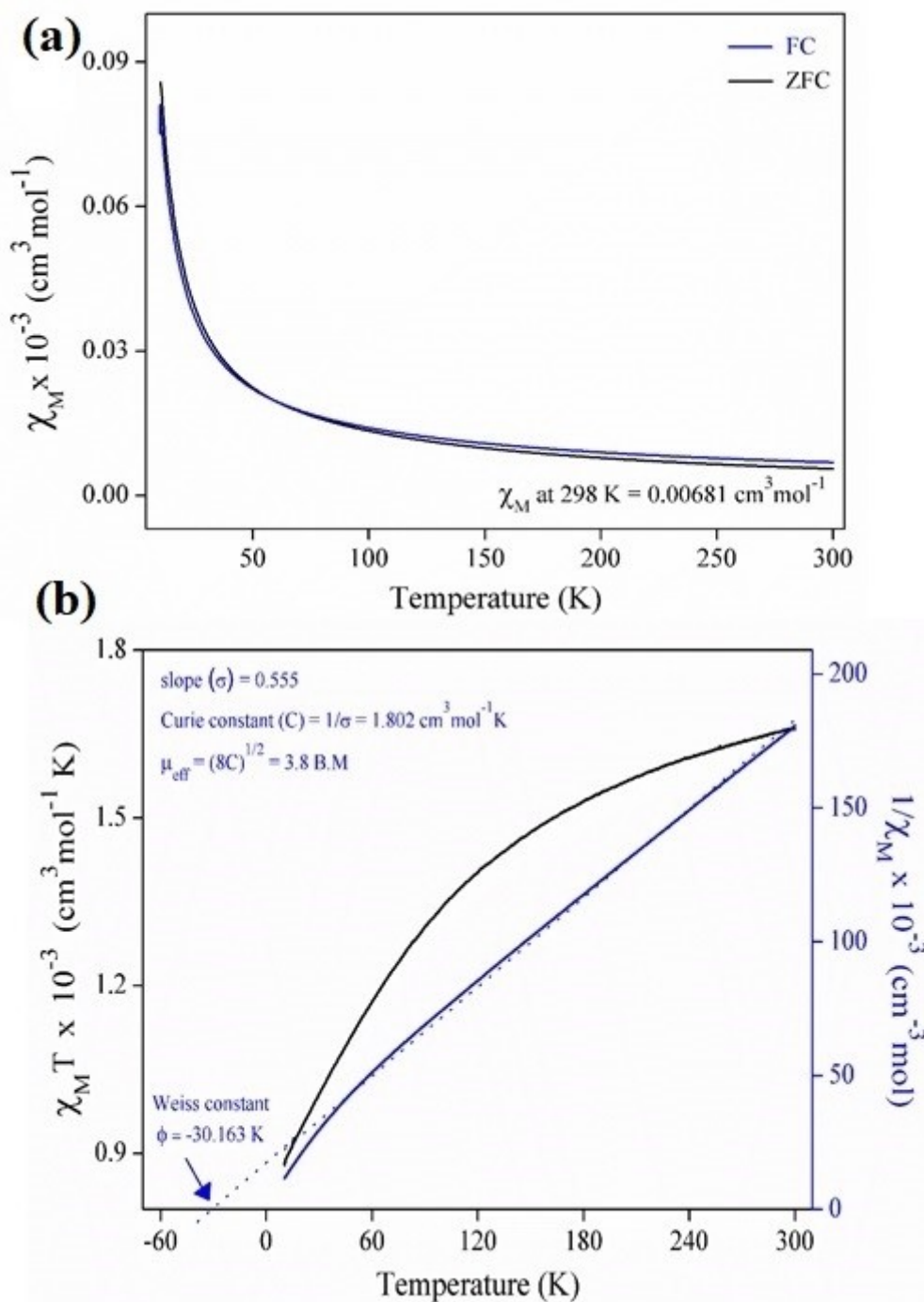


Figure 8. a) The plot of Zero Field Cooled (ZFC)–Field Cooled (FC) magnetic susceptibility for 1 as a function of temperature under an applied field of 1000 G between 10 to 300 K. b) Temperature dependence of $\chi_M T$ and $1/\chi_M$ for 1 under an applied field of 1000 G between 10–300 K. The solid blue line is the theoretical fit to the Curie-Weiss law.

$\text{cm}^3 \text{ mol}^{-1} \text{ K}$, T is the temperature in Kelvin and ϕ is the Weiss constant in Kelvin. A fitting of the Curie-Weiss law on the data gave Curie Constant (C) = $1.803 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ obtained from inverse of the slope and a negative Weiss constant (ϕ) = -30.163 K , suggesting weak antiferromagnetic (AF) exchange interactions, evinced from declining $\chi_M T$ values upon cooling

with an effective magnetic moment of 3.8 BM using $\mu_{\text{eff}} = (8C)^{1/2}$ [1,3,18,21,22,26–29,32,33]

Employing 1 as an additive in the decomposition of ammonium nitrate (AN)

We evaluated the thermal characteristics of AN with 1 by performing thermo gravimetric analysis (TGA)-Differential Thermal analysis (DTA)-Derivative Thermal analysis (DTG) and Differential Scanning Calorimetric (DSC) studies by heating the sample between 35–400 °C in a nitrogen atmosphere at 5 °C min⁻¹ while DSC experiments were conducted on Perkin Elmer DSC 8000 between 50–400 °C in a nitrogen atmosphere at 2 °C min⁻¹.

From the thermal decomposition profile of neat AN (Figure 9a), AN start disintegrating at ~200 °C and thereafter undergoes complete decomposition at 276 °C evidenced by a sharp endothermic peak at 276 °C in the DTA and DTG patterns. The thermal behaviour of AN/1 (20 wt%) (Figure 9b) showed complete decomposition at 248 °C indicated by exothermic and endothermic peaks in the DTA and DTG patterns. Hence, this revealed that the burning rate of AN/1 (20 wt%) as an additive deteriorated faster than the additive-free one (neat AN) with decomposition at 276 °C and 248 °C respectively. Thus, AN/1 (20 wt%) burnt 28 °C lower than that of neat AN, the

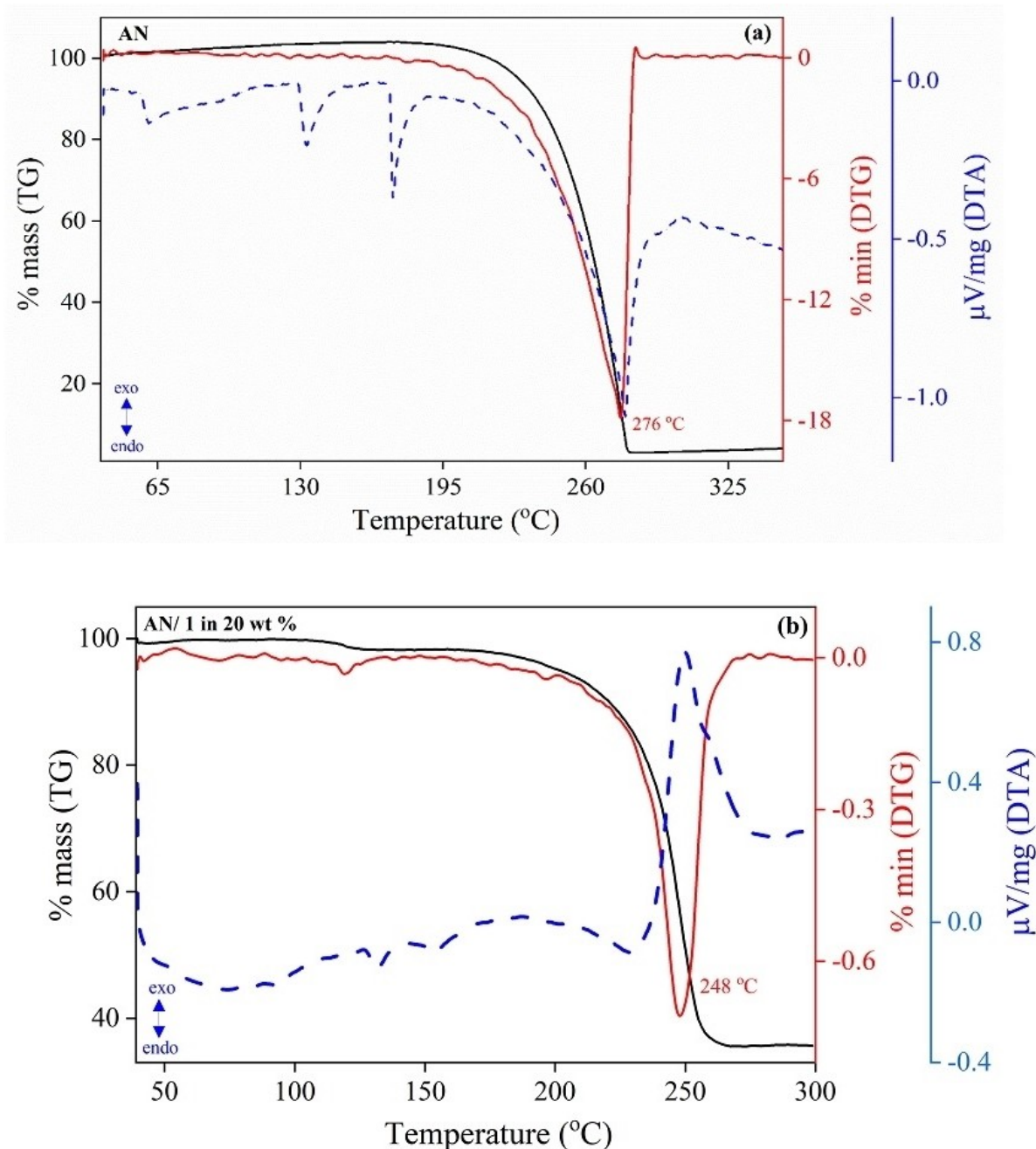


Figure 9. The TG-DTA-DTG plots of (a) neat AN and (b) AN/1 in 20 wt % were carried out between 35–400 °C at a heating rate of 5 °C min⁻¹ in nitrogen atmosphere.

comparative decomposition values for various compounds chosen as an additive in AN decomposition are shown in Table 2.

Moreover, the DSC traces of AN and AN/1 in 20 wt % also revealed similar observations. The DSC traces of neat AN and AN with 1 heated between 50–400 °C at a heating rate of 2 °C min⁻¹ in a nitrogen atmosphere are shown in Figure 10. The DSC of neat AN displayed four distinct endothermic peaks at ~50 °C, and ~120 °C attributed to the phase transitions of AN while that at 169 °C indicated the melting point of AN. The large endothermic event at ~276 °C, represented the thermal decomposition of AN. On comparing the decomposition behaviour of a mixture of AN and 1, we observed only three distinct peaks, at ~50 °C and ~120 °C due to phase transitions with the melting point of AN poorly defined followed by a sharp endothermic peak at 248 °C due to AN decomposition. Hence, these results corroborated with the thermal studies asserting the potential of 1 as an additive in AN-based fuels with less heat evolution.^[34–37]

Table 2. An overview of the compounds used as additive with AN.

Sr. No.	Compound	Decomposition of AN (°C)	Reference
1	AN/Nano triaminoguanidine nitrate	252	[35]
2	AN/NaCl	264	[36]
	AN/NH ₄ Cl	256	
	AN/KCl	256	
	AN/CaCl ₂	266	
3	AN/Basic Cu(II) nitrate	260	[37]
4	Neat AN	276	Our work
5	AN/1 in 20 wt %	248	Our work

Conclusions

A new coordination polymer, [Co(suc)(bpm)] · 2H₂O (1) has been synthesised and characterized by several techniques. The crystal structure of 1 exhibits a flower-like supramolecular network. The bridging succinate and bpm mediates magnetic exchange interactions between the Co(II) centres with weak antiferromagnetic exchange interactions. Compound 1 demonstrated a type VI nitrogen adsorption isotherm and was an efficient additive in lowering the exothermic decomposition of AN.

Experimental section

Materials and analysis

All chemicals and solvents were commercially available and used without further purification. The disodium salt of succinic acid (Na₂suc) was prepared by the slow addition of NaHCO₃ to the hot aqueous solution of succinic acid (2:1), followed by slow evaporation to give white crystalline flakes. The composition of Na₂suc was studied by IR spectroscopy and elemental analysis (C, H, & N). The necessary safety measures were taken during autoclave syntheses using Teflon-lined stainless steel vessels heated in a temperature-controlled oven (ANTS). The IR spectrum of the powdered compound was recorded on dilution with KBr on Shimadzu (IR Prestige-21) FT-IR spectrometer in the region 4000–350 cm⁻¹ at a resolution of 4 cm⁻¹. Elemental analyses (C, H & N) were performed on ElementarVarioMicro Cube CHNS Analyzer. The variable-temperature magnetic susceptibility data were obtained on a Vibrating Sample Magnetometer with the sensitivity of a SQUID (Superconducting Quantum Interference Device) of model Quantum Design, MPMS-3 operated between 10–300 K with an applied field of 1000 G. Thermogravimetric analysis accompanied

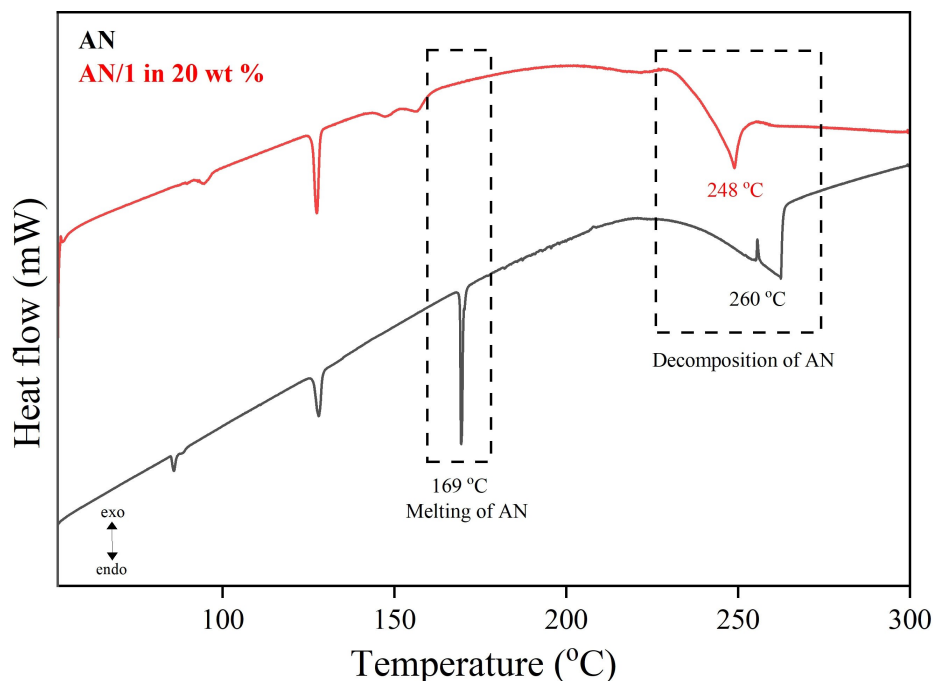
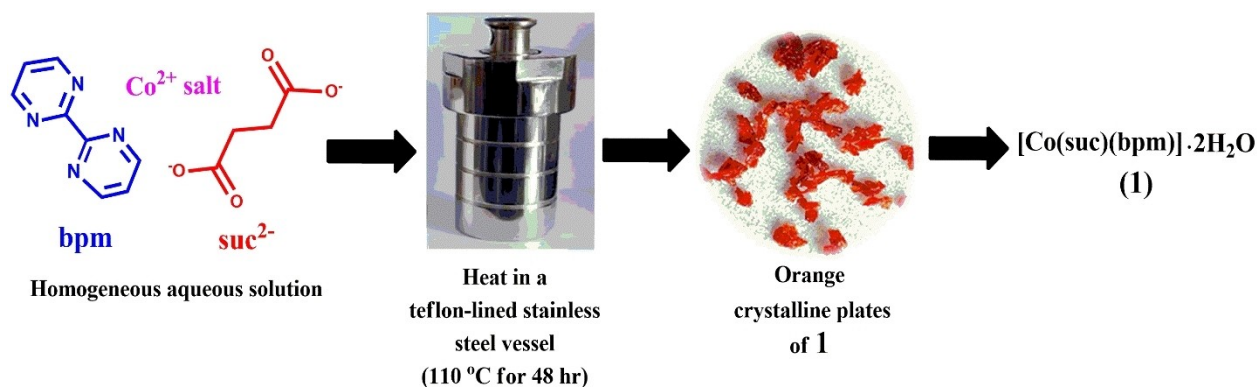


Figure 10. The DSC traces of AN and AN/1 in 20 wt % were carried out between 50–400 °C at a heating rate of 2 °C min⁻¹ in nitrogen atmosphere.



Scheme 1. Synthetic methodology for compound 1.

by Differential thermal analysis (DTA) and Derivative thermal gravimetry (DTG) were carried out on Netzsch STA 409 analyzer under air atmosphere from RT to 650 °C at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) was performed on Perkin Elmer DSC 8000 analyzer under a nitrogen atmosphere from 50–650 °C at a heating rate of 2 °C min⁻¹. X-ray powder diffraction (PXRD) patterns were collected on a RIGAKU ULTIMA IV diffractometer using Cu–K α (λ = 1.5418 Å) with a Ni filter. The ambient pressure volumetric N₂ adsorption–desorption measurements were performed at 77 K maintained by low-temperature liquid nitrogen assembly. The sample was outgassed at 100 °C for 2 h. The adsorption data in the pressure range < 0.1 P/P₀ were fitted to the Brunauer–Emmett–Teller (BET) equation to determine the surface area. The Field Emission Scanning Electron Microscope (FESEM) imaging was done on Quanta FEG 250 at 20 KV with a magnification ranging 10000X–25000X.

Single crystal X-ray diffraction

The single crystals of **1** were structurally analyzed on a Bruker D8 Quest Eco model X-ray diffractometer equipped with Mo-(K α) = 0.71073 Å radiation at 100 K. The X-ray diffraction intensities were collected, integrated, and scaled and unit cell parameters were determined using the program suite APEX3 (Version 2018.1). The structure was solved by direct methods with SHELXS and subsequent refinements on F² using full-matrix least-squares methods were performed with SHELXL.^[48] The non-hydrogen atoms were refined with the anisotropic displacement parameters while the hydrogen atoms were located at the calculated positions.

Synthesis of [Co(suc)(bpm)] · 2H₂O (**1**)

An aqueous solution (2 mL) of Co(NO₃)₂ · 6H₂O (1 mmol, 0.291 g) was added dropwise to an aqueous mixture (3 mL) of disodium succinate (1 mmol, 0.162 g) and bpm (3 mmol, 0.474 g). The resulting orange solution was stirred at room temperature (RT) for 5 mins and then transferred into a 10 mL Teflon-lined stainless steel autoclave which was heated at 110 °C for 48 hours under autogenous pressure (Scheme 1). Orange plate-like crystals of **1** were obtained, separated and dried in air (Yield = 0.055 g). *Anal. Calc.* for 1 C₁₂H₁₄N₄O₆Co (Mr = 369.2): C, 39.04; H, 3.82; N, 15.18. *Found*: C, 38.55; H, 3.75; N, 15.01. *IR* (KBr, cm⁻¹): 3680 (w), 3300 (br), 3033 (w), 2327 (w), 1970 (w), 1765 (w), 1560 (s), 1424 (s), 1245 (s),

1155 (s), 1117 (s), 1040 (s), 937 (s), 900 (s), 835 (s), 758 (s), 670 (s), 502 (s), 464 (s).

CCDC: Deposition Number 2179421, contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Acknowledgements

SND and LRD gratefully acknowledge financial support from CSIR (Grant No. 01(2923)/18/EMR-II). The authors acknowledge IISER Bhopal for assisting with the SQUID-VSM facility and BITS Pilani Goa for FESEM imaging

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Ammonium nitrate · anti-ferromagnetic · bipyrimidine · coordination polymer · hydrothermal

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Submitted: August 2, 2022

Accepted: November 18, 2022

Construction of Pyrazine-Appended 1D and 3D Cobalt(II) Succinate Coordination Polymers: Influence of Solvent on Architectures and Applications in Gas Adsorption and NAC Detection

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Cite This: *ACS Omega* 2022, 7, 5698–5712



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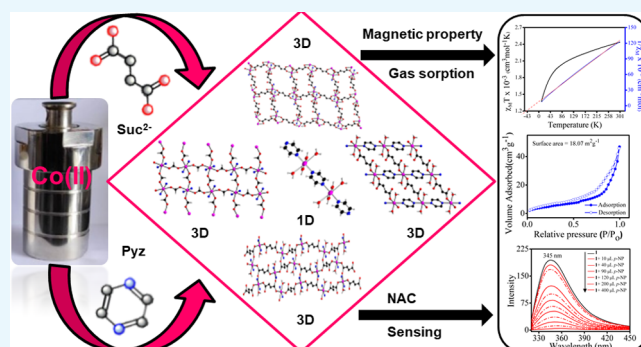


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Supporting Information

ABSTRACT: An underexplored reaction of pyrazine (rigid and linear) and succinic acid (flexible) with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ afforded four new coordination polymers (CPs): $[\text{Co}(\text{H}_2\text{O})(\text{pyz})(\text{suc})]$ (1), $[\text{Co}(\text{H}_2\text{O})_2(\text{pyz})(\text{suc})]$ (2), $[\text{Co}(\text{H}_2\text{O})_4(\text{pyz})(\text{suc})]$ (3) and $[\text{Co}_2(\text{H}_2\text{O})_2(\text{pyz})(\text{suc})_2]$ (4), as well as $[\text{Co}(\text{HCO}_2)_2(\text{pyz})]$ (5) being lately reported along with well-known 6 and 7. The CPs were obtained as stable crystalline materials and characterized by conventional solid-state techniques, including X-ray crystallography. Hydrothermally produced compounds 1 and 2 were both 3D CPs. While 3 and 4 obtained under ambient/solvothermal conditions in DMSO generated 1D and 3D structures, 5 isolated from DMF under solvothermal conditions had a 3D structure. The topologies of the coordination polymers 1–7 were described by underlying nets 3D 5-c *fet*, 3D 4-c *cds*, 1D 2-c *2C1*, 3D 5-c *bnn*, 3D 6-c *rob*, 1D 2-c *2C1*, and 3D 6-c *pcu*, respectively. The plot of χ_M^{-1} versus T was essentially linear in the entire temperature range following the Curie–Weiss law with a Curie constant (C) of 2.525 and a negative Weiss constant (ϕ) of -46.24 K, suggesting weak antiferromagnetic (AF) exchange interactions. CO_2 and N_2 adsorption studies of 1–5 featured type III isotherms. 1 was found to show remarkably higher quenching efficiencies for nitrophenols ($\eta = 98\%$ for *o*-NP) over other NACs. The Stern–Volmer plot exhibited deviation in linearity with K_{sv} values about 200 times greater than that for the simplest nitroaromatic compound (NB), signifying its exclusive quenching ability toward 1. The LOD for *p*-NP addition to 1 was found to be 0.995 ppm.



INTRODUCTION

Coordination polymers and metal–organic frameworks (MOFs) form an interdisciplinary area of research with MOFs endorsing high porosity, thermal stability, robustness, tunable metrics, and organic functionality, resulting in intriguing structural diversities.^{1–4} The sewing of molecular building units by strong bonds into predetermined extended structures alongside weak noncovalent interactions (hydrogen-bonding, π – π stacking, and van der Waals forces) generates supramolecular assemblies.^{5–9} These play promising roles in applications such as catalysis,^{10–12} chemical adsorption,^{13,14} gas adsorption,^{15–19} and magnetism.^{20–24} Hydro(solvo)-thermal conditions alongside the compositional and process parameters assist the formation of M–O–M extensions having a profound effect on the overall structure and stability.^{25–30} The employment of mixed ligands favors frameworks with diverse structural motifs, in comparison to using only one type of ligands. Flexible dicarboxylates in combination with linear rodlike ligands mediate the construction of coordination polymers (CPs) ranging from 1D to 3D networks. Hence, the ligands chosen, i.e., succinic acid and pyrazine, serve as

suitable candidates. Succinic acid is flexible containing two carboxylate groups in 1,4-positions adopting monodentate, bridging, and bridging chelate coordination modes to the metal as seen in our work, while pyrazine is a rigid-planar bidentate diimine ligating through the μ_2 bridging mode. There is growing recognition for such systems in the field of molecular magnetism as they act as antiferromagnetic (AF) couplers in transition-metal complexes.

With industrialization, there has been exploitation of organic dyes, nitroaromatic compounds (NACs), causing a serious threat to the environment and health. This has triggered the development of fluorescent sensor materials for the selective and judicious detection of organic dyes and removal of harmful

Received: September 20, 2021

Accepted: January 21, 2022

Published: February 10, 2022



Table 1. Crystal Data and Structure Refinement Parameters for 1–4

empirical formula	C ₈ H ₁₀ CoN ₂ O ₅ 1	C ₈ H ₁₂ CoN ₂ O ₆ 2	C ₄ H ₁₆ CoN ₂ O ₈ 3	C ₁₂ H ₁₆ Co ₂ N ₂ O ₁₀ 4
formula weight (g mol ^{−1})	273.11	291.13	327.16	466.13
temperature (K)	296(2)			
wavelength (Å)	0.71073			
crystal system	monoclinic	monoclinic	orthorhombic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> <i>n</i> <i>n</i> <i>m</i>	<i>P</i> <i>1</i>
<i>a</i> (Å)	7.1468(2)	12.7414(5)	10.316(4)	7.7368(4)
<i>b</i> (Å)	17.7533(6)	6.7729(2)	7.114(3)	9.0843(5)
<i>c</i> (Å)	8.5534(2)	13.4227(4)	9.458(4)	11.321(6)
α (deg)	90	90	90	90.118(1)
β (deg)	103.3180(1)	107.6590(1)	90	99.312(1)
γ (deg)	90	90	90	97.756(1)
volume (Å ³)	1056.06(5)	1103.75(6)	694.1(5)	777.78(7)
<i>Z</i>	4	4	2	2
calcd density (mg m ^{−3})	1.718	1.752	1.565	1.99
absorption coefficient (mm ^{−1})	1.632	1.574	1.271	2.194
<i>F</i> (000)	556	596	338	472
diffractometer	Bruker D8 Quest Eco			
theta range for data collection (deg)	2.703–28.302	3.185–28.283	2.922–28.319	2.872–28.264
completeness to theta	98.4	99.7	100	100
index ranges	−8 ≤ <i>h</i> ≤ 9 −21 ≤ <i>k</i> ≤ 23 −11 ≤ <i>l</i> ≤ 9	−16 ≤ <i>h</i> ≤ 14 −9 ≤ <i>k</i> ≤ 8 −17 ≤ <i>l</i> ≤ 17	−13 ≤ <i>h</i> ≤ 13 −9 ≤ <i>k</i> ≤ 9 −12 ≤ <i>l</i> ≤ 12	−10 ≤ <i>h</i> ≤ 10 −12 ≤ <i>k</i> ≤ 12 −15 ≤ <i>l</i> ≤ 15
reflections collected	10 816	8722	8915	11 979
independent reflections	2586 (<i>R</i> _{int} = 0.0314)	1364 (<i>R</i> _{int} = 0.049)	924 (<i>R</i> _{int} = 0.0326)	3853 (<i>R</i> _{int} = 0.0315)
refinement method	full-matrix least-squares on <i>F</i> ²			
absorption correction	semiempirical from equivalents			
data/restraints/parameters	2586/0/151	1364/0/85	924/0/56	3845/0/247
goodness-of-fit on <i>F</i> ²	1.063	1.066	1.196	1.054
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0281, <i>wR</i> ₂ = 0.0629	<i>R</i> ₁ = 0.0294, <i>wR</i> ₂ = 0.0676	<i>R</i> ₁ = 0.0357, <i>wR</i> ₂ = 0.0793	<i>R</i> ₁ = 0.0309, <i>wR</i> ₂ = 0.0664
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0389, <i>wR</i> ₂ = 0.0693	<i>R</i> ₁ = 0.0472, <i>wR</i> ₂ = 0.0772	<i>R</i> ₁ = 0.0422, <i>wR</i> ₂ = 0.083	<i>R</i> ₁ = 0.0449, <i>wR</i> ₂ = 0.0737
largest diff. peak and hole (e Å ^{−3})	0.516, −0.424	0.317, −0.425	0.573, −0.451	0.472, −0.541
CCDC number	2098543	2098544	2098545	2098548

substances. One promising approach toward NAC detection is the use of fluorescent electron-rich MOFs undergoing quenching on interaction with electron-deficient nitroaromatic molecules. Fluorescence sensing is a promising strategy to tackle the detection of nitro explosives owing to its low cost, electronic tunability, portability, and easy operation.^{31–37} To the best of our knowledge, the MOFs with succinate and pyrazine linkers together have not been explored, and only the coordination polymer [Cd₂(H₂O)₂(pyz)(suc)₂] has been reported.³⁸ In addition to this, compounds [Co(HCOO)₂(pyz)] **5** and [Co(H₂O)₄(suc)] **6** are well-known.^{39,40} Hence, bearing in mind the less explored chemistry of cobalt(II) with succinate and pyrazine, we have attempted the synthesis of five cobalt(II) coordination polymers by tuning the synthetic conditions and the solvent. On our way to prepare compounds **1**–**5**, we obtained **6** and **7** as secondary products. We investigated the gas sorption ability of the compounds for N₂ and CO₂ gases. In addition, we have tested **1** for its selective detection of nitroaromatic compounds (NACs).

RESULTS AND DISCUSSION

Structural Description. Single-Crystal Structure Determination. The single crystals of **1**–**7** were determined using a Bruker D8 Quest Eco X-ray diffractometer at 296 K, equipped

with Mo K α (λ = 0.71073 Å) radiation. The program suite APEX3 (version 2018.1) was used to integrate the frames, perform absorption correction, and determine the unit cell. The structures were solved with SHELXS, and subsequent refinements on *F*² using full-matrix least-squares methods were performed with SHELXL.⁴¹ The refinement of nonhydrogen atoms was performed in an anisotropic manner, while the hydrogen atoms were located at calculated positions.

[Co(H₂O)(pyz)(suc)] (**1**). X-ray analysis of **1** revealed its crystallization in the monoclinic *P*2₁/*c* space group (Table 1). The asymmetric unit consists of one Co(II), one pyz, one suc^{2−}, and one water molecule. Three oxygen atoms from each succinate ligand (O1, O3ⁱ, O4ⁱⁱ), one water molecule (O5w), and two nitrogen atoms from the bridging pyrazine (N1 and N2ⁱⁱⁱ) complete the octahedral coordination of Co(II) (Figure 1). The typical Co–O bond length varies from 2.061 to 2.101 Å, with Co–N distances ranging 2.169–2.188 Å, and that for Co–O5w is 2.083 Å (Table S1), which clearly indicates distortion from the ideal octahedral geometry. These measures are comparable to Co(II) compounds containing succinate or pyrazine (Table S2).^{8,42–46} The oxygen atoms of succinate adopt monodentate coordination to cobalt i.e., one oxygen atom coordinated to cobalt (κ -O) (mode I depicted in Table 2). The succinate ligands adopt anti–anti conformation with torsion angle χ [C(1)C(2)C(3)C(4)] = −168.62°. The

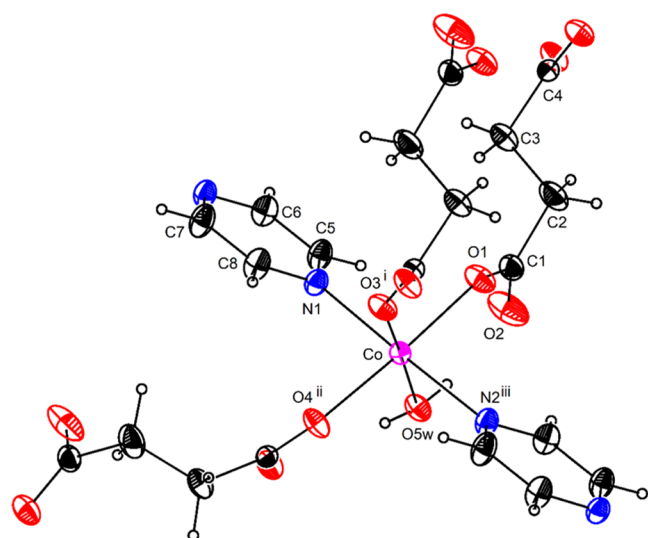


Figure 1. Crystal structure of $[\text{Co}(\text{H}_2\text{O})(\text{pyz})(\text{suc})]$ **1**, showing the thermal ellipsoids drawn at the 50% probability level for all of the atoms except for the H atoms that are shown as spheres of arbitrary radii. Symmetry code: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, y + 1/2, -z + 3/2$; and (iii) $x + 1, y, z$.

orientation of carboxylate with respect to the backbone line of succinate generates angles $[\text{O}(1)\text{C}(1)\text{C}(2)]$, $[\text{O}(4)\text{C}(4)-\text{C}(3)]$, and $[\text{O}(3)\text{C}(4)\text{C}(3)]$ equal to 116.63° , 117.86° , and 119.37° , respectively.^{38,47} Pyrazine ligates cobalt via κ -N mode.^{38,48–54} On viewing **1** along the c direction, pyz forms a bridge between the cobalt centers with an intrachain Co...Co separation distance of $7.147(0)$ Å (Figure 2). While on perceiving **1** in the a -axis (Figure S1), two rings are seen: a 14-membered ring built from two cobalt centers $[\text{Co}(\text{a})$ and $\text{Co}(\text{b})]$ stitched in a *cis* fashion by sharing two succinate oxygen atoms ($\text{O}1$ and $\text{O}3^{\text{i}}$) in the *bis*-monodentate mode and a larger 22-membered ring composed of four cobalt centers $[\text{Co}(\text{b})$ and $\text{Co}(\text{e})]$ connected by $\text{O}4^{\text{ii}}$ and $\text{O}1$ of succinate in the *bis*-monodentate fashion and $\text{Co}(\text{c})$ and $\text{Co}(\text{d})$ linked via $\text{O}1$ and $\text{O}4^{\text{ii}}$ of succinate in the same mode. On observing the ring structures, it can be seen that the water molecules lie within the bigger ring, while they are disposed of outside the 14-membered ring. The Co...Co separation distance in the smaller ring is $7.275(1)$ Å, while that in the larger ring is

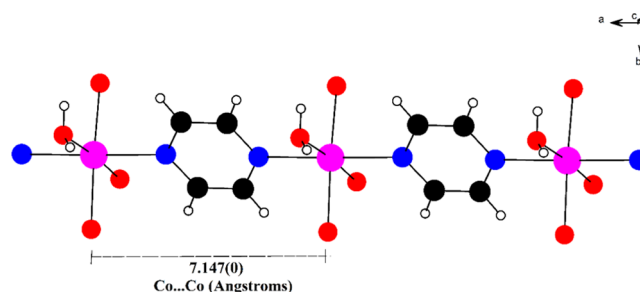


Figure 2. View of **1** showing extension of pyrazine along the c -axis.

$12.412(1)$ Å. The molecular packing of **1** viewed along the a^* -axis displays a 3D array (Figure S2).

To understand the coordination modes of the ligands forming the framework, we performed a topological analysis of **1**.⁵⁵ The succinate ligand bridges three cobalt centers by involving three oxygen donor atoms. Following the notation of the coordination mode for succinate anion as T^3 , the overall coordination formula of **1** is $\text{AT}^3\text{B}^2\text{M}^1$. The underlying net of **1** is 3,5-*c* *fet* due to succinate that coordinates three Co atoms (hence 3-*c*) and 5-*c* Co atoms that connect two pyrazine and three succinate molecules (Table 3).^{56–58} The hydrogen-bonding interactions of **1** are summarized in Table S3.

$[\text{Co}(\text{H}_2\text{O})_2(\text{pyz})(\text{suc})]$ (**2**). It crystallizes in the monoclinic $\text{C}2/c$ space group (Table 1). The asymmetric unit is composed of two oxygen atoms ($\text{O}2$ and $\text{O}2^{\text{i}}$) of succinate, two nitrogen atoms from two different pyrazine ligands ($\text{N}1$ and $\text{N}1^{\text{i}}$), and two water molecules ($\text{O}1\text{w}$ and $\text{O}1\text{w}^{\text{i}}$) (Figure 3). Succinate also adopts monodentate coordination to cobalt, i.e., one oxygen atom coordinated to cobalt (κ -O) and one pyz ligated cobalt via κ -N mode, as seen in **1**. The typical Co–O, Co–N, and Co– $\text{O}1\text{w}$ bond distances measure 2.064 , 2.207 , and 2.111 Å, respectively (Table S1), lying in accordance with **1** and reported cobalt(II) compounds containing succinate or pyrazine (Table S2).^{8,42–46} The succinate ligands adopt *gauche* conformation with torsion angle $\chi[\text{C}(3)\text{C}(4)\text{C}(4')-\text{C}(3')] = -59.41^\circ$, and the orientation of the carboxylate groups with respect to the C–C backbone of succinate generates angle $[\text{O}(2)\text{C}(3)\text{C}(4)] = 116.71^\circ$. The intrachain Co...Co separation distance through bridging pyz is $7.215(0)$ Å, and that bridged by succinate is $7.726(5)$ Å (Figure S3a,b).^{38,47–54} The propagation of **2** in the b direction through succinate results in the formation of rectangular grids of

Table 2. Observed Coordination Modes for Succinate in **1–6**

Sr. No.	Oxygen atoms of suc^{2-} coordinating	Coordination mode to Co
1		Mode I: Monodentate κ -O seen in 1 , 2 and 6 .
2		Mode II: Bridging κ -O for Co1 and Co2 seen in 4 .
3		Mode III: Bridging chelate κ^2 -O, O' and κ -O seen in 4 .

Table 3. Coordination Formulae and Net Representations for 1–6

compound	chemical formula	space group	dimension	coordination formula	ligand composition	observed net
1	C ₈ CoH ₁₀ N ₂ O ₅	<i>P21/c</i>	3D	AT ³ B ² M ¹	H ₂ O[M ¹] C ₄ H ₄ O ₄ [T ³] C ₄ H ₄ N ₂ [B ²]	fet
2	C ₈ CoH ₁₂ N ₂ O ₆	<i>C2/c</i>	3D	AB ₂ ² M ₂ ¹	C ₄ H ₄ N ₂ [B ²] H ₂ O[M ¹] C ₄ H ₄ O ₄ [B ²]	cds
3	C ₈ CoH ₁₄ N ₂ O ₈	<i>Pnmm</i>	1D	AB ² M ₄ ¹	C ₄ H ₄ N ₂ [B ²] H ₂ O[M ¹] C ₄ H ₄ O ₄ [0D-not coordinated]	linear chain
4	C ₆ CoH ₈ NO ₅	$\bar{P}1$	3D	A ₄ K ²² K ⁴ T ₂ ¹¹ B ₂ ² M ₄ ¹	C ₄ H ₄ N ₂ [B ²] H ₂ O[M ¹] C ₄ H ₄ O ₄ [K ⁴] C ₄ H ₄ O ₄ [K ²²] C ₄ H ₄ O ₄ [T ¹¹]	twofold bnn
5	C ₆ CoH ₆ N ₂ O ₄	<i>C2/c</i>	3D	AB ₃ ²	C ₄ H ₄ N ₂ [B ²] CHO ₂ [B ²]	rob
6	C ₄ CoH ₁₂ O ₈	<i>P21/c</i>	1D	AB ² M ₄ ¹	H ₂ O[M ¹] C ₄ H ₄ O ₄ [B ²]	linear chain

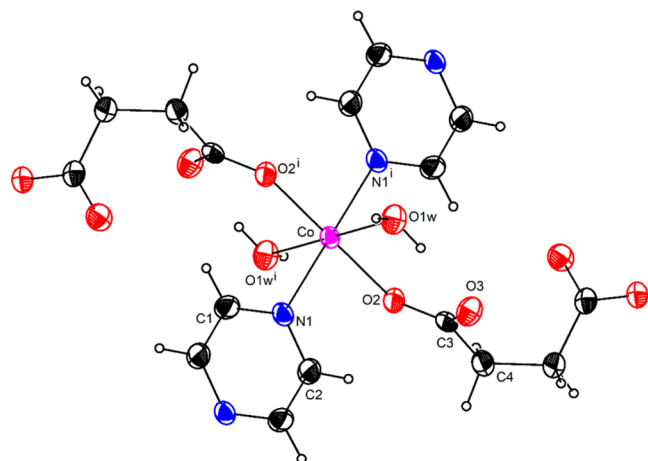


Figure 3. Crystal structure of [Co(H₂O)₂(pyz)(suc)] (**2**), showing the thermal ellipsoids drawn at the 50% probability level for all of the atoms except for the H atoms that are shown as spheres of arbitrary radii. Symmetry code: (i) $-x + 3/2, -y + 3/2, -z + 1$.

7.215(0) × 7.726(5) Å dimensions (Figure 4). Topological study of **2** reveals succinate bridging of two cobalt centers in

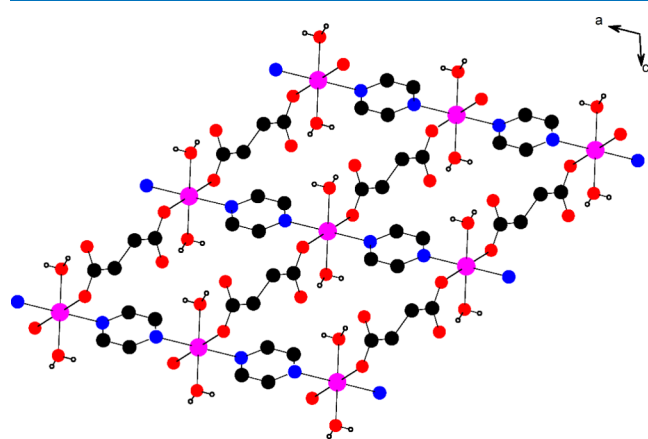


Figure 4. Packing diagram of **2** viewed along the *b* direction displaying rectangular channels formed between interlayered pyrazine bridges.

the *bis*-monodentate fashion by coordination of two oxygen atoms of one succinate linking to two cobalt atoms. Hence, the coordination mode for succinate is B (two donor oxygen atoms used in total), and since $m = 2$, it becomes B². On the other hand, pyrazine adopts coordination mode B^{2*} since it uses two donor atoms (N atoms) for coordination and connects to two cobalt atoms via one donor atom each ($m = 2$). Finally, two terminal water molecules have coordination mode M¹ as each water molecule possesses one donor atom and coordinates one

cobalt atom ($m = 1$). The coordination formula of **2** is represented as AB²B²M¹.⁵⁵ The topological analysis of **2** resulted in the 4-connected underlying net **cds** with both pyrazine and succinate 2-*c* bridged (Table 3).^{56,59} The subnets {Co(pyrazine)} and {Co(suc)} are represented by 2-*c* simple chains intersecting at the Co atoms. The hydrogen-bonding interactions in **2** are shown in Table S3.

[Co(H₂O)₄(pyz)₂](suc) (**3**). On switching the reaction in DMSO under room temperature conditions, bright orange crystalline plates of **3** were obtained, which crystallized in the orthorhombic *Pnmm* space group (Table 1). The crystal structure shows cobalt coordinated to two nitrogen atoms of pyz (N1 and N1ⁱⁱⁱ), four oxygen atoms of water (O1w, O1wⁱ⁻ⁱⁱⁱ), and an uncoordinated succinate dianion (Figure 5).

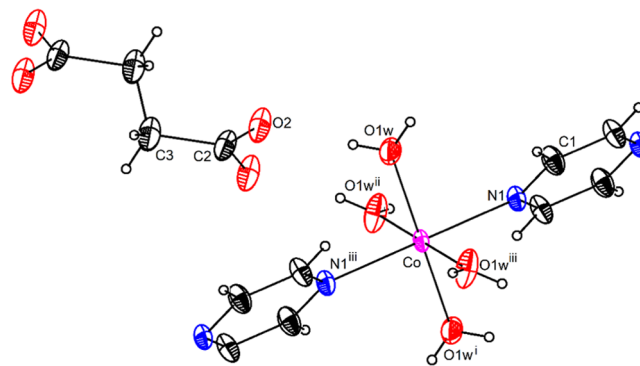


Figure 5. Crystal structure of [Co(H₂O)₄(pyz)](suc) (**3**) showing the thermal ellipsoids drawn at the 50% probability level for all of the atoms except for the H atoms that are shown as spheres of arbitrary radii. Symmetry code: (i) $-x + 1, -y + 1, -z + 1$ (ii) $x, y, -z + 1$ (iii) $-x + 1, -y + 1, z$.

The uncoordinated succinate plays a templating as well as charge compensating role and adopts *anti* conformation with torsion angle $\chi[C(2)C(3)C(3')C(2')] = 180^\circ$, and the orientation of the carboxylate with respect to the succinate backbone is $[O(2)C(2)C(3)] = 117.54^\circ$.^{38,47} The Co–N distance of 2.166(2) Å in **3** is consistent with the reported [CoCl₂(pyz)₂]_n and [CoCl₂(pyz)]_n compounds (Table S2), where one pyz ligates one cobalt atom in the κ -N mode.^{60–65} The cobalt centers are terminated (M¹ mode) by four water molecules and bridged (B² mode) via pyz with a Co...Co spacing of 7.114 Å to form coordination formula AB²M₄.^{1,55} This coordination mode results in topology **2C1** for simple 2-*c* linear chains (Table 3 and Figure S4).⁵⁶ The uncoordinated succinate anions connect the coordination chains into 3D supramolecular architecture through H-bonds with coordinated water molecules.

[Co₂(H₂O)₂(pyz)(suc)]₂ (**4**). Subjecting the reaction under solvothermal conditions in DMSO gave purple crystalline

cubes of 4 crystallizing in the triclinic $\bar{P}1$ space group (Table 1). The crystal structure is composed of succinate oxygen atoms (O2 and O3) adopting bridging coordination to Co1 and Co2, respectively (mode II, Table 2), while O4 and O5 of succinate coordinate Co1 and Co2 via bridging the chelate (mode III, Table 2). In total, four carboxylate oxygen atoms of three different succinate ligands coordinate a single cobalt ion (κ^4 -O,O',O'',O''' mode), while one pyz ligates per cobalt via the κ -N mode (Figure 6).^{8,38,48–54} The Co1–O bond distances

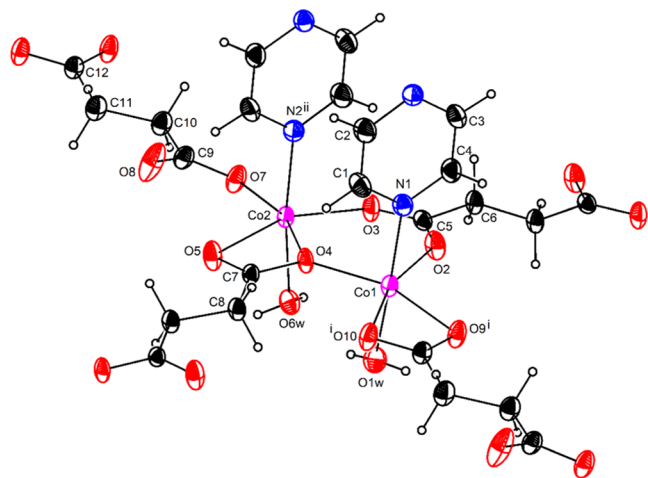


Figure 6. Crystal structure of $[\text{Co}_2(\text{H}_2\text{O})_2(\text{pyz})(\text{suc})_2]$ (4) showing the thermal ellipsoids drawn at the 50% probability level for all of the atoms except for the H atoms that are shown as spheres of arbitrary radii. Symmetry code: (i) $x - 1, y + 1, z$ (ii) $-x, -y + 1, -z + 1$.

range from 2.0154(17) to 2.2137(17) Å, while that of Co1–N1 is 2.164(2) Å. However, the bond distances for Co2–O lie between 1.9956(16) and 2.2786(17) Å and that for Co2–N2 is 2.179(2) Å (Table S1). The view of 4 along the a -axis shows succinate extending between two cobalt centers with the Co1...Co2 separation distance of 3.625(0) Å, and the distance bridged by pyz is 7.133(5) Å (Figure S5a). The succinate ligands adopt the anti–anti conformation with torsion angles $\chi[\text{C}(12)\text{C}(11)\text{C}(10)\text{C}(9)]$, $\chi[\text{C}(7)\text{C}(8)\text{C}(8')\text{C}(7')]$, and $\chi[\text{C}(5)\text{C}(6)\text{C}(6')\text{C}(5')]$ equal to 172.4, -180 , and 180° , respectively (Figure S5b). The orientation of the carboxylate groups with respect to the C–C backbone of succinate generates angles $[\text{O}(2)\text{C}(5)\text{C}(6)]$, $[\text{O}(3)\text{C}(5)\text{C}(6)]$, $[\text{O}(4)\text{C}(7)\text{C}(8)]$, $[\text{O}(5)\text{C}(7)\text{C}(8)]$, $[\text{O}(7)\text{C}(9)\text{C}(10)]$, $[\text{O}(9)\text{C}(12)\text{C}(11)]$, and $[\text{O}(10)\text{C}(12)\text{C}(11)]$ equal to 117.3, 116.8, 118.68, 124, 115.02, 120.89, and 119.39°, respectively.^{38,47} The four or three donor atoms of the succinate anion participating in the formation of coordination bonds give coordination modes K^{22} and K^4 or T^{11} , respectively. Pyrazine adopts the B^2 mode using two donor atoms to coordinate two Co1 or two Co2. The terminal water molecules have coordination mode M^1 since each water molecule possesses one donor atom and is coordinated to Co1 or Co2. Therefore, the coordination formula of 4 is represented as $\text{A}_4\text{K}^{22}\text{K}^4\text{T}_2^{11}\text{B}_2\text{M}_4^1$. The succinate forms the $\{\text{Co}(\text{suc})\}$ subnet with 2D 4-c sql net topology and the layers are interconnected in an alternate fashion by pyrazine ligands into two interpenetrating frameworks. A pair of carboxylate groups from the succinate anion connect pairs of Co atoms into dimeric cluster $\{\text{Co}_2(\text{COO})_2\}$. This cluster can be simplified into a five-coordinated node: four edges incident to the node

are formed by four succinate anions, and one edge is formed by a pair of pyrazine molecules. The underlying net is therefore five-coordinated **bnn** with the dimeric cluster as the node (Table 3 and Figure S6).^{55,56} The hydrogen-bonding interactions prevailing in 4 are shown in Table S3.

Very recently reported is $[\text{Co}(\text{HCO}_2)_2(\text{pyz})]$ (5) by Sahoo and co-workers.³⁹ They have described the synthesis of $[\text{Co}(\text{HCOO})_2(\text{C}_4\text{H}_4\text{N}_2)]$ (5) in DMF under solvothermal conditions using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and pyrazine (1:2). The crystal structure was determined at 298 K and crystallizes in the monoclinic $\text{C2}/c$ space group. Both the formate anion and pyz molecule exhibit the B^2 mode of coordination to complete the coordination formula AB_3^2 (Table 3).^{55,56} This coordination formula results in the formation of a 3D framework from undulated sublayers $\{\text{Co}(\text{HCO}_2)_2\}$ bridged by pyrazine molecules in two directions $[1\bar{1}0]$ and $[110]$. The underlying topology of the framework is described by 6-c net **rob** with pyrazine and formate both 2-c bridged. It is curious that a very similar topology has been described for $[\text{Cd}(\text{CN})_2(\text{pyz})]$.⁶⁶ The compound has been characterized by FTIR, TGA–DSC, high-resolution XPS, PXRD, FESEM, TEM analysis, and various temperature-dependent magnetic measurements. The compound shows in situ transformation owing to hydrolysis of DMF under high-temperature and basic conditions. On investigating the electrochemical catalytic performance of the compound, its promising role as an efficient electrocatalyst for the oxygen evolution reaction (OER) in alkaline media is revealed, thereby serving potential roles in applications for energy storage and conservation. In our work, we attempted to study the effect of solvent (DMF) in the reaction between $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, disodium succinate, and pyrazine under solvothermal conditions. We anticipated the compound to contain succinate and pyrazine with enhanced dimensionality or nuclearity. However, to our utter surprise, we obtained the compound reported by Sahoo et al., incorporating the hydrolysis product of DMF. We determined its crystal structure and found that it crystallized in the monoclinic $\text{C2}/c$ space group (Table S4) with cobalt surrounded by four oxygen atoms of formate ($\text{O1}, \text{O2}^{\text{i-iii}}$) and two nitrogen atoms of two pyz (N1 and N1^{ii}) (Figure 7). The Co–N distance is 2.186(2) Å, and that of Co–O ranges from 2.0740(18) to 2.0853(18) Å, showing distortion from ideal octahedra (Table

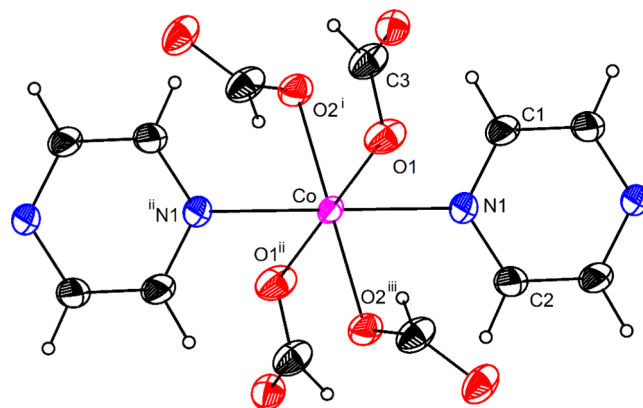
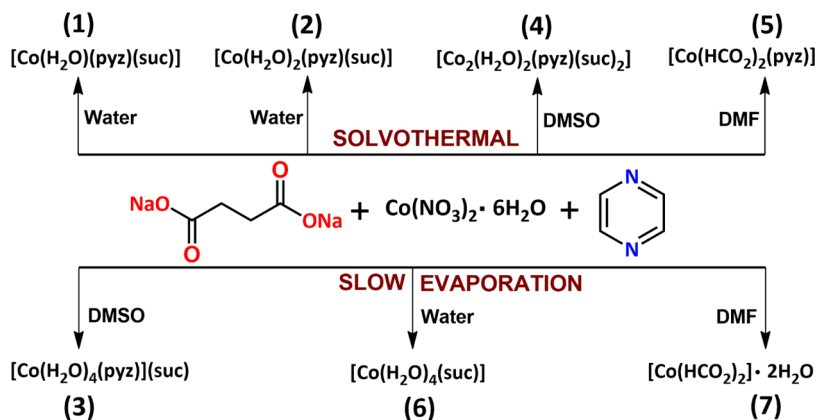


Figure 7. Crystal structure of $[\text{Co}(\text{HCO}_2)_2(\text{pyz})]$ (5) showing the thermal ellipsoids drawn at the 50% probability level for all of the atoms except for the H atoms that are shown as spheres of arbitrary radii. Symmetry code: (i) $x, -y + 2, z - 1/2$ (ii) $-x + 1/2, -y + 3/2, -z + 1$ (iii) $-x + 1/2, y - 1/2, -z + 3/2$.

Scheme 1. Synthetic Procedure for Compounds 1–7



S1), which is in agreement with the reported crystal data. On viewing **5** along *c*-axis, the intrachain $\text{Co} \cdots \text{Co}$ distance bridged by *pyz* is 7.158(0) Å, while along the *a*-axis, the $\text{Co} \cdots \text{Co}$ distance linked via formate is 5.738(0) Å (Figure S7a,b). Formate adopts the κ -O mode to cobalt. Compound **5** shows a 3D packing of cobalt with *pyz* and formate along the *c*-direction (Figure S8).

The crystal structure of cobalt succinate tetrahydrate, i.e., $[\text{Co}(\text{H}_2\text{O})_4(\text{suc})]$ (**6**) is well documented in the literature and isostructural with Ni, Fe, Mg, and Mn analogues.^{40,67–70} The refinement details for **6** are presented in Table S4. It crystallizes in the monoclinic $P2_1/c$ space group, where cobalt is octahedrally coordinated to two succinate oxygen atoms (O6 and O8ⁱ) and four water molecules (O1w–O4w) (Figure S9). Succinate ligands adopt the anti–anti conformation with torsion angle $\chi[\text{C}(1)\text{C}(2)\text{C}(3)\text{C}(4)] = 173.53^\circ$, and the orientation of the carboxylate with respect to the C–C backbone of succinate generates angles $[\text{C}(6)\text{C}(4)\text{C}(3)]$ and $[\text{C}(8)\text{C}(1)\text{C}(2)]$ equal to 116.41 and 117.72°, respectively.^{38,47} Each succinate ligates cobalt via the κ -O mode with coordination formula AB^2M_4^1 (Table 3). The intrachain $\text{Co} \cdots \text{Co}$ separation distance through the succinate bridge is 9.792(6) Å, which is in close agreement with that reported by Roy and co-workers, thereby resulting in a one-dimensional (1D) coordination network topology 2C1 with simple 2-*c* linear chains (Figure S10).⁷¹ On comparing crystal structures of 1–7, there is an enhancement in the dimensionality of the coordination network to 3D for structures with ratios of metal to bridging ligands of 1:2 (compounds **1** and **2**) and 1:3 (compounds **5** and **7**) in comparison to 1D coordination polymers with a ratio of 1:1 (compounds **3** and **6**). The *pyz* ligand usually accepts coordination mode B², while the succinate anion can be coordinated in different modes (B², T³, K²², K⁴, T¹¹) or noncoordinated at all when H-bonds compete with coordination bonds. Aprotic solvents DMSO and DMF bind a part of *pyz* or succinic acid, tuning the content of the ligands in precipitating crystalline compounds. Li and co-workers have mentioned the role of solvents in coordination supramolecular systems. *N,N*-Dimethylformamide (DMF) can readily coordinate to metal centers; however, it hydrolyzes during reactions giving byproducts of formate anions and dimethylammonium cations, which can be incorporated into the structure.^{72,73} In our work, we have demonstrated the in situ generation of formate from the reaction in DMF subjected to autoclave conditions, yielding **5** and **7**. We have not examined the crystal structure of **7** as

under fast scan we obtained structure parameters as trigonal space group $R\bar{3}c$, with parameters $a = b = 8.1951(3)$, $c = 22.2502(17)$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, and $V = 1294.12 \text{ \AA}^3$, which matched with the reported structure of **7**. Compound $(\text{Me}_2\text{H}_2\text{N})[\text{Co}(\text{HCOO})_3]$ (**7**) has one of the most symmetrical 3D 6-*c* underlying nets of topology *pcu*.⁵⁵ This net shows only three directions for spreading the edges, while edges of *rob* net spread in four directions. Such a difference in the structure of **7** is attributed to the presence of $\text{Me}_2\text{H}_2\text{N}^+$ cations in the voids.^{74–77}

Syntheses and Spectroscopic Properties of 1–7. It is remarkable that the same starting materials $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Na_2suc , and *pyz* under the influence of temperature (conventional slow evaporation and hydro(solvo)thermal methods at 105 °C for 2 days) and solvent (water, DMSO, and DMF) were vital for obtaining the desired compounds (Scheme 1). Hydrothermal conditions yielded orange crystals of **1** along the walls of the Teflon vessel, and slow evaporation of the mother liquor afforded red crystals of **2**. Subjecting to steam bath heating, we obtained copious amounts of $[\text{Co}(\text{H}_2\text{O})_4(\text{suc})]$ (**6**) coordination polymer.^{25,26} Bearing in mind the literature on aprotic solvents (DMSO and DMF) acting as linkers or guest molecules in MOFs, we simply mixed the aforesaid reagents (1:1:3) at ambient conditions in DMSO, forming bright orange crystalline blocks of **3**. Under solvothermal conditions, fine purple crystalline cubes of **4** were obtained. On allowing the filtrate to slowly evaporate at room temperature, **6** crystallized out as the secondary product. On the other hand, DMF gave an appreciable yield of **6** under normal reaction conditions. However, under solvothermal conditions, maroon blocks of **5** concomitant with purple crystals of **7** were isolated. Surprisingly, **5** contained the hydrolysis product of DMF (formate) along with pyrazine, without the incorporation of the succinate ligand as reported by Sahoo and co-workers.³⁹ Compound **7** obtained in larger quantity was devoid of pyrazine and succinate ligands and contained only formates coordinated to cobalt.

The infrared spectra of 1–4 were compared with that of **6**, as shown in Figure S11a. All of the compounds exhibited broad vibrations between ~ 3230 and 3560 cm^{-1} , suggesting the presence of water molecules. Medium-to-weak absorptions between ~ 2890 and 3080 cm^{-1} for all compounds are due to C–H vibrations. Strong-to-medium absorptions for 1–4 and **6** at ~ 1500 – 1550 and ~ 1380 – 1430 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations, respectively, of succinate. The separation distances between $\nu_{\text{asym}}(\text{COO}^-)$

and $\nu_{\text{sym}}(\text{COO}^-)$, i.e., Δ , are 144 and 161 cm^{-1} for 1 and 2, respectively, consistent for the *bis*-bidentate coordination mode. The Δ value of 90 cm^{-1} for 4 is in accordance with the bridging coordination modes observed. For 5 and 7, the ν_{asym} and ν_{sym} vibrations due to formate ions appear at ~ 1540 – 1550 and ~ 1330 – 1365 cm^{-1} , respectively (Figure S11b).^{78–82}

Raman spectra of 1–3, 5, and 7 when compared with the corresponding IR spectra (Figure S12a–e) depicted in-plane bending modes of pyrazine at ~ 1000 cm^{-1} . The $\text{s}(\text{CH}_2)$ scissoring band of succinate can be seen as a weak doublet at ~ 1443 and ~ 1415 cm^{-1} . Weak intensity at ~ 1210 cm^{-1} is due to the $\text{w}(\text{CH}_2)$ wagging mode of succinate. A weak $\delta(\text{OCO})$ bending mode of succinate is at ~ 634 cm^{-1} . The symmetrical $\nu_{\text{sym}}(\text{CH})$ vibrations at ~ 2855 cm^{-1} are observed for both succinate and pyrazine along with the $\nu(\text{OH})$ mode at ~ 3560 cm^{-1} , all seen as sharp peaks.^{79–81} The UV–vis absorption spectra of 1–6 are shown in Figure S13, and an inset displays d–d bands. The bands between ~ 260 and 308 nm are assigned to π – π^* and n – π^* transitions of the linkers. The d–d band at ~ 510 nm corresponds to ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$ transition for a distorted octahedral Co(II) center.^{82,83}

Magnetic Properties of 1–5. We resorted to studying the magnetic properties in the solid state by performing temperature-dependent magnetic susceptibility (χ_{M}) measurements on the finely powdered samples of 1–5 under an applied magnetic field of 100 Oe in the temperature range of 60–310 K. The plot of χ_{M} versus T shows the influence of temperature on the zero-field-cooled–field-cooled (ZFC–FC) curves. In the case of 1 (Figure 8), the magnetic susceptibility (χ_{M})

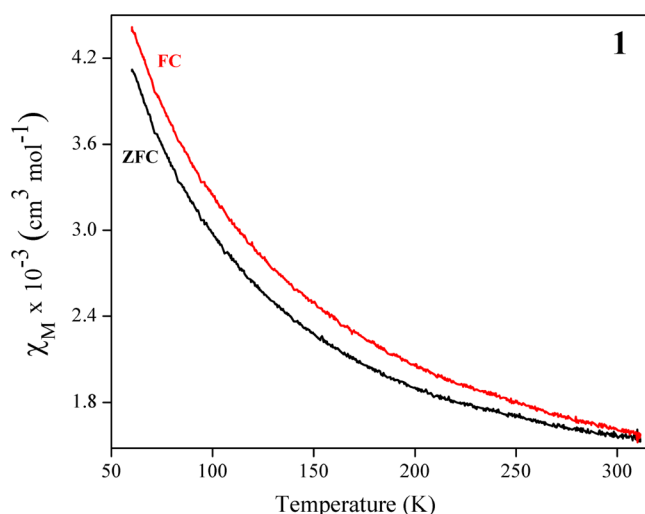


Figure 8. Plot of zero-field-cooled (ZFC)–field-cooled (FC) magnetic susceptibility for 1 as a function of temperature under an applied field of 100 G between 60 and 310 K.

values were found to increase monotonically with decreasing temperature (i.e., high χ_{M} values at 60 K). The ZFC–FC curves displayed an appreciable extent of bifurcation suggestive of magnetic ordering. This trend is also pronounced in all of the compounds (Figure S14a for 4). Hence, the higher χ_{M} values for FC measurements are due to the unpaired electron spins aligned with respect to the applied magnetic field (100 Oe), while lower χ_{M} values in the ZFC situation are attributed to randomization of spins due to the absence of applied field.^{46,72}

Moreover, the curve of $\chi_{\text{M}}T$ against T for 1–5 presented a continuous decrease of $\chi_{\text{M}}T$ values upon cooling. As seen in the case of 4 (Figure S14b), the $\chi_{\text{M}}T$ value descended from 1.180 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 310 K to 0.605 $\text{cm}^3 \text{mol}^{-1} \text{K}$ on cooling to 60 K. This outcome is relevant to cobalt(II) compounds, suggesting magnetic exchange interactions between the cobalt(II) centers. From the crystal structure analysis (vide infra), the cobalt(II) centers are bridged by succ^{2-} as well as pyz along different dimensions for 1, 2, and 4, while only pyz bridges the cobalt(II) centers in 3, along with bridging pyz and formate in 5. The average Co...Co distance flanked by pyrazine is 7.2 Å, which is sufficiently good for magnetic interactions to take place. These observations draw conclusions from single-ion anisotropy and antiferromagnetic (AF) interactions mediated by ligands bridging the cobalt(II) centers.^{42,43,48,61} So, to gather evidence on the AF interactions persisting in the compound, we performed various temperature susceptibility (χ_{M}) measurements on compound 1. From the plot of χ_{M} versus T (Figure S15a), there was a gradual decrease in χ_{M} from 0.136 $\text{cm}^3 \text{mol}^{-1}$ at RT to 0.00854 $\text{cm}^3 \text{mol}^{-1}$ at 298 K with effective magnetic moment calculated using $\mu_{\text{eff}} = 2.82 (\chi_{\text{M}}T)^{1/2}$ of 4.5 BM, which deviates from the calculated spin-only magnetic moment ($\mu_{\text{so}} = 3.87$ BM) for a high-spin Co(II) $3d^7$ system with $S = 3/2$. The plot of χ_{M}^{-1} versus T (Figure S15b) was essentially linear over the entire temperature range following the Curie–Weiss law given as follows: $\chi_{\text{M}} = \frac{C}{T - \phi}$, where χ_{M} is the magnetic susceptibility in $\text{cm}^3 \text{mol}^{-1}$, C is the Curie constant, T is the temperature in kelvin, and ϕ is the Weiss constant in kelvin. A fitting of the Curie–Weiss law on the data gave a Curie constant (C) of 2.525 obtained from the inverse of the slope and a negative Weiss constant (ϕ) of -46.24 K, suggesting weak antiferromagnetic (AF) exchange interactions. The declining $\chi_{\text{M}}T$ values upon cooling confirm this behavior. The effective magnetic moment calculated using $\mu_{\text{eff}} = (8C)^{1/2}$ was 4.51 BM.^{38,72}

Thermogravimetric Analyses, X-ray Powder Diffraction Patterns, and Gas Adsorption Properties. We investigated the thermal stability of 1–7 by TG–DTG measurements in the temperature range of 30–650 °C. The TG curve of 1 shows a mass loss of 6.1% from 32 to 85 °C due to water (calcd 6.6%). On increasing the temperature up to 345 °C, there was gradual degradation of pyrazine and succinate to 68.5% (calcd 71.8%) as evidenced by peaks at 200 and 345 °C in DTG; a residue of 23.6% (calcd 27.4%) was obtained for CoO (Figure 9).

Compound 2 is stable up to 110 °C and thereafter disintegrates to give a mass loss of 12.5% due to two water molecules (calcd 12.36%), evident at 150 °C in DTG. Pyrazine decomposes to 26.46% (calcd 27.48%) followed by succinate to 39.84% (calcd 35.83%), indicated at 332 °C in DTG. A residue of 26.17% corresponding to CoO (calcd 25.76%) is obtained (Figure S16a). Compound 3 is stable until 90 °C followed by a mass loss of 22.5% at 135 °C due to the elimination of four water molecules (calcd 22.0%). This is associated with the corresponding peak at 132 °C in DTG. The dehydrated compound then disintegrates to a total mass loss of 57.1% due to ligand decomposition (calcd 59.9%), evident at 342 °C in DTG, giving a residue of 20.1% of CoO (Figure S16b). In the case of 4, stability up to 80 °C with two subsequent weight losses of 25.73% from 90 to 200 °C and 51.6% up to 400 °C can be assigned to the concomitant loss of two water molecules, pyrazine (calcd 24.88%) and succinate (calcd 49.77%) as confirmed by DTG peaks at 202 and 366

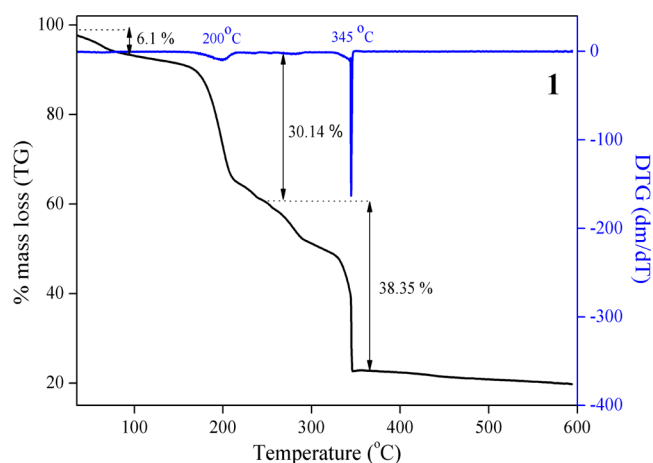


Figure 9. TG–DTG plot of **1** recorded between 30 and 600 °C in air at 10 °C min⁻¹.

°C, respectively. A residue of 17.65% of CoO was formed (Figure S16c). Compound **5** recorded the highest stability of 250 °C and thereafter decomposes until 315 °C to 66.0% (calcd 74.30%) due to the loss of formate (CO₂, water, and CO) and pyrazine as characterized by a sharp DTG peak at 306 °C, with a residue of 33.48% (Figure S16d). Cobalt(II) succinate tetrahydrate **6** shows thermal stability up to 80 °C followed by a sharp weight loss of 30.23% between 78 and 130 °C due to four water molecules (calcd 29.14%). This is associated with a corresponding peak at 130 °C in DTG. The dehydrated compound is stable up to 320 °C and then abruptly disintegrates until 340 °C with a mass loss of 40.1% (calcd 40.5%), assignable to ligand decomposition with a sharp peak at 345 °C in DTG. The final decomposed product of 28.6% is probably CoO (Figure S16e). The thermal pattern of **7** is associated with the loss of two water molecules at 19.3% (calcd 19.47%) followed by subsequent decomposition of formate up to 300 °C of 46.13% (calcd 48.67%) with a residue of 35.32% of CoO (Figure S16f).

Thermal analyses of **1–7** revealed moderate to high thermal stabilities, and, crystal structural analyses revealed diverse architectures with the presence of minute pores as visualized by the crystal structure visualization tool (Mercury 4.2).⁸⁴ This observation lies on the fact that MOFs possess the properties of modest thermal stability and robust architecture, thereby serving as traps for selective gas adsorption. Here, we investigated the CO₂ and N₂ adsorption properties of our compounds to determine their porosity. In adsorption studies, the compounds were degassed at 80 °C for ~15 h to ensure that the samples were free from adsorbed moisture. The N₂ and CO₂ adsorption performance was then investigated for the degassed samples **1–7** at 77 and 298 K, respectively. The reversible N₂ sorption profiles for **4** at 77 K (Figure 10) demonstrate type III adsorption isotherm behavior (characteristic of non/macroporous substances) with a modest uptake value of ~47 cm³ g⁻¹, suggesting only surface adsorption. The BET surface area (Figure 10, inset) and total pore volume of **4** are 18.07 m² g⁻¹ and 0.072 cm³ g⁻¹, respectively. The reversible N₂ sorption plots for the other compounds are shown in Figure S17. The adsorption and desorption curves do not agree with each other, indicating a type H3 hysteresis loop (according to the IUPAC classification). The N₂ uptake values have been found as 5.54 (**1**), 12.54 (**2**), 29.32 (**3**), 47.40 (**4**), 34.60 (**5**), and 22.11 (**6**) cm³ g⁻¹ at P/P₀ ~0.99. All of the

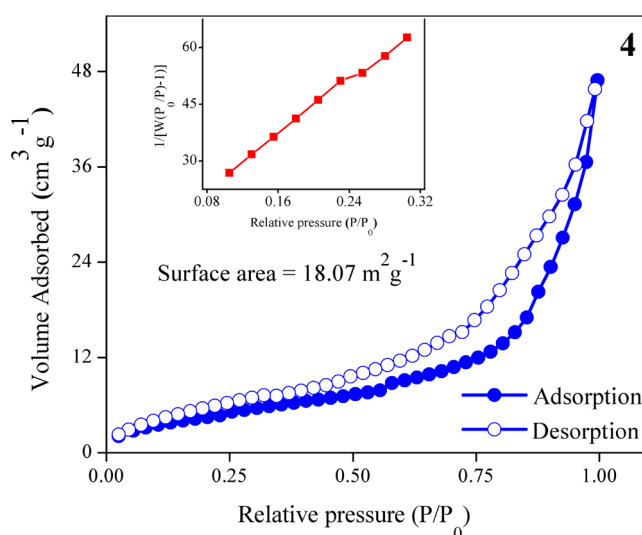


Figure 10. Nitrogen adsorption/desorption isotherms at 77 K for **4** displaying the highest surface area; filled spheres, adsorption; empty spheres, desorption (inset: BET plot).

compounds show a negligible amount of N₂ uptake with a type III surface adsorption isotherm, thereby having low BET surface areas of 3.53, 9.12, 10.52, 18.07, 9.28, 11.16, and 2.75 m² g⁻¹ for **1–7**, respectively (Table S5). The observed pore volumes in cm³ g⁻¹ are 0.008 (**1**), 0.019 (**2**), 0.072 (**4**), and 0.034 (**6**). However, the formate containing compounds **5** and **7** had pore volumes of 0.053 and 0.010 cm³ g⁻¹, respectively. The calculated pore volumes for **1–6** are 64.76, 40.66, 48.08, 14.66, 51.80, and 9.85 in Å³, respectively, as obtained from Mercury 4.2. The low N₂ uptake could stem from the fact that the low thermal energy of N₂ at 77 K makes it unable to overcome the high diffusion barrier, thereby causing N₂ gas to escape.

A similar phenomenon was observed for CO₂ gas adsorption, resulting in very low uptake due to the blocking of the windows of unidirectional pores to the incoming CO₂ molecules. The CO₂ adsorption isotherms recorded at 298 K showed adsorption of 15.22 cm³ g⁻¹ for **1**, 4.09 cm³ g⁻¹ for **2**, 5.80 cm³ g⁻¹ for **3**, and 4.46 cm³ g⁻¹ for **4**, while the formate counterparts, **5** and **7** exhibited CO₂ uptake of 4.18 and 3.32 cm³ g⁻¹, respectively. Cobalt succinate tetrahydrate **6** exhibited a CO₂ uptake of 6.57 cm³ g⁻¹ (Figure 11). The desorption curves did not trace the adsorption curves and showed hysteric nature due to the strong interaction of CO₂ molecules with the framework on account of the strong quadrupole moment of CO₂. The adsorption profiles were of type III with poor sorption, suggesting strong attraction of gaseous adsorbate to the pore surface, thereby preventing interaction of other molecules.^{85–88}

The X-ray powder diffraction patterns of the bulk samples of compounds **1–6** were measured and compared with the calculated X-ray powder patterns obtained from Mercury 4.2. Both experimental and calculated X-ray powder patterns of compounds **3**, **4**, and **6** perfectly matched, while those of others (**1**, **2** and **5**) showed trace impurities, which are evident from profile fitting of the powder patterns using the Le Bail method with the help of FullProf software (Figures S18–S23).^{89,90} After understanding the X-ray powder patterns of **1–6**, they were further inspected for surface morphology using scanning electron microscopy (SEM). The SEM images were

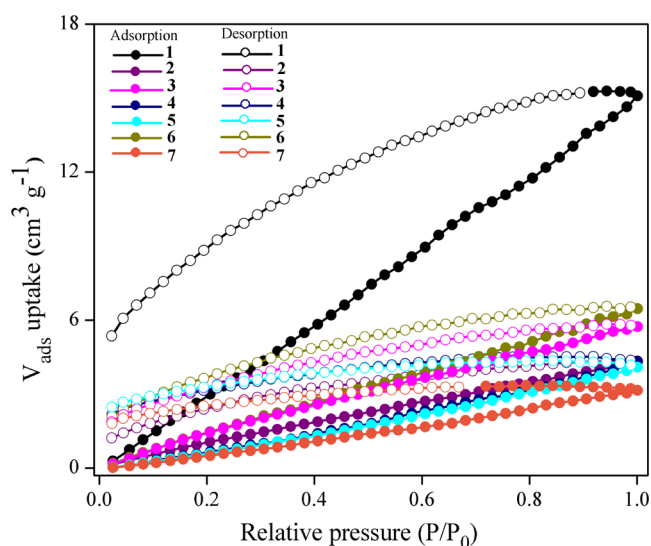


Figure 11. Carbon dioxide sorption isotherms at 298 K for 1–7 (filled spheres, adsorption; empty spheres, desorption).

obtained at 20 kV with a magnification of up to 40 000× (Figure S24). The morphological examination of the powdered sample of **1** showed well-defined octahedral-shaped particles, while the SEM image of **2** showed particles arranged as small rods with irregular edges. Compound **3** exhibited globular-shaped particles with agglomeration; on the other hand, well-defined rectangular plates stacked onto each other to form bundles were observed for compound **4**. Only formate- and pyrazine-containing compound **5** appeared as agglomerated rod-shaped particles along with irregular globular-shaped particles; similarly, succinate- and hydrate-containing **6** also showed particles of irregular shape and varying size. Formate compound **7** exhibited a morphology in which the particles were viewed as well-defined rectangular rods along with lozenge-shaped particles (Figure S24).^{85–88} With complete characterization on structural and morphological aspects, we then diverted our attention to understanding the luminescence properties of compound **1** as the results obtained for **2** and **3** did not show any pronounced difference. It was observed that succinic acid showed an emission band at 393 nm due to the $\pi^* \rightarrow n$ or $\pi \rightarrow \pi^*$ transitions upon excitation at 350 nm.

Fluorescence Sensing Properties of 1. The fluorescence properties of **1** in the solid state and as a suspension in water and DMSO were investigated. As a suspension in water and DMSO, **1** emitted strongly at 345 nm upon excitation at 300 nm, while the solid-state spectra for **1** showed emission at 428 nm upon excitation at a longer wavelength of 370 nm (Figure S25a,b). These emissions are likely attributed to the $\pi^* \rightarrow n$ or $\pi \rightarrow \pi^*$ transitions arising from the succinate ligand.⁵⁰ Hence, we observed a blue shift (decrease in λ) on moving from solid-state fluorescence emission to the suspension phase.

For the fluorescence sensing titrations, 2 mL of aqueous suspension of **1** (2 mM) was placed in a quartz cell of 1 cm width and aqueous solution of NAC (1 mM) was added gradually in an incremental fashion of 10 μ L. The emission spectra were recorded upon excitation at 300 nm at 298 K, and the corresponding emission wavelength at 345 nm was monitored. Both the excitation and emission slit widths were 10 nm for all of the measurements. Each titration was repeated at least three times to obtain concordant values. From the fluorescence sensing experiments, we observed consistent

emission spectra for **1** in water (ex. 300 nm, em. 345 nm) upon addition of NACs with gradual decay of the emission band; unlike for DMSO showing a drastic shift in λ upon the same excitation with NAC addition (Figure S26). Hence, water was chosen as the medium for carrying out sensing experiments. The relative fluorescence emission spectra were measured for an aqueous suspension of **1** in various analytes (NACs) used as a quencher in water. In the current study, the NACs employed were nitrobenzene (NB), *o*-nitrotoluene (*o*-NT), *p*-nitrotoluene (*p*-NT), *o*-nitrophenol (*o*-NP), *p*-nitrophenol (*p*-NP), 2,4-dinitrophenol (DNP), and 2,4,6-trinitrophenol (TNP). No change was observed in the shape of the emission spectra of **1**, although only quenching of the initial fluorescence emission intensity upon titration with the electron-deficient NACs was seen. The representative titration of *p*-NP with **1** is shown in Figure 12, while titration with other NACs is provided in the Supporting Information (Figures S27 and S28).

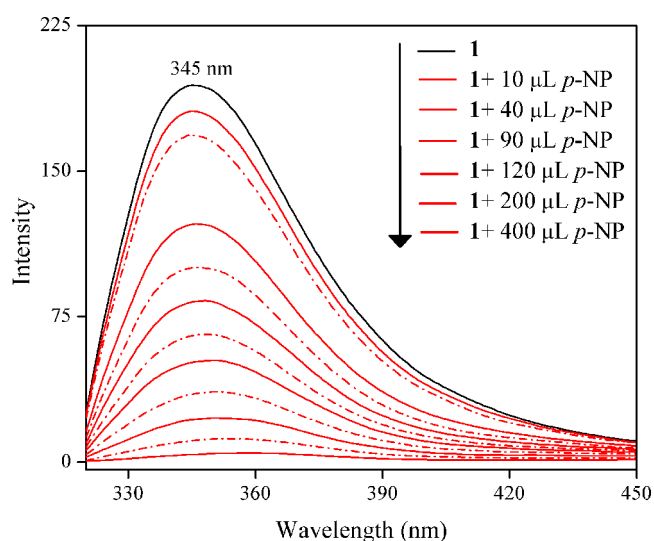


Figure 12. Reduction of the fluorescence emission of **1** upon gradual addition of 1 mM *p*-nitrophenol (*p*-NP).

In all cases, the initial fluorescence intensity of **1** was found to show a considerable decrease upon gradual addition of the NACs. The fluorescence efficiency (η) was calculated as $[(I_0 - I)/I_0] \times 100\%$, where I_0 and I are the fluorescence intensities before and after addition of the respective NACs. The initial emission intensity of **1** was quenched by approximately 98% (η) after the addition of 400 μ L of *p*-NP. On the other hand, a sluggish decline in the intensity of **1** was observed with only 26% quenching with the addition of 410 μ L of NB. The addition of 500 μ L of *o*-NT gave 7.4% quenching. The emission intensity decreased to a minimum at 69% quenching efficiency with the addition of 740 μ L of *p*-NT. Furthermore, the intensity of **1** was quenched to 82% after adding 950 μ L of *o*-NP. On adding DNP (300 μ L), there was 86% quenching of the emission intensity of **1**. Moreover, the addition of TNP (380 μ L) showed 94% quenching of the emission intensity of **1**. Therefore, in terms of fluorescence quenching efficiencies, the NACs follow the trend *o*-NT < NB < *p*-NT < *o*-NP < DNP < TNP < *p*-NP. Hence, **1** was found to show remarkably higher efficiencies toward nitrophenols with 98% for *p*-NP than the nitrotoluene compounds. The sensing ability of **1** toward the different NACs is plotted in terms of their quenching

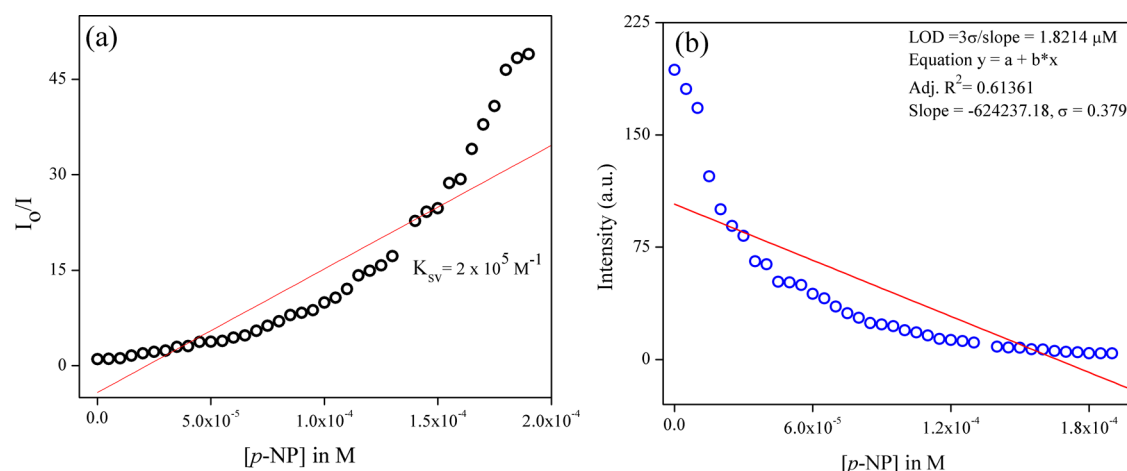


Figure 13. (a) Stern–Volmer plot for **1** with *p*-NP exhibiting the highest K_{sv} value among other NACs. (b) Plot for the determination of the limit of detection (LOD) for *p*-NP.

efficiencies (%), as depicted in Figure S29. Thus, it unambiguously suggests that **1** can be selectively used as a chemical sensing reagent in the detection of *p*-NP from an aqueous mixture of other NACs.^{91–95}

The Stern–Volmer quenching constant (K_{sv}) was calculated employing the normalized fluorescence emission intensity (I_0/I) as a function of increasing quencher concentration $[Q]$ by the following relation; $I_0/I = 1 + K_{sv} [Q]$, where I_0 and I are the emission intensities of **1**, before and after addition of NACs, respectively, K_{sv} is the quenching constant (M^{-1}), and $[Q]$ is the molar concentration of NACs. The Stern–Volmer plot of **1** with *p*-NP is depicted in Figure 13a, while that with the other NACs are provided in the Supporting Information (Figure S30). It can be seen that that Stern–Volmer plot followed a linear path at low concentrations; however, at higher concentrations, the linearity deviated as an upwardly bent curve as a consequence of static and collisional quenching mechanisms. The K_{sv} values for **1** toward all of the NACs used are given in Table 4. The quenching constant for *p*-NP was

Table 4. Quenching Efficiencies, Stern–Volmer Constants, and LODs upon Addition of Different NACs to **1**

sr. no.	NAC	quenching efficiency η (%)	Stern–Volmer constant K_{sv} (M^{-1})	limit of detection (LOD)	
				μM	ppm
1	NB	26	1.1×10^3	14.026	7.661
2	<i>o</i> -NT	7.4	3.3×10^2	32.480	17.741
3	<i>p</i> -NT	69	5×10^3	5.000	2.731
4	<i>o</i> -NP	82	7×10^3	7.680	4.195
5	<i>p</i> -NP	98	2×10^5	1.821	0.995
6	DNP	86	2.8×10^4	3.053	1.668
7	TNP	94	5.7×10^4	3.242	1.771

200 times greater than that for the simplest NB, while *p*-NP showed K_{sv} values about 29, 6.5, and 3.5 times greater than the nitrophenol compounds (*o*-NP, DNP, and TNP), respectively. This signified the exclusive quenching ability of *p*-NP toward luminescent **1** in water among other NACs.^{95–98}

Determining the Limit of Detection (LOD). The LOD was calculated from the plot of fluorescence intensity with increasing concentration of NACs. The slope of the line (m) was calculated from the plot, while the standard deviation (σ)

was taken from three blank measurements of **1**. The LOD was calculated based on the following formula: $3\sigma/m$. The LOD could be expressed in molar or ppm (parts per million), as calculated in Figure S31 and Table 4. The limit of detection of *p*-NP was found to be as low as 0.995 ppm or 1.821 μM (Figure 13b). This clearly depicts that **1** has high selectivity for *p*-NP over the other potentially interfering NACs.^{95,98}

With a view to understanding the mechanism prevailing between **1** and respective NACs, we recorded the absorption spectra of the individual NACs and the completely quenched mixture (**1** + NAC); the observations are summarized in Table S6 and Figure S32, displaying red and blue shifts with no new peak formation. Thus, we speculated dynamic quenching since the fluorophore (**1**) was quenched on collision with the quencher (NAC) without formation of a new species. However, from the S–V plot showing deviation in linearity, we could infer that both static and collisional quenching mechanisms are active. We can rule out the encapsulation of NACs in the pores of **1** as evident from the low surface properties of **1** already discussed in the previous section (vide supra). Due to the dispersible nature of the micro-sized fine particles of **1** in water, there was close contact with NACs, thus relating the fluorescence turn-off (quenching) to the photo-induced electron transfer (PET) mechanism. Generally in PET, the conduction band (CB) of **1** lies at higher energy than the LUMOs of the NACs to facilitate electron transfer, thereby favoring effective quenching. Apart from this, the nonlinear nature of S–V plots for the NACs also suggested the resonance energy transfer (RET) mechanism for enhanced quenching. The probability of RET depended on the extent of spectral overlap between the absorption band of the NACs and the emission band of **1**. As can be seen in Figure 14, the absorption spectra of *p*-NP, TNP, and DNP showed a considerable overlap with the 345 nm emission band of **1**, while marginal or no spectral overlap is observed for the other NACs. As a result, high quenching responses were observed for *p*-NP (98%), TNP (94%), and DNP (86%) compared to the rest of the NACs. These furnished the fact that the concomitant effect of PET and RET mechanisms is responsible for the effective fluorescence quenching of **1** by the NACs. Thus, **1** responded more selectively to *p*-NP than the other NACs with a quenching efficiency of 98%.^{31,94,96–100}

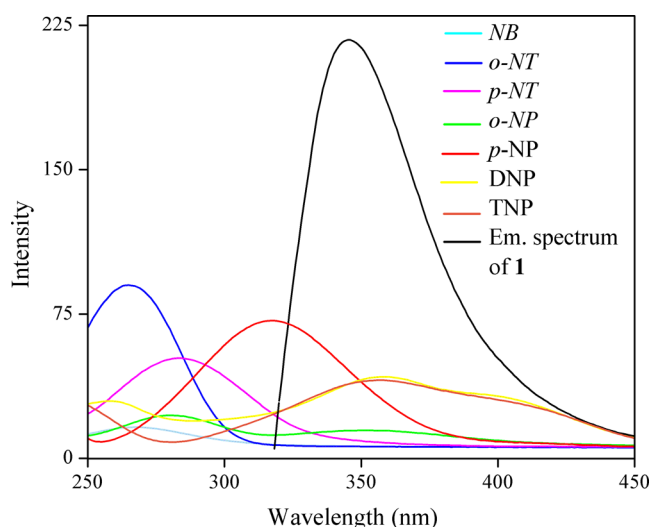


Figure 14. Spectral overlap between the absorption spectra of NACs and the emission spectrum of **1** in water.

CONCLUSIONS

We explored the chemistry of cobalt(II) with pyrazine (rigid) and succinic acid (flexible) in water/DMSO/DMF under ambient/solvothermal conditions generating CPs with diverse architectures (1D to 3D). The construction of CPs was influenced by different binding modes adopted by the carboxylate ligand and the μ_2 bridging mode of pyrazine, mediated by the reaction conditions. The topologies of the coordination polymers **1–7** were described by underlying nets 3D 3,5-*c* **fet**, 3D 4-*c* **cds**, 1D 2-*c* **2C1**, 3D 5-*c* **bnn**, 3D 6-*c* **rob**, 1D 2-*c* **2C1**, and 3D 6-*c* **pcu**, respectively. The plot of χ_M^{-1} versus T was essentially linear over the entire temperature range following the Curie–Weiss law with a Curie constant (C) = 2.525 and a negative Weiss constant (ϕ) = −46.24 K, suggesting weak antiferromagnetic (AF) exchange interactions. The gas adsorption measurements revealed a type III isotherm, indicating the macroporous nature of the compounds. Scanning electron microscopy images presented assorted surface morphologies. The present data unambiguously suggested that **1** can be selectively used as a chemical sensing reagent in the detection of *p*-NP (highest η) from a mixture of NACs, with a detection limit of 0.995 ppm for *p*-NP. The Stern–Volmer plot exhibited deviation in linearity with K_{sv} values about 200 times greater than that for the simplest nitroaromatic compound (NB), signifying its exclusive quenching ability toward **1**.

EXPERIMENTAL SECTION

Materials and Instrumentation. All chemicals and solvents were commercially available and used as received. The disodium salt of succinic acid (Na_2suc) was prepared by the slow addition of NaHCO_3 to the hot aqueous solution of succinic acid (2:1), followed by slow evaporation to give white crystalline flakes. The composition of Na_2suc was studied by IR spectroscopy and elemental analysis (C, H, and N). Necessary safety measures were taken during autoclave syntheses using Teflon-lined stainless steel vessels heated in a temperature-controlled oven (ANTS make). The IR spectra of powdered compounds **1–7** were recorded on dilution with KBr on a Shimadzu (IR Prestige-21) FTIR spectrometer in the region 4000–350 cm^{-1} at 4 cm^{-1} resolution. Solid-state

Raman spectra were measured using 785 nm laser radiation for excitation with the laser power set to 100 mW on an Agiltron PeakSeeker Pro Raman instrument using a 1 mm quartz cell. The absorption spectra were recorded on an Agilent UV–vis spectrophotometer (Model 8453). Elemental analyses (C, H, and N) were performed on an Elementar Variomicro Cube CHNS analyzer. The field-dependent magnetization studies, viz., zero-field cooling (ZFC) and field cooling (FC), were performed between temperatures 60 and 310 K under an applied magnetic field of 100 G. The variable-temperature magnetic susceptibility data for only **1** was obtained on a vibrating sample magnetometer (VSM) with the sensitivity of a SQUID (Superconducting Quantum Interference Device) magnetometer. The SQUID-VSM magnetometer (Quantum Design, MPMS-3) was operated in the temperature range of 10–300 K under an applied field of 1000 G. Thermogravimetric analysis (TG–DTG) were carried out on a PerkinElmer TGA 4000 analyzer in air at a heating rate of 10 $^\circ\text{C min}^{-1}$ from room temperature to 650 $^\circ\text{C}$. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance X-ray diffractometer using $\text{Cu K}\alpha_1$ ($\lambda = 1.5406 \text{ \AA}$) with a Ni filter. Surface morphologies of the compounds were evaluated on a Carl-Zeiss Evo scanning electron microscope (SEM) operating at 20 kV. The solution-state fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer. The ambient pressure volumetric N_2 adsorption–desorption measurements were performed at 77 K maintained by low-temperature liquid nitrogen Dewar and those of CO_2 were performed at 298 K in the pressure range 0–760 Torr using an AutosorbIQ (Quantachrome Inc.) gas sorption analyzer. Before analysis, **1–7** were soaked in chloroform for 24 h to remove water molecules. Subsequently, the supernatant chloroform was poured and the procedure was repeated twice with fresh chloroform. Further, the outgassing process was carried out at 80 $^\circ\text{C}$ for 15 h under a dynamic vacuum of 10^{-3} Torr until a stable weight was obtained. Warm and cold free space correction measurements were carried out utilizing ultrapure (99.999% purity) He gas. For analysis, high-purity (99.999%) N_2 and CO_2 were used, which were again purified by calcium aluminosilicate adsorbents to remove any trace amounts of moisture before analysis. The adsorption data in the pressure range $<0.1 P/P_0$ were fitted to the Brunauer–Emmett–Teller (BET) equation to determine the surface area. The fluorescence spectra of **1** in the solid state and in suspension in water and DMSO were recorded by a xenon flash lamp technology-based Cary Eclipse Fluorescence Spectrophotometer (G9800A) from Agilent Technologies. For nitroaromatic compound (NAC) sensing, 2 mM suspension of **1** in 2 mL of DMSO/water was placed in a 1 cm quartz cuvette, to which an aqueous solution of 1 mM NAC was added. Excitation was carried out at 300 nm with slit widths of excitation and emission of 10 nm, respectively.

Synthesis of $[\text{Co}(\text{H}_2\text{O})(\text{pyz})(\text{suc})]$ (1**) and $[\text{Co}(\text{H}_2\text{O})_2(\text{pyz})(\text{suc})]$ (**2**).** An aqueous solution (2 mL) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 0.291 g) was added dropwise to an aqueous mixture (3 mL) of disodium succinate (1 mmol, 0.162 g) and pyrazine (3 mmol, 0.24 g). The orange solution was stirred at room temperature (RT) for 30 min and then transferred into a 10 mL Teflon-lined stainless steel autoclave, which was heated to 105 $^\circ\text{C}$ for 48 h. On cooling, orange plate-shaped crystals of **1** deposited along the walls of the Teflon cup separated from the mother liquor and were air-dried (yield = 0.085 g). Slow evaporation of the mother liquor at room temperature gave red

crystalline blocks of **2**, which were isolated and air-dried (yield: 0.23 g).

Anal. Calcd for **1** $C_8H_{10}N_2O_5Co$ (Mr. = 273.11): C, 35.18; H, 3.69; N, 10.26. Found: C, 35.02; H, 3.67; N, 10.12. IR (KBr, cm^{-1}): 3223 (br), 2890 (m), 2323 (m), 1656 (w), 1542 (s), 1430 (m), 1328 (w), 1243 (m), 1170 (m), 1045 (m), 1040 (w), 975 (m), 890 (w), 801 (w), 678 (m), 540 (m), 420 (w). UV-vis in water (λ_{max} nm, ϵ): 267 (6520), 308 (860), 510 (7), 641 (1).

Anal. Calcd for **2** $C_8H_{12}N_2O_6Co$ (Mr. = 291.13): C, 33.01; H, 4.15; N, 9.62. Found: C, 33.52; H, 4.07; N, 9.63. IR (KBr, cm^{-1}): 3340 (br), 2907 (m), 2423 (m), 1520 (s), 1360 (s), 1260 (m), 1190 (m), 1130 (m), 1030 (m), 763 (m), 610 (m), 520 (m), 412 (m). UV-vis in water (λ_{max} nm, ϵ): 263 (14872), 306 (1624), 470 (13), 510 (15).

Synthesis of $[Co(H_2O)_4(pyz)_2](suc)$ (3**).** Compound **3** was synthesized using the same reactants as those for **1** and **2**, except that DMSO/ H_2O (5 mL, v/v, 3:2) was used instead of H_2O and the reaction was performed at room temperature with stirring for 30 min. Elongated bright orange crystalline blocks of **3** started to grow after 2 days, which were isolated and air-dried (yield: 0.37 g).

Anal. Calcd for **3** $C_8H_{16}N_2O_8Co$ (Mr. = 327.16): C, 29.37; H, 4.93; N, 8.56. Found: C, 29.12; H, 5.10; N, 8.12. IR (KBr, cm^{-1}): 3250 (br), 2990 (m), 2230 (m), 1895 (m), 1840 (m), 1873 (s), 1710 (w), 1630 (m), 1490 (s), 1380 (s), 1260 (m), 1130 (m), 1060 (m), 1100 (m), 940 (w), 835 (w), 790 (w), 760 (w), 640 (m), 570 (m), 430 (m). UV-vis in water (λ_{max} nm, ϵ): 265 (7480), 308 (860), 478 (6), 510 (7).

Synthesis of $[Co_2(H_2O)_2(pyz)_2](suc)_2$ (4**).** The synthesis method was similar to those of **1** and **2** under autoclavable conditions, except that DMSO/ H_2O (5 mL, v/v, 3:2) was used instead of H_2O . Purple crystals of **4** were obtained after 2 days along with pink crystalline blocks of compound **6**. The crystals of **4** were first picked by a stainless steel spatula and then air-dried (yield = 0.192 g). The remaining pink crystals of **6** were isolated by filtration and air-dried (yield = 0.324 g).

Anal. Calcd for **4** $C_{12}H_{16}N_2O_{10}Co_2$ (Mr. = 466.13): C, 30.92; H, 3.46; N, 6.01. Found: C, 30.45; H, 3.27; N, 5.97. IR (KBr, cm^{-1}): 3380 (br), 2895 (m), 2290 (m), 1970 (m), 1890 (m), 1680 (m), 1540 (s), 1441 (s), 1306 (m), 1180 (m), 1100 (m), 1070 (m), 995 (m), 850 (w), 670 (m), 471 (m). UV-vis in water (λ_{max} nm, ϵ): 264 (463), 304 (52), 474 (15), 512 (5).

Anal. Calcd for **6** $C_4H_{12}O_8Co$ (Mr. = 247.07): C, 19.45; H, 4.90. Found: C, 19.40; H, 4.91. IR (KBr, cm^{-1}): 3330 (br), 2889 (m), 2440 (m), 1660 (m), 1650 (w), 1555 (s), 1473 (w), 1411 (s), 1350 (m), 1290 (m), 1250 (m), 1190 (m), 1050 (m), 980 (w), 888 (w), 672 (w), 530 (w), 415 (m). UV-vis in water (λ_{max} nm, ϵ): 202 (19050), 267 (678), 516 (31).

Synthesis of $[Co(HCO_2)_2pyz](5)$. The synthesis method was similar to those of **1** and **2** under autoclavable conditions, except that DMF/ H_2O (5 mL, v/v, 3:2) was used instead of H_2O . After 2 days, a mixture of two compounds containing dark red and purple crystals was formed in the solution. The red crystalline blocks of **5** were isolated first using a spatula and air-dried (yield = 0.181 g). Purple crystals of **7** were then filtered and dried in air (yield = 0.252 g).

Anal. Calcd for **5** $C_6H_6N_2O_4Co$ (Mr. = 229.06): C, 31.46; H, 2.64; N, 12.23. Found: C, 30.23; H, 2.17; N, 12.1. IR (KBr, cm^{-1}): 3050 (m), 2998 (w), 2896 (m), 2800 (s), 2680 (m), 2400 (w), 2260 (w), 1910 (m), 1840 (m), 1730 (w), 1530 (s), 1370 (m), 1320 (s), 1100 (m), 1070 (m), 997 (m), 940 (m),

740 (m), 422 (m). UV-vis in water (λ_{max} nm, ϵ): 267 (868), 307 (193), 650 (6).

Anal. Calcd for **7** $C_2H_6O_6Co$ (Mr. = 126.02): C, 19.06; H, 4.76. Found: C, 18.95; H, 4.43. IR (KBr, cm^{-1}): 3320 (br), 2930 (m), 2880 (m), 2400 (m), 1910 (w), 1530 (s), 1360 (s), 1260 (m), 1190 (m), 1133 (m), 1010 (w), 740 (m), 850 (m), 760 (m), 610 (m), 520 (m), 450 (m).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c05216>.

FTIR, Raman, and UV-vis spectra; bond measurements and angles for **1–6**; hydrogen bond measurements for **1–6**; comparative table of bond measures and synthesis method of synthesized compounds **1–6** with that of literature reported compounds; crystal structures of compounds **1–6**; crystal refinement details of **5** and **6**; thermogravimetric analysis, magnetic properties, adsorption data, PXRD patterns, and Le Bail fitting; SEM images; and fluorescence spectral data for **1** (PDF)

Crystallographic data for $[Co(H_2O)(pyz)(suc)]$ (CIF)

Crystallographic data for $[Co(H_2O)_2(py_2)(suc)]$ (CIF)

Crystallographic data for $[Co(H_2O)_4(py_2)](suc)$ (CIF)

Crystallographic data for $[Co_2(H_2O)_2(py_2)(suc)_2]$ (CIF)

Crystallographic data for $[Co(HCOO)_2(py_2)]$ (CIF)

Crystallographic data for $[Co(H_2O)_4(suc)]$ (CIF)

Accession Codes

CCDC Numbers 2098543, 2098544, 2098545, 2098548, 2098547, and 2098546 contain the supplementary crystallographic data of compounds **1–6** reported in this work, and this data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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<https://pubs.acs.org/doi/10.1021/acsomega.1c05216>

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

S.N.D. gratefully acknowledges the financial support from CSIR (Grant No. 01(2923)/18/EMR-II). The authors

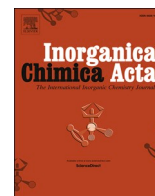
acknowledge the DST-FIST program for the Bruker D8 Quest Eco X-ray diffractometer. L.R.D. acknowledges CSIR (Grant No. 01(2923)/18/EMR-II) for the SRF and Goa University for the Research Studentship. Financial assistance to the School of Chemical Sciences (formerly Department of Chemistry), Goa University under the Special Assistance Program (DSA-1) of UGC-India is gratefully acknowledged. The authors acknowledge the Central Instrumentation facility at IISER Bhopal for assisting us with the SQUID-VSM facility. The authors thank Prof. B. R. Srinivasan for his valuable discussions on single-crystal X-ray data and Dr. Venkatesha R. Hathwar for his valuable inputs on the interpretation of simulated and experimental X-ray powder patterns of our compounds.

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Research paper

Structural characterization of benzoate anion-supported supramolecular assemblages of Co(III) and Ni(II) cyclam compounds with catecholase-like and antibacterial activities

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ARTICLE INFO

Dedicated to Prof. S. P. Kamat on the occasion of his 74th Birthday

Keywords:

Cyclam

Cobalt(III)

Nickel(II)

Benzoate

Spectroscopy

Crystal structure

Catecholase-like activity

Antibacterial

ABSTRACT

Two mononuclear compounds, *cis*-[Co(cyclam)(Bz)₂](Bz)·H₂O (**1**), and *trans*-[Ni(cyclam)(H₂O)₂](MOBA)₂·4H₂O (**2**) (where Bz = benzoate and MOBA = *o*-methoxy benzoate) have been synthesized and characterized by elemental analyses, spectroscopy, X-ray diffraction, and thermogravimetric techniques. Compounds **1** and **2** crystallize in a monoclinic crystal system with *P*₂₁/*c* and *P*₂₁/*n* space groups, respectively. The carboxylate ligand in compound **1** enables the cyclam ligand to adopt a *cis*-V conformation, while in compound **2**, cyclam adopts a stable *trans*-III conformation. Hirshfeld surface analyses were carried out to elucidate the intricate intermolecular forces shaping the crystal structure. The ability of compounds **1** and **2** to imitate the activities of the catechol oxidase enzyme was evaluated using 3,5-di-*tert*-butyl catechol (3,5-DTBC) as the model substrate. The antibacterial activity was investigated using the Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli* bacterial strains. Interestingly, compound **1** exhibited higher catecholase-like activity than compound **2** and enhanced antibacterial activity.

1. Introduction

The architectural and functional attributes of supramolecular compounds, built upon transition metals in combination with the macrocyclic ligands, have significantly influenced the domain of inorganic chemistry. Such compounds have shown substantial records in the fields of catalysis [1,2], molecular sensors [3,4], magnetism [5,6], and in the biological realm [7,8]. Compared to the open-chain analogs, the macrocyclic ligands are well-recognized for offering outstanding thermodynamic and kinetic stability [9]. Within the diverse array of macrocyclic ligands, saturated cyclam linkers are particularly notable for their extensive use in synthesizing metal complexes that exhibit a broad spectrum of functional properties [10,11]. The ancillary ligands in mixed ligand complexes are often known to influence the conformation of macrocyclic ligands around the metal ion. A Cambridge Structural Database (CSD) search on cyclam-related complexes indicated that the cyclam can adopt five different conformations, among which the *trans*-III (S,S,R,R) is the most stable conformation in solid state [12–14]. Other conformations, namely *trans*-I, II, IV, and V, are rare and predominantly

exist in the solution state. Another notable conformation is *cis*-V (R,R,R,R) observed with certain bidentate co-ligands [15,16]. The mode of interaction between the co-ligand and the metal-cyclam moiety significantly influences the type of conformation adopted by the macrocyclic ligand. Consequently, the metallocyclams can serve as effective recognition probes for proteins and anionic ligands primarily due to two reasons: (i) the kinetic inertness of the metal-cyclam core, which confers resistance to demetallation, and (ii) the availability of unsaturated sites that allow the binding of the anions without any steric constraints [17]. Liang and coworkers have highlighted the influence of different anions on the conformational selectivity of Zn(II)-cyclam complexes. In their report, the acetate anions were known to be more effective in promoting the stability of the *cis*-V conformation of Zn(II)-cyclam complexes in the aqueous medium compared to chloride or perchlorate anions thus suggesting importance of the choice of anions leading to the rich structural diversity [18]. Additionally, metal compounds featuring cyclam and its derivatives are being studied as potential analogs to mimic the metal active sites in certain metalloenzymes. Their ability to activate dioxygen molecules paves the way for chemical transformations, which would

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<https://doi.org/10.1016/j.ica.2024.122139>

Received 7 February 2024; Received in revised form 6 April 2024; Accepted 12 May 2024

Available online 15 May 2024

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otherwise be difficult to achieve without these metal compounds. This property enriches cyclam-based compounds potential in biochemical research and applications [19–21]. Catechol oxidase, a well-known enzyme, catalyzes the oxidation of *o*-diphenols to the corresponding *o*-quinones. The enzyme's metal active site features a hydroxo-bridged dicopper(II) core, with each copper ion coordinated to three histidine residues in a trigonal pyramidal geometry. Inspired by the active site of the catechol oxidase enzyme, numerous copper compounds have been investigated to mimic the catecholase-like activity, including those of manganese, iron, cobalt, nickel, and zinc, under standard laboratory conditions [22,23]. This broadens the scope of research in replicating enzymatic functions using various metal compounds. Metallocyclams are increasingly recognized in antibiotic research for their ability to imitate metalloenzyme active sites, which is essential in biological processes. The study of transition metal ions is vital, offering promising avenues for novel therapeutic approaches, including antibiotics, and enhancing our understanding of their medical and biochemical applications [24]. The research into transition metal ions is expanding therapeutic options and understanding their roles in health and disease. The rise in antimicrobial resistance has prompted the exploration of new metallodrugs with distinct actions from organic antibiotics and strategies to boost current antibiotics effectiveness, a key strategy against resistant infections [25,26]. The active roles of the metal compounds for antibacterial [27,28] and antifungal [29,30] activities are well known. The two accessible oxidation states of cobalt compounds, one being the kinetically inert Co(III) and the other labile high spin Co(II) oxidation state, make them particularly interesting and suitable candidates for anticancer agents [31–34]. One of the most promising drugs containing Co(III) includes CTC-96, a powerful inhibitor of herpes simplex virus type 1 (HSV-1) comprising N and O-donor ligands [35]. Recently, Fang and coworkers reported the cytotoxic and immunogenic-activating properties of cobalt(III)-cyclam complex decorated with flufenamic acid on breast cancer stem cells (CSCs). According to mechanistic studies, the compound induces DNA damage, inhibits cyclooxygenase-2 expression, and promotes caspase-dependent apoptosis in breast CSCs [36]. Our current work highlights the role of the benzoate anions in shaping the coordination environment and cyclam conformation in *cis*-[Co(cyclam)(Bz)₂](Bz)·H₂O (**1**), and *trans*-[Ni(cyclam)(H₂O)₂](MOBA)₂·4H₂O (**2**). It delves into the intermolecular interaction via Hirshfeld surface analysis and assesses the catechol oxidase-like behavior and antibacterial properties of compounds **1** and **2**.

2. Experimental

2.1. Materials and instruments

The chemicals namely, cobalt acetate tetrahydrate (99 %, Loba Chemie), nickel acetate tetrahydrate (98 %, Avra), benzoic acid (98 %, Avra), *o*-methoxy benzoic acid (>98 %, TCI chemicals), 1,4,8,11-tetraazacyclotetradecane (cyclam) (98 %, Avra) and 3,5-di-*tert*-butyl catechol (98 %, Sigma Aldrich) were used as received without any further purification. Infrared (IR) spectra were measured on Shimadzu (IR Prestige-21) FT-IR spectrometer with a resolution of 4 cm^{−1} from 4000–400 cm^{−1}. UV–Vis spectra were recorded in the 200–800 nm range on a UV–Vis spectrophotometer (Agilent 8453). X-ray photoelectron spectroscopy (XPS) experiments were done on PHI 5000Versa Probe II (FEI Inc.) at IIT Kanpur (ACMS). Elemental analyses were carried out on the Elementar Variomicro Cube CHNS analyzer. Thermogravimetric analysis was carried out on DTG-60 00,826 SHIMADZU with a heating rate of 10 °C/min under N₂ atmosphere from room temperature to 500 °C. The bulk purity of the compounds was determined using a RIGAKU SMAR-TLAB powder diffractometer equipped with Cu-Kα radiation (1.5418 Å) with a Ni filter. ESI-MS spectra of **1** and **2** were recorded on the Xevo G2-XS QT instrument at IIT Ropar. Molecular Hirshfeld surface analysis and related 2D fingerprint plots were obtained using Crystal Explorer software (version 21.5) [37].

2.2. Synthetic aspects

2.2.1. Synthesis of [Co(cyclam)(Bz)₂](Bz)·H₂O (**1**)

2 mmol (0.24 g) of benzoic acid was added to the 25 mL of hot distilled water. To this solution, 1 mmol (0.25 g) of Co(OAc)₂·4H₂O and 1 mmol (0.20 g) of 1,4,8,11-tetraazacyclotetradecane (cyclam) were added. The reaction mixture was further stirred for about 30 min. at 80 °C and kept for crystallization at normal laboratory temperature. After a week, the purple plate-shaped crystals formed were isolated from solution. Yield: 36 % (0.23 g). *Anal. Calc.* (%) for C₃₁H₄₁CoN₄O₇ **1** C, 58.11; N, 8.75; H, 6.46. Experimental (%) C, 58.45; N, 9.01; H, 6.71. IR (KBr, cm^{−1}): 3441 (br), 3076 (br), 2872 (br), 1598(s), 1562 (s), 1377 (s), 1355 (s), 1220 (m), 1172(m), 1068 (m), 1024(m), 839 (m), 719 (s), 684 (m) 449 (m). UV–Vis spectra were measured in CH₃CN (λ_{max}, nm): 378 (ε = 325 M^{−1}cm^{−1}), 530 (ε = 260 M^{−1}cm^{−1}). ESI-MS in CH₃CN: 501.1717 [Co(cyclam)(Bz)₂]⁺

2.2.2. Synthesis of [Ni(cyclam)(H₂O)₂](MOBA)₂·4H₂O (**2**)

The preparation of compound **2** was accomplished by adopting a similar procedure as used in the preparation of **1**, except that the carboxylic acid and metal source were different. 2 mmol (0.33 g) of *o*-methoxy benzoic acid was reacted with 1 mmol (0.25 g) of Ni(OAc)₂·4H₂O and 1 mmol (0.20 g) of 1,4,8,11-tetraazacyclotetradecane. After a week, the pale purple plate-shaped crystals were isolated from the solution. Yield: 61 % (0.36 g). *Anal. Calc.* (%) for C₂₆H₅₀NiN₄O₁₂ **2** C, 46.65; N, 8.37; H, 7.54. Experimental (%) C, 46.95; N, 8.56; H, 7.85. IR (KBr, cm^{−1}): 3460 (br), 3255 (m), 2931 (m), 1654 (m), 1537 (s), 1377 (s), 1247 (m), 1101 (s), 989 (m), 769 (s), 655 (m) 567 (m). UV–Vis spectra were measured in CH₃CN (λ_{max} nm): 520 (ε = 13 M^{−1}cm^{−1}). ESI-MS in CH₃CN: *m/z* = 257.1198 deprotonated [Ni(cyclam)]⁺ and fragment peaks at *m/z* = 129.0664 [Ni(cyclam)]²⁺ and *m/z* = 409.1559 [Ni(cyclam)(MOBA)]⁺.

2.3. The X-ray data collection and refinement

The single crystals obtained from the solution were chosen under the microscope for diffraction purposes. The data was collected at 296 K on a Bruker D8 Quest Eco X-ray diffractometer using monochromated Mo Kα (λ = 0.7107 Å) radiation. The integrating, scaling, and absorption correction steps were performed using Bruker's APEX 4 program package (Version 2021.10–0). The structures were solved with SHELXT and subsequent refinements using full-matrix least-squares on F² with SHELXL [38,39]. Non-hydrogen atoms were refined anisotropically. All the calculations were on WinGX software [40]. All the hydrogen atoms were placed geometrically and refined using a riding model. The oxygen of the water molecule in compound **1** was disordered; the hydrogens were fixed using the Olex 2 program [41].

2.4. Catalytic transformation of the 3,5-DTBC by **1** and **2**

The catecholase-like activity of compounds **1** and **2** was tested utilizing 3,5-di-*tert*-butyl catechol (3,5-DTBC) as the model substrate in dioxygen-saturated acetonitrile solution [42]. In a typical catalytic reaction, 100 equivalent of 3,5-DTBC in acetonitrile was reacted with 0.5 mM solution of compounds **1** and **2** separately for 30 min. The spectral changes were monitored on a UV–Vis spectrophotometer at 400 nm at a regular interval of 30 s for 30 min. The increase in the intensity of the new band at around 400 nm suggests the formation of the corresponding quinone product [43,44]. To investigate the dependence of the rates on the substrate concentration, 0.5 mM solution of the compound **1** was treated with 20–100 equivalents of 3,5-DTBC in acetonitrile under aerobic conditions at room temperature. The kinetic data was treated with the Michaelis-Menten model. The kinetics parameters such as (*V*_{max}), binding constant (*K*_m), and turnover number (*K*_{cat}) were extracted from the Lineweaver-Bruk plot.

2.5. Antibacterial activity

The antibacterial activity of compound **1** against Gram-positive *S. aureus* ATCC 25923 and Gram-negative *E. coli* ATCC 25922 were determined according to our earlier work by D'souza *et al.* [45]. The fresh loopful inoculum of *E. coli* and *S. aureus* was inoculated in two separate flasks containing 25 mL of nutrient broth. After 24 h of incubation, 100 μ L of inoculum was spread plated on nutrient agar plates in triplicates and allowed for adsorption for 30 min. The stock solutions of compound **1** (1 mg/mL) were prepared in dimethyl sulfoxide (DMSO) and water in a ratio of 1:1. The lowest concentration of **1** inhibiting the pathogens was determined by preparing different concentrations of **1** (10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 300, 500, 700, 900 and 1000 μ g/mL). Nalidixic acid (10 μ g/mL) and DMSO: H₂O were positive and negative controls, respectively. The cyclam, Co(OAc)₂·4H₂O, benzoic acid, compound **2**, and Ni(OAc)₂·4H₂O were evaluated for antibacterial activity at 1 mg/mL concentration. Each concentration was added to 6 mm wells bored on nutrient agar plates marked appropriately. The plates were kept in the BOD incubator at 37 °C. After 24 h, each plate was monitored for zones of growth inhibition in mm or no growth around the wells. The results were expressed as mean $\pm$ standard error for all experiments.

3. Results and discussion

3.1. Preparation and spectroscopic characterization of **1** and **2**

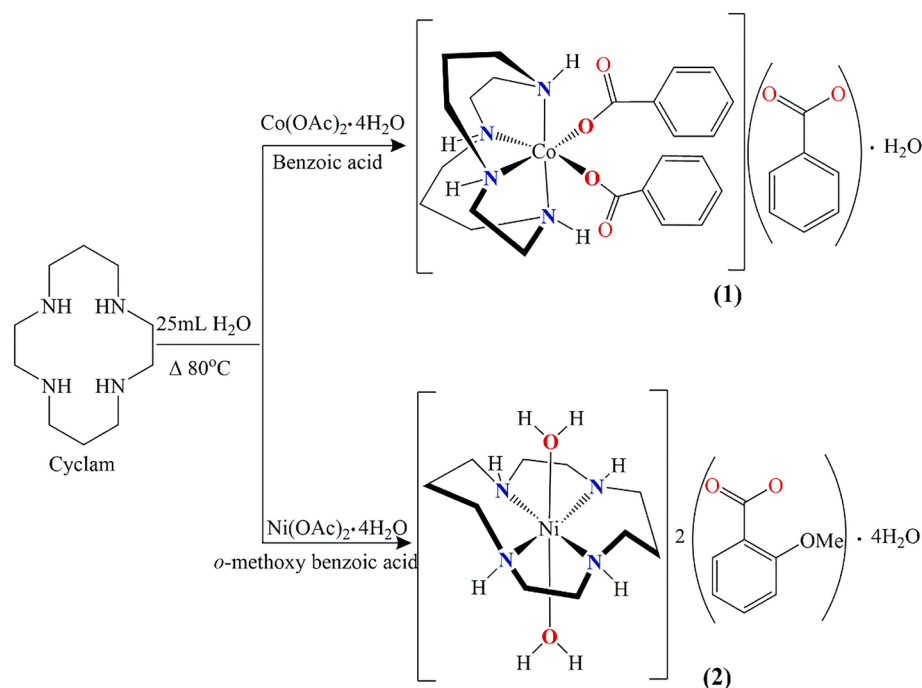
Hasnan and coworkers, in their article, mention the preparation of a dark brown semi-solid Co(II) complex titled a [Co(C₆H₅COO)₂(cyclam)]. This complex was synthesized through the reaction between [Co₂(C₆H₅COO)₃Cl]·H₂O and cyclam, which was then further reacted with pyridine-based ligands to obtain the other desired products [46,47]. However, the article does not elaborate on the structural or spectroscopic features of the [Co(C₆H₅COO)₂(cyclam)] compound. Herein we attempted a slightly different methodology, using a benzoic acid instead of sodium benzoate to obtain the single crystal of compound **1**. The metalocyclam compounds supported by the benzoate in **1** and *o*-methoxy benzoate **2** were prepared *via* the synthetic route presented in

(Scheme 1).

Infrared spectra of compounds **1** and **2** were compared with those of their respective acid precursors (benzoic acid and *o*-methoxy benzoic acid), as shown in Figs. S1 and S2. It was observed that their spectra do not overlap, indicating the formation of new compounds. Unlike the precursor spectrum, compound **1** exhibits a broad band centered at 3415 cm⁻¹, attributed to the O—H stretching vibration of the aqua molecules. The broad nature of the band suggests possible hydrogen bonding within the compound. A similar observation was seen in the case of compound **2**, where the broad band appeared in the range of 3585 to 3433 cm⁻¹ [48,49]. In addition to the bands due to water molecules, the spectra exhibit strong bands in the 1700 to 1300 cm⁻¹ region in both compounds assigned to the carboxylate functionality.

The shift of strong vibration bands in compounds **1** and **2** towards the lower frequency compared to the carbonyl stretching vibration of benzoic acid (1690 cm⁻¹) and *o*-methoxy benzoic acid (1680 cm⁻¹) suggests the presence of benzoate and *o*-methoxy benzoate anions respectively. The strong and sharp vibrational bands due to the asymmetric $\nu_{\text{asym}}(\text{COO}^-)$ and symmetric $\nu_{\text{sym}}(\text{COO}^-)$ stretching vibrations of the carboxylate ion in compound **1** arise at 1598–1560 and 1379–1355 cm⁻¹ respectively, while for compound **2** the bands are observed at 1587–1544 and 1381 cm⁻¹ respectively [50]. The strong to medium bands due to C—O stretching vibrations are seen in regions of 1070 to 1020 cm⁻¹ [51].

UV–Vis spectra of compounds **1** and **2** were recorded in CH₃CN (2x10⁻³ M) at room temperature, as shown in Fig. S3. The intra-ligand transitions below 300 nm are attributed to the π - π^* or n - π^* transitions which are originating from organic moieties. The absorption bands in compound **1** appears at 378 nm and 530 nm, assignable to the spin-allowed *d-d* transitions (¹A_{1g} $\rightarrow$ ¹T_{1g} and ¹A_{1g} $\rightarrow$ ¹T_{2g}, respectively) of the octahedral geometry in the diamagnetic spin state, thus indicating the presence of low spin Co(III) in **1** [52,53]. On the other hand, compound **2** exhibits a very weak shoulder band at $\sim$ 340 nm and another broad band at 520 nm assigned to ³A_{2g} (F) $\rightarrow$ ¹T_{1g} (F) (inset of Fig. S3). The *d-d* band at 520 nm, indicates a high spin octahedral Ni(II) ion similar to those reported in the literature [54]. Both compounds were characterized by ESI-mass technique in their respective CH₃CN solutions. ESI-MS depicted in Fig. S4 and S5 for compounds **1** and **2**,



Scheme 1. Synthetic routes for the preparation of **1** and **2**.

respectively, showed a prominent parent ion mass peaks at m/z = 501.1717 and 257.1198, which are assigned to the $[\text{Co}(\text{cyclam})(\text{C}_6\text{H}_5\text{COO})_2]^+$ and deprotonated $[\text{Ni}(\text{cyclam})]^+$ species respectively [55].

3.2. Characterization by X-ray techniques

3.2.1. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was utilized to elucidate the core-level electronic structure and binding energy of the elements present in the cobalt compound **1**. The high-resolution XPS spectrum of Co2p, depicted in (Fig S6) was plotted and deconvoluted using the peak fitting software. The spectrum of Co2p featured two dominant peaks and two weak satellite signals. The Co2p peaks corresponding to spin-orbit components Co2p_(3/2) and Co2p_(1/2) exhibited binding energies of 780.808 eV and 795.876 eV, respectively. Typically, the energy separation is ~16 eV for high-spin Co(II) and approximately 15 eV for low-spin Co(III) [56]. The measured binding energy separation of 15.068 eV was consistent with low spin Co(III), accompanied by two satellite peaks near the spin-orbit doublets at 787.330 and 801.727 eV. The XPS analysis thus suggests that cobalt in **1** exists in the +3 oxidation state, which is very well corroborated by the findings from UV-Vis spectroscopy.

3.2.2. The X-ray single crystal structure description of **1** and **2**

The X-ray single crystal structure analysis indicates that compounds **1** and **2** crystallize in centrosymmetric monoclinic crystal systems with $P2_1/c$ and $P2_1/n$ space groups, respectively. The technical details of data acquisition and selected refinement parameters for both compounds are given in Table 1. Fig. 1 displays an asymmetric unit of compound **1**, which includes a cationic core, $[\text{Co}(\text{cyclam})(\text{Bz})_2]^+$, featuring a centrally located cobalt ion. This core is coordinated by two

crystallographically independent benzoate anions and one tetradentate cyclam ligand, which adopts the *cis-V* conformation. This cationic core is balanced by one uncoordinated benzoate ligand, and together with a lattice aqua molecule, it contributes to the stabilization of compound **1**. The coordination environment of Co(III) comprises of four nitrogen atoms from the cyclam ligand (N1-N4) and two oxygen atoms (O1 & O3) from each of the benzoate ligands, connected via monodentate coordination mode, thus forming the $\{\text{CoN}_4\text{O}_2\}$ chromophore.

The selected bond lengths and bond angles are presented in Table 2. The distortion from the ideal octahedral geometry around the Co(III) atom is evident from the Co-O and Co-N bond distances, which are 1.923 (2) (Co1-O1), 1.947(2) (Co1-O3) and Co-N bond ranging from 1.971(3)-1.979(3) Å. Notably, the Co-O bond distances are shorter than that of the Co-N bond. The *trans* and *cis* bond angles also indicate the distortion with (O-Co-O, O-Co-N, N-Co-N) falling in the range 171.57(14) to 174.48(15)° and 85.96(14) to 95.96(14)° respectively. These observations derived from the Co-O and Co-N bond distances suggest that the cobalt is in a (+3) oxidation state in **1**, endorsed by UV-Vis and XPS analysis data. The bond distances align closely with those of related cyclam complexes [57–62], further supporting the change in the oxidation state from (+2) to (+3) upon coordinating with the cyclam ligand. Cyclam's inherent flexibility enables it to adopt the conformations described in the literature, with the *trans*-III form being the most stable. In compound **1**, the coordination of the benzoate ligands induces a diagonal folding of the cyclam ligand at N2 and N4 atoms, resulting in a *cis-V* conformation. The five-membered chelate rings of cyclam adopts the *gauche* conformation with average fold angles around the Co (III) ion of 86.16(15)°, which is less than the fold of the six-membered rings, that adopt a chair conformation.

The crystal lattice of compound **1** is stabilized by various non-covalent interactions, including N—H...O, O—H...O, and C—H...O bond, emanating from the organic components and the aqua molecule within the crystal lattice. All the hydrogens attached to the nitrogen atoms of the cyclam ligand participate in hydrogen bonds with the adjacent anions and the lattice water molecules, contributing to a supramolecular network structure. The hydrogen bonding parameters for **1** and **2** are outlined in Table 3. The ladder-shaped structure of compound **1** is constructed through inter- and intra-molecular hydrogen bonds. The one-dimensional zig-zag chain is formed by two units of $[\text{Co}(\text{Cyclam})(\text{Bz})_2](\text{Bz})\cdot\text{H}_2\text{O}$, linked via C1-H1A...O1W bond, and these units are further extended in a one-dimensional array through the intermolecular hydrogen bond C6-H6A...O6 as illustrated in Fig. S7.

Compound **2**, as described in this study, crystallizes in centrosymmetric monoclinic space group $P2_1/n$. The crystal structure is composed of an ionic pair, in which the cationic unit $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2]^{2+}$ includes a nickel ion situated at an inversion center. Two terminal water molecules are coordinated at the axial position (O1W and O1Wⁱ). The cyclam ligand occupies the equatorial positions through the nitrogen atoms (N1, N1ⁱ, N2, and N2ⁱ), thus forming an octahedral arrangement around the central metal ion, as depicted in Fig. 2. This cationic unit is counterbalanced by two uncoordinated *o*-methoxy benzoate anions, one among which is symmetry generated and engages in extensive hydrogen bonding with the lattice water molecules, contributing to the stability of the supramolecular assembly. Although the $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2]^{2+}$ core is very well documented in the literature, its interaction with *o*-methoxy benzoate is explored for the first time in this paper. The influence of anions on the conformation of the cyclam is detailed in Table S1.

The cyclam ligand in compound **2** adapts the *trans*-III conformation, which is the most thermodynamically stable isomer. This stability is due to the four- and six-membered chelate rings assuming the *gauche* and chair conformations, respectively [63]. Compound **2** displays a slight tetragonal distortion, as evidenced by the axial Ni-O bonds (2.1666 Å) from the aqua ligands being marginally more extended than the average Ni-N bond length (average 2.0653), aligning well with similar nickel cyclam compounds reported in the literature [64–67]. The selected bond distances and bond angles are listed in Table 2. Additionally, compound

Table 1

The crystal data and structure refinement parameters for compounds **1** and **2**.

Compound	1	2
Empirical formula	C ₃₁ H ₄₁ CoN ₄ O ₇	C ₂₆ H ₅₀ NiN ₄ O ₁₂
Temperature/K	296(2)	296(2)
Formula weight	640.61	669.39
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
<i>a</i> / Å	9.2901(3)	8.6697(2)
<i>b</i> / Å	35.1546(11)	7.8613(2)
<i>c</i> / Å	9.6023(3)	23.0083(6)
α / °	90	90
β / °	103.024(1)	91.6860(10)
γ / °	90	90
Volume / Å ³	3055.34(17)	1567.45(7)
<i>Z</i>	4	2
<i>D</i> _{calc} . [Mg cm ⁻³]	1.393	1.418
μ / mm ⁻¹	0.615	0.685
<i>F</i> (000)	1352	716
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
Crystal size/mm	0.29 × 0.16 × 0.05	0.21 × 0.14 × 0.09
θ range for data collection (°)	2.53 to 28.28	2.54 to 28.31
Index ranges	$-12 \leq h \leq 11, -46 \leq k \leq 46, -12 \leq l \leq 12$	$-11 \leq h \leq 11, -10 \leq k \leq 10, -30 \leq l \leq 30$
Reflections collected	30,131	21,437
Independent reflections	7590 [R(int) = 0.0756]	3905 [R(int) = 0.0279]
Completeness to θ = 25.242 (%)	99.9	99.9
SGoodness-of-fit on <i>F</i> ²	1.095	1.048
Final R indexes [<i>I</i> > 2 σ (<i>I</i>)]	R1 = 0.0754, wR2 = 0.1294	R1 = 0.0307, wR2 = 0.0709
Final R indexes [all data]	R1 = 0.1338, wR2 = 0.1492	R1 = 0.0363, wR2 = 0.0733
Largest diff. peak/hole/e Å ⁻³	0.39 and -0.45	0.38 and -1.26
CCDC No	2206672	2284051

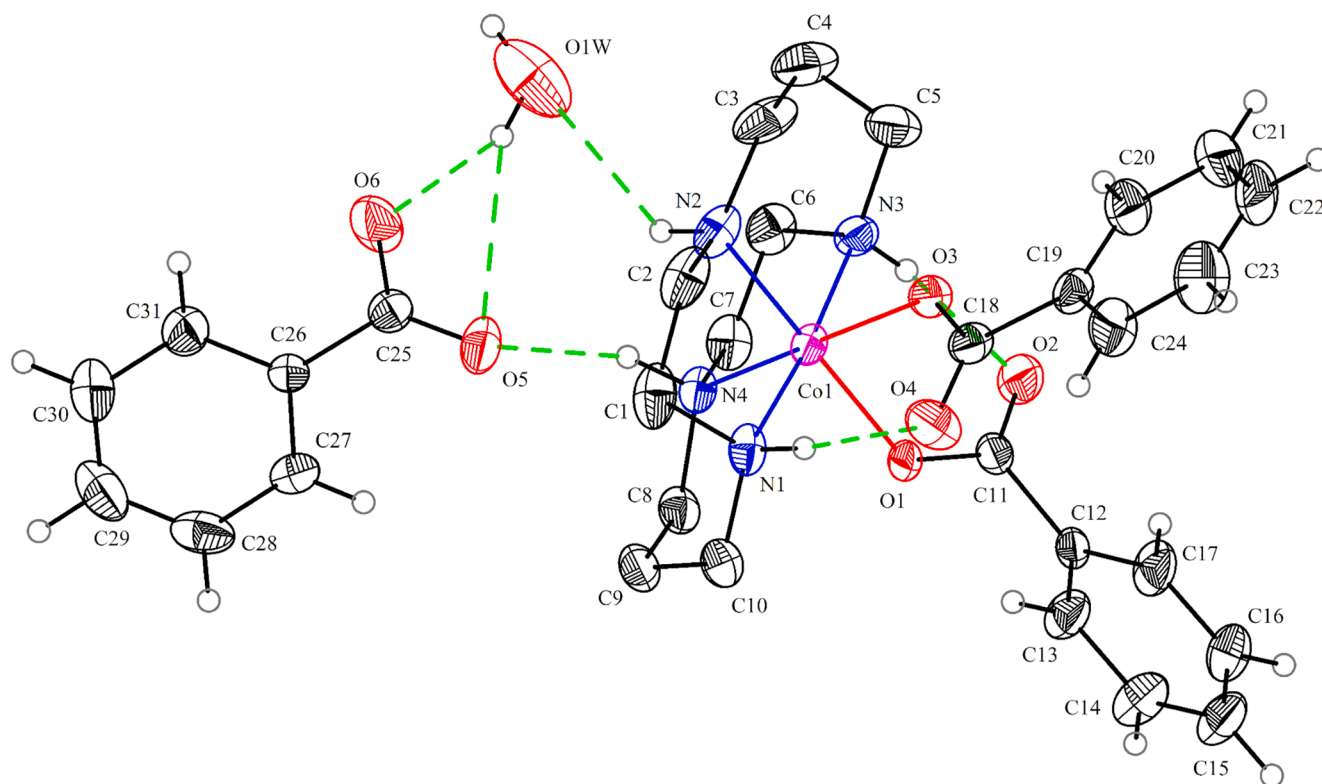


Fig. 1. The asymmetric unit of **1** is depicted with labeled atoms, excluding hydrogens of the cyclam carbon skeleton, for clarity. Thermal ellipsoids show atom positions at a 30% probability. The intramolecular hydrogen bonds are represented in green dotted lines.

Table 2
Selected bond lengths (Å) and angles (°).

Compound 1			
Bond distance		Bond angle	
Co1–O1	1.923(2)	O1–Co1–O3	86.74(11)
Co1–O3	1.947(2)	O3–Co1–N2	87.78(13)
Co1–N1	1.979(3)	N2–Co1–N4	95.96(14)
Co1–N2	1.978(3)	N4–Co1–O1	90.10(12)
Co1–N3	1.971(4)	N1–Co1–N3	174.48(15)
Co1–N4	1.971(3)		
Compound 2			
Bond distance		Bond angle	
Ni1–N1	2.0705(12)	N1–Ni1–N2	85.39(5)
Ni1–N1 ⁱ	2.0705(12)	N2–Ni1–N1 ⁱ	94.61(5)
Ni1–N2	2.0602(12)	N2 ⁱ –Ni1–N1 ⁱ	85.39(5)
Ni1–N2 ⁱ	2.0602(12)	N2 ⁱ –Ni1–N1	94.61(5)
Ni1–O1W	2.1666(10)	O1W–Ni1–O1W ⁱ	180.00(7)
Ni1–O1W ⁱ	2.1666(10)		

Symmetry code (i = 1 – x, 1 – y, 1 – z).

2 exhibits a network of hydrogen bonds, specifically N–H⋯O and O–H⋯O, which contributes to the stabilization of the supramolecular architecture. The hydrogens attached to the oxygen of the coordinated/lattice waters and the nitrogen atoms on the cyclam ligand act as hydrogen donors. This results in ten hydrogen bonds, half of which are intramolecular. The intermolecular hydrogen bond O3W–H8⋯O1 links the individual nickel units into an infinite chain propagating along the *a* axes as shown in Fig. S8. The hydrogen bond parameters of compound **2** are summarized in Table 3. The packing diagram of compound **2** and the hydrogen bonding network extending along the *ab* plane are illustrated in Fig. S9.

Table 3
Hydrogen bonding parameters (Å, °) for **1** and **2**.

D–H⋯A	d(D–H)	d(H⋯A)	<DHA	d(D⋯A)	Symmetry code
[Co(cyclam)(Bz) ₂](Bz)H ₂ O (1)					
N1–H1⋯O4	0.895	1.815	167.2	2.695	
N2–H2⋯O1W	0.818	2.609	135.18	3.241	
N3–H3⋯O2	0.794	1.955	167.52	2.736	
N4–H4⋯O5	0.980	1.919	159.41	2.857	
C1–H1A⋯O1W	0.970	2.643	130.55	3.355	[1 – x, 1 – y, 2 – z]
C6–H6A⋯O6	0.970	2.590	139.67	3.388	[–x, 1 – y, 2 – z]
O1W–H1W⋯O5	0.85	2.592	142.62	3.308	
O1W–H1W⋯O6	0.85	1.938	154.03	2.728	
[Ni(cyclam)(H ₂ O) ₂](MOBA) ₂ ·4H ₂ O (2)					
N1–H1⋯O3W	0.871	2.498	160.48	3.331	[–x, –y + 1, –z + 1]
N2–H2⋯O2	0.98	1.945	167.86	2.91	[–x + 1, –y, –z + 1]
O2W–H6⋯O3W	0.739	2.086	166.26	2.809	[–x, –y + 1, –z + 1]
O1W–H3⋯O1	0.795	2.061	172.49	2.851	[–x + 1, –y + 1, –z + 1]
O3W–H8⋯O1	0.773	2.147	158.34	2.879	[1 – x, y, z]
O3W–H8⋯O3	0.773	2.531	124.73	3.039	[1 – x, y, z]
O1W–H4⋯O1	0.833	1.995	172.45	2.823	
O1W–H4⋯O2	0.833	2.59	131.33	3.201	
O2W–H5⋯O2	0.736	2.111	176.4	2.846	
O3W–H7⋯O2W	0.806	2.027	161.29	2.809	

3.2.3. Comparative powder X-ray diffraction (PXRD)

Prior to the solution state investigations of compounds **1** and **2**, X-ray powder diffraction was employed to assess the bulk purity of the solid compounds. The diffraction patterns from bulk samples were matched with the stimulated patterns generated by Mercury software from the single crystal structure data of **1** and **2**. As seen in (Fig. 3a and b), the

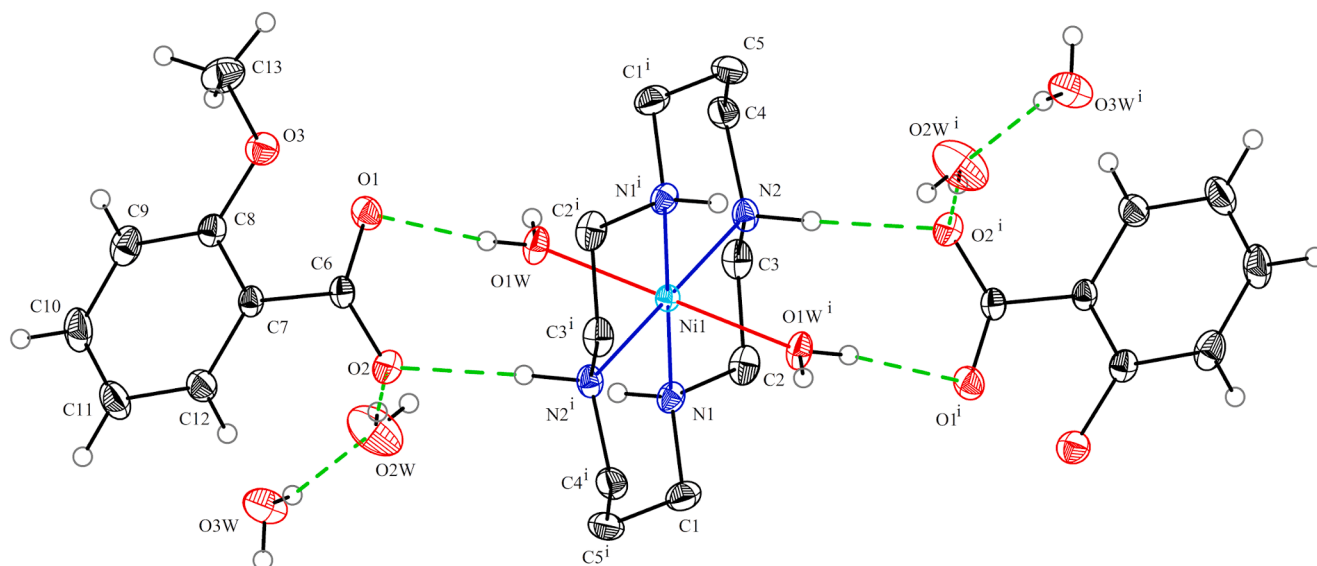


Fig. 2. The crystal structure of **2** shows the atom labeling scheme. The thermal ellipsoids are drawn at 30% probability except for the H atoms, shown as spheres of arbitrary radius. The hydrogen atoms on the cyclam carbon skeleton are omitted for clarity. The intramolecular hydrogen bonds are shown as green dotted lines.

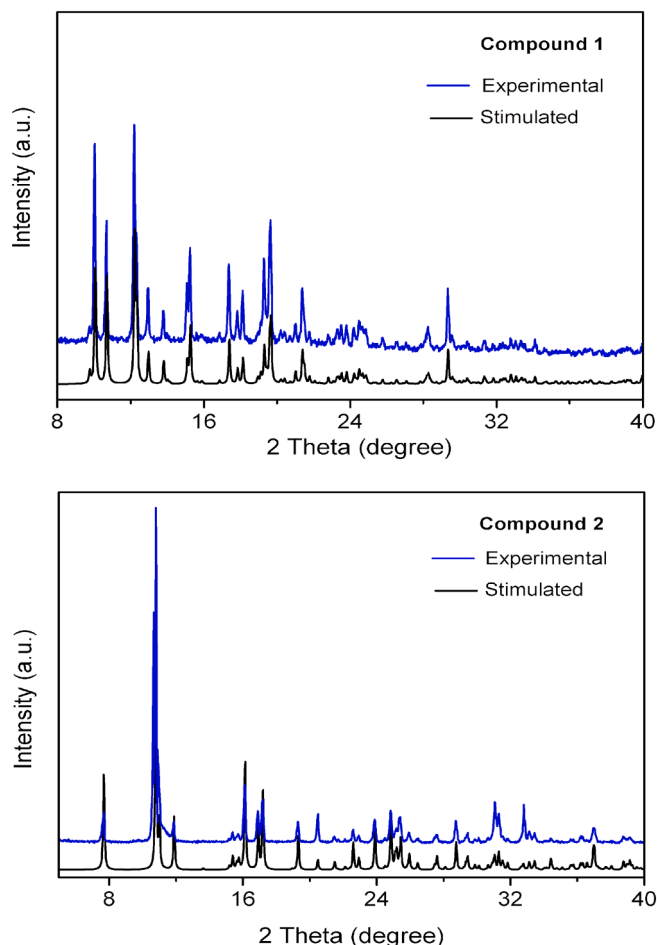


Fig. 3. a) Experimental PXRD pattern of **1** (black) overlaid with the stimulated pattern (blue); b) The experimental powder pattern of **2** (black) overlaid with the stimulated pattern (blue).

near-perfect alignment of the experimental and the stimulated patterns verified the bulk purity of compounds **1** and **2**. With the confirmed solid-state structure and bulk purity by diffraction techniques, the powdered samples were then utilized for catecholase reactivity and antimicrobial activities.

3.3. Thermogravimetric analysis

TG-DTA analysis was utilized to evaluate the thermal stability of compounds **1** and **2**. The TG plots, recorded under a nitrogen atmosphere, indicate that both compounds are stable below 200 °C after elimination of the lattice and coordinated water molecules (Fig. S10). For compound **1**, the initial decomposition event, marked by an endothermic peak in the DTA, occurs at ~100 °C, corresponding to 2.63 % mass loss (calcd. 2.81 %), signifying complete dehydration of compound **1**. A further mass loss of 48.62 % (Calcd. 50.17 %) is observed, associated with the thermal decomposition of cyclam and benzoate, with exothermic and endothermic peaks at 180 °C and 261 °C, respectively, in the DTA plot. Above 300 °C, a mass loss of 34.09 % (Calcd. 34.06 %) is attributed to the loss of two benzoate ligands, with a sharp endotherm at 350 °C. The final residue is 14.66 %, close to the calculated 14.19 %, for Co₃O₄ oxide, with no further weight loss observed beyond 400 °C. TG-plot of compound **2** reveals two successive mass loss events; the first mass loss of 16.06 % (Calcd. 16.15 %) corresponds to the loss of six water molecules between ~50–100 °C (Fig. S11). This is followed by a mass loss of 72.12 % (Calcd. 72.7 %) between 210–380 °C due to the decomposition of cyclam and two moles of *o*-methoxy benzoate, with two DTA peaks centered at 222 °C and 340 °C. Above 380 °C, there is no mass loss, and the final residue of 11.77 % corresponds to the formation of nickel oxide (Calcd. 11.16 %).

3.4. Molecular Hirshfeld surface analysis

The structures of compounds **1** and **2** were analyzed using Hirshfeld surface studies to gain in-depth visualization of the 3D intermolecular interactions responsible for crystal packing in lattice. The 2D fingerprint plots identified the key contributors to these intermolecular interactions. The interactions between the molecules can be quantitatively studied based on the color-mapping of functions of the Hirshfeld surface (HS). The red and blue spots represent distances indicating shorter and longer contacts, while the white color denotes contacts with distances

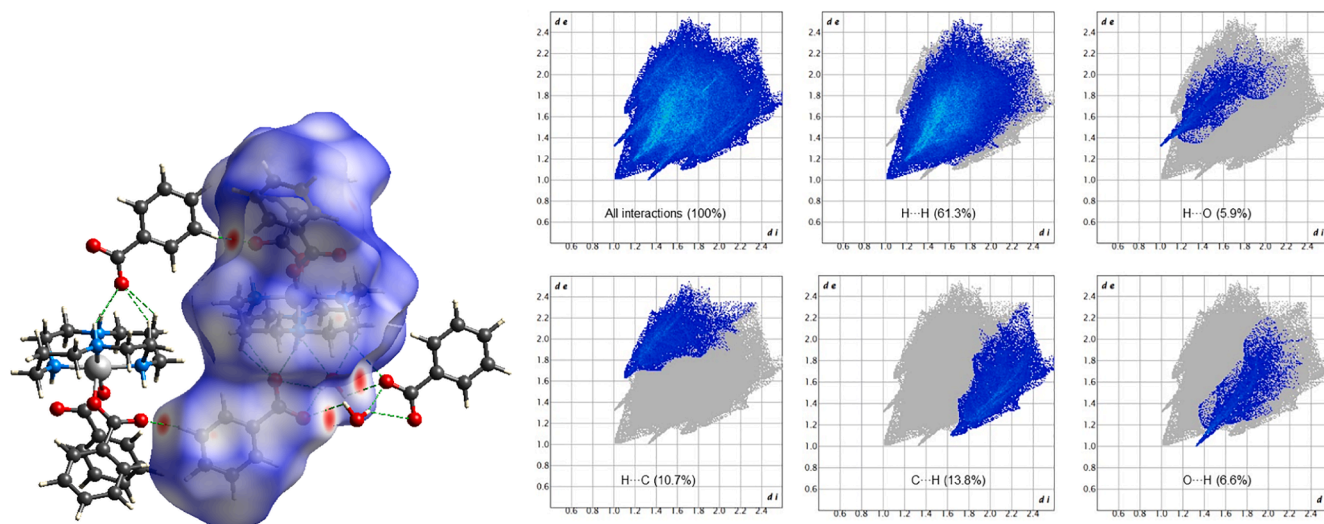


Fig. 4. a) HS mapped with the d_{norm} function for 1 showing the intermolecular interactions. b) 2D fingerprint plots with the relative contribution in % of interaction to HS area.

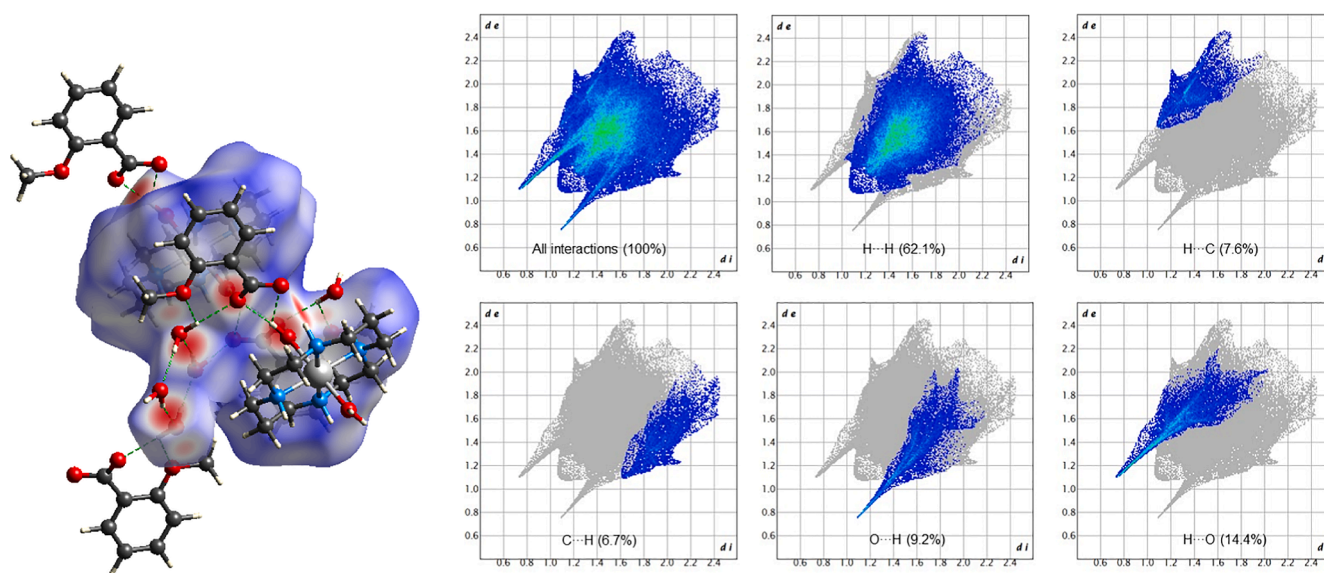


Fig. 5. a) HS mapped with the d_{norm} function for 2 showing the intermolecular interactions. b) 2D fingerprint plots with the relative contribution in % of interaction to HS area.

equal to the sum of van der Waals radii of the atoms [68]. The Hirshfeld surface plots for compounds 1 and 2 are displayed in Figs. 4a and 5a, respectively. The HS of compounds 1 and 2 were mapped with d_{norm} (normalized contact distance), which is defined by the internal d_i and the external d_e distance and the van der Waals radii of the atoms expressed as:

$$d_{\text{norm}} = \frac{d_i - r_i^{\text{vdw}}}{r_i^{\text{vdw}}} + \frac{d_e - r_e^{\text{vdw}}}{r_e^{\text{vdw}}}$$

where r_i^{vdw} and r_e^{vdw} are the van der Waals radii of the atoms [69]. The d_{norm} surfaces of 1 and 2, with short contacts, are defined by the red regions, which arise primarily from donor O—H and acceptor O atoms. Other significant interactions and characteristics of close-contact environments can be visualized using a 2D fingerprint plot. The 2D fingerprint plots and the relative contributions of various interactions for 1 and 2 are illustrated in Figs. 4b and 5b, respectively. The fingerprint plot can be further segmented into individual close contacts, each detailing

their specific share of the total intermolecular interactions, quantified as percentages. The molecular packing in the crystal structure is predominantly driven by H...H, H...O, and H...C interactions. The 2D fingerprint plots indicate that the principal contributors to the supramolecular assembly are the H...H interaction, accounting for 61.3 % in 1 and 62.1 % in compound 2. In addition to the H...H interactions, compound 2 displays a more significant percentage of O—H interactions compared to compound 1, attributable to increased water content and the substitution of the carboxylate group from benzoate to o-methoxy benzoate.

3.5. Catecholase-like activity of compounds 1 and 2

Several mononuclear and dinuclear cobalt and nickel complexes have been examined for their catalytic efficacy in oxidizing 3,5-di-*tert*-butyl catechol (3,5-DTBC) [70–74]. However, the literature needs to include specific findings on the oxidation of catechol by carboxylate-supported cobalt and nickel cyclam coordination complexes. Consequently, the impact of carboxylate binding in compounds 1 and 2 on the

catecholase activity was explored by employing 3,5-DTBC as a model substrate. Due to the quinone-catechol pair's lower reduction potential, 3,5-DTBC is commonly utilized in catechol oxidation studies [75]. The reaction kinetics were evaluated by monitoring the time-dependent change in absorbance at 400 nm during the oxidation process, as shown in Figs. 6 and 7 for compounds 1 and 2, respectively, in acetonitrile solvent. The initial rate method was utilized to elucidate the kinetics of the oxidation of 3,5-DTBC to 3,5-DTBQ at room temperature. The change in absorbance (ΔA) at 400 nm was plotted against time to determine the initial rate of the reaction. The Ni(II) based catalyst (compound 2) exhibited less activity towards the oxidation of 3,5-DTBC than compound 1. To determine the kinetic parameters of the reaction catalyzed by compound 1, a 0.5 mM solution of the catalyst was reacted with varying substrate concentrations (20–100 equivalent). The rate for each substrate concentration was ascertained using the initial rate method. The rate versus substrate concentration plot was analyzed using the Michaelis-Menten model to derive the Lineweaver-Burk plot, as shown in Fig. 8. Additionally, the kinetic parameters are summarized in Table 4 for compound 1. The product was identified by ^1H NMR spectroscopy, as shown in Fig. S12. The higher catalyst concentration required for the conversion of substrate to the product, compared to those reported in the literature using catalysts is in the range of 10^{-4} to 10^{-5} M [76–78], and suggests that this catalyst exhibits moderate to low activity towards the oxidation of the 3, 5-DTBC. This may be due to competitive carboxylate ligands, which render the compound less effective in the oxidation process at lower concentrations.

3.6. Antibacterial activity

It has been documented that cyclam and its salts have shown potent antiviral properties [79], but there have been few reports of their antimicrobial activity [80]. The antimicrobial activity of metal-cyclam complexes and their derivatives against *Mycobacterium tuberculosis*, which causes tuberculosis, was the principal focus initiated by researchers [81,82]. Interestingly, research has progressed towards evaluating the antimicrobial properties of cyclam salt derivatives against bacterial (*E. coli*, *Pseudomonas aeruginosa*, *S. aureus*) and fungal (*Candida* sp.) pathogens [80,83,84]. Additionally, the coordination of metal ions in cyclam-based systems enhances or diminishes efficiency toward pathogens. This is supported by the previously published reports on the antimicrobial properties of cyclam-based metal complexes against bacterial and fungal pathogens [85–87]. Although various studies are being carried out to evaluate the antimicrobial performance of cyclam-based metal complexes, there are scarce reports on carboxylate-supported

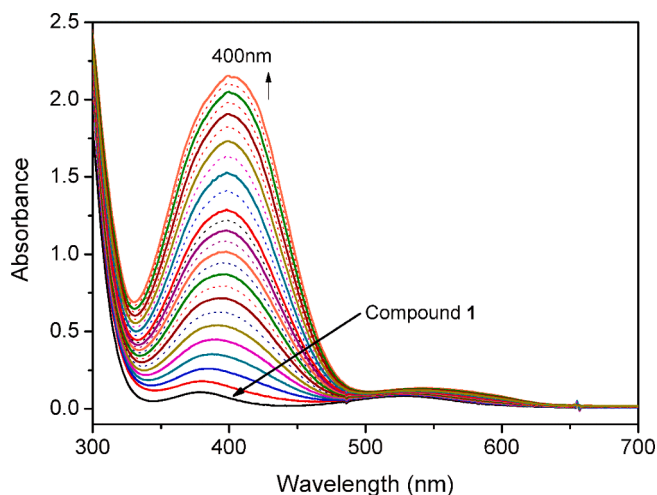


Fig. 6. Escalated absorbance around 400 nm after adding 100 equivalents of 3,5-DTBC to a 0.5 mM solution of compound 1 in acetonitrile.

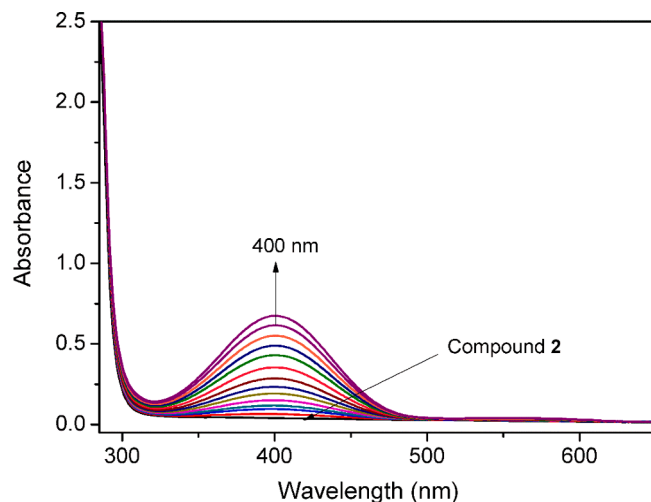


Fig. 7. Escalated absorbance around 400 nm after adding 100 equivalents of 3,5-DTBC to a 0.5 mM solution of compound 2 in acetonitrile.

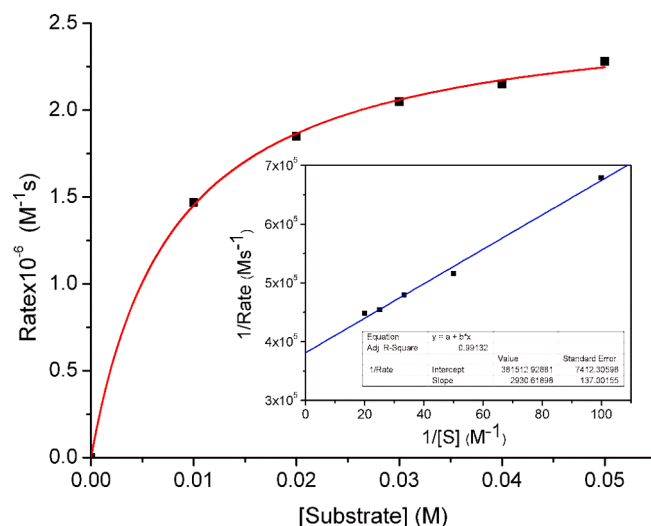


Fig. 8. The plot of the initial rates versus substrate concentration. The inset shows the Lineweaver-Burk plot.

Table 4

Kinetic parameters for the oxidation of 3,5-DTBC.

Compound	$V_{\max}$ (M/s)	K_M (M)	K_{cat} (h^{-1})
1	2.62×10^{-6}	7.68×10^{-2}	18.9

Note: Standard error for $V_{\max}$ (M min^{-1}) = 0.0353×10^{-6} and $K_M = 4.5288 \times 10^{-4}$.

metal cyclam complexes for biological activity [88]. Considering this, the antibacterial properties of newly synthesized compounds, 1 and 2, along with cyclam, $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, and benzoic acid against *E. coli* ATCC 25922 and *S. aureus* ATCC 25923 were evaluated using agar well diffusion method. Among different concentrations of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 300, 500, 700, 900, and 1000 $\mu\text{g/ml}$ of 1, 90 $\mu\text{g/ml}$ was the lowest concentration found effective against *E. coli* and *S. aureus*. Moreover, as seen in Fig. 9, the antibacterial activity of 1 against *E. coli* and *S. aureus* varied in a dose-dependent manner ranging from 11.0–27.3 mm and 9.33–26.0 mm, respectively, for concentrations 100, 300, 500, 700, 900 and 1000 $\mu\text{g/mL}$. However, compound 1 was more effective against Gram-negative *E. coli* than *S. aureus*. Alves et al. [80] reported the minimum inhibitory

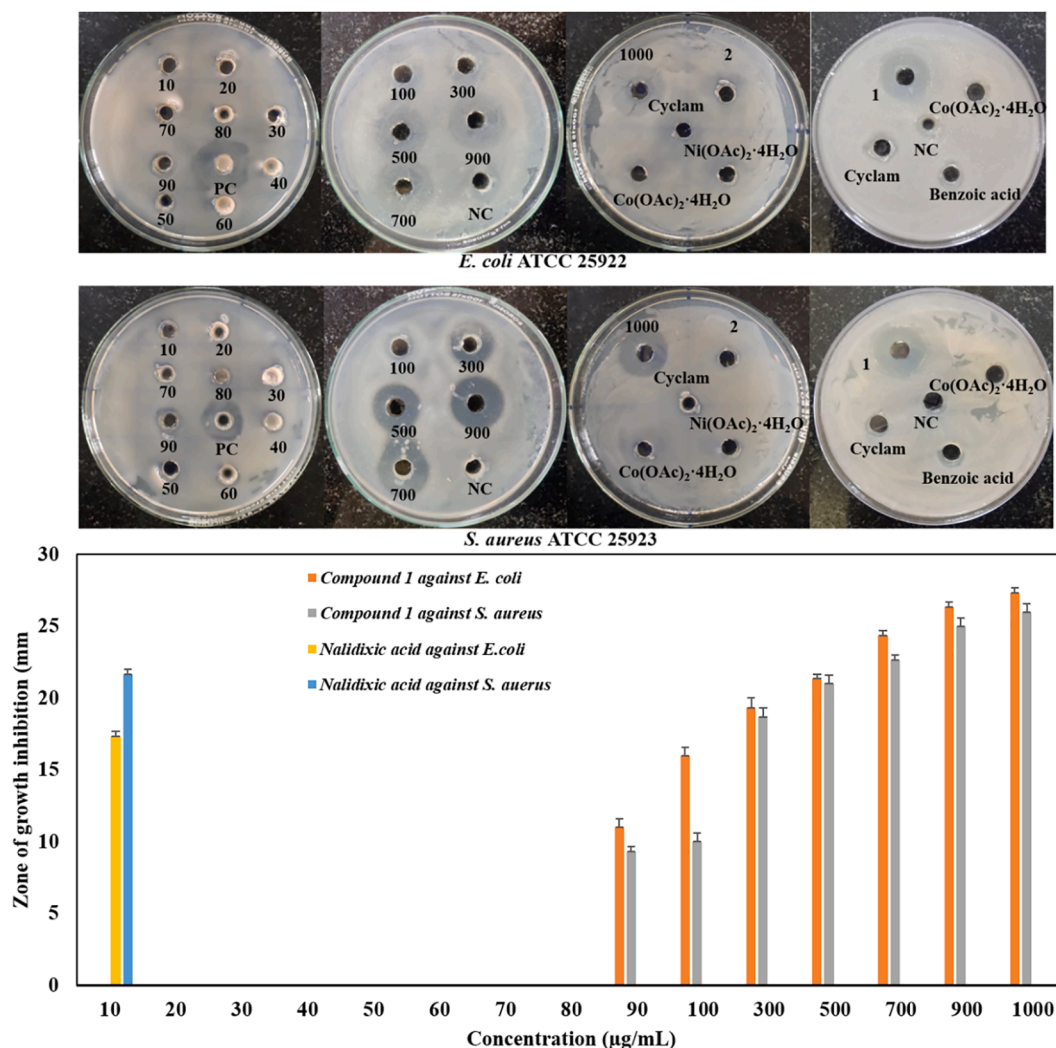


Fig. 9. Antibacterial activity of **1** at different concentrations (10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 300, 500, 700, 900 and 1000 µg/ml); NC, negative control (DMSO: H₂O); PC, positive control (Nalidixic acid, 10 µg/ml); **2**, [Ni(cyclam)(H₂O)₂](MOBA)₂·4H₂O.

concentration (MIC) of 9, 261, and 15 µg/mL for [H₂{H₂(3-CF₃PhCH₂)₂Cyclam}](CH₃COO)₂·(CH₃COOH)₂ against *E. coli*, *P. aeruginosa*, and *S. aureus* strains respectively, by the broth dilution method. Furthermore, protonated cyclam [H₄(H₄Cyclam)Cl₄] showed MIC of > 512 µg/mL for *E. coli* ATCC 25922 and *S. aureus* strains, respectively [83]. Nikolić and co-workers [88] examined Cu and Co-based substituted cyclam derivatives for antimicrobial activity. Their results revealed significant antimicrobial activity of Co₄(pm)(topic)₂ (ClO₄)₄·6H₂O against *Bacillus subtilis*, *Klebsiella pneumoniae*, and *S. aureus* strains with a MIC of 53 µg/mL, whereas the MIC was 212 µg/mL for *E. coli* and *Enterococcus faecalis*. In contrast, [Cu₂(pma)(tpmc)]·8H₂O failed to exhibit activity against the pathogenic strains. Recently, the newly synthesized cyclam-based iron and copper complexes have been known to exhibit activity against unicellular and multicellular fungal pathogens [89]. Archana and Sreedaran [90,91] synthesized and evaluated DNA cleavage, antitumor, and antimicrobial activities of a series of cyclam-based macrobicyclic binuclear Zn(II) and Mn(II) complexes. It is important to note that cyclam, Co(OAc)₂·4H₂O, and benzoic acid at 1000 µg/ml did not exhibit antibacterial activity. Similarly, compound **2** and Ni(OAc)₂·4H₂O failed to inhibit the growth of *E. coli*, and *S. aureus* at 1000 µg/ml (Fig. 9). In contrast, Sreedaran *et al.* [87] reported antimicrobial activity of cyclam-based nickel(II) complexes at 100 µg/mL against *E. coli* ATCC 11775, *P. aeruginosa* ATCC 10145, *K. pneumoniae* ATCC 13883, *B. subtilis* ATCC 6633, and *S. aureus* ATCC

12600. The lack of activity by individual components suggests that they do not contribute effectively at 1 mg/mL against the tested pathogens, implying a synergistic effect of these components in **1** that could be responsible for antibacterial activity. Furthermore, the differences in the antibacterial activity in terms of zone of growth inhibition could be attributed to the morphological and structural difference between *E. coli* and *S. aureus*, as previously reported [92]. Additionally, the presence of lipopolysaccharide in *E. coli* may account for the pathogen's sensitivity to antimicrobial agents. In conclusion, the current investigations have revealed the antimicrobial performance of **1**, which could be explored as a potent antimicrobial agent in the future.

4. Conclusions

Two mononuclear compounds [Co(cyclam)(Bz)₂](Bz)₂H₂O (**1**) and [Ni(cyclam)-(H₂O)₂](MOBA)₂·4H₂O (**2**), were synthesized and characterized using various techniques. These compounds exhibited structural diversity, as revealed by single-crystal X-ray diffraction studies. The use of benzoate in compound **1** and *o*-methoxy benzoate in compound **2** resulted in distinct structural features. Notably, the cyclam ligand adopted *cis*-V conformation in **1** in contrast to the *trans*-III conformation in **2**. Although stabilized by carboxylates and lattice waters, the supramolecular networks collapse relatively at lower temperatures to form simple oxides, as evidenced by thermogravimetry.

Herhsfeld studies support the key role of hydrogen bond interactions in the 3D packing of the supramolecular assembly, wherein H...H type of weak interaction predominated in both the compounds. With regards to their reactivity, compound **1** demonstrated enhanced catecholase-like activity in oxidizing 3,5-di-*tert*-butyl catechol as compared to Ni(II) compound **2**, with 3,5-di-*tert*-quinone as the sole product. Compound **1** exhibited antibacterial activity against gram-positive and gram-negative bacteria, making it a potential antibacterial agent.

CRedit authorship contribution statement

Nikita N. Harmalkar: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **San- ket Gaonkar:** Writing – original draft, Methodology, Data curation. **Delicia A. Barretto:** Writing – review & editing, Writing – original draft, Data curation. **Sunder N. Dhuri:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors are unable or have chosen not to specify which data has been used.

Acknowledgments

The authors thank the Department of Science and Technology (DST), New Delhi, India, for DST-FIST (SR/FST/CSII-034/2014(C) and the University Grants Commission (UGC), New Delhi, India, for the UGC-SAP (F.504/14/DSA-I/2015) for the support of instrumental facilities. SND thanks the Council of Scientific and Industrial Research (CSIR), New Delhi, India (No. 01(2923)/18/EMR-II) for financial support. SND also thank Goa State Research Foundation, Goa (GSRF/Schemes/MajorGR/13/2023/187/ii) for research support. NNK acknowledges UGC for providing her financial support under the Savitribai Jyotirao Phule Fellowship for Single Girl Child (SJSJC) [UGCES-22-OB-GOA-F-SJSGC-6907]. Author SG is grateful to the Department of Microbiology, Goa Medical College, Bambolim, Goa, India, for the microbial pathogens used in the study.

Appendix A. Supplementary data

Supplementary data (Additional crystallographic information can be found in the joint Cambridge Crystallographic Data Centre (CCDC) and is available without charge: the deposition number CCDC 2206672 (**1**) and 2284051 (**2**). [Supplementary Data \(Figs. S1 and S12\) and \(Table S1\)](#) associated with this article are electronic.) to this article can be found online at <https://doi.org/10.1016/j.ica.2024.122139>.

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Cite this: *New J. Chem.*, 2024, 48, 3472

Weakly antiferromagnetic vanillin and acetate bridged dinuclear Ni(II) compound exhibiting catecholase-like activity and biological properties†

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A dinuclear nickel compound that features vanillin (van) and acetate (OAc) bridging ligands, [Ni₂(μ-van)₂(μ-OAc)(NCS)₃(H₂O)]·5H₂O **1**, was synthesized and characterized using various techniques. Crystal structure analysis revealed a pair of Ni(II) ions bridged by an acetate anion through a μ₂-η¹:η¹ coordination mode. At the same time, vanillin bridges both nickel(II) centers through phenolic oxygen, separating the two Ni ions by a distance of 3.001(7) Å. The temperature-dependent magnetism indicates weak antiferromagnetic behaviour in compound **1**, following the Curie–Weiss law with Curie constant $C = 1.0145 \text{ cm}^3 \text{ K mol}^{-1}$ and Weiss constant $\theta = -4.1 \text{ K}$. Compound **1** was evaluated for its ability to mimic the catechol oxidase enzyme using 3,5-di-*tert*-butylcatechol as a model substrate with a K_{cat} value of $157.1 \times 10^2 \text{ h}^{-1}$. Furthermore, compound **1** was tested for its cytotoxicity against HepG2 cancer cells and DNA cleavage properties.

Received 6th October 2023,
Accepted 15th January 2024

DOI: 10.1039/d3nj04662a

rsc.li/njc

1. Introduction

The nickel(II) ion presents versatile coordination chemistry due to its inherent ability to adopt various geometries. For many decades, nickel was not thought to be involved in biological processes. Later, the discovery of urease by Zerner in 1975,^{1,2} to possess nickel in its active center, was a game changer and served as an initial impetus for bioinorganic chemists to understand significant roles played by Ni(II) in biological metabolism. In many enzymes, such as *E. coli* glyoxalase-I and superoxide dismutase, its functional utility is transparently visible.^{3–5} The nickel(II) ion plays a vital role in metalloproteins like hydrogenases, such as carbon monoxide dehydrogenase and acetyl-CoA synthase.^{6,7} These enzymes have the ability to activate molecular oxygen at ambient temperatures, and thus there has been a significant focus on nickel(II) enzymes in the

past.^{8–10} Nickel(II) compounds serving as functional models have been utilized as competent catalysts for several synthetic transformations of industrial importance.^{11,12} Metalloenzyme models with oxidase activity have attracted many researchers, in the pursuit of creating bio-inspired catalysts for organic oxidation.¹³

Nickel(II) has been implicated in the pathogenesis of certain diseases: for example, nickel(II) ions can interact with proteins and induce immune responses in individuals who are allergic to nickel.¹⁴ Furthermore, a plethora of nickel(II) compounds with biological activities, such as anti-tumor antibiotics,¹⁵ anticonvulsants, antiepileptic drugs, or vitamins, have been reported.^{16–18} In an attempt to evaluate nickel(II) compounds biologically, many of them that exhibit noteworthy potential as antibacterial and anti-fungal agents,^{19–21} as well as those that show anti-inflammatory²² and antioxidant^{23–25} activity, have been explored and verified. Additionally, various nickel(II) compounds have been reported to act as DNA intercalators^{26,27} and DNA cleavage agents.^{28,29} These compounds possess effective anti-proliferative activity towards diverse cell lines and have been adequately substantiated in the literature.^{30–32}

Dinuclear transition metal compounds play prominent roles in electron transfer processes in metallobiomolecules,^{33–37} which can be confirmed by citing an example of a unique representation of a heteroleptic paddlewheel complex of nickel(II) that has been synthesized and structurally characterized.³⁸ Extensive research has been dedicated to the

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† Electronic supplementary information (ESI) available. CCDC 2285723. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3nj04662a>

synthesis of dinuclear metal compounds that mimic several metalloproteins like urease^{39–41} and catecholase.^{42–44} Dinuclear nickel(II) compounds have been known to catalyze catechol oxidation.^{45,46} The ligating groups play indispensable roles in establishing a linkage between the biological function and relevance of the compound. A well-known and multifaceted ligand studied in large applications is *p*-vanillin (4-hydroxy-3-methoxybenzaldehyde), which occurs naturally in various plants. It is synthetically obtained as a by-product of the sulfite process in the manufacture of wood pulp.⁴⁷ *p*-Vanillin is commonly used as a flavouring or fragrance agent in food items, perfumes, beverages, cosmetics, and the pharmaceutical industry.⁴⁸ *p*-Vanillin exhibits non-linear properties with second harmonic generation efficiency, and thus, it has potential for use in the fabrication of optical devices.⁴⁹

Apart from its industrial and economic value, *p*-vanillin has been effectively authenticated as a significant bioactive substance. It is an effective anti-mutagenic agent and reduces certain species that induce mutations in bacteria and subsequently inhibits spontaneous mutations.⁵⁰ The bioactivity of *p*-vanillin is propagated through the fact that it can significantly reduce mutations caused by ultraviolet light and X-rays in mammalian cells and hamster lung cells (V79).⁵¹ The innate ability of *p*-vanillin to cause DNA cleavage and its ability to induce the apoptosis of HepG2 cancer cells were very well supported in our recent study.⁵² Our up-to-date search of the CSD provided us with a few structures of transition metal complexes incorporating *p*-vanillin^{53–56} and a single mononuclear compound has been specifically reported for nickel.⁵⁷ Considering the importance of *p*-vanillin in biology and scarcity of studies on nickel-vanillin compounds, we herein report the structural, spectroscopic, and magnetic properties of a new dinuclear nickel(II)-vanillin compound **1** with subordinate acetate and isothiocyanate ligands. The catecholase-like activity of the dinuclear compound is demonstrated along with a presentation of the efficacy of compound **1** in cytotoxicity studies and DNA cleavage.

2. Experimental section

2.1. Materials and methods

The chemicals used in this study were procured from local chemical vendors and used as received without further purification or recrystallization. Infrared spectra of powdered compound **1** and associated ligands were measured on a Shimadzu FTIR spectrophotometer (IR-Prestige-21) in the region 4000–400 cm^{−1} at 4 cm^{−1} resolution in a KBr matrix. UV-Vis absorption spectra were recorded on a diode array photocathode Agilent UV-Vis spectrophotometer (model-8453). Elemental analyses were achieved using an Elementar Vario MACRO cube CHNS analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance X-ray diffractometer using Cu Kα₁ (λ = 1.5406 Å) with an Ni filter. Temperature-dependent magnetic measurements of polycrystalline sample **1** were carried out using a SQUID-VSM MPMS3 magnetometer in the temperature range of 60 to 310 K. The temperature-dependent variation of

field-cooled (FC) and zero-field-cooled (ZFC) magnetization (M) was measured with a magnetic field of 100 Oe. The ¹H NMR spectra were recorded on a Bruker 500 MHz instrument with tetramethylsilane (TMS) as an internal standard in CDCl₃ at IIT Goa.

2.2. Single crystal X-ray diffraction (SCXRD)

The single crystal X-ray structure determination of compound **1** was achieved using a Bruker D8 QUEST ECO X-ray diffractometer equipped with graphite-monochromated MoKα (λ = 0.7107 Å) radiation. The collected frames were integrated, scaled, and merged, and absorption correction was performed using Bruker's APEX 4 program package. The structure of **1** was solved using SHELXS and subsequent refinements were carried out against F² using SHELXL-2014.⁵⁸ All non-hydrogen atoms were refined anisotropically. The H-atoms of water molecules were located from a difference map, and hydrogens attached to carbon atoms were refined in calculated positions [C–H = 0.93 Å and O–H = 0.85 Å] with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ [1.5 for $U_{\text{eq}}(\text{O})$] using a riding model. The technical details of data acquisition and selected refinement results for **1** are given in Table 1.

2.3. Synthesis of [Ni₂(μ-van)₂(μ-OAc)(NCS)₃(H₂O)]·5H₂O

A methanolic solution (10 mL) of nickel(II) acetate tetrahydrate (1 mmol, 0.249 g) was added dropwise to a methanolic solution (10 mL) of vanillin (2 mmol, 0.304 g) and ammonium thiocyanate (2 mmol 0.152 g). The reaction mixture was stirred for two

Table 1 Crystal parameters and selected refinement details for compound **1**

Empirical formula	C ₂₁ H ₃₁ N ₃ Ni ₂ O ₁₄ S ₃
Formula weight (g mole ^{−1})	763.09
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions (Å/°)	$a = 10.637(14)$ $\alpha = 90$ $b = 22.981(3)$ $\beta = 106.458(4)$ $c = 14.427(17)$ $\gamma = 90$
Volume (Å ³)	3382.4(7)
Z	4
Density (calculated) (Mg m ^{−3})	1.498
Absorption coefficient (mm ^{−1})	1.361
$F(000)$	1576
Crystal size (mm ³)	0.4 × 0.22 × 0.12
2 theta range for data collection (°)	2.184 to 28.364
Index ranges	$-14 \leq h \leq 14$, $-30 \leq k \leq 30$, $-16 \leq l \leq 19$
Reflections collected	49 980
Independent reflections	8412 [$R(\text{int}) = 0.0479$]
Completeness to theta = 25.242° (%)	99.3
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8412/2/420
Goodness-of-fit on F^2	1.031
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0465$, $wR_2 = 0.1295$
R indices (all data)	$R_1 = 0.0661$, $wR_2 = 0.1334$
Extinction coefficient	n/a
Largest diff. peak and hole e (Å ^{−3})	0.82 and −0.74
CCDC	2285723

hours, and the green-colored solution was then allowed to evaporate slowly. After two weeks, the green-colored crystals were isolated from mother liquor, washed with isopropanol and ether, and air-dried. Yield of **1** is 0.472 g (55%). Anal. calcd for **1**: $C_{21}H_{31}O_{14}N_3S_3Ni_2$ (M.W. = 763.09 g) C, 33.05; H, 4.10; and N, 5.51 Found: C, 33.77; H, 4.21; and N, 5.39. IR (KBr, cm^{-1}): 3207 (br), 2833 (br), 2113, 2058, 1870 (sh), 1665 (sh), 1562 (sh), 1487 (sh), 1282 (sh), 1001 (sh), and 815 (sh). UV-Vis (DMSO) (λ_{max} , nm): 252, 281, 317, 673 and 742.

2.4. Catecholase-like activity

The catecholase-like activity of dinuclear compound **1** was investigated using 3,5-di-*tert*-butylcatechol (3,5-DTBC) as a model substrate. 3,5-DTBC is known to offer a low quinone-catechol reduction potential, making it an ideal substrate for such studies.^{59,60} The efficacy of the Ni(II) compound in catalyzing the oxidation of 3,5-DTBC was studied by adding 100 equivalents of 3,5-DTBC to a 10^{-4} M methanolic solution of **1** saturated with oxygen atmosphere. The reaction proceeds with the formation of a new absorption band at 405 nm, which is attributed to the respective quinone with a distinct color change from light green to yellow for a duration of 30 minutes. A blank experiment was conducted without a catalyst, which showed no quinone formation in MeOH for up to 2 h. The kinetics of the oxidation of 3,5-DTBC in the presence of the catalyst was measured by the initial rate method.⁶¹ The dependence of the initial rate on substrate concentration (100–600 eq.) was spectrophotometrically monitored at 405 nm. Compound **1** showed saturation kinetics; hence, the data was treated with the Michaelis–Menten model. The maximum velocity (V_{max}), binding constant (K_M), and rate constant (K_{cat}) were calculated using the Lineweaver–Burk graph. NMR spectroscopy was used to characterize the isolated product after the catalytic study of compound **1** which was identified to be 3,5-DTBQ (Fig. S5, ESI†). 1H NMR (400 MHz, $CDCl_3$): δ = 6.85 (s, 1H), 6.15 (s, 1H), 1.20 (s, 9H), and 1.16 (s, 9H).

2.5. Detection of H_2O_2 in reaction medium

The generation of hydrogen peroxide during the reaction was determined by an iodometric method. The catalytic reaction was carried out as described in the kinetics experiment. After 1 h, to stop further oxidation, the solution was acidified with H_2SO_4 to pH 2. To the acidified solution, 10% KI solution (1 mL) was added, followed by the addition of 3% ammonium molybdate solution to increase the rate of the reaction.⁶² 3,5-DTBQ was then extracted twice with CH_2Cl_2 from the reaction medium. The formation of I^{3-} could then be spectrophotometrically monitored using the aqueous layer. In blank experiments under identical conditions, only minor formation of I^{3-} was observed in the presence of just 3,5-DTBC or the catalyst.

2.6 Cytotoxicity studies

The cytotoxic effect of compound **1** was determined by a colorimetric assay that measures the reduction of yellow 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) to an insoluble and dark purple formazan product by mitochondrial succinate dehydrogenase of viable cells. HepG2 cell lines were

used for this study. The cell lines were cultured in Dulbecco's modified Eagle medium with low glucose (Gibco, Invitrogen) supplemented with 10% foetal bovine serum (FBS) (Gibco, Invitrogen) and antimycotic 100 $\times$ solution (Thermo Fisher Scientific). The cells were seeded in a 96-well flat-bottom microplate and maintained at 37 °C in 95% humidity and 5% CO_2 overnight. Different concentrations (100, 50, 25, 12.5, 6.25, and 3.125 $\mu g\ mL^{-1}$) of **1** were treated with cells for a duration of 48 hours. The wells were washed twice with PBS; 20 μL of the MTT staining solution was added to each well, and the plate was incubated at 37 °C. After 4 h, 100 μL of DMSO was added to each well to dissolve the formazan crystals, and the absorbance was recorded using a microplate reader at 570 nm. Untreated cells with media and *cis*-platin were maintained as negative and positive controls, respectively. The experiments were carried out in triplicates, and the cell viability relative to untreated cells was determined using eqn (1).

$$\text{Surviving cells (\%)} = \frac{\text{mean OD of test compound}}{\text{mean OD of negative control}} \times 100 \quad (1)$$

2.7. DNA cleavage activity

The DNA cleavage activity of compound **1** was determined according to the procedure developed by Banerjee *et al.* with a slight modification.⁶³ Briefly, a supercoiled pBR322 (200 μg) artificial plasmid DNA was treated with prepared compound **1** (10 μM , 20 μM , 40 μM , and 80 μM) in Tris buffer (5 mM Tris-HCl, 50 mM NaCl, pH $\sim$ 7.2) to yield a total volume of 10 μL and incubated in the dark for 1 h at 37 °C. The reaction was quenched by adding 3 μL of loading buffer, and resulting solutions were loaded on 1% agarose gel. Electrophoresis was carried out at 80 V for 1 h in Tris-acetate-EDTA (TAE) buffer (pH $\sim$ 8.0). The DNA bands were visualized under UV light and the band intensities and fragmentation patterns observed in the absence and presence of the compound. The results were expressed qualitatively based on the appearance of supercoiled (SC) (form I), nicked circular (NC) (form II), and linear (L) (form III) forms of DNA.

3. Results and discussion

3.1. Synthetic protocol of $[Ni_2(\mu\text{-van})_2(\mu\text{-OAc})(NCS)_3(H_2O)] \cdot 5H_2O$

The synthesis of the dinuclear compound **1** was achieved by reacting 1 mole of nickel(II) acetate tetrahydrate, 2 moles of *p*-vanillin, and 2 moles of ammonium thiocyanate in the ratio 1:2:2 by a slow evaporation method at room temperature. After 2 weeks, the green-colored crystals that had formed were isolated and washed with isopropanol followed by diethyl ether. Single crystals of **1** were subjected to various characterization techniques like spectroscopy, elemental analysis, SCXRD, and powder diffraction. The synthetic approach for compound **1** is shown in Scheme 1.

3.2. Infrared and UV-Vis spectroscopic studies

The IR spectrum of **1** is depicted in Fig. S1, ESI†. A broad band in the range of $3207\ cm^{-1}$ has been attributed to the water molecules in compound **1** and can also be assigned to the

phenolic –OH group, which is characteristic of a free *p*-vanillin moiety and the weak band at 2833 cm^{-1} is due to C–H vibrations.^{64,65} The broadening of this band suggests intra-molecular H-bonding with phenolic oxygen. Vanillin bound to Ni(II) in a bridged manner exhibited a stretching band at 1665 cm^{-1} assigned to an aldehydic C=O stretching vibration. Several sharp-to-medium vibrations between $\sim 1590^{-1}$ and 1420 cm^{-1} could be assigned to C–C vibrations, while those at $\sim 1277\text{ cm}^{-1}$ and $\sim 1150\text{ cm}^{-1}$ could be typical signatures for C–N and methoxy functionalities, respectively.^{64–66} The characteristic signatures at $1487\text{--}1413\text{ cm}^{-1}$ may be attributed to the symmetric stretching of C–O and the methyl group.⁶⁷ The presence of a strong absorption band at 2113 cm^{-1} with a shoulder at 2058 cm^{-1} indicates coordination of isothiocyanate (NCS anion) to the two nickel atoms.⁶⁸ The electronic spectrum of compound **1** (2 mM) showed a low-intensity broadband in the region of 600–800 nm when recorded in MeOH solvent. These bands are attributed to d–d transitions (inset Fig. S2, ESI†). The molar extinction of bands arising at 673 and 742 nm is 20.3 and $19\text{ mol}^{-1}\text{ L cm}^{-1}$, respectively. Upon diluting the solution to 0.1 mM, we could see bands appearing at 252, 281, and 317 nm, which can be assigned to intra-ligand $\pi\text{--}\pi^*$ and $n\text{--}\pi^*$ transitions, suggesting the presence of the vanillin moiety in the compound when compared with the spectrum of free vanillin (Fig. S2, ESI†).⁶⁹

3.3. Single crystal structure of **1**

The single crystal data of $[\text{Ni}_2(\mu\text{-van})_2(\mu\text{-OAc})(\text{NCS})_3(\text{H}_2\text{O})]\cdot 5\text{H}_2\text{O} **1** reveals that the compound crystallizes in the centrosymmetric monoclinic crystal system with $P2_1/c$ space group. The asymmetric unit of **1** discloses the presence of two crystallographically independent nickel(II) ions (Ni1 and Ni2) held together by a bridging acetate ligand in a $\mu\text{-}\eta^1:\eta^1$ (*syn-syn*) type of coordination mode and phenolic oxygen (O3 and O6) of *p*-vanillin ligands with Ni–Ni separation of $3.001(7)\text{ \AA}$. Apart from the bridging ligand, the asymmetric unit also contains three terminal isothiocyanate moieties of which two show a linear and one a bent coordination mode. The asymmetric unit also comprises one coordinated water molecule attached to the Ni1 and five water molecules in the crystal lattice, as shown in Fig. 1. Both the Ni(II) centers adopt the octahedral geometry; however, the coordination environments are significantly different. The octahedron of the Ni1 centre consists of five oxygen and one nitrogen atom forming an $\{\text{NiO}_5\text{N}\}$ coordination environment$

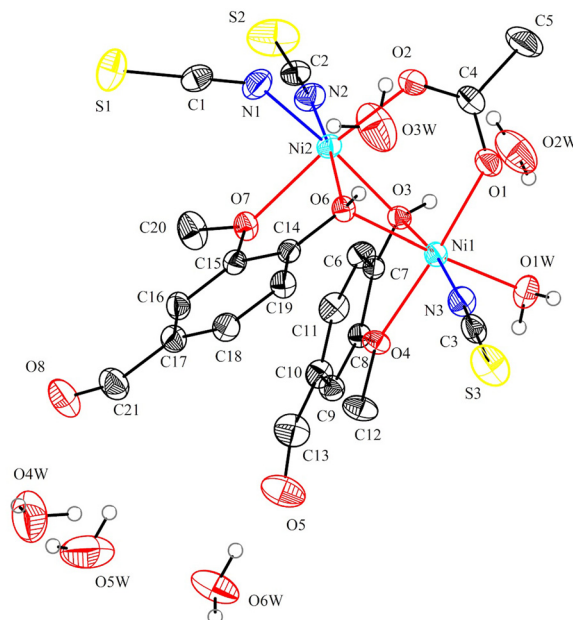
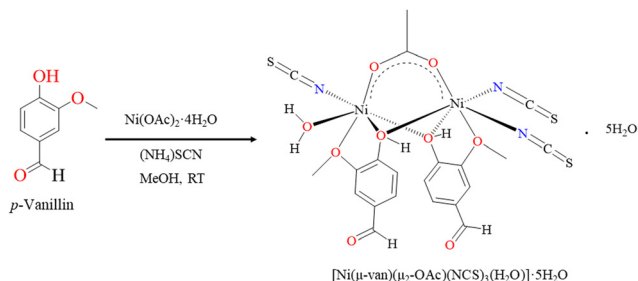


Fig. 1 Asymmetric unit of **1** with atom labelling scheme. The thermal ellipsoids are drawn at a 30% probability level for all non-hydrogen atoms. The hydrogen atoms on the carbon backbone of acetate and *p*-vanillin apart from one on phenolic oxygen have been removed for clarity.

(Fig. S3(left) ESI†). The phenolic oxygen atoms (O3 and O6) occupy two equatorial positions, originating from two-bridging *p*-vanillin, with an average Ni–O bond distance of $2.05\text{ \AA}$. The remaining equatorial sites are occupied by one water molecule (O1W) and one terminal isothiocyanate ligand (N3), adopting linear coordination mode. The Ni–O1W and Ni–N3 bond distances are $2.083(3)$ and $1.994(3)\text{ \AA}$, respectively, agreeing with compounds bearing terminal water and isothiocyanates.^{70–72} The axial positions are occupied by two oxygen atoms (O1 and O4) from the bridging acetate and methoxy substituent on the *p*-vanillin ligand, with Ni–O bond distances of $2.031(2)$ and $2.148(19)\text{ \AA}$, respectively, again showing good agreement with related compounds.^{73,74} The *cis* N–Ni1–O bond angles range from $92.64(12)^\circ$ to $95.87(10)^\circ$, and the *trans* angle is 171.8° . The *cis* O–Ni1–O bond angles range from $77.11(7)^\circ$ to $92.13(8)^\circ$, with the average *trans* angle being 17° . The deviation from the regular octahedron is discernible from bond distances and bond angles around Ni1.

The Ni2 center in the dinuclear compound also adopts an octahedral coordination, exhibits deviation from a regular octahedron, and tends to form the $\{\text{NiO}_4\text{N}_2\}$ coordination environment depicted in Fig. S3 (right), ESI†. Since *p*-vanillin is involved in bridging, two equatorial sites are occupied by oxygen atoms (O6 and O3), as at the Ni1 center. Moreover, the axial positions here are occupied by two oxygen atoms (O2 and O7) from the bridging acetate and methoxy substituent similar to that in the Ni1 center. The difference lies in the occupancy at equatorial sites, which are now occupied by two nitrogen atoms (N1 and N2), forming the coordination of isothiocyanate ligands. One of the isothiocyanate ligands coordinated through N1 shows bent-type coordination mode, forming a bond angle



Scheme 1 Preparation of **1** using the above methodology.

of $139.6(3)^\circ$ for Ni2–N1–C1. Further, the N1 of the isothiocyanate ligand with bent mode forms a slightly longer Ni–N bond $2.057(2)$ Å compared to the one coordinating *via* the linear isothiocyanate ligand with an average Ni–N bond length of 2 Å. These values are in good agreement with reported compounds with bent and linear isothiocyanate ligands.^{75,76} The *cis* N–Ni2–O bond angle ranges from $87.68(11)^\circ$ to $96.27(10)^\circ$, and the average *trans*-N–Ni2–O bond angle is 17° . Selected bond distances and angles are given in Table S1 (ESI†). The bridge mediated by phenolic oxygens between the two Ni centers is asymmetric, as can be seen from varying bond distances between Ni and the phenolic oxygen. The O3 oxygen is attracted more towards the Ni1 center with a bond distance of $2.027(19)$, whereas the distance from O3 to Ni2 is slightly longer $2.092(2)$. A similar observation is made for the O6 atom, which lies more towards the Ni2 atom with a bond distance of $2.032(19)$. This asymmetric type of binding is made possible because of the presence of a methoxy group adjacent to the phenolic oxygen in the *p*-vanillin ligand, which has its oxygen atom coordinating with metal centers. Thus, it can be said that the variation in substituents adjacent to the phenolic oxygen will undoubtedly influence the structural, and therefore, magnetic properties of the material. Moreover, the bridging of the acetate molecule is responsible for the non-planarity of the equatorial base at each Ni(II) site. This results in slight structural folding, with an Ni1–O3–Ni2 bond angle of $93.52(8)^\circ$ and Ni2–O6–Ni1 of $93.73(8)^\circ$.

The geometric parameters of two crystallographically unique *p*-vanillin, acetate, and isothiocyanate ligands are in the normal range as reported in the literature (Table S2, ESI†).^{77–79} The hydrogens attached to the coordinated aqua ligand bound to Ni1 of one dinuclear unit function as hydrogen donors, while the S atom of the isothiocyanate ligand coordinated to Ni2 *via* the N atom of the other unit acts as an acceptor, resulting in O1W–H1A...S1 intermolecular hydrogen bonding interactions. The extension of this hydrogen bond along *a*-axes results in a 1D supramolecular chain structure. These 1D chains are then extended along *b*-axes to form a 2D layer structure through hydrogen bonding interaction with the hydrogen atom bonded to the terminal carbon of the acetate group (C5) which acts as a donor atom to the unit in the layer above. The carbonyl oxygen (O8) functions as a hydrogen bond acceptor, thereby interlinking the layers in the *ab* plane, as shown in Fig. 2. These 2D supramolecular layers are further connected through C13–H13...S1 to a 3D hydrogen-bonded network (Fig. 3). The hydrogen bonding parameters of **1** are listed in Table S3 (ESI†).

3.4. X-ray powder diffraction

The phase purity of the crystalline powder of **1** was determined by comparing the experimental X-ray powder pattern of **1** with its simulated powder pattern obtained using single crystal structure data (Fig. S4, ESI†). The powder patterns closely matched, suggesting that compound **1** is in the pure phase.

3.5. Catechol oxidation by **1**

The catechol oxidase enzyme catalyzes the oxidation of various *o*-diphenols to corresponding *o*-quinones.⁸⁰ The active site of

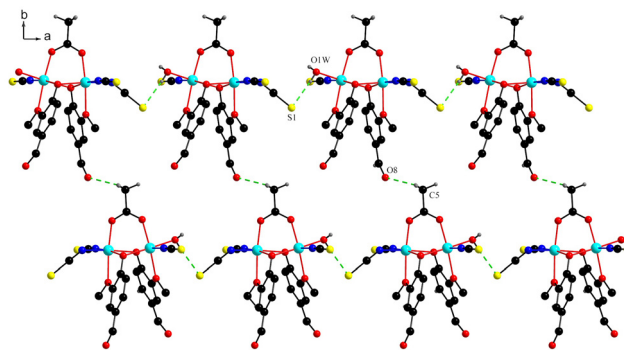


Fig. 2 Intermolecular hydrogen bond O1W–H1A...S1ⁱ is responsible for the formation of 1D supramolecular chain assembly along the axes, and the C5–H5A...O8ⁱⁱ bond aids in interlinking the chains into 2D layers along the *ab* plane.

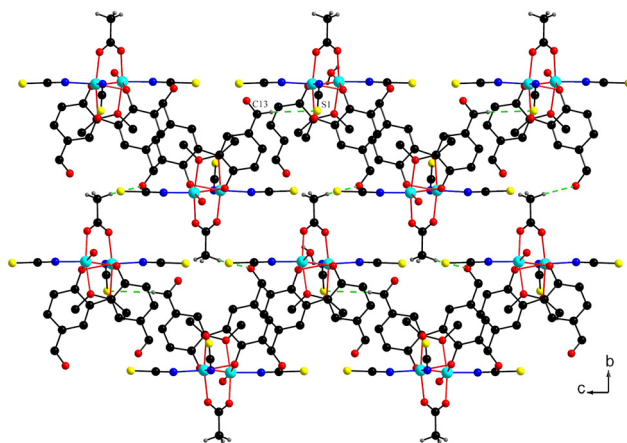


Fig. 3 Further extension of 2D layers along *c*-axes through the C13–H13...S1ⁱⁱⁱ intermolecular hydrogen bond.

the enzyme comprises a hydroxo-bridged Cu(II) core wherein copper binds to three histidine nitrogens, forming a trigonal pyramidal structure: a type-3 active site. Due to the advantage of lower redox potential for the quinone-catechol couple, 3,5-di-*tert*-butylcatechol is the most commonly utilized substrate to determine the catalytic potency of a catalyst.⁸¹ To uncover the potential of the titled compound in the oxidation of 3,5-DTBC, we reacted a 1×10^{-4} M methanolic solution of **1** with 1×10^{-2} M (100 equiv.) of 3,5-DTBC. The solvent was saturated with O₂ by bubbling through O₂ gas for about 2 minutes prior to analysis. The course of the reaction was then traced as a function of time with the aid of a UV-Vis spectrophotometer. The time-dependent spectral scans of **1** in the presence of 100 equiv. of substrate are depicted in Fig. 4. From the figure, it is clear that a new band appeared at around 405 nm, the intensity of which increases with time, suggesting the formation of the product in the reaction mixture. To identify the oxidised product, the reaction medium was allowed to evaporate at room temperature, resulting in the formation of dark brown crystals which were isolated and further purified using column chromatography and characterized using NMR spectroscopy in

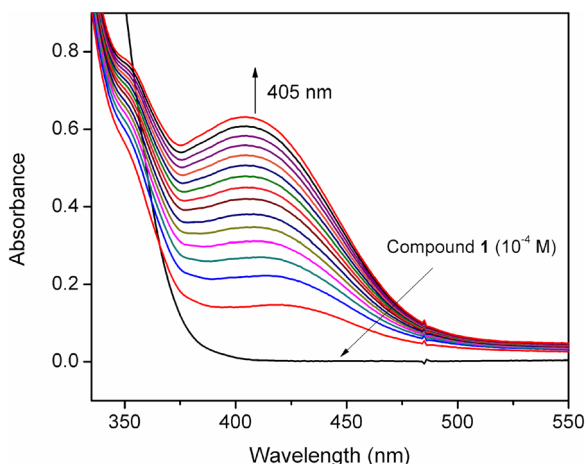


Fig. 4 Increase in the absorbance band at 405 nm upon the addition of 100 equivalents of 3,5-DTBC to a 10^{-4} M oxygen-saturated methanolic solution of **1**.

CDCl_3 . The ^1H NMR data of the product shown in Fig S5, ESI† is similar to that reported in the literature for 3,5-DTBQ,⁸² thereby confirming the formation of the *o*-quinone derivative in the reaction medium at 405 nm. The kinetics for the oxidation of 3,5-DTBC to 3,5-DTBQ were determined by the initial rate method at room temperature. The concentration of the substrate was varied in the range from 0.001 to 0.006 M in methanolic solution to a total volume of 2 mL. To each of these substrate solutions, 50 μL from the stock solution of the complex was added to make the concentration of the catalyst as 1×10^{-4} M. The dependence of the initial rate on the concentration of the substrate was monitored spectrophotometrically at 405 nm. Moreover, the initial rate method exhibited first-order dependence on the catalyst and exhibited saturation kinetics at higher substrate concentrations. The Michaelis-Menten model was thus applied to analyze the observed rate *vs.* substrate concentration, while the binding constant (K_M), maximum velocity (V_{max}) and turnover number (K_{cat}) were obtained from the Lineweaver-Burk graph of $1/V$ *vs.* $1/[S]$ shown as an inset in Fig. 5. The kinetic parameters (V_{max} , K_M , and K_{cat}) for compound **1** are presented in Table 2.

The catecholase activity exhibited by compound **1** was compared with that of compounds reported by various groups, as summarized in Table S4 (ESI†). The catalytic efficiency of the present compound was found to be either comparable, higher, or lower than mono- or dinuclear transition metal compounds reported in the literature, especially in methanol solvent. Upon comparing Table 2 with Table S4 (ESI†), it may be stated that compound **1** belongs to a fairly efficient group of catalysts.

The formation of 3,5-DTBQ is associated with the generation of water or hydrogen peroxide as the end product during the oxidation process, as reported for several compounds in the literature.⁶¹ Some reports suggest that the formation of H_2O_2 largely depends on the metal center involved during the oxidation process.⁸² Hence, it was essential to know which species are formed during the reaction; hence, we utilized the iodometric

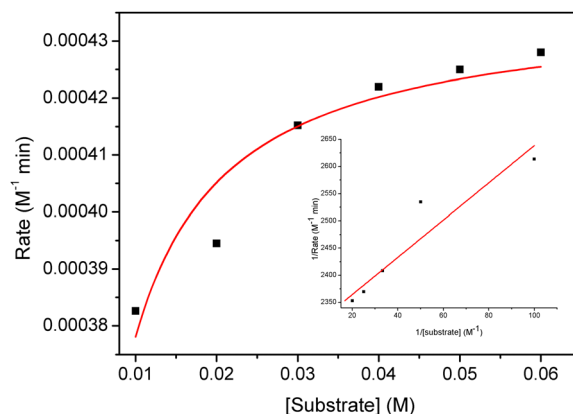


Fig. 5 Plot of initial rates *versus* substrate concentration from the oxidation of 3,5-DTBC catalyzed by **1**. The inset shows the Lineweaver-Burk plot.

Table 2 Kinetic parameters for the oxidation of 3,5-DTBC

Compound	V_{max} (M min^{-1})	K_M (M)	K_{cat} (h^{-1})
1	4.364×10^{-4}	1.54×10^{-3}	157.1×10^2

Note: standard error for V_{max} (M min^{-1}) = 4.839×10^{-6} and for K_M = 2.622×10^{-4} .

method. The oxidation of I^- species to iodine followed by the generation of I^{3-} species is evident in our case from the absorption band obtained near 353 nm from the UV-Vis spectral study (Fig. S6, ESI†).

3.6. Magnetic properties

The temperature (T) dependence of the magnetization (M) in the presence of an applied magnetic field of $H = 100$ Oe, was measured for compound **1**. The inverse magnetic susceptibility [$\chi(T) = M/H$] in the temperature range 60–310 K is shown in Fig. 6. These data show a broad hump-like feature below ≈ 260 K. However, there is no signature for long-range magnetic ordering in compound **1**. We analyzed the $\chi(T)$ data quantitatively. A closer look at the high-temperature data above 260 K shows that the inverse magnetic susceptibility is linear with temperature. We fitted the data with the Curie-Weiss law, $\chi(T) = C/(T - \theta)$ in the high-temperature range (260–310 K), and the fitted line is shown by the solid straight line in Fig. 6a. Here, C is the Curie constant and θ is the Curie-Weiss temperature. From the fitting, we get $C = 1.0145 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -4.1$ K. The low and negative value of θ indicates weak antiferromagnetic interaction between Ni(II) spins in compound **1**. The effective moment of the compound was calculated from the Curie constant obtained from the fitting according to the formula:

$$\mu_{\text{eff}} = \sqrt{(3k_B C/N_A)},$$

where k_B is the Boltzmann constant and N_A is the Avogadro number. We got $\mu_{\text{eff}} \approx 2.85 \mu_B/\text{Ni}^{2+}$, which is very close to the expected spin-only moment of Ni^{2+} ($S = 1$), $2.83 \mu_B$. Concerning to the analysis of the T -dependence of susceptibility, the Curie-Weiss

law works well in the high-temperature range, but fails to reproduce the hump-like nature below 260 K. This broad hump-like signature represents the existence of short-range magnetic ordering in the system. From the crystal structure of compound **1**, it is pertinent that Ni forms the dinuclear part. Hence, a dimer model is one of the possibilities for modelling the magnetic properties of this compound. We can consider this system as an isolated $S = 1$ dimer. Hence, we can write down the Heisenberg interaction as:

$$H = -2JS_1 \cdot S_2$$

where S_1 and S_2 are the spins of two Ni^{2+} in the Ni-dimer and J is the exchange interaction between them.⁸³ Now, we can write down the temperature-dependent magnetic susceptibility as:

$$\chi(T) = \frac{N_A g^2 \mu_B^2}{3k_B T} \frac{\sum_{S=0}^2 S(S+1)(2S+1) \exp\left(-\frac{E}{k_B T}\right)}{\sum_{S=0}^2 (2S+1) \exp\left(-\frac{E}{k_B T}\right)} + \chi_0$$

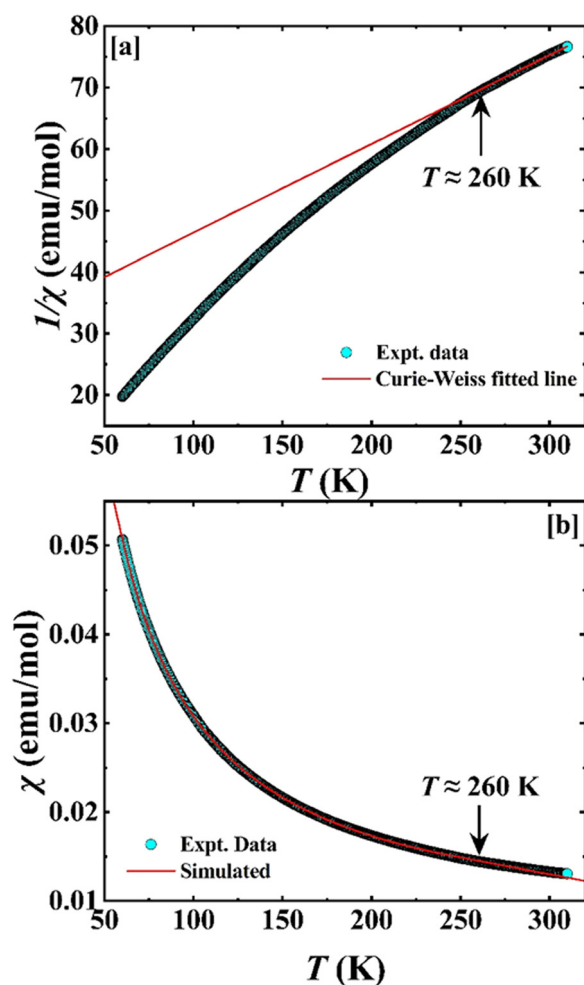


Fig. 6 (a) Temperature-dependent inverse magnetic susceptibility. Scattered points represent the experimental data, while the red solid line is obtained from Curie-Weiss fitting. (b) The $\chi(T)$ data along with the simulated pattern using the isolated dimer model.

where χ_0 is the Curie contribution, g is the Lande- g factor (we consider here the standard value of $g = 2$) and we can write down the energy. Inserting the value of energy for a spin 1 dimer, we can rewrite the above equation as:

$$\chi(T) = \frac{N_A g^2 \mu_B^2}{3k_B T} \frac{\sum_{S=0}^2 \left[6 \exp\left(-\frac{2J}{k_B T}\right) + 30 \exp\left(-\frac{6J}{k_B T}\right) \right]}{1 + 3 \exp\left(-\frac{2J}{k_B T}\right) + 5 \exp\left(-\frac{6J}{k_B T}\right)} + \chi_0$$

This equation fits the experimental data satisfactorily, as shown in Fig. 6b. We got $\chi_0 = 2 \times 10^{-5} \text{ cm}^3 \text{ mol}^{-1}$ and $J/k_B = 3.08 \pm 0.04365 \text{ K}$. Therefore, it is evident that Ni(II) forms a dinuclear compound because of isolated dimeric interactions in compound **1**. The major contribution controlling the magnetic coupling ($J_{\text{Ni-Ni}}$) in compound **1** is the phenoxide bridge from *p*-vanillin, which works as a magnetic exchange pathway between the Ni(II) centers.^{84,85} From the theoretical and experimental data, the literature discussed in Table S1 (ESI[†]) suggests that the phenoxide-based Ni-O-Ni angle could be one of the determining factors for the nature of the magnetic interaction shown by compound **1**. It is expected that the phenoxide-bridged dinuclear Ni(II) will show a more negative $J_{\text{Ni-Ni}}$ with larger Ni-O-Ni bond angle than $93\text{--}96^\circ$. In compound **1**, the average Ni-O-Ni bond angle is 93.5° , responsible for feeble antiferromagnetic interactions between the two nickel centers and is in good agreement with the well-established magneto-structural correlation.^{86–89}

4. Biological evaluation

4.1. Cytotoxicity studies of **1**

Compound **1** showed dose-dependent toxicity toward HepG2 cancer cells, as depicted in Fig. 7a. Compared with *cis*-platin, only $6.67 \pm 0.120\%$ cell viability was observed for **1** against HepG2 cell lines at $100 \mu\text{g mL}^{-1}$. The growth inhibition effect on HepG2 cell lines increased with an increase in concentration of **1**, with $78.9 \pm 0.11\%$ cell viability at $3.12 \mu\text{g mL}^{-1}$. Three dicobalt(II) complexes of *p*-cresol-based “end-off” compartmental ligands 2,6-bis(R-iminomethyl)-4-methyl-phenolate, where R = *N*-ethylpiperazine, 2-ethylpyridine or *N*-ethylpiperidine for three different compounds inhibited the proliferation of HepG2 by more than 50% at $100 \mu\text{M mL}^{-1}$ ($\sim 88.86 \mu\text{g mL}^{-1}$).⁶³ However, in the present study, $33.15 \mu\text{M}$ concentration ($\sim 25 \mu\text{g mL}^{-1}$) resulted in $> 50\%$ cell death. In another study by Biswas *et al.*,⁹⁰ a new azido-bridged dinuclear copper(II) thiosemicarbazide complex showed cytotoxicity against AGS and A549 cancer cells. The complex showed concentration-dependent cytotoxic activity with $> 50\%$ killing observed for $0.5 \mu\text{g mL}^{-1}$ ($\sim 0.83 \mu\text{M mL}^{-1}$) in both cell lines.

The cytotoxic effect of the synthesized complex on the cancer cell line was also observed using light microscopy (Fig. 7b). The untreated HepG2 cells were highly dense, confluent, and abundant, but treatment with different concentrations of **1** inhibited the proliferation of cells. Additionally, the shrinkage of cells

was observed after circularization, resulting in a decrease in the adherence and density of cells. Similar morphological alterations in the HeLa cervical cell line (spherical and granular changes in shape) have been reported recently in the presence of nickel with the Schiff base vanillin-4-methyl-4-phenyl-3-thiosemicarbazone complex.⁹¹ It was observed that *cis*-platin showed an IC₅₀ value of $2.23 \pm 0.02 \mu\text{g mL}^{-1}$ ($2.95 \mu\text{M mL}^{-1}$) which is eleven times more effective than **1**, *i.e.* $22.82 \pm 0.09 \mu\text{g mL}^{-1}$ ($30.26 \mu\text{M mL}^{-1}$), on HepG2 cancerous cells. However, an IC₅₀ value of $54.3 \pm 1.7 \mu\text{g mL}^{-1}$ was observed against HeLa cervical cell lines by a complex of nickel with Schiff base vanillin-4-methyl-4-phenyl-3-thiosemicarbazone.⁹¹ In contrast, IC₅₀ of 4.3 μM and 10 μM were observed for an azido-bridged dinuclear copper(II) thiosemicarbazide complex against AGS and A549 cancer cells, respectively.⁹⁰ Although compound **1** has a high IC₅₀ value, it is apparent that the complex can inhibit the proliferation of HepG2 cells in a dose-dependent manner, indicating that this complex can be used as an effective agent for antitumor activity. The individual action of free ligand and Ni(OAc)₂ can be ruled out according to an earlier report for the [Cu(phen)(van)]₂ complex. The authors observed individual properties of vanillin, phenanthroline, and CuCl₂ above 150 mmol mL⁻¹, indicating the non-cytotoxic effect of these isolated species. The activity of **1** in cancer cells may be due to the generation of reactive oxygen species (ROS) through the transfer of electrons from metal ions to oxygen, resulting in cell death.⁶⁵ Generally, the metal complexes of copper, cobalt, zinc, and nickel with various ligands, and specifically vanillin complexes with these metals have been reported for their cytotoxicity against various cancer cell lines, such as B16-F10, HUH-7, 786-0, MCF-7, MDA-MB-231, A375, LNcaP, HK-2, HepG2 and HeLa.^{63,66,90,92–96} However, a recent study has highlighted the applicability of nickel(II) complexes derived from vanillin with much higher anticancer activities than other metal complexes, indicating that the anticancer potency is also metal-dependent.⁹⁷ In another study, the low cytotoxicity of ligands (L1, benzyl 2-(cyclobutanylidene)hydrazinecarboxylate; L2, benzyl 2-(cyclopentanylidene)hydrazinecarboxylate; L3, benzyl

2-(cyclohexanylidene)hydrazinecarboxylate and ammonium thiocyanate) and nitrate salts of Co(II) or Ni(II) used to form a series of mononuclear cobalt and nickel complexes were reported.⁹⁸ Similarly, Liu *et al.*⁹⁹ documented the low cytotoxicity and absence of DNA cleavage activity for free ligand (H-ClQ) and NiCl₂ used for the preparation of a dinuclear Ni(II) complex with 5,7-dichloro-8-hydroxyl quinolone (H-ClQ).

4.2. DNA cleavage activity

The direct activity of compound **1** on DNA cleavage was determined by the formation of a relaxed or nicked circular form (form II) due to a single-strand break or by a linear form (form III) *via* a double-strand break from circular supercoiled plasmid DNA (form I). This study is important since DNA is reported to be a specific target for metal complexes of transition elements such as cobalt⁶³ and copper,⁶⁵ exhibiting potential antitumor properties. Fig. 8 shows the differential electrophoresis pattern for DNA cleavage after interacting with **1**. From the assay, it is clear that **1** showed a dose-dependent rise in forms II and III. It was observed that, at 80 μM concentration, DNA cleavage is very prominent with diffused form I compared to 10, 20, and 40 μM concentrations. However, decreases in the fluorescence intensity of supercoiled (SC) (form I), nicked circular (NC) (form II), and linear (L) (form III) forms were observed for all complex concentrations tested for DNA cleavage activity, while no DNA cleavage activity was observed for the control. In the case of the [Cu(phen)(van)]₂ complex, maximum DNA cleavage activity was observed in the presence of hydrogen peroxide initiated at 10 μM , resulting in the formation of relaxed (form II) and linear (form III) DNA compared to only the relaxed (form II) in the presence of glutathione.⁶⁵ The authors also confirmed the improved DNA cleavage activity due to the vanillin ligand compared to its precursor complex [Cu(phen)Cl₂]. In another study, dicobalt(II) complexes of *p*-cresol-based ligands have been reported to cleave DNA prominently at a concentration above 100 μM , exhibiting the form II of DNA.⁶³ The mechanism of pBR322 cleavage in this study can be explained by hydrolytic cleavage and the generation of free radicals by compound **1** at various concentrations, as observed for vanillin or polypyridyl or

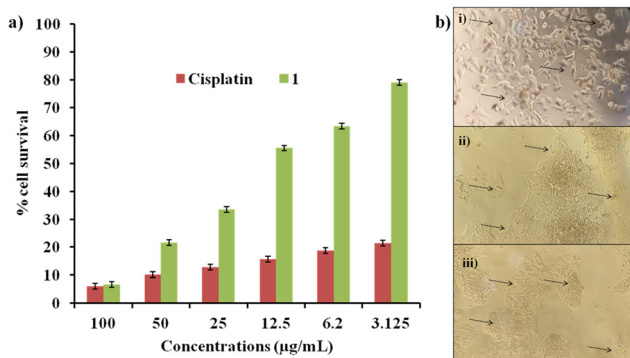


Fig. 7 Cytotoxicity studies of compound **1** against HepG2 cancerous cells determined using an MTT assay. (a) Percentage cell survival of HepG2 cancerous cells *via* the dose-dependent anti-proliferative activity of **1**. (b) Microscopic images of HepG2 cells: control cells without **1** (i), cells treated with 3.25 $\mu\text{g mL}^{-1}$ of **1** (ii), and cells treated with 12.5 $\mu\text{g mL}^{-1}$ of **1**.

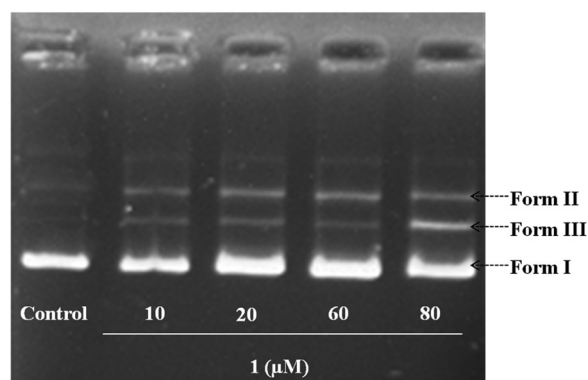


Fig. 8 DNA cleavage assay employing plasmid DNA pBR322 with **1** at different concentrations (10, 20, 60, and 80 μM).

N-ethylpiperazine, 2-ethylpyridine, and *N*-ethylpiperidine based metal complexes.^{63,66,100,101}

5. Conclusions

A new dinuclear nickel(II) compound **1** bearing vanillin, acetate, isothiocyanate, and aqua ligands has been synthesized. Acetate ligands act as the capping agent binding the two nickel(II) ions through *syn-syn* coordination mode, while the *p*-vanillin exhibits bridging through the phenolic oxygen contributing towards magnetic interactions. Compound **1** showed weak antiferromagnetic interaction, indicated by the low θ value (−4.1 K), obtained by fitting the magnetic data with the Curie–Weiss law. Compound **1** exhibits catecholase activity in the oxidation of 3,5-di-*tert*-butylcatechol to corresponding quinone with $K_{\text{cat}} = 157.1 \times 10^2 \text{ h}^{-1}$. Compound **1** also exhibited potent cytotoxicity and DNA cleavage in biological activity studies.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Authors acknowledge the financial support to School of Chemical Sciences, Goa University by DST, New Delhi under DST-FIST Scheme (No. SR/FST/CSII-034/2014(C) and UGC, New Delhi under SAP programme (No. F.504/14/DSA-I/2015). Beena K. Vernekar thanks the Directorate of Higher Education, Government of Goa for the grant of sabbatical leave and the Dean, School of Chemical Sciences, Goa University for laboratory facilities during the leave. Beena K. Vernekar also acknowledge DST-Goa for the sanction of project (grant no. 6-331-2018/S&T-DIR/302). Nikita N. Harmalkar acknowledge UGC for the Savitribai Jyotirao Phule Fellowship for Single Girl Child (SJS GC) [UGCES-22-OB-GOA-F-SJSGC-6907]. JS thank SERB, DST-India for the Ramanujan Fellowship [R/JF/2019/000046 (SQUID-1986-JS-3632)]. Authors acknowledge ACMS, IIT, Kanpur, CSIF, BITS Goa campus and Central Instrumentation Facility, IISER, Bhopal for XPS, PXRD and SQUID facilities, respectively. Authors acknowledge the Maratha Mandal's Central Research Laboratory, Belgavi, Karnataka for DNA cleavage and cytotoxicity studies. Authors thank Dr Venkatesha R. Hathwar, School of Physical and Applied Sciences, Goa University for the valuable discussions on crystal structure of **1** and refinement of data.

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Variation in Structural Features Induced by *ortho*-Substituted Benzoate Ligands in Zinc Cyclam-Based Compounds: Synthesis, Characterization, and Hirshfeld Studies

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This paper investigates the structural diversity and non-covalent interactions in eight newly synthesized $[\text{Zn}(\text{II})(\text{cyclam})]^{2+}$ compounds (1–8) featuring *ortho*-substituted benzoate ligands. Compounds (1) and (2) exhibit 1D polymeric structures, wherein aqua ligands bridge the cationic and anionic units, resulting in $[\text{Zn}_2(\mu\text{-H}_2\text{O})_2(\text{cyclam})(\text{L})_4]$ compounds. Here, L = *o*-methyl benzoate in 1, L = *o*-methoxy benzoate in 2, cyclam = 1,4,8,11-tetraazacyclotetradecane. Conversely, using hydroxy and nitro substituents at the *ortho* position results in the formation of zero-dimensional compounds 3 and 4, $[\text{Zn}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{L})_2]$

(L = *o*-hydroxybenzoate in 3, L = *o*-nitrobenzoate in 4). Interestingly, the application of benzoate, *o*-chlorobenzoate, *o*-(methylthio)benzoate, and *o*-aminobenzoate led to significant variation in the crystal packing, resulting in discrete ionic compounds 5–8. The analysis of geometric descriptors revealed the disruption of isostructurality in related isomorphous compounds upon switching the *ortho* substituents. To gain a deeper understanding of the non-covalent interactions that govern the supramolecular self-assemblies, we conducted Hirshfeld surface analysis on the compounds.

1. Introduction

Cyclam (1,4,8,11-tetraazacyclotetradecane) is a macrocyclic N-donor ligand that has been generously employed in the synthesis of metal complexes due to its ability to render chemical stability to the metal compounds in its parent form or when it is suitably *N*-functionalized.^[1–2] The metal chelates prepared using cyclam find their application in various fields, including medicine, catalysis, and molecular sensors.^[3–6] Besides offering high binding affinity to small transition metal ions, cyclam also adopts various configurations due to its flexibility when interacting with the metal ions and the other supporting ligands. In 1965, Bosnich et al. described five configurations adopted by the cyclam ligand under the influence of the transition metal ion.^[7] The orientation of the N–H group in coordinated cyclam defines the type of isomer, which can be classified as *trans*-I–IV, and the unusual folded *cis*-V configuration in the metal compounds. Among these, the *trans*-III configuration is the most stable and predominates in the cyclam-based compounds compared to the other forms.^[8–11] The nature of the counter anion greatly influences the relative population of the different configurations present in the solution state.^[12] In 2003, Sadler et al., via the NMR technique, highlighted the influence of the counterion on the type of isomer present in the solution state. In addition, the solid-state examination of the crystal structure pro-

vided valuable information on the configuration adopted by the cyclam ligand.

The structural insights into the metal compounds, such as those involving cyclam ligands, play a crucial role in understanding their properties and potential applications, such as their inhibitory effect on the replication of human immunodeficiency virus (HIV). In the case of cyclam-based compounds, the interaction with the co-receptor CXCR4 is indeed intriguing. The carboxylate group of the aspartate residue in CXCR4 likely forms non-covalent interactions with the cyclam ligand, contributing to its binding affinity.^[13,14] Given these, the effective development of new anti-HIV drugs based on cyclam compounds hinges on a thorough understanding of the different conformations that N-donor ligands can adopt and the interaction between the carboxylates and the metal cyclam units. This is critical because the different configurations of the cyclam ligand can alter how the receptor molecules recognize it. The increased activity has been observed in studying the interaction of the carboxylate moieties with the metal cyclam core. In 2005, Jo et al. studied the molecular interaction of four compounds $[\text{Zn}(\text{L})(\text{tp})]\cdot\text{H}_2\text{O}$, $[\text{Zn}(\text{L})(\text{H}_2\text{bta})]\cdot 2\text{H}_2\text{O}$, $[\text{Zn}_2(\text{L})_2(\text{ox})]_2\cdot\text{ClO}_4\cdot 2\text{DMF}$ and $[\text{Zn}(\text{L})(\text{H}_2\text{bta})]\cdot 2\text{H}_2\text{O}$ where L = cyclam, tp = 1,4-benzenedicarboxylate, H₂bta = 1,2,4,5-benzenetetracarboxylate, ox = oxalate, and H₂btc = 1,3,5-benzenetricarboxylate ions. The structural analysis of the compounds mentioned above reveals strong coordination of the carboxylate anions with the $[\text{Zn}(\text{cyclam})]^{2+}$ core. When the oxalate ligand was employed, a dinuclear compound containing $[\text{Zn}_2(\text{L})_2(\text{Ox})]^{2+}$ cationic units was obtained, where the oxalate ligand adopted a bis-bidentate coordination mode. Consequently, the cyclam in $[\text{Zn}_2(\text{L})_2(\text{ox})]_2\cdot\text{ClO}_4\cdot 2\text{DMF}$ adopts the *cis*-V configuration. Meanwhile, aromatic carboxylate ligands such as 1,4-benzenedicarboxylate and 1,2,4,5-benzenetetracarboxylate

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Supporting information for this article is available on the WWW under
<https://doi.org/10.1002/slct.202404167>

facilitated the formation of 1D coordination polymers.^[15] The CSD search further highlights similar compounds with extensions in 1D aided by various linear or bent ditopic or polytopic carboxylic linkers.^[16–18] In 2006, Kim et al. studied the molecular interaction of two metal cyclam compounds, namely $[\text{Zn}(\text{L})(\text{maleate})]\cdot\text{H}_2\text{O}$, $[\text{Zn}(\text{L})(\text{H}_2\text{O})_2](\text{fumarate})\cdot 4\text{H}_2\text{O}$ where $\text{L} = \text{cyclam}$. In the presence of a maleate ligand, a 1D coordination polymer was obtained wherein the maleate ligand bridges the two $[\text{Zn}(\text{cyclam})]^{2+}$ cores, while the fumarate ligand, having a similar basicity as that of a maleate, does not coordinate to the metal ion. This selective strong interaction with zinc was assumed to be because of the conformation of the ligand, which enables the formation of hydrogen bonds as compared to the fumarate ligand, where the carboxylate groups are trans to each other.^[19] In the same year, Kim et al. also reported a nickel cyclam compound with maleate ligand $[\text{Ni}(\text{L})(\text{maleate})]\cdot\text{H}_2\text{O}$ exhibiting 1D coordination polymer analogous to $[\text{Zn}(\text{L})(\text{maleate})]\cdot\text{H}_2\text{O}$.^[20] Similarly, Lim et al. in 2010 reported a nickel compound that is identified to be analogous to the $[\text{Zn}(\text{L})(\text{H}_2\text{O})_2](\text{fumarate})\cdot 4\text{H}_2\text{O}$.^[21] As the example above shows, the crystal packing arrangements can be altered by changing the chemical composition, which can also be achieved by modifying the substituents. For instance, the influence on the crystal packing is evident from the structural investigation of metal cyclam compounds bearing benzoate and its derivatives with substituents at the *para* position. The elucidation of the structural features suggests that the related compounds either crystallize in the same or different space group: $[\text{Ni}(\text{L})(\text{benzoate})_2]$ (*Pbca*),^[22] $[\text{Ni}(\text{L})(4\text{-nitrobenzoate})_2]$ (*P2₁/n*), $[\text{Ni}(\text{L})(4\text{-aminobenzoate})_2]$ (*C2/c*),^[16] and $[\text{Ni}(\text{L})(4\text{-hydroxybenzoate})_2]$ (*P2₁/n*).^[23] Furthermore, the effect of variation in the carboxylate is also observed in the copper compounds, such as when nickel is replaced with copper ions, the compound $[\text{Cu}(\text{L})(4\text{-hydroxybenzoate})_2]$ crystallizes in *P2₁/c*. However, the same compound crystallized in the *Pbca* space group when *para*-methoxybenzoate was utilized instead of 4-hydroxybenzoate.^[24] Their type and placement in a multi-component system can gradually influence the crystal packing arrangement, potentially leading to the formation of either isostructural compounds or may lead to disruption in isostructurality. For related compounds to exhibit isostructurality, they must share a similar chemical composition and conformation of the compounds, with the highly analogous supramolecular arrangement in the crystal lattice having the same space group.^[25–27] Bombicz and coworkers highlighted various methods to recognize isostructurality in related compounds. These methods include numerical descriptors such as cell similarity (π), isostructurality (*Is*), and molecular isometricity indices. Statistical approaches help investigate the extent of isostructurality exhibited by related compounds with the same space group and *Z*.^[25] Our work intends to expand the literature on zinc-cyclam-based compounds with varying *ortho* substituents and further extend our understanding of the mode of interaction of the carboxylate anions with the zinc-cyclam unit and their influence on the supramolecular arrangement.

2. Results and Discussion

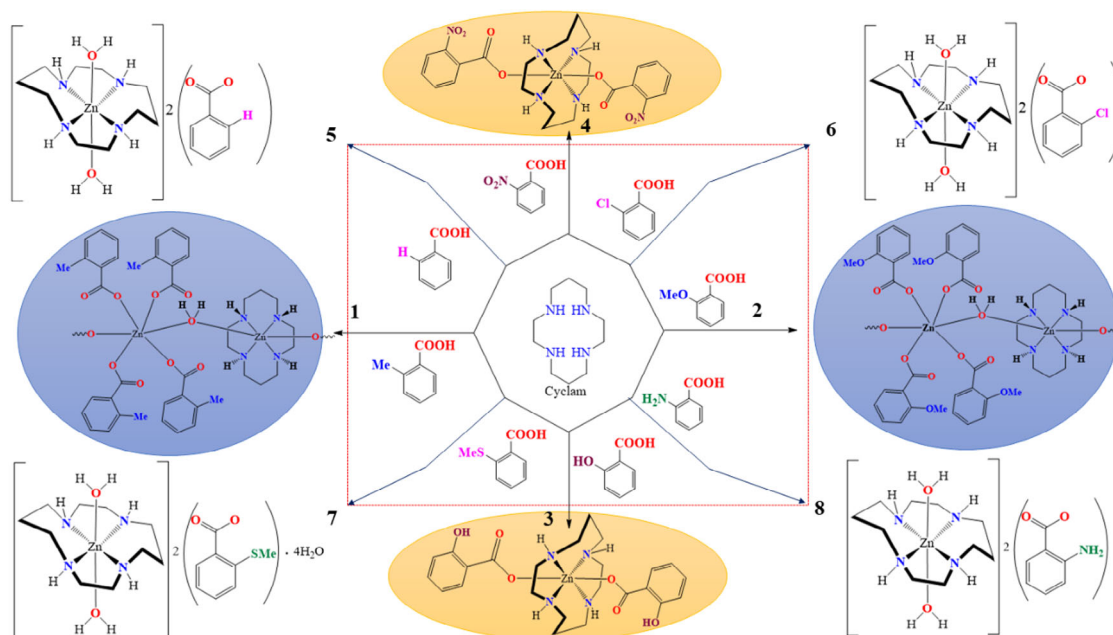
2.1. Synthetic Aspects, Spectroscopic, and Structural Characterization of 1–8

The crystallographic data and the refinement parameters of compounds 1–8 are given in Table 1. Compounds 1–8 were obtained via the slow evaporation method at room temperature, wherein aqueous $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ solution was initially mixed with the corresponding carboxylic acid separately and stirred at 80 °C until a clear solution was obtained. The resulting solution was then reacted with the cyclam ligand for 1 h. Upon standing at room temperature, this reaction mixture afforded suitable single crystals of compounds 1–8, which were then washed using cold distilled water and used for further analysis. A general scheme showing the synthetic route for 1–8 is shown in Scheme 1. The IR spectroscopic analysis revealed that compounds exhibit sharp bands in the region of ~ 1700 and 1400 cm^{-1} , which are attributed to the characteristic absorption bands for asymmetric and symmetric stretching vibration of the carboxylate (COO^-) anion, thus suggesting the incorporation of the carboxylate moieties in the respective compounds as depicted in Figure S1. The broad absorption bands centered at 3369 (1), 3398 (2), 3310 (3), 3340 (4), 3412 (5), and 3378 (6) cm^{-1} are attributed to the O–H stretching vibrations of the aqua molecules. Medium to weak stretching vibration bands in all eight compounds due to C–H and N–H vibrations in the organic moieties were seen in the $3100\text{--}2800\text{ cm}^{-1}$ range.

2.2. Thermal Investigation of Compounds 1 and 5

The thermal decomposition pattern of compound 1 was compared with the decomposition pattern of 5, consisting of the parent benzoate ligand. The thermal profiles of 1 are depicted in Figure 1. The first mass loss in both compounds is due to the removal of the coordinated water molecules. In compound 1, the first mass loss occurs between 90 and 150 °C, accounting for 3.91% (calcd. 3.97%) mass loss attributed to the loss of the bridging type of aqua molecules with two endotherms in the DTA pattern centered at 118 and 145 °C. In contrast, in compound 5 (Figure S2), the aqua molecules are lost at a much lower temperature range, between 80 and 125 °C, due to the monodentate coordination mode of the water molecules. This process is evident from an endotherm at 87 °C in the DTA pattern. The following mass loss of 22.72% (calcd. 22.07% in 1) and 36.92% (calcd. 37% in 5) is attributed to the decomposition of the cyclam ligand in the range of 250–350 °C. Upon dehydration and decomposition of the cyclic amine, further heating in 1 until 700 °C results in a mass loss of 56.15% in 1 (calcd. 56.05%) and 39.28% in 5 (calcd. 41.6%) is observed due to the decomposition of the carboxylate ligands (*o*-methoxybenzoate and benzoate) in respective compounds. The final residue of 17.22 was observed in the case of compound 1 and is in good agreement with the calcd. % for ZnO (17.91). Whereas a little higher percentage of residue (17.7%)

Table 1. The crystallographic data and structure refinement parameters for 1–4.							
Compound	1	2	3	4	5	6	7
Empirical formula	C ₄₂ H ₅₆ N ₄ O ₁₀ Zn ₂	C ₄₂ H ₅₆ N ₄ O ₁₄ Zn ₂	C ₂₄ H ₃₄ N ₄ O ₆ Zn	C ₂₄ H ₃₂ N ₆ O ₈ Zn	C ₂₄ H ₃₈ N ₄ O ₆ Zn	C ₂₄ H ₃₆ Cl ₂ N ₄ O ₆ Zn	C ₂₆ H ₅₀ N ₄ O ₁₀ S ₂ Zn
Formula weight (g)	907.68	971.68	539.94	597.95	543.97	612.86	708.21
T (K)	296 (2)	296 (2)	296 (2)	296 (2)	296 (2)	296 (2)	296 (2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	C 2/m	C 2/m	Pbca	Pbca	P 2 ₁ /n	P 2 ₁ /n	P 2 ₁ /n
Unit cell dimensions (Å/°)	a = 8.6359(7) b = 22.2604(16) c = 11.6583(9) β = 103.563(3)	a = 8.5789(8) b = 22.352(2) c = 11.6195(10) β = 97.157(3)	a = 13.2057(6) b = 10.6115(5) c = 17.6741(8) β = 90	a = 13.3732(5) b = 11.096(4) c = 17.8362(7) β = 90	a = 8.6104(2) b = 10.7391(3) c = 14.157(3) β = 104.43(10)	a = 8.6444(2) b = 12.0356(3) c = 14.1167(3) β = 106.761(1)	a = 9.012 (11) b = 8.3398(6) c = 22.593(2) β = 92.04(4)
Volume (Å ³)	2178.7(3)	2210.8(3)	2476.7(2)	2646.70(17)	1267.77(5)	1406.31(6)	1697.0(3)
Z	4	4	4	4	2	2	2
ρ (calcd.) (Mg/m ³)	1.384	1.46	1.448	1.501	1.425	1.447	1.386
Absorption coefficient (mm ^{−1})	1.16	1.155	1.039	0.987	1.015	1.108	0.902
F(000)	952	1016	1136	1248	576	640	752
Crystal size (mm ³)	0.30 × 0.11 × 0.09	0.31 × 0.25 × 0.15	0.42 × 0.31 × 0.15	0.43 × 0.27 × 0.12	0.21 × 0.12 × 0.09	0.12 × 0.09 × 0.08	0.47 × 0.30 × 0.14
θ range (°)	2.593–28.325	2.538–28.358	2.719–28.294	2.745–28.284	2.971–28.303	2.266–28.381	2.604–28.286
Index ranges	−11 ≤ h ≤ 11, −29 ≤ k ≤ 29, −15 ≤ l ≤ 15	−11 ≤ h ≤ 11, −29 ≤ k ≤ 29, −15 ≤ l ≤ 15	−17 ≤ h ≤ 17, −14 ≤ k ≤ 14, −23 ≤ l ≤ 23	−17 ≤ h ≤ 17, −14 ≤ k ≤ 14, −23 ≤ l ≤ 23	−11 ≤ h ≤ 11, −14 ≤ k ≤ 14, −18 ≤ l ≤ 18	−11 ≤ h ≤ 11, −16 ≤ k ≤ 16, −18 ≤ l ≤ 18	−12 ≤ h ≤ 12, −11 ≤ k ≤ 11, −30 ≤ l ≤ 30
Reflections collected	32271	25506	69830	85827	42805	32990	33021
Independent reflections	2781 [R(int) = 0.0335]	2830 [R(int) = 0.0713]	3078[R(int) = 0.0547]	3279 [R(int) = 0.0379]	3158 [R(int) = 0.0392]	3512 [R(int) = 0.0327]	4190 [R(int) = 0.0266]
Completeness to θ = 25.242° (%)	99.8	99.9	100	99.8	99.7	99.8	99.8
Data/restraints/parameters	2781/0/142	2830/120/156	3078/0/172	3279/0/186	3158/0/172	3521/0/178	4190/0/218
Goodness-of-fit on F ²	1.018	1.149	1.15	1.075	1.057	1.051	1.05
Final R indices [I > 2σ(I)]	R1 = 0.0335, wR2 = 0.084	R1 = 0.0577, wR2 = 0.148	R1 = 0.0343, wR2 = 0.085	R1 = 0.0315, wR2 = 0.080	R1 = 0.027, wR2 = 0.07	R1 = 0.041, wR2 = 0.112	R1 = 0.026, wR2 = 0.067
R indices (all data)	R1 = 0.0437, wR2 = 0.089	R1 = 0.0799, wR2 = 0.163	R1 = 0.0604, wR2 = 0.113	R1 = 0.041, wR2 = 0.092	R1 = 0.031, wR2 = 0.076	R1 = 0.051, wR2 = 0.119	R1 = 0.031, wR2 = 0.069
Largest diff. peak and hole (e.Å ^{−3})	0.266 and −0.888	0.788 and −1.045	0.294 and −0.524	0.472 and −0.405	0.368 and −0.399	0.771 and −0.741	0.339 and −0.368
CCDC No.	2376524	2376525	2376526	2376527	2376528	2376529	2376530
Absorption correction: semi-empirical from equivalents. Refinement method: full-matrix least-squares on F ² .							2376531



Scheme 1. General preparative scheme for compounds 1–8.

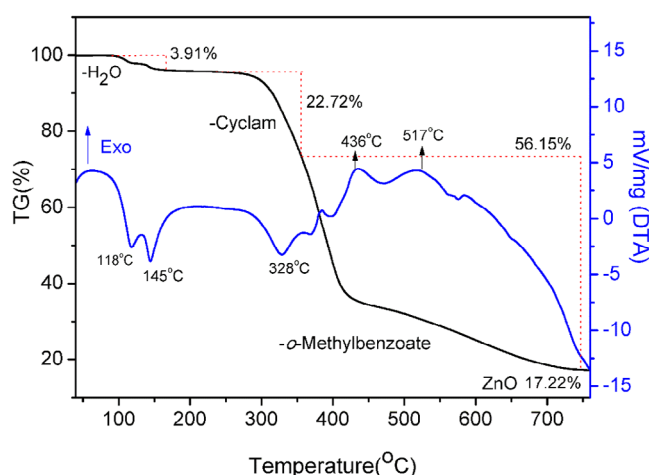


Figure 1. The thermal decomposition plot of compound 1 was recorded in the nitrogen atmosphere between RT–760 °C at a heating rate of 10 °C min^{−1}.

is observed in the thermal pattern of compound 5 as compared with calculated value of 15% for ZnO.

2.3. Structural Description of Crystal Structure, Isostructurality Descriptors, and Hirshfeld Analysis 1–8

The structural analysis of the eight compounds reveals that the macrocyclic ligand consistently adopts the *trans*-III configuration irrespective of the carboxylate anion, and hence the structural variations are primarily attributed to the interactions between the carboxylate anions with varying *ortho* substituents and the zinc cyclam core. Moreover, the compounds were classified based on the similarities in their unit cell parameters and examined for isostructurality. For a compound to demonstrate

isostructurality, it must have unit cell parameters similar to those of related compounds. The zinc series, consisting of eight compounds, was divided into three groups to elucidate the structural relationships and variation among them. Compounds 1 and 2 were placed in Group I as they crystallized in the monoclinic system with the *C2/m* space group. Compounds 3 and 4 were assigned to Group II as they crystallized in the orthorhombic system with *Pbca* space group. Group III included compounds 5, 6, and 7 crystallized in the monoclinic *P2₁/n* space group. Compound 8 did not fit into these groups, as it crystallized in the monoclinic crystal system with the *C2/c* space group.

The crystal structure of compounds 1 and 2 (Group I) exhibits a 1D zig-zag chain structure due to bridging aqua molecules located on a two-fold crystallographic axis that binds to the [Zn(cyclam)]²⁺ cationic and the anionic units [Zn(L)₄].^[2] The crystal structure of compound 1, shown in Figure 2a, comprises two crystallographically independent Zn²⁺ ions occupying the special positions (Zn1 and Zn2) and adopts distorted octahedral geometry. The Zn...Zn separation in the coordination polymer (CP) is 4.318 Å. The Zn1 ion is coordinated with the cyclam ligand and via four nitrogen atoms (N1, N1i, N1ii, N1iii) on the equatorial plane. The axial positions are occupied by the oxygen atom (O 1W and O 1Wⁱⁱⁱ) from the bridging aqua molecules, thus forming the {ZnN₄O₂} coordination environment. On the other hand, the Zn²⁺ ion is coordinated to six oxygen atoms forming the {ZnO₆} core, wherein the four oxygen atoms are contributed by the carboxylate group of *o*-methyl benzoate ligands, as depicted in Figure 2b. The O-donor ligand adopts a monodentate coordination mode, and axial oxygen atoms are contributed by the bridging aqua molecules (O1 W and O 1Wⁱⁱⁱ). A similar crystal structural arrangement is identified in compound 2, shown in the ORTEP diagram (Figure S3).

The Zn1 and Zn2 atoms in both compounds display distorted octahedral geometries due to the elongation of the axial

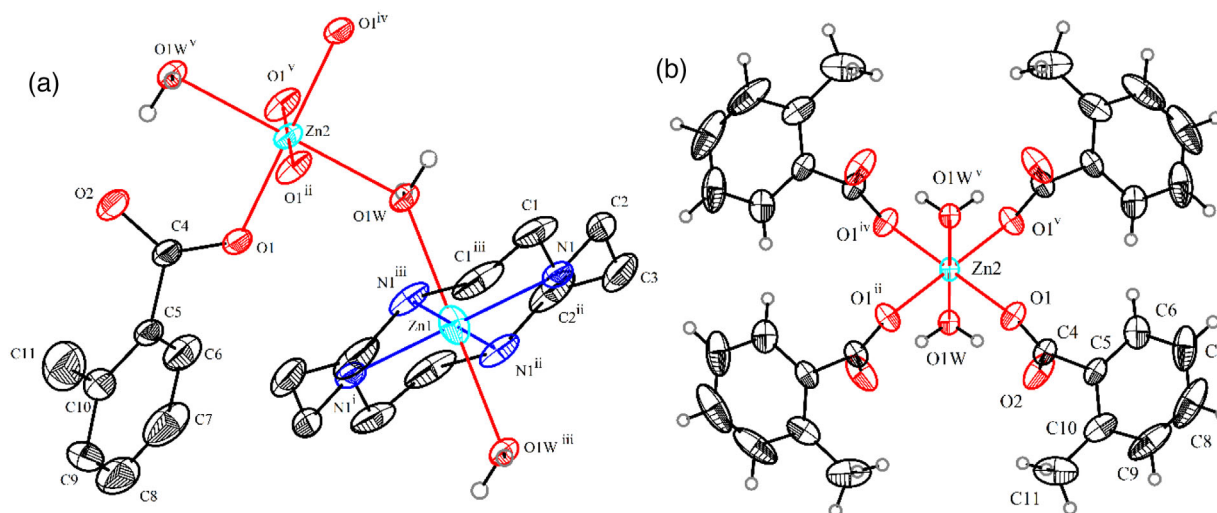


Figure 2. (a) The ORTEP diagram of compound **1** shows a portion of the chain with an atom labeling scheme. Thermal ellipsoids are drawn at 30% probability except for the hydrogen atoms. For clarity, the hydrogen atoms on the cyclam and the carboxylate ligand have been omitted. Symmetry codes: i) $-x, 1-y, 1-z$; ii) $x, 1-y, z$; iii) $-x, y, 1-z$; iv) $1-x, 1-y, 1-z$; and v) $1-x, y, 1-z$. (b) *o*-Methylbenzoate-adopting monodentate coordination mode around Zn2 ion in compound **1**.

bonds, which is attributed to the bridging aqua molecules. The Zn—O1W_(aqua-bridged) bond (1) 2.448 (17) and (2) 2.463 (4) Å is comparatively longer than the Zn—O1W_(aqua-monodentate) reported in the literature^[13,28] as well as the Zn—O bonds arising from the coordinated carboxylate ligands, 2.0564 (3) and 2.065 (3) in compounds **1** and **2**, respectively. Despite the different acid counterparts, the Zn1—O1W—Zn2 bond angles in both compounds are very similar to one another, measured at **1** 133.23° (19) and **2** 132.49° (17) and are in good agreement with the bond angle observed in compounds containing Zn—O_(aqua)—Zn type bridges.^[29–31] The selected bond distances and angles for **1** and **2** are summarized in Table 2.

Dissem et al. synthesized a similar mixed-ligand CP, $[\text{Cu}(\text{H}_2\text{btca})_2(\text{H}_2\text{O})_2\text{Cu}(\text{cyclam})]\cdot\text{H}_2\text{O}$ here ($\text{H}_2\text{btca} = 1,2,4,5$ -benzene tetracarboxylic dianion) in methanol at room temperature. Some of the structural features of the title compound are akin to those of compounds **1** and **2**. The asymmetric unit contains two crystallographically independent Cu(II) ions located in a special position; one of the ions is coordinated with the cyclam molecule, forming the $[\text{Cu}(\text{cyclam})]^{2+}$ cationic core, which is further bridged by an aqua molecule present in a special position with a site occupancy of 0.5, as seen in case of **1** and **2**. However, due to the extending nature of the H_2btca linker, it adopts the μ_2 -bidentate coordination mode, with two of the $-\text{COOH}$ groups remaining protonated, resulting in a 3D CP. The macrocyclic unit $[\text{Cu}(\text{cyclam})]^{2+}$ exhibits tetragonal distortion due to the bridging aqua molecules with an average $\text{Cu}-\text{O}_{(\text{aqua-bridged})}$ distance of 2.52 Å. Compared to the bonds of zinc compounds **1** and **2**, the bonds are slightly longer and can be attributed to the Jahn–Teller distortion in copper compounds.^[32]

A better understanding of the non-covalent interactions, such as N—H...O, O—H...O, and C—H...O, along with π – π stacking interactions between aromatic benzene rings of the acid component, can be achieved through structural analysis. These

interactions contribute to stabilizing the crystal lattice. Each cationic unit interacts with an anionic unit with the help of $\text{N1-H1}_{(\text{cyclam})}\cdots\text{O1}_{(\text{carboxylate})}$ with a donor-acceptor distance of 3.012 Å (Table 3). Additionally, the hydrogen atoms of the bridging aqua ligand are also involved in hydrogen bonding with the uncoordinated oxygen atoms of the carboxylate ligand $\text{O1W-H1W}_{(\text{aqua})}\cdots\text{O2}_{(\text{carboxylate})}$ with a donor-acceptor distance of 2.62 Å, thus playing significant roles in the stabilization of the structure. The formation of a 1D CP with intermolecular hydrogen bonds is shown in Figure 3a. Moreover, the 1D chain is also supported through $\text{C-H}\cdots\text{O}$ and π - π interactions. Each adjacent aromatic ring of the carboxylate interacts with weak π - π stacking interaction (centroid distance of 4.82 Å), as shown in Figure 3b. These weaker interactions extend the 1D chain into a 3D supramolecular network and stabilize the crystal structure.

The extent of isostructurality in molecular pairs can be described based on geometrical descriptors such as cell similarity (π), isostructurality (I_s), and molecular isometricity indices. The isostructurality index offers a strict criterion for structural similarity, accounting for the geometrical and positional differences caused by rotation and translation.^[25,33] The cell similarity index obtained for the molecular pair **1** and **2** was 0.037, close to zero, suggesting similar unit cell parameters. However, the lower isostructurality index of 37% indicates a considerable difference in the close packing of the two compounds. Furthermore, the Mercury software was used to overlay the asymmetric unit of the related molecules, as depicted in Figure 4a, to obtain the rmsD and max D values. A higher deviation of the max D (3.7119 Å) from zero can be attributed to varying orientations of the substituents, which assume almost opposite directions. Analysis of the geometrical parameters of the carboxylate anion highlights how substituents disrupt the isostructurality in compounds **1** and **2**. Due to the ortho effect, the carboxylate group exhibits a slight bend around the ring in both compounds. The dihedral angles between the ring carrying the substituent (C5–C6–C7–

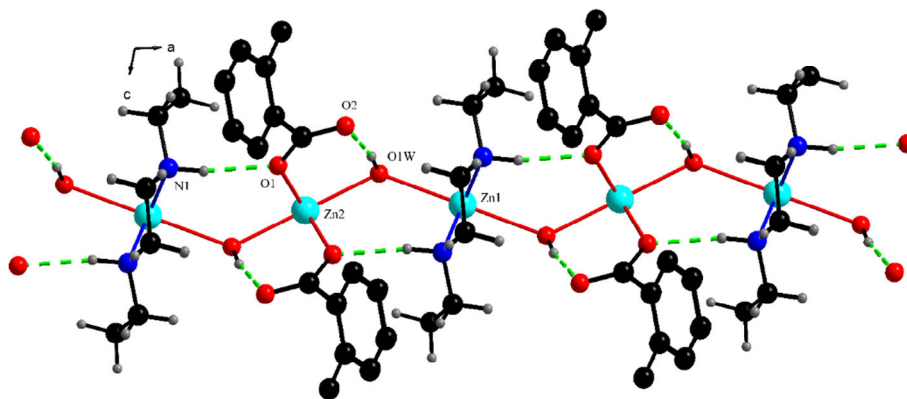


Figure 3a. 1D chain structure due to bridging aqua molecules running along *a* axis. Green dotted lines show the intermolecular hydrogen bonds.

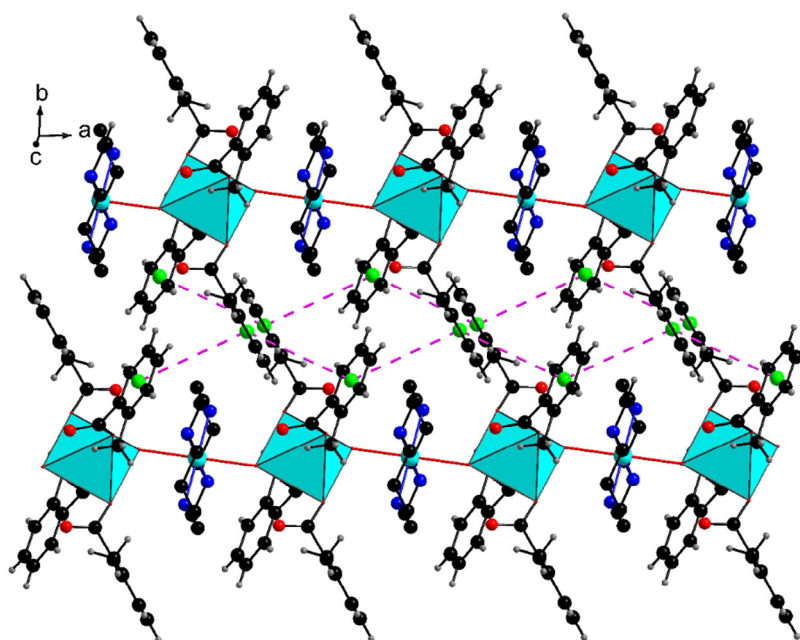


Figure 3b. The weak π - π interactions between the aromatic rings of the adjacent chains with a centroid distance of 4.82 Å.

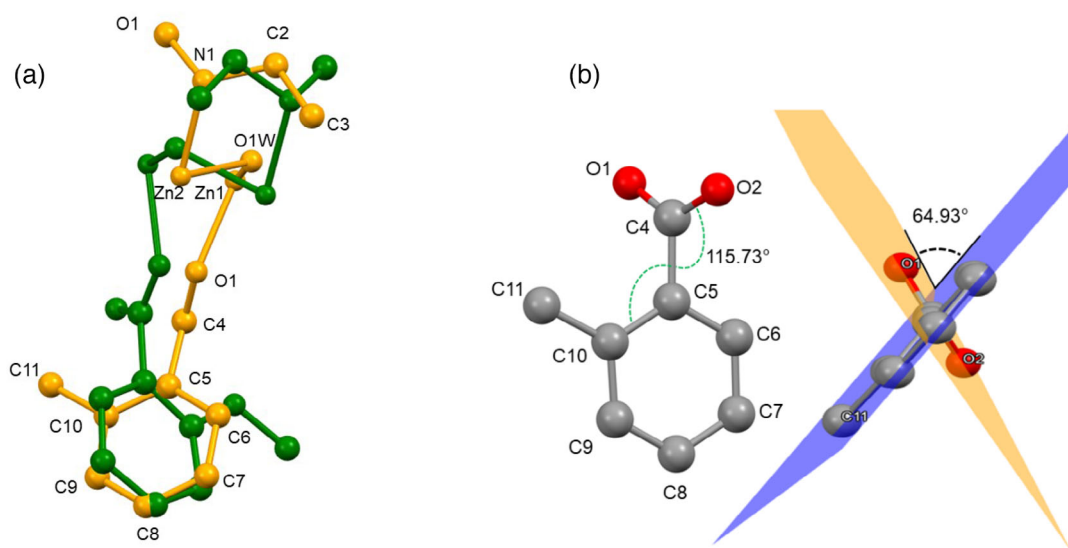


Figure 4. (a) Overlay diagram of the asymmetric units of 1 (yellow) and 2 (green) compounds with rmsD = 1.9347 and max = 3.711 Å. (b) View along the carboxylate anion highlighting the orientation of the substituents (left) and dihedral angle between the mean plane through benzene ring (C5-C6-C7-C8-C9-C10) and (O1-C4-O2) (right).

Table 2. Selected hydrogen bond distance and bond angles for 1 and 2.

1					
Bond Distance		Bond Angle			
Zn1–N1	2.078(17)	N1–Zn1–O1W	91.89(5)	O1W–Zn2–O1	86.41(5)
Zn1–N1 ⁱ	2.078(17)	N1 ⁱⁱ –Zn1–O1W	88.1(5)	O1W–Zn2–O1 ⁱⁱ	86.41(5)
Zn1–N1 ⁱⁱ	2.078(17)	N1 ⁱ –Zn1–O1W	91.9(5)	O1W–Zn2–O1 ^{iv}	93.59(5)
Zn1–N1 ⁱⁱⁱ	2.078(17)	N1 ⁱⁱⁱ –Zn1–O1W	91.9(5)	O1W–Zn2–O1 ^v	93.59(5)
Zn1–O1W ⁱⁱⁱ	2.448(17)	N1–Zn1–N1 ⁱⁱ	94.34(12)	O1–Zn2–O1 ⁱⁱ	91.73(9)
Zn1–O1W	2.448(17)	N1 ⁱ –Zn1–N1 ⁱⁱ	85.66(12)	O1 ⁱⁱ –Zn2–O1 ^{iv}	88.27(9)
Zn2–O1 ^{iv}	2.056(13)	N1 ⁱ –Zn1–N1 ⁱⁱⁱ	94.34(12)	O1 ^{iv} –Zn2–O1 ^v	91.73(9)
Zn2–O1 ⁱⁱ	2.056(13)	N1–Zn1–N1 ⁱⁱⁱ	85.66(12)	O1 ^v –Zn2–O1	88.27(9)
Zn2–O1 ^v	2.056(13)	N1 ⁱⁱⁱ –Zn1–N1 ⁱⁱ	180(7)	O1W–Zn2–O1W ^v	180
Zn2–O1	2.056(13)	N1 ⁱ –Zn1–N1	180(7)	O1–Zn2–O1 ^{iv}	180
Zn2–O1W	2.255(17)	O1W–Zn1–O1W ⁱⁱⁱ	180(7)	O1 ⁱⁱ –Zn2–O1 ^v	180
Zn2–O1W ^v	2.255(17)				
2					
Bond Distance		Bond Angle			
Zn1–N1	2.074(3)	N1–Zn1–O1W	91.53(11)	O1W–Zn2–O1	86.99(1)
Zn1–N1 ⁱ	2.074(3)	N1 ⁱⁱ –Zn1–O1W	91.53(11)	O1W–Zn2–O1 ⁱⁱ	86.99(1)
Zn1–N1 ⁱⁱ	2.074(3)	N1 ⁱ –Zn1–O1W	88.47(11)	O1W–Zn2–O1 ^{iv}	93.01(1)
Zn1–N1 ⁱⁱⁱ	2.074(3)	N1 ⁱⁱⁱ –Zn1–O1W	88.47(11)	O1W–Zn2–O1 ^v	93.01(1)
Zn1–O1W ⁱⁱⁱ	2.463(4)	N1–Zn1–N1 ⁱⁱ	94.4(3)	O1–Zn2–O1 ⁱⁱ	91.12(18)
Zn1–O1W	2.463(4)	N1 ⁱ –Zn1–N1 ⁱⁱ	85.6(3)	O1 ⁱⁱ –Zn2–O1 ^{iv}	88.88(18)
Zn2–O1 ^{iv}	2.065(3)	N1 ⁱ –Zn1–N1 ⁱⁱⁱ	94.4(3)	O1 ^{iv} –Zn2–O1 ^v	91.12(18)
Zn2–O1 ⁱⁱ	2.065(3)	N1–Zn1–N1 ⁱⁱⁱ	85.6(3)	O1 ^v –Zn2–O1	88.88(18)
Zn2–O1 ^v	2.065(3)	N1 ⁱⁱⁱ –Zn1–N1 ⁱⁱ	180(15)	O1W–Zn2–O1W ^v	180
Zn2–O1	2.065(3)	N1 ⁱ –Zn1–N1	180	O1–Zn2–O1 ^{iv}	180
Zn2–O1W	2.222(3)	O1W–Zn1–O1W ⁱⁱⁱ	180	O1 ⁱⁱ –Zn2–O1 ^v	180

Symmetry code (1): i = –x, 1–y, 1–z; ii = x, 1–y, z; iii = –x, y, 1–z; iv = 1–x, 1–y, 1–z; v = 1–x, y, 1–z. (2): i = 2–x, 1–y, 1–z; ii = x, 1–y, z; iii = 2–x, y, 1–z; iv = 1–x, 1–y, 1–z; v = 1–x, y, 1–z.

C8–C9–C10) and the plane defined by (O1–C4–O2) are 64.93 in (1), as shown in Figure 4b, and 73.82° in compound 2. Additionally, the torsion angle in compound 1 is 115.73° and –106.81 in compound 2. These variations suggest that substituents might greatly induce conformational changes, leading to a loss of isostructurality between the related compounds.

To further investigate the supramolecular non-covalent interactions in compounds 1 and 2, Hirshfeld surface (HS) analysis was performed. HS effectively quantifies the intermolecular interaction in the crystals. The d_{norm} surfaces with short contacts, where the distance between the atoms is shorter than the sum of their van der Waals radii, are indicated in red. The d_{norm} mapping reveals strong hydrogen bonds, such as N–H...O contacts, between the N atoms of the cyclam in the cationic unit and oxygen of the neighboring carboxylate ligand as a bright red area in the surface, as shown in Figure 5a,e for compounds 1 and 2, respectively. In both compounds, the predominant interactions are of the H...H type, accounting for up to 67% in compound 1, which consists of methyl benzoate anion as the anion. However, with the introduction of methoxy benzoate in the structure of compound 2, the H...H type interaction reduces by 9.4%. Other

significant interactions include C...H/H...C and O...H/H...O type seen in both compounds. Given the change as mentioned earlier in the anion source, an increment of 10% is observed in the contribution from the O...H/H...O type of interaction in compound 2, with compound 1 accounting for 12.2%. The intermolecular interactions arising due to C...H/H...C are nearly the same in both compounds, contributing 19.4% and 18.9% in 1 and 2, respectively. The 2D fingerprint plots are illustrated in Figure 5b–d,f–h for compounds 1 and 2, respectively.

Additionally, the Hirshfeld surfaces of 1 and 2 have been mapped with shape index and curvedness to identify the characteristic way the adjacent molecules interact. The effect of the substituents can be easily seen from the HSs of compounds 1 and 2, which are distinct, suggesting that the two molecules possibly show variation in the close packing arrangements. Figure 6 illustrates the front view of the HSs of compound 1, along with the shape index and curvedness plot (top) and the HSs, shape index, and cuteness plot of compound 2 (bottom). Curvature is an intrinsic property of any surface and shows large regions marked in green, representing a flatter surface, indicating stacking interaction.^[34,35] In compound 1, the curvedness plot shows

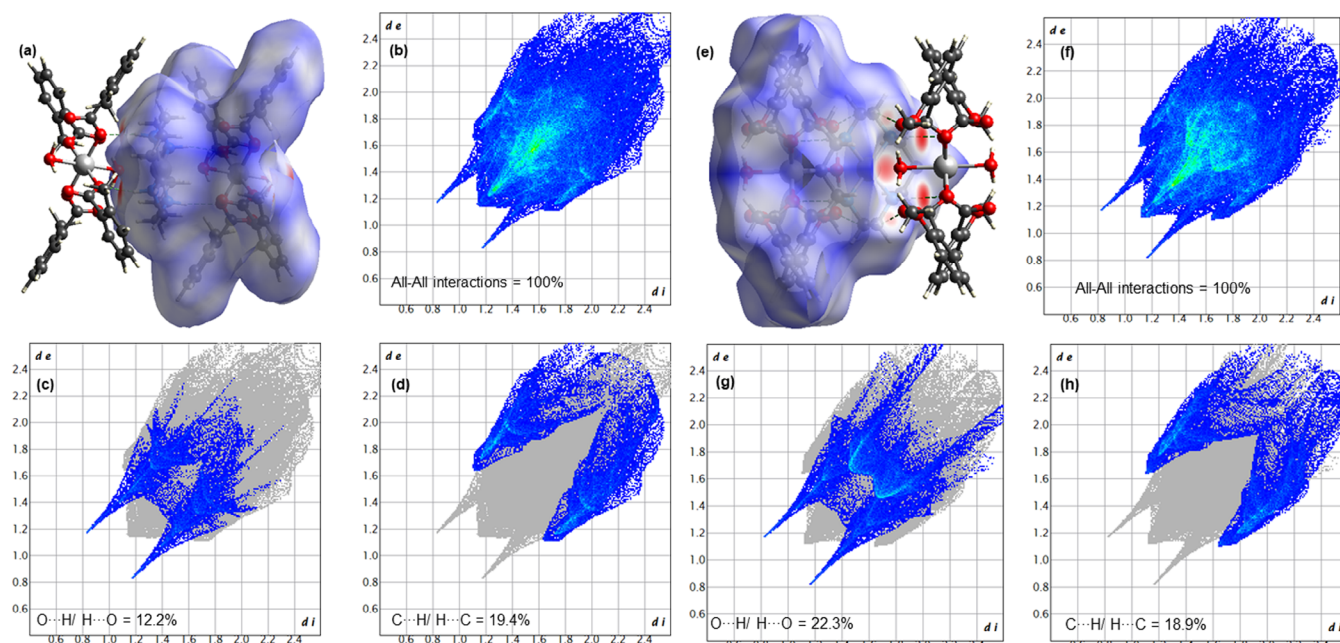


Figure 5. Intermolecular N–H...O interactions in **1** (a) and **2** (e). 2D fingerprint showing full, O...H/H...O and C...H/H...C type interactions with the percentage of contribution to the total Hirshfeld surface area in compound **1** (b–d) and **2** (f–h).

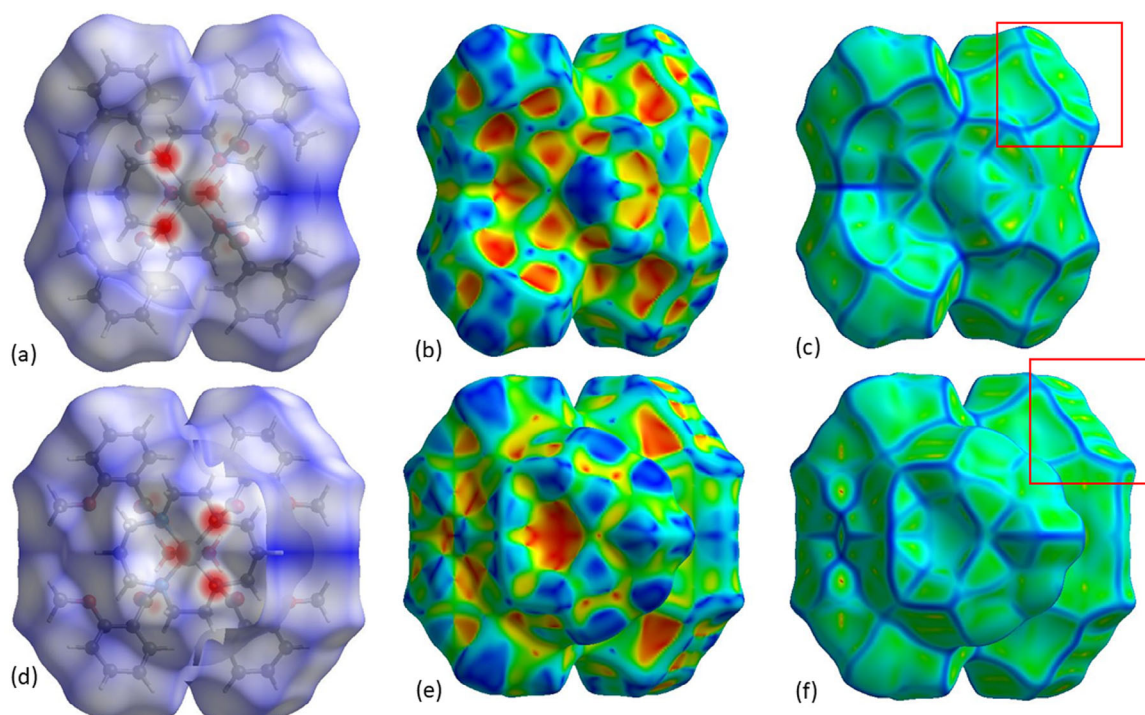


Figure 6. Hirshfeld surface mapped with (a) d_{norm} ranging from -0.40 Å (red) to 2.04 Å (blue) (b) shape index, and (c) curvedness of **1** and (d) d_{norm} ranging from -0.47 Å to 1.74 Å (e) shape index, and (f) curvedness of **2** (view along a-axis).

similar flat surface patches above the aromatic ring, thereby supporting the presence of $\pi\cdots\pi$ interactions. Furthermore, a more distinctive feature is the red concave region on the surface around the acceptor atom and the blue region around the donor atom, further supporting the inclusion of $\pi\cdots\pi$ interactions between the aromatic rings, which are more prominent in compound **1** than in compound **2**.

Interestingly, the 1D chain structure in compound **2** was retained by substituting the methyl group with the methoxy group. This observation prompted further investigation with other simple substituents. Compound **3** was synthesized using the *o*-hydroxybenzoic acid. Structural analysis revealed that **3** formed a discrete zero-dimensional compound rather than a one-dimensional polymeric structure. Compound **3** crystallized

Table 3. Selected hydrogen bond parameters for 1–8.

D–H...A	d(D–H)	d(H...A)	<DHA	d(D...A)	Symmetry Code
1					
O1–H1W...O2	0.83	1.8	169.17	2.62	1–x, 1–y, 1–z
N1–H1...O1	0.98	2.052	165.8	3.012	–x, 1–y, 1–z
C1–H1A...O2	0.97	2.594	158.56	3.515	1–x, 1–y, 1–z
2					
O1W–H1W...O2	0.804	1.852	165.46	2.638	1–x, y, 1–z
N1–H1...O1	0.764	2.235	170.99	2.992	2–x, 1–y, 1–z
C1–H1A...O2	0.97	2.545	159.48	3.47	1–x, 1–y, 1–z
3					
O3–H1...O2	0.92	1.661	154.67	2.523	
N2–H2...O2	0.834	2.153	162.57	2.959	1–x, 1–y, 1–z
C9–H9A...O2	0.97	2.531	139	3.325	1/2–x, 1/2–y, 1–z
4					
N1–H1...O2	0.852	2.498	141.79	3.211	
C4–H4A...O1	0.97	2.608	113.82	3.129	
C1–H1A...O1	0.97	2.543	116.35	3.098	1–x, 1–y, 1–z
5					
O1W–H1W...O1	0.796	1.887	176.47	2.682	
O1W–H2W...O2	0.765	1.98	159.77	2.711	1–x, 1–y, 1–z
N1–H1...O2	0.98	1.972	169.18	2.94	1–x, y, z
6					
O1W–H1W...O2	0.77	1.892	171.29	2.656	
O1W–H2W...O1	0.795	1.921	157.34	2.673	1–x, 1–y, 1–z
N1–H1...O1	0.98	1.946	168.94	2.914	1 + x, y, z
7					
O3W–H1E...O2	0.757	2.131	169.93	2.879	
O3W–H2E...O2W	0.821	2.006	174.46	2.825	
O1W–H2C...O2	0.822	1.923	175.52	2.744	
O1W–H1C...O1	0.829	1.964	169.46	2.783	1–x, 1–y, 1–z
O2W–H1D...O1	0.833	2.037	169.27	2.859	1–x, 1–y, 1–z
8					
N3–H3...O1	0.86	2.075	128.36	2.695	
O1W–H1W...O1	0.707	2.097	173.68	2.801	
O1W–H2W...O1	0.691	2.175	159.74	2.833	x + 3/2, 1/2–y, 1–z
O1W–H2W...O2	0.691	2.611	147.49	3.215	x + 3/2, 1/2–y, 1–z
N3–H3A...O2	0.86	2.041	167.39	2.887	x, 1–y, 1/2–z

in an orthorhombic crystal system with *Pbca* space group. The crystal structures consist of a unique zinc ion on the inversion center, due to which half of the molecule is symmetry generated. The zinc ion adopts the octahedral geometry with four equatorial positions of the octahedron occupied by the nitrogen atoms of the cyclam ligand (N1, N1ⁱ, N2, N2ⁱ). The axial positions are taken by the oxygen atoms (O1 and O1ⁱ) contributed by the corresponding carboxylate anion, coordinating with the central metal ion via monodentate coordination mode shown in Figure 7a. Compound **3** is isomorphous to **4**, synthesized using *o*-nitrobenzoic acid. **4** exhibited similar unit cell parameters and coordination environment, as seen in **3**, depicted in Figure 7b.

The distortion in the octahedron of **3** is evident from the slightly longer Zn–O (2.187 (12) Å) bonds as compared to the Zn–N (2.092 (14) Å) bond lengths. Similar observations were made for **4**. The selected bond lengths and angles of compounds **3** and **4** are summarized in Table S1.

The crystal packing is stabilized by non-covalent N–H...O, O–H...O, and C–H...O hydrogen bonds. The intermolecular bonding situation in **3**, wherein C9 (donor atom) of the cyclam ligand interacts with the adjacent molecules through the uncoordinated oxygen atom O2 (acceptor atom) with a D...A distance of 3.325 Å, as a result of which a supramolecular network is formed. A view of the supramolecular assembly of **3** is shown in Figure 8b. The hydrogen bonding parameters are summarized in Table 3.

Compounds **3** and **4** showed isomorphism, reflected in the cell similarity index (π) with a value of 0.0192, which is very close to zero, suggesting a higher resemblance in the unit cell parameters. However, these two compounds do not exhibit isostructurality. The asymmetric units were further overlaid to obtain the rmsD and max D values, as Figure S4 depicts. A higher deviation of the max D value of 3.5487 indicates a variation in the crystal structure packing of the two compounds influenced by the different substituents. Unlike the methyl or methoxy substituent, the hydroxy substituent is involved in intramolecular hydrogen bonding with the carboxylate group through the uncoordinated oxygen atom (O2), which does not allow the carboxylate group to bend to a greater extent. The dihedral angle between the aromatic ring (C2–C3–C4–C5–C6–C7) carrying the substituent and the plane defined by O1–C1–O2 is 10° in (**1**). On the contrary, the dihedral angle observed in **4** is 44.25 between the plane defined by C7–C8–C9–C10–C11–C12 and O1–C6–O2 shown in Figure 9. This variation could be one of the factors in disrupting the isostructurality between the two isomorphous compounds.

Additionally, we conducted Hirshfeld surface analysis on the two isomorphous compounds to gain insights into the supramolecular non-covalent interactions. The HS for **3** and **4** is mapped over the d_{norm} range (–0.17 to 1.78 Å) and (–0.22 to 1.34), respectively. The d_{norm} surfaces are indicative of short contacts such as N–H...C formed between the cyclam ligand and the carbon atom of the carboxylate ligand of neighboring molecule seen as a bright red area in the Hirshfeld surfaces (Figure 10a). In the case of **4**, short contacts C–H...O are observed between the carbon atoms of the coordinated carboxylate (Figure 10b), the oxygen atoms of the nitro group, and the uncoordinated oxygen atom of the carboxylate group. Comparatively, more O...H/H...O-type interactions are witnessed in **4** with 32.2% than in **3**, as depicted in the 2D figure print plot of **3** (c and d) and **4** in (e and f). The difference in the interaction between the adjacent molecules indicates different packing of the molecules in the crystal lattice, resulting in disruption in isostructurality. The shape index of **3** and **4** exhibits red triangles above the aromatic ring and a relatively flatter region in the crudeness plot, indicating the presence of π – π stacking interactions illustrated in Figure S5.

Compounds **5**–**8** were synthesized using benzoic acid as the parent acid and other substituted benzoic acids with chloro,

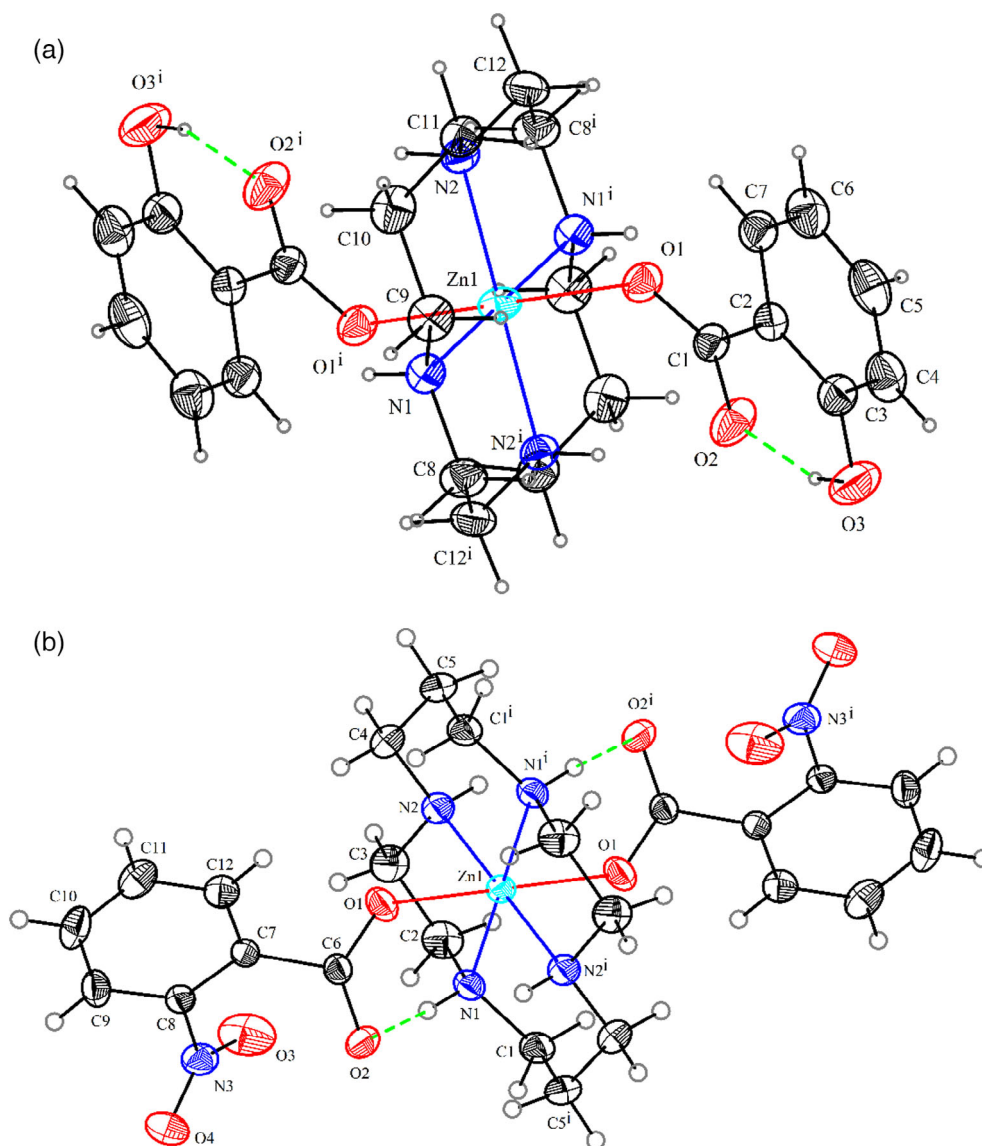


Figure 7. The thermal ellipsoid plot of compounds 3 (a) and 4 (b) with atom labeling scheme.

methyl(thio), and amino groups at the ortho position. The crystal structure analysis revealed that, except for 8, others showed isomorphism with similar unit cell parameters. Compounds 5–7 crystallize in a monoclinic crystal system with the $P2_1/n$ space group, while 8 crystallizes in the $C2/c$ space group. All these compounds 5–8 have zinc ions placed in a special position. The asymmetric unit of compound 5 contains a Zn(II) ion coordinated to the cyclam ligand on the equatorial positions via the nitrogen atoms (N1, N2, N1i, and N2i) where $i = -x, 1-y,$ and $1-z$. In contrast, the axial positions are occupied by the oxygen atoms from the coordinated aqua molecules, forming a $[ZnN_4O_2]$ coordination environment. The bond length of the metal to nitrogen of the cyclam $Zn1-N1 = 2.105(1)$ Å, slightly shorter than the metal to the oxygen atom of the coordinated aqua ligand $Zn-O$ bond distance is $2.245(1)$ Å. Similar observations are made for compounds 6, 7, and 8. The selected bond angles and bond distances are summarized in Table S1. These bond distances and angles are consistent with the similarly reported compound

having $[Zn(cyclam)]^{2+}$ cationic core.^[36,37] This cationic unit then interacts with the uncoordinated carboxylate anions through intramolecular hydrogen bonds, arising from the O–H of the aqua molecules with the uncoordinated oxygen atom of the carboxylate group acting as the hydrogen bond acceptor atoms and resulting in the formation of a zero-dimensional mononuclear compound. Compound 7 differs slightly from its isomorphous group (5 and 6). It contains four aqua molecules in its crystal lattice, which results in additional hydrogen bonding. The crystal structure of compounds 5 and 7 is shown in Figure 11, while the figures for compounds 6 and 8 are in the Supporting Information (Figure S6).

Several non-covalent interactions are found in the crystal packing in the isomorphous compounds 5–7, majorly of the type $O-H\cdots O$, $N-H\cdots O$, and $C-H\cdots O$ hydrogen bonding interactions (Table 3). Compounds 5 and 6 both exhibit a total of four hydrogen bonds, among which two are intermolecular $N-H\cdots O$ and $O-H\cdots O$ type hydrogen bonds responsible for the

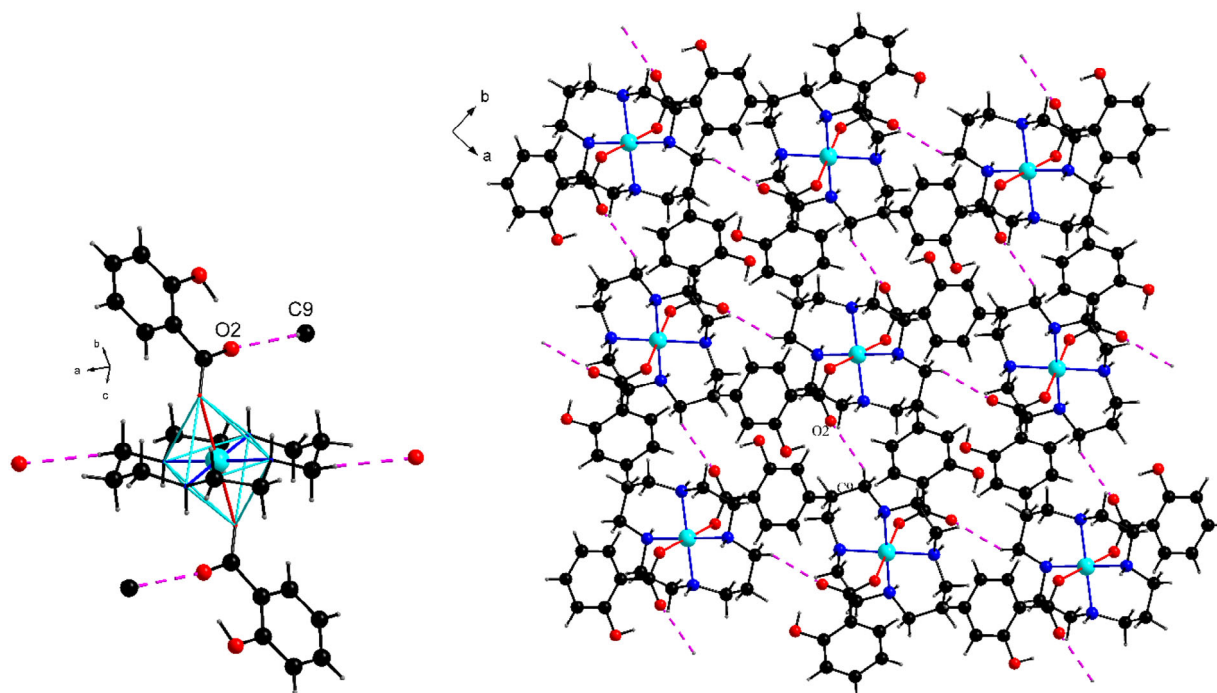


Figure 8. (a) The C—H...O intermolecular hydrogen bonding situation in **3**. (b) A view of 2D supramolecular network in **3**.

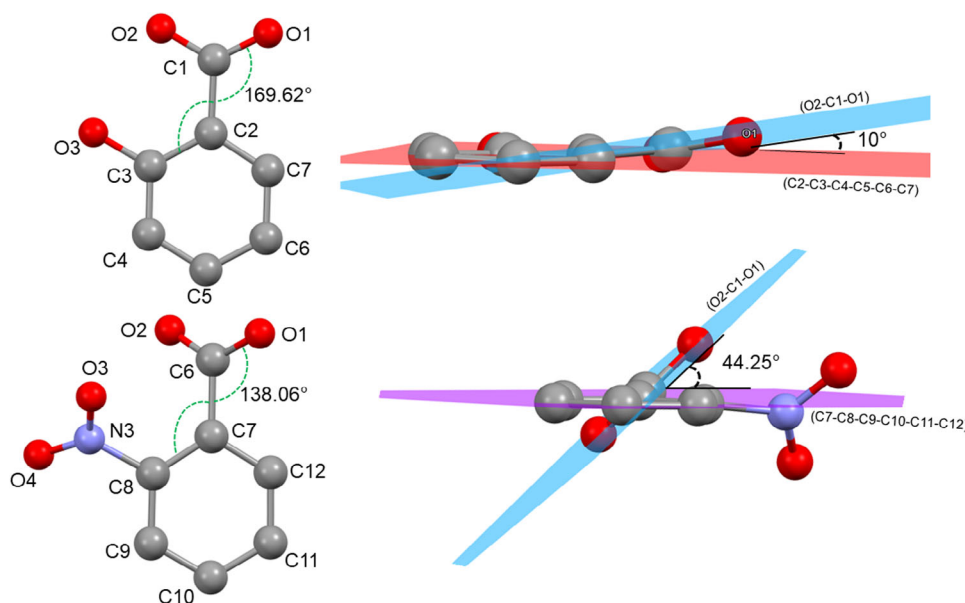


Figure 9. View along the carboxylate anion in **3** and **4** highlighting the orientation of the substituents (left) and dihedral angle between the mean plane through the benzene ring (C2–C3–C4–C5–C6–C7) and (O2–C1–O1) (**3**) and (C7–C8–C9–C10–C11–C12) and (O2–C6–O1) (right).

extension of the discrete unit in a 1D supramolecular chain along the axes depicted in Figure 12a. It can be further seen that the ligated aqua molecules are involved in hydrogen bonding with the oxygen of the carboxylate group O1W—H1W...O1_(intra) and O1W—H2W...O2_(inter), resulting in the formation of edge-fused R_2^2 (8) ring along the *ac* plane with H...A distances of 1.887 and 1.980 Å, accompanied by the D—H...A of 176.47° and 159.77°, respectively in **5**. A similar arrangement was observed in compound **6**. On the other hand, compound **7** exhibits

more hydrogen bonding interaction due to non-ligated water molecules in its structure. Compound **7** exhibits 11 hydrogen bonds, 4 intramolecular, and 7 intermolecular hydrogen bonds. The cationic unit interacts with the charge-balancing carboxylate anion via intramolecular hydrogen bond interaction (O1W—H2C...O2), where O1 W atoms act as the donor and O2 acts as the acceptor atoms with H...A distance of 1.923 Å. The other hydrogen of the O1 W is involved in interlinking the adjacent units via (O1W—H1C...O1ⁱⁱ) interaction, where (*ii* = (1–*x*, 1–*y*, 1–*z*),

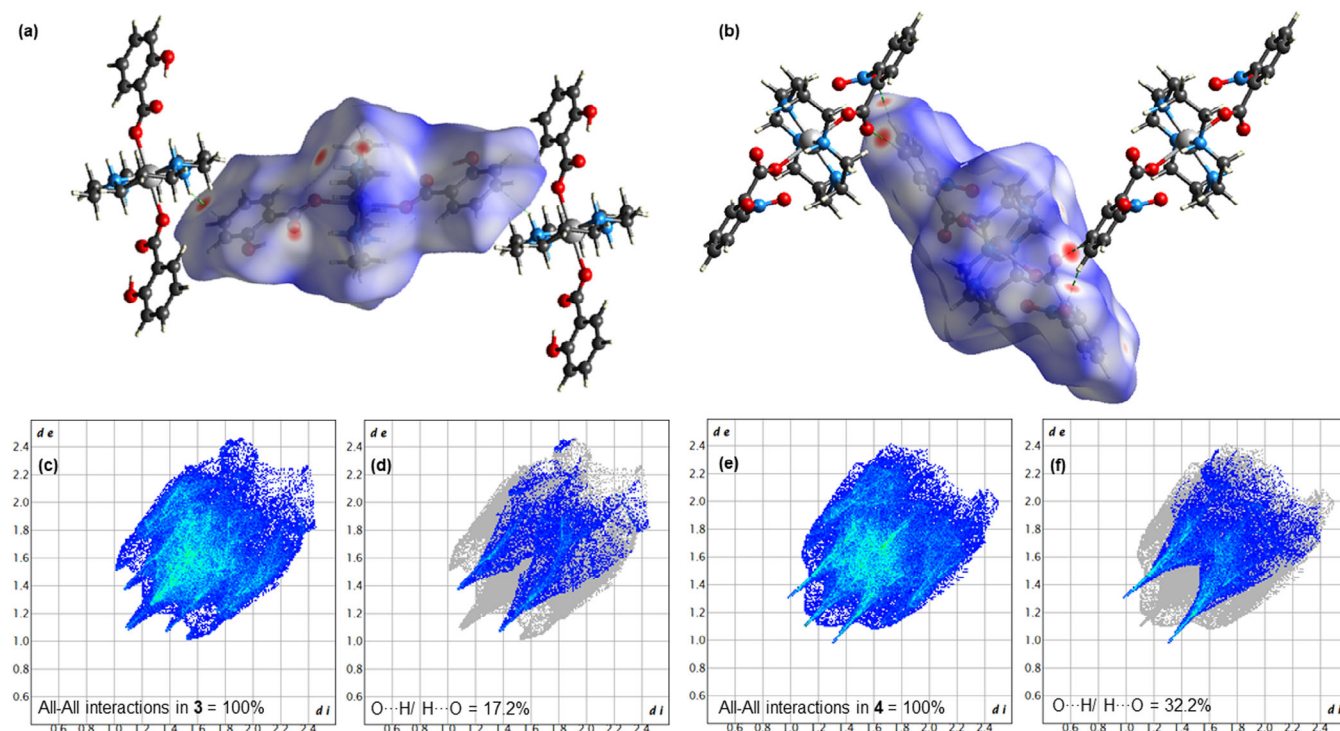


Figure 10. Intermolecular N—H...C interactions in **3** (a) and C—H...O in **4** (b). 2D Fingerprint showing full and O...H/H...O type interactions with the percentage of contribution to the total Hirshfeld surface area in **3** and **4**.

thus forming a similar eight-membered ring structure as seen in **5** and **6** resulting in a 1D supramolecular chain structure along the **b** axes (Figure 12b). The non-ligated ligand aids in interlinking the individual chain structure by forming a four-membered water cluster, which extends along the ac plane, thereby rendering a 2D-layered supramolecular network in compound **7**, as depicted in the Supporting Information (Figure S7). These structural changes indicate little or no isostructurality between **5**, **6**, and **7**.

A view of the supramolecular assembly of **8** is exhibited in Figure 13. The crystal packing here is stabilized mainly by N—H...O and O—H...O type of interactions (Table 3) with H...O distance in the range of 2.041–2.611 Å. compound **8** exhibits two intra- and four intermolecular hydrogen bonding interactions responsible for stabilizing the crystal structure. The amino group, unlike other substituents, participates in hydrogen bonding with the unbounded carboxylate oxygen (O2), resulting in the formation of a chain-like structure, interlinking the cationic units, thus resulting in the formation of a 1D ladder-shaped supramolecular layer.

It is evident that compounds **5–7** lack isostructurality due to significant variations in the hydrogen bonding situation in the crystal structure upon including different substituents. The cell similarity index π value for the molecular pair **5/6** is 0.0197, whereas, for **5/7**, it increases up to 0.2452. The highest deviation of the cell similarity index from zero is seen in the case of a **5/7** pair. It is attributed to the intense hydrogen bonding situation in compound **7**, which comprises non-ligated water molecules.

The Hirshfeld surface is mapped over d_{norm} range (−0.7068 to 1.4553) in **5**, (−0.72 to 1.3264) in **6**, and (−0.6574 to 1.6115) in **7**. The red spots on the surface indicate the dominant interactions. The HS analysis indicates strong hydrogen bond interactions, such as O—H...O and N—H...O, co-exist between the cationic and the anionic unit in **5–7** shown in (Figure 14a–c), respectively. The 2D fingerprint plots **5–7** shown in the Supporting Information (Figure S8) exhibit the crucial contributors to crystal packing; the results are also expressed as a pie chart in Figure 14d–f for compounds **5–7**. The majority of the contribution in all isomorphous compounds arises from the H...H type in the order of **5** > **7** > **6**. Compared to the parent compounds **5**, **6**, and **7** exhibits H...Cl with 13.4% contribution and H...S type with 6.7% contribution in the respective compounds. Consequently, the additional interactions seen in **6** and **7** alter the crystal packing, thereby preventing the attainment of isostructurality. Aromatic rings in the crystal structure enable close molecular packing through π – π stacking interactions. These interactions are illustrated by red triangles above the aromatic rings in the shape index plot and flatter regions in the curvedness plot of compounds **5–7** depicted in Figure S9. This observation underscores the role these interactions play in stabilizing the overall structure.

To estimate the effect of substituents on the final architecture, we calculated the void spaces generated during molecular packing. The presence and distribution of these voids are generally studied to understand the response of molecular crystals to external pressures.^[38–41] The quantitative measures, such as volume (VH), surface area (SH), globularity (G), and asphericity, were

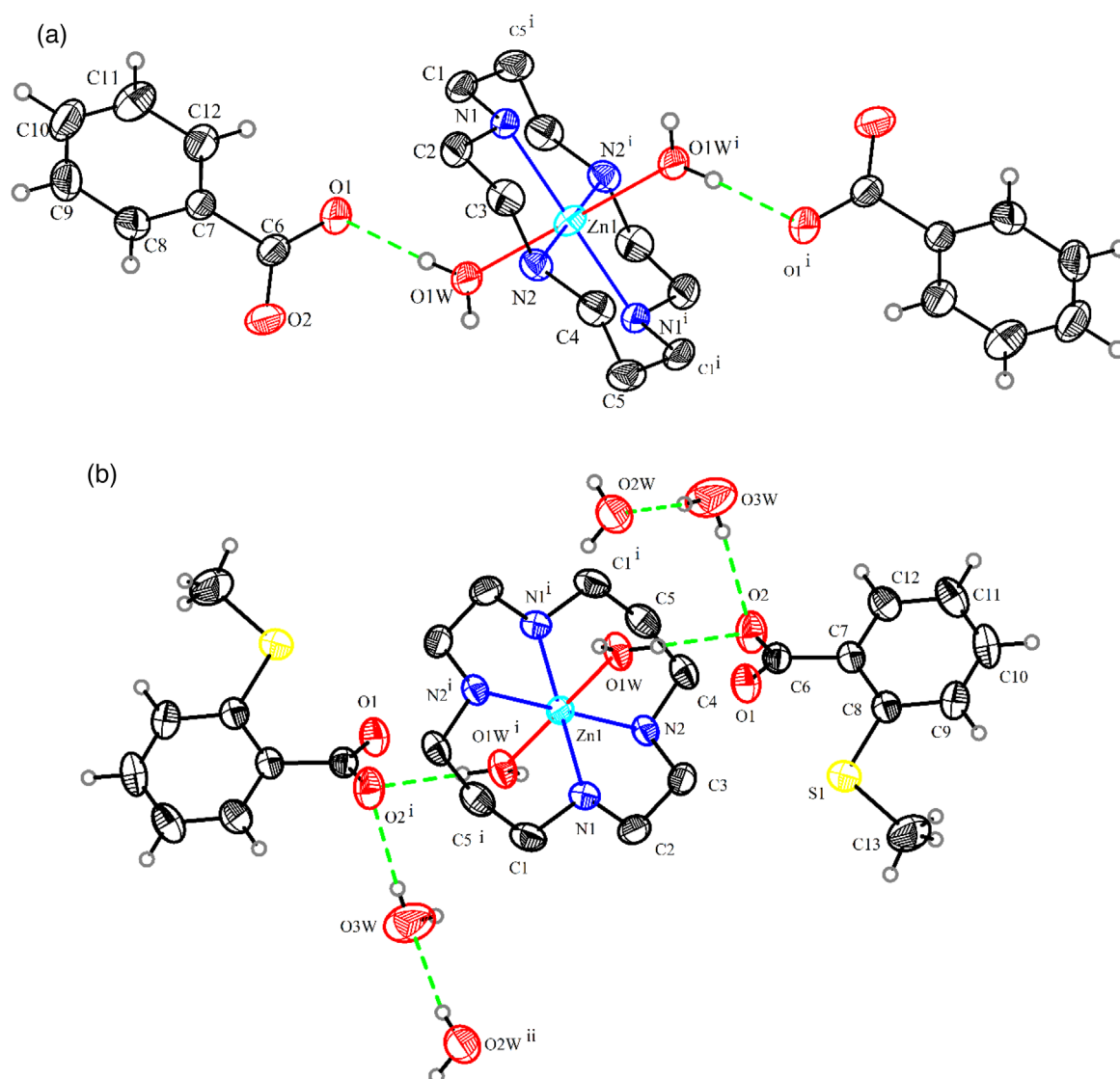


Figure 11. The thermal ellipsoid plot of compounds 5 (a) and 7 (b) with atom-labeling scheme.

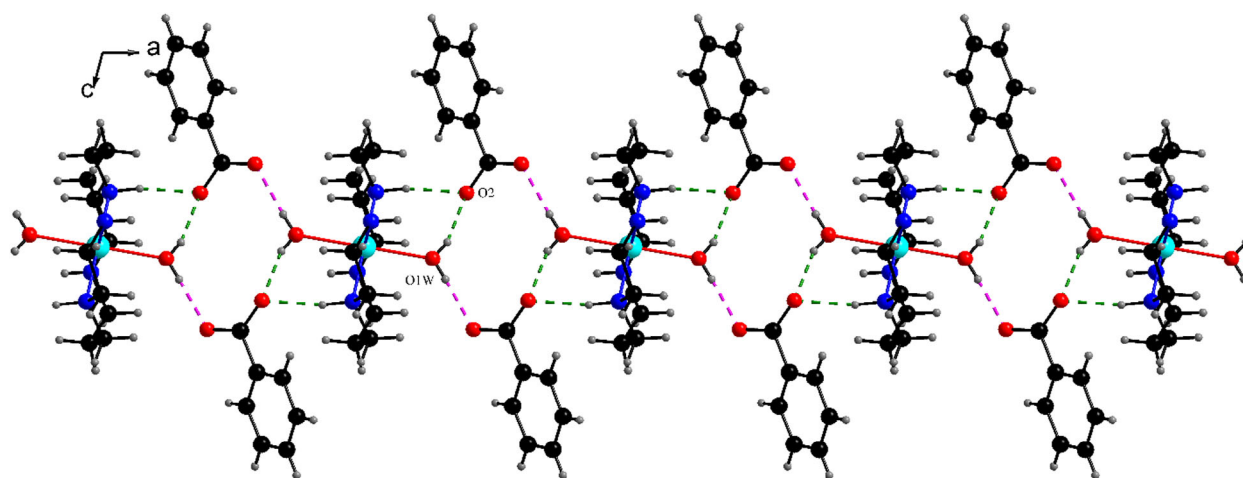


Figure 12a. Formation of 1D supramolecular chain through N1—H1...O2 and O1W—H...O2 shown in purple dotted lines in 5.

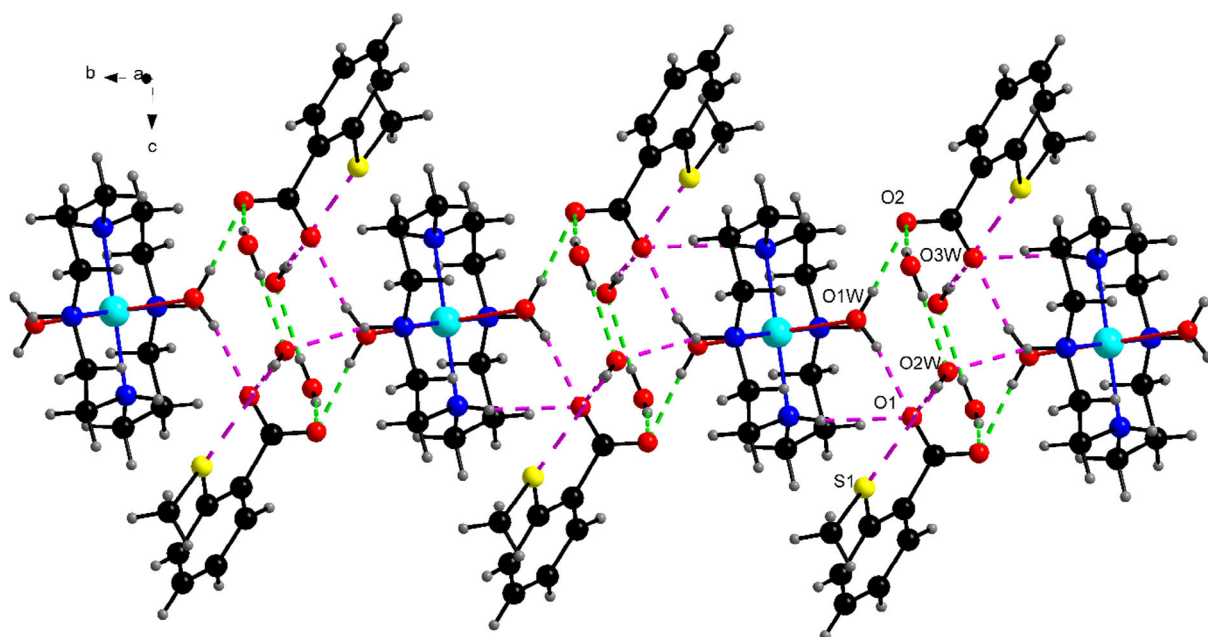


Figure 12b. Formation of 1D supramolecular chain structure via N—H...O, O—H...O and O—H...S type of intermolecular interactions shown in purple dotted lines in 7.

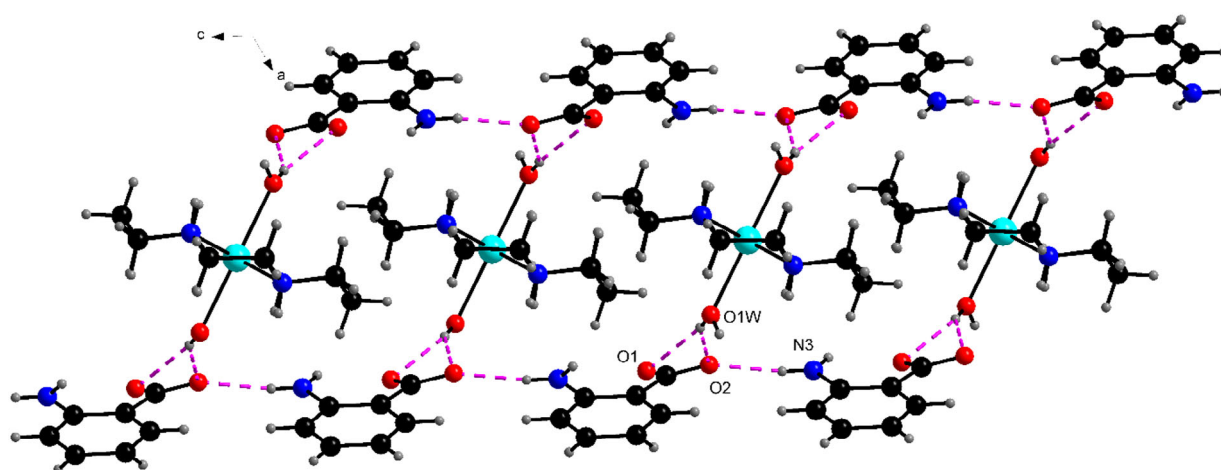


Figure 13. Formation of 1D supramolecular double chain structure via N—H...O and O—H...O interactions shown in purple dotted lines in 8.

computed from the HSS of compounds 1–7 and summarized in Table S2. The void volume of Group I compounds illustrated in Figure S10 shows that compound 2 has a void volume of 281.16 Å³ (void percentage of 12.7%), which is relatively lesser than compound 1, 329.16 Å³ (void percentage of 15%). The small difference in the void volume may be attributed to the variation in the ortho substituents. The globularity in all the compounds is found to be <1, which indicates that the molecular surfaces are more structured. The asphericity is the measure of anisotropy and follows the order of Group III (7) > Group I (1) ≈ (2) > Group III (5) ≈ (6) > Group II (3) ≈ (4). From the computed values, it can also be learned that the molecules have occupied the major space in the crystal. Thus, the compounds can bear considerable pressure before undergoing any permanent change in their shape.

3. X-Ray Powder Diffraction

We then recorded the powder X-ray diffraction patterns to investigate the phase purity of the bulk material. The stimulated data for all the compounds were obtained from the Mercury 4.0 software. The diffractograms for compounds 1 and 2 are shown in Figure 15, whereas for compounds 3/4 and 5–8, the powder patterns are given in Figures S11 and S12, respectively. The diffraction peaks in the simulated pattern exactly matched the experimental data collected at room temperature, suggesting that the single crystal model represents the bulk crystalline material. Powder diffractograms can be a suitable technique for identifying isostructurality in related compounds as they show unique fingerprints of the solid compounds. Upon comparing the powder patterns of the related compounds, such as 1 with

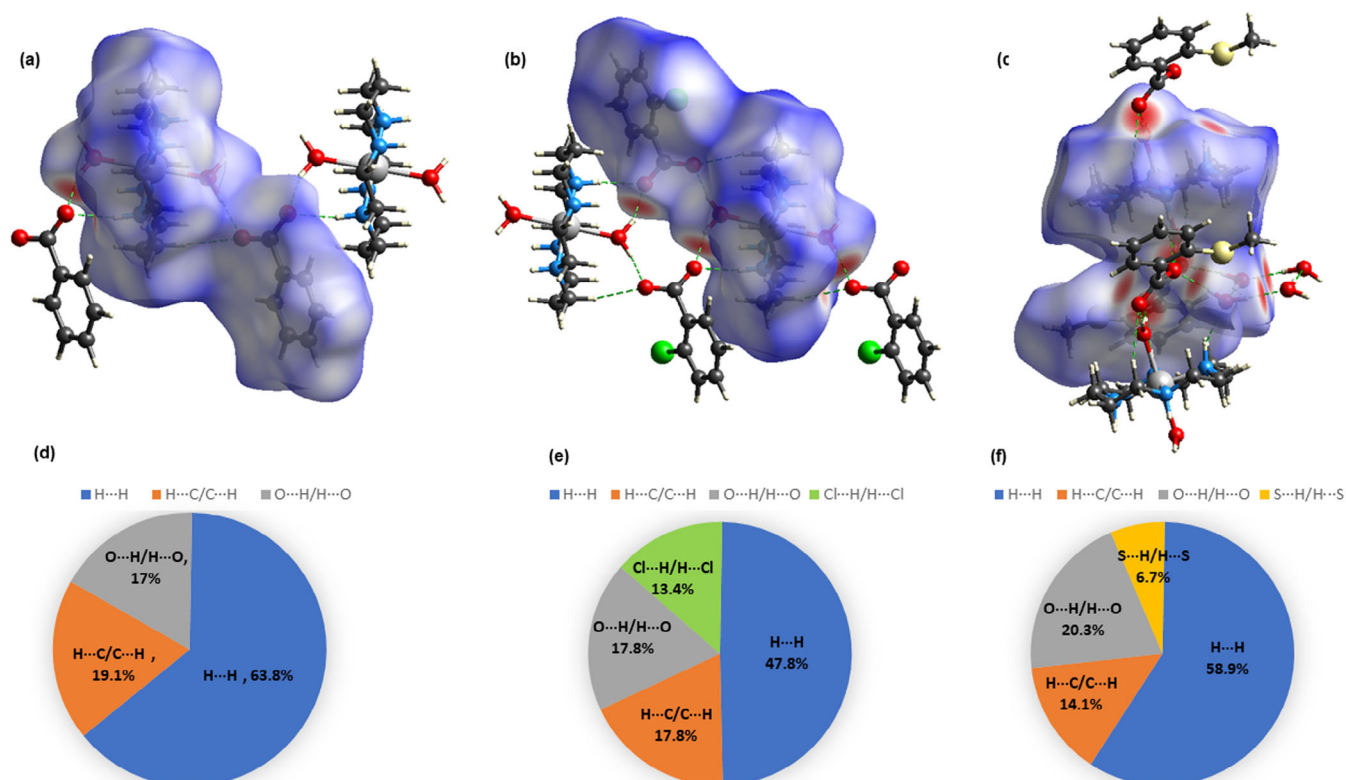


Figure 14. Intermolecular O—H...O and N—H...O type non-covalent interactions in 5 (a), 6 (b), and 7 (c).

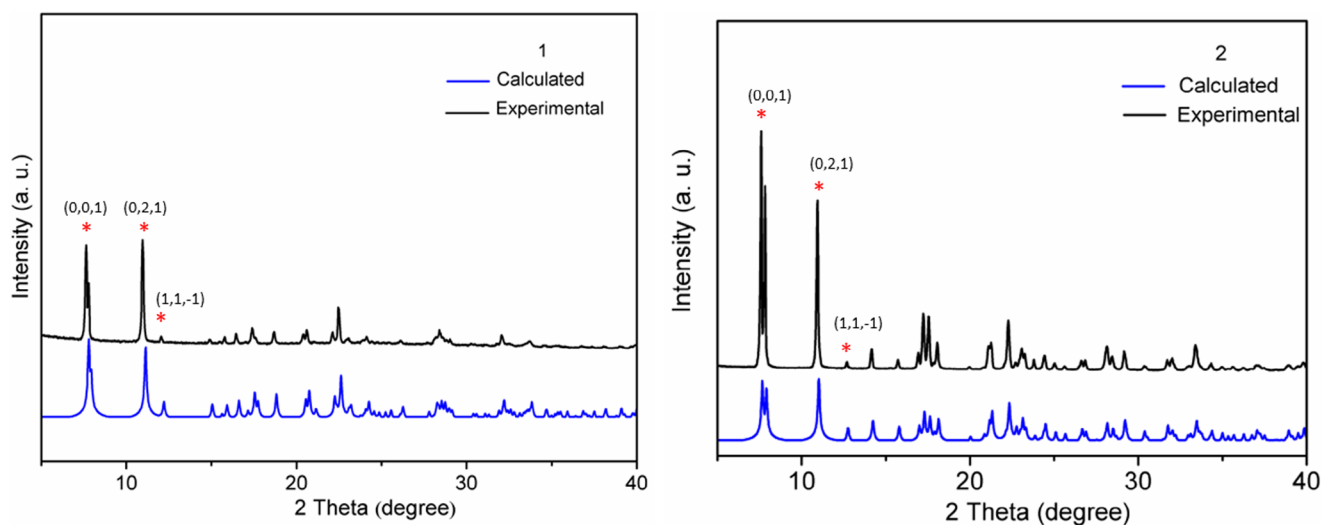


Figure 15. The XRD powder patterns of 1 and 2.

2, 3 with 4, and 5–7, it was observed that the powder patterns slightly varied, again suggesting that the related compounds sharing similar unit cell parameters are not isostructural.

4. Conclusion

Eight compounds (1–8) were synthesized and characterized using analytical techniques. The structural analysis reveals signif-

icant structural diversity in zinc cyclam compounds on varying the substituents at the ortho position. Introducing the methyl and methoxy substituents (1) and (2) resulted in 1D coordination polymers, where aqua molecules bridged the cationic and anionic units. Compounds 1 and 2 further shared similar unit cell parameters and were identified as isomorphous in nature by ISOS software, a lower isostructurality index and a larger deviation in the $D_{\max}$ value obtained by overlaying the asymmetric units of 1 and 2 in Mercury software suggested they were not truly isostructural. This discrepancy was due to differences in

non-covalent interactions and substituent orientation relative to the coordinating carboxylate group, further supported by Hirshfeld surface analysis. Similarly, compound **3** was isomorphous to **4**, with the carboxylate ligand directly coordinating to the zinc ions, resulting in a zero-dimensional compound. Compounds **5**–**8** were identified as zero-dimensional, in which the carboxylate ligands were held by $[\text{Zn}(\text{cyclam})]^{2+}$ cationic units by intramolecular hydrogen bonds, with compound **7** also exhibiting additional aqua molecules in the crystal lattice. The compounds **5**–**7** showed isomorphism, with a significant variation in the close packing arrangement of the molecules due to the chloro and (methylthio) substituents in the lattice compared to the parent benzoate ligand. The introduction of these substituents breaks the isostructurality as they introduce the additional $\text{Cl}\cdots\text{H}/\text{H}\cdots\text{Cl}$ and $\text{S}\cdots\text{H}/\text{H}\cdots\text{S}$ type of non-covalent interactions as identified theoretically by Hirshfeld surface analysis.

Supporting Information

The Deposition Number(s) [2376524](#) (for **1**), [2376525](#) (for **2**), [2376526](#) (for **3**), [2376527](#) (for **4**), [2376528](#) (for **5**), [2376529](#) (for **6**), [2376530](#) (for **7**), [2376531](#) (for **8**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe [Access Structures Service](#). The supporting figures (Figures [S1](#) and [S12](#)) and tables (Tables [S1](#) and [S2](#)) associated with this article are available in the [Supporting Information](#) file, which is freely downloadable.

Author Contributions

Nikita N. Harmalkar: Investigation; methodology; data curation; formal analysis; conceptualization; visualization; writing—original draft; writing—review and editing. **Sunder N. Dhuri:** Methodology; conceptualization; writing—original draft; writing—review and editing; project administration; funding acquisition; supervision; visualization; validation.

Acknowledgements

The authors thank the Department of Science and Technology (DST), New Delhi, India, for the DST-FIST (SR/FST/CSII-034/2014(C)) project and the University Grants Commission (UGC), New Delhi, India, for the UGC-SAP (F.504/14/DSA-I/2015) project. SND thanks the Council of Scientific and Industrial Research (CSIR), New Delhi, India (No. 01(2923)/18/EMR-II), for financial support. SND thanks the Goa State Research Foundation (GSRF/Schemes/MajorGR/13/2023/187/ii) for its research support. NNH acknowledges UGC for providing her financial support under the Savitribai Jyotirao Phule Fellowship for Single Girl Child (SJS GC) [UGCES-22-OB-GOA-F-SJSGC-6907]. The authors thank Dr. Hathwar Venkatesha for his valuable inputs on crystal structures.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

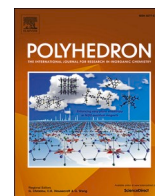
The data that support the findings of this study are available in the [Supporting Information](#) of this article.

Keywords: Carboxylate interaction · Hirshfeld analysis · Isostructurality · Supramolecular · Zinc cyclam crystal structures

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Manuscript received: August 31, 2024



Bis(4-aminopyridinium) and bis(2-amino-6-methylpyridinium) cations stabilised by $[MS_4]^{2-}$ anions: Synthesis, crystal structures, Hirshfeld surface analysis and sulfur transfer reactions

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ARTICLE INFO

Dedicated to Professor Vijayendra P. Kamat on the occasion of his 69th Birthday

Keywords:

Tetrasulfidometallate
4-Aminopyridinium
2-Amino-6-methylpyridinium
X-ray crystallography
Hirshfeld
Sulfur

ABSTRACT

Four new organic ammonium tetrasulfidometallates: (4-aminopyridinium)₂[MoS₄]·H₂O **1**, (4-aminopyridinium)₂[WS₄]·H₂O **2**, (2-amino-6-methylpyridinium)₂[MoS₄] **3**, and (2-amino-6-methylpyridinium)₂[WS₄] **4** have been synthesized by a well-known base promoted cation exchange method. All compounds were characterized by elemental analysis, IR/Raman/UV–Vis spectroscopy, thermogravimetric analysis, and X-ray crystallography. The structures of **1** and **2** consist of unique tetrahedral $[MoS_4]^{2-}$ and $[WS_4]^{2-}$ dianions, which are charge-balanced by crystallographically independent 4-aminopyridinium monocations. Additionally, both have a lattice water molecule, which contributes to the overall stability of their structures. In compounds **3** and **4**, 4-aminopyridinium of **1** and **2** are replaced by 2-amino-6-methylpyridinium cation and lack lattice water. The different H-bonding interactions viz $N-H\cdots S$, $C-H\cdots S$, $N-H\cdots O$ and $O-H\cdots O$ are observed in **1** and **2**, which are reduced to two viz $N-H\cdots S$ and $C-H\cdots S$ in **3** and **4**. The weak interactions ($N-H\cdots O$ and $O-H\cdots O$) originating from lattice water further interlink cations with $[MoS_4]^{2-}$ and $[WS_4]^{2-}$ anions forming extended networks in **1** and **2**. To understand the importance of intermolecular interactions in the structures of **1–4**, the Hirshfeld surface analyses were performed. The enrichment ratio (E) in the structures of compounds **1–4** was obtained. Compounds **1–4** were tested for their sulfur transfer ability. Only compound **1** showed a predominant disulfide product formation in reaction with 1,3-dibromopropane.

1. Introduction

Tetrasulfidometallate, $[MS_4]^{2-}$ (M = Mo or W) anions are advantageous owing to their conventional synthesis and solubility in aqueous or polar hydrocarbon solvents and tunability by selecting the right cation candidates [1]. These tetrahedral inorganic anions first discovered by Berzelius [2] gained importance because of their unique attributes such as intermediate Mo–S bond lengths [3], highest to lowest oxidation state of Mo/W and S respectively, and minimal energy difference between *p* & *d* orbitals of sulfur and Mo/W respectively [4–6]. A large number of structurally diverse Mo- or W-sulfide-bridged heterometallic compounds have been synthesized from their precursor complexes $(NH_4)_2[MS_4]$ (M = Mo, W) [3,7–10]. The ligating modes of sulfide donors, ranging from terminal to side-on to bridging in polysulfide complexes of Mo and W, have given rise to a varying range of complexity in their structures,

which have been understood very well over the years [11]. From the bioinorganic point of view, the soluble polysulfide metal complexes originating through $[MS_4]^{2-}$ have been reviewed as functional models of hydrogenases wherein desulfurization is a primary step [12]. The tetrahedral tetrasulfidometallate, $[MS_4]^{2-}$ (M = Mo, W) core exhibits extraordinary kinetic stability in the presence of ammonia or organic amines, which serve as ammonium/organic ammonium cations for charge balance [13–25]. Solid-state organic ammonium tetrasulfidomolybdates are comparatively more stable than $(NH_4)_2[MoS_4]$, which slowly decomposes to release H₂S gas, solid MoS₃, and NH₃ gas [26,27]. In the last two decades, there has been a lot of work established that demonstrates the versatility of organic ammonium ligands in tuning the distortions of M–S bonds of MS_4 tetrahedron [12–24].

The acentric tetrahedral $[MS_4]^{2-}$ unit has been utilized as a foundation block to produce non-centrosymmetric compounds by selecting

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<https://doi.org/10.1016/j.poly.2024.117272>

Received 2 September 2024; Accepted 19 October 2024

Available online 28 October 2024

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appropriate organic ammonium counter cations. The strong secondary interactions involved in affecting the M—S bond distances, such as M—S...H—N, M—S...H—C, and sometimes M—S...H—O arising from lattice waters, form the extended networks as evidenced by their crystal structures [12–24]. These reports also showed that the significant distortions in $[MS_4]$ tetrahedra were identified from the IR-Raman spectra of organic ammonium tetrasulfidometallates, which showed a distinct split of Mo-S or W-S vibrations (vide infra). The degree of split of M—S vibration was proportional to the difference in longest and shortest M—S bond distances of $[MS_4]^{2-}$ tetrahedron and can be fine-tuned by the use of different organic ammonium cations.

Sulfidometallates find utility in various realms, from biological systems [28–30] to organic synthesis [31] and catalyst precursors [32,33]. Among the many applications, ammonium tetrasulfidometallates have been used as MS_2/MS_3 (M = Mo, W) catalyst precursors in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) processes. From the perspective of biomedical fields, an example of such a therapeutic intervention, regarded as one of the most critical, is anti-copper therapy for Wilson's disease, where tetrasulfidomolybdate is identified as a copper-sequestering drug [34,35]. Organic ammonium tetrathiosulfidotungstates have shown their usefulness in complex 33S MAS NMR spectra for natural abundance analysis [36–38].

The efficacy of tetrasulfidometallate reactivity in sulfur transfer and induced internal redox reactions has gained significant attention. Both solid-state and solvent-assisted reactions of tetrasulfidometallate have greatly simplified the synthesis of organic disulfides [39–41]. The development of various methodologies, from reducing organic azides to synthesizing thiolactams [42,43], depends on the induced internal redox reactions of tetrasulfidometallates [44–47]. The reactions of aqueous $(NH_4)_2[MoS_4]$ with Ni^{2+} , Co^{2+} , and Mn^{2+} salts in the presence of ethylenediamine (en) have resulted in polymorphisms of $[M(en)_3][MoS_4]$ ($M' = Ni, Co$ or Mn) [48].

The importance of H-bonding interactions in the structural chemistry of tetrasulfidometallates has been evidenced by the fact that in some of the reported organic salts, the organic amine handles are only partially protonated [24]. Our current work exploits the utility of the H-bonding interactions to optimize the M—S bond distances through a choice of selective organic amines of varying numbers of H-atom donors and bulky groups. Here, we have employed the pyridine-based amines, namely 4-aminopyridine and 2-amino-6-methylpyridine, to understand the influence of substitution with methyl group on the structural and functional properties of $[MS_4]^{2-}$ tetrahedra. The synthesis, characterization, and Hirshfeld surface analyses of compounds 1–4 have been investigated. The application of compounds 1–4 in the transformation of 1,3-dibromopropane to 1,2-dithiolane has been discussed.

2. Experimental

2.1. Materials and methods

All chemicals and solvents were obtained from commercial sources and used without further purification. The ammonium salts of $[MS_4]^{2-}$ (M = Mo and W) were prepared following literature procedures [49]. Infrared (IR) spectra of the powdered compounds were recorded by diluting with KBr using a Shimadzu (IR Prestige-21) FT-IR spectrometer in the region 4000–350 cm^{-1} at a resolution of 4 cm^{-1} . Raman spectra were recorded using a Labram HR Evolution Raman Spectrometer. Elemental analyses (C, H, N, S) were performed on the Elementar Vario-micro Cube CHNS Analyzer. Using standard mode, UV–Vis spectra were recorded using an Agilent spectrophotometer (8453 model). Thermal investigations were performed on simultaneous DTA/TG apparatus, DTG-60 00826 SHIMADZU, under N_2 atmosphere from room temperature to 600 $^{\circ}C/800$ $^{\circ}C$ at a heating rate of 10 $^{\circ}C$ min^{-1} . Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance X-ray diffractometer using Cu $K\alpha_1$ ($\lambda = 1.5406$ Å) with a nickel filter.

2.2. Preparation of compounds 1–4

Compound 1 was synthesized using a base-promoted cation exchange method in a 1:2 M to amine ratio [24]. A freshly prepared ammonium tetrasulfidomolybdate, $(NH_4)_2[MoS_4]$ (260 mg, 1.0 mmol) was taken in 10 mL of water to which 4-aminopyridine (188 mg, 2 mmol) dissolved in 5 mL of water was added in dropwise manner. The resulting red solution was kept in the refrigerator for slow crystallization. After 24 h, many needle-shaped red crystals were formed in the flask. The single crystals were isolated by decantation and washed with cold isopropyl alcohol (10 mL), followed by washing with diethyl ether. The crystals of 1 were vacuum-dried and stored in a desiccator. Yield of compound 1 was 74 %.

Compound 3 was synthesized using the base-promoted cation exchange method, using ammonium salt as the source for $[MoS_4]^{2-}$. Freshly prepared crystalline $(NH_4)_2[MoS_4]$ (260 mg, 1.0 mmol) was dissolved in water (~10 mL), a few drops of aqueous ammonia were added, and the solution was filtered. Into this clear red filtrate, 2-amino-6-methylpyridine (216 mg, 2.0 mmol) was added, and the reaction mixture was left aside for crystallization in the refrigerator. After a day, the red blocks of compound 3 were slowly separated. The single crystals were filtered, washed with ice-cold water (2 mL), followed by isopropyl alcohol (~10 mL) and diethyl ether (10 mL), and air dried. Yield of compound 3 was 69 %.

A reaction of $(NH_4)_2[WS_4]$ instead of $(NH_4)_2[MoS_4]$ with 4-aminopyridine and 2-amino-6-methylpyridine under identical reaction conditions afforded 2 and 4 with yield of 74 and 66 %, respectively.

Analysis of $(C_5H_7N_2)_2[MoS_4] \cdot H_2O$ (1): Calc.: C, 27.77; H, 3.73; N, 12.95; S, 29.66; MoS_4 , 51.89 %. Found: C, 27.06; H, 3.96; N, 12.69; S, 29.39; MoS_4 , 51.71 %. IR data (cm^{-1}): 2947(ν_{N-H}), 2722, 2577, 1725, 1646, 1355, 1288, 1226, 973, 783, 459(ν_1). Raman data (cm^{-1}): 1047, 998, 954, 851, 527, 424(ν_1), 287, 194(ν_2, ν_4). UV–Vis data (in nm): 468, 315, 241.

Analysis of $(C_5H_7N_2)_2[WS_4] \cdot H_2O$ (2): Calc.: C, 23.08; H, 3.10; N, 10.77; S, 24.65; WS_4 , 59.98 %. Found: C, 23.98; H, 3.15; N, 10.16; S, 24.18; WS_4 , 59.91 %. IR data (cm^{-1}): 2970, 2857, 2426, 1907, 1654, 1185, 996, 756, 563, 499, 453. Raman data (cm^{-1}): 1048, 1008, 855, 479(ν_1), 399, 182(ν_2, ν_4). UV–Vis data (in nm): 392, 277, 218.

Analysis of $(C_6H_9N_2)_2[MoS_4]$ (3): Calc.: C, 32.57; H, 4.10; N, 12.66; S, 28.98; MoS_4 , 50.67 %. Found: C 32.26, H 4.15, N 12.83, S, 28.48; MoS_4 , 50.21 %. IR data (cm^{-1}): 2916(ν_{N-H}), 2834, 2754, 1727, 1660, 1470, 1294, 1118, 943, 782, 646, 552, 470(ν_1). Raman data (cm^{-1}): 947, 736, 560, 534, 428, 270, 191(ν_2, ν_4). UV–Vis data (in nm): 468, 315, 241.

Analysis of $(C_6H_9N_2)_2[WS_4]$ (4): Calc.: C, 27.23; H, 3.24; N, 10.58; S, 24.23; W, 34.73; WS_4 , 58.84 %. Found: C, 19.21; H, 5.27; N, 15.13; S, 34.23, WS_4 , 58.70 %. IR data (cm^{-1}): 3030(ν_{N-H}), 2880, 2716, 2591, 1736, 1648, 1460, 1359, 1208, 1007, 781, 479(ν_1). Raman data (cm^{-1}): 1389, 1304, 998, 731, 557, 528, 479(ν_1), 475, 457, 446, 419, 182(ν_2, ν_4). UV–Vis data (in nm): 392, 277, 218.

2.3. Single crystal X-ray diffraction

Single crystals of 1–4 were analyzed on a Bruker D8 Quest Eco model X-ray diffractometer equipped with graphite monochromated Mo- $K\alpha$ ($\lambda = 0.71073$ Å) radiation at 296 K. The X-ray diffraction intensities were collected, integrated, and scaled, and unit cell parameters were determined using the program suite APEX3 (Version 2018.1). The structures were solved using direct methods with SHELXS-97, and subsequent refinements on F^2 using full-matrix least-squares methods were performed with SHELXL-2016 [50]. All non-hydrogen atoms were refined anisotropically. The N—H hydrogen atoms were taken from the difference map; their bond lengths were set to idealized geometry and refined isotropically with $U_{iso}(H) = 1.2/1.5$ Ueq (N) using a riding model. In contrast, the hydrogen atoms were located at the calculated positions. The technical details of the data acquisition and selected refinement for

Table 1

The technical details of the data acquisition and selected refinement for 1–4.

Compound	1	2	3	4
Empirical formula	C ₁₀ H ₁₆ MoN ₄ OS ₄	C ₁₀ H ₁₆ WN ₄ OS ₄	C ₁₂ H ₁₈ MoN ₄ S ₄	C ₁₂ H ₁₈ WN ₄ S ₄
Temperature/K	296(2)	296(2)	296(2)	296(2)
Formula weight	432.45	520.35	442.48	530.38
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P2 ₁ /c	P2 ₁ /n	P $\bar{1}$	P $\bar{1}$
a/Å	7.1593(5)	7.172(2)	7.5408(5)	7.5606(9)
b/Å	13.4523(9)	13.515(4)	8.1207(6)	8.1181(10)
c/Å	17.7034(12)	17.726(6)	15.4365(11)	15.5155(19)
$\alpha/^\circ$	90	90	81.080(2)	81.017(3)
$\beta/^\circ$	96.289(2)	96.29(9)	79.763(2)	79.674(3)
$\gamma/^\circ$	90	90	87.436(2)	87.639(3)
Volume/Å ³	1694.7(2)	1707.7(10)	918.76(11)	925.3(2)
Z	4	4	2	2
D _{calc.} [Mg cm ⁻³]	1.695	2.024	1.599	1.904
μ /mm ⁻¹	1.266	7.253	1.166	6.691
F(000)	872	1000	448	512
Crystal size/mm	0.29 × 0.16 × 0.05	0.50 × 0.41 × 0.31	0.21 × 0.16 × 0.08	0.21 × 0.15 × 0.07
θ range for data collection (°)	1.906–28.29	2.76–28.32	2.75–28.24	2.70–28.32
Index ranges	−9 ≤ h ≤ 9, −17 ≤ k ≤ 17, −23 ≤ l ≤ 23	−9 ≤ h ≤ 9, −18 ≤ k ≤ 18, −23 ≤ l ≤ 23	−10 ≤ h ≤ 10, −10 ≤ k ≤ 10, −20 ≤ l ≤ 20	−10 ≤ h ≤ 10, −10 ≤ k ≤ 10, −20 ≤ l ≤ 20
Reflections collected	59,985	57,894	27,711	31,259
Independent reflections	4214 [R(int) = 0.0596]	4258 [R(int) = 0.0374]	4556 [R(int) = 0.0311]	4600 [R(int) = 0.0349]
Completeness to $\theta = 25.242$ (%)	100	99.9	99.9	99.7
Goodness-of-fit on F ²	1.096	1.103	1.086	1.117
Final R indexes [I > 2 σ (I)]	R1 = 0.0272, wR2 = 0.0559	R1 = 0.0139, wR2 = 0.0322	R1 = 0.0319, wR2 = 0.0656	R1 = 0.0155, wR2 = 0.0372
R indexes [all data]	R1 = 0.0426, wR2 = 0.0643	R1 = 0.0171, wR2 = 0.0343	R1 = 0.0453, wR2 = 0.0738	R1 = 0.0176, wR2 = 0.0386
Largest diff. peak/hole/eÅ ⁻³	0.719 and −0.594	0.612 and −0.70	0.498 and −0.485	0.56 and −0.72
CCDC No	2381453	2381454	2381455	2381456

1–4 are given in Table 1.

2.4. Hirshfeld surface analyses and enrichment ratios

Crystal Explorer Software generated Hirshfeld surfaces through experimental electron density data [51–53]. The software employs the Hirshfeld method to divide the electron density between atoms engaged in interactions, facilitating the analysis of intermolecular interactions between cations and anions. During the Hirshfeld surface analysis, the surface is mapped over the normalised contact distance parameter d_{norm} , defined by Eq. (i) as follows.

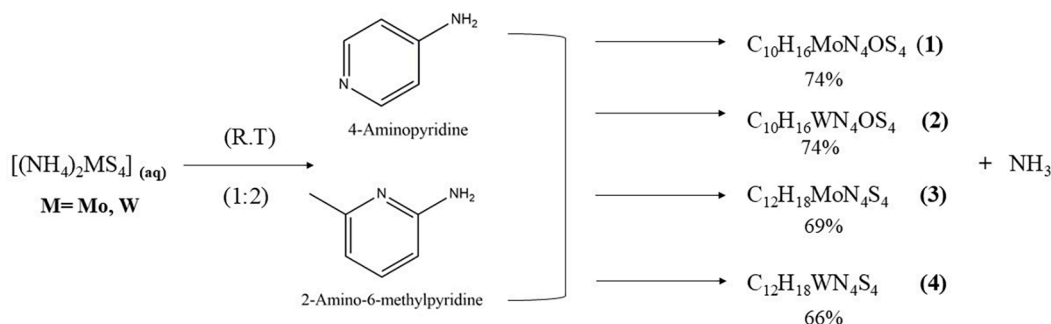
$$d_{\text{norm}} = (d_i - r_i^{\text{vdw}})/r_i^{\text{vdw}} + (d_e - r_e^{\text{vdw}})/r_e^{\text{vdw}} \quad (\text{i})$$

The parameter d_e represents the distance between the Hirshfeld surface and the closest nucleus outside the surface. On the other hand, d_i denotes the corresponding distance to the nearest nucleus present inside the surface. On the d_{norm} surface, intermolecular contacts are visually emphasized in red at distances shorter than the sum of the Van der Waals radii (r_{vdw}) of the atoms involved. The contacts longer than the sum of

the Van der Waals radii appear in blue, while contacts around the sum of the Van der Waals radii are represented by white. The 2D fingerprint of the Hirshfeld surface is a unique and comprehensive visualization method for representing the intermolecular interactions in a molecular crystal. Derived from the Hirshfeld surface, it condenses complex information into a single, full-color plot. It provides a “fingerprint” of the crystal’s intermolecular interactions by summarizing the frequency and relative surface area of different interaction types. Each point on the 2D fingerprint corresponds to a unique (d_e , d_i) pair, with colors indicating the contribution level, ranging from blue for minor contributions to red for significant contributions. The plots are consistently colored to enable easy comparison between different molecules. The enrichment ratio E for the single crystals of 1–4 was calculated indirectly from the crystal packing information obtained from Crystal Explorer Software as per the procedure given elsewhere [54,55]. Briefly, the Hirshfeld surface contacts for element pair X,Y (C_{XY}) were used to calculate the proportion of chemical type X on the molecular surface S_X as,

$$S_X = C_{XX} + 0.5 \sum_{Y \neq X} C_{XY} \quad (\text{ii})$$

The ratio of random contacts R_{XY} between two elements X and Y are

**Scheme 1.** Synthetic routes for the preparation of compounds 1–4.

calculated by probability products as,

$$R_{XX} = S_X S_X \text{ and } R_{XY} = 2S_X S_Y \quad (\text{iii})$$

The enrichment ratio (E) for elemental pair X, Y is then obtained by

$$E_{XY} = C_{XY}/R_{XY} \quad (\text{iv})$$

3. Results and discussion

3.1. Syntheses and spectroscopic characterization of compounds 1–4

Compounds 1–4 were synthesized by a well-known base-promoted cation exchange reaction [14–24] using $(\text{NH}_4)_2[\text{MS}_4]$ (M = Mo for 1 and 3 or W for 2 and 4) salts and the corresponding organic amine. In this method, a weaker base NH_3 is substituted by 4-aminopyridine in 1 and 2 while 2-amino-6-methylpyridine in 3 and 4, respectively, as shown in Scheme 1.

Unlike ammonium tetrathiomolybdate, $(\text{NH}_4)_2[\text{MoS}_4]$, which undergoes slow surficial degradation with time, the organic tetrasulfido-molybdates 1 and 3 are very stable and retain their red colour for several days without any morphological changes. Compounds 1–4 slowly dissolve in water but are freely soluble in dilute aqueous ammonical solutions, DMSO, DMF, and insoluble in other organic solvents. Depending upon the protonation of the amine nitrogen, the four different structures are possible depicting monoprotection of two amines (II, III and V, VI) resulting in 1 $[\text{MS}_4]^{2-}$ (MS = Mo, W): 2 (organic ammonium) stoichiometry and another two structures (I and IV) with $[\text{MoS}_4]^{2-}$: diprotonated cation stoichiometry (Scheme S1). The formulae of the compounds 1–4 were derived from the elemental analytical data (CHNS) and the gravimetric analysis of $[\text{MS}_4]^{2-}$ content, which indicated $[\text{MS}_4]^{2-}$: organic ammonium ratio as 1:2 in compounds 1–4. IR, Raman, and UV–Vis spectroscopies, thermal analysis, and single crystal X-ray diffraction were used to get insight into the structures of 1–4.

IR and Raman spectra of compounds 1–4 indicated the presence of organic ammonium cations, 4-aminopyridinium, and 2-amino-6-methylpyridinium, and the M–S vibrations of $[\text{MS}_4]^{2-}$ (M = Mo, W) tetrahedral anions. For a free tetrahedral $[\text{MS}_4]^{2-}$ anion, four characteristic vibrations namely $\nu_1(\text{A}_1)$, $\nu_2(\text{E})$, $\nu_3(\text{F}_2)$ and $\nu_4(\text{F}_2)$ are expected. All these four bands are Raman active while only ν_3 and ν_4 are IR active. When the $[\text{MS}_4]$ tetrahedron is distorted, the symmetry is reduced. As a result,

the symmetric vibration $\nu_1(\text{A}_1)$ appears in the infrared spectrum as a signal of medium intensity and an intense signal for the triply degenerate $\nu_3(\text{F}_2)$ asymmetric stretching M–S vibration [56]. Compounds 1–4 exhibit several signals in their mid-infrared spectra up to 500 cm^{-1} , originating from the organic ammonium cations. The M–S vibrations of the $[\text{MS}_4]^{2-}$ anions are observed at lower energies below 500 cm^{-1} (Fig. S2). The signals due to the vibrations of $[\text{MoS}_4]^{2-}$ unit occur at slightly higher energies, even though their spectra are quite identical with that of their W analogs [17,22,63]. The strong absorption bands occurring at 3312 and 3336 cm^{-1} can be assigned to the O–H stretching vibrations of water in 1 and 2, respectively. For all four compounds the N–H region appears broad and has shifted to lower wave numbers compared to the free organic amines. This can be attributed to the change of the amine group into the ammonium cation and the hydrogen bonding interactions between the organic ammonium cations and $[\text{MoS}_4]^{2-}$ anions. A broad signal due to the N–H vibration occurs at $\sim 3085 \text{ cm}^{-1}$ for 1, while for 2–4, this vibration occurs at ~ 3062 , ~ 3050 , and $\sim 3041 \text{ cm}^{-1}$, respectively. The N–H region of 1–4 exhibits extra bands that have been assigned to the N–H vibrations of a free amine functionality of the organic cations, indicating that the amines used in this study are partially protonated [14,21]. We have also recorded Raman spectra 1–4 to trace the signals that are forbidden in IR spectra. The Mo–S and W–S Raman bands arising from $[\text{MS}_4]^{2-}$ unit are observed in the expected region ranging between 430 – 480 cm^{-1} (ν_1, ν_3), while the degenerate (ν_2, ν_4) signals are seen at $\sim 180 \text{ cm}^{-1}$ (Fig. S1–S4). UV–Vis spectra of 1–4 in water containing a few drops of ammonia were measured to confirm the unique absorption bands corresponding to $[\text{MoS}_4]^{2-}$ and $[\text{WS}_4]^{2-}$ chromophores. Electronic spectra of the red colour solutions of 1 and 3 are nearly identical, and the bands arising are exclusively assigned to charge transfer transitions of $[\text{MoS}_4]^{2-}$ chromophore [3,8]. The longest wavelength of absorption occurs at $\sim 468 \text{ nm}$ for both $[\text{MoS}_4]^{2-}$ compounds (1 and 3), while this signal is blue-shifted to 392 nm for $[\text{WS}_4]^{2-}$ compounds (2 and 4) (Fig. S5).

3.2. Thermal analyses of 1–4

The thermal stability of compounds 1–4 was investigated using TG-DTA measurements, and their corresponding TG-DTA plots are given in Figs. S6–S9. The studies on thermal decomposition patterns further helped to understand the structural aspects of 1–4. As observed in Fig. S6, compound 1 showed a mass loss of 4.1% (Calc. 4.15%) that has

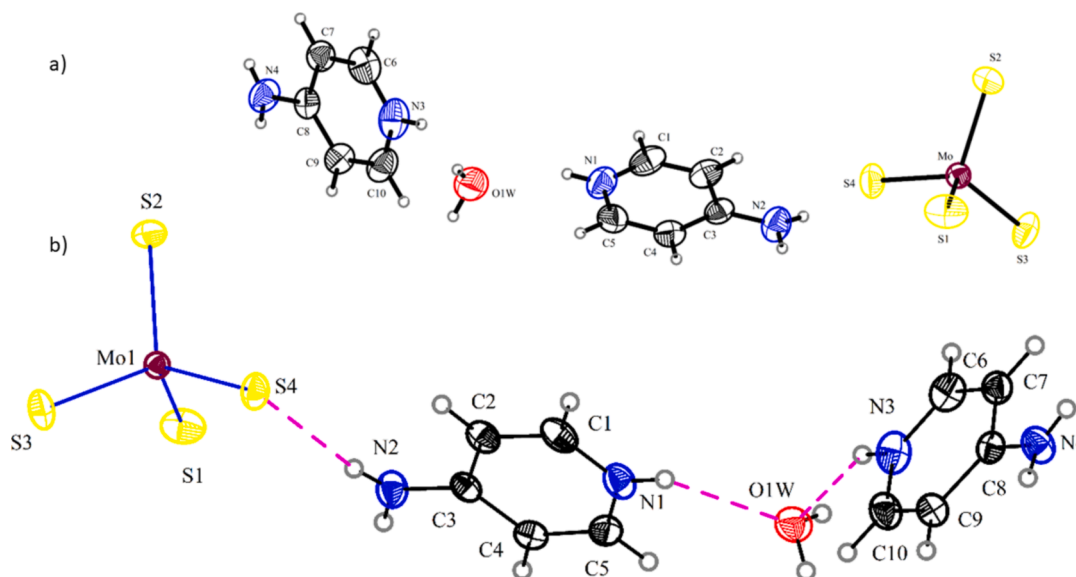


Fig. 1. a) Crystal structure of $(4\text{-aminopyridinium})_2[\text{MoS}_4]\cdot\text{H}_2\text{O}$ 1 showing atom labeling scheme. The thermal ellipsoids are drawn at 30 % probability, and the H atoms are shown as circles with an arbitrary radius. b) Intramolecular hydrogen bonds are shown in purple dotted lines in 1.

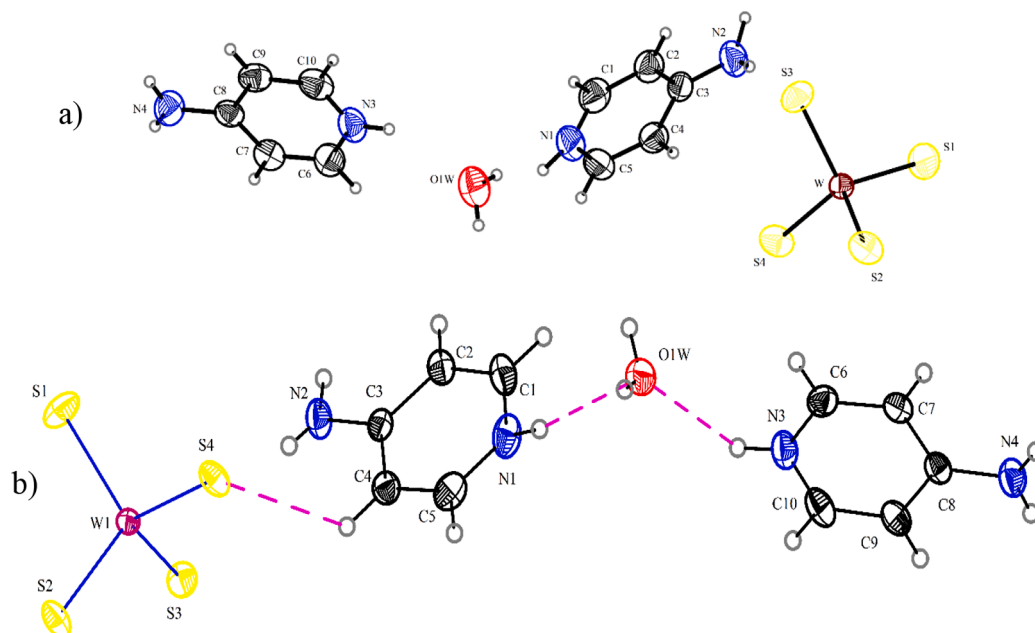


Fig. 2. a) Crystal structure of (4-aminopyridinium)₂[WS₄]·H₂O **2** showing atom labeling scheme. The thermal ellipsoids are drawn at 30 % probability, and the H atoms are shown as circles with an arbitrary radius. b) Intramolecular hydrogen bonds are shown in purple dotted lines in **2**.

been assigned to the loss of a crystal lattice water molecule giving rise to an anhydrous organic ammonium (4-ampH)₂[MoS₄]. On further heating, the anhydrous compound showed a mass loss of 44.32 %, corresponding to the decomposition of the organic ammonium portion. The weight of undecomposed residue was 45.2 %, which closely matches the formation of MoS₃ (*Calc.* 44.2 %). It has been reported that MoS₃ is unstable at high temperatures and changes exothermically to MoS₂ as in ammonium tetrasulfidomolybdate [3,57–59]. In compound **2**, the first mass loss of 3.5 % is assigned to the elimination of a water molecule as water vapor in the TG furnace associated with the corresponding endo peak at ~80 °C (Fig. S7). The observed mass loss is in close agreement with the calculated mass loss of 3.46 % for a single water molecule. Thus, TG-DTA data support supports IR spectra of **1** and **2**, which showed O–H vibrations for water molecules. The anhydrous complex (4-ampH)₂[WS₄] of **2** on further heating up to 600 °C showed a significant mass loss of 43.0 % (*Calc.* 43.1 %) due to the decomposition of organic ammonium moiety accompanied by two closely related exothermic events. The weight of black residue (53.1 %) left in the TG crucible very well matched the expected value for the formation of WS₃ (*Calc.* 53.78 %). In the TG-DTA plots of compounds **3** and **4**, there was no weight loss observed up to 120 °C, suggesting the absence of any water molecules, unlike in **1** and **2**. Compound **3** starts decomposing at around 121 °C, which is indicated by rapid mass loss (56.99 %) in the TG curve corresponding to loss of the organic amine moiety and H₂S (*Calc.* 56.56 %) (Fig. S8). The weight of the remaining black residue was 43.01 %, and this value closely matched with the formation of MoS₃ (*Calc.* 44.2 %). Compound **4** is thermally more stable, as evidenced by its TG-DTA plot. Compound **4** starts decomposing at a temperature of ~133 °C, which is accompanied by a rapid mass loss of 47.3 % until 600 °C (Fig. S9). The observed mass loss is in good agreement with the loss of organic amine moiety (*Calc.* 47.2 %). The resulting residue of 52.7 % closely matched with the formation of WS₃ (*Calc.* 52.79 %).

3.3. Description of crystal structures 1–4

We recorded the powder X-ray diffraction patterns of compounds **1–4** (Fig. S10) to confirm the phase purity of the single crystals and the bulk material. The experimental powder patterns were compared with the simulated PXRD patterns obtained from single crystal structure data

Table 2
Selected geometric parameters (Å, °) for 1–4.

Compound 1			
Mo1–S1	2.1620(8)	Mo1–S3	2.1857(7)
Mo1–S2	2.1745(7)	Mo1–S4	2.1935(7)
S1–Mo1–S3	110.19(3)	S2–Mo1–S3	109.79(3)
S1–Mo1–S2	109.13(3)	S1–Mo1–S4	109.57(4)
S2–Mo1–S4	109.83(3)	S3–Mo1–S4	108.33(3)
Compound 2			
W1–S1	2.1700(10)	W1–S2	2.1928(10)
W1–S3	2.1801(10)	W1–S4	2.2014(10)
S1–W1–S3	109.20(4)	S3–W1–S2	109.71(4)
S1–W1–S2	110.17(4)	S1–W1–S4	109.64(5)
S2–W1–S4	108.35(4)	S3–W1–S4	109.76(4)
Compound 3			
Mo1–S1	2.1669(9)	Mo1–S4	2.1865(8)
Mo1–S2	2.1702(8)	Mo1–S3	2.1950(8)
S1–Mo1–S3	107.86(4)	S2–Mo1–S3	109.90(4)
S1–Mo1–S2	110.89(4)	S1–Mo1–S4	110.78(5)
S2–Mo1–S4	108.46(3)	S4–Mo1–S3	108.94(4)
Compound 4			
W1–S2	2.1741(8)	W1–S3	2.1937(7)
W1–S1	2.1765(7)	W1–S4	2.1988(7)
S1–W1–S3	108.51(3)	S2–W1–S3	110.69(4)
S2–W1–S1	110.95(4)	S1–W1–S4	109.84(3)
S2–W1–S4	107.91(3)	S3–W1–S4	108.91(3)

(*vide infra*) using Mercury 4.0 software [60]. The single crystals of **1–4** were obtained in copious amounts by a slow evaporation method. Crystal structures of compounds **1** and **2** revealed that both **1** and **2** crystallize in a centrosymmetric monoclinic crystal space group $P2_1/c$ (Table 1). The asymmetric unit of **1** and **2** are composed of unique anions [MS₄]^{2–} (M = Mo **1** and W **2**), which are stabilized by two crystallographically independent 4-aminopyridinium cations located in general positions (Fig. 1 and Fig. 2). As evidenced from IR and TG data, the crystal structures showed a lattice water molecule in **1** and **2**.

The selected bond distances and bond angles of compounds **1–4** are summarized in Table 2. As evidenced from the data, compound **1** show

Table 3
Hydrogen bonding parameters (Å, °) for **1–4**.

D—H...A	d (D—H)	d (H...A)	∠DHA	d (D...A)	Symmetry code
Compound 1					
O1W—H1W...S1	0.741	2.865	144.42	3.495 (3)	$[-x, -y + 1, -z + 1]$
C10—H10...S1	0.930	2.869	160.07	3.757 (4)	$[-x + 1, -y + 1, -z + 1]$
N2—H2A...S2	0.838	2.918	138.77	3.591 (3)	$[-x + 1, y - 1/2, -z + 3/2]$
N4—H4B...S2	0.757	2.701	174.42	3.456 (3)	$[-x, y - 1/2, -z + 1/2]$
O1W—H2W...S3	0.809	2.681	164.70	3.460 (3)	$[-x, -y + 1, -z + 1]$
N2—H2A...S3	0.838	2.959	145.56	3.681 (3)	$[-x + 1, y - 1/2, -z + 3/2]$
N4—H4A...S3	0.857	2.998	121.27	3.519 (2)	$[-x + 1, y - 1/2, -z + 1/2]$
N4—H4A...S4	0.857	2.668	161.31	3.489 (3)	$[-x + 1, y - 1/2, -z + 1/2]$
C9—H9...S4	0.930	2.877	146.24	3.686 (3)	$[-x + 1, y - 1/2, -z + 1/2]$
C7—H7...S4	0.930	2.864	123.02	3.460 (3)	$[-x, y - 1/2, -z + 1/2]$
N2—H2B...S4	0.805	2.586	168.16	3.377 (3)	
N1—H1N...O1W	0.797	2.235	145.59	2.927 (4)	
N3—H3N...O1W	0.815	2.150	150.22	2.886 (4)	
Compound 2					
O1W—H1A...S1	0.760	2.811	151.01	3.490 (3)	$[x - 1, -y + 3/2, z + 1/2]$
C1—H1A...S1	0.930	2.881	159.91	3.771 (3)	$[x, -y + 3/2, z + 1/2]$
O1W—H1B...S2	0.781	2.722	164.26	3.475 (3)	$[x, -y + 3/2, z + 1/2]$
N2—H2A...S2	0.861	3.014	120.41	3.523 (2)	
N4—H4A...S3	0.712	3.041	140.34	3.615 (3)	$[x, y, z + 1]$
N2—H2B...S3	0.863	2.612	170.51	3.459 (3)	$[1 - x, y, z]$
O1W—H4...O1	0.833	1.995	172.45	2.823 (4)	
O1W—H4...O2	0.833	2.59	131.33	3.201 (3)	
C4—H4...S4	0.931	2.871	123.12	3.468 (3)	$[1 - x, y, z]$
N4—H4B...S4	0.871	2.530	168.12	3.378 (3)	$[-x + 2, y - 1/2, -z + 3/2]$
N2—H2A...S4	0.861	2.681	159.91	3.502 (3)	
C2—H2...S4	0.931	2.881	146.61	3.693 (3)	
Compound 3					
N2—H6...S1	0.818	2.635	163.09	3.426 (4)	$[x, y + 1, z]$
C8—H8...S1	0.930	2.930	140.99	3.700 (4)	$[x, y + 1, z]$
N1—H12...S2	0.836	2.727	163.44	3.536 (3)	$[x - 1, y, z]$
C2—H2...S2	0.930	2.967	129.85	3.634 (3)	$[-x + 1, -y, -z + 1]$
C6—H6B...S2	0.960	2.973	144.30	3.794 (4)	
N3—H1...S3	0.805	2.538	162.55	3.315 (3)	
N2—H7...S3	0.829	2.882	139.96	3.556 (3)	
N1—H11...S3	0.817	2.740	151.52	3.480 (4)	

Table 3 (continued)

D—H...A	d (D—H)	d (H...A)	∠DHA	d (D...A)	Symmetry code
N1—H12...S4	0.836	2.878	117.50	3.347 (4)	$[x - 1, y, z]$
N4—H5...S4	0.830	2.407	171.32	3.230 (3)	
Compound 4					
C4—H4...S1	0.930	2.985	129.44	3.647 (5)	$[-x + 1, -y, -z + 1]$
N2—H2B...S1	0.860	2.698	164.68	3.535 (3)	$[x - 1, y, z]$
C6—H6B...S1	0.960	2.982	145.42	3.811 (6)	$[x - 1, y, z]$
N4—H4B...S2	0.860	2.605	159.10	3.423 (3)	$[x, y + 1, z]$
C8—H8...S2	0.930	2.932	141.19	3.703 (6)	$[x, y + 1, z]$
N2—H2B...S3	0.860	2.886	116.38	3.357 (6)	$[x - 1, y, z]$
N3—H5...S3	0.835	2.413	168.85	3.236 (2)	
N4—H4A...S3	0.860	2.990	141.50	3.702 (5)	
N1—H1...S4	0.861	2.495	161.83	3.324 (2)	
N2—H2A...S4	0.860	2.710	150.74	3.486 (3)	

the shortest Mo—S bond length of 2.1620 (8) Å (Mo1—S1), while the most elongated Mo—S bond length is 2.1935 (7) Å (Mo(1)—S(4)). The difference (Δ) between the longest and the shortest Mo—S bond in **1** is 0.0315 Å, which is in good agreement with related $[\text{MoS}_4]^{2-}$ cores attributed to a slight distortion of tetrahedron [61]. The distortion of the tetrahedron is further evident from the deviation S—Mo—S bond angles from the ideal bond angle of 109.5° seen in the case of a perfect tetrahedron. The S—Mo—S bond angles in **1** range between 108.33 (3) to 110.19 (3)°. The distortion of $[\text{MoS}_4]^{2-}$ gets further credence from the IR and Raman data, which showed a split of Mo—S vibration in **1** and **2** (Fig. S1).

The structural insights show that compound **1** is composed of N—H...S and N—H...O type intra-molecular hydrogen bonds. Also comprised of intermolecular hydrogen bonds, namely O—H...S, N—H...S, and C—H...S, which gave rise to 3D supramolecular networks (Table 3). The nature, number, and strength of M—S...H interaction all lead to the distortion of Mo—S bond lengths, as seen in the case of **1**. The reports on similar compounds suggest that longest S...H distance is associated with smaller D—H...A angle and results in shorter Mo—S bond distance. In comparison, shorter S...H distance is associated with a larger D—H...A angle, resulting in elongated Mo—S bonds. For instance, the interaction between S2...H is fragile with a distance of 2.918 Å accompanied by a smaller N2—H2A...S2 bond angle of 138.77° as a result of which the Mo—S2 bond is shorter with a bond distance of 2.1745(7) Å. In contrast, S4...H interaction is shorter, 2.668 Å, along with a significantly larger bond angle of 161°, which explains the long Mo—S bond of 2.1935(7) Å. Each $[\text{MoS}_4]^{2-}$ anion interacts with four neighboring 4-aminopyridinium cations via N—H...S intermolecular hydrogen bonds and three weak C—H...S interactions. The $[\text{MoS}_4]^{2-}$ anion is further connected to the neighboring $[\text{MoS}_4]^{2-}$ anions with the aid of lattice water molecules (Fig. 3). Along the *ab* plane, the crystal structure **1** shows a double layer alternating with the cations and the anions. The lattice aqua molecules show hydrogen bonding with the $[\text{MoS}_4]^{2-}$ anion, thus forming a 1D extended chain structure (Fig. 4).

The crystal structure of compound **2** displays a distortion in the $[\text{WS}_4]^{2-}$ anion with the S—W—S bond angles ranging from 108.35 (4) to 110.17 (4)° while the shortest W—S bond length is 2.1700 (10) Å (W1—S1) and longer bond distance is 2.2014 (10) Å (W1—S4). The difference between the longest and the shortest W—S bond in **2** is

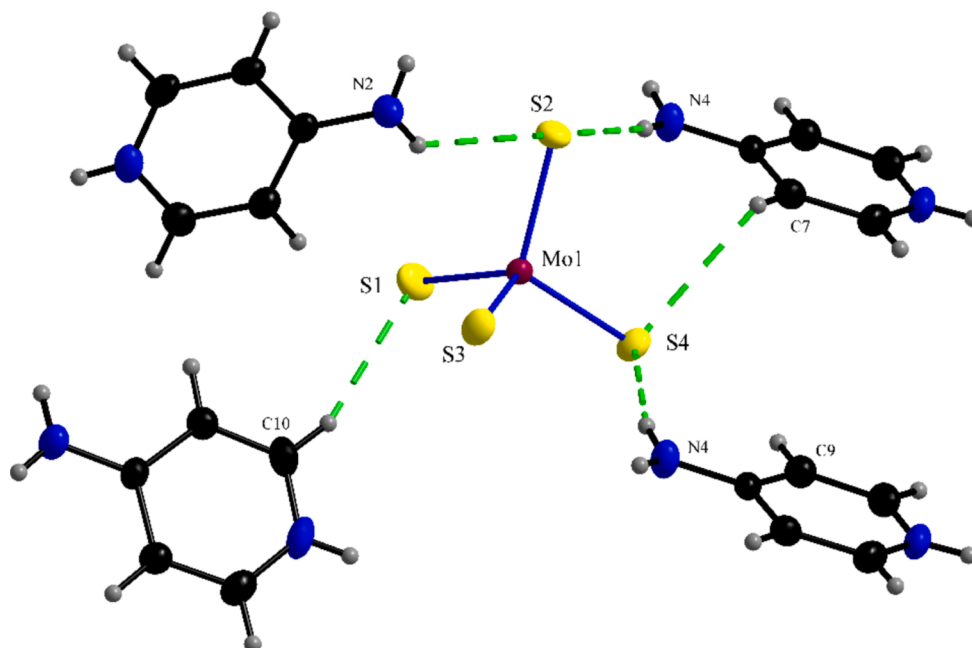


Fig. 3. Hydrogen bonding interactions between tetrahedral $[\text{MoS}_4]^{2-}$ and 4-aminopyridinium cations in **1**.

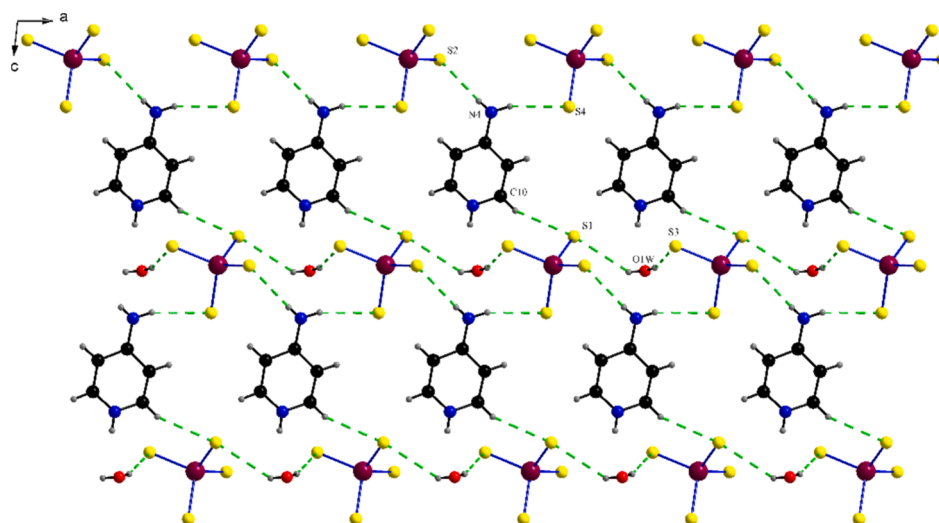


Fig. 4. A view showing the arrangement of the tetrahedrons, cationic units, and the lattice waters in compound **1** along the ab plane. The intermolecular hydrogen bonds are shown in green dotted lines.

Table 4

Comparison of M—S bond distances and bond angles leading to distortion (Δ) of $[\text{MS}_4]^{2-}$ tetrahedra in **1–4**.

Compound	1	2	3	4
M—S (longest) (Å)	2.1935(7)	2.2014(10)	2.1950(8)	2.1988(7)
M—S (shortest) (Å)	2.1620(8)	2.1700(10)	2.1669(9)	2.1741(8)
$\Delta(\text{M—S})$ (Å)	0.0315	0.0314	0.0281	0.0247
S—M—S (largest) (Å)	110.19(3)	110.17(4)	110.89(4)	110.95(4)
S—M—S (smallest) (Å)	108.33(3)	108.35(4)	108.46(4)	107.91(4)

0.0314 Å (Table 4), which is close to the difference observed in **1** and other related compounds of $[\text{WS}_4]^{2-}$ tetrahedron [17,21,22]. Each $[\text{WS}_4]^{2-}$ anion interacts with four neighboring 4-aminopyridinium cations via four N—H...S hydrogen bonds and a weak C—H...S interaction. The hydrogen bonding situation around the $[\text{WS}_4]^{2-}$ tetrahedron in compound **2** is shown in Fig. S11. The $[\text{WS}_4]^{2-}$ anions are further

connected with the aid of O—H...S interactions originating from the lattice water molecules, thus forming a 1D extended chain structure in **2**. Along the ab plane, the crystal structure **2** shows a double layer alternating with the cations and the anions (Fig. S12).

Hirshfeld surface analyses were carried out to extract more information on the intermolecular interactions of the cations and the anions in the supramolecular assembly. Our results report similar interactions in compounds **1** and **2**. It is observed that in comparison to 2-amino-6-methylpyridinium cations, the 4-aminopyridinium cations showed many red regions in the Hirshfeld surface of the anion (Fig. 5(a) and 6(a)). Both the compounds exhibit two spikes, the first at $d_e/d_i = 0.85/1.5$ due to S...H interaction having 95.2 and 95.1 % contribution, respectively, while the second spike appears at $d_e/d_i \cong 1.8/1.8$ due to S...S interactions from the neighboring anions, and these interactions contribute 2.7 % and 2.6 % in **1** and **2**, respectively. As discussed earlier, the red regions in Fig. 5(b) and 6(b) show shorter interactions than the

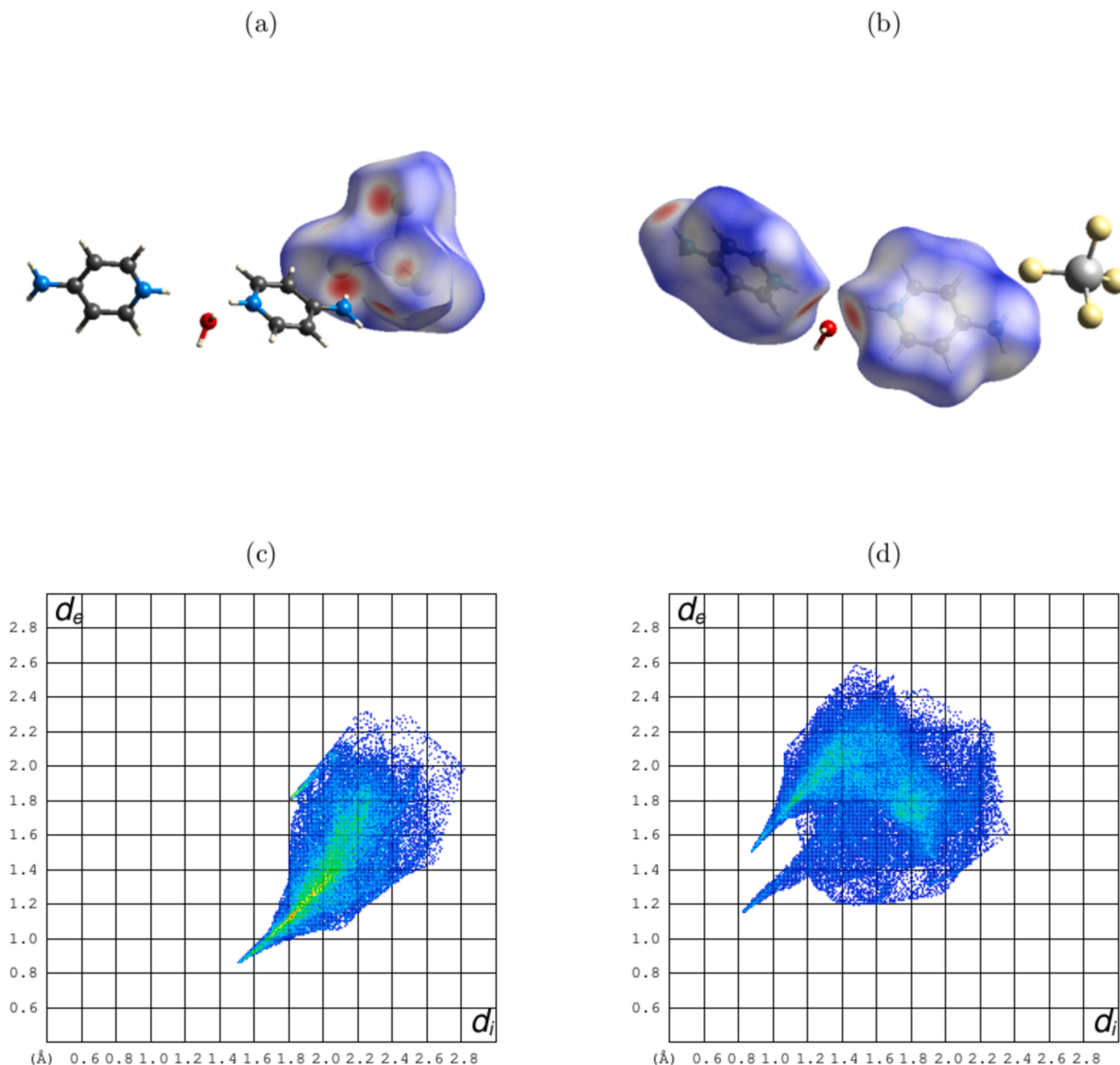


Fig. 5. Top: Hirshfeld surfaces of the anion (left) and the cation (right) of 1. Bottom: the corresponding fingerprint plots.

sum of the Van der Waals radii of the corresponding atoms. Fig. 5(d) and 6(d) show the cations' fingerprint plots displaying various interactions. A spike at $d_e/d_i \approx 1.18/0.8$ is due to H...O interaction and contributes 4.9 and 4.7 % in 1 and 2, respectively. H...H interactions due to the hydrogens in neighboring cations culminate into a broad spike at $d_e/d_i \approx 1.2/0.9$ and $d_e/d_i \approx 1.3/0.95$, contributing 32.6 % and 31.8 %, respectively, in 1 and 2. It is also observed that in compounds of 4-aminopyridinium cation (1 and 2), irrespective of the metal ion (W or Mo) used, there exists the presence of an S...S interaction between the neighboring anions, which is absent in compounds 3 and 4 containing 2-amino-6-methylpyridinium cations. The decomposed fingerprint plots for the above interactions in compounds 1 and 2 are given in Fig. S13 and Fig. S14, respectively.

Compounds 3 and 4 are isostructural and crystallize in the centrosymmetric triclinic crystal system with the $P1$ space group. The crystal structures of 3 and 4 are composed of a unique anionic core $[\text{MS}_4]^{2-}$

stabilized by two crystallographically independent 2-amino-6-pyridinium cationic units located in the general positions (Fig. 7, Fig. 8). The selected bond distances and bond angles of 3 and 4 are summarized in Table 2. Compounds 3 and 4 exhibit distortion of $[\text{MS}_4]^{2-}$ tetrahedron which is evident from the stretching and compression of M—S bond distances and S—M—S bond angles. In compound 3, the shortest Mo—S bond distance of 2.1669 (9) Å (Mo1—S1) is accompanied by the longest Mo—S bond distance of 2.1950 (8) Å (Mo1—S3). The difference (Δ) between the longest and the shortest Mo—S bond in 3 is 0.0281 Å (Table 4). In case of 4, the shortest W—S bond distance of 2.1741 (8) Å (W1—S2) is accompanied by the longest bond distance of 2.1988 (7) Å (W1—S4). The difference (Δ) of 0.0247 Å is observed in compound 4. Interestingly, the difference (Δ) between the smallest and the longest M—S bond distances in 3 and 4 is comparatively less than that observed in compounds 1 and 2, indicating that hydrogen bonding strength in 1 and 2 is relatively higher than in 3 and 4. This observation has been

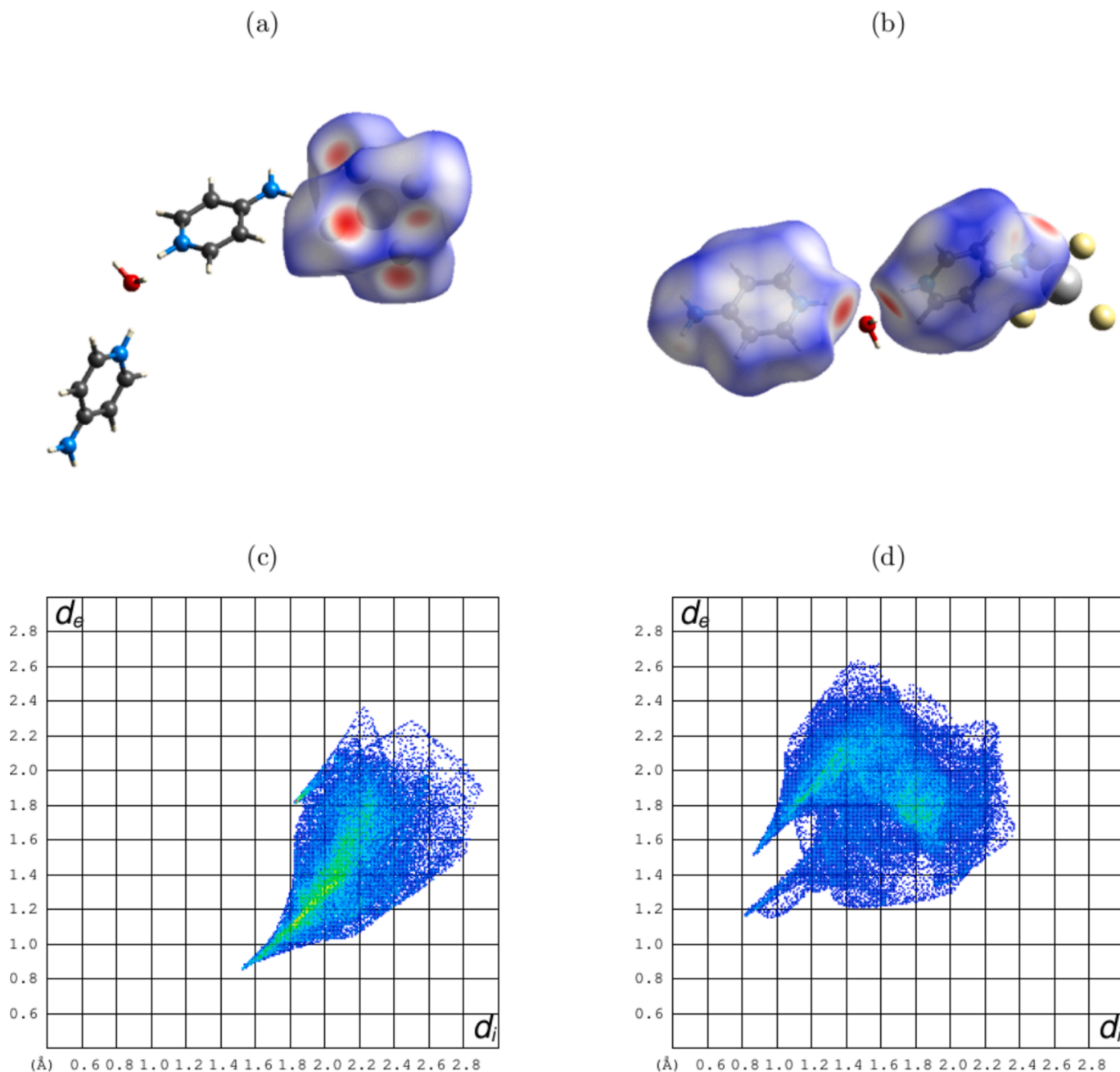


Fig. 6. Top: Hirshfeld surfaces of the anion (left) and the cation (right) of **2**. Bottom: the corresponding fingerprint plots.

attributed to the presence of two different amines, namely 4-aminopyridine and 2-amino-6-methylpyridine, in compounds **1**, **3**, and **2**, **4** pairs, respectively. Additionally the structures of **1** and **2** are stabilized by a lattice of water, which is lacking in **3** and **4**. The steric credibility of the two amines differs from the positions of the amino groups with respect to pyridine N as well as the additional methyl group in **3** and **4** further attributes to this observation. The crystal structure analysis revealed that both the compounds show N—H...S and C—H...S type inter- and intramolecular interactions responsible for packing the molecules in the crystal lattice (Table 3). Each $[\text{MoS}_4]^{2-}$ anion in **3** interacts with the three nearest 2-amino-6-pyridinium cations via N—H...S hydrogen bonds and weak C—H...S interactions as shown in Fig. S15. Similar observations are also drawn for compound **4**; the hydrogen bonding situation around the tetrahedron is depicted in Fig. S16.

On comparing the Hirshfeld surface analysis data of anion and

cations in compound **3** (with molybdenum, Mo) and compound **4** (with tungsten, W), it is observed that they exhibit nearly similar interactions. In Fig. 9(a) and (b) of compound **3**, the red area on the Hirshfeld surface indicates the S...H contact, which remains consistent between the two compounds. Since both compounds contain the same cation, the d_e/d_i values are expected to be identical, as seen in the case of compound **4** (Fig. 10). However, it is essential to note that the contribution of each interaction to the Hirshfeld surface may vary slightly between the two compounds.

In the 2D fingerprint plot for the anion, Fig. 9(c), the S...H interaction is observed at $d_e/d_i = 0.8/1.42$, contributing 94.9 % to the surface in compound **3**. This interaction is prominently represented in the fingerprint plot. In Fig. 9(d), the fingerprint plot for the cations is shown, and it shows two distinct interactions. The interaction at $d_e/d_i = 1.4/0.8$ corresponds to the H...S interaction, contributing 29.6 % to the surface.

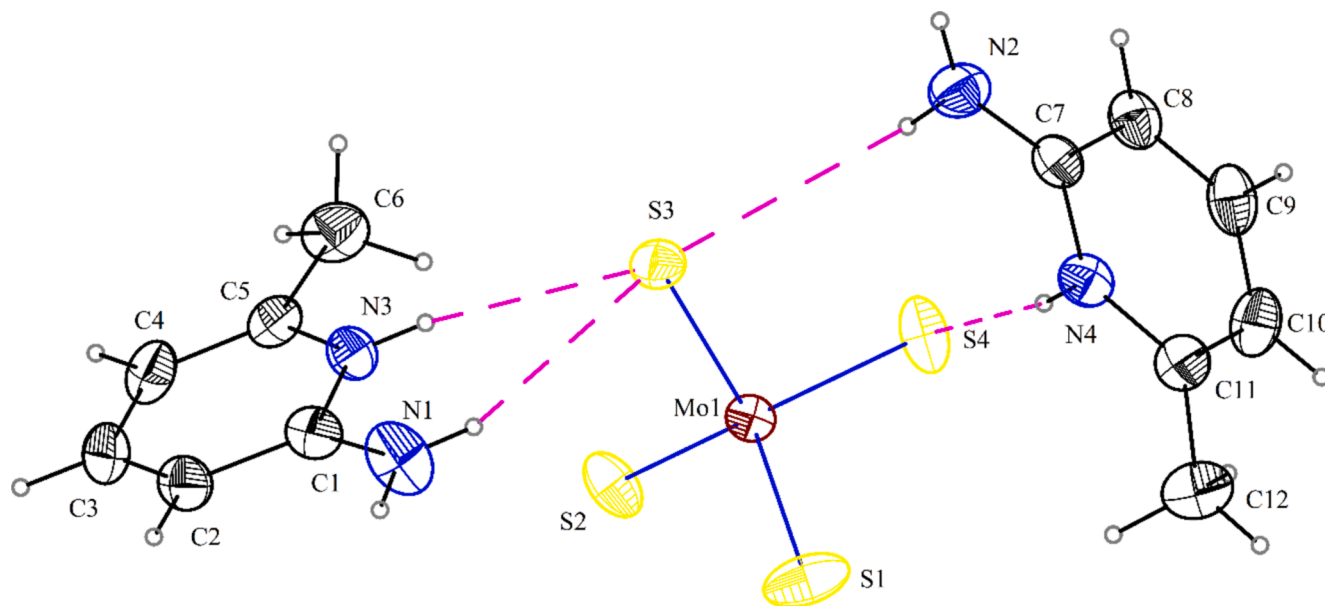


Fig. 7. The crystal structure of (2-amino-6-methylpyridinium)₂[MoS₄] **3** showing atom labeling scheme. The thermal ellipsoids are drawn at 30 % probability, and the H atoms are shown as circles with an arbitrary radius. The intramolecular hydrogen bonds are shown in purple dotted lines.

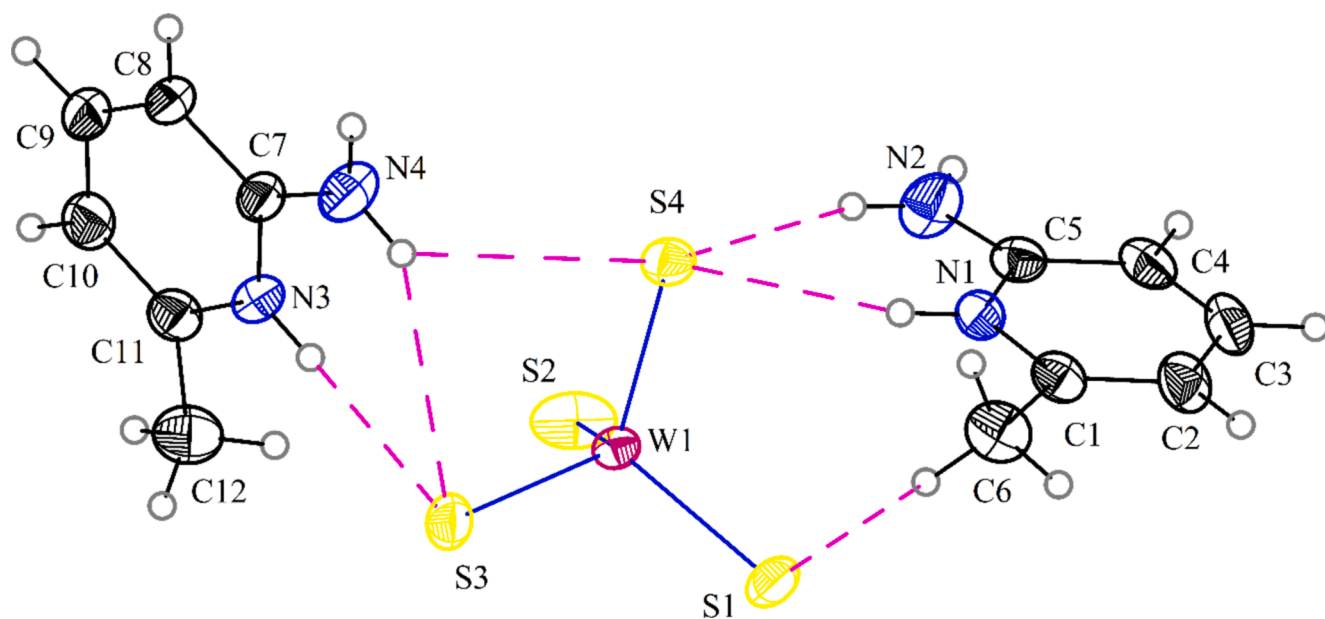


Fig. 8. The crystal structure of (2-amino-6-methylpyridinium)₂[WS₄] **4** showing atom labeling scheme. The thermal ellipsoids are drawn at 30 % probability, and the H atoms are shown as circles with an arbitrary radius.

Additionally, the interaction at $d_e/d_i = 1.15/1.15$ represents H...H contacts between neighboring cations, accounting for 45.4 % of the surface.

In Fig. 10(a) and (b) of **4**, the red regions highlight interatomic distances that are shorter than the sum of the Van der Waals radii of the corresponding atoms. The 2D fingerprint plots, shown in Fig. 10(c) and Fig. 10(d) of **4**, provide a detailed analysis of the contacts observed in Fig. 10(a) and Fig. 10(b). The anion's fingerprint plot (Fig. 10(c)) shows a spike at $d_e/d_i = 0.8/1.42$, corresponding to an S...H interaction accounting for 95.1 % of the total contribution. In the cation's fingerprint plot (Fig. 10(d)), two distinct spike-like features represent different types of interactions. The first spike at $d_e/d_i = 1.15/1.15$ indicates H...H interactions due to hydrogens in neighboring cations, contributing 45 % to the surface. The second spike at $d_e/d_i = 1.42/0.8$ corresponds to H...S

interactions, contributing 29.7 % to the surface.

Furthermore, one of the cations exhibits an H...S interaction at $d_e/d_i = 1.5/0.82$, accounting for 29.3 % of the contribution. The second cation, on the other hand, displays an H...S interaction at $d_e/d_i = 1.42/0.8$, contributing 30.1 % to the surface. The decomposed fingerprint plots for the interactions discussed for compounds **3** and **4** are given in Fig. S17 and Fig. S18, respectively.

The plots of d_{norm} of Hirshfeld surface area, shape index, curvedness, and decomposed fingerprint plots of C_π/C_π interactions for the entire single crystal for compounds **1–4** are given in Fig. S19 to Fig. S22, respectively. The presence of red- and blue-colored triangles in shape index (Fig. S19 to Fig. S22(b)) and flat surfaces in curvedness surface (Fig. S19) to Fig. S22(c)) confirms the π ... π stacking interactions in the crystals [62]. The decomposed fingerprint plot for these interactions in

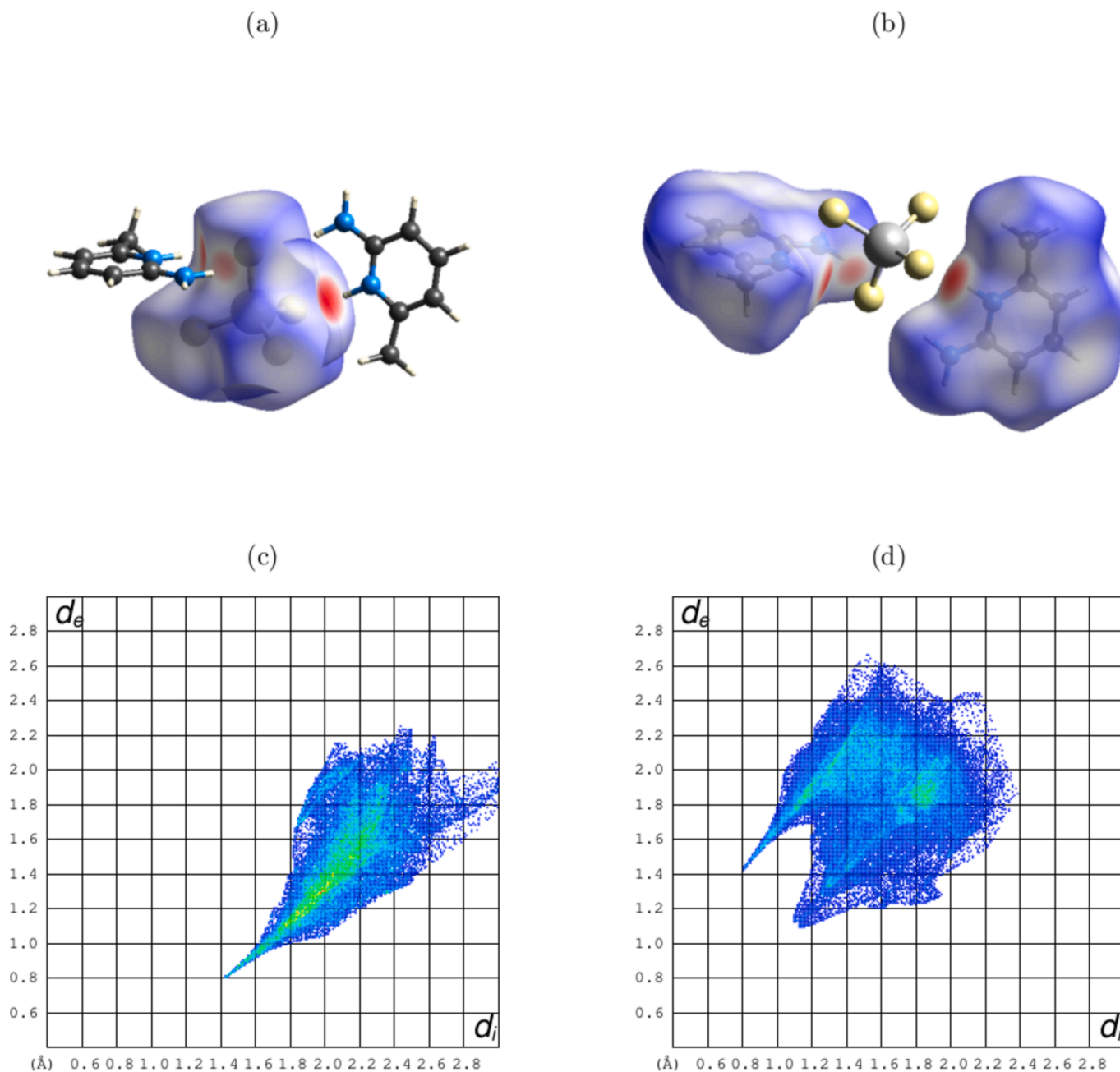


Fig. 9. Top: Hirshfeld surfaces of the anion (left) and the cation (right) of **3**. Bottom: the corresponding fingerprint plots.

compounds **1** to **4** are given in (Figs. S19 to Fig. S22(d)) which accounts for 3.7 % for compounds **1** and **4** and 3.8 % for compounds **2** and **3**.

The contact percentages and enrichment ratios calculated for the elemental pairs from the fingerprint plot for compounds **1** to **4** are given in Tables S1 to S4 and S5 to S8, respectively. The values of E greater than 1 represent the contacts that are favored in crystal packing [54]. From Figs. S19, S20, and Tables S5, and S6, it can be noted that in compounds **1** and **2**, S...H, C...C, and N...N interactions are favored. Whereas the contacts having a value of E_{XY} less than 1 are avoided. Similar observations can be made for compounds **3** and **4** in which C...C and N...N contacts are favored in the crystal packing (Figs. S21, S22, and Table S7, S8).

Various weak interactions arising during the crystal packing were visualized using non-covalent interaction (NCI) analysis based on promolecular density [63] as implemented in Multiwfn software [64]. Figs. S23 to S26 show the (a) NCI plot index and (b) RDG vs. sign (λ_2)p

scatter plot of **1** to **4**, respectively. The NCI plot index visually represents the coloured surface at the site of weak interactions [62,65]. In RDG vs. sign (λ_2)p scatter plot, the red coloured region indicates the repulsive interactions present in the crystal, whereas the blue regions represent the attractive interactions, and the green region represents the Van der Waals interactions. As seen from Figs. S23 and S24, many weak interactions are observed in compounds **1** and **2**, respectively. The weak interaction arising due to C...C and N...N interactions can be clearly observed in Figs. S25(a) and S26(a) for compounds **3** and **4**. Thus, NCI analysis visually complements the results obtained by enrichment ratio to identify the aforementioned results.

3.4. Utility of **1–4** as sulfur transfer reagents

S. Chandrasekaran and co-workers have proven benzyl triethylammonium tetrathiomolybdate as an efficient sulfur transfer reagent in

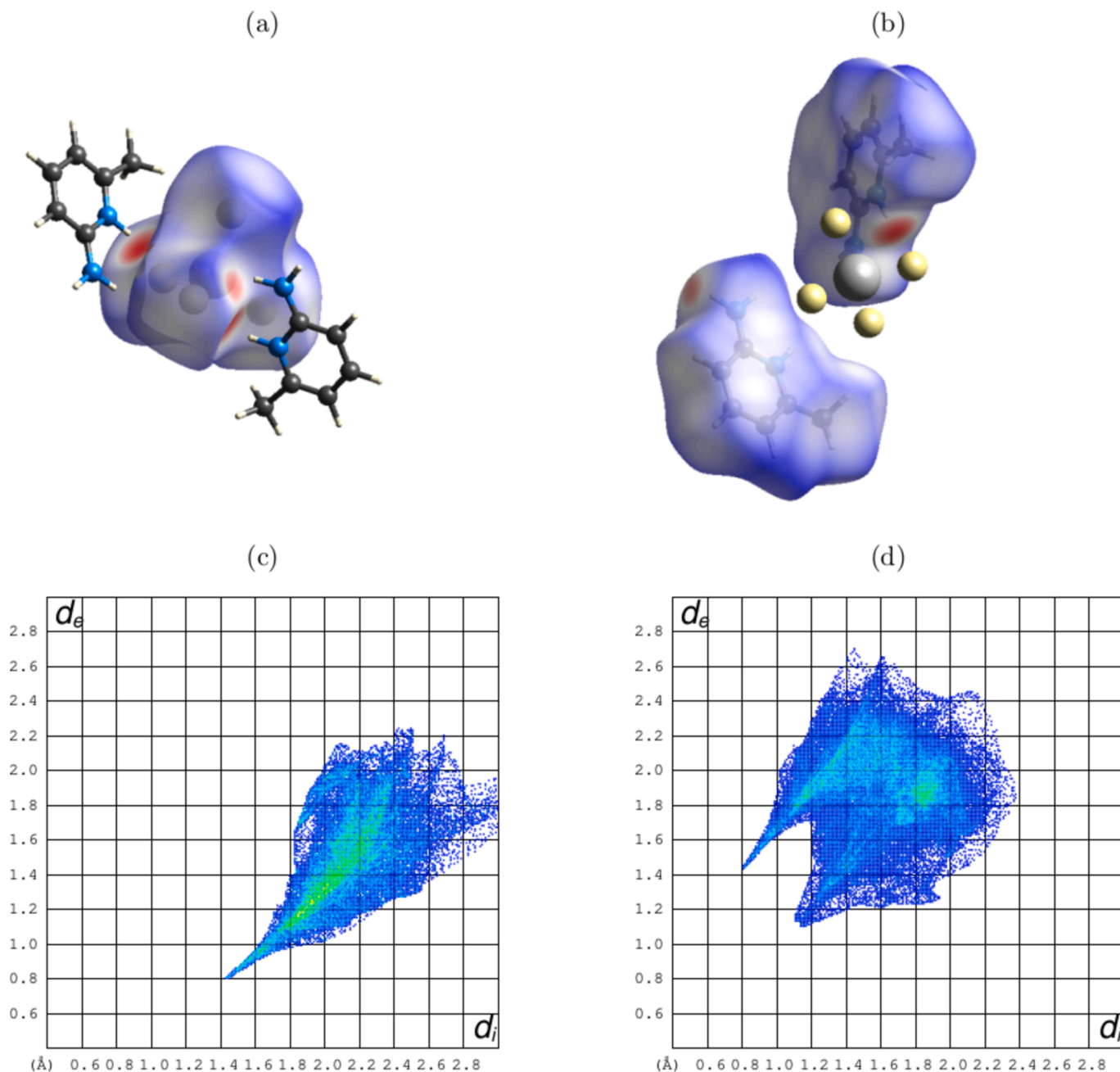
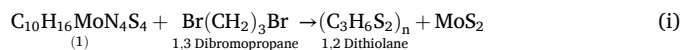


Fig. 10. Top: Hirshfeld surfaces of the anion (left) and the cation (right) of compound 4. Bottom: the corresponding fingerprint plots.

organic synthesis [66]. They also used piperidinium tetrathiotungstate as a sulfur transfer reagent to convert alkyl halides into corresponding disulfide compounds [67]. It was interesting to find out whether cyclic disulfides can be formed efficiently from *n*-halo compounds via intramolecular pathways in compounds 1–4. UV–Vis. spectroscopy was used as a tool to study the formation of disulfide and the corresponding UV–Vis spectra followed a pseudo-first-order kinetic pattern [40,68]. Several thiosugars have been synthesized using benzyl triethylammonium tetrathiomolybdate as a sulfur transfer reagent [69]. We tested tetrathiomolybdates 1, 3 and tetrathiotungstates 2, 4 for their sulfur transfer ability to a dihaloalkane such as 1,3-dibromopropane. Before using them in S-transfer reactions, the phase purity of powdered samples of 1–4 was confirmed by PXRD and SCXRD, as discussed in section 3.3 (*vide supra*). In a representative experiment, the tetrathiomolybdate 1 (1×10^{-4} M, 2 mL) in DMF was taken in a quartz cuvette and the corresponding UV–Vis bands at 323 and 476 nm for $[\text{MoS}_4]^{2-}$ chromophore were recorded.

Under the time-dependent mode, 50 equivalents of 1,3-dibromopropane were added to the solution of 1, and the spectral changes at 323 and 476 nm were monitored. The absorption bands of 1 decayed with pseudo-first-order rate constant, $k_{\text{obs}} = 4.33 \times 10^{-4} \text{ s}^{-1}$ (Fig. 11).



We then carried out the same reaction of 1 with 1, 3-dibromopropane in 1:1 stoichiometry with measurable quantities (See SI for procedure). A black precipitate was immediately thrown out in the reaction mixture. The precipitate was isolated and dried under a vacuum, and its powder XRD was measured. The PXRD powder of the black solid was nearly featureless lacking peaks, indicating the amorphous phase of MoS_2 (Fig. S27) (reaction (i)). The filtrate was then evaporated under a high-pressure vacuum, resulting in a yellow semi-solid product. The IR spectrum of the product indicated the formation of a disulfide product

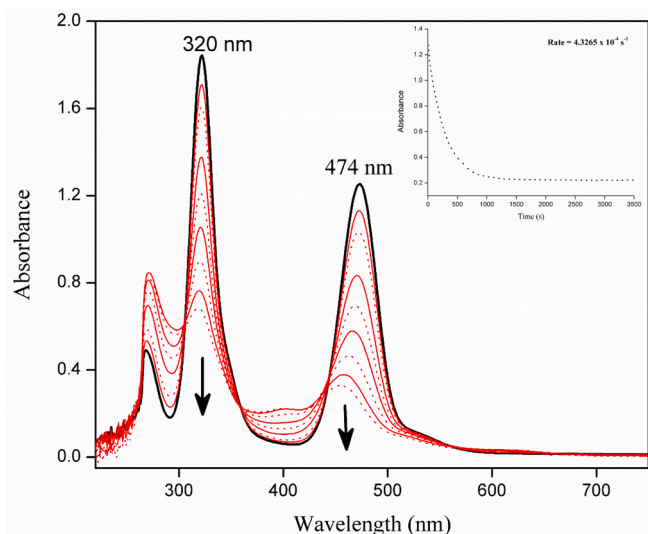


Fig. 11. UV-Vis. spectral changes on the addition of 50 equivalent of 1,3 dibromopropane to the DMF solution of (4-aminopyridinium)₂[MoS₄] **1** (1×10^{-4} M, 2 mL). The inset shows a decay of **1** at 474 nm with time.

[70] (Fig. S28). We then carried out the reactions of **2–4** with 50 equivalents of 1,3 dibromopropane; however, the reactions were quite sluggish for W analog (**2** and **4**), which can be attributed to the strength of strong W—S bonds. Further, the use of substituted organic ammonium cation (2-amino-6-methylpyridinium) in **3** instead of 4-aminopyridinium showed very slow reactivity. The time trace for the reaction of **2** with 1,3 dibromopropane is shown in Fig. S29, while the pseudo-first-order rate constants of all compounds are listed in Table S1.

4. Conclusions

Four new organic ammonium tetrasulfidometalates, **1–4**, were synthesized and characterized, and their correct formulae were arrived. Crystal structures of **1–4** revealed the existence of several hydrogen bonding interactions between the organic cation and the inorganic [MS₄]^{2−} anion. Methyl substitution in 2-aminopyridine led to dehydrated compounds **3** and **4**. The structural and spectroscopic analysis confirmed the elongation and compression of Mo—S and W—S bonds in compounds **1–4**, leading to distortion of [MoS₄]^{2−} and [WS₄]^{2−} tetrahedra. Hirshfeld surface analyses demonstrated the role of intermolecular S...H interactions between the anions and cations. The intermolecular H...H contacts contribute to the overall arrangement of the structural constituents in **1–4** and further support the ability of [MS₄]^{2−} to stabilize partially protonated organic ammonium cations. The values of enrichment ratios (E) higher than 1 represented the strength of short contacts in crystal packing of **1–4**. Compound **1** showed higher efficiency of conversion of 1,3-dibromopropane to 1,2-dithiolane, making this compound an active sulfur transfer reagent in future studies on the synthesis of organic disulfides.

5. Declaration by Authors

Authors declare that:

- the work described has not been published previously except in the form of a preprint, an abstract, a published lecture, an academic thesis, or a registered report.
- the article is not under consideration for publication elsewhere.
- the article's publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out.

- if accepted, the article will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.
- No generative AI in scientific writing is used.

CRediT authorship contribution statement

Milagrina D'Souza: Writing – review & editing, Writing – original draft, Validation, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Nikita N. Harmalkar:** Writing – original draft, Visualization, Software, Funding acquisition, Formal analysis, Data curation. **Vishnu R. Chari:** Writing – original draft, Software, Resources, Investigation. **Beena K. Vernekar:** Methodology, Formal analysis. **Sunder N. Dhuri:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors greatly acknowledge the support from the Department of Science and Technology, New Delhi (DST-FIST; SR/FST/CSII-034/2014(C); PURSE; (SR/PURSE/2023/198)) and the University Grants Commission, New Delhi, (UGC-SAP; F.504/14/DSA-I/2015). SND acknowledges support from Goa State Research Foundation, Goa, (GSRF/Schemes/MajorGR/13/2023/187/ii). NNH acknowledges UGC for the Savitribai Jyotirao Phule Fellowship for Single Girl Child (SJS GC) [UGCES-22-OB-GOA-F-SJSGC-6907].

Appendix A. Supplementary data

The Supplementary material file contains Scheme S1, additional figures (Figs. S1–S29), Tables S1–S9, and CheckCIF reports of **1–4**. CCDC No. 2381453, 2381454, 2381455, and 2381456 contain the supplementary crystallographic data for compounds **1–4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/-conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033). Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2024.117272>.

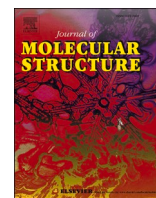
Data availability

Data will be made available on request.

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In vitro cytotoxicity and DNA interaction studies of nickel(II) mefenamate compounds with substituted α -diimines

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ARTICLE INFO

Keywords:

Nickel(II) ion
Mefenamic acid
Crystallography
Cytotoxicity
DNA cleavage
Molecular docking
Dynamics

ABSTRACT

Two bioactive nickel(II) compounds of mefenamic acid (Hmef) with substituted α -diimines as co-ligands have been characterised using various spectroscopic methods and evaluated for cytotoxicity, DNA interaction and antioxidant studies, molecular docking and dynamics studies. Single crystal structures of $[\text{Ni}(\text{Mef-O})_2(\text{etobpy})(\text{H}_2\text{O})]$ **1** and $[\text{Ni}(\text{Mef-O})_2(\text{dmbpy})(\text{H}_2\text{O})(\text{DMF})]$ **2**, (etobpy = 4,4'-diethoxy 2,2'-bipyridine, dmbpy = 4,4'-dimethyl-2,2'-bipyridine and DMF = N, N'-dimethylformamide) have been determined using single crystal X-ray diffraction technique. The mefenamate ligand adopts two types of coordination modes (mono- and bidentate) in **1**, while in compound **2** both mef ligands display monodentate behaviour. The Ni(II) ion in both compounds shows a distorted octahedral geometry binding to two N and four O atoms. The cytotoxicity results revealed the activity of **1** and **2** against cancerous HepG2 in a dose-dependent manner. % DPPH free radical scavenging activity of **1** and **2** when performed, they exhibited IC_{50} values of $17.02 \pm 0.85 \mu\text{M}$ and $19.89 \pm 0.73 \mu\text{M}$ respectively, depicting their antioxidant nature. DNA binding properties of **1** and **2** were assessed by UV absorption spectroscopy, which suggested an intercalating binding between the complexes and the DNA. Both complexes act as potential agents towards DNA cleavage with the dose-dependent rise of Form II and III DNA. Further, Their interactions with DNA were studied using molecular docking and molecular dynamics simulations. Both **1** and **2** are intercalating in the major groove of DNA fragment, destabilizing the double helix strand during simulation, proving as potential candidates for cytotoxicity.

1. Introduction

The chemistry of transition metal compounds with nonsteroidal anti-inflammatory drug (NSAID) properties is a cornerstone of medicinal inorganic chemistry. Such compounds have exhibited diverse structures and reactivity patterns, which makes them useful in several industrial and biological applications [1,2]. NSAIDs are a class of medications commonly used to alleviate pain, reduce inflammation, and lower fever by inhibiting the release of prostaglandins produced in the body by enzymatic transformations [3]. Several groups have successfully incorporated the transition metal ions into NSAIDs, enhancing their pharmacological potency [4–9]. NSAIDs can inhibit the

cyclooxygenase-mediated production of prostaglandins, resulting in reduced pain and swelling. They also exhibit effective antiproliferative activity against a series of cancer cell lines, including apoptosis [10]. Additionally, the consistent interest in NSAIDs containing carboxylate groups as ligands can be accredited to the fact that they possess the inherent ability to tune the structural properties of transition metal complexes and produce new structures with varied nuclearities, geometries, oxidation states, and coordination numbers [11,12]. In light of this, many metal complexes of NSAIDs have been isolated and studied, and their crystal structures have been investigated extensively [13–15].

Nickel has played a vital role in coordination chemistry due to its innate competency in adopting various geometries. It is a trace element

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<https://doi.org/10.1016/j.molstruc.2025.141694>

Received 16 October 2024; Received in revised form 12 January 2025; Accepted 6 February 2025

Available online 9 February 2025

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for many living organisms, and its role in bioinorganic chemistry is intriguing. It is a cofactor for enzymes and is intrinsically involved in various activities in enzymes like urease, hydrogenase, superoxide dismutase, etc. [16–19]. The discovery of nickel as the active center of urease by Zerner in 1975 triggered a paradigm shift in the understanding of the role of nickel in other metalloprotein molecules. This has led to the spur among bioinorganic chemists investigating the paramount ability of nickel in several biological processes [20,21]. Furthermore, the various nickel complexes possessing biological activity have been substantiated in the literature as having efficacy as antitumor antibiotics, anticonvulsants, antiepileptic drugs, or vitamins [22–25]. To decipher the biological evaluation of Ni-complexes, many of them exhibit remarkable potential as antibacterial and anti-fungal [26–28], anti-inflammatory [29], and antioxidant [30–32] have been well documented. Moreover, many Ni(II) compounds are known to function as DNA intercalators [33,34] and DNA cleavage agents [35,36]. These complexes also exhibit efficacious anti-proliferative activity toward diverse cell lines and have been well documented in the literature [37, 38].

Mefenamic acid, (2-[(2,3-dimethylphenyl)amino]benzoic acid) (Hmef) is a derivative of N-aryl anthranilic acid and shares its resemblance with NSAIDs like tolfeamic acid and flufenamic acid. Like many NSAIDs, mefenamic acid binds to cyclooxygenase (COX), thus inhibiting the synthesis of prostaglandins [39]. In the present decade, special attention has been focused on the synthesis, structural characterisation, and biological evaluation of nickel mefenamates with α -diimines like o-phenanthroline, 2,2'-bipyridine by Totta et al. [40] and In another study, Nnabuike et al. have explored the structures of new nickel(II) mefenamate complexes, in the presence of monodentate nitrogen donor ligands [41]. In accordance with the above viewpoint, apart from the biological significance of mefenamic acid, it is well known that the α -diimines like o-phenanthroline, 2,2'-bipyridine, and their derivatives are found to possess profound affinity towards biochemical activities, and the complexes of them have exhibited antiproliferative properties [42,43]. These aspects have been an impetus to researchers in this field to use these nitrogen donor molecules as co-ligands.

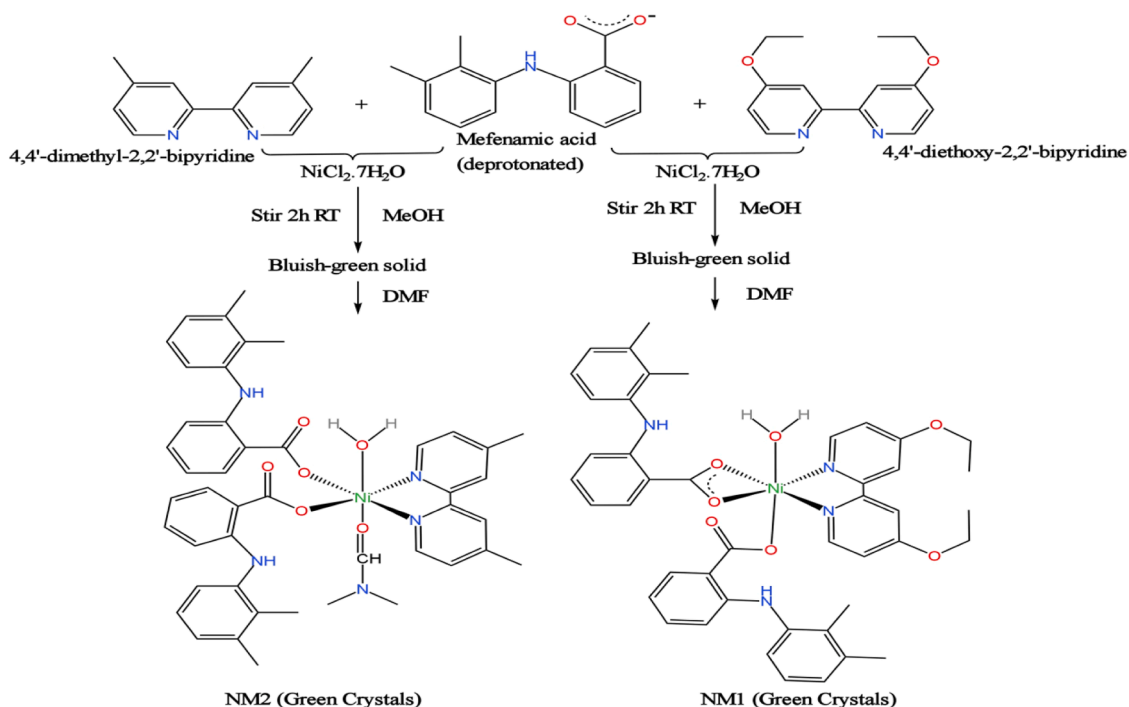
Understanding the insight of the bioinorganic chemistry of nickel(II)

ion with mefenamic acid is crucial in elucidating its role and developing novel therapeutic associated strategies. Such a study explains the importance of a coordination environment and intermolecular interactions, emphasising their structure-function connections and facilitating the design of novel and active metal-based drugs. It can be perceived from the literature that the evaluation of cytotoxicity has been probed mostly on breast cancer cells (MCF-7) and lung cancer cells [44, 45]. In contrast, few studies have been investigated on liver cell lines; with this perspective in consideration, we have centred our studies on probing the cytotoxicity of such complexes for liver cancer HepG2 cell lines and substantiating their biological impact. With this view, herein the present study aimed to design two new Ni(II) complexes (1 and 2) of mefenamic acid co-hosted by nitrogen donor ligands, namely, 4, 4'-diethoxy 2,2'-bipyridine and 4,4'-dimethyl-2,2'-bipyridine (Scheme 1). The new compounds have been characterized by elemental, spectroscopic, and thermal analysis. More importantly, the single crystal structures of $[\text{Ni}(\text{Mef}-\text{O})_2(\text{etobpy})(\text{H}_2\text{O})]$ 1 and $[\text{Ni}(\text{Mef}-\text{O})_2(\text{dmbpy})(\text{H}_2\text{O})]$ 2 are described. The anticancer activity using HepG2 cancer cell lines and antioxidant activity by 1 %DPPH free radical scavenging activity was carried out. Further DNA interaction study was carried out by DNA binding, cleavage, molecular docking and dynamics studies.

2. Experimental details

2.1. Materials and methods

The chemicals and solvents used in this work were obtained commercially and used as received. 4,4'-diethoxy-2,2'-bipyridine was synthesised according to the reported procedure [42]. IR spectra of powdered compounds 1 and 2 were recorded by diluting with KBr on a Shimadzu (IR-Prestige –21) FTIR spectrophotometer in the region 4000–400 cm^{-1} with 4 cm^{-1} resolution. UV–visible spectra were recorded on a Shimadzu UV–Vis spectrophotometer (model-UV-2600). Elemental analysis (C, H, N) was performed on the elementary Variomicrocube CHNS analyser. Thermo-gravimetric analysis (TG-DTA) studies were performed on simultaneous DTA/TG apparatus, DTG-60 00,826



Scheme 1. The synthetic methodology adopted to obtain single crystals of 1(NM1) and 2 (NM2).

SHIMADZU, in a nitrogen atmosphere at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from room temperature to $1000\text{ }^{\circ}\text{C}$. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance X-ray diffractometer using $\text{Cu K}\alpha_1$ ($\lambda = 1.5406\text{ \AA}$) with a Ni filter.

2.2. Synthesis of 1 and 2

A methanolic solution (10 mL) containing Hmef (96 mg, 0.4 mmol) and KOH (22 mg 0.4 mmol) was stirred for one hour at room temperature. The resultant solution was simultaneously added to the methanolic solution (5 mL) of 4,4'-diethoxy-2,2'-bipyridine (49 mg, 0.2 mmol), followed by dropwise addition to a methanolic solution of $\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$ (48 mg, 0.2 mmol). The solution was stirred for around two hours and left for evaporation; the bluish-green microcrystalline powder was formed after a few days. The residue was then dissolved in dimethylformamide (DMF) and left aside for slow evaporation. After two weeks, the green crystals of **1** suitable for single X-ray structure determination were collected, washed with isopropyl alcohol followed by diethyl ether, and air dried. {Yield: 145 mg, 90 %} Anal. Calcd. for $\text{C}_{44}\text{H}_{46}\text{N}_4\text{NiO}_7$ (MW= 801.54 g/mol) (%): C, 65.9; H, 5.7; N, 6.99. Found: C, 65.96; H, 5.91 N, 7.34. IR: ν_{max} , cm^{-1} : 3290 ($\nu(\text{O}-\text{H})$), 1609 ($\nu_{\text{asym}}(\text{C}=\text{O})$), 1570, 1494 $\nu_{\text{sym}}(\text{C}-\text{O})$; 1393 $\nu_{\text{sym}}(\text{C}=\text{O})$, (s) 1293 $\nu_{\text{sym}}(\text{C}-\text{O})$ UV-vis: λ/nm 291.

2 was synthesised by adopting a procedure similar to the synthesis of **1**. A methanolic solution (5 mL) of 4,4'-dimethyl- 2,2'-bipyridine (37 mg, 0.2 mmol) was added instead of 4,4'-diethoxy 2,2' bipyridine in **1**. The solution was stirred for around two hours and left for evaporation; the bluish-green microcrystalline powder was formed after a few days. The residue was then dissolved in dimethyl formamide (DMF), followed by slow evaporation. Green-coloured crystals of **2** suitable for single-crystal X-ray diffraction studies were collected after two weeks, washed with isopropyl alcohol followed by diethyl ether and air dried. {Yield: 151 mg, 92 %}. Anal. Calcd. for $\text{C}_{45}\text{H}_{49}\text{N}_5\text{O}_6$ (MW= 814.58) (%): C, 66.29; H, 6.01 N, 8.59. Found: C, 67.28; H, 6.216; N, 8.65 IR: ν_{max} , cm^{-1} 3253 ($\nu(\text{O}-\text{H})$), 1617 ($\nu_{\text{asym}}(\text{C}=\text{O})$), 1543, 1487 $\nu_{\text{sym}}(\text{C}-\text{O})$; 1282 $\nu_{\text{sym}}(\text{C}=\text{O})$, (s), UV-vis: λ/nm 293. Both compounds are stable in air and soluble in DMSO and DMF.

2.3. Single crystal X-ray data collection and refinement

The single crystal X-ray diffraction data of compounds **1** and **2** were collected at 296 K on Bruker D8 Quest Eco X-ray diffractometer using monochromated $\text{Mo K}\alpha$ ($\lambda = 0.7107\text{ \AA}$) radiation. The integrating, scaling, and absorption correction steps were performed using Bruker's APEX 4 program package (Version 2021.10-0). Absorption corrections were performed using a multiscan method. The structures were solved with SHELXT and subsequent refinements using full-matrix least-squares on F^2 with SHELXL [46,47]. Non-hydrogen atoms were refined anisotropically. All the calculations were done using the WinGX crystallographic software package [48]. All the hydrogen atoms were placed geometrically and refined using a riding model. The crystal parameters and refinement details of compounds **1** and **2** are summarized in Table S1. The checkcif report of **1** and **2** is shown in supporting material.

2.4. Anticancer activity

The anticancer activity of **1** and **2** compounds was determined by 3-(4, 5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT) colorimetric assay [36]. Briefly, the enzymatic reduction of yellow MTT to an insoluble purple-coloured formazan by viable cells was measured after the reaction assay. HepG2 and normal liver cell lines were used for this study. The cell lines were cultured in Dulbecco's modified Eagle medium with low glucose (Gibco, Invitrogen) supplemented with 10 % Foetal Bovine Serum (FBS) (Gibco, Invitrogen) and Antimycotic 100X solution (Thermofisher Scientific). The cells were seeded in a 96-well flat-bottom microplate and maintained at $37\text{ }^{\circ}\text{C}$ in 95 % humidity and

5 % CO_2 overnight. Different concentrations (100, 50, 25, 12.5, 6.25, 3.125 $\mu\text{g/ml}$) of each **1** and **2** were treated separately with cells for 48 h. The wells were washed twice with PBS, 20 μL of the MTT staining solution was added to each well, and the plate was incubated at $37\text{ }^{\circ}\text{C}$. After 4 h, 100 μL of DMSO was added to each well to dissolve the formazan crystals, and absorbance was recorded with a 570 nm using a microplate reader. Untreated cells with media and *cis*-platin were maintained as a negative and positive control, respectively. The experiment was carried out in triplicates, and cell viability relative to untreated cells was determined using Eq. (1).

$$\text{Surviving cells (\%)} = \text{Mean OD of test compound} / \text{mean OD of negative control} \times 100 \quad (1)$$

2.5. Antioxidant activity

The *invitro* antioxidant potential of compounds **1** and **2** was determined by % DPPH (1,1-diphenyl-2-picrylhydrazyl) free radical scavenging activity [65]. 1 mL of various concentrations (10, 20, 40, 60, 80 μM) of compounds were added to 2 mL DPPH reagent (0.1 mM in methanol). The reaction mixture was mixed thoroughly and incubated in the dark for 30 min at room temperature. Ascorbic acid was used as the standard antioxidant and respective solvent (DMSO for compounds and distilled water for ascorbic acid) as control. The absorbance was recorded at 517 nm. The experiments were performed in triplicate and the data are expressed as mean $\pm$ standard deviation (SD).

The antioxidant activity of the synthesized compounds was calculated based on the percentage of DPPH radical scavenged using Eq. (2).

$$\text{DPPH free radical scavenging (\%)} = \left[\frac{(\text{Ac} - \text{As})}{\text{Ac}} \right] \times 100 \quad (2)$$

where Ac = absorbance of the control reaction mixture, As = absorbance of the test

2.6. DNA binding studies

The DNA binding studies were performed for compounds **1** and **2** by UV-visible spectroscopy as described by Jayaseelan et al. [66]. Briefly, the concentration of calf-thymus (CT) DNA was calculated from its known extinction coefficient at 260 nm ($6600\text{ M}^{-1}\text{ cm}^{-1}$) [67]. Further, varied concentrations of calf-thymus (CT) DNA prepared with Tris-HCl/NaCl buffer (50 mM Tris-HCl/1 mM NaCl buffer, pH 7.5) (20, 40, 60, 80 μM) was mixed with the solution of compounds **1** and **2**. After the addition of DNA to the metal complexes **1** and **2**, the resulting solution was allowed to equilibrate at $27\text{ }^{\circ}\text{C}$ for 20 min, after which absorption readings were noted.

2.7. DNA cleavage activity

DNA cleavage activity of the **1** and **2** complexes was determined according to Banerjee et al. [49] with modification. Briefly, the supercoiled pBR322 (200 ng) artificial plasmid DNA was treated separately with prepared **1** and **2** complexes (10, 20, 40, and 80 μM) in Tris buffer (5 mM *tris*-HCl, 50 mM NaCl, pH = 7.2) to yield a total volume of 10 μL and then incubated in the dark for 1 h at $37\text{ }^{\circ}\text{C}$. The reaction was quenched by adding 3 μL loading buffer, and then the resulting solutions were loaded on a 1 % agarose gel. Electrophoresis was carried out at 80 V for 1 h in TAE buffer (pH = 8.0). The DNA bands were visualised under UV light and observed for band intensities and fragmentation patterns in the absence and presence of the complex. The results were expressed qualitatively based on supercoiled (SC) (*Form I*), nicked circular (NC) (*Form II*), and linear (L) (*Form III*) forms of DNA.

2.8. Computational studies (molecular docking and molecular dynamic studies)

Crystal structures of **1** and **2** were prepared using *OpenBabel* (v. 3.1.1) [50], assigning Electronegativity Equalization Method (EEM) atomic partial charges to the complexes [51]. Subsequently, the complexes were docked using *AutoDock-Vina* (v. 1.2.5) [52] into the major groove of the crystal structure B-DNA dodecamer fragment [53]. The top-ranking poses for complexes **1** and **2** were prepared for Molecular Dynamics Simulations for a prolonged period of 100 ns using *Desmond* (v. 7.2) [54]. The interactions between the **1/2** complexes and DNA fragments were analyzed using *Maestro* (v. 13.4). The detailed computational studies are in line with the reference quoted [55].

2.9. Evaluation of stability of compounds

The stability study of compounds **1–2** was performed by UV-visible spectroscopy [68]. The compounds were assessed for their stability at varied pH (4, 5, 6, 7, and 8) and temperature (4, 27, 37 and 50 °C) conditions. The pH was maintained constant (pH 7), and the temperatures were varied for the determination of the stability of compounds for 24 h. For determining the stability of compounds at pH variations, a constant temperature of 27 °C was maintained for 24 h. The biological activities performed in this study, like the DNA cleavage, anticancer studies and others, were performed at temperatures of 27 and 37 °C and 5–7.5 pH. Also, 4 °C was evaluated to check the stability of compounds. The stability of compounds at a temperature of 50 °C was evaluated to check for their stability at higher temperatures. Similarly, pH 4 and 8 were assessed to check their stability at acidic and basic conditions. Thus, these criteria were followed for stability testing of compounds **1–2**.

3. Results and discussion

3.1. Synthetic details for **1** and **2**

Both compounds **1** and **2** were synthesized in high yields via aerobic reaction of deprotonated mefenamic acid with N, N' donor substituted α -diimines namely 4,4'-diethoxy-2,2'-bipyridine and 4,4'-dimethyl-2,2'-bipyridine and $\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$ in methanol with 2:1:1 stoichiometry (Scheme 1)

3.2. Spectroscopic characterization

3.2.1. Infrared and UV-Vis spectroscopy

Infrared spectra of the **1** and **2** compounds are depicted in (Fig. S1). The IR spectra of the complexes revealed the binding modes of the mefenamato ligand. An absorption band at $\sim 3370 \text{ cm}^{-1}$ seen in free mefenamic acid is attributed to O—H stretching vibration. This peak is expected to vanish in the complexes due to deprotonation of the carboxylic acid group and, thereafter, binding of the carboxylate group to the nickel ion. The bands at 3282 and 3253 cm^{-1} for **1** and **2**, respectively, are observed for the O—H vibrations of water molecules. The bands at 1650 cm^{-1} and 1255 cm^{-1} are attributed to the stretching frequency of C = O and C—O, respectively, of the mefenamic group [56]. These values are shifted in the IR spectrum of both the compounds to 1609 and 1570 cm^{-1} and 1494 and 1293 cm^{-1} for **1** and 1617 and 1543 cm^{-1} , 1487 and 1282 cm^{-1} in **2**, these signatures are assigned to asymmetric and symmetric stretching respectively [40]. The stretching modes of both complexes are not identical as the binding mode in **1** is different from that in **2**, which is consistent with the X-ray crystallographic investigations. UV-visible spectra of **1** and **2** in DMSO exhibited similar bands, thus suggesting retention of their structures in solution. The bands at 291 and 293 cm^{-1} in **1** and **2**, respectively, are ascribed to π - π^* and n - π^* transitions of the mefenamato ligand [44] (Fig. S2).

3.3. TG-DTA studies of **1** and **2**

The thermal stability of **1** and **2** was investigated using TG analysis under the nitrogen atmosphere (Fig. S3a and b). A mass loss of 2.5 % at ~ 100 °C in the thermogram of **1** is assigned to the loss of water molecules accompanied by an endothermic peak in DTA. Thereafter, the complex starts melting; the melting point of 4,4'-diethoxy-2,2'-bipyridine is around 124 °C seen in the broad endo peak merged with that of water. The significant mass loss of 67 % in one step is attributed to the loss of two mefenamic acid molecules, and thereafter, the concomitant loss of the co-ligand 4,4'-diethoxy-2,2'-bipyridine is ascertained by the sharp endothermic event at 346 °C and an exothermic event at 370 °C. The expected mass loss differs marginally from the experimental mass loss observed, indicating that the final phase formed may differ entirely from NiO. In the thermal profile of **2**, the initial mass loss of 2.4 % indicates the coordinated water molecule, which is supported by the endo event at around 100 °C. Thereafter, the mass loss of 6.68 % is attributed to the elimination of dimethyl formamide coordinated to nickel, and consecutively, the mass loss of 64.54 % is indicative of the loss of two mefenamic acids and concomitant loss of the co-ligand 4,4'-dimethyl-2,2'-bipyridine. The expected mass loss of 90.7 % is well in agreement with the experimental mass loss of 90.4 %, which indicates that the phase formed is of NiO [44,57,58].

3.4. Description of crystal structures of **1** and **2**

Single-crystal X-ray diffraction analysis of **1** revealed its crystallization in the monoclinic $P2_1/n$ space group. The asymmetric unit is built from one crystallographically independent Ni(II) ion, two unique mefenamato (mef) ligands, one unique 4,4'-diethoxy-2,2'-bipyridine ligand, and a coordinated water molecule (Fig. 1). Each Ni(II) ion adopts a distorted octahedral coordination geometry. The (etobpy) ligand contributes two nitrogen atoms for biding in bidentate chelate mode with a bite angle of 78.88° ; one of the nitrogen coordinates at the equatorial site (N1) while the other (N2) binds at the axial position. A coordinated aqua molecule (O1 W) occupies the other axial site. The remaining equatorial sites are occupied by the oxygen atoms (O3–O5) of the mef ligands, thus completing the *cis*-NiO4N2 coordination environment. Both mefenamato ligands adopt different coordination modes; one mef ligand exhibits a bidentate chelating type of coordination mode with an O—O bite angle of 62.41° while the other mef ligand exhibits a simple monodentate coordinated mode with the Ni(II) ion as shown in (Fig. S4). The average Ni–N lies at $2.0547 \text{ \AA}$, while the Ni–O bond lengths due to chelating mef ligand lie at $2.1127 \text{ \AA}$, which is slightly longer than the mef ligand coordinating via monodentate mode (Ni–O bond length $2.0388 (12) \text{ \AA}$) as shown in Table S2. The bond lengths and angles are in good agreement with related Ni(II) complexes reported in the literature [14,40,41]. The mefenamic acid and related compounds are conformationally flexible molecules with different conformers. The molecules can exhibit rotation over the $\text{C}_{\text{ar}}\text{--N}$ bond (where the carbon belongs to the benzene ring carrying the methyl substitutes) more freely than the rotation over the $\text{C}_{\text{ar}}\text{--N}$ and $\text{C}_{\text{ar}}\text{--C}_{\text{ar}}$ (where the carbons belong to the benzene ring carrying the carboxylate group). The rotation over the latter bonds is hindered due to the intramolecular hydrogen bonds between the N—H and oxygen of the carboxylate group [59]. The mef moieties are non-planar, as is evident from their torsion angle. The torsion angle measured from the chelating mef unit (C21 N3 C22 C27) is -71.80° while that from the monodentate mef unit is -66.60° (C36 N4 C37 C42), thus attaining the most stable conformer.

An interplay of non-covalent interactions such as O—H $\cdots$ O, N—H $\cdots$ O, and C—H $\cdots$ O type hydrogen bonds results in the stabilization of the crystal lattice. The analysis of the structure revealed that each molecule interacts with the neighbouring molecule via O—H $\cdots$ O interaction between the oxygen atom of the coordinated aqua molecule (donor atom) and the uncoordinated oxygen atom (O4) of the mef ligand (acceptor atom). This unit is further extended along *a* axes with the aid

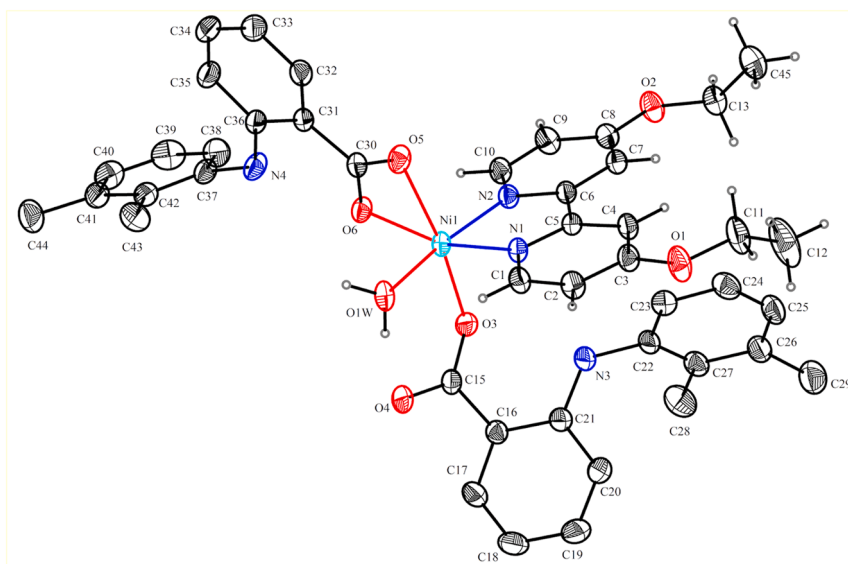


Fig. 1. The crystal structure of compound $[\text{Ni}(\text{mef})_2(\text{etobpy})(\text{H}_2\text{O})]$ **1** reveals the thermal ellipsoid plot drawn at 30 % probability for all the non-hydrogen atoms. The hydrogens are shown as spheres of arbitrary radii. The hydrogen atoms of the (etobpy) ligands have been removed for clarity purposes.

of C7-H7...O5 type of interaction, resulting in the formation of a dimensional supramolecular chain structure as depicted in (Fig. 2). The hydrogen bonding parameters for compound **1** are summarized in Table S3. Within the chain, the molecules also exhibit π - π stacking interactions due to aromatic rings originating from the mef and diamine ligands. (Fig. S5) shows the interaction between the two aromatic rings of the bipyridine derivative. The distance between the centroid of one aromatic ring of 4,4'-diethoxy-2,2'-bipyridine ligand and the closet centroid of another ring is 3.741 Å, as observed in the cases of similar compounds [15,40].

Compound **2** crystallizes in a Triclinic crystal system with $P\bar{1}$ space group. The asymmetric unit consists of one unique Ni(II) ion, one N-donor ligand, 4,4'-dimethyl-2,2'-bipyridine, two unique mef ligands, one coordinated aqua molecule, and one coordinated solvent molecule, N, N'-dimethylformamide (DMF) depicted in (Fig. 3). The Ni(II) ion also adopts a distorted octahedral coordination geometry. The 4,4'-dimethyl-2,2'-bipyridine ligand adopts a bidentate chelate mode with a bite angle of 78.65° and contributes two nitrogen atoms (N1, N2) to the coordination at the equatorial sites. The other two equatorial sites are occupied by two oxygen atoms (O2 and O4), each contributed by the carboxylate group of the mef ligand. Both the mef moieties in **2** adopt the monodentate coordination mode. One of the axial positions is occupied by the coordinated aqua molecule (O1 W). In contrast, the other is occupied by an oxygen atom (O1) contributed by the DMF solvent molecule, thus completing the NiN_2O_4 shown in (Fig. S6). The average Ni-N lies at 2.0706 Å, while the Ni-O bond lengths range from 2.0396 (12) Å to 2.1318 (13) Å. The distortion in the octahedron is visible from the bond

distances, wherein the Ni-O bond formed by the mef ligands is shorter than the bond formed by the aqua and DMF molecules, as shown in Table S2. The non-planarity of the two mef moieties is evident from the torsion angles, where one exhibits a torsion angle of (C37 N5 C38 C44) $112.9(3)^\circ$ while the other shows an angle of $123.2(2)^\circ$ (C22 N4 C23 C29).

The structural analysis reveals that each molecule interacts with the neighbouring molecule via non-covalent interactions. A total of ten hydrogen bonding interactions were identified, nine of which are intramolecular hydrogen bonds and one inter-molecular hydrogen bond. The hydrogen bonding parameters are summarized in Table S3. The inter-molecular bond between two molecules via the donor atom of the diamine ligand (C8) and the acceptor atom (O1 W) of the aqua ligand is depicted in (Fig. S7). This unit is further interacted by π - π stacking interaction between the aromatic rings of the mef ligands to form the supramolecular network, thereby stabilizing the crystal lattice.

3.5. Powder X-ray diffraction (PXRD)

Both compounds **1** and **2** were characterized by PXRD to prove the phase purity of the bulk and single crystals. The experimental PXRD patterns of **1** and **2** were compared with their stimulated PXRD patterns obtained from single crystal structure data using Mercury software (Figs. S8 and S9). Both stimulated and experimental patterns on overlapping were found to match exactly, suggesting the same phase in bulk and single crystals.

4. Biological evaluation

4.1. Anticancer studies of **1** and **2**

As seen in (Fig. 4), **1** and **2** complexes showed significant dose-dependent anticancer activity towards cancerous HepG2 cells. In comparison with *cis*-platin at 100 $\mu\text{g/mL}$, interestingly, $4.95 \pm 0.09\%$ and $19.1 \pm 0.10\%$ cell viability was observed for **1** and **2**, respectively, against HepG2. Overall, the anticancer effect on HepG2 cell lines by **1** was more significant than **2**, with more than 85 and 95 % cell viability at 3.12 $\mu\text{g/mL}$. It is important to note that *cis*-platin and **1** at 25 $\mu\text{g/mL}$ exhibited similar per cent cell survival, indicating the efficacy of the prepared complex contributing towards significant anticancer properties. The difference in the anticancer activity at different dose-

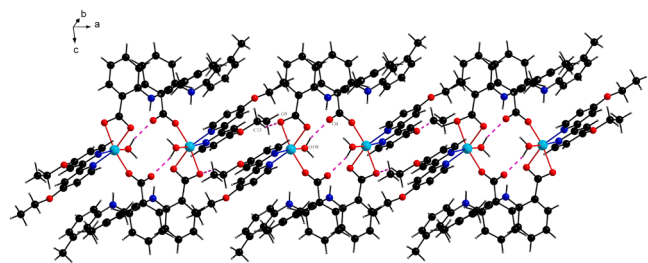


Fig. 2. View of the crystal structure of **1** showing the extension of the supramolecular chain along the *a* axes. (Symmetry code *i* = 1-*x*, 1-*y*, 1-*z*, *ii* = 2-*x*, 1-*y*, 1-*z*).

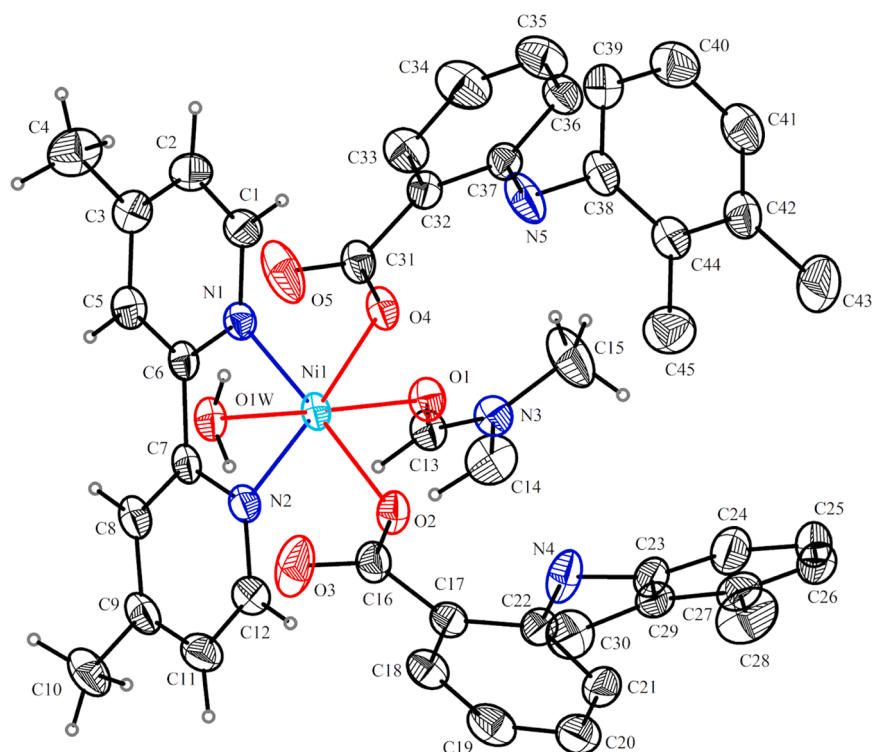


Fig. 3. The crystal structure of compound $[\text{Ni}(\text{mef})_2(\text{dmbpy})(\text{H}_2\text{O})(\text{DMF})]$ **2** reveals the thermal ellipsoid plot drawn at 30 % probability for all the non-hydrogen atoms. The hydrogens are shown as spheres of arbitrary radii. The hydrogen atoms of the mef ligand have been removed for clarity purposes.

concentration is related to the presence of 4,4'-diethoxy 2,2'-bipyridine in **1** and 4,4'-dimethyl-2,2'-bipyridine and N, N'-dimethylformamide in **2**. Previously, the presence of diimine co-ligands like 4,4'-bis(alkyl)-2,2'-bipyridine along with coordination to platinum complexes are known to enhance the anticancer activity [42,70]. Concerning N, N'-dimethylformamide, dose-dependent effects of DMF on apoptosis and proliferation in nontumorous MCF-12A cells and breast cancer MCF-7 is reported. At high concentrations (100 mM), DMF inhibited MCF-7 cell growth while at a low dose (1 mM) stimulated the growth [73]. In the present study, the additional co-ligand DMF in **2** at lower concentrations may be less effective on cancer HepG2 cells. Further, the anticancer effect of synthesised complexes on HepG2 was monitored by light microscopy (Fig. 4). As seen in the negative control (untreated), the cells were abundant, dense, and highly confluent. After treatment with complexes with increasing concentration, the proliferation of cells was inhibited, resulting in less dense cells and abundance. Also, the cells become circularised, resulting in shrinkage from the tapering ends, which leads to a decrease in adherence of the cells. Similar morphological alterations in HepG2 have been reported recently for dinuclear nickel compound stabilised by vanillin and acetate bridging ligands [37]. Also, nickel with Schiff base vanillin-4-methyl-4-phenyl-3-thosemicarbazone complex showed a similar effect on the morphology of Hela cells [60].

Furthermore, an IC_{50} value of $4.33 \pm 0.02 \mu\text{g/mL}$ was observed for **1** against HepG2 in comparison with an IC_{50} value of $2.23 \pm 0.02 \mu\text{g/mL}$ for Cisplatin. This shows that the significant effect of **1** on the cancerous cells is comparable to cis-platin. However, the IC_{50} value of $47.1 \pm 0.10 \mu\text{g/mL}$ was observed for **2** against HepG2. The comparable IC_{50} values of **1** and cis-platin was related to the structure-activity relationship. The synthesised compounds were considered as cis-platin analogues that utilise the nitrogen donors, diimine [4,4'-diethoxy 2,2'-bipyridine in **1** and 4,4'-dimethyl-2,2'-bipyridine in **2**] in place of the ammonia in cisplatin. In addition, the coordination of these co-ligands to Ni(II) ion and mefenamic acid stimulated anticancer activity. Such structure-activity relationship is observed between synthesised $[\text{PtCl}_2(4,4'$ -

dialkoxy-2,2'-bipyridine)] and cis-platin. Further, their study highlighted increased activity with an increased carbon chain length of the alkyl groups [42]. Kumar et al. [60] reported an IC_{50} value of $54.3 \pm 1.7 \mu\text{g/mL}$ for nickel with Schiff base vanillin-4-methyl-4-phenyl-3-thosemicarbazone complex against Hela cells. Although **2** showed a high IC_{50} value, its activity is shown to increase in a dose-dependent manner, resulting in the inhibition of cell proliferation. Although various studies are reported on cytotoxicity and DNA binding activities of nickel(II) complexes [61], the effect of mefenamic acid in conjugation with ligands like diamine-like 4,4'-dimethyl-2,2'-bipyridine and 4,4'-diethoxy-2,2'-bipyridine on cancer cells are rarely reported. Previously, the mefenamic acid with nickel metal complex exhibited anti-proliferative activity against MCF-7, T24, and I-929 cancer cell lines [13]. The variations in the cytotoxic effects of the different metal complexes with non-steroidal drugs are attributed to the existence of different nitrogen donor ligands contributing to uplifting the biological performance of the complexes [44]. A recent report highlighted the applicability of nickel(II) complexes linked to vanillin with an IC_{50} value of $22.82 \pm 0.09 \mu\text{g/mL}$ against HepG2 cancer cell lines, indicating its anticancer potential [37].

4.2. Antioxidant activity by % DPPH free radical scavenging activity

The synthesised complexes depicted very good % DPPH free radical scavenging activity, wherein **NM1** exhibited a maximum of 94.78 ± 0.82 % DPPH free radical scavenging activity than **NM2** 88.15 ± 1.02 % at 80 μM concentration (Fig. S10 and Table 1). In addition, **1** and **2** showed an IC_{50} values of $17.02 \pm 0.85 \mu\text{M}$ and $19.89 \pm 0.73 \mu\text{M}$ which was comparable to the IC_{50} value of ascorbic acid ($14.38 \pm 0.64 \mu\text{M}$). X Totta et al. reported DPPH scavenging activity of nickel mefenamic acid and nitrogen donor ligand complexes in the range of (7.42–13.03 %) at 0.1 mM concentration [40].

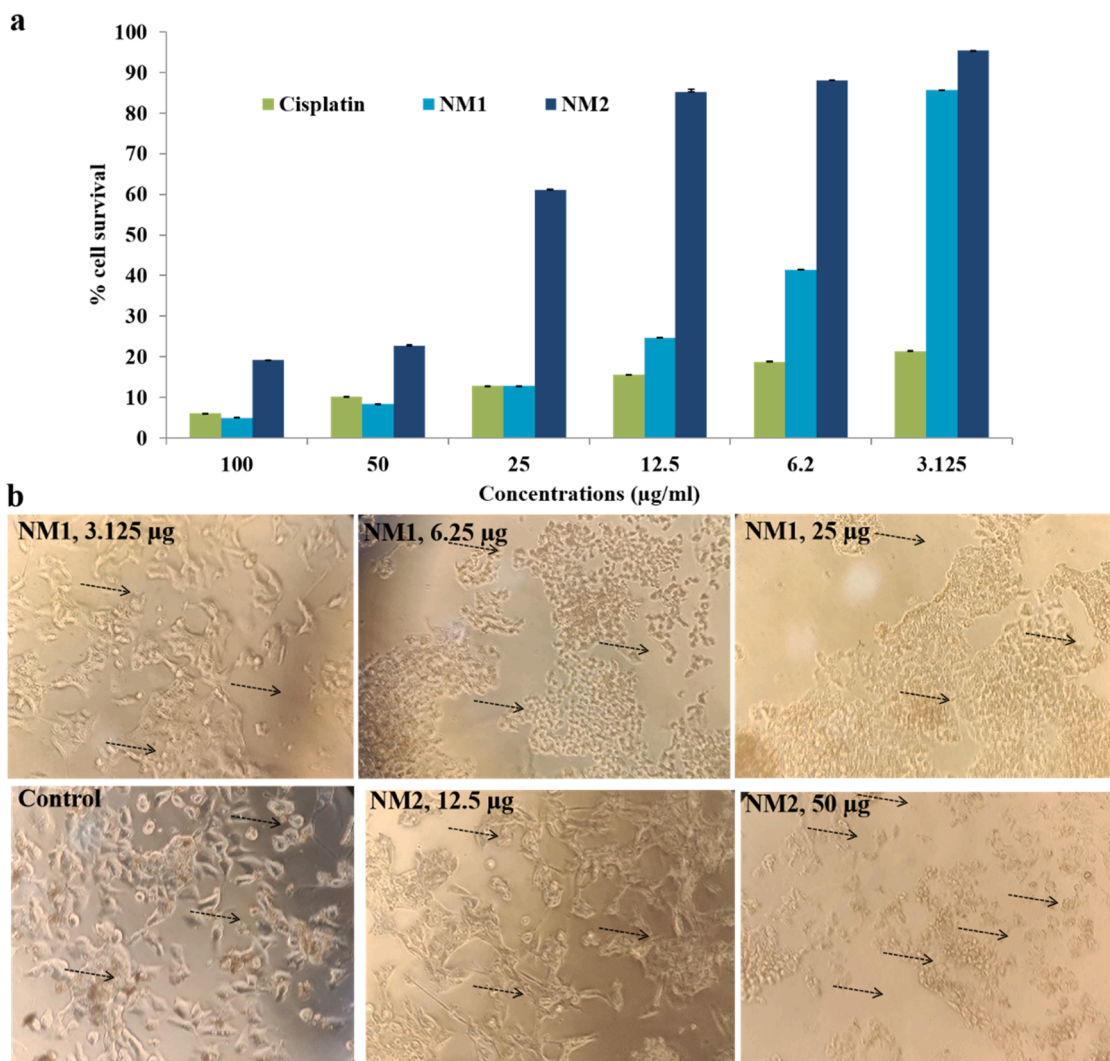


Fig. 4. Anticancer studies of 1(NM1) and 2(NM2) against HepG2 cancerous cells. a) Percent cell survival of HepG2 via the dose-dependent anti-proliferative activity of 1 and 2; b) Microscopic images of HepG2 cells: Cells treated separately with 1 (3.25, 6.25 and 25 µg/mL) and 2 (12.5 and 50 µg/mL); control cells without 1 and 2 treatment.

Table 1

Antioxidant activity of compounds NM1 and NM2 by % DPPH free radical scavenging activity.

Concentration (µM)	% DPPH free radical scavenging activity		
	NM1	NM 2	Ascorbic acid
10	47.45±0.41	41.34±0.53	58.78±1.05
20	58.76±0.78	50.26±0.51	69.56±0.38
40	72.87±0.49	62.77±0.67	80.56±0.69
60	85.56±0.77	76.89±0.19	92.65±0.27
80	94.78±0.82	88.15±1.02	99.98±0.89
IC ₅₀ value (µM)	17.02±0.85	19.89±0.73	14.38±0.64

Values are expressed as mean ± SD, *n* = 3.

4.3. DNA binding studies

The changes in the spectra of the compounds in the presence of increasing CT-DNA concentration are widely employed to study the

interaction of the metal complexes with DNA. The absorbance spectra of complexes 1 and 2 in the presence and absence of the CT-DNA are shown in Fig. 5. The intercalative binding mode of the complexes with the DNA is usually associated with hypochromic and bathochromic shifts due to their stacking interactions [69]. Furthermore, the hypochromic shift is particularly attributed to the strength of such binding [67]. In complexes 1 and 2, the absorption intensity is seen decreasing (hypochromism) upon the addition of increasing concentration of CT-DNA to the complexes, suggesting an intercalating binding between the complexes and the DNA.

4.4. DNA cleavage activity of 1 and 2

Direct activity of 1 and 2 on disruption and cleavage of DNA was monitored by the appearance of nicked circular form II or the linear form III due to single and double-strand break, respectively, from highly supercoiled circular plasmid DNA (form I). Fig. 6 depicts the differential electrophoresis pattern of cleavage of pBR322 DNA. It is clear that both

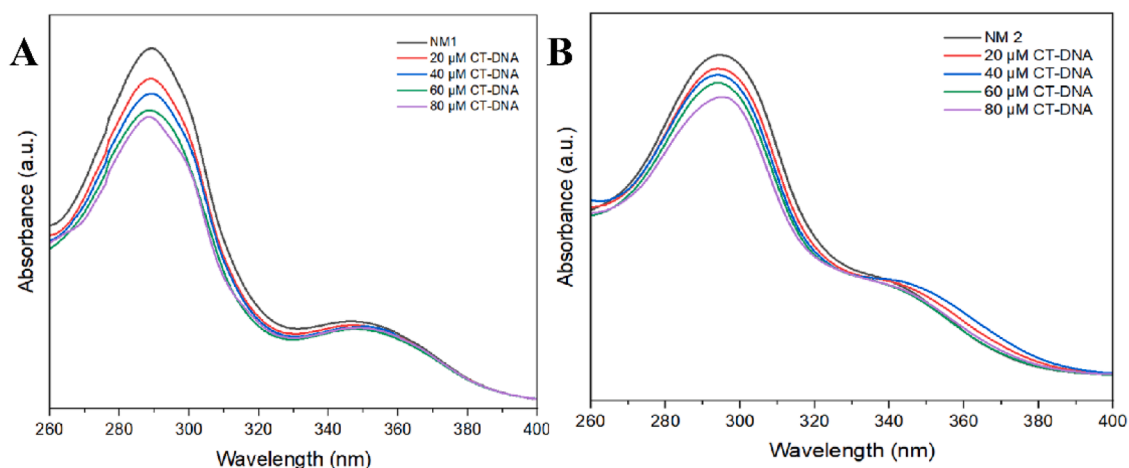


Fig. 5. Absorption spectra of compounds 1 (A) and 2 (B) in the presence and absence of varying CT-DNA concentrations (20, 40, 60, 80 μM).

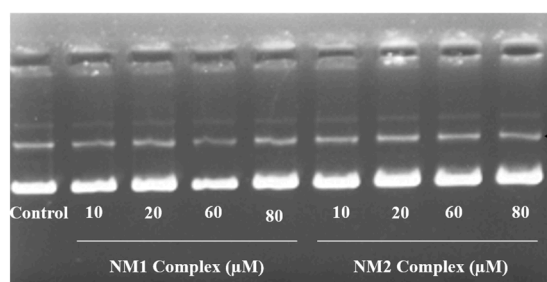


Fig. 6. Plasmid DNA pBR322 cleavage assay employing 1(NM1) and 2(NM2) at 10, 20, 60, and 80 μM concentrations.

1 and 2 showed a dose-dependent rise in *Forms II* and *III*. Further, as seen in the gel electropherogram, DNA cleavage is very prominent and observed as diffused *Form I* for 80 μM concentrations of 1 and 2. However, for control, the least diffusion fluorescence intensity bands of *Form I*, *II*, and *III* were seen than tested complexes. Also, an increase in the fluorescence intensity of the DNA bands was observed with increasing concentrations of 1 and 2, which were tested for DNA cleavage activity. A dinuclear compound of nickel with vanillin and acetate as a bridging ligand showed maximum DNA cleavage activity at 80 μM [37]. Generally, hydrolysis of phosphodiester bonds in the nucleic acid (reversible reaction) or oxidation of sugar/nitrogenous base by ROS (irreversible reaction) are responsible for DNA cleavage activity. Further, complexes or compounds having metal centers such as zinc, cobalt and copper with Lewis acidity are mostly reported to cleave nucleic acids via hydrolytic reaction [71]. For instance, Simunkova and co-workers documented hydrolytic cleavage of pBSK DNA by Cu (II) complexes containing mixed ligands of phen and NSAID drugs consisting of flufenamic, mefenamic, tolafenamic acid as redox-cycling functional moieties [72]. Concerning, cleavage of PBR322 DNA, generation of free radicals and hydrolysis of phosphodiester bonds in DNA is reported for several ligand and complexes of copper [37,50,62–64].

4.5. Molecular docking and molecular dynamics studies results

To get insightful information on the interactions of 1 and 2 with DNA, we performed Molecular Docking and Molecular Dynamics

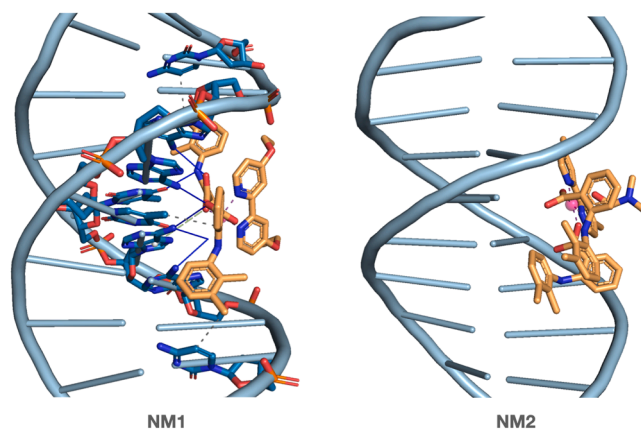


Fig. 7. Intercalating interactions were determined by docking 1 (NM1) and 2 (NM2) compounds with B-DNA dodecamer.

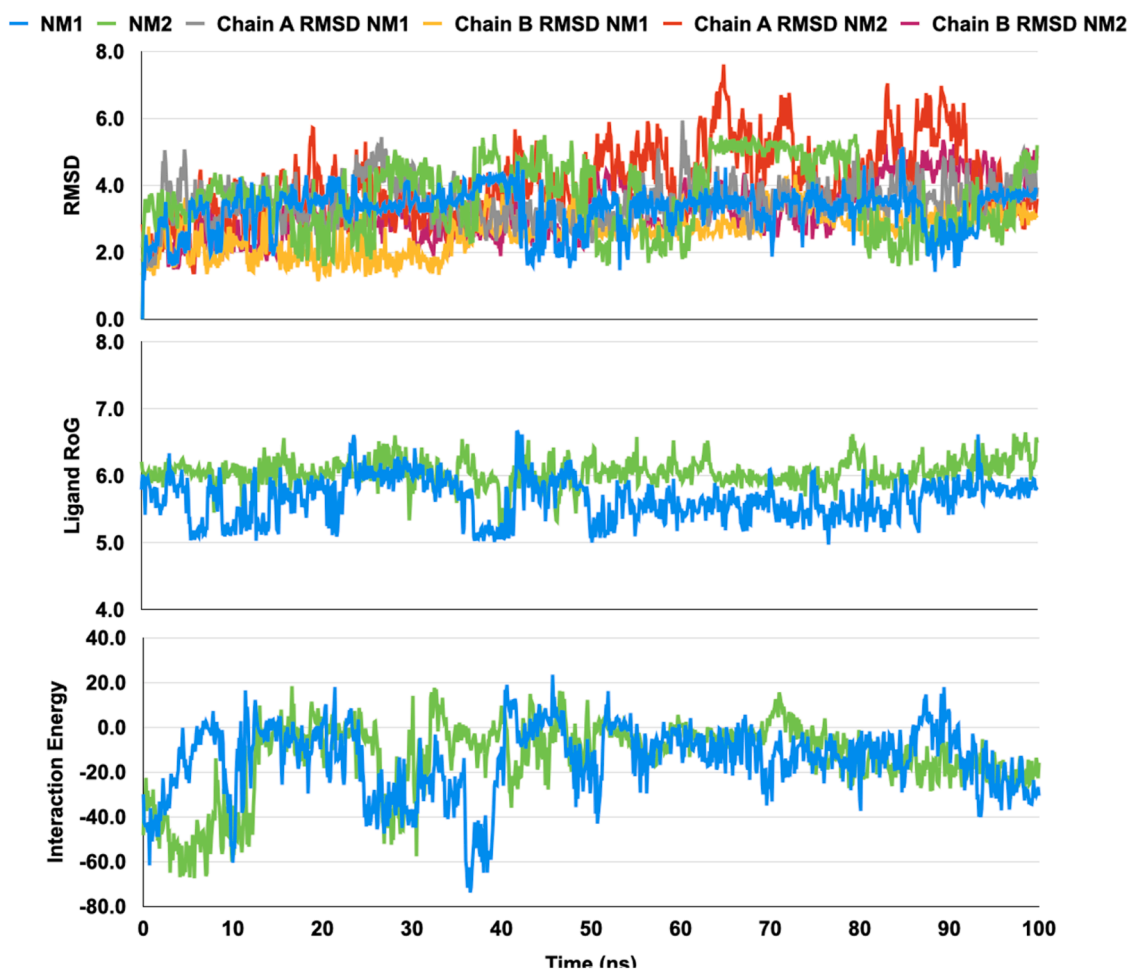
studies. The docking studies reveal that 1 and 2 intercalate with the DNA fragment at the major groove, interacting with the DNA bases as depicted in Fig. 7. The stability of the intercalated DNA-NM complexes was tested using molecular dynamics simulations over 100 ns. Subsequent analysis of the trajectories in terms of RMSD and RoG and Interactions Energies validate the stability of the DNA-NM complexes, which were calculated over 1000 frames captured during simulation, are depicted in Table 2 and Fig. 8. The RMSD fluctuation in the DNA indicates the intercalation of the NM complexes at the major groove has the potential to destabilize the DNA. The interaction energies indicate the strength of the DNA-NM complexes over a period of time.

4.6. Stability studies of compounds 1–2

The compounds 1–2 were evaluated for their stability at varied pH (4, 5, 6, 7 and 8) and temperature (4, 27, 37 and 50 $^{\circ}\text{C}$) conditions by UV-visible spectroscopy. It was observed that compounds 1–2 were stable at all the assessed pH and temperature conditions as a single peak showing intense signal at 291 nm and 293 nm for 1 and 2, respectively, was observed for the compounds with varied conditions (Fig. 9). As the compounds assessed were found to be stable at the tested temperature

Table 2Analysis of molecular dynamics simulations of B-DNA dodecamer in complex with **1** and **2** complexes.

	Interaction Energies (Kcal/mol)		Radius of Gyration (Å)		RMSD (Å)					
	1	2	1	2	Chain A (1)	Chain B (1)	Chain A (2)	Chain B (2)	1	2
Min	73.8	67.5	5.0	5.2	1.5	1.1	1.3	1.4	0.0	0.0
Max	23.5	18.4	6.7	6.6	5.9	4.3	7.6	5.4	5.2	5.5
Average	14.8	13.6	5.7	6.1	3.5	2.6	4.1	3.2	3.3	3.7
SD	15.7	16.5	0.3	0.2	0.6	0.6	1.1	0.8	0.6	1.0

**Fig. 8.** Analysis of molecular dynamics simulations of B-DNA dodecamer with **1** (NM1) and **2** (NM2).

and pH conditions, it can be concluded that the efficiency of their biological activities will not get affected depending upon the physiological conditions of the tests.

5. Conclusions

Two novel compounds of nickel(II) **1** and **2** have been synthesised for the first time and fully characterised by single crystal X-ray diffraction technique and spectroscopic studies. Crystal structures suggested that both are non-isostructural and, thus, differed in viable efficiency in their applications described in the work. In compound **1**, mefenamic acid

exhibits monodentate and bidentate modes of chelation, while in **2**, both the mefenamate molecules coordinate to Ni(II) *via* monodentate ligation. Thermal studies showed both compounds are stable up to 175 °C and above that organic moieties decompose and get eliminated from the compounds to produce oxide of Nickel at 900 °C. Anti-cancer studies and DNA interaction revealed the potential ability of **1** and **2** to be promising candidates for anti-tumour agents in biomedical applications. The complexes **1** and **2** also showed DPPH free radical scavenging efficiency and thus were found to be very good antioxidative agents. DNA binding studies revealed the intercalative mode of **1** and **2** for binding to DNA. The complexes **1** and **2** were also able to undergo DNA cleavage.

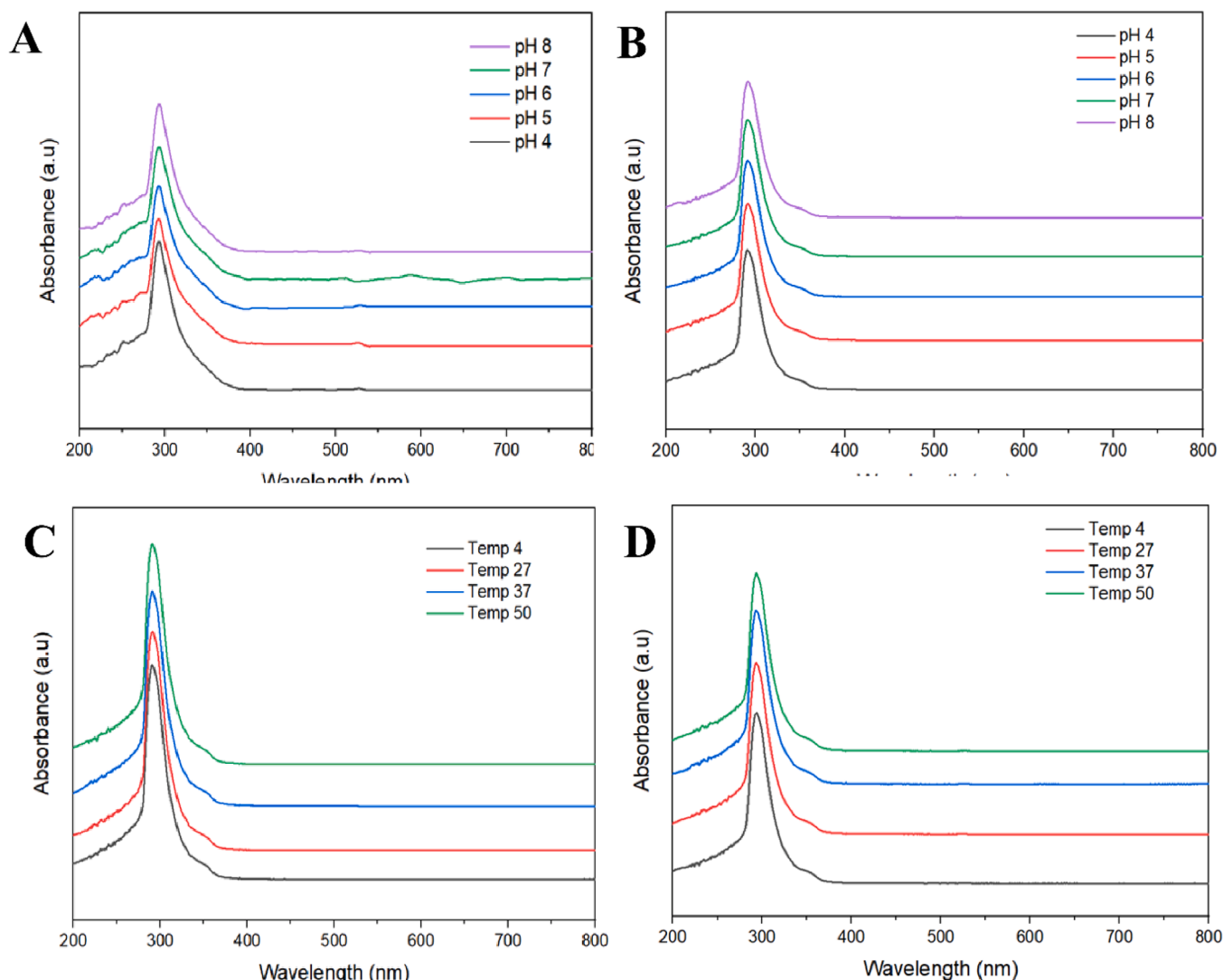


Fig. 9. Stability study of compounds **1** and **2** at varied pH and temperature conditions: (A, B) depicts UV–Vis spectra of compounds **1** and **2** respectively with pH variations (pH 4, 5, 6, 7, 8); (C, D) depicts UV–Vis spectra of compounds **1** and **2** respectively with temperature variations (4, 27, 37, 50 °C).

Further, the docking and molecular dynamics studies helped to understand the interactions of the **1** and **2** complexes with the DNA fragment to conclude that these compounds could intercalate in the major groove of the DNA fragment and thereby destabilize the double helix, thus proving effective potential for anti-cancer activity and DNA interaction.

Ethics approval and consent to participate

Ethics approval and consent to participate are not applicable as the data is obtained from Maratha Mandal's Central Research Laboratory, for which due acknowledgement is made.

Consent for publication

Not applicable.

Funding

School of Chemical Sciences, Goa University was financially supported by the Department of Science and Technology, New Delhi, India, under the FIST program (No. SR/FST/CSII-034/2014(C)). School of Chemical Sciences was also supported by the University Grants Commission, New Delhi, India, under the SAP program (No. F.504/14/DSA-

I/2015). BKV was financially supported through DST-Goa, India grant No.6-331-2018/S&T-DIR/302.

CRedit authorship contribution statement

Beena K. Vernekar: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Nikita N. Harmalkar:** Writing – review & editing, Writing – original draft, Visualization, Software, Formal analysis, Data curation. **Sanket K. Gaonkar:** Writing – review & editing, Writing – original draft, Validation, Resources, Investigation, Formal analysis, Data curation, Conceptualization. **Delicia A. Barretto:** Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Deepika Maliwal:** Software, Formal analysis. **Raghuvir R. Pissurlenkar:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Methodology, Investigation, Data curation, Conceptualization. **Pradip K. Bhowmik:** Writing – review & editing, Writing – original draft, Resources, Methodology, Investigation. **Sunder N. Dhuri:** Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

B.K.V acknowledges the Department of Science and Technology – Waste Management Goa for grant No. 6-331-2018/S&T-DIR/302. BKV thanks the School of Chemical Sciences, Goa University, for providing laboratory and instrumental facilities during the study leave duration. BKV also thanks the Directorate of Higher Education, Government of Goa, for granting sabbatical leave. Authors acknowledge CSIF, BITS Pilani Goa, for measuring PXRD. and Maratha Mandal's Central Research Laboratory, Belgavi, Karnataka, India, for providing the investigations of DNA cleavage and Cytotoxicity studies. The authors are grateful to Mr. Saurav Sattarker for his experimental work on DNA binding studies. PKB sincerely acknowledges the Knowledge Fund administered by the Nevada Governor's Office of Economic Development (GOED) and the University of Nevada Las Vegas (UNLV).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2025.141694](https://doi.org/10.1016/j.molstruc.2025.141694).

Data availability

<http://www.ccdc.cam.ac.uk/-conts/retrieving.html> (Authors declare that the supporting data is available in the Supplementary Information file. CCDC No. 2375640 (for compound 1) and 2375641 (for compound 2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).)

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