A Thesis Entitled

SYNTHESES, SPECTRA, STRUCTURES AND PROPERTIES OF METAL BENZENE DICARBOXYLATES

Submitted to Goa University for the Award of the Degree of

DOCTOR OF PHILOSOPHY
In
CHEMISTRY

By
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MAY 2019

CERTIFICATE

This is to certify that the thesis entitled, "**Syntheses, Spectra, Structures and Properties of Metal Benzene Dicarboxylates**" submitted by Ms. **RITA NINGAPPA JYAI**, is a record of research work carried out by the candidate during the period of study under my supervision and that it has not previously formed the basis for the award of any degree or diploma or other similar titles.

Goa University
May 2019

Prof. B. R. SRINIVASAN
Research Guide
School of Chemical Sciences
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DECLARATION

I hereby declare that the work embodied in the thesis entitled “**Syntheses, Spectra, Structures and Properties of Metal Benzene Dicarboxylates**” is the result of investigations carried out by me under the guidance of **PROF. B. R. SRINIVASAN** at School of Chemical Sciences, Goa University and that it has not previously formed the basis for the award of any degree or diploma or other similar titles.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Goa University
May 2019

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.......Ms. Rita Ningappa Jyai

Dedicated
to my
Beloved
parents

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SYNOPSIS

Syntheses, Spectra, Structures and Properties of Metal Benzene Dicarboxylates

The study of metal carboxylates is an active area of research in view of the diverse structures and a variety of applications of these compounds. Recent years have witnessed a steady growth of publications in this area especially pertaining to studies of metal benzene carboxylates[1-3]. In the literature, a variety of terms viz. coordination polymers (CP), metal organic framework (MOF), coordination networks, hybrid organic-inorganic materials etc. are employed to designate these compounds. A coordination polymer can be defined as a metal-ligand compound that extends infinitely into one dimension (1D), two dimensions (2D) or three dimensions (3D) via metal-ligand bonding. The primary requirement to build an extended structure is the use of a bridging ligand or a multitopic ligand which can bind to at least two or more metal ions. The carboxylate group ($–COO^-$) can serve this purpose in view of its well documented versatile binding modes [4]. In this context, the present work on metal benzene dicarboxylates was undertaken and the results of these studies are described in the thesis entitled '*Syntheses, spectra, structures and properties of metal benzene dicarboxylates*'.

The introductory chapter presents an overview of the known chemistry of metal benzene dicarboxylates with special emphasis on coordination polymers. The next chapter illustrates the different instrumentation methods employed for the characterization of the compounds synthesised in this study and the details of the synthetic procedures employed to prepare metal phthalates and 3-nitrophthalate compounds. The third chapter describes the results and discussion of the synthetic aspects, spectral characterization, crystal structure determination, thermal investigations, electrochemical studies and magnetic properties of the synthesised compounds (Table 1). The last chapter summarises the results and the thesis ends with a few recommendations for future prospects.

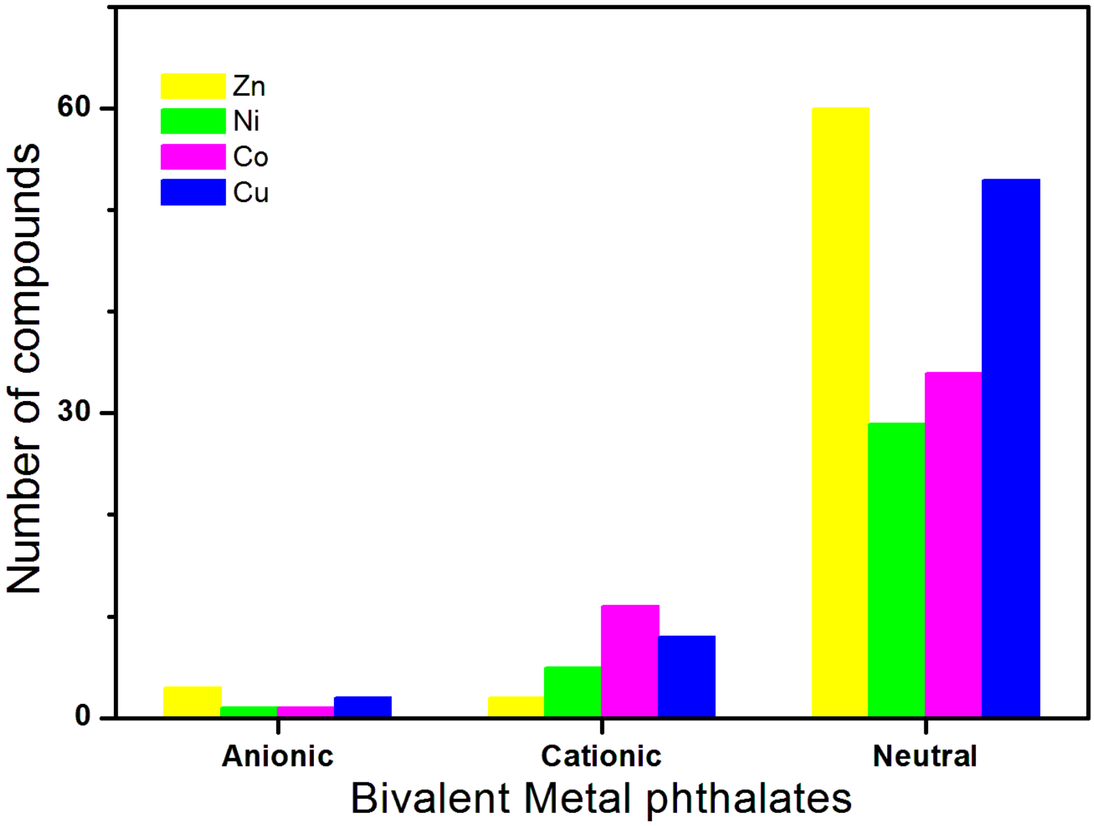
Table 1: Partial list of synthesised compounds

Compound Formula	Space group	Dimensionality
$(pipH_2)[Zn(pht)_2]\cdot H_2O$	$P2_1/c$	1D
$[(enH_2)[Zn(pht)_2(H_2O)]$	-	-
$(pipH_2)[Ni(pht)_2(H_2O)_4]\cdot 8H_2O$	$P\bar{1}$	0D
$(pipH_2)[Co(pht)_2(H_2O)_4]\cdot 8H_2O$	$P\bar{1}$	0D
$(pipH_2)[Cu(pht)_2(H_2O)_4]\cdot 8H_2O$	$P\bar{1}$	0D
$[Cu(pht)_2(pipH_2)]$	-	-
$[Ni(im)_6]pht\cdot H_2O$	$P2_1/c$	0D
$[Co(im)_6]pht\cdot H_2O$	$P2_1/c$	0D
$[Co(im)_3(pht)(H_2O)_2]$	-	-
$[Cu_2(im)_4(pht)_2(H_2O)]\cdot H_2O$	$P2_1/n$	2D
$[Li(3\text{-}nphtH)(H_2O)_3]$	-	-
$[Li_2(3\text{-}npht)(H_2O)_3]$	-	-
$[Na(3\text{-}nphtH)(H_2O)_3]\cdot H_2O$	$P\bar{1}$	1D
$[Na_2(3\text{-}npht)(H_2O)_2]$	-	-
$[K(3\text{-}nphtH)]$	$P2_1/c$	2D
$[K_2(3\text{-}npht)]$	-	-
$[Rb(3\text{-}nphtH)(H_2O)_2]$	$Pcca$	1D
$[Rb_2(3\text{-}npht)]$	$P2_1/n$	3D
$[Cs(3\text{-}nphtH)(H_2O)]$	$Pcca$	1D
$[Cs_2(3\text{-}npht)]$	$P2_1/n$	3D
$[K_7Na_{11}(pht)_9(H_2O)_{12}]$	$P-31c$	-

Abbreviations used : $pipH_2$= piperazinediium; pht= phthalate; enH_2= ethylenediaminiium im= imidazole; 3-npht= 3-nitrophthalate.

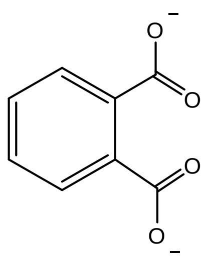
The choice of benzene dicarboxylic acid as ligands for the present work is due to the fact that it contains two –COOH functionalities present on a six membered ring, which can provide a rigid support to the –COOH group attached to it. Based on the disposition of the –COOH groups with respect to each other, three isomers viz. *para*-benzene dicarboxylic acid (terephthalic acid), *meta*-benzene dicarboxylic acid (isophthalic acid) and *ortho*-benzene dicarboxylic acid (phthalic acid) are possible. It is well documented that terephthalic acid with two –COOH groups disposed '*trans'* to each other extends the structure linearly and isophthalic acid extends the structure in a zig-zag fashion. The '*ortho'* isomer namely phthalic acid ($phtH_2$) has been shown to exhibit twenty six different types of binding modes by Baca *et al* [5].

A literature survey as well as an analysis of the Cambridge Structure Database (CSD) for metal phthalate compounds was performed to understand the structural diversity of the first row transition bivalent metal phthalates. The metal phthalates of Zn(II)[6], Ni(II), Co(II) and Cu(II) based on metal to phthalate ratio can be classified into neutral (1:1), cationic (2:1) and anionic (1:2) compounds. The analysis revealed that a majority of the reported compounds are neutral and only very few examples of anionic phthalates are reported (Scheme 1). In view of this, the present work was undertaken with an aim to prepare more examples of anionic metal phthalates. For this purpose organic amines were employed as structure directing agent cum charge balancing cation.

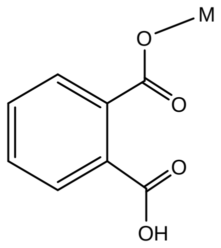


Scheme 1 – Anionic (1:2), cationic (2:1) and neutral (1:1) bivalent metal phthalates

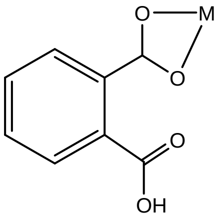
Of the several binding modes reported for the phthalate anion[5], nineteen different binding modes (Scheme 2) were identified in bivalent metal phthalates.



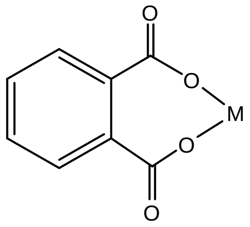
Free phthalate



Monodentate



Bidentate



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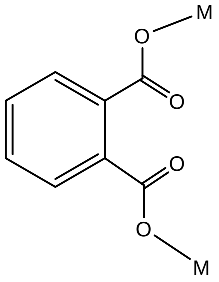
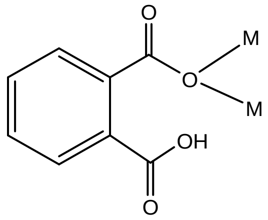


μ_2-bidentate



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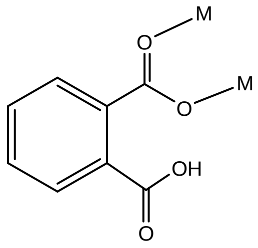

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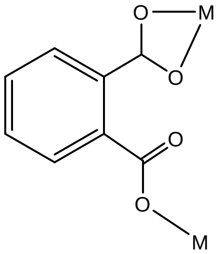
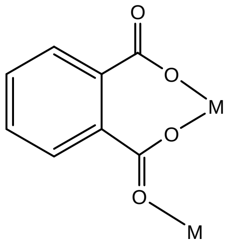


μ_2-tridentate



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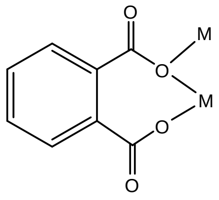
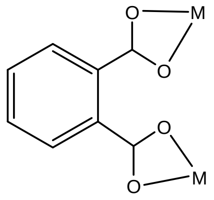
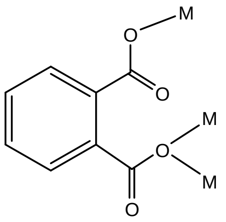


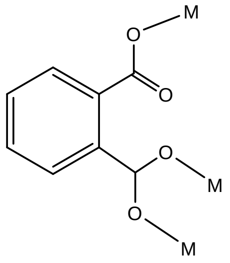
μ_2-tridentate



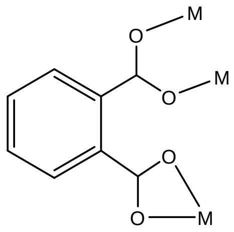
μ_2-tetradentate



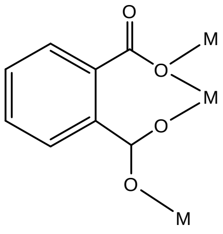
μ_3-tridentate



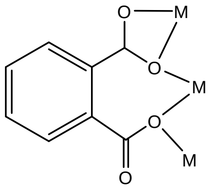
μ_3-tridentate



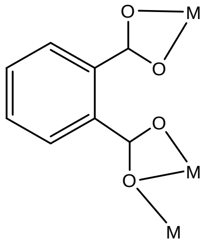
μ_3-tetradentate



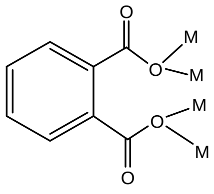
μ_3-tetradentate



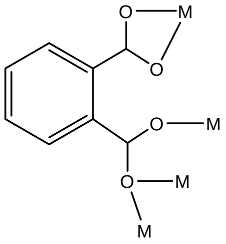
μ_3-pentadentate



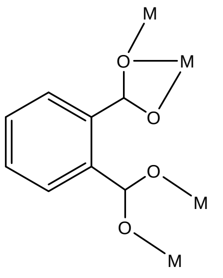
μ_3-pentadentate



μ_4-tetradentate



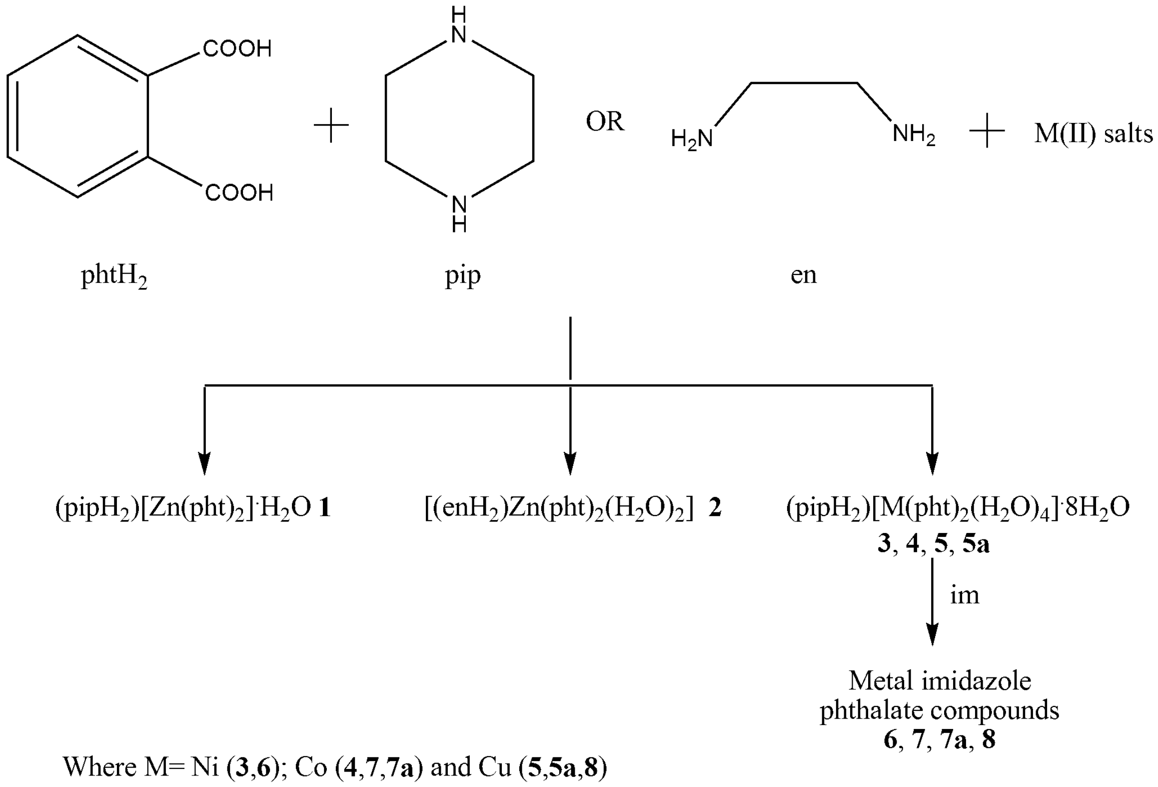
μ_4-pentadentate



μ_4-pentadentate

Scheme 2: Binding modes of phthalate anion where M= Zn, Ni, Co and Cu

In the present work the reactions of bivalent metal salts were investigated with phthalic acid in the presence of organic amines (Scheme 3).



Scheme 3

Phthalic acid ($phtH_2$) can form two different anions viz. phthalate $(pht)^{2-}$ dianion and hydrogen phthalate $(phtH)^{-}$ monoanion. The use of a cyclic amine viz. piperazine (pip) which is known to act as a charge balancing cation and structure directing agent (Table 2) afforded an anionic zinc(II) phthalate **1** which contains Zn and pht in 1:2 ratio. The structural characterization of **1** containing an unique Zn^{2+} ion, two crystallographically independent phthalate $(pht)^{2-}$ dianions, piperazinediium $(pipH_2)^{2+}$ dication and a lattice water molecule reveals one dimensional (1D) ladder coordination polymeric architecture (Fig. 1). The use of acyclic amine viz. ethylenediamine (en) in place of pip results in the formation of $[(enH_2)Zn(pht)_2(H_2O)_2]$ **2**.

Table 2- List of known piperazinediium compounds.

S.No.	Compound	S.No.	Compounds	S.No.	Compounds
1	$(pipH_2)[MoS_4]$	6	$(pipH_2)[CoCl_4]\cdot H_2O$	11	$(pipH_2)[ZnBr_4]$
2	$(pipH_2)[WS_4]$	7	$(pipH_2)[SeO_4]\cdot H_2O$	12	$(pipH_2)[ZnI_4]$
3	$(pipH_2)[CrO_4]$	8	$(pipH_2)[SO_4]\cdot H_2O$	13	$(pipH_2)[HgBr_4]$
4	$(pipH_2)[Cr_2O_7]$	9	$(pipH_2)[S_2O_3]\cdot H_2O$	14	$(pipH_2)[HgI_4]$
5	$(pipH_2)[CdBr_4]\cdot H_2O$	10	$(pipH_2)(phtH)_2\cdot 2H_2O$	15	$(pipH_2)[CdI_4]$

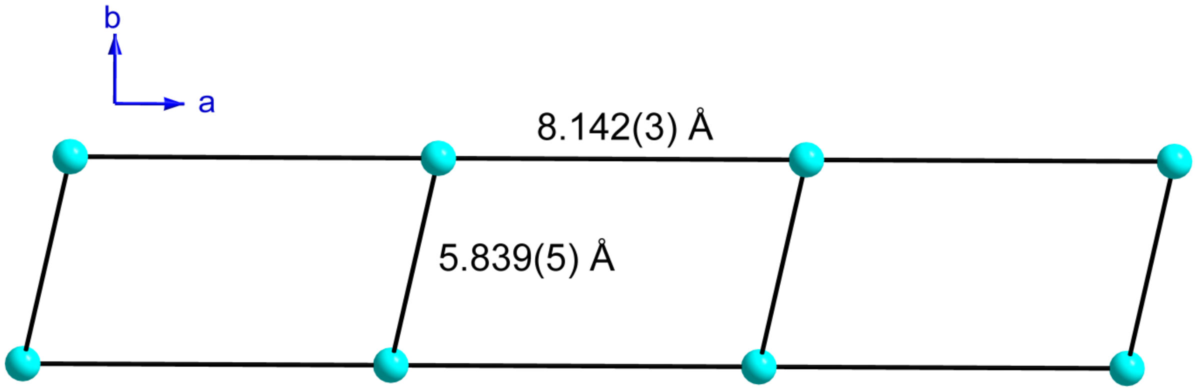


Fig. 1 – A portion of the infinite Zn(II) ladder in **1** extending along a-axis. For clarity only the Zn(II) points in the ladder are shown.

The use of other 3*d* metal ions Ni(II), Co(II) and Cu(II) in place of Zn(II) in the above case results in water-rich anionic metal phthalate compounds with the basic hexacoordinated $[M(pht)_2(H_2O)_4]^{2-}$ (M=Ni(II) **3**, Co(II) **4** and Cu(II) **5** anionic unit charge balanced by $(pipH_2)^{2+}$ dication and eight water molecules in the crystal lattice. A representative scheme is displayed in Fig. 2. In all the compounds, the $(pht)^{2-}$ dianion functions as a monodentate ligand. The H-bonding interactions amongst lattice water molecules lead to the formation of a water dodecamer (Fig. 3). The inter- and the intramolecular H-bonding interactions results in the formation of a metal cage structure shown for the Ni(II) compound (Fig. 4). The other analogues form similar cages. Monodentate behaviour of phthalate ligand in contrast to a bridging mode can probably be explained due to the presence of twelve water molecules in **3**-**5**.

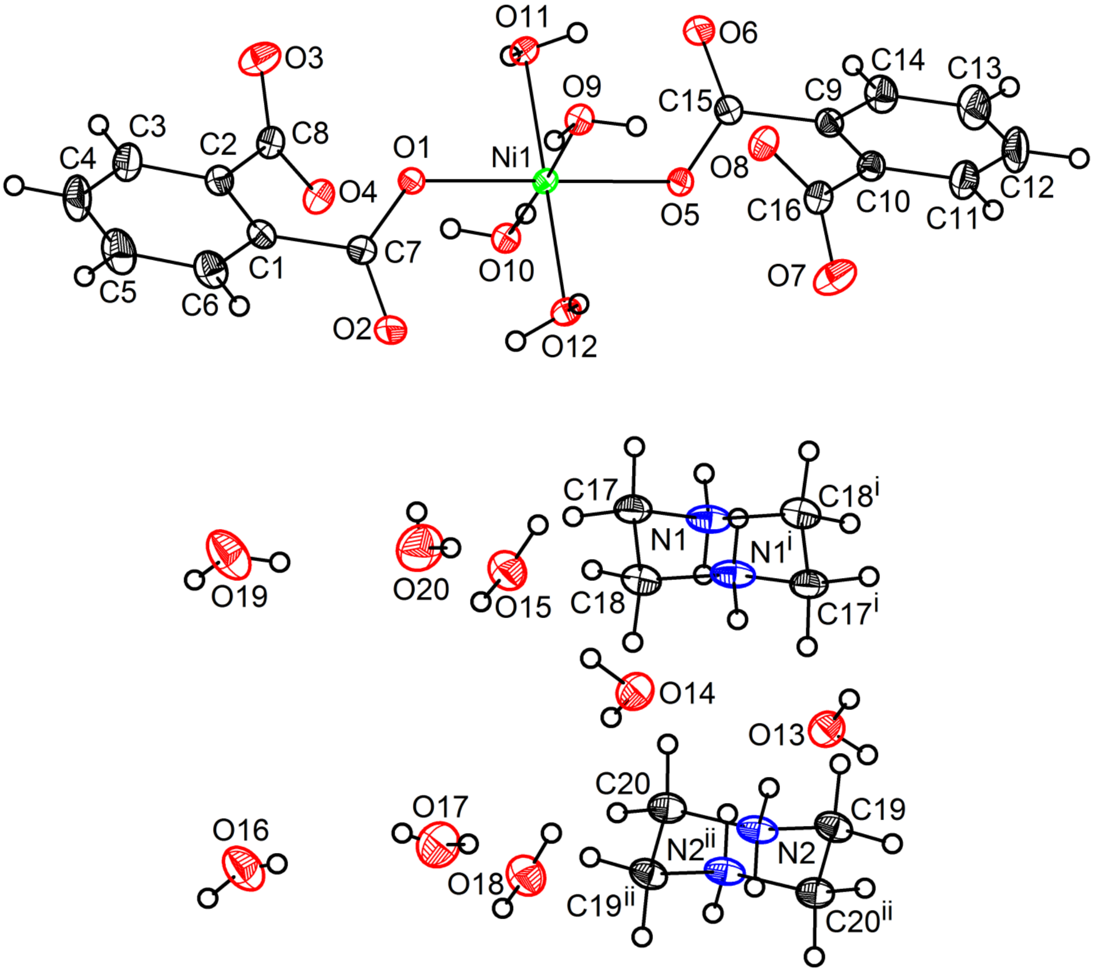


Fig. 2 – The crystal structure of $(pipH)_2[Ni(pht)_2(H_2O)_4]\cdot 8H_2O$ **3** showing the atom labelling scheme and the coordination sphere of Ni(II). Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as circles of arbitrary radius. Symmetry code: i) 1-x, 1-y, 1-z; ii) 2-x,-y, 1-z.

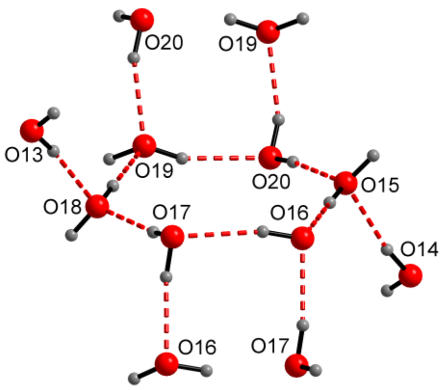


Fig. 3 – A water dodecamer formed by H-bonding interactions among lattice water molecules.

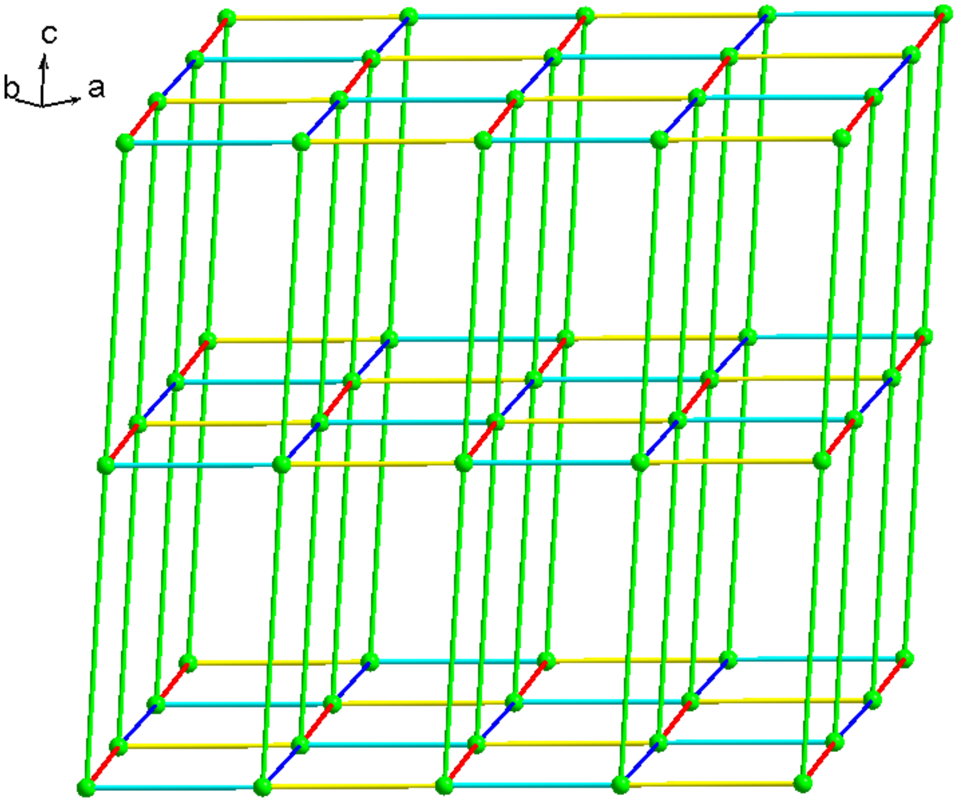


Fig. 4 – Disposition of Ni(II) centres in the crystal structure of $(pipH)_2[Ni(pht)_2(H_2O)_4]\cdot 8H_2O$ **3** forming 3-D cage architecture with Ni···Ni distance of 12.496 Å (Green), 8.684 Å (Red), 9.580 Å (Blue), 7.072 Å (Cyan) and 7.112 Å (Yellow).

The thermal investigations of the water-rich compounds show interesting dehydration-rehydration properties displaying gradual changes in the infrared spectra (Fig. 5) and X-ray powder pattern (Fig. 6) accompanied by distinct colour changes. The X-ray powder pattern indicates crystalline-amorphous-crystalline phase transformation in the nickel and cobalt compounds.

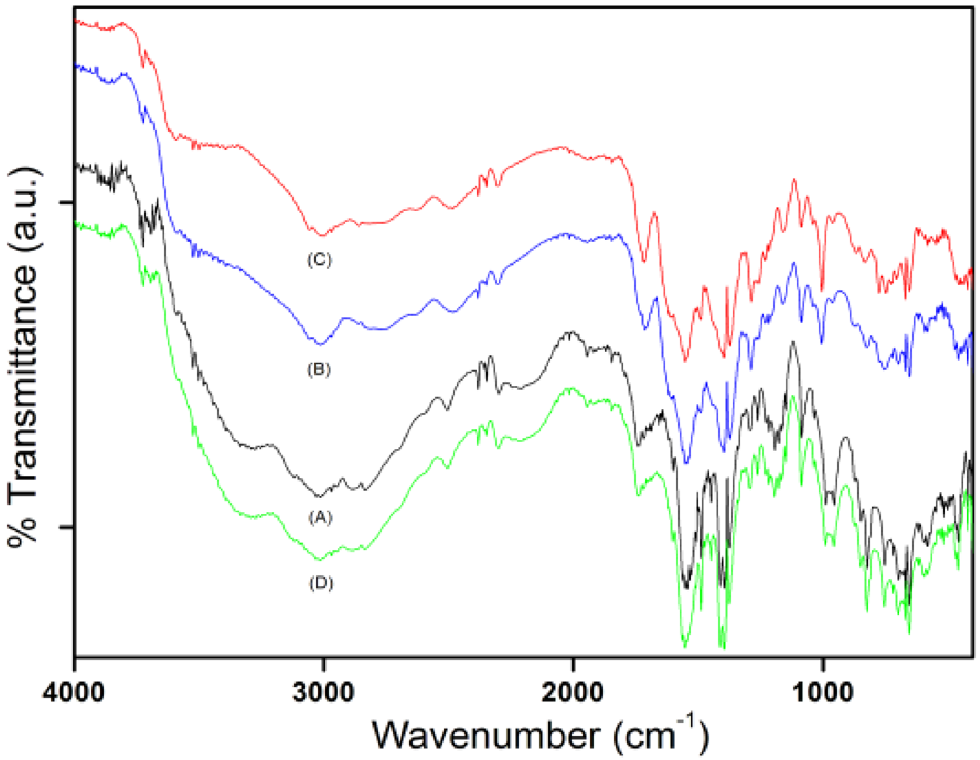


Fig. 5 – IR spectrum of $(pipH)_2[Ni(pht)_2(H_2O)_4]\cdot8H_2O$ **3** dehydrated at different temperatures (A) Starting compound, (B) at 100°, (C) at 180° and (D) Rehydrated compound.

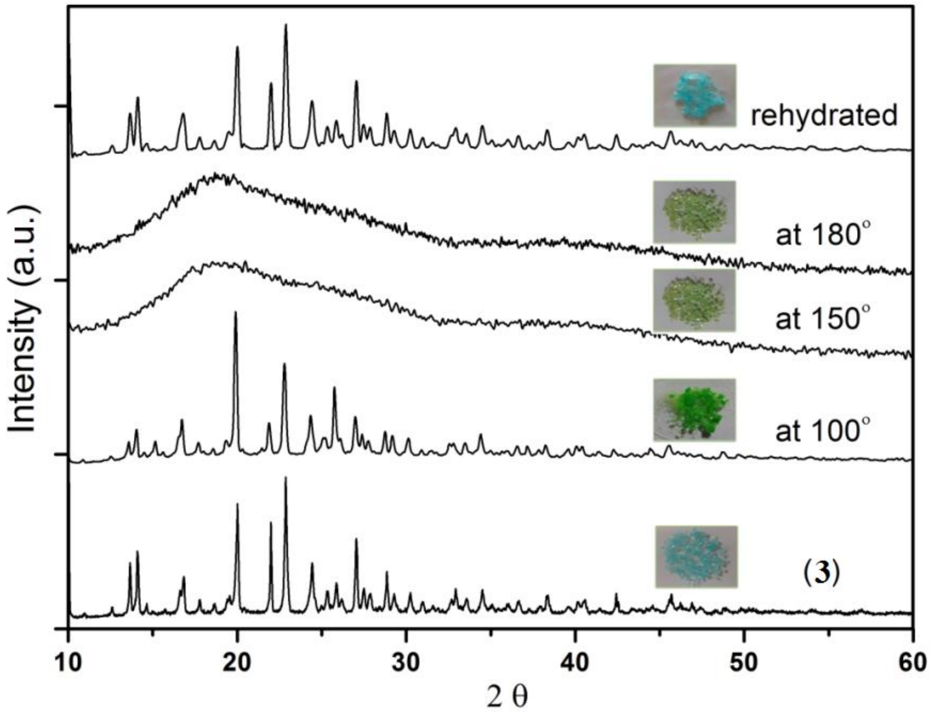


Fig. 6 – X-ray powder pattern of $(pipH)_2[Ni(pht)_2(H_2O)_4]\cdot8H_2O$ **3** dehydrated at different temperatures.

The electrochemical studies of Ni(II) and Co(II) phthalate compounds reveal a pair of reversible redox events (Fig. 7). The scan rate effect on the electrochemical behaviour was also investigated showing the quasi-reversible behaviour of the compounds. The temperature-dependent magnetic susceptibility data for polycrystalline samples were measured at an applied magnetic field of 250 Oe in the temperature range 50-300K. A representative χ_M versus T plot is displayed in Fig. 8. All the χ_M versus T plots depict a typical paramagnetic behaviour of the compounds, which is in accordance with the crystal structure.

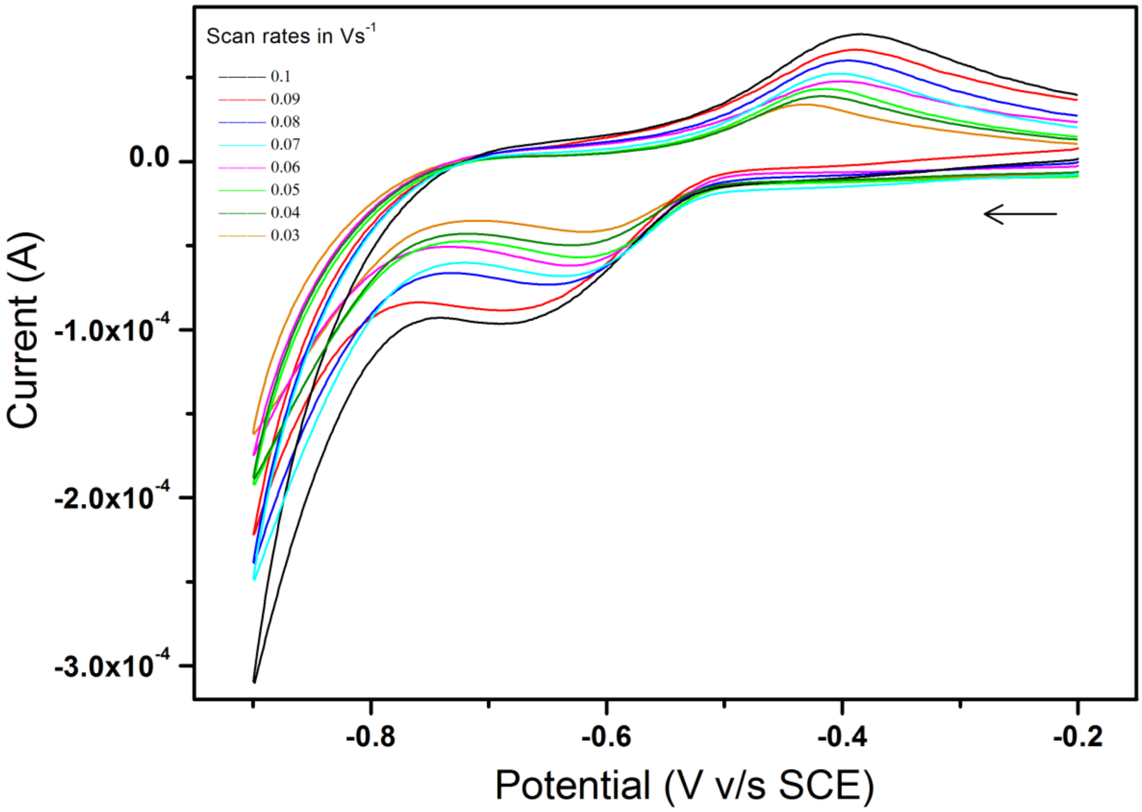


Fig. 7 – Cyclic voltammograms of $(pipH)_2[Ni(pht)_2(H_2O)_4]\cdot8H_2O$ **3** at different scan rates.

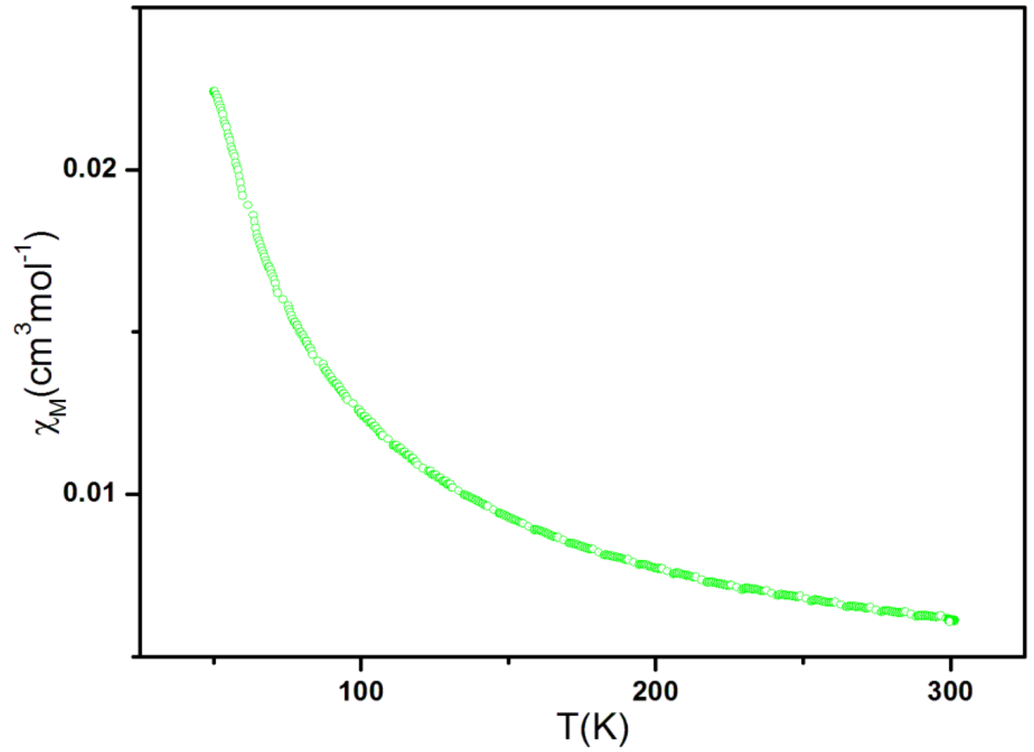


Fig. 8 – Plot of χ_M versus T for $(pipH)_2[Ni(pht)_2(H_2O)_4]\cdot 8H_2O$ **3**.

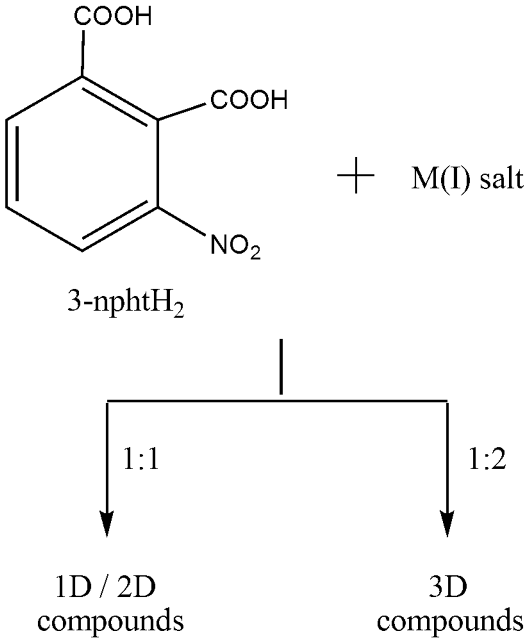
The reaction of $(pipH_2)[Ni(pht)_2(H_2O)_4]\cdot 8H_2O$ **3**, $(pipH_2)[Co(pht)_2(H_2O)_4]\cdot 8H_2O$ **4** and $(pipH_2)[Cu(pht)_2(H_2O)_4]\cdot 8H_2O$ **5** with imidazole results in the formation of $[Ni(im)_6]\cdot pht$ **6**, $[Ni(im)_6]\cdot pht$ **7** and $[Cu_2(im)_4(pht)_2(H_2O)]\cdot H_2O$ **8** (Scheme 3).

It is well documented that $NaHpht\cdot ½H_2O$ (sodium hydrogen phthalate hemihydrate)[7] and KHpht (potassium hydrogen phthalate)[8] crystallise in the non-centrosymmetric space groups *Aba2* and *P2₁ab* respectively. The mixed crystals of formula $[K_{0.78}Na_{1.22}(pht)_2]\cdot H_2O$ reported in literature can be correctly reformulated as a hetero bimetallic compound $[K_7Na_{11}(pht)_9(H_2O)_{12}]$. Several claims have appeared in recent literature reporting incorporation of bivalent, trivalent metal ions/amino acids/organics into the crystal structure of $NaHpht\cdot ½H_2O$ and KHpht (Table 3). A reinvestigation of these reports reveals that all such claims are inappropriate.

Table 3: List of reported dopants used to incorporate in KHpht

METAL ION	AMINO ACIDS	ORGANIC COMPOUNDS
Fe(III)	L-lysine	Anthracene
Ni(II)	L-alanine	EDTA
Cu(II)	Glycine	1,10-Phenanthroline
Zn(II)	L-arginine	
Ca(II)	L-histidine	
Mg(II)	L-aspartic acid	
Sr(II)		
Ba(II)		
Li(I)		
Al(III)		

The presence of an additional functional group on phthalic acid can result in the formation of new compounds with interesting structural features. In view of this, the $-NO_2$ group which is isoelectronic to –COOH was chosen for this purpose. Hence the reactions of 3-nitrophthalic acid (3-nphtH$_2$) with the structurally flexible alkali metals were investigated (Scheme 4). This study resulted in the formation of compounds of differing dimensionalities viz. 1D, 2D and 3D.



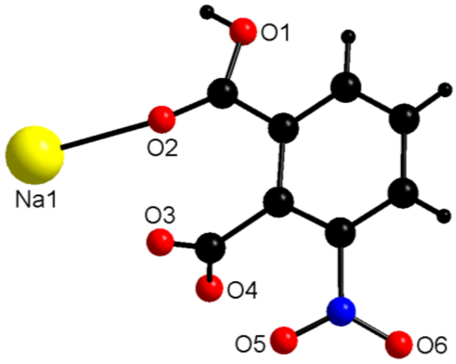
Scheme 4

An analysis of the structural features of the 3-nitrophthalate compounds of alkali and alkaline earth metal ions (Table 4) reveals new binding modes for 3-nitrophthalate (Fig. 9) including coordination of oxygen atom of nitro group.

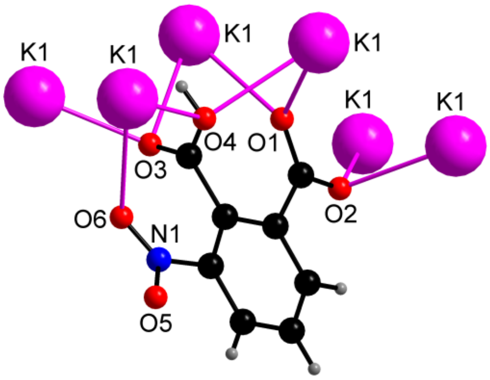
Table 4: List of structurally characterized 3-nitrophthalate compounds in literature.

Compound formula	Space group	Dimensionality	C.N	Binding mode of 3-nitrophthalate ligand	$-NO_2$ group binding
Alkali metal 3-nitrophthalates					
$[Na(H_2O)_3(3\text{-}nphtH)] \cdot H_2O$	$P\bar{1}$	1D	6	Monodentate	zero
$[Na_4(H_2O)_3(3\text{-}npht)_2]$	$P\bar{1}$	2D	5,6, 6,7	μ_6-octadentate μ_8-dodecadentate	1 bond
$[K(3\text{-}nphtH)]$*	$P2_1/c$	2D	9	μ_6-nonadentate	1 bonds
$[Cs(3\text{-}nphtH)(H_2O)]$*	$Pcca$	1D	10	μ_2-tetradentate	2 bonds
$[Cs_2(3\text{-}npht)]$*	$P2_1/n$	3D	7,10	μ_{10}-polydentate	3 bonds
$[Rb_2(3\text{-}npht)]$*	$P2_1/n$	3D	7,10	μ_{10}-polydentate	3-bonds
Alkaline earth metal 3-nitrophthalates					
$[Mg(H_2O)_5(3\text{-}npht)] \cdot 2H_2O$	$P\bar{1}$	0D	6	Monodentate	zero
$[Ca(H_2O)_2(3\text{-}npht)] \cdot H_2O$	$P2_1/c$	1D	7	μ_3-pentadentate	zero
$[Ba(3\text{-}npht)]$	$P\bar{1}$	2D	9	μ_6-nonadentate	1 bond

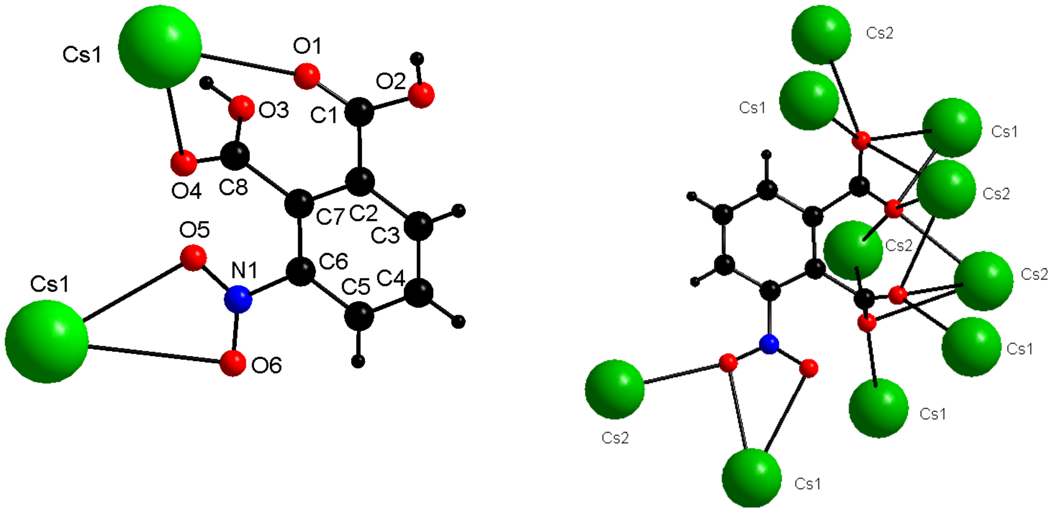
*Present work



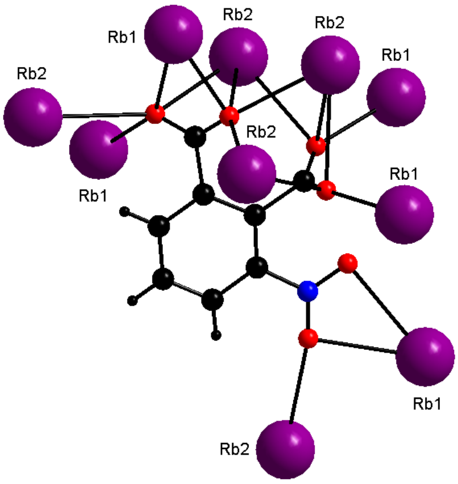
Monodentate in $[Na(3\text{-}nphtH)(H_2O)_3] \cdot H_2O$



μ_6-nonadentate in $[K(3\text{-}nphtH)]$



μ_2-tetradentate in [Cs(3-nphtH)(H_2O)] μ_{10}-polydentate in [Cs_2(3-npht)]



μ_{10}-polydentate in [Rb_2(3-npht)]

Fig. 9 - Binding modes of 3-npht ligand observed in synthesised alkali metal 3-nitrophthalate compounds displaying binding nature of –NO_2 group.

In summary, the present work has resulted in the structural characterization of new examples of anionic bivalent metal phthalates, some of which exhibit interesting water cluster architecture. The thermal investigations reveal interesting crystalline-amorphous-crystalline phase transformation along with marked colour changes. The transition metal phthalates show typical paramagnetic behaviour in accordance with their structures. The studies of alkali metal 3-nitrophthalates reveal a very rich structural chemistry of these compounds.

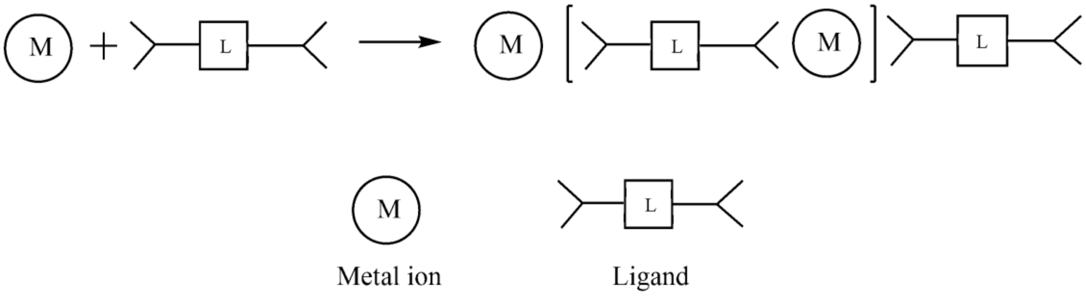
Selected references

1. C. Janiak, *Engineering coordination polymers towards applications*, Dalton Trans. (2003) 2781-2804.
2. J.R. Long, O.M. Yaghi, *The pervasive chemistry of metal–organic frameworks*, Chem. Soc. Rev., 38 (2009) 1213–1214.
3. H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, *Design and synthesis of an exceptionally stable and highly porous metal-organic framework*, Nature 402 (1999) 276-279.
4. F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bachmann, Advanced Inorganic Chemistry, Sixth Edition (2014).
5. S.G. Baca, I.G. Filippova, O.A. Gherco, M. Gdaniec, Y.A. Simonov, N.V. Gerbeleu, P. Franz, R. Basler, S. Decurtins, *Nickel(II)-, cobalt(II)-, copper(II)-, and zinc(II)-phthalate and 1-methylimidazole coordination compounds: synthesis, crystal structures and magnetic properties*, Inorg. Chim. Acta 357 (2004) 3419-3429.
6. R.N. Jyai & B.R. Srinivasan, *Piperazinediium bis(μ_2-phthalato)zincate(II) monohydrate: A new ladder coordination polymer with an unique supramolecular architecture*,Indian Journal of Chemistry, 54A (2015) 1402-1408.
7. R.A. Smith, *The crystal structures of a series of salts of phthalic acid. II. The crystal structure of sodium acid phthalate hemihydrate*,, Acta Cryst., B31 (1975) 2345-2347.
8. Y. Okaya, *The crystal structure of potassium acid phthalate, $KC_6H_4COOH.COO$*, Acta Cryst., 19 (1965) 879-882.

INTRODUCTION

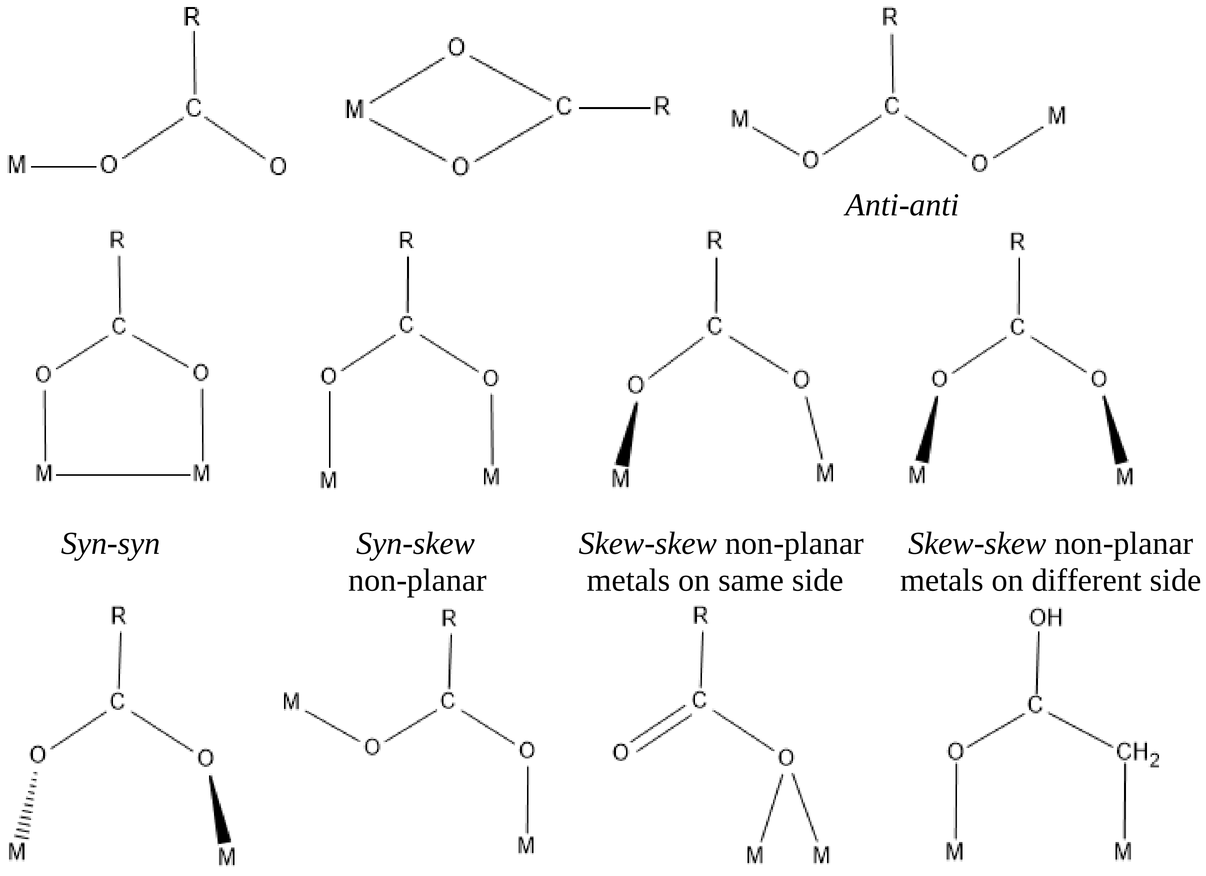
The study of coordination polymers (CP) or metal organic frameworks (MOF) is a topical area of research in view of their fascinating architectures and potential applications in adsorption (gas storage) [1-4], separation processes [1, 3, 5], catalysis [1-3, 6-7], luminescence [2-3, 8], non-linear optical properties [1, 3], magnetism [1, 3, 9], conductivity [1, 3, 10], chemical sensor [1, 3, 11], biomedical [1-3, 12-13] etc. In the literature, the terms viz. porous coordination polymers, organic-inorganic hybrid materials, metal organic networks, coordination networks are also employed by many research groups [14-17]. According to the International Union of Pure and Applied Chemistry (IUPAC) recommendations 2013 [15], coordination polymer is defined as a coordination compound with repeating coordination entities extending in one or two or three dimensions and MOF as a three dimensional coordination network with organic ligands containing potential voids. Moreover, the structures extending via H-bonding are considered as supramolecular architecture/ networks and it does not define the dimensionality of the compound. Coordination polymers have attracted the attention of many researchers for their easy methods of synthesis which includes saturation methods (slow evaporation and slow cooling), diffusion methods, hydro(solvo)thermal methods and microwave & ultrasonic methods. The synthesis of coordination polymers invariably depends on various factors like pH of the solution, reaction temperature, quantity of the solvent used, molar ratio of the metal and ligand, geometry of central metal ion, the nature of the ligand used, counter ion etc. These aspects of synthesis effect the compound formation as well as the structure of the final product.

Coordination polymers are obtained by combining metal sources with a bridging ligand or a multitopic ligand which can bind to at least two or more metal ions (Scheme 1.1).



Scheme 1.1 – Bridging ligand facilitating structure extension.

In this context, the carboxylate group (–COO)$^-$ can serve the purpose of obtaining coordination polymers in view of its well documented [18] bridging binding modes in addition to the well known mono and bidentate modes resulting in a variety of structures (Fig. 1.1).



Anti-anti

Syn-syn

Syn-skew non-planar

Skew-skew non-planar metals on same side

Skew-skew non-planar metals on different side

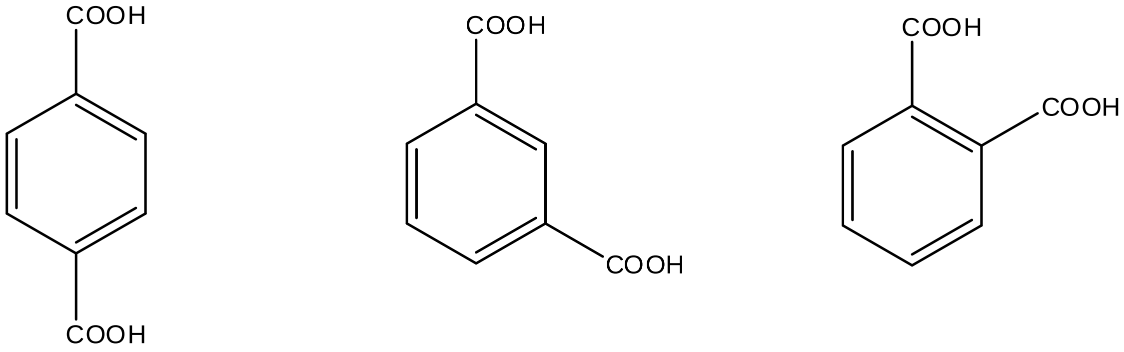
Anti-syn

Monoatomic

Fig. 1.1 – Different binding modes of carboxylate (RCOO)$^-$ group.

Recent years have witnessed a steady growth of publications in this area especially pertaining to studies of metal benzene carboxylates [19-21] as the benzene ring provides a rigid support to the carboxyl group and additionaly π-π stacking secondary interactions of aromatic rings adds to the stability of the structure [22- 26]. Depending on the number of carboxyl groups attached to the aromatic ring, the prefix di-, tri- tetra- or poly- is used for carboxylic acids to indicate the number of carboxyl group present on aromatic ring. The study of metal benzene dicarboxylates became an active area of research with the pioneering work by the Yaghi group of employing 1,4-benzene dicarboxylic acid (1,4-BDC) for the construction of metal organic framework system namely MOF-5 having composition $[Zn_4O(BDC)_3(DMF)_8(C_6H_5Cl)]$ in 1999 [27].

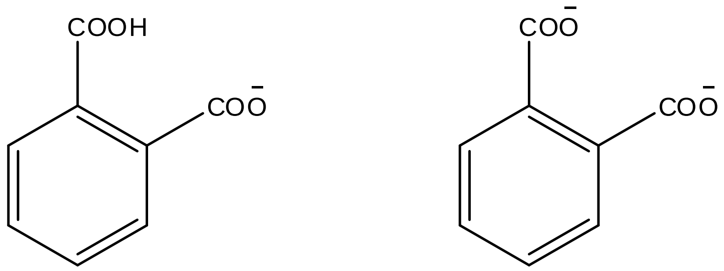
In the present thesis entitled '*Syntheses, Spectra, Structures and Properties of Metal Benzene Dicarboxylates*', the chemistry of phthalates of first row bivalent metal ions viz. Zn(II), Ni(II), Co(II), Cu(II) ions and *s*-block metal ions has been studied. The choice of benzene dicarboxylic acid as ligand for the present work is due to the fact that it contains two –COOH functionalities with characteristic binding features and a six membered ring providing a rigid support to the –COOH groups attached to it. Based on the disposition of the –COOH groups with respect to each other, three isomers viz. *para*-benzene dicarboxylic acid (terephthalic acid), *meta*-benzene dicarboxylic acid (isophthalic acid) and *ortho*-benzene dicarboxylic acid (phthalic acid) are possible (Fig. 1.2). It is well documented that terephthalic acid with two –COOH groups disposed '*trans*' to each other extends the structure linearly [27] and isophthalic acid extends the structure in a zig-zag fashion. The '*ortho*' isomer namely phthalic acid (ptH_2) has been shown to exhibit several different types of binding modes by Baca *et al* [28] resulting in extended structures which can be one-dimensional (1D) or 2D or 3D and also takes part in secondary interactions forming supramolecular architectures via hydrogen bonding and/or stacking forces and other weak interactions.



Terephthalic acid Isophthalic acid Phthalic acid

Fig. 1.2 – The three isomers of benzene dicarboxylic acids.

Transition metal ions are frequently employed to construct coordination polymers in view of their well defined coordination number, variable oxidation states and magnetic properties. Transition metal ions with multidentate phthalate ligand can result in construction of polymeric structures with interesting architectures. Phthalic acid having two carboxyl groups form either mono-deprotonated or di-deprotonated anions namely hydrogen phthalate or acid phthalate $(phtH)^-$ anion and phthalate $(pht)^{2-}$ dianion (Fig. 1.3) which subsequently offer different structural arrangements.



Hydrogen phthalate anion $(phtH)^-$ phthalate dianion $(pht)^{2-}$

Fig. 1.3 – Mono and dianion of phthalic acid.

The formation of either hydrogen phthalate anion or phthalate dianion generally depends on the molar ratio of metal(II) sources and phthalic acid taken in the reaction mixture. Depending on the metal: phthalate ratio, different types of compounds are obtained which can be classified into neutral, cationic and anionic. Neutral compounds are obtained by taking bivalent metal ion and phthalate in 1:1 molar ratio or in 2:1 molar ratio whereas cationic compounds are results of 2:1 molar ratio charge balanced by an anion (Scheme 1.2). The molar ratio of metal ion and phthalate in 1:2 results in anionic compounds charge balanced by a cation.

Neutral metal phthalate

$$M^{2+} : (pht)^{2-} \longrightarrow [M(pht)]$$

$$2M^{2+} : (pht)^{2-} \longrightarrow [M_2(pht)(L)]$$

L = Dianionic ligand

Cationic metal phthalate

$$2M^{2+} : (pht)^{2-} \longrightarrow [M_2(pht)]^{2+}$$

Anionic metal phthalate

$$M^{2+} : 2(pht)^{2-} \longrightarrow [M(pht)_2]^{2-}$$

Scheme 1.2 – Classification of metal phthalates.

A charge balancing species for cationic metal phthalates $[M_2(pht)]^{2+}$ can be an anion like perchlorate. In the literature other anions like sulfate, iodide, nitrite have been employed in addition to $(ClO_4)^-$. For bis(phthalato) metalates, a variety of cations viz. ammonium, organic ammonium or cationic metal containing species like $[M(L)_x]^{n+}$ (L= neutral ligand) can be employed for charge balance.

A survey of literature of phthalate compounds of first row bivalent metal viz. zinc, nickel, cobalt and copper reveals several neutral compounds as per the classification in Scheme 1.2. A few cationic and anionic phthalates are also known (Fig. 1.4-1.7).

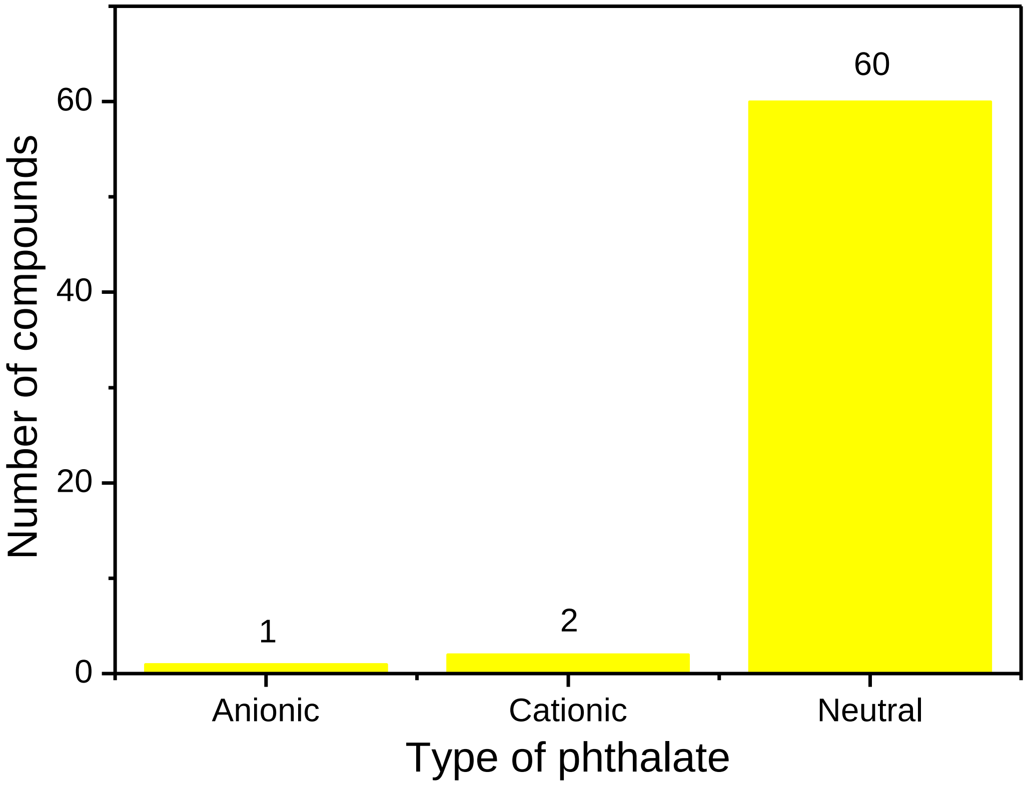


Fig. 1.4 – Anionic (1:2), cationic (2:1) and neutral (1:1 and 2:1) zinc phthalates.

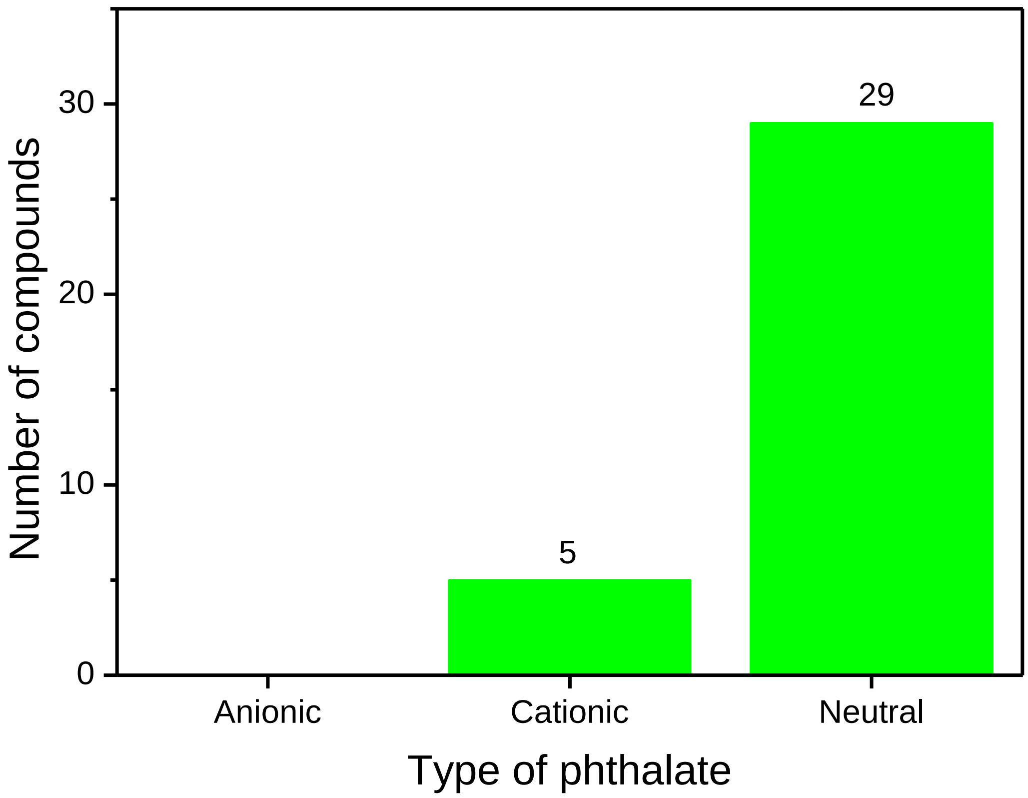


Fig. 1.5 – Anionic (1:2), cationic (2:1) and neutral (1:1) nickel phthalates

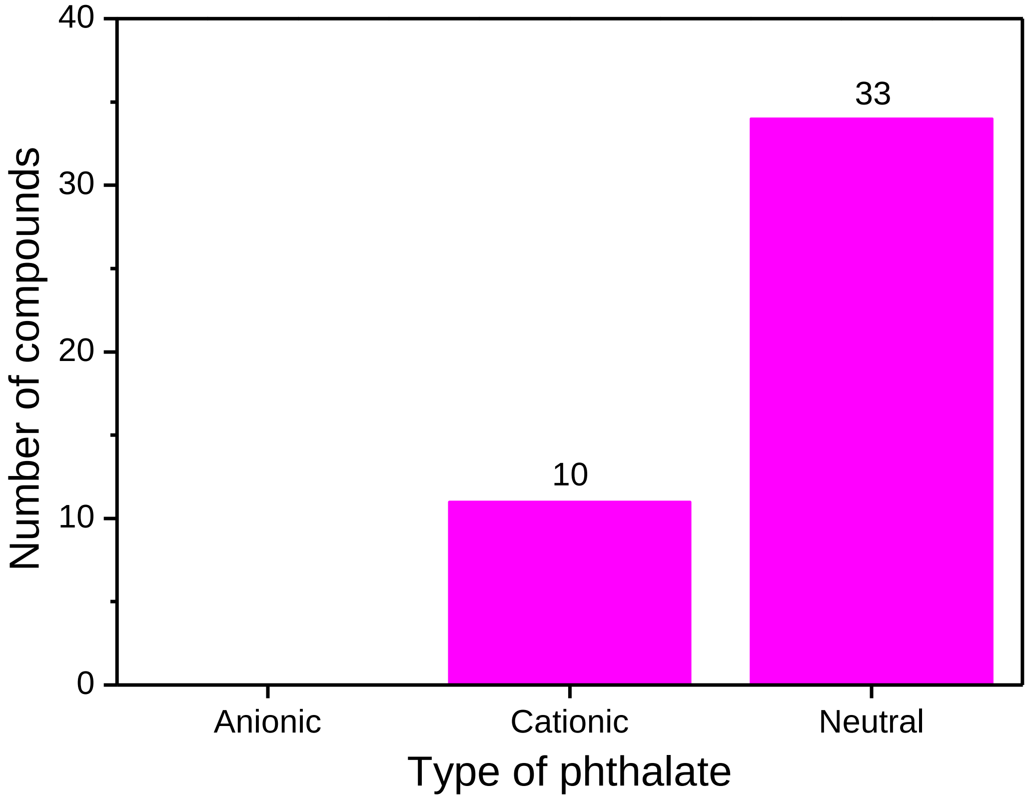


Fig. 1.6 – Anionic (1:2), cationic (2:1) and neutral (1:1) cobalt phthalates.

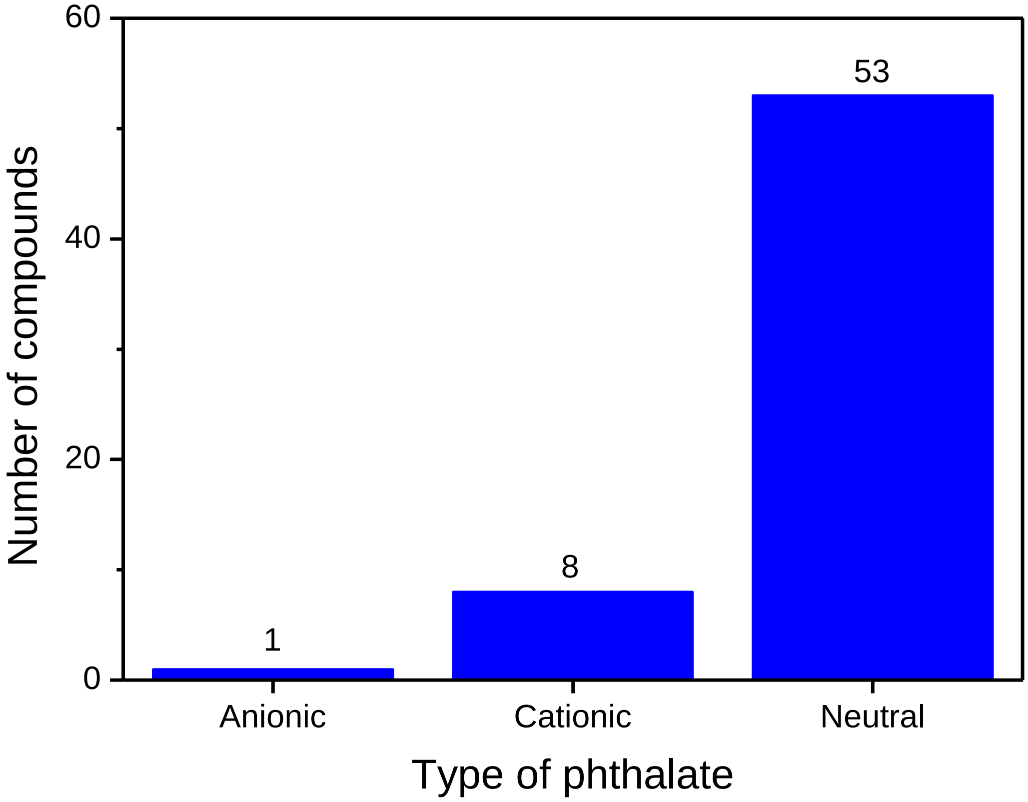


Fig. 1.7 – Anionic (1:2), cationic (2:1) and neutral (1:1) copper phthalates.

A search of the Cambridge Structural Database (CSD) [29-30] for Zn(II) phthalates (Table 1.1) reveals a similar trend namely most of the compounds are neutral having Zn:pht ratio 1:1 [31-76]. Out of 63 zinc phthalates sixty are neutral (95 %) while two are (3 %) cationic. Only a single anionic compound is reported till date. The analysis of structure data of reported compounds further shows that a majority (78 %) of the structurally characterized zinc phthalates crystallize in centrosymmetric space groups viz. $P2_1/c$, $P2_1/n$, $P\bar{1}$, $C2/c$, $Pccn$, $Pbca$, $P2/n$ and $Pbcn$ which is in line with the space group statistics reported in the Cambridge Database [77]. The remaining 22 % of the Zn(II) phthalates crystallize in non-centrosymmetric space groups viz. $P2_12_12_1$, $P2_1$, Cc, Pn, $Pnc2$, $Pna2_1$ and $Pca2_1$.

Table 1.1 – List of zinc(II) phthalate compounds

No.	Compound	C.N.	Coordination sphere	Phthalate binding mode	Space group	Dimensionality	Ref.
	Neutral compounds whose Zn:pht = 1:1						
1	[Zn(pht)(Im)(H_2O)]$_2$	4	NO_3	μ_2-bidentate	$P2_1/c$	0D	31
2	[Zn(pht)(metu)$_2$]$_2$·4H_2O	4	S_2O_2	μ_2-bidentate	$P2_1/c$	0D	32
3	[Zn(pht)(1-MeIm)$_2$]	4	N_2O_2	μ_2-bidentate	*Pccn*	1D	28
4	[Zn(pht)(Pyridine)$_2$]	4	N_2O_2	μ_2-bidentate	*Pbca*	1D	33
5	[Zn(pht)(β-Pic)$_2$]	4	N_2O_2	μ_2-bidentate	$P2_1/c$	1D	33
6	[Zn(pht)(γ-Pic)$_2$]	4,5	N_2O_2, N_2O_3	μ_2-bidentate, μ_2-tridentate	$P2_1$	1D	33
7	[Zn(pht)(γ-Pic)]	4,6	NO_3,NO_5	μ_3-tetradentate	*Cc*	1D	33
8	[Zn(pht)(Im)$_2$]	4	N_2O_2	μ_2-bidentate	*Pn*	1D	31
9	[Zn(pht)(2-MeIm)$_2$]	4	NO_3	μ_2-tridentate	*Pnc2*	1D	31
10	[Zn(pht)(fimp)]	5	N_2O_3	μ_2-tridentate	*C2/c*	1D	34
11	[Zn(pht)(1-VnIm)]	4	N_2O_2	μ_2-bidentate	$P2_1/c$	1D	35
12	[Zn(pht)(Phen)(H_2O)]	6	N_2O_4	μ_2-tridentate	$P2_1/n$	1D	36
13	[Zn(pht)(2,2’-bpy)(H_2O)]	6	N_2O_4	μ_2-tridentate	$Pna2_1$	1D	37
14	[Zn(pht)(cyclam)]·2(CH_3OH)	6	N_4O_2	μ_2-bidentate	$P\bar{1}$	1D	38
15	[Zn(pht)(Phen)(H_2O)]	6	N_2O_4	μ_2-bidentate	$P2_1/n$	1D	39
16	[Zn(pht)(dpz)]	5	N_2O_3	μ_2-bidentate	$P\bar{1}$	1D	40
17	[Zn(pht)(μ-4,4’-bpp)]·H_2O	4	N_2O_2	μ_2-bidentate	$P\bar{1}$	1D	41
18	[Zn(pht)(bbip)]·H_2O	4	N_2O_2	μ_2-bidentate	$P\bar{1}$	1D	42
19	[Zn(pht)(dmetu)$_2$]	4	S_2O_2	μ_2-bidentate	$Pna2_1$	1D	32
20	[Zn(pht)(tu)$_2$]	4	S_2O_2	μ_2-bidentate	$P2_12_12_1$	1D	43
21	[Zn(pht)(pyrazole)$_2$]	4	N_2O_2	μ_2-bidentate	$P2_1/c$	1D	44
22	[Zn(pht)(2,3’-tmbpht)(H_2O)]	5	N_2O_3	μ_2-bidentate	$P\bar{1}$	1D	45
23	[Zn(pht)(3,3’-tmbpht)]·H_2O	5	N_2O_3	μ_2-bidentate	$P\bar{1}$	1D	45
24	[Zn(pht)(3-dpaa)]	4	N_2O_2	μ_2-bidentate	$P\bar{1}$	1D	46
25	[Zn(pht)(1-allylimidazole)$_2$]	4	N_2O_2	μ_2-bidentate	$Pca2_1$	1D	47
26	[Zn(pht)(bdmb)]	4	N_2O_2	μ_2-bidentate	$P2_1/c$	1D	48

27	[Zn(pht)(4,4’-bpht)]	5	N_2O_3	μ_2-tridentate	$P2_1/c$	2D	49
28	[Zn(pht)(biim-5)]	4	N_2O_2	μ_2-bidentate	*Pbca*	2D	50
29	[Zn(pht)(4,4’-bipy)(H_2O)$_2$]·2H_2O	6	N_2O_4	μ_2-bidentate	$P2/n$	2D	51
30	[Zn(pht)]	4	O_4	μ_4-pentadentate	$P2_1/c$	2D	52
31	[Zn(pht)(biim-6)]	4	N_2O_2	μ_2-bidentate	$P\bar{1}$	2D	53
32	[Zn(pht)(bmb)$_{0.5}$(H_2O)]·0.5(bmb)·H_2O	5	NO_4	μ_2-bidentate	$P\bar{1}$	2D	54
33	[Zn(pht)(thim)]·2H_2O	4	N_2O_2	μ_2-bidentate	$P2_1/n$	2D	55
34	[Zn(pht)(mib)]·3H_2O	4	N_2O_2	μ_2-bidentate	$P2_1/c$	2D	56
35	[Zn(pht)(mib)$_{0.5}$]	4	NO_3	μ_3-tridentate	$P2_1/c$	3D	56
36	[Zn(pht)(imp)(H_2O)]	4	N_2O_2	μ_2-bidentate	$P2_12_12_1$	3D	57
37	[Zn(pht)(ib)]	4	N_2O_2	μ_2-bidentate	$P2_1/c$	3D	58
38	[Zn(pht)(tppa)]·2H_2O	6	N_2O_4	μ_2-tetradentate	*Pbcn*	3D	59
39	[Zn(pht)(bimb)]	4	N_2O_2	μ_2-bidentate	*Cc*	3D	60
40	[Zn_2(pht)$_2$(Dpq)$_2$(H_2O)$_4$]·2H_2O	6	N_2O_4	μ_2-bidentate	$C2/c$	0D	61
41	[Zn_2(pht)$_2$(Dpds)$_2$]·2H_2O	4,4	N_2O_2, N_2O_2	μ_2-bidentate, μ_2-bidentate	$C2/c$	0D	61
42	[Zn_2(pht)$_2$(tpht)$_2$]	5,5	N_3O_2, N_3O_2	μ_2-bidentate, μ_2-bidentate	*Pbca*	0D	62
43	[Zn_2(pht)$_2$(2,2’-bpy)$_2$(H_2O)$_2$]	5,5	N_2O_3, N_2O_3	μ_2-bidentate, μ_2-bidentate	$P\bar{1}$	0D	63
44	[Zn_2(pht)$_2$(bpp)]	4,6	NO_3, NO_5	μ_3-tetradentate	*Cc*	1D	64
45	[Zn_2(pht)$_2$(3,4’-bpht)]	4,4	NO_3, NO_3	μ_3-tridentate	$P2_1/c$	1D	49
46	[Zn_2(pht)$_2$(bpp)$_2$]·H_2O	4	N_2O_2	μ_2-bidentate	$P2_1$	1D	65
47	[Zn_2(pht)$_2$(2,2’-bpy)$_2$(H_2O)]·H_2O	4,5	N_2O_2, N_2O_3	μ_2-bidentate, μ_2-bidentate	$P2_1/n$	1D	66
48	[Zn_2(pht)$_2$(pmmi)$_2$]·6H_2O	4,4	N_2O_2, N_2O_2	μ_2-bidentate, μ_2-bidentate	$P2_1/c$	1D	67
49	[Zn_2(pht)$_2$(ttmt)$_2$]·H_2O	4	N_2O_2	μ_2-bidentate	$P\bar{1}$	1D	68
50	[Zn_2(pht)$_2$(4-dpaa)(H_2O)$_2$]·2H_2O	4	NO_3	μ_2-bidentate	$P\bar{1}$	1D	46
51	[Zn_2(pht)$_2$(Dpq)$_2$]·H_2O	5	N_2O_3	μ_3-tridentate	$P2_1/c$	2D	53
52	[Zn_2(pht)$_2$(bte)$_2$]·4H_2O	4	N_2O_2	μ_2-bidentate	$Pna2_1$	2D	69
53	[Zn_2(pht)$_2$(bib)]	5	NO_4	μ_3-tetradentate	$P\bar{1}$	2D	70
54	[Zn_2(pht)$_2$(imb)]·2H_2O	4	NO_3	μ_2-tridentate	$P2_1/c$	3D	71
55	[Zn_2(pht)$_2$(imm)]·3.5H_2O	4,5	N_2O_2, N_2O_3	μ_2-tridentate,μ_2-bidentate	$C2/c$	3D	72
56	[Zn_4(pht)$_4$(tib)$_2$]·2H_2O	4,5,5,5	N_2O_2, NO_4, NO_4,N_2O_3	μ_2-bidentate	$Pca2_1$	2D	73

Neutral compounds whose Zn:pht = 2:1							
57	$[Zn_2(pht)(ppa)(H_2O)]\cdot 2H_2O$	5,6	N_2O_3, N_2O_4	μ_2-bidentate	$P\bar{1}$	1D	74
58	$[Zn_2(pht)(pp)_2(H_2O)]$	6,6	N_4O_2, N_2O_4	μ_4-pentadentate	$P2_1/c$	1D	75
59	$[Zn_2(pht)(tib)Cl_2]$	4,4	N_2O_2, $NOCl_2$	μ_2-bidentate	$P2_1/n$	3D	73
Cationic compounds whose Zn:pht = 2:1							
60	$[Zn_2(pht)(tib)](NO_3)_2$	4	N_3O	μ_2-bidentate	$C2/c$	3D	73
61	$[Zn_2(pht)(tib)_2]I_2$	4	N_3O	μ_2-bidentate	$C2/c$	3D	73
Anionic compounds whose Zn:pht = 1:2							
62	$[1,3\text{-}pnH_2][Zn(pht)_2]$	4	O_4	μ_2-bidentate	$Pbca$	1D	76

Abbreviations: Im= imidazole, metu=N-methylthiourea; 1-MeIm= 1-methylimidazole, β-Pic=3-methylpyridine; γ-Pic=4-methylpyridine; 2-MeIm= 2-methylimidazole, fimp=2-(2-furyl)-1H-imidazo[4,5-f](1,10-phenanthroline); 1-VnIm =1-vinylimidazole; Phen=1,10-phenanthroline; 2,2'-bpy= 2,2'-bipyridine; dpz=dipyrido[3,2-a:2'3'-c]phenazine; μ-4,4'-bpp= 2,2'-bis(4-pyridylmethyleneoxy)-1,10 -biphenylene; bbip=1,1'-(1,4-butanediyl)bis(imidazole-2-phenyl); dmetu=N,N'-dimethyl thiourea; tu= thiourea; 2,3'-tmbpht= 1-((1H-1,2,4-trizol-1-yl)methyl)-3-(3-pyridyl)-5-(2-pyridyl)-1,2,4-trazole; 3,3'-tmbpht= 1-((1H-1,2,4-trizol-1-yl)methyl)-3,5-bis(3-pyridyl)-1,2,4-trazole; 3-dpaa= N,N'-di(3-pyridyl)adipoamide; bdmb= 1,1'-(Biphenyl-4,4'-diyl)bis(methylene)bis(1H-benzimidazole); 4,4'-bpht=1H-3,5-bis(4-pyridyl)-1,2,4-triazole; biim-5=1,1'-(1,5-pentanedidyl)bis(imidazole); 4,4'-bpy= 4,4'-bipyridine; biim-6=1,1'-(1,6-hexane-didyl)bis(imidazole); bmb=1,4-bis(2-methyl benzimidazol-1-ylmethyl); thim= 2,5-bis(imidazol-1-yl)thiophene; mib= 1,4-bis(2-methylimidazole-3-ium-1-yl)biphenyl; imp=3,5-Bis(imidazole-1-yl)pyridine; ib= 1,4-bis(imidazol-1-yl)benzene; tppa= tri(4-pyridylphenyl)amine; bimb= 1,4-bis(imidazol-1-yl-methyl)benzene; Dpq=dipyrido[3,2-d:2',3'-f]quinoxaline; Dpds= 4,4'-Dipyridyldisulfide; tpht= 4'-4(1,2,4-triazol-1-yl)phenyl-2,2':6',2"-terpyridine; bpp=1,3-bis(4-pyridyl)propane; 3,4'-bpht=1H-3-(3-pyridyl)-5-(4-pyridyl)-1,2-4-triazole; pmmi= bis(1,1'-((2,3,5,6-tetramethyl-1,4-phenylene)bis(methylene))bis(2-methyl-1H-imidazole)); ttmt= 1,3,5-tris(1H-1,2,4-triazol-1-ylmethyl)-2,4,6-trimethylbenzene; 4-dpaa= N,N'-di(4-pyridyl)adipoamide; bte=bis(1,2,4-triazole-1-yl)ethane; bib=4,4'-bis(2-methylimidazol-1-ylmethyl)biphenyl; imb=1,4-di(1H-imidazol-4-yl)benzene; imm= tetrakis(imidazol-1-ylmethyl)methane; tib=1,3,5-tris(1-imidazolyl)benzene; ppa=2-[3-(pyridin-2-yl)-1H-pyrazol-1-yl]acetate; pp=3-(2-pyridyl)pyrazole.

In these compounds, the coordination number of Zn varies from 4 to 6 with tetracoordination being the most preferred geometry. Out of seventy nine Zn(II) centres in sixty three structurally characterised compounds, forty eight centres are tetracoordinated (61 %), nineteen pentacoordinated (24 %) and twelve hexacoordinated (15 %). In addition to phthalate ligand these compounds contain neutral N-donor or S-donor ligands like imidazole, pyrazole, pyridine, thiourea etc and their derivatives (Table 1.1). Zn(II) mostly forms mono- or dinuclear phthalates with few tri- and tetranuclear compounds. An analysis of the binding modes of the phthalate reveals that in many of the compounds one oxygen of each of the carboxylate $(\text{-COO})^-$ is bonded in monodentate fashion resulting in net μ_2-bridging bidentate commonly called as 1,6-bridging bidentate coordination mode (Fig. 1.8). Phthalic acid usually forms 1D compounds with Zn(II) metal ion playing a primary role in extending the structure. The N- or S-donor ligands generally functions as monodentate or chelating ligand.

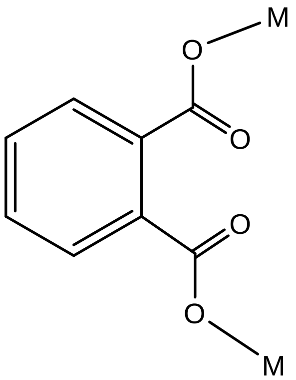


Fig. 1.8 - μ_2-bridging (or 1,6-bridging) bidentate binding mode of phthalate ligand.

The structural details of the phthalates of Ni(II), Co(II) and Cu(II) obtained by a CSD search are given in Table 1.2 [78-100], 1.3 [101-136] and 1.4 [137-185] respectively.

Table 1.2 – Structural details of known nickel(II) phthalate compounds.

No.	Compounds	C.N.	Coordination sphere	Phthalate binding mode	Space Group	Dimensionality	Ni:H_2O ratio	Ref
				Cationic compounds				
2	$[Ni(1\text{-}MeIm)_6]2phtH\cdot 2H_2O$	6	N_6	-	$P2_1/c$	0D	1:4	28
3	$[Ni(1,2\text{-}bib)_2(H_2O)_2]2phtH$	6	N_4O_2	-	$Pbca$	2D	1:2	60
4	$[Ni(Im)_6]pht\cdot H_2O$	6	N_6	-	$P2_1/c$	0D	1:1	78
5	$[Ni(2,2'\text{-}biim)_3]pht$	6	N_6	-	$P2_1/c$	0D	-	79
6	$[Ni(Ettsc)_3]pht\cdot 4H_2O$	6	N_3S_3	-	$P2_1/c$	0D	1:4	80
				Neutral compounds				
7	$[Ni(phtH)_2(H_2O)_2]$	4	O_4	Monodentate	$P2_1/c$	0D	1:2	81
8	$[Ni(phtH)_2(H_2O)_4]\cdot 2H_2O$	6	O_6	Monodentate	$P2_1/c$	0D	1:6	82
9	$[Ni(pht)(Bpybc)(H_2O)_4]\cdot 9H_2O$	6	O_6	Monodentate	$P2_1/c$	0D	1:13	83
10	$[Ni(pht)(en)_2(H_2O)]\cdot 0.5H_2O$	6	N_4O_2	Monodentate	$C2/c$	0D	1:3	84
11	$[Ni(pht)(Im)_3(H_2O)_2]\cdot H_2O$	6	N_3O_3	Monodentate	$P2_1/n$	0D	1:3	78
12	$[Ni(pht)(2\text{-}MeIm)_2(H_2O)_3]\cdot H_2O$	6	N_2O_4	Monodentate	$P\bar{1}$	0D	1:4	78
13	$[Ni(pht)(4\text{-}MeIm)_2(H_2O)]$	6	N_2O_4	μ_2-tridentate	$P2_1/n$	1D	1:1	78
14	$[Ni(pht)(1\text{-}MeIm)_2(H_2O)_3]$	6	N_2O_4	Monodentate	$P\bar{1}$	0D	1:3	85
15	$[Ni(pht)(3\text{-}MePy)_2(H_2O)_3]\cdot H_2O$	6	N_2O_4	Monodentate	$P2_1/c$	0D	1:4	85
16	$[Ni(pht)(Py)_2(H_2O)_3]$	6	N_2O_4	Monodentate	$P2_1/n$	0D	1:3	85
17	$[Ni(pht)(2,2'\text{-}bipy)(H_2O)_3]\cdot H_2O$	6	N_2O_4	Monodentate	$P2_12_12_1$	0D	1:4	86
18	$[Ni(pht)(2,2'\text{-}bipy)(H_2O)_3]$	6	N_2O_4	Monodentate	$P\bar{1}$	0D	1:3	87
19	$[Ni(pht)(4,4'\text{-}bipy)(H_2O)]\cdot 3H_2O$	6	N_2O_4	μ_2-tridentate	$P2_1$	2D	1:4	88
20	$[Ni(pht)(4,4'\text{-}bipy)(H_2O)_2]\cdot 2H_2O$	6	N_2O_4	μ_2-bidentate	$P2/c$	3D	1:4	89
21	$[Ni(pht)(2,2'\text{-}dipa)(H_2O)_3]\cdot 2H_2O$	6	N_2O_4	Monodentate	$P2_1/n$	0D	1:5	90
22	$[Ni(pht)(OxOm)_2]\cdot 4H_2O$	6	N_4O_2	μ_2-bidentate	$P2_1/c$	1D	1:4	91
23	$[Ni(pht)(Tddc)(H_2O)_2]\cdot 4H_2O$	6	N_3O_3	Monodentate	$P\bar{1}$	0D	1:6	92
24	$[Ni(pht)(Dbt)_2]\cdot 3.5H_2O$	6	N_4O_2	bidentate	$P2_1/c$	0D	1:3.5	93
25	$[Ni(pht)(Tpht)_3(H_2O)]$	6	N_3O_3	μ_2-bidentate	$P3_221$	1D	1:1	94
26	$[Ni(pht)(1,10\text{-}Phen)(H_2O)_3]\cdot H_2O$	6	N_2O_4	Monodentate	$P2_1/n$	0D	1:4	90
27	$[Ni(pht)(1,10\text{-}Phen)(H_2O)]\cdot H_2O$	5	N_2O_3	μ_2-bidentate	$Pbcm$	1D	1:2	95

28	$[Ni(pht)(1,10\text{-}Phen)(H_2O)]\cdot H_2O$	5	N_2O_3	μ_2-bidentate	$Pca2_1$	1D	1:2	96
29	$[Ni(pht)(1,10\text{-}Phen)]\cdot 2H_2O$	4	N_2O_2	μ_2-bidentate	$Pbcm$	1D	1:2	66
30	$[Ni(pht)(1,4\text{-}bib)]$	6	N_2O_4	μ_2-tetradentate	$P2_1/n$	2D	-	60
31	$[Ni(pht)(Me_3tsc)_2]\cdot 2H_2O$	6	$N_2S_2O_2$	bidentate	$P2_1/n$	0D	1:2	80
32	$[Ni_2(pht)_2(dpq)_2(H_2O)_4]\cdot 2H_2O$	6,6	N_2O_4, N_2O_4	μ_2-bidentate, μ_2-bidentate	$C2/c$	0D	2:6	98
33	$[Ni_2(pht)_2(4,4'\text{-}dipa)_2(H_2O)_4]\cdot H_2O$	6,6	N_2O_4, N_2O_4	Bidentate, bidentate	$C2/c$	0D	2:5	99
34	$[Ni_2(pht)(bhbhaim)(H_2O)]\cdot 3MeOH$	6,6	N_2O_4, N_2O_4	μ_2-tridentate, μ_2-tridentate	$P2_1/n$	0D	2:1	100
35	$[Ni_2(pht)(hhaim)(H_2O)]\cdot MeOH$	6,6	N_2O_4, N_2O_4	Monodentate, Monodentate	$P2_1/c$	0D	2:1	100

Abbreviations: $pipH_2$= piperazinediium; pht= phthalate dianion; phtH= hydrogen phthalate anion; 1-MeIm= 1-methylimidazole; 1,2-bib= 1,2-bis(imidazol-1-yl-methyl)benzene; Im= imidazole; 2,2'-biim= 2,2'-biimidazole; Ettsc= 4-ethylthiosemicarbazide; Bpybc= 1,1'-bis(4-carboxylatobenzyl)-4,4'-bipyridinium; en= ethylenediamine; 2-MeIm= 2-methylimidazole; 4-MeIm= 4-methylimidazole; 3-MePy= 3-methylpyridine; Py= pyridine; 2,2'-bipy= 2,2'-bipyridine; 4,4'-bipy= 4,4'-bipyridine; 2,2'-dipa= 2,2'-dipyridylamine; OxOm= Oxamide oxime; Tddc= 1,12,15-triaza-3,4:9,10-dibenzo-5,8-dioxacyclohephtadecane; Dbt= 2,2'-Diamino-4,4'-bi-1,3-thiazole; Tpht= 2,4,6-tri(pyridine-4-yl)-1,3,5-triazine; 1,10-Phen= 1,10-Phenanthroline; 1,4-bib= 1,4-bis(imidazol-1-yl-methyl)benzene; Me_3tsc= Methylthiosemicarbazide; dpq= dipyrido[3,2-d:2',3'-f]quinoxaline; 4,4'-dipa= 4,4'dipyridylamine; bhbhaim= (2-(5-bromo-2-hydroxyphenyl)-1,3-bis[4-(5-bromo-2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine); hhaim= (2-(2-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine.

Table 1.3 –Structural details of known cobalt(II) phthalate compounds.

No.	Compounds	C.N.	Coordination sphere	Phthalate binding mode	Space Group	Dimensionality	Co:H_2O ratio	Ref
				Cationic compounds				
2	$[Co(H_2O)_6]2phtH$	6	O_6	-	$P2_1/c$	0D	1:6	101
3	$[Co(H_2O)_6]2phtH$	6	O_6	-	$C2/m$	0D	1:6	102
4	$[Co(H_2O)_6]2phtH$	6	O_6	-	$P2_1/a$	0D	1:6	103
5	$[Co(1\text{-}MeIm)_6]2phtH\cdot 2H_2O$	6	N_6	-	$P2_1/c$	0D	1:2	28
6	$[Co(btp)_2(H_2O)_2]2phtH\cdot 2H_2O$	6	N_4O_2	-	$P\bar{1}$	1D	1:4	104
7	$[Co_2(phtH)_2(1,10\text{-}Phen)_4]2phtH\cdot 2H_2O$	6,6	N_2O_4, N_2O_4	Monodentate, monodentate	$P\bar{1}$	1D	2:2	105
8	$[Co(Pyz)(H_2O)_4]pht$	6	N_2O_4	-	$Immm$	1D	1:4	106
9	$[Co(nicotinamide)_2(H_2O)_4]pht\cdot 2H_2O$	6	N_2O_4	-	$C2/c$	0D	1:6	107
10	$[Co(4,4'\text{-}Bipy)(H_2O)_4]pht\cdot 2H_2O$	6	N_2O_4	-	$P2/c$	1D	1:6	108
				Neutral compounds				
11	$[Co(phtH)_2(4,4'\text{-}Bipy)]$	6	N_2O_4	μ_2-bidentate	$I4_122$	3D	-	109
12	$[Co(pht)(H_2MBP)_2]\cdot EtOH$	6	N_4O_2	μ_2-bidentate	$P2_1/n$	2D	-	110
13	$[Co(pht)(2,2'\text{-}BiIm)_2]$	6	N_4O_2	bidentate	$P2_1/n$	0D	-	111
14	$[Co(pht)(4\text{-}pin)(H_2O)_2]\cdot 2.36H_2O$	6	N_2O_4	bidentate	$P2_1/n$	1D	1:4.36	112
15	$[Co(pht)(ppdox)(H_2O)_2]\cdot 2H_2O$	6	N_2O_4	μ_2-bidentate	$P2_1/c$	1D	1:4	113
16	$[Co(pht)(1,10\text{-}Phen)(H_2O)_3]\cdot H_2O$	6	N_2O_4	Monodentate	$P2_1/n$	0D	1:4	114
17	$[Co(pht)(4,4'\text{-}Bipy)(H_2O)_2]\cdot 2H_2O$	6	N_2O_4	μ_2-bidentate	$P2/n$	2D	1:4	115
18	$[Co(pht)(4\text{-}bpmp)(H_2O)]\cdot 5.5H_2O$	6	N_2O_4	μ_2-tridentate	$P\bar{1}$	2D	1:6.5	116
19	$[Co(pht)(4\text{-}bpfp)(H_2O)_2]\cdot H_2O$	6	N_2O_4	μ_2-bidentate	$P2_1$	2D	1:3	117
20	$[Co(pht)(4,4'\text{-}Bipy)(H_2O)]\cdot 3H_2O$	6	N_2O_4	μ_2-tridentate	$P2_1$	2D	1:4	118
21	$[Co(pht)(tdod)(H_2O)]$	6	N_3O_3	μ_2-bidentate	$P2_1/n$	0D	1:1	119
22	$[Co(pht)(CH_3OH)_2(H_2O)_2]$	6	O_6	μ_2-bidentate	$P2_1/c$	1D	1:2	120
23	$[Co(pht)(1,10\text{-}Phen)(H_2O)]\cdot EtOH$	6	N_2O_4	μ_2-tridentate	$P2_1/n$	1D	1:1	121
24	$[Co(pht)(4,4'\text{-}Bipy)(H_2O)_2]$	6	N_2O_4	μ_2-bidentate	$Pmn2_1$	2D	1:2	122
25	$[Co(pht)(4\text{-}MeIm)_2(H_2O)]$	6	N_2O_4	μ_2-tridentate	$P2_1/n$	1D	1:1	123

26	$[Co(pht)(poa)_{1.5}(H_2O)]$	6	N_3O_3	bidentate	$C2/c$	1D	1:1	124
27	$[Co(pht)(oeim)(H_2O)]\cdot 0.5H_2O$	5	N_2O_3	μ_2-bidentate	$P2_1/n$	1D	1:1.5	125
28	$[Co(pht)(Pyzl)_2]$	4	N_2O_2	μ_2-bidentate	$P2_1/c$	1D	-	126
29	$[Co(pht)(pmbim)]$	4	N_2O_2	μ_2-bidentate	$P\bar{1}$	1D	-	127
30	$[Co(pht)(2\text{-}MeIm)_2]$	4	N_2O_2	μ_2-bidentate	$Pca2_1$	1D	-	128
31	$[Co(pht)(biim\text{-}5)]$	4	N_2O_2	μ_2-bidentate	$Pbca$	2D	-	129
32	$[Co(pht)(bix)]$	4	N_2O_2	μ_2-bidentate	Cc	3D	-	130
33	$[Co(pht)(hbim)]$	4	N_2O_2	μ_2-bidentate	$P2_1/c$	2D	-	131
34	$[Co(pht)(Im)_2]$	4	N_2O_2	μ_2-bidentate	Pn	1D	-	132
35	$[Co(pht)(1\text{-}MeIm)_2]$	4	N_2O_2	μ_2-bidentate	$Pccn$	1D	-	28
36	$[Co(pht)(bimb)]$	4	N_2O_2	μ_2-bidentate	Cc	3D	-	131
37	$[Co(pht)(bimb)]\cdot H_2O$	4	N_2O_2	μ_2-bidentate	$I4_1/a$	3D	1:1	133
38	$[Co(pht)(bmbim)]$	4	N_2O_2	μ_2-bidentate	$P2_1/c$	1D	-	134
39	$[Co(pht)(bim)_2]$	4	N_2O_2	μ_2-bidentate	$C2/c$	1D	-	135
40	$[Co_2(pht)_2(3\text{-}pin)(H_2O)_6]\cdot H_2O$	6,6	N_2O_4, N_2O_4	Monodentate, Monodentate	$P2_1/n$	1D	2:7	112
41	$[Co_2(pht)_2(4\text{-}pn)(H_2O)_6]\cdot 1.12H_2O$	6,6	N_2O_4, N_2O_4	Monodentate, Monodentate	$P2_1/c$	1D	2:7.12	112
42	$[Co_2(pht)_2(apy)_2(H_2O)_6]$	6,6	N_2O_4, N_2O_4	Monodentate, Monodentate	$P2_1/c$	1D	2:6	136
43	$[Co_2(pht)_2(dpa)_2(H_2O)_4]\cdot H_2O$	6,6	N_2O_4, N_2O_4	μ_2-bidentate, μ_2-bidentate	$C2/c$	1D	2:5	99

Abbreviations: pipH_2= piperazinediium; pht= phthalate dianion; phtH= hydrogen phthalate anion;1-MeIm=1-methylimidazole; btp=1,3-bis(1,2,4-triazol-1-yl)propane; 1,10-Phen=1,10-Phenanthroline; Im=imidazole; Pyz=pyrazine; 4,4'-Bipy=4,4'-Bipyridine; H_2MBP= 4,4'-methylene-bispyrazole; 2,2'-BiIm=2,2'-Biimidazole; 4-pin=N-(4-pyridyl)isonicotinamide; ppdox=N,N'-bis(pyridine-3-yl)pyridine-2,6-dicarboxamide; 4-bpmp= bis(4-pyridylmethyl)piperazime; 4-bpfp=bis(4-pyridylformyl)piperazine; tdod=1,12,15-triiaza-3,4:9,10-dibenzo-5,8-dioxacyclo hephtadecane; 4-MeIm=4-methylimidazole; poa=N,N'-bis(pyridine-3-yl)octanediamide; oeim=1,1'-(2,2'-oxybis(ethane-2-1-diyl))bis(1H-imidazole); Pyzl=pyrazole; pmbim= 1,1'-(1,3-propane)bis(2-methylbenzimidazole); 2-MeIm=2-methylimidazole; biim-5=1,1'-(1,5-pentanediyl)bis(imidazole); bix=1,4-bis(imidazol-1-yl-methylene)-benzene; hbim=1,1'-(1,4-hexanediyl)bis(imidazole); bimb=1,4-bis(imidazol-1-yl-methyl)-benzene; bmbim=1,1'-(biphenyl-4,4'-diyl)bis(methylene)bis(1H-benzimidazole); bim=benimidazolate; 3-pin=N-(3-pyridyl)isonicotinamide; 4-pn=N-(4-pyridyl)nicotinamide; apy=4,4'-Azopyridine; dpa=4,4'-Dipyridylamine.

Table 1.4 - Structural details of known copper(II) phthalate compounds.

No.	Compounds	C.N.	Coordination sphere	Phthalate binding mode	Space Group	Dimensionality	$Cu:H_2O$ ratio	Ref
	Anionic compounds							
2	$[Cu(dap)_2(H_2O)_2][Cu(pht)_2(dap)_2]$	6,6	N_4O_2, N_4O_2	Monodentate, Monodentate	*Pī*	0D	-	137
	Cationic compounds							
3	$[Cu(Dpds)_2(H_2O)_2]2phtH \cdot H_2O$	6	N_4O_2	-	$Pna2_1$		1:3	138
4	$[Cu(Daf)_2(H_2O)_2]2phtH$	6	N_4O_2	-	$P2_1/a$		1:2	139
5	$[Cu(phtH)(Abpht)_2]2phtH$	6	N_4O_2	-	$P2_1/c$		-	140
6	$[Cu_2(pht)(deta)_2(ClO_4)]ClO_4$	5,6	N_3O_2, N_3O_3	μ_2-bidentate, μ_2-bidentate	$P2_1$	0D	-	141
7	$[Cu_2(phtH)_2(1,10\text{-}Phen)_2(NO_3)(H_2O)]NO_3 \cdot 2H_2O$	5,5	N_3O_2, N_3O_2	Monodentate, Monodentate	$P2_1/n$	0D	2:1	142
8	$[Cu_2(pht)_2(H4\text{-}bpmp)_2(H_2O)_2]2NO_3 \cdot H_2O$	5,5	N_2O_3, N_2O_3	μ_2-bidentate, μ_2-bidentate	P_1	2D	2:3	143
9	$[Cu_2(pht)_2(H4\text{-}bpmp)_2(H_2O)_2]2SO_4 \cdot 2H_2O$	5,5	N_2O_3, N_2O_3	μ_2-bidentate, μ_2-bidentate	P_1		2:4	143
10	$[Cu(Daf)_2(H_2O)_2]2phtH$	4	N_2O_2	-	$P2_1/c$		1:2	144
	Neutral compounds							
11	$[Cu(phtH)_2(H_2O)_2]$	6	O_6	μ_2-bidentate	$P2_1/c$	1D	1:2	145
12	$[Cu(phtH)_2(H_2O)_2]$	4	O_4	Monodentate	$P2_1/c$	0D	1:2	146
13	$[Cu(phtH)_2(1\text{-}MeIm)_2]$	4	N_2O_2	μ_2-bidentate	$C2/c$	1D	-	147
14	$[Cu(pht)(Pap)] \cdot EtOH \cdot H_2O$	6	N_5O	Monodentate	$C2/c$		1:1	148
15	$[Cu(pht)(4,4'\text{-}Bipy)(H_2O)_2] \cdot 2H_2O$	6	N_2O_4	μ_2-bidentate	$P2/c$	2D	1:4	149
16	$[Cu(pht)(Im)_2]$	6	N_2O_4	μ_2-tetradentate	$Pna2_1$	1D	-	150
17	$[Cu(pht)(H_2O)_3]$	5	O_5	μ_3-tridentate	$P2_1$		1:2	151
18	$[Cu(pht)(H_2bbbz)] \cdot phtH_2$	5	N_3O_2	μ_2-bidentate	*Pī*		-	152
19	$[Cu(pht)(3\text{-}bpfp)(H_2O)] \cdot 2H_2O$	5	N_2O_3	μ_2-bidentate	Pc	3D	1:3	153
20	$[Cu(pht)(Deta)] \cdot 0.5CH_3OH$	5	N_3O_2	μ_2-bidentate	$I2/a$	1D	-	154
21	$[Cu(pht)(1,10\text{-}Phen)(H_2O)] \cdot 0.5H_2O$	5	N_2O_3	μ_2-bidentate	$Pbcm$	1D	1:1.5	155

22	[Cu(pht)(1,10-Phen)(H$_2$O)]·CH$_3$OH	5	N$_2$O$_3$	μ_2-bidentate	*Pbcm*		1:1	156
23	[Cu(pht)(1,10-Phen)$_2$]·2EtOH·3H$_2$O	5	N$_4$O	Monodentate	$P\bar{1}$	0D	1:3	157
24	[Cu(pht)(1,10-Phen)(H$_2$O)]·H$_2$O	5	N$_2$O$_3$	μ_2-bidentate	*Pbcm*	1D	1:2	158
25	[Cu(pht)(1,10-Phen)(H$_2$O)]·H$_2$O	5	N$_2$O$_3$	μ_2-bidentate	$Pca2_1$	1D	1:2	159
26	[Cu(pht)(terpyOH)]·H$_2$O	5	N$_3$O$_2$	μ_2-bidentate	$P2_1/c$	1D	1:1	160
27	[Cu(pht)(Nic)$_2$(H$_2$O)]·0.5H$_2$O	5	N$_2$O$_3$	μ_2-bidentate	$P2_1/c$	1D	1:1.5	161
28	[Cu(pht)(Py)$_2$]	5	N$_2$O$_2$	μ_2-bidentate	$P2_1/c$	1D	-	162
29	[Cu(pht)(2,2’-BiPy)(H$_2$O)]·3.5H$_2$O	5	N$_2$O$_3$	μ_2-bidentate	$P2_1/c$	1D	1:4.5	163
30	[Cu(pht)(4-MeIm)$_2$(H$_2$O)]	5	N$_2$O$_3$	μ_2-bidentate	$P2_1/n$	1D	1:1	123
31	[Cu(pht)(Dpk)]·0.33CH$_3$OH	5	N$_2$O$_3$	μ_3-tridentate	*R-3*	3D	-	164
32	[Cu(pht)(Bpnd)]	5	N$_3$O$_2$	μ_2-bidentate	C2/c	2D	-	165
33	[Cu(pht)(HPz)$_2$]·CH$_2$Cl$_2$	5	N$_2$O$_3$	μ_3-tridentate	$P2_1/c$	2D	-	166
34	[Cu(pht)(Ammonium)$_2$]	4	N$_2$O$_2$	μ_2-bidentate	$P2_1/c$	1D	-	167
35	[Cu(pht)(isoconazole)$_2$]	4	N$_2$O$_2$	μ_2-bidentate	$P2_1/n$	1D	-	168
36	[Cu(pht)(1-MeIm)$_2$]	4	N$_2$O$_2$	μ_2-bidentate	*C2/c*	1D	-	28
37	[Cu(pht)(1-VIm)$_2$]	4	N$_2$O$_2$	μ_2-bidentate	*C2/c*	1D	-	169
38	[Cu(pht)(Isonic)$_2$]·H$_2$O	4	N$_2$O$_2$	μ_2-bidentate	$P2_1/n$	1D	1:1	170
39	[Cu$_2$(pht)$_2$(H$_2$O)$_2$]	6,6	O$_6$, O$_6$	μ_2-bidentate, μ_2-bidentate	*B112/b*	3D	2:2	171
40	[Cu$_2$(pht)$_2$(4-pmpmd)$_2$(CH$_3$OH)$_2$]·2H$_2$O	6,6	N$_2$O$_4$	Monodentate, Monodentate	*Ibca*	3D	2:2	172
41	[Cu$_2$(pht)$_2$(4-pmpmd)$_2$(H$_2$O)$_2$]·2H$_2$O	6,6	N$_2$O$_4$	μ_2-bidentate, μ_2-bidentate	*Ibca*	3D	2:4	173
42	[Cu$_2$(pht)$_2$(2,2’-Bipy)$_2$]·4H$_2$O	5,5	N$_2$O$_3$	μ_2-tridentate, μ_2-tridentate	$P2_1/n$	0D	2:4	173
43	[Cu(pht)(2,2’-Bipy)(H$_2$O)]·3.5H$_2$O	5	N$_2$O$_3$	μ_2-bidentate	$P2_1/c$	1D	2:4	174
44	[Cu$_2$(pht)$_2$(2,2’-Bipy)$_2$]·4H$_2$O	5,5	N$_2$O$_3$, N$_2$O$_3$	μ_2-tridentate, μ_2-tridentate	$P2_1/n$	0D	2:4	175
45	[Cu$_2$(pht)$_2$(Im)$_4$(H$_2$O)]·H$_2$O	5,5	N$_2$O$_3$, N$_2$O$_3$	μ_2-bidentate, μ_3-tridentate	$P2_1/n$	3D	2:2	176
46	[Cu$_2$(pht)$_2$(4-bpfp)(H$_2$O)$_2$]	5,5	NO$_4$, NO$_4$	μ_2-bidentate, μ_2-bidentate	$P\bar{1}$	2D	2:2	117
47	[Cu$_2$(pht)$_2$(Dpa)]·H$_2$O	5,5	NO$_4$, NO$_4$	μ_2-tridentate, μ_2-tridentate	$P6_5$	1D	2:1	124
48	[Cu$_2$(pht)$_2$(HPz)$_4$]·0.5H$_2$O	5,5	N$_2$O$_3$, N$_2$O$_3$	μ_2-tridentate, μ_2-tridentate	$P2_1/n$	2D	2:0.5	166
49	[Cu$_2$(pht)$_2$(4-MePy)$_4$(H$_2$O)]	4,5	N$_2$O$_2$, N$_2$O$_3$	μ_2-bidentate, μ_2-bidentate	$P\bar{1}$	1D	2:1	177
50	[Cu$_2$(pht)$_2$(Im)$_2$]·3H$_2$O	4,4	N$_2$O$_2$, N$_2$O$_2$	μ_2-bidentate, μ_2-bidentate	*Pbca*	1D	2:3	28
51	[Cu$_2$(pht)$_2$(HPz)$_2$]	4,4	N$_2$O$_2$, N$_2$O$_2$	μ_2-bidentate, μ_2-bidentate	$P\bar{1}$	1D	-	166

52	$[Cu_2(pht)_2(4\text{-}pmpmd)_2]\cdot 2H_2O$	4,4	N_2O_2, N_2O_2	Monodentate, Monodentate	*Ibca*	3D	2:2	172
53	$[Cu_4(pht)_4(Btm)_6]\cdot 4DMF\cdot 3H_2O$	5,5, 5,5	N_2O_3, N_2O_3, N_2O_2P, N_2O_2P	μ_2-bidentate, μ_2-bidentate, μ_2-bidentate, μ_2-bidentate	*Pnma*	2D	4:3	178
54	$[Cu(pht)_2(4\text{-}bpfp)(H_2O)_2]\cdot 2H_2O$	5,6	N_2O_5, N_2O_6	μ_3-tridentate, μ_3-tridentate	$P2_1/c$	3D	1:2	153
55	$[Cu\ (pht)_6(HPz)_3]\cdot 3.5HPz\cdot H_2O$	6	N_4O_2	μ_2-bidentate	$P2_1/n$	1D	3:1	166
56	$[Cu_2(pht)(phtH)_2(3\text{-}bpmp)_2(H_2O)_2]\cdot 3H_2O$	6,4	N_2O_4, N_2O_2	Monodentate, Monodentate	$P\bar{1}$	1D	2:4	179
57	$[Cu_2(pht)(terpyridine)_2Cl]\cdot 4H_2O$	5,5	N_3OCl, N_3OCl	Monodentate	$P\bar{1}$	0D	2:4	180
58	$[Cu_2(pht)(terpyO)_2(H_2O)_2]\cdot 11H_2O$	5,5	N_3O_2	μ_2-bidentate	$P\bar{1}$	1D	2:13	160
59	$[Cu_2(pht)(Bpca)_2(H_2O)]\cdot 5H_2O$	5,5	N_3O_2, N_3O_2	μ_3-tridentate, μ_3-tridentate	*C2/c*	1D	2:6	181
60	$[Cu_2(pht)(Bapo)]\cdot 4H_2O$	5,5	N_2O_3, N_2O_3	μ_2-bidentate, μ_2-bidentate	*C2/c*	3D	2:4	182
61	$[Cu_2(pht)(Oxen)]\cdot 2H_2O$	5,5	N_2O_3, N_2O_3	μ_2-tetradentate, μ_2-tetradentate	$Pca2_1$	2D	2:2	183
62	$[Cu_2(pht)(Oxpn)]\cdot 2H_2O$	5,4	N_3O_2, N_2O_2	μ_2-bidentate, μ_2-bidentate	$P2_1/c$	1D	2:2	184
63	$[Cu_2(pht)(Dasa)_2]\cdot 3H_2O$	4,4	N_2O_2, N_2O_2	μ_2-bidentate	$P2_1/c$	0D	2:3	185

Abbreviations: $pipH_2$= piperazinediium; pht= phthalate dianion; phtH= hydrogen phthalate anion;dap= 1,3-diaminopropane; Dpds= Di-4-pyridyl disulfide; Daf= 4,5-diazaflouren-9-one; Abpht= 4-Amino-3,5-bis(pyridine-2-yl)-4H-1,2,4-triazole; deta= Diethyltriamine; Phen= 1,10-Phenanthroline; H4-bpmp= 1,4-bis(pyridin-4-ylmethyl)piperazin-1-ium; 1-MeIm= 1-Methylimidazole; Pap=1,2R,3,4S,5-Pentaaminopentane; 4,4'-Bipy= 4,4'-Bipyridine; Im= Imidazole; H_2bbbz= 1,2-bis(benzimidazolyl) benzene; 3-bpfp= (3-pyridylformyl)piperazine; terpyO= 4'-hydroxy-2,2':6',2"-terpyridine; Nic= Nicotinamide; Isonic= isonicotinamide; Py= Pyridine; 2,2'-Bipy= 2,2'-Bipyridine; 4-MeIm= 4-Methylimidazole; Dpk= 4,4'-dipyridylketone; Bpnd= N,N'-bis(pyridine-3-yl)naphthalene-1,4-dicarboxamide-N^3:$N^{3'}$; HPz= Pyrazole; 1-VIm= 1-vinyl-1*H*-imidazole; 4-pmpmd = 2,6-Bis(4-pyridinylmethyl)benzo[1,2-c:4,5']dipyrrole-1,3,5,7-(2*H*,6*H*)-tetrone; 4-bpfp= (4-pyridylformyl)piperazine; Dpa= 4,4'dipyridylamine; 4-MePy= 4-Methylpyridine; Btm= bis(1,2,4-triazol-1-yl)methane; 3-bpmp= N.N'-bis(3-pyridylmethyl)piperazine; Bpca= bis(2-pyridylcarbonyl)amide anion; Bapo= N,N'-bis(2-aminopropyl)oxamide; Oxen= N,N'-bis(2-aminoethyl)oxamide; Oxpn= N,N'-bis(2-aminopropyl)oxamide; Dasa= N-(2-diethylaminoethyl)salicyldenaminato.

The phthalates of nickel, cobalt and copper exhibit similar structural features like their zinc counterparts described earlier. Of the known thirty four Ni(II) phthalates, twenty nine are neutral (85 %) and the rest (15 %) are cationic. The analysis of Co(II) phthalates shows that out of forty three compounds thirty three are neutral (77 %) and remaining ten are cationic. In case of Cu(II), an anionic compound is reported with cationic metal containing species for charge balance. Fifty three (86 %) compounds out of sixty two Cu(II) phthalates are neutral and eight (13 %) are cationic. Like in Zn(II), majority (more than 80 %) of the structurally characterized nickel / cobalt / copper phthalates crystallize in one of the centrosymmetric space groups viz. $P2_1/c$, $P2_1/n$, $P\bar{1}$, $P2/c$, $Pbcm$, $Pbca$, $C2/c$, $P2_1/a$, $C2/m$, $Pccn$, $Immm$, $I4_1/a$, $Ibca$, $Pnma$, $R\text{-}3$, $B112/b$ and the rest in non-centrosymmetric space groups viz. $P2_12_12_1$, $P2_1$, Cc, Pn, $Pnc2$, $Pna2_1$ and $Pca2_1$. Unlike Zn, Ni(II) and Co(II) prefer hexacoordination while Cu(II) exhibits pentacoordination. Out of thirty eight Ni(II) centres in thirty four structurally characterised compounds, two centres (5 %) are tetracoordinated, two (5 %) pentacoordinated and thirty four (90 %) hexacoordinated. Likewise, out of forty eight Co(II) centres in forty three structurally characterised compounds, twelve centres (25 %) are tetracoordinated, one (2 %) pentacoordinated and thirty five hexacoordinated (73 %). In sixty two structurally characterised Cu(II) phthalates with ninety one metal centres, nineteen centres are tetracoordinated (21 %), fifty three pentacoordinated (58 %) and nineteen hexacoordinated (21 %). These metal ions mostly form mono- and dinuclear compounds.

Ni(II), Co(II) and Cu(II) metal ions generally form several hydrated compounds containing coordinated and lattice water molecules (Fig. 1.9-1.11).

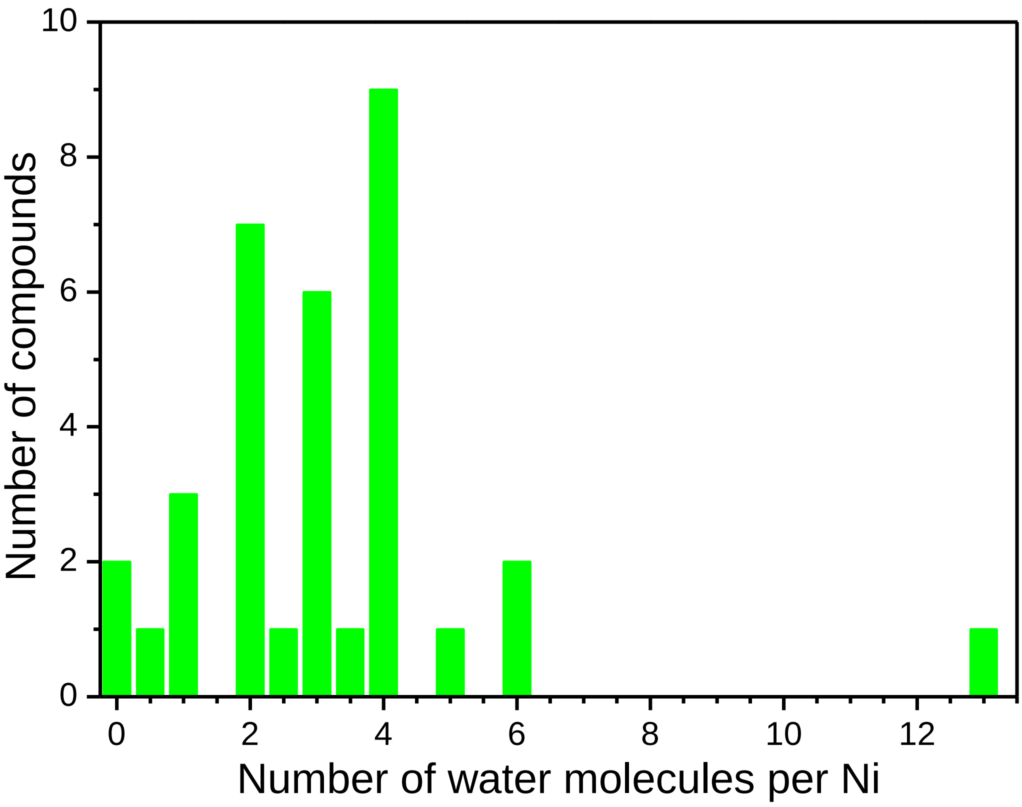


Fig. 1.9 – Degree of hydration of Ni(II) phthalates.

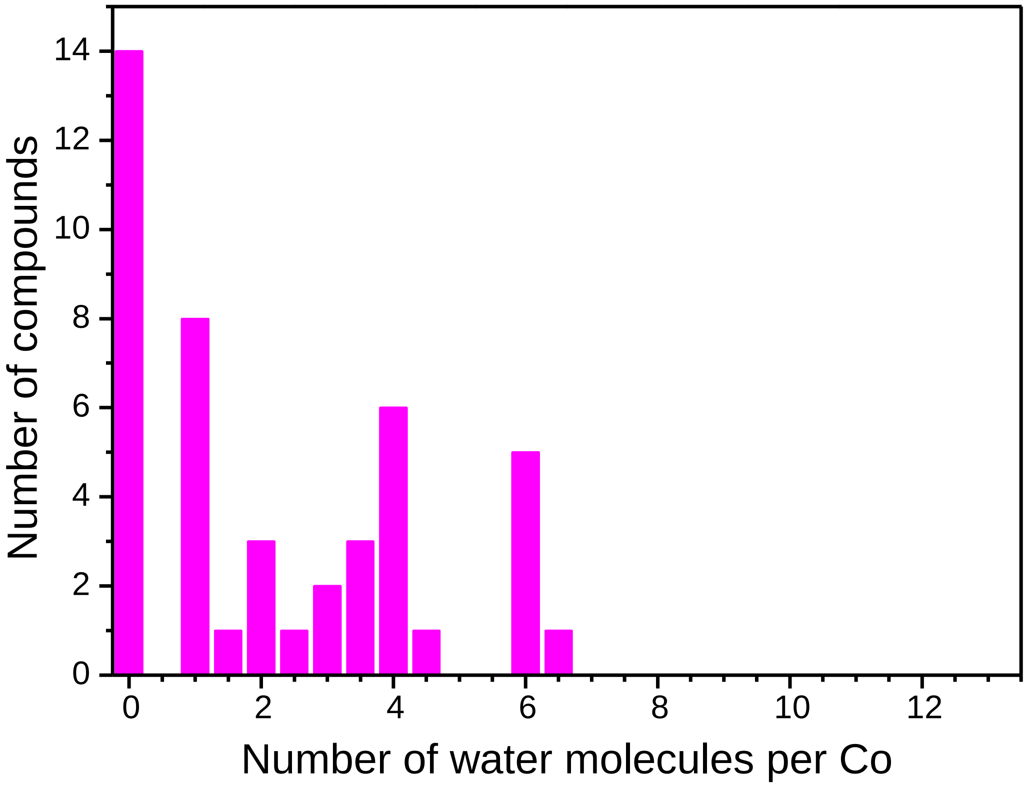


Fig. 1.10 – Degree of hydration of Co(II) phthalates.

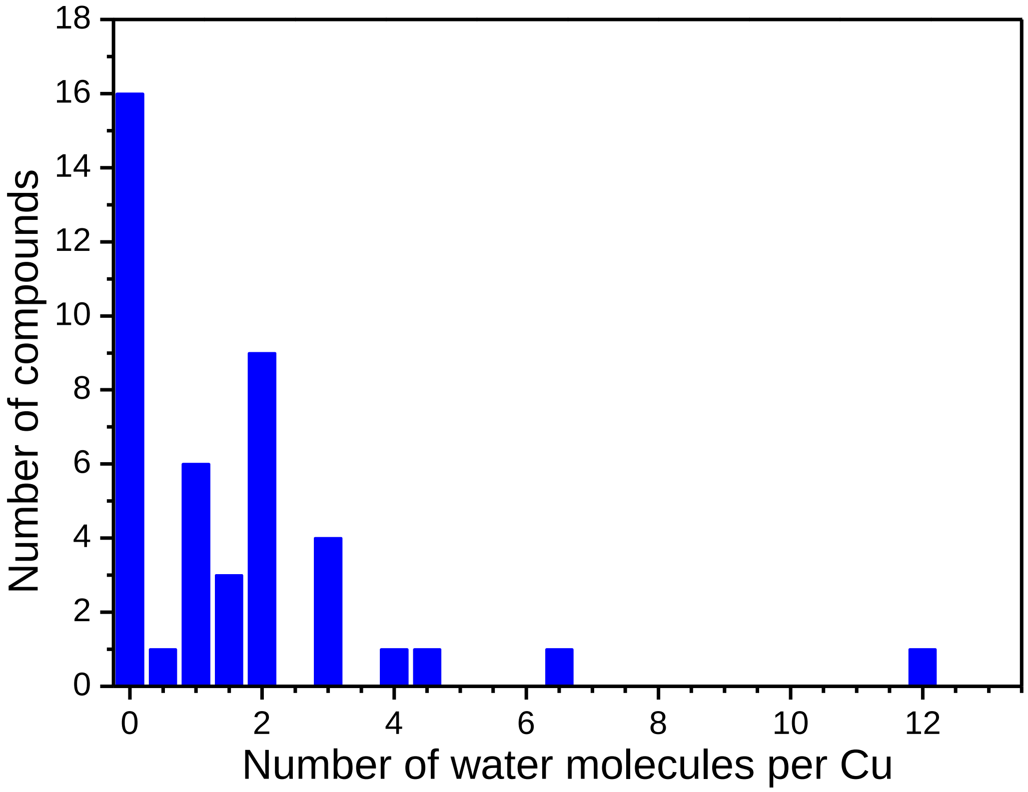
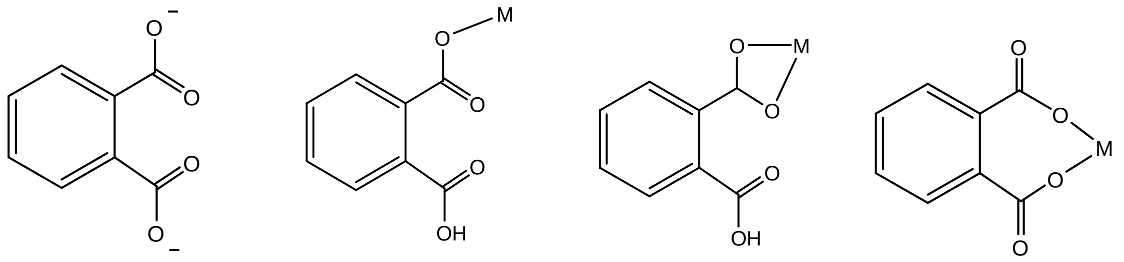


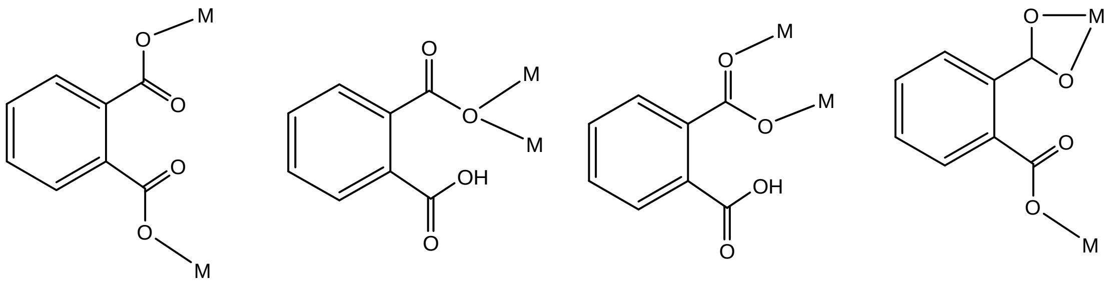
Fig. 1.11 – Degree of hydration of Cu(II) phthalates.

The binding mode of phthalate can be correlated to the degree of hydration. In the compounds with M^{2+}: H_2O ratio more than 1:4, the phthalate ligand which exhibits bridging bidentate binding mode instead functions as a monodentate ligand with only one $(–COO)^-$ group binding to metal ion and the other $(–COO)^-$ group is free. This is due to the fact that the coordination requirement of the central metal ion is satisfied by the aqua ligands which can probably explain the monodentate binding mode of phthalate.

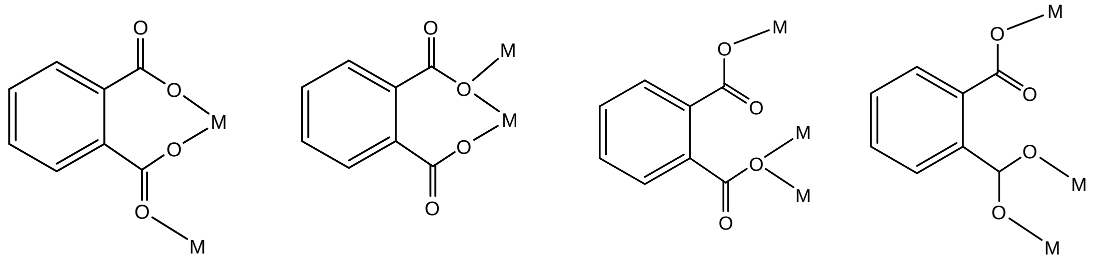
The phthalate ligand exhibits a variety of binding modes (Fig. 1.12) with Zn(II), Ni(II), Co(II) and Cu(II) metal ions.



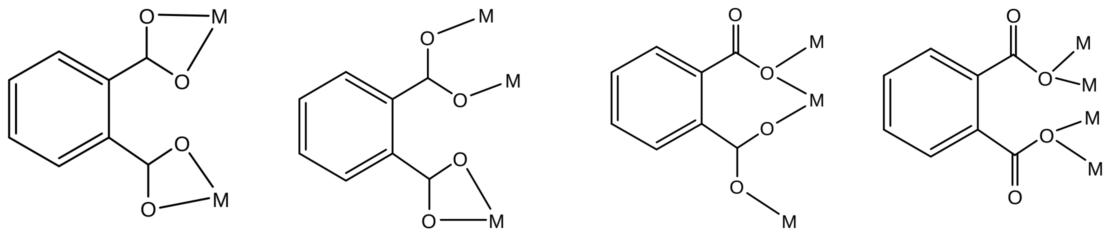
Free phthalate (A) Monodentate (B) Bidentate (C) Bidentate (D)



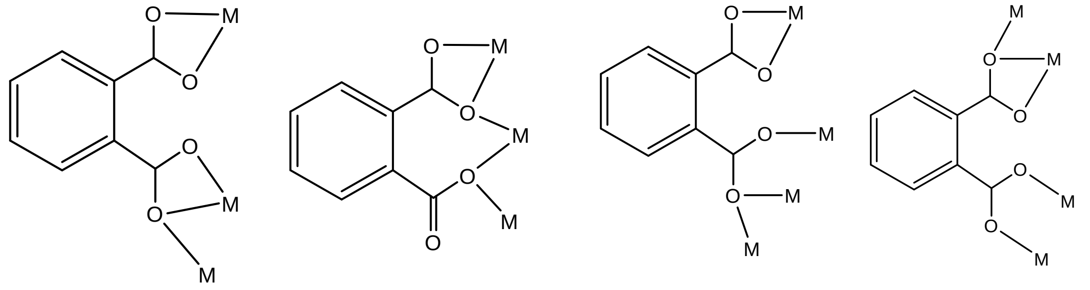
μ_2-bidentate (E) μ_2-bidentate (F) μ_2-bidentate (G) μ_2-tridentate (H)



μ_2-tridentate (I) μ_2-tridentate (J) μ_3-tridentate (K) μ_3-tridentate (L)



μ_2-tetradentate (M) μ_3-tetradentate (N) μ_3-tetradentate (O) μ_4-tetradentate (P)



μ_3-pentadentate (Q) μ_3-pentadentate (R) μ_4-pentadentate (S) μ_4-pentadentate (T)

Fig. 1.12 - Different modes of binding of the phthalate anion with first row bivalent metals.

The free phthalate acts as a charge balancing anion. The phthalate ligand possess four O-donor sites from two $(–COO)^-$ groups. Phthalate exhibits mono-, bi-, tri-, tetra- and pentadentate binding modes. It can display five different bidentate binding modes of which three are bridging (mode E, F and G). Two bidentate binding modes (mode C and D) results in chelation where two oxygens of either same $(–COO)^-$ group or adjacent $(–COO)^-$ groups are involved. Five different types of tridentate binding modes involving three monodentate oxygens (mode L) or one monodentate-one bidentate oxygen (mode H, I, J and K) are observed. Phthalate also shows μ_2- (mode M) , μ_3- (mode N and O) and μ_4-tetradentate (mode P) binding mode. It displays μ_3- (mode Q and R) and μ_4-pentadentate (mode S and T) binding modes. The binding modes (mode D, I, J, O and R) involving a common metal atom shared between two $(–COO)^-$ groups is a consequence of *-ortho* positioning of two carboxylates in phthalate ligand.

In compounds which contain both coordinated and free (lattice) water molecules, the H-bonding among lattice water molecules lead to the formation of water clusters. The crystal host provides the lattice space for the stabilization of variety of supramolecular water architecture. These water clusters in turn have profound influence on the overall stabilization of the crystal structure. Extensive experimental and theoretical structural investigations of water molecules have been carried out for diverse water patterns present in nature and importantly due to fundamental importance in human life and in biological and chemical processes [186-187]. The H-bonding interactions among lattice water molecules can form i) discrete water clusters viz. dimer, tetramer, hexamer, octamer, decamer etc [188]; ii) 1D water chains or tapes [189]; ii) 2D layers with ring structures [190] or iii) 3D water cluster networks [191]. The water rich compounds with flexible framework hold their very important material properties and are usually observed to show reversible change in their structures and properties in response to external stimuli especially temperature [192-193].

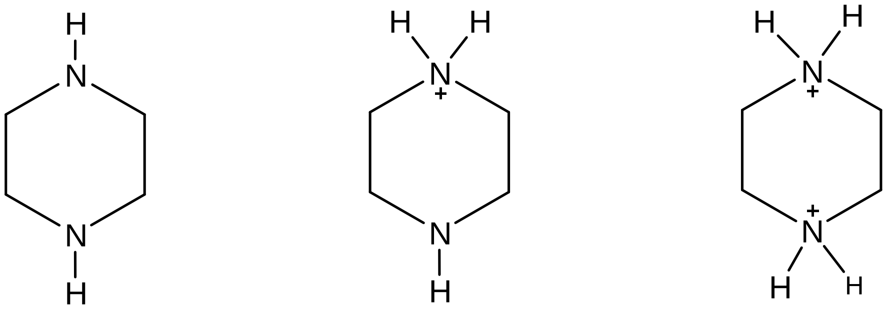
In view of the availability of very few anionic phthalates in the literature, the present work has been undertaken. As mentioned earlier for the synthesis of metal bis(phthalato) compounds, an organic amine viz. piperazine (pip) is chosen to serve as i) charge balance and ii) structure directing agent. Piperazine is considered to be a good candidate as it is well documented (Table 1.5) to act as a charge balancing cation cum structure directing agent [194-206].

Table 1.5 – Structural details of known piperazinediium compounds

S.No	Compound	Space group	Secondary interactions	Ref.
1	$(pipH_2)[MoS_4]$	$P2_1/c$	N–H···S, C–H···S	194
2	$(pipH_2)[WS_4]$	$P2_1/c$	N–H···S, C–H···S	195
3	$(pipH_2)[Cr_2O_7]$	$P2_1/c$	N–H···O, C–H···O	196
4	$(pipH_2)[CdBr_4]\cdot H_2O$	$P2_1/c$	N–H···O, N–H···Br, O–H···Br	197
5	$(pipH_2)[S_2O_3]\cdot H_2O$	$P2_1/c$	N–H···O, N–H···S, O–H···O, O–H···S, C–H···O, C–H···S	198
6	$(pipH_2)(phtH)_2\cdot 2H_2O$	$P2_1/c$	N–H···O, C–H···O, O–H···O	199
7	$(pipH_2)[Zn(pht)_2]\cdot H_2O$	$P2_1/c$	N–H···O, C–H···O, O–H···O	200
8	$(pipH_2)[CrO_4]$	$P2_1/n$	N–H···O, C–H···O	201
9	$(pipH_2)[SeO_4]\cdot H_2O$	$P2_1/n$	N–H···O, O–H···O	202
10	$(pipH_2)[SO_4]\cdot H_2O$	$P2_1/n$	N–H···O, O–H···O, C–H···O	203
11	$(pipH_2)[CoCl_4]\cdot H_2O$	$P2_1/a$	N–H···Cl, O–H···Cl, C–H···Cl	204
12	$(pipH_2)[ZnBr_4]$	$P2_12_12_1$	N–H···Br	205
13	$(pipH_2)[ZnI_4]$	$P2_12_12_1$	N–H···I	205
14	$(pipH_2)[HgBr_4]$	$P2_12_12_1$	N–H···Br	205
15	$(pipH_2)[HgI_4]$	$P2_12_12_1$	N–H···I	205
16	$(pipH_2)[CdI_4]$	$P2_12_12_1$	N–H···I	197
17	$(pipH_2)[CoCl_4]$	$P2_12_12_1$	N–H···Cl	206
18	$(pipH_2)\ [Ni(mal)_2(H_2O)_2]$	$P\bar{1}$	N–H···O, C–H···O, O–H···O	206
19	$(pipH_2)[Co(mal)_2(H_2O)_2]$	$P\bar{1}$	N–H···O, C–H···O, O–H···O	206
20	$(pipH_2)[Cu(mal)_2(H_2O)_2]\cdot 2H_2O$	$P\bar{1}$	N–H···O, C–H···O, O–H···O	206

Abbreviations: $pipH_2$= piperazine dication, phtH= hydrogen phthalate, mal= malonate.

In addition to forming a dication viz. piperazinediium as in Table 1.5, pip can form a monocation called as piperazinium (Fig. 1.13). Piperazine is a well known structure directing species via secondary interactions. The H atoms attached to N of pip (>N-H) can function as good H-donor towards oxygen, sulphur and halogens.



Piperazine (pip) Piperaziniium (pipH)$^{+}$ Piperaziendiium (pipH$_2$)$^{2+}$

Fig. 1.13 - Piperazine and the two cations formed by piperazine.

The recent studies have shown that the coordination polymers of *s*-block metal ions have numerous advantages over *d*-block metal ions [207-208]. Although *s*-block metal cations lack properties like magnetism and variable oxidation states shown by *d*-block metal ions because of closed shell configuration these are preferred due to easy method of preparation, solubility, ready availability of starting materials and their commercial importance. The alkali and alkaline-earth metal ions are typically used in pharmaceutical, dyes and pigment industries for their advantage of non-toxicity, low cost and solubility in aqueous medium. The use of *s*-block metal ions is quite challenging due to numerous possible coordination geometries due to lack of ligand field stabilization effect seen in transition metal which makes the structural chemistry much more interesting but difficult and unpredictable. The alkali and alkaline-earth metal cations form strong binding interaction with carboxylate oxygen atoms due to their affinity for O-donor ligands, ionic nature and high charge density.

A list of phthalate compounds of *s*-block metal ions [209-229] retrieved from the CSD is given in Table 1.6.

Table 1.6 – List of *s*-block metal phthalates

S.No	Compound	Space group	References
1	$[Li(phtH)]\cdot 2H_2O$	$Pnma$	209
2	$[Li(phtH)]\cdot H_2O$	$P\bar{1}$	210
3	$[Li(phtH)]\cdot CH_3OH$	$P\bar{1}$	211
4	$[Na_2(pht)]\cdot 3.5H_2O$	$Pbca$	212
5	$[Na(phtH)]\cdot 0.5H_2O$	$Aba2$	213
6	$[K_2(pht)]\cdot H_2O$	$Pbca$	214
7	$[K(phtH)]$	$P2_1ab$	215
8	$[K(phtH)]\cdot 0.5H_2O_2$	$Pbca$	216
9	$[K(C_{16}H_{11}O_8)^{1-}(H_2O)_2]n$	$C2/c$	217
10	$[Rb(phtH)]$	$P2_1ab$	213
11	$[Rb(C_{16}H_{11}O_8)^{1-}]\cdot 2H_2O$	$C2/c$	218
12	$[Rb(phtH)]$	$P2_122_1$	219
13	$[Cs(C_{16}H_{11}O_8)^{1-}]$	$Pbcn$	220
14	$[Cs(phtH)]$	$P2_12_12_1$	219
15	$[Cs(phtH)]$	$Pca2_1$	221
16	$[Mg(H_2O)_6(phtH)_2]$	$P2_1/c$	222
17	$[Mg(H_2O)_6(phtH)_2]\cdot 2H_2O$	$P\bar{1}$	222
18	$[Mg(H_2O)_4(phtH)_2(CH_3OH)_2]$	$P2_1/c$	223
19	$[Ca(pht)]\cdot H_2O$	$P2_1/c$	224
20	$[Ca(pht)(H_2O)]$	$P2_1/c$	225
21	$[Ca(pht)]$	$P2_1/m$	226
22	$[Sr(phtH)_2]\cdot 2H_2O$	$Cmc2_1$	227
23	$[Ba(phtH)_2]$	$P2_1/c$	228
24	$[K_{0.78}Na_{1.22}(pht)_2]\cdot H_2O$	$P\bar{3}1c$	229

It is observed that the metal ions are differently hydrated. The hydrogen phthalates of K, Rb and Cs are isostructural and crystallise in the non-centrosymmetric space group $P2_1ab$. Amongst all, sodium hydrogen phthalate hemihydrate ($NaHpht\cdot{}^1/_2H_2O$) and potassium hydrogen phthalate (KHpht) are well explored as non linear optical (NLO) crystals for their second harmonic generation (SHG) properties which is of current interest due to their wide applications. $NaHpht\cdot½H_2O$ is easily prepared in laboratory by an aqueous reaction of phthalic acid with $NaHCO_3$ in 1:1 molar ratio. The anhydrous KHpht is a commercially available compound and is employed as a standard in titrimetry. The compounds $NaHpht\cdot½H_2O$ and KHpht crystallise in the non-centrosymmetric orthorhombic space groups *Aba2* [213] and *P2$_1$ab* [215] respectively. It is thus seen that although both are monovalent and are from the same group they differ completely in their structures and more importantly the degree of hydration.

The structure of sodium hydrogen phthalate (NaHpht·½H_2O) hemihydrate was described as early as 1975 by Smith [213] and constitutes of an unique sodium ion, an independent hydrogen phthalate ion and a water molecule shared by a pair of sodium ions. The Na^+ ion is surrounded by six O-atoms, four from the ionized carboxyl groups, one from an unionized carboxyl group and one from the water molecule. The molecules are joined through an O–H···O hydrogen bond between the water molecule and two oxygen atoms of the ionized carboxylic group. NaHpht·½H_2O exhibits a two-dimensional (2D) polymeric structure in which the hydrogen phthalate anion functions as a μ_4-bridging pentadentate ligand (Fig. 1.14). The water molecule located on a special position functions as a μ_2-bridging bidentate ligand resulting in hexacoordination around the central metal.

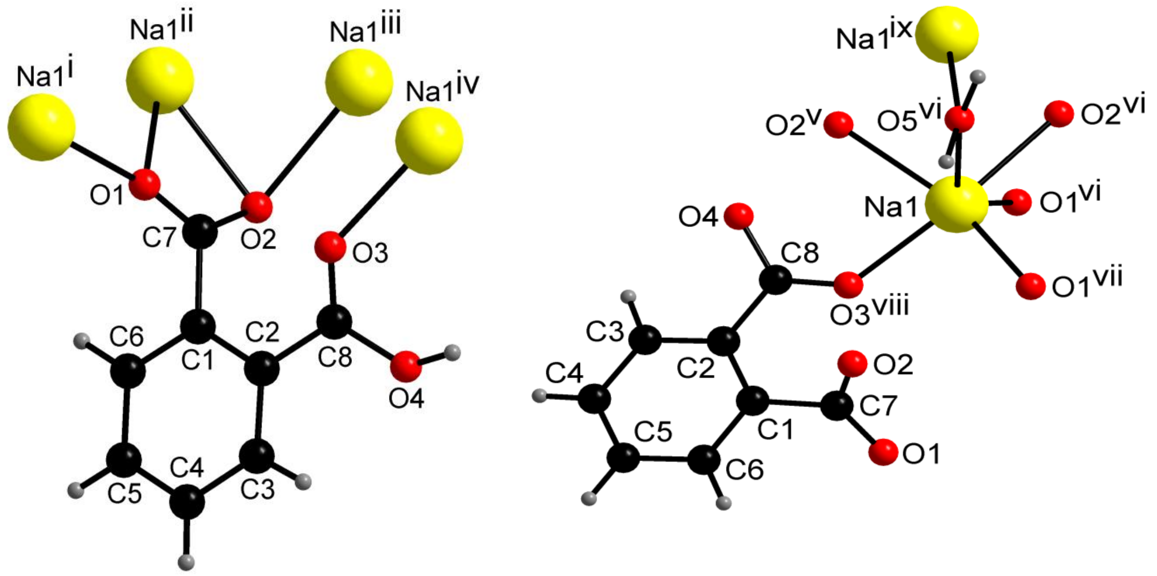


Fig. 1.14 - The μ_4-bridging pentadentate hydrogen phthalate ligand (left); The coordination environment of Na^+ in NaHpht·½H_2O showing the μ_2-bridging bidentate water. Symmetry code i) (-1+x,-y,-z); ii) (-0.5+x,0.5+y,-z); iii) (-0.5+x,0.5-y,z); iv) (-1+x,y,z); v) (0.5+x,0.5-y,z) vi) (0.5+x,0.5+y,-z);vii) (1+x,-y,-z); viii) (1+x,y,z); ix) (x,1-y,-z). Figure drawn using CIF file from [213].

The crystal structure of anhydrous KHpht was first reported by Okaya in 1965 [215] and it contains potassium and hydrogen phthalate ions. The potassium ion is surrounded by seven oxygen atoms, five from the ionised carboxyl groups and two from unionised carboxyl groups. KHpht exhibits a three dimensional (3D) polymeric structure where hydrogen phthalate anion function as a μ_4- bridging heptadentate ligand (Figure 1.15).

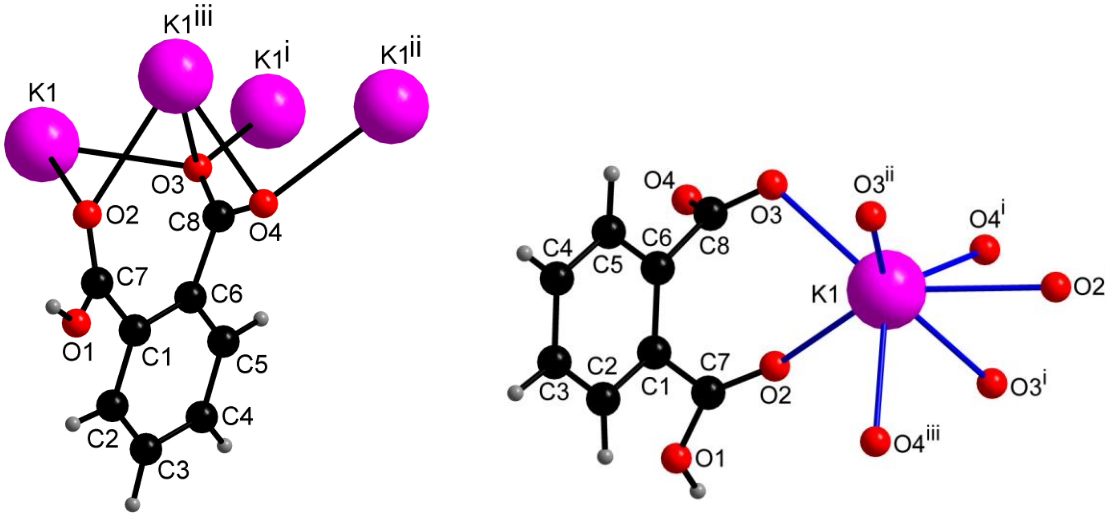
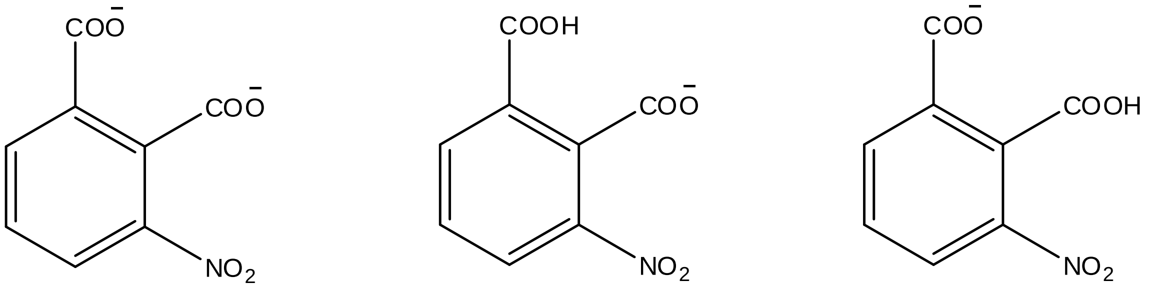


Fig. 1.15 - The μ_4-bridging heptadentate hydrogen phthalate ligand (left); Symmetry code i) -0.5+ x, 0.5- y, z ii) -1+ x, y, z iii) -0.5+ x, -y, -z. The crystal structure of potassium hydrogen phthalate showing the hepta coordination around the unique K^+ ion linked to four symmetry related hydrogen phthalate ligands (right). For clarity, only the O atoms of three other ligands are shown. K-O bonds are shown in blue. Symmetry code i) 0.5+ x, -y, -z ii) 0.5+ x, 0.5- y, z iii) 1+ x, y, z. Figures drawn using the CIF file reported in [215].

Several papers have been published in literature (Appendix-I, Table A1-A2) reporting incorporation of metal ions, amino acids and organic compounds into the crystal structure of NaHpht·½H_2O / KHpht and increase its NLO property. In view of the structural properties of NaHpht·½H_2O / KHpht described above, a reinvestigation work was undertaken to verify if other metal ions can be incorporated in their structures or not.

The presence of an additional functional group on phthalic acid can result in the formation of new compounds with interesting structural features. A –NO_2 functionality was chosen for the present work as it functions as a hard hydrogen bond acceptor and being isoelectronic to carboxyl (-COOH) group it was of interest to study for its binding behaviour. 3-nitrophthalic acid (3-nphtH_2) can in principle form three types of anions namely 3-nitrophthalate (3-npht) – a dianion; 2-carboxy-6-nitrobenzoate (2-carboxy-6-nba) when carboxyl group present *ortho* to nitro group is deprotonated and 2-carboxy-3-nitrobenzoate (2-carboxy-3-nba) if the carboxyl group positioned *meta*- to nitro group is deprotonated (Fig. 1.16). Anion formation of 3-nitrophthalic acid depends on the molar ratio of metal source and 3-nphtH_2 taken. The presence of –NO_2 and two –COOH groups leads to secondary interactions resulting in interesting architecture.



3-nitrophthalate 2-carboxy-6-nitrobenzoate 2-carboxy-3-nitrobenzoate

Fig. 1.16 - Types of anions obtained from 3-nitrophthalic acid.

A list of structurally characterized 3-nitrophthalates with organic amines [230-265] and metal ions [266-273] are given in Table 1.7 and Table 1.8 respectively. Many of the reported 3-nitrophthalate compounds are generally synthesised under ambient conditions.

Table 1.7 - Known 3-nitrophthalate compounds with organic amines

S.No	Compounds formula	Compound name	Space group	Ref
		3-nphtH$_2$ = ($C_8H_5NO_6$)		
1	$(C_8H_5NO_6)$	3-Nitrophthalic acid	$P2_1/n$	230
2	$(C_8H_5NO_6)(C_{10}H_8N_2)$	3-nitrophthalic acid 4,4'-bipyridine	$P2_1/n$	231
3	$(C_8H_5NO_6)(C_{12}H_{11}N_5)\cdot H_2O$	3-nitrophthalic acid N-benzyl-9H-purin-6-amine monohydrate	$P\bar{1}$	232
4	$(C_8H_5NO_6)(C_6H_6N_2O_3)$	3-Nitrophthalic acid 3-methyl-4-nitropyridine N-oxide	$P\bar{1}$	233
5	$2(C_8H_5NO_6)(C_8H_{12}N_2)\cdot 2H_2O$	bis(3-Nitrophthalic acid) tetramethylpyrazine dihydrate	$P\bar{1}$	234
6	$(C_8H_5NO_6)(C_6H_8N_2)$	2,3-dimethylpyrazine 3-nitrophthalic acid	$P\bar{1}$	235
7	$(C_8H_5NO_6)(C_9H_{11}NO)$	3-nitrophthalic acid 4-(dimethylamino)benzaldehyde	$P\bar{1}$	236
		3-nphth = ($C_8H_3NO_6$)		
8	$(C_8H_3NO_6)(C_4H_8N_3O)_2\cdot H_2O$	bis(1-methyl-4-oxoimidazolidin-2-iminium) 3-nitrophthalate monohydrate	$P2_1/c$	237
9	$(C_8H_3NO_6)(C_6H_9N_2)_2$	bis(2-Amino-6-methylpyridinium) 3-nitrobenzene-1,2-dicarboxylate	$P2_1/n$	238
10	$(C_8H_3NO_6)(C_{17}H_{18}N_4)$	1,1'-(propane-1,3-diyl)bis(1H-benzimidazol-3-ium) 3-nitrobenzene-1,2-dicarboxylate	$P21/n$	239
11	$(C_8H_3NO_6)(C_7H_{10}N)_2\cdot 2H_2O$	bis(phenylmethanaminium) 3-nitrophthalate dihydrate	$P\bar{1}$	240
12	$(C_8H_3NO_6)(C_4H_{12}N_2)\cdot 2H_2O$	Piperazinediium 3-nitrophthalate dihydrate	$Pna2_1$	241
		(2-carboxy-3-nitrobenzoate) = ($C_8H_4NO_6$)		
13	$(C_8H_4NO_6)(C_{15}H_{17}N_2)\cdot H_2O$	(E)-4-[4- (dimethylamino)styryl]pyridinium 2-carboxy-3-nitrobenzoate monohydrate	$P2_1/c$	242
		(2-carboxy-6-nitrobenzoate) = ($C_8H_4NO_6$)		
14	$(C_8H_4NO_6)(C_9H_8NO)\cdot H_2O$	8-Hydroxyquinolinium 3-nitrophthalate monohydrate	$P2_1/c$	243
15	$(C_8H_4NO_6)(CH_6N_3)\cdot H_2O$	Guanidinium 2-carboxy-6-nitrobenzoate monohydrate	$P2_1/c$	244
16	$(C_8H_4NO_6)(C_2H_6NO_2)$	Glycinium 3-nitrophthalate	$P2_1/c$	245
17	$(C_8H_4NO_6)(C_9H_8N)\cdot H_2O$	Quinolinium 3-nitrophthalate monohydrate	$P2_1/c$	246
18	$(C_8H_4NO_6)_2(C_4H_{12}N_2)$	Piperazine-1,4-diium bis(hydrogen-3-nitrophthalate)	$P2_1/c$	247
19	$(C_8H_4NO_6)(C_6H_7IN)$	3-Iodoanilinium 2-carboxy-6-nitrobenzoate	$P2_1/c$	248
20	$(C_8H_4NO_6)(C_{12}H_{12}N_3)$	4-(phenyldiazenyl)anilinium 2-carboxy-6-nitrobenzoate	$P2_1/c$	249
21	$(C_8H_4NO_6)(C_{12}H_9N_2)$	1,10-Phenanthrolin-1-ium 2-carboxy-6-nitrobenzoate	$P2_1/c$	250
22	$(C_8H_4NO_6)(C_6H_7IN)$	4-Iodoanilinium 3-nitrophthalate	$P2_1/c$	251
23	$(C_8H_4NO_6)(C_3H_5N_2)$	1H-pyrazol-2-ium 2-carboxy-6-nitrobenzoate	$P2_1/c$	252

24	$(C_8H_4NO_6)(C_6H_7ClN)$	4-chloroanilinium 2-carboxy-6-nitrobenzoate	$P2_1/c$	253
25	$(C_8H_4NO_6)(C_6H_8N)$	4-methylpyridin-1-ium 2-carboxy-6-nitrobenzoate	$P2_1/c$	254
26	$(C_8H_4NO_6)(C_6H_8N)$	2-Methylpyridinium 2-carboxy-6-nitrobenzoate	$P2_1/c$	255
27	$(C_8H_4NO_6)(C_7H_7N_2)$	1H-benzimidazol-3-ium 2-carboxy-6-nitrobenzoate	$P2_1/c$	256
28	$(C_8H_4NO_6)_2(C_{10}H_{16}N_4)\cdot 2H_2O$	1,1'-(butane-1,4-diyl)bis(1H-imidazol-3-ium) bis(2-carboxy-6-nitrobenzoate) dihydrate	$P2_1/c$	257
29	$(C_8H_4NO_6)(C_7H_8NO_2)$	4-Ammoniobenzoic acid 2-carboxy-6-nitrobenzoate	$P2_1/a$	258
30	$(C_8H_4NO_6)(C_8H_9NO_3)(C_8H_{10}NO_3)$	4-Carboxy-2-methoxyanilinium 4-carboxy-2-methoxyaniline 2-carboxy-6-nitrobenzoate	$P\bar{1}$	259
31	$(C_8H_4NO_6)(C_4H_6ClN_4)$	2,6-diamino-4-chloropyrimidin-1-ium 2-carboxy-3-nitrobenzoate	$P\bar{1}$	260
32	$(C_8H_4NO_6)(C_4H_8N_5)\cdot H_2O$	2,4,6-triaminopyrimidinium 2-carboxy-6-nitrobenzoate monohydrate	$P\bar{1}$	261
33	$(C_8H_4NO_6)(C_{23}H_{27}N_2O_4)\cdot 2H_2O$	Brucinium 2-carboxy-6-nitrophthalate dihydrate	$P2_12_12_1$	262
34	$(C_8H_4NO_6)(C_{11}H_{14}N_3O)$	1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-aminium 2-carboxy-6-nitrobenzoate	$P2_12_12_1$	263
35	$(C_8H_4NO_6)(C_6H_6N_3)\cdot H_2O$	1H-benzotriazol-3-ium 2-carboxy-6-nitrobenzoate monohydrate	*Pbca*	264
36	$(C_8H_4NO_6)_2(C_7H_{10}N_4)\cdot 3H_2O$	1,1'-methylenebis(1H-imidazol-3-ium) 2-carboxy-6-nitrobenzoate trihydrate	*Iba2*	265

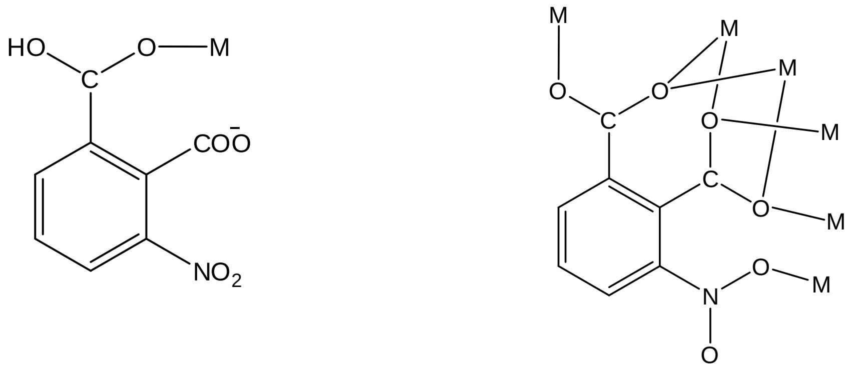
Table 1.8 - Known 3-nitrophthalate compounds containing metal ions

S.No.	Compound formula	Space group	Dimensionality	C.N	Binding mode of 3-nitrophthalate	$-NO_2$ grp binding	Extending via H_2O	Ref
1	$[Na(H_2O)_3(2\text{-carboxy-6nba})]\cdot H_2O$	$P\bar{1}$	1D	6	Monodentate	zero	Yes	266
2	$[Na_4(H_2O)_3(3\text{-nphth})_2]$	$P\bar{1}$	2D	5,6,6,7	μ_6-octadentate μ_8-dodecadentate	1 bond	Yes	267
3	$[Mg(H_2O)_5(3\text{-nphth})]\cdot 2H_2O$	$P\bar{1}$	0D	6	Monodentate	zero	No	268
4	$[Ca(H_2O)_2(3\text{-nphth})]\cdot H_2O$	$P2_1/c$	1D	7	μ_3-pentadentate	zero	No	268, 269
5	$[Ba(3\text{-nphth})]$	$P\bar{1}$	2D	9	μ_6-nonadentate	1 bond	No	270
6	$[Co(3\text{-nphth})(4,4'\text{-bpy})]$	$P2_1/c$	3D	6	μ_3-tetradentate	zero	No	271
7	$[Co(3\text{-nphth})_2(tsc)_2]\cdot 4H_2O$	$P\bar{1}$	0D	6	Monodentate, monodentate	zero	No	272
8	$[Zn(2\text{-carboxy-3-nba})_2(bpe)]$	$P\bar{1}$	1D	5	μ_2-bidentate, Monodentate	zero	No	273

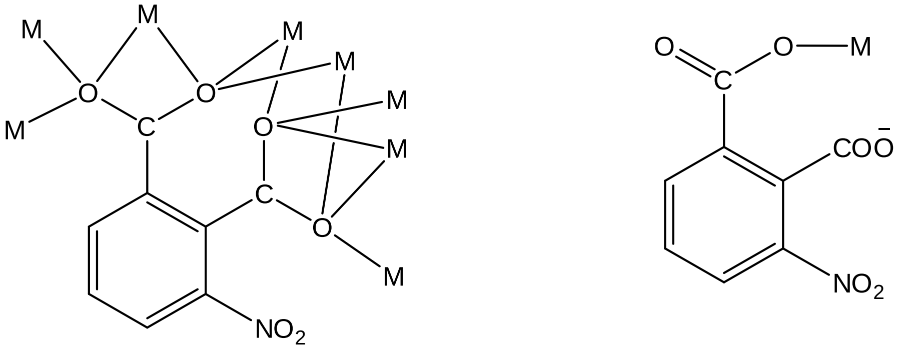
Abbreviations : 2-carboxy-6-nba= 2-carboxy-6-nitrobenzoate, 3-nphth= 3-nitrophthalate, 2-carboxy-3-nba= 2-carboxy-3-nitrobenzoate, 4,4'-bpy= 4,4'-bipyridine, tsc= thiosemicarbazide, bpe= 1,2-bis(4-pyridylethylene)

A maximum number of 3-nitrophthalate compounds are with organic amines generally containing 2-carboxy-6-nba anion and most of them are hydrated. A very few 3-nitrophthalates with metal ions are reported. The metal 3-nitrophthalates crystallize in the centrosymmetric $P\bar{1}$ (six compounds) or $P2_1/c$ (two compounds) space groups. The 2D compounds reported are obtained only under hydro(solvo)thermal conditions. Amongst the reported compounds, metal ions form polymeric structure except for Mg which is known to form discrete compounds as evidenced by the presence of $[Mg(H_2O)_6]^{2+}$ moiety in many compounds. Na(I) metal ion generally forms compounds with coordinated water molecules, which exhibit μ_2-bridging bidentate binding mode. This behaviour of sodium is observed even when prepared under hydrothermal conditions. 3-nitrophthalates of only Na(I) from alkali and Mg(II), Ca(II), Ba(II) from alkaline-earth metal ions are reported so far. The coordination number of metal ions observed in reported metal 3-nitrophthalate compounds are as follows: Na = 5 - 7; Mg = 6; Ca = 7; Ba = 9; Co= 6 and Zn=5.

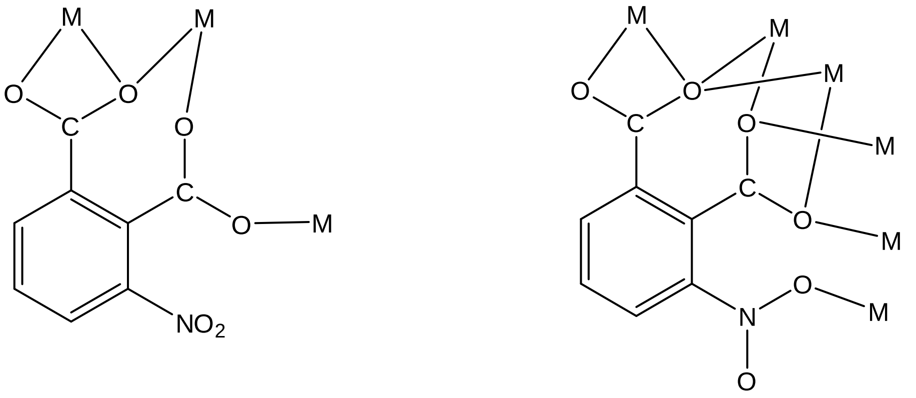
An analysis of the structural features of the 3-nitrophthalate compounds of alkali and alkaline earth metal ions reveals new binding modes for 3-nitrophthalate (Fig. 1.17) including coordination of oxygen atom of nitro group.



Monodentate μ6-octadentate



μ8-dodecadentate Monodentate



μ3-pentadentate μ6-nonadentate

Fig. 1.17 – Different binding modes of 3-nitrophthalate ligand in known structures.

In view of few reports on metal bis(phthalato) and metal 3-nitrophthalate compounds in literature, the present work has been undertaken. The details of syntheses, spectral characterization, thermal investigations, crystal structures, electrochemical and magnetic properties are described in the subsequent chapters.

SYNTHESES AND EXPERIMENTAL DETAILS

2.1 General considerations

All the reagents employed in this study were of analytical reagent grade and were used as received without any further purification. All the reactions were performed by using distilled water as a solvent. Infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer from 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. Raman spectra were recorded using 785 nm laser radiation for excitation on an Agiltron PeakSeeker Pro Raman instrument. UV-Visible spectra were recorded using a Shimadzu UV-2450 double beam spectrophotometer in water using matched quartz cells. Diffuse-reflectance spectra were recorded in the same instrument using $BaSO_4$ as reference (100% reflectance). Absorption data were calculated from the reflectance data using the Kubelka- Munk function ($a/S = (1-R)^2/2R$, where a is the absorption coefficient, R is the reflectance, and S is the Scattering coefficient. Isothermal weight loss studies were performed in a temperature controlled electric furnace. Elemental analysis (C, H and N) was performed on a Elementar vario Micro cube CHNS analyser. TG-DTA study was performed in flowing air in Al_2O_3 crucibles at heating rate of 10 K min^{-1} using a STA-409 PC simultaneous thermal analyser from Netzsch. X-ray powder pattern were recorded on a Rigaku Miniflex II powder diffractometer using Cu-K$_\alpha$ radiation with Ni filter. ^{1}H NMR spectra was recorded (in d^6-DMSO or D_2O) using a Bruker 400 MHz (Avance) FT-NMR spectrometer. The EPR spectra of powdered solid sample was recorded in JOEL JES-FA200 instrument with Frequency used 9.451 GHz. Conductivity measurements of compounds were carried out at room temperature using a Digital conductivity meter (LT-16) from Labtronics equipped with a standard conductometric cell composed of two platinum black electrodes. Cyclic voltammetry was performed in Electrochemical workstation-CH Instrument (Inc. CH16107), by using platinum as working electrode, platinum wire as counter electrode and saturated calomel electrode (SCE) as the reference. The redox properties of the aqueous solutions of the compounds were studied using 0.1 M KCl solution as supporting electrolyte at varying scan rates. Magnetic properties were studied as a function of temperature (M–T) using a vibrating sample magnetometer (VSM) on a Quantum Design-Versa Lab model.

X-ray intensity data were collected by using: 1) Bruker Smart Apex CCD diffractometer at School of Chemistry, University of Hyderabad for $(pipH_2)[Zn(pht)_2]\cdot H_2O$ **1** and $(pipH_2)[Ni(pht)_2(H_2O)_4]\cdot 8H_2O$ **3**; 2) Bruker AXS Kappa Apex II CCD Diffractometer at Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of Technology (IIT) Madras for $(pipH_2)[Co(pht)_2(H_2O)_4]\cdot 8H_2O$ **4**, $(pipH_2)[Cu(pht)_2(H_2O)_4]\cdot 8H_2O$ **5**, $[Ni(im)_6]pht\cdot H_2O$ **6**, $[Co(im)_6]pht\cdot H_2O$ **7**, $[Cu_2(im)_4(pht)_2(H_2O)]$ **8**, $[Cs(2\text{-carboxy-6-nba})(H_2O)]$ **13**, $[Rb_2(3\text{-npht})]$ **17**, $[Cs_2(3\text{-npht})]$ **18**, $[NaRb(2\text{-carboxy-6-nba})_2(H_2O)_3]\cdot 2H_2O$ **19**; 3) Image Plate Diffraction System (IPDS-1) from STOE, at the single X-ray facility in Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Germany for $[Na(2\text{-carboxy-6-nba})(H_2O)_3]\cdot H_2O$ **10** and $[K(2\text{-carboxy-3-nba})]$ **11**. Integration and scaling of intensity data were accomplished using the program SAINT [274]. The structures were solved with direct methods using SHELXS-97 [275] (SIR92 [275]) and refinement was done against F^2 using SHELXL-97 [275] (SHELXL-2014 [275]). The detailed structure protocol of the compounds and their checkCIF/PLATON reports are given in Appendix-II and Appendix-III respectively.

2.2 Synthetic protocol of metal phthalates

2.2.1 Syntheses of bivalent transition metal phthalates with piperazine

Synthesis of [Zn(phtH)$_2$(H$_2$O)$_2$] (precursor A)

A mixture of phthalic acid (phtH$_2$) (0.3323 g, 2 mmol) and zinc acetate dihydrate (Zn(OAc)$_2$·2H$_2$O) (0.2195 g, 1 mmol) was taken in ~15 mL distilled water and was heated on a water bath to obtain a clear solution (pH 4.5). Methanol (~10 mL) was added and the reaction mixture was kept undisturbed for crystallization in a refrigerator. Transparent crystals which separated after 24 hrs were isolated by filtration, washed with methanol and dried in air to yield 0.3885 g of [Zn(phtH)$_2$(H$_2$O)$_2$] in 90 % yield.

Anal. Found (Calcd.) for $ZnC_{16}O_{10}H_{14}$ (431.69) (%): C 44.22 (44.51); H 3.18 (3.28); phtH$_2$ 76.92 (76.97); ZnO 18.74 (18.85); IR data (cm^{-1}): 3557-2527 (b), 1688 (s), 1585 (s), 1393 (s), 1283 (w), 1146 (w), 897 (w), 758 (w), 669 (w); Raman data (cm^{-1}): 3083 (s), 1638 (s), 1587 (s), 1416 (w), 1382 (w), 1260 (s), 1159 (w), 1041 (s), 769 (s), 642 (w), 546 (w), 436 (w). UV-Vis data (nm): 282.

Synthesis of (pipH$_2$)(phtH)$_2$·2H$_2$O (precursor B)

A mixture of phtH$_2$ (0.3323 g, 2 mmol) and pip (0.0861 g, 1 mmol) was taken in ~20 mL distilled water and the reaction mixture was heated on a steam bath to obtain a clear solution. The clear reaction mixture thus obtained was left undisturbed for crystallization. The transparent crystals isolated by filtration after 4 days was washed with little ice cold water followed by methanol and air dried to yield 0.4318 g (95 %) of (pipH$_2$)(phtH)$_2$·2H$_2$O.

Anal. Found (Calcd.) for $C_{20}O_{10}N_2H_{26}$ (454.48) (%): C 52.39 (52.85), N 6.11 (6.17), H 5.81 (5.78); IR data (cm^{-1}): 3588-2306 (b), 1715 (s), 1548 (s), 1396 (s), 1369 (w), 1219 (w), 1158 (w), 1082 (s), 750 (w), 658 (w); Raman data (cm^{-1}): 3928 (w), 3060 (s), 2970 (w), 1656 (s), 1148 (s), 1035 (s), 807 (s); UV-Vis data (nm): 282.

Synthesis of ($pipH_2$)[Zn($pht)_2$]·H_2O **1**

Method I

[Zn($phtH)_2(H_2O)_2$] (0.4317 g, 1 mmol) prepared from above reaction was taken in ~15 mL distilled water with pip (0.0861 g, 1 mmol). The volume of the reaction mixture was reduced to ~10 mL by heating it on a steam bath and the clear solution obtained (pH=7) was then kept undisturbed for crystallization at room temperature. The needle shaped transparent crystals obtained in 4 days was washed with ice cold water followed by methanol and dried in air to yield 0.4098 g (82 %) of **1**.

Anal. Found (Calcd.) for $ZnC_{20}O_9N_2H_{22}$ (499.83) **1** (%): C 48.12 (48.06); H 4.41 (4.45); N 5.59 (5.61); $phtH_2$ 66.4 (66.47); ZnO 16.38 (16.28). IR data (cm^{-1}): 3660, 3427, 3030, 1608, 1552, 1371, 1083, 962, 833, 761, 459; Raman data (cm^{-1}): 3928 (w), 3067 (s), 2968 (w), 2764 (w), 1582 (s), 1392 (s), 1148 (s), 1040 (s), 834 (s); UV-DRS data (nm): 274. DTA (°C): 155 (endo), 347 (exo), 472 (exo).

Method II

$Zn(OAc)_2·2H_2O$ (0.2195 g, 1 mmol), pip (0.0861 g, 1 mmol) and $phtH_2$ (0.3323 g, 2 mmol) were taken in ~40 mL distilled water to get a clear solution. The reaction mixture was heated on a steam bath for ~15 min to reduce the volume to ~25 mL. The solution thus obtained was cooled and left undisturbed for crystallization at room temperature. The needle shaped transparent crystals isolated by filtration after 5 days was washed with ice cold water followed by methanol and dried in air to yield 0.3998 g (80 %) of **1**.

Method III

$(pipH_2)(phtH)_2·2H_2O$ (0.4545 g, 1 mmol) and $Zn(OAc)_2·2H_2O$ (0.2195 g, 1 mmol) were mixed together in ~20 mL distilled water to get a clear solution. The reaction mixture was then heated on a steam bath to reduce the volume to ~15 mL and kept for crystallization at room temperature. The crystals obtained in 2 days were isolated as before to yield 0.3749 g (75 %) of **1**. The IR spectrum of the compound obtained was found identical to **1** obtained from method *I* and *II*.

Synthesis of [(enH$_2$)Zn(pht)$_2$H$_2$O] **2**

Method I

$[Zn(phtH)_2(H_2O)_2]$ (0.4317 g, 1 mmol) prepared from above reaction was taken in ~15 mL distilled water with ethylenediamine (0.07 mL, 1 mmol). The volume of the reaction mixture was reduced to ~10 mL by heating it on a steam bath and the clear solution obtained (pH=7) was then kept undisturbed for crystallization at room temperature. The needle shaped transparent crystals obtained in 4 days was washed with ice cold water followed by methanol and dried in air to yield 0.4027 g (85 %) of **2**.

Anal. Found (Calcd.) for $ZnC_{18}O_9N_2H_{20}$ (473.79) **2** (%): C 45.71 (45.63); H 4.32 (4.26); N 5.89 (5.91); ZnO 17.2 (17.18); IR data (cm^{-1}): 3664, 3312 - 2512, 1588, 1566, 1366, 1088, 858, 772, 455; Raman data (cm^{-1}): 3926 (w), 3056 (s), 2980 (w), 1586 (s), 1398 (s), 1149 (s), 1040 (s), 831 (s), 658 (w); UV-DRS data (nm): 283.

Method II

$Zn(OAc)_2·2H_2O$ (0.2195 g, 1 mmol), ethylenediamine (0.07 mL, 1 mmol) and $phtH_2$ (0.3323 g, 2 mmol) were taken in ~40 mL distilled water to get a clear solution. The reaction mixture was heated on a steam bath for ~15 min to reduce the volume to

~25 mL. The solution thus obtained was cooled and left undisturbed for crystallization at room temperature. The needle shaped transparent crystals isolated by filtration after 5 days was washed with ice cold water followed by methanol and dried in air to yield 0.3791 g (80 %) of **2**.

Method III

To the mixture of phtH$_2$ (0.3323 g, 2 mmol) and NaHCO$_3$ (0.3360 g, 4 mmol), ethylenediamine dihydrochloride (0.1330 g, 1 mmol) and ZnCl$_2$·7H$_2$O (0.1363 g, 1 mmol) was added and a clear solution was obtained. The transparent crystals obtained after 2 days (0.3885 g, 82 %) were filtered, washed with methanol, dried. The IR spectrum of the compound obtained was found identical to **2** obtained from method *I* and *II*.

Synthesis of (pipH$_2$)[Ni(pht)$_2$(H$_2$O)$_4$]·8H$_2$O ***3***

Method I

Aqueous solutions of KHpht (0.4084 g, 2 mmol), pip (0.0861 g, 1 mmol) and nickel chloride hexahydrate [Ni(H$_2$O)$_6$]Cl$_2$ (0.2377 g, 1 mmol) were mixed together to obtain a clear solution. The reaction mixture (pH=7) was heated on a water bath to reduce the volume to ~15 mL and was kept undisturbed for crystallization at room temperature. Green crystals which separated after 24 hrs were isolated by filtration, washed with ice cold water followed by methanol and dried in air to yield 0.6222 g (90 %) of **3**.

Anal. Calcd for NiC$_{20}$O$_{20}$N$_2$H$_{44}$ (649.00) **3** (%): C, 34.74; N, 4.05; H, 6.43. Found: C, 34.79; N, 4.07; H, 6.38 %. IR (KBr, cm^{-1}): 3588-2506(br), 1549(s), 1414(s), 1394(s), 956(w), 818(w), 654(w). Raman (cm^{-1}): 3057(w), 1546(s), 1397(s), 1160(s), 810(s), 652(s). UV-Vis (nm): 278 ($\mathcal{E}$ = 1760 mol^{-1} L cm^{-1}), 395. ^{1}H NMR (DMSO-d_6, δ from

TMS): 8.171 (s, 4H), 7.496 (s, 4H), 2.884 (m, 8H). DTA (°C): 90 (endo), 320 (exo), 400 (exo). Molar conductivity (Λ_m, S cm^2 mol^{-1}) (0.01 M): 211.

Method II

KHpht (0.4084 g, 2 mmoL), pip (0.0861 g, 1 mmol) and nickel nitrate hexahydrate $Ni(NO_3)_2 \cdot 6H_2O$ (0.2908 g, 1 mmol) were taken in ~30 mL distilled water to get a clear solution. The reaction mixture was heated on a steam bath to reduce the volume to ~15 mL. The solution thus obtained was cooled and left undisturbed for crystallization at room temperature. The green crystals isolated by filtration after 2 days was washed with ice cold water followed by methanol and dried in air to yield 0.6360 g (92 %) of **3**.

Method III

KHpht (0.4084 g, 2 mmol), pip (0.0861 g, 1 mmol) and nickel sulphate hexahydrate $NiSO_4 \cdot 6H_2O$ (0.2628 g, 1 mmol) were taken in ~30 mL distilled water to get a clear solution. The reaction mixture was heated on a steam bath to reduce the volume to ~15 mL. The solution thus obtained was cooled and left undisturbed for crystallization at room temperature. The green crystals isolated by filtration after 3 days was washed with ice cold water followed by methanol and dried in air to yield 0.6153 g (89 %) of **3**.

Method IV

(pip)($phtH_2$)$\cdot 2H_2O$ (0.4545 g, 1 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (0.2489 g, 1 mmol) were taken in ~15 mL distilled water to get a clear solution. The reaction mixture was heated on a steam bath to reduce the volume to ~10 mL and the solution thus obtained was cooled and left undisturbed for crystallization. The green crystals isolated by filtration after 3 days was washed with little ice cold water followed by methanol and air dried to yield 0.5599 g (81 %) of **3**.

Method V

phtH$_2$ (0.3323 g, 2 mmol), pip (0.0861 g, 1 mmol) and nickel acetate tetrahydrate Ni(OAc)$_2$·4H$_2$O (0.2489 g, 1 mmol) were taken in ~40 mL distilled water to get a clear solution. The reaction mixture was heated on a steam bath and the solution (~15 mL) thus obtained was cooled and left undisturbed for crystallization. The green coloured crystals isolated by filtration after 3 days was washed with ice cold water followed by methanol and dried in air to yield 0.5531 g (80 %) of **3**.

Method VI

To the freshly prepared nickel carbonate obtained by adding aqueous solution (~10 mL) of Na$_2$CO$_3$ (0.1059 g, 1 mmol) to the aqueous solution (~10 mL) of [Ni(H$_2$O)$_6$]Cl$_2$ (0.2377 g, 1 mmol), phtH$_2$ (0.3323 g, 2 mmol) and pip (0.0861 g, 1 mmol) was added. The reaction mixture was heated on a steam bath to get a clear solution. The solution thus obtained was cooled and left undisturbed for crystallization at room temperature. The green crystals isolated by filtration after 4 days was washed with ice cold water followed by methanol and air dried to yield 0.5876 g (85 %) of **3**.

Method VII

To the mixture of phtH$_2$ (0.3323 g, 2 mmol) and NaHCO$_3$ (0.3360 g, 4 mmol) in ~30 mL distilled water, 0.1590 g (1 mmol) of pipH$_2$Cl$_2$ and [Ni(H$_2$O)$_6$]Cl$_2$ (0.2377 g, 1 mmol) was added. The reaction mixture was heated on a steam bath to reduce the volume to ~15 mL. The solution thus obtained was left undisturbed for crystallization at room temperature. The green crystals isolated by filtration after 4 days was washed with ice cold water followed by methanol and dried in air to yield 0.5669 g (82 %) of **3**. The IR spectrum of the compound obtained was found identical to **3** obtained from method *I* to *VI*.

Synthesis of $(pipH_2)[Co(pht)_2(H_2O)_4]\cdot 8H_2O$ **4**

Method I

Aqueous solutions of KHpht (0.4084 g, 2 mmol), pip (0.0861 g, 1 mmol) and cobalt chloride hexahydrate $[Co(H_2O)_6]Cl_2$ (0.2379 g, 1 mmol) were mixed together to obtain a clear solution (~20 mL). The reaction mixture (pH = 7) was heated on a water bath to reduce the volume to ~10 mL and was kept undisturbed for crystallization at room temperature. Pink crystals which separated after 2 days were isolated by filtration, washed with ice cold water and dried in air to yield 0.6362 g (92 %) of **4**.

Anal. Found (Calcd.) for $CoC_{20}O_{20}N_2H_{44}$ **4** (%): C 34.63 (34.73), N 4.06 (4.05), H 6.46 (6.43); IR data (cm^{-1}): 3622-2308(b), 1552(s), 1396(s), 1377(s), 1084(w), 821(w), 654(w); Raman data (cm^{-1}): 3076(w), 1566(s), 1417(s), 1180(s), 1056(s), 831(s), 672(s); UV-DRS data (nm): 275 (ε = 1890 mol^{-1} L cm^{-1}), 510; ^1H NMR (d^6-DMSO, δ from TMS): 8.6 (b, 4H), 7.7 (b, 4H); DTA (°C): 87 (endo), 119 (endo), 351 (exo), 390 (exo), 403 (exo); Molar conductivity (λm, S cm^2 mol^{-1}) (0.01 M): 222.

Method II

KHpht (0.4084 g, 2 mmoL), pip (0.0861 g, 1 mmol) and cobalt nitrate hexahydrate $Co(NO_3)_2\cdot 6H_2O$ (0.2910 g, 1 mmol) were taken in ~30 mL distilled water to get a clear solution. The reaction mixture was heated on a steam bath to reduce the volume to ~15 mL. The solution thus obtained was cooled and left undisturbed for crystallization at room temperature. The pink crystals isolated by filtration after

2 days was washed with ice cold water followed by methanol and dried in air to yield 0.6571 g (95 %) of **4**.

Method III

(pip)(phtH$_2$)·2H$_2$O (0.4545 g, 1 mmol) and cobalt acetate tetrahydrate Co(OAc)$_2$·4H$_2$O (0.2491 g, 1 mmol) were taken in ~15 mL distilled water to get a clear solution. The reaction mixture was heated on a steam bath to reduce the volume to ~10 mL and the solution thus obtained was cooled and left undisturbed for crystallization. The pink crystals isolated by filtration after 3 days was washed with little ice cold water followed by methanol and air dried to yield 0.6224 g (90 %) of **4**.

Method IV

phtH$_2$ (0.3323 g, 2 mmol), pip (0.0861 g, 1 mmol) and cobalt acetate tetrahydrate Co(OAc)$_2$·4H$_2$O (0.2491 g, 1 mmol) were taken in ~40 mL distilled water to get a clear solution. The reaction mixture was heated on a steam bath and the solution (~15 mL) thus obtained was cooled and left undisturbed for crystallization. The pink coloured crystals isolated by filtration after 3 days was washed with ice cold water followed by methanol and dried in air to yield 0.6362 g (92 %) of **4**.

Method V

To the freshly prepared cobalt carbonate obtained by adding aqueous solution (~10 mL) of Na$_2$CO$_3$ (0.1059 g, 1 mmol) to the aqueous solution (~10 mL) of [Co(H$_2$O)$_6$]Cl$_2$ (0.2379 g, 1 mmol), phtH$_2$ (0.3323 g, 2 mmol) and pip (0.0861 g, 1 mmol) was added. The reaction mixture was heated on a steam bath to get a clear solution. The solution thus obtained was cooled and left undisturbed for crystallization at room temperature. The pink crystals isolated by filtration after

4 days was washed with ice cold water followed by methanol and air dried to yield 0.6432 g (93 %) of **4**.

Method VI

To the mixture of phtH$_2$ (0.3323 g, 2 mmol) and 4NaHCO$_3$ (0.3360 g, 4 mmol) in ~30 mL distilled water, 0.1590 g (1 mmol) of pipH$_2$Cl$_2$ and [Co(H$_2$O)$_6$]Cl$_2$ (0.2379 g, 1 mmol) was added. The reaction mixture was heated on a steam bath to reduce the volume to ~15 mL. The solution thus obtained was left undisturbed for crystallization at room temperature. The pink crystals isolated by filtration after 4 days was washed with ice cold water followed by methanol and dried in air to yield 0.6086 g (92 %) of **4**. The IR spectrum of the compound obtained was found identical to **4** obtained from method *I* to *V*.

*Synthesis of (pipH$_2$)[Cu(pht)$_2$(H$_2$O)$_4$]·8H$_2$O **5** and [Cu(pht)$_2$(pipH$_2$)] **5a***

Method I

Aqueous solutions of KHpht (0.4084 g, 2 mmol), pip (0.0861 g, 1 mmol) and copper chloride dihydrate CuCl$_2$·2H$_2$O (0.1704 g, 1 mmol) were mixed together to obtain a clear solution (~30 mL). The reaction mixture (pH = 7) was kept undisturbed for crystallization. Blue crystals which separated after 4 days were isolated by filtration, washed with ice cold water and dried in air to yield **(**0.4177 g, 60 %) of **5** along with some green crystals of **5a**.

Anal. Found (Calcd.) for CuC$_{20}$O$_{20}$N$_2$H$_{44}$ **5** (%): C 34.61 (34.50), N 4.14 (4.02), H 6.28 (6.38); IR data (cm^{-1}): 3514-2382(b), 1553(s), 1394(s), 1375(s), 1217(w), 1085(w), 820(w), 654(w); Raman data (cm^{-1}): 3057(w), 1560(s), 1412(s), 1174(s), 1051(s), 831(s), 667(s); UV-DRS data (nm): 274, 750; DTA (°C): 77 (endo), 114 (endo), 280 (exo), 324 (exo), 390 (exo).

Anal. Found (Calcd.) for $CuC_{20}O_8N_2H_{20}$ **5a** (%): C 49.98 (50.04); N 5.80 (5.84); H 4.23 (4.21); IR data (cm^{-1}): 3601(s), 3109(b), 1562(s), 1390(s), 1365(s), 1083(w), 856(w), 831(w), 759(w), 696(w), 651(w), 516(w); UV-DRS data (nm): 270, 750. DTA (°C): 270 (exo), 305 (exo), 347 (exo).

Method II

KHpht (0.4084 g, 2 mmol), pip (0.0861 g, 1 mmol) and copper sulphate pentahydrate $CuSO_4 \cdot 5H_2O$ (0.2497 g, 1 mmol) were dissolved in ~30 mL distilled water to get a clear solution and left undisturbed for crystallization. The crystals isolated by filtration after 3 days was washed with ice cold water and dried in air to yield 0.4594 g (66 %) of blue crystals of **5** and green compound **5a**.

Method III

(pip)($phtH_2$)$\cdot 2H_2O$ (0.4545 g, 1 mmol) and copper acetate dihydrate $Cu_2(OAc)_4 \cdot 2H_2O$ (0.1996 g, 0.5 mmol) were taken in ~15 mL distilled water to get a clear solution and left undisturbed for crystallization. The crystals isolated by filtration after 4 days was washed with ice cold water and dried in air to yield 0.4873 g (70 %) of blue crystals **5** and green compound **5a**.

Method IV

$phtH_2$ (0.3323 g, 2 mmol), pip (0.0861 g, 1 mmol) and $Cu_2(OAc)_4 \cdot 2H_2O$ (0.1996 g, 1 mmol) were taken in ~30 mL distilled water to get a clear solution and left undisturbed for crystallization. The crystals isolated by filtration after 5 days was washed with ice cold water and dried in air to yield 0.4525 g (65 %) of blue crystals of **5** and green compound **5a**.

Method V

To the freshly prepared copper carbonate obtained by adding aqueous solution (~10 mL) of Na_2CO_3 (0.1059 g, 1 mmol) to the aqueous solution (~10 mL) of $CuCl_2{\cdot}2H_2O$ (0.1704 g, 1 mmol), $phtH_2$ (0.3323 g, 2 mmol) and pip (0.0861 g, 1 mmol) was added. The reaction mixture obtained was left undisturbed for crystallization. The crystals isolated by filtration after 6 days was washed with ice cold water and air dried to yield 0.5012 g (72 %) of blue crystals of **5** and green compound **5a**.

Method VI

To the mixture of $phtH_2$ (0.3323 g, 2 mmol) and $NaHCO_3$ (0.3360 g, 4 mmol) in ~30 mL distilled water, 0.1590 g (1 mmol) of $pipH_2Cl_2$ and $CuCl_2{\cdot}2H_2O$ (0.1704 g, 1 mmol) was added. The reaction mixture obtained was left undisturbed for crystallization. The crystals isolated by filtration after 5 days was washed with ice cold water and air dried to yield 0.5708 g (82 %) of blue crystals of **5** and green compound **5a**. The IR spectrum of the compound obtained was found identical to **5** and **5a** obtained from method *I* and *V*.

2.2.2 Syntheses of metal phthalates with imidazole

Synthesis of $[Ni(im)_6]pht{\cdot}H_2O$ ***6***

To an aqueous solution of $(pipH_2)[Ni(pht)_2(H_2O)_4]{\cdot}8H_2O$ **3** (0.6913 g, 1 mmol) in ~20 mL of distilled water, imidazole (0.2723 g, 4 mmol) was added. The reaction mixture was stirred well to dissolve the N-donor ligand and left undisturbed for crystallization at room temperature. The violet crystals obtained after 7 days were isolated by filtration, washed with ice cold water and methanol and dried in air to yield 0.3571 g (55 %) of **6.**

Anal. Found (Calcd.) for $NiC_{26}O_5N_{12}H_{30}$ **6** (%): C 48.11 (48.09), N (25.89) 25.95, H 4.63 (4.67); IR data (cm^{-1}): 3438-2630(br), 1554(s), 1379(s), 1322(w), 1250(w), 1144(w), 1072(w), 935(w), 823(w), 752(w), 665(w), 621(w), 426(w); Raman data (cm^{-1}): 1597(w), 1413(w), 1328(w), 1254(s), 1160(s), 1041(w), 818(w); UV-DRS data (nm): 276, 390; DTA (°C): 140 (endo), 200 (endo), 395 (exo).

Synthesis of $[Co(im)_6]pht{\cdot}H_2O$ ***7*** *and* $[Co(im)_3(pht)(H_2O)_2]$ ***7a***

To an aqueous solution of $(pipH_2)[Co(pht)_2(H_2O)_4]{\cdot}8H_2O$ **4** (0.6916 g, 1 mmol) in ~20 mL of distilled water, imidazole (0.2723 g, 4 mmol) was added. The reaction mixture was stirred well to dissolve the N-donor ligand and left undisturbed for crystallization at room temperature. The orange crystals obtained after 7 days were isolated by filtration, washed with ice cold water and methanol and dried in air to yield (0.2598 g, 40 %) **7** and pink compound **7a** (0.1912 g, 30 %) .

Anal. Found (Calcd.) for $CoC_{26}O_5N_{12}H_{30}$ **7** (%): C 48.17 (48.07), N 25.92 (25.88), H 4.57 (4.66); IR data (cm^{-1}): 3630-2714(b), 1566(s), 1413(s), 1087(w), 752(w), 652(w), 494(w); Raman data (cm^{-1}): 3143(w), 1453(w), 1320(w), 1253(s), 1148(s), 1095(w), 821(w); UV-DRS (nm): 239, 273, 494; DTA (°C): 148 (endo), 216 (endo), 415 (exo).

Anal. Found (Calcd.) for $CoC_{17}O_6N_6H_{20}$ **7a** (%): C 44.15 (44.06), N 18.01 (18.14), H 4.5 (4.36); IR data (cm^{-1}): 3464-2623(b), 1578(s), 1493(s), 1329(s), 1255(w), 1165(w), 1070(w), 943(w), 817(w), 754(w), 698(w), 659(w), 619(w), 446(w); Raman data (cm^{-1}): 1600(s), 1492(s), 1412(s), 1327(s), 1254(s), 1162(w), 1101(w), 1041(w), 818(w); UV-DRS data (nm): 256, 496; DTA (°C): 129 (endo), 210 (endo), 263 (endo), 421 (exo).

Synthesis of [$Cu_2(im)_4(pht)_2(H_2O)$] **8**

To an aqueous solution of $(pipH_2)[Cu(pht)_2(H_2O)_4]\cdot 8H_2O$ **5** (0.6961 g, 1 mmol) in ~20 mL of distilled water, imidazole (0.1362 g, 2 mmol) was added. The reaction mixture was stirred well to dissolve the N-donor ligand and left undisturbed for crystallization at room temperature. The blue crystals obtained after 7 days were isolated by filtration, washed with ice cold water and methanol and dried in air to yield (0.4583 g, 60 %) of **8.**

Anal. Found (Calcd.) for $Cu_2C_{28}O_{10}N_8H_{28}$ **8** (%): C 44.08 (44.03), N 14.66 (14.67), H 3.75 (3.70); IR data (cm^{-1}): 3390-2756(br), 1552(s), 1379(s), 1265(w), 1145(w), 1074(s), 954(w), 862(w), 750(w), 660(w), 462(w); Raman data (cm^{-1}): 1549(s), 1362(s), 1276(s), 1205(s), 1110(s), 992(w), 770(w); UV-DRS data (nm): 258, 725. DTA (°C): 148 (endo), 241 (exo), 394 (exo), 427 (exo).

2.3 Syntheses of s-block metal 3-nitrophthalates

Synthesis of [$Li(3\text{-}nphtH)(H_2O)_3$] **9**

3-nphtH$_2$ (0.2111 g, 1 mmol) and Li_2CO_3 (0.0369 g, 0.5 mmol) were mixed in ~20 mL distilled water and a clear solution was obtained with the evolution of effervescence. The mixture was then heated on water bath to reduce the volume to ~15 mL and kept undisturbed for crystallization at room temperature. Transparent crystals separated after 10 days were isolated by filtration, washed with ice cold water followed by methanol and dried in air to yield 0.2114 g (78 %) of **9**.

Anal. Found (Calcd.) for $LiC_8O_9NH_7$ **9** (271.13) (%): C 35.32 (35.44), N 5.11 (5.17), H 3.79 (3.73); IR data (cm^{-1}): 3601-3096 (b), 1722 (w), 1572 (w), 1537 (w), 1464 (w), 1390 (w), 1346 (w), 1273 (s), 912 (s), 781 (s), 685 (w); Raman data (cm^{-1}): 1566 (w), 1349 (s), 1150 (w), 1079 (w), 808 (w). DTA (°C): 95 (endo), 214 (endo), 271 (endo), 410 (exo).

Synthesis of [Na(2-carboxy-6-nba)(H_2O)$_3$]·H_2O **10**

To an aqueous solution of 3-nphtH$_2$ (0.2111 g, 1 mmol) in ~20 mL of distilled water, Na_2CO_3 (0.0529 g, 0.5 mmol) was added and a clear solution was obtained with the evolution of effervescence. The mixture was then heated on water bath to reduce the volume to ~10 mL and kept undisturbed for crystallization at room temperature. Transparent crystals separated after 7 days were isolated by filtration, washed with ice cold water followed by methanol and dried in air to yield 0.2380 g (78 %) of **10**.

Anal. Found (Calcd.) for $NaC_8O_{10}NH_{12}$ **10** (305.21) (%): C 31.61 (31.48), N 4.45 (4.59), H 3.88 (3.97); IR data (cm^{-1}): 3600-2484 (b), 2158 (w), 1715 (w), 1572 (w), 1530 (w), 1464 (w), 1360 (w), 1252 (w), 1157 (w), 1070 (w), 914 (w), 754 (w), 678 (w); Raman data (cm^{-1}): 1720 (w), 1567 (w), 1530 (w), 1355 (w), 1153 (w), 1072 (w), 830 (w); UV-Vis (nm): 270;. ^{1}H NMR (D_2O, δ from TMS): 8.205 (d, 1H), 8.142 (d, 1H), 7.529 (t, 1H).

Synthesis of [K(2-carboxy-3-nba)] **11**

To the aqueous solution of 3-nphtH$_2$ (0.2111 g, 1 mmol) in ~20 mL of distilled water, K_2CO_3 (0.0691 g, 0.5 mmol) was added and a clear solution was obtained with the evolution of effervescence. The mixture was then heated on water bath to reduce the volume to ~10 mL and kept undisturbed for crystallization at room temperature. Transparent crystals separated after 7 days were isolated by filtration, washed with ice cold water followed by methanol and dried in air to yield 0.1993 g (80 %) of **11**.

Anal. Found (Calcd.) for $KC_8O_6NH_4$ **11** (249.23) (%): C 38.48 (38.53), N 5.59 (5.62), H 1.57 (1.62); IR data (cm^{-1}): 1663 (w), 1609 (w), 1533 (w), 1454 (w), 1344 (w), 914 (w), 808 (w), 785 (w), 750 (w), 704 (w), 667 (w), 580 (w), 550 (w), 430 (w); Raman data (cm^{-1}): 1562 (w), 1528 (s), 1342 (w), 1154 (w), 1066 (w), 806 (w). UV-Vis (nm):

270. DTA: 290 (endo), 345 (exo), 476 (exo), 527°C (exo). ^{1}H NMR (D_2O, δ from TMS): 8.190 (d, 1H), 8.127 (d, 1H), 7.514 (t, 1H).

Synthesis of [Rb(3-nphtH)]·2H$_2$O **12**

To the aqueous solution of 3-nphtH$_2$ (0.2111 g, 1 mmol) in ~20 mL of distilled water, Rb_2CO_3 (0.1155 g, 0.5 mmol) was added and a clear solution was obtained with the evolution of effervescence. The mixture was then heated on water bath to reduce the volume to ~15 mL and kept undisturbed for crystallization at room temperature. Transparent crystals separated after 10 days were isolated by filtration, washed with ice cold water followed by methanol and dried in air to yield 0.4071 g (75 %) of **12**. Anal. Found (Calcd.) for $RbC_{16}O_{14}N_2H_{13}$ **12** (542.78) (%): C 35.33 (35.40), N 5.20 (5.16), H 2.35 (2.42); IR data (cm^{-1}): 1649 (w), 1522 (w), 1450 (w), 1346 (s), 914 (w), 785 (w), 667 (w); Raman data (cm^{-1}): 1559 (w), 1526 (w), 1343 (s), 1154 (w), 1068 (w), 807 (w). DTA (°C): 102 (endo), 342 (exo), 406 (exo).

Synthesis of [Cs(2-carboxy-6-nba)(H$_2$O)] **13**

To the aqueous solution of 3-nphtH$_2$ (0.2111 g, 1 mmol) in ~20 mL of distilled water, Cs_2CO_3 (0.1629 g, 0.5 mmol) was added and a clear solution was obtained with the evolution of effervescence. The mixture was then heated on water bath to reduce the volume to ~15 mL and kept undisturbed for crystallization at room temperature. Transparent crystals separated after 10 days were isolated by filtration, washed with ice cold water followed by methanol and dried in air to yield 0.4722 g (80 %) of **13**. Anal. Found (Calcd.) for $CsC_8O_7NH_6$ **13** (361.15) (%): C 26.51 (26.60), N 3.77 (3.88), H 1.61 (1.68); IR data (cm^{-1}): 3099 (w), 1667 (w), 1605(w), 1520 (w), 1452 (w), 1355 (s), 912 (w), 706 (w); Raman data (cm^{-1}): 1562 (w), 1528 (w), 1348 (s), 1155 (w), 1068 (w), 807 (w). DTA (°C): 80 (endo), 106 (endo), 250 (exo), 470 (exo).

Synthesis of [Li_2(3-npht)(H_2O)$_3$] **14**

3-nphtH_2 (0.2111 g, 1 mmol) and Li_2CO_3 (0.0738 g, 1 mmol) were mixed in ~15 mL distilled water and a clear solution was obtained with the evolution of effervescence. The mixture was then heated on water bath to reduce the volume to ~10 mL and kept undisturbed for crystallization at room temperature. The cluster of crystals obtained in 5 days were redissolved in aqueous medium and few good quality crystals for single crystal determination were isolated by filtration in 10 days, washed with ice cold water followed by methanol and dried in air to yield 0.2077 g (75 %) of **14**.

Anal. Found (Calcd.) for $Li_2C_8O_6NH_3$ (277.06) **14** (%): C 34.73 (34.68); N 4.98 (5.06); H 3.18 (3.28); IR data (cm^{-1}): 3615-3084 (b), 1604 (s), 1535 (w), 1454 (s), 1394 (s), 1354 (s), 926 (s), 714 (w); Raman data (cm^{-1}): 3078 (w), 1556 (w), 1526 (w), 1461 (w), 1404 (w), 1347 (s), 1158 (w), 1070 (w), 830 (w). DTA (°C): 100 (endo), 406 (exo).

Synthesis of [Na_2(3-npht)(H_2O)$_2$] **15**

3-nphtH_2 (0.2111 g, 1 mmol) and Na_2CO_3 (0.1059 g, 1 mmol) were mixed in ~15 mL distilled water and a clear solution was obtained with the evolution of effervescence. The mixture was then heated on water bath to reduce the volume to ~10 mL and kept undisturbed for crystallization at room temperature. The cluster of crystals obtained in 5 days were redissolved in aqueous medium and few good quality crystals for single crystal determination were isolated by filtration in 10 days, washed with ice cold water followed by methanol and dried in air to yield 0.2388 g (82 %) of **15**.

Anal. Found (Calcd.) for $Na_2C_8O_8NH_7$ **15** (291.16) (%): C 33.22 (33.00), N 4.76 (4.81), H 2.28 (2.43); IR data (cm^{-1}): 3626 (s), 3516-2978 (b), 1589 (s), 1524 (w), 1452 (w), 1352 (s), 1157 (w), 1072 (w), 923 (s), 823 (w), 713 (w); Raman data (cm^{-1}):

1561 (w), 1349 (s), 1150 (w), 1073 (w), 828 (w). DTA (°C): 116 (endo), 168 (endo), 386 (exo), 483 (exo) and 666 (exo).

Synthesis of [K_2(3-npht)] **16**

To the aqueous solution of 3-nphtH$_2$ (0.2111 g, 1 mmol) in ~20 mL of distilled water, K_2CO_3 (0.1382 g, 1 mmol) was added and a clear solution was obtained with the evolution of effervescence. The mixture was then heated on water bath to reduce the volume to ~10 mL and kept undisturbed for crystallization at room temperature. Transparent needle shaped crystals obtained in 10 days, isolated by filtration, washed with ice cold water followed by methanol and dried in air to yield 0.2385 g (83 %) of **16**.

Anal. Found (Calcd.) for $K_2C_8O_6NH_3$ **16** (287.33) (%): C 33.51 (33.44), N 4.83 (4.88), H 0.98 (1.05); IR data (cm^{-1}): 3543-3094 (b), 1597 (s), 1458 (w), 1344 (s), 1163 (w), 924 (s), 822 (w), 713 (w); Raman data (cm^{-1}): 1559 (s), 1334 (s), 1159 (w), 1068 (w), 818 (w). DTA (°C): 299 (exo), 344 (exo), 487 (exo).

Synthesis of [Rb_2(3-npht)] **17**

To the aqueous solution of 3-nphtH$_2$ (0.2111 g, 1 mmol) in ~20 mL of distilled water, Rb_2CO_3 (0.2309 g, 1 mmol) was added and a clear solution was obtained with the evolution of effervescence. The mixture was then heated on water bath to reduce the volume to ~15 mL and kept undisturbed for crystallization at room temperature. Transparent crystals separated after 10 days were isolated by filtration, washed with ice cold water followed by methanol and dried in air to yield 0.3154 g (83 %) of **17**.

Anal. Found (Calcd.) for $Rb_2C_8O_6NH_3$ **17** (380.06) (%): C 25.31 (25.28); N 3.74 (3.69), H 0.75 (0.8); IR data (cm^{-1}): 3096 (w), 1589 (s), 1516 (w), 1450 (w), 1356 (s), 920 (w), 750 (w), 712 (s); Raman data (cm^{-1}): 1564(w), 1526(w), 1343 (s), 1296(w), 1154 (w), 807 (w). DTA (°C): 384 (exo), 490 (exo), 560 (exo).

Synthesis of [Cs_2(3-npht)] **18**

To the aqueous solution of 3-nphtH$_2$ (0.2111 g, 1 mmol) in ~20 mL of distilled water, Cs_2CO_3 (0.3258 g, 1 mmol) was added and a clear solution was obtained with the evolution of effervescence. The mixture was then heated on water bath to reduce the volume to ~15 mL and kept undisturbed for crystallization at room temperature. Transparent crystals separated after 10 days were isolated by filtration, washed with ice cold water followed by methanol and dried in air to yield 0.4038 g (85 %) of **18**.

Anal. Found (Calcd.) for $Cs_2C_8O_6NH_3$ **18** (475.12) (%): C 20.31 (20.22), N 2.89 (2.95), H 0.55 (0.64); IR data (cm^{-1}): 3090 (s), 2937 (w), 1589 (s), 1516 (w), 1446 (w), 1356 (s), 916 (w), 750 (w), 710 (w), 553 (w); Raman data (cm^{-1}): 1580(w), 1556 (w), 1515(w), 1416 (w), 1376 (w), 1333 (s), 1148 (w), 1070 (s), 813 (w). DTA (°C): 346 (exo), 357 (exo), 508 (exo) and 602 (exo).

Synthesis of [NaRb(2-carboxy-6-nba)$_2$(H_2O)$_3$]·2H_2O **19**

3-nphtH$_2$ (0.2111 g, 1 mmol), Na_2CO_3 (0.0529 g, 0.5 mmol) and RbCl (0.0605 g, 1 mmol) were mixed in ~20 mL distilled water and a clear solution was obtained. The mixture was then heated on water bath to reduce the volume to ~15 mL and kept undisturbed for crystallization at room temperature. Transparent crystals obtained after 6 days were isolated by filtration, washed with ice cold water followed by methanol and dried in air to yield 0.3713 g (60 %) of **19**.

Anal. Found (Calcd.) for $NaRbC_{16}O_{17}N_2H_{18}$ **19** (618.83) (%): C 30.86 (31.05), N 4.62 (4.53), H 2.84 (2.94); IR data (cm^{-1}): 3593-3104 (br), 1670(w), 1570(s), 1537(w), 1456 (s), 1387 (s), 1344(s), 1273 (w), 912 (w), 841 (w), 779 (w), 685 (w), 538 (w);

Raman data (cm^{-1}): 1562 (w), 1528 (w), 1347 (s), 1154 (w), 1067 (w), 808 (w). DTA (°C): 106 (endo), 238 (endo), 345 (exo), 480 (exo).

2.4 Syntheses of *s*-block metal phthalates in presence of piperazine

Synthesis of pure metal phthalate compounds for reference:

To an aqueous solution of $phtH_2$ (0.1661 g, 1 mmol) in ~20 mL distilled water, $NaHCO_3$ (0.084 g, 1 mmol) was added and a clear solution was obtained. The reaction mixture was heated on a steam bath to reduce the volume to ~10 mL. The solution thus obtained was cooled and left undisturbed for crystallization at room temperature. The hexagonal shaped crystals isolated by filtration after 3 days was washed with ice cold water followed by methanol and dried in air to yield 0.1812 g of $NaHpht{\cdot}½H_2O$ **20**.

The commercially available potassium hydrogen phthalate, KHpht (**21**) was used for all experiments.

A mixture of metal(II) chloride (Cu^{+2}, Ni^{+2}, Mg^{+2}) and Na_2CO_3 in 1:1 stoichiometric ratio was prepared in minimum amount of distilled water resulting in *in situ* generation of metal carbonate. To this solution, phthalic acid was added maintaining the ratio of metal to phthalate as 1:1. The phthalic acid dissolved slowly giving brisk effervescence. The reaction mixture was then heated on water bath for a short period. The clear solution obtained was then left undisturbed to get the product at room temperature. The same procedure was repeated for the other metal ions by taking metal carbonate/acetate (Sr^{+2}, Ba^{+2}, Ca^{2+}, Zn^{+2}) as the starting material. (**22**= Ca, **23**=Mg, **24**=Ni, **25**=Cu, **26**=Zn, **27**=Sr, **28**=Ba phthalates).

Investigation of reactions of s-block metal ions with phthalic acid in presence of piperazine.

Synthesis of sodium phthalate in presence of piperazine.

To an aqueous solution of phtH$_2$ (0.3323 g, 2 mmol) and NaHCO$_3$ (0.1680 g, 2 mmol) in ~20 mL distilled water, pip (0.0861 g, 1 mmol) was added and a clear solution was obtained. The reaction mixture was heated on a steam bath to reduce the volume to ~15 mL. The solution thus obtained was cooled and left undisturbed for crystallization at room temperature. The hexagonal shaped crystals isolated by filtration after 3 days was washed with ice cold water followed by methanol and dried in air to yield 0.1608 g of **29**.

IR data (cm^{-1}): 3506(s), 2455(br), 1697(w), 1597(w), 1350(w), 1097(w), 814(s), 754(s), 550(w), 444(w).

Synthesis of potassium phthalate in presence of piperazine

To an aqueous solution of KHpht (0.4084 g, 2 mmol) in ~20 mL distilled water, pip (0.0861 g, 1 mmol) was added to get a clear solution. The reaction mixture was heated on a steam bath to reduce the volume to ~15 mL. The solution thus obtained was cooled and left undisturbed for crystallization at room temperature. The needle shaped crystals isolated by filtration after 3 days was washed with ice cold water followed by methanol and dried in air to yield 0.1727 g of **30**.

IR data (cm^{-1}): 2789-2482 (br), 1936(w), 1678(s), 1560(s), 1485(s), 1375(s), 1288(s), 1152(w), 1092(w), 854(w), 808(s), 764(s), 688(w), 552(w).

Synthesis of calcium phthalate in presence of piperazine

Method I

To an aqueous solution of phtH$_2$ (0.3323 g, 2 mmol) and piperazine (0.0861 g, 1 mmol) in ~20 mL distilled water, calcium acetate (0.1582 g, 1 mmol) was added and a clear solution was obtained. The reaction mixture thus obtained was left undisturbed for crystallization at room temperature. The white powdery material obtained by filtration after 3 days was washed with distilled water followed by methanol and dried in air to yield 0.1971 g of **31a**.

IR data (cm^{-1}): 3550-3238 (br), 1639 (s), 1591(s), 1548(s), 1492(s), 1456(s), 1433(s), 1408(s), 1367(w), 1261(w), 1090(w), 960(w), 877(s), 833(s), 817(s), 775(s), 725(s), 694(s), 657(s), 561(s), 437(s), 409(w).

Method II

To an aqueous solution of $CaCl_2 \cdot 2H_2O$ (0.1470 g, 1 mmol) and Na_2CO_3 (0.1059 g, 1 mmol) in ~20 mL distilled water, pip (0.0861 g, 1 mmol) and $phtH_2$ (0.3336 g, 2 mmol) mixture in ~20 mL distilled water was added and a clear solution was obtained. The solution thus obtained was left undisturbed for crystallization at room temperature. The fine crystals isolated by filtration after 7 days was washed with distilled water followed by methanol and dried in air to yield 0.3101 g of **31b**.

Method III

$CaCO_3$ (0.100 g, 1 mmol) was added to ~25 mL of distilled water containing $phtH_2$ (0.3323 g, 2 mmol) and a clear solution was obtained with evolution of effervescence. To this solution, pip (0.0861 g, 1 mmol) dissolved in ~10 mL of distilled water was added and a reaction mixture obtained was left undisturbed for crystallisation. The fine crystals obtained in 24 hrs was washed with methanol and dried in air to yield 0.2854 g of **31c**.

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Synthesis of magnesium phthalate in presence of piperazine.

To an aqueous solution of $Mg(OAc)_2 \cdot 4H_2O$ (0.2145 g, 1 mmol) in ~10 mL distilled water, the aqueous mixture of pip (0.0861 g, 1 mmol) and ptH_2 (0.3323 g, 2 mmol) in ~20 mL distilled water was added. The reaction mixture was heated on a steam bath to reduce the volume to ~15 mL. The solution thus obtained was cooled and left undisturbed for crystallization at room temperature. The transparent crystals isolated by filtration after 5 days was washed with ice cold water followed by methanol and dried in air to yield 0.4008 g of **32**.

IR data (cm^{-1}): 3331-2198 (br), 1552(s), 1448(s), 1390(s), 1335(s), 1285(s), 1140(s), 1076(w), 956(w), 845(w), 745(w), 685(s), 592(s), 428(s).

Synthesis of strontium phthalate in presence of piperazine.

To an aqueous solution of $phtH_2$ (0.3323 g, 2 mmol) and $SrCO_3$ (0.1476 g, 1 mmol) in ~40 mL distilled water, pip (0.0861 g, 1 mmol) was added and the solution was heated to obtain clear solution. The solution thus obtained was cooled and left undisturbed at room temperature. The white powdery material isolated by filtration after 24 hrs was washed with ice cold water followed by methanol and dried in air to yield 0.395 g of **33**.

Synthesis of barium phthalate in presence of piperazine.

To an aqueous solution of $phtH_2$ (0.3323 g, 2 mmol) and $BaCO_3$ (0.1973 g, 1 mmol) in ~40 mL distilled water, pip (0.0861 g, 1 mmol) was added and the solution was heated to obtain clear solution. The solution thus obtained was cooled and left undisturbed at room temperature. The white powdery material isolated by filtration after 24 hrs was washed with ice cold water followed by methanol and dried in air to yield 0.4190 g of **34**.

2.5 Crystal growth reactions of KHpht in presence of metal ions/ amino acids/ organic compounds

Reinvestigation of crystal growth of KHpht in presence of bivalent metal ions (Cu^{2+}*,* Ni^{2+}*,* Zn^{2+}*,* Sr^{2+}*,* Mg^{2+}*,* Ca^{2+} *and* Ba^{2+}*) and trivalent metal ion (*Fe^{3+}*):*

Copper

The aqueous solution of KHpht (2.036 g) was prepared. To this solution (~20 mL) $CuCl_2{\cdot}2H_2O$ (0.005 g) was added. Then the solution (pH ~ 6.5) was kept for slow evaporation at room temperature. Blue coloured (**35a**) compound obtained after 4 days (0.012 g) were isolated by filtration and the filtrate was kept for further evaporation. Hexagonal transparent crystals were isolated after 10 days. The crystals obtained (**35b**) were washed with cold H_2O and methanol, dried and yield (0.1632 g) was recorded.

A similar reaction was carried out by reacting KHpht with nickel chloride hexahydrate, zinc acetate dihydrate, strontium carbonate, barium carbonate, magnesium carbonate, calcium chloride dihydrate. The products obtained from these reactions were isolated, washed with ice cold water, dried and analysed.

Fe (III) ion

KHpht (2.04 g, 10 mmol) was dissolved using distilled water (~15 mL). To this solution of $Fe(NO_3)_3{\cdot}9H_2O$ (8 mg, 0.2 M %) was added. The immediate brown coloured precipitate (**36a**) that formed was filtered and the filtrate (pH=5) was kept for slow evaporation at room temperature without disturbance. Transparent hexagonal shaped crystals (**36b**) were obtained after 12 days. It was washed with ice cold water and methanol; dried and yield was recorded (1.603 g, 78.55 %).The same reaction was carried out with different concentration of $Fe(NO_3)_3{\cdot}9H_2O$ (0.3 mg, 0.5 %) and the reactions were repeated to check the reproducibility.

Reinvestigation of crystal growth of potassium hydrogen phthalate KHpht in presence of amino acids.

Glycine

An aqueous solution of KHpht (1.981 g, 10 mmol) was prepared in ~15mL water. To this solution Glycine (22.5 mg, 3 M %,) was added. This solution (pH~4.5) was kept for slow evaporation at room temperature. Transparent crystals were obtained (**37**) after 5days. It was washed with ice cold water & methanol; dried & yield was recorded (1.259 g, 64 %).The same reaction was carried out with different concentration of Glycine (0.1 mg, 0.2 M %).

A similar reaction was carried out by reacting KHpht with *L*-lysine and *L*-alanine. The products obtained from these reactions were isolated, washed with ice cold water, dried and analysed.

Reinvestigation of crystal growth of potassium hydrogen phthalate (KHpht) in presence of organic compounds.

EDTA

The reaction was carried out in 1:1 ratio. An aqueous solution of KHpht (0.204 g, 1 mmol) was prepared in ~15 mL water. To this solution EDTA (0.372 g, 1 mmol) was added. This solution (pH~4.5) was kept for slow evaporation at room temperature. A powdered compound (**38**) was obtained after 7 days. It was washed with ice cold water & methanol; dried & yield was recorded (0.311 g, 84 %).

Anthracene

The reaction was carried out in 1:1 ratio An aqueous solution of KHpht (0.089 g, 0.5 mmol) was prepared in ~15 mL water. To this solution Anthracene (0.178 g, 0.5 mmol) in 50 mL ethanol was added. This solution (pH~4.5) was kept for slow evaporation at room temperature. A powdered compound (**39**) was obtained after

6 days. It was washed with ice cold water & methanol; dried & yield was recorded (0.075 g, 84 %).The same reaction was carried out with Anthracene dissolved in DMSO.

2.6 Crystal growth reactions of NaHpht·½H_2O in presence of metal ions/ amino acids/ organic compounds

Reinvestigation of crystal growth of sodium hydrogen phthalate hemihydrate NaHpht.$^1/_2H_2O$ in presence of metal ions:

Copper

To the aqueous solution of NaHpht·½H_2O prepared in situ by taking phtH_2 (0.164 g, 99 mmol %) and $NaHCO_3$ (0.166 g, 99 mmol %) in ~15 mL distilled water, an aqueous solution of $CuCl_2·2H_2O$ (1 mmol %) was added. The solution was then kept for slow evaporation at room temperature. Blue coloured crystals obtained initially were isolated by filtration and the filtrate was further kept for crystallisation. Hexagonal shaped transparent crystals were isolated after 5 days. The crystal was then washed with ice cold H_2O and methanol, dried and yield was recorded.

The same above procedure was followed for the other metal ions also and the products obtained were analysed.

The reactions were repeated to check its reproducibility and to optimize the conditions by keeping the stoichiometric ratio constant.

Fe(III) ion

To the aqueous solution of NaHpht·½H_2O (1.9712 g) aqueous solution of $Fe(NO_3)_2{}^{·}9H_2O$ (0.008 g) was added. The immediate precipitate that formed was filtered (0.011 g) and the filtrate obtained was stirred for 30 min to get a homogeneous solution (pH~5.5). Then the solution was kept for slow evaporation at room temperature. Hexagonal shaped transparent crystals were isolated after days.

The crystal was washed with ice cold H_2O and ethanol; dried and yield was recorded (1.44 g).

Reinvestigation of crystal growth of sodium hydrogen phthalate hemihydrates (NaHpht·½H_2O) in presence of amino acids.

L-valine

To an aqueous solution of NaHpht·½H_2O (1.971 g, 10 mmol) *L*- valine (0.585 g, 5 mmol) was added. The reaction mixture was heated on the water bath (pH~5) and was left undisturbed at room temperature. Good transparent hexagonal shaped crystals was isolated after 20 days. The crystals were thoroughly washed with ice cold H_2O and ethanol; dried and yield was recorded (1.402 g, 71 %). The reaction was carried out twice to check its reproducibility. The use of a very small amount of *L*-valine (0.012 g) also resulted in isolation of crystals in 72 % yield and all these crystals were characterized.

A similar reaction was carried out by reacting KHpht with Glycine, *L*-lysine and *L*-alanine. The products obtained from these reactions were isolated, washed with ice cold water, dried and analysed.

Reinvestigation of crystal growth of sodium hydrogen phthalate hemihydrates (NaHpht·½H_2O) in presence of organic compounds.

EDTA

To the aqueous solution of NaHpht·½H_2O (phtH$_{2\ (1mmol)}$ 0.1661 g + NaHCO$_{3\ (1mmol)}$ 0.0840 g) aqueous solution of EDTA (1 mmol, 0.3722 g) was added. The solution was then stirred for ~15 min to get it homogenized (pH~4.5). Then the covered solution was kept for slow evaporation at room temperature. Hexagonal shaped transparent crystals were isolated after 13 days. The crystal was then washed with ice cold H_2O and ethanol; dried and yield was recorded (1.243 g).

Anthracene

To the aqueous solution of NaHpht·½H_2O (phtH$_{2\ (1mmol)}$ 0.1661 g + NaHCO$_{3\ (1mmol)}$ 0.0840 g in minimum amount of H_2O), solution of Anthracene (1 mmol, 0.1782 g) in ethanol (till dissolution) was added. The solution was then stirred for ~20 min to get it homogenized (pH~5). Then the covered solution was kept for slow evaporation at room temperature. The same was repeated with another solvent that is DMSO. Flaked crystals were found in both the cases which were isolated after 17 and 20 days respectively. The crystal was then washed with ice cold H_2O dried and yield was recorded (1.032 g and 0.765 g) respectively.

2.7 Crystal growth reactions of *crystal growth of $ZnSO_4·7H_2O$ in presence of L-valine*

A mixture of zinc sulphate heptahydrate (1.438 g, 5 mmol) and *L*-valine (0.586 g, 5 mmol) was taken in water 25 ml and the reac-tion mixture was stirred well to obtain a clear colourless solution. The clear reaction mixture (pH~4.5) was left undisturbed at room temperature. Slow evaporation of the solvent resulted in the separation of transparent crystals (**40**), which were isolated by filtration and dried in air to yield 0.45 g of crystalline product.

In addition, we investigated crystal growth reaction by taking *L*-valine (0.586 g, 5 mmol) and zinc sulphate heptahydrate (0.144 g, 0.5 mmol) in a 10:1 mol ratio and the crystalline product from this experiment was isolated as before. We performed one more crystal growth experiment by employing a large excess of zinc sulphate heptahydrate (10 mmol) and *L*-valine (1 mmol) and the crystalline product from this experiment was isolated and analysed.

2.8 Crystal growth reactions of *crystal growth of KNO_3 / $NaNO_3$ in presence of L-glutamine:*

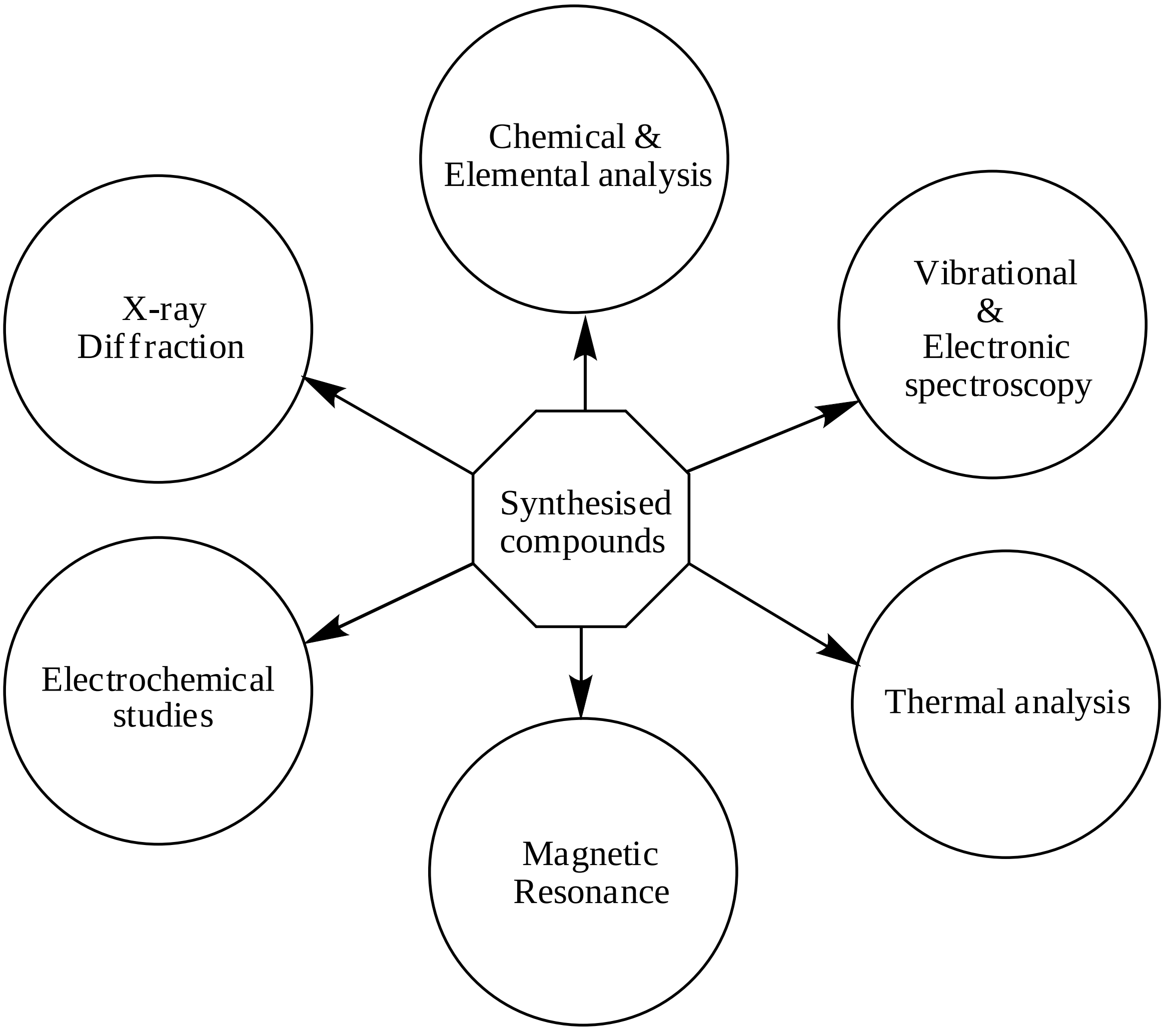
A mixture of potassium nitrate (0.5056 g, 5 mmol) and *L*-glutamine (1.4615 g, 10 mmol) was taken in water 15 mL and was stirred well to obtain a clear colourless solution (pH~5.5). H_2O_2 (2 mL) was added to this and the reaction mixture was left undisturbed at ambient temperature. Slow evaporation of the solvent resulted in the separation of crystals (**41**) in 7 days, which were isolated by filtration, washed with little cold water and dried in air to yield 1.215 g of crystalline material.

The use of sodium nitrate (0.425 g, 5 mmol) instead of potassium nitrate in the above crystal growth reaction resulted in the formation of transparent crystals (**42**) (1.147 g) which were isolated by following the same procedure as given above.

In addition, we investigated crystal growth reaction by taking alkali metal nitrate and *L*-glutamine in a 1:1 molar ratio. The products obtained were isolated as before and analysed.

RESULTS AND DISCUSSIONS

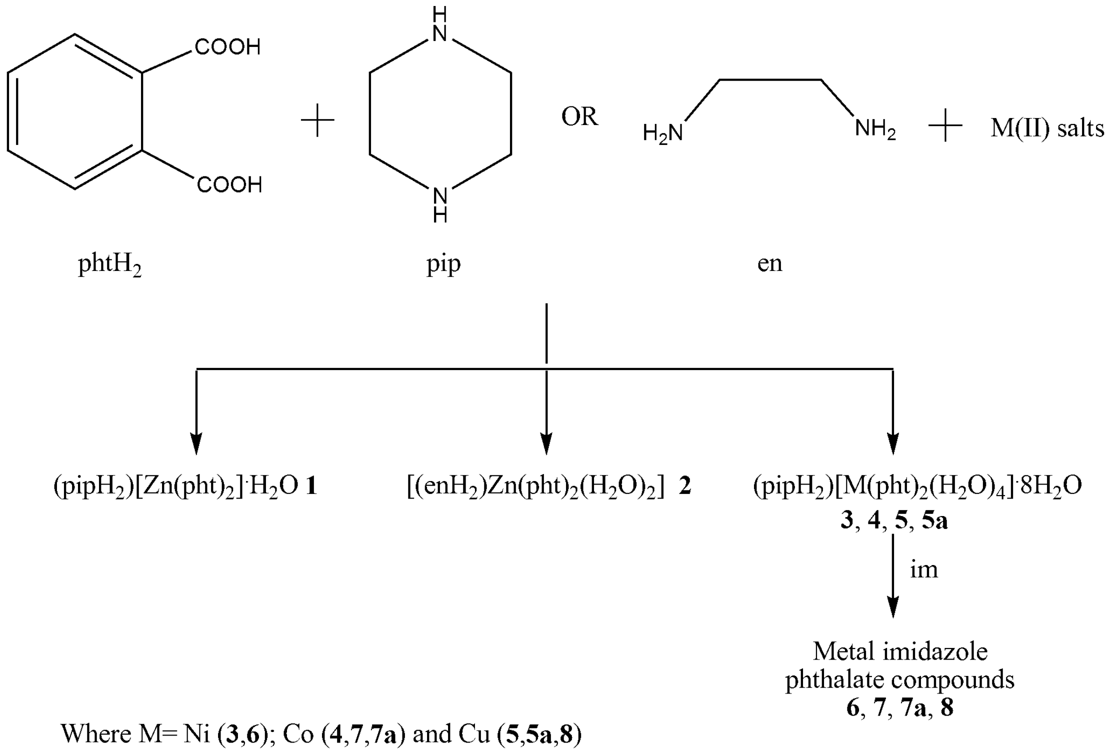
The synthetic aspects, spectroscopic characterization, structural analysis and investigations of thermal, electrochemical and magnetic properties of the synthesized compounds are described in this chapter. The various chemical and instrumental techniques of analysis employed in the present work are as follows**:**



Investigation of synthesised metal bis(phthalato) compounds

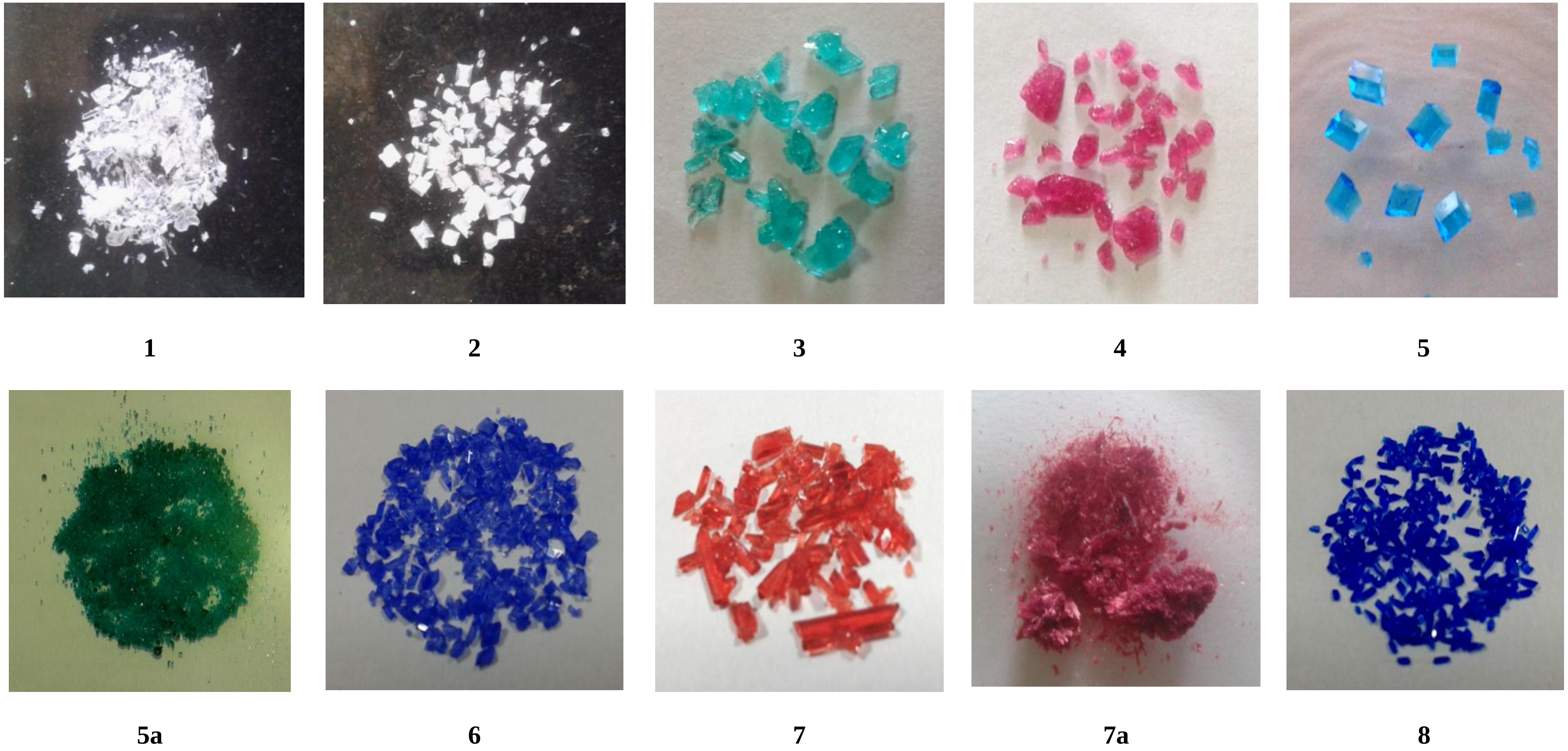
3.1 Investigation of Zn(II), Ni(II), Co(II) and Cu(II) phthalates

A general protocol for the synthesis of metal phthalates in presence of amines viz. piperazine, ethylenediamine and imidazole is depicted in Scheme 3.1.



Scheme 3.1 – Syntheses of metal phthalates in presence of pip, en and im.

The morphology and colour of the synthesised Zn(II), Ni(II), Co(II) and Cu(II) phthalate compounds are depicted in Fig. 3.1.



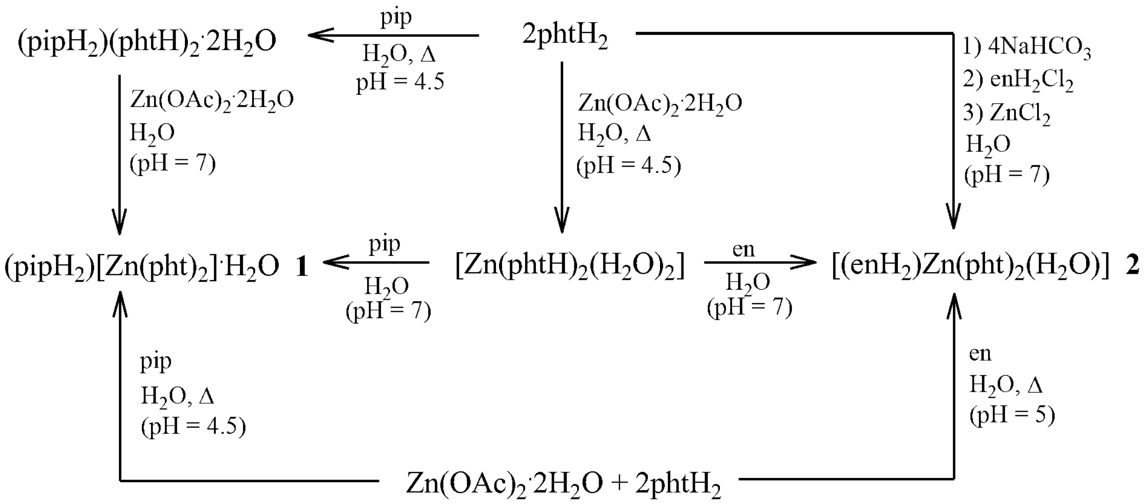
1 2 3 4 5

5a 6 7 7a 8

Fig. 3.1 – Crystals of synthesised metal phthalates **1**-**8**.

*3.1.1 Synthetic aspects, spectral characteristics and thermal studies for **1** and **2***

We have employed a carboxylate exchange reaction involving the reaction of $Zn(OAc)_2{\cdot}2H_2O$ with $phtH_2$ in 1:2 mole ratio to afford $[Zn(phtH)_2(H_2O)_2]$ in high yield, which is used as a precursor for the synthesis of compound **1** (Scheme 3.2). The bis(hydrogenphthalate) compound $[Zn(phtH)_2(H_2O)_2]$ thus obtained was then reacted with piperazine (pip) in 1:1 mole ratio wherein it deprotonates hydrogenphthalate to phthalate resulting in compound **1** forming $[Zn(pht)_2]^{2-}$ anion and piperazinediium as charge balancing cation. Alternatively, a single pot reaction between $Zn(OAc)_2{\cdot}2H_2O$, $phtH_2$ and pip in 1:2:1 mole ratio in aqueous medium with mixing of these reagents in any order resulted in **1** explaining the thermodynamic stability of **1**. Compound **1** could also be obtained by reacting piperazinediium bis(hydrogenphthalate) $(pipH_2)(phtH)_2{\cdot}2H_2O$ which was prepared as per the reported procedure [199] with $Zn(OAc)_2{\cdot}2H_2O$ in aqueous medium at room temperature in 1:1 mole ratio.



Scheme 3.2– Syntheses of Zn(II) phthalates in presence of pip and en

The generality of this methodology can be evidenced by the formation of $[(enH_2)[Zn(pht)_2](H_2O)]$ **2** by use of ethylenediamine (en) in the above reaction instead of piperazine. Compound **2** was also crystallised from an aqueous mixture of disodium salt of $phtH_2$ (generated *in situ*) by reacting it with $NaHCO_3$, ethylenediamine dihydrochloride and $ZnCl_2$ (Scheme 3.2). The composition of precursor zinc(II) phthalate compound $[Zn(phtH)_2(H_2O)_2]$, **1** and **2** was arrived at based on elemental analysis, ZnO formed on pyrolysis and weight loss studies. The IR spectra of **1** (Fig. 3.2) and **2** (Fig. 3.3) exhibits several sharp bands in the mid-infrared region, clearly indicating the presence of the organic moieties.

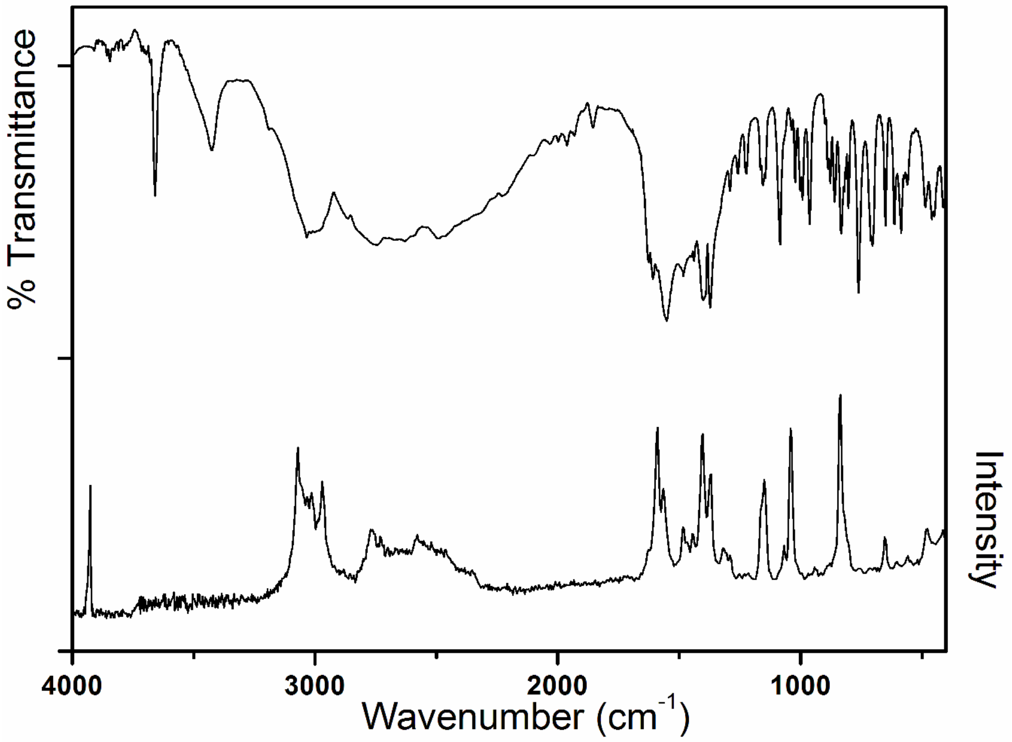


Fig. 3.2 – IR and Raman spectra of $(pipH_2)[Zn(pht)_2]\cdot H_2O$ **1**

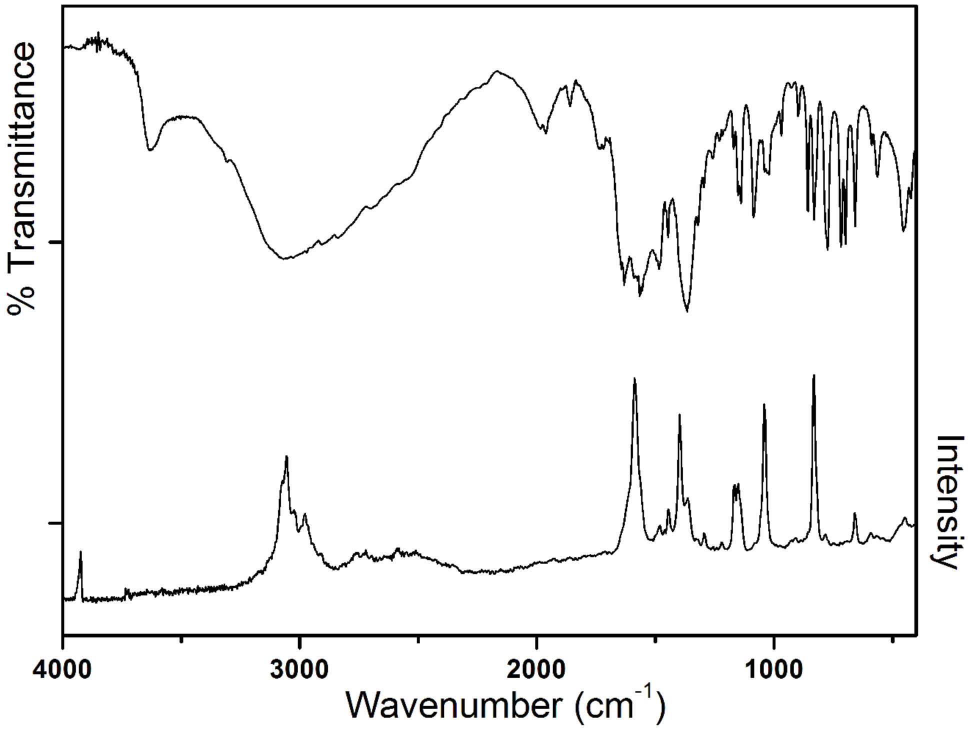


Fig. 3.3 – IR and Raman spectra of $[(enH)_2Zn(pht)_2(H_2O)]$ **2**

Characteristic signals due to asymmetric (υ_{as}) and symmetric (υ_s) stretching vibrations of the carboxylate group in **1** are observed at 1552 and 1371 cm^{-1} and for **2** at 1566 and 1366 cm^{-1} respectively.

The UV-visible spectrum of precursor compound $[Zn(phtH)_2(H_2O)_2]$ in water was similar to free $phtH_2$ spectrum, which can be assigned to the intra ligand charge transfer of aromatic phthalate (Fig. 3.4). The UV-DRS spectrum of **1** show bands at 274 nm and **2** at 283 nm that can be attributed to intra ligand charge transfer of aromatic phthalate (Fig. 3.5).

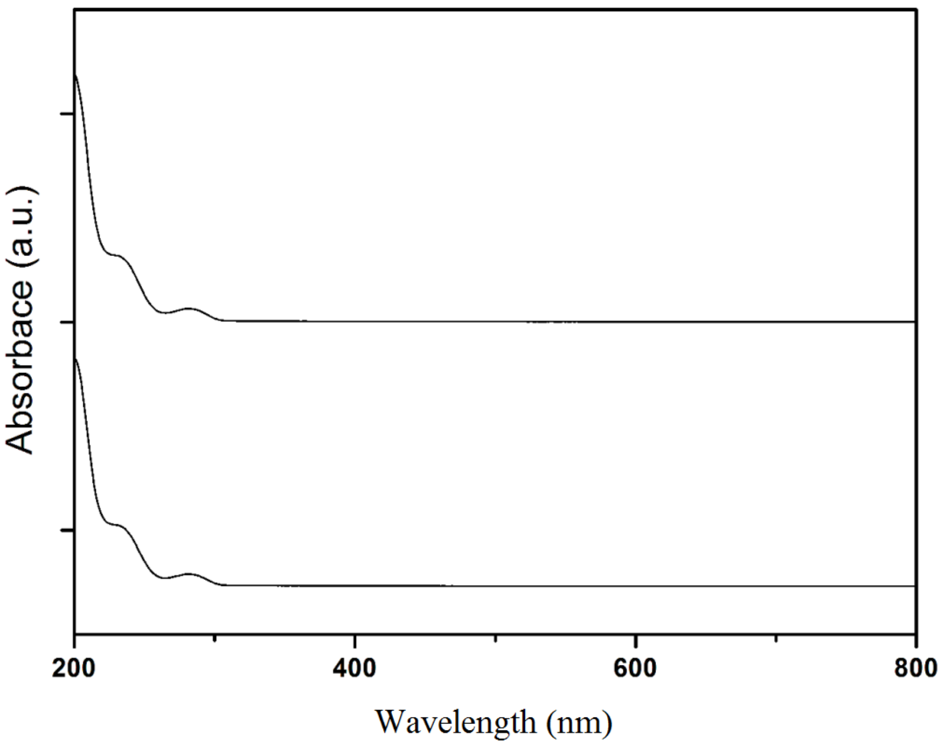


Fig. 3.4 – UV-Visible spectra of phtH$_2$ (top) and [Zn(phtH)$_2$(H$_2$O)$_2$] in H$_2$O (bottom)

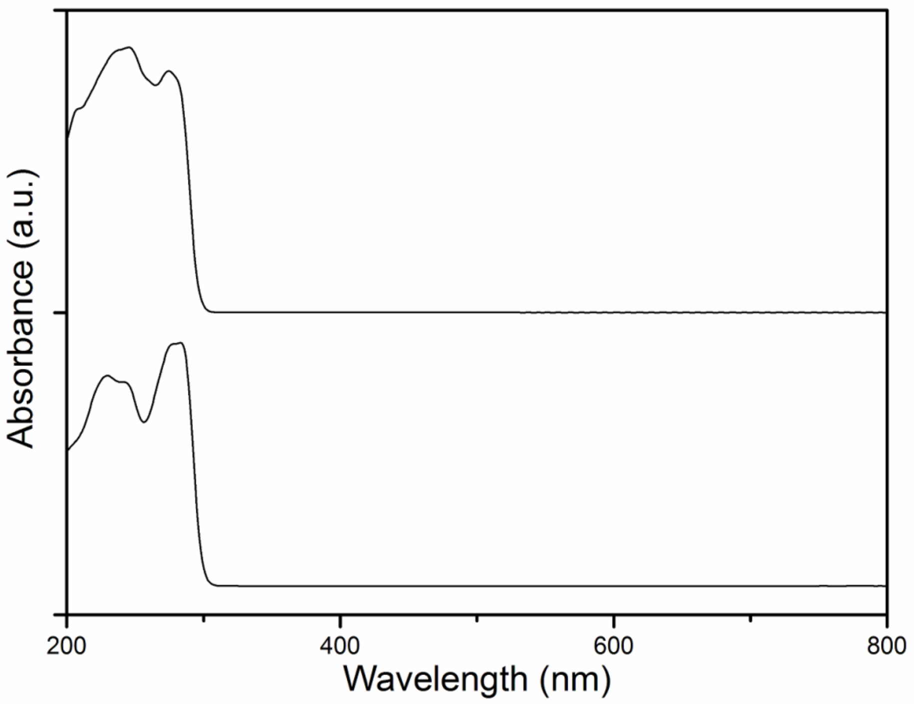


Fig. 3.5 – Diffused reflectance spectra of **1** and **2**

The precursor compound [Zn(phtH)$_2$(H$_2$O)$_2$], **1** and **2** is decomposed to ZnO by heating in a furnace at 500°C, which was confirmed from the featureless IR spectrum of the three residues (Fig. 3.6).

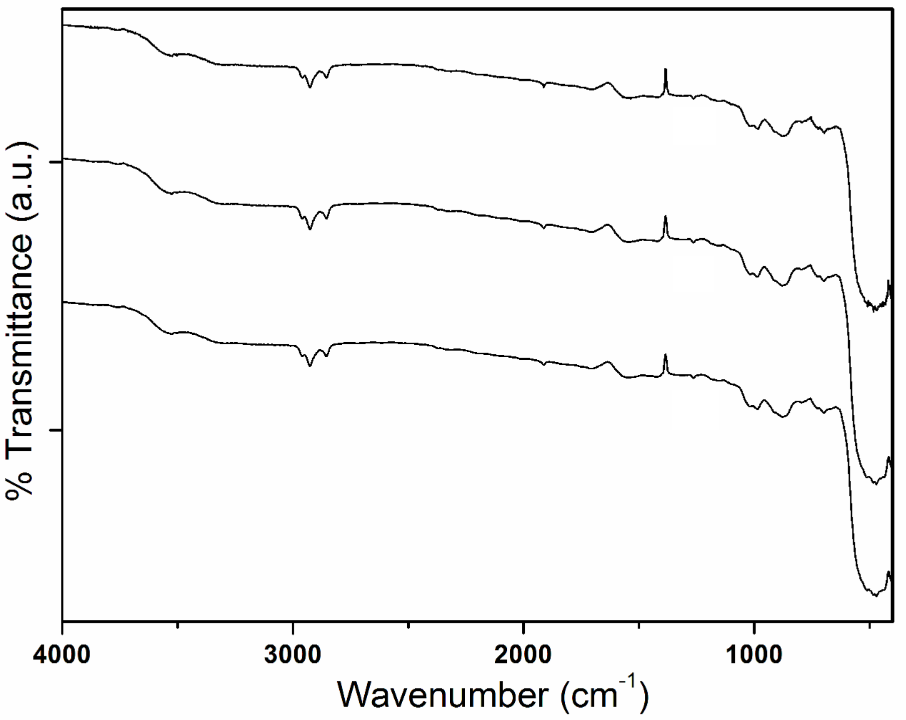


Fig. 3.6 – IR spectra of residues obtained after heating at 500°C [Zn(phtH)$_2$(H$_2$O)$_2$] (top), **1** (middle) and **2** (bottom)

The phase purity of **1** was confirmed by its identical theoretical and experimental X-ray powder patterns (Fig. 3.7). On the basis of these spectral analysis, weight loss study and CHN data, compound **2** can be formulated as [(enH$_2$)Zn(pht)$_2$H$_2$O].

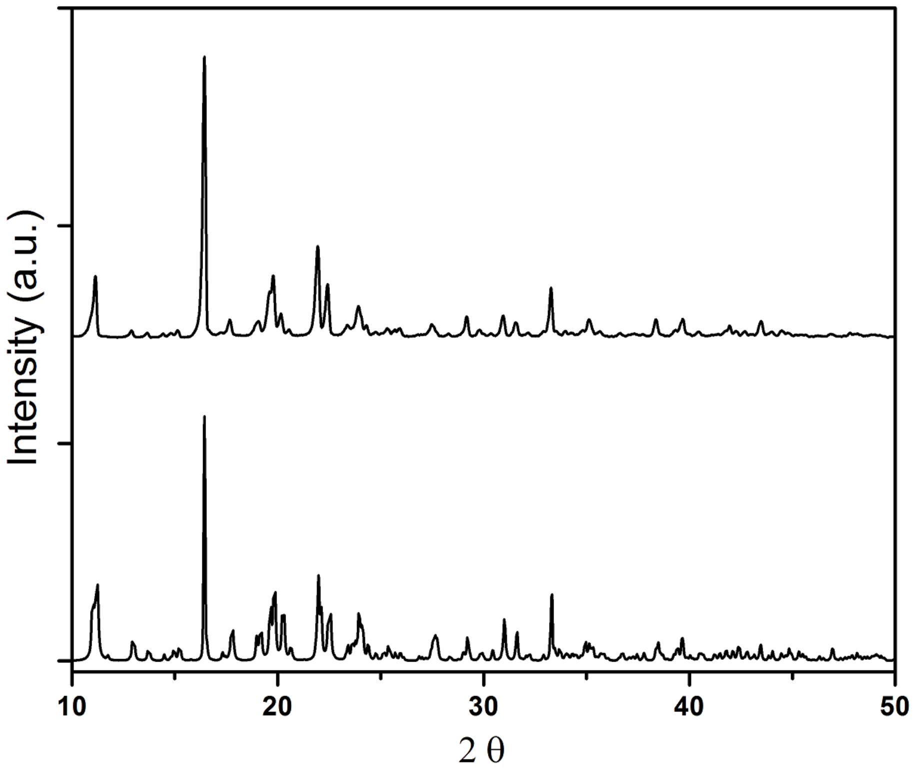


Fig. 3.7 – Experimental (top) and theoretical (bottom) X-ray powder pattern of **1**

The TG-DTA curve of **1** (Fig. 3.8) exhibits an endothermic event with the peak in DTA at 155°C. TG curve is parallel to the *x-axis* till 150°C. From temperature 150-200°C, TG shows a gradual decrease in mass by 3 % equivalent to loss of one water molecule. Above 200°C, the DTA curve shows only exothermic peak with signals at 347°C and 470°C, accompanied by a rapid drop in mass that can be attributed to decomposition of **1**. In the absence of mass spectral data of the emitted fragments, no detailed description of the thermal decomposition processes can be made. However, the obtained residual mass of 16.82 % is in good the agreement for formation of ZnO. The formation of the oxide phase can also be evidenced by the featureless infrared spectrum of the residue as well as its powder pattern (Fig. 3.9). The results of weight loss study at 500°C in a furnace add more credence to the TG-DTA data.

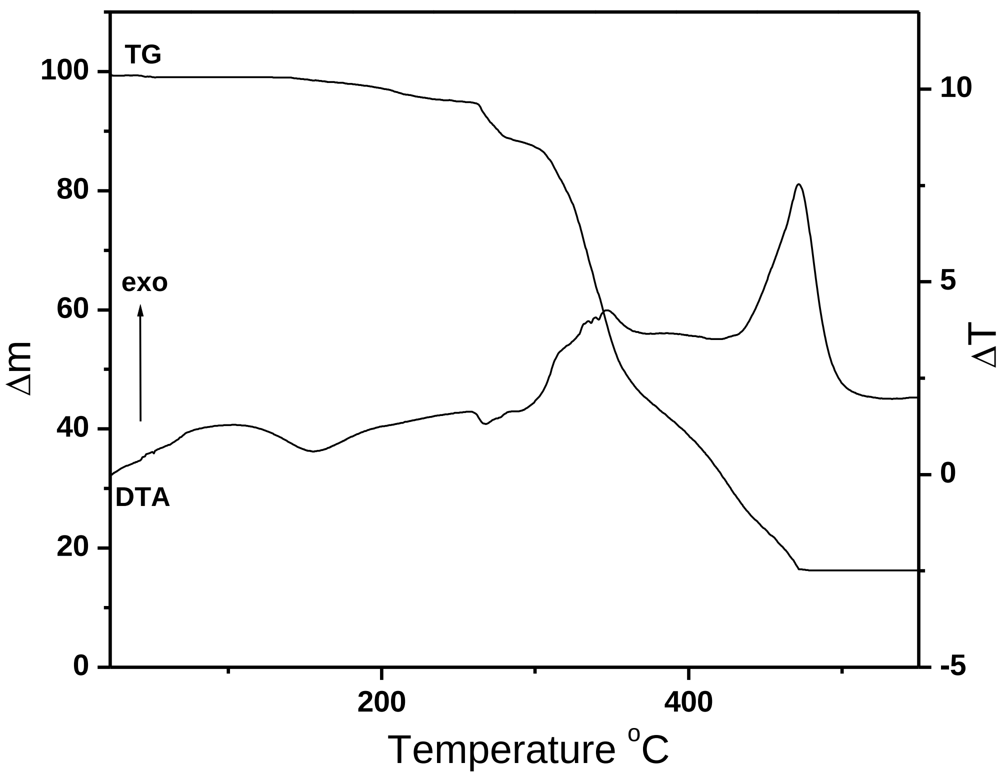


Fig. 3.8 – TG-DTA curve of **1**

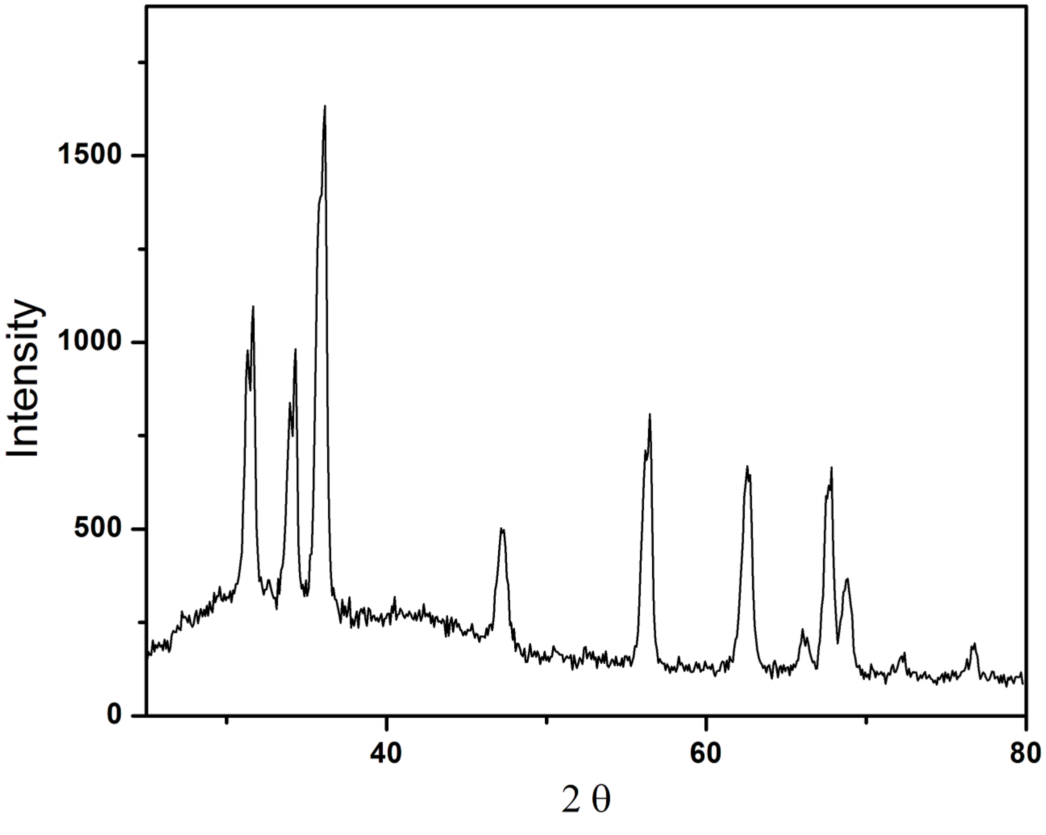


Fig. 3.9 – X-ray powder pattern of **1** after heating at 500°C

3.1.2 Crystal structure of $(pipH_2)[Zn(pht)_2]\cdot H_2O$ **1**

The zinc bis(phthalato) compound **1** crystallises in the centrosymmetric monoclinic $P2_1/c$ space group. Its crystal structure consists of an unique Zn(II) ion, two crystallographically independent phthalate ligands, a lattice water molecule all of which are located in general positions and two unique piperazinium $(pipH_2)^{2+}$ dication located on inversion centres (Fig. 3.10). The details of structure refinement for **1** are given in Table 3.1. It is interesting to note that many known $(pipH_2)$ compounds crystallize in the $P2_1/c$ space group [194-206]. The geometric parameters of the cations are in the normal range and are comparable with data of other reported piperazinediium cations in the literature.

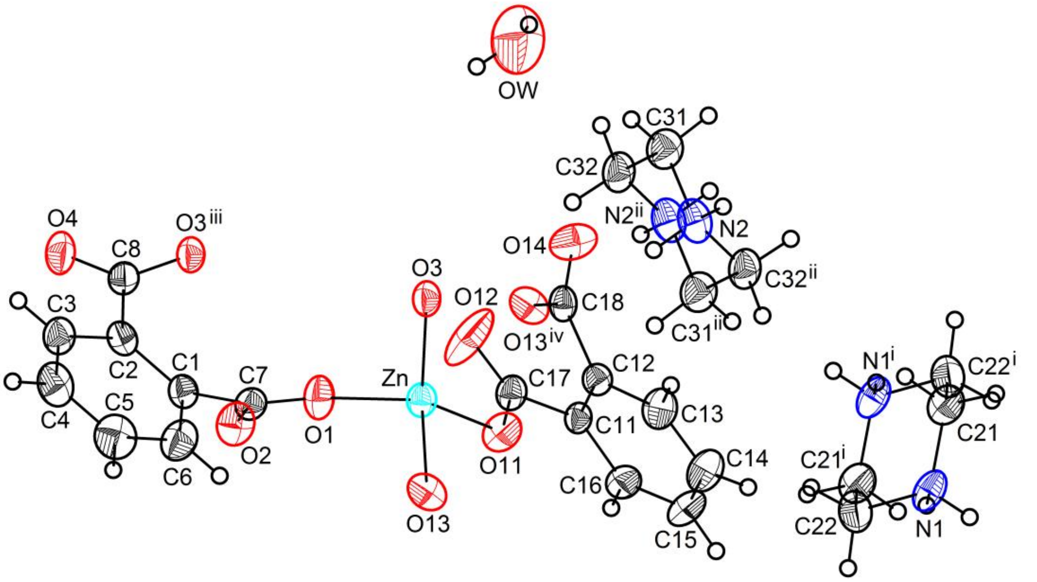


Fig. 3.10 – The crystal structure of $(pipH_2)[Zn(pht)_2]\cdot H_2O$ **1** showing the atom labelling scheme and the coordination sphere of Zn(II) in **1**. Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as circles of arbitrary radius. Symmetry code: i) 2-x, 1-y, -z; ii) –x, 1-y, 1-z; iii) 1-x, 1-y, 2-z; iv) -1+x, y, z

Table 3.1 – Crystal data and structure refinement for $(pipH_2)[Zn(pht)_2]\cdot H_2O$ **1**

Empirical formula	$C_{20}H_{22}N_2O_9Zn$
Formula weight (g mol^{-1})	499.77
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	8.142(3)
b (Å)	21.537(8)
c (Å)	11.782(5)
α (°)	90.00
β (°)	99.441(7)
γ (°)	90.00
Volume (Å^3)	2038.1(14)
Z	4
D_{calc} (mg/m^3)	1.629
Absorption coefficient (mm^{-1})	1.263
F(000)	1032
Crystal size (mm^3)	0.16 x 0.14 x 0.12
θ range for data collect. (°)	1.89 to 26.50
Index ranges	$-10 \leq h \leq 10$
	$-26 \leq k \leq 26$
	$-14 \leq l \leq 14$
Reflections collected / unique	20445 / 4201 [R(int) = 0.0698]
Completeness to θ = 26.50°	99.5 %
Absorption correction	Multi scan
Max. and min. transmission	0.859 and 0.817
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4201 / 3 / 286
Goodness-of-fit on F^2	0.981
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.1038
R indices (all data)	R1 = 0.0627, wR2 = 0.1107
Largest diff. peak and hole (e Å^{-3})	0.616 and -0.481

The two piperazines are diprotonated present on an inversion centre serving as a charge balancing cation for $[Zn(pht)_2]^{2-}$ unit in the structure. The central Zn is tetrahedrally coordinated to four oxygen atoms from four symmetry related phthalate anions. The Zn-O bond distances range from 1.953(2) to 1.992(6) Å while the O-Zn-O angles vary between 99.07(10) to 122.22(9)° indicating a distorted $\{ZnO_4\}$ tetrahedron (Table 3.2).

Table 3.2 – Selected bond lengths [Å] and angles [°] for $(pipH_2)[Zn(pht)_2]\cdot H_2O$ **1**

Bond lengths			
Zn-O(11)	1.953(2)	Zn-O(3)	1.968(2)
Zn-O(1)	1.965(2)	Zn-O(13)	1.992(2)
Bond angles			
O(11)-Zn-O(1)	108.70(10)	O(11)-Zn-O(13)	99.07(10)
O(11)-Zn-O(3)	122.22(9)	O(1)-Zn-O(13)	110.13(9)
O(1)-Zn-O(3)	104.17(9)	O(3)-Zn-O(13)	112.38(9)

The two unique phthalate ligands in the crystal structure display μ_2-bridging bidentate binding mode (Fig. 3.11).

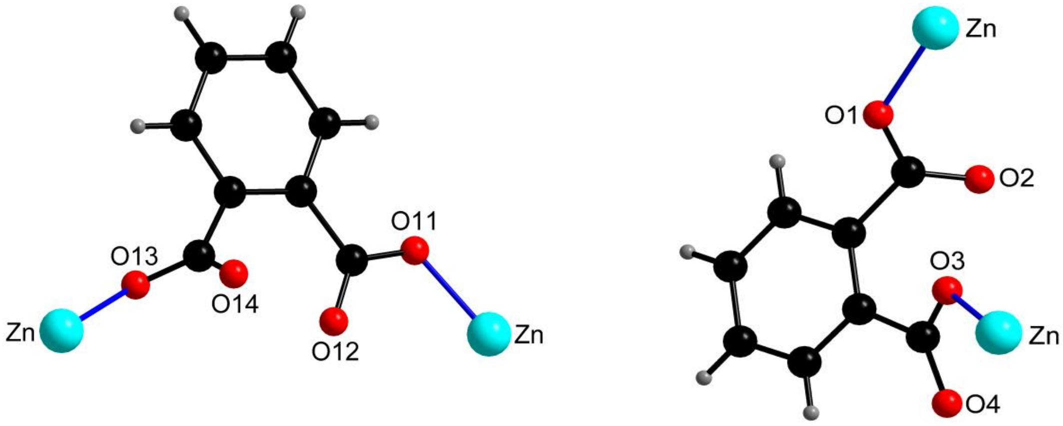


Fig 3.11 – μ_2-bidentate bridging binding modes shown by two unique phthalate ligands in **1.** First unique phthalate ligand linking to two Zn(II) ions via O13 and O11 (Left) and second unique phthalate ligand linking to two Zn(II) ions via O3 and O1 (Right) with two carboxylate groups displaying monodentate coordination in both. Zn-O bonds are shown in blue.

One of the unique phthalate in each formula unit links two Zn(II) ions via O11 and O13 atoms with Zn-O distance of 1.953(2) and 1.992(2) Å resulting in the formation of a chain extending along *a-axis* with Zn···Zn separation of 8.142(5) Å and the second unique phthalate ligand binds to another symmetry related Zn(II) ion along *c-axis* with a shorter Zn···Zn separation of 5.839(6) Å via O1 and O3 with Zn-O distance of 1.968(2) and 1.965(2) Å, which further forms a chain via O11 and O13 to complete its coordination but antiparallel to previous chain. The net result of the μ$_2$-bridging bidentate binding modes of the unique pht ligands in **1** is the formation of a one-dimensional Zn(II) ladder (Fig. 3.12).

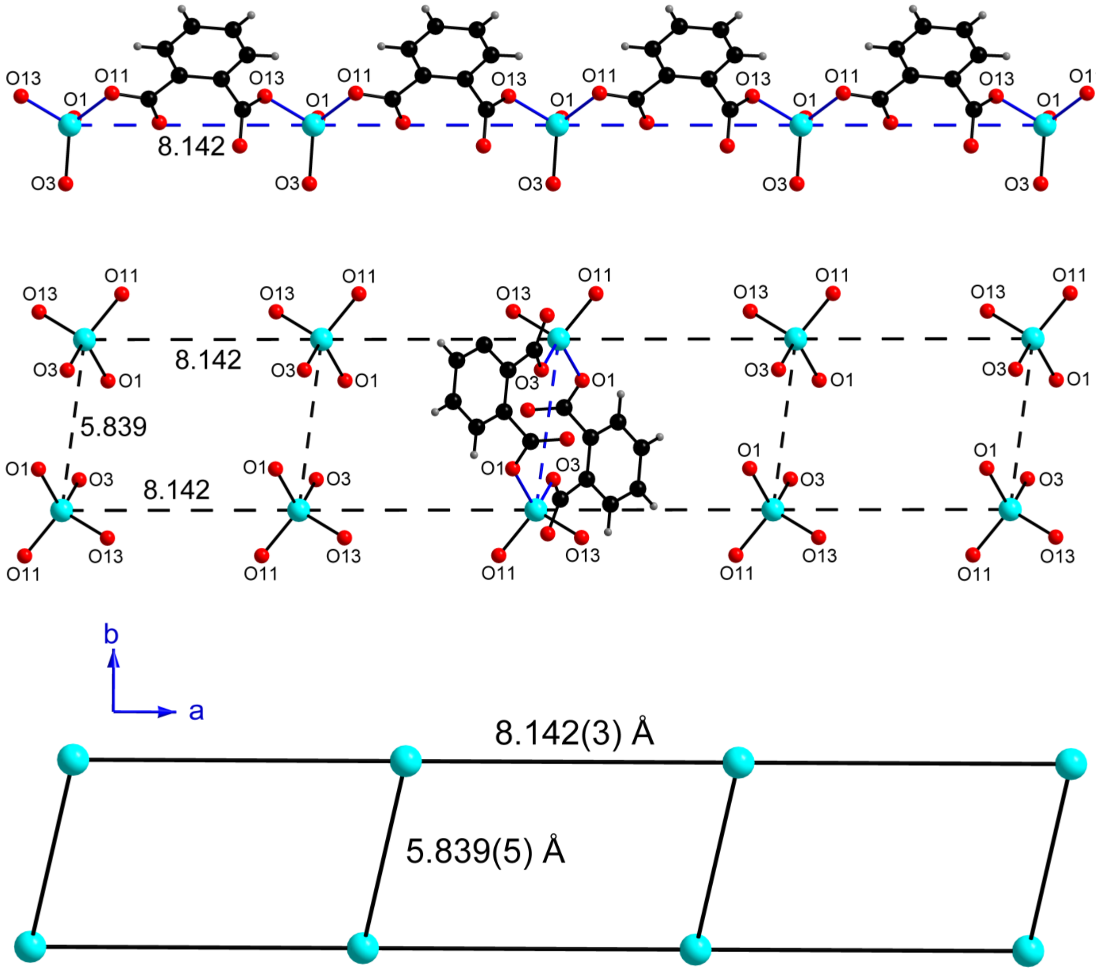


Fig. 3.12 – A portion of the infinite chain extending along *a-axis* with Zn···Zn separation of 8.142 Å due to the bridging bidentate coordination mode of the first unique phthalate (O11, O13) ligand (Top). A pair of the second unique (O1, O3) ligands cross link two infinte chains with Zn···Zn separation of 5.839 Å. For clarity the crosslink is shown only for the middle Zn(II) ion in each chain (Middle). A portion of the infinite Zn(II) ladder in **1** extending along *a-axis*. For clarity only the Zn(II) points in the ladder are shown (Bottom).

The two unique (pipH$_2$)$^{2+}$ cations adopt the chair conformation as seen earlier in reported compounds with (pipH$_2$)$^{2+}$ cation (*vide supra*) having bond lengths and angles in the similar range. The two dication shows different hydrogen bonding environment around them (Fig. 3.13). The first unique (pipH$_2$)$^{2+}$ cation (N1) shows two types of hydrogen bonding N-H···O and C-H···O with the distances and angles in the range 2.645(2) to 3.142(3) Å and 125.44 to 152.97°. The second unique (pipH$_2$)$^{2+}$ cation (N2) displays only N-H···O hydrogen bonding interaction with the D···A distance ranging between 2.627(1) to 2.727(3) Å with angles 162.92(4) to 166.44(7)°. The two unique dications being on inversion centre, the hydrogen bonding for only half of the molecule is being shown. On the other hand, [Zn(pht)$_2$]$^{2-}$ is hydrogen bonded with three (pipH$_2$)$^{2+}$ cation in its surrounding and one lattice water with the distance 2.818(2) Å and angle 178.74°.

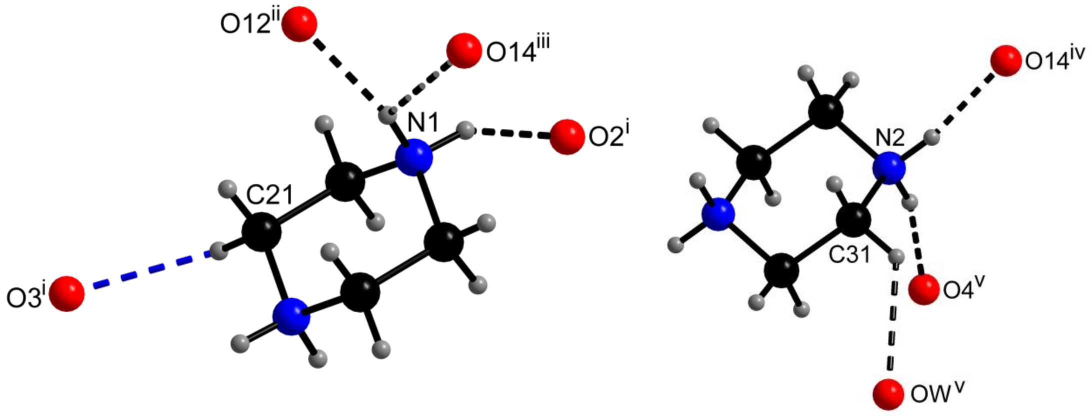


Fig. 3.13 – The H-bonding surroundings of the unique cations showing N-H···O and C-H···O interactions (shown in broken lines) Symmetry code: i) x, y, z-1 ii) x+1, y, z-1 iii) x, y, z-1 iv) –x+1, -y+1, -z+1 v) x, y, z.

The lattice water makes this structure more remarkable as each of the unique cations are lined by water molecules on either side. The OWH2W···O2 (symmetry code -x+1, -y+1, -z+2) interaction between the lattice water and the phthalate oxygen O2 organises the water molecules on either side of the ladder. The net effect of the C31-H18B···OW and OW-H2W···O2 interactions involving the N2 cation, lattice water and the phthalate oxygen is an assembly of an unique supramolecular architecture such that each layer of N2 cations or the ladder anion is on either side of water layers resulting in the following H-bonded sequence viz. water···cation···water···ladder···water and so on in the crystallographic *ac* plane (Fig. 3.14).

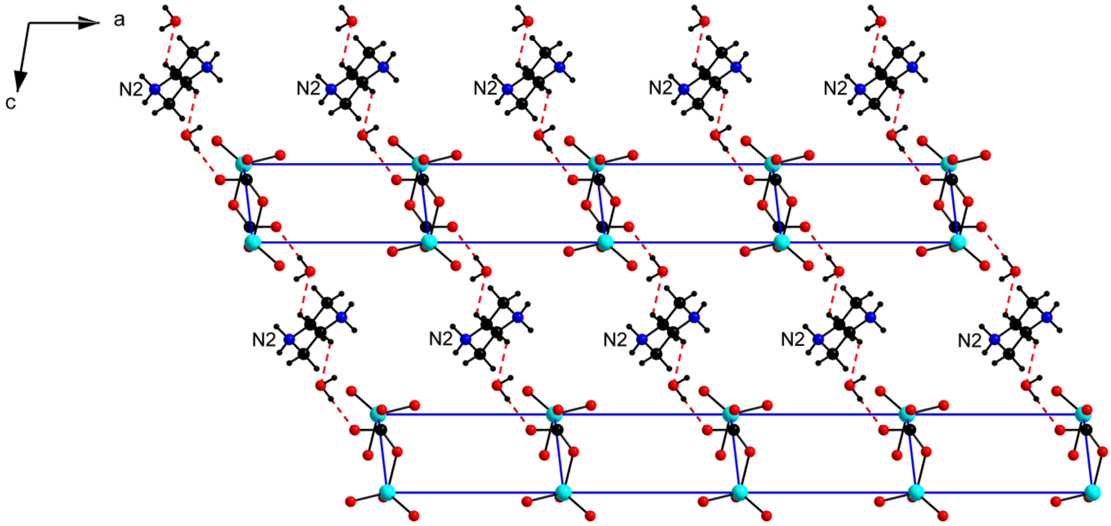


Fig. 3.14 – The supramolecular architecture of (pipH$_2$)[Zn(pht)$_2$]·H$_2$O **1** showing (*For clarity only the N2 cations are shown*) the sequence viz. water···cation···water···ladder···water and so on in the crystallographic *ac* plane. H-bonds are shown in red broken lines.

The unique cations are differently disposed in the crystal structure, with the N1 cations located in the ladder cavity, and the N2 cations positioned on either side of a water decorated ladder in the crystallographic *ac* plane (Fig. 3.15). This actually amounts to sandwiching an infinite Zn(II) chain between the two unique cations, resulting in alternate layers of cations and anions. The geometric parameters of all the hydrogen bonds are listed in Table 3.3.

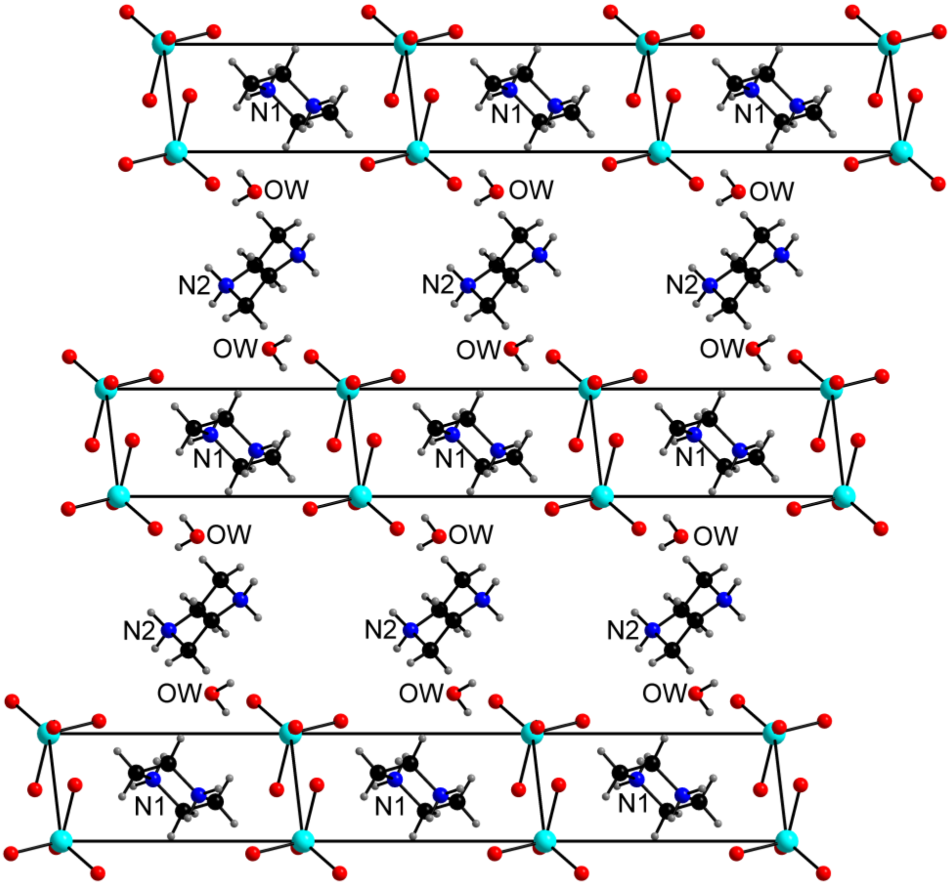


Fig. 3.15 – The disposition of the unique piperazinediium (N1 and N2) in the crystal structure of **1.**

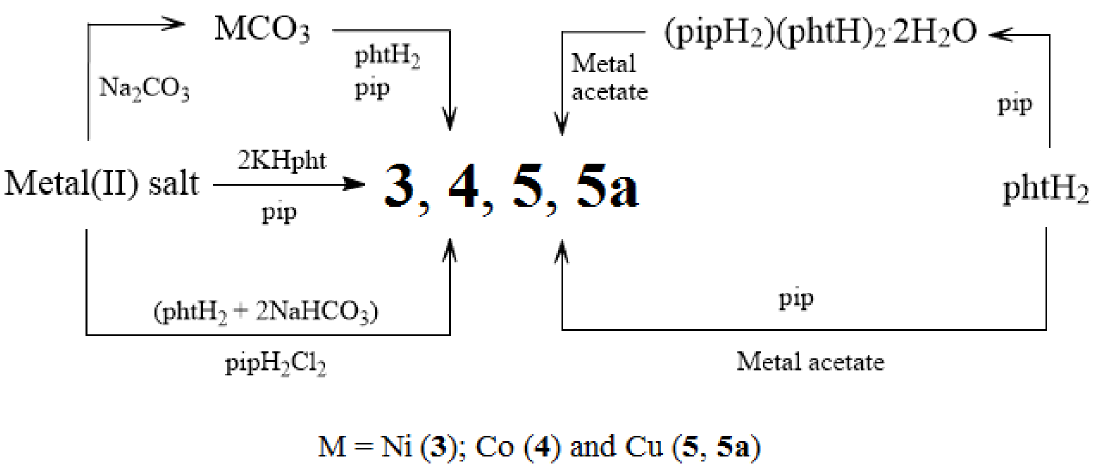
Table 3.3 – Hydrogen bonding geometry [Å and °] for (pipH$_2$)[Zn(pht)$_2$]·H$_2$O **1**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<DHA	Symmetry code
N1-H12A···O2	0.900	1.828	2.645	149.83	x, y, z-1
N1-H11B···O12	0.900	1.843	2.676	152.97	x+1, y, z-1
N1-H11B···O14	0.900	2.554	3.162	125.44	x, y, z-1
N2-H15A···O14	0.900	1.744	2.627	166.44	-x+1, -y+1, -z+1
N2-H16B···O4	0.900	1.854	2.727	162.90	x, y, z
C21-H9B···O3	0.970	2.345	3.142	149.91	x, y, z-1
C31-H18B···OW	0.970	2.386	3.117	131.61	x, y, z
OW-H2W···O2	0.850	1.967	2.818	179.74	-x+1, -y+1, -z+2

D= Donor and A= Acceptor

*3.1.3 Synthetic aspects, spectral characteristics and thermal studies for **3, 4**, **5**and **5a***

Green coloured **3** was crystallised from an aqueous mixture of potassium hydrogen phthalate (KHpht), piperazine (pip) and $NiCl_2·6H_2O$ ($NiSO_4·4H_2O$/ $Ni(NO_3)_2·7H_2O$) in 2:1:1 molar ratio irrespective of their order of mixing (Scheme 3.3). The formation of only compound **3** from the reaction mixture (using any Ni source) unambiguously shows that the anion present (Cl^- /SO_4^{2-} /NO_3^-) has no effect on product formation and bis(phthalato) compound charge balanced by $(pipH_2)^{2+}$ is the only preferred product. The facile formation of **3** is further revealed by a single pot reaction of $Ni(OAc)_2·2H_2O$ (OAc = acetate), phthalic acid ($phtH_2$) and pip in 1:2:1 mole ratio in aqueous medium or by an aqueous reaction of reported compound $(pipH_2)(phtH)_2·2H_2O$ [199] with $Ni(OAc)_2·4H_2O$ at room temperature. Alternatively, an acid-base reaction of freshly precipitated $NiCO_3$ from the mixture of $NiCl_2·6H_2O$ and Na_2CO_3 in 1:1 molar ratio with $phtH_2$ and then adding pip resulted in **1**. Also, a reaction of $NiCl_2·6H_2O$ with *in situ* generated disodium salt of $phtH_2$ and pip was used as an alternative method for the compound preparation (Scheme 3.3). By taking Co(II) and Cu(II) salt instead of Ni(II) salt in above reactions results in pink coloured compound **4** and blue coloured compound **5** (Scheme 3.3) respectively. In the case of Cu in addition to **5**, a green coloured compound **5a** is obtained in low yield which loses its crystallinity on removal from the reaction mixture.



Scheme 3.3 – Detailed synthesis of compounds **3**, **4**, **5** and **5a**

The IR spectra of **3, 4, 5** and **5a** exhibit several sharp signals in the mid-IR region indicating the presence of organic moieties (Fig. 3.16 - 3.19). The absence of a signal in the region 1680-1710 cm^{-1} clearly indicates the formation of the fully deprotonated phthalate dianion in these compounds. In the IR spectrum of **3**, an intense band at 1549 cm^{-1} (1552 in **4**; 1553 in **5**; 1562 in **5a**) can be assigned for the asymmetric stretching vibration of the carboxylate group (υ_{asym}) and the bands observed at 1414 and 1394 cm^{-1} (1396 and 1377 in **4**; 1394 and 1375 in **5**; 1390 and 1365 in **5a**) for symmetric stretching vibration (υ_{sym}). Interestingly compound **3** exhibits two signals at 1546 and 1397 cm^{-1} in its Raman spectrum (1566 and 1417 in **4**; 1560 and 1412 in **5**) (Fig. 3.16 - 3.19) with the former being more intense and assignable for asymmetric (υ_{asym}) and symmetric stretching vibration (υ_{sym}) of the carboxylate group respectively.

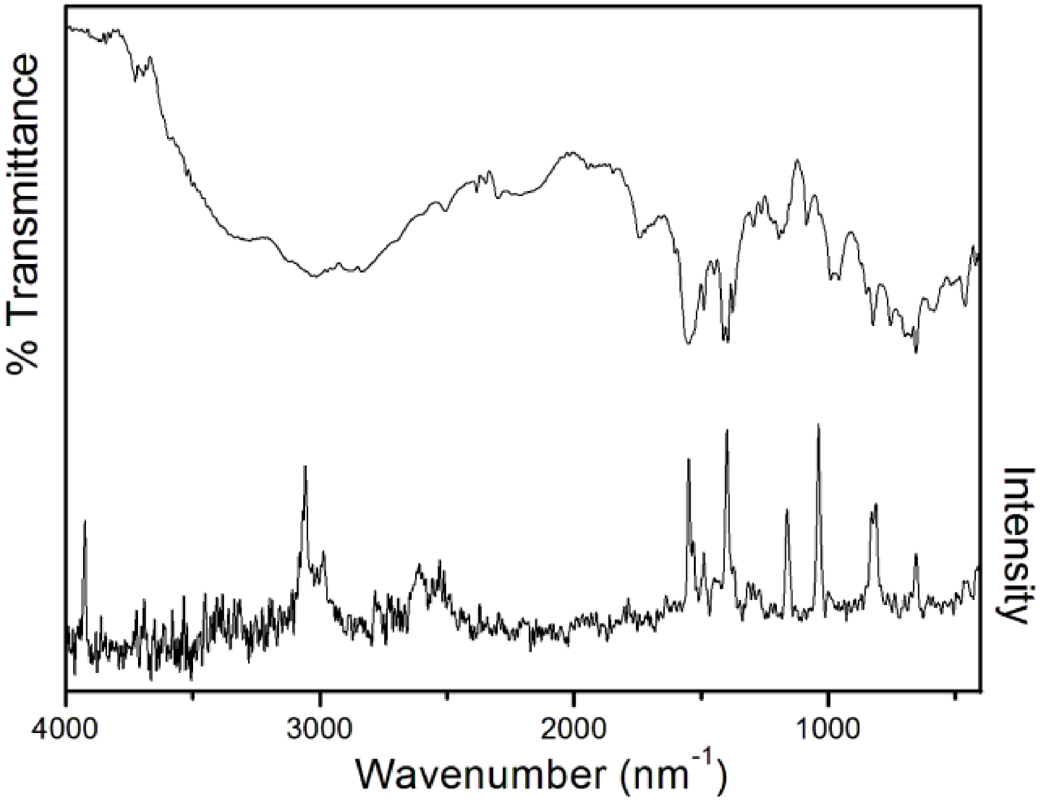


Fig. 3.16 – IR and Raman spectra of **3**

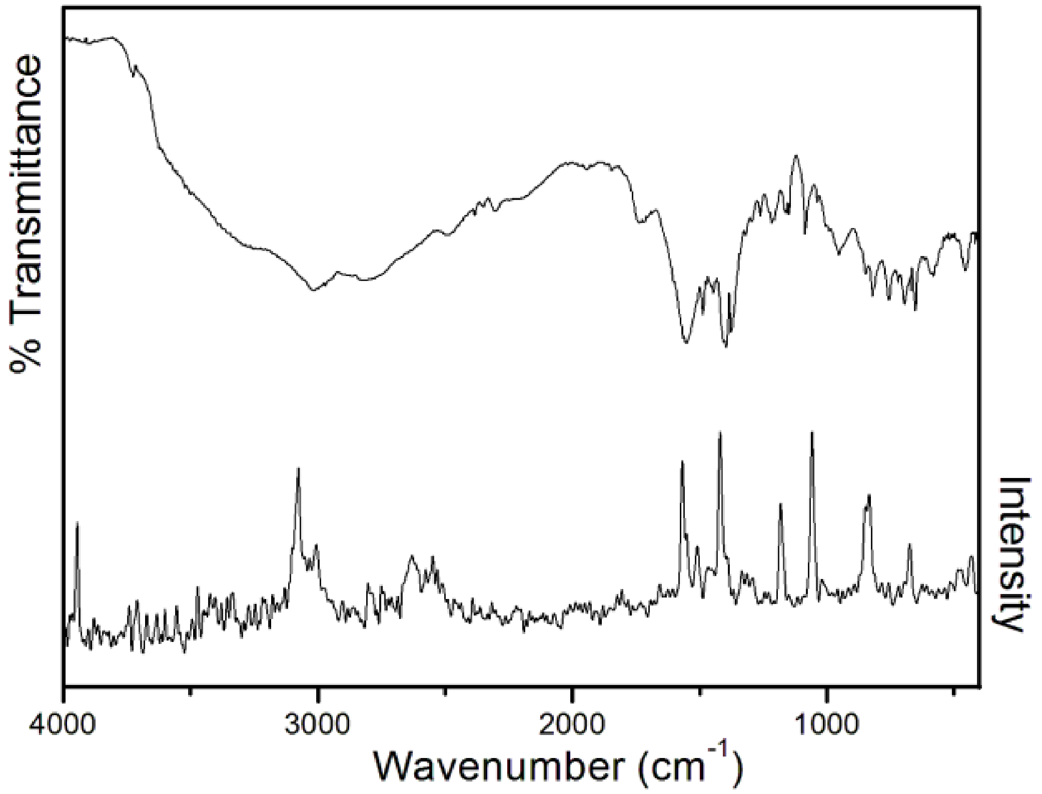


Fig. 3.17 – IR and Raman spectra of **4**

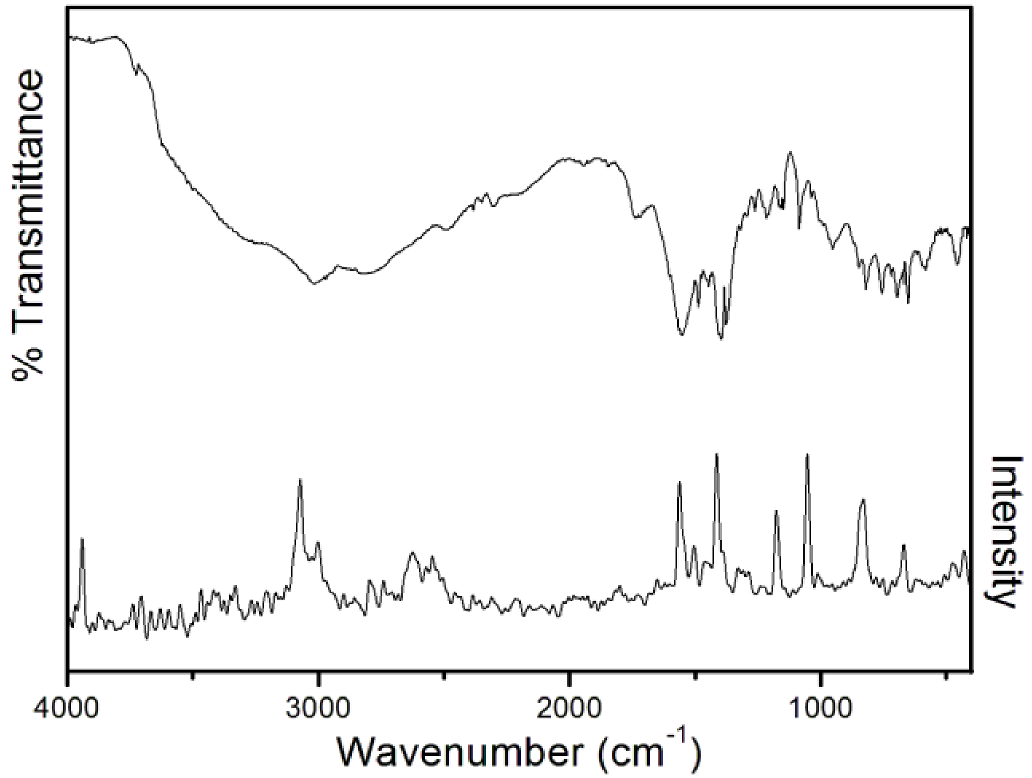


Fig. 3.18 – IR and Raman spectra of **5**

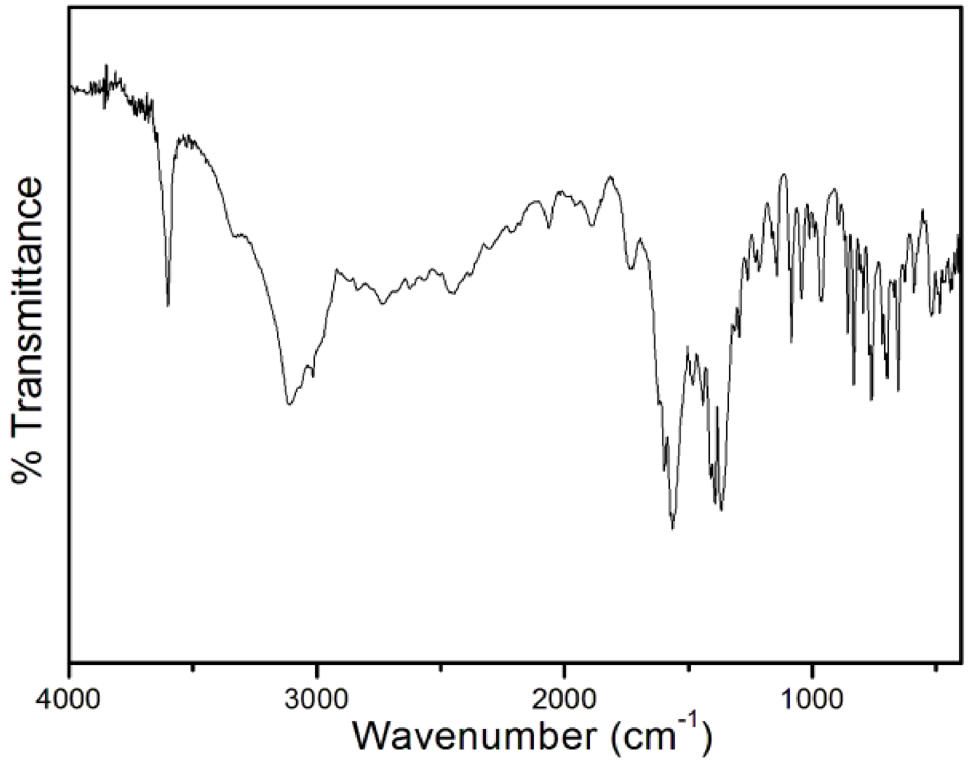


Fig. 3.19 – IR and Raman spectra of **5a**

The UV-Vis spectra of all compounds are characteristic of an absorption at ~275 nm. The optical spectra (Fig. 3.20 - 3.21) in water and in solid-state (Fig. 3.22 - 3.23) of **3-4** exhibit a band around 275 nm that can be assigned for the intra-ligand charge transfer of the aromatic phthalate. The band at 395 nm for **3** (510 nm for **4**) can be attributed to the *d-d* transition of the respective bivalent metal ions. Due to solubility issues compounds **5** and **5a** were studied by diffuse reflectance spectra (DRS). Compound **5** (**5a**) (Fig. 3.24 - 3.25) exhibits a band at 252 (270 nm) for intra-ligand charge transfer of aromatic phthalate group and a broad band above 750 nm.

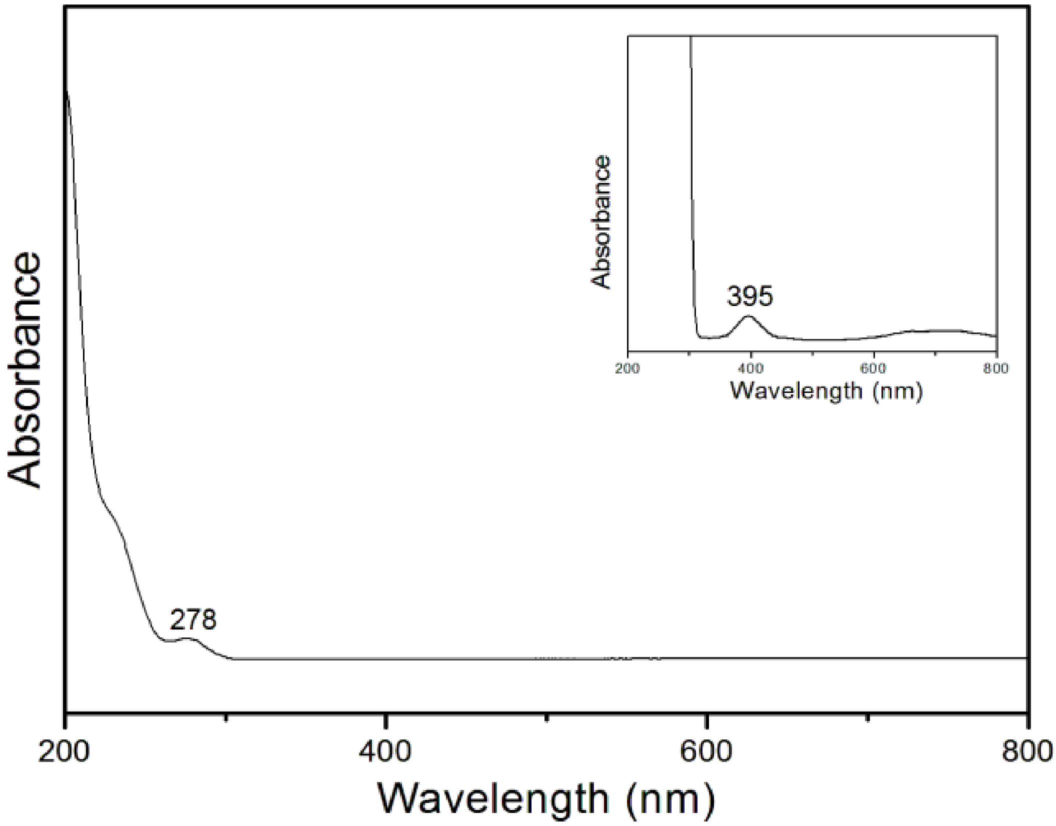


Fig. 3.20 – UV-Visible spectra of **3**

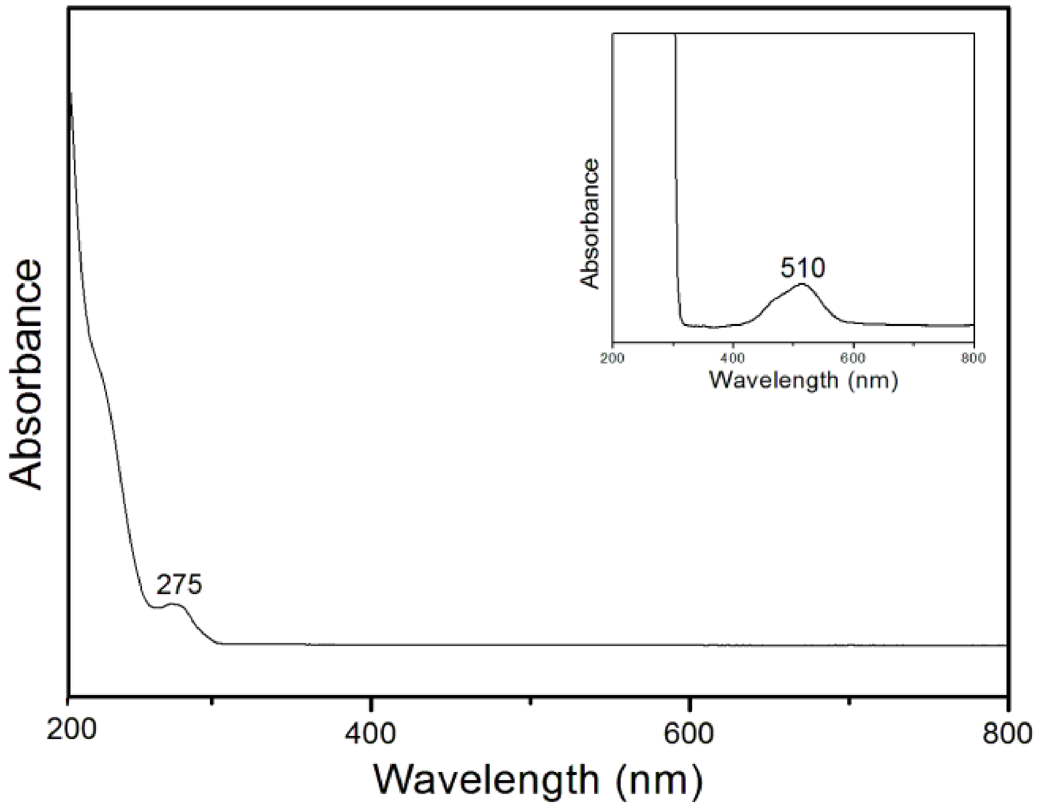


Fig. 3.21 – UV-Visible spectra of **4**

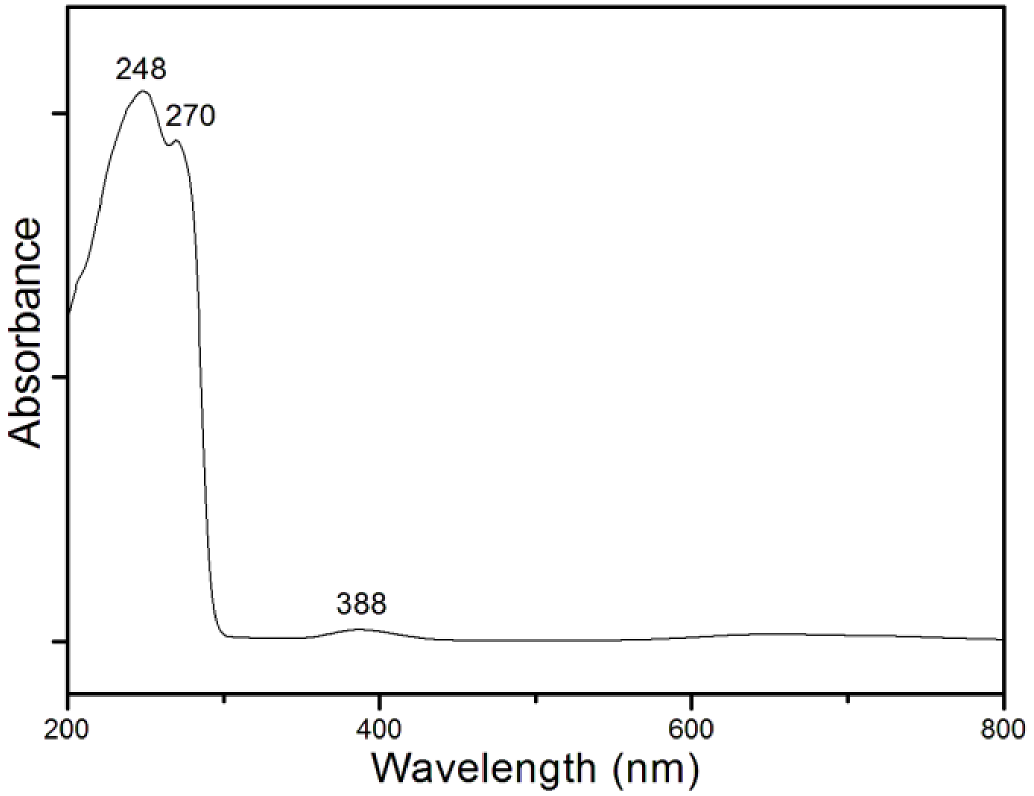


Fig. 3.22 – Diffused reflectance spectra of **3**

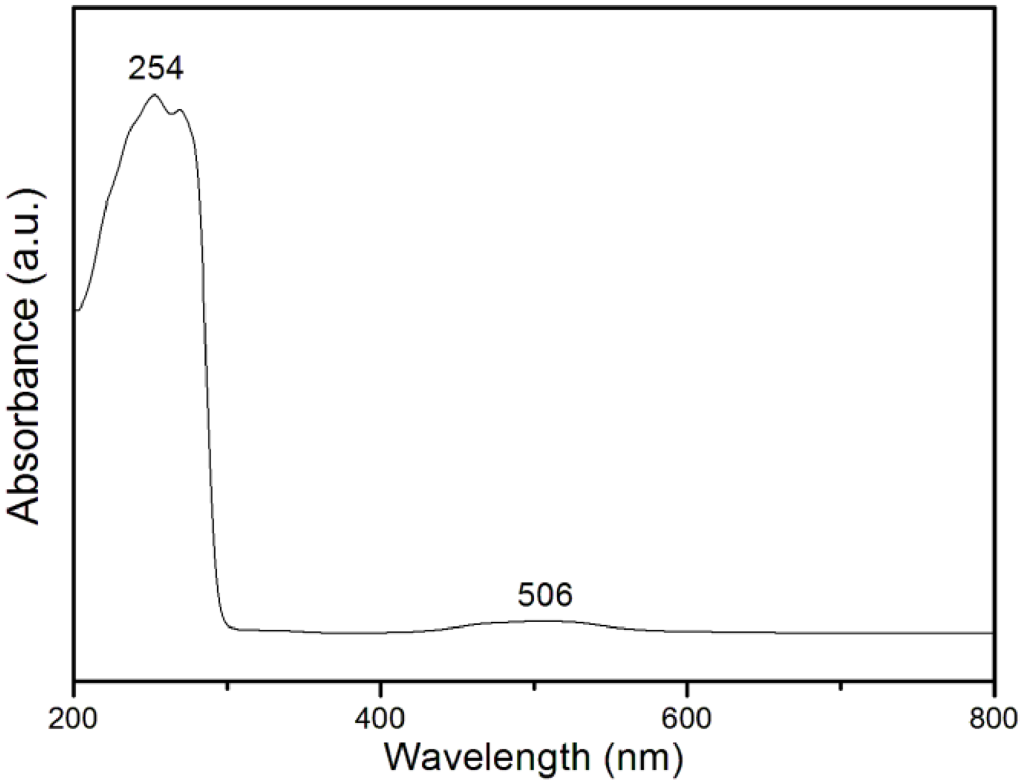


Fig. 3.23 – Diffused reflectance spectra of **4**

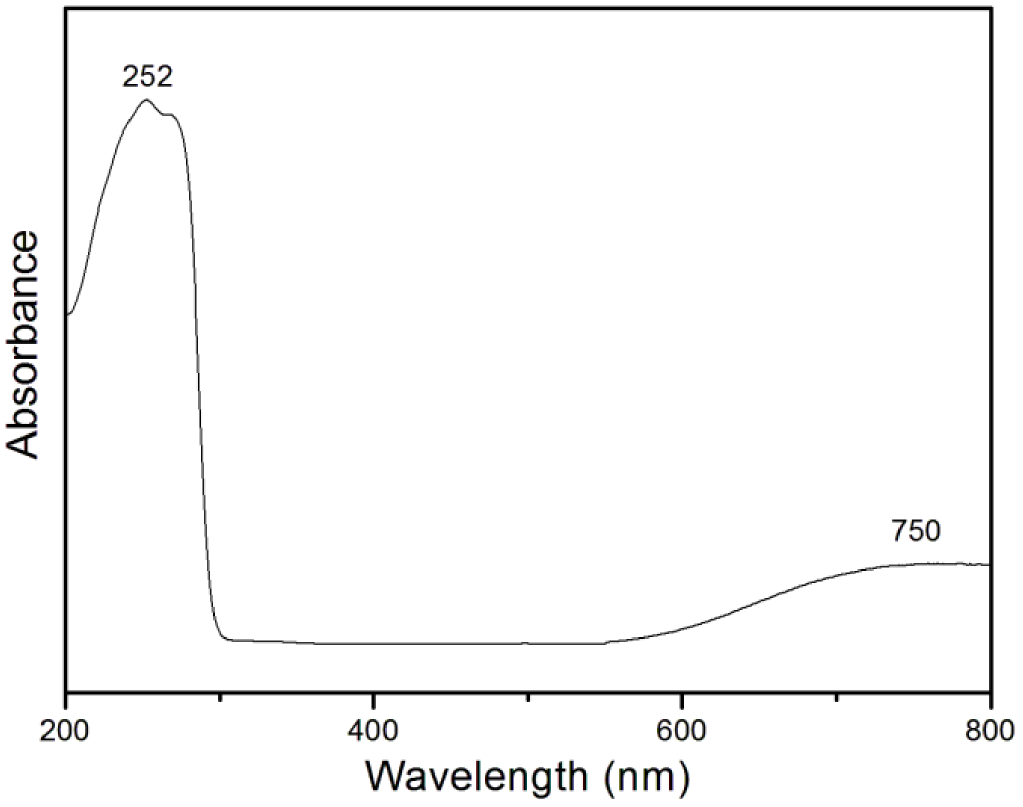


Fig. 3.24 – UV-Visible spectra of **5**

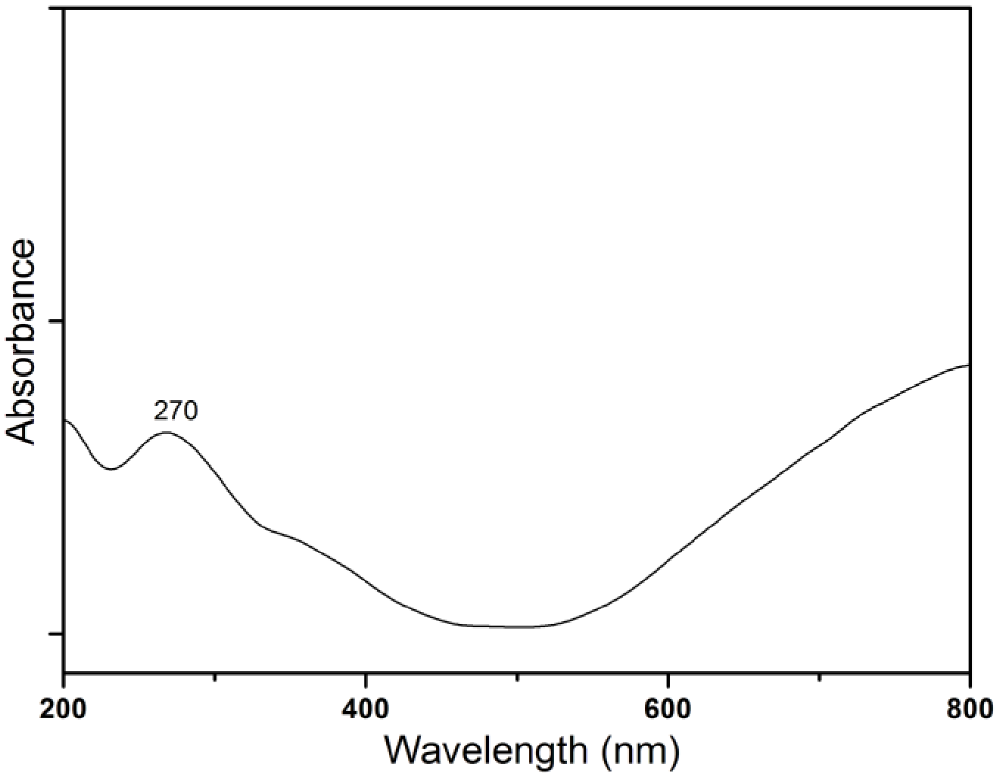


Fig. 3.25 – Diffused reflectance spectra of **5a**

^{1}H NMR spectrum of compound **3** in *d*^{6}-DMSO (Fig. 3.26) shows two sharp signals for aromatic -CH protons of phthalate ligand at δ 8.171 ppm for 4H and δ 7.496 ppm for 4H in addition with a broad signal for -CH_2 of piperazine protons at δ 2.884 ppm for 8H, confirming the composition of compound **1** having pht : pip in the ratio of 2:1. ^{1}H NMR spectrum of compound **4** in *d*^{6}-DMSO (Fig. 3.27) shows two broad signals for aromatic -CH protons of phthalate ligand at δ 8.6 ppm for 4H and δ 7.7 ppm for 4H but the signal for -CH_2 of piperazine protons overlaps with *d*^{6}-DMSO.

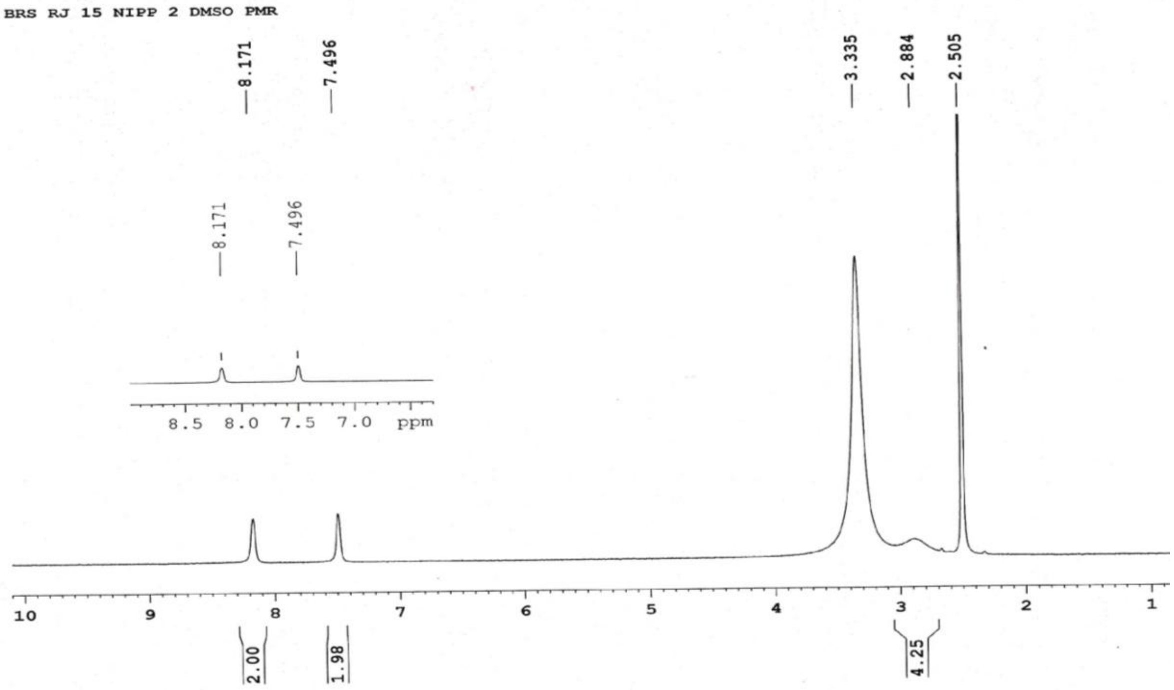


Fig. 3.26 – ^{1}H NMR spectrum (in d^6-DMSO) of **3**

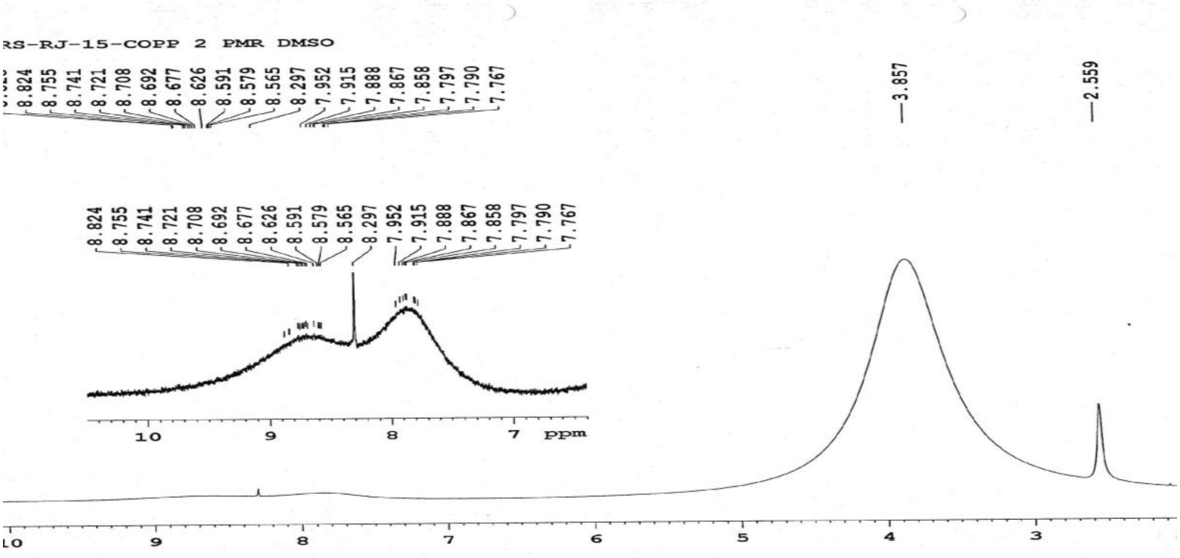


Fig. 3.27 – ^{1}H NMR spectrum (in d^6-DMSO) of **4**

The powder pattern of compounds **3-5a** exhibit sharp Bragg lines indicating their crystalline nature (Fig. 3.28 – 3.31). The minor product **5a** exhibit differing powder pattern as compared to the water rich compound **5**. The experimental powder pattern of the bulk sample is in very good agreement with the theoretical powder pattern calculated from the single crystal data of **3**-**5**. The results of powder pattern experiments, reproducible thermo analytical data and spectral data reveal that the compounds **3**-**5** can be obtained in a state of high purity.

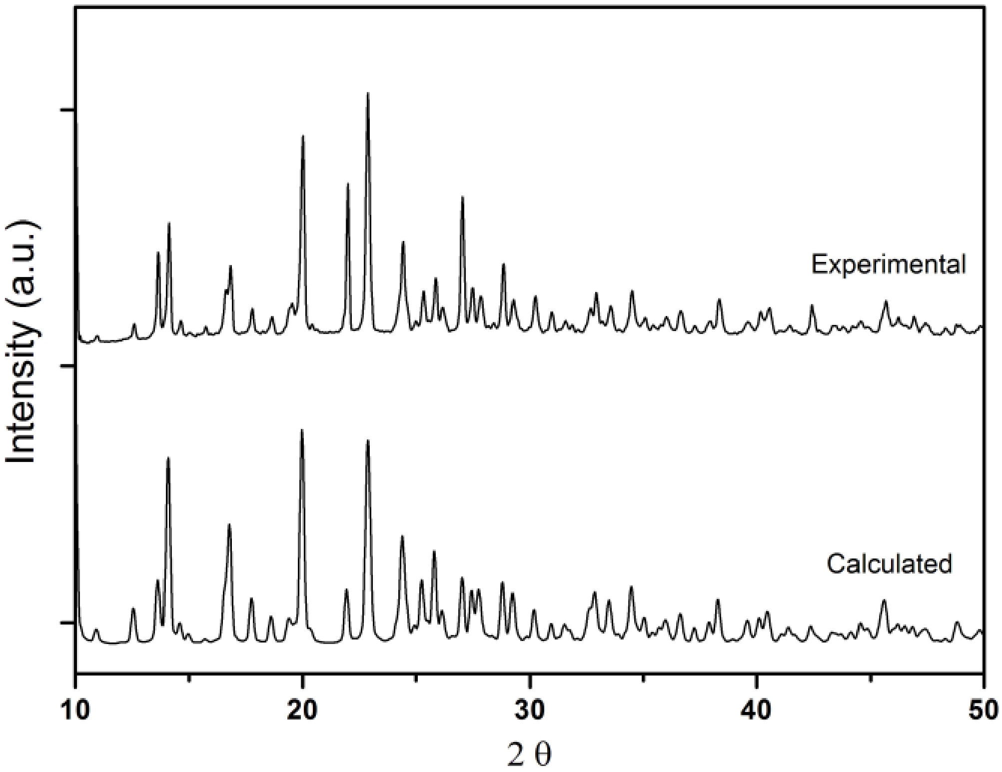


Fig. 3.28 – Experimental and theoretical X-ray powder pattern of **3**

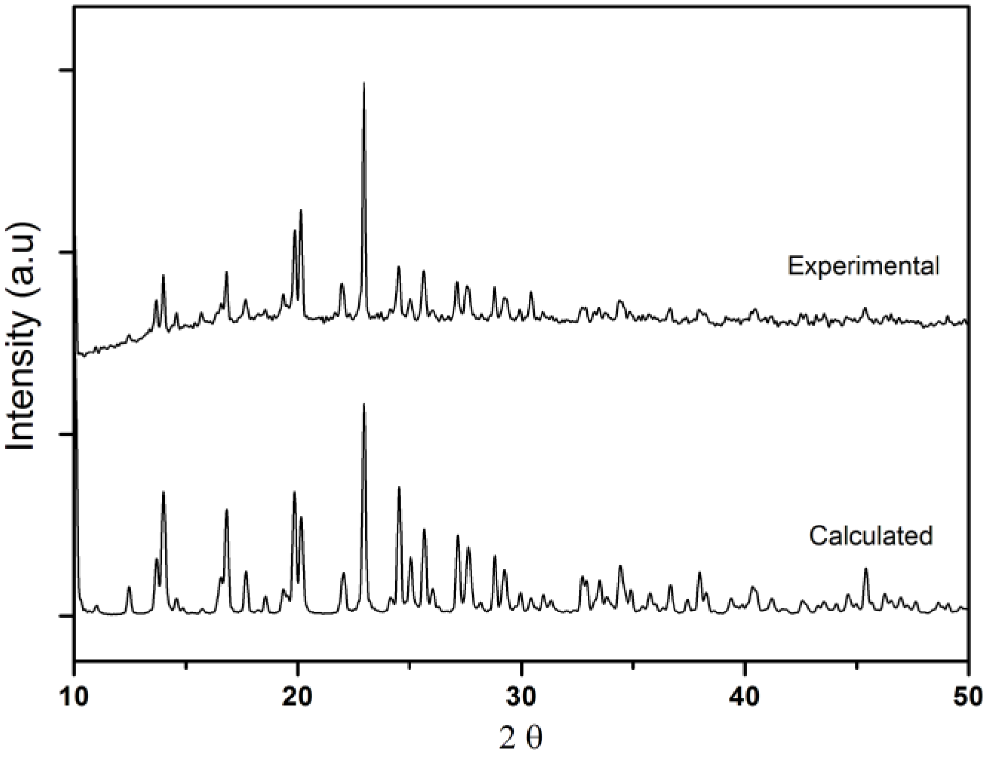


Fig. 3.29 – Experimental and theoretical X-ray powder pattern of **4**

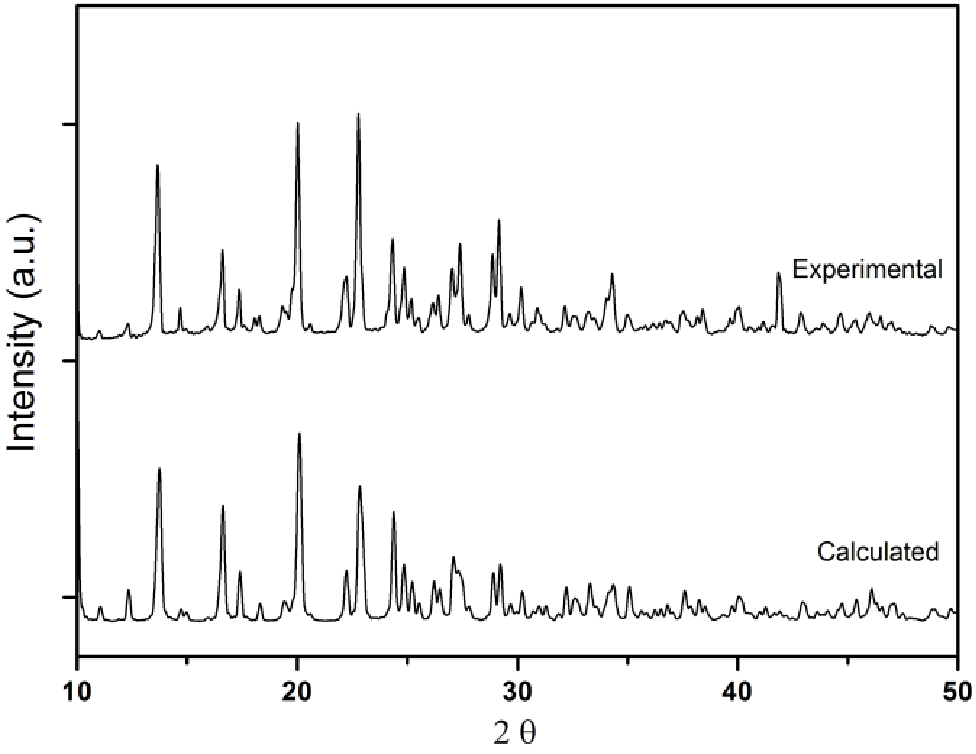


Fig. 3.30 – Experimental and theoretical X-ray powder pattern of **5**

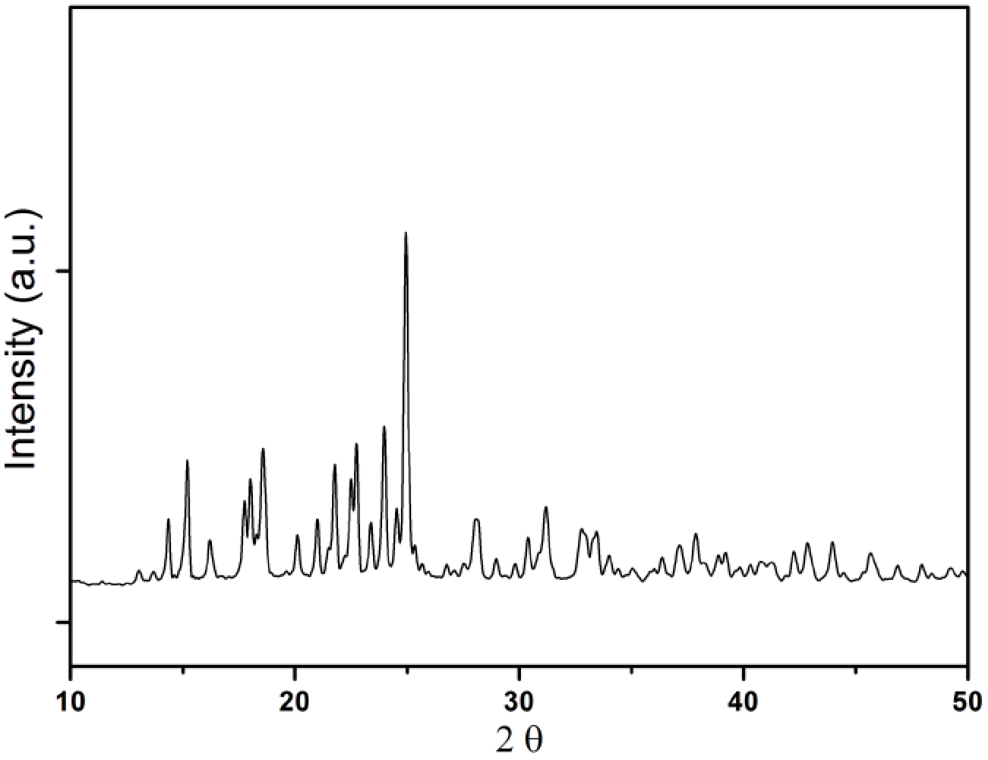


Fig. 3.31 – Experimental X-ray powder pattern of **5a**

Nickel bis(phthalato) compound **3** exhibits an endothermic event with a peak in DTA at 90°C in its TG-DTA graph (Fig. 3.32). The TG curve shows a decrease in mass by 26.13 % equivalent to loss of 10 water molecules at 100°C and a gradual decrease by 31.83 % at 180°C equivalent to 12 water molecules (fully dehydrated compound). Above 200°C, the DTA curve shows only exothermic peaks at 320°C and 400°C, accompanied by a rapid drop in mass that can be attributed to decomposition of **3**. The residual mass of 10.93 % is in very good agreement for the formation of NiO.

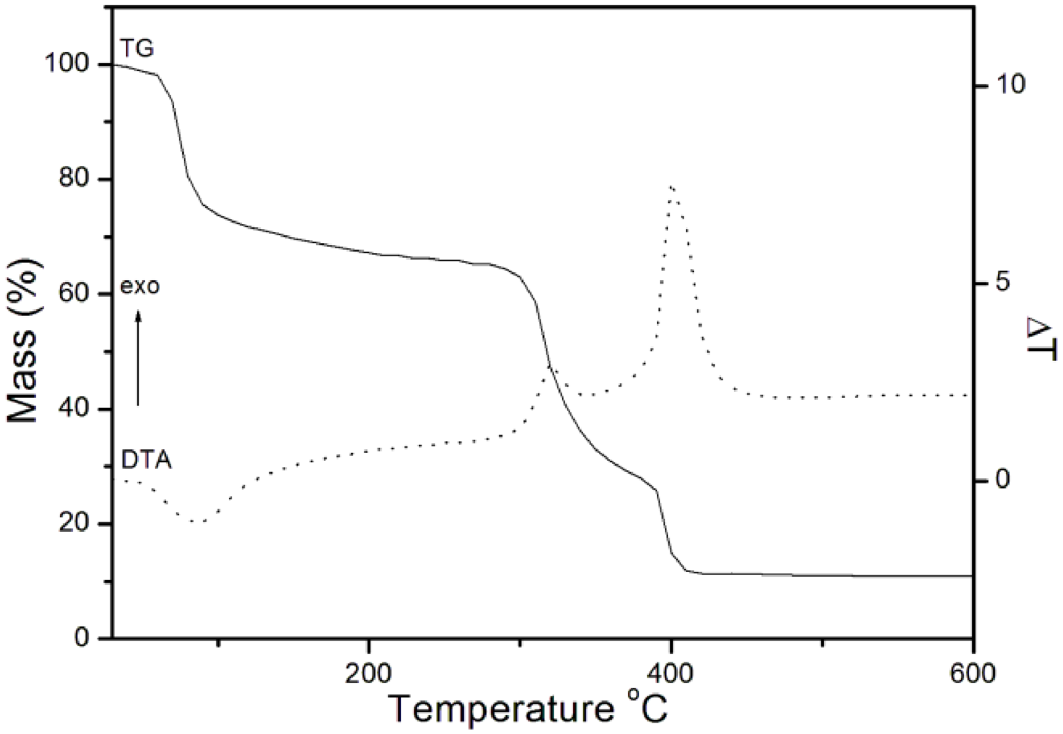


Fig. 3.32 – TG-DTA curves of **3**

Cobalt bis(phthalate) compound **4** shows an endothermic peak at 87°C and 119°C in its TG-DTA graph (Fig. 3.33). The TG curve shows a decrease in mass by 22.28 % equivalent to loss of 8 water molecules at 100°C and a gradual decrease by 31.53 % at 180°C equivalent to 12 water molecules (fully dehydrated compound). Above 200°C, the DTA curve shows only exothermic peaks at 351°C, 390°C and 403°C with rapid mass loss due to decomposition of **4**. The residual mass of 11.5 % corresponds to Co_3O_4 as confirmed by powder pattern (*vide infra*).

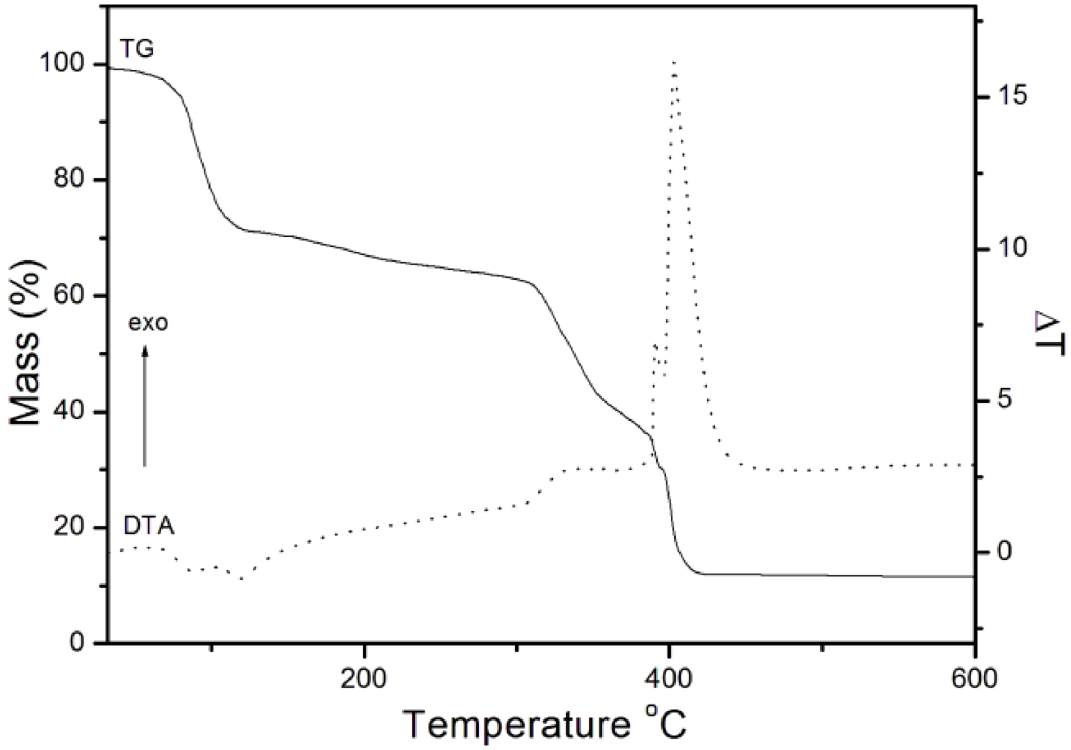


Fig. 3.33 – TG-DTA curves of **4**

Similarly, an endothermic peak in DTA at 77°C and 114°C was observed for compound **5** in its TG-DTA curve (Fig. 3.34). Its TG curve shows a decrease in mass by 27.23 % equivalent to loss of 10 water molecules at 100°C and a gradual decrease by 30.89 % at 180°C equivalent to 12 water molecules (fully dehydrated compound). Above 200°C, the DTA curve shows only exothermic peaks at 280°C, 324°C and 390°C, followed by a rapid drop in mass due to decomposition of **5**. The residual mass of 11.35 % is in accordance with the formation of CuO.

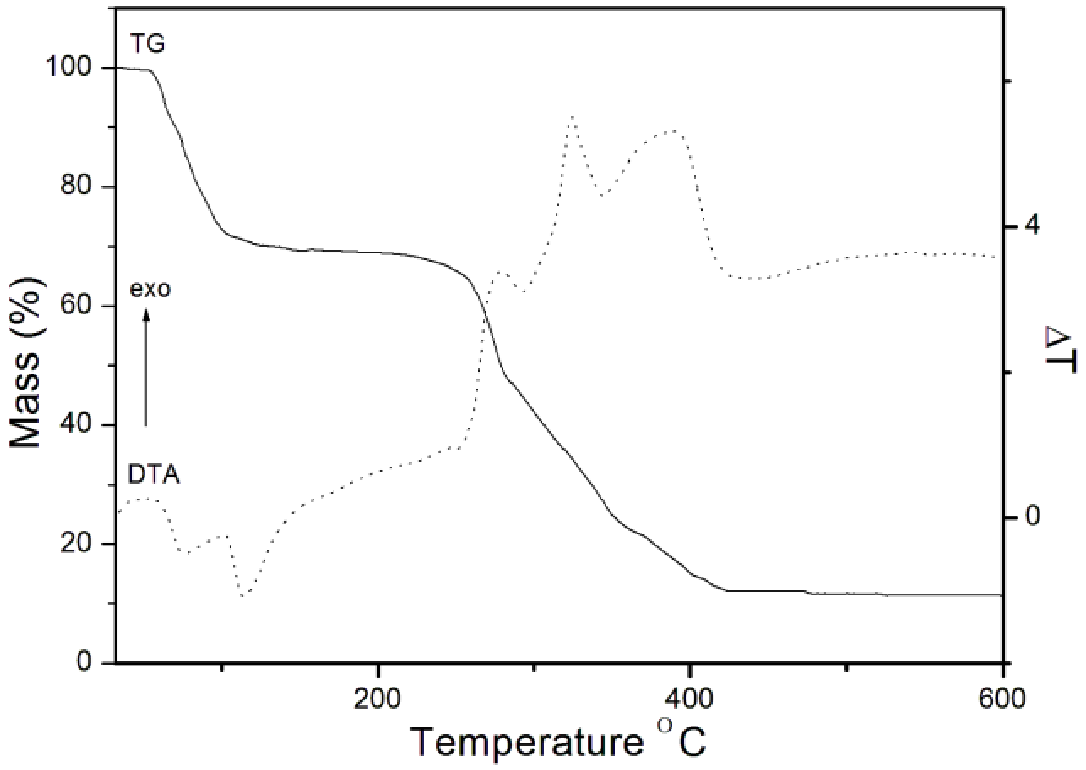


Fig. 3.34 – TG-DTA curves of **5**

The TG curve of **5a** (Fig. 3.35) shows no weight loss till 240°C indicating the anhydrous nature of the compound. Above 250°C, the DTA curve of **5a** shows a similar pattern to compound **5** with exothermic peaks at 270°C, 305°C and 347°C. The % residue obtained 17.13 % matched to the CuO formed on heating the compound at 600°C in the electric furnace.

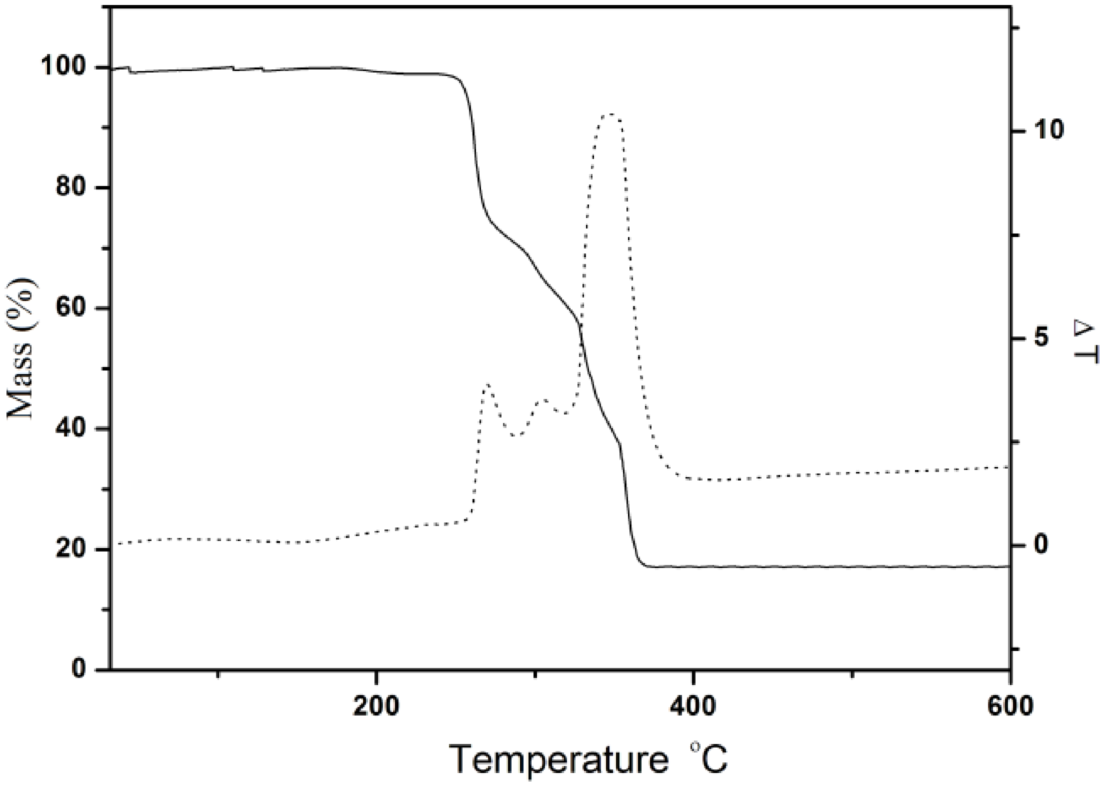


Fig. 3.35 – TG-DTA curves of **5a**

The featureless IR spectra of the residues (Fig. 3.36) obtained and their matching powder patterns with corresponding oxides (Fig. 3.37) provide evidence for the complete removal of organic moiety with oxide formation. The results of isothermal mass loss study performed at different temperatures viz. 100°, 150°, 180°, 200° and 600°C add credence to the thermal data of the compounds.

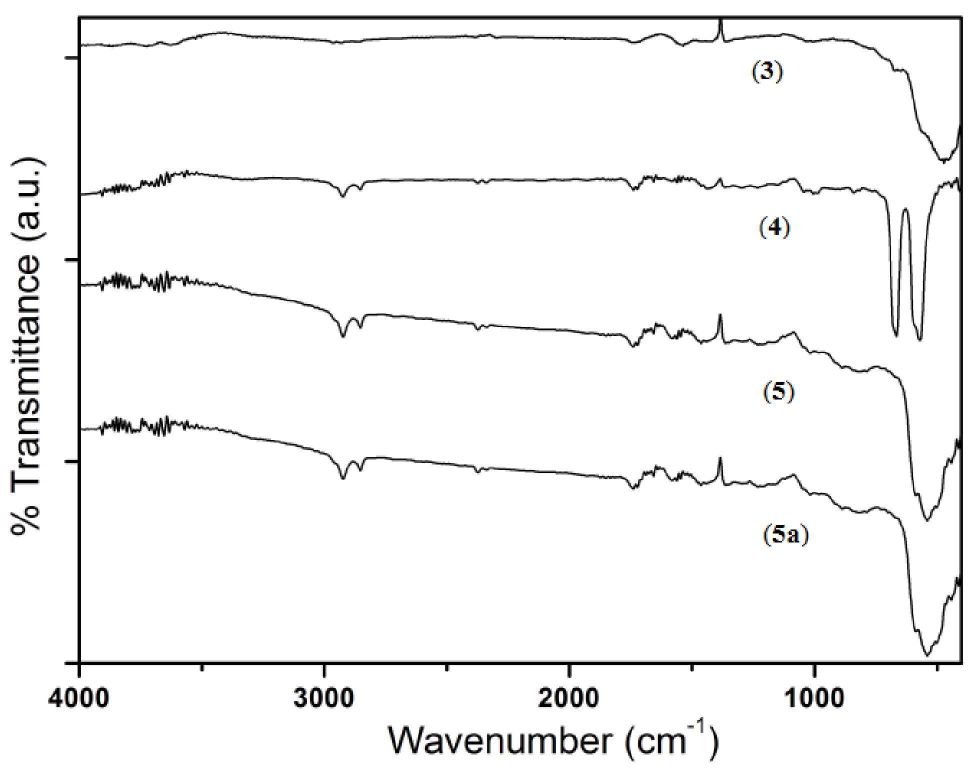


Fig. 3.36 – IR spectra of residues obtained after heating **3**; **4**; **5** and **5a** at 600°C

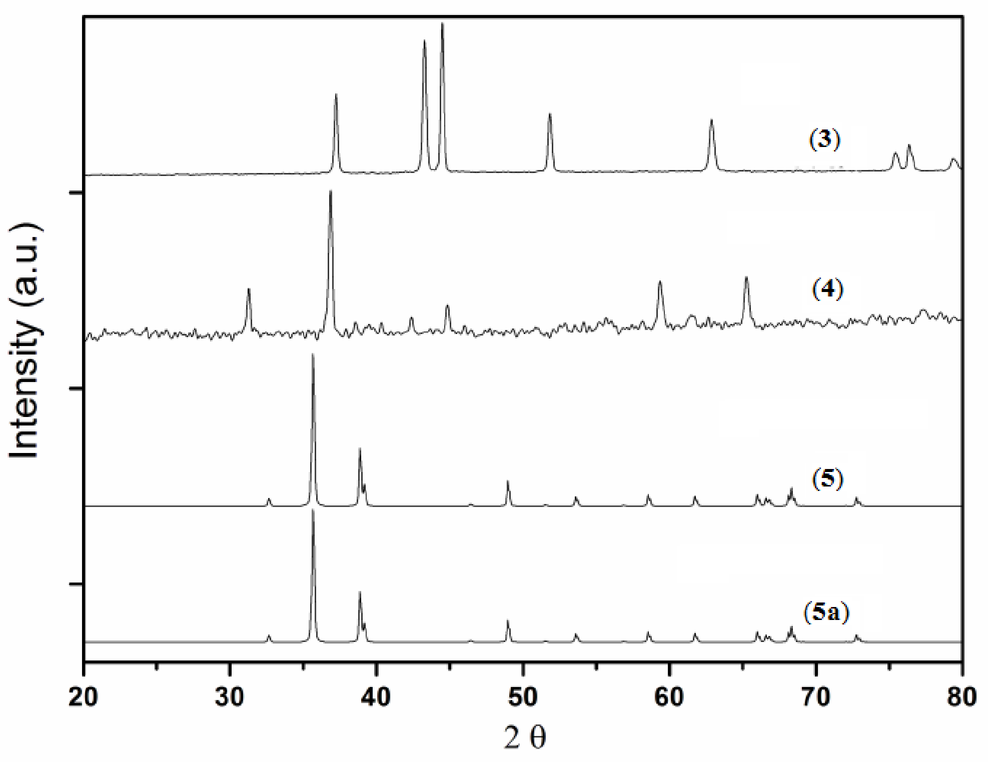


Fig. 3.37 –X-ray powder pattern of residues obtained after heating **3**; **4**; **5** and **5a** at 600°C

The EPR spectrum of polycrystalline sample of **5** was recorded in X-band at room temperature. The spectrum shows axial symmetry with $g_{||} > g_{\perp} > 2.03$ ($g_{||} = 2.3119$ and $g_{\perp} = 2.0920$) with the unpaired electron localized in $d_{x^2-y^2}$ orbital giving $^2B_{1g}$ as ground state (Fig. 3.38).

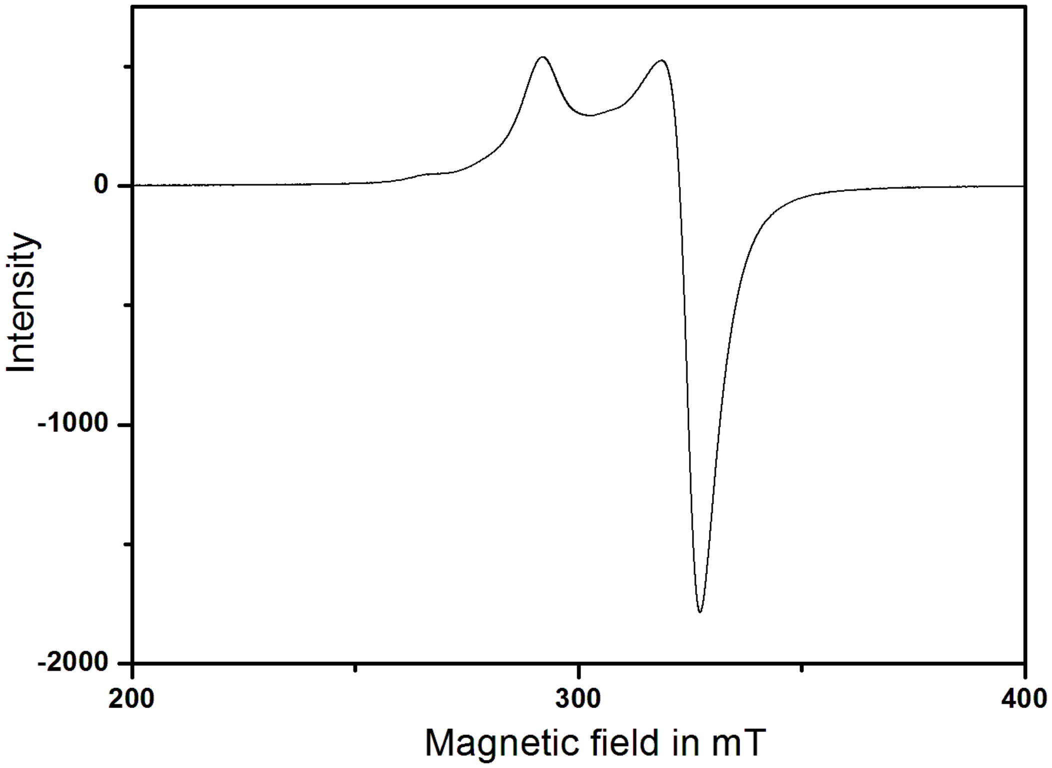


Fig. 3.38 – Room temperature ESR spectrum of polycrystalline compound **5**

*3.1.4 Dehydration-rehydration studies of **3**, **4** and **5***

The three water rich compounds **3**, **4** and **5** could be completely dehydrated and rehydrated back to the original compound by first heating the compounds at 180°C in oven with a marked colour change from green to yellowish green (for **3**), pink to violet (for **4**), blue to dark green (for **5**) and then equilibrating in water atmosphere in a dessicator for 4 days (Fig. 3.39).

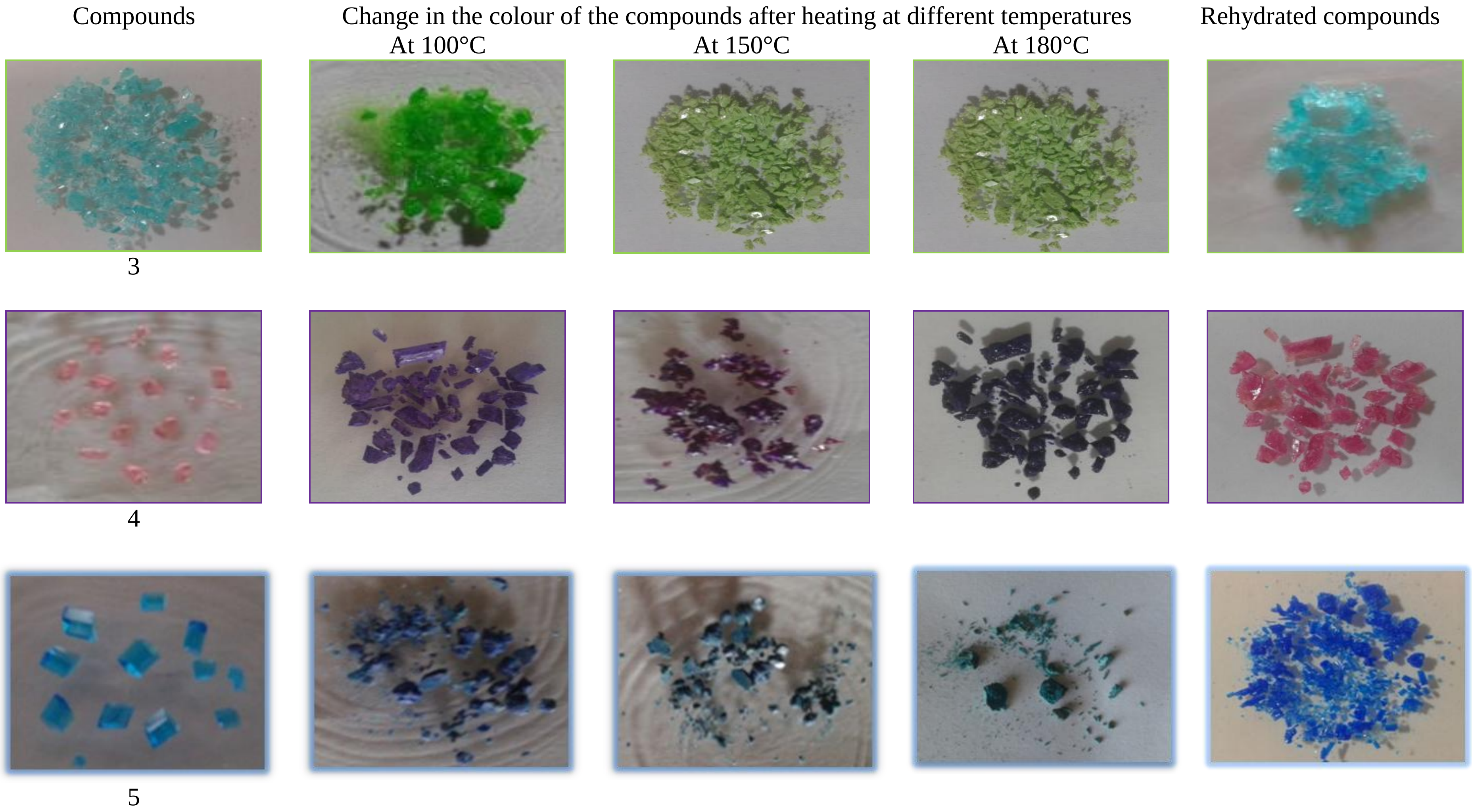


Fig. 3.39 – Dehydration - rehydration studies of water rich compounds **3-5**

A weighed amount (100 mg) of **3**, **4** and **5** taken separately were heated at 180°C in an oven for 15 minutes. The measured weight loss of 31.32 mg (31.32 %) for **3**, 31.30 mg (31.30 %) for **4** and 31.15 mg (31.15 %) for **5** was equivalent to the loss of 12 water molecules and formation of completely anhydrous compounds. This is in agreement with the elemental analysis. (Dehydrated compound **3**): Anal. (%): Found (calcd) for $NiC_{16}\ N_2O_9H_{12}$ (475.11): C 40.42 (40.45), H 2.57 (2.55), N 5.7 (5.9); (Dehydrated compound **4**): Anal. (%): Found (calcd) for $CoC_{16}\ N_2O_9H_{12}$ (475.35): C 40.39 (40.42), H 2.58 (2.54), N 5.85 (5.89); (Dehydrated compound **5**): Anal. (%): Found (calcd) for $CuC_{16}\ N_2O_9H_{12}$ (479.97): C 40.01 (40.04), H 2.55 (2.53), N 5.81 (5.84).

The anhydrous compounds of **3**, **4** and **5** when kept over water in a dessicator, get regenerated back to the original compound after 4 days with increase in the weight of 31.32 mg for **3**, 31.30 mg for **4** and 31.15 mg for **5** equivalent to the gain of 12 water molecules. The IR spectrum of these compounds at different temperature (100, 150, 180°C) depicts a stepwise removal of water molecules from the crystal structure (Fig. 3.40-3.42), and the simultaneous powder XRD pattern at these temperatures (Fig. 3.43-3.45) shows the phase change in the compounds. The regenerated material regains their original identity with identical IR spectrum and powder XRD pattern with those of the respective starting compounds. Interestingly, Compound **5a** when kept over water in dessicator absorbs moisture and gets hydrated to **5** over a period of 5 days (Fig. 3.46). Thus, compounds **3-5** can be considered as a water reservoir as the lattice water molecules could be completely removed and added back from the crystal host regaining its original crystal structure.

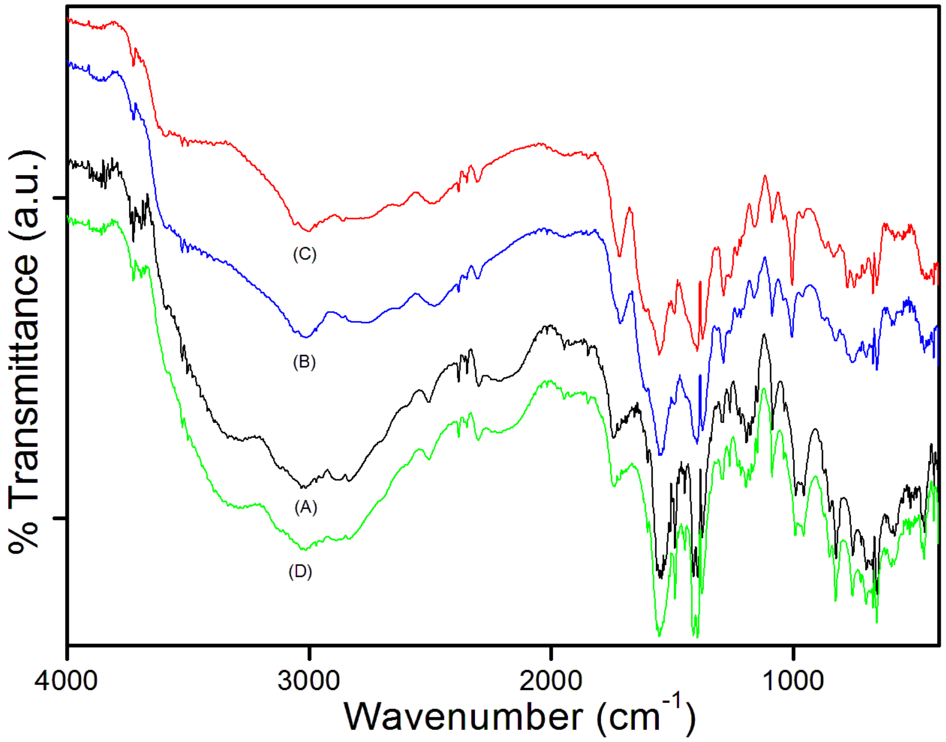


Fig. 3.40 – IR spectra of **3** dehydrated at different temperatures (A) Starting compound, (B) at 100°C, (C) at 180°C and (D) rehydrated compound.

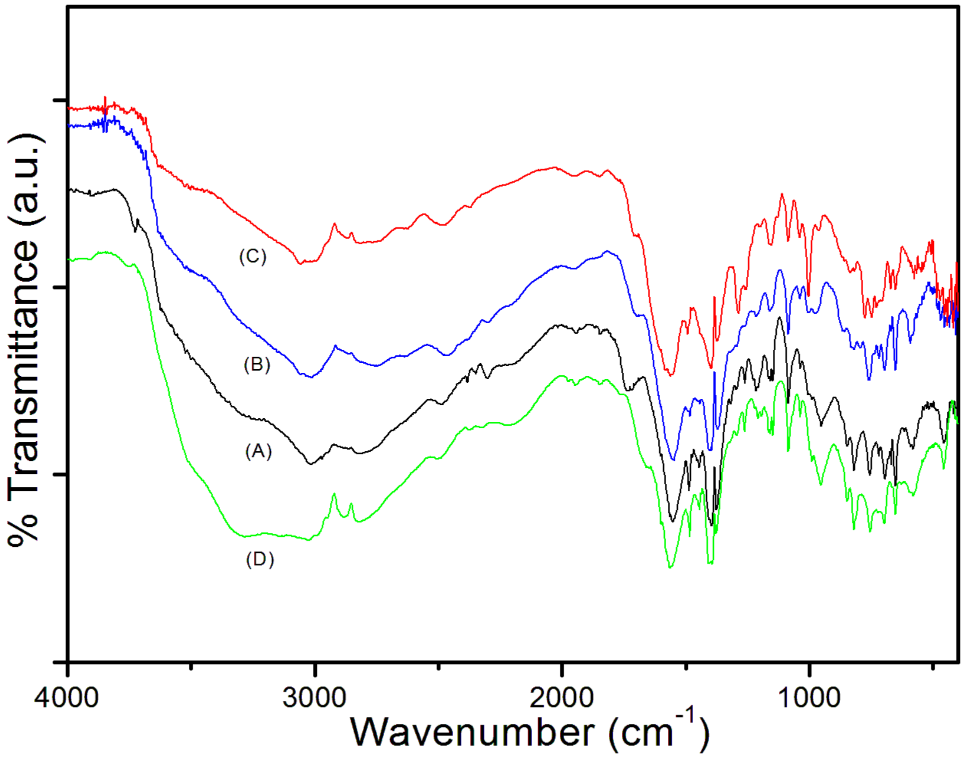


Fig. 3.41 – IR spectra of **4** dehydrated at different temperatures (A) Starting compound, (B) at 100°, (C) at 180° and (D) Rehydrated compound.

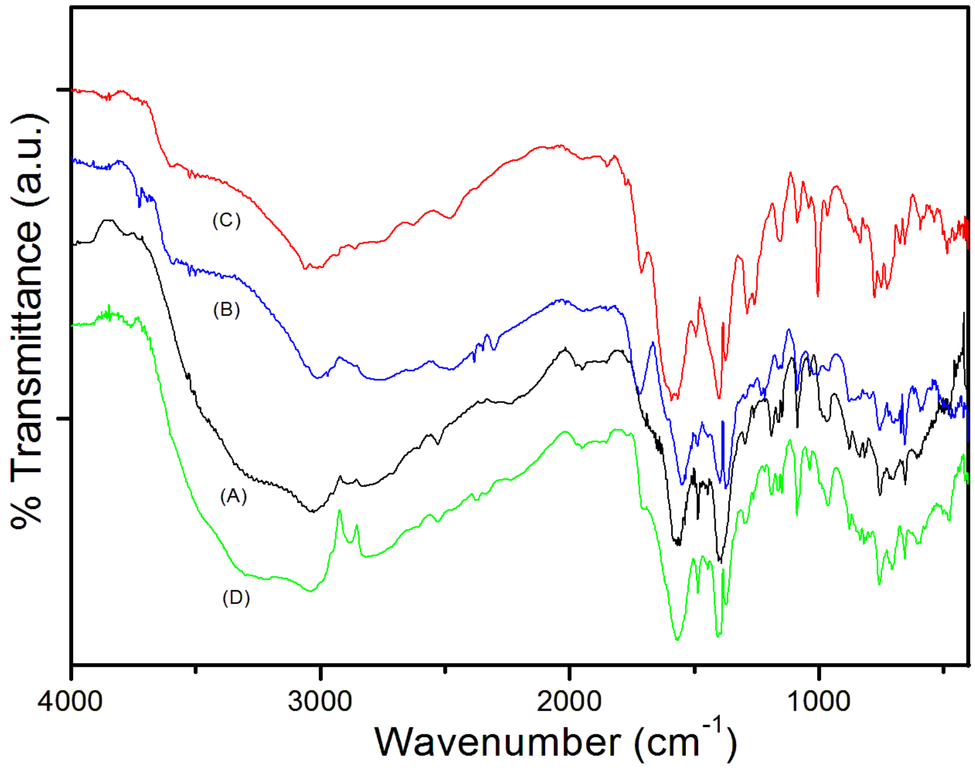


Fig. 3.42 – IR spectra of **5** dehydrated at different temperatures (A) Starting compound, (B) at 100°C, (C) at 180°C and (D) rehydrated compound.

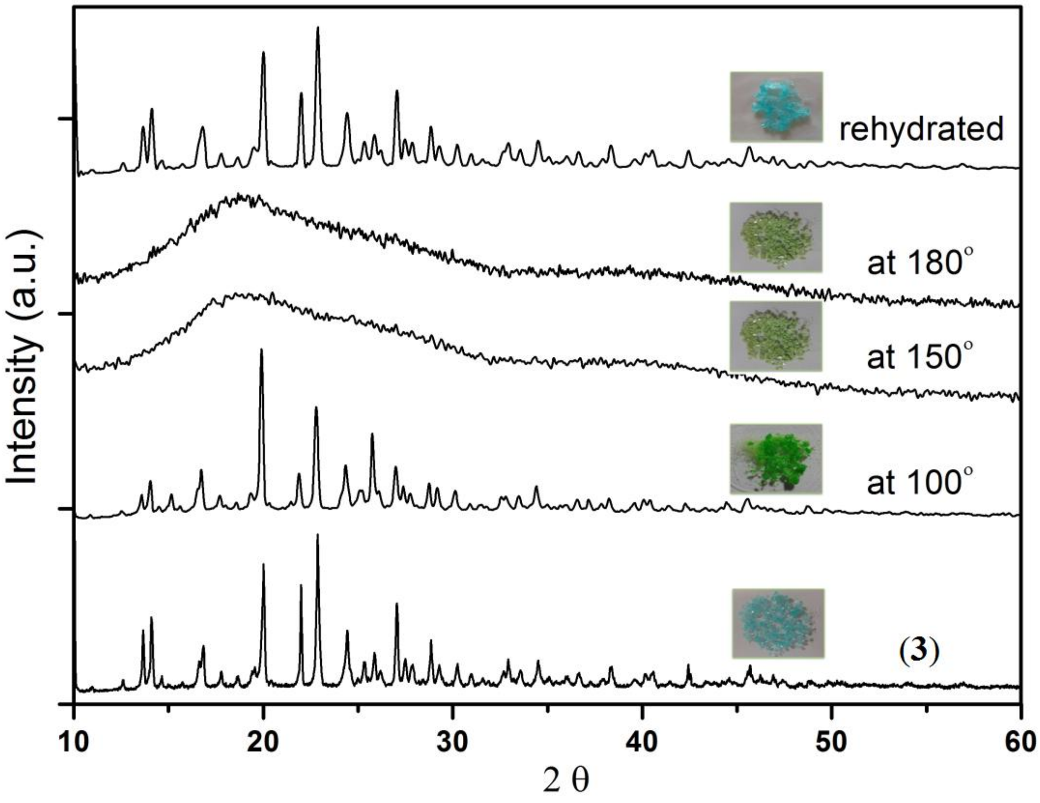


Fig. 3.43 – X-ray powder pattern of **3** at different temperatures

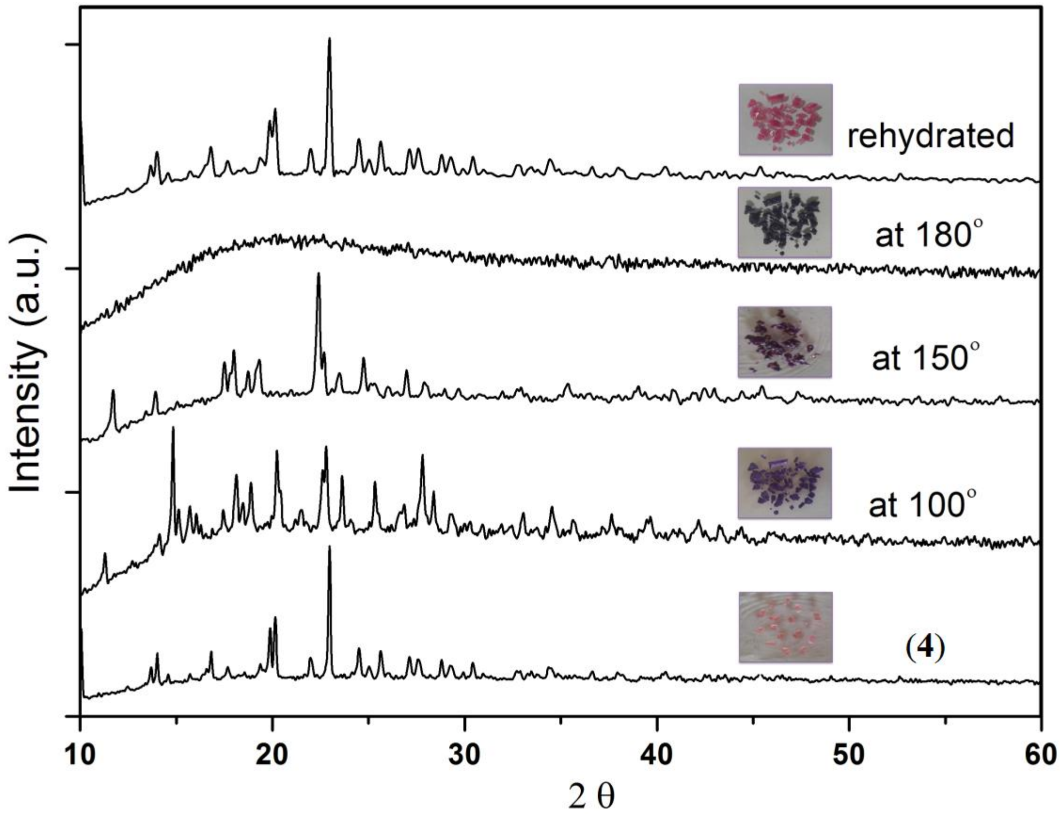


Fig. 3.44 – X-ray powder pattern of **4** at different temperatures

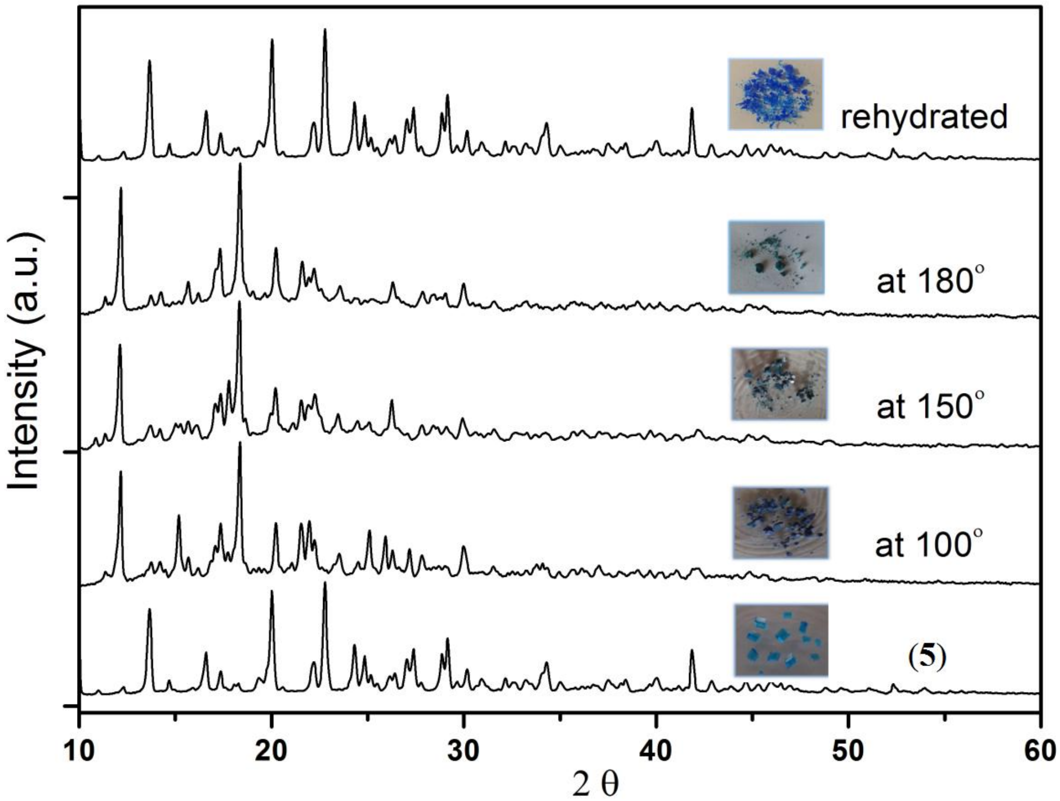


Fig. 3.45 – X-ray powder pattern of **5** at different temperatures

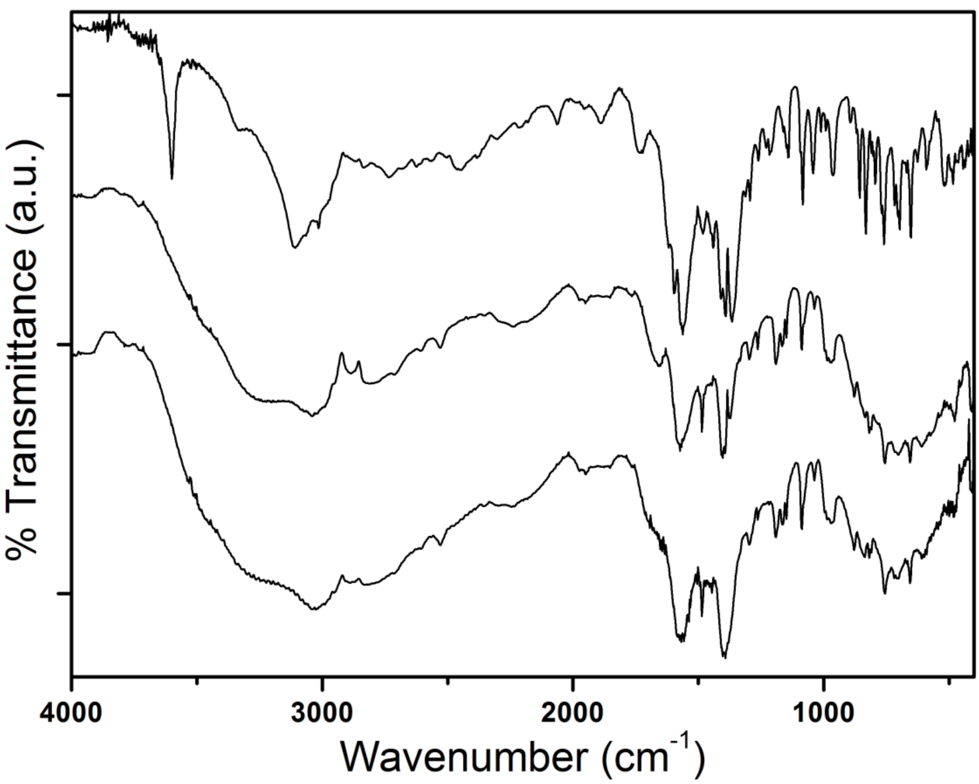


Fig. 3.46 – IR spectrum of **5a** (top); hydrated compound of **5a** (middle) and **5** (bottom)

*3.1.5 Conductivity, electrochemical and magnetic studies of **3**, **4** and **5***

The room temperature conductivity of aqueous solutions of **3** and **4** (Table 3.4) exhibits an increase in molar conductivity values with increasing dilution indicating the dissociation of both compounds in dilute solution.

Table 3.4 - Specific conductivity (Ƙ) and molar conductivity (Λ_m) data for **3** and **4** at room temperature

Molar concentration (M)	Specific conductivity (Ƙ) (in S cm^{-1}) **3**	**4**	Molar conductivity (Λ_m) (S cm^2 mol^{-1}) **3**	**4**
0.1	7.12	8.29	71	83
0.08	6.53	7.12	82	89
0.06	5.72	6.53	95	109
0.04	4.78	5.37	119	134
0.02	3.26	3.62	163	181
0.01	2.11	2.22	211	222
0.001	0.49	0.65	494	645

The electrochemistry of **3-4** was studied by cyclic voltametry at room temperature in the potential range 1 to -1 V using 0.1 M KCl aqueous solution as a supporting electrolyte (Fig. 3.47-3.48). A pair of redox events was observed in the potential range of -0.2 to -0.9 V and -0.1 to -0.9 for **3** and **4** respectively, which can be attributed to a ligand (phthalate) centred process. The effect of varying the scan rate from 0.02 to 0.1 Vs^{-1} does not show any remarkable changes in $E_{1/2}$ excepting a slight increase in the peak-to-peak separations.

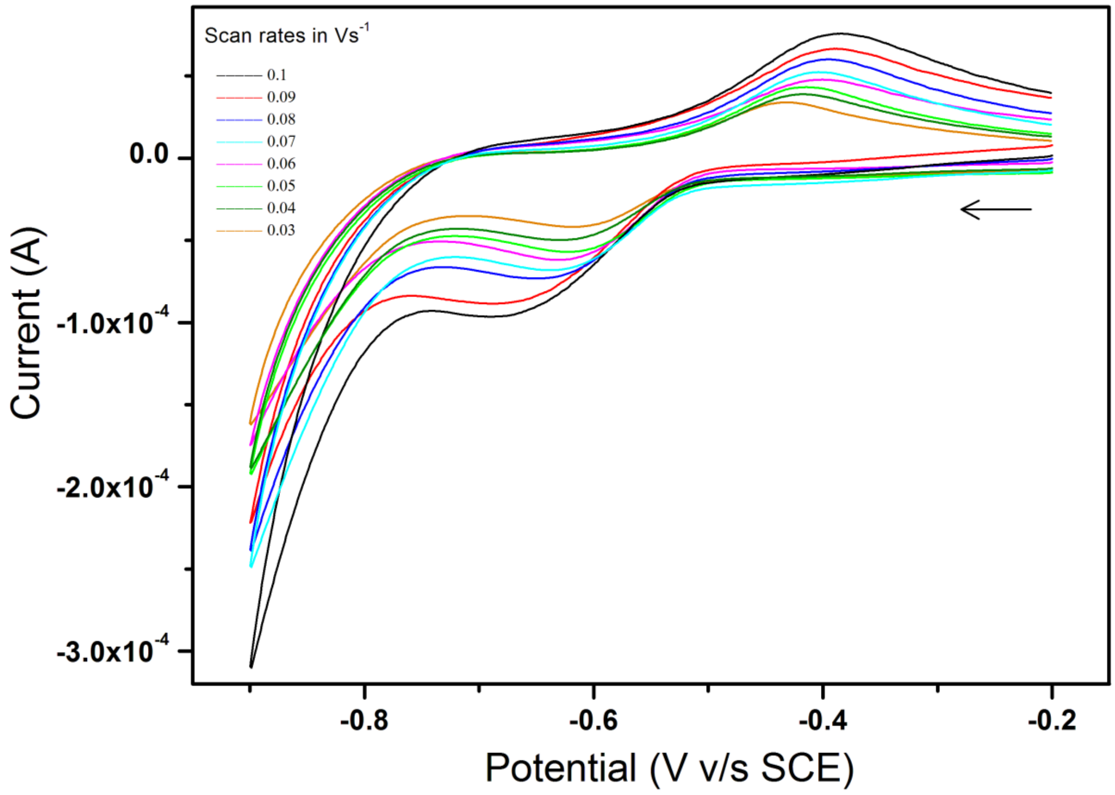


Fig. 3.47 - Cyclic voltammograms of **3** at different scan rates (from inner to outer) of 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 and 0.1Vs^{-1} in the potential range of -0.9 to -0.2V in 0.1M aqueous KCl solution.

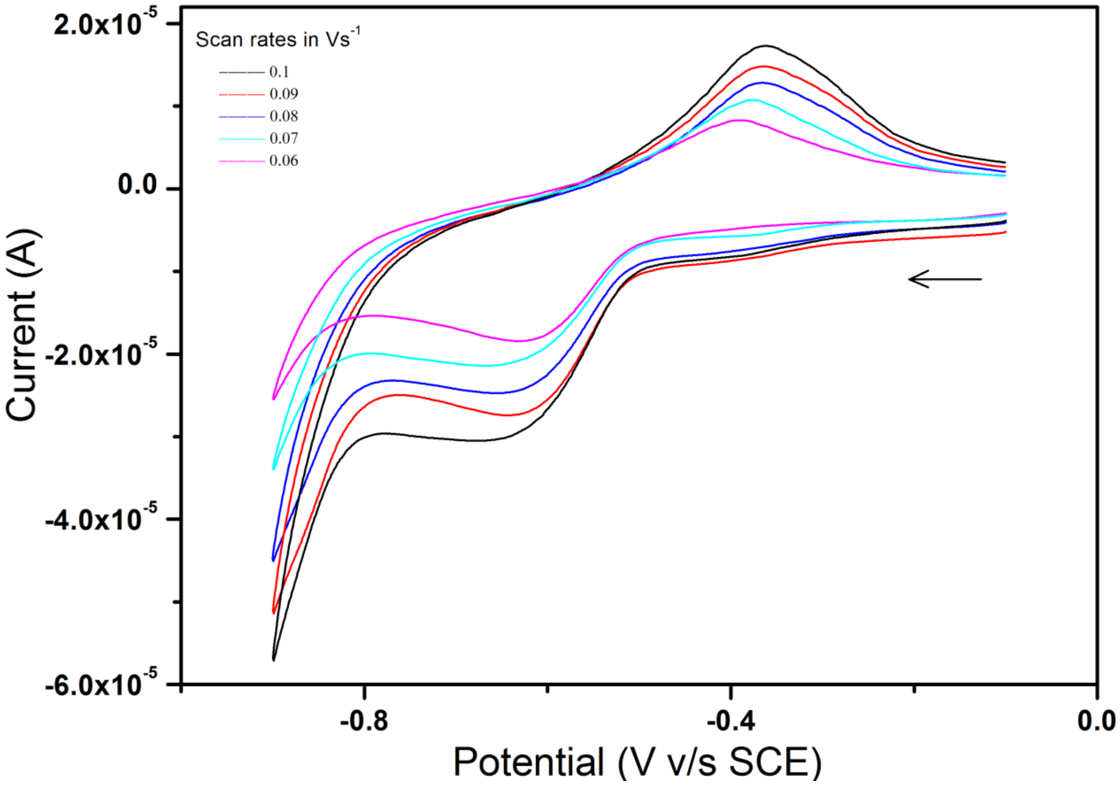


Fig. 3.48 - Cyclic voltammograms of **4** at different scan rates (from inner to outer) of 0.06, 0.07, 0.08, 0.09 and 0.1Vs^{-1} in the potential range of -0.9 to -0.1V in 0.1M aqueous KCl solution.

The temperature-dependent magnetic susceptibility of polycrystalline samples of **3**, **4**, **5** and **5a** have been measured at an applied magnetic field of 250 Oe in the temperature range 50-300K (Fig. 3.49-3.51). The χ_M versus T plots depict a simple paramagnetic behaviour of all indicating the absence of exchange interactions. This behaviour is in accordance with the central structures which show that the metal centres are located far apart from each other (*vide infra*).

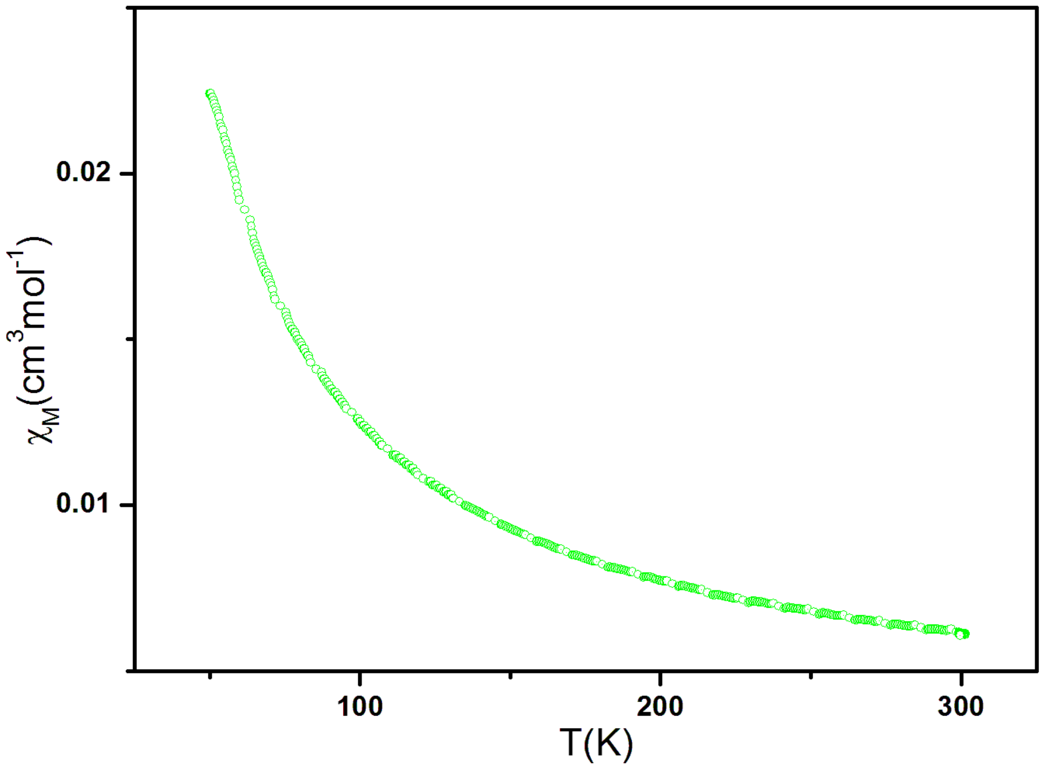


Fig. 3.49 – Plot of χ_M versus T for **3**

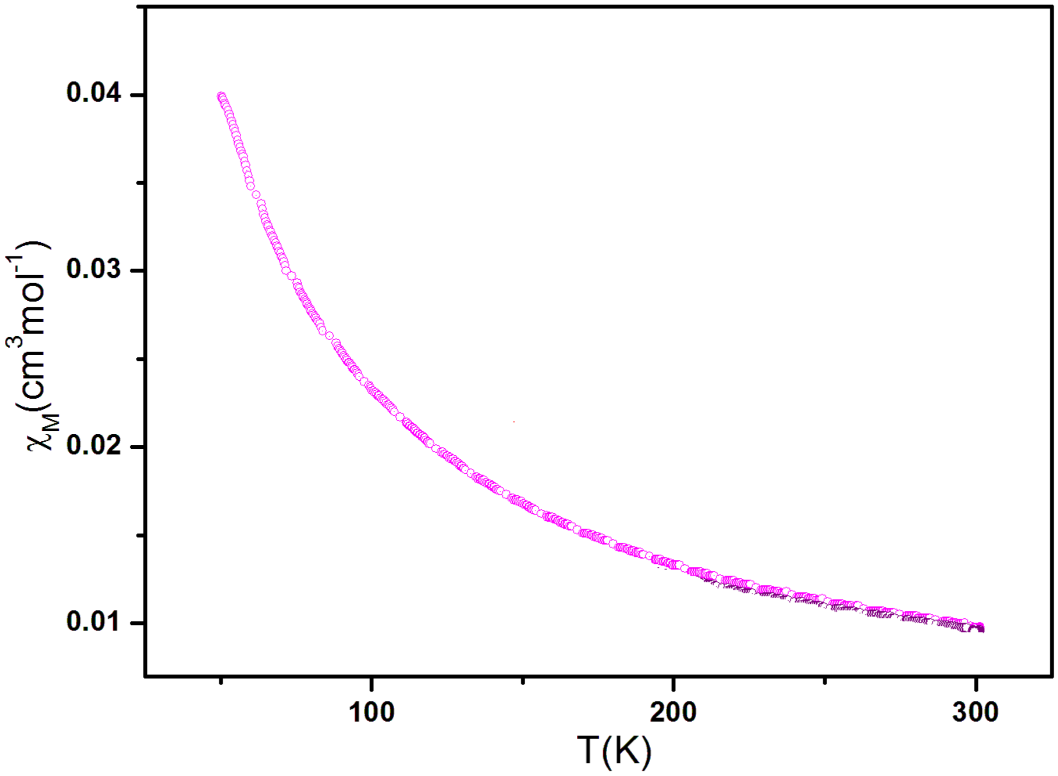


Fig. 3.50 – Plot of χ_M versus T for **4** **(-o-)**

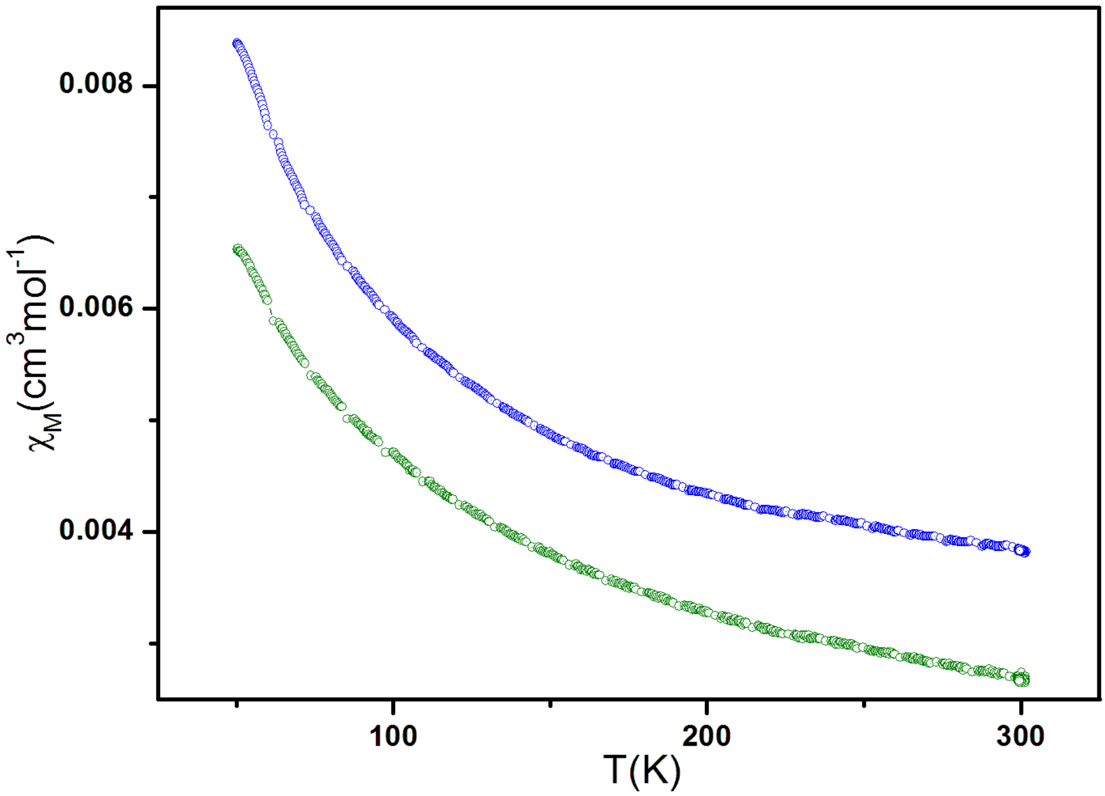


Fig. 3.51 – Plot of χ_M versus T for **5 (-o-)** and **5a (-o-)**

*3.1.6 Description of Crystal structure of **3**, **4** and **5***

The details of structure refinements for **3 - 5** are given in Table 3.5.

Table 3.5 – Crystal data and structure refinement for **3 – 5**.

Empirical formula	$C_{20}H_{44}N_2NiO_{20}$	$C_{20}H_{44}CoN_2O_{20}$	$C_{20}H_{44}CuN_2O_{20}$
Formula weight (g mol^{-1})	691.28	691.5	696.11
Temperature (K)	293(2)	296(2)	296(2)
Wavelength (Å)	1.54184	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	11.2600(6)	11.8572(3)	11.9101(5)
b (Å)	11.8393(7)	12.4961(3)	12.3555(6)
c (Å)	12.4959(7)	27.2165(6)	16.6034(7)
α (°)	82.000(5)	79.0500(10)	100.649(2)
β (°)	77.409(5)	88.6480(10)	97.357(2)
γ (°)	75.538(5)	82.0290(10)	96.264(2)
Volume (Å^3)	1567.92(15)	3920.95(16)	2359.23(18)
Z	2	5	3
D_{calc} (mg/m^3)	1.464	1.464	1.4703

Absorption coefficient (mm^{-1})	1.660	0.632	0.779
F(000)	732	1825	1101
Crystal size (mm^{3})	0.37 x 0.27 x 0.26	0.30 x 0.25 x 0.20	0.25 x 0.20 x 0.20
θ range for data collection (°)	3.64 to 67.08	1.70 to 25.00	1.90 to 25.00
Index ranges	$-9 \le h \le 13$	$-14 \le \mathrm{h} \le 14$	$-14 \le \mathrm{h} \le 14$
	$-14 \le k \le 14$	$-14 \le \mathrm{k} \le 14$	$-14 \le \mathrm{k} \le 14$
	$-14 \le l \le 14$	$-32 \le \mathrm{l} \le 32$	$-19 \le \mathrm{l} \le 19$
Reflections collected / unique	9530/5572 [R(int) = 0.0166]	97359 / 13783 [R(int) = 0.0371]	61059 / 8318 [R(int)=0.0383]
Completeness to θ = 26.50°	99.8 %	99.9%	99.9%
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Max. and min. Transmission	0.6721 and 0.5787	0.8840 and 0.8330	0.8598 and 0.8291
Refinement method	Full-matrix least-squares on F^{2}	Full-matrix least-squares on F^{2}	Full-matrix least-squares on F^{2}
Data / restraints / parameters	5572/ 1 /447	13783 / 99 / 1151	8318 / 54 / 714
Goodness-of-fit on F^{2}	1.037	1.052	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0993	R1 = 0.0311, wR2 = 0.0850	R1 = 0.0290, wR2 = 0.0755
R indices (all data)	R1 = 0.0366, wR2 = 0.1009	R1 = 0.0515, wR2 = 0.1001	R1 = 0.0474, wR2 = 0.0876
Largest diff. peak and hole (e Å^{-3})	0.374 and -0.415	0.406 and -0.442	0.286 and -0.467

The anionic water rich bis(phthalato) compounds **3**-**5** crystallise in the centrosymmetric triclinic *Pī* space group. The structures of all three compounds are based on a metal bis(phthalato) anionic unit with two independent monodentate pht^{2-} ligands disposed *trans* to each other and charge balanced by an organic cation $(pipH_2)^{2+}$. The geometric parameters of the phthalate ligands are in the normal range and are in agreement with reported data [31-76]. The unique organic cations are diprotonated and adopt a chair conformation with their geometric parameters in normal range. The central metal ion viz. Ni(II) in **3** and Co(II) in **4** Cu(II) in **5** exhibit hexacoordination forming a distorted $\{MO_6\}$ octahedron. Although compounds **3**-**5** have similar anionic units, they differ from each other in terms of the number of unique metal ions present in the crystal structure. Compound **3** contains an unique Ni(II) ion situated in a general position while three independent Co(II) ions one of which (Co3) is situated on an inversion centre are present in **4**. Compound **5** contains two unique metal ions one of which (Cu2) is located on an inversion centre (Fig. 3.52 – 3.54).

Despite the presence of more than one unique metal in **4** and **5**, all metal centres exhibit the same hexacoordination viz. four terminal aqua ligands and two monodentate phthalates, due to the presence of five crystallographically unique phthalate ligands in **4** and three independent phthalates in **5**. The M-O bond distances range from 2.0402(11) to 2.1070(11) Å (Ni-O) and 2.0697(13) to 2.1509(13) Å (Co-O). The O-M-O angles vary between 86.36(5) to 94.65(5)° (cis angles) and 177.08(4) to 179.29(4)° (trans angles) in **3**, 85.00(5) to 95.81(5)° (cis angles) and 176.58(5) to 179.43(5)° (trans angles) in **4** indicating a slightly distorted $\{MO_6\}$ octahedra (Table 3.8). Four Cu-O bond distances in **5** range from 1.941(7) to 1.988(8) Å (Cu-O) while the O-Cu-O cis angles vary between 88.2(3) to 92.5(3)° and trans angles from

177.7(3) to 178.8(3)°. In addition, two longer Cu-O(H_2O) distances at 2.445(2) and 2.528(5) Å in Cu1 are observed indicating a Jahn-Teller distorted {CuO_6} octahedron (Table 3.8). The second unique Cu2 in **5** exhibits a similar distorted {CuO_6} octahedron.

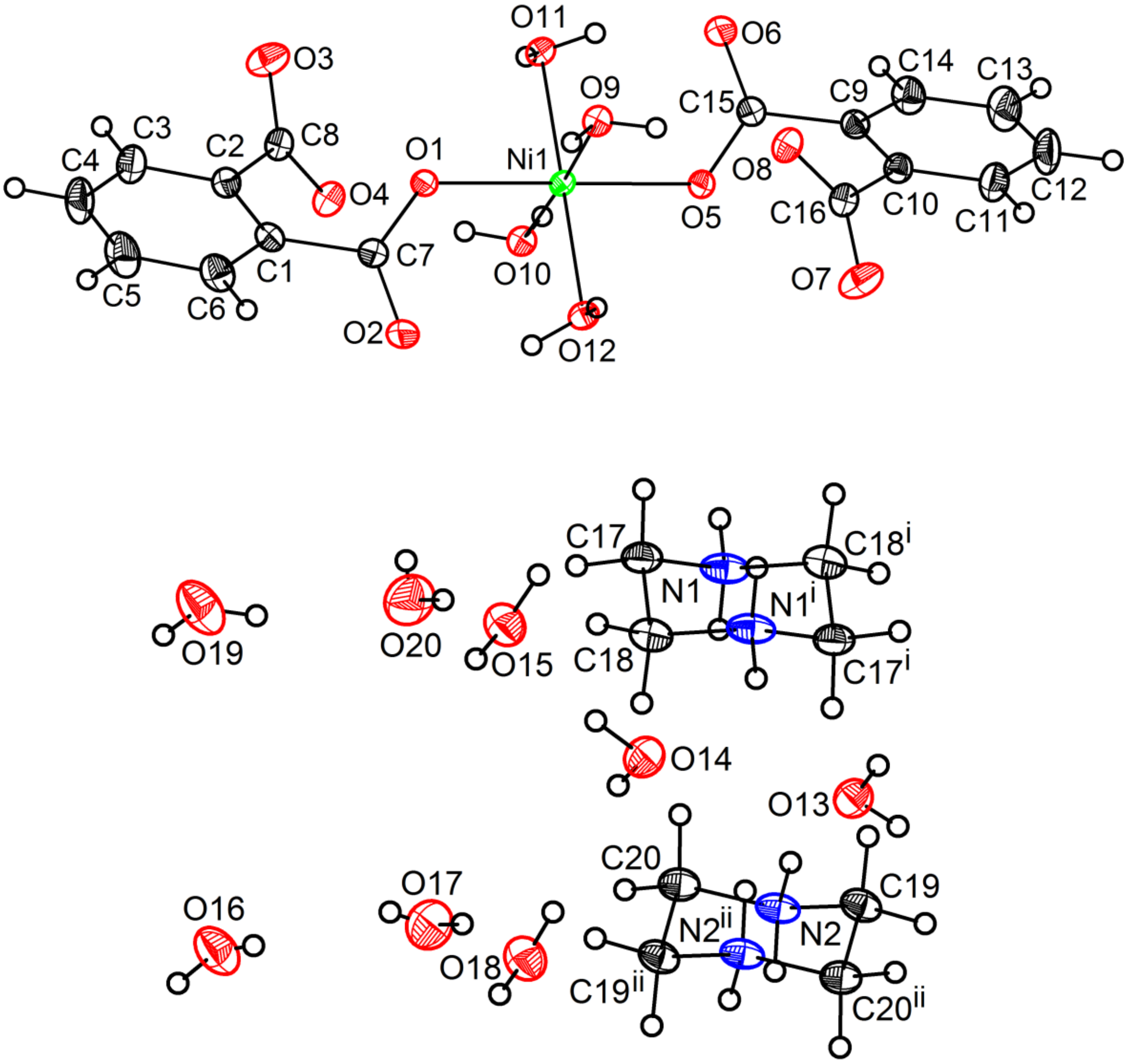


Fig. 3.52 – The crystal structure of (pipH_2)[Ni(H_2O)$_4$(pht)$_2$]·8H_2O **3** showing the atom labelling scheme and the coordination sphere of Ni(II) in **3**. Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as circles of arbitrary radius. Symmetry code: i) 1-x, 1-y, 1-z; ii) 2-x,-y, 1-z.

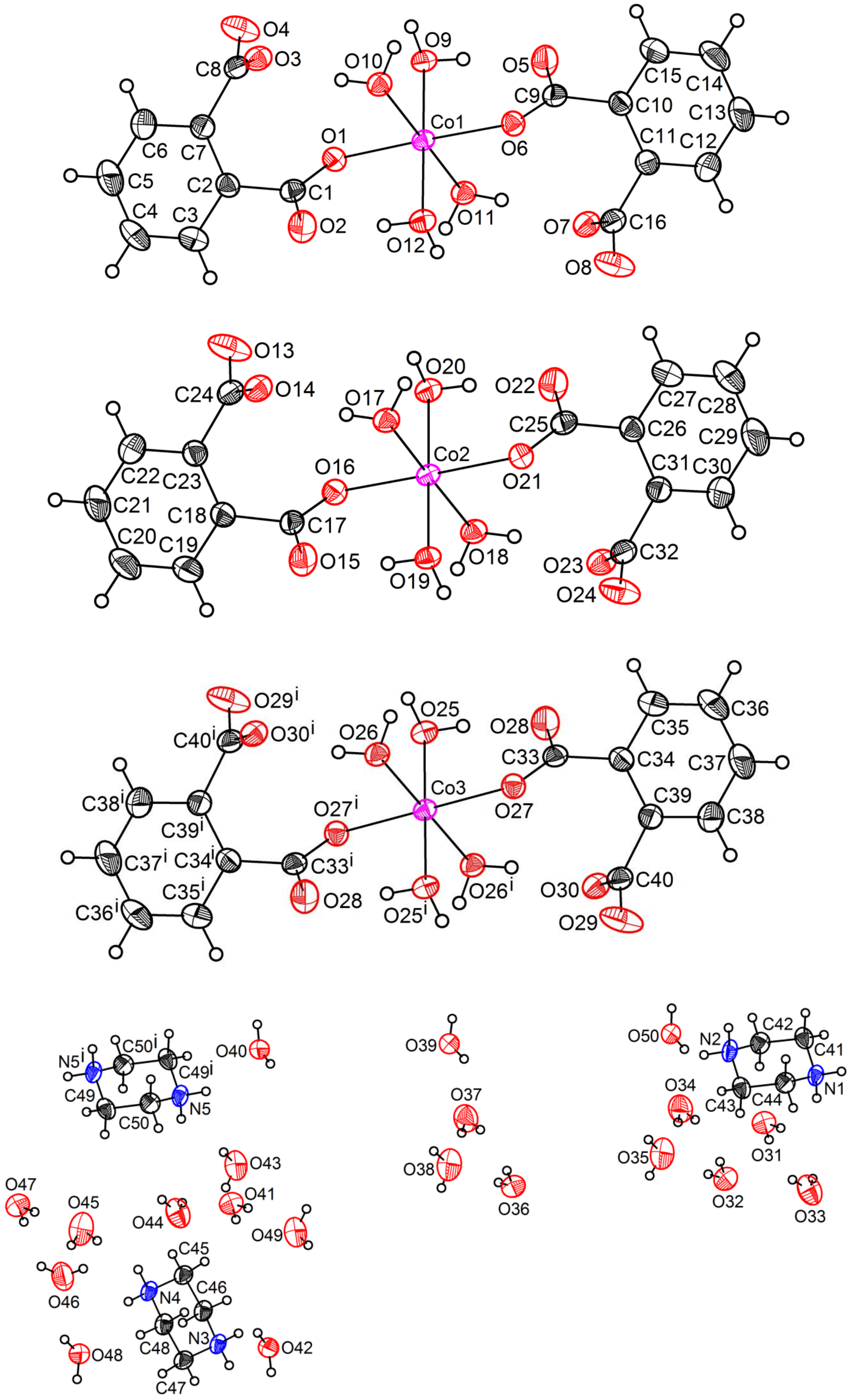


Fig. 3.53 – The crystal structure of $(pipH)_2[Co(H_2O)_4(pht)_2]\cdot 8H_2O$ **4** showing the atom labelling scheme and the coordination sphere of Co(II) in **4**. Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as spheres of arbitrary radius. Symmetry code: i) 1-x, 1-y, 2-z; ii) 2-x, 1-y, 1-z.

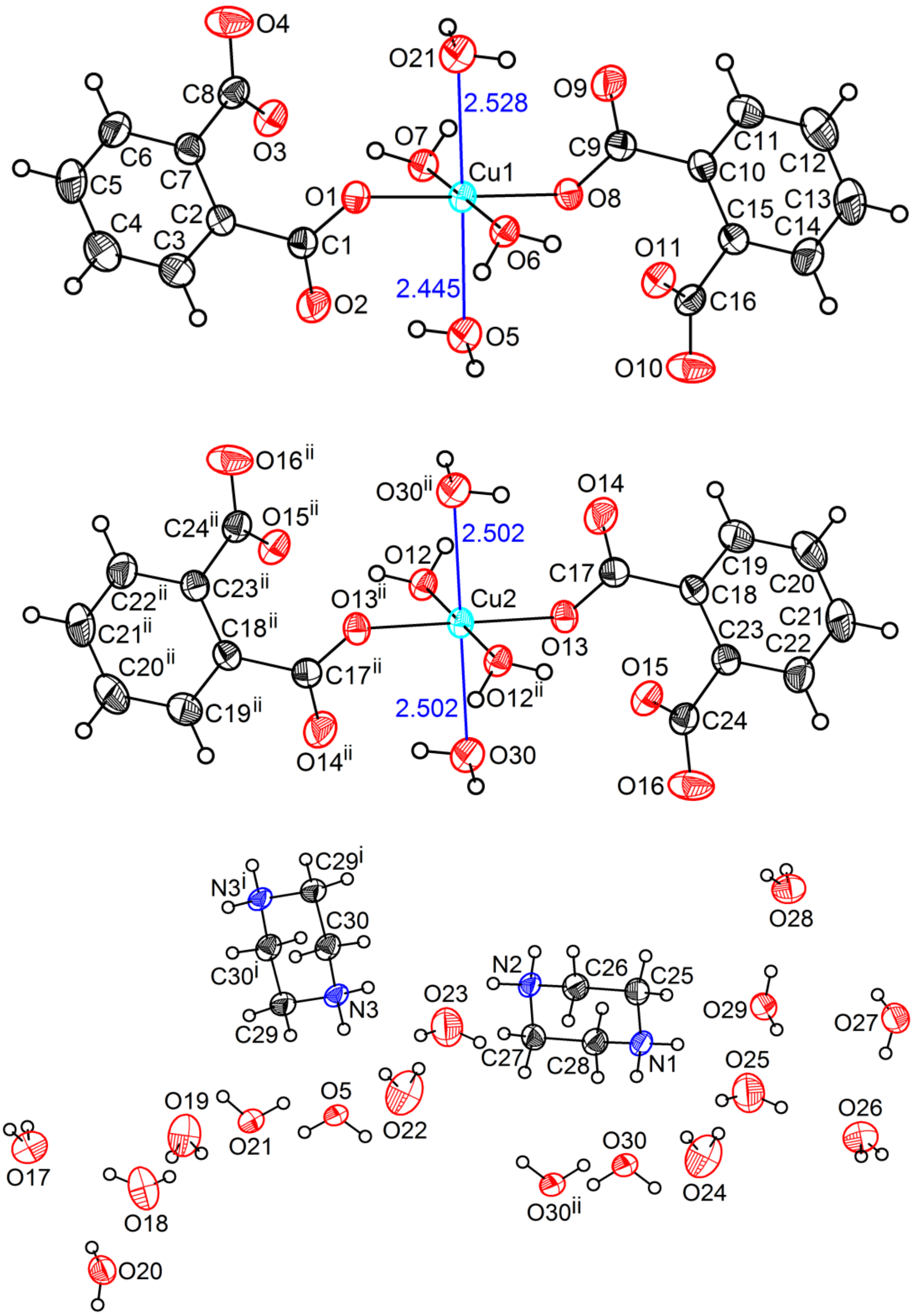


Fig. 3.54 – An anionic unit, cation and lattice water in the crystal structure of (pipH$_2$)[Cu(H$_2$O)$_4$(pht)$_2$]·8H$_2$O **5** showing the atom labelling scheme and the coordination sphere of Cu(II) in **5**. Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as spheres of arbitrary radius. Symmetry code: i) -x, 1-y, 1-z; ii) -x, 1-y, -z.

Table 3.8 – Selected bond lengths [Å] and angles [°]

Compound **3**

Bond lengths

Ni1-O1	2.0402(11)	Ni1-O9	2.0532(12)	Ni1-O11	2.0844(11)
Ni1-O5	2.0475(11)	Ni1-O10	2.0698(11)	Ni1-O12	2.1070(11)

Bond angles

O1-Ni1-O9	91.52(5)	O5-Ni1-O11	93.63(5)	O9-Ni1-O12	89.99(5)
O5-Ni1-O9	87.50(5)	O9-Ni1-O11	89.38(5)	O10-Ni1-O12	92.10(5)
O1-Ni1-O10	86.36(5)	O10-Ni1-O11	88.51(5)	O11-Ni1-O12	179.29(4)
O5-Ni1-O10	94.65(5)	O1-Ni1-O12	92.45(5)	O1-Ni1-O5	178.69(4)
O1-Ni1-O11	87.23(5)	O5-Ni1-O12	86.68(5)	O9-Ni1-O10	177.08(4)

Compound **4**

Bond lengths

Co1-O1	2.0697(13)	Co1-O12	2.1469(13)	Co2-O21	2.0733(13)
Co1-O6	2.0775(13)	Co2-O16	2.0759(13)	Co2-O20	2.1509(13)
Co1-O9	2.1214(13)	Co2-O17	2.0839(12)	Co3-O25	2.1423(13)
Co1-O10	2.1074(13)	Co2-O18	2.0907(12)	Co3-O26	2.0895(12)
Co1-O11	2.0852(13)	Co2-O19	2.1315(13)	Co3-O27	2.0862(12)

Bond angles

O1-Co1-O11	92.07(5)	O10-Co1-O12	92.56(5)	O18-Co2-O19	88.02(5)
O6-Co1-O11	86.87(5)	O1-Co1-O6	178.52(4)	O21-Co2-O20	92.21(5)
O1-Co1-O10	85.76(5)	O11-Co1-O10	176.58(5)	O16-Co2-O20	87.26(5)
O6-Co1-O10	95.35(5)	O9-Co1-O12	179.43(5)	O17-Co2-O20	89.49(5)
O1-Co1-O9	88.03(5)	O21-Co2-O17	92.62(5)	O18-Co2-O20	92.54(5)
O6-Co1-O9	92.97(5)	O16-Co2-O17	86.58(5)	O21-Co2-O16	179.05(5)
O11-Co1-O9	89.38(5)	O21-Co2-O18	85.00(5)	O17-Co2-O18	176.93(5)
O10-Co1-O9	87.91(5)	O16-Co2-O18	95.81(5)	O19-Co2-O20	179.37(5)
O1-Co1-O12	91.69(5)	O21-Co2-O19	87.56(5)	O27-Co3-O26	93.29(5)
O6-Co1-O12	87.29(5)	O16-Co2-O19	92.96(5)	O27-Co3-O25	93.07(5)
O11-Co1-O12	90.14(5)	O17-Co2-O19	89.94(5)	O26-Co3-O25	89.61(5)

Compound **5**

Bond lengths

Cu1-O1	1.945(7)	Cu1-O6	1.988(8)	Cu2-O12	1.973(7)
Cu1-O8	1.941(7)	Cu1-O7	1.972(8)	Cu2-O13	1.954(7)
Cu1-O5	2.445(2)	Cu1-O21	2.528(2)	Cu2-O30	2.502(2)

Bond angles

O8-Cu1-O7	90.2(3)	O5-Cu1-O1	95.28(0)	O21-Cu1-O8	95.29(0)
O1-Cu1-O7	89.1(3)	O5-Cu1-O6	85.28(0)	O21-Cu1-O7	86.88(0)
O8-Cu1-O6	88.2(3)	O5-Cu1-O8	85.76(0)	O21-Cu1-O5	178.95(0)
O1-Cu1-O6	92.5(3)	O5-Cu1-O7	92.98(0)	O13-Cu2-O12	90.8(3)
O7-Cu1-O6	177.7(3)	O21-Cu1-O1	83.68(0)	O30-Cu2-O12	87.5(0)
O8-Cu1-O1	178.8(3)	O21-Cu1-O6	94.89(0)	O30-Cu2-O13	96.0(0)

The phthalate anion in **3-5** functions as a monodentate ligand and not as a bridging ligand which is often observed in many other bivalent metal phthalates. The observed monodentate ligation of $(pht)^{2-}$ can be correlated to the degree of hydration of these compounds (*vide supra*). All these compounds contain four terminal aqua ligands and eight lattice water molecules.

It is interesting to note that compounds **3-5** are rare examples of metal phthalates containing a dozen water molecules per metal and hence we have used the terminology 'water rich' to designate these compounds. In the Ni(II) series only one compound viz. $[Ni(pht)(Bpybc)(H_2O)_4]\cdot 9H_2O$ (Bpybc= 1,1'-bis(4-carboxylatobenzyl)-4,4'-bipyridinium) [82] is reported so far containing high metal: H_2O ratio of 1:13 (*vide supra*). Since the hydrogens of the lattice waters were not located an analysis of the water architecture was not reported. An analysis of the crystal structures of **3-5** (Table 3.9) reveals that the coordinated and lattice water molecules exhibit several intra- and intermolecular H-bonding interactions (Fig. 3.55 – 3.60) due to the presence of a dozen water molecules, resulting in an intricate 3D supramolecular architecture. The intramolecular H-bonding among the lattice water molecules in **3-5** results in the formation of a water dodecamer cluster (R6 water motif) which extends on both sides forming a tetramer with the next cyclic hexameric unit resulting in an alternate arrangement of edge-shared hexameric and tetrameric units of water dodecamer having T4(2)6(2) extended motif. Based on the nomenclature of various types of water clusters, extended water motifs reported by Infantes *et al* [187] the water cluster in **3-5** is designated as R6 and the extended motif is termed as T4(2)6(2). The observed average O···O distance in water dodecamer cluster in **3**-**5** is 2.824 Å, which is shorter than those observed in liquid water (2.854 Å) and thus comparable to those in the ice phase (2.77 - 2.84 Å) [276-278].

Table 3.9 – Hydrogen bonding geometry [Å and °] for **3**, **4** and **5**

D-H···A	d(D-H)	(H···A)	d(D···A)	<DHA	Symmetry code
$(pipH_2)[Ni(H_2O)_4(pht)_2]\cdot 8H_2O$ **3**					
O9-H9A···O8	0.858	1.939	2.797	177.21	x, y, z
O9-H9B···O7	0.811	1.817	2.626	175.28	-x+2, -y+1, -z+1
O10-H10A···O4	0.832	2.015	2.845	175.83	x, y, z
O10-H10B···O3	0.744	1.904	2.647	178.74	-x+1, -y+2, -z+1
O11-H11A···O4	0.860	1.914	2.701	151.47	-x+1, -y+2, -z+1
O11-H11B···O6	0.830	1.799	2.602	162.32	x, y, z
O12-H12A···O2	0.861	1.855	2.610	145.47	x, y, z
O12-H12B···O8	0.871	2.028	2.847	156.32	-x+2, -y+1, -z+1
N1-H1A···O13	0.920	2.158	2.939	142.14	-x+1, -y+1, -z+1
N1-H1A···O14	0.920	2.271	2.987	134.30	-x+1, -y+1, -z+1
N1-H1B···O12	0.920	2.189	2.987	144.63	-x+1, -y+1, -z+1
N1-H1B···O5	0.920	2.409	3.161	138.87	-x+1, -y+1, -z+1
N2-H2A···O11	0.920	2.096	2.847	138.08	-x+2, -y+1, -z+1
N2-H2A···O1	0.920	2.287	2.998	133.77	-x+2, -y+1, -z+1
N2-H2B···O13	0.920	2.183	2.936	138.41	-x+2, -y, -z+1
N2-H2B···O14	0.920	2.264	3.025	139.71	-x+2, -y, -z+1
O13-H13A···O7	0.739	2.054	2.758	159.19	x, y, z
O13-H13B···O18	0.838	2.011	2.846	174.68	-x+2, -y, -z+1
O14-H14A···O15	0.926	1.921	2.837	169.61	x, y, z
O14-H14B···O3	0.787	2.059	2.793	155.16	x, y-1, z
O15-H15A···O16	0.870	1.924	2.789	172.26	-x+2, -y, -z+2
O15-H15B···O8	0.870	1.980	2.843	170.64	-x+2, -y+1, -z+1
O16-H16A···O17	0.491	2.362	2.849	172.60	x, y, z
O16-H16B···O6	0.897	1.861	2.746	169.06	x, y-1, z+1
O17-H17C···O16	0.584	2.351	2.849	144.93	-x+2, - y, -z+2
O17-H17D···O18	0.974	1.840	2.792	164.99	x, y, z
O18-H18C···O19	0.839	1.965	2.801	174.20	-x+2, -y, -z+2
O18-H18D···O4	0.800	2.096	2.880	166.58	x+1, y-1, z
O19-H19C···O20	0.753	2.057	2.793	165.78	x, y, z
O19-H19D···O2	0.834	1.882	2.709	170.67	-x+1, -y+1, -z+2
O20-H20C···O19	0.538	2.345	2.876	169.33	-x+1, -y+1, -z+2
O20-H20D···O15	0.872	1.934	2.799	171.60	x, y, z
C17-H17B···O10	0.990	2.395	3.320	155.10	x, y, z
C18-H18B···O5	0.990	2.636	3.363	130.35	-x+1, -y+1, -z+1
C18-H18B···O3	0.990	2.675	3.467	137.16	x, y-1, z
C18-H18B···O20	0.990	2.620	3.535	153.63	x, y, z
C19-H19B···O7	0.990	2.655	3.644	177.49	x, y, z
C20-H20B···O17	0.990	2.700	3.590	149.76	x, y, z
C20-H20A···O9	0.990	2.475	3.315	142.37	-x+2, -y+1, -z+1
C20-H20A···O14	0.990	2.703	3.385	126.39	x, y, z

$(pipH_2)[Co(H_2O)_4(pht)_2]\cdot 8H_2O$ **4**

O9-H9C···O3	0.851	1.874	2.686	159.21	-x, -y+1, -z+2
O9-H9D···O5	0.846	1.786	2.61	163.84	x, y, z
O10-H10C···O3	0.848	1.997	2.835	169.64	x, y, z
O10-H10D···O4	0.854	1.793	2.645	174.88	-x, -y+1, -z+2
O11-H11C···O7	0.841	1.96	2.797	173.04	x, y, z
O11-H11D···O13	0.861	1.758	2.617	174.52	x, y, z
O12-H12C···O14	0.858	2.029	2.828	154.55	x, y, z
O12-H12D···O2	0.834	1.805	2.618	164.24	x, y, z
O17-H17C···O8	0.857	1.763	2.619	176.3	x, y, z
O17-H17D···O14	0.842	1.968	2.799	168.64	x, y, z
O18-H18C···O29	0.841	1.794	2.632	173.71	-x+2, -y+1, -z+1
O18-H18D···O23	0.877	1.993	2.862	170.59	x, y, z
O19-H19C···O30	0.845	1.938	2.735	156.84	-x+2, -y+1, -z+1
O19-H19D···O15	0.84	1.779	2.601	165.76	x, y, z
O20-H20C···O22	0.851	1.781	2.616	166.29	x, y, z
O20-H20C···O21	0.851	2.644	3.045	110.22	x, y, z
O20-H20D···O7	0.884	1.998	2.823	154.66	x, y, z
O25-H25C···O23	0.876	1.951	2.785	158.67	x, y, z
O25-H25D···O28	0.83	1.822	2.618	160.07	x, y, z
O26-H26C···O30	0.845	1.948	2.783	169.31	-x+2, -y+1, -z+1
O26-H26D···O24	0.853	1.783	2.633	174.78	x, y, z
N1-H1A···O42	0.9	2.196	2.942	139.86	-x+2, -y+1, -z+1
N1-H1A···O39	0.9	2.236	2.949	135.88	-x+3, -y+1, -z+1
N1-H1B···O20	0.9	2.213	2.996	145.08	-x+2, -y+1, -z+1
N1-H1B···O16	0.9	2.491	3.218	138.18	-x+2, -y+1, -z+1
N2-H2A···O25	0.9	2.213	2.983	143.28	x+1, y, z
N2-H2A···O27	0.9	2.429	3.165	139.13	-x+3, -y+1, -z+1
N2-H2B···O50	0.9	2.167	2.881	135.77	x, y, z
N2-H2B···O50	0.9	2.207	2.944	138.73	-x+3, -y+1, -z+1
N3-H3A···O19	0.9	2.147	2.876	137.46	x-1, y, z
N3-H3A···O21	0.9	2.283	2.981	134.24	x-1, y, z
N3-H3B···O42	0.9	2.162	2.897	138.41	x, y, z
N3-H3B···O39	0.9	2.261	2.995	138.43	x-1, y, z
N4-H4A···O40	0.9	2.192	2.93	138.74	x-1, y, z
N4-H4A···O48	0.9	2.274	3.016	139.61	x, y, z
N4-H4B···O9	0.9	2.141	2.869	137.5	x, y, z
N4-H4B···O1	0.9	2.325	3.013	133.21	x, y, z
N5-H5A···O40	0.9	2.159	2.927	142.94	x, y, z
N5-H5A···O48	0.9	2.288	2.985	134.15	x+1, y, z
N5-H5B···O12	0.9	2.227	3.006	144.56	x, y, z
N5-H5B···O6	0.9	2.44	3.169	138.21	x, y, z
O31-H31C···O7	0.836	2.071	2.86	157.1	-x+1, -y+2, -z+1
O31-H31D···O43	0.843	1.981	2.796	162.47	-x+1, -y+2, -z+1
O32-H32C···O35	0.876	1.944	2.795	163.8	x, y, z
O32-H32D···O30	0.827	2.098	2.875	156.46	x, y, z
O33-H33C···O32	0.799	2.14	2.788	138.21	x, y, z
O33-H33D···O43	0.833	1.998	2.826	172.31	-x+1, -y+2, -z+1

O34-H34C···O31	0.813	2.196	2.8	131.19	x, y, z
O34-H34D···O35	0.83	1.973	2.795	170.88	x, y, z
O35-H35C···O28	0.869	1.899	2.724	158.04	x, y, z
O35-H35D···O37	0.82	2.21	2.874	138.19	-x+1, -y+2, -z+1
O36-H36C···O38	0.817	2.029	2.817	161.8	x, y, z
O36-H36D···O23	0.845	1.993	2.793	157.71	x, y, z
O37-H37C···O36	0.802	2.237	2.778	125.26	-x+1, -y+2, -z+1
O37-H37D···O38	0.858	1.916	2.773	176.69	x, y, z
O38-H38C···O34	0.784	2.376	2.871	122.19	-x+1, -y+2, -z+1
O38-H38D···O22	0.873	1.868	2.703	159.52	x, y, z
O39-H39C···O24	0.825	2.01	2.8	159.97	x, y, z
O39-H39D···O31	0.82	2.019	2.836	174.42	-x+2, -y+2, -z+1
O40-H40C···O47	0.827	2.024	2.849	175.26	-x+1, -y+1, -z+2
O40-H40D···O8	0.817	1.973	2.754	159.51	x, y, z
O41-H41C···O49	0.857	1.976	2.796	159.98	x, y, z
O41-H41D···O14	0.828	2.052	2.841	159.03	x, y, z
O42-H42C···O32	0.823	2.02	2.841	175.79	-x+1, -y+1, -z+1
O42-H42D···O13	0.831	1.959	2.746	157.71	x, y, z
O43-H43C···O5	0.844	1.942	2.751	160.41	x, y, z
O43-H43D···O44	0.796	2.168	2.815	138.69	x, y, z
O44-H44C···O47	0.809	2.176	2.793	133.25	-x, -y+1, -z+2
O44-H44D···O49	0.828	1.998	2.823	174.08	x-1, y+1, z
O45-H45C···O2	0.858	1.854	2.699	167.8	x, y, z
O45-H45D···O46	0.801	2.037	2.801	159.22	x, y, z
O46-H46C···O45	0.765	2.124	2.867	164.09	-x+1, -y, -z+2
O46-H46D···O41	0.833	2.016	2.797	155.78	-x+1, -y, -z+2
O47-H47C···O3	0.827	2.091	2.88	159.4	x, y, z
O47-H47D···O45	0.89	1.927	2.797	165.53	x, y, z
O48-H48C···O41	0.826	2.01	2.835	176.75	x-1, y, z
O48-H48D···O4	0.834	2.006	2.788	155.87	x, y, z
O49-H49C···O15	0.832	1.948	2.751	161.64	x, y, z
O49-H49D···O33	0.831	2.138	2.811	137.97	-x+2, -y+1, -z+1
O50-H50C···O29	0.85	1.892	2.709	160.82	x, y, z
O50-H50D···O36	0.846	1.963	2.808	176.05	x+1, y, z
C41-H41B···O26	0.970	2.473	3.389	157.46	-x+3, -y+1, -z+1
C43-H43A···O18	0.970	2.439	3.340	154.34	-x+2, -y+1, -z+1
C45-H45B···O44	0.970	2.718	3.588	149.51	x, y, z
C46-H46A···O8	0.970	2.680	3.649	177.68	x-1, y, z
C46-H46A···O17	0.970	3.075	3.758	128.66	x-1, y, z
C46-H46A···O40	0.970	2.943	3.537	120.65	x-1, y, z
C47-H47A···O33	0.970	2.740	3.619	151.01	-x+1, -y+1, -z+1
C48-H48B···O13	0.970	2.749	3.718	177.97	-x+2, -y+1, -z+1
C48-H48B···O42	0.970	2.896	3.494	120.65	x, y, z
C49-H49A···O10	0.970	2.427	3.329	154.38	x, y, z
C49-H49A···O12	0.970	3.031	3.651	123.07	x, y, z
C50-H50A···O4	0.970	2.729	3.491	135.84	x+1, y, z
C50-H50A···O6	0.970	2.626	3.341	130.82	-x+1, -y+1, -z+2
C50-H50A···O10	0.970	2.798	3.598	140.29	-x+1, -y+1, -z+2
C50-H50B···O46	0.970	2.658	3.556	154.14	-x+1, -y+1, -z+2

(pipH$_2$)[Cu(H$_2$O)$_4$(pht)$_2$]·8H$_2$O **5**

N1-H1A···O30	0.9	2.026	2.815	145.62	x, y, z
N1-H1B···O29	0.9	2.114	2.871	141.22	x, y, z
N1-H1B···O29	0.9	2.198	2.899	134.25	-x+1, -y+1, -z
N2-H2A···O20	0.9	2.152	2.901	140.28	x+1, y, z
N2-H2A···O27	0.9	2.223	2.928	134.89	-x, -y, -z
N2-H2B···O21	0.9	2.002	2.815	149.64	x+1, y, z
N3-H3A···O5	0.9	1.97	2.728	140.91	x, y, z
N3-H3A···O8	0.9	2.456	3.114	130.2	x, y, z
N3-H3B···O20	0.9	2.185	2.918	138.26	x+1, y, z
N3-H3B···O27	0.9	2.219	2.941	136.93	-x, -y, -z
O17-H17A···O24	0.849	1.949	2.783	166.75	x, y+1, z+1
O17-H17B···O15	0.835	2.084	2.904	166.98	x, y+1, z+1
O18-H18A···O17	0.845	1.966	2.81	175.46	x, y, z
O18-H18B···O19	0.797	1.997	2.792	176.15	-x, -y+2, -z+1
O19-H19A···O2	0.835	1.909	2.735	169.98	x, y, z
O19-H19B···O18	0.825	1.992	2.793	163.82	x, y, z
O22-H22A···O9	0.836	1.87	2.689	165.9	x, y, z
O22-H22B···O23	0.846	1.942	2.772	166.85	x, y, z
O23-H23A···O28	0.839	1.984	2.82	173.89	-x, -y, -z
O23-H23B···O24	0.812	2.051	2.855	169.97	-x-1, -y, -z
O24-H24A···O14	0.839	1.884	2.712	168.96	x, y, z
O24-H24B···O25	0.84	1.963	2.79	167.92	x, y, z
O25-H25C···O22	0.829	2.051	2.864	166.97	-x-1, -y, -z
O25-H25D···O26	0.846	1.98	2.825	176.59	x, y, z
O5-H5A···O2	0.823	1.843	2.65	166.35	x, y, z
O5-H5B···O15	0.835	1.909	2.729	166.71	-x, -y+1, -z
O6-H6A···O11	0.856	1.941	2.796	175.77	x, y, z
O6-H6B···O16	0.833	1.795	2.622	171.69	-x, -y+1, -z
O7-H7A···O4	0.84	1.772	2.608	173.62	-x-1, -y+1, -z+1
O7-H7B···O3	0.86	1.884	2.743	179.61	x, y, z
O12-H12A···O15	0.845	1.883	2.728	179.08	-x, -y+1, -z
O12-H12B···O10	0.837	1.781	2.615	173.94	x, y, z
O20-H20A···O4	0.822	1.984	2.775	161.48	x, y, z
O20-H20B···O17	0.824	2.034	2.854	173.44	-x-1, -y+2, -z+1
O21-H21A···O3	0.838	2.03	2.845	163.96	-x-1, -y+1, -z+1
O21-H21B···O9	0.851	1.843	2.666	162.23	x, y, z
O26-H26C···O19	0.847	1.942	2.778	168.92	x, y-1, z-1
O26-H26D···O3	0.83	2.07	2.888	168.27	x, y-1, z-1
O27-H27C···O26	0.846	1.989	2.826	169.98	x, y, z
O27-H27D···O10	0.844	2.017	2.813	157.06	-x, -y, -z
O28-H28C···O22	0.835	1.979	2.803	168.52	x+1, y,
O28-H28D···O11	0.827	1.985	2.793	165.34	x+1, y, z
O29-H29C···O16	0.824	1.942	2.742	163.57	x, y, z
O29-H29D···O28	0.846	1.95	2.794	176.54	x, y, z
O30-H30C···O14	0.85	1.85	2.672	162.33	-x, -y+1, -z
O30-H30D···O11	0.854	1.979	2.818	167.37	-x, -y+1, -z
C25-H25A···O6	0.970	2.660	3.498	144.80	1+x, y, z
C26-H26A···O10	0.970	2.711	3.450	133.41	x, y, z
C26-H26A···O12	0.970	2.699	3.563	148.69	x, y, z

C26-H26A···O13	0.970	2.607	3.358	134.48	x, y, z
C26-H26B···O25	0.970	2.644	3.575	160.98	-x, -y, -z
C27-H27B···O12	0.970	2.689	3.557	149.07	x, y, z
C28-H28A···O23	0.970	2.670	3.607	162.60	1+x, 1+y, z
C28-H28B···O1	0.970	2.477	3.270	138.82	1+x, y, z
C28-H28B···O6	0.970	2.625	3.471	145.92	1+x, y, z
C29-H29A···O7	0.970	2.654	3.448	139.28	x, y, z
C29-H29B···O18	0.970	2.684	3.600	157.52	-x, 2-y, 1-z

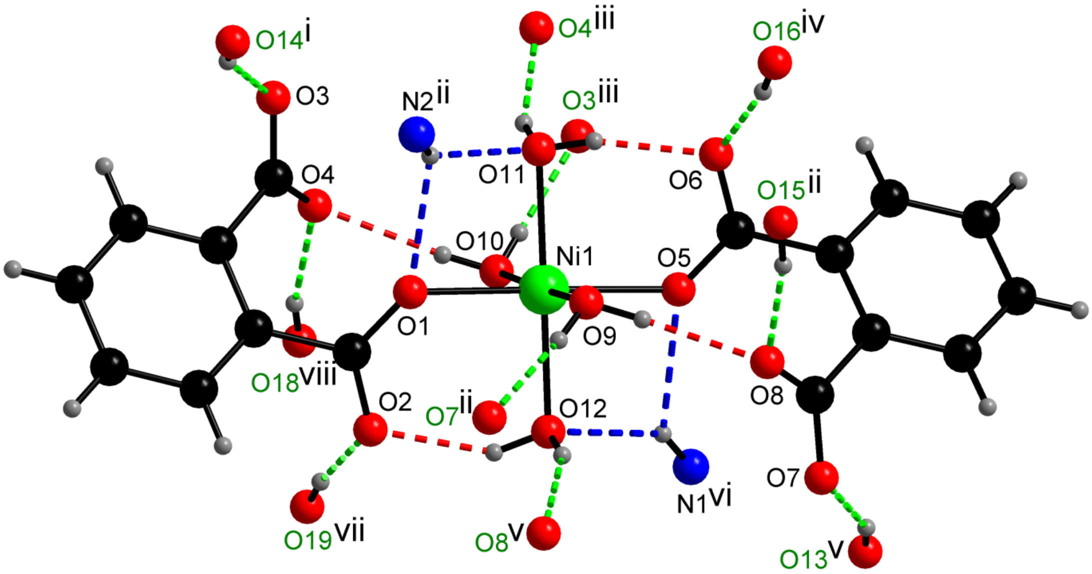
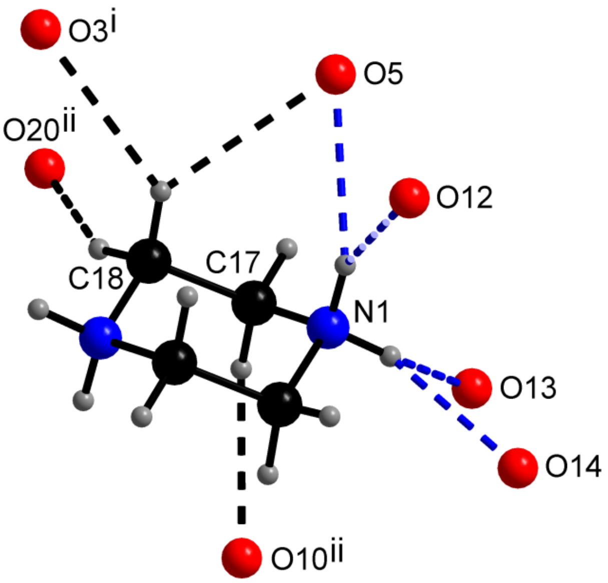


Fig. 3.55 – The H-bonding surroundings of $[Ni(H_2O)_4(pht)_2]^{2-}$ anion (Symmetry code: i) x, 1+y, z ii) 2-x, 1-y,1-z iii) 1-x, 2-y, 1-z iv) x, 1+y, -1+z v) x, y, z vi) 1-x, 1-y, 1-z vii) 1-x, 1-y, 2-z viii) -1+x, 1+y, z) in **3** showing N-H···O, C-H···O and O-H···O interactions (shown in broken lines)



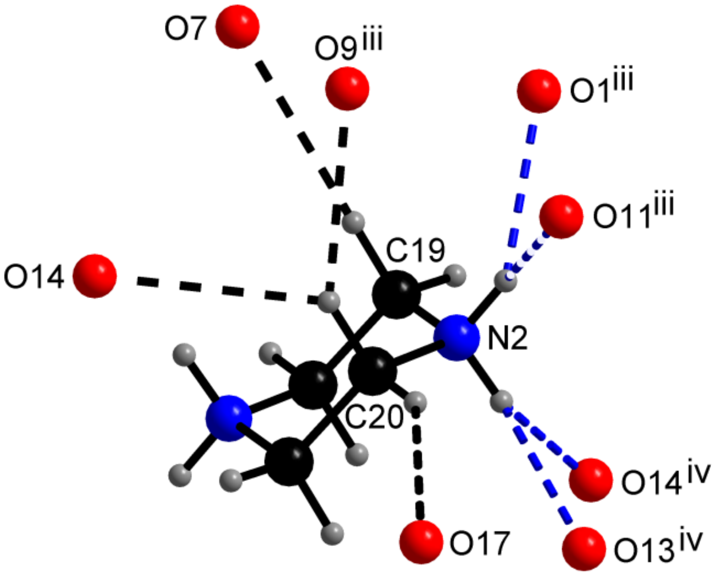


Fig. 3.56 – The H-bonding surroundings of the unique cations (Symmetry code: i) 1-x, 2-y, 1-z ii) 1-x, 1-y, 1-z iii) 2-x, 1-y, 1-z iv) 2-x, -y, 1-z) in **3** showing N-H···O, C-H···O and O-H···O interactions (shown in broken lines)

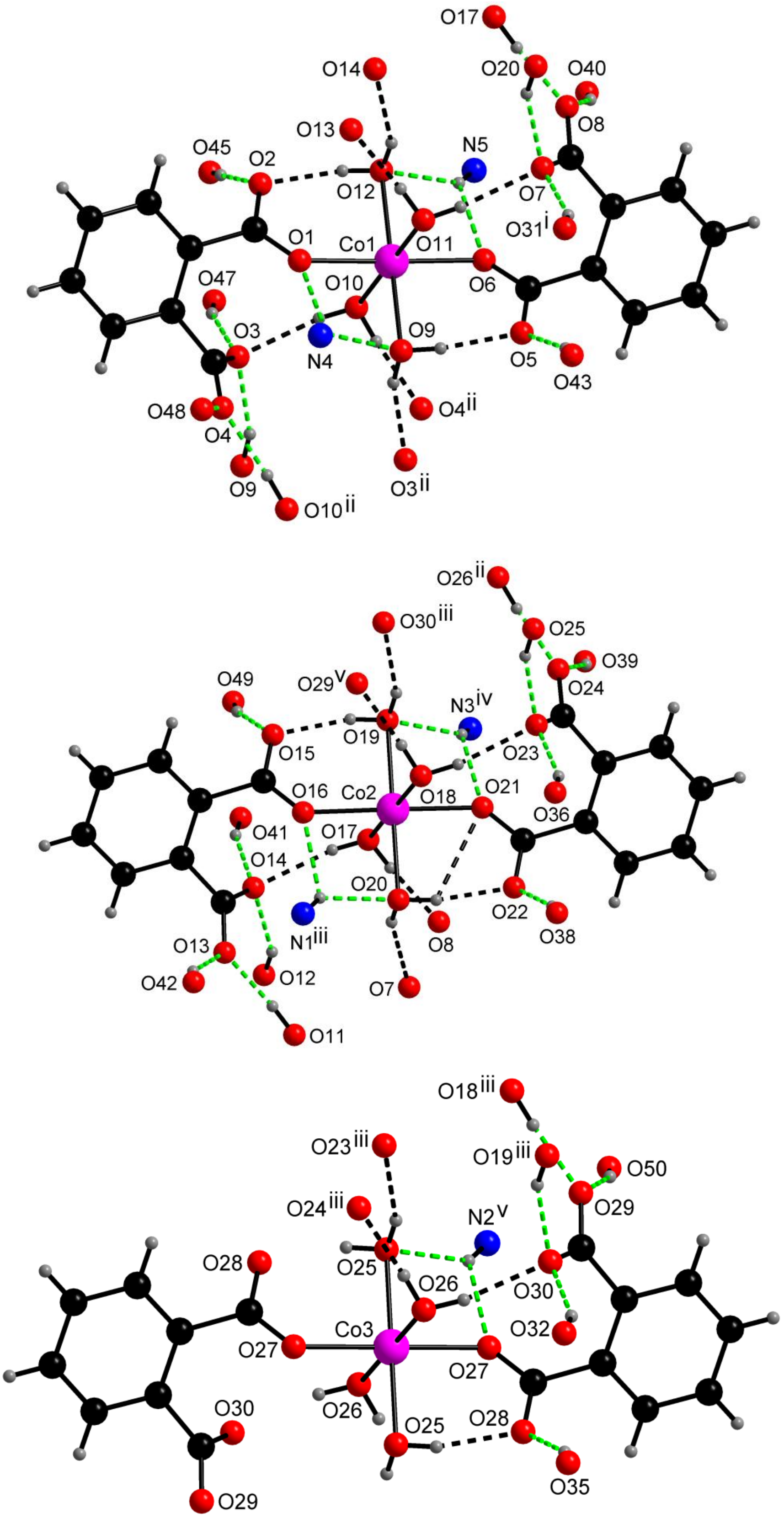


Fig. 3.57 – The H-bonding surroundings of $[Co(H_2O)_4(pht)_2]^{2-}$ anions (Symmetry code: i) 1-x, 2-y, 1-z ii) -x, 1-y, 2-z iii) 2-x, 1-y, 1-z iv) 1+x, y, z v) 2-x, 1-y, 1-z) in **4** showing N-H···O, C-H···O and O-H···O interactions (shown in broken lines)

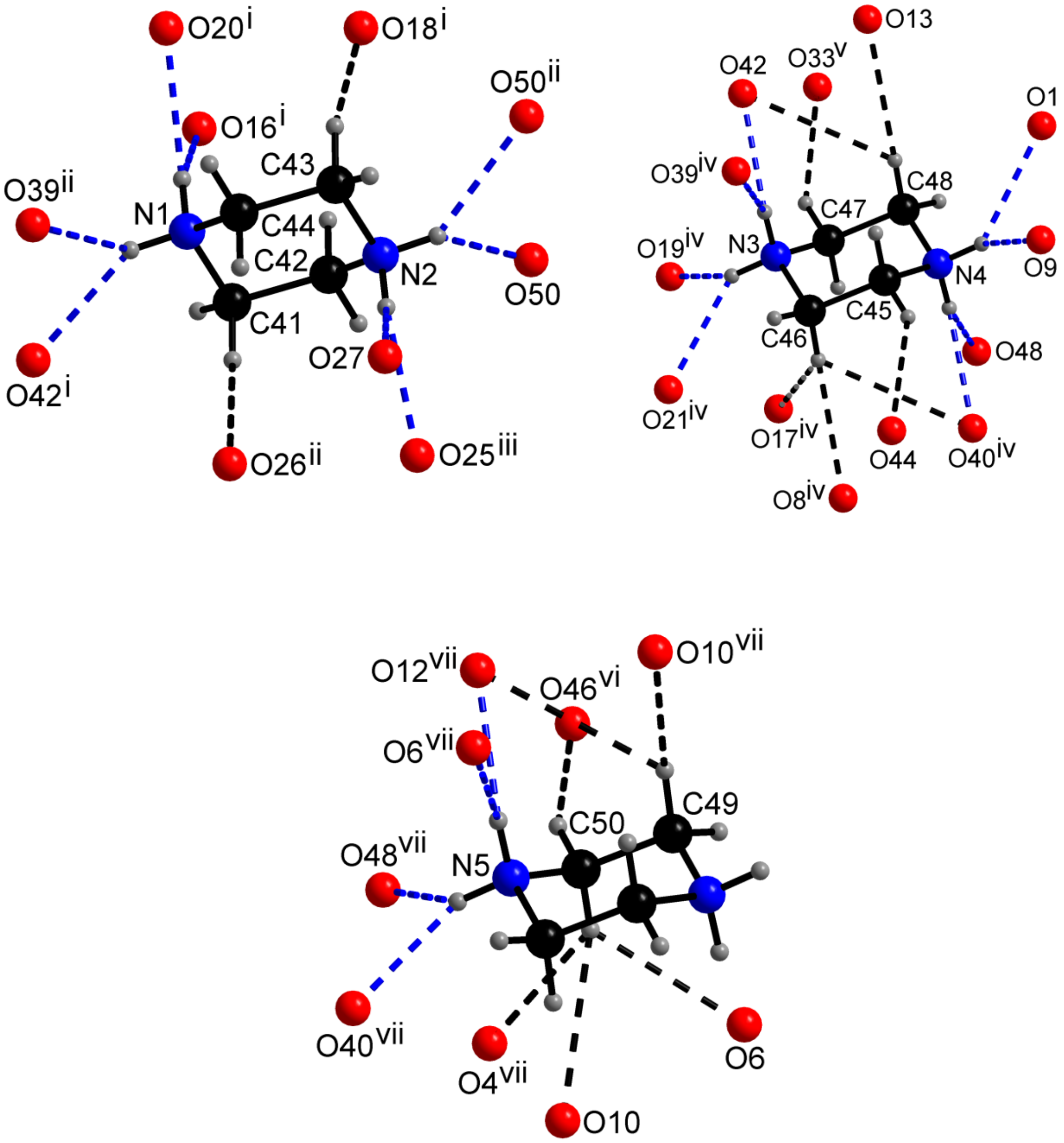


Fig. 3.58 – The H-bonding surroundings of the unique cations (Symmetry code: i) 2-x, 1-y, 1-z ii) 3-x, 1-y, 1-z iii) 1+x, y, z iv) -1+x, y, z v) 1-x, 1-y, 1-z vi) x, 1+y, z vii) 1-x, 1-y, 2-z) in **4** showing N-H···O, C-H···O and O-H···O interactions (shown in broken lines)

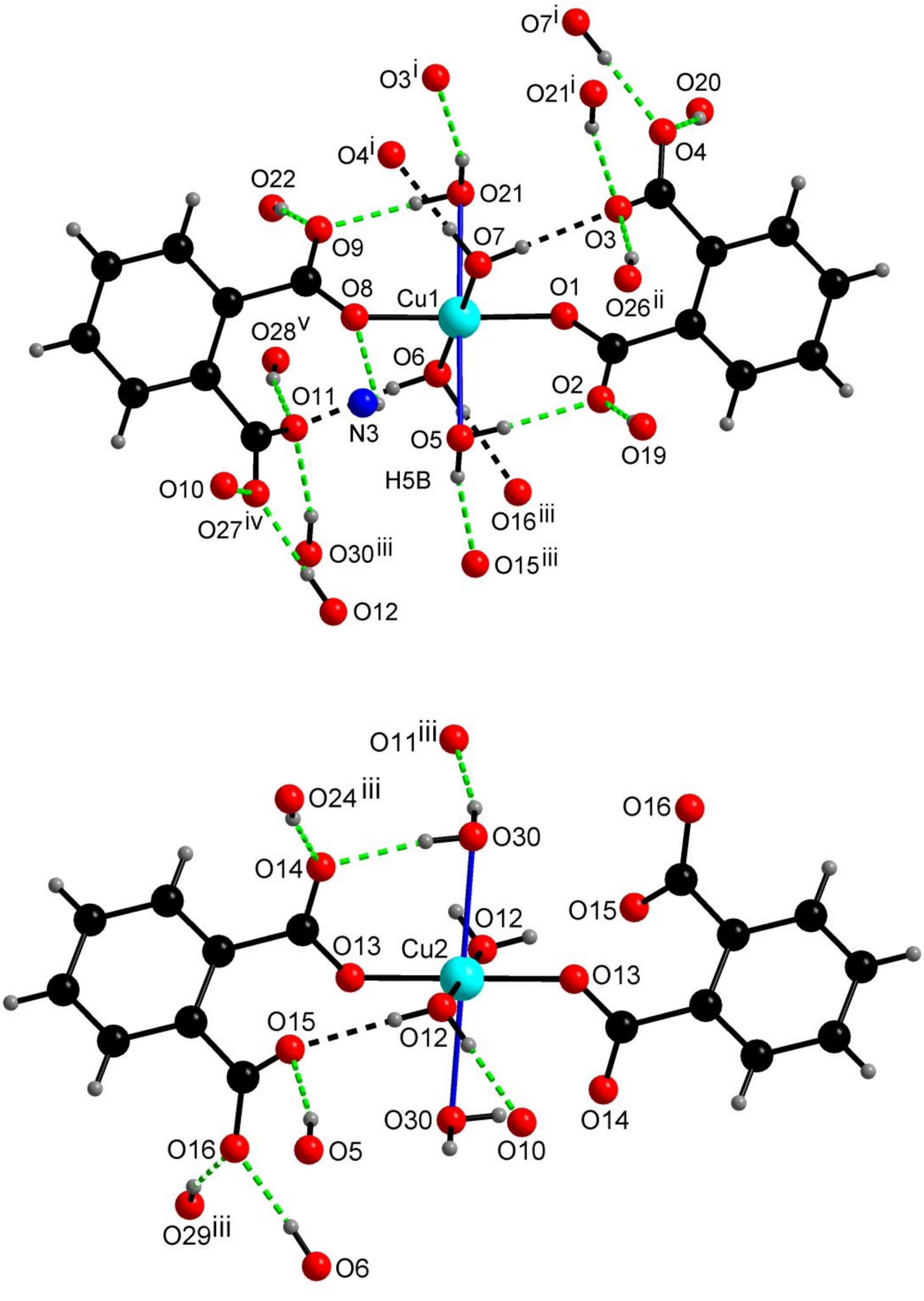


Fig. 3.59 – The H-bonding surroundings of $[Cu(H_2O)_4(pht)_2]^{2-}$ anions in **5** (Symmetry code: i) -1-x, 1-y, 1-z ii) x, 1+y, 1+z iii) -x, 1-y, -z iv) -x, -y, -z v) -1+x, y, z) and the unique cations (Symmetry code: i) 1+x, y, z ii) -x, -y, -z iii) 1+x, 1+y, z iv) 1-x, 1-y, -z v) -x, 2-y, 1-z) in **5** showing N-H···O, C-H···O and O-H···O interactions (shown in broken lines)

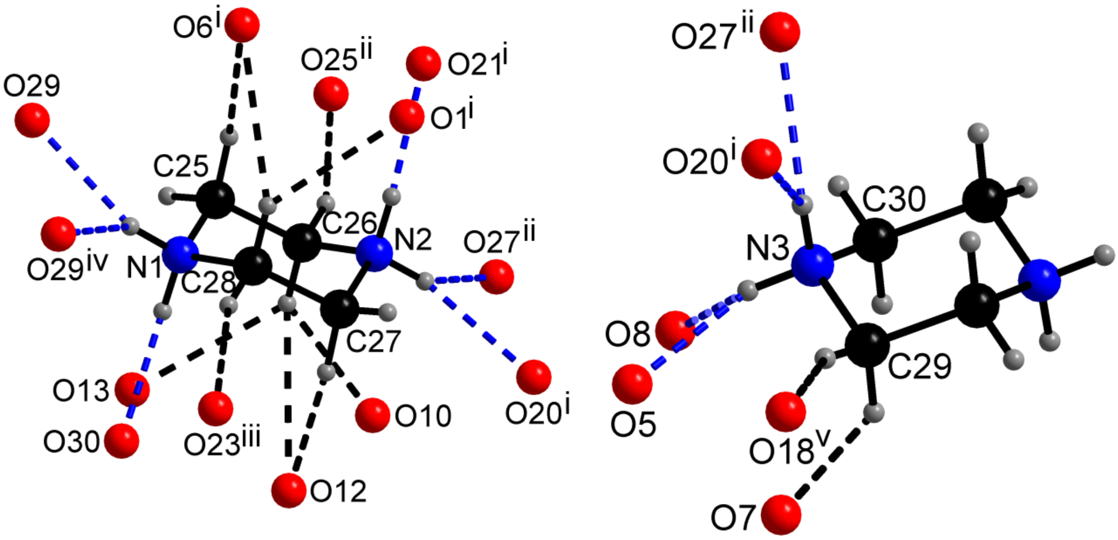


Fig. 3.60 – The H-bonding surroundings the unique cations in **5**. Symmetry code: i) 1+x, y, z ii) -x, -y, -z iii) 1+x, 1+y, z iv) 1-x, 1-y, -z v) -x, 2-y, 1-z) in **5** showing N-H···O, C-H···O and O-H···O interactions (shown in broken lines)

In **3**, a water dodecamer cluster of type ‘A’ (Fig. 3.61) is formed by O15, O16, O17, O18, O19 and O20 with six water molecules O13, O14, O16, O17, O19 and O20 bonded to every corner. The cyclic hexamer is non-planar and extends on one side via O16 and O17 and on the opposite side via O19 and O20 forming a tetramer with the next identical cyclic hexameric unit ‘A’. This results in an alternate arrangement of edge-shared hexameric and tetrameric units resulting in a H-bonded sequence ‘-A-A-A-’ of water dodecamer having T4(2)6(2) extended motif (Fig. 3.61). Due to the non-planar nature of the hexameric unit, the extended water cluster resembles a staircase pattern when viewed along *c-axis* (Fig. 3.62).

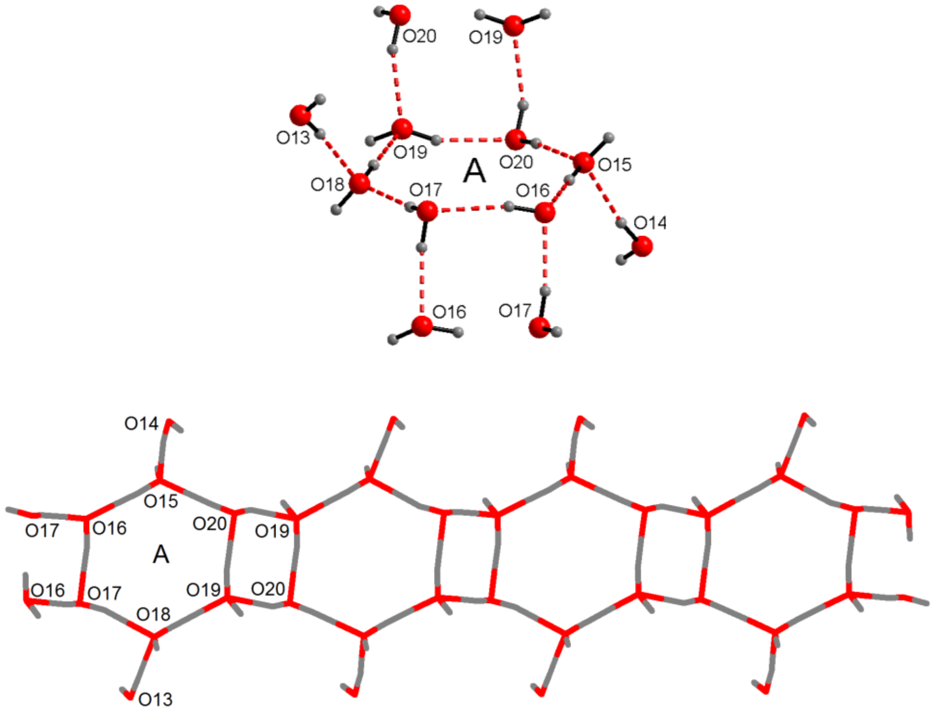


Fig. 3.61 - A water dodecamer ‘A’ formed by H-bonding interactions among lattice water molecules (top) extending on either side having an alternate arrangement of edge-shared hexameric and tetrameric unit in the sequence ‘-A-A-A-’ (bottom) in **3**.

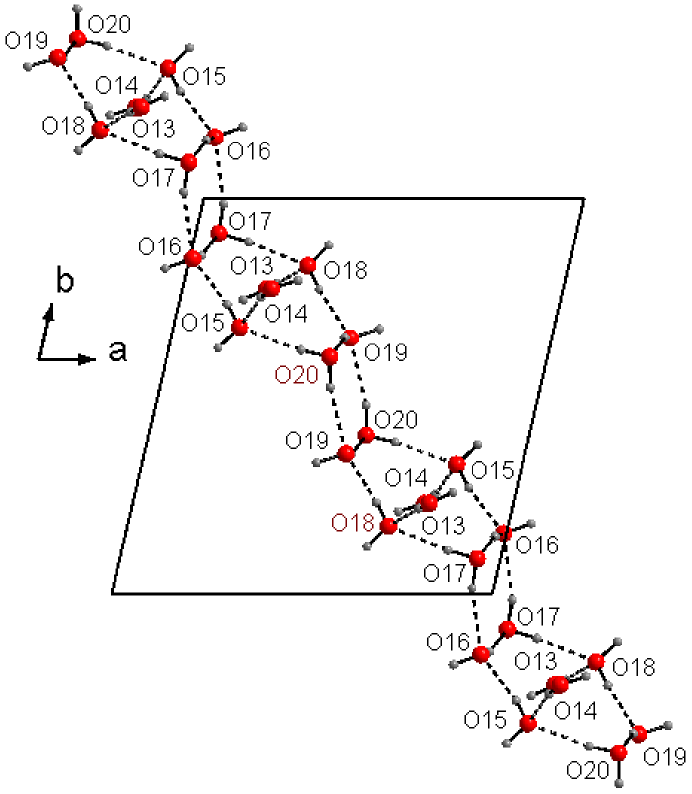


Fig. 3.62 – A portion of the infinite staircase architecture extending along *c-axis* in **3**

Due to the presence of three unique bis(phthalato) Co(II) in **4**, three types of water dodecamer clusters are formed viz. ‘A’, ‘B’ and ‘C’ with ‘A’ located on an inversion centre (Fig. 3.63). The water dodecamer cluster ‘A’ is formed using O34, O35, O36, O37, O38 and O50; cluster ‘B’ via H-bonding between 031, O32, O33, O34, O35, O37, O38, O39, O42, O43, O44, and O49 while cluster ‘C’ is formed of O33, O40, O41, O43, O44, O45, O46, O47, O48 and O49. Water cluster ‘A’ extends on either side via O34 and O35; cluster ‘B’ using O37 and O38 on one side and on the other side via O44 and O49 whereas cluster ‘C’ extends by means of O33 and O43 on one side and O45 and O46 on the other side in the order ‘-B-A-B-C-C-B-A-B-‘ (Fig. 3.63).

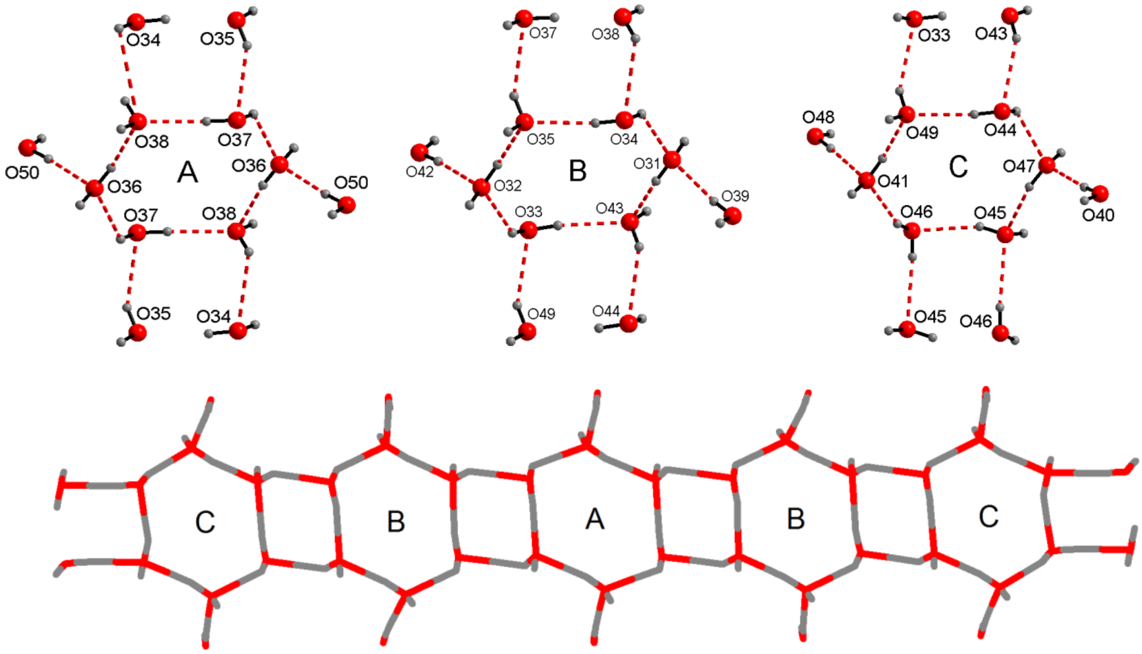


Fig. 3.63 – Three types of water dodecamers ‘A’, ‘B’ and ‘C’ in **4** with ‘A’ on inversion centre formed by intramolecular H-bonding interactions among lattice water molecules (top) extending with an alternate arrangement of edge-shared hexameric and tetrameric unit in the sequence ‘-B-A-B-C-C-B-A-B-’ (bottom)

The extension of these water dodecamer units again results in a staircase pattern as in **3** when viewed along *b-axis*. The two types of water dodecamer clusters namely 'A' and 'B' in **5** can be explained due to the presence of the two unique bis(phthalato)Cu(II) units, with 'A' located on an inversion centre (Fig. 3.64). The water dodecamer cluster 'A' is made up of O22, O23, O24, O25, O28 and O29 while cluster 'B' is formed using O17, O18, O19, O20, O22, O23, O24, O25, O26 and O27. Water cluster 'A' extends on either side using O24 and O25 whereas cluster 'B' extends by means of O18 and O19 on one side and O22 and O23 on the other side in the sequence '-A-B-B-A-B-B-A-' resembling a staircase structure motif as in **3** and **4** when viewed along *b-axis*.

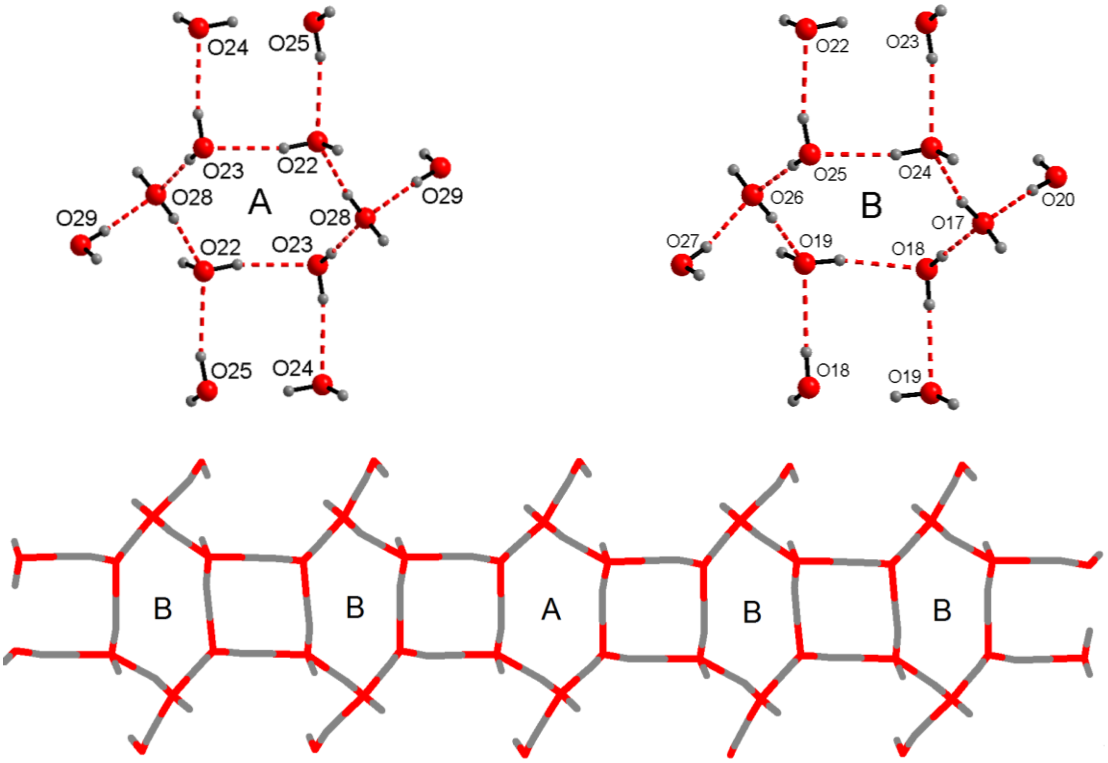


Fig. 3.64 – Two types of water dodecamers 'A' and 'B' with 'A' on inversion centre formed by intramolecular H-bonding interactions among lattice water molecules (top) extending with an alternate arrangement of edge-shared hexameric and tetrameric unit in the sequence '-B-A-B-C-C-B-A-B-' (bottom) in **5.**

Further, the unique cations serve as crosslinks between two successive extended water motifs via N-H···O interactions forming a two dimensional (2D) sheet. In **3**, the two water molecules O13 and O14 attached to the cyclic hexamer but not involved in its extension are H-bonded to the nitrogen atoms N1 and N2 of two unique organic cations pipN1 and pipN2 interlinking the two cations via N1···O13···N2 and N1···O14···N2 linkages. The two unique cations pipN1 and pipN2 serve as crosslinks between two successive water staircases forming a 2D sheet in the crystallographic *ac* plane (Fig. 3.65).

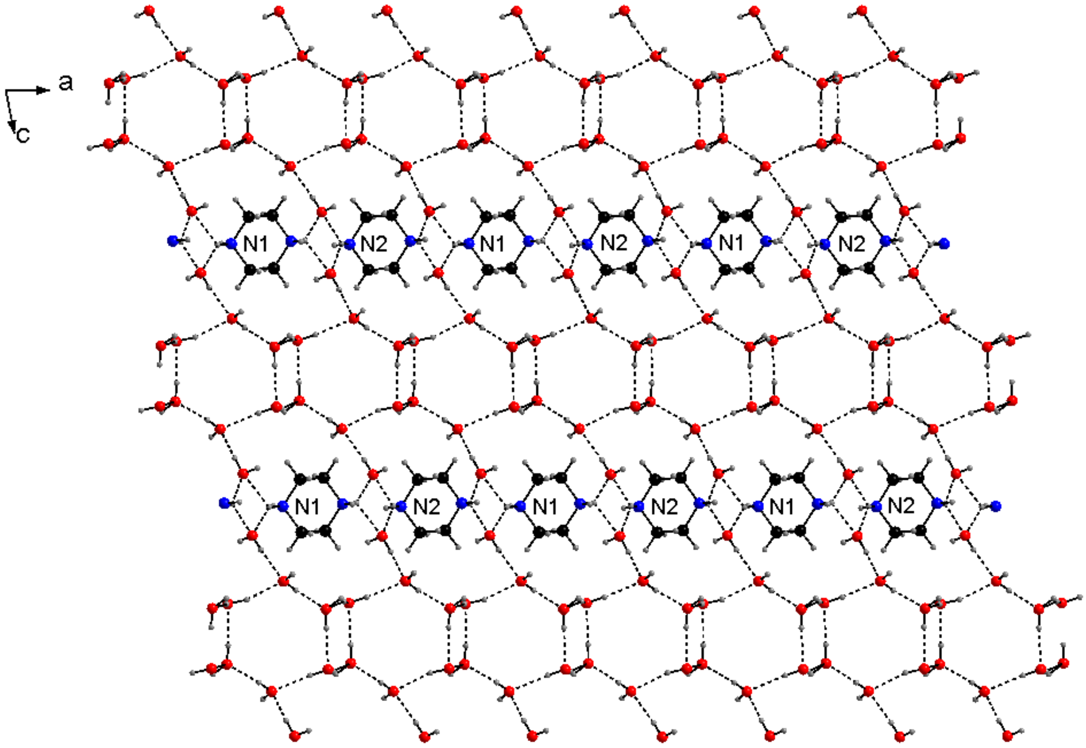


Fig. 3.65 - The unique piperazinediium pipN1 and pipN2 cross links two infinte water staircase via N-H···O H-bonding interaction forming a cation-water sheet in the crystallographic *ac* plane in **3**

In **4**, the free water molecule O50 of water dodecamer 'A' is H-bonded to nitrogen atom N2 of pipN1/N2 (N2-H···O50···H-N2); O39 and O42 water molecule of cluster 'B' is linked to N1 of pipN1/N2 and N3 of pipN3/N4 (N1-H···O39···H-N3) whereas

O40 and O48 free water molecule of ‘C’ is connected to N4 and N5 of pipN3/N4 and pipN5 (N4-H···O40···H-N5, N4-H···O48···H-N5) respectively. Such an organised H-bonding results into a sheet of these water cluster and three unique piperazinediium cations in the crystallographic *bc* plane (Fig. 3.66).

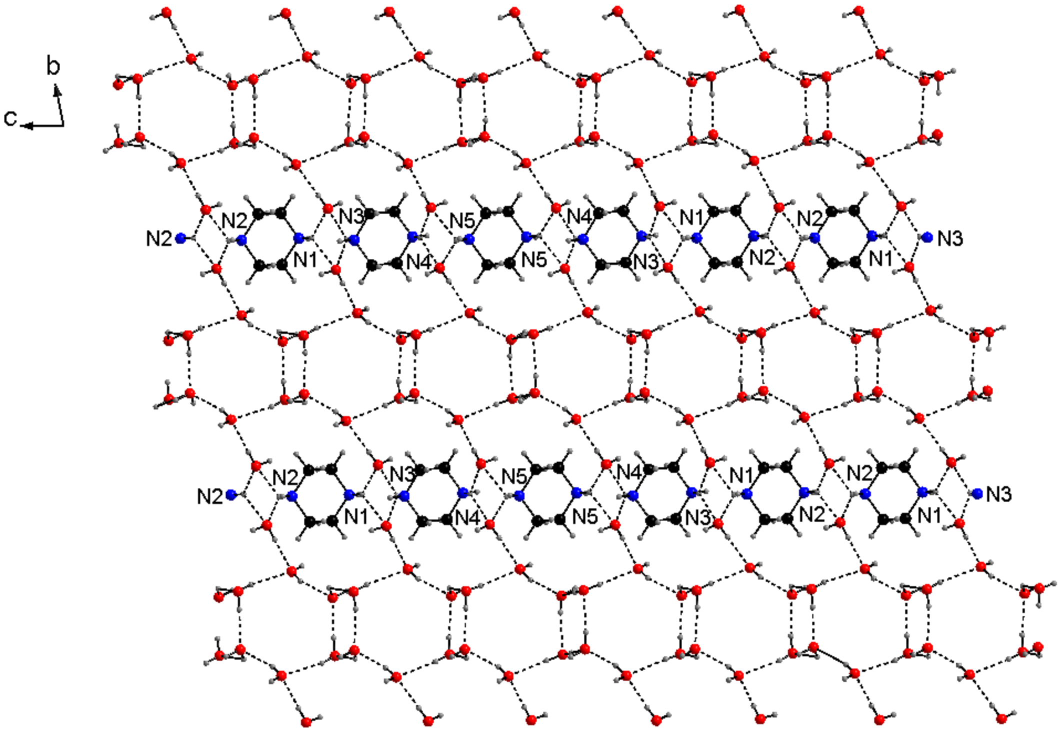


Fig. 3.66 – The unique piperazinediium pipN1/N2, pipN3/N4 and pipN5 cross link two infinte water staircase via N-H···O interaction forming a cation-water sheet in the crystallographic *bc* plane in **4**

In **5**, the free water molecule O29 of water dodecamer ‘A’ not involved in extension of water cluster is H-bonded to nitrogen atom N1of pipN1/N2 (N1-H···O29···H-N1) whereas O20 and O27 free water molecule of ‘B’ is linked to N2 and N3 of pipN1/N2 and pipN3 (N2···O20···N3, N2···O29···N3) respectively. The extended water dodecamer staircase structure crosslinked by means of organic cations forms a sheet structure in the crystallographic *bc* plane (Fig. 3.67).

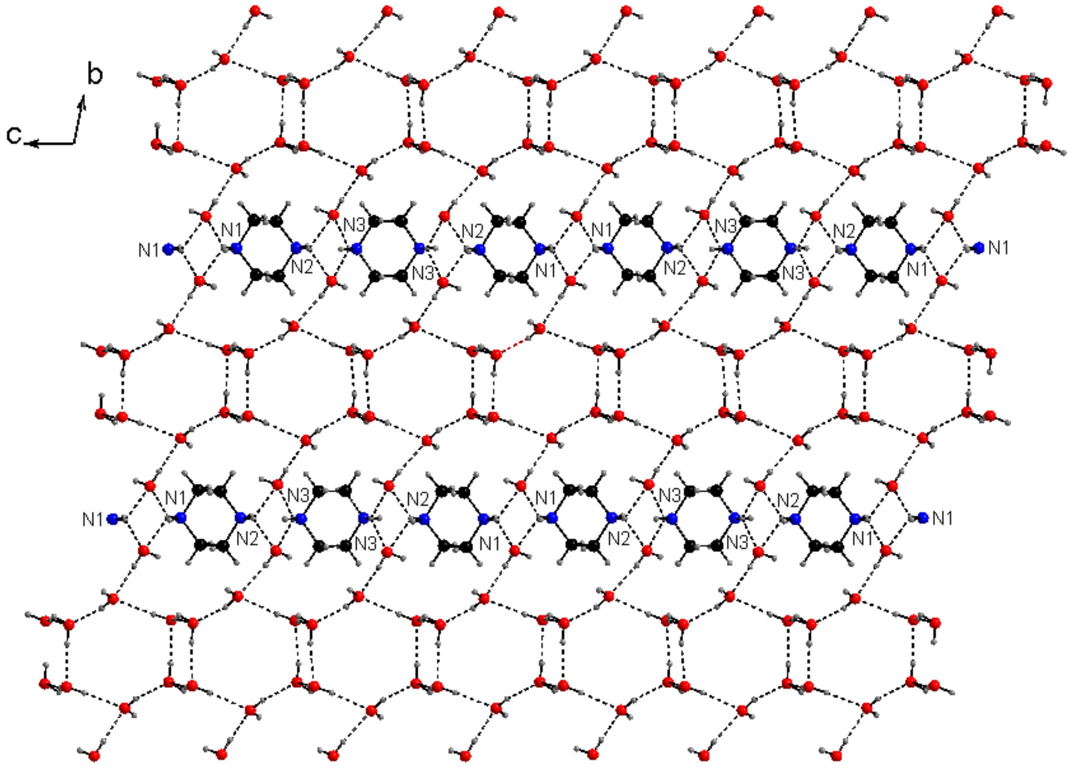


Fig. 3.67 – The unique piperazinediium pipN1/N2 and pipN3 cross link two infinte water staircase via N-H···O interaction forming a cation-water sheet in the crystallographic *bc* plane in **5**

The crystal structure of **3** further reveals the H-bonding amongst cation, anion and water cluster leads to a cage architecture of the metal centres with the Ni···Ni distance of 8.684 Å and 9.580 Å along *a*-axis; 7.072 Å and 7.112 Å along *b*-axis and the longest Ni···Ni distance of 12.496 Å along *c*-direction (Fig. 3.68). A top view of the cage (Fig. 3.69) shows along a-axis: the cation pipN1 donates hydrogen to the metal coordinated oxygen atom O5 of phthalate ligand and coordinated water molecule O12, similarly pipN2 functions as a H-donor to the metal coordinated oxygen atom O1 of symmetry related phthalate ligand and coordinated water molecule O11 leading to Ni1···pipN1···Ni1···pipN2···Ni1···pipN1···Ni1···pipN2···Ni1 cation-anion arrangement while along b-axis: a H-bonding between cations and lattice water molecules is observed. When the structure is viewed from the front (Fig. 3.70), a pair of water clusters extending the structure via O-H···O bonding interactions between free carboxylate oxygens, coordinated water molecules and lattice water molecules. On the other hand, a side view of the cage (Fig. 3.71) displayed a cation anion extension in one direction via N-H···O interaction and O-H···O interaction in another direction.

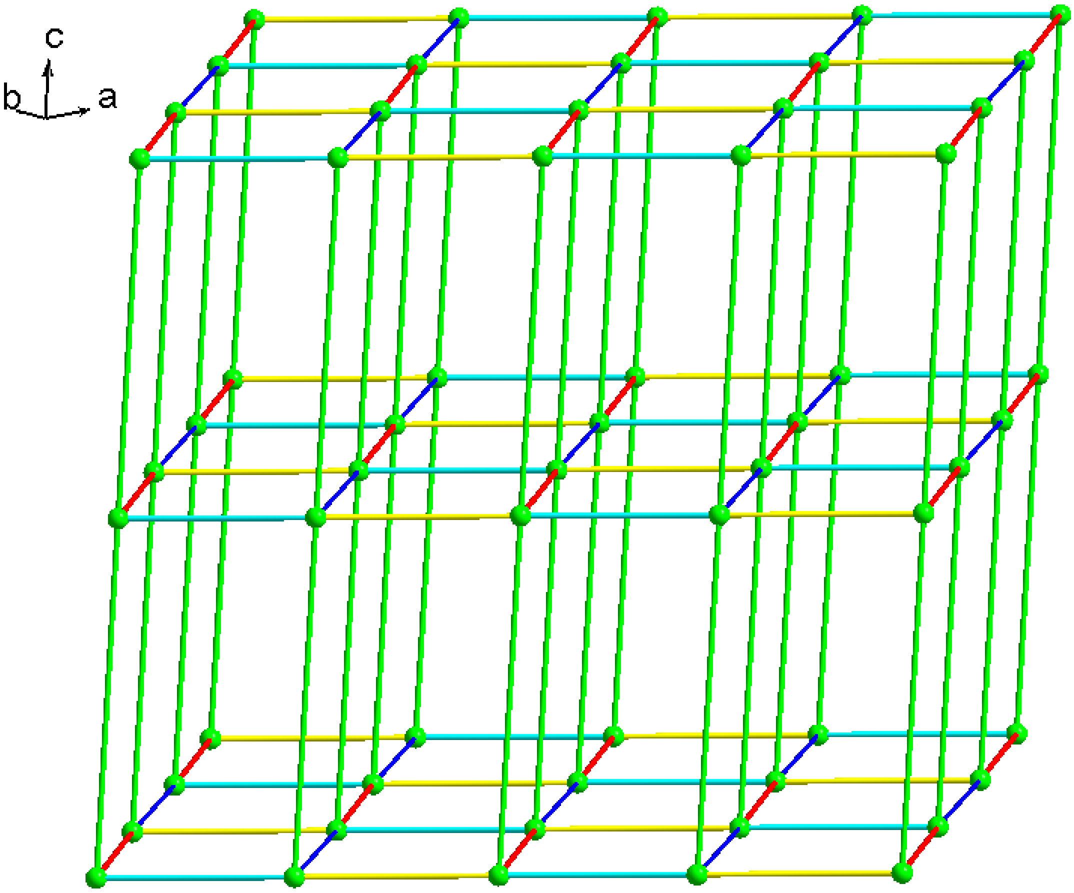


Fig. 3.68 – The organisation of Ni(II) centres in the crystal structure of **3** showing a 3D cage architecture with Ni···Ni separation of 12.496 Å (Green), 8.684 Å (Red), 9.580 Å (Blue), 7.072 Å (Cyan) and 7.112 Å (Yellow).

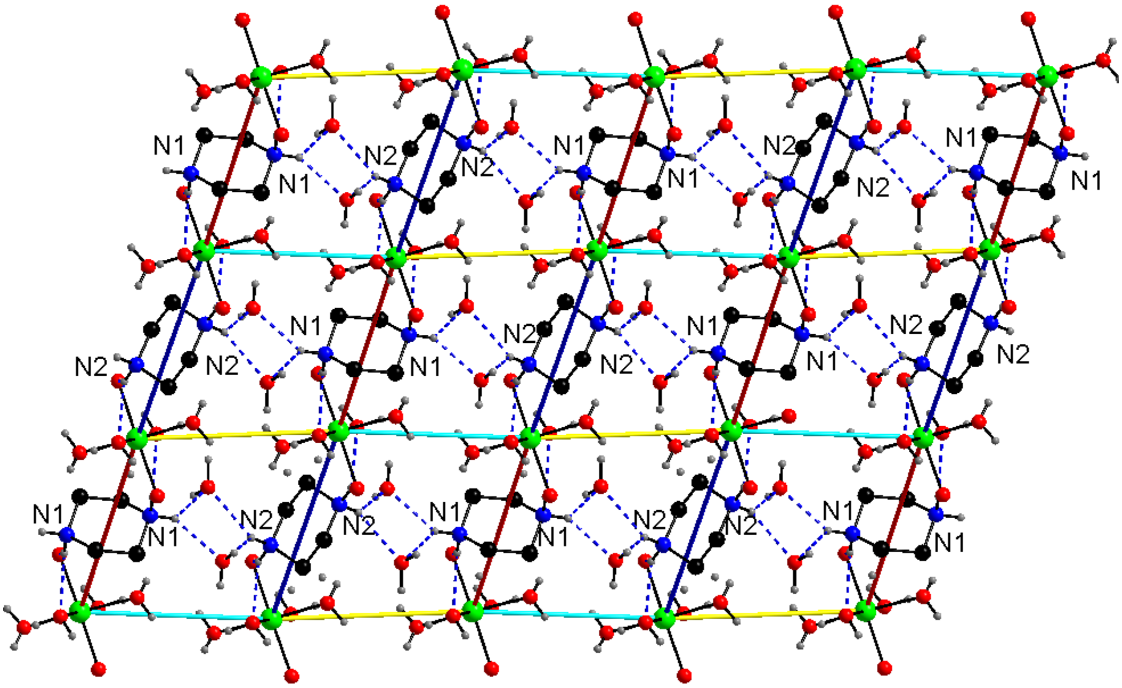


Fig 3.69 – A view from top of the cage architecture showing N-H···O H-bonding interaction between the cation and the anion forming cation···anion···cation···anion sequence in *ab* plane in **3.** (*For clarity the phthalate ligand is not shown*)

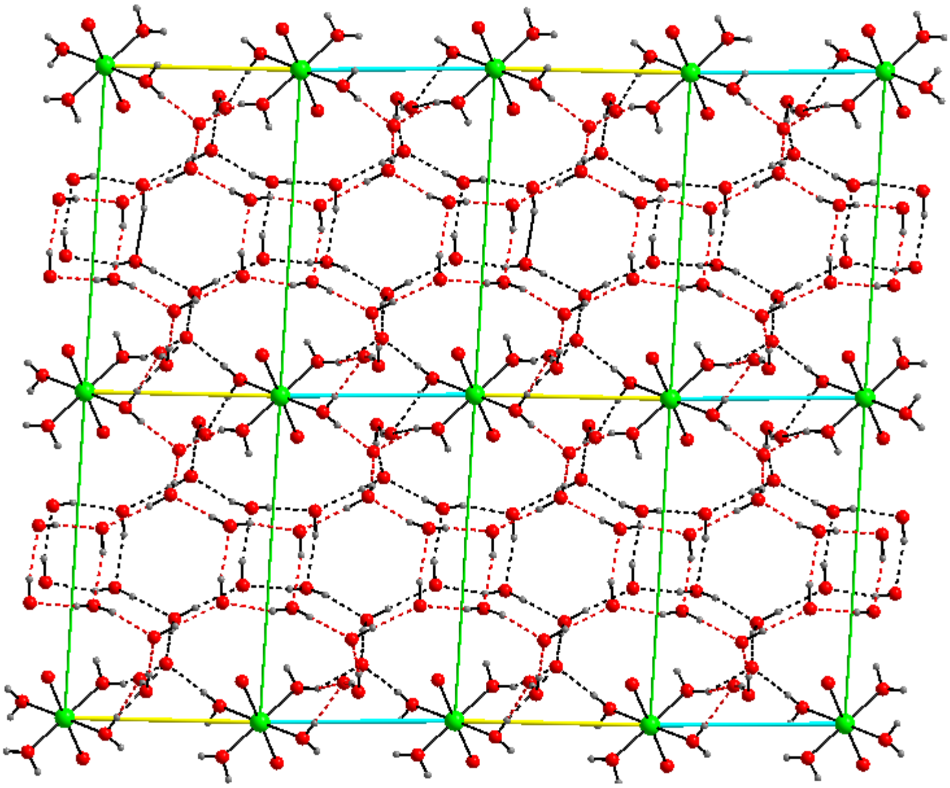


Fig. 3.70 – A view from the front of the cage architecture showing O-H···O H-bonding interaction between the anion and infinte water staircase in **3**.

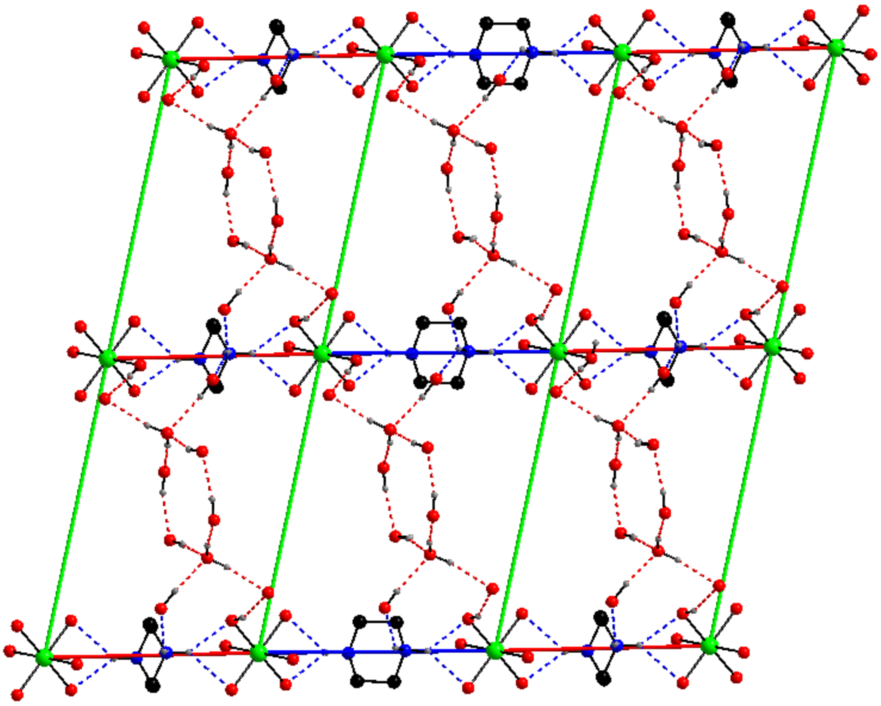


Fig. 3.71 – A view from the side displaying N-H···O and O-H···O H-bonding interaction between cation, anion and water cluster in **3**.

The crystal structure of **4** reveals the H-bonding amongst cation, anion and water cluster leads to a cage architecture of the metal centres with the Co···Co distance of 7.090 Å, 7.138 Å and 7.185 Å along *a*-axis; 8.671 Å, 9.566 Å and 8.748 Å along *c*-axis and the longest Co···Co distance of 12.496 Å along *b*-direction (Fig. 3.72). A top view of the cage (Fig. 3.73) shows along *a*-axis: the first $[Co(pht)_2(H_2O)_4]^{2-}$ anion H-bonded to nitrogen atom N4 and N5 of pipN3/N4 and pipN5 respectively whereas the second $[Co(pht)_2(H_2O)_4]^{2-}$ anion H-bonded to N1 of pipN1/N2 and N3 of pipN3/N4 while third $[Co(pht)_2(H_2O)_4]^{2-}$ anion on inversion centre H-bonded to N2 of pipN1/N2. The three anionic units labelled as 'Co1', 'Co2' and 'Co3' in conjugation with three unique cations pipN1/N2, pipN3/N4 and pipN5 are arranged in an alternate cation···anion···cation···anion···cation···anion sequence viz. Co2···pipN3/N4···Co1···pipN5···Co1···pipN3/N4···Co2···pipN1/N2···Co3···pipN1/N2···

Co2 in *ac*-plane. When the structure is viewed from the front (Fig. 3.74), a pair of water clusters extending the structure via O-H···O H-bonding interactions between free carboxylate oxygens, coordinated water molecules and lattice water molecules. On the other hand, a side view of the cage (Fig. 3.75) displayed a cation anion extension in one direction via N-H···O interaction and O-H···O interaction in another direction.

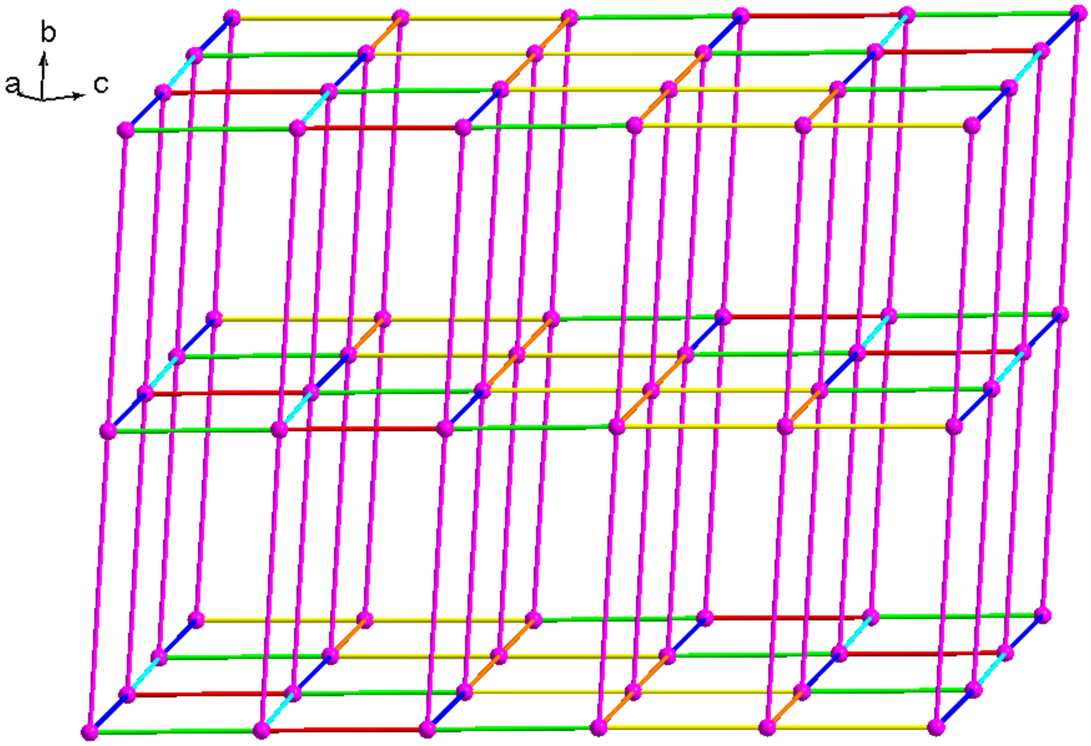


Fig. 3.72 – Disposition of Co(II) centres in the crystal structure of **4** forming 3D cage architecture with Co···Co distance of 12.496 Å (Pink), 7.090 Å (Red), 7.138 Å (Green), 7.185 Å (Yellow), 8.671 Å (Cyan), 9.566 Å (Blue) and 8.748 Å (Orange)

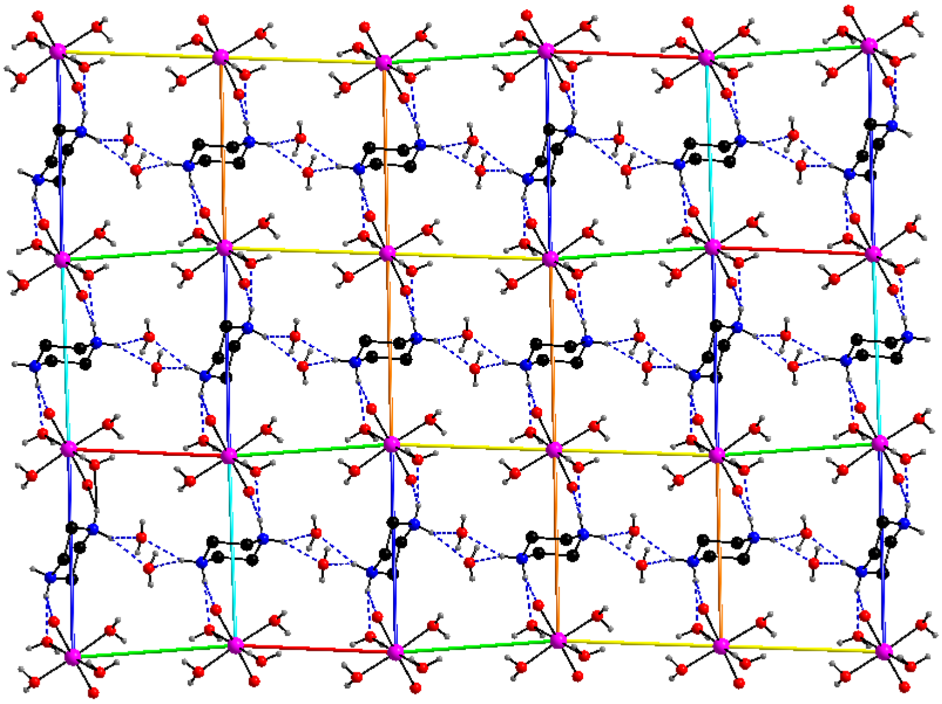


Fig. 3.73 - A view from top of the cage architecture showing N-H···O H-bonding interaction between the cation and the anion forming cation···anion···cation···anion sequence in *ab* plane in **4.** (*For clarity the phthalate ligand is not shown*)

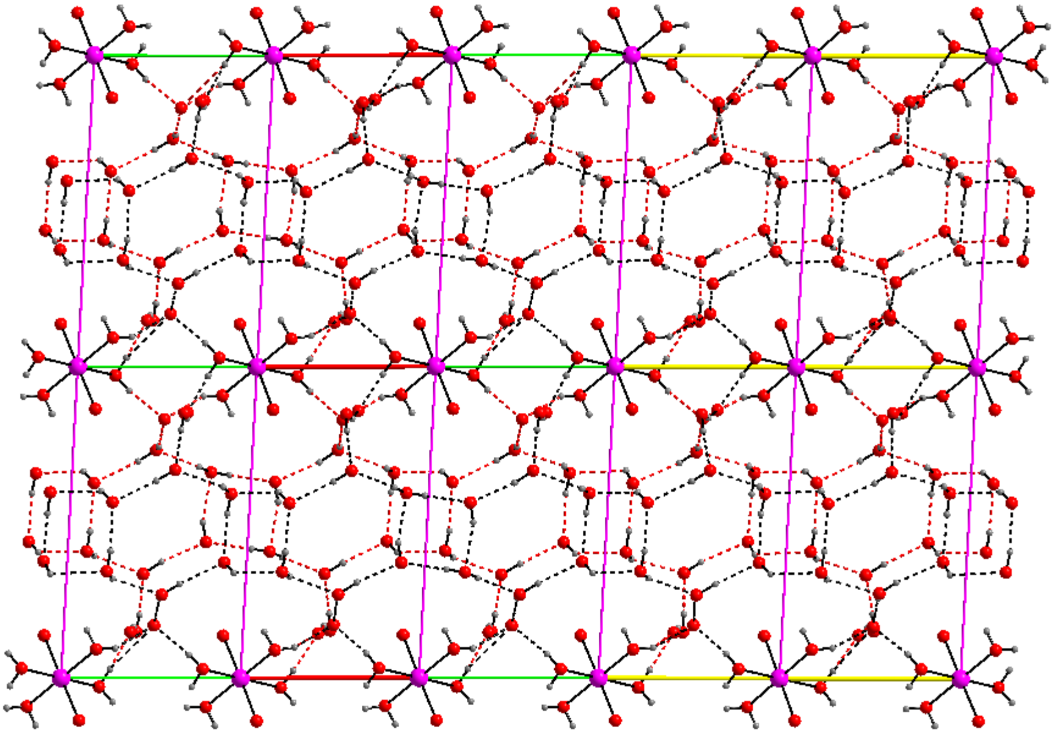


Fig. 3.74 – A view from the front of the cage architecture showing O-H···O H-bonding interaction between the anion and infinte water staircase in **4**.

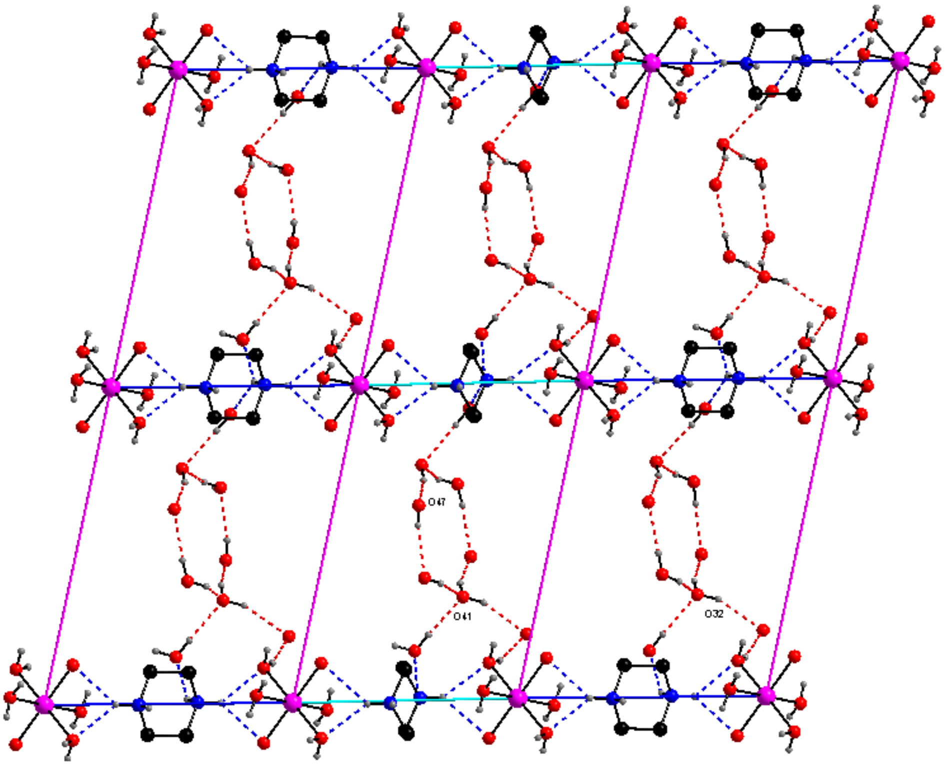


Fig. 3.75 – A view from the side displaying N-H···O and O-H···O H-bonding interaction between cation, anion and water cluster in **4**.

The crystal structure of **5** reveals the H-bonding amongst cation, anion and water cluster leads to a cage architecture of the metal centres with the Cu···Cu distance of 7.234 Å and7.214 Å along *a*-axis; 9.568 Å and 8.834 Å along *c*-axis and the longest Cu···Cu distance of 12.356 Å along *b*-direction (Fig. 3.76). A top view of the cage (Fig. 3.77) shows along *a*-axis: the first $[Cu(pht)_2(H_2O)_2]^{2-}$ anion is H-bonded to N3 of pipN3 and the second anion on inversion centre is connected to N1 of pipN1/N2. Due to H-bonding between two unique anions labelled ‘Cu1’ and ‘Cu2’ and cations namely pipN1/N2 and pipN3, an alternate anion···cation···anion···cation arrangement is observed with the sequence Cu2···pipN1/N2···Cu1···pipN3···Cu1···pipN1/N2···Cu2 in *ac* plane. When the structure is viewed from the front (Fig. 3.78), a pair of water clusters extending the structure via O-H···O H-bonding interactions between free carboxylate oxygens, coordinated water molecules and lattice water molecules. On the other hand, a side view of the cage (Fig. 3.79) displayed a cation anion extension in one direction via N-H···O interaction and O-H···O interaction in another direction.

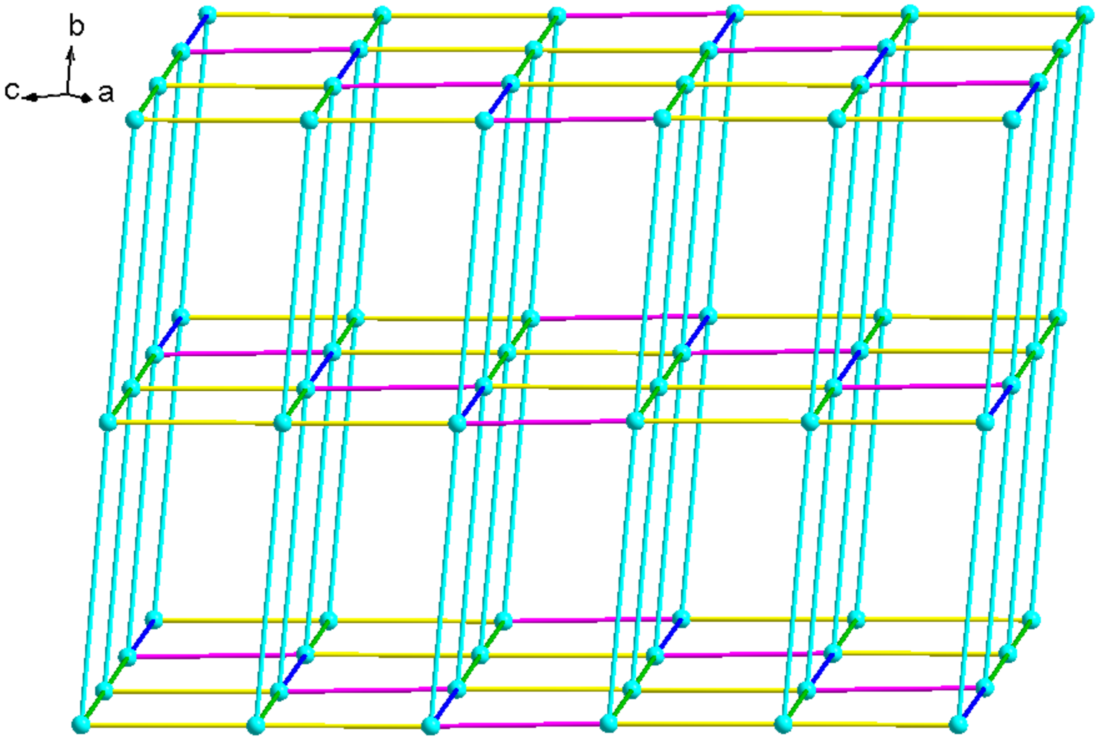


Fig. 3.76 – Disposition of Cu(II) centres in the crystal structure of **5** forming 3-D cage architecture with Cu···Cu distance of 12.356 Å (Cyan), 7.234 Å (Pink), 7.214 Å (Yellow), 9.568 Å (Blue) and 8.834 Å (Green)

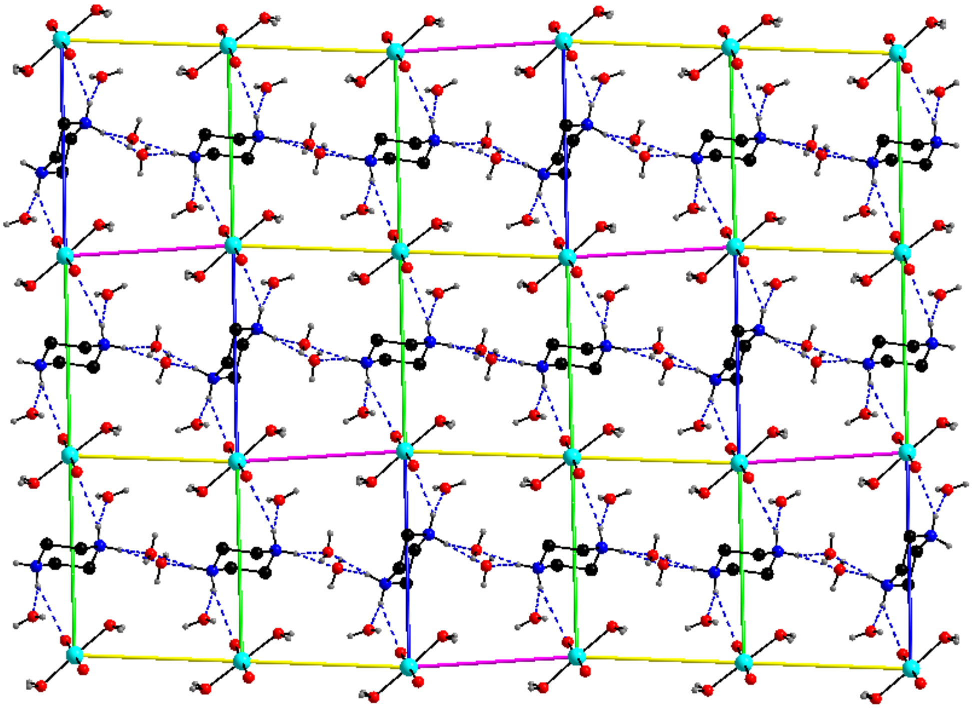


Fig. 3.77 – A view from top of the cage architecture showing N-H···O H-bonding interaction between the cation and the anion forming cation···anion···cation···anion sequence in *ab* plane in **5.** (*For clarity the phthalate ligand is not shown*)

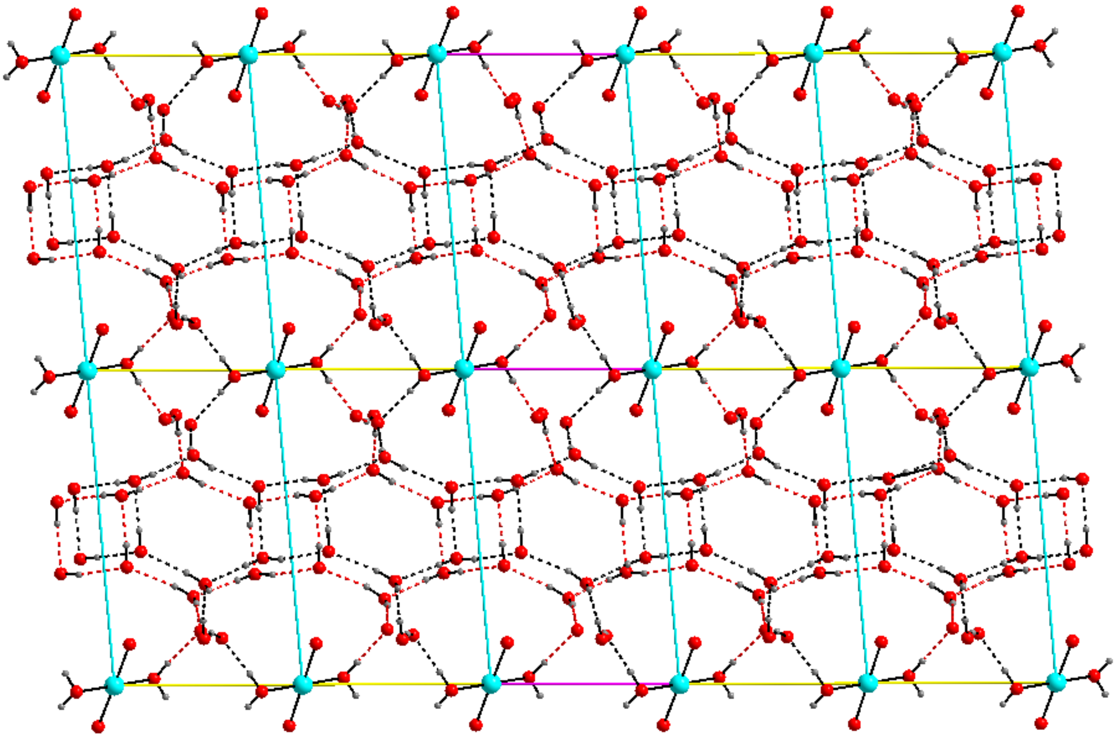


Fig. 3.78 – A view from the front of the cage architecture showing O-H···O H-bonding interaction between the anion and infinte water staircase in **5**.

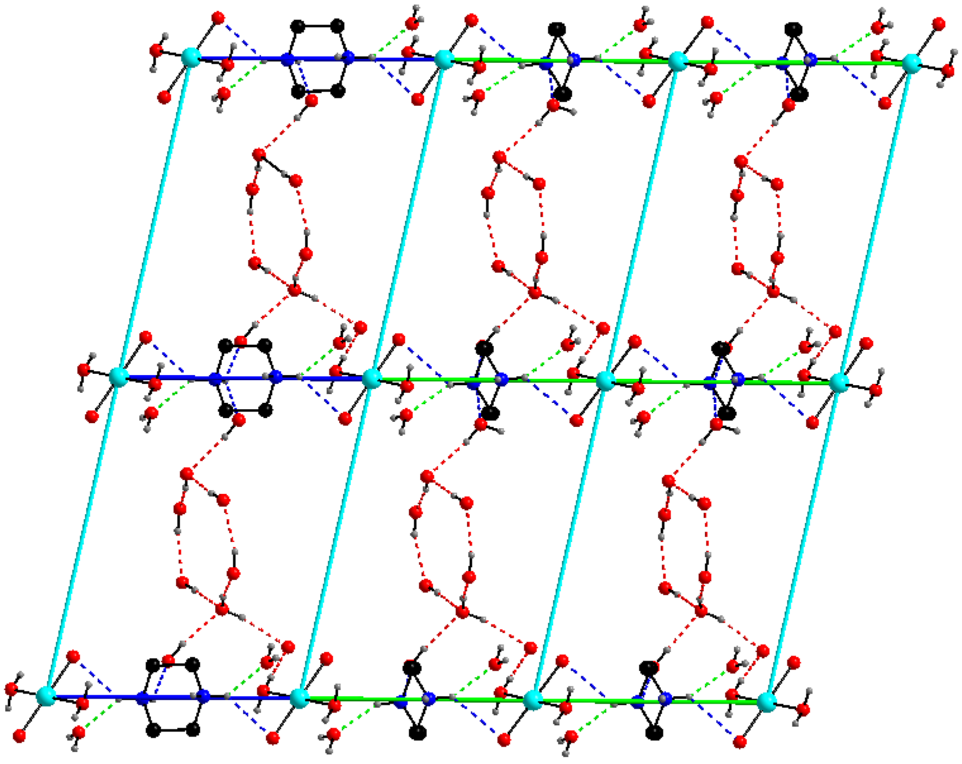


Fig. 3.79 – A view from the side displaying N-H···O and O-H···O H-bonding interaction between cation, anion and water cluster in **5**.

On the whole, H-bonding amongst cation, anion and water cluster in **3-5** disposes the metal centres in all three directions forming cage architecture that can be explained as follows: (i) a view from top of the cage shows the N-H···O H-bonding interaction between organic cations and the anionic units extending the structure with alternate cation···anion···cation···anion sequence in one direction and perpendicaular to it extending via N-H···O H-bonding interaction between organic cations and the lattice water molecule; (ii) a front view shows a pair of water cluster extending the structure in second direction via O-H···O H-bonding interactions between free carboxylate oxygens, coordinated water molecules and lattice water molecules and (iii) a view from the side displays a cation anion extension in one direction and perpendicular to it the extended architecture using water cluster via H-bonding.

*3.1.7 π···π stacking interactions study in **3-5***

In addition to the H-bonding interactions described above, the water rich compounds **3-5** exhibit π···π stacking interactions [25]. In compounds **3-5** the ring centroid to ring centroid distances (Cg···Cg) between adjacent phthalates are found to be of the order of 4 Å. The shortest Cg···Cg distances in **3**, **4** and **5** are 4.0964, 4.0772 and 4.0876 Å respectively. As it has been reported that stacking interactions between benzene rings can exist at very long Cg···Cg (Cg = ring centroid) distances up to 7 Å [26], the observed (Cg···Cg) distances can be attributed to π···π stacking of the six membered rings. A π···π stacking interaction in **3-5** is displayed in Fig. 3.80 – 3.82. For the analysis of short ring interactions in **3-5** the program Platon [279] was used and the details are listed in Table 3.10.

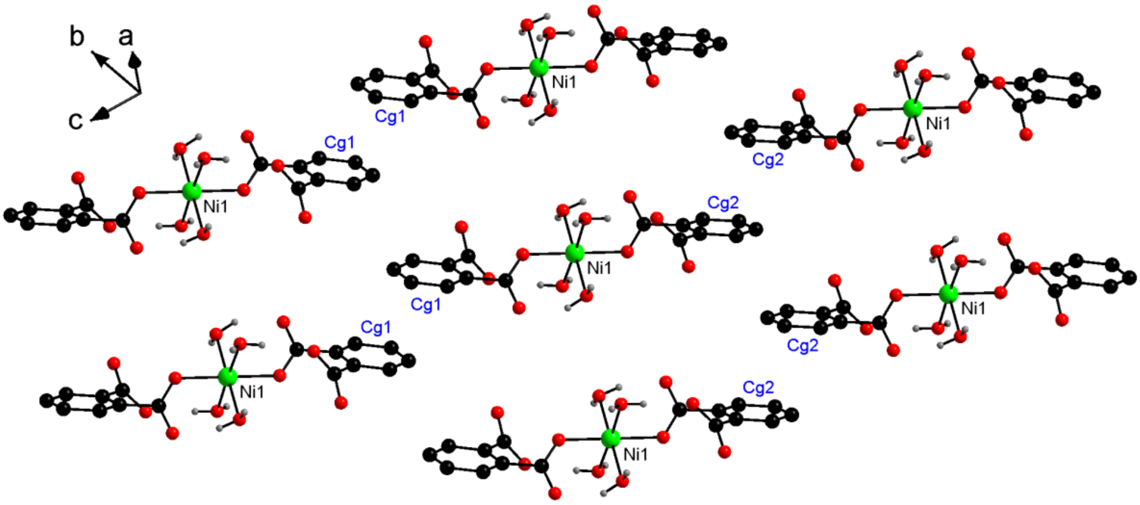


Fig. 3.80 – Centroid to centroid distances of the unique phthalate rings in **3** Cg(1)···Cg(1) = 4.0964 Å and Cg(2)···Cg(2) = 4.1616 Å

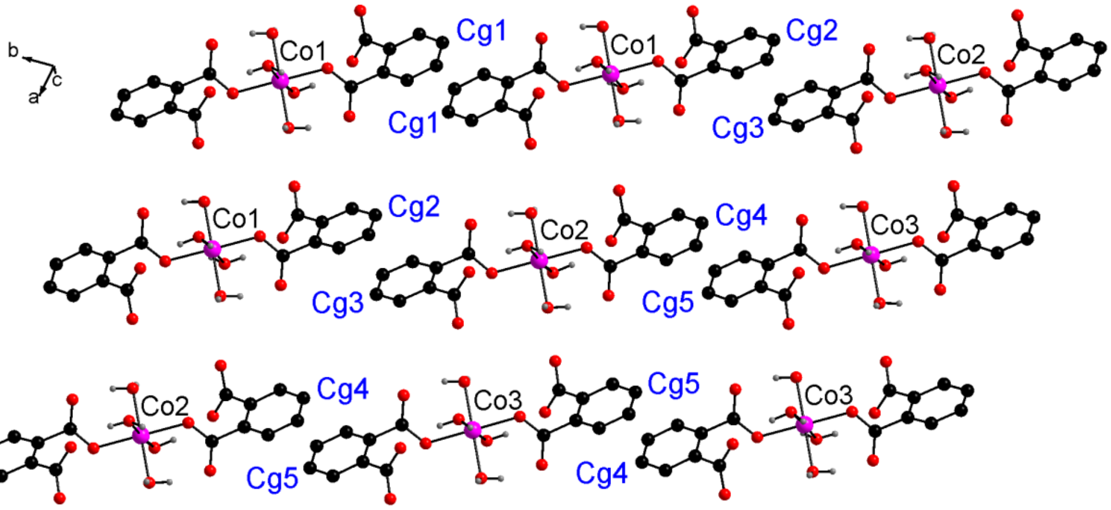


Fig. 3.81 – Centroid to centroid distances of the unique phthalate rings in **4** Cg(1)···Cg(1) = 4.0772 Å, Cg(2)···Cg(3) = 4.1148 Å and Cg(4)···Cg(5) = 4.1222 Å.

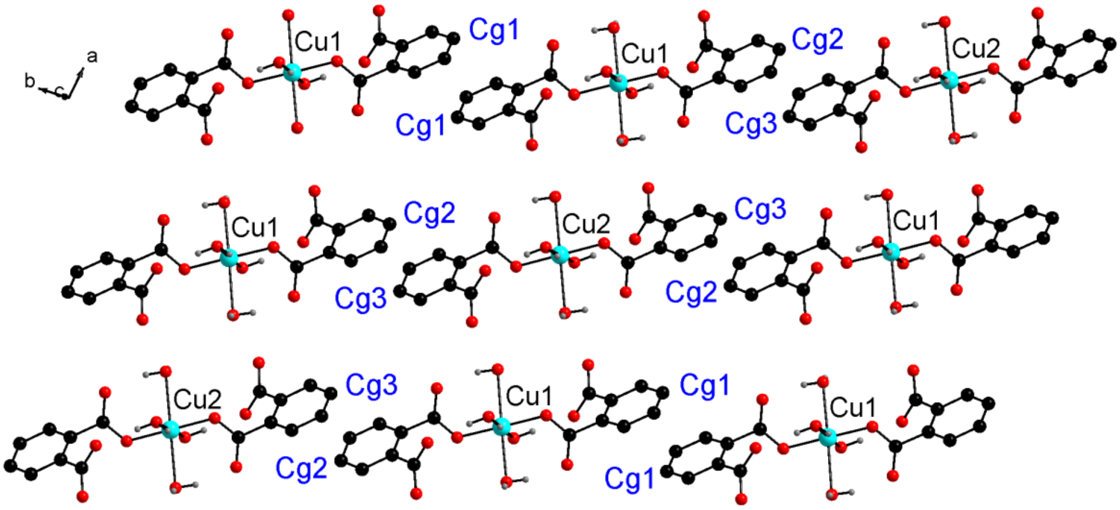


Fig. 3.82 – Centroid to centroid distances of the unique phthalate rings in **5** Cg(1)···Cg(1) = 4.0876 Å and Cg(2)···Cg(3) = 4.1116 Å.

Table 3.10 - Analysis of Short Ring-Interactions with Cg-Cg Distances < 6.0 Å and β < 60.0^0

Cg(I)	Res(I)	Cg(J)	[ARU(J)]	Cg-Cg	α	B	γ	CgI_Perp	Cg J_Perp	Slippage
(pipH$_2$)[Ni(H$_2$O)$_4$(pht)$_2$]·8H$_2$O **3**										
Cg(1)	[1] ->	Cg(1)	[2655.01]	4.0964(11)	0	26	26	3.6824(8)	3.6824(8)	1.795
Cg(2)	[1] ->	Cg(2)	[2567.01]	4.1616(12)	0	24	24	-3.8030(8)	-3.8030(8)	1.69
Where, Cg(1)= first phthalate (C1-C6) and Cg(2)= second unique phthalate (C9-C14)										
(pipH$_2$)[Co(H$_2$O)$_4$(pht)$_2$]·8H$_2$O **4**										
Cg(1)	[1] ->	Cg(1)	[2775.01]	4.0772(13)	0	25.5	25.5	-3.6804(9)	-3.6804(9)	1.754
Cg(2)	[1] ->	Cg(3)	[1545.02]	4.1148(13)	0.55(11)	23.5	23.8	-3.7638(9)	3.7723(9)	
Cg(4)	[2] ->	Cg(5)	[1545.03]	4.1222(13)	1.78(11)	26.6	26.8	-3.6808(9)	3.6867(9)	
Where, Cg(1)= first phthalate (C2-C7), Cg(2)= second unique phthalate (C10-C15), Cg(3)= third unique phthalate (C18-C23), Cg(4)= fourth unique phthalate (C26-C31) and Cg(5)= fifth unique phthalate (C34-C39)										
(pipH$_2$)[Cu(H$_2$O)$_4$(pht)$_2$]·8H$_2$O **5**										
Cg(1)	[1] ->	Cg(1)	[2676.01]	4.0876(14)	0	22.7	22.7	3.7706(10)	3.7707(10)	1.578
Cg(2)	[1] ->	Cg(3)	[1545.02]	4.1116(14)	1.79(11)	27	26.4	3.6815(10)	-3.6642(9)	
Where, Cg(1)= first phthalate (C2-C7), Cg(2)= second unique phthalate (C10-C15) and Cg(3)= third unique phthalate (C18-C23)										

- Cg(I) = Plane number I (= ring number in () above)
- Alpha = Dihedral Angle between Planes I and J (Deg)
- Beta = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg)
- Gamma = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg)
- Cg-Cg = Distance between ring Centroids (Ang.)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Ang.)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)
- Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Ang.)

Investigation of synthesied metal phthalate compounds with imidazole

*3.1.8 Synthetic aspects, spectral characteristics and thermal studies for **6, 7, 7a** and **8***

With a view to substitute the terminal aqua ligands in **3**-**5** by N-donors, a ligand exchange reaction was performed by reaction of **3**-**5** with imidazole in a 1:4 mole ratio. Contrary to our expectations these reactions did not give rise to any anionic bis(phthalates) but resulted in the formation of 1:1 phthalates devoid of any organic cation viz. blue crystals of **6** and orange crystals of **7** with a metal:im stoichiometry of 1:6, and blue crystals of **8** showing a 1:2 Cu:im composition (Fig. 3.1). In the literature, compounds **6** and **8** have been prepared without use of piperazine [45, 176]. The reaction of imidazole with **4** afforded pink crystals of **7a** in addition to **7** which exhibits a Co:im ratio of 1:3 (Fig. 3.1). Compounds **5a** could be easily separated manually from the reaction mixture and were formulated based on analytical data. The composition of all compounds was initially arrived at based on elemental analysis, mass loss studies and metal oxide formed on pyrolysis and unambiguously confirmed by single crystal X-ray studies for **6**-**8**.

The IR spectra of compounds **6**-**8** exhibit several signals in the mid-IR region indicating the presence of organic moieties (Fig. 3.83- 3.86). The absence of a signal in the region 1680-1710 cm^{-1} (expected for –COOH) clearly indicates the formation of the fully deprotonated phthalate dianion in all these compounds. In the IR spectrum of **4**, an intense band at 1558 (1566 in **5**; 1578 in **5a** and 1552 in **6**) can be assigned for the asymmetric stretching vibration of the carboxylate group (υ_{asym}) and the bands observed at 1379 in **6** (1413 in **7**; 1406 in **7a** and 1379 in **8**) for symmetric stretching vibration (υ_{sym}). The IR stretching vibrations expected for the $\upsilon_{N\text{-}H}$ vibration of the imidazole ligand group in 3500 – 3350 cm^{-1} region is masked in the broad –OH band in compounds **6**-**8**. Interestingly compound **6** exhibits two signals at 1597 and 1413 (1453 and 1320 in **7;** 1600 and 1412 in **7a**; 1549 and 1362 in **8**) (Fig. 3.83- 3.86) with the latter being more intense and assignable for the asymmetric (υ_{asym}) and symmetric stretching vibrations (υ_{sym}) of the carboxylate group respectively.

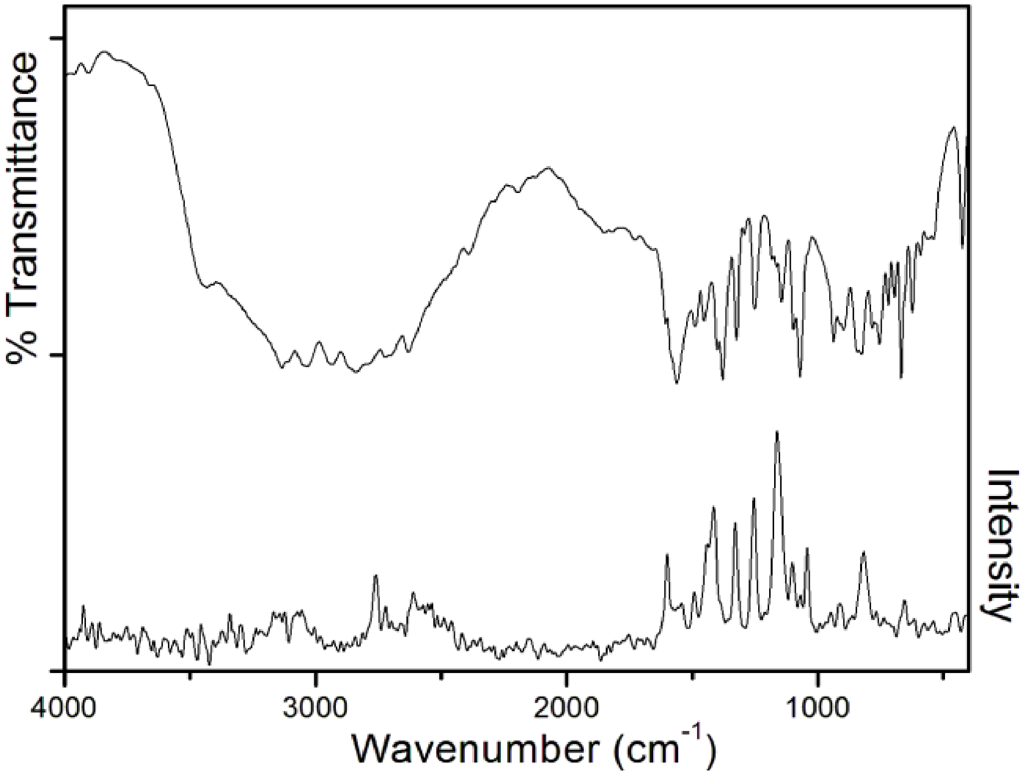


Fig. 3.83 – IR and Raman spectra of **6**

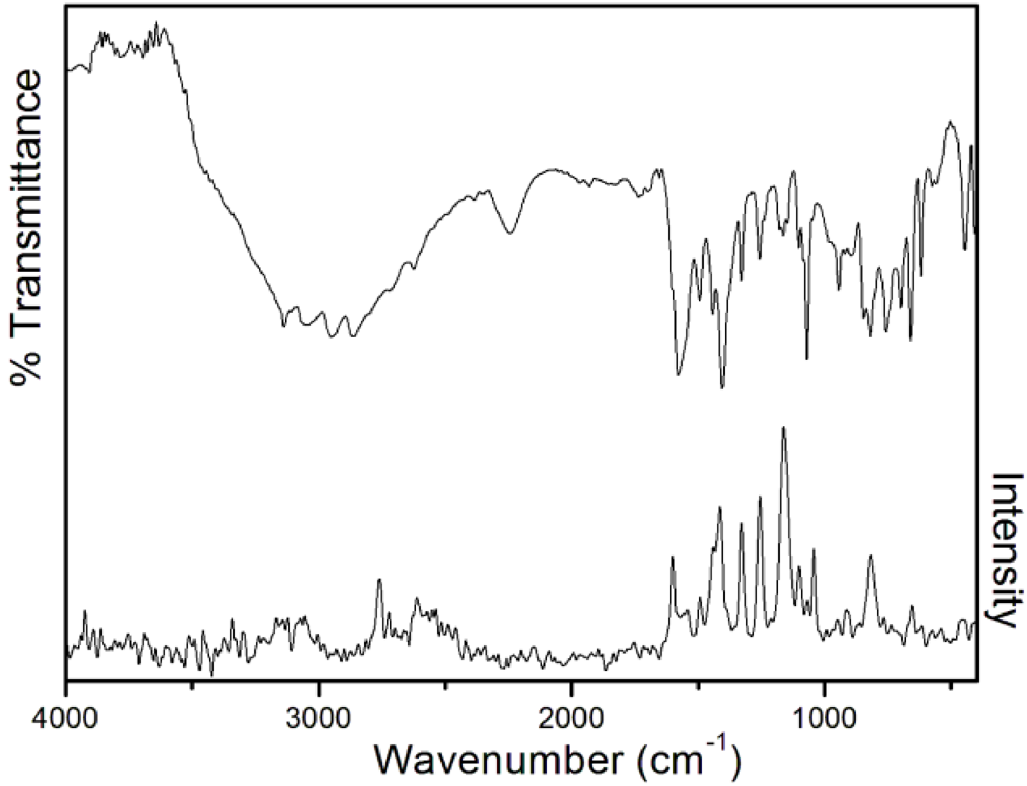


Fig. 3.84 – IR and Raman spectra of **7**

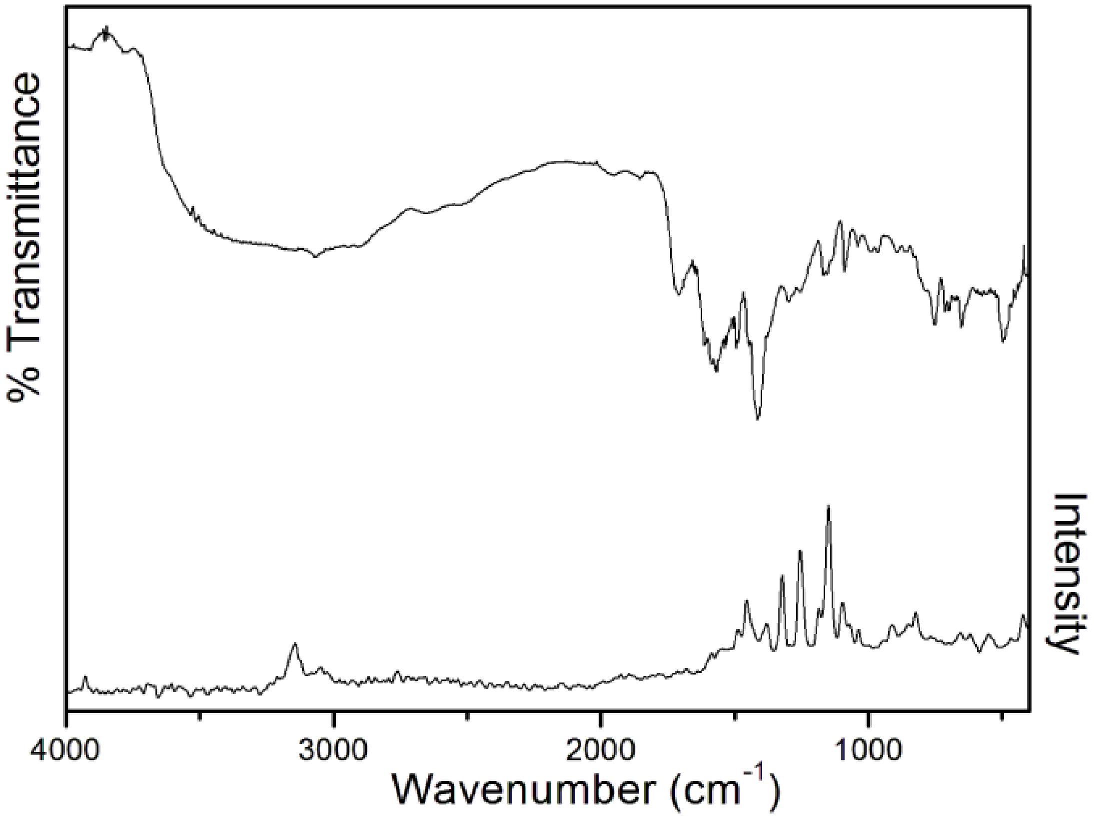


Fig. 3.85 – IR and Raman spectra of **7a**

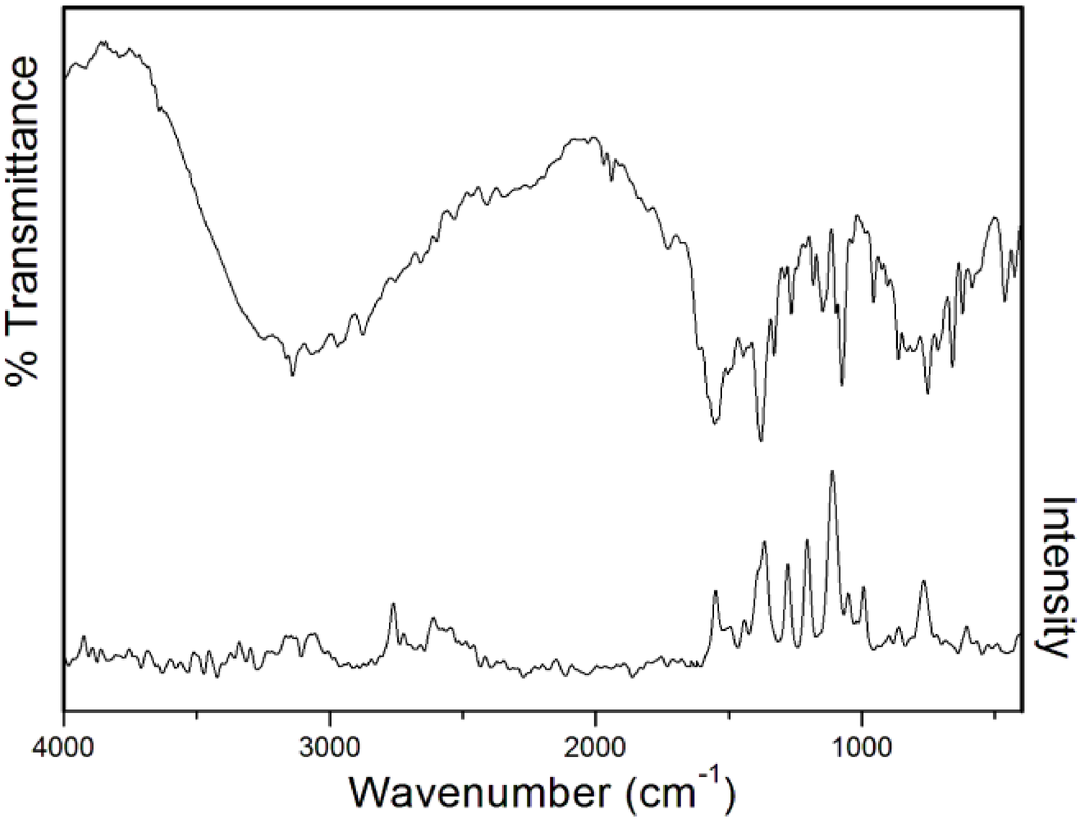


Fig. 3.86 – IR and Raman spectra of **8**

The diffuse reflectance spectra (DRS) of **6** (Fig. 3.87 - 3.90) exhibits bands at 276 (239 and 273 nm for **7**; 256 for **7a**; 258 for **8**) for intra-ligand charge transfer and 390 nm (494 nm for **7**; 496 for **7a**; 725 for **8**) assignable for a possible metal cantered transition of the respective metal ion (Fig. 3.87 – 3.90). The powder pattern of compound **7** and **7a** exhibit sharp Bragg lines indicating their crystalline nature (Fig. 3.91 - 3.92). The minor product **7a** exhibit differing powder pattern as compared to the compound **7**. The experimental powder pattern of the bulk sample is in very good agreement with the theoretical powder pattern calculated from the single crystal data of **7**. The results of powder pattern experiments, reproducible thermo analytical data and spectral data reveal that the compounds **7** and **7a** can be obtained in a state of high purity.

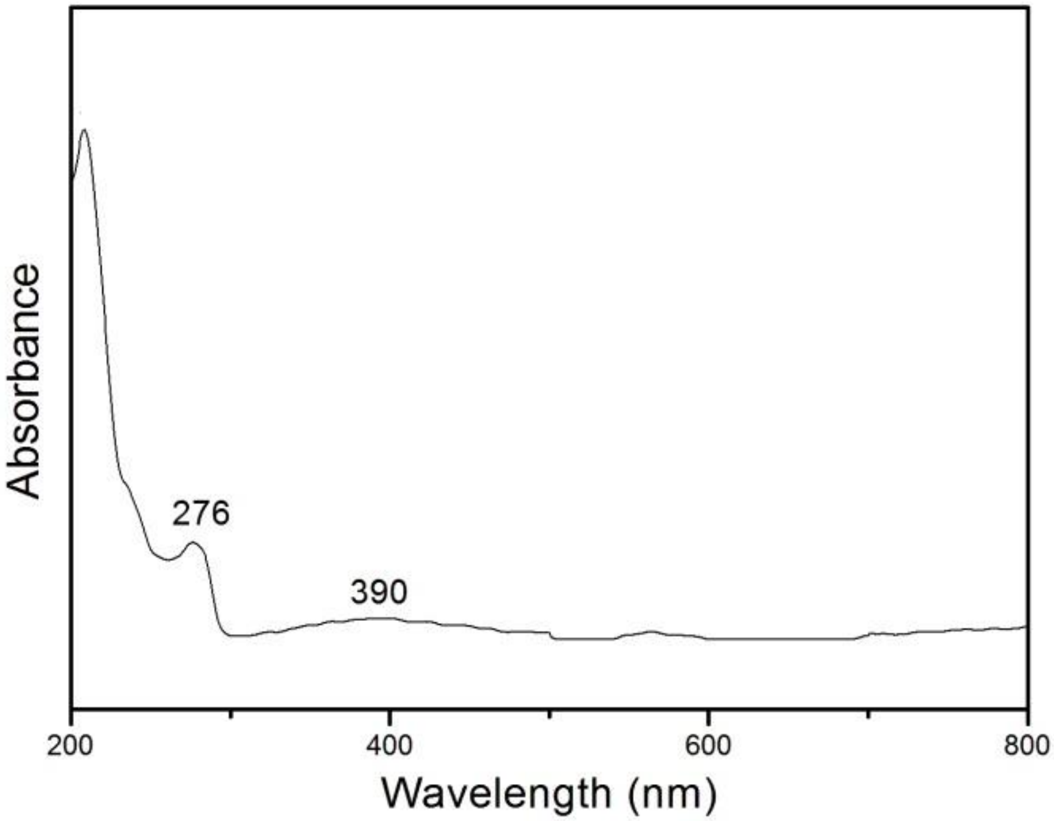


Fig. 3.87 – Diffused reflectance spectra of **6**

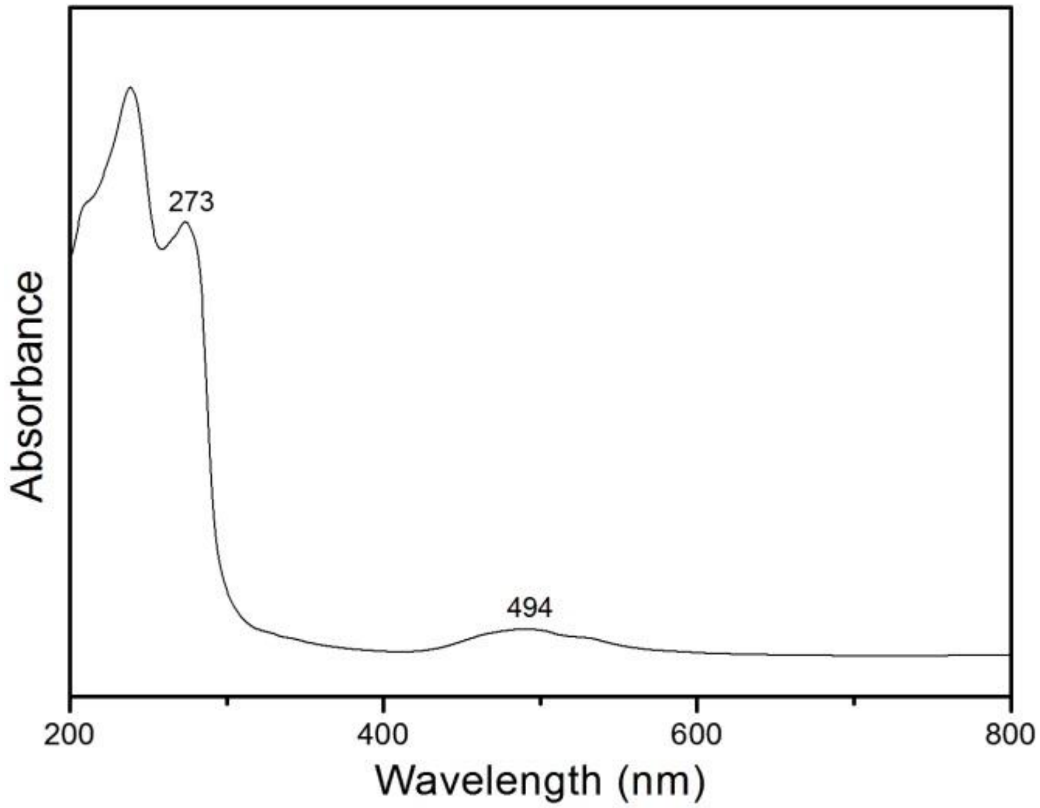


Fig. 3.88 – Diffused reflectance spectra of **7**

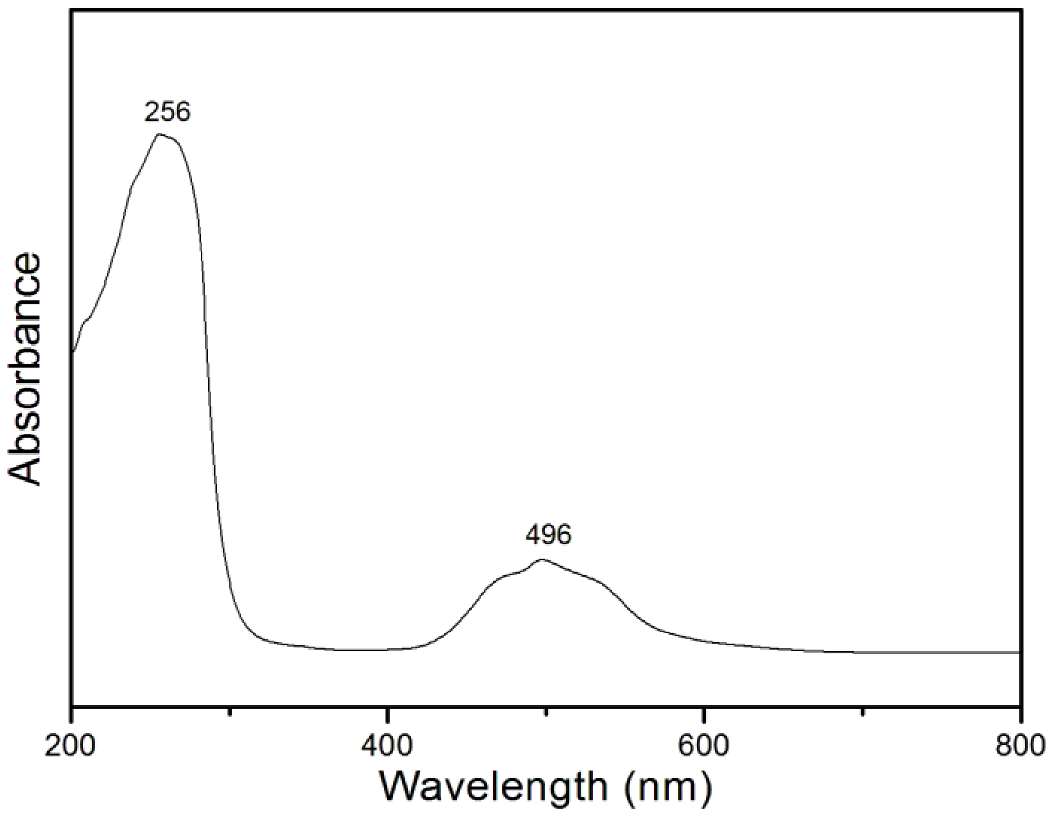


Fig. 3.89 – Diffused reflectance spectra of **7a**

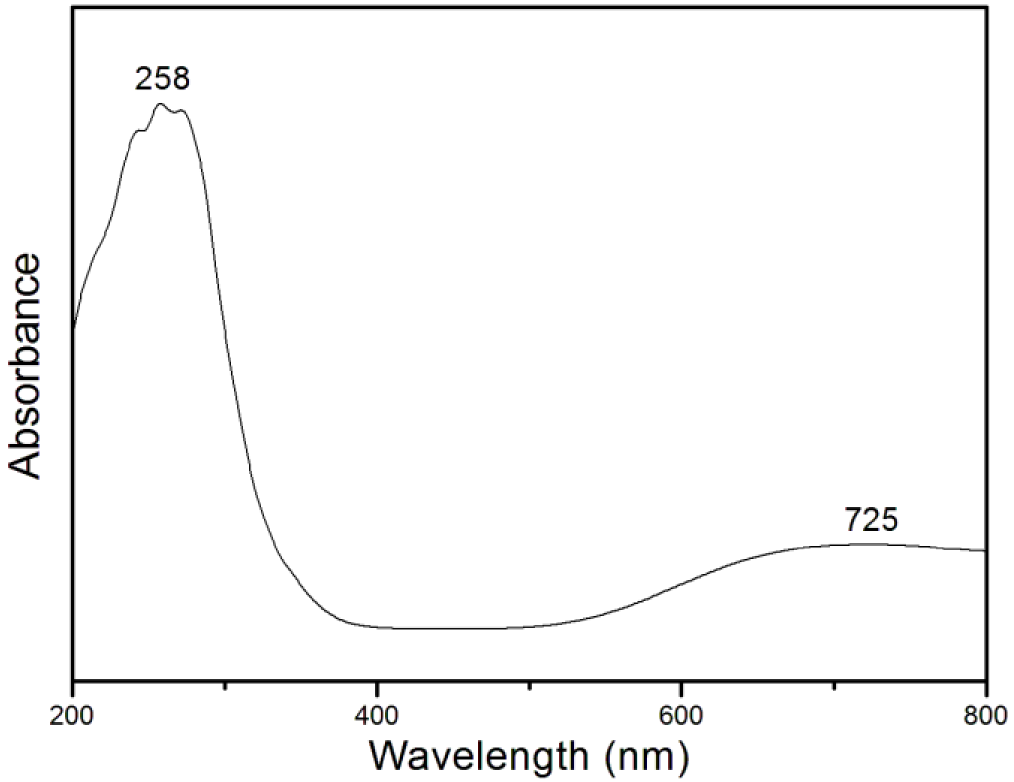


Fig. 3.90 – Diffused reflectance spectra of **8**

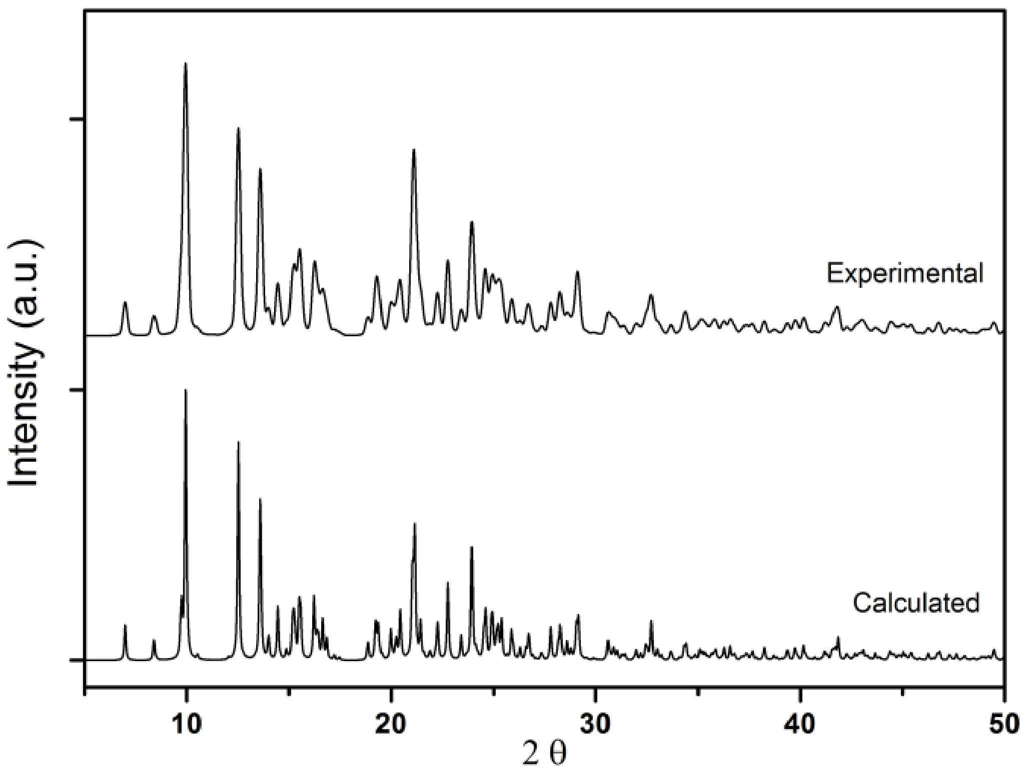


Fig. 3.91 – Experimental and theoretical X-ray powder pattern of **7**

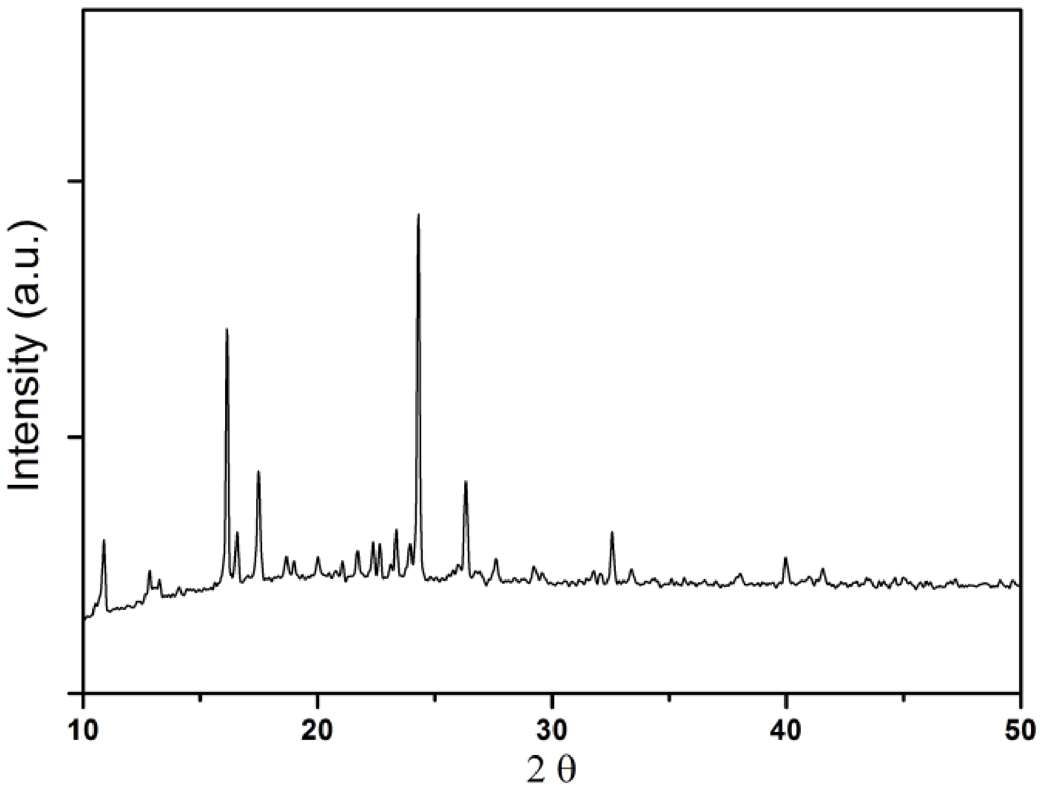


Fig. 3.92 – Experimental X-ray powder pattern of **7a**

Nickel hexaimidazole compound **6** exhibits an endothermic event at 140°C in its TG-DTA graph (Fig. 3.93). The TG curve shows a decrease in mass by 2.77 % equivalent to the loss of a single water molecule by 150°C. The DTA curve shows an endothermic and exothermic peak at 200°C and 395°C respectively, accompanied by a rapid drop in mass that can be attributed to decomposition of **6**. The residual mass of 11.5 % is in very good agreement for the formation of NiO.

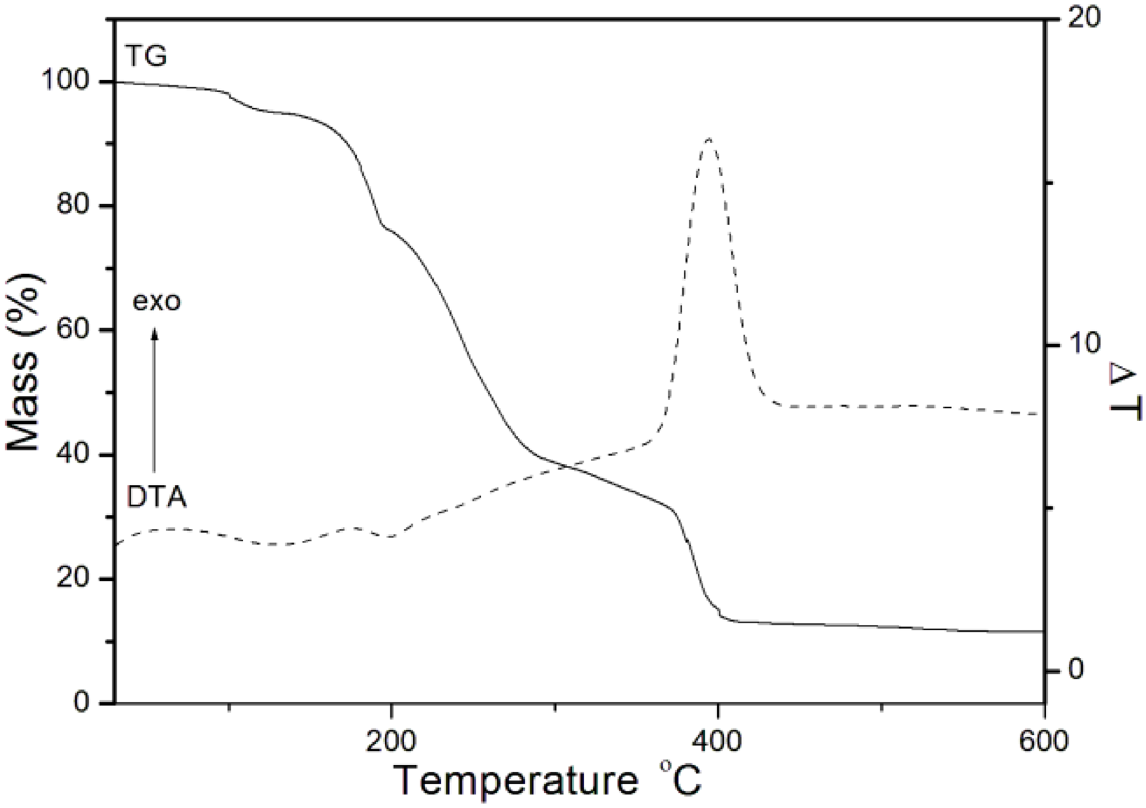


Fig. 3.93 – TG-DTA curves of **6**

Cobalt hexaimidazole compound **7** shows an endothermic peak at 148°C in its TG-DTA graph (Fig. 3.94). The TG curve shows a decrease in mass by 2.8 % equivalent to loss of one water molecule at 150°C. Above 200°C, the DTA curve shows an endothermic peak at 216°C and an exothermic peak at 415°C, accompanied by a rapid mass loss that can be attributed to the decomposition of **7**. The residual mass of 12.32 % is in good agreement for the formation of Co_3O_4 further confirmed by powder pattern.

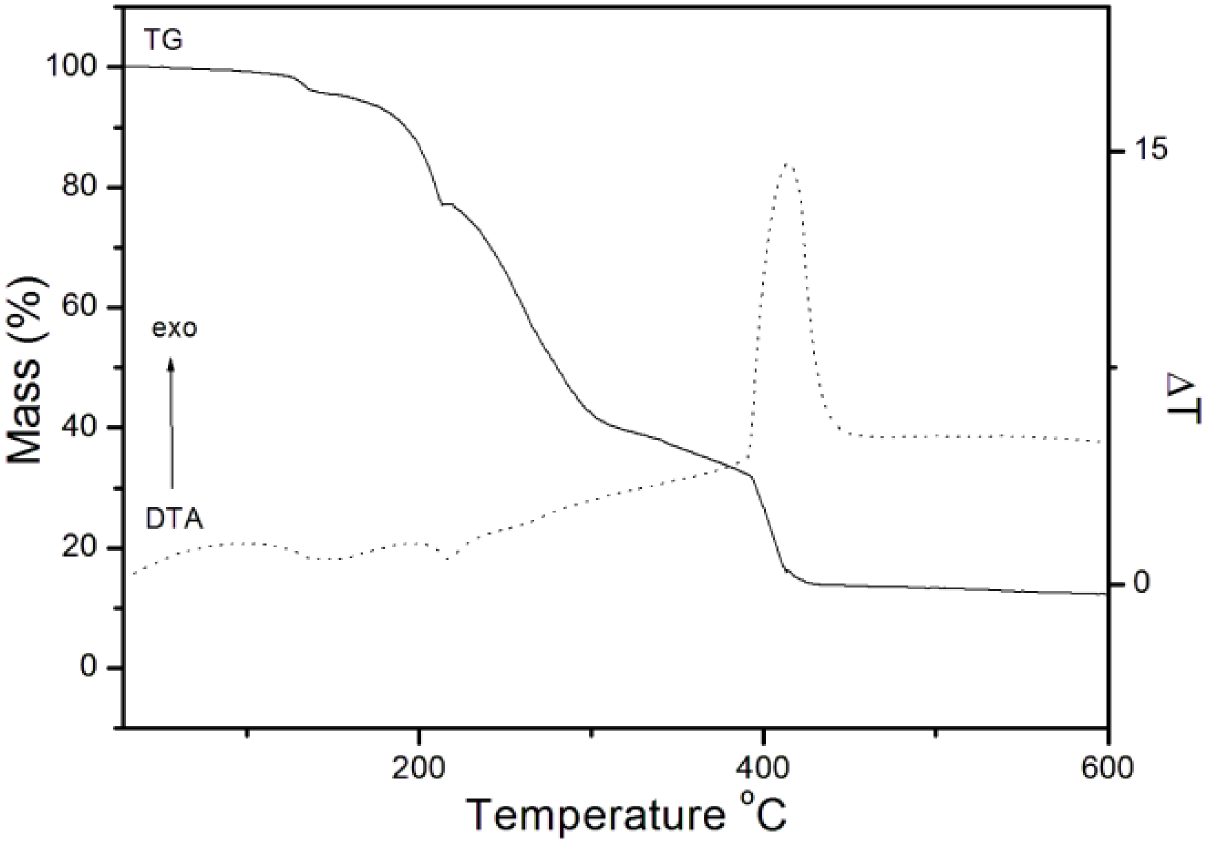


Fig. 3.94 – TG-DTA curves of **7**

The DTA curve of compound **7a** shows three endothermic peaks 129, 210, 263°C and an exothermic peak at 421°C, accompanied by a rapid mass loss in its TG-DTA curve (Fig. 3.95) that can be attributed to the decomposition of **7a**. The residual mass of 17.25 % is in good agreement for the formation of Co_3O_4.

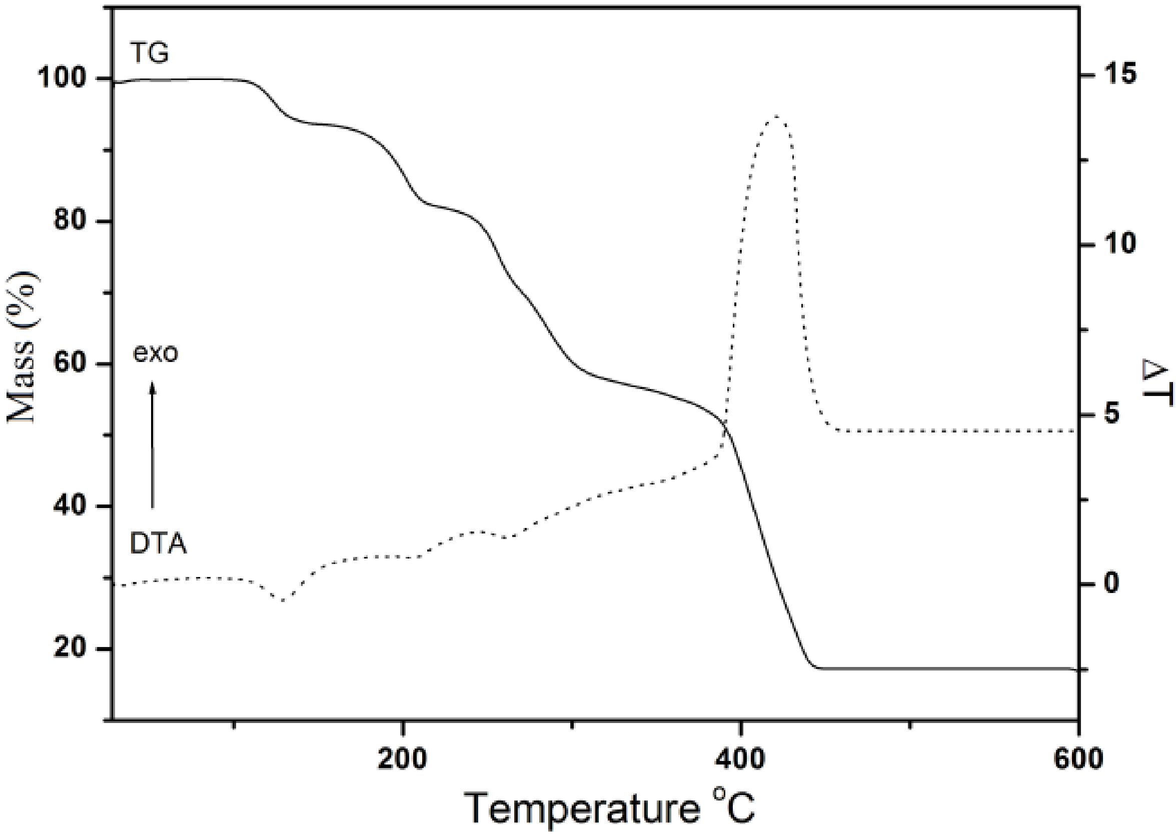


Fig. 3.95 – TG-DTA curves of **7a**

Dinuclear copper compound **8** exhibits an endothermic event at 150°C in its TG-DTA curve (Fig. 3.96). The TG curve shows a decrease in mass by 4.72 % assignable for the loss of 2 water molecules at 150°C. Above 200°C, the DTA curve shows only exothermic peaks at 241, 394 and 427°C, accompanied by a rapid drop in mass that can be attributed to decomposition of **8**. The residual mass of 21.28 % is in very good agreement for the formation of CuO.

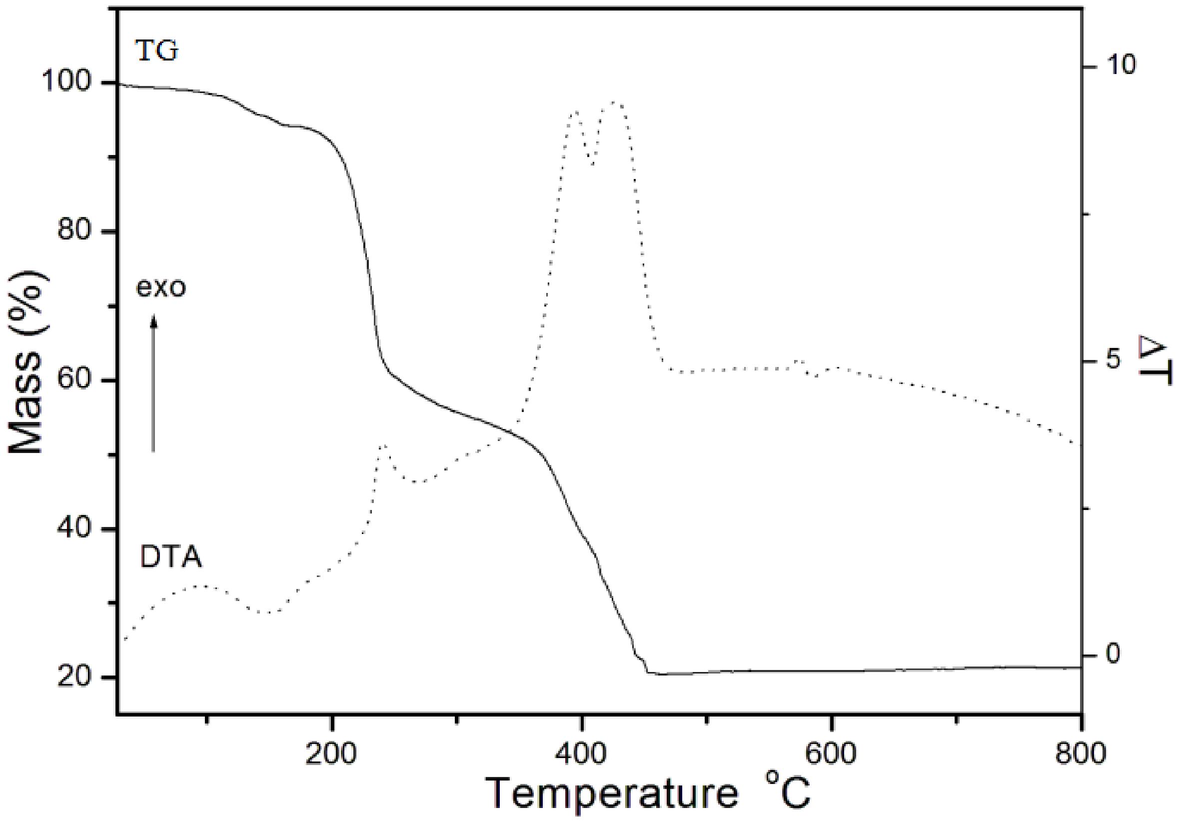


Fig. 3.96 – TG-DTA curves of **8**

The featureless IR spectra (Fig. 3.97) of the residues obtained and their matching powder patterns with corresponding oxides (Fig. 3.98) provide evidence for the complete removal of organic moiety with oxide formation. The results of isothermal mass loss studies performed at different temperatures viz. 100°, 150°, 180°, 200° and 600°C add credence to the thermal data of the compounds.

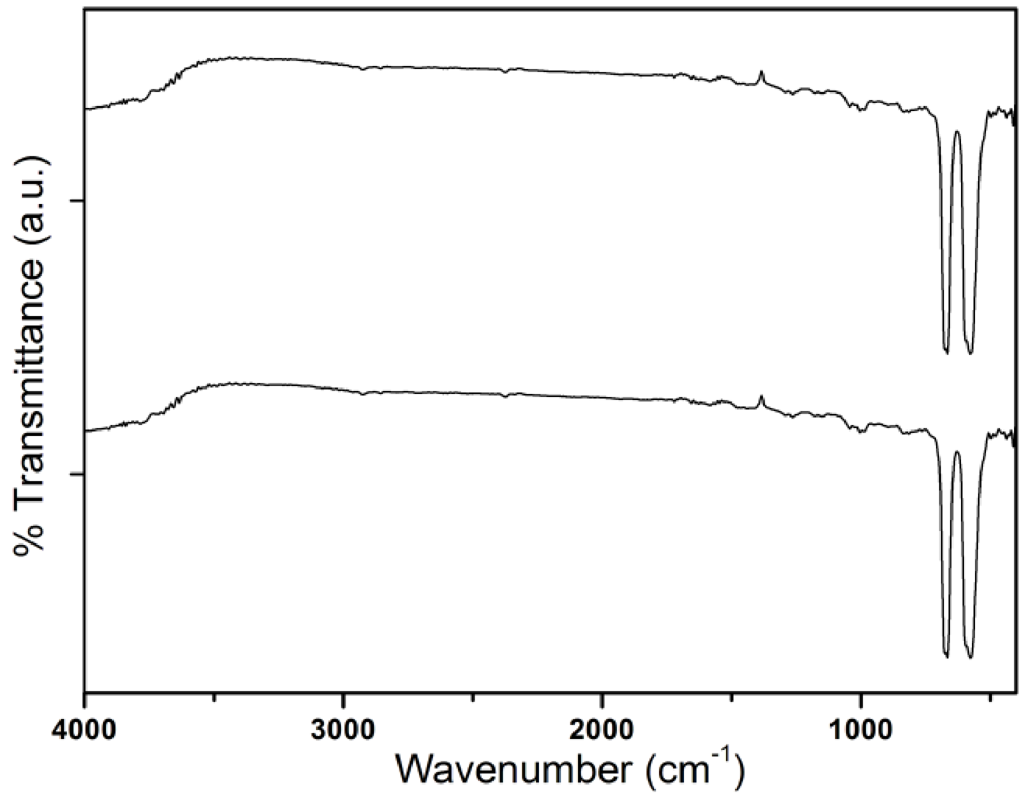


Fig. 3.97 – IR spectra of residues obtained after heating **7** (top) and **7a** (bottom) at 600°C

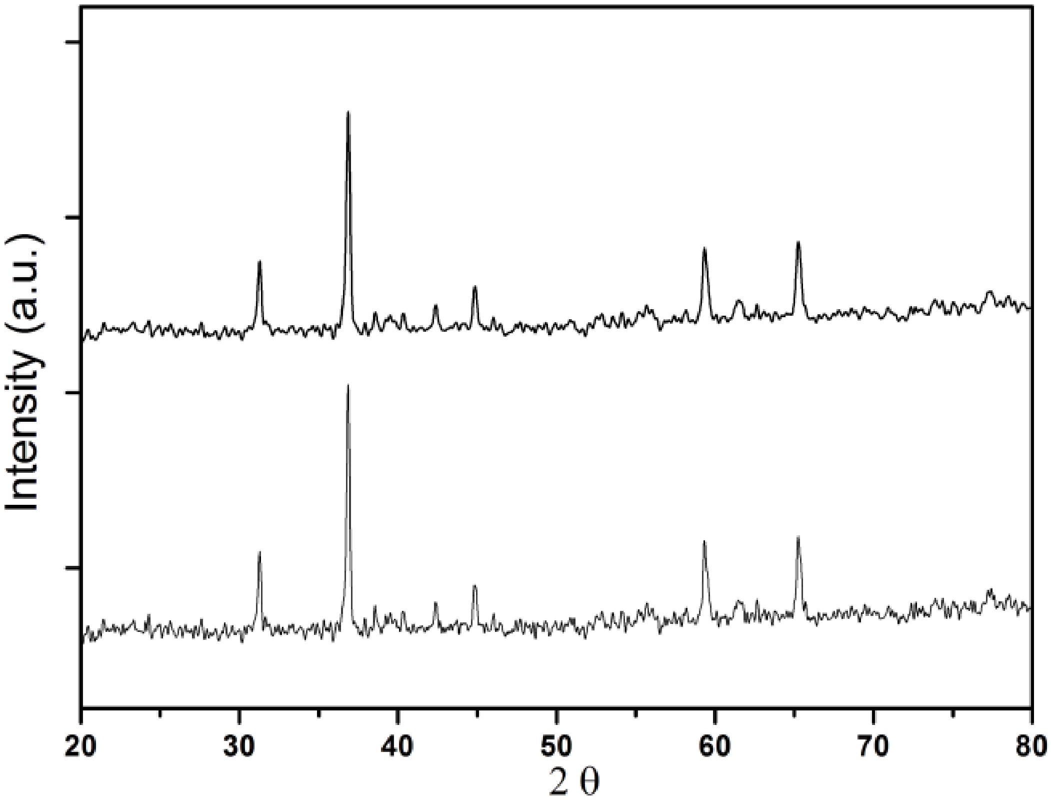


Fig. 3.98 –X-ray powder pattern of residues obtained after heating **7** (top) and **7a** (bottom) at 600°C

*3.1.9 Magnetic studies **7** and **7a***

The temperature-dependent magnetic susceptibility data for polycrystalline samples of compounds **7** and **7a** have been measured at an applied magnetic field of 250 Oe in the temperature range 50-300K (Fig. 3.99). The χ_M versus T plots depict a typical paramagnetic behaviour of the compounds.

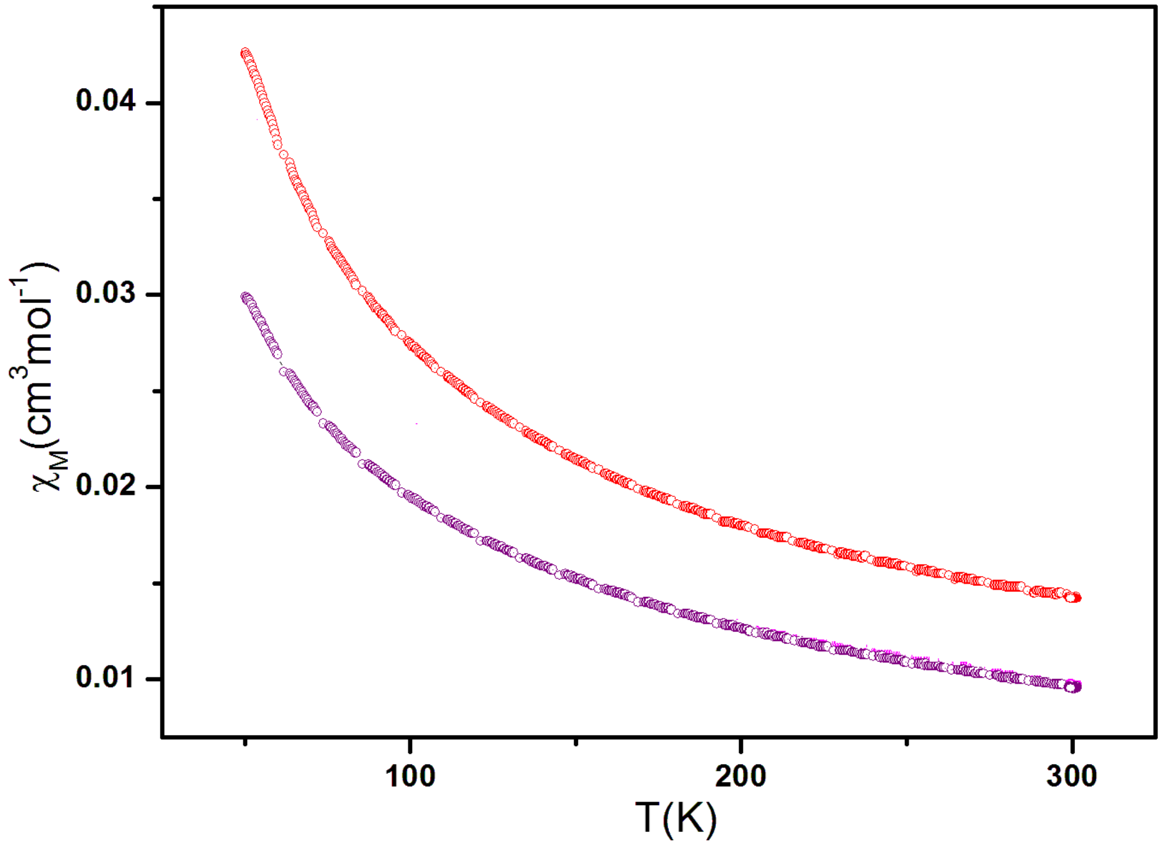


Fig. 3.99 – Plot of χ_M versus T for **7** **(-o-)**, and **7a** **(-o-)**

3.1.10 Description of Crystal structure of 7

Compounds **6** and **7** contain the hexaimidazole metal unit $[M(im)_6]^{2+}$ (M= Ni **6**; Co **7**) charge balanced by phthalate anion while **8** is a dinuclear copper compound containing terminal imidazole and bridging phthalate ligand. Compound **6** and **7** are isostructural whereas **6** and **8** being identical to reported compounds the crystal structure is not been discussed.

Compound **7** crystallises in the centrosymmetric monoclinic $P2_1/c$ space group. The crystal structure of **7** consists of an unique Co(II) ion, six crystallographically independent imidazole ligands, an unique phthalate and a lattice water molecule, all of which are situated in general positions (Fig. 3.100). The central metal ion is octahedrally coordinated to six nitrogen atoms from six terminal imidazole ligands. In this case, the phthalate dianion acts as a charge balancing counter anion. The details of structure refinements for **6 - 8** are given in Table 3.11.

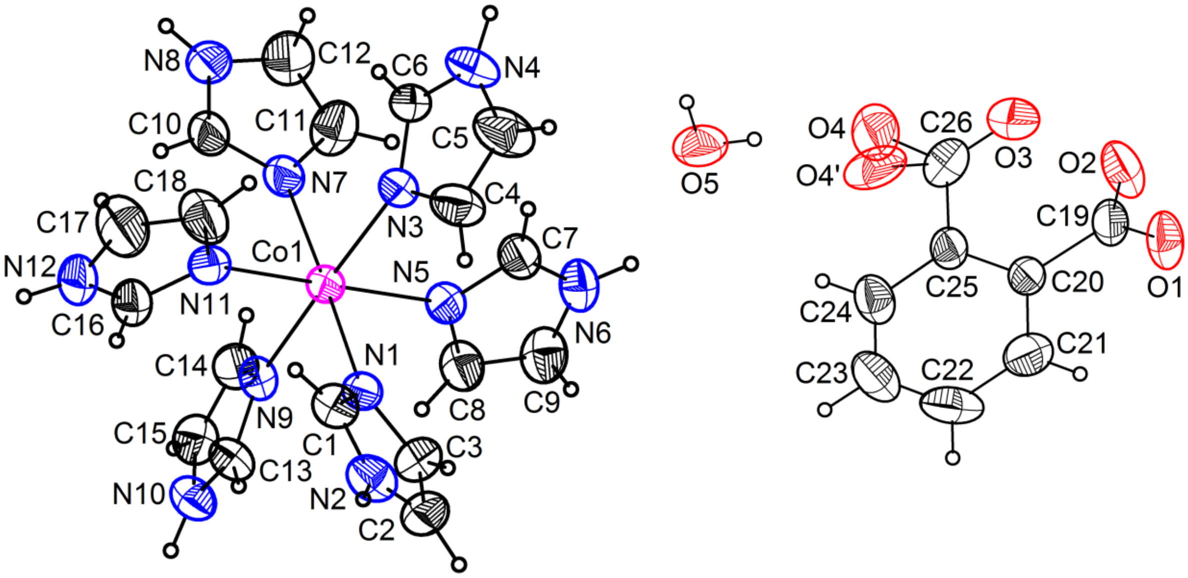


Fig. 3.100 – The crystal structure of $[Co(im)_6](pht)\cdot H_2O$ **7** showing the atom labelling scheme and the coordination sphere of Co(II) in **7**. Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as spheres of arbitrary radius

Table 3.11 – Crystal data and structure refinement for **6 – 8.**

Empirical formula	$C_{26}H_{30}N_{12}NiO_5$	$C_{26}H_{30}CoN_{12}O_5$	$C_{28}H_{28}Cu_2N_8O_{10}$
Formula weight (g mol^{-1})	649.33	649.55	763.66
Temperature (K)	293(2)	293(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
Unit cell dimensions			
a (Å)	13.0759(6)	13.1134(4)	8.8768(4)
b (Å)	13.0309(7)	13.0374(4)	22.3595(12)
c (Å)	18.4208(9)	18.4269(6)	16.1084(9)
α (°)	90	90	90
β (°)	105.636(2)	105.388(2)	105.454(2)
γ (°)	90	90	90
Volume (Å^3)	3022.6(3)	3037.41(17)	3081.6(3)
Z	4	4	4
D_{calc} (mg/m^3)	1.427	1.420	1.646
Absorption coefficient (mm^{-1})	0.699	0.622	1.451
F(000)	1352	1348	1560
Crystal size (mm^3)	0.4 x 0.3 x 0.3	0.40 x 0.30 x 0.30	0.30 x 0.30 x 0.25

θ range for data collection (°)	2.25 to 25.00	2.244 to 25.00	2.245 to 26.999
Index ranges	$-15 \le h \le 15$	$-15 \le h \le 15$	$-11 \le h \le 11$
	$-15 \le k \le 15$	$-15 \le h \le 15$	$-28 \le k \le 28$
	$-21 \le l \le 21$	$-15 \le h \le 15$	$-20 \le l \le 20$
Reflections collected / unique	51915/5305 (R(int) = 0.0428)	45501 / 5337 [R(int) = 0.0386]	51507/6736 (R(int) = 0.0308)
Completeness to θ = 25.00°	99.8 %	100.00%	100.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empiricalfrom equivalents	Semi-empirical from equivalents
Max. and min. Transmission	0.90 and 0.75	0.82 and 0.71	0.73 and 0.55
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5305/3/405	5337 / 10 / 416	6736 / 15 / 449
Goodness-of-fit on F^2	1.082	1.146	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.1053	R1 = 0.0376, wR2 = 0.0820	R1 = 0.0298, wR2 = 0.0683
R indices (all data)	R1 = 0.0625, wR2 = 0.1295	R1 = 0.0583, wR2 = 0.1009	R1 = 0.0407, wR2 = 0.0732
Largest diff. peak and hole (e $Å^{-3}$)	0.464 and -0.430	0.368 and -0.374	0.416 and -0.308

The Co-N bond distances range from 2.153(2) to 2.195(2) Å. The cis N-Co-N angles vary between 87.74(9) to 92.52(9)° and the trans angles range from 177.01(8) to 177.93(9)° indicating a distorted {CoN_6} octahedron (Table 3.12).

Table 3.12 – Selected bond lengths [Å] and angles [°]

Compound **7**					
Bond lengths					
Co1-N7	2.153(2)	Co1-N9	2.165(2)	Co1-N3	2.187(2)
Co1-N1	2.154(2)	Co1-N11	2.175(2)	Co1-N5	2.195(2)
Bond angles					
N7-Co1-N9	90.85(8)	N7-Co1-N3	88.25(8)	N9-Co1-N5	89.20(8)
N1-Co1-N9	89.37(8)	N1-Co1-N3	91.65(8)	N3-Co1-N5	87.97(8)
N7-Co1-N11	89.82(9)	N11-Co1-N3	90.33(8)	N7-Co1-N1	177.56(9)
N1-Co1-N11	87.74(9)	N7-Co1-N5	91.30(9)	N9-Co1-N3	177.01(8)
N9-Co1-N11	92.52(9)	N1-Co1-N5	91.13(8)	N11-Co1-N5	177.93(9)

An analysis of the crystal structure reveals the presence of N-H···O, C-H···O and O-H···O H-bonding interactions (Table 3.13).

Table 3.13– Hydrogen bonding geometry [Å and °] for **7**

D-H···A	d(D-H)	(H···A)	d(D···A)	<DHA	Symmetry code
[Co(Im)$_6$]pht·H_2O **7**					
C2-H2···O2	0.93	2.42	3.260(4)	150.3	-x+1,-y,-z+1
C6-H6 ···O2	0.93	2.63	3.112(3)	112.6	x+1,-y+1/2,z+1/2
N2-H2A ···O3	0.86	2.42	3.068(4)	132.4	-x+1,y-1/2,-z+3/2
N2-H2A ···O4	0.86	1.93	2.781(10)	169.9	-x+1,y-1/2,-z+3/2
N4-H4A ···O1	0.86	2.23	3.049(3)	159.5	x+1,-y+1/2,z+1/2
N4-H4A ···O2	0.86	2.45	2.999(3)	121.9	x+1,-y+1/2,z+1/2
N6-H6A ···O3	0.86	1.89	2.742(3)	170	x+1,y,z
N8-H8A ···O2	0.86	1.92	2.759(3)	164.3	-x+1,y+1/2,-z+3/2
N10-H10A ···O1	0.86	1.96	2.813(3)	173.1	x, y, z
N12-H12A ···O5	0.86	1.95	2.804(3)	169.6	x, y, z
O5-H5A ···O1	0.845(18)	1.919(18)	2.756(3)	171(4)	x,-y+1/2,z+1/2
O5-H5B ···O4	0.858(18)	1.85(2)	2.703(7)	170(5)	x, y, z

The $[Co(im)_6]^{2+}$ cation acts as a H-donor via uncoordinated nitrogens of imidazole ligand and the carbon atoms via N-H···O and C-H···O interactions respectively (Fig. 3.101). On the other hand, phthalate acts as H-acceptor accepting hydrogens from the cation and the lattice water molecule. The lattice water accepts proton from the cation and donates the hydrogens to phthalate anion (Fig. 3.101).

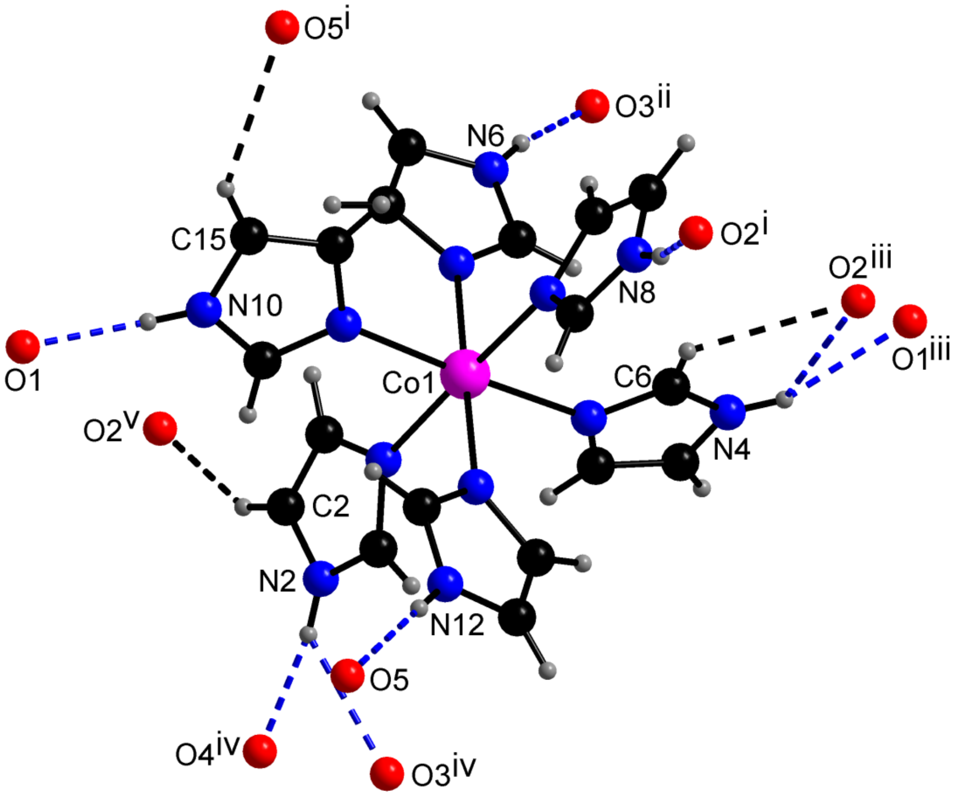


Fig. 3.101 – The H-bonding surroundings of $[Co(im)_6]^{2+}$ cation in **7** showing N-H···O, C-H···O and O-H···O interactions (shown in broken lines)

$[Co(im)_6]^{2+}$ cation is H-bonded to six symmetry related phthalate dianions and a lattice water molecule in its surrounding (Fig. 3.102).

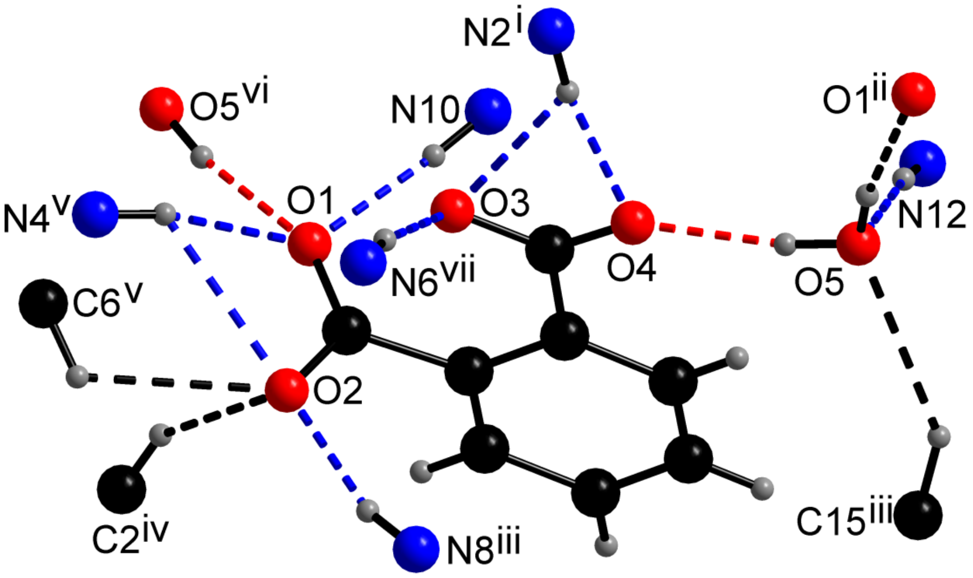


Fig. 3.102 – The H-bonding surroundings of pht^{2-} anion and lattice water O5 in **7** showing N-H···O, C-H···O and O-H···O interactions (shown in broken lines)

The $[Co(im)_6]^{2+}$ unit, phthalate and lattice water molecules are organised in a zig-zag fashion in crystallographic *ab* plane (Fig. 3.103 - 3.105).

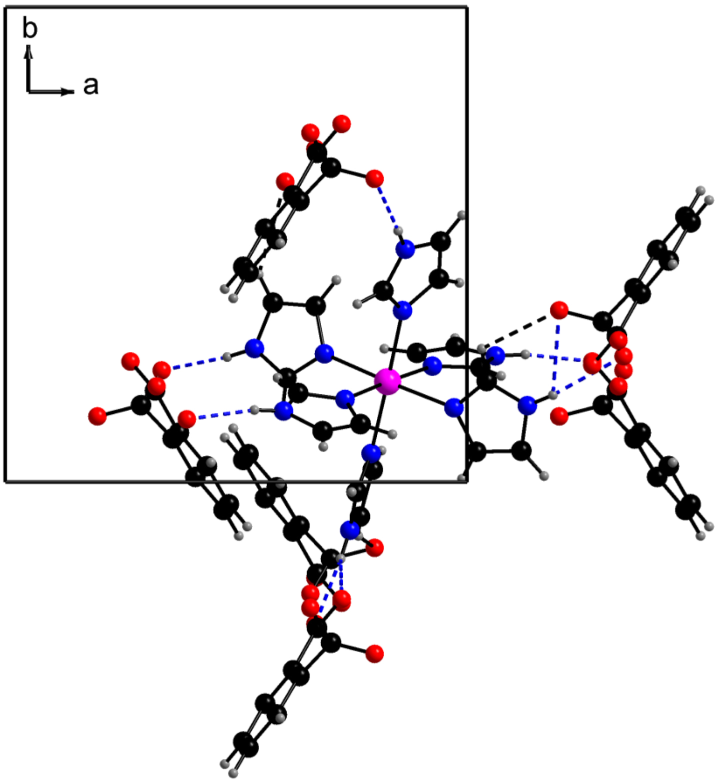


Fig. 3.103 – $[Co(im)_6]^{2+}$ cation surrounded by six phthalate anions and a lattice water molecule via H-bonding interaction in **7**

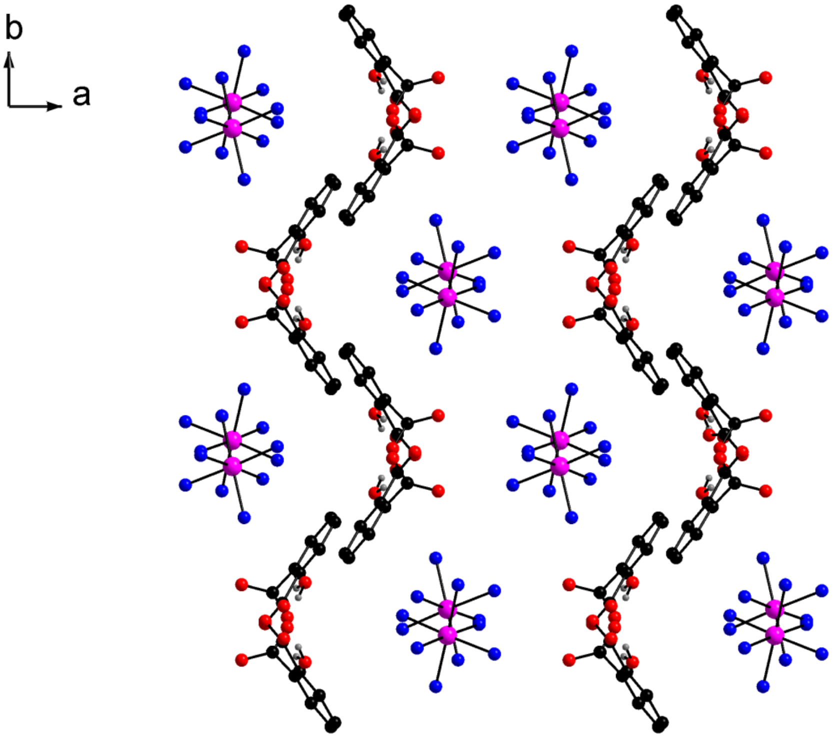


Fig. 3.104 – A view along c-axis showing the disposition of $[Co(im)_6]^{2+}$ unit and the phthalate anion in the crystal structure of **7** (for clarity the imidazole ring are not shown)

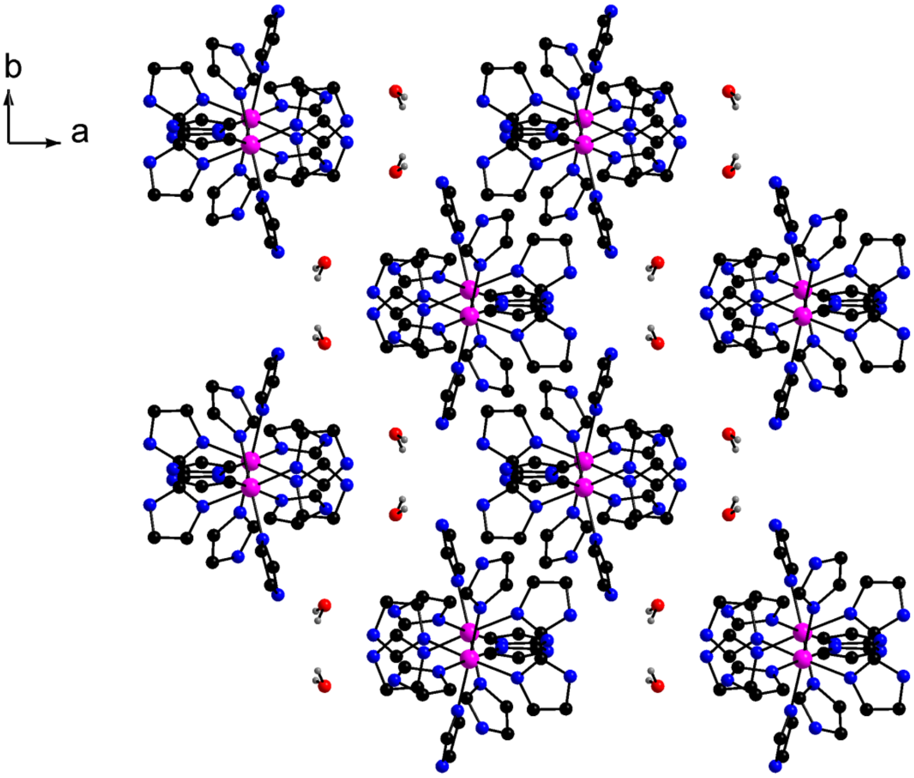


Fig. 3.105 – A view along *c-axis* showing the disposition of $[Co(im)_6]^{2+}$ unit and the lattice water molecule in the crystal structure of **7**

An O-H···O interaction between phthalate and lattice water leads to a 1-D zig-zag chain along *c-axis* (Fig. 3.106).

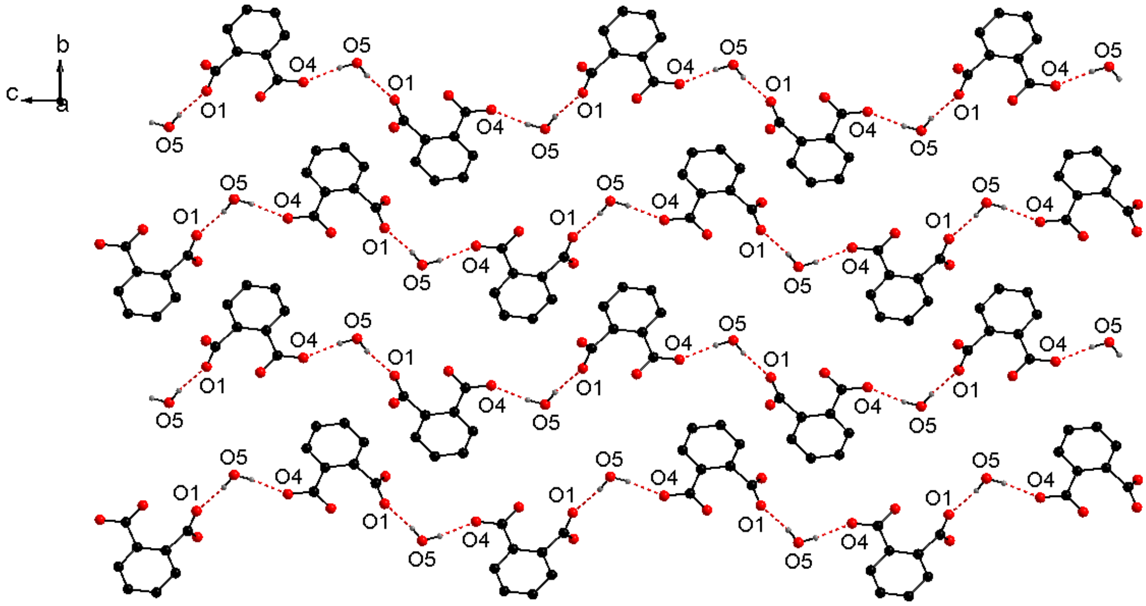


Fig. 3.106 – The O-H···O interaction between phthalate anion and lattice water molecule extending in zig zag fashion along *c*-direction in **7**

H-bonding interactions between cation, anion and lattice water molecule results in 3D supramolecular architecture (Fig. 3.107).

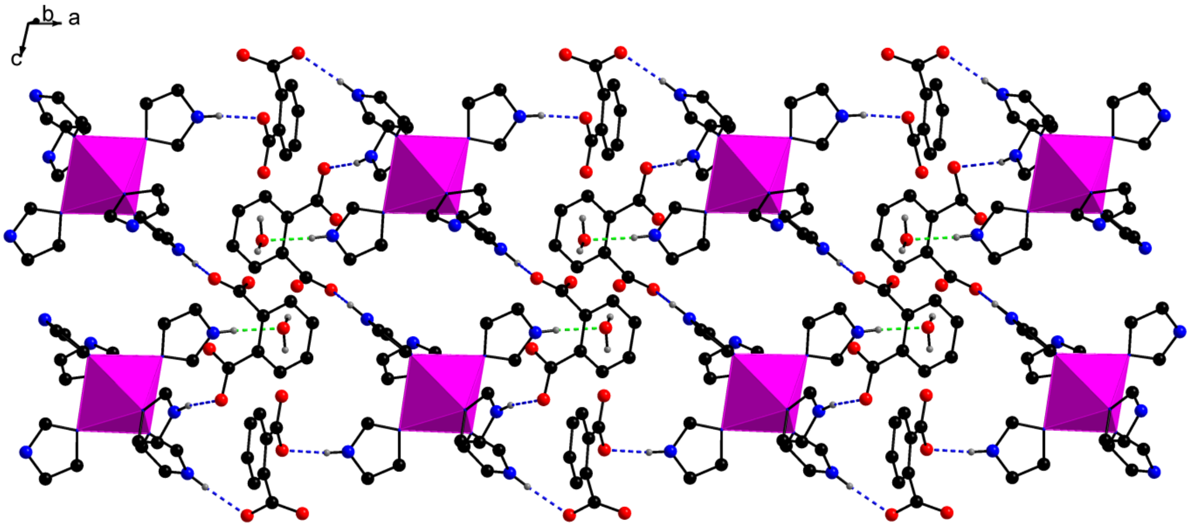


Fig. 3.107 – The two dimensional (2D) supramolecular architecture in **7** formed due to N-H···O interaction between $[Co(im)_6]^{2+}$ cation and phthalate anion in *ac* plane

Unlike in **3-5**, no Cg···Cg distances involving phthalate ring is observed in **6** and **7** which can be explained due to presence of a single unique phthalate in the crystal structure of these 1:1 phthalates. Compound **8** exhibits Cg···Cg distances between the centroids of two unique phthalate rings of the order 4.5 Å and more which are longer than in **3-5** (Table 3.14).

Table 3.14 - Analysis of Short Ring-Interactions between phthalate rings in **8** with Cg···Cg Distances < 6.0 Å and β < 60°

Cg(I)	Res(I)	Cg(J)	[ARU(J)]	Cg-Cg	α	β	γ	CgI_Perp	Cg J_Perp	Slippage
$[Cu_2(H_2O)(im)_4(pht)_2]\cdot H_2O$ **8**										
Cg(7)	[1] ->	Cg(8)	[2455.01]	4.6297(15)	55.82(12)	51.9	8.2	-4.5819(11)	-2.8579(10)	
Cg(7)	[1] ->	Cg(8)	[2555.01]	5.4821(15)	55.82(12)	35.6	55.3	3.1208(11)	4.4555(10)	
Cg(8)	[1] ->	Cg(8)	[3656.01]	5.5843(14)	0	58.3	58.3	2.9341(10)	2.9341(10)	4.751

Where, Cg(7)= unique phthalate (C9-C14) and Cg(8)= second unique phthalate (C23-C28)

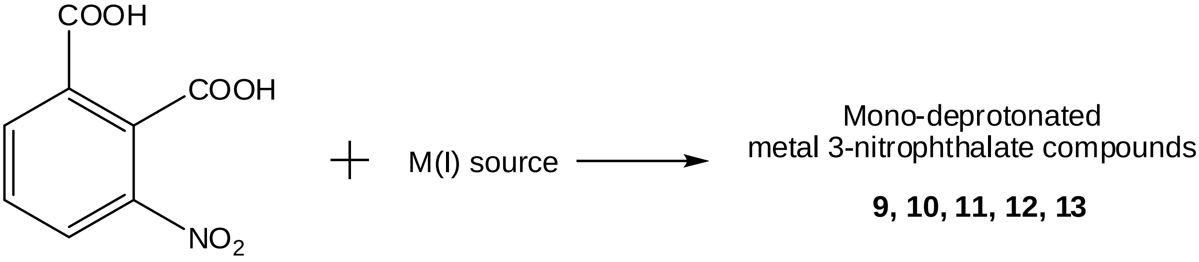
Analysis of Short Ring-Interactions with Cg-Cg Distances < 6.0 Angstrom and Beta < 60.0Deg.

- Cg(I) = Plane number I (= ring number in () above)
- Alpha = Dihedral Angle between Planes I and J (Deg)
- Beta = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg)
- Gamma = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg)
- Cg-Cg = Distance between ring Centroids (Ang.)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Ang.)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)
- Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Ang.)

Investigation of synthsised alkali metal 3-nitrophthalate compounds

3.2 Syntheses of alkali metal 3-nitrophthalates

A general protocol for the syntheses of metal 3-nitrophthalate in 1:1 molar ratio is depicted in Scheme 3.4.



Scheme 3.4 - Syntheses of mono-deprotonated 3-nitrophthalates.

3.2.1 Synthetic aspects, spectral characteristics and thermal studies for [Li(3-nphtH)$(H_2O)_3$] **9**, *[Na(2-carboxy-6-nba)$(H_2O)_3$]$\cdot H_2O$* **10**, *[K(2-carboxy-3-nba)]* **11**, *[Rb(3-nphtH)]$\cdot 2H_2O$* **12** and *[Cs(2-carboxy-6-nba)(H_2O)]* **13**

Compound **9-13** were prepared from an aqueous medium acid base reaction of respective metal carbonates with 3-nitrophthalic acid (3-nphtH$_2$) in 1:1 mole ratio respectively. Crystals suitable for X-ray structure analysis were obtained by recrystallising it from an aqueous solution. The compositions of **9-13** were determined based on analytical data and metal carbonate formed on pyrolysis at 800°C.

The IR spectra of compounds **9-13** exhibit several signals in the mid-IR region indicating the presence of organic moieties (Fig 3.108-3.112). An analysis of the signal in the region 1680-1720 cm^{-1} for –COOH gives information on resultant mono- or di- deprotonated 3-nitrophthalate ligand. A weak –COOH signal at ~1720 cm^{-1} in **9-13** indicates formation of mono-deprotonated 3-nitrophthalate ligand. In the IR spectrum of **9**, bands at 1572 cm^{-}

^{1} (1572 in **10**; 1652 and 1602 in **11,** 1522 in **12**; 1520 in **13)** can be assigned for the asymmetric stretching vibration of the carboxylate group (υ_{asym}) and the bands observed at 1464 and 1390 cm^{-1} (1464 in **10**; 1456 in **11,** 1450 in **12**; 1452 in **13)** for symmetric stretching vibration (υ_{sym}). The IR stretching vibrations expected for the $\upsilon_{N\text{-}O}$ vibration of the –NO_2 group of the ligand is seen at 1346 cm^{-1} (**9**), 1360 (**10**), 1346 (**11**), 1346 (**12**), 1355 (**13**). Interestingly sharp signal assignable for –NO_2 group stretching vibrations was observed in Raman spectrum (Fig 3.108-3.112) of the compounds at 1349 (**9**), 1355 (**10**), 1342 (**11**)1343 (**12**), 1348 (**13**).

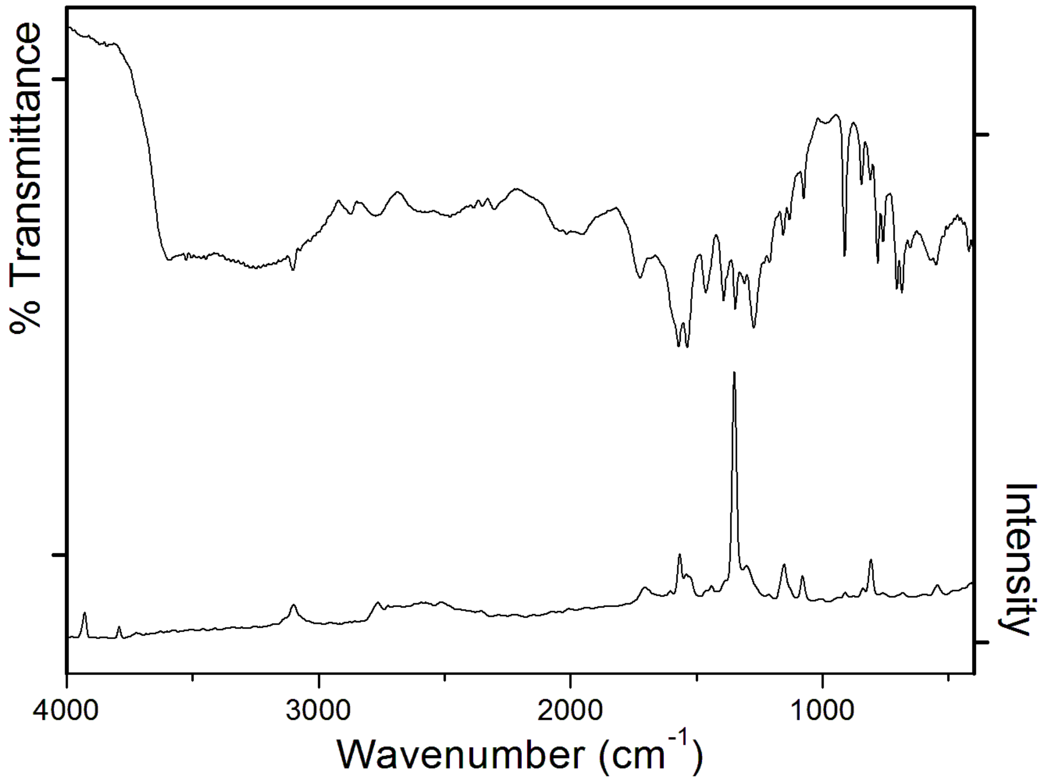


Fig. 3.108 – IR and Raman spectrum of **9**

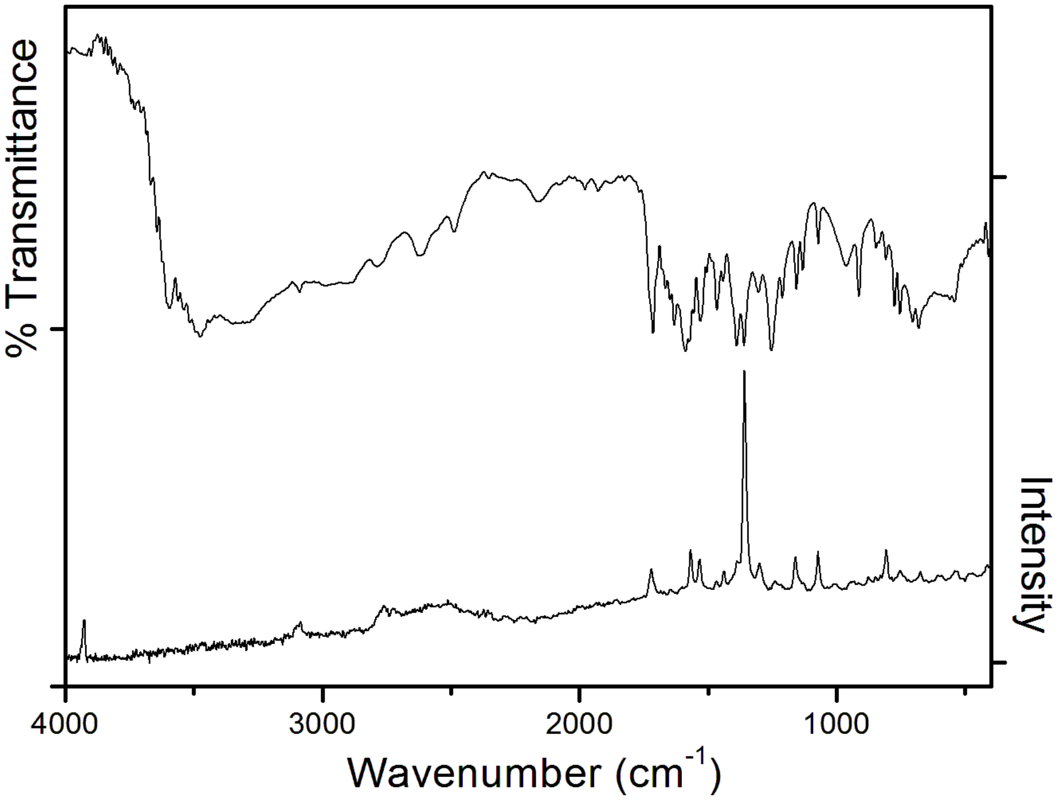


Fig. 3.109 – IR and Raman spectrum of **10**

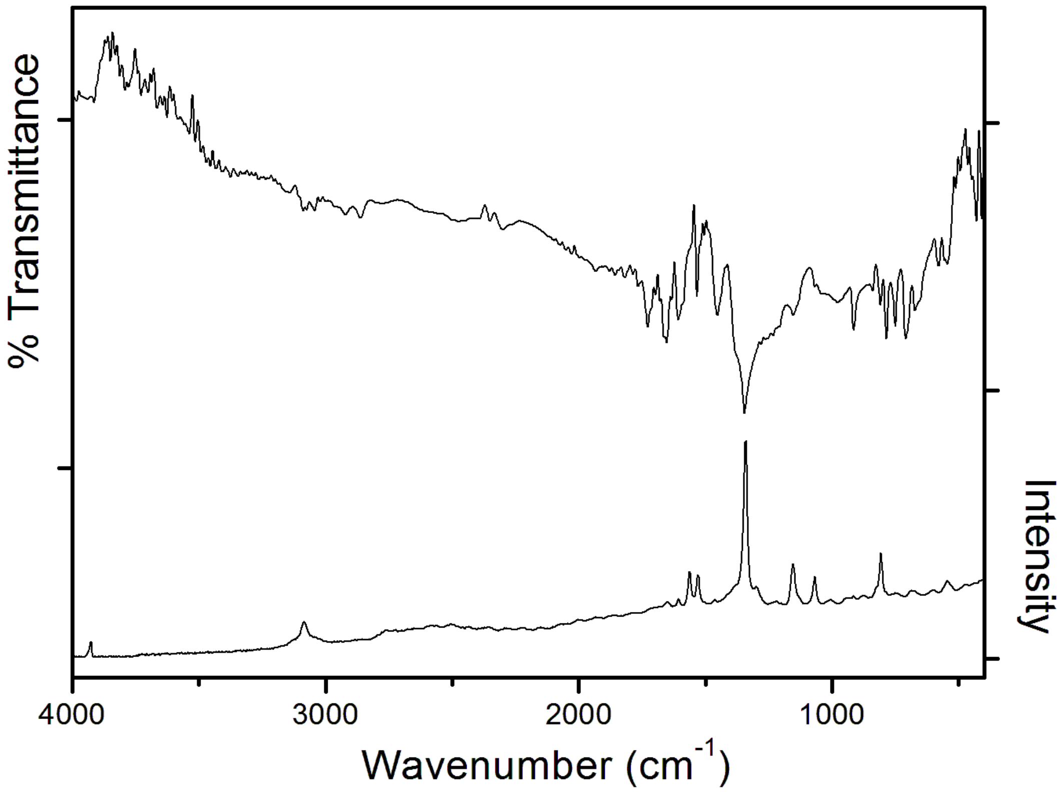


Fig. 3.110 – IR and Raman spectrum of **11**

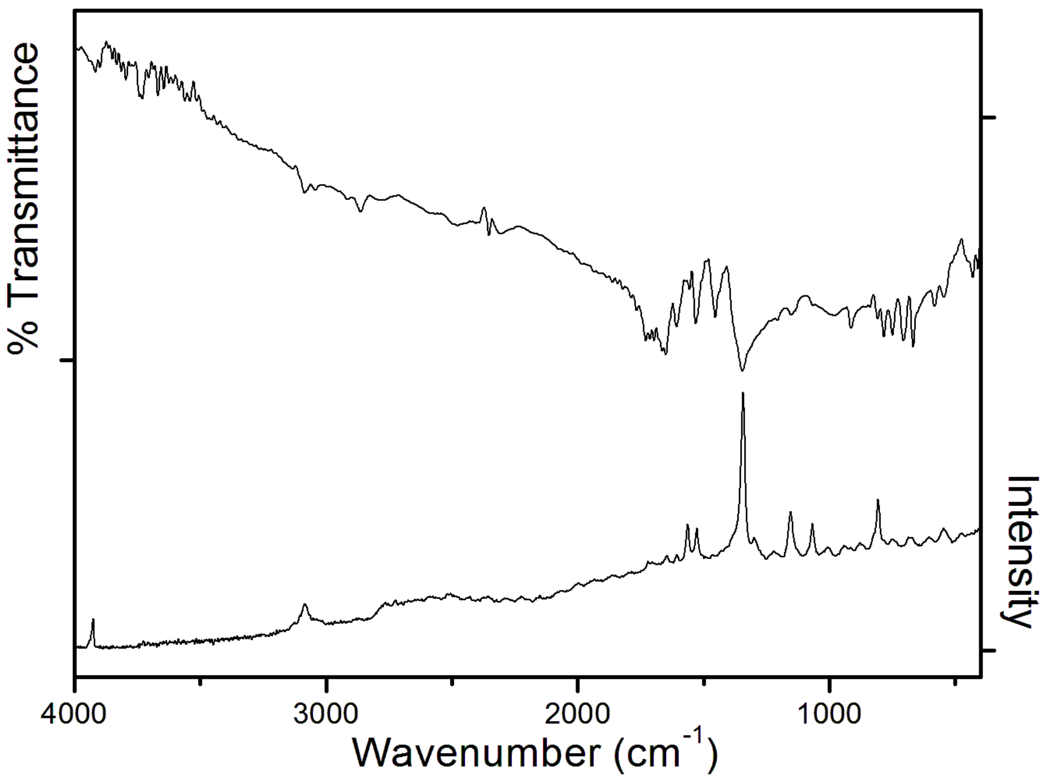


Fig. 3.111 – IR and Raman spectrum of **12**

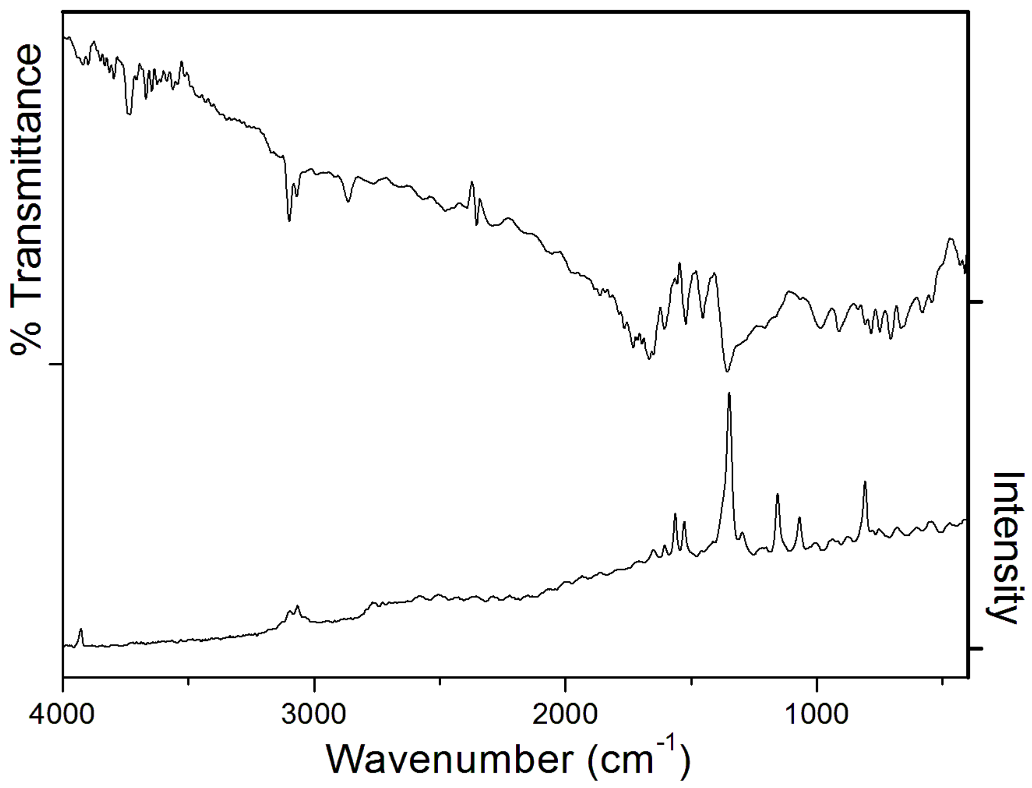


Fig. 3.112 – IR and Raman spectrum of **13**

The UV-visible spectra (Fig. 3.113-3.117) of compounds **9-13** shows an absorbance ~273 nm assignable for intra ligand charge transfer band for aromatic 3-nitrophthalate ligand.

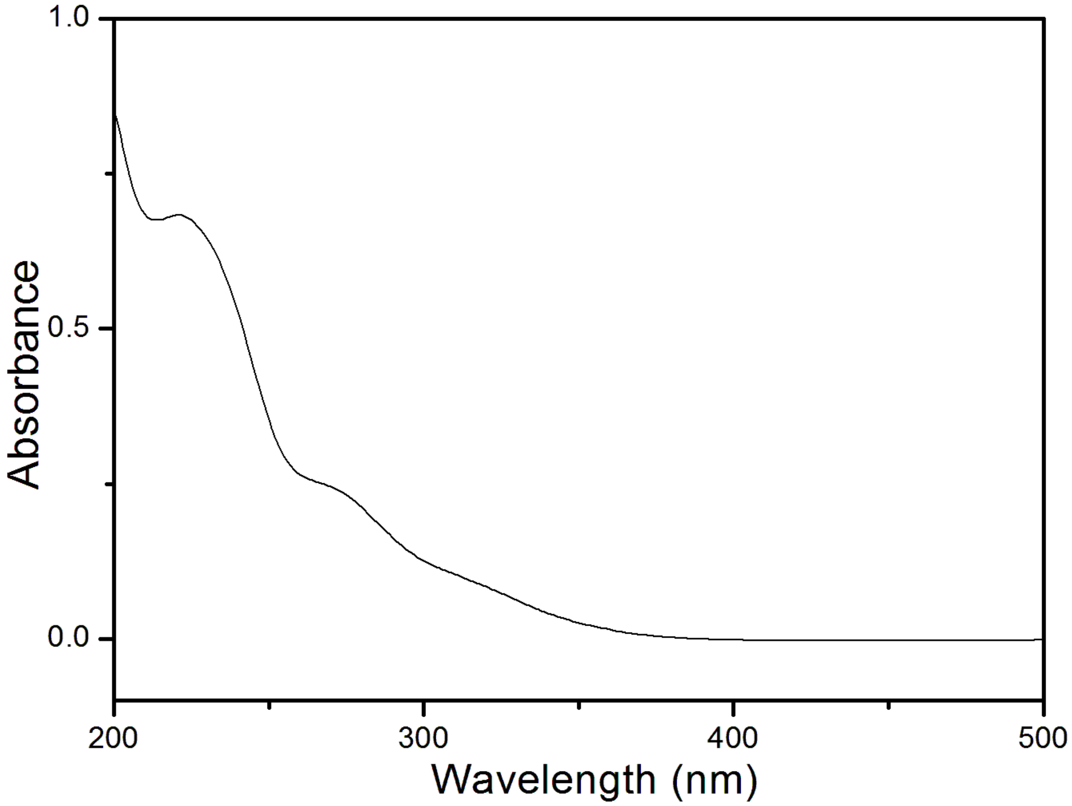


Fig. 3.113 – UV-Visible spectrum of **9**

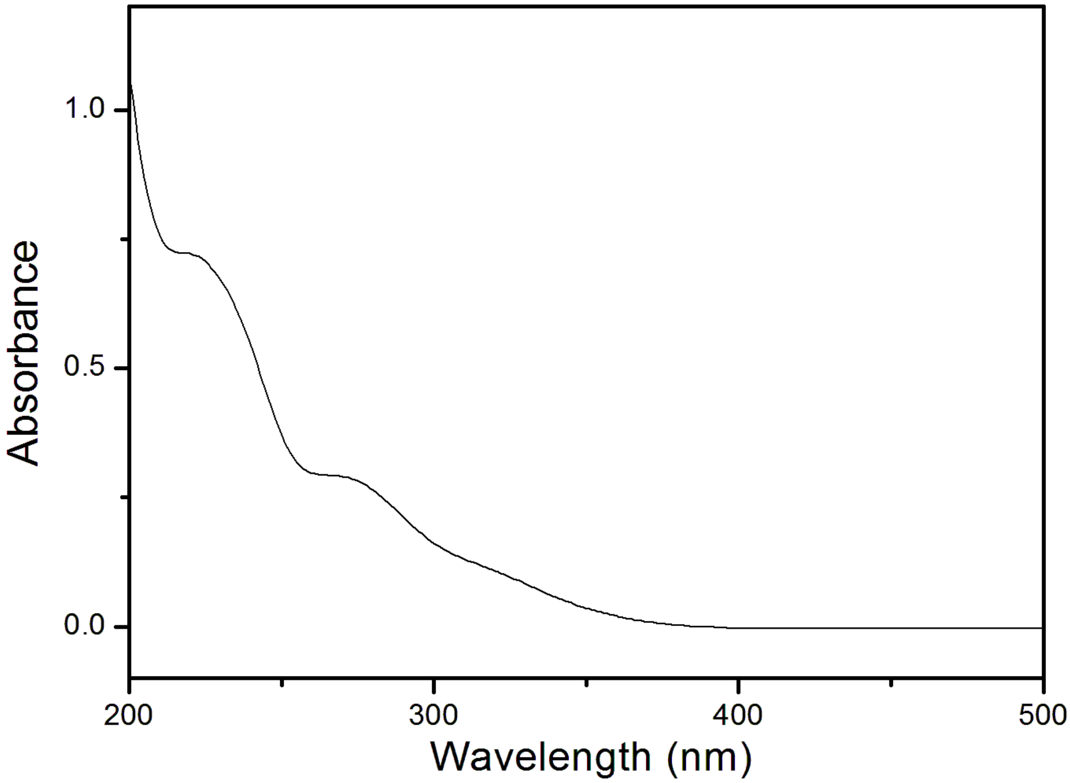


Fig. 3.114 – UV-Visible spectrum of **10**

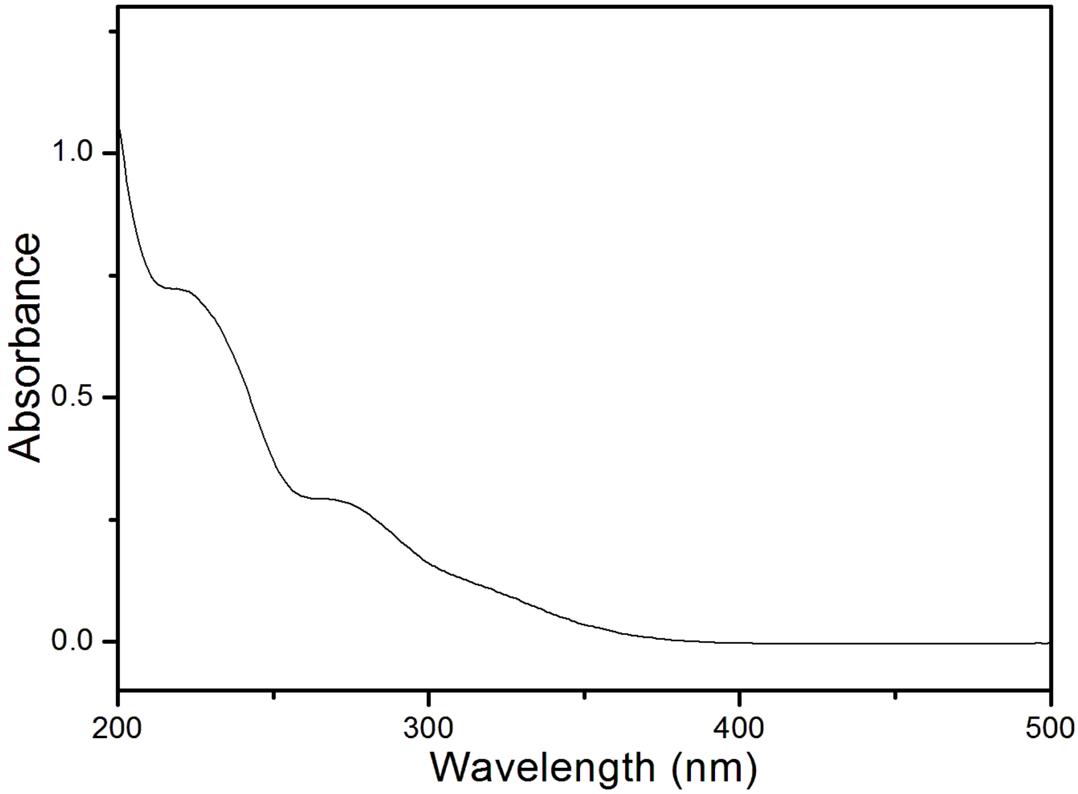


Fig. 3.115 – UV-Visible spectrum of **11**

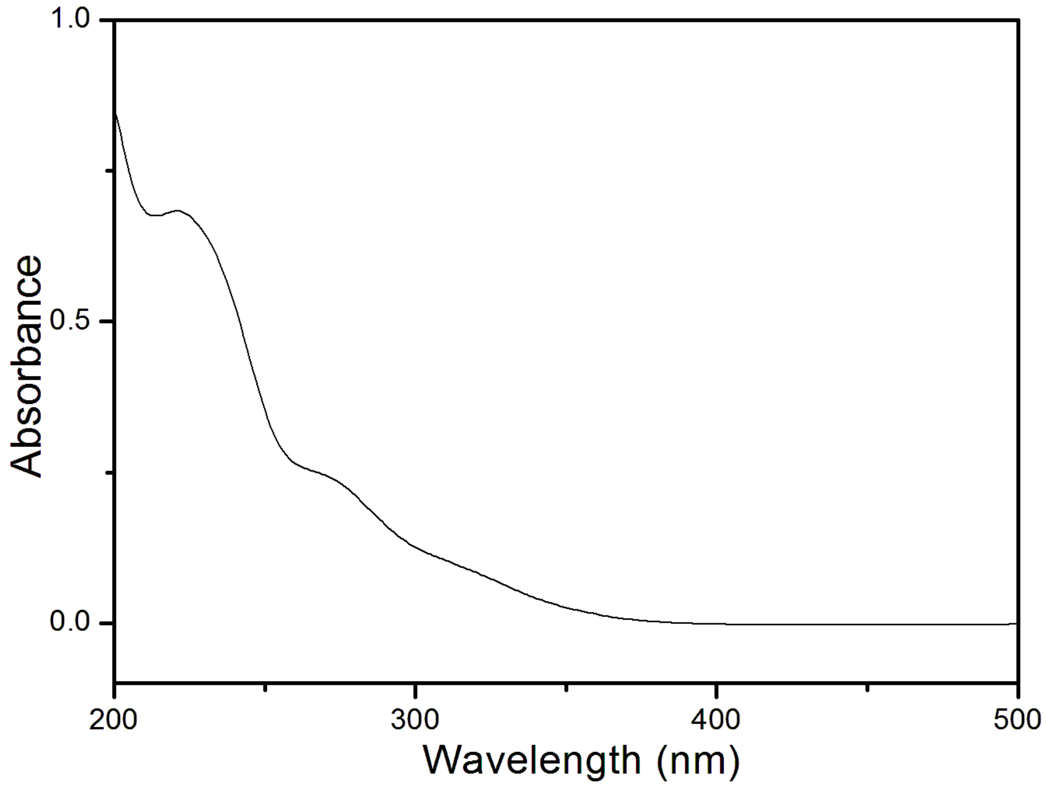


Fig. 3.116 – UV-Visible spectrum of **12**

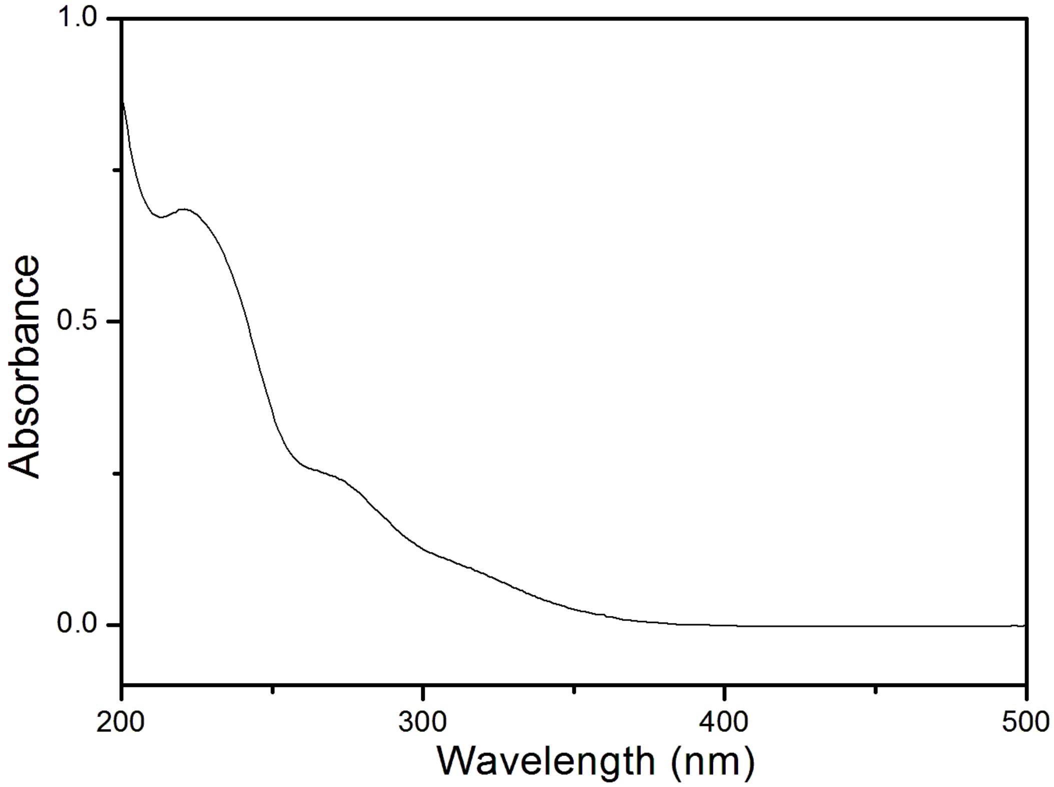


Fig. 3.117 – UV-Visible spectrum of **13**

Lithium compound **9** exhibits an endothermic event with a peak in DTA at 95°C in its TG-DTA graph (Fig. 3.118). The TG curve shows a decrease in mass by 19.75 % equivalent to loss of three water molecules by 100°C. Above 200°C, the DTA curve shows peaks at 214°C (endo), 271°C (endo) and 410°C (exo), accompanied by a rapid drop in mass that can be attributed to decomposition of **1**. The residual mass of 13.87 % is in very good agreement for the formation of Li_2CO_3.

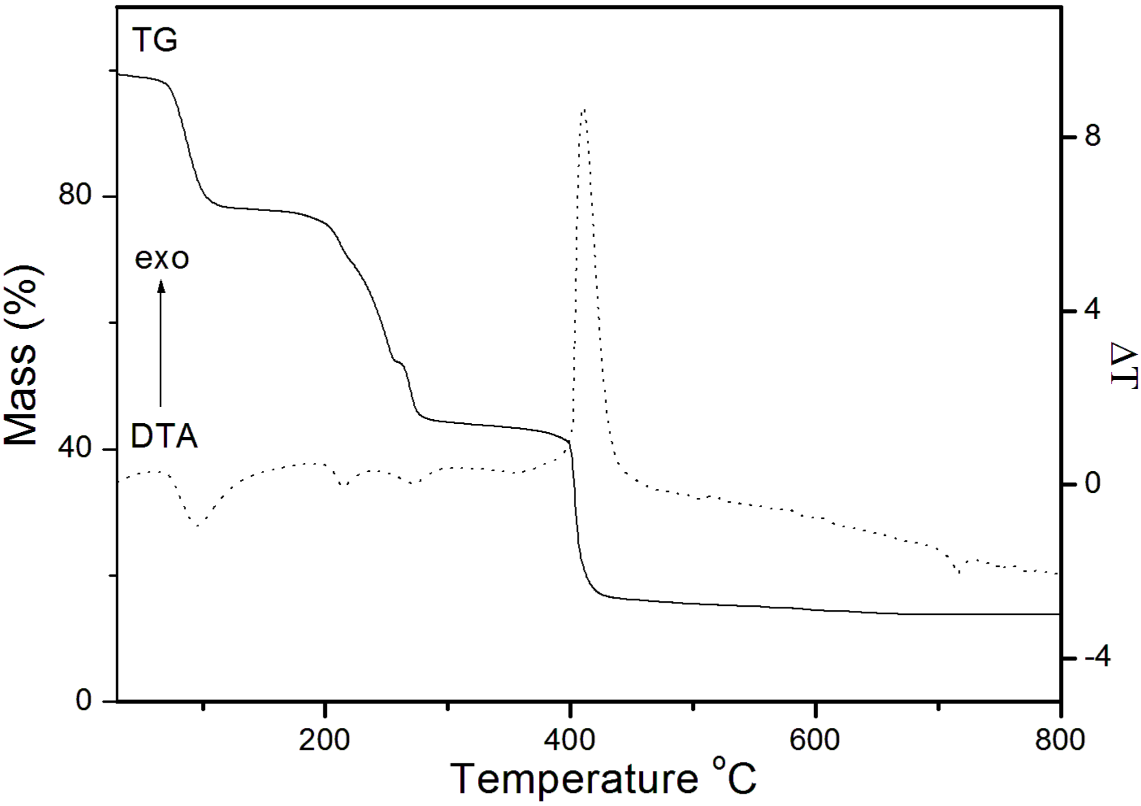


Fig. 3.118 – TG-DTA curve of **9**

Sodium compound **10** exhibits endothermic event at 102°C in its TG-DTA graph (Fig. 3.119). The TG curve shows a decrease in mass by 18.05 % equivalent to loss of three water molecules by 110°C. Above 200°C, the DTA curve shows an endothermic peak at 250°C and an endothermic peak at 370°C with rapid mass loss due to decomposition of **10**. The residual mass of 18.7 % corresponds to Na_2CO_3.

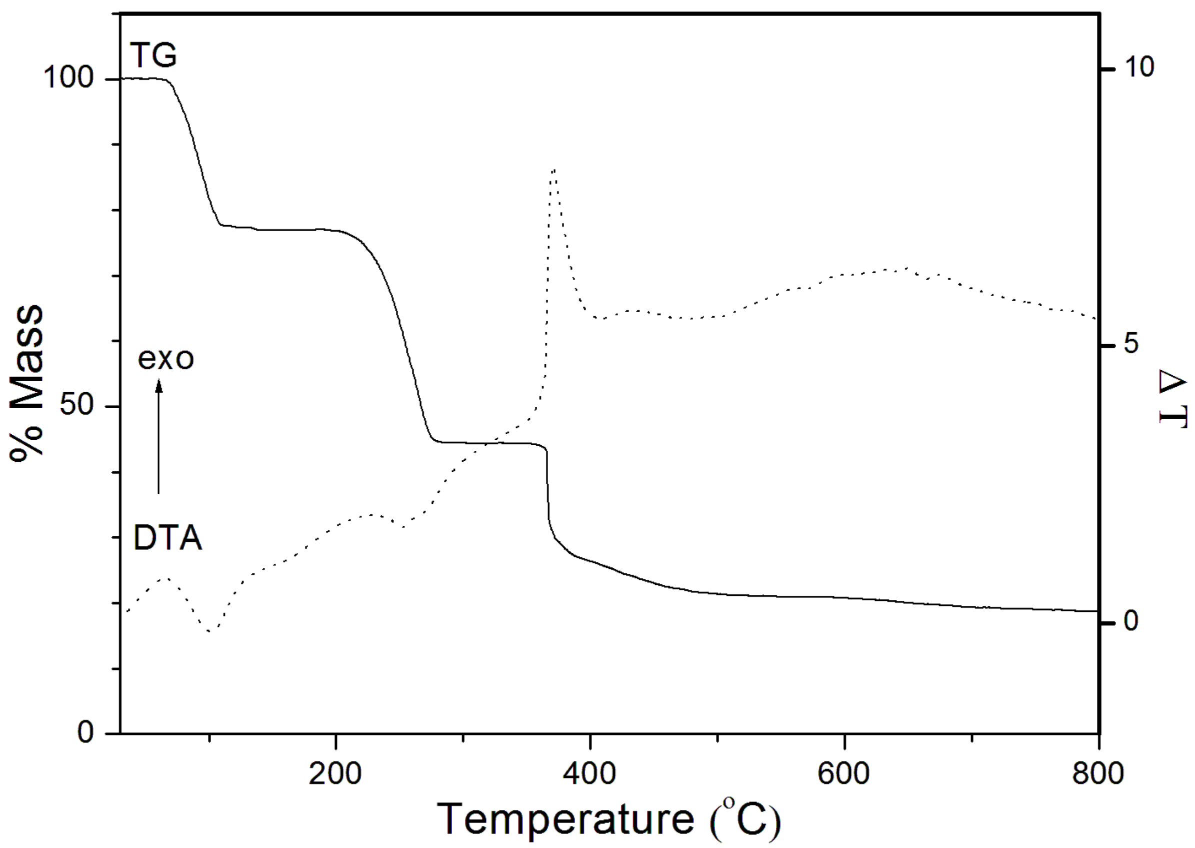


Fig. 3.119 – TG-DTA curve of **10**

Potassium compound **11** shows a straight curve till 250°C indicating no weight loss in its TG-DTA graph (Fig. 3.120). Above 250°C, the DTA curve shows an endothermic event at 290°C and exothermic peaks at 345, 476 and 527°C accompanied by a rapid drop in mass that can be attributed to decomposition of **11**. The residual mass of 27.84 % is in very good agreement for the formation of K_2CO_3.

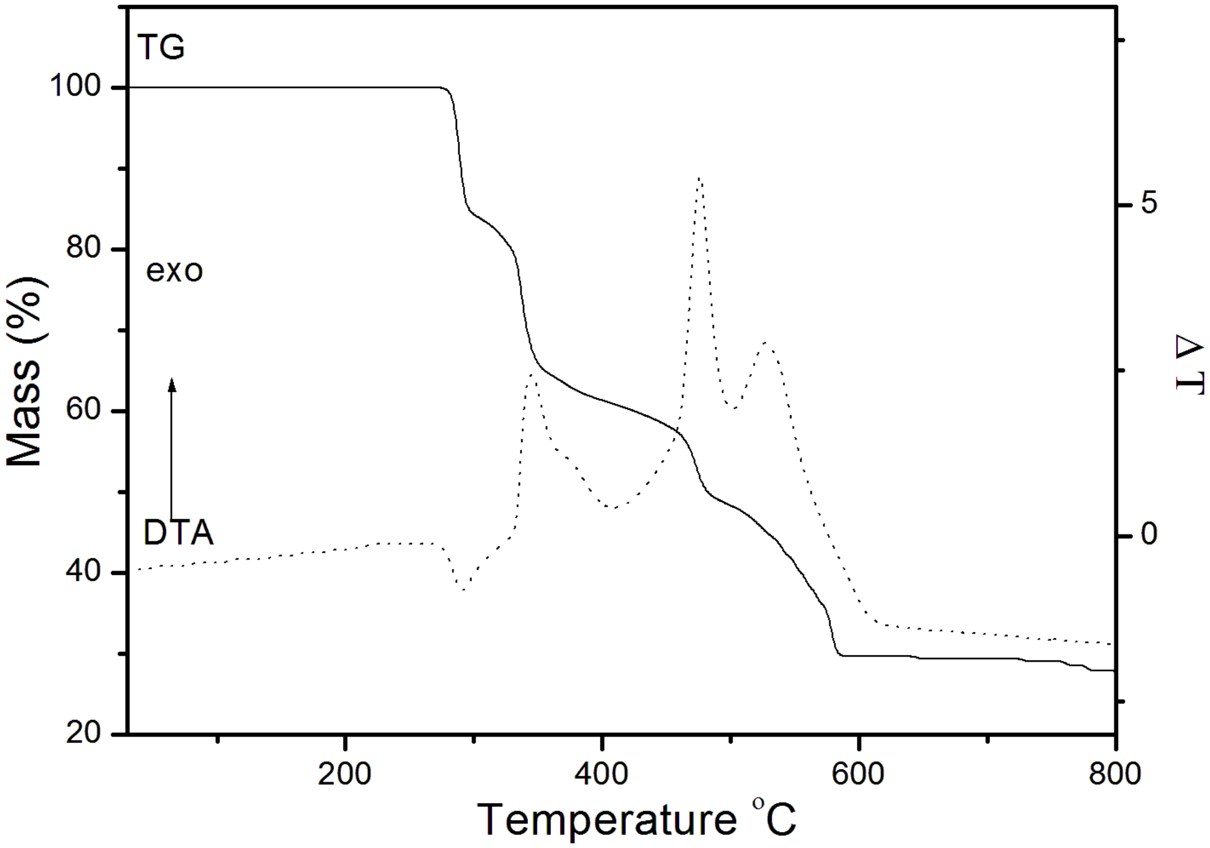


Fig. 3.120 – TG-DTA curve of **11**

Rubidium compound **12** exhibits endothermic event at 102°C in its TG-DTA graph (Fig. 3.121). The TG curve shows a decrease in mass by 9.08 % equivalent to loss of one water molecules by 110°C. Above 200°C, the DTA curve shows only an exothermic peak at 342°C and 460°C with rapid mass loss due to decomposition of **12**. The residual mass of 34.82 % corresponds to Rb_2CO_3.

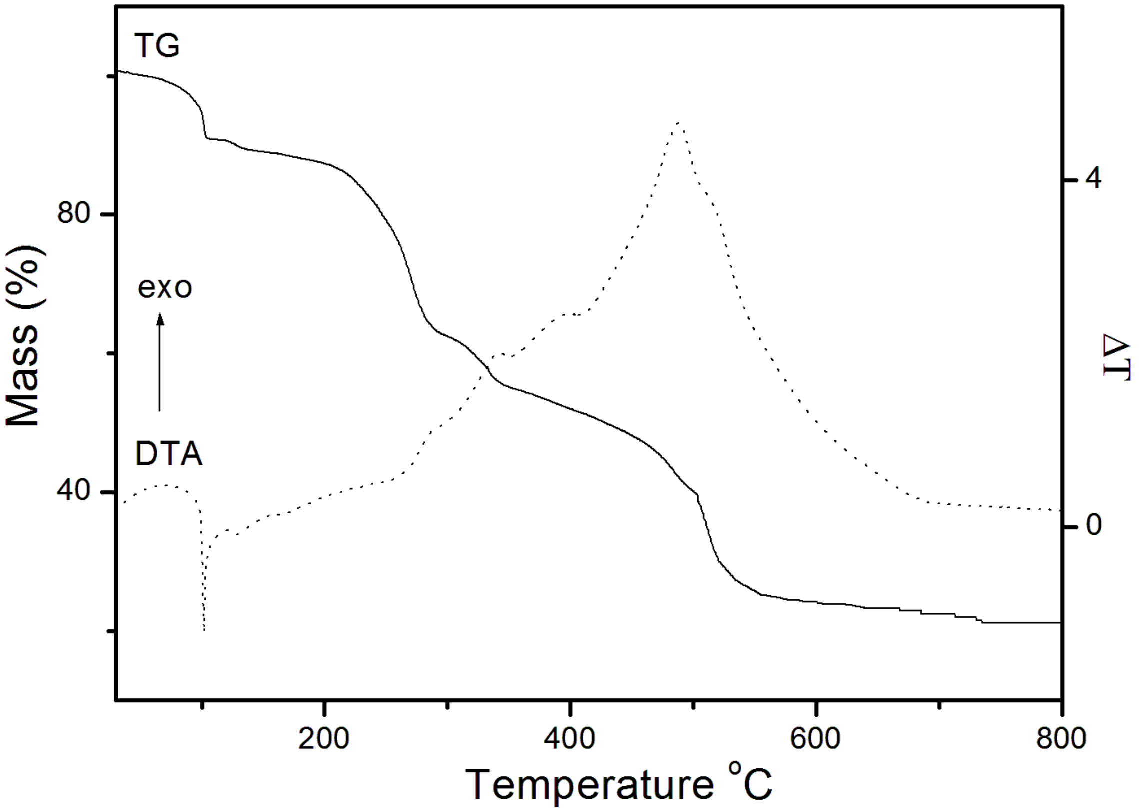


Fig. 3.121 – TG-DTA curve of **12**

Ceasium compound **13** exhibits endothermic event at 80°C and 106°C in its TG-DTA graph (Fig. 3.122). The TG curve shows a decrease in mass by 5.11 % equivalent to loss of one water molecules by 150°C. Above 200°C, the DTA curve shows only an exothermic peak at 250°C and 470°C with rapid mass loss due to decomposition of **13**. The residual mass of 45.19 % corresponds to Cs_2CO_3.

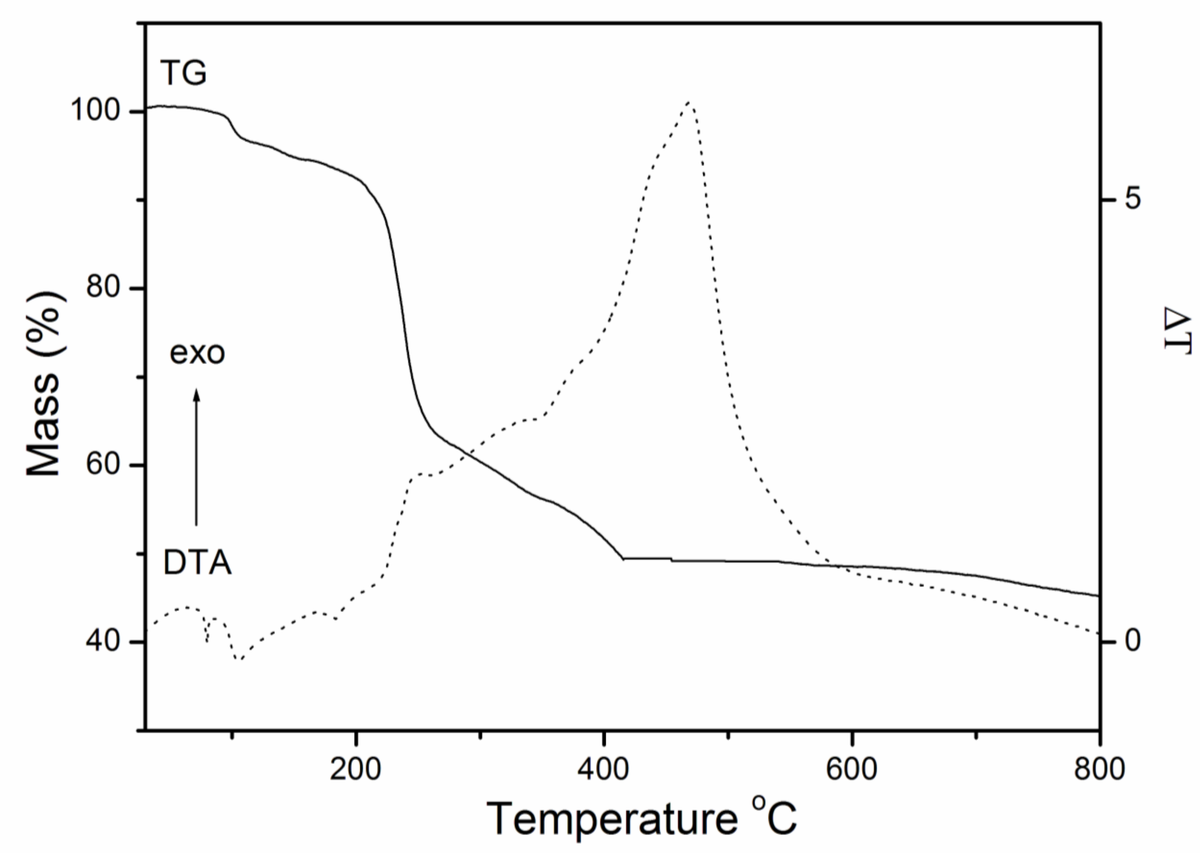


Fig. 3.122 – TG-DTA curve of **13**

The ^{1}H NMR spectrum of **10** (**11**) (Fig. S3-S4) exhibits the characteristic resonances of the aromatic protons of 2-carboxy-3-nba (2-carboxy-6-nba) ligand at δ 8.190, 8.127 and 7.514 ppm (δ 8.205, 8.142 and 7.549 ppm).

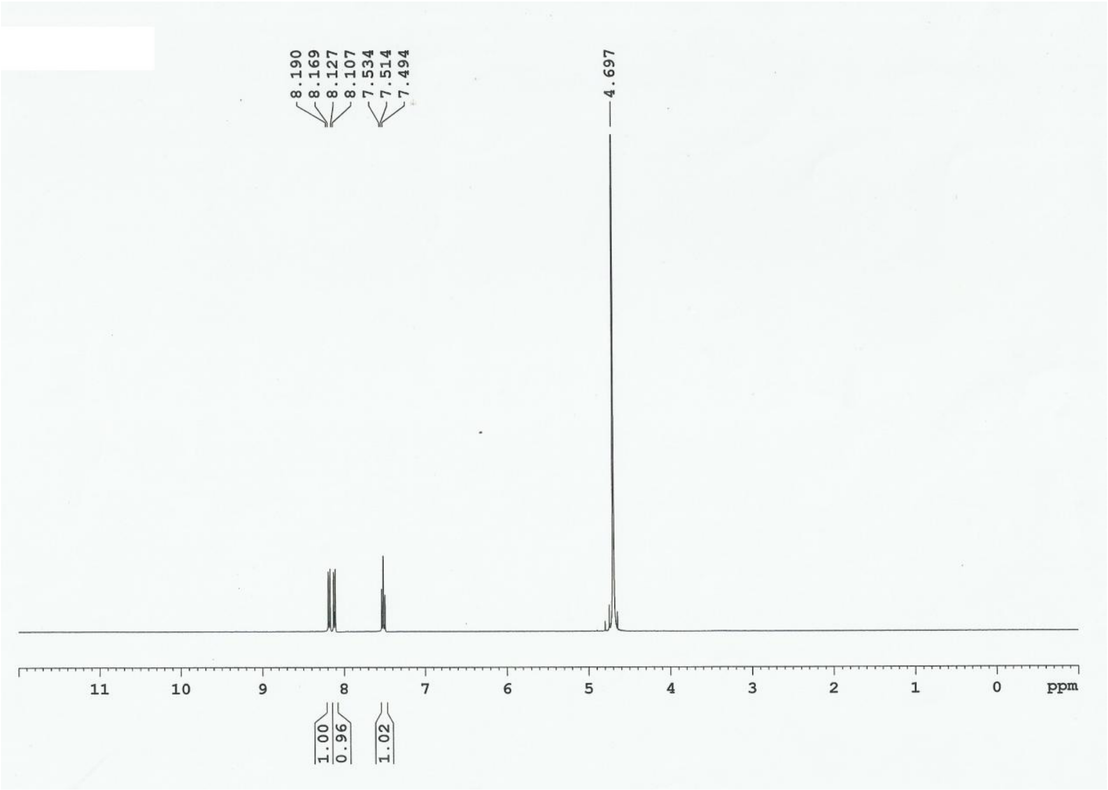


Fig. 3.123 – ^{1}H NMR spectrum of **10**

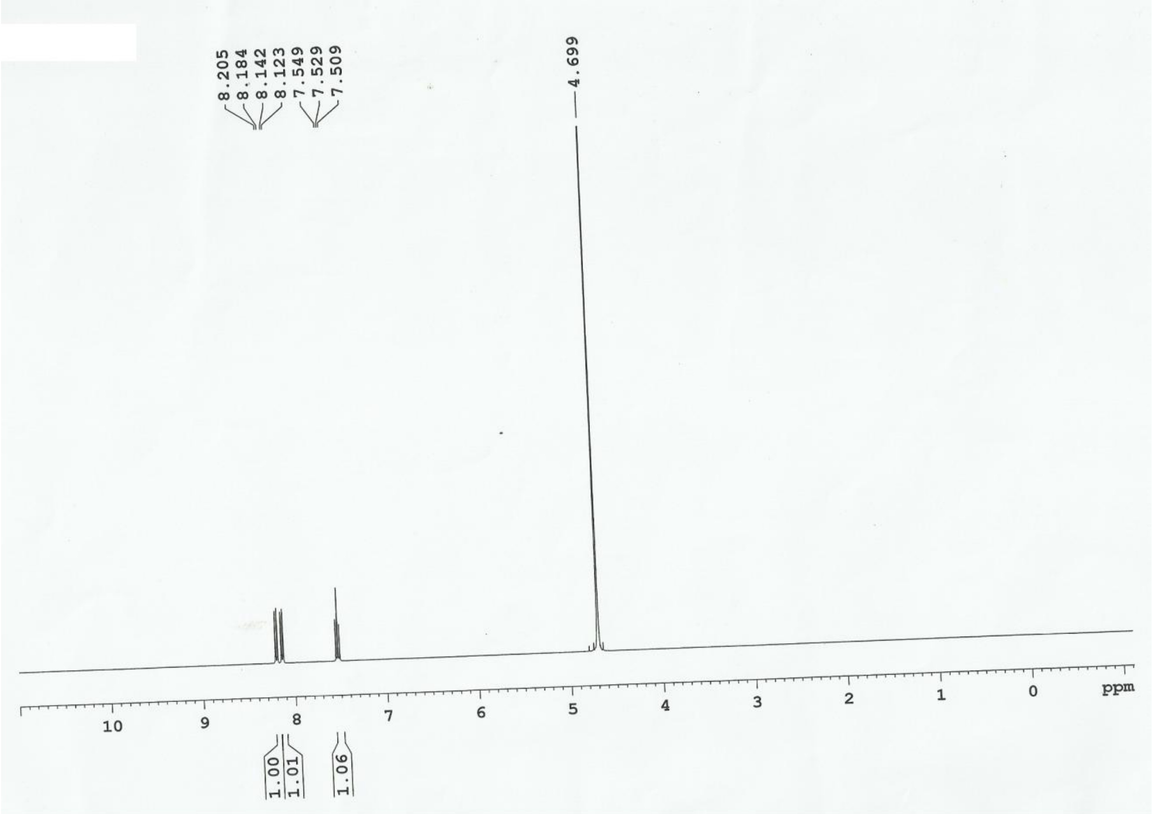


Fig. 3.124 – ^{1}H NMR spectrum of **11**

The powder pattern of **10** and **11** exhibit sharp Bragg lines indicating their crystalline nature. The experimental powder pattern of the bulk sample is in very good agreement with the theoretical powder pattern calculated from the single crystal data (*vide infra*) of **10** and **11** (Fig. 3.125-3.126). The results of powder pattern experiments, reproducible thermo analytical data and spectral data reveal that the compounds can be obtained in a state of high purity.

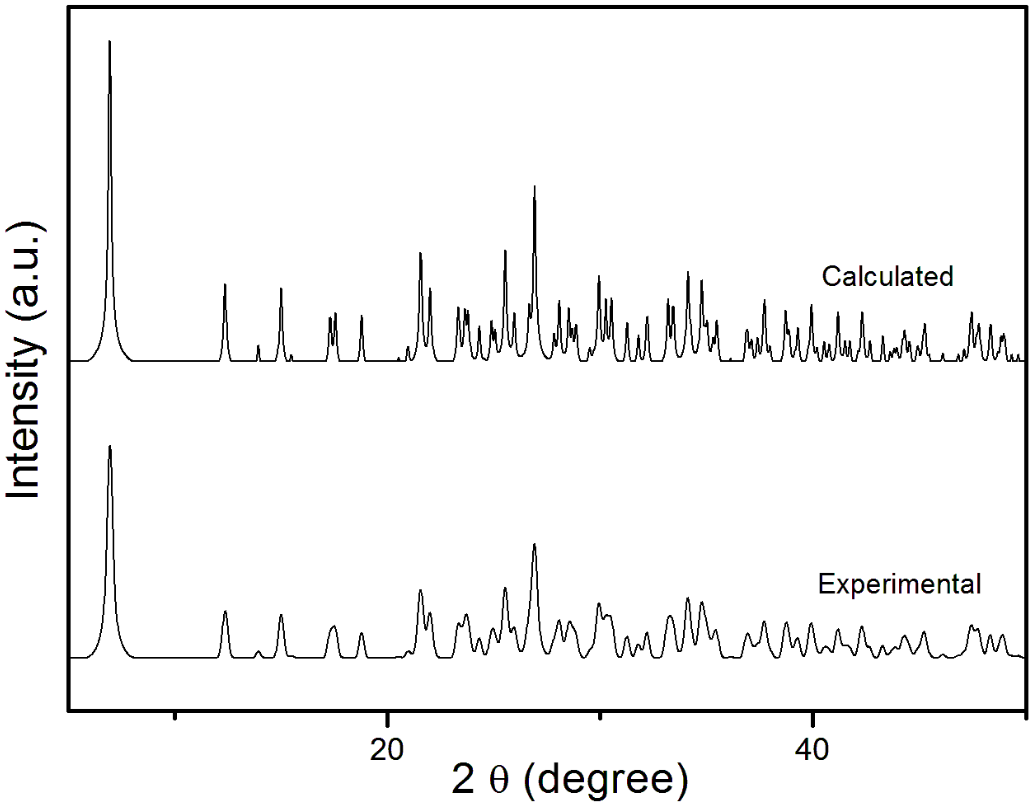


Fig. 3.125 – X-ray powder pattern of **10**

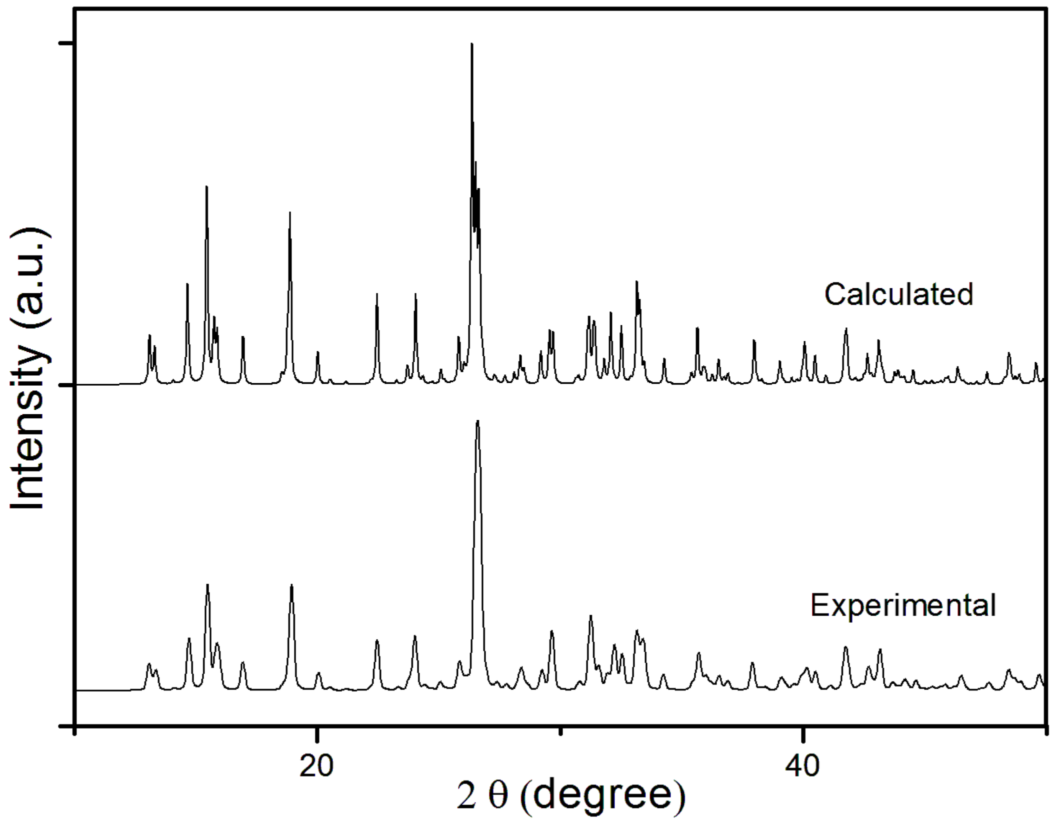


Fig. 3.126 – X-ray powder pattern of **11**

3.2.2 Description of crystal structure of [Na(2-carboxy-6-nba)(H_2O)$_3$]·H_2O **10**

Mono-deprotonated 3-nitrophthalate compound **10** containing Na(I) crystallises in the centrosymmetric triclinic *P*$\bar{1}$ space group. Its crystal structure consists of an unique Na(I) ion, crystallographically independent 2-carboxy-6-nitrobenzoate ligand, three coordinated and one lattice water molecule all of which are located in general positions (Fig. 3.127). The geometric parameters of 2-carboxy-6-nitrobenzoate (2-carboxy-6-nba) are in the normal range comparable with reported data [266-273].

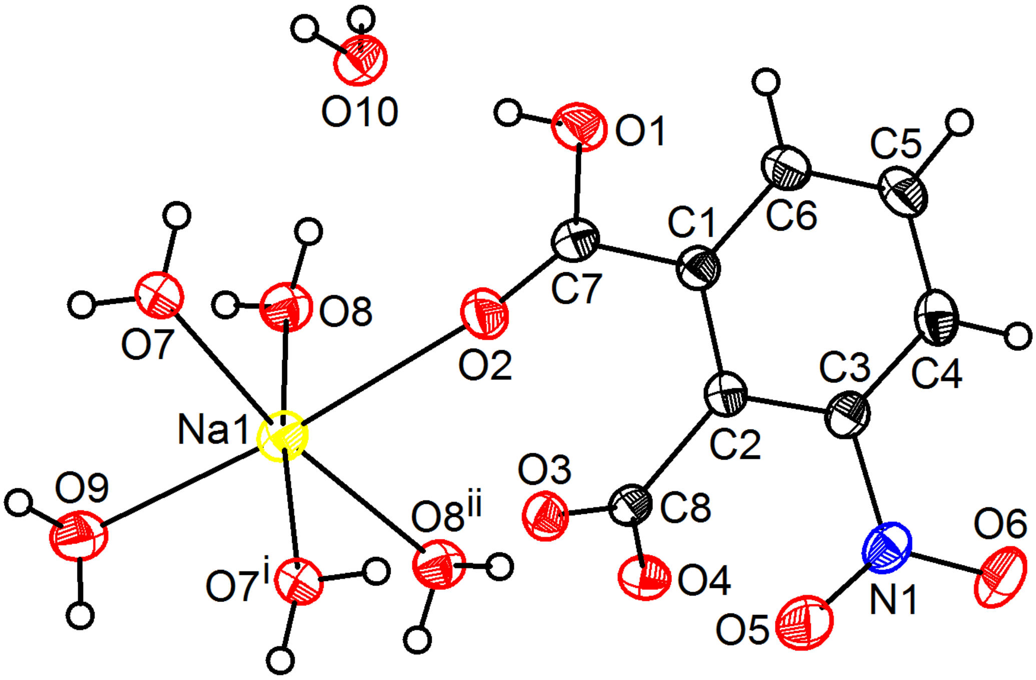


Fig. 3.127 – The crystal structure of $[Na(H_2O)_3(2\text{-carboxy-6-nba})]\cdot H_2O$ **10** showing the atom labelling scheme and the coordination sphere of Na^+ in **10**. Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as circles of arbitrary radius. Symmetry codes: i) 1-x, -0.5+y, 0.5-z; ii) 1-x, 1-y, 1-z.

The central metal ion Na^+ ion is hexacoordinated to one oxygen atom of carboxyl group of the monodentate ligand and five water molecules with $\{NaO_6\}$ coordination sphere. 2-carboxy-6-nitrobenzoate acts as a monodentate ligand coordinating to Na(I) via carboxyl group (Fig. 3.128).

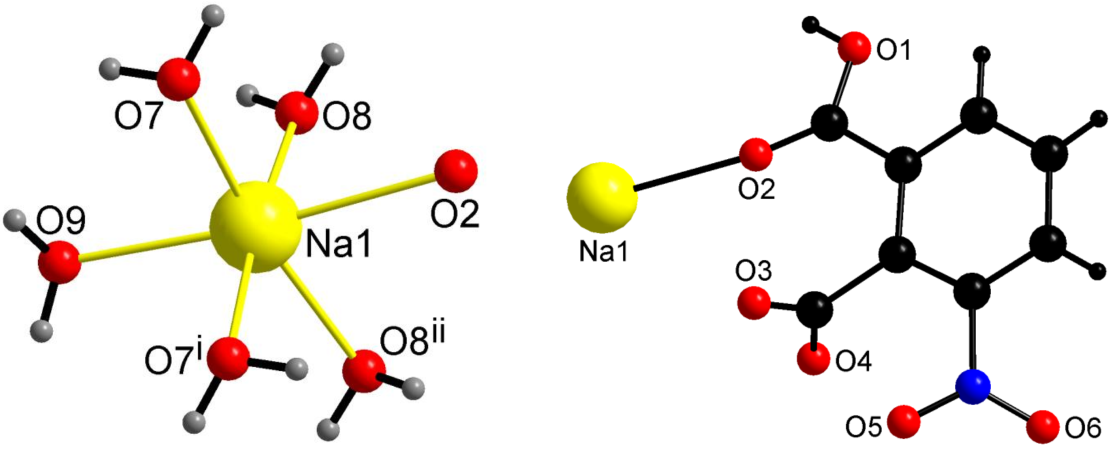


Fig. 3.128 – The coordination environment around the unique Na^+ ion in **10**. For clarity only the O atoms of the 2-carboxy-6-nba and not the entire 2-carboxy-6-nba ligand is shown. Monodentate bridging binding mode of 2-carboxy-6-nba ligand. Symmetry codes: i) 1-x, -0.5+y, 0.5-z; ii) 1-x, 1-y, 1-z.

The details of structure refinement for 9 are given in Table 3.15.

Table 3.15. Crystal data and structure refinement of $[Na(2\text{-carboxy-6-nba})(H_2O)_3]\cdot H_2O$ **10**

Empirical formula	$C_8H_{12}NNaO_{10}$
Formula weight (g mol^{-1})	305.18
Temperature (K)	170(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	6.8903(5)
b (Å)	7.5137(5)
c (Å)	12.8854(9)
α (°)	77.567(6)
β (°)	83.374(6)
γ (°)	74.389(6)
Volume (Å^3)	626.25(8)
Z	2
D_{calc} (mg/m^3)	1.618
Absorption coefficient (mm^{-1})	0.179
F(000)	316
Crystal size (mm^3)	0.08 x 0.12 x 0.35
θ range for data collection (°)	1.621 to 28.004
Index ranges	$-9 \leq h \leq 9$
	$-8 \leq k \leq 9$
	$-17 \leq l \leq 17$
Reflections collected / unique	8266/3002 (R(int) = 0.0330)
Completeness to θ = 25.00°	99.5 %
Absorption correction	Numerical
Max. and min. Transmission	0.8175 and 0.9609
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3002 / 0 /182
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0316, wR2 = 0.0857
R indices (all data)	R1 = 0.0377, wR2 = 0.0877
Largest diff. peak and hole (eÅ^{-3})	0.340 and -0.217

The Na-O bond distances range from 2.3318(9) to 2.5434(10) Å while the O-Na-O angles vary between 81.30(3) to 103.07(3)° (Table 3.16).

Table 3.16 – Selected bond lengths [Å] and angles [°] for **10**

Bond lengths			
Na(1)-O(8)	2.3318(9)	O(7)-Na(1)#2	2.4241(9)
Na(1)-O(8)#1	2.3666(10)	Na(1)-O(9)	2.4346(10)
Na(1)-O(7)	2.3825(10)	Na(1)-O(2)	2.5434(10)
Na(1)-O(7)#2	2.4241(9)	O(8)-Na(1)#1	2.3665(10)
Bond angles			
O(8)-Na(1)-O(8)#1	85.55(3)	O(7)-Na(1)-O(9)	87.53(3)
O(8)-Na(1)-O(7)	97.66(3)	O(7)#2-Na(1)-O(9)	90.86(3)
O(8)#1-Na(1)-O(7)	168.86(4)	O(8)-Na(1)-O(2)	85.86(3)
O(8)-Na(1)-O(7)#2	174.17(4)	O(8)#1-Na(1)-O(2)	81.30(3)
O(8)#1-Na(1)-O(7)#2	88.80(3)	O(7)-Na(1)-O(2)	88.28(3)
O(7)-Na(1)-O(7)#2	87.62(3)	O(7)#2-Na(1)-O(2)	91.86(3)
O(8)-Na(1)-O(9)	91.82(3)	O(9)-Na(1)-O(2)	174.90(4)
O(8)#1-Na(1)-O(9)	103.07(3)		

Symmetry transformations used to generate equivalent atoms:#1 -x+2,-y+1,-z+1
#2 -x+1,-y+1,-z+1

The {$NaO_3(H_2O)_3$} unit and the unique 2-carboxy-6-nba ligand shows (Fig. 3.129) O-H···O and C-H···O type of H-bonding interactions (Table 3.17).

Table 3.17 – Hydrogen bonding geometry [Å and °] for **10**

D-H···A	d(D-H)	H···A)	d(D···A)	<DHA	Symmetry code
O7-H7A...O3	0.84	1.91	2.7414(11)	169.7	-x+1, -y+1, -z+1
O7-H7B...O4	0.84	2.11	2.9263(11)	164.9	x, y-1, z
O8-H8A...O4	0.84	2	2.8368(12)	178	-x+2, -y+1, -z+1
O8-H8B...O10	0.84	1.96	2.7975(12)	176.1	X, y, z
O9-H9A...O3	0.84	2.03	2.8269(13)	157.9	-x+1, -y+1, -z+1
O9-H9B...O5	0.84	2.12	2.9558(13)	170.8	-x+1, -y+2, -z+1
O10-H10A...O4	0.84	1.91	2.7155(12)	160.5	x, y-1, z
O10-H10B...O3	0.84	1.91	2.7419(11)	171.1	x+1, y-1, z

D=Donor and A=Acceptor

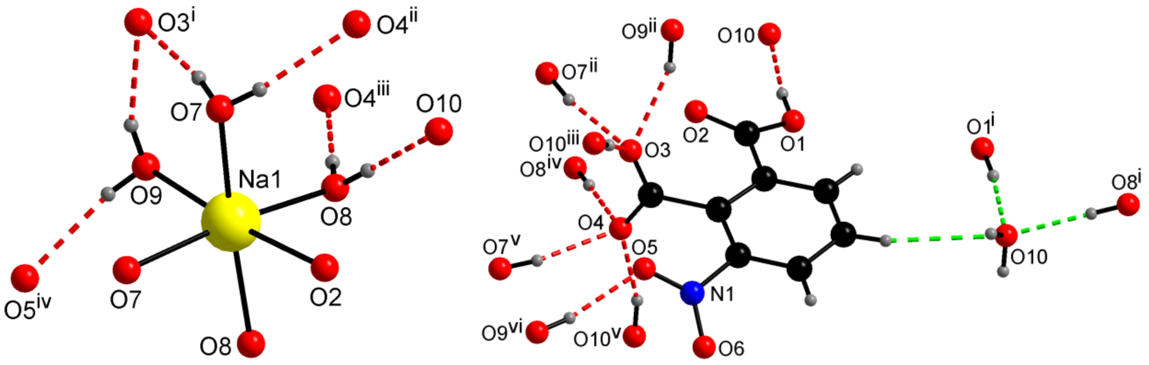


Fig. 3.129 – The H-bonding surroundings of {$NaO_3(H_2O)_3$} and the unique 2-carboxy-6-nba ligand O-H···O and C-H···O interactions (shown in broken lines) Symmetry code: i) x, y, z-1 ii) x+1, y, z-1 iii) x, y, z-1 iv) -x+2,-y+1,-z+1 v) -x+1,-y+1,-z+1

A pair of water molecules via O7 and O8 in **10** is involved in extending the structure in 1D (Fig. 3.130). 2-carboxy-6-nba and one coordinated water molecule trans to each other are arranged in a zig-zag fashion around {---$(H_2O)_2Na(H_2O)_2Na(H_2O)_2$---} chain with alternate Na1···Na1 distance of 3.449 and 3.469 Å.

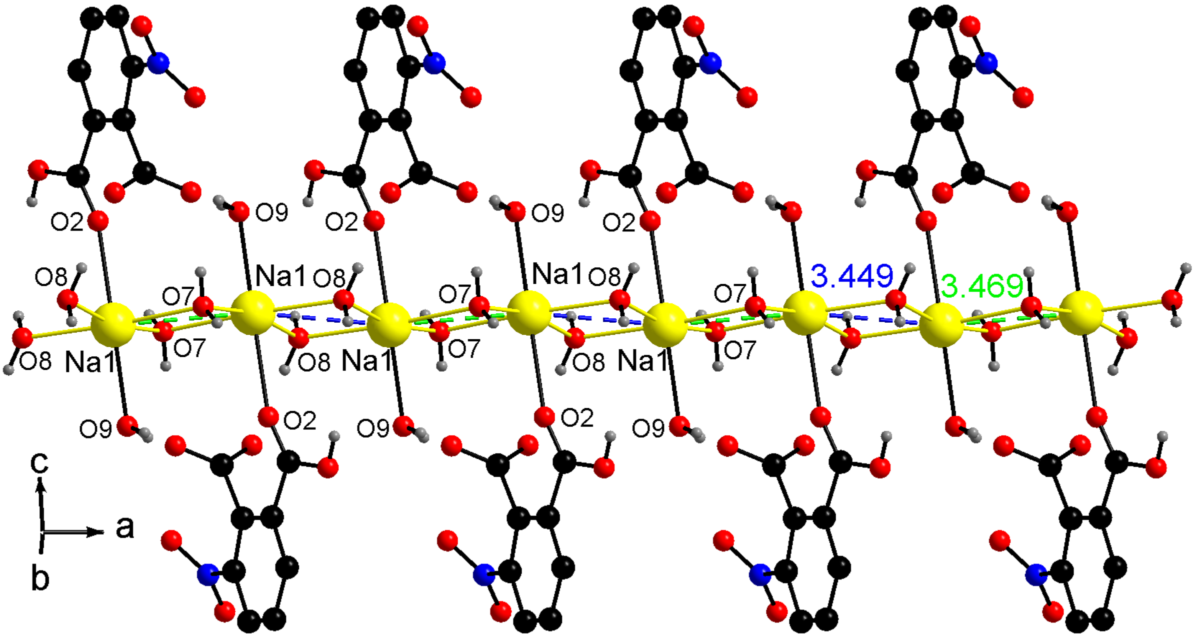


Fig. 3.130 – A portion of one dimensional chain of **10** along *a*-axis with an alternate Na1···Na1 distance of 3.449 Å (blue dash bond) and 3.469 Å (green dash bond).

The H-bonding interactions in the crystal structure leads to supramolecular architecture in **10** (Fig. 3.131).

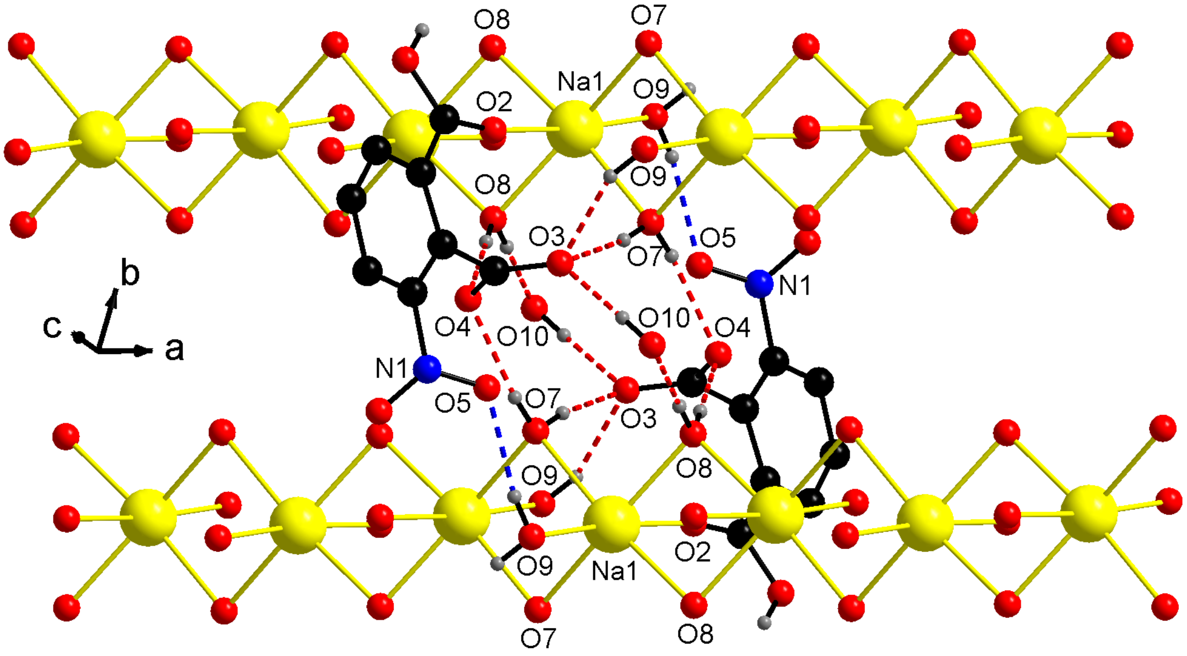


Fig. 3.131 – The supramolecular architecture of [Na(H_2O)$_3$(2-carboxy-6-nba)]·H_2O **10**. H-bonds are shown in red and blue broken lines.

3.2.3Description of crystal structure of [K(2-carboxy-3-nba)] ***11***

Anhydrous K(I) compound **11** crystallises in the centrosymmetric monoclinic *P2₁/c* space group. Its crystal structure consists of an unique K(I) ion and crystallographically independent 2-carboxy-3-nitrobenzoate ligand all of which are located in general positions (Fig. 3.132). The geometric parameters of 2-carboxy-3-nitrobenzoate (2-carboxy-3-nba) are in the normal range comparable with reported data [266-273].

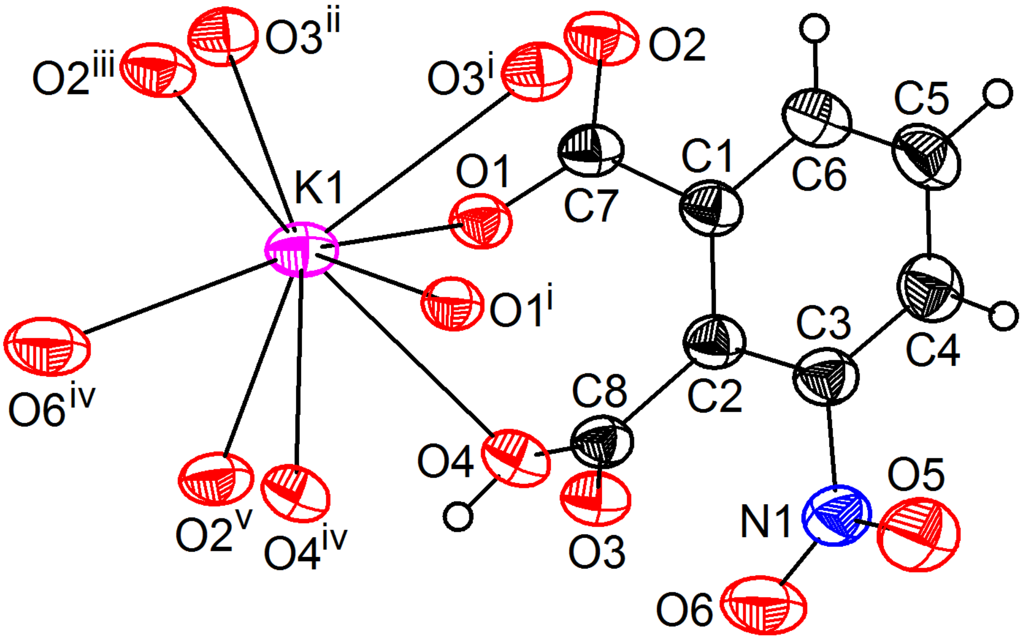


Fig. 3.132 – The crystal structure of [K(2-carboxy-3nba)] **11** showing the atom labelling scheme and the coordination sphere of K^+ in **11**. Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as circles of arbitrary radius.

The central metal ion K^+ ion is nonacoordinated to two oxygen atoms of carboxylate group, two oxygen atoms of carboxyl group and one oxygen atom of nitro group with $\{KO_9\}$ coordination sphere (Fig. 3.133).

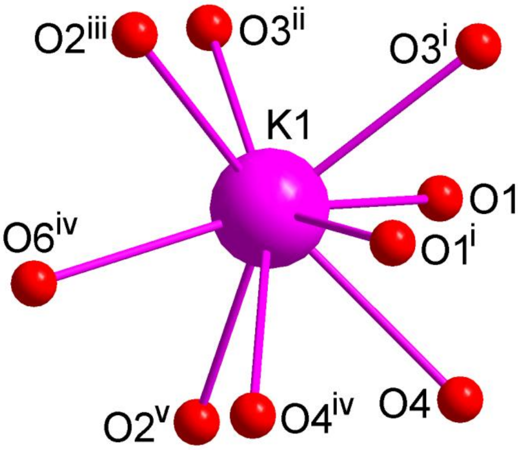


Fig. 3.133 – The coordination environment around the unique K^+ ion in **11**. For clarity only the O atoms of the 2-carboxy-3-nba and not the entire 2-carboxy-3-nba ligand is shown. Symmetry codes: i) 1-x, 2-y, 1-z; ii) 1-x, 0.5+y, 0.5-z; iii) x, 1.5-y, 0.5+z; iv) 1-x, 1-y, 1-z; v) 1-x, -0.5+y, 0.5-z.

The details of structure refinement for **11** are given in Table 3.18.

Table 3.18. Crystal data and structure refinement of [K(2-carboxy-3-nba)] **11**

Empirical formula	$C_8H_4KNO_6$
Formula weight (g mol^{-1})	249.22
Temperature (K)	170(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	13.0237(8)
b (Å)	8.6490(4)
c (Å)	8.2763(4)
α (°)	90°
β (°)	102.771(4)
γ (°)	90°
Volume (Å^3)	909.20(8)
Z	4
D_{calc} (mg/m^3)	1.821
Absorption coefficient (mm^{-1})	0.598
F(000)	504
Crystal size (mm^3)	0.08 x 0.12 x 0.20
θ range for data collection (°)	1.603 to 26.00
Index ranges	$-16 \leq h \leq 16$ $-10 \leq k \leq 10$ $-8 \leq l \leq 10$
Reflections collected / unique	6839 / 1783 [R(int) = 0.0651]
Completeness to θ = 25.00°	99.8%
Absorption correction	Numerical
Max. and min. Transmission	0.9287 and 0.7856
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1783 / 0 / 145
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1273
R indices (all data)	R1 = 0.0529, wR2 = 0.1324
Largest diff. peak and hole (eÅ^{-3})	0.490 and -0.547

The K-O bond distances range from 2.7328(18) to 3.108(3) Å while the O-K-O angles vary between 49.75(4) to 162.53(5)° (Table 3.19).

Table 3.19 – Selected bond lengths [Å] and angles [°] for **11**

Bond lengths			
K(1)-O(2)#1	2.7328(18)	K(1)-O(4)	2.9522(18)
K(1)-O(3)#2	2.7552(17)	K(1)-O(3)#3	2.9630(18)
K(1)-O(1)	2.8190(17)	K(1)-O(4)#5	3.0226(17)
K(1)-O(1)#3	2.8324(17)	K(1)-O(6)#5	3.108(3)
K(1)-O(2)#4	2.879(2)		
Bond angles			
O(2)#1-K(1)-O(3)#2	104.73(5)	O(1)#3-K(1)-O(3)#3	61.21(5)
O(2)#1-K(1)-O(1)	84.40(5)	O(2)#4-K(1)-O(3)#3	83.31(5)
O(3)#2-K(1)-O(1)	68.92(5)	O(4)-K(1)-O(3)#3	83.04(5)
O(2)#1-K(1)-O(1)#3	113.68(5)	O(2)#1-K(1)-O(4)#5	68.39(5)
O(3)#2-K(1)-O(1)#3	141.37(5)	O(3)#2-K(1)-O(4)#5	162.53(5)
O(1)-K(1)-O(1)#3	109.90(6)	O(1)-K(1)-O(4)#5	124.37(5)
O(2)#1-K(1)-O(2)#4	130.39(7)	O(1)#3-K(1)-O(4)#5	49.75(4)
O(3)#2-K(1)-O(2)#4	76.71(5)	O(2)#4-K(1)-O(4)#5	95.35(5)
O(1)-K(1)-O(2)#4	136.77(5)	O(4)-K(1)-O(4)#5	61.98(5)
O(1)#3-K(1)-O(2)#4	81.53(5)	O(3)#3-K(1)-O(4)#5	110.15(5)
O(2)#1-K(1)-O(4)	66.15(5)	O(2)#1-K(1)-O(6)#5	75.06(6)
O(3)#2-K(1)-O(4)	131.34(5)	O(3)#2-K(1)-O(6)#5	107.99(5)
O(1)-K(1)-O(4)	62.75(4)	O(1)-K(1)-O(6)#5	157.82(6)
O(1)#3-K(1)-O(4)	65.64(5)	O(1)#3-K(1)-O(6)#5	86.39(5)
O(2)#4-K(1)-O(4)	147.09(5)	O(2)#4-K(1)-O(6)#5	58.41(5)
O(2)#1-K(1)-O(3)#3	146.09(6)	O(4)-K(1)-O(6)#5	114.39(5)
O(3)#2-K(1)-O(3)#3	84.66(5)	O(3)#3-K(1)-O(6)#5	133.72(5)
O(1)-K(1)-O(3)#3	68.45(5)	O(4)#5-K(1)-O(6)#5	55.18(5)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y-1/2,-z+1/2 #2 -x+1,y+1/2,-z+1/2 #3 x,-y+3/2,z+1/2 #4 -x+1,-y+2,-z+1 #5 -x+1,-y+1,-z+1 #6 x,-y+3/2,z-1/2

The 2-carboxy-3-nba ligand shows a μ_6-nonadentate binding mode in the crystal structure with carboxy, carboxylate and nitro group involved in bonding (Fig. 3.134).

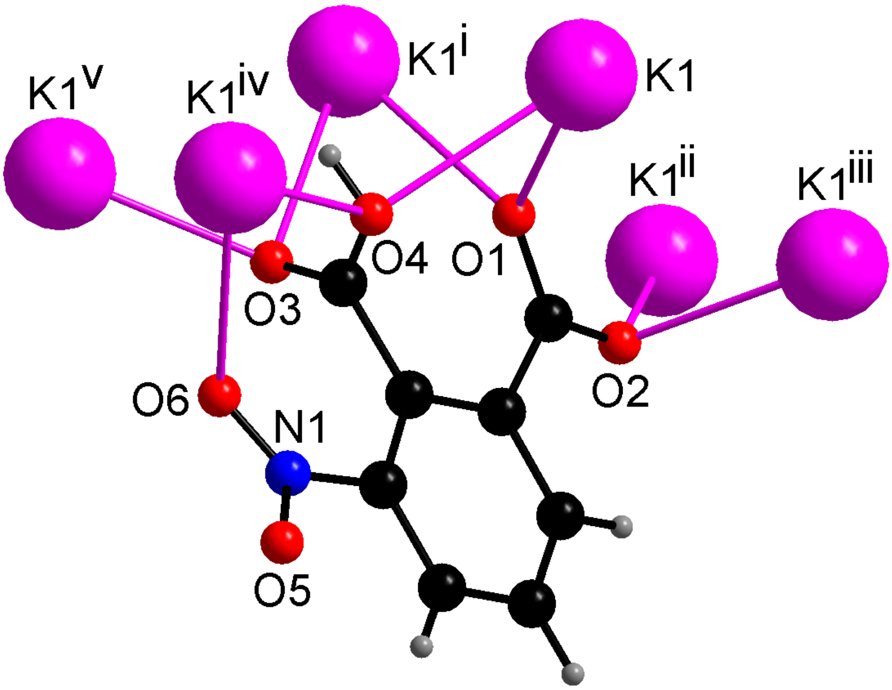


Fig. 3.134 – μ_6-nonadentate bridging binding mode of 2-carboxy-3-nba ligand in **11**. Symmetry codes: i) 1-x, -0.5+y, 0.5-z; ii) 1-x, 1-y, 1-z; iii) x, 1.5-y, -0.5+z; iv) 1-x, 0.5+y, 0.5-z; v) 1-x, 2-y, 1-z

It extends the structure in two directions via O1 and O2 along *c* axis while O3 and O4 along *b* axis forming a sheet parallel to *bc* plane (Fig. 3.135). The 2-D sheet is non-planar with a uniform K···K separation of 4.166 Å along *c*-axis arranged in zig-zag fashion and two alternate distances of 4.230 and 5.122 Å along *b* axis. It is observed that two oxygens are being shared by the adjacent K^+ ions in either direction. Along *c* direction it forms repeating K1···O1···K1···O2 tetramer whereas along *b* direction forms alternate K1···O3···K1···O3 and K1···O4···K1···O4 tetramer units with shared K1 edges (Fig. 3.135).

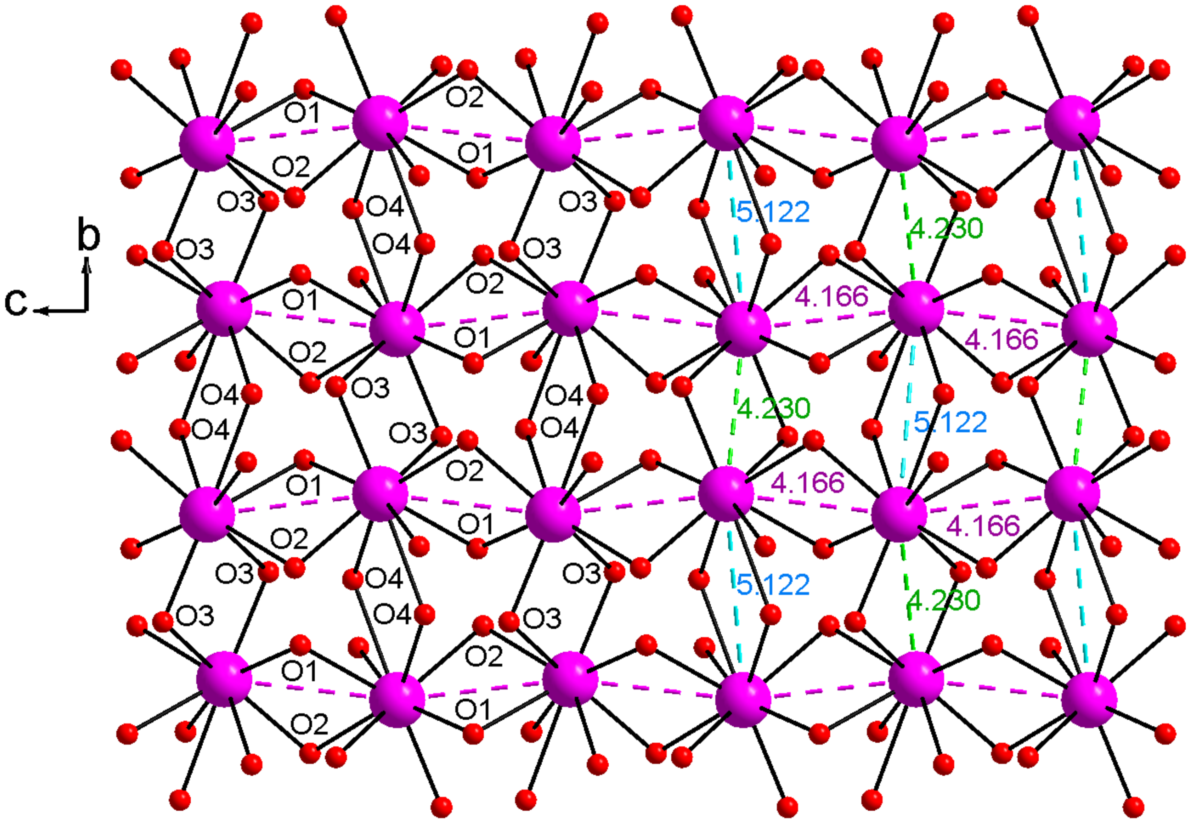


Fig. 3.135 – A portion of two dimensional zig-zag sheet/layer of **11** in *bc* plane with K1···K1 distance of 4.166 Å (pink dash bond) along *c* axis and alternate 4.230 Å (green dash bond) and 5.122 Å (blue dash bond) along *b* axis.

Interestingly, the -NO_2 group further participates in building a supramolecular structure via C5-H5···O5 H-bonding with the symmetry code 2-x, 0.5+y, 1.5-z (Table 3.20) connecting the two layers along a-axis resulting into a 3D supramolecular architecture of **11** (Fig. 3.136).

Table 3.20 – Hydrogen bonding geometry [Å and °] for **11**

D-H···A	d(D-H)	H···A)	d(D···A)	<DHA	Symmetry code
C5-H5···O5	0.95	2.506	3.257	136.06	2-x, 0.5+ y, 1.5-z
O4-H4A···O1	0.84	1.640	2.469	168.57	1-x, -0.5+y, 0.5-z

D=Donor and A=Acceptor

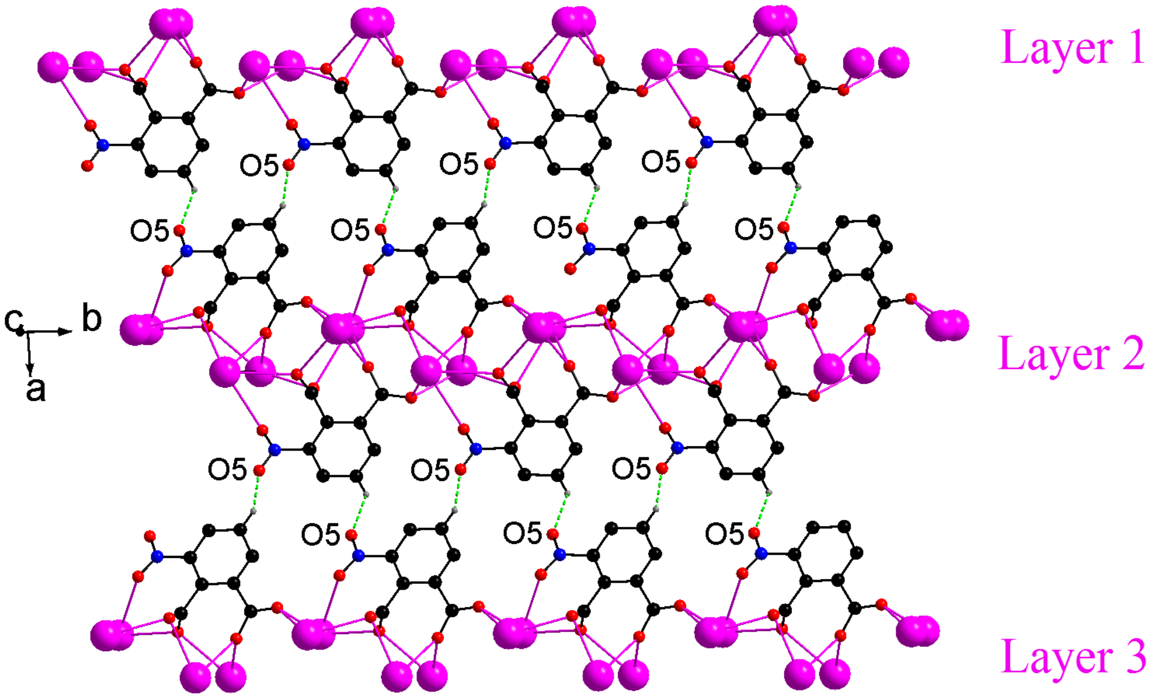


Fig. 3.136 – A portion of supramolecular architecture of **11** along *c* axis via C5–H5···O5 H-bonding interaction connecting the two layers.

3.2.4 Description of crystal structure of [Cs(2-carboxy-6-nba)(H_2O)] **13**

Ceasium containing compound **13** crystallises in the centrosymmetric orthorhombic *Pcca* space group. Its crystal structure consists of an unique Cs(I) ion, one crystallographically independent 2-carboxy-6-nba ligand and a coordinated water molecule all of which are located in general positions (Fig. 1.137). The geometric parameters of 2-carboxy-6-nba are in the normal range (Table 3.21).

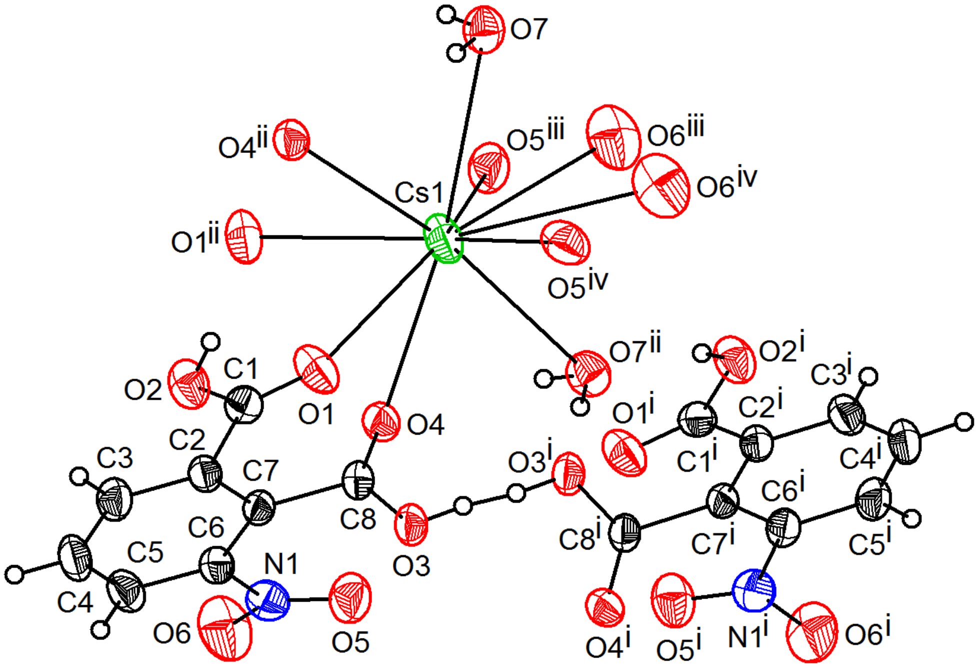


Fig. 3.137 – The crystal structure of [Cs(2-carboxy-6-nba)(H_2O)] **13** showing the atom labelling scheme and the coordination sphere of Cs(I) in **13**. Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as spheres of arbitrary radius. Symmetry code: i) 1.5-x, 1-y, z; ii) 1-x, y, 0.5-z; iii) x, 1-y, -0.5+z; iv) 1-x, 1-y, 1-z.

A unique metal ion Cs1 is decacoordinated to ten oxygen atoms from four symmetry related 3-nitrophthalate anion and two symmetry related water molecules (Fig. 3.138).

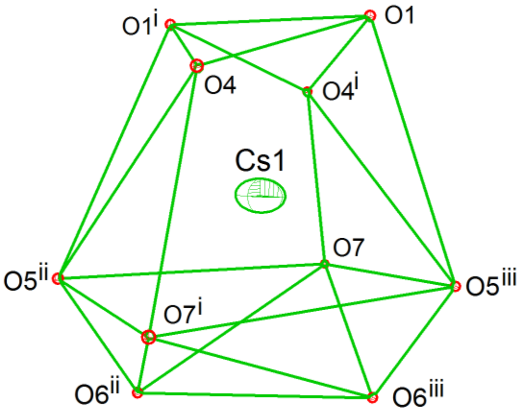


Fig. 3.138 –The distorted decahedron {CsO_{10}} coordination around Cs^{+1} in **13**. Symmetry code: i) 1-x, y, 0.5-z; ii) 1-x, 1-y, 1-z; iii) x, 1-y, -0.5+z.

The details of structure refinement for **11** are given in Table 3.18.

Table 3.21 - Crystal data and structure refinement for [Cs(2-carboxy-6-nba)(H_2O)] **13**

Empirical formula	$C_{16}H_{13}N_2O_{14}Cs$
Formula weight (g mol^{-1})	590.19
Temperature (K)	296(2) K
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pcca
Unit cell dimensions	
a (Å)	13.1768(5)
b (Å)	11.6552(3)
c (Å)	13.4456(5)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	2064.95(12)
Z	4
D_{calc} (mg/m^3)	1.898
Absorption coefficient (mm^{-1})	1.872
F(000)	1160
Crystal size (mm^3)	0.15 x 0.10 x 0.10
θ range for data collection (°)	3.402 to 28.407
Index ranges	$-17 \leq h \leq 17$ $-15 \leq k \leq 15$ $-18 \leq l \leq 16$
Reflections collected / unique	42355 / 3551 [R(int) = 0.0240]
Completeness to θ = 25.00°	97.2%
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.7462 and 0.5603
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3551 / 0 / 154
Goodness-of-fit on F^2	1.094
Final R indices [I>2sigma(I)]	R1 = 0.0245, wR2 = 0.0481
R indices (all data)	R1 = 0.0353, wR2 = 0.0505
Largest diff. peak and hole (e Å^{-3})	0.682 and -0.747

The Cs-O bond distances range from 3.075(3) to 3.649(2) Å while the O-Cs-O angles vary between 35.86(6) to 165.69(7)° indicating a distorted {CsO_{10}} decahedron (Table 3.22).

Table 3.22 – Selected Bond lengths [Å] and angles [°] for **13**

Bond lengths

Cs1-O1	3.075(2)	Cs1-O5#1	3.300(3)
Cs1-O4	3.116(2)	Cs1-O5#3	3.300(3)
Cs1-O7	3.649(2)	Cs1-O6#1	3.582(3)
Cs1-O1#2	3.075(2)	Cs1-O6#3	3.582(3)
Cs1-O4	3.116(2)	Cs1-O7#2	3.649(2)

Bond angles

O5#1-Cs1-O5#3	132.19(8)	O1#2-Cs1-O7#2	112.55(6)
O1-Cs1-O6#1	165.69(7)	O4#2-Cs1-O7#2	170.00(5)
O1#2-Cs1-O6#1	119.39(7)	O4-Cs1-O7#2	57.30(5)
O4#2-Cs1-O6#1	127.32(6)	O5#1-Cs1-O7#2	60.05(5)
O4-Cs1-O6#1	109.89(6)	O5#3-Cs1-O7#2	99.80(6)
O5#1-Cs1-O6#1	35.86(6)	O6#1-Cs1-O7#2	58.12(6)
O5#3-Cs1-O6#1	96.33(6)	O6#3-Cs1-O7#2	80.03(6)
O1-Cs1-O6#3	119.39(7)	O7-Cs1-O7#2	132.11(7)
O1#2-Cs1-O6#3	165.69(7)	O1-Cs1-O1#2	64.70(10)
O4#2-Cs1-O6#3	109.89(6)	O1-Cs1-O4#2	66.90(6)
O4-Cs1-O6#3	127.32(6)	O1#2-Cs1-O4#2	57.78(5)
O5#1-Cs1-O6#3	96.33(6)	O1-Cs1-O4	57.78(5)
O5#3-Cs1-O6#3	35.86(6)	O1#2-Cs1-O4	66.90(6)
O6#1-Cs1-O6#3	60.48(9)	O4#2-Cs1-O4	113.58(7)
O1-Cs1-O7	112.55(6)	O1-Cs1-O5#1	140.60(6)
O1#2-Cs1-O7	107.60(6)	O1#2-Cs1-O5#1	84.95(6)
O4#2-Cs1-O7	57.30(5)	O4#2-Cs1-O5#1	118.37(5)
O4-Cs1-O7	170.00(5)	O4-Cs1-O5#1	88.21(5)
O5#1-Cs1-O7	99.80(6)	O1-Cs1-O5#3	84.95(6)
O5#3-Cs1-O7	60.05(5)	O1#2-Cs1-O5#3	140.60(6)
O6#1-Cs1-O7	80.03(6)	O4#2-Cs1-O5#3	88.21(5)
O6#3-Cs1-O7	58.12(6)	O4-Cs1-O5#3	118.37(5)
O1-Cs1-O7#2	107.59(6)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1; #2 -x+1,y,-z+1/2; #3 x,-y+1,z-1/2

The unique 3-nitrophthalate ligand in the crystal structure exhibits a μ_2-bridging tetradentate binding coordination mode (Fig. 3.139).

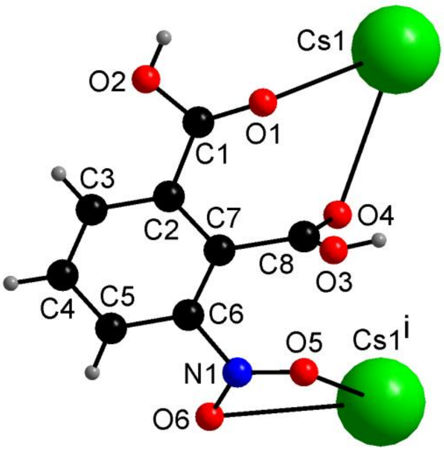


Fig. 3.139 –The μ$_2$-bridging tetradentate binding mode of 2-carboxy-6-nba ligand in **13**.

The crystal structure reveals that **13** is a 1D coordination polymer with a pair of 3-nitrophthalate ligand extending the structure in one dimension via its μ$_2$-bridging tetradentate binding mode using O1, O4, O5 and O6 oxygen atoms (Fig. 3.140). The 1D chain extends in a zig-zag fashion along c-axis with a uniform Cs1···Cs1 distance of 6.917 Å.

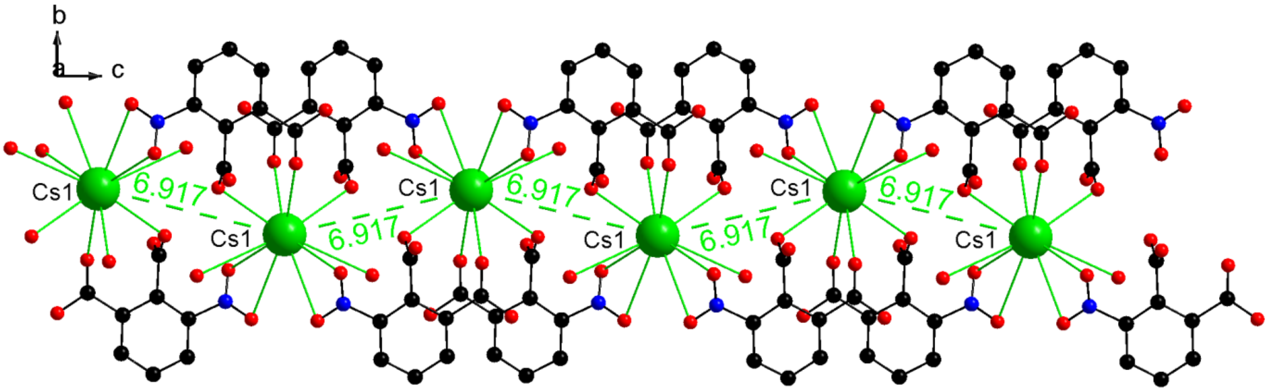


Fig. 3.140 – A portion of the infinite chain extending along c-*axis* with Cs···Cs separation of 6.917 Å due to μ$_2$-bridging tetradentate coordination mode of 3-nphth ligand in **13**.

The structure reveals that the oxygen atoms of carboxylate and $–NO_2$ group of 3-nitrophthalate ligand and the coordinated water molecule are involved in O-H···O, C-H···O H-bonding interactions (Table 3.23) (Fig. 3.141). These inter- and intramolecular H-bonding interactions lead to supramolecular architecture along *b*-axis with Cs1···Cs1 distance of 11.655 Å (Fig. 3.141).

Table 3.23 - Hydrogen bonding geometry [Å and °] for [Cs(2-carboxy-6-nba)(H_2O)] **13**

D-H···A	d(D-H)	(H···A)	d(D···A)	<DHA	Symmetry code
C3-H3 ···O2	0.930(.003)	2.394(.002)	2.728(.004)	100.92(0.19)	x, y, z
C3-H3 ···O6	0.930(.003)	2.485(.003)	3.303(.004)	146.88(0.19)	x,-y+2,+z-1/2
C4 -H4 ···O7	0.930(.003)	2.822(.002)	3.666(.004)	151.44(0.19)	-x+1,+y+1,-z+1/2
C5 -H5 ···O2	0.930(.003)	2.489(.002)	3.335(.004)	151.31(0.19)	x,-y+2,+z+1/2
O2-H2A ···O7	0.820(.002)	1.801(.002)	2.614(.003)	170.83(0.17)	-x+1,-y+1,-z
O7-H7B ···O1	0.844(.031)	2.946(.036)	3.245(.003)	103.20(2.68)	-x+1,-y+1,-z
O3-H3A ···O4	0.820(.002)	2.701(.002)	3.195(.003)	120.40(0.14)	-x+1/2+1,-y+1,+z
O3-H3A ···O3	0.820(.002)	1.626(.002)	2.444(.003)	175.55(0.15)	-x+1/2+1,-y+1,+z
O7-H7B ···O4	0.844(.031)	1.993(.031)	2.794(.003)	158.22(2.92)	x,-y+1,+z-1/2
O7-H7B ···O4	0.844(.031)	2.883(.030)	3.277(.003)	110.63(2.24)	-x+1,+y,-z+1/2
O7-H7A ···O4	0.843(.033)	2.961(.037)	3.277(.003)	104.66(2.84)	-x+1,+y,-z+1/2
O7-H7A ···O3	0.843(.033)	1.966(.035)	2.802(.003)	171.09(3.00)	x-1/2,-y+1,-z+1/2

D=Donor and A=Acceptor

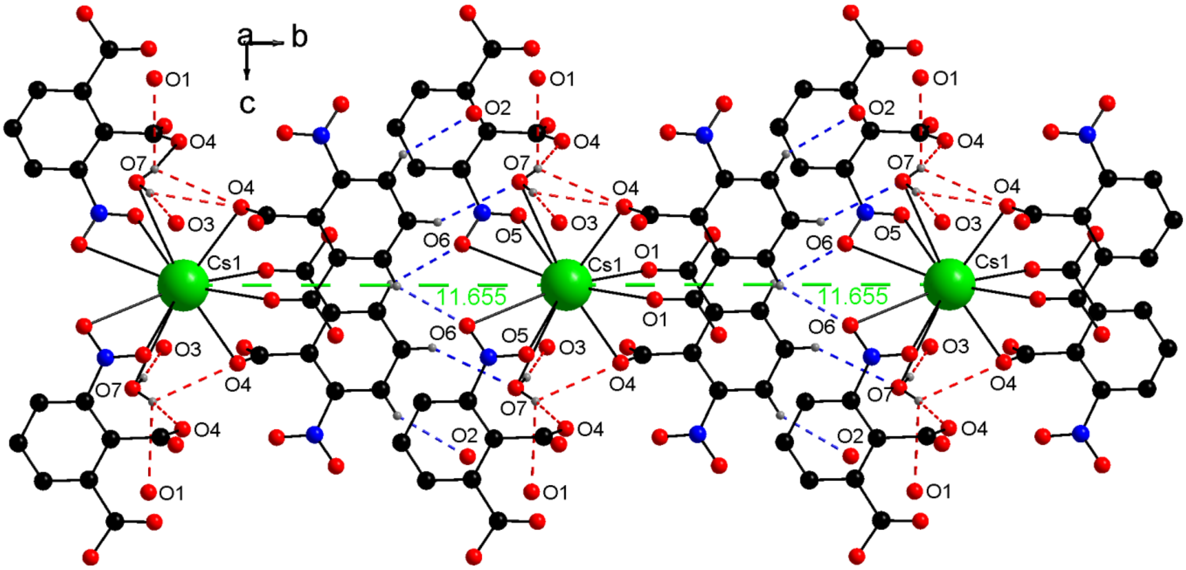


Fig. 3.141 - The two dimensional (2D) supramolecular architecture in **13** formed due to O-H···O and C-H···O interaction along *b*-axis.

The central metal atoms are organised in a zig zag fashion in crystallographic *bc* plane (Fig. 3.142). with Cs···Cs distance of 6.917 Å along *c*-axis and 11.655 Å along *b*-axis

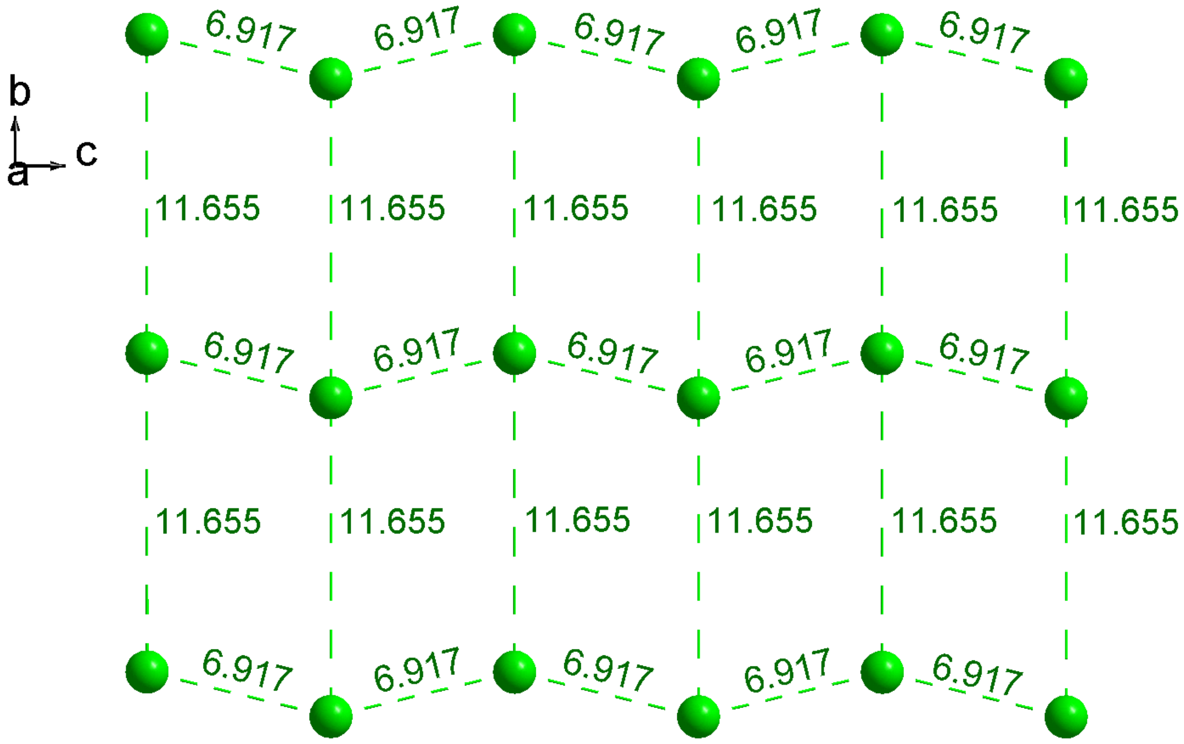
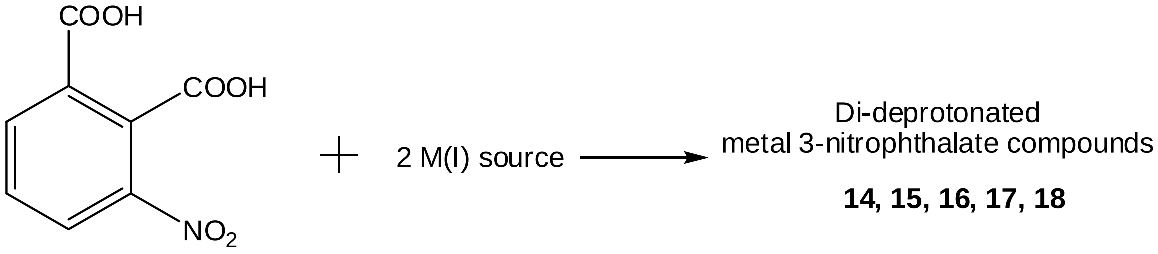


Fig. 3.142 – Disposition of Cs(I) centres in the crystal structure of **13** forming 2D architecture with Cs···Cs distance of 6.917 Å along *c*-axis and 11.655 Å along *b*-axis.

A general protocol for the synthesis of metal 3-nitrophthalate in 2:1 molar ratio is depicted in Scheme 3.5.



Scheme 3.5 - Syntheses of di-deprotonated 3-nitrophthalates.

3.1.5 Synthetic aspects, spectral characteristics and thermal studies for [Li_2(3-npht)(H_2O)$_3$] **14,** *[Na_2(3-npht)(H_2O)$_2$]* **15,** *[K_2(3-npht)]* **16,** *[Rb_2(3-npht)]* **17** and *Synthesis of [Cs_2(3-npht)]* **18**

Compound **14-18** were prepared from an aqueous medium acid base reaction of respective metal carbonates with 3-nitrophthalic acid (3-nphtH$_2$) in 2:1 molar ratio respectively. Crystals suitable for X-ray structure analysis were obtained by recrystallising it from an aqueous solution. The composition of **14-18** were determined based on analytical data and metal carbonate formed on pyrolysis at 800°C.

The IR spectra of all compounds studied in this work exhibit several signals in the mid-IR region indicating the presence of organic moieties (Fig. 3.143-3.1147). An analysis of the signal in the region 1680-1710 cm^{-1} for –COOH gives information on resultant mono- or di- deprotonated 3-nitrophthalate ligand. The absence of –COOH signal in **14-18** indicates complete deprotonation of the ligand and formation of 3-nitrophthalate dianion. In the IR spectrum **14** a band at 1604 in **14** (1589 in **15**; 1658 in **16**; 1589 in **17**; 1589 in **18**) can be assigned for the asymmetric stretching vibration of the carboxylate group (υ_{asym}) and the bands observed at 1454 and 1394 in **14**; 1452 in **15**; 1460 in **16**; 1450 in **17**; 1446 in **18**) for symmetric stretching vibration (υ_{sym}). The IR stretching vibrations expected for the $\upsilon_{N\text{-}O}$ vibration of the $-NO_2$ group of the ligand is seen at 1354 (**14**), 1352 (**15**), 1340 (**16**), 1356 (**17**) and 1356 (**18**). Interestingly sharp signal assignable for $-NO_2$ group stretching vibrations was observed in Raman spectrum (Fig. 3.143-3.147) of the compounds at 1347 (**14**), 1349 (**15**), 1334 (**16**), 1343 (**17**) and 1333 (**18**).

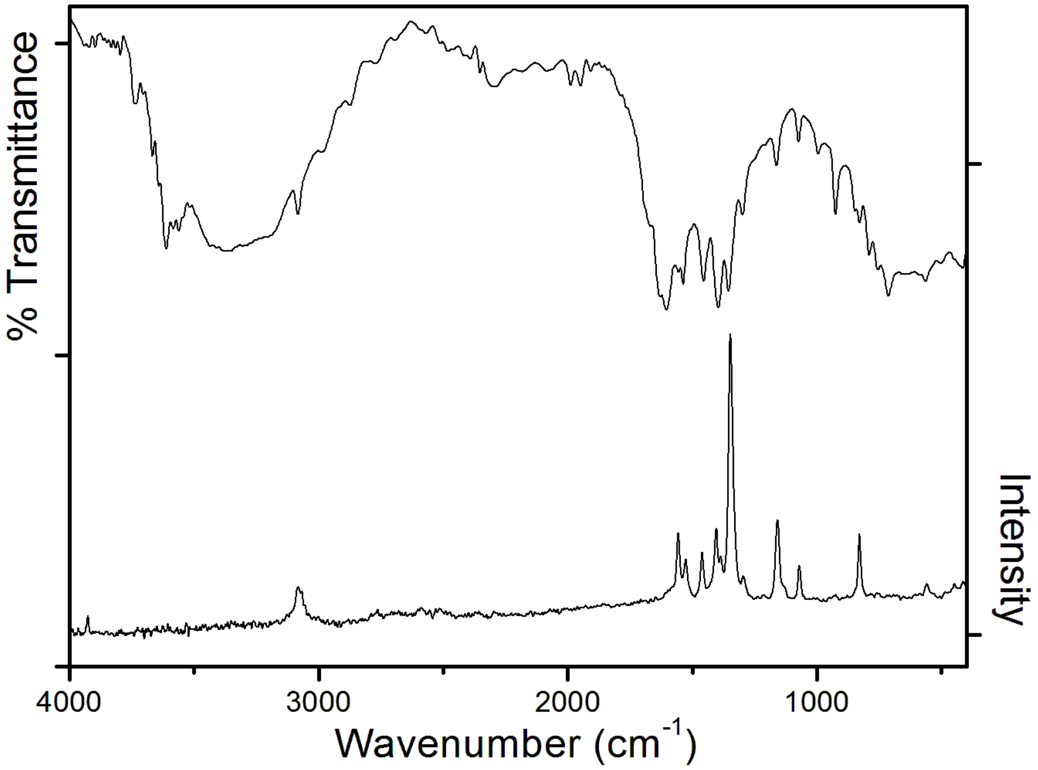


Fig. 3.143– IR and Raman spectrum of **14**

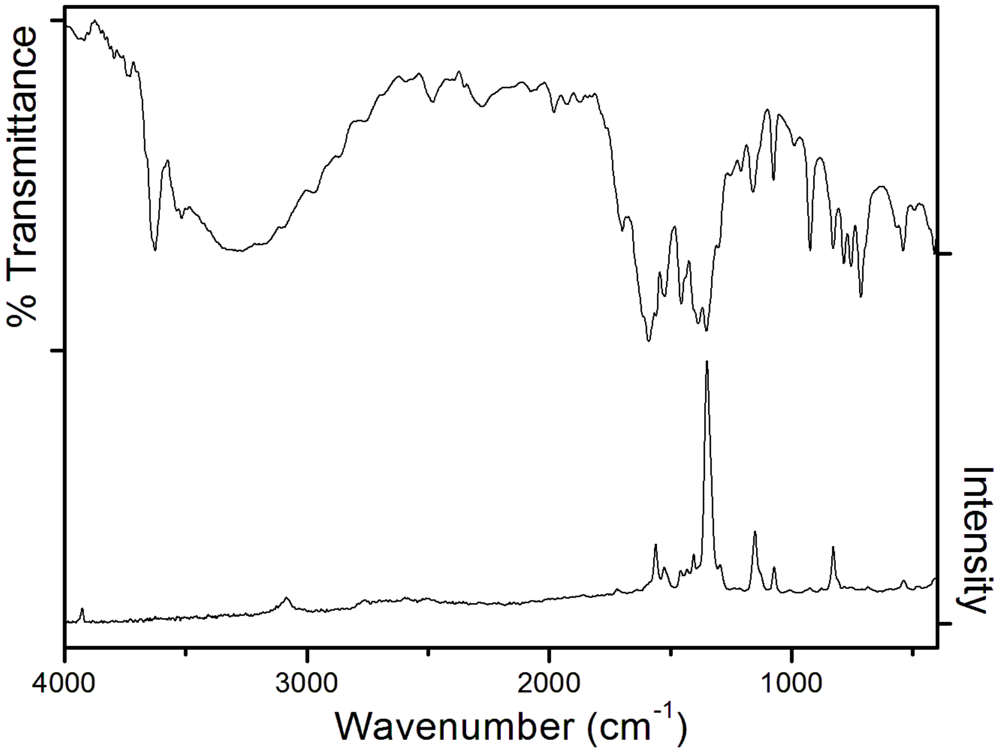


Fig. 3.144 – IR and Raman spectrum of **15**

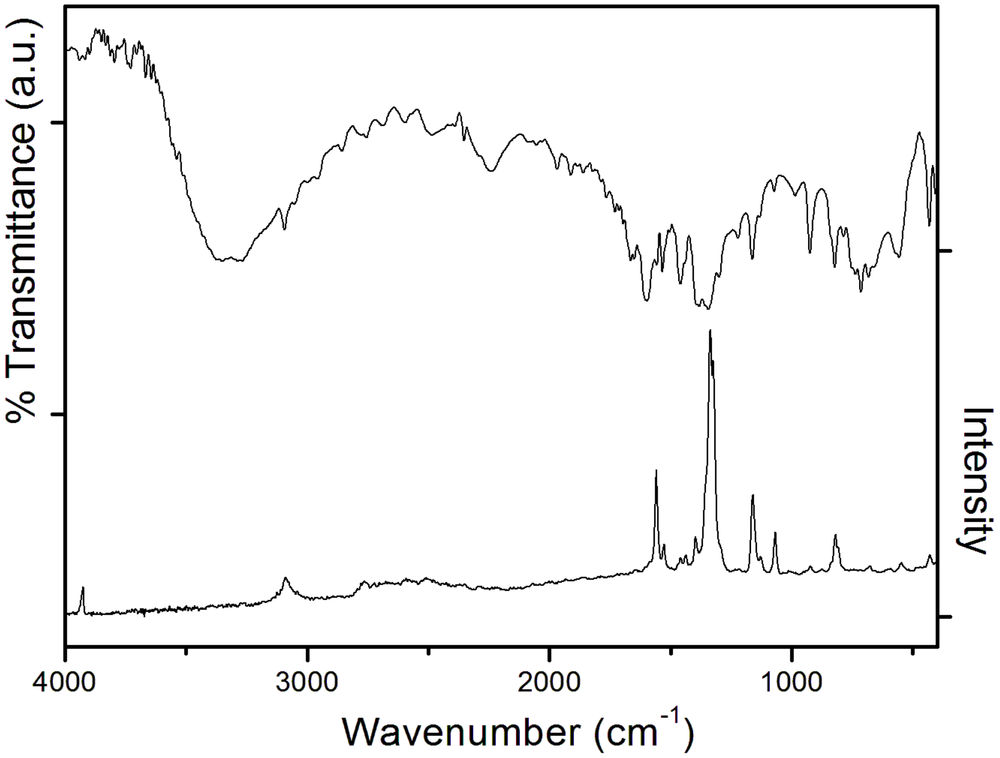


Fig. 3.145 – IR and Raman spectrum of **16**

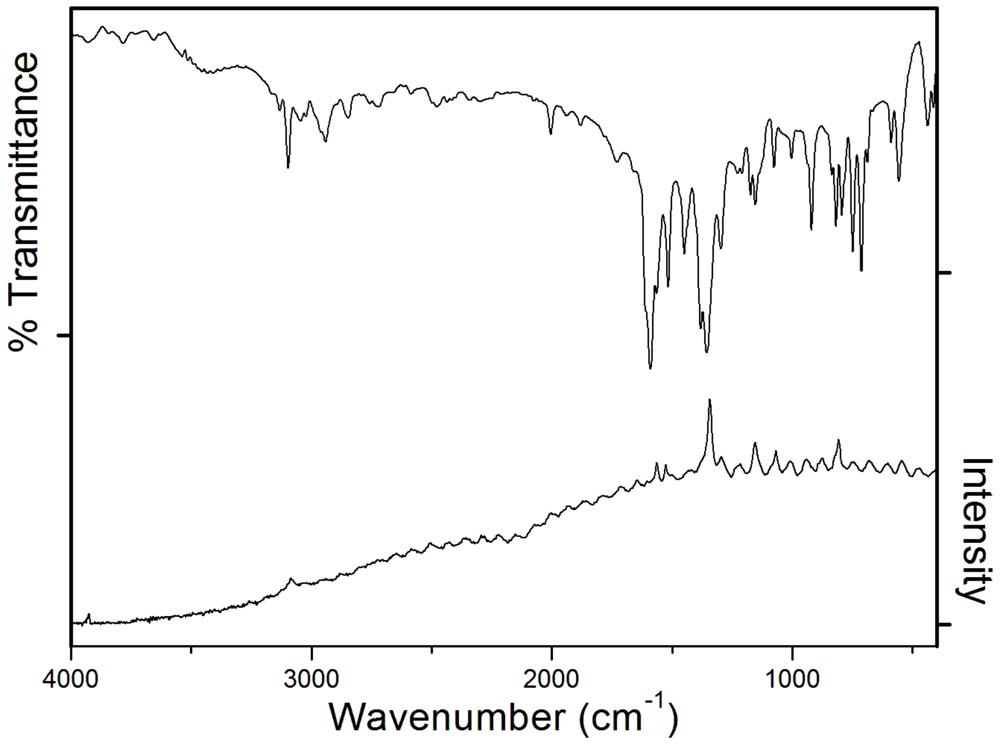


Fig. 3.146 – IR and Raman spectrum of **17**

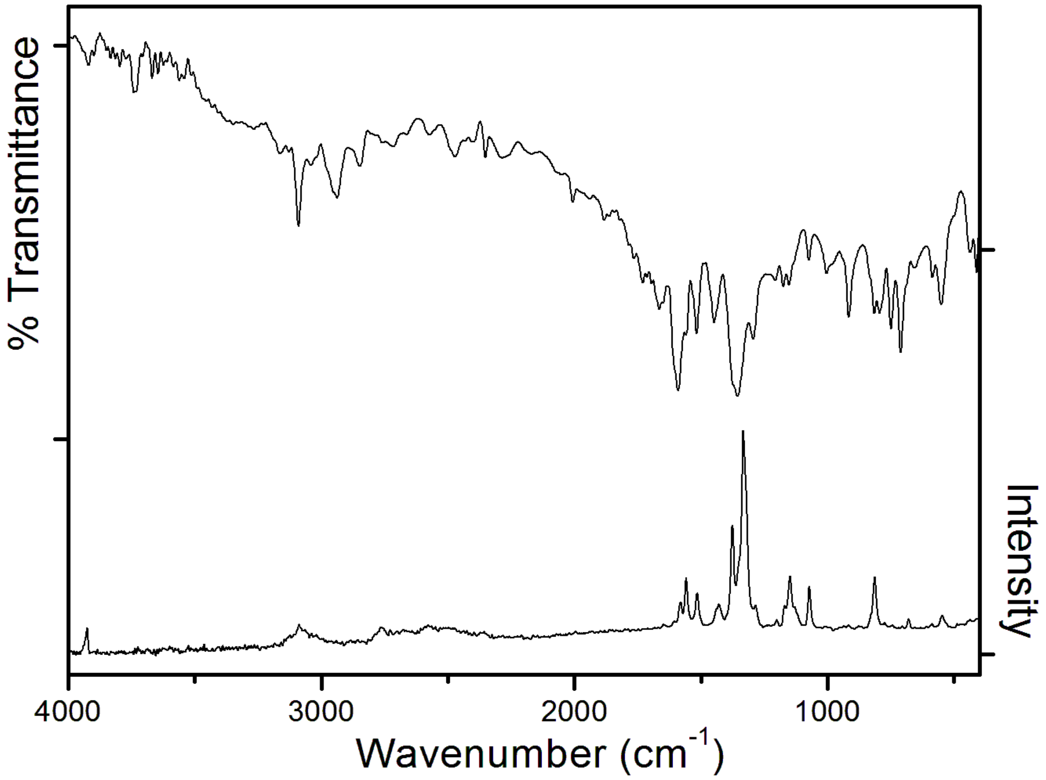


Fig. 3.147 – IR and Raman spectrum of **18**

The UV-visible spectra (Fig. 3.148-3.152) of compounds **14-18** shows an absorbance ~273 nm assignable for intra ligand charge transfer band for aromatic 3-nitrophthalate ligand.

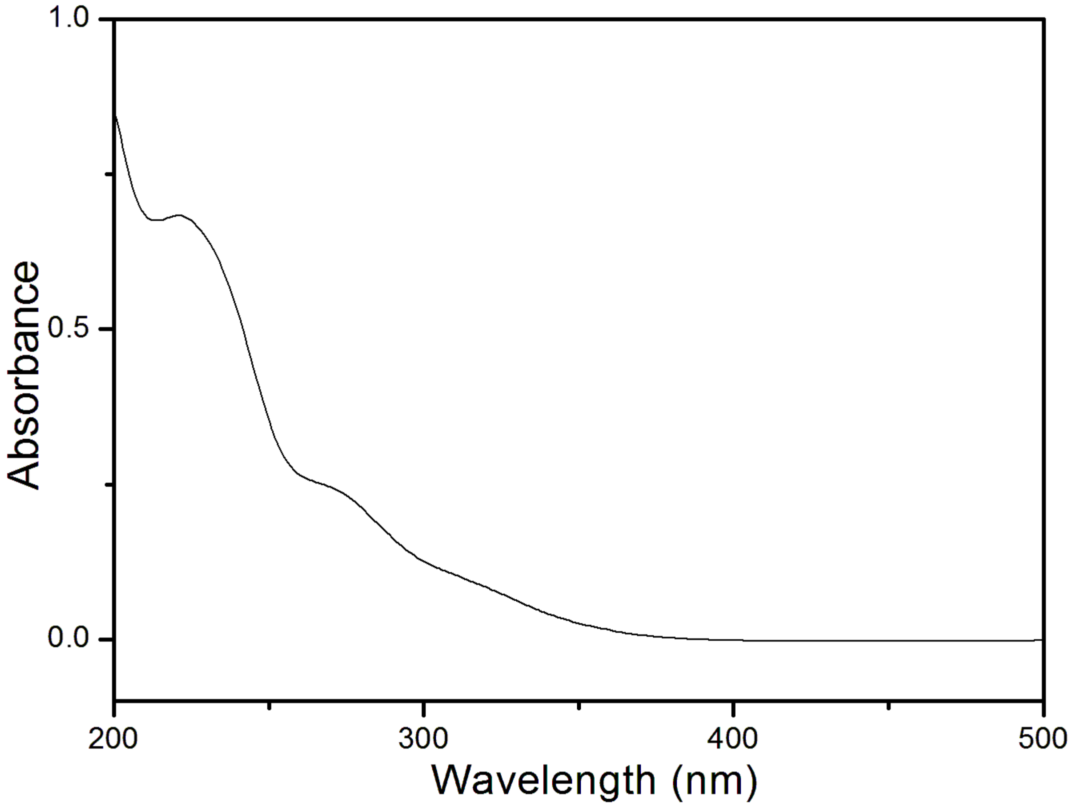


Fig. 3.113 – UV-Visible spectrum of **14**

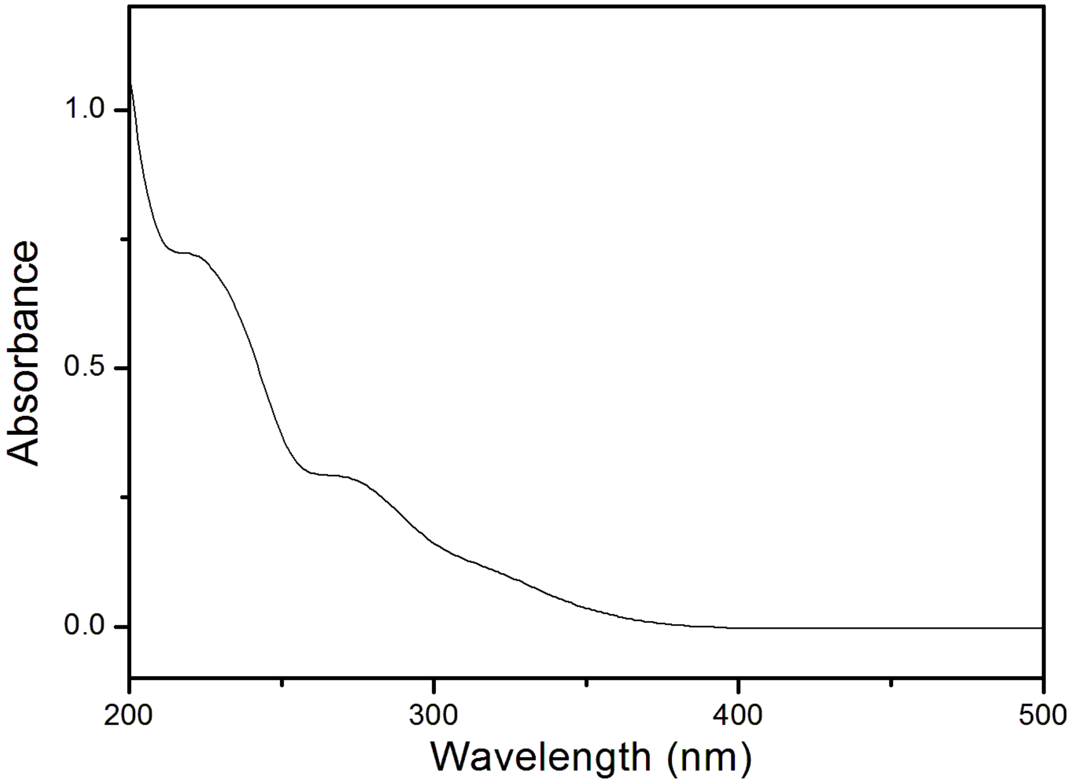


Fig. 3.114 – UV-Visible spectrum of **15**

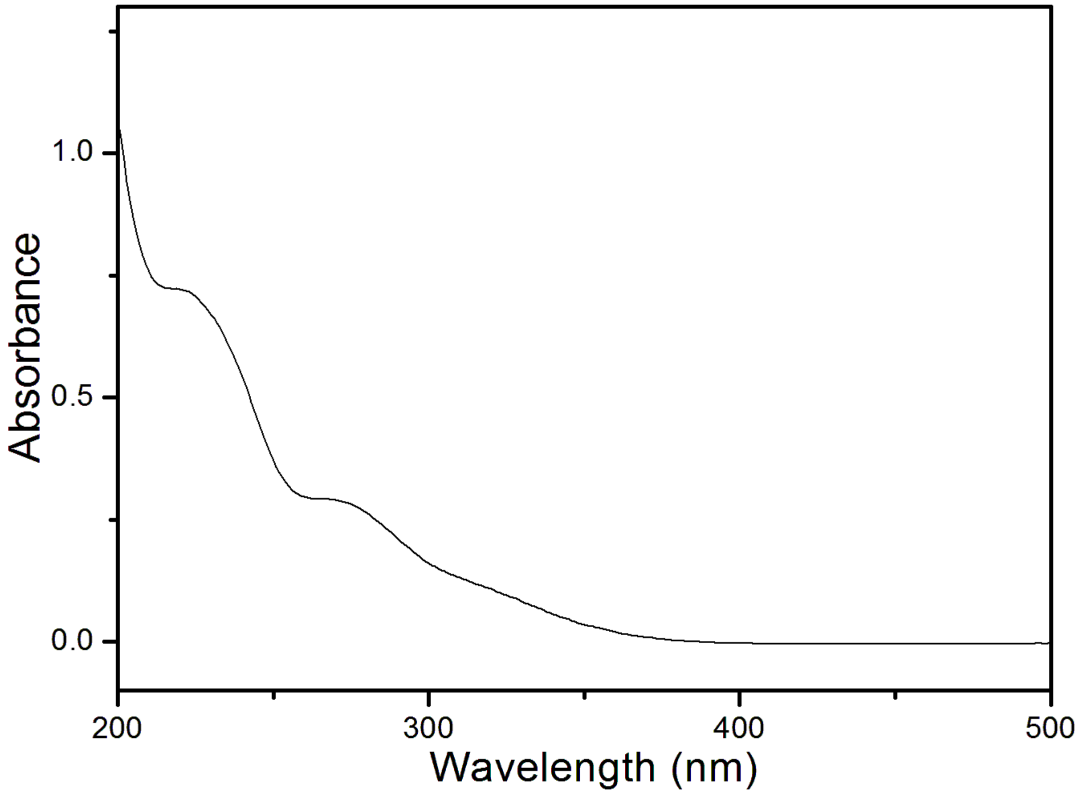


Fig. 3.115 – UV-Visible spectrum of **16**

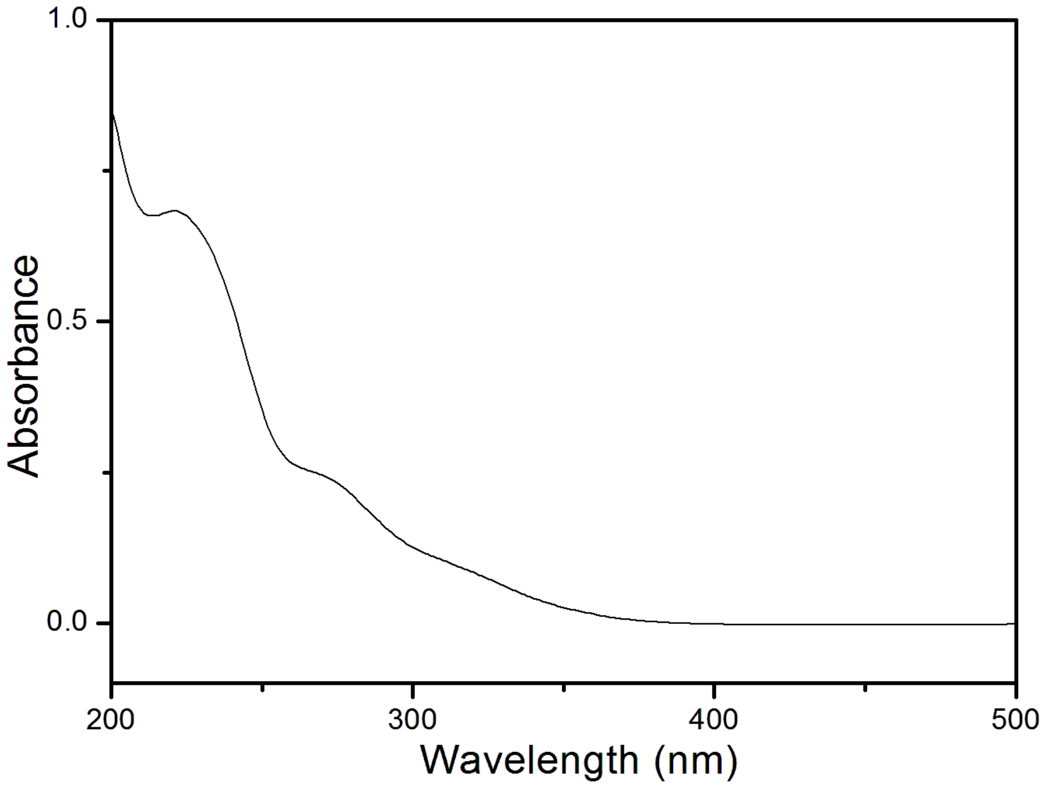


Fig. 3.116 – UV-Visible spectrum of **17**

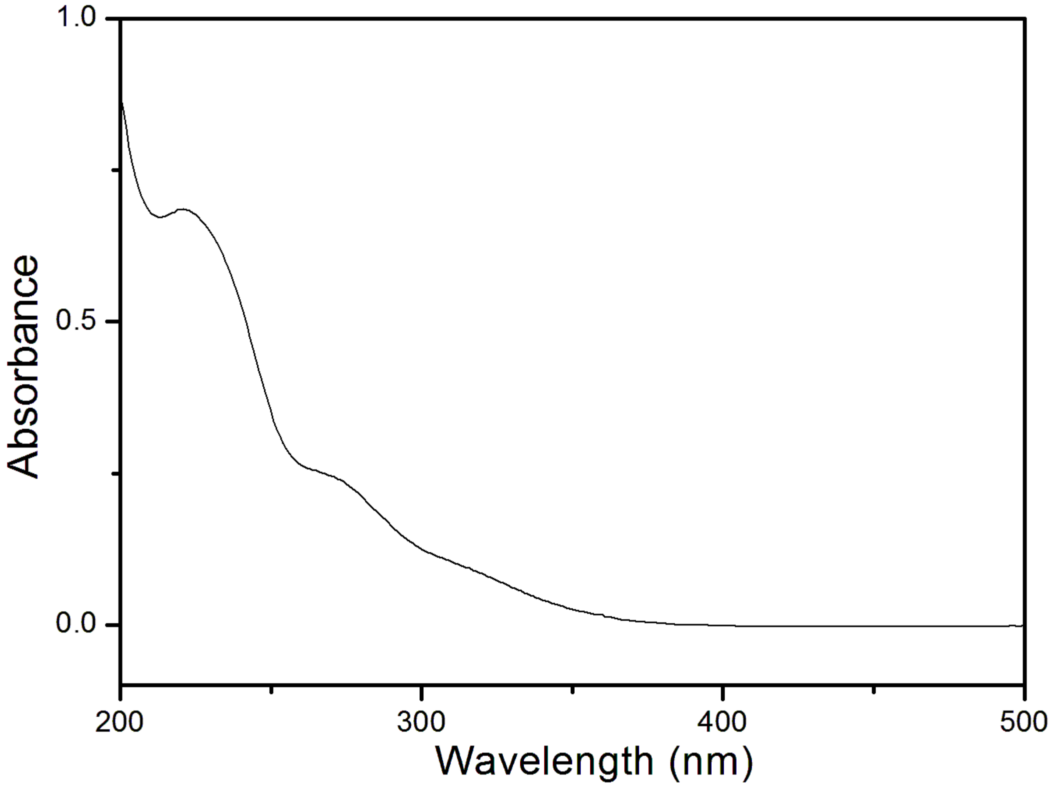


Fig. 3.117 – UV-Visible spectrum of **18**

Lithium 3-nitrophthalate compound **14** exhibits endothermic event at 100°C in its TG-DTA graph (Fig. 3.153). The TG curve shows a decrease in mass by 19.17 % equivalent to loss of three water molecules by 100°C. Above 200°C, the DTA curve shows only an exothermic peak at 406°C with rapid mass loss due to decomposition of **14**. The residual mass of 13.27 % corresponds to Li_2CO_3.

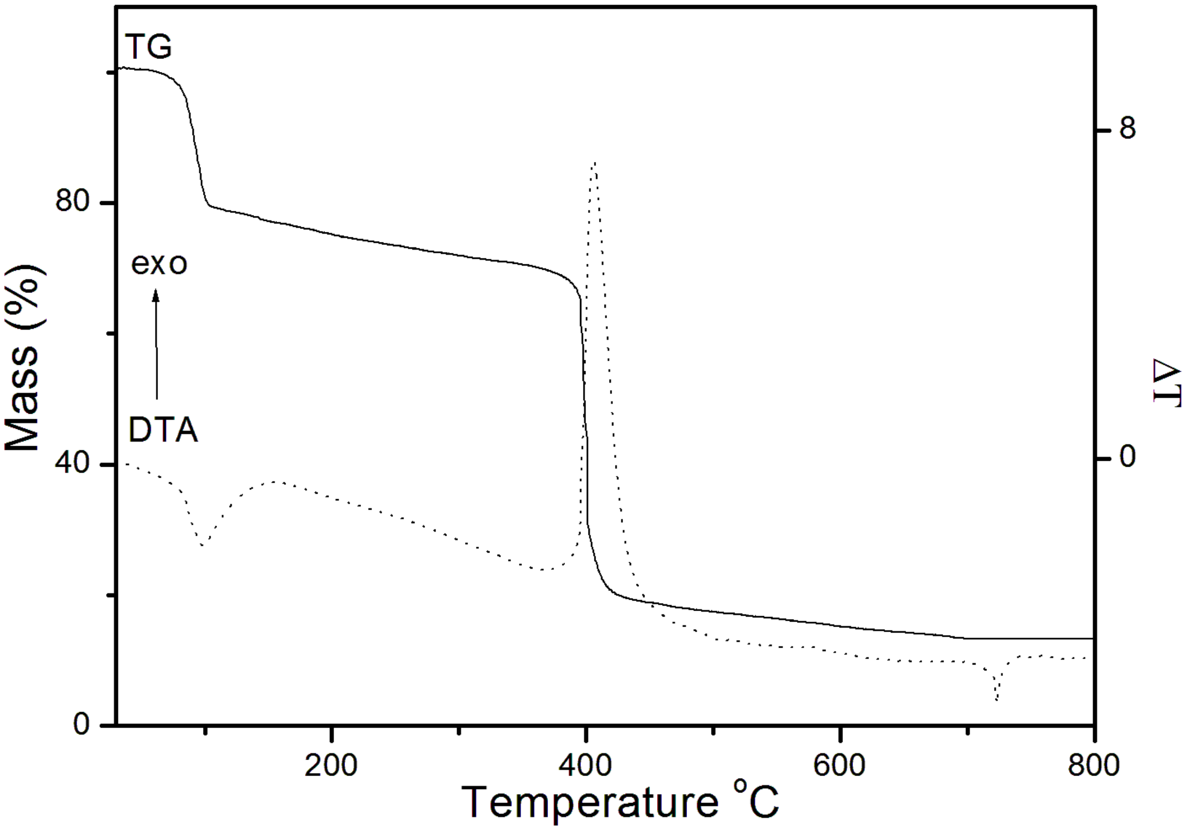


Fig. 3.153 – TG-DTA curve of **14**

Sodium 3-nitrophthalate compound **15** exhibits endothermic event at 116°C and 168°C in its TG-DTA graph (Fig. 3.154). The TG curve shows a decrease in mass by 7.07 % equivalent to loss of one water molecule by 120°C. Above 200°C, the DTA curve shows only exothermic peaks at 386°C, 483°C and 666°C with rapid mass loss due to decomposition of **15**. The residual mass of 36.35 % is in accordance with the formation of Na_2CO_3.

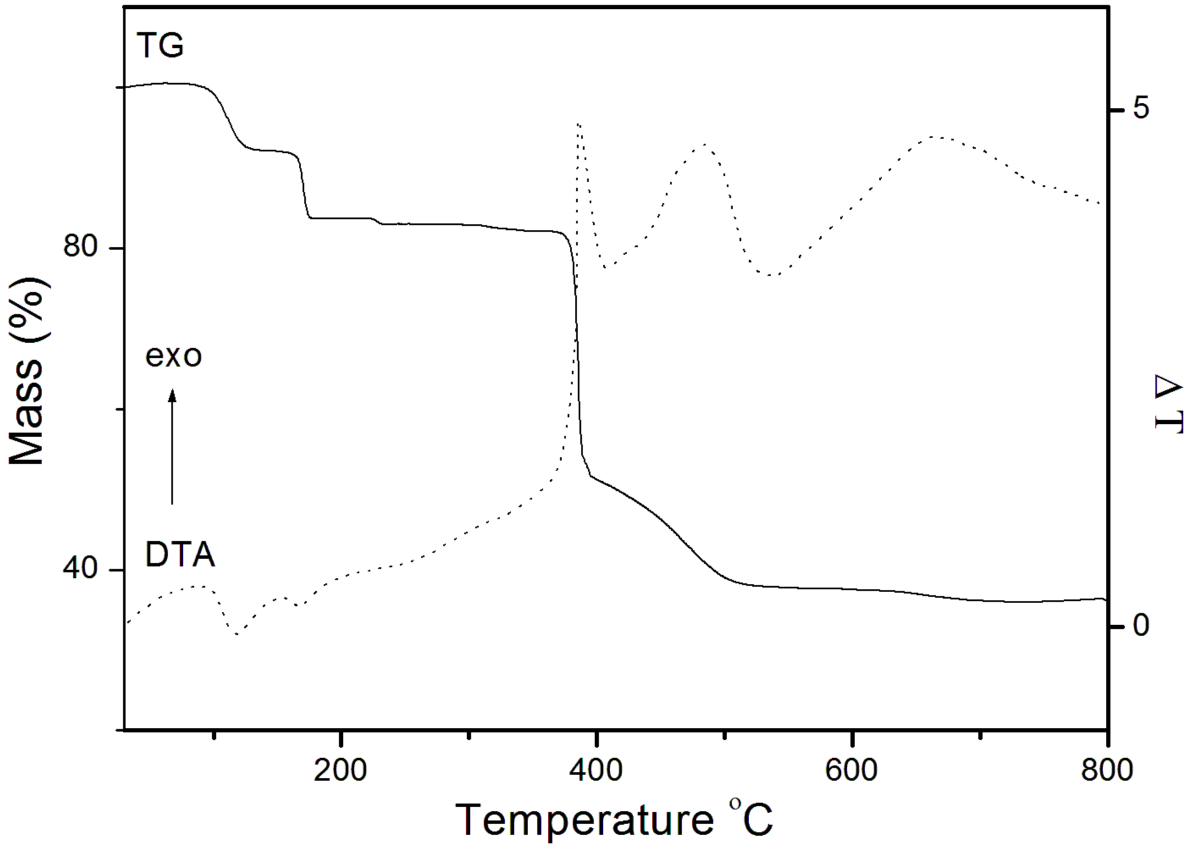


Fig. 3.154 – TG-DTA curve of **15**

TG-DTA curve of **16** does not show any weight loss below 200°C in DTA (Fig. 3.155). Above 200°C, the DTA curve shows only exothermic peaks at 299°C, 344°C and 487°C, followed by a rapid drop in mass due to decomposition of **16**. The residual mass of 47.89 % is in accordance with the formation of K_2CO_3.

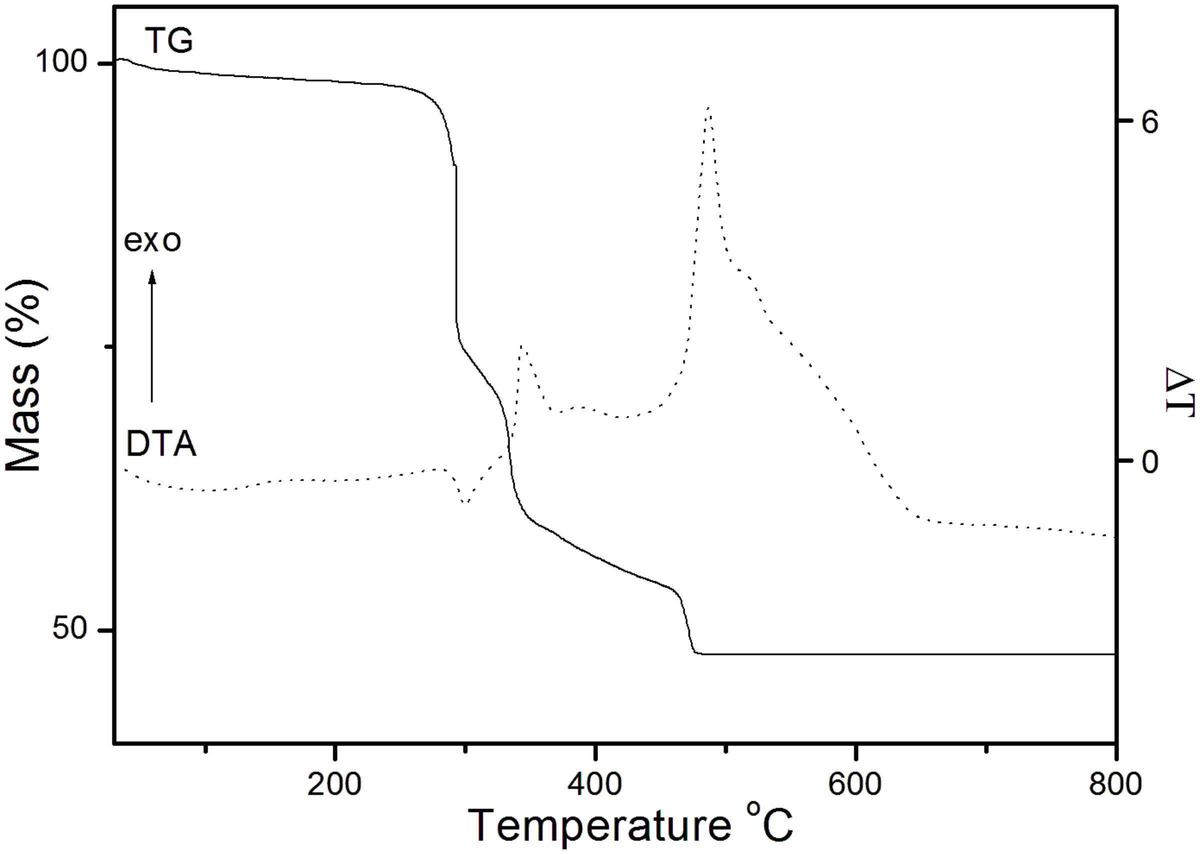


Fig. 3.155 – TG-DTA curve of **16**

TG-DTA curve of **17** does not show any weight loss below 200°C in DTA (Fig. 3.156). Above 200°C, the DTA curve shows exothermic peaks at 384°C, 490°C and 560°C, followed by a rapid drop in mass due to decomposition of **17**. The residual mass of 60.84 % is in accordance with the formation of Rb_2CO_3.

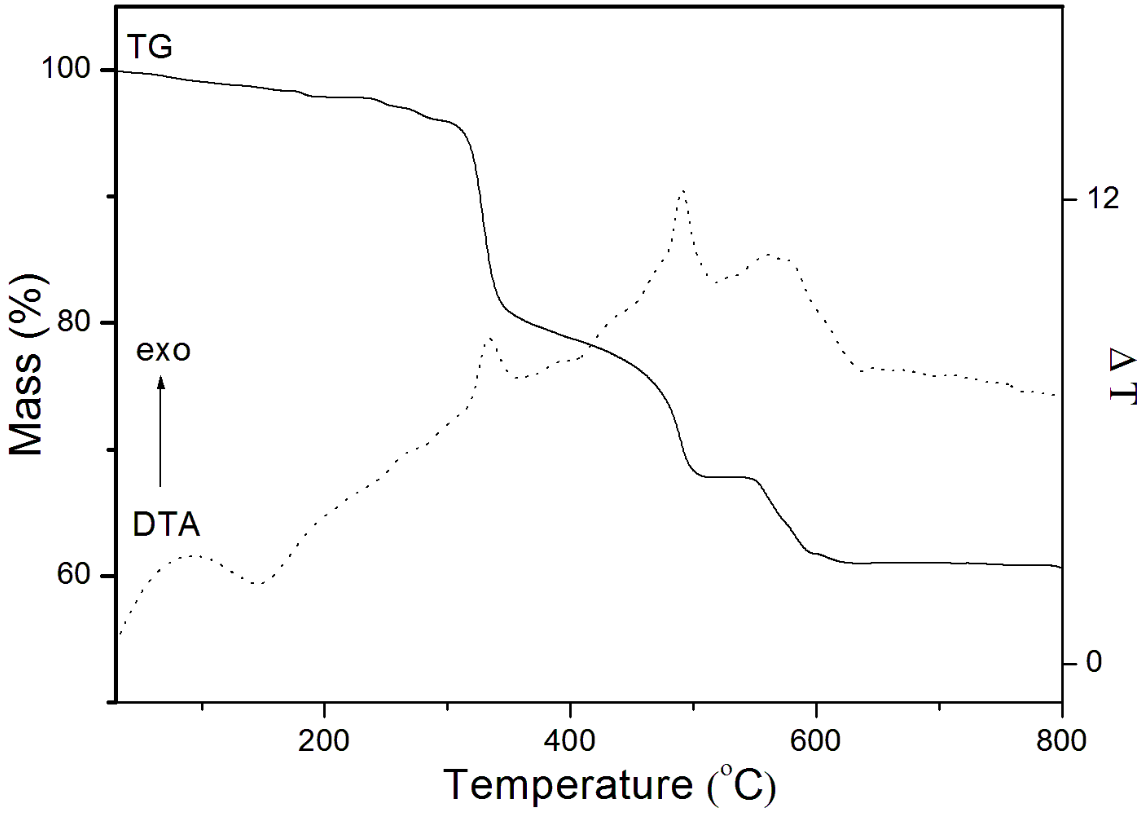


Fig. 3.156 – TG-DTA curve of **17**

The TG curve of **18** (Fig. 3.157) shows no weight loss till 200°C indicating the anhydrous nature of the compound. Above 250°C, the DTA curve of **18** shows exothermic peaks at 346°C, 357°C, 508°C and 602°C. The % residue obtained 68.51 % is in good agreement with the Cs_2CO_3.

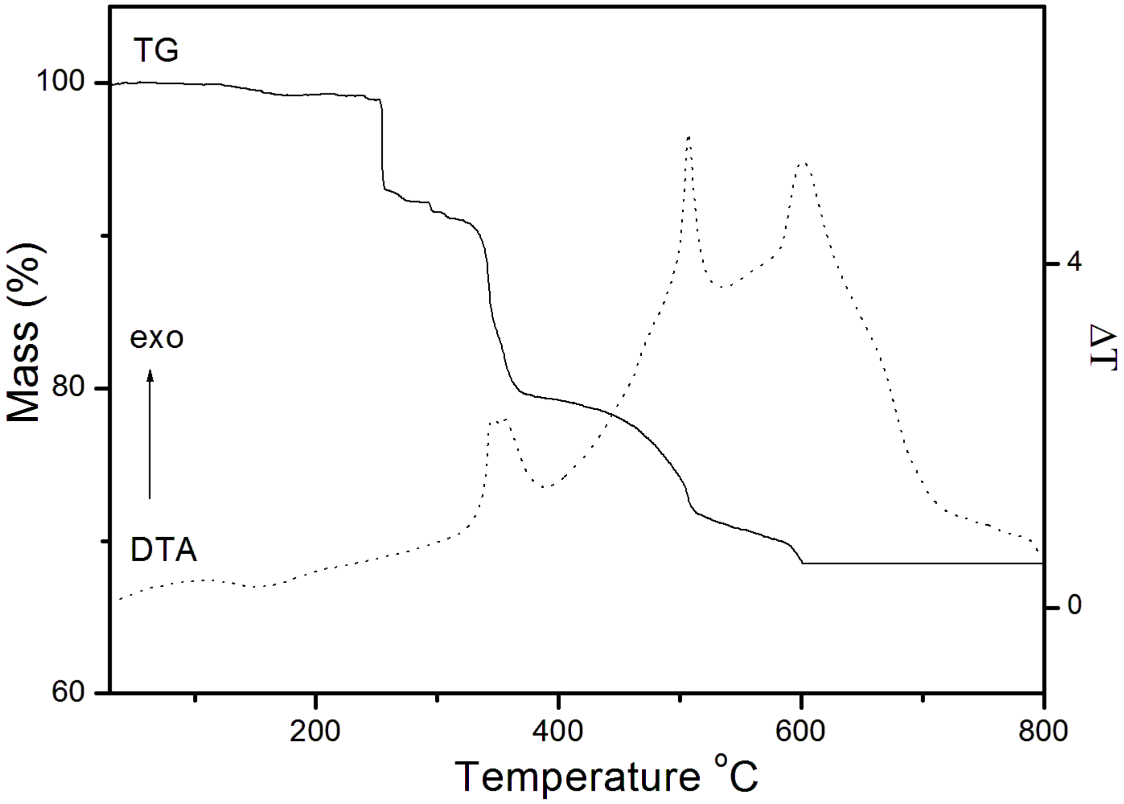


Fig. 3.157 – TG-DTA curve of **18**

3.2.6 Description of crystal structure of [Rb_2(3-npht)] ***17***

Rubidium 3-nitrophthalate **18** crystallises in the centrosymmetric monoclinic *$P2_1/n$* space group. Its crystal structure consists of two unique Rb(I) ions and one crystallographically independent 3-nitrophthalate ligand all of which are located in general positions (Fig. 3.158). The geometric parameters of 3-nitrophthalate are in the normal range.

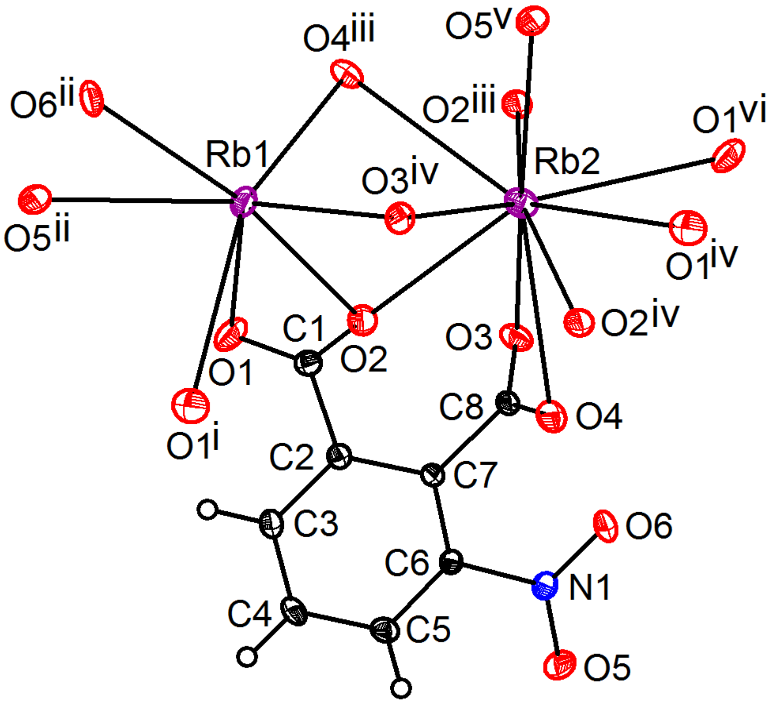


Fig. 3.158 – The crystal structure of [Rb$_2$(3-npht)] **17** showing the atom labelling scheme and the coordination sphere of two unique Rb^{+1} (Rb1 and Rb2). Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as spheres of arbitrary radius. Symmetry code: i) 1.5-x, -0.5+y, 0.5-z; ii) 0.5+x, 0.5-y, -0.5+z; iii) 0.5-x, 0.5+y, 0.5-z; iv) 0.5-x, -0.5+y, 0.5-z; v) -0.5+x, 0.5-y, -0.5+z; vi) -1+x, y, z.

The two unique metal ions Rb1 and Rb2 exhibits different coordination viz. heptacoordination and decacoordination respectively (Fig. 3.159).

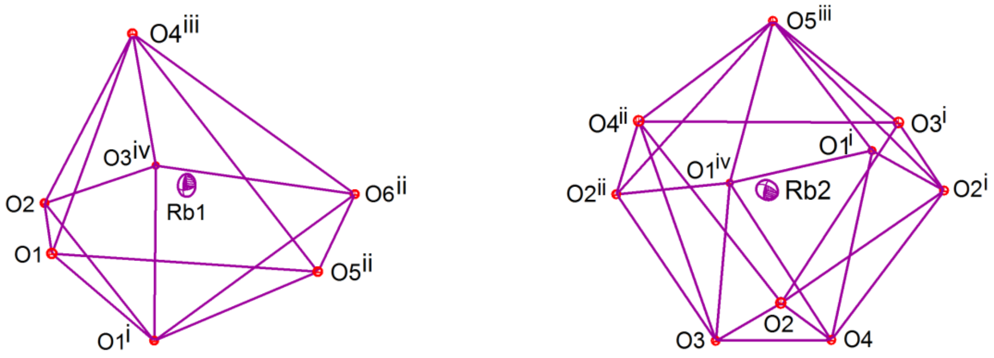


Fig. 3.159 –The distorted pentagonal bipyramidal {RbO$_7$} coordination around Rb1 (Symmetry code: i) 1.5-x, -0.5+y, 0.5-z; ii) 0.5+x, 0.5-y, -0.5+z; iii) 0.5-x, 0.5+y, 0.5-z; iv) 0.5-x, -0.5+y, 0.5-z) and decahedral {RbO$_{10}$} coordination around Rb2 in **17** (Symmetry code: i) 0.5-x, 0.5+y, 0.5-z; ii) 0.5-x, -0.5+y, 0.5-z; iii) -0.5+x, 1.5-y, -0.5+z; iv) -1+x, y, z).

The details of structure refinement for **17** are given in Table 3.24.

Table 3.24 - Crystal data and structure refinement for [Rb_2(3-npht)] **17**

Empirical formula	$C_8H_3NO_6Rb_2$
Formula weight (g mol^{-1})	380.05
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2₁/n
Unit cell dimensions	
a (Å)	7.6198(9)
b (Å)	6.3293(7)
c (Å)	20.350(2)
α (°)	90
β (°)	94.480(4)
γ (°)	90
Volume (Å^3)	978.4(2)
Z	4
D_{calc} (mg/m^3)	2.580
Absorption coefficient (mm^{-1})	10.019
F(000)	720
Crystal size (mm^3)	0.10 x 0.10 x 0.05
θ range for data collection (°)	3.372 to 32.618
Index ranges	$-11 \leq h \leq 11$ $-9 \leq k \leq 9$ $-30 \leq l \leq 30$
Reflections collected / unique	26790 / 3551 [R(int) = 0.0357]
Completeness to θ = 25.00°	99.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.7462 and 0.5603
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3551 / 0 / 154
Goodness-of-fit on F^2	1.094
Final R indices [I>2sigma(I)]	R1 = 0.0245, wR2 = 0.0481
R indices (all data)	R1 = 0.0353, wR2 = 0.0505
Largest diff. peak and hole (e Å^{-3})	0.682 and -0.747

The Rb-O bond distances range from 2.823(0) to 3.432(2) Å while the O-Rb-O angles vary between 40.68(3) to 169.67(4)° forming a distorted {RbO_7} pentagonal bipyramidal polyhedron and {RbO_{10}} decahedron (Table 3.25).

Table 3.25 – Selected Bond lengths [Å] and angles [°] for **1**7

Bond lengths			
Rb1-O3#2	2.8230(13)	Rb2-O1#2	3.1559(16)
Rb1-O4#1	2.9559(13)	Rb2-O3#2	3.1995(14)
Rb1-O5#8	3.0242(15)	Rb2-O4#1	3.2274(14)
Rb1-O1#3	3.1424(14)	Rb2-O1#10	3.2667(15)
Rb1-O6#8	3.1657(14)	Rb2-O2#2	3.4322(15)
Rb1-O1	3.1406(15)	Rb2-O2	2.8723(14)
Rb1-O2	2.7491(14)	Rb2-O3	3.0284(14)
Rb2-O2#1	2.9382(15)	Rb2-O4	3.1681(14)
Rb2-O5#9	3.1316(13)		
Bond angles			
O2-Rb1-O3#2	74.79(4)	O3-Rb2-O4	42.30(4)
O2-Rb1-O4#1	78.23(4)	O5#9-Rb2-O4	153.71(4)
O3#2-Rb1-O4#1	90.47(4)	O1#2-Rb2-O4	82.93(4)
O2-Rb1-O5#8	132.96(4)	O2-Rb2-O3#2	67.51(4)
O3#2-Rb1-O5#8	136.00(4)	O2#1-Rb2-O3#2	138.76(4)
O4#1-Rb1-O5#8	124.28(4)	O3-Rb2-O3#2	125.57(3)
O2-Rb1-O1	43.99(4)	O5#9-Rb2-O3#2	68.74(4)
O3#2-Rb1-O1	117.93(4)	O1#2-Rb2-O3#2	82.64(3)
O4#1-Rb1-O1	86.71(4)	O4-Rb2-O3#2	97.47(4)
O5#8-Rb1-O1	92.56(4)	O2-Rb2-O4#1	72.13(4)
O2-Rb1-O1#3	70.75(4)	O2#1-Rb2-O4#1	59.50(4)
O3#2-Rb1-O1#3	88.92(4)	O3-Rb2-O4#1	99.78(4)
O4#1-Rb1-O1#3	147.99(4)	O5#9-Rb2-O4#1	71.48(4)
O5#8-Rb1-O1#3	75.05(4)	O1#2-Rb2-O4#1	144.38(4)
O1-Rb1-O1#3	65.599(18)	O4-Rb2-O4#1	129.65(2)
O2-Rb1-O6#8	169.67(4)	O3#2-Rb2-O4#1	79.37(4)
O3#2-Rb1-O6#8	105.32(4)	O2-Rb2-O1#10	144.08(4)
O4#1-Rb1-O6#8	112.04(4)	O2#1-Rb2-O1#10	66.78(4)
O5#8-Rb1-O6#8	40.68(3)	O3-Rb2-O1#10	83.23(4)
O1-Rb1-O6#8	132.78(4)	O5#9-Rb2-O1#10	88.27(4)
O1#3-Rb1-O6#8	98.93(4)	O1#2-Rb2-O1#10	63.973(18)
O2-Rb2-O2#1	99.92(4)	O4-Rb2-O1#10	91.54(4)
O2-Rb2-O3	60.94(4)	O3#2-Rb2-O1#10	144.06(3)
O2#1-Rb2-O3	69.10(4)	O4#1-Rb2-O1#10	120.21(3)
O2-Rb2-O5#9	126.85(4)	O2-Rb2-O2#2	89.31(4)
O2#1-Rb2-O5#9	93.56(4)	O2#1-Rb2-O2#2	166.95(5)
O3-Rb2-O5#9	162.56(4)	O3-Rb2-O2#2	108.31(3)
O2-Rb2-O1#2	127.58(4)	O5#9-Rb2-O2#2	88.15(3)
O2#1-Rb2-O1#2	129.16(4)	O1#2-Rb2-O2#2	39.39(3)
O3-Rb2-O1#2	115.67(4)	O4-Rb2-O2#2	66.02(3)
O5#9-Rb2-O1#2	73.40(4)	O3#2-Rb2-O2#2	53.56(3)
O2-Rb2-O4	60.86(4)	O4#1-Rb2-O2#2	132.90(3)
O2#1-Rb2-O4	110.49(4)	O1#10-Rb2-O2#2	100.37(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1/2,-z+1/2; #2 -x+1/2,y-1/2,-z+1/2; #3 -x+3/2,y-1/2,-z+1/2; #4 -x+3/2,y+1/2,-z+1/2; #5 x+1,y,z; #6 x-1/2,-y+1/2,z+1/2; #7 x+1/2,-y+1/2,z+1/2; #8 x+1/2,-y+1/2,z-1/2; #9 x-1/2,-y+1/2,z-1/2; #10 x-1,y,z.

The unique 3-nitrophthalate ligand in the crystal structure of **17** exhibits μ_{10}-bridging polydentate binding mode with $-NO_2$ group involved in binding with central metal ion (Fig. 3.160). The $-NO_2$ group of the 3-nitrophthalate ligand shows μ_2-tridentate binding mode.

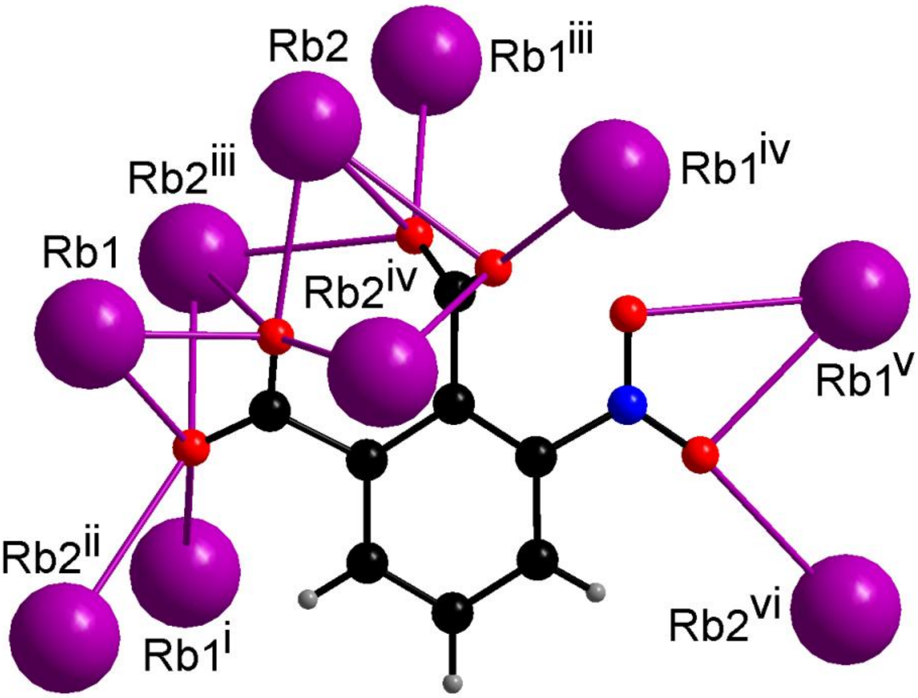


Fig. 3.160 – The μ_{10}-bridging polydentate binding mode of 3-npht ligand in **17**. Symmetry code: i) 1.5-x, -0.5+y, 0.5-z; ii) 1+x, y, z; iii) 0.5-x, -0.5+y, 0.5-z; iv) 0.5-x, 0.5+y, 0.5-z; v) -0.5+x, 1.5-y, 0.5+z; vi) 0.5+x, 1.5-y, 0.5+z.

The crystal structure reveals that **17** is a 3D coordination polymer. A unique 3-nitrophthalate ligand with its bridging binding mode extends the structure forming a zig-zag 1D chain along *a*-axis (Fig. 3.161).

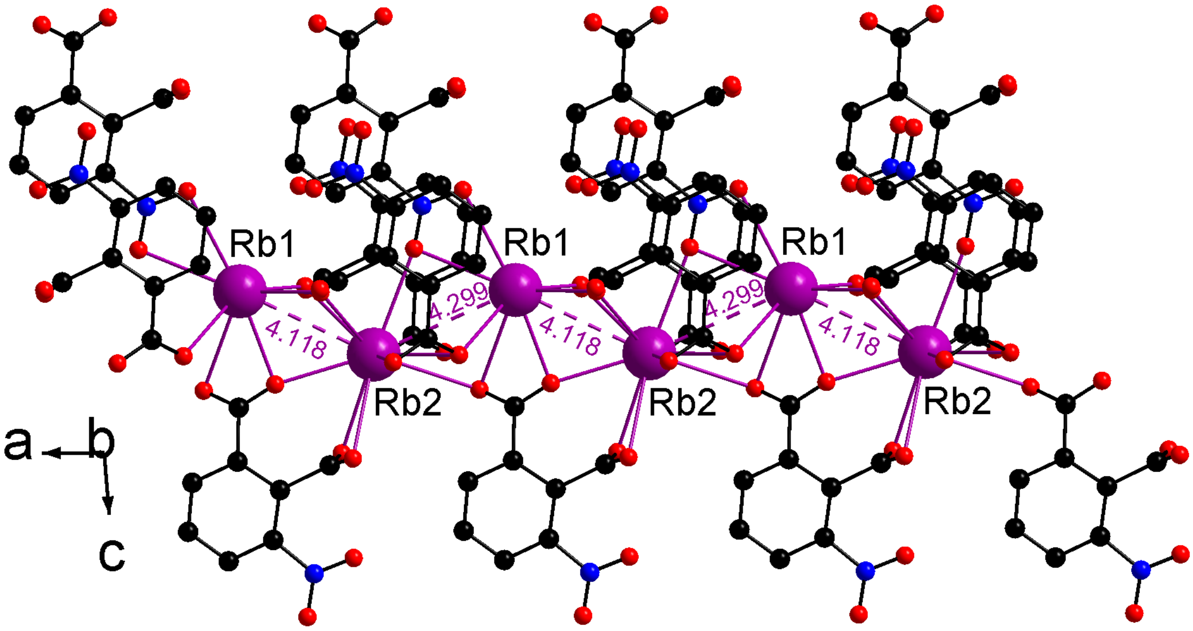


Fig. 3.161 – A portion of the infinite chain extending along *a-axis* with Rb···Rb separation of 4.118 and 4.299 Å alternatively due to μ_{10}-bridging polydentate coordination mode of a unique 3-npht ligand in **17**.

The two metal ions Rb1 and Rb2 are connected via two sets of three oxygen atoms viz. set I of carboxylate oxygens (O1, O2 and O3) and set II of two symmetry related carboxylate oxygens (O4 and O4) and a $-NO_2$ oxygen (O6) (Fig. 3.162). This extension via Rb1···O2··· Rb2, Rb1···O3··· Rb2, Rb1···O4··· Rb2, Rb1···O1··· Rb2 and Rb1···O5··· Rb2 leads to alternate arrangement of the two unique metal ions as Rb1··· Rb2··· Rb1··· Rb2 with alternate distances of 4.118 and 4.299 Å. A similar type of arrangement via Rb1···O1··· Rb2, Rb1···O2··· Rb2, Rb1···O3··· Rb2 and Rb1···O4··· Rb2 results in extension along *b*-axis forming 2D sheet structure in *ab*-plane with alternate Rb1···Rb2 distance of 4.190 and 4.580 Å (Fig. 3.162).

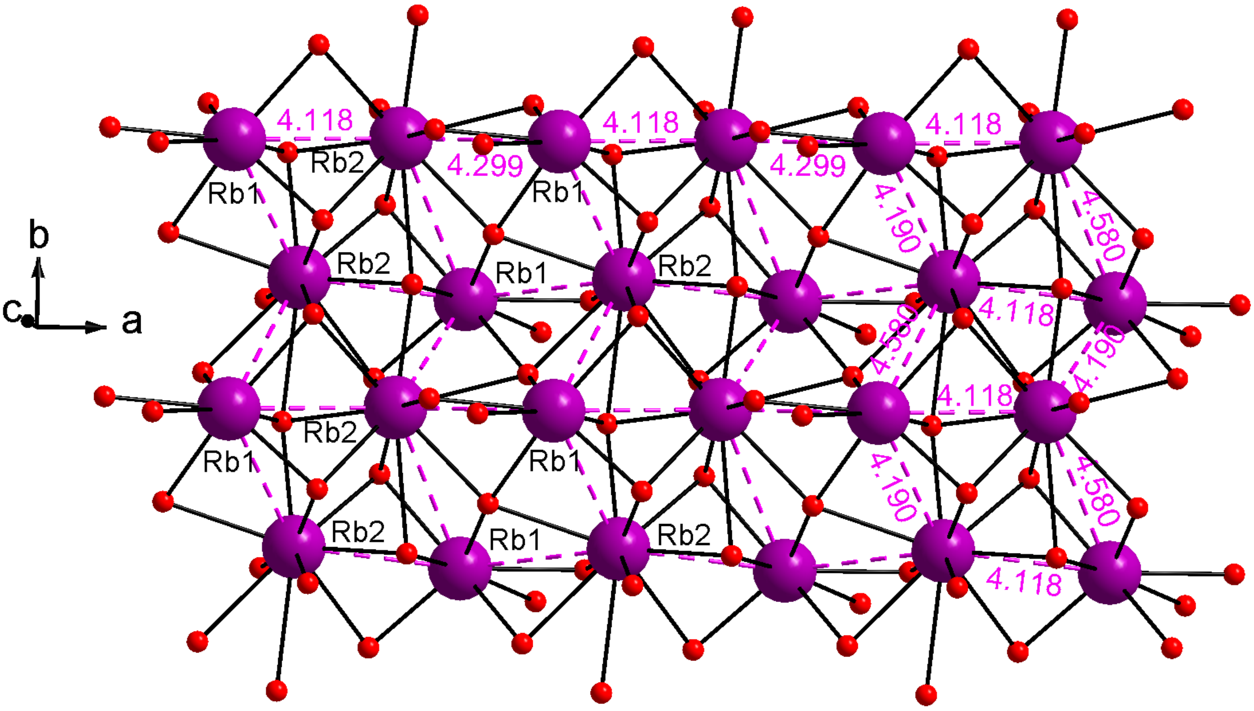


Fig. 3.162 – A portion of two dimensional zig-zag sheet/layer of **17** in *ab* plane with alternate Rb···Rb distance of 4.118 and 4.299 Å along *a-axis* and alternate 4.190 and 4.580 Å along *b-axis* (pink broken lines). For clarity only the O atoms of the ligand are shown.

The structure further extends along *c*-axis resulting in 3D coordination polymer (Fig. 3.163). Interestingly **17** show only C-H···O H-bonding interactions in its crystal structure (Table 3.26).

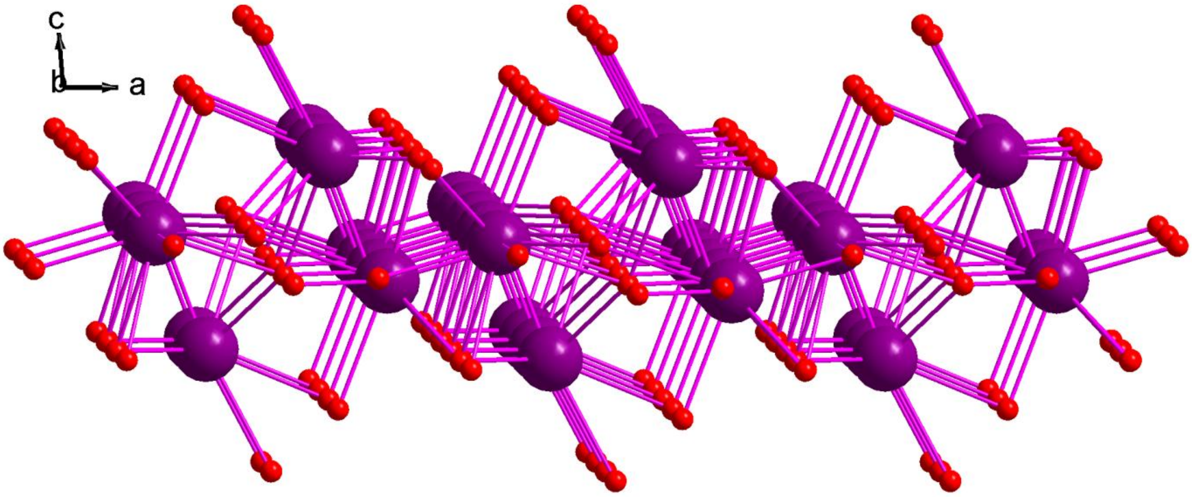


Fig. 3.163 – A portion of three dimensional architecture of **17** *(for clarity only oxygen atoms of the ligands are shown).*

Table 3.26 - Hydrogen bonding geometry [Å and °] for [Rb_2(3-npht)] **1**

D-H···A	d(D-H)	(H···A)	d(D···A)	<DHA	Symmetry code
C3-H3 ···O1	0.950(.002)	2.571(.001)	2.829(.002)	95.70(0.11)	x, y, z
C5-H5 ···O5	0.950(.002)	2.340(.001)	2.666(.002)	99.44(0.11)	x, y. z
C3-H3 ···O4	0.950(.002)	2.656(.001)	3.433(.002)	139.27(0.11)	x+1,+y,+z
C4-H4 ···O6	0.950(.002)	2.294(.001)	3.145(.002)	148.80(0.11)	x+1,+y,+z
C3-H3 ···O3	0.950(.002)	2.922(.001)	3.732(.002)	143.94(0.11)	x+1,+y,+z
C5-H5 ···O3	0.950(.002)	2.814(.001)	3.408(.002)	121.49(0.11)	-x+1,-y+1,-z+1
C5-H5 ···O4	0.950(.002)	2.653(.001)	3.425(.002)	138.65(0.11)	-x+1,-y,-z+1

D=Donor and A=Acceptor

3.2.7 Description of crystal structure of [Cs_2(3-npht)] ***18***

Compound **18** crystallises in the centrosymmetric monoclinic *$P2_1/n$* space group. Its crystal structure consists of two unique Cs(I) ions and one crystallographically independent 3-nitrophthalate ligand all of which are located in general positions (Fig. 3.164). The geometric parameters of 3-nitrophthalate are in the normal range (Table 3.27).

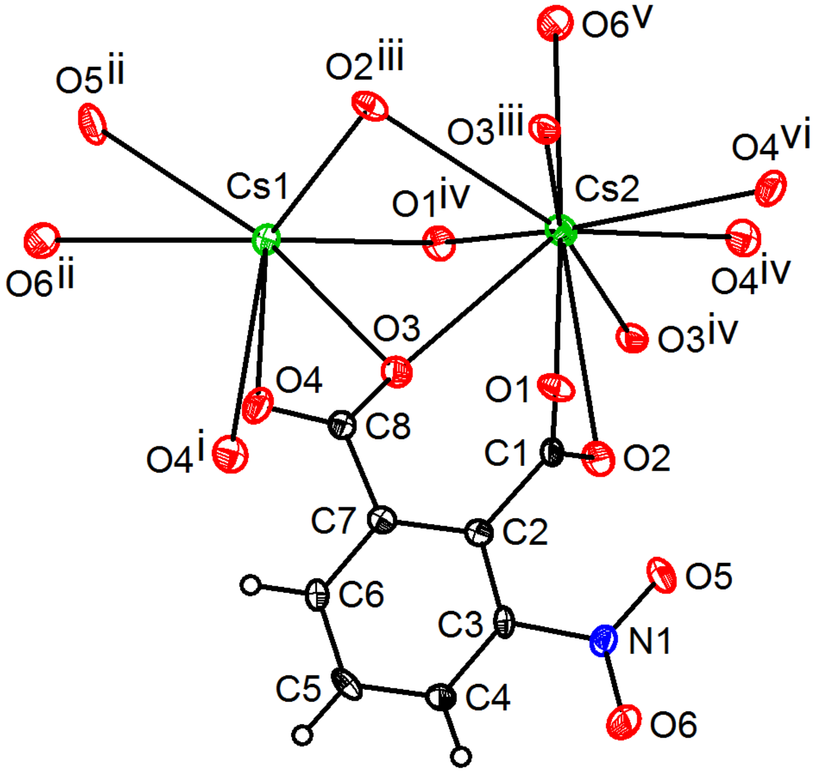


Fig. 3.164 – The crystal structure of [Cs_2(3-npht)] **18** showing the atom labelling scheme and the coordination sphere of two unique Cs^{+1} (Cs1 and Cs2). Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as spheres of arbitrary radius. Symmetry code: i) 1.5-x, 0.5+y, 0.5-z; ii) 0.5+x, 1.5-y, -0.5+z; iii) 0.5-x, -0.5+y, 0.5-z; iv) 0.5-x, 0.5+y, 0.5-z; v) -0.5+x, 1.5-y, -0.5+z; vi) -1+x, y, z.

The two unique metal ions Cs1 and Cs2 exhibits different coordination viz. heptacoordination and decacoordination respectively (Fig. 3.165).

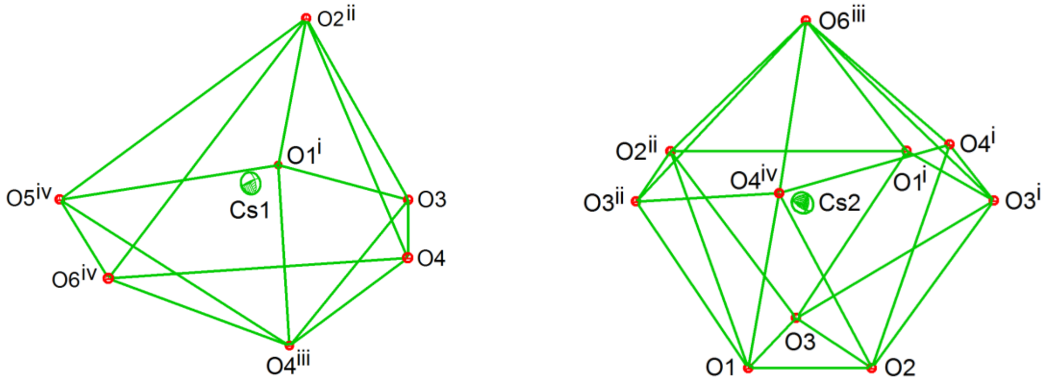


Fig. 3.165 –The distorted pentagonal bipyramidal {CsO_7} coordination around Cs1 (Symmetry code: i) 0.5-x, 0.5+y, 0.5-z; ii) 0.5-x, -0.5+y, 0.5-z; iii) 1.5-x, 0.5+y, 0.5-z; iv) 0.5+x, 1.5-y, -0.5+z) and Sphenocorna {CsO_{10}} coordination around Cs2 in **18** (Symmetry code: i) 0.5-x, 0.5+y, 0.5-z; ii) 0.5-x, -0.5+y, 0.5-z; iii) -0.5+x, 1.5-y, -0.5+z; iv) -1+x, y, z).

The details of structure refinement for **18** are given in Table 3.27.

Table 3.27 - Crystal data and structure refinement for [Cs_2(3-npht)] **18**

Empirical formula	$C_8H_3NO_6Cs_2$
Formula weight (g mol^{-1})	474.93
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	7.776(2)
b (Å)	6.526(2)
c (Å)	21.086(7)
α (°)	90
β (°)	95.058(11)
γ (°)	90
Volume (Å^3)	1065.8(6)
Z	4
D_{calc} (mg/m^3)	2.960
Absorption coefficient (mm^{-1})	6.856
F(000)	864
Crystal size (mm^3)	0.10 x 0.10 x 0.05
θ range for data collection (°)	3.269 to 25.992
Index ranges	$-9 \leq h \leq 9$ $-8 \leq k \leq 8$ $-26 \leq l \leq 26$
Reflections collected / unique	13128 / 2066 [R(int) = 0.0390]
Completeness to θ = 25.00°	98.6%
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.7457 and 0.5617
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2066 / 0 / 155
Goodness-of-fit on F^2	1.132
Final R indices [I>2sigma(I)]	R1 = 0.0161, wR2 = 0.0353
R indices (all data)	R1 = 0.0195, wR2 = 0.0363
Largest diff. peak and hole (e Å^{-3})	0.477 and -0.506

The Cs-O bond distances range from 2.935(2) to 3.463(2) Å while the O-Cs-O angles vary between 38.00(5) to 169.09(5)° forming a distorted {CsO_7} pentagonal bipyramidal polyhedron and {CsO_{10}} decahedron (Table 3.28).

Table 3.28 – Selected Bond lengths [Å] and angles [°] for **18**

Bond lengths

Cs1-O1#5	2.9754(19)	Cs2-O1#5	3.287(2)
Cs1-O2#4	3.075(2)	Cs2-O2#4	3.317(2)
Cs1-O6#8	3.173(2)	Cs2-O4#5	3.332(2)
Cs1-O4#2	3.240(2)	Cs2-O6#9	3.332(2)
Cs1-O5#8	3.415(2)	Cs2-O3#5	3.463(2)
Cs1-O3	2.935(2)	Cs2-O1	3.195(2)
Cs1-O4	3.334(2)	Cs2-O2	3.273(2)
Cs2-O3#4	3.101(2)	Cs2-O3	3.053(2)
Cs2-O4#10	3.249(2)		

Bond angles

O3-Cs1-O1#5	76.23(5)	O3#4-Cs2-O1#5	137.95(5)
O3-Cs1-O2#4	78.06(5)	O1-Cs2-O1#5	124.65(4)
O1#5-Cs1-O2#4	90.30(6)	O2-Cs2-O1#5	97.48(5)
O3-Cs1-O6#8	133.49(5)	O3-Cs2-O2#4	72.80(5)
O1#5-Cs1-O6#8	134.01(5)	O3#4-Cs2-O2#4	57.15(5)
O2#4-Cs1-O6#8	125.27(5)	O1-Cs2-O2#4	98.42(5)
O3-Cs1-O4#2	70.31(5)	O4#10-Cs2-O2#4	121.30(5)
O1#5-Cs1-O4#2	85.17(6)	O2-Cs2-O2#4	127.51(3)
O2#4-Cs1-O4#2	148.23(5)	O1#5-Cs2-O2#4	81.02(5)
O6#8-Cs1-O4#2	77.59(5)	O3-Cs2-O4#5	128.34(5)
O3-Cs1-O4	41.17(5)	O3#4-Cs2-O4#5	130.19(5)
O1#5-Cs1-O4	115.89(5)	O1-Cs2-O4#5	117.59(5)
O2#4-Cs1-O4	88.96(5)	O4#10-Cs2-O4#5	65.24(3)
O6#8-Cs1-O4	94.99(5)	O2-Cs2-O4#5	85.77(5)
O4#2-Cs1-O4	65.30(3)	O1#5-Cs2-O4#5	80.87(5)
O3-Cs1-O5#8	169.09(5)	O2#4-Cs2-O4#5	143.86(5)
O1#5-Cs1-O5#8	106.10(5)	O3-Cs2-O6#9	126.54(5)
O2#4-Cs1-O5#8	112.34(5)	O3#4-Cs2-O6#9	92.22(5)
O6#8-Cs1-O5#8	38.00(5)	O1-Cs2-O6#9	162.97(5)
O4#2-Cs1-O5#8	99.09(5)	O4#10-Cs2-O6#9	93.63(5)
O4-Cs1-O5#8	132.69(5)	O2-Cs2-O6#9	156.23(5)
O3-Cs2-O3#4	98.55(5)	O1#5-Cs2-O6#9	67.27(5)
O3-Cs2-O1	57.48(5)	O2#4-Cs2-O6#9	70.03(5)
O3#4-Cs2-O1	70.81(5)	O4#5-Cs2-O6#9	74.18(5)
O3-Cs2-O4#10	138.90(5)	O3-Cs2-O3#5	91.20(5)
O3#4-Cs2-O4#10	68.24(5)	O3#4-Cs2-O3#5	167.69(7)
O1-Cs2-O4#10	81.59(5)	O1-Cs2-O3#5	108.95(5)
O3-Cs2-O2	58.07(5)	O2-Cs2-O3#5	68.34(5)
O3#4-Cs2-O2	110.68(5)	O1#5-Cs2-O3#5	52.83(5)
O1-Cs2-O2	40.62(5)	O2#4-Cs2-O3#5	133.79(5)
O4#10-Cs2-O2	89.28(5)	O4#5-Cs2-O3#5	38.36(5)
O3-Cs2-O1#5	70.15(5)	O6#9-Cs2-O3#5	87.92(5)

Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,-y+3/2,z+1/2 ; #2 -x+3/2,y+1/2,-z+1/2; #3 -x+3/2,y-1/2,-z+1/2;
#4 -x+1/2,y-1/2,-z+1/2; #5 -x+1/2,y+1/2,-z+1/2; #6 x-1/2,-y+3/2,z+1/2;
#7 x+1,y,z; #8 x+1/2,-y+3/2,z-1/2; #9 x-1/2,-y+3/2,z-1/2; #10 x-1,y,z.

The unique 3-nitrophthalate ligand in the crystal structure of **18** exhibits μ_{10}-bridging polydentate binding mode with $-NO_2$ group involved in binding with central metal ion (Fig. 3.166). The $-NO_2$ group of 3-nitrophthalate ligand shows μ_2-tridentate binding mode.

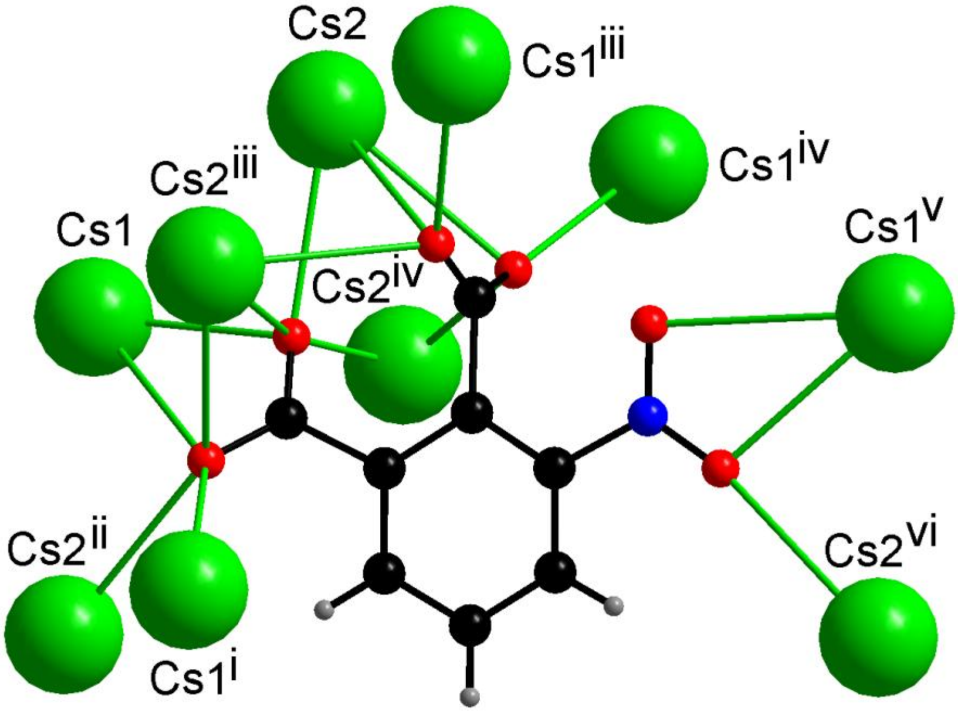


Fig. 3.166 – The μ_{10}-bridging polydentate binding mode of 3-npht ligand in **18**. Symmetry code: i) 1.5-x, -0.5+y, 0.5-z; ii) -1+x, y, z; iii) 0.5-x, -0.5+y, 0.5-z; iv) 0.5-x, 0.5+y, 0.5-z; v) -0.5+x, 1.5-y, 0.5+z; vi) 0.5+x, 1.5-y, 0.5+z.

The crystal structure reveals that **18** is a 3D coordination polymer. A unique 3-nitrophthalate ligand with its bridging binding mode extends the structure forming a zig-zag 1D chain along *a*-axis (Fig. 3.167).

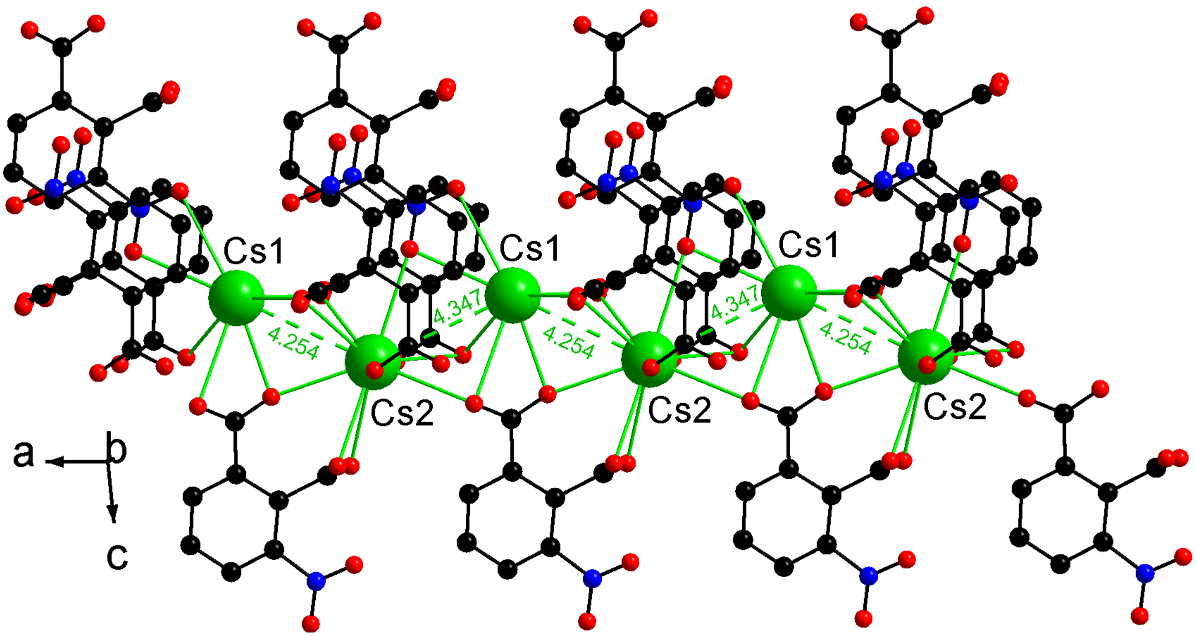


Fig. 3.167 – A portion of the infinite chain extending along *a-axis* in **18** with Cs···Cs separation of 4.254 and 4.347 Å alternatively due to μ_{10}-bridging polydentate coordination mode of a unique 3-npht ligand.

The two metal ions Cs1 and Cs2 are connected via two sets of three oxygen atoms viz. set I of carboxylate oxygens (O1, O2 and O3) and set II of two symmetry related carboxylate oxygens (O4 and O4) and a $-NO_2$ oxygen (O6). This extension via Cs1···O1···Cs2, Cs1···O2···Cs2, Cs1···O3···Cs2, Cs1···O4···Cs2 and Cs1···O6···Cs2 leads to alternate arrangement of the two unique metal ions as Cs1···Cs2···Cs1···Cs2 with alternate distances of 4.254 and 4.347 Å. A similar type of arrangement via Cs1···O1···Cs2, Cs1···O3···Cs2, Cs1···O4···Cs2, Cs1···O2···Cs2, Cs1···O3···Cs2 and Cs1···O4···Cs2 results in extension along *b*-axis forming 2D sheet structure in *ab*-plane with alternate Cs1···Cs2 distance of 4.392 and 4.702 Å (Fig. 3.168).

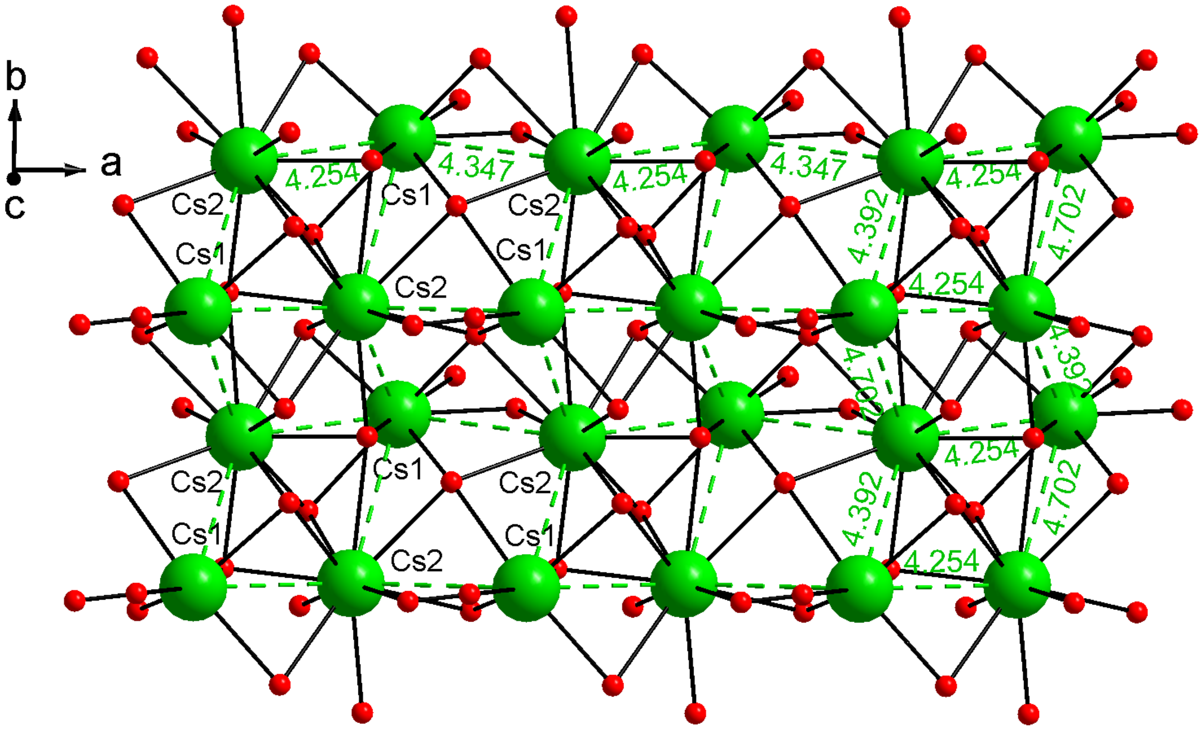


Fig. 3.168 – A portion of two dimensional zig-zag sheet/layer of **18** in *ab* plane with alternate Cs···Cs distance of 4.254 and 4.347 Å along *a-axis* and alternate 4.392 and 4.702 Å along *b-axis* (green broken lines). For clarity only the O atoms of the ligand are shown.

The structure further extends along *c*-axis resulting in 3D coordination polymer (Fig. 3.169). Interestingly the crystal structure of **18** shows only C-H···O H-bonding interactions (Table 3.29).

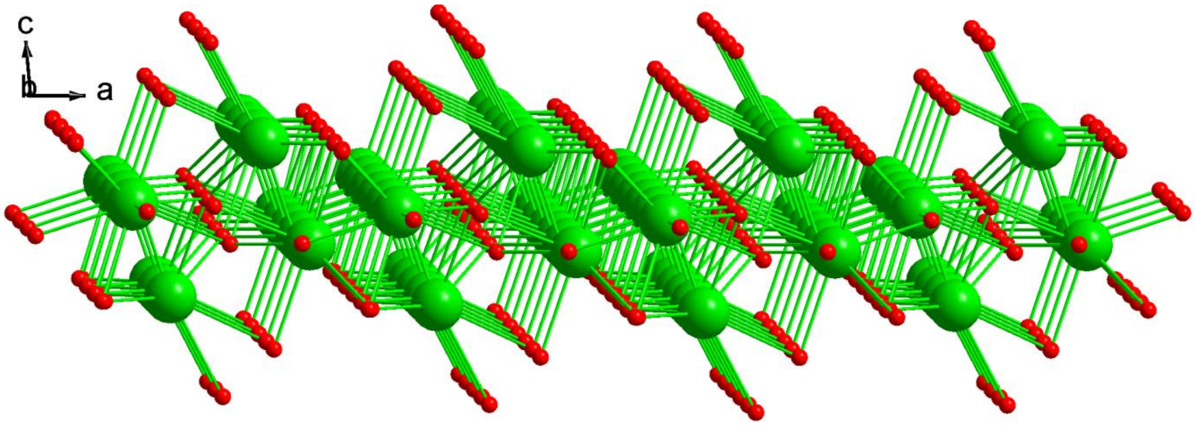


Fig. 3.169 – A portion of three dimensional (3D) architecture of **18** *(for clarity only oxygen atoms of the ligands are shown).*

Table 3.29 - Hydrogen bonding geometry [Å and °] for [Cs_2(3-npht)] **18**

D-H···A	d(D-H)	(H···A)	d(D···A)	<DHA	Symmetry code
C4-H4 ···O1	0.950(.003)	2.909(.002)	3.526(.003)	123.69(0.17)	-x+1,-y+1,-z+1
C4-H4 ···O2	0.950(.003)	2.855(.002)	3.616(.003)	137.83(0.17)	-x+1,-y+2,-z+1
C5-H5 ···O5	0.950(.003)	2.360(.002)	3.217(.004)	149.88(0.19)	x+1,+y,+z
C6-H6 ···O2	0.950(.003)	2.822(.002)	3.627(.004)	143.11(0.17)	x+1,+y,+z
D=Donor and A=Acceptor					

3.2.8 Synthetic aspects, spectral characteristics and thermal studies for [NaRb(2-carboxy-6-nba)$_2$(H_2O)$_3$]·2H_2O **19**

The mixed metallic compound **19** was prepared from an aqueous medium acid base reaction of rubidium carbonate, sodium bicarbonate and 3-nitrophthalic acid (3-nphtH$_2$) in 1:1:1 mole ratio. Crystals suitable for X-ray structure analysis were obtained by recrystallising it from an aqueous solution. The composition of **19** was determined based on analytical data and metal carbonate formed on pyrolysis at 800°C.

The IR spectra of **19** exhibit several signals in the mid-IR region indicating the presence of organic moieties (Fig. 3.170). In the IR spectrum of **19**, the band at 1578 cm^{-1} can be assigned for the asymmetric stretching vibration of the carboxylate group (υ_{asym}) and the band observed at 1485 cm^{-1} for symmetric stretching vibration (υ_{sym}). The IR stretching vibrations expected for the υ_{N-O} vibration of the –NO$_2$ group of the ligand is seen at 1344 cm^{-1}. Interestingly sharp signal assignable for –NO$_2$ group stretching vibrations was observed in Raman spectrum (Fig. 3.170) of the compound at 1347 cm^{-1}.

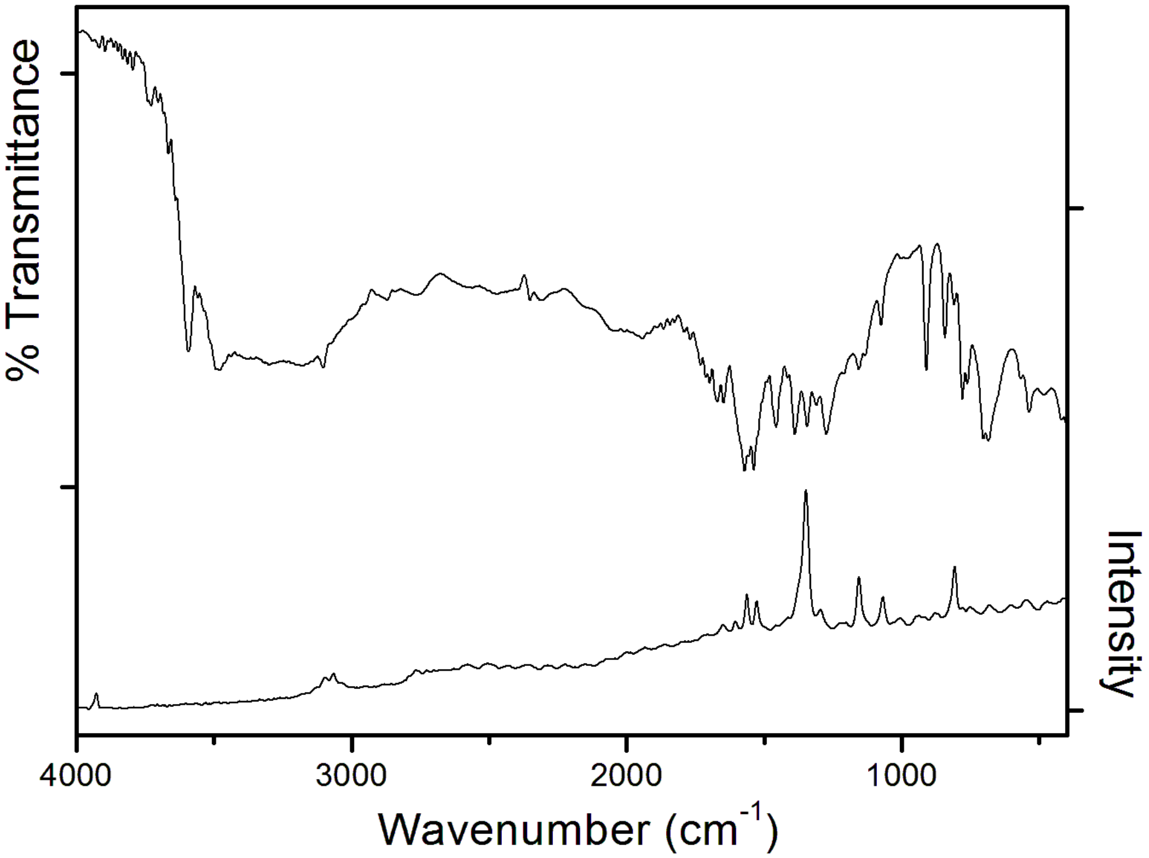


Fig. 3.170 – IR and Raman spectrum of **19**

The UV-visible spectrum (Fig. 3.171) of the compound show an absorbance ~273 nm assignable for intra ligand charge transfer band for aromatic 2-carboxy-6-nba ligand.

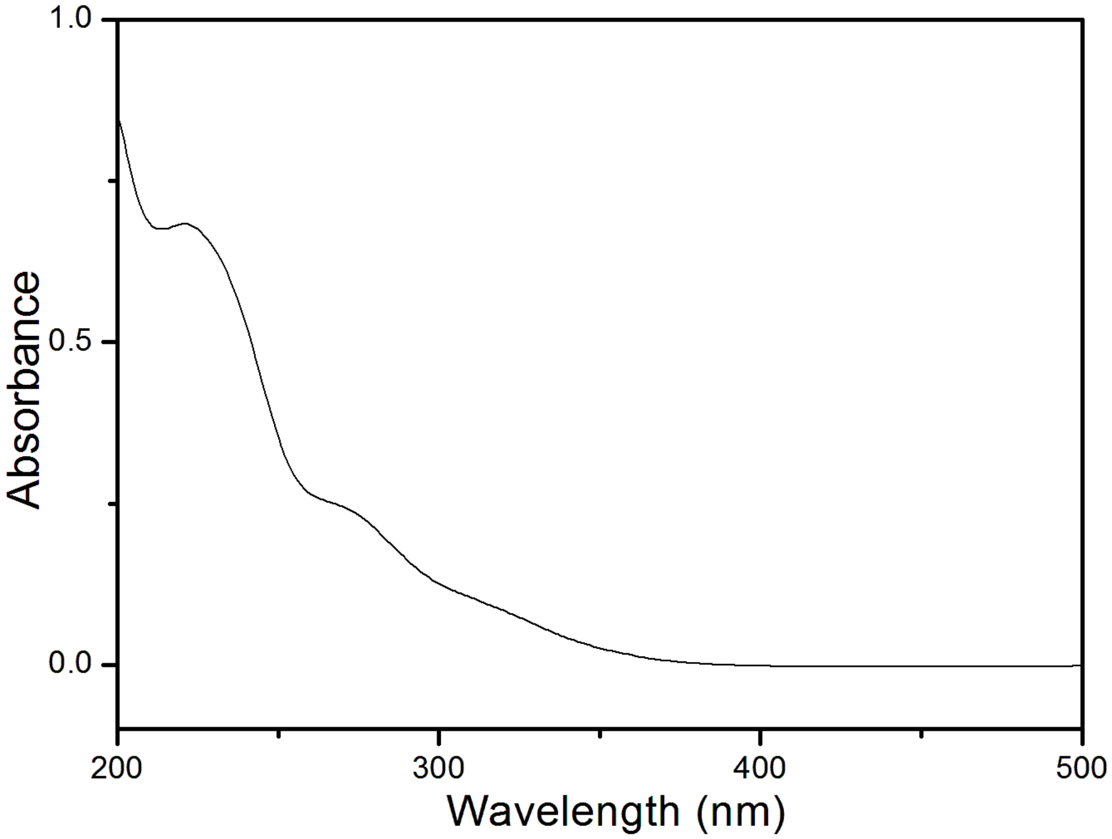


Fig. 3.171 – UV-Visible spectrum of **19**

Compound **19** exhibits endothermic event at 109°C in its TG-DTA graph (Fig.3.172). The TG curve shows a decrease in mass by 14.71 % equivalent to loss of five water molecules by 120°C. Above 200°C, the DTA curve shows an endothermic peak at 236°C and exothermic peaks at 344°C and 480°C with rapid mass loss due to decomposition of **19**. The residual mass of 27.19 % corresponds to Na_2CO_3-Rb_2CO_3.

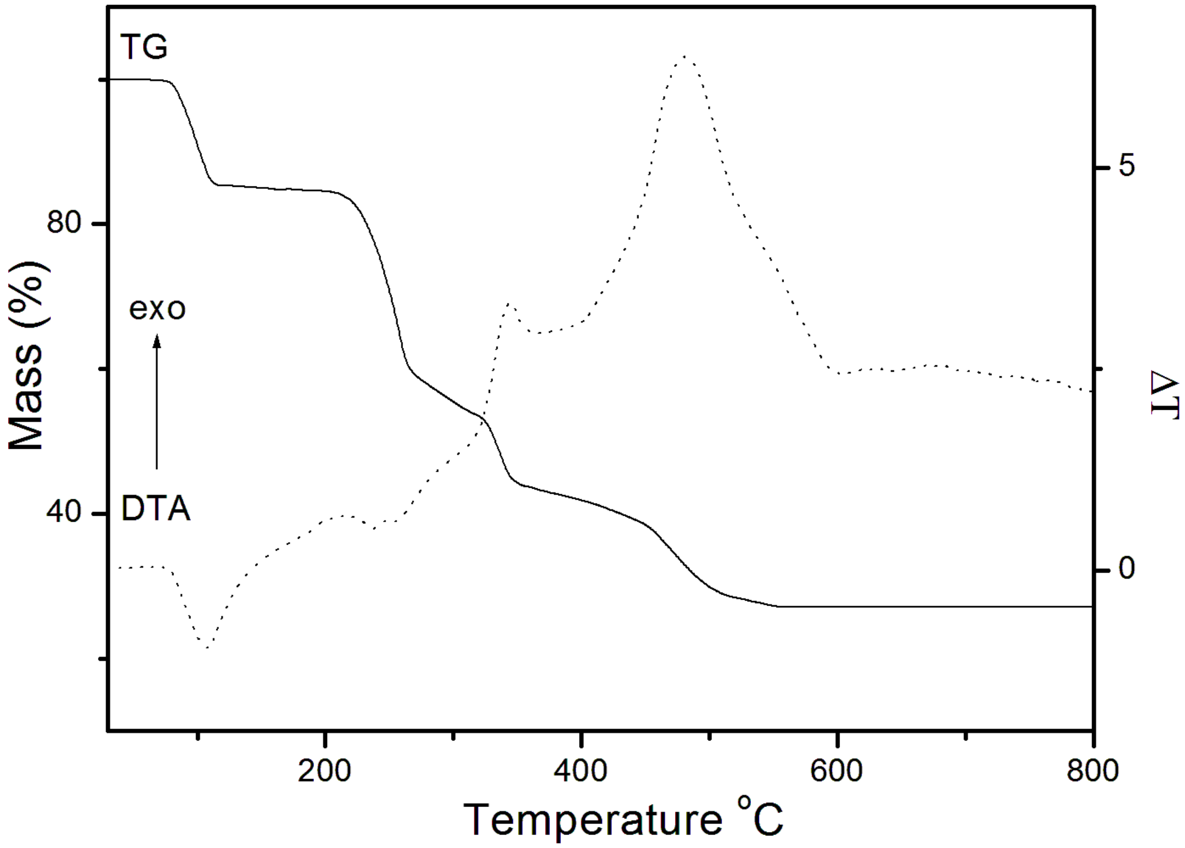


Fig. 3.172 – TG-DTA curve of **19**

3.2.9 Description of crystal structure of [NaRb(2-carboxy-6-nba)$_2$(H$_2$O)$_3$]·2H$_2$O **19**

Compound **19** crystallises in the centrosymmetric monoclinic *P2$_1$/n* space group. Its crystal structure consists of an unique Rb(I) ion, an unique Na(I) ion, two crystallographically independent 2-carboxy-6-nba ligands, three independent coordinated and two lattice water molecules (Fig. 3.173). The geometric parameters of 2-carboxy-6-nba are in the normal range.

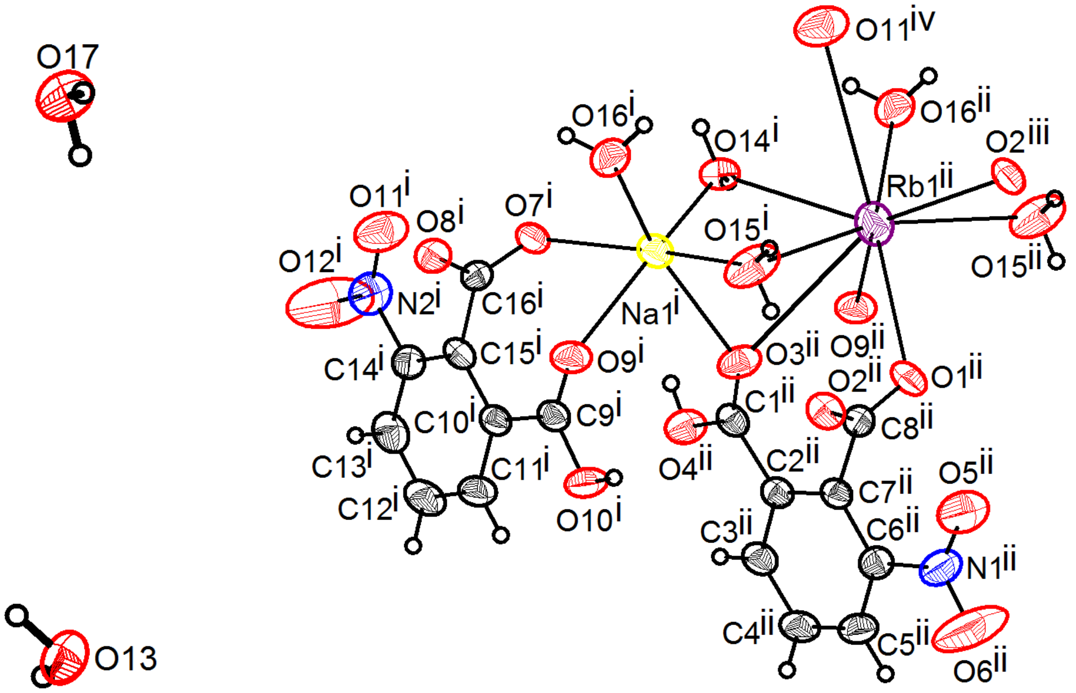


Fig. 3.173 - The crystal structure of [NaRb(2-carboxy-6-nba)$_2$(H$_2$O)$_3$]·2H$_2$O **19** showing the atom labelling scheme and the coordination sphere of the unique Na(I) and Rb(I) atoms in **19**. Displacement ellipsoids are drawn at the 50% probability level excepting for the H atoms, which are shown as spheres of arbitrary radius. Symmetry code: i) 0.5-x, -0.5+y, -0.5-z; ii) 0.5-x, -1.5+y, -0.5-z; iii) x, -2+y, -1+z; iv) -0.5+x, 0.5-y, -1.5+z.

The unique Na ion is hexacoordinated to three oxygens of carboxylate groups and three water molecules whereas Rb is nonacoordinated to five oxygens of carboxylate groups and four water molecules (Fig. 3.174).

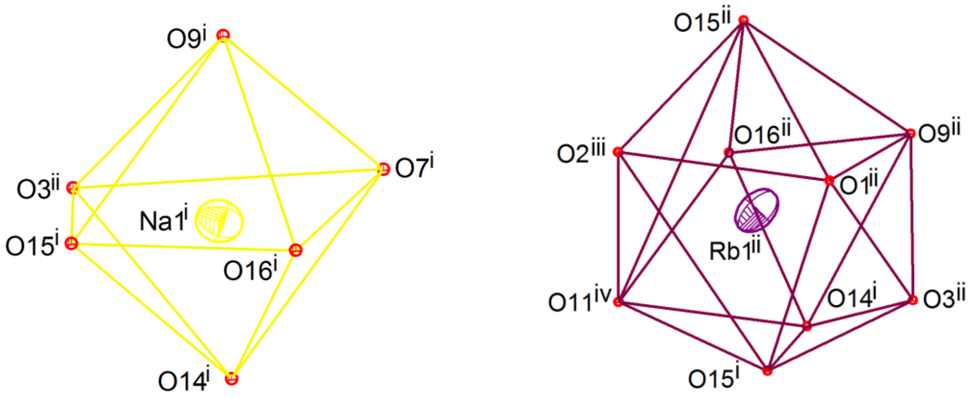


Fig. 3.174 - The distorted hexagonal {NaO$_6$} coordination around Na1 and biaugmented triangular prism {NaO$_9$} coordination around Rb1 in **19** Symmetry code: i) 0.5-x, -0.5+y, -0.5-z; ii) 0.5-x, -1.5+y, -0.5-z; iii) x, -2+y, -1+z; iv) -0.5+x, 0.5-y, -1.5+z.

The structural details of **19** are given in Table 3.30.

Table 3.30 - Crystal data and structure refinement for [NaRb(2-carboxy-6-nba)$_2$(H$_2$O)$_3$] ·2H$_2$O **19**

Empirical formula	$C_{16}H_{18}N_2O_{17}RbNa$
Formula weight (g mol^{-1})	618.78
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	18.7330(14)
b (Å)	6.6818(5)
c (Å)	18.8092(14)
α (°)	90
β (°)	93.359(3)
γ (°)	90
Volume (Å^3)	2350.3(3)
Z	4
D_{calc} (mg/m^3)	1.749
Absorption coefficient (mm^{-1})	2.213
F(000)	1248
Crystal size (mm^3)	0.15 x 0.10 x 0.10
θ range for data collection (°)	3.049 to 24.999
Index ranges	$-22 \le h \le 22$ $-7 \le k \le 7$ $-22 \le l \le 22$
Reflections collected / unique	66259 / 4133 [R(int) = 0.0552]
Completeness to θ = 25.00°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.7456 and 0.5705
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4133 / 15 / 371
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.0979
R indices (all data)	R1 = 0.0415, wR2 = 0.1017
Largest diff. peak and hole (e Å^{-3})	0.767 and -0.782

The Na-O bond distances range from 2.316(3) to 2.552(3) Å while the O-Na-O angles vary between 73.24(10) to 166.45(14)° forming a distorted {NaO$_6$} octahedron. The Rb-O bond distances range from 2.870(3) to 3.587(4) Å while the O-Rb-O angles vary between 53.25(9) to 152.98(9)° forming a distorted {RbO$_9$} polyhedron (Table 3.31).

Table 3.31 – Selected Bond lengths [Å] and angles [°] for **19**.

Bond lengths			
Rb(1)-O(1)	2.870(3)	Rb(1)-O(11)#3	3.587(4)
Rb(1)-O(14)#1	2.899(3)	Na(1)-O(14)	2.316(3)
Rb(1)-O(2)#2	2.973(3)	Na(1)-O(16)	2.332(3)
Rb(1)-O(16)	2.976(4)	Na(1)-O(15)	2.360(4)
Rb(1)-O(15)#1	3.277(5)	Na(1)-O(9)	2.455(3)
Rb(1)-O(9)	3.298(3)	Na(1)-O(7)	2.464(3)
Rb(1)-O(3)	3.337(3)	Na(1)-O(3)#4	2.552(3)
Rb(1)-O(15)	3.476(5)		
Bond angles			
O(1)-Rb(1)-O(14)#1	122.93(8)	O(9)-Rb(1)-O(15)	64.55(8)
O(1)-Rb(1)-O(2)#2	86.16(8)	O(3)-Rb(1)-O(15)	125.59(9)
O(14)#1-Rb(1)-O(2)#2	141.29(8)	O(1)-Rb(1)-O(11)#3	152.98(9)
O(1)-Rb(1)-O(16)	144.56(8)	O(14)#1-Rb(1)-O(11)#3	62.03(8)
O(14)#1-Rb(1)-O(16)	73.58(9)	O(2)#2-Rb(1)-O(11)#3	80.53(8)
O(2)#2-Rb(1)-O(16)	97.84(9)	O(16)-Rb(1)-O(11)#3	61.27(9)
O(1)-Rb(1)-O(15)#1	73.29(8)	O(15)#1-Rb(1)-O(11)#3	85.46(10)
O(14)#1-Rb(1)-O(15)#1	70.69(8)	O(9)-Rb(1)-O(11)#3	123.38(8)
O(2)#2-Rb(1)-O(15)#1	98.38(8)	O(3)-Rb(1)-O(11)#3	120.58(9)
O(16)-Rb(1)-O(15)#1	139.66(9)	O(15)-Rb(1)-O(11)#3	105.85(10)
O(1)-Rb(1)-O(9)	82.38(8)	O(14)-Na(1)-O(16)	101.03(13)
O(14)#1-Rb(1)-O(9)	78.86(8)	O(14)-Na(1)-O(15)	100.13(16)
O(2)#2-Rb(1)-O(9)	134.57(8)	O(16)-Na(1)-O(15)	82.45(13)
O(16)-Rb(1)-O(9)	69.75(8)	O(14)-Na(1)-O(9)	155.96(12)
O(15)#1-Rb(1)-O(9)	119.63(9)	O(16)-Na(1)-O(9)	97.38(13)
O(1)-Rb(1)-O(3)	58.44(7)	O(15)-Na(1)-O(9)	97.48(15)
O(14)#1-Rb(1)-O(3)	64.61(7)	O(14)-Na(1)-O(7)	91.71(11)
O(2)#2-Rb(1)-O(3)	138.20(8)	O(16)-Na(1)-O(7)	88.87(12)
O(16)-Rb(1)-O(3)	123.79(8)	O(15)-Na(1)-O(7)	166.45(14)
O(15)#1-Rb(1)-O(3)	53.25(9)	O(9)-Na(1)-O(7)	73.24(10)
O(9)-Rb(1)-O(3)	66.80(8)	O(14)-Na(1)-O(3)#4	86.90(12)
O(1)-Rb(1)-O(15)	92.09(9)	O(16)-Na(1)-O(3)#4	156.28(13)
O(14)#1-Rb(1)-O(15)	125.26(8)	O(15)-Na(1)-O(3)#4	74.12(12)
O(2)#2-Rb(1)-O(15)	72.16(8)	O(9)-Na(1)-O(3)#4	82.31(11)
O(16)-Rb(1)-O(15)	56.65(9)	O(7)-Na(1)-O(3)#4	113.41(10)
O(15)#1-Rb(1)-O(15)	163.35(11)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1/2,-z+1/2; #2 x,y+1,z; #3 -x+1,-y+2,-z+1; #4 x,y-1,z ;
#5 -x+1/2,y-1/2,-z+1/2.

The two unique 2-carboxy-6-nba ligands in the crystal structure of **19** exhibits μ_3-tetradentate binding mode (Fig. 3.175).

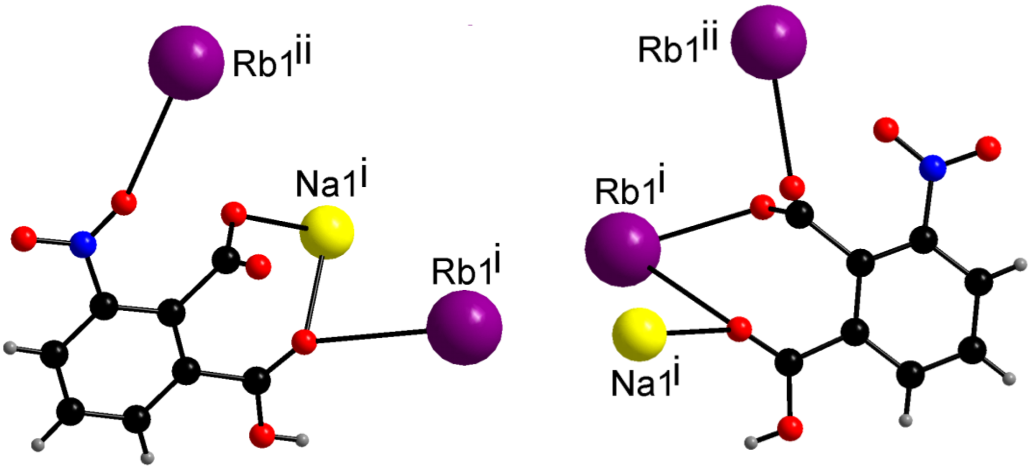
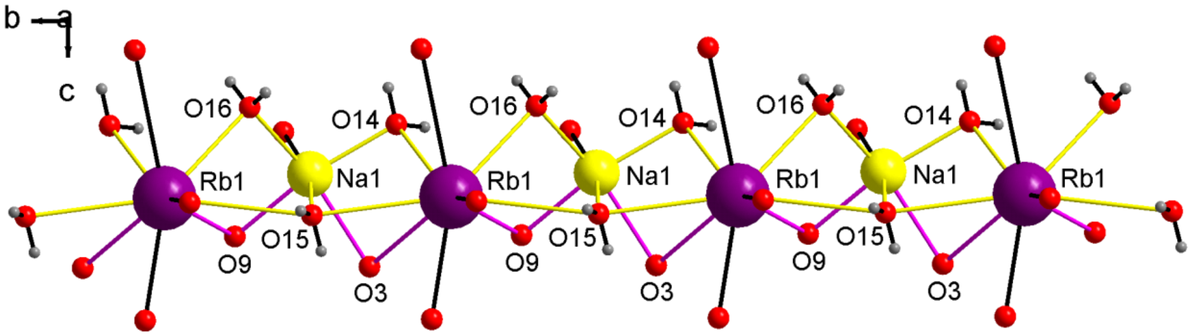


Fig. 3.175 - The μ_3-bridging tetradentate binding mode of two unique 2-carboxy-6-nba ligands in **19**. Symmetry code: i) 0.5-x, -0.5+y, -0.5-z; ii) 0.5-x, -1.5+y, -0.5-z.

Interestingly in **19**, the coordinated aqua ligands show bridging binding mode of which two water molecules exhibit μ_2-bridging bidentate binding mode connecting the Na and Rb centres as Rb1-O16-Na1-O14-Rb1 (Fig. 3.176). The third coordinated aqua ligand exhibit μ_3- bridging tridentate binding mode binded to one Na and two symmetry related Rb centres. The oxygen atoms O3 and O9 of carboxylate group of two symmetry related 2-carboxy-6-nba ligand also acts as a bridge connecting the two metal centres via Rb1-O9-Na1-O3-Rb1. The bridging behaviour of coordinated water molecules and 2-carboxy-6-nba ligands extends the structure into 1D polymeric chain along *b*-axis. The two 1D chains are further interconnected via Rb1 centres using one of the carboxylate group oxygens O1 and O2 of the ligand forming 1D rail structure (Fig. 3.176).



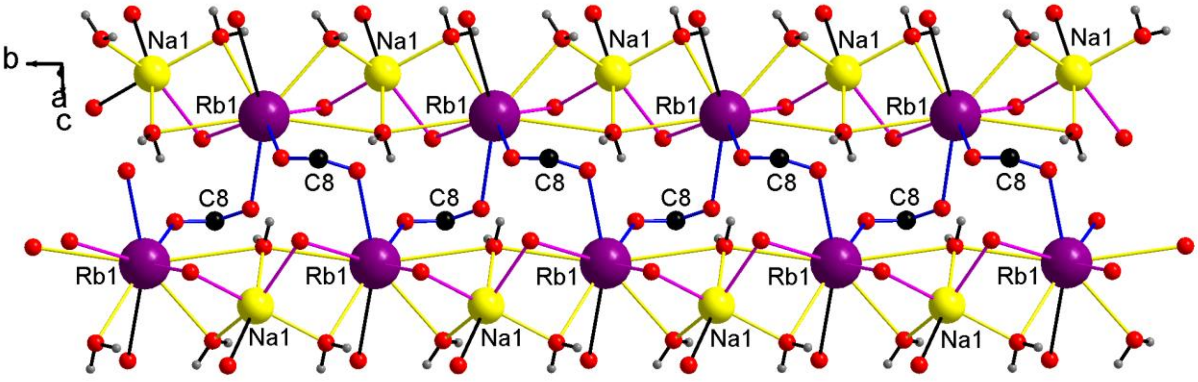


Fig. 3.176 – The μ_2- bridging bidentate and μ_3-bridging tridentate binding mode of coordinated water molecules in **19** extending the structuere along *b*-axis forming a chain of Rb1-Na1-Rb1-Na1-Rb1 (top). The two chains are further interconnected via carboxylate group of the 3-nitrophthalate ligand (bottom).

The two unique 2-carboxy-6-nba ligands (Fig. 3.177) show C-H···O and O-H···O H-bonding interactions (Table 3.32).

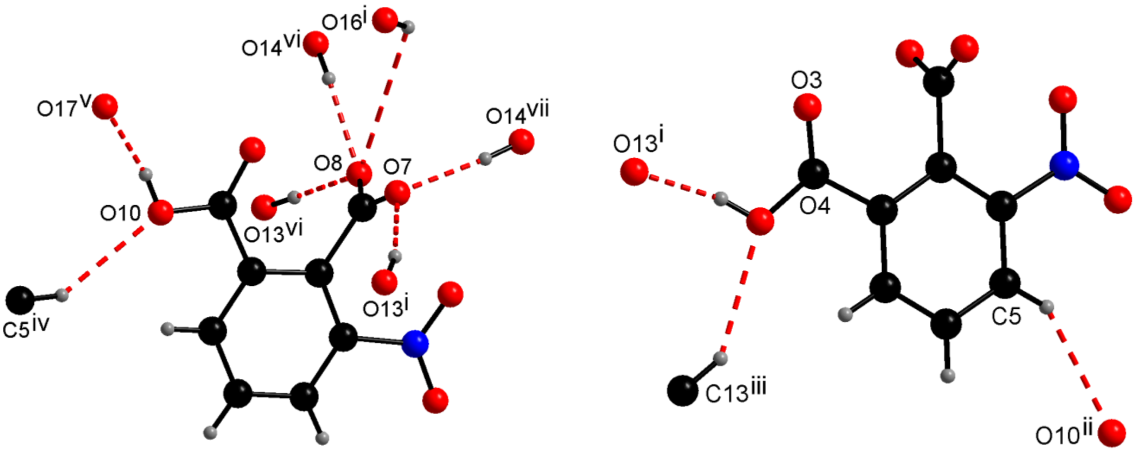


Fig. 3.177 - The H-bonding surroundings of two unique 2-carboxy-6-nba ligands in **19** showing C-H···O and O-H···O interactions (shown in broken lines)

Table 3.32 – Hydrogen bonds [Å and °] for [NaRb(2-carboxy-6-nba)$_2$(H$_2$O)$_3$]·2H$_2$O **19**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)	Symmetry codes
C5-H5 ···O10	0.93	2.59	3.399(5)	146.3	-x+1,-y+2,-z
C13-H13 ···O4	0.93	2.61	3.423(5)	146.7	-x+3/2,y-1/2,-z+1/2
O4-H4A ···O13	0.82	1.75	2.538(4)	161.9	x,y+1,z #3 -x+1,-y+2,-z+1
O10-H10A ···O17	0.82	1.73	2.532(5)	165	-x+1/2,y+1/2,-z+1/2
O13-H13A ···O8	0.861(19)	1.887(19)	2.747(4)	179(5)	x,y-1,z
O13-H13B ···O7	0.873(18)	1.87(2)	2.732(4)	167(5)	x,y,z

O14-H14A ···O8	0.844(19)	2.02(2)	2.841(4)	164(5)	x,y-1,z
O14-H14B ···O7	0.870(19)	1.93(2)	2.796(4)	171(4)	-x+1,-y+1,-z+1
O15-H15A ···O2	0.860(19)	1.97(2)	2.819(4)	169(6)	x,y-1,z
O15-H15B ···O1	0.86(2)	1.98(3)	2.822(4)	168(7)	-x+1/2,y-1/2,-z+1/2
O16-H16A ···O5	0.828(19)	2.25(4)	2.913(5)	137(6)	-x+1/2,y-1/2,-z+1/2
O16-H16B ···O8	0.85(2)	2.02(3)	2.827(5)	159(5)	-x+1,-y+2,-z+1
O17-H17A ···O1	0.854(19)	1.887(19)	2.732(4)	170(5)	-x+1/2,y-1/2,-z+1/2
O17-H17B ···O2	0.841(19)	1.91(2)	2.741(4)	171(5)	-x+1/2,y-3/2,-z+1/2

One such H-bonding interaction between coordinated water molecule O14 and carboxylate oxygen O7 that is not involved in Bridging extends the structure in 2D via O14-H···O7 H-bonding along c-axis forming a supramolecular architecture (Fig. 3.178).

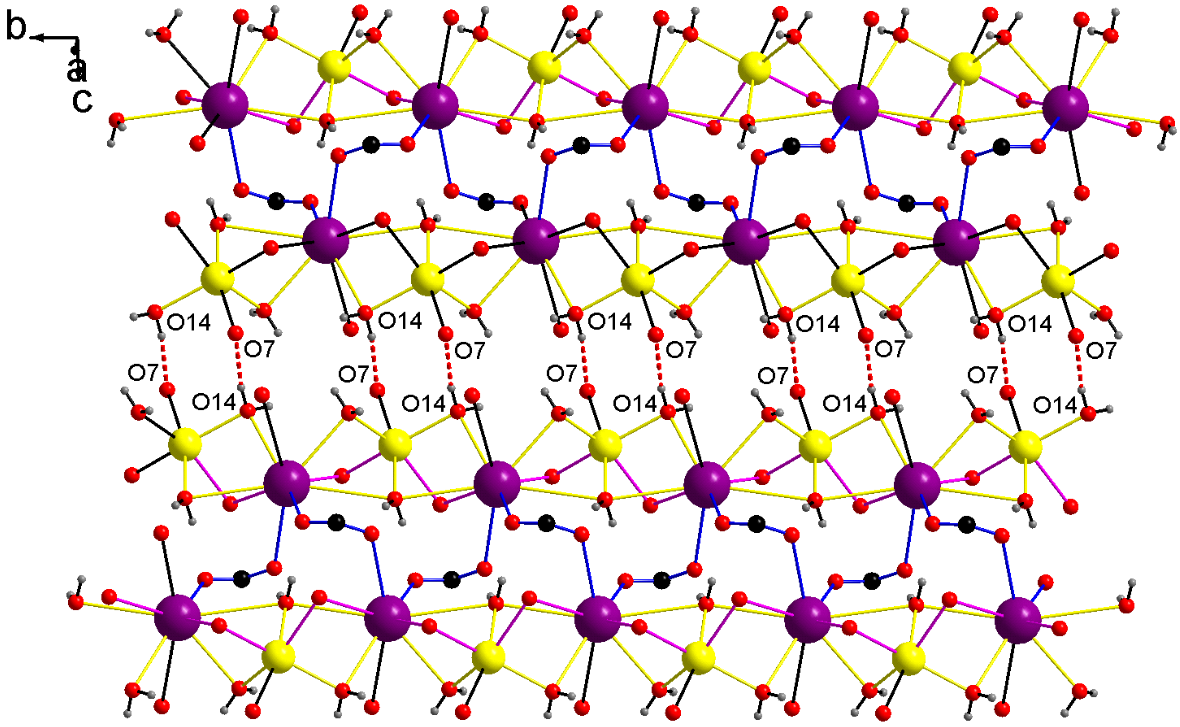


Fig. 3.178 – The H-bonding interaction between coordinated water molecule O14 and the oxygen O7 of 2-carboxy-6-nba ligand extends the structure along *c*-axis and forms a 2D supramolecular architecture via O14-H···O7 H-bonding.

Investigations of crystal growth of s-block metal phthalates in presence of piperazine

3.3.1 Synthesis of pure metal phthalate compounds for reference:

Pure metal phthalates of Na, Ca, Mg, Ni, Cu, Zn, Sr, Ba are synthesised by an aqueous reaction of metal source and phthalic acid. No efforts are made to formulate the compound as these compounds are prepared for only comparison purpose in further investigations using IR spectrum. The IR spectrum of NaHpht·½H_2O **20** (Fig. 3.179), KHpht **21** (Fig. 3.180), calcium phthalate **22a** (Fig. 3.181), calcium hydrogen phthalate **22b** (Fig. 3.182), magnesium phthalate **23** (Fig. 3.183), nickel phthalate **24** (Fig. 3.184), copper phthalate **25** (Fig. 3.185), zinc hydrogen phthalate **26** (Fig. 3.186), strontium phthalate **27** (Fig. 3.187), barium phthalate **28** (Fig. 3.188) are shown below:

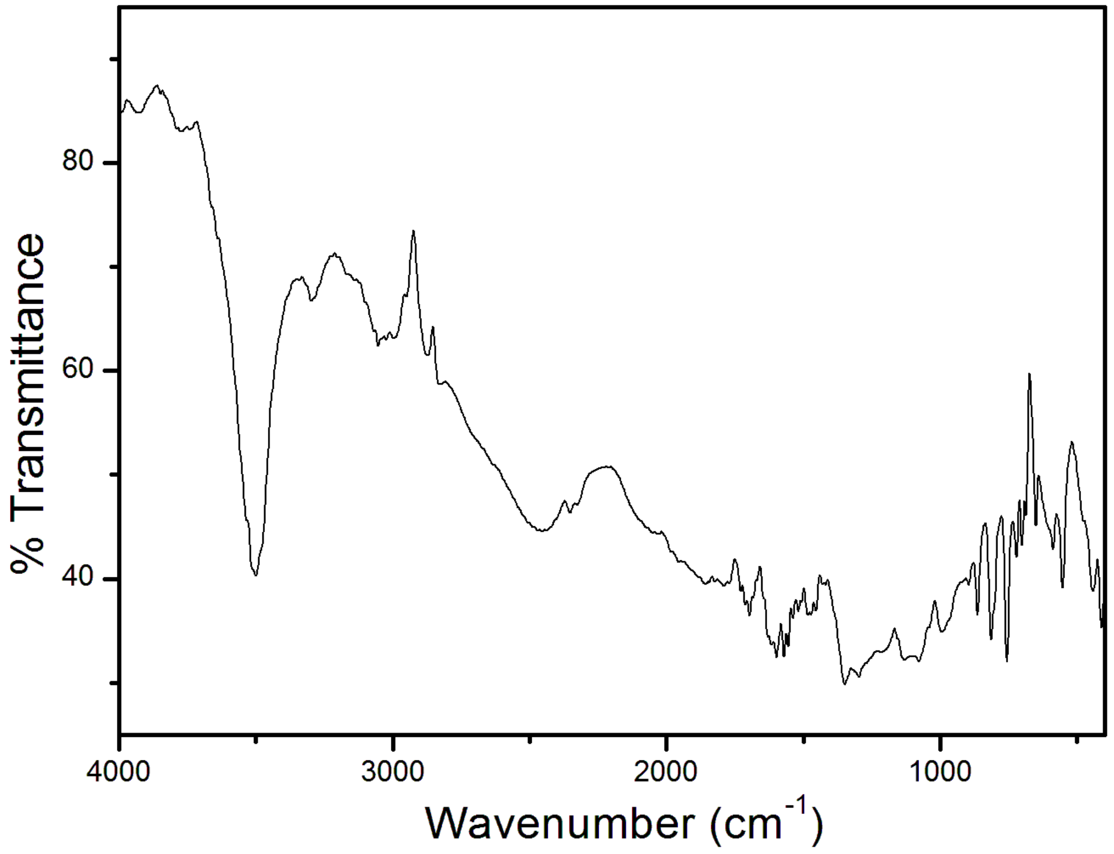


Fig. 3.179 – IR spectrum of **20**

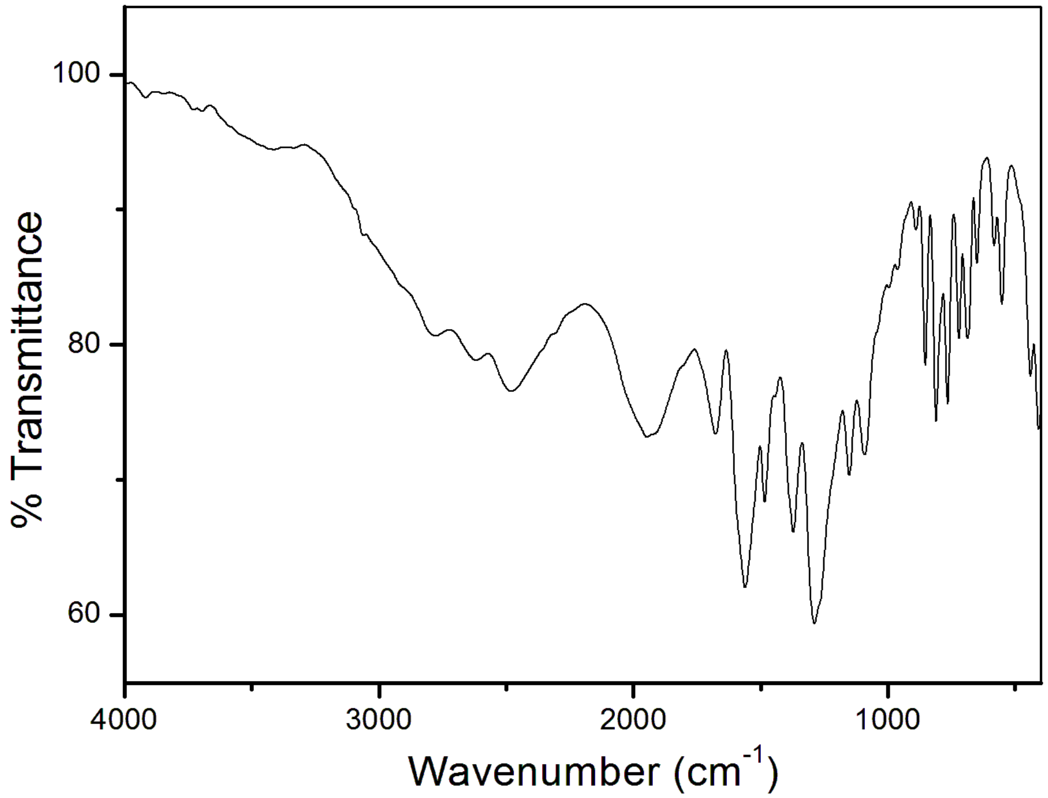


Fig. 3.180 – IR spectrum of **21**

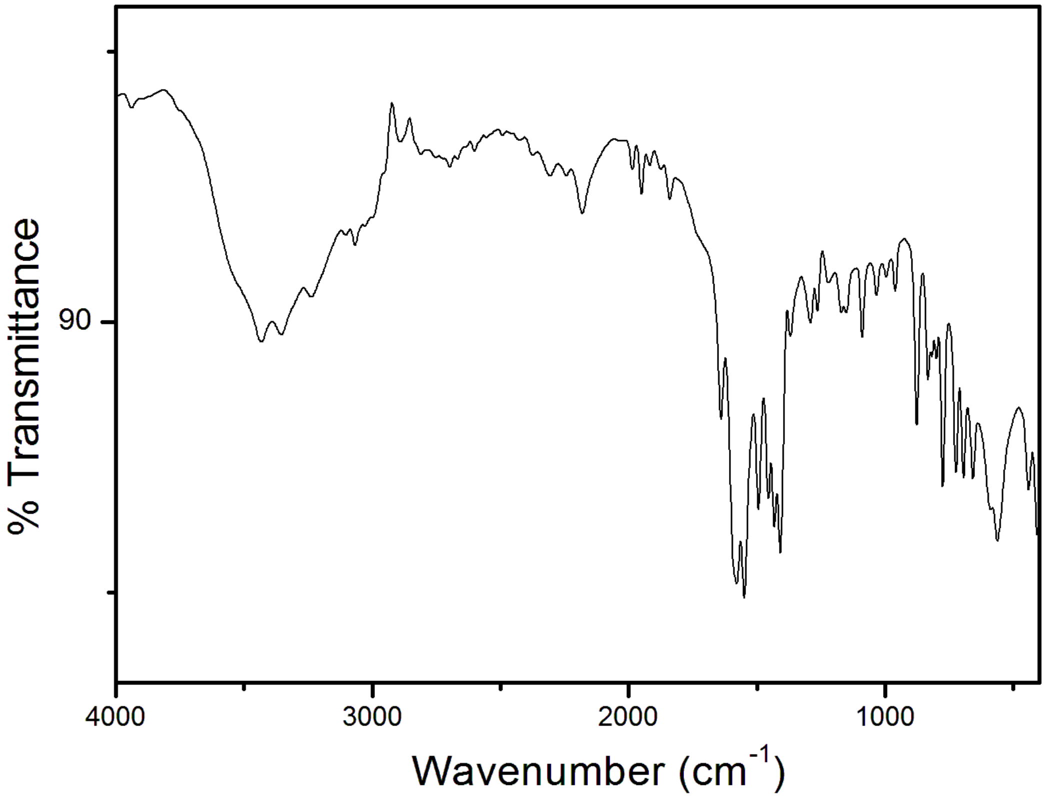


Fig. 3.181 – IR spectrum of **22a**

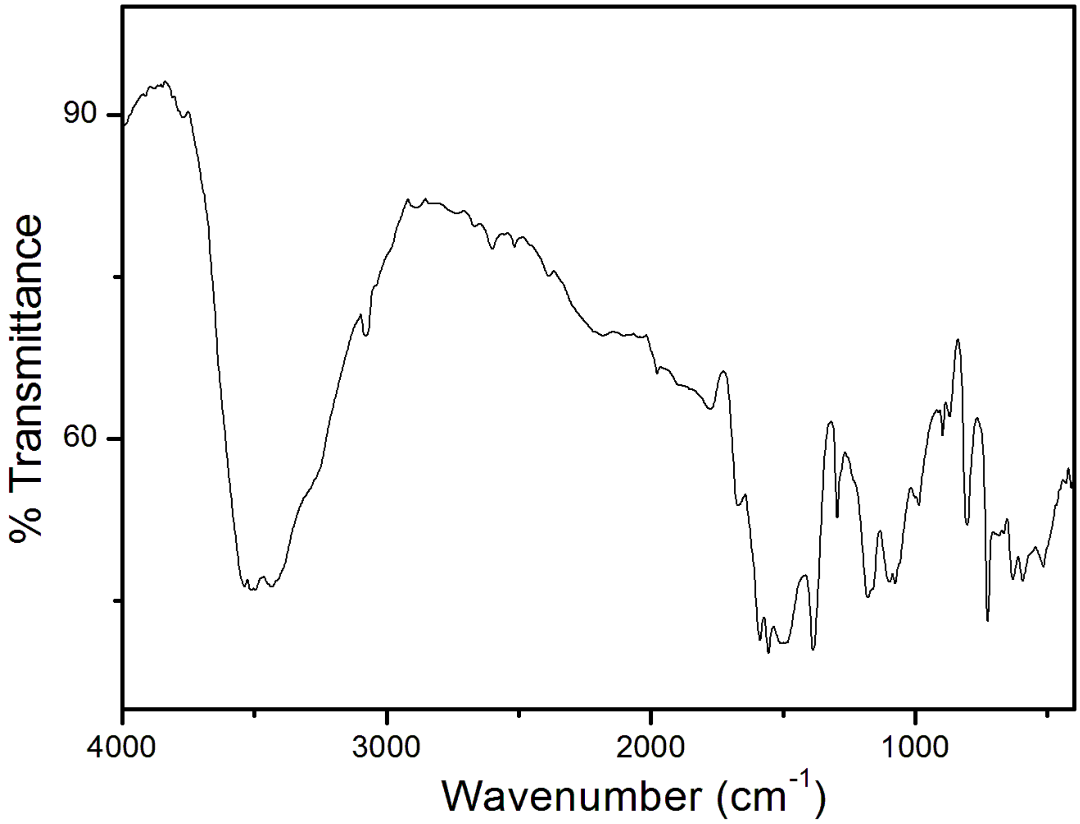


Fig. 3.182 – IR spectrum of **22b**

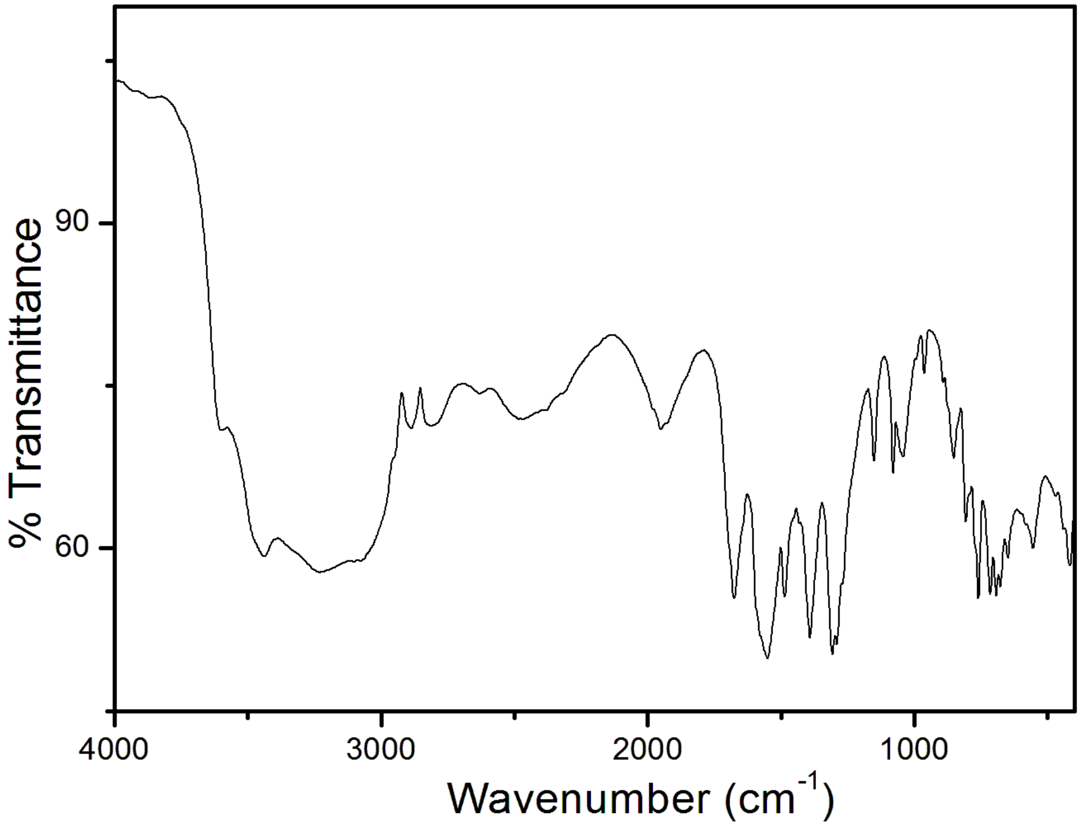


Fig. 3.183 – IR spectrum of **23**

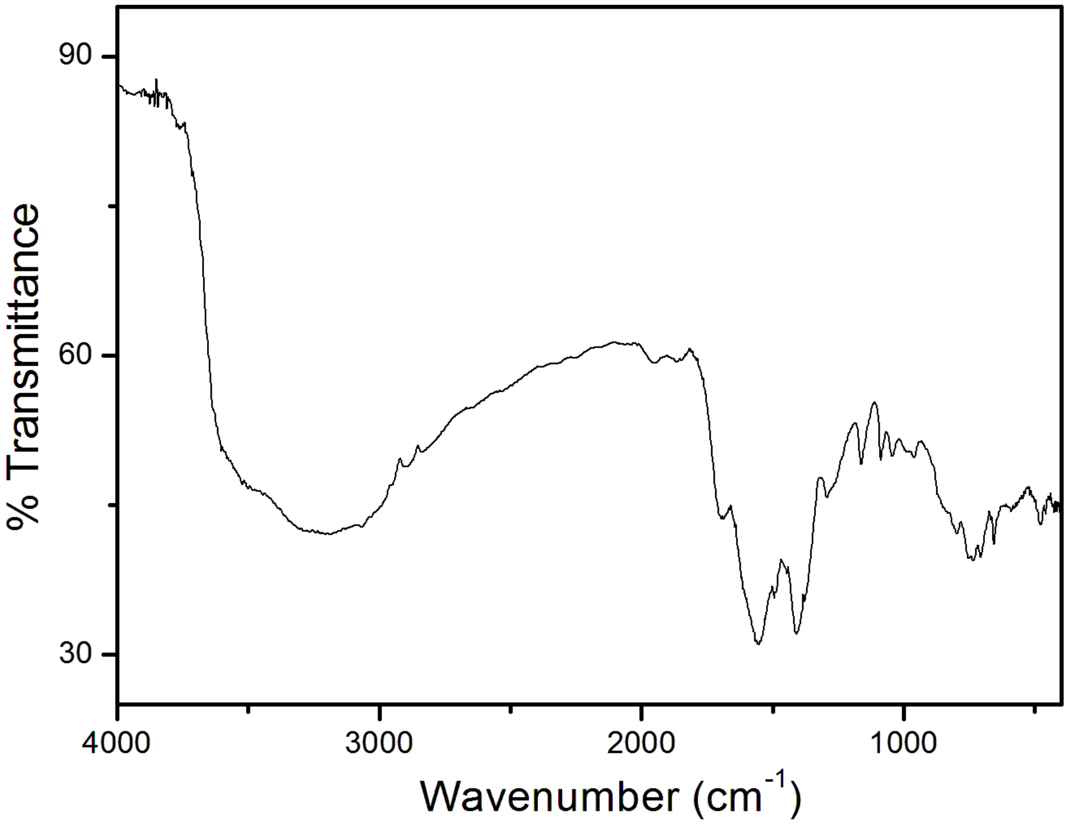


Fig. 3.184 – IR spectrum of **24**

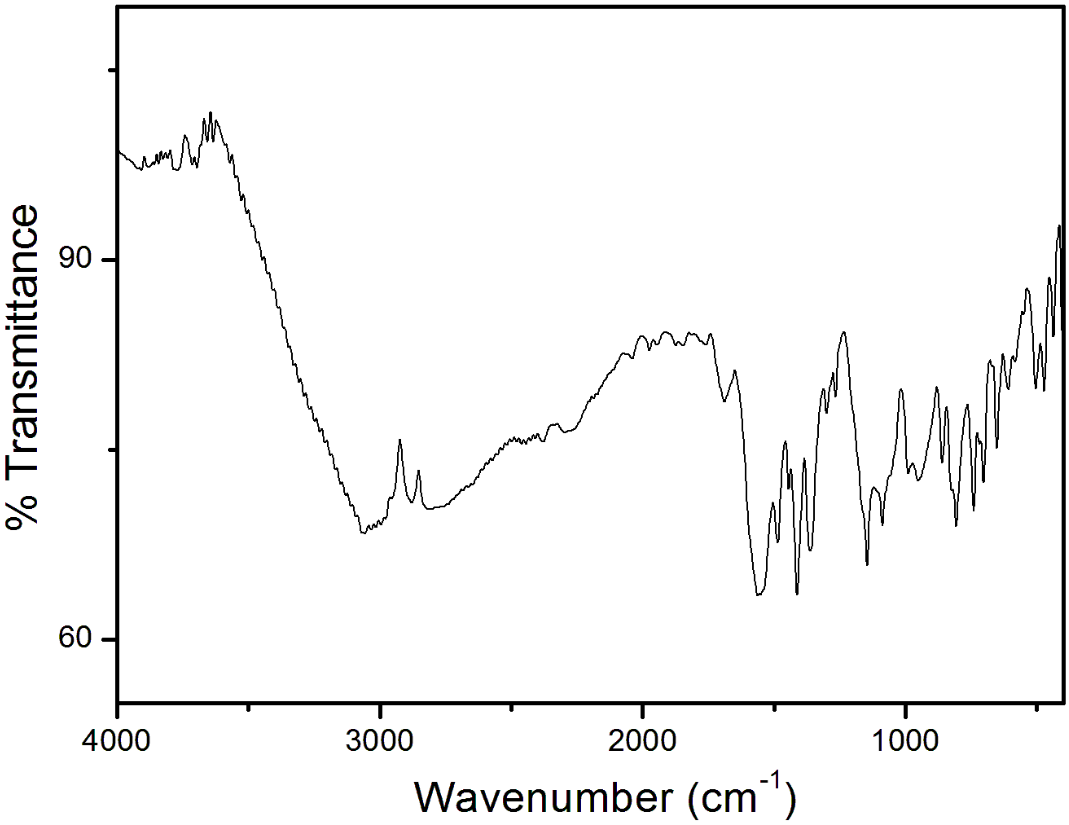


Fig. 3.185 – IR spectrum of **25**

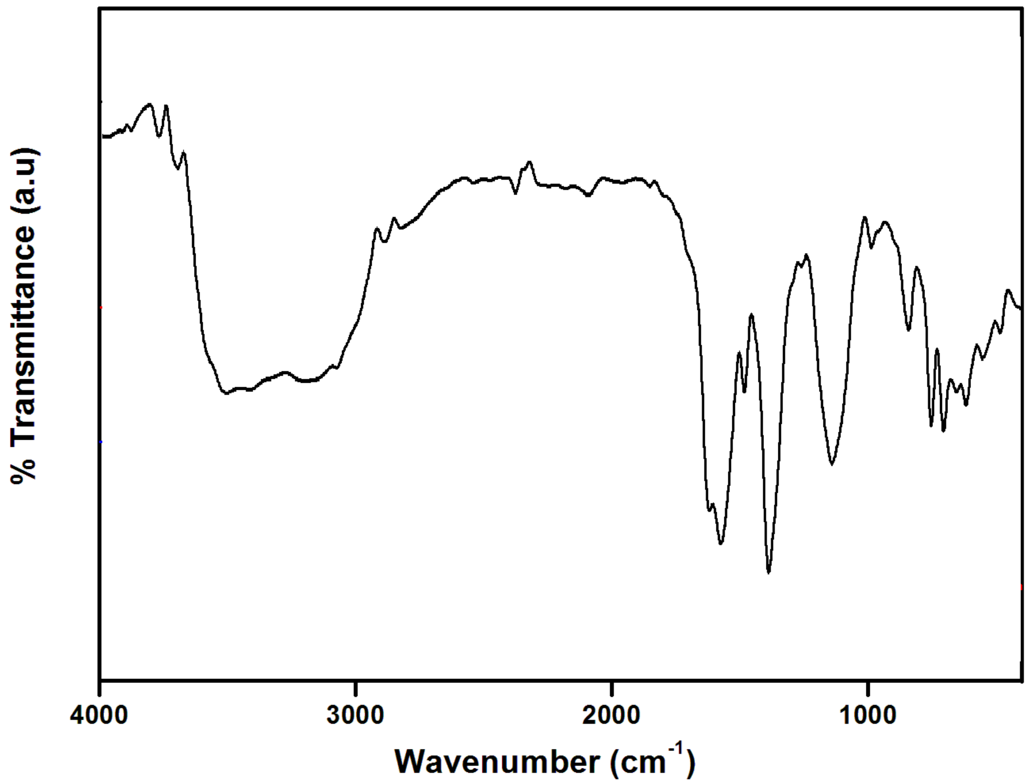


Fig. 3.186 – IR spectrum of **26**

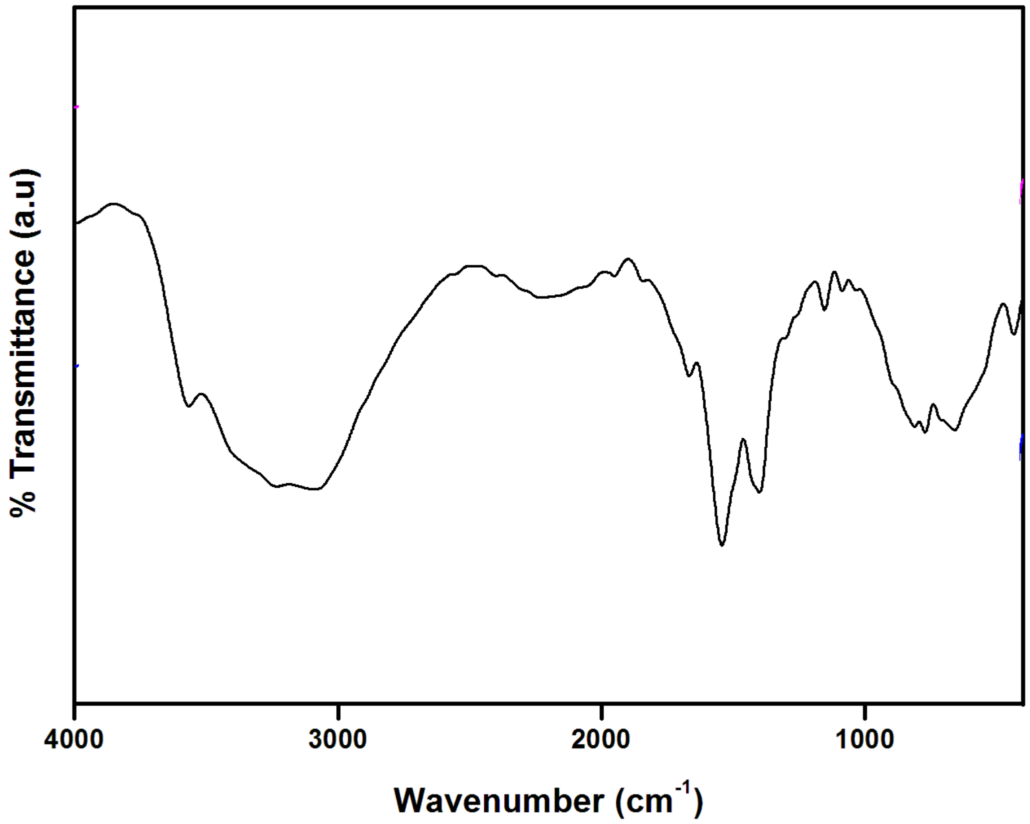


Fig. 3.187 – IR spectrum of **27**

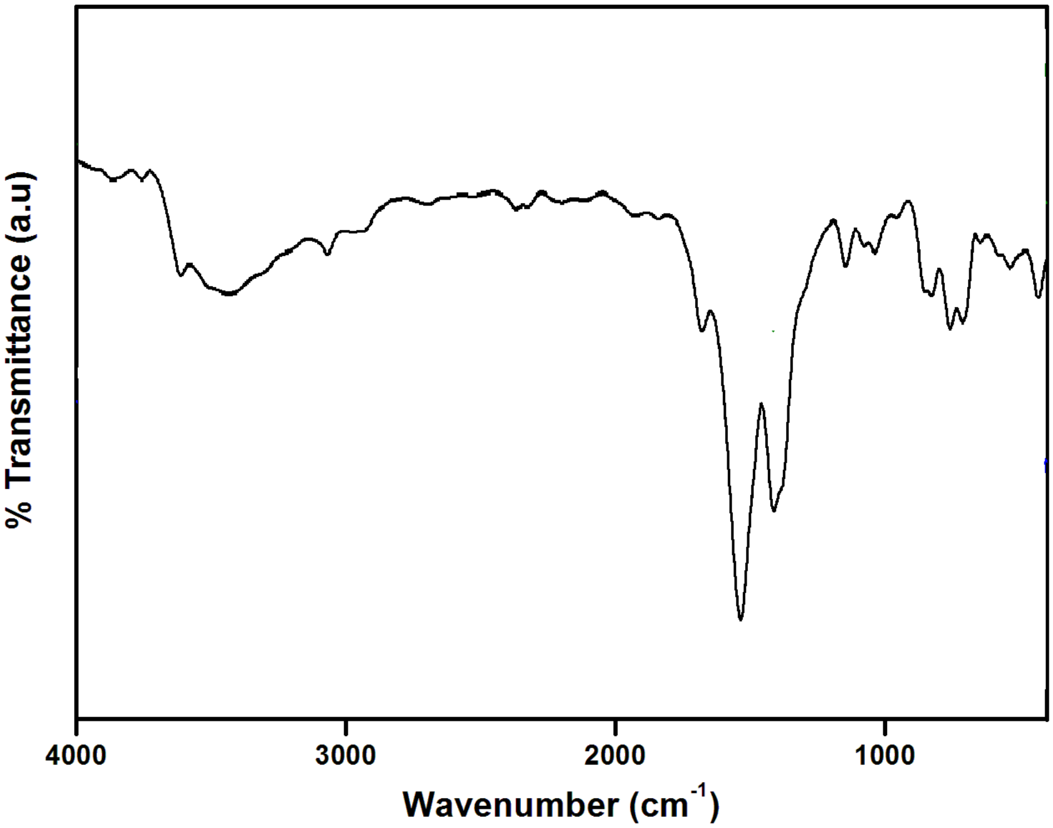


Fig. 3.188 – IR spectrum of **28**

3.3.2 Investigation of reactions of s-block metal ions with phthalic acid in presence of piperazine.

An aqueous reaction of alkali metal ions viz. Na / K, phthalic acid and piperazine is carried out in 1:1:0.5 molar ratio. The IR spectrum of the crystalline product (**29** and **30**) obtained was found identical to NaHpht·½H_2O and KHpht respectively.

The IR spectrum of the product obtained from the reaction mixture of containing calcium, phthalic acid and pip was compared with that of pure calcium phthalate (**22a**) and calcium hydrogen phthalate (**22b**). The IR spectrum of the product obtained from method I (**31a**) is identical to **22a**. The IR spectrum of the products obtained from method II (**31b**) and III (**31c**) is identical to **17b**.

IR spectroscopy is used as a characterization tool to infer new product formation. As it is well documented that every compound exhibits a characteristic IR spectrum, a comparison of the IR spectra of the starting reagents and the product material of a crystal growth reaction constitutes an useful procedure for product characterization. A new product crystal is expected to show differences in its IR spectrum in terms of disappearance of existing IR bands in the spectrum of the starting reagents or appearance of new signals.

The reaction of alkaline earth metal ions (Mg, Sr, Ba) with phthalic acid in presence of pip resulted in products **32**, **33** and **34** respectively. The IR spectrum (Fig. 3.189-3.191) of these compounds differed from the IR spectrum of pure metal phthalates or the other possible product $(pipH_2)(phtH)_2 \cdot 2H_2O$ precursor **B** [199]. This infers the formation of a metal phthalate compound containing pip.

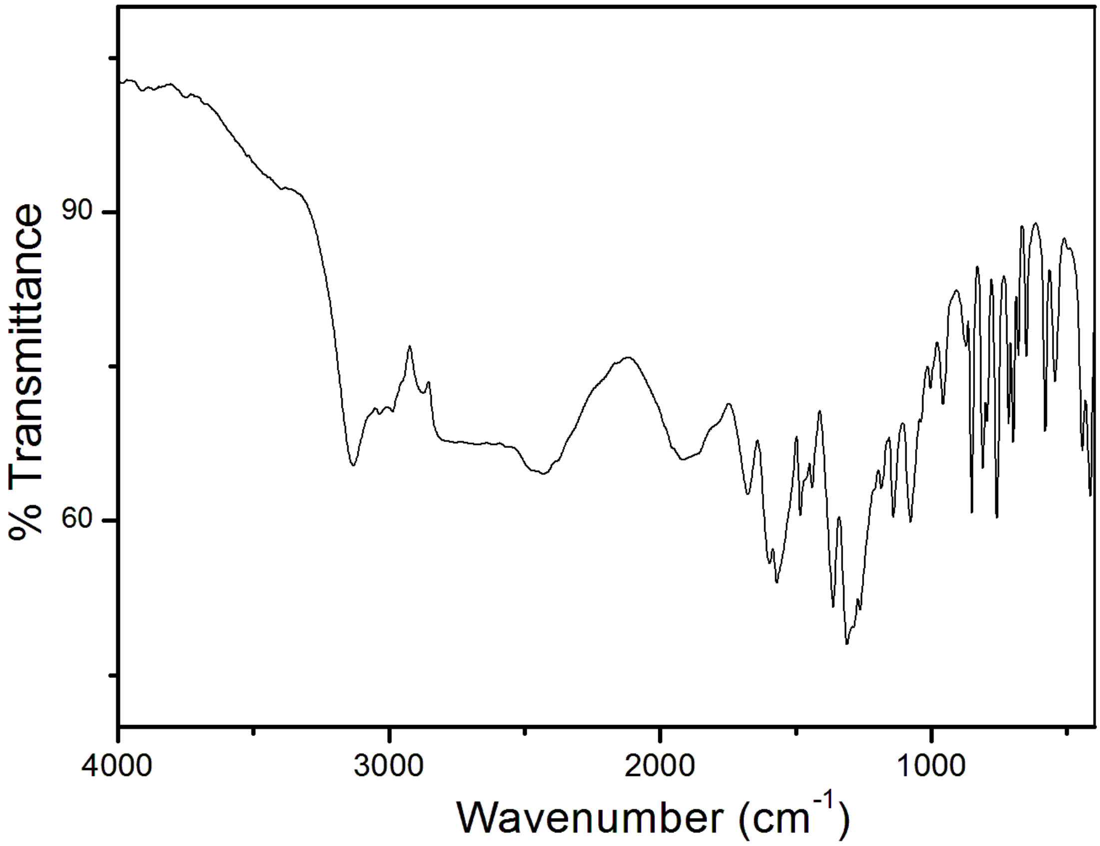


Fig. 3.189 – IR spectrum of **32**

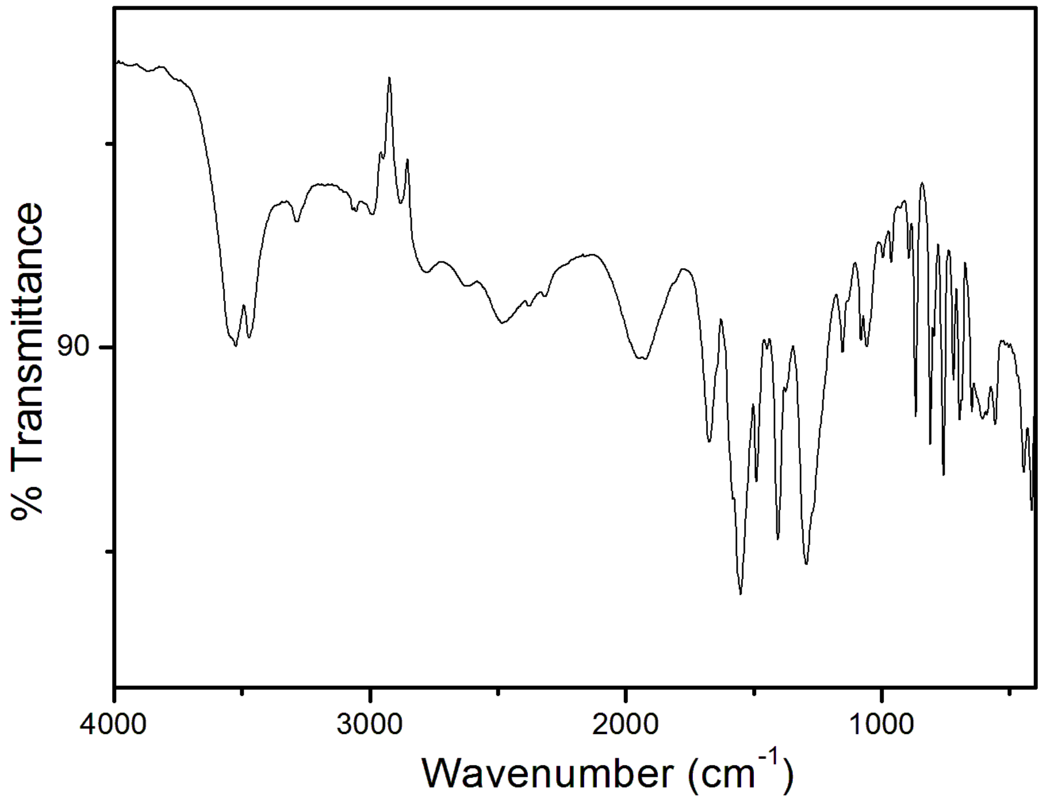


Fig. 3.190 – IR spectrum of **33**

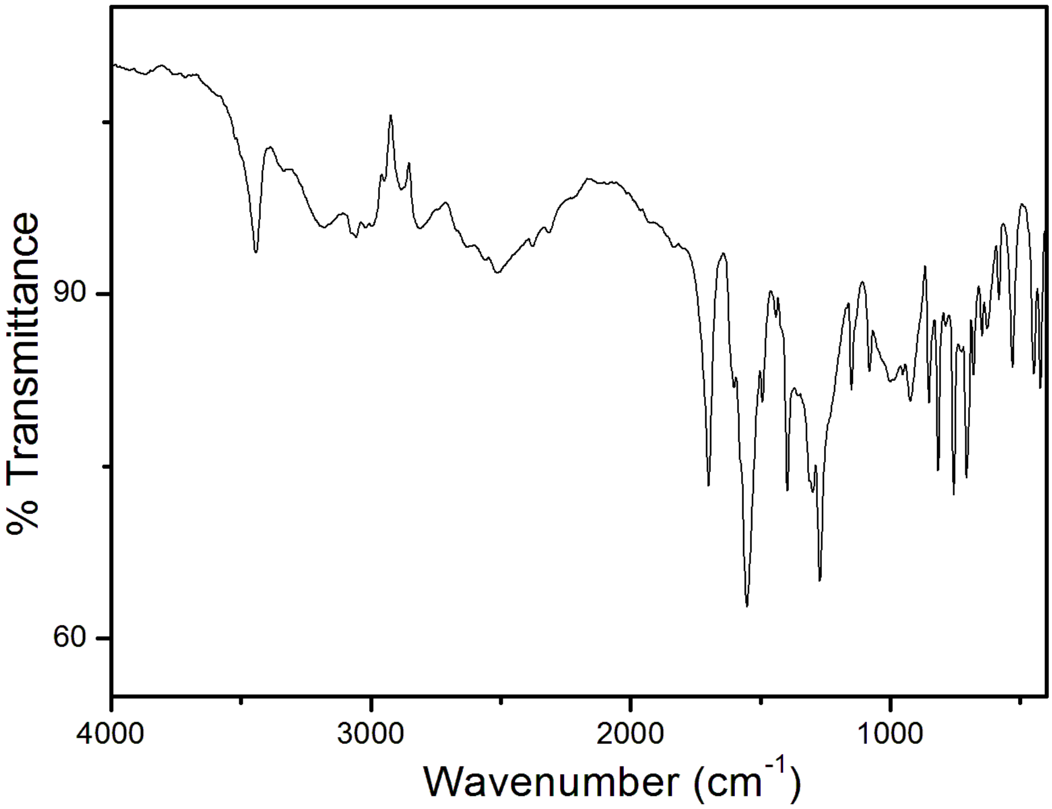


Fig. 3.191 – IR spectrum of **34**

3.3.3 Reinvestigation of crystal growth of KHpht in presence of bivalent metal ions (Cu^{2+}, Ni^{2+}, Zn^{2+}, Sr^{2+}, Mg^{2+}, Ca^{2+} and Ba^{2+}) and trivalent metal ion (Fe^{3+}) / amino acids / organic compounds.

The claims (Appendix I, Table A1) of incorporation of bivalent metal ions into the crystal structure of KHpht are reinvestigated. This work was undertaken, as during our metal phthalate studies zinc hydrogen phthalate is prepared by reacting zinc salt with KHpht. These reactions resulted in the formation of respective pure metal phthalates as expected. The results are confirmed from their identical IR spectrum with pure metal phthalates. A representative spectrum of product (**35**) obtained from Ni^{2+} and KHpht reaction is shown in Fig. 3.192.

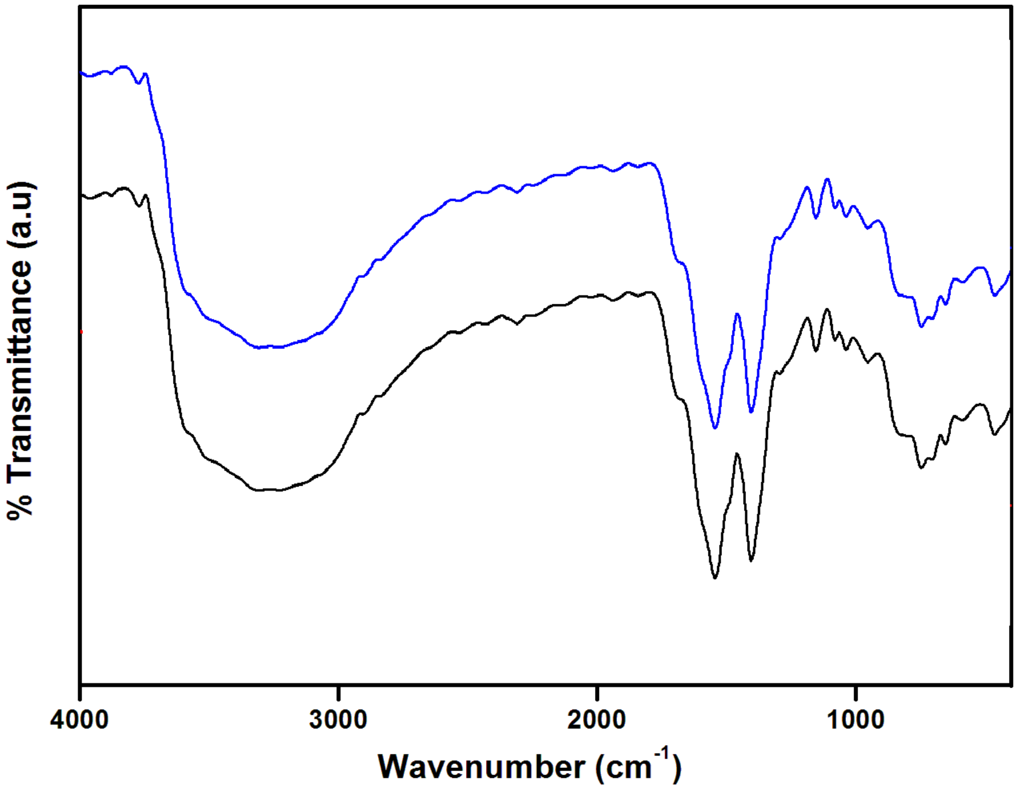


Fig 3.192 – Comparative IR spectra of **35** (top) and pure copper phthalate (bottom)

The reaction of Fe(III) ion with KHpht leads to immediate precipitation of brown coloured compound **36**. The IR spectrum (Fig. 3.193) of the precipitate was identical to pure Fe(III) phthalate. Further evaporation of the reaction mixture led to recrystallization of KHpht.

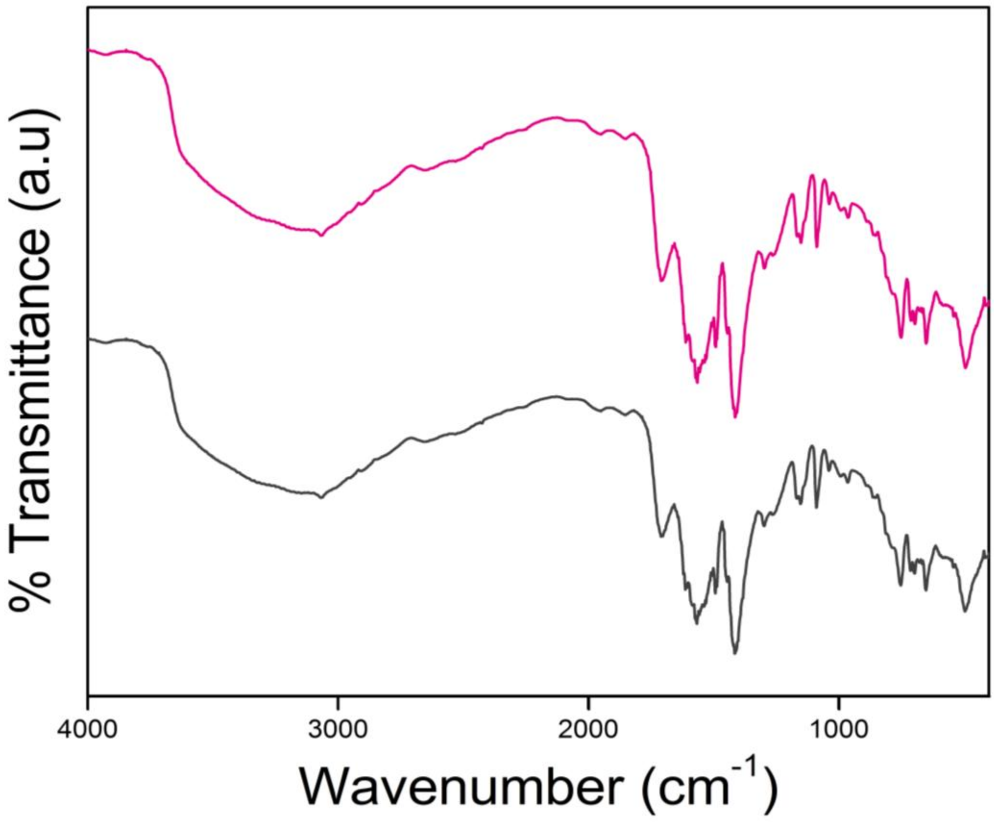


Fig. 3.193 – Comparative IR spectra of **36** (top) and pure Fe(III) phthalate (bottom)

The crystal growth reaction of KHpht in presence of amino acids (Glycine, *L*-valine and *L*-alanine etc) results in fractional crystallization of KHpht without incorporation of amino acids. A representative IR spectrum of the product (**37**) in presence of one of the amino acid namely glycine is given below (Fig. 3.194).

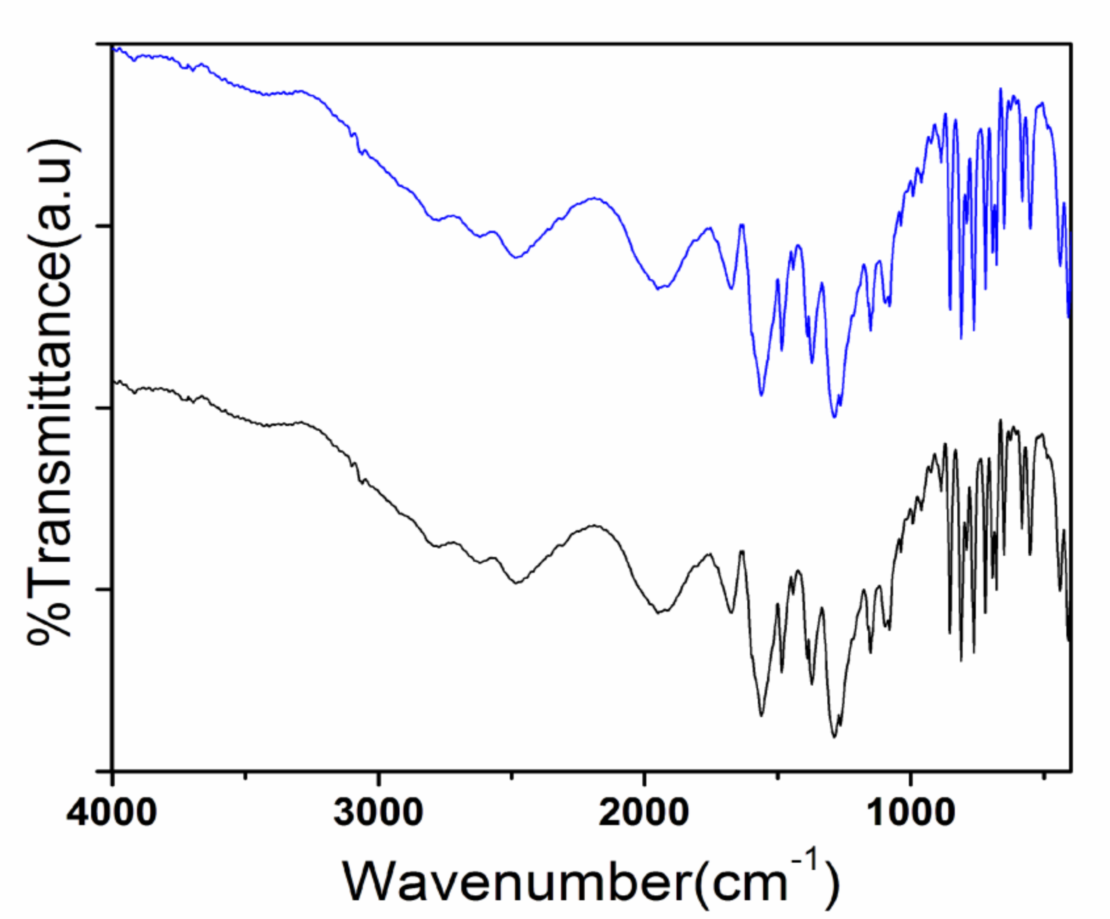


Fig. 3.194 – Comparative IR spectra of **37** (top) and pure KHpht (bottom)

An aqueous reaction of KHpht with organic compounds results in fractional crystallization of less soluble organic compounds EDTA and anthracene. This is confirmed from the identical IR spectrum of the products **38** (Fig. 3.195) and **39** (Fig. 3.196) with that of pure EDTA and anthracene respectively.

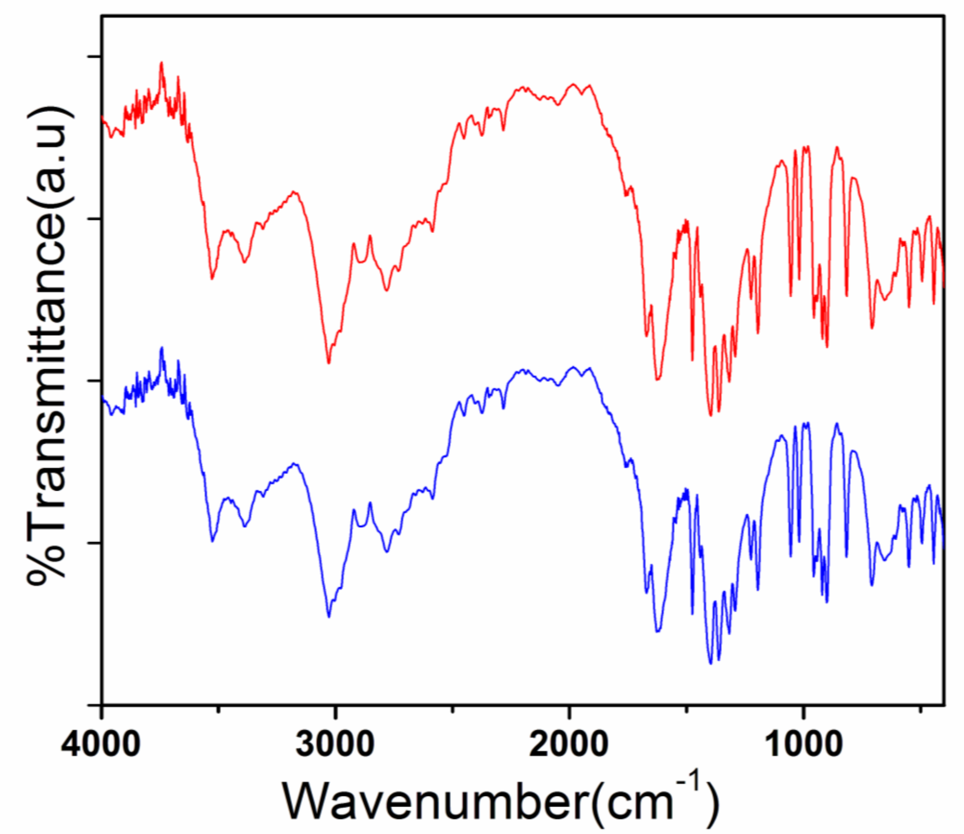


Fig. 3.195 – Comparative IR spectra of **38** (top) and pure EDTA (bottom)

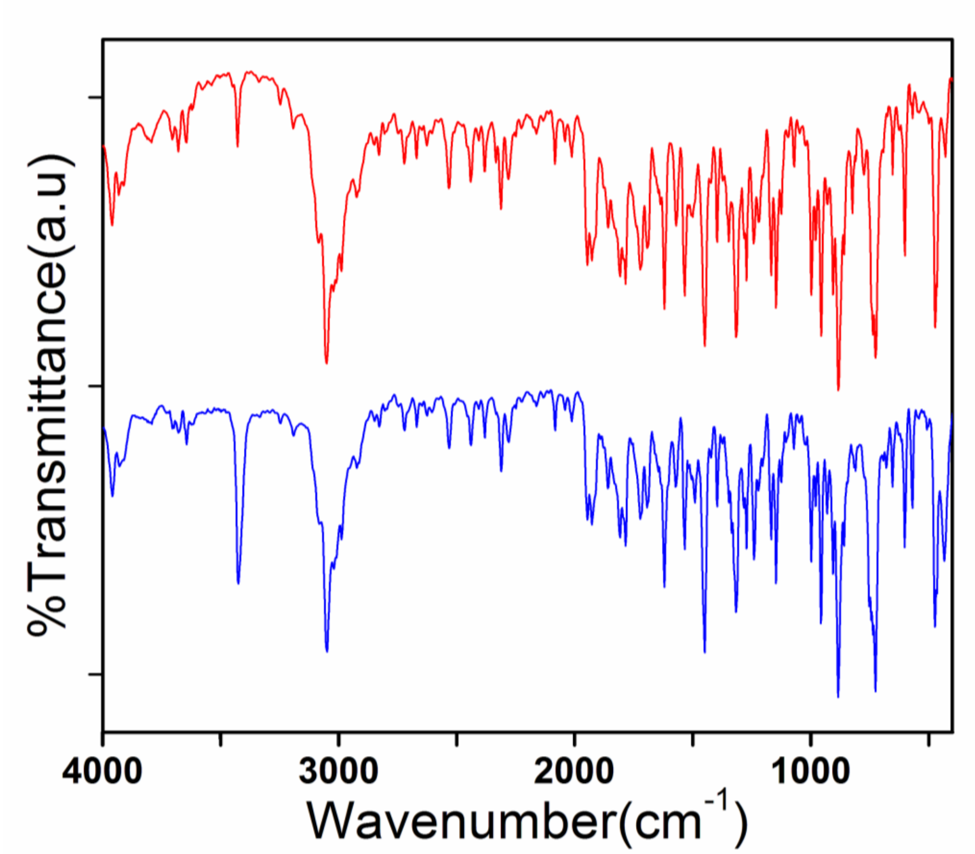


Fig. 3.196 – Comparative IR spectra of **39** (top) and pure anthracene (bottom)

3.3.4 Reinvestigation of crystal growth of sodium hydrogen phthalate hemihydrate NaHpht.$^1/_2H_2O$ in presence of metal ions / amino acids / organic compounds.

The results obtained from this reinvestigation were similar to crystal growth reaction of KHpht in presence of metal ions/ amino acids/ organic compounds. Our studies to incorporate metal ions results in formation of respective metal phthalates; fractional crystallization of NaHpht and organic compounds in case of amino acids and organic compounds respectively.

3.3.5 Reinvestigation of crystal growth of so called L-valine $ZnSO_4·7H_2O$, L-glutamine $KNO_3/NaNO_3$.

The reported growth of *L*-valine zinc sulphate [280] and *L-glutamine* $KNO_3/NaNO_3$ [281-282] are reinvestigated in the present work. The studies reveal that the above reactions result in fractional crystallization of the less soluble *L*-valine (**40**) and L-glutamine (**41, 42**) respectively. The more soluble metal salts ($ZnSO_4$ and KNO_3/ $NaNO_3$) remain in solution. This is confirmed by IR spectral studies (Fig. 3.198-3.199).

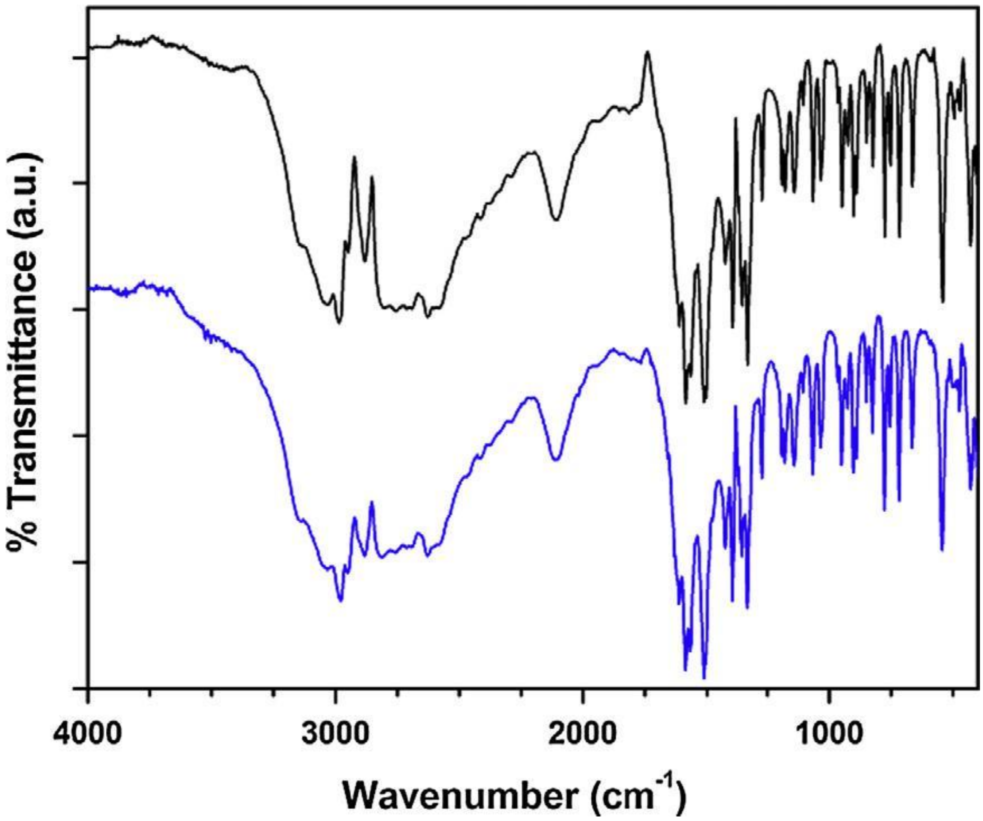


Fig. 3.198 - IR spectral comparison reveals that *L*-valine (top) and **40** (bottom)

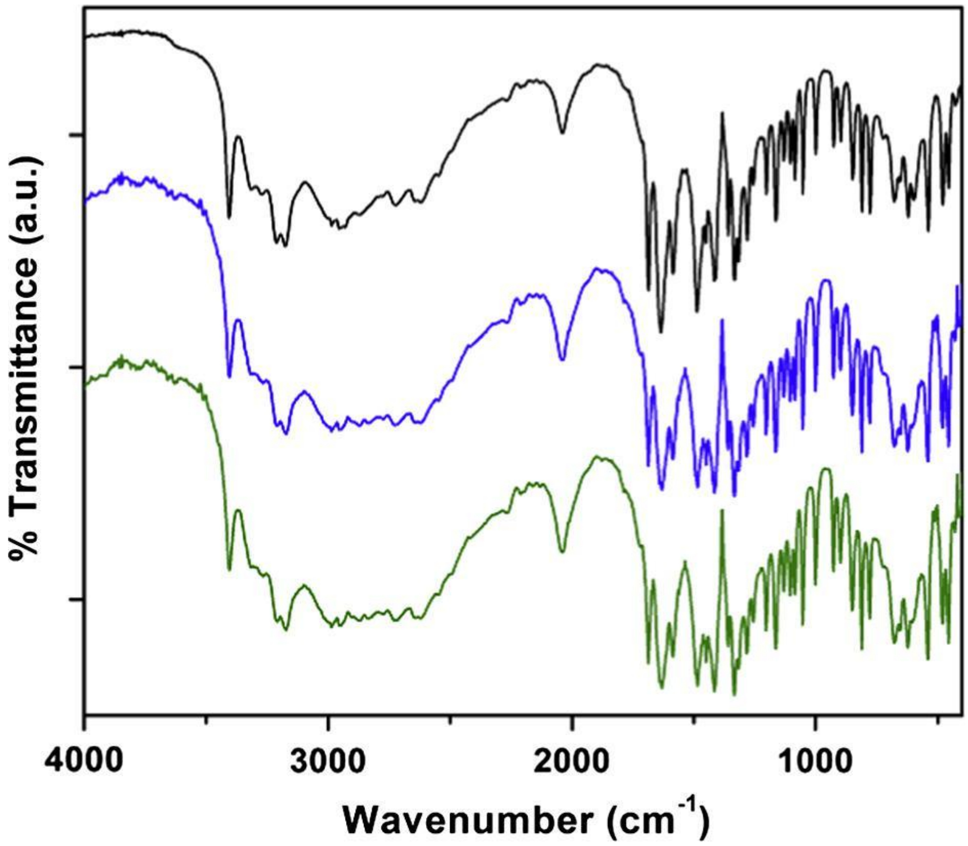


Fig. 3.199 - Infrared spectra of pure L-glutamine (top) and **41** (middle) and **42** (bottom)

SUMMARY AND CONCLUSIONS

The thesis describes syntheses, spectral characterization, crystal structures and properties of metal phthalates and 3-nitrophthalates. The structurally characterized compounds in the present work are listed in Table 4.1.

Table 4.1 – List of structurally characterized compounds.

No.	Compound	Coordination sphere	Space group	Phthalate binding mode	D
1	$(pipH_2)[Zn(pht)_2]\cdot H_2O$ **1**	$\{ZnO_4\}$	$P2_1/c$	μ_2-bidentate	1D
2	$(pipH_2)[Ni(pht)_2(H_2O)_4]\cdot 8H_2O$ **3**	$\{NiO_6\}$	$P\bar{1}$	Monodentate	0D
3	$(pipH_2)[Co(pht)_2(H_2O)_4]\cdot 8H_2O$ **4**	$\{CoO_6\}$	$P\bar{1}$	Monodentate	0D
4	$(pipH_2)[Cu(pht)_2(H_2O)_4]\cdot 8H_2O$ **5**	$\{CuO_6\}$	$P\bar{1}$	Monodentate	0D
5	$[Ni(im)_6]pht\cdot H_2O$ **6**	$\{NiN_6\}$	$P2_1/c$	-	0D
6	$[Co(im)_6]pht\cdot H_2O$ **7**	$\{CoN_6\}$	$P2_1/c$	-	0D
7	$[Cu_2(H_2O)(im)_4(pht)_2]\cdot H_2O$ **8**	$\{CuN_2O_3\}$ $\{CuN_2O_3\}$	$P2_1/n$	μ_2-bidentate	0D
8	$[Na(H_2O)_3$(2-carboxy-6-nba)$]\cdot H_2O$ **10**	$\{NaO_6\}$	$P\bar{1}$	Monodentate	1D
9	[K(2-carboxy-3-nba)] **11**	$\{KO_9\}$	$P2_1/c$	μ_6-nonadentate	2D
10	[Cs(2-carboxy-6-nba)(H_2O)] **13**	$\{CsO_{10}\}$	$Pcca$	μ_2-tetradentate	1D
11	$[Rb_2$(3-npht)] **17**	$\{RbO_7\}$, $\{RbO_{10}\}$	$P2_1/n$	μ_{10}-polydentate	3D
12	$[Cs_2$(3-npht)] **18**	$\{CsO_7\}$, $\{CsO_{10}\}$	$P2_1/n$	μ_{10}-polydentate	3D
13	[NaRb(2-carboxy-6-nba)$_2(H_2O)_3]\cdot 2H_2O$ **19**	$\{NaO_6\}$, $\{RbO_9\}$	$P2_1/n$	μ_3-tetradentate, μ_3-tetradentate	1D

Abbreviations: D = dimensionality, $pipH_2$ = piperazinediium, pht = phthalate, im = imidazole, 2-carboxy-6-nba = 2-carboxy-6-nitrobenzoate, 2-carboxy-3-nba = 2-carboxy-3-nitrobenzoate, 3-npht = 3-nitrophthalate.

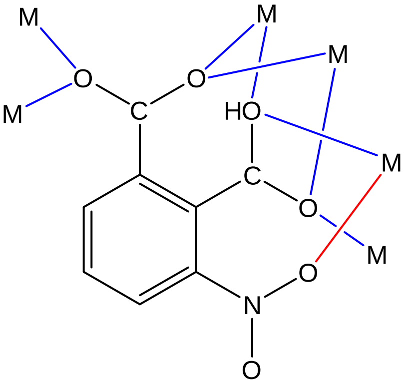
The synthesized compounds crystallize in centrosymmetric space groups. The dimensionality of the synthesized compounds range from zero dimensional to three dimensional. The bis(phthalato) compounds of Zn, Ni, Co and Cu which is charge balanced by $(pipH_2)^{2+}$ dication are amongst the few anionic metal phthalates reported so far [200, 283]. The tetracoordinated Zn(II) phthalate, $(pipH_2)[Zn(pht)_2]\cdot H_2O$ **1** ($pipH_2$=piperazinediium, pht=phthalate) with μ_2-bridging bidentate phthalate ligand exhibits 1D ladder architecture. The metal bis(phthalato) compounds

$(pipH_2)[M(pht)_2(H_2O)_4]\cdot 8H_2O$ [M= Ni (**3**), Co (**4**) and Cu (**5**)] are rare examples of water rich compounds exhibiting metal:water ratio of 1:12. The phthalate ligand in these compounds exhibit monodentate binding mode. The lattice water molecules form water dodecamer cluster with the aid of H-bonding interactions. The secondary interactions in the crystal structure lead to $\pi\cdots\pi$ stacking of the phthalate rings with (Cg···Cg) distances of ~4.0 Å. The thermal investigation of water rich compounds showed dehydration-rehydration property wherein **3** and **4** undergo crystalline-amorphous-crystalline transformation.

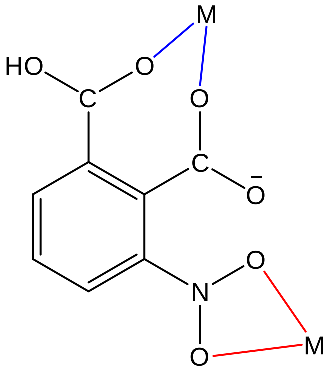
The reaction of bis(phthalato) compounds **3-5** with imidazole in 1:4 mole ratio afforded hexaimidazole compounds **6** and **7** and the dinuclear compound **8** respectively. Phthalate in **6** and **7** is a charge balancing anion and in **8** it displays μ_2-bridging bidentate binding mode.

The nitrophthalate compounds $[Na(2\text{-carboxy-6-nba})(H_2O)_3]\cdot H_2O$ **10** (2-carboxy-6-nba= 2-carboxy-6-nitrobenzoate), [K(2-carboxy-3-nba)] **11** (2-carboxy-3-nba=2-carboxy-3-nitrobenzoate), $[Cs(2\text{-carboxy-6-nba})(H_2O)]$ **13**, $[Rb_2(3\text{-npht})]$ **17** (3-npht= 3-nitrophthalate), $[Cs_2(3\text{-npht})]$ **18** and $[NaRb(2\text{-carboxy-6-nba})_2(H_2O)_3]\cdot 2H_2O$ **19** are the products of reaction of alkali metal ion with 3-nitrophthalic acid in 1:1 and 2:1 molar ratio. The mononuclear compounds **10**, **11** and **13** and mixed metal compound **19** are obtained by mono-deprotonation of 3-nitrophthalate ligand and are 1D coordination polymers. The dinuclear compounds **17** and **18** consist of completely deprotonated 3-nitrophthalate ligand and exhibit 3D polymeric structures. The central metal ions Na and K show hexa- and nona-coordination respectively. The metal ions Rb / Cs exhibits hepta- and deca-coordination in dinuclear compounds **17** and **18**. In the mixed metal compound **19**, Rb shows nonacoordination.

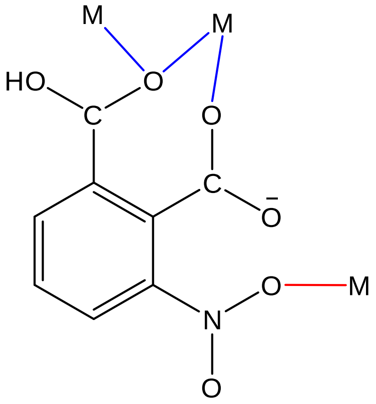
The 3-nitrophthalate ligand exhibits a variety of new binding modes viz monodentate μ_2- tetradentate, μ_3-tetradentate, μ_6-nonadentate and μ_{10}- polydentate binding modes (Fig. 4.1) that resulted in 1/2/3D polymeric compounds.



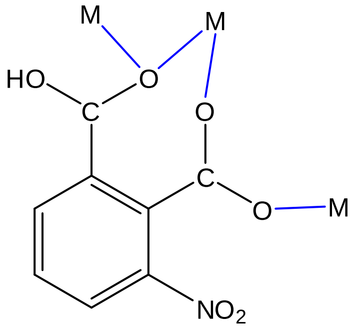
μ_6-nonadentate



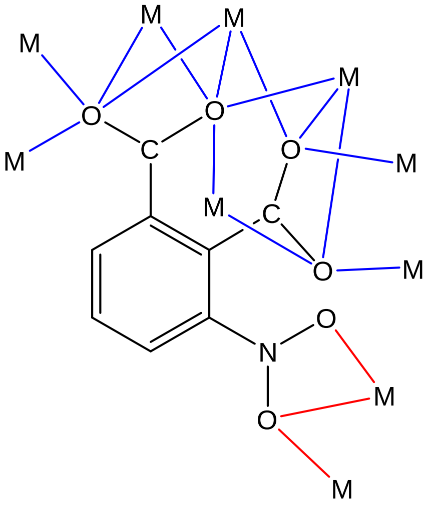
μ_2- tetradentate



μ_3-tetradentate



μ_3-tetradentate



μ_{10}- polydentate

Fig. 4.1 – New binding modes obtained for 3-nitrophthalate ligand.
M–O (carboxylate) bond is shown in blue and M–O (nitro) bond is shown in red.

It is interesting to note that in the synthesised 3-nitrophthalates, the oxygen of the –NO_2 group is involved in metal binding. Earlier, only mono-coordination for –NO_2 group of 3-nitrophthalate ligand was known which was observed in 2D Na and Ba compounds synthesized under hydro/solvothermal conditions [267, 270]. In the present study, in addition to mono-coordinated –NO_2 group in **10** and **11**, a –NO_2 group exhibiting bidentate binding in case of **13** and μ_2-bridging tridentate binding mode in 3D [M_2(3-npht)] [M= Rb(**17**) and Cs (**18**)] is observed.

A reinvestigation of the growth of *L*-valine zinc sulphate crystal by slow evaporation of an aqueous solution containing *L*-valine and zinc sulphate heptahydrate results in the fractional crystalliza-tion of *L*-valine [284]. The slow evaporation of an aqueous solution containing *L*-glutamine and potassium nitrate in 2:1 mol ratio results in the fractional crystallization of *L*-glutamine and not the formation of a so called bis (*L*-glutamine) potassium nitrate [285].

REFERENCES

1. R.-B. Lin, S. Xiang, B. Li, Y. Cui, G. Qian, W. Zhou, B. Chen, '*Our journey of developing multifunctional metal-organic frameworks'* Coordination Chemistry Reviews 384 (2019) 21–36. https://doi.org/10.1016/j.ccr.2019.01.009

2. J.D. Evans, B. Garai, H. Reinsch, W. Li , S. Dissegna , V. Bon, I. Senkovska, R.A. Fischer, S. Kaskel, C. Janiak, N. Stock, D. Volkmere '*Metal–organic frameworks in Germany: From synthesis to function'* Coordination Chemistry Reviews 380 (2019) 378–418. https://doi.org/10.1016/j.ccr.2018.10.002

3. N.F. Sunday, *'Emerging Trends in Coordination Polymers and Metal-Organic Frameworks: Perspectives, Synthesis, Properties and Applications'* Arc. Org. Inorg. Chem. Sci. 1 (2018) 39-50. http://dx.doi.org/10.32474/AOICS.2018.01.000106

4. J. Yu, L.-H. Xie, J.-R. Li, Y. Ma, J.M. Seminario, P.B. Balbuena. *'CO_2 Capture and Separations Using MOFs: Computational and Experimental Studies'* Chem. Rev., 117 (2017) 9674-9754. http://dx.doi.org/10.1021/acs.chemrev.6b00626

5. X. Zhao, Y. Wang, D.-S. Li, X. Bu, P. Feng, '*Metal–Organic Frameworks for Separation'* Adv. Mater. 30 (2018) 1705189. https://doi.org/10.1002/adma.201705189

6. E. Loukopoulos, G.E. Kostakis '*Recent advances of one-dimensional coordination polymers as catalysts'* Journal of Coordination Chemistry 71 (2018) 371–410. https://doi.org/10.1080/00958972.2018.1439163

7. Y.-S. Kang, Y. Lu, K. Chen, Y. Zhao, P. Wang, W.-Y. Sun, *'Metal–organic frameworks with catalytic centers: From synthesis to catalytic application'* Coordination Chemistry Reviews 378 (2019) 262–280. https://doi.org/10.1016/j.ccr.2018.02.009

8. T.-T. Zheng, J. Zhao, Z.-W. Fang, M. -T. Li, C.-Y. Sun, X. Li, X.-L. Wang, Z.-M. Su, '*A luminescent metal organic framework with high sensitivity for detecting and removing copper ions from simulated biological fluid*s' Dalton Trans., 46 (2017) 2456-2461. https://doi.org/10.1039/C6DT04630D

9. M.H. Zeng, Z. Yin, Y.X. Tan, W.X. Zhang, Y.P. He, M. Kurmoo, '*Nanoporous Cobalt(II) MOF Exhibiting Four Magnetic Ground States and Changes in Gas Sorption upon Post-Synthetic Modification*' J. Am. Chem. Soc. 136 (2014) 4680-4688. https://doi.org/10.1021/ja500191r

10. Y. Ye, W. Guo, L. Wang, Z. Li, Z. Song, J. Chen, Z. Zhang, S. Xiang, B. Chen, '*Straightforward Loading of Imidazole Molecules into Metal–Organic Framework for High Proton Conduction'* J. Am. Chem. Soc. 139 (2017) 15604–15607. https://doi.org/10.1021/jacs.7b09163

11. R.-B. Lin, S.-Y. Liu, J.-W. Ye, X.-Y. Li, J.-P. Zhang, '*Photoluminescent Metal-Organic Frameworks for Gas Sensing,'* Adv. Sci. 3 (2016) 1500434. https://doi.org/10.1002/advs.201500434

12. S. Rojas, F.J. Carmona, C.R. Maldonado, P. Horcajada, T. Hidalgo, C. Serre, J.A.R. Navarro, E. Barea, '*Nanoscaled Zinc Pyrazolate Metal–Organic Frameworks as Drug-Delivery Systems'* Inorg. Chem., 55 (2016) 2650–2663. https://doi.org/10.1021/acs.inorgchem.6b00045

13. T. Simon-Yarza, A. Mielcarek, P. Couvreur, C. Serre, '*Nanoparticles of Metal-Organic Frameworks: On the Road to In Vivo Efficacy in Biomedicine'* Adv. Mater. 30 (2018) 1707365. https://doi.org/10.1002/adma.201707365

14. L. Öhrström, *'Let's Talk about MOFs—Topology and Terminology of Metal-Organic Frameworks and Why We Need Them'* Crystals 5 (2015) 154-162. https://doi.org/10.3390/cryst5010154

15. S.R. Batten, N.R. Champness, X.M. Chen, J.G. Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M. Paik Suh, J. Reedijk, *'Terminology of metal–organic frameworks and coordination polymers'* (IUPAC Recommendations 2013) Pure Appl. Chem. 85 (2013) 1715–1724. https://doi.org/10.1351/PAC-REC-12-11-20

16. S.R. Batten, N.R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M. Paik Suh, J. Reedijk, *'Coordination polymers, metal–organic frameworks and the need for terminology guidelines'* Cryst. Eng. Comm. 14 (2012) 3001–3004. https://doi.org/10.1039/C2CE06488J

17. K. Biradha, A. Ramanan, J.J. Vittal, *'Coordination Polymers Versus Metal-Organic Frameworks, Perspectives'* Cryst. Growth & Des. 9 (2009) 2969-2970. https://doi.org/10.1021/cg801381p

18. F.A. Cotton, G. Wilkinson, C.A. Murillo and M. Bochmann, '*Advanced inorganic chemistry'* Wiley, Sixth edition.

19. Y.Z. Zhenga, Z. Zhenga, X.M. Chenb, *'A symbol approach for classification of molecule-based magnetic materials exemplified by coordination polymers of metal carboxylates'* Coord. Chem. Rev. 258-259 (2014) 1– 15. http://dx.doi.org/10.1016/j.ccr.2013.08.03

20. X.L.Wang, J. Luan, F.F. Sui, H.Y. Lin, G.C. Liu, C. Xu, '*Structural Diversities and Fluorescent and Photocatalytic Properties of a Series of Cu(II) Coordination Polymers Constructed from Flexible Bis-pyridyl-bis-amide Ligands with Different Spacer Lengths and Different Aromatic carboxylates*' Cryst. Growth & Des. 13 (2013) 3561-3576. http://dx.doi.org/10.1021/cg400538c

21. F.J. Liu, J. Hao, J. Cheng, X.H. Lin, H.P. Chen, R.B. Huang, L.S. Zheng, , '*Syntheses, Structures, and Photoluminescences of Four Cd(II) Coordination Architectures Based on 1-(4-Pyridylmethyl)-2-methylimidazole and Aromatic carboxylates: From One-Dimensional Chain to Three-Dimensional Coordination Architecture*' Cryst. Growth & Des. 12 (2012) 2004-2012. http://dx.doi.org/10.1021/cg201708x

22. G.R. Desiraju, *'Supramolecular Synthons in Crystal Engineering — A New Organic Synthesis'* Angew. Chem., Int. Ed. 35 (1995) 2311-2327. https://doi.org/10.1002/anie.199523111

23. C. Janiak, *'A critical account on π–π stacking in metal complexes with aromatic nitrogen-containing ligands'* J. Chem. Soc., Dalton Trans. (2000) 3885-3896. https://doi.org/10.1039/B003010O

24. A.N. Khlobystov, A.J. Blake, N.R. Champness, D.A. Lemenovskii, A.G. Majouga, N.V. Zyk, M. Schroder, *'Supramolecular design of one-dimensional coordination polymers based on silver(I) complexes of aromatic nitrogen-donor ligands'* Coord. Chem. Rev. 222 (2001) 155-192. https://doi.org/10.1016/S0010-8545(01)00370-8

25. C.A. Hunter, J.K.M. Sanders, *'The nature of .pi.-.pi. interactions'* J. Am. Chem. Soc. 112 (1990) 5525-5534. https://doi.org/10.1021/ja00170a016

26. R. Kruszynski, T. Sierański, Cryst. Growth Des. 16 (2016) 587−595. https://doi.org/10.1021/acs.cgd.5b00852

27. H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, *'Design and synthesis of an exceptionally stable and highly porous metal-organic framework'* Nature 402 (1999) 276. https://doi.org/10.1038/46248

28. S.G. Baca, I.G. Filippova, O.A. Gherco, M. Gdaniec, A.S. Yu, N.V. Gerbeleu, P. Franz, R. Basler, S. Decurtins, '*Nickel(II)-, cobalt(II)-, copper(II)-, and zinc(II)-phthalate and 1-methylimidazole coordination compounds: synthesis, crystal structures and magnetic properties'* Inorg. Chim. Acta 357 (2004) 3419. https://doi.org/10.1016/S0020-1693(03)00498-5

29. CSD version 5.38 (2017).

30. C.R. Groom, I.J. Bruno, M.P. Lightfoot, S.C. Ward, '*The Cambridge Structure Database*' Acta Cryst. B72 (2016) 171-179.

31. G. Baca, I.G. Filippo, N. V Gerbeleu, Y.A. Simono, M. Gdaniec, G.A. Timco, O.A. Gherco, Y.L. Malaestean, '*Zinc(II) carboxylates with imidazole and 2-methylimidazole : unprecedented cyclic dimer and polynuclear coordination polymers based on bridging phthalate ions*' Inorg. Chim. Acta. 344 (2003) 109–116.

32. N.J. Burke, A.D. Burrows, A.S. Donovan, R.W. Harrington, M.F. Mahon, C.E. Price, '*Zinc dicarboxylate polymers and dimers : thiourea substitution as a tool in supramolecular synthesis'* 2 (2003) 3840–3849. https://doi.org/10.1039/ b307420j.

33. S.G. Baca, Y.A. Simonov, N.V. Gerbeleu, M. Gdaniec, P.N. Bourosh, G.A. Timco, '*Synthesis and X-ray diffraction study of Zn (II) complexes with o -phthalic acid and aromatic amines'* Polyhedron. 20 (2001) 831–837.

34. C. Li, Y. Li, W. Fang, B. Liu, D. Li, *'catena-Poly[[[2-(2-furyl)-1H-imidazo[4,5-f][1,10]- phenanthroline]zinc(II)]-μ-benzene-1,2-di-carboxylato]*' Acta Crystallogr. E62 (2006) m3541–m3543. https://doi.org/10.1107/S1600536806049592.

35. R.-X Li, S.-X Li, Q.-Y Wu, G.-Y Liu, F.-Q Liu, '*catena-Poly[[bis(1-vinylimidazole-*κN^3*)- zinc(II)]-μ-phthalato-*$\kappa^2 O^1{:}O^2$*]*' Acta Crystallogr. E63 (2007) m2874. https://doi.org/10.1107/S160053680705355X.

36. A. Thirumurugan, C.N.R. Rao, '*1,2-, 1,3- and 1,4-Benzenedicarboxylates of Cd and Zn of differentdimensionalities : Process of formation of the three-dimensional structure*' J. Mater. Chem. 25 (2005) 3852–3858. https://doi.org/10.1039/b504666a.

37. J. Yao, W. Huang, B. Li, S. Gou, Y. Xu, '*A novel one-dimensional single helix derived from 2,2'-bipyridine based Zn(II) species directed self-assembly with 1,2-benzenedicarboxylate*' Inorg. Chem. Commun. 5 (2002) 711–714.

38. X. Liang, M. Weishäupl, J.A. Parkinson, S. Parsons, P.A. Mcgregor, P.J. Sadler, '*Selective Recognition of Configurational Substates of Zinc Cyclam by Carboxylates : Implications for the Design and Mechanism of Action of Anti-HIV Agents*' Chem. Eur. J. 9 (2003) 4709–4717. https://doi.org/10.1002/chem.200304808.

39. X. Lu, Y. Chen, P. Li, Y. Bi, C. Yu, X.-D. Shi, Z.-X. Chi, '*Self-assembly of three 1-D zinc – benzenedicarboxylate coordination polymers with 1 , 10- phenanthroline'* J. Coord. Chem. 63 (2015) 3923–3932. https://doi.org/10.1080/00958972.2010.523826.

40. S. Zhang, J. Sun, '*Poly[[(dipyrido[3,2-a:2',3'-c]phenazine)zinc(II)]- µ3-benzene-1,2-dicarboxylato]*' Acta Crystallogr. E62 (2006) m3107–m3109. https://doi.org/10.1107/S1600536806044217.

41. Y. Gong, R. Wang, D. Yuan, W. Su, Y. Huang, C. Yue, F. Jiang, M. Hong, '*Chains , ladders and sheets of d^{10} metal – organic polymers generated from the flexible bipyridyl ligands*' Polyhedron. 26 (2007) 5309–5316. https://doi.org/10.1016/j.poly.2007.07.048.

42. Y. Liu, J.-F. Ma, J. Yang, M.J. -Cheng, G. Ping '*Structures of metal-organic networks based on flexible 1,10-(1,4-butanediyl)bis(imidazole-2-phenyl) ligand*' CrystEngComm. 10 (2008) 565–572. https://doi.org/10.1039/b714399k.

43. A.D. Burrows, R.W. Harrington, M.F. Mahon, C.E. Price, '*The influence of hydrogen bonding on the structure of zinc co-ordination polymers*' J. Chem. Soc., Dalt. Trans. 2 (2000) 3845–3854. https://doi.org/10.1039/b003210g.

44. J. Li, J.-H Zhou, Y.-Z Li, X.-T Chen, Wuji Huaxue Xuebao, 20 (2004) 841.

45. W.-Q Kan, J. Yang, Y.-Y Liu, J.-F Ma, '*Effect of organic anions on the self-assembly of Zn(II)-containing coordination polymers based on trigonal N-donor ligands'* CrystEngComm, 14 (2012) 6934. https://doi.org/10.1039/C2CE25907A

46. P.-C Cheng, P.-T Kuo, Y.–H Liao, M.-Y Xie, W. Hsu, J.-D Chen, '*Ligand-Isomerism Controlled Structural Diversity of Zn(II) and Cd(II) Coordination Polymers from Mixed Dipyridyladipoamide and Benzenedicarboxylate Ligands'* Crystal Growth and Design, 13 (2013) 623. https://doi.org/10.1021/cg301311m

47. R.-X Li, Q.-Y Wu, F.-Q Liu, *'catena-Poly[[bis(1-allylimidazole)zinc(II)]-μ-phthalato-κ^{2}O^1:O^2]'* Acta Crystallographica Section E: Structure Reports Online, 66 (2010) m258. https://doi.org/10.1107/S1600536810003892

48. Tao Z -L, Cui J -H, Qin L, Zheng H -G, *Wuji Huaxue Xuebao*, 28 (2012) 2633.

49. F. Huang, J. Tian, G. Chen, D. Li, W. Gu, X. Liu, S. Yan, D.-Z. Liao, P. Cheng, '*A*

case study of the Zn II -BDC / bpt mixed-ligand system : positional isomeric effect , structural diversification and luminescent properties' CrystEngComm. 12 (2010) 1269–1279. https://doi.org/10.1039/b915506f.

50. W. Zhang, Y. Liu, J. Ma, H. Jiang, J. Yang, '*Syntheses and characterizations of nine coordination polymers of transition metals with carboxylate anions and bis (imidazole) ligands*' Polyhedron. 27 (2008) 3351–3358. https://doi.org/10.1016/j.poly.2008.07.026.

51. Y.A. Simonov, S.G. Baca, I.G. Filippova, M. Gdaniec, O.A. Gerko, N. V Gerbeleu, '*Two-Dimensional Coordination Polymer* $\{[Zn(Pht)(4,4'\text{-}Bipy)(H_2O)_2]\cdot 2H_2O\}n$ *: Synthesis and Structure*' Russ. J. Coord. Chem. 30 (2004) 727–732.

52. W. Xiong, Q. Liu, N. Zhang, L. Wang, '*A two-dimensional coordination polymer containing a two-dimensional zinc – carboxylate layer constructed from helical chains : poly [(*μ_4*-benzene-1,2-dicarboxylato)zinc(II)]*' Acta Crystallogr. C68 (2012) m235–m237. https://doi.org/10.1107/S0108270112033045.

53. X. Wang, Y. Bi, G. Liu, H. Lin, T. Hu, X. Bu, '*Zn(II) coordination architectures with mixed ligands of benzenedicarboxylate : syntheses, crystal structures, and photoluminescence properties*' CrystEngComm. 10 (2008) 349–356. https://doi.org/10.1039/b706071h.

54. C. Xu, Q. Guo, X. Wang, H. Hou, Y. Fan, '*A Case Study of Zn II -bmb Meso-Helical Coordination Polymers upon the Spacer Angles and Lengths of Dicarboxylate Coligands*' Cryst. Growth Des. 11 (2011) 1869–1879. https://doi.org/10.1021/cg200052t.

55. N. Singh, G. Anantharaman, '*Structural diversity and luminescence properties of coordination polymers based on mixed ligands, 2,5-bis(imidazol-1-yl)thiophene (*$thim_2$*) and aromatic multicarboxylates*' CrystEngComm, 16 (2014) 7914. https://doi.org/10.1039/C4CE00927D

56. B. Liu, '*Hydrothermal Syntheses, Crystal Structure and Luminescent Properties of Two New Zn(II) Coordination Polymers'* Journal of Inorganic and Organometallic Polymers and Materials, 24 (2014) 536.

57. J. Xu, X. Sun, L. Yang, X. Yan, C. Bi, M. Sun, '*Coordination Frameworks based on 3,5-Bis(imidazole-1-yl) pyridine and Aromatic Dicarboxylate Ligands : Synthesis, Crystal Structures, and Photoluminescent Properties*' Z. Anorg. Allg. Chem. 640 (2014) 236–242. https://doi.org/10.1002/zaac.201300276.

58. Y.-W Li, H. Ma, Y.-Q Chen, K.-H He, Z.-X Li, X.-H Bu, '*Structure Modulation in Zn(II)–1,4-Bis(imidazol-1-yl)benzene Frameworks by Varying Dicarboxylate Anions'* Crystal Growth and Design, 12 (2012) 189. https://doi.org/10.1021/cg200926z
59. M.-D Zhang, L. Qin, H.-T Yang, Y.-Z Li, Z.-J Guo, H.-G Zheng, '*Series of Metal–Organic Frameworks Including Novel Architectural Features Based on a Star-like Tri(4-pyridylphenyl)amine Ligand' Crystal Growth and Design,* 13 (2013) 1961. https://doi.org/10.1021/cg3018612

60. N. Zhao, Y. Deng, P. Liu, C. An, T. Wang, Z. Lian, '*Syntheses , structures and third-order nonlinear optical properties of three coordination polymers based on bis(imidazol-l-yl-methyl) benzene and aromatic dicarboxylic ligands*' Polyhedron. 85 (2015) 607–614.

https://doi.org/10.1016/j.poly.2014.09.021.

61. X.-L Wang, B.-K Chen, H.-Y Lin, Y.-F Bi, G.-C Liu, '*Two Isostructural Complexes Constructed from Mixed Ligands of Dipyrido[3,2-d:2',3'-f]quinoxaline and Phthalate with Novel Oxygen Clusters'* Journal of Chemical Crystallography, 38 (2008) 339. https://doi.org/10.1007/s10870-007-9299-1

62. H.-L Zhu, J.-L Lin, W. Xu, J. Zhang, Y.-Q Zheng, ' *Self-assembly of new Zn(II) supramolecular complexes from 4,4'-dipyridyldisulfide'* Journal of Coordination Chemistry, 64 (2011) 2088. https://doi.org/10.1080/00958972.2011.588706

63. Q.-L Chen, H.-B Chen, Z.-H Zhou, '*Solid and solution evidences on the temperature effect of N-chelated zinc phthalates'* Journal of Molecular Structure, 1035 (2013) 198.

64. Y.-B Chen, J. Zhang, J.-K. Cheng, Y. Kang, Z.-J. Li, Y.-G. Yao, '*1D chain structure, NLO and luminescence properties of [Zn2-bpp(pht)2]*' Inorg. Chem. Commun. 7 (2004) 1139–1141. https://doi.org/10.1016/j.inoche.2004.08.018.

65. Y. Zheng, J. Zhang, J. Liu, '*New Zn(II) coordination polymers with 1,3-bis(4-pyridyl)-propane : syntheses, crystal structures and properties'* CrystEngComm. 2 (2010) 2740–2748. https://doi.org/10.1039/b927448k.

66. Y.-S Song, B. Yan, Z.-X Chen, '*Synthesis of two luminescent coordination polymers based on self-assembly of Zn(II) with polycarboxylic acids ligands and heteroaromatic N-donor'* Applied Organometallic Chemistry, 20 (2006) 44. https://doi.org/10.1002/aoc.1009

67. Y.-J Mu, X.-L Ma, B. Han, G.-F Qin, Y.-Y Niu, H -X Lü, '*A series of Zn(II) coordination polymers derived from dicarboxylate acids and flexible imidazole-based ligands: Syntheses, crystal structures and photoluminescent properties'* Polyhedron, 67 (2014) 44.

68. Y.-Y Liu, H.-Y Liu, J.-F Ma, Y. Yang, J. Yang, '*Syntheses, structures and photoluminescent properties of Zn(II) and Cd(II) coordination polymers with flexible tripodal triazole-containing ligands'* CrystEngComm, 15 (2013) 1897. https://doi.org/10.1039/C2CE26958A

69. B. Li, B. Li, X. Zhu, X. Lu, Y. Zhang, '*Two novel zinc coordination polymers based on bis(1,2,4-triazole-1-yl)ethane and benzenedicarboxyl'* J Coord Chem, 57, 16, (2004) 1361. https://doi.org/10.1080/00958970412331281827

70. L. Zhou, '*Synthesis and Crystal Structure of a Two-Dimensional Zn(II) Coordination Polymer'* Asian journal of chemistry 24 (2012) 1415.

71. S.-S Chen, J. Fan, T.-A Okamura, M.-S Chen, Z. Su, W.-Y Sun, N. Ueyama, '*Synthesis , Crystal Structure, and Photoluminescence of a Series of Zinc (II) Coordination Polymers with 1 , 4-Di (1 H -imidazol-4-yl) benzene and Varied Carboxylate Ligands*' Cryst. Growth Des. 10 (2010) 812–822. https://doi.org/10.1021/cg9011857.

72. H.-Y Bai, J.-F Ma, J. Yang, L.-P Zhang, J.-C Ma, Y.-Y Liu, '*Eight Two-Dimensional and Three-Dimensional Metal−Organic Frameworks Based on a Flexible Tetrakis(imidazole) Ligand: Synthesis, Topological Structures, and Photoluminescent Properties'* Crystal Growth and Design, 10 (2010) 1946. https://doi.org/10.1021/cg100032n

73. Z. Su, J. Xu, J. Fan, D. Liu, Q. Chu, M. Chen, S. Chen, G. Liu, X. Wang, W. Sun, '*Synthesis , Crystal Structure , and Photoluminescence of Coordination Polymers with Mixed Ligands and Diverse Topologies*' Cryst. Growth Des. 9 (2009) 2801–2811. https://doi.org/10.1021/cg900059m.

74. H. Cai, Y. Xiao, Y. Guo, J. Li, '*Controllable assembly of a three- dimensional metal – organic supra- molecular framework displaying hydrogen-bonding and p – p stacking interactions*' Acta Crystallogr. C70 (2014) 722–725. https://doi.org/10.1107/S2053229614014247.

75. T.-L Hu, R.-Q Zou, J.-R Li, X.-H Bu, '*d^{10} Metal complexes assembled from isomeric benzenedicarboxylates and 3-(2-pyridyl) pyrazole showing 1D chain structures : syntheses, structures and luminescent properties*' Dalt. Trans. (2008) 1302–1311. https://doi.org/10.1039/b716398c.

76. M. Padmanabhan, K.C. Joseph, V.G. Puranik, X. Huang, J. Li, 'An unprecedented two-dimensional polymeric $[Zn(OOC\text{-}C_6H_4\text{-}COO)_2]_n^{2-}[^{+}H_3N\text{-}(CH_2)_3\text{-}NH_3^{+}]n$ system bearing one-dimensional chain of zinc(II)bis(phthalate) dianions held by propane-1,3-diammonium cations : Crystal structure' Solid State Sci. 9 (2007) 491–495. https://doi.org/10.1016/j.solidstatesciences.2007.04.009.

77. For space group statistics see http://www.ccdc.cam.ac.uk/products/csd/statistics/

78. I.G. Filippova, O.A. Gherco, Y.A. Simonov, A.A. Deseatnic-ciloci, S.F. Clapco, J.P. Tiurina, S.G. Baca, '*Synthesis , structures and biological properties of nickel (II) phthalates with imidazole and its derivatives*' Polyhedron. 29 (2010) 1102–1108. https://doi.org/10.1016/j.poly.2009.11.016.

79. L.-N. Yang, J. Li, F. Zhang, '*Tris(2,2'-biimidazole)nickel(II) phthalate*' Acta Crystallogr. E61 (2005) m2169–m2171. https://doi.org/10.1107/S1600536805030941.

80. A.D. Burrows, R.W. Harrington, M.F. Mahon, S.J. Teat, '*Manipulation of Molecular and Supramolecular Structure in Nickel (II) Complexes through the Orientation of Dicarboxylate Hydrogen Bonding Faces*' Cryst. Growth Des. 4 (2004) 813–822. https://doi.org/10.1021/cg049930a.
81. Y.-W Xuan, W. Wu, D.-P Xie, N.-X. Yuan, '*Diaquabis(2-carboxybenzoato-κO)-nickel(II)*' Acta Crystallogr. E64 (2008) m101. https://doi.org/10.1107/S1600536807064604.

82. G. Adiwidjaja, H. Kuppers, '*Nickel Dihydrogen Diphthalate Hexahydrate*' Acta Crystallogr. B32 (1976) 1571–1574. https://doi.org/10.1107/S0567740876005840

83. Q.-X. Yao, X.-H. Jin, Z.-F. Ju, H.-X. Zhang, J. Zhang, '*Supramolecular Borromean sheet consisting of threefold parallel interwoven 44-sql layers assembled by a flexible bipyridinium ligand*' Cryst. Growth Des. 11 (2009) 1502–1504.

https://doi.org/10.1039/b901516g.

84. N. P. Kozlova, V. M. Agre, V. K. Trunov, S. S. Makarevich, N. N. Barkhanova, *'Crystal structure of o-phthalato (aquo) bis (ethylenediamine) nickel (II) hemihydrate'* Zhurnal Strukturnoi Khimii, 1982, 23, 108-13.

85. S.G. Baca, I.G. Filippova, P. Franz, C. Ambrus, M. Gdaniec, H. Stoeckli-evans, Y.A. Simonov, O.A. Gherco, T. Bejan, N. Gerbeleu, S. Decurtins, '*Ni (II) coordination compounds based on mixed phthalate and aromatic amine ligands : synthesis, crystal structures and magnetic properties*' Inorganica Chim. Acta. 358 (2005) 1762–1770. https://doi.org/10.1016/j.ica.2004.10.028.

86. D. Poleti, L. Karanovi, B. V. Prelesnik, '*Structure of triaqual [1,2-benzenedicarboxylato(2-)](2,2'-bipyridine)nickel(ll) Monohydrate*' Acta Crystallogr. C46 (1990) 2465–2467. https://doi.org/10.1107/S0108270190006059.

87. F.-C Xue, Z.-H Jiang, D.-Z Liao, S.-L. Ma, S.-L Yan, G.-L Wang, X.-K. Yao, R.-J. Wang, '*Novel structure of nickel(II) complex Ni(phth)py)(H_2O), (phth= the dianion of phthalic acid; bpy = 2,2'-bipyridine)*' Polyhedron. 12 (1993) 2787–2789.

88. S.–Y. Yang, L.–S. Long, R.–B. Huang, L.–S. Zhenga, S.W. Ng, *'Aqua(4,4-bipyridine) phthalatonickel(II) Trihydrate'* Acta Cryst. E59 (2003) m507-m509. https://doi.org/10.1107/S1600536803013448

89. X. Zhang, Z. Yi, W. Xia, C. Yang, B. Li, '*Poly[[diaqua-l2-4,4'-bipyridyl-l2-o-phthalato-nickel(II)] dihydrate]*' Acta Crystallogr. E64 (2008) m345–m346. https://doi.org/10.1107/S1600536807064562.

90. D. Poleti, D.R. Stojakovic, B.V. Prelesnik, L. Manojlovic-Muir**,** '*Structures of triaqua[1,2-benzenedicarboxylato(2-)](1,10-phenanthroline)nickel(II) monohydrate (I) and triaqua[1,2-benzenedicarboxylato(2-)](2,2'-dipyridylamine)nickel(II) dihydrate (II)'* Acta Cryst. C46 (1990) 399-402. https://doi.org/10.1107/S0108270189007791

91. H. Endres, 'Formation of Octahedral Complexes via cis-Addition to Square Planar Bis (oxamideoximato)nickel(II): Three Structure Examples' *Zeitschrift fur Anorganische und Allgemeine Chemie*, 513 (1984) 78-88. https://doi.org/10.1002/zaac.19845130609

92. H. Bai, Y. Liu, *'Crystal structure of diaqua(benzene-1,2-dicarboxylato)-(1,12,15-triaza-3,4:9,10-dibenzo-5,8-dioxacycloheptadecane-"3N,N',N")-nickel(II) tetrahydrate,* $Ni(H_2O)_2(C_8H_4O_4)(C_{20}H_{27}N_3O_2)\cdot 4H_2O$*'* Z. Krist. NCS. 225 (2010) 507–508. https://doi.org/10.1524/ncrs.2010.0222.

93. B.-X. Liu, D.-J. Xu, '*Bis(2,2'-diamino-4,4'-bi-1,3-thiazole-κ2N,N')-(phthalato-κ2O,O')nickel(II) 3.5-hydrate*' Acta Crystallogr. E59 (2003) m1096–m1098. https://doi.org/10.1107/S1600536803024516.

94. D.-S Zhang, Z. Chang, Y.-F Li, Z.-Y Jiang, Z.-H Xuan, Y.-H Zhang, J.-R. Li, Q. Chen, T.-L. Hu, X.-H. Bu, '*Fluorous Metal-Organic Frameworks with Enhanced Stability and High* H_2/CO_2 *Storage Capacities*' Sci. Rep. (2013) 1–7. https://doi.org/10.1038/srep03312.

95. L. Tian, L. Chen, S. Shen, C. Wen, S.-L. Liu, ‘*Synthesis , crystal structure and magnetic properties of a 1D coordination polymer [Ni(phth)(phen)(*H_2O*)] n·n*H_2O*’* J. Coord. Chem. 60 (2007) 683–689. https://doi.org/10.1080/00958970600899856.

96. L. Tian, L. Chen, L.-H Yi, Huaxue Yanjiu, 16 (2005) 9-11.

97. L. Tian, L.-h Yi, L. Chen, Y.-c Yi, L.-c Yu, Xiangtan Daxue Ziran Kexue Xuebao, 29 (2007) 70.

98. X.–L. Wang, B.–K. Chen, H.–Y. Lin, Y.–F. Bi, G.–C. Liu, *Journal of Chemical Crystallography* 38 (2007) 9299.

99. M.A. Braverman, R.M. Supkowski, R.L. Laduca, ‘*One-dimensional nickel and cobalt phthalate coordination polymers incorporating the kinked dipodal organodiimine 4,4’-dipyridylamine: Hydrothermal synthesis,structural characterization and thermal properties*’ Inorganica Chim. Acta. 360 (2007) 2353–2362. https://doi.org/10.1016/j.ica.2006.12.004.

100. M. Fondo, A.M. Garc´ıa-Deibe, N. Ocampo, J. Sanmart´ın, M.R. Bermejo, A.L. Llamas-saiz, ‘*Dinuclear nickel complexes with a* Ni_2O_2 *core : a structural and magnetic study*’ Dalt. Trans. (2006) 4260–4270. https://doi.org/10.1039/b606414k.

101. G. Adiwidjaja, E. Rossmanith, H. Kuppers, ‘*Cobalt dihydrogen diphthalate hexahydrate*’ Acta Cryst. (1978) B34, 3079. https://doi.org/10.1107/S0567740878010110

102. H. Küppers, ‘*The structure of a second modification of cobalt(II) dihydrogen diphthalate hexahydrate’* Zeitschrift fur Kristallographie, (1990) 192-97.

103. B. M. Kariuki, W. Jones, ‘*Structure of hexaaquacobalt hydrogen phthalate*’ Acta Cryst. C49 (1993) 2100-2102. https://doi.org/10.1107/S0108270193005918

104. X. Qian, J. Wang, Y.F Cui, B. Li, H. Li, ‘H*ydrogen Bond Networks of Three Cobalt Coordination Polymers Based on Bis(triazole) and Benzenebiscarboxylate Isomers’* Chinese Journal of Chemistry, 2011, 29, 2591-2596. https://doi.org/10.1002/cjoc.201180432

105. D. Poleti, L. Karanovic, G. A. Bogdanovic, A. Spasojevic-de Biré, ‘*Bis[*μ*-(hydrogen benzene-1,2-dicarboxylato)-O:O']bis[bis(1,10-phenanthroline-N,N')cobalt(II)] bis(hydrogen benzene-1,2-dicarboxylate) dihydrate’* Acta Cryst. C55 (1999) 2061-2063. https://doi.org/10.1107/S0108270199010720

106. S.-Y Yang, L.-S Long, R.-B. Huang, L.-S. Zheng, S.W. Ng, ‘*catena-Poly[[[tetraaquacobalt(II)]-*μ*-pyrazine] phthalate]*’ Acta Crystallogr. E59 (2003) m961–m963. DOI: 10.1107/S1600536803021573

107. A.S. Antsyshkina, G.G. Sadikov, T. V Koksharova, I.S. Gritsenko, V.S. Sergienko, ‘*Synthesis, Crystal and Molecular Structure of Tetraaqua-bis(nicotinamide) cobalt(II) Phthalate Dihydrate’* Russ. J. Inorg. Chem. 54 (2009) 1310–1315.

108. C.-Z Xie, B.-F Zhang, X.-Q Wang, G.-Q. Shen, D.-Z. Shen, ‘*catena-*

poly[[tetraaquacobalt(II)]-l-4,4'-bipyridine-j2N:N'] phthalate dihydrate]' Acta Crystallogr. E60 (2004) m1703–m1705. https://doi.org/10.1107/S1600536804025930.

109. P. Lightfoot, A. Snedden, '*Metal–organic co-ordination frameworks based on mixed N- and O-donor ligands: crystal structures of* $[Co(phth)_2(bipy)]$ *and* $[Co_2(mal)_2(bipy)(H_2O)_2]$*(phth=phthalate, mal=malonate'* J. Chem. Soc., Dalt. Trans. (1999) 3549–3551.

110. S. Sengupta, S. Ganguly, A. Goswami, S. Bala, S. Bhattacharya, R. Mondal, Construction of Co(II) coordination polymers comprising of helical units using a flexible pyrazole based ligand, CrystEngComm. 14 (2012) 7428–7437. https://doi.org/10.1039/c2ce25256b.

111. B.-H. Ye, B.-B. Ding, Y.-Q. Weng, X.-M. Chen, '*Multidimensional Networks Constructed with Isomeric Benzenedicarboxylates and 2,2'-Biimidazole Based on Mono-, Bi-, and Trinuclear Units'* Cryst. Growth Des. 5 (2005) 801–806. https://doi.org/10.1021/cg049742k.

112. D.K. Kumar, A. Das, P. Dastidar, '*Exploring hydrogen-bond capable backbone and ligating topologies : Co(II) coordination polymers derived from mixed ligand systems'* J. Mol. Struct. 796 (2006) 139–145. https://doi.org/10.1016/j.molstruc.2006.02.033.

113. L.-L. Liu, J.-J. Huang, U.-W. Zhang, G.-C. Liu, X.-L. Wang, H.-Y. Lin, N.-L. Chen, Y. Qu, '*Polycarboxylate-assisted assembly of cobalt(II) metal – organic coordination polymers from a 'V'-shaped tri-pyridyl-bis-amide ligand*' Transit. Met Chem. 38 (2013) 689–697. https://doi.org/10.1007/s11243-013-9738-0.

114. L. Tian, L. Chen, X. Zhang, '*Synthesis and Crystal Structure of 2D Supramolecular Compound* $[Co(phth)(phen)(H_2O)_3]\cdot H_2O$' J Chem Crystallogr. 40 (2010) 664–667. https://doi.org/10.1007/s10870-010-9716-8.

115. R. Köferstein, C. Robl, '$M(H_2O)_2(4,4'\text{-}bipy)[C_6H_4(COO)_2]\cdot 2H_2O$(M_Mn$_2$_,Co$_2$_)_ *Two Isotypic Coordination Polymers with Layered Structure*' Z. Anorg. Allg. Chem. 633 (2007) 1127–1130. https://doi.org/10.1002/zaac.200700118.

116. A.L. Pochodylo, K.M. Blake, M.A. Braverman, G.A. Farnum, R.L. Laduca, '*Chiral and achiral layered divalent metal aromatic ortho-dicarboxylate coordination polymers with bis(4-pyridylmethyl) piperazine ligands : Luminescent behavior and magnetic properties'* Inorganica Chim. Acta. 363 (2010) 3951–3958. https://doi.org/10.1016/j.ica.2010.07.061.

117. C.Y. Wang, Z.M. Wilseck, M. Supkowski, R.L. Laduca, '*Metal and ligand binding mode dependent topologies in phthalate coordination polymers with bis(4-pyridylformyl) piperazine co-ligands*' CrystEngComm. 13 (2011) 1391–1399. https://doi.org/10.1039/c0ce00632g.

118. M.A. Harvey, S. Suarez, F. Doctorovich, F.D. Cukiernikc, R. Baggio, '*The structure of* $\{[Co(pht)(bpy)\text{-}(H_2O)]\cdot 3H_2O\}n$ *(pht is phthalate and bpy is 4,4'-bipyridine) and the role of solvent water clusters in structure stability*' Acta Crystallogr. C70 (2014) 440–444. https://doi.org/10.1107/S2053229614006950.

119. H.-Y Bai, J. Yang, '*Crystal structureofaqua(μ_2-benzene-1,2-dicarboxylato)-(1,12,15-triaza-3,4:9,10-dibenzo-5,8-dioxacycloheptadecane-k3N,N',N'')cobalt(II),* $Co(H_2O)(C_8H_4O_4)(C_{20}H_{27}N_3O_2)$*'* Z. Krist. NCS. 225 (2010) 401–402. https://doi.org/10.1524/ncrs.2010.0176.

120. C.-Q Liu, X.-T Yang, L.-L An, R. Li, J.-M Shi, '*catena-Poly[[diaquabis(methanol)-cobalt(II)]-μ-phthalato]*' Acta Crystallogr. E63 (2007) m2311. https://doi.org/10.1107/S1600536807038573.

121. L. Gao, Q.-Y. Cheng, Y.-J. Wang, '*Synthesis and crystal structure of a coordination polymer* $\{[Co(phth)(phen)(H_2O)]\cdot(C_2H_5OH)\}_n$*'* Jiegou Huaxue, 25 (2006) 1193-1196.

122. M.A. Harvey, S. Suarez, F.D. Cukiernik, R. Baggio, '*The topotactic dehydration of monoclinic* $\{[Co(pht)(bpy)(H_2O)_2]\cdot 2H_2O\}_n$ *into orthorhombic* $[Co(pht)(bpy)(H_2O)_2]_n$*(pht is phthalate and bpy is 4,4'-bipyridine)*' Acta Cryst C70 (2014) 978. https://doi.org/10.1107/S2053229614020427

123. S.G. Baca, S.T. Malinovskii, P. Franz, C. Ambrus, H. Stoeckli-evans, N. Gerbeleu, S. Decurtins, '*Synthesis, structure and magnetic properties of cobalt (II) and copper (II) coordination polymers assembled by phthalate and 4-methylimidazole*' J. Solid State Chem. 177 (2004) 2841–2849. https://doi.org/10.1016/j.jssc.2004.05.001.

124. X.-L Wang, F.-F Sui, H.-Y Lin, C. Xu, G.-C Liu, J.-W Zhang, A.-X Tian, '*Role of aromatic dicarboxylates in the structural diversity of cobalt(II) and copper(II) coordination polymers containing a flexible N,N'-di(3-pyridyl)octanediamide ligand*' CrystEngComm. 15 (2013) 7274–7284. https://doi.org/10.1039/c3ce40825f.

125. Y. Qi, Y. Che, F. Luo, S.R. Batten, Y. Liu, J. Zheng, '*A Variety of 1D to 3D Metal-Organic Coordination Architectures Assembled with 1,1'-(2,2'-Oxybis(ethane-2,1-diyl))bis(1H-imidazole)*' Crystal Growth & Design 8 (2008) https://doi.org/10.1021/cg7011217

126. J. Jin, D. Li, L. Li, X. Han, S. Cong, Y. Chi, S. Niu, '*Synthesis , crystal structure and surface photo-electric property of a series of Co(II) coordination polymers and supramolecules*' Inorganica Chim. Acta. 379 (2011) 44–55. https://doi.org/10.1016/j.ica.2011.09.040.

127. L. Liu, X. Li, C. Xu, G. Han, Y. Zhao, H. Hou, Y. Fan, '*Construction of six coordination networks based on a flexible bis(methylbenzimidazole) ligand and isomeric benzenedicarboxylates*' Inorganica Chim. Acta. 391 (2012) 66–74. https://doi.org/10.1016/j.ica.2012.04.043.

128. Y.A. Simonov, M. Gdaniec, I.G. Filippova, S.G. Baca, G.A. Timco, N. V Gerbeleu, '*Synthesis and Structure of Catena -[Bis(2-Methylimidazole)(m-Phthalato) cobaltate (II)]*' Russ. J. Coord. Chem. 27 (2001) 353–359.

129. L.-P Zhang, J.-F Ma, J. Yang, Y.-Y Liu, G.-H Wei, '*1D , 2D , and 3D Metal - Organic Frameworks Based on Bis(imidazole) Ligands and Polycarboxylates : Syntheses,*

Structures, and Photoluminescent Properties' Cryst. Growth Des. 9 (2009) 4660–4673. https://doi.org/10.1021/cg900460k.

130. Y. Wang, F. Zhao, A. Shi, Y. Che, J. Zheng, '*Magnetic and ferroelectric properties of two Co (II) complexes based on flexible bis(imidazole) ligands'* Inorg. Chem. Commun. 20 (2012) 23–26. https://doi.org/10.1016/j.inoche.2012.02.005.

131. Y. Qi, F. Luo, Y. Che, J. Zheng, '*Hydrothermal Synthesis of Metal-Organic Frameworks Based on Aromatic Polycarboxylate and Flexible Bis(imidazole) Ligands'* Cryst. Growth Des. 8 (2008) 606–611. https://doi.org/10.1021/cg700758c.

132. S.G. Baca, M.T. Reetz, R. Goddard, I.G. Filippova, Y.A. Simonov, M. Gdaniec, N. Gerbeleu, '*Coordination polymers constructed from o -phthalic acid and diamines : Syntheses and crystal structures of the and [Co(Pht)(Im)2]n and their application in oxidation catalysis*' Polyhedron 25 (2006) 1215–1222. https://doi.org/10.1016/j.poly.2005.09.003.

133. G.-F Hou, B. Wen, Y.-H Yu, J.-S Gao, X.-D Wang, P.-F Yan, '*Two novel 2-fold interpenetration frameworks constructed by 4,4'-bis(1H-imidazol-1-yl-methyl)biphenyl cobalt(II)coordination polymer and the effect of dicarboxylic acid*' Inorganica Chim. Acta. 402 (2013) 128–132. https://doi.org/10.1016/j.ica.2013.03.046.

134. Z. Tao, L.-l Liang, H.-b Xue, Rengong Jingti Xuebao, 41 (2012) 1478.

135. Y.-H Xue, L. Zhang, D.-J Xu, '*Crystal engineering of coordination polymers using 4,4'-bipyridine as a bond between transition metal atoms'* Jiegou Huaxue, 24 (2005) 1043.

136. L.-N Zhu, M. Liang, Q.-L Wang, W.-Z Wang, D.-Z Liao, Z.-H Jiang, S.-P Yan, P. Cheng, '*Synthesis , structure and magnetic properties of a novel 4,4'-azopyridine-bridged cobalt coordination polymer*' J. Mol. Struct. 657 (2003) 157–163. https://doi.org/10.1016/S0022-2860(03)00365-X.

137. M.R. Sundberg, R. Uggla, '*Conformational flexibility of the di(1,3-diaminopropane)copper(H) cation Part 3. Structure determination for trans-diaquabis(1,3-diaminopropane-N,N')copper(Ii)trans-di(ortho-phthalato-O)bis(1,3-diaminopropane- N,N')cuprate(II) monohydrate and D'* Inorganica Chim. Acta. 254 (1997) 259–265.

138. H.-L. Zhu, J. Zhang, J.-L. Lin, '*catena-Poly[[[diaquacopper(II)]-bis([mu]2-di-4-pyridyl disulfide-[kappa]2N:N')] bis(hydrogen phthalate) monohydrate]*' Acta Crystallogr. E66 (2010) m185. https://doi.org/10.1107/S1600536810001716.

139. Xue-Yan He, Xun-Gao Liu, Bao-Long Li, Yong Zhang, Jiegou Huaxue, *24* (2005*) 831.*

140. Yan Yan, Wen-Jing Yu, Jing Chen, 'Bis[4-amino-3,5-bis(pyridine-2-yl)-4H-1,2,4-triazole-k2N2,N3]bis(benzene-1,2-dicarboxylic acid-k0)copper(II)bis(2-carboxybenzoate)' Acta Crystallogr E68 (2012) m129-m130. https://doi.org/10.1107/S1600536812000128

141. S.K. Shakhatreh, E.G. Bakalbassis, I. Brudgam, H. Hartl, J. Mrozinski, C.A. Tsipis, '*Strong Ferromagnetism between Copper(I1) Ions Separated by 6.7 A in a New Phthalato-Bridged Copper (11) Binuclear Complex*' Inorg. Chem. 30 (1991) 2801–2806. https://doi.org/10.1021/ic00013a018

142. L. Li, D. Liao, Z. Jiang, S. Yan, '*Synthesis , structure and magnetic properties of di-carboxylato-bridged complex* $[Cu_2(phen)_2(Hpht)_2(NO_3)(H_2O)]NO_3{\cdot}2H_2O$' Polyhedron. 19 (2000) 2529–2532.

143. A.L. Pochodylo, K.M. Blake, M.A. Braverman, G.A. Farnum, R.L. Laduca, '*Chiral and achiral layered divalent metal aromatic ortho -dicarboxylate coordination polymers with bis (4-pyridylmethyl) piperazine ligands : Luminescent behavior and magnetic properties*' Inorganica Chim. Acta. 363 (2010) 3951–3958. 10.1016/j.ica.2010.07.061.

144. J.-S Zhao, R.-L Zhang, B.-Y Su, A.-P Gu, S.-Y He, G.-L Xue, J.-N Liu, J.-M Dou, D. –Qi, Wang,Huaxue Xuebao, 60 (2002) 2069.

145. B.L. Rodrigues, M.D.D. Costa, N.G. Fernandes, '*Diaquabis(hydrogen phthalato) copper(II), a new phase*' Acta Crystallogr C55 (1999) 1997-2000. https://doi.org/10.1107/S0108270199011610

146. W. Wen, X. Jimin, '*The influence of pH on coordination of phthalate to copper (II)*' J. Coord. Chem. 61 (2008) 2288–2295. https://doi.org/10.1080/00958970801905270.

147. O.A. Gherco, '*Synthesis and Structure of the Copper (II) Complex with ortho - Phthalic Acid and 1-Methylimidazole* $[\ Cu(HPht)_2(1\text{-}CH_3Im)_2]$' Russ. J. Coord. Chem. 31 (2005) 597–602.

148. A. Zimmer, T. Weyhermuller, K. Hegetschweiler, Monograph Series International Conferences on Coordination Chemistry 6 (2003) 201.

149. H. Xu, R. Sun, Y. Li, J.-F. Bai, '*Poly[[diaqua-μ-1,2-benzene-1,2-dicarboxylato- l-4,4'-bipyridine-copper(II)] dihydrate]: a two-dimensional copper(II) polymer*' Acta Crystallogr. E62 (2006) m1156–m1158. https://doi.org/10.1107/S1600536806014711.

150. H.-X Zhao, G.-L Zhuang, S.-T Wu, L.-S Long, H.-Y Guo, Z.-G. Ye, R.-B. Huang, L.-S. Zheng, '*Experimental and theoretical demonstration of ferroelectric anisotropy in a one-dimensional copper (II)-based coordination polymer*' Chem. Commun. (2009) 1644–1646. https://doi.org/10.1039/b820500k.

151. M.B. Cingi, A.M.M. Lanfredi, A. Tiripicchio, M. T. Camellini, '*The crystal and molecular structure of o-phthalato copper (II)dihydrate*' Acta Crystallogr B34 (1978) 134. https://doi.org/10.1107/S0567740878002459

152. F.-Y Meng, B.-L Jiang, C.-W Lin, L. Wang, X.-H Tan, '*Syntheses, Crystal Structures , and Spectral Properties of Two Coordination Compounds Based on 1,2-Bis(benzimidazolyl) benzene*' Bull. Korean Chem. Soc. 32 (2011) 1017–1021. https://doi.org/10.5012/bkcs.2011.32.3.1017.

153. H.-Y Lin, B. Mu, X.-L Wang, P. Liu, C. Xu, C. Liu, ‘*Two Novel 3D Copper Phthalate Coordination Complexes Incorporating Isomeric Flexible Bis(pyridylformyl) piperazine Ligands*’ Z. Anorg. Allg. Chem. 638 (2012) 1504–1511. https://doi.org/10.1002/zaac.201200193.

154. E.G. Bakalbassis, D.G. Paschalidis, C.P. Raptopoulou, V. Tangoulis, ‘*Synthesis , Crystal Structure , and Magnetic Properties of a One-Dimensional Polymeric Copper (II) Complex , Containing Unicoordinated Phthalato Bridges*’ Inorg. Chem. 37 (1998) 4735–4737.

155. I. Krstanovic, L. Karanovic, D. Stojakovic, ‘*Structure of catena-aqua(1,10-phenanthroline)-μ-phthalatocopper(II)hemihydrates,* $[Cu(C_8H_4O_4)(H_2O)(1,10\text{-}C_{12}H_8N_2)]\cdot 0.5H_2O$’ Acta Crystallogr C41 (1985) 43-45. https://doi.org/10.1107/S0108270185002724

156. L.-l Wu, R. He, Z. Wei, H.-h Song, ‘*Syntheses, structures and properties of five coordination polymers involving phthalic acid’* Chemical Research in Chinese Universities, 27 (2011) 724-729.

157. A. Kellett, M. O’Connor, M. McCann, M. McNamara, P. Lynch, G. Rosair, V. Mckee, B. Creaven, M. Walsh, S. McClean, A. Foltyn, D. O’Shea, O. Howea, M. Devereux, ‘*Bis-phenanthroline copper(II) phthalate complexes are potent in vitro antitumour agents with ‘self-activating’ metallo-nuclease and DNA binding properties*’ Dalt. Trans. 40 (2011) 1024–1027. https://doi.org/10.1039/c0dt01607a.

158. C. Ye, H. Sun, X. Wang, R. Huang, J.-R. Li, S. Gao, ‘*Synthesis and crystal structure of a phthalate-bridged copper (II) complex* $\{[Cu(L)(Phen)(H_2O)]\cdot H_2O\}n$*’* J Chem Crystallogr. 35 (2005) 381–384. https://doi.org/10.1007/s10870-005-1692-z.

159. Li Tian, Lin Chen Lin Chen, Lan-Hua Yi, ‘*Synthesis and crystal structure of phthalate copper(II) polymer*’ Xiangtan Daxue Ziran Kexue Xuebao 25 (2003) 113.

160. Y. Wang, S. Cui, L. Wang, X. Zhang, B. Li, J. Zhang, ‘*Encapsulated different forms of water molecules by Cu (II) complexes with diverse structures’* CrystEngComm. 12 (2010) 2734–2739. https://doi.org/10.1039/b925615f.

161. G.G. Sadikov, T. V Koksharova, A.S. Antsyshkina, I.S. Gritsenko, V.S. Sergienko, ‘*Synthesis and Crystal Structure of catena -Bis (nicotinamide) aqua (μ-phthalato) copper (II) Hemihydrate*’ Crystallogr. Reports. 53 (2008) 631–638. https://doi.org/10.1134/S1063774508040135.

162. M.B. Cingi, A.M.M. Lanfredi, A. Tiripicchio, M.T. Camellini, ‘*The structure of (o-phthalato)bis(pyridine)copper(II) with bridging and chelating o-phthalate anions’* Acta Cryst. B37 (1981) 2159-2163. https://doi.org/10.1107/S0567740881008297

163. Y. Zhang, J. Li, Q. Su, Q. Wang, X. Wu, ‘*Synthesis, structure and spectroscopic properties of an o-phthalate-bridged copper (II) chain complex*’ J. Mol. Struct. 516 (2000) 231–236.

164. M.A. Braverman, J.H. Nettleman, R.M. Supkowski, R.L. Laduca, '*Copper Phthalate Coordination Polymers Incorporating Kinked Dipyridyl Ligands : An Unprecedented 8-Connected Network and One-Dimensional Chiral Nanobarrels with Hydrophobic Channels Constructed from Septuple Helical Motifs*' Inorg. Chem. 48 (2009) 4918–4926. https://doi.org/10.1021/ic900331m.

165. R.-G. Lin, Y.-L. Wang, Q. Liang, '*Structure and magnetic properties of a mixed-ligand copper(II) complex'* Acta Cryst. C71 (2015) 44-47. https://doi.org/10.1107/S205322961402556X

166. C. D. Nicola, F. Garau, A. Lanza, M. Monari, L. Pandolfo, C. Pettinari, A. Zorzi, '*Influence of the solvent in the formation of different 1D and 2D coordination polymers from the reaction of copper (II) phthalate with pyrazole*' Inorganica Chim. Acta. 416 (2014) 186–194. https://doi.org/10.1016/j.ica.2014.03.024.

167. M. B. Cingi, C. Guastini, A. Musatti, M. Nardelli, '*The crystal and molecular structure of diammine-(o-phthalato)copper(II)*' Acta Cryst. B26 (1970) 1836-1843. https://doi.org/10.1107/S0567740870004971

168. G.M. Dulcevscaia, V.C. Kravtsov, F.Z. Macaev, G.G. Duca, E.P. Stingachi, S.I. Pogrebnoi, V. V Boldescu, S.F. Clapco, J.P. Tiurina, A.A. Deseatnic-ciloci, J. Lipkowski, S. Liu, S. Decurtins, S.G. Baca, '*New copper (II) complexes with isoconazole : Synthesis , structures and biological properties*' Polyhedron. 52 (2013) 106–114. https://doi.org/10.1016/j.poly.2012.10.040.

169. S.-X. Li, G.-F. Zhao, F.-Q. Liu, Z.-G. Huang, W.-H. Li, G.-Y. Liu, '*Synthesis , Crystal Structure and Electrochemical Studies of catena-Poly ([bis(1-vinyl-1H-imidazole-κN3) copper (II)]-μ-phthalato-κ2O:O')*' Chinese J. Chem. 26 (2008) 1732–1736.

170. X.-G. Zhou, '*Poly[[[bis(isonicotinamide)copper(II)]-μ-benzene-1,2-dicarboxylato] monohydrate]*' Acta Cryst E63 (2007) m3166. https://doi.org/10.1107/S1600536807060217

171. C. K. Prout, J. R. Carruthers and F. J. C. Rossotti , '*Structure and stability of carboxylate complexes. Part IX. Crystal and molecular structure of copper(II) phthalate monohydrate*' J. Chem. Soc. A (1971) 3350-3354. https://doi.org/10.1039/J19710003350

172. G.-B Li, L. Li, J.-M Liu, T. Yang, C.-Y Su, '*A $CdSO_4$ - Type 3D Metal − Organic Framework Showing Coordination Dynamics on Cu^{2+} Axial Sites: Vapochromic Response and Guest Sorption Selectivity*' Cryst. Growth Des. 13 (2013) 1518–1525. https://doi.org/10.1021/cg3017563.

173. J. Zdravkovic, D. Poleti, J. Rogan, D.M. Minic, '*Bis(2,2'-bipyridine)-bis(l3-phthalato)-dicopper(II) tetrahydrate as molecular sieve with zero-dimensional structure'* Polyhedron. 80 (2014) 256–264. https://doi.org/10.1016/j.poly.2014.05.026.

174. D. Poleti, Lj. Karanovic, B.V. Prelesnik, '*A polymeric copper(II) complex with 2,2'bipyridine and 1,2-benzenedicarboxylate(2-)*' Acta Crystallogr C49 (1993) 1249-1251. https://doi.org/10.1107/S0108270193001404

175. X. Zhao, H. Peng, L. Yu, '*Syntheses and crystal structures of two o-phthalate*

based transition metal complexes' African J. Pure Appl. Chem. 5 (2011) 436–441.

176. X. Fu, X. Wang, M. Li, C. Wang, X. Deng, '*Poly[[aquatetraimidazoledi-l-phthalato-dicopper(II)] monohydrate]*' Acta Crystallogr. C62 (2006) m343–m345. https://doi.org/10.1107/S0108270106019068.

177. N.V. Gerbeleu, Yu.A. Simonov, G.A. Timko, P.N. Bourosh, J. Lipkovskii, S.G. Baka, D.I. Saburov, M.D. Mazus, Zhurnal Neorganicheskoi Khimii, 44 (1999) 1264.

178. L. Zhang, Y. Ling, J. Li, H. Gao, '*Supramolecular self-assembly of two Cu (II) complexes with 1,2,4-triazole derivatives : syntheses, crystal structures and magnetic properties*' Struct. Chem. 19 (2008) 911–916. https://doi.org/10.1007/s11224-008-9375-y.

179. L.L. Johnston, D.P. Martin, R.M. Supkowski, R.L. Laduca, '*One- and two-dimensional copper benzenedicarboxylate coordination polymers incorporating the flexible tethering diimine N,N'-bis(3-pyridylmethyl) piperazine : Synthesis , structure , and thermal properties'* Inorg. Chim. Acta. 361 (2008) 2887–2894. https://doi.org/10.1016/j.ica.2008.02.040.

180. J. Cano, G.De Munno, J.L. Sanz, R. Ruiz, F. Lloret, J. Faus, M. Julve, '*Synthesis, crystal-structure and magnetic-properties of terephthalate-bridged, isophthalate-bridged and phthalate-bridged copper(ii) dinuclear complexes'* Anales de Quimica, 93(1997) 174-181.

181. W. Xu, W. Pan, Y. Zheng, '*Syntheses and crystal structures of phthalato-, succinato-, maleato-, acetylenedicarboxylato-bridged [bis(2-pyridylcarbonyl)amide] copper(II) complexes'* J. Coord. Chem. 66 (2013) 4415–4429. https://doi.org/10.1080/00958972.2013.862789.

182. J. Chen, Z.-H Jiang, D.-Z Liao, S.-P Yan, Jiegou Huaxue 24 (2005) 1017.

183. H.-X Zhang, B.-S Kang, A.-W Xu, Z.-N Chen, Z.-Y Zhou, A.S.C. Chan, K. Yu, C. Ren, '*Supramolecular architectures from the self-assembly of trans-oxamidato-bridged dicopper(II) building blocks and phenyldicarboxylates*' J. Chem. Soc., Dalt. Trans. (2001) 2559–2566. https://doi.org/10.1039/b102570h.

184. Z.-N Chen, H.-X Zhang, K.-B Yu, B.-S Kang, H. Cai, C.-Y Su, T.-W Wang, Z.-L Lu, '*3D Extended Supramolecular Structures via H-Bonded Linkages of 2D Sheetlike or 1D Zigzag Coordination Polymers*' Inorg. Chem. 37 (1998) 4775–4781.

185. C.E. Xanthopoulos, C.C. Hadjikostas, G.A. Katsoulos, A. Terzis, M.P. Sigalas, C.C. Hadjikostas, 'Molecular Structure and Magnetic Properties of the Binuclear Phthalato-Bridged Species Bis[(N-(2-(Diethylamino)Ethyl)Salicylidenaminato)-Copper(II)] Trihydrate' J. Coord. Chem. 55 (2010) 563–572. https://doi.org/10.1080/00958970290020874.

186. R. Ludwig, '*Water: From Clusters to the Bulk',* Angew. Chem. Int. Ed. 40 (2001) 1808–1827. https://www.ncbi.nlm.nih.gov/pubmed/11385651

187. L. Infantes, J. Chisholm, S. Matherwell, CrystEngComm 5 (2003) 480-486. https://doi.org/10.1039/B312846F

188. S. Supriya, S.K. Das, '*Small Water Clusters in Crystalline Hydrates*', Journal of Cluster Science, 14 (2003) 337-366. https://link.springer.com/article/10.1023/B:JOCL.0000005068.77622.a4

189. B.K. Saha, A. Nangia, 'First example of an ice-like water hexamer boat tape structure in a supramolecular organic host', Chem. Commun. (2006) 1825–1827. https://doi.org/10.1039/B600348F

190. P.S. Lakshminarayanan, E. Suresh, P. Ghosh, '*Formation of an Infinite 2D-Layered Water of* $(H_2O)_{45}$ *Cluster in a Cryptand−Water Supramolecular Complex: A Template Effect',* J. Am. Chem. Soc. 127 (2005) 13132–13133. https://doi.org/10.1021/ja054068w

191. C.H. Li, K.L. Huang, J.M. Dou, Y.N. Chi, Y.Q. Xu, L. Shen, D.Q. Wang, C.W. Hu, *'An Interesting Six-Connected 3D Nanowater Framework Constructed from Turbine-Type* $(H_2O)_{18}$ *Clusters Based on a Mn(III) Complex',* Cryst. Growth Des. 8 (2008) 3141–3143. https://doi.org/10.1021/cg800504a

192. K. Takaoka, M. Kawano, M. Tominaga and M. Fujita, '*In Situ Observation of Reversible Single-Crystal-to-Single-Crystal Apical Ligand Exchange Reaction in a Hydrogen-Bonded 2-D Coordination Network*' Angew. Chem. 44 (2005) 2151-2154. https://doi.org/10.1002/anie.200462214

193. M.P. Suh, J.W. Ko, H. J. Choi, '*A Metal−Organic Bilayer Open Framework with a Dynamic Component: Single-Crystal-to-Single-Crystal Transformations*' J. Am. Chem. Soc. 124 (2002) 10976. https://doi.org/10.1021/ja017560y

194. B.R. Srinivasan, S.N. Dhuri, M. Poisot, C. Näther, W. Bensch, 'Synthesis, Crystal Structures and Properties of Three New Tetrathiomolybdates with Organic Ammonium Cations' Z Naturforsch 59b (2005) 1083-1092.

195. B.R. Srinivasan, S.N. Dhuri, M. Poisot, C. Näther, W. Bensch, '*Synthesis, X-ray Structures, Spectroscopic and Thermal Characterization of Two New Organic Ammonium Tetrathiotungstates*' Z Anorg. Allg. Chem. 631 (2005) 1087-1094. https://doi.org/10.1002/zaac.200400513

196. B.R. Srinivasan, A.R. Naik, C. Näther, W. Bensch, '*Piperazinium dichromate(VI)'* Acta Cryst. E60 (2004) m1384-1386. https://doi.org/10.1107/S1600536804021543

197. H. Ishihara, K. Horiuchi, T.M. Gesing, S.-q. Dou, J.-C. Buhl, P. Erk, '*Crystal Structures of Piperazinium Tetrabromocadmate(II)-Monohydrate* $[C_4H_{12}N_2]CdBr_4 \cdot H_2O$*, Piperazinium Tetraiodocadmate(II)* $[C_4H_{12}N_2]CdI_4$*, and Bis(trimethylsulphonium) Tetrabromocadmate(II)* $[(CH_3)_3S]_2CdBr_4$*'* Z Naturforsch 57b (2002) 503-508.

198. B.R. Srinivasan, A.R. Naik, S.N. Dhuri, C. Näther, W. Bensch, '*Synthesis, properties and supramolecular structure of piperazinediium thiosulfate monohydrate*' J. Chem. Sci. 123 (2011) 55-61. https://doi.org/10.1007/s12039-011-0064-9

199. Z.M. Jin, Y.J. Pan, L. He, Z.G. Li, K.B. Yu, '*Crystal Structure of the 1:2:2 Adduct of Piperazine, o-Phthalic Acid and Water'* Anal. Sci. 19 (2003) 333-334. https://doi.org/10.2116/analsci.19.333

200. R.N. Jyai, B. R. Srinivasan, '*Piperazinediium bis(μ2-phthalato)zincate(II) monohydrate: A new ladder coordination polymer with a unique supramolecular architecture*' Indian J. Chem 54A (2015) 1402-1408. http://nopr.niscair.res.in/handle/123456789/33428

201. B.R. Srinivasan, C. Näther, W. Bensch, '*Piperazinium chromate(VI)*' Acta Cryst. E59 (2003) m639-m641. https://doi.org/10.1107/S1600536803014879

202. D. Havlíček, J. Plocek, I. Němec, R. Gyepes, Z. Mička, 'The Crystal Structure, Vibrational Spectra, and Thermal Behavior of Piperazinium(2+) Selenate Monohydrate and N, N′-Dimethylpiperazinium(2+) Selenate Dihydrate' J. Solid State Chem. 150 (2000) 305-315. https://doi.org/10.1006/jssc.1999.8595

203. K. Jayaraman, A. Choudhury, C.N.R. Rao, '*Sulfates of organic diamines: hydrogen-bonded structures and properties*' Solid State Sci. 4 (2002) 413-422. https://doi.org/10.1016/S1293-2558(02)01269-4

204. D.T. Qui, E. Palacios, '*Structure of piperazinium tetrachlorocobaltate monohydrate'* Acta Cryst. C46 (1990) 1212-1215. https://doi.org/10.1107/S0108270189011571

205. H. Ishihara, K. Horiuchi, I. Svoboda, H. Fuess, T. M. Gesing, J.-C. Buhl, H. Terao, '*Crystal Structures of Piperazinium Tetrahalogenometallates (II)* $[C_4H_{12}N_2]MX_4$ *(M = Zn, Hg; X = Br, I)'* Z Naturforsch 61b (2006) 69-72.

206. K.R. Mote, J. Thomas, A. Ramanan, '*Crystal engineering of molecular to nonmolecular metal malonates in presence of piperazine: Role of metal ions in tuning architectures*' Indian J. Chem 57A (2018) 1081-1091. http://nopr.niscair.res.in/handle/123456789/44893

207. K.M. Fromm, *'Coordination polymer networks with s-block metal ions'* Coord. Chem. Rev. 252 (2008) 856–885. https://doi.org/10.1016/j.ccr.2007.10.032

208. B. Yan, R.K. Vakiti, N. Fedorka, X. Liu, Y. Cao, W.P. Pan, *'3-D metal-organic frameworks based on s-block metal ions'* Inorg. Chim. Acta 421 (2014) 544–548. https://doi.org/10.1016/j.ica.2014.07.039

209. W. Gonschorek, H. Küppers, *'The crystal structure of lithium hydrogen phthalate dihydrate, containing a very short hydrogen bond'* Acta Cryst. B31 (1975) 1068-1072. https://doi.org/10.1107/S0567740875004517

210. H. Kuppers,*'Lithium hydrogen phthalate monohydrate'* Acta Cryst. B34 (1978) 3763-3765. https://doi.org/10.1107/S0567740878012121

211. H. Kuppers, A. Kvick, I. Olovsson, '*Hydrogen bond studies. CXLII. Neutron diffraction study of the two very short hydrogen bonds in lithium hydrogen phthalate-methanol'* Acta Cryst. B37 (1981) 1203-1207. https://doi.org/10.1107/S0567740881005517

212. L.M. Avdonina, G.M. Serebrennikova, Yu. V. Oboznenko, T.M. Okhrimenko, G.S. Belikova, Yu. A. Velikodni (1980) Zh. Neorg. Khim.(Russ.)(Russ.J.Inorg.Chem.), 25, 542.

213. R.A. Smith, '*The crystal structures of a series of salts of phthalic acid. II. The crystal structure of sodium acid phthalate hemihydrate'* Acta Cryst. B31 (1975) 2345-2347. https://doi.org/10.1107/S0567740875007546

214. J.Z. Gougoutas, W.H. Ojala, J.A. Miller (1980) Cryst.Struct.Commun. , 9**,** 519.

215. Y. Okaya, *'The crystal structure of potassium acid phthalate, $KC_6H_4COOH.COO$'* Acta Cryst. 19 (1965) 879-882. https://doi.org/10.1107/S0365110X65004590

216. B. M. Kariuki, W. Jones, *'Potassium Hydrogen Phthalate Hemiperhydrate'* Acta Cryst. C51 (1995) 1128-1130. https://doi.org/10.1107/S0108270194012497

217. J.B. Benedict, T. Bullard, W. Kaminsky, B. Kahr, *'Potassium hydrogen diphthalate dihydrate: a new structure and correction to the literature'* Acta Cryst. C60 (2004) m551-m553. https://doi.org/10.1107/S0108270104019043

218. H. Kuppers, Z. Kristallogr., Kristallgeom.,Kristallphys.,Kristallchem. 146 (1977) 269.

219. Y. Okaya, R. Pepinsky, *'The crystal structure of amonium acid phthalate'* Acta Cryst. 10 (1957) 324-328. https://doi.org /10.1107/S0365110X57000936

220. I.A. Krol, V.M. Agre, V.K. Trunov, L.M. Avdonina, Koord.Khim. (Russ.)(Coord.Chem.) 9 (1983) 687.

221. H. Mancheng, G. Chunyu, L. Shuni, L. Zhihong, J. Yucheng, Z. Guofang, *'Caesium(I) hydrogen phthalate'* Acta Cryst. 60 (2004) m1713-m1715. https://doi.org/ 10.1107/S1600536804026479

222. B. M. Kariuki, W. Jones, '*Structures of hexaaquamagnesium hydrogen phthalate and hexaaquamagnesium hydrogen phthalate dihydrate'* Acta Cryst. C45 (1989) 1297-1299. https://doi.org/10.1107/S0108270189004385.

223. A. Langkilde, D. Madsen, S. Larsen, '*Structures of three salts of phthalic acid; variation in crystal packing and geometry of the hydrogen phthalate ion'* Acta Cryst. B60 (2004) 502-511. https://doi.org /10.1107/S0108768104018051

224. M. P. Gupta, R. P. Sinha, Cryst.Struct.Commun. 4 (1975) 207

225. W. Schuckmann, H. Fuess, J. W. Bats, *'Refinement of the structure of calcium phthalate monohydrate'* Acta Cryst. B34 (1978) 3754-3756. https://doi.org/10.1107/S056774087801208X

226. A.A.A. Terkawi, G. Scholz, C. Prinz, A. Zimathies, F. Emmerling, E. Kemnitz, '*Hydrated and dehydrated Ca-coordination polymers based on benzene-dicarboxylates: mechanochemical synthesis, structure refinement, and spectroscopic characterization'* CrystEngComm 2018, 20, 946-961. https://doi.org/10.1039/C7CE01906H

227. J.W. Bats, W. Schuckmann, H.Fuess, '*Strontium dihydrogen diphthalate dihydrate'* Acta Crystallogr. 34B (1978) 2627. https://doi.org/10.1107/S0567740878008778

228. R.A.Smith, Acta Crystallogr. 33B (1977) 1594.

229. G. Ramasamy, S. Meenakshisundaram, *'Synthesis and crystal structure of potassium hydrogen phthalate mixed crystal* $K_{0.78}Na_{1.22}[C_6H_4(COO)_2]\cdot H_2O$*'* J. Cryst. Growth, 375 (2013) 26–31. https://doi.org/10.1016/j.jcrysgro.2013.03.046

230. C. Glidewell, J. N. Low, J. M. S. Skakle, J. L. Wardell, *'A 1, 2, 4 - diazaphospholane complex of rhodium'* Acta Cryst. C59 (2003) 144. https://doi.org/10.1107/S0108270103002142

231. A. Amani, Z. Derikvand, A. Azadbakht, B. Notash *'Synthesis, crystal structure and Hirshfeld surface analysis of acidic salt [4-methyl phenyl ammonium][(O-phenyl)(hydroxyl)phosphate],* $[4\text{-}CH_3\text{-}C_6H_4NH_3][(C_6H_5O)P(O)(O)(OH)]$*'* Iranian Journal of Crystallography and Mineralogy' 25 (2017) 199-206.

232. L. Wang, M. Guo, S. Jin, L. Sun, Y. Wang, W. Xu, D. Wang, *'Crystal Structures of Three Organic Adducts Produced by N6 -Benzyladenine, Trichloroacetic Acid, 3-Nitrophthalic Acid, and Citric Acid'* J.Chem.Cryst. 46 (2016) 399.

233. Y. Wang, W. Feng, L. Xue, J. M. Zheng, *Jiegou Huaxue(Chin.)* 25 (2006) 923.

234. L. Wang, R. Xue, Y. Li, Y. Zhao, F. Liu, K. Huang *'Hydrogen-bonding patterns in a series of multi-component molecular solids formed by 2,3,5,6-tetramethylpyrazine with selected carboxylic acids'* Cryst. Eng.Comm. 16 (2014) 7074-7089. http://dx.doi.org/10.1039/C4CE00749B

235. X. Wang, K. Zhang, Y. Geng, Y. Sun, F. Chen, L. Wang, '*A series of cocrystals formed by 2,3-dimethylpyrazine bridging various aromatic acids through hydrogen bonds: Synthesis, structural characterization and synthon discussion*' J. Mol. Struct. 1165 (2018) 106-119. https://doi.org/10.1016/j.molstruc.2018.03.105

236. S. Jin, L. Wang, Y. Lou, L Liu, B. Li, L. Li, C. Feng, H. Liu, D. Wang '*A series of cocrystals formed by 2,3-dimethylpyrazine bridging various aromatic acids through hydrogen bonds: Synthesis, structural characterization and synthon discussion*' J.Mol.Struct. 1108 (2016) 735. https://doi.org/10.1016/j.molstruc.2018.03.105

237. V. Thayanithi, P. P. Kumar, B. Gunasekaran, *'Bis(creatininium) 3-nitrophthalate monohydrate'* (2016) *IUCr Data* ,1 , x160989. https://doi.org/10.1107/S2414314616009895

238. P. Sivakumar, S. Sudhahar, S. Israel, G. Chakkaravarthi, '*Bis (2-amino-6-methyl-pyridinium) 3-nitrobenzene-1,2-dicarboxylate'*
(2016) IUCrData, 1, x161233. https://doi.org/10.1107/S2414314616012335

239. A. Ding, S. Jin, S. Jin, K. K. Hu, Z. Lin, H. Liu, D. Wang *'Crystal structures of eight 3D molecular adducts derived from bis-imidazole, bis(benzimidazole), and organic acids'* J.Mol.Struct.1151 (2018) 17-38. https://doi.org/10.1016/j.molstruc.2017.09.009

240. X. Gao, X. L. Li, S. Jin, K. Hu, J. Guo, M. Guo, W. Xu, D. Wang, *'Hydrogen bonded 1D-3D supramolecular structures from Benzylamine and organic acidic components' J.Mol.Struct.,*1155 (2018) 39-50.
https://doi.org/10.1016/j.molstruc.2017.09.051

241. M. L. Guo, *'Piperazinediium 3-nitrophthalate dihydrate'* E60 (2004) o1236- o1238. https://doi.org/10.1107/S1600536804014692

242. R. W. Seidel, R. Goddard, M. Spiteller, T. M. Kolev, J.Chem.Cryst. 45 (2015) 86

243. M. D. Bharathi, G. Ahila, J. Mohana, G. Chakkaravarthi, G. Anbalagan Acta Crystallogr.,Sect.E:Cryst.Commun. E**71** (2015)

244. G. Smith, U. D. Wermuth, P. C. Healy, *'Guanidinium 2-carb-oxy-6-nitro-benzoate monohydrate: a two-dimensional hydrogen-bonded network structure'* Acta Cryst. E63 (2007) o3527-o3528. https://doi.org/10.1107/S1600536807034356

245. Z. S. Li, J. S. Chai, *'Glycinium 3-nitro-phthalate'* Acta Cryst. 63 (2007) o2857-o2859. https://doi.org/10.1107/S1600536807019253

246. J. Mohana, M. D. Bharathi, G. Ahila, G. Chakkaravarthi, G. Anbalagan, *Acta Cryst.* E71.

247. Y. D. S. Y. Wang, J. Liu, Y. L. Yang, F. Zang, H. W. Ma, Huaxue Xuebao (Chin.)(Acta Chim.Sinica) 65 (2007) 809

248. C. Glidewell, J. N. Low, J. M. S. Skakle, J. L. Wardell *'3-Iodo-anilinium 2-carb-oxy-6-nitro-benzoate: a three-dimensional framework built from O-H...O and N-H...O hydrogen bonds and a two-centre iodo-nitro inter-action'* Acta Cryst. C61 (2005) o246-o248. https://doi.org/10.1107/S0108270105006013

249. G. Smith, U. D. Wermuth, D. J. Young, J. M. White, *'The 1:1 proton-transfer compounds of 4-(phenyl-diazen-yl)aniline (aniline yellow) with 3-nitro-phthalic, 4-nitro-phthalic and 5-nitro-isophthalic acids'*,64 (2008) o123-o127. https://doi.org/10.1107/S0108270108001595

250. Ming-Lin Guo (2005) *Acta Crystallogr., Sect.E:Struct.Rep.Online* **61** o1728

251. C. Glidewell, J. N. Low, J. M. S.Skakle, J. L. Wardell, *'4-Iodo¬anilinium 3-nitro¬phthalate(1–): tripartite sheets built from O—H···O and N—H···O hydrogen bonds'* Acta Cryst. C59 (2003) o509-o511. https://doi.org/10.1107/S0108270103014434

252. S. Balachandar, M. Sethuram, P. Muthuraja, T. Shanmugavadivu, M. Dhandapani, *J.Photochem.Photobiol. B* 163 (2016) 352.

253. K. Singaravelan, A.Chandramohan, M. Saravanabhavan, I. V. Muthu Vijayan Enoch, V. S. Suganthi, *'Hydrogen bonded charge transfer molecular salt (4-chloro anilinium-3-nitrophthalate) for photophysical and pharmacological applications'* Spectrochim.Acta Part A 184 (2017) 318. https://doi.org/10.1016/j.saa.2017.05.016

254. S. R. Devi, S. Kalaiyarasi, R. Akilan, R. M. Kumar, G. Chakkaravarthi, *4-Methylpyridinium 2-carboxy-6-nitrobenzoate*, IUCrData ,1 (2016) x161803. https://doi.org/10.1107/S2414314616018034

255. P. Sivakumar, S. Sudhahar, S. Israel, G. Chakkaravarthi, *2-Methylpyridinium 2-carboxy-6-nitrobenzoate*, IUCrData ,1 (2016) x161104. https://doi.org/10.1107/S2414314616011044

256. R. Mekala, R. Mani, I. B. Rietveld, P. Jagdish, R. Mathammal, H. Jiang, *Crystal growth and physical properties of the organic salt benzimidazolium 3-nitrophthalate*, CrystEngComm 18 (2016) 8194-8206. https://doi.org/10.1039/C6CE01712F

257. A. Ding, S. Jin, S. Jin, K. Hu, Z. Lin, H. Liu, D. Wang, *Crystal structures of eight 3D molecular adducts derived from bis-imidazole, bis(benzimidazole), and organic acids,* J. Mol. Struct. 1151 (2018) 17-28. https://doi.org/10.1016/j.molstruc.2017.09.009

258. K. Chadwick, G. Sadiq, R. J. Davey, C. C. Seaton, R. G. Pritchard, A. Parkin, *Designing Acid Acid Co-Crystals−The Use of Hammett Substitution Constants*, Cryst. Growth Des. 9 (2009) 1278-1279. https://doi.org/10.1021/cg801225s

259. C. C. Seaton, K. Chadwick, G. Sadiq, K. Guo, R. J. Davey, *Designing Acid/Acid Co-Crystals through the Application of Hammett Substituent Constants*, Cryst. Growth Des. 10 (2010) 726-733. https://doi.org/10.1021/cg9011235

260. M. Mohana, P. T. Muthiah, R. J. Butcher, *Supramolecular interactions in carboxylate and sulfonate salts of 2,6-diamino-4-chloropyrimidinium*, Acta Cryst. C73 (2017) 536-540. https://doi.org/10.1107/S2053229617008798

261. P. Xing, Q. Li, Y. Li, K. Wang, Q. Zhang, L. Wang, *Organic salts formed by 2,4,6-triaminopyrimidine and selected carboxylic acids via a variety of hydrogen bonds: Synthons cooperation, and crystal structures*, J. Mol. Struct. 1136 (2017) 59-68. http://dx.doi.org/10.1016/j.molstruc.2017.01.066

262. G.Smith, U.D.Wermuth, D.J.Young, P.C.Healy, *Brucinium 2-carb-oxy-6-nitro-phthalate dihydrate: the 1:1 proton-transfer compound of brucine with 3-nitro-phthalic acid*, Acta Cryst. E61 (2005) o2008-o2011. https://doi.org/10.1107/S1600536805017149

263. M. G.Smith, A. Lemmerer, *Novel crystal forms of 4-aminoantipyrine and its derivatives: Co-crystallizing a reluctant molecule*, J. Mol. Struct. ,1175 (2019) 307-313. https://doi.org/10.1016/j.molstruc.2018.07.062

264. R. Mekala, R. Mani, P. Jagdish, R. Mathammal, *Design, structural investigation and physicochemical properties of benzotriazolium* m*-nitrophthalate monohydrate single crystals*, J. Mol. Struct. 1157 (2018) 40-51. https://doi.org/10.1016/j.molstruc.2017.12.026

265. A. Ding, S. Jin, S. Jin, K. Hu, Z. Lin, H. Liu, D. Wang, *Crystal structures of eight 3D molecular adducts derived from bis-imidazole, bis(benzimidazole), and organic acids*, J. Mol. Struct. 1151 (2018) 17-28. http://dx.doi.org/10.1016/j.molstruc.2017.09.009

266. M. –L. Guo, c*atena-Poly[[[aqua(2-carboxy-6-nitrobenzoato-κO)sodium]-di-μ-aqua] monohydrate]*, Acta Cryst. E60 (2004) m1684-m1685. https://doi.org/10.1107/S1600536804026273

267. Q. Shuai, Y. -Y. Di, Z. -B. Li, L. Li, D. -H. He, *Poly[[diaqua(μ_3-3-nitrophthalato)-calcium(II)] monohydrate]*, Acta Cryst. E66 (2010) m1509-m1510. https://doi.org/10.1107/S0108270109036130

268. B. R. Srinivasan, S. Y. Shetgaonkar, C. Näther, Preparation, *Crystal Structures, and Thermal Studies of Alkaline Earth Nitrocarboxylates*, Z. Anorg. Allg. Chem. 637 (2011) 130-136 http://dx.doi.org/10.1002/zaac.201000214

269. M. -L. Guo, *Poly[[diaqua(μ_3-3-nitrophthalato)calcium(II)] monohydrate]*, Acta Cryst. C65 (2009) m395-m397. https://doi.org/10.1107/S0108270109036130

270. P. -F. Wang, X. -L. Tao, J. -L. Wang, G. -Z. Wu, X. Wang, *A New 2D Layered Barium Coordination Polymer [Ba(3-NPA)]n: Synthesis, Crystal Structure, Thermal Stability and Luminescent Properties*, Chinese J. Struct. Chem. 33 (2014) 339-344.

271. S. -Y. Zhang, N. Xu, W. Shi, P. Cheng, D. –Z. Liao, *Syntheses, structural diversities and magnetic properties of four new Co(II) coordination polymers with phthalic acid derivatives*, 51 (2013) Polyhedron 283-291. https://doi.org/10.1016/j.poly.2012.12.032

272. R. Yang, X. -Q. Shen, H. -Y. Mao, H. -Y. Zhang, Q. -A. Wu, H. Wang, H. -W. Hou, Y. Zhu, *Synthesis and Crystal Structure of a Novel Supra-Molecular Compound* $[Co(tsc)_2][NPA]_2 \cdot 4H_2O$ *(tsc=Thiosemicarbazide,* H_2NPA*=3-Nitro-Phthalic Acid)*, 36 (2006) Synth.React.Inorg.,Met.-Org.,Nano-Met.Chem. 617-620. https://doi.org/10.1080/15533170600910538

273. G. -L. Li, W. –D. Yin, G. –Z. Liu, L. –F. Ma, L. –L. Huang, L. Li, L. –Y. Wang, *Single-crystal to single-crystal photochemical structure transformation of a ladder-like coordination polymer with dinuclear Zn(II) platform*, 43 (2014) Inorg.Chem.Commun.165-168 https://doi.org/10.1016/j.inoche.2014.02.037

274. Bruker SMART V5.630, SAINT-PLUS V6.45 and SADABS Bruker-Nonius Analytical X-ray Systems Inc., Madison, Wisconsin, USA, 2003.

275. G.M. Sheldrick, Acta Cryst. C71 (2015) 3-8. https://doi.org/10.1107/S2053229614024218

276. J.-H. Wang, G.-M. Tang, Y.-T. Wang, T.-X. Qin, S.W. Ng, CrystEngComm 16 (2014) 2660- 2683. https://doi.org/10.1039/C3CE42099J

277. An Introduction to Hydrogen Bonding, ed. G.A. Jeffrey, Oxford University Press, New York, (1997).

278. A.H. Narten, W.E. Thiessen, L. Blum, Sci. 217 (1982) 1033-1034. https://doi.org/10.1126/science.217.4564.1033

279. A.L. Spek, Acta Cryst. D65 (2009) 148-155. https://doi.org/10.1107/S090744490804362X

280. *A.P. Raj, C.R. Raja, 'Studies on the synthesis, spectral, optical* and *thermal properties of L-valine zinc sulphate: an organic inorganic hybrid nonlinear optical crystal'* Spectrochimica Acta 97A (2012) 83–87.

281. R. Hanumantharao, S. Kalainathan, *'Growth and spectroscopic investigation of a new crystal for NLO applications:*$C_{10}H_{20}KN_5O_9$*'* Spectrochim. Acta *A99* (2012) 181–188.

282. R. Hanumantharao, S. Kalainathan, '*Studies on structural, thermal and optical properties of novel NLO crystal bis L-glutamine sodium nitrate'* Mater. Lett. 74 (2012) 74–77.

283. R.N.Jyai & B.R.Srinivasan, *Syntheses, structures, reactivity studies and properties of anionic water rich bivalent metal phthalates*, Journal of Molecular Structure 1178 (2019) 89-99. https://doi.org/10.1016/j.molstruc.2018.10.012

284. B.R. Srinivasan & R.N. Jyai, *Reinvestigation of growth of 'L-valine zinc sulphate' crystal*, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 120 (2014) 621–624. http://dx.doi.org/10.1016/j.saa.2013.11.062

285. B.R. Srinivasan, S.K. Shyama, S.G. Naik & R.N. Jyai, *On the existence of 'bis (L-glutamine) potassium nitrate' crystal,* Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 136 (2015) 334–337. http://dx.doi.org/10.1016/j.saa.2014.08.148

APPENDIX

Table A1: List of reported dopants used to incorporate in NaHpht$^{.1}/_2H_2O$.

Sr. No.	Dopant	Reference
	Metal ions	
1	Fe^{3+}	1
2	Zn^{2+}	2
	Amino acids	
3	L-Histidine monohydrochloride dihydrate	3
4	L-valine	4
5	L-alanine,	5
6	L-histidine	5
7	L-arginine	5, 6

References:

1] N. Goel, B. Kumar, *Remarkable enhancement in optical and thermal properties of sodium hydrogen phthalate hemihydrates crystals due to Fe3+ doping*, Journal of Crystal Growth 361 (2012) 44-50. http://dx.doi.org/10.1016/j.jcrysgro.2012.08.044

2] N. Goel, N. Sinha, B. Kumar, *Enhanced optical, NLO, dielectric and thermal properties of novel sodium hydrogen phthalate single crystals doped with zinc*, Optical Materials 35 (2013) 479-486. http://dx.doi.org/10.1016/j.optmat.2012.10.020

3] S. S. Dhavud and J. T. J. Prakash, *Effect of semiorganic additive on the growth and characterization of NLO properties of NaAP single crystals for optoelectronic applications*, Int. J. Adv. Res. 4(8) (2016) 685-695. http://dx.doi.org/10.21474/ijar01/1264

4] L. R. Nirmala , J. T. J. Prakash, *Effect of L-Valine on the growth and characterization of Sodium Acid Phthalate (SAP) single crystal*, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 110 (2013) 425-429. http://dx.doi.org/10.1016/j.saa.2013.03.070

5] S. Nirmala S. Devi, R. A. Kumar & E. K. Girija, *Growth and characterization of amino acids doped sodium acid phthalate single crystals,* Materials Research Innovations, 20 (2016) 293-299. https://doi.org/10.1080/14328917.2015.1133020

6] M. Iyanar, J. T. J. Prakash, S. Ekadevasena, S. S. Dhavud, J. M. S. Gnanaraj, *Investigations on the structural, optical, mechanical and microstructural properties of l–arginine doped sap crystals – a potential material for nlo applications*, International Journal of Advanced Scientific Research & Development (IJASRD), 02 (2015) 149-158. http://www.ijasrd.org/in

Table A2: List of reported dopants used to incorporate in KHpht.

S. No.	Dopant	References
	Metal ions	
1	Li^{+}	1
2	Na^{+}	2, 1
3	Rb^{+}	1
4	Mg^{2+}	3, 4, 5, 6
5	Ca^{2+}	6
6	Sr^{2+}	7
7	Ba^{2+}	8, 6
8	Co^{2+}	9
9	Ni^{2+}	10
10	Cu^{2+}	11, 12, 5
11	Zn^{2+}	11, 13
12	Pd^{2+}	5, 14
13	Cd^{2+}	15
14	Hg^{2+}	3, 16
15	Cr^{3+}	17, 18
16	Fe^{3+}	19, 17, 20, 18
17	Al^{3+}	17
18	Ce^{2+}	21
19	Sm^{+}	22
20	Os^{6+}	23
21	Li^{1+}-Mg^{2+}	24
22	Co^{2+}-Mg^{2+}	24, 25
23	Ni^{2+}-Mg^{2+}	24
24	NaCl	26
25	$CaCl_2$	27
26	$HgCl_2$	28
27	$PbCl_2$	28
28	Potassium dihydrogen phosphate	29
29	Boric acid	30
	Amino acids	
30	Glycine	31, 32
31	L-Lysine	33
32	L-Alanine	34
33	DL-Alanine	35
34	L-Histidine	36, 37, 38
35	L-Glutamic acid	39
36	L-Asparagine	39
37	L-Serine	39
38	L-Aspartic acid	36, 40, 41
39	L-Arginine phosphate	29
40	L-Methionine	35
41	L-Citrulline	40, 41
	Organic compounds	
42	Trytophan	42
43	Anthracene	43
44	Ethylenediamine tetra acetic acid	44
45	Polyvinyl pyrrolidone	45
46	Urea	29
	Dyes	
47	Coumarin 6	46
48	Rhodamine 6G	45
49	Amaranth	47
50	Crystal violet	48, 49

References:

1] S. K. Geetha, R. Perumal, S. M. Babu, P. M. Anbarasan, *Habit modification and improvement in properties of potassium hydrogen phthalate (KAP) crystals doped with metal ions* Cryst. Res. Technol. 41, 221-224 (2006). http://dx.doi.org/10.1002/crat.200510563

2] G. Ramasamy , S. Parthiban, S. P. Meenakshisundaram, S. C. Mojumdar, *Influence of alkali metal sodium doping on the properties of potassium hydrogen phthalate (KHP) crystals* J Therm Anal Calorim (2010) 100:861-865. http://dx.doi.org/10.1007/s10973-010-0678-z

3] G. Bhagavannarayana, S. Parthiban, C. Chandrasekaran, S. Meenakshisundaram, *Effect of alkaline earth and transition metals doping on the properties and crystalline perfection of potassium hydrogen phthalate (KHP) crystals* CrystEngComm, 2009, 11, 1635-1641. http://dx.doi.org/10.1039/b904220b

4] V. Niraimathia, V. Aroulmojib, G. Rajarajanb, *Effect of Mg2+dopant on structural, optical and mechanical propertiesof potassium acid phthalate (KAP) single crystals*, Optik 126 (2015) 1567-1571. http://dx.doi.org/10.1016/j.ijleo.2015.04.054

5] D. V. Niraimathi, C. Shanthi, *A comparative study on the effect of Cu, Pd, Mg dopant during the growth of KAP single crystals*, J. Chem. Pharm. Res., 2016, 8(3):926-929. www.jocpr.com ISSN : 0975-7384

6] P. Kanchana C. Sekar, *Effect of divalent metal ion impurities (Ba , Ca and Mg) on the growth, structural and physical properties of KAP crystals,* Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 103 (2013) 187-192. https://doi.org/10.1016/j.saa.2012.10.051

7] A. C. Sajikumar, S. Vinu, C. Krishnan, *Effects of strontium metal ion doping on the thermal, optical and electrical properties of potassium hydrogen phthalate single crystals,* J Therm Anal Calorim (2015) 119: 1047-1052. https://doi.org/10.1007/s10973-014-4237-x

8] A. C. Sajikumar, S. Vinu, C. Krishnan, *Growth and Characterization of Barium doped Potassium Hydrogen Phthalate Single Crystal* Int. Journal of Engineering Research and Applications 5 (2) 2015 50-52. www.ijera.com ISSN : 2248-9622

9] P. Rajasekar · K. Thamizharasan, *Effect of cobalt (Co2+) concentration on structural, optical, thermal and mechanical properties of potassium acid phthalate (KAP) crystals*, Journal of Materials Science Materials in Electronics, 29 (2018) 1777-1784. https://doi.org/10.1007/s10854-017-8086-9

10] J. T. J. Prakash, J. M. S. Gnanaraj, S. Ekadevasena, *Synthesis, Growth and Characterization of Ni2+ incorporated Potassium Acid Phthalate crystal: A Potential material for NLO applications* Optik 126 (2015) 1821-1825. http://dx.doi.org/10.1016/j.ijleo.2015.05.020

11] V. Chithambaram , S. J. Das, R. A. Nambi, K. Srinivasan, S. Krishnan, *Effect of metallic dopants on potassium acid phthalate (KAP) single crystals* Physica B 405 (2010) 2605-2609. https://doi.org/10.1016/j.physb.2010.03.004

12] D. V. Niraimathi, C. Shanthi, *Influence of Copper Doping on the Structural, Optical and Dielectric Properties of Potassium Acid Phthalate (KAP) Single Crystals* J Chem Crystallogr (2015) 45:376-382. https://doi.org/10.1007/s10870-015-0604-0

13] S. Parthiban , S. Murali, G. Madhurambal, S. P. Meenakshisundaram, S. C. Mojumdar, *Effect of zinc(II) doping on thermal and optical properties of potassium hydrogen phthalate (KHP) crystals* J Therm Anal Calorim (2010) 100:751-756. https://doi.org/10.1007/s10973-010-0677-0

14] V. Niraimathi, V. Aroulmoji, G. Rajarajan, *Effect of Pd 2+ Doped on the Growth, Optical, Mechanical and Dielectric Properties of KAP Single Crystal*, American Journal of Materials Science and Engineering, 2 (2014) 36-41. https://doi.org/10.12691/ajmse-2-3-2

15] P. Punitha, S. Senthilkumar, S. Parthiban, *Influence of Cd(II) doping on the properties of potassium hydrogen phthalate(KHP) crystals* International Journal of ChemTech Research, 7 (2015) 3171-3180 CODEN (USA): IJCRGG ISSN: 0974-4290

16] P. Girija, S. Kumaravel, C. Vidya and P. M. Anbarasan, *Synthesis and Characteristic Studies of Mercury Doped Potassium Hydrogen Phthalate for Optoelectronic Applications,* Int. J. Adv. Sci. Eng. 3 (2017) 373-378. https://doi.org/10.13140/RG.2.2.34319.28321

17] P. Kanchana, A. Elakkina Kumaran, C. Sekar, *Effect of trivalent metal ion impurities (Al3+, Cr3+ and Fe3+) on the growth structural and physical properties of potassium acid phthalate (KAP) crystals* Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 112 (2013) 21-26

18] N. Kejalakshmy, K. Srinivasan, *Growth, optical and electro-optical characterisations of potassium hydrogen phthalate crystals doped with Fe3+ and Cr3+ ions* Optical Materials 27 (2004) 389-394. https://doi.org/10.1016/j.optmat.2004.09.005

19] N. Sivakumar, N. K. Geetha, J. Venkatamuthukumar**,** V. Jayakumar, *Mechanical Studies on Pure and Fe3+ Doped Potassium Hydrogen Phthalate Single Crystals for Device Fabrications* Indian Journal of Science and Technology, 9(36), 2016. https://doi.org/10.17485/ijst/2016/v9i36/100852

20] R. Ashok Kumar, N. Sivakumar, R. Ezhil Vizhi, D. Rajan Babu, *The effectofFe3+ doping inPotassiumHydrogenPhthalatesinglecrystalson structuralandopticalproperties* Physica B 406 (2011) 985–991. https://doi.org/10.1016/j.physb.2010.12.044

21] L. Kasthuri,a G. Bhagavannarayana, S. Parthiban, G. Ramasamy, K. Muthua, Subbiah Meenakshisundaram, *Rare earth cerium doping effects in nonlinear optical materials: potassium hydrogen phthalate (KHP) and tris(thiourea)zinc(II) sulfate (ZTS),* CrystEngComm, 2010, 12, 493–499. https://doi.org/10.1039/b907513e

22] S. Sudhahar, M. K. Kumar, V. Jayaramakrishnan, R. Muralidharan, R. M. Kumar, *Effect of Sm+ Rare Earth Ion on the Structural, Thermal, Mechanical and Optical Properties of Potassium Hydrogen Phthalate Single Crystals,* Journal of Materials Science & Technology, 30 (2014) 13-18.

23] K. Muthu, G. Bhagavannarayana, C. Chandrasekaran, S. Parthiban, S. Meenakshisundaram, S. Mojumdar, *Os(VIII) doping effects on the properties and crystalline perfection of potassium hydrogen phthalate (KHP) crystals,* Journal of Thermal Analysis and Calorimetry,100 (2010) 793–799. https://doi.org/10.1007/s10973-010-0759-z

24] S. A. Begum, J. Podder, *Effects of Co-Doped Bimetallic Impurities on the Growth and Nucleation Kinetics of Potassium Acid Phthalate (KAP),* Journal of Bangladesh Academy of Sciences, 33 (2) 189-197, 2009. https://doi.org/10.3329/jbas.v33i2.4102

25] M. Hossain, S. A. Begum, J. Podder, *Growth, Structural, Thermal and Optical properties of Mg2+-Co2+ doped potassium acid phthalate crystals,* Journal of Bangladesh Academy of Sciences, 37 (2013) 165-172. https://doi.org/10.3329/jbas.v37i2.17557

26] R. K. Raju, S. M. Dharamaprakash, H. S. Jayanna, Effect of NaCl Doping on Growth, Characterization, Optical and Dielectric Properties of Potassium Hydrogen Phthalate (KHP) Crystals *Advances in Materials Physics and Chemistry*, 5, (2015) 399-407.
http://dx.doi.org/10.4236/ampc.2015.510040

27] U. Pisipaty, M. P. Megala, S. Abirami, *Effect of calcium chloride on potassium drogen phthalate* International journal of frontiers in science and technology (2015) 3 75-100.

28] G. Vasudevan, P. AnbuSrinivasan, G. Madhurambal, S. C. Mojumdar, *Thermal analysis, effect of dopants, spectral characterisation and growth aspects of KAP crystals*, Journal of Thermal Analysis and Calorimetry, (2009) 96(1) 99–102.

29] P. Murugakoothan, R. M. Kumar, P. M. Ushasree, R. Jayavel, R. Dhanasekaran, P. Ramasamy, *Habit modification of potassium acid phthalate (KAP) single crystals by impurities* Journal of Crystal Growth 207 (1999) 325-329

30] V. Thendral, P. Suganthi, G. Marudhu, A. Thayumanavan, G. Pasupathi, S. Krishnan, M. Prabhaharan, *Growth, structural, vibrational, optical, mechanical studies of Boric acid doped KAP single crystal,* International Journal of ChemTech Research, 11 (2018) 231-238.
DOI : http://dx.doi.org/10.20902/IJCTR.2018.110326

31] T. Baraniraja, P. Philominathan, *Growth, Thermal, Mechanical and Dielectric Studies of Glycine Doped Potassium Acid Phthalate Single Crystals* Journal of Minerals & Materials Characterization & Engineering, 10 (2011) 805-815

32] N. Sivakumara, R. Mohan Kumarb and G. Anbalagan, *Effect of Glycine doping in Potassium Hydrogen Phthalate (KHP) crystals on structural and optical properties,* Advanced Materials Research, 584 (2012) 116-120. doi:10.4028/www.scientific.net/AMR.584.116

33] S. R. Thilagavathy, P. Rajesh, P. Ramasamy, K. Ambujam, *Growth and characterization of pure and doped KHP NLO single crystals* Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 127 (2014) 248–255. http://dx.doi.org/10.1016/j.saa.2014.01.137

34] F. Akhtar , J. Podder, *Studies on the effect of L-alanine on the structural, optical and thermal properties of potassium acid phthalate crystals* Journal of applied sciences 11 (16): 2974-2983 (2011) ISSN 1812-5654. https://doi.org/10.3923/jas.2011.2974.2983

35] K. Uthayarani, R. Sankar, C. K. Shashidharan Nair, *Growth, spectral and thermal properties of KAP single crystals in the presence of DL-Alanine and L-Methionine amino acid dopants* Cryst. Res. Technol. 43, No. 7, 733 – 739 (2008). https://doi.org/10.1002/crat.200711091

36] C. Amuthambigai1, X. S. Shajan, *Growth, optical and XRD studies on pure and doped potassium hydrogen phthalate single crystals* International Journal of ChemTech Research, 6 (2014) 3256-3258.

37] C. Amuthambigaia, C. Guzman-Afonsob, M. E. Torresb, X. Sahaya Shajan, *Optical, spectral and dielectric studies of l-histidine added potassium hydrogen phthalate crystals*, Optik 127 (2016) 3292–3298. http://dx.doi.org/10.1016/j.ijleo.2015.12.022

38] A. C. Sajikumar, S. Vinu, C. Krishnan, *Studies on Structural, Optical and Thermal Properties of L-Histidine Doped Potassium Hydrogen Phthalate Single Crystal* International Journal of Engineering Research & Technology (IJERT) 4 (2015) 525-527.

39] S. S. Dhavud and J. T. J. Prakash, *Influence of amino acid dopants on the growth and properties of potassium hydrogen phthalate single crystals for nonlinear optical applications* Int. J. Adv. Res. 5(2), 886-897. http://dx.doi.org/10.21474/ijar01/3230

40] C. Amuthambigai, C. K. Mahadevan, X. S. Shajan, *Optical studies of potassium acid phthalate single crystals added with amino acids*, *Optik* 127(15) 2016, 5935-5941.
https://doi.org/10.1016/j.ijleo.2016.04.047

41] C. Amuthambigai, C. K. mahadevan, X. S. Shajan, *X-Ray, Thermal and Mechanical Studies of Potassium Acid Phthalate Single Crystals Added with Aspartic Acid/L-Citrulline,* Chem Sci Trans., 2015, 4(4) 1095. https://doi.org/10.7598/cst2015.1119

42] J. Bhuvana, G. Madhurambal, *Effect of trytophan as dopant on potassium acid phthalate single crystals,* Chemistry International, 1 (2015) 87-91

43] S. Meenakshisundaram, S. Parthiban, U. R. Pisipaty, G. Madhurambal, S. C. Mojumdar, *Effect of anthracene doping on potassium hydrogen phthalate crystals* J Therm Anal Calorim (2010) 100:821–826. https://doi.org/10.1007/s10973-010-0738-4

44] K. Srinivasan, K. Meera, P. Ramasamy, *Enhancement of metastable zone width for solution growth of potassium acid phthalate* Journal of Crystal Growth 205 (1999) 457-459.

45] M. Enculescu, *Morphologicalandopticalpropertiesofdopedpotassiumhydrogen phthalate crystals*, Physica B 405 (2010) 3722–3727. https://doi.org/10.1016/j.physb.2010.05.074

46] M. Enculescu, *Growth and optical characteristics of coumarin 6 doped potassium hydrogen phthalate (KAP) crystals*, Optical Materials 32 (2009) 281–285. https://doi.org/10.1016/j.optmat.2009.08.002

47] G. B. Rao, P. Rajesh , P. Ramasamy, *Enhanced optical, thermal and piezoelectric behavior in dye doped potassium acid phthalate (KAP) single crystal*, Journal of Crystal Growth, 468 (2017) 411-415. https://doi.org/10.1016/j.jcrysgro.2016.11.083

48] G. B. Rao, P. Rajesh, P. Ramasamy, *A study on the growth, optical, thermal, mechanical, dielectric and piezoelectric properties of dye doped KAP single crystals Materials Research Bulletin*, 60 (2014) 709-713. https://doi.org/10.1016/j.materresbull.2014.09.063

49] G. B. Rao, P. Rajesh, P. Ramasamy, *Investigations on the growth, optical, thermal, dielectric, and laser damage threshold properties of crystal violet dye-doped potassium acid phthalate single crystal*, Applied Physics A 122 (2016) 175. https://doi.org/10.1007/s00339-016-9693-7

Structure protocol for $(\mathrm{pipH_2})[\mathrm{Zn(pt)_2}]\cdot\mathrm{H_2O}$ **1**

Crystal data and structure refinement for $(\mathrm{pipH_2})[\mathrm{Zn(pt)_2}]\cdot\mathrm{H_2O}$ **1**

Identification code	skd1189m
Empirical formula	$C_{20}H_{22}N_2O_9Zn$
Formula weight (g mol^{-1})	499.77
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*P2$_1$/c*
Unit cell dimensions	
a (Å)	8.142(3)
b (Å)	21.537(8)
c (Å)	11.782(5)
α (°)	90.00
β (°)	99.441(7)
γ (°)	90.00
Volume (Å^3)	2038.1(14)
Z	4
D_{calc} (mg/m^3)	1.629
Absorption coefficient (mm^{-1})	1.263
F(000)	1032
Crystal size (mm^3)	0.16 x 0.14 x 0.12
θ range for data collect. (°)	1.89 to 26.50
Index ranges	$-10 \le h \le 10$
	$-26 \le k \le 26$
	$-14 \le l \le 14$
Reflections collected / unique	20445 / 4201 [R(int) = 0.0698]
Completeness to θ = 26.50°	99.5 %
Absorption correction	Multi scan
Max. and min. transmission	0.859 and 0.817
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4201 / 3 / 286
Goodness-of-fit on F^2	0.981
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.1038
R indices (all data)	R1 = 0.0627, wR2 = 0.1107
Largest diff. peak and hole (e Å^{-3})	0.616 and -0.481

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(\mathrm{pipH_2})[\mathrm{Zn(pt)_2}]\cdot\mathrm{H_2O}$ **1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Zn	4367(1)	3943(1)	8438(1)	29(1)
O2	6808(3)	3968(1)	10937(2)	43(1)
O11	2634(2)	3451(1)	7506(2)	42(1)
O13	6362(2)	3497(1)	8077(2)	37(1)
O3	4534(2)	4848(1)	8256(2)	31(1)
N1	9001(3)	4456(1)	-231(2)	36(1)
O1	4187(3)	3832(1)	10069(2)	41(1)
O4	3483(3)	4783(1)	6404(2)	42(1)
C7	5311(4)	3900(1)	10945(3)	31(1)
C1	4745(4)	3845(1)	12089(2)	29(1)
C8	4249(3)	5069(1)	7239(2)	29(1)
C2	5063(3)	4295(1)	12945(2)	29(1)
C3	4608(4)	4177(2)	14008(3)	35(1)
C4	3849(4)	3626(2)	14234(3)	44(1)
C21	8266(4)	5085(2)	-419(3)	42(1)
C5	3546(4)	3183(2)	13389(3)	49(1)
C6	3988(4)	3291(2)	12319(3)	44(1)
C22	10476(4)	4455(2)	689(3)	45(1)

O14	7391(3)	4264(1)	7162(2)	47(1)
O12	692(3)	3903(1)	8284(3)	76(1)
C18	7273(3)	3702(2)	7388(2)	28(1)
N2	1376(3)	5245(1)	4558(2)	40(1)
C17	1122(4)	3540(2)	7593(2)	31(1)
C12	8143(4)	3231(1)	6758(2)	27(1)
C32	-421(4)	5282(2)	6021(3)	39(1)
C31	326(4)	5654(2)	5154(3)	42(1)
C11	9870(3)	3177(1)	6785(2)	25(1)
C13	7082(4)	2861(2)	5989(3)	41(1)
C16	10444(4)	2768(1)	6026(3)	36(1)
C15	9358(5)	2419(2)	5249(3)	48(1)
C14	7661(4)	2472(1)	5223(2)	51(1)
OW	845(4)	6537(1)	7279(2)	132(2)

Bond lengths [A] and angles [deg] for (pipH$_2$)[Zn(pt)$_2$]·H$_2$O **1**

Zn-O11	1.9532	C21-C22#2	1.4965
Zn-O1	1.9652	C5-C6	1.3865
Zn-O3	1.9682	C22-C21#2	1.4965
Zn-O13	1.9922	O14-C18	1.2464
O2-C7	1.2294	O12-C17	1.2224
O11-C17	1.2664	C18-C12	1.5014
O13-C18	1.2654	N2-C32#3	1.4784
O3-C8	1.2753	N2-C31	1.4824
N1-C22	1.4814	C17-C11#4	1.4974
N1-C21	1.4834	C12-C13	1.3954
O1-C7	1.2714	C12-C11	1.4064
O4-C8	1.2403	C32-N2#3	1.4784
C7-C1	1.4994	C32-C31	1.5044
C1-C6	1.3884	C11-C16	1.3904
C1-C2	1.3934	C11-C17#5	1.4974
C8-C2#1	1.5084	C13-C14	1.3714
C2-C3	1.3874	C16-C15	1.3854
C2-C8#1	1.5084	C15-C14	1.3824
C3-C4	1.3835	OW-H1W	0.9108
C4-C5	1.3725	OW-H2W	0.8502
O11-Zn-O1	108.701	N1-C21-C22#2	111.33
O11-Zn-O3	122.229	C4-C5-C6	120.03
O1-Zn-O3	104.179	C5-C6-C1	120.83
O11-Zn-O13	99.071	N1-C22-C21#2	110.13
O1-Zn-O13	110.139	O14-C18-O13	123.33
O3-Zn-O13	112.389	O14-C18-C12	119.43
C17-O11-Zn	119.62	O13-C18-C12	117.23
C18-O13-Zn	123.62	C32#3-N2-C31	112.03
C8-O3-Zn	117.8618	O12-C17-O11	122.63
C22-N1-C21	111.72	O12-C17-C11#4	121.33
C7-O1-Zn	128.42	O11-C17-C11#4	116.13
O2-C7-O1	126.23	C13-C12-C11	118.53
O2-C7-C1	117.93	C13-C12-C18	114.53
O1-C7-C1	115.73	C11-C12-C18	126.63
C6-C1-C2	119.53	N2#3-C32-C31	109.73
C6-C1-C7	117.23	N2-C31-C32	109.53
C2-C1-C7	123.23	C16-C11-C12	118.73
O4-C8-O3	123.43	C16-C11-C17#5	118.33
O4-C8-C2#1	119.23	C12-C11-C17#5	123.03
O3-C8-C2#1	117.42	C14-C13-C12	122.23
C3-C2-C1	118.73	C15-C16-C11	121.53
C3-C2-C8#1	117.23	C14-C15-C16	119.93
C1-C2-C8#1	123.93	C13-C14-C15	119.13

C4-C3-C2	121.73	H1W-OW-H2W	98.4
C5-C4-C3	119.33		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+2 #2 -x+2,-y+1,-z #3 -x,-y+1,-z+1 #4 x-1,y,z #5 x+1,y,z

Anisotropic displacement parameters (A^2 x 10^3) for (pipH$_2$)[Zn(pt)$_2$]·H$_2$O **1**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Zn	26(1)	36(1)	25(1)	-1(1)	6(1)	-1(1)
O2	35(1)	58(2)	40(1)	-2(1)	16(1)	-3(1)
O11	27(1)	49(2)	48(1)	-13(1)	5(1)	-2(1)
O13	33(1)	45(1)	38(1)	13(1)	19(1)	7(1)
O3	37(1)	35(1)	21(1)	1(1)	4(1)	-2(1)
N1	30(1)	48(2)	33(1)	-14(1)	12(1)	-9(1)
O1	41(1)	57(2)	24(1)	0(1)	7(1)	-4(1)
O4	48(1)	48(2)	28(1)	-4(1)	-5(1)	-9(1)
C7	38(2)	28(2)	27(2)	-1(1)	8(1)	-1(1)
C1	30(2)	33(2)	24(2)	2(1)	5(1)	0(1)
C8	22(1)	38(2)	26(2)	-2(1)	7(1)	5(1)
C2	23(1)	39(2)	26(2)	5(1)	6(1)	4(1)
C3	34(2)	46(2)	27(2)	0(2)	9(1)	4(2)
C4	44(2)	60(2)	32(2)	12(2)	17(2)	1(2)
C21	27(2)	54(2)	45(2)	-13(2)	0(1)	2(2)
C5	55(2)	46(2)	48(2)	10(2)	17(2)	-15(2)
C6	53(2)	42(2)	37(2)	-4(2)	12(2)	-9(2)
C22	46(2)	53(2)	34(2)	1(2)	-1(2)	2(2)
O14	62(2)	36(2)	53(2)	3(1)	41(1)	0(1)
O12	35(1)	117(3)	78(2)	-70(2)	12(1)	-5(2)
C18	21(1)	40(2)	22(1)	-1(1)	3(1)	-1(1)
N2	36(1)	55(2)	31(1)	11(1)	11(1)	-4(1)
C17	30(2)	38(2)	26(2)	-2(1)	8(1)	0(1)
C12	30(2)	28(2)	24(2)	2(1)	7(1)	-1(1)
C32	40(2)	51(2)	27(2)	0(2)	11(1)	2(2)
C31	50(2)	44(2)	35(2)	2(2)	14(2)	-3(2)
C11	29(1)	26(2)	20(1)	0(1)	5(1)	-2(1)
C13	35(2)	45(2)	39(2)	-5(2)	0(1)	-8(2)
C16	39(2)	36(2)	35(2)	-3(2)	10(1)	5(2)
C15	63(2)	40(2)	41(2)	-16(2)	11(2)	5(2)
C14	56(2)	46(2)	46(2)	-16(2)	-5(2)	-10(2)
OW	139(4)	148(4)	97(3)	-21(3)	-20(3)	10(3)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for (pipH$_2$)[Zn(pt)$_2$]·H$_2$O **1**.

	x	y	z	U(eq)
H12A	8231	4194	-40	43
H11B	9299	4319	-890	43
H1	4818	4475	14584	42
H2	3548	3557	14951	53
H10A	7845	5217	267	51
H9B	7337	5072	-1050	51
H3	3044	2810	13533	59
H4	3775	2990	11749	52
H13A	10967	4043	758	54
H14B	10141	4560	1418	54
H15A	1809	5469	4033	48
H16B	2226	5098	5074	48
H19A	455	5127	6611	46
H20B	-1151	5543	6387	46
H17A	-552	5836	4598	51

H18B	997	5989	5539	51
H8	5942	2879	5996	49
H5	11584	2727	6040	44
H6	9770	2150	4746	57
H7	6922	2246	4694	61
H1W	1538	6797	6973	159
H2W	1551	6385	7819	159
H2W	1551	6385	7819	159

Hydrogen bonding geometry [Å and °] for (pipH$_2$)[Zn(pt)$_2$]·H$_2$O **1**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<DHA	Symmetry code
N1-H12A···O2	0.900	1.828	2.645	149.83	x, y, z-1
N1-H11B···O12	0.900	1.843	2.676	152.97	x+1, y, z-1
N1-H11B···O14	0.900	2.554	3.162	125.44	x, y, z-1
N2-H15A···O14	0.900	1.744	2.627	166.44	-x+1, -y+1, -z+1
N2-H16B···O4	0.900	1.854	2.727	162.90	X, y, z
C21-H9B···O3	0.970	2.345	3.142	149.91	x, y, z-1
OW-H2W···O2	0.850	1.967	2.818	179.74	-x+1, -y+1, -z+2

D=Donor and A=Acceptor

Structure protocol for $(pipH_2)[Ni(pt)_2(H_2O)_4]\cdot 8H_2O$ **3**

Crystal data and structure refinement for $(pipH_2)[Ni(pt)_2(H_2O)_4]\cdot 8H_2O$ **3**

Identification code	NiPP
Empirical formula	$C_{20}H_{44}N_2NiO_{20}$
Formula weight (g mol^{-1})	691.28
Temperature (K)	293(2)
Wavelength (Å)	1.54184
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.2600(6)
b (Å)	11.8393(7)
c (Å)	12.4959(7)
α (°)	82.000(5)
β (°)	77.409(5)
γ (°)	75.538(5)
Volume (Å^3)	1567.92(15)
Z	2
D_{calc} (mg/m^3)	1.464
Absorption coefficient (mm^{-1})	1.660
F(000)	732
Crystal size (mm^3)	0.37 x 0.27 x 0.26
θ range for data collection (°)	3.64 to 67.08
Index ranges	$-9 \leq h \leq 13$ $-14 \leq k \leq 14$ $-14 \leq l \leq 14$
Reflections collected / unique	9530/5572 [R(int) = 0.0166]
Completeness to θ = 26.50°	99.8 %
Absorption correction	Multi-scan
Max. and min. Transmission	0.6721 and 0.5787
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5572/ 1 /447
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0993
R indices (all data)	R1 = 0.0366, wR2 = 0.1009
Extinction coefficient	0.0199(6)
Largest diff. peak and hole (e Å^{-3})	0.374 and -0.415

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(pipH_2)[Ni(pt)_2(H_2O)_4]\cdot 8H_2O$ **3**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ni1	7355(1)	7390(1)	5028(1)	20(1)
O1	7322(1)	8278(1)	6324(1)	24(1)
O2	6810(1)	6995(1)	7723(1)	44(1)
O3	5640(1)	11291(1)	6291(1)	47(1)
O4	4761(1)	9762(1)	6713(1)	32(1)
C1	6728(1)	8914(1)	8108(1)	27(1)
C2	6062(1)	10053(1)	7871(1)	28(1)
C3	5938(2)	10902(2)	8574(2)	41(1)
C4	6457(2)	10623(2)	9515(2)	54(1)
C5	7107(2)	9498(2)	9751(2)	55(1)
C6	7249(2)	8644(2)	9050(1)	40(1)
C7	6963(1)	7993(1)	7330(1)	26(1)
C8	5448(1)	10387(1)	6877(1)	28(1)
O5	7422(1)	6471(1)	3736(1)	25(1)
O6	8050(1)	7747(1)	2371(1)	42(1)
O7	9640(1)	3508(1)	3646(1)	50(1)
O8	10228(1)	5198(1)	3300(1)	32(1)

C9	8196(1)	5831(1)	1955(1)	27(1)
C10	9008(2)	4750(1)	2141(1)	28(1)
C11	9225(2)	3903(2)	1414(2)	42(1)
C12	8655(2)	4136(2)	500(2)	54(1)
C13	7853(2)	5198(2)	321(2)	54(1)
C14	7617(2)	6044(2)	1049(1)	41(1)
C15	7875(1)	6757(1)	2743(1)	26(1)
C16	9671(1)	4474(1)	3106(1)	29(1)
O9	9271(1)	7051(1)	4637(1)	27(1)
O10	5423(1)	7817(1)	5426(1)	26(1)
O11	7281(1)	8980(1)	4060(1)	25(1)
O12	7452(1)	5785(1)	6011(1)	27(1)
N1	3731(1)	5647(1)	5048(1)	40(1)
C17	4305(2)	5415(2)	6036(2)	41(1)
C18	5316(2)	4302(2)	5978(2)	42(1)
N2	11293(1)	-55(1)	4938(1)	35(1)
C19	10716(2)	332(2)	3956(2)	37(1)
C20	10372(2)	223(2)	5970(2)	37(1)
O13	7796(1)	2295(1)	3839(1)	43(1)
O14	7664(1)	2292(1)	6193(1)	47(1)
O15	8269(1)	3268(1)	7898(1)	52(1)
O16	10074(2)	-1535(2)	11063(2)	66(1)
O17	10610(2)	-885(2)	8757(2)	74(1)
O18	13141(2)	-1718(2)	7904(1)	54(1)
O19	5299(2)	3537(2)	11027(2)	74(1)
O20	5714(2)	4008(2)	8739(2)	75(1)

Bond lengths[Å] and angles [^{o}]for(pipH$_2$)[Ni(pt)$_2$(H$_2$O)$_4$]·8H$_2$O **3**

Ni1-O1	2.0392(10)	Ni1-O10	2.0699(11)
Ni1-O5	2.0462(10)	Ni1-O11	2.0853(10)
Ni1-O9	2.0526(10)	Ni1-O12	2.1063(10)
O1-C7	1.2599(18)	C9-C14	1.390(2)
O2-C7	1.252(2)	C9-C10	1.398(2)
O3-C8	1.248(2)	C9-C15	1.499(2)
O4-C8	1.2585(19)	C10-C11	1.387(2)
C1-C6	1.391(2)	C10-C16	1.509(2)
C1-C2	1.397(2)	C11-C12	1.392(3)
C1-C7	1.497(2)	C12-C13	1.374(3)
C2-C3	1.387(2)	C13-C14	1.385(3)
C2-C8	1.509(2)	N1-C17	1.477(3)
C3-C4	1.388(3)	N1-C18#1	1.486(2)
C4-C5	1.376(3)	C17-C18	1.510(3)
C5-C6	1.385(3)	C18-N1#1	1.486(2)
O5-C15	1.2681(18)	N2-C19	1.476(2)
O6-C15	1.246(2)	N2-C20	1.487(2)
O7-C16	1.249(2)	C19-C20#2	1.509(2)
O8-C16	1.256(2)	C20-C19#2	1.509(2)

O1-Ni1-O5	178.74(4)	O9-Ni1-O11	89.23(4)
O1-Ni1-O9	91.63(4)	O10-Ni1-O11	88.53(4)
O5-Ni1-O9	87.41(4)	O1-Ni1-O12	92.48(4)
O1-Ni1-O10	86.50(5)	O5-Ni1-O12	86.71(4)
O5-Ni1-O10	94.49(5)	O9-Ni1-O12	90.17(4)
O9-Ni1-O10	177.15(4)	O10-Ni1-O12	92.05(4)
O1-Ni1-O11	87.14(4)	O11-Ni1-O12	179.28(4)
O5-Ni1-O11	93.67(4)		
C7-O1-Ni1	127.06(10)	C10-C9-C15	121.69(13)
C6-C1-C2	119.54(15)	C11-C10-C9	119.34(15)
C6-C1-C7	119.12(14)	C11-C10-C16	118.61(14)
C2-C1-C7	121.23(13)	C9-C10-C16	122.05(14)

C3-C2-C1	119.49(15)	C10-C11-C12	120.26(17)
C3-C2-C8	118.73(15)	C13-C12-C11	120.28(17)
C1-C2-C8	121.78(14)	C12-C13-C14	119.97(17)
C2-C3-C4	120.51(18)	C13-C14-C9	120.37(17)
C5-C4-C3	119.95(18)	O6-C15-O5	125.20(14)
C4-C5-C6	120.20(17)	O6-C15-C9	117.82(13)
C5-C6-C1	120.31(17)	O5-C15-C9	116.97(13)
O2-C7-O1	124.72(14)	O7-C16-O8	124.68(15)
O2-C7-C1	118.16(13)	O7-C16-C10	116.05(14)
O1-C7-C1	117.10(13)	O8-C16-C10	119.25(14)
O3-C8-O4	124.82(14)	C17-N1-C18#1	111.43(14)
O3-C8-C2	116.69(14)	N1-C17-C18	110.69(15)
O4-C8-C2	118.46(14)	N1#1-C18-C17	110.84(15)
C15-O5-Ni1	124.08(10)	C19-N2-C20	111.59(13)
C14-C9-C10	119.78(15)	N2-C19-C20#2	110.49(14)
C14-C9-C15	118.46(14)	N2-C20-C19#2	109.95(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1, #2 -x+2,-y,-z+1.

Anisotropic displacement parameters (A^2 x 10^3) for (pipH$_2$)[Ni(pt)$_2$(H$_2$O)$_4$]·8H$_2$O **3**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Ni1	19(1)	19(1)	23(1)	-2(1)	-5(1)	-5(1)
O1	26(1)	25(1)	23(1)	-2(1)	-4(1)	-8(1)
O2	63(1)	29(1)	34(1)	0(1)	4(1)	-14(1)
O3	63(1)	40(1)	50(1)	14(1)	-35(1)	-23(1)
O4	27(1)	30(1)	42(1)	-6(1)	-14(1)	-4(1)
C1	26(1)	33(1)	23(1)	-1(1)	-4(1)	-7(1)
C2	26(1)	31(1)	28(1)	-4(1)	-7(1)	-6(1)
C3	49(1)	37(1)	40(1)	-12(1)	-12(1)	-5(1)
C4	72(1)	58(1)	40(1)	-22(1)	-20(1)	-10(1)
C5	68(1)	70(1)	32(1)	-8(1)	-26(1)	-10(1)
C6	44(1)	45(1)	30(1)	0(1)	-15(1)	-1(1)
C7	21(1)	27(1)	28(1)	-1(1)	-5(1)	-3(1)
C8	27(1)	27(1)	31(1)	-5(1)	-10(1)	-2(1)
O5	27(1)	26(1)	25(1)	-4(1)	-5(1)	-8(1)
O6	60(1)	28(1)	34(1)	-2(1)	2(1)	-12(1)
O7	70(1)	38(1)	57(1)	14(1)	-43(1)	-23(1)
O8	28(1)	30(1)	41(1)	-8(1)	-12(1)	-5(1)
C9	28(1)	29(1)	25(1)	-2(1)	-5(1)	-7(1)
C10	29(1)	29(1)	28(1)	-4(1)	-7(1)	-6(1)
C11	51(1)	33(1)	41(1)	-11(1)	-13(1)	-1(1)
C12	81(2)	49(1)	38(1)	-20(1)	-21(1)	-8(1)
C13	76(2)	55(1)	37(1)	-8(1)	-31(1)	-9(1)
C14	50(1)	41(1)	33(1)	-1(1)	-19(1)	-3(1)
C15	23(1)	26(1)	26(1)	-2(1)	-7(1)	-3(1)
C16	27(1)	28(1)	33(1)	-6(1)	-10(1)	-2(1)
O9	22(1)	28(1)	31(1)	-4(1)	-8(1)	-4(1)
O10	22(1)	28(1)	30(1)	-3(1)	-7(1)	-6(1)
O11	23(1)	22(1)	30(1)	-1(1)	-9(1)	-4(1)
O12	28(1)	23(1)	31(1)	1(1)	-8(1)	-6(1)
N1	26(1)	24(1)	70(1)	-7(1)	-8(1)	-4(1)
C17	40(1)	30(1)	51(1)	-9(1)	2(1)	-13(1)
C18	42(1)	31(1)	54(1)	-1(1)	-14(1)	-9(1)
N2	22(1)	26(1)	58(1)	-2(1)	-8(1)	-9(1)
C19	30(1)	32(1)	50(1)	1(1)	-4(1)	-12(1)
C20	33(1)	34(1)	49(1)	-4(1)	-10(1)	-13(1)
O13	42(1)	44(1)	43(1)	-6(1)	-10(1)	-8(1)
O14	44(1)	51(1)	48(1)	-10(1)	-9(1)	-10(1)
O15	52(1)	54(1)	50(1)	3(1)	-11(1)	-19(1)

O16	58(1)	56(1)	67(1)	11(1)	10(1)	-9(1)
O17	76(1)	68(1)	68(1)	-14(1)	6(1)	-7(1)
O18	52(1)	58(1)	53(1)	2(1)	-9(1)	-19(1)
O19	58(1)	72(1)	74(1)	19(1)	7(1)	-15(1)
O20	65(1)	75(1)	77(1)	-19(1)	2(1)	-10(1)

Hydrogen bonding geometry [Å and °] for (pipH$_2$)[Ni(pt)$_2$(H$_2$O)$_4$]·8H$_2$O **3**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<DHA	Symmetry code
O9-H9A···O8	0.858	1.939	2.797	177.21	x, y, z
O9-H9B···O7	0.811	1.817	2.626	175.28	-x+2, -y+1, -z+1
O10-H10A···O4	0.832	2.015	2.845	175.83	x, y, z
O10-H10B···O3	0.744	1.904	2.647	178.74	-x+1, -y+2, -z+1
O11-H11A···O4	0.860	1.914	2.701	151.47	-x+1, -y+2, -z+1
O11-H11B···O6	0.830	1.799	2.602	162.32	x, y, z
O12-H12A···O2	0.861	1.855	2.610	145.47	x, y, z
O12-H12B···O8	0.871	2.028	2.847	156.32	-x+2, -y+1, -z+1
N1-H1A···O13	0.920	2.158	2.939	142.14	-x+1, -y+1, -z+1
N1-H1A···O14	0.920	2.271	2.987	134.30	-x+1, -y+1, -z+1
N1-H1B···O12	0.920	2.189	2.987	144.63	-x+1, -y+1, -z+1
N1-H1B···O5	0.920	2.409	3.161	138.87	-x+1, -y+1, -z+1
N2-H2A···O11	0.920	2.096	2.847	138.08	-x+2, -y+1, -z+1
N2-H2A···O1	0.920	2.287	2.998	133.77	-x+2, -y+1, -z+1
N2-H2B···O13	0.920	2.183	2.936	138.41	-x+2, -y, -z+1
N2-H2B···O14	0.920	2.264	3.025	139.71	-x+2, -y, -z+1
O13-H13A···O7	0.739	2.054	2.758	159.19	x, y, z
O13-H13B···O18	0.838	2.011	2.846	174.68	-x+2, -y, -z+1
O14-H14A···O15	0.926	1.921	2.837	169.61	x, y, z
O14-H14B···O3	0.787	2.059	2.793	155.16	x, y-1, z
O15-H15A···O16	0.870	1.924	2.789	172.26	-x+2, -y, -z+2
O15-H15B···O8	0.870	1.980	2.843	170.64	-x+2, -y+1, -z+1
O16-H16A···O17	0.491	2.362	2.849	172.60	x, y, z
O16-H16B···O6	0.897	1.861	2.746	169.06	x, y-1, z+1
O17-H17C···O16	0.584	2.351	2.849	144.93	-x+2, - y, -z+2
O17-H17D···O18	0.974	1.840	2.792	164.99	x, y, z
O18-H18C···O19	0.839	1.965	2.801	174.20	-x+2, -y, -z+2
O18-H18D···O4	0.800	2.096	2.880	166.58	x+1, y-1, z
O19-H19C···O20	0.753	2.057	2.793	165.78	x, y, z
O19-H19D···O2	0.834	1.882	2.709	170.67	-x+1, -y+1, -z+2
O20-H20C···O19	0.538	2.345	2.876	169.33	-x+1, -y+1, -z+2
O20-H20D···O15	0.872	1.934	2.799	171.60	x, y, z
C17-H17B···O10	0.990	2.395	3.320	155.10	x, y, z
C18-H18B···O5	0.990	2.636	3.363	130.35	-x+1, -y+1, -z+1
C18-H18B···O3	0.990	2.675	3.467	137.16	x, y-1, z
C18-H18B···O20	0.990	2.620	3.535	153.63	x, y, z
C19-H19B···O7	0.990	2.655	3.644	177.49	x, y, z
C20-H20B···O17	0.990	2.700	3.590	149.76	x, y, z
C20-H20A···O9	0.990	2.475	3.315	142.37	-x+2, -y+1, -z+1
C20-H20A···O14	0.990	2.703	3.385	126.39	x, y, z

D=Donor and A=Acceptor

Structure protocol for $(pipH_2)[Co(pt)_2(H_2O)_4]\cdot 8H_2O$ **4**

Crystal data and structure refinement for $(pipH_2)[Co(pt)_2(H_2O)_4]\cdot 8H_2O$ **4**

Identification code	CoPP
Empirical formula	$C_{20}H_{44}CoN_2O_{20}$
Formula weight (g mol^{-1})	691.5
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.8572(3)
b (Å)	12.4961(3)
c (Å)	27.2165(6)
α (°)	79.0500(10)
β (°)	88.6480(10)
γ (°)	82.0290(10)
Volume (Å^3)	3920.95(16)
Z	5
D_{calc} (mg/m^3)	1.464
Absorption coefficient (mm^{-1})	0.632
F(000)	1825
Crystal size (mm^3)	0.30 x 0.25 x 0.20
θ range for data collection (°)	1.70 to 25.00
Index ranges	$-14 \leq h \leq 14$ $-14 \leq k \leq 14$ $-32 \leq l \leq 32$
Reflections collected / unique	97359 / 13783 [R(int) = 0.0371]
Completeness to θ = 25.00°	99.9%
Absorption correction	Multi-scan
Max. and min. Transmission	0.8840 and 0.8330
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13783 / 99 / 1151
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0311, wR2 = 0.0850
R indices (all data)	R1 = 0.0515, wR2 = 0.1001
Extinction coefficient	0.00327(17)
Largest diff. peak and hole (e Å^{-3})	0.406 and -0.442

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(pipH_2)[Co(pt)_2(H_2O)_4]\cdot 8H_2O$ **4**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Co1	2112(1)	4972(1)	9057(1)	20(1)
Co2	5779(1)	5011(1)	6938(1)	21(1)
Co3	10000	5000	5000	21(1)
O1	1221(1)	3654(1)	9072(1)	25(1)
O2	2611(1)	2254(1)	9272(1)	43(1)
O3	297(1)	3261(1)	10099(1)	31(1)
O4	-1405(1)	3703(1)	9737(1)	46(1)
O5	1625(1)	7649(1)	8779(1)	42(1)
O6	3031(1)	6283(1)	9027(1)	26(1)
O7	3686(1)	6717(1)	7903(1)	32(1)
O8	5495(1)	6350(1)	8145(1)	50(1)
C1	1584(2)	2645(2)	9214(1)	26(1)
C2	716(2)	1869(2)	9309(1)	27(1)
C3	861(2)	927(2)	9100(1)	41(1)
C4	37(2)	236(2)	9157(1)	55(1)
C5	-942(2)	476(2)	9418(1)	55(1)
C6	-1102(2)	1410(2)	9623(1)	42(1)

C7	-279(2)	2115(2)	9575(1)	28(1)
C8	-471(2)	3102(2)	9819(1)	28(1)
C9	2652(2)	7275(2)	8847(1)	26(1)
C10	3507(2)	8059(2)	8718(1)	26(1)
C11	4406(2)	7868(2)	8392(1)	28(1)
C12	5204(2)	8596(2)	8304(1)	42(1)
C13	5108(2)	9501(2)	8532(1)	54(1)
C14	4219(2)	9686(2)	8853(1)	53(1)
C15	3424(2)	8969(2)	8947(1)	40(1)
C16	4531(2)	6905(2)	8130(1)	29(1)
O9	525(1)	5976(1)	9087(1)	26(1)
O10	2072(1)	4570(1)	9845(1)	26(1)
O11	2047(1)	5368(1)	8278(1)	27(1)
O12	3714(1)	3952(1)	9020(1)	28(1)
O13	2397(1)	3656(1)	7842(1)	53(1)
O14	4198(1)	3280(1)	8094(1)	32(1)
O15	6266(1)	2330(1)	7202(1)	42(1)
O16	4854(1)	3704(1)	6975(1)	26(1)
O21	6691(1)	6322(1)	6911(1)	24(1)
O22	5298(1)	7722(1)	6729(1)	43(1)
O23	7613(1)	6704(1)	5867(1)	31(1)
O24	9303(1)	6268(1)	6239(1)	47(1)
C17	5237(2)	2708(2)	7146(1)	25(1)
C18	4382(2)	1920(2)	7280(1)	27(1)
C19	4461(2)	1008(2)	7056(1)	41(1)
C20	3671(2)	287(2)	7155(1)	54(1)
C21	2783(2)	484(2)	7475(1)	54(1)
C22	2684(2)	1395(2)	7697(1)	42(1)
C23	3481(2)	2123(2)	7606(1)	28(1)
C24	3358(2)	3090(2)	7864(1)	29(1)
C25	6328(2)	7331(2)	6774(1)	26(1)
C26	7195(2)	8107(2)	6667(1)	26(1)
C27	7057(2)	9052(2)	6870(1)	42(1)
C28	7868(2)	9754(2)	6803(1)	55(1)
C29	8836(2)	9512(2)	6533(1)	55(1)
C30	8990(2)	8576(2)	6329(1)	42(1)
C31	8174(2)	7866(2)	6390(1)	27(1)
C32	8373(2)	6867(2)	6150(1)	28(1)
O17	5841(1)	4625(1)	7717(1)	27(1)
O18	5807(1)	5416(1)	6156(1)	27(1)
O19	7369(1)	3997(1)	6903(1)	25(1)
O20	4180(1)	6038(1)	6980(1)	28(1)
O27	10921(1)	6301(1)	5012(1)	26(1)
O28	9551(1)	7689(1)	4754(1)	43(1)
O29	13544(1)	6338(1)	4236(1)	53(1)
O30	11783(1)	6728(1)	3936(1)	31(1)
C33	10570(2)	7304(2)	4840(1)	26(1)
C34	11440(2)	8079(2)	4742(1)	27(1)
C35	11306(2)	9005(2)	4961(1)	39(1)
C36	12114(2)	9715(2)	4896(1)	50(1)
C37	13067(2)	9502(2)	4616(1)	50(1)
C38	13220(2)	8582(2)	4400(1)	39(1)
C39	12407(2)	7866(2)	4456(1)	27(1)
C40	12585(2)	6901(2)	4194(1)	29(1)
O25	8392(1)	6027(1)	4986(1)	28(1)
O26	9907(1)	4603(1)	5780(1)	27(1)
N1	17561(1)	5020(2)	3467(1)	40(1)
N2	16784(1)	4963(2)	4472(1)	40(1)
C41	17466(2)	6015(2)	3693(1)	41(1)
C42	16557(2)	5980(2)	4090(1)	42(1)
C43	16886(2)	3968(2)	4247(1)	41(1)

C44	17796(2)	4004(2)	3851(1)	42(1)
N3	-1292(1)	5048(2)	7487(1)	34(1)
N4	-863(1)	4936(2)	8522(1)	35(1)
C45	-779(2)	5958(2)	8155(1)	38(1)
C46	-1559(2)	6036(2)	7717(1)	37(1)
C47	-1380(2)	4026(2)	7853(1)	38(1)
C48	-596(2)	3948(2)	8291(1)	38(1)
N5	5388(1)	5047(2)	9495(1)	40(1)
C49	4734(2)	3965(2)	10274(1)	40(1)
C50	5640(2)	4026(2)	9876(1)	42(1)
O31	8186(1)	12099(2)	2704(1)	50(1)
O32	9992(2)	7900(2)	3269(1)	53(1)
O33	10313(2)	8773(2)	2262(1)	73(1)
O34	7944(2)	11234(2)	3722(1)	71(1)
O35	8544(2)	8950(2)	3909(1)	70(1)
O36	5845(1)	7966(2)	5269(1)	50(1)
O37	3731(2)	11263(2)	5736(1)	70(1)
O38	4304(2)	8996(2)	5895(1)	72(1)
O39	10670(1)	6204(1)	7071(1)	45(1)
O40	7098(1)	6160(1)	8883(1)	41(1)
O41	6063(1)	2084(2)	8688(1)	50(1)
O42	728(1)	3827(1)	7138(1)	43(1)
O43	459(2)	8946(2)	7968(1)	62(1)
O44	-1819(2)	8753(2)	8241(1)	71(1)
O45	3618(2)	1044(2)	10114(1)	72(1)
O46	4151(2)	-1251(2)	10291(1)	73(1)
O47	2131(1)	2085(2)	10746(1)	51(1)
O48	-2862(1)	3801(1)	8936(1)	45(1)
O49	7416(2)	1034(2)	8016(1)	62(1)
O50	15043(1)	6151(1)	4994(1)	42(1)

Bond lengths [Å] and angles [°] for (pipH$_2$)[Co(pt)$_2$(H$_2$O)$_4$]·8H$_2$O **4**

Co1-O1	2.0697(13)	Co2-O18	2.0907(12)
Co1-O6	2.0775(13)	Co2-O19	2.1315(13)
Co1-O11	2.0852(13)	Co2-O20	2.1509(13)
Co1-O10	2.1074(13)	Co3-O27^{i}	2.0862(12)
Co1-O9	2.1214(13)	Co3-O27	2.0862(12)
Co1-O12	2.1469(13)	Co3-O26	2.0895(12)
Co2-O21	2.0733(13)	Co3-O26^{i}	2.0895(12)
Co2-O16	2.0759(13)	Co3-O25^{i}	2.1423(13)
Co2-O17	2.0839(12)	Co3-O25	2.1423(13)
O1-C1	1.263(2)	C25-C26	1.495(3)
O2-C1	1.249(2)	C26-C27	1.384(3)
O3-C8	1.261(2)	C26-C31	1.399(2)
O4-C8	1.249(2)	C27-C28	1.376(3)
O5-C9	1.247(2)	C28-C29	1.376(3)
O6-C9	1.267(2)	C29-C30	1.376(3)
O7-C16	1.261(2)	C30-C31	1.387(3)
C3-C4	1.379(3)	C31-C32	1.503(3)
C4-C5	1.374(3)	O27-C33	1.267(2)
C5-C6	1.375(3)	O28-C33	1.246(2)
C6-C7	1.391(3)	O29-C40	1.247(2)
C7-C8	1.496(3)	O30-C40	1.259(2)
C9-C10	1.496(3)	C33-C34	1.497(3)
C10-C15	1.38\9(3)	C34-C35	1.388(3)
C10-C11	1.395(2)	C34-C39	1.395(2)
C11-C12	1.388(3)	C35-C36	1.381(3)
C11-C16	1.499(3)	C36-C37	1.371(3)
C12-C13	1.379(3)	C37-C38	1.377(3)
C13-C14	1.375(3)	C38-C39	1.390(3)

C14-C15	1.376(3)	C39-C40	1.503(3)
O13-C24	1.251(2)	N1-C41	1.477(3)
O14-C24	1.261(2)	N1-C44	1.481(3)
O15-C17	1.247(2)	N2-C43	1.477(3)
O16-C17	1.267(2)	N2-C42	1.478(3)
O21-C25	1.262(2)	C41-C42	1.507(3)
O22-C25	1.251(2)	C43-C44	1.504(3)
O23-C32	1.262(2)	N3-C47	1.477(3)
O24-C32	1.245(2)	N3-C46	1.480(3)
C17-C18	1.501(3)	N4-C45	1.478(3)
C18-C19	1.383(3)	N4-C48	1.482(3)
C18-C23	1.400(2)	C45-C46	1.507(3)
C19-C20	1.376(3)	C47-C48	1.508(3)
C20-C21	1.376(3)	N5-C49#2	1.477(3)
C21-C22	1.377(3)	N5-C50	1.482(3)
C22-C23	1.387(3)	C49-N5#2	1.477(3)
C23-C24	1.497(3)	C49-C50	1.506(3)

O1-Co1-O6	178.52(4)	O17-Co2-O19	89.94(5)
O1-Co1-O11	92.07(5)	O18-Co2-O19	88.02(5)
O6-Co1-O11	86.87(5)	O21-Co2-O20	92.21(5)
O1-Co1-O10	85.76(5)	O16-Co2-O20	87.26(5)
O6-Co1-O10	95.35(5)	O17-Co2-O20	89.49(5)
O11-Co1-O10	176.58(5)	O18-Co2-O20	92.54(5)
O1-Co1-O9	88.03(5)	O19-Co2-O20	179.37(5)
O6-Co1-O9	92.97(5)	O27^{i}-Co3-O27	180.0
O11-Co1-O9	89.38(5)	O27^{i}-Co3-O26	86.71(5)
O10-Co1-O9	87.91(5)	O27-Co3-O26	93.29(5)
O1-Co1-O12	91.69(5)	O27^{i}-Co3-O26^{i}	93.29(5)
O6-Co1-O12	87.29(5)	O27-Co3-O26^{i}	86.71(5)
O11-Co1-O12	90.14(5)	O26-Co3-O26^{i}	180.000(1)
O10-Co1-O12	92.56(5)	O27^{i}-Co3-O25^{i}	93.07(5)
O9-Co1-O12	179.43(5)	O27-Co3-O25^{i}	86.93(5)
O21-Co2-O16	179.05(5)	O26-Co3-O25^{i}	90.39(5)
O21-Co2-O17	92.62(5)	O26^{i}-Co3-O25^{i}	89.61(5)
O16-Co2-O17	86.58(5)	O27^{i}-Co3-O25	86.93(5)
O21-Co2-O18	85.00(5)	O27-Co3-O25	93.07(5)
O16-Co2-O18	95.81(5)	O26-Co3-O25	89.61(5)
O17-Co2-O18	176.93(5)	O26^{i}-Co3-O25	90.39(5)
O21-Co2-O19	87.56(5)	O25^{i}-Co3-O25	180.000(1)
O16-Co2-O19	92.96(5)		

C14-C13-C12	120.0(2)	C2-C7-C8	121.82(17)
C13-C14-C15	120.1(2)	O4-C8-O3	124.35(18)
C14-C15-C10	120.4(2)	O4-C8-C7	116.91(16)
O8-C16-O7	124.20(18)	O3-C8-C7	118.71(17)
O8-C16-C11	116.51(16)	O5-C9-O6	125.11(18)
O7-C16-C11	119.27(17)	O5-C9-C10	117.81(18)
C17-O16-Co2	124.48(11)	O6-C9-C10	117.06(16)
C25-O21-Co2	127.02(11)	C15-C10-C11	119.74(18)
O15-C17-O16	125.11(17)	C15-C10-C9	118.70(17)
O15-C17-C18	117.74(18)	C11-C10-C9	121.50(16)
O16-C17-C18	117.13(16)	C12-C11-C10	118.95(18)
C19-C18-C23	119.83(18)	C12-C11-C16	119.06(17)
C19-C18-C17	118.86(17)	C10-C11-C16	121.99(17)
C23-C18-C17	121.23(17)	C13-C12-C11	120.8(2)
C20-C19-C18	120.7(2)	C26-C31-C32	122.31(16)
C19-C20-C21	119.7(2)	O24-C32-O23	124.40(18)
C20-C21-C22	120.4(2)	O24-C32C31	116.73(16)
C21-C22-C23	120.74(19)	O23-C32-C31	118.84(17)
C22-C23-C18	118.68(18)	C33-O27-Co3	124.93(11)

C22-C23-C24	119.11(17)	O28-C33-O27	124.56(18)
C18-C23-C24	122.21(17)	O28-C33-C34	118.03(18)
O13-C24-O14	123.97(18)	O27-C33-C34	117.40(16)
O13-C24-C23	116.45(16)	C35-C34-C39	119.33(18)
O14-C24-C23	119.56(17)	C35-C34-C33	119.05(17)
O22-C25-O21	124.43(18)	C39-C34-C33	121.55(17)
O22-C25-C26	118.22(18)	C36-C35-C34	120.7(2)
O21-C25-C26	117.34(16)	C37-C36-C35	120.0(2)
C27-C26-C31	119.29(18)	C36-C37-C38	120.2(2)
C27-C26-C25	119.35(17)	C37-C38-C39	120.7(2)
C31-C26-C25	121.26(16)	C38-C39-C34	119.20(18)
C28-C27-C26	120.9(2)	C38-C39-C40	118.78(17)
C27-C28-C29	119.8(2)	C34-C39-C40	121.99(17)
C30-C29-C28	120.2(2)	O29-C40-O30	124.36(18)
C29-C30-C31	120.6(2)	O29-C40-C39	116.71(16)
C30-C31-C26	119.20(18)	O30-C40-C39	118.89(17)
C30-C31-C32	118.49(17)	C41-N1-C44	111.40(16)
C1-O1-Co1	127.33(11)	C43-N2-C42	111.81(16)
C9-O6-Co1	124.28(11)	N1-C41-C42	110.49(17)
O2-C1-O1	124.62(18)	N2-C42-C41	110.70(17)
O2-C1-C2	118.19(18)	N2-C43-C44	110.47(17)
O1-C1-C2	117.18(16)	N1-C44-C43	110.59(17)
C3-C2-C7	119.38(18)	C47-N3-C46	111.78(15)
C3-C2-C1	119.54(17)	C45-N4-C48	111.61(15)
C7-C2-C1	120.93(17)	N4-C45-C46	110.28(17)
C4-C3-C2	120.5(2)	N3-C46-C45	110.12(17)
C5-C4-C3	120.3(2)	N3-C47-C48	109.93(17)
C4-C5-C6	119.9(2)	N4-C48-C47	110.20(17)
C5-C6-C7	120.9(2)	C49#2-N5-C50	111.47(16)
C6-C7-C2	119.01(18)	N5#2-C49-C50	110.59(17)
C6-C7-C8	119.16(17)	N5-C50-C49	110.73(17)

Symmetry tranformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+1   #2 -x+1,-y+1,-z+2

Anisotropic displacement parameters (A^2 x 10^3) for (pipH$_2$)[Co(pt)$_2$(H$_2$O)$_4$]·8H$_2$O **4**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Co1	17(1)	25(1)	20(1)	-6(1)	1(1)	-3(1)
Co2	18(1)	27(1)	19(1)	-6(1)	1(1)	-3(1)
Co3	18(1)	25(1)	21(1)	-6(1)	1(1)	-3(1)
O1	24(1)	25(1)	28(1)	-6(1)	-2(1)	-3(1)
O2	26(1)	34(1)	63(1)	3(1)	2(1)	3(1)
O3	30(1)	41(1)	28(1)	-14(1)	2(1)	-9(1)
O4	34(1)	50(1)	61(1)	-34(1)	-9(1)	6(1)
O5	26(1)	34(1)	60(1)	1(1)	3(1)	-2(1)
O6	24(1)	26(1)	30(1)	-6(1)	-1(1)	-5(1)
O7	30(1)	40(1)	29(1)	-12(1)	2(1)	-11(1)
O8	33(1)	57(1)	69(1)	-42(1)	-8(1)	5(1)
C1	28(1)	29(1)	21(1)	-5(1)	1(1)	-2(1)
C2	31(1)	22(1)	26(1)	-3(1)	0(1)	-2(1)
C3	48(1)	32(1)	45(1)	-15(1)	10(1)	-2(1)
C4	72(2)	30(2)	72(2)	-28(1)	9(1)	-15(1)
C5	58(2)	40(2)	74(2)	-18(1)	5(1)	-25(1)
C6	39(1)	39(2)	51(1)	-12(1)	7(1)	-16(1)
C7	29(1)	28(1)	27(1)	-7(1)	0(1)	-6(1)
C8	26(1)	32(1)	27(1)	-10(1)	5(1)	-7(1)
C9	27(1)	27(1)	24(1)	-7(1)	3(1)	-4(1)
C10	27(1)	23(1)	28(1)	-5(1)	0(1)	-2(1)
C11	28(1)	28(1)	29(1)	-7(1)	0(1)	-6(1)
C12	35(1)	42(2)	52(1)	-13(1)	12(1)	-15(1)

C13	52(1)	38(2)	81(2)	-21(1)	11(1)	-25(1)
C14	58(2)	35(2)	76(2)	-30(1)	7(1)	-14(1)
C15	41(1)	33(1)	51(1)	-18(1)	8(1)	-4(1)
C16	27(1)	35(1)	26(1)	-9(1)	3(1)	-7(1)
O9	23(1)	31(1)	24(1)	-9(1)	2(1)	-3(1)
O10	27(1)	30(1)	24(1)	-8(1)	1(1)	-6(1)
O11	29(1)	32(1)	24(1)	-9(1)	2(1)	-7(1)
O12	24(1)	33(1)	28(1)	-8(1)	1(1)	-1(1)
O13	34(1)	58(1)	77(1)	-47(1)	-10(1)	6(1)
O14	30(1)	41(1)	28(1)	-13(1)	3(1)	-11(1)
O15	24(1)	35(1)	62(1)	0(1)	4(1)	-2(1)
O16	24(1)	28(1)	27(1)	-5(1)	-1(1)	-5(1)
O21	23(1)	24(1)	24(1)	-4(1)	-3(1)	-2(1)
O22	25(1)	35(1)	62(1)	4(1)	4(1)	3(1)
O23	31(1)	41(1)	26(1)	-13(1)	1(1)	-8(1)
O24	31(1)	52(1)	63(1)	-35(1)	-9(1)	8(1)
C17	29(1)	27(1)	22(1)	-6(1)	3(1)	-7(1)
C18	26(1)	24(1)	30(1)	-6(1)	1(1)	-3(1)
C19	42(1)	35(1)	51(1)	-20(1)	8(1)	-7(1)
C20	57(2)	36(2)	78(2)	-31(1)	9(1)	-15(1)
C21	50(1)	40(2)	81(2)	-21(1)	12(1)	-26(1)
C22	34(1)	42(2)	52(1)	-12(1)	13(1)	-14(1)
C23	28(1)	26(1)	30(1)	-6(1)	0(1)	-5(1)
C24	26(1)	35(1)	28(1)	-10(1)	5(1)	-8(1)
C25	27(1)	30(1)	19(1)	-4(1)	1(1)	-2(1)
C26	29(1)	23(1)	26(1)	-3(1)	-1(1)	-1(1)
C27	46(1)	32(1)	48(1)	-14(1)	7(1)	-1(1)
C28	69(2)	32(2)	71(2)	-25(1)	7(1)	-15(1)
C29	56(2)	40(2)	78(2)	-19(1)	5(1)	-24(1)
C30	37(1)	40(2)	53(1)	-11(1)	8(1)	-15(1)
C31	28(1)	28(1)	26(1)	-6(1)	0(1)	-5(1)
C32	26(1)	33(1)	27(1)	-10(1)	5(1)	-7(1)
O17	30(1)	31(1)	23(1)	-9(1)	2(1)	-6(1)
O18	28(1)	32(1)	22(1)	-8(1)	1(1)	-5(1)
O19	24(1)	31(1)	21(1)	-9(1)	2(1)	-4(1)
O20	24(1)	33(1)	27(1)	-8(1)	2(1)	-3(1)
O27	27(1)	26(1)	26(1)	-5(1)	-1(1)	-5(1)
O28	27(1)	35(1)	62(1)	3(1)	0(1)	0(1)
O29	35(1)	58(1)	74(1)	-45(1)	-13(1)	9(1)
O30	29(1)	41(1)	26(1)	-14(1)	1(1)	-11(1)
C33	29(1)	27(1)	21(1)	-6(1)	3(1)	-2(1)
C34	31(1)	24(1)	24(1)	-5(1)	-1(1)	-2(1)
C35	44(1)	35(1)	43(1)	-16(1)	6(1)	-3(1)
C36	63(2)	32(2)	63(2)	-24(1)	2(1)	-12(1)
C37	52(1)	37(2)	68(2)	-17(1)	3(1)	-23(1)
C38	34(1)	40(1)	45(1)	-10(1)	5(1)	-14(1)
C39	28(1)	28(1)	25(1)	-6(1)	0(1)	-6(1)
C40	29(1)	33(1)	26(1)	-11(1)	4(1)	-6(1)
O25	24(1)	32(1)	27(1)	-7(1)	3(1)	-1(1)
O26	28(1)	30(1)	24(1)	-8(1)	3(1)	-7(1)
N1	24(1)	72(2)	25(1)	-10(1)	2(1)	-10(1)
N2	23(1)	72(2)	23(1)	-8(1)	2(1)	-5(1)
C41	28(1)	55(2)	38(1)	2(1)	-1(1)	-10(1)
C42	33(1)	53(2)	39(1)	-11(1)	2(1)	-2(1)
C43	28(1)	55(2)	36(1)	3(1)	-1(1)	-8(1)
C44	30(1)	56(2)	42(1)	-14(1)	3(1)	-5(1)
N3	21(1)	60(1)	21(1)	-7(1)	-4(1)	-4(1)
N4	22(1)	62(1)	22(1)	-9(1)	-4(1)	-5(1)
C45	31(1)	54(2)	31(1)	-11(1)	-3(1)	-7(1)
C46	28(1)	52(2)	29(1)	-4(1)	-4(1)	-1(1)
C47	31(1)	51(2)	32(1)	-10(1)	-5(1)	-7(1)

C48	30(1)	52(2)	29(1)	-3(1)	-4(1)	-1(1)
N5	23(1)	73(2)	26(1)	-10(1)	2(1)	-8(1)
C49	25(1)	53(2)	40(1)	3(1)	-2(1)	-9(1)
C50	29(1)	53(2)	43(1)	-13(1)	2(1)	-4(1)
O31	48(1)	49(1)	53(1)	-11(1)	-5(1)	-1(1)
O32	51(1)	53(1)	51(1)	-11(1)	-6(1)	1(1)
O33	67(1)	65(2)	78(1)	9(1)	8(1)	-8(1)
O34	81(2)	65(1)	61(1)	3(1)	0(1)	-14(1)
O35	61(1)	78(2)	57(1)	2(1)	1(1)	15(1)
O36	49(1)	48(1)	51(1)	-9(1)	-9(1)	0(1)
O37	79(1)	65(1)	62(1)	3(1)	1(1)	-14(1)
O38	63(1)	80(2)	59(1)	3(1)	-2(1)	17(1)
O39	47(1)	48(1)	43(1)	-10(1)	3(1)	-12(1)
O40	42(1)	42(1)	41(1)	-10(1)	2(1)	-9(1)
O41	48(1)	50(1)	53(1)	-13(1)	-6(1)	-1(1)
O42	41(1)	44(1)	45(1)	-11(1)	2(1)	-9(1)
O43	48(1)	68(1)	57(1)	6(1)	4(1)	8(1)
O44	67(1)	67(2)	72(1)	7(1)	7(1)	-9(1)
O45	73(1)	69(1)	57(1)	7(1)	-2(1)	23(1)
O46	74(1)	85(2)	58(1)	2(1)	10(1)	-23(1)
O47	51(1)	50(1)	52(1)	-10(1)	-7(1)	0(1)
O48	50(1)	45(1)	42(1)	-10(1)	1(1)	-12(1)
O49	49(1)	68(1)	58(1)	6(1)	4(1)	6(1)
O50	45(1)	44(1)	37(1)	-10(1)	2(1)	-9(1)

Torsion angles [°] for (pipH$_2$)[Co(pt)$_2$(H$_2$O)$_4$]·8H$_2$O **4**

O2-C1-C2-C3	-48.0(3)	O21-C25-C26-C31	44.4(2)
O1-C1-C2-C3	130.89(19)	C31-C26-C27-C28	0.1(3)
O2-C1-C2-C7	136.47(19)	C25-C26-C27-C28	176.5(2)
O1-C1-C2-C7	-44.7(2)	C26-C27-C28-C29	-0.5(4)
C7-C2-C3-C4	-0.4(3)	C27-C28-C29-C30	0.3(4)
C1-C2-C3-C4	-176.0(2)	C28-C29-C30-C31	0.3(4)
C2-C3-C4-C5	0.6(4)	C29-C30-C31-C26	-0.7(3)
C3-C4-C5-C6	0.0(4)	C29-C30-C31-C32	178.7(2)
C4-C5-C6-C7	-0.6(4)	C27-C26-C31-C30	0.5(3)
C5-C6-C7-C2	0.8(3)	C25-C26-C31-C30	-175.78(18)
C5-C6-C7-C8	-178.0(2)	C27-C26-C31-C32	-178.81(19)
C3-C2-C7-C6	-0.3(3)	C25-C26-C31-C32	4.9(3)
C1-C2-C7-C6	175.29(18)	C30-C31-C32-O24	52.0(3)
C3-C2-C7-C8	178.49(18)	C26-C31-C32-O24	-128.7(2)
C1-C2-C7-C8	-6.0(3)	C30-C31-C32-O23	-126.2(2)
C6-C7-C8-O4	-50.2(3)	C26-C31-C32-O23	53.1(3)
C2-C7-C8-O4	131.0(2)	O28-C33-C34-C35	53.9(3)
C6-C7-C8-O3	128.1(2)	O27-C33-C34-C35	-125.1(2)
C2-C7-C8-O3	-50.6(3)	O28-C33-C34-C39	-129.1(2)
O5-C9-C10-C15	57.4(3)	O27-C33-C34-C39	51.9(2)
O6-C9-C10-C15	-121.2(2)	C39-C34-C35-C36	0.4(3)
O5-C9-C10-C11	-125.5(2)	C33-C34-C35-C36	177.5(2)
O6-C9-C10-C11	55.9(2)	C34-C35-C36-C37	-0.7(4)
C15-C10-C11-C12	0.2(3)	C35-C36-C37-C38	0.0(4)
C9-C10-C11-C12	-176.92(18)	C36-C37-C38-C39	0.9(4)
C15-C10-C11-C16	-179.45(19)	C37-C38-C39-C34	-1.2(3)
C9-C10-C11-C16	3.5(3)	C37-C38-C39-C40	177.2(2)
C10-C11-C12-C13	-0.6(3)	C35-C34-C39-C38	0.5(3)
C16-C11-C12-C13	179.0(2)	C33-C34-C39-C38	-176.47(18)
C11-C12-C13-C14	0.6(4)	C35-C34-C39-C40	-177.78(18)
C12-C13-C14-C15	0.0(4)	C33-C34-C39-C40	5.2(3)
C13-C14-C15-C10	-0.5(4)	C38-C39-C40-O29	47.8(3)
C11-C10-C15-C14	0.4(3)	C34-C39-C40-O29	-133.9(2)
C9-C10-C15-C14	177.5(2)	C38-C39-C40-O30	-130.2(2)

C12-C11-C16-O8	48.2(3)	C34-C39-C40-O30	48.2(3)
C10-C11-C16-O8	-132.2(2)	N1-C41-C42-N2	55.7(2)
C12-C11-C16-O7	-130.1(2)	N2-C43-C44-N1	-56.0(2)
C10-C11-C16-O7	49.5(3)	N4-C45-C46-N3	-56.2(2)
O15-C17-C18-C19	-55.7(3)	N3-C47-C48-N4	56.5(2)
O16-C17-C18-C19	122.9(2)	N5#1-C49-C50-N5	-55.9(2)
O15-C17-C18-C23	127.6(2)	C42-C41-N1-C44	-56.7(2)
O16-C17-C18-C23	-53.9(2)	C43-C44-N1-C41	57.0(2)
C23-C18-C19-C20	-0.9(3)	C44-C43-N2-C42	56.2(2)
C17-C18-C19-C20	-177.7(2)	C41-C42-N2-C43	-56.1(2)
C18-C19-C20-C21	1.0(4)	C48-C47-N3-C46	-57.5(2)
C19-C20-C21-C22	-0.2(4)	C45-C46-N3-C47	57.4(2)
C20-C21-C22-C23	-0.6(4)	C46-C45-N4-C48	57.1(2)
C21-C22-C23-C18	0.7(3)	C47-C48-N4-C45	-57.3(2)
C21-C22-C23-C24	-178.6(2)	C49-C50-N5-C49#1	56.4(2)
C19-C18-C23-C22	0.1(3)	O2-C1-O1-Co1	-15.8(3)
C17-C18-C23-C22	176.78(18)	C2-C1-O1-Co1	165.45(11)
C19-C18-C23-C24	179.31(19)	O5-C9-O6-Co1	18.8(2)
C17-C18-C23-C24	-4.0(3)	C10-C9-O6-Co1	-162.74(11)
C22-C23-C24-O13	-49.4(3)	O15-C17-O16-Co2	-18.4(2)
C18-C23-C24-O13	131.4(2)	C18-C17-O16-Co2	163.14(11)
C22-C23-C24-O14	129.5(2)	O22-C25-O21-Co2	15.7(2)
C18-C23-C24-O14	-49.8(3)	C26-C25-O21-Co2	-165.51(11)
O22-C25-C26-C27	46.9(3)	O28-C33-O27-Co3	18.6(2)
O21-C25-C26-C27	-131.90(19)	C34-C33-O27-Co3	-162.54(11)
O22-C25-C26-C31	-136.74(19)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+2 #2 -x+2,-y+1,-z+1

Hydrogen bonding geometry [Å and °] for (pipH$_2$)[Co(pt)$_2$(H$_2$O)$_4$]·8H$_2$O **4**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<DHA	Symmetry code
O9-H9C···O3	0.851	1.874	2.686	159.21	-x, -y+1, -z+2
O9-H9D···O5	0.846	1.786	2.61	163.84	x, y, z
O10-H10C···O3	0.848	1.997	2.835	169.64	x, y, z
O10-H10D···O4	0.854	1.793	2.645	174.88	-x, -y+1, -z+2
O11-H11C···O7	0.841	1.96	2.797	173.04	x, y, z
O11-H11D···O13	0.861	1.758	2.617	174.52	x, y, z
O12-H12C···O14	0.858	2.029	2.828	154.55	x, y, z
O12-H12D···O2	0.834	1.805	2.618	164.24	x, y, z
O17-H17C···O8	0.857	1.763	2.619	176.3	x, y, z
O17-H17D···O14	0.842	1.968	2.799	168.64	x, y, z
O18-H18C···O29	0.841	1.794	2.632	173.71	-x+2, -y+1, -z+1
O18-H18D···O23	0.877	1.993	2.862	170.59	x, y, z
O19-H19C···O30	0.845	1.938	2.735	156.84	-x+2, -y+1, -z+1
O19-H19D···O15	0.84	1.779	2.601	165.76	x, y, z
O20-H20C···O22	0.851	1.781	2.616	166.29	x, y, z
O20-H20C···O21	0.851	2.644	3.045	110.22	x, y, z
O20-H20D···O7	0.884	1.998	2.823	154.66	x, y, z
O25-H25C···O23	0.876	1.951	2.785	158.67	x, y, z
O25-H25D···O28	0.83	1.822	2.618	160.07	x, y, z
O26-H26C···O30	0.845	1.948	2.783	169.31	-x+2, -y+1, -z+1
O26-H26D···O24	0.853	1.783	2.633	174.78	x, y, z
N1-H1A···O42	0.9	2.196	2.942	139.86	-x+2, -y+1, -z+1
N1-H1A···O39	0.9	2.236	2.949	135.88	-x+3, -y+1, -z+1
N1-H1B···O20	0.9	2.213	2.996	145.08	-x+2, -y+1, -z+1
N1-H1B···O16	0.9	2.491	3.218	138.18	-x+2, -y+1, -z+1
N2-H2A···O25	0.9	2.213	2.983	143.28	x+1, y, z
N2-H2A···O27	0.9	2.429	3.165	139.13	-x+3, -y+1, -z+1
N2-H2B···O50	0.9	2.167	2.881	135.77	x, y, z

N2-H2B···O50	0.9	2.207	2.944	138.73	-x+3, -y+1, -z+1
N3-H3A···O19	0.9	2.147	2.876	137.46	x-1, y, z
N3-H3A···O21	0.9	2.283	2.981	134.24	x-1, y, z
N3-H3B···O42	0.9	2.162	2.897	138.41	x, y, z
N3-H3B···O39	0.9	2.261	2.995	138.43	x-1, y, z
N4-H4A···O40	0.9	2.192	2.93	138.74	x-1, y, z
N4-H4A···O48	0.9	2.274	3.016	139.61	x, y, z
N4-H4B···O9	0.9	2.141	2.869	137.5	x, y, z
N4-H4B···O1	0.9	2.325	3.013	133.21	x, y, z
N5-H5A···O40	0.9	2.159	2.927	142.94	x, y, z
N5-H5A···O48	0.9	2.288	2.985	134.15	x+1, y, z
N5-H5B···O12	0.9	2.227	3.006	144.56	x, y, z
N5-H5B···O6	0.9	2.44	3.169	138.21	x, y, z
O31-H31C···O7	0.836	2.071	2.86	157.1	-x+1, -y+2, -z+1
O31-H31D···O43	0.843	1.981	2.796	162.47	-x+1, -y+2, -z+1
O32-H32C···O35	0.876	1.944	2.795	163.8	x, y, z
O32-H32D···O30	0.827	2.098	2.875	156.46	x, y, z
O33-H33C···O32	0.799	2.14	2.788	138.21	x, y, z
O33-H33D···O43	0.833	1.998	2.826	172.31	-x+1, -y+2, -z+1
O34-H34C···O31	0.813	2.196	2.8	131.19	x, y, z
O34-H34D···O35	0.83	1.973	2.795	170.88	x, y, z
O35-H35C···O28	0.869	1.899	2.724	158.04	x, y, z
O35-H35D···O37	0.82	2.21	2.874	138.19	-x+1, -y+2, -z+1
O36-H36C···O38	0.817	2.029	2.817	161.8	x, y, z
O36-H36D···O23	0.845	1.993	2.793	157.71	x, y, z
O37-H37C···O36	0.802	2.237	2.778	125.26	-x+1, -y+2, -z+1
O37-H37D···O38	0.858	1.916	2.773	176.69	x, y, z
O38-H38C···O34	0.784	2.376	2.871	122.19	-x+1, -y+2, -z+1
O38-H38D···O22	0.873	1.868	2.703	159.52	x, y, z
O39-H39C···O24	0.825	2.01	2.8	159.97	x, y, z
O39-H39D···O31	0.82	2.019	2.836	174.42	-x+2, -y+2, -z+1
O40-H40C···O47	0.827	2.024	2.849	175.26	-x+1, -y+1, -z+2
O40-H40D···O8	0.817	1.973	2.754	159.51	x, y, z
O41-H41C···O49	0.857	1.976	2.796	159.98	x, y, z
O41-H41D···O14	0.828	2.052	2.841	159.03	x, y, z
O42-H42C···O32	0.823	2.02	2.841	175.79	-x+1, -y+1, -z+1
O42-H42D···O13	0.831	1.959	2.746	157.71	x, y, z
O43-H43C···O5	0.844	1.942	2.751	160.41	x, y, z
O43-H43D···O44	0.796	2.168	2.815	138.69	x, y, z
O44-H44C···O47	0.809	2.176	2.793	133.25	-x, -y+1, -z+2
O44-H44D···O49	0.828	1.998	2.823	174.08	x-1, y+1, z
O45-H45C···O2	0.858	1.854	2.699	167.8	x, y, z
O45-H45D···O46	0.801	2.037	2.801	159.22	x, y, z
O46-H46C···O45	0.765	2.124	2.867	164.09	-x+1, -y, -z+2
O46-H46D···O41	0.833	2.016	2.797	155.78	-x+1, -y, -z+2
O47-H47C···O3	0.827	2.091	2.88	159.4	x, y, z
O47-H47D···O45	0.89	1.927	2.797	165.53	x, y, z
O48-H48C···O41	0.826	2.01	2.835	176.75	x-1, y, z
O48-H48D···O4	0.834	2.006	2.788	155.87	x, y, z
O49-H49C···O15	0.832	1.948	2.751	161.64	x, y, z
O49-H49D···O33	0.831	2.138	2.811	137.97	-x+2, -y+1, -z+1
O50-H50C···O29	0.85	1.892	2.709	160.82	x, y, z
O50-H50D···O36	0.846	1.963	2.808	176.05	x+1, y, z
C41-H41B···O26	0.970	2.473	3.389	157.46	-x+3, -y+1, -z+1
C43-H43A···O18	0.970	2.439	3.340	154.34	-x+2, -y+1, -z+1
C45-H45B···O44	0.970	2.718	3.588	149.51	x, y, z
C46-H46A···O8	0.970	2.680	3.649	177.68	x-1, y, z
C46-H46A···O17	0.970	3.075	3.758	128.66	x-1, y, z
C46-H46A···O40	0.970	2.943	3.537	120.65	x-1, y, z
C47-H47A···O33	0.970	2.740	3.619	151.01	-x+1, -y+1, -z+1
C48-H48B···O13	0.970	2.749	3.718	177.97	-x+2, -y+1, -z+1

C48-H48B···O42	0.970	2.896	3.494	120.65	x, y, z
C49-H49A···O10	0.970	2.427	3.329	154.38	x, y, z
C49-H49A···O12	0.970	3.031	3.651	123.07	x, y, z
C50-H50A···O4	0.970	2.729	3.491	135.84	x+1, y, z
C50-H50A···O6	0.970	2.626	3.341	130.82	-x+1, -y+1, -z+2
C50-H50A···O10	0.970	2.798	3.598	140.29	-x+1, -y+1, -z+2
C50-H50B···O46	0.970	2.658	3.556	154.14	-x+1, -y+1, -z+2

Structure protocol for $(\mathrm{pipH_2})[\mathrm{Cu(pt)_2(H_2O)_4}]\cdot 8\mathrm{H_2O}$ **5**

Crystal data and structure refinement for $(\mathrm{pipH_2})[\mathrm{Cu(pt)_2(H_2O)_4}]\cdot 8\mathrm{H_2O}$ **5**

Identification code	rj2
Empirical formula	$C_{20}H_{44}CuN_2O_{20}$
Formula weight (g mol^{-1})	696.11
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.9101(5)
b (Å)	12.3555(6)
c (Å)	16.6034(7)
α (°)	100.649(2)
β (°)	97.357(2)
γ (°)	96.264(2)
Volume (Å^3)	2359.23(18)
Z	3
D_{calc} (mg/m^3)	1.4703
Absorption coefficient (mm^{-1})	0.779
F(000)	1101
Crystal size (mm^3)	0.25 x 0.20 x 0.20
θ range for data collection (°)	1.90 to 25.00
Index ranges	$-14 \leq h \leq 14$
	$-14 \leq k \leq 14$
	$-19 \leq l \leq 19$
Reflections collected / unique	61059 / 8318 [R(int)=0.0383]
Completeness to θ = 25.00°	99.9%
Absorption correction	Multi-scan
Max. and min. Transmission	0.8598 and 0.8291
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8318 / 54 / 714
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0290, wR2 = 0.0755
R indices (all data)	R1 = 0.0474, wR2 = 0.0876
Extinction coefficient	0.0050(19)
Largest diff. peak and hole (e Å^{-3})	0.286 and -0.467

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(\mathrm{pipH_2})[\mathrm{Cu(pt)_2(H_2O)_4}]\cdot 8\mathrm{H_2O}$ **5**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cu1	-3506(1)	5004(1)	3236(1)	23(1)
Cu2	0	5000	0	23(1)
C1	-3928(10)	7269(10)	3612(7)	25(3)
C2	-4758(10)	8065(9)	3815(7)	26(3)
C3	-4789(12)	8961(11)	3426(8)	41(3)
C4	-5562(13)	9693(12)	3570(10)	53(4)
C5	-6329(13)	9531(12)	4099(10)	52(4)
C6	-6323(11)	8629(11)	4489(8)	39(3)
C7	-5536(10)	7893(10)	4356(7)	27(3)
C8	-5531(10)	6951(10)	4812(7)	29(3)
O1	-4354(6)	6268(6)	3306(4)	25(2)
O2	-2895(7)	7631(7)	3728(6)	44(2)
O3	-4593(7)	6731(7)	5133(5)	32(2)
O4	-6486(8)	6454(8)	4858(6)	49(3)
C9	-3106(10)	2721(10)	2926(6)	25(3)
C10	-2277(10)	1913(9)	2760(7)	26(3)
C11	-2331(12)	986(11)	3124(8)	41(3)
C12	-1546(14)	254(12)	3022(10)	55(4)

C13	-689(13)	443(12)	2568(10)	54(4)
C14	-619(11)	1360(11)	2203(8)	39(3)
C15	-1417(10)	2097(9)	2289(7)	26(3)
C16	-1329(10)	3068(10)	1860(7)	28(3)
O8	-2679(6)	3729(6)	3180(4)	24(2)
O9	-4139(7)	2368(8)	2830(6)	46(2)
O10	-358(7)	3597(8)	1921(6)	47(2)
O11	-2218(7)	3268(7)	1451(5)	31(2)
O5	-1677(7)	6065(7)	3163(5)	31(2)
O6	-3725(7)	4724(7)	2004(5)	26(2)
O7	-3223(7)	5274(7)	4458(5)	26(2)
O21	-5412(8)	3941(8)	3317(6)	36(2)
C17	444(10)	2730(10)	-293(7)	26(3)
C18	1290(10)	1933(9)	-429(7)	25(3)
C19	1248(12)	1032(11)	-37(8)	39(3)
C20	2039(13)	301(12)	-121(9)	49(4)
C21	2891(13)	468(11)	-584(9)	47(4)
C22	2952(11)	1366(11)	-973(8)	36(3)
C23	2150(10)	2095(9)	-906(7)	26(3)
C24	2207(10)	3027(10)	-1374(7)	28(3)
O13	854(6)	3738(6)	10(4)	26(2)
O14	-589(7)	2372(8)	-463(6)	45(2)
O15	1292(7)	3232(7)	-1745(5)	31(2)
O16	3175(8)	3521(8)	-1385(6)	48(3)
O12	126(7)	5284(7)	1219(5)	26(2)
O30	1924(8)	6073(8)	54(5)	35(2)
N1	3492(8)	4980(9)	913(6)	33(2)
N2	2894(8)	4970(9)	2523(6)	33(2)
C25	3369(10)	3942(11)	1229(7)	35(3)
C26	2535(10)	3989(11)	1838(7)	36(3)
C27	3012(10)	6013(11)	2207(7)	35(3)
C28	3844(10)	5965(11)	1594(7)	36(3)
N3	-361(8)	5010(9)	4154(6)	31(2)
C29	-301(10)	6022(11)	4801(7)	34(3)
C30	-601(10)	3991(11)	4480(7)	33(3)
O17	-734(9)	12119(9)	7117(6)	53(3)
O18	-717(10)	11219(11)	5437(8)	72(4)
O19	-1434(10)	8930(10)	5041(7)	62(3)
O20	-8396(9)	6201(8)	3658(7)	41(2)
O22	-5481(11)	1063(10)	1504(7)	71(4)
O23	-5920(10)	-1236(11)	1229(7)	68(3)
O24	-1945(11)	1118(10)	-1827(7)	69(3)
O25	-2413(11)	-1196(11)	-2154(8)	71(3)
O26	-2502(10)	-2105(9)	-3856(7)	52(3)
O27	-1277(9)	-3749(8)	-3333(7)	44(2)
O28	5822(10)	2027(9)	463(6)	48(2)
O29	4935(8)	3805(8)	-94(6)	39(2)

Bond lengths [Å] and angles [°] for (pipH_2)[Cu(pt)$_2$(H_2O)$_4$]·8H_2O **5**

Cu1-O8	1.941(7)	Cu2-O13	1.954(7)
Cu1-O1	1.945(7)	Cu2-O13^i	1.954(7)
Cu1-O7	1.972(8)	Cu2-O12	1.973(7)
Cu1-O6	1.988(8)	Cu2-O12^i	1.973(7)
C1-O2	1.240(14)	C16-O11	1.256(13)
C1-O1	1.269(13)	C17-O14	1.239(14)
C1-C2	1.495(15)	C17-O13	1.271(13)
C2-C3	1.382(16)	C17-C18	1.493(15)
C2-C7	1.397(15)	C18-C19	1.389(16)

C3-C4	1.371(18)	C18-C23	1.392(15)
C4-C5	1.37(2)	C19-C20	1.376(18)
C5-C6	1.388(18)	C20-C21	1.37(2)
C6-C7	1.386(16)	C21-C22	1.383(18)
C7-C8	1.502(16)	C22-C23	1.384(16)
C8-O4	1.251(14)	C23-C24	1.504(15)
C8-O3	1.254(14)	C24-O16	1.247(14)
C9-O9	1.239(14)	C24-O15	1.256(14)
C9-O8	1.265(13)	N1-C25	1.473(15)
C9-C10	1.493(15)	N1-C28	1.481(15)
C10-C11	1.389(16)	N2-C27	1.478(16)
C10-C15	1.391(15)	N2-C26	1.482(16)
C11-C12	1.375(19)	C25-C26	1.505(16)
C12-C13	1.37(2)	C27-C28	1.507(16)
C13-C14	1.381(19)	N3-C30	1.473(15)
C14-C15	1.389(16)	N3-C29	1.479(15)
C15-C16	1.506(16)	C29-C30#2	1.504(16)
C16-O10	1.247(14)	C30-C29#2	1.504(16)
O8-Cu1-O1	178.8(3)	O13-Cu2-O13^{i}	180.000(1)
O8-Cu1-O7	90.2(3)	O13-Cu2-O12	90.8(3)
O1-Cu1-O7	89.1(3)	O13^{i}-Cu2-O12	89.2(3)
O8-Cu1-O6	88.2(3)	O13-Cu2-O12^{i}	89.2(3)
O1-Cu1-O6	92.5(3)	O13^{i}-Cu2-O12^{i}	90.8(3)
O7-Cu1-O6	177.7(3)	O12-Cu2-O12^{i}	180.0(5)
O2-C1-O1	125.2(10)	O10-C16-O11	124.9(11)
O2-C1-C2	118.6(11)	O10-C16-C15	116.6(10)
O1-C1-C2	116.2(10)	O11-C16-C15	118.5(10)
C3-C2-C7	119.5(11)	C9-O8-Cu1	126.2(7)
C3-C2-C1	118.9(10)	O14-C17-O13	124.8(11)
C7-C2-C1	121.5(10)	O14-C17-C18	118.9(11)
C4-C3-C2	121.1(12)	O13-C17-C18	116.3(10)
C5-C4-C3	119.7(12)	C19-C18-C23	119.1(11)
C4-C5-C6	120.1(12)	C19-C18-C17	118.9(10)
C7-C6-C5	120.6(12)	C23-C18-C17	121.9(10)
C6-C7-C2	118.9(11)	C20-C19-C18	120.7(12)
C6-C7-C8	118.9(10)	C21-C20-C19	120.1(12)
C2-C7-C8	122.2(10)	C20-C21-C22	120.0(12)
O4-C8-O3	124.6(11)	C21-C22-C23	120.4(12)
O4-C8-C7	116.4(10)	C22-C23-C18	119.6(11)
O3-C8-C7	119.0(11)	C22-C23-C24	119.0(10)
C1-O1-Cu1	124.9(7)	C18-C23-C24	121.4(10)
O9-C9-O8	124.9(10)	O16-C24-O15	124.6(11)
O9-C9-C10	119.0(10)	O16-C24-C23	117.0(10)
O8-C9-C10	116.1(10)	O15-C24-C23	118.3(11)
C11-C10-C15	119.3(11)	C17-O13-Cu2	124.8(7)
C11-C10-C9	119.0(10)	C25-N1-C28	111.7(9)
C15-C10-C9	121.6(10)	C27-N2-C26	111.5(9)
C12-C11-C10	120.7(12)	N1-C25-C26	110.7(10)
C13-C12-C11	120.0(13)	N2-C26-C25	110.3(10)
C12-C13-C14	120.2(12)	N2-C27-C28	110.5(10)
C13-C14-C15	120.4(12)	N1-C28-C27	110.6(10)
C14-C15-C10	119.3(11)	C30-N3-C29	111.7(9)
C14-C15-C16	118.7(10)	N3-C29-C30#2	110.0(10)
C10-C15-C16	122.0(10)	N3-C30-C29#2	109.9(10)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z, #2 -x,-y+1,-z+1

Anisotropic displacement parameters (A^2 x 10^3) for $(pipH_2)[Cu(pt)_2(H_2O)_4]\cdot 8H_2O$ **5**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cu1	24(1)	24(1)	20(1)	5(1)	2(1)	7(1)
Cu2	26(1)	24(1)	20(1)	6(1)	3(1)	8(1)
C1	29(7)	27(7)	20(6)	6(5)	5(5)	6(5)
C2	28(6)	23(6)	28(6)	4(5)	5(5)	3(5)
C3	47(8)	35(8)	49(8)	21(6)	18(7)	11(6)
C4	63(10)	36(9)	76(11)	34(8)	23(9)	21(7)
C5	54(9)	37(9)	76(11)	20(8)	20(8)	27(7)
C6	38(7)	38(8)	49(8)	13(6)	18(6)	15(6)
C7	27(6)	26(7)	28(6)	6(5)	4(5)	5(5)
C8	31(7)	33(7)	27(6)	10(5)	9(5)	10(6)
O1	26(4)	25(5)	25(4)	4(3)	3(3)	7(3)
O2	27(5)	37(6)	63(6)	-2(5)	11(4)	3(4)
O3	34(5)	40(5)	27(4)	12(4)	7(4)	15(4)
O4	35(5)	55(7)	67(7)	41(5)	10(5)	5(5)
C9	28(7)	27(7)	20(6)	4(5)	3(5)	2(5)
C10	28(6)	22(6)	25(6)	2(5)	2(5)	3(5)
C11	50(8)	33(8)	47(8)	17(6)	19(7)	5(6)
C12	71(11)	34(9)	74(11)	30(8)	18(9)	20(8)
C13	60(10)	38(9)	73(11)	19(8)	15(8)	28(7)
C14	36(7)	39(8)	48(8)	11(6)	13(6)	15(6)
C15	27(6)	25(7)	26(6)	5(5)	3(5)	3(5)
C16	27(7)	32(7)	27(6)	10(5)	9(5)	9(5)
O8	24(4)	23(5)	24(4)	4(3)	1(3)	5(3)
O9	25(5)	39(6)	68(7)	-7(5)	11(4)	0(4)
O10	30(5)	56(6)	64(6)	40(5)	5(4)	2(4)
O11	32(5)	40(5)	26(4)	12(4)	6(4)	13(4)
O5	35(5)	39(6)	25(5)	14(4)	6(4)	12(4)
O6	27(4)	28(5)	24(4)	9(4)	5(3)	8(4)
O7	30(5)	28(5)	24(4)	8(4)	6(3)	8(4)
O21	39(5)	43(6)	30(5)	12(4)	6(4)	11(4)
C17	31(7)	28(7)	21(6)	7(5)	5(5)	5(5)
C18	29(6)	22(6)	24(6)	4(5)	3(5)	3(5)
C19	47(8)	35(8)	41(7)	17(6)	14(6)	7(6)
C20	64(10)	32(8)	61(9)	27(7)	12(8)	16(7)
C21	52(9)	35(8)	62(9)	16(7)	9(8)	24(7)
C22	36(7)	35(8)	42(7)	10(6)	9(6)	13(6)
C23	28(6)	25(6)	24(6)	6(5)	2(5)	6(5)
C24	32(7)	32(7)	24(6)	10(5)	9(5)	11(6)
O13	30(4)	25(5)	24(4)	6(3)	2(3)	9(3)
O14	27(5)	40(6)	64(6)	-2(5)	9(4)	5(4)
O15	33(5)	42(5)	26(4)	14(4)	8(4)	16(4)
O16	32(5)	57(7)	65(6)	41(5)	5(5)	2(5)
O12	29(5)	29(5)	24(4)	9(4)	5(3)	10(4)
O30	37(5)	42(6)	31(5)	15(4)	8(4)	12(4)
N1	24(5)	54(7)	22(5)	10(5)	5(4)	9(5)
N2	25(5)	54(7)	24(5)	12(5)	7(4)	12(5)
C25	30(7)	43(8)	30(6)	3(6)	4(5)	7(6)
C26	29(7)	45(8)	36(7)	11(6)	8(6)	5(6)
C27	30(7)	44(8)	31(6)	4(6)	4(5)	11(6)
C28	30(7)	45(8)	33(7)	8(6)	6(6)	5(6)
N3	23(5)	51(7)	21(5)	10(5)	0(4)	8(5)
C29	31(7)	45(8)	30(6)	11(6)	3(5)	10(6)
C30	28(7)	43(8)	27(6)	6(6)	2(5)	1(6)
O17	50(6)	54(7)	53(7)	15(5)	2(5)	-4(5)
O18	68(8)	68(8)	79(9)	-2(7)	30(7)	14(7)
O19	59(7)	56(7)	58(7)	-7(6)	12(6)	-15(6)
O20	42(6)	39(6)	46(6)	10(5)	13(5)	9(5)
O22	71(8)	69(8)	58(7)	-3(7)	5(6)	-24(7)

O23	70(8)	74(9)	60(7)	2(7)	16(7)	16(7)
O24	70(8)	68(8)	55(7)	-1(6)	5(6)	-20(7)
O25	71(8)	77(9)	62(7)	3(7)	17(7)	17(7)
O26	51(7)	48(7)	56(7)	14(5)	4(6)	0(5)
O27	48(6)	42(6)	46(6)	9(5)	14(5)	11(5)
O28	47(7)	47(7)	49(6)	11(5)	-1(6)	2(5)
O29	42(6)	38(6)	40(6)	10(5)	11(5)	11(5)

Torsion angles [°] for (pipH$_2$)[Cu(pt)$_2$(H$_2$O)$_4$]·8H$_2$O **5**

O2-C1-C2-C3	58.4(3)	C11-C10-C15-C16	178.3(2)
O1-C1-C2-C3	-119.5(2)	C9-C10-C15-C16	-5.2(3)
O2-C1-C2-C7	-124.8(2)	C14-C15-C16-O10	-45.4(3)
O1-C1-C2-C7	57.3(3)	C10-C15-C16-O10	135.3(2)
C7-C2-C3-C4	0.9(4)	C14-C15-C16-O11	132.6(2)
C1-C2-C3-C4	177.7(2)	C10-C15-C16-O11	-46.7(3)
C2-C3-C4-C5	-0.9(4)	O14-C17-C18-C19	-57.1(3)
C3-C4-C5-C6	0.1(4)	O13-C17-C18-C19	121.4(2)
C4-C5-C6-C7	0.7(4)	O14-C17-C18-C23	125.9(2)
C5-C6-C7-C2	-0.7(3)	O13-C17-C18-C23	-55.6(3)
C5-C6-C7-C8	177.9(2)	C23-C18-C19-C20	-0.5(3)
C3-C2-C7-C6	-0.1(3)	C17-C18-C19-C20	-177.6(2)
C1-C2-C7-C6	-176.8(2)	C18-C19-C20-C21	1.1(4)
C3-C2-C7-C8	-178.6(2)	C19-C20-C21-C22	-0.6(4)
C1-C2-C7-C8	4.6(3)	C20-C21-C22-C23	-0.6(4)
C6-C7-C8-O4	42.6(3)	C21-C22-C23-C18	1.3(3)
C2-C7-C8-O4	-138.8(2)	C21-C22-C23-C24	-176.9(2)
C6-C7-C8-O3	-135.8(2)	C19-C18-C23-C22	-0.7(3)
C2-C7-C8-O3	42.8(3)	C17-C18-C23-C22	176.32(19)
O9-C9-C10-C11	-50.4(3)	C19-C18-C23-C24	177.4(2)
O8-C9-C10-C11	127.6(2)	C17-C18-C23-C24	-5.6(3)
O9-C9-C10-C15	133.1(2)	C22-C23-C24-O16	-41.2(3)
O8-C9-C10-C15	-48.9(3)	C18-C23-C24-O16	140.7(2)
C15-C10-C11-C12	-0.1(4)	C22-C23-C24-O15	136.5(2)
C9-C10-C11-C12	-176.6(2)	C18-C23-C24-O15	-41.6(3)
C10-C11-C12-C13	1.0(4)	N1-C25-C26-N2	-56.2(2)
C11-C12-C13-C14	-0.9(4)	N2-C27-C28-N1	55.7(2)
C12-C13-C14-C15	-0.2(4)	C26-C25-N1-C28	56.5(2)
C13-C14-C15-C10	1.1(3)	C27-C28-N1-C25	-56.2(2)
C13-C14-C15-C16	-178.2(2)	C28-C27-N2-C26	-56.8(2)
C11-C10-C15-C14	-1.0(3)	C25-C26-N2-C27	56.9(2)
C9-C10-C15-C14	175.46(19)		

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1 #2 -x,-y+1,-z

Hydrogen bonding geometry [Å and °] for (pipH$_2$)[Cu(pt)$_2$(H$_2$O)$_4$]·8H$_2$O **5**

D-H···A	d(D-H)	d(H..A)	d(D..A)	<DHA	Symmetry code
N1-H1A···O30	0.9	2.026	2.815	145.62	x, y, z
N1-H1B···O29	0.9	2.114	2.871	141.22	x, y, z
N1-H1B···O29	0.9	2.198	2.899	134.25	-x+1, -y+1, -z
N2-H2A···O20	0.9	2.152	2.901	140.28	x+1, y, z
N2-H2A···O27	0.9	2.223	2.928	134.89	-x, -y, -z
N2-H2B···O21	0.9	2.002	2.815	149.64	x+1, y, z
N3-H3A···O5	0.9	1.97	2.728	140.91	x, y, z
N3-H3A···O8	0.9	2.456	3.114	130.2	x, y, z
N3-H3B···O20	0.9	2.185	2.918	138.26	x+1, y, z
N3-H3B···O27	0.9	2.219	2.941	136.93	-x, -y, -z
O17-H17A···O24	0.849	1.949	2.783	166.75	x, y+1, z+1
O17-H17B···O15	0.835	2.084	2.904	166.98	x, y+1, z+1

O18-H18A···O17	0.845	1.966	2.81	175.46	x, y, z
O18-H18B···O19	0.797	1.997	2.792	176.15	-x, -y+2, -z+1
O19-H19A···O2	0.835	1.909	2.735	169.98	x, y, z
O19-H19B···O18	0.825	1.992	2.793	163.82	x, y, z
O22-H22A···O9	0.836	1.87	2.689	165.9	x, y, z
O22-H22B···O23	0.846	1.942	2.772	166.85	x, y, z
O23-H23A···O28	0.839	1.984	2.82	173.89	-x, -y, -z
O23-H23B···O24	0.812	2.051	2.855	169.97	-x-1, -y, -z
O24-H24A···O14	0.839	1.884	2.712	168.96	x, y, z
O24-H24B···O25	0.84	1.963	2.79	167.92	x, y, z
O25-H25C···O22	0.829	2.051	2.864	166.97	-x-1, -y, -z
O25-H25D···O26	0.846	1.98	2.825	176.59	x, y, z
O5-H5A···O2	0.823	1.843	2.65	166.35	x, y, z
O5-H5B···O15	0.835	1.909	2.729	166.71	-x, -y+1, -z
O6-H6A···O11	0.856	1.941	2.796	175.77	x, y, z
O6-H6B···O16	0.833	1.795	2.622	171.69	-x, -y+1, -z
O7-H7A···O4	0.84	1.772	2.608	173.62	-x-1, -y+1, -z+1
O7-H7B···O3	0.86	1.884	2.743	179.61	x, y, z
O12-H12A···O15	0.845	1.883	2.728	179.08	-x, -y+1, -z
O12-H12B···O10	0.837	1.781	2.615	173.94	x, y, z
O20-H20A···O4	0.822	1.984	2.775	161.48	x, y, z
O20-H20B···O17	0.824	2.034	2.854	173.44	-x-1, -y+2, -z+1
O21-H21A···O3	0.838	2.03	2.845	163.96	-x-1, -y+1, -z+1
O21-H21B···O9	0.851	1.843	2.666	162.23	x, y, z
O26-H26C···O19	0.847	1.942	2.778	168.92	x, y-1, z-1
O26-H26D···O3	0.83	2.07	2.888	168.27	x, y-1, z-1
O27-H27C···O26	0.846	1.989	2.826	169.98	x, y, z
O27-H27D···O10	0.844	2.017	2.813	157.06	-x, -y, -z
O28-H28C···O22	0.835	1.979	2.803	168.52	x+1, y,
O28-H28D···O11	0.827	1.985	2.793	165.34	x+1, y, z
O29-H29C···O16	0.824	1.942	2.742	163.57	x, y, z
O29-H29D···O28	0.846	1.95	2.794	176.54	x, y, z
O30-H30C···O14	0.85	1.85	2.672	162.33	-x, -y+1, -z
O30-H30D···O11	0.854	1.979	2.818	167.37	-x, -y+1, -z
C25-H25A···O6	0.970	2.660	3.498	144.80	1+x, y, z
C26-H26A···O10	0.970	2.711	3.450	133.41	x, y, z
C26-H26A···O12	0.970	2.699	3.563	148.69	x, y, z
C26-H26A···O13	0.970	2.607	3.358	134.48	x, y, z
C26-H26B···O25	0.970	2.644	3.575	160.98	-x, -y, -z
C27-H27B···O12	0.970	2.689	3.557	149.07	x, y, z
C28-H28A···O23	0.970	2.670	3.607	162.60	1+x, 1+y, z
C28-H28B···O1	0.970	2.477	3.270	138.82	1+x, y, z
C28-H28B···O6	0.970	2.625	3.471	145.92	1+x, y, z
C29-H29A···O7	0.970	2.654	3.448	139.28	x, y, z
C29-H29B···O18	0.970	2.684	3.600	157.52	-x, 2-y, 1-z

Structure protocol for $[Ni(Im)_6]pt\cdot H_2O$ **6**

Crystal data and structure refinement for $[Ni(Im)_6]pt\cdot H_2O$ **6**

Identification code	NiImpt
Empirical formula	$C_{26}H_{30}N_{12}NiO_5$
Formula weight (g mol^{-1})	649.33
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	13.0759(6)
b (Å)	13.0309(7)
c (Å)	18.4208(9)
α (°)	90
β (°)	105.636(2)
γ (°)	90
Volume (Å^3)	3022.6(3)
Z	4
D_{calc} (mg/m^3)	1.427
Absorption coefficient (mm^{-1})	0.699
F(000)	1352
Crystal size (mm^3)	0.4 x 0.3 x 0.3
θ range for data collection (°)	2.25 to 25.00
Index ranges	$-15 \le h \le 15$ $-15 \le k \le 15$ $-21 \le l \le 21$
Reflections collected / unique	51915/5305 (R(int) = 0.0428)
Completeness to θ = 25.00°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.90 and 0.75
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5305/3/405
Goodness-of-fit on F^2	1.082
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.1053
R indices (all data)	R1 = 0.0625, wR2 = 0.1295
Largest diff. peak and hole (e Å^{-3})	0.464 and -0.430

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $[Ni(Im)_6]pt\cdot H_2O$ **6**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ni(1)	8276(1)	2103(1)	7781(1)	34(1)
N(1)	7930(2)	612(2)	7315(1)	36(1)
N(2)	7476(2)	-1006(2)	7172(2)	50(1)
C(1)	7614(2)	-198(2)	7627(2)	44(1)
C(2)	7702(2)	-720(2)	6532(2)	52(1)
C(3)	7978(2)	272(2)	6625(2)	46(1)
N(3)	9693(2)	1564(2)	8570(1)	37(1)
N(4)	11295(2)	1604(2)	9345(2)	54(1)
C(4)	10190(2)	637(3)	8566(2)	54(1)
C(5)	11168(3)	661(3)	9031(2)	69(1)
C(6)	10403(2)	2125(2)	9057(2)	40(1)
N(5)	9223(2)	2431(2)	7013(1)	40(1)
N(6)	10592(2)	2642(2)	6553(2)	49(1)
C(7)	10265(2)	2395(3)	7155(2)	46(1)
C(8)	9721(3)	2841(3)	5984(2)	55(1)
C(9)	8882(3)	2713(2)	6268(2)	49(1)
N(7)	8592(2)	3578(2)	8276(1)	42(1)
N(8)	8661(2)	4870(2)	9051(2)	53(1)
C(10)	8187(2)	3990(2)	8789(2)	52(1)

C(11)	9369(3)	4257(2)	8217(2)	57(1)
C(12)	9410(3)	5045(3)	8690(2)	62(1)
N(9)	6919(2)	2682(2)	6967(1)	38(1)
N(10)	5411(2)	2793(2)	6090(1)	46(1)
C(13)	6100(2)	2174(2)	6554(2)	41(1)
C(14)	6738(2)	3691(2)	6742(2)	45(1)
C(15)	5808(2)	3762(2)	6200(2)	47(1)
N(11)	7368(2)	1734(2)	8550(1)	42(1)
N(12)	6033(2)	1499(2)	9036(2)	54(1)
C(16)	6347(2)	1879(2)	8461(2)	45(1)
C(17)	6888(3)	1072(4)	9523(2)	79(1)
C(18)	7706(3)	1222(3)	9225(2)	68(1)
O(1)	3380(2)	2351(2)	5133(1)	56(1)
O(2)	1982(2)	1367(2)	5101(1)	61(1)
O(3)	2688(2)	2523(2)	6558(2)	65(1)
O(4)	3386(3)	2009(2)	7707(2)	108(1)
C(19)	2934(2)	1607(2)	5362(2)	44(1)
C(20)	3626(2)	909(2)	5945(2)	37(1)
C(21)	4118(3)	99(3)	5690(2)	54(1)
C(22)	4741(3)	-598(3)	6202(3)	64(1)
C(23)	4851(3)	-473(3)	6956(2)	61(1)
C(24)	4371(2)	326(3)	7209(2)	50(1)
C(25)	3762(2)	1023(2)	6716(2)	39(1)
C(26)	3231(3)	1922(3)	7011(2)	52(1)
O(5)	3935(2)	1318(2)	9139(2)	63(1)
O(5)	3935(2)	1318(2)	9139(2)	63(1)

Bond lengths [Å] and angles [°] for [Ni(Im)$_6$]pt·H_2O **6**

Ni1-N7	2.120(2)	N8-C12	1.343(4)
Ni1-N1	2.123(2)	C11-C12	1.339(5)
Ni1-N9	2.128(2)	N9-C13	1.314(4)
Ni1-N11	2.135(2)	N9-C14	1.379(4)
Ni1-N3	2.143(2)	N10-C13	1.334(4)
Ni1-N5	2.158(2)	N10-C15	1.360(4)
N1-C1	1.321(4)	C14-C15	1.352(4)
N1-C3	1.362(4)	N11-C16	1.314(4)
N2-C1	1.328(4)	N11-C18	1.375(4)
N2-C2	1.343(4)	N12-C16	1.331(4)
C2-C3	1.340(4)	N12-C17	1.350(5)
N3-C6	1.324(4)	C17-C18	1.341(5)
N3-C4	1.373(4)	O1-C19	1.261(4)
N4-C6	1.330(4)	O2-C19	1.249(4)
N4-C5	1.350(4)	O3-C26	1.222(4)
C4-C5	1.334(5)	O4-C26	1.248(4)
N5-C7	1.317(4)	C19-C20	1.508(4)
N5-C9	1.375(4)	C20-C21	1.383(4)
N6-C7	1.331(4)	C20-C25	1.391(4)
N6-C8	1.349(4)	C21-C22	1.402(5)
C8-C9	1.346(5)	C22-C23	1.366(5)
N7-C10	1.315(4)	C23-C24	1.361(5)
N7-C11	1.374(4)	C24-C25	1.376(4)
N8-C10	1.330(4)	C25-C26	1.534(4)
N7-Ni1-N1	177.88(9)	C10-N7-Ni1	127.6(2)
N7-Ni1-N9	90.61(9)	C11-N7-Ni1	127.7(2)
N1-Ni1-N9	89.63(9)	C10-N8-C12	107.3(3)
N7-Ni1-N11	89.82(9)	N7-C10-N8	112.0(3)
N1-Ni1-N11	88.07(9)	C12-C11-N7	110.0(3)
N9-Ni1-N11	92.28(9)	C11-C12-N8	106.5(3)
N7-Ni1-N3	88.42(9)	C13-N9-C14	105.0(2)

N1-Ni1-N3	91.44(9)	C13-N9-Ni1	128.6(2)
N9-Ni1-N3	177.02(9)	C14-N9-Ni1	126.34(19)
N11-Ni1-N3	90.54(9)	C13-N10-C15	107.5(3)
N7-Ni1-N5	91.34(9)	N9-C13-N10	111.8(3)
N1-Ni1-N5	90.77(9)	C15-C14-N9	109.6(3)
N9-Ni1-N5	89.16(9)	C14-C15-N10	106.1(3)
N11-Ni1-N5	178.15(9)	C16-N11-C18	104.5(3)
N3-Ni1-N5	88.04(9)	C16-N11-Ni1	127.8(2)
C1-N1-C3	104.2(2)	C18-N11-Ni1	127.5(2)
C1-N1-Ni1	127.8(2)	C16-N12-C17	107.7(3)
C3-N1-Ni1	128.04(19)	N11-C16-N12	111.6(3)
C1-N2-C2	108.1(3)	C18-C17-N12	106.1(3)
N1-C1-N2	111.3(3)	C17-C18-N11	110.0(3)
C3-C2-N2	105.7(3)	O2-C19-O1	124.6(3)
C2-C3-N1	110.8(3)	O2-C19-C20	117.8(3)
C6-N3-C4	104.1(2)	O1-C19-C20	117.4(3)
C6-N3-Ni1	126.8(2)	C21-C20-C25	119.0(3)
C4-N3-Ni1	127.51(19)	C21-C20-C19	117.6(3)
C6-N4-C5	107.5(3)	C25-C20-C19	123.3(3)
C5-C4-N3	110.4(3)	C20-C21-C22	120.3(3)
C4-C5-N4	106.4(3)	C23-C22-C21	119.4(3)
N3-C6-N4	111.5(3)	C24-C23-C22	120.4(3)
C7-N5-C9	104.3(2)	C23-C24-C25	121.1(3)
C7-N5-Ni1	127.5(2)	C24-C25-C20	119.7(3)
C9-N5-Ni1	128.24(19)	C24-C25-C26	120.4(3)
C7-N6-C8	107.4(3)	C20-C25-C26	119.9(3)
N5-C7-N6	112.0(3)	O3-C26-O4	123.1(3)
C9-C8-N6	106.3(3)	O3-C26-C25	118.9(3)
C8-C9-N5	110.0(3)	O4-C26-C25	118.0(3)
C10-N7-C11	104.1(3)		

Anisotropic displacement parameters (A^2 x 10^3) for $[Ni(Im)_6]pt\cdot H_2O$ **6**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Ni1	29(1)	36(1)	37(1)	-4(1)	9(1)	-3(1)
N1	31(1)	37(1)	37(1)	-2(1)	5(1)	-1(1)
N2	45(1)	32(1)	68(2)	-3(1)	7(1)	-4(1)
C1	43(2)	44(2)	44(2)	2(1)	9(1)	-3(1)
C2	53(2)	45(2)	54(2)	-15(2)	11(2)	2(2)
C3	53(2)	44(2)	42(2)	-3(1)	13(1)	-1(1)
N3	29(1)	42(1)	38(1)	-4(1)	8(1)	-4(1)
N4	36(1)	62(2)	50(2)	0(1)	-9(1)	-5(1)
C4	44(2)	45(2)	63(2)	-10(2)	-4(2)	-1(2)
C5	49(2)	51(2)	89(3)	-7(2)	-9(2)	10(2)
C6	37(2)	45(2)	37(2)	-4(1)	8(1)	-4(1)
N5	37(1)	41(1)	43(1)	-3(1)	13(1)	-3(1)
N6	41(1)	54(2)	58(2)	2(1)	25(1)	-1(1)
C7	37(2)	57(2)	45(2)	0(2)	12(1)	-2(1)
C8	57(2)	63(2)	50(2)	14(2)	23(2)	2(2)
C9	44(2)	59(2)	46(2)	11(2)	15(1)	4(2)
N7	33(1)	40(1)	50(2)	-9(1)	9(1)	-1(1)
N8	43(1)	45(2)	68(2)	-24(1)	9(1)	1(1)
C10	35(2)	53(2)	70(2)	-22(2)	17(2)	-6(1)
C11	70(2)	40(2)	71(2)	-4(2)	34(2)	-10(2)
C12	64(2)	36(2)	88(3)	-10(2)	26(2)	-11(2)
N9	31(1)	40(1)	45(1)	1(1)	12(1)	0(1)
N10	34(1)	55(2)	45(2)	7(1)	3(1)	0(1)
C13	32(2)	41(2)	47(2)	5(1)	6(1)	-4(1)
C14	44(2)	37(2)	54(2)	0(1)	13(1)	1(1)
C15	47(2)	43(2)	51(2)	6(2)	12(2)	10(1)

N11	39(1)	49(2)	40(1)	-8(1)	13(1)	-7(1)
N12	42(1)	75(2)	49(2)	-3(1)	23(1)	0(1)
C16	40(2)	51(2)	47(2)	-1(1)	16(1)	1(1)
C17	58(2)	138(4)	44(2)	22(2)	20(2)	4(2)
C18	41(2)	119(3)	42(2)	12(2)	9(2)	2(2)
O1	55(1)	62(1)	47(1)	21(1)	6(1)	-14(1)
O2	40(1)	66(2)	65(2)	28(1)	-4(1)	-6(1)
O3	62(2)	68(2)	71(2)	7(1)	29(1)	21(1)
O4	184(4)	90(2)	50(2)	-2(2)	35(2)	37(2)
C19	45(2)	50(2)	35(2)	10(1)	9(1)	0(1)
C20	31(1)	40(2)	42(2)	9(1)	12(1)	-1(1)
C21	51(2)	55(2)	62(2)	-1(2)	27(2)	3(2)
C22	46(2)	42(2)	110(3)	-1(2)	32(2)	8(2)
C23	39(2)	56(2)	83(3)	29(2)	6(2)	2(2)
C24	40(2)	53(2)	52(2)	18(2)	6(1)	-7(2)
C25	31(1)	45(2)	40(2)	9(1)	8(1)	-5(1)
C26	54(2)	61(2)	45(2)	-3(2)	21(2)	-9(2)
O5	56(1)	81(2)	55(2)	-14(1)	17(1)	17(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for [Ni(Im)$_6$]pt·H$_2$O **6**

	x	y	z	U(eq)
H2A	7278	-1607	7270	60
H1	7501	-201	8105	53
H2	7673	-1125	6111	62
H3	8175	674	6268	56
H4A	11851	1828	9672	64
H4	9887	72	8280	65
H5	11664	132	9121	82
H6	10292	2800	9183	48
H6A	11240	2669	6531	58
H7	10718	2217	7620	55
H8	9704	3030	5494	66
H9	8176	2801	5998	59
H8A	8515	5255	9388	64
H10	7636	3701	8950	63
H11	9804	4180	7895	69
H12	9868	5605	8756	74
H10A	4823	2612	5777	56
H13	6012	1468	6582	49
H14	7187	4237	6933	54
H15	5502	4355	5954	57
H12A	5399	1520	9088	64
H16	5900	2207	8047	54
H17	6907	742	9973	95
H18	8400	1009	9443	82
H21	4036	16	5176	64
H22	5076	-1140	6031	77
H23	5256	-937	7299	74
H24	4456	403	7724	60
H5A	3710(30)	1790(30)	9384(19)	99(16)
H5B	3650(40)	1460(40)	8670(11)	115(19)

Torsion angles [°] for [Ni(Im)$_6$]pt·H_2O **6**

N7-Ni1-N1-C1	-15(2)	C11-N7-C10-N8	-0.2(4)
N9-Ni1-N1-C1	-111.8(2)	Ni1-N7-C10-N8	171.6(2)
N11-Ni1-N1-C1	-19.5(2)	C12-N8-C10-N7	0.2(4)
N3-Ni1-N1-C1	70.9(2)	C10-N7-C11-C12	0.1(4)
N5-Ni1-N1-C1	159.0(2)	Ni1-N7-C11-C12	-171.6(2)
N7-Ni1-N1-C3	164(2)	N7-C11-C12-N8	0.0(4)
N9-Ni1-N1-C3	67.7(2)	C10-N8-C12-C11	-0.1(4)
N11-Ni1-N1-C3	160.0(2)	N7-Ni1-N9-C13	-159.9(3)
N3-Ni1-N1-C3	-109.5(2)	N1-Ni1-N9-C13	17.9(3)
N5-Ni1-N1-C3	-21.4(2)	N11-Ni1-N9-C13	-70.1(3)
C3-N1-C1-N2	0.6(3)	N3-Ni1-N9-C13	129.1(16)
Ni1-N1-C1-N2	-179.79(18)	N5-Ni1-N9-C13	108.7(3)
C2-N2-C1-N1	-0.5(3)	N7-Ni1-N9-C14	22.8(2)
C1-N2-C2-C3	0.2(3)	N1-Ni1-N9-C14	-159.3(2)
N2-C2-C3-N1	0.1(4)	N11-Ni1-N9-C14	112.6(2)
C1-N1-C3-C2	-0.4(3)	N3-Ni1-N9-C14	-48.2(18)
Ni1-N1-C3-C2	179.9(2)	N5-Ni1-N9-C14	-68.5(2)
N7-Ni1-N3-C6	-6.1(2)	C14-N9-C13-N10	-0.6(3)
N1-Ni1-N3-C6	176.0(2)	Ni1-N9-C13-N10	-178.36(19)
N9-Ni1-N3-C6	64.9(18)	C15-N10-C13-N9	0.7(4)
N11-Ni1-N3-C6	-95.9(2)	C13-N9-C14-C15	0.4(3)
N5-Ni1-N3-C6	85.3(2)	Ni1-N9-C14-C15	178.2(2)
N7-Ni1-N3-C4	-169.4(3)	N9-C14-C15-N10	0.0(3)
N1-Ni1-N3-C4	12.7(3)	C13-N10-C15-C14	-0.4(3)
N9-Ni1-N3-C4	-98.4(17)	N7-Ni1-N11-C16	90.0(3)
N11-Ni1-N3-C4	100.8(3)	N1-Ni1-N11-C16	-90.2(3)
N5-Ni1-N3-C4	-78.0(3)	N9-Ni1-N11-C16	-0.7(3)
C6-N3-C4-C5	-0.7(4)	N3-Ni1-N11-C16	178.4(3)
Ni1-N3-C4-C5	165.5(3)	N5-Ni1-N11-C16	-142(3)
N3-C4-C5-N4	0.9(4)	N7-Ni1-N11-C18	-95.4(3)
C6-N4-C5-C4	-0.7(4)	N1-Ni1-N11-C18	84.4(3)
C4-N3-C6-N4	0.3(3)	N9-Ni1-N11-C18	174.0(3)
Ni1-N3-C6-N4	-166.12(19)	N3-Ni1-N11-C18	-7.0(3)
C5-N4-C6-N3	0.3(4)	N5-Ni1-N11-C18	33(3)
N7-Ni1-N5-C7	80.0(3)	C18-N11-C16-N12	0.5(4)
N1-Ni1-N5-C7	-99.8(3)	Ni1-N11-C16-N12	176.1(2)
N9-Ni1-N5-C7	170.6(3)	C17-N12-C16-N11	-0.7(4)
N11-Ni1-N5-C7	-48(3)	C16-N12-C17-C18	0.7(5)
N3-Ni1-N5-C7	-8.4(3)	N12-C17-C18-N11	-0.4(5)
N7-Ni1-N5-C9	-100.8(3)	C16-N11-C18-C17	0.0(5)
N1-Ni1-N5-C9	79.4(3)	Ni1-N11-C18-C17	-175.6(3)
N9-Ni1-N5-C9	-10.2(3)	O2-C19-C20-C21	87.7(4)
N11-Ni1-N5-C9	131(3)	O1-C19-C20-C21	-87.1(4)
N3-Ni1-N5-C9	170.8(3)	O2-C19-C20-C25	-90.3(4)
C9-N5-C7-N6	0.5(4)	O1-C19-C20-C25	94.9(3)
Ni1-N5-C7-N6	179.9(2)	C25-C20-C21-C22	0.3(4)
C8-N6-C7-N5	-0.6(4)	C19-C20-C21-C22	-177.8(3)
C7-N6-C8-C9	0.4(4)	C20-C21-C22-C23	0.4(5)
N6-C8-C9-N5	-0.1(4)	C21-C22-C23-C24	-0.7(5)
C7-N5-C9-C8	-0.3(4)	C22-C23-C24-C25	0.3(5)
Ni1-N5-C9-C8	-179.6(2)	C23-C24-C25-C20	0.5(4)
N1-Ni1-N7-C10	-11(2)	C23-C24-C25-C26	-179.8(3)
N9-Ni1-N7-C10	85.2(3)	C21-C20-C25-C24	-0.8(4)
N11-Ni1-N7-C10	-7.1(3)	C19-C20-C25-C24	177.2(3)
N3-Ni1-N7-C10	-97.6(3)	C21-C20-C25-C26	179.5(3)
N5-Ni1-N7-C10	174.4(3)	C19-C20-C25-C26	-2.5(4)
N1-Ni1-N7-C11	158(2)	C24-C25-C26-O3	-179.4(3)
N9-Ni1-N7-C11	-104.9(3)	C20-C25-C26-O3	0.4(4)
N11-Ni1-N7-C11	162.8(3)	C24-C25-C26-O4	1.4(5)

N3-Ni1-N7-C11	72.3(3)	C20-C25-C26-O4	-178.8(3)
N5-Ni1-N7-C11	-15.7(3)		

Hydrogen bonding geometry [Å and °] for [Ni(Im)$_6$]pt·H_2O **6**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)	Symmetry code
C2-H2···O2	0.93	2.41	3.255(4)	150.3	-x+1,-y,-z+1
C6-H6···N7	0.93	2.6	3.070(4)	111.9	x, y, z
C6-H6···O2	0.93	2.63	3.111(4)	112.9	x+1,-y+1/2,z+1/2
C7-H7···N3	0.93	2.62	3.095(4)	112.5	x, y, z
C10-H10···N11	0.93	2.66	3.119(4)	111	x, y, z
N2-H2A···O3	0.86	2.43	3.076(4)	132.7	-x+1,y-1/2,-z+3/2
N2-H2A···O4	0.86	2.01	2.854(4)	168.6	-x+1,y-1/2,-z+3/2
N4-H4A···O1	0.86	2.22	3.043(3)	159	x+1,-y+1/2,z+1/2
N4-H4A···O2	0.86	2.47	3.010(4)	121.2	x+1,-y+1/2,z+1/2
N6-H6A···O3	0.86	1.89	2.743(3)	170.9	x+1,y,z
N8-H8A···O2	0.86	1.93	2.768(3)	163.6	-x+1,y+1/2,-z+3/2
N10-H10A···O1	0.86	1.97	2.823(3)	171.7	x, y, z
N12-H12A···O5	0.86	1.96	2.810(4)	169.8	x, y, z
O5-H5A···O1	0.859(19)	1.915(19)	2.757(3)	166(4)	x,-y+1/2,z+1/2
O5-H5B···O4	0.863(19)	1.86(2)	2.695(4)	163(5)	x, y, z
C2-H2···O2	0.93	2.41	3.255(4)	150.3	-x+1,-y,-z+1
C6-H6···N7	0.93	2.6	3.070(4)	111.9	x, y, z
C6-H6···O2	0.93	2.63	3.111(4)	112.9	x+1,-y+1/2,z+1/2
C7-H7···N3	0.93	2.62	3.095(4)	112.5	x, y, z
C10-H10···N11	0.93	2.66	3.119(4)	111	x, y, z
N2-H2A···O3	0.86	2.43	3.076(4)	132.7	-x+1,y-1/2,-z+3/2
N2-H2A···O4	0.86	2.01	2.854(4)	168.6	-x+1,y-1/2,-z+3/2
N4-H4A···O1	0.86	2.22	3.043(3)	159	x+1,-y+1/2,z+1/2
N4-H4A···O2	0.86	2.47	3.010(4)	121.2	x+1,-y+1/2,z+1/2
N6-H6A···O3	0.86	1.89	2.743(3)	170.9	x+1,y,z
N8-H8A···O2	0.86	1.93	2.768(3)	163.6	-x+1,y+1/2,-z+3/2
N10-H10A···O1	0.86	1.97	2.823(3)	171.7	x, y, z
N12-H12A···O5	0.86	1.96	2.810(4)	169.8	x, y, z
O5-H5A···O1	0.859(19)	1.915(19)	2.757(3)	166(4)	x,-y+1/2,z+1/2
O5-H5B···O4	0.863(19)	1.86(2)	2.695(4)	163(5)	x, y, z

Structure protocol for [Co(Im)$_6$]pt·H$_2$O **7**

Crystal data and structure refinement for [Co(Im)$_6$]pt·H$_2$O **7**

Identification code	CoImpt
Empirical formula	$C_{26}H_{30}CoN_{12}O_5$
Formula weight	649.55
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	13.1134(4)
b (Å)	13.0374(4)
c (Å)	18.4269(6)
α (°)	90
β (°)	105.388(2)
γ (°)	90
Volume (Å^3)	3037.41(17)
Z	4
D_{calc} (mg/m^3)	1.420
Absorption coefficient (mm^{-1})	0.622
F(000)	1348
Crystal size (mm^3)	0.40 x 0.30 x 0.30
θ range for data collection (°)	2.244 to 25.00
Index ranges	$-15 \leq h \leq 15$ $-15 \leq h \leq 15$ $-15 \leq h \leq 15$
Reflections collected / unique	45501 / 5337 [R(int) = 0.0386]
Completeness to theta = 25.00°	100.00%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.82 and 0.71
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5337 / 10 / 416
Goodness-of-fit on F^2	1.146
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0820
R indices (all data)	R1 = 0.0583, wR2 = 0.1009
Extinction coefficient	0.0076(4)
Largest diff. peak and hole (e Å $^{-3}$)	0.368 and -0.374

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for [Co(Im)$_6$]pt·H$_2$O **7**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
C1	7611(2)	-207(2)	7616(2)	45(1)
C2	7683(2)	-727(2)	6519(2)	53(1)
C3	7960(2)	263(2)	6612(2)	47(1)
C4	10202(2)	638(2)	8580(2)	56(1)
C5	11178(3)	660(3)	9042(2)	73(1)
C6	10428(2)	2128(2)	9054(1)	39(1)
C7	10288(2)	2411(2)	7133(2)	47(1)
C8	9756(3)	2847(3)	5969(2)	56(1)
C9	8915(2)	2720(2)	6250(2)	49(1)
C10	8190(2)	4029(2)	8777(2)	54(1)
C11	9393(3)	4278(2)	8226(2)	58(1)
C12	9431(3)	5065(2)	8700(2)	62(1)
C13	6091(2)	2193(2)	6539(2)	42(1)
C14	6725(2)	3705(2)	6720(2)	46(1)
C15	5799(2)	3778(2)	6189(2)	49(1)
C16	6344(2)	1875(2)	8468(2)	45(1)

C17	6876(3)	1073(4)	9526(2)	89(1)
C18	7696(3)	1221(4)	9228(2)	75(1)
C19	2943(2)	1619(2)	5368(2)	44(1)
C20	3628(2)	918(2)	5947(2)	36(1)
C21	4119(2)	110(2)	5690(2)	54(1)
C22	4731(2)	-587(2)	6200(2)	64(1)
C23	4843(2)	-467(3)	6954(2)	61(1)
C24	4369(2)	336(2)	7208(2)	50(1)
C25	3763(2)	1038(2)	6717(2)	38(1)
C26	3246(3)	1930(3)	7014(2)	52(1)
N1	7924(2)	602(2)	7304(1)	36(1)
N2	7464(2)	-1014(2)	7163(2)	51(1)
N3	9719(2)	1564(2)	8578(1)	38(1)
N4	11308(2)	1609(2)	9345(1)	55(1)
N5	9251(2)	2443(2)	6994(1)	39(1)
N6	10617(2)	2656(2)	6537(1)	49(1)
N7	8606(2)	3611(2)	8275(1)	42(1)
N8	8665(2)	4902(2)	9045(2)	54(1)
N9	6913(2)	2701(2)	6944(1)	39(1)
N10	5400(2)	2812(2)	6081(1)	47(1)
N11	7360(2)	1741(2)	8558(1)	44(1)
N12	6029(2)	1496(2)	9043(1)	56(1)
O1	3390(2)	2351(2)	5134(1)	57(1)
O2	1999(2)	1384(2)	5113(1)	62(1)
O3	2714(2)	2539(2)	6564(1)	65(1)
O4	3280(20)	2016(7)	7703(4)	90(4)
O4'	3720(20)	1960(30)	7715(8)	73(6)
O5	3935(2)	1322(2)	9134(2)	64(1)
Co1	8283(1)	2114(1)	7772(1)	35(1)

Bond lengths [Å] and angles [°] for $[Co(Im)_6]pt\cdot H_2O$ **7**

Co1-N7	2.153(2)	Co1-N11	2.175(2)
Co1-N1	2.154(2)	Co1-N3	2.187(2)
Co1-N9	2.165(2)	Co1-N5	2.195(2)
N1-C1	1.317(3)	N9-C14	1.375(3)
N1-C3	1.362(3)	N10-C13	1.334(3)
N2-C1	1.325(4)	N10-C15	1.358(4)
N2-C2	1.344(4)	C14-C15	1.345(4)
C2-C3	1.340(4)	N11-C16	1.309(3)
N3-C6	1.320(3)	N11-C18	1.376(4)
N3-C4	1.364(4)	N12-C16	1.330(4)
N4-C6	1.323(4)	N12-C17	1.343(4)
N4-C5	1.350(4)	C17-C18	1.344(5)
C4-C5	1.336(4)	C19-O2	1.240(3)
N5-C7	1.315(3)	C19-O1	1.255(3)
N5-C9	1.372(4)	C19-C20	1.507(4)
N6-C7	1.322(4)	C20-C21	1.382(4)
N6-C8	1.343(4)	C20-C25	1.392(4)
C8-C9	1.347(4)	C21-C22	1.398(5)
N7-C10	1.310(4)	C22-C23	1.367(5)
N7-C11	1.371(4)	C23-C24	1.363(5)
N8-C10	1.329(4)	C24-C25	1.381(4)
N7-Co1-N1	177.56(9)	C25-C26	1.519(4)
N8-C12	1.340(4)	C26-O3	1.223(4)
C11-C12	1.341(4)	C26-O4	1.265(6)
N9-C13	1.315(3)	C26-O4'	1.276(14)
N7-Co1-N9	90.85(8)	N7-Co1-N5	91.30(9)
N1-Co1-N9	89.37(8)	N1-Co1-N5	91.13(8)
N7-Co1-N11	89.82(9)	N9-Co1-N5	89.20(8)

N1-Co1-N11	87.74(9)	N3-Co1-N5	87.97(8)
N9-Co1-N11	92.52(9)	N7-Co1-N1	177.56(9)
N7-Co1-N3	88.25(8)	N9-Co1-N3	177.01(8)
N1-Co1-N3	91.65(8)	N11-Co1-N5	177.93(9)
N11-Co1-N3	90.33(8)		
N7-Co1-N9	90.85(8)	C10-N8-C12	107.2(3)
N1-Co1-N9	89.37(8)	N7-C10-N8	112.2(3)
N7-Co1-N11	89.82(9)	C12-C11-N7	109.9(3)
N1-Co1-N11	87.74(9)	N8-C12-C11	106.5(3)
N9-Co1-N11	92.52(9)	C13-N9-C14	104.7(2)
N7-Co1-N3	88.25(8)	C13-N9-Co1	128.61(18)
N1-Co1-N3	91.65(8)	C14-N9-Co1	126.65(18)
N9-Co1-N3	177.01(8)	C13-N10-C15	107.3(2)
N11-Co1-N3	90.33(8)	N9-C13-N10	111.8(2)
N7-Co1-N5	91.30(9)	C15-C14-N9	109.9(3)
N1-Co1-N5	91.13(8)	C14-C15-N10	106.2(3)
N9-Co1-N5	89.20(8)	C16-N11-C18	104.5(3)
N11-Co1-N5	177.93(9)	C16-N11-Co1	127.9(2)
N3-Co1-N5	87.97(8)	C18-N11-Co1	127.3(2)
C1-N1-C3	104.0(2)	C16-N12-C17	107.6(3)
C1-N1-Co1	128.17(19)	N11-C16-N12	111.8(3)
C3-N1-Co1	127.84(19)	N12-C17-C18	106.4(3)
C1-N2-C2	107.8(2)	C17-C18-N11	109.7(3)
N1-C1-N2	111.7(3)	O2-C19-O1	124.7(3)
C3-C2-N2	105.6(3)	O2-C19-C20	117.7(2)
C2-C3-N1	110.8(3)	O1-C19-C20	117.3(2)
C6-N3-C4	104.3(2)	C21-C20-C25	119.4(3)
C6-N3-Co1	126.63(19)	C21-C20-C19	117.6(3)
C4-N3-Co1	127.45(18)	C25-C20-C19	123.0(2)
C6-N4-C5	107.5(2)	C20-C21-C22	120.1(3)
C5-C4-N3	110.4(3)	C23-C22-C21	119.8(3)
C4-C5-N4	106.2(3)	C24-C23-C22	120.1(3)
N3-C6-N4	111.7(3)	C23-C24-C25	121.3(3)
C7-N5-C9	104.2(2)	C24-C25-C20	119.3(3)
C7-N5-Co1	127.79(19)	C24-C25-C26	120.4(3)
C9-N5-Co1	127.98(18)	C20-C25-C26	120.3(2)
C7-N6-C8	107.5(2)	O3-C26-O4	119.0(7)
N5-C7-N6	112.2(3)	O3-C26-O4'	134.5(19)
N6-C8-C9	106.4(3)	O4-C26-O4'	26.1(7)
C8-C9-N5	109.7(3)	O3-C26-C25	118.8(3)
C10-N7-C11	104.2(2)	O4-C26-C25	122.0(6)
C10-N7-Co1	127.6(2)	O4'-C26-C25	104.4(19)
C11-N7-Co1	127.70(19)		

Anisotropic displacement parameters (Å^{2}x 10^3) for [Co(Im)$_6$]pt·H$_2$O **7**. The anisotropicn displacement factor exponent takes the form: -2□^{2}[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U11	U22	U33	U23	U13	U12
C1	44(2)	43(2)	45(2)	4(1)	9(1)	-3(1)
C2	56(2)	47(2)	55(2)	-15(2)	12(2)	2(2)
C3	56(2)	46(2)	40(2)	-4(1)	14(1)	-1(1)
C4	48(2)	44(2)	67(2)	-10(2)	-5(2)	-1(1)
C5	53(2)	54(2)	94(3)	-9(2)	-14(2)	11(2)
C6	36(1)	44(2)	35(1)	-5(1)	7(1)	-4(1)
C7	38(2)	58(2)	45(2)	1(1)	11(1)	-1(1)
C8	60(2)	63(2)	52(2)	15(2)	25(2)	4(2)
C9	44(2)	59(2)	47(2)	12(1)	14(1)	5(1)
C10	36(2)	54(2)	73(2)	-25(2)	16(2)	-7(1)
C11	70(2)	40(2)	73(2)	-7(2)	36(2)	-8(2)
C12	65(2)	38(2)	87(3)	-12(2)	28(2)	-11(2)

C13	33(1)	40(2)	47(2)	6(1)	5(1)	-4(1)
C14	48(2)	37(2)	53(2)	-2(1)	14(1)	-2(1)
C15	52(2)	44(2)	50(2)	7(1)	14(1)	9(1)
C16	40(2)	52(2)	47(2)	0(1)	17(1)	0(1)
C17	60(2)	167(4)	43(2)	22(2)	19(2)	3(3)
C18	43(2)	142(4)	39(2)	16(2)	9(2)	2(2)
C19	46(2)	50(2)	35(2)	10(1)	8(1)	-1(1)
C20	31(1)	39(1)	40(2)	9(1)	12(1)	-1(1)
C21	52(2)	55(2)	61(2)	-1(2)	26(2)	2(2)
C22	45(2)	44(2)	111(3)	1(2)	33(2)	10(2)
C23	40(2)	57(2)	79(3)	28(2)	5(2)	1(2)
C24	39(2)	54(2)	52(2)	18(2)	5(1)	-6(1)
C25	32(1)	44(2)	39(2)	10(1)	8(1)	-5(1)
C26	55(2)	59(2)	45(2)	-4(2)	21(2)	-8(2)
N1	33(1)	36(1)	37(1)	-3(1)	6(1)	-1(1)
N2	45(1)	33(1)	69(2)	-2(1)	6(1)	-2(1)
N3	31(1)	43(1)	38(1)	-4(1)	8(1)	-4(1)
N4	39(1)	64(2)	50(2)	-1(1)	-9(1)	-5(1)
N5	36(1)	41(1)	42(1)	-3(1)	12(1)	-4(1)
N6	42(1)	53(2)	59(2)	3(1)	25(1)	0(1)
N7	34(1)	39(1)	52(1)	-10(1)	9(1)	-1(1)
N8	44(1)	46(2)	68(2)	-26(1)	9(1)	1(1)
N9	33(1)	40(1)	45(1)	1(1)	12(1)	1(1)
N10	36(1)	55(2)	46(1)	6(1)	4(1)	-1(1)
N11	40(1)	54(1)	38(1)	-9(1)	11(1)	-8(1)
N12	43(1)	80(2)	51(2)	-4(1)	23(1)	-1(1)
O1	58(1)	61(1)	46(1)	23(1)	6(1)	-14(1)
O2	44(1)	67(1)	65(1)	31(1)	-4(1)	-6(1)
O3	62(1)	66(1)	72(2)	7(1)	29(1)	22(1)
O4	137(11)	88(3)	50(3)	7(2)	35(3)	54(5)
O4'	58(11)	111(12)	54(7)	-38(9)	22(6)	7(8)
O5	58(1)	80(2)	55(2)	-14(1)	18(1)	18(1)
Co1	31(1)	36(1)	37(1)	-5(1)	9(1)	-3(1)

Torsion angles [°] for [Co(Im)$_6$]pt·H$_2$O **7**

N2-C2-C3-N1	0.3(3)	C3-C2-N2-C1	0.0(3)
N3-C4-C5-N4	0.9(4)	N4-C6-N3-C4	-0.1(3)
N6-C8-C9-N5	-0.4(4)	N4-C6-N3-Co1	-166.28(18)
N7-C11-C12-N8	-0.4(4)	C5-C4-N3-C6	-0.5(4)
N9-C14-C15-N10	0.2(3)	C5-C4-N3-Co1	165.5(3)
N12-C17-C18-N11	0.1(5)	N3-C6-N4-C5	0.6(4)
O2-C19-C20-C21	88.2(3)	C4-C5-N4-C6	-0.9(4)
O1-C19-C20-C21	-86.1(3)	N6-C7-N5-C9	0.6(3)
O2-C19-C20-C25	-90.3(4)	N6-C7-N5-Co1	-179.85(19)
O1-C19-C20-C25	95.4(3)	C8-C9-N5-C7	-0.1(3)
C25-C20-C21-C22	1.0(4)	C8-C9-N5-Co1	-179.7(2)
C19-C20-C21-C22	-177.5(3)	N5-C7-N6-C8	-0.9(4)
C20-C21-C22-C23	-0.1(5)	C9-C8-N6-C7	0.7(4)
C21-C22-C23-C24	-0.7(5)	N8-C10-N7-C11	-0.4(4)
C22-C23-C24-C25	0.6(5)	N8-C10-N7-Co1	171.33(19)
C23-C24-C25-C20	0.3(4)	C12-C11-N7-C10	0.5(4)
C23-C24-C25-C26	-179.7(3)	C12-C11-N7-Co1	-171.2(2)
C21-C20-C25-C24	-1.1(4)	N7-C10-N8-C12	0.1(4)
C19-C20-C25-C24	177.3(3)	C11-C12-N8-C10	0.2(4)
C21-C20-C25-C26	179.0(3)	N10-C13-N9-C14	-0.4(3)
C19-C20-C25-C26	-2.6(4)	N10-C13-N9-Co1	-179.63(18)
C24-C25-C26-O3	180.0(3)	C15-C14-N9-C13	0.1(3)
C20-C25-C26-O3	-0.1(4)	C15-C14-N9-Co1	179.35(19)
C24-C25-C26-O4	-5.9(15)	N9-C13-N10-C15	0.5(3)
C20-C25-C26-O4	174.0(15)	C14-C15-N10-C13	-0.5(3)

C24-C25-C26-O4'	15.2(11)	N12-C16-N11-C18	1.4(4)
C20-C25-C26-O4'	-164.9(11)	N12-C16-N11-Co1	175.82(19)
N2-C1-N1-C3	0.6(3)	C17-C18-N11-C16	-0.9(5)
N2-C1-N1-Co1	180.00(17)	C17-C18-N11-Co1	-175.4(3)
C2-C3-N1-C1	-0.6(3)	N11-C16-N12-C17	-1.4(4)
C2-C3-N1-Co1	-179.99(19)	C18-C17-N12-C16	0.8(5)
N1-C1-N2-C2	-0.4(3)		

Hydrogen bonding geometry [Å and °] for [Co(Im)$_6$]pt·H$_2$O **7**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)	Symmetry codes
C2-H2···O2	0.93	2.42	3.260(4)	150.3	-x+1,-y,-z+1
C6-H6 ···O2	0.93	2.63	3.112(3)	112.6	x+1,-y+1/2,z+1/2
N2-H2A ···O3	0.86	2.42	3.068(4)	132.4	-x+1,y-1/2,-z+3/2
N2-H2A ···O4	0.86	1.93	2.781(10)	169.9	-x+1,y-1/2,-z+3/2
N4-H4A ···O1	0.86	2.23	3.049(3)	159.5	x+1,-y+1/2,z+1/2
N4-H4A ···O2	0.86	2.45	2.999(3)	121.9	x+1,-y+1/2,z+1/2
N6-H6A ···O3	0.86	1.89	2.742(3)	170	x+1,y,z
N8-H8A ···O2	0.86	1.92	2.759(3)	164.3	-x+1,y+1/2,-z+3/2
N10-H10A ···O1	0.86	1.96	2.813(3)	173.1	x, y, z
N12-H12A ···O5	0.86	1.95	2.804(3)	169.6	x, y, z
O5-H5A ···O1	0.845(18)	1.919(18)	2.756(3)	171(4)	x,-y+1/2,z+1/2
O5-H5B ···O4	0.858(18)	1.85(2)	2.703(7)	170(5)	x, y, z

Structure protocol for $[Cu_2(Im)_4(pt)_2(H_2O)]\cdot H_2O$ **8**

Crystal data and structure refinement for $[Cu_2(Im)_4(pt)_2(H_2O)]\cdot H_2O$ **8**

Identification code	CuImpt
Empirical formula	$C_{28}H_{28}Cu_2N_8O_{10}$
Formula weight (g mol^{-1})	763.66
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	8.8768(4)
b (Å)	22.3595(12)
c (Å)	16.1084(9)
α (°)	90
β (°)	105.454(2)
γ (°)	90
Volume (Å^3)	3081.6(3)
Z	4
D_{calc} (mg/m^3)	1.646
Absorption coefficient (mm^{-1})	1.451
F(000)	1560
Crystal size (mm^3)	0.30 x 0.30 x 0.25
θ range for data collection (°)	2.245 to 26.999
Index ranges	$-11 \leq h \leq 11$ $-28 \leq k \leq 28$ $-20 \leq l \leq 20$
Reflections collected / unique	51507/6736 (R(int) = 0.0308)
Completeness to θ = 26.999°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.73 and 0.55
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6736 / 15 / 449
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0298, wR2 = 0.0683
R indices (all data)	R1 = 0.0407, wR2 = 0.0732
Extinction coefficient	n/a
Largest diff. peak and hole (e Å^{-3})	0.416 and -0.308

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $[Cu_2(Im)_4(pt)_2(H_2O)]\cdot H_2O$ **8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	11335(2)	1052(1)	3278(1)	23(1)
C2	12108(3)	3048(1)	4114(2)	36(1)
C3	13582(3)	2959(1)	3240(2)	48(1)
C4	12626(3)	2485(1)	3152(2)	40(1)
C5	6679(2)	1617(1)	3219(1)	29(1)
C6	6642(3)	688(1)	3596(2)	42(1)
C7	8085(3)	914(1)	3930(2)	36(1)
C8	8164(2)	2816(1)	2659(1)	21(1)
C9	7276(2)	3360(1)	2271(1)	24(1)
C10	7731(3)	3919(1)	2625(2)	34(1)
C11	6973(3)	4429(1)	2252(2)	52(1)
C12	5757(4)	4387(1)	1525(2)	63(1)
C13	5297(3)	3836(1)	1158(2)	50(1)
C14	6044(2)	3317(1)	1518(1)	27(1)
C15	5424(2)	2733(1)	1090(1)	24(1)
C16	781(3)	2141(1)	1045(1)	32(1)
C17	125(3)	2918(1)	211(2)	42(1)

C18	1471(3)	2689(1)	120(2)	42(1)
C19	7053(2)	1289(1)	1312(1)	29(1)
C20	7105(3)	461(1)	637(3)	81(1)
C21	5656(3)	688(1)	406(3)	73(1)
C22	2240(2)	614(1)	1729(1)	23(1)
C23	2580(2)	264(1)	2561(1)	23(1)
C24	2298(2)	492(1)	3312(1)	23(1)
C25	2807(3)	173(1)	4077(2)	33(1)
C26	3533(3)	-377(1)	4089(2)	42(1)
C27	3759(3)	-610(1)	3343(2)	43(1)
C28	3298(3)	-291(1)	2582(2)	34(1)
N1	11697(2)	2544(1)	3707(1)	28(1)
N2	13246(2)	3311(1)	3854(1)	43(1)
N3	8111(2)	1501(1)	3692(1)	24(1)
N4	5767(2)	1140(1)	3150(1)	35(1)
N5	1877(2)	2196(1)	645(1)	28(1)
N6	-288(2)	2568(1)	800(1)	38(1)
N7	5614(2)	1208(1)	844(1)	30(1)
N8	7975(2)	844(1)	1211(1)	41(1)
O1	10513(2)	1219(1)	2567(1)	31(1)
O2	11388(2)	1314(1)	3984(1)	29(1)
O3	8509(2)	2760(1)	3483(1)	26(1)
O4	8542(2)	2447(1)	2187(1)	28(1)
O5	5254(2)	2673(1)	307(1)	38(1)
O6	5022(2)	2343(1)	1562(1)	26(1)
O7	2876(2)	1385(1)	-448(1)	33(1)
O8	3079(2)	1065(1)	1729(1)	31(1)
O9	1204(2)	417(1)	1099(1)	37(1)
O10	15169(2)	4297(1)	4417(1)	37(1)
Cu1	9954(1)	2023(1)	3782(1)	23(1)
Cu2	3770(1)	1711(1)	779(1)	27(1)

Bond lengths [Å] and angles [°] for $[Cu_2(Im)_4(pt)_2(H_2O)]\cdot H_2O$ **8**

C1-O1	1.241(2)	C17-C18	1.343(3)
C1-O2	1.270(2)	C17-N6	1.353(3)
C1-C24#1	1.509(3)	C18-N5	1.377(3)
C2-N1	1.307(3)	C19-N7	1.311(3)
C2-N2	1.329(3)	C19-N8	1.325(3)
C3-C4	1.343(3)	C20-C21	1.339(4)
C3-N2	1.359(3)	C20-N8	1.343(3)
C4-N1	1.375(3)	C21-N7	1.367(3)
C5-N3	1.321(3)	C22-O8	1.253(2)
C5-N4	1.325(3)	C22-O9	1.254(2)
C6-C7	1.349(3)	C22-C23	1.511(3)
C6-N4	1.359(3)	C23-C28	1.390(3)
C7-N3	1.370(3)	C23-C24	1.395(3)
C8-O4	1.227(2)	C24-C25	1.390(3)
C8-O3	1.286(2)	C24-C1#2	1.509(3)
C8-C9	1.495(3)	C25-C26	1.386(3)
C9-C10	1.389(3)	C26-C27	1.374(4)
C9-C14	1.403(3)	C27-C28	1.383(3)
C10-C11	1.378(3)	N1-Cu1	1.9660(17)
C11-C12	1.368(4)	N3-Cu1	1.9825(16)
C12-C13	1.380(4)	N5-Cu2	1.9618(17)
C13-C14	1.384(3)	N7-Cu2	1.9661(17)
C14-C15	1.510(3)	O2-Cu1	2.0033(14)
C15-O5	1.236(2)	O3-Cu1	2.0662(14)
C15-O6	1.270(2)	O6-Cu2	2.0183(14)
C16-N5	1.308(3)	O7-Cu2	2.0572(16)
C16-N6	1.331(3)	O8-Cu2	2.3040(14)

O1-C1-O2	124.03(18)	C26-C25-C24	120.5(2)
O1-C1-C24#1	118.15(18)	C27-C26-C25	120.0(2)
O2-C1-C24#1	117.80(17)	C26-C27-C28	120.1(2)
N1-C2-N2	111.0(2)	C27-C28-C23	120.5(2)
C4-C3-N2	106.2(2)	C2-N1-C4	105.88(19)
C3-C4-N1	109.1(2)	C2-N1-Cu1	126.81(16)
N3-C5-N4	111.3(2)	C4-N1-Cu1	126.99(15)
C7-C6-N4	106.3(2)	C2-N2-C3	107.8(2)
C6-C7-N3	109.4(2)	C5-N3-C7	105.28(18)
O4-C8-O3	123.05(18)	C5-N3-Cu1	125.15(15)
O4-C8-C9	119.28(17)	C7-N3-Cu1	128.16(15)
O3-C8-C9	117.67(17)	C5-N4-C6	107.66(18)
C10-C9-C14	119.44(19)	C16-N5-C18	105.66(18)
C10-C9-C8	119.88(18)	C16-N5-Cu2	128.39(15)
C14-C9-C8	120.56(18)	C18-N5-Cu2	125.90(15)
C11-C10-C9	120.7(2)	C16-N6-C17	108.54(19)
C12-C11-C10	119.8(2)	C19-N7-C21	104.91(19)
C11-C12-C13	120.3(2)	C19-N7-Cu2	128.47(15)
C12-C13-C14	120.9(2)	C21-N7-Cu2	126.62(16)
C13-C14-C9	118.7(2)	C19-N8-C20	107.55(19)
C13-C14-C15	117.2(2)	C1-O2-Cu1	110.49(12)
C9-C14-C15	124.00(18)	C8-O3-Cu1	106.26(12)
O5-C15-O6	124.0(2)	C15-O6-Cu2	107.58(12)
O5-C15-C14	119.32(19)	C22-O8-Cu2	140.19(14)
O6-C15-C14	116.55(18)	N1-Cu1-N3	172.51(7)
N5-C16-N6	110.6(2)	N1-Cu1-O2	90.11(7)
C18-C17-N6	105.7(2)	N3-Cu1-O2	91.34(7)
C17-C18-N5	109.5(2)	N1-Cu1-O3	87.85(7)
N7-C19-N8	111.5(2)	N3-Cu1-O3	90.19(6)
C21-C20-N8	106.5(2)	O2-Cu1-O3	175.59(6)
C20-C21-N7	109.6(2)	N5-Cu2-N7	176.60(8)
O8-C22-O9	126.16(19)	N5-Cu2-O6	89.75(7)
O8-C22-C23	116.00(17)	N7-Cu2-O6	93.14(6)
O9-C22-C23	117.76(18)	N5-Cu2-O7	89.40(7)
C28-C23-C24	119.42(19)	N7-Cu2-O7	87.20(7)
C28-C23-C22	117.76(19)	O6-Cu2-O7	148.83(6)
C24-C23-C22	122.67(17)	N5-Cu2-O8	92.77(6)
C25-C24-C23	119.39(19)	N7-Cu2-O8	88.34(7)
C25-C24-C1#2	120.26(19)	O6-Cu2-O8	102.93(6)
C23-C24-C1#2	120.16(18)	O7-Cu2-O8	108.23(6)

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z   #2 x-1,y,z

Anisotropic displacement parameters (Å^{2}x 10^3) for [Cu$_2$(Im)$_4$(pt)$_2$(H$_2$O)]·H$_2$O **8**. The anisoropic displacement factor exponent takes the form: -2□^{2}[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U11	U22	U33	U23	U13	U12
C1	19(1)	23(1)	27(1)	1(1)	5(1)	-2(1)
C2	31(1)	35(1)	42(1)	-6(1)	9(1)	-5(1)
C3	42(1)	55(2)	50(2)	-2(1)	20(1)	-10(1)
C4	34(1)	48(1)	38(1)	-11(1)	12(1)	-8(1)
C5	26(1)	33(1)	27(1)	2(1)	5(1)	-3(1)
C6	43(1)	31(1)	51(2)	0(1)	11(1)	-12(1)
C7	37(1)	28(1)	39(1)	2(1)	6(1)	0(1)
C8	18(1)	22(1)	23(1)	-1(1)	4(1)	-3(1)
C9	28(1)	22(1)	22(1)	1(1)	10(1)	-1(1)
C10	44(1)	26(1)	31(1)	-1(1)	8(1)	-6(1)
C11	72(2)	19(1)	60(2)	-1(1)	11(2)	-2(1)
C12	73(2)	26(1)	79(2)	12(1)	0(2)	14(1)

C13	50(2)	33(1)	53(2)	10(1)	-8(1)	8(1)
C14	28(1)	25(1)	27(1)	4(1)	5(1)	2(1)
C15	19(1)	29(1)	23(1)	2(1)	1(1)	5(1)
C16	32(1)	37(1)	27(1)	5(1)	9(1)	0(1)
C17	39(1)	38(1)	47(2)	11(1)	9(1)	10(1)
C18	36(1)	52(2)	43(1)	22(1)	17(1)	7(1)
C19	26(1)	32(1)	28(1)	-5(1)	4(1)	0(1)
C20	38(2)	47(2)	140(3)	-48(2)	-10(2)	15(1)
C21	32(1)	44(2)	121(3)	-46(2)	-17(2)	5(1)
C22	21(1)	22(1)	25(1)	1(1)	5(1)	4(1)
C23	20(1)	21(1)	26(1)	1(1)	2(1)	-2(1)
C24	20(1)	22(1)	25(1)	2(1)	3(1)	0(1)
C25	36(1)	36(1)	27(1)	5(1)	7(1)	3(1)
C26	47(1)	36(1)	40(1)	18(1)	6(1)	9(1)
C27	53(2)	23(1)	52(2)	8(1)	10(1)	12(1)
C28	39(1)	26(1)	37(1)	0(1)	9(1)	6(1)
N1	22(1)	30(1)	30(1)	-2(1)	4(1)	-4(1)
N2	39(1)	35(1)	52(1)	-4(1)	8(1)	-14(1)
N3	25(1)	25(1)	22(1)	-4(1)	5(1)	-2(1)
N4	26(1)	42(1)	34(1)	0(1)	4(1)	-11(1)
N5	23(1)	36(1)	25(1)	4(1)	5(1)	4(1)
N6	31(1)	47(1)	40(1)	0(1)	18(1)	6(1)
N7	21(1)	28(1)	39(1)	-6(1)	2(1)	1(1)
N8	21(1)	37(1)	59(1)	-6(1)	-1(1)	5(1)
O1	31(1)	35(1)	26(1)	3(1)	4(1)	12(1)
O2	29(1)	29(1)	25(1)	-4(1)	3(1)	5(1)
O3	28(1)	26(1)	22(1)	0(1)	4(1)	2(1)
O4	27(1)	30(1)	27(1)	-6(1)	7(1)	4(1)
O5	49(1)	42(1)	22(1)	-1(1)	7(1)	-1(1)
O6	26(1)	27(1)	25(1)	0(1)	5(1)	-1(1)
O7	32(1)	40(1)	24(1)	1(1)	4(1)	-5(1)
O8	26(1)	33(1)	31(1)	9(1)	5(1)	-5(1)
O9	44(1)	34(1)	27(1)	-2(1)	-4(1)	-5(1)
O10	42(1)	27(1)	38(1)	-3(1)	5(1)	-1(1)
Cu1	19(1)	22(1)	26(1)	-2(1)	3(1)	0(1)
Cu2	19(1)	30(1)	29(1)	-4(1)	2(1)	2(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for $[Cu_2(Im)_4(pt)_2(H_2O)]\cdot H_2O$ **8**

	x	y	z	U(eq)
H2	11664	3202	4531	43
H3	14325	3033	2940	57
H4	12597	2167	2775	47
H5	6354	1985	2966	35
H6	6313	299	3658	50
H7	8932	704	4270	43
H10	8557	3950	3119	41
H11	7287	4802	2495	62
H12	5237	4730	1278	76
H13	4473	3813	661	60
H16	753	1844	1446	38
H17	-412	3248	-72	50
H18	2041	2840	-240	51
H19	7384	1617	1669	35
H20	7442	108	440	98
H21	4809	517	9	88
H25	2660	330	4584	40
H26	3866	-588	4603	50
H27	4222	-984	3349	52
H28	3470	-448	2080	41

H2A	13690	3645	4042	52
H4A	4795	1121	2873	42
H6A	-1105	2615	985	45
H8	8953	808	1467	49
H7A	2900(30)	1652(10)	-809(15)	49(8)
H7B	2000(20)	1225(12)	-557(19)	64(10)
H10A	14750(30)	4605(10)	4172(16)	55(9)
H10B	15460(40)	4346(14)	4953(11)	81(12)

Torsion angles [°] for $[Cu_2(Im)_4(pt)_2(H_2O)]\cdot H_2O$ **8**

N2-C3-C4-N1	0.3(3)	C26-C27-C28-C23	-1.1(4)
N4-C6-C7-N3	-0.3(3)	C24-C23-C28-C27	-1.2(3)
O4-C8-C9-C10	-133.3(2)	C22-C23-C28-C27	174.5(2)
O3-C8-C9-C10	46.1(3)	N2-C2-N1-C4	-0.3(3)
O4-C8-C9-C14	42.7(3)	N2-C2-N1-Cu1	-174.23(15)
O3-C8-C9-C14	-137.89(19)	C3-C4-N1-C2	0.0(3)
C14-C9-C10-C11	0.9(3)	C3-C4-N1-Cu1	173.93(18)
C8-C9-C10-C11	177.0(2)	N1-C2-N2-C3	0.5(3)
C9-C10-C11-C12	0.0(4)	C4-C3-N2-C2	-0.4(3)
C10-C11-C12-C13	-0.7(5)	N4-C5-N3-C7	0.2(2)
C11-C12-C13-C14	0.4(5)	N4-C5-N3-Cu1	167.56(14)
C12-C13-C14-C9	0.5(4)	C6-C7-N3-C5	0.0(3)
C12-C13-C14-C15	177.8(3)	C6-C7-N3-Cu1	-166.79(17)
C10-C9-C14-C13	-1.2(3)	N3-C5-N4-C6	-0.4(3)
C8-C9-C14-C13	-177.2(2)	C7-C6-N4-C5	0.4(3)
C10-C9-C14-C15	-178.3(2)	N6-C16-N5-C18	0.3(3)
C8-C9-C14-C15	5.7(3)	N6-C16-N5-Cu2	177.74(15)
C13-C14-C15-O5	52.2(3)	C17-C18-N5-C16	-0.6(3)
C9-C14-C15-O5	-130.6(2)	C17-C18-N5-Cu2	-178.13(17)
C13-C14-C15-O6	-123.7(2)	N5-C16-N6-C17	0.1(3)
C9-C14-C15-O6	53.4(3)	C18-C17-N6-C16	-0.5(3)
N6-C17-C18-N5	0.7(3)	N8-C19-N7-C21	-1.8(3)
N8-C20-C21-N7	-0.9(5)	N8-C19-N7-Cu2	177.71(16)
O8-C22-C23-C28	-107.9(2)	C20-C21-N7-C19	1.6(4)
O9-C22-C23-C28	69.1(3)	C20-C21-N7-Cu2	-177.9(3)
O8-C22-C23-C24	67.8(2)	N7-C19-N8-C20	1.3(3)
O9-C22-C23-C24	-115.2(2)	C21-C20-N8-C19	-0.2(4)
C28-C23-C24-C25	3.0(3)	O1-C1-O2-Cu1	0.6(2)
C22-C23-C24-C25	-172.55(19)	C24#1-C1-O2-Cu1	-177.67(13)
C28-C23-C24-C1#2	-171.94(18)	O4-C8-O3-Cu1	6.4(2)
C22-C23-C24-C1#2	12.5(3)	C9-C8-O3-Cu1	-172.93(13)
C23-C24-C25-C26	-2.5(3)	O5-C15-O6-Cu2	-9.5(2)
C1#2-C24-C25-C26	172.4(2)	C14-C15-O6-Cu2	166.21(13)
C24-C25-C26-C27	0.2(4)	O9-C22-O8-Cu2	-13.3(3)
C25-C26-C27-C28	1.6(4)	C23-C22-O8-Cu2	163.43(14)

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z   #2 x-1,y,z

Hydrogen bonding geometry [Å and °] for $[Cu_2(Im)_4(pt)_2(H_2O)]\cdot H_2O$ **8**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)	Symmetry code
C5-H5···O6	0.93	2.39	3.135(3)	136.7	x, y, z
C16-H16···O1	0.93	2.34	3.259(3)	170.7	x-1, y, z
C16-H16···O8	0.93	2.65	3.157(3)	115.2	x, y, z
C18-H18···N3	0.93	2.63	3.532(3)	164.8	x-1/2, -y+1/2, z-1/2
C19-H19···O4	0.93	2.18	3.073(3)	161.5	x, y, z
N2-H2A···O10	0.86	1.95	2.788(3)	165.1	x, y, z
N4-H4A···O8	0.86	2.06	2.837(2)	150.2	x, y, z
N6-H6A···O4	0.86	2.08	2.717(2)	130.6	x-1, y, z
N8-H8···O1	0.86	2.14	2.815(2)	134.6	x, y, z
N8-H8···O9	0.86	2.4	3.072(3)	135.9	x+1, y, z
O7-H7A···O3	0.838(16)	1.909(16)	2.730(2)	166(3)	x-1/2, -y+1/2, z-1/2
O7-H7B···O10	0.831(16)	1.993(16)	2.805(2)	166(3)	x-3/2, -y+1/2, z-1/2
O10-H10A···O9	0.831(16)	2.001(19)	2.812(2)	165(3)	-x+3/2, y+1/2, -z+1/2
O10-H10B···O9	0.839(17)	1.865(19)	2.695(2)	170(3)	x+3/2, -y+1/2, z+1/2
C5-H5···O6	0.93	2.39	3.135(3)	136.7	x, y, z
C16-H16···O1	0.93	2.34	3.259(3)	170.7	x-1, y, z
C16-H16···O8	0.93	2.65	3.157(3)	115.2	x, y, z
C18-H18···N3	0.93	2.63	3.532(3)	164.8	x-1/2, -y+1/2, z-1/2
C19-H19···O4	0.93	2.18	3.073(3)	161.5	x, y, z
N2-H2A···O10	0.86	1.95	2.788(3)	165.1	x, y, z
N4-H4A···O8	0.86	2.06	2.837(2)	150.2	x, y, z
N6-H6A···O4	0.86	2.08	2.717(2)	130.6	x-1, y, z
N8-H8···O1	0.86	2.14	2.815(2)	134.6	x, y, z
N8-H8···O9	0.86	2.4	3.072(3)	135.9	x+1, y, z
O7-H7A···O3	0.838(16)	1.909(16)	2.730(2)	166(3)	x-1/2, -y+1/2, z-1/2
O7-H7B···O10	0.831(16)	1.993(16)	2.805(2)	166(3)	x-3/2, -y+1/2, z-1/2
O10-H10A···O9	0.831(16)	2.001(19)	2.812(2)	165(3)	-x+3/2, y+1/2, -z+1/2
O10-H10B···O9	0.839(17)	1.865(19)	2.695(2)	170(3)	x+3/2, -y+1/2, z+1/2

Structure protocol for [Na(H_2O)$_3$(2-carboxy-6-nba)].H_2O **9**

Crystal data and structure refinement for [Na(H_2O)$_3$(2-carboxy-6-nba)].H_2O **9**

Empirical formula	$C_8H_{12}NNaO_{10}$
Formula weight (g mol^{-1})	305.18
Temperature (K)	170(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	6.8903(5)
b (Å)	7.5137(5)
c (Å)	12.8854(9)
α (°)	77.567(6)
β (°)	83.374(6)
γ (°)	74.389(6)
Volume (Å^3)	626.25(8)
Z	2
D_{calc} (mg/m^3)	1.618
Absorption coefficient (mm^{-1})	0.179
F(000)	316
Crystal size (mm^3)	0.08 x 0.12 x 0.35
θ range for data collection (°)	1.621 to 28.004
Index ranges	$-9 \leq h \leq 9$ $-8 \leq k \leq 9$ $-17 \leq l \leq 17$
Reflections collected / unique	8266/3002 (R(int) = 0.0330)
Completeness to θ = 25.242°	99.5 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3002 / 0 /182
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0316, wR2 = 0.0857
R indices (all data)	R1 = 0.0377, wR2 = 0.0877
Extinction coefficient	n/a
Largest diff. peak and hole (e Å^{-3})	0.340 and -0.217

Comments

A numerical absorption correction was performed (Tmin/max: 0.8175/0.9609). All non-hydrogen atoms were refined anisotropic. The C-H H atoms were located in difference map but were positioned with idealized geometry and refined isotropic with U_{iso}(H) = 1.2 U_{eq}(C) using a riding model. The water O-H H atoms were located in difference map, their bond lengths were set to ideal values and finally they were refined isotropic with U_{iso}(H) = 1.5 U_{eq}(O) using a riding model. The hydroxyl H atom was located in difference map but were positioned with idealized geometry allowed to rotate but not to tip and refined isotropic with U_{iso}(H) = 1.2 U_{eq}(C) using a riding model.

Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for [Na(H_2O)$_3$(2-carboxy-6-nba)].H_2O **9**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Na1	7534(1)	4838(1)	5096(1)	25(1)
C1	7965(2)	7918(2)	1371(1)	19(1)
C2	6986(2)	9601(2)	1715(1)	18(1)
C3	6651(2)	11239(2)	937(1)	21(1)
C4	7098(2)	11263(2)	-144(1)	25(1)
C5	7929(2)	9565(2)	-465(1)	26(1)
C6	8407(2)	7913(2)	286(1)	23(1)
C7	8580(2)	6124(2)	2169(1)	20(1)
O1	9924(1)	4807(1)	1755(1)	29(1)
O2	7934(1)	5923(1)	3090(1)	28(1)
C8	6350(2)	9672(1)	2877(1)	19(1)
O3	4691(1)	9306(1)	3212(1)	23(1)
O4	7506(1)	10110(1)	3402(1)	24(1)
N1	5812(2)	13066(1)	1258(1)	24(1)
O5	4557(2)	13155(1)	2014(1)	40(1)
O6	6410(2)	14413(1)	759(1)	38(1)
O7	5630(1)	2804(1)	4786(1)	24(1)
O8	10736(1)	2822(1)	4933(1)	25(1)
O9	7166(1)	3523(1)	6986(1)	32(1)
O10	10817(1)	1515(1)	3050(1)	25(1)

Bond lengths [Å] and angles [°] for [Na(H_2O)$_3$(2-carboxy-6-nba)].H_2O **9.**

Na1-O8	2.3318(9)	Na1-O9	2.4346(10)
Na1-O8#1	2.3666(10)	Na1-O2	2.5434(10)
Na1-O7	2.3825(10)	Na1-Na1#1	3.4487(9)
Na1-O7#2	2.4241(9)	Na1-Na1#2	3.4687(9)
O7-Na1#2	2.4241(9)	O8-Na1#1	2.3665(10)
O8-Na1-O8#1	85.55(3)	O7-Na1-O9	87.53(3)
O8-Na1-O7	97.66(3)	O7#2-Na1-O9	90.86(3)
O8#1-Na1-O7	168.86(4)	O8-Na1-O2	85.86(3)
O8-Na1-O7#2	174.17(4)	O8#1-Na1-O2	81.30(3)
O8#1-Na1-O7#2	88.80(3)	O7-Na1-O2	88.28(3)
O7-Na1-O7#2	87.62(3)	O7#2-Na1-O2	91.86(3)
O8-Na1-O9	91.82(3)	O9-Na1-O2	174.90(4)
O8#1-Na1-O9	103.07(3)		

C1-C6	1.3978(15)	C5-C6	1.3864(17)
C1-C2	1.4009(15)	C7-O2	1.2112(13)
C1-C7	1.5002(15)	C7-O1	1.3199(13)
C2-C3	1.3941(15)	C8-O4	1.2497(14)
C2-C8	1.5191(14)	C8-O3	1.2543(13)
C3-C4	1.3877(16)	N1-O6	1.2208(14)
C3-N1	1.4675(14)	N1-O5	1.2258(14)
C4-C5	1.3808(17)		

C6-C1-C2	120.12(10)	C5-C6-C1	120.94(11)
C6-C1-C7	119.79(10)	O2-C7-O1	124.12(10)
C2-C1-C7	120.07(9)	O2-C7-C1	123.65(10)
C3-C2-C1	116.66(10)	O1-C7-C1	112.22(9)

C3-C2-C8	120.89(10)	O4-C8-O3	126.33(10)
C1-C2-C8	122.43(9)	O4-C8-C2	117.33(9)
C4-C3-C2	123.81(11)	O3-C8-C2	116.34(9)
C4-C3-N1	116.92(10)	O6-N1-O5	123.67(11)
C2-C3-N1	119.26(9)	O6-N1-C3	118.03(10)
C5-C4-C3	118.08(10)	O5-N1-C3	118.30(9)
C4-C5-C6	120.08(10)		

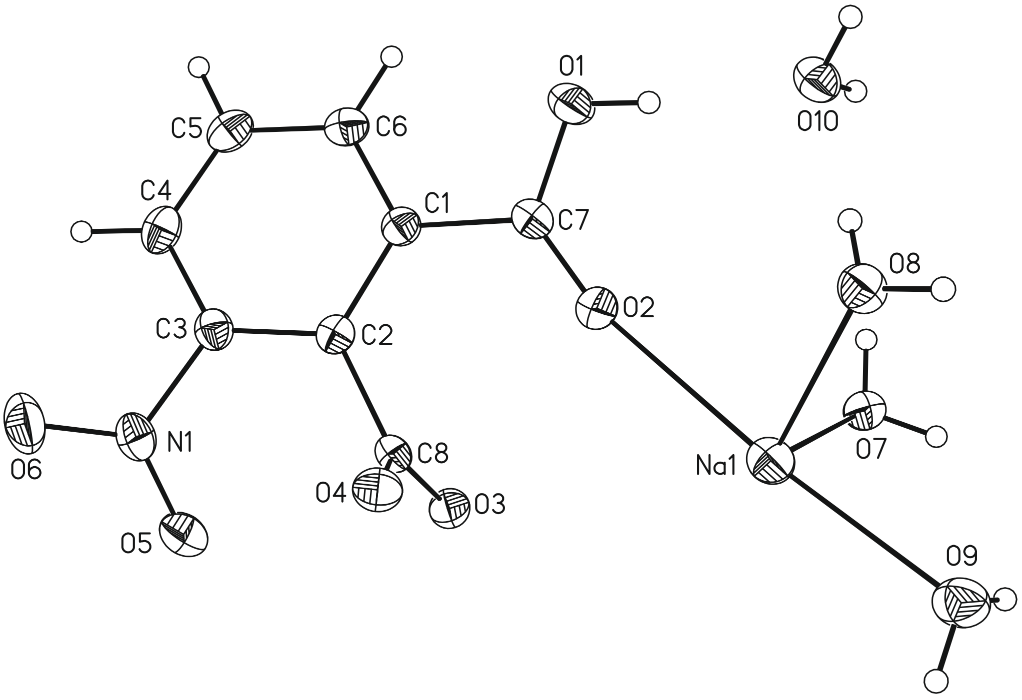
Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+1   #2 -x+1,-y+1,-z+1

Anisotropic displacement parameters (Å^{2}x 10^3) for [Na(H$_2$O)$_3$(2-carboxy-6-nba)].H$_2$O **9**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2 a^{*2}U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

	U11	U22	U33	U23	U13	U12
Na1	22(1)	24(1)	30(1)	-6(1)	0(1)	-6(1)
C1	18(1)	20(1)	20(1)	-4(1)	-1(1)	-6(1)
C2	16(1)	20(1)	18(1)	-3(1)	-2(1)	-5(1)
C3	19(1)	19(1)	23(1)	-3(1)	-2(1)	-5(1)
C4	26(1)	27(1)	21(1)	2(1)	-4(1)	-9(1)
C5	28(1)	33(1)	17(1)	-5(1)	0(1)	-9(1)
C6	23(1)	26(1)	21(1)	-7(1)	1(1)	-6(1)
C7	20(1)	19(1)	23(1)	-6(1)	-2(1)	-4(1)
O1	33(1)	23(1)	25(1)	-5(1)	-1(1)	4(1)
O2	33(1)	23(1)	22(1)	-2(1)	3(1)	-2(1)
C8	20(1)	14(1)	20(1)	-3(1)	-1(1)	-1(1)
O3	20(1)	22(1)	25(1)	-4(1)	3(1)	-5(1)
O4	26(1)	26(1)	22(1)	-8(1)	-2(1)	-7(1)
N1	26(1)	19(1)	27(1)	-1(1)	-7(1)	-4(1)
O5	45(1)	23(1)	45(1)	-9(1)	14(1)	-2(1)
O6	51(1)	23(1)	43(1)	-2(1)	-2(1)	-17(1)
O7	28(1)	24(1)	22(1)	-6(1)	1(1)	-6(1)
O8	27(1)	25(1)	24(1)	-5(1)	-5(1)	-4(1)
O9	36(1)	31(1)	34(1)	-12(1)	2(1)	-11(1)
O10	22(1)	22(1)	31(1)	-6(1)	-2(1)	-3(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for [Na(H$_2$O)$_3$(2-carboxy-6-nba)].H$_2$O **9**.

	x	y	z	U(eq)
H4	6841	12414	-647	30
H5	8172	9529	-1202	31
H6	9045	6761	59	28
H1	10168	3803	2211	44
H7A	5569	2040	5363	37
H7B	6073	2195	4296	37
H8A	11266	1973	5432	38
H8B	10817	2401	4373	38
H9A	6408	2788	7065	48
H9B	6603	4388	7320	48
H10A	9971	875	3092	38
H10B	11996	820	3033	38



Hydrogen bonding geometry [Å and °] for [Na(H_2O)$_3$(2-carboxy-6-nba)].H_2O **9**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)	Symmetry code
O7-H7A...O3	0.84	1.91	2.7414(11)	169.7	-x+1, -y+1, -z+1
O7-H7B...O4	0.84	2.11	2.9263(11)	164.9	x, y-1, z
O8-H8A...O4	0.84	2	2.8368(12)	178	-x+2, -y+1, -z+1
O8-H8B...O10	0.84	1.96	2.7975(12)	176.1	X, y, z
O9-H9A...O3	0.84	2.03	2.8269(13)	157.9	-x+1, -y+1, -z+1
O9-H9B...O5	0.84	2.12	2.9558(13)	170.8	-x+1, -y+2, -z+1
O10-H10A...O4	0.84	1.91	2.7155(12)	160.5	x, y-1, z
O10-H10B...O3	0.84	1.91	2.7419(11)	171.1	x+1, y-1, z

Structure Protocol for [K(3-npht)] **10**

Crystal data and structure refinement for [K(3-npht)] **10**

Identification code	srini165
Empirical formula	$C_8 H_4 K N O_6$
Formula weight (g mol^{-1})	763.66
Temperature (K)	249.22
Wavelength (Å)	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	13.0237(8)
b (Å)	8.6490(4)
c (Å)	8.2763(4)
α (°)	90
β (°)	102.771(4)
γ (°)	90
Volume (Å^3)	909.20(8)
Z	4
D_{calc} (mg/m^3)	1.821
Absorption coefficient (mm^{-1})	0.598
F(000)	504
Crystal size (mm^3)	0.08 x 0.12 x 0.20
θ range for data collection (°)	1.603 to 26.000°.
Index ranges	$-16 \leq h \leq 16$
	$-10 \leq k \leq 10$
	$-8 \leq l \leq 10$
Reflections collected / unique	6839/1783 [R(int) = 0.0651]
Completeness to θ = 26.50°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1783 / 0 / 145
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1273
R indices (all data)	R1 = 0.0529, wR2 = 0.1324
Extinction coefficient	n/a
Largest diff. peak and hole (e Å^{-3})	0.490 and -0.547

Comments

A numerical absorption correction was performed (Tmin/max: 0.7856/0.9287). All non-hydrogen atoms were refined anisotropic. The C-H H atoms were positioned with idealized geometry and refined isotropic with $U_{iso}(H) = 1.2\ U_{eq}(C)$ using a riding model. The K-H H atom was located in difference map, its bond length were set to ideal values and finally it was refined isotropic with $U_{iso}(H) = 1.5\ U_{eq}(O)$ using a riding model.

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for [K(3-npht)] **10**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
K1	4304(1)	7779(1)	4753(1)	37(1)
C1	7390(2)	8441(3)	3808(3)	32(1)
C2	7359(2)	6825(3)	3905(3)	32(1)
C3	8238(2)	6107(3)	4887(3)	36(1)
C4	9114(2)	6900(3)	5721(3)	42(1)
C5	9137(2)	8499(3)	5575(3)	44(1)
C6	8277(2)	9252(3)	4618(3)	40(1)
C7	6459(2)	9395(3)	2951(3)	33(1)
O1	5564(1)	8696(2)	2557(2)	33(1)
O2	6579(1)	10782(2)	2725(2)	42(1)
C8	6409(2)	5923(3)	3007(3)	32(1)
O3	6260(1)	5675(2)	1526(2)	36(1)
O4	5793(1)	5477(2)	3962(2)	36(1)
N1	8265(2)	4409(3)	5078(3)	43(1)
O5	8933(2)	3848(2)	6188(3)	60(1)
O6	7619(2)	3636(2)	4125(3)	62(1)

Bond lengths [Å] and angles [°] for [K(3-npht)] **10.**

K1-O2#1	2.7328(18)	K1-O3#3	2.9630(18)
K1-O3#2	2.7552(17)	K1-O4#5	3.0226(17)
K1-O1	2.8190(17)	K1-O6#5	3.108(3)
K1-O1#3	2.8324(17)	K1-K1#3	4.1662(2)
K1-O2#4	2.879(2)	K1-K1#6	4.1662(2)
K1-O4	2.9522(18)	O3-K1#1	2.7552(17)
O1-K1#6	2.8324(17)	O3-K1#6	2.9631(18)
O2-K1#2	2.7328(18)	O4-K1#5	3.0226(17)
O2-K1#4	2.879(2)	O1-K1-O3#3	68.45(5)
O6-K1#5	3.108(3)	O1#3-K1-O3#3	61.21(5)
O2#1-K1-O3#2	104.73(5)	O2#4-K1-O3#3	83.31(5)
O2#1-K1-O1	84.40(5)	O4-K1-O3#3	83.04(5)
O3#2-K1-O1	68.92(5)	O2#1-K1-O4#5	68.39(5)
O2#1-K1-O1#3	113.68(5)	O3#2-K1-O4#5	162.53(5)
O3#2-K1-O1#3	141.37(5)	O1-K1-O4#5	124.37(5)
O1-K1-O1#3	109.90(6)	O1#3-K1-O4#5	49.75(4)
O2#1-K1-O2#4	130.39(7)	O2#4-K1-O4#5	95.35(5)
O3#2-K1-O2#4	76.71(5)	O4-K1-O4#5	61.98(5)
O1-K1-O2#4	136.77(5)	O3#3-K1-O4#5	110.15(5)
O1#3-K1-O2#4	81.53(5)	O2#1-K1-O6#5	75.06(6)
O2#1-K1-O4	66.15(5)	O3#2-K1-O6#5	107.99(5)
O3#2-K1-O4	131.34(5)	O1-K1-O6#5	157.82(6)
O1-K1-O4	62.75(4)	O1#3-K1-O6#5	86.39(5)
O1#3-K1-O4	65.64(5)	O2#4-K1-O6#5	58.41(5)
O2#4-K1-O4	147.09(5)	O4-K1-O6#5	114.39(5)
O2#1-K1-O3#3	146.09(6)	O3#3-K1-O6#5	133.72(5)
O3#2-K1-O3#3	84.66(5)	O4#5-K1-O6#5	55.18(5)
C1-C6	1.390(3)	C5-C6	1.383(4)
C1-C2	1.401(3)	C7-O2	1.230(3)
C1-C7	1.509(3)	C7-O1	1.289(3)
C2-C3	1.395(3)	C8-O3	1.217(3)
C2-C8	1.511(3)	C8-O4	1.303(3)
C3-C4	1.379(3)	N1-O5	1.217(3)
C3-N1	1.477(3)	N1-O6	1.218(3)
C4-C5	1.389(4)	C6-C5-C4	119.2(2)
C6-C1-C2	120.5(2)	C5-C6-C1	121.3(2)
C6-C1-C7	116.5(2)	O2-C7-O1	123.9(2)

C2-C1-C7	122.8(2)	O2-C7-C1	119.2(2)
C3-C2-C1	116.5(2)	O1-C7-C1	116.8(2)
C3-C2-C8	122.3(2)	O3-C8-O4	125.2(2)
C1-C2-C8	121.2(2)	O3-C8-C2	121.1(2)
C4-C3-C2	123.5(2)	O4-C8-C2	113.64(19)
C4-C3-N1	116.3(2)	O5-N1-O6	123.1(2)
C2-C3-N1	120.2(2)	O5-N1-C3	118.2(2)
C3-C4-C5	118.9(2)	O6-N1-C3	118.7(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y-1/2,-z+1/2 #2 -x+1,y+1/2,-z+1/2 #3 x,-y+3/2,z+1/2
#4 -x+1,-y+2,-z+1 #5 -x+1,-y+1,-z+1 #6 x,-y+3/2,z-1/2

Anisotropic displacement parameters (Å^{2}x 10^3) for [K(3-npht)] **10**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
K1	50(1)	26(1)	33(1)	1(1)	6(1)	0(1)
C1	37(1)	30(1)	30(1)	-1(1)	4(1)	-1(1)
C2	36(1)	29(1)	30(1)	-3(1)	4(1)	0(1)
C3	40(1)	30(1)	37(1)	1(1)	4(1)	1(1)
C4	39(1)	44(1)	41(1)	4(1)	-1(1)	0(1)
C5	41(1)	41(1)	43(1)	0(1)	-3(1)	-8(1)
C6	44(1)	33(1)	40(1)	-2(1)	5(1)	-6(1)
C7	41(1)	27(1)	28(1)	-3(1)	4(1)	1(1)
O1	36(1)	27(1)	34(1)	1(1)	2(1)	0(1)
O2	51(1)	25(1)	43(1)	2(1)	-1(1)	-4(1)
C8	37(1)	24(1)	32(1)	1(1)	3(1)	2(1)
O3	46(1)	30(1)	31(1)	-4(1)	6(1)	-3(1)
O4	42(1)	32(1)	30(1)	-1(1)	3(1)	-8(1)
N1	44(1)	32(1)	50(1)	1(1)	1(1)	5(1)
O5	61(1)	43(1)	62(1)	11(1)	-12(1)	10(1)
O6	65(1)	31(1)	74(2)	-5(1)	-17(1)	2(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for [K(3-npht)] **10.**

	x	y	z	U(eq)
H4	9693	6362	6385	51
H5	9736	9069	6127	52
H6	8293	10345	4511	47
H4A	5300	4972	3368	53

Hydrogen bonding geometry [Å and °] for [K(3-npht)] **10.**

D-H···A	d(D-H)	(H···A)	d(D···A)	<DHA	Symmetry code
C5-H5···O5	0.95	2.506	3.257	136.06	2-x, 0.5+ y, 1.5-z
O4-H4A···O1	0.84	1.640	2.469	168.57	1-x, -0.5+y, 0.5-z
D=Donor and A=Acceptor					

Structure protocol for *[Cs(3-nphtH)]·2H$_2$O* **11**

Crystal data and structure refinement for *[Cs(3-nphtH)]·2H$_2$O* **11.**

Identification code	RJCS21
Empirical formula	$C_{16}H_{13}CsN_2O_{14}$
Formula weight (g mol^{-1})	590.19
Temperature (K)	296(2) K
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pcca*
Unit cell dimensions	
a (Å)	13.1768(5)
b (Å)	11.6552(3)
c (Å)	13.4456(5)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	2064.95(12)
Z	4
D$_{calc}$ (mg/m^3)	1.898
Absorption coefficient (mm^{-1})	1.872
F(000)	1160
Crystal size (mm^3)	0.15 x 0.10 x 0.10
θ range for data collection (°)	3.402 to 28.407
Index ranges	$-17 \leq h \leq 17$ $-15 \leq k \leq 15$ $-18 \leq l \leq 16$
Reflections collected / unique	42355 / 3551 [R(int) = 0.0240]
Completeness to θ = 25.00°	97.2%
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.7457 and 0.6504
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2543 / 3 / 159
Goodness-of-fit on F^2	1.240
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.0748
R indices (all data)	R1 = 0.0473, wR2 = 0.0804
Extinction coefficient	0.0174(13)
Largest diff. peak and hole (e Å^{-3})	0.695 and -0.678

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for *[Cs(3-nphtH)]·2H$_2$O* **11**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cs1	5000	4302(1)	2500	46(1)
C1	6285(2)	7558(2)	2216(2)	31(1)
C2	6326(2)	8245(2)	3157(2)	28(1)
C3	6221(2)	9431(2)	3125(2)	36(1)
C4	6177(2)	10075(2)	3983(2)	41(1)
C5	6226(2)	9537(2)	4893(2)	37(1)
C6	6333(2)	8351(2)	4923(2)	30(1)
C7	6395(2)	7677(2)	4074(2)	26(1)
C8	6510(2)	6383(2)	4122(2)	29(1)
O1	6210(2)	6531(2)	2199(2)	47(1)
O2	6302(2)	8195(2)	1405(2)	44(1)
O3	7426(2)	6046(2)	3976(2)	36(1)
O4	5782(2)	5766(2)	4281(2)	35(1)
O5	6685(2)	6845(2)	5982(2)	50(1)
O6	6023(3)	8353(2)	6608(2)	69(1)

O7	4177(2)	3031(2)	154(2)	43(1)
N1	6358(2)	7814(2)	5909(2)	38(1)

Bond lengths [Å] and angles [°] for $[Cs(3\text{-}nphtH)]\cdot 2H_2O$ **11.**

Cs1-O1	3.075(2)	C2-C3	1.390(3)
Cs1-O4	3.116(2)	C2-C7	1.403(4)
Cs1-O7	3.649(2)	C3-C4	1.377(4)
Cs1-O1#2	3.075(2)	C4-C5	1.377(4)
Cs1-O4	3.116(2)	C5-C6	1.390(3)
Cs1-O5#1	3.300(3)	C6-C7	1.388(4)
Cs1-O5#3	3.300(3)	C6-N1	1.466(4)
Cs1-O6#1	3.582(3)	C7-C8	1.517(3)
Cs1-O6#3	3.582(3)	C8-O4	1.218(3)
Cs1-O7#2	3.649(2)	C8-O3	1.284(3)
C1-O1	1.202(3)	O5-N1	1.213(3)
C1-O2	1.319(3)	O6-N1	1.213(3)
C1-C2	1.498(4)		
O5#1-Cs1-O5#3	132.19(8)	O1-Cs1-O4#2	66.90(6)
O1-Cs1-O6#1	165.69(7)	O1#2-Cs1-O4#2	57.78(5)
O1#2-Cs1-O6#1	119.39(7)	O1-Cs1-O4	57.78(5)
O4#2-Cs1-O6#1	127.32(6)	O1#2-Cs1-O4	66.90(6)
O4-Cs1-O6#1	109.89(6)	O4#2-Cs1-O4	113.58(7)
O5#1-Cs1-O6#1	35.86(6)	O1-Cs1-O5#1	140.60(6)
O5#3-Cs1-O6#1	96.33(6)	O1#2-Cs1-O5#1	84.95(6)
O1-Cs1-O6#3	119.39(7)	O4#2-Cs1-O5#1	118.37(5)
O1#2-Cs1-O6#3	165.69(7)	O4-Cs1-O5#1	88.21(5)
O4#2-Cs1-O6#3	109.89(6)	O1-Cs1-O5#3	84.95(6)
O4-Cs1-O6#3	127.32(6)	O1#2-Cs1-O5#3	140.60(6)
O5#1-Cs1-O6#3	96.33(6)	O4#2-Cs1-O5#3	88.21(5)
O5#3-Cs1-O6#3	35.86(6)	O4-Cs1-O5#3	118.37(5)
O6#1-Cs1-O6#3	60.48(9)	O6-N1-O5	123.3(3)
O1-Cs1-O7	112.55(6)	O6-N1-C6	118.1(3)
O1#2-Cs1-O7	107.60(6)	O5-N1-C6	118.5(2)
O4#2-Cs1-O7	57.30(5)	O1-C1-O2	123.1(3)
O4-Cs1-O7	170.00(5)	O1-C1-C2	123.4(3)
O5#1-Cs1-O7	99.80(6)	O2-C1-C2	113.4(2)
O5#3-Cs1-O7	60.05(5)	C3-C2-C7	120.2(2)
O6#1-Cs1-O7	80.03(6)	C3-C2-C1	120.1(2)
O6#3-Cs1-O7	58.12(6)	C7-C2-C1	119.6(2)
O1-Cs1-O7#2	107.59(6)	C4-C3-C2	121.4(3)
O1#2-Cs1-O7#2	112.55(6)	C5-C4-C3	119.6(3)
O4#2-Cs1-O7#2	170.00(5)	C4-C5-C6	118.9(3)
O4-Cs1-O7#2	57.30(5)	C7-C6-C5	123.0(3)
O5#1-Cs1-O7#2	60.05(5)	C7-C6-N1	120.0(2)
O5#3-Cs1-O7#2	99.80(6)	C5-C6-N1	116.9(2)
O6#1-Cs1-O7#2	58.12(6)	C6-C7-C2	116.9(2)
O6#3-Cs1-O7#2	80.03(6)	C6-C7-C8	122.3(2)
O7-Cs1-O7#2	132.11(7)	C2-C7-C8	120.8(2)
C8-O4-Cs1	116.65(17)	O4-C8-O3	125.9(2)
N1-O5-Cs1#1	100.83(19)	O4-C8-C7	121.0(2)
N1-O6-Cs1#1	87.09(19)	O3-C8-C7	113.1(2)
O1-Cs1-O1#2	64.70(10)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,y,-z+1/2 #3 x,-y+1,z-1/2

Anisotropic displacement parameters (Å^{2}x 10^3) for $[Cs(3\text{-}nphtH)]\cdot 2H_2O$ **11**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
Cs1	70(1)	27(1)	41(1)	0	-2(1)	0
C1	29(1)	32(1)	32(1)	2(1)	2(1)	0(1)
C2	27(1)	24(1)	35(1)	-1(1)	1(1)	1(1)
C3	39(1)	27(1)	43(2)	6(1)	-1(1)	1(1)
C4	44(2)	22(1)	56(2)	-2(1)	2(1)	4(1)
C5	39(1)	28(1)	45(2)	-9(1)	4(1)	1(1)
C6	30(1)	27(1)	33(1)	-3(1)	0(1)	2(1)
C7	22(1)	23(1)	33(1)	1(1)	0(1)	2(1)
C8	30(1)	23(1)	32(1)	0(1)	0(1)	5(1)
O1	71(2)	31(1)	39(1)	-2(1)	3(1)	-10(1)
O2	66(1)	34(1)	33(1)	4(1)	2(1)	1(1)
O3	30(1)	25(1)	54(1)	-2(1)	0(1)	5(1)
O4	31(1)	28(1)	45(1)	3(1)	1(1)	-3(1)
O5	67(2)	42(1)	41(1)	4(1)	-7(1)	10(1)
O6	109(2)	60(2)	39(1)	-12(1)	14(1)	10(2)
O7	42(1)	40(1)	46(1)	0(1)	5(1)	4(1)
N1	41(1)	39(1)	35(1)	-3(1)	-1(1)	-2(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for $[Cs(3\text{-}nphtH)]\cdot 2H_2O$ **11.**

	x	y	z	U(eq)
H3	6180	9797	2512	44
H4	6114	10869	3947	49
H5	6189	9960	5478	45
H2A	6217	7786	916	53
H3A	7446	5343	3984	43
H7B	4530(20)	3530(30)	-140(30)	50(11)
H7A	3650(20)	3340(30)	380(30)	77(15)

Torsion angles [°] for $[Cs(3\text{-}nphtH)]\cdot 2H_2O$ **11.**

Cs1#1-O6-N1-O5	-36.6(3)	C4-C5-C6-N1	-178.6(3)
Cs1#1-O6-N1-C6	141.2(2)	C5-C6-C7-C2	-1.1(4)
Cs1#1-O5-N1-O6	41.2(3)	N1-C6-C7-C2	177.6(2)
Cs1#1-O5-N1-C6	-136.6(2)	C5-C6-C7-C8	-179.9(3)
O2-C1-O1-Cs1	-106.2(4)	N1-C6-C7-C8	-1.3(4)
C2-C1-O1-Cs1	71.1(5)	C3-C2-C7-C6	1.2(4)
O3-C8-O4-Cs1	-70.9(3)	C1-C2-C7-C6	-174.1(2)
C7-C8-O4-Cs1	108.9(2)	C3-C2-C7-C8	-179.9(2)
O1-C1-C2-C3	-167.9(3)	C1-C2-C7-C8	4.7(4)
O2-C1-C2-C3	9.7(4)	C6-C7-C8-O4	79.5(3)
O1-C1-C2-C7	7.5(4)	C2-C7-C8-O4	-99.2(3)
O2-C1-C2-C7	-175.0(2)	C6-C7-C8-O3	-100.7(3)
C7-C2-C3-C4	-0.4(4)	C2-C7-C8-O3	80.6(3)
C1-C2-C3-C4	175.0(3)	C7-C6-N1-O6	-159.5(3)
C2-C3-C4-C5	-0.7(5)	C5-C6-N1-O6	19.3(4)
C3-C4-C5-C6	0.8(5)	C7-C6-N1-O5	18.5(4)
C4-C5-C6-C7	0.1(4)	C5-C6-N1-O5	-162.8(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Hydrogen bonding geometry [Å and °] for $[Cs(3\text{-}nphtH)]\cdot 2H_2O$ **11.**

D-H···A	d(D-H)	(H···A)	d(D···A)	<DHA	Symmetry code
C3-H3···O2	0.930(.003)	2.394(.002)	2.728(.004)	100.92(0.19)	x, y, z
C3-H3···O6	0.930(.003)	2.485(.003)	3.303(.004)	146.88(0.19)	x,-y+2,+z-1/2
C4-H4···O7	0.930(.003)	2.822(.002)	3.666(.004)	151.44(0.19)	-x+1,+y+1,-z+1/2
C5-H5···O2	0.930(.003)	2.489(.002)	3.335(.004)	151.31(0.19)	x,-y+2,+z+1/2
O2-H2A···O7	0.820(.002)	1.801(.002)	2.614(.003)	170.83(0.17)	-x+1,-y+1,-z
O7-H7B···O1	0.844(.031)	2.946(.036)	3.245(.003)	103.20(2.68)	-x+1,-y+1,-z
O3-H3A···O4	0.820(.002)	2.701(.002)	3.195(.003)	120.40(0.14)	-x+1/2+1,-y+1,+z
O3-H3A···O3	0.820(.002)	1.626(.002)	2.444(.003)	175.55(0.15)	-x+1/2+1,-y+1,+z
O7-H7B···O4	0.844(.031)	1.993(.031)	2.794(.003)	158.22(2.92)	x,-y+1,+z-1/2
O7-H7B···O4	0.844(.031)	2.883(.030)	3.277(.003)	110.63(2.24)	-x+1,+y,-z+1/2
O7-H7A···O4	0.843(.033)	2.961(.037)	3.277(.003)	104.66(2.84)	-x+1,+y,-z+1/2
O7-H7A···O3	0.843(.033)	1.966(.035)	2.802(.003)	171.09(3.00)	x-1/2,-y+1,-z+1/2

D=Donor and A=Acceptor

Structure protocol for [Rb_2(3-npht)] **12**

Crystal data and structure refinement for [Rb_2(3-npht)] **12.**

Identification code	RB11
Empirical formula	$C_8H_3NO_6Rb_2$
Formula weight (g mol^{-1})	380.05
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	7.6198(9)
b (Å)	6.3293(7)
c (Å)	20.350(2)
α (°)	90
β (°)	94.480(4)
γ (°)	90
Volume (Å^3)	978.4(2)
Z	4
D_{calc} (mg/m^3)	2.580
Absorption coefficient (mm^{-1})	10.019
F(000)	720
Crystal size (mm^3)	0.10 x 0.10 x 0.05
θ range for data collection (°)	3.372 to 32.618
Index ranges	$-11 \leq h \leq 11$ $-9 \leq k \leq 9$ $-30 \leq l \leq 30$
Reflections collected / unique	26790 / 3551 [R(int) = 0.0357]
Completeness to θ = 25.00°	99.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.7462 and 0.5603
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3551 / 0 / 154
Goodness-of-fit on F^2	1.094
Final R indices [I>2sigma(I)]	R1 = 0.0245, wR2 = 0.0481
R indices (all data)	R1 = 0.0353, wR2 = 0.0505
Extinction coefficient	n/a
Largest diff. peak and hole (e Å^{-3})	0.682 and -0.747

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for [Rb_2(3-npht)] **12**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rb1	5543(1)	2664(1)	1388(1)	16(1)
Rb2	856(1)	3091(1)	2258(1)	18(1)
C1	5891(2)	3412(3)	2974(1)	13(1)
C2	6125(2)	2913(3)	3705(1)	11(1)
C3	7835(2)	2620(3)	3989(1)	14(1)
C4	8162(2)	2187(3)	4655(1)	16(1)
C5	6779(2)	2170(3)	5057(1)	14(1)
C6	5082(2)	2496(3)	4772(1)	10(1)
C7	4675(2)	2779(2)	4093(1)	9(1)
C8	2790(2)	2905(3)	3763(1)	12(1)
O1	7052(2)	4540(2)	2745(1)	23(1)
O2	4542(2)	2698(2)	2657(1)	19(1)
O3	2223(2)	4698(2)	3604(1)	18(1)
O4	2022(2)	1175(2)	3663(1)	18(1)
O5	4088(2)	2138(2)	5818(1)	19(1)
O6	2191(2)	3000(2)	5022(1)	20(1)
N1	3694(2)	2543(2)	5232(1)	13(1)

Bond lengths [Å] and angles [°][Rb$_2$(3-npht)] **12.**

Rb1-O3#2	2.8230(13)	Rb2-O4	3.1681(14)
Rb1-O4#1	2.9559(13)	C1-O1	1.254(2)
Rb1-O5#8	3.0242(15)	C1-O2	1.254(2)
Rb1-O1#3	3.1424(14)	C1-C2	1.518(2)
Rb1-O6#8	3.1657(14)	C2-C3	1.396(2)
Rb1-O1	3.1406(15)	C2-C7	1.409(2)
Rb1-O2	2.7491(14)	C3-C4	1.387(3)
Rb2-O2#1	2.9382(15)	C4-C5	1.383(3)
Rb2-O5#9	3.1316(13)	C5-C6	1.391(2)
Rb2-O1#2	3.1559(16)	C6-C7	1.404(2)
Rb2-O3#2	3.1995(14)	C6-N1	1.467(2)
Rb2-O4#1	3.2274(14)	C7-C8	1.539(2)
Rb2-O1#10	3.2667(15)	C8-O3	1.248(2)
Rb2-O2#2	3.4322(15)	C8-O4	1.251(2)
Rb2-O2	2.8723(14)	O5-N1	1.2342(19)
Rb2-O3	3.0284(14)	O6-N1	1.2254(19)

Rb1-O1-Rb1#4	152.74(5)	O2#1-Rb2-O1#2	129.16(4)
C1-O1-Rb2#1	83.74(11)	O3-Rb2-O1#2	115.67(4)
Rb1-O1-Rb2#1	93.35(4)	O5#9-Rb2-O1#2	73.40(4)
Rb1#4-O1-Rb2#1	86.08(4)	O2-Rb2-O4	60.86(4)
C1-O1-Rb2#5	128.38(12)	O2#1-Rb2-O4	110.49(4)
Rb1-O1-Rb2#5	84.25(4)	O3-Rb2-O4	42.30(4)
Rb1#4-O1-Rb2#5	81.63(3)	O5#9-Rb2-O4	153.71(4)
Rb2#1-O1-Rb2#5	147.00(5)	O1#2-Rb2-O4	82.93(4)
C1-O2-Rb1	102.08(11)	O2-Rb2-O3#2	67.51(4)
C1-O2-Rb2	149.10(12)	O2#1-Rb2-O3#2	138.76(4)
Rb1-O2-Rb2	94.17(4)	O3-Rb2-O3#2	125.57(3)
C1-O2-Rb2#2	114.27(11)	O5#9-Rb2-O3#2	68.74(4)
Rb1-O2-Rb2#2	94.86(4)	O1#2-Rb2-O3#2	82.64(3)
Rb2-O2-Rb2#2	89.97(4)	O4-Rb2-O3#2	97.47(4)
C1-O2-Rb2#1	71.84(10)	O2-Rb2-O4#1	72.13(4)
Rb1-O2-Rb2#1	95.00(4)	O2#1-Rb2-O4#1	59.50(4)
Rb2-O2-Rb2#1	80.79(3)	O3-Rb2-O4#1	99.78(4)
Rb2#2-O2-Rb2#1	166.94(5)	O5#9-Rb2-O4#1	71.48(4)
C8-O3-Rb1#1	147.86(12)	O1#2-Rb2-O4#1	144.38(4)
C8-O3-Rb2	90.93(10)	O4-Rb2-O4#1	129.65(2)
Rb1#1-O3-Rb2	91.40(4)	O3#2-Rb2-O4#1	79.37(4)
C8-O3-Rb2#1	126.03(11)	O2-Rb2-O1#10	144.08(4)
Rb1#1-O3-Rb2#1	86.03(4)	O2#1-Rb2-O1#10	66.78(4)
Rb2-O3-Rb2#1	82.49(3)	O3-Rb2-O1#10	83.23(4)
C8-O4-Rb1#2	164.51(12)	O5#9-Rb2-O1#10	88.27(4)
C8-O4-Rb2	84.57(10)	O1#2-Rb2-O1#10	63.973(18)
Rb1#2-O4-Rb2	96.77(4)	O4-Rb2-O1#10	91.54(4)
C8-O4-Rb2#2	111.99(11)	O3#2-Rb2-O1#10	144.06(3)
Rb1#2-O4-Rb2#2	83.38(3)	O4#1-Rb2-O1#10	120.21(3)
Rb2-O4-Rb2#2	79.92(3)	O2-Rb2-O2#2	89.31(4)
N1-O5-Rb1#6	101.80(10)	O2#1-Rb2-O2#2	166.95(5)
N1-O5-Rb2#7	165.61(11)	O3-Rb2-O2#2	108.31(3)
Rb1#6-O5-Rb2#7	88.57(4)	O5#9-Rb2-O2#2	88.15(3)
N1-O6-Rb1#6	94.98(10)	O1#2-Rb2-O2#2	39.39(3)
O2-Rb1-O3#2	74.79(4)	O4-Rb2-O2#2	66.02(3)
O2-Rb1-O4#1	78.23(4)	O3#2-Rb2-O2#2	53.56(3)
O3#2-Rb1-O4#1	90.47(4)	O4#1-Rb2-O2#2	132.90(3)
O2-Rb1-O5#8	132.96(4)	O1#10-Rb2-O2#2	100.37(3)
O3#2-Rb1-O5#8	136.00(4)	C1-O1-Rb1	83.72(10)
O4#1-Rb1-O5#8	124.28(4)	C1-O1-Rb1#4	123.18(11)
O2-Rb1-O1	43.99(4)	O6-N1-O5	122.43(15)
O3#2-Rb1-O1	117.93(4)	O6-N1-C6	118.87(14)

O4#1-Rb1-O1	86.71(4)	O5-N1-C6	118.69(14)
O5#8-Rb1-O1	92.56(4)	O1-C1-O2	125.99(17)
O2-Rb1-O1#3	70.75(4)	O1-C1-C2	116.73(15)
O3#2-Rb1-O1#3	88.92(4)	O2-C1-C2	117.26(16)
O4#1-Rb1-O1#3	147.99(4)	C3-C2-C7	120.55(15)
O5#8-Rb1-O1#3	75.05(4)	C3-C2-C1	117.86(15)
O1-Rb1-O1#3	65.599(18)	C7-C2-C1	121.58(15)
O2-Rb1-O6#8	169.67(4)	C4-C3-C2	121.40(16)
O3#2-Rb1-O6#8	105.32(4)	C5-C4-C3	119.52(16)
O4#1-Rb1-O6#8	112.04(4)	C4-C5-C6	118.61(16)
O5#8-Rb1-O6#8	40.68(3)	C5-C6-C7	123.79(16)
O1-Rb1-O6#8	132.78(4)	C5-C6-N1	115.45(15)
O1#3-Rb1-O6#8	98.93(4)	C7-C6-N1	120.76(15)
O2-Rb2-O2#1	99.92(4)	C6-C7-C2	115.83(15)
O2-Rb2-O3	60.94(4)	C6-C7-C8	124.26(15)
O2#1-Rb2-O3	69.10(4)	C2-C7-C8	119.90(14)
O2-Rb2-O5#9	126.85(4)	O3-C8-O4	127.32(16)
O2#1-Rb2-O5#9	93.56(4)	O3-C8-C7	116.91(15)
O3-Rb2-O5#9	162.56(4)	O4-C8-C7	115.71(15)
O2-Rb2-O1#2	127.58(4)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1/2,-z+1/2 #2 -x+1/2,y-1/2,-z+1/2 #3 -x+3/2,y-1/2,-z+1/2,
#4 -x+3/2,y+1/2,-z+1/2 #5 x+1,y,z #6 x-1/2,-y+1/2,z+1/2 #7 x+1/2,-y+1/2,z+1/2 #8 x+1/2,-y+1/2,z-1/2 #9 x-1/2,-y+1/2,z-1/2 #10 x-1,y,z

Anisotropic displacement parameters (Å^{2}x 10^{3}) for [Rb$_2$(3-npht)] **12**. The anisotropic displacement factor exponent takes the form: $-2\square^{2}[\,h^{2}\,a^{*2}U^{11} + ... + 2\,h\,k\,a^{*}\,b^{*}\,U^{12}\,]$

	U11	U22	U33	U23	U13	U12
Rb1	16(1)	19(1)	14(1)	0(1)	5(1)	-2(1)
Rb2	18(1)	17(1)	19(1)	-2(1)	-3(1)	-1(1)
C1	14(1)	12(1)	13(1)	0(1)	2(1)	3(1)
C2	11(1)	10(1)	13(1)	-1(1)	1(1)	-1(1)
C3	10(1)	14(1)	17(1)	0(1)	2(1)	0(1)
C4	8(1)	20(1)	19(1)	1(1)	-3(1)	-1(1)
C5	13(1)	16(1)	12(1)	0(1)	-3(1)	-1(1)
C6	10(1)	10(1)	11(1)	-1(1)	1(1)	-1(1)
C7	9(1)	8(1)	11(1)	0(1)	0(1)	0(1)
C8	9(1)	17(1)	9(1)	-1(1)	0(1)	1(1)
O1	27(1)	23(1)	19(1)	5(1)	5(1)	-9(1)
O2	16(1)	29(1)	13(1)	-1(1)	0(1)	-2(1)
O3	17(1)	18(1)	18(1)	1(1)	-1(1)	7(1)
O4	14(1)	20(1)	21(1)	-1(1)	-3(1)	-5(1)
O5	21(1)	25(1)	11(1)	0(1)	2(1)	-1(1)
O6	9(1)	30(1)	21(1)	3(1)	3(1)	2(1)
N1	13(1)	12(1)	13(1)	-1(1)	2(1)	-2(1)

Hydrogen coordinates (x 10^{4}) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for [Rb$_2$(3-npht)] **12**.

	x	y	z	U(eq)
H3	8796	2719	3720	17
H4	9327	1904	4834	19
H5	6985	1940	5518	17

Torsion angles [°] for [Rb_2(3-npht)] **12.**

Rb1#5-O6-N1-O5	-3.46(17)	C7-C8-O4-Rb1#2	128.6(4)
Rb1#5-O6-N1-C6	177.24(12)	O3-C8-O4-Rb2	41.66(18)
Rb1#5-O5-N1-O6	3.69(18)	C7-C8-O4-Rb2	-135.61(13)
Rb2#6-O5-N1-O6	-131.7(4)	O3-C8-O4-Rb2#2	118.48(17)
Rb1#5-O5-N1-C6	-177.01(11)	C7-C8-O4-Rb2#2	-58.78(16)
Rb2#6-O5-N1-C6	47.6(5)	C5-C6-N1-O6	173.89(16)
Rb2#6-O5-N1-Rb1#5	-135.4(5)	C7-C6-N1-O6	-5.8(2)
C2-C7-C8-Rb2	5.9(2)	C5-C6-N1-O5	-5.4(2)
O2-C1-O1-Rb1	-20.55(18)	C7-C6-N1-O5	174.89(15)
C2-C1-O1-Rb1	161.02(14)	O1-C1-C2-C3	-35.4(2)
O2-C1-O1-Rb1#3	154.68(14)	O2-C1-C2-C3	146.08(17)
C2-C1-O1-Rb1#3	-23.7(2)	O1-C1-C2-C7	143.64(17)
O2-C1-O1-Rb2#1	73.54(18)	O2-C1-C2-C7	-34.9(2)
C2-C1-O1-Rb2#1	-104.90(14)	C7-C2-C3-C4	0.1(3)
O2-C1-O1-Rb2#4	-98.1(2)	C1-C2-C3-C4	179.14(16)
C2-C1-O1-Rb2#4	83.47(18)	C2-C3-C4-C5	-4.0(3)
O1-C1-O2-Rb1	24.1(2)	C3-C4-C5-C6	2.9(3)
C2-C1-O2-Rb1	-157.52(12)	C4-C5-C6-C7	2.1(3)
O1-C1-O2-Rb2	-96.1(3)	C4-C5-C6-N1	-177.60(15)
C2-C1-O2-Rb2	82.3(3)	C5-C6-C7-C2	-5.7(2)
O1-C1-O2-Rb2#2	125.10(17)	N1-C6-C7-C2	173.97(14)
C2-C1-O2-Rb2#2	-56.48(17)	C5-C6-C7-C8	173.22(16)
O1-C1-O2-Rb2#1	-67.29(18)	N1-C6-C7-C8	-7.1(2)
C2-C1-O2-Rb2#1	111.13(15)	C3-C2-C7-C6	4.5(2)
O4-C8-O3-Rb1#1	50.3(3)	C1-C2-C7-C6	-174.49(15)
C7-C8-O3-Rb1#1	-132.47(17)	C3-C2-C7-C8	-174.48(15)
O4-C8-O3-Rb2	-43.82(19)	C1-C2-C7-C8	6.6(2)
C7-C8-O3-Rb2	133.42(13)	C6-C7-C8-O3	102.6(2)
O4-C8-O3-Rb2#1	-125.19(17)	C2-C7-C8-O3	-78.5(2)
C7-C8-O3-Rb2#1	52.04(19)	C6-C7-C8-O4	-79.8(2)
O3-C8-O4-Rb1#2	-54.1(5)	C2-C7-C8-O4	99.07(19)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1/2,-z+1/2 #2 -x+1/2,y-1/2,-z+1/2 #3 -x+3/2,y+1/2,-z+1/2 #4 x+1,y,z #5 x-1/2,-y+1/2,z+1/2 #6 x+1/2,-y+1/2,z+1/2

Hydrogen bonding geometry [Å and °] for [Rb_2(3-npht)] **12.**

D-H···A	d(D-H)	(H···A)	d(D···A)	<DHA	Symmetry code
C3-H3 ···O1	0.950(.002)	2.571(.001)	2.829(.002)	95.70(0.11)	x, y, z
C5-H5 ···O5	0.950(.002)	2.340(.001)	2.666(.002)	99.44(0.11)	x, y. z
C3-H3 ···O4	0.950(.002)	2.656(.001)	3.433(.002)	139.27(0.11)	x+1,+y,+z
C4-H4 ···O6	0.950(.002)	2.294(.001)	3.145(.002)	148.80(0.11)	x+1,+y,+z
C3-H3 ···O3	0.950(.002)	2.922(.001)	3.732(.002)	143.94(0.11)	x+1,+y,+z
C5-H5 ···O3	0.950(.002)	2.814(.001)	3.408(.002)	121.49(0.11)	-x+1,-y+1,-z+1
C5-H5 ···O4	0.950(.002)	2.653(.001)	3.425(.002)	138.65(0.11)	-x+1,-y,-z+1

D=Donor and A=Acceptor

ructure protocol for [Cs$_2$(3-npht)] **13**

Crystal data and structure refinement for [Cs$_2$(3-npht)] **13**

Identification code	CS11
Empirical formula	$C_8H_3Cs_2NO_6$
Formula weight (g mol^{-1})	474.93
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	7.776(2)
b (Å)	6.526(2)
c (Å)	21.086(7)
α (°)	90
β (°)	95.058(11)
γ (°)	90
Volume (Å^3)	1065.8(6)
Z	4
D$_{calc}$ (mg/m^3)	2.960
Absorption coefficient (mm^{-1})	6.856
F(000)	864
Crystal size (mm^3)	0.10 x 0.10 x 0.05
θ range for data collection (°)	3.269 to 25.992
Index ranges	$-9 \leq h \leq 9$
	$-8 \leq k \leq 8$
	$-26 \leq l \leq 26$
Reflections collected / unique	13128 / 2066 [R(int) = 0.0390]
Completeness to θ = 25.00°	98.6%
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.7457 and 0.5617
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2066 / 0 / 155
Goodness-of-fit on F^2	1.132
Final R indices [I>2sigma(I)]	R1 = 0.0161, wR2 = 0.0353
R indices (all data)	R1 = 0.0195, wR2 = 0.0363
Extinction coefficient	0.00244(14)
Largest diff. peak and hole (e Å^{-3})	0.477 and -0.506

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for [Cs$_2$(3-npht)] **13**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cs1	5517(1)	7314(1)	1376(1)	16(1)
Cs2	791(1)	6984(1)	2245(1)	17(1)
C1	2873(4)	7126(4)	3756(1)	14(1)
C2	4725(4)	7246(4)	4083(1)	11(1)
C3	5095(4)	7494(4)	4742(1)	13(1)
C4	6746(4)	7747(4)	5037(1)	18(1)
C5	8122(4)	7713(4)	4672(2)	20(1)
C6	7831(4)	7348(4)	4021(1)	14(1)
C7	6159(4)	7117(4)	3726(1)	12(1)
C8	5976(3)	6669(4)	3017(1)	13(1)
N1	3693(3)	7476(3)	5171(1)	15(1)
O1	2315(2)	5376(3)	3612(1)	19(1)
O2	2129(2)	8808(3)	3649(1)	20(1)
O3	4622(3)	7262(3)	2700(1)	19(1)
O4	7179(2)	5673(3)	2798(1)	22(1)
O5	2224(3)	7097(3)	4950(1)	27(1)
O6	4069(3)	7824(3)	5742(1)	24(1)

Bond lengths [Å] and angles [°] for [Cs_2(3-npht)] **13.**

Cs1-O1#5	2.9754(19)	O3-Cs2	3.053(2)
Cs1-O2#4	3.075(2)	C1-O1	1.250(3)
Cs1-O6#8	3.173(2)	C1-O2	1.252(3)
Cs1-O4#2	3.240(2)	C1-C2	1.543(4)
Cs1-O5#8	3.415(2)	C2-C7	1.401(4)
Cs1-O3	2.935(2)	C2-C3	1.403(4)
Cs1-O4	3.334(2)	C3-C4	1.386(4)
Cs2-O3#4	3.101(2)	C3-N1	1.476(4)
Cs2-O4#10	3.249(2)	C4-C5	1.372(4)
Cs2-O1#5	3.287(2)	C5-C6	1.392(4)
Cs2-O2#4	3.317(2)	C6-C7	1.399(4)
Cs2-O4#5	3.332(2)	C7-C8	1.518(4)
Cs2-O6#9	3.332(2)	C8-O3	1.257(3)
Cs2-O3#5	3.463(2)	C8-O4	1.259(3)
O1-Cs2	3.195(2)	N1-O5	1.220(3)
O2-Cs2	3.273(2)	N1-O6	1.236(3)
Cs1#4-O1-Cs2	90.69(5)		
C1-O1-Cs2#4	125.91(17)	O3#4-Cs2-O2	110.68(5)
Cs1#4-O1-Cs2#4	85.43(5)	O1-Cs2-O2	40.62(5)
Cs2-O1-Cs2#4	82.75(5)	O4#10-Cs2-O2	89.28(5)
C1-O2-Cs1#5	162.45(18)	O3-Cs2-O1#5	70.15(5)
C1-O2-Cs2	87.09(16)	O3#4-Cs2-O1#5	137.95(5)
Cs1#5-O2-Cs2	95.53(5)	O1-Cs2-O1#5	124.65(4)
C1-O2-Cs2#5	114.18(17)	O4#10-Cs2-O1#5	144.88(5)
Cs1#5-O2-Cs2#5	83.36(5)	O2-Cs2-O1#5	97.48(5)
Cs2-O2-Cs2#5	81.12(5)	O3-Cs2-O2#4	72.80(5)
C8-O3-Cs1	104.54(16)	O3#4-Cs2-O2#4	57.15(5)
C8-O3-Cs2	153.71(17)	O1-Cs2-O2#4	98.42(5)
Cs1-O3-Cs2	90.52(6)	O4#10-Cs2-O2#4	121.30(5)
C8-O3-Cs2#5	111.77(16)	O2-Cs2-O2#4	127.51(3)
Cs1-O3-Cs2#5	93.33(5)	O1#5-Cs2-O2#4	81.02(5)
Cs2-O3-Cs2#5	88.26(5)	O3-Cs2-O4#5	128.34(5)
C8-O3-Cs2#4	75.60(14)	O3#4-Cs2-O4#5	130.19(5)
Cs1-O3-Cs2#4	94.23(5)	O1-Cs2-O4#5	117.59(5)
Cs2-O3-Cs2#4	81.99(5)	O4#10-Cs2-O4#5	65.24(3)
Cs2#5-O3-Cs2#4	167.69(7)	O2-Cs2-O4#5	85.77(5)
C8-O4-Cs1#3	123.07(17)	O1#5-Cs2-O4#5	80.87(5)
C8-O4-Cs2#7	133.54(17)	O2#4-Cs2-O4#5	143.86(5)
Cs1#3-O4-Cs2#7	85.20(5)	O3-Cs2-O6#9	126.54(5)
C8-O4-Cs2#4	81.23(15)	O3#4-Cs2-O6#9	92.22(5)
Cs1#3-O4-Cs2#4	82.81(5)	O1-Cs2-O6#9	162.97(5)
Cs2#7-O4-Cs2#4	143.08(6)	O4#10-Cs2-O6#9	93.63(5)
C8-O4-Cs1	85.53(15)	O2-Cs2-O6#9	156.23(5)
Cs1#3-O4-Cs1	148.49(6)	O1#5-Cs2-O6#9	67.27(5)
Cs2#7-O4-Cs1	82.63(5)	O2#4-Cs2-O6#9	70.03(5)
Cs2#4-O4-Cs1	89.71(5)	O4#5-Cs2-O6#9	74.18(5)
N1-O5-Cs1#6	93.70(16)	O3-Cs2-O3#5	91.20(5)
N1-O6-Cs1#6	105.44(16)	O3#4-Cs2-O3#5	167.69(7)
N1-O6-Cs2#1	167.16(17)	O1-Cs2-O3#5	108.95(5)
Cs1#6-O6-Cs2#1	83.81(5)	O4#10-Cs2-O3#5	99.46(5)
O3-Cs1-O1#5	76.23(5)	O2-Cs2-O3#5	68.34(5)
O3-Cs1-O2#4	78.06(5)	O1#5-Cs2-O3#5	52.83(5)
O1#5-Cs1-O2#4	90.30(6)	O2#4-Cs2-O3#5	133.79(5)
O3-Cs1-O6#8	133.49(5)	O4#5-Cs2-O3#5	38.36(5)
O1#5-Cs1-O6#8	134.01(5)	O6#9-Cs2-O3#5	87.92(5)
O2#4-Cs1-O6#8	125.27(5)	C1-O1-Cs1#4	148.53(18)
O3-Cs1-O4#2	70.31(5)	C1-O1-Cs2	90.66(16)
O1#5-Cs1-O4#2	85.17(6)	O1-C1-O2	127.8(3)
O2#4-Cs1-O4#2	148.23(5)	O1-C1-C2	116.4(2)

O6#8-Cs1-O4#2	77.59(5)	O2-C1-C2	115.7(2)
O3-Cs1-O4	41.17(5)	C7-C2-C3	115.8(2)
O1#5-Cs1-O4	115.89(5)	C7-C2-C1	120.8(2)
O2#4-Cs1-O4	88.96(5)	C3-C2-C1	123.4(2)
O6#8-Cs1-O4	94.99(5)	C4-C3-C2	124.0(3)
O4#2-Cs1-O4	65.30(3)	C4-C3-N1	115.5(2)
O3-Cs1-O5#8	169.09(5)	C2-C3-N1	120.5(2)
O1#5-Cs1-O5#8	106.10(5)	C5-C4-C3	118.9(3)
O2#4-Cs1-O5#8	112.34(5)	C4-C5-C6	119.3(3)
O6#8-Cs1-O5#8	38.00(5)	C5-C6-C7	121.4(3)
O4#2-Cs1-O5#8	99.09(5)	C6-C7-C2	120.4(3)
O4-Cs1-O5#8	132.69(5)	C6-C7-C8	117.5(2)
O3-Cs2-O3#4	98.55(5)	C2-C7-C8	122.1(2)
O3-Cs2-O1	57.48(5)	O3-C8-O4	125.4(3)
O3#4-Cs2-O1	70.81(5)	O3-C8-C7	117.7(2)
O3-Cs2-O4#10	138.90(5)	O4-C8-C7	116.9(2)
O3#4-Cs2-O4#10	68.24(5)	O5-N1-O6	122.8(2)
O1-Cs2-O4#10	81.59(5)	O5-N1-C3	119.0(2)
O3-Cs2-O2	58.07(5)	O6-N1-C3	118.2(2)

Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,-y+3/2,z+1/2 #2 -x+3/2,y+1/2,-z+1/2 #3 -x+3/2,y-1/2,-z+1/2 #4 -x+1/2,y-1/2,-z+1/2
#5 -x+1/2,y+1/2,-z+1/2 #6 x-1/2,-y+3/2,z+1/2 #7 x+1,y,z #8 x+1/2,-y+3/2,z-1/2
#9 x-1/2,-y+3/2,z-1/2 #10 x-1,y,z

Anisotropic displacement parameters (Å^{2}x 10^3) for [Cs_2(3-npht)] **13**. The anisotropic displacement factor exponent takes the form: -2□^{2}[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U11	U22	U33	U23	U13	U12
Cs1	15(1)	19(1)	15(1)	-1(1)	4(1)	0(1)
Cs2	15(1)	16(1)	18(1)	1(1)	-1(1)	1(1)
C1	10(1)	20(2)	11(1)	0(1)	3(1)	1(1)
C2	12(1)	7(1)	14(1)	1(1)	-1(1)	2(1)
C3	8(1)	13(1)	17(1)	1(1)	4(1)	3(1)
C4	15(2)	27(2)	10(1)	-2(1)	-2(1)	0(1)
C5	8(2)	28(2)	24(2)	-1(1)	-5(1)	0(1)
C6	10(1)	16(1)	17(2)	0(1)	4(1)	1(1)
C7	13(1)	8(1)	14(1)	1(1)	0(1)	0(1)
C8	13(1)	10(1)	15(1)	2(1)	3(1)	-3(1)
N1	14(1)	15(1)	15(1)	-1(1)	3(1)	4(1)
O1	18(1)	17(1)	21(1)	-2(1)	-3(1)	-8(1)
O2	16(1)	21(1)	22(1)	1(1)	-3(1)	7(1)
O3	15(1)	27(1)	14(1)	1(1)	0(1)	2(1)
O4	21(1)	23(1)	21(1)	-4(1)	6(1)	6(1)
O5	11(1)	47(1)	24(1)	-4(1)	2(1)	-3(1)
O6	24(1)	35(1)	14(1)	-2(1)	4(1)	2(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) For [Cs_2(3-npht)] **13.**

	x	y	z	U(eq)
H4	6922	7940	5485	21
H5	9261	7937	4862	25
H6	8788	7254	3772	17

Torsion angles [°] for [Cs$_2$(3-npht)] **13.**

O2-C1-O1-Cs1#3	-50.3(5)	C7-C8-O4-Cs1	-163.8(2)
C2-C1-O1-Cs1#3	132.1(3)	O6-N1-O5-Cs1#5	2.3(3)
Cs2-C1-O1-Cs1#3	-92.4(3)	C3-N1-O5-Cs1#5	-178.69(18)
O2-C1-O1-Cs2	42.1(3)	O5-N1-O6-Cs1#5	-2.5(3)
C2-C1-O1-Cs2	-135.5(2)	C3-N1-O6-Cs1#5	178.42(16)
O2-C1-O1-Cs2#3	123.6(3)	O5-N1-O6-Cs2#1	132.6(7)
C2-C1-O1-Cs2#3	-54.0(3)	O1-C1-C2-C7	79.7(3)
Cs2-C1-O1-Cs2#3	81.52(14)	O2-C1-C2-C7	-98.2(3)
O1-C1-O2-Cs1#4	58.3(8)	Cs2-C1-C2-C7	-6.8(4)
C2-C1-O2-Cs1#4	-124.2(5)	O1-C1-C2-C3	-100.6(3)
Cs2-C1-O2-Cs1#4	99.2(6)	O2-C1-C2-C3	81.6(3)
O1-C1-O2-Cs2	-40.9(3)	Cs2-C1-C2-C3	172.98(19)
C2-C1-O2-Cs2	136.7(2)	C7-C2-C3-C4	4.5(4)
O1-C1-O2-Cs2#4	-119.8(3)	C1-C2-C3-C4	-175.3(2)
C2-C1-O2-Cs2#4	57.8(3)	C7-C2-C3-N1	-174.9(2)
Cs2-C1-O2-Cs2#4	-78.91(10)	C1-C2-C3-N1	5.3(4)
O4-C8-O3-Cs1	-21.7(3)	C2-C3-C4-C5	-1.5(4)
C7-C8-O3-Cs1	160.58(18)	N1-C3-C4-C5	177.9(2)
O4-C8-O3-Cs2	101.4(4)	C3-C4-C5-C6	-2.5(4)
C7-C8-O3-Cs2	-76.3(4)	C4-C5-C6-C7	3.3(4)
Cs1-C8-O3-Cs2	123.1(4)	C5-C6-C7-C2	-0.1(4)
O4-C8-O3-Cs2#4	-121.4(2)	C5-C6-C7-C8	-178.5(2)
C7-C8-O3-Cs2#4	60.9(2)	C3-C2-C7-C6	-3.6(3)
Cs1-C8-O3-Cs2#4	-99.68(12)	C1-C2-C7-C6	176.2(2)
O4-C8-O3-Cs2#3	69.0(3)	C3-C2-C7-C8	174.7(2)
C7-C8-O3-Cs2#3	-108.7(2)	C1-C2-C7-C8	-5.5(4)
O3-C8-O4-Cs1#2	-147.4(2)	C6-C7-C8-O3	-151.5(2)
C7-C8-O4-Cs1#2	30.3(3)	C2-C7-C8-O3	30.2(3)
O3-C8-O4-Cs2#6	93.8(3)	C6-C7-C8-O4	30.6(3)
C7-C8-O4-Cs2#6	-88.4(3)	C2-C7-C8-O4	-147.8(2)
O3-C8-O4-Cs2#3	-72.0(3)	C4-C3-N1-O5	-174.2(2)
C7-C8-O4-Cs2#3	105.8(2)	C2-C3-N1-O5	5.2(4)
Cs1-C8-O4-Cs2#3	-90.40(4)	C4-C3-N1-O6	4.9(3)
O3-C8-O4-Cs1	18.4(3)	C2-C3-N1-O6	-175.7(2)

Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,-y+3/2,z+1/2 #2 -x+3/2,y-1/2,-z+1/2 #3 -x+1/2,y-1/2,-z+1/2
#4 -x+1/2,y+1/2,-z+1/2 #5 x-1/2,-y+3/2,z+1/2 #6 x+1,y,z

Hydrogen bonding geometry [Å and °] for [Cs$_2$(3-npht)] **13.**

D-H···A	d(D-H)	(H···A)	d(D···A)	<DHA	Symmetry code
C4-H4···O1	0.950(.003)	2.909(.002)	3.526(.003)	123.69(0.17)	-x+1,-y+1,-z+1
C4-H4···O2	0.950(.003)	2.855(.002)	3.616(.003)	137.83(0.17)	-x+1,-y+2,-z+1
C5-H5···O5	0.950(.003)	2.360(.002)	3.217(.004)	149.88(0.19)	x+1,+y,+z
C6-H6···O2	0.950(.003)	2.822(.002)	3.627(.004)	143.11(0.17)	x+1,+y,+z

D=Donor and A=Acceptor

Structure protocol for $[NaRb(3\text{-}nphtH)_2(H_2O)_3]\cdot 2H_2O$ **14**

Crystal data and structure refinement for $[NaRb(3\text{-}nphtH)_2(H_2O)_3]\cdot 2H_2O$ **14.**

Empirical formula	$C_{16}H_{18}N_2NaO_{17}Rb$
Formula weight (g mol^{-1})	618.78
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	18.7330(14)
b (Å)	6.6818(5)
c (Å)	18.8092(14)
α (°)	90
β (°)	93.359(3)
γ (°)	90
Volume (Å^3)	2350.3(3)
Z	4
D_{calc} (mg/m^3)	1.749
Absorption coefficient (mm^{-1})	2.213
F(000)	1248
Crystal size (mm^3)	0.15 x 0.10 x 0.10
θ range for data collection (°)	3.049 to 24.999
Index ranges	$-22 \leq h \leq 22$ $-7 \leq k \leq 7$ $-22 \leq l \leq 22$
Reflections collected / unique	66259 / 4133 [R(int) = 0.0552]
Completeness to θ = 25.00°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.7456 and 0.5705
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4133 / 15 / 371
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.0979
R indices (all data)	R1 = 0.0415, wR2 = 0.1017
Largest diff. peak and hole (e Å^{-3})	0.767 and -0.782

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $[NaRb(3\text{-}nphtH)_2(H_2O)_3]\cdot 2H_2O$ **14**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rb1	3400(1)	10743(1)	3387(1)	54(1)
Na1	4424(1)	5765(2)	3690(1)	36(1)
C1	4943(2)	13395(5)	2111(2)	29(1)
C2	4740(2)	13066(5)	1340(2)	28(1)
C3	5286(2)	12881(6)	871(2)	34(1)
C4	5135(2)	12544(8)	158(2)	39(1)
C5	4430(2)	12373(6)	-93(2)	39(1)
C6	3888(2)	12541(6)	374(2)	32(1)
C7	4023(2)	12901(5)	1097(2)	27(1)
C8	3406(2)	13041(5)	1603(2)	27(1)
C9	5335(2)	8379(6)	2515(2)	31(1)
C10	6121(2)	8396(5)	2720(2)	29(1)
C11	6612(2)	8404(6)	2198(2)	40(1)
C12	7342(2)	8380(7)	2364(3)	46(1)
C13	7586(2)	8321(7)	3063(3)	42(1)
C14	7095(2)	8314(6)	3584(2)	33(1)

C15	6356(2)	8387(5)	3439(2)	28(1)
C16	5824(2)	8439(5)	4021(2)	26(1)
N1	3152(2)	12277(7)	82(2)	50(1)
N2	7390(2)	8221(7)	4332(2)	52(1)
O1	3229(2)	11430(4)	1880(2)	37(1)
O2	3147(1)	14716(4)	1696(2)	37(1)
O3	4510(2)	13721(5)	2552(2)	44(1)
O4	5636(2)	13295(5)	2263(2)	44(1)
O5	2664(2)	12258(7)	460(2)	73(1)
O6	3046(3)	12116(15)	-545(2)	145(3)
O7	5596(2)	6801(4)	4230(2)	33(1)
O8	5664(2)	10124(5)	4240(2)	35(1)
O9	4864(2)	8443(5)	2937(2)	43(1)
O10	5192(2)	8261(5)	1824(2)	44(1)
O11	6998(2)	8285(7)	4803(2)	70(1)
O12	8027(2)	8051(15)	4437(3)	148(3)
O13	6097(2)	3509(4)	3557(2)	40(1)
O14	4476(2)	2749(4)	4298(2)	37(1)
O15	3250(2)	5593(7)	3165(2)	68(1)
O16	3877(2)	7805(5)	4504(2)	48(1)
O17	1110(2)	3108(4)	3616(2)	43(1)

Bond lengths [Å] and angles [°] for *[NaRb(3-nphtH)$_2$(H$_2$O)$_3$]·2H$_2$O* **14.**

Rb1-O1	2.870(3)	C6-N1	1.465(6)
Rb1-O14#1	2.899(3)	C7-C8	1.543(5)
Rb1-O2#2	2.973(3)	C8-O2	1.237(5)
Rb1-O16	2.976(4)	C8-O1	1.249(5)
Rb1-O15#1	3.277(5)	C9-O9	1.222(5)
Rb1-O9	3.298(3)	C9-O10	1.313(5)
Rb1-O3	3.337(3)	C9-C10	1.499(6)
Rb1-O15	3.476(5)	C10-C11	1.383(6)
Rb1-O11#3	3.587(4)	C10-C15	1.399(6)
Rb1-Na1	3.8660(16)	C11-C12	1.386(7)
Rb1-Na1#1	3.8906(16)	C12-C13	1.366(7)
Na1-O14	2.316(3)	C13-C14	1.382(6)
Na1-O16	2.332(3)	C14-C15	1.396(5)
Na1-O15	2.360(4)	C14-N2	1.483(6)
Na1-O9	2.455(3)	C15-C16	1.523(5)
Na1-O7	2.464(3)	C16-O8	1.242(5)
Na1-O3#4	2.552(3)	C16-O7	1.247(4)
Na1-Rb1#4	3.8906(16)	N1-O6	1.190(6)
C1-O3	1.213(5)	N1-O5	1.191(5)
C1-O4	1.314(5)	N2-O11	1.183(5)
C1-C2	1.494(5)	N2-O12	1.202(6)
C2-C3	1.394(5)	O2-Rb1#5	2.973(3)
C2-C7	1.398(5)	O3-Na1#1	2.552(3)
C3-C4	1.371(6)	O11-Rb1#3	3.587(4)
C4-C5	1.381(6)	O14-Rb1#4	2.899(3)
C5-C6	1.385(6)	O15-Rb1#4	3.277(5)
C6-C7	1.389(5)		

O1-Rb1-O14#1	122.93(8)	O15-Na1-O3#4	74.12(12)
O1-Rb1-O2#2	86.16(8)	O9-Na1-O3#4	82.31(11)
O14#1-Rb1-O2#2	141.29(8)	O7-Na1-O3#4	113.41(10)
O1-Rb1-O16	144.56(8)	O14-Na1-Rb1	145.86(9)
O14#1-Rb1-O16	73.58(9)	O16-Na1-Rb1	50.25(10)
O2#2-Rb1-O16	97.84(9)	O15-Na1-Rb1	62.47(11)
O1-Rb1-O15#1	73.29(8)	O9-Na1-Rb1	57.86(8)
O14#1-Rb1-O15#1	70.69(8)	O7-Na1-Rb1	103.98(7)

O2#2-Rb1-O15#1	98.38(8)	O3#4-Na1-Rb1	113.08(9)
O16-Rb1-O15#1	139.66(9)	O14-Na1-Rb1#4	47.83(8)
O1-Rb1-O9	82.38(8)	O16-Na1-Rb1#4	111.61(10)
O14#1-Rb1-O9	78.86(8)	O15-Na1-Rb1#4	57.13(12)
O2#2-Rb1-O9	134.57(8)	O9-Na1-Rb1#4	136.34(9)
O16-Rb1-O9	69.75(8)	O7-Na1-Rb1#4	136.29(8)
O15#1-Rb1-O9	119.63(9)	O3#4-Na1-Rb1#4	58.03(8)
O1-Rb1-O3	58.44(7)	Rb1-Na1-Rb1#4	118.96(4)
O14#1-Rb1-O3	64.61(7)	O3-C1-O4	123.5(4)
O2#2-Rb1-O3	138.20(8)	O3-C1-C2	123.2(3)
O16-Rb1-O3	123.79(8)	O4-C1-C2	113.3(3)
O15#1-Rb1-O3	53.25(9)	C3-C2-C7	120.8(4)
O9-Rb1-O3	66.80(8)	C3-C2-C1	118.3(3)
O1-Rb1-O15	92.09(9)	C7-C2-C1	121.0(3)
O14#1-Rb1-O15	125.26(8)	C4-C3-C2	121.1(4)
O2#2-Rb1-O15	72.16(8)	C3-C4-C5	119.0(4)
O16-Rb1-O15	56.65(9)	C4-C5-C6	119.9(4)
O15#1-Rb1-O15	163.35(11)	C5-C6-C7	122.5(4)
O9-Rb1-O15	64.55(8)	C5-C6-N1	117.5(4)
O3-Rb1-O15	125.59(9)	C7-C6-N1	120.0(3)
O1-Rb1-O11#3	152.98(9)	C6-C7-C2	116.7(3)
O14#1-Rb1-O11#3	62.03(8)	C6-C7-C8	121.1(3)
O2#2-Rb1-O11#3	80.53(8)	C2-C7-C8	122.2(3)
O16-Rb1-O11#3	61.27(9)	O2-C8-O1	127.2(3)
O15#1-Rb1-O11#3	85.46(10)	O2-C8-C7	117.2(3)
O9-Rb1-O11#3	123.38(8)	O1-C8-C7	115.7(3)
O3-Rb1-O11#3	120.58(9)	O2-C8-Rb1	103.0(2)
O15-Rb1-O11#3	105.85(10)	O1-C8-Rb1	41.2(2)
O1-Rb1-C8	16.65(8)	C7-C8-Rb1	125.4(2)
O14#1-Rb1-C8	107.82(8)	O9-C9-O10	122.1(4)
O2#2-Rb1-C8	95.94(8)	O9-C9-C10	124.6(4)
O16-Rb1-C8	154.16(8)	O10-C9-C10	113.3(3)
O15#1-Rb1-C8	58.52(9)	C11-C10-C15	120.0(4)
O9-Rb1-C8	85.03(8)	C11-C10-C9	120.1(4)
O3-Rb1-C8	44.66(7)	C15-C10-C9	119.9(3)
O15-Rb1-C8	107.91(9)	C10-C11-C12	122.0(4)
O11#3-Rb1-C8	143.09(10)	C13-C12-C11	119.1(4)
O1-Rb1-Na1	108.00(6)	C12-C13-C14	119.0(4)
O14#1-Rb1-Na1	89.34(6)	C13-C14-C15	123.6(4)
O2#2-Rb1-Na1	106.44(6)	C13-C14-N2	116.6(4)
O16-Rb1-Na1	37.06(6)	C15-C14-N2	119.8(4)
O15#1-Rb1-Na1	155.18(7)	C14-C15-C10	116.3(3)
O9-Rb1-Na1	39.08(6)	C14-C15-C16	123.0(4)
O3-Rb1-Na1	105.35(6)	C10-C15-C16	120.8(3)
O15-Rb1-Na1	37.02(6)	O8-C16-O7	126.6(3)
O11#3-Rb1-Na1	98.32(8)	O8-C16-C15	116.1(3)
C8-Rb1-Na1	117.65(6)	O7-C16-C15	117.2(3)
O1-Rb1-Na1#1	91.85(6)	O6-N1-O5	120.1(5)
O14#1-Rb1-Na1#1	36.32(6)	O6-N1-C6	118.7(4)
O2#2-Rb1-Na1#1	132.66(6)	O5-N1-C6	121.2(4)
O16-Rb1-Na1#1	109.90(7)	O11-N2-O12	122.3(5)
O15#1-Rb1-Na1#1	37.22(6)	O11-N2-C14	119.7(4)
O9-Rb1-Na1#1	91.66(6)	O12-N2-C14	118.0(4)
O3-Rb1-Na1#1	40.46(6)	C8-O1-Rb1	122.2(3)
O15-Rb1-Na1#1	155.10(6)	C8-O2-Rb1#5	126.2(2)
O11#3-Rb1-Na1#1	80.38(8)	C1-O3-Na1#1	138.4(3)
C8-Rb1-Na1#1	75.32(6)	C1-O3-Rb1	132.4(3)
Na1-Rb1-Na1#1	118.96(4)	Na1#1-O3-Rb1	81.52(8)
O14-Na1-O16	101.03(13)	C16-O7-Na1	115.5(2)
O14-Na1-O15	100.13(16)	C9-O9-Na1	129.0(3)
O16-Na1-O15	82.45(13)	C9-O9-Rb1	145.7(3)

O14-Na1-O9	155.96(12)	Na1-O9-Rb1	83.06(8)
O16-Na1-O9	97.38(13)	C9-O10-H10A	109.5
O15-Na1-O9	97.48(15)	N2-O11-Rb1#3	152.8(3)
O14-Na1-O7	91.71(11)	Na1-O14-Rb1#4	95.85(10)
O16-Na1-O7	88.87(12)	Na1-O15-Rb1#4	85.66(12)
O15-Na1-O7	166.45(14)	Na1-O15-Rb1	80.50(12)
O9-Na1-O7	73.24(10)	Rb1#4-O15-Rb1	163.35(11)
O14-Na1-O3#4	86.90(12)	Na1-O16-Rb1	92.69(11)
O16-Na1-O3#4	156.28(13)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1/2,-z+1/2   #2 x,y+1,z   #3 -x+1,-y+2,-z+1 #4 x,y-1,z   #5 -x+1/2,y-1/2,-z+1/2

Anisotropic displacement parameters (Å^{2}x 10^3) for *[NaRb(3-nphtH)$_2$(H$_2$O)$_3$]·2H$_2$O* **14**. The anisotropic displacement factor exponent takes the form: -2□^{2}[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

	U11	U22	U33	U23	U13	U12
Rb1	50(1)	60(1)	52(1)	13(1)	-12(1)	-15(1)
Na1	34(1)	37(1)	38(1)	1(1)	9(1)	-1(1)
C1	26(2)	26(2)	36(2)	2(1)	8(2)	1(1)
C2	28(2)	25(2)	30(2)	0(1)	7(2)	2(1)
C3	32(2)	36(2)	37(2)	0(2)	12(2)	-1(2)
C4	39(3)	45(2)	36(2)	-3(2)	19(2)	2(2)
C5	46(2)	42(2)	28(2)	-3(2)	10(2)	2(2)
C6	32(2)	34(2)	32(2)	-1(2)	4(2)	2(2)
C7	31(2)	20(2)	30(2)	2(1)	7(2)	2(1)
C8	18(2)	34(2)	30(2)	-5(2)	5(1)	1(1)
C9	38(2)	24(2)	31(2)	2(1)	8(2)	-2(2)
C10	35(2)	22(2)	32(2)	-1(1)	11(2)	-1(1)
C11	45(3)	42(2)	33(2)	-2(2)	16(2)	-2(2)
C12	41(3)	47(2)	52(3)	-2(2)	27(2)	-1(2)
C13	24(2)	47(2)	56(3)	-3(2)	11(2)	-2(2)
C14	30(2)	34(2)	35(2)	-3(2)	4(2)	0(2)
C15	28(2)	20(2)	35(2)	1(1)	12(2)	1(1)
C16	23(2)	30(2)	24(2)	-2(1)	2(1)	3(1)
N1	42(2)	74(3)	33(2)	-8(2)	0(2)	-3(2)
N2	30(2)	75(3)	51(2)	-5(2)	-1(2)	0(2)
O1	33(1)	34(1)	46(2)	5(1)	16(1)	-4(1)
O2	34(2)	32(1)	46(2)	-2(1)	14(1)	7(1)
O3	32(2)	71(2)	30(2)	-8(1)	4(1)	6(1)
O4	28(2)	70(2)	34(2)	-4(1)	4(1)	3(1)
O5	36(2)	132(4)	49(2)	-9(2)	0(2)	-6(2)
O6	66(3)	326(10)	42(3)	-44(4)	-3(2)	-13(5)
O7	38(2)	30(1)	32(1)	1(1)	12(1)	-5(1)
O8	41(2)	30(1)	36(2)	-6(1)	11(1)	5(1)
O9	31(2)	67(2)	32(2)	0(1)	8(1)	-2(1)
O10	41(2)	66(2)	26(2)	-2(1)	7(1)	1(1)
O11	45(2)	124(4)	42(2)	-2(2)	-2(2)	2(2)
O12	34(2)	340(11)	68(3)	4(5)	-2(2)	33(4)
O13	50(2)	35(1)	36(2)	-1(1)	13(1)	-1(1)
O14	41(2)	42(2)	30(2)	2(1)	7(1)	6(1)
O15	32(2)	125(3)	48(2)	-31(2)	4(1)	20(2)
O16	42(2)	60(2)	42(2)	-13(2)	7(1)	-4(2)
O17	42(2)	34(2)	53(2)	-1(1)	10(1)	-1(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for $[NaRb(3\text{-}nphtH)_2(H_2O)_3]\cdot 2H_2O$ **14**.

	x	y	z	U(eq)
H3	5759	12989	1044	41
H4	5503	12432	-151	47
H5	4320	12145	-575	46
H11	6446	8427	1722	47
H12	7662	8404	2004	55
H13	8074	8286	3186	50
H4A	5713	13203	2695	66
H10A	4759	8357	1738	66
H13A	5970(30)	2450(40)	3770(20)	48
H13B	5980(30)	4500(40)	3830(20)	48
H17A	1350(20)	4050(50)	3430(30)	51
H17B	1350(20)	2050(40)	3570(30)	51
H14A	4770(20)	1790(50)	4270(20)	44(13)
H14B	4450(30)	3020(70)	4748(12)	53(15)
H15A	3280(30)	5280(100)	2724(15)	90(20)
H15B	2814(17)	5940(110)	3210(40)	100(30)
H16A	3540(20)	7220(80)	4680(30)	70(19)
H16B	4110(30)	8490(80)	4820(20)	80(20)

Torsion angles [°] for $[NaRb(3\text{-}nphtH)_2(H_2O)_3]\cdot 2H_2O$ **14.**

O1-Rb1-Na1-O14	-133.93(18)	C5-C6-N1-O6	-6.8(8)
O14#1-Rb1-Na1-O14	101.47(19)	C7-C6-N1-O6	174.6(7)
O2#2-Rb1-Na1-O14	-42.64(19)	C5-C6-N1-O5	174.5(5)
O16-Rb1-Na1-O14	38.46(19)	C7-C6-N1-O5	-4.1(7)
O15#1-Rb1-Na1-O14	137.1(2)	C13-C14-N2-O11	177.2(5)
O9-Rb1-Na1-O14	174.5(2)	C15-C14-N2-O11	-2.9(7)
O3-Rb1-Na1-O14	164.86(17)	C13-C14-N2-O12	-3.9(8)
O15-Rb1-Na1-O14	-65.5(2)	C15-C14-N2-O12	176.1(7)
O11#3-Rb1-Na1-O14	39.88(18)	O2-C8-O1-Rb1	-64.1(5)
C8-Rb1-Na1-O14	-148.68(17)	C7-C8-O1-Rb1	115.3(3)
Na1#1-Rb1-Na1-O14	123.45(16)	O14#1-Rb1-O1-C8	-26.8(3)
O1-Rb1-Na1-O16	-172.38(13)	O2#2-Rb1-O1-C8	125.9(3)
O14#1-Rb1-Na1-O16	63.01(13)	O16-Rb1-O1-C8	-136.0(3)
O2#2-Rb1-Na1-O16	-81.10(13)	O15#1-Rb1-O1-C8	26.0(3)
O15#1-Rb1-Na1-O16	98.6(2)	O9-Rb1-O1-C8	-98.2(3)
O9-Rb1-Na1-O16	136.02(15)	O3-Rb1-O1-C8	-30.8(2)
O3-Rb1-Na1-O16	126.41(13)	O15-Rb1-O1-C8	-162.1(3)
O15-Rb1-Na1-O16	-103.92(17)	O11#3-Rb1-O1-C8	65.5(3)
O11#3-Rb1-Na1-O16	1.42(13)	Na1-Rb1-O1-C8	-128.1(3)
C8-Rb1-Na1-O16	172.86(13)	Na1#1-Rb1-O1-C8	-6.7(3)
Na1#1-Rb1-Na1-O16	84.99(12)	O1-C8-O2-Rb1#5	-49.3(6)
O1-Rb1-Na1-O15	-68.46(14)	C7-C8-O2-Rb1#5	131.3(3)
O14#1-Rb1-Na1-O15	166.94(13)	Rb1-C8-O2-Rb1#5	-86.7(2)
O2#2-Rb1-Na1-O15	22.83(14)	O4-C1-O3-Na1#1	34.4(6)
O16-Rb1-Na1-O15	103.92(17)	C2-C1-O3-Na1#1	-145.6(3)
O15#1-Rb1-Na1-O15	-157.4(3)	O4-C1-O3-Rb1	-102.2(4)
O9-Rb1-Na1-O15	-120.05(15)	C2-C1-O3-Rb1	77.8(5)
O3-Rb1-Na1-O15	-129.67(13)	O1-Rb1-O3-C1	-66.3(3)
O11#3-Rb1-Na1-O15	105.35(14)	O14#1-Rb1-O3-C1	117.4(4)
C8-Rb1-Na1-O15	-83.22(14)	O2#2-Rb1-O3-C1	-102.7(4)
Na1#1-Rb1-Na1-O15	-171.09(12)	O16-Rb1-O3-C1	71.4(4)
O1-Rb1-Na1-O9	51.60(11)	O15#1-Rb1-O3-C1	-158.4(4)
O14#1-Rb1-Na1-O9	-73.01(10)	O9-Rb1-O3-C1	29.1(3)
O2#2-Rb1-Na1-O9	142.88(11)	O15-Rb1-O3-C1	0.9(4)
O16-Rb1-Na1-O9	-136.02(15)	O11#3-Rb1-O3-C1	145.3(3)
O15#1-Rb1-Na1-O9	-37.39(19)	C8-Rb1-O3-C1	-78.3(4)

O3-Rb1-Na1-O9	-9.62(10)	Na1-Rb1-O3-C1	35.7(4)
O15-Rb1-Na1-O9	120.05(15)	Na1#1-Rb1-O3-C1	152.6(4)
O11#3-Rb1-Na1-O9	-134.60(11)	O1-Rb1-O3-Na1#1	141.16(11)
C8-Rb1-Na1-O9	36.84(12)	O14#1-Rb1-O3-Na1#1	-35.12(8)
Na1#1-Rb1-Na1-O9	-51.03(11)	O2#2-Rb1-O3-Na1#1	104.78(12)
O1-Rb1-Na1-O7	111.11(9)	O16-Rb1-O3-Na1#1	-81.16(12)
O14#1-Rb1-Na1-O7	-13.49(9)	O15#1-Rb1-O3-Na1#1	49.00(9)
O2#2-Rb1-Na1-O7	-157.60(9)	O9-Rb1-O3-Na1#1	-123.45(10)
O16-Rb1-Na1-O7	-76.50(13)	O15-Rb1-O3-Na1#1	-151.61(8)
O15#1-Rb1-Na1-O7	22.12(19)	O11#3-Rb1-O3-Na1#1	-7.21(13)
O9-Rb1-Na1-O7	59.52(11)	C8-Rb1-O3-Na1#1	129.12(14)
O3-Rb1-Na1-O7	49.90(10)	Na1-Rb1-O3-Na1#1	-116.87(8)
O15-Rb1-Na1-O7	179.57(15)	O8-C16-O7-Na1	82.7(4)
O11#3-Rb1-Na1-O7	-75.08(10)	C15-C16-O7-Na1	-97.6(3)
C8-Rb1-Na1-O7	96.36(10)	O14-Na1-O7-C16	177.0(3)
Na1#1-Rb1-Na1-O7	8.49(10)	O16-Na1-O7-C16	-82.0(3)
O1-Rb1-Na1-O3#4	-12.34(11)	O15-Na1-O7-C16	-32.0(7)
O14#1-Rb1-Na1-O3#4	-136.94(10)	O9-Na1-O7-C16	16.0(2)
O2#2-Rb1-Na1-O3#4	78.95(11)	O3#4-Na1-O7-C16	89.6(3)
O16-Rb1-Na1-O3#4	160.05(15)	Rb1-Na1-O7-C16	-33.6(2)
O15#1-Rb1-Na1-O3#4	-101.33(19)	Rb1#4-Na1-O7-C16	157.1(2)
O9-Rb1-Na1-O3#4	-63.93(12)	O10-C9-O9-Na1	102.0(4)
O3-Rb1-Na1-O3#4	-73.55(9)	C10-C9-O9-Na1	-77.1(5)
O15-Rb1-Na1-O3#4	56.12(14)	O10-C9-O9-Rb1	-53.8(7)
O11#3-Rb1-Na1-O3#4	161.47(11)	C10-C9-O9-Rb1	127.1(4)
C8-Rb1-Na1-O3#4	-27.10(11)	O14-Na1-O9-C9	21.1(5)
Na1#1-Rb1-Na1-O3#4	-114.96(9)	O16-Na1-O9-C9	160.9(3)
O1-Rb1-Na1-Rb1#4	-77.37(7)	O15-Na1-O9-C9	-115.8(4)
O14#1-Rb1-Na1-Rb1#4	158.02(7)	O7-Na1-O9-C9	74.3(3)
O2#2-Rb1-Na1-Rb1#4	13.91(8)	O3#4-Na1-O9-C9	-43.1(3)
O16-Rb1-Na1-Rb1#4	95.01(12)	Rb1-Na1-O9-C9	-166.6(4)
O15#1-Rb1-Na1-Rb1#4	-166.36(16)	Rb1#4-Na1-O9-C9	-66.8(4)
O9-Rb1-Na1-Rb1#4	-128.97(11)	O14-Na1-O9-Rb1	-172.4(3)
O3-Rb1-Na1-Rb1#4	-138.58(6)	O16-Na1-O9-Rb1	-32.57(11)
O15-Rb1-Na1-Rb1#4	-8.91(12)	O15-Na1-O9-Rb1	50.73(11)
O11#3-Rb1-Na1-Rb1#4	96.43(8)	O7-Na1-O9-Rb1	-119.15(9)
C8-Rb1-Na1-Rb1#4	-92.13(8)	O3#4-Na1-O9-Rb1	123.50(9)
Na1#1-Rb1-Na1-Rb1#4	180	Rb1#4-Na1-O9-Rb1	99.78(11)
O3-C1-C2-C3	174.4(4)	O1-Rb1-O9-C9	30.0(5)
O4-C1-C2-C3	-5.6(5)	O14#1-Rb1-O9-C9	-95.8(5)
O3-C1-C2-C7	-7.1(6)	O2#2-Rb1-O9-C9	106.9(5)
O4-C1-C2-C7	172.9(3)	O16-Rb1-O9-C9	-172.2(5)
C7-C2-C3-C4	0.3(6)	O15#1-Rb1-O9-C9	-35.8(5)
C1-C2-C3-C4	178.9(4)	O3-Rb1-O9-C9	-28.8(5)
C2-C3-C4-C5	-0.4(7)	O15-Rb1-O9-C9	126.0(5)
C3-C4-C5-C6	0.0(7)	O11#3-Rb1-O9-C9	-141.2(5)
C4-C5-C6-C7	0.6(7)	C8-Rb1-O9-C9	13.5(5)
C4-C5-C6-N1	-177.9(4)	Na1-Rb1-O9-C9	161.3(5)
C5-C6-C7-C2	-0.7(6)	Na1#1-Rb1-O9-C9	-61.6(5)
N1-C6-C7-C2	177.8(4)	O1-Rb1-O9-Na1	-131.24(10)
C5-C6-C7-C8	-178.8(4)	O14#1-Rb1-O9-Na1	102.93(9)
N1-C6-C7-C8	-0.3(5)	O2#2-Rb1-O9-Na1	-54.34(14)
C3-C2-C7-C6	0.3(5)	O16-Rb1-O9-Na1	26.49(9)
C1-C2-C7-C6	-178.3(3)	O15#1-Rb1-O9-Na1	162.95(9)
C3-C2-C7-C8	178.3(3)	O3-Rb1-O9-Na1	169.91(11)
C1-C2-C7-C8	-0.2(5)	O15-Rb1-O9-Na1	-35.25(9)
C6-C7-C8-O2	-90.7(4)	O11#3-Rb1-O9-Na1	57.54(14)
C2-C7-C8-O2	91.3(4)	C8-Rb1-O9-Na1	-147.79(10)
C6-C7-C8-O1	89.8(4)	Na1#1-Rb1-O9-Na1	137.11(9)
C2-C7-C8-O1	-88.1(4)	O12-N2-O11-Rb1#3	24.1(13)

C6-C7-C8-Rb1	136.8(3)	C14-N2-O11-Rb1#3	-157.1(5)
C2-C7-C8-Rb1	-41.2(4)	O16-Na1-O14-Rb1#4	109.25(11)
O1-Rb1-C8-O2	132.6(4)	O15-Na1-O14-Rb1#4	25.06(13)
O14#1-Rb1-C8-O2	-70.8(2)	O9-Na1-O14-Rb1#4	-111.4(3)
O2#2-Rb1-C8-O2	78.3(2)	O7-Na1-O14-Rb1#4	-161.56(9)
O16-Rb1-C8-O2	-159.8(2)	O3#4-Na1-O14-Rb1#4	-48.20(10)
O15#1-Rb1-C8-O2	-17.9(2)	Rb1-Na1-O14-Rb1#4	80.10(17)
O9-Rb1-C8-O2	-147.4(2)	O14-Na1-O15-Rb1#4	-21.95(11)
O3-Rb1-C8-O2	-85.7(2)	O16-Na1-O15-Rb1#4	-121.88(12)
O15-Rb1-C8-O2	151.4(2)	O9-Na1-O15-Rb1#4	141.62(10)
O11#3-Rb1-C8-O2	-3.9(3)	O7-Na1-O15-Rb1#4	-172.5(5)
Na1-Rb1-C8-O2	-169.7(2)	O3#4-Na1-O15-Rb1#4	61.86(10)
Na1#1-Rb1-C8-O2	-54.3(2)	Rb1-Na1-O15-Rb1#4	-170.71(11)
O14#1-Rb1-C8-O1	156.6(3)	O14-Na1-O15-Rb1	148.76(10)
O2#2-Rb1-C8-O1	-54.3(3)	O16-Na1-O15-Rb1	48.84(11)
O16-Rb1-C8-O1	67.6(3)	O9-Na1-O15-Rb1	-47.67(10)
O15#1-Rb1-C8-O1	-150.5(3)	O7-Na1-O15-Rb1	-1.8(6)
O9-Rb1-C8-O1	80.0(3)	O3#4-Na1-O15-Rb1	-127.43(12)
O3-Rb1-C8-O1	141.7(3)	Rb1#4-Na1-O15-Rb1	170.71(11)
O15-Rb1-C8-O1	18.8(3)	O1-Rb1-O15-Na1	117.72(12)
O11#3-Rb1-C8-O1	-136.5(3)	O14#1-Rb1-O15-Na1	-16.07(16)
Na1-Rb1-C8-O1	57.7(3)	O2#2-Rb1-O15-Na1	-156.99(14)
Na1#1-Rb1-C8-O1	173.0(3)	O16-Rb1-O15-Na1	-44.45(11)
O1-Rb1-C8-C7	-89.7(4)	O15#1-Rb1-O15-Na1	145.8(4)
O14#1-Rb1-C8-C7	67.0(3)	O9-Rb1-O15-Na1	37.18(10)
O2#2-Rb1-C8-C7	-144.0(3)	O3-Rb1-O15-Na1	65.89(14)
O16-Rb1-C8-C7	-22.1(4)	O11#3-Rb1-O15-Na1	-82.71(12)
O15#1-Rb1-C8-C7	119.8(3)	C8-Rb1-O15-Na1	112.42(11)
O9-Rb1-C8-C7	-9.7(3)	Na1#1-Rb1-O15-Na1	18.8(2)
O3-Rb1-C8-C7	52.0(3)	O1-Rb1-O15-Rb1#4	151.9(5)
O15-Rb1-C8-C7	-70.9(3)	O14#1-Rb1-O15-Rb1#4	18.1(5)
O11#3-Rb1-C8-C7	133.9(3)	O2#2-Rb1-O15-Rb1#4	-122.8(5)
Na1-Rb1-C8-C7	-31.9(3)	O16-Rb1-O15-Rb1#4	-10.3(4)
Na1#1-Rb1-C8-C7	83.4(3)	O15#1-Rb1-O15-Rb1#4	180.000(2)
O9-C9-C10-C11	-177.2(4)	O9-Rb1-O15-Rb1#4	71.4(5)
O10-C9-C10-C11	3.6(5)	O3-Rb1-O15-Rb1#4	100.1(5)
O9-C9-C10-C15	3.2(6)	O11#3-Rb1-O15-Rb1#4	-48.5(5)
O10-C9-C10-C15	-175.9(3)	C8-Rb1-O15-Rb1#4	146.6(5)
C15-C10-C11-C12	0.8(6)	Na1-Rb1-O15-Rb1#4	34.2(4)
C9-C10-C11-C12	-178.7(4)	Na1#1-Rb1-O15-Rb1#4	53.0(6)
C10-C11-C12-C13	0.8(7)	O14-Na1-O16-Rb1	-159.17(10)
C11-C12-C13-C14	-0.9(7)	O15-Na1-O16-Rb1	-60.26(14)
C12-C13-C14-C15	-0.7(7)	O9-Na1-O16-Rb1	36.36(11)
C12-C13-C14-N2	179.2(4)	O7-Na1-O16-Rb1	109.31(10)
C13-C14-C15-C10	2.3(6)	O3#4-Na1-O16-Rb1	-51.3(4)
N2-C14-C15-C10	-177.7(4)	Rb1#4-Na1-O16-Rb1	-110.36(8)
C13-C14-C15-C16	-178.2(4)	O1-Rb1-O16-Na1	12.6(2)
N2-C14-C15-C16	1.9(6)	O14#1-Rb1-O16-Na1	-111.73(12)
C11-C10-C15-C14	-2.2(5)	O2#2-Rb1-O16-Na1	106.96(11)
C9-C10-C15-C14	177.3(3)	O15#1-Rb1-O16-Na1	-140.13(12)
C11-C10-C15-C16	178.2(3)	O9-Rb1-O16-Na1	-27.81(10)
C9-C10-C15-C16	-2.3(5)	O3-Rb1-O16-Na1	-69.04(13)
C14-C15-C16-O8	88.7(5)	O15-Rb1-O16-Na1	44.40(11)
C10-C15-C16-O8	-91.8(4)	O11#3-Rb1-O16-Na1	-178.40(15)
C14-C15-C16-O7	-91.0(4)	C8-Rb1-O16-Na1	-14.6(3)
C10-C15-C16-O7	88.5(4)	Na1#1-Rb1-O16-Na1	-112.03(10)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1/2,-z+1/2 #2 x,y+1,z #3 -x+1,-y+2,-z+1 #4 x,y-1,z #5 -x+1/2,y-1/2,-z+1/2

Hydrogen bonds for $[NaRb(3\text{-}nphtH)_2(H_2O)_3]\cdot 2H_2O$ **14** [Å and °].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)	Symmetry codes
C5-H5 ···O10	0.93	2.59	3.399(5)	146.3	-x+1,-y+2,-z
C13-H13 ···O4	0.93	2.61	3.423(5)	146.7	-x+3/2,y-1/2,-z+1/2
O4-H4A ···O13	0.82	1.75	2.538(4)	161.9	x,y+1,z #3 -x+1,-y+2,-z+1
O10-H10A ···O17	0.82	1.73	2.532(5)	165	-x+1/2,y+1/2,-z+1/2
O13-H13A ···O8	0.861(19)	1.887(19)	2.747(4)	179(5)	x,y-1,z
O13-H13B ···O7	0.873(18)	1.87(2)	2.732(4)	167(5)	x,y,z
O14-H14A ···O8	0.844(19)	2.02(2)	2.841(4)	164(5)	x,y-1,z
O14-H14B ···O7	0.870(19)	1.93(2)	2.796(4)	171(4)	-x+1,-y+1,-z+1
O15-H15A ···O2	0.860(19)	1.97(2)	2.819(4)	169(6)	x,y-1,z
O15-H15B ···O1	0.86(2)	1.98(3)	2.822(4)	168(7)	-x+1/2,y-1/2,-z+1/2
O16-H16A ···O5	0.828(19)	2.25(4)	2.913(5)	137(6)	-x+1/2,y-1/2,-z+1/2
O16-H16B ···O8	0.85(2)	2.02(3)	2.827(5)	159(5)	-x+1,-y+2,-z+1
O17-H17A ···O1	0.854(19)	1.887(19)	2.732(4)	170(5)	-x+1/2,y-1/2,-z+1/2
O17-H17B ···O2	0.841(19)	1.91(2)	2.741(4)	171(5)	-x+1/2,y-3/2,-z+1/2

CheckCIF/PLATON report for (pipH$_2$)[Zn(pht)$_2$]·H$_2$O 1

Datablock: ZnPP

Bond precision:	C-C = 0.0044 A	Wavelength=0.71073	
Cell:	a=8.142(3)	b=21.537(8)	c=11.782(5)
	alpha=90	beta=99.441(7)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	2038.0(14)	2038.1(14)	
Space group	P 21/c	P2(1)/c	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C16 H8 O8 Zn, C4 H12 N2, H2 O	C16 H8 O8 Zn, C4 H12 N2, H2 O	
Sum formula	C20 H22 N2 O9 Zn	C20 H22 N2 O9 Zn	
Mr	499.79	499.77	
Dx,g cm-3	1.629	1.629	
Z	4	4	
Mu (mm-1)	1.263	1.263	
F000	1032.0	1032.0	
F000'	1033.66		
h,k,lmax	10,27,14	10,26,14	
Nref	4221	4201	
Tmin,Tmax	0.817,0.859	0.817,0.859	
Tmin'	0.817		

Correction method= # Reported T Limits: Tmin=0.817 Tmax=0.859 AbsCorr = MULTI SCAN
Data completeness= 0.995 Theta(max)= 26.500
R(reflections)= 0.0412(3058) wR2(reflections)= 0.1107(4201)
S = 0.981 Npar= 286

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert type_alert-level**.

Click on the hyperlinks for more details of the test

Alert level B

PLAT420_ALERT_2_B D-H Without Acceptor Ow - H1W ..Please Check

Alert level C

PLAT165_ALERT_3_CNr. of StatusR Flagged Non-Hydrogen Atoms 1

PLAT242_ALERT_2_CLow Ueqas Compared to Neighbors for C17Check

Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	3Note
PLAT004_ALERT_5_G	Polymeric Structure Found with Maximum Dimension	1Info
PLAT005_ALERT_5_G	No _iucr_refine_instructions_details in the CIF	PleaseDo !
PLAT007_ALERT_5_G	Number of Unrefined Donor-H Atoms	6Report
PLAT066_ALERT_1_G	Predicted and Reported Tmin&Tmax Range Identical	? Check
PLAT093_ALERT_1_G	No su's on H-positions, refinement reported as .	mixed
PLAT199_ALERT_1_G	Reported _cell_measurement_temperature ..... (K)	293Check
PLAT200_ALERT_1_G	Reported _diffrn_ambient_temperature ..... (K)	293Check
PLAT720_ALERT_4_G	Number of Unusual/Non-Standard Labels	1Note
PLAT764_ALERT_4_G	Overcomplete CIF Bond List Detected (Rep/Expd) .	1.12Ratio
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	3Note
PLAT899_ALERT_4_G SHELXL97	is Deprecated and Succeeded by SHELXL	2014Note

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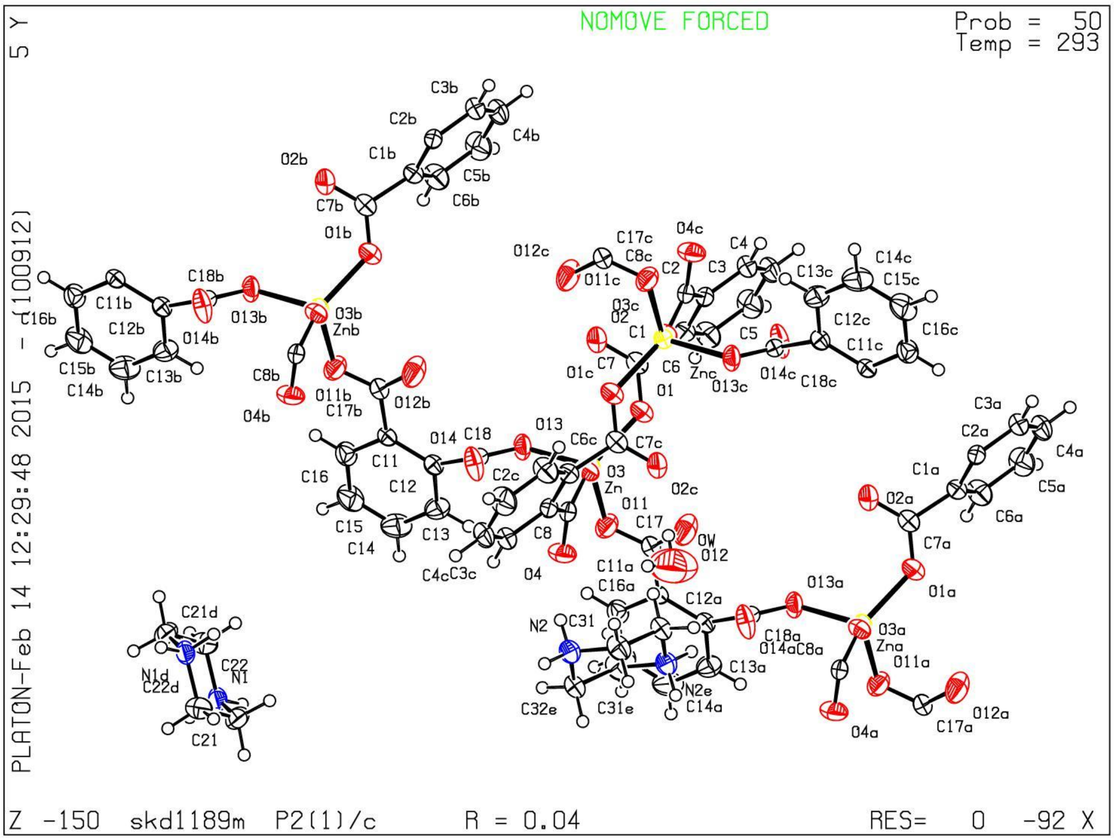
0 **ALERT level A** = Most likely a serious problem - resolve or explain 1 **ALERT level B** = A potentially serious problem, consider carefully

2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight 12 **ALERT level G** = General information/check it is not something unexpected

4ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3ALERT type 2 Indicator that the structure model may be wrong or deficient
2ALERT type 3 Indicator that the structure quality may be Low
3ALERT type 4Improvement, methodology, query or suggestion
3ALERT type 5Informative message, check

PLATON version of 29/01/2015; check.def file version of 29/01/2015

Datablock for ZnPP - ellipsoid plot



CheckCIF/PLATON report for (pipH$_2$)[Ni(pht)$_2$(H$_2$O)$_4$]·8H$_2$O 3

Datablock: NiPP

Bond precision: C-C = 0.0026 A Wavelength=1.54184

Cell:	a=11.2600(6)	b=11.8393(7)	c=12.4959(7)
	alpha=82.000(5)	beta=77.409(5)	gamma=75.538(5)
Temperature:	293 K		

	Calculated	Reported
Volume	1567.92(16)	1567.92(15)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C16 H16 Ni O12, C4 H12 N2, 8(H2 O)	C16 H16 Ni O12, 2(C2 H6 N), 8(H2 O)
Sum formula	C20 H44 N2 Ni O20	C20 H44 N2 Ni O20
Mr	691.26	691.28
Dx,g cm-3	1.464	1.464
Z	2	2
Mu (mm-1)	1.660	1.660
F000	732.0	732.0
F000'	728.71	
h,k,lmax	13,14,14	13,14,14
Nref	5582	5572
Tmin,Tmax	0.613,0.649	0.579,0.672
Tmin'	0.515	

Correction method= # Reported T Limits: Tmin=0.579 Tmax=0.672 AbsCorr = MULTI-SCAN
Data completeness= 0.998 Theta(max)= 67.080
R(reflections)= 0.0354(5256) wR2(reflections)= 0.1026(5572)
S = 1.054 Npar= 438

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**. Click on the hyperlinks for more details of the test.

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 2Note
PLAT005_ALERT_5_G No Embedded Refinement Details found in the CIF PleaseDo !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms 16Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ PleaseCheck
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note) 0.005Degree
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K) 293Check
PLAT200_ALERT_1_G Reported _diffrn_ambient_temperature ..... (K) 293Check
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Ni1 --O9 .. 5.8s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Ni1 --O10 .. 5.2s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Ni1 --O11 .. 5.7s.u.

PLAT432_ALERT_2_G Short Inter X...Y Contact O1 ..C19 .. 3.01Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact O11 ..C20 .. 3.01Ang.
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 20Do !
C7 -O1 -NI1 -O5 -74.90 1.90 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 45Do !
C15 -O5 -NI1 -O1 -100.80 1.80 1.555 1.555 1.555 1.555
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 7Note
H2 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 9Note
H2 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 10Note
H2 O
PLAT860_ALERT_3_G Number of Least-Squares Restraints 1Note

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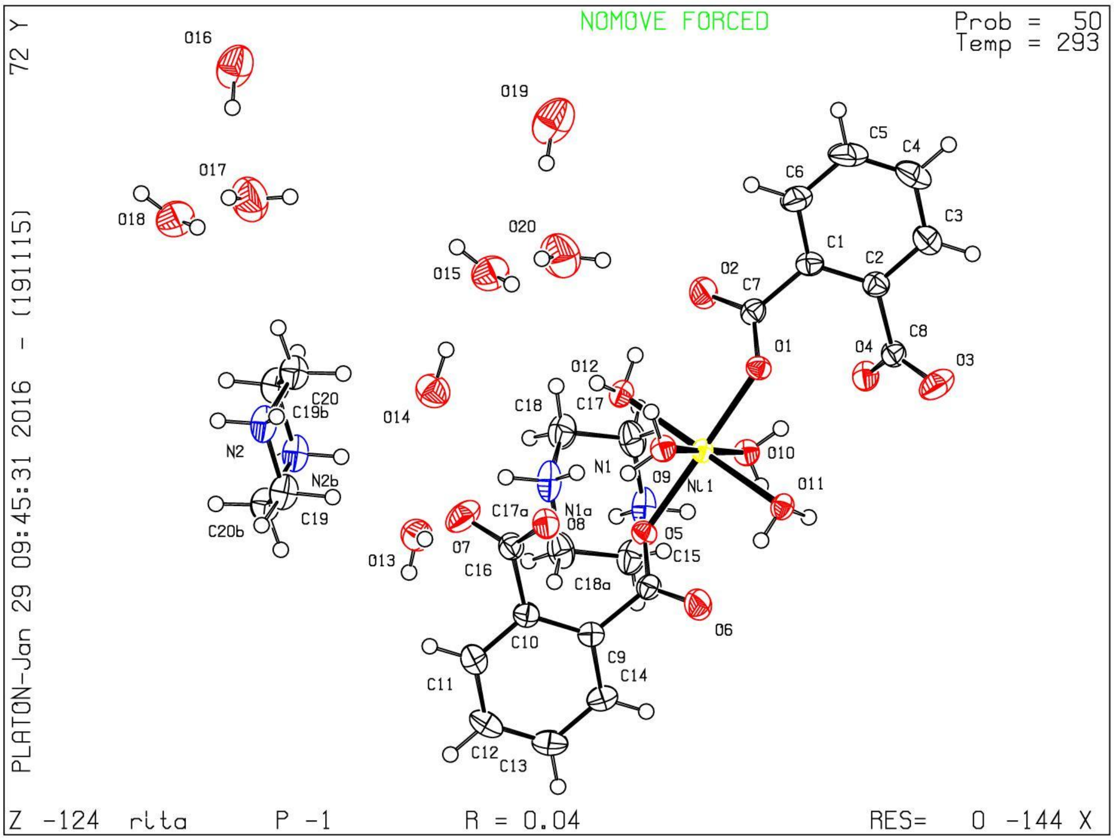
0 **ALERT level A** = Most likely a serious problem - resolve or explain 0 **ALERT level B** = A potentially serious problem, consider carefully

0 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight 18 **ALERT level G** = General information/check it is not something unexpected

4ALERT type 1 CIF construction/syntax error, inconsistent or missing data
6ALERT type 2 Indicator that the structure model may be wrong or deficient
1ALERT type 3 Indicator that the structure quality may be low
5ALERT type 4Improvement, methodology, query or suggestion
2ALERT type 5Informative message, check

PLATON version of 19/11/2015; check.def file version of 17/11/2015

Datablock NiPP - ellipsoid plot



CheckCIF/PLATON report for $(pipH_2)[Co(pht)_2(H_2O)_4]\cdot 8H_2O$ 4

Datablock: CoPP

Bond precision: C-C = 0.0031 A Wavelength=0.71073

Cell:	a=11.8572(3)	b=12.4961(3)	c=27.2165(6)
	alpha=79.050(1)	beta=88.648(1)	gamma=82.029(1)
Temperature:	296 K		

	Calculated	Reported
Volume	3920.95(16)	3920.95(16)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	N2,C16 H16 Co O12,8(H2 O)	C4 H12 N2 O12, C4,8(H2 O)
Sum formula	C20 H44 Co N2 O20	C20 H44 Co N2 O20
Mr	691.50	691.50
Dx,g cm-3	1.464	1.464
Z	5	5
Mu (mm-1)	0.632	0.632
F000	1825.0	1825.0
F000’	1827.95	
h,k,lmax	14,14,32	14,14,32
Nref	13795	13783
Tmin,Tmax	0.827,0.881	0.833,0.884
Tmin’	0.827	

Correction method= # Reported T Limits: Tmin=0.833 Tmax=0.884
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.000R(reflections)= 0.0311(9968) wR2(reflections)= 0.1001(13783) S = 1.052 Npar= 1151

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert- type_alert-level**. Click on the hyperlinks for more details of the test.

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the_exptl_absorpt_process_details field.
Absorption correction given as multi-scan

PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Co1 -- O9 .. 6.3 su PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Co1 -- O12 .. 6.0 su PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Co2 -- O19 .. 6.1 su PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Co2 -- O20 .. 5.6 su PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Co3 -- O25 .. 5.8 su
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.3 Note
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.4 Note

Alert level G

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  PLAT005_ALERT_5_ No _iucr_refine_instructions_details   in the CIF              Please       Do !
  PLAT007_ALERT_5_ Number of Unrefined Donor-H Atoms ..............                         10 Report
  PLAT066_ALERT_1_ Predicted and Reported Tmin&Tmax Range Identical                          ? Check
  PLAT112_ALERT_2_ ADDSYM Detects Additional (Pseudo) Symm. Elem...           sub          Check
  PLAT154_ALERT_1_ The su's on the Cell Angles are Equal ..........           0.00100      Degree
  PLAT432_ALERT_2_ Short Inter X...Y Contact   O1      ..  C48      ..        3.00         Ang.
  PLAT432_ALERT_2_ Short Inter X...Y Contact   O9      ..  C45      ..        3.01         Ang.
  PLAT432_ALERT_2_ Short Inter X...Y Contact   O19     ..  C47      ..        3.02         Ang.
  PLAT432_ALERT_2_ Short Inter X...Y Contact   O21     ..  C46      ..        2.99         Ang.
  PLAT710_ALERT_4_ Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #                          1 Do !
O6   -CO1 -O1   -C1     70.00   2.00    1.555    1.555    1.555    1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #          6 Do !
O1   -CO1 -O6   -C9     105.00  2.00    1.555    1.555    1.555    1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #        53 Do !
O21 -CO2 -O16 -C17    -97.00  3.00    1.555    1.555    1.555    1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #         58 Do !
O16 -CO2 -O21 -C25    -79.00  3.00    1.555    1.555    1.555    1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #        105 Do !
O27 -CO3 -O27 -C33      4.00   0.00    2.766    1.555    1.555    1.555
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #          4 Note
C4 H12 N2
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #          5 Note
C4 H12 N2
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #          7 Note
H2 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #        10 Note
H2 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #         13 Note
H2 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #         20 Note
H2 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #         22 Note
H2 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #         24 Note
H2 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #         26 Note
H2 O
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         99 Note
PLAT899_ALERT_4_G SHELXL97     is Deprecated and Succeeded by SHELXL      2014 Note
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
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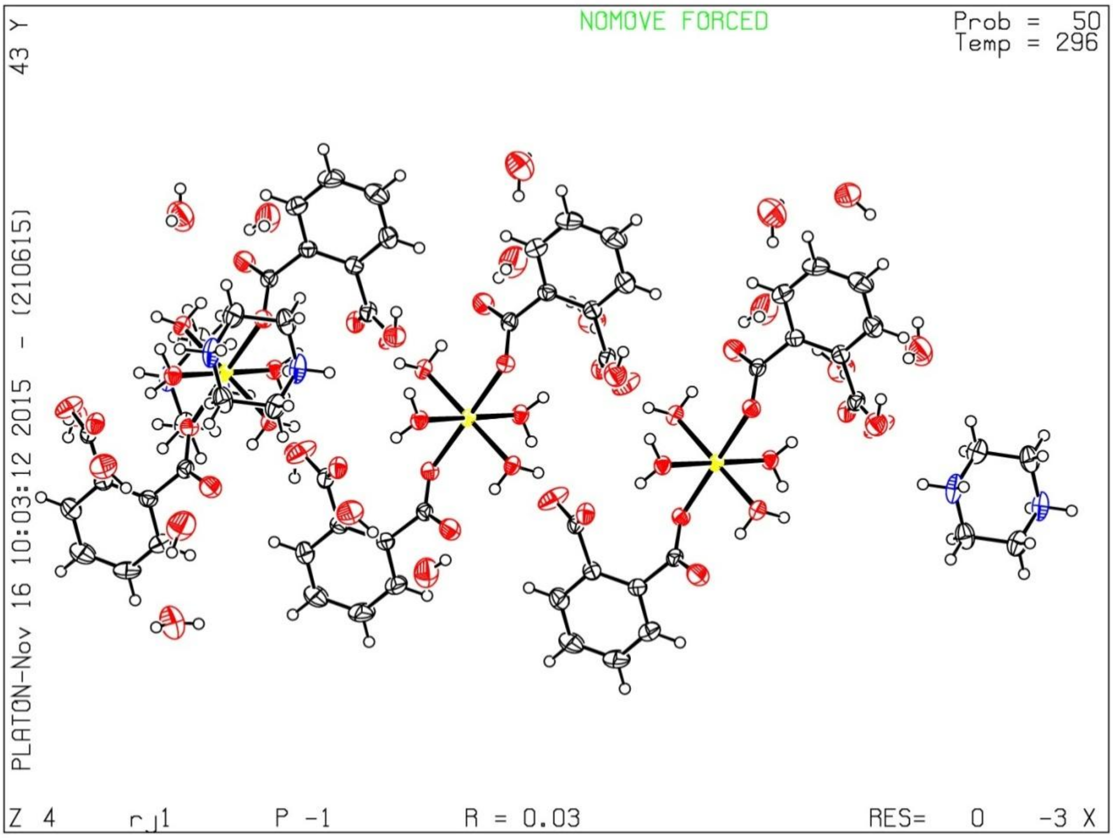
26 **ALERT level G** = General information/check it is not something unexpected
3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
13 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
15 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

PLATON version of 21/06/2015; check.def file version of 21/06/2015

Datablock CoPP - ellipsoid plot



CheckCIF/PLATON report for $(pipH_2)[Cu(pht)_2(H_2O)_4]\cdot 8H_2O$ 5

Datablock: C uPP

Bond precision: C-C = 0.0182 A Wavelength=0.71073

Cell:	a=11.9101(5)	b=12.3555(6)	c=16.6034(7)
	alpha=100.649(2)	beta=97.357(2)	gamma=96.264(2)
Temperature:	296 K		

	Calculated	Reported
Volume	2359.23(18)	2359.23(18)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C16 H16 Cu 8(H2 O)	N2,C16 H16 Cu O12, C4 H12 N2, 8(H2 O)
Sum formula	C20 H44 Cu N2 O20	C20 H44 Cu N2 O20
Mr	696.12	696.11
Dx,g cm-3	1.470	1.470
Z	3	3
Mu (mm-1)	0.779	0.779
F000	1101.0	1101.0
F000’	1102.67	
h,k,lmax	14,14,19	14,14,19
Nref	8323	8318
Tmin,Tmax	0.829,0.856	0.829,0.860
Tmin’	0.823	

Correction method= # Reported T Limits: Tmin=0.829 Tmax=0.860
AbsCorr = MULTI-SCAN
Data completeness= 0.999 Theta(max)= 25.000

R(reflections)= 0.0290(6460) wR2(reflections)= 0.0876(8318)
S = 1.054 Npar= 714

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.

Click on the hyperlinks for more details of the test.

Alert level B

PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds .... 0.0182 Ang.

Alert level
C

```
PLAT314_ALERT_2_  Check  Small Angle   for  H2O:  Metal-O5    -H5A        83.34     Degree
PLAT314_ALERT_2_  Check  Small Angle   for  H2O:  Metal-O21   -H21B       82.47     Degree
PLAT314_ALERT_2_  Check  Small Angle   for  H2O:  Metal-O30   -H30C       83.43     Degree
PLAT480_ALERT_4_  Long  H...A   H-Bond  Reported   H26A ..    O13  ..     2.61      Ang.
PLAT480_ALERT_4_  Long  H...A   H-Bond  Reported   H26B ..    O25  ..     2.64      Ang.
PLAT480_ALERT_4_  Long  H...A   H-Bond  Reported   H28B ..    O6   ..     2.62      Ang.
PLAT480_ALERT_4_  Long  H...A   H-Bond  Reported   H29A ..    O7   ..     2.65      Ang.
PLAT758_ALERT_4_  D-H..A   Calc      176.00, Rep        175(20)     ......    Senseless   su
               O18 -H18A   -O17      1.555    1.555      1.555       #        165
PLAT758_ALERT_4_  D-H..A   Calc      167.00, Rep        167(19)     ......    Senseless   su
               O22 -H22B   -O23      1.555    1.555      1.555       #        165
PLAT758_ALERT_4_  D-H..A   Calc      168.00, Rep        168(18)     ......    Senseless   su
               O24 -H24B   -O25      1.555    1.555      1.555       #        165
PLAT758_ALERT_4_  D-H..A   Calc      177.00, Rep        177(18)     ......    Senseless   su
               O25 -H25D   -O26      1.555    1.555      1.555       #        165
PLAT758_ALERT_4_  D-H..A   Calc      177.00, Rep        177(15)     ......    Senseless   su
               O29 -H29D   -O28      1.555    1.555      1.555       #        165
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.   #     1 Note

C16 H16 Cu O12
```

Alert level
G

```
PLAT005_ALERT_5_  No _iucr_refine_instructions_details  in the CIF              Please      Do !
PLAT007_ALERT_5_  Number of Unrefined Donor-H Atoms ..............                         6 Report
PLAT066_ALERT_1_  Predicted and Reported Tmin&Tmax Range Identical                          ? Check
PLAT112_ALERT_2_  ADDSYM Detects Additional (Pseudo) Symm. Elem...             sub         Check
PLAT154_ALERT_1_  The su's on the Cell Angles are Equal ..........             0.00200     Degree
PLAT432_ALERT_2_  Short Inter X...Y Contact   O5     ..  C29     ..            3.00        Ang.
PLAT432_ALERT_2_  Short Inter X...Y Contact   O8     ..  C30     ..            3.02        Ang.
PLAT710_ALERT_4_  Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #                        22 Do !
O8   -CU1 -O1   -C1     121.00 15.00    1.555    1.555    1.555    1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #      46 Do !
O1   -CU1 -O8   -C9      55.00 16.00    1.555    1.555    1.555    1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... #      70 Do !
O13 -CU2 -O13 -C17     14.00   0.00    2.565    1.555    1.555    1.555
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #        5 Note
H2 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #        6 Note
H2 O
 PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #       7 Note
H2 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #      8 Note
H2 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #       9 Note
H2 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #      10 Note
H2 O
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #      11 Note
H2 O
   PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #     12 Note
  H2 O
   PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #    13 Note
  H2 O
  PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.   #     14 Note
 H2 O
PLAT794_ALERT_5_G  Tentative  Bond  Valency  for  Cu1        (II)       .....          2.09   Note
PLAT794_ALERT_5_G  Tentative  Bond  Valency  for  Cu2        (II)       .....          2.07   Note
```

PLAT860_ALERT_3_G Number of Least-Squares Restraints .... 54 Note
PLAT899_ALERT_4_G SHELXL97 is Deprecated and Succeeded by SHELXL 2014 Note

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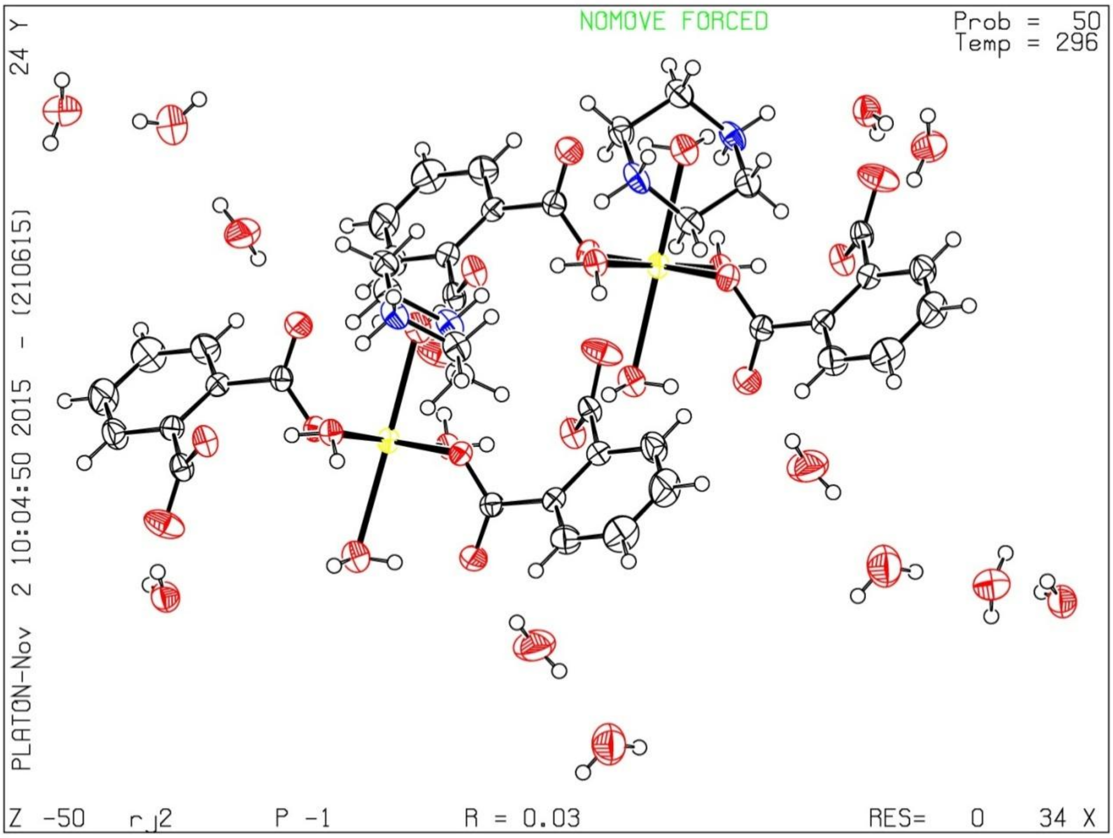
7 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
25 ALERT type 4 Improvement, methodology, query or suggestion
4 ALERT type 5 Informative message, check

PLATON version of 21/06/2015; check.def file version of 21/06/2015

Datablock CuPP - ellipsoid plot



CheckCIF/PLATON report for $[Ni(Im)_6]pht\cdot H_2O$ 6

Datablock: NiImpt

Bond precision:	C-C = 0.0049 A		Wavelength=0.71073
Cell:	a=13.0759(6)	b=13.0309(7)	c=18.4208(9)
	alpha=90	beta=105.636(2)	gamma=90
Temperature:	293 K		

	Calculated	Reported
Volume	3022.6(3)	3022.6(3)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C18 H24 N12 Ni, C8 H4 O4, H2 O	C18 H24 N12 Ni, C8 H4 O4,H2 O
Sum formula	C26 H30 N12 Ni O5	C26 H30 N12 Ni O5
Mr	649.31	649.33
Dx,g cm-3	1.427	1.427
Z	4	4
Mu (mm-1)	0.699	0.699
F000	1352.0	1352.0
F000'	1353.80	
h,k,lmax	15,15,21	15,15,21
Nref	5316	5305
Tmin,Tmax	0.778,0.811	0.750,0.900
Tmin'	0.756	

Correction method= # Reported T Limits: Tmin=0.750 Tmax=0.900 AbsCorr = MULTI-SCAN
Data completeness= 0.998 Theta(max)= 25.000
R(reflections)= 0.0398(4017) wR2(reflections)= 0.1295(5305)
S = 1.082 Npar= 405

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level C

PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of						C17	Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of						C26	Check
PLAT369_ALERT_2_C Long C(sp2)-C(sp2) Bond	C25	-	C26	..		1.53	Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported	H6	..	O2	..		2.63	Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported	H10	..	N11	..		2.66	Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported	H6	..	O2	..		2.63	Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported	H10	..	N11	..		2.66	Ang.

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or        Angle Restraints on AtSite                3        Note
PLAT005_ALERT_5_G No Embedded Refinement    Details found          in the CIF            Please   Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............                       6        Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ                       Please   Check
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)                       293      Check
PLAT200_ALERT_1_G Reported  _diffrn_ambient_temperature ..... (K)                        293      Check
PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4       Linear Torsion Angle ... #                1        Do !
N7                  -NI1 -N1     -C1    -15.00    2.00    1.555     1.555     1.555     1.555
PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4       Linear    Torsion Angle ... #             6        Do !
N7                  -NI1 -N1     -C3    164.00    2.00    1.555     1.555     1.555     1.555
PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4       Linear    Torsion Angle ... #             20       Do !
N9                  -NI1 -N3     -C6    64.90     1.80    1.555     1.555     1.555     1.555
PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4       Linear    Torsion Angle ... #             25       Do !
N9                  -NI1 -N3     -C4    -98.40    1.70    1.555     1.555     1.555     1.555
PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4       Linear    Torsion Angle ... #             38       Do !
N11                 -NI1 -N5     -C7    -48.00    3.00    1.555     1.555     1.555     1.555
PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4       Linear    Torsion Angle ... #             43       Do !
N11                 -NI1 -N5     -C9    131.00    3.00    1.555     1.555     1.555     1.555
PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4       Linear    Torsion Angle ... #             52       Do !
N1                  -NI1 -N7     -C10   -11.00    2.00    1.555     1.555     1.555     1.555
PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4       Linear    Torsion Angle ... #             57       Do !
N1                  -NI1 -N7     -C11   158.00    2.00    1.555     1.555     1.555     1.555
PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4       Linear    Torsion Angle ... #             72       Do !
N3                  -NI1 -N9     -C13   129.10    1.60    1.555     1.555     1.555     1.555
PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4       Linear    Torsion Angle ... #             77       Do !
N3                  -NI1 -N9     -C14   -48.20    1.80    1.555     1.555     1.555     1.555
PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4       Linear    Torsion Angle ... #             90       Do !
N5                  -NI1 -N11 -C16  -142.00       3.00    1.555     1.555     1.555     1.555
PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4       Linear    Torsion Angle ... #             95       Do !
N5                  -NI1 -N11 -C18      33.00     3.00    1.555     1.555     1.555     1.555
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............                       3        Note
PLAT899_ALERT_4_G
SHELXL97                         is Deprecated and Succeeded by SHELXL                   2014     Note
```

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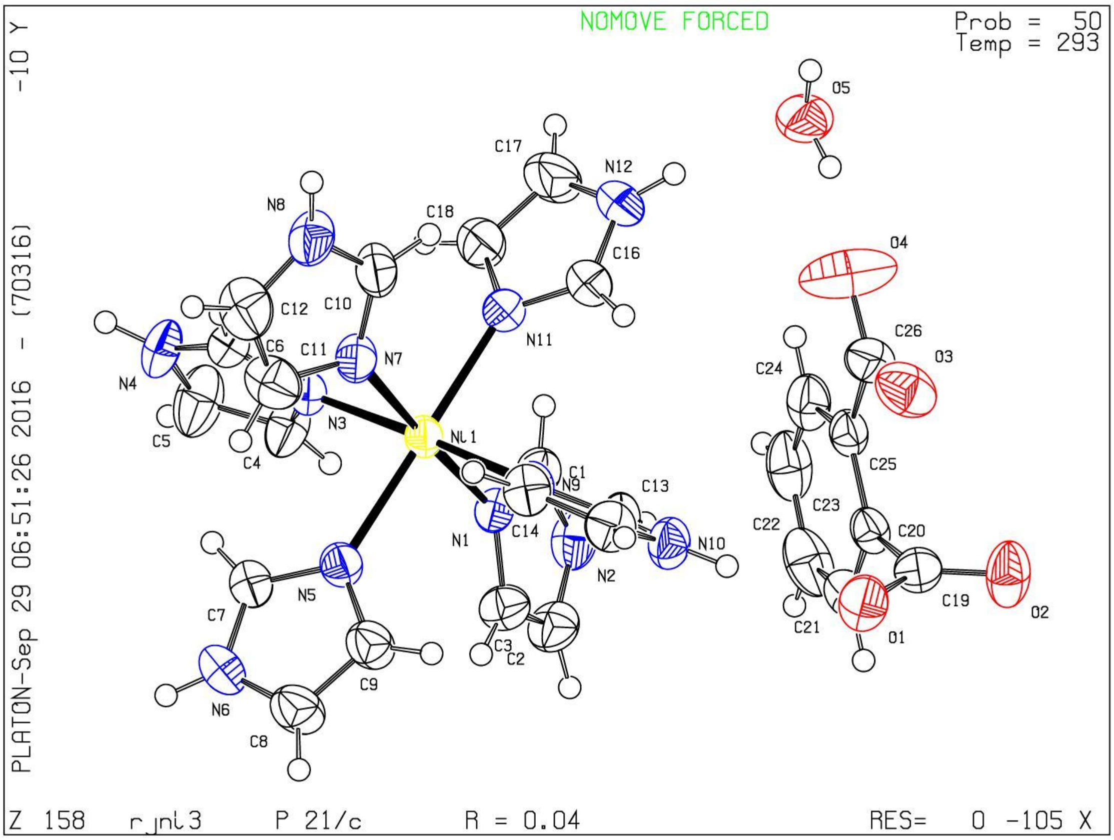
20 **ALERT level G** = General information/check it is not something unexpected

```
3      ALERT type   1  CIF construction/syntax error, inconsistent                or missing data
4      ALERT type   2  Indicator that the          structure model may be wrong or deficient
1      ALERT type   3  Indicator that the          structure quality may be       low
17     ALERT type   4  Improvement, methodology, query or suggestion
2      ALERT type   5  Informative message, check
```

PLATON version of 11/08/2016; check.def file version of 04/08/2016

Datablock NiImpt - ellipsoid plot



CheckCIF/PLATON report for $[\mathrm{Co(Im)_6}]$pht·$\mathrm{H_2O}$ 7

Datablock: CoImPt

Bond precision:	C-C = 0.0044 A		Wavelength=0.71073
Cell:	a=13.1134(4)	b=13.0374(4)	c=18.4269(6)
	alpha=90	beta=105.388(2)	gamma=90
Temperature:	293 K		

	Calculated	Reported
Volume	3037.41(17)	3037.41(16)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C18 H24 Co N12, C8 H4 O4, H2 O	C18 H24 Co N12, C8 H4 O4, H2 O
Sum formula	C26 H30 Co N12 O5	C26 H30 Co N12 O5
Mr	649.55	649.55
Dx,g cm-3	1.420	1.420
Z	4	4
Mu (mm-1)	0.622	0.622
F000	1348.0	1348.0
F000'	1349.85	
h,k,lmax	15,15,21	15,15,21
Nref	5339	5337
Tmin,Tmax	0.799,0.830	0.789,0.835
Tmin'	0.780	

Correction method= # Reported T Limits: Tmin=0.789 Tmax=0.835 AbsCorr = MULTI-SCAN
Data completeness= 1.000 Theta(max)= 25.000
R(reflections)= 0.0376(4191) wR2(reflections)= 0.1009(5337)
S = 1.146 Npar= 416

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

● Alert level C

PLAT230_ALERT_2_C	Hirshfeld Test Diff for	C22	-- C23	..	5.7s.u.
PLAT241_ALERT_2_C	High 'MainMol' Ueq as Compared to Neighbors of				C5Check
PLAT241_ALERT_2_C	High 'MainMol' Ueq as Compared to Neighbors of				C17Check
PLAT480_ALERT_4_C	Long H...A H-Bond Reported	H6	.. O2	..	2.63Ang.
PLAT480_ALERT_4_C	Long H...A H-Bond Reported	H7	.. N3	..	2.66Ang.
PLAT480_ALERT_4_C	Long H...A H-Bond Reported	H10	.. N11	..	2.70Ang.
PLAT480_ALERT_4_C	Long H...A H-Bond Reported	H6	.. O2	..	2.63Ang.
PLAT480_ALERT_4_C	Long H...A H-Bond Reported	H7	.. N3	..	2.66Ang.
PLAT480_ALERT_4_C	Long H...A H-Bond Reported	H10	.. N11	..	2.70Ang.

Alert level G

```
 PLAT002_ALERT_2_G
Number                          of Distance or                 Angle Restraints on AtSite                6 Note
 PLAT003_ALERT_2_G Number of Uiso or Uij                      Restrained non-H Atoms ...                2 Report
 PLAT005_ALERT_5_G No Embedded Refinement          Details found              in the CIF          Please Do !
 PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............                                     6 Report
 PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)                                   293 Check
 PLAT200_ALERT_1_G Reported                 _diffrn_ambient_temperature ..... (K)                     293 Check
 PLAT301_ALERT_3_G Main Residue   Disorder                              ............ Percentage =          2 Note
 PLAT367_ALERT_2_G Long?   C(sp?)-C(sp?) Bond          C25        -     C26    ..                     1.52 Ang.
 PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4         Linear             Torsion Angle ... #                1 Do !
N7                 -CO1 -N1     -C1          -17.00    2.00        1.555      1.555   1.555           1.555
 PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4         Linear             Torsion Angle ... #                6 Do !
N7                 -CO1 -N1     -C3          162.00    1.90        1.555      1.555   1.555           1.555
 PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4         Linear             Torsion Angle ... #               20 Do !
N9                 -CO1 -N3     -C6           65.40    1.70        1.555      1.555   1.555           1.555
 PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4         Linear             Torsion Angle ... #               25 Do !
N9                 -CO1 -N3     -C4          -97.70    1.60        1.555      1.555   1.555           1.555
 PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4         Linear             Torsion Angle ... #               38 Do !
N11 -CO1 -N5                    -C7          -43.00    2.00        1.555      1.555   1.555           1.555
 PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4         Linear             Torsion Angle ... #               43 Do !
N11 -CO1 -N5                    -C9          136.00    2.00        1.555      1.555   1.555           1.555
 PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4         Linear             Torsion Angle ... #               52 Do !
N1                 -CO1 -N7     -C10         -11.00    2.00        1.555      1.555   1.555           1.555
 PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4         Linear             Torsion Angle ... #               57 Do !
N1                 -CO1 -N7     -C11         158.70    1.90        1.555      1.555   1.555           1.555
 PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4         Linear             Torsion Angle ... #               72 Do !
N3                 -CO1 -N9     -C13         128.60    1.60        1.555      1.555   1.555           1.555
 PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4         Linear             Torsion Angle ... #               77 Do !
N3                 -CO1 -N9     -C14         -50.40    1.70        1.555      1.555   1.555           1.555
 PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4         Linear             Torsion Angle ... #               90 Do !
N5                 -CO1 -N11         -C16  -146.00    2.00        1.555      1.555   1.555           1.555
 PLAT710_ALERT_4_G Delete  1-2-3 or 2-3-4         Linear             Torsion Angle ... #               95 Do !
N5                 -CO1 -N11    -C18          27.00    2.00        1.555      1.555   1.555           1.555
 PLAT779_ALERT_4_G Suspect or Irrelevant            (Bond) Angle in           CIF .... #              129 Check
O4                 -C26         -O4'          1.555        1.555       1.555                       26.10 Deg.
 PLAT860_ALERT_3_G Number of Least-Squares Restraints .............                                    10 Note
 PLAT899_ALERT_4_G
SHELXL97                                       is Deprecated and Succeeded by SHELXL                 2014 Note
```

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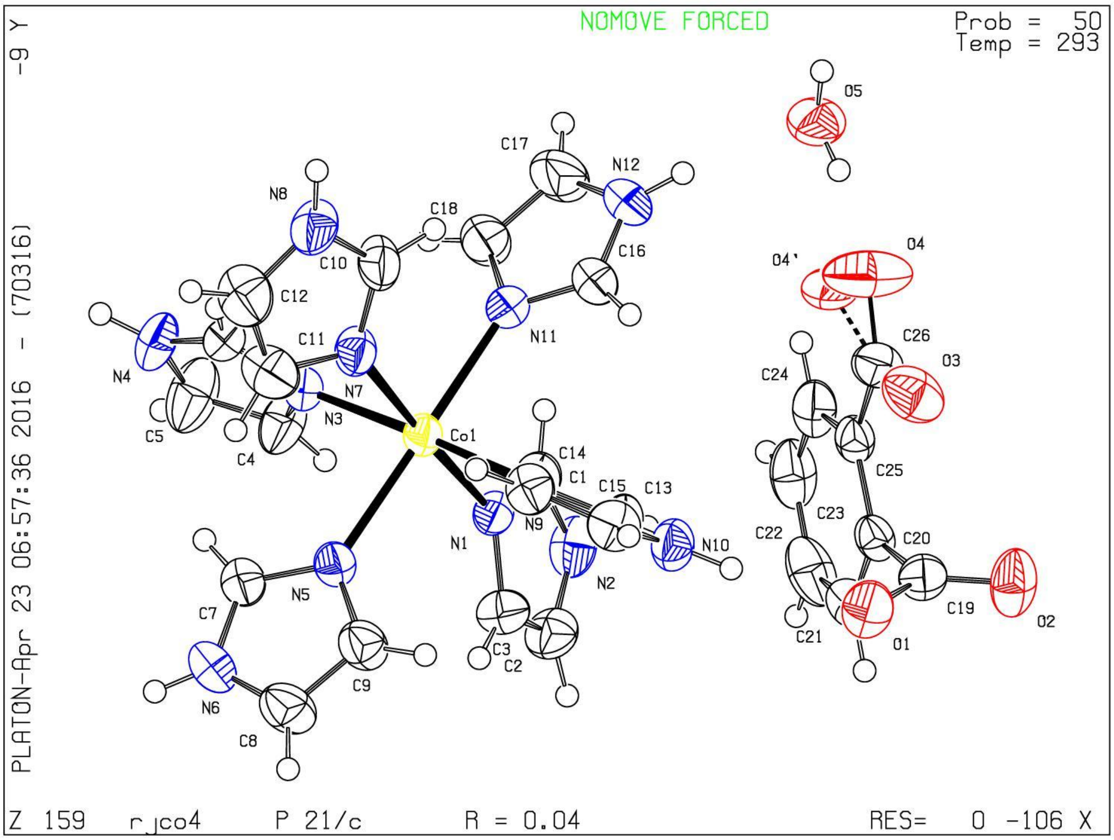
9 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight 23 **ALERT level G** = General information/check it is not something unexpected

```
    2ALERT type    1CIF construction/syntax error, inconsistent               or missing data
    6ALERT type    2Indicator that the          structure model may be wrong or deficient
    2ALERT type    3Indicator that the          structure quality may be            low
   20ALERT type    4Improvement, methodology, query or suggestion
    2ALERT type    5Informative message, check
```

PLATON version of 30/03/2016; check.def file version of 30/03/2016

Datablock CoImPt - ellipsoid plot



CheckCIF/PLATON report for [$Cu_2(Im)_4(pht)_2(H_2O)$] 8

Datablock: CuImpt

Bond precision:	C-C = 0.0033 A	Wavelength=0.71073	
Cell:	a=8.8768(4)	b=22.3595(12)	c=16.1084(9)
	alpha=90	beta=105.454(2)	gamma=90
Temperature:	296 K		

	Calculated	Reported
Volume	3081.6(3)	3081.6(3)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C28 H26 Cu2 N8 O9, H2 O	C28 H26 Cu2 N8 O9, H2 O
Sum formula	C28 H28 Cu2 N8 O10	C28 H28 Cu2 N8 O10
Mr	763.68	763.66
Dx,g cm-3	1.646	1.646
Z	4	4
Mu (mm-1)	1.451	1.451
F000	1560.0	1560.0
F000'	1563.18	
h,k,lmax	11,28,20	11,28,20
Nref	6738	6736
Tmin,Tmax	0.654,0.696	0.550,0.730
Tmin'	0.641	

Correction method= # Reported T Limits: Tmin=0.550 Tmax=0.730 AbsCorr = MULTI-SCAN
Data completeness= 1.000 Theta(max)= 26.999
R(reflections)= 0.0298(5657) wR2(reflections)= 0.0732(6736)
S = 1.045 Npar= 449

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

● **Alert level B**

PLAT232_ALERT_2_B Hirshfeld Test Diff (M-X) Cu2 -- O8 ..17.5 s.u.

Author Response: The bond Cu2-O8(2.304 angstoms) is not a covalent bond. Itis is a weak coordnation bond and hence may not be rigid. Rigid bond conditions needed for Hirshfeld test is not applicable to the situation.

● **Alert level C**

PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 3.9Ratio
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C20Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C21Check
PLAT480_ALERT_4_C Long H...A H-Bond Reported H16 .. O8 .. 2.65Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported H16 .. O8 .. 2.65Ang.

● **Alert level G**

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 6Note

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 3Report
PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension 2Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms 4Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records 2Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records 1Report
PLAT794_ALERT_5_G Tentative Bond Valency for Cu1 (II) 1.97Note
PLAT794_ALERT_5_G Tentative Bond Valency for Cu2 (II) 2.07Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints 15Note

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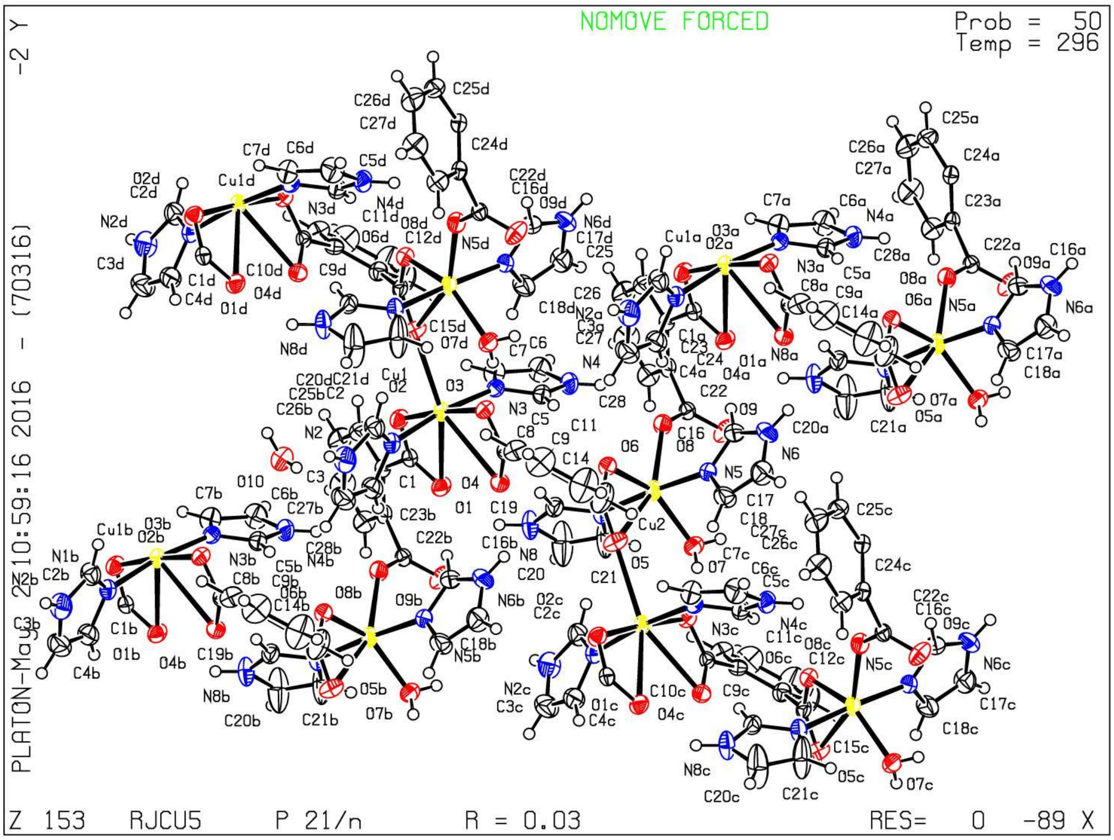
0 **ALERT level A** = Most likely a serious problem - resolve or explain 1 **ALERT level B** = A potentially serious problem, consider carefully

5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight 9 **ALERT level G** = General information/check it is not something unexpected

0ALERT type 1 CIF construction/syntax error, inconsistent or missing data
6ALERT type 2 Indicator that the structure model may be wrong or deficient
1ALERT type 3 Indicator that the structure quality may be low
4ALERT type 4Improvement, methodology, query or suggestion
4ALERT type 5Informative message, check

PLATON version of 30/03/2016; check.def file version of 30/03/2016

Datablock CuImpt - ellipsoid plot



CheckCIF/PLATON report for [Na(2-carboxy-6-nba)(H_2O)$_3$]·H_2O 9

Datablock: Na 3-npaH

Bond precision: C-C = 0.0016 A Wavelength=0.71073

Cell: a=6.8903(5) b=7.5137(5) c=12.8854(9)
alpha=77.567(6) beta=83.374(6) gamma=74.389(6)
Temperature: 170 K

	Calculated	Reported
Volume	626.25(8)	626.25(8)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C8 H10 N Na O9, H2 O	C8 H10 N Na O9, H2 O
Sum formula	C8 H12 N Na O10	C8 H12 N Na O10
Mr	305.18	305.18
Dx,g cm-3	1.618	1.618
Z	2	2
Mu (mm-1)	0.179	0.179
F000	316.0	316.0
F000'	316.30	
h,k,lmax	9,9,17	9,9,17
Nref	3013	3002
Tmin,Tmax	0.975,0.986	0.817,0.961
Tmin'	0.939	

Correction method= # Reported T Limits: Tmin=0.817 Tmax=0.961 AbsCorr = NUMERICAL
Data completeness= 0.996 Theta(max)= 28.004
R(reflections)= 0.0316(2594) wR2(reflections)= 0.0877(3002)
S = 1.062 Npar= 182

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.

Click on the hyperlinks for more details of the test.

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field.

Absorption correction given as numerical

Alert level G

PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension 1Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms 9Report
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note) 0.006Degree
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) . 1.19Ratio

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain

0 **ALERT level B** = A potentially serious problem, consider carefully

1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

4 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

0 ALERT type 2 Indicator that the structure model may be wrong or deficient

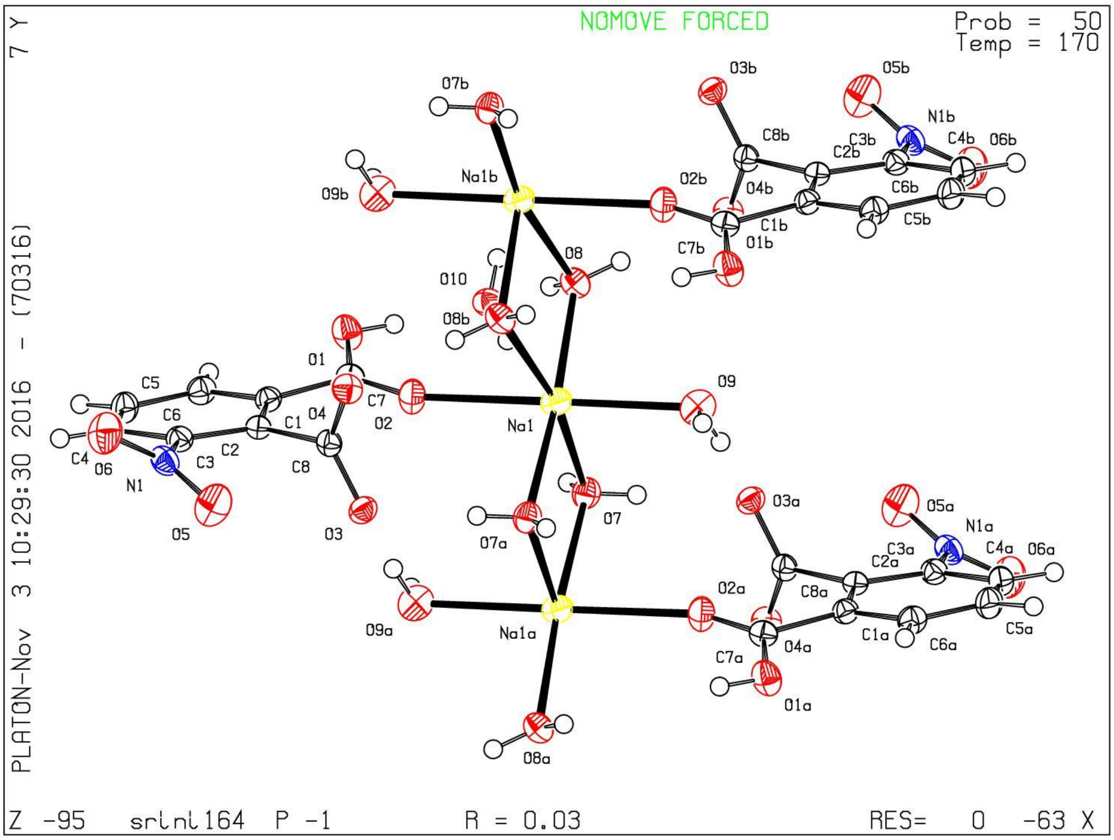
0 ALERT type 3 Indicator that the structure quality may be low

1 ALERT type 4 Improvement, methodology, query or suggestion

2 ALERT type 5 Informative message, check

PLATON version of 11/08/2016; check.def file version of 04/08/2016

Datablock Na 3-npaH - ellipsoid plot



CheckCIF/PLATON report for [K(2-carboxy-3-nba)] 10

Datablock: K 3-npaH

Bond precision:	C-C = 0.0039 A	Wavelength=0.71073	
Cell:	a=13.0237(8)	b=8.6490(4)	c=8.2763(4)
	alpha=90	beta=102.771(4)	gamma=90
Temperature:	170 K		

	Calculated	Reported	
Volume	909.20(8)	909.20(8)	
Space group	P 21/c	P 21/c	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C8 H4 K N O6	C8 H4	K N O6
Sum formula	C8 H4 K N O6	C8 H4	K N O6
Mr	249.22	249.22	
Dx,g cm-3	1.821	1.821	
Z	4	4	
Mu (mm-1)	0.598	0.598	
F000	504.0	504.0	
F000'	505.12		
h,k,lmax	16,10,10	16,10,10	
Nref	1786	1783	
Tmin,Tmax	0.917,0.953	0.786,0.929	
Tmin'	0.887		

Correction method= # Reported T Limits: Tmin=0.786 Tmax=0.929
AbsCorr = NUMERICAL

Data completeness= 0.998 Theta(max)= 26.000
R(reflections)= 0.0470(1576) wR2(reflections)= 0.1324(1783)
S = 1.039 Npar= 145

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.

Click on the hyperlinks for more details of the test.

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field.
Absorption correction given as numerical

```
PLAT731_ALERT_1_C Bond  Calc    4.1662(7), Rep    4.1662(2) ......    4 su-Rat
K1                -K1           1.555   4.576 ............  #       11  Check
PLAT731_ALERT_1_C Bond  Calc    4.1662(7), Rep    4.1662(2) ......    4 su-Rat
K1                -K1           1.555   4.575 ............  #       12  Check
```

Alert level G

PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension 2 Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .... 1 Report
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) . 1.46 Ratio
PLAT774_ALERT_1_G Suspect X-Y Bond in CIF: K1 -- K1 .. 4.17 Ang.
PLAT774_ALERT_1_G Suspect X-Y Bond in CIF: K1 -- K1 .. 4.17 Ang.

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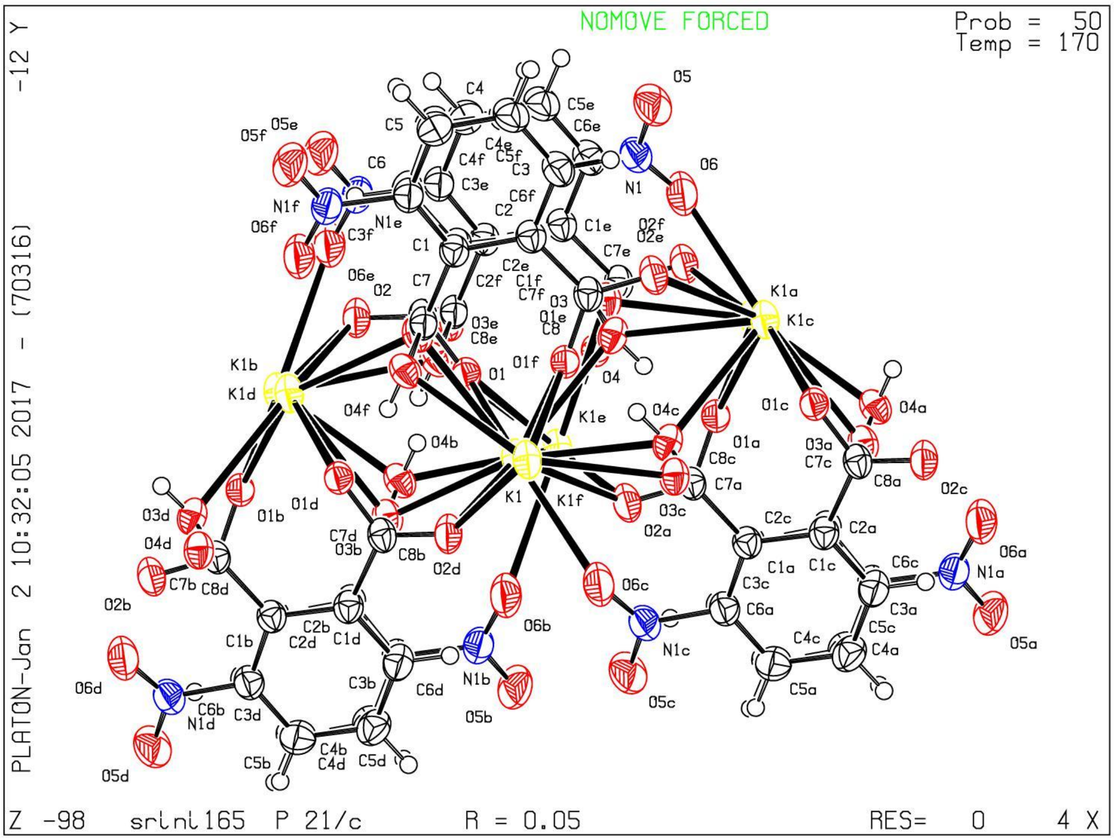
0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected
5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

PLATON version of 24/11/2016; check.def file version of 23/11/2016

Datablock K 3-npaH - ellipsoid plot



CheckCIF/PLATON report for [Cs(3-nphtH)]·$2H_2O$ 11

Datablock: Cs3npa21

Bond precision:	C-C = 0.0036 A	Wavelength=0.71073	
Cell:	a=13.1768(5)	b=11.6552(3)	c=13.4456(5)
	alpha=90	beta=90	gamma=90
Temperature:	296 K		

	Calculated	Reported
Volume	2064.95(12)	2064.95(12)
Space group	P c c a	P c c a
Hall group	-P 2a 2ac	-P 2a 2ac
Moiety formula	C16 H9 Cs N2 O12, 2(H2 O)	C16 H9 Cs N2 O12, 2(H2 O)
Sum formula	C16 H13 Cs N2 O14	C16 H13 Cs N2 O14
Mr	590.19	590.19
Dx,g cm-3	1.898	1.898
Z	4	4
Mu (mm-1)	1.872	1.872
F000	1160.0	1160.0
F000'	1159.24	
h,k,lmax	17,15,17	17,15,18
Nref	2598	2543
Tmin,Tmax	0.799,0.829	0.650,0.746
Tmin'	0.755	

Correction method= # Reported T Limits: Tmin=0.650 Tmax=0.746 AbsCorr = MULTI-SCAN
Data completeness= 0.979 Theta(max)= 28.407
R(reflections)= 0.0393(2130) wR2(reflections)= 0.0804(2543)
S = 1.240 Npar= 159

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.

Click on the hyperlinks for more details of the test.

Alert level C

PLAT417_ALERT_2_C Short Inter D-H..H-D	H2A	..H7B	2.10	Ang.
PLAT905_ALERT_3_C Negative K value in the Analysis		of Variance ...	-0.422	Report
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin &		STh/L= 0.600	49	Report
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in		FCF	19	Note

Alert level G

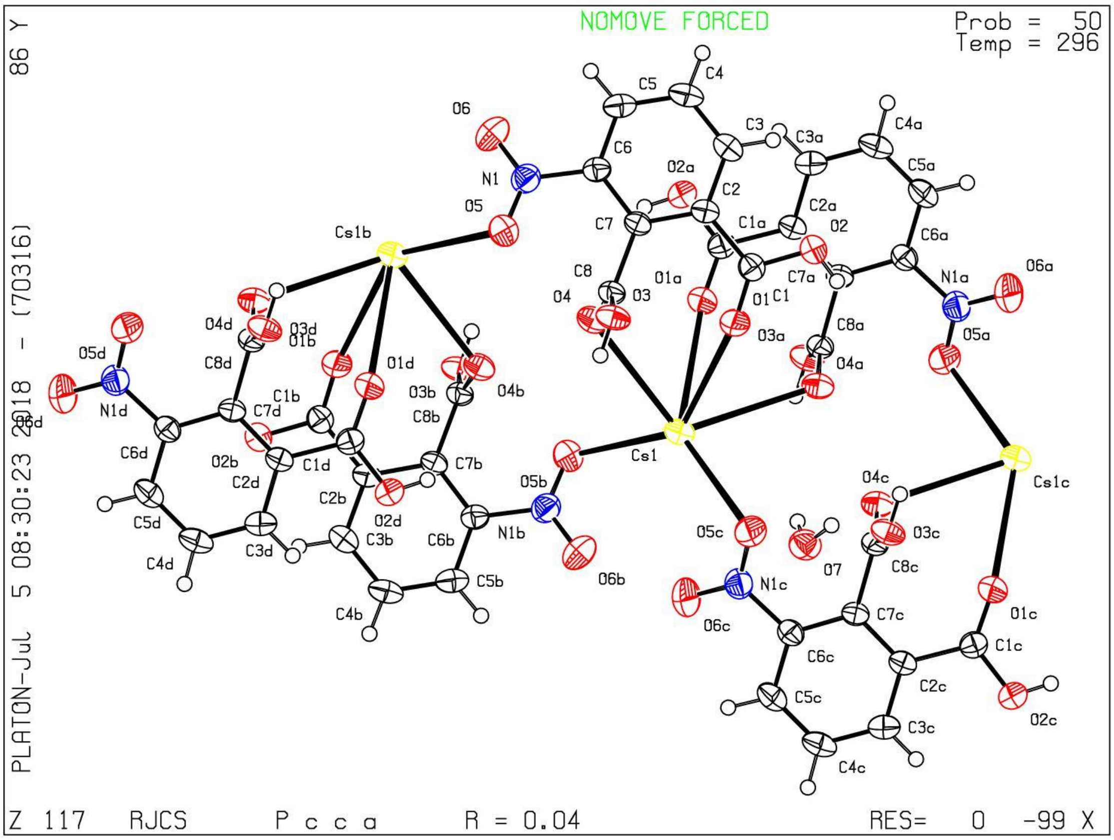
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite	3	Note
PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension	1	Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms	2	Report
PLAT019_ALERT_1_G _diffrn_measured_fraction_theta_full/*_max < 1.0	0.994	Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records	2	Report
PLAT300_ALERT_4_G Atom Site Occupancy of H3A Constrained at	0.5	Check
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) .	1.48	Ratio
PLAT860_ALERT_3_G Number of Least-Squares Restraints	3	Note

PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).	4	Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600	3	Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...	1	Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.	3	Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
12 **ALERT level G** = General information/check it is not something unexpected
1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

PLATON version of 23/04/2018; check.def file version of 23/04/2018

Datablock Cs3npa21 - ellipsoid plot



CheckCIF/PLATON report for [Rb$_2$(3-npht)] 12

Datablock: Rb3npa11

Bond precision:	C-C = 0.0021 A	Wavelength=0.71073	
Cell:	a=7.6198(9)	b=6.3293(7)	c=20.350(2)
	alpha=90	beta=94.480(4)	gamma=90
Temperature:	200 K		

	Calculated	Reported
Volume	978.44(19)	978.4(2)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C8 H3 N O6 Rb2	C8 H3 N O6 Rb2
Sum formula	C8 H3 N O6 Rb2	C8 H3 N O6 Rb2
Mr	380.05	380.05
Dx,g cm-3	2.580	2.580
Z	4	4
Mu (mm-1)	10.019	10.019
F000	720.0	720.0
F000'	713.04	
h,k,lmax	11,9,30	11,9,30
Nref	3576	3551
Tmin,Tmax	0.382,0.606	0.560,0.746
Tmin'	0.353	

Correction method= # Reported T Limits: Tmin=0.560 Tmax=0.746 AbsCorr = MULTI-SCAN
Data completeness= 0.993 Theta(max)= 32.618
R(reflections)= 0.0245(3034) wR2(reflections)= 0.0505(3551)
S = 1.094 Npar= 154

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

● Alert level C

PLAT112_ALERT_2_C ADDSYM Detects New (Pseudo) Symm. Elem	B		82	%Fit
PLAT369_ALERT_2_C Long C(sp2)-C(sp2) Bond	C7	- C8 .	1.54	Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported	H5	..O4	2.65	Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=	0.600		2	Report

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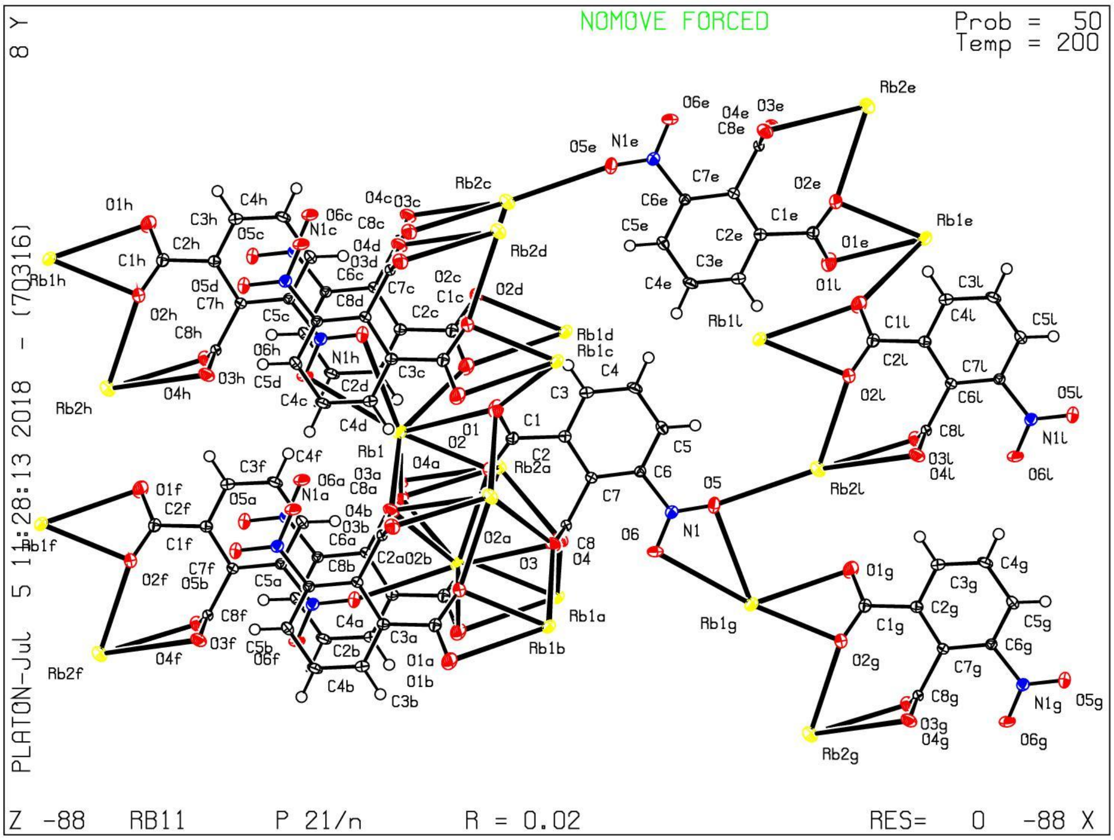
● Alert level G

PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension		3	Info
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) .		1.90	Ratio
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).		3	Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600		21	Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in	FCF	1	Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res	File ...	1	Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual	Density.	5	Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
7 **ALERT level G** = General information/check it is not something unexpected
0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

PLATON version of 23/04/2018; check.def file version of 23/04/2018

Datablock Rb3npa11 - ellipsoid plot



CheckCIF/PLATON report for [Cs$_2$(3-npht)] 13

Datablock: Cs3npa11

Bond precision:	C-C = 0.0040 A	Wavelength=0.71073	
Cell:	a=7.776(2)	b=6.526(2)	c=21.086(7)
	alpha=90	beta=95.058(11)	gamma=90
Temperature:	200 K		

	Calculated		Reported	
Volume	1065.9(6)		1065.8(6)	
Space group	P 21/n		P 21/n	
Hall group	-P 2yn		-P 2yn	
Moiety formula	C8 H3	Cs2 N O6	C8 H3	Cs2 N O6
Sum formula	C8 H3	Cs2 N O6	C8 H3	Cs2 N O6
Mr	474.93		474.93	
Dx,g cm-3	2.960		2.960	
Z	4		4	
Mu (mm-1)	6.856		6.856	
F000	864.0		864.0	
F000'	861.45			
h,k,lmax	9,8,26		9,8,26	
Nref	2096		2066	
Tmin,Tmax	0.509,0.710		0.562,0.746	
Tmin'	0.499			

Correction method= # Reported T Limits: Tmin=0.562 Tmax=0.746 AbsCorr = MULTI-SCAN
Data completeness= 0.986 Theta(max)= 25.992
R(reflections)= 0.0161(1906) wR2(reflections)= 0.0363(2066)
S = 1.132 Npar= 155

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT112_ALERT_2_C ADDSYM	Detects New (Pseudo) Symm. Elem	B	82	%Fit
PLAT369_ALERT_2_C Long	C(sp2)-C(sp2) Bond C1 - C2	.	1.54	Ang.
PLAT911_ALERT_3_C Missing	FCF Refl Between Thmin & STh/L=	0.600	23	Report
PLAT934_ALERT_3_C Number of	(Iobs-Icalc)/SigmaW > 10 Outliers		1	Check

---

Alert level G

PLAT004_ALERT_5_G	Polymeric Structure Found with Maximum Dimension	3	Info
PLAT343_ALERT_2_G	Unusual Angle Range in Main Residue for	C8	Check
PLAT367_ALERT_2_G	Long? C(sp?)-C(sp?) Bond C7 - C8 .	1.52	Ang.
PLAT764_ALERT_4_G	Overcomplete CIF Bond List Detected (Rep/Expd) .	1.76	Ratio
PLAT779_ALERT_4_	Suspect or Irrelevant (Bond) Angle in CIF .... #	18	Check

G								
CS1	-C4	-H4	4.676	1.555	1.555		41.10 Deg.	
PLAT779_ALERT_4_								
G	Suspect or Irrelevant (Bond) Angle in CIF .... #						24	Check
CS1	-C5	-H5	4.676	1.555	1.555		42.40 Deg.	
PLAT910_ALERT_3_								
G	Missing # of FCF Reflection(s) Below Theta(Min).						3	Note
PLAT912_ALERT_4_								
G	Missing # of FCF Reflections Above STh/L=					0.600	4	Note
PLAT913_ALERT_3_								
G	Missing # of Very Strong Reflections in FCF						2	Note
PLAT933_ALERT_2_								
G	Number of OMIT Records in Embedded .res File ...						4	Note
PLAT955_ALERT_1_								
G	Reported (CIF) and Actual (FCF) Lmax Differ by .						1	Units
PLAT978_ALERT_2_								
G	Number C-C Bonds with Positive Residual Density.						3	Info

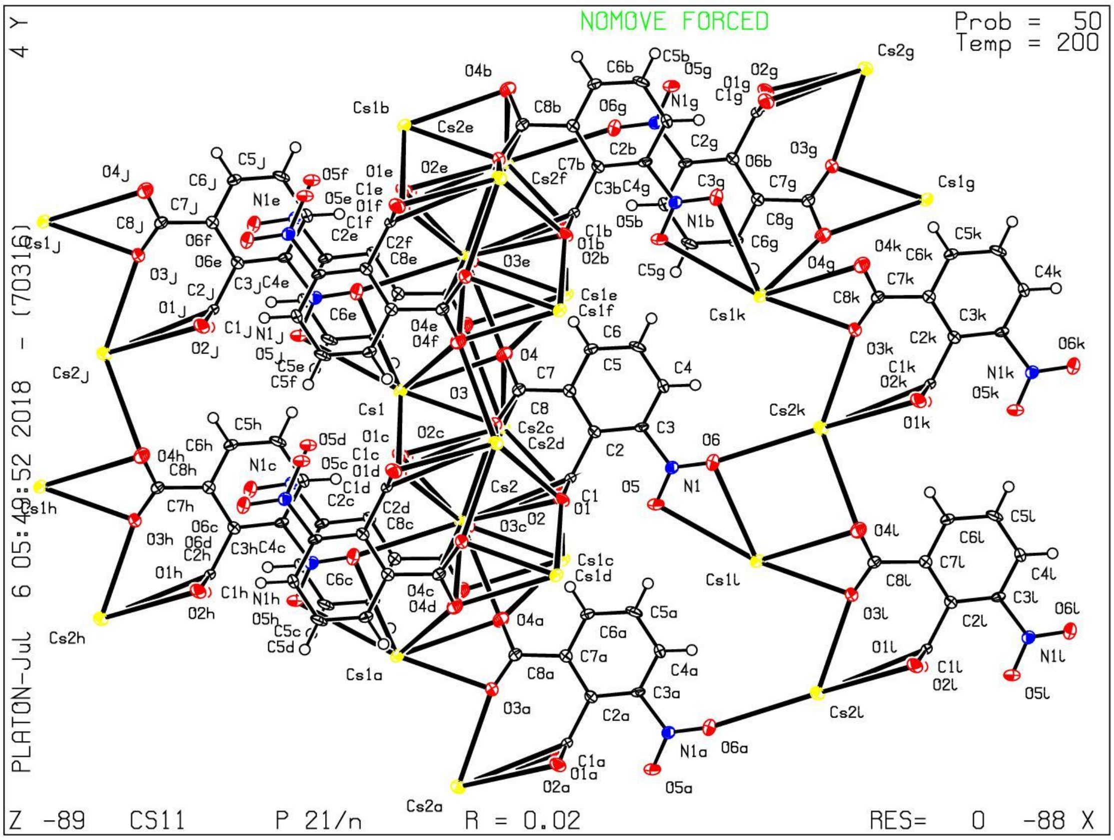
---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
12 **ALERT level G** = General information/check it is not something unexpected

1	ALERT type 1	CIF construction/syntax error, inconsistent or missing data
6	ALERT type 2	Indicator that the structure model may be wrong or deficient
4	ALERT type 3	Indicator that the structure quality may be low
4	ALERT type 4	Improvement, methodology, query or suggestion
1	ALERT type 5	Informative message, check

PLATON version of 23/04/2018; check.def file version of 23/04/2018

Datablock Cs3npa11 - ellipsoid plot



CheckCIF/PLATON report for [NaRb(3-nphtH)$_2$(H$_2$O)$_3$]·2H$_2$O 14

Datablock: NaRb3npa21

Bond precision:	C-C = 0.0052 A		Wavelength=0.71073
Cell:	a=18.7330(14)	b=6.6818(5)	c=18.8092(14)
	alpha=90	beta=93.359(3)	gamma=90
Temperature:	296 K		

	Calculated	Reported
Volume	2350.3(3)	2350.3(3)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C16 H14 N2 Na O15 Rb, 2(H2 O)	C16 H14 N2 Na O15 Rb, 2(H2 O)
Sum formula	C16 H18 N2 Na O17 Rb	C16 H18 N2 Na O17 Rb
Mr	618.78	618.78
Dx,g cm-3	1.749	1.749
Z	4	4
Mu (mm-1)	2.213	2.213
F000	1248.0	1248.0
F000'	1245.18	
h,k,lmax	22,7,22	22,7,22
Nref	4143	4133
Tmin,Tmax	0.767,0.801	0.571,0.746
Tmin'	0.718	

Correction method= # Reported T Limits: Tmin=0.571 Tmax=0.746
AbsCorr = MULTI-SCAN
Data completeness= 0.998 Theta(max)= 24.999
R(reflections)= 0.0375(3859) wR2(reflections)= 0.1017(4133)
S = 1.073 Npar= 371

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT018_ALERT_1_C	_diffrn_measured_fraction_theta_max	.NE. *_full	!	Check
PLAT213_ALERT_2_C	Atom O6	has ADP max/min Ratio	3.1	prolat
PLAT213_ALERT_2_C	Atom O12	has ADP max/min Ratio	3.4	prolat
PLAT220_ALERT_2_C	Non-Solvent Resd 1	O Ueq(max)/Ueq(min) Range	4.4	Ratio
PLAT242_ALERT_2_C	Low 'MainMol' Ueq	as Compared to Neighbors of	N1	Check
PLAT242_ALERT_2_C	Low 'MainMol' Ueq	as Compared to Neighbors of	N2	Check
PLAT250_ALERT_2_C	Large U3/U1 Ratio for Average U(i,j) Tensor		2.1	Note
PLAT369_ALERT_2_C	Long C(sp2)-C(sp2) Bond	C7 - C8 .	1.54	Ang.
PLAT417_ALERT_2_C	Short Inter D-H..H-D	H4A ..H13A	2.11	Ang.
PLAT417_ALERT_2_C	Short Inter D-H..H-D	H10A ..H17A	2.13	Ang.
PLAT480_ALERT_4_C	Long H...A H-Bond Reported H13	..O4	2.61	Ang.
PLAT910_ALERT_3_C	Missing # of FCF Reflection(s) Below Theta(Min).		5	Note
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L=	0.595	5	Report

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite	15	Note
PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension	1	Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms	2	Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records	3	Report
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) .	1.35	Ratio
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #	26	Check
O1 -C8 -RB1 1.555 1.555 1.555	41.20 Deg.	
PLAT804_ALERT_5_G Number of ARU-Code Packing Problem(s) in PLATON	1	Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints	15	Note
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed ..	!	Info
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still	79%	Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF	3	Note
PLAT931_ALERT_5_G Found Twin Law ( )[1 0 -1] Est. BASF	0.42	Check
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...	2	Note

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
13 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
13 **ALERT level G** = General information/check it is not something unexpected
1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
11 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
5 ALERT type 4 Improvement, methodology, query or suggestion
4 ALERT type 5 Informative message, check

PLATON version of 23/04/2018; check.def file version of 23/04/2018

Datablock NaRb3npa21 - ellipsoid plot