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Synthesis, structure characterization, and properties of a new heterometallic coordination polymer containing two μ_3-bridging tridentate ligands

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The synthesis, spectral characterization, single crystal structure and properties of a new potassium coordination polymer $[K(LH_2)(MoO_4)]$ **1** (LH_2 = 1,3-dihydroxy-2-(hydroxymethyl)propan-2-aminium) are reported. The bimetallic compound **1** crystallizes in the non-centrosymmetric trigonal $P3c1$ space group with K^+, $(LH_2)^+$ and $(MoO_4)^{2-}$ located on three-fold axes. The K^+ ion exhibits hexa coordination and both $(LH_2)^+$ and $(MoO_4)^{2-}$ function as μ_3-bridging tridentate ligands resulting in the formation of a three-dimensional (3D) polymeric structure. In the 3D polymer, the $\{KO_6\}$ octahedra and $\{MoO_4\}$ tetrahedra are interlinked into a hexagonal array of alternating $\{KO_6\}$ and $\{MoO_4\}$ polyhedra connected *via* corner-sharing with enclosure of $(LH_2)^+$ ion in the cavity. The $(LH_2)^+$ and $(MoO_4)^{2-}$ units in **1** are interlinked with the aid of three varieties of hydrogen bonding interactions. Thermal decomposition of **1** at 600°C results in the formation of $K_2Mo_2O_7$. Comparative structural chemistry of several $(LH_2)^+$ containing compounds is described.

Keywords: 1,3-Dihydroxy-2-(hydroxymethyl)propan-2-aminium, Potassium, Non-centrosymmetric, Coordination polymer, Hexagonal array

The synthesis and characterization of non-centrosymmetric (NCS) compounds is a topical area of research as these materials possess properties like second harmonic generation, piezoelectricity, dipole moment, *etc.*[1-6] It is well known that any solid material can crystallize in one of the two hundred and thirty space groups of which a hundred and thirty-eight are non-centrosymmetric[7]. The NCS space groups are classified under two categories *viz.* seventy-three space groups with mirror planes and or glides and sixty-five Sohncke space groups, which contain only operations of the first kind *viz.* rotations, roto-translations and translations. Since chiral molecules can only crystallize in one of the sixty-five Sohncke space groups, preparation of NCS compounds can in principle be accomplished using chiral starting reagents for example naturally occurring amino acids[8]. In addition, NCS compounds of different compositions can also be prepared by employing specific strategies[9-19]. Some of these strategies involve (i) the use of asymmetric building units such as second-order Jahn-Teller active cations or transition metal oxide fluorides, (ii) a combination of acentric organic linkers and tetrahedral inorganic nodes in extended hybrid materials by prohibiting intraframework inversion centers and (iii) making use of known compounds having a tendency to crystallize in NCS space groups.

2-Amino-2-(hydroxymethyl)propane-1,3-diol (LH) referred to as Tris is a non-toxic compound. It is used extensively in biological studies as a low-cost component in buffer solutions and has a pK_a of about 8.5 and pH range of 7-9 in buffer solutions which fits it in the physiological pH range of most living organism[20-23]. The amino alcohol can function as a monoanion $(L)^-$ or monocation[24] $(LH_2)^+$. A search of the Cambridge Structural Database[25] for compounds containing the monoprotonated cation of LH namely $(LH_2)^+$ reveals several hits showing its flexibility to exist in different anionic environments (Table S1). The family of $(LH_2)^+$ containing compounds crystallize in both centrosymmetric and NCS space groups. Interestingly nineteen out of the sixty-six compounds (entry nos. 1-19 in Table S1) crystallize in NCS space groups[26-41].

This indicates a good possibility of synthesizing NCS compounds using LH as a starting reagent. In a recent study, we have shown that a mixed cationic tetraoxidomolybdate charge balanced by $(NH_4)^+$ and $(LH_2)^+$ crystallizes in the polar space group $P3c1$[41]. As it is well-known that ammonium and the corresponding potassium compounds tend to be isostructural for example the isomorphous ammonium and potassium molybdates and heptamolybdates[42,43] we set out to synthesize the potassium analog of $(NH_4)(LH_2)(MoO_4)$ and determine if the oxophilic K can bind to the hydroxy groups of the organic ligand and or the oxygen atoms of the molybdate ion giving rise to a bimetallic coordination network[44,45]. The last two decades have witnessed good progress in the study of *s*-block metal-based networks[44-51]. In the literature, many s-block-based materials have been synthesized by hydrothermal methods[45,48]. However, in this work, we report a non-hydrothermal method for the synthesis of $[K(LH_2)(MoO_4)]$ **1**, in which K^+ ion exhibits three-dimensional connectivity. In this report, we describe the details of the synthesis, crystal structure, spectral characterization and thermal study of **1**.

Experimental Section

Materials and methods

All the chemicals used in this study were of reagent grade and were used as received from commercial sources without any further purification. Potassium heptamolybdate tetrahydrate $[K_6(Mo_7O_{24})(H_2O)_4]$ was prepared by a similar procedure reported for its Rb analog[52]. The instrumentation (supplementary material) used for infrared, Raman and optical spectra, thermal study, X-ray powder pattern, solution conductivity study and piezoelectric measurement are the same as reported in our earlier papers[41,46-50]. The X-ray intensity data of compound **1** were collected with the aid of a Bruker D8 Quest Eco single crystal X-ray diffractometer using monochromated Mo*Kα* (λ= 0.7107 Å) radiation. The collected frames were integrated, scaled, merged and absorption correction was performed using APEX3 the program package of Bruker (Version 2018.1). The structure was solved by SHELXS and refined against F^2 by weighted full-matrix least-squares using SHELXL[53]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Selected refinement results are listed in Table 1.

Synthesis of $[K(LH_2)(MoO_4)]$, 1

Potassium heptamolybdate tetrahydrate (1.36 g, 1 mmol) was dissolved in distilled water (~15 mL) to obtain a clear solution. To this, an aqueous solution containing LH (0.726 g, 6 mmol) was added and the reaction mixture was stirred well for 10-15 min and filtered. The colourless filtrate was left undisturbed at RT. Transparent crystals of **1** obtained after a few days were isolated by filtration, washed with ice-cold water and dried in air to obtain 1.14 g of **1**. The isolated product contained several single crystals suitable for X-ray diffraction.

Compound **1**: Anal. Calcd: C, 14.96; H, 3.77; N, 4.36. Found: C, 14.88; H, 3.69; N, 4.31%. UV-Vis data: λ_{max} 208 nm; IR: 3614-3118 (broad), 3350, 3234, 2872, 2796, 2664, 2565, 2449, 2235, 2103, 2004, 1904, 1797, 1624, 1524, 1459, 1401, 1302, 1195, 1144, 1070, 922, 889, 839, 773, 674, 607, 491 cm^{-1}; Raman data: 1461, 1296, 1189, 1072, 891, 848, 812, 753, 610, 377, 312 cm^{-1}; DTA (°C): 146 (exo), 229 (exo), 308 (exo), 493 (exo); Molar conductivity (λ_m) (0.02 M): 292 S $cm^2\,mol^{-1}$.

Results and Discussion

Description of the crystal structure of $[K(LH_2)(MoO_4)]$, 1

The title coordination polymer crystallizes in the non-centrosymmetric trigonal space group *P*3*c*1. The piezoelectric response of **1** (see Supplementary material) confirms the correct choice of the non-centrosymmetric *P*3*c*1 space group[6]. $[K(LH_2)(MoO_4)]$ **1** is isostructural with the recently reported $(NH_4)(LH_2)(MoO_4)$[41]. The unit cell parameters of **1** exhibit a decrease resulting in

Table 1 — Crystal data and structure refinement for $[K(LH_2)(MoO_4)]$ **1**

Empirical formula	$C_4H_{12}KMoNO_7$
Formula weight	321.18
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, Space group	Trigonal, *P*3*c*1
Unit cell dimensions	a = 6.9394(1) Å b = 6.9394(1) Å c = 11.9594(4) Å $\alpha = \beta = 90°$, $\gamma = 120°$
Volume	498.75(2) $Å^3$
Z, calculated Density	2, 2.139 mg m^{-3}
Absorption coefficient	1.745 mm^{-1}
F(000)	320
Crystal size	0.316×0.199×0.125 mm^3
θ range for data collection	6.122 to 29.576°
Index ranges	$-9 \le h \le 9, -9 \le k \le 9, -16 \le l \le 16$
Reflections collected, unique	6556 / 929 [R(int) = 0.0234]
Completeness to θ = 25.242°	95.80%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	929/1/48
Goodness-of-fit on F^2	1.309
Final R indices [I>2σ(I)]	R1 = 0.0178, wR2 = 0.0443
R indices (all data)	R1 = 0.0183, wR2 = 0.0449
Absolute structure parameter	0.012 (17)
Largest diff. peak and hole	0.420 and –1.059 e.$Å^{-3}$
CCDC Deposition No.	2101429

a reduction (~16.53 Å^3) of the cell volume (Table 1) compared to 515.28(5) Å^3 for the ammonium analogue. The structure of **1** consists of an unique K^+ cation, an independent $(LH_2)^+$ cation and a crystallographically unique $(MoO_4)^{2-}$ dianion all of which are located on three-fold axes (Fig. 1).

In $(LH_2)^+$ the three-fold axis is situated along the bond connecting C1 and N1 atoms, while in $(MoO_4)^{2-}$ the three-fold axis passes *via* Mo1 and O1 atoms (Fig. 1). The geometric parameters of the $(LH_2)^+$ cation and the $(MoO_4)^{2-}$ dianion are in normal range (Table S2) and are in agreement with reported data[41].

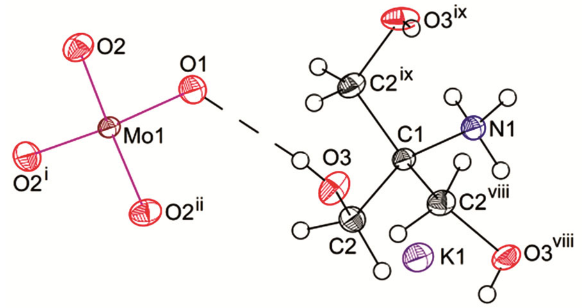

Fig. 1 — The crystal structure of $[K(LH_2)(MoO_4)]$ **1** showing the atom labelling scheme. Displacement ellipsoids of the non-hydrogen atoms are drawn at 50% probability level. Broken line represents intramolecular H-bonding. Symmetry code: i) -y+1, x-y+1, z ii) -x+y, -x+1, z viii) -y+1, x-y, z ix) -x+y+1, -x+1, z.

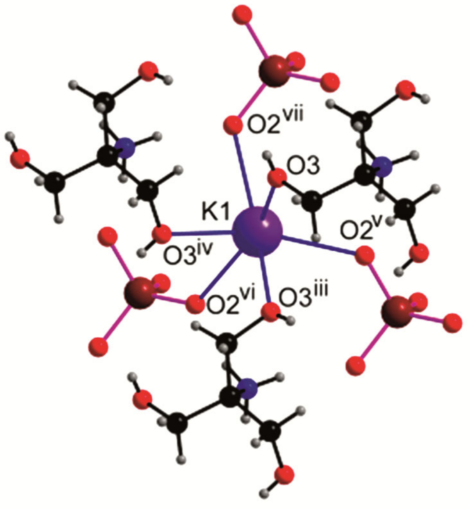

Fig. 2 — The coordination environment around the unique K^+ ion in $[K(LH_2)(MoO_4)]$ **1**. Symmetry code: iii) -x+y, -x, z iv) -y, x-y, z v) -x+y, y-1, z-1/2 vi) x-1, x-y, z-1/2 vii) -y+1, -x+1, z-1/2

Potassium is known to exhibit a range of coordination numbers *viz.* seven[47] or eight[51]. In **1**, the central potassium exhibits hexacoordination and is bonded to three symmetry related molybdate dianions and three different $(LH_2)^+$ cations (Fig. 2).

A comparison of the crystal structures of the isostructural **1** and $(NH_4)(LH_2)(MoO_4)$ reveals that the six K-O bonds in **1** are the equivalent of the six N-H···O interactions around the $(NH_4)^+$ cation in $(NH_4)(LH_2)(MoO_4)$. The K-O bond distances scatter in a narrow range between 2.714(3) and 2.834(17) Å (Table S2). The *cis* O-K-O angles vary from 71.34(5) to 115.64(4)° while all the *trans-O-K-O* angles are identical at 149.17(11)° and deviate considerably from the ideal value indicating a severe distortion of the $\{KO_6\}$ octahedron (Table S2).

The unique molybdate dianion as well as $(LH_2)^+$ cation function as μ_3-tridentate ligands and bridge three symmetry-related K^+ ions (Fig S1). Two features of the crystal structure are noteworthy *viz.* (i) $(LH_2)^+$ cation bridging three different K^+ ions *via* the symmetry equivalent oxygens of the hydroxy groups and (ii) both the tridentate ligands bridge K^+ ions resulting in identical K···K separations of 6.939 Å (Fig S1), which is a consequence of the three-fold symmetry around the central metal. The μ_3-bridging coordination mode of the unique ligands results in a three-dimensional connectivity of the K^+ ions as the alternate vertices of the distorted $\{KO_6\}$ octahedron are contributed by each of the unique μ_3-bridging ligands located on three-fold axes (Fig S2, Fig S3).

In the three-dimensional polymer, the $\{KO_6\}$ octahedra and $\{MoO_4\}$ tetrahedra are interlinked into a hexagonal array of alternating $\{KO_6\}$ and $\{MoO_4\}$ polyhedra connected *via* corner-sharing, with enclosure of the $(LH_2)^+$ cation in the cavity (Fig S4). The $(LH_2)^+$ cation and the $(MoO_4)^{2-}$ anion are interlinked with the aid of three varieties of H-bonding interactions *viz.* O-H···O, N-H···O and C-H···O (Table 2).

Table 2 — Geometric parameters (Å, °) of the hydrogen bonds in **1**

D-H···A	d(D-H)	d(H···A)	<(DHA)	d(D···A)	Symmetry code
O3-H3···O1	0.71(4)	2.08(4)	171(4)	2.788(3)	x, y, z
N1-H1A···O2	0.89	1.98	166.9	2.856(2)	-x+y, y-1, z-1/2
N1-H1B···O2	0.89	1.98	166.9	2.856(2)	-y+2, -x+1, z-1/2
N1-H1C···O2	0.89	1.98	166.9	2.856(2)	x, x-y+1, z-1/2
C2-H2A···O3	0.97	2.56	141.5	3.373(3)	-x+y, -x, z
C2-H2B···O2	0.97	2.54	151.1	3.418(4)	-x+y, -x+1, z

All the H atoms in **1** function as hydrogen bond donors while the O atoms O1, O2 of $(MoO_4)^{2-}$ and O3 of $(LH_2)^+$ are hydrogen acceptors. Of the six hydrogen bonds in (Table 2), the O2-H3···O1 bond at a D···A distance of 2.788 (3) Å and accompanied by a large DHA angle is intramolecular while the rest are intermolecular. Because of its three-fold symmetry, O1 makes a total of three O2-H3···O1 bonds, (Fig S5A) which can explain the elongation of Mo-O1 bond. In contrast, the O2 site and the symmetry equivalent $O2^{i}$ and $O2^{ii}$ atoms of $(MoO_4)^{2-}$ are each involved in a single C-H···O and an N-H···O interaction (Fig. 3).

Due to hydrogen bonding and the three-fold symmetry, each $(MoO_4)^{2-}$ anion is linked with six symmetry-related $(LH_2)^+$ cations. In addition to the C-H···O and an N-H···O interactions mentioned above the $(LH_2)^+$ is involved in a C2-H2B···O2 interaction which interlinks a $(LH_2)^+$ with symmetry-related organic cation. Hence, each $(LH_2)^+$ is hydrogen bonded with symmetry-related $(MoO_4)^{2-}$ ions (Fig S5B) and three different organic cations.

Synthetic aspects, spectral, thermal and conductivity studies

An aqueous reaction of $K_6[Mo_7O_{24}]\cdot 4H_2O$ with LH resulted in the formation of $[K(LH_2)(MoO_4)]$ **1**. It is interesting to note that the aqueous reaction mixture (*p*H ~6) of alkali metal heptamolybdate and LH, which is normally expected to favour the formation of heptamolybdate core resulted in the formation of a tetraoxidomolybdate containing compound **1**. The synthetic methodology employed in this study is analogous to the aqueous reaction of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ with LH which afforded the polar tetraoxidomolybdate $(NH_4)(LH_2)(MoO_4)$[41]. A powdered sample taken from the bulk of **1** was studied by powder X-ray diffraction (PXRD). A comparison of the experimental pattern with that calculated from the single-crystal data (Fig. 4) reveals the monophasic nature of **1**.

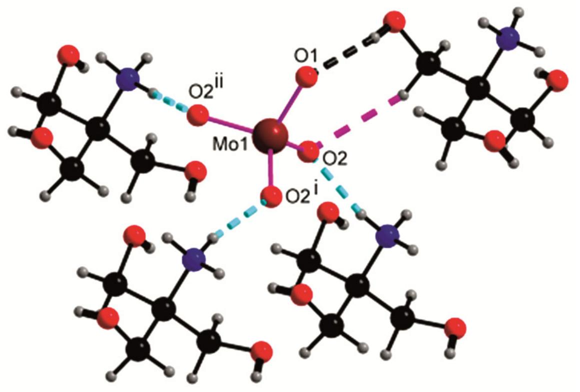

Fig. 3 — The H-bonding surroundings of the $(MoO_4)^{2-}$ ion showing O-H···O (black), N-H···O (cyan) and C-H···O (pink) interactions in **1**. For clarity, C-H···O around $O2^{i}$ and $O2^{ii}$ are not shown. In view of three-fold symmetry O1 makes three O-H···O bonds (see **Fig S5**).

In view of the isostructural nature of the heptamolybdates of K and Rb, we investigated the synthesis of $[Rb(LH_2)(MoO_4)]$ by an analogous procedure. However, our attempts were unsuccessful as the reaction of $[Rb_6(H_2O)_4(Mo_7O_{24})]$ with LH afforded a viscous product preventing further analysis.

The absence of the 936 cm^{-1} band in the Raman spectrum of **1** (Fig S6) proves that it is not a heptamolybdate[54]. The reaction mixture (*p*H ~6) of $K_6[Mo_7O_{24}]\cdot 4H_2O$ and LH exhibits strong Raman signal (Fig S6) at 891 cm^{-1} which can be assigned for the symmetric stretching υ_1 (A_1) vibration of the $\{MoO_4\}$ tetrahedron[55] and a weak band at 936 cm^{-1} (Fig S6) which is quite a characteristic of heptamolybdate. Usually, in an acidic solution (*p*H ~6) heptamolybdate species are present but in this case Raman study indicates formation of a tetrahedral $(MoO_4)^{2-}$ anion. The solid obtained after slow evaporation of reaction mixture exhibits strong Raman signal at 891 cm^{-1} confirming the formation of tetrahedral $(MoO_4)^{2-}$ (Fig S6).

Based on a comparison of the Raman spectrum of **1** with that of $Na_2MoO_4\cdot 2H_2O$, the weaker signals at 848 and 312 cm^{-1} can be assigned for υ_3 and υ_2 bands of $(MoO_4)^{2-}$respectively (Fig S7). A comparison of the Raman spectrum of **1** with the hydrochloride salt of LH (Fig S8) enables identification of the bands of

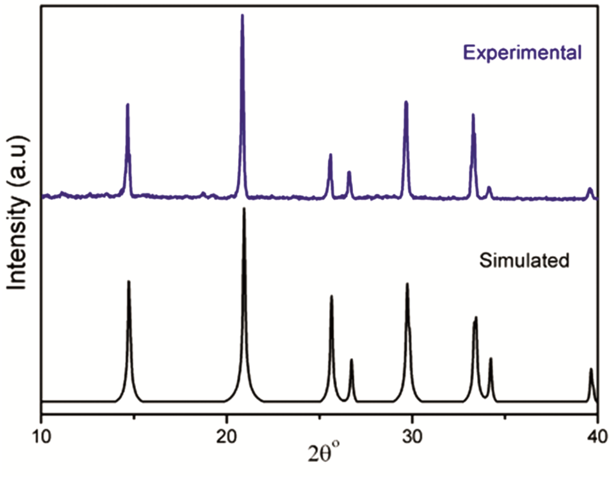

Fig. 4 — X-ray powder pattern of $[K(LH_2)(MoO_4)]$ **1** simulated from single crystal data (**bottom**) and experimental pattern of the bulk sample (**top**).

Table 3 — Specific conductivity (Ꝁ) and molar conductivity (λ_m) data of [$K(LH_2)(MoO_4)$] **1** and $(NH_4)(LH_2)(MoO_4)$ **2**

Conc. (M)	Ꝁ (S cm^{-1})		λ_m (S cm^2 mol^{-1})	
	1	**2**	**1**	**2**
0.1	0.0196	0.0184	196	184
0.08	0.0169	0.0158	211	198
0.06	0.0140	0.0134	234	224
0.04	0.0101	0.0092	253	230
0.02	0.0058	0.0056	292	281

the $(LH_2)^+$ cation. The IR spectrum of **1** (Fig S9) exhibits several sharp signals in the mid-IR region indicating the presence of the organic cation. The asymmetric Mo-O stretching vibration of the {MoO_4} tetrahedron occurs as an intense signal at 839 cm^{-1}. Aqueous solutions containing different concentrations of **1** and that of the isostructural ammonium compound $(NH_4)(LH_2)(MoO_4)$ were investigated for their conductivity. In both cases, increase in molar conductivity is observed with increasing dilution (Table 3).

The conductivity data of **1** are nearly identical to that of $(NH_4)(LH_2)(MoO_4)$[41] which consists of discrete ammonium, $(LH_2)^+$ and $(MoO_4)^{2-}$ anions in its crystal structure. The increased conductivity on dilution can be explained due to identical situation in solution for the isostructural compounds namely the presence of same number of ions in **1** as in $(NH_4)(LH_2)(MoO_4)$. Hence, the conductivity study proves that in solution compound **1** loses its identity and the K^+ ion is hydrated and the $(MoO_4)^{2-}$ as well as $(LH_2)^+$ are no longer bonded to K^+ as observed in the solid state. The presence of $(MoO_4)^{2-}$ in solution can also be evidenced from the optical spectrum of **1**, which is nearly identical to that of the solution spectrum of $Na_2MoO_4{\cdot}2H_2O$ (Fig S10).

Thermal study (Fig S11) reveals **1** is stable up to 145°C as evidenced by a TG curve parallel to X-axis indicating the absence of any water molecule. Above this temperature, a gradual mass loss is observed accompanied by exothermic events at 146, 229, 308 and 493°C in the DTA curve, which can be attributed to the decomposition of the organic cation. The final residual mass obtained (60.14%) is in close agreement with the calculated residual mass (59.47%) for a probable composition of $MoO_3{\cdot}1/2K_2O$. The final composition obtained corresponds to $K_2Mo_2O_7$ which is confirmed by its matching powder pattern of the final metal oxide obtained after pyrolysis of **1** at 600°C with the reported phase (JCPDS 01-072-1894) (Fig S12).

Conclusions

In summary, we report the room tempearure synthesis and characterization of a new non-centrosymmetric potassium coordination polymer consisting of bridging $(LH_2)^+$ and $(MoO_4)^{2-}$ ligands. The μ_3-tridentate binding mode of the unique ligands results in the formation of a hexagonal array of alternating {KO_6} and {MoO_4} polyhedra connected *via* corner-sharing with the enclosure of the organic cation in the cavity. The usefulness of Raman spectroscopy for compound identification is demonstrated. Thermal decomposition of **1** results in the formation of the triclinic $K_2Mo_2O_7$ phase. **1** is a new example of a non-centrosymmetric compound based on $(LH_2)^+$ which exhibits a piezoelectric effect, comparable to that of α-quartz. The title compound is a new addition to the list of structurally characterized *s*-block coordination polymers. As pointed out by Fromm in a very early review of this subject[45] a rich structural chemistry of *s*-block elements still remains to be explored and this subject is very interesting[49].

Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776. CCDC-2101429 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif. Additional figures and tables (Figures S1 to S12; Tables S1-S2) pertaining to the structure, spectra and thermal study are given in Electronic supplementary information.

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