Coordination polymers with pyridine-2,4,6-tricarboxylic acid and alkaline-earth/lanthanide/transition metals: synthesis and X-ray structures[†]

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Pyridine-2,4,6-tricarboxylic acid (ptcH₃) reacts with Cd(II), Mn(II), Ni(II), Mg(II), Ca(II), Sr(II), Ba(II), Dy(III) salts forming different products depending on the reaction conditions. In the presence of pyridine at room temperature the acetate, chloride or nitrate salt of Cd(II) breaks the ligand to form an open framework structure with the empirical formula, $\{ [Cd(Ox)(H_2O)_2|H_2O) \}_n$ (Ox = oxalate), 1. In the absence of pyridine, no crystalline compound could be isolated at room temperature (RT). However, under hydrothermal conditions and in the absence of pyridine, a discrete tetrameric complex with the formula, { $[Cd_2(cda)_2(H_2O)_4](H_2O)_3$ }, $(cdaH_2 = 4$ -hydroxypyridine-2,6-dicarboxylic acid), **2**, is formed where the carboxylate group at the 4-position of the ligand is reduced to a hydroxyl group. When Ni(II), Mn(II), Mg(II), Ca(II), Sr(II), Ba(II), Dy(III) salts are used in place of Cd(II), no crystalline product could be isolated at RT. But under hydrothermal conditions, coordination polymers $\{[Ni_{1,5}(ptc)(pip)_{0,5}(H_2O)_4] \cdot H_2O\}_n, (pip = piperazine), 3; \{Mn_{1,5}(ptc) \cdot 2H_2O\}_n, 4; \{Mg_3(ptc)_2 \cdot 8H_2O\}_n, 5; \{Mg_3(ptc)_2$ $\{[Mg(ptc)(H_2O)_2] \cdot 1/2 [Mg(H_2O)_6] \cdot H_2O\}_n, 6; \{Ca_{1.5}(ptc) \cdot 2H_2O\}_n, 7; \{Sr_{1.5}(ptc) \cdot 5H_2O\}_n, 8;$ $\{[Ba(ptc)(H_2O)][Ba(ptcH_2)H_2O]\}_n$, 9; $\{[Dy(ptc)\cdot 3H_2O]\cdot H_2O]_n$, 10) are formed. The structures exhibit different dimensionality depending on the nature of the metal ions. In 1 a discrete acyclic water hexamer is also identified. All the compounds are characterized in the solid state by X-ray crystallography, IR and elemental analysis.

Introduction

The development and identification of novel solid-state architectures is a general theme in the pursuit of new functional materials. However, at times, finding strategies to prepare a designed solidstate architecture can be highly empirical, and obtaining a phase with the desired organization of components becomes a trial and error process. Metal–organic framework (MOF) structures can be synthesized by hydro(solvo)thermal or room temperature reactions between metal ions and multi-dentate ligands. In most cases, it may not be possible to predict the structural pattern by looking at the ligand structure while, in a few cases, unexpected reactions¹⁻³ such as ligand oxidative coupling, hydrolysis or substitution, can occur making it almost impossible to predict the final structure. However, such ligand transformations provide alternate routes for the construction of new MOFs.

The vast majority of work on coordination polymers has used transition metals. However the chemistry of alkaline earth metals has been a largely undeveloped area. There have been a few studies⁴ on the coordination behavior of these metals in both aqueous and nonaqueous media. However, the pioneering work on

^aDepartment of Chemistry, Indian Institute of Technology, Kanpur, 208016, India. E-mail: pkb@iitk.ac.in coordination polymers with s-block metal ions by K. M. Fromm has improved this literature a lot.4a,4b Transition metals are more natural choices owing to the well-defined coordination geometries of d-block cations and cation clusters. Compared to this, reluctance in using alkaline earth cations as building blocks arises from their unpredictable coordination numbers and geometries as no ligand field stabilization effects govern their bonding.⁵ The main issue for framework assembly with alkaline earth ions is their high affinity for oxygen donors, particularly water. Given the less predictable nature of alkaline earth assemblies, it seems counter-intuitive to use them as building blocks although less structural predictability does not preclude high degrees of order or functionality. Also, lack of intrinsically useful properties (*i.e.* magnetism or variable oxidation states) might appear to make alkaline earth metals less interesting. However these metals do have some advantages for application in materials science; they are nontoxic, cheap and generally amenable to aqueous preparation. For these reasons alkaline earth salts are the preferred formulations for a host of commercial materials, including many common pharmaceuticals and colorants.

We⁶ and others⁷ are exploring the coordination chemistry of pyridine-2,4,6-tricarboxylic acid (ptcH₃) to construct MOFs with different dimensionality. This ligand has been chosen as aromatic carboxylates are known to form thermally stable MOFs with different types of metal ions. Another reason for choosing aromatic polycarboxylates is the inherent negative charge associated with them that helps in the charge compensation of the metal ion in the framework. We have used transition, alkaline earth and lanthanide metals to build MOFs with different structures. Taking into account all the previous studies⁶⁻⁷ along with the present one,

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[†] Electronic supplementary information (ESI) available: X-Ray crystallographic files in CIF format for the structure determination of compounds **1–10**; additional figures, selected bond lengths and angles for the compounds **1–10**. CCDC reference numbers 697859–697868. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b814066a

Table 1 Symmetric stretching (v_s) , asymmetric stretching (v_{as}) , their differences (Δv) and the binding mode of the carboxylate groups of compounds **3–10**

Compound	V _{as}	Vs	Δv	Binding mode
3	1639	1390, 1360	249, 279	Unidentate
4	1608, 1556	1367	241, 189	Unidentate
5	1629, 1563	1365	246, 198	Unidentate
6	1630, 1533	1395	235, 138	Unidentate, chelate
7	1624	1384, 1356	240, 268	Unidentate
8	1617, 1510	1370	247, 140	Unidentate, chelate
9	1642, 1583	1440	202, 143	Unidentate, chelate
10	1608, 1528	1394	214, 134	Unidentate, chelate

we have attempted to rationalize how the dimensionality of the MOFs formed by the ligand $ptcH_3$ varies with the nature of the metal ion.

Results and discussion

All the compounds are stable in air, sparingly soluble in water and insoluble in common organic solvents. High yields of the products indicate that they are thermodynamically stable under the prevailing reaction conditions. Each exhibits a strong absorption band in the region, 1350–1550 cm⁻¹ diagnostic⁸ of coordinated carboxylates. The uni-dentate and chelate mode of coordination of carboxylate groups in **2–10** can be distinguished by FTIR spectra.⁹ A separation (Δv) of 40–120 cm⁻¹ between asymmetric v_{as} (O–C–O) and symmetric v_s (O–C–O) indicates chelating mode, while a separation of 210–270 cm⁻¹ is indicative of the uni-dentate mode of binding (Table 1). The absence of characteristic bands at around 1700 cm⁻¹ rules out the presence of protonated carboxylate groups in the complexes **2–10**¹⁰ except for complex **9**.

Structures

Structure of $\{[Cd(Ox)(H_2O)_2|H_2O\}_n, (1).$ The Cd(II) ion breaks the ligand in the presence of pyridine forming a Cd(II)– oxalate coordination polymer, **1**. The counter anion does not play any role in this transformation as the same product (1) is formed with different salts of Cd(II) such as acetate, chloride or nitrate. In the absence of pyridine or in the presence of a different base such as piperazine or tetraalkylammonium hydroxide, reaction between a Cd(II) salt and the ligand affords a white precipitate of indefinite composition almost instantaneously. The reaction under hydrothermal condition in the absence of a base, affords a discrete tetrameric compound (2) in good yield. With a Co(II) salt and pyridine at room temperature, the ligand forms a 1D coordination polymer (the same can be prepared^{7b} without using pyridine as reported by Cheng et al.) without any ligand cleavage. The same reaction under hydrothermal condition, does not give any crystalline product. Several Ni(II) salts when allowed to react with the ligand, with or without a base like pyridine or piperazine, give a mixture of products but on hydrothermal reaction in the presence of piperazine afford only the crystalline product 3 in high yields (40% or more). Thus, the breakage of the ligand to oxalate is observed only with Cd(II) and Zn(II)^{6a} in the presence of pyridine. However, neither Cd(II) nor Zn(II) can break the ligand when a base other than pyridine is used. At this stage, we are unable to suggest a mechanism for the cleavage of the ligand. Further studies are underway to access the role of various metal ions and presence of pyridine on the cleavage of this ligand to form various polymeric metal oxalate compounds.

Literature survey reveals existence of several cadmium oxalate structures under different reaction conditions. The compound $[Cd_2(\mu_5-C_2O_4)(\mu_3-OH)_2]^{11}$ which was synthesized from hydrothermal reaction of CdCl₂, H₂C₂O₄, imidazole and H₂O shows a fivebridging coordination mode of oxalate unit having inter-crossed $[Cd(OH)]_{\infty}$ corrugated sheets and a 3D $[Cd_2(ox)]_{\infty}$ network. Rao et al. reported alkali halide incorporated cadmium oxalate¹²⁻¹³ synthesized by metathetic reaction employing hydrothermal methods. The same group also reported¹⁴ a 3D cadmium oxalate open framework constructed from amine and K⁺ ion. A polymeric cadmium oxalate species quite similar to 1, was prepared¹⁵ by decomposition of ascorbic acid in the presence of Cd(II) ion under mildly acidic condition. The structure of 1 consists of oxalate anions bonded to Cd(II) forming a 2D open framework structure. Each oxalate anion binds four Cd(II) ions extending along the crystallographic b axis where two of the O atoms act as bridging ones. Along the crystallographic a axis, however, each oxalate shows D_{2h} symmetry binding two Cd(II) ions. The almost square voids thus formed have the dimension, 5.99×6.00 Å² (atom to atom distance). Each Cd(II) shows hepta-coordinated pentagonal bipyramidal geometry with ligation from five O atoms of three oxalate groups and two water molecules (Fig. 1). All bond



Fig. 1 A perspective view of 2D open framework structure of complex 1.

distances and bond angles are within normal ranges. Selected bond lengths and bond angles involving the metal ion are collected in the ESI (Table S1).† The present structure appears to be identical to that of $\{Cd_2(C_2O_4)\cdot 6H_2O\}_n$ ¹⁵ reported by Orioli *et al.* Although the crystal data parameters of this reference compound is the same as that of ours, the space group for the triclinic system used by them is *P*1 (No. 1) whereas we have used the higher symmetric *P* $\overline{1}$ (No. 2) to solve the structure.

A striking feature of this complex is identification of a discrete acyclic water hexamer that was also present in the crystal structure of the above reference compound¹⁵ but not mentioned by the authors. Among small water clusters, the hexamer is subjected to a number of experimental and theoretical studies as this cluster is the building block of ice16 and also exhibits17 some of the properties of bulk water. Theoretical calculations¹⁸ have predicted five low energy isomers for this cluster that are iso-energetic. While chair,¹⁹ boat,²⁰ and planar cyclic²¹ forms of hexamers have been identified in crystal hydrates, the 'cage' conformer predicted to be most stable at very low temperature has been observed²² by vibration-rotation tunneling spectroscopy and to the best of our knowledge, so far, no organic or metallo-organic compound is known where an acyclic water hexamer has been detected. This water hexamer has a center of inversion symmetry and is made up of one 'free' and two metal-bound water molecules with their symmetry related molecules through H-bonding interactions, and is depicted in Fig. 2 along with its immediate H-bonding coordination environment. In the hexameric unit, the average distance between the oxygen atoms is 2.863 Å, which is comparable with the $O \cdots O$ distance in liquid water (2.85 Å), while for the gas phase this value is ca. 0.1 Å longer.16b,17b The water molecules present in clefts of biological/abiological molecules are very different from the gas phase or bulk liquid water. Here, the principle of maximizing H-bonding interactions is followed where the environment plays a major role. While Ow1 acts as two H-bond donors to two different carboxylate O atoms, Ow3 acts as two Hbond donors to one carboxylate O atom and a water molecule (Ow1). The H-bonding parameters are listed in Table S2 (ESI[†]). Interestingly, the hexameric water clusters act as pillars separating two layers of coordination polymers with an approximate distance of 5.488 Å between the layers leading to an overall H-bonded 3-D structure.

Structure of $\{ [Cd_2(cdaH)_2(H_2O)_4](H_2O)_3 \}_2$, (2). The structure of 2 consists of a discrete tetra nuclear Cd(II) cluster where the carboxylic acid group at the 4-position of the ligand is converted to hydroxyl group and remain uncoordinated (Fig. 3). This conversion of pyridine-2,4,6-tricarboxylic acid $(ptcH_3)$ to chelidamic acid $(cdaH_3)$ is readily achieved under hydrothermal condition. Each terminal Cd(II) ion in 2 is bonded to the pyridine N and two carboxylate O at the 2- and 6-positions of one cdaH²⁻ and two carboxylate O at the 2-positions of another cdaH²⁻ ligands giving a NO₄ coordination in the pentagonal plane. Two water molecules occupy the axial sites completing pentagonal bipyramidal coordination geometry. Each of the two Cd(II) ions in the middle is bonded to one carboxylate O at the 5-position of the previous cdaH2- and the pyridine N and two carboxylate O at the 2and 6-positions of the neighboring cdaH2-, along with one water molecule equatorially. Two water molecules are bonded axially giving each metal ion a hepta-coordinated pentagonal bipyramidal geometry.

Structure of {[**Ni**_{1.5}(**ptc**)(**pip**)_{0.5}(**H**₂**O**)₄]·**H**₂**O**}_n, (3). The structure consists of Ni(II), ptc³⁻, piperazine and water. It can be described as a piperazine-bridged dimer where each Ni(II) ion is equatorially coordinated to the pyridine N, carboxylate O at 2- and 6-positions and a piperazine N and the two axial sites are occupied by two water molecules showing a distorted octahedral coordination geometry. Another Ni(II) ion is axially coordinated to the carboxylate present at the 4-position of the ptc³⁻ in a monodentate fashion thus joining the dimeric molecules and form a 1D coordination polymeric chain along the crystallographic *a* axis. The ligand ptc³⁻ has a μ_4 coordination mode (Type II, Scheme 1) in this complex. Free water molecules occupy the voids in between the parallel chains (Fig. 4). These water molecules are involved in H-bonding interactions to 'O' of carboxylates as well as metal-bound water molecules of neighboring chains to reinforce the structure.

Structure of { $Mn_{1.5}(ptc)\cdot 2H_2O$ }_n, (4); { $Ca_{1.5}(ptc)\cdot 2H_2O$ }_n, (7). Compounds 4 and 7 are isomorphous and hence only the structural description of 4 is presented. The asymmetric unit consists of one ptc³⁻ unit, two Mn(II) and two metal-bound water molecules (Fig. 5). Atom Mn(2), exhibits a distorted octahedral surrounding (Fig. S1, ESI[†]), in which the basal plane is formed



Fig. 2 A view of the discrete acyclic water hexamer in 1. Symmetry codes: (i) 2 - x, 1 - y, -1 - z; (ii) 2 - x, 1 - y, -z; (iii) 1 + x, y, z.; (iv) 2 - x, 1 - y, 1 - z; (v) 4 - x, -1 - y, 1 - z; (vi) -x, 1 - y, -1 - z; (vii) x, y, 1 + z; (viii) x, y, -1 + z.



Fig. 3 A view of the discrete tetranuclear Cd(II) complex in 2.



Scheme 1 Coordination modes of ligand ptc.

by four carboxylate O atoms from four ptc^{3-} ligands. This plane is almost perpendicular to the mean plane of the pyridine ring (*ca.* 86.7°). Two water molecules occupy the axial positions. On the other hand, Mn(1) forms two five-membered chelate rings with one ptc^{3-} ligand (bite angle = 68.99°, 66.90°). One carboxylate O atom and one O atom of a water molecule (Ow1) along with the chelating atoms form a basal plane of pentagonal bipyramidal geometry. Axial sites are occupied by two carboxylate O atoms from two ptc^{3-} units. All M–O and M–N distances are within normal ranges²³ and are listed in Table S1 (ESI[†]). There is a μ_7 coordination motif of the ligand ptc³⁻ in this complex (Type VII, Scheme 1).

Two sidewise pillars constructed from alternate repeating units of Mn(1) and a carboxylate group [C(7)O(1)O(2)] are bridged by two symmetry related carboxylate O atoms (O3) forming four-membered Mn₂O₂ sets of Mn(1) dimers. In each of the ladders, the pyridine rings of ptc³⁻ units are involved in two different π - π stacking interactions (centroid-to-centroid distances



Fig. 4 The 1D coordination polymeric structure in complex 3.



Fig. 5 Coordination environment of 4 (ORTEP drawing with 50% probability of ellipsoids). Symmetry codes: (i) 1 + x, y, z; (ii) x, -1 + y, z; (iii) -x, 1 - y, 1 - z; (iv) -1 - x, 1 - y, -z; (v) x, 1 + y, z; (vi) -1 + x, y, z; (vii) -1 - x, 1 - y, 1 - z; (viii) -x, -y, 1 - z; (iv) 1 + x, 1 + y, z; (x) -x, 1 - y, -z; (x) -x, -y, -z; (x) -x, -z; (x) -x; -z; (x) -x, -z; (x) -x; (x) -x; -z; (x) -x; -z; (x) -x; (x) -x; (x) -x; (x)

are 3.205(4) and 3.299(4) Å with offset distance of 0.51 and 0.69 Å respectively) in opposite faces with two different Mn(1)-Mn(1) corner distances of 7.819 and 7.385 Å respectively (Fig. 6). These layers of ladder-cum-pillars run along the crystallographic *a* axis. Octahedrally coordinated Mn(2) connects these layers through two different carboxylate O atoms to form a robust 3-D network. (Fig. 7).

For complex 7, bond lengths and angles at the calcium atoms are compiled in Table S1 (ESI[†]). The Ca–O (carboxylate) bond lengths in 7 lie in the ranges of 2.266(4)–2.551(4) Å. A study based on the data extracted from the Cambridge Structural Database (CSD) found a range of 2.27–2.49 Å for Ca–O bonds involving monodentate carboxylate.²⁴ So, the values observed in this case are thus exceptional only for Ca2–O1 = 2.551(4) Å. The CSD study mentioned also gives 2.31–2.49 Å and 2.33–2.60 Å for Ca–OH₂ bond lengths in seven- and eight-coordinate complexes, respectively. This is consistent for the Ca–OH₂ (terminal) bond lengths which lie between 2.340(5)–2.382(4) Å in complex 7. Here also, the pyridine rings of ptc^{3–} units are π -stacked in opposite faces with two different centroid-to-centroid distances of 3.350(4) and 3.455(4) Å (offset distances are 0.58 and 1.13 Å respectively).

Structure of $\{Mg_3(ptc)_2 \cdot 8H_2O\}_n$, (5). The asymmetric unit of 5 consists of three Mg(II), two ptc³⁻ units and eight water molecules. The Mg(2) is coordinated by six atoms to form a distorted octahedral geometry where four water molecules are bonded equatorially. The axial sites are occupied by two carboxylate O atoms (O3, O5) from two different ptc³⁻ units. Mg(1) also exhibits a distorted octahedral geometry with equatorial coordination from ring N and two O atoms from two carboxylate groups at the 2- and 6- positions of a ptc³⁻ ligand (*i.e.* NO₂ donor set). The remaining equatorial site is occupied by another carboxylate O atom at the 2-position belonging to a different ptc³⁻ unit and the axial sites are occupied by two water molecules (Ow5, Ow6). The same geometry is attained by Mg(3) atom with similar mode of bonding. There are two different coordination modes for ptc³⁻ unit in this complex: one with a connectivity number of μ_6 and the other μ_3 (Type I, VI, Scheme 1). Fig. 8 represents the coordination environment of 5, in which the trinuclear unit is the building block of the structure. These building units are propagating the 1D coordination polymeric chains along the crystallographic a axis. The pyridine rings of one chain are involved in π - π stacking interactions (centroid-to-centroid distance of 3.478(4) Å with offset distance of 1.09 Å) with the pyridine rings of neighboring



Fig. 6 π - π stacking interactions among ptc units in complex 4.



Fig. 7 View of 3D framework of 4.

chains along the *b* direction. The metal-bound water molecules of one chain are involved in an intricate array of H-bonding interactions to 'O' of carboxylates as well as the water molecules of another chains. These H-bonding interactions among the chains extend the structure along the crystallographic *b* axis (Fig. S2, Table S3, ESI†). The lengths of the Mg–O bonds fall in the narrow range 2.008(5)–2.200(5) which are within normal limits^{4d,g,m} and are summarized in Table S1 (ESI†).

Structure of $\{[Mg(ptc)(H_2O)_2]\cdot 1/2[Mg(H_2O)_6]\cdot H_2O\}_n$ (6). For this compound, the asymmetric unit comprises of one ptc^{3-1} ligand, one Mg(II) ion in a general position, another Mg(II) ion on a crystallographic center of symmetry, five metal-bound water molecules and one free water molecule. The Mg(II) ion in the general position (Mg1) shows a distorted pentagonal bipyramidal geometry with equatorial coordination from two ptc³⁻ units (NO₄ donor set), while the axial sites are occupied by two water molecules (Type V, Scheme 1). Thus each organic anion binds two Mg1 ions to form a coordination polymeric chain. These chains runs parallel to the *b* axis making void spaces in between that are occupied by inorganic hexa-aqua magnesium cations (the Mg2 position coinciding with a crystallographic center of symmetry), and free water molecules (Fig. 9). These water molecules are involved in an intricate array of H-bonding interactions to unbound 'O' of carboxylates as well as metal-bound water molecules of neighboring 1D chains. Calculation of the solvent accessible



Fig. 8 Coordination environment of **5** (ORTEP drawing with 50% probability of ellipsoids). Symmetry codes: (i) -0.5 + x, -0.5 + y, z; (ii) 0.5 + x, 0.5 - y, 0.5 + z; (iii) x, -y, -0.5 + z; (iv) -0.5 + x, 0.5 - y, -0.5 + z; (v) 0.5 + x, 0.5 + y, z; (vi) x, -y, 0.5 + z.

volume²⁵ reveals that **6** contains ~13% void volume. All Mg–O bond lengths and angles are within limits ranging from 2.039(3) to 2.251(3) Å and are listed in Table S1 (ESI†). The presence of a free water molecule in the asymmetric unit differs this structure slightly from $\{[M(H_2O)_6][M(ptc)(H_2O)_2]_2 \cdot 2H_2O\}_n$ (M = Fe/Co).^{7b}

Structure of $\{Sr_{1.5}(ptc)-5H_2O\}_n$, (8). The asymmetric unit in this structure comprises of one ptc³⁻ ligand, two Sr(II) atoms and 5 metal-bound water molecules. Fig. 10 shows the coordination environment of two crystallographically independent Sr(II) ions. Quite differently from the coordination environments in 1–6, the metal Sr(2) in 8 is nine-coordinated by O atoms, of which five are from water molecules and remaining are from three different ptc³⁻ units out of which two are involved in chelation, resulting in a singly capped square antiprism (Fig. S3, ESI†). On the other



Fig. 10 View of the coordination environment of the metal center in complex 8 (ORTEP drawing with 50% probability of ellipsoids). Symmetry codes: (i) 0.5 - x, 0.5 + y, z; (ii) 1 - x, 1 - y, -z; (iii) 0.5 - x, -0.5 + y, z; (iv) 1 - x, y, 0.5 - z; (v) -x, y, 0.5 - z.

hand, Sr(1) is also coordinated to nine atoms, including (O1, N1, O6) the pair of symmetry related NO₂ donor set, another pair of symmetry related oxygen (O3) from a carboxylate group. The remaining oxygen atom comes from a coordinated water molecule (Ow5) to give Sr(1) an overall singly capped square antiprism geometry (Fig. S3, ESI[†]). The Sr-O and the carboxylate C-O bond distances in this network span the range 2.542(4)-2.849(4) Å and 1.228(6)-1.269(6) Å respectively, consistent with the values observed in other metal complexes.^{4p} Selected bond distances and angles for this complex are summarized in Table S1 (ESI^{\dagger}). The ligand ptc³⁻ has a μ_8 coordination mode in this complex (Type X, Scheme 1). It is interesting to note that there are three μ_2 carboxylate oxygen atoms (O1, O3, O6) which bridge the independent Sr atoms to form a Sr(1)Sr(2) dimer (3.982(3) Å). To the best of our knowledge no such metallo-dimer is yet known where the dimer is formed by μ_2 bridging of three different carboxylate oxygen atoms. Another dimer, namely Sr(2)Sr(2) dimer, is formed (4.353(3) Å) by the bridging of two symmetry related water molecules (Ow1) with a tetrahedral bridging angle (Sr2- $Ow1-Sr2 = 108.47(15)^{\circ}$) suggesting a tetrahedral coordination



Fig. 9 A perspective view of complex 6.

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environment (others angles are: H1W1–Ow1–H2W1 = $106(6)^{\circ}$, $H1W1-Ow1-Sr2 = 105(5)^{\circ}, 116(5)^{\circ}; H2W1-Ow1-Sr2 = 103(3)^{\circ},$ $119(3)^{\circ}$ around the water molecule. While Sr(1) is shared by the two Sr(1)Sr(2) dimeric units, Sr(2) is shared by one Sr(1)Sr(2)and another Sr(2)Sr(2) dimeric units. Thus these dimeric chains can be best described as $[Sr(2)Sr(2)Sr(1)]_n$ which run along the crystallographic c axis. The other point to note is that these two types of metals do not lie in a plane but rather form puckered sheets. These metal oxide layers are interconnected by ptc³⁻ ligands as pillars to form a 3D network as shown in Fig. 11. These pillars are approximately perpendicular to the puckered metal oxide sheets and the pyridine rings of these pillars are parallel with respect to each other with a centroid-to-centroid distance of 3.483(4) Å (offset distance = 1.21 Å) showing π - π interactions. The faces of the aromatic rings are alternate with respect to the position of ring N atom as can be seen in 5.

Structure of $\{[Ba(ptc)(H_2O)]|Ba(ptcH_2)H_2O]\}_n$, (9). This compound displays a complicated 3D structure, containing two crystallographically independent Ba atoms, two ptc³⁻ ligands and

Sr(2)Sr(2

Sr(1)Sr(2) dimer



two water molecules coordinated to each of the Ba atoms (Fig. 12). There is no uncoordinated water molecule in the structure. The coordination polyhedra around Ba(II) ions can be described as a trigonal hexadecahedron and trigonal dodecahedron for Ba1 and Ba2 respectively (Fig. S4, ESI[†]). The Ba(1) ion is bonded to four mono-dentate carboxylate O atoms (O3, O4, O8, O11) from four ptc³⁻ units, two chelate oxygen atoms (O9, O10) from a different ptc3- unit, one NO2 donor set (O1, N1, O6) from another ptc3- unit, and a water molecule (Ow2) completing ten coordination. This is a rare example of six multicarboxylate ligands coordinating to one metal center. The coordination environment of Ba(2) is quite different. Here, the metal ion is bound to two mono-dentate carboxylate oxygen atoms (O9, O10) from two ptc3- ligands, two chelate oxygen atoms (O3, O4) from another ligand unit, and a water molecule (Ow1) attaining eight coordination geometry. The ligand has two coordination modes in this structure, one with a connectivity number of μ_9 and the other μ_7 (Type VIII, IX, Scheme 1). All bond distances involving the metal ion are within normal range.²⁶ The N(1)-Ba(1) and N(2)-Ba(2) distances in 9 (2.947(10) and 2.991(9) Å respectively) are larger than N(1)–Sr(1) distance (2.708(4) Å) found in 8, which is in accordance with the larger radius of barium than strontium. The Ba...O bond distances are also within normal range.^{40,p} In contrast to 8, in which two types of metal dimers form puckered sheets, the metals in 9 (Ba1, Ba2), form a zigzag type of dimer (namely Ba1Ba2 dimer) with a Ba-Ba separation of 4.523(2) and 4.455(2) Å. It is worth noting that there are two sets of chelate oxygen atoms (O3, O4 and O9, O10) from two unique ligand moieties which are basis of these dimeric chains where each type of metal ions sit in separate rows of the zigzag chain (Fig. 13). These metal oxide dimeric sheets are running along crystallographic a axis. Moreover, each of the two unique ligands simultaneously chelates to two unique cations and bridges to two neighboring metal oxide chains like a pillar. The π - π interaction is the total interaction between two aromatic moieties including van der Waals' and other electrostatic interactions having energies in the 3-10 kcal mol⁻¹ range that stabilize molecules in many crystals.²⁷ The pillars in 9 are also held together by significant π - π interactions. The pillars which bridges Ba(2), appears to have significant π - π interactions, with two different centroid-to-centroid distances of 3.573(4) and



Fig. 12 A view of the coordination environment of **9**. Symmetry codes for (a): (i) -x, 2 - y, -1 - z; (ii) -x, 2 - y, -z; (iii) -1 - x, 1 - y, -z; (iv) 2 - x, 2 - y, -1 - z; (v) 1 - x, 1 - y, -2 - z; (vi) x, y, 1 + z; (vii) x, -1 + y, z; (viii) 1 - x, 2 - y, -1 - z; (ix) -1 - x, -y, -z. For (b): (i) -x, 2 - y, -1 - z; (ii) -1 - x, 1 - y, -z; (iv) 2 - x, 2 - y, -z; (iii) -1 - x, 1 - y, -z; (iv) 2 - x, 2 - y, -z; (iii) -1 - x, 1 - y, -z; (iv) 2 - x, 2 - y, -z; (iii) -x, 1 - y, -z; (iv) 2 - x, 2 - y, -z; (iii) -x, 1 - y, -z; (iv) 2 - x, 2 - y, -z; (iv) -x, 1 - y, -z; (iv) -x, -x, -y, -z; (iv) -x, -x, -y, -z; (iv) -x, -x, -y, -z; (iv) -x, -x, -x; (iv) -x; (iv) -x, -x; (iv) -x



Fig. 13 π - π stacking interactions among ptc units in complex 9.



Fig. 14 View of the 3D structure of 9.

3.909(4) Å (offset distances of 1.45 and 1.91 Å respectively) among the participating pyridine rings. On the other hand, the pyridine rings of the pillars connecting Ba1 atoms appear to have a short centroid-to-centroid distance of 3.382(4) Å (offset distance = 0.96 Å) which is clearly attributed to strong π - π interaction. Another centroid-to-centroid distance of 4.127(4) Å which is large enough, cannot be involved in π - π interaction. Fig. 14 represents the 3D structure of 9.

Structure of { $[Dy(ptc)\cdot 3H_2O]\cdot H_2O]_n$, (10). The single crystal analysis reveals that complex 10 is a 3D open MOF constructed with ptc³⁻, Dy(III) ion and water molecules. The asymmetric unit consists of one Dy(III) ion, one ptc³⁻, three metal-bound and one free water molecules. The Dy(III) ion is nine coordinated (Fig. 15) and is described as singly-capped square anti-prism with bonding from five carboxylate O atoms from three ptc³⁻ units, one ring N atom from one of the ligands and three water molecules (Fig. S5, ESI†). The Dy–O and Dy–N bond lengths are within the normal range. Each ptc³⁻ unit links five Dy(III) centers and four O atoms in addition to the ring N atom (Type XI, Scheme 1). A striking feature of this structure is the arrangement of Dy(III) ions in infinite single helices extending along the crystallographic *b* axis with intervening ptc³⁻ ligands. As the compound crystallizes in the centro-symmetric space group $P2_1/c$, there are equal numbers of left and right-handed chains. A left-handed helix is depicted in the Fig. 16. The helical structure is a result of metal–ligand interactions coupled with stereoelectronic characteristics of the ligand and the conditions prevailing during the synthesis. The pitch of the helix is calculated to be 7.24 Å based on the repeated unit containing two Dy(III) ions and 2 ligands. The stability of the final helical structure relies on the coordinate bonds that each metal makes with ptc³⁻ ligand and the medium value of the pitch is a result of topology of this ligand along with electrostatic repulsive interactions among the metal centers.

Magnetic measurements

Variable temperature magnetic susceptibility data were collected for **4** in the 2 to 300 K temperature range with an applied magnetic field of 0.3 T. The susceptibility variation with temperature is



Fig. 15 View of the coordination environment around Dy(III) in 10. Symmetry codes: (i) x, -0.5 - y, 0.5 + z; (ii) 2 - x, -y, 2 - z; (iii) x, 1 + y, z.



Fig. 16 View of the left-handed single helix in compound **10**:(a) ball-and-stick representation and (b) space-filling representation.

shown in Fig. 17a. As the temperature decreases, the susceptibility increases, following the Curie–Weiss law, with a negative Weiss temperature, indicating weak antiferromagnetic coupling between the Mn(II) ions. The χ T vs T plot decreases slowly as temperature goes down, until at temperatures below 80 K the decrease in the χ T product is more pronounced. The magnetization increases with increasing field in a nearly linear fashion, and is at all times well below the calculated Brillouin curve for an isolated Mn(II) with g = 2.0, which supports the antiferromagnetic coupling in 4 (Fig. 17b). A close look at the structure shows a 3D grid of Mn(II) ions where each Mn(II) ion is linked to four other Mn(II) by *syn, anti*-carboxylato arms of the ptc³⁻ ligands. This bridging mode will favour weak antiferromagnetic interactions between the metal centres, as observed in the magnetic data presented here.



Fig. 17 (a) Temperature dependence for the susceptibility per Mn(II) ion in 4 (χ is shown in circles, χ T is shown as triangles). (b) Magnetization plot per Mn(II) ion in 4. The solid line is the Brillouin function for Mn(II) ion with g = 2.0.

Structural trends

The strategies to control network structure are important for design and synthesis of functional solids whose properties are inherent in their 1D, 2D or 3D structures. There have been recent trends in studying the dimensionality of s-block coordination networks. Fromm has investigated²⁸ the polymeric structures of hydrated Ca(II) and Ba(II) polyether complexes as their iodide salts where the M(II) units are cross-linked between metal-bound water molecules and uncomplexed iodide ions by H-bonding interactions with concluding remarks by the authors that the dimensionality of the polymers formed were primarily related to the number of water molecules per cationic complex, which in turn, could be controlled by the denticity of the polyether ligands and the radii of the cations used. In a more specific approach with sulfate ions, Squattrito and Cai have studied the coordination behavior of mono-4n and disulfonate4m ligands with alkali and alkaline earth cations to obtain lamellar structures. Here, the authors have shown that with the decreasing charge/radius ratio of the cation there is the increment in coordination ability of the ligand.

The nature of the metal largely governs which class of structure is formed and this can be understood by considering the interplay of the basic factors governing s-block metal coordination, that is, charge, size and electronegativity. As the most electronegative metal investigated, Mg–ligand bonds have a higher covalent

contribution than the others, whilst as the smallest group 2 ion, the higher charge density on Mg(II) means that it tends to make stronger interactions with Lewis bases. It is known that Mg-OH₂ bonds are considerably more stable than the other M-OH₂ bonds considered here.²⁹ As can be seen, the asymmetric unit of 5 contains eight water molecules, the highest among the complexes discussed here. Crystallization from water is in effect a competition reaction between the carboxylate groups and neutral water molecules; the higher covalent nature of magnesium thus appears to favor direct hydration of metal over less interaction with the carboxylate group as can be seen for 6. In the 3D structure of Ca(II), Sr(II) and Ba(II) (complex 7, 8, 9 respectively), there is markedly lower level of hydration. Previous studies on this ligand by us⁶ and others⁷ have shown that this ligand readily reacts with transition metals as well as lanthanides to yield a wide variety of structures. In this present paper, we have extended our investigation to systems containing alkaline earth metals, a few of the transition metals and a lanthanide ion. A schematic representation showing the various coordination modes of the ligand ptc³⁻ with different connectivity numbers (μ) used in this study as well as in previous studies^{6,7} are given (Scheme 1). As a comparison, atomic radii of ions, ligand connectivity (µ), range in coordination number and structural variation are listed in Table 2, which provides an understanding of the key factors determining variation in these structures. The coordination numbers of the transition metals vary from 6 to 7 and for the lanthanides and alkaline earth metals this span is 8-10 except for Ca(II) ion. So, coordination number increases as a result of increase in ionic radii. Although the ligand connectivity numbers down the table is not in gradual increment order, it can be said that metals with higher radii have generally higher connectivity numbers. For the case of Fe, the connectivity number is high which may be considered in a very little difference in radii among the transition metal ions (maximum difference is 0.10 Å between Fe and Zn) except for the case of Mn, which is relatively larger in size. Either 1D or 2D structures are obtained for the first row transition metals (exception for Mn) as well as Mg whose ionic radii, ligand connectivity and coordination numbers are very similar. Thus, we can divide the whole Table 2 in two parts: the

first part contains the metal ions from Fe to Zn (ionic radii 0.64 to 0.74 Å) and second part contains metal ions from Mn to Ba (ionic radii 0.80 to 1.35 Å). In contrast, the other alkaline earth metals along with lanthanides have higher 3D networks due to their high ligand connectivity number and coordination number. So, in general, structures of higher dimensions are obtained going down the table.

Conclusion

We have shown the formation of a Cd-oxalate coordination polymer as a result of breakage of the ligand, pyridine-2,4,6tricarboxylic acid (ptcH₃) at RT in the presence of pyridine. The solid-state structure also shows the presence of a discrete acyclic water hexamer. However, under hydrothermal condition, ligand ptcH₃ is reduced to chelidamic acid that binds Cd(II) forming a 1D coordination polymer. Prior to this study, structures of coordination polymers of seven transition and three lanthanide metals with the ptcH₃ ligand were known.⁶⁻⁷ We have now expanded this series by adding few more transition and lanthanide metals as well as several alkaline earth metals. With this structural information now available, it is possible to rationalize the seemingly random variety of coordination networks formed with this ligand. Thus, a tentative trend in the coordination ability of metal ions toward aromatic carboxylates is emerging: alkalineearth metals \approx trivalent lanthanides > divalent transition metals. This study presents a strategy to form coordination networks not only with different levels of aggregation between metal ions and the ligand, but also with different degrees of dimensionality difference in the number of metal-carboxylate interactions that can form, as rationalized by cation radii and coordination number, manifests into a dimensional evaluation between the networks, propagating down Table 2. This study also presents a strategy to form coordination networks with soft closed shell cations of Group 2. These metals should not be discounted as potential candidates for building blocks in extended coordination networks for potential applications.

Table 2 Ionic radii, ligand connectivity (μ), metal coordination number (CN), and structure dimensionality (D) of M-ptc compounds

Complex	Metal ion	Ionic radii	μ	CN	D	Reference
$\{ [Fe(H_2O)_k] [Fe(ptc)(H_2O)_2]_2 \cdot 2H_2O \}_n $	Fe	0.64	5	6/7	1	7b
${Mg_3(ptc)_2 \cdot 8H_2O}_n$	Mg	0.65	3/6	6	1	This work
$\{[Mg(ptc).1/2[Mg(H_2O)_6]\cdot H_2O]\}$	Mg	0.65	5	7	1	This work
$\{[Ni_{15}(ptc)(pip)_{05}(H_2O)_4]\cdot H_2O\}_{n}$	Ni	0.72	4	6	1	This work
$\{[Ni(ptcH)_2][Ni(bpy)(H_2O)_4]\cdot 6H_2O\}$	Ni	0.72	3	6	1	6d
$\{Cu_{3}(ptc)_{2}(H_{2}O)_{8}\} \cdot 4H_{2}O\}_{n}$	Cu	0.72	5	6	1	7b
$\{ [Cu(ptc)] \cdot 1/2 [Cu((H_2O)_6] \cdot H_2O]_n \}$	Cu	0.72	4	6	1	6c
$\{ [Co(H_2O)_6] [Co(ptc)(H_2O)_2]_2 \cdot 2H_2O \}_n$	Со	0.74	5	6/7	1	7b
$\{ [Co_2(ptcH)_2(4,4'-bipy)(H_2O)_4] \cdot 2H_2O \}$	Со	0.74	3	6	1	6e
$\{Zn_{15}(ptc)(H_2O)_6\}_n$	Zn	0.74	5	6	2	6a
$\{Zn_1(ptcH)(H_2O)_{433}\}_3$	Zn	0.74	3	6	2	6a
$\{Mn_{1,5}(ptc)\cdot 2H_2O\}_n$	Mn	0.80	7	6	3	This work
${[Pr(ptc)\cdot 2H_2O]\cdot 2H_2O]}$	Pr	0.90	7	9	3	6b, 7a
$\{Na_2NiPr(ClO_4)(C_2H_6O_2)(ptc)_2(H_2O)_8\} \cdot 4.5H_2O\}_n$	Pr	0.90	6	10	3	7a
${[Dy(ptc)\cdot 3H_2O]\cdot H_2O]_n}$	Dy	0.91	6	9	3	This work
$\{Ca_{1,5}(ptc)\cdot 2H_2O\}_n$	Ca	0.99	7	6/7	3	This work
$\{ [Nd(ptc) \cdot 2H_2O] \cdot 2H_2O \}$	Nd	1.00	7	9	3	6b
$\{Sr_{15}(ptc)\cdot 5H_2O\}_n$	Sr	1.13	8	9	3	This work
${Ba_2(ptcH)_2 \cdot 2H_2O}_n$	Ba	1.35	7/9	8/10	3	This work

Materials

The metal salts and 2,4,6-trimethylpyridine were acquired from Aldrich and used as received. All solvents were obtained from S.D. Fine Chemicals (India) and were purified prior to use following standard procedures.

Physical measurements

The IR spectra (KBr pellets) were recorded on a Perkin-Elmer Model 1320 spectrometer in the 4000–400 cm⁻¹ spectral regions. Elemental analyses (C, H, and N) were performed on a LECO CHNS-932 microanalytical analyzer. Magnetic measurements were performed at the Servei de Mesures Magnètiques (Universitat de Barcelona) on crushed polycrystalline samples using a Quantum Design SQUID MPMS-XL magnetometer equipped with a 5 T magnet. The diamagnetic corrections were evaluated from Pascal's constants.

X-Ray structural studies

Single crystal X-ray data on 1-10 were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphitemonochromated Mo-K α radiation ($\lambda = 0.71069$ Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The data integration and reduction were processed with SAINT³⁰ software. An empirical absorption correction was applied to the collected reflections with SADABS³¹ using XPREP.³² The structure was solved by the direct method using SHELXTL³³ and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97³⁴ program package. The non-hydrogen atoms were refined anisotropically while the hydrogen atoms attached to carbon atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters. The hydrogen atoms of water molecules were located from difference Fourier maps and refined freely keeping the O-H bond distances constrained to ~0.82 Å with the DFIX command. In 2, Ow6 is disorder over two positions with occupancy of 0.5 and both were refined as isotropic. For complex 5, the Flack parameter did not refine to a sensible value and therefore the polar direction in the crystal could not be determined. The crystal and refinement data are collected in Table 3.

Synthesis

Pyridine-2,4,6-tricarboxylic acid, (ptcH₃). This compound was synthesized in 50% yield by oxidation of 2,4,6trimethylpyridine with aqueous alkaline KMnO4 following a literature method.35

 $\{ [Cd(Ox)(H_2O)_2]H_2O \}_n$, (1). Reaction of $Cd(NO_3)_2 \cdot 4H_2O$ and ptcH₃ in 2:1 molar ratio at room temperature in the presence of excess pyridine afforded crystals of 1 in 1 h in ~50% yield. The same product as crystals could be isolated in comparable yield when acetate or chloride salt of Cd(II) was used in place of the nitrate salt. Anal. calcd for C₂H₆O₇Cd: C, 9.44; H, 2.3%. Found: C, 9.50; H, 2.42%. Main IR features (cm⁻¹, KBr pellet): 3439 vs for v(O-H); 3095 w for v(C-H); 1615 vs, 1534 s for $[v_{as}(O-C-O) +$

v(C=C + C=N)]; 1483 w for $v(C_{ar}-C)$; 1384 s, 1323 w, 1311 w for $v_{\rm s}$ (O–C–O); 1161 w, 1070 w, 1052 m for $\delta_{\rm ip}$ (C–H); 937 w for $\delta_{\rm ring}$; 826 m for $\delta(O-C-O)$; 777 m for $\delta_{op}(C-H)$; 608 w for π (CO₂); 530 w, 485 w for v(M–O).

 $\{ [Cd_2(cdaH)_2(H_2O)_4](H_2O)_3 \}_2$, (2). Synthesis of this compound was achieved hydrothermally by reacting 1 mmol amounts of Cd(NO₃)₂·4H₂O and ptcH₃ in 5 ml of water in a 25 ml Teflonlined stainless steel autoclave. The autoclave was heated under autogenous pressure to 180 °C for 2 days and then kept at 60 °C for a further 12 h period. Upon cooling to RT, the desired product appeared as long colorless rectangular parallelopipeds in $\sim 60\%$ yield. In this reaction condition, the carboxylic acid group at the 4-position of ptcH₃ was converted to hydroxyl to afford chelidamic acid ($cdaH_3$ = chelidamic acid). Anal. Calcd. for $C_{14}H_{20}N_2O_{17}Cd_2$: C, 23.58; H, 2.82; N, 3.92%. Found: C, 23.63; H, 2.85; N, 3.86%. Main IR features (cm⁻¹, KBr pellet): 3420 vs for v(O–H); 3050 w for v(C-H); 1606 vs for $[v_{as}(O-C-O) + v(C=C + C=N)]$; 1443 m for v(C_{ar}-C); 1363 s, 1272 m for v_s(O-C-O); 1105 w, 1027 w, 1015 m for δ_{ip} (C–H); 939 w for δ_{ring} ; 827 m for δ (O–C–O); 783 m for $\delta_{op}(C-H)$; 589 w for π (CO₂); 470 w, 438 w for ν (M–O + M–N).

 $\{[Ni_{1,5}(ptc)(pip)_{0,5}(H_2O)_4]\cdot H_2O\}_n$, (3). This compound was synthesized hydrothermally, as above by reacting $Ni(NO_3)_2 \cdot 6H_2O_1$, piperazine (pip) and ptcH₃ in one molar amount each in the presence of 6 ml water for three days at 170 °C and then cooled for 7 h. The final product obtained as long green needles, were collected by filtration, washed with water, then MeOH, and finally with ether. Yield ~40%. Anal. calcd for $C_{10}H_{17}N_2O_{11}Ni_{15}$: C, 27.98; H, 3.99; N, 6.53%. Found: C, 27.93; H, 4.03; N, 6.42%. Main IR features (cm⁻¹, KBr pellet): 3368 vs for v(O–H); 1639 vs for [v_{as} (O– C-O) + v(C=C + C=N)]; 1390 s, 1360 s for v_s (O-C-O); 921 m for δ_{ring} ; 758 m for δ_{op} (C–H); 595 w for π (CO₂); 558 w, 490 w, 467 w for v(M-O + M-N).

 ${Mn_{1.5}(ptc) \cdot 2H_2O}_n$, (4). This compound was synthesized by mixing 1 mmol of ptcH₃ and 1 mmol of MnCl₂·4H₂O in 4 ml of water in Teflon-lined autoclave, which was heated under autogenous pressure to 180 °C for 84h. Upon cooling to room temperature the desired product appeared as pale pink cubic in ca. 60% yield. The same crystalline product could be obtained when acetate or sulfate salt of Mn(II) is used in place of chloride salt. Anal. calcd for C₈H₆N₁O₈Mn_{1.5}: C, 29.42; H, 1.85; N, 4.29%. Found: C, 29.46; H, 1.89; N, 4.25%. Main IR features (cm⁻¹, KBr pellet): 3381 vs for v(O-H); 3050 w for v(C-H); 1608 vs, 1556 s for $[v_{as}(O-C-O) + v(C=C + C=N)]$; 1455 m for $v(C_{ar}-C)$; 1367 vs, 1278 m for v_s (O–C–O); 1226 m, 1105 w, 1025 w for δ_{in} (C–H); 944 w for δ_{ring} ; 747 m for δ_{op} (C–H); 618 w for π (CO₂); 498 w, 467 w for v(M-O + M-N).

 $\{Mg_3(ptc)_2 \cdot 8H_2O\}_n$, (5). This was prepared in *ca*. 54% yield as colorless needles on hydrothermal reaction of 1 mmol of ptcH₃ and 1 mmol of Mg(NO₃)₂·6H₂O (or MgCl₂·6H₂O) in 5 ml of water in Teflon-lined autoclave which was heated under autogenous pressure to 140 °C for 72 h. Upon cooling to room temperature the final product was collected by filtration, washed with water and then MeOH. Anal. calcd for C₁₆H₂₀N₂O₂₀Mg₃: C, 30.34; H, 3.18; N, 4.45%. Found: C, 30.36; H, 3.14; N, 4.48%. Main IR features (cm⁻¹, KBr pellet): 3469 vs for v(O–H); 3101 m for v(C–H); 1629 vs, 1563 s for $[v_{as}(O-C-O) + v(C=C + C=N)]$; 1452 m for $v(C_{ar}-C-O) + v(C=C + C=N)$ C); 1365 s, 1284 m for v_s (O–C–O); 1108 m, 1029 m for δ_{ip} (C–H);

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 $Table \ 3 \quad {\rm Crystal} \ {\rm data} \ {\rm and} \ {\rm structure} \ {\rm refinement} \ for \ 1-10$

		1	2	3	4	S	9	7	8	6	10
Empiric	al	$C_2H_6O_7Cd$	$C_{14}H_{20}N_2O_{17}Cd_2\\$	$C_{10}H_{17}N_2O_{11}Ni_{1.5}$	$C_8H_6N_1O_8Mn_{1.5}$	$C_{16}H_{20}N_2O_{20}Mg_3$	$C_8 H_{\rm l4} NO_{\rm l2} Mg_{\rm l.5}$	$C_8H_6NO_8Ca_{1.5}$	$C_8H_{12}NO_{10.5}Sr_{1.5}$	$C_{16}H_{10}Ba_2N_2O_{14}$	$C_8H_{10}NO_{10}Dy$
Formula	1 weight	254.47	713.12	429.32	326.55	633.27	352.67	304.26	424.62	728.94	442.67
Tempera	ature	100(2) K	100(2) K	100(2) K	100(1) K	100(2) K	100(1) K	100(1) K	100(2) K	100(2) K	100(1) K
Radiatic	nc	Mo-Ka	Mo-Ka	Mo-Ka	Mo-Ka	Mo-Ka	Mo-Ka	Mo-Ka	Mo-Ka	Mo-Ka	Mo-Ka
Wavelen	ıgth	0.71069 Å	$0.71069 { m \AA}$	$0.71069 m \AA$	0.71069 Å	0.71069 Å	0.71069 Å	0.71069 Å	0.71069 Å	$0.71069 { m \AA}$	0.71069 Å
Crystal	system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Orthorhombic	Triclinic	Monoclinic
Space gi	toup	$P\overline{1}$	P21/c	$P\overline{1}$	$P\overline{1}$	Cc	$P\overline{1}$	$P\overline{1}$	Pbcn	$P\overline{1}$	P21/c
a/Å		5.998(4)	10.403(5)	7.472(3)	6.434(3)	19.708(4)	7.274(5)	6.714(2)	16.493(5)	7.310(3)	11.822(6)
$b/\text{\AA}$		6.592(3)	17.963(6)	8.752(4)	8.585(4)	6.799(5)	8.955(4)	8.773(3)	6.820(6)	7.851(4)	7.240(5)
$c/ m \AA$		8.459(4)	13.090(6)	11.646(4)	9.880(3)	19.461(4)	11.032(5)	10.070(3)	22.220(7)	17.242(4)	13.466(4)
α (°)		74.674(5)	90.00	92.638(5)	110.107(5)	90.00	74.722(6)	108.977(5)	90.00	101.448(5)	90.00
β (°)		74.278(4)	105.904(8)	101.187(4)	95.052(4)	116.873(5)	74.713(6)	97.689(4)	90.00	92.926(4)	96.142(7)
γ(°)		81.171(5)	90.00	90.541(5)	102.072(5)	90.00	79.032(7)	100.447(5)	90.00	90.140(4)	90.00
$V/Å^3$		309.3(3)	2352.5(17)	746.2(5)	493.5(4)	2326.1(18)	663.0(6)	539.6(3)	2499(2)	968.5(7)	1146.0(10)
N		2	2	1	1	4	1	1	4	2	4
$\rho_{\rm c}/{\rm Mg}$ 1	n^{-3}	2.732	2.013	1.911	2.198	1.808	1.766	1.873	2.236	2.500	2.566
μ/mm^{-1}		3.514	1.892	1.977	1.988	0.237	0.229	0.856	6.485	4.127	6.577
F(000)		244	1400	442	325	1304	366	310	1656	688	844
Indepen	dent refl.	1451	5118	3266	2094	4154	2463	2057	2302	4023	2319
. Refl. use	pe	1458	5821	3537	2434	4550	3290	2561	3087	4630	2788
$(I > 2\sigma)$	(1)										
$R_{\rm int}$ valu	le	0.0146	0.0316	0.0177	0.0132	0.0265	0.0203	0.0157	0.0549	0.0183	0.0288
- Refinem	nent	Full-matrix	Full-matrix	Full-matrix	Full-matrix	Full-matrix	Full-matrix	Full-matrix	Full-matrix	Full-matrix	Full-matrix
method		least-squares	least-squares on	least-squares on	least-squares	least-squares on	least-squares on	least-squares	least-squares on	least-squares on	least-squares
		on F^2	F^2	F^2	on F^2	F^2	F^2	on F^2	F^2	F^2	on F^2
GOF		1.126	1.041	1.030	1.105	1.119	1.109	1.106	1.130	1.160	1.115
Final R	indices	$R_1 = 0.0291$	$R_1 = 0.0648$	$R_1 = 0.0313$	$R_1 = 0.0483$	$R_1 = 0.0566$	$R_1 = 0.0677$	$R_1 = 0.0550$	$R_1 = 0.0368$	$R_1 = 0.0529$	$R_1 = 0.0396$
$\left \left[I > 2\sigma \right] \right $	[()]	$wR_2 = 0.0826$	$wR_2 = 0.1851$	$wR_2 = 0.0844$	$wR_2 = 0.1057$	$wR_2 = 0.1344$	$wR_2 = 0.1758$	$wR_2 = 0.1102$	$wR_2 = 0.0726$	$wR_2 = 0.1249$	$wR_2 = 0.0838$
R indice	S	$R_1 = 0.0292$	$R_1 = 0.0825$	$R_1 = 0.0339$	$R_1 = 0.0731$	$R_1 = 0.0700$	$R_1 = 0.0905$	$R_1 0.0869$	$R_1 = 0.0634$	$R_1 = 0.0766$	$R_1 = 0.0604$
(all data	1)	$WR_2 = 0.0827$	$WR_2 = 0.2145$	$wR_2 = 0.0863$	$WR_2 = 0.1796$	$WR_2 = 0.1684$	$WR_2 = 0.2475$	$WR_2 = 0.1729$	$WR_2 = 0.1050$	$wR_2 = 0.2091$	$wR_2 = 0.1472$

934 w, 919 w for δ_{ring} ; 838 m for $\delta(O-C-O)$; 733 m for $\delta_{op}(C-H)$; 534 w, 490 w for v(M-O + M-N).

{[Mg(ptc)(H₂O)₂]-1/2[Mg(H₂O)₆]·H₂O}₁, (6). The filtrate from the reaction of Mg(NO₃)₂·6H₂O and ptcH₃ on further evaporation afforded **6** as colorless hexagonal-shaped crystals in ~15% yield. Anal. calcd for C₈H₁₄N₁O₁₂Mg_{1.5}: C, 27.25; H, 4.00; N, 3.97%. Found: C, 27.28; H, 4.05; N, 4.02%. Main IR features (cm⁻¹, KBr pellet): 3366 vs for v(O–H); 3045 w for v(C–H); 1662 vs, 1611 s for [v_{as} (O–C–O) + v(C=C + C=N)]; 1452 m for v(C_{ar}– C); 1365 s, 1284 m for v_s (O–C–O); 1108 m, 1029 m for δ_{ip} (C–H); 934 w, 919 w for δ_{ing} ; 838 m for δ (O–C–O); 733 m for δ_{op} (C–H); 534 w, 490 w for v(M–O + M–N).

{**Ca**_{1.5}(**ptc**)-**2H**₂**O**}_n, (7). Standard hydrothermal conditions did not afford compound 7. A different approach was adopted for its synthesis. In a typical experiment, 1 mmol of ptcH₃ and 1 mmol of Ca(NO₃)₂·4H₂O and few drops of triethylamine were taken in a 10 ml of water in Teflon-lined autoclave. The autoclave was heated under autogenous pressure to 180 °C for 96 h and then left to cool to room temp. Colorless prismatic crystals were obtained in *ca*. 58% yield. Anal. calcd for C₈H₆N₁O₈Ca_{1.5}: C, 31.58; H, 1.99; N, 4.60%. Found: C, 31.60; H, 2.04; N, 4.64%. Main IR features (cm⁻¹, KBr pellet): 3424 vs for v(O–H); 3063 m for v(C–H); 1624 vs for [*v*_{as}(O–C–O) + *v*(C=C + C=N)]; 1445 m for *v*(C_{ar}–C); 1384 m, 1356 m, 1322 s for *v*_s(O–C–O); 1010 m for δ_{ip} (C–H); 944 w, 930 w for δ_{ring} ; 785 m for δ_{op} (C–H); 591 w for π (CO₂); 514 w, 469 w for *v*(M–O + M–N).

{**Sr**_{1.5}(**ptc**)-**5H**₂**O**}_{**n**}, (8). When Sr(NO₃)₂ (or SrCl₂·6H₂**O**) was taken in place of Ca(NO₃)₂·4H₂O keeping the reaction condition the same as in 7, compound 8 could be isolated in ~55% yield as colorless rectangular parallelopipeds. Anal. calcd for C₈H₁₂N₁O_{10.5}Sr_{1.5}: C, 22.79; H, 2.86; N, 3.32%. Found: C, 22.84; H, 2.83; N, 3.35%. Main IR features (cm⁻¹, KBr pellet): 3475 vs for *v*(O–H); 3060 w for *v*(C–H); 1630 vs, 1533 s for [*v*_{as}(O–C–O) + *v*(C=C + C=N)]; 1463 m for *v*(C_{ar}–C); 1395 s, 1348 m for *v*_s(O–C–O); 1277 w, 1230 m for δ_{ip} (C–H); 930 w for δ_{ring} ; 784 m for δ_{op} (C–H); 550 w, 491 w, 469 w for *v*(M–O + M–N).

{**[Ba(ptc)(H₂O)][Ba(ptcH₂)H₂O]**_n, **(9).** When Ba(NO₃)₂ (or BaCl₂·6H₂O) was taken in place of Ca(NO₃)₂·4H₂O keeping the reaction condition the same as in 7, compound 9 could be isolated in ~58% yield as colorless rectangular parallelopipeds. Anal. calcd for C₁₆H₁₀N₂O₁₄Ba₂: C, 26.36; H, 1.38; N, 3.84%. Found: C, 26.41; H, 1.35; N, 3.89%. Main IR features (cm⁻¹, KBr pellet): 3423 vs for v(O–H); 3068 m for v(C–H); 1727 m for protonated carboxylate; 1642 vs, 1582 s for [v_{as} (O–C–O) + v(C=C + C=N)]; 1548 m for v(C_{ar}–C); 1440 m, 1390 m for v_s (O–C–O); 1246 m, 1192 m, 1108 w for δ_{ip} (C–H); 1001 w, 942 w, 902 w for δ_{ring} ; 787 m for δ_{op} (C–H); 555 w for π (CO₂); 520 w, 468 w for v(M–O + M–N).

{[**Dy(ptc)·3H₂O]·H₂O**}_n, (10). This was prepared in ~55% yield as light purple rectangular parallelopipeds crystals on hydrothermal reaction of 1 mmol of Dy(NO₃)₃·5H₂O with 1 mmol of the ligand under identical experimental condition as 7. Anal. calcd for C₈H₁₀N₁O₁₀Dy₁: C, 21.70; H, 2.27; N, 3.16%. Found: C, 21.68; H, 2.30; N, 3.13%. Main IR features (cm⁻¹, KBr pellet): 3383 vs for v(O–H); 3055 w for v(C–H); 1631 m, 1645 vs, 1580 s for [v_{as} (O–C–O) + v(C=C + C=N)]; 1447 m for v(C_{ar}–C); 1394 s, 1353 m, 1278 w for v_s (O–C–O); 1236 w, 1110 m, 1026 m for

 $\delta_{rp}(C-H)$; 952 w for δ_{ring} ; 792 m for $\delta_{op}(C-H)$; 535 w, 516 w for v(M-O + M-N).

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