Acid-Driven Dimensionality Control of Cd(II) Complexes: From Discrete Double Open Cubane to One- and Three-Dimensional Networks

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Supporting Information

ABSTRACT: Reaction of CdCl₂ with hep-H [hep-H = 2-(2-hydroxyethyl)pyridine] in MeOH at 298 K yields the double open cubane tetramer \([\text{Cd}_2(\mu_2-\text{Cl})_2(\mu_3-\text{Cl})(\text{hep-H})_2\text{Cl}]_2\) (1). On reaction with methanolic HCl, HNO₃, and H₂SO₄ transforms into a one-dimensional (1D) polymeric chain \([\text{Cd}(\mu_2-\text{Cl})_2(\text{Cl})(\text{hep-H})_2]_n\) (2), ribbon-shaped polymeric structure \([\text{Cd}_{12}(\text{H}_2\text{O})_3]_2(\text{hep-H})_2\) (3), and three-dimensional network \([\text{Cd}(...\text{SO}_4)(...\text{H}_2\text{O})_n][\text{Cd}(...\text{SO}_4)(...\text{H}_2\text{O})_n][\text{Cd}(...\text{SO}_4)(...\text{H}_2\text{O})_n]\) (4) with topology seh-4,6-C₂/c net, respectively. The similar reactions of CdCl₂ with other pyridine alcohols such as hmp-H [hmp-H = 2-(2-hydroxymethyl)pyridine] and hpp-H [hpp-H = 2-(2-hydroxypropyl)pyridine] yield 1D polymeric chains \([\text{Cd}(\mu_2-\text{Cl})_2(\text{hmp-H})_2]_n\) (5) and \([\text{Cd}(\mu_2-\text{Cl})_2(\text{hpp-H})]_n\) (6), respectively. Similar to 1, upon treatment with methanolic HCl 5 and 6 also transform into respective 1D polymeric chains \([\text{Cd}(\mu_2-\text{Cl})_2(\text{Cl})(\text{hmp-H})_2\text{Cl}]_2\) (7) and \([\text{Cd}(\mu_2-\text{Cl})_2(\text{Cl})(\text{hpp-H})_2\text{Cl}]_2\) (8), analogous to 2. However, their reactions with methanolic HNO₃ and H₂SO₄ result in nonisolable products. In 1, 5, and 6, the pyridine alcohols are bonded to Cd(II) in bidentate fashion via their O and N atoms, whereas in 2, 7, and 8 due to protonation of pyridine nitrogen these ligands are bonded in a monodentate fashion via the alcoholic O atom.

INTRODUCTION

Coordination polymers (CPs) are of great importance because of their significant role in combining synthetic chemistry and applied materials field, and provide broader perspective of arrangement of molecules and their functions.¹ A general practice for design and construction of coordination polymers (CPs) is to employ appropriate bridging ligands or spacers or oxyanions to extend the primary-building units; this makes the crystal engineering field very active.²⁻⁸

Recent trends show increasing interest in the fabrication of Cd(II)-based coordination polymers (CPs) due to their potential applications in optical properties, catalysis, biological activity, and molecular metal wires.³ Cd(II)-based one-, two- and three-dimensional (1D, 2D, and 3D) CPs are in great demand because of their ability to form molecular-based materials with interesting magnetic and luminescent properties.¹⁰ Varying coordination numbers and geometries of soft Cd(II) metal make it a suitable candidate to explore the structural dimensionalities by using a precursor such as CdCl₂ to devise self-assembled CPs.¹¹ A speedy development has been made in designing and construction of CPs with varying dimensionalities, but the dimensionality control still remains the challenging task in the field of crystal engineering¹² and metallo-supramolecular chemistry.¹³ Most of these polymers are constructed by the self-assembly of transition metal salts with carboxylic acids and multidentate N-donor ligands.¹⁴ The self-assembly of coordination complexes is largely dependent on suitable intra- and intermolecular interactions such as metal–ligand interactions and supramolecular contacts (hydrogen bonding and other weak interactions), and the scope of

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manipulation in these interactions always exists to obtain self-assemblies of altered structures with improved properties. Such manipulations can be done by tuning of metal ions, ligands involved, and reaction conditions such as solvents, temperature, and pH of the reaction medium.15

Herein, we discuss the systematic study of the effect of three different acids (HCl, HNO₃, and H₂SO₄) on molecular assemblies of Cd-pyridine alcohol complexes and report on (i) discrete double open cubane tetramer complex and its acid induced transformations to diverse 1D polymeric chain and to 3D network with topology seh-4,6-C₂/c net and (ii) transformation of the 1D polymeric chain into another 1D polymeric chain with varying coordination of ligands. Moreover, we also studied the extended structures of all the complexes via supramolecular contacts. Although the acid-driven supramolecular tuning of metal salts, particularly those of Co, Zn, Re, and Tc, are known,15−g hitherto, this is the first report on transformations of discrete Cd(II) complexes to polymeric species to the best of our knowledge.

■ RESULTS AND DISCUSSION

The double open cubane [Cd₂(μ₂-Cl)₂(μ₃-Cl)(hep-H)₂Cl]₂ (1) was obtained by the reaction of CdCl₂ with hep-H (hep-H = 2-(2-hydroxyethyl)pyridine) in methanol at 298 K, where hep-H is bonded to Cd(II) ion in a bidentate fashion through its N, O donor atoms. The effect of methanolic HCl on 1 leads to protonation of pyridine N and addition of Cl⁻, which results in transformation of a double open cubane tetramer to the 1D polymeric chain [Cd(μ₂-Cl)₂(Cl)(hep-H)]₈ (2). Use of methanolic HNO₃ affords a 1D polymeric ribbon shape structure (3) in which each repeating unit contains a dianionic [Cd₂Cl₁₂(H₂O)₃]²⁻ and two pyridinium-2-ethanol [hep-H]⁺ as countercations. Furthermore, treatment of methanolic H₂SO₄ on 1 results in complete removal of hep-H and Cl⁻ ligands and forms a seh-4,6-C₂/c net of [Cd(SO₄)(H₂O)]₅₄ (4) (Scheme 1). 1D polymeric chains of 5 and 6 were formed by the reactions of CdCl₂ with hmp-H [(hmp-H = 2-(2-hydroxymethyl)pyridine) and hpp-H (hpp-H = 2-(2-hydroxypropyl)pyridine)], respectively, where hmp-H and hpp-H are coordinated to Cd(II) ion in a N, O bidentate fashion. Further the effect of acids on 5 and 6 was also observed, as with methanolic HCl they transform in isostructural 1D polymeric chains 7 and 8 formed by addition of H⁺ and Cl⁻ as observed in 2 (Scheme 2). However, the reaction of 5 and 6 with methanolic HNO₃ and H₂SO₄ gives nonisolable products. 1, 2, and 5–8 are characterized by microanalytical, IR spectral studies, thermal analysis, and powder X-ray diffraction techniques. 1–8 are authenticated by their single crystal X-ray studies.

The different course of reactivities of HCl, HNO₃, and H₂SO₄ can be attributed to different conjugate bases Cl⁻, NO₃⁻, and SO₄²⁻ present in these acids. The empirical formulas of 2, 7, and 8 suggest that their formation results from a formal addition of a HCl molecule to their respective parent complexes 1, 5, and 6. This was perhaps feasible due to smaller Cl⁻ ions from HCl occupying the vacant coordination site on Cd(II)
generated by a change in coordination mode of pyridine alcohol from bidentate to monodentate as a result of protonation, which satisfies the octahedral coordination of Cd(II). However, in the case of HNO₃, protonation of pyridine is not followed by subsequent addition of anion, probably because of its larger size. This causes removal of the hep-H ligand and triggers rearrangement of Cl⁻ groups in the double open cubane structure of 1, which through Cl⁻ bridging forms a cationic 1D ribbon structure of 3 having [hep-H₂]⁺ units as counteractation.

Effect of H₂SO₄ on 1 leads to complete removal of Cl⁻ and hep-H ligands and affords a sech-4,6-C2/c net of 4. This prompted us to reinvestigate this transformation in the presence of other SO₄²⁻ sources Na₂SO₄ and MgSO₄ instead of H₂SO₄. It was observed that either Na₂SO₄ or MgSO₄ fail to transform 1 into 4. This suggests that SO₄²⁻ alone is unable to bring transformation, and the presence of H⁺ is necessary to protonate the pyridine alcohol to weaken its binding with Cd(II) through disruption of its chelate, thereby allowing binding of SO₄²⁻ to Cd(II). In order to study the fate of the detached hep-H ligand in reaction of 1 with H₂SO₄, we extracted the organic product from neutralized reaction mixture whose 1H NMR spectrum confirms the presence of hep-H and thus corroborates that during the reaction hep-H does not undergo any chemical transformation.

In order to reach an optimum acid concentration, we also studied the effect of the varying concentration of three acids on these transformations. It was observed that the monobasic acids HCl and HNO₃ show similar concentration dependence in their reactions. The optimum concentration for these two acids was found to be 1 M, which completes the reaction in 3 h (same time for 2–6 M solutions). However, dilute solutions 0.5 and 0.1 M take longer time 8 h and 2 days, respectively, to complete the reaction. With further dilution of HCl and HNO₃ solutions (0.01 M), no observable transformation was seen. In the case of dibasic acid H₂SO₄, the optimum concentration of the acid was found to be 0.1 M to complete the conversion of 1 to 4 in 3 h (same time for 1–6 M solutions). As observed, 0.01 M solutions of HCl and HNO₃ were insufficient to bring any substantial transformation; at the same concentration, complete transformation was observed with H₂SO₄ but in longer duration of 14 h. However, no reaction was observed with 0.001 M H₂SO₄ solution.

### CRYSTAL STRUCTURES

1 crystallizes in triclinic P1 space group with a crystallographically imposed inversion center (Table 1, Figure 1). 1 consists of two dimeric [Cd(μ-Cl)Cl]₂ units that link together to form tetranuclear [Cd₂(μ-Cl)₂(μ₃-Cl)(hep-H)₂Cl]₂ with double open cubane core (inset Figure 1). The Cd(II) ions in the core are linked through chloride bridges. The hep-H links the Cd(II) centers via N and O atoms in bidentate mode, creating six-membered rings around the metal centers with metal bite angles 80.2°{(N(1)−Cd(1)−O(1)} and 81.5°{(N(2)−Cd(2)−O(2)} (Table S1). Both the Cd(II) atoms are present in the hexacoordinated environment forming distorted octahedral geometry. In Cd(1), out of the six coordination sites two are occupied by μ₂-Cl and two by μ₃-Cl, and the remaining two sites are occupied by N, O of the hep-H ligand. However, in Cd(2) two positions are occupied by μ₂-Cl, two by N and O atoms of hep-H ligand, one by μ₃-Cl, and the remaining one by terminal Cl (Table S1, Supporting Information). Cd(2) differs from Cd(1) by the presence of one terminal Cl atom. Cd−Cl bond lengths are in the range of 2.537(2)−2.886(2) Å. The bond distance between Cd(2)
Table 1. Crystallographic Details of 1–8

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and $\mu_3$-Cl is relatively larger ($2.886(2)$ Å) than Cd(2) and $\mu_2$-Cl ($2.668(3)$ Å).

3 crystallizes in monoclinic $P2_1/n$ space group with a crystallographically imposed inversion center (Table 1, Figure 2). Asymmetric unit in 3 consists of dianionic $[[\text{CdCl}_3(\text{H}_2\text{O})_3]^- \cdot (\text{hep-H}_2)]^2-$ and two protonated $[\text{hep-H}_2]^+$ ligands in the lattice as countercation, which on further expansion generates a ribbon-shaped polymeric structure. The geometry around each Cd(II) atom is distorted octahedral with two different types of coordination environments. Cd(1), Cd(4), and Cd(5) are surrounded by three Cl atoms of $\mu_3$-Cl, two Cl atoms of $\mu_2$-Cl, and one O atom of the coordinated water molecule. However, in Cd(2) and Cd(3), all the coordination sites are occupied by Cl atoms (three by Cl atoms of $\mu_3$-Cl, two by Cl atoms of $\mu_2$-Cl, and one by terminal Cl atom. Cd−Cl distances are in the range of $2.515(7)$−$2.786(7)$ Å, whereas the Cd−O distances are observed to be Cd(1)−O(101) $2.352(15)$ Å, Cd(5)−O(102) $2.343(14)$ Å, Cd(4)−O(103) $2.313(17)$ Å (Table S1, Supporting Information). The two $[\text{hep-H}_2]^+$ cations present in the lattice are involved in strong hydrogen bonding for extension of supramolecular networks.

4 crystallizes in monoclinic $P2_1/n$ space group with crystallographically imposed inversion center (Table 1, Figure 3), as reported earlier.\(^{18}\) We have observed better refinement parameters, and the topology for this 3D network which has not been discussed so far. Moreover, the synthetic route discussed by us is also different. Asymmetric unit of 4 consists of Cd(II) metal ions with identical hexacoordinated ($O_6$) environment. Cd−O bond distances are in the range of $2.240(4)$−$2.405(4)$ Å (Table S1, Suppporting Information). Each Cd(II) metal is linked through the O atoms of sulfate and H$_2$O molecule in all directions yielding a seh-4,6-C2/c like 3D network.

The structure of CdSO$_4$(H$_2$O) (4) is formed by cations Cd$^{2+}$ and two ligands SO$_4^{2−}$ and H$_2$O (Figure 3a). The Cd$^{2+}$ ion has coordination number 6, and the sulfate ion is coordinated by four cadmium atoms. The water molecule is a bridging ligand coordinated by two cadmium atoms. The following simplified standard representation can be proposed. The cadmium and sulfur atoms are represented by 4- and 6-coordinated nodes, while the oxygen atoms of ligands H$_2$O and SO$_4^{2−}$ are represented by edges of the underlying net. The topological type of the underlying net for the structure in standard representation is seh-4,6-C2/c, which mean a 4,6-coordinated binodal net of the maximal symmetry C2/c (Figure 3b) derived from the seh net according to the procedure described.\(^{19}\) Moreover Cd$^{2+}$ ions and H$_2$O molecules form zigzag-like parallel chains arranged in hexagonal rod packing according to classification.\(^{20}\) The seh-4,6-C2/c net is described by an isohedral natural tiling\(^{21}\) with only one type of tile $[3^2 \cdot 4^2 \cdot 6^4]$ (Figure 4) (each tile represents a cage in the structure). The symbol $[3^2 \cdot 4^2 \cdot 6^4]$ means that the tile consists of two 3-rings, two 4-rings, and four 6-rings. The rings correspond to the channel sections separating the cages (tiles). The transitivity of the tiling is $[2561]$, where 2, 5, 6, and 1 are the numbers of inequivalent vertices, edges, faces (windows of channels) and tiles in the natural tiling, respectively.

Figure 1. Perspective view of 1 (double open cubane core in inset).

Figure 2. Perspective view of the ribbonlike structure of 3.
The topological motif of the arrangement of tiles in the natural tiling is described by the net that arises from dualization of the tiling. The vertices of the dual net coincide with the centers of the tiles, and the edges pass through the faces of the tiles to link the center. Since tiles correspond to cages, the dual net characterizes the system of cages and channels. The dual net in the structure of CdSO₄(H₂O) is 8-coordinated (Figure 5) and has transitivity [1652] (the reverse of 2651).

According to the data from the TTO collection, the isoreticular series with topology seh-4,6-C2/c is presented by 89 inorganic structures. These structures are of three types: monohydrate salts (14 structures), oxo salts (69 structures), and oxy salts (6 structures). All inorganic frameworks of the isoreticular series are composed of six-coordinated metal atoms (Ti, Zr, V, Nb, Ta, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sb), bridging ligand (molecules of water, hydroxide or oxygen ions), and 4-coordinated anion (SO₄²⁻,SeO₄²⁻,PO₄³⁻,AsO₄³⁻,SiO₄⁴⁻,GeO₄⁴⁻,AlO₄³⁻) (Table S2, Supporting Information).

5 and 6 crystallize in orthorhombic Pbcn and monoclinic P2₁/c space group, respectively, with crystallographically imposed inversion center (Table 1, Figures 6–7). Each Cd atom exhibits hexacoordinated environment with distorted octahedral geometry. The four coordination sites are occupied by bridging Cl atoms {Cd(1)–Cl(1) 2.5484(6) Å, Cd(1)–Cl(1′) 2.6656(6) Å, Cd(1)–Cl(2) 2.5352(7) Å, Cd(1)–Cl(2′) 2.7129(7) Å/Cd(1)–Cl(1) 2.6748(9) Å, Cd(1)–Cl(1′) 2.6015(9) Å, Cd(1)–Cl(2) 2.5767(9) Å, Cd(1)–Cl(2′) 2.6444(9) Å}, while the remaining two are occupied by N, O donor atoms of pyridine alcohol {Cd(1)–N(1) 2.294(2) Å, Cd(1)–O(1) 2.411(2) Å/Cd(1)–N(1) 2.331(3) Å, Cd(1)–O(1) 2.432(3) Å}. Cl(1) and Cl(2) form a doubly bridging unit between two successive Cd(1) ions, producing zigzag 1D polymeric chains. In the polymeric chain of the complexes, the hmp-H and hpp-H ligands are present in trans fashion. In 5, hmp-H binds the Cd(II) center via N and O atoms in bidentate manner, creating a five-membered ring around the metal center with a metal bite angle of 70.22° (Table S1, Supporting Information). However, hpp-H is attached to the Cd(II) center through N and O atoms, resulting in a rare seven-membered ring around the Cd(II) center with a metal bite angle of 89.30° (Table S1, Supporting Information). The observed bite angles in 1, 5, and 6 suggest that a successive increase in the number of methylene groups from hmp-H to hpp-H leads to a stepwise increase in the bite angle by approximately 10°.

2, 7, and 8 crystallize in orthorhombic P2₁₂₁₂, Pna21, P₂1₂₁₂₁ space groups, respectively (Table 1, Figures 8–10). Each Cd(II) center exhibits distorted octahedral geometry.
The six coordination sites are bound with five Cl atoms and one O atom, where four are bridging Cl (i.e., Cl(1) and Cl(2)), one is terminal Cl (i.e., Cl(3)), and one is the alcoholic O atom of ligand. Due to unavailability of the N lone pair of protonated pyridine, in complexes 2, 7, and 8 the ligands bind to the metal in monodentate fashion through their alcoholic O atom. Like complexes 5 and 7 here also Cl(1) and Cl(2) form a doubly bridging unit between two successive Cd(1) units, resulting in 1D polymeric chains. The Cd–O bond distances observed in 2, 7, and 8 are 2.376(2) Å, 2.478(5) Å/2.529(4) Å and 2.463(6) Å, respectively. The Cd–O bond distance in 2 is shorter than 7 and 8. In the case of 2, 7, and 8, the O atom of alcoholic (OH) and terminal Cl atom are found to be quite close to each other, which involve in intramolecular H-bonding (see below).

Comparative Structural Motif in 1–8. It is interesting to mention here that when CdCl₂ is treated with hmp-H, hep-H, and hpp-H, the ligand binds to the metal in a bindentate manner via N and O atoms (complexes 1, 5, and 6). However, on treating these complexes with acids, either the binding mode of the ligand changes (monodentate in 2, 7, and 8, on treatment with HCl) or the ligands remain as countercation [hep-H²⁺] (in complex 3 on treatment with HNO₃) or get detached from the metal center (in complex 4, on treatment with H₂SO₄). Besides changes in bonding between pyridine alcohols and cadmium metals, the gradual increase in acid strength also affects a systematic increase in Cd–Cd separations in the acid treated products. The Cd–Cd separations before acid treatment in 1, 5, and 6 are observed to be in the range 3.761(5)–3.992(4) Å, and after treating with HCl the Cd–Cd separations in 2, 7, 8 are found to be in the range 3.750(1)–3.914(1) Å, which shows a slight decrease compared to HNO₃ in 3 where Cd–Cd separations are in the range of 3.796(9)–4.060(2) Å. In the case of the H₂SO₄-treated product 4, the Cd–Cd separation ranges are found to be 4.077(3)–5.547(3) Å larger than others. An increase in Cd–Cd separation is observed by employing stronger acids from HCl to HNO₃ to H₂SO₄.

Supramolecular Expansion. The extended supramolecular interactions were observed in 1–3 and 5–8. The double open cubane tetramer 1 shows strong intermolecular H-bonding involving the alcoholic (OH) and terminal Cl atom of the adjacent tetramer leading to the formation of a H-bonded octamer, which further extended to form a linear 1D polymeric chain. The linear 1D chain is extended via the pyridine H atom and bridging Cl atom forming a hydrogen-bonded 3D network. Two ribbon-shaped 1D polymeric chains of 3 linked via intermolecular H-bonding involve the H atom of uncoordinated hep-H and μ-Cl atoms of neighbor polymeric chains, which further extend yielding a 3D network (Table S3, Figures 11, 13 and S1).

The polymeric chains in 5 and 6 show presence of intermolecular H-bonding involving pyridine H and bridging Cl atoms, however, intramolecular H-bonding also found in 6 involving H atom of alcoholic (OH) of pyridine ring and bridging Cl atom. Each 1D polymeric chain is extended to H-bonding 2D network through the pyridine H atom of one layer and bridging Cl-atom of adjacent layer, further, in complex 6 π–π interactions (3.345 Å) between pyridine rings of two layers generates 2D polymeric network (Table S3, Figures 14, 15, and S3, S4).
The packing diagrams of 1D polymeric chains in 2, 7, and 8 show intramolecular O–H···Cl hydrogen bonding between the alcoholic (OH) and terminal Cl atom of neighboring Cd(II) ion. Each 1D polymeric chain is extended to a hydrogen bonding 2D network through the pyridine H atom of one layer to the terminal and bridging Cl atom of another layer. In 8 the extension of these supramolecular interactions involve π–π stacking (3.371 Å) between two pyridine rings of adjacent two layers. This 2D network is further extended via H-bonding forming a H-bonded 3D network (Table S3, Figures 12, 16, 17, S2 and S5, S6).

**Powder X-ray Diffraction, Thermal Analysis and IR Studies.** Powder X-ray diffraction (PXRD) patterns of 1–2 and 5–8 are consistent with the simulated PXRD pattern generated from single crystal data that imply the structural identity and phase purity of the bulk product (Figure S7, Supporting Information).

In order to check the thermal stability of these complexes, thermogravimetric analysis (TGA) was performed (Figure S8, Supporting Information). All these complexes are stable until 210 °C with two steps decomposition. However, the stability of complex 6 is increased by 50 °C with three-step decomposition. The order of thermal stability in 1, 2, 5–8 is hmp-H > hep-H > hpp-H with the final end set temperature ≈ 650 °C. 1, 2, 5–8 showed ~99% weight loss, while 6 and 8 showed ~87% weight loss. The IR spectra of 1, 2, and 5–8 show one new strong intensity vibration in the region 762–783 cm⁻¹ due to the formation of the Cd–O bond. The ν(\text{C=\text{N}}) absorptions of pyridine appeared in the region 1603–1625 cm⁻¹.

**CONCLUSION**

The present study demonstrates the effect of three different acids (HCl, HNO₃, and H₂SO₄) on coordination behavior of
discrete double open cubane tetramer and 1D chain formed by the complexation of pyridine alcohols with CdCl₂. The three acids having different conjugate bases affect the intra- and intermolecular interactions of Cd(II) complexes in different ways and lead to their transformation into diverse 1D polymeric chains and 3D networks. In the case of HCl, transformation involves protonation of the pyridine nitrogen of the pyridine alcohol ligand causing a bidentate to monodentate change in its coordination mode, which is subsequently followed by addition of a Cl⁻ to the vacant coordination site on Cd(II). With HNO₃.
and H\textsubscript{2}SO\textsubscript{4} protonation of the pyridine nitrogen is accompanied by detachment of the hep-H ligand from Cd(II) in the case of HNO\textsubscript{3}, whereas in the case of H\textsubscript{2}SO\textsubscript{4}, complete removal of hep-H and all Cl\textsuperscript{-} ligands and binding of SO\textsubscript{4}\textsuperscript{2-} were observed.

\section*{EXPERIMENTAL DETAILS}

\textbf{Materials.} The commercially available starting materials, CdCl\textsubscript{2}, 2-(2-hydroxyethyl)pyridine (hep-H), 2-(2-hydroxymethyl)pyridine (hmp-H), 2-(2-(2-hydroxypropyl)pyridine (hpp-H), and reagent grade methanol were used as received.

\textbf{Physical Measurements.} IR spectra [4000−400 cm\textsuperscript{-1}] were recorded with a Bio-Rad FTS 3000MX instrument on KBr pellets. Thermogravimetric analyses were performed on Metler Toledo thermal analysis system. The measurements were done at a heating rate of 10 °C/min from 25 to 900 °C under flowing nitrogen environment. Elemental analyses were carried out with a Flash 2000 elemental analyzer.

\textbf{Powder X-ray diffraction.} For complexes were recorded on a Rigaku Smart Lab X-ray diffractometer using monochromated Cu K-alpha radiation (0.154 nm).

\textbf{X-ray Crystallography.} Single crystal X-ray structural studies of 1−8 were performed on a CCD Agilent technology supernova diffractometer equipped with a low-temperature attachment. Data were collected at 150(2) K using graphite-monochromated Mo K\textalpha\ (\lambda = 0.71073 Å) and Cu K\textalpha\ (\lambda = 1.54814 Å). The strategy for the data collection was evaluated by using the CrystAlisPro CCD software. The data were collected by the standard phi-omega scan techniques.

Figure 13. (a) Hydrogen bonded 2D network of 3 through tilted b axis. (b) Packing diagram showing uncoordinated hep-H\textsubscript{2} trapped between two ribbon-shaped 1D polymeric chains in 3 forming a 3D network along the a axis.
and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on $F^2$. The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally $1.2 \times U_{eq}$ of their parent atoms. All the H-bonding interactions, mean plane analysis, and molecular drawings were obtained using the program Diamond (version 3.1d). In 5 the disordered solvent molecule was observed, which was omitted by applying SQUEEZE option from Platon. In the case of 3 after many attempts the H atom of uncoordinated (OH) of hep-H and coordinated water molecule could not be located. The crystal and refinement data are summarized in Table 1, and selected bond distances and bond angles are shown in Table S1.

Figure 14. H-bonded 3D-network of 5 along the c axis.

Figure 15. Intermolecular H-bonding and $\pi-\pi$ interactions 3.345 Å between pyridine rings of two layers forming 2D polymeric network of 6 tilted along the b axis (A represents centroid of the pyridine ring).
Synthesis of $[\text{Cd}_2(\mu^-\text{Cl})_2(\mu^3-\text{Cl})_2\text{hep-H}_2\text{Cl}]_2$ (1). A solution of hep-H (0.123 g, 1 mmol) in methanol (5 mL) was added to a solution of CdCl$_2$ (0.201 g, 1 mmol) in methanol (40 mL), and the resultant solution was stirred magnetically for 10 h at 298 K. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was then allowed to stand at 298 K for crystallization. On slow evaporation of the solvent, colorless single crystals of 1 were obtained after 10 d. Anal. Calcd: C$_{28}$H$_{36}$Cd$_4$Cl$_8$N$_4$O$_4$, (Mw = 1225.89): C 27.45, H 2.63, N 4.57. Found: C 27.77, H 2.96, N 4.69. IR (KBr, cm$^{-1}$): $\nu_{\text{C=N}}$ 1603 cm$^{-1}$ $\nu_{\text{Cd-O}}$ 783 cm$^{-1}$, $\nu_{\text{Cd-N}}$ 641 cm$^{-1}$.

Synthesis of $[\text{Cd} (\mu^-\text{Cl})_2\text{Cl} (\text{hep-H}_2)]_n$ (2). Compound 1 (0.1225 g, 0.1 mmol) was dissolved in 1 M solution of HCl in methanol (20 mL) and stirred magnetically for 3 h at 298 K. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was then allowed to stand at 298 K for crystallization. On slow evaporation of the solvent, colorless single crystals of 2 were obtained after two months. Anal. Calcd: C$_7$H$_{10}$CdCl$_3$NO·HCl, (Mw = 379.39): C 22.16, H 2.92, N 3.69.

Figure 16. Intermolecular H-bonded 3D network in 7 through the b axis.

Figure 17. Intermolecular H-bonding and $\pi-\pi$ interactions 3.371 Å forming a 3D network of 8 along the a axis (A represents centroid of the pyridine ring).
Synthesis of $[\text{Cd(Cl)}_3\{\text{H}_2\text{O}\}]_{2}\{\text{hmp-H}\}$ (3). Compound 1 (0.1225 g, 0.1 mmol) was dissolved in 1 M solution of HNO$_3$ in methanol (20 mL) and stirred magnetically for 3 h at 298 K. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was then allowed to stand at 298 K for crystallization. On slow evaporation of the solvent, very low yield colorless single crystals of 3 were obtained after ~30 days. Anal. Calcld: C$_{29}$H$_{12}$Cd$_3$Cl$_6$N$_2$O$_2$ (Mw = 1283.69): C 32.08, H 1.26, N 4.15. Found: C 32.06, H 1.22, N 4.16. IR (KBr, cm$^{-1}$): $\nu$ = 1640 cm$^{-1}$ $\nu$(Cd-O) 763 cm$^{-1}$ $\nu$(Cd-N) 646 cm$^{-1}$.

Synthesis of $[\text{Cd}([\mu_2-\text{Cl}]_2\{\text{hmp-H}\})]_n$ (5). A solution of hmp-H (0.137 g, 1 mmol) was added to a solution of CdCl$_3$ (0.0584 g, 0.1 mmol) which was then passed through the filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was then allowed to stand at 298 K for crystallization. On slow evaporation of the solvent, colorless single crystals of 5 were obtained after 10 days. Anal. Calcld: C$_{32}$H$_{32}$Cd$_4$Cl$_{10}$N$_2$O$_4$ (Mw = 320.48): C 29.64, H 3.43, N 4.28. Found: C 29.64, H 3.45, N 4.36. IR (KBr, cm$^{-1}$): $\nu$(Cd-O) 762 cm$^{-1}$ $\nu$(Cd-N) 658 cm$^{-1}$.

Synthesis of $[\text{Cd}([\mu_2-\text{Cl}]_2\{\text{hmp-H}\})_2]_n$ (7). Compound 5 (0.0584 g, 0.1 mmol) was dissolved in 1 M solution of HCl in methanol (20 mL) and stirred magnetically for 3 h at 298 K. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was then allowed to stand at 298 K for crystallization. On slow evaporation of the solvent, colorless single crystals of 7 were obtained after 2 months. Anal. Calcld: C$_{40}$H$_{24}$Cd$_4$Cl$_{12}$N$_2$O$_4$ (Mw = 657.77): C 21.84, H 2.75, N 4.25. Found: C 21.06, H 2.28, N 4.01. IR (KBr, cm$^{-1}$): $\nu$(Cd-O) 1609 cm$^{-1}$ $\nu$(Cd-O) 1673 cm$^{-1}$ $\nu$(Cd-O) 647 cm$^{-1}$.

Synthesis of $[\text{Cd}([\mu_2-\text{Cl}]_2\{\text{hmp-H}\})_2]_n$ (6). A solution of hmp-H (0.137 g, 1 mmol) was added to a solution of CdCl$_3$ (0.201 g, 1 mmol) in methanol (40 mL), and the resultant solution was stirred magnetically for 10 h at 298 K. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was then allowed to stand at 298 K for crystallization. On slow evaporation of the solvent, very low yield colorless single crystals of 6 were obtained after 10 days. Anal. Calcld: C$_{18}$H$_{16}$Cd$_2$Cl$_6$N$_2$O$_2$ (Mw = 369.64): C 26.92, H 3.39, N 3.92. Found: C 27.13, H 3.36, N 3.91. IR (KBr, cm$^{-1}$): $\nu$(Cd-O) 1624 cm$^{-1}$ $\nu$(Cd-O) 781 cm$^{-1}$.

ASSOCIATED CONTENT

Supporting Information
Crystallographic data, including selected bond length and angles, CIF files, PXRD, and TGA of complexes 1–8 and some figures. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic information files (CIF) of the compounds were deposited with the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition numbers 1002558–1002565.

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