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Formation of Two 1D Polymeric Water Morphologies

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Two complexes with double- or triple-stranded chain structures, $\{[Cd(pg)(phen)]\cdot 3H_2O\}_n$ (**1**) and $\{[Cd_3(cpg)_3(phen)_2]\cdot 3H_2O\}_n$ (**2**), have been hydrothermally synthesized [H_2pg = 3-phenylglutaric acid, H_2cpg = 3-(4-chlorophenyl)glutaric acid, phen = 1,10-phenanthroline]. In the crystal lattices of **1** and **2**, two 1D polymeric water morphologies are observed (a treelike chain for **1** and a staircaselike tape for **2**), both of which contain $(H_2O)_6$ subunits. The geometrical parameters of water chains and tapes are similar to those in ice, I_h, and liquid water, respectively.

Introduction

The fundamental importance of water in physical, biological, and chemical processes has prompted intensive research efforts, however, some properties of water still remain "anomalous".[1–4] The structural information of discrete water clusters is the first step to understanding the behavior of water.[5] In recent years, extensive structural studies on discrete water clusters have significantly advanced our preliminary comprehension of water.[6] A comparison between the physical properties of discrete water clusters and polymeric clusters, which structurally lie between small water clusters and bulk water/ice, shows that the properties of polymeric clusters are more closely associated with those of bulk water. Thus, studies involving polymeric water clusters are a further step towards understanding water. With the development of polymeric water clusters, three morphologies of polymeric water clusters[7] including infinite 1D-chain,[8] tape,[9] and 2D-layer[10] structures, have been observed. Among the three morphologies, 1D water chains and tapes are of great interest since many fundamental biological processes[11] and properties of materials[12] appear to depend on the unique properties of 1D water morphologies. Structural studies have shown that 1D water morphologies exist in gramicidin A membrane channels,[13] bacteriorhodopsin,[14] and α-amylase[15] for the rapid transport of protons and act as "proton wires". Thus, it is essential that 1D water morphologies can be rationally and predictably designed. However, most water clusters are obtained occasionally, and the rational design of such water morphologies still remains a challenge.

The lattices of crystal hosts offer environments for stabilizing various topologies of water clusters, which play important roles in the formation of different water morphologies. To obtain 1D water morphologies, it is necessary to construct suitable host frameworks for water molecules extending into chains or tapes. Without a doubt, a host channel, which can encapsulate the water chains or tapes, generated by organic or inorganic moieties is a good choice.[16] If a host chain can provide hydrogen-bond donors and/or acceptors, it may induce the free water molecules or discrete water clusters to extend with itself, and finally lead to 1D water morphologies. A metal–organic chain may be another good choice. In this paper, we report on two complexes, $[Cd_3(cpg)_3(phen)_2]\cdot 3H_2O$ (**1**) and $[Cd(cpg)(phen)]\cdot 3H_2O$ (**2**) [H_2pg = 3-phenylglutaric acid, H_2cpg = 3-(4-chlorophenyl) glutaric acid, phen = 1,10-phenanthroline], which both have 1D host frameworks and result in 1D water chains and tapes, respectively.

Results and Discussion

Carboxyl groups can provide hydrogen-bond donors and/or acceptors, so we have chosen two similar benzoic carboxylates (H_2pg and H_2cpg) as organic ligands to construct the host frameworks. In order to obtain 1D metal–organic chains, we selected 1,10-phen as a secondary ligand. The induction of the terminal ligand can prevent the chain from extending to intricate 2D and 3D architectures.

Crystal Structure of $\{[Cd(pg)(1,10\text{-}Phen)]\cdot 3H_2O\}_n$ (1)

Single-crystal X-ray analysis reveals that **1** is a 1D double-stranded chain. As shown in Figure 1, each central cadmium ion is coordinated by two oxygen atoms from two monatomic bridging carboxylate groups (Scheme 1a), two

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oxygen atoms from one chelating carboxylate group (Scheme 1b) and two nitrogen atoms from one 1,10-phen molecule. Two pg^{2-} ligands link two cadmium ions forming a metal–organic ring, and these are bridged into a double-stranded chain through the monatomic bridging carboxylate groups (Figure 2).

In the crystal lattice of **1**, three crystallographically independent water molecules (O1w, O2w, and O3w) are observed, which are associated by hydrogen bonds to form a water trimer. The water trimer is hydrogen bonded to its equivalent, derived by the crystallographic 2_1 axis along the [010] direction, forming a $(H_2O)_6$ unit. The geometric parameters of the hexamers are summarized in Table 1. The 2_1 axis in symmetry operations of generating $(H_2O)_6$ clusters leads to a water hexamer with an opening structure. Such an open structure is different from any hexamer conformation revealed by theoretical calculations (ring, book, bag, cage, and prism).[19,20,6a] With O1w and equivalent molecules dangling at two sides, the hexamers are self-assembled into treelike chains along the [010] direction (Figure 3). The average O···O distance of 2.796 Å is very close to the corresponding value of 2.759 Å in ice, I_h, at –90 °C.[1] However, there is a wide variation in the O–O–O angles with an average of 131.2°, which deviates considerably from the corresponding value found in ice, I_h. The water chains link adjacent double-stranded metal–organic chains into a 2D network through the O1w–H···O6 and O3w–H···O4 hydrogen bonds. Neighbor layers are extended into a three-dimensional architecture through π–π interactions (3.367 Å) between two phenanthroline rings of the 1,10-phen ligand.

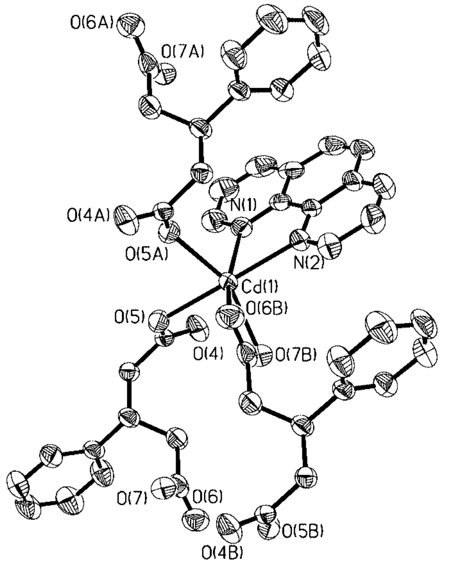
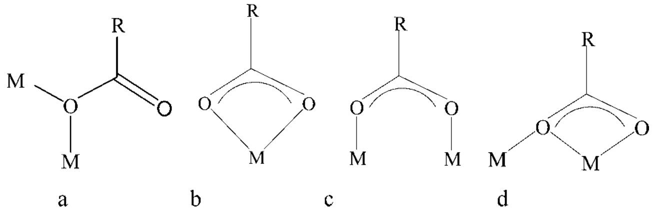


Figure 1. The coordination environment of cadmium ions in **1** with the thermal ellipsoids at the 50% probability level (all H atoms were omitted for clarity). Symmetry codes: #A: –*x* + 1, –*y* + 1, –*z*; #B: –*x* + 1, –*y* + 2, –*z*.



Scheme 1. The coordination modes assumed by the carboxylate ligands.

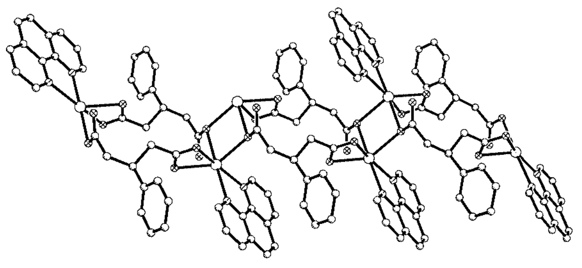


Figure 2. The double-stranded host chain of **1**.

Table 1. Hydrogen-bonding parameters ([Å] and [°]) for{$[Cd(pg)(phen)]\cdot 3H_2O\}_n$ (**1**) and $\{[Cd_3(cpg)_3(phen)_2]\cdot 3H_2O\}_n$ (**2**).[a]

O–H···O	O–H	O···O	H···O	O–H···O
1				
O6–H(6WA)···O7$^{\#1}$	0.96(5)	2.763(6)	1.87(6)	154.7(7)
O7–H(7WB)···O1$^{\#2}$	1.02(8)	2.816(4)	1.80(8)	174.8(2)
O6–H(6WB)···O7	1.01(2)	2.857(8)	2.19(9)	122.0(5)
O5–H(5WA)···O3$^{\#2}$	0.92(5)	2.728(4)	1.82(5)	172.1(5)
O5–H(5WB)···O6	1.21(3)	2.769(6)	1.99(3)	117.9(3)
2				
O(1)–H(1WA)···O3$^{\#3}$	0.74(9)	2.765(1)	2.08(1)	153(1)
O(1)–H(1WB) ···O2	0.75(9)	2.812(2)	2.10(1)	161(1)
O(2)–H(2WB)···O4	0.67(9)	2.853(1)	2.18(9)	175(1)
O(2)–H(2WA)···O3	0.79(9)	2.997(2)	2.23(9)	165(1)
O(3)–H(3WB)··· O6$^{\#4}$	0.80(9)	2.755(1)	1.96(9)	175(9)
O(3)–H(3WA)···O1$^{\#5}$	1.07(9)	2.875(2)	1.84(9)	164(7)

[a] Symmetry codes: #1: – *x*, *y* + 1/2, –*z* + 1/2; #2: –*x* + 1, *y* – 1/2, –*z* + 1/2; #3: –*x* + 1, –*y*, –*z* + 2; #4: *x* + 1, *y*, *z*; #5: *x* + 1, *y*, *z*.

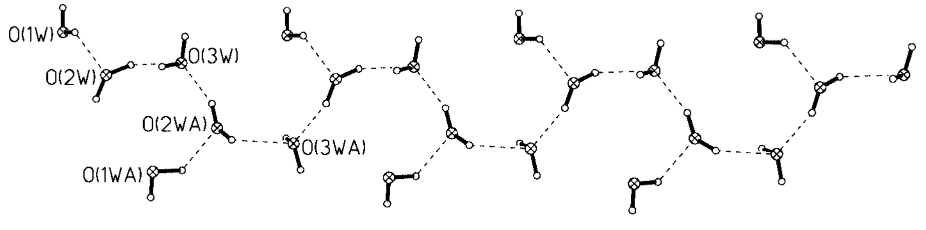


Figure 3. The 1D treelike water chain with dangling molecules in **1**.

Crystal Structure of {[Cd_3(cpg)$_3$(1,10-Phen)$_2$]·$3H_2O$}$_n$ (2)

In the asymmetric unit of **2**, there are three crystallographically independent Cd^{II} ions, three cpg$^{2–}$ ligands, two 1,10-phen ligands, and three water molecules, as revealed by X-ray crystallography. The coordination environments around the three Cd^{II} ions are different, however, they all exhibit an octahedral-coordination geometry (Figure 4). Cd(1) is coordinated by two nitrogen atoms from one 1,10-phen ligand, one oxygen atom from one *syn,syn*-$\eta^1:\eta^1:\mu_2$ bridging carboxylate group (Scheme 1c), one oxygen atom from one monatomic bridging carboxylate group (Scheme 1a), and two oxygen atoms from one chelate bridging carboxylate group (Scheme 1d). Cd(2) is coordinated by two nitrogen atoms from one 1,10-phen ligand, two oxygen atoms from two *syn,syn*-$\eta^1:\eta^1:\mu_2$ bridging carboxylate groups (Scheme 1c), and two oxygen atoms from one chelate bridging carboxylate group (Scheme 1d). Cd(3) is coordinated by three oxygen atoms from three *syn,syn*-$\eta^1:\eta^1:\mu_2$ bridging carboxylate groups (Scheme 1c), two oxygen atoms from one chelate bridging carboxylate group (Scheme 1d), and one oxygen atom from one monatomic bridging carboxylate group (Scheme 1a). As a result of the coordination diversity of carboxylate groups, three Cd^{II} ions are connected to form a trinuclear cluster. As a basic building unit, the trinuclear clusters are fused to an infinite triple-stranded chain bridged by the carboxylate groups of the cpg$^{2–}$ ligands. To accommodate the role of the bridging trinuclear clusters, the alkyl chain of the cpg$^{2–}$ ligands rotates from the most stable *anti* form to the gauche form, which is higher in energy. The rotation of the flexible cpg$^{2–}$ ligand allows each strand to twist in order to form a helical chain. By sharing cadmium ions, the three strands are attached to produce a novel triple-stranded helical chain (Figure 5). In the case of the infinite double and higher order helices there are two kinds of possibilities: (i) The strands of the helix are independent infinite chains held together by noncovalent forces, analogous to the situation in DNA;[21] and (ii) The strands are not independent, but are attached through coordinative bonds to a column of metal atoms, which form the axis of the helix. To the best of our knowledge, complex **1** is the first infinite triple-stranded helical chain of type (ii).

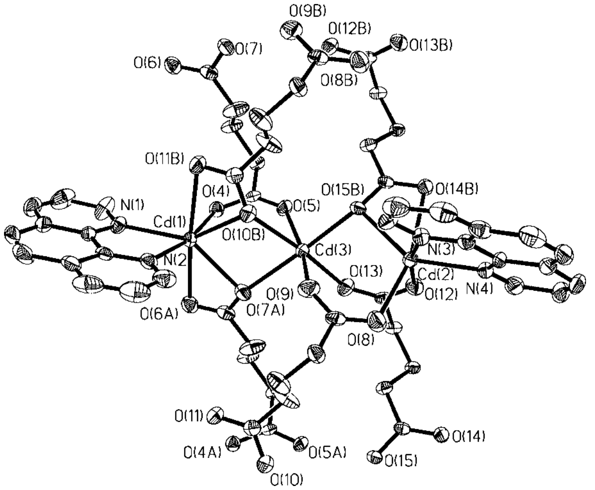


Figure 4. The coordination environment of cadmium ions in **2** with the thermal ellipsoids at the 30% probability level (all hydrogen atoms and the chlorophenyl groups of the cpg$^{2–}$ ligand were omitted for clarity). Symmetry codes: #A: $x + 1, y, z$; #B: $x – 1, y, z$.

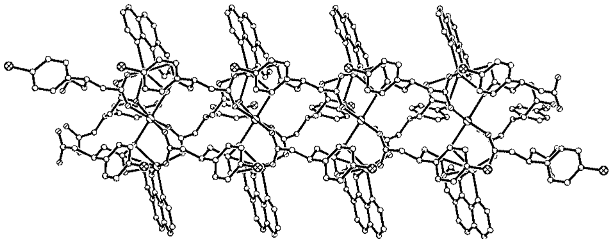


Figure 5. The triple-stranded host chain of **2**.

Similar to **1**, there are three crystallographically independent free water molecules in the crystal lattice of complex **2**. These three water molecules and their equivalents, generated by a crystallographic inversion center, are associated by O–H···O hydrogen bonds in a cyclic centrosymmetric hexamer. The mean deviation of the three atoms from the plane is 0.0088 Å, which shows that these atoms are almost located on the same plane and the hexamer ring exists as a planar conformation. The geometric parameters of the hexamers are summarized in Table 1. The average O···O distance of 2.858 Å is longer than the value of 2.759 Å in ice, I_h,[1] but very similar to the O···O distance of 2.85 Å in liquid water.[22] The average value of the O–O–O angles is 119.3°, which deviates considerably from the corresponding value found in liquid water. The hexamers are self-assembled by O3w–H···O1w hydrogen bonds into extended water tapes along the [100] direction, consisting of fused four- and six-membered water rings (Figure 6). The dihedral angle between four- and six-membered rings is 44.1°, which makes the water tape "staircase"-like. The interhexamer O1···O3B distance of 2.892 Å is also close to the corresponding O···O distance in liquid water. Additional O2w–H···O4 and O3w–H···O6 hydrogen bonds anchor the water tapes to two adjacent metal–organic chains, resulting in triple helical chain pairs. The triple chain pairs are extended

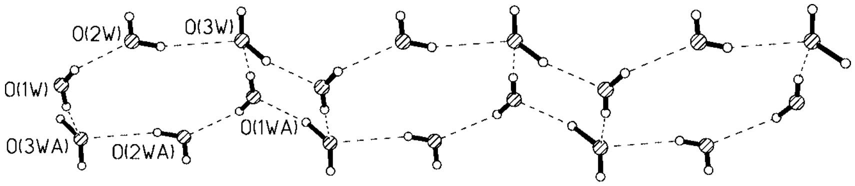


Figure 6. The staircaselike water tape in **2**.

into a three-dimensional architecture through π–π interactions (3.779 Å) between two phenanthroline rings of 1,10-phen ligands from neighboring chains.

Thermal Analysis and X-ray Powder Diffraction

Samples of **1** and **2** were examined by TGA, which show similar TGA curves (Figure 7). TGA analyses of **1** show a 4.11% weight loss from 63 to 108 °C, which corresponds to 1.26 of the 3 free water molecules. The remaining water molecules are eventually lost at 345 °C. For **2**, the weight loss of 1.92% from 61 to 91 °C is equivalent to the loss of 1.57 of the three free water molecules. The remaining water molecules are lost slowly until a temperature of 268 °C is reached. After all the free water molecules were released from the structure the metal–organic host chains started to decompose. To confirm the TGA, the original samples and dehydrated samples of **1** and **2** were characterized by X-ray Powder diffraction (XRPD) at room temperature (Figure 8 and Figure 9). The patterns that were simulated from the single-crystal X-ray data of **1** and **2** were in good agreement with those that were observed. However, after water molecules were lost as a result of heat, total changes in the pattern were observed, suggesting decomposition of the metal–organic framework. This is expected, as the water chain or tape acts as a "glue" to assemble the overall structure.

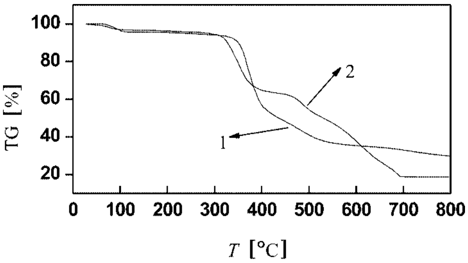


Figure 7. TGA curves for **1** and **2**.

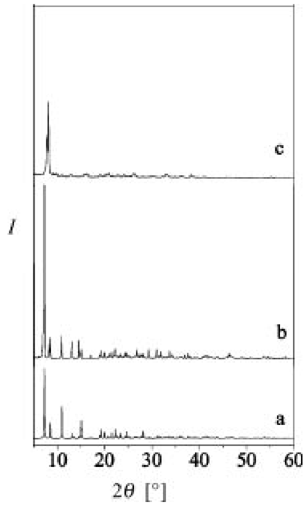


Figure 8. XRPD patterns for **1**: (a) calculated from single-crystal X-ray data; (b) taken at room temperature; (c) after heating at 350 °C for 2 h.

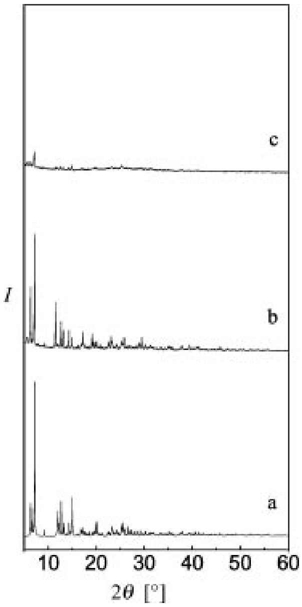


Figure 9. XRPD patterns for **2**: (a) calculated from single-crystal X-ray data; (b) taken at room temperature; (c) after heating at 300 °C for 2 h.

Vibrational Spectra

The FT-IR spectroscopy of **1** shows strong bands at 1574 and 1428 cm^{-1} due to the $\upsilon_{\mathrm{asym}}(\mathrm{CO_2})$ and $\upsilon_{\mathrm{sym}}(\mathrm{CO_2})$ stretching vibrations, respectively. For **2**, the $\upsilon_{\mathrm{asym}}(\mathrm{CO_2})$ and $\upsilon_{\mathrm{sym}}(\mathrm{CO_2})$ stretching vibrations appear at 1585 cm^{-1} and 1402 cm^{-1}, respectively. The spectra of **1** and **2** exhibit broad bands centered around 3375 and 3406 cm^{-1}, respectively. The O–H stretching vibration for the quasiplanar water hexamer appears[23] as a broad band centered around 3400 cm^{-1}; the O–H stretching vibration for the same cluster in a helium droplet appears at 3325 cm^{-1}.[6b] In comparison, this vibration of the planar hexamers in the ice I and II phases occurs at 3220 cm^{-1}.[1] After removing the water from the crystal lattices of **1** and **2** by heating, the bands centered around 3375 and 3406 cm^{-1} disappear. Therefore, in the case of **1** and **2**, these bands are attributable to the O–H stretching frequency of the $(\mathrm{H_2O})_6$ core structure. The difference in the stretching vibration may arise from their different conformations and environments. Deliberate exposure to water vapor for 3 d does not lead to reabsorption of water into the lattice as monitored by FTIR spectroscopy.

Conclusions

In conclusion, two complexes with metal–organic host chains have been synthesized successfully, in which two 1D water morphologies are observed. When the host chains change from double stranded to triple stranded, the water morphologies are observed as treelike chains and staircaselike tapes, respectively, which contain $(\mathrm{H_2O})_6$ subunits with different conformations. The water morphologies act as building blocks extending the host frameworks into a higher dimensionality. In this sense, the water chains and tapes are different from other 1D water morphologies encapsulated in the host channels generated by organic or inorganic moieties. We propose that the metal–organic chain, with selected hydrophilic groups, may be a good host framework to induce the formation of 1D water morphologies. This discovery may be helpful in the rational design of 1D water morphologies.

Experimental Section

General Methods: All chemicals were obtained commercially and used without further purification. Elemental analyses were carried out with an Elementar Vario EL III analyzer. Infrared (IR) spectra were recorded with a PerkinElmer Spectrum One as KBr pellets in the range 4000–400 cm^{-1}. Thermogravimetric analyses were carried out with a NETZSCH STA 449C unit at a heating rate of 10 °C min^{-1} under nitrogen. X-ray Powder diffraction measurements were recorded with a RIGAKU DMAX2500PC diffractometer using Cu-K_{α} radiation.

Preparation of Complexes

{[Cd(pg)(1,10-Phen)]·3H$_2$O}$_n$ (1): A mixture of H$_2$pg (0.021 g, 0.1 mmol), 1,10-phen (0.020 g, 0.1 mmol), and Cd(NO$_3$)$_2$·4H$_2$O (0.031 g, 0.1 mmol) in distilled water (15 mL) was sealed in a Teflon-lined Stainless autoclave and heated at 165 °C for 3 d under autogenous pressure and then cooled to room temperature for 2 d. Colorless crystals (26 mg) were isolated in 47% yield and washed with distilled water. $C_{23}H_{24}N_2O_7Cd$ (552.84): calcd. C 49.81, H 4.37, N 5.05; found C 49.80, H 4.38, N 5.06. IR (KBr): ṽ = 3375 (m), 3063 (w), 1574 (vs), 1515 (s), 1428 (vs), 1251 (w), 1103(w), 973(w), 864 (s), 854 (vs), 775 (m), 729 (s) cm^{-1}.

{[Cd$_3$(cpg)$_3$(1,10-Phen)$_2$]·3H$_2$O}$_n$ (2): A mixture of H$_2$cpg (0.024 g, 0.1 mmol), 1,10-phen (0.020 g, 0.1 mmol), and Cd(NO$_3$)$_2$·4H$_2$O (0.031 g, 0.1 mmol) in distilled water (15 mL) was sealed in a Teflon-lined Stainless autoclave and heated at 165 °C for 3 d under autogenous pressure and then cooled to room temperature for 2 d. Yellow prism-like crystals (47 mg) suitable for X-ray analysis were isolated in 32% yield and washed with distilled water. $C_{57}H_{49}N_4O_{15}Cl_3Cd_3$ (1473.55): calcd. C 46.46, H 3.35, N 3.80; found C 46.48, H 3.34, N 3.81. IR (KBr): ṽ = 3406 (m), 1581 (vs), 1518 (m), 1493 (m), 1402 (s), 1281 (w), 1092 (w), 1014 (w), 976 (w), 866 (m), 831 (m), 729 (s) cm^{-1}.

Table 2. Selected bond lengths [Å] and angles [°] for {[Cd(pg)(phen)]·3H$_2$O}$_n$ (**1**)[a] and {[Cd$_3$(cpg)$_3$(phen)$_2$]·3H$_2$O}$_n$ (**2**).[a]

1			
Cd(1)–N(1)	2.299(2)	Cd(1)–O(7)$^{\#1}$	2.310(2)
Cd(1)–N(2)	2.385(2)	Cd(1)–O(5)$^{\#2}$	2.3294(19)
Cd(1)–O(5)	2.3035(19)	Cd(1)–O(6)$^{\#1}$	2.438(2)
O(7)$^{\#1}$–Cd(1)–O(6)$^{\#1}$	54.94(8)	N(1)–Cd(1)–O(7)$^{\#1}$	136.06(8)
N(1)–Cd(1)–O(5)$^{\#2}$	88.86(8)	O(5)–Cd(1)–N(2)	174.75(7)
O(5)$^{\#2}$–Cd(1)–O(6)$^{\#1}$	83.32(8)		
2			
Cd(1)–N(1)	2.316(7)	Cd(2)–N(3)	2.363(8)
Cd(1)–N(2)	2.331(7)	Cd(2)–N(4)	2.301(7)
Cd(1)–O(4)	2.264(6)	Cd(2)–O(14)$^{\#4}$	2.454(6)
Cd(1)–O(6)$^{\#3}$	2.513(6)	Cd(3)–O(5)	2.286(6)
Cd(1)–O(7)$^{\#3}$	2.351(7)	Cd(3)–O(7)$^{\#3}$	2.309(6)
Cd(2)–O(8)	2.247(7)	Cd(3)–O(9)	2.281(7)
Cd(1)–O(10)$^{\#4}$	2.368(7)	Cd(3)–O(10)$^{\#4}$	2.280(7)
Cd(1)–O(11)$^{\#4}$	2.609(8)	Cd(3)–O(13)	2.228(6)
Cd(2)–O(12)	2.220(6)	Cd(3)–O(15)$^{\#4}$	2.265(5)
Cd(2)–O(15)$^{\#4}$	2.296(6)		

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, -y + 2, -z$; #2: $-x + 1, -y + 1, -z$; #3: $x + 1, y, -z$; #4: $x - 1, y, z$.

Table 3. Crystallographic data for {[Cd(pg)(phen)]·3H$_2$O}$_n$ (**1**) and {[Cd$_3$(cpg)$_3$(phen)$_2$]·3H$_2$O}$_n$ (**2**).

	1	**2**
Empirical formula	$C_{23}H_{24}N_2O_7Cd$	$C_{57}H_{49}N_4O_{15}Cl_3Cd_3$
Formula mass [g mol^{-1}]	552.84	1473.55
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a [Å]	11.1744(6)	7.674(3)
b [Å]	8.5230(5)	27.815(9)
c [Å]	26.1459(14)	26.611(9)
α [°]	90	90
β [°]	111.879(3)	94.640(7)
γ [°]	90	90
V [Å^3]	2310.8(2)	5661(3)
Z	4	4
$\rho_{\text{calcd.}}$ [mg m^{-3}]	1.589	1.729
μ (Mo-K_{α}) [mm^{-1}]	0.991	1.330
No. of data collected	17114	35940
No. of unique data (all)	5296 [R(int) = 0.0195]	9979 [R(int) = 0.0663]
No. of obsd. data [$F > 2(\sigma F)$]	4912	8329
Parameters	304	763
R_1,[a] wR_2[b] [$I > 2\sigma(I)$]	0.0327, 0.0873	0.0777, 0.1719
R_1,[a] wR_2[b] (all data)	0.0362, 0.0902	0.0972, 0.1823
GOF	1.005	1.162

[a] $R = \Sigma\|F_o\| - \|F_c\| / \Sigma\|F_o\|$. [b] $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0530P)^2 + 1.6272P]$, where $P = (F_o^2 + 2F_c^2)/3$ for **1**. $w = 1/[\sigma^2(F_o^2) + (0.0550P)^2 + 18.1927P]$, where $P = (F_o^2 + 2F_c^2)/3$ for **2**.

X-ray Crystallography

X-ray diffraction data were collected with a Rigaku diffractometer with a Mercury CCD area detector (Mo-K_α; λ = 0.71073 Å) for **1** and **2** at 173(2) K. Empirical absorption corrections were applied to the data using the CrystalClear program.[17] The structures were solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXTL-97 program.[18] The hydrogen atoms on the organic ligands were generated by the riding mode (C–H = 0.95 Å), and hydrogen atoms on water molecules were located from difference maps. Bond lengths and bond angles are listed in Table 2. Crystallographic data and other pertinent information for **1** and **2** are summarized in Table 3.

CCDC-289131 and CCDC-281815 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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