Inorganic Chemistry

ARTICLE

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Family of Cadmium Acetate Coordination Networks With Structurally Diverse $[Cd_4(OAc)_9(\mu_3\text{-}OH)]^{2-}$ Secondary Building Units

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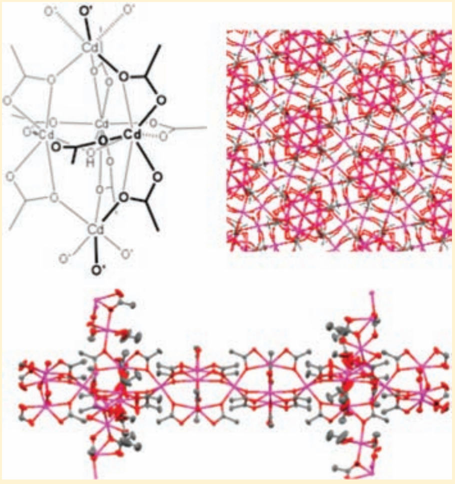
Supporting Information

ABSTRACT: By subtly varying crystallization conditions, four distinct cadmium acetate coordination networks with unit cell formulas $Cd_{87}(H_2O)_{36}(EtOH)_{18}(OH)_{12}(CH_3CO_2)_{162}$ (**1**), $Cd_{87}(H_2O)_{72}(OH)_{12}(CH_3CO_2)_{162}$ (**2**), $Cd_{10}(H_2O)_6(OH)_2(CH_3CO_2)_{18}$ (**3**), and $Cd_{20}(H_2O)_{20}(OH)_4(CH_3CO_2)_{36}$ (**4**) have been isolated. The coordination networks exhibit interesting structural diversity and have been investigated by powder X-ray diffraction, elemental analysis, thermal gravimetric analysis, infrared spectroscopy, and single-crystal X-ray diffraction. All four complexes are composed of secondary building units with the general formula $[Cd_4(OAc)_9(\mu_3\text{-}OH)]^{2-}$. Complexes **1** and **2** exhibit a remarkable three-dimensional network composed of aligned columns, each 4.5 nm long, containing three different cadmium acetate clusters. Complexes **3** and **4** extend in two-dimensions with each unit cell repeating a different linkage isomer of the $[Cd_4(OAc)_9(\mu_3\text{-}OH)]^{2-}$ cluster.



INTRODUCTION

Metal acetate complexes are of great interest for studies of supramolecular chemistry,[1] as precursors for metal-organic chemical vapor deposition,[2] and for developing molecular magnetic materials.[3] Zinc carboxylate clusters, in particular, are important structural components of metal−organic frameworks (MOFs),[4] which have vast potential for applications including catalysis,[5] sensing,[6] gas storage,[7] and separation.[8] Much of the progress in this field has been guided by the coordination chemistry of Zn^{2+} forming so-called secondary building units (SBUs) in a predictable way.[9]

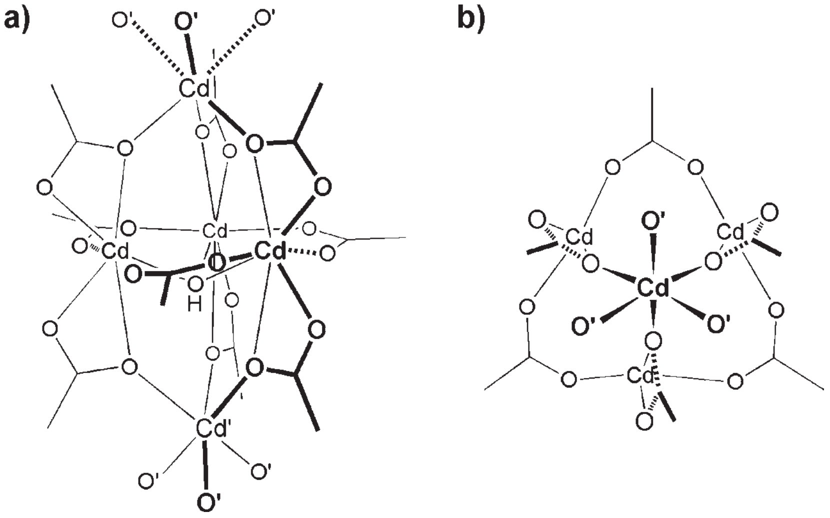
On the other hand, the structures of Cd^{2+} in the solid-state are generally unpredictable. Cadmium(II) has been reported in tetrahedral, trigonal bipyramidal, octahedral, distorted pentagonal bipyramidal, and distorted dodecahedral coordination geometries.[10] This structural variation in Cd^{2+} coordination geometry arises from two effects: (i) the large ionic radius of Cd^{2+} allows flexibility in terms of coordination number; and (ii) the d^{10} electronic configuration of Cd^{2+} ions serves to eliminate ligand field effects and thereby permits diverse geometries. Therefore, the coordination modes of cadmium are predominantly influenced by steric interactions. The structural unpredictability of Cd^{2+} may be an impediment to developing a series of structurally related complexes, but it may also enable access to diverse structures unobtainable with Zn^{2+} ions.

Increased interest surrounding Cd^{2+} coordination chemistry has yielded a number of varied and complex structures. For example, it was demonstrated that by replacing zinc with cadmium in the MOF preparations, new cadmium carboxylate-containing MOFs with unique properties can be obtained.[11] Cadmium ions also participate in biological systems,[12] most often as toxins, further increasing the interest surrounding its varied coordination chemistry. Recently, a Cd-containing carbonic anhydrase metalloenzyme that participates in the capture of inorganic carbon for photosynthesis was isolated from the marine diatom *Thalassiosira weissflogii*.[13] This provided an example of the biological role of cadmium ions in the ocean where, as in many marine diatoms, cadmium, cobalt, and zinc are functionally interchangeable because of very low concentrations of many essential trace metals in seawater.[14]

Many metal-acetato structures have been reported in which the ligand is bridging or chelating.[15] It has been demonstrated by Carrell et al., using data from the Cambridge Structural Database, that carboxylates more commonly behave as bidentate chelating ligands when binding to cadmium.[16] Crystals of cadmium(II) carboxylate complexes have been synthesized that exhibit a variety of carboxylate binding modes. In 2005 Baggio et al. synthesized the first monomeric cadmium complex that has two chelating acetato ligands in its coordination sphere in the form of a heptacoordinated cadmium terpyridine complex.[17] Mak et al. reported a polymeric complex with cadmium in four distinct coordination modes.[18]

Received: November 30, 2010
Published: March 10, 2011

Chart 1. (a) Side-on View and (b) Top-down View of the $[Cd_4(OAc)_9(\mu_3\text{-}OH)]^{2-}$ Secondary Building Unit Found in All of the Cadmium Carboxylate Networks[a]



[a] O′ and Cd′ are is not included in the formula. The lower half is omitted for clarity from part b.

Our interest in cadmium carboxylate chemistry first arose from the discovery of novel heptametallic cadmium hydroxo acetate clusters templated inside Schiff base macrocycles.[19,20] During our synthetic investigations, we unintentionally isolated and crystallographically characterized a new and unusual cadmium acetate cluster network, thus prompting this investigation. We have discovered two new coordination polymers based on cadmium hydroxy-acetate clusters with the unit cell formulas $Cd_{87}(H_2O)_{36}(EtOH)_{18}(OH)_{12}(CH_3CO_2)_{162}$ (complex **1**) and $Cd_{87}(H_2O)_{72}(OH)_{12}(CH_3CO_2)_{162}$ (complex **2**). The structure of both coordination polymers is complex, with cadmium ions existing in seven different environments and two different coordination geometries: octahedral and distorted pentagonal bipyramidal. The three-dimensional structure consists of 4.5 nm long columns each containing 23 cadmium ions within three distinct cadmium clusters supported by acetato ligands. Two of the three distinct cadmium clusters are $[Cd_4(OAc)_9(\mu_3\text{-}OH)]^{2-}$ SBUs which appear to be particularly stable in cadmium acetate compounds. A general representation of these SBUs is found in Chart 1. These clusters are similar to the ones observed in our previous work on cadmium hydroxo acetate clusters templated inside Schiff base macrocycles,[19] but are markedly different from the most common zinc acetate cluster, $Zn_4O(CH_3COO)_6$.[21]

In this paper, we describe the synthesis, characterization, and crystallographic studies of four cadmium acetate-based complexes that have two-dimensional (2-D) and three-dimensional (3-D) structures based upon repeating $[Cd_4(OAc)_9(\mu_3\text{-}OH)]^{2-}$ SBUs. These results, which illustrate the complex and flexible nature of cadmium coordination chemistry and demonstrate that the $[Cd_4(OAc)_9(\mu_3\text{-}OH)]^{2-}$ cluster is a persistent motif in cadmium carboxylate chemistry, are important for the development of cadmium-based MOFs.

■ EXPERIMENTAL SECTION

Cadmium acetate was obtained from Mallinckrodt, cadmium oxide was obtained from Alfa Aesar, and solvents were obtained from common suppliers. All chemicals and solvents were used without further purification. Thermal gravimetric analysis (TGA) data were obtained using a Perkin-Elmer TGA6 instrument. Powder X-ray diffraction (XRD) data were obtained with rotating disk samples using graphite-monochromated Cu−Kα radiation on a Bruker D8 Advance powder X-ray diffractometer. FT-IR spectra were collected neat in the solid state on a Thermo Nicolet 6700 FT-IR spectrometer equipped with a Smart Orbit attenuated total reflectance (ATR) attachment. Elemental analyses (CHN) were performed at the UBC Microanalytical Services Laboratory.

Synthesis of Complex 1. A flask was charged with $Cd(OAc)_2 \cdot 2H_2O$ (6.57 g, 24.7 mmol), CdO (0.234 g, 1.82 mmol), 100 mL of EtOH, and 2.00 mL of water, and the mixture was heated to reflux. After 10 min, a white precipitate formed and, after 30 h, the reaction mixture was removed from the heat and cooled to room temperature. The reaction mixture was filtered, and the colorless filtrate dried under reduced pressure to give a white solid. Yield: 5.67 g (0.02 mmol, 89%). Crystals were grown from a hot, saturated solution of **1** in 1:1 toluene and EtOH.

Data for Complex 1. Anal. Calc'd for complex **1**, $Cd_{87}(H_2O)_{36}(EtOH)_{18}(OH)_{12}(CH_3CO_2)_{162}$: C, 20.56; H, 3.25. Found: C, 20.70; H, 3.08 (formula determined from the crystal structure data). FT-IR: $\bar{\nu}$ = 3288, 1585, 1539, 1408 1339, 1045, 1019, 947, 679. 657, 613, 467, 416 cm^{-1}.

Synthesis of Complexes 2, 3, and 4. Complexes **2**−**4** were synthesized by crystallizing complex **1** (prepared in ethanol) in a 1:1 mixture of toluene and MeOH, 1-butanol or *tert*-butanol, respectively. Complex **3** can also be crystallized in 1-propanol.

Data for Complex 2. Anal. Calc'd for complex **2**, $Cd_{87}(H_2O)_{72}(OH)_{12}(CH_3CO_2)_{162}$: C, 18.65; H, 2.84. Found: C, 18.64; H, 3.28 (this formula was determined from the crystal structure data). FT-IR: $\bar{\nu}$ = 3246, 1541, 1407, 1341, 1020, 948, 679, 658, 614, 401 cm^{-1}.

Data for Complex 3. Anal. Calc'd for complex **3**, $Cd_{10}(H_2O)_6(OH)_2(CH_3CO_2)_{18}$: C, 18.57; H, 2.84. Found: C, 18.82; H, 3.01 (this formula was determined from the crystal structure data). FT-IR: $\bar{\nu}$ = 3218, 1605, 1575, 1539, 1406, 1385, 1334, 1018, 676, 663, 653, 611, 458 cm^{-1}.

Data for Complex 4. Anal. Calc'd for complex **4**, $Cd_{20}(H_2O)_{20}(OH)_4(CH_3CO_2)_{36}$: C, 17.99; H, 3.16. Found: C, 18.55; H, 2.91 (this formula was determined from the crystal structure data). FT-IR: $\bar{\nu}$ = 3207, 2361, 2342, 1574, 1538, 1404, 1385, 1333, 1044, 1017, 947, 947, 792, 676, 664, 652, 611, 458 cm^{-1}.

Single-Crystal XRD. Crystals of **1**−**4** were obtained by slow evaporation from the crystallization solvents described above. In each case, toluene was used to decrease the solubility of complex **1** in the crystallization solvent. The single crystal of complex **1** was a colorless

Table 1. Crystallographic Parameters for Complexes 1−4

	complex **1**	complex **2**	complex **3**	complex **4**
empirical formula	$C_{60}H_{98}O_{65}Cd_{14.5}$	$C_{54}H_{83}O_{68}Cd_{14.5}$	$C_9H_{16.5}O_{11}Cd_{2.5}$	$C_{18}H_{38}O_{24}Cd_5$
M (g mol^{-1})	3489.18	3450.00	581.72	1200.48
cryst syst	rhombohedral	rhombohedral	triclinic	monoclinic
space group	$R\bar{3}$	$R\bar{3}$	$P\bar{1}$	$P2_1/n$
a (Å)	19.095(1)	19.060(2)	10.989(3)	10.890(5)
b (Å)	19.095(1)	19.060(2)	11.088(3)	15.645(5)
c (Å)	50.580(2)	50.017(6)	16.011(5)	20.493(5)
α (deg)	90	90	96.271(11)	90
β (deg)	90	90	95.918(11)	93.224(5)
γ (deg)	120	120	118.105(8)	90
V (Å^3)	15972(2)	15736(3)	1683.7(8)	3486(2)
Z	6	6	4	4
T (K)	173(2)	173(2)	173(2)	173(2)
ρ_{calcd} (g cm^{-3})	2.175	2.184	2.295	2.287
λ(Mo Kα) (Å)	0.71069	0.71073	0.71073	0.71073
F(000)	10044	9882	1114	2312
$2\theta_{max}$ (deg)	56	65	62	34
reflns collected	45216	77286	22163	38513
indep reflns	8773	12964	8914	13811
obsd reflns ($I > 2\sigma$)	8773	12964	8227	13811
R_{int}	0.0281	0.0323	0.0344	0.0456
R_1	0.037	0.052	0.030	0.040
wR_2	0.098	0.130	0.076	0.082
GoF	1.036	1.051	1.073	1.012

octahedron, complex **2** was a colorless cube, and complexes **3** and **4** were colorless rods. Single-crystal XRD for complexes **1** and **4** was performed on a Bruker APEX Duo diffractometer with graphite monochromated Mo−Kα radiation. Data for complexes **2** and **3** were collected on a Bruker X8 APEX II CCD with graphite monochromated Mo−Kα radiation. Structures of all complexes were solved by direct methods[22] and the refinements were performed using SHELXL-97.[23] The hydrogen atoms attached to aqua and ethanol ligands were not modeled; however, they must all be fully protonated for charge balance. In complexes **1** and **2** one acetato ligand (C15, C16, O15, O16), linking Cd6 to Cd7, was found in two orientations rotated about C16 in a 7:3 ratio. The atoms in the 30% abundant orientation were labeled as 'b' atoms. The aqua ligand, O22, found axial to O15 on Cd7 was also found in two orientations in a 7:3 ratio. The 30% abundant orientation was labeled O22b and is axial to O15b. The μ_3-O ligand in complexes **3** and **4** is disordered above and below the plane of Cd ions 2−4 and is modeled in the plane to account for this disorder. For charge balance, a hydrogen atom must also be bound to the μ_3-O making it a μ_3-OH. This hydrogen atom was not modeled in complex **3** because of the disorder of the oxygen atom. The hydrogen atoms attached to oxygen in complex **3** were located in the difference map. In complex **4**, the hydrogen atoms attached to aqua ligands and the μ_3 hydroxo ligand were found in the difference map and modeled accordingly. The su ratio for the proton of the μ_3 hydroxo ligand is quite large and this is attributed to the fact that the proton is disordered on either side of the oxygen atom; however, it is only modeled on one side. Methyl group hydrogen atoms were included at fixed positions. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms not mentioned earlier were included at fixed positions. The crystallographic parameters are shown in Table 1.

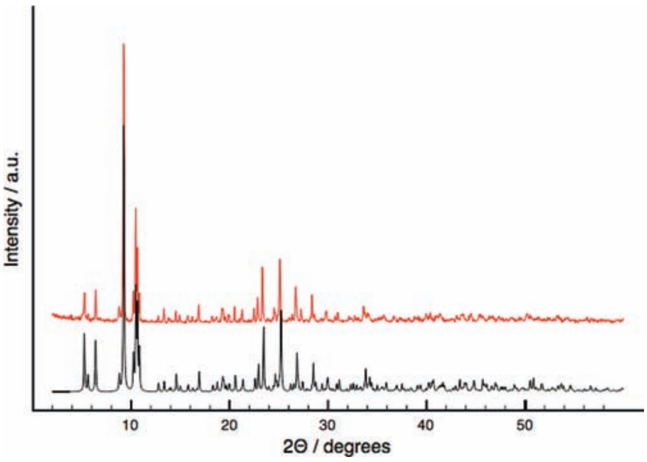


Figure 1. PXRD pattern of a microcrystalline sample of complex **1** (top) compared to the PXRD pattern predicted from SCXRD of complex **1** (bottom).

RESULTS AND DISCUSSION

As noted in the introduction, we first obtained crystals of complex **1** from an experiment that involved combining a Schiff base macrocycle with cadmium acetate in ethanol. Although the structure contained no macrocycle, we thought that it was very interesting, and so we felt that developing a reproducible synthesis of this material as well as exploring its generality would be worthwhile. The synthesis and characterization of the product obtained from recrystallizing **1** from ethanol and methanol is first described, followed by a discussion of the products obtained by recrystallizing **1** from other alcohols.

Complexes 1 and 2: 3-D Cross-Linked 4.5 nm Columns from EtOH/MeOH. Reaction of $Cd(OAc)_2 \cdot 2H_2O$ and CdO in 13.7:1 ratio in ethanol afforded a white microcrystalline powder following filtration and evaporation of the filtrate. Powder XRD (PXRD) analysis of the powder (Figure 1) indicated that it had the same structure as the network originally analyzed by single crystal XRD (SCXRD). Elemental analysis was also in agreement with the chemical formula determined from the SCXRD analysis. Single crystals suitable for XRD were grown from a hot, saturated solution of this microcrystalline powder in 1:1 toluene and EtOH. A colorless octahedron was subjected to SCXRD analysis, and the results are depicted in Figure 2a. Complex **1** has the symmetry-reduced structural formula $Cd_{29}(H_2O)_{12}(EtOH)_6(OH)_4(CH_3CO_2)_{54}$ and crystallizes in the rhombohedral space group $R\bar{3}$ with unit cell dimensions $a = b = 19.095(1)$ and $c = 50.580(2)$ Å. Unit cell data and refinement statistics for complexes **1**−**4** are shown in Table 1. As depicted in Figure 1, the PXRD pattern predicted from the SCXRD data of complex **1** matches well with the PXRD pattern of the starting material from which complex **1** was crystallized. This shows that the bulk reaction described above between $Cd(OAc)_2 \cdot 2H_2O$ and CdO produces a microcrystalline form of complex **1** with the same structure as determined by SCXRD.

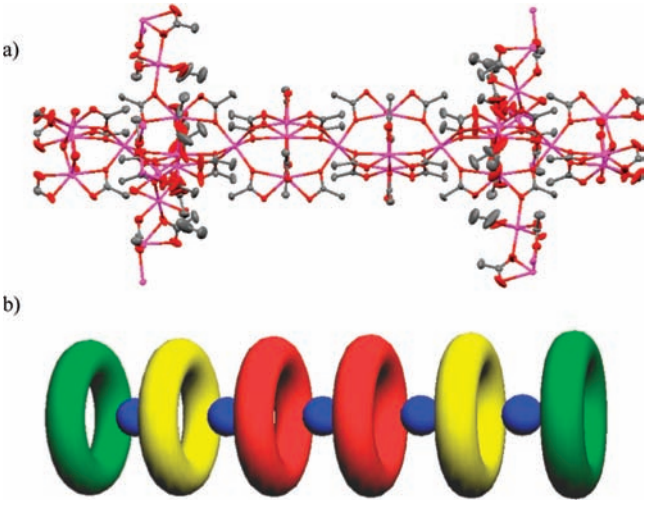


Figure 2. (a) Thermal ellipsoid plot of complex **1** with ellipsoids at 50% probability (C = gray, O = red, Cd = pink). Hydrogen atoms have been omitted for clarity. (b) Representation of an individual column within complex **1** showing the color-coded distinct cadmium rings and intracolumn cadmium linkers. Red = ring 1, yellow = ring 2, green = ring 3, blue = cadmium ions linking rings by acetato groups. Intercolumn linking cadmium ions are bound to rings 2 and 3 but are omitted from this representation.

Since ethanol is incorporated into the structure of **1**, we wondered whether a series of isostructural frameworks could be obtained by using other recrystallization solvents. When microcrystalline **1** was recrystallized from a hot, saturated solution of **1** in 1:1 toluene/MeOH, colorless cubes were obtained. The crystals were subjected to SCXRD analysis and a new complex, **2**, that has the symmetry-reduced structural formula $Cd_{29}(H_2O)_{24}(OH)_4(CH_3CO_2)_{54}$ was obtained. Complex **2** is essentially isostructural with complex **1** and also crystallizes in the rhombohedral space group $R\bar{3}$.

The three-dimensional structure of both complexes **1** and **2** can be described as finite columns consisting of three distinct cadmium clusters supported by acetato ligands. As shown in Figure 2a, each column is composed of six Cd_3O_x rings within $[Cd_4(OAc)_9(\mu_3\text{-}OH)]^{2-}$ clusters. There is an inversion center on the central intracolumn linking cadmium ion that bridges ring 1 to its symmetry equivalent ring. Each column is then joined to six other columns by a cadmium linker perpendicular to the long axis of the column. The +58 charge of 29 Cd^{2+} ions is balanced by 54 acetates (−54 total charge) and 4 central μ_3-hydroxo ligands (−4 total charge).

The three distinct rings, shown in Figure 2b (hereafter referred to as rings 1, 2 and 3), are arranged in each column in the following

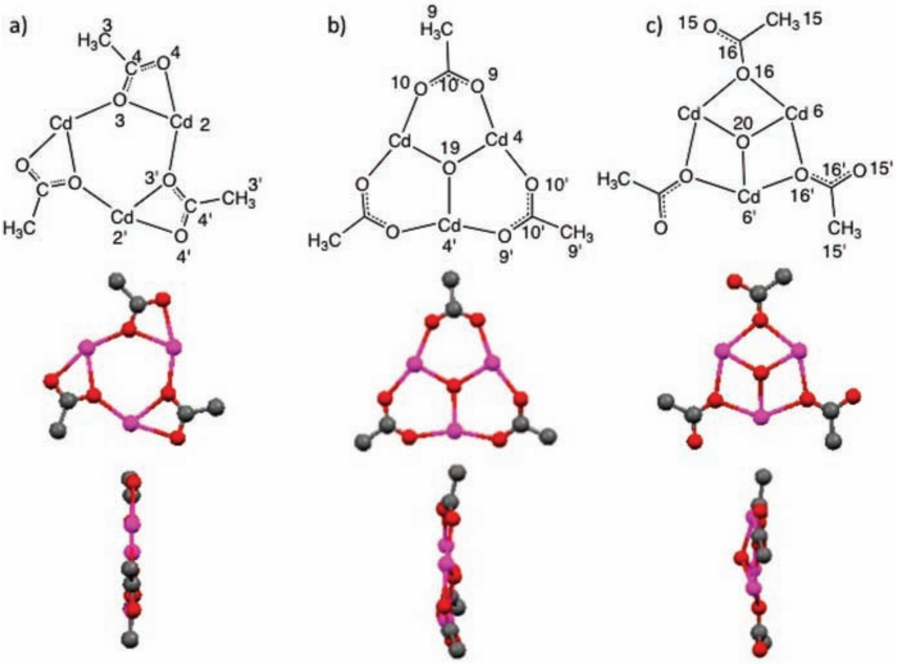


Figure 3. Representations of (a) ring 1, (b) ring 2, and (c) ring 3 with front and side views of each ring from the solid-state structure of **1** (C = gray, O = red, Cd = pink). Primes denote symmetry-equivalent atoms and are included for description of the cluster. Hydrogen atoms have been omitted for clarity.

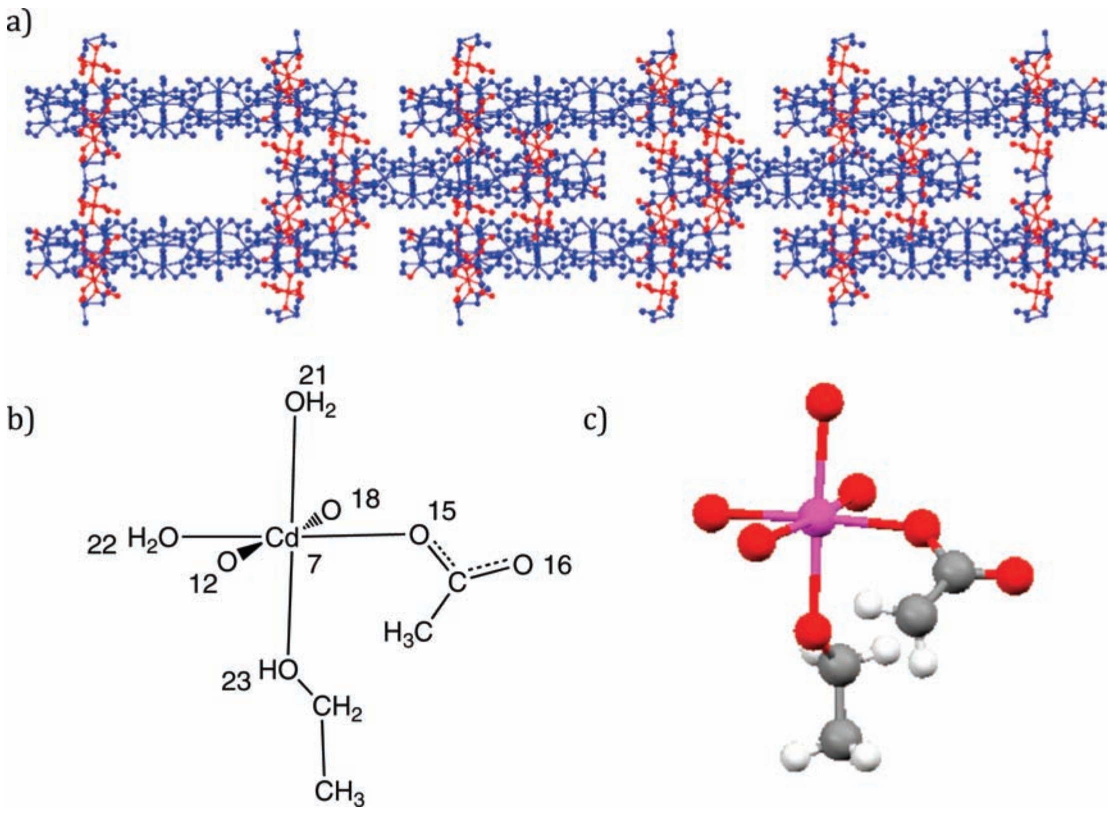


Figure 4. (a) Solid-state structure of eight symmetry-related columns in complex **1** demonstrating how they are connected via cadmium linkers between rings 2 and 3. Hydrogen atoms have been omitted from the structure for clarity. (b) Representation and (c) solid-state structure of the intercolumnar cadmium linker in complex **1** (C = gray, O = red, Cd = pink, H = white).

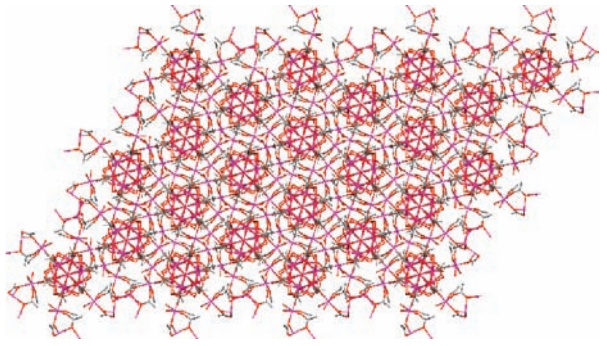


Figure 5. Top-down view of the extended solid-state packing of complex **1**.

order: 3-2-1-1′-2′-3′ where 1′, 2′, and 3′ represent the corresponding inverted ring. Structural details of each ring are found in Figure 3. The three cadmium ions in each ring are heptacoordinate and exhibit distorted pentagonal bipyramidal geometry. This seven coordinate geometry is more unusual for cadmium than the octahedral geometry observed for the cadmium ions that link the rings together.

The following discussion uses the labeling scheme from Figure 3 and refers to complex **1**; it should be noted, however, that all bond lengths and angles in complex **1** and complex **2** are very similar except where otherwise specified. Ring 1 consists of three cadmium ions connected by μ-1,1-acetato ligands. The cadmium ions and acetato oxygen ions that make up the 6-membered ring all lie within the same plane. Ring 1 is linked to ring 1′ and ring 2 via acetato groups in a μ-1,1-fashion connected to an intracolumn cadmium ion linker. The Cd(2)-O(3′) bond length is 2.220(3) Å and the Cd(2)−O(3) bond length is 2.315(3) Å. These bonds are considerably shorter than the equivalent bond (2.597(3) Å) in $Cd(OAc)_2 \cdot 2H_2O$.[24]

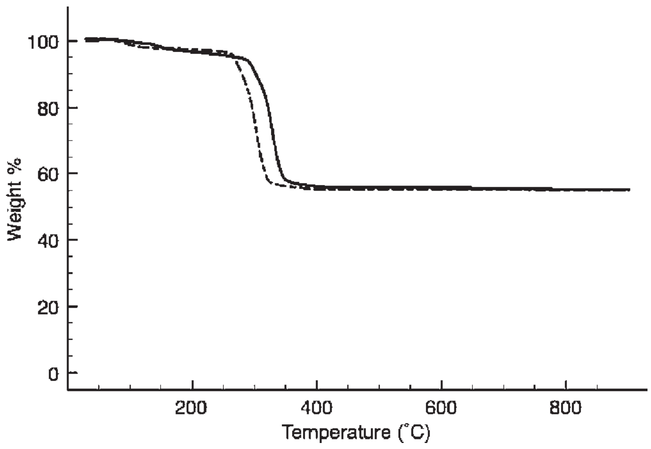


Figure 6. TGA trace of complex **1** (solid line) and complex **2** (dashed line) in an atmosphere of nitrogen (20 °C min^{-1}).

In ring 2, the three cadmium ions are connected by μ-1,3-acetato groups, forming a ring surrounding a central oxygen atom. The Cd(4)−O(19)−Cd(4′) angle is 117.3(2)°, indicating that the central oxygen ion in ring 2 has more sp^2 character than in ring 3 and implying that O19 is a μ_3-oxo ligand. However, there are no other basic sites within the crystal structure where a proton (necessary for charge balance of the framework) might be

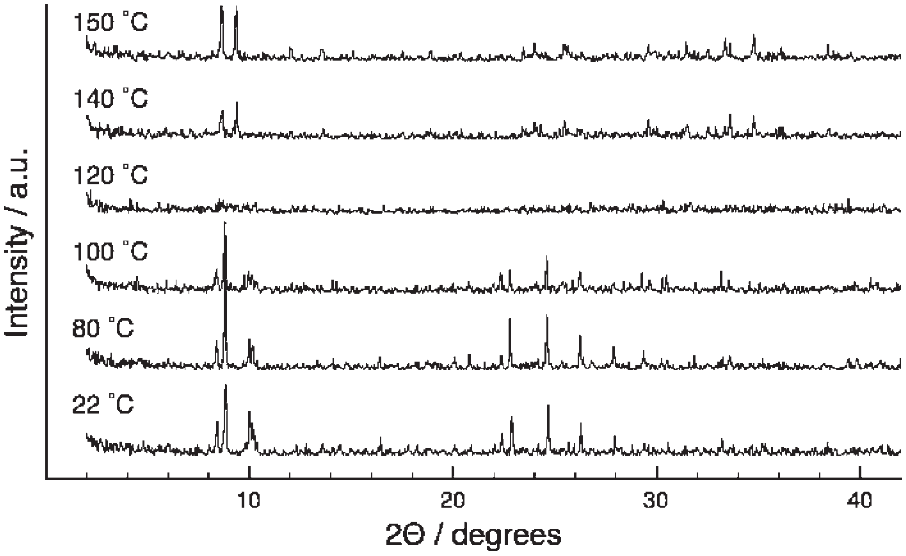


Figure 7. Variable temperature PXRD pattern of complex **1** showing changes in crystallinity occurring as a function of increased temperature.

expected to lie. Close examination of ring 2 reveals that in the space above O19 there is a cage-like environment formed by three acetato ligands. It is possible that in this environment the proton could be mostly trapped between the 3 symmetry equivalent acetate ligands (O7 in particular) leaving the μ_3-O as a pseudo oxo ligand. The O7−Cd4 distance of 2.815(3) Å indicates there is very little bonding present and a large amount of electron density available for the proton. This cage-like environment does not exist for ring 3, where the acetato ligands near the μ_3-OH are twisted outward to facilitate intercolumnar linking. A search of the Cambridge Structural Database reveals that a tetrahedral μ_3-oxo ligand bridging three cadmium ions is very rare with only a few compounds having previously been reported.[25] The planarity of the ring could also result from disorder, but judging from the size and shape of the ellipsoid for the μ_3-O in ring 2, this is not the case. Residual electron density suggests that there is a proton in a position consistent with a μ_3-OH ligand, but this too is ambiguous. From the above evidence we suggest it is more likely that the central oxygen atom is in a distorted tetrahedral geometry characteristic of a μ_3-OH ligand, but we are unable to fully discount the possibility of a pseudo μ_3-oxo ligand based on the data collected.

Ring 3 is composed of three cadmium ions and three acetato oxygen atoms where the cadmium ions are bridged by a μ_3-hydroxo ligand. The Cd(6)−O(20)−Cd(6′) bond angle between adjacent cadmium ions is 112.8(3)°, revealing the distorted tetrahedral arrangement of the central μ_3-hydroxo ligand. The Cd(6)−O(20) bond length in ring 3 (2.207(2) Å) is longer than the Cd(4)−O(19) bond length in ring 2, which is 2.182(1) Å. This difference presumably arises because the outer ring of ring 2 is composed of more atoms than ring 3, thereby limiting bond lengths to allow the structural motif to fit within the columns. The outer ring is similar to that of ring 1, but the acetato ligands in the plane of the ring bridge to a cadmium ion that links separate columns in a μ_3-1,1,3 fashion. Bond lengths Cd(6)−O(16′) = 2.353(7) Å and Cd(6)−O(16) = 2.403(7) Å are longer than the equivalent bonds in ring 2 allowing the acetato ligands on ring 3 to coordinate to the intercolumnar Cd linker.

Each ring is then connected to its neighboring rings via acetato groups bound to an octahedral 6-coordinate intracolumnar cadmium ion. The Cd_3O_x rings and Cd intracolumnar linkers form $[Cd_4(OAc)_9(\mu_3\text{-}OH)]^{2-}$ secondary building units that appear to be particularly stable and are present in various forms in all the structures described in this paper. To our surprise, this secondary building unit is very different from the most common basic zinc acetate cluster, which consists of four zinc ions held together by a tetrahedral μ_4-O and six bridging μ-1,3-acetato ligands.

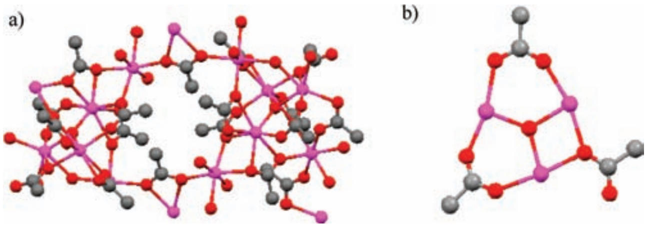


Figure 8. (a) Solid-state structure and (b) Cd_3 ring of complex **3** (C = gray, O = red, Cd = pink). Hydrogen atoms have been omitted from the structure for clarity.

In the solid-state structure of complexes **1** and **2**, each column is connected to six equivalent columns via a second octahedral intercolumnar cadmium ion linker as shown in Figure 4a. The coordination environment at the linker is different in complexes **1** and **2**. In complex **1**, two aqua ligands and one EtOH molecule are bound to the linking cadmium ion, with the remaining three bonds linking two columns via acetato groups in rings 2 and 3 as shown in Figures 4b and 4c. The intercolumnar linking Cd(7) binds to ring 3 of one column through a bridging μ-1,3-acetato ligand via O(15) and a μ-1,1-acetato ligand via O(18). Cd(7) also binds to ring 2 of another column through μ-1,1-acetato ligand via O(12). The cylindrical columns and linkers can be clearly seen in a top-down view of the extended solid-state packing as shown in Figure 5.

Since complex **2** was crystallized in MeOH rather than EtOH, it cannot have an identical intercolumnar linker to complex **1**. Unexpectedly, in place of the EtOH bound to the cadmium ion linker there is an aqua ligand instead of a MeOH molecule, bringing the total number of aqua ligands bound to Cd(7) to three. There is an additional uncoordinated water molecule positioned behind the coordinated aqua ligand. Its presence

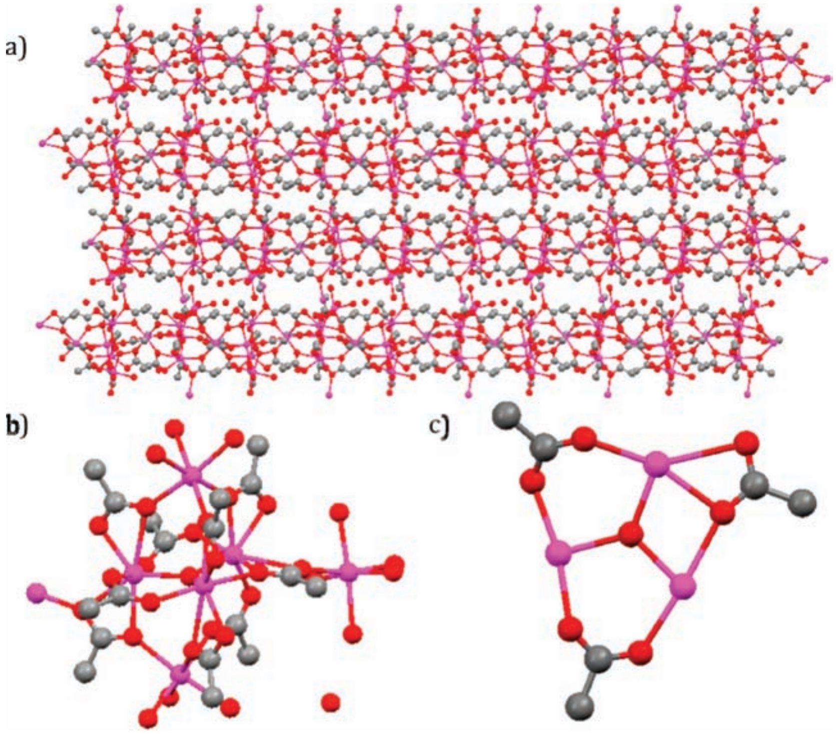


Figure 9. (a) Extended solid-state packing of complex **4**. Solid-state structure of (b) the repeating unit and (c) the Cd-ring of complex **4** (C = gray, O = red, Cd = pink). Hydrogen atoms have been omitted for clarity.

may help to occupy space left with the removal of the larger EtOH molecule in complex **1**. This uncoordinated water molecule hydrogen bonds with the coordinated aqua ligand (O21) and an acetate group (O17) (O−O bond lengths are 2.59 Å and 2.72 Å, respectively).

Both complexes **1** and **2** have 3-D open framework structures with included solvent. We undertook TGA studies to test whether the solvent could be removed to yield frameworks with accessible porosity. The TGA curves for complexes **1** and **2** are shown in Figure 6. Complex **1** shows a 6 wt % loss from 100 to 260 °C that closely matches a complete loss of EtOH and water from the structure (calculated 7%). This broad weight loss is followed by a distinct mass loss at 300−350 °C. Elemental analysis was conducted on the residue obtained after complex **1** was heated to 400 °C. The analysis indicated that the product is primarily CdO, with a small amount of carbon (0.37%) retained. Complex **2** shows similar stability to complex **1**, with a weight loss of about 6% at 70−240 °C which corresponds to loss of water from the structure.

We undertook a variable temperature PXRD study of complex **1** in the microcrystalline form to probe the lattice stability upon removal of EtOH and water (Figure 7). As the temperature was increased beyond 80 °C, crystallinity was gradually lost and then above 120 °C the compound regained crystallinity, albeit with a different structure. The results indicate that the compound loses order as the water and EtOH are removed, then a new crystalline substance is formed above 120 °C. Nitrogen adsorption was conducted after heating a sample to 150 °C and showed the new network is nonporous, suggesting that the restructuring of the crystalline frameworks results in collapse of any potential void space. Attempts to study the new crystalline material by SCXRD were unsuccessful.

Complex 3: Isolated SBU from 1-BuOH and 1-PrOH. To further explore the generality of the cadmium structures, we investigated the crystallization of microcrystalline samples of complex **1** in other alcohol solvents. Crystals of complex **3**, with formula $Cd_{10}(H_2O)_6(OH)_2(CH_3CO_2)_{18}$, were obtained from solutions of **1** in either 1-butanol or 1-propanol and toluene. Complex **3** (Figure 8a) was previously reported by Poul et al.[26] In their report, complex **3** was synthesized by heating $Cd(OAc)_2 \cdot 2H_2O$ in a polyol solution. They found that the resulting crystals decomposed immediately upon removal from solution, thus rendering single-crystal analysis difficult. The crystals of complex **3** we isolated from 1-butanol and toluene are more robust than those previously reported and maintain crystallinity even upon standing in air at room temperature for 3 months as confirmed by SCXRD. Complex **3** consists of 2-D layers composed of nearly isolated $[Cd_4(OAc)_9(\mu_3\text{-}OH)]^{2-}$ SBUs. The $[Cd_4(OAc)_9(\mu_3\text{-}OH)]^{2-}$ cluster in complex **3** is slightly different than those in complexes **1** and **2**, with the main difference being the absence of 3-fold symmetry. The ring within the SBU (Figure 8b) contains two separate motifs, one similar to ring 2 of complex **1** is repeated twice in each ring and one similar to that of ring 3 of complex **1** completes the ring.

Complex 4: Lamellar Columns from *t*-BuOH. When a microcrystalline sample of complex **1** is crystallized in *t*-butanol, single crystals of complex **4** are formed. Complex **4** has a unit cell formula of $Cd_{20}(H_2O)_{20}(OH)_4(CH_3CO_2)_{36}$ and is structurally similar to complexes **1** and **2** in that it consists of columns joined together by intercolumnar cadmium linkers (Figure 9a). However, complex **4** has a 2-D structure with only one cluster type (compared to three in complexes **1** and **2**), and the columns are infinitely long.

The $[Cd_4(OAc)_9(\mu_3\text{-}OH)]^{2-}$ cluster that is present in complex **4** lacks 3-fold symmetry (Figure 9c). This cluster is then linked to a cluster in an adjacent column by an intercolumnar linker similar to that of complex **2** (with aqua ligands, not alcohol). The octahedral linker is coordinated by four aqua ligands and bound to two clusters, each through a μ_3-1,1,3-acetato ligand. An uncoordinated water molecule is also positioned behind a bound water molecule. As in complex **2**, this uncoordinated water molecule participates in hydrogen bonding with the extended network (O(24)−O(11) distance is 2.85 Å and O(24)−O(22) distance is 2.87 Å). The repeating unit is shown in Figure 9b.

Other Solvents. To determine the solvent limitations for making complex **1** and analogues, 2-PrOH was used to grow crystals from a microcrystalline sample of complex **1**. SCXRD showed that these were $Cd(OAc)_2 \cdot 2H_2O$. It appears that the extended 3-D structure formed in complex **1** does not form with alcohol solvents larger than ethanol. It is surprising that while crystallization from the bulkier solvent, *t*-BuOH, yields complex **4**, crystallization from 2-PrOH does not. Crystals with unit cells matching complexes **1**−**4** were also grown from mixtures of hexanes and alcohols, but the crystals were more difficult to obtain and were of lower quality than those obtained using toluene as cosolvent.

FT-IR Spectroscopy. FT-IR spectra were recorded for complexes **1**−**4**. By comparison with the IR spectra of known cadmium acetate dihydrate and cobalt acetate dihydrate, many of the bands could be assigned.[27] The peaks corresponding to acetato ligands can clearly be seen in each spectrum. For example, in the spectrum of complex **1** the peaks at 1017 and 1052 cm^{-1} correspond to CH_3 rocking while the peak at 1333 cm^{-1} corresponds to CH_3 symmetrical stretching. Each spectrum also has a clear O−H stretching peak attributed to water at 3200−3300 cm^{-1}.

CONCLUSIONS

Novel cadmium hydroxo acetate cluster complexes have been prepared and studied. Two new coordination networks with 3-D open-framework structures were obtained from ethanol and methanol. Both complexes **1** and **2** form a network composed of truncated 4.5 nm long columns, each containing three distinct Cd_3O_x rings. Six of these rings are linked by intracolumnar cadmium linkers to form the truncated columns, and each column is then connected to six others via intercolumnar cadmium ions yielding the open-framework. Both complexes **1** and **2** decompose around 300−350 °C to give CdO as the major product.

Other structures were obtained when compound **1** was recrystallized from other alcohols. We report a route affording much more stable crystals of the previously described 2-D structure, complex **3**, after recrystallizing complex **1** from a mixture of *n*-butanol and toluene. Although the crystals were previously found to immediately decompose upon removal from solvent, crystals prepared by our method are air stable for months. Complex **4** was obtained from *t*-butanol, and exhibits a 2-D structure consisting of infinite columns containing a repeating $[Cd_4(OAc)_9(\mu_3\text{-OH})]^{2-}$ cluster.

We have observed a strong propensity for $Cd(OAc)_2$ to form cadmium cluster SBUs with the general formula $[Cd_4(OAc)_9(\mu_3\text{-OH})]^{2-}$ when crystallized from alcohol solutions. Each SBU is composed of a central planar ring containing 3 Cd ions and 2 Cd 'linker' ions with one linker above and one below the plane. This cadmium cluster, similar to those observed in macrocycle-cadmium cluster metallocavitands previously reported, appears to be an important SBU for cadmium carboxylate chemistry.

To drive discovery and application of useful cadmium-containing MOFs and supramolecular structures, it is important to understand the coordination modes of cadmium and to be able to predict the geometry of potential SBUs. This article describes several cadmium acetate-based structures with complex architectures that illustrate numerous cadmium coordination modes. These results clearly show that the carboxylate coordination chemistry of cadmium is rich and provide a starting point for those wishing to construct cadmium-carboxylate MOFs based on $[Cd_4(OAc)_9(\mu_3\text{-OH})]^{2-}$ SBUs.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** PXRD patterns and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

We thank NSERC and UBC for funding this research. P.D.F. is grateful to UBC for a graduate fellowship. We are grateful to Brian Patrick for assistance with the SCXRD analyses.

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