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Inorganic Chemistry Article

Self-Assembly of a Mixed-Ligand Metal-Coordination Polymeric Network of Cadmium(II) Croconate with 4,4′-Bipyridine

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A new cadmium croconate ($C_5O_5^{2-}$) complex, $[Cd_2(C_5O_5)_2(4,4'\text{-bpy})(H_2O)]_\infty$ (4,4-bpy = 4,4′-bipyridine) with an extended network has been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction studies. The title compound crystallizes in the monoclinic system, space group $P2_1/n$, with empirical formula $C_{20}H_{12}Cd_2N_2O_{12}$, $a = 15.9623(3)$ Å, $b = 7.5837(1)$ Å, $c = 18.1181(3)$ Å, $\beta = 99.95(2)°$, and $Z = 4$. Structural determination reveals that the title compound has a bilayered network, containing two crystallographically independent Cd(II) ions in different coordination environments. Cd(1) lies in a distorted pentagonal bipyramidal environment, consisting of three croconate ions and one 4,4′-bpy nitrogen donor, while Cd(2) lies in a distorted octahedral environment, consisting of two croconate anions, one 4,4′-bpy nitrogen donor, and one water molecule. Of the two crystallographic independent croconate ligands, one presents a bis-bidentate adjacent μ_3-coordination mode and the other a new bidentate/three-adjacent μ_5-coordination mode. A two-dimensional hybrid layer is formed by two rectangular boxes as the building units through the connectivity between Cd(II) and croconate and 4,4′-bpy ligands.

Introduction

Crystal engineering of metal coordination frameworks[1−5] (MOFs) has attracted great attention not only because of their wide variety of structural topologies but also for their potential application as a zeolite-like solid,[6−9] for molecular selection, ion exchange, and catalysis. The design and synthesis of metal−organic networks via self-assembly of metal ions and multifunctional ligands depend both on the selection of the coordination geometry of metal centers and on the coordination behavior of the organic ligands. Many of these frameworks have been obtained using N,N′-donor spacer ligands with rodlike characteristics, such as 4,4′-bipyridine (4,4′-bpy)[10−16] or 1,2-bis(4-pyridyl)ethane (bpe)[17−20] with the gauche and anti conformation. During the past few years, the bonding characteristics of croconate ($C_5O_5^{2-}$, dianion of 4,5-dihydroxycyclopent-4-ene-1,2,3-trione) with first transi-

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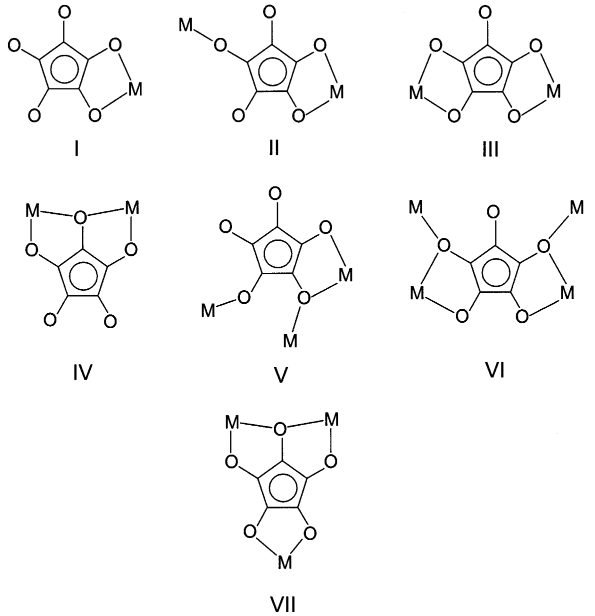
Chart 1



tion-metal ions and some complexes of croconate associated with another coligand such as imidazole, histamine, 2,2′-bipyridine, and bis(2-pyridylvarbonyl)amido anion have been investigated and show that this cyclic oxocarbon ligand can be coordinated to the metal ions using various bonding modes as a terminal bidentate (Chart 1, **I**),[21−29] bridging bidentate/monodentate (Chart 1, **II**),[22,30,31] or bridging bis-bidentate ligand through either four (Chart 1, **III**)[32,34] or three adjacent (Chart 1, **IV**)[34,36] croconate oxygen atoms. Recently, two new bonding and bridging modes as a tridentate ligand (Chart 1, **V**) and tetradentate ligand (Chart 1, **VI**) have been found in the Cd(II)− and Ag(I)−Na complexes.[37] We have employed croconate alone with 4,4′-bpy ligands on Cd(II) to create a new mixed-ligand bridging network. In this paper we report the synthesis, crystal structure, and thermogravimeteric analysis of a novel three-dimensional extended network in which the croconate functions as a bridging bis-bidentate through three-adjacent (μ_3) bridge mode (**IV** in Chart 1) and a new bidentate/three-adjacent (μ_5) bridge mode (**VII** in Chart 1).

Experimental Section

Materials and Physical Techniques. All chemicals were of reagent grade and were used as commercially obtained without further purification. The infrared spectra were recorded on a Nicolet Fourier transform IR MAGNA-IR 500 spectrometer in the range of 500−4000 cm^{-1} using the KBr disk technique. Thermogravimetric analyses (TGA) was performed on a computer-controlled Perkin-Elmer 7 Series/UNIX TGA7 analyzer. Single-phase powder samples (4.014 mg) were loaded into aluminum pans and heated with a ramp rate of 5 °C/min from room temperature to 900 °C under nitrogen flux. In situ variable-temperature synchrotron XRD data ($\lambda = 1.3268$ Å) were obtained at the National Synchrotron Radiation Research Center BL17A1. The title compound was sealed in a 1 mm capillary for XRD studies. The diffraction data were recorded at room temperature and 230 °C, respectively, by using a curved Fuji BASIII imaging plate, which covers a 2θ range from 3° to 120°. After being cooled to room temperature, the sample was dipped into deionization water for 2 h and its powder diffraction remeasured.

Synthesis of $\{[Cd_2(C_5O_5)_2(4,4'\text{-bpy})(H_2O)]\cdot(H_2O)\}_\infty$. Reaction of $Cd(NO_3)_2\cdot4H_2O$ (0.0326 g, 0.1 mmol), $Na_2C_5O_5$ (0.0198 g, 0.1 mmol), 4,4′-bpy (0.0171 g, 0.1 mmol) and deionized water (6 mL) in a mole ratio of 1:1:1:3333 at 180 °C for 3 days produced pale-yellow needlelike crystals in a yield of 0.0253 g, 36.29% (based on Cd^{II}). The final pH value of the solution was 6.05. The yields can be raised to 75% or 78% by the same reaction using stoichiometric ratios of 2:2:1:3333 or 2.2:2:1:3333 instead of the above 1:1:1:3333. Anal. Found: C, 34.41; H, 1.52; N, 4.20. Calcd for $C_{20}H_{12}Cd_2N_2O_{12}$: C, 34.46; H, 1.73; N, 4.02.

Crystallographic Data Collection and Refinement. Single-crystal structure analysis was performed on a Siemens SMART diffractomer with a CCD detector with Mo radiation ($\lambda = 0.71073$ Å) at room temperature. A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 15 frames each, each frame corresponding to a 0.3° scan in 10 s, following by spot integration and least-squares refinement. For each structure, data were measured using ω scans of 0.3° per frame for 20 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART[38] software and refined with SAINT[39] on all observed reflections. Data reduction was performed with the SAINT[39] software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[40] Direct phase determination and subsequent difference Fourier map synthesis yielded the positions of all non-hydrogen atoms, which were subjected to anisotropic refinements. Hydrogen atoms were placed in their geometrically generated positions. The final full-matrix, least-squares refinement on F^2 was applied for all observed reflections [$I > 2\sigma(I)$]. All calculations were performed using the SHELXTL-PC V 5.03 software package.[41] Crystallographic data and details of the data collection and structure refinement are listed in Table 1.

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Table 1. Crystal Data and Refinement Details of the Complex $\{[Cd_2(C_5O_5)_2(4,4'\text{-bpy})(H_2O)]\cdot H_2O\}_\infty$

empirical formula	$C_{20}H_{12}Cd_2N_2O_{12}$	fw	697.12
crystal syst	monoclinic	space group	$P2_1/n$
a (Å)	15.9623(3)	α (deg)	90.0
b (Å)	7.5837(1)	β (deg)	99.95(1)
c (Å)	18.1181(3)	γ (deg)	90.0
V (Å^3)	2160.25(6)	Z	4
μ (mm^{-1})	2.042	θ range (deg)	1.57−27.50
total no. of data collected	22287	no. of obsd data ($I > 2\sigma(I)$)	4953
R1, wR2[a] ($I > 2\sigma(I)$)	0.0227, 0.0528	R1, wR2[a] (all data)	0.0339, 0.0660
GOF	1.008	no. of variables	338

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w|F_o^2 - F_c^2|^2/\sum w(F_o^4)]^{1/2}$.

CCDC. The CCDC for the title compound contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, U.K.; fax +44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk].

Result and Discussion

Synthesis and IR Spectroscopy. The title compound was synthesized by stoichiometric mixing of $Cd(NO_3)_2$ and disodium croconate ($Na_2C_5O_5$) with 4,4′-bpy and H_2O under hydrothermal conditions. The reaction was carried out in 23 mL acid-digestion bombs at 180 °C for 3 days. The compound is very stable in air at ambient temperature and is insoluble in common solvents such as water, alcohol, and acetonitrile. The synthetic reproducibility is very nice. The yield can be raised to 75−78% when the synthesis is repeated with different ratios of the reactants. This implies that the synthesis is not so rigorous in its stoichiometry demands. The infrared spectrum shows a broad band in the region 3300−3500 cm^{-1}, which can be assigned to the stretching vibration ν(O−H) of the water molecules. The most relevant IR features are those associated with the chelating croconate ligands. The peak at 1718 cm^{-1} is assigned to the uncoordinated carbonyl groups, which exhibits double bond character. The coordinated CO groups are characterized by medium absorptions at 1664 and 1603 cm^{-1}. A very strong and broad band is centered at around 1511 cm^{-1}, which is attributed to vibrational modes representing mixtures of C−O and C−C stretching motions and is in agreement with the characteristic of the $(CO)_n^{2-}$ salts.[42]

Structure Description. The X-ray structure determination reveals a covalently bonded complicated three-dimensional network of composition $[Cd_2(C_5O_5)_2(4,4'\text{-bpy})(H_2O)]\cdot(H_2O)$ containing two crystallographically independent cadmium(II) ions with different coordination geometries. The metal coordination environments of Cd(1) and Cd(2) are illustrated in Figures 1 and 2, respectively, and relevant bond lengths and angles are listed in Table 2. Cd(1) lies in a distorted pentagonal bipyramidal environment, consisting of one nitrogen atom from the 4,4′-bpy ligand with a bond distance of Cd(1)−N(1) = 2.255(3) Å and six oxygen atoms from three bridging croconate ligands with bond distances of Cd(1)−O(1) = 2.467(2) Å, Cd(1)−O(2) = 2.296(2) Å, Cd(1)−O(6) = 2.423(2) Å, Cd(1)−O(7) = 2.420(2) Å, Cd(1)−O(8) = 2.359(2) Å, and Cd(1)−O(9) = 2.568(2) Å (Figure 1), while Cd(2) lies in a distorted octahedral environment, consisting of one nitrogen atom from the 4,4′-bpy ligand with a bond distance of Cd(2)−N(2) = 2.275(3) Å and five oxygen atoms from two bridging croconate ligands and one water molecule with bond distances of Cd(2)−O(2) = 2.314(2) Å, Cd(2)−O(3) = 2.331(2) Å, Cd-

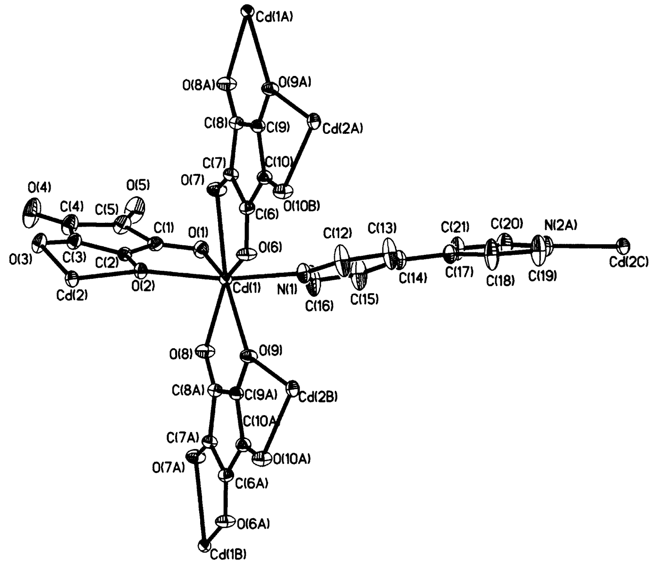

Figure 1. Distorted pentagonal bipyramidal coordination sphere about Cd(1) with the atom labeling scheme (ORTEP drawing, 50% thermal ellipsoids).

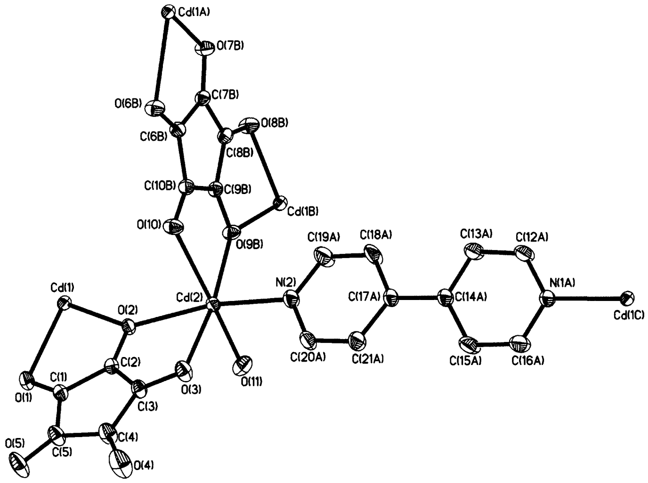

Figure 2. Distorted octahedral coordination sphere about Cd(2) with the atom labeling scheme (ORTEP drawing, 50% thermal ellipsoids).

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Table 2. Bond Lengths (Å) and Angles (deg) for Cd(1) and Cd(2) Coordination Spheres in $\{[Cd_2(C_5O_5)_2(4,4'\text{-bpy})(H_2O)]\cdot H_2O\}_\infty$

Cd(1)−O(1)	2.467(2)	Cd(2)−O(2)	2.314(2)
Cd(1)−O(2)	2.296(2)	Cd(2)−O(3)	2.331(2)
Cd(1)−O(6)	2.423(2)	Cd(2)−O(9)[a]	2.422(2)
Cd(1)−O(7)	2.420(2)	Cd(2)−O(10)	2.350(2)
Cd(1)−O(8)	2.359(2)	Cd(2)−$O(11)_w$	2.259(2)
Cd(1)−O(9)	2.568(2)	Cd(2)−N(2)	2.275(3)
Cd(1)−N(1)	2.255(3)		
N(1)−Cd(1)−O(2)	158.42(9)	O(7)−Cd(1)−O(8)	146.49(7)
N(1)−Cd(1)−O(1)	83.55(8)	O(7)−Cd(1)−O(9)	141.06(6)
N(1)−Cd(1)−O(6)	96.76(8)	O(8)−Cd(1)−O(9)	71.18(6)
N(1)−Cd(1)−O(7)	93.16(9)	N(2)−Cd(2)−O(2)	165.87(8)
N(1)−Cd(1)−O(8)	94.39(8)	N(2)−Cd(2)−O(3)	89.58(9)
N(1)−Cd(1)−O(9)	92.07(8)	N(2)−Cd(2)−O(9)[a]	97.04(9)
O(2)−Cd(1)−O(1)	75.04(7)	N(2)−Cd(2)−O(10)	96.93(9)
O(2)−Cd(1)−O(6)	99.32(7)	N(2)−Cd(2)−O(11)	95.37(9)
O(2)−Cd(1)−O(7)	78.65(7)	O(2)−Cd(2)−O(3)	76.30(7)
O(2)−Cd(1)−O(8)	82.49(7)	O(2)−Cd(2)−O(9)[a]	97.08(7)
O(2)−Cd(1)−O(9)	106.91(7)	O(2)−Cd(2)−O(10)	86.71(7)
O(1)−Cd(1)−O(6)	145.39(6)	O(2)−Cd(2)−O(11)	84.82(8)
O(1)−Cd(1)−O(7)	74.29(6)	O(3)−Cd(2)−O(9)[a]	172.70(7)
O(1)−Cd(1)−O(8)	74.20(7)	O(3)−Cd(2)−O(10)	102.01(8)
O(1)−Cd(1)−O(9)	144.65(6)	O(3)−Cd(2)−O(11)	92.31(8)
O(6)−Cd(1)−O(7)	71.13(6)	O(9)[a]−Cd(2)−O(10)	74.24(7)
O(6)−Cd(1)−O(8)	71.13(6)	O(9)[a]−Cd(2)−O(11)	90.11(7)
O(6)−Cd(1)−O(9)	69.94(6)	O(10)−Cd(2)−O(11)	161.14(8)

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

(2)−O(9) = 2.422(2) Å, Cd(2)−O(10) = 2.350(2) Å, and Cd(2)−$O(11)_w$ = 2.259(2) Å (Figure 2). The 4,4′-bpy ligand acts as a bis-monodentate bridging ligand to connect Cd(1) and Cd(2) ions (Figure 1) with a Cd(1)···Cd(2C) separation of 11.595 Å which is comparable with those of other related metal−(4,4′-bpy) complexes.[10−16] It is important to note that the croconate ligand ($C_5O_5^{2-}$) plays a key role in the construction of the novel three-dimensional network. It acts as a bridging ligand with two different bridging modes. The first one is a bridging bis-bidentate mode through three adjacent[34,36] (μ_3) croconate oxygen atoms (O(1), O(2), O(3)) (**IV** in Scheme 1) to link Cd(1) and Cd(2) ions with a Cd(1)···Cd(2) separation of 4.381 Å which is comparable with that of 4.355 Å in $[Cd(C_5O_5)(NH_3)_2]_n$.[37] The uncoordinated oxygens (O(4) and O(5)) show a ketonic form with shorter bond distances (C(4)−O(4) = 1.221(4) Å, C(4)−O(4) = 1.217(4) Å) compared to the C−O distances (C(1)−O(1) = 1.242(4) Å, C(2)−O(2) = 1.282(4) Å, C(3)−O(3) 1.271(4) Å) of the metal-coordinated oxygen atoms due to a partial localization of the π-electrons upon complexation.[37] The other one adopts a new bidentate/three-adjacent (μ_5) bridging mode (**VII** in Scheme 1) through five oxygen atoms (O(6), O(7)/(O(8), O(9), O(10)) of croconate to link two crystallographically identical Cd(1) ions and one Cd(2) ion as an isosceles triangle Cd_3 unit (Figure 1) with Cd(1)···Cd(1A), Cd(1)···Cd(2A), and Cd(1A)···Cd(2A) separations of 7.584, 7.501, and 4.785 Å, respectively. It is noted that, unlike the former μ_3-croconate, the differences among the five C−O distances of μ_5-croconate are not so obvious and in the range of 1.235(3)−1.264(3), which indicates a more π-delocalized bridging mode close to a free croconate ring.

The overall three-dimensional architecture is depicted in Figure 3, and can be described as a hybrid two-dimensional layer formed by the connectivity between the Cd and croconate and 4,4′-bpy ligands. Two rectangular boxes shown in Figure 4a,b are the basic building units to construct the hybrid two-dimensional layer (Figure 3) in which the same boxes are repeatedly arranged along the *b* axis and different boxes are then alternatively arranged along the *a* axis. The first rectangular box in Figure 4a shows that four Cd(1) and four Cd(2) ions occupy the box corners and are linked by four μ_3-croconate and two μ_5-croconate bridging ligands to complete the small box with a size of 7.584 × 4.785 × 4.381 Å. To the best of our knowledge, this is the first metal−croconate complex that uses two kinds of croconate bridging modes to construct its metal−organic framework. The other rectangular box in Figure 3b shows that four Cd(1) and four Cd(2) ions also occupy the box corners but are linked by four 4,4′-bpy and two μ_5-croconate bridging ligands to complete the larger box with a size of 11.595 × 7.584 × 4.785 Å. Both of the rectangular boxes share their faces with neighboring ones, forming a two-dimensional extended framework along the [100] and [010] directions. This is indeed an important and novel structure wherein croconate binds to Cd atoms, giving rise to different sizes of channels along the crystallographic *a* axis (Figure 4c). Adjacent independent networks with identical connectivity are interlocked with each other with the uncoordinated oxygen atoms of μ_3-croconate ligands inserting into the vacant space of the large rectangular box, completing a three-dimensional architecture (Figure 3). Two hydrogen bonds are found between the coordinated oxygen atoms of the croconate ligands and coordinated water ($O(11)\cdots O(6)_i$ = 2.812 Å and $O(11)\cdots O(3)_{ii}$ = 2.834 Å; i, $x, -1 + y, z$; ii, $0.5 - x, -0.5 + y, 1.5 - z$), which provide the extra intra- and intermolecular interactions in the stabilization of the three-dimensional network.

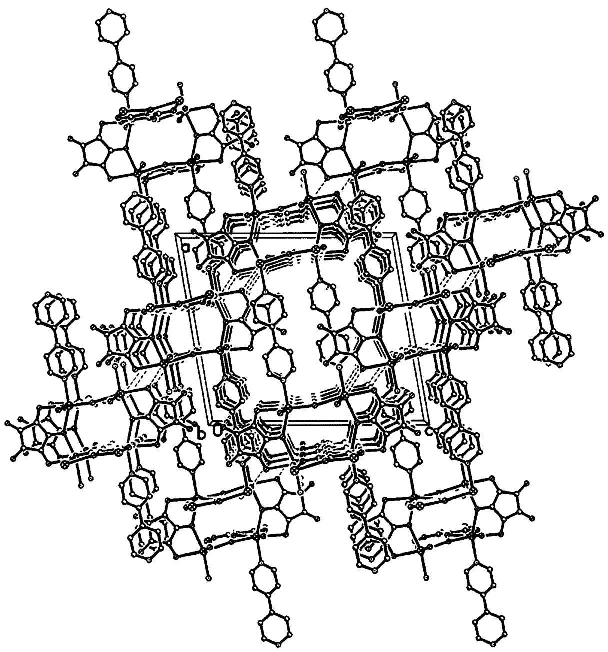

Figure 3. Three-dimensional network of $\{[Cd_2(C_5O_5)_2(4,4'\text{-bpy})(H_2O)]\cdot H_2O\}_\infty$ viewed along the *b*-axis.

Thermogravimetric and Powder X-ray Diffraction (PXRD) Analysis. To assess the thermal stability and its

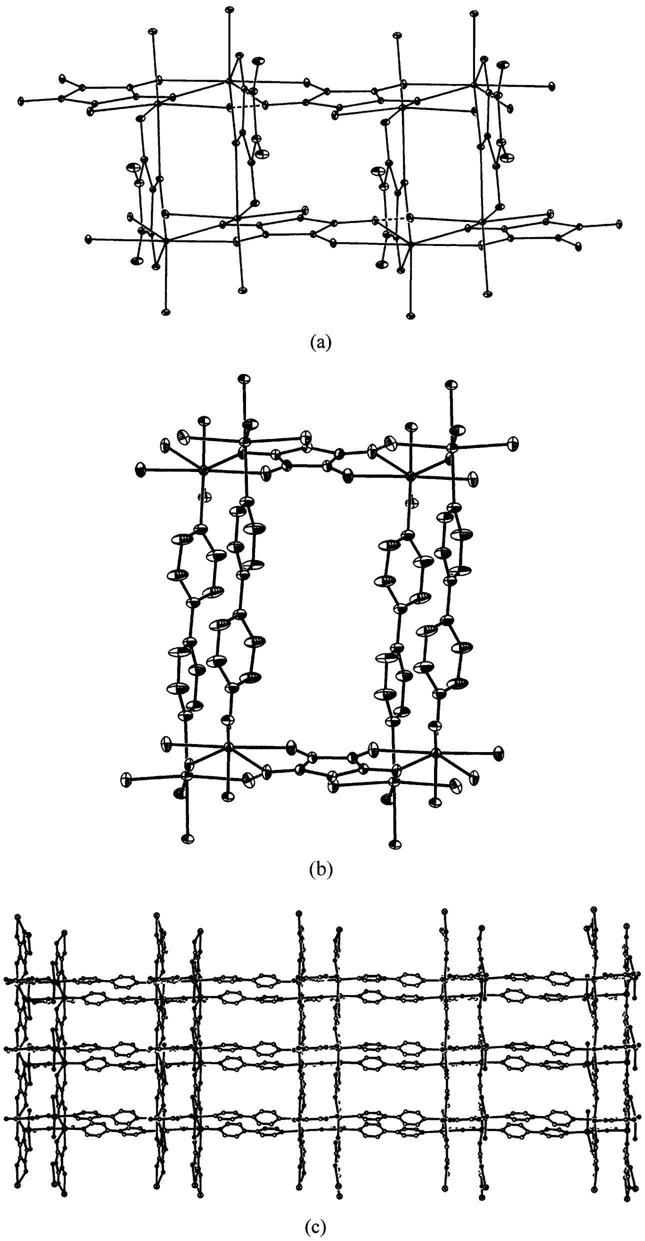

Figure 4. (a) Small rectangular box formed via the connectivity between Cd(II) ions and μ_3- and μ_5-croconates. (b) Large rectangular box formed via the connectivity between the Cd(II) ions and 4,4′-bpy and μ_5-croconates. Dotted lines represent the hydrogen-bonding interactions (O(11)···O(3)). (c) A two-dimensional layered architecture formed by two rectangular boxes extended along the [100] and [010] directions.

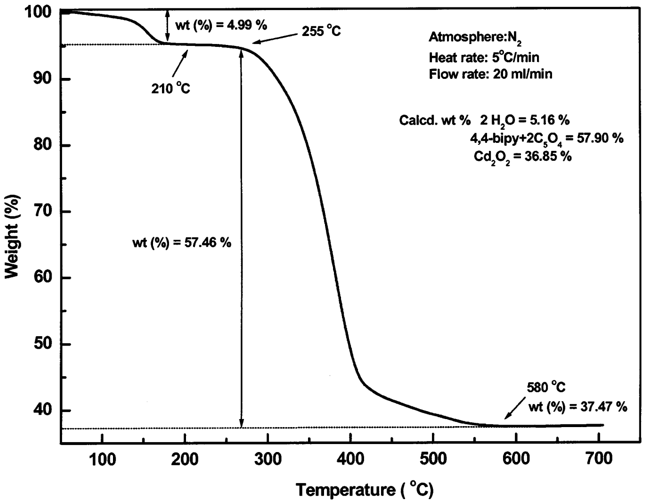

Figure 5. Thermogravimetric analysis of $\{[Cd_2(C_5O_5)_2(4,4'\text{-bpy})(H_2O)]\cdot H_2O\}_\infty$.

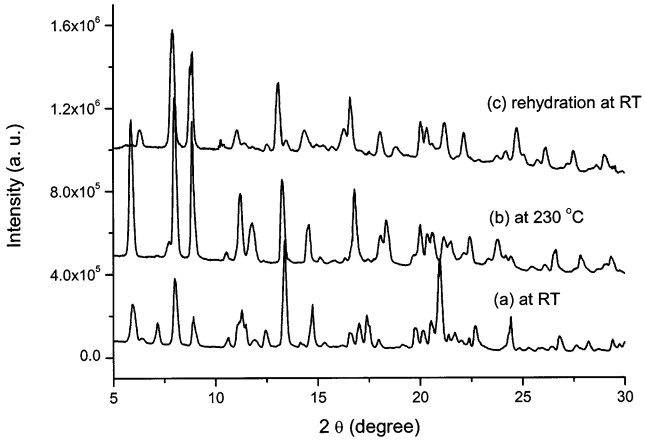

Figure 6. Variable-temperature synchrotron powder XRD measurements ($\lambda = 1.3268$ Å). The temperature ramps to 230 °C and back to 25 °C for rehydration. The baseline for each temperature was shifted for clarity.

structural variation as a function of the temperature, thermogravimetric analysis (TGA) was performed on single-phase polycrystalline samples. During the heating process, the TGA analysis (Figure 5) shows that the first weight loss of 4.99% (calcd 5.16%), corresponding to the loss of crystallized and coordinated water molecules, occurred in the range of approximately 50−175 °C. In the temperature range of approximately 180−255 °C, the complex is stable without any weight loss. On further heating, these samples decomposed at approximately 260−580 °C with loss of 57.46% (calcd 57.90%) corresponding to the loss of 4,4′-bipyridine and croconate, to yield the cadmium oxide. The XRD patterns of the solids at room temperature and 230 °C and the solids rehydrated at room temperature are shown in Figure 6 to demonstrate the stability of guest removal/readsorption. Compared to solids at room temperature, the dehydrated solid obtained by heating to 230 °C and rehydrated solid after being immersed in water for 2 h both show similar XRD patterns. This result is consistent with TGA measurement and suggests that the two-dimensional framework is preserved during dehydration and the de- and rehydration processes are reversible.

Conclusions

In theis paper, we have presented the synthesis, crystal structure, and thermal stability studies of a metal-coordination polymer, $\{[Cd_2(C_5O_5)_2(4,4'\text{-bpy})(H_2O)]\cdot(H_2O)\}_\infty$. Two crystallographically independent Cd(II) ions are found with distorted pentagonal bipyramidal and octahedral coordination spheres. It is interesting to note that 4,4′-bpy and croconate ligands, which adopt two bridging modes as a bis-bidentate three-adjacent (μ_3) bridging mode and a new bidentate/three-adjacent (μ_5) bridging mode, are both used in the construction of two rectangular boxes as the building units. A two-dimensional layered framework is formed via the two face-shared rectangular boxes.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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