Pillared, 3D Metal-Organic Frameworks with Rectangular Channels. Synthesis and Characterization of Coordination Polymers Based on Tricadmium Carboxylates

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Hydro(solvo)thermal reactions between cadmium(II) perchlorate and 4-pyridinecarboxaldehyde in the presence of various guest molecules have resulted in a series of 3-D coordination polymers based on tricadmium carboxylates $[Cd_6(isonicotinate)_{10}(H_2O)_2](ClO_4)_2(EtOH)_4(H_2O)_4$, **1**, $[Cd_3(isonicotinate)_5(EtOH)](ClO_4)(EtOH)(4\text{-nitroaniline})_{0.5}$, **2**, and $[Cd_6(isonicotinate)_{11}](ClO_4)(EtOH)_2(H_2O)_2(4\text{-cyanopyridine})_{0.5}$, **3**. X-ray single crystal structure determinations show that they exhibit similar pillared, 3D framework structures based on tricadmium carboxylate building blocks. Rectangular channels are clearly present in these polymeric networks and are occupied by perchlorate anions and disordered guest molecules. Quantitative NMR and X-ray powder diffraction studies and thermogravimetric analyses (TGA) reveal that these coordination networks are capable of accommodating different guest molecules. More significantly, the guest molecules can be readily removed via evacuation to result in nanoporous polymeric coordination networks retaining the framework structures of the pristine solids. Crystal data for **1**: monoclinic space group $P2_1/n$, $a = 19.041(1)$ Å, $b = 23.654(1)$ Å, $c = 21.568(1)$ Å, $\beta = 95.440(1)°$, and $Z = 4$. Crystal data for **2**: triclinic space group $P\bar{1}$, $a = 12.050(1)$ Å, $b = 12.277(1)$ Å, $c = 19.103(1)$ Å, $\alpha = 91.669(1)°$, $\beta = 96.850(1)°$, $\gamma = 117.945(1)°$, and $Z = 2$. Crystal data for **3**: monoclinic space group $P2_1/n$, $a = 19.038(1)$ Å, $b = 23.834(1)$ Å, $c = 21.756(1)$ Å, $\beta = 97.580(1)°$, and $Z = 4$.

Introduction

The ability to construct polymeric metal−organic coordination networks with interesting structures and potentially useful functions has been clearly established in recent years.[1−8] The synthesis of nanoporous metal−organic frameworks has been particularly fruitful; these zeolitic solids can be potentially exploited for size- and functional-group-selective separation and catalysis.[5−8] Despite significant progress in the synthesis of numerous polymeric metal−organic coordination networks in recent years, there is yet no generally successful approach to predict and control the structures of coordination networks assembled from a particular combination of metal centers and bridging ligands. Over the past few years, we have focused our efforts on the rational synthesis of polar solids using unsymmetrical rigid bridging ligands such as pyridinecarboxylates.[9−11] In the course of this research, we have discovered that nanoporous cadmium coordination networks can be obtained by reactions of Cd(II) salt with 4-cyanopyridine in the presence of ethanol or pyrazine guest molecules under hydro(solvo)thermal conditions.[12] Under these conditions, 4-cyanopyridine slowly hydrolyzes to form isonicotinic acid which acts as the bridging ligand for 3D coordination networks based on interpenetrated diamondoid structures in its deprotonated form. In the present work, we have examined hydro(solvo)thermal reactions of cadmium(II) perchlorate and 4-pyridinecarboxyaldehyde in the presence of different guest molecules. The use of 4-pyridinecarboxyaldehyde as the precursor to the isonicotinate bridging ligand has led to Cd(II) coordination polymers with pillared, 3D Cd(II) framework structures based on tricadmium carboxylate building blocks which are entirely different from the interpenetrated diamondoid networks reported earlier.[12] These pillared, 3D Cd(II) coordination networks are capable of accommodating different guest molecules. Herein we wish to report the synthesis and X-ray structures of three pillared, 3D Cd(II) coordination networks $[Cd_6(isonicotinate)_{10}(H_2O)_2](ClO_4)_2(EtOH)_4(H_2O)_4$, **1**, $[Cd_3(isonicotinate)_5(EtOH)](ClO_4)(EtOH)(4\text{-nitroaniline})_{0.5}$, **2**, and $[Cd_6(isonicotinate)_{11}](ClO_4)(EtOH)_2(H_2O)_2(4\text{-cyanopyridine})_{0.5}$, **3**, and the generation of nanoporous solids via the removal of guest molecules from **1**−**3**.

Experimental Section

Materials and Methods. Cadmium (II) perchlorate hexahydrate, pyridine-4-carboxaldehyde, 4-nitroaniline, 4-cyanopyridine, and

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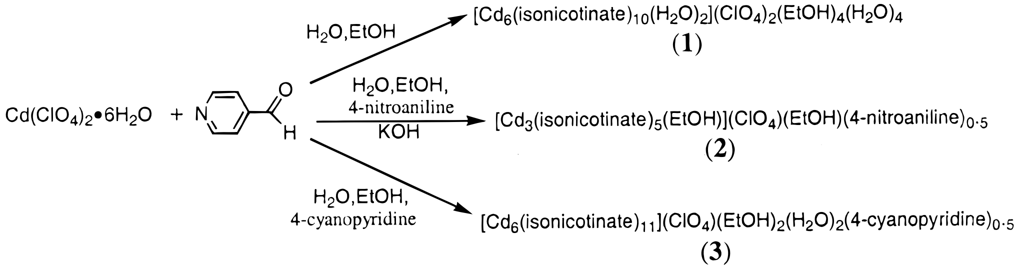
Table 1. Data for the X-ray Diffraction of **1**, **2**, and **3**[a]

chem formula	$Cd_6C_{68}H_{76}Cl_2N_{10}O_{38}$, **1**	$Cd_3C_{37}H_{35}ClN_6O_{17}$, **2**	$Cd_6C_{73}H_{62}ClN_{12}O_{30}$, **3**
cryst syst	monoclinic	triclinic	monoclinic
a, Å	19.0412(3)	12.050(1)	19.038(1)
b, Å	23.6540(4)	12.277(1)	23.834(1)
c, Å	21.5681(3)	19.103(1)	21.756(1)
α, deg	90	91.669(1)	90
β, deg	95.440(1)	96.850(1)	97.580(1)
γ, deg	90	117.945(1)	90
V, Å^3	9670.5(3)	2467.09(1)	9785.5(3)
Z	4	2	4
FW	2386.69	1208.36	2297.20
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
T, °C	−75 (1)	−75 (1)	25(1)
λ (Mo Kα), Å	0.710 73	0.710 73	0.710 73
ρ_{calcd}, g/cm^3	1.64	1.63	1.56
μ, cm^{-1} (Mo Kα)	14.4	14.1	13.8
min and max residual density, e/Å^3	−2.63, 3.70	−2.93, 2.86	−0.80, 1.18
R1	0.088	0.108	0.051
$_wR2$	0.255	0.308	0.179
goodness of fit	1.07	1.84	1.06

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $_wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; GOF $= [\Sigma[w(F_o^2 - F_c^2)^2]/(\text{no. of reflections} - \text{no. of parameters})]^{1/2}$.

Scheme 1



Na_2(EDTA) were purchased from Aldrich and used without further purification. *Caution! $Cd(ClO_4)_2{\cdot}6H_2O$ is potentially explosive and should be used with care!* Thermogravimetric analysis was performed under nitrogen at a scan speed of 10 °C/min on a Shimadzu TGA-50 TG analyzer. ^{1}H NMR spectra were taken on a Varian Inova 400 MHz spectrometer with a relaxation time (T_1) of 5 s. Infrared spectra were measured from KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. XRPD data were recorded on a Rigaku RU300 diffractometer at 60 kV, 300 mA for Cu Kα (λ = 1.5418 Å), with a scan speed of 2 deg/min and a step size of 0.02° in 2θ. The calculated XRPD patterns were produced using the SHEXTL-XPOW program and single-crystal reflection data.

Synthesis of [Cd_6(isonicotinate)$_{10}$(H_2O)$_2$](ClO_4)$_2$(EtOH)$_4$(H_2O)$_4$, 1. A mixture of $Cd(ClO_4)_2{\cdot}6H_2O$ (0.210 g, 0.5 mmol) and 4-pyridinecarboxaldehyde (0.107 g, 1.0 mmol) was thoroughly mixed with ethanol (0.5 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 110 °C. After 48 h of heating, colorless rectangular crystals were obtained. Yield: 0.0641 g (32.2%). Anal. Calcd for $Cd_6C_{68}H_{76}Cl_2N_{10}O_{38}$: C, 34.2; H, 3.21; N, 5.87; Found: C, 35.0; H, 2.90; N, 5.63. IR (cm^{-1}): 3425 (m), 2968 (w), 1630 (s), 1551 (s), 1398 (s), 1229 (w), 1103 (m), 1057 (m), 1016 (m), 865 (w), 772 (m), 709 (m), 687 (m), 623 (w).

Synthesis of [Cd_3(isonicotinate)$_5$(ClO_4)(EtOH)][(4-nitroaniline)$_{0.5}$-(EtOH)], 2. A mixture of $Cd(ClO_4)_2{\cdot}6H_2O$ (0.210 g, 0.5 mmol), 4-pyridinecarboxaldehyde (0.107 g, 1.0 mmol), and 4-nitroaniline (0.135 g, 1.0 mmol) was thoroughly mixed with ethanol (0.5 mL), deionized water (0.1 mL), and 1 M KOH (0.1 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 110 °C. After 48 h of heating light yellow rectangular crystals were obtained. Yield: 0.117 g (58.2%). Anal. Calcd for $Cd_3C_{37}H_{35}ClN_6O_{17}$: C, 36.8; H, 2.92; N, 6.95; Found: C, 37.1; H, 3.06; N, 7.41. IR (cm^{-1}): 3366 (m), 1630 (s), 1553 (s), 1498 (m), 1418 (sh), 1398 (s), 1330 (sh), 1311 (s), 1228 (w), 1213 (w), 1110 (m), 1058 (m), 1016 (m), 864 (w), 842 (w), 772 (m), 708 (m), 686 (m), 624 (w).

Synthesis of [Cd_6(isonicotinate)$_{11}$(ClO_4)][(4-cyanopyridine)$_{0.5}$-(EtOH)$_2$(H_2O)$_2$], 3. A mixture of $Cd(ClO_4)_2{\cdot}6H_2O$ (0.210 g, 0.5 mmol), 4-pyridinecarboxaldehyde (0.107 g, 1.0 mmol), and 4-cyanopyridine (0.104 g, 1.0 mmol) was thoroughly mixed with ethanol (0.5 mL) and deionized water (0.1 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 90 °C. After 48 h of heating colorless rectangular crystals were obtained. Yield: 0.0759 g (39.7%). IR (cm^{-1}): 3421 (m), 2967 (m), 1622 (s), 1552 (s), 1403 (sh), 1397 (s), 1229 (w), 1095 (m), 1057 (m), 1016 (m), 864 (w), 844 (w), 772 (m), 708 (m), 687 (s), 624 (m), 560 (w).

Quantitative NMR Experiments. A mixture of disodium ethylenediamine tetraacetic acid (0.0085 g, 0.0229 mmol) and a freshly prepared and ground sample of **1** (0.0077 g, 0.0064 mmol) was added to a clean and dry NMR tube. Absolute methanol (0.0125 g, 0.3910 mmol) and deuterium oxide (0.4 mL) were added and the sealed NMR tube was sonicated at room temperature for a period of 1 h. The amount of ethanol in **1** was determined from the ratio of the integral of the methanol singlet at $\sim\delta$ 3.3 vs the integral of the ethanol triplet at $\sim\delta$ 1.0. The experiment revealed that **1** contained ~4.4 mol of ethanol per formula unit. NMR quantification of the guest molecules (except water) for **2** and **3** was carried out in a similar fashion. The experiments revealed that **2** contained approximately 0.43 mol of 4-nitroaniline and 1.9 mol of ethanol per formula unit and **3** contained approximately 0.56 mol of 4-cyanopyridine and 2.2 mol of ethanol per formula unit, respectively.

Removal of Guest Molecules. A freshly ground sample of **1** (272 mg, 0.23 mmol) was subjected to a vacuum at 55 °C. After 24 h, **1** exhibited a weight loss of 30.0 mg (11.03%), equivalent to the loss of four ethanol molecules and four water molecules per formula unit (calculated 29.4 mg, 10.74%). Evacuation of **2** and **3** were performed

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for **1**, **2**, and **3**[a,b]

1			**2**			**3**		
atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Cd1	O1	2.231(9)	Cd1	O1	2.277(10)	Cd1	O2	2.333(5)
Cd1	O5	2.246(8)	Cd1	O5	2.232(10)	Cd1	O13	2.241(6)
Cd1	O7	2.277(8)	Cd1	O8	2.435(10)	Cd1	O17	2.233(7)
Cd1	O9	2.423(7)	Cd1	O9	2.328(10)	Cd1	O20	2.319(5)
Cd1	N6	2.339(8)	Cd1	O11	2.392(19)	Cd1	N11_c	2.394(8)
Cd1	N7_d	2.358(9)	Cd1	N2_a	2.349(16)	Cd1	N8_f	2.355(8)
Cd2	O2	2.255(6)	Cd2	O4	2.272(12)	Cd2	O4	2.442(6)
Cd2	O3	2.224(7)	Cd2	O6	2.254(11)	Cd2	O6	2.236(7)
Cd2	O8	2.304(7)	Cd2	O8	2.391(10)	Cd2	O8	2.227(7)
Cd2	O9	2.317(6)	Cd2	O10	2.301(8)	Cd2	O11	2.269(6)
Cd2	O22	2.349(11)	Cd2	N1_g	2.325(13)	Cd2	N1	2.345(8))
Cd2	N3_b	2.330(10)	Cd2	N4_j	2.352(10)	Cd2	N7_d	2.356(9)
Cd3	O4	2.271(7)	Cd3	O2	2.258(12)	Cd3	O3	2.295(6)
Cd3	O6	2.259(7)	Cd3	O3	2.275(11)	Cd3	O5	2.251(7)
Cd3	O8	2.385(7)	Cd3	O7	2.279(10)	Cd3	O10	2.254(7)
Cd3	O10	2.291(8)	Cd3	O9	2.387(9)	Cd3	O12	2.393(6)
Cd3	N10_a	2.326(10)	Cd3	N3_h	2.345(13)	Cd3	N10_a	2.337(8)
Cd3	N8_e	2.328(9)	Cd3	N5_i	2.324(12)	Cd3	N9_e	2.331(9)

1				**2**				**3**			
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O1	Cd1	O5	175.9(3)	O1	Cd1	O5	161.6(4)	O2	Cd1	O13	96.1(2)
O1	Cd1	O7	95.0(3)	O1	Cd1	O8	81.4(4)	O2	Cd1	O17	93.0(2)
O1	Cd1	O9	87.4(3)	O1	Cd1	O9	98.9(4)	O2	Cd1	O20	83.20(19)
O1	Cd1	N6	88.0(3)	O1	Cd1	O11	93.9(8)	O2	Cd1	N11_c	84.1(2)
O1	Cd1	N7_d	90.0(3)	O1	Cd1	N2_a	81.4(5)	O2	Cd1	N8_f	166.8(3)
O5	Cd1	O7	88.7(3)	O5	Cd1	O8	89.9(4)	O13	Cd1	O17	170.0(3)
O5	Cd1	O9	90.1(3)	O5	Cd1	O9	95.7(4)	O13	Cd1	O20	87.2(2)
O5	Cd1	N6	88.6(3)	O5	Cd1	O11	99.0(8)	O13	Cd1	N11_c	89.6(3)
O5	Cd1	N7_d	92.3(3)	O5	Cd1	N2_a	86.7(5)	O13	Cd1	N8_f	84.5(3)
O7	Cd1	O9	101.9(2)	O8	Cd1	O9	80.7(3)	O17	Cd1	O20	97.9(2)
O7	Cd1	N6	171.1(3)	O8	Cd1	O11	162.5(7)	O17	Cd1	N11_c	87.4(3)
O7	Cd1	N7_d	81.4(3)	O8	Cd1	N2_a	111.3(4)	O17	Cd1	N8_f	85.6(3)
O9	Cd1	N6	86.6(3)	O9	Cd1	O11	83.4(7)	O20	Cd1	N11_c	166.5(2)
O9	Cd1	N7_d	176.0(3)	O9	Cd1	N2_a	167.8(4)	O20	Cd1	N8_f	110.0(3)
N6	Cd1	N7_d	90.2(3)	O11	Cd1	N2_a	84.4(7)	N8_f	Cd1	N11_c	82.7(3)
O2	Cd2	O3	167.4(3)	O4	Cd2	O6	173.7(4)	O4	Cd2	O6	91.0(2)
O2	Cd2	O8	95.4(2)	O4	Cd2	O8	94.9(4)	O4	Cd2	O8	86.3(2)
O2	Cd2	O9	94.9(2)	O4	Cd2	O10	90.8(4))	O4	Cd2	O11	101.4(2)
O2	Cd2	O22	89.9(4)	O4	Cd2	N1_g	89.6(5)	O4	Cd2	N1	86.7(2)
O2	Cd2	N3_b	85.4(3)	O4	Cd2	N4_j	86.1(4)	O4	Cd2	N7_d	174.1(2)
O3	Cd2	O8	97.1(3)	O6	Cd2	O8	89.1(4)	O6	Cd2	O8	175.2(2)
O3	Cd2	O9	85.9(3)	O6	Cd2	O10	93.5(4)	O6	Cd2	O11	89.0(3)
O3	Cd2	O22	92.2(4)	O6	Cd2	N1_g	86.6(5)	O6	Cd2	N1	87.8(3)
O3	Cd2	N3_b	82.5(3)	O6	Cd2	N4_j	88.9(4)	O6	Cd2	N7_d	93.0(3)
O8	Cd2	O9	84.0(2)	O8	Cd2	O10	97.7(3)	O8	Cd2	O11	95.3(2)
O8	Cd2	O22	82.9(3)	O8	Cd2	N1_g	175.3(4)	O8	Cd2	N1	88.1(2)
O8	Cd2	N3_b	166.8(3)	O8	Cd2	N4_j	90.0(3)	O8	Cd2	N7_d	89.4(3)
O9	Cd2	O22	166.5(3)	O10	Cd2	N1_g	80.7(4)	O11	Cd2	N1	171.4(2)
O9	Cd2	N3_b	109.1(3)	O10	Cd2	N4_j	172.0(4)	O11	Cd2	N7_d	83.0(3)
O22	Cd2	N3_b	83.9(4)	N1_g	Cd2	N4_j	91.9(4)	N1	Cd2	N7_d	89.1(3)
O4	Cd3	O6	175.4(3)	O2	Cd3	O3	177.7(4)	O3	Cd3	O5	91.0(2)
O4	Cd3	O8	92.3(2)	O2	Cd3	O7	89.8(4)	O3	Cd3	O10	88.3(2)
O4	Cd3	O10	88.1(3)	O2	Cd3	O9	92.0(4)	O3	Cd3	O12	94.2(2)
O4	Cd3	N10_a	93.1(3)	O2	Cd3	N3_h	86.6(4)	O3	Cd3	N10_a	176.3(3)
O4	Cd3	N8_e	85.5(3)	O2	Cd3	N5_i	94.3(4)	O3	Cd3	N9_e	87.3(3)
O6	Cd3	O8	92.2(3)	O3	Cd3	O7	88.1(4)	O5	Cd3	O10	176.7(2)
O6	Cd3	O10	91.8(3)	O3	Cd3	O9	89.2(4)	O5	Cd3	O12	92.0(2)
O6	Cd3	N10_a	86.8(3)	O3	Cd3	N3_h	92.3(4)	O5	Cd3	N10_a	86.5(2)
O6	Cd3	N8_e	89.9(3)	O3	Cd3	N5_i	87.7(4)	O5	Cd3	N9_e	91.3(3)
O8	Cd3	O10	94.8(2)	O7	Cd3	O9	99.4(3)	O10	Cd3	O12	91.3(2)
O8	Cd3	N10_a	88.0(3)	O7	Cd3	N3_h	85.6(4)	O10	Cd3	N10_a	94.0(2)
O8	Cd3	N8_e	177.7(3)	O7	Cd3	N5_i	173.5(5)	O10	Cd3	N9_e	85.4(3)
O10	Cd3	N10_a	176.9(3)	O9	Cd3	N3_h	174.9(3)	O12	Cd3	N10_a	88.6(2)
O10	Cd3	N8_e	85.8(3)	O9	Cd3	N5_i	85.6(4)	O12	Cd3	N9_e	176.3(3)
N8_e	Cd3	N10_a	91.4(3)	N3_h	Cd3	N5_i	89.6(4)	N9_e	Cd3	N10_a	90.0(3)

[a] Symmetry operations: a = $-1 + x, y, z$; b = $^{1}/_{2} - x, -^{1}/_{2} + y, ^{1}/_{2} - z$; c = $-^{1}/_{2} - x, -^{1}/_{2} + y, ^{3}/_{2} - z$; d = $-^{1}/_{2} + x, ^{1}/_{2} - y, -^{1}/_{2} + z$; e = $-^{1}/_{2} + x, ^{1}/_{2} - y, ^{1}/_{2} + z$; f = $^{1}/_{2} - x, -^{1}/_{2} + y, ^{3}/_{2} - z$; g = $x, -1 + y, z$; h = $1 + x, 1 + y, z$; i = $-1 - x, -1 - y, -z$; j = $-1 - x, -1 - y, 1 - z$. [b] Bond distances and angles of only one of the two crystallographically independent tricadmium carboxylate moieties are listed.

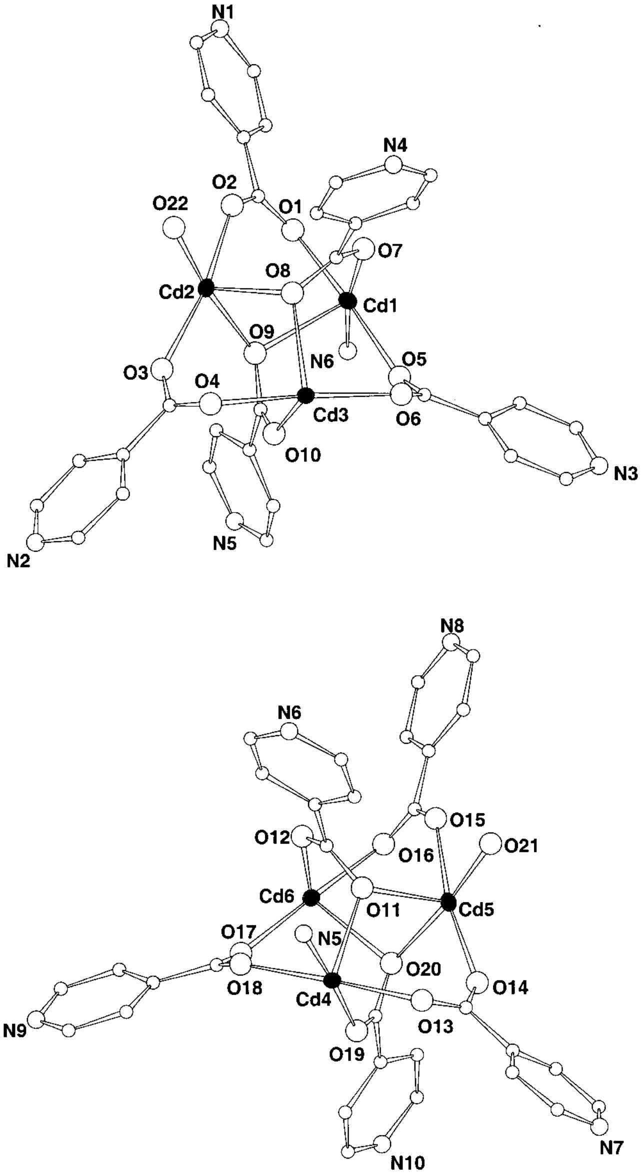


Figure 1. View of the asymmetric unit in **1**. The dark ellipsoids represent the cadmium atoms, while the circles with increasing sizes represent C, N, and O atoms, respectively. For clarity, included guest molecules and perchlorate anions are omitted. The asymmetric unit has been broken up into two $[Cd_3(isonicotinate)_5(H_2O)]^+$ building blocks. N5 and N6 have been duplicated to show the connectivity between the two tricadmium building blocks.

similarly. A freshly ground sample of **2** (85.1 mg, 0.037 mmol) was subjected to a vacuum at 55 °C. After 24 h, **2** exhibited a weight loss of 9.8 mg (7.0%), equivalent to the loss of 2 molecules of ethanol per formula unit (calculated 10.8 mg, 7.5%). A freshly ground sample of **3** (141 mg, 0.12 mmol) was subjected to a vacuum at 55 °C. After 24 h, **3** exhibited a weight loss of 6.1 mg (7.2%), equivalent to the loss of two ethanol molecules, two water molecules, and one-half molecule of 4-cyanopyridine per formula unit (calculated 6.7 mg, 7.8%).

X-ray Data Collections and Structure Determinations. Data collection for **1** (**2**) was carried out with a crystal of dimensions of 0.12 × 0.16 × 0.32 mm (0.12 × 0.14 × 0.16 mm) on a Siemens SMART system equipped with a CCD detector using MoKα radiation. Of the 23 018 (10 162) reflections measured, 14 859 (7326) reflections with $I > 2\sigma(I)$ were used in structure solution and refinement for **1** (**2**). The structures were solved by direct method using SHELX-TL.[13]

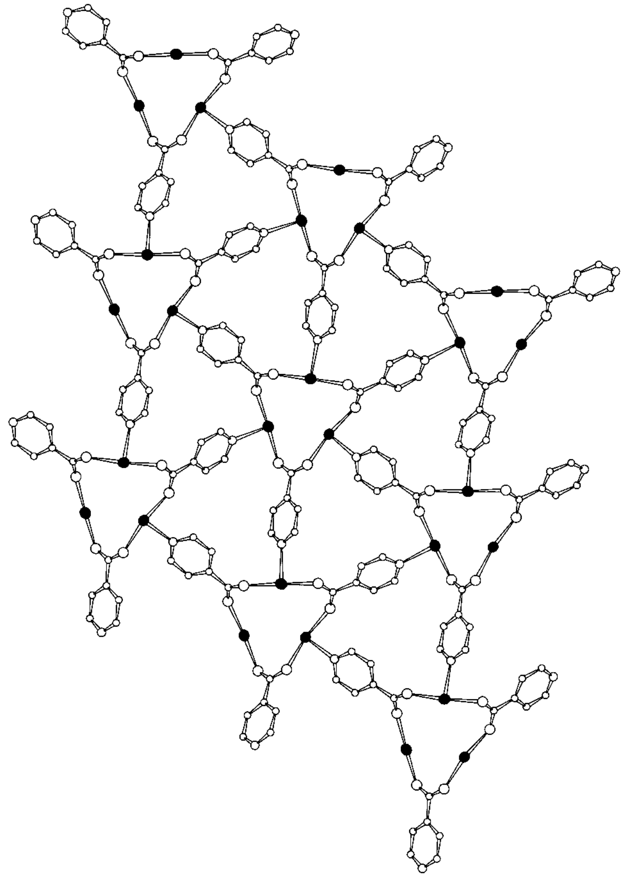


Figure 2. View of the *pseudo*-trigonal sheet in **1** lying in the *bc*-plane formed by cadmium centers and *exo*-tridentate isonicotinate groups. The dark ellipsoids represent the cadmium centers, while the circles with increasing sizes represent C, N, and O, respectively.

All of the non-hydrogen atoms of the host polymeric network of $\{[Cd_3(isonicotinate)_5(H_2O)]^+\}_\infty$ and chlorine atoms in **1** were refined by full-matrix least-squares methods using anisotropic displacement parameters. All of the guest molecules and perchlorate oxygen atoms in **1** are disordered and have been refined isotropically; their positions are only approximate.

All the non-hydrogen atoms of the host polymeric network in **2** were refined by full-matrix least-squares methods using anisotropic displacement parameters. The guest molecules and perchlorate anions in **2** are highly disordered and could not be readily located in electron density maps; their identities were inferred from IR, TGA, and quantitative NMR studies. The hydrogen atoms of the isonicotinate groups in both **1** and **2** have been located by geometric placing.

Data collection for **3** was carried out on an Enraf-Nonius CAD4-Turbo diffractometer equipped with MoKα radiation using the Nonius EXPRESS program.[14] Of the 14 783 reflections measured, 9375 reflections with $I > 2\sigma(I)$ were used in structure solution and refinement. The structure was solved by direct method using SHELX-TL.[13] All the non-hydrogen atoms of the host polymeric network and chlorine atoms were refined by full-matrix least-squares methods using anisotropic displacement parameters. Perchlorate anions have been modeled with two orientations with partial occupancies. All the guest molecules and perchlorate oxygen atoms were refined isotropically. The hydrogen atoms of the isonicotinate groups have been located by geometric placing. Experimental details for X-ray data collections of **1**−**3** are tabulated in Table 1. Selected bond distances and angles for **1**−**3** are listed in Table 2. All drawings were produced using either the Oxford University program CAMERON[15] or the SHELX-TL (XP) package.[13]

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(13) SHELX-TL Version 5.1, Bruker Analytical X-ray Systems, Inc., Madison, WI., 1997.

(14) Straver, L. H. *CAD4-EXPRESS*; Enraf-Nonius: Delft, The Netherlands, 1992.

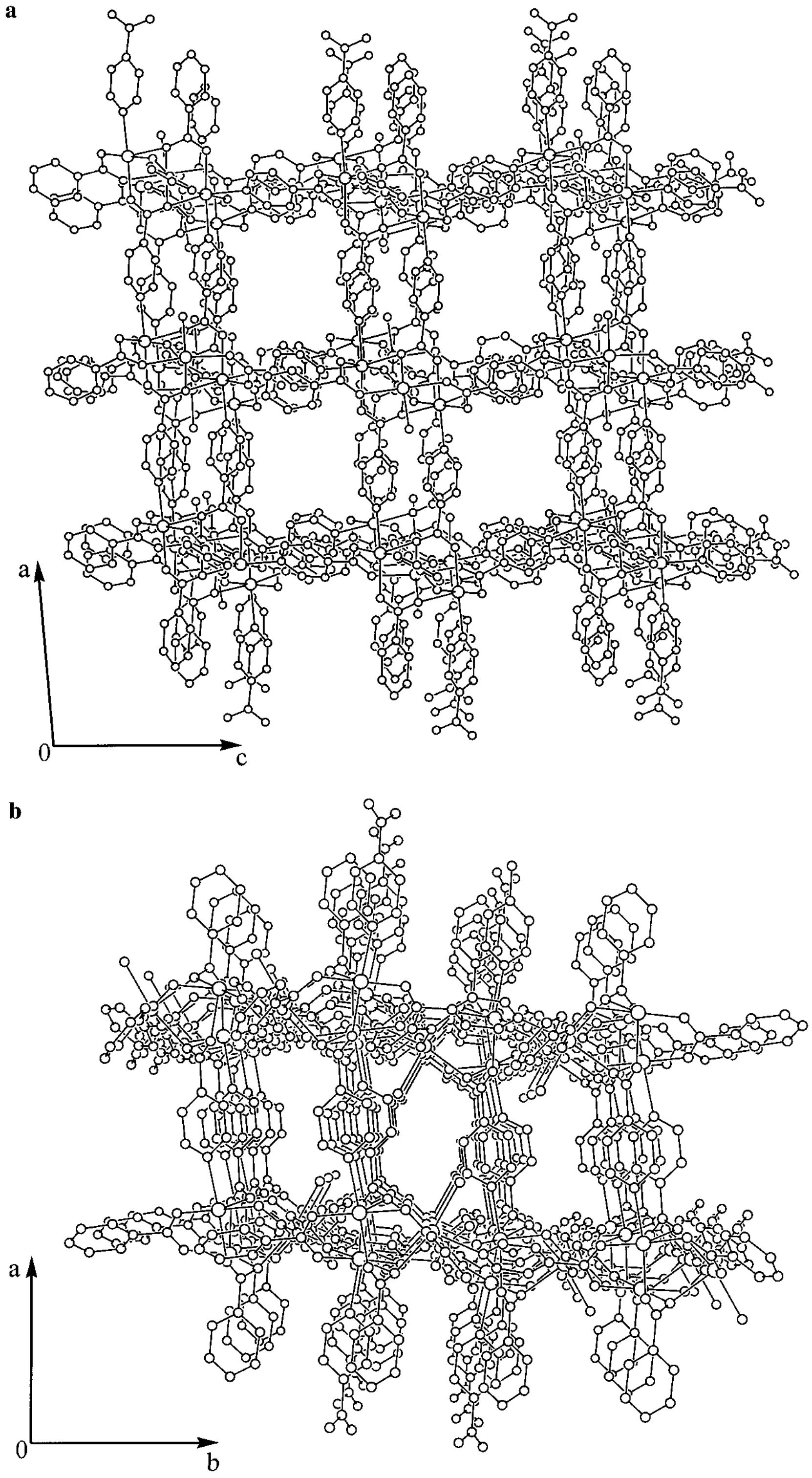

Figure 3. View of the framework in **1** as viewed (a) down the *b*-axis and (b) down the *c*-axis. Included ethanol, water, and perchlorate molecules are omitted for clarity.

Results and Discussion

Synthesis and Characterization. Compound **1** was obtained by a hydro(solvo)thermal reaction between $Cd(ClO_4)_2{\cdot}6H_2O$ and 4-pyridinecarboxaldehyde in a mixture of ethanol and water at 110 °C (Scheme 1). The IR spectrum of **1** shows peaks at 1551 and 1398 cm^{-1} due to the asymmetric and symmetric carboxylate stretches, respectively.[16] The absence of an aldehyde carbonyl peak (1680−1720 cm^{-1}) indicates that 4-pyridinecarboxaldehyde has been oxidized to isonicotinate groups under the reaction conditions.[17] The IR spectrum of **1** also shows broad peaks at 1000−1103 cm^{-1} due to perchlorate Cl−O stretches.

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(15) Watkin, D. J.; Prout, C. K.; Pearce, L. J. *CAMERON*; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1996.

(16) Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic Press: New York, 1983.

(17) We believe that perchlorate anions act as oxidants in this hydro(solvo)-thermal reaction. See also: Xiong, R. G.; Wilson, S. R.; Lin, W. *J. Chem. Soc., Dalton Trans.* **1998**, 4089−4090.

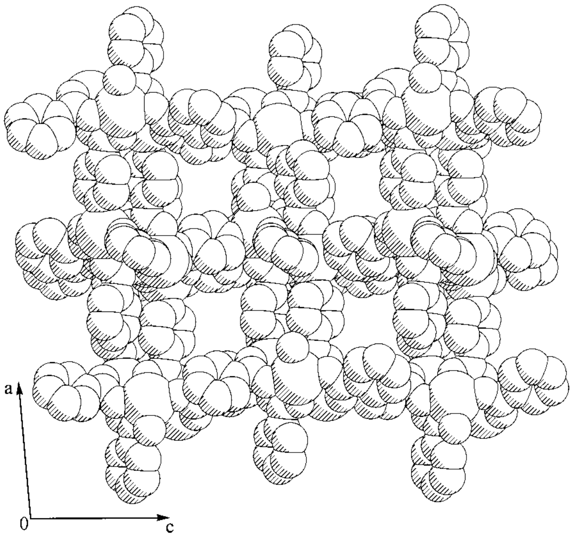

Figure 4. Space-filling model of **1** as viewed along the *b*-axis. Cavities are occupied by water, ethanol, and perchlorate molecules, which have been removed for clarity.

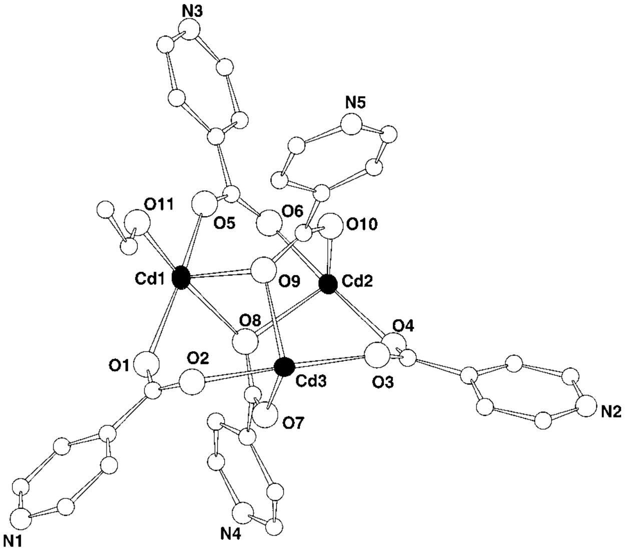

Figure 5. View of the asymmetric unit in **2**. The dark ellipsoids represent the cadmium centers, while the circles with increasing sizes represent C, N, and O, respectively. For clarity, included guest molecules and perchlorate anions are omitted.

The formulation of **1** has been established via single-crystal X-ray diffraction, quantitative NMR, TGA, and elemental analyses. Although the host polymeric network of $\{[Cd_3(isonicotinate)_5(H_2O)]^+\}_\infty$ in **1** is easily established from an X-ray structure analysis, the guest molecules and even the perchlorate anions cannot be accurately located owing to their disordered nature. We have thus carried out quantitative NMR and TGA studies to characterize the guest molecules and perchlorate anions. Quantitative NMR experiments using methanol as an internal standard revealed that **1** contained approximately 4.4 mol of ethanol per formula unit. The water content cannot be determined due to interference from residual water in NMR solvents. TGA analysis of **1** revealed a weight loss of 11.91% by 200 °C, corresponding to the loss of 4 mol of ethanol and 6 mol of water per formula unit (calculated 12.23%). **1** thus has a formula of $[Cd_6(isonicotinate)_{10}(H_2O)_2](ClO_4)_2(EtOH)_4(H_2O)_4$, which is further substantiated by elemental analysis results.

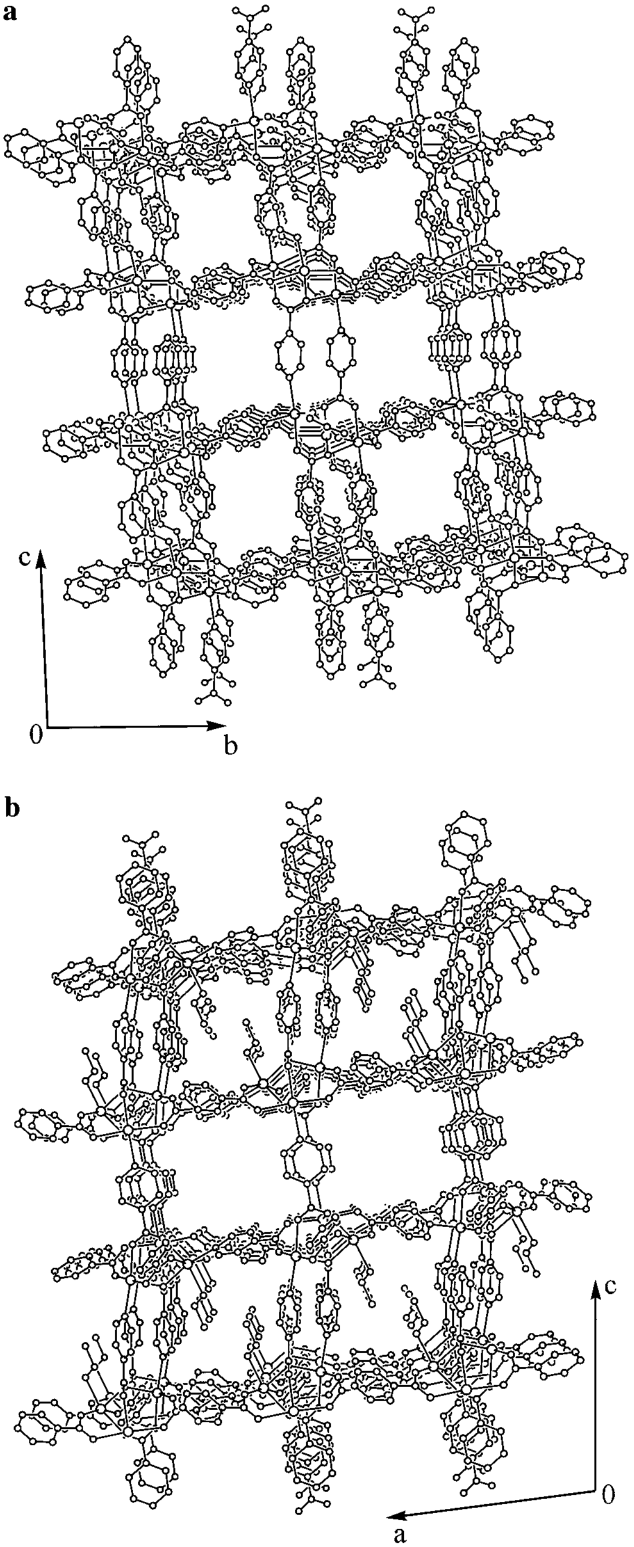

Figure 6. View of the framework in **2** as viewed (a) down the *a*-axis and (b) down the *b*-axis. Included ethanol and 4-nitroaniline molecules and perchlorate anions are omitted for clarity.

Compound **2** was obtained by a hydro(solvo)thermal reaction between $Cd(ClO_4)_2\cdot 6H_2O$ and 4-pyridinecarboxyaldehyde in a mixture of ethanol, water, potassium hydroxide, and 4-nitroaniline at 110 °C (Scheme 1). The host polymeric network of $\{[Cd_3(isonicotinate)_5(EtOH)]^+\}_\infty$ in **2** was established by a single-crystal X-ray diffraction study. The IR spectrum of **2** indicated the presence of isonicotinate and perchlorate groups. Furthermore, strong peaks at 1330 and 1311 cm^{-1} can be

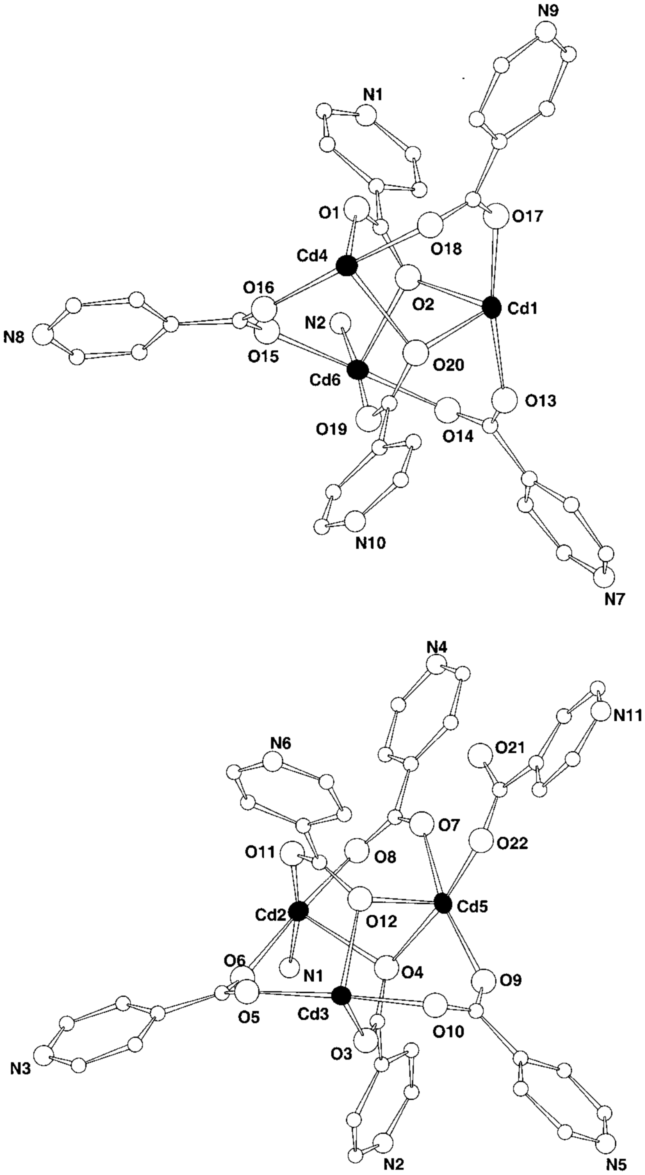

Figure 7. View of the asymmetric unit in **3**. The dark ellipsoids represent the cadmium centers, while the circles with increasing sizes represent C, N, and O, respectively. For clarity, included ethanol, water, 4-cyanopyridine, and perchlorate molecules are omitted. The asymmetric unit has been broken up into two $[Cd_3(isonicotinate)_5(H_2O)]^+$ building blocks. N5 and N6 have been duplicated to show the connectivity between the two tricadmium building blocks.

assigned to an a nitro group, while weak but defined peaks at ~3400 cm^{-1} can be assigned to the N−H stretching bands of 4-nitroaniline. Quantitative NMR experiments revealed that **2** contained approximately 1.9 mol of ethanol and 0.43 mol of 4-nitroaniline per formula unit. TGA analysis showed that **2** had a gradual weight loss of 7.6% by 260 °C, corresponding to the loss of 2 mol of ethanol per formula unit (calculated 7.5%). Further heating to 285 °C resulted in complete loss of 4-nitroaniline. **2** is thus formulated as $[Cd_3(isonicotinate)_5(EtOH)](ClO_4)(EtOH)(4\text{-nitroaniline})_{0.5}$; this formulation is further supported by elemental analysis results.

Compound **3** was obtained by a hydro(solvo)thermal reaction between $Cd(ClO_4)_2{\cdot}6H_2O$ and 4-pyridinecarboxaldehyde in a mixture of ethanol, water, and 4-cyanopyridine at 100 °C (Scheme 1). Quantitative NMR experiments revealed that **3** contained approximately 2.2 mol of ethanol and 0.56 mol of 4-cyanopyridine per formula unit. TGA analysis revealed that **3** exhibited a weight loss of 7.7% by 280 °C, corresponding to the loss of 2 mol of ethanol, 2 mol of water, and $^1/_2$ mol of 4-cyanopyridine per formula unit (calculated 7.8%) which is consistent with the above formulation.

Single-Crystal X-ray Structures. A single-crystal X-ray diffraction study of **1** revealed a complex 3-D coordination network. **1** crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit consists of six Cd(II) centers, 10 bridging isonicotinate groups, two coordinated water molecules, two perchlorate anions and four ethanol and four water guest molecules (Figure 1). The asymmetric unit contains two inequivalent $[Cd_3(isonicotinate)_5(H_2O)]^+$ building blocks that are composed of Cd1, Cd2, and Cd3 centers and Cd4, Cd5, and Cd6 centers, respectively (Figure 1). The five isonicotinate groups within each $[Cd_3(isonicotinate)_5(H_2O)]^+$ building block adopt two different bridging modes: two isonicotinate ligands adopt an *exo*-tetradentate bridging mode (with a coordinating pyridyl group and a μ_3,η^1,η^2-carboxylato bridge) and orient along the *a*-axis while the other three isonicotinate ligands adopt an *exo*-tridentate bridging mode (with a coordinating pyridyl group and a μ_2,η^2-carboxylato bridge) and lie in the *bc*-plane. The five isonicotinate groups of each $[Cd_3(isonicotinate)_5(H_2O)]^+$ building block provide a total of 17 binding sites. With the addition of a coordinated water, all the Cd centers adopt six coordinate distorted octahedral geometry.

The three Cd atoms in each $[Cd_3(isonicotinate)_5(H_2O)]^+$ building block form roughly an isosceles triangle with two sides having a Cd−Cd separation of ~3.70 Å and the third having a Cd−Cd separation of ~4.42 Å. The roughly isosceles triangles formed by the three Cd centers have angles of ~72.8, 52.7, and 54.5°. It is instructive to view this complex structure as a pillared solid. The *exo*-tridentate isonicotinate groups lying in the *bc* plane bridge two crystallographically independent $[Cd_3(isonicotinate)_5(H_2O)]^+$ building blocks to form a 2D sheet with *pseudo*-trigonal symmetry (Figure 2). The *exo*-tetradentate isonicotinate groups along the *a*-axis act as pillars and serve to link adjacent *pseudo*-trigonal sheets to form an extended 3D coordination network (Figure 3). Adjacent *pseudo*-trigonal sheets are rotated 180° along the *a*-axis and displaced ~2.13 Å along the *b*-axis from each other. The *exo*-tetradentate isonicotinate pillars form $\pi-\pi$ stacks along the *c*-axis with a centroid to centroid distance of ~3.54 Å. Analogous pillared networks based on hydrogen-bonded guanidinium sulfonate salts have been extensively studied by Ward et al.[18−20] A space-filling model of **1** viewed down the *b*-axis reveals large rectangular channels of ~3.3 × 2.8 Å which are occupied by disordered ethanol and water guest molecules and perchlorate anions (Figure 4).

Compound **2** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of three Cd centers, five bridging isonicotinate groups, one coordinated ethanol molecule, one perchlorate anion, one ethanol guest and one-half disordered nitroaniline guest molecules (Figure 5). Similar to **1**, the isonicotinate groups adopt two different bridging modes: three isonicotinate groups adopt an *exo*-tridentate bridging mode and lie in the *ab* plane, while the other two isonicotinate groups adopt and *exo*-tetradentate bridging mode and orient along the *c*-axis. Each Cd atom in **2** also adopts a 6-coordinate distorted octahedral geometry. The three Cd atoms of each [Cd3-

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(18) Russell, V. A.; Etter, M. C.; Ward, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 1941−1952.

(19) Russell, V. A.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575−579.

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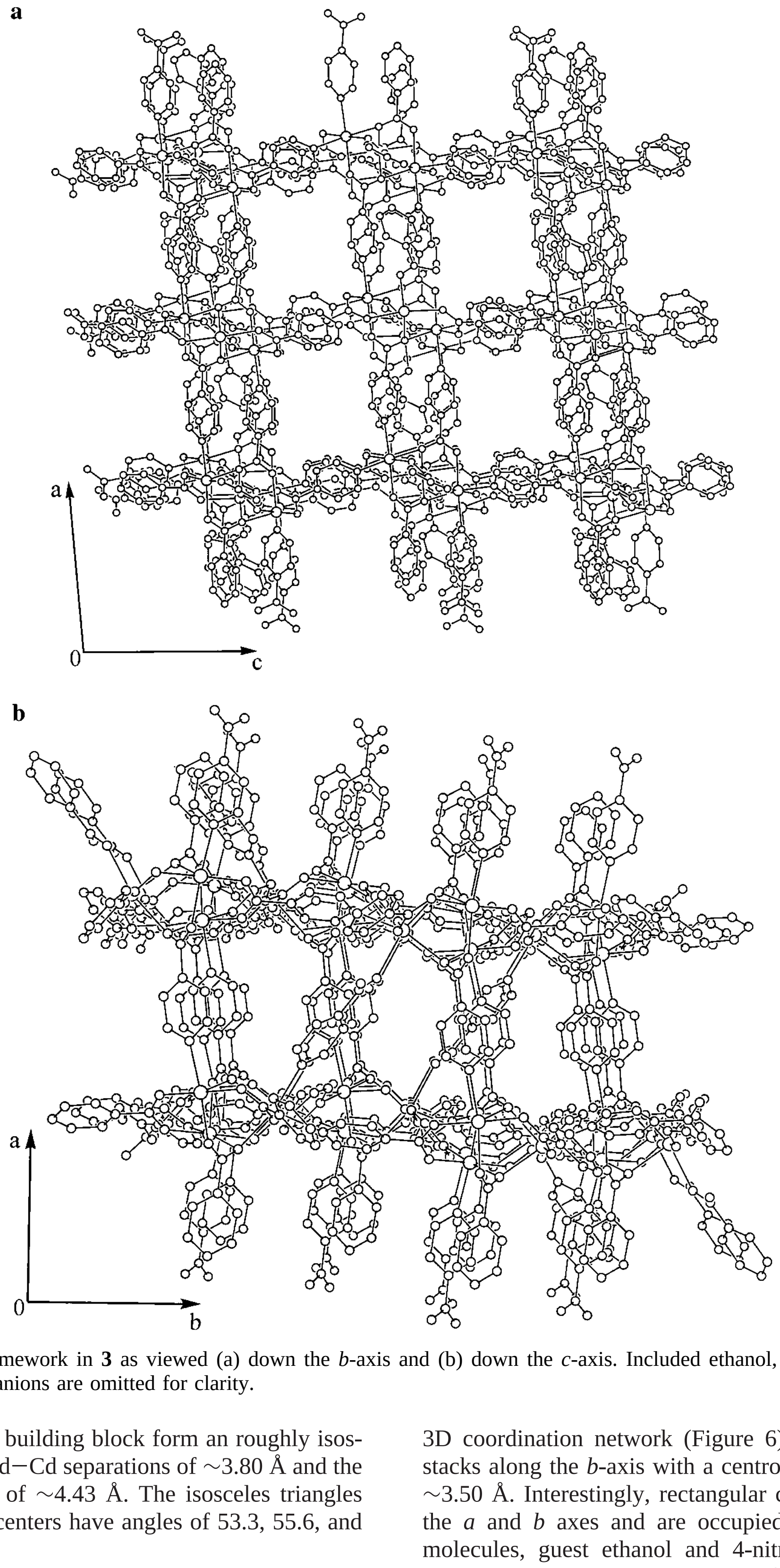

Figure 8. View of the framework in **3** as viewed (a) down the *b*-axis and (b) down the *c*-axis. Included ethanol, water, and 4-cyanopyridine molecules and perchlorate anions are omitted for clarity.

(isonicotinate)$_5$(EtOH)]$^+$ building block form an roughly isosceles triangle with two Cd−Cd separations of ~3.80 Å and the third Cd−Cd separation of ~4.43 Å. The isosceles triangles formed by the three Cd centers have angles of 53.3, 55.6, and 71.1°.

Compound **2** has a 3D pillared structure similar to **1**. The *exo*-tridentate isonicotinate groups lying in the *ab* plane bridge the [Cd$_3$(isonicotinate)$_5$(EtOH)]$^+$ building blocks to form a 2D sheet with *pseudo*-trigonal symmetry (see Supporting Information). Adjacent *pseudo*-trigonal sheets are rotated 180° about the *c*-axis and displaced ~2.29 Å along the *a*-axis. The *exo*-tetradentate isonicotinate groups along the *c*-axis serve as pillars to link adjacent *pseudo*-trigonal sheets to afford an extended 3D coordination network (Figure 6). The pillars form $\pi-\pi$ stacks along the *b*-axis with a centroid to centroid distance of ~3.50 Å. Interestingly, rectangular channels exist along both the *a* and *b* axes and are occupied by coordinated ethanol molecules, guest ethanol and 4-nitroaniline molecules, and perchlorate anions (Figure 6). Space-filling models revealed that the rectangular channels of **2** along the *a*-axis have a size of ~4.4 × 3.7 Å while those along the *b*-axis have a size of ~4.5 × 5.0 Å (see Supporting Information).

Compound **3** crystallizes in the monoclinic space group *P2$_1$/n*. The asymmetric unit of **3** consists of six Cd centers, 11 bridging isonicotinate groups, one perchlorate anion, and two ethanol, two water, and one-half disordered 4-cyanopyridine

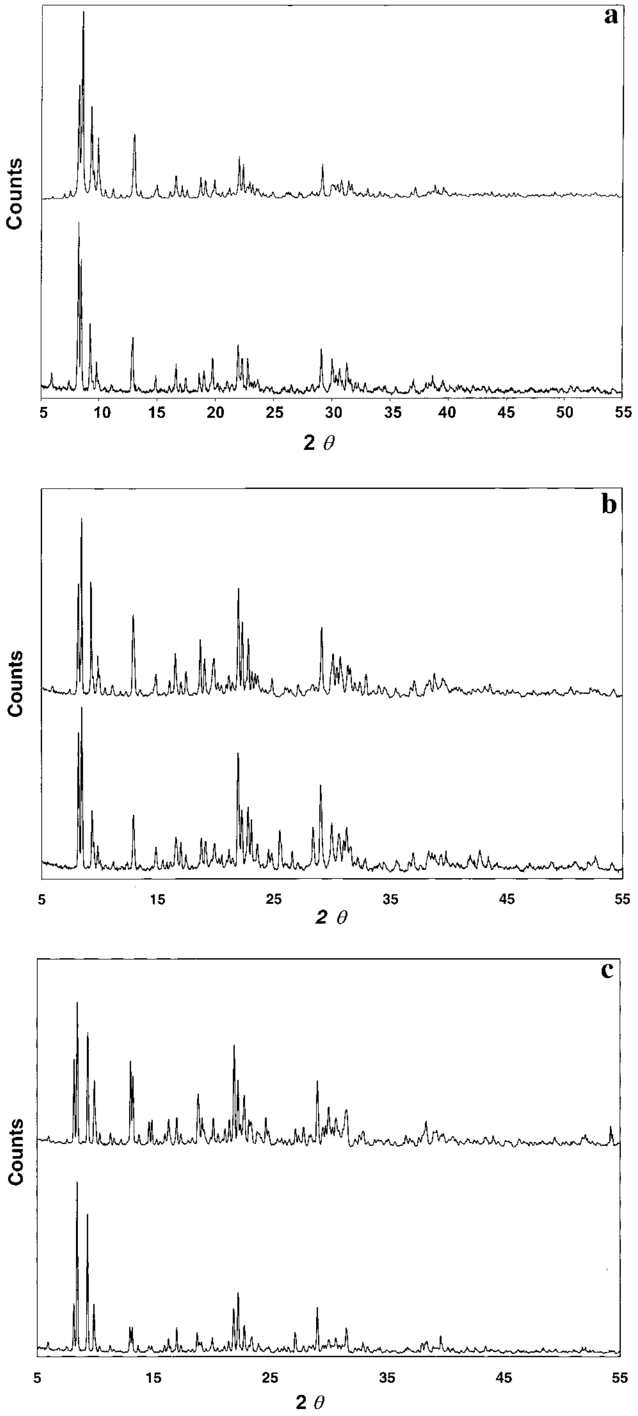

Figure 9. (a) XRPD for **1** before (top) and after (bottom) the removal of guest molecules. (b) XRPD for **2** before (top) and after (bottom) the removal of guest molecules. (c) XRPD for **3** before (top) and after (bottom) the removal of guest molecules.

molecules (Figure 7). Similar to **1**, six isonicotinate groups adopt *exo*-tridentate (in the *bc* plane) binding mode and four isonicotinate groups adopt *exo*-tetradentate (along the *a* axis) binding mode to bridge the six Cd centers to form two inequivalent $[Cd_3(isonicotinate)_5]^+$ building blocks. The 3D structure of **3** shares similar feature to those of **1** and **2** except there is an additional isonicotinate bridging ligand. The *exo*-tridentate isonicotinate groups in the *bc* plane and Cd centers of each $[Cd_3(isonicotinate)_5]^+$ building block form an isosceles triangle with two Cd−Cd separations of ~3.75 Å and the other at ~4.45 Å. The three Cd−Cd−Cd angles of each isosceles triangle are 72.4, 54.5, and 53.1°. The *exo*-tridentate isonicotinate groups in the *bc* plane bridge two inequivalent $[Cd_3(isonicotinate)_5]^+$ building blocks to form a similar *pseudo*-trigonal sheets as **1** (see Supporting Information). Adjacent *pseudo*-trigonal sheets are rotated 180° along the *a*-axis and displaced 1.85 Å along the *b*-axis from each other. The *exo*-tetradentate isonicotinate groups along the *a*-axis serve as pillars to link adjacent *pseudo*-trigonal sheets to form a 3D coordination network (Figure 8). The isonicotinate pillars form $\pi-\pi$ stacks with a centroid to centroid distance of ~3.62 Å. There is however a major difference between the structure of **3** and that of **1**: the 11th isonicotinate group in the asymmetric unit adopts an *exo*-bidentate bridging mode (with the carboxylate group being monodentate) and has replaced the two coordinated water molecules in **1**. The distance from the Cd5 center of one *pseudo*-trigonal sheet to the Cd1 center of an adjacent sheet is 9.81 Å and can easily accommodate the coordination of an isonicotinate group. The 11th isonicotinate group connects Cd1 and Cd5 centers and serves as additional bridges between adjacent *pseudo*-trigonal sheets. Therefore, **3** exhibits a similar topology to **1**, with the substitution of a cross-linking isonicotinate bridge for the coordinated water. Despite the additional cross-linking group, a space filling model of **3** along the *b*-axis reveals large rectangular channels of ~4.1 × 3.4 Å (see Supporting Information). These large channels are occupied by perchlorate anions and 4-cyanopyridine, ethanol, and water guest molecules.

Removal of Guest Molecules: TGA, XRPD, and Quantitative NMR studies. We have recently systematically explored the potential of coordination networks as nonlinear optical materials and as nanoporous solids. In particular, we have previously described an interpenetrated diamondoid coordination network possessing interesting nanoporous characteristics.[12] The X-ray crystal structures of **1**, **2**, and **3** clearly indicate the presence of large rectangular channels occupied by guest molecules. These guest molecules and even the coordinated solvent molecules can potentially be removed to generate nanoporous solids which may retain the framework structures of the pristine samples.

When a freshly prepared and ground sample of **1** was evacuated under a 10^{-2} Torr vacuum at 55 °C for 24 h, the sample experienced a weight loss corresponding to the removal of 4 mol of ethanol and 4 mol of water per formula unit. The absence of ethanol guest molecules in the evacuated solid was confirmed by a quantitative NMR experiment. Interestingly, an XRPD of the evacuated solid is very similar to that of the pristine sample of **1** (Figure 9a). This result demonstrates that the removal of guest molecules from **1** has led to a nanoporous solid which maintains the structural integrity of the Cd-isonicotinate framework in **1**.

Evacuation of **2** under identical conditions led to a weight loss corresponding to the removal of 2 mol of ethanol. A quantitative NMR experiment confirmed this assignment; the 4-nitroaniline guest molecule is retained while both coordinated and guest ethanol molecules have been removed during the evacuation. An XRPD of **2** after evacuation is very similar to that of pristine sample of **2** (Figure 9b). It is also interesting to note that the coordinated ethanol molecules in **2** have been removed during the evacuation. It is thus possible to obtain nanoporous metal−organic frameworks with coordinatively unsaturated metal centers which may be exploited for their catalytic actions. However, TGA analysis indicated that the evacuated sample of **2** readily readsorbed water from air, probably to attain 6-coordinate Cd centers.

Evacuation of **3** has led to a weight loss corresponding to the removal of 2 mol of ethanol, 2 mol of water, and $^1/_2$ mol of 4-cyanopyridine per formula unit. A NMR spectrum of the digested evacuated solid confirmed the absence of both ethanol and 4-cyanopyridine molecules. The XRPD of the evacuated solid is very similar to that of pristine compound **3** (Figure 9c). The removal of 4-cyanopyridine from **3** is in stark contrast to the inability to remove 4-nitroaniline from **2** under identical conditions. We believe that this difference is a result of different vapor pressures of 4-cyanopyridine and 4-nitroaniline, but not a consequence of different channel sizes in **2** and **3**.[21] The removal of an aromatic molecule from **3** with the retention of the Cd-isonicotinate framework is significant, indicating that the channels within the nanoporous solid are large enough to allow the removal of the relatively large 4-cyanopyridine molecule.

There has been much recent research on the synthesis of zeolitic materials based on metal−organic coordination networks.[5−8,22−27] Unlike conventional zeolites, the shapes, sizes, and functions of the cavities in nanoporous coordination networks can be systematically engineered by changing the molecular building blocks. Such tunable and well-defined cavities are potentially exploitable for interesting separation and even catalytic applications.[28] Attempts to generate nanoporous metal−organic frameworks are typically complicated by the formation of interpenetrated networks as well as by the fragility of the metal−organic frameworks. Consequently, examples of metal−organic frameworks that can maintain their structural integrity upon the removal of guest molecules are still limited. The above results have clearly demonstrated the ready removal of included guest molecules from **1**, **2**, and **3** and the generation of nanoporous solids that retain the framework structure integrity of the pristine solids. The stability of the framework structures in these solids is undoubtedly due to the multidentate functionality of the pyridinecarboxylates. We believe that multidentate functionality of the bridging ligands is also at least partly responsible for the aggregation of cadmium cations to lead to carboxylate-bridged tricadmium building blocks. Large metal-containing building blocks tend to disfavor the formation of an interpenetrated solid.[29,30] Finally, the metal−organic frameworks of **1**, **2**, and **3** exhibit an interesting ability in accommodating different guest molecules, probably owing to the templating effect of the guest molecules.

Acknowledgment. We acknowledge NSF (CHE-9875544) and ACS-PRF for financial support. We also thank Dr. Scott R. Wilson and the Materials Chemistry Laboratory at University of Illinois at Urbana-Champaign for X-ray data collections of **1** and **2**, Dr. Bruce M. Foxman for X-ray data collection of **3**, and Dr. X. Ren for initial experiments. W.L. is an Alfred P. Sloan Fellow, a Cottrell Scholar of Research Corporation, and an Arnold and Mabel Beckman Young Investigator.

Supporting Information Available: Eleven figures (depictions of X-ray structures and TGA curves of **1**−**3**) and X-ray crystallographic files in CIF format for the structure determinations of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) 4-Cyanopyridine has a vapor pressure of 3.14×10^{-1} Torr at 25 °C while 4-nitroaniline has a vapor pressure of 3.2×10^{-6} Torr at 25 °C. See: Howard, P. H., Meylan, W. M., Eds. *Handbook of Physical Properties of Organic Chemicals*; CRC Press: Boca Raton, FL, 1997.

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