Three-Dimensional Open Frameworks Based on Cobalt(II) and Nickel(II) *m*-Pyridinecarboxylates

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Three-dimensional open frameworks $[Co_2(nicotinate)_4(\mu\text{-}H_2O)]\cdot CH_3CH_2OH\cdot H_2O$, **1**, and $[Ni_2(nicotinate)_4(\mu\text{-}H_2O)]\cdot CH_3CH_2OH\cdot H_2O$, **2**, were obtained by hydro(solvo)thermal reactions between 3-cyanopyridine and cobalt-(II) nitrate and nickel(II) perchlorate, respectively. Both **1** and **2** exhibit complicated 3-D structures based on $[M_2(nicotinate)_4(\mu\text{-}H_2O)]$ (M = Co or Ni) building blocks and possess open channels that are occupied by removable solvent molecules. 3-D open frameworks $[M_2L_4(\mu\text{-}H_2O)]\cdot HL\cdot(H_2O)_x$ (where M = Co, x = 2, **3**, and M = Ni, x = 1, **4**, and L = *trans*-3-(3-pyridyl)acrylate) were similarly prepared with *trans*-3-(3-pyridyl)acrylic acid in place of 3-cyanopyridine. Compounds **3** and **4** are isostructural and exhibit network topologies similar to that of **1** with open channels occupied by disordered *trans*-3-(3-pyridyl)acrylic acid and water guest molecules. Crystal data for **1**: triclinic space group $P\bar{1}$, a = 10.534(1) Å, b = 11.907(1) Å, c = 14.046(1) Å, α = 106.645(1)°, β = 101.977-(1)°, γ = 112.078(1)°, and Z = 4. Crystal data for **2**: tetragonal space group $P4/ncc$, a = 20.089(1) Å, c = 14.016(1) Å, and Z = 4. Crystal data for **3**: monoclinic space group $C2/c$, a = 14.082(2) Å, b = 15.278(2) Å, c = 18.537(2) Å, β = 105.360(2)°, and Z = 2. Crystal data for **4**: monoclinic space group $C2/c$, a = 14.082(1) Å, b = 15.250(1) Å, c = 18.606(1) Å, β = 106.747(1)°, and Z = 2.

Introduction

The field of coordination polymers has undergone explosive growth over the past decade.[1−6] In particular, there have been numerous reports on coordination polymers with micropores and nanopores that are stable upon the removal of solvent (guest) molecules.[7−15] However, in order for such coordination polymers to be potentially useful, it is essential that their structures can be rationally and predictably tuned via variation and functionalization of their constituent building blocks. Unfortunately, predicting and controlling the structures of such com-

plicated supramolecular assemblies are still at a very primitive stage.

The use of rigid linking ligands thus far represents the most promising approach toward the synthesis of porous metal−organic frameworks.[1−6] A majority of these materials are based on either neutral donor ligands (e.g., 4,4′-bipyridine)[16−21] or strictly anionic groups (e.g., carboxylates).[6] For example, Yaghi et al. have successfully synthesized a variety of remarkable nanoporous coordination networks based on 1,3,5-benzenetri-carboxylic acid (BTC).[6] Our research effort in this area focuses on coordination polymers with multifunctional ligands. First, the presence of different functional groups should allow the incorporation of interesting properties into the resulting coordination networks. We have rationally synthesized polar solids based on Zn(II) and Cd(II) pyridinecarboxylates using the molecular building block approach.[22−25] Some of these acentric solids exhibit second-order nonlinear optical properties that are comparable to and exceeding technologically important lithium niobate. Second, both neutral and anionic donor groups in such multifunctional bridging ligands can coordinate to metal centers

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potentially to result in neutral polymeric structures. The absence of counterions in such neutral polymeric networks simplifies the control of their structures and should also increase the chance of obtaining porous solids. In this context, we have recently synthesized porous metal−organic frameworks based on interpenetrated diamondoid networks and pillared three-dimensional networks.[26−28] Herein we wish to report the hydro(solvo)thermal synthesis and X-ray structures of four 3-D metal−organic frameworks based on the [M$_2$(pyridinecarboxylate)$_4$(μ-H$_2$O)] building blocks and the generation of microporous solids via the removal of the solvent molecules in these solids.

Experimental Section

Materials and Methods. Cobalt(II) nitrate hexahydrate, nickel(II) perchlorate hexahydrate, *trans*-3-(3-pyridyl)acrylic acid, 3-cyanopyridine, and pyridine were purchased from Adrich and used without further purification. ***CAUTION:*** *Ni(ClO$_4$)$_2$·6H$_2$O is potentially explosive and should be used with care!* Thermogravimetric analysis was performed in air at a scan speed of 4 °C/min on a Shimadzu TGA-50 analyzer. Infrared spectra were measured from KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrometer.

Synthesis of [Co$_2$(nicotinate)$_4$(μ-H$_2$O)]·CH$_3$CH$_2$OH·H$_2$O, 1. A mixture of Co(NO$_3$)$_2$·6H$_2$O (0.073 g, 0.25 mmol) and 3-cyanopyridine (0.051 g, 0.5 mmol) was thoroughly mixed with ethanol (1.4 mL) and deionized water (0.3 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 130 °C. After 48 h of heating, violet rectangular crystals were obtained. Yield: 0.065 g (68.7%). IR (cm^{-1}): 3475 (w), 1700 (m), 1635 (s), 1594 (m), 1401 (s), 1191 (ms), 1155 (ms), 1093 (ms), 1047 (ms), 827 (ms), 758 (s), 699 (s), 642 (w), 574 (w).

Synthesis of [Ni$_2$(nicotinate)$_4$(μ-H$_2$O)]·CH$_3$CH$_2$OH·H$_2$O, 2. A mixture of Ni(ClO$_4$)$_2$·6H$_2$O (0.091 g, 0.25 mmol) and 3-cyanopyridine (0.051 g, 0.5 mmol) was thoroughly mixed with ethanol (1.4 mL) and deionized water (0.3 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 130 °C. After 48 h of heating, tabular blue crystals were obtained. Yield: 0.0690 g (80.0%). IR (cm^{-1}): 2475(w), 3136 (w), 3072 (w), 2052 (w), 1750 (w), 1643 (s), 1593 (s), 1550 (s), 1404 (s), 1317 (ms), 1192 (s), 1157 (ms), 1095 (ms), 1050 (s), 1034 (ms), 894 (w), 834 (s), 758 (s), 698 (s), 644 (ms), 581 (w).

Synthesis of [Co$_2$(*trans*-3-(3-pyridyl)acrylate)$_4$(μ-H$_2$O)]·(*trans*-3-(3-pyridyl)acrylic acid)·2H$_2$O, 3. A mixture of Co(NO$_3$)$_2$·6H$_2$O (0.0727 g, 0.25 mmol) and *trans*-3-(3-pyridyl)acrylic acid (0.075 g, 0.5 mmol) was thoroughly mixed with methanol (1.2 mL) and pyridine (0.4 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 130 °C. After 24 h of heating, brown cubic crystals were obtained. Yield: 0.070 g (64.0%). Anal. Calcd for C$_{40}$H$_{37}$N$_5$O$_{13}$Co$_2$: C, 52.6; H,4.08; N, 7.67. Found: C, 53.8; H, 3.70; N, 7.87 (the microanalysis results are more consistent with one included water molecule, probably due to facile loss of an included water molecule). IR (cm^{-1}): 3854 (s), 1715 (w), 1652 (s), 1607 (s), 1479 (w), 1435 (ms), 1394 (s), 1256 (w), 1302 (w), 966 (w), 805 (w), 716 (w), 690 (w), 644 (w), 599 (w).

Synthesis of [Ni$_2$(*trans*-3-(3-pyridyl)acrylate)$_4$(μ-H$_2$O)]·(*trans*-3-(3-pyridyl)acrylic acid)·H$_2$O, 4. A mixture of Ni(ClO$_4$)$_2$·6H$_2$O (0.0914 g, 0.25 mmol) and *trans*-3-(3-pyridyl)acrylic acid (0.075 g, 0.5 mmol) was thoroughly mixed with methanol (1.2 mL) and pyridine (0.4 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 130 °C. After 24 h of heating, pale green rectangular crystals were obtained. Yield: 0.072 g (65.0%). Anal. Calcd for C$_{40}$H$_{35}$N$_5$O$_{12}$Ni$_2$: C, 53.7; H, 3.94; N, 7.82. Found: C, 53.6; H, 3.71; N, 7.85. IR (cm^{-1}): 3475 (w), 1737 (w), 1650 (ms), 1602 (s), 1476 (ms), 1437 (m), 1395 (s), 1350 (w), 1043 (w), 970 (ms), 881 (w), 825 (w), 722 (ms), 695 (ms), 646 (w).

Removal of Guest Molecules. A freshly ground sample of **1** (62.4 mg) was subjected to a vacuum at 40 °C. After 18 h, **1** exhibited a weight loss of 4.6 mg (7.4%), equivalent to the loss of one ethanol molecule and one water molecule per formula unit (calcd 8.1%). Similar evacuation of **1** at 60 °C for 18 h results in a weight loss of 9.1%. Evacuation of **2** was performed similarly on a freshly ground sample of **2** (115.1 mg) at 60 °C. After 18 h, **2** exhibited a weight loss of 7.1 mg (6.2%), slightly less than the loss of one ethanol molecule and one water molecule per formula unit (calcd 8.1%). Similar evacuation of **2** at 90 °C for 48 h results in a weight loss of 10.1%.

X-ray Collections and Structure Determinations. The X-ray single-crystal data collections for all four crystals were performed using a Siemens SMART system equipped with a CCD detector using Mo Kα radiation. The structures were solved by direct methods using SHELX-TL.[29] Of the 6525 (3505) reflections measured for the violet crystal of **1** (tubular blue crystal of **2**), 4478 (2228) reflections with $I > 2\sigma(I)$ were used in structure solution and refinement. All the non-hydrogen atoms of the framework structures were refined by full-matrix least squares using anisotropic displacement parameters, while the guest water and ethanol molecules were refined using isotropic displacement parameters. Final refinement gave R1 = 0.074 (0.054), wR2 = 0.135 (0.179), and goodness of fit = 1.173 (1.04) for **1** (**2**).

Of the 3387 (4590) reflections measured for the brown cubic crystal of **3** (**4**), 1864 (3230) reflections with $I > 2\sigma(I)$ were used in structure solution and refinement. All the non-hydrogen atoms belonging to the framework structures were refined by full-matrix least squares using anisotropic displacement parameters. Despite numerous attempts, only parts of the highly disordered *trans*-3-(3-pyridyl)acrylic acid guest molecules in both **3** and **4** were located and refined with isotropic displacement parameters. Final refinements gave R1 = 0.1060 (0.0707), wR2 = 0.2159 (0.1631), and goodness of fit = 1.128 (1.109) for **3** (**4**). Experimental details for X-ray data collection of **1**−**4** are presented in Table 1, while selected bond distances and angles for **1**−**4** are listed in Table 2.

Results and Discussion

1. Synthesis and Characterization. Compound **1** was obtained as violet hexagonal platy crystals by a hydro(solvo)-thermal reaction between Co(NO$_3$)$_2$·6H$_2$O and 3-cyanopyridine in a mixture of ethanol and water at 130 °C. Compound **2** was obtained as bluish green platy crystals by a hydro(solvo)thermal reaction between Ni(ClO$_4$)$_2$·6H$_2$O and 3-cyanopyridine in a mixture of ethanol and water at 130 °C. The IR spectra of **1** and **2** show clearly the presence of carboxylate peaks at ~1550 and ~1400 cm^{-1}.[30] The absence of characteristic peaks for cyano groups (at ~2200 cm^{-1}) indicates that the nicotinate (3-pyridinecarboxylate) ligand results from the hydrolysis of 3-cyanopyridine. Such in situ slow hydrolysis of pyridine-carboxylate precursor ligands has recently been utilized in our group to synthesize novel 2-D and 3-D coordination polymers.[22,24−26] Compounds **3** and **4** were obtained as brown cubic and pale green rectangular crystals by hydro(solvo)thermal reactions between *trans*-3-(3-pyridyl)acrylic acid and Co(NO$_3$)$_2$·6H$_2$O or Ni(ClO$_4$)$_2$·6H$_2$O in a mixture of methanol and pyridine, respectively. The IR spectra of **3** and **4** show clearly the presence of coordinated carboxylate peaks at ~1550 and ~1400 cm^{-1} as well as the peaks at ~1710 cm^{-1} which are characteristic of free carboxylic acid.

The TGA curve of **1** shows a weight loss of 7.7% from room temperature to 220 °C, which corresponds to the loss of both included ethanol and water molecules (calcd 8.1%). Further heating results in the loss of bridging water molecules and the collapse of the framework structure, as indicated by powder

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Table 1. Crystallographic Data for Compounds **1**−**4**[a]

compound	**1**	**2**	**3**	**4**
empirical formula	$Co_2C_{26}H_{26}N_4O_{11}$	$NiC_{23}H_{23}N_2O_{5.5}$	$CoC_{23}H_{18.5}N_{2.5}O_{6.5}$	$NiC_{23}H_{17.5}N_{2.5}O_6$
fw	687.86	339.19	492.83	386.88
space group	$P\bar{1}$	$P4/ncc$	$C2/c$	$C2/c$
a, Å	10.5344(1)	20.0890(5)	14.082(2)	14.0821(1)
b, Å	11.9073(2)	20.0890(5)	15.278(2)	15.2498(3)
c, Å	14.0461(3)	14.0156(5)	18.537(2)	18.6058(2)
α, deg	106.645(1)	90.00	90.00	90.00
β, deg	101.977(1)	90.00	105.360(2)	106.747(1)
γ, deg	112.078(1)	90.00	90.00	90.00
V, Å	1462.39(4)	5656.2(3)	3845.8(6)	3826.11(9)
Z	2	16	8	8
T, °C	−75	−75	−75	−75
λ (Mo Kα)	0.71073	0.71073	0.71073	0.71073
ρ_{calc}, g/cm^3	1.56	1.61	1.70	1.68
μ, cm^{-1}	11.89	13.92	9.28	12.88
R1	0.0740	0.0542	0.1060	0.0707
wR2	0.1346	0.1788	0.2159	0.1631

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(\text{no. of reflections} - \text{no. of parameters})]^{1/2}$.

X-ray diffraction studies. The TGA curve of **2** shows a gradual weight loss of 3.0% from room temperature to 200 °C, followed by an abrupt weight loss at 260 °C. We believe that the gradual weight loss corresponds to the removal of the included water molecule, while the included ethanol molecule can only be removed at higher temperatures (in air) because of the small openings for the cavities where they reside (see Scheme 1).

The TGA of **3** shows a weight loss of 4.8% in the 40−140 °C temperature range, which is slightly larger than the 3.9% weight loss expected for one included water molecule. Heating of **3** to higher temperatures results in the loss of *trans*-3-(3-pyridyl)acrylic acid and collapse of the framework structure of **3**. The TGA curve of **4** shows a weight loss of 2.3% in the 40−150 °C temperature range, which is consistent with the loss of one included water molecule (expected 2.0%). Further heating of **4** leads to the loss of *trans*-3-(3-pyridyl)acrylic acid and collapse of the framework structure.

Although the host polymeric frameworks of $M_2(L)_4(\mu\text{-}H_2O)$ of compounds **1**−**4** were easily established from single-crystal X-ray structural analyses (see below), the guest molecule of free *trans*-3-(3-pyridyl)acrylic acid in **3** and **4** cannot be accurately located owing to their highly disordered nature. The identity of free *trans*-3-(3-pyridyl)acrylic acid in **3** and **4** was instead established from IR spectroscopy and elemental analysis results. The TGA of **3** and **4** are also consistent with their formulation.

2. Single-Crystal X-ray Structures. [Co$_2$(nicotinate)$_4$(μ-H$_2$O)]·(CH$_3$CH$_2$OH)·(H$_2$O), 1. The polymeric structure of **1** was confirmed by an X-ray single-crystal structural determination. **1** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit of **1** consists of two Co(II) centers, four nicotinate groups, one bridging water molecule, one ethanol guest molecule, and one water guest molecule (Figure 1). There are two coordination modes for the four bridging nicotinate groups: two of them adopt an exo-tridentate linkage with a coordinating pyridyl group and a μ_2,η^2-carboxylate bridge, while the other two adopt an exo-bidentate linkage with a coordinating pyridyl group and a monodentate carboxylate group. Each Co-(II) center in **1** is coordinated to one oxygen atom of the monodentate carboxylate group, and two oxygen atoms of two different μ_2,η^2-carboxylate groups, one oxygen atom of the bridging water molecule, and two pyridyl nitrogen atoms in a cis geometry. The geometry around both Co atoms is slightly distorted octahedral: the bond angles between the cis ligands and the Co1 center range from 85.8° to 94.2°, while the bond

angles between the cis ligands and the Co2 center range from 86.6° to 97.3°. The Co−N and Co−O distances are all within the normal range. The angle between the two Co centers and the water oxygen atom is 113.9(2)°.

The framework structure of **1** is built from the Co$_2$-(nicotinate)$_4$(μ-H$_2$O) unit. First, the exo-bidentate nicotinate ligands link the dicobalt building units to form 1-D ladders of [Co$_2$(μ-H$_2$O)(nicotinate)$_2$]$_\infty$ along the c axis (Figure S1). Each Co$_4$(μ-H$_2$O)$_2$(nicotinate)$_4$ unit is then doubly bridged by exo-tridentate nicotinate ligands to four other Co$_4$(μ-H$_2$O)$_2$-(nicotinate)$_4$ units from four adjacent 1-D ladders to form a complicated 3-D framework structure (Figure 2). Finally, four 1-D ladders of [Co$_2$(μ-H$_2$O)(nicotinate)$_2$]$_\infty$ are linked by the exo-tridentate nicotinate ligands to form rhomboid channels with diagonal lengths of 5.4 × 8.4 Å (Figure S2). These channels are running along the a axis and occupied by removable ethanol and water guest molecules. The guest molecules inside these channels have been further characterized by TGA results and evacuation studies (see below).
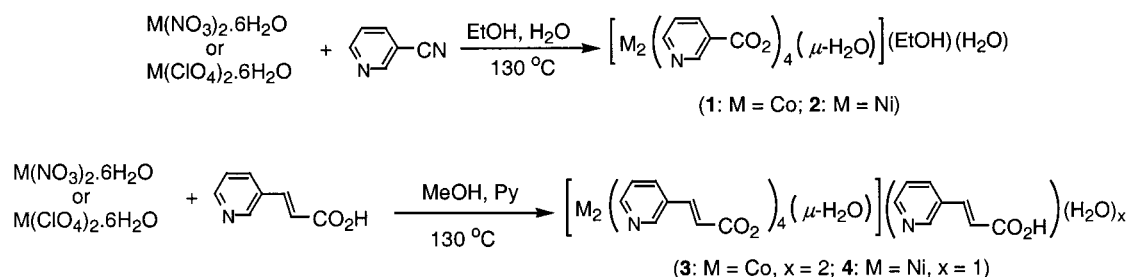
[Ni$_2$(nicotinate)$_4$(μ-H$_2$O)]·(CH$_3$CH$_2$OH)·(H$_2$O), 2. Compound **2** crystallizes in the tetragonal space group $P4/ncc$. The asymmetric unit of **2** consists of one Ni atom, two nicotinate ligands, one bridging water molecule, one-half water guest molecule, and one-half ethanol guest molecule (Figure 3). The bridging water molecule sits on a 2-fold axis. Similar to **1**, there are two different coordination modes for the two bridging isonicotinate groups: one of them adopts the exo-tridentate linkage while the other one adopts the exo-bidentate linkage. The Ni(II) center in **2** is thus coordinated to one oxygen atom of the monodentate carboxylate group, and two oxygen atoms of the μ_2,η^2-carboxylate group, one oxygen atom of the bridging water molecule, and two pyridyl nitrogen atoms in a cis geometry. The geometry around the Ni atom is distorted octahedral with the bond angles between the cis ligands and the Ni1 center ranging from 81.4° to 95.8°. The Ni−N and Ni−O distances are all within the normal range. The angle between the two Ni centers and the water oxygen atom is 112.3-(2)°.

Although compounds **1** and **2** have the same empirical formula and nicotinate coordination modes, they exhibit entirely different 3-D framework structures. The 3-D framework structure of **2** is similarly built from the Ni$_2$(nicotinate)$_4$(μ-H$_2$O) unit. However, in stark contrast to **1**, the exo-bidentate nicotinate ligands in **2** link the dinickel building units to form 1-D barrels of [Ni$_2$(μ-H$_2$O)(nicotinate)$_2$]$_\infty$ along the c axis (Figure S3). These

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for **1**−**4**

1[a]		**2**[b]		**3**[c]		**4**[d]	
Co1−O2	2.052(4)	Ni1−O4A	2.018(3)	Co1−O3	2.054(6)	Ni1−O1	2.040(3)
Co1−O5	2.098(4)	Ni1−N2C	2.075(3)	Co1−O4A	2.073(7)	Ni1−O2A	2.081(3)
Co1−O7	2.111(3)	Ni1−O1	2.080(3)	Co1−O1	2.094(6)	Ni1−N1B	2.087(4)
Co1−N2B	2.131(5)	Ni1−O3	2.086(3)	Co1−N2C	2.130(8)	Ni1−O3	2.093(3)
Co1−N3C	2.144(4)	Ni1−N1B	2.103(3)	Co1−O5	2.151(5)	Ni1−O5	2.103(2)
Co1−O9	2.161(4)	Ni1−O5	2.117(2)	Co1−N1B	2.178(8)	Ni1−N2C	2.131(4)
Co2−O4	2.069(4)						
Co2−O6	2.072(4)	O4A−Ni1−N2C	91.4(2)	O3−Co1−O4A	96.5(3)		
Co2−O1	2.112(4)	O4A−Ni1−O1	177.1(2)	O3−Co1−O1	176.3(3)	O1−Ni1−O2A	95.23(13)
Co2−N1A	2.147(4)	N2C−Ni1−O1	88.0(2)	O4A−Co1−O1	87.1(3)	O1−Ni1−N1B	91.81(14)
Co2−O9	2.150(4)	O4A−Ni1−O3	95.8(2)	O3−Co1−N2C	92.6(3)	O2A−Ni1−N1B	87.45(14)
Co2−N4D	2.200(5)	N2C−Ni1−O3	88.1(2)	O4B−Co1−N2C	88.8(3)	O1−Ni1−O3	178.39(13)
		O1−Ni1−O3	81.4(2)	O1−Co1−N2C	88.3(3)	O2A−Ni1−O3	86.27(13)
O2−Co1−O5	94.2(2)	O4A−Ni1−N1B	90.8(2)	O3−Co1−O5	89.7(2)	N1B−Ni1−O3	87.65(13)
O2−Co1−O7	178.2(2)	N2C−Ni1−N1B	90.3(2)	O4A−Co1−O5	88.7(2)	O1−Ni1−O5	90.31(11)
O5−Co1−O7	85.8(2)	O1−Ni1−N1B	92.0(2)	O1−Co1−O5	89.6(2)	O2A−Ni1−O5	89.36(12)
O2−Co1−N2B	88.7(2)	O3−Ni1−N1B	173.2(2)	N2C−Co1−O5	176.8(2)	N1B−Ni1−O5	176.32(11)
O5−Co1−N2B	177.1(2)	O4A−Ni1−O5	89.9(1)	O3−Co1−N1B	87.4(3)	O3−Ni1−O5	90.30(11)
O7−Co1−N2B	91.3(2)	N2C−Ni1−O5	178.4(1)	O4A−Co1−N1B	175.8(3)	O1−Ni1−N2C	87.98(14)
O2−Co1−N3C	90.6(2)	O1−Ni1−O5	90.7(1)	O1−Co1−N1B	89.0(3)	O2A−Ni1−N2C	175.84(13)
O5−Co1−N3C	87.5(2)	O3−Ni1−O5	91.0(1)	N2C−Co1−N1B	89.4(3)	N1B−Ni1−N2C	89.81(15)
O7−Co1−N3C	87.8(2)	N1B−Ni1−O5	90.5(1)	O5−Co1−N1B	92.9(3)	O3−Ni1−N2C	90.50(14)
N2B−Co1−N3C	92.1(2)					O5−Ni1−N2C	93.27(14)
O2−Co1−O9	91.6(2)						
O5−Co1−O9	88.6(2)						
O7−Co1−O9	89.9(2)						
N2B−Co1−O9	91.7(2)						
N3C−Co1−O9	175.6(2)						
O4−Co2−O6	175.9(2)						
O4−Co2−O1	86.8(2)						
O6−Co2−O1	97.3(2)						
O4−Co2−N1A	88.6(2)						
O6−Co2−N1A	91.9(2)						
O1−Co2−N1A	87.0(2)						
O4−Co2−O9	90.9(2)						
O6−Co2−O9	88.8(2)						
O1−Co2−O9	90.4(2)						
N1A−Co2−O9	177.3(2)						
O4−Co2−N4D	89.1(2)						
O6−Co2−N4D	86.8(2)						
O1−Co2−N4D	175.3(2)						
N1A−Co2−N4D	90.8(2)						
O9−Co2−N4D	91.9(2)						

[a] Symmetry transformations: A = 1 − x, 1 − y, 1 − z; B = 1 − x, −y, 1 − z; C = −x, −y, −z; D = 1 − x, −y, −z. [b] Symmetry transformations: A = −0.5 + y, −0.5 + x, 0.5 − z; B =1 − y, −0.5 − x, −z; C = 1 − x, −y, −z. [c] Symmetry transformations: A = −x, y, 0.5 − z; B = x, −1 − y, 0.5 − z; C = −0.5 + x, −0.5 − y, −0.5 + z. [d] Symmetry transformations: A = 1 − x, y, 0.5 − z; B = 0.5 − x, 0.5 − y, −z; C = x, 1 − y, 0.5 + z.

Scheme 1

$$M(NO_3)_2\cdot 6H_2O \text{ or } M(ClO_4)_2\cdot 6H_2O + \text{(3-cyanopyridine)} \xrightarrow[130\,^\circ C]{EtOH, H_2O} \left[M_2\left(\text{(nicotinate)}CO_2\right)_4(\mu\text{-}H_2O)\right](EtOH)(H_2O)$$

(1: M = Co; 2: M = Ni)

$$M(NO_3)_2\cdot 6H_2O \text{ or } M(ClO_4)_2\cdot 6H_2O + \text{(trans-3-(3-pyridyl)acrylic acid)}CO_2H \xrightarrow[130\,^\circ C]{MeOH, Py} \left[M_2\left(CO_2\right)_4(\mu\text{-}H_2O)\right]\left(CO_2H\right)(H_2O)_x$$

(3: M = Co, x = 2; 4: M = Ni, x = 1)

1-D barrels of [Ni$_2$(μ-H$_2$O)(nicotinate)$_2$]$_\infty$ are further linked by the exo-tridentate nicotinate ligands to form a complicated 3-D framework structure (Figure 4). Interestingly, there is a round-shaped open channel formed inside the 1-D barrel of [Ni$_2$(μ-H$_2$O)(nicotinate)$_2$]$_\infty$ which runs along the c axis. These open channels have a diameter of ∼4.3 Å. In addition, the walls of four adjacent barrels of [Ni$_2$(μ-H$_2$O)(nicotinate)$_2$]$_\infty$ are linked by the exo-tridentate nicotinate ligands to form spherical cages with a diameter of ∼8.0 Å; these cages have a cross-shaped

opening with a maximum width of ∼2.0 Å (Figure S4). The water guest molecules reside in the round-shaped channels, and the ethanol guest molecules residing in the cages can be removed without the collapse of the 3-D framework structure of **2**.

[M$_2$(*trans*-3-(3-pyridyl)acrylate)$_4$(μ-H$_2$O)]·[*trans*-3-(3-pyridyl)acrylic acid]·(H$_2$O)$_x$ (3 and 4, M = Co and Ni). Compounds **3** and **4** are isomorphous, and both crystallize in the monoclinic space group $C2/c$. Only the structure of **3** will be described here. The asymmetric unit of **3** consists of one
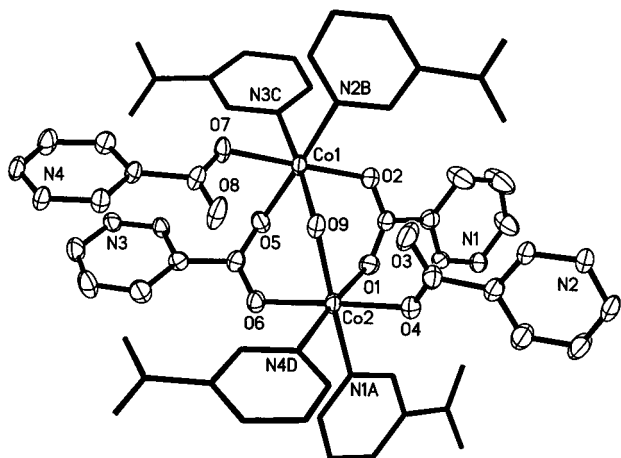
Figure 1. Coordination environment of **1**. The asymmetric unit (excluding ethanol and water) is shown with ellipsoids at 50% probability.
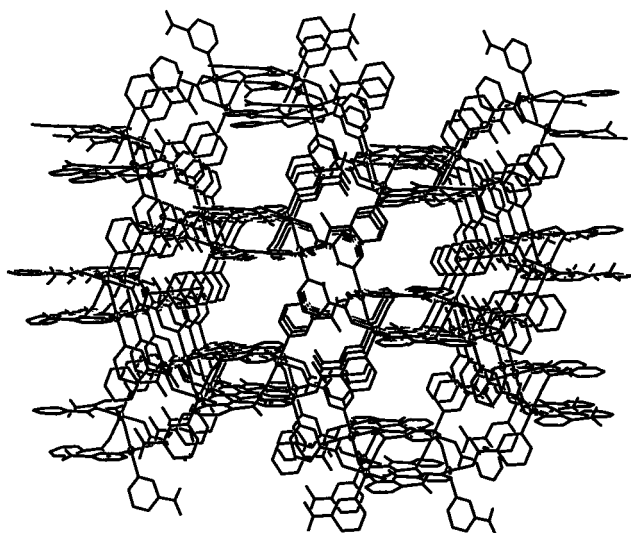

Figure 2. 3-D framework of **1** as viewed down the *a* axis. Included ethanol and water molecules are omitted for clarity.
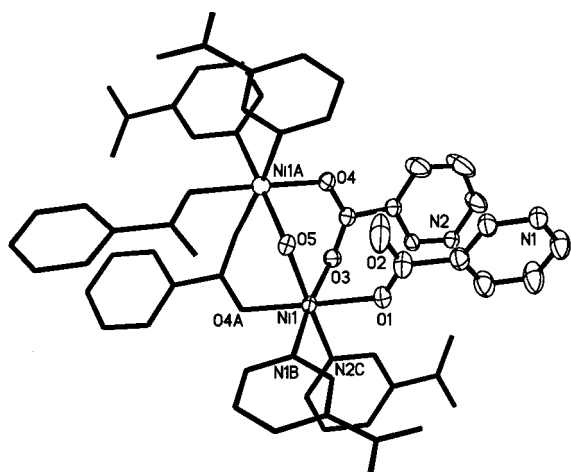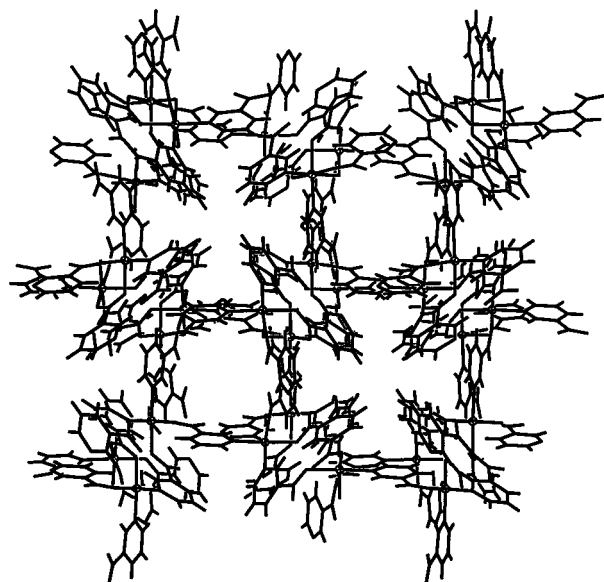

Figure 3. Coordination environment of **2**. The asymmetric unit (excluding ethanol and water) is shown with ellipsoids at 50% probability.

cobalt atom, two L ligands, one bridging water molecule, one-half guest molecule of disordered *trans*-3-(3-pyridyl)acrylic acid, and one-half disordered water guest molecule (Figure 5). One of the two L ligands adopts an exo-bidentate linkage, while the

Figure 4. 3-D framework of **2** as viewed down the *c* axis. Included ethanol and water molecules are omitted for clarity.
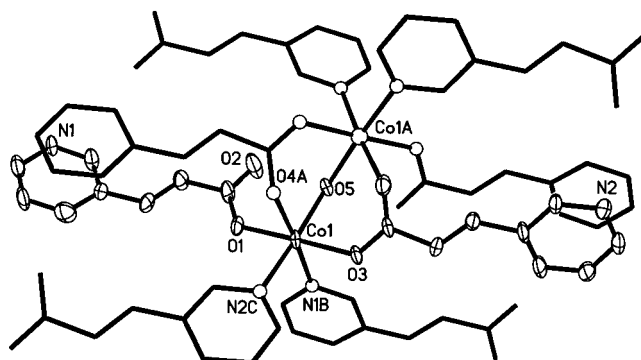

Figure 5. Coordination environment of **3**. The asymmetric unit excluding the guest molecules is shown with ellipsoids at 50% probability.

other L ligand adopts an exo-tridentate linkage. The coordination environment of Co1 in **3** is similar to those of the Co and Ni atoms in **1** and **2** and can be described as a distorted octahedron. The detailed coordination environments for the Co1 center in **3** and the Ni1 center in **4** are listed in Table 2.

The framework structures of **3** and **4** are built from the M_2-(*trans*-3-(3-pyridyl)acrylate)$_4$(μ-H$_2$O) unit. The network topologies of **3** and **4** are very similar to that of **1**. The exo-bidentate L ligands link the bimetallic building units to form 1-D ladders of $[M_2(\mu$-H$_2$O)(*trans*-3-(3-pyridyl)acrylate)$_2]_\infty$ along the *c* axis (Figures S5−S10). These 1-D ladders are then doubly bridged by exo-tridentate L ligands to four adjacent 1-D ladders to form a complicated 3-D framework structure (Figure 6). Interestingly, four 1-D ladders of $[M_2(\mu$-H$_2$O)(*trans*-3-(3-pyridyl)acrylate)$_2]_\infty$ are linked by the exo-tridentate L ligands to form rhomboid channels with diagonal lengths of ~6.6 × 8.7 and ~6.7 × 8.6 Å for **3** and **4**, respectively. These channels are running along the [1 −1 0] axis and occupied by highly disordered free *trans*-3-(3-pyridyl)acrylic acid and water guest molecules.

3. Removal of Guest Molecules. When a freshly prepared and ground sample of **1** was evacuated at 10^{-2} Torr and 40 °C for 18 h, the sample experienced a weight loss corresponding to the removal of 90% of the ethanol and water guest molecules. Interestingly, an XRPD of the evacuated solid is very similar to that of the pristine sample of **1** (Figure S13). Similar evacuation of **1** at 10^{-2} Torr and 60 °C for 18 h results in the
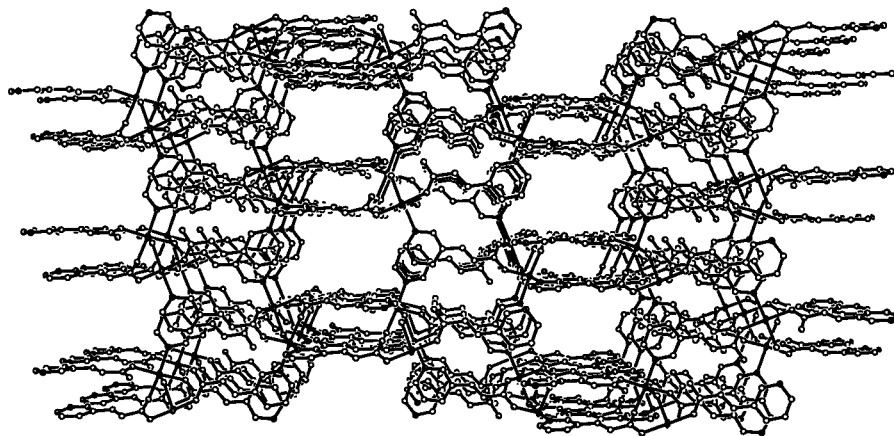
Figure 6. 3-D framework of **3** as viewed down the [1 −1 0] axis. Included guest molecules are omitted for clarity.

complete removal of all the ethanol and water guest molecules, and yet the X-ray powder diffraction studies indicated that the framework structure of **1** remains intact. This result demonstrates that the removal of guest molecules from **1** has led to a porous solid which maintains its structural integrity.

Evacuation of compound **2** at 10^{-2} Torr and 60 °C for 18 h led to a weight loss corresponding to the partial removal of the guest molecules, while evacuation of **2** at 10^{-2} Torr and 90 °C for 48 h resulted in the loss of all the guest molecules. The fact that the included ethanol molecules are more difficult to remove is entirely consistent with the structure of **2** which shows that ethanol guest molecules reside in the spherical cages with relatively small cross-shaped openings. Moreover, it is even more intriguing that **2** can lose included ethanol molecules without the collapse of the 3-D framework structure (Figure S13). There is apparently significant flexibility for the coordinated 3-pyridyl rings in the solid state so that adjacent 3-pyridyl rings in the cross-shaped openings can work cooperatively to "breathe" out included ethanol molecules. We also note that evacuation of **2** at 10^{-2} Torr and 90 °C for 48 h has resulted in partial loss of bridging water molecules. XRPD results clearly indicated the partial decomposition of the 3-D framework structure. We have failed to remove the included free *trans*-3-(3-pyridyl)acrylic acid in **3** and **4** without the collapse of their framework structures evidently due to the high boiling (or sublimation) temperature of *trans*-3-(3-pyridyl)acrylic acid. Compounds **1**−**4** are air stable and do not dissolve in common solvents.

In summary, we have demonstrated the synthesis of 3-D metal−organic polymeric frameworks based on *m*-pyridinecarboxylate bridging ligands. Compounds **1**−**4** are all built from the M_2(*m*-pyridinecarboxylate)$_4$(H_2O) units. Despite different bridging ligand lengths, compounds **1**, **3**, and **4** exhibit the same network topologies and open channels. On the contrary, compound **2** exhibits very different network topologies and possesses both open channels and spherical cages with small cross-shaped openings. Evacuation and powder X-ray diffraction studies have shown that the guest molecules in **1** and **2** can be removed to afford porous metal−organic frameworks that retain the structures of the pristine solids.

Supporting Information Available: Thirteen figures, one table, and X-ray crystallographic files in CIF format for the structures of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010343D