Nanoporous, Interpenetrated Metal−Organic Diamondoid Networks

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Reactions of $Cd(NO_3)_2 \cdot 4H_2O$ with 4-cyanopyridine in the presence of ethanol or pyrazine guest molecules under hydro(solvo)thermal conditions afford two new cadmium coordination polymers, $[Cd(isonicotinate)_2(EtOH)][EtOH]$, **1**, and $[Cd(isonicotinate)_2(H_2O)][pyrazine]$, **2**. The Cd centers in both **1** and **2** are seven-coordinate with distorted pentagonal bipyrimidal structures via coordination to two pyridyl nitrogen atoms, one oxygen atom from a solvent molecule, one chelating carboxylate, and one semichelating carboxylate group. The bridging isonicotinate groups link each Cd center to four adjacent Cd centers, resulting in three-dimensional polymeric networks based on doubly interpenetrated diamondoid structures. One molecule of ethanol or pyrazine is also included in **1** or **2**, respectively, to fill the void space left within the solid after the twofold interpenetration. Thermogravimetric analyses (TGA) showed that the included and coordinated ethanol molecules in **1** could be removed stepwise at 100 and 160 °C, respectively. After the removal of the guest ethanol molecules, the resulting nanoporous solid exhibits the same X-ray powder diffraction (XRPD) pattern as **1**. Guest ethanol molecules can be reintroduced into the evacuated sample of **1** via exposure to ethanol vapor at room temperature. Further heating results in the loss of coordinated ethanol molecules and the collapse of the polymeric network structure. On the other hand, XRPD shows that removal of pyrazine in **2** is accompanied by the loss of the coordinated water molecules and, consequently, the collapse of the polymeric network structure. These results demonstrate that nanopores can be designed based on interpenetrated coordinated networks. Crystal data for **1**: orthorhombic space group *Pbca*, $a = 12.691(1)$ Å, $b = 15.545(1)$ Å, $c = 18.342(1)$ Å, and $Z = 8$. Crystal data for **2**: orthorhombic space group *Pbca*, $a = 12.081(1)$ Å, $b = 15.323(2)$ Å, $c = 19.705(3)$ Å, and $Z = 8$.

Introduction

The prospect of generating new materials with interesting structures and prescribed functions provides significant motivation for the recent surge of research activities in organic and metal−organic supramolecular frameworks.[1] Many organic and metal−organic polymeric networks have recently been demonstrated to possess nanopores that are potentially useful for size-selective and functional-group-selective sorptions.[2] The construction of functional coordination polymers based on diamondoid structures is of particular interest owing to the general robustness of three-dimensionally interconnected diamondoid networks.[3] Although Wuest and co-workers have recently demonstrated the construction of diamondoid networks of hydrogen-bonded molecular tectons possessing large pores that are occupied by included guest molecules,[4] the synthesis of nanoporous diamondoid metal−organic frameworks has yet to be realized. The scarcity of nanoporous diamondoid frameworks stems from the high propensity of diamondoid nets to interpenetrate, thereby providing an efficient pathway for filling the void space.[5] Moreover, nearly all metal−organic diamondoid networks have been constructed with neutral linking groups such as bipyridines,[6] dicyanobenzenes,[7] and cyanopyridines[8] to result in cationic polymeric frameworks; in these coordination networks, counterions provide an additional means for filling any open space left after interpenetration. Accordingly, we have devised an interesting approach to the synthesis of diamondoid metal−organic frameworks using anionic bifunctional linking groups, 4-pyridinecarboxylates.[9] The metal centers can be linked by 4-pyridinecarboxylate groups to afford neutral, interpene-

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trated diamondoid networks. Without the counterions, open cavities can exist in these interpenetrated diamondoid networks; these cavities can be occupied by exchangeable and removable guest molecules. Herein we report the synthesis and X-ray single-crystal structures of two interpenetrated diamondoid networks [Cd(isonicotinate)$_2$(EtOH)][EtOH], **1**, and [Cd(isonicotinate)$_2$(H_2O)][pyrazine], **2**, and the generation of nanoporous coordination networks via the removal of guest ethanol molecules from **1**.

Experimental Section

Materials and Methods. All chemicals were purchased from Aldrich and used without further purification. The IR spectra were recorded as 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 ($\lambda = 1.5406$ 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 SHELXTL-XPOW program and single-crystal reflection data. Density measurements were carried out by the neutral buoyancy method using a mixture of chlorobenzene and dibromomethane. Elemental and thermogravimetric analyses were done at the Microanalytical Laboratory of University of Illinois at Urbana-Champaign. TGA experiments were carried out at a heating rate of 20 °C/min under nitrogen.

Synthesis of [Cd(isonicotinate)$_2$(EtOH)][EtOH], 1. A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (1.617 g, 5.25 mmol) and 4-cyanopyridine (1.092 g, 10.5 mmol) was thoroughly mixed with ethanol (4 mL) and H_2O (1 mL) in a 23 mL Teflon-lined autoclave (Parr bomb). The autoclave was sealed and heated in an oven at 110 °C. Colorless rectangular plate crystals were obtained after 72 h of heating. Yield: 1.541 g (65.4%). **1** always analyzes low in C and H, and high in N, suggestive of the facile loss of guest ethanol molecules. Density: 1.60(1) g/cm^3. IR (cm^{-1}): 3418 (m), 2972 (w), 1592 (s), 1550 (s), 1400 (s), 1227 (w), 1086 (w), 1058 (m), 1015 (m), 862 (m), 776 (m), 696 (s).

Synthesis of [Cd(isonicotinate)$_2$(H_2O)][pyrazine], 2. A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.616 g, 2.0 mmol), 4-cyanopyridine (0.416 g, 4.0 mmol), and pyrazine (0.500 g, 4.0 mmol) was thoroughly mixed with H_2O (4 mL) in a 23 mL Teflon-lined autoclave (Parr bomb). The autoclave was sealed and heated in an oven at 130 °C. Colorless rectangular plate crystals were obtained after 48 h of heating. Yield: 0.509 g (56.1%). Anal. Calcd for $C_{16}H_{14}N_4O_5Cd$: C, 42.2; H, 3.08; N, 12.3. Found: C, 41.6; H, 3.02; N, 11.9. Density: 1.66(1) g/cm^3. IR (cm^{-1}): 3375 (m), 3072 (m), 1595 (s), 1550 (s), 1400 (s), 1229 (w), 1147 (w), 1123 (w), 1059 (w), 1028 (w), 861 (w), 775 (m), 694 (s), 620 (w).

Removal and Reintroduction of Guest Molecules. A freshly ground sample of **1** (390 mg, 0.87 mmol) was subjected to vacuum at room temperature. After 24 h, the sample exhibited a weight loss of 43.0 mg, equivalent to the loss of one ethanol molecule per formula unit (calcd 40.0 mg).

Guest ethanol molecules can be reintroduced into the evacuated sample of **1** via exposure to ethanol vapor. When 107.7 mg of an evacuated sample of **1** was exposed to ethanol vapor at room temperature for 4 h, the sample experienced a weight gain of 12.3 mg (calcd 12.3 mg).

Evacuation of [Cd(isonicotinate)$_2$(H_2O)][pyrazine] was performed similarly. However, no weight loss was observed until the sample was heated. A freshly ground sample of **2** (100 mg, 0.22 mmol) was placed inside an oven at 140 °C. After 24 h, the sample exhibited a weight loss of 21.2 mg, equivalent to the loss of both guest pyrazine and coordinated water molecules (calcd 21.1 mg). The guest pyrazine and coordinated water molecules can also be removed under vacuum at 95 °C. After several attempts, we have not been able to remove only guest pyrazine molecules (without the loss of coordinated water molecules).

X-ray Data Collections and Structure Determinations. Data collection for **1** was carried out with a colorless crystal of dimensions 0.18 × 0.20 × 0.24 mm on a Siemens SMART system equipped with a CCD detector using Mo Kα radiation. Of the 4393 reflections measured, 1821 reflections with $I > 3\sigma(I)$ were used in structure solution and refinement. The structures were solved using SIR92[10] and refined using the CRYSTALS software package by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms except the included ethanol molecule.[11] H(111) was located in the electron density difference map and refined isotropically. All of the other hydrogen atoms were located by geometric placing. Final refinement gave $R = 0.033$, $R_w = 0.035$, and goodness of fit = 1.12. Experimental details for X-ray data collection of **1** are presented in Table 1. Selected bond distances and angles for **1** are listed in Table 2.

Table 1. Data for the X-ray Diffraction of **1** and **2**^{a}

empirical formula	$CdC_{16}H_{18}N_2O_6$, **1**	$CdC_{16}H_{14}N_4O_5$, **2**
a, Å	12.691(1)	12.081(1)
b, Å	15.545(1)	15.323(2)
c, Å	18.342(1)	19.705(3)
V, Å^3	3618.7(1)	3647.7(2)
Z	8	8
fw	447.74	454.72
space group	*Pbca* (No. 61)	*Pbca* (No. 61)
T, °C	−75 (1)	25(1)
λ (Mo Kα), Å	0.710 73	0.710 73
ρ_{obs}, g/cm^3	1.60(1)	1.64(1)
ρ_{calc}, g/cm^3	1.64	1.66
μ, cm^{-1} (Mo Kα)	12.3	10.2
min and max resid dens, e/Å^3	−0.49, 1.46	−1.22, 0.89
R	0.033	0.036
R_w	0.035	0.045
goodness of fit	1.12	1.02

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$.

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

1		2	
Cd1−O2	2.664(4)	Cd1−O2	2.573(2)
Cd1−O4	2.279(5)	Cd1−O4	2.306(2)
Cd1−N8	2.343(5)	Cd1−N8	2.318(2)
Cd1−O11	2.327(4)	Cd1−O11	2.465(2)
Cd1−O14	2.442(4)	Cd1−O13	2.355(2)
Cd1−O16	2.384(4)	Cd1−O20	2.334(3)
Cd1−N20	2.366(5)	Cd1−N17	2.396(3)
O2−Cd1−O4	52.5(2)	O2−Cd1−O4	53.1(1)
O2−Cd1−N8	82.5(2)	O2−Cd1−N8	82.0(1)
O2−Cd1−O11	102.6(2)	O2−Cd1−O11	161.4(1)
O2−Cd1−O14	135.5(2)	O2−Cd1−O13	139.2(1)
O2−Cd1−O16	165.2(2)	O2−Cd1−O20	95.7(1)
O2−Cd1−N20	85.0(2)	O2−Cd1−N17	85.6(1)
O4−Cd1−N8	134.3(2)	O4−Cd1−N8	134.4(1)
O4−Cd1−O11	89.7(2)	O4−Cd1−O11	140.6(1)
O4−Cd1−O14	84.7(2)	O4−Cd1−O13	86.8(1)
O4−Cd1−O16	139.1(2)	O4−Cd1−O20	88.8(1)
O4−Cd1−N20	92.8(2)	O4−Cd1−N17	90.3(1)
N8−Cd1−O11	93.0(2)	N8−Cd1−O11	84.8(1)
N8−Cd1−O14	141.1(2)	N8−Cd1−O13	138.6(1)
N8−Cd1−O16	86.7(2)	N8−Cd1−O20	88.3(1)
N8−Cd1−N20	90.7(2)	N8−Cd1−N17	94.3(1)
O11−Cd1−O14	86.9(2)	O11−Cd1−O13	54.4(1)
O11−Cd1−O16	88.0(2)	O11−Cd1−O20	97.7(1)
O11−Cd1−N20	172.0(2)	O11−Cd1−N17	82.3(1)
O14−Cd1−O16	54.4(2)	O13−Cd1−O20	90.0(1)
O14−Cd1−N20	85.7(2)	O13−Cd1−N17	87.5(1)
O16−Cd1−N20	85.0(2)	O20−Cd1−N17	177.3(1)

A single crystal of **2** with dimensions of 0.25 × 0.32 × 0.36 mm was mounted with epoxy on a Pyrex fiber affixed to a brass pin and transferred to an Enraf-Nonius CAD4-Turbo diffractometer equipped with Mo Kα radiation. Data were collected using the Nonius EXPRESS program.[12] Of the 3842 reflections measured, 3378 reflections with I

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(10) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

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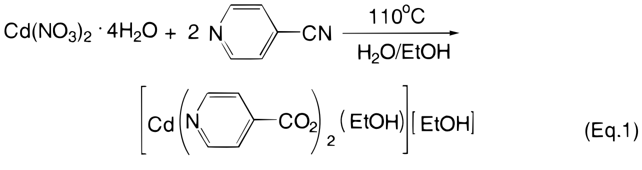
$> 1.96\sigma(I)$ were used in structure solution and refinement. The structure was solved using SIR92 and refined by full-matrix least squares using the CRYSTALS software package and anisotropic displacement parameters for all non-hydrogen atoms.[11] H(201) and H(202) were located in the electron density difference map and refined isotropically. All of the other hydrogen atoms were located by geometric placing. Final refinement gave $R = 0.036$, $R_w = 0.045$, and goodness of fit = 1.02. All drawings (except space-filling models) were produced using the Oxford University program CAMERON.[13] Space-filling models were generated with the SHELX-TL (XP) package.[14] Experimental details for X-ray data collection of **2** are presented in Table 1. Selected bond distances and angles for **2** are listed in Table 2.

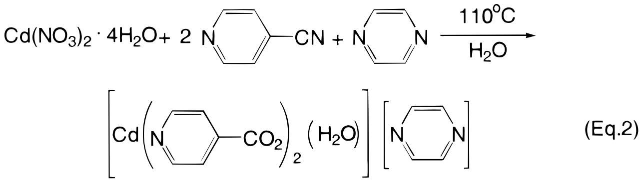
Results and Discussion

Synthesis. Compound **1** was obtained as colorless rectangular plate crystals in 56% yield by a hydro(solvo)thermal reaction between $Cd(NO_3)_2 \cdot 4H_2O$ and 4-cyanopyridine in a mixture of ethanol and water at 110 °C. The IR spectrum of **1** clearly indicates the presence of strong peaks at 1550 and 1400 cm^{-1}, suggesting the formation of carboxylate groups during the reaction.[15] Elemental analysis and TGA results further confirmed the formulation of $[Cd(isonicotinate)_2(EtOH)][EtOH]$ for **1**. The absence of characteristic peaks for cyano groups (at ~2200 cm^{-1}) indicates that the isonicotinate (4-pyridinecarboxylate) ligand results from the hydrolysis of 4-cyanopyridine. The in situ slow hydrolysis of 4-cyanopyridine to the isonicotinate group is very crucial for the synthesis of **1**. Excess cadmium ions in the solution ensure the formation of 3-dimensional coordination polymers by coordinating to both the pyridine and carboxylate ends of the isonicotinate group. In fact, if isonicotinic acid is used in place of 4-cyanopyridine in the hydro(solvo)thermal synthesis, a known mononuclear complex $[Cd(isonicotinate)_2(H_2O)_4]$ with only the pyridyl nitrogen atoms coordinating the Cd center is obtained.[16] The synthesis of 2- and 3-dimensional coordination polymers via "controlled release" of desired ligands by slow hydrolysis of cyanopyridines has recently been explored in our group.[9,17] Similarly compound **2** was prepared in 65% yield by reacting $Cd(NO_3)_2 \cdot 4H_2O$ and 4-cyanopyridine in the presence of pyrazine guest molecules in H_2O at 130 °C (eq 2). **1** and **2** were also prepared in comparable yields when cadmium perchlorate was used in place of cadmium nitrate.



(Eq.1)

1



(Eq.2)

2

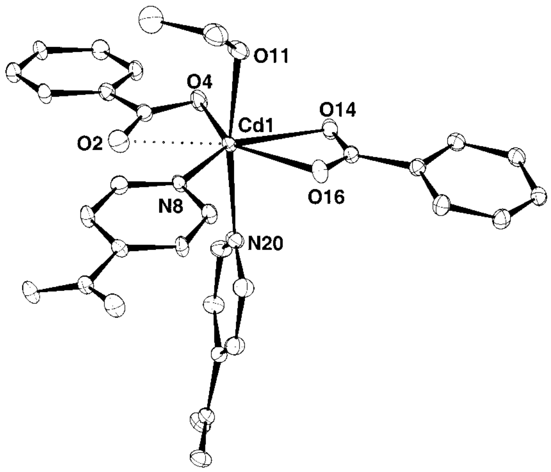


Figure 1. Coordination environment of **1**. The ellipsoids are shown at 30% probability.

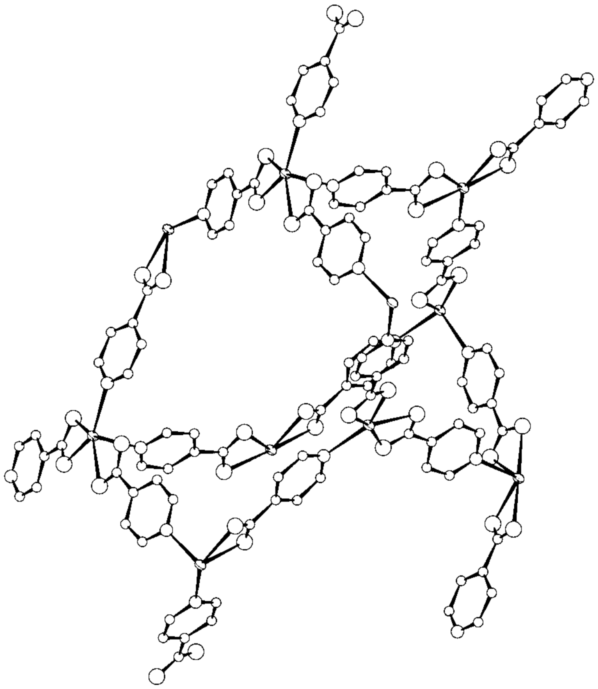


Figure 2. Diamondoid structure of **1**. The ellipsoids represent Cd, while the circles with increasing sizes represent C, N, and O, respectively.

X-ray Single-Crystal Structures. The polymeric structure of **1** was revealed by an X-ray single-crystal structure determination. Each asymmetric unit of **1** contains one Cd atom, two isonicotinate groups, one coordinated ethanol, and one included ethanol molecule. All of the atoms lie on general positions. The local coordination geometry around the Cd1 center can be described as a distorted pentagonal bipyramid (Figure 1). In the equatorial plane, the Cd1 center coordinates to one pyridyl nitrogen atom, to one carboxylate group in a chelating fashion with a Cd1−O16 distance of 2.385(4) Å and a Cd1−O14 distance of 2.442(4) Å, and to one carboxylate group in a semichelating fashion with a Cd1−O4 distance of 2.279(4) Å and a Cd1−O2 distance of 2.664(4) Å. The Cd1 center binds to one ethanol molecule and one pyridyl nitrogen atom in the apical positions (angle O11−Cd1−N20, 172.0(1)°).

The Cd1 center is connected to four adjacent Cd centers through the isonicotinate bridges to result in a 3-dimensional

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[12] Straver, L. H. *CAD4-EXPRESS*; Enraf-Nonius: Delft, The Netherlands, 1992.

[13] Watkin, D. J.; Prout, C. K.; Pearce, L. J. *CAMERON*; Chemical Crystallography Laboratory, University of Oxford: Oxford, 1996.

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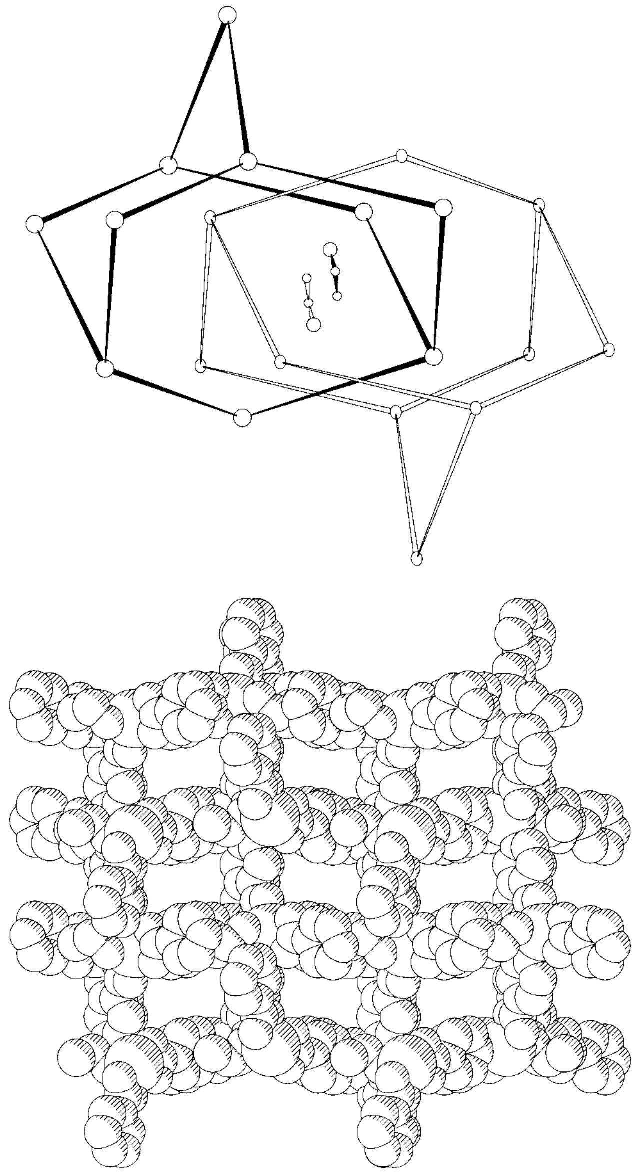

Figure 3. (a) Diagram illustrating the twofold interpenetration in **1**. Only the Cd centers and guest ethanol molecules are shown. (b) Space-filling model of the doubly interpenetrated diamondoid network viewed down the *a* axis. Cavities are occupied by the included ethanol molecules, which have been omitted for clarity.

polymeric network with a diamondoid structure (Figure 2). The Cd−Cd separations are 9.31(1) and 9.38(1) Å within the diamondoid network. If the isonicotinate groups are omitted, the Cd−Cd−Cd angles in **1** range from 75.4° to 129.0° and deviate significantly from the 109.45° expected for an idealized diamond network. Compound **1** thus adopts a highly distorted diamondoid structure, probably in order to accommodate the coordination of one ethanol molecule. As evidenced in Figure 2, a very large cavity exists within a single diamondoid network. However, compound **1** avoids potentially large open space by forming a doubly interpenetrated diamondoid structure (Figure 3a). Moreover, the space-filling model clearly shows that even after the twofold interpenetration, open space still exists within the coordination network of **1** which has been occupied by the included ethanol molecules (Figure 3a). If the guest ethanol molecules are omitted, channels with an opening size of ∼4.5 × 3.4 Å are clearly visible along the crystallographic *a* axis (Figure 3b). The flexibility of the included ethanol molecules allows their removal without destruction of the framework structure of **1**, evidently through the open channels along the *a* axis (see below).

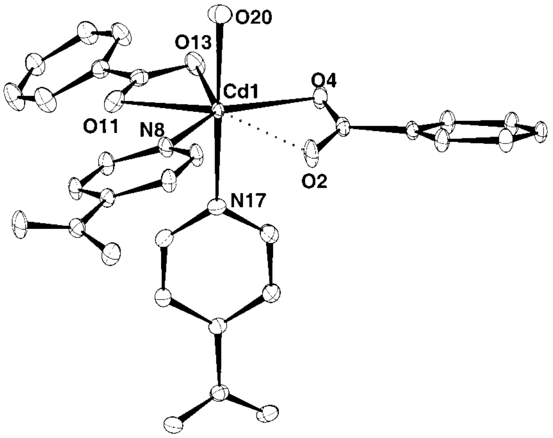

Figure 4. Coordination environment of **2**. The ellipsoids are shown at 30% probability.

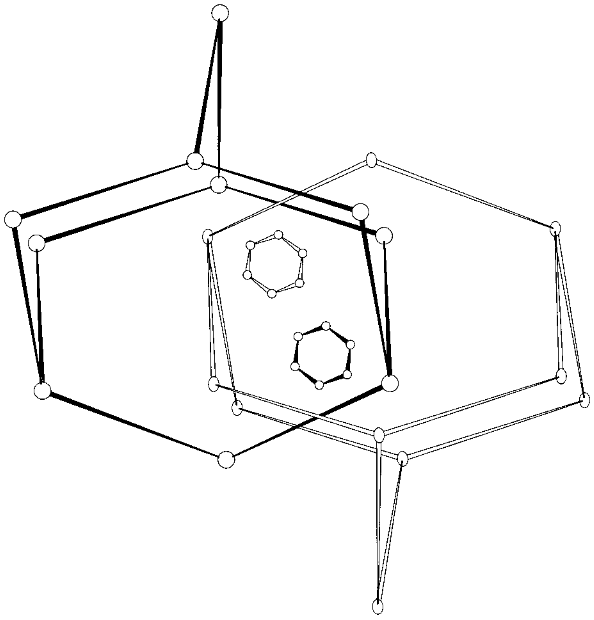

Figure 5. Diagram illustrating the twofold interpenetration in **2**. Only the Cd centers and guest pyrazine molecules are shown.

Compound **2** is very similar in structure to compound **1**. The coordination environment of **2** is essentially identical to that of **1** with the exception that the coordinated ethanol molecule in the apical position of **1** has been replaced with a coordinated water molecule in **2** (Figure 4). Compound **2** also adopts a twofold diamondoid structure with one included pyrazine molecule (Figure 5). The Cd−Cd separations within the diamond network are 9.30(1) and 9.35(1) Å, and the Cd−Cd−Cd angles in each diamond net range from 81.0° to 127.2°. **2** thus adopts a less distorted diamond network than **1**, probably because the coordinated water is not as sterically demanding as the ethanol molecule. A space-filling model also indicates the presence of channels with an opening size of ∼4.4 × 3.4 Å along the *a* axis in **2**. In contrast to **1**, the channel openings in **2** are smaller than the size of the pyrazine molecules.

The formation of a twofold diamondoid structure of **1** and **2** is also worth noting. Bis(isonicotinato)zinc was previously synthesized by reacting $Zn(ClO_4)_2 \cdot 6H_2O$ and 4-cyanopyridine

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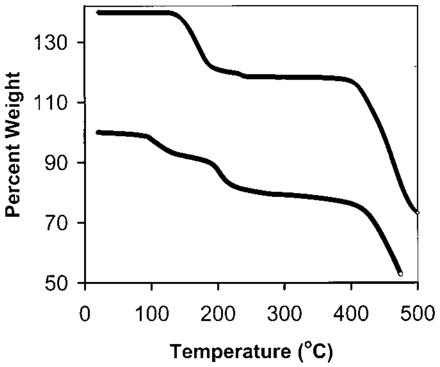
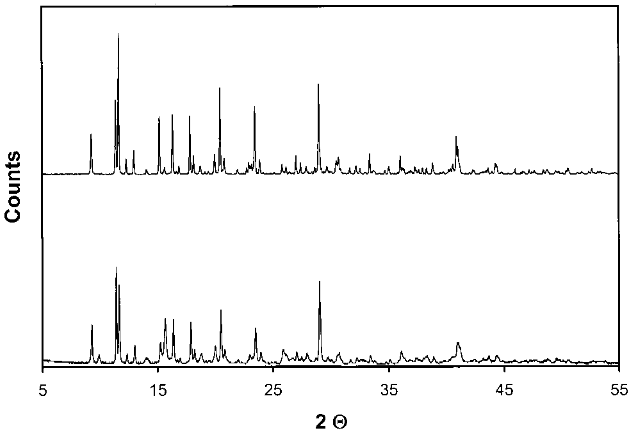


Figure 6. TGA curves for **1** (bottom) and **2** (top). For clarity, the curve for **2** has been shifted up by 40% in percent weight.

under similar conditions. In contrast to **1** and **2**, bis(isonicotinato)zinc adopts a threefold diamondoid structure. This difference can be probably attributed to the tendency of Cd^{II} ions to adopt higher coordination numbers than Zn^{II} ions. The length of the isonicotinate group cannot accommodate a threefold interpenetration in either **1** or **2** with coordinated solvent molecules. Instead, the structural flexibility of metal–ligand coordination allows **1** and **2** to adopt a twofold diamondoid structure by including appropriate guest molecules. This result demonstrates that interpenetrated diamondoid networks with open cavities can be obtained with a judicious choice of ligand length and metal centers.

Removal of Guest Molecules: TGA and XRPD Studies. X-ray single-crystal structures clearly indicate that open channels along the *a* axes exist in both **1** and **2**. We were intrigued by the possibility of generating nanoporous, interpenetrated diamondoid networks by removing the guest molecules in **1** and **2**. The TGA curve of **1** showed that two discrete weight losses occur at onset temperatures of 100 and 160 °C, corresponding to the stepwise removal of the included and coordinated ethanol molecules, respectively (Figure 6). Interestingly, an XRPD for the sample after removal of the included ethanol molecules remains essentially identical to those of pristine compound **1** (Figure 7a). Moreover, guest ethanol molecules can be readily reintroduced into the evacuated sample of **1** by exposure to ethanol vapor at room temperature. This result conclusively demonstrates that the guest ethanol molecules in **1** have been successfully removed to result in a nanoporous material with the same twofold diamondoid network structure as **1**. However, upon the removal of the coordinated ethanol molecules from **1**, an essentially amorphous material was obtained and the framework structure of **1** likely collapsed.

In stark contrast to the above results, a TGA curve of **2** shows that the removal of guest pyrazine molecules is inevitably accompanied by the loss of coordinated water molecules (Figure 6). XRPD studies indicate that the framework structure of **2** has collapsed after the removal of the guest pyrazine molecules (Figure 7b). The different behavior between **1** and **2** can be rationalized on the basis of their X-ray single-crystal structures. Although **1** and **2** have essentially the same open channels along their crystallographic *a* axes, the flexibility of included ethanol molecules allows their removal from **1** through the open channels without destroying the framework structure of **1**, while rigid pyrazine molecules cannot pass through the open channels in **2**. Consequently, the removal of guest pyrazine molecules will result in the collapse of the framework structure of **2**.



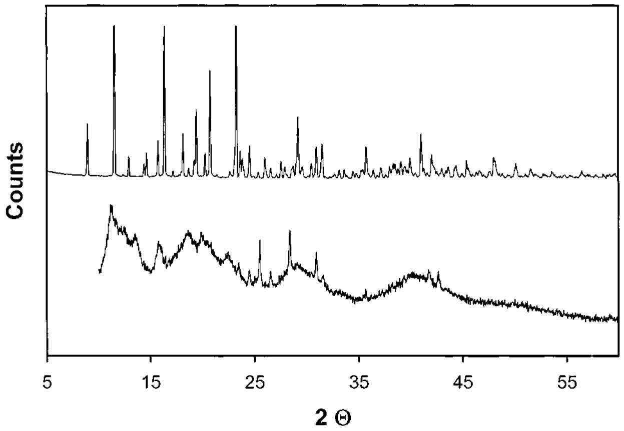


Figure 7. (a) XRPD for **1** before (top) and after (bottom) the removal of guest ethanol molecules. (b) XRPD for **2** before (top) and after (bottom) the removal of guest pyrazine molecules.

Conclusions

Two new 3-dimensional cadmium isonicotinate coordination polymers have been synthesized via in situ slow hydrolysis of 4-cyanopyridines under hydro(solvo)thermal conditions. Both **1** and **2** adopt twofold interpenetrated diamondoid structures and also contain ethanol or pyrazine guest molecules to fill the void space left within the solid after the twofold interpenetration. TGA and XRPD indicated that the guest ethanol molecules in **1** can be removed to result in a nanoporous material with the same twofold diamondoid network structure as **1**. The present work demonstrates that potentially exploitable nanopores can be designed based on interpenetrated coordinated networks with a judicious choice of ligand length and metal centers.

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Supporting Information Available: Two figures and tables listing detailed crystallographic data, fractional atomic coordinates, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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