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A Novel Noninterpenetrating Polycyclohexane Network: A New Inorganic/Organic Coordination Polymer Structural Motif Generated by Self-Assembly of "T-Shaped" Moieties

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The new bidentate nitrogen-donor ligand 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (**4**) has been synthesized (monoclinic, $P2_1/c$, $a = 11.074(2)$ Å, $b = 4.737(1)$ Å, $c = 11.475(2)$ Å, $\beta = 115.861(9)°$, $V = 541.7(1)$ Å^3, $Z = 4$) and its coordination chemistry with cadmium and cobalt nitrate hydrates investigated. Two new noninterpenetrating coordination polymers based on "T-shaped" building blocks have been obtained: $[Cd(NO_3)_2(C_{12}H_{10}N_4)_{1.5}\cdot CH_2Cl_2]_n$ (**5**) (monoclinic, $P2_1/n$, $a = 7.891(1)$ Å, $b = 17.172(3)$ Å, $c = 18.576(4)$ Å, $\beta = 97.72(1)°$, $V = 2494.5(7)$ Å^3, $Z = 4$) and $[Co(NO_3)_2(C_{12}H_{10}N_4)_{1.5}\cdot CH_2Cl_2]_n$ (**6**) (monoclinic, $P2_1/n$, $a = 7.7954(8)$ Å, $b = 17.026(3)$ Å, $c = 18.412(3)$ Å, $\beta = 97.89(1)°$, $V = 2420.6(6)$ Å^3, $Z = 4$). Both **5** and **6** adopt a novel "polycyclohexane" structural motif, consisting of "all-equatorially" condensed cyclohexane-like M_6(ligand)$_6$ units. They are open-framework materials with unusually large cavities (ca. 28 × 15 Å), and reversibly absorb and desorb guest molecules between room temperature and 213 °C without framework decomposition.

Introduction

The construction of new polymeric networks through the rational combination of organic ligands and metal ions is an area of intense current interest.[1−4] In this context, rigid organic ligands containing pyridine rings separated by various spacers such as 4,4′-bipyridine (**1**), 1,2-bis(4-pyridyl)ethene (**2**), and 1,2-bis(4-pyridyl)ethyne (**3**) (Figure 1), have proven popular in recent years and have resulted in a rich variety of structural motifs.[2,5] In general, the polymer topology generated from the self-assembly of inorganic (metal) species and organic ligands can be modified by the chemical structure of the ligands chosen, the coordination geometry preferred by

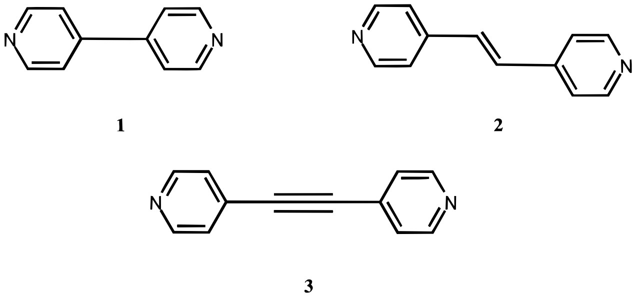

Figure 1. Rigid organic bipyridyl-based ligands used in the construction of coordination polymer frameworks.

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the metal, the inorganic counterions, the solvent system, and sometimes the metal-to-ligand ratio. Among these factors, the choice of organic ligand is certainly extremely important in determining the ultimate topology of the product. As we know, the organic ligands serve to tether the metal centers and to propagate the structural information expressed in metal coordination preferences throughout the extended structure; therefore, properties of organic ligands such as coordination ability, length, geometry, and relative orientation of the donor groups play a very important role in dictating polymer framework topology. In other words, the network topology can be controlled and modified by selecting the chemical structure of the organic ligand. The generation of such frameworks is a promising path in the search for stable microporous inorganic/organic networks that exhibit reversible guest exchange and, possibly, selective catalytic activity.[6,7] We have been investigating the effect of ligand functionality in the construction of arrays based on Cd(II), Co(II), and Cu(II) metal centers with the rigid ligands **1**, **2**, and **3**,[5b,e,8] and report here the syntheses and X-ray structure determinations of the new organic ligand 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene **(4)**, along with two new coordination polymers adopting a novel "polycyclohexane" structure: $[Cd(NO_3)_2(C_{12}H_{12}N_4)_{1.5}\cdot CH_2Cl_2]_n$ (**5**) and $[Co(NO_3)_2(C_{12}H_{12}N_4)_{1.5}\cdot CH_2Cl_2]_n$ (**6**), generated from the reaction of **4** with $Cd(NO_3)_2\cdot 4H_2O$ and $Co(NO_3)_2\cdot 6H_2O$, respectively. Compound **5** is air-stable and exhibits reversible absorption of small organic guest molecules at room temperature.

Experimental Section

Materials and Methods. $Cd(NO_3)_2\cdot 4H_2O$, $Co(NO_3)_2\cdot 6H_2O$, 3-pyridine carboxaldehyde, and hydrazine (35 wt % solution in water) were purchased from Aldrich and used without further purification. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer as KBr pellets in the 4000−400 cm^{-1} range. Differential thermal analysis and thermogravimetric analysis (DTA−TGA) were conducted on a TA Instruments SDT 2960 simultaneous DTA−TGA in a helium atmosphere using a heating rate of 10 °C/min. Compounds **5** and **6** were heated from 30 to 650 °C. Elemental analyses were carried out by National Chemical Consulting.

Synthesis. Preparation of 4. 3-Pyridine carboxaldehyde (2.2 mL, 22 mmol) was dissolved in ethanol (15 mL), followed by dropwise addition of hydrazine (35 wt % solution in water, 1 mL, 11 mmol). After addition of two drops of formic acid, the mixture was stirred at room temperature for 24 h and filtered, and the resulting yellow crystalline solid was washed with ethanol/hexane (1:1) several times and dried in air. Yield: 89%. ^1H NMR ($CDCl_3$, ppm): 8.98 (s, 2 H, pyridyl), 8.70 (d, 2 H, pyridyl), 8.66 (s, 2 H, H−C=N), 8.21, 8.19 (t, t, 2 H, pyridyl), 7.39 (q, 2 H, pyridyl). IR (KBr, cm^{-1}): 1633.5 (s), 1615.3 (s), 1585.7 (s), 1482.1 (s), 1410.6 (s), 1335.0 (s), 1302.6 (s). Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.57; H, 4.76. Found: C, 68.26; H, 4.59.

Preparation of 5. A colorless solution of $Cd(NO_3)_2\cdot 4H_2O$ (92 mg, 0.30 mmol) in MeOH (5 mL) was layered onto a solution of **4** (126 mg, 0.60 mmol) in methylene chloride. Diffusion between the two phases over a period of one month produced bright yellow triangular crystals in 81% yield. IR (KBr, cm^{-1}): 1629.4 (s), 1601.4 (s), 1570.2 (s), 1458.7 (s), 1448.6 (s), 1427.9 (s), 1379.6 (s), 1312.2 (s), 1127.6 (m), 1029.9 (s), 975.6 (s), 875.5 (s), 810.3 (s), 734.1 (w), 690.7 (s), 643.5 (s). Anal. Calcd for $CdC_{18}H_{15}N_8O_6$: C, 41.35; H, 2.72. Found: C, 41.87; H, 2.92.

Preparation of 6. An ethanol solution (10 mL) of $Co(NO_3)_2\cdot 6H_2O$ (87 mg, 0.30 mmol) was allowed to diffuse into a methylene chloride solution (8 mL) of **4** (126 mg, 0.60 mmol) in a test tube for 1 month. Large deep red crystals formed at the bottom of the test tube. Crystals were collected by filtration. Yield: 83%. IR (KBr, cm^{-1}): 1632.4 (s), 1629.7 (s), 1600.6 (S), 1467.6 (m), 1456.0 (s), 1432.9 (m), 1383.6 (s), 1311.4 (w), 1189.8 (s), 1130.1 (m), 1054.9 (m), 1031.4 (s), 881.3 (s), 825.4 (m), 808.0 (s), 694.3 (s), 648.0 (m). Anal. Calcd for $CoC_{18}H_{15}N_8O_6$: C, 39.11; H, 2.92. Found: C, 39.94; H, 2.57.

Crystal Structure Determination. Single crystals of **4** and **5** used for data collection were epoxied in air onto the end of thin glass fibers; **6** was encased in epoxy on the end of the fiber to prevent solvent loss (vide infra). Intensity measurements for each were made at 20 °C on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation ($\lambda = 0.710\,69$ Å). Unit cells for each compound were initially determined from 15 randomly selected reflections obtained using the AFC6 automatic search, center, index, and least-squares routines, and ultimately refined using 25 high-angle reflections after data collection. Data processing was performed on a Silicon Graphics INDIGO^2 computer using the TEXSAN structure solving program library obtained from the Molecular Structure Corporation, The Woodlands, TX. Lorentz−polarization (Lp) and absorption (DIFABS) corrections were applied to each data set. Full-matrix least-squares refinements minimized the function

$$\Sigma_{hkl}\, w(|F_o| - |F_c|)^2$$

where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

The intensities of three standard reflections measured every 150 reflections for each compound showed no significant deviations during data collection. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters; the hydrogen atoms were calculated and not refined. Crystal data, data collection parameters, and analysis statistics for **4**−**6** are listed in Table 1. Relevant interatomic bond distances and bond angles for **4**−**6** are collected in Tables 2−4, respectively.

Results and Discussion

Synthesis. The long rigid bidentate ligand 1,4-bis-(3-pyridyl)-2,3-diaza-1,3-butadiene **(4)** was prepared in 89% yield by the Schiff-base condensation reaction of 3-pyridine carboxaldehyde with hydrazine (35 wt % solution in water) in ethanol at room temperature. Single crystals of **4** were obtained by slow diffusion of *n*-hexane into a solution of **4** in methylene chloride at room temperature. When a solution of **4** in methylene chloride was treated with $Cd(NO_3)_2\cdot 4H_2O$ in methanol and $Co(NO_3)_2\cdot 6H_2O$ in ethanol, respectively, in a molar ratio of 1:2 (metal−ligand), compounds **5** and **6** were obtained as polymeric compounds with a novel two-dimensional noninterpenetrating polycyclohexane motif in chair conformation. It is worthwhile to point out that the coordination chemistry of **4** with transition metal templates, such as Cd(II) and Co(II), appears to be quite versatile. Recently, a series of novel solvent-dependent polymeric structures based on Cd(II) and Co(II) metal centers and **4** have been synthesized in our lab.[9] In these

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Table 1. Crystallographic Data for 4−6

formula	$C_{12}H_{10}N_4$, **4**	$CdC_{19}H_{17}N_8O_6Cl_2$, **5**	$CoC_{19}H_{17}N_8O_6Cl_2$, **6**
fw	210.24	636.71	583.23
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	11.074(2)	7.891(1)	7.7954(8)
b (Å)	4.737(1)	17.172(3)	17.026(3)
c (Å)	11.475(2)	18.576(4)	18.413(3)
α (deg)	90	90	90
β (deg)	115.861(9)	97.72(1)	97.86(1)
γ (deg)	90	90	90
V (Å^3)	541.7(1)	2494.5(7)	2420.6(6)
Z	4	4	4
ρ(calcd) (g/cm^3)	1.289	1.695	1.600
μ (Mo Kα) (cm^{-1})	0.822	11.422	9.826
temp (°C)	23	23	23
no. of reflcns ($I > 3\sigma$)	583	3590	3310
residuals:^{a} R; R_w	0.052; 0.057	0.044; 0.059	0.062; 0.083

^{a} $R = \sum_{hkl}(||F_{obs}| - |F_{calc}||)/\sum_{hkl}|F_{obs}|$; $R_w = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|^2)/\sum_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$.

Table 2. Interatomic Distances (Å) and Bond Angles (deg) with Esds for 4

N(1)−C(1)	1.331(4)	N(1)−C(5)	1.336(4)
N(2)−N(2)	1.414(4)	N(2)−C(6)	1.284(5)
C(1)−C(2)	1.391(5)	C(2)−C(3)	1.369(4)
C(3)−C(4)	1.389(4)	C(4)−C(5)	1.395(5)
C(1)−N(1)−C(5)	117.0(3)	N(2)−N(2)−C(6)	112.1(3)
N(1)−C(1)−C(2)	123.1(3)	C(2)−C(3)−C(4)	119.9(3)
N(1)−C(5)−C(4)	124.5(3)	N(2)−C(6)−C(4)	122.2(3)

Table 3. Interatomic Distances (Å) and Bond Angles (deg) with Esds for 5

Cd−O(1)	2.394(5)	Cd−O(2)	2.403(4)
Cd−O(4)	2.362(4)	Cd−O(5)	2.508(4)
Cd−N(1)	2.334(4)	Cd−N(4)	2.377(4)
Cd−N(5)	2.342(4)	O(1)−N(7)	1.275(7)
O(2)−N(7)	1.267(7)	O(4)−N(8)	1.267(6)
O(5)−N(8)	1.253(6)	N(1)−C(1)	1.349(7)
N(2)−N(3)	1.417(7)	N(2)−C(6)	1.269(7)
N(6)−N(6)	1.42(1)	N(6)−C(18)	1.282(7)
C(1)−C(2)	1.389(7)	C(4)−C(5)	1.377(7)
N(1)−Cd−N(4)	175.3(1)	N(1)−Cd−N(5)	92.8(1)
N(5)−Cd−N(4)	83.6(1)	O(5)−Cd−N(5)	85.0(1)
O(1)−Cd−O(2)	53.6(2)	O(1)−Cd−O(4)	135.5(1)
O(1)−Cd−O(5)	171.9(1)	O(1)−Cd−N(1)	92.9(2)
O(1)−Cd−N(4)	90.0(1)	O(1)−Cd−N(5)	87.0(1)
O(2)−Cd−N(4)	82.0(1)	O(2)−Cd−O(5)	134.2(1)
O(2)−Cd−N(1)	94.8(2)	O(2)−Cd−N(4)	89.9(1)
Cd−N(1)−C(1)	124.0(3)	C(1)−N(1)−C(5)	116.5(4)
N(3)−N(2)−C(6)	111.5(5)	N(6)−N(6)−C(18)	111.4(6)
C(1)−C(2)−C(3)	118.9(5)	N(3)−C(7)−C(8)	120.1(5)

Table 4. Interatomic Distances (Å) and Bond Angles (deg) with Esds for 6

Co−O(1)	2.216(5)	Co−O(2)	2.285(4)
Co−O(4)	2.172(4)	Co−O(5)	2.294(4)
Co−N(1)	2.188(4)	Co−N(4)	2.193(4)
Co−N(5)	2.137(4)	O(1)−N(7)	1.249(7)
O(2)−N(7)	1.259(6)	O(4)−N(8)	1.276(7)
O(5)−N(8)	1.263(7)	N(1)−C(1)	1.332(7)
N(2)−N(3)	1.412(6)	N(2)−C(6)	1.263(6)
N(6)−N(6)	1.406(9)	N(6)−C(18)	1.355(7)
C(1)−C(2)	1.397(7)	C(4)−C(5)	1.391(7)
N(1)−Co−N(4)	178.6(2)	N(1)−Co−N(5)	92.7(1)
N(5)−Co−N(4)	86.3(1)	O(5)−Co−N(5)	143.2(2)
O(1)−Co−O(2)	56.1(2)	O(1)−Co−O(4)	132.5(2)
O(1)−Co−O(5)	76.0(2)	O(1)−Co−N(1)	87.2(2)
O(1)−Co−N(4)	92.9(2)	O(1)−Co−N(5)	140.5(2)
O(2)−Co−N(4)	88.5(1)	O(2)−Co−O(5)	84.5(2)
O(2)−Co−N(1)	90.5(1)	O(2)−Co−N(4)	88.5(1)
Co−N(1)−C(1)	124.6(3)	C(1)−N(1)−C(5)	116.7(4)
N(3)−N(2)−C(6)	112.8(4)	N(6)−N(6)−C(18)	111.9(5)
C(1)−C(2)−C(3)	119.0(5)	N(3)−C(7)−C(8)	120.3(5)

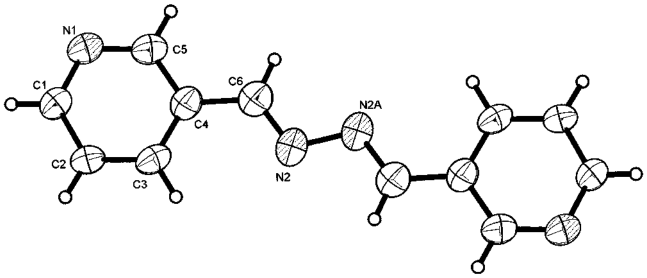

Figure 2. ORTEP drawing of the new ligand 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (**4**) used to construct the polycyclohexane frameworks. Ellipsoids are shown at the 50% probability level.

specific reactions, the products depend only on the solvent systems used instead of the ligand-to-metal ratio. However, increasing the ligand-to-metal ratio resulted in a somewhat higher yield.

Both compounds **5** and **6** are insoluble in water and common organic solvents, such as CH_2Cl_2, CH_3COCH_3, CH_3CN, and THF. Crystals of **5** retain their structural integrity at room temperature for a considerable length of time. The CH_2Cl_2 guest molecules are liberated very slowly at room temperature (72% lost in 2 weeks upon exposure to air). Crystals of **6**, on the other hand, lose solvent molecules rapidly, and turn opaque within minutes under ambient atmosphere. Because of its instability, the host−guest chemistry of **6** could not be investigated.

Structures. The molecular structure of **4** (Figure 2) reveals that the two pyridyl groups are separated by a zigzag −CH=N−N=CH− linkage at the *meta* position on the pyridine rings, resulting in a different orientation of the nitrogen donors compared to **1**, **2**, and **3**. The terminal (pyridyl) N···N separation in **4** is 10.729(4) Å, significantly longer than the terminal N···N separations of 7.122(4), 9.385(5), and 9.685(4) Å found in **1**, **2**, and **3**, respectively. Crystal packing of **4** (Figure 3) shows two sets of molecules connected to one another by two identical "head−head" hydrogen bonds (N(1)···H(1)−C(1): N(1)···C(1) = 3.374(4) Å, N(1)···(1) = 2.640(5) Å, N(1)···H(1)−C(1) = 132.28(6)°[10]) to produce two one-dimensional chains perpendicular to each other. Additionally, these two sets of chains are held together by an additional hydrogen bond (N(2)···H(2)−C(2): N(1)···C(2) = 3.624(4) Å, N(1)···H(2) = 2.706(5) Å, N(1)···C(2) = 157.14(6)°[10]) to produce a 3-D framework.

The X-ray structure of **5** reveals that the Cd(II) atoms lie in a heptacoordinate environment (Figure 4) with

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[10] Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441.

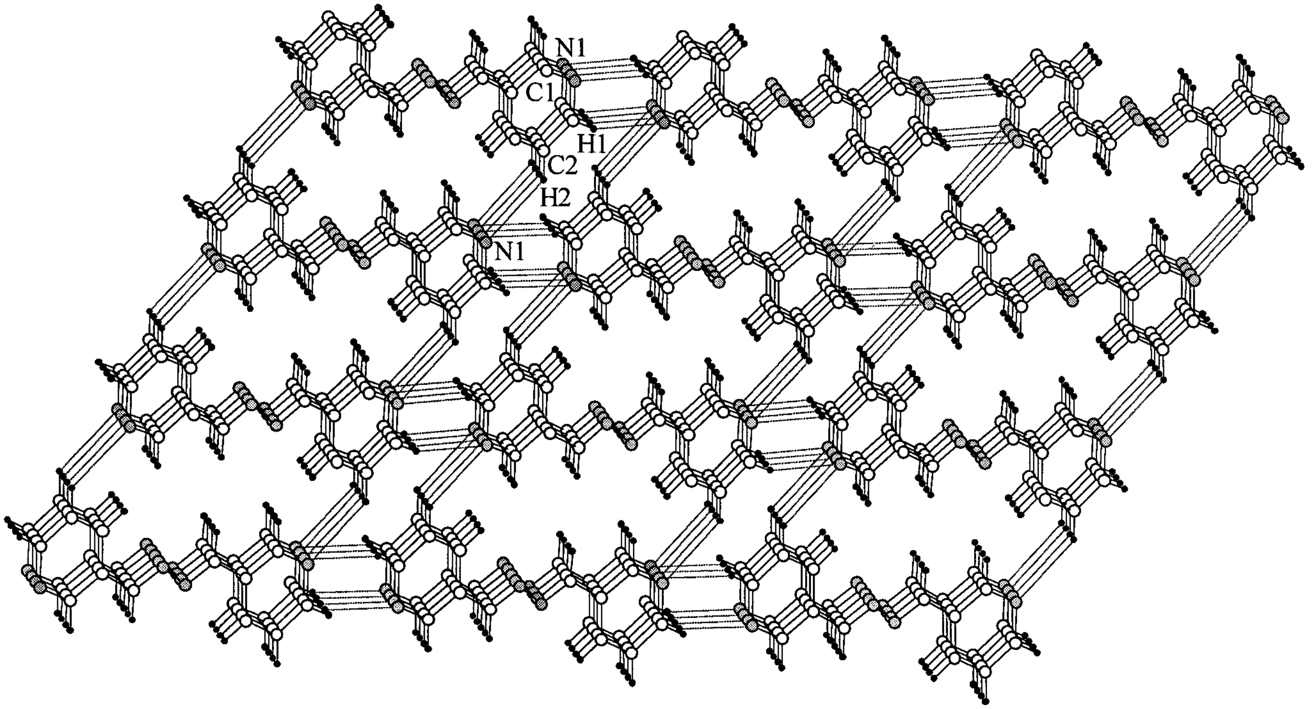

Figure 3. Crystal packing of **4** (3-D framework). Nitrogen, carbon, and hydrogen atoms are shown as gray, open and black circles, respectively. Hydrogen bonds are shown as lines linking the molecules.

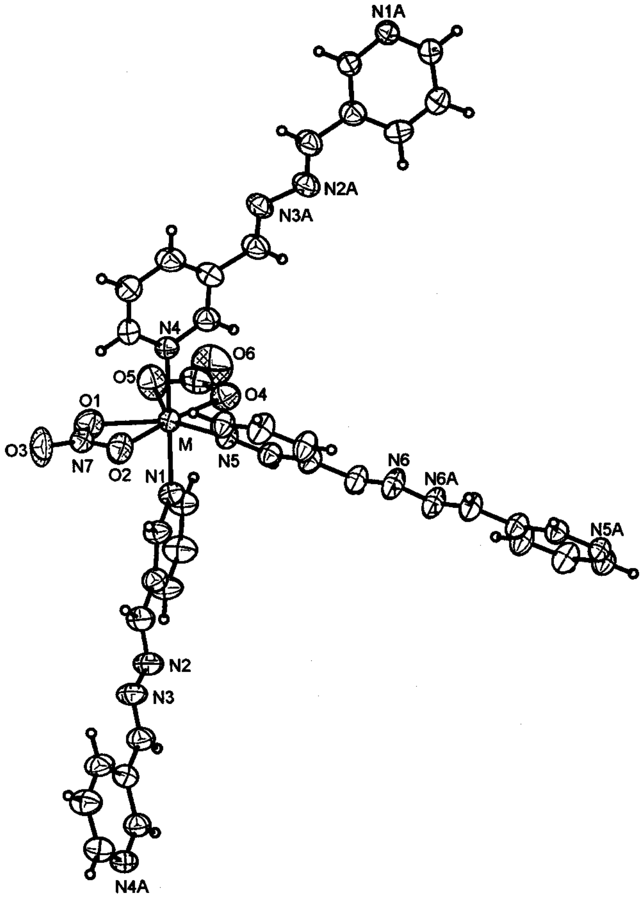

Figure 4. "T-shaped" environment at the metal centers of **5** (M = Cd) and **6** (M = Co), with 50% probability ellipsoids.

three ligands of **4** forming a distorted "T-joint" at the Cd(II) center (N(6)−Cd−N(7) = 83.6(1)°, N(3)−Cd−N(7) = 92.81(1)° and N(3)−Cd−N(6) = 175.3(1)°). The remaining Cd(II) coordination sites are occupied by two bidentate nitrate anions. The Cd−N and Cd−O bond distances range from 2.334(4)−2.343(4) Å and 2.394-(4)−2.508(4) Å, respectively (Table 3), which are consistent with the corresponding bond lengths found in the $[Cd(NO_3)_2(4,4'\text{-bipy})_2]\cdot 2C_6H_4Br_2$[11] and $[Cd(dpb)_{1.5}(NO_3)_2]$.[2e] These "T-joints" connect to each other to produce a novel polycyclohexane structural motif (Figure 5), in which each 66-membered "cyclohexane ring" consists of six ligands and six cadmium ions. The "cyclohexane ring" adopts the chair conformation and repeats along the crystallographic *ab* plane with alternating reversion of the geometry around Cd(II) centers. Alternately, the extended structure can be envisaged as an "all-equatorial" condensation of cyclohexane-like $[Cd_6(N_4C_{12}H_{10})_6]$ units, with the "axial" positions occupied by the nitrate ions.

Single-crystal X-ray analysis shows that the local geometry of the Co(II) center in compound **6** (Figure 4) is similar to the geometry of the cadmium center in compound **5**. The Co−N and Co−O bond lengths lie in the range of 2.137(4)−2.193(4) Å and 2.172(4)−2.294-(4) Å, respectively (Table 4), which are comparable to those of corresponding bond distances found in $[Co(4,4'\text{-bipy})_{1.5}(NO_3)_2]\cdot 2CHCl_3$, $[Co(4,4'\text{-bipy})_{1.5}(NO_3)_2]\cdot 2MeCN$,[2f] $[Co(1,4\text{-bis}(4\text{-pyridyl})\text{ethane})_{1.5}(NO_3)_2]\cdot MeCN$, and $[Co(1,4\text{-bis}(4\text{-pyridyl})\text{ethane})_{1.5}(NO_3)_2]\cdot 3CHCl_3$.[12] However, the Co−O bond distances are significantly shorter than those in $[Co(1,2\text{-bis}(4\text{-pyridyl})\text{ethyne})_{1.5}(NO_3)_2]\cdot MeOH$ (2.351−2.444 Å).[5e] In the solid state, compound **6** adopts the same polycyclohexane pattern as compound **5** (Figure 5). As shown in Figure 6, both **5** and **6** exist as noninterpenetrating open framework coordination polymers with remarkably large cavities and channels (Cd·

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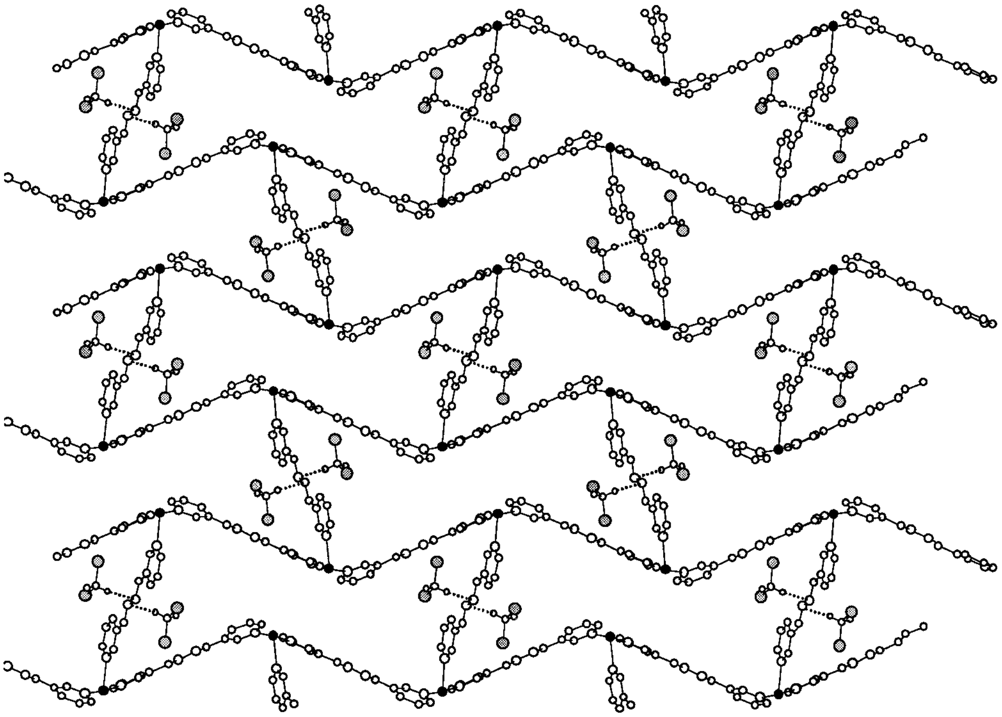

Figure 5. Molecular polycyclohexane motif (viewed down the crystallographic *c*-axis). Cadmium or cobalt centers are shown as black circles, chlorine atoms are shown as gray circles. Nitrogen, carbon, and hydrogen atoms are shown as large, medium, and small open circles. CH_2Cl_2 guest molecules are included in the "cyclohexane" rings (N⋯H−C hydrogen bonds are shown as dotted lines). The NO_3^- ions and the hydrogen atoms on the ligands are omitted for clarity.

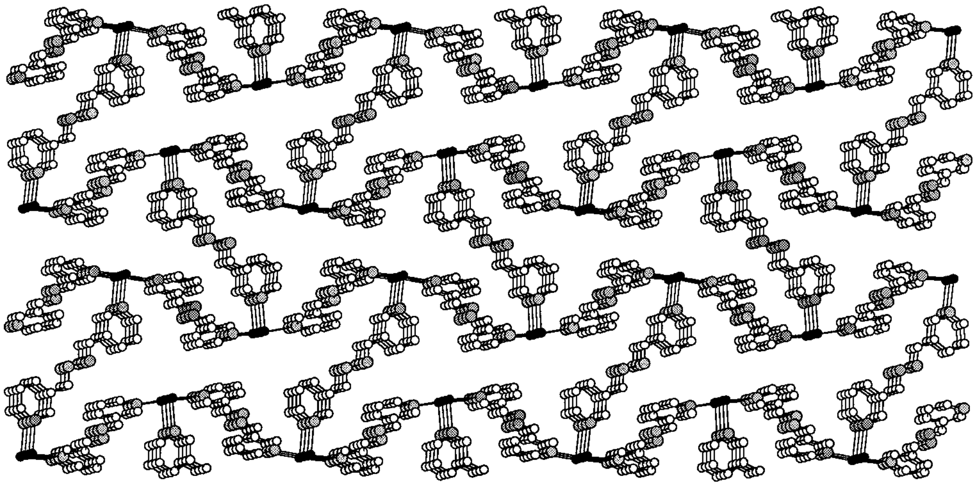

Figure 6. Noninterpenetrating polycyclohexane framework with large cavities and channels. Cadmium or cobalt centers are shown as the black circles. Nitrogen and carbon atoms are shown as gray and open circles, respectively. CH_2Cl_2 guest molecules and NO_3^- ions are omitted for clarity.

⋯Cd = 14.750(4) Å, Co⋯Co = 14.373(3) Å, effective cross section of ca. 28 × 15 Å for **5** and 28 × 14 Å for **6**. The pore dimensions are crystallographic scalar quantities, and do not account for the van der Waals radii of the atoms defining the pore.). To date, most two- and three-dimensional frameworks found in coordination polymers are interpenetrated or self-inclusive,[2f] which always reduces the volume of the cavities and channels. We are aware of only one other crystallographically characterized coordination polymer with dimensions similar in size to **5** and **6**, the square-geometry compound Zn_4O(1,4-benzenedicarboxylate)$(DMF)_8(C_6H_5Cl)$, reported recently by Yaghi.[2h]

It is well-known that the cyclohexane-based extended structural motif (especially in the chair conformation) is commonly found in inorganic chemistry, for example in the gray form of elemental arsenic, and the network of silicon atoms in the Zintl compound $CaSi_2$.[13] Likewise it is common in organic chemistry where the cyclohexane pattern is familiar from cyclohexane itself to diverse polycondensed aliphatic hydrocarbons. Compounds **5** and **6**, then, represent inorganic−organic hybrids that fill a void between purely organic and purely inorganic manifestations of this structural motif. Recently, several types of polymer framework patterns have been constructed by "T-joint" building blocks comprised of 4-pyridyl-based bidentate ligands, including molecular

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ladder,[2e,f,5b] brick wall,[2e,f] molecular bilayer,[5e] 3-D framework,[5d] and parquet motifs.[5e,14] The polycyclohexane motif described here differs distinctly from the patterns mentioned above, and is, to our knowledge, unprecedented. We believe that this unique motif results from the different "transoid" orientation of nitrogen donors on the pyridyl rings in the new ligand **4**. In both compounds **5** and **6**, there is one crystallographically independent CH_2Cl_2 molecule per metal atom lying in the large "cyclohexane ring" as a guest molecule. Each "cyclohexane ring" contains two CH_2Cl_2 guest molecules, which are all oriented so that they appear to be hydrogen bonded, very weakly, to nitrogen atoms on the $-CH{=}N-N{=}CH-$ linkages in the ligands ($N\cdots CH_2Cl_2 = 3.621(4)$ Å).[2f,10]

Thermogravimetric Analyses. Thermogravimetric analyses were carried out using a TA Instrument SDT 2960 simultaneous DTA−TGA under flowing helium at a heating rate of 10 °C/min. For **5**, the TGA shows a weight loss of 13.6% from 135 − 178 °C corresponding to the loss of the CH_2Cl_2 guest molecules (calculated 13.4%). A second weight loss of 32.5% from 213 to 304 °C corresponds to removal of two of the three ligands of **4** (calculated 33.0%). The third weight loss, observed from 310 to 392 °C, corresponds to the release of the remaining ligand (observed 16.4%, calculated 16.5%). A brown amorphous residue (observed 19.3%, calculated for CdO 20.2%) remained. For **6**, the CH_2Cl_2 guest molecules were lost in the range of 123−188 °C (calculated 14.6% observed, 13.6%), followed by a weight loss of 36.0% (225−250 °C), which compares with a calculated value of 36.0% for the loss of two of the three ligands of **4**. An additional ligand molecule is lost in the temperature range 260−370 °C (calculated 18.1% observed 19.6%). A further weight loss was observed above 370 °C, resulting in a black and amorphous final residue.

Host−Guest Chemistry of Compound 5. The most important factor in seeking and developing new molecular-based porous materials is whether the frameworks of such materials are stable even after removal of guest molecules.[15] As we know, many porous systems, upon removal of the included guest molecules, often undergo phase transitions to other more dense structures.[16−19] Crystals of **5** retain their structural integrity at room temperature for a considerable length of time. The empty polycyclohexane framework of **5** is stable at room temperature and does not decompose until 213 °C. Moreover, it exhibits a clear affinity for methylene chloride, and can reversibly desorb and re-absorb this guest molecule at room temperature. X-ray powder diffraction (XRD) patterns of thermally desolvated samples of **5** are compared with those of as-synthesized, solvent-containing **5** in Figure 7. The desolvated samples were obtained by heating crystals of **5** to 160 °C. Total removal of the CH_2Cl_2 guests was confirmed by TGA before performing the powder diffraction experiment. The XRD patterns after heating show that the shapes and intensities of some reflections are slightly changed relative to those of the original sample. Guest loss does not, however, result in symmetry change or cavity volume collapse! Moreover, when the desolvated solids are immersed in CH_2Cl_2 for 24 h at room temperature, XRD patterns nearly identical to those obtained for the original crystals are regenerated, indicating the CH_2Cl_2 moieties were re-incorporated into the framework under these mild conditions. Since **5** is insoluble in CH_2Cl_2, the possibility of a dissolution−recrystallization mechanism to explain the solvent reabsorption is unlikely. TGA analysis confirmed the re-uptake of CH_2Cl_2 to the extent of 92%.

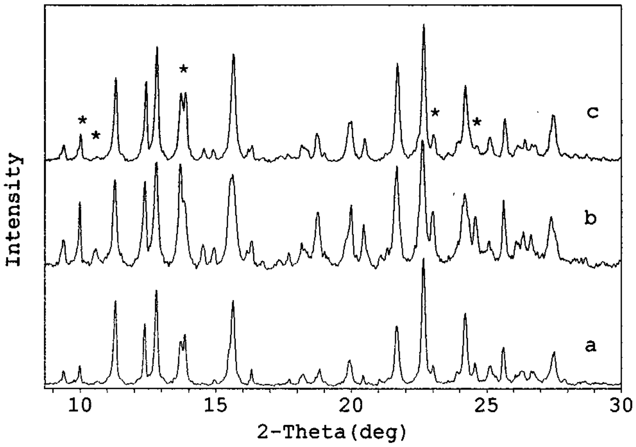

Figure 7. X-ray powder diffraction patterns of **5**: (a) the original crystals of **5**; (b) **5** heated to 160 °C; (c) sample obtained by immersing sample b in CH_2Cl_2 for 24 h at room temperature. The starred peaks indicate reflections whose intensities change most significantly upon loss or uptake of CH_2Cl_2.

Conclusions

In conclusion, we have been able to synthesize isostructural cadmium and cobalt coordination polymers with a novel noninterpenetrating polycyclohexane structural motif by reaction of the new ligand 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (**4**) with $Cd(NO_3)_2{\cdot}4H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$, respectively. Compound **5** was shown to reversibly absorb and desorb CH_2Cl_2 guest molecules at room temperature. We are currently extending this result by preparing open frameworks with pore channels of diverse hole sizes through variation of the guest molecules and counterions and the orientation of the nitrogen donors on Schiff-base ligands structurally related to the new ligand (**4**) reported herein.

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, bond distances and angles, structure factors, and further crystallographic data for **4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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