Organizing Chain and Square-Grid Architectures by Employing Coordination Bonds between Inorganic and Organic Components. New Coordination Polymers Formed from Cd(II), Co(II), and Cu(II) Nitrate Salts and 1,4-Bis(4-pyridyl)butadiyne

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Four new coordination polymers containing the long conjugated bidentate ligand 1,4-bis-(4-pyridyl)butadiyne (**2**) and cadmium, cobalt, and copper nitrate hydrates are reported. The coordination polymers were synthesized using almost identical solution reaction conditions utilizing the same mixed methanol/methylene chloride solvent system. The first compound $[Cd(1,4\text{-bis}(4\text{-pyridyl})butadiyne)(NO_3)_2(H_2O)\cdot CH_2Cl_2]_n$ (**3**; monoclinic, $C2/c$; $a = 28.135(3)$ Å, $b = 8.535(1)$ Å, $c = 17.642(2)$ Å, $\beta = 91.797(2)°$, $Z = 8$) is obtained by combination of **2** with $Cd(NO_3)_2\cdot 6H_2O$. The structure includes a rare sinusoidal-type polymer chain architecture, effected by a combination of hydrogen-bonding interactions and $\pi-\pi$ interactions between adjacent alkyne regions of the ligand. The second species $[Co(1,4\text{-bis}(4\text{-pyridyl})butadiyne)(NO_3)_2(H_2O)_2\cdot 2H_2O]_n$ (**4**; orthorhombic, $Pccn$; $a = 22.999(3)$ Å, $b = 23.338(3)$ Å, $c = 7.388(1)$ Å, $Z = 8$) is generated from the reaction of **2** and $Co(NO_3)_2\cdot 6H_2O$ and forms a straight-chain polymeric architecture consisting of double chains that crisscross each other, generating a new layer architecture. The third species $[Cu(1,4\text{-bis}(4\text{-pyridyl})butadiyne)_2(NO_3)_2\cdot CH_2Cl_2]_n$ (**5**; orthorhombic, $C222_1$; $a = 14.382(1)$ Å, $b = 22.755(2)$ Å, $c = 8.975(1)$ Å, $Z = 4$) is prepared from the reaction of **2** and $Cu(NO_3)_2\cdot 3H_2O$. The structure of **5** exhibits a two-dimensional interpenetrating square-grid-type architecture from the coordination of four pyridyl rings at the copper center. The intersection of the grids generates large continuous rhombic channels that can be occupied by organic molecules. The fourth species $[Co(1,4\text{-bis}(4\text{-pyridyl})butadiyne)_2(NO_3)_2\cdot CH_2Cl_2]_n$ (**6**; orthorhombic, $C222_1$; $a = 14.0364(12)$ Å, $b = 23.7595(19)$ Å, $c = 8.9706(7)$ Å, $Z = 4$) is generated from the reaction of **2** and $Co(NO_3)_2\cdot 6H_2O$ and is isostructural with **5**.

Introduction

Crystal engineering research on coordination polymers[1] is continuing to undergo a rapid expansion because of promising technological applications in the areas of catalysis, gas storage, magnetism, electrical conductivity, and molecular recognition.[1−9] Special interest centers on the design of appropriate organic ligands and on an understanding of their mode of interaction with transition metal centers. As part of our research program to develop new polydentate ligands, we have recently designed and synthesized new types of long, conjugated Schiff-base ligands [1,4-bis-(x-pyridyl)-2,3-diaza-1,3-butadienes; $x = 2, 3, 4$] and reported several new inorganic/organic coordination polymers with novel network patterns.[5] The specific local geom-

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etry, the different orientations of N-donors and the zigzag conformation of the spacer moiety (−CH═N−N═HC−) in these ligands has been quite useful in the construction of unusual building blocks for use in assembling a large variety of new coordination polymers. In general, the polymer topology generated in these systems can be controlled by the rational choice of organic ligands containing two pyridyl donor units interconnected by the spacer, which yields a variety of lengths, linear or nonlinear geometries, and conformationally rigid or nonrigid molecular skeletons. The most popular and commercially available ligand, 4,4′-bipyridine (**1**),[6] has already been used to construct a striking variety of crystalline architectures, including chains,[6a] ladders,[6b] squares,[6c] diamondoids,[6d] and so forth and several novel coordination polymer networks exhibiting a high degree of porosity. The use of alkane,[7] alkene,[8] and alkyne[8a,9] units as inserts for bipyridine ligands has also led to a large variety of very interesting structural motifs, both in inorganic networks and in hydrogen-bonded organic assemblies. The length of such ligands can be easily increased by lengthening the spacer, and utilization of the di-alkyne species, namely 1,4-bis(4-pyridyl)butadiyne (**2**), has resulted in several new coordination polymers. For example, the reaction of **2** with (a) $[Cu(CH_3CN)_4]X$ (X = PF_6, BF_4) and AgX (X = NO_3, ClO_4, CF_3SO_3) affords 1-D, 2-D, and 3-D coordination polymers;[10] (b) $[Rh(cod)_2]X$ (X = BF_4, PF_6, or ClO_4; cod = cycloocta-1,5-diene) gives 1-D zigzag chain polymers;[11] (c) $Cp_2Mo_2(CO)_4$ and $Co_2(CO)_6$ forms organometallic monomers for use in the construction of polymers.[12] This ligand **2** is ≈5.0 Å longer than **1** (12.17 vs 7.12 Å) due to the (−C≡C−C≡C−) spacer, which can influence and possibly control the size of the cavities.

Our goal in this paper is to highlight the utility of conjugated pyridyl ligands incorporating an alkyne entity[8a,13] and to illustrate their usefulness in the preparation of new inorganic−organic coordination polymers, potentially leading to large pore framework architectures. Our strategy is based on the construction of stable microporous inorganic−organic networks that exhibit reversible guest exchange and, possibly, selective catalytic activity. We report herein three new coordination polymers based on the 1,4-bis(4-pyridyl)butadiyne ligand (**2**) and metal nitrate salts (M = Cd, Co, Cu) exhibiting three kinds of crystalline architectures. The first architecture, obtained for M = Cd ($[Cd(C_{14}N_2H_8)(NO_3)_2(H_2O)\cdot CH_2Cl_2]_n$, **3**) is a novel layer-type coordination polymer consisting of sinusoidal chains bridged by nitrate anions into a two-dimensional network. In addition, interlayer hydrogen bonding and, interestingly, $\pi-\pi$ interactions between the alkyne units play an important structure-directing role. For M = Co, the second type of architecture is formed, constructed from layers of hydrogen-bonded pairs of infinite straight chains that stack in a crisscrossing manner (**4**, $[Co(C_{14}N_2H_8)(NO_3)_2(H_2O)_2\cdot 2H_2O]_n$). The third type of architecture consists of well-known two-dimensional interpenetrating square grids and is found for $[Cu(C_{14}N_2H_8)_2(NO_3)_2\cdot CH_2Cl_2]_n$ (**5**), and $[Co(C_{14}N_2H_8)_2(NO_3)_2\cdot CH_2Cl_2]_n$ (**6**) featuring cavities suitable for incorporation of methylene chloride guest molecules.

Experimental Section

Materials and Methods. The ligand 1,4-bis(4-pyridyl)butadiyne (**2**) was prepared according to the literature method[14] and single crystals suitable for X-ray analysis were obtained by recrystallization from a mixture of methanol and dichloromethane. The crystal data for **2** were previously reported[15] and are not included here. The metal salts $Cd(NO_3)_2\cdot 4H_2O$, $Co(NO_3)_2\cdot 6H_2O$ (both Aldrich, 98%), and $Cu(NO_3)_2\cdot 3H_2O$ (Alfa Aesar, Technical Grade) were used without further purification. IR spectra were recorded on a Nicolet 740 FTIR spectrometer as KBr pellets in the 4000−400-cm^{-1} range. Thermogravimetric analyses were carried out on a TA Instruments SDT 2960 simultaneous DTA−TGA under flowing helium. Compounds **3**, **5**, and **6** were heated from 50 to 800 °C at a rate of 10 °C/min.

X-ray Structure Determinations. Crystal data and refinement statistics for compounds **3**−**6** are given in Table 1. All crystals were mounted on the tips of glass fibers and encased in epoxy for the room-temperature measurements except for **6**, which was coated in inert (Paratone-N) oil and frozen onto the tip of a glass fiber in the nitrogen cold stream for data collection at −100 °C. For each sample, 1350 frames constituting a hemisphere of X-ray intensity data were collected with a frame width of 0.3° in omega and a counting time of 20 s/frame, using a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å).[16] The first 50 frames were re-collected at the end of each data collection to monitor crystal decay; no significant decay was observed in any case. The raw data frames for **3**−**6** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT+.[16] A correction for incident

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Table 1. Crystallographic Data for 3, 4, 5, and 6

	3	4	5	6
empirical formula	$C_{15}H_{12}Cl_2CdN_4O_7$	$C_{14}H_{12}CoN_4O_{10}$	$C_{29}H_{18}Cl_2CuN_6O_6$	$C_{29}H_{18}Cl_2CoN_6O_6$
M_w	543.59	455.21	680.93	676.32
cryst. syst.	monoclinic	orthorhombic	orthorhombic	orthorhombic
a (Å)	28.135(3)	22.999(3)	14.382(1)	14.0364(12)
b (Å)	8.535(1)	23.338(3)	22.755(2)	23.7595(19)
c (Å)	17.642(2)	7.388(1)	8.975(1)	8.9706(7)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	91.797(2)	90.00	90.00	90.00
γ (deg)	90.00	90.00	90.00	90.00
V (Å^3)	1484.6(8)	3966.1(10)	2937.6(4)	2991.7(4)
space group	*C*2/*c*	*Pccn*	*C*222$_1$	*C*222$_1$
Z value	8	8	4	4
ρ_{calc} (g/cm^3)	1.726	1.525	1.540	1.502
μ(Mo Kα) (cm^{-1})	0.0134	0.0092	0.0098	0.0081
λ (Å)	0.71073	0.71073	0.71073	0.71073
temp (K)	293(2)	293(2)	293(2)	173(2)
residuals:[a] R; wR2	0.039; 0.094	0.064; 0.124	0.035; 0.102	0.036; 0.098
GOF	1.01	0.92	1.07	1.061

[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 $= \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ (n = no. refl; p = no. refined parameters). $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where P is $[2F_c^2 + \max(F_o^2, 0)]/3$.

and diffracted beam absorption effects based on the multiple measurement of equivalent reflections was applied to each data set using SADABS.[16] All structures were solved by direct methods and refined against F^2 by the full-matrix least-squares technique, using the SHELXTL software package.[16] Hydrogen atoms, except those associated with water molecules, were calculated and refined as riding atoms; all non-hydrogen atoms including solvent molecules were refined with anisotropic displacement parameters. Water hydrogens were located and refined with isotropic displacement parameters. Relevant interatomic bond distances and bond angles for all compounds are given in Table 2.

Synthesis: $[Cd(C_{14}N_2H_8)(NO_3)_2(H_2O)\cdot CH_2Cl_2]_n$ (3). A colorless solution of $Cd(NO_3)_2\cdot 4H_2O$ (30.9 mg, 0.1 mmol) in methanol (3 mL) was carefully layered onto a solution of **2** (20.4 mg, 0.1 mmol) in methylene chloride (5 mL). Diffusion between the two phases over a period of 2 days produced multifaceted white crystals in 90% yield based on cadmium nitrate. IR (KBr, cm^{-1}): 1761 (w), 1601 (s), 1538 (m), 1474 (w), 1466 (s), 1383 (s), 1224 (s), 1060 (s), 1030 (m), 822 (s), 784 (s), 726 (w).

Synthesis: $[Co(C_{14}N_2H_8)(NO_3)_2(H_2O)_2\cdot 2H_2O]_n$ (4) and $[Co(C_{14}N_2H_8)_2(NO_3)_2\cdot CH_2Cl_2]_n$ (6). A methanol solution of $Co(NO_3)_2\cdot 6H_2O$ (30.0 mg, 0.1 mmol) was slowly added to a methylene chloride (5 mL) solution of **2** (20.0 mg, 0.1 mmol). After 1 week, the red solution was evaporated (at room temperature) over a period of 2 days to half the initial volume. After 2 more days, reddish orange crystals grew at the bottom of the test tube in 68% yield based on cobalt nitrate. IR (KBr, cm^{-1}): 1609 (s), 1552 (w), 1465 (m), 1424 (s), 1383 (s), 1301 (s), 1235 (m), 1061 (m), 1015 (m), 953 (w), 871 (w). **4** and **6** form simultaneously in the same batch of crystals and, consequently, the yield and IR data applies to the mixture of **4** and **6**. On the basis of powder X-ray diffraction, **4** is the minor product and **6** the major product.

Synthesis: $[Cu(C_{14}N_2H_8)_2(NO_3)_2\cdot CH_2Cl_2]_n$ (5). A solution of $Cu(NO_3)_2\cdot 3H_2O$ (24.2 mg, 0.1 mmol) in a 5:1 methanol:water (5 mL) mixture was allowed to diffuse slowly into a methylene chloride (5 mL) solution of **2** (20.1 mg, 0.1 mmol). Immediately, a blue precipitate formed at the interface of two layers. Greenish blue crystals formed in this mixture after 1 day. The yield was 47% based on copper nitrate trihydrate. IR (KBr, cm^{-1}): 1761 (w), 1613 (m), 1548 (m), 1498 (w), 1414 (m), 1382 (s), 1308 (m), 1234 (m), 1058 (m), 1016 (m), 947 (w).

Results and Discussion

Synthesis. Four new coordination polymers were synthesized by solution reactions between the ligand **2** (1,4-bis(4-pyridyl)butadiyne) and the metal salts $M(NO_3)_2\cdot xH_2O$; M = Cd(II), Co(II), and Cu(II); $x = 3-6$. Single crystals of compounds **3**–**6** were all obtained from same methanol/methylene chloride solvent system, though the preparative route differed slightly. When a solution of **2** in methylene chloride was treated with $M(NO_3)_2\cdot xH_2O$ in methanol, using a metal-to-ligand ratio of 1:1, compounds **3**, **4**, **5**, and **6** were obtained as crystalline polymeric compounds displaying two principle types of architectures: layers (**3**, **5**, **6**) and chains (**4**). Slow diffusion of $Cd(NO_3)_2\cdot 6H_2O$ in methanol into a methylene chloride solution of **2** afforded the coordination polymer **3** as light yellow crystals within 1 day. When compound **3** was removed from the mother liquor, the crystals quickly lost solvent, became opaque and brittle, and eventually collapsed into a white powder. When coated with a viscous oil, they are sufficiently stable for crystallographic analysis. We were not able to grow high-quality single crystals of **4** and **6** by an analogous slow diffusion of $Co(NO_3)_2\cdot 6H_2O$ in methanol into a methylene chloride solution of **2**; however, we were able to grow large reddish orange crystals of **4** and **6** by overnight slow evaporation of the above diffused reaction mixture in a test tube. The interpenetrating polymeric square-grid architecture of compound **5** was obtained from a methanol/methylene chloride system as well. Deep blue-green crystals of **5** were obtained overnight by allowing a methanol solution of $Cu(NO_3)_2\cdot 3H_2O$ to diffuse into a methylene chloride solution of **2**. Compounds **4**, **5**, and **6** also decomposed when removed from the mother liquor, though not as quickly as **3**, presumably because of loss of incorporated solvent from the framework. Compounds **3**, **4**, **5**, and **6** are insoluble in water and common organic solvents.

Polymeric Chain Architectures. The immediate coordination environment around the cadmium center in compound **3** is shown in Figure 1. The Cd(II) ions lie in a heptacoordinate environment, consisting of two oxygen donors from one bidentate nitrate anion, two oxygen donors from two crystallographically equivalent bridging nitrate anions, one oxygen donor from a water molecule, and two pyridyl nitrogen atoms from two ligands. Bond distances around the Cd center are typical of other cadmium-based coordination polymers containing nitrogen donor ligands: N(2)–Cd = 2.320 Å and N(1)–Cd = 2.318 Å, with Cd–O bond distances in the

Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) for 3, 4, and 5

$C_{15}H_{12}Cl_2CdN_4O_7$, **3**[a]			
Cd−N(1)	2.318(4)	N(3)−O(1)	1.217(6)
Cd−N(2)	2.320(4)	N(3)−O(2)	1.258(6)
Cd−O(1)	2.616(5)	N(4)−O(4)	1.261(5)
Cd−O(2)	2.398(4)	N(4)−O(5)	1.227(5)
Cd−O(4)	2.541(3)	N(4)−O(6)	1. 254(5)
Cd−O(6)	2.332(3)	O(6)−Cd#4	2.332(3)
Cd−O(7)	2.274(4)	N(3)−O(3)	1.205(6)
N(1)−Cd−N(2)	162.04(15)	O(7)−Cd−O(2)	81.08(17)
N(1)−Cd−O(1)	123.67(15)	O(6)#1−Cd−O(2)	110.44(13)
N(2)−Cd−O(1)	74.12(15)	O(7)−Cd−O(4)	101.01(16)
N(1)−Cd−O(2)	79.14(15)	O(6)#1−Cd−O(4)	68.70(12)
N(2)−Cd−O(2)	116.10(15)	O(2)−Cd−O(4)	161.18(13)
N(1)−Cd−O(4)	82.25(13)	O(7)−Cd−O(1)	102.26(19)
N(2)−Cd−O(4)	82.72(12)	O(6)#1−Cd−O(1)	84.90(17)
N(1)−Cd−O(6)#1	95.89(14)	O(2)−Cd−O(1)	49.19(14)
N(2)−Cd−O(6)#1	87.74(13)	O(4)−Cd−O(1)	145.48(14)
O(7)−Cd−N(1)	87.82(16)	N(4)−O(4)−Cd	119.1(3)
O(7)−Cd−N(2)	85.46(16)	N(4)−O(6)−Cd#4	117.9(3)
O(7)−Cd−O(6)#1	168.35(16)		
$C_{14}H_{12}CoN_4O_{10}$, **4**[b]			
Co−N(1)	2.115(3)	N(3)−O(1)	1.284(5)
Co−N(2)#1	2.125(3)	N(3)−O(2)	1.210(6)
Co−O(1)	2.135(3)	N(3)−O(3)	1.204(5)
Co−O(4)	2.135(4)	N(4)−O(4)	1.212(6)
Co−O(7)	2.074(4)	N(4)−O(5)	1.246(7)
Co−O(8)	2.069(4)	N(4)−O(6)	1.253(7)
N(1)−Co−N(2)#1	177.00(16)	N(1)−Co−O(4)	90.20(15)
O(8)−Co−O(7)	178.59(17)	N(2)#1−Co−O(4)	89.55(16)
O(8)−Co−N(1)	91.68(16)	O(8)−Co−O(1)	100.05(16)
O(7)−Co−N(1)	87.54(14)	O(7)−Co−O(1)	81.18(14)
O(8)−Co−N(2)#1	91.22(16)	N(1)−Co−O(1)	93.94(13)
O(7)−Co−N(2)#1	89.55(15)	N(2)#1−Co−O(1)	86.33(13)
O(8)−Co−O(4)	79.42(18)	N(3)−O(1)−Co	126.7(3)
O(7)−Co−O(4)	99.40(16)	N(4)−O(4)−Co	130.5(5)
O(4)−Co−O(1)	175.84(14)		
$C_{29}H_{18}Cl_2CuN_6O_6$, **5**[c]			
Cu−N(1)	2.033(2)	N(3)−O(1)	1.262(3)
Cu−N(1)#3	2.033(2)	N(3)−O(2)	1.222(5)
Cu−N(2)#1	2.028(2)	N(3)−O(3)	1.239(4)
Cu−N(2)#2	2.028(2)	Cu−O(1)#3	2.412(2)
Cu−O(1)	2.412(2)		
N(2)#1−Cu−N(2)#2	89.28(12)	N(1)−Cu−O(1)#3	86.75(9)
N(2)#1−Cu−N(1)#3	174.01(9)	N(2)#1−Cu−O(1)	87.31(8)
N(2)#1−Cu−N(1)	89.88(8)	N(2)#2−Cu−O(1)	89.44(9)
N(2)#2−Cu−N(1)#3	89.88(8)	N(1)#3−Cu−O(1)	86.75(9)
N(2)#2−Cu−N(1)	174.01(9)	N(1)−Cu−O(1)	96.44(8)
N(1)#3 −Cu−N(1)	91.56(13)	O(1)#3−Cu−O(1)	175.43(12)
N(2)#1−Cu−O(1)#3	89.44(9)	N(3)−O(1)−Cu	125.10(19)
N(2)#2−Cu−O(1)#3	87.31(8)		
N(1)#3−Cu−O(1)#3	96.44(8)		
$C_{29}H_{18}Cl_2CoN_6O_6$, **6**[d]			
Co−N(1)	2.144(2)	N(3)−O(1)	1.286(3)
Co−N(1)#1	2.144(2)	N(3)−O(2)	1.234(3)
Co−N(2)#2	2.151(2)	N(3)−O(3)	1.218(4)
Co−N(2)#3	2.151(2)	Co−O(1)#1	2.1115(18)
Co−O(1)	2.1115(18)		
N(1)#1−Co−N(2)#2	89.31(8)	O(1)#1−Co−N(1)#1	87.65(8)
N(1)−Co−N(2)#2	174.09(9)	O(1)−Co−N(2)#2	86.86(8)
N(1)−Co−N(1)#1	88.36(12)	O(1)#1−Co−N(2)#2	96.76(8)
N(1)#1−Co−N(2)#2	89.31(8)	O(1)−Co−N(2)#3	96.76(8)
N(1)#1−Co−N(2)#3	174.09(9)	O(1)#1−Co−N(2)#3	86.86(8)
N(1)−Co−N(2)#3	89.31(8)	O(1)−Co−O(1)#1	174.74(11)
O(1)−Co−N(1)	87.65(8)	N(3)−O(1)−Co	126.39(16)
O(1)#1−Co−N(1)	88.58(8)		
O(1)−Co−N(1)#1	88.58(8)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1/2, y - 1/2, -z + 3/2$; #4, $-x + 1/2, y + 1/2, -z + 3/2$. [b] Symmetry transformations used to generate equivalent atoms: #1, $x + 1/2, y + 1/2, -z + 2$. [c] Symmetry transformations used to generate equivalent atoms: #1, $-x + 3/2, y - 1/2, -z + 3/2$; #2, $x + 1/2, y - 1/2, z + 1$; #3, $-x + 2, y, -z + 5/2$. [d] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1, y, -z + 5/2$; #2, $x - 1/2, y + 1/2, z + 1$; #3, $-x + 3/2, y + 1/2, -z + 3/2$.

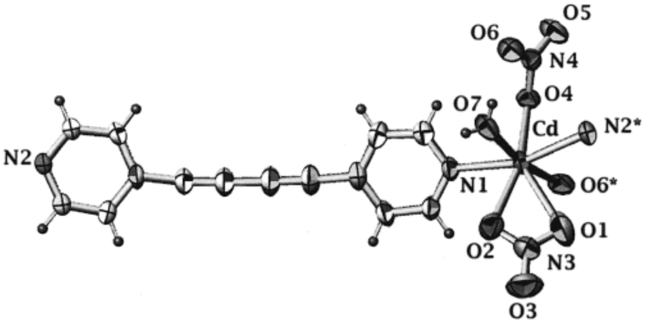

Figure 1. Heptacoordinate environment around the Cd center in **1**, shown with 50% probability ellipsoids. Asterisks denote symmetry-equivalent atoms.

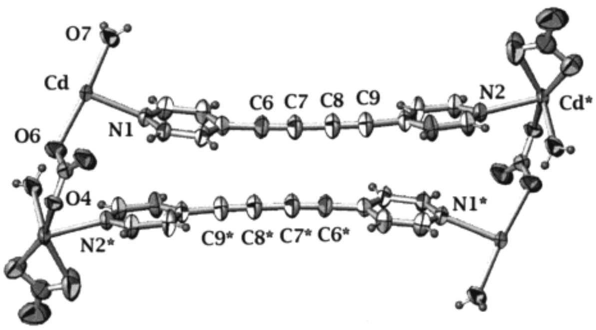

Figure 2. View of the curvature of adjacent 1,4-bis(4-pyridyl)-butadiyne ligands toward one another in **3**. An inversion center is present in the center of the figure. The C7−C7* distance is 3.47 Å. Ellipsoids are plotted at the 50% probability level.

range 2.274(4)−2.616(5) Å, consistent with corresponding bond lengths found in $[Cd(NO_3)_2(1,2\text{-bis(4-pyridyl)-ethene/ethyne})_{1.5}]_n$,[8a] $[Cd(NO_3)_2(4,4'\text{-bipy})_2\cdot 2C_6H_4Br_2]_n$,[6c] and $[Cd(NO_3)_2(dpb)_{1.5}]_n$.[17a] The ligands are coordinated in a trans fashion, with N(1)−Cd−N(2)* = 162.0°. The pyridyl rings are rotated 79.7° relative to one another. This coordination geometry, in combination with the ligand's own nonlinearity, results in a sinusoidal chain motif. The deformation of the 1,4-bis(4-pyridyl)-butadiyne ligand is due to $\pi-\pi$ interactions between the neighboring alkyne portions, which can be clearly seen in Figure 2. These sinusoidal chains are not isolated, but are themselves linked into two-dimensional corrugated sheets via bridging nitrate ions, as illustrated by Figure 3. An intralayer hydrogen bond is present between the coordinated water molecule and the bridging nitrate (O7−H1w···O4; d(H···A) = 2.07(7) ∠(D−H···A) = 168(8)°). The full three-dimensional crystal structure is completed by stacking of these layers such that the "hydrophilic" $Cd(NO_3)_2(H_2O)$ centers are superimposed along [001]. An interlayer hydrogen bond between the second hydrogen atom of the water molecule (H2w) and the unbridged nitrate ion of an adjacent layer assists in this alignment (O7−H2w···O2; d(H2w···O2) = 2.04(6) Å, ∠(O7−H2w···O2) = 164(6)°). Figure 4 shows two adjacent sheets, viewed roughly parallel to the layers and down the direction of the sinusoidal chain fragments, more clearly showing the linking of the chains by nitrate ions to form the

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(17) (a) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287. (b) Fujita, M.; Kwon, Y. J.; Miyazawa, M.; Ogura, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1977. (c) Hennigar, T. L.; Donald, M. C.; Losier, P.; Rogers, R. D.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 972.

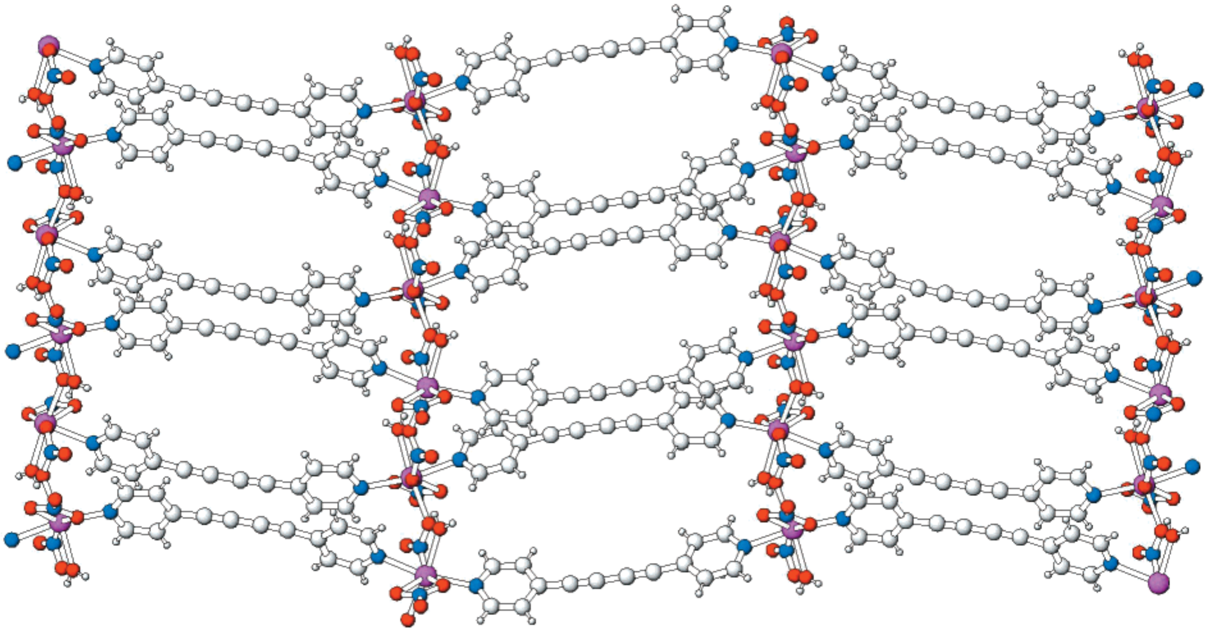

Figure 3. Linking of the sinusoidal chains in **3** via bidentate nitrate ions to form 2-D layers. The view is roughly perpendicular to the layers. Successive layers are stacked such that the hydrophilic {$Cd(NO_3)_2(H_2O)$} regions and the hydrophobic ligand regions directly superimpose. Methylene chloride solvent molecules reside in the oval spaces created by the bowed ligands. Cd atoms, large pink circles; oxygen atoms, red circles; nitrogen atoms, blue circles; hydrogen atoms, small gray circles.

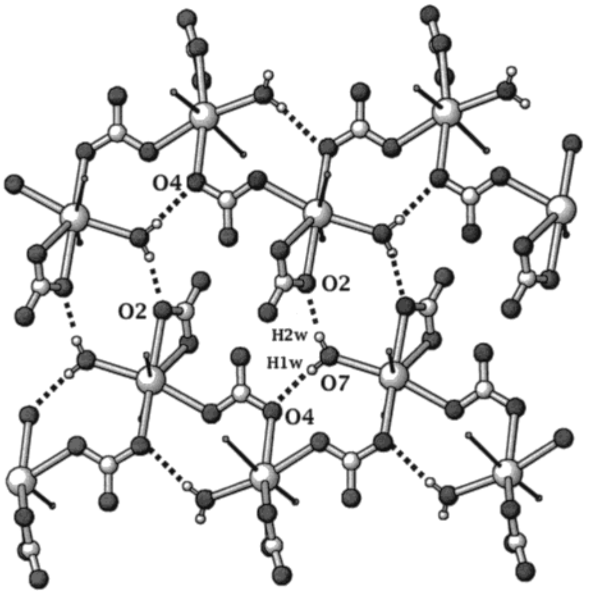

Figure 4. View roughly parallel to the chain direction of two adjacent corrugated layers in **3**. All but the nitrogen atoms of the ligands are omitted for clarity; Cd−N bonds (dark solid lines) are retained for orientation. Intra- and interlayer hydrogen bonds are shown as dotted lines. Large circles, Cd atoms; gray circles, oxygen; open circles, nitrogen; small circles; hydrogen.

corrugated layers. This stacking mode also creates “hydrophobic” regions in the structure consisting of the alkyne portion of the ligand in which small cavities are present (i.e., the larger spaces between ligands in Figure 3). These small cavities enclose methylene chloride guest molecules.

It is well-demonstrated that the coordination geometry around Cd(II) centers is typically heptacoordinate, often forming a T-shaped building block (Cd plus three pyridine rings).[5,6a,17] There are a few cases where Cd(II) atoms lie in an octahedral geometry consisting of four pyridyl groups in the equatorial positions and two nitrate ions at the apical positions.[6c] Such octahedral geometries have also been found in $[Cd(NO_3)_2(1,2\text{-bis(4-pyridyl)ethene})_{1.5}]_n$,[8a] where two types of pyridine rings are coordinated to the Cd(II) atoms and form novel infinite noninterpenetrating zigzag chains. The structural motif of compound **3**, however, consists of only two pyridine rings coordinated to the Cd(II) atom, although the metal centers are heptacoordinate. This kind of $[CdN_2O_5]$ coordination sphere is unusual and results from the long diacetylene spacer in the ligand **2**.

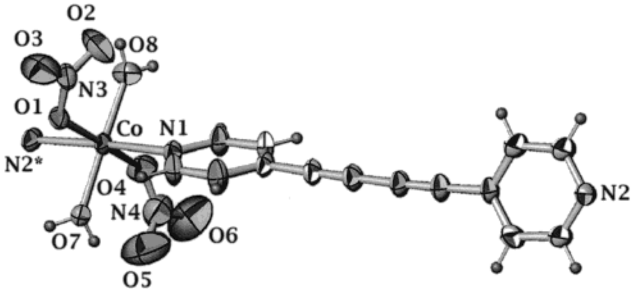

Figure 5. The pseudooctahedral coordination environment around the Co center in **4** (50% probability ellipsoids), showing the rigid rodlike conformation of the ligand, and the 90° rotation of the opposite pyridyl groups. Asterisks denote symmetry-equivalent atoms.

Compared to **3**, a different coordination environment is found for the cobalt center in compound **4**, although the same ligand **2** is used. As shown in Figure 5, the Co(II) centers lie in an unusual pseudooctahedral {CoN_2O_4} environment with the axial positions occupied by two pyridyl nitrogen donors from the ligand **2** (N(1)−Co = 2.115(3) Å and N(2)−Co = 2.125(3) Å) and the equatorial positions occupied by two trans oxygen atoms from two nitrate anions (Co−O(1) = 2.135(3) Å; Co−O(4) = 2.135(4) Å) and two trans oxygen atoms from two water molecules (Co−O(7) = 2.074(4) Å; Co−O(8)

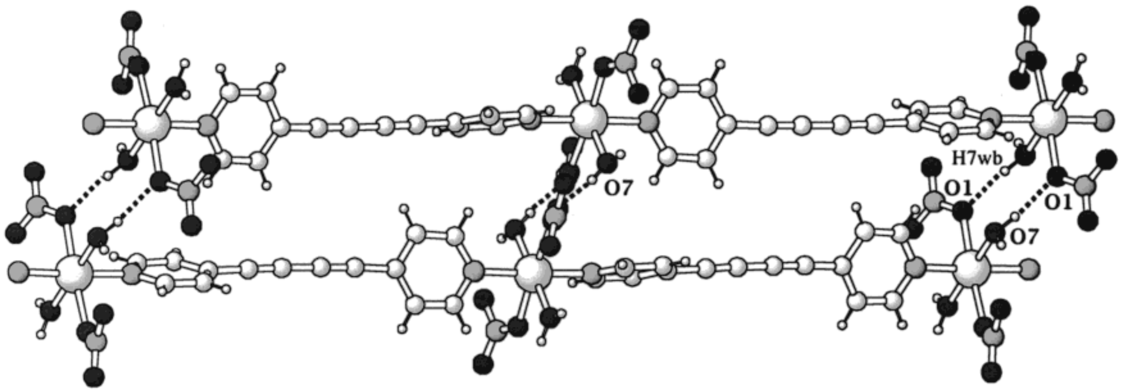

Figure 6. Linking of individual [$Co(H_2O)_2(NO_3)_2(\mathbf{2})$] chains into pairs via hydrogen bonding (dotted lines: O7−H7wb···O1; *d*(H7wb−O1) = 1.98(2) Å; ∠(O7−H7wb···O1 = 171(7)°). Large circles, Co atoms; dark circles, oxygen; gray circles, nitrogen; open circles, carbon and hydrogen.

= 2.069(4) Å). Interestingly, the pyridine rings of ligand **2** are found to be rotated 70.3° from coplanarity relative to each other, sterically resulting in two different Co−N coordination bond lengths, both of which are shorter than corresponding bond lengths in previously reported Co(II) coordination polymers.[5,18] The bond distances between the Co(II) and the two nitrate oxygens and two oxygens belonging to the water molecules are also shorter than those found in the related compounds.[5a,b,18] It is also worth pointing out that the connection between the Co(II) center and the oxygens of nitrate anions and water molecules are nearly linear, with a O(4)−Co−O(1) angle of 175.8° and O(8)−Co−O(7) angle of 178.6°, respectively.

The {CoN_2O_4} coordination sphere in **4** is unusual in coordination polymers. [$Co(H_2O)_4$(1,2-bis(4-pyridyl)-ethene)$_2$]$_n$ [18a] and [$Co(H_2O)_4$(4,4′-bipy)][PF_6]$_2$·3bipy[5c] also have a {CoN_2O_4} coordination sphere, but consisting of four water molecules and two ligands, not two nitrate anions, two water molecules, and two ligands as in compound **4**. Other Co(II) centers in coordination polymers are more typically heptacoordinate and have {CoN_3O_4}[5a−d,18] coordination environments. Also, cobalt centers which are exclusively N-coordinated (by thiocyanate and *N*,*N*′-bidentate ligands, e.g.) can adopt an octahedral coordination, as in {$CoN_4N'_2$}.[18] This less sterically crowded six-coordinate {CoN_2O_4} environment in **4** is primarily responsible for the slightly shorter Co−N and Co−O bond distances observed.

Similar to compound **3**, in **4** the two pyridyl nitrogen atoms of the two ligands are coordinated to the metal center in a trans fashion (N(1)−Co−N(2) = 177.0(2)°) and form a one-dimensional linear polymeric chain. In **4**, however, these 1-D chains are not linked by nitrate ions, though they are associated by hydrogen bonding into pairs of chains that traverse the face diagonal to the unit cell. Figure 6 shows the linking of two crystallographically equivalent chains into the dual strands that make up compound **4**. The pairs of associated chains are arranged in layers parallel to the crystallographic *ab* plane, though side-by-side chain pairs do not interact. Rotation by 90° followed by stacking along [001] of these layers of dual chains completes the three-dimensional crystal structure. Figure 7 shows a view perpendicular to the stacking direction ([001]), showing the orthogonal crisscrossing of chains. Again, the metal nitrate/H_2O nodes at successive heights along the stacking direction are vicinal, and there is clear hydrogen bonding between layers (O8−H8wb···O5; *d*(H8wb−O5) = 2.012() Å; ∠(O8−H8wb···O5) = 165(5)°). Large dumbbell-shaped cavities (cross-sectional area 11.7 × 8.5 Å) are present, which contain disordered water molecules of crystallization. The structures of **3** and **4** reported herein are, to the best of our knowledge, unprecedented and represent new polymeric frameworks generated from the long linear spacer ligand **2**.

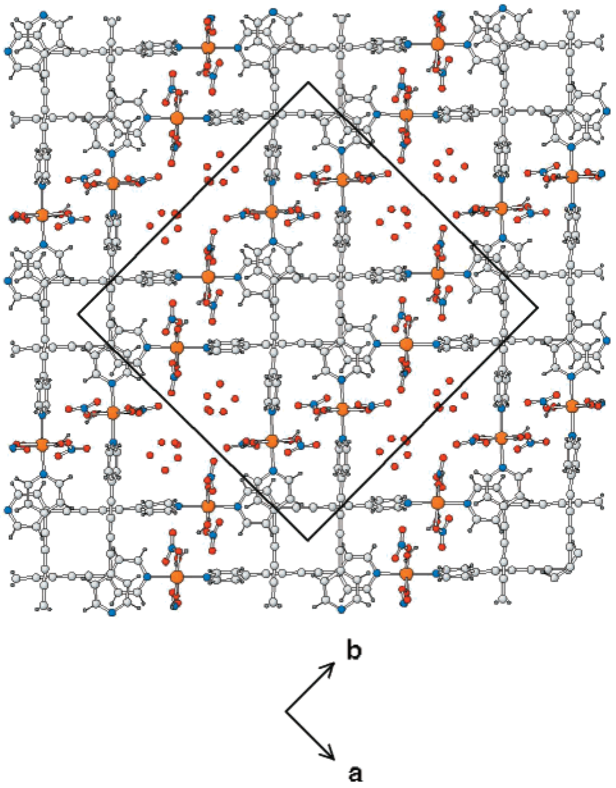

Figure 7. View down the stacking direction ([001]) of two crisscrossing layers of double chains in **4**. Disordered water molecules located in the cavities are shown as isolated red circles. The unit cell is also shown. Larger orange circles, Co atoms; red circles, oxygen; blue circles, nitrogen; gray circles, carbon and hydrogen.

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[18] (a) Jung, O.-S.; Park, S. H.; Kim, K. M.; Jang, H. G. *Inorg. Chem.* **1998**, *37*, 5781. (b) Lloret, F.; Munno, G. D.; Miguel, J.; Cano, J.; Ruiz, R.; Caneschi, A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 135. (c) Power, K. N.; Hennigar, T. L.; Zaworotko, M. J. *New. J. Chem.* **1998**, 177. (d) Carlucci, L.; Ciani, G.; Proserpio, D. M. *J. Chem. Soc., Dalton Trans.* **1999**, *39*, 1799.

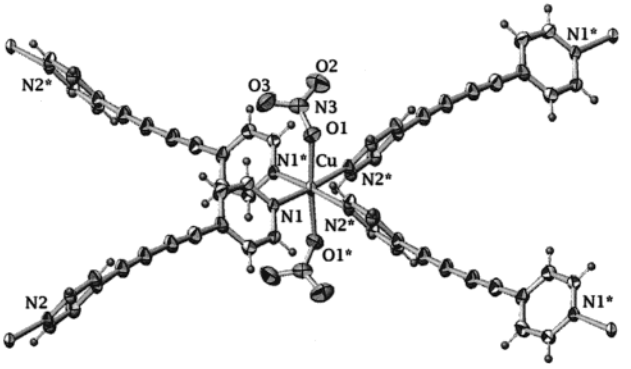

Figure 8. The coordination environment around the Cu atom in **5**, giving rise to the square-grid structural motif. Ellipsoids drawn at the 50% probability level; asterisks indicate symmetry-equivalent atoms.

Polymeric Square-Grid Architecture: The third polymeric structural motif is exemplified by the polymeric structure of **5**, produced by copper nitrate and ligand **2**. The pseudooctahedral 4 + 2 coordination environment of the Cu(II) center is shown in Figure 8. Four crystallographically equivalent ligands of **2** are situated in a square planar fashion about the Cu center (Cu−N(1) = 2.033(2) and Cu−N(2) = 2.028(2) Å); two crystallographically equivalent nitrate ions (Cu−O(1) = 2.412(2) Å) occupy the axial positions. The pyridyl rings of each ligand are again twisted, by 78.0°. The polymeric structure of **5** generated from such coordination consists of familiar two-dimensional square-grid-type layers, in this case with inner square cavity dimensions of 16.17 × 16.17 Å^2, comparable to those of related compounds[19] but of course larger than that generated from 4,4′-bipyridine with similar metals (Zn, Ni, Cu, Cd).[6c,20] The square-grid layers are strictly flat, and crystallographically equivalent sets interpenetrate at an angle of 60.4° to one another. Though the interpenetration severely reduces the porosity, the intersection of grids formed from such a long ligand is still capable of giving rise to large continuous rhombic channels that can be occupied by organic molecules. In the case of **5**, the channels are occupied by one methylene chloride molecule per metal center, located approximately in the middle of the channel. Figure 9 shows a view down the channel direction (the *c*-axis) showing the beautiful pattern of rhombic-shaped channels and also the solvent molecules residing therein.

Compound **6**, $[Co(C_{14}N_2H_8)_2(NO_3)_2 \cdot CH_2Cl_2]_n$, is isostructural with **5**. Four crystallographically equivalent ligands of **2** are situated in a square planar fashion about the Co center (Co−N(1) = 2.144(2) and Co−N(2) = 2.151(2) Å); two crystallographically equivalent nitrate ions (Co−O(1) = 2.1115(18) Å) occupy the axial positions. The pyridyl rings of each ligand are again twisted, by 78.0°. The polymeric structure of **6** generated from such coordination consists of familiar two-dimensional square-grid-type layers. The square-grid layers are strictly flat, and crystallographically equivalent sets interpenetrate at an angle of 60.4° to one another. As in the case of **5**, the intersection of grids generates channels that are occupied by one methylene chloride molecule per metal center.

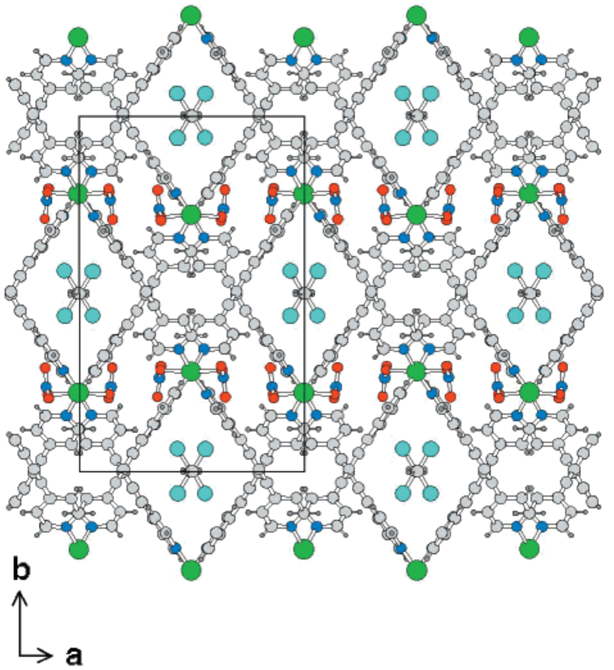

Figure 9. View down the *c*-axis of the interpenetrating square-grid structure of **5**, showing the rhombic channels occupied by columns of methylene chloride solvent. Large green circles, Cu; red circles, oxygen; blue circles, nitrogen; large cyan circles, Cl; gray circles, carbon and hydrogen atoms.

This square-grid structure seems to form readily with this ligand and we have also successfully prepared an isostructural nickel analogue in which it is possible to incorporate a large variety of diverse organic molecules into the channels, which we will report on soon.

Thermogravimetric Analysis. To characterize the thermal stability of compounds **3**−**6**, simultaneous differential thermal analysis and thermogravimetric analysis (DTA−TGA) were performed on samples consisting of numerous single crystals of each compound. All samples were heated at a rate of 10 °C min^{-1} under flowing helium to 800 °C. Because of the facile loss of solvent from all compounds, initially the samples were brought to ≈50 °C to remove the guest molecules, held at this temperature until a stable weight was achieved, after which time the heating was resumed. Even with this approach, compound **3** showed a broad weight loss terminating at ≈100 °C, which is due to loss of remaining CH_2Cl_2 guests. Above 100 °C the solvent-free compound shows no weight loss until 228 °C, where a loss of 3.8% is observed, corresponding to the removal of the coordinated water molecule (calculated 3.7%). A second poorly defined weight loss begins at ≈257 °C and begins to level off near 425 °C; however, a stable flat baseline is never achieved, and a steady weight loss occurs up to the maximum temperature measured. This broad transition is most likely due to the combined decomposition of the framework and nitrate ions. The TGA behavior of compound **5** shows that the guest CH_2Cl_2 molecules were lost slowly from room temper-

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[19] (a) Biradha, K.; Hongo, Y.; Fujita, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3843. (b) Biradha, K.; Fujita, M. *Dalton* **2000**, 3805. (c) Aakeroy, C. B.; Beatty, A. M.; Leinen, D. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 1815.

[20] (a) MacGillivray, L. R.; Groeneman, R. H.; Atwood, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 2676. (b) Biradha, K.; Domasevitch, K. V.; Moulton, B.; Seward, C.; Zaworotko, M. J. *J. Chem. Commun.* **1999**, 1327. (c) Biradha, K.; Mondal, A.; Moulton, B.; Zaworotko, M. J. *Dalton* **2000**, 3837.

ature to 181 °C. At this temperature a drastic multistep weight loss occurs, for which there are no clear endpoints. The thermal decomposition behavior of compound **6** is similar to that of **5**. (It was possible to adjust the growth conditions by using very dry solvents to minimize the amount of **4** and, consequently, to carry out measurements on **6**, but not on **4**.) An initial broad weight loss occurs essentially from room temperature to 196 °C, corresponding to removal of the guest solvent molecules. This is followed immediately by a sharp decrease in weight of 54.8%, terminating at 288 °C, corresponding to the loss of both coordinated water molecules and the ligand **2** (calculated 56.7%). Above this temperature a gradual weight loss accompanying decomposition of the nitrate ions is observed. From these data it appears that the frameworks of **3**, **5**, and **6** are thermally stable up to 228, 181, and 196 °C, respectively, which is quite typical for organic−inorganic coordination polymers consisting of metal cations and *N*,*N′*-bidentate-type ligands.

Powder X-ray Diffraction Analysis. Powder samples (crushed crystals) of compounds **3**, **5**, and **6** were examined by X-ray powder diffraction (XRPD) to investigate the stability of the framework before and after removal of solvent. As mentioned earlier, compound **3** loses solvent quickly and is unstable outside of the mother liquor. This was confirmed by powder diffraction, which showed a poorly crystalline solid that became increasingly amorphous as solvent was removed by heating in air. The crystalline square-grid frameworks of **5** and **6**, however, proved to be quite thermally stable. After acquiring the XRPD pattern of freshly prepared, solvent-containing crystals, the powdered samples of **5** and **6** were heated at 180 °C in air for 20 min. The experimental XRPD patterns acquired before and after heat treatment were then compared with the XRPD patterns calculated from the single-crystal data for the solvent-containing structure and for the same framework structure where the solvent molecules were removed. In both cases the powder patterns showed no change in diffraction peak position in 2θ, but did show marked change in the intensities of certain reflections. Furthermore, the affected reflections and the relative changes in intensity of those reflections agreed well with the patterns calculated without solvent molecules, providing strong evidence that the frameworks of **5** and **6** remain intact upon removal of the solvent. This is not very surprising, as other square-grid frameworks are known to remain intact upon removal of solvent.[19]

Conclusions

The self-assembly of four new organic−inorganic hybrid materials described in this paper were prepared from the same ligand using very similar reaction conditions and identical solvent systems. Nonetheless, the four new compounds display very different crystalline architectures and coordination geometries. The results reported herein illustrate two new structural motifs for Cd(II) and Co(II) ions, which generated sinusoidal and crisscrossing straight-chain-type polymeric arrangements, respectively. Moreover, we introduced a new open and interpenetrating two-dimensional network containing square grids of dimension $\approx 16 \times 16$ Å. Such coordination polymers are obtained from Cu(II) and Co(II) (and Ni(II)) salts and the 1,4-bis(4-pyridyl)butadiyne ligand that are potentially important in the context of understanding the structure and stoichiometry of the host−guest chemistry. We are currently extending this result in the nickel system by preparing open frameworks with pore channels of diverse sizes through the variation of the guest molecules and counterions and the orientation of the nitrogen donors on longer bipyridyl ligands structurally related to the ligand (**2**) reported herein.

These results again underscore that numerous different possibilities exist even for relatively simple systems such as those described here. The rational design and selection of appropriate ligands and metals allow us to “lead” a reaction along a certain path, increasing the chances of producing the desired structure. Clearly, experimental verification of design strategies is both essential and liable to produce unexpected surprises. The formation of chains (**3** and **4**) from the coordination of two ligands at the metal center and square-grid architectures (**5** and **6**) from the coordination of four ligands at the metal center represents an elegant illustration of the challenges faced in developing approaches toward inorganic crystal engineering.

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Supporting Information Available: X-ray crystallographic data for **3**−**6** (CIF). Tables of observed and calculated structure factors for **3**−**6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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