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New Cd(II)-, Co(II)-, and Cu(II)-Containing Coordination Polymers Synthesized by Using the Rigid Ligand 1,2-Bis(3-pyridyl)ethyne (3,3′-DPA)

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Four new organic/inorganic coordination polymers, $[Cd(C_{10}H_8N_2)_2(H_2O)_2(NO_3)_2]_n$ (**1**), $[Co(C_{10}H_8N_2)(H_2O)NO_3CH_3OH]_n$ (**2**), $[Cu(C_{10}H_8N_2)(CH_3OH)(NO_3)_2]_n$ (**3**), and $[Cu(C_{10}H_8N_2)(hfac)_2]_n$ (**4**), were synthesized by using the rigid ligand 1,2-bis(3-pyridyl)ethyne (3,3′-DPA). Complex **1** crystallizes in space group *P2/n*: $a = 12.462(2)$ Å, $b = 9.485(1)$ Å, $c = 13.383(2)$ Å, $\beta = 96.629(2)°$, $V = 1559.6(3)$ Å^3, Z = 4. Complex **2** crystallizes in space group *Fddd*: $a = 9.248(4)$ Å, $b = 19.982(7)$ Å, $c = 35.093(16)$ Å, $V = 6485.0(4)$ Å^3, $Z = 8$. Complex **3** crystallizes in space group *I2/a*: $a = 18.315(2)$ Å, $b = 8.517(1)$ Å, $c = 20.494(3)$ Å, $\beta = 104.042(2)°$, $V = 3101.2(7)$ Å^3, $Z = 8$. Complex **4** crystallizes in space group *P21/c*: $a = 6.576(1)$ Å, $b = 16.189(1)$ Å, $c = 11.653(1)$ Å, $\beta = 91.337(1)°$, $V = 1240.3(2)$ Å^3, $Z = 2$. The coordination polymers display a variety of structural architectures, ranging from sinusoidal and zigzag chains (**1**, **3**, **4**) to two-dimensional channel-type architectures (**2**). The effects of the orientation of the nitrogen atom in the pyridine rings on the resultant structures are discussed.

Introduction

Great advances in the synthesis and characterization of new network topologies have been made in the field of supramolecular chemistry.[1−5] One driving force behind the syntheses of new network structures has been the implicit understanding that the simple association of a pair of starting compounds through metal coordination and/or noncovalent interactions can be used to assemble new coordination polymers exhibiting properties that are not displayed by either of the components alone. Certainly the appeal of creating functionally valuable materials continues to motivate researchers to explore the syntheses of new structures, to elucidate the principles that guide molecular assembly and, thereby, to direct the network topology. Such exploratory syntheses can help in understanding the formation of new crystalline frameworks and may lead to the ability to rationalize, in advance, crystal structures containing new linkers. Within this framework, we are pursuing the assembly of new crystalline network topologies utilizing two complementary organic and inorganic starting materials.[5−11]

Bridging 4,4′-bipyridine based ligands have been used extensively for the synthesis of a variety of one-, two-, and three-dimensional organic−inorganic polymeric network structures, as well as for pure organic networks.[2−4,7−9] We have been investigating the effect of the 2,2′-, 3,3′-, and 4,4′-positional orientation of the nitrogen atoms in acetylene-bridged *N*,*N*′-bidentate ligands (Scheme 1) on the resultant structures.[12] The different crystalline architectures resulting

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(1) *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Lehn, J.-M., Eds.; Pergamon: Oxford, UK, 1996; Vol. 6.

(2) *Crystal Engineering: The Design and Applications of Functional Solids*; Seddon, K. R., Zaworotko, M. J., Eds.; NATO ASI Series; Kluwer Academic: Dordrecht, The Netherlands, 1998.

(3) *Crystal Engineering: From Molecules and Crystals of Materials*; Braga, D., Grepioni, F., Orpen, A. G., Eds.; NATO ASI Series; Kluwer Academic: Dordrecht, The Netherlands, 1999.

(4) Weber, E., Ed. *Design of Organic Solids*; Topics in Current Chemistry Series; Springer-Verlag: Berlin, Heidelberg,Germany, 1998; Vol. 198.

(5) Fujita, M., Ed. *Molecular Self-Assembly Organic Versus Inorganic Approaches*; Structure and Bonding Series; Springer-Verlag: Berlin, Heidelberg, Germany, 2000; Vol. 96.

(6) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Withersby, M. A.; Schroder, M. *Coord. Chem. Rev.* **1999**, *183*, 117.

(7) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.

(8) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474.

(9) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.

(10) Leninger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.

(11) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, *23*, 283.

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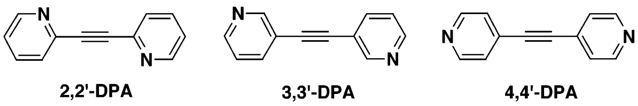
Scheme 1



from these three rigid organic ligands are influenced both by the nitrogen position and by the linking of the hydrogen-bonded supramolecular synthon[13] in the solid state. The nitrogen position also impacts the metal−ligand coordination environments that can be influenced by the judicious choice of the metal center. The generation of such coordination polymers with multiple frameworks is of potential interest with regard to their physical, electronic, catalytic, and structural (mainly porosity) properties.[14−19]

Recently, we have reported the syntheses and structural characterization of organic/inorganic coordination polymers containing 1,2-bis(4-pyridyl)ethyne [4,4′-dipyridylacetylene, 4,4′-DPA] with cadmium and cobalt salts.[20,21] Moreover, Carlucci et al. have also reported structural studies of five crystalline polymers based on the same 4,4′-DPA ligand.[22−24] Likewise, 2,2′-DPA and 3,3′-DPA turn out to be interesting ligands due to their rigidity and structure-directing abilities. In the course of our investigation of structures resulting from DPA ligands, we synthesized metal complexes of 2,2′-DPA, 3,3′-DPA, and 4,4′-DPA in a common solvent system with identical reaction conditions. Our first experimental results with the 2,2′-DPA ligand led to the formation of single crystals from $Cd(NO_3)_2{\cdot}4H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ salts by using a methylene chloride−methanol solvent system. We found that the $Cd(II)(2,2'\text{-DPA})(NO_3)_2(H_2O)$ complex is new[25] while the structure of $[Co(II)(2,2'\text{-DPA})(NO_3)_2]_n$, prepared in the same solvent system, had been reported previously by Neenann et al.[26] We have since expanded our work to include 3,3′-DPA, because ligands where the nitrogen atoms are at the 3-position of the pyridine ring have resulted in intriguing polymeric coordination structures.[27−31]

In this report we focus on 1,2-bis(3-pyridyl)ethyne (3,3′-DPA) in which the two nitrogens are joined by a metal center and form one-dimensional and two-dimensional polymeric networks. The synthesis, structure, and properties of four new Cd(II)-, Co(II)-, and Cu(II)-containing coordination polymers are described within. The four structures $[Cd(C_{10}H_8N_2)_2(H_2O)_2(NO_3)_2]_n$ (**1**), $[Co(C_{10}H_8N_2)(H_2O)NO_3CH_3OH]_n$ (**2**), $[Cu(C_{10}H_8N_2)(CH_3OH)(NO_3)_2]_n$ (**3**), and $[Cu(C_{10}H_8N_2)(hfac)_2]_n$ (**4**) display a variety of structural architectures, ranging from sinusoidal and zigzag chains (**1**, **3**, **4**) to two-dimensional channel-type architectures (**2**).

Experimental Section

Materials. All the solvents were of reagent grade quality and were used as received except for triethylamine, which was distilled from KOH immediately before use. The metal salts $Cd(NO_3)_2{\cdot}4H_2O$ (Aldrich, 98%), $Co(NO_3)_2{\cdot}6H_2O$ (Aldrich, 98%), $Cu(NO_3)_2{\cdot}3H_2O$ (Alfa Aesar, Technical Grade), and $Cu(hfac)_2{\cdot}H_2O$ (hfac = hexafluoroacetylacetonate) (Aldrich) were used without further purification.

Physical Measurements. Elemental analyses were performed by Robertson Microlit Laboratories. IR spectra were recorded on a Nicolet 740 FTIR spectrometer as KBr pellets in the 4000−400 cm^{-1} range. ^1H NMR spectra were recorded on a 400-MHz Varian U400 spectrometer; chemical shifts are reported in δ relative to $CHCl_3$-d_6. Thermogravimetric analyses were carried out on a TA Instruments SDT 2960 simultaneous DTA-TGA under flowing helium. Compounds **1**−**4** 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 **1**−**4** are given in Table 1. All crystals were mounted on the tips of glass fibers encased in epoxy for the room-temperature measurements. 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 per frame, using a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å).[32] 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 frame data for **1**−**4** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects with SAINT.[32] Corrections for incident and diffracted beam absorption effects were applied with SADABS.[32] All structures were solved by direct methods and refined against F^2 by the full-matrix least-squares technique, using the SHELXTL software package.[32] Hydrogen atoms were calculated and refined as riding atoms; all non-hydrogen atoms including solvent molecules were refined with anisotropic displacement parameters. Relevant interatomic bond distances and bond angles for all compounds are given in Tables 2−5.

Synthesis: Ligands. The synthetic procedure of all three ligands (2,2′-DPA, 3,3′-DPA, and 4,4′-DPA) has been reported previously.[33−36] A practical and straightforward procedure is described below (Scheme 2) for the preparation of 3,3′-DPA ligand. This

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(12) Zaman, M. B.; Tomura, M.; Yamashita, Y. *Org. Lett.* **2000**, *2*, 273.
(13) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.
(14) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M., *Nature (London)* **1999**, *402*, 276.
(15) Noro, S.-I.; Kitagawa, S.; Kondo, M.; Seki, K. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2082.
(16) Tabares, L. C.; Navarro, L. A. R.; Salas, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 383.
(17) Real, A. J.; Andres, E.; Munno, G. D.; Julve, M.; Granier, T.; Bousseksou, A.; Varret, F. *Science* **1995**, *268*, 265.
(18) Lloret, F.; Munno, G. D.; Julve, M.; Cano, J.; Ruiz, R.; Caneschi, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 135.
(19) Matsuda, K.; Takayama, K.; Irei, M. *Chem. Commun.* **2001**, 363.
(20) Dong, Y.-B.; Layland, R. C.; Smith, M. D.; Pschirer, N. G.; Bunz, U. H. F.; zur Loye, H.-C. *Inorg. Chem.* **1999**, *38*, 3056.
(21) Dong, Y.-B.; Layland, R. C.; Pschirer, N. G.; Smith, M. D.; Bunz, U. H. F.; zur Loye, H.-C. *Chem. Mater.* **1999**, *11*, 1413.
(22) Carlucci, L.; Ciani, G.; Macchi, P.; Proserpio, D. M. *Chem. Commun.* **1998**, 1837.
(23) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Chem. Commun.* **1999**, 449.
(24) Carlucci, L.; Ciani, G.; Proserpio, D. M. *J. Chem. Soc., Dalton Trans.* **1999**, 1799.
(25) We prepared the dinuclear complex of 2,2′-DPA from cadmium nitrate salts: Zaman, M. B.; Smith, M. D.; zur Loye, H.-C. *Acta Crystallogr. C.* Submitted for publication.
(26) Neenann, T. X.; Driessen, W. L.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chim. Acta* **1996**, *247*, 43.
(27) Dong, Y.-B.; Smith, M. D.; zur Loye, H.-C. *Inorg. Chem.* **2000**, *39*, 4927.
(28) Dong, Y.-B.; Smith, M. D.; Layland, R. C.; zur Loye, H.-C. *Chem. Mater.* **2000**, *12*, 1156.
(29) Dong, Y.-B.; Smith, M. D.; zur Loye, H.-C. *J. Solid State Chem.* **2000**, *155*, 143.
(30) Bosch, E.; Barnes, C. L. *New J. Chem.* **2001**, *25*, 1376.
(31) Lopez, S.; Kahraman, M.; Harmata, M.; Keller, S. W. *Inorg. Chem.* **1997**, *36*, 6138.
(32) SMART, SAINT, and SHELX software; Bruker Analytical X-ray Systems Inc.: Madison, WI, 1997.

Table 1. Crystallographic Data for **1**, **2**, **3**, and **4**

	1	**2**	**3**	**4**
empirical formula	$C_{12}H_{12}CdN_4O_8$	$C_{26}H_{20}CoN_6O_{10}$	$C_{13}H_{12}CuN_4O_7$	$C_{22}H_{10}CuF_{12}N_2O_4$
mw	452.66	634.41	399.81	657.86
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	P2/n	*Fddd*	*I*2/*a*	*P*21/*c*
a (Å)	12.462(2)	9.248(4)	18.315(2)	6.576(1)
b (Å)	9.485(1)	19.982(7)	8.517(1)	16.189(1)
c (Å)	13.383(2)	35.093(16)	20.494(3)	11.653(1)
β (deg)	96.629(2)	90.00	104.042(2)	91.337(1)
V (Å^3)	1559.6(3)	6485.0(4)	3101.2(7)	1240.3(2)
Z value	4	8	8	2
r_{calcd} (g/cm^3)	1.928	1.302	1.713	1.762
μ(Mo Kα) (cm^{-1})	0.145	0.059	0.146	0.100
temp (K)	283(2)	293(2)	273(2)	193(2)
residuals:[a] *R*; *R*$_w$	0.066; 0.145	0.058; 0.164	0.038; 0.084	0.045; 0.129
GOF	1.09	1.45	0.99	1.07

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; GOF $= \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ (n = number of reflections; p = number of refined parameters). $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [2F_c^2 + \max(F_o^2, 0)]/3$.

Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) around the Cd(II) Center for **1**

Cd−N(1)	2.240(6)	Cd−O(4)	2.408(5)
Cd−N(2)#1	2.246(6)	Cd−O(7)	2.382(6)
Cd−O(2)	2.490(6)	Cd−O(8)	2.468(6)
N(1)−Cd−N(2)#1	171.9(2)	N(2)#1-Cd−O(2)	99.2(2)
N(1)−Cd−O(7)	88.0(2)	O(7)−Cd−O(4)	105.2(2)
N(2)#1−Cd−O(7)	84.9(2)	O(7)−Cd−O(8)	172.5(2)
N(1)−Cd−O(4)	95.0(2)	O(4)−Cd−O(8)	67.4(2)
N(2)#1−Cd−O(4)	90.7(2)	O(7)−Cd−O(2)	118.7(2)
N(1)−Cd−O(8)	91.6(2)	O(4)−Cd−O(2)	135.6(2)
N(2)#1−Cd−O(8)	95.9 (2)	O(8)−Cd−O(2)	68.6(2)
N(1)−Cd−O(2)	80.7(2)		

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg) around the Co(II) Center for **2**

Co−N(1)	2.169(2)	Co−O(1W)	2.098(3)
N(1)−Co−N(1)#2	179.44(11)	N(1)−Co−N(1)#1	88.90(13)
N(1)#2−Co−N(1)#1	91.11(13)	N(1)−Co−O(1W)	90.28(5)
O(1W)#1−Co−O(1W)	180.00(1)	O(1W)#1−Co−N(1)#2	89.72(5)

Table 4. Selected Interatomic Distances (Å) and Bond Angles (deg) around the Cu(II) Center for **3**

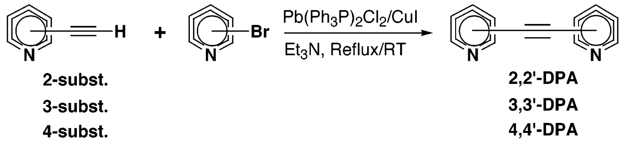
Cu−N(1)	2.016(3)	Cu−O(1)	1.999(2)
Cu−N(2)	2.032(3)	Cu−O(5)	2.007(2)
Cu−O(1S)	2.280 (2)		
N(1)−Cu−N(2)	168.80(10)	N(1)−Cu−O(1)	91.15(10)
N(1)−Cu−O(5)	92.97(10)	N(2)−Cu−O(1)	89.00(10)
N(2)−Cu−O(5)	88.37(10)	O(1)−Cu−O(5)	171.62(9)
O(5)−Cu−O(1S)	89.72(9)	O(1)−Cu−O(1S)	82.52(8)
N(1)−Cu−O(1S)	97.17(9)	N(2)−Cu−O(1S)	93.95(9)

Table 5. Selected Interatomic Distances (Å) and Bond Angles (deg) around the Cu(II) Center for **4**

Cu−N(1)	2.061(3)	Cu−O(1)	1.966(2)
Cu−O(2)	2.281(2)		
N(1)#1−Cu−N(1)	180.00	O(1)−Cu−N(1)	90.70(9)
O(1)−Cu−O(1)	87.42(7)	O(1)−Cu−N(2)#1	89.30(9)
O(1)−Cu−O(1)#1	92.58(8)	N(1)−Co−O(2)	86.03(9)

method can also be used for the preparation of the 2,2′-DPA and 4,4′-DPA ligands.

Scheme 2



According to the literature method, the starting 3-ethynylpyridine was prepared in good yield.[33] This compound was coupled with 3-bromopyridine, using $Pb(PPh_3)_2Cl_2$ as a catalyst, CuI as the reducing agent, and diethlyamine as the base. The mixture was refluxed for 12 h, the black suspension was quenched with water, and the solvent was evaporated under vacuum. The product was extracted with methylene chloride and dried over $MgSO_4$. After the solid was dried in vacuo, 58% crude product was obtained as a pale yellow powder. This powder was recrystallized from the mixture of methylene chloride and methanol as yellow thin plate crystals. ^{1}H NMR (400 MHz, $CHCl_3$-d_6): δ 7.32 (dd, J = 7.9, 2H), 7.83 (dt, J = 6.8, 2H), 8.58 (dd, J = 5.4, 2H), 8.79 (br s, 2H).

$[Cd(C_{10}N_2H_8)(NO_3)_2(H_2O)_2]_n$ (1). A colorless solution of Cd(NO_3)$_2$·4H_2O (30.9 mg, 0.1 mmol) in methanol (3 mL) was carefully layered onto a solution of 3,3′-DPA (20.4 mg, 0.1 mmol) in acetonitrile (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}): 1959 (w), 1766 (w) 1609 (s), 1558 (m), 1534 (w), 1510 (s), 1395 (s), 1303 (s), 1234 (s), 1122 (w), 1088 (s), 1070 (m), 882 (s), 784 (s), 726 (w). Anal. Calcd: C, 31.84; H, 2.67; N, 12.38. Found: C, 31.56; H, 2.54; N, 12.30.

$[Co(C_{10}N_2H_8)(NO_3)_2(H_2O)_2]_n$ (2). A methanol solution of Co(NO_3)$_2$·6H_2O (30.0 mg, 0.1 mmol) was slowly added to a methylene chloride (5 mL) solution of 3,3′-DPA (20.0 mg, 0.1 mmol). After 2 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). Anal. Calcd: C, 36.09; H, 3.01; N, 14.04. Found: C, 36.55; H, 3.01; N, 14.14.

$[Cu(C_{10}H_8N_2)(CH_3OH)(NO_3)_2]_n$ (3). A solution of Cu(NO_3)$_2$·3H_2O (24.2 mg, 0.1 mmol) in a 5:1 methanol/water (5 mL) mixture was allowed to diffuse slowly into a chloroform (5 mL) solution of **2** (20.1 mg, 0.1 mmol). Immediately, a blue precipitate formed at the interface of the two layers. Greenish blue single crystals formed, together with unidentified products, in this mixture after 15 days. The yield was 48% based on copper nitrate. IR (KBr, cm^{-1}): 1761 (w), 1652 (m), 1613 (m), 1548 (m), 1498 (w), 1414

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(33) For 2,2′-DPA, see: Teitei, T.; Collin, P. J.; Sasse, W. H. F. *Aust. J. Chem.* **1972**, *25*, 171.
(34) For 3,3′-DPA, see: Teitei, T.; Wells, D.; Sasse, W. H. F. *Aust. J. Chem.* **1973**, *26*, 2129.
(35) For 4,4′-DPA, see: Tanner, M.; Ludi, A. *Chimica* **1980**, *34*, 23.
(36) Ciana, L. D.; Haim, A. *J. Hetrocycl. Chem.* **1984**, *21*, 607.

(m), 1382 (s), 1308 (m), 1234 (m), 1058 (m), 1016 (m), 947 (w). Anal. Calcd: C, 39.09; H, 3.01; N, 14.01. Found: C, 39.41; H, 2.83; N, 14.18.

$[Cu(hfac)_2(C_{10}N_4H_8)_{1.5}(NO_3)_2]_n$ (4). An ethanol solution of 3,3′-DPA (0.1 mmol) was slowly diffused over a methylene chloride solution of $Cu(hfac)_2{\cdot}H_2O$ (0.1 mmol, 3 mL) through a layer of an ethanol/hexane (2:1) mixture. After a day, bright green crystals formed in 78% yield based on copper(II) hexafluoroacetylacetonate hydrate. IR (KBr, cm^{-1}): 3072 (w), 1659 (s), 1644 (s), 1558 (s), 1495 (m), 1454 (w), 1422 (s), 1301 (s), 1255 (m), 1081 (m), 1025 (m), 933 (s), 811 (s), 778 (s), 751 (m), 735 (m), 678 (s). Anal. Calcd: C, 40.17; H, 1.53; N, 4.26. Found: C, 40.06; H, 1.40; N, 4.28.

Results and Discussion

Synthesis. The rigid bidentate ligand 1,2-bis(3-pyridyl)-ethyne (3,3′-DPA) was prepared in 58% yield by a standard palladium-catalyzed coupling of 3-ethylenepyridine with 3-bromopyridine.[34] The compound was purified by recrystallization from a mixture of methylene chloride and methanol in the form of thin yellow crystal plates.

3,3′-DPA was reacted with commercially available nitrate salts of Cd(II), Co(II), and Cu(II) as well as with copper(II) hexafluoroacetylacetonate yielding in all cases polymeric compounds. Four compounds, **1**−**4**, were obtained from different solvent systems. The highest quality single crystals of $[Cd(C_{10}N_2H_8)(NO_3)_2(H_2O)_2]_n$ **(1)** were grown out of a methanol/acetonitrile system. Slow diffusion of $Cd(NO_3)_2{\cdot}4H_2O$ in methanol into an acetonitrile solution of 3,3′-DPA afforded the infinite coordination polymer **1** as white creamy crystals within 2 days. Other solvent systems, such as methanol/methylene chloride, only gave poor-quality (but single phase) materials. By contrast, several high-quality crystals of $[Co(C_{10}N_2H_8)(NO_3)_2(H_2O)_2]_n$ (**2**) were obtained from the methanol/methylene chloride system. Large reddish orange crystals of **2** formed at the bottom of the test tube when a methanol solution of $Co(NO_3)_2{\cdot}6H_2O$ was allowed to diffuse into a methylene chloride solution of 3,3′-DPA. An ethanol/methylene chloride and/or methanol/acetonitrile system afforded only poor-quality crystals of **2**. Greenish-blue crystals of $[Cu(C_{10}H_8N_2)(CH_3OH)(NO_3)_2]_n$ **(3)** were obtained after 15 days when a methanol/water (5:1) solution of $Cu(NO_3)_2{\cdot}3H_2O$ was allowed to diffuse into a chloroform solution of 3,3′-DPA. Crystals of **3**, not suitable for single-crystal X-ray analysis, can also be grown within a few days from the layered ethanol/methanol solution of $Cu(NO_3)_2{\cdot}3H_2O$ over the solution of 3,3′-DPA in methylene chloride, benzene, toluene, xylene, and acetonitrile.

Bright green crystals of $[Cu(hfac)_2(C_{10}N_4H_8)_{1.5}(NO_3)_2]_n$ **(4)** were obtained overnight by layering a methanol or ethanol solution of 3,3′-DPA over a methylene chloride solution of copper(II) hexafluoroacetylacetonate. It is also important to note that when the solvents for 3,3′-DPA and copper(II) hexafluoroacetylacetonate are reversed, layering is not possible at all and only powders are obtained.

Crystal Structures. The immediate coordination arrangement around the cadmium center in compound **1** is shown in Figure 1. The Cd(II) ions lie in an octahedral environment, consisting of two pyridyl nitrogen atoms from two ligands, two oxygen atoms from two nitrate anions, and two oxygen atoms from two water molecules. The Cd−N and Cd−O bond lengths [Cd−N(2) = 2.246(6) Å, Cd−N(1) = 2.240(6) Å, Cd−O = 2.382(6)−2.490(6) Å] are shorter than the corresponding bond lengths found in the literature.[20,24,37−39] The 3,3′-DPA ligands are coordinated in a trans fashion, with N(1)−Cd−N(2)* = 171.9(2)°. The pyridyl rings are rotated almost 90° relative to one another similar to what was previously observed in copper−3,3′-bipyridine compounds.[30,31] The coordination geometry, in combination with the orientation of nitrogen atoms at the 3-position of the ligand, results in a sinusoidal chain motif. A view of this novel sinusoidal chain architecture is shown in Figure 2. Two of the sinusoidal polymer chains are intertwined via an intralayer hydrogen bond between the coordinated water molecule and the nitrate ions (O7−H7WB···O4: d(H···A) = 2.00(1) Å, ∠(D−H···A) = 173(6)°; O7−H7WA···O5: d(H···A) = 2.24(1) Å, ∠(D−H···A) = 175(8)°) forming $Cd-(H_2O)_2\cdots(NO_3)_2-Cd$ bridges, with a Cd···Cd distance of 3.892 Å. The adjacent bridges (pair of polymeric chains) are in turn hydrogen bonded between the coordinated water molecule and the nitrate anions (O8−H8WB···O6: d(H···A) = 2.11(3) Å, ∠(D−H···A) = 164(9)°; O8−H8WA···O5: d(H···A) = 2.57(3) Å, ∠(D−H···A) = 159(6)°) thereby completing the layers and making this a two-dimensional structure.

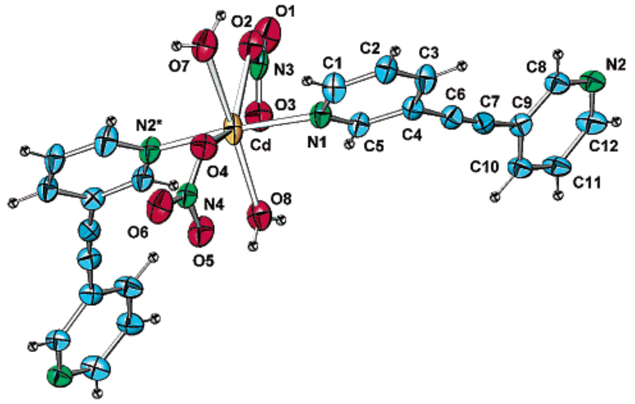

Figure 1. Cadmium coordination environment with atom numbering scheme for **1**. Displacement ellipsoids are shown at the 50% probability level. Asterisks denote symmetry-equivalent atoms.

The $\{CdN_2O_4\}$ coordination sphere in **1** is unusual in coordination polymers. This less sterically crowded six-coordinate environment is primarily responsible for the slightly shorter Cd−N and Cd−O bond distances observed. Such octahedral geometries have also been found in $[Cd(NO_3)_2(1,2\text{-bis(4-pyridyl)ethene})_{1.5}]_n$,[20] where two types of pyridine rings are coordinated to the Cd(II) atoms and form infinite zigzag chains. In the case of **1**, the unusual sinusoidal-chain motif is generated by the location of the nitrogen atoms in the three position of the pyridine rings.

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(37) Fujita, M.; Kwon, Y. J.; Washizy, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151.

(38) MacGillivray, L. R.; Groeneman, R. H.; Atwood, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 2676.

(39) Zaman, M. B.; Smith, M. D.; zur Loye, H.-C. *Chem. Mater.* **2001**, *13*, 3534.

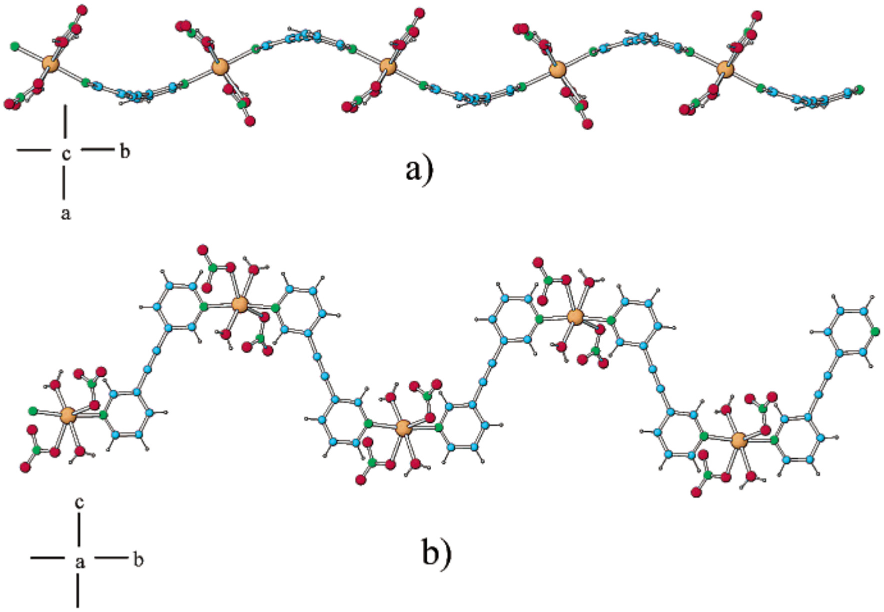

Figure 2. View of the one-dimensional sinusoidal chain architecture of **1. T**he chains are shown along the crystallographic *b*-axis (a) and rotated by 90° (b).

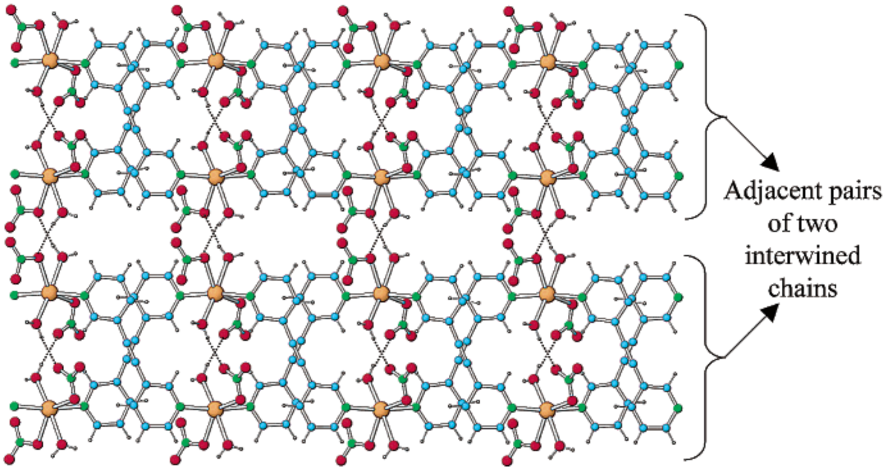

Figure 3. Hydrogen-bonding interactions of the sinusoidal chains in **1** via the oxygen atoms of the nitrate ions and water molecules which form 2D layers. The view is roughly perpendicular to the layers. Cd atoms are shown in yellow, oxygen in red, nitrogen in green, and carbon in blue; hydrogen is indicated with small gray circles.

In compound **2**, an analysis of the local site symmetry reveals that each Co(II) center is positioned on a 2/*m* symmetry site, with a crystallographic mirror plane passing through the two water molecules. Similar symmetry environments were recently found in a coordination polymer composed of a cobalt atom connected to the 3-position N-atoms in the long rigid bidentate Schiff-base ligand, 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene.[29]

The coordination environment around the cobalt atom in **2** is shown in Figure 4, where the Co(II) atoms lie in a pseudooctahedral *trans*-CoO_2N_4 coordination environment. Four equatorial nitrogen donors originate on four equivalent bridging 3,3′-DPA ligands [N(1)−Co = 2.169(2) (× 4)] while two oxygen donors come from two axial water molecules [O(1W)−Co = 2.098(3) (× 2)]. A similar mode of water coordination to Co(II) atoms is found in the mixed ligand 4,4′-bipyridine and pyridine-4-carboxylate Co(II) coordination polymer.[38] As a consequence of this ligand arrangement connecting the cobalt atoms, a new two-dimensional sheet structure is generated; the layers lie almost exactly parallel to the crystallographic *ab* plane (Figure 5a). These layers stack along the crystallographic *c*-axis in an ABAB fashion. Each repeat unit in the layer consists of four Co(II) atoms and four 3,3′-DPA ligands, which form a 36-membered ring structure resembling a distorted square. The cross-sectional dimensions of the “square” outlined by the ligands are approximately 10 Å by 11 Å.

A view down the polymer *a*-axis (Figure 5b) shows that channels of approximately 11 Å × 6 Å exist within this structure; they are, however, occupied by disordered methanol molecules and nitrate ions.

The structure of compound **3**, emphasizing the coordination environment around the copper, is shown in Figure 6. Each copper atom is in a pseudo-square-pyramidal coordination environment consisting of two pyridyl nitrogen atoms from two 3,3′-DPA ligands, two oxygen atoms from two

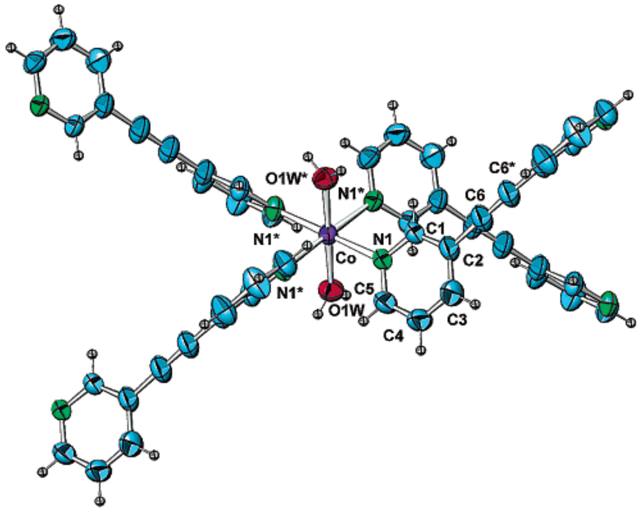

Figure 4. The pseudooctahedral coordination environment around the Co center in **2** (50% probability ellipsoids) shows the rigid rodlike conformation of the ligand and the 90° rotation of the opposite pyridyl rings. Asterisks denote symmetry-equivalent atoms.

nitrate ions, and one oxygen atom from the methanol solvent. The Cu−N bond lengths range between 2.016(2) and 2.032(3) Å, and the Cu−O bond lengths for the nitrate ions range from 1.999(2) to 2.007(2) Å, consistent with the corresponding bond lengths found in 3,3′-bipyridine[31] and 4,4′-bipyridine-type bridging ligands.[22,39−42] The coordinated methanol forms a relatively long bond [Cu−O(1S) = 2.280(2) Å]. The 3,3′-DPA ligands are coordinated in a trans fashion, with N(1)−Cu−N(2)* = 168.8°. Although the five-coordinate $\{CuO_3N_2\}$ square-pyramidal arrangement of the copper compound in **3** is quite different from the octahedral coordination environment for the cadmium atom in **1**, both structures exhibit a sinusoidal chain-type architecture. Figure 7 shows a view of the sinusoidal chain of **3** lying within the crystallographic *ab* plane. Similar to the chains in **1**, the sinusoidal polymeric chains in **3** are connected pair wise by hydrogen bonds between the coordinated methanol molecule and the nitrate ions (O1S−H1S···O1: d(H···A) = 1.91(1) Å, $\angle$(D−H···A) = 1724)°).

The repeat unit of the polymeric compound **4** is shown in Figure 8. The copper atom is in a six-coordinate 4+2 pseudooctahedral geometry defined by two nitrogen donors from two *trans*-3,3′-DPA ligands and four oxygen donors from two hfca chelating ligands. This geometry is quite similar to the geometry of the copper centers found in $Cu(hfac)_2(pyrazine)_2$,[43] $[Cu(hfac)_2\{1,2bis(4\text{-}pyridyl)ethane\}]_n$,[43] and $Cu(hfac)_2\{$3- and 4-(*N*-oxyl-*trans*-butylamino)pyridines$\}_2$.[44] The Cu−N bond length of 2.061(3) Å in **4**, which is very close to the Cu−N bond length {2.07 (1) Å} found in the Cu(hfac) complex with 3-(*N*-oxyl-*trans*-butylamino)pyridine,[44] is significantly longer than that in the polymeric compounds we have previously reported, $[Cu(hfac)_2\{1,2bis(4\text{-}pyridyl)ethane\}]_n$ [Cu−N = 2.014(7) Å] and $[Cu(hfac)_2\{4,4'\text{-}trimethylenebipyridine\}]_n$ [Cu−N = 1.992(6) and 2.017(6) Å].[43] The Cu−O bond lengths in **4** are 1.966(2) and 2.281(2) Å, where Cu−O(1) is significantly shorter than Cu−O(2). Similar length differences can be found in other cis-coordinated Cu(II) complexes[44] [Cu−O = 2.019(8) and 2.327(10) Å].

Each copper center is connected by 3,3′-DPA ligands through the pyridyl nitrogen atoms into a one-dimensional zigzag chain along the crystallographic *c*-axis (Figure 9). In this compound, the Cu···Cu intrapolymer distance is 11.653 Å and the interpolymer distance is 6.576 Å. The trans-coordinated compound **4** connected via 3,3′-DPA affords a close contact between neighboring polymeric chains. Moreover, the fluorine atoms of the hfac ligand and hydrogen on the 3,3′-DPA ligand of the neighboring chains (along the *bc* plane) are involved in weak interactions (F···H = 2.92 Å).

Orientation Effect of Nitrogen Atoms in Coordination Chemistry. This study suggests that the relative orientation of the pyridyl nitrogen donors (Scheme 1) can control the coordination framework and influence the polymeric architectures of the crystalline materials. The 2,2′-DPA ligand has so far only produced a coordination polymer with cobalt nitrate, whereas the other metal nitrate salts yielded dinuclear complexes.[25,26] In each of the compounds, in the solid state, the metals are coordinated by two molecules of the pyridyl ligands in a nonchelating, monodentate fashion or in a chelating, bidentate arrangement with two of the nitrate ions further coordinated to the metal center to form tetrahedral and/or octahedral arrangements.

The 3,3′-DPA and 4,4′-DPA ligands, one the other hand, have yielded numerous polymeric structures with common metal nitrate salts. The coordination arrangements of the 3,3′-DPA ligand result in some interesting features, such as coordination environments that lead to novel sinusoidal chain architectures in Cd(II) and Cu(II) systems. These chains are additionally hydrogen bonded via coordinated solvent and water molecules to create two-dimensional frameworks. The 3,3′-DPA can also be successfully combined with $Co(NO_3)_2\cdot 6H_2O$ to yield a distorted square-grid two-dimensional coordination polymer containing relatively large pores. In this case, the architecture is solely influenced by the coordination of the ligand and water molecules to the metal center, since no nitrate ions are coordinated. In contrast, 4,4′-DPA-coordination polymers form in one- and two-dimensional ladder-like architectures with well-known T-shaped building blocks, taking advantage of "head-on" linkages between the metal and the coordinating ligand.[21−24] One can anticipate that when coordinated to different metal salts, these ligands may lead to new organic−inorganic polymeric frameworks having sizable pores and channels.[23] One must of course bear in mind that longer organic spacers may result in higher degrees of interpenetration.

The copper chemistry with these ligands has resulted in several new network structures. Single crystals suitable for

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(40) Tong, M.-L.; Chen, X.-M.; Yu, X.-L.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1998**, 5.

(41) Batten, S. R.; Harris, A. R.; Jensen, P.; Murray, K. S.; Ziebell, A. *J. Chem. Soc., Dalton Trans.* **2000**, 3929.

(42) Carlucci, L.; Ciani, G.; Proserpio, D. M. *J. Chem. Soc., Dalton Trans.* **2000**, 3821.

(43) Dong, Y.-B.; Smith, M. D.; Layland, R. C.; zur Loye, H.-C. *Inorg. Chem.* **1999**, *38*, 5027.

(44) Ishimaru, Y.; Kitano, M.; Kumada, H.; Koga, N.; Iwamura, H. *Inorg. Chem.* **1998**, *37*, 2272.

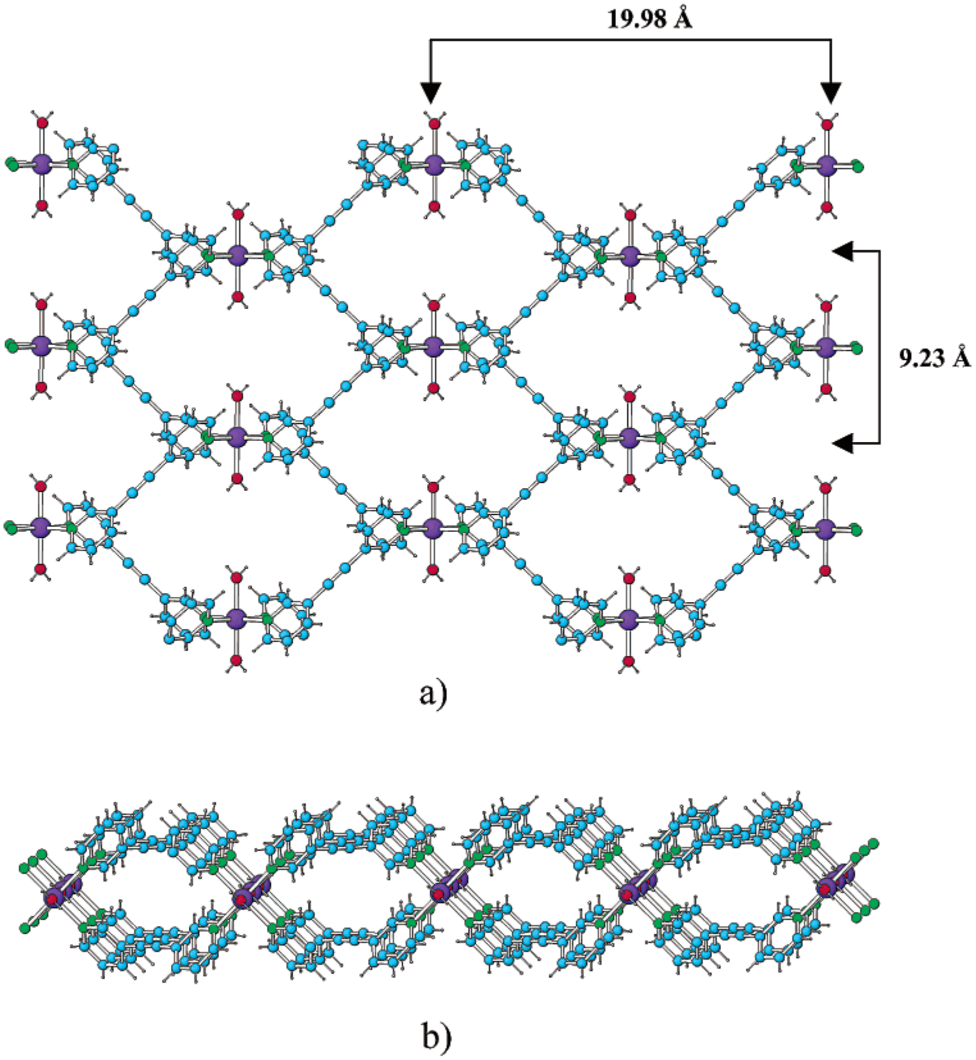

Figure 5. (a) Two-dimensional distorted "square" layer in **2** viewed down the crystallographic *c*-axis. (b) View down the *a*-axis. The nitrate ions and the methanol molecules are omitted for clarity. Co(II) centers are shown in violet, carbon atoms in blue, nitrogen atoms in green, and oxygen atoms in red.

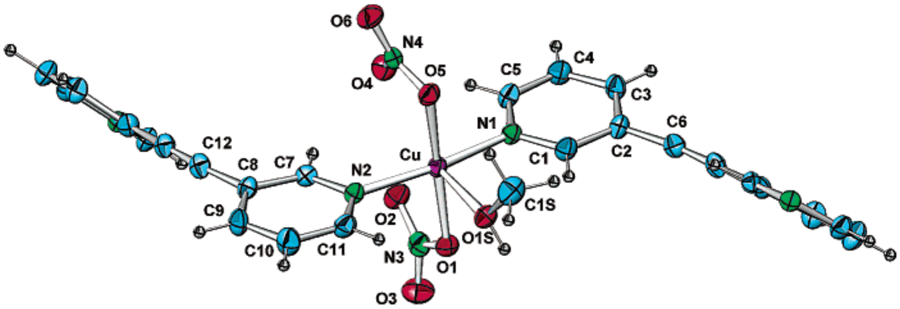

Figure 6. The local coordination environment around the copper atom in **3** is shown with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

X-ray analysis were obtained from the reaction between 3,3′-DPA and Cu(hfac)$_2$ (**4**). In contrast, the reaction between 2,2′-DPA and 4,4′-DPA and Cu(hfac)$_2$ formed only solutions and poor quality crystals, respectively, under the same reaction conditions with the same solvent. These types of complexes can be classified into two groups having trans- and cis-coordinated pyridyl nitrogen atoms and/or acetonate oxygen atoms, respectively. Compound **4** has a trans occupied coordination sphere that contains one short and one long Cu−O bond. The ligand orientation in **4** is also affected by intermolecular interactions; a twisted ligand structure similar to that of 3,3′-DPA is found in the coordination features and the architecture of Cd(NO$_3$)$_2$(1,2-bis(4-pyridyl)-ethane)$_{1.5}$.[45]

Thermogravimetric Analysis. To investigate the thermal stability of the framework of compounds **1**−**4**, thermogravi-

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(45) Fujita, M.; Aoyagi, M.; Ogura, K. *Bull Chem. Soc. Jpn.* **1998**, *71*, 1799.

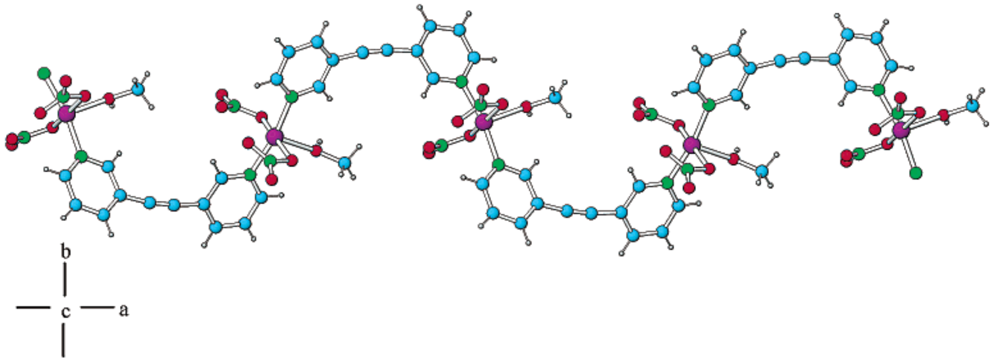

Figure 7. View of one sinusoidal chain in compound **3**. Cu atoms are shown in pink, N atoms in green, O atoms in red, C atoms in blue, and hydrogen atoms in gray.

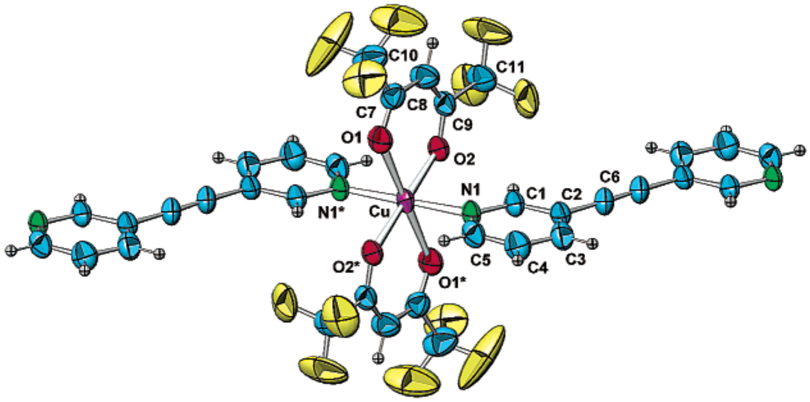

Figure 8. The local coordination environment around the Cu atom in **4** is shown with the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level, and asterisks indicate symmetry-equivalent atoms.

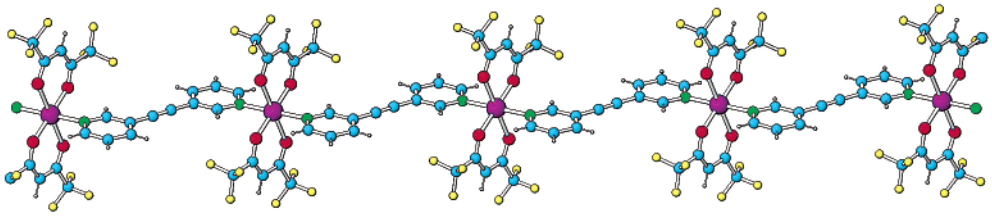

Figure 9. A one-dimensional zigzag chain in **4** is shown.

metric analyses (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. TGA data suggest that the framework of **1** is stable up to 226 °C, although the first weight loss of 7.92% (calculated 7.96%) corresponding to the loss of the two H_2O molecules coordinated at the cadmium center occurred over the range 102−125 °C. In the temperature range of 226−268 °C, **1** underwent complicated multiple weight loss steps, with the total loss corresponding to one ligand and two nitrate ions (obsd 73.18%, calcd 73.08%). The thermal decomposition behavior of the distorted square compound **2** is quite different from that of **1**. The TGA data for **2** show that the first weight loss (9.79%) occurs by 166 °C, corresponding to the loss of two molecules of methanol solvent (calcd 10.07%). A second weight loss occurs between 166 and 206 °C, corresponding to the loss of the coordinated H_2O molecules (obsd 6.65%, calcd 6.28%). The framework apparently collapses due to the release of one 3,3′-DPA ligand and a nitrate ion per formula unit, which occurs between 250 and 284 °C with an observed weight loss of 51% (calcd 51.23%). The decomposition sequence of **3** is similar of **1**. For **3**, the first weight loss, 8.20% (calcd 8.00%), corresponding to the loss of the coordinated methanol solvent, occurs between 95 and 115 °C. A second weight loss is observed between 215 and 236 °C, which is presumably due to framework collapse and the loss of ligands and nitrate ions in the compound. A single-step weight loss was observed in compound **4** and the final product is black and amorphous. The weight loss from 200 to 248 °C is believed to be due to the loss of the 3,3′-DPA and hfac ligands, which is quite typical for organic−inorganic coordination polymers consisting of Cu(hfac)$_2$ cations and N,N′-bidentate-type ligands.[43]

Conclusions

The four frameworks described in this paper are some of the first reported examples of extended coordination poly-

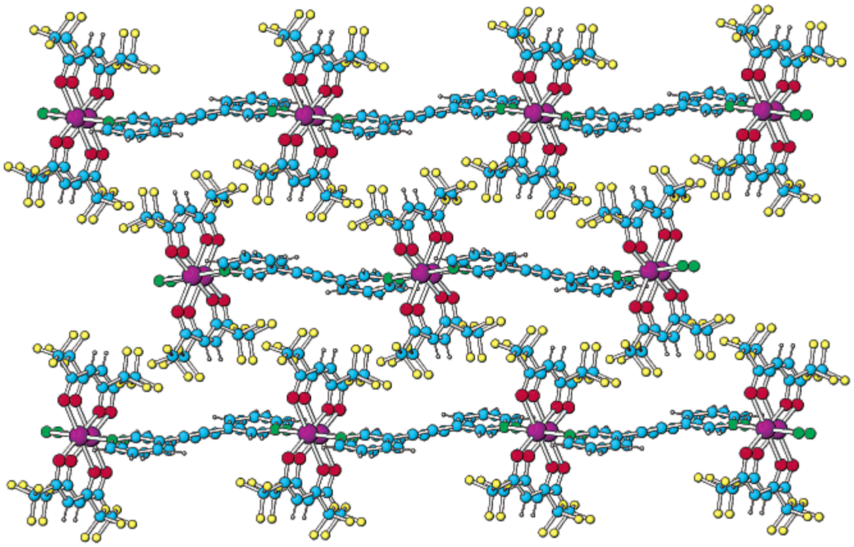

Figure 10. A packing diagram of the zigzag chains in **4**. The short Cu···Cu and F···F interchain distances can be seen in this view.

mers incorporating the 3,3′-DPA ligand. These polymers illustrate the propensity of these metal−ligand systems to adopt chain- and layerlike architectures, even when containing dramatically angular bridging ligands. We demonstrated that the three different orientations of the pyridyl nitrogen atoms with an acetylene spacer can strongly bind to the nitrate salts of Cd(II), Co(II), Cu(II), and Cu(hfac)$_2$ and form crystalline polymeric compounds (**1**−**4**). The results presented in this article not only include diverse structural motifs, but also highlight the usefulness of the three different nitrogen positions of the pyridyl ligands and the potential for obtaining novel supramolecular architectures based on similar components.

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Supporting Information Available: X-ray crystallographic data (CIF files) for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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