

Syntheses and Characterizations of One-Dimensional Coordination Polymers Generated from Cadmium Nitrate and Bipyridine Ligands

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Two new one-dimensional organic/inorganic composite polymers were synthesized by the reaction of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with 1,2-bis(4-pyridyl)ethyne or *trans*-1,2-bis(4-pyridyl)ethene in several solvent systems. $[\text{Cd}(\text{NO}_3)_2(1,2\text{-bis}(4\text{-pyridyl)ethyne})_{1.5}]_n$ (**1**), which has an infinite one-dimensional structure with interpenetrating molecular ladders, was obtained by reacting $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with 1,2-bis(4-pyridyl)ethyne in a methylene chloride/methanol solvent system. It crystallized in the monoclinic space group $C2/c$ (No. 15), with $a = 20.713(3)$ Å, $b = 17.450(2)$ Å, $c = 14.451(3)$ Å, $\beta = 129.203(8)^\circ$, $Z = 8$. $[\text{Cd}(\text{NO}_3)_2(1,2\text{-bis}(4\text{-pyridyl)ethene})_{1.5}]_n$ (**2**) was generated from the reaction of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with the *trans*-1,2-bis(4-pyridyl)ethene ligand in an ethanol/water system. It has a novel infinite non-interpenetrating zigzag chain structure which is made up of *trans*-1,2-bis(4-pyridyl)ethene–Cd–*trans*-1,2-bis(4-pyridyl)ethene–Cd–*trans*-1,2-bis(4-pyridyl)ethene building units. Compound **2** crystallized in the triclinic space group $P\bar{1}$ (No. 2), with $a = 10.725(2)$ Å, $b = 10.814(2)$ Å, $c = 9.517(2)$ Å, $\alpha = 104.21(2)^\circ$, $\beta = 94.60(1)^\circ$, $\gamma = 106.62(1)^\circ$, $Z = 2$. In compound **1**, the Cd(II) centers lie in a heptacoordinate environment, while in compound **2**, the Cd(II) atoms adopt an octahedral geometry. The two kinds of polymer structures are based on a T-shape and a linear building block, respectively. $[\text{Cd}(\text{NO}_3)_2(1,2\text{-bis}(4\text{-pyridyl)ethane})_{1.5}]_n$ (**3**) was also synthesized by the reaction of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with the 1,2-bis(4-pyridyl)ethane ligand in a methylene chloride/methanol system. Polymer **3** forms square units, which are linked through the two Cd(II) centers to give infinite linear chains. The synthesis of compound **3** was reported by Fujita (Fujita, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1977) using a different solvent system.

Introduction

Crystal engineering and the design of solid-state architectures have recently become areas of increasing interest.^{1–4} Assembling extended structure compounds by selecting the chemical structure of organic spacers and the coordination geometry of inorganic metal ion species may yield a series of novel networks with various sizes and shapes of channels or cavities. However, while an accurate prediction of the overall crystal structure currently is almost impossible,⁵ it may be achieved in the future.

Meanwhile, new structural motifs must be identified and the reaction chemistry leading to new structural motifs investigated. This will generate a sufficiently large database from which crystal packing rules for specific classes of materials can be deduced. Self-assembly is currently the most efficient approach toward the design of one-, two-, and three-dimensional organic/inorganic hybrid materials of potential utility in fields such as catalysis,⁶ nonlinear optics,⁷ molecular magnetic materials,⁸ electrical conductivity,⁹ and molecular recognition.¹⁰

Among a number of basic building blocks employed in the design of solid-state architectures, the “T-shape” unit has been proven to play an important role in the construction strategy of networks. To date, a large group of novel organic/inorganic composite materials has been obtained using T-shaped building blocks including ladders,^{4b,11} brick walls,^{3a} molecular bilayers,¹²

- (1) (a) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375. (b) Abrahams, B. F.; Hoskins, B. F.; Michall, D. M.; Robson, R. *Nature* **1995**, *374*, 727. (c) Keller, S. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 247. (d) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. (e) Yaghi, O. M.; Li, H. L.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474. (f) Gardner, G. B.; Venkataraman, D.; Moore, J. S.; Lees, S. *Nature* **1995**, *374*, 792.
- (2) (a) Lu, J.; Paliwala, T.; Lim, S. C.; Yu, C.; Niu, T.; Jacobson, A. J. *Inorg. Chem.* **1997**, *36*, 923. (b) Lu, J.; Harrison, W. T. A.; Jacobson, A. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2557. (c) Lu, J.; Yu, C.; Niu, T.; Paliwala, T.; Crisci, G.; Somosa, F.; Jacobson, A. J. *Inorg. Chem.* **1998**, *37*, 4637 and references therein. (d) Mayr, A.; Mao, L. F. *Inorg. Chem.* **1998**, *37*, 5776. (e) Hirsch, K. A.; Wilson, S. R.; Moore, J. S. *Inorg. Chem.* **1997**, *36*, 2960.
- (3) (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.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (c) Fujita, M.; Oguro, D.; Milyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469.
- (4) (a) Losier, P.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2779. (b) Hennigar, T. L.; MacQuarrie, D. C.; Losier, P.; Rogers, R. D.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 972. (c) Power, K. N.; Hennigar, T. L.; Zaworotko, M. J. *Chem. Commun.* **1998**, 595.

- (5) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.
- (6) Maruoka, K.; Murase, N.; Yamamoto, H. *J. Org. Chem.* **1993**, *58*, 2938.
- (7) Chen, C.; Suslick, K. S. *Coord. Chem. Rev.* **1993**, *128*, 293 and references therein.
- (8) (a) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Grandjean, D.; Kahn, O. *Science* **1993**, *261*, 447. (b) Lloret, F.; Munno, G. D.; Julve, M.; Cano, J.; Ruiz, R.; Caneschi, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 135. (c) Real, J. A.; Andrés, E.; Munoz, M. C.; Julve, M.; Granier, T.; Bousseksou, A.; Varret, F. *Science* **1995**, *268*, 265.
- (9) (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. (b) Bowes, C. L.; Ogini, G. A. *Adv. Mater.* **1996**, *8*, 13.
- (10) (a) Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1725. (b) Venkataraman, D.; Gardner, G. F.; Lee, S.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 11600.
- (11) Jung, O. S.; Park, S. H.; Kim, K. M.; Jang, H. G. *Inorg. Chem.* **1998**, *37*, 5781.

3D frameworks,¹³ and parquet motifs.¹⁴ An excellent choice of an inorganic species for constructing T-shaped building blocks is the nitrate anion, which, due to its donor ability, is known to give rise to T-shaped metal centers.^{3a,4a,15} As for the organic spacers, linked bidentate pyridines such as the rigid ligands 4,4'-bipyridine and *trans*-1,2-bis(4-pyridyl)ethene, the flexible ligand 1,2-bis(4-pyridyl)ethane, and other structurally similar ligands are popular for the construction of T-shaped building units.^{3a,4a,b,12}

A second, more common type of basic building block is a linear unit. A number of one-dimensional polymer chains have been generated by linear units through the coordination of ligands to metal centers in a wide variety of ways.^{2c} Pyrazine, 4,4'-bipyridine, and related species with pseudotetrahedrally and octahedrally coordinated metal centers are chosen in order to construct linear building blocks. Linear chain structures can often be modified to form more complicated patterns such as double chains with ladder-type motifs^{2c,15} and 2D or 3D networks,^{13b} by choice of the coordinating anions and the metal-metal interactions.

In the present work, we report the preparation, crystal structures, and thermogravimetric analysis (TGA) of a novel series of organic/inorganic composite materials consisting of both T-shaped and linear building blocks. These materials are formed by the reaction of Cd(NO₃)₂·4H₂O and the rigid linked bidentate pyridine ligands 1,2-bis(4-pyridyl)ethyne and *trans*-1,2-bis(4-pyridyl)ethene, or a flexible bidentate pyridine ligand 1,2-bis(4-pyridyl)ethane. In different solvent systems, three molecular polymers were formed: [Cd(NO₃)₂(1,2-bis(4-pyridyl)ethyne)_{1.5}]_n (**1**), [Cd(NO₃)₂(1,2-bis(4-pyridyl)ethene)_{1.5}]_n (**2**), and [Cd(NO₃)₂(1,2-bis(4-pyridyl)ethane)_{1.5}]_n (**3**). Compounds **1** and **2** are new molecular polymers while the structure of **3** has been reported previously.¹⁶ Compounds **1** and **3** form interpenetrating lattices, while compound **2** forms a non-interpenetrating linear polymer.

Experimental Section

Materials. Cd(NO₃)₂·4 H₂O (Aldrich, 98%), 1,2-bis(4-pyridyl)ethane (Aldrich, 99%), and *trans*-1,2-bis(4-pyridyl)ethene (Aldrich, 97%) were used as obtained from commercial sources without further purification. 1,2-Bis(4-pyridyl)ethyne was prepared according to the literature method.¹⁷

Methods. 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 **1** and **2** were heated from 30 to 500 °C, while **3** was heated from 30 to 600 °C. Infrared spectra (IR) were obtained in the 4000–400 cm⁻¹ range using a Perkin-Elmer 1600 FTIR spectrometer. The samples were prepared as KBr pellets.

[Cd(NO₃)₂(1,2-bis(4-pyridyl)ethyne)_{1.5}]_n. Compound **1** was obtained upon carefully layering a solution of Cd(NO₃)₂·4H₂O (43 mg, 0.14 mmol) in methanol (5 mL) onto a solution of 1,2-bis(4-pyridyl)ethyne (50 mg, 0.28 mmol) in methylene chloride (5 mL). Large pale yellow crystals formed at the methanol/methylene chloride interface and were collected by filtration to give a yield of 50%. IR (KBr, cm⁻¹): 1955.5 (w), 1762.1 (w), 1603.3 (s), 1545.4 (m), 1528.1 (w), 1507.9 (s), 1384.3

(s), 1290.1 (sh), 1210.9 (s), 1124.3 (w), 1088.1 (w), 1074.0 (m), 1007.0 (s), 868.4 (s), 830.0 (s). Anal. Calcd for C₁₈H₁₂N₃CdO₆: C, 42.63; H, 2.37; N, 13.81. Found: C, 42.52; H, 2.60; N, 13.45.

[Cd(NO₃)₂(1,2-bis(4-pyridyl)ethene)_{1.5}]_n. An ethanol solution (7 mL) of *trans*-1,2-bis(4-pyridyl)ethene (102 mg, 0.56 mmol) was allowed to diffuse into an aqueous solution (5 mL) of Cd(NO₃)₂·4H₂O (83 mg, 0.28 mmol) in a test tube for 1 day. Large colorless crystals formed at the ethanol/water interface. Crystals were collected by filtration and washed several times with *n*-hexane, giving a yield of 75%. IR (KBr, cm⁻¹): 3416.3 (br, s), 1762.5 (w), 1605.6 (s), 1558.2 (m), 1504.1 (s), 1385.1 (s), 1316.2 (s), 1302.8 (s), 1232.0 (s), 1255.8 (m), 1220.0 (m), 1205.9 (s), 1074.1 (m), 1010.5 (s), 977.4 (s), 841.3 (s), 826.5 (s). Anal. Calcd for C₁₈H₁₇N₃CdO₇: C, 40.93; H, 3.22; N, 13.26. Found: C, 41.31; H, 3.30; N, 12.98.

[Cd(NO₃)₂(1,2-bis(4-pyridyl)ethane)_{1.5}]_n. Compound **3** was synthesized using a procedure similar to that for **1** except that 1,2-bis(4-pyridyl)ethane was used instead of 1,2-bis(4-pyridyl)ethyne. Colorless crystals were obtained overnight and collected by filtration with a yield of 72%. IR (KBr, cm⁻¹): 1726.9 (m), 1613.7 (s), 1557.1 (s), 1504.7 (s), 1384.5 (s), 1285.8 (s), 1222.9 (s), 1098.3 (w), 1075.3 (s), 1015.5 (s), 832.9 (s), 814.2 (s), 731.9 (w), 688.3 (m).

X-ray Structure Analysis. A cube-shaped (0.6 × 0.6 × 0.5 mm) crystal of **1**, a plate shaped (0.5 × 0.6 × 0.3 mm) crystal of **2**, and a cube-shaped (0.5 × 0.5 × 0.4 mm) crystal of **3** were selected for the single-crystal measurements. The crystals used for the intensity measurements were mounted on glass fibers. Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. The unit cells were determined from 25 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. All data processing was performed on a Silicon Graphics INDIGO² computer with the TEXSAN structure solving program library obtained from the Molecular Structure Corporation, The Woodlands, TX. Lorentz-polarization (Lp) and an absorption correction were applied to the data. Neutral atom scattering factors were calculated by the standard procedures.¹⁸ Anomalous dispersion corrections were applied to all atoms.¹⁹ Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{\text{raw}})^2 + (0.02I_{\text{net}})^2]^{1/2}/Lp$. The intensities of three standard reflections were measured every 150 reflections. These reflections showed no significant deviations during the data collection process.

Compound **1** crystallized in the monoclinic crystal system. The pattern of systematic absences observed in the data was consistent with either the space group *C2/c* or *Cc*. The centric space group *C2/c* was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All atoms were refined with anisotropic thermal parameters.

Compound **2** crystallized in the triclinic crystal system. The centric space group *P1* was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All atoms were refined with anisotropic thermal parameters.

Polymer **3** crystallized in the monoclinic crystal system. The pattern of systematic absences observed during the data collection was consistent with the space group *P2₁/n*, which was confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All atoms were refined with anisotropic thermal parameters.

Results and Discussion

Synthesis. Compounds **1–3** were obtained from different solvent systems. It is well-known that the solvent system plays a crucial role in determining the quality of the crystals and the

(12) Power, K. N.; Hennigar, T. L.; Zaworotko, M. J. *New J. Chem.* **1998**, 22, 177.

(13) (a) Robinson, F.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1995**, 2413. (b) Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1996**, 118, 295.

(14) Dong, Y.-B.; Layland, R. C.; Pschirer, N. G.; Smith, M. D.; Bunz, U. H. F.; zur Loye, H.-C. Submitted.

(15) Carlucci, L.; Ciani, C.; Macchi, P.; Proserpio, D. M. *Chem. Commun.* **1998**, 1837.

(16) (a) Fujita, M.; Kwon, Y. J.; Miyazawa, M.; Ogura, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1977. (b) Fujita, M.; Aoyagi, M.; Ogura, K. *Bull. Chem. Soc. Jpn.* **1998**, 71, 1799.

(17) Tanner, M.; Ludi, A. *Chimia* **1980**, 34, 23.

(18) *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B.

(19) *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.3.1.

Table 1. Crystallographic Data for **1** and **2**

empirical formula	CdO ₆ N ₅ C ₁₈ H ₁₂ , 1	CdO ₇ N ₅ C ₁₈ H ₁₇ , 2
fw	506.73	527.77
cryst syst	monoclinic	triclinic
<i>a</i> (Å)	20.713(3)	10.725(2)
<i>b</i> (Å)	17.450(2)	10.814(2)
<i>c</i> (Å)	14.451(3)	9.517(2)
α (deg)	90	104.21(2)
β (deg)	129.203(8)	94.60(1)
γ (deg)	90	106.62(1)
<i>V</i> (Å ³)	4048(1)	1011.8(4)
space group	<i>C2/c</i> (No. 15)	<i>P1</i> (No. 2)
<i>Z</i> value	8	2
ρ _{calc} (g/cm ³)	1.663	1.732
μ (Mo Kα) (cm ⁻¹)	11.258	11.329
temp (°C)	23.0	23.0
no. of observations (<i>I</i> > 3σ)	2094	2513
residuals: ^a <i>R</i> ; <i>R</i> _w	0.042; 0.050	0.037; 0.055

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

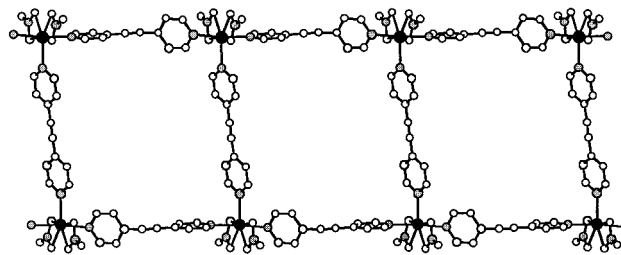
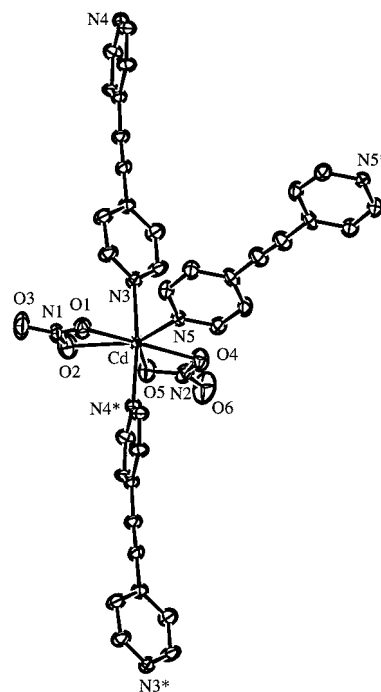
Table 2. Interatomic Distances (Å) and Bond Angles (deg) with Esds () for **1**

Cd—O(1)	2.419(6)	Cd—N(3)	2.312(6)
Cd—O(2)	2.419(7)	Cd—N(4)	2.314(6)
Cd—O(4)	2.456(6)	Cd—N(5)	2.354(6)
Cd—O(5)	2.435(6)		
O(1)—Cd—O(2)	53.0(2)	O(1)—Cd—O(4)	168.2(2)
O(1)—Cd—O(5)	137.9(2)	O(1)—Cd—N(3)	91.2(2)
O(1)—Cd—N(4)	86.2(2)	O(1)—Cd—N(5)	87.2(2)
O(2)—Cd—O(4)	137.5(2)	O(2)—Cd—O(5)	85.4(3)
O(2)—Cd—N(3)	85.5(2)	O(2)—Cd—N(4)	88.5(2)
O(2)—Cd—N(5)	139.5(3)	O(4)—Cd—O(5)	52.5(2)
O(4)—Cd—N(3)	94.9(2)	O(4)—Cd—N(4)	88.6(2)
O(4)—Cd—N(5)	82.9(2)	O(5)—Cd—N(3)	90.9(2)
O(5)—Cd—N(4)	87.2(2)	O(5)—Cd—N(5)	134.8(2)
N(3)—Cd—N(4)	173.8(2)	N(3)—Cd—N(5)	88.7(2)
N(4)—Cd—N(5)	96.8(2)	Cd(1)—O—N(1)	94.6(5)

nature of the structures.^{4a,b} For example, the best single crystals of **1** were obtained from a methanol/methylene chloride system. Slow diffusion of Cd(NO₃)₂·4H₂O in methanol into a methylene chloride solution of 1,2-bis(4-pyridyl)ethyne afforded the infinite coordination polymer **1** as light yellow crystals within 1 day. Other solvent systems, such as the ethanol/water system, only gave poor-quality (but single-phase) materials. However, high-quality single crystals of compound **2** were obtained from the ethanol/water system. Large colorless crystals of **2** formed overnight at the ethanol/water interface when an ethanol solution of *trans*-1,2-bis(4-pyridyl)ethene was allowed to diffuse into an aqueous solution of Cd(NO₃)₂·4H₂O in a test tube. A methylene chloride/methanol system afforded only poor-quality crystals of **2**. It is interesting that only two *trans*-1,2-bis(4-pyridyl)ethene ligands participate in the coordination with the Cd(II) centers in compound **2**. This unexpected result differs from our expectation of a polymeric ladder motif constructed from three *trans*-1,2-bis(4-pyridyl)ethene ligands coordinated to the Cd(II) center forming a T-shaped unit.^{3a,4a}

Compound **3** was also obtained from a methanol/methylene chloride system. The colorless crystals of **3** were obtained overnight in 72% yield when a methanol solution of Cd(NO₃)₂·4H₂O was allowed to diffuse into a methylene chloride solution of 1,2-bis(4-pyridyl)ethane.

Crystal Structure Determinations. Compounds **1–3** were investigated by single-crystal X-ray analysis. Crystal data, data collection parameters, and the results of the analysis for compounds **1** and **2** can be found in Table 1. Selected interatomic bond distances and bond angles for compounds **1** and **2** are given in Tables 2 and 3, respectively. The structure

**Figure 1.** View of a single ladder in the infinite 1D structure of **1**.**Figure 2.** Coordination environment around the cadmium atom in **1**. The atoms are drawn with 50% probability ellipsoids.**Table 3.** Interatomic Distances (Å) and Bond Angles (deg) with Esds () for **2**

Cd—O(1)	2.567(4)	Cd—O(1)*	2.460(4)
Cd—O(4)	2.361(4)	Cd—O(7)	2.303(4)
Cd—N(3)	2.295(4)	Cd—N(4)	2.246(4)
O(1)—Cd—O(1)*	62.7(1)	O(1)—Cd—O(4)	149.4(1)
O(1)—Cd—O(7)	122.6(1)	O(1)—Cd—N(3)	86.4(1)
O(1)—Cd—N(4)	81.4(1)	O(1)*—Cd—O(4)	89.2(1)
O(1)*—Cd—O(7)	174.3(1)	O(1)*—Cd—N(3)	87.7(1)
O(1)*—Cd—N(4)	85.8(1)	O(4)—Cd—O(7)	85.2(1)
O(4)—Cd—N(3)	80.4(1)	O(4)—Cd—N(4)	109.8(1)
O(7)—Cd—N(3)	90.3(1)	O(4)—Cd—N(4)*	97.1(1)
N(3)—Cd—N(4)	167.8(1)	Cd—O(1)—Cd*	117.3(1)

of the infinite ladder **1** is shown in Figure 1. The coordination geometry around the cadmium atom in **1** can be seen in Figure 2. The structure of the infinite zigzag chain of **2** is depicted in Figure 3, while the detailed coordination geometry around the cadmium atom in **2** is displayed in Figure 4.

The X-ray structural analysis of **1** revealed that the Cd(II) centers assume a heptacoordinate environment (Figure 2). The three 1,2-bis(4-pyridyl)ethyne ligands form a "T-joint" at the Cd(II) atoms (Cd(1)—N(3) = 2.312(6) Å, Cd(1)—N(4) = 2.314(6) Å, Cd(1)—N(5) = 2.354(6) Å), which is slightly distorted: N(3)—Cd—N(4) = 173.8(2)°, N(3)—Cd—N(5) = 88.7(2)°, N(4)—Cd—N(5) = 96.8(2)°. The remaining four coordination sites are occupied by the two bidentate nitrate anions. The bond distances (Å) between the Cd(II) atom and the four oxygen

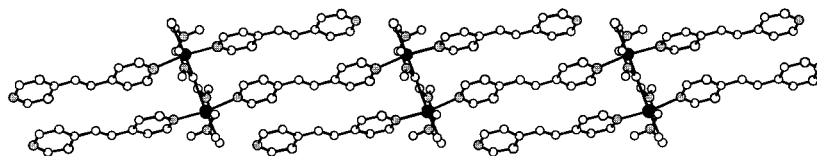


Figure 3. View of a single infinite molecular zigzag chain of **2**.

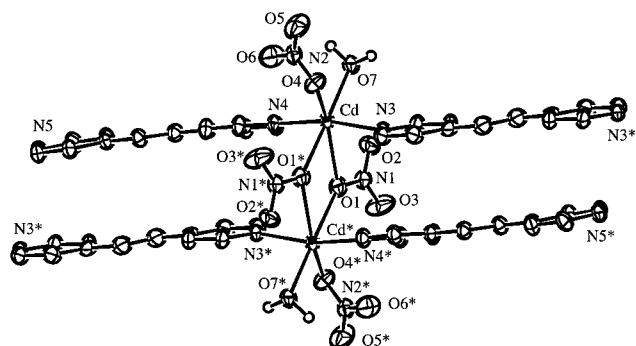


Figure 4. Coordination environment around the cadmium atoms in **2**. The atoms are drawn with 50% probability ellipsoids.

atoms in the two incorporated nitrate anions are Cd–O(1) = 2.419(6), Cd–O(2) = 2.419(2), Cd–O(4) = 2.456(6), and Cd–O(5) = 2.435(6). The T-shaped building blocks in compound **1** are connected to each other to form an infinite 1D structure with interpenetrating molecular ladders which involve 44-membered square rings. Each large square ring has dimensions of 14.249(4) Å × 14.315(4) Å and is enclosed by four 1,2-bis(4-pyridyl)ethyne ligands and four Cd(II) atoms (Figure 1).

The coordination geometry of the metal center plays an important role in the packing arrangement of the polymer. The coordination geometry around the Cd(II) center in compound **1** is similar to that around the Cd(II) atom in [Cd(NO₃)₂(1,4-methylenepyridyl)benzene]_{1.5}_n.^{3a} Such heptacoordinate environments have also been found in cobalt analogues: [Co(NO₃)₂(1,2-bis(4-pyridyl)ethane)_{1.5}]_n.^{4b} and [Co(NO₃)₂(4,4'-bipyridine)_{1.5}]_n.^{4a} All of the metal centers mentioned above adopt a pseudo-octahedral or octahedral coordination geometry from which a flat ladder pattern with all coplanar ligands is generated. It is, however, distinctly different from the ladder pattern generated from the reaction of [Cu(MeCN)₄]PF₆ with 1,4-bis(4-pyridyl)-butadiyne, the structure of which contains an undulating ladder resulting from the tetrahedral Cu(I) centers.²⁰

It is worth pointing out that two of the three ligands in this T-shaped building block in compound **1** have the terminal pyridine groups rotated by 90° with respect to one another, while the pyridine groups in the third coordinating ligand are strictly coplanar.

The situation for compound **2** is quite different from that of compound **1**, both in the coordination geometry of the Cd(II) centers and in the structure. In **2**, the Cd(II) atoms adopt an octahedral geometry. The coordination sphere is defined by two pyridyl nitrogen donors from two *trans*-1,2-bis(4-pyridyl)ethene ligands (Cd–N(3) = 2.295(4) Å, Cd–N(4) = 2.246(4) Å), one oxygen donor from the water molecule (Cd–O(7) = 2.303(4) Å), and three oxygen donors from two nitrate anions (Figure 4). Two of three oxygen atoms of the nitrate anions are shared by two Cd(II) centers to form a Cd–O–Cd–O four-membered ring, with Cd–O distances of 2.567(4) and 2.460(4) Å, respectively. It is worth noticing that there are two types of 1,2-bis(4-pyridyl)ethene ligands in compound **2**. One type forms

a bridge between two Cd(II) centers using two terminal pyridine groups. However, the other type of ligand only uses one terminal pyridine group to coordinate to the Cd(II) atoms, while the other terminal pyridine group is uncoordinated. Two types of *trans*-1,2-bis(4-pyridyl)ethene ligands and Cd(II) centers form a *trans*-1,2-bis(4-pyridyl)ethene–Cd–*trans*-1,2-bis(4-pyridyl)ethene–Cd–*trans*-1,2-bis(4-pyridyl)ethene linear structural unit. These units are linked by two oxygen atoms from the nitrate anions through the cadmium atoms to form a novel infinite non-interpenetrating zigzag molecular chain (Figure 3), which is unlike the one-dimensional double-chain patterns found in [Cu(NO₃)₂(1,2-bis(4-pyridyl)ethyne)]·0.5EtOH¹⁵ and [Co(4,4'-bipyridine)(CH₃COO)₂]_{2c} polymers. Double-chain structures consist of two one-dimensional linear chains which extend in parallel pairs joined by bridging incorporated anions in a ladder fashion. The structural motif of compound **2**, however, is made up of only one stairlike chain, although the metal centers are all in octahedral environments. This kind of unique motif results from the different coordination of the two types of 1,2-bis(4-pyridyl)ethene ligands in **2** (Figure 4). Zigzag chains containing other metals, such as Cu,^{21–24} Ag,²⁵ and Mn,^{26,27} have been reported previously. Compound **2** is the first example of a zigzag chain containing cadmium atoms. It is worth noting that the direction of the chain is almost perpendicular to the Cd₂O₂ plane (for O(1)–Cd–N(3) = 87.7(1)°, O(1)–Cd–N(3) = 85.8(1)°).

Compound **3** is made up of infinite one-dimensional chains in which there are also two types of 1,2-bis(4-pyridyl)ethene ligands. Two ligands of the first type adopt a *gauche* configuration to connect two Cd(II) centers to form square units, which are linked through the two Cd(II) centers by the second type of ligand (*anti*) to give infinite linear chains. This pattern is the same as the structure reported by Fujita.¹⁶

Thermogravimetric Analysis. Figure 5a–c show the results of the thermogravimetric analyses performed on compounds **1–3**. Compounds **1** and **2** were heated to 500 °C and **3** was heated to 600 °C in a helium atmosphere. For **1**, TGA shows that the skeleton of the ladder structure is stable up to 156 °C. Compound **1** went through complicated multiple weight loss steps in the temperature range of 156–386 °C. The total weight loss corresponds to loss of all 1,2-bis(4-pyridyl)ethyne ligands (observed 53.9%, calculated 53.3%) (Figure 5a). The thermal decomposition behavior of compound **2** is quite different from that of compound **1** (Figure 5b). The first weight loss of 3.4%, from 151 to 173 °C, corresponds to the loss of the one water

(20) Blake, A. J.; Champness, N. R.; Khlobystov, A.; Lemenovskii, D. A.; Li, W. S.; Schröder, M. *Chem. Commun.* **1997**, 2027.

(21) (a) Otieno, T.; Rettig, S. J.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1990**, *68*, 1901. (b) Otieno, T.; Rettig, S. J.; Thompson, R. C.; Trotter, J. *Can. J. Chem.* **1989**, *67*, 1964.
 (22) Li, M. X.; Xu, Z.; You, X. Z.; Dong, Z. C.; Guo, G. C. *Polyhedron* **1993**, *8*, 921.
 (23) Lu, J.; Crisci, G.; Niu, T.; Jacobson, A. J. *Inorg. Chem.* **1997**, *36*, 5140.
 (24) Kitagawa, S.; Munakata, M.; Tanimura, T. *Inorg. Chem.* **1992**, *31*, 1714.
 (25) (a) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1995**, *117*, 4562. (b) Carlucci, L.; Ciani, G.; Gudenberg, D. W.; Proserpio, D. M. *Inorg. Chem.* **1997**, *36*, 3812.
 (26) Cortes, R.; Lezama, L.; Pizarro, J. L.; Arriortua, M. I.; Solans, X.; Rojo, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2488.
 (27) Andruh, M.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H. G. *Z. Naturforsch.* **1994**, *49b*, 31.

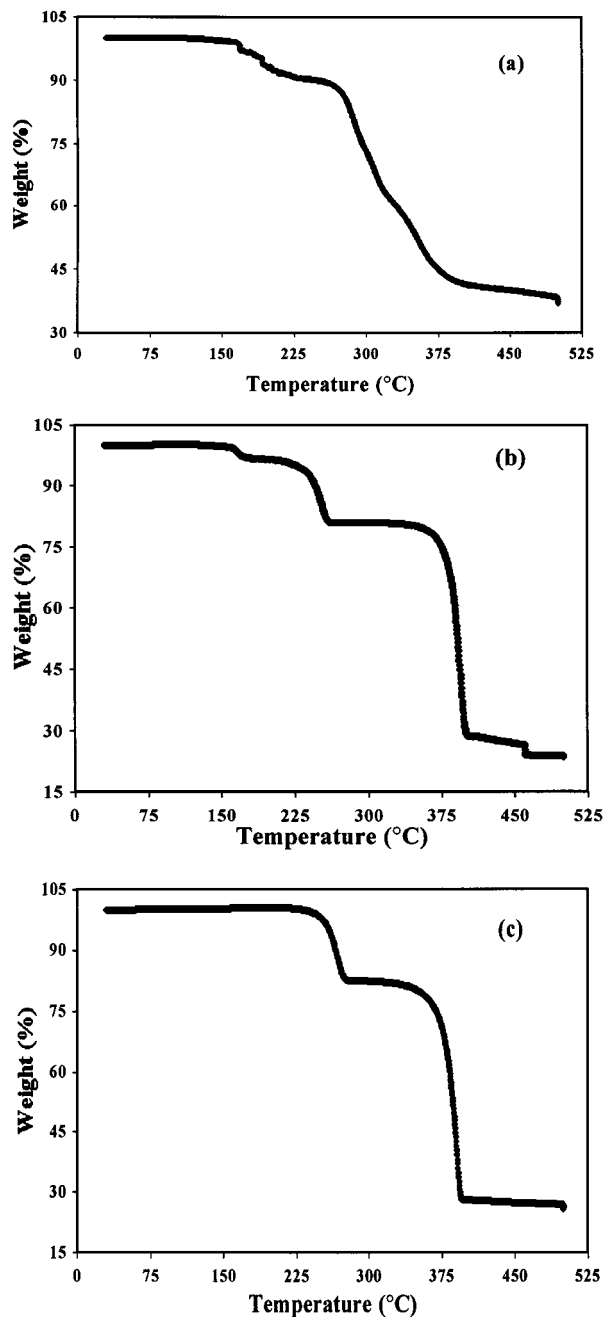


Figure 5. Thermogravimetric analysis results for (a) **1**, (b) **2**, and **3** molecule (calculated 3.4%). A second weight loss corresponding to one of the three *trans*-1,2-bis(4-pyridyl)ethene ligands (observed 16.6%, calculated 17.2%) was found in the temperature range 208–264 °C. A drastic weight loss was observed

from 356 to 475 °C, corresponding to the remaining two *trans*-1,2-bis(4-pyridyl)ethene ligands. This final process is accompanied by the decomposition of the nitrate ions, ultimately giving a brown, amorphous solid that appears to be CdO (observed 23.9%, calculated 24.4%). As for compound **3**, no weight loss was observed below 233 °C (Figure 5c). A weight loss of 17.9% was observed between 233 and 280 °C, which compares with a calculated value of 18.0% for the loss of one of the three 1,2-bis(4-pyridyl)ethane ligands. This ligand loss is followed by a 74.0% (calculated 74.6%) weight loss from 330 to 400 °C, corresponding to the release of the rest of the two 1,2-bis(4-pyridyl)ethane ligands, also accompanied by the decomposition of the nitrate anions. A brown amorphous residue of CdO (observed 26.0%, calculated 25.1%) remained.

Three kinds of *N,N'*-bidentate ligand molecules thermally decomposed from their structures at different temperatures, although the Cd–N bond distances of compounds **1–3** are very similar. Such different thermal behaviors of **1–3** may result from different decomposition mechanisms, which in turn should depend on different topological and energetic factors.^{28,29}

Conclusions

Two new organic/inorganic composite polymers were synthesized by the reaction of 1,2-bis(4-pyridyl)ethyne or *trans*-1,2-bis(4-pyridyl)ethene with Cd(NO₃)₂·4H₂O. A known coordination polymer [Cd(NO₃)₂(1,2-bis(4-pyridyl)ethane)_{1.5}]_n was also obtained from a different solvent system. All three compounds were determined by single-crystal X-ray diffraction. We found that the solvent systems affect not only the quality of the crystals, reaction time, and yield but also the metal coordination geometry and final polymer structure. In the future, we will expand the types of ligands to trimeric and tetrameric pyridine-capped ligands which should give access to porous networks with larger, yet still well-defined pores.

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Supporting Information Available: Tables of crystallographic data, structure solutions and refinements, atomic coordinates, interatomic bond distances and angles, and anisotropic thermal parameters for compounds **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC9814569

(28) Hagerman, D.; Hammond, R. P.; Hanshalter, R.; Zubieta, J. *Chem. Mater.* **1998**, *10*, 2091.

(29) Petit, S.; Coquerel, G. *Chem. Mater.* **1996**, *8*, 2247.