

## Two- and Three-Dimensional Cadmium Coordination Polymers Based on *N,N*-(2-Pyridyl)-(4-pyridylmethyl)amine

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The synthesis of a bipyridine ligand with a flexible spacer and a noncoordinating amine group *N,N*-(2-pyridyl)-(4-pyridylmethyl)amine, **L**<sub>2</sub>, and its coordination chemistry with cadmium have been investigated. Two-dimensional (2D) coordination polymers of **L**<sub>2</sub> with empirical formulas [Cd(**L**<sub>2</sub>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]<sub>∞</sub>, **1**, or [Cd(**L**<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>∞</sub>, **2**, were prepared by hydro(solvo)thermal reactions of **L**<sub>2</sub> and Cd(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O or Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in mixtures of water and ethanol, respectively. Single-crystal X-ray diffraction studies reveal that **1** and **2** have similar structures in which each **L**<sub>2</sub> ligand bridges two cadmium centers with both the 4-pyridyl and 2-pyridyl nitrogen atoms to result in 2D rhombohedral polymeric grids. The two rings of **L**<sub>2</sub> are essentially perpendicular to each other, likely to accommodate the coordination of both pyridyl nitrogen atoms to the Cd centers as well as the “intramolecular” hydrogen bonds between the amine group in the flexible spacer and the coordinated anion group. When the hydro(solvo)thermal reaction was carried out between **L**<sub>2</sub> and CdSO<sub>4</sub>·6H<sub>2</sub>O, a 3D Cd coordination polymer [Cd<sub>2</sub>(**L**<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>]<sub>∞</sub>, **3**, resulted. Two distinct Cd centers reside in the asymmetric unit in **3**. One Cd center coordinates to four 4-pyridyl nitrogen atoms of **L**<sub>2</sub> ligands and two sulfate groups, while the other Cd center binds to two 2-pyridyl nitrogen atoms, two sulfate groups, and two water molecules. The two distinct cadmium centers are bridged by both **L**<sub>2</sub> ligands and sulfate groups to result in an unusual 3D polymeric structure. Crystal data for **1**: monoclinic space group *C2/c*, *a* = 8.4931(6) Å, *b* = 17.264(1) Å, *c* = 16.699(1) Å, β = 99.517(6)°, *V* = 2559.4(1) Å<sup>3</sup>, *Z* = 4, *R* = 0.034, *R*<sub>w</sub> = 0.039. Crystal data for **2**: monoclinic space group *C2/c*, *a* = 8.6231(5) Å, *b* = 17.288(1) Å, *c* = 16.1675(7) Å, β = 94.730(2)°, *V* = 2401.9(1) Å<sup>3</sup>, *Z* = 4, *R* = 0.050, *R*<sub>w</sub> = 0.058. Crystal data for **3**: monoclinic, space group *P2<sub>1</sub>/n*, *a* = 11.7188(2) Å, *b* = 15.7525(3) Å, *c* = 12.8528(1) Å, β = 93.064(1)°, *V* = 2369.2(1) Å<sup>3</sup>, *Z* = 2, *R* = 0.042, *R*<sub>w</sub> = 0.047.

### Introduction

The recent surge of research activity in the area of coordination polymers has been motivated by the ability of metal–ligand coordination in providing a facile approach to the controlled assembly of one-, two-, and three-dimensional extended solids. Incorporation of active groups into coordination polymers presents an excellent opportunity for the construction of functional materials with interesting second-order nonlinear optical,<sup>1</sup> electronic,<sup>2</sup> magnetic,<sup>3</sup> inclusion,<sup>4</sup> and catalytic properties.<sup>5</sup> Extensive work has been carried out using rigid bridging ligands such as 4,4'-bipyridine,<sup>6</sup> 2,4,6-tris(4-pyridyl)-1,3,5-

triazine,<sup>7</sup> 1,3,5-tris(4-ethynylbenzonitrile)benzene,<sup>8</sup> and 1,3,5-benzenetricarboxylic acid,<sup>9</sup> and a variety of 1D, 2D, and 3D frameworks with novel topologies and inclusion behaviors have been obtained. On the other hand, bridging ligands with flexible spacers have not been extensively exploited except in a few cases.<sup>10</sup> To this end, we have designed and synthesized an unsymmetrical flexible bridging ligand with a noncoordinating amine group in the spacer, *N,N*-(2-pyridyl)-(4-pyridylmethyl)-

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amine,  $L_2$ . The flexible spacer in  $L_2$  may allow the synthesis of coordination polymers that are not possible with rigid linking groups such as 4,4'-bipyridine. Moreover, the amine group in the flexible spacer of  $L_2$  can potentially form hydrogen bonds with the acceptor groups to direct the self-assembly of interesting supramolecular systems. Additionally, we are interested in exploiting the potential of directing the inclusion behaviors of guest molecules via potential hydrogen bonding with the amine group as well as inducing the crystallization of the target coordination polymers in acentric space groups by using an unsymmetrical bridging ligand. We report in this paper the synthesis and X-ray single-crystal structures of 2D and 3D coordination polymers of cadmium(II) perchlorate, nitrate, and sulfate with the ligand  $L_2$ . We have demonstrated that the bipyridine ligand  $L_2$  is capable of linking metal centers to yield coordination polymers, and more importantly, the combination of flexible spacer and hydrogen bonding ability of the amine group in  $L_2$  can direct the self-assembly of novel polymeric coordination networks.

## Experimental Section

**Materials and Methods.** All chemicals were purchased from Aldrich, and used without further purification. **Caution!**  $Cd(ClO_4)_2 \cdot 6H_2O$  is potentially explosive and should be used with care! The IR spectra were recorded as KBr pellets on a Paragon 1000 FT-IR spectrometer.  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra were taken on a Varian XL-300 spectrometer. Density measurements were carried out by the neutral buoyancy method using a mixture of chlorobenzene and 1,4-dibromobenzene. Elemental analyses were done at the Microanalytical Laboratory of the University of Illinois at Urbana-Champaign.

**Synthesis of  $N,N$ -(2-Pyridyl)-(4-pyridylmethyl)amine,  $L_2$ .** A clear solution of 4-pyridinecarboxaldehyde (9.2 mL, 96 mmol) and 2-aminopyridine (7.5 g, 80 mmol) in 150 mL of benzene was refluxed with a Dean-Stark trap for 12 h. Benzene was removed in vacuo, and the residue was dissolved in 200 mL of ethanol. To the ethanol solution was added  $NaBH_4$  (4.0 g, 105.8 mmol), and the resulting mixture was stirred at room temperature for 18 h. Excess  $NaBH_4$  was quenched with water and then with saturated  $NH_4Cl$  solution at 70 °C. The volatiles were removed in vacuo, and the residue was dissolved in 200 mL water and extracted with  $3 \times 150$  mL of ethyl acetate. The extract was dried over  $MgSO_4$ , and upon removal of the solvent, analytically pure off-white product was obtained. Yield: 14.5 g (98%).  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  8.48 (dd,  $^3J_{HH} + ^5J_{HH} = 6.1$  Hz, 2H), 8.05 (m, 1H), 7.37 (m, 1H), 7.22 (dd,  $^3J_{HH} + ^5J_{HH} = 6.1$  Hz, 2H), 6.58 (m, 1H), 6.32 (d,  $^3J_{HH} = 8.4$  Hz, 1H), 5.00 (br., 1H), 4.50 (d,  $^3J_{HH} = 6.1$  Hz, 2H).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 75 MHz):  $\delta$  150.1, 149.0, 148.4, 137.7, 122.2, 121.3, 113.8, 107.3, 45.1.

**Synthesis of  $[Cd(L_2)_2(ClO_4)_2]_{\infty}$ , **1**.** A mixture of  $Cd(ClO_4)_2 \cdot 6H_2O$  (0.42 g, 1 mmol) and  $L_2$  (0.37 g, 2 mmol) was thoroughly mixed with ethanol (0.5 mL) and  $H_2O$  (0.05 mL) in a heavy-walled Pyrex tube. The Pyrex tube was sealed under vacuum and heated in an oven at 90 °C. Colorless crystals were obtained after 24 h of heating. Yield: 0.16 g (23.5%). Anal. Calcd for  $C_{22}H_{22}Cl_2N_6O_8Cd$ : C, 38.76; H, 3.25; N, 12.33. Found: C, 38.78; H, 3.26; N, 12.05. Density: 1.76(1) g/cm<sup>3</sup>. IR (cm<sup>-1</sup>, KBr): 3365 (s), 1612 (s), 1572 (s), 1528 (m), 1466 (s), 1427 (s), 1368 (w), 1342 (m), 1314 (m), 1296 (vw), 1276 (vw), 1241 (w), 1227 (w), 1147 (s), 1122 (s), 1024 (s), 916 (m), 824 (w), 790 (w), 768 (m), 738 (w), 718 (w), 669 (vw), 631 (w), 616 (m), 532 (vw), 511 (w), 478 (m).

**Synthesis of  $[Cd(L_2)_2(NO_3)_2]_{\infty}$ , **2**.** A heavy-walled Pyrex tube containing a mixture of  $Cd(NO_3)_2 \cdot 4H_2O$  (0.31 g, 1 mmol) and  $L_2$  (0.37

g, 2 mmol) in ethanol (0.5 mL) and  $H_2O$  (0.05 mL) was sealed under vacuum and placed inside an oven at 95 °C. Colorless crystals were obtained after 24 h of heating. Yield: 0.28 g (46.1%). Anal. Calcd for  $C_{22}H_{22}N_8O_6Cd$ : C, 43.54; H, 3.65; N, 18.46. Found: C, 43.04; H, 3.64; N, 17.81. Density: 1.67(1) g/cm<sup>3</sup>. IR (cm<sup>-1</sup>): 3273 (m), 1610 (s), 1575 (m), 1539 (w), 1472 (w), 1436 (s), 1384 (w), 1362 (w), 1315 (m), 1301 (m), 1282 (m), 1221 (w), 1162 (m), 1136 (w), 1065 (w), 1038 (m), 1021 (m), 999 (m), 818 (w), 794 (vw), 768 (m), 636 (vw), 561 (w), 532 (w), 519 (w), 479 (m).

**Synthesis of  $[Cd_2(L_2)_4(H_2O)_2(SO_4)_2]_{\infty}$ , **3**.** A mixture of  $CdSO_4 \cdot 2H_2O$  (0.13 g, 0.5 mmol) and  $L_2$  (0.185 g, 1 mmol) was thoroughly mixed in ethanol (0.5 mL) and  $H_2O$  (0.03 mL) in a heavy-walled Pyrex tube. The Pyrex tube was sealed under vacuum and heated in an oven at 90 °C. Colorless crystals were obtained after 12 h of heating. Yield: 0.27 g (98.4%). Density: 1.65(1) g/cm<sup>3</sup>. IR (cm<sup>-1</sup>, KBr): 3371 (s), 3049 (br), 1607 (s), 1572 (s), 1527 (s), 1459 (m), 1429 (s), 1377 (w), 1368 (w), 1340 (m), 1315 (s), 1286 (w), 1277 (vw), 1226 (m), 1164 (s), 1113 (s), 1036 (s), 992 (m), 952 (m), 818 (w), 790 (w), 770 (m), 736 (w), 718 (w), 656 (vw), 605 (s), 519 (m), 484 (w), 474 (m).

**X-ray Data Collections and Structure Determinations.** A single crystal of **1** with dimensions of 0.10  $\times$  0.34  $\times$  0.42 mm was mounted with epoxy on a Pyrex fiber affixed to a brass pin and transferred to an Enraf-Nonius CAD4-Turbo diffractometer equipped with Mo K $\alpha$  radiation. Data were collected using the Nonius EXPRESS program.<sup>11</sup> Of the 3232 reflections measured, 2498 reflections with  $I > 1.96\sigma(I)$  were used in structure solution and refinement. The structure was solved using SIR92<sup>12</sup> and refined using the CRYSTALS software package by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms.<sup>13</sup> H2 was located in the difference electron density map and refined isotropically. All the other hydrogen atoms were located by geometric placing. Final refinement gave  $R = 0.034$  and  $R_w = 0.039$ . All the drawings were produced using the Oxford University program CAMERON.<sup>14</sup> Experimental details for X-ray data collections of **1** are tabulated in Table 1. Selected bond distances and angles for **1** are listed in Table 2.

Data collections for **2** and **3** were carried out with colorless crystals of dimensions of 0.15  $\times$  0.18  $\times$  0.22 mm and 0.07  $\times$  0.08  $\times$  0.38 mm, respectively on a Siemens SMART system equipped with a CCD detector using Mo K $\alpha$  radiation. Of the 2840 (5589) reflections measured, 1316 (3065) reflections with  $I > 3\sigma(I)$  [ $2\sigma(I)$ ] were used in structure solution and refinement for **2** (**3**). The structures were solved using SIR92, and refined using the CRYSTALS software package by full matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms. H22 in **2** and H81, H82, H91, and H401 in **3** were located in difference electron density maps, and refined isotropically. All the other hydrogen atoms in **2** and **3** were located by geometric placing. Final refinement gave an  $R = 0.050$  (0.042) and  $R_w = 0.058$  (0.047) for **2** (**3**). Experimental details for X-ray data collections of **2** and **3** are tabulated in Table 1. Selected bond distances and angles for **2** and **3** are listed in Tables 2 and 3, respectively.

## Results and Discussion

**Synthesis.** The ligand used for this study,  $N,N$ -(2-pyridyl)-(4-pyridylmethyl)amine,  $L_2$ , was synthesized in nearly quantitative yields according to Scheme 1. Both  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra are consistent with the formulation of  $L_2$ . The hydro-(solvo)thermal reactions of  $L_2$  and  $Cd(ClO_4)_2 \cdot 6H_2O$  and  $Cd(NO_3)_2 \cdot 4H_2O$  in the molar ratios of 2:1 at 90 °C afford two novel cadmium 2D coordination polymers with empirical formulas of  $[Cd(L_2)_2(ClO_4)_2]_{\infty}$ , **1**, and  $[Cd(L_2)_2(NO_3)_2]_{\infty}$ , **2**, respectively. While the microanalyses suggested the formula-

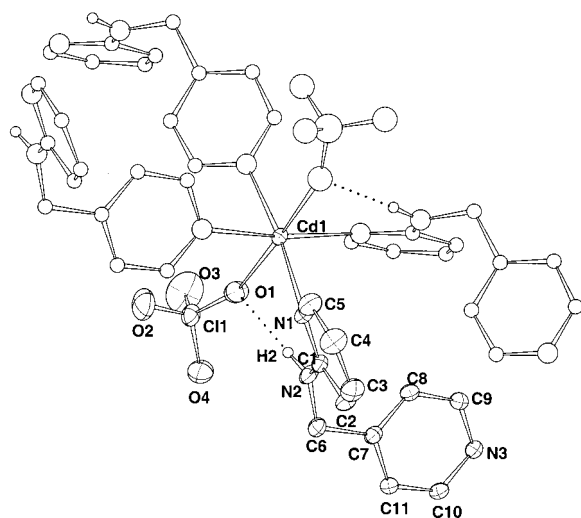
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**Table 1.** Data for the X-ray Diffraction of **1**, **2**, and **3**<sup>a</sup>

empirical formula	CdC <sub>22</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>8</sub> , <b>1</b>	CdC <sub>22</sub> H <sub>22</sub> N <sub>8</sub> O <sub>6</sub> , <b>2</b>	Cd <sub>2</sub> C <sub>44</sub> H <sub>48</sub> N <sub>12</sub> S <sub>2</sub> O <sub>10</sub> , <b>3</b>
<i>a</i> , Å	8.4931(6)	8.6231(5)	11.7188(2)
<i>b</i> , Å	17.264(1)	17.288(1)	15.7525(3)
<i>c</i> , Å	17.699(1)	16.1675(7)	12.8528(1)
$\alpha$ , deg	90	90	90
$\beta$ , deg	99.517(6)	94.730(2)	93.064(1)
$\gamma$ , deg	90	90	90
<i>V</i> , Å <sup>3</sup>	2559.5(1)	2402.0(1)	2369.2(1)
<i>Z</i>	4	4	2
fw	681.77	606.88	1193.89
space group	<i>C2/c</i>	<i>C2/c</i>	<i>P2<sub>1</sub>/n</i>
<i>T</i> , °C	21(1)	25(1)	25(1)
$\lambda$ (Mo K $\alpha$ ), Å	0.710 73	0.710 73	0.710 73
$\rho_{\text{obs}}$ , g/cm <sup>3</sup>	1.76(1)	1.67(1)	1.65(1)
$\rho_{\text{calc}}$ , g/cm <sup>3</sup>	1.77	1.68	1.67
$\mu$ , cm <sup>-1</sup> (Mo K $\alpha$ )	11.2	9.6	10.5
min and max residual density, e/Å <sup>3</sup>	-0.48, 0.61	-1.14, 0.84	-0.58, 0.57
<i>R</i>	0.034	0.050	0.042
<i>R<sub>w</sub></i>	0.039	0.058	0.047
goodness of fit	1.08	1.02	0.39

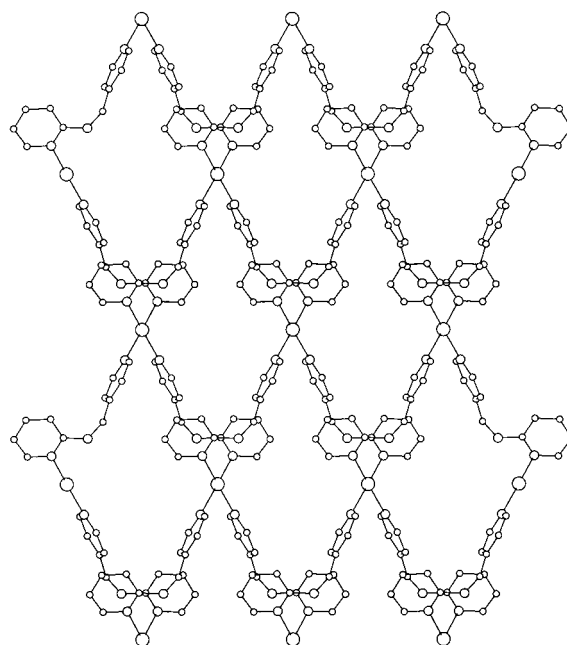
<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $R_w = \{\sum w[|F_o| - |F_c|]^2 / \sum w|F_o|^2\}^{1/2}$ .



**Figure 1.** Coordination environment of **1**. The asymmetric unit is represented as ellipsoids at 30% probability. The open circles with increasing sizes represent H, C, N, O, and Cl, respectively. The “intramolecular” hydrogen bonding between the amine and the coordinated perchlorate group is also shown.

tions of **1** and **2**, the IR spectra clearly indicated the presence of perchlorate (1146–1024 cm<sup>-1</sup>) and nitrate groups (1426–1280 cm<sup>-1</sup>) in **1** and **2**, respectively. The strong splitting of the perchlorate and nitrate peaks is also suggestive of the coordination of the perchlorate and nitrate groups to the cadmium centers in **1** and **2**, which has been confirmed by the single-crystal structure determinations. Interestingly, when the hydro(solvo)-thermal reaction was carried out between **L<sub>2</sub>** and CdSO<sub>4</sub>·2.7H<sub>2</sub>O, a product with the formulation of [Cd<sub>2</sub>(L<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>]<sub>∞</sub>, **3**, was obtained. The IR spectrum clearly indicated the presence of both water and the sulfate group in **3**. The fact that all three products are quite insoluble in water, ethanol, and common organic solvents suggests that they are polymeric in nature.

**X-ray Single-Crystal Structures of 1 and 2.** The polymeric structure of **1** was confirmed by an X-ray single-crystal structure determination. Each asymmetric unit of **1** contains one L<sub>2</sub> ligand, one perchlorate group, and one Cd center lying on a crystallographic 2-fold axis. The local coordination geometry around the Cd center can be described as a slightly distorted octahedron (Figure 1). The Cd center coordinates to two monodentate perchlorate groups with a Cd–O distance of 2.430(3) Å in the



**Figure 2.** View of 2D rhombohedral structure of **1** in the *ab* plane. Hydrogen atoms and perchlorate groups have been omitted, and the open circles with increasing sizes represent H, C, N, O, and Cd, respectively.

axial positions and to two 2-pyridyl and two 4-pyridyl nitrogen atoms of four different L<sub>2</sub> ligands in a *cis* fashion with Cd–N distances of 2.344(2) and 2.320(2) Å, respectively. The O1–Cd–O1' angle is 177.7(1)°, whereas the N–Cd–N angles around the Cd center range from 87.1(1) to 95.5(1)°. Each Cd center is linked to four different Cd atoms via the four different L<sub>2</sub> ligands to result in a 2D rhombohedral grid in the *ab* plane (Figure 2). In the Cd<sub>4</sub> rhombus, the Cd–Cd distance through the bridging L<sub>2</sub> ligands is 9.62 Å, while the Cd–Cd separations through the diagonals of the Cd<sub>4</sub> rhombus are 8.49 and 17.26 Å (the internal angles of the rhombus are 52.4 and 127.6°, respectively). The next layer of 2D rhombohedral grid is displaced by 4.07 Å along the *b* axis, so that the 2D rhombohedral grids form an ABAB repeat along the crystallographic *c* axis. The layer spacing between the rhombohedral grids is 8.73 Å; the adjacent layers stack via van der Waals interactions.

The geometry of the coordinated L<sub>2</sub> ligand in **1** is also worth noting. The 4-pyridyl and 2-pyridyl rings of L<sub>2</sub> are essentially



**Table 2.** Selected Bond Distances (Å) and Bond Angles (deg) for **1** and **2**<sup>a</sup>

1		2	
Cd1—O1	2.430(3)	Cd1—O1	2.357(8)
Cd1—N1	2.345(2)	Cd1—N1	2.375(6)
Cd1—N3	2.320(2)	Cd1—N3	2.321(6)
C11—O1	1.429(4)	O1—N4	1.213(11)
C11—O2	1.395(4)	O2—N4	1.212(13)
C11—O3	1.382(5)	O3—N4	1.158(12)
C11—O4	1.413(4)	N1—C1	1.340(9)
N1—C1	1.352(4)	N1—C5	1.358(10)
N1—C5	1.347(4)	N2—C1	1.349(10)
N2—C1	1.354(4)	N2—C6	1.448(10)
N2—C6	1.448(4)	N3—C9	1.330(11)
N3—C9	1.336(4)	N3—C10	1.336(10)
N3—C10	1.340(4)	C1—C2	1.407(10)
C1—C2	1.403(5)	C2—C3	1.363(14)
C2—C3	1.372(6)	C3—C4	1.362(14)
C3—C4	1.372(6)	C4—C5	1.370(13)
C4—C5	1.380(6)	C6—C7	1.501(10)
C6—C7	1.513(5)	C7—C8	1.385(10)
C7—C8	1.373(5)	C7—C11	1.376(10)
C7—C11	1.388(5)	C8—C9	1.369(11)
C8—C9	1.382(5)	C10—C11	1.383(10)
C10—C11	1.373(5)	N2—H22	0.81(8)
N2—H2	0.85(4)		
O1—Cd1—N1	91.10(10)	O1—Cd1—N1	87.5(2)
O1—Cd1—O1(a)	177.71(12)	O1—Cd1—O1(d)	172.7(2)
O1—Cd1—N1(a)	90.43(10)	O1—Cd1—N1(d)	97.7(2)
O1—Cd1—N3(b)	94.60(10)	O1—Cd1—N3(e)	87.1(2)
O1—Cd1—N3(c)	83.73(10)	O1—Cd1—N3(f)	87.7(2)
N1—Cd1—N1(a)	95.53(7)	O1(d)—Cd1—N1	97.7(2)
N1—Cd1—N3(b)	88.95(7)	N1—Cd1—N1(d)	90.7(2)
N1—Cd1—N3(c)	173.20(6)	N1—Cd1—N3(e)	90.9(2)
N3(b)—Cd1—N3(c)	87.06(7)	N1—Cd1—N3(f)	175.1(2)
Cd1—N1—C1	128.1(2)	N3(e)—Cd1—N3(f)	87.8(2)
Cd1—N1—C5	112.67(18)	Cd1—N1—C1	127.9(5)
N2—C1—C2	122.1(3)	Cd1—N1—C5	113.0(5)
N1—C1—C2	120.7(3)	C1—N1—C5	118.1(6)
N1—C1—N2	117.1(3)	C1—N2—C6	124.3(6)
C1—C2—C3	119.5(3)	C9—N3—C10	116.3(6)
C2—C3—C4	119.6(4)	N2—C1—C2	121.9(7)
C3—C4—C5	118.7(4)	N1—C1—C2	121.2(7)
N1—C5—C4	123.0(3)	N1—C1—N2	116.9(6)
N2—C6—C7	114.3(3)	C1—C2—C3	118.9(7)
C7—C8—C9	119.6(3)	C2—C3—C4	120.0(8)
N3—C9—C8	122.9(3)	C3—C4—C5	119.2(8)
N3—C10—C11	123.0(3)	N1—C5—C4	122.5(8)
C1—N1—C5	118.4(3)	N2—C6—C7	115.5(6)
C9—N3—C10	117.3(3)	C8—C7—C11	116.7(6)
C8—C7—C11	117.6(3)	C6—C7—C8	122.7(6)
C6—C7—C8	122.0(3)	C6—C7—C11	120.5(6)
C6—C7—C11	120.2(3)	C7—C8—C9	119.3(7)
C7—C11—C10	119.5(3)	N3—C9—C8	124.5(7)
C1—N2—C6	123.9(3)	N3—C10—C11	122.8(7)
		C7—C11—C10	120.3(6)

<sup>a</sup> Symmetry transformations: a = 2 - x, y, 1/2 - z; b = 1/2 + x, -1/2 + y, z; c = 3/2 - x, -1/2 + y, 1/2 - z; d = 2 - x, y, 3/2 - z; e = 1/2 + x, 1/2 + y, z; f = 3/2 - x, 1/2 + y, 3/2 - z.

perpendicular to each other with a dihedral angle of 83.4 degrees. The C1—N2—C6—C7 torsion angle is 89.3°. The amine group on the flexible spacer of **L**<sub>2</sub> forms “intramolecular” hydrogen bond with the O1 atom of the coordinated perchlorate group; the N2—H2...O1 distance is 2.93(1) Å and the N2—H2...O1 angle is 172(4)°. The 4-pyridyl and 2-pyridyl rings probably adopt their mutually perpendicular orientation to accommodate the coordination of both pyridyl nitrogen atoms to the Cd center and the “intramolecular” hydrogen bond between the amine group on the flexible spacer and the coordinated perchlorate group. Finally, the distance between the

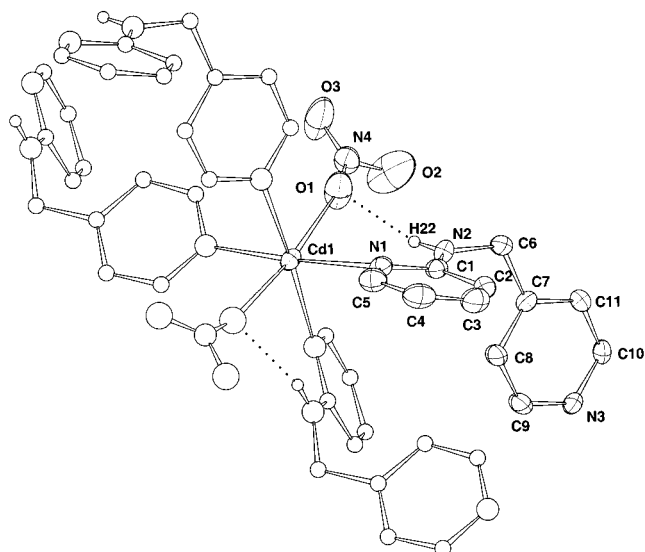
**Table 3.** Selected Bond Distances (Å) and Bond Angles (deg) for **3**<sup>a</sup>

Cd1—O4	2.362(4)	C16—C17	1.370(14)
Cd1—O8	2.238(5)	C17—C18	1.386(16)
Cd1—N34	2.448(6)	C18—C19	1.356(12)
Cd2—O6	2.282(5)	C24—C29	1.374(9)
Cd2—N27	2.326(6)	C24—C25	1.378(10)
Cd2—N48	2.426(6)	C25—C26	1.371(11)
N9—C10	1.446(10)	C45—C50	1.382(10)
N9—C14	1.353(9)	C45—C46	1.387(11)
N15—C16	1.344(13)	C46—C47	1.379(11)
N15—C14	1.345(10)	C49—C50	1.374(11)
N27—C26	1.347(10)	C28—C29	1.395(11)
N27—C28	1.343(10)	C35—C36	1.377(12)
N34—C39	1.353(9)	C36—C37	1.395(12)
N34—C35	1.354(9)	C37—C38	1.376(11)
N40—C42	1.431(10)	C38—C39	1.410(9)
N40—C39	1.362(9)	C42—C45	1.525(10)
N48—C49	1.331(10)	O8—H82	0.80(10)
N48—C47	1.344(10)	O8—H81	0.87(8)
C10—C24	1.536(10)	N9—H91	0.9(2)
C14—C19	1.407(11)	N40—H401	0.78(8)
O4—Cd1—O8	85.22(18)	C45—C50—C49	120.1(7)
O4—Cd1—N34	89.44(17)	N15—C14—C19	120.9(7)
O4—Cd1—O8(d)	94.78(18)	N9—C14—C19	123.7(7)
O4—Cd1—N34(d)	90.56(17)	N15—C16—C17	124.9(10)
O8—Cd1—N34	84.9(2)	C16—C17—C18	117.0(10)
O8—Cd1—N34(d)	95.1(2)	C17—C18—C19	120.0(8)
O6—Cd2—N27	92.0(2)	C14—C19—C18	119.8(8)
O6—Cd2—N48(a)	81.8(2)	C10—C24—C25	119.3(6)
O6—Cd2—N27(c)	88.0(2)	C10—C24—C29	122.0(6)
N27—Cd2—N48(e)	92.3(2)	C25—C24—C29	118.7(7)
O6—Cd2—N48(e)	98.2(2)	C24—C25—C26	119.7(7)
N27—Cd2—N48(a)	87.7(2)	N27—C26—C25	122.9(7)
C10—N9—C14	123.3(6)	N27—C28—C29	123.1(6)
C14—N15—C16	117.4(7)	C24—C29—C28	118.6(7)
Cd2—N27—C26	118.7(5)	N34—C35—C36	124.4(7)
Cd2—N27—C28	124.1(5)	C35—C36—C37	118.2(7)
C26—N27—C28	117.1(6)	C36—C37—C38	118.8(7)
C35—N34—C39	117.0(6)	C37—C38—C39	119.8(6)
Cd1—N34—C35	112.2(5)	N40—C39—C38	121.6(6)
Cd1—N34—C39	129.4(4)	N34—C39—N40	116.8(6)
C39—N40—C42	125.1(6)	N34—C39—C38	121.6(6)
C47—N48—C49	116.5(6)	N40—C42—C45	115.6(6)
Cd2(b)—N48—C47	124.7(5)	C42—C45—C46	122.4(6)
Cd2(b)—N48—C49	117.8(5)	C42—C45—C50	120.6(6)
N48—C47—C46	123.4(7)	C46—C45—C50	116.9(7)
N9—C10—C24	115.2(6)	C45—C46—C47	119.5(7)
N48—C49—C50	123.6(7)	H81—O8—H82	106(9)
N9—C14—N15	115.4(7)		

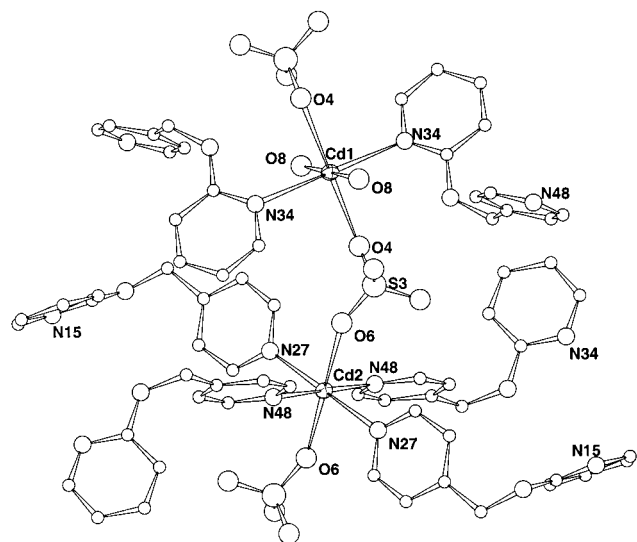
<sup>a</sup> Symmetry transformation: a = 5/2 - x, -1/2 + y; 5/2 - z; c = 2 - x, -y, 2 - z; d = 2 - x, -y, 3 - z; e = -1/2 + x, 1/2 - y, -1/2 + z.

two coordinated nitrogen atoms of **L**<sub>2</sub> is 6.81 Å, about 1.73 Å longer than that of 2,4'-bipyridine which only coordinates to metal centers via the 4-pyridyl nitrogen atom.<sup>15</sup>

**2** is isostructural with **1** except that the coordinated perchlorate groups are replaced by two monodentate nitrate groups. The Cd center possesses C<sub>2</sub> crystallographic symmetry and a slightly distorted octahedral geometry with its equatorial sites occupied by two 4-pyridyl and two 2-pyridyl nitrogen atoms of **L**<sub>2</sub> and its axial positions occupied by two monodentate nitrate groups (Figure 3). The Cd centers also form a 2D rhombohedral grid with a Cd—Cd distance through the bridging **L**<sub>2</sub> ligands of 9.66 Å in the *ab* plane. The Cd—Cd separations through the diagonals of the rhombus are 8.62 and 17.29 Å and the internal angles of the rhombus are 53.0 and 127.0°. The 2D rhombohedral grids in **2** also form an *ABAB* repeat along the crystallographic *c* axis.



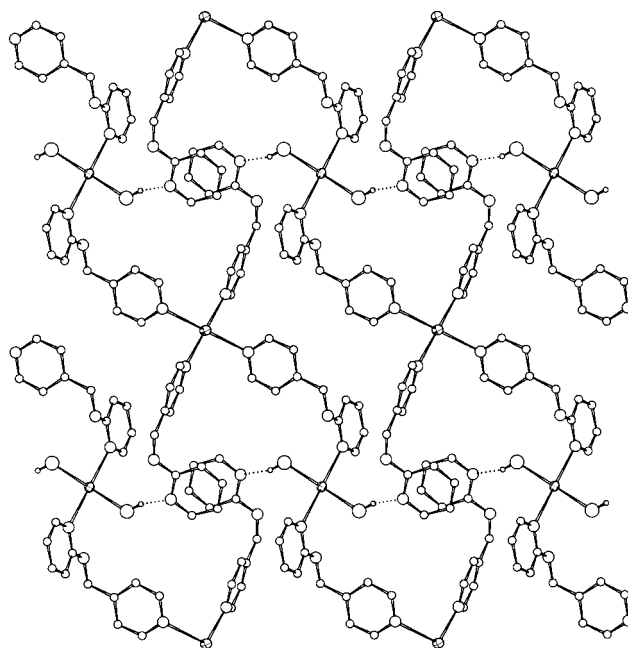
**Figure 3.** Coordination environment of **2**. The asymmetric unit is represented as ellipsoids at 30% probability. The open circles with increasing sizes represent H, C, N, and O, respectively. The “intramolecular” hydrogen bonding between the amine and the coordinated nitrate group is also shown.



**Figure 4.** Coordination environments of Cd1 and Cd2 in **3**. Hydrogen atoms have been omitted, and the open circles with increasing sizes represent C, N, O, and S, respectively.

The rhombohedral grid is displaced by 4.69 Å along the *b* axis, and the layer spacing between the rhombohedral grids is 8.06 Å. That **1** has a larger layer spacing between the rhombohedral grids than **2** is simply because the perchlorate group is larger than the nitrate group.

The amine group of the *L*<sub>2</sub> ligand and the coordinated oxygen atom of the nitrate group also form an “intramolecular” hydrogen bond with an N2–H22···O1 distance of 2.87(1) Å and an angle of 157(8)°. The N–H stretching frequency of 3273 cm<sup>−1</sup> is lower than those of secondary amines, supporting the formation of “intramolecular” hydrogen bond between the amine group of the *L*<sub>2</sub> ligand and the coordinated oxygen atom of the nitrate group. The dihedral angle between the 4-pyridyl and 2-pyridyl rings of *L*<sub>2</sub> in **2** is 87.2°. It is interesting to note that the rhombohedral grid structures of **1** and **2** are rather unusual. Most of the known 2D polymers adopt square grid structures because linear *exo*-bidentate ligands (e.g., 4,4′-bipyridine) have thus far been almost exclusively used to link the metal centers.



**Figure 5.** View of the Cd1–*L*<sub>2</sub>–Cd2 zigzag chains in the *ab* plane. The sulfate group and hydrogen atoms except H81 have been omitted. Cd atoms are shown as ellipsoids, while H, C, N, and O atoms are represented with open circles with increasing sizes. The hydrogen bonding between the 2-pyridyl group and coordinated water is also shown.

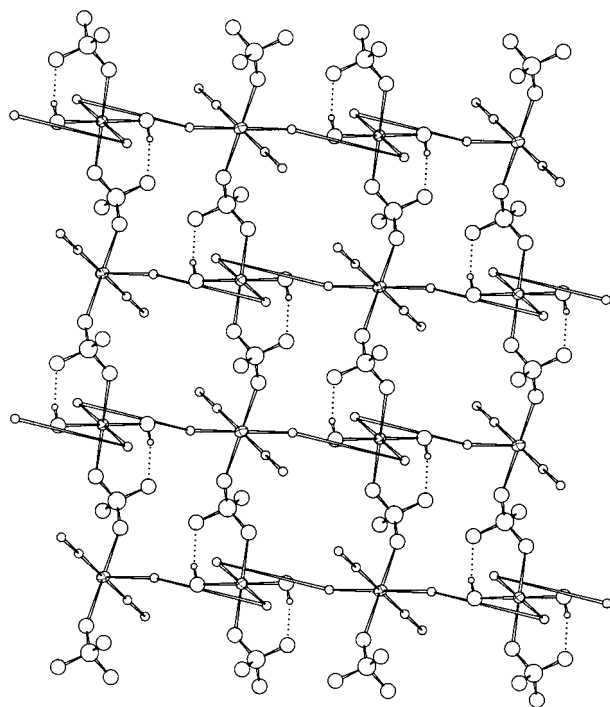
In combination with six-coordinate, octahedral metal centers or four-coordinate, square planar metal centers, square grid structures will be expected. It was previously reported that rhombohedral grid structures may be obtained when a nonlinear *exo*-bidentate ligand such as 1,2-bis(4-pyridyl)ethylene is used.<sup>16</sup> The combination of the flexible spacer in *L*<sub>2</sub> and the potential of forming “intramolecular” hydrogen bonds between the amine nitrogen and coordinated anion groups results in two highly bent pyridyl groups which may have directed the formation of the 2D rhombohedral grids in **1** and **2**. Residual volume analyses with PLATON indicate that no solvent-accessible voids exist in either **1** or **2**.<sup>17</sup>

**X-ray Single-Crystal Structure of 3.** The crystal structure of **3** is drastically different from those of **1** and **2**. The asymmetric unit of **3** contains two distinct Cd centers, a  $\mu_2$ -bridged sulfate group, a coordinated water molecule, and two *L*<sub>2</sub> ligands. Both Cd1 and Cd2 centers in the asymmetric unit lie on inversion centers, and have slightly distorted octahedral coordination geometry. The bond angles around the Cd1 center range from 85.2(2) to 94.8(2)°, while the bond angles around the Cd2 center range from 81.7(2) to 98.3(2)°. The Cd1 center coordinates to two 2-pyridyl nitrogen atoms of the *L*<sub>2</sub> ligands and two water molecules in the equatorial plane and to two  $\mu_2$ -bridged sulfate groups in the axial positions (Figure 4). The Cd2 center binds to four 4-pyridyl nitrogen atoms of the *L*<sub>2</sub> ligands in the basal plane and to two  $\mu_2$ -bridged sulfate groups in the axial positions (Figure 4). In each formula unit, two of the four 4-pyridyl nitrogen atoms of the *L*<sub>2</sub> ligands do not coordinate to metal centers; instead they form very strong hydrogen bonds with the water molecules coordinated to the Cd1 center (see below).

Each Cd1 center in **3** is linked to four adjacent Cd2 centers via two *L*<sub>2</sub> ligands and two sulfate groups. In the *ab* plane, Cd1

(16) Real, J. A.; Andrés, E.; Muñoz, M. C.; Julve, M.; Granier, T.; Bousseksou, A.; Varet, F. *Science* **1995**, 268, 265–2267.

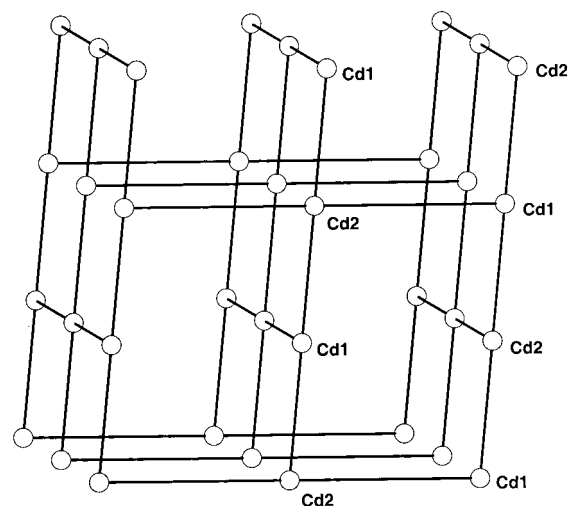
(17) Sluis, P. v. d.; Spek, A. L. *Acta Crystallogr.* **1990**, A46, 194.



**Figure 6.** Connection of Cd1–L<sub>2</sub>–Cd2 zigzag chains (running into the paper) by sulfate groups as projected down the *b* axis. The L<sub>2</sub> ligands are shown with two pyridyl nitrogen atoms linked by a straight line. Cd atoms are shown as ellipsoids, while H, N, O, and S atoms are represented with open circles with increasing sizes. The hydrogen bonding between the 2-sulfate group and coordinated water is also shown.

and Cd2 centers form zigzag chains bridged by L<sub>2</sub> ligands (Figure 5); all the Cd centers in the zigzag chain are collinear. The uncoordinated 2-pyridyl rings on the Cd1–L<sub>2</sub>–Cd2 chains form strong interchain  $\pi$ – $\pi$  stacks in the *ab* plane (Figure 5). The separation between each pair of uncoordinated 2-pyridyl rings is 4.06 Å. Additionally, the uncoordinated 2-pyridyl nitrogen atoms form very strong interchain hydrogen bonds with the coordinated water molecules (Figure 5). The O8–H81...N15 distance is 2.659(8) Å, while the O8–H81...N15 angle is 159(8) degrees. Through these  $\pi$ – $\pi$  stack and hydrogen bond interactions, the Cd1–L<sub>2</sub>–Cd2 zigzag chains in the *ab* plane are highly interdigitated. The dihedral angle between the 4-pyridyl and coordinated 2-pyridyl rings of the L<sub>2</sub> ligand is 79.28°, while the dihedral angle between the 4-pyridyl and uncoordinated 2-pyridyl rings of the L<sub>2</sub> ligand is 78.44°.

The Cd1–L<sub>2</sub>–Cd2 zigzag chains in the adjacent layers run along the [1 1 0] and  $[-1\ 1\ 0]$  directions, and orient with each other at 73.3°. They are connected to each other by the doubly bridged sulfate groups along the *c* axis. Adjacent layers of the Cd1–L<sub>2</sub>–Cd2 zigzag chains are displaced in such a way that the Cd1 centers are linked by the sulfate groups to two Cd2 centers in two immediately adjacent layers (Figure 6). Because of such a displacement of the zigzag chains, each Cd1–L<sub>2</sub>–Cd2 chain is linked to all the chains in the two adjacent layers by the sulfate groups to result in an unusual three-dimensional



**Figure 7.** Connectivity of **3** in three dimensions. Only Cd atoms are shown. The vertical chains are linked by sulfate groups and coincide with the *c* axis. All the other chains represent Cd1–L<sub>2</sub>–Cd2 zigzag chains.

coordination polymer (Figure 7). Finally, the hydrogen atom (H82) of the coordinated water molecule also forms a strong “intramolecular” hydrogen bond with one of the sulfate oxygen atoms (O5). The O8–H82...O5 distance and angle are 2.684(7) Å and 167(10)°, respectively (Figure 6). Residual volume analysis with PLATON indicates the absence of solvent-accessible voids in **3**.

## Conclusions

This work demonstrates that the bipyridine ligand *N,N*-(2-pyridyl)-(4-pyridylmethyl)amine (L<sub>2</sub>) with a flexible spacer and a noncoordinating amine group is capable of coordinating to metal centers with both pyridyl nitrogen atoms to result in novel 2D and 3D coordination polymers. Three 2D and 3D Cd coordination polymers based on L<sub>2</sub> have been synthesized and structurally characterized. The amine hydrogen atom has a tendency to form “intramolecular” hydrogen bonds with coordinated anions, and therefore becomes inaccessible for desired “intermolecular” hydrogen bonding interactions with potential guest molecules. Future work is directed toward increasing the distance of the amine nitrogen from the pyridyl nitrogen atom in order to prevent “intramolecular” hydrogen bonding interactions with coordinated anions.

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**Supporting Information Available:** Tables of fractional atomic coordinates and anisotropic displacement parameters and a figure for the asymmetric unit of **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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