

## New Open Frameworks Based on Metal Pyridylphosphonates

Ponnaiyan Ayyappan,<sup>†</sup> Owen R. Evans,<sup>†</sup> Bruce M. Foxman,<sup>‡</sup> Kraig A. Wheeler,<sup>§</sup> Timothy H. Warren,<sup>†</sup> and Wenbin Lin<sup>\*,†</sup>

Departments of Chemistry, Venable and Kenan Laboratories CB#3290, University of North Carolina, Chapel Hill, North Carolina 27599, Brandeis University, Waltham, Massachusetts 02454, Delaware State University, Dover, Delaware 19901, and Georgetown University, Washington, D.C. 20057

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A family of new 1D, 2D, and 3D coordination networks based on metal–pyridylphosphonates have been synthesized under hydro(solvo)thermal conditions. Zn(3-pyridylphosphonate)(bromide), **1**, adopts a 1D ladder structure, while Co(4-pyridylphosphonate)(H<sub>2</sub>O)<sub>3</sub>, **2**, adopts a 2D grid structure. [Cu<sub>2</sub>(4-pyridylphosphonate)<sub>2</sub>]·2H<sub>2</sub>O, **3**, [Cd(3-pyridylphosphonate)<sub>2</sub>]·DMSO, **4**, Cd(4-pyridylphosphonate)<sub>2</sub>, **5**, and Cd(ethyl 4-pyridylphosphonate)<sub>2</sub>, **6**, all adopt 3D framework structures. While **3** possesses open channels that are occupied by water molecules, **4** exhibits cavities that accommodate DMSO guest molecules. The present work demonstrates that interesting open frameworks can be readily synthesized on the basis of metal pyridylphosphonates. Crystal data for **1**: monoclinic space group *C2/c*; *a* = 15.267(4), *b* = 11.903(2), *c* = 10.380(2) Å;  $\beta$  = 98.68(2)°; *Z* = 8. Crystal data for **2**: monoclinic space group *P2<sub>1</sub>/c*; *a* = 9.634(12), *b* = 7.611(9), *c* = 11.901(1) Å;  $\beta$  = 97.830(2)°; *Z* = 4. Crystal data for **3**: triclinic spacegroup *P1̄*; *a* = 7.464(8), *b* = 9.203(1), *c* = 11.602(2) Å;  $\alpha$  = 100.289(1)°,  $\beta$  = 104.532(1)°,  $\gamma$  = 94.569(1)°; *Z* = 2. Crystal data for **4**: tetragonal space group *I4<sub>1</sub>/a*; *a* = 15.114(2), *b* = 15.114(2), *c* = 13.128(3) Å; *Z* = 8. Crystal data for **5**: monoclinic space group *P2<sub>1</sub>/c*; *a* = 8.344(2), *b* = 10.589(2), *c* = 14.384(3) Å;  $\beta$  = 91.77(3)°; *Z* = 4. Crystal data for **6**: monoclinic space group *P2<sub>1</sub>/n*; *a* = 5.606(1), *b* = 11.198(1), *c* = 14.176(2) Å;  $\beta$  = 94.518(1)°; *Z* = 2.

### Introduction

Metal–phosphonate chemistry has undergone a rapid growth over the past two decades owing to their perceived wide range of applications in catalysis,<sup>1–3</sup> molecular recognition,<sup>4</sup> ion exchanging,<sup>5</sup> and nonlinear optics.<sup>6,7</sup> Facile preparations at relatively low temperatures and high thermal and chemical stabilities make metal phosphonates an excellent candidate for supramolecular assembly of novel inorganic–organic hybrid materials.<sup>8,9</sup> Although earlier work was mostly focused on layered materials, recent metal phosphonate chemistry has afforded many 1D, 2D, and 3D coordination networks with interesting micropores and active catalytic sites.<sup>10–15</sup> In com-

parison to more labile metal–pyridine<sup>16–21</sup> and metal–carboxylate<sup>22</sup> linkages which have been extensively used to construct metal–organic coordination networks in recent years, metal phosphonates tend to produce microcrystalline materials and are thus more difficult to characterize. Despite this difficulty, Clearfield et al.<sup>8,23–28</sup> and Bujoli et al.<sup>29–32</sup> have synthesized and characterized many metal phosphonates with varying

\* Corresponding author. Email: wlin@unc.edu.

<sup>†</sup> University of North Carolina.

<sup>‡</sup> Brandeis University.

<sup>§</sup> Delaware State University.

<sup>||</sup> Georgetown University.

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dimensionality using a combination of single-crystal and powder X-ray diffraction techniques.

To design novel functional materials based on metal phosphonates, it is important to incorporate other functional groups into the frameworks. There have been several reports on the synthesis of hybrid metal phosphonates that contain carboxylate,<sup>12,33,34</sup> amino,<sup>35,36</sup> and even crown ether functionalities.<sup>4,37</sup> The incorporation of these groups also makes them more amenable to the growth of X-ray diffraction quality single-crystalline samples. Motivated by our recent success in the rational synthesis of NLO-active polar solids based on multi-functional ligands such as pyridinecarboxylates,<sup>38–44</sup> we have decided to explore the synthesis of metal–organic frameworks based on pyridylphosphonate bridging ligands. We report here the synthesis of two new pyridylphosphonic acids and their use in the construction of a family of new 1D, 2D, and 3D coordination networks based on metal–pyridylphosphonates under hydro(solvo)thermal conditions.

## Experimental Section

**Materials and Methods.** 4-Bromopyridine hydrochloride was purchased from TCA America, while all the other chemicals were purchased from Aldrich Chemical Co. They were used without further purification. *Caution: Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O are potentially explosive and should be used with care!* The IR spectra were recorded from KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Thermogravimetric analyses (TGA) were carried out under air on a Shimadzu TGA-50 instrument at a heating rate of 4 °C/min. <sup>1</sup>H and <sup>13</sup>C NMR spectra were taken on a Varian Unity-Plus 400 MHz spectrometer. Microanalyses were performed on crystalline samples by the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois at Urbana-Champaign.

**Synthesis of Diethyl 4-Pyridylphosphonate.** A mixture of 4-bromopyridine hydrochloride (4.0 g, 20.56 mmol) and diethyl phosphite (4.42 g, 32 mmol) in 80 mL of anhydrous toluene and 8 mL of triethylamine was refluxed in the presence of tetrakis(triphenylphosphine)palladium (600 mg, 0.5 mmol) under nitrogen atmosphere for 16 h. After cooling, the reaction mixture was washed three times with deionized water (30 mL), dried over MgSO<sub>4</sub>, and concentrated dry. Silica gel chromatography eluting with a mixture of chloroform and acetone (2:1, v/v) afforded 3.127 g of diethyl 4-pyridylphosphonate (71% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.7 (dd, 2H, <sup>3</sup>J<sub>H-H</sub> = 5.5 Hz, <sup>4</sup>J<sub>H-P</sub> = 5.5 Hz), 7.6 (dd, 2H, <sup>3</sup>J<sub>H-H</sub> = 5.5 Hz, <sup>3</sup>J<sub>H-P</sub> = 13.4 Hz), 4.1 (m, 4H, POCH<sub>2</sub>CH<sub>3</sub>), 1.3 (t, 6H, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz, POCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 43.8 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 150.3 (d, <sup>2</sup>J<sub>C-P</sub> = 12.2 Hz), 137.6 (d, <sup>1</sup>J<sub>C-P</sub> = 185.4 Hz), 125.4 (d, <sup>3</sup>J<sub>C-P</sub> = 7.6 Hz), 62.9 (d, <sup>2</sup>J<sub>C-P</sub> = 5.3 Hz, POCH<sub>2</sub>CH<sub>3</sub>), 16.5 (d, <sup>3</sup>J<sub>C-P</sub> = 6.1 Hz, POCH<sub>2</sub>CH<sub>3</sub>).

**Synthesis of Diethyl 3-Pyridylphosphonate.** A mixture of 3-bromopyridine (2.0 g, 12.65 mmol) and diethyl phosphite (2.3 g, 16 mmol) in 35 mL of anhydrous benzene and 4 mL of triethylamine was refluxed in the presence of tetrakis(triphenylphosphine)palladium (300 mg, 0.25 mmol) under nitrogen atmosphere for 16 h. After cooling, the reaction mixture was washed three times with deionized water (15 mL), dried over MgSO<sub>4</sub>, and concentrated dry. Silica gel chromatography eluting with a mixture of chloroform and acetone (2:1, v/v) afforded 1.61 g of diethyl 3-pyridylphosphonate (60% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.95 (dd, 1H, <sup>2</sup>J<sub>H-P</sub> = 5.5 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.22 Hz), 8.75 (ddd, 1H, <sup>3</sup>J<sub>H-H</sub> = 4.7 Hz, <sup>4</sup>J<sub>H-H</sub> = 2.3 Hz, <sup>5</sup>J<sub>H-P</sub> = 1.8 Hz), 8.08 (dddd, 1H, <sup>3</sup>J<sub>H-P</sub> = 7.9 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.8 Hz, <sup>3</sup>J<sub>H-H</sub> = 1.83, <sup>3</sup>J<sub>H-H</sub> = 13.4 Hz), 7.4 (ddd, 1H, <sup>3</sup>J<sub>H-H</sub> = 13.4 Hz, <sup>3</sup>J<sub>H-H</sub> = 4.7 Hz, <sup>4</sup>J<sub>H-P</sub> = 4.3 Hz), 4.1 (m, 4H, POCH<sub>2</sub>CH<sub>3</sub>), 1.33 (t, 6H, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz, POCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 60.0 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 153.1 (s), 152.3 (d, <sup>2</sup>J<sub>C-P</sub> = 12.2 Hz), 139.6 (d, <sup>3</sup>J<sub>C-P</sub> = 7.6 Hz), 137.3 (d, <sup>1</sup>J<sub>C-P</sub> = 185.0 Hz), 123.5 (d, <sup>2</sup>J<sub>C-P</sub> = 11.5 Hz), 62.6 (d, <sup>2</sup>J<sub>C-P</sub> = 6.1 Hz, POCH<sub>2</sub>CH<sub>3</sub>), 16.4 (d, <sup>3</sup>J<sub>C-P</sub> = 6.9 Hz, POCH<sub>2</sub>CH<sub>3</sub>).

**Synthesis of 4-Pyridylphosphonic Acid–Hydrogen Bromide, L1.** A mixture of diethyl 4-pyridylphosphonate (3.2 g, 15 mmol) and trimethylsilyl bromide (4.6 g, 30 mmol) in 25 mL of methylene chloride was stirred at room temperature for 16 h. The solvent was then removed under reduced pressure, and the residue was dissolved in 50 mL of methanol and stirred at room temperature for an additional 30 min. The methanol was then removed under reduced pressure to afford 3.579 g of L1 (98% yield). <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ 8.9 (ddd, 2H, <sup>3</sup>J<sub>H-H</sub> = 19.3 Hz, <sup>5</sup>J<sub>H-H</sub> = 6.7 Hz, <sup>4</sup>J<sub>H-P</sub> = 3.1 Hz), 8.3 (ddd, 2H, <sup>3</sup>J<sub>H-H</sub> = 13.5 Hz, <sup>5</sup>J<sub>H-H</sub> = 6.7 Hz, <sup>4</sup>J<sub>H-P</sub> = 6.7 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (D<sub>2</sub>O): δ 33.0 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (D<sub>2</sub>O): δ 156.2 (d, <sup>1</sup>J<sub>C-P</sub> = 162.5 Hz), 141.1 (d, <sup>2</sup>J<sub>C-P</sub> = 12.2 Hz), 128.1 (d, <sup>3</sup>J<sub>C-P</sub> = 8.4 Hz).

**Synthesis of 3-Pyridylphosphonic Acid–Hydrogen Bromide, L2.** A mixture of diethyl 3-pyridylphosphonate (2.01 g, 9.35 mmol) and trimethylsilyl bromide (3.06 g, 20 mmol) in 25 mL of methylene chloride was stirred at room temperature for 16 h. The solvent was then removed under reduced pressure, and the residue was dissolved in 50 mL of methanol and stirred at room temperature for an additional 30 min. The methanol was then removed under reduced pressure to afford 2.18 g of L2 (98% yield). <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ 9.1 (d, 1H, <sup>3</sup>J<sub>H-P</sub> = 8.5 Hz), 9.0 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 5.5 Hz), 8.9 (dd, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.9 Hz, <sup>3</sup>J<sub>H-P</sub> = 12.2 Hz), 8.2 (ddd, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.9 Hz, <sup>3</sup>J<sub>H-H</sub> = 6.1 Hz, <sup>4</sup>J<sub>H-P</sub> = 3.1 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>OD): δ 34.4 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (D<sub>2</sub>O): δ 148.6 (d, <sup>3</sup>J<sub>C-P</sub> = 6.1), 142.5 (s), 142.3 (d, <sup>2</sup>J<sub>C-P</sub> = 15.3), 136.3 (d, <sup>1</sup>J<sub>C-P</sub> = 176.2 Hz), 127.6 (d, <sup>3</sup>J<sub>C-P</sub> = 11.4 Hz).

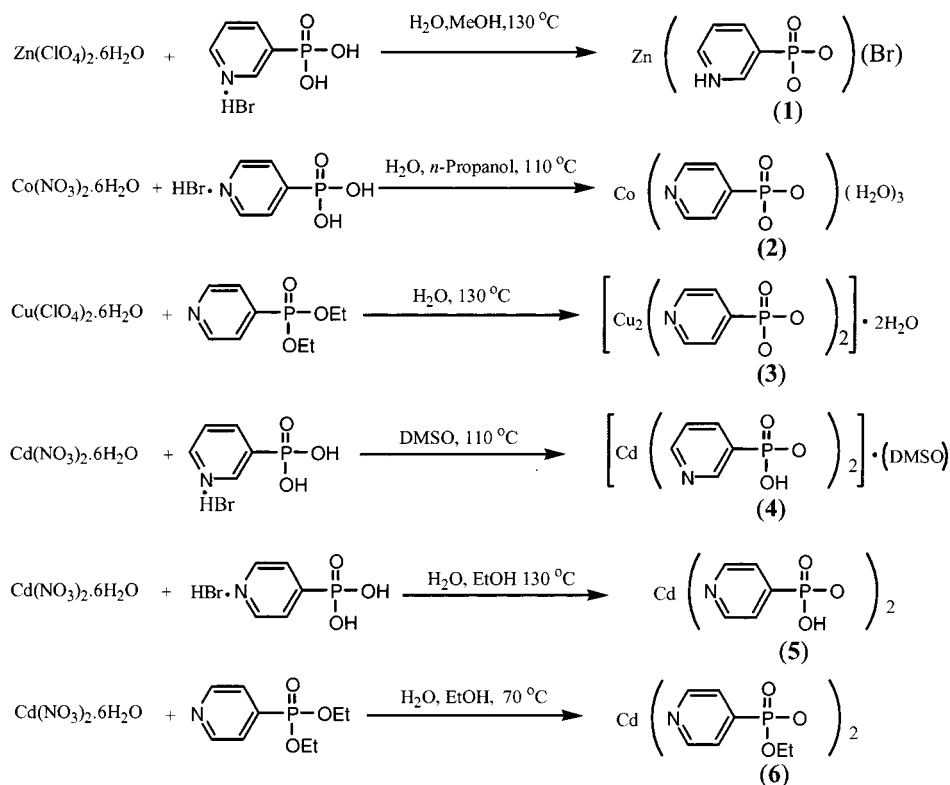
**Synthesis of Zn(3-pyridylphosphonate)(Br), 1.** A mixture of Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.0047 g, 0.0125 mmol) and L2 (0.0060 g, 0.025 mmol) was thoroughly mixed with methanol (0.6 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 130 °C. After 24 h of heating brown rod-shape single crystals were obtained. Yield: 0.0031 g (80.1%). Anal. Calcd for C<sub>5</sub>H<sub>3</sub>BrNO<sub>3</sub>PZn: C, 19.80; H, 1.66; N, 4.62. Found: C, 21.09; H, 1.88; N, 4.42. IR (KBr, cm<sup>-1</sup>): 3446 (w), 3059 (s), 2644 (w), 1628 (ms), 1618 (ms), 1457 (ms), 1349 (w), 1285 (w), 1263 (w), 1152 (s), 1104 (s), 1028 (s), 1063 (s), 998 (s), 870 (w), 806 (w), 728 (w), 712 (w), 680 (s), 600 (ms), 561 (s), 534 (w), 499 (w).

**Synthesis of Co(4-pyridylphosphonate)(H<sub>2</sub>O)<sub>3</sub>, 2.** A mixture of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.0072 g, 0.025 mmol) and L1 (0.0080 g, 0.05 mmol) was thoroughly mixed with *n*-propanol (0.4 mL) and water (0.4 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 110 °C. After 18 h of heating, pink rectangular single crystals were obtained. Yield: 0.0040 g (60.0%). Anal. Calcd for C<sub>5</sub>H<sub>10</sub>NO<sub>6</sub>PCo: C, 22.24; H, 3.73; N, 5.19. Found: C, 21.90; H, 3.59; N, 4.99. IR (KBr, cm<sup>-1</sup>): 3594 (ms), 2870 (w), 1956 (w), 1607 (s), 1413 (ms), 1317 (w), 1225 (w), 1145 (s), 1107 (s), 1058 (s), 985 (s), 818 (ms), 731 (w), 699 (w), 636 (w), 556 (s).

**Synthesis of [Cu<sub>2</sub>(4-pyridylphosphonate)<sub>2</sub>·2H<sub>2</sub>O], 3.** A mixture of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.0741 g, 0.2 mmol) and diethyl 4-pyridylphosphonate ester (0.0430 g, 0.2 mmol) was thoroughly mixed with water (0.4 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 130 °C. After 1 week of heating, greenish blue rod-shape single crystals were obtained. Yield: 0.0090 g (9.4%). Anal. Calcd for C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>Cu<sub>2</sub>: C, 25.15; H, 2.51;

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## Scheme 1

Table 1. Crystallographic Data for Compounds 1–6<sup>a</sup>

param	1	2	3	4	5	6
empirical formula	ZnBrPC <sub>5</sub> H <sub>5</sub> NO <sub>3</sub>	CoPC <sub>5</sub> H <sub>10</sub> NO <sub>6</sub>	Cu <sub>2</sub> P <sub>2</sub> C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O <sub>8</sub>	CdP <sub>2</sub> SC <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O <sub>7</sub>	CdP <sub>2</sub> C <sub>10</sub> H <sub>10</sub> N <sub>2</sub> O <sub>6</sub>	CdP <sub>2</sub> C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub>
fw	303.35	270.04	477.24	504.15	428.54	484.64
cryst system	monoclinic	monoclinic	triclinic	tetragonal	monoclinic	monoclinic
space group	<i>C2/c</i> (No. 15)	<i>P2<sub>1/c</sub></i> (No. 14)	<i>P1</i> (No. 2)	<i>I4<sub>1/a</sub></i> (No. 88)	<i>P2<sub>1/c</sub></i> (No. 14)	<i>P2<sub>1/n</sub></i> (No. 14)
<i>a</i> , Å	15.267(4)	9.6346(12)	7.4642(8)	15.114(2)	8.3444(17)	5.6057(4)
<i>b</i> , Å	11.903(2)	7.6113(9)	9.2033(10)	15.114(2)	10.589(2)	11.1980(8)
<i>c</i> , Å	10.380(2)	11.9014(14)	11.6017(15)	13.128(3)	14.384(3)	14.1758(11)
α, deg	90.00	90.00	100.289(12)	90.00	90.00	90.00
β, deg	98.68(2)	97.830(2)	104.532(12)	90.00	91.77(3)	94.5180(10)
γ, deg	90.00	90.00	94.569(12)	90.00	90.00	90.00
<i>V</i> , Å <sup>3</sup>	1864.6(8)	864.61(18)	752.57(15)	2998.8(8)	1270.4(4)	887.09(11)
<i>Z</i>	8	4	2	8	4	2
<i>T</i> , °C	25	100	25	25	25	75
λ(Mo Kα)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
ρ <sub>calc</sub> , g/cm <sup>3</sup>	2.161	2.075	2.106	2.233	2.241	1.814
μ, cm <sup>-1</sup>	70.57	21.74	30.83	18.53	20.01	14.44
R1	0.076	0.028	0.090	0.036	0.031	0.030
wR2	0.164	0.070	0.262	0.084	0.103	0.078
goodness of fit	1.03	1.06	1.13	1.06	1.32	0.621
min and max resid density, e/Å <sup>3</sup>	0.74, 2.36	0.42, 0.49	1.16, 2.60	0.72, 1.41	1.67, 1.01	0.56, 1.45

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}; GOF = [\sum [w(F_o^2 - F_c^2)^2] / (\text{no. of reflections} - \text{no. of parameters})]^{1/2}.$$

N, 5.87. Found: C, 24.39; H, 2.45; N, 5.64. IR (KBr, cm<sup>-1</sup>): 3420 (w), 3045 (w), 2980 (w), 2892 (w), 1640 (s), 1611 (s), 1421 (ms), 1387 (w), 1358 (w), 1317 (w), 1208 (s), 1154 (s), 1088 (w), 1065 (s), 960 (ms), 830 (ms), 762 (ms), 830 (ms), 782 (w), 782 (ms), 733 (w), 533 (s), 489 (ms).

**Synthesis of [Cd(3-pyridylphosphonate)<sub>2</sub>·DMSO], 4.** A mixture of Cd(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.075 g, 0.25 mmol) and L2 (0.119 g, 0.5 mmol) was thoroughly mixed with dimethyl sulfoxide (0.6 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 110 °C. After 24 h of heating yellow single crystals were obtained. Yield: 0.0742 g (60.0%). Anal. Calcd for C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O<sub>7</sub>P<sub>2</sub>SCd: C, 28.43; H, 3.16; N, 5.53. Found: C, 28.15; H, 2.75; N, 5.90. IR (KBr, cm<sup>-1</sup>): 3448 (s), 1654 (ms), 1560 (ms), 1247 (ms), 1165 (s), 1140 (s), 1031 (s), 921 (s), 807 (w), 744 (w), 707 (w), 648 (w), 560 (s), 498 (w).

**Synthesis of Cd(4-pyridylphosphonate)<sub>2</sub>, 5.** A mixture of Cd(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.0185 g, 0.060 mmol) and L1 (0.0287 g, 0.12 mmol) was thoroughly mixed with ethanol (0.8 mL) and deionized water (0.4 mL) in a heavy-walled Pyrex tube. The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 130 °C. After 24 h of heating, colorless rod-shaped single crystals were obtained. Yield: 0.0152 g (59.0%). Anal. Calcd for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>Cd: C, 28.01; H, 2.33; N, 6.53. Found: C, 27.72; H, 2.38; N, 6.40. IR (KBr, cm<sup>-1</sup>): 3450 (w), 2806 (w), 1605 (ms), 1413 (ms), 1383(w), 1220 (ms), 1171 (s), 1145 (s), 1097 (ms), 1070 (ms), 1035 (s), 1016 (s), 946 (s), 819 (ms), 730 (w), 563 (s), 539 (s), 486 (ms).

**Synthesis of Cd(ethyl 4-pyridylphosphonate)<sub>2</sub>, 6.** A mixture of Cd(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.0750 g, 0.50 mmol) and diethyl 4-pyridinephosphonate ester (0.0800 g, 0.50 mmol) was thoroughly mixed with ethanol (0.4 mL) and deionized water (0.1 mL) in a heavy-walled Pyrex tube.

**Table 2.** Selected Bond Distances (Å) and Bond Angles (deg) for **1–3**

<b>1<sup>a</sup></b>		<b>2<sup>b</sup></b>		<b>3<sup>c</sup></b>	
Zn1–O2B	1.924(7)	Co1–O5A	2.015(2)	Cu1–O1	1.954(8)
Zn1–O1A	1.952(7)	Co1–O2	2.045(2)	Cu1–O5B	1.959(8)
Zn1–O3	1.966(8)	Co1–O1	2.137(2)	Cu1–N1A	1.990(8)
Zn1–Br1	2.362(2)	Co1–N1	2.137(2)	Cu1–O4	1.990(9)
P1–O1	1.508(9)	Co1–O6B	2.190(2)	Cu2–O2C	1.920(8)
P1–O3	1.510(7)	Co1–O3	2.227(2)	Cu2–O3	1.957(8)
P1–O2	1.521(8)	P1–O5	1.518(2)	Cu2–N2D	2.010(10)
P1–C1	1.84(2)	P1–O4	1.528(2)	Cu2–O6B	2.010(9)
O2B–Zn1–O1A	110.8(3)	P1–O6	1.539(2)	P1–O2	1.520(8)
O2B–Zn1–O3	109.2(3)	P1–C1	1.819(2)	P1–O1	1.526(8)
O1A–Zn1–O3	105.4(3)	O5A–Co1–O2	177.80(6)	P1–O3	1.534(9)
O2B–Zn1–Br1	108.0(2)	O5A–Co1–O1	82.39(6)	P1–C1	1.809(11)
O1A–Zn1–Br1	117.4(2)	O2–Co1–O1	95.59(6)	P2–O5	1.522(8)
O3–Zn1–Br1	105.7(2)	O5A–Co1–N1	94.88(7)	P2–O4	1.523(8)
O1–P1–O3	110.7(5)	O2–Co1–N1	86.03(7)	P2–O6	1.528(9)
O1–P1–O2	113.1(5)	O1–Co1–N1	91.74(7)	P2–C6	1.819(12)
O3–P1–O2	114.7(5)	O5A–Co1–O6B	92.86(6)	O1–Cu1–O5B	86.6(3)
O1–P1–C1	106.9(5)	O2–Co1–O6B	86.23(6)	O1–Cu1–N1A	90.0(3)
O3–P1–C1	105.4(5)	O1–Co1–O6B	89.19(6)	O5B–Cu1–N1A	165.0(3)
O2–P1–C1	105.3(5)	N1–Co1–O6B	172.26(6)	O1–Cu1–O4	167.7(4)
		O5–Co1–O3	91.40(6)	O5B–Cu1–O4	92.1(4)
		O2–Co1–O3	90.59(6)	N1A–Cu1–O4	94.3(4)
		O1–Co1–O3	173.46(6)	O2C–Cu2–O3	92.5(3)
		N1–Co1–O3	90.82(7)	O2C–Cu2–N2D	90.9(4)
		O6B–Co1–O3	89.07(6)	O3–Cu2–N2D	164.4(4)
		O5–P1–O4	112.89(9)	O2C–Cu2–O6B	147.0(4)
		O5–P1–O6	112.97(8)	O3–Cu2–O6B	95.8(3)
		O4–P1–O6	111.86(8)	N2D–Cu2–O6B	89.5(4)
		O5–P1–C1	105.48(9)	O2–P1–O1	113.5(5)
		O4–P1–C1	105.23(9)	O2–P1–O3	112.0(5)
		O6–P1–C1	107.75(9)	O1–P1–O3	113.7(5)
				O2–P1–C1	103.7(5)
				O1–P1–C1	106.2(5)
				O3–P1–C1	106.7(5)
				O5–P2–O4	117.6(5)
				O5–P2–O6	110.1(5)
				O4–P2–O6	111.4(5)
				O5–P2–C6	104.0(5)
				O4–P2–C6	106.4(5)

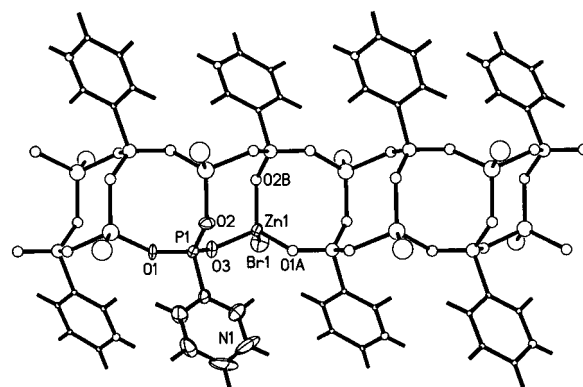
<sup>a</sup> Symmetry transformations: A =  $x, 1 - y, 0.5 + z$ ; B =  $1 - x, 1 - y, 1 - z$ . <sup>b</sup> Symmetry transformations: A =  $-x, 0.5 + y, 0.5 - z$ ; B =  $1 + x, y, z$ . <sup>c</sup> Symmetry transformations: A =  $x, 1 + y, z$ ; B =  $-x, -y, 1 - z$ ; C =  $1 - x, -y, 1 - z$ , D =  $x, y, -1 + z$ .

The tube was frozen under liquid nitrogen, sealed, and placed inside an oven at 60 °C for 12 h and then moved to an oven at 70 °C. After an additional 3 h of heating, colorless rod-shaped single crystals were obtained. Yield: 0.0723 g (61.0%). Anal. Calcd for  $C_{14}H_{18}N_2O_6P_2Cd$ : C, 34.69; H, 3.74; N, 5.78. Found: C, 34.28; H, 3.64; N, 5.69. IR (KBr,  $cm^{-1}$ ): 3407 (w), 2985 (w), 2938 (w), 2808 (w), 1601 (ms), 1414 (ms), 1228 (s), 1148 (ms), 1107 (ms), 1089 (s), 1070 (ms), 1044 (s), 1009 (w), 953 (s), 829 (ms), 789 (s), 748 (w), 724 (w), 662 (w), 560 (s), 540 (s), 484 (w), 464 (w).

**X-ray Collection and Structure Determinations.** Data collection for **1** and **3–5** was carried out with Siemens P4 (**1** and **3**) and Enraf-Nonius CAD4-Turbo (**4** and **5**) diffractometers equipped with Mo  $K\alpha$  radiation, while data collection for **2** and **6** was performed using a Siemens SMART system equipped with a CCD detector using Mo  $K\alpha$  radiation. The structures were solved by direct methods using SHELX-TL<sup>45</sup> and refined on  $F^2$  by full-matrix least squares using anisotropic displacement parameters for all framework non-hydrogen atoms. The water guest molecules in **3** and disordered DMSO molecules in **4** were refined using isotropic displacement parameters. Experimental details for X-ray data collection of **1–6** are presented in Table 1, while selected bond distances and angles for **1–6** are listed in Tables 2 and 3.

## Results and Discussion

**Synthesis and Characterization.** Compound **1** was obtained in 80.1% yield by a hydro(solvo)thermal reaction between Zn-



**Figure 1.** View of 1D ladders of **1**. The asymmetric unit is shown with ellipsoids at 50% probability.

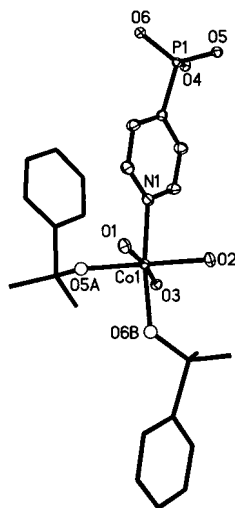
( $ClO_4$ )<sub>2</sub>·6H<sub>2</sub>O and **L2** in methanol at 130 °C (Scheme 1). The polymeric network of **1** was established by a single-crystal X-ray diffraction study. TGA shows no weight loss up to 400 °C, which clearly indicates that there is no included solvent molecules in **1**. Compound **2** was obtained in 60.0% yield by reacting  $Co(NO_3)_2 \cdot 6H_2O$  and **L1** in *n*-propanol and water at 110 °C. TGA shows a weight loss of 20.0% in the 100–150 °C range, consistent with the loss of three water molecules/formula unit (expected 19.9%). Compound **3** was obtained in 9.4% yield by a hydro(solvo)thermal reaction between

(45) SHELX-TL Version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

**Table 3.** Selected Bond Distances (Å) and Bond Angles (deg) for **4–6**

4 <sup>a</sup>		5 <sup>b</sup>		6 <sup>c</sup>	
Cd1–O1A	2.284(2)	Cd1–O5D	2.255(2)	Cd1–O1	2.259(2)
Cd1–N1	2.313(3)	Cd1–O2B	2.265(2)	Cd1–O3B	2.296(2)
Cd1–O2B	2.393(3)	Cd1–N1	2.306(2)	Cd1–N–1D	2.360(3)
P1–O1	1.494(3)	Cd1–N2	2.327(2)	P1–O1	1.492(3)
P1–O2	1.507(3)	Cd1–O4C	2.377(2)	P1–O3	1.494(3)
P1–O3	1.578(3)	Cd1–O1A	2.413(2)	P1–O2	1.604(3)
P1–C1	1.809(4)	P1–O2	1.498(2)	P1–C1	1.813(4)
O1A–Cd1–O1E	180.0(2)	P1–O1	1.507(2)	O1–Cd1–O3B	91.6(1)
O1A–Cd1–N1	94.1(1)	P1–O3	1.576(2)	O1–Cd1–O3C	88.4(1)
O1E–Cd1–N1	85.9(1)	P1–C3	1.809(2)	O1–Cd1–N1D	90.7(1)
N1–Cd1–N1D	180.0(2)	P2–O5	1.485(2)	O1–Cd1–N1E	89.3(1)
O1A–Cd1–O2B	92.71(9)	P2–O4	1.516(2)	O3B–Cd1–N1D	85.8(1)
O1E–Cd1–O2B	87.29(9)	P2–O6	1.571(2)	O3B–Cd1–N1E	94.2(1)
N1–Cd1–O2B	95.0(1)	P2–C8	1.812(2)	O1–P1–O3	119.8(2)
N1–Cd1–O2C	85.0(1)	O5D–Cd1–O2B	91.28(6)	O1–P1–O2	105.1(2)
O1–P1–O2	117.1(2)	O5D–Cd1–N1	87.63(7)	O3–P1–O2	111.7(2)
O1–P1–O3	110.4(2)	O2B–Cd1–N1	93.51(7)	O1–P1–C1	108.1(2)
O2–P1–O3	107.5(2)	O5D–Cd1–N2	96.03(7)	O3–P1–C1	107.9(2)
O1–P1–C1	110.2(2)	O2B–Cd1–N2	87.54(7)	O2–P1–C1	102.9(2)
O2–P1–C1	106.8(2)	N1–Cd1–N2	176.18(6)		
O3–P1–C1	104.1(2)	O5D–Cd1–O4C	81.59(6)		
		O2B–Cd1–O4C	170.82(6)		
		N1–Cd1–O4C	91.96(7)		
		N2–Cd1–O4C	87.48(6)		
		O5D–Cd1–O1A	169.41(6)		
		O2B–Cd1–O1A	98.27(6)		
		N1–Cd1–O1A	87.25(7)		
		N2–Cd1–O1A	88.97(7)		
		O4CCd1O1A	89.33(6)		
		O2–P1–O1	114.2(1)		
		O2–P1–O3	112.9(1)		
		O1–P1–O3	107.9(1)		
		O2–P1–C3	105.8(1)		
		O1–P1–C3	109.9(1)		
		O3–P1–C3	105.8(1)		
		O5–P2–O4	115.9(1)		
		O5–P2–O6	108.4(1)		
		O4–P2–O6	109.93(9)		
		O5–P2–C8	109.8(1)		
		O4–P2–C8	106.1(1)		
		O6–P2–C8	106.4(1)		

<sup>a</sup> Symmetry transformations: A = 1 - x, 1 - y, 1 - z; B = 0.25 + y, 1.25 - x, 0.25 + z; C = 0.75 - y, -0.25 + x, 0.75 - z; D = 1 - x, 0.5 - y, z; E = x, 0.5 + y, 1 - z. <sup>b</sup> Symmetry transformations: A = 1 + x, 1 + y, 1 + z; B = x, 0.5 - y, -0.5 + z; C = x, 1.5 - y, 0.5 - z; D = -x, 1 - y, -z. <sup>c</sup> Symmetry transformations: A = -2 - x, 2 - y, 2 - z; B = -1 - x, y, z; C = -1 - x, 2 - y, 2 - z; D = 1.5 - x, 0.5 + y, 1.5 - z; E = -0.5 + x, 1.5 - y, 0.5 + z.

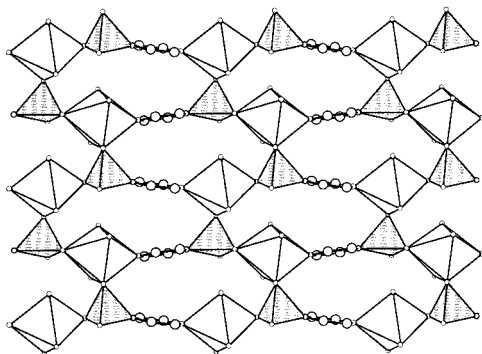
**Figure 2.** Coordination environment of **2**. The asymmetric unit is shown with ellipsoids at 50% probability.

$\text{Cu}(\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$  and diethyl 4-pyridylphosphonate ester in water at 130 °C. TGA shows a weight loss of 8.8% in the 50–

80 °C range, indicating the presence of two water guest molecules in **3**. Compound **4** was obtained in 60.0% yield by reacting  $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and **L2** in dimethyl sulfoxide at 130 °C. TGA shows a weight loss of 14.0% in the 280–360 °C range, which corresponds to 1 DMSO molecule/formula unit (calcd 15.4%). Compound **5** was obtained in 59.0% yield by reacting  $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and **L1** in a mixture of ethanol and water at 130 °C, while **6** was obtained in 61.0% yield by reacting  $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and ethyl 4-pyridylphosphonate ester in a mixture of ethanol and water at 60 °C. TGA indicates the absence of solvent molecules in both **5** and **6**.

The IR spectra of **1–6** show asymmetric and symmetric stretching vibrations at 3610 and 3540  $\text{cm}^{-1}$  corresponding to the P–OH stretching vibrations.<sup>46</sup> The IR spectra also exhibit the corresponding deformation band near 1605  $\text{cm}^{-1}$ . There are several bands between 1250 and 950  $\text{cm}^{-1}$  that correspond to the characteristic stretching modes of the  $\text{PO}_3$  groups. The IR spectra of these compounds also show the characteristic C–C and C–N pyridine ring stretching frequencies in the 1620–

(46) Corbridge, D. E. C. *Phosphorus: An outline of its chemistry, Biochemistry and Technology*, 4th ed.; Elsevier Scientific Publishing Co: Amsterdam, 1990.



**Figure 3.** View of 2D gridlike network of **2** down the *c* axis. The 1D sinusoidal chain with alternate corner-sharing  $\text{CoO}_5\text{N}$  octahedra and  $\text{PO}_3\text{C}$  tetrahedra is running along the *b* axis.

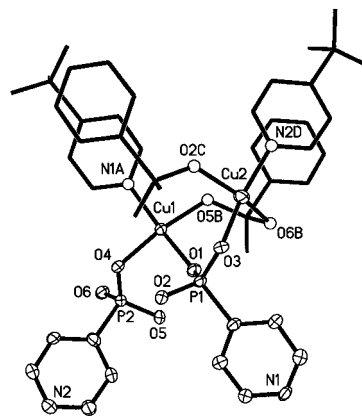
1595 and 1460–1410  $\text{cm}^{-1}$  ranges for the pyridyl groups. The formulations of **1–6** are supported by elemental analyses.

**X-ray Structure of Zn(3-pyridylphosphonate)(bromide), 1.** The polymeric structure of **1** was confirmed by an X-ray single-crystal structural determination. Compound **1** crystallizes in the monoclinic space group  $C2/c$ . The asymmetric unit of **1** consists of one zinc center, one 3-pyridylphosphonate group, and one bromide (Figure 1). The pyridylphosphonate ligand possesses a  $\mu_3, \eta^3$ -phosphonate group with the pyridyl group protonated and thus noncoordinating. Each zinc center is thus coordinated to three oxygen atoms from three different  $\mu_3, \eta^3$ -phosphonate units and a bromide ion to adopt a distorted tetrahedral coordination environment. The Zn–O distance varies from 1.92(7) to 1.97(8) Å, while the Zn–Br distance is 2.36(6) Å. The bond angles around the Zn center range from 105.3(3) to 117.4(2) °C.

Each zinc center is doubly bridged to another zinc center via two pyridylphosphonate oxygen atoms to form 1D ladders of  $\text{Zn}_2(3\text{-pyridylphosphonate})_2\text{Br}_2$  along the *b* axis (Figure 1). The coordination of terminal bromide ions to the Zn centers and noncoordination of 3-pyridyl groups have limited the dimensionality of **1**. As a consequence, no solvent molecules are included in **1**. Interestingly, the 3-pyridyl rings from the adjacent 1D ladders form a highly interdigitated structure via the  $\pi$ – $\pi$  stacking interactions with a centroid-to-centroid distance of 3.596 Å.

**X-ray Structure of Co(4-pyridylphosphonate)(H<sub>2</sub>O)<sub>3</sub>, 2.** Compound **2** crystallizes in the monoclinic space group  $P2_1/c$ . The asymmetric unit of **2** consists of one cobalt atom, one 4-pyridylphosphonate group, and three water molecules (Figure 2). The 4-pyridylphosphonate ligand adopts an exo-tridentate linkage with a  $\mu_2, \eta^2$ -phosphonate bridge and a coordinating pyridyl group. Each Co atom is coordinated to three water molecules and to two phosphonate oxygen atoms and a pyridyl nitrogen atom from three different 4-pyridylphosphonate ligands. The Co center has a slightly distorted octahedral geometry with the bond distances ranging from 2.015(1) to 2.227(1) Å and bond angles ranging from 82.4(1) to 95.59(0)°.

The Co centers in **2** are connected via phosphonate oxygen atoms to form a 1D sinusoidal chain with alternate corner-sharing  $\text{CoO}_5\text{N}$  octahedra and  $\text{PO}_3\text{C}$  tetrahedra along the *b* axis (Figure 3). These 1D sinusoidal chains are further connected to adjacent chains via the coordination of the 4-pyridyl nitrogen atoms along the *a* axis to form a 2D gridlike network lying in the *ab* plane (Figure 3). The centroid-to-centroid distance between adjacent 4-pyridyl rings is 3.927 Å. The noncoordinating phosphonate oxygen (O4) atom forms two sets of intralayer hydrogen bonding interactions with coordinated water



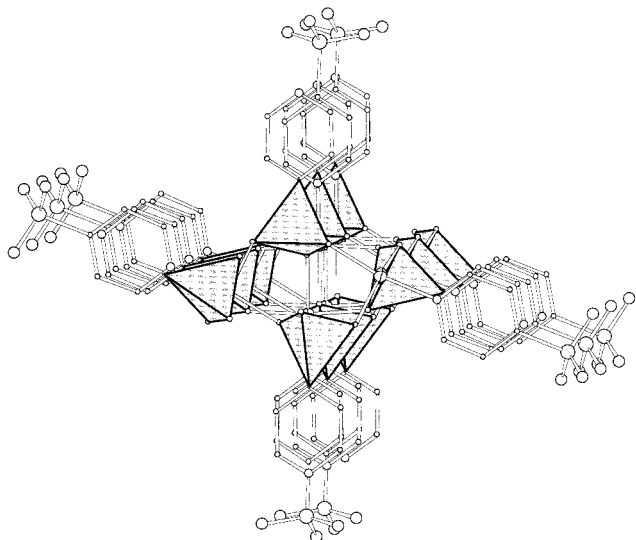
**Figure 4.** Coordination environment of **3**. The asymmetric unit is shown with ellipsoids at 50% probability.

molecules (O1 and O3). The O1···O4 distance is 2.741(0) Å, while the O1–H1B···O4 angle is 172.06(0)°. The O3···O4 distance is 2.681(1) Å, while the O3–H3A···O4 angle is 162.41(1)°. O4 also forms an interlayer hydrogen bond to the other coordinated water molecule (O2) with the O2···O4 distance of 2.683(0) Å and the O2–H2A···O4 angle of 167.66(1)°. In addition, the coordinated water molecules from adjacent layers also form a hydrogen bond with the O1···O3 distance of 2.864(2) Å and the O1–H1A···O3 angle of 169.24(1)°. The 2D coordination networks shown in Figure 3 are thus further linked to adjacent grids via interlayer hydrogen bonds to form a 3D network structure.

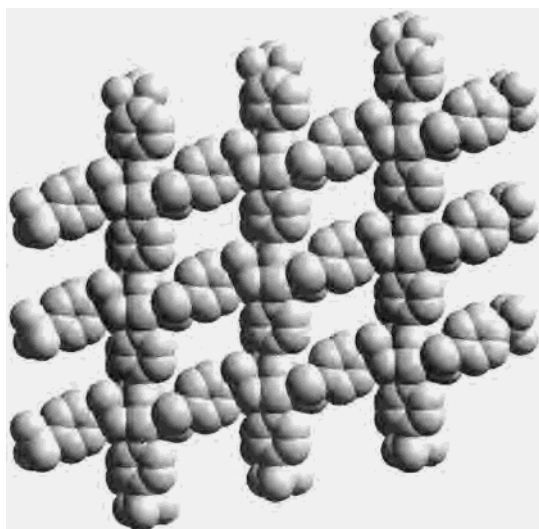
**X-ray Structure of [Cu<sub>2</sub>(4-pyridylphosphonate)<sub>2</sub>·2H<sub>2</sub>O], 3.** Compound **3** crystallizes in the triclinic space group  $P\bar{1}$ . The asymmetric unit of **3** consists of two copper centers, two 4-pyridylphosphonate groups, and two water molecules (Figure 4). Both pyridylphosphonate groups have an exo-tetradentate linkage with a coordinating pyridyl group and a  $\mu_3, \eta^3$ -phosphonate bridge. Each copper center is coordinated to three phosphonate oxygen atoms and a pyridyl nitrogen atom of four different pyridylphosphonate groups in a slightly distorted square planar arrangement. The Cu–O and Cu–N bond distances are normal while the angles around the Cu atom range from 86.6(3) to 95.8(3)°.

The Cu centers in **3** link triple corner-sharing  $\text{PO}_3\text{C}$  tetrahedra to form 1D zigzag chains along the *a* axis (Figure 5). Such 1D chains are further linked to four adjacent 1D chains via the 4-pyridylphosphonate bridging ligands to form a complex 3D coordination network with rectangular channels of dimension 4.2 × 4.7 Å along the *a* axis (Figure 6). The void space within each unit cell measures 141.2 Å<sup>3</sup>, which corresponds to 18.7% of the total unit cell volume, and is occupied by removable water guest molecules. Compound **3** thus represents a new type of metal phosphonate open-framework structure.

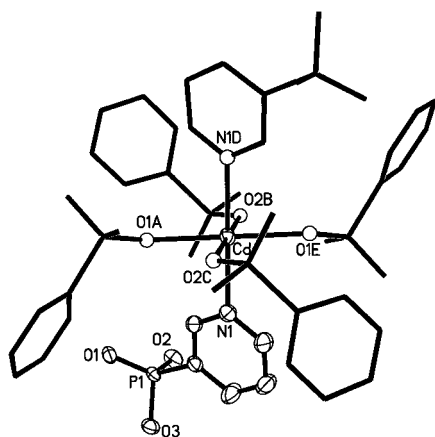
**X-ray Structure of [Cd(3-pyridylphosphonate)<sub>2</sub>·DMSO], 4.** Compound **4** crystallizes in the tetragonal space group  $I4_1/a$ . The asymmetric unit of **4** consists of one cadmium center and one 3-pyridylphosphonate group and a disordered DMSO molecule (Figure 7). The Cd1 center lies on a  $\bar{4}$  axis. The 3-pyridylphosphonate ligand adopts an exo-tridentate linkage with a coordinating pyridyl nitrogen atom and a  $\mu_2, \eta^2$ -phosphonate bridge. The Cd1 center adopts a slightly distorted octahedral geometry by coordinating to four phosphonate oxygen atoms in the equatorial positions and to two 3-pyridyl nitrogen atoms in the apical positions. These phosphonate oxygen and 3-pyridyl nitrogen atoms come from six different 3-pyridylphosphonate bridging ligands.



**Figure 5.** View of 1D zigzag chains formed by the Cu centers and triple corner-sharing  $\text{PO}_3\text{C}$  tetrahedra in **3** slightly off the  $a$  axis.

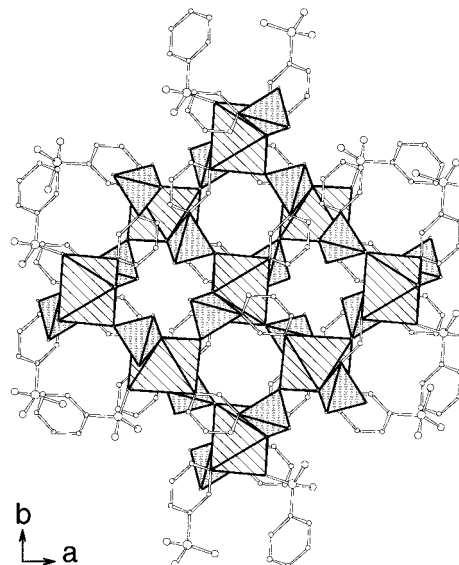


**Figure 6.** Space filling model of **3** as viewed down the  $a$  axis. Rectangular channels are occupied by water molecules which have been omitted for clarity.

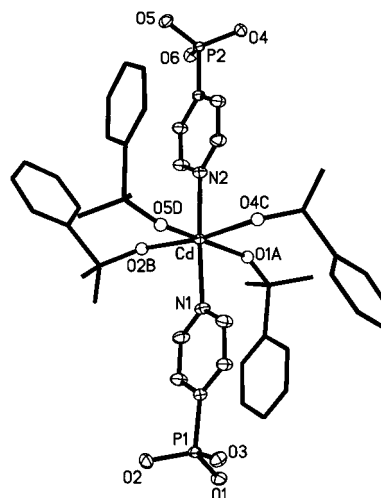


**Figure 7.** Coordination environment of **4**. The asymmetric unit is shown with ellipsoids at 50% probability.

Each Cd center is connected via six bridging 3-pyridylphosphonate ligands (four corner-sharing  $\text{PO}_3\text{C}$  tetrahedra and two pyridyl groups) to six adjacent Cd centers to form a complex 3D coordination network (Figure 8a). Spherical cavities with a



**Figure 8.** View of 3D coordination network of **4** down the  $c$  axis. Each Cd center is connected via six bridging 3-pyridylphosphonate ligands to six adjacent Cd centers.

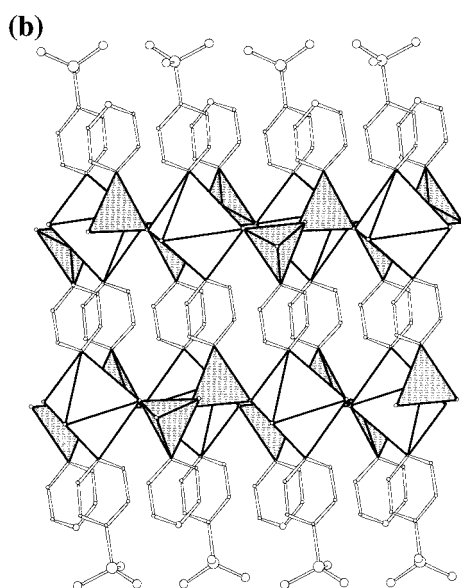
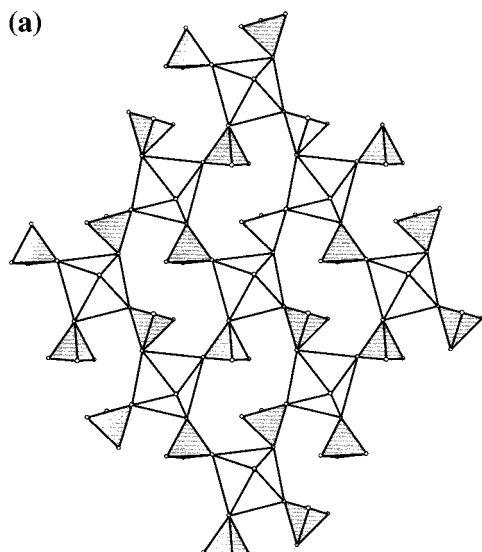


**Figure 9.** Coordination environment of **5**. The asymmetric unit is shown with ellipsoids at 50% probability.

small opening are formed with the 3D network and are occupied by disordered DMSO molecules (Figure 8b). The presence of DMSO molecules in **4** has been independently confirmed by  $^1\text{H}$  NMR studies and TGA analysis.

**X-ray Structure of  $\text{Cd}(\text{4-pyridylphosphonate})_2$ , **5**.** Compound **5** crystallizes in the monoclinic space group  $P2_1/c$  with all the atoms lying in general positions. The asymmetric unit of **5** consists of one cadmium center and two 4-pyridylphosphonate groups (Figure 9). The 4-pyridylphosphonate ligand adopts an exo-tridentate linkage with a coordinating pyridyl nitrogen atom and a  $\mu_2, \eta^2$ -phosphonate bridge. The Cd1 center adopts a slightly distorted octahedral geometry by coordinating to four phosphonate oxygen atoms in the equatorial positions and to two 4-pyridyl nitrogen atoms in the axial positions.

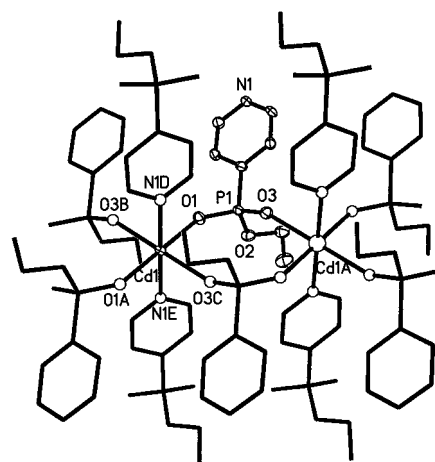
Each  $\text{CdO}_4\text{N}_2$  octahedron is connected to four adjacent  $\text{CdO}_4\text{N}_2$  octahedra via four corner-sharing  $\text{PO}_3\text{C}$  tetrahedra to form a 2D network in the  $ab$  plane (Figure 10a). Such 2D networks are further linked via the 4-pyridyl pillars to form an interesting 3D pillared coordination network (Figure 10b). There are significant  $\pi$ - $\pi$  stacking interactions among these pyridyl pillars with centroid-to-centroid distances of 3.527 and 3.593 Å between pyridyl rings.



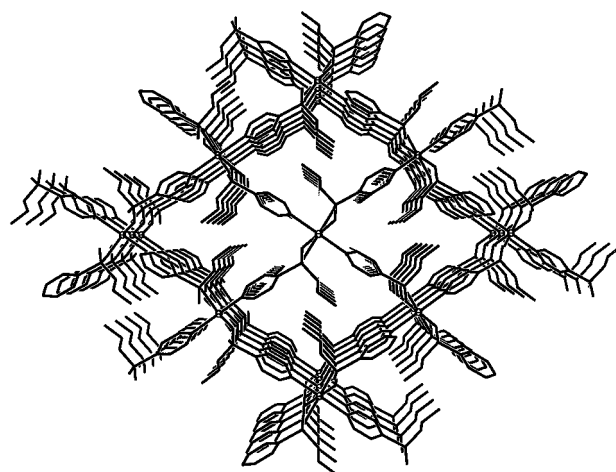
**Figure 10.** (a) 2D network of **5** in the *ab* plane formed by corner-sharing  $\text{CdO}_4\text{N}_2$  octahedra and  $\text{PO}_3\text{C}$  tetrahedra. (b) Linking of the above 2D networks by 4-pyridyl groups to form a regular 3D pillared coordination network as viewed down the *a* axis.

**X-ray Structure of  $\text{Cd}(\text{ethyl 4-pyridylphosphonate})_2$ , **6**.** Compound **6** crystallizes in the monoclinic space group  $P2_1/n$ . The asymmetric unit of **6** consists of one cadmium center and one ethyl 4-pyridylphosphonate group (Figure 11). The pyridylphosphonate ligand adopts an exo-tridentate linkage with a coordinating pyridyl nitrogen atom and a  $\mu_2, \eta^2$ -phosphonate bridge. The Cd center adopts a slightly distorted octahedral geometry by coordinating to four oxygen atoms equatorially and to two pyridyl nitrogen atoms axially.

Compound **6** has the same network topology as the 3D coordination polymer bis(isonicotinato)iron(II), which was reported by us recently.<sup>47</sup> Each cadmium atom is connected to four different cadmium centers through four different pyridylphosphonate moieties. First, Cd centers are doubly bridged by phosphonate oxygen atoms to form infinite Cd–Cd chains along the *a* axis. These 1D doubly phosphonate-bridged Cd–Cd chains are linked by the 4-pyridyl rings to four adjacent Cd–Cd chains to form a highly regular 3D coordination network



**Figure 11.** Coordination environment of **6**. The asymmetric unit is shown with ellipsoids at 50% probability.



**Figure 12.** Perspective view of 3D network in **6** slightly off the *a* axis.

(Figure 12). The ethoxy groups of the phosphonate esters have effectively filled the void space generated within the 3D network, and there thus exists no cavity that is accessible to solvent molecules.

In summary, we have designed two new pyridylphosphonic acid ligands and successfully shown their potential in the construction of a family of new metal phosphonate coordination networks with 1D, 2D, and 3D structures. Among the six metal pyridylphosphonate coordination networks, compounds **3** and **4** have interesting open-framework structures and clearly demonstrate the utility of rigid pyridylphosphonate ligands as new building blocks for porous solids. We are currently designing longer pyridylphosphonate building blocks to synthesize open frameworks with larger pores.

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**Supporting Information Available:** Seven figures and X-ray crystallographic files in CIF format for the structures of **1–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(47) Xiong, R. G.; Wilson, S. R.; Lin, W. J. *Chem. Soc., Dalton Trans.* **1998**, 4089.