

# Metal Phosphonates Based on {[(Benzimidazol-2-ylmethyl)imino]bis(methylene)}bis(phosphonic Acid): Syntheses, Structures and Magnetic Properties of the Chain Compounds $[M\{(C_7H_5N_2)CH_2N(CH_2PO_3H)_2\}]$ ( $M = Mn, Fe, Co, Cu, Cd$ )

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**Keywords:** Chain structures / Magnetic properties / N,O ligands / Organic–inorganic hybrid composites / Transition metals

Five compounds based on {[(benzimidazol-2-ylmethyl)imino]bis(methylene)}bis(phosphonic acid)  $[(C_7H_5N_2)CH_2N(CH_2PO_3H)_2]$  [ $M = Mn$  (**1**),  $Fe$  (**2**),  $Co$  (**3**),  $Cu$  (**4**),  $Cd$  (**5**)] have been synthesized under hydrothermal conditions. These compounds are isostructural, crystallizing in the orthorhombic space group *Pbca*, with  $a = 15.331(2)$ ,  $b = 10.7150(16)$ , and  $c = 16.715(2)$  Å for **1**;  $a = 15.320(3)$ ,  $b = 10.477(2)$ , and  $c = 16.764(3)$  Å for **2**;  $a = 15.207(2)$ ,  $b = 10.4626(16)$ , and  $c = 16.794(3)$  Å for **3**;  $a = 15.101(3)$ ,  $b = 10.3517(17)$ , and  $c = 16.997(3)$  Å for **4**; and  $a = 15.4679(19)$ ,  $b = 10.8923(13)$ , and  $c = 16.6175(19)$  for **5**. Each

compound shows a one-dimensional chain structure where  $\{MO_3N_2\}$  trigonal bipyramids are connected by  $\{CPO_3\}$  tetrahedra through corner-sharing. The chains are further connected to each other through aromatic stacking of the benzimidazole rings and extensive hydrogen bonds, forming a supramolecular 3D structure. Magnetic susceptibility studies of **1–4** reveal that weak antiferromagnetic interactions occur between the metal centers.

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## Introduction

Increasing attention has been paid in recent years to metal phosphonate materials due to their potential applications in catalysis, nonlinear optics, magnetism, and biotechnology etc.<sup>[1]</sup> Meanwhile, the rapid development in the rational design and synthesis of coordination polymers, by using different organic ligands, has provided a variety of compounds with interesting architectures and possible functionalities.<sup>[2]</sup> The integration of the inorganic phosphonate ( $CPO_3$ ) group and numerous rigid or flexible organic functional groups within the same composite would, therefore, be expected to result in new inorganic–organic hybrid materials with interesting structures and properties. Efforts along this line have been made where the organic moieties of the phosphonate ligand contain amino,<sup>[3]</sup> carboxylate,<sup>[4]</sup> pyridyl,<sup>[5]</sup> macrocyclic,<sup>[6]</sup> and ferrocene<sup>[7]</sup> groups etc. In this article, we report a new route to the synthesis of {[(benzimidazol-2-ylmethyl)imino]bis(methylene)}bis(phosphonic acid)  $[(C_7H_5N_2)CH_2N(CH_2PO_3H)_2]$ ,

bibmpH<sub>4</sub>], where a benzimidazole group is incorporated into the diphosphonic acid. Five isostructural compounds based on this ligand, namely  $[M\{(C_7H_5N_2)CH_2N(CH_2PO_3H)_2\}]$  [ $M = Mn$  (**1**),  $Fe$  (**2**),  $Co$  (**3**),  $Cu$  (**4**),  $Cd$  (**5**)] are obtained by hydrothermal reactions; all exhibit one-dimensional chain structures. The magnetic properties of **1–4** were also investigated.

## Results and Discussion

### Syntheses and Preliminary Characterization

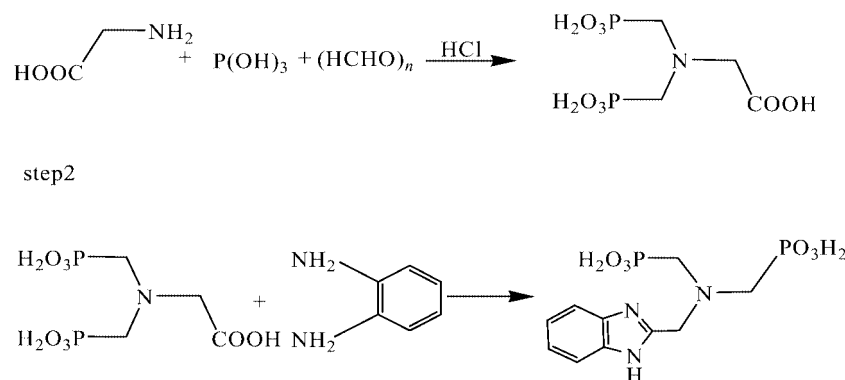
The synthesis of bibmpH<sub>4</sub> was previously reported from 2-(2-aminomethyl)benzimidazole, phosphorus, and formaldehyde by a Mannich reaction.<sup>[8]</sup> In this paper we describe a new synthetic route to the same acid from the reaction between *N,N*-bis(phosphonomethyl)aminoacetic acid and 1,2-diaminobenzene (Scheme 1). The final product can be easily isolated with a much higher yield (82%) than that reported in the patent (17%).<sup>[8]</sup>

The hydrothermal reaction of bibmpH<sub>4</sub> and the appropriate metal sulfate at 140 °C for one day resulted in compounds **1–5**, which have identical structures even though the experimental conditions for the formation of these compounds are slightly different. A series of experiments was conducted by changing the molar ratio of the starting materials and the pH of the reaction mixture. It was found that

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Scheme 1.

pure phases of compounds **1**, **3**, and **5** can be obtained with good yields when the molar ratio of M/ligand and the pH are 1:1 and 2.5–3.5 for **1**, 1:1 and 3.0–4.0 for **3**, and 1:1 and 2.0–4.0 for **5**, respectively. For compounds **2** and **4**, the crystallization of the products is always accompanied by the formation of brown powdery impurities when the molar ratio of M/ligand and the pH are 1:0.75–1 and 2.9–7.0 for **2** and 1:0.75–1 and 3.0–5.9 for **4**, respectively. Crystals with the best quality are formed when the pH is 7.03 for **2** and 4.90 for **4**. In preparing compound **2**, Me<sub>4</sub>NOH was used instead of NaOH to adjust the pH of the reaction mixture in order to improve the crystal quality. The same product can also be obtained with NaOH.

The IR spectra of compounds **1–5** are almost identical. The broad bands appearing around 3000 cm<sup>−1</sup> can be assigned to NH and OH stretching vibrations with the presence of extensive hydrogen bonds.<sup>[9]</sup> The sharp bands at around 1622, 1598, and 1522 cm<sup>−1</sup> are characteristic of the phenyl ring, and the bands near 1467 and 1455 cm<sup>−1</sup> are typical for ν(C=N) of the imidazole ring.<sup>[10]</sup> A series of bands between 1236 and 915 cm<sup>−1</sup> correspond to the CPO<sub>3</sub> groups.<sup>[11]</sup>

### Crystal Structures of Compounds 1–5

Compounds **1–5** are isostructural and crystallize in the orthorhombic space group *Pbca*. Crystallographic and re-

Table 1. Selected bond lengths [Å] and angles [°] for **1–5**.<sup>[a]</sup>

|           | <b>1</b>   | <b>2</b>   | <b>3</b>   | <b>4</b>   | <b>5</b>   |
|-----------|------------|------------|------------|------------|------------|
| M1–O1     | 2.032(3)   | 1.980(3)   | 1.978(3)   | 2.000(2)   | 2.148(3)   |
| M1–O4     | 2.090(3)   | 2.029(3)   | 2.004(3)   | 2.142(2)   | 2.198(3)   |
| M1–N1     | 2.486(4)   | 2.364(3)   | 2.345(4)   | 2.137(3)   | 2.551(3)   |
| M1–N2     | 2.127(4)   | 2.067(3)   | 2.024(4)   | 1.981(3)   | 2.213(4)   |
| M1–O5A    | 2.033(3)   | 2.035(3)   | 2.005(3)   | 1.926(2)   | 2.152(3)   |
| P1–O1     | 1.496(4)   | 1.501(3)   | 1.504(3)   | 1.509(2)   | 1.492(3)   |
| P1–O2     | 1.517(4)   | 1.494(3)   | 1.495(4)   | 1.513(2)   | 1.494(3)   |
| P1–O3     | 1.580(4)   | 1.569(3)   | 1.573(3)   | 1.564(2)   | 1.604(3)   |
| P2–O4     | 1.507(4)   | 1.524(3)   | 1.524(3)   | 1.501(2)   | 1.525(3)   |
| P2–O5     | 1.506(4)   | 1.494(3)   | 1.493(3)   | 1.513(2)   | 1.487(3)   |
| P2–O6     | 1.552(3)   | 1.558(3)   | 1.563(3)   | 1.554(2)   | 1.573(3)   |
| O1–M1–O4  | 115.95(15) | 122.72(12) | 118.82(14) | 113.52(9)  | 111.24(10) |
| O1–M1–N1  | 79.21(13)  | 82.30(11)  | 82.49(13)  | 87.18(9)   | 78.53(10)  |
| O1–M1–N2  | 114.37(17) | 113.09(13) | 115.30(15) | 125.68(11) | 117.01(12) |
| O1–M1–O5A | 105.68(14) | 101.24(12) | 100.05(13) | 96.31(9)   | 110.01(12) |
| O4–M1–N1  | 79.16(13)  | 81.87(11)  | 82.12(12)  | 84.55(9)   | 77.49(10)  |
| O4–M1–N2  | 115.67(15) | 115.80(13) | 118.10(14) | 117.56(10) | 114.86(12) |
| O4–M1–O5A | 98.01(13)  | 94.78(12)  | 95.24(12)  | 91.09(9)   | 95.16(11)  |
| N1–M1–N2  | 73.63(15)  | 76.41(12)  | 77.25(14)  | 80.52(10)  | 72.34(12)  |
| O5A–M1–N1 | 175.09(14) | 176.11(12) | 177.02(13) | 175.25(10) | 170.52(11) |
| O5A–M1–N2 | 104.32(16) | 103.45(13) | 102.92(14) | 99.92(10)  | 106.06(13) |
| M1–N1–C1  | 106.4(3)   | 105.7(2)   | 106.5(3)   | 107.95(17) | 105.1(2)   |
| M1–N1–C2  | 106.2(3)   | 107.9(2)   | 107.5(3)   | 109.77(19) | 105.7(2)   |
| M1–N1–C3  | 108.1(3)   | 107.8(2)   | 107.2(3)   | 107.02(19) | 105.5(2)   |
| M1–N2–C4  | 119.8(5)   | 118.0(3)   | 118.5(3)   | 114.9(2)   | 119.4(3)   |
| M1–N2–C5  | 135.3(4)   | 136.5(3)   | 136.1(3)   | 139.9(2)   | 134.8(3)   |
| M1–O1–P1  | 124.9(2)   | 122.96(17) | 122.6(2)   | 117.48(12) | 122.86(15) |
| M1–O4–P2  | 123.58(19) | 122.01(16) | 122.37(17) | 116.85(14) | 121.94(16) |
| M1B–O5–P2 | 135.5(2)   | 138.15(19) | 137.95(19) | 136.27(15) | 128.28(19) |

[a] Symmetry codes: A:  $-x, y + 1/2, -z + 1/2$ ; B:  $-x, y - 1/2, -z + 1/2$ .

finement details of **1–5** are listed in the Experimental Section, and selected bond lengths and angles are given in Table 1. Figure 1 displays the building unit of **1** with the atomic labeling scheme. The asymmetric unit of compound

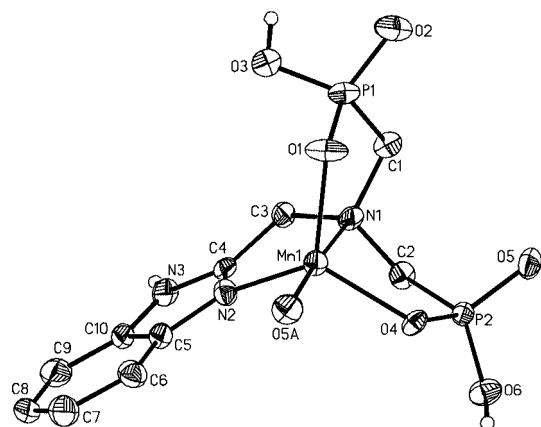


Figure 1. Asymmetric building unit of compound **1** with atomic labeling scheme (50% probability). All H atoms except H3A, H3B and H6A are omitted for clarity.

**1** contains one  $\text{Mn}^{\text{II}}$  ion and one  $\text{bibmpH}_2^{2-}$  ligand. The Mn1 atom has a distorted trigonal bipyramidal geometry, with the basal plane defined by the atoms O1, O4, and N2 from the same  $\text{bibmpH}_2^{2-}$  ligand. The Mn1–O1, Mn1–O4, and Mn1–N2 bond lengths are 2.032(3), 2.090(3), and 2.127(4) Å, respectively, while the O1–Mn1–O4, O1–Mn1–N2, and O4–Mn1–N2 bond angles are 116.0(2)°, 114.4(2)°, and 115.7(2)°, respectively. The axial positions are occupied by the atom N1 from the same  $\text{bibmpH}_2^{2-}$  ligand and O5A from the other equivalent  $\text{bibmpH}_2^{2-}$  ligand. The N1–Mn1–O5A bond angle is 175.1(1)°, and the Mn1–N1 and Mn1–O5A bond lengths are 2.486(4) and 2.033(3) Å, respectively.

Each  $\text{bibmpH}_2^{2-}$  behaves as a pentadentate ligand, binding through three phosphonate oxygen atoms (O1, O4, O5), one imino nitrogen atom (N1), and one benzimidazole nitrogen atom (N2). Two phosphonate oxygen atoms (O3, O6), each from a  $\{\text{CPO}_3\}$  terminus, are protonated [P1–O3 = 1.580(4), P2–O6 = 1.552(3) Å]. The remaining phosphonate oxygen (O2) is pendant [P1–O2 = 1.517(4) Å]. The equivalent Mn atoms are bridged by phosphonate oxygen atoms O4 and O5 to form a zigzag chain along the *b*-axis

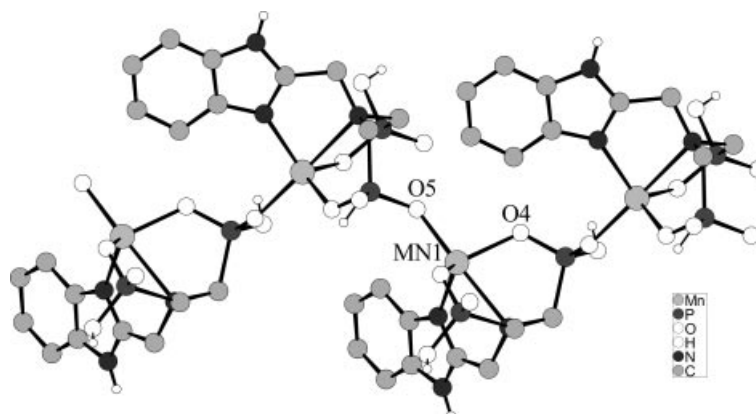


Figure 2. A fragment of chain in structure **1**. All H atoms except H3A, H3B and H6A are omitted for clarity.

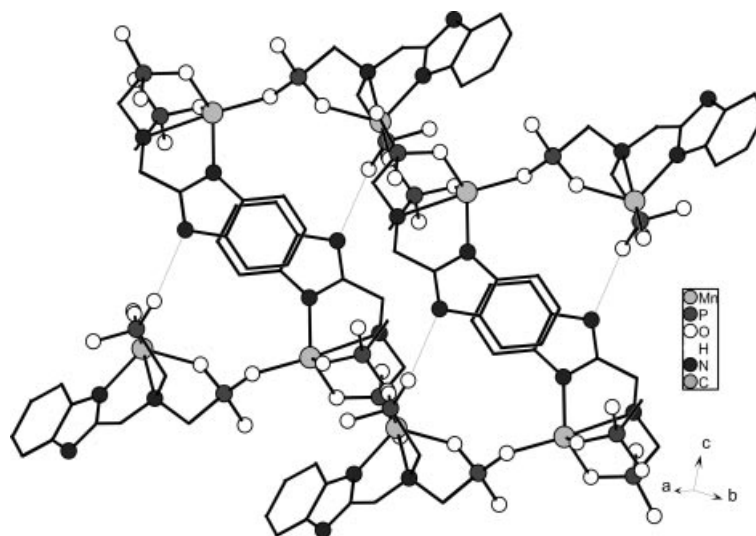


Figure 3. The inter-chain  $\pi$ - $\pi$  stacking and  $\text{N}\cdots\text{O}$  hydrogen bond interactions in structure **1**. All H atoms are omitted for clarity.

(Figure 2). The Mn1...Mn1A distance over the O4–P2–O5 bridge is 5.849 Å. The benzimidazole rings are arranged tilted on two sides of the chain.

Between the chains, the benzimidazole rings are approximately parallel and are  $\pi$ – $\pi$  stacked (the average centroid–centroid distance between the two phenyl rings of the benzimidazole groups is 3.547 Å for **1**; Figure 3).<sup>[12]</sup> Hydrogen-bond interactions are found between the imidazole nitrogen atom (N3) and the phosphonate oxygen atom (O2) approximately along the *c*-axis, and among phosphonate oxygen atoms along the *a*-axis (Figures 3 and 4). The N3...O2<sup>i</sup>, O3...O4<sup>ii</sup>, and O6...O2<sup>iii</sup> distances are 2.753(6), 2.723(5), and 2.536(5) Å, respectively (symmetry codes: i: *x*,  $-y + 3/2$ , *z* – 1/2; ii: *x* + 1/2, *y*,  $-z + 1/2$ ; iii: *x* – 1/2, *y*,  $-z + 1/2$ ). Therefore, a three-dimensional network structure is built

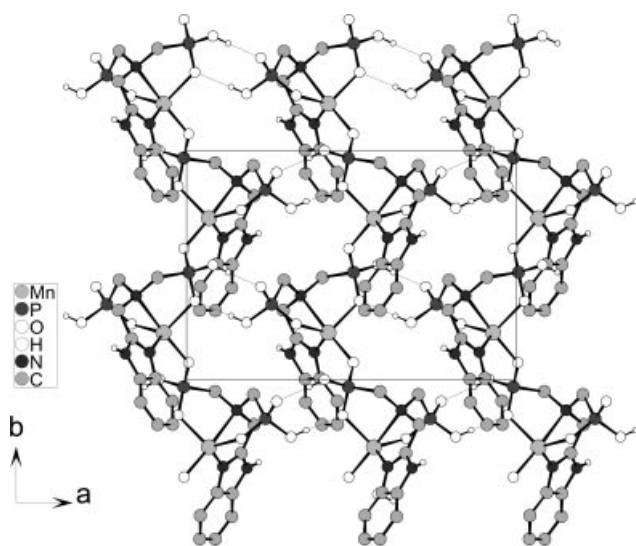


Figure 4. The inter-chain hydrogen bond interactions among the phosphonate oxygen atoms in structure **1**. All H atoms except H3A, H3B and H6A are omitted for clarity.

up. Figure 5 shows the packing diagram of compound **1** viewed down the *b*-axis.

The structures of compounds **2–4** are analogous to **1** except that the Mn<sup>II</sup> ion in **1** is replaced by Fe<sup>II</sup> in **2**, Co<sup>II</sup> in **3**, Cu<sup>II</sup> in **4**, and Cd<sup>II</sup> in **5**. The cell volume decreases in the sequence **5** > **1** > **2** > **3** > **4**, in accordance with the decreasing sequence of the ionic radii of the corresponding metal ions.<sup>[13]</sup> Therefore, the metal atoms in **2–5** also have distorted trigonal bipyramidal geometries. The M–N1 distance [2.364(3) Å in **2**, 2.345(4) Å in **3**, 2.137(3) Å in **4**, and 2.551(3) Å in **5**] is significantly longer than the other M–O(N) bond lengths, although the Cu1–N1 bond length in **4** [2.137(3) Å] is much shorter. The metal atoms are bridged by O–P–O units to form infinite chains. The M...M distances across the O–P–O unit within the chain are 5.813 Å for **2**, 5.794 Å for **3**, 5.767 Å for **4**, and 5.941 Å for **5**. These chains are connected by hydrogen-bond interactions as well as  $\pi$ – $\pi$  stacking interactions. The average centroid–centroid distances between the two phenyl rings of the benzimidazole groups are 3.482 Å for **2**, 3.470 Å for **3**, 3.490 Å for **4**, and 3.620 Å for **5**. The N3...O2<sup>i</sup>, O3...O4<sup>ii</sup>, and O6...O2<sup>iii</sup> distances are 2.757(4), 2.690(4), and 2.583(4) Å for **2**, 2.739(5), 2.699(4), and 2.570(4) Å for **3**, 2.715(3), 2.632(3), and 2.550(3) Å for **4**, and 2.805(5), 2.702(4), and 2.529(4) Å for **5**, respectively.

It could be of interest to compare the coordination capabilities of the bibmp<sup>4-</sup> ligand with that of *N,N*-bis(phosphonomethyl)aminoacetate (bpmaa<sup>5-</sup>; Scheme 2) as both can offer up to six phosphonate oxygen atoms for coordination with the metal ions. For the bpmaa<sup>5-</sup> ligand, the carboxylate group has additional two oxygen donors. Thus, several transition metal/bpmada<sup>5-</sup> compounds have been prepared that show two- and three-dimensional structures.<sup>[14]</sup> For the bibmp<sup>4-</sup> ligand, only one nitrogen atom of each benzimidazole group can be used for the coordination when the reaction pH is not high enough. Besides, the benzimidazole group present in this ligand also provides a topologi-

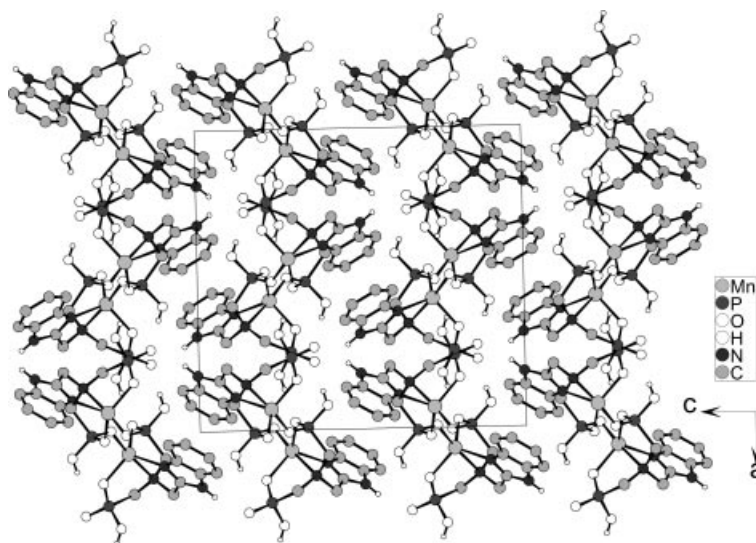
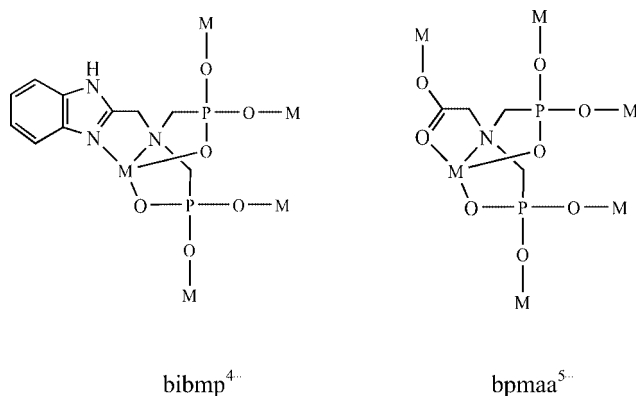


Figure 5. Packing diagram of structure **1** projected along *b*-axis. All H atoms are omitted for clarity.

cal hydrophobic environment, possible  $\pi$ - $\pi$  stacking interactions between the phenyl rings, and steric hindrance as well. Hence, it is not unexpected that different structures will be constructed when metal sources react with bibmpH<sub>4</sub> and bpmaaH<sub>5</sub> acids. This paper shows that metal/bibmpH<sub>2</sub><sup>2-</sup> compounds with zigzag chain structures can be obtained through hydrothermal reactions of metal sulfates and the acid bibmpH<sub>4</sub>.



Scheme 2.

### Magnetic Properties

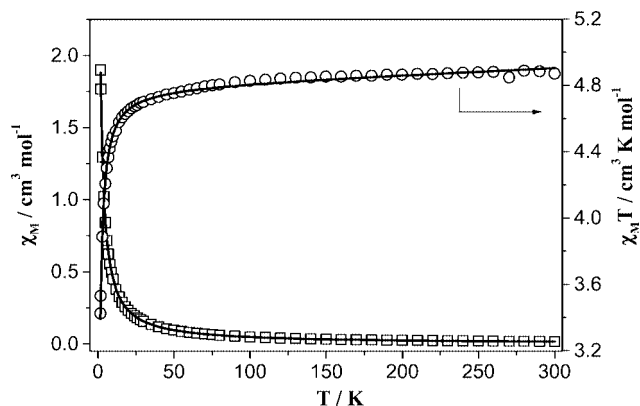
The temperature-dependent magnetic behaviors of compounds **1–4** were investigated in the temperature range 1.8–300 K. The room-temperature effective magnetic moments are 6.24  $\mu_B$ /Mn for **1** (expected 5.92  $\mu_B$  for  $S = 5/2$ ), 5.12  $\mu_B$ /Fe for **2** (expected 4.90  $\mu_B$  for  $S = 2$ ), 4.57  $\mu_B$ /Co for **3** (expected 3.87  $\mu_B$  for  $S = 3/2$ ), and 1.82  $\mu_B$ /Cu for **4** (expected 1.73  $\mu_B$  for  $S = 1/2$ ). Figure 6 shows the  $\chi_M$  and  $\chi_M T$  vs.  $T$  plots for compound **1**. The continuous decrease of  $\chi_M T$  upon cooling suggests a dominant antiferromagnetic exchange coupling between the Mn<sup>II</sup> centers. Since structure **1** is one-dimensional and the Mn<sup>II</sup> ions are linked purely through O–P–O units, the susceptibility data can be analyzed by Fisher's expression for a uniform chain based on the Heisenberg Hamiltonian  $H = -J \sum S_{Ai} \cdot S_{Ai+1}$ , with the classical spins scaled to a real quantum spin  $S = 5/2$  [Equation (1)],<sup>[15]</sup>

$$\chi_M = \frac{Ng^2\beta^2 S(S+1)}{3kT} \frac{1+u}{1-u} + N_a$$

$$u = \coth \left[ \frac{JS(S+1)}{kT} \right] - \left[ \frac{kT}{JS(S+1)} \right] \quad (1)$$

where  $J$  is the coupling constant,  $N$ ,  $g$ ,  $\beta$  and  $k$  have their usual meanings, and  $N_a$  accounts for both the diamagnetic and TIP contributions. A good fit, shown as the solid line in Figure 6, gives the parameters  $g = 2.09$ ,  $J = -0.075$  cm<sup>-1</sup>, and  $N_a = 4.0 \times 10^{-4}$  cm<sup>3</sup> mol<sup>-1</sup>. The value of  $g$  is higher than that expected for a high-spin Mn<sup>II</sup> ion ( $g = 2$ ). A higher  $g$  value has also been reported for the compounds [Mn(N<sub>3</sub>)<sub>2</sub>(bte)] [bte = 1,2-bis(1,2,4-triazol-1-yl)ethane] ( $g = 2.06$ ),<sup>[16]</sup> [Mn(oda)(H<sub>2</sub>O)]<sub>n</sub> [oda = O(CH<sub>2</sub>COO)<sub>2</sub>]<sup>2-</sup> ( $g =$

2.07),<sup>[17]</sup> and [Mn(OAc)(terpy)( $\mu_{1,5}$ -dca)]<sub>n</sub> [dca = N(CN)<sub>2</sub><sup>-</sup>, OAc = acetate, terpy = 2,2':6',2''-terpyridine] ( $g = 2.15$ ).<sup>[18]</sup>

Figure 6. The  $\chi_M T$  and  $\chi_M$  vs.  $T$  plots for **1**.

Dominant antiferromagnetic interactions are also observed in compounds **2** and **3** (Figures 7 and 8, respectively). As is well known, both Fe<sup>II</sup> and Co<sup>II</sup> ions in octahedral environments show significant single-ion anisotropies or spin-orbital couplings. When the symmetry of the molecule is lowered, the orbital contribution can be partially removed. In the present case each metal atom has a distorted trigonal-bipyramidal geometry, therefore the orbital contributions of both Fe<sup>II</sup> and Co<sup>II</sup> would be reduced. The susceptibility data were initially fitted by the Fisher formula [Equation (1)], with  $S = 2$  for **2** and  $S = 3/2$  for **3**, which leads to the parameters  $g = 2.07$ ,  $J = -0.33$  cm<sup>-1</sup>, and  $N_a = 2.0 \times 10^{-4}$  cm<sup>3</sup> mol<sup>-1</sup> for **2** and  $g = 2.15$ ,  $J = -0.35$  cm<sup>-1</sup>, and  $N_a = 1.7 \times 10^{-3}$  cm<sup>3</sup> mol<sup>-1</sup> for **3**. The  $J$  value of compound **2** is comparable to that for [NH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>]-[Fe{HO<sub>3</sub>PC(CH<sub>3</sub>)(OH)(PO<sub>3</sub>H)}<sub>2</sub>·2H<sub>2</sub>O], in which the Fe<sup>II</sup> ions are doubly bridged by O–P–O units ( $J = -0.46$  cm<sup>-1</sup>) and the same equation was employed for the data fitting.<sup>[19]</sup> The Fisher formula, however, is a simplified model that assumes Heisenberg exchange couplings between all spins and does not take into account the single-ion anisotropy or spin-orbit coupling of either Fe<sup>II</sup> or Co<sup>II</sup> ions. A theoretical analysis considering both zero-field splitting (ZFS) and a small antiferromagnetic interaction would be a more logical approach. In order to fit the  $\chi_M T$  vs.  $T$  plots of compounds **2** and **3**, we calculated the magnetic susceptibility of six-membered closed rings. Due to the high-spin value we can suppose that the magnetic behavior of these closed rings is very similar to that of an infinite chain.<sup>[20]</sup> The Hamiltonian can therefore be used in its simplified axial form with an axial ZFS parameter ( $D$ ), the antiferromagnetic exchange interaction ( $J$ ), an axial  $g$  vector, and a temperature-independent paramagnetism (TIP). The analysis of the data was performed with the full-matrix diagonalization program MAGPACK.<sup>[21]</sup> After a least-squares fitting the following parameters were found:  $J = -0.1$  cm<sup>-1</sup>,  $D = 0.51$  cm<sup>-1</sup>,  $g = 2.09$ , and TIP =  $3.3 \times 10^{-4}$  for the Fe<sup>II</sup> complex **2** and  $J = -0.15$  cm<sup>-1</sup>,  $D = 7.6$  cm<sup>-1</sup>,  $g_z = 2.33$ ,  $g_{xy} = 2.08$ , and TIP =  $1.1 \times 10^{-3}$  for the Co<sup>II</sup> complex **3**, shown as solid lines in

Figures 7 and 8, respectively. The  $J$  values obtained for compounds **2** and **3** are comparable to that of compound **1**.

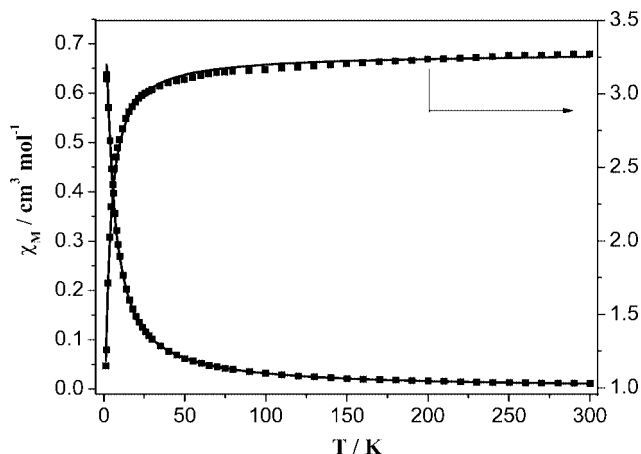


Figure 7. The  $\chi_M T$  and  $\chi_M$  vs.  $T$  plots for **2**.

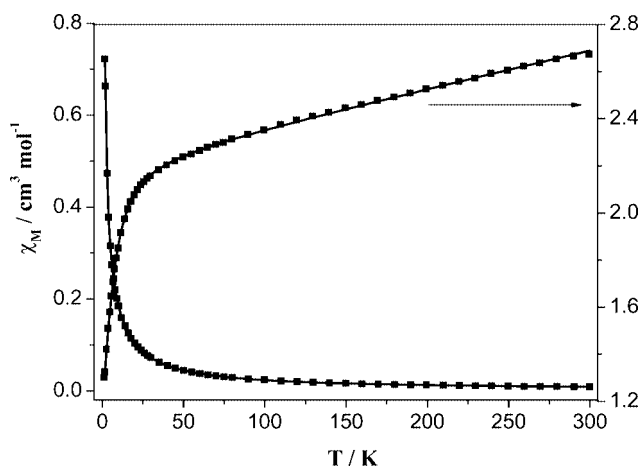


Figure 8. The  $\chi_M T$  and  $\chi_M$  vs.  $T$  plots for **3**.

For compound **4** there is a maximum at around 3 K in the  $\chi_M$  vs.  $T$  plot (Figure 7), which is consistent with the antiferromagnetic nature of the magnetic interactions. Considering that compound **4** also has a chain structure with equally spaced  $\text{Cu}^{\text{II}}$  ions ( $S = 1/2$ ), the susceptibility data can be fitted by the following equation based on the Heisenberg Hamiltonian  $H = -J\sum S_{\text{Ai}} \cdot S_{\text{Ai}+1}$  [Equation (2)],<sup>[15]</sup>

$$\chi_M = \frac{Ng^2\beta^2}{kT} \frac{0.25 + 0.074975x + 0.075235x^2}{1 + 0.9931x + 0.172135x^2 + 0.757825x^3} + N_\alpha \quad (2)$$

where  $x = |J|/kT$ . A good fit, shown as the solid line in Figure 9, results in the parameters  $g = 2.18$ ,  $J = -2.96 \text{ cm}^{-1}$ , and  $N_\alpha = -2.9 \times 10^{-5} \text{ cm}^3 \text{ mol}^{-1}$ . The  $J$  value is smaller than those found for compounds  $[\{\text{Cu}_3(\text{di-2-pyridylamine})_3(\mu\text{-HPO}_4)(\mu\text{-PO}_4)(\text{H}_2\text{O})\}(\text{PF}_6)(\text{H}_2\text{O})_3]_n$  ( $-4.98 \text{ cm}^{-1}$ )<sup>[22]</sup> and  $[\{(\text{bipy})\text{Cu}(\text{H}_2\text{O})\}_2(\mu\text{-P}_2\text{O}_7) \cdot 7\text{H}_2\text{O}]$  ( $J = -20 \text{ cm}^{-1}$ ),<sup>[23]</sup> where the  $\text{Cu}^{\text{II}}$  ions are also linked by O–P–O units.

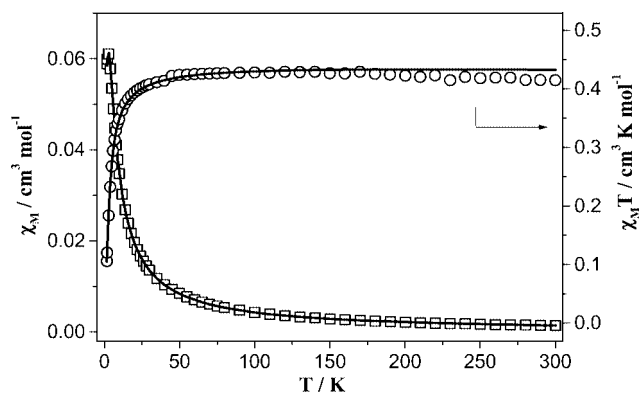


Figure 9. The  $\chi_M T$  and  $\chi_M$  vs.  $T$  plots for **4**.

## Conclusion

Hydrothermal reactions of metal sulfates and (benzimidazol-2-ylmethyl)imino bis(methylenephosphonic acid) have resulted in five isostructural compounds with the formula  $[\text{M}\{(\text{C}_7\text{H}_5\text{N}_2)\text{CH}_2\text{N}(\text{CH}_2\text{PO}_3\text{H})_2\}]$  [ $\text{M} = \text{Mn}$  (**1**),  $\text{Fe}$  (**2**),  $\text{Co}$  (**3**),  $\text{Cu}$  (**4**), and  $\text{Cd}$  (**5**)]. Each compound shows a one-dimensional chain structure where  $\{\text{MO}_3\text{N}_2\}$  trigonal bipyramids are connected by  $\{\text{CPO}_3\}$  tetrahedra through corner-sharing. The benzimidazole rings are involved in both aromatic stacking and hydrogen bonds. Further work is in progress to explore new materials with other topologies based on the same phosphonate ligand.

## Experimental Section

**Materials and Methods:** *N,N*-Bis(phosphonomethyl)aminoacetic acid was synthesized according to the literature procedure.<sup>[14a]</sup> All other reagents were purchased as reagent-grade chemicals and used without further purification. Elemental analyses were performed with a Perkin–Elmer 240C elemental analyzer. The IR spectra were obtained as KBr disks on a VECTOR 22 spectrometer. Variable-temperature magnetic susceptibility data were obtained for microcrystalline samples using a Quantum Design MPMS-XL7 SQUID magnetometer.

**Synthesis of  $\{[(\text{Benzimidazol-2-ylmethyl})\text{imino}]\text{bis}(\text{methylene})\}\text{bis}(\text{phosphonic Acid})[(\text{C}_7\text{H}_5\text{N}_2)\text{CH}_2\text{N}(\text{CH}_2\text{PO}_3\text{H})_2, \text{bibmpH}_4]$ :** Bis-(phosphonomethyl)imino acetic acid (5.26 g, 20 mmol) and 1,2-diaminobenzene (2.06 g, 20 mmol) were fully mixed by grinding. The mixture was transferred to an open, single-necked flask and then heated at  $190^\circ\text{C}$  until no steam was produced. After cooling, 6 M hydrochloric acid (8 mL) was added to the flask. The resulting solution was refluxed at  $120^\circ\text{C}$  for 2 h, and then concentrated to dryness. The blue solid was taken up in water (20 mL) and KOH was added until the solid had dissolved (pH about 5–6). After refluxing with decoloring charcoal for 30 min, the solution was filtered off. The filtrate was acidified with 6 M HCl until  $\text{pH} \leq 1.0$ . The white precipitate was collected, washed with methanol, and dried in vacuo. Yield: 5.5 g (82%). IR (KBr):  $\tilde{\nu} = 3153\text{--}2346$  (br)  $\text{cm}^{-1}$ , 1625 (m), 1573 (w), 1524 (w), 1491 (w), 1460 (m), 1438 (w), 1418 (w), 1400 (m), 1383 (w), 1367 (w), 1344 (m), 1308 (m), 1285 (m), 1252 (s), 1219 (s), 1159 (s), 1134 (s), 1059 (s), 1019 (s), 992 (s), 958 (s), 926 (s), 899 (m), 887 (m), 851 (m), 828 (m), 752 (s), 727 (w), 620 (w), 572 (w), 544 (w), 496 (s), 468 (m), 456 (m), 434 (w),

411 (w),  $C_{10}H_{15}N_3O_6P_2$ : calcd. C 35.85, H 4.51, N 12.54; found C 35.72, H 4.82, N 12.55.

**Synthesis of  $[Mn\{(C_7H_5N_2)CH_2N(CH_2PO_3H)_2\}]$  (1):** A mixture of bibmpH<sub>4</sub> (0.15 mmol, 0.0495 g) and  $MnSO_4 \cdot H_2O$  (0.15 mmol, 0.0253 g) in 8 mL of H<sub>2</sub>O, adjusted to pH 2.5–3.5 with 1 M NaOH, was kept in a Teflon-lined autoclave at 140 °C for 24 h. After slow cooling to room temperature, gray-blue, block-shaped crystals were obtained as a monophasic material (according to the powder X-ray diffraction pattern). Yield: 23 mg (40%).  $C_{10}H_{13}MnN_3O_6P_2$ : calcd. C 30.92, H 3.35, N 10.82; found C 30.93, H 3.21, N 10.80. IR (KBr):  $\tilde{\nu}$  = 3104 (m, br)  $cm^{-1}$ , 2939 (w), 2874 (w), 1622 (w), 1598 (w), 1522 (w), 1467 (m), 1455 (m), 1432 (m), 1387 (w), 1377 (w), 1343 (w), 1324 (w), 1309 (w), 1282 (w), 1266 (w), 1236 (m), 1181 (s), 1133 (s), 1100 (m), 1073 (s), 1035 (m), 958 (w), 941 (w), 915 (s), 852 (w), 832 (w), 754 (m), 686 (w), 651 (w), 576 (s), 505 (w), 499 (w), 472 (w), 448 (w), 408 (w).

**Synthesis of  $[Fe\{(C_7H_5N_2)CH_2N(CH_2PO_3H)_2\}]$  (2):** A mixture of bibmpH<sub>4</sub> (0.10 mmol, 0.0330 g) and  $FeSO_4 \cdot 7H_2O$  (0.20 mmol, 0.0556 g) in 8 mL of H<sub>2</sub>O, adjusted to pH 7.03 by adding 0.2 mmol of Me<sub>4</sub>NOH, was kept in a Teflon-lined autoclave at 140 °C for 24 h. After slow cooling to room temperature, gray-green, block-shaped crystals were obtained together with a brown powder. The crystals were selected manually and were used for single-crystal structural determination and physical measurements. Yield: 16 mg (41% based on bibmpH<sub>4</sub>).  $C_{10}H_{13}FeN_3O_6P_2$ : calcd. C 30.85, H 3.34, N 10.80; found C 30.35, H 3.56, N 10.46. IR (KBr):  $\tilde{\nu}$  = 3104–2886 (m, br)  $cm^{-1}$ , 1623 (w), 1598 (w), 1524 (w), 1467 (m), 1456 (m), 1434 (m), 1420 (m), 1387 (w), 1377 (w), 1342 (m), 1323 (w), 1309 (w), 1281 (w), 1264 (w), 1236 (m), 1185 (s), 1140 (s), 1091 (m), 1065 (s), 1036 (s), 1021 (s), 981 (m), 968 (m), 955 (m), 941 (m), 918 (s), 898 (m), 833 (m), 778 (m), 756 (m), 704 (w), 653 (w), 577 (s), 560 (m), 509 (w), 496 (w), 470 (w), 447 (w), 420 (w).

**Synthesis of  $[Co\{(C_7H_5N_2)CH_2N(CH_2PO_3H)_2\}]$  (3):** A mixture of bibmpH<sub>4</sub> (0.15 mmol, 0.0495 g) and  $CoSO_4 \cdot 7H_2O$  (0.15 mmol, 0.0422 g) in 8 mL of H<sub>2</sub>O, adjusted to pH 3.0–4.0 with 1 M NaOH, was kept in a Teflon-lined autoclave at 140 °C for 24 h. After slow cooling to room temperature, magenta, block-shaped crystals were obtained as a monophasic material (according to the powder X-ray diffraction pattern). Yield: 46 mg (78%). Anal. found (calcd.) for  $C_{10}H_{13}CoN_3O_6P_2$ : calcd. C 30.60, H 3.32, N 10.71; found C 30.66, H 3.30, N 10.53. IR (KBr):  $\tilde{\nu}$  = 3100–2887 (m, br)  $cm^{-1}$ , 1625 (w), 1598 (w), 1529 (w), 1469 (m), 1457 (m), 1433 (m), 1420

(w), 1388 (w), 1342 (w), 1323 (w), 1311 (w), 1282 (w), 1184 (s), 1132 (s), 1093 (m), 1067 (s), 1040 (m), 1021 (w), 982 (w), 969 (w), 918 (s), 834 (w), 781 (w), 756 (m), 714 (w), 653 (w), 578 (s), 513 (w), 499 (w), 472 (w), 448 (w), 423 (w), 408 (w).

**Synthesis of  $[Cu\{(C_7H_5N_2)CH_2N(CH_2PO_3H)_2\}]$  (4):** A mixture of bibmpH<sub>4</sub> (0.10 mmol, 0.0330 g) and  $CuSO_4$  (0.13 mmol, 0.0208 g) in 8 mL of H<sub>2</sub>O, adjusted to pH 4.90 with 1 M NaOH, was kept in a Teflon-lined autoclave at 140 °C for 24 h. After slow cooling to room temperature, green, block-shaped crystals were obtained together with a brown powder. The crystals were selected manually and were used for single-crystal structural determination and physical measurements. Yield: 22 mg (55% based on bibmpH<sub>4</sub>).  $C_{10}H_{13}CuN_3O_6P_2$ : calcd. C 30.25, H 3.28, N 10.59; found C 30.34, H 3.43, N 10.62. IR (KBr):  $\tilde{\nu}$  = 3121–2900 (m, br)  $cm^{-1}$ , 1622 (w), 1597 (w), 1529 (w), 1494 (w), 1473 (m), 1456 (m), 1434 (m), 1419 (m), 1378 (w), 1341 (w), 1320 (w), 1281 (w), 1256 (m), 1238 (s), 1193 (s), 1128 (s), 1095 (m), 1059 (m), 1035 (m), 988 (w), 961 (w), 944 (w), 918 (s), 834 (w), 784 (w), 767 (m), 757 (m), 721 (w), 653 (w), 584 (s), 560 (m), 512 (w), 499 (w), 474 (w), 447 (w), 414 (w).

**Synthesis of  $[Cd\{(C_7H_5N_2)CH_2N(CH_2PO_3H)_2\}]$  (5):** A mixture of bibmpH<sub>4</sub> (0.15 mmol, 0.0495 g) and  $CdSO_4 \cdot 2.7H_2O$  (0.15 mmol, 0.0380 g) in 8 mL of H<sub>2</sub>O, adjusted to pH 3.0–4.0 with 1 M NaOH, was kept in a Teflon-lined autoclave at 140 °C for 24 h. After slow cooling to room temperature, gray-blue block-shaped crystals were obtained as a monophasic material (according to the powder X-ray diffraction pattern). Yield: 37 mg (55%). Anal. found (calcd.) for  $C_{10}H_{13}CdN_3O_6P_2$ : calcd. C 26.93, H 2.92, N 9.43; found C 26.82, H 2.85, N 9.28. IR (KBr):  $\tilde{\nu}$  = 3102 (m)  $cm^{-1}$ , 2939 (w), 2868 (w), 1619 (w), 1598 (w), 1521 (w), 1490 (w), 1469 (m), 1456 (m), 1432 (m), 1386 (w), 1377 (w), 1344 (w), 1325 (w), 1311 (w), 1286 (w), 1266 (w), 1238 (m), 1206 (m), 1176 (s), 1129 (s), 1097 (m), 1072 (s), 1038 (m), 979 (w), 967 (w), 955 (w), 942 (w), 913 (s), 853 (w), 830 (w), 765 (w), 754 (m), 684 (w), 649 (w), 576 (s), 502 (w), 487 (w), 460 (w), 442 (w), 410 (w).

**X-ray Crystallographic Studies:** Single crystals of dimensions  $0.1 \times 0.04 \times 0.04$  mm<sup>3</sup> for **1**,  $0.1 \times 0.05 \times 0.05$  mm<sup>3</sup> for **2**,  $0.15 \times 0.15 \times 0.15$  mm<sup>3</sup> for **3**,  $0.04 \times 0.02 \times 0.02$  mm<sup>3</sup> for **4**, and  $0.1 \times 0.05 \times 0.05$  mm<sup>3</sup> for **5** were used for structural determinations on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo- $K_\alpha$  radiation ( $\lambda$  = 0.71073 Å) at room temperature. Further details can be found in Table 2. A hemisphere of

Table 2. Crystallographic data and refinement parameters for **1–5**.

| Compound                                                                    | 1                         | 2                         | 3                         | 4                         | 5                         |
|-----------------------------------------------------------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| Empirical formula                                                           | $C_{10}H_{13}MnN_3O_6P_2$ | $C_{10}H_{13}FeN_3O_6P_2$ | $C_{10}H_{13}CoN_3O_6P_2$ | $C_{10}H_{13}CuN_3O_6P_2$ | $C_{10}H_{13}CdN_3O_6P_2$ |
| $F_w$                                                                       | 388.11                    | 389.02                    | 392.10                    | 396.71                    | 445.57                    |
| Crystal system                                                              | orthorhombic              | orthorhombic              | orthorhombic              | orthorhombic              | orthorhombic              |
| Space group                                                                 | <i>Pbca</i>               | <i>Pbca</i>               | <i>Pbca</i>               | <i>Pbca</i>               | <i>Pbca</i>               |
| $a$ [Å]                                                                     | 15.331(2)                 | 15.320(3)                 | 15.207(2)                 | 15.101(3)                 | 15.4679(19)               |
| $b$ [Å]                                                                     | 10.7150(16)               | 10.477(2)                 | 10.4626(16)               | 10.3517(17)               | 10.8923(13)               |
| $c$ [Å]                                                                     | 16.715(2)                 | 16.764(3)                 | 16.794(3)                 | 16.997(3)                 | 16.6175(19)               |
| $V$ [Å <sup>3</sup> ]                                                       | 2745.8(6)                 | 2690.7(9)                 | 2672.0(7)                 | 2656.9(7)                 | 2799.7(6)                 |
| $Z$                                                                         | 8                         | 8                         | 8                         | 8                         | 8                         |
| $\rho_{\text{calcd.}}$ [g cm <sup>−3</sup> ]                                | 1.878                     | 1.921                     | 1.949                     | 1.984                     | 2.114                     |
| $F(000)$                                                                    | 1576                      | 1584                      | 1592                      | 1608                      | 1760                      |
| $R_{\text{int}}$                                                            | 0.0835                    | 0.0585                    | 0.073                     | 0.0517                    | 0.056                     |
| Goodness of fit on $F^2$                                                    | 1.042                     | 1.042                     | 1.090                     | 1.136                     | 1.141                     |
| $R_1, wR_2$ [ $I > 2\sigma(I)$ ]                                            | 0.0641, 0.1169            | 0.0484, 0.1105            | 0.0564, 0.0998            | 0.0426, 0.0901            | 0.0429, 0.0599            |
| $R_1, wR_2^{\text{[a]}}$ (all data)                                         | 0.1107, 0.1281            | 0.0715, 0.1205            | 0.0876, 0.1110            | 0.0557, 0.0926            | 0.0707, 0.0636            |
| $(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}}$ [e Å <sup>−3</sup> ] | 0.407, −0.438             | 0.979, −1.231             | 0.550, −0.458             | 0.397, −0.433             | 0.870, −0.952             |

[a]  $R_1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

data were collected in the  $\theta$  range 2.62–26.00° for **1**, 2.43–26.00° for **2**, 2.43–25.99° for **3**, 2.40–25.99° for **4**, and 2.45–26.00° for **5** using a narrow-frame method with scan widths of 0.30° in  $\omega$  and an exposure time of 5 s per frame. Numbers of observed and unique [ $I > 2\sigma(I)$ ] reflections are 13496 and 2700 ( $R_{\text{int}} = 0.0835$ ) for **1**, 13174 and 2634 ( $R_{\text{int}} = 0.0585$ ) for **2**, 13176 and 2618 ( $R_{\text{int}} = 0.073$ ) for **3**, 12675 and 2605 ( $R_{\text{int}} = 0.0517$ ) for **4**, and 14077 and 2754 ( $R_{\text{int}} = 0.056$ ) for **5**, respectively. The data were integrated using the Siemens SAINT program,<sup>[24]</sup> with the intensities corrected for Lorentz factors, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Multi-scan absorption corrections were applied. The structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares using SHELXTL.<sup>[25]</sup> All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded.

CCDC-283019 to -283023 (for **1–5**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Acknowledgments

We thank the NNSF of China (No. 20325103), the Ministry of Education of China and the NSF of Jiangsu province (No. BK2002078) for financial supports, Mr. Yong-Jiang Liu for crystal data collections, Dr. You Song and Mr. Tian-Wei Wang for magnetic measurements.

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Received: September 7, 2005  
Published Online: March 13, 2006