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Chiral-Layered Metal Phosphonate Formed via Spontaneous Resolution Showing Dehydration-Induced Antiferromagnetic to Ferromagnetic Transformation

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Metal phosphonates $M^{II}\{(2\text{-}C_5H_4N)CH_2NHCH_2PO_3\}(H_2O)$ [M = Mn (**1**), Cd (**2**)] with chiral-layered structures are obtained by spontaneous resolution using achiral starting materials. The magnetic behavior of **1** is transformed from antiferromagnetic to ferromagnetic upon dehydration.

Molecular materials combining chirality with magnetism have been of considerable interest since a weak magnetochiral dichroism effect was observed in a paramagnetic chiral species.[1−3] So far, examples of homochiral magnetic materials are rather few, most of which are formed by using enantiopure chiral coligands.[2] Spontaneous resolution upon crystallization may occur by using achiral or racemic ligands, which usually results in optically inactive conglomerates, e.g., a mechanical and racemic mixture of enantiomeric chiral crystals.[4−6] Nonzero enantiomeric excess that arises spontaneously from an achiral or a racemic state through chiral symmetry breaking is rarely reported.[7,8] On the other hand, molecule-based materials with their physical properties sensitive to the external stimulus are of intense current interest because of their potential applications as switches and sensors.[9] Although magnetic property changes induced by light, temperature, and guest adsorption, etc., have been observed in many compounds,[10] few of them are concerned with a chiral magnetic system.[11]

Metal phosphonates are attractive inorganic−organic hybrid materials in which the organic group may be designed for particular chemical or physical properties.[12] On the basis of enantiopure phosphonate ligands, a few homochiral metal phosphonates have been prepared.[13−16] Spontaneous resolution can also be achieved by using achiral and asymmetric phosphonate ligands as starting materials, leading to racemic

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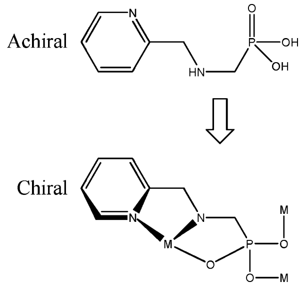
Scheme 1



conglomerates.[17] With the aim of exploring new chiral magnetic materials based on phosphonate, we focus our attention on an unsymmetrical phosphonate ligand, i.e., (2-pyridylmethylamino)methyl phosphonate [$(2\text{-}C_5H_4N)CH_2NHCH_2PO_3^{2-}$, 2-pmamp^{2-}] (Scheme 1), which contains two additional N atoms besides three phosphonate O donors. This ligand can chelate to metal ions, forming two five-membered rings, thus providing a potential source for the generation of chirality. Two layer compounds $M^{II}\{(2\text{-}C_5H_4N)CH_2NHCH_2PO_3\}(H_2O)$ [M = Mn (**1**), Cd (**2**)] are obtained successfully. The spontaneous resolution in crystallization leads to the formation of **2** as a racemic conglomerate and, more interestingly, **1** with bulk chirality.

Compound **1** was obtained by the hydrothermal treatment of a mixture of $MnCl_2\cdot 4H_2O$ (0.1 mmol, 0.0198 g) and 2-pmampH$_2$$\cdot$HCl[18] (0.1 mmol, 0.0238 g) in 8 mL of H_2O, adjusted to pH = 8.99 with 1 M NaOH, at 140 °C for 24 h. Brown crystals were obtained as a monophasic material in a yield of 55%. Compound **2** was prepared similarly except by using $CdSO_4\cdot {}^8/_3H_2O$ instead of $MnCl_2\cdot 4H_2O$ with a pH of 5.50 (yield 58%).[19]

Single-crystal X-ray diffraction (XRD) analyses reveal that compound **1** crystallizes in monoclinic noncentrosymmetric space group $P2_1$, while **2** crystallizes in orthorhombic noncentrosymmetric space group $P2_12_12_1$.[20] As shown in Figure 1, the asymmetric unit of **1** consists of one Mn atom, one 2-pmamp^{2-}, and one coordination H_2O molecule. Each Mn is chelated by 2-pmamp^{2-} through phosphonate oxygen O1, pyridyl nitrogen N1, and amino nitrogen N2, forming a neutral Mn(2-pmamp) unit that contains two five-membered rings. The Mn(2-pmamp) units are interlocked by coordination of the other two phosphonate O atoms (O2 and O3), forming a layer in the *ab* plane (Figure 2a). A H_2O molecule completes the distorted octahedral environment around the Mn atom. The Mn−O(N) bond lengths are in the range of 2.144(6)−2.474(8) Å.

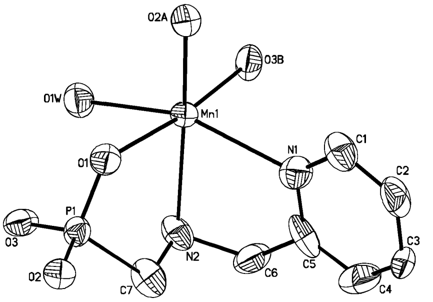


Figure 1. Building unit of structure **1** with the atomic labeling scheme (50% probability). All H atoms are omitted for clarity.

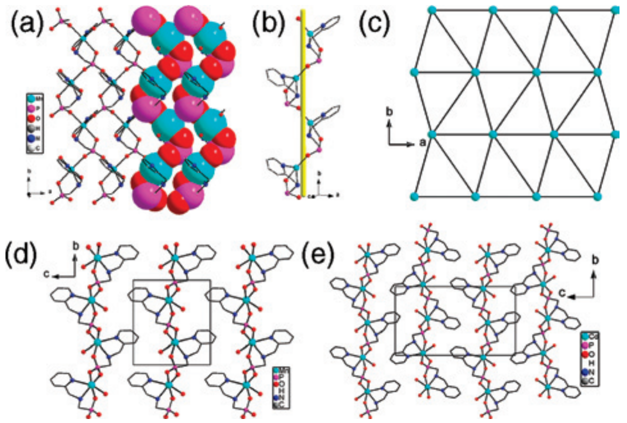


Figure 2. One layer of structure **1** viewed along the *c* axis (a); right-handed helical chain running along the *b* axis (b); topology of the inorganic layer in **1**, where O−P−O units are simplified as black lines (c); packing diagrams of structures **1** (d) and **2** (e).

It is notable that each Mn atom is a chiral center (with Λ configuration) induced by the twist in the ligand. The chirality is transmitted to layers discriminatively via O−P−O linkages along the *a* and *b* axes. Right-handed 2_1 helical chains can be observed along the *b* axis (Figure 2b). The chiral inorganic layer can be viewed as an irregular triangular topology in which the Mn atoms are linked purely through O−P−O bridges (Figure 2c). The Mn•••Mn distances over O−P−O bridges are 5.0875, 5.4753, and 6.3865 Å. The pyridyl groups are tilted on the two sides of the inorganic chiral layer, with van der Waals interactions dominant between the layers (Figure 2d). Compound **2** possesses a chiral layer structure very similar to that of **1**. However, the stacking of the layers is different in the two cases. Adjacent layers are packed in

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(19) Anal. Found (calcd) for $C_7H_{11}O_4N_2PMn$ (**1**): C, 30.78 (30.79); N, 10.12 (10.26); H, 4.00 (4.01). Anal. Found (calcd) for $C_7H_{11}O_4N_2PCd$ (**2**): C, 25.42 (25.43); N, 8.34 (8.47); H, 3.33 (3.35).

(20) Crystals of dimensions 0.07 × 0.05 × 0.04 mm for **1** and 0.10 × 0.08 × 0.06 mm for **2** were selected for indexing and intensity data collection at room temperature on a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. Crystal data for **1**: $C_7H_{11}O_4N_2PMn$, monoclinic, space group $P2_1$, a = 5.0875(10) Å, b = 10.437(2) Å, c = 9.5129(19) Å, V = 505.09(17) Å^3, Z = 2, D_c = 1.796 g cm^{-3}, μ = 1.460 mm^{-1}, $F(000)$ = 278. Unique reflections: 1731 (R_{int} = 0.0357). Least-squares refinements were based on F^2 and converged at R1 = 0.0638 and wR2 = 0.1266. Crystal data for **2**: $C_7H_{11}O_4N_2PCd$, orthorhombic, space group $P2_12_12_1$, a = 5.1070(12) Å, b = 10.461(3) Å, c = 18.714(5) Å, V = 999.8(5) Å^3, Z = 4, D_c = 2.196 g cm^{-3}, μ = 2.339 mm^{-1}, $F(000)$ = 648. Unique reflections: 1961 (R_{int} = 0.0245). Least-squares refinements were based on F^2 and converged at R1 = 0.0278 and wR2 = 0.0745. CCDC 696826 and 696827 contain the supplementary crystallographic data for this paper.

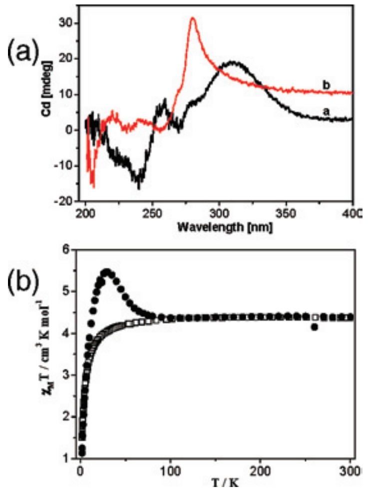

Figure 3. (a) Solid-state CD spectra for compounds **1** (a, black) and **1-de** (b, red). (b) χ_M and $\chi_M T$ vs T plots for compounds **1** (open squares) and **1-de** (filled circles).

the sequence of ···AA··· in **1** and ···ABAB··· in **2** (Figure 2e). Hence, the cell parameter is nearly doubled in the *c* direction for **2** [18.714(5) vs 9.513(2) Å for **1**].

Thermal analyses show a clear two-step decomposition for both compounds. The first-step weight loss is attributed to the release of coordination H_2O in the temperature ranges of 170−230 °C for **1** (found, 6.8%; calcd, 6.6%) and 180−260 °C for **2** (found, 5.3%; calcd, 5.4%). The second-step weight loss occurs above 350 °C in both cases, corresponding to the decomposition of the organic ligands and the collapse of the structure. In order to determine whether the layer structures are maintained after the dehydration process, compounds **1** and **2** are calcined at 260 °C for 2.5 h. The XRD measurements confirm that the layer structure of **1** remains in the dehydrated sample of **1** (**1-de**) with the interlayer distance shortened, while that of **2** collapses after removal of the coordination H_2O (Supporting Information).

Solid-state circular dichroism (CD) spectra were measured from KBr pellets for compounds **1**, **2**, and **1-de**. As shown in Figure 3a, positive Cotton effects of **1** are evident at 258 and 310 nm and a negative dichroic signal is centered at 239 nm. For **1-de**, four signals appear at 205(−), 220(+), 241(+), and 280(+) nm (Figure 3a). Apparently, both compounds **1** and **1-de** show bulk chiralities in the solid state, while compound **2** is CD-silent, indicating that **2** crystallizes as a racemic conglomerate. The second harmonic generation (SHG) properties of powder samples **1** and **1-de** were also studied. The results indicate that both exhibit SHG responses about 0.6 times that of urea.

The magnetic properties of **1** and **1-de** are measured at 1 kOe in the temperature range 2−300 K. Figure 3b shows the $\chi_M T$ vs T plots for both samples. For **1**, the room temperature effective magnetic moment of 5.92 μ_B per Mn agrees well with the expected spin-only value for $S = {}^5/_2$ (5.92 μ_B). The magnetic behavior follows the Curie−Weiss law in the whole temperature range with a Curie constant of 4.44 cm^3 K mol^{-1} and a Weiss constant of −3.02 K. The negative Weiss constant indicates a weak antiferromagnetic (AF) interaction between Mn^{II} centers. This is confirmed by the monotonous decreasing of $\chi_M T$ upon cooling. For **1-de**, the interaction between Mn^{II} ions becomes ferromagnetic, as suggested by the continuous increasing of $\chi_M T$ on cooling from 300 K (4.39 cm^3 K mol^{-1}) to 30 K (5.46 cm^3 K mol^{-1}). Below 30 K, $\chi_M T$ decreases with decreasing temperature, attributed to zero-field splitting of the ground state and/or the interlayer AF interactions. The magnetic susceptibility data in the temperature range 300−50 K can be fitted by the Curie−Weiss law, yielding a Curie constant of 4.32 cm^3 K mol^{-1} and a Weiss constant of +2.46 K.

AF interactions are commonly found in other manganese phosphonate compounds where Mn atoms are bridged by O−P−O units.[21] The observation of a ferromagnetic interaction in **1-de** is unexpected. Although the origin of this ferromagnetic interaction is still not clear to us, it could be related to the structural transformation upon heating, e.g., from a distorted octahedral environment in **1** to a distorted trigonal-bipyramidal environment around the Mn centers in **1-de**.

In summary, we describe here the first examples of metal phosphonates based on an unsymmetrical multidentate (2-pyridylmethylamino)methyl phosphonate ligand. Spontaneous resolution upon crystallization leads to the formation of compound **2** as a racemic conglomerate and **1** with enantiomeric excess. As far as we are aware, compound **1** provides one of the rare examples that nonzero enantiomeric excess can arise spontaneously from an achiral or a racemic state. It is interesting that bulk chirality is maintained for **1** after removal of the coordination H_2O. Moreover, the dehydration process also induces a transformation of the magnetic properties, e.g., from antiferromagnetic to ferromagnetic. Such behaviors could have potential applications as switches or sensors. Further work is in progress to explore new metal phosphonates combining chirality and magnetism.

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Supporting Information Available: Crystallographic files in CIF format and six figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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