

Two-Dimensional Homochiral Manganese(II)-Azido Frameworks Incorporating an Achiral Ligand: Partial Spontaneous Resolution and Weak Ferromagnetism

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The design of chiral magnets combining magnetism and optical activity has been one of the major challenges in the pursuit of polyfunctional materials. Recent interest has been encouraged by the observation of a weak effect of magneto-chiral dichroism (MChD) in paramagnetic chiral species.¹ It is expected that chiral magnets may open the prospect for observing a stronger MChD effect.² A few chiral molecular magnets, all based on coordination polymers, have been prepared, but their MChD effect remains unreported.^{2,3}

Chiral coordination compounds can be obtained either by stereoselective synthesis using chiral species^{2,4} or by spontaneous resolution upon crystallization without any chiral auxiliary.^{3,5} Spontaneous resolution, which yields a conglomerate (racemic mixture of chiral crystals), is a relatively scarce phenomenon and cannot be predicted a priori because the laws of physics determining the processes are not yet fully understood. However, if there are preferential and extended homochiral interactions between neighboring chiral components, the chirality would be able to extend to higher dimensionality, and hence the probability of spontaneous resolution should increase. The chirally discriminative interactions may arise from coordination bonds and/or hydrogen bonds.^{3,5,6}

Along these lines, we focus our attention on building chiral azido-bridged magnets. The use of the azido ion as a bridge has been an intriguing synthetic approach to molecular magnets due to their remarkable diversities in structural and magnetic behaviors.⁷ To impart chirality, we are interested in open-chain diazine ligands bearing two bidentate sites, such as 2-pyridylmethylketazine (PMK), because these achiral ligands are potential sources of atropisomeric chirality: upon coordination as a bridge, the freedom of the ligands to rotate about the N–N bonds is restrained, and the ligands are locked in a twisted chiral conformation. In fact, single-, two-, and three-strand binuclear helicates have been prepared from these ligands, but spontaneous resolution rarely occurred due to the lack of homochiral intermolecular interactions.⁸ Our strategy is to link the binuclear units into higher dimensionality with azido bridges. In this Communication, we reported an interesting Mn(II)-azido-diazine system that exhibits *partial spontaneous resolution*, in which the chiral binuclear units generated from achiral components are connected into a homochiral 2D layer via 1D helical coordination bonds, and the layers are stacked in a hetero- and homochiral fashion to yield simultaneously racemic and chiral crystals. Both compounds behave as spin-canted weak ferromagnets.

When the solution obtained from the reaction of PMK with $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and NaN_3 in methanol was allowed to evaporate slowly at room temperature, two kinds of yellow crystals with different shapes, prism (**1**) and hexagonal plate (**2**), appeared and were separated manually (see Supporting Information for experi-

mental details). X-ray analyses revealed a racemic structure for **1** and a chiral one for **2**.⁹ In both structures, two neighboring Mn(II) ions are triply linked by a N–N diazine and two end-on azido bridges to form a dinuclear unit, and each dinuclear unit is connected to four neighboring identical motifs through single end-to-end bridges, generating a homochiral 2D layer with an interesting fish-scalelike topology (Figure 1a and b). The 2D network may be denoted as a (6,3) net (each Mn(II) as a node) or a (4,4) net (each dinuclear unit as a node).

Each metal ion, ligated by an unsymmetric bidentate pyridylimine group and two different pairs of cisoid azido ligands, is obviously a chiral center (Δ configuration in Figure 1). What interests us is how the homochirality is induced and transmitted within the 2D layer. The chirality of the dimeric unit is induced primarily by the lock of the diazine ligand in a twisted chiral conformation (*M* helicity in Figure 1) upon coordination. The dihedral angles between the two halves of the ligand are 79.2° for **1** and 58.7° for **2**, and the Mn–N–N–Mn torsion angles are 32.6° and 27.9° , respectively. This imparts chirality to the triply bridged moiety, which consists of two end-on azido bridges plus the N–N bridge. The chiral linkage attached with two chelate groups is chirally discriminative and requires that the two metal coordination spheres exhibit the same absolute configuration. The chirality is preserved when the dimers are interlinked into the 2D network. The homochiral interdimer interactions arise from the unique bridging topology of the azido bridges. Each Mn(II) ion is linked to two others from adjacent dimers via two cisoid end-to-end bridges with the Mn–N–N–Mn linkage in a gauche configuration (the Mn–N₃–Mn torsion angles are 25.2° for **1** and 67.3° for **2**). This results in an infinite helical Mn–N₃ chain around a 2_1 screw axis (*P*-helicity in Figure 1). The helical linkage is also chirally discriminative, and it is obligatory that all metal ions in a helix have the same chirality. Therefore, considering that the two Mn(II) sites in a dimer are also homochiral, all of the Mn(II) sites in a layer must be homochiral, as must all of the helical chains in the layer. One may say that the chirality of the dimer is transmitted via the discriminative helical linkage or, alternatively, that the chirality of the helical chain is transmitted via the discriminative triply bridged units.

In both crystals, the chiral layers extend parallel to the *ab* plane and are stacked along the *c* direction. In **1**, adjacent layers are related by inversion centers and exhibit opposite chirality, so the whole crystal is heterochiral and hence racemic. In **2**, however, adjacent layers are related by 3_1 screw axes and stacked in an *ABCABC* fashion (*A*, *B*, and *C* represent layers of different orientations but of the same chirality), resulting in a homochiral crystal. There is no preferential interlayer interaction for homochiral discrimination. The simultaneous crystallization of the racemic and chiral crystals

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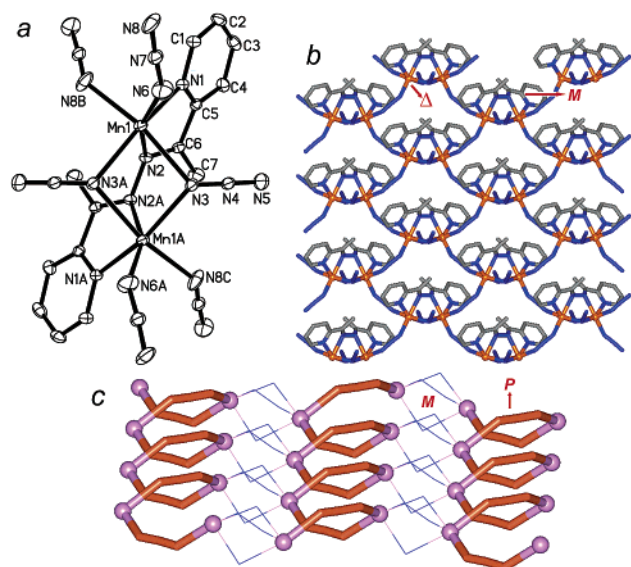


Figure 1. Views of the binuclear unit (a) and the 2D layer showing the scalelike network (b) and highlighting the homochiral 1D helical linkage (c, only Mn and the bridging atoms are shown for clarity) in **1**.

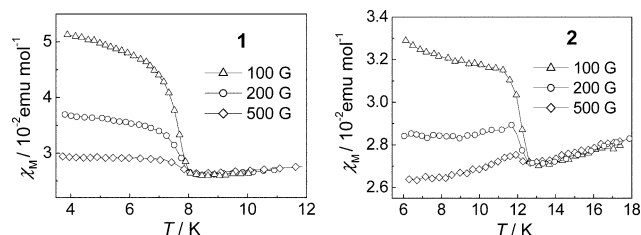


Figure 2. Field-cooled susceptibility of **1** and **2** at different fields.

suggests that a *partial spontaneous resolution* occurs and that the energetic difference between them should be very small, if any.

The magnetic susceptibilities of the racemic compound and the conglomerate were measured in the 2–300 K range at 5000 G (see Supporting Information for the $\chi_M T$ – T and $\chi_M T$ – T plots). For both compounds, the $\chi_M T$ values at 300 K are ca. 3.8 emu K mol^{−1}, lower than the spin-only value (4.38 emu K mol^{−1}) for a high-spin Mn(II) ion. Upon cooling, $\chi_M T$ decreases monotonically, while χ_M increases to a rounded maximum at about 40 K and then decreases on further cooling. These features indicate a global antiferromagnetic interaction in these compounds.

Field-cooled magnetization measurements were performed under lower fields (Figure 2). Under these fields, both **1** and **2** exhibit weak spontaneous magnetization characteristic of weak ferromagnets, but the critical temperatures are different, as indicated by the abrupt rise in the χ_M values below 8 K for **1** and 12.5 K for **2**. The weak ferromagnetic transitions should be due to the phenomenon of spin canting, which is consistent with the field dependence of the cryomagnetic behaviors: the magnetic transitions are less pronounced at higher fields, and the spontaneous moments are so weak that they are nearly repressed by a field of 5000 G. In the absence of single-ion magnetic anisotropy [Mn(II), high spin], the spin-canted structure should arise from the antisymmetric exchange mechanism,¹⁰ consistent with the lack of inversion center between neighboring Mn(II) ions and the systematic alternation of differently oriented metal chromophores within the layer.^{10c,d} Further evidence for the weak ferromagnetism comes from the field-dependent magnetization and zero-field-cooled magnetization (see Supporting Information).

In summary, we present here the first example of a simple synthetic strategy for building chiral molecular magnets with azido bridges.¹¹ By incorporating an achiral ligand that can be locked in a chiral conformation, we induced a homochiral 2D layer, in which the chirality is transmitted via extended homochiral coordination interactions, and different packing fashions of the layers lead to a partial spontaneous resolution. This shows an unusual example of *incomplete evolution in chirality*, a progression from achiral species, to chiral dimers, to chiral 2D layers, and finally to both racemic and chiral crystals. The resulting compounds exhibit weak ferromagnetic behaviors at different critical temperatures. Further investigations are underway, including magnetic and optical measurements of the present magnets and an extension of the strategy into other systems.

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Supporting Information Available: Experimental details, supplementary magnetic studies (PDF), and crystallographic data (CIF) for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) Crystal data for [Mn₂(PMA)(N₃)₄]_n (**1**): 293 K, monoclinic, $C2/c$, $a = 15.0691(4)$, $b = 7.8290(3)$, $c = 17.4369(4)$ Å, $\beta = 96.088(2)^\circ$, $V = 2045.53(11)$ Å³, $Z = 4$, $R = 0.0346$, $\text{GOF} = 1.012$. Crystal data for [Mn₂(PMA)(N₃)₄]_n·*n*(MeOH) (**2**): 293 K, trigonal, $P3_121$, $a = 8.0488(11)$, $b = 8.0488(11)$, $c = 30.552(6)$ Å, $V = 1714.1(5)$ Å³, $Z = 3$, $R = 0.0425$, $\text{GOF} = 1.026$ (see Supporting Information for further details).
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