A Manganese Carboxylate with Geometrically Frustrated Magnetic Layers of Novel Topology

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A new two-dimensional coordination polymer, $Mn_2(THFTC)(H_2O)_3$ (THFTC = tetrahydrofuran-2,3,4,5-tetracarboxylate), was hydrothermally synthesized and characterized by single-crystal X-ray diffraction and magnetic measurements. The Mn^{2+} cations, linked by the carboxylate groups of the THFTC, form a geometrically frustrated network with a novel $(3.5^3)(3.5.3.5)$ topology. This topology is closely related to the widely investigated triangular and Kagome lattices. According to the magnetic measurements, the compound does not establish a long-range ordered state down to 1.8 K, a sign for possible spin frustration.

Introduction

Geometrically frustrated antiferromagnetic (AF) systems built of polygons with odd numbers of edges, triangles for example, are of great interest because of their fascinating magnetic properties and pertinence to some fundamental physics such as high-temperature superconductivity and spin chirality.[1] The AF interactions between the spins (nearest interactions only) in such polygons compete with each other and cannot be completely satisfied. For an infinite lattice this geometric frustration might result in a very large number of ground states with similar energies that can exist simultaneously. Thus, the frustration of the spins tends to prevent establishment of long-range magnetic order, even at very low temperatures, and often leads to observation of novel low-temperature magnetic phenomena such as spin-glasses,[2] spin-liquids,[3] and spin-ice.[4] The theoretical parameter $F_c = -1/(1 - p)$, where p is the number of spins in a cluster, has been proposed in order to rank the geometric frustration of different lattices. For example, F_c is -1 for a nonfrustrated lattice and -0.5 for triangular and Kagome lattices. However, this parameter works well for simple lattices with one unique node, and its significance is primarily at the theoretical level. Experimentally, another frustration parameter, defined as $f = |\theta/T_c|$, where θ is the Weiss constant of the Curie−Weiss law and T_c is an eventual critical

temperature for ordering in the system,[1] is widely used to measure the relative degree of the spin frustration. The Weiss constant θ is a measure of the energy of the magnetic interactions and a rough sum of all exchange interactions [$\theta = 2S(S + 1)/3k\sum_n z_n J_n$, where n and J_n are the nth neighbor and corresponding magnetic coupling]. For a nonfrustrated lattice, f is relatively small (f is about 1 for a ferromagnet and 2−4 for an antiferromagnet), but for a spin-frustrated lattice, it is usually quite larger since the long-range ordering is prohibited by the competing interactions. This parameter is usually larger than 10 for significantly frustrated lattices.

Numerous geometrically frustrated networks, from one-dimensional to three-dimensional, have been discovered and thoroughly investigated in recent years.[1−5] Among them, the 2D Heisenberg triangular and Kagome antiferromagnets are two of the most interesting topologies because, in addition to the experimental efforts, they are susceptible to theoretical modeling.[6] Although in theory there are many possible frustrated 2D lattices,[6a] their experimental realization has been very rare.[1a,b] Herein, we report the synthesis and characterization of a manganese carboxylate coordination polymer, $Mn_2(THFTC)(H_2O)_3$, where THFTC = tetrahydrofuran-2,3,4,5-tetracarboxylate, with a two-dimensional geometrically frustrated network of a $(3.5^3)(3.5.3.5)$ topology. The magnetic measurements show that long-range magnetic

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ordering does not occur all the way down to 1.8 K, and this suggests possible spin-frustration.

Experimental Section

All starting materials (reagent grade) were used as purchased without further purification. The magnetizations of a polycrystalline sample were measured at different temperatures and different fields on a Quantum Design MPMS SQUID system. All experimental magnetic data were corrected for the diamagnetism of the sample holders and of the constituent atoms.[7]

$Mn_2(THFTC)(H_2O)_3$ was synthesized by a hydrothermal reaction of $MnCl_2 \cdot 4H_2O$ (530 mg, 2.68 mmol), THFTC (55 mg, 0.22 mmol), and NaOH (1.2 mmol, 1.2 mL for 1 M) in 3 mL of water (final pH $\sim$ 5.0) carried out in a 23 mL Teflon-lined autoclave at 140 °C for 2 days. Colorless wedge-shaped crystals of the compound were recovered (40% yield based on H_4THFTC) together with a very small amount of yellow powder.

X-ray diffraction data of a single crystal of $Mn_2(THFTC)(H_2O)_3$ ($0.24 \times 0.19 \times 0.05$ mm) were collected on an Enraf-Nonius CAD4 diffractometer at room temperature with Mo Kα radiation ($\lambda = 0.71073$ Å, $\theta_{max} = 25°$). The structure was solved by direct method and refined by a full-matrix least-squares technique based on F^2 using the SHELXL97 program. All hydrogen atoms of the framework were refined as riding on the corresponding non-hydrogen atoms while they were fixed to the ideal geometry for the coordinated H_2O molecules. Crystal data: monoclinic, $P2_1/c$, $a = 14.8704(3)$ Å, $b = 7.6902(2)$ Å, and $c = 10.6506(3)$ Å, $\beta = 102.570(2)°$, $V = 1188.77 (5)$ Å,^{3} $Z = 4$, R1 = 0.0555 for 224 parameters and 1871 unique reflections with $I > 2\sigma(I)$, and wR2 = 0.1418 for all 2086 reflections. Atomic coordinates, equivalent isotropic displacement parameters, and important distances are available as Supporting Information.

Results and Discussion

The structure of $Mn_2(THFTC)(H_2O)_3$ is made of layers that are held together only by hydrogen bonds between coordinated water molecules and carboxylic groups. The asymmetric unit contains two different Mn atoms, one fully deprotonated THFTC ligand, and three coordinated water molecules (Figure 1a). Both Mn atoms are octahedrally coordinated: Mn1 by three different THFTC linkers and two water molecules in a cis position and Mn2 by three different THFTC linkers and one water molecule. The octahedra are slightly distorted with ranges of Mn−O distances of 2.14−2.21 and 2.12−2.29 Å for Mn1 and Mn2, respectively. The THFTC linker uses all of its nine oxygen atoms to coordinate to five Mn atoms, two Mn1 and three Mn2. There are two bridging modes for the carboxylic groups: syn−anti for two of them and anti−anti for the other two. This leads to four different Mn−Mn distances: Mn1−Mn1C = 5.99 Å, Mn1C−Mn2 = 6.05, Mn1−Mn2B = 4.64 Å, and Mn2−Mn2A = 5.81 Å (Figure 1). These four bridging carboxylic groups can transmit moderate magnetic coupling, mostly antiferromagnetic,[8] and present four different magnetic pathways between Mn^{2+} ions, as shown in different colors in Figure 1c.

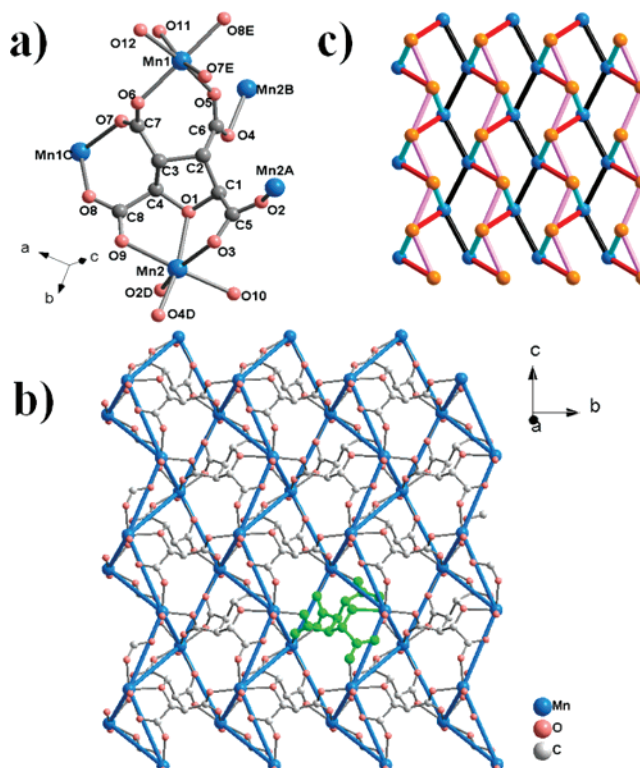The layers in $Mn_2(THFTC)(H_2O)_3$ (Figure 1b) are parallel to the *bc* plane, and each layer has the stoichiometry of the

Figure 1. (a) The local coordination environments of Mn1, Mn2, and THFTC in $Mn_2(THFTC)(H_2O)_3$. (b) The 2D network of the compound with blue lines showing the connectivity between the Mn^{2+} ions linked by carboxylic groups (highlighted in green is one THFTC molecule). (c) The simplified 2D network with lines in different colors showing different distances (blue and orange spheres correspond to Mn1 and Mn2, respectively).

compound itself. The Mn-atoms in a layer are not coplanar but rather form two planes, one containing Mn1 and the other Mn2 (Figure 2). In the layer, although the Mn^{2+} ions are interconnected by the THFTC linkers, magnetic coupling is possible only via the carboxylic groups (COO). In other words, there is no magnetic coupling via the C−C and C−O bonds of the organic core of the linker. This simplifies greatly the magnetic array to a simple 2D topology, as shown in Figure 1c, where the four different Mn−Mn distances and two different Mn atoms are shown in different colors. Each Mn atom in this magnetic lattice is a four-connected node with two Mn1 and two Mn2 neighbors. Interestingly, this topology contains two different polygons with odd numbers of atoms, triangles and pentagons. Although all nodes are four-connected, they are of two different types, and this leads to a binodal novel topology denoted as $(3.5^3)(3.5.3.5)$. The layers are held together by very short hydrogen bonds between coordinated water molecules and carboxylic groups with distances of 2.73 and 2.75 Å (Figure 2), and this results in a short interlayer Mn−Mn distance of 5.14 Å.

The novel topology of the layers is closely related to and apparently can be derived from a simple triangular lattice or its Kagome derivative. As shown in Figure 3, the

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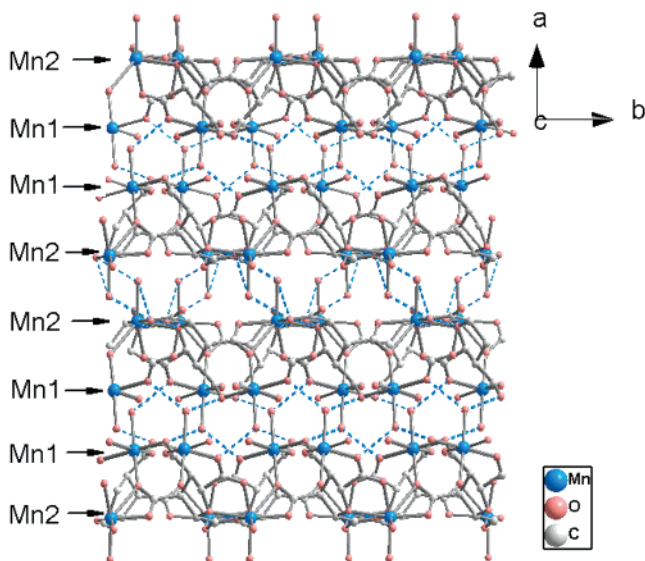
Figure 2. The structure of $Mn_2(THFTC)(H_2O)_3$ viewed along the layers (the c-axis). Each layer has two levels, one that contains only Mn1 and another with Mn2 only.
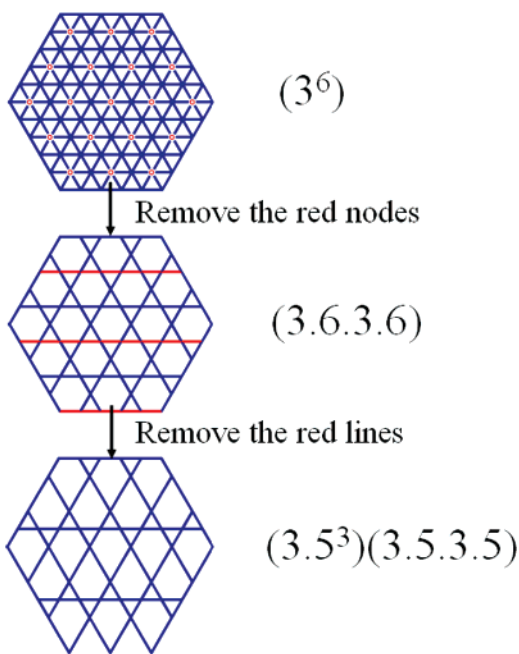

Figure 3. The relationship between the triangular lattice (top), Kagome net (middle), and the $(3.5^3)(3.5.3.5)$ topology in $Mn_2(THFTC)(H_2O)_3$.

triangular lattice, a hexagonal close-packed layer, has one six-bonded unique node and is denoted as (3^6). The Kagome lattice, denoted as $(3.6.3.6)$, is derived from the triangular lattice by removal of every third node without generating neighboring defects (Figure 3). Although the resulting nodes are all equivalent and four-bonded, the lattice is made of two kinds of polygons, triangles and hexagons. The decrease in the number of neighbors from six in the triangular lattice to four in the Kagome lattice permits more freedom for the alignment of the magnetic moments, so that Kagome antiferromagnets are anticipated to exhibit more ground states with similar energy.[6a] Further removal of a quarter of the vertices in the Kagome net, specifically those in straight lines as shown in Figure 3, lowers the lattice symmetry further and results in the observed here topology $(3.5^3)(3.5.3.5)$ of the layers of $Mn_2(THFTC)(H_2O)_3$. Along the "evolution"

chain, this binodal topology can be viewed as a Kagome lattice with ordered defects.

Although the topology $(3.5^3)(3.5.3.5)$ can be easily predicted by the removal of vertices in a Kagome net as described above, it appears that $Mn_2(THFTC)(H_2O)_3$ is the first real compound with such a lattice. Like the Kagome net, this topology contains two different polygons, but this time they are triangles and pentagons. Both polygons have odd numbers of vertices, and antiferromagnetic spin coupling is expected to lead to spin frustration. The polygons are connected to each other by sharing corners (triangles) or both edges and corners (pentagons). Also, like the Kagome net, all nodes in $(3.5^3)(3.5.3.5)$ are four-bonded. Half of them are surrounded by one triangle and three pentagons while the other half have two triangles and two pentagons as neighbors.

Another important aspect of $Mn_2(THFTC)(H_2O)_3$ is the short interlayer Mn−Mn distance of 5.14 Å, which is much sorter than in most 2D magnetically frustrated lattices. For example, the interlayer distance in the jarosite compounds $AFe_3(SO_4)_2(OH)_6$ with Kagome lattices and $f > 10$ is about 6 Å,[9] it is 8 Å in the triangular lattices of $AM(SO_4)_2$ ($f = 6-10$),[10] and about 13 Å in $(4,4'-bpy)Cu_3(OH)_2(MoO_4)_2$ ($f = 19.4$) and $Co(N_3)_2(bpg)(DMF)_{4/3}$ ($f = 10$) with complex layer structures.[5a,11] The interlayer magnetic exchange through dipole−dipole interactions (which increases with the magnitude of the spin) and/or through hydrogen bonding does play an undeniable role in these frustrated systems and leads to magnetic long-range ordering in all of them. In this respect, the short interlayer distance in $Mn_2(THFTC)(H_2O)_3$ suggests some three-dimensionality of the magnetic interactions. This, in turn, would be an indication of a three-dimensional magnetically frustrated system of triangular plaquettes. Compared with the long-range ordered ground states of the compounds mentioned above and despite its short interlayer distance, hydrogen bonding, and expected stronger interlayer magnetic interactions, $Mn_2(THFTC)(H_2O)_3$ does not show long-range ordering above 1.8 K (vide infra). In other words, the absence of long-range ordering in $Mn_2(THFTC)(H_2O)_3$ is more likely due to geometric spin frustration than low-dimensionality, as in many layered compounds.

Shown in Figure 4 are the field dependence of the magnetization of $Mn_2(THFTC)(H_2O)_3$ measured at 2 K as well as the temperature dependence of its magnetic susceptibility measured at 1 kOe and displayed as $\chi_m T(T)$ and $\chi_m^{-1}(T)$. The room-temperature value of 4.24 cm³mol⁻¹K for $\chi_m T$ (theoretical value of 4.375 cm³ mol⁻¹ K for a spin-only weak-field Mn^{2+} ion) decreases monotonously to 0.6 cm³ mol⁻¹ K at 2 K. The inverse molar susceptibility above 50 K fits well the Curie−Weiss law with a Curie constant $C = 4.38$ cm³ mol⁻¹ K and a Weiss temperature $\theta = -10.8$ K. The negative Weiss constant indicates overall antiferromagnetic coupling between the Mn^{2+} ions. The AF coupling is also confirmed by the field dependence of the isothermal

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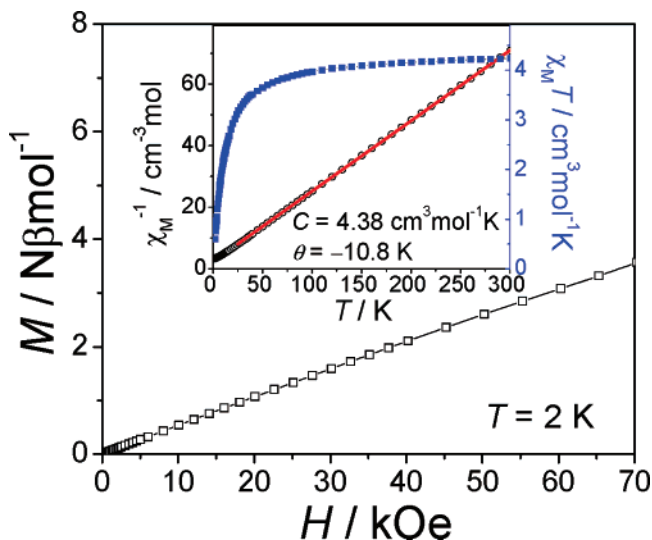(11) Shores, M. P.; Bartlett, B. M.; Nocera, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 17986.

Figure 4. The field dependence of the magnetization of $Mn_2(THFTC)$-$(H_2O)_3$ at 2 K. Shown in the inset is the temperature dependence of $\chi_m T$ and χ_m^{-1} at 1 kOe and the Curie$-$Weiss fit (red line) of the latter.

Figure 5. The field-cooled and zero-field-cooled magnetization of Mn_2-$(THFTC)(H_2O)_3$ at 20 Oe.

magnetization $M(H)$ at 2 K, which shows a linear increase with the field and reaches 3.56 μ_B at 70 kOe, a value that is far below the saturation value 5 μ_B expected for a spin-only Mn^{2+} ion.

The field-cooled (FC) and zero-field-cooled (ZFC) magnetizations of the compound were measured at a low field of 20 Oe down to 1.8 K (the lowest reachable temperature in our SQUID system) in order to check for eventual long-range ordering at low temperatures. The two curves are identical and completely superimposed on each other (Figure 5), suggesting there is no spontaneous magnetization of $Mn_2(THFTC)(H_2O)_3$ down to 1.8 K. They are smooth from 20 K down to 2.6 K, where a very small abnormality appears on the ZFC and FC curves. The origin of the abnormality is not clear and might be due to impurities or short-range order. However, the absence of a peak on the curves rules out antiferromagnetic long-range ordering. This suggests that the compound retains its paramagnetic state and does not order above 1.8 K. Therefore its frustration parameter $f = |\theta/T_N|$ is at least larger than 6.0 (10.8/1.8). This indicates a reasonable frustration in this geometrically frustrated antiferromagnetic network. It compares well with, for example, the frustration factors for the well-known family of compounds with triangular lattices $RFeSO_4$ (R = K, Rb, Cs) with
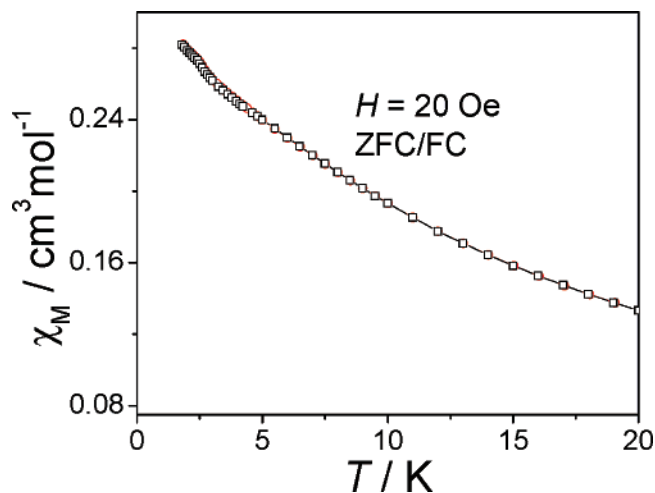
f in the range 6$-$10 and the frustrated lattice of $CoTi_2O_6$ with f of 5.0.[10,12]

In summary, a novel geometrically frustrated metal$-$organic coordination polymer with binodal topology denoted as $(3.5^3)(3.5.3.5)$ was synthesized and characterized structurally and magnetically. The topology is closely related to the widely investigated triangular and Kagome lattices. It is the first experimental realization of this specific topology and enriches the family of two-dimensional geometrically frustrated lattices. Magnetic measurements also suggest the existence of the spin-frustration in this compound.

Supporting Information Available: X-ray crystallographic CIF file and tables with atomic coordinates, equivalent isotropic displacement parameters, and important distances. This material is available free of charge via the Internet at http://pubs.acs.org.

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