Communication

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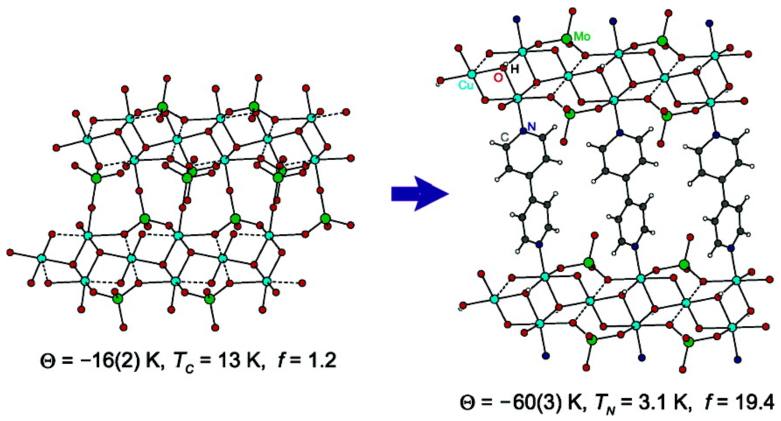

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Spin-Frustrated Organic-Inorganic Hybrids of Lindgrenite

Matthew P. Shores, Bart M. Bartlett, and Daniel G. Nocera*

Department of Chemistry, 6-335, Massachusetts Institute of Technology, 77 Massachusetts Avenue,
Cambridge, Massachusetts 02139-4307

Received September 28, 2005; E-mail: nocera@mit.edu

Geometric spin frustration occurs when the structural arrangement of spins precludes the simultaneous satisfaction of all nearest-neighbor interactions.[1] The determination of the magnetic ground state(s) arising from such frustration is important to the understanding of highly correlated systems. Of particular interest are $S = {}^1/_2$ systems, in which quantum fluctuations can dominate the ground-state properties.[2] Compounds with $S = {}^1/_2$ ions residing on a triangular lattice, however, are uncommon.[3] One intriguing system possessing such a structure is the rare copper molybdate mineral lindgrenite, $Cu_3(OH)_2(MoO_4)_2$, the crystal structure of which is shown in Figure 1.[4] The mineral crystallizes in the space group $P2_1/n$ and is composed of alternating corner- and edge-sharing triangular chains of $CuO_4(OH)_2$ octahedra comprising two crystallographically distinct Cu atoms. The triangular chains are organized into layers by molybdate anions to form the three-dimensional structure shown in Figure 1b. We report here that although lindgrenite is a ferromagnet, the incorporation of organic pillaring agents disrupts ferromagnetic exchange to unveil a spin-frustrated antiferromagnetism consonant with the presence of $Cu_3(\mu_3\text{-}OH)$ triangles composing the layers.

We have developed hydrothermal protocols to synthesize triangular layered materials composed of magnetic ions of various spin states.[3,5] Survey studies were undertaken to adapt such methods for the preparation of lindgrenite in the presence of ditopic bases such as 4,4′-dipyridyl and piperazine as pillaring agents since it is established that nitrogen donor ligands effectively separate Cu(II) molybdate layers in hybrid organic−inorganic materials.[6] A hydrothermal reaction employing stoichiometric amounts of $Cu(OH)_2$, $Cu_2(OH)_2CO_3$, 4,4′-dipyridyl, and ammonium dimolybdate proceeds cleanly to afford a single Cu(II)-containing product, (4,4′-bpy)$Cu_3(OH)_2(MoO_4)_2$ (**1**), according to the following:

$$\begin{aligned}&(4,4'\text{-bpy}) + Cu_2(OH)_2CO_3 + Cu(OH)_2 + \\ &(NH_4)_2Mo_2O_7 \rightarrow (4,4'\text{-bpy})Cu_3(OH)_2(MoO_4)_2 + 2\,NH_3 + \\ &2\,H_2O + CO_2 \quad (1)\end{aligned}$$

A similar hydrothermal method employing piperazine has been developed to form (pip)$Cu_3(OH)_2(MoO_4)_2$ (**2**). Full experimental details are provided in the Supporting Information.

The inorganic portion of the single-crystal X-ray structure of **1** is shown in Figure 1a; the structure of **2** is homologous. Two crystallographically distinct Cu sites are found. On the Cu(1) site, three oxygen atoms from molybdate anions, two hydroxides, and one nitrogen atom from the 4,4′-dipyridyl ligand surround the Cu center, with the hydroxide ligands arranged in a cis fashion. On the Cu(2) site, four oxygen atoms from the molybdates and two trans hydroxides compose the primary coordination sphere. Jahn−Teller distorted Cu(II) octahedra form complex chains of alternating corner- and edge-sharing $Cu_3(\mu_3\text{-}OH)$ triangles. The chains are then linked by three of the four oxygen atoms of the molybdate anions to form $Cu_3(OH)_2(MoO_4)_2$ layers. The connectivity of Cu(II) ions through the pyramidal base of MoO_4^{2-} is structurally analogous to lindgrenite (Figure 1b). However, the Cu−O−Mo linkage involving the apical oxygen of the MoO_4^{2-} pyramids of lindgrenite is disrupted in **1** and **2** by the pillaring agents. Instead, interlayer communication in **1** and **2** is established by coordination of the ditopic base to Cu ions in adjacent layers. Though the organic spacer lowers the overall symmetry of the structure to $P\bar{1}$, as shown in Table S1, the structure of the inorganic layers is conserved across the series. Structurally, the main effect of the organic spacers is to increase the interlayer separation from 7.012(3) Å in lindgrenite to 13.456(2) Å in **1** (and to 9.447(2) Å in **2**).

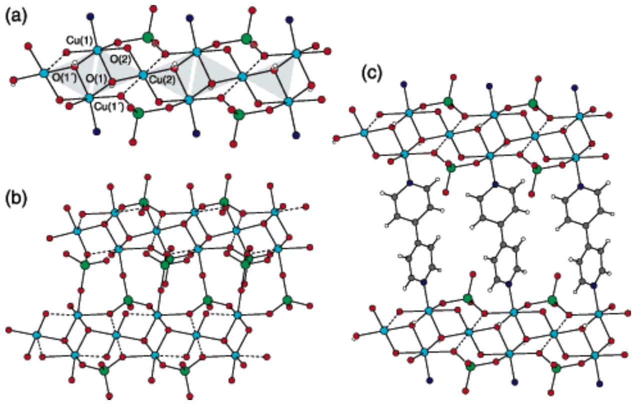

Figure 1. (a) $Cu_3(OH)_2$ chains in lindgrenite and (4,4′-bpy)$Cu_3(OH)_2(MoO_4)_2$ (**1**); structure of latter is shown. Gray triangles highlight nearest-neighbor magnetic coupling through hydroxide bridges. Chains are linked by molybdate anions to form $Cu_3(OH)_2(MoO_4)_2$ layers (see Supporting Information). Molybdate anions and dipyridyl ligands link the layers in (b) lindgrenite and (c) **1**, respectively. Light blue, red, green, blue, gray, and white spheres represent Cu, O, Mo, N, C, and H atoms, respectively. H atoms are omitted in the lindgrenite structure.

A microcrystalline sample of lindgrenite was prepared,[7] and its magnetic susceptibility was examined to provide a point of reference for the organic-hybrid structures. Fits of the high-temperature susceptibility data of lindgrenite to the Curie−Weiss law indicate a net antiferromagnetic nearest-neighbor coupling, with $\Theta_{CW} = -16$ K. Low temperature data show ferromagnetic long range ordering occurring at $T_C = 13$ K (Figure S2a). This presence of a dominant ferromagnetic exchange interaction was confirmed by the observation of hysteresis loops in M(H) plots (Figure S2b).

The magnetic properties of (4,4′-bpy)$Cu_3(OH)_2(MoO_4)_2$ (**1**) shown in Figure 2 are notably distinct from lindgrenite. A Curie−Weiss fit to the high-temperature susceptibility data yields a Θ_{CW} of −60 K. Consistent with the observed antiparallel nearest-neighbor coupling, antiferromagnetic ordering is observed at low temperature and low field ($H_{meas} = 100$ Oe, $T_N = 3.1$ K). Ramirez has provided a measure for spin frustration by defining $f = |\Theta_{CW}|/T_N$, with values of $f > 10$ signifying a strong effect.[8] As is evident from $f = 19.4$, **1** exhibits the signature of a highly frustrated magnetic system. In

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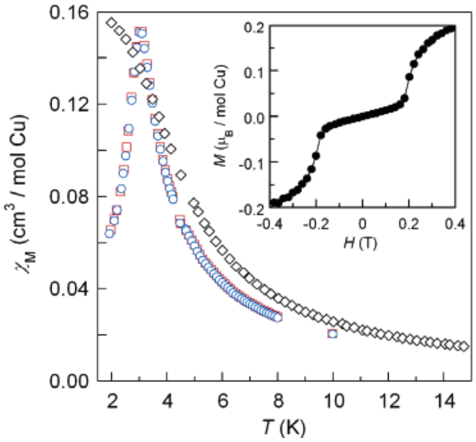


Figure 2. Temperature dependence of χ_M for **1** as measured at 100 Oe under zero-field cooled (□) and field-cooled (○) conditions, and at 1 T under zero-field cooled conditions (◇). Inset: field dependence of the magnetization per mole of Cu for **1**, measured at 2 K. The line is drawn to guide the eye.

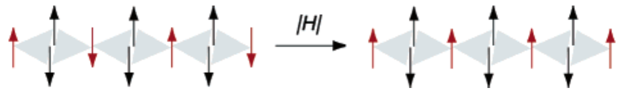
a larger measuring field (1 T), all ordering is suppressed down to the lowest temperature that we measured, 2 K.

The magnetization vs field plot at 2 K (Figure 2, inset) for **1** shows no hysteresis at very low fields, which is consistent with antiferromagnetic ordering. Starting at slightly larger fields (±0.16 T), however, the magnitude of the magnetization increases rapidly with increasing field relative to the low field response. At the highest fields (5 T), the magnetization saturates at 0.34 μ_B/mol Cu, which is consistent with one unpaired electron for every three Cu centers (Figure S3b).

The nearest-neighbor exchange interactions of lindgrenite and **1** are expected to be similar owing to the structural homology of the inorganic layers**.** Within each layer, Cu(II)-based spins most directly communicate via an oxygen atom of the bridging hydroxide of $Cu_3(\mu_3\text{-OH})$ triangles (Cu(1)−O(1)−Cu(2)) and of the pyramidal base of the MoO_4^{2-} anion (Cu(1)−O(2)−Cu(2)). An orbital analysis for Cu−O(H)−Cu bond angles (98−112°) in the $Cu_3(\mu_3\text{-OH})$ triangles for both compounds is consistent with an antiferromagnetic exchange interaction,[9] whereas the more acute angle Cu−O(Mo)−Cu bond angle of <90° is expected to show a ferromagnetic exchange interaction. In a competitive environment, antiferromagnetic interactions tend to dominate,[10] consistent with the observed values of Θ_{CW} for **1** and lindgrenite.

Despite the similar intralayer magneto structure, the properties of **1** and lindgrenite diverge significantly when interlayer interactions are considered. As shown in Figure 1b, a Cu−O−Mo−O−Cu interlayer exchange pathway is established via the MoO_4^{2-} anions, which directly bridge layers through the apical oxygen. This exchange pathway is precluded by the organic pillars of **1**; studies of model complexes show that coupling of Cu(II) spin centers through 4,4′-bipyridyl is negligible.[11] Presumably, the ferromagnetic transition in lindgrenite is associated with interlayer coupling, as this is the only significant difference in exchange pathways between the native and inorganic−organic hybrid layered structures.

With interlayer exchange prevented by pillaring, the antiferromagnetism within layers of **1** is clearly uncovered. As shown in the scheme below, the Cu(1) centers compose Cu(1)[(μ-O(1))(μ-O(1′))]Cu(1′) (d(Cu(1)−Cu(1′) = 3.049 Å) chains of antiferromagnetically coupled dimers (black spins):



Spins on Cu(2) centers (red), which connect these chains within the intralayer, are geometrically frustrated (d(Cu(1)−Cu(2) = 3.106 Å). To maintain antiferromagnetic long range order below T_N, the Cu(2) centers must alternate spin orientation within each chain, thus accounting for the $f = 19.4$ in **1**. We believe that this frustration underpins the observed field-dependent jumps in the magnetization shown in Figure 2 (inset). As the field is increased beyond a critical point ($T < T_N$), competing antiferromagnetic interactions become strong for enough to disrupt the Cu(2) spin orientations. As a result of this metamagnetic transition, the Cu(2) spins attain parallel alignment within the chain, resulting in a net one spin per $Cu_3(\mu_3\text{-OH})$ triangle.

Organic−inorganic hybrid structures formed from the introduction of organic pillars within 2D layers can give rise to a variety of interesting properties, including ion exchange, ionic and electronic conduction, sorption, and catalysis.[12] The foregoing results demonstrate that the interesting magnetic phenomenon of spin frustration can be exposed when the magnetism of inorganic layers is isolated by organic pillars.

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Supporting Information Available: Synthetic protocols and characterizations of lindgrenite, **1**, and **2** and crystallographic tables for **1** and **2** (PDF). Full X-ray crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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