Frustrated Magnets

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A “Star” Antiferromagnet: A Polymeric Iron(III) Acetate That Exhibits Both Spin Frustration and Long-Range Magnetic Ordering**

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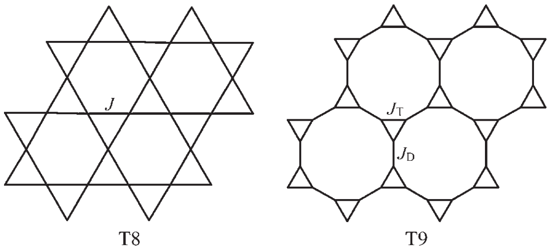
The preparation of new geometrically spin-frustrated magnetic materials[1] that approximate theoretical models[1,2] is a challenge. Although the Mermin–Wagner theorem[3] indicates that long-range magnetic order can exist in two dimensions at zero Kelvin, order can be destroyed either by quantum fluctuations or geometric frustration even at this temperature. Theoretical studies indicate that the ground state of a spin-1/2 Heisenberg antiferromagnet is most likely to be semi-classically ordered.[4] However, the interplay of geometric frustration and quantum fluctuations has been found to give rise to a paramagnetic ground state without semi-classical long-range order in two types of lattice.

The first of these lattices is the famous Kagomé lattice (T8) and the second is the so-called “star” lattice (T9; Scheme 1), which may serve as a new example of a quantum paramagnet.[4,5] The triangles are corner-sharing in the Kagomé lattice whereas they are separated by a bridge in the star lattice, which means that their next-nearest-neighbor exchange interactions are different.[4,5] The magnetic J exchange pathways in the Kagomé lattice are all equivalent, whereas the intra-triangular J_T pathway in the star lattice is weaker than the inter-triangular J_D pathway. In contrast to the rapid development of Kagomé-type antiferromagetic lattices[6,7] and related, geometrically spin-frustrated lattices,[8] there appears to date to be no report of a compound with a genuine star lattice.



Scheme 1. A comparison of the Kagomé (T8, left) and star (T9, right) lattices with indication of the magnetic *J* exchange pathways.

Triangular clusters with superexchange pathways, such as the widely employed $M_3(\mu_3\text{-}O)$ clusters, where M may be Fe^{III}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, V^{III}, or Cr^{III}, can be used to generate frustrated lattices,[7–9] including the desired magnetically frustrated star lattice. This star lattice can be described in vertex notation as 3.12^2 (see Scheme S1 in the Supporting Information), a lattice that is a uniform, three-connected two-dimensional net with large voids.[10] Three-connected node subunits that prefer to bond in a planar fashion, such as the basic cationic iron(III) carboxylate cluster $[Fe_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6L_3]^+$,[11] where L may be water, methanol, or pyridine, must be used to avoid three-dimensional connections. These carboxylate clusters are good potential building blocks because they are easily prepared, prefer planar bonding, and the R groups and L ligands can easily be varied.[12]

The cationic $[Fe_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6L_3]^+$ moiety has previously served as a six- or three-connected node (see Scheme S2 in the Supporting Information) to form either three-[12a–e] or zero-dimensional[12f] porous frameworks depending upon the nature of the carboxylate, which may be either fully or partially substituted by dicarboxylates; the L ligands are usually retained as terminal ligands. Although no example is known to date, it should be possible to substitute the L ligands located in the triangular $[Fe_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6L_3]^+$ cation plane with other bridging bidentate ligands that are better at both mediating antiferromagnetic interactions and producing a two-dimensional star lattice. Herein, we report the use of bidentate acetate bridging ligands to link $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6]^+$ cations together to form $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3][Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_{7.5}]_2\cdot 7\,H_2O$ (**1**), a new compound with the desired star lattice.

Single-crystal X-ray diffraction studies of **1** at 293 and 90 K revealed that isolated $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3]^+$ cations (Figure 1) occupy the dodecagonal channels formed by the stacking of acetate-bridged $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_{7.5}]^{1/2-}$ anionic layers; the dihedral angle between the triangular $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3]^+$ cations and the $[Fe_3(\mu_3\text{-}O)(\mu\text{-}$

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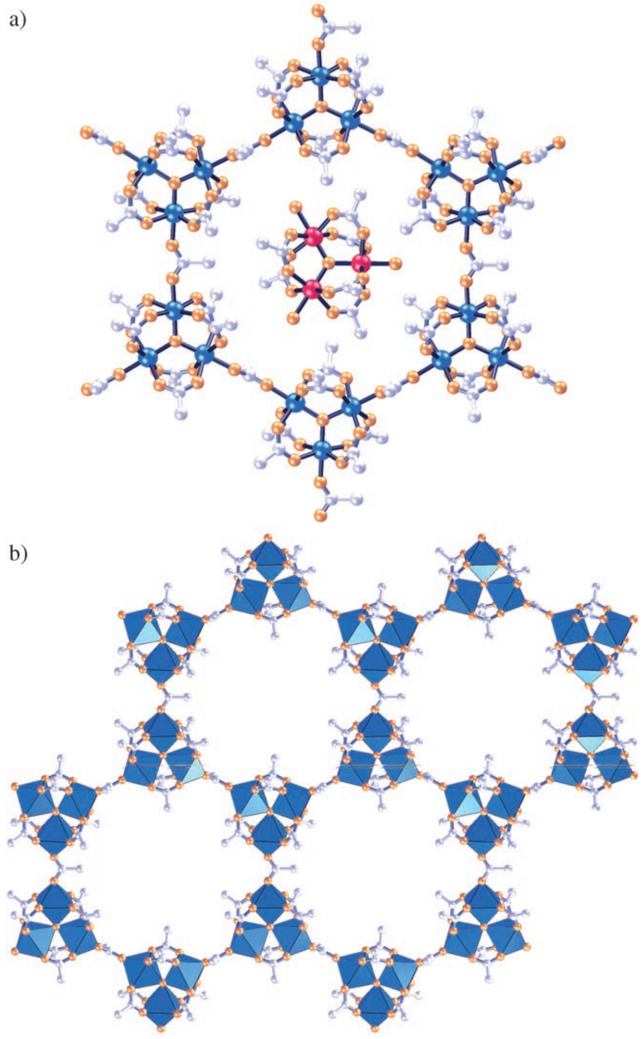

Figure 1. The structural unit (a) and the "star" anionic framework (b) of **1** viewed down the *c* axis. The guest water molecules have been omitted for clarity. The Fe^{III} ions in the anionic layer are colored blue and are highlighted as blue polyhedra in (b); the Fe^{III} ions in the isolated cations are red in (a) and these cations have been omitted in (b); oxygen atoms are colored orange and carbon atoms grey.

$OAc)_{7.5}]^{1/2-}$ anionic layers is 42° (see Figure S1 in the Supporting Information). It should be noted that an extended network containing its own building blocks as templates is unusual in host–guest chemistry.

The anionic layers are packed in an AAA fashion along the *c* axis and all the Fe^{III} ions have a pseudooctahedral coordination environment with mean Fe–O(oxo), Fe–O(carboxy), and Fe–O(aqua) bond lengths of 1.907(2), 2.018(3), and 2.065(4) Å, respectively, which are in the normal range for Fe^{III}–O bonds. The mean Fe–O(oxo)–Fe bond angles in the anionic layer and in the cationic "isolated" trimer are 120.0(1)° and 120.3(1)°, respectively. Bond valence sum calculations[13] with an r_0(Fe–O) value of 1.759 Å yield a mean iron valence of 3.14 in **1**, thereby confirming that the iron is unambiguously trivalent, a conclusion that is fully supported by the Mössbauer spectral results presented below.

The mean intra- and inter-trimer Fe···Fe distances in the anionic layer are 3.307 and 6.130 Å, respectively, and the expected magnetic interactions within the anionic layer are consistent with the formation of a "star" lattice. The major interactions between both the anionic layers and the anionic layers and the "isolated" cations are hydrogen bonds. The shortest Fe···Fe distance between the "isolated" cations and the anionic layers is 6.990 Å, and the shortest Fe···Fe distance between the anionic layers is 7.424 Å.

The Mössbauer spectra (Figure 2 and Figure S2 in the Supporting Information) indicate both that **1** is paramagnetic between 295 and 10 K and that it exhibits long-range magnetic order at 4.2 K. The paramagnetic spectra can be fitted with two doublets in a 2:1 ratio, the resulting hyperfine parameters of which are characteristic of Fe^{III} (see Table S1a in the Supporting Information). Full details of the analysis of the paramagnetic spectra are given in the Supporting Information.

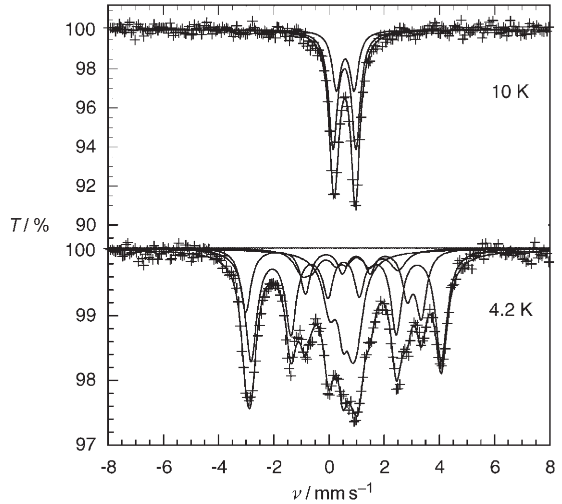

Figure 2. Mössbauer spectra of **1** obtained at 10 and 4.2 K; *T*: transmission; υ: velocity. The fitting lines are assigned according to the ratio of anions and cations.

The spectrum at 4.2 K (Figure 2) can be fitted using four magnetic components with an area ratio of 4/9:2/9:2/9:1/9. The first two of these components can be assigned to the $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_{7.5}]^{1/2-}$ anions and the second two to the $[Fe_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3]^+$ cations; the resulting hyperfine parameters are given in Table S1b of the Supporting Information. Two sextets are required for each ion because the principal axis of the electric field gradient at the Fe^{III} ion makes two different angles, θ, with the easy magnetization axis, an axis that is normal to the *c* axis and collinear with the *a* axis. As expected, the two θ values are 0° and 60° for the anions. In contrast, although one of the angles for the cation is 90°, as expected, the second is 0° rather than the expected value of 50° based on the 42° tilt of the Fe_3O plane of the cation relative to the plane of the anion (see Figure S1 in the Supporting Information).

In agreement with the magnetic results presented below, the hyperfine fields of about 20 T observed for the anions indicate that the magnetization, which most probably results from long-range magnetic coupling of the moments in the layered anions, is not saturated at 4.2 K. In contrast, the much smaller fields observed for the isolated cations result from a transferred field arising from the anions; the isolated cations do not contribute to the exchange coupling. In the absence of information about the magnetic structure, it is difficult to determine the reason for the very different transferred fields on the Fe^{III} ions in the isolated cations.

The influence of structure on the magnetic properties of **1** is interesting. The dc susceptibility indicates that χT at 300 K is 12.44 $cm^3 mol^{-1} K$ (see Figure S4 in the Supporting Information), a value that is much smaller than the expected 39.39 $cm^3 mol^{-1} K$ spin-only χT for nine fully spin-decoupled $S = {}^5\!/_2$ Fe^{III} ions. It thus appears that there is significant antiferromagnetic coupling between the three high-spin Fe^{III} ions through the oxo bridge.[11] The magnetic susceptibility observed between 105 and 300 K exhibits Curie–Weiss behavior (Figure 3) with a Curie constant, C, of 36.52 $cm^3 mol^{-1} K$, a corresponding effective magnetic moment, μ_{eff}, of 5.78 μ_B per Fe^{III} ion, and a Weiss temperature, θ, of −581 K. The reduction of μ_{eff} from the expected value of 5.92 μ_B and the large negative θ value confirm the presence of antiferromagnetic interactions in **1**.

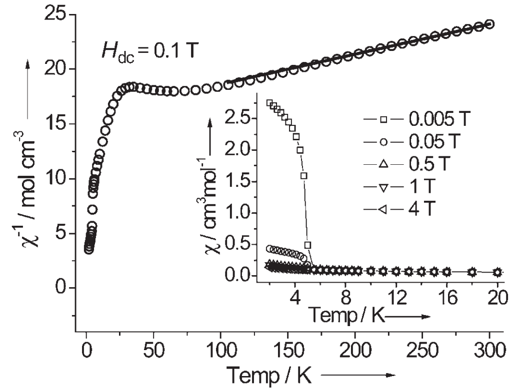

Figure 3. The temperature dependence of the inverse molar magnetic susceptibility of **1** obtained in an applied dc field of 0.1 T; the solid line represents the behavior according to the Curie–Weiss law. Inset: The field dependence of the molar magnetic susceptibility of **1** obtained below 20 K.

A measure of magnetic spin frustration, f, is given by $|\theta/T_N|$, and an f value above 10 indicates the presence of strong frustration.[1] From the above θ value and the T_N value of 4.5 K determined from the dc and ac susceptibility presented below, a value for f of 129 is obtained for **1**, which indicates the presence of strong spin frustration.[1,2] χT decreases continuously upon cooling to reach a minimum of 0.56 $cm^3 mol^{-1} K$ at 5.1 K and then increases to a maximum of 0.75 $cm^3 mol^{-1} K$ at about 3.9 K; this increase is probably because the number of metal centers is odd, which prevents the total cancellation of the antiferromagnetically coupled spins, and/or because a spin-canting behavior is induced by Dzyaloshinsky–Moriya interactions,[14] which lead to the presence of weak ferromagnetism. To confirm this possibility, we measured χ in applied fields of 0.005–4 T between 3 and 20 K (see the inset to Figure 3). The observed increase in χ below about 4.5 K in a field of 0.005 T unambiguously indicates the presence of both canted antiferromagnetism and long-range magnetic order below 4.5 K.

The occurrence of magnetic order in **1** below 4.5 K was further confirmed by the observed difference in its field-cooled and zero-field-cooled susceptibility (Figure 4), the irreversible spontaneous magnetization observed at 4 and 2 K, and the sharp peak observed at 4.5 K in both the real and imaginary components of the ac susceptibility (see Figure S5 in the Supporting Information). In addition, the ac susceptibility of **1** is independent of frequency, which precludes the presence of any spin-glass like behavior.[15] Further, the small molar magnetization of **1** (1.38 Nμ_B) observed at 2 K in an applied field of 7 T (see Figure S5 in the Supporting Information) as well as the hysteresis loop with a coercive field of only 0.01 and 0.02 T and a remnant magnetization of only 0.010 and 0.015 Nμ_B at 4 and 2 K, respectively (see the inset to Figure 4), again indicate the presence of weak ferromagnetism in **1**. This behavior is very similar to that previously reported for some related layered magnets.[16]

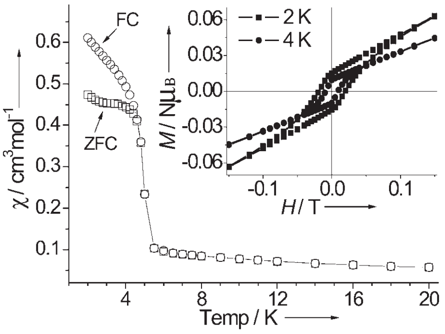

Figure 4. The zero-field-cooled (ZFC) and field-cooled (FC) molar magnetic susceptibility of **1** obtained in a dc applied field of 0.03 T. Inset: The magnetic hysteresis observed in **1** at the indicated temperatures.

Unfortunately, **1** does have limitations as an ideal "star" antiferromagnet both because of the presence of the $[Fe^{III}_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3]^+$ cations, even though they are paramagnetic at 4.2 K (by Mössbauer spectroscopy) and because the bridging acetate ligands do not yield magnetic exchange interactions within the anionic layers that are stronger than the "localized" exchange interactions within the $\{Fe^{III}_3(\mu_3\text{-}O)\}$ triangular clusters.[17–19] Thus, in the absence of an appropriate model, we cannot determine the extent of the magnetic frustration attributable to the star lattice directly. We also cannot qualitatively compare the f values with those reported previously for $\{Fe^{III}_3(\mu_3\text{-}O)\}$-based compounds as it is impossible to calculate the latter because of the absence of a Néel temperature in such oligomeric complexes[11] or magnetically dilute coordination polymers.[12] The only compounds that can be used as a reference point are the Fe^{III}-containing jarosites.[7] Although the f values (10–51) of these jarosites are all smaller than that of **1**,[7] it does not follow that the frustration is stronger in **1** as the inter-trimer magnetic interactions are very different in the two lattices.

Jarosites and analogous Kagomé lattice complexes with Fe^{III}, Co^{II}, and Cr^{III} ions exhibit frustrated low-temperature antiferromagnetism and, occasionally, long-range order in the ground state.[6,7] The quantum many body Heisenberg interaction theory[6g] indicates that such Kagomé complexes with half-odd-integer spins will exhibit strong magnetic frustration. In contrast, the degeneracy of the spin excitations in integer-spin and mixed-spin complexes will produce a spin-gap that partially or fully removes any geometric lattice-induced magnetic frustration. If this theory applies to star complexes, the half-odd-integer spins of **1** should yield ground-state lattice-induced frustration. However, because of the somewhat reduced lattice symmetry of **1**, Dzyaloshinsky–Moriya interactions may induce spin-canting out of the plane of the star, which means that the interlayer coupling between the canted moments[6h] at low temperature, either through the extensive hydrogen-bonding network between the layers of **1** or through space,[15] may lead to long-range magnetic order.

In summary, we have obtained an iron(III) acetate hybrid material[20] with a star lattice, which exhibits spin frustration and long-range magnetic order simultaneously, by linking triangular $\{Fe_3O(OAc)_6\}$ clusters. More importantly, this "bottom-up" strategy provides a practical way to prepare frustrated magnetic materials with a specific topology.

Experimental Section

Synthesis of **1**: A solution of $[Fe_3O(OAc)_6(H_2O)_3]Cl\cdot 6H_2O$ (0.076 g, 0.1 mmol) in MeCN (10 mL) was carefully layered on an aqueous solution (10 mL) of $FeCl_3\cdot 4H_2O$ (0.117 g, 0.5 mmol) and NaOAc (0.166 g, 2 mmol) in a long tube (0.6×25 cm^2). The tube was sealed with Parafilm and kept at room temperature. Red plate-like crystals of **1** were obtained from the bottom of the tube after 4 months (yield: 0.064 g, 37% based on Fe). A simulation of the powder X-ray diffraction pattern of **1** indicates that it is phase-pure (see Figure S4 in the Supporting Information). IR data for **1** (KBr): $\tilde{\nu}=3425$ (s,br), 2925 (w), 2853 (w), 1599 (vs), 1558 (s), 1519 (s), 1446 (s), 1020 (w), 850 (w), 726 (w), 663 (w), 611 cm^{-1} (w). Anal. calcd. for **1**: C 25.60, H 4.25; found: C 25.25, H 4.39.

Crystal data for **1** at 293(2) K: $C_{42}H_{83}Fe_9O_{55}$, $M=1970.73$ g mol^{-1}, monoclinic, space group $C2/c$, $a=29.661(2)$, $b=17.2693(8)$, $c=16.0180(8)$ Å, $\beta=111.053(1)°$, $V=7657.0(6)$ Å^3, $Z=4$, $\rho=1.710$ g cm^{-3}, $\theta_{max}=26.0°$, total data 21114, unique data 7483, $\mu=1.762$ mm^{-1}, 521 parameters, $R_1=0.0426$ for $I\geq 2\sigma(I)$ and $wR_2=0.1207$ for all data.

Crystal data for **1** at 90(2) K: $a=29.396(1)$, $b=17.3372(9)$, $c=15.7527(8)$ Å, $\beta=111.600(1)°$, $V=7464.4(6)$ Å^3, $Z=4$, $\rho=1.754$ g cm^{-3}, $\theta_{max}=26.0°$, total data 28063, unique data 7317, $\mu=1.808$ mm^{-1}, 521 parameters, $R_1=0.0340$ for $I\geq 2\sigma(I)$ and $wR_2=0.0880$ for all data. The intensity data were recorded with a Bruker SMART Apex CCD system with $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). The structure was solved by direct methods and refined on F^2 using SHELXTL. CCDC 643841 and 643842 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The Mössbauer spectra of **1** were recorded with a constant-acceleration spectrometer equipped with a rhodium matrix cobalt-57 source that had been calibrated at room temperature with α-iron foil.

Magnetic susceptibility measurements for **1** were performed with a Quantum Design MPMS-XL7 SQUID magnetometer. A diamagnetic correction of -8.86×10^{-4} emu mol^{-1} (calculated from Pascal's constants) was applied.

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[18] To the best of our knowledge, there is only one example of a study of the magnetic interaction between Fe^{III} ions through an *anti-anti* bridging carboxylate, which gives a coupling constant in the range −5.1 to −4.0 cm^{-1}, depending on the coplanarity of the system: P. Angaridis, J. W. Kampf, V. L. Pecoraro, *Inorg. Chem.* **2005**, *44*, 3626.

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