DOI:10.1021/cm901765n

CHEMISTRY OF MATERIALS
Communication

$Co_3(SO_4)_3(OH)_2[enH_2]$: A New $S = 3/2$ Kagome-Type Layered Sulfate with a Unique Connectivity

Anthony V. Powell,*,† Patricia Leyva-Bailen,† Paz Vaqueiro,† and Rodolfo D. Sanchez‡

†*Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, U.K., and* ‡*Centro Atomico Bariloche, 8400 Bariloche (RN), Argentina*

Received June 24, 2009
Revised Manuscript Received August 14, 2009

The Kagome lattice, comprising a two-dimensional array of corner-sharing equilateral triangles, is central to the exploration of magnetic frustration.[1] In such a lattice, antiferromagnetic coupling between ions in triangular plaquettes prevents all of the exchange interactions being simultaneously satisfied, and a variety of novel magnetic ground states may result at low temperature. Experimental realization of a Kagome lattice remains difficult. The jarosite family of materials of nominal composition $AM_3(SO_4)_2(OH)_6$ (A = monovalent cation; $M = Fe^{3+}$, Cr^{3+}), offers perhaps one of the most promising manifestations of the phenomenon of magnetic frustration in two dimensions. The magnetic properties of jarosites are however extremely sensitive to the degree of coverage of magnetic sites. Consequently, there is considerable interest in the use of soft chemical techniques for the design and synthesis of novel materials in which to explore the effects of spin, degree of site coverage, and connectivity on magnetic frustration.[2]

Tetrahedral anions are attractive candidates as building blocks for the construction of novel frustrated materials. The threefold rotational symmetry of species such as SO_4^{2-} affords the potential to direct the assembly of metal-centered octahedra to form the triangular units that represent the canonical example of a frustrated system. Structure-directed synthesis in a sulfuric acid medium has been shown to be a versatile method for the preparation of novel metal sulfates,[3] including those with structures comprising vertex-linked $M(O,F)_6$ octahedra with the Kagome topology.[4] Here we have exploited this method to synthesize[5] a new sulfate, $Co_3(SO_4)_3(OH)_2[enH_2]$, that provides a rare example of an $S = 3/2$ Kagome lattice[6] in which, despite the 100% coverage of magnetic sites, magnetic ordering occurs at low temperatures. This appears to be due to a unique connectivity of metal-centered octahedra in a Kagome lattice.

In the structure[7] (Figure S1, Supporting Information) of $Co_3(SO_4)_3(OH)_2[enH_2]$, pairs of Co(5)-centered octahedra, related by a plane of symmetry, share a common edge. The outer *trans* edges of this unit are shared with two $Co(3)O_6$ octahedra. Each of the latter are in turn connected to a dimeric unit of edge-sharing Co(2) and Co(4)-centered octahedra via edges that are cis to the Co(3)−Co(5) linkage. This results in a three-connected oxygen (O(24)) that is common to Co(3), Co(4), and Co(5). An analogous arrangement is produced by the linkage of pairs of $Co(2)O_6$ octahedra through $Co(1)O_6$, with which the former share edges. Protonation of each of the three-connected oxygen atoms, required for charge balancing and consistency with the bond valence sums, yields a (μ_3−OH) species.

Linkage of CoO_6 octahedra produces a nine-octahedron triangular unit of stoichiometry $[Co_9O_{36}]$. Each Co_9 triangle is linked to six neighboring triangles through (μ_3−OH) ions. Sulfate ions cap three octahedral vertices above or below each of the hydroxyl groups to generate an anionic layer of stoichiometry $[Co_3(SO_4)_3(OH)_2]^{2-}$ (Figure 1a). The layers are stacked along the [001] direction in an *AA* fashion, with Co···Co interlayer distances of ca. 8.9 Å. Terminal atoms of the sulfate anions are directed above and below the layers into the interlayer space, where diprotonated ethylenediamine cations

*Corresponding author. E-mail: a.v.powell@hw.ac.uk.

(1) (a) Ramirez, A. P. *Annu. Rev. Mater. Sci.* **1994**, *24*, 453. (b) Greedan, J. E. *J. Mater. Chem.* **2001**, *11*, 37. (c) Moessner, R.; Ramirez, A. P. *Phys. Today* **2006**, 24. (d) Pati, S. K.; Rao, C. N. R. *Chem. Commun.* **2008**, 4783.
(2) Nocera, D. G.; Bartlett, B. M.; Grohol, D.; Papoutskakis, D.; Shores, M. P. *Chem. Eur. J.* **2004**, *10*, 3850.
(3) (a) Rujiwatra, A.; Keppert, C. J.; Claridge, J. B.; Rosseinsky, M. J.; Kumagai, H.; Kurmooo, M. *J. Am. Chem. Soc.* **2001**, *123*, 10584. (b) Rao, C. N. R.; Behera, J. N.; Dan, M. *Chem. Soc. Rev.* **2006**, *35*, 375. (c) Behera, J. N.; Gopalkrishnan, K. V.; Rao, C. N. R. *Inorg. Chem.* **2004**, *43*, 2636. (d) Paul, G.; Choudhury, A.; Rao, C. N. R. *Chem. Mater.* **2003**, *15*, 1174. (e) Fan, Y.; Li, G. H.; Yang, L.; Zhang, Z. M.; Chen, Y.; Song, T. Y.; Feng, S. H. *Eur. J. Inorg. Chem.* **2005**, 3359.
(4) (a) Behera, J. N.; Rao, C. N. R. *J. Am. Chem. Soc.* **2006**, *128*, 9334. (b) Rao, C. N. R.; Sampathkumaran, E. V.; Nagarajan, R.; Paul, G.; Behera, J. N.; Choudhury, A. *Chem. Mater.* **2004**, *16*, 1441. (c) Paul, G.; Choudhury, A.; Sampathkumaran, E. V.; Rao, C. N. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 4297. (d) Paul, G.; Choudhury, A.; Rao, C. N. R. *Chem. Commun.* **2002**, 1904.

(5) Single crystals of $Co_3(SO_4)_3(OH)_2[enH_2]$ were prepared from a mixture of $Co(SO_4)\cdot 7H_2O$ (0.56 g; 2 mmol), ethylenediamine (0.135 mL; 2 mmol), H_2SO_4 (0.11 mL; 2 mmol), and H_2O, with an approximate molar composition $CoSO_4$:en:H_2SO_4:H_2O of 1:1:1:1. The mixture in a sealed 23 mL Teflon-lined stainless autoclave was heated at 443 K for 5 days, and cooled to room temperature at 1 K min^{-1}. The product was filtered, washed with deionized water, methanol, and acetone, and dried in air at room temperature. Anal. Calcd: (%) C, 4.28; H, 4.99; N, 2.16. Found: C, 4.30; H, 4.79; N, 2.20. TGA, Calcd wt loss (%) 60.03; found 59.43.

(6) (a) Behera, J. N.; Paul, G.; Choudhury, A.; Rao, C. N. R. *Chem. Commun.* **2004**, 456. (b) Wang, X.-Y.; Wang, L.; Wang, Z.-M.; Gao, S. *J. Am. Chem. Soc.* **2006**, *128*, 674.

(7) Crystal structure: monoclinic, space group *Cm*, a = 11.6795(3), b = 19.9926(6), c = 8.9249(3) Å, β = 93.168(1)°, V = 2080.81(11) $Å^3$, Z = 6. Crystal dimensions: 0.40 × 0.60 × 0.80 mm^3, M = 1687.39. 14191 reflections measured, 5545 unique (R_{merg} = 0.021, 5337 observed with $I > 3\sigma(I)$) which were used in all calculations. Final values of R(F) and wR(F) are 0.021 and 0.026, respectively. Data collected at 293 K, using a Bruker-AXS X8 Apex CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved using the direct methods program SIR92 and the model refined using the CRYSTALS suite of programs.

 Published on Web 08/20/2009

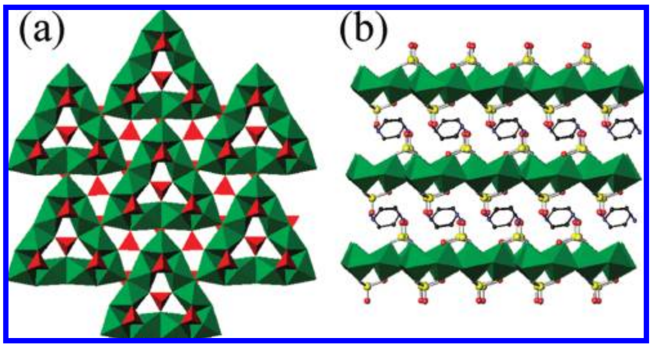

Figure 1. (a) View onto the (001) plane of a $[Co_3(SO_4)_3(OH)_2]^{2-}$ layer of edge- and vertex-linked CoO_6 octahedra (green), capped by sulfate tetrahedra (red). (b) $Co_3(SO_4)_3(OH)_2[enH_2]$ viewed along [010] illustrating the vertices of the tetrahedra directed into the interlayer space where diprotonated ethylenediamine molecules reside.

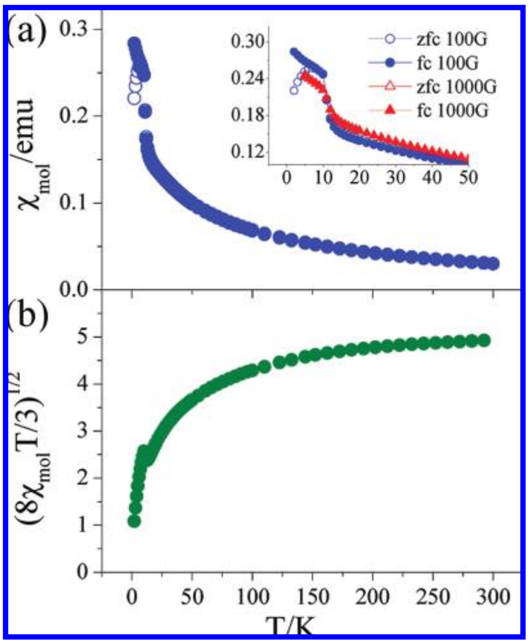

Figure 2. (a) Zero-field cooled and field-cooled molar susceptibility in a field of 100 G (inset: comparison of the low-temperature susceptibility in fields of 100 and 1000 G). (b) Temperature dependence of μ_{eff} per Co ion.

(Figure 1b) reside. These balance the anionic charges of the layers and provide linkage between layers through an extensive network of hydrogen bonds between amino cations and the terminal oxygen atoms of the SO_4^{2-} anions.

ZFC magnetic susceptibility data (Figure 2) collected in a measuring field of 100 G[8] are well described by a Curie−Weiss law (μ_{eff} = 5.27(1) μ_B per cobalt ion, θ = −54.8(3) K), the reciprocal susceptibility deviating from linearity below 17 K. The magnetic moment is consistent with octahedral *hs*-Co^{2+}:d^7 with an orbital enhancement of the spin-only value of the moment (3.87 μ_B). At 100 G, ZFC and FC data overlie to low temperatures, both increasing sharply at 12 K. The ZFC data reach a maximum at T_c = 7 K, where ZFC and FC data begin to diverge. Measurements in a measuring field of 1000 G show similar Curie−Weiss behavior at higher temperatures, but the rise in susceptibility at 12 K is less pronounced and the maximum in the ZFC susceptibility, together with the divergence between ZFC and FC data, is suppressed.

(8) Magnetic susceptibility data (2 ≤ T/K ≤ 300) were collected on hand-picked crystals using a Quantum Design MPMS2 SQUID susceptometer after cooling in zero applied field (ZFC) and in the measuring field (FC). Magnetization measurements (−10000 ≤ H/G ≤ 10000) were carried out at 5 K.

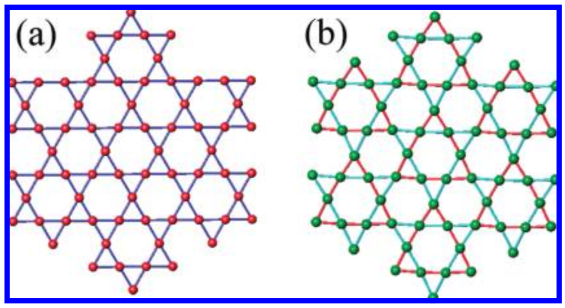

Figure 3. Kagome network of (a) iron cations in $(H_3O)Fe_3(SO_4)_2(OH)_6$ and (b) cobalt cations in $Co_3(SO_4)_3(OH)_2[enH_2]$. In (b) short and long Co−Co distances are denoted by red and blue lines, respectively.

The effective magnetic moment per cobalt ion decreases on cooling from 300 to 12 K, owing to a combination of a reduction in the orbital contribution and antiferromagnetic correlations. Below 12 K, μ_{eff} increases slightly before passing through a local maximum at 10 K. Magnetization measurements (Supporting Information) provide no evidence for hysteresis nor any significant spontaneous magnetization at 5 K.

The cobalt lattice in $Co_3(SO_4)_3(OH)_2[enH_2]$ exhibits the topology of the 2D Kagome network (Figure 3) of corner-linked triangles. For antiferromagnetic exchange between nearest-neighbor cations, this arrangement is inherently frustrated. The ratio $|\theta|/T_c$ is commonly taken as a measure of the degree of frustration.[1a,b] The value $|\theta|/T_c$ = 8 determined here is consistent with a magnetically frustrated system and is slightly larger than for the Kagome-like $[Mn_3\{C_6H_3(COO)_3\}_2]$ ($|\theta|/T_c$ = 3.55), which exhibits a canted antiferromagnetic state at low temperatures[9] (T_c = 13 K). The ratio $|\theta|/T_c$ typically lies in the range 11−16 for jarosites containing appreciable levels of vacancies on the magnetic sublattice. Defective materials exhibit long-range antiferromagnetic magnetic order at low temperatures, adopting the $\mathbf{q} = 0$ structure below T_c.[10] However, when the occupancy of magnetic sites approaches 100%, as occurs in $(H_3O)Fe_3(SO_4)_2(OH)_6$, the ratio $|\theta|/T_c$ rises markedly, and the material behaves as a spin glass.[11] An "order by disorder" mechanism has been proposed and is supported by measurements on the magnetically diluted materials $(D_3O)Fe_{3-x}Al_x(SO_4)_2(OD)_6$.[10] However, Grohol et al.[12] have subsequently prepared stochiometrically pure samples of $AFe_3(SO_4)_2(OH)_6$ (A = Na^+, K^+, Rb^+, NH_4^+) and demonstrated that

(9) Mahata, P.; Sen, D.; Natarajan, S. *Chem. Commun.* **2008**, 1278.
(10) Wills, A. S.; Harrison, A.; Ritter, C.; Smith, R. I. *Phys. Rev. B* **2000**, *61*, 6156.
(11) (a) Wills, A. S.; Harrison, A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2161. (b) Wills, A. S.; Harrison, A.; Mentink, S. A. M.; Mason, T. E.; Tun, Z. *Europhys. Lett.* **1998**, *42*, 325.
(12) Grohol, D.; Nocera, D. G.; Papoutsakis, D. *Phys. Rev. B.* **2003**, *67*, 064401.

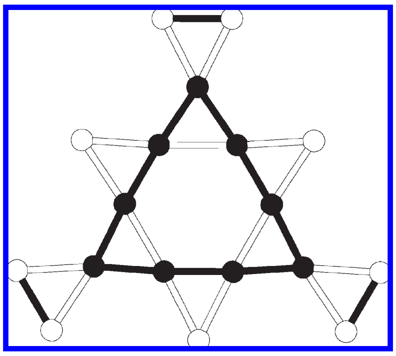

Figure 4. Magnetic exchange pathways between cobalt ions in $Co_3(SO_4)_3(OH)_2[enH_2]$. Cobalt ions that form a single $[Co_9O_{36}]$ triangular cluster are denoted by solid circles. Antiferromagnetic couplings across shared octahedral edges are likely to be the strongest exchange interactions and are indicated by solid bonds while the weaker interactions via common octahedral vertices are represented by open bonds. All nonmetal atoms are omitted for clarity.

these materials undergo long-range magnetic order at temperatures in the range 61−65 K, that are essentially independent of the size of the A-cation. In the light of this result, they propose that the anomalous nature of the hydronium iron jarosite may be ascribed to structural and magnetic disorder arising from protonation of the μ-hydroxo bridge by proton transfer from interlayer hydronium ions.

While there is 100% coverage of magnetic sites in $Co_3(SO_4)_3(OH)_2[enH_2]$, the frustration parameter is significantly lower than in the hydronium iron jarosite. Furthermore, magnetic susceptibility data indicate magnetic ordering at $T_c = 7$ K, which, given the absence of a spontaneous moment, appears to be to an antiferromagnetic state. The origin of this behavior may be traced to the differences in connectivity of the octahedra in the material reported here compared with the jarosites (Figure 3). In the latter, all cation−cation separations are approximately 3.7 Å. However, the presence of both edge- and corner-sharing CoO_6 octahedra in $Co_3(SO_4)_3(OH)_2[enH_2]$ leads to short (3.1−3.2 Å) and long (3.5−3.6 Å) Co−Co distances across common octahedral edges and vertices, respectively. While neutron diffraction data will be required to establish the detailed spin structure, some qualitative conclusions about the magnetic coupling may be drawn. The triangular plaquettes characteristic of the Kagome lattice are intrinsically frustrated. However, each plaquette contained wholly within a triangular Co_9 cluster contains two short and one long Co−Co distance, whereas plaquettes that serve to link clusters contain two long and one short Co−Co distance (Figure 4). Thus within each plaquette, there are two exchange constants of different magnitudes, which may provide a mechanism for relieving frustration. However, the short Co−Co separations define an exchange pathway (Figure 4) around the Co_9 triangular cluster, in which magnetic coupling occurs across shared octahedral edges. Even at these shorter Co−Co distances, interaction between neighboring moments is dominated by superexhange via the intervening oxygen anion. These interactions are of the 90° $d\sigma-p\sigma/p\pi-d\pi$ type and are likely to be moderately strong and antiferromagnetic in origin. Consequently, given the odd number of cobalt ions present in the cluster, the Co_9 unit is itself magnetically frustrated. Coupling between clusters occurs through shared octahedral vertices at the apexes and midpoints of the edges of each Co_9 triangular unit. The Co−O−Co angles involving common vertices, both within the Co_9 unit and at sites that link these units, are significantly larger (ca. 118−120°) than those involving shared edges. Overlap with anion p-orbitals is less effective, and the (probable) antiferromagnetic exchange interaction is likely to be considerably weaker.

Interaction between clusters which are geometrically frustrated has been shown to introduce considerable complexity into the macroscopic magnetic behavior. For example, Zaharko et al.[13] have shown that in $Cu_2Te_2O_5X_2$ (X = Cl, Br), intercluster exchange between tetrahedral Cu_4 clusters that are geometrically frustrated, leads to a complex incommensurate antiferromagnetically ordered state at low temperatures that appears to contain helical arrangements of Cu^{2+} moments. A similar degree of complexity in the material reported here will necessitate detailed neutron measurements as a function of temperature to characterize the nature of the ordered state and elucidate the precise details of the spin orientations.

Acknowledgment. We thank the UK EPSRC for an Advanced Research Fellowship for P.V. and a grant to support X-ray diffraction facilities, ScotCHEM for a studentship for P.L.B. and The Royal Society for a Joint Project Grant.

Supporting Information Available: Crystallographic and magnetic data for the title compound, together with thermogravimetric and optical data (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

(13) Zaharko, O.; Daoud-Aladine, A.; Streule, S.; Mesot, J.; Brown, P. J.; Berger, H. *Phys. Rev. Lett.* **2004**, *93*, 217206.