J|A|C|S
COMMUNICATIONS

A Ni^{2+} ($S = 1$) Kagome Compound Templated by 1,8-Diazacubane

J. N. Behera and C. N. R. Rao*

*Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research,
Jakkur P. O., Bangalore 560064, India, and Solid State and Structural Chemistry Unit,
Indian Institute of Science, Bangalore 560012, India*

Received May 15, 2006; E-mail: cnrrao@jncasr.ac.in

Transition metal compounds with the Kagome structure have been of great academic interest because of their novel magnetic properties. Most of the Kagome compounds investigated belong to the family of jarosites, which are difficult to obtain in pure form.[1] Magnetic properties of the jarosites comprising Fe^{3+} ions generally show magnetic frustration or long-range antiferromagnetic order at low temperatures. Nocera et al. have found that pure iron jarosites prepared by redox-based methods exhibit long-range antiferromagnetic order at 61.4 K, involving antiferromagnetic stacking of an out-of-plane moment arising from spin canting.[2] These workers have also shown that a phase pure $S = {}^1/_2$ copper Kagome layer exhibits spin frustration.[3] Interestingly, in V^{3+} jarosites, there is ferromagnetic coupling within the triangles of the Kagome layers.[4] The presence of ferromagnetic interactions has also been reported in Fe^{2+} and mixed-valent Fe (2+, 3+) Kagome compounds.[5] The corresponding Co^{2+} Kagome compound, however, behaves similar to the Fe^{3+} jarosites.[6] A theoretical study employing many-body Heisenberg models has enabled us to rationalize the variety of low-temperature magnetic properties exhibited by Kagome compounds and suggests the crucial role of the magnitude of the spin of the transition metal ion.[7] Thus, integral spins are suggested to give rise to ferro/ferrimagnetic interactions, while odd-half integer spins cause frustration. To test such a hypothesis and to prepare a novel Kagome compound with an entirely different transition metal ion, we have carried out experiments to prepare and characterize a Ni^{2+} ($S = 1$) Kagome compound. Interestingly, a phase-pure compound of the formula $[C_6N_2H_8][NH_4]_2[Ni_3F_6(SO_4)_2]$, **I**, prepared by us under solvothermal conditions[8] shows novel magnetic properties. Another unusual feature of **I** is that a novel organic species, diazacubane, formed under the synthetic conditions, templates the structure.

The asymmetric unit of **I** consists of eight non-hydrogen atoms, out of which five belong to the inorganic framework and three to the extra framework guest molecules, including the nitrogen of the ammonium ion (Figure 1a). The structure of **I** consists of anionic layers of vertex-sharing $Ni^{II}F_4O_2$ octahedra and SO_4 tetrahedra fused together by Ni−F−Ni and Ni−O−S bonds. Each NiF_4O_2 unit shares four of its Ni−F vertices with similar neighbors with the Ni−F−Ni bonds roughly aligned in the *ab*-plane. The Ni−O bond is canted from the *ab*-plane, and the Ni−O vertex forces a three-ring trio of apical Ni−O bonds closer together to allow them to be capped by the SO_4 tetrahedra. The sulfate groups are positioned alternately up and down about the hexagonal network. The three and six rings formed by the octahedra give rise to the in-plane connectivity of the hexagonal tungsten bronze sheets, characteristic of the Kagome lattice, as shown in Figure 1b.

The Ni−O/F bond distances in **I** are in the range of 2.018 (2)−2.050 (3) Å [(Ni−O) = 2.050 and $(Ni-F)_{av}$ = 2.019(2) Å]. Bond valence sum (BVS) calculations[9] using r_0 (Ni−F) of 1.596 and r_0 (Ni−O) of 1.654 Å gave a valence sum of 1.95 for Ni.

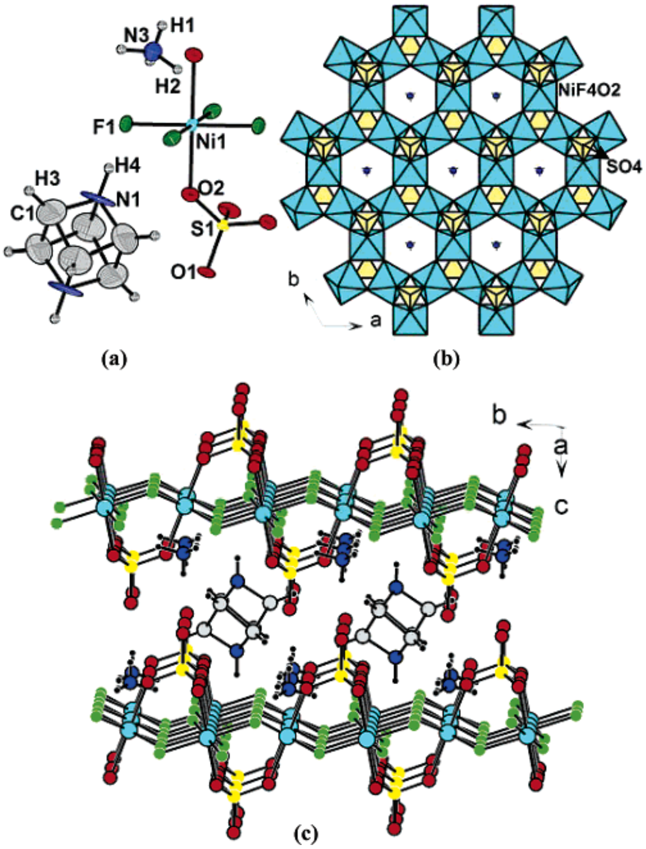

Figure 1. (a) Labeled asymmetric unit of **I**. Thermal ellipsoids are given at 50% probability. (b) Polyhedral view of the hexagonal Kagome layer in **I**. Note the presence of ammonium ion in the hexagonal channel. (c) Structure of **I** showing the presence of the 1,8-diazacubane in the interlayer space.

The position of the fluorine is also supported by these calculations [F(1) = 0.62)]. The framework stoichiometry of $[Ni_3F_6(SO_4)_2]$ with −4 charge is balanced by the presence of protonated 1,8-diazacubane (see Figure 1a, C−N = 1.572(10) Å, C−C = 1.697(12) Å) and NH_4^+ ions in the interlayer space and hexagonal channels, respectively (Figure 1c). Both of these are formed by the decomposition of piperazine under the synthetic conditions. Diazacubane is not a known compound, and its 1,8-isomer has been theoretically predicted as most stable.[10] Both NH_4^+ and protonated diazacubane form hydrogen bonds with the inorganic layers and ensure the stability of the structure.

In Figure 2, we present the results of magnetic measurements on **I**. The high-temperature inverse susceptibility data give a Weiss temperature of −60 K and an effective magnetic moment per nickel atom is 3.02 μ_B, which is slightly higher than the spin only $S = 1$ value of 2.83 μ_B. This is to be compared with the magnetic moment

10.1021/ja063385f CCC: $33.50 © 2006 American Chemical Society

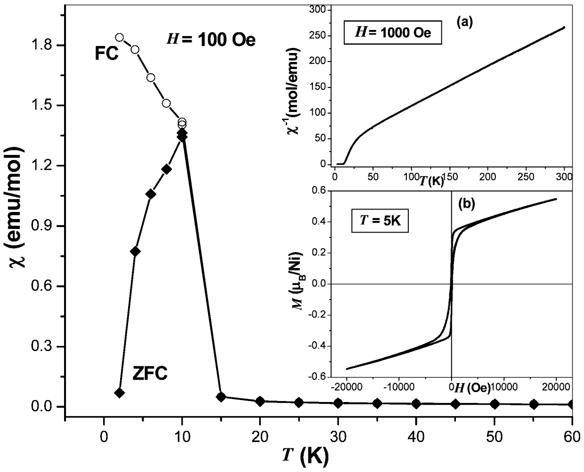

Figure 2. Temperature dependence of the magnetic susceptibility of **I** (100 Oe) under field-cooled (FC) and zero-field-cooled (ZFC) conditions. Inset (a) shows the temperature variation of the inverse susceptibility at 1000 Oe. Inset (b) shows magnetic hysteresis at 5 K.

of V^{3+} jarosites, which lie in the range between 3.02 and 3.16 μ_B.[4c] Furthermore, **I** shows magnetic hysteresis at low temperatures (inset in Figure 2). The susceptibility (χ) data can be considered to have three different regions corresponding to three different energy scales. In the high-temperature regime down to 15 K, χ decreases due to antiferromagnetic superexchange coupling between the spin ($S = 1$) moments, as given by the Curie−Weiss law. Below 15 K, the coupling is primarily angle-dependent (canted) antiferromagnetic (AFM) induced by Dzyaloshinskii−Moriya (DM) interactions. It may be noted that both the in-plane and the out-of-plane DM vectors would be nonzero in this system, with the in-plane component inducing canted spin moments in the out-of-plane directions. At low temperatures below 10 K, χ decreases due to weak AFM coupling between the layers, which is field-dependent. The occurrence of such diverse interactions of different magnitudes and signs is due to the interplay between the frustrated Kagome geometry and the integer spins of the Ni^{2+} ions.

In conclusion, we have prepared and characterized an organically templated Ni(II) Kagome compound. Significantly, the Ni^{2+} compound with $S = 1$ shows canted antiferromagnetism. A novel side observation is the formation of the stable isomer of 1,8-diazacubane in the inter-sheet space.

Acknowledgment. J.N.B. thanks CSIR, India, for a research fellowship. Thanks are due Dr. S. K. Pati for useful discussions.

Supporting Information Available: TGA curve, crystallographic tables, bond distances and angles, hydrogen bonding interactions of **I** (pdf). Full X-ray crystallographic information, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Ramirez, A. P. *Annu. Rev. Mater. Sci.* **1994**, *24*, 453. (b) Greedan, J. E. *J. Mater. Chem.* **2001**, *11*, 37. (c) Nocera, D. G.; Bartlett, B. M.; Grohol, D.; Papoutsakis, D.; Shores, M. P. *Chem.*−*Eur. J.* **2004**, *10*, 3850.
(2) Bartlett, B. M.; Nocera, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 8985.
(3) Shores, M. P.; Nytko, E. A.; Bartlett, B. M.; Nocera, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 13462.
(4) (a) Grohol, D.; Nocera, D. G.; Papoutsakis, D. *Phys. Rev. B* **2003**, *67*, 064401. (b) Grohol, D.; Huang, Q.; Toby, B. H.; Lynn, J. W.; Lee, Y. S.; Nocera, D. G. *Phys. Rev. B* **2003**, *68*, 094404. (c) Papoutsakis, D.; Grohol, D.; Nocera, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 2647.
(5) (a) Rao, C. N. R.; Sampathkumaran, E. V.; Nagarajan, R.; Paul, G.; Behera, J. N.; Choudhury, A. *Chem. Mater.* **2004**, *16*, 1441. (b) Paul, G.; Choudhury, A.; Sampathakumaran, E. V.; Rao, C. N. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 4297.
(6) Behera, J. N.; Paul, G.; Choudhury, A.; Rao, C. N. R. *Chem. Commun.* **2004**, 456.
(7) Pati, S. K.; Rao, C. N. R. *J. Chem. Phys.* **2005**, *123*, 234703.
(8) **Synthesis and initial characterizations:** In a typical synthesis of **I**, 0.281 g (1 mmol) of Ni $(NO_3)_2{\cdot}H_2O$ was dissolved in 4.6 mL (80 mmol) of ethylene glycol (EG) under constant stirring. To this mixture were added 0.22 mL (4 mmol) of sulfuric acid (H_2SO_4, 98%) and 0.344 g (4 mmol) of piperazine (pip), followed by the addition of 0.35 mL (8 mmol) of HF (40%). The resultant mixture was taken in a 23 mL PTFE-lined acid digestion bomb and heated at 180 °C for 3 days. The product (yield: 40% with respect to Ni) containing green rhombohedral crystals was monophasic. **I** was characterized by powder X-ray diffraction (PXRD), energy dispersive analysis of X-rays (EDAX), chemical analysis, thermogravimetric analysis (TGA), and IR spectroscopy. Magnetic measurements were performed at temperatures between 2 and 300 K, in a vibrating sample magnetometer using a physical property measurement system (quantum design). EDAX analysis indicated the ratio of Ni:S to be 3:2. The percentage of Ni and sulfate in **I** were 26 and 29% compared to 28 and 30% expected on the basis of the formula. The loss of ammonia in TGA (∼6%) corresponded to the theoretically calculated value (5.4%). The IR spectrum of **I** shows the expected bands of the sulfate, NH_4^+, and other species. TGA showed a two-step weight loss, the first loss corresponding to the loss of ammonia in the 100−150 °C range. The second weight loss occurs in the 300−650 °C range due to the removal of amine, HF, F_2, and SO_3 (obs = 61.7%, calcd = 59.3%). The end product was characterized to be NiO (JCPDS file card 00-001-1239). **Single-crystal structure determination:** Single-crystal data were collected on a Siemens SMART-CCD diffractometer [graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å ($T = 298$ K)]. An absorption correction based on symmetry-equivalent reflections was applied using SADABS.[11] The structure was solved using SHELXS-86[12] and SHELXTL-PLUS[13] package of programs. **Crystal data:** $[C_6N_2H_8][NH_4]_2[Ni_3F_6(SO_4)_2]$, **I**, $M_r = 626.44$, trigonal, space group = $R3$, $a = 7.3166(3)$ Å, $b = 7.3166(3)$ Å, $c = 26.1924(13)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $V = 1214.30(92)$ Å^3, $Z = 3$, $\rho_{calc} = 2.570$ g cm^{-3}. A total of 1673 reflections were collected in the θ range 2.33−23.26 and merged to give 394 unique data ($R_{int} = 0.0475$). Final $R = 0.0328$, $wR = 0.0933$, and $S = 1.16$ were obtained for 53 parameters.
(9) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244.
(10) (a) Engelke, R. *J. Am. Chem. Soc.* **1993**, *115*, 2961. (b) Zhou, G.; Pu, X.-M.; Wong, N.-B.; Tian, A.; Zhou, H. *J. Phys. Chem. A* **2006**, *110*, 4107. (c) Engelke, R. *J. Org. Chem.* **1992**, *57*, 4841.
(11) Sheldrick, G. M. *SADABS*: *Siemens Area Detector Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1994.
(12) Sheldrick, G. M. *SHELXS-86 Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1986.
(13) Sheldrick, G. M. *SHELXTL-PLUS Program for Crystal Structure Solution and Refinement*; University of Göttingen: Göttingen, Germany, 1993.

JA063385F