An organically templated Co(II) sulfate with the kagome lattice, prepared for the first time, exhibits magnetic properties comparable to those of the analogous Fe(III) compounds.

Transition metal compounds with the kagome structure have been of considerable interest because of their novel magnetic properties such as geometric frustration. 1 Thus, investigations of Fe3+ jaro sites with the kagome structure have shown that, by and large, they exhibit geometric magnetic frustration, with some of them showing long-range antiferromagnetic ordering at low temperatures. 2 A Cr3+ compound with the kagome lattice also exhibits antiferromagnetic order. 3 Kagome structures of V3+ and mixed valent Fe (+2 and +3) have been found to exhibit ferro/ ferrimagnetic behavior. 4 To our knowledge, no kagome compound of cobalt appears to be known to date. We were interested in the synthesis of cobalt compounds with the kagome lattice in order to compare their magnetic properties with those of the iron compounds. In this communication, we report the synthesis†, structure‡ and magnetic properties of the first organically templated cobalt(II) sulfate of the composition, [H2N(CH2)4NH2][NH4]2-[Co(II)3F6(SO4)2], I, with the kagome lattice.

The asymmetric unit (Fig. 1a) of I contains 27 non-hydrogen atoms, out of which 19 belong to the inorganic-framework and 8 to the extra-framework guest molecules, including the nitrogens of the ammonium ions. The structure of I consists of anionic layers of vertex-sharing CoF4O2 octahedra and tetrahedral SO4 units, which are fused together by Co–F–Co and Co–O–S bonds. Each CoF4O2 unit shares four of its CoF4O2 units with similar neighbors with the Co–F–Co bonds roughly aligned in the bc-plane. The Co–O bond is canted from the bc-plane and the Co–O vertex forces a three-ring trio of apical Co–O bonds closer together to allow them to be capped by the SO4tetrahedra. The three- and six-rings of octahedra from the in-plane connectivity are shown in Fig. 1b). Such a layer consisting of hexagonal tungsten bronze sheets is characteristic of the kagome lattice. 5 The structure is akin to that of the mineral jaro site where all the Fe atoms are in the +3 state. The Co–O bond distances in I are in the range 2.104(3)–2.155(3) Å, |Co(I)–O|av = 2.134(3), (Co(2)–O)av = 2.112(3) and (Co(3)–O)av = 2.155(3) Å. The Co–F bond distances are in the range 2.032(2)–2.064(2) Å, |(Co(1))–F| = 2.046(5), (Co(2)–F) = 2.052(2) and (Co(3)–F)|av = 2.053(2) Å. The values of the bond angles and distances indicate a distorted octahedral coordination of Co and near-perfect tetrahedral coordination of sulfur. Bond valence sum calculations 8 [Co(1)] = 1.94, Co(2) = 1.95 and Co(3) = 1.91] and the values of the bond distances indicate that the valence state of the Co atoms to be +2. The position of the fluorine is also supported by these calculations. Thus, the framework stoichiometry of [Co(II)3F6(SO4)2]5− with a –4 charge requires the amine to be doubly protonated besides the presence of two ammonium ions. The anionic kagome sheets of [Co(II)3F6(SO4)2]5− are stacked one over the other and are held strongly by the hydrogen bond interaction of the amine and ammonium ions, residing in the inter-layer space. The amine and the ammonium ions form N–H–O (θ(N–H–O) = 150.8(4)–168.5(5), d(N–O) = 2.737(5)–3.040(7) Å) and N–H–F hydrogen bonds (θ(N–H–F) = 166(5)°–176(5)°, d(N–F) = 2.761(6)–2.870(6) Å) with the framework oxygens and fluorines.

The DC magnetic susceptibility data recorded at 100 Oe (Fig. 2) show marginal divergence between the field-cooled (FC) and the zero-field-cooled (ZFC) samples, along with a transition around 2.8 K (Tc). The divergence decreases even further at higher fields (500 Oe or above). Thus, the DC susceptibility data at 5000 Oe shows only the transition at 2.8 K. The inverse susceptibility data in the 150–300 K region is linear and can be fitted to the Curie–Weiss law...
mixture was taken in a 23 ml PTFE-lined acid digestion bomb and heated at 180 °C for 4 days. The product (yield: 60% with respect to Co) containing pink rhombohedral crystals suitable for single crystal X-ray diffraction, was filtered and washed with water. Compound I was characterized by powder X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Energy Dispersive X-ray (EDX) Analysis, elemental CHN analysis and IR spectroscopy. Magnetic measurements were performed at temperatures between 1.8 and 300 K using a Quantum Design SQUID magnetometer. EDX analysis indicated the ratio of Co : S to be 3 : 2. CHN analysis: obs. C = 7.82%, H = 4.02%, N = 9.06%; calc. C = 7.89%, H = 3.56%, N = 9.20%. The IR spectrum of I showed characteristic bands for the amine as well as the ammonium moieties. The ammonium ions are resulted from the decomposition of the pipernazine molecules used in the starting synthesis mixture. The stretching mode of −N-H bond (of the amine) is observed around 3004 cm⁻¹ (ν1). The N-H bending modes of the amine and NH₄⁺ are observed in the range 1440–1586 cm⁻¹. The characteristic stretching bands, ν₁(N–H) and 2ν₁(N–H) of the NH₄⁺ ion are observed at 2432 and 2830 cm⁻¹ respectively. Multiple C–N stretching modes are observed in the range 1080–1220 cm⁻¹. Strong bands in the region 850–1015 cm⁻¹ corresponds to ν1 and ν2 while bands in the region 583–644 cm⁻¹ can be assigned to ν1 and ν4 fundamental modes of sulfate ion.™ TGA shows a mass loss of 7% in the range 150–250 °C which could be accounted for the removal of ammonia (theo. = 6%). A major weight loss in the region 350–480 °C was observed corresponding to the loss of amine, HF and F₂ [theo. = 33.3%, obs. = 32.1%], followed by a third weight loss in the range 530–600 °C corresponding to the decomposition of the sulfate [theo. = 23.71%, obs. = 23.8%]. The end product was characterised to be condensed CoO.

† Single Crystal Structure Determination: Single crystal data were collected on a Siemens SMART-CCD diffractometer [graphite-monochromated MoKα radiation, λ = 0.71073 Å (T = 298 K)]. An absorption correction based on symmetry-equivalent reflections was applied using SADABS. The structures were solved by direct methods using SHELXS-86 and difference Fourier synthesis. Full-matrix least-squares structure refinement against F² was carried out using the SHELXTL-PLUS™ package of programs. The non-hydrogen atoms were refined anisotropically.

Crystal data: [H₂(N(CH₃)₂)₂NH][NH₄][Co₆(SO₄)₁] · 2H₂O, M = 607.15, Monoclinic, space group = P2₁/c (no. 14), α = 17.6655(5) Å, b = 7.477(10) Å, c = 12.8216(4) Å, β = 90°, β = 104.361(2)°, γ = 90°, V = 1639.46(7) Å³, Z = 4, μ = 3.367 mm⁻¹, μ_{calc} = 2.460 Mg m⁻³. A total of 6465 reflections were collected in the θ range 1.9–23.2 and merged to give 2331 unique data (R_{int} = 0.0327) of which 1688 with I > 2σ(I) were considered to be observed. Final R = 0.0516, R_{wp} = 0.0784 and S = 1.018 were obtained for 278 parameters. CCDC 211914. See http://www.ccdc.cam.ac.uk/supdata/cdb/33831394v4 for crystallographic data in cif format.


Notes and references

† Synthesis and initial characterization: I was synthesized under mild solvothermal conditions. In a typical synthesis, 0.2911 g of Co(NO₃)₂·6H₂O was dissolved in 4.6 ml of ethylene glycol under constant stirring. To this mixture, 0.3445 g of pipernazine (pip) and 0.22 ml of sulfuric acid (98%) were added, followed by the addition of 0.45 ml HF (40%). The resultant mixture with the molar composition, Co(NO₃)₂·6H₂O : 4H₂SO₄ : 4 pip : 80 ethylene glycol : 10HF had an initial pH < 2 after stirring for 5 h. The

Fig. 2. Temperature variation of the DC magnetic susceptibility I at 100 Oe showing the ZFC and FC curves. Inset shows inverse DC susceptibility vs temperature plot at 5000 Oe.

Fig. 3. Isothermal M–H cycles of I at 2 and 5 K.

(see the inset of Fig. 2) although a kagome lattice need not obey this law.² We obtain a θB of −35.5 K and an effective magnetic moment of 5.2 μB per Co from the Curie–Weiss fit. This θB value is much lower than that of the Fe³⁺ kagome compounds ( > ~600 K). The calculated χ_meff (spin only) for high-spin Co²⁺ is 3.87 μB. A slightly higher value I is due to the orbital contribution as found in many of the Co²⁺ compounds.³ The relatively high negative θB value indicates strong antiferromagnetic interactions between the Co²⁺ sites within the layer. The large θB/|T| ratio ( > 10) demonstrates the presence of magnetic frustration¹ as can be expected from the triangular lattice formed by the Co²⁺ ions in the kagome net. Isothermal magnetization data at 2 and 5 K (Fig. 3) do not show hysteresis. While there is no sharp increase in magnetization with the field, there is a small change in slope around 25 kOe in the 2 K data, possibly due to weak magnetic interactions between the layers.

In conclusion, a Co(n) kagome compound has been synthesized and characterized for the first time. Significantly, the magnetic properties of the Co(n) compound with d³ ions are not unlike those of the well-known Fe(n) kagome compounds with d⁵ ions, some of which exhibit antiferromagnetic ordering at low temperatures.² The magnetic parameters of the Co(n) compound however, suggest weaker antiferromagnetic interactions compared to the Fe(n) compounds.

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