

An organically templated Co(II) sulfate with the kagome lattice

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An amine-templated cobalt(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⁺ jarosites 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 Co^{II}F₄O₂ 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 Co–F vertices 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 SO₄ tetrahedra. The three- and six-rings of octahedra from the in-plane connectivity are shown in Fig. 1(b). 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 jarosite 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(1)–O)_{av} = 2.134(3), (Co(2)–O)_{av} = 2.112(3) and (Co(3)–O)_{av} = 2.1355(3) Å]. The Co–F bond distances are in the range 2.033(2)–2.064(2) Å [(Co(1)–F)_{av} = 2.0465(2), (Co(2)–F)_{av} = 2.0527(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 calculations⁶ [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] 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]^{4–} 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 ($\theta_{\text{N–H...O}}$ = 150.8(4)–168(5)°, $d_{\text{(N...O)}}$ = 2.737(5)–3.040(7) Å) and N–H...F hydrogen bonds ($\theta_{\text{N–H...F}}$ = 166(5)°–176(5)°, $d_{\text{(N...F)}}$ = 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 (T_N). 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

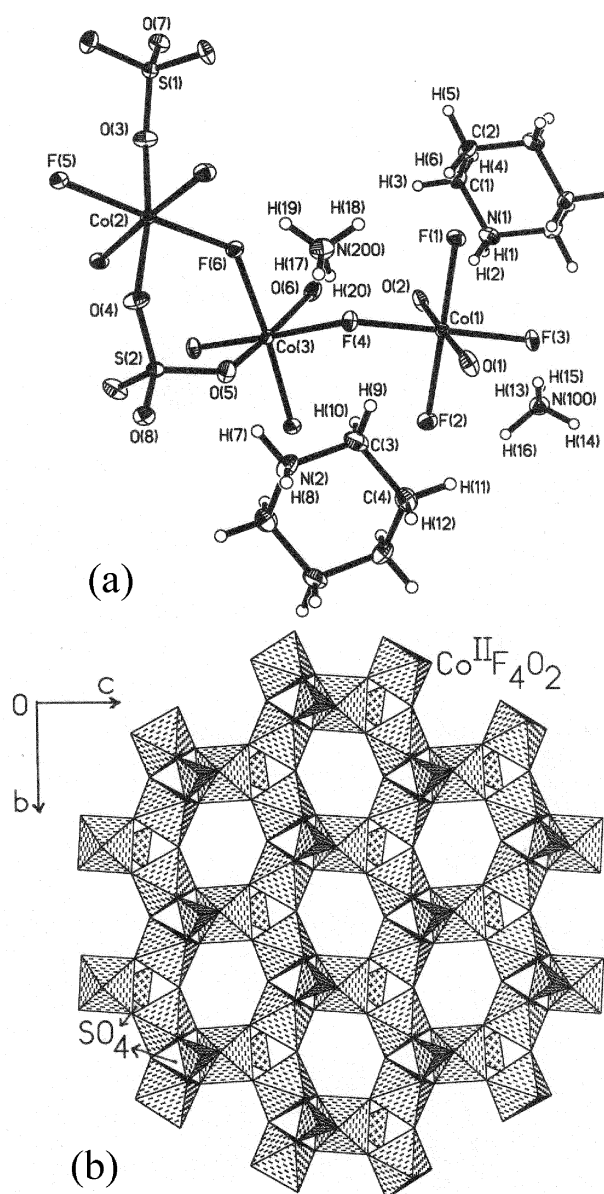


Fig. 1 (a) Asymmetric unit of **I**. Thermal ellipsoids are given at 45% probability. Only the asymmetric unit is labeled. (b) Polyhedral view of the kagome layer in **I**.

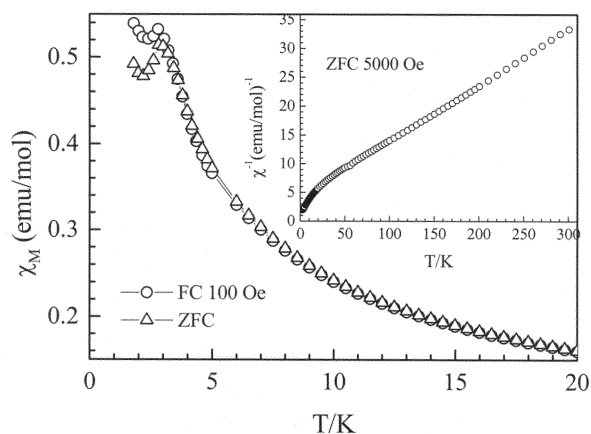


Fig. 2 Temperature variation of the DC magnetic susceptibility of **I** at 100 Oe showing the ZFC and FC curves. Inset shows inverse DC susceptibility vs temperature plot at 5000 Oe.

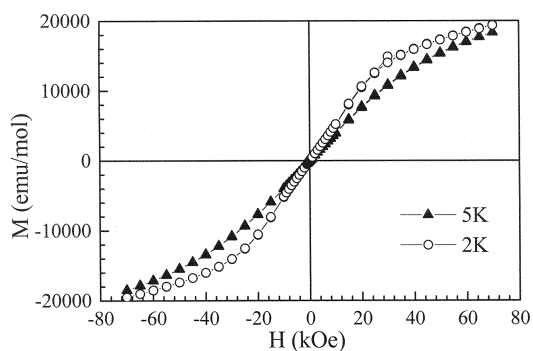


Fig. 3 Isothermal M-H cycles of **I** at 2 and 5 K.

(see the inset of Fig. 2) although a kagome lattice need not obey this law.² We obtain a θ_p of -35.5 K and an effective magnetic moment of $5.2 \mu_B$ per Co from the Curie-Weiss fit. This θ_p value is much lower than that of the Fe^{3+} kagome compounds (> -600 K). The calculated μ_{eff} (spin only) for high-spin Co^{2+} is $3.87 \mu_B$. A slightly higher value in **I** is due to the orbital contribution as found in many of the Co^{2+} compounds.⁷ The relatively high negative θ_p value indicates strong antiferromagnetic interactions between the Co^{2+} sites within the layer. The large θ_p/T_N ratio (> 10) demonstrates the presence of magnetic frustration¹ as can be expected from the triangular lattice formed by the Co^{2+} 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 $\text{Co}(\text{II})$ kagome compound has been synthesized and characterized for the first time. Significantly, the magnetic properties of the $\text{Co}(\text{II})$ compound with d^7 ions are not unlike those of the well-known $\text{Fe}(\text{III})$ kagome compounds with d^5 ions, some of which exhibit antiferromagnetic ordering at low temperatures.² The magnetic parameters of the $\text{Co}(\text{II})$ compound however, suggest weaker antiferromagnetic interactions compared to the $\text{Fe}(\text{III})$ compounds.

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Notes and references

† *Synthesis and initial characterization*: **I** was synthesized under mild solvothermal conditions. In a typical synthesis, 0.2911 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 4.6 ml of ethylene glycol under constant stirring. To this mixture, 0.3445 g of piperazine (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, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} : 4\text{H}_2\text{SO}_4 : 4 \text{ pip} : 80$ ethylene glycol : 10HF had an initial pH < 2 after stirring for 5 h. The

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 piperazine molecules used in the starting synthesis mixture. The stretching mode of $-\text{N}-\text{H}$ bond (of the amine) is observed around 3004 cm^{-1} (ν_1). The $\text{N}-\text{H}$ bending modes of the amine and NH_4^+ are observed in the range $1440-1586 \text{ cm}^{-1}$. The characteristic stretching bands, $\nu_3(\text{N}-\text{H})$ and $2\nu_4(\text{N}-\text{H})$ of the NH_4^+ ion are observed at 3243 and 2830 cm^{-1} respectively. Multiple C-N stretching modes are observed in the range $1080-1220 \text{ cm}^{-1}$. Strong bands in the region $850-1015 \text{ cm}^{-1}$ corresponds to ν_1 and ν_3 while bands in the region $583-644 \text{ cm}^{-1}$ can be assigned to ν_2 and ν_4 fundamental modes of sulfate ion.⁸ TGA shows a mass loss of 7% in the range $150-250^\circ\text{C}$ which could be accounted for the removal of ammonia (theo. = 6%). A major weight loss in the region $350-480^\circ\text{C}$ was observed corresponding to the loss of amine, HF and F_2 [theo. = 33.3%, obs. = 32.1%], followed by a third weight loss in the range $530-600^\circ\text{C}$ 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 $\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ ($T = 298 \text{ K}$)]. An absorption correction based on symmetry-equivalent reflections was applied using SADABS.⁹ The structures were solved by direct methods using SHELXS-86¹⁰ and difference Fourier synthesis. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS¹¹ package of programs. The non-hydrogen atoms were refined anisotropically.

Crystal data: $[\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2][\text{NH}_4]_2[\text{Co}^{13}\text{F}_6(\text{SO}_4)_2]$, **I**, $M_r = 607.15$, Monoclinic, space group = $P2_1/c$ (no. 14), $a = 17.6655(5) \text{ \AA}$, $b = 7.47170(10) \text{ \AA}$, $c = 12.8216(4) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 104.361(2)^\circ$, $\gamma = 90^\circ$, $V = 1639.46(7) \text{ \AA}^3$, $Z = 4$, $\mu = 3.367 \text{ mm}^{-1}$, $\rho_{\text{calcd}} = 2.460 \text{ Mg m}^{-3}$. A total of 6465 reflections were collected in the θ range $1.9-23.2$ and merged to give 2331 unique data ($R_{\text{int}} = 0.0327$) of which 1688 with $I > 2\sigma(I)$ were considered to be observed. Final $R = 0.0516$, $R_w = 0.0784$ and $S = 1.018$ were obtained for 278 parameters. CCDC 211914. See <http://www.rsc.org/suppdata/cc/b3/b313594b/> for crystallographic data in .cif format.

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