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$Co^{II}_5(OH)_6(SO_4)_2(H_2O)_4$: the first ferromagnet based on a layered cobalt–hydroxide pillared by inorganic $\cdots OSO_3–Co(H_2O)_4–O_3SO\cdots$

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The synthetic mineral $Co^{II}_5(OH)_6(SO_4)_2(H_2O)_4$ (1), obtained by hydrothermal reaction of $CoSO_4{\cdot}7H_2O$ and NaOH at 165 °C and consisting of brucite-like $Co_4(OH)_6O_2$ layers pillared by $OSO_3–Co(H_2O)_4–O_3SO$, is a ferromagnet (T_{Curie} = 12 K, H_c = 580 Oe).

Layered transition-metal hydroxides, in particular those having the brucite or hydrotalcite structure, are of major interest to both chemists and physicists due primarily to the rigidity of the metal–oxygen network brought about by the μ_3-OH and the edge-sharing of the octahedra.[1] The chemical interest stems from intercalation chemistry, to purification, to chromatography and most importantly, for their potential applications as catalysts.[1a] The interest for physics is due to the presence of short metal–metal distances (*ca.* 3 Å) and favourable angles for strong near-neighbour magnetic exchange interactions within the layer.[2] They are, therefore, model compounds to study certain aspects of magnetism; in particular, the mechanism for long-range magnetic ordering in two dimensions and its dependence on the tuneable interlayer distance.[3] However, the lack of structurally well-defined compounds and of single crystals have hampered the development in this area as evidenced by the number of variable interpretations.[4] To our knowledge, there exists only four such reports on structurally characterised magnetic materials, all prepared by the hydrothermal technique, but in these cases the layers are not truly brucite but are modified by having some of the octahedra within the layer replaced by tetrahedra above and below the vacancies.[5] However, a truly brucite-type magnetic layered compound has never been prepared in the laboratory but there are several reports of the structures of naturally occurring minerals.[6] Here, we report the structure of the first example prepared in a laboratory and its thermal and magnetic properties.

The crystals, very thin pale pink platelets, were reproducibly synthesised by hydrothermal treatment of a suspension of $CoSO_4{\cdot}7H_2O$ and sodium hydroxide at 165 °C for 24 h.‡ While the stoichiometry of the compound has a Co/OH ratio of 1.2, the optimised ratio of starting materials Co/OH is only 0.17. Under stoichiometric conditions $Co_3(OH)_2(SO_4)_2(H_2O)_2$ is obtained.[7] Thermogravimetric analysis performed under argon exhibits three weight losses corresponding to the departure of the coordinated water, the OH as H_2O and the decomposition of SO_4 as SO_2 or SO_3. The results confirm the formulation. **1** consists of a succession of brucite-like layers built up of edge-shared cobalt octahedra (Fig. 1) and pillared by inorganic $\cdots OSO_3–Co(H_2O)_4–O_3SO\cdots$.§ The formula of **1** can, therefore, be rewritten as $[Co(1)_2Co(2)_2(OH)_6O_{2/2}][Co(3)(H_2O)_4(SO_3O_{1/2})_2]$. Within the layer, Co(1) and Co(2) form alternate parallel chains running along the *b*-axis (Fig. 2). The O(2) oxygen atoms of the sulfate group are shared between two Co(1) and one Co(2) and alternate positions are occupied. On the other face of the layer, the complementary positions are now occupied. The pillaring Co(3) interlayer octahedron connects the sulfate groups. The octahedron around Co(1) is axially distorted with four short Co–O bonds with hydroxy groups (⟨Co–O⟩ = 2.035 Å) and two long ones with the sulfate group (⟨Co–O⟩ = 2.264 Å). Co(2) is bonded to five hydroxy

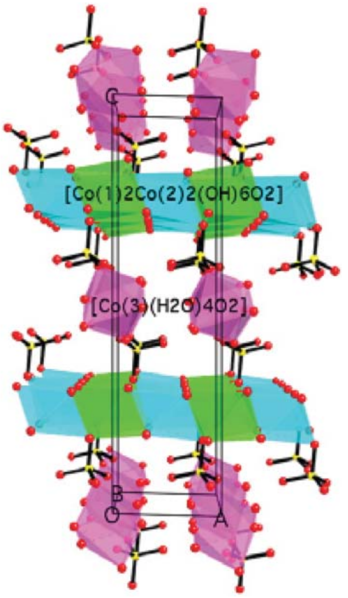

Fig. 1 Perspective view of the structure of (**1**) along the *b*-axis showing the brucite-like layers (Co(1) in blue and Co(2) in green) pillared by the $\cdots OSO_3–Co(H_2O)_4–O_3SO\cdots$ links (Co(3) in pink).

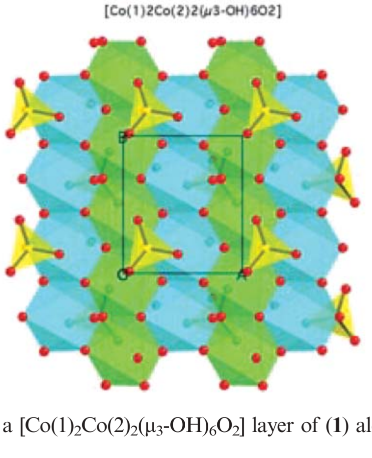

Fig. 2 View of a $[Co(1)_2Co(2)_2(\mu_3\text{-}OH)_6O_2]$ layer of (**1**) along the *c*-axis.

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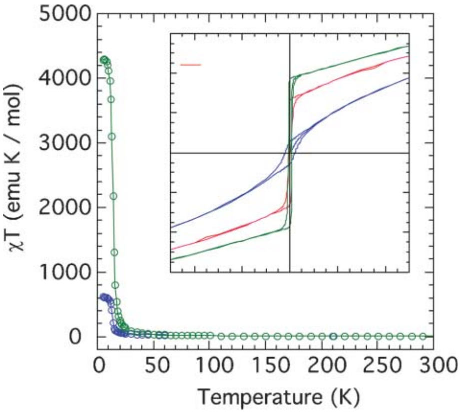

Fig. 3 Temperature dependence of the magnetic susceptibility in field of 1 kOe applied parallel (green) and perpendicular (blue) to the layers. Inset: isothermal magnetization at 2 K for the same orientations as well as for a polycrystalline sample (red).

groups (⟨Co–O⟩ = 2.079 Å) and one sulfate (Co–O = 2.309 Å). The Co(3) octahedron is nearly regular with four equal bonds with water molecules (Co–O = 2.103 Å) and two bonds with the sulfate (Co–O = 2.090 Å). The sulfate tetrahedron is nearly regular (⟨S–O⟩ = 1.477 Å).

The magnetic susceptibility has been measured on a polycrystalline sample and on an array of aligned crystals set in a PMMA matrix[5c] by use of a SQUID magnetometer between 2 and 300 K under an applied field of 1, 100 or 1000 Oe (Fig. 3). The isothermal magnetization was measured at different temperatures (2–20 K) in field range of ±50 kOe. In the paramagnetic region, above 100 K, the susceptibility of a powder sample obeys the Curie–Weiss law with Curie constant, $C = 14.5(2)$ emu K mol^{-1}, and Weiss constant, $\theta = +3(3)$ K, giving an effective moment $\mu_{\text{eff}} = (8C)^{1/2} = 4.82\ \mu_{\text{B}}$. This value is higher than the spin only value ($3.87\ \mu_{\text{B}}$) but falls within the experimental range for octahedral Co^{2+}.[8] The increase of μ_{eff} is due to spin–orbit coupling. The positive Weiss constant suggests ferromagnetic interaction between near-neighbours.[9] Spontaneous magnetization is observed at 12 K. Similar behaviour is observed for the aligned crystals but with slightly different values of Curie and Weiss constants. The bifurcation in the ZFC/FC magnetization in a field of 1 Oe and the non-zero imaginary ac-susceptibility (not shown) confirm the long-range magnetic ordering. The isothermal magnetization of a powder sample at 2 K presents a narrow hysteresis loop with a coercive field of 580 Oe and a magnetization in 50 kOe of $9.67\ \mu_{\text{B}}$. A value of $11\ \mu_{\text{B}}$ is expected taking into account an $S_{\text{eff}} = 1/2$ and $<g> = 13/3$. The behaviour for the aligned sample[5c] demonstrates the intrinsic anisotropy and indicates that the easy axis of magnetization lies within the layer. From the shape of the hysteresis loop and from the linear dependence above 2 kOe, it can be concluded that the moments on Co(1) and Co(2) are well ordered within the layers but this may not be the case for Co(3). Preliminary heat capacity measurements and frequency dependence ac-susceptibility suggest possible randomness of the moment of Co(3). The determination of the magnetic structure from neutron powder data will give more insight into the arrangement of the magnetic moment. Given that structurally well-characterised examples having different layer topology are available, their physics should enhance our understanding of the variable ground states, Curie temperatures,[5] magnetic hardness and furthermore, shed some light on the controversial long-range magnetic ordering mechanism.[4]

Notes and references

‡ Hydrothermal treatment of a suspension of $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (2.5 g, 8.9 mmol, 15 ml H_2O) and sodium hydroxide (0.06 g, 1.5 mmol, 5 ml H_2O) at 165 °C for 24 h, using boiled and degassed distilled water to prevent oxidation of Co^{2+}, gave very thin pale pink platelets which were separated by filtration, washed with distilled water, ethanol and acetone, and dried in air at 40 °C.

§ *Crystal data* for $\text{Co}_5(\text{OH})_6(\text{SO}_4)_2(\text{H}_2\text{O})_4$, (**1**), $M = 660.67$, monoclinic, space group $P2_1/c$, $a = 5.4698(2)$, $b = 6.3435(3)$, $c = 20.5471(8)$ Å, $\beta = 91.709(2)°$, $V = 712.62(9)$ Å^3, $Z = 2$, $D_c = 3.079$ Mg m^{-3}, $T = 293$ K, μ(Mo-Kα) = 6.06 mm^{-1}, $wR2 = 0.1291$ (for 2035 independent reflections ($R_{\text{int}} = 0.0391$)), $R1 = 0.0535$ [$I > 2\sigma(I)$]. CCDC 245726. See http://www.rsc.org/suppdata/cc/b4/b411304g/ for crystallographic data in .cif or other electronic format.

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