The organo-pillared porous magnetic framework $Co_4(SO_4)(OH)_6(H_2NC_2H_4NH_2)_{0.5}\cdot 3H_2O$

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The organo-pillared octahedral–tetrahedral (O/T) layer solid $Co_4(SO_4)(OH)_6(H_2NC_2H_4NH_2)_{0.5}\cdot 3H_2O$ is robust to loss of water molecules within the galleries, thermally stable to 300 °C and orders as a metamagnet below 14 K.

Pillared layered solids are an increasingly important class of materials of interest in the areas of sorption, separation and catalysis, as exemplified by the study of layered double hydroxides (positive layer charge),[1] smectite and other classes of clay (negative layer charge)[2] and the metal phosphonates (neutral layers).[3] Here, we report the direct synthesis and structural characterisation by single crystal X-ray diffraction of a novel type of layered hydroxide derived by organic pillaring of the namuwite[4,5]/basic zinc sulfate structure.[6] The multi-component nature of the new solid, its hydration/dehydration behaviour and the straightforward low temperature synthesis all suggest a broad family of such magnetic porous materials should be accessible.

Hydrothermal synthesis is a widely exploited low-temperature route to new solids.[6] Initial attempts to prepare microporous cobalt sulfates with a variety of amine templates at pH of below 7 led to the formation of dense, stable mineral phases such as $Co_3(SO_4)_2(OH)_2\cdot 2H_2O$ which only contain octahedral cobalt.[7] Increasing the pH of the initial synthesis gel from 7.7 to 10.8 led to precipitation of a brown sol (amorphous to X-rays) which on hydrothermal treatment for three days at 180 °C yielded small blue crystals of $Co_4(SO_4)(OH)_6(H_2NC_2H_4NH_2)_{0.5}\cdot 3H_2O$.§ Single crystal X-ray diffraction¶ showed the structure of this phase to arise from the stacking of layers formed by edge-sharing $Co^{II}(OH)_6$ octahedra regularly decorated by tetrahedral Co^{II} sites located above and below the layer at the 1/7 of the octahedral sites which are vacant (Fig. 1). Layer neutrality is completed by sulfate groups projected out from the layer which share one oxygen atom with three neighbouring CoO_6 octahedra and give the layer composition $Co_3^{oct}(SO_4)(OH)_5\cdot Co^{tet}(OH)$.

The coordination at the pseudo-tetrahedral metal site pulled out of the layer consists of three basal hydroxide anions (whose orientation is stabilised by hydrogen bonding to the neighbouring sulfate group) with the apical site occupied by the amine group of the bidentate ethylenediamine ligands. These organic units thus link two adjacent layers covalently *via* the decorating tetrahedral cobalt cations (Fig. 1). The synthesis pH controls whether cobalt is able to adopt this tetrahedral co-ordination.

The void space between the O/T layers separated by the en pillars contains three waters of crystallisation located by hydrogen bonding. The free dimensions of the channels between the pillars are 4.7 × 2.8 Å, occupying 16.5% of the crystal volume. One of the interlayer water molecules is readily lost at ambient temperature as elemental analysis indicates only two water molecules per formula unit. The difference from the composition derived from the low temperature crystallographic study is due to kinetic trapping of this water by the supporting oil at the low measuring temperature. The thermal analysis data in Fig. 2 shows that the remaining interlayer water is lost in two steps at *ca.* 100 and 200 °C to yield $Co_4(SO_4)(OH)_6(H_2NC_2H_4NH_2)_{0.5}\cdot H_2O$ [(b) c = 9.426 Å at 100(2) °C] and the fully dehydrated phase $Co_4(SO_4)(OH)_6(H_2NC_2H_4NH_2)_{0.5}$ [(c) c = 9.339 Å at 200(2) °C], respectively. The retention of the en pillars within the framework up to 200 °C was confirmed by the characteristic vibrational spectrum of the methylene group. Further heating leads to loss of the organic pillars as confirmed by loss of the methylene bending vibrations (Fig. 2, inset) and formation of Co_2O_3 *via* an unidentified crystalline intermediate above 450 °C. Water loss to stage (c) is fully reversible as demonstrated by TGA and *in situ* X-ray powder diffraction measurements of $Co_4(SO_4)(OH)_6(H_2NC_2H_4NH_2)_{0.5}$ on cooling from 200 °C to room temperature in water-saturated gas streams: the *c*-parameter increases sharply on cooling below 60 °C as water is reabsorbed within the interlayer region (Fig. 2 inset).‖

The *ca.* 1 Å decrease in the *c* parameter is consistent with a slippage of the layers occurring within the *ab*-plane. The bridging en units, having an N···N distance of 3.1 Å, may facilitate this interlayer compression if there is a tilting of the C–C bond resulting from a 120° rotation about each of the C–N bonds and change in N–C–C–N torsion angle from 60 to 180°.

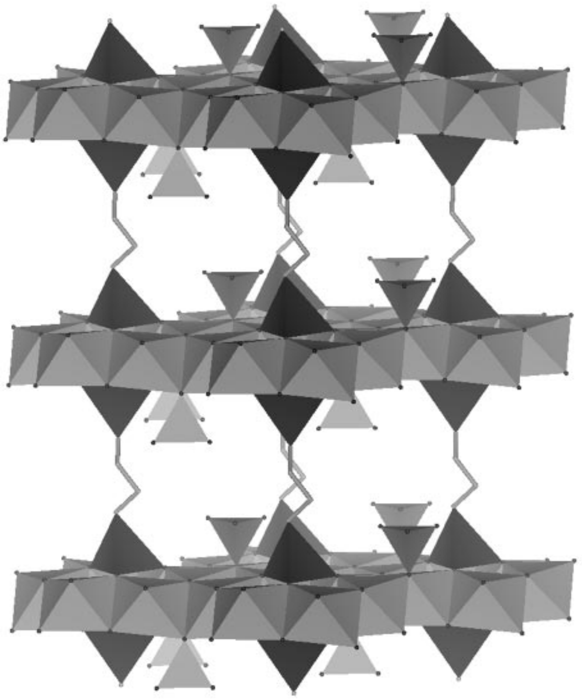

Fig. 1 The octahedral–tetrahedral (O/T) cobalt hydroxide layers of $Co_4(SO_4)(OH)_6(H_2NC_2H_4NH_2)_{0.5}\cdot 3H_2O$ are connected to each other by ethylenediamine pillars through the tetrahedral cobalt ions. The sulfate anions are the light grey tetrahedra decorating the layer. The interlayer water molecules, which can be removed while retaining the structure, are omitted for clarity.

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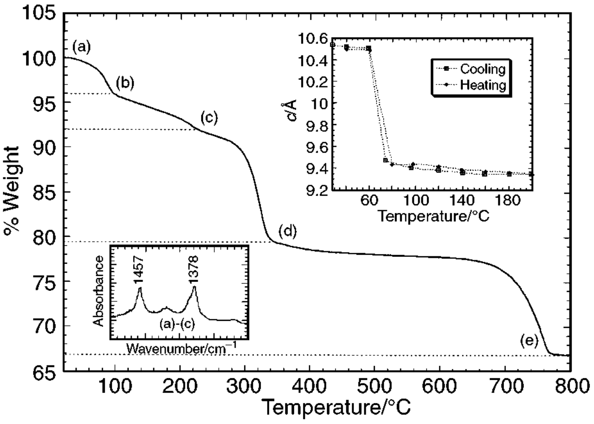

Fig. 2 TGA data under flowing nitrogen for $Co_4(SO_4)(OH)_6(H_2NC_2H_4NH_2)_{0.5}\cdot 2H_2O$ (a), showing loss of the interlayer water to yield the dehydrated pillared phase at (c). Insets show the temperature dependence of the *c*-parameter on heating and cooling in H_2O saturated helium and the IR spectra showing bending and stretching modes of the methylene groups (at 1457, 1378 and 2952, 2891 cm^{-1}).

The loss of 3D ordering with desolvation, as seen by the retention of only the 00l reflections, indicates there is no long range correlation in the direction of the resulting slippages for neighbouring sets of layers.

The magnetic susceptibility obeys the Curie–Weiss law above 190 K with an effective magnetic moment of 4.92(1) μ_B per cobalt, and a Weiss constant of −43(1) K. The downturn in the ZFC magnetisation at 14 K is consistent with antiferromagnetic ordering below this temperature.** Deviation from linearity in *M*(*H*) below 190 K indicates the development of short-range order well above this temperature. The magnetisation isotherm at 5 K (Fig. 3) and the corresponding first derivative curve (dM/dH) indicates metamagnetic behaviour with a saturation moment of 1.07 μ_B per Co at 5.0 T and 5 K. Manipulation of the metal sites, pillar and tetrahedral oxyanion based on this structure promises enhancement of void volume size, guest sorption and magnetic behaviour in this new class of magnetic porous material.

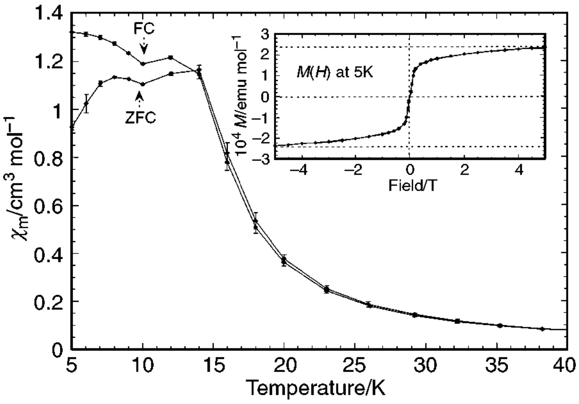

Fig. 3 Temperature dependent molar susceptibility (per mole of cobalt ions: ZFC and FC data collected in an applied field of 100 G). The field dependent magnetisation at 5 K is shown as an inset. The hysteresis at 5 K yields r_m of 336(9) emu mol^{-1} and H_c of 55(1) G.

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Notes and references

§ *Experimental*: $Co_4(SO_4)(OH)_6(H_2NC_2H_4NH_2)_{0.5}\cdot 3H_2O$ was synthesised hydrothermally from a mixture of $Co(NO_3)_2\cdot 6H_2O$ (98% Aldrich), H_2SO_4 (98% aq.), ethylenediamine (99% Aldrich) and concentrated aqueous 6 M KOH (pellet, 85+% Aldrich) in a molar ratio 1:2:0.6:5.4:100. The initial pH of the mixture was < 2 and became about 11 after addition of concentrated $KOH_{(aq)}$, then decreasing gradually to 8 after stirring for 1 h. A dark brown sol was obtained at this stage. The reaction was performed (180 °C, 3 days, autogeneous pressure) in a sealed hydrothermal bomb (22 cm^3 bomb volume and 70% fill factor) fitted with a Teflon liner. Blue plate-like (0.30 × 0.20 × 0.05 mm) crystals mixed with monophasic powder of the same product obtained were washed and rinsed with deionised water and acetone respectively. The elemental analytical formula was $Co_4(SO_4)(OH)_6(H_2NC_2H_4NH_2)_{0.45}\cdot 2.2H_2O$. Found: C, 2.16; H, 2.82; N, 2.52; Co, 47.10; S, 6.41. Calc. C, 2.32; H, 3.11; N, 2.70; Co, 45.51; S, 6.19%.

¶ Diffraction data collection was conducted at 150 K with an Enraf-Nonius DIP2000 diffractometer equipped with fine-focus molybdenum X-ray tube and a graphite monochromator. *Crystal data*: $CH_{16}Co_4NO_{13}S$, *M* = 517.93, trigonal, space group $P\bar{3}$ (no. 147), *a* = 8.298(1), *c* = 10.519(2) Å, *U* = 627.3(2) Å^3, *Z* = 2, μ(Mo-Kα) = 5.43 mm^{-1} 3396 reflections measured, 875 unique (R_{int} = 0.054) which were used in all calculations. The en pillar and surrounding water molecules are disordered about a threefold axis and were modelled with 1/3-occupation. *R*(*F*) = 0.0881 and *R*(F^2) = 0.2193 for all data. CCDC 182/1437. See http://www.rsc.org/suppdata/cc/1999/2307/ for crystallographic files in .cif format.

‖ Powder diffraction data collection was carried out using a Phillips X-ray diffractometer with Cu-Kα radiation to confirm the purity of the bulk synthesis. High temperature data were collected for $30 \leqslant T/°C \leqslant 400$ using a Siemens D5005 X-ray diffractometer with Cu-Kα radiation from a Gobel mirror multilayer monochromator: the sample was under a He or He–H_2O stream within an Anton-Parr HTK1200 high-temperature cell.

** Susceptibility measurements on a monophasic polycrystalline sample were made using a Quantum Design MPMS-SQUID magnetometer with a sample mass of 31.5 mg. Field cooled (FC) and zero-field cooled (ZFC) measurements were performed in applied fields of 100 and 1000 G over the temperature range of 5–300 K.

FTIR data were collected with a Nicolet Magna-IR 560 spectrometer with samples as self-supporting pellets.

Thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) data were collected on a Rheometric Scientific STA 1500 instrument for $20 \leqslant T/°C \leqslant 800$ under a nitrogen flow with a heating rate of 2 °C min^{-1}.

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