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The first 3-D ferrimagnetic nickel fumarate with an open framework: $[Ni_3(OH)_2(O_2C–C_2H_2–CO_2)(H_2O)_4]\cdot 2H_2O$†

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A three-dimensional nickel fumarate has been isolated by hydrothermal reaction and its structure solved from powder X-ray diffraction; its organisation reveals an unusual topology not previously seen in nickel chemistry and provided a scarce ferrimagnetic behaviour below 20 K.

The construction of infinite topologies using co-ordination chemistry tools, as transition metals and N- or O-donors ligands, is currently one of the most productive and promising focuses of chemistry research. Polymeric complexes at the frontier of solid state and molecular chemistry associate, in one material, electronic properties of transition metals with flexibility of the organic.[1–3] Co-operative magnetism in the solid state depends on the dimensionality of the exchange pathways; using fumarate or other linkers with π-delocalisation allows couplings through the organic and the opportunity to combine 3-D electronic interactions and open frameworks.[4–9] The interest of nickel lies in the construction, under hydrothermal conditions, of unusual inorganic networks with polyhedra linked by edges, vertices or faces.[10–12] This characteristic is well illustrated by the recent synthesis of two succinate compounds with unprecedented metal oxide organisations.[10,11] Herein, we describe the synthesis, structure, magnetic and thermal properties of the first three-dimensional nickel fumarate with a 3-D open framework.

The title compound was isolated as a pure green crystalline powder under hydrothermal conditions.‡ Its structure solved from X-ray powder diffraction data leads to the formula $[Ni_3(OH)_2(C_4H_2O_4)_2(H_2O)_4]\cdot 2H_2O$.§ Pattern indexing (DICVOL91)[13] yielded a monoclinic unit cell [a = 6.5561(3), b = 8.1194(3), c = 15.5027(6) Å and β = 96.370(2)°; V = 820.13(5) Å^3; Z = 2] with satisfactory figures of merit [M_{20} = 124 and F_{20} = 270 (0.0021, 36)]. Systematic absences were consistent with the $P2_1/c$ space group. The final Rietveld plot (Fig. 1) corresponds to satisfactory crystal structure model indicators (R_B = 0.089 and R_F = 0.071) and profile factors (R_P = 0.097 and R_{WP} = 0.122).

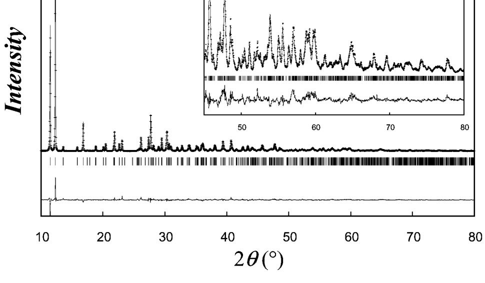

Fig. 1 Final Rietveld plot of the nickel fumarate. A zoom of the region at high angles is shown as inset.

The asymmetric unit contains two independent nickel atoms: Ni_1 (*4*) and Ni_2 (*2a*), one fumarate, three water molecules and a hydroxide ion. The organization consists of 1-D chains of nickel octahedra, parallel to the *a*-axis, and connected by fumarate ions to form a 3-D framework.

A remarkable feature is the presence of 2-D pores running along *a* and *b* axes. Tunnels down the *a*-axis are delineated by four walls of fumarate and four nickel oxide chains (free space taking into account van der Waals radii: 13.5/1.5 Å) (Fig. 2). Tunnels down the *b*-axis are delimited by the space between two pillar fumarates (3.0/5.5 Å) (Fig. 3). Each cavity at the intersection of the two perpendicular tunnels contains one water molecule.

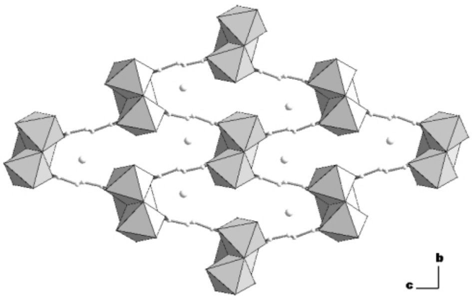

Fig. 2 View of nickel oxide chains running along the *a*-axis.

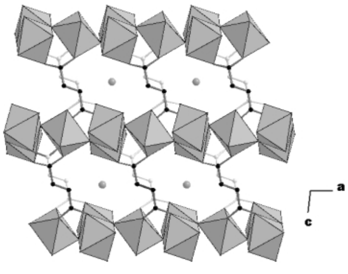

Fig. 3 View of the tunnels running along the *b*-axis.

The repeating structural motif in the nickel oxide chain is a trimer consisting of two edge-sharing symmetry-related nickel octahedra ($Ni_1–Ni_1$) linked *via* μ_3-OH to a vertex of Ni_2 octahedron (Fig. 4). Ni_1 is co-ordinated to oxygens from two hydroxide groups, two water molecules and two carboxylates. Ni_2 co-ordination is ensured by two hydroxide groups and four carboxylate oxygen atoms. The two polyhedra are quite symmetrical with bond lengths ranging from 2.03(1) to 2.16(1)

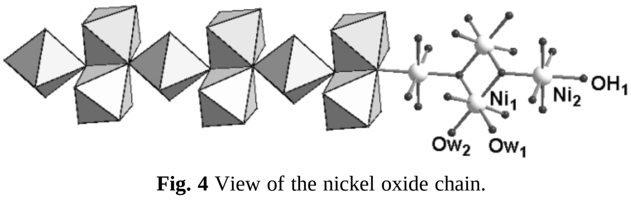

Fig. 4 View of the nickel oxide chain.

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† Electronic supplementary information (ESI) available: table of X-ray crystallographic data for $[Ni_3(OH)_2(C_4H_2O_4)_3(H_2O)_4]\cdot 2H_2O$. See http://www.rsc.org/suppdata/cc/b2/b207133a/

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Å. Carboxylic functions are bidentate ligands, bridging successive nickel atoms, while alkyl chains act as spacers between the chains. The structural organisation is novel, but the large lozenge shaped tunnels bear a striking resemblance to a vanadium terephthalate recently isolated by K. Barthelet *et al.*[14] The latter phase is constructed from infinite chains of V(III) octahedra linked by vertices and connected in a three-dimensional array by the carboxylates.

The thermal behaviour of $[Ni_3(OH)_2(C_4H_2O_4)_2(H_2O)_4]\cdot 2H_2O$ was studied by gravimetric analysis, X-ray powder diffraction and differential calorimetry. Four weight losses were associated with the departure of water molecules. Below 100 °C, a weight loss is probably due to adsorbed molecules. Around 110 °C, a loss, corresponding to occluded molecules, induces a phase transformation (obs. 6.6, calc. 6.2%). Between 200 and 250 °C a removal is attributed to the first co-ordinating water and is associated with XRD pattern modifications (obs. 5.7, calc. 6.2%). The removal of the second water ligand (280 °C) happens just before combustion of the organic and involves a last structural transformation before nickel oxide formation. The porosity was measured by gas sorption isotherm experiments performed in liquid nitrogen but the solid did not present any capacity for nitrogen adsorption whatever the temperature of gas evacuation. This non-reachable porosity is certainly due to the structural modification accompanying the removal of occluded water molecules.

The magnetic behaviour is displayed as $\chi_m T$ *vs* T in Fig. 5.¶ Through cooling from room temperature to 50 K, $\chi_m T$ remains practically constant and equal to 3.94 cm^3 K mol^{-1}, a value expected for three non-interacting Ni(II) atoms. Then, a small decrease is followed by a sharp and important increase (9.54 cm^3 K mol^{-1}) of $\chi_m T$ down to 4 K whatever the applied field (ZFC or FC). This behaviour is characteristic of ferromagnetic exchanges, but the small decrease at 50 K and a θ_p value of -7 K indicates competition between magnetic interactions. Considering the 1-D nickel chain, the main interactions occur from nickel polyhedra sharing edges ($d_{Ni-Ni} = 2.95$Å) and vertices ($d_{Ni-Ni} = 3.55$ and 3.66Å). A plausible model of magnetic interactions can be made using orbital overlap arguments.[15] The sign of the exchange depends on Ni–O–Ni angles (α): j is expected to be positive (F) for α values close to 90°, and negative (AF) when α is large. For the edge-sharing nickels with α of 89.7°, a ferromagnetic superexchange is expected, whereas vertices connections with large angles of 118.9° and 123.5° should favour antiferromagnetic interactions. A plot of the field dependent magnetisation measurement at 4.5 K is shown as inset in Fig. 5. Saturation is not yet reached, nonetheless, an extrapolated value can be estimated at around 2.6 μB mol^{-1}.

This clearly indicates a transition to a magnetised state at low temperature, but the value is slightly above that calculated for co-operative ferrimagnetism assuming $g = 2$, $M_s = 2$ μB mol^{-1}. Two parameters can explain this difference: first spin-orbit coupling with a g-factor estimated from our data close to 2.29,[16] and secondly a small spin frustration due to additional exchange pathway through fumarate ions. The possible orbital overlaps through fumarate should ensure a three-dimensional co-operative magnetisation.

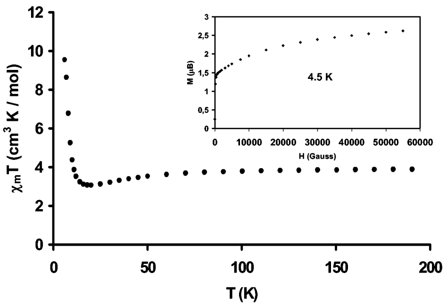

Fig. 5 Thermal dependence of the $\chi_m T$ product. The inset shows the magnetisation *vs* the applied magnetic field at 4.5 K.

We have for the first time synthesised a transition metal fumarate with a 3-D covalent organisation. The originality of the metal-oxide chain illustrates the plasticity of nickel inorganic condensation. It is a nice example of the versatility of nickel networks under hydrothermal conditions.

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Notes and references

‡ The title compound crystallised under hydrothermal conditions from a reaction mixture of 1 $NiCl_2\cdot 6H_2O$ (0.55 g)/1.5 fumaric acid (0.403 g)/4 KOH (0.520 g) and 120 H_2O. The reactants were sealed in a Teflon-lined 23 mL autoclave and heated at 180 °C for two days. After cooling, the solid product was recovered by filtration. Elemental analysis are in agreement with calculated values: $Ni_3C_8H_{18}O_{16}$ (% calc./obs.; Ni : 32.3/33.6, C : 17.6/17.6, H : 3.3/3.3). IR (KBr pellet, cm^{-1}): broad triplet at 3400 (water molecules) superimpose with a sharp band at 3600 characteristic of hydroxide groups (ν, O–H), doublet at 1575 *vs* (ν_{as}, O–C=O), band at 1400 *vs* (ν_s, O–C=O).

§ X-ray powder diffraction data were collected at 293 K on a Siemens D-5000 diffractometer using CuKα radiation [$\lambda = 1.5418$ Å; step size 0.02° (2θ); angular range 10–80° (2θ)]. Calculations were performed with the EXPO package for pattern matching (495 I_{int}) and direct methods,[17] and by using SHELXL for successive difference Fourier maps.[18] The Rietveld refinement was performed by using FullProf[19] integrated in WinPLOTR.[20] Calculated density 2.139 g cm^{-3} and measured one 2.204 g cm^{-3}; *M*w = 546.2 g mol^{-1}.

¶ Magnetic susceptibility measurement were carried out with a Quantum Design SQUID Magnetometer with an applied field of 5000 G.

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