A chromium(III) nickel(II) cyanide-bridged ferromagnetic layered structure with corrugated sheets

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An infinite stair-like layered ferromagnetic system is obtained from the reaction of $K_3[Cr^{III}(CN)_6]$ with $[Ni^{II}(cyclam)][ClO_4]_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane); a quasi-two-dimensional magnetic behaviour is suggested by the absence of three-dimensional magnetic order down to 2 K.

Bimetallic cyanide-bridged systems, built from the molecular precursors $[M(CN)_6]^{n-}$ and hexaaqua complexes $\{M'(OH_2)_6\}^{m+}$, present a three-dimensional Prussian blue-like structure,[1] exhibit magnetic order below T_C as high as 315 K[2,3] and present magneto-optical properties.[4] The magnetism of molecular assemblies is closely linked to their dimensionality.[5] Hexacyanometalates behave as versatile precursors to tune the dimensionality when combined with the assembler unit Lewis-acid complex $\{M'L_x(OH_2)_{6-x}\}^{m+}$, in which a polydentate ligand L blocks selected coordination sites and imposes the stereochemistry of the assembler.[6] Thus, the reaction of $[M(CN)_6]^{n-}$ with $\{M'L_x(OH_2)_{6-x}\}^{m+}$ affords low-dimensional systems.[7] Using a pentadentate ligand leads to heptanuclear species, with high-spin ground states and a superparamagnetic behaviour.[8,9]

Here, we report the single-crystal X-ray structure of $[Ni(cyclam)]_3[Cr(CN)_6]_2\cdot20H_2O$ (cyclam = 1,4,8,11-tetraazacyclotetradecane), an infinite two-dimensional system and a preliminary magnetic study of the powdered derivative $[Ni(cyclam)]_3[Cr(CN)_6]_2\cdot5H_2O$ **1**.†

The microcrystalline powder **1** is obtained by reacting an aqueous solution of *trans*-$[Ni(cyclam)(H_2O)_2][ClO_4]_2$ with $K_3[Cr(CN)_6]$. Parallelepiped, yellow single crystals are grown by the slow diffusion technique in an H-tube. The IR spectra of the powder and of the single crystals are identical. The important feature is the presence of two cyanide ν_{as} stretching bands at 2160 and 2130 cm^{-1} indicating the simultaneous presence of bridging and non-bridging cyanides respectively. X-Ray crystallography‡ reveals a monoclinic layered structure

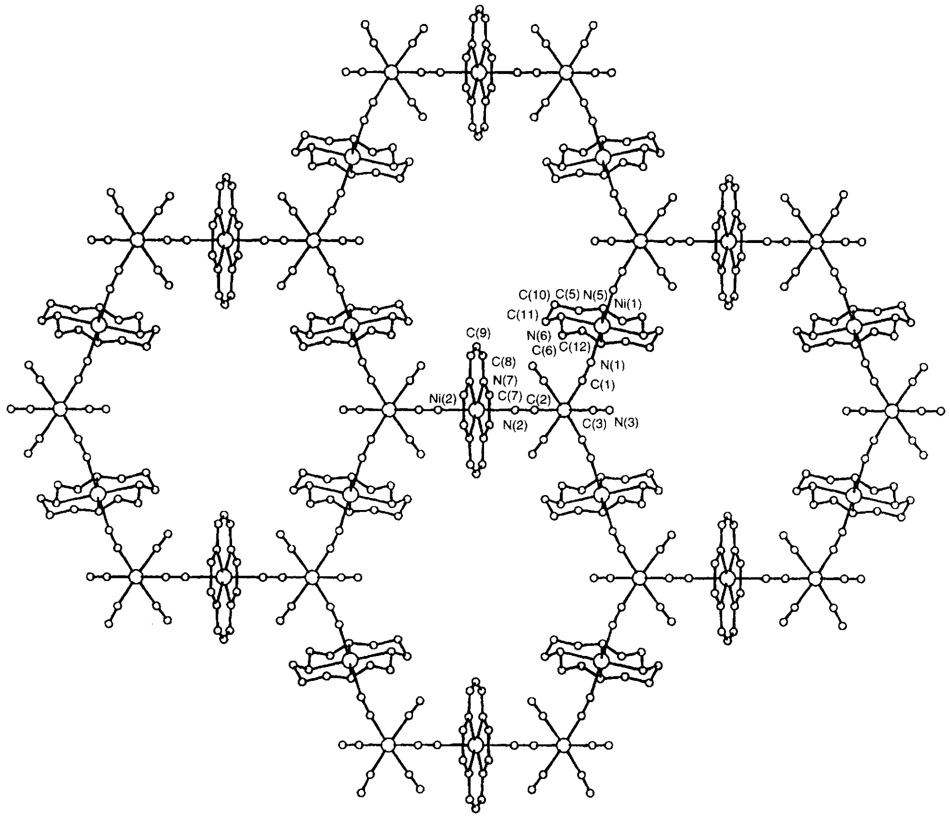

Fig. 1 View of a sheet down the *c* axis. Hydrogen atoms and water molecules are omitted for clarity. A selected tetranuclear $CrNi_3$ unit showing the facial disposition of the Ni(cyclam) molecules with labelled atoms is shown. Intermolecular distances (Å): Cr–C(1) 2.06(2), Cr–C(2) 2.01(3), Cr–C(3) 2.05(2), Cr–C(4) 2.11(2), Ni(1)–N(1) 2.12(1), Ni(1)–N(5) 2.06(2), Ni(1)–N(6) 2.23(3), Ni(2)–N(2) 2.06(2), Ni(2)–N(7) 2.11(2).

with the layers lying perpendicular to the *c* axis. Within the layers, each [Cr(CN)$_6$] entity is surrounded by three Ni(cyclam) moieties through cyanide bridges, leading to electrical neutrality of the layer, whereas each Ni(cyclam) unit is linked to two hexacyanochromate(III) molecules in *trans* positions (Fig. 1). The three Ni(cyclam) units adopt a facial configuration around the chromium ion, leaving three uncoordinated cyanides. Each nickel ion possesses an idealized inversion centre. The Cr···Ni(1) and Cr···Ni(2) distances through the cyanides bridge are 5.29 and 5.15 Å respectively, close to that observed for Prussian blue analogues.[1] The geometry around the nickel atoms is compressed octahedral; the nickel–cyanide nitrogen distances (apical positions) are slightly shorter (2.06 Å) than the equatorial ones (Fig. 1). The particular local molecular arrangement leads to a honeycomb-like structure, revealed when looking along the *c* axis (Fig. 1). The repeating hexagonal-like units adopt a chair conformation.§ The layers can be described as an infinite stair with the chromium ions lying at the edges of the steps and the nickel ions within the steps (Fig. 2). The corrugated two-dimensional structure is similar to that of black arsenic. Water molecules occupy the interlayer space, forming a network of hydrogen bonds, with O···N(3), O···N(3) and O···O distances being close to 2.90 Å. The shortest interlayer Cr···Cr, Cr···Ni(1), Cr···Ni(2) and Ni···Ni separations are 9.06, 8.06, 8.16 and 9.06 Å respectively.

The magnetic properties of **1** were investigated in the temperature range 2–300 K for molar susceptibility and in the range 0–70 kOe for magnetization. The $\chi_M T$ *vs.* T curve (Fig. 3) indicates a short-range ferromagnetic exchange interaction between Cr^{III} (t_{2g}^3) and Ni^{II} (e_g^2), as expected from the orthogonality of the t_{2g} (Cr^{III}) and e_g (Ni^{II}) orbitals.[2,8] This ferromagnetic coupling between Cr^{III} and Ni^{II} through the cyanide bridge was confirmed by the M *vs.* H curve, which at 70 kOe exhibits a value of 11.8 μ_B (expected value 12 μ_B for a Cr$_2$Ni$_3$ unit). At T = 10 K, $\chi_M T$ is at a maximum (25 cm^3 K mol^{-1}) and below 10 K, it decreases and reaches a value of 5 cm^3 K mol^{-1} at 2 K. This behaviour can be ascribed to an antiferromagnetic interaction between the layers. However, heat capacity measurements in the range 2–300 K range do not reveal any phase transitions.

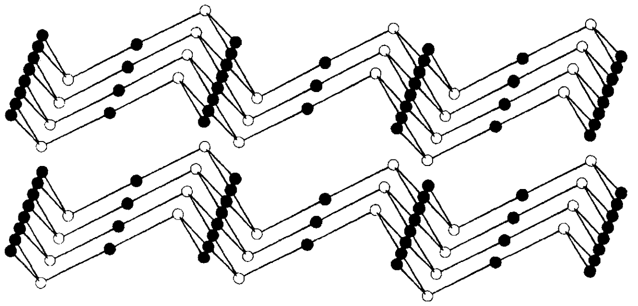

Fig. 2 View of two sheets showing the corrugated structure; only metal ions are shown for clarity: (○) Cr, (●) Ni

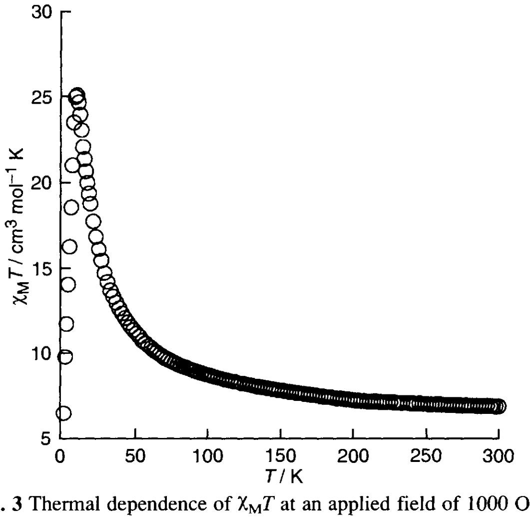

Fig. 3 Thermal dependence of $\chi_M T$ at an applied field of 1000 Oe

The present example is a new demonstration of the versatility of hexacyanometalates in building molecule-based assemblies of tunable dimensionality from discrete species[8,9] to three-dimensional networks,[1–3] *via* low-dimensional systems.[7]

Footnotes

† Chemical analysis of sample **1** is in accord with the proposed formula.

‡ The single crystals are destroyed when removed from their mother-liquor. The X-ray diffraction experiment was performed with the crystal in a Lindeman tube filled with water.

Crystal data: monoclinic, space group C_2/m, a = 25.980(4), b = 17.090(4), c = 9.057(1) Å, β = 91.54(1)°, U = 4020(2) Å^3, D_c = 1.27 g cm^{-3}, μ = 10.2 cm^{-1}, 3915 data collected at room temperature on a Enraf-Nonius CAD4 diffractometer. Empirical absorption correction using DIFABS (min. 0.88, max. 1.09) was adopted. Anomalous dispersion correction was applied. The structure was solved by standard Patterson Fourier techniques and refined by least-squares analysis using anisotropic thermal parameters for Ni, Cr and N atoms and isotropic thermal parameters for C atoms. Reflections [2157 with $I > 3\sigma(I)$, out of 3915 collected] were used to solve and refine the structure to R = 0.109 and R_w = 0.139, with 140 least-squares parameters. The program used was the PC version of CRYSTALS.[10] Three possible space groups are compatible with the observed extinctions: Cc, C_2/m and C_2/c. The best results are obtained with C_2/m. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/257.

§ Another alternate description of the hexagonal-like units is that of a cube having lost two vertices along one of the ternary axes.

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Received, 6th August 1996; Com. 6/05503F