

A novel two-dimensional honeycomb-like bimetallic iron(III)–nickel(II) cyanide-bridged magnetic material [Ni(cyclam)]₃[Fe(CN)₆]₂·*n*H₂O (cyclam = 1,4,8,11-tetraazacyclodecane)

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The 2D honeycomb-like layered iron(III)–nickel(II) cyanide-bridged complex [Ni(cyclam)]₃[Fe(CN)₆]₂·*n*H₂O exhibits ferromagnetic intralayer and antiferromagnetic interlayer interactions; above 3 K the magnetic properties are typical of a metamagnet with *H*_c = 5000 G, whereas below 3 K a canted structure is formed, leading to a long range ferromagnetic ordering.

Bimetallic assemblies with Prussian blue-like structure form a family of materials that exhibit spontaneous magnetization at *T*_c as high as 315 K,¹ and interesting electro-chemical, opto-electronic and magneto-optical properties.² The crystallization of Prussian blue analogues, however, is very difficult and it has been only quite recently that Kahn and coworkers³ have succeeded in growing crystals of [Mn₂(H₂O)₅Mo(CN)₇]₂·*n*H₂O (α and β forms), which ferromagnetically order at 51 K.

One alternative route to bimetallic cyanide-bridged extended arrays is that of using hexacyanometalate building blocks with metal complexes containing polydentate ligands. This hybrid approach favours the crystallization and then their magneto-structural study. Depending on the nature of the building blocks different and fascinating extended network structures can be obtained, some of which are magnetically ordered.⁴

On reacting [Ni(cyclam)]²⁺ and [Fe(CN)₆]³⁻ in water using a 1:1 molar ratio the compound [Ni(cyclam)]₃[Fe(CN)₆]₂·12H₂O is obtained as a fine brown precipitate, however, by using a 1:10 molar ratio the complex [Fe(cyclam)][Fe(CN)₆]₆·6H₂O is obtained.⁵ Slow diffusion of two aqueous solutions of the reactants, into a U-tube containing silica gel, provided two kinds of well formed dark brown block-like single crystals of formula [Ni(cyclam)]₃[Fe(CN)₆]₂·*n*H₂O (*n* = 12 and 22.5). X-ray analysis[†] reveals that both phases exhibit similar structures, which only differ in the number of water molecules (hereafter we shall discuss the results for *n* = 22.5, whose structure is more accurately determined). The structure consists of honeycomb-like layers (Fig. 1) and crystal water molecules that occupy the interlayer space. To form the layers, each [Fe(CN)₆]³⁻ is coordinated to three [Ni(cyclam)]²⁺ cations, at facial positions, through cyanide bridges, with Fe...Ni distances ranging from 5.037 to 5.202 Å, whereas each [Ni(cyclam)]²⁺ cation is linked to two [Fe(CN)₆]³⁻ units in *trans* positions. The *cis*-C–Fe–C angles are close to 90°, whereas the Fe–C distances are in the range 1.934(4)–1.954(4) Å. Ni^{II} ions, which are located on centres of symmetry, exhibit a *trans*-octahedral geometry; the nickel–cyanide nitrogen distances [2.123(3)–2.144(3) Å] being longer than the equatorial ones [2.059(4)–2.070(4) Å]. The Fe–C–N angles are close to linear and only vary in the small range 174.0(3)–179.1(3)°, whereas the Ni–N–C angles [165.4(3) and 154.9(3)°] deviate significantly from linearity. The layers are

not planar but form an infinite staircase structure and align along the *a* axis with shortest interlayer separations of 7.688 Å, for Fe...Ni(2). This structure is similar to that reported for a hexacyanochromate(III) analogue.^{4k}

The $\chi_M T$ vs. *T* plot per Fe₂Ni₃ unit (*H* = 50 G) is shown in Fig. 2. ‡ On cooling, $\chi_M T$ increases reaching a maximum value of 15 cm³ mol⁻¹ K at 8 K, indicating a ferromagnetic interaction between Fe^{III} (*t*_{2g}⁵) and Ni^{II} (*e*_g²). The χ_M curve shows a maximum at *ca.* 8 K, for *H* < 5000 G, a clear indication of an antiferromagnetic interaction between the ferromagnetic sheets.

Below 6 K, $\chi_M T$ sharply increases again reaching a value of 60 cm³ mol⁻¹ K at 2 K, suggesting a canting of the local spins, which may arise from the local magnetic anisotropy of Ni^{II} and low-spin Fe^{III} ions. This phase transition is confirmed by ac susceptibility measurements which show an intense signal at 3 K. Above 3 K, the magnetic properties are typical of a metamagnet with a critical field *H*_c = 5000 G. For *H* < 5000 G,

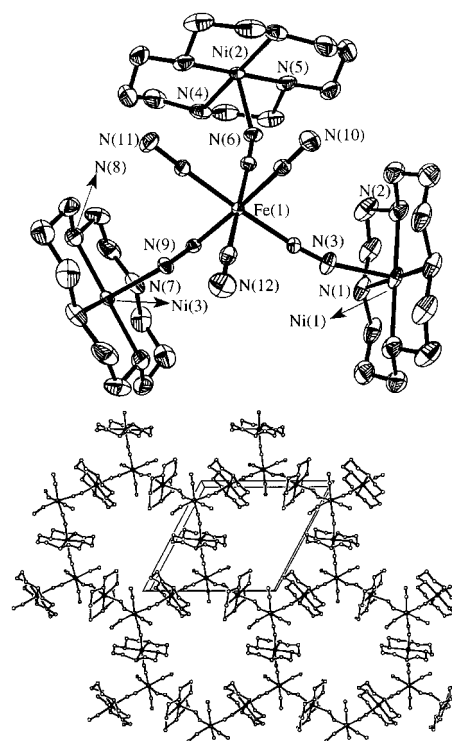


Fig. 1 Views of the asymmetric unit and 2D honeycomb-like layered. Water molecules are omitted for clarity.

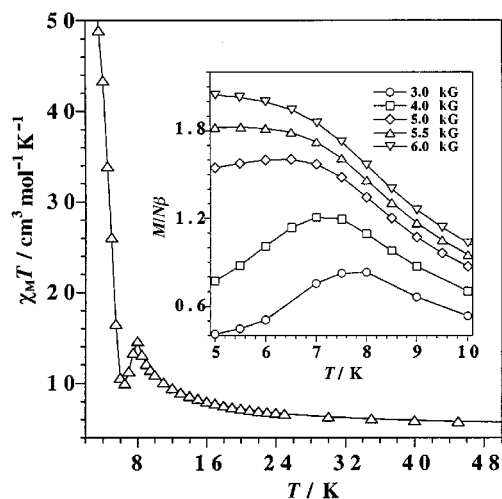


Fig. 2 $\chi_M T$ vs. T for $H = 50$ G. Inset: $(M/N\beta)$ vs. T at various fields.

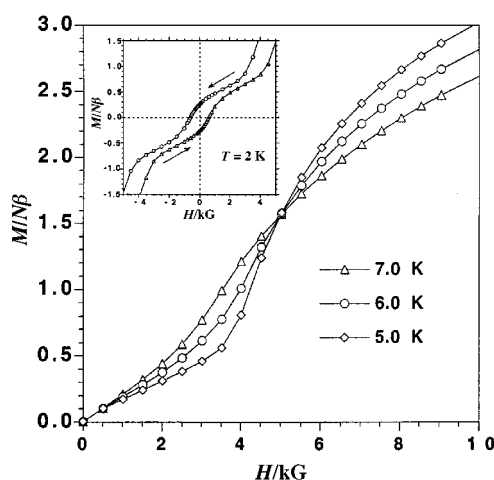


Fig. 3 $(M/N\beta)$ vs. H at different temperatures. Inset: hysteresis loop at 2 K.

the $(M/N\beta)$ vs. T curves (Fig. 2 inset) display a maximum which broadens as H is increased and finally disappears for $H > 5000$ G, demonstrating that a field-induced transition from an antiferro- to a ferro-magnetic ground state occurs. To confirm this metamagnetic behaviour, $(M/N\beta)$ vs. H was measured at various temperatures (Fig. 3). As the temperature is lowered, the isotherms become increasingly sigmoidal and present a crossing point at ca. 5000 G, corresponding to H_c .

Below 3 K, a canted structure is formed. The magnetization curves present hysteresis loops with a remanent magnetization of $0.26 N\beta$ and a coercive field of 600 G at 2 K (Fig. 3 inset). This canted structure is also broken when $H > 5000$ G, which is sufficient to overcome the intersheet interactions, responsible for the spin canting ground state. The chromium(III) analogue,^{4k} does not exhibit any phase transition above 2 K.

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Notes and references

† *Crystal structure analysis:* $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 22.5\text{H}_2\text{O}$, $\text{C}_{42}\text{H}_{113}\text{Fe}_2\text{N}_{24}\text{Ni}_3\text{O}_{22.5}$, $M_w = 1606.4$, monoclinic, space group $A2/n$, $a = 17.9384(12)$, $b = 16.7894(12)$, $c = 25.764(2)$ Å, $\beta = 91.176(9)^\circ$, $V = 7757.7(10)$ Å³, $Z = 4$, $D_c = 1.375$ Mg m⁻³, $F(000) = 3396$, $\mu = 1.157$ mm⁻¹, $T = 223(2)$ K, $0.50 \times 0.50 \times 0.40$ mm, 7366 independent ($R_{\text{int}} = 0.0497$) with 4326 [$I > 2\sigma(I)$] observed data, $R1 = 0.0457$, $wR2 = 0.1326$. $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$, $\text{C}_{42}\text{H}_{96}\text{Fe}_2\text{N}_{24}\text{Ni}_3\text{O}_{12}$, $M_w = 1417.3$, monoclinic, space group $C2/m$, $a = 27.384(3)$, $b = 14.3128(11)$, $c = 8.4772(8)$ Å, $\beta = 90.176(13)^\circ$, $V = 3322.6(6)$ Å³, $Z = 2$, $D_c = 1.417$ Mg m⁻³, $F(000) = 1496$, $\mu = 1.330$ mm⁻¹, $T = 193(2)$ K, $0.25 \times 0.20 \times 0.20$ mm, 3357 independent ($R_{\text{int}} = 0.197$) with 1571 [$I > 2\sigma(I)$] observed data, $R1 = 0.0764$, $wR2 = 0.1840$. Disordered macrocycle, atoms N21 and C21 (atoms A and B, were given an occupancy of 0.5 each). Graphite monochromatized Mo-K α radiation, $\lambda = 0.71073$ Å, STOE Image Plate diffractometer. No absorption corrections. Solution by direct methods (SHELXS-97) and refinements on F^2 by full-matrix least squares. Non-hydrogen atoms were refined anisotropically, H-atoms in calculated positions as riding atoms, except those of the water molecules that were ignored. CCDC 182/1234. See <http://www.rsc.org/suppdata/cc/1999/987/> for crystallographic files in .cif format

‡ Magnetic measurements were carried out on a SQUID-based sample magnetometer using a Quantum Design Model MPMS instrument.

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