

# A novel two-dimensional honeycomb-like bimetallic iron(III)–nickel(II) cyanide-bridged magnetic material $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ (cyclam = 1,4,8,11-tetraazacyclodecane)

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The 2D honeycomb-like layered iron(III)–nickel(II) cyanide-bridged complex  $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$  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,<sup>1</sup> and interesting electro-chemical, opto-electronic and magneto-optical properties.<sup>2</sup> The crystallization of Prussian blue analogues, however, is very difficult and it has been only quite recently that Kahn and coworkers<sup>3</sup> have succeeded in growing crystals of  $[\text{Mn}_2(\text{H}_2\text{O})_5\text{Mo}(\text{CN})_7] \cdot n\text{H}_2\text{O}$  ( $\alpha$  and  $\beta$  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.<sup>4</sup>

On reacting  $[\text{Ni}(\text{cyclam})]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  in water using a 1:1 molar ratio the compound  $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$  is obtained as a fine brown precipitate, however, by using a 1:10 molar ratio the complex  $[\text{Fe}(\text{cyclam})][\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$  is obtained.<sup>5</sup> 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  $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$  ( $n = 12$  and  $22.5$ ). X-ray analysis<sup>†</sup> 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  $[\text{Fe}(\text{CN})_6]^{3-}$  is coordinated to three  $[\text{Ni}(\text{cyclam})]^{2+}$  cations, at facial positions, through cyanide bridges, with Fe...Ni distances ranging from 5.037 to 5.202 Å, whereas each  $[\text{Ni}(\text{cyclam})]^{2+}$  cation is linked to two  $[\text{Fe}(\text{CN})_6]^{3-}$  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<sup>II</sup> 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.<sup>4k</sup>

The  $\chi_M T$  vs.  $T$  plot per  $\text{Fe}_2\text{Ni}_3$  unit ( $H = 50$  G) is shown in Fig. 2.† On cooling,  $\chi_M T$  increases reaching a maximum value of  $15 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 8 K, indicating a ferromagnetic interaction between Fe<sup>III</sup> ( $t_{2g}^5$ ) and Ni<sup>II</sup> ( $e_g^2$ ). The  $\chi_M$  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  $60 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 2 K, suggesting a canting of the local spins, which may arise from the local magnetic anisotropy of Ni<sup>II</sup> and low-spin Fe<sup>III</sup> 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,

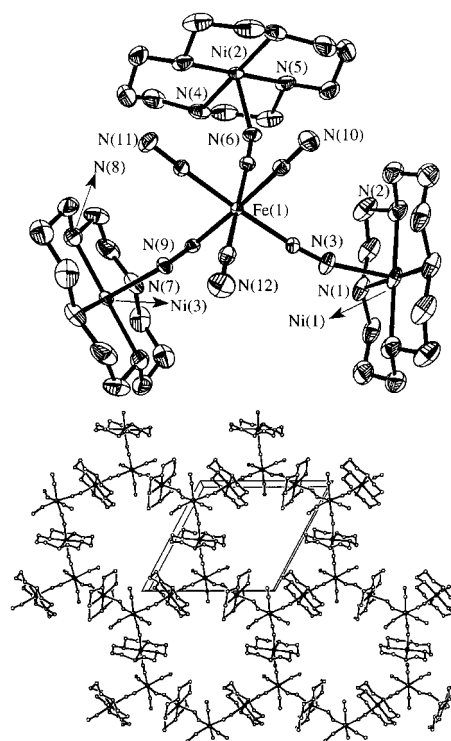


Fig. 1 Views of the asymmetric unit and 2D honeycomb-like layered. Water molecules are omitted for clarity.

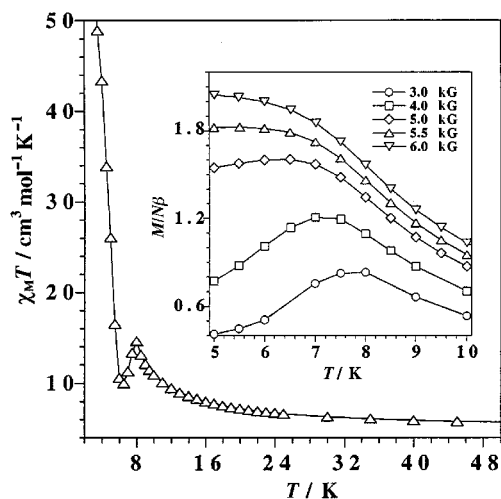


Fig. 2  $\chi_M T$  vs.  $T$  for  $H = 50$  G. Inset:  $(M/N\beta)$  vs.  $T$  at various fields.

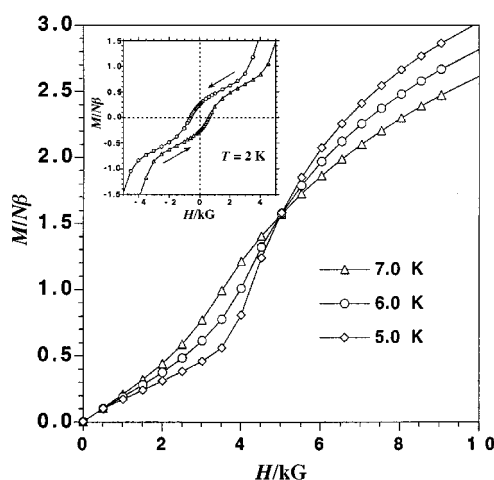


Fig. 3  $(M/N\beta)$  vs.  $H$  at different temperatures. Inset: hysteresis loop at 2 K.

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,<sup>4k</sup> 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,  $\beta = 91.176(9)^\circ$ ,  $V = 7757.7(10)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.375$  Mg m<sup>-3</sup>,  $F(000) = 3396$ ,  $\mu = 1.157$  mm<sup>-1</sup>,  $T = 223(2)$  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,  $\beta = 90.176(13)^\circ$ ,  $V = 3322.6(6)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.417$  Mg m<sup>-3</sup>,  $F(000) = 1496$ ,  $\mu = 1.330$  mm<sup>-1</sup>,  $T = 193(2)$  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 $\alpha$  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.

- 1 M. Verdager, *Science*, 1996, **272**, 698; W. Entley and G. S. Girolami, *Science*, 1995, **268**, 397; O. Kahn, *Nature*, 1995, **378**, 667; S. Ferlay, T. Mallah, R. Ouahes, P. Veillet and M. Verdager, *Nature*, 1995, **378**, 701; E. Dujardin, S. Ferlay, X. Phan, C. Desplanches, C. Cartier dit Moulin, P. Sainctavit, F. Baudelet, E. Dartyge, P. Veillet and M. Verdager, *J. Am. Chem. Soc.*, 1998, **120**, 11 347.
- 2 K. R. Dumbard and R. A. Heintz, *Prog. Inorg. Chem.*, 1997, **45**, 283; O. Sato, T. Iyoda, A. Fujishina and K. Hashimoto, *Science*, 1996, **271**, 46; O. Sato, T. Iyoda, A. Fujishina and K. Hashimoto, *Science*, 1996, **272**, 704.
- 3 J. Larionova, R. Clerac, J. Sanchiz, O. Kahn, S. Golhen and L. Ouahab, *J. Am. Chem. Soc.*, 1998, **120**, 13 088.
- 4 (a) M. Ohba, H. Okawa, N. Fukita and Y. Hashimoto, *J. Am. Chem. Soc.*, 1997, **119**, 1011; (b) N. Fukita, M. Ohba, H. Okawa, K. Matsuda and H. Iwamura, *Inorg. Chem.*, 1998, **37**, 842 and references therein; (c) M. Ohba, N. Usuki, N. Fukita and H. Okawa, *Inorg. Chem.*, 1998, **37**, 3349 and references therein; (d) H. Miyasaka, N. Matsumoto, N. Re, E. Gallo and C. Floriani, *Inorg. Chem.*, 1997, **36**, 670; (e) H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo and C. Floriani, *J. Am. Chem. Soc.*, 1996, **118**, 981; (f) N. Re, E. Gallo, C. Floriani, H. Miyasaka and N. Matsumoto, *Inorg. Chem.*, 1996, **35**, 6004; (g) H.-Z. Kou, D.-Z. Liao, P. Cheng, Z.-H. Jiang, S.-P. Yan, G. L. Wang, X.-K. Yao and H.-G. Wang, *J. Chem. Soc., Dalton Trans.*, 1997, 1503; (h) M. Salah El Fallah, E. Rentschler, A. Caneschi, R. Sessoli and D. Gatteschi, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 9047; (i) T. Mallah, C. Auberger, M. Verdager and P. Veillet, *J. Chem. Soc., Chem. Commun.*, 1995, 61; (j) A. Sculler, T. Mallah, M. Verdager, A. Nivorozhkin, J. Tholence and P. Veillet, *New J. Chem.*, 1996, **20**, 1; (k) S. Ferlay, T. Mallah, J. Vaisserman, F. Bartolomé, P. Veillet and M. Verdager, *Chem. Commun.*, 1996, 2481; (l) K. Van Langenberg, S. R. Batten, K. J. Berry, D. C. R. Hockless, B. Moubaraki and K. S. Murray, *Inorg. Chem.*, 1997, **36**, 5006; (m) N. Matsumoto, Y. Sunatsuki, H. Miyasaka, Y. Hashimoto, D. Luneau and J. P. Tuchagues, *Angew. Chem., Int. Ed.*, 1998, **38**, 171; (n) H.-Z. Kou, W.-M. Bu, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan, Y.-G. Fan and G.-L. Wang, *J. Chem. Soc., Dalton Trans.*, 1998, 4161; (p) J. Larionova, O. Kahn, S. Gohlen, L. Ouahab and R. Clerac, *J. Am. Chem. Soc.*, 1999, **121**, 3349.
- 5 E. Colacio, J. M. Domínguez-Vera, M. Ghazi, R. Kivekas, M. Klinga and J. M. Moreno, *Chem. Commun.*, 1998, 1071.

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