

# A cyano bridged iron(III) linear chain with alternating $\text{Fe}(\text{CN})_6\text{--Fe}(\text{cyclam})$ (cyclam = 1,4,8,11-tetraazacyclodecane) units and unexpected ferromagnetic behaviour

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The X-ray crystal structure and magnetic properties of a cyano-bridged iron(III) linear chain containing alternating iron sites and unexpected ferromagnetic behaviour, justified on the basis of the axial distortion from regular octahedral geometry of one of the iron(III) ions, are reported.

The design and elaboration of new systems with original magnetic, optical and/or electrical properties is at the heart of molecular magnetism.<sup>1</sup> In the last few years, there has been a considerable interest in the preparation and properties of molecular magnets.<sup>2</sup> One potential general route to the synthesis of molecular magnets is to make analogues of Prussian blue, in which all the centres are paramagnetic.<sup>3</sup> Following this route, several Prussian analogues have been prepared with the aim of enhancing the ordering temperature by changing the nature of the interaction between the paramagnetic ions through the cyanide bridge. Recently, the room temperature barrier was overcome at 315 K with a  $\text{Cr}^{\text{III}}/[\text{V}^{\text{II}}\text{--V}^{\text{III}}]$  compound.<sup>4</sup> Even though these materials can be synthesized by applying the techniques of molecular chemistry and then considered as molecular-based magnets, however, because their magnetic properties can only be tuned by changing the pair of interacting paramagnetic ions, they are close to the ionic magnets. Lately, a hybrid approach has been used in order to obtain molecular-based magnets. It consists of combining  $[\text{M}(\text{CN})_6]^{n-}$  building blocks with transition metal ion complexes. Following this approach several cyano-bridged bimetallic complexes with 2D<sup>5</sup> and 3D<sup>6</sup> structures have been prepared, which undergo magnetic phase transitions at lower temperature than the Prussian blue analogues. Because they are molecular systems their magnetic properties can be chemically tuned by not only varying the metal ions but also the ligands. By using the same synthetic strategy it is possible to design  $\text{MM}'_6$  cyano bridged heptanuclear entities ( $\text{M} = \text{Fe}^{\text{III}}$  or  $\text{Cr}^{\text{III}}$ ;  $\text{M}' = \text{Cu}^{\text{II}}$  or  $\text{Ni}^{\text{II}}$  and  $\text{Mn}^{\text{II}}$ , respectively).<sup>7</sup> Among them, the  $\text{CrNi}_6$  and  $\text{CrMn}_6$  species exhibit high-spin ground states of  $S = 15/2$  and  $27/2$ , respectively. We have now found that from the building blocks  $[\text{Ni}(\text{cyclam})]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ , two different cyano-bridged complexes can be obtained, depending on the stoichiometric ratio of the reactants. Thus, by dropwise addition of an aqueous solution of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (1 mmol, 20 ml) to an aqueous solution of  $[\text{Ni}(\text{cyclam})][\text{ClO}_4]_2$  (1 mmol, 50 ml) a brown precipitate is immediately obtained, whose analytical data point to the formula  $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 6\text{H}_2\text{O}$ . Preliminary magnetic measurements suggest that this compound orders ferromagnetically below 8 K. It is noteworthy that the precipitate dissolves upon addition of a large excess of  $[\text{Fe}(\text{CN})_6]^{3-}$  (10:1 molar ratio), leading to a dark green solution, from which prismatic dark brown crystals of  $[\text{Fe}(\text{cyclam})][\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$  **1** appear within one week.<sup>‡</sup> It is noteworthy that the presence of a large excess of  $[\text{Fe}(\text{CN})_6]^{3-}$  promotes the substitution of  $\text{Ni}^{\text{II}}$  from  $[\text{Ni}(\text{cyclam})]^{2+}$  by  $\text{Fe}^{\text{III}}$ . Consequently, complex **1** can also be prepared from cyclam and

$\text{K}_3[\text{Fe}(\text{CN})_6]$ . The structure<sup>§</sup> of **1** was determined by X-ray analysis (Fig. 1) and it consists of polymeric chains of alternating  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{cyclam})]^{3+}$  ions running along the *a* axis, and crystal water molecules. In the chain two  $\text{CN}^-$  groups of each  $[\text{Fe}(\text{CN})_6]^{3-}$  unit bridge two iron(III) atoms with  $\text{Fe}\cdots\text{Fe}$  distances of 5.129(1) Å. Both types of iron atoms are located on symmetry elements *2/m*, and the bridging  $\text{CN}^-$  ions as well as the C(6) atom of the cyclam ligand lie on the mirror plane. The chains are almost linear as the bond angles for the bridging  $\text{CN}^-$  group are *ca.* 175°. The  $\text{Fe--C--N}$  angles for terminal  $\text{CN}^-$  groups in  $[\text{Fe}(\text{CN})_6]^{3-}$  do not deviate significantly from linearity. The iron centre in the  $[\text{Fe}(\text{CN})_6]^{3-}$  unit adopts a minimally distorted octahedral environment, where the *cis*- $\text{C--Fe--C}$  angles are close to 90° and  $\text{Fe--C}$  distances equal for bridging [1.925(8) Å] and terminal [1.936(6) Å]  $\text{CN}^-$  groups. Owing to coordination of the  $\text{CN}^-$  groups, the iron centre of the  $[\text{Fe}(\text{cyclam})]^{3+}$  unit assumes an axially distorted octahedral  $\text{FeN}_6$  chromophore. The two axial positions are occupied by the nitrogen atoms of the bridging  $\text{CN}^-$  groups with  $\text{Fe--N}$  distances of 2.069(6) Å and the equatorial positions by the  $\text{N}_4$  set of donor atoms from the cyclam ligand with  $\text{Fe--N}$  distances of 1.963(5) Å. The equatorial coordination planes of Fe(1) and Fe(2) are not parallel but form a dihedral angle of 10.7(1)°. In the crystal, the chains are linked by hydrogen bonds involving the lattice water molecules and the N(2) and N(4) nitrogen atoms of the  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{cyclam})]^{3+}$  units, respectively, thus leading to a two dimensional layer structure. The donor-acceptor distances range from 2.738(8) to 2.836(7) Å, whereas the nearest  $\text{Fe}\cdots\text{Fe}$  interchain separation is 8.101(1)

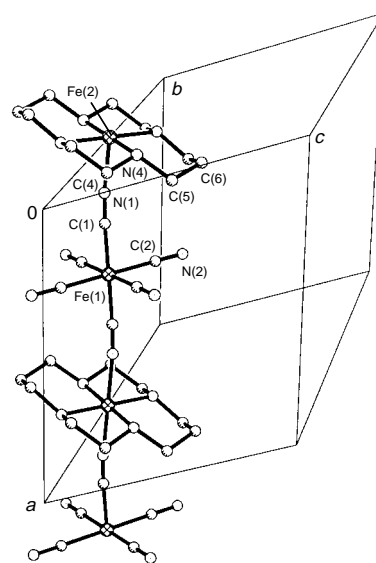
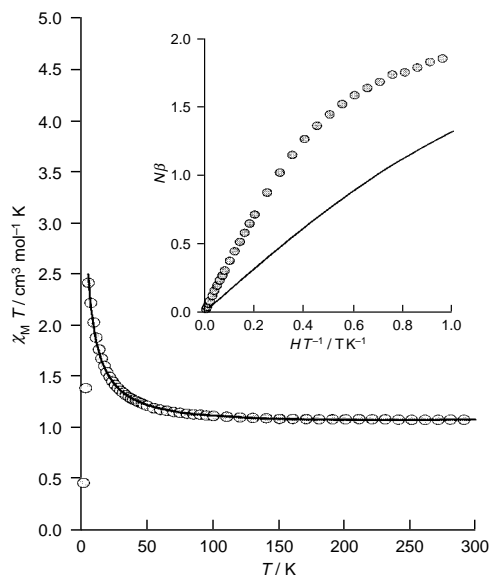


Fig. 1 A perspective view of the chain complex **1**



**Fig. 2** Magnetic data ( $\chi_M T$  vs.  $T$ ) of **1**. Inset: magnetization data ( $N\beta$  vs.  $H/T$ ) of **1** (solid line represents the theoretical value of the Brillouin function for  $S = \frac{1}{2}$ ).

Å. It should be noted that, among Fe<sup>III</sup> polymers, structurally characterized chain complexes are rare and those with alternating iron sites are rarer still,<sup>8</sup> compound **1** being the first example of an iron(III) chain containing alternating iron sites but not alternating bridging ligands.

The temperature dependence of the  $\chi_M T$  product per Fe<sub>2</sub> unit in the range 2–295 K is shown in Fig. 2. The  $\chi_M T$  product at room temperature, 1.06 cm<sup>3</sup> mol<sup>-1</sup> K, is significantly larger than the spin-only value of 0.75 cm<sup>3</sup> mol<sup>-1</sup> K expected for two isolated low spin iron(III) ions ( $S = \frac{1}{2}$ ), assuming  $g = 2.00$ , probably because of an orbital contribution to the magnetic moment of the low-spin Fe<sup>III</sup> ions. As the temperature is lowered,  $\chi_M T$  remains almost constant until around 100 K, then increases smoothly to reach a maximum of 2.41 cm<sup>3</sup> mol<sup>-1</sup> K at 6 K and finally decreases sharply to 0.45 cm<sup>3</sup> mol<sup>-1</sup> K upon cooling to 2 K. Such magnetic behaviour is characteristic of a dominant ferromagnetic coupling within the chain and inter-chain antiferromagnetic interactions, which are responsible for the decrease of  $\chi_M T$  at very low temperature. The experimental magnetization values per Fe<sub>2</sub> unit as a function of the applied field at 5 K (Fig. 2) are greater than those predicted by the Brillouin function for two magnetically isolated iron(III) with  $S = \frac{1}{2}$ , thus confirming the existence of a ferromagnetic interaction between iron(III) ions. Apparently, **1** is the first example of an iron(III) chain exhibiting ferromagnetic intra-chain exchange interactions. For estimating the magnitude of the ferromagnetic coupling, first, the magnetic susceptibility data ( $T > 6$  K) were fitted to the Baker's expression<sup>9</sup> for a  $S = \frac{1}{2}$  uniformly spaced ferromagnetic chain with the Hamiltonian in the form  $H = -J \sum_i^{n-1} S_i S_{i+1}$ .

The best fit parameters were  $J = 8.6$  cm<sup>-1</sup> and  $g = 2.27$ . The polycrystalline powder EPR spectrum at 100 K seems to be axial with  $g_{\perp} = 2.21$  and  $g_{\parallel} = 2.03$ . At first glance, the ferromagnetic behaviour observed for **1** is rather unexpected taking into account the magnetic orbitals involved in the exchange interaction. Low-spin iron(III) ion in octahedral surroundings ( $t_{2g}^5$ ) has the unpaired electron density on  $xy$ ,  $xz$  and  $yz$  d orbitals, which are degenerate. If the Fe(1)–CN–Fe(2) bond is considered to lie along the  $z$  axis, with the  $x$  and  $y$  axes pointing toward the equatorial CN<sup>-</sup> groups for Fe(1) and toward the nitrogen atoms of the macrocycle for Fe(2), the  $xz$  and  $yz$  orbitals on both iron(III) ions would overlap through the  $\pi$  orbitals of the CN<sup>-</sup> group to give rise to antiferromagnetic contributions. A closer examination of the structure of **1**,

however, reveals that while the coordination polyhedron of Fe(1) is almost perfectly octahedral ( $O_h$  point symmetry), that of Fe(2) is axially elongated along the CN–Fe(2)–NC direction ( $D_{4h}$ ). For this tetragonal distortion the ground state configuration becomes  $(xz, yz)^4(xy)^1$ . Then, the ferromagnetic interaction might be the result of the orthogonality between the  $(xy)^1$  orbital ( $b_{2g}$ ) on Fe(2) and the  $xz$  and  $yz$  ( $t_{2g}$ ) orbitals on Fe(1). It is of note that a similar unexpected ferromagnetic coupling has been also observed between two cyano-bridged Cr<sup>III</sup>[ $d^3, (t_{2g})^3$ ], in the compound *catena*-cyano(phthalocyaninato)chromium(III).<sup>10</sup> Even though no crystal structure determination has been reported for this compound, the Cr<sup>III</sup> ions in the chain should be in a distorted octahedral surrounding. If so, a similar orbital explanation to that for **1** can be applied to the Cr<sup>III</sup> compound in order to justify the observed ferromagnetic interaction. In view of these results, more examples are needed of cyano-bridged chain Cr<sup>III</sup> and Fe<sup>III</sup> complexes in order to definitively clarify the origin of the ferromagnetic exchange interaction. In this sense, the reaction of  $[M(CN)_6]^{3-}$  ( $M = Cr^{III}$  and  $Fe^{III}$ ) toward metal–macrocycle complexes is currently under examination.

This work was supported by the Dirección General de Investigación Científica y Técnica (project PB94-0764) and by the Junta of Andalucía.

## Notes and References

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‡ IR (cm<sup>-1</sup>):  $\nu(OH)$  3583, 3480;  $\nu(NH)$  3349, 3100;  $\nu(CN)$  2151, 2125. Anal. Calc. for C<sub>16</sub>H<sub>36</sub>Fe<sub>2</sub>N<sub>10</sub>O<sub>6</sub>: C, 33.32; H, 6.30; N, 24.30; Found: C, 33.29; H, 6.38; N, 24.04%.

§ *Crystal structure analysis for 1*: Rigaku AFC7S diffractometer, graphite monochromatized Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å, 298 K. Lorentz-polarisation and absorption corrections ( $\psi$  scan). C<sub>16</sub>H<sub>36</sub>Fe<sub>2</sub>N<sub>10</sub>O<sub>6</sub>, monoclinic, space group  $C2/m$ ,  $a = 10.259(2)$ ,  $b = 16.201(3)$ ,  $c = 8.892(2)$  Å,  $\beta = 110.99(3)^\circ$ ,  $U = 1379.8(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.387$  Mg m<sup>-3</sup>,  $F(000) = 604$ ,  $\mu = 1098$  mm<sup>-1</sup>, crystal dimensions  $0.22 \times 0.10 \times 0.09$  mm. 1335 Reflections were collected with 932 considered as observed [ $I > 2\sigma(I_o)$ ]. Structure was solved by direct methods (SHELX-86) and refined on  $F^2$  by full-matrix least squares to  $R_1 = 0.0568$  ( $wR_2 = 0.1124$ ). CCDC 182/827.

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Received in Basel, Switzerland, 6th January 1998; 8/00188J