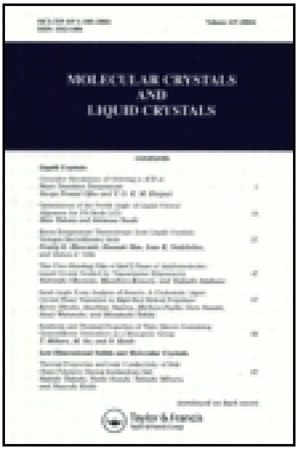

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

One-Dimensional Iron(III) and Two-Dimensional Iron(III)Nickel(II) Cyanide-Bridged Ferromagnetic Arrays from Hexacyanoferrate(III) and $[Ni(cyclam)]^{2\pm}$ Building Blocks: Synthesis, Crystal Structure and Magnetic Properties

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One-Dimensional Iron(III) and Two-Dimensional Iron(III)Nickel(II) Cyanide-Bridged Ferromagnetic Arrays from Hexacyanoferrate(III) and $[Ni(cyclam)]^{2+}$ Building Blocks: Synthesis, Crystal Structure and Magnetic Properties

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The X-ray structures and magnetic properties of a iron(III) linear chain and a honeycomb-like layered iron(III)-nickel(II) cyanide-bridged compound are reported. The former contains alternating iron sites and unexpected ferromagnetic behaviour, justified on the basis of the axial distortion from regular octahedral geometry of one of the iron ions. The latter is metamagnetic with ferromagnetic intralayers and antiferromagnetic interlayers interactions with a Néel temperature, T_N= 7.7 K. The field-induced transition from an antiferro- to a ferromagnetic state takes place at Hc= 5000 G. The antiferromagnetic ordered phase exhibits spin-canting and long range ferromagnetic ordering at 3 K with a characteristic hysteresis loop.

Keywords: cyanide-bridged; metamagnet; spin-canting; ferromagnetic; two-dimensional; linear-chain

INTRODUCTION

The design and elaboration of new systems with original magnetic, optical and/or electrical properties are at the heart of molecular magnetism [1-2]. In the last few years, there has been a considerable interest in the preparation and *properties of molecular magnets* [3,4]*. The aim is not to synthesize compounds* in order to replace already existing magnets but to imagine and to conceive new system exhibiting new properties. One potential general route to the synthesis of molecular magnets is to use $[M(CN)_6]^{n-}$ and $[M(H_2O)_6]^{n+}$ complexes as molecular building blocks to prepare bimetallic cyanide-bridged assemblies with three-dimensional Prussian-like structure, which exhibit long-range magnetic ordering temperatures, Tc, as high as 315 K.[5] The origin of the magnetic behaviour is associated with the three-dimensional structure of the compounds, in which the interaction between the metal ions are strong ferro- or antiferromagnetic. Recent work has shown that the tunning of T_c is possible through a molecular excitation induced by photons or electrochemically,[6] which opens new routes to the design of molecule-based magneto-optical devices, and then to the so called molecular electronics. The crystallization of Prussian blue analogues, however, is very difficult and it has been only quite recently that Kahn *et al.*[7] have succeeded in growing crystals of $[Mn_2(H_2O)_5Mo(CN)_7]\cdot nH_2O$ (α and β forms), two bimetallic cyanide-bridged compounds with tridimensional structure, which order ferromagnetically at 51 K and exhibit a pronounced magnetic anisotropy in the magnetically-ordered phase. However, in this kind of compounds, their magnetic properties can only be tunned by changing the pair of interacting paramagnetic ions and not by modifying their peripheral ligands.

One alternative route to bimetallic cyanide-bridged extended arrays is that of using hexacyanometalates building blocks with metal complexes containing polydentate ligands. This hybrid approach favours the crystallization of the bimetallic assemblies, thus allowing their magneto-structural study. Depending on the nature of the $[ML_n]^{m+}$ building blocks (available coordination sites on M and their geometrical disposition, steric hindrance of L, oxidation state of M, etc) different and fascinating extended network structures can be obtained, some of which are *magnetically ordered*.[8] Because they are molecular systems, their magnetic properties can be chemically tuned not only varying the metal ions but also the ligands. By using this strategy it is possible to design [MM'$_6$] cyanide-bridged heptanuclear entities (M=Fe(III) or Cr(III); M'=Cu(II) or Ni(II) and Mn(II), respectively).[9] Among them, the CrNi$_6$[9a] and CrMn$_6$[9b] species exhibit high-spin ground states of S=15/2 and 27/2, respectively.

RESULTS AND DISCUSSION

We have now found that from the building blocks [Ni(cyclam)]$^{2+}$ and [Fe(CN)$_6$]$^{3-}$ two different cyano-bridged complexes can be obtained depending on the stoichiometric ratio of the reactants. Thus, when a large excess of [Fe(CN)$_6$]$^{3-}$ *to [Ni(cyclam)]*$^{2+}$ is used *(10/1 molar ratio), after removing* a green powder that immediately precipitates, prismatic dark brown crystals of [Fe(cyclam)][Fe(CN)$_6$]·6H$_2$O **1** appear within one week from the dark green solution.[10] It is noteworthy that the presence of a large excess of [Fe(CN)$_6$]$^{3-}$ promotes the substitution of Ni(II) from [Ni(cyclam)]$^{2+}$ by Fe(III). Consequently, complex **1** can also be prepared from cyclam and K$_3$*[Fe(CN)$_6$]*. On the other hand, by dropwise addition of an aqueous solution of K$_3$[Fe(CN)$_6$] (1mmol, 20 ml) to an aqueous solution of [Ni(cyclam)](ClO$_4$)$_2$ (1mmol, 50 ml) the compound [Ni(cyclam)]$_3$[Fe(CN)$_6$]$_2$·12H$_2$O **2** can be obtained as a fine brown precipitate. Slow diffusion of two aqueous solutions of the reactants into a U-tube containing silica gel, provided well formed dark brown block-like single crystals. The structure of **1** was determined by X-ray analysis (Fig. 1) and it consists of polymeric chains of alternated [Fe(CN)$_6$]$^{3-}$ and [Fe(cyclam)]$^{3+}$ ions running along the *a* axis, and crystal water molecules. In the chain two CN$^-$ groups of each [Fe(CN)$_6$]$^{3-}$ unit bridge two iron(III) atoms with Fe···Fe distances of 5.129(1) Å. Both types of iron atoms are located on symmetry elements *2/m*, and the bridging 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 CN$^-$ group are ca. 175°. The iron centre in the $[Fe(CN)_6]^{3-}$ unit adopts a minimally distorted octahedral environment, whereas the iron centre of the $[Fe(cyclam)]^{3+}$ unit assumes an axially distorted octahedral FeN_6 chromophore. The two axial positions are occupied by the nitrogen atoms of the bridging CN$^-$ groups with Fe-N distances of 2.069(6) Å and the equatorial positions by the N_4 set of donor atoms from the cyclam ligand with 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)°.

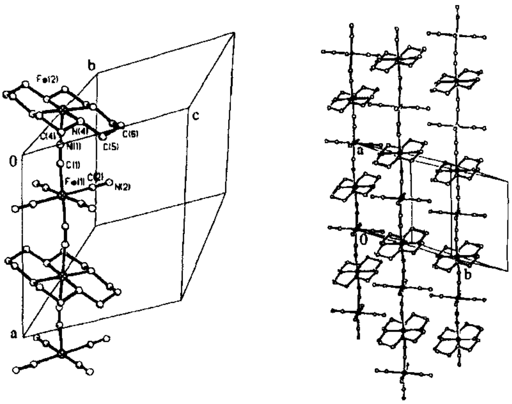

FIGURE 1 Perspective views of the chain complex and the packing of **1**.

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 $[Fe(CN)_6]^{3-}$ and $[Fe(cyclam)]^{3+}$ units, respectively, thus leading to a two dimensional layer structure. The Fe···Fe interchain separation is 8.101(1) Å. To our knowledge compound **1** represents 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_2 unit in the temperature range 2-295 K (Fig. 2) shows that, as temperature is lowered, $\chi_M T$ remains almost constant until around 100 K, then increases smoothly to reach a maximum at 6 K and finally decreases sharply upon cooling down to 2 K.

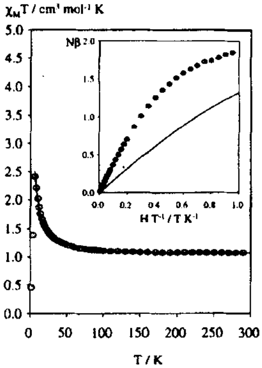

FIGURE 2 Magnetic data (*$\chi_M T$ vs. T*) of **1**. Inset: magnetization data (*$N\beta$ vs. H/T*) of **1** (solid line represents the theoretical value of Brillouin function for S= 1/2).

Such magnetic behaviour is characteristic of a dominant ferromagnetic coupling within the chain and interchain antiferromagnetic interactions, which are responsible of the decrease of $\chi_M T$ at very low temperature. The experimental magnetization values per Fe_2 unit as a function of the applied field at 5 K (inset Fig. 2) support the existence of an ferromagnetic interaction between iron(III) ions. Apparently, **1** is the first example of an iron(III) chain exhibiting ferromagnetic intrachain exchange interactions. The magnetic susceptibility data (T> 6 K) were fitted to the Baker's expression for a S= 1/2 uniformly spaced ferromagnetic chain leading to J= 8.6 cm^{-1} and g= 2.27. The polycrystalline powder EPR spectrum at 100 K seems to be axial with $g_{\parallel}$= 2.21 and $g_{\perp}$= 2.03. In spite of the two different kind of iron(III) atoms in **1**, the Mössbauer spectra at room temperature and 90 K shows a single sharp doublet with IS and QS parameters at 90 K of -0.0679 mm/s and 2.447 mm/s, respectively. The large size of the QS reflects the asymmetry around the low-spin centers and the delocalization along the chain.

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 surrounding (t_{2g}^5) has the unpaired electron density on xy, xz and yz d orbitals, which are degenerate and then equally populated with a statistical factor of 1/3. If the Fe(1)-CN-Fe(2) bond is considered to lie along the z axis, with the x and y axis pointing toward the equatorial CN^- 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 orbitals of the CN^- group to give rise to antiferromagnetic contributions. A closer examination of the structure of **1**, however, allows a possible orbital explanation for the observed ferromagnetic coupling. Thus, while the coordination polyhedron of Fe(1) is almost perfect octahedral (O_h point symmetry), however, 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). Noteworthy, a similar unexpected ferromagnetic coupling has been also observed between two cyano-bridged $Cr[d^3,(t_{2g})^3]$, in the catena-cyano(phthalocyaninato) chromium(III).[11]

The structure of **2** consists of honeycomb-like layers and crystal water molecules that occupy the interlayers space (Fig. 3). To form the layers, each $[Fe(CN)_6]^{3-}$ is coordinated to three $[Ni(cyclam)]^{2+}$ cations 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 hexacyanoferrate(III) units in *trans* positions. The iron centre in the $[Fe(CN)_6]^{3-}$ unit adopts a minimally distorted octahedral environment with the $[Ni(cyclam)]^{2+}$ units located at facial positions. Ni^{II} ions, which are located on centres of symmetry, exhibit a *trans* octahedral geometry with cyanide nitrogen atoms at axial positions; 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). In the crystal the layers, which are not planar but forming an infinite stair, align along the *a* axis Fig. 3). The layers are linked by a network of hydrogen bonds involving the lattice water molecules and the unco-ordinated CN groups. It should be point that the honeycomb-like structure observed for **2** is very similar to that recently reported for the hexacyanochromate(III) analogue.[8i]

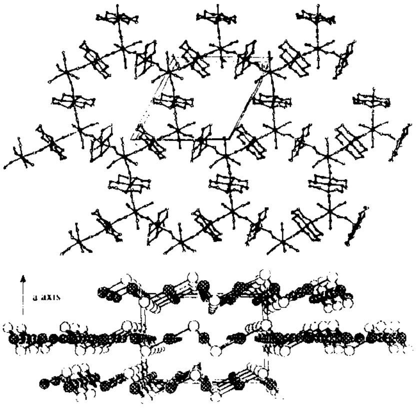

FIGURE 3 Perspective views of the 2D honeycomb-like layered structure and the packing (open and cross-hatched balls represent Fe^{III} and Ni^{II} atoms, respectively) of **2**. Water molecules have been omitted for clarity.

The temperature dependence of the product $\chi_M T$ per Fe_2Ni_3 unit in the temperature range 2-295 K under an applied field of 50 G (low temperature region) and 1 T (high temperature region) is shown in Fig. 4 (left). Between 30 K and 295 K $\chi_M T$ values are essentially independent of the temperature. On further lowering the temperature, $\chi_M T$ increases reaching a maximum value of 15 $cm^3mol^{-1}K$ at 8 K. This behaviour is indicative of a short range ferromagnetic interaction between Fe^{III} (t_{2g}^5) and Ni^{II} (e_g^2) through the cyanide bridge, as a result of the orthogonality of the magnetic orbitals on the metal ions. Below 6 K and applied field of 50 G, $\chi_M T$ rapidly increases again reaching a value of 60 cm^{3}mol^{-1}K at 2 K. The temperature dependence of χ_M shows a similar behaviour with a maximum at about 8 K (for applied fiels lower than 5000 G, Fig. 4 rigth), which is a clear indication of a three-dimensional antiferromagnetic ordering of the ferromagnetic sheets.

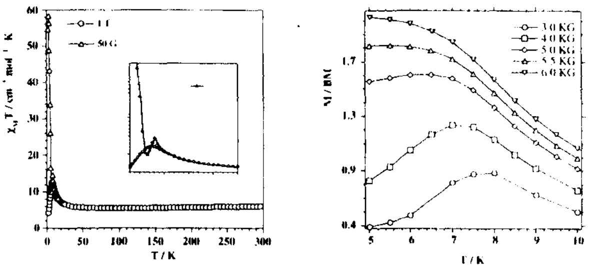

FIGURE 4 (Left) Plot $\chi_M T$ *vs.* T of a polycrystalline sample of **2** at applied fields of 50 G (Δ) and 10 kG (o). Inset: amplification of the 2-25 K zone. (Right) Field-cooled magnetization in different applied fields.

The increasing tendency in $\chi_M T$ below 6 K suggests a magnetic ordering over the lattice, which is probably due to a canting of the local spins. This canted structure 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 a weak out-of-phase signal at 7.7 K and an intense one at 3 K, which are not frequency dependents. The intense signal at 3 K is due to a long-range ferromagnetic ordering leading to a net magnetic moment and spontaneous magnetization below Tc= 3 K. Above 3 K, the magnetic properties are typical of a metamagnet with a crytical field of 5000 G. The temperature dependence of the magnetization at variuos fields is shown in Figure 4 (right). For values of the applied field less than 5000 G, the curves display a maximum which broadens as H is increased and finally disappears for H> 5000 G, demonstring that a field-induced transition from an antiferro- to a ferromagnetic ground state occurs. To confirm this metamagnetic behaviour, the magnetization vs applied field was measured at various temperatures (Figure 5 left). As temperature is lowered, the isotherms become increasing sigmoidal and present a crossing point at ca 5000 G, corresponding to the critical field.

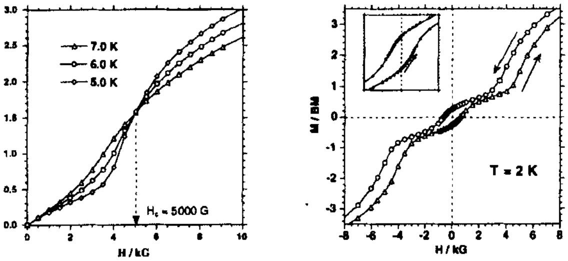

FIGURE 5 (Left) Magnetization isotherms for **2** at T > 3K. (Right) Hysteresis loop at 2 K for **2**.

Below 3 K, a canted structure is formed. The magnetization curves present the characteristic hysteresis loop with a remanent magnetization of 0.26 BM and a coercive field of 600 G at 2 K (Figure 5 right). This canted structure is also broken when applied fields greater than 5000 G are used. Such a critical field is sufficient to overcome the weak intersheet antiferromagnetic interactions which are responsible of the spin canting ground state. It should be pointed out that, in contrast to **2**, the chromium(III) analogue $[Ni(cyclam)]_3[Cr(CN)_6]_2 \cdot 5H_2O$,[8i] does not exhibit any phase transition in the 2-300 K range.

The title compound is a new example of the versatility of hexacyanometalates to build a rich variety of molecular extended arrays with relevant and intriguing magnetic properties. In order to definitively clarify the origin of the ferromagnetic exchange interactions in homometallic cyanide-bridged iron(III) systems and to know how the intersheet separation affects the magnetic properties in cyanide-bridged complexes with honeycomb-like structure, we are currently exploring the assembling between hexacyanometallate(III) and other [M(macrocycle)]$^{n+}$ complexes.

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