A cyano-bridged molecular magnet with a novel two-dimensional brick wall structure

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Slow diffusion of $K_3[Fe(CN)_6]$ and $[NiL](ClO_4)_2$ (L = 3,10-diethyl-1,3,5,8,10,12-hexaazacyclotetradecane) yields a novel cyano-bridged 2D brick wall-like assembly which is ferromagnetically ordered below 9.1 K with considerably strong hard magnetic behaviour.

It is well known that the cyanide ion can coordinate to one metal ion through the carbon atom acting as a monodentate ligand or connect two metal ions as a bridging ligand through both the carbon and nitrogen atoms. Recently, magnetic interactions between paramagnetic metal ions through the cyanide bridge have been extensively investigated. In particular, the cyanide-bridged 3D bimetallic assemblies of Prussian Blue type, derived from $[M(CN)_6]^{3-}$ (M = Cr^{III}, Fe^{III}) and simple transition metal ions $[M']^{n+}$, have attracted great attention owing to the fact that many of them exhibit a considerably high magnetic critical (Curie) temperature.[1] However, the difficulty in obtaining single crystals suitable for X-ray diffraction analysis precludes the clarification of the magneto–structural correlation. Furthermore, the face-centred cubic structures (based on powder XRD results) they usually possess result in low or no magnetic anisotropy, which would give low or no magnetic coercivity.[1] To overcome these problems, hybrid Prussian Blue analogues have been synthesized by the reaction of coordinately unsaturated transition metal complexes $[M'L]^{m+}$ (L = polydentate ligand) with hexacyanometalate building blocks $[M(CN)_6]^{3-}$ (M = Fe, Cr or Mn).[2,3] Consequently, the introduction of organic ligands could lower the symmetry of the lattice, and afford various molecular structures.[2,3]

Most recently, stair-shaped 2D honeycomb networks, [Ni-(cyclam)]$_3$[Cr(CN)$_6$]$_2$·20H$_2$O,[3a] [Ni(cyclam)]$_3$[Fe(CN)$_6$]$_2$·xH$_2$O,[3b,c] [NiL^1]$_3$[Fe(CN)$_6$]$_2$·9H$_2$O[3d] and [NiL^1]$_3$[Cr(CN)$_5$-(NO)]$_2$·10H$_2$O[3e] (L^1 = 3,10-dimethyl-1,3,6,8,10,12-hexaazacyclotetradecane 3,10-dimethyl-1,3,6,8,10,12-hexaazacyclotetradecane) have been reported. According to Mallah *et al.*, for Ni$_3$M$_2$ systems containing *trans* nickel macrocyclic complexes a meridional arrangement might lead to either a 2D flat brick wall-like layer or a double chain stair-like structure. However, this arrangement of five moieties [two M(CN)$_6$ and three Ni(macrocycle)] in a plane imposes a steric hindrance between the macrocycle ligands.[4] Therefore, only stair-shaped 2D honeycomb networks have been obtained so far. We have found, however, that the reaction between a bulky planar macrocyclic nickel(II) complex [NiL](ClO$_4$)$_2$[5] (L = 3,10-diethyl-1,3,5,8,10,12-hexaazacyclotetradecane) and K$_3$[Fe(CN)$_6$] afforded a complex of similar formula, [NiL]$_3$[Fe(CN)$_6$]$_2$·12H$_2$O **1**, which does have the flat brick wall-like structure.

Well shaped red–brown crystals of **1** for X-ray structure analysis† and magnetic measurements were grown at room temperature by the slow diffusion of an orange DMF solution (30 mL) of [NiL](ClO$_4$)$_2$ (0.15 mmol) and a yellow aqueous solution (30 mL) of K$_3$[Fe(CN)$_6$] (0.15 mmol) in an H-tube.‡

The structure consists of neutral flat layers with slightly distorted rectangles. Unlike the honeycomb-like complexes

mentioned above, in which three [Ni(cyclam)] or [NiL^1] groups connect with three cyanide groups in a *fac* arrangement at an iron(III), chromium(II) or chromium(III) cation,[3] in the present complex each [Fe(CN)$_6$]$^{3-}$ unit uses three cyanide groups in a meridional arrangement to connect with three *trans*-[NiL]$^{2+}$ units [Fig. 1(a)]. This particular local molecular disposition extends to give rise to a brick wall-like structure [Fig. 1(b)], as predicted by Mallah *et al.*[4] The bridging cyanide ligands coordinate to the nickel(II) ions in a considerably bent fashion with Ni–N≡C bond angles of 148.5(9)° for C(1)–N(1)–Ni(2), 151.4(9)° for C(4)–N(4)–Ni(1) and 152.1(9)° for C(3)–N(3)–Ni(3), which prevents the steric hindrance of L. The coordination environment of the nickel ions can be described as axially elongated octahedral. Adjacent Fe···Ni distances are 5.003(2) Å for Fe···Ni(1), 4.987(2) Å for Fe···Ni(2) and 4.985(2) Å for Fe···Ni(3), respectively. In the crystal, the layers align along the
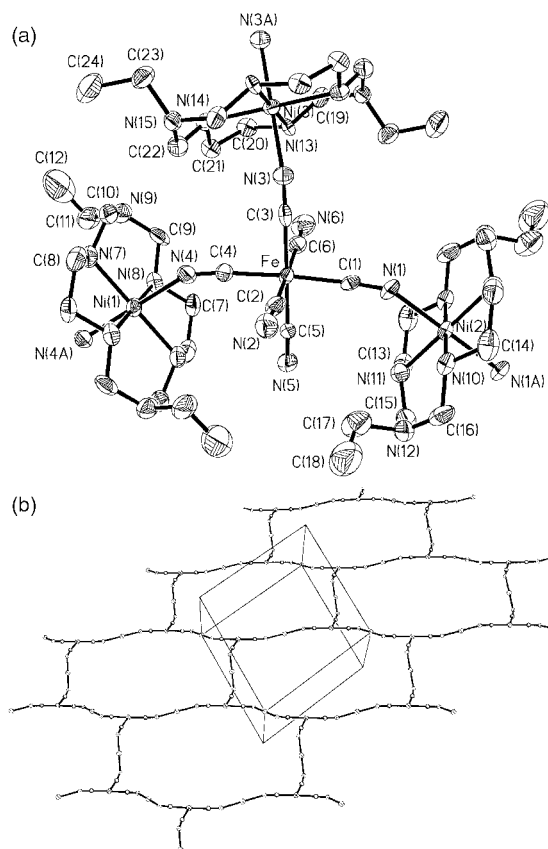
Fig. 1 (a) ORTEP plot of complex **1**. Selected bond distances (Å): Ni(2)–N(10) 2.050(9), Ni(2)–N(11) 2.053(9), Ni(2)–N(1) 2.126(8), Ni(3)–N(13) 2.064(8), Ni(3)–N(14) 2.066(8), Ni(3)–N(3) 2.111(9), Ni(1)–N(8) 2.072(10), Ni(1)–N(7) 2.074(8), Ni(1)–N(4) 2.139(10). (b) Projection along the *a* axis showing the brick wall-like backbone containing Fe$_6$Ni$_6$ rectangles.
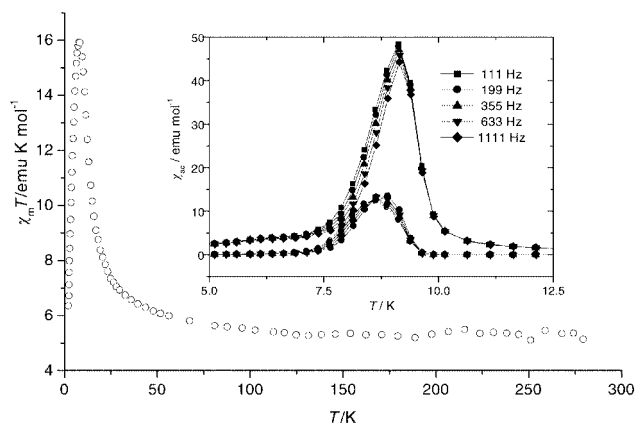
Fig. 2 Temperature dependence of $\chi_M T$ for **1**. Real (χ') and imaginary (χ'') ac magnetic susceptibilities in zero applied dc field and an ac field of 2 Oe at different frequencies for **1** are shown in the inset.

[110] direction with a separation of *ca.* 8.33 Å, and the nearest interlayer metal–metal distance is 8.53 Å for Ni(2)···Fe. Water molecules are positioned between the layers and are linked to the terminal CN^- ligands of $Fe(CN)_6^{3-}$ and other water molecules *via* hydrogen bonding.

The magnetic susceptibility of **1** has been measured on a crystalline sample confined within a gelatine capsule under a field of 10 kOe in the temperature range 2–280 K. A plot of $\chi_m T$ *vs. T* is shown in Fig. 2, where χ_m is the magnetic susceptibility per Ni_3Fe_2 unit. The $\chi_m T$ value at 280 K is *ca.* 5.3 emu K mol^{-1} (6.5 μ_B) which increases smoothly and then sharply with decreasing temperature, reaching a maximum value of 15.9 emu K mol^{-1} (11.3 μ_B) at 7.8 K, strongly suggestive of the occurrence of magnetic ordering. Below 7.8 K, $\chi_m T$ decreases rapidly, which may be due to interlayer antiferromagnetic interactions, a saturation effect and/or the zero-field splitting effect of nickel(II) ions in axially elongated octahedral surroundings. The magnetic susceptibility above 8.4 K obeys the Curie–Weiss law with a positive Weiss constant, θ, of +7.0 K.

The onset of a long-range magnetic phase transition is confirmed by the temperature dependence of the ac magnetic susceptibility displayed in the inset of Fig. 2. The real part of the ac magnetic susceptibility, χ', has a maximum at *ca.* 9.1 K for a frequency of 111 Hz, suggesting that T_c of complex **1** is *ca.* 9.1 K. The weak frequency dependence of χ_{ac}' and χ_{ac}'' suggests a degree of glassy behaviour.

The field dependence of the magnetization (0–50 kOe) measured at 1.6 K shows rapid saturation of magnetization reaching a value of 7.4 $N\beta$ at 50 kOe which is close to the expected $S = 4$ value of 8 $N\beta$ for a ferromagnetic Ni_3Fe_2 system. A hysteresis loop at 1.6 K was observed with a coercive field as large as 1500 Oe and a remnant magnetization of *ca.* 1.36 $N\beta$ per Ni_3Fe_2 unit, typical of a hard ferromagnet. To our knowledge, the coercivity in **1** is the highest measured for

hybrid Prussian Blue analogues, probably due to the presence of the magnetic anisotropy of the paramagnetic ions, the grain size of the sample used and/or irreversible movements of the domain walls.[1a,2b,6] Magnetic studies on samples of different sizes should bring some insights into the origins of the large coercive field and remnant magnetization. Further work to this end is in progress in our laboratory.

In conclusion, we have obtained a hybrid Prussian Blue analogue with a unique brick wall-like molecular structure which serves as a new molecule-based ferromagnet showing hard magnetic behaviour.

Notes and references

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