A Two-dimensional Bimetallic Assembly, $[Ni(pn)_2]_2[Fe(CN)_6]ClO_4{\cdot}2H_2O$, with a Square Structure

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A bimetallic assembly, $[Ni(pn)_2]_2[Fe(CN)_6]ClO_4{\cdot}2H_2O$, has a two-dimensional square network structure, formed from Fe–CN–Ni(pn)$_2$–NC–Fe linkages, and shows ferromagnetic ordering.

Design of high-dimensional molecular systems is closely linked to interest in unique physicochemical phenomena occurring in the bulk of such systems.[1,2] Ferri- and ferro-magnetism are remarkable examples that appear as specific properties in two- (2-D) and three-dimensional (3-D) systems of paramagnetic centres. So far there have been obtained complex-based assemblies exhibiting spontaneous magnetization[1–15] and X-ray crystallography has revealed a high-dimensional bulk structure for some of them.[11–15] However, complex-based ferri- and ferro-magnets of real 2-D or 3-D network structures are still limited.

It is shown that hexacyanometallate ions $[M(CN)_6]^{n-}$ are good building blocks to provide bimetallic assemblies exhibiting spontaneous magnetization.[6–9] Recently, we have reported a bimetallic assembly $[Ni^{II}(en)_2]_3[Fe^{III}(CN)_6]_2{\cdot}\ 2H_2O$[16] that possesses a rare rope-ladder chain structure constructed by $[Fe(CN)_6]^{3-}$, *cis*-$[Ni(en)_2]^{2+}$ and *trans*-$[Ni(en)_2]^{2+}$ (2 : 2 : 1). In the crystal, the chains align along a line to form a quasi 2-D sheet structure which leads to the ferromagnetic spin ordering at T_C = 18.6 K. As the extension of this study we describe here a new bimetallic assembly $[Ni(pn)_2]_2[Fe(CN)_6]ClO_4{\cdot}2H_2O$ (pn = 1,2-diaminopropane) with a 2-D network structure.

The bimetallic assembly is obtained as black crystals by the reaction of $K_3[Fe(CN)_6]$ and $[Ni(R,S\text{-}pn)_2](ClO_4)_2$ in an aqueous solution.† X-Ray crystallography reveals that the asymmetric unit consists of each one-half of $[Fe(CN)_6]^{3-}$ and ClO_4^- anions, each one-half of $[Ni(R\text{-}pn)_2]^{2+}$ and $[Ni(S\text{-}pn)_2]^{2+}$ cations, and one water molecule (Fig. 1).‡ All the metal ions and the Cl atom are at the special equivalent positions [Fe(0, 1/2, 0), Ni1(1/2, 1/2, 0), Ni2(0,0,0), Cl(1/2, 0, 0)]. Hexacyanoferrate(III) ion coordinates to four $[Ni(pn)_2]^{2+}$ cations through four cyano nitrogens [N(1), N(1*), N(2), N(2*)] on a plane to provide a 2-D square-shaped structure constructed by Fe–CN–Ni linkages (Fig. 2). The mean Fe–C, C–N, and N–Ni bond distances are 1.949, 1.142, and 2.105 Å, respectively, and the Fe···Ni(1) and Fe···Ni(2) separations are 5.062(2) and 5.126(3) Å, respectively. The Fe–C and C–N bond distances of the axial Fe–CN moiety are 1.942(8) and 1.153(8) Å, respectively. The quadrangle formed by four Fe ions is nearly equilateral [10.123(5) and 10.252(3) Å] and is slightly distorted to a rhombus (interior angles: 85.0 and 95.0°). All the Ni ions assume a *trans*-octahedral geometry together with cyanide nitrogens at the axial sites. The Ni–N(pn) bond lengths range from 2.085(7) to 2.109(6) Å. It is noted that $[Ni(R\text{-}pn)_2]^{2+}$ and $[Ni(S\text{-}pn)_2]^{2+}$ align along *a* and *b* axes, respectively, through Fe–CN–Ni–NC–Fe linkages. Perchlorate ion resides in each quadrangle (Fig. 2) and assumes two arrangements (O2–5); the occupancy factors of the oxygen atoms are determined to be 0.5 on the basis of the peak heights.

In the bulk the 2-D sheets align along *c* axis (Fig. 3). The intersheet Fe···Fe(0, 1/2, 1) separation along *c* axis is 8.978(5) Å. The nearest intersheet Fe···Ni(1) (*x*, *y*, *z* + 1), Fe···Ni(2) (*x*, *y* + 1, *z* + 1) and Ni(1)···Ni(2) (*x* + 1, *y* + 1, *z* + 1) separations are 9.852, 8.613 and 9.754 Å, respectively. The water molecule exists between 2-D sheets and is hydrogen-bonded to N(3*) [O(1)···N(3*), 2.841 Å].

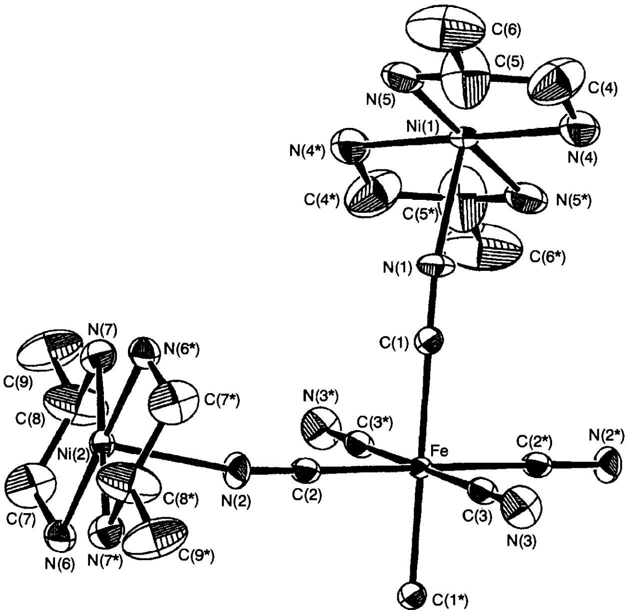

Fig. 1 ORTEP drawing for $\{[Ni(pn)_2]_2[Fe(CN)_6]\}^+$ part. Selected bond distances (Å) and angles (°) are as follows: Fe–C(1) 1.954(7), Fe–C(2) 1.943(7), Fe–C(3) 1.942(8), Ni(1)–N(1) 2.107(6), Ni(1)–N(4) 2.085(7), Ni(1)–N(5) 2.099(7), Ni(2)–N(2) 2.103(6), Ni(2)–N(6) 2.109(6), Ni(2)–N(7) 2.100(6), C(1)–Fe–C(2) 91.5(3), C(1)–Fe–C(3) 88.5(3), C(2)–Fe–C(3) 91.6(3), N(1)–Ni(1)–N(4) 91.6(3), N(1)–Ni(1)–N(5) 91.9(2), N(4)–Ni(1)–N(5) 83.1(3), N(2)–Ni(2)–N(6) 90.9(2), N(2)–Ni(2)–N(7) 89.0(2), N(6)–Ni(2)–N(7) 82.4(2).

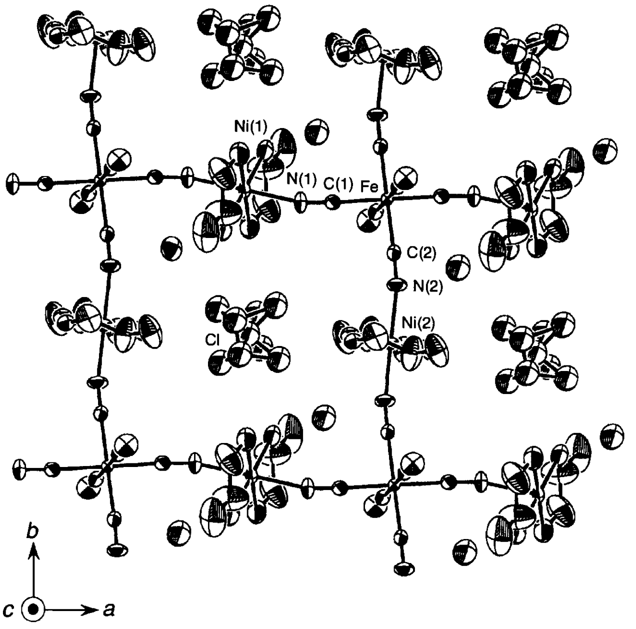

Fig. 2 View along *c* axis of 2 D network showing the $Fe^{III}_4Ni^{II}_4$ squares

The cryomagnetic property of the assembly is shown in Fig. 4 in the form of $\chi_M T$ *vs.* T plot. The χ_M *vs.* T plot in the low temperature region is given in the insert. At room temperature, $\chi_M T$ is 3.21 cm^3 K mol^{-1} per FeNi$_2$ (5.07 μ_B) which increases with decreasing temperature up to the maximum value of 12.21 cm^3 K mol^{-1} (9.89 μ_B) at 9.0 K and then decreases below this temperature. The maximum $\chi_M T$ value is larger than the value expected for S_T = 5/2 of ferromagnetically coupled FeNi$_2$ (4.38 cm^3 K mol^{-1}, 5.91 μ_B). This fact suggests the ferromagnetic ordering within the two-dimensional network through the Fe–CN–Ni linkages. Our preliminary study has revealed the magnetic phase transition near 10 K. The drop in $\chi_M T$ value below 9.0 K is probably due to antiferromagnetic interaction between 2-D sheets.

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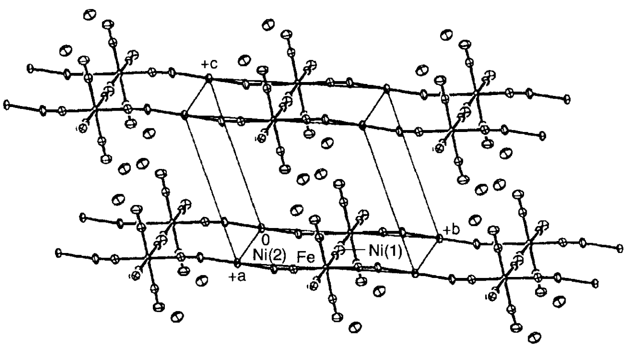

Fig. 3 The packing mode of 2 D sheets

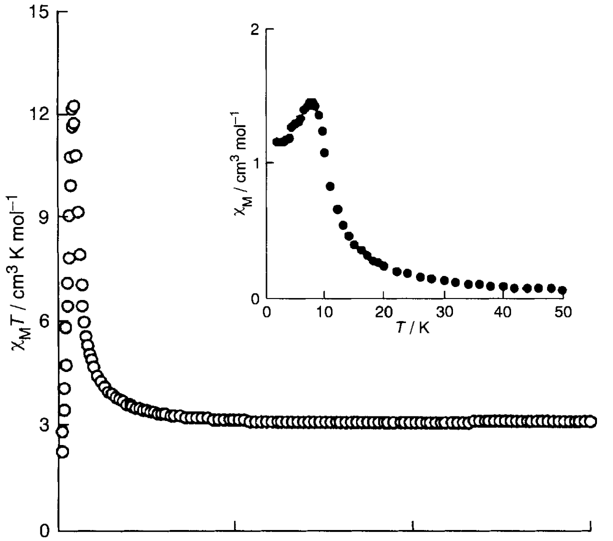

Fig. 4 The temperature-dependence of the $\chi_M T$ per FeNi$_2$. The insert is the χ_M *vs.* T plot in the low temperature region.

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Footnotes

† Yield: almost quantitative. IR: 2130, 2140 cm^{-1}. Satisfactory elemental analyses were obtained.

‡ *Crystal data* for [Ni(pn)$_2$]$_2$[Fe(CN)$_6$]ClO$_4$·2H$_2$O at room temp. black plate, space group $P\bar{1}$ with Z = 2, a = 10.123(5), b = 10.252(3), c = 8.978(5) Å, α = 110.80(3)°, β = 95.78(5)°, γ = 85.04(3)°, V = 865.3(7) Å^3, D_c = 1.461 g cm^{-3}, $F(000)$ = 397.0, μ(Mo-Kα) = 16.19 cm^{-1}. Crystal size 0.2 × 0.2 × 0.15 mm. Cell parameters were defined by 24 reflections with 20.6 < 2θ < 24.5°. 3039 unique reflections were measured with 2θ_{max} = 50°. All the measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation and a 12 kW rotation anode generator. The structure was determined by the direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1824 observed [$I > 3\sigma(I)$] and 215 variable parameters and converged with R = 0.047 and Rw = 0.043. Atomic coordinates, thermal parameters, bond lengths and bond angles, and hydrogen atom location of [Ni(pn)$_2$]$_2$[Fe(CN)$_6$]ClO$_4$·2H$_2$O are deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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