$[NiL]_2[Fe(CN)_6]\cdot 4H_2O$ [L = 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane]: a novel three-dimensional iron(II)–nickel(II) cyanide-bridged bimetallic assembly with a vat-like structure

Letter

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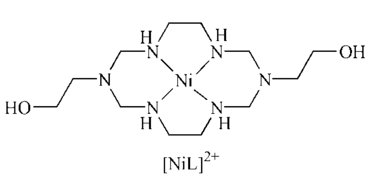
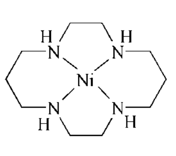
Reaction of either $[Fe(CN)_6]^{3-}$ or $[Fe(CN)_6]^{4-}$ with a macrocyclic Ni(II) complex leads to the same product with a new type of 3-D structure, which shows a weak ferromagnetic interaction between the nearest Ni(II) ions through the diamagnetic Fe(II) ion.

Supramolecular assembly and molecular architecture have recently attracted much attention.[1] A number of supramolecular species with one- two- and three-dimensional networks of various sizes and shapes have been synthesized, and some of them show useful molecular recognition, electronic, magnetic, optical and catalytic properties.[2–5] Four-coordinate macrocyclic complexes can react with different bridging ligands to construct coordination polymers with different structures. Reaction of the nickel(II) complexes $[NiL]^{2+}$ and $[NiL^1]^{2+}$ with BTC^{3-} [L = 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaaza-cyclotetradecane, L^1 = 1,4,8,11-tetraazacyclodecane, BTC = 1,3,5-benzenetricarboxylate] gives 2-D networks with brick wall and honeycomb structures.[6] Reaction of $[NiL^1]^{2+}$ with $[Fe(CN)_6]^{3-}$ leads to a 2-D network of $[NiL^1]_3[Fe(CN)_6]_2$ with a honeycomb structure,[7] while reaction of $[NiL^1]^{2+}$ with an excess of $[Fe(CN)_6]^{3-}$ leads to a 1-D linear chain of $Fe[Fe(CN)_6]$,[8] in which the nickel(II) ion is replaced by the Fe(III) ion. Reaction of $[CuL]^{2+}$ with $[Fe(CN)_6]^{3-}$ leads to a 1-D zigzag chain, $[CuL(H_2O)_2]\{[CuL]_3[Fe(CN)_6]\}_2$.[9,10] In this paper, we demonstrate that reaction of $[NiL]^{2+}$ with either $[Fe(CN)_6]^{3-}$ or $[Fe(CN)_6]^{4-}$ leads to the same product, $[NiL]_2[Fe(CN)_6]\cdot 4H_2O$, with a novel vat-like 3-D structure. To the best of our knowledge, this is the first example of a 3-D network constructed by a macrocyclic complex with a bridging ligand that does not include hydrogen bond linkages.



$[NiL]^{2+}$



$[NiL^1]^{2+}$

Slow diffusion of aqueous solutions of $[NiL](ClO_4)_2$[9] with $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ into a U-shaped tube containing silica gel gave crystals with the same colour and crystal shape, and X-ray analysis† confirmed that the product was the same in both cases. The asymmetric unit of complex **1** $\{[NiL]_2[Fe(CN)_6]\cdot 4H_2O\}$ contains one $[Fe(CN)_6]^{4-}$, one $[NiL]^{2+}$, two halves of $[NiL]^{2+}$, and four water molecules (Fig. 1). In the complex, each Ni(II) ion is six-coordinate with four nitrogen atoms from the macrocyclic ligand in the equatorial plane, and two nitrogen atoms from the bridging cyanide groups in axial positions, forming a distorted octahedral geometry. The Ni–N bond lengths range from 2.046(4) to 2.127(6) Å. Each $[Fe(CN)_6]^{4-}$ is coordinated to four $[NiL]^{2+}$ cations through four cyano nitrogen atoms [N(3), N(4B) (symmetry transformation B: $-x + 1/2$, $y + 1/2$, $-z + 1/2$), N(5), N(6)], in which two cyano nitrogen atoms [N(3), N(5)] coordinate with $[NiL]^{2+}$ to form a $\{[Fe(CN)_6][NiL]\}_n$ chain; the other two cyano nitrogen atoms connect the adjacent chains through the coordination with $[NiL]^{2+}$, forming a novel 3-D network with vat-like structure (Fig. 2). All the water molecules are located in the lattice, and there are no obvious hydrogen bonds between these water molecules and other molecules.

Thermogravimetric analysis (TGA) of the crystalline sample **1** was carried out on a Netzsch–Geräte GmbH Thermobalance in the 26–800 °C temperature range with a heating rate of 10 °C min^{-1}; the result showed that all four water molecules per formula unit were lost below 100 °C. The dehydrated compound was heated to 220 °C without any additional weight loss. The crystals of **1** were heated in the dark at 100 °C and 20 mm Hg for 2 h; the XRPD patterns showed that the lines broadened and their positions changed compared with those of the crystals of **1.** However, when the solid was immersed in water for 1 h, the major features reappeared in the powder pattern. Magnetic susceptibility data were collected in the 5.03–289.13 K temperature range with a SQUID magnetometer in an applied field of 1 T. The plots of $\chi_M T$ and $1/\chi_M$ *vs.* T per Ni_2Fe unit (H = 1 T) are shown in Fig. 3. The $\chi_M T$ value at room temperature, 1.98 cm^3 K mol^{-1}, is close to the value of 2.00 cm^3 K mol^{-1} expected for the magnetically dilute spin system $(S_{Ni}, S_{Ni}) = (1, 1)$, where the spin-only value was calculated by assuming $g_{Ni} = 2.00$. The $\chi_M T$ value gradually increases with decreasing temperature up to the maximum value of 2.17 cm^3 K mol^{-1} (4.17 μ_B) at 22 K and then decreases below this temperature. The plot of $1/\chi_M$ *vs.* T in the range 40–290 K obeys the Curie–Weiss law with a small positive Weiss constant of $\Theta = +0.99$ K. This observation suggests a weak ferromagnetic interaction between the nearest Ni(II) ions through the –NC–Fe–CN–

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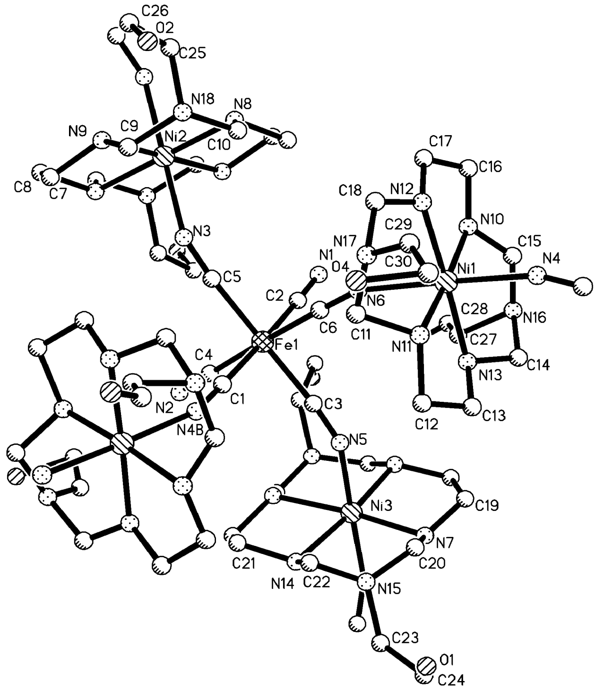

Fig. 1 ORTEP drawing of $[NiL]_2[Fe(CN)_6]\cdot 4H_2O$ (H_2O molecules are omitted). Selected bond lengths (Å) and angles (°): Fe(1)–C(6) 1.893(3), F3(1)–C(5) 1.893(3), Fe(1)–C(3) 1.901(4), Fe(1)–C(1) 1.905(3), Fe(1)–C(2) 1.906(4), Fe(1)–C(4) 1.913(4), Ni(1)–N(12) 2.047(4), Ni(1)–N(13) 2.070(4), Ni(1)–N(10) 2.095(6), Ni(1)–N(4) 2.104(3), Ni(1)–N(6) 2.107(3), Ni(1)–(11) 2.127(6), Ni(2)–N(8) 2.051(3), Ni(2)–N(9) 2.062(3), Ni(2)–N(3) 2.106(3), Ni(3)–N(7) 2.046(4), Ni(3)–N(5) 2.107(3); C(5)–Fe(1)–C(3) 179.65(16), C(6)–Fe(1)–C(1) 93.37(14), N(4)–Ni(1)–N(6) 178.01(14), N(3)–Ni(2)–Ni(3)^a 180.0(2), N(5)–Ni(3)–N(5)^b 179.0(2). Symmetry transformations used to generate equivalent atoms: (*a*) $-+\frac{1}{2}, -y+\frac{1}{2}$, (*b*) $-x, y, -z+\frac{1}{2}$.

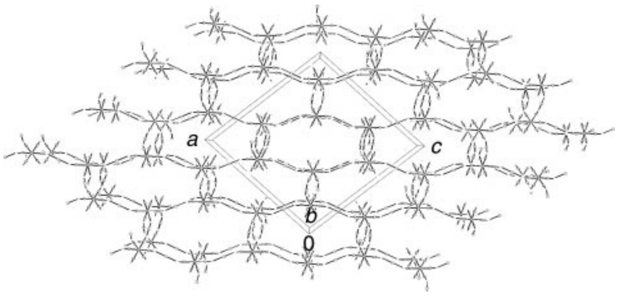

Fig. 2 Projection of the 3-D vat-like structure onto the *ac* plane (macrocyclic and water molecules are omitted for clarity).

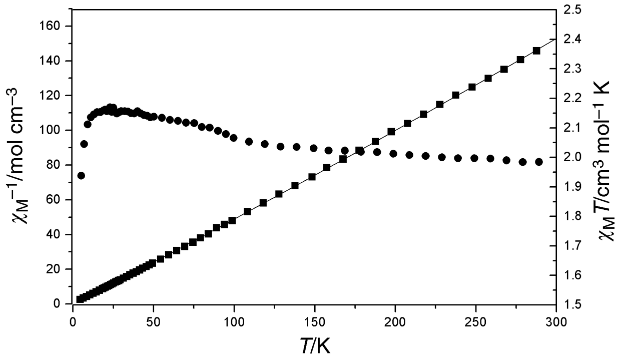

Fig. 3 Temperature dependence of $\chi_M T$ (●) and $1/\chi_M$ (■) for $[NiL]_2[Fe(CN)_6]\cdot 4H_2O$.

bridge, and the ferromagnetic interaction is proposed to occur by a σ-superexchange pathway between the nearest Ni(II) ions through the empty d_σ orbital of the Fe(II) ion.

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Notes and references

† Crystal data for complex **1**: $[NiL]_2[Fe(CN)_6]\cdot 4H_2O$, $C_{30}H_{68}FeNi_2N_{18}O_8$, $M = 982.29$, monoclinic, space group $C2/c$, $a = 24.684(4)$, $b = 15.202(2)$, $c = 25.368(4)$ Å, $\beta = 97.780(3)°$, $U = 9432(2)$ Å^3, $Z = 8$, $T = 293(2)$ K, 8215 independent ($R_{int} = 0.0578$) with 5224 $[I > 2\sigma(I)]$ observed data, $R_1 = 0.0789$, $wR_2 = 0.1783$. Disordered atoms C(27), O(1), O(2), O(2w) and O(4w) were treated isotropically (s.o.f. = 0.5). Data were collected on a Bruker Smart 1000 CCD diffractometer using λ(Mo-Kα) = 0.71 073 Å radiation. The structure was solved by direct methods (SHELXL 93) and refined by the full-matrix least-squares method.

CCDC reference number 440/243. See http://www.rsc.org/suppdata/nj/b0/b007406n/ for crystallographic files in .cif format.

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