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Magnetic characteristics of two two-dimensional bimetallic assemblies, $[Ni(diamine)_2]_2[Fe(CN)_6]NO_3 \cdot nH_2O$ (diamine = 1,3-diaminopropane, $n = 2$; ethylenediamine, $n = 3$), with a square molecular structure

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Two bimetallic assemblies, $[Ni(diamine)_2]_2[Fe(CN)_6]NO_3 \cdot nH_2O$ [diamine = 1,3-diaminopropane (tn), $n = 2$ (**1**); ethylenediamine (en), $n = 3$ (**2**)], were prepared and their magnetic properties studied. The structure of **1** consists of a two-dimensional sheet of polycations containing Ni–N≡C–Fe linkages and NO_3^- anions. In the crystal the four CN^- ligands of $Fe(CN)_6^{3-}$ co-ordinate to the *trans*-$[Ni(tn)_2]^{2+}$ cations in a bent fashion which is significantly different from similar 2-D sheet-like Ni_2Fe complexes. The complexes both exhibit intramolecular ferromagnetic interaction and the magnetic data have been analysed giving the intramolecular Fe–Ni exchange integral of 0.88 cm^{-1} for **1** and 0.92 cm^{-1} for **2**, respectively.

Introduction

Cyanide-bridged bimetallic assemblies of Prussian Blue type, derived from $[M(CN)_6]^{n-}$ ($M = Cr^{III}$, Mn^{III}, Fe^{III} or V^{II}), have attracted much attention in the area of molecular-based magnets.[1–12] These complexes exhibit spontaneous magnetisation at considerably high temperatures and form a family of magnetic materials.

In order to clarify the magneto-structural correlation of cyano-bridged bimetallic systems, a wide variety of hybrid Prussian Blue complexes derived from $[M(CN)_6]^{3-}$ ($M = Cr^{III}$, Mn^{III}, or Fe^{III}) and transition metal complexes have been studied structurally and magnetically.[13–29] They assume oligonuclear,[13,14] 1-D,[15–19] 2-D[17,20–27] and 3-D[28,29] structures and exhibit ferro- or meta-magnetic behaviour. Among them, the Ni^{II}–Fe^{III} bimetallic assemblies, *e.g.* pentanuclear cluster $[Ni(bpm)_2]_3[Fe(CN)_6]_2 \cdot 7H_2O$ [bpm = bis(pyrazol-1-yl)methane],[13] 1-D chain complexes $[Ni(en)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$[15] and $[PPh_4][Ni(pn)_2][Fe(CN)_6]$ (pn = propane-1,2-diamine)[17] and 2-D sheet $[Ni(diamine)_2]_2[Fe(CN)_6]X$ (diamine = 1,1-dimethylethylenediamine or pn; $X = ClO_4^-$, NO_3^-, $PhCO_2^-$, I^- or N_3^-)[20–22] as well as 3-D $[Ni(tren)]_3[Fe(CN)_6]_2 \cdot 6H_2O$ [tren = tris(2-aminoethyl)amine],[28] have been synthesized and characterised in much detail and invariably exhibit a ferromagnetic interaction between the adjacent nickel(II) and iron(III) ions through the CN^- bridges. Significantly, it has been found that the 2-D complexes $[Ni(diamine)_2]_2[Fe(CN)_6]X \cdot nH_2O$ exhibit ferro- or metamagnetic behaviour dependent on the difference in intersheet separations.[21] As an extension of those studies, two 2-D complexes, $[Ni(tn)_2]_2[Fe(CN)_6]NO_3 \cdot 2H_2O$ **1** (tn = propane-1,3-diamine) and $[Ni(en)_2]_2[Fe(CN)_6]NO_3 \cdot 3H_2O$ **2**, were prepared. The crystal structure of **1** was determined by X-ray crystallography revealing a 2-D network extended by Fe^{III}–CN–Ni^{II} linkages. Magnetic properties of the compounds are also reported.

Experimental

The physical measurements have been performed as described previously.[18]

Preparations

$[Ni(tn)_2]_2[Fe(CN)_6]NO_3 \cdot 2H_2O$ 1. To an aqueous solution of $[Ni(tn)_3][NO_3]_2$ prepared by mixing $Ni(NO_3)_2 \cdot 6H_2O$ (1 mmol, 290.8 mg) and tn (3 mmol, 222.3 mg) in 20 cm^3 of water was added $K_3Fe(CN)_6$ (0.5 mmol, 165 mg) in water (15 cm^3) at room temperature. Brown microcrystals precipitated from the resulting brown solution in 10 min. They were collected by suction filtration, washed with water and ethanol, and dried *in vacuo* over P_2O_5. Yield 253.3 mg, 70% (Found: C, 29.9; H, 6.0; N, 28.5. $C_{18}H_{44}FeN_{15}Ni_2O_5$ requires C, 29.9; H, 6.1; N, 29.0%). IR: ν_{max}/cm^{-1} 2150, 2140 and 2060 (C≡N) and 1380 (N–O).

Brown crystals suitable for X-ray single crystal analysis were obtained by slow evaporation of the above filtrate in a refrigerator.

$[Ni(en)_2]_2[Fe(CN)_6]NO_3 \cdot 3H_2O$ 2. This complex was prepared as black crystals in a way similar to that of **1**, except for the use of en (3 mmol, 180.3 mg) instead of tn. Yield 205.7 mg, 60% (Found: C, 24.6; H, 5.8; N, 30.8. $C_{14}H_{38}FeN_{15}Ni_2O_6$ requires C, 24.5; H, 5.6; N, 30.6%). IR: ν_{max}/cm^{-1} 2150, 2130 and 2110 (C≡N) and 1380 (N–O).

Crystal structure determination of complex 1

Crystal data. $C_{18}H_{44}FeN_{15}Ni_2O_5$, $M = 723.95$, triclinic, space group $P1$, $a = 8.9298(8)$, $b = 9.9358(9)$, $c = 10.1319(7)$ Å, $U = 806.97(12)$ Å^3, $T = 293(2)$ K, $Z = 1$, μ(Mo-Kα) = 1.651 mm^{-1}, 3440 reflections measured and considered unique ($R_{int} = 0.062$) used in all calculations. The final wR was 0.053. $R1(F) = 0.0466$.

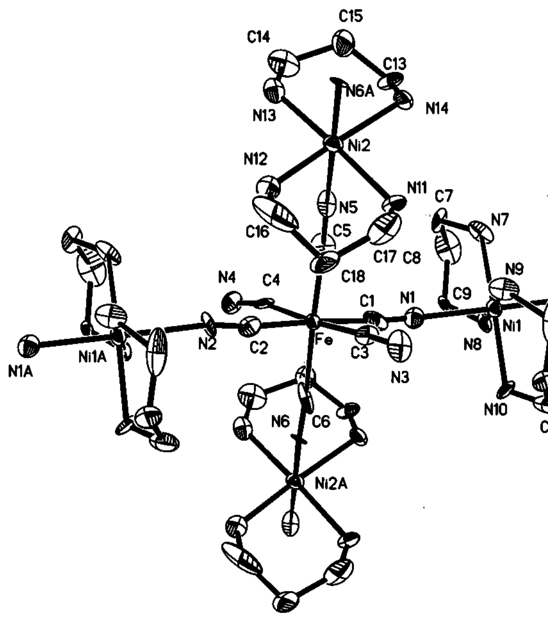


Fig. 1 An ORTEP[30] drawing of complex **1** with the atom numbering scheme.

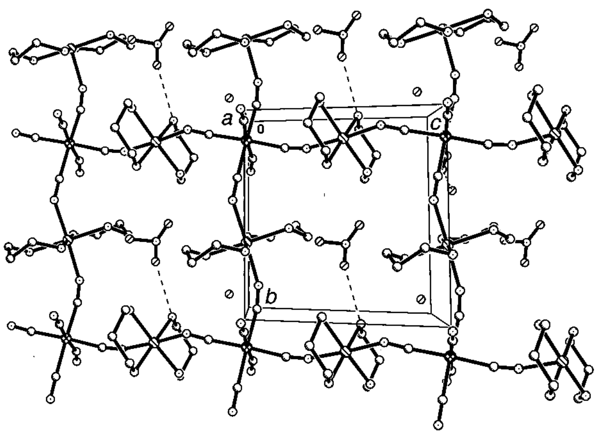


Fig. 2 Projection of the polymeric sheet-like structure along the *a* axis showing Fe_4Ni_4 squares and hydrogen bonds (---).

CCDC reference number 186/1212.

See http://www.rsc.org/suppdata/dt/1998/4161/ for crystallographic files in .cif format.

Results and discussion

The complexes **1** and **2** were obtained as crystals when $Fe(CN)_6^{3-}$ reacted with $[Ni(diamine)_3][NO_3]_2$ (diamine = tn or en). The synthetic method has been commonly used to prepare cyanide-bridged bimetallic complexes of different structures.[16]

The IR spectral data of the complexes given in the Experimental section show three sharp bands at 2150, 2140 and 2060 cm^{-1} for **1** and 2150, 2130 and 2110 cm^{-1} for **2**, respectively, which are attributed to C≡N stretching modes. The shift of *ν*(C≡N) to higher wavenumber compared with that of $K_3Fe(CN)_6$ (2119 cm^{-1}) suggests a lowered symmetry about the $Fe(CN)_6^{3-}$ entity and the formation of CN^- bridges, as observed for other cyano-bridged systems.[13–16,22,23,29] The appearance of the sharp band at 1380 cm^{-1} in the spectra indicates the presence of free NO_3^- anions.

Crystal structure of complex 1

The asymmetric unit is shown in Fig. 1. Selected bond distances and angles are listed in Table 1 and intermolecular contacts involving H atoms in Table 2.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Fe–C(3)	1.901(2)	Fe–C(5)	1.914(2)
Fe–C(2)	1.925(2)	Fe–C(1)	1.982(3)
Fe–C(6)	1.996(2)	Fe–C(4)	2.023(3)
C(1)–N(1)	1.132(3)	C(4)–N(4)	1.122(3)
C(2)–N(2)	1.163(2)	Ni(1^{i})–N(2)	2.174(2)
C(3)–N(3)	1.177(3)	Ni(1)–N(1)	2.127(2)
C(5)–N(5)	1.141(2)	Ni(2)–N(5)	2.146(2)
C(6)–N(6)	1.132(2)	Ni(1)–N(7)	2.072(2)
Ni(1)–N(9)	2.116(2)	Ni(1)–N(8)	2.124(2)
Ni(1)–N(10)	2.155(2)	Ni(1)–N(2^{iii})	2.177(2)
Ni(2)–N(12)	2.031(2)	Ni(2)–N(13)	2.094(2)
Ni(2)–N(11)	2.1561(2)	Ni(2)–N(14)	2.165(2)
Ni(2)–N(6^{iv})	2.144(2)	Fe···Ni(1)	5.081
Fe···Ni(2)	4.958		
N(1)–C(1)–Fe	168.8(7)	C(1)–N(1)–Ni(1)	161.3(7)
N(2)–C(2)–Fe	173.7(9)	C(2)–N(2)–Ni(1^{i})	148.3(9)
N(3)–C(3)–Fe	176.8(9)	N(4)–C(4)–Fe	164.7(8)
N(5)–C(5)–Fe	167.7(7)	C(5)–N(5)–Ni(2)	153.7(6)
N(6)–C(6)–Fe	174.3(8)	C(6)–N(6)–Ni(2^{ii})	144.2(6)
N(7)–Ni(1)–N(10)	177.8(8)	N(8)–Ni(1)–N(2^{iii})	88.5(7)
N(13)–Ni(2)–N(5)	92.1(7)	N(12)–Ni(2)–N(14)	176.4(6)
N(11)–Ni(2)–N(14)	88.7(8)	N(5)–Ni(2)–N(6^{iv})	177.3(9)

Symmetry transformations: i *x*, *y*, *z* − 1; ii *x*, *y* + 1, *z*; iii *x*, *y*, *z* + 1; iv *x*, *y* − 1, *z*.

Table 2 Intermolecular contacts (Å) involving H atoms

Ow(1)···N(4^{v})	2.802	O(2)···N(7)	2.932
Ow(2)···N(3^{vi})	2.866		

Symmetry transformations: v *x* + 1, *y* − 1, *z*; vi *x* − 1, *y*, *z* + 1.

The asymmetric unit consists of two *trans*-$[Ni(tn)_2]^{2+}$ cations, one $Fe(CN)_6^{3-}$, one NO_3^- anion and two water molecules. No atom is sited at a special equivalent position. The 2-D sheet-like $\{[Ni(tn)_2]_2[Fe(CN)_6]\}_n^{n+}$ polycations are formed by the Ni–N≡C–Fe linkages and can be described as a square network constructed by the cross-linking of snake-shaped Ni–Fe chains (Fig. 2).

Hexacyanoferrate(III) ion co-ordinates to four adjacent *trans*-$[Ni(tn)_2]^{2+}$ cations through four cyano nitrogen atoms [N(1), N(2), N(5), N(6)] on a plane [Ni(1)–N 2.127(2) and 2.177 Å; Ni(2)–N 2.146(2) and 2.144(2) Å]. The Ni–N (tn) lengths range from 2.072(2) to 2.155(2) Å for Ni(1) and 2.031(2) to 2.165(2) Å for Ni(2). The tn molecules in *trans*-$[Ni(tn)_2]^{2+}$ assume a chair conformation similar to that in $[Ni(tn)_2]_3[Fe^{II}(CN)_6][PF_6]_2$.[28]

The average Fe–C and C≡N distances are 1.957(2) and 1.144(2) Å, respectively, which are within the normal range whereas the Fe–C≡N bond angles vary in the range 164.7(8)–176.8(9)°. It should be noted that the Ni–N≡C bond angles range from 144.2(6) to 161.3(7)°, *i.e.* the bridging CN ligands co-ordinate to nickel(II) ions in a considerably bent fashion, which is unique for the 2-D sheet-like Ni_2Fe complexes. The adjacent Fe···Ni distances are 5.081 Å for Fe···Ni(1) and 4.958 Å for Fe···Ni(2). The NO_3^- ion is situated within each Ni_4Fe_4 square and linked to N(7) of the tn ligand [O(2)···N(7) 2.932 Å]. In the crystal the sheets align along the *a* axis with a separation of *ca.* 8.9 Å. The water molecules are positioned between the sheets and linked to the terminal CN ligands of $Fe(CN)_6^{3-}$ *via* hydrogen bonding (Table 2).

Every effort to determine the structure of complex **2** has failed owing to the weak diffraction peaks obtained during data collection. Based on IR, microelemental analyses and the structure of complex **1**, we presume that **2** has a 2-D sheet structure similar to that of **1**. As pointed out by Ohba *et al.*, the square cavity formed by the Ni_4Fe_4 moiety plays an important role in the construction of Ni_2Fe type complexes.[22] The authors predicted that the en compound $[Ni(en)_2]_2[Fe(CN)_6]X$

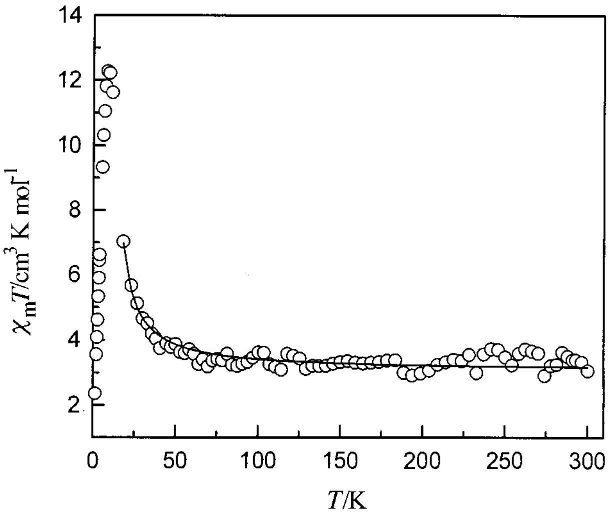


Fig. 3 Temperature dependence of $\chi_M T$ for complex **1**. The solid line is the calculated curve discussed in the text.

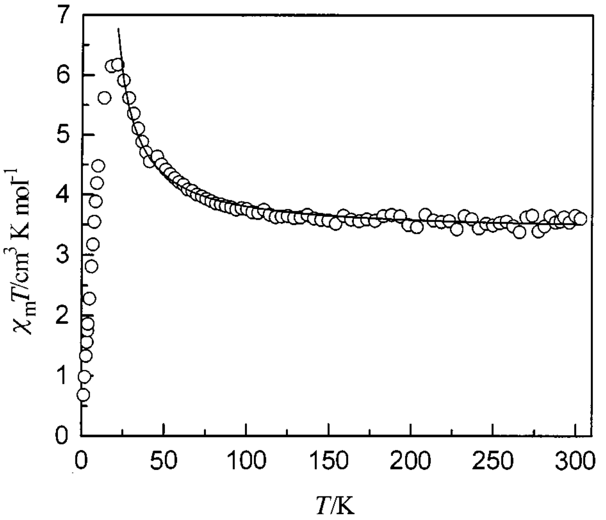


Fig. 4 Temperature dependence of $\chi_M T$ for complex **2**. The solid line represents the fit discussed in the text.

($X = ClO_4^-$, BF_4^- or PF_6^-) cannot have a 2-D network structure as a result of the shallow cavity which is insufficient to accommodate the counter anions within it. We chose the less bulky and planar NO_3^- anion and obtained the 2-D $[Ni(en)_2]_2[Fe(CN)_6]NO_3$ complex.

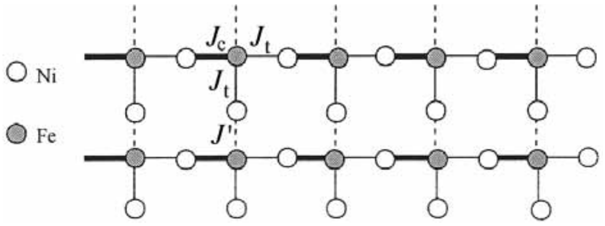
Magnetic properties

The magnetic susceptibilities of complexes **1** and **2** have been measured in the temperature range 1.5–300 K with a model CF-1 vibrating-sample magnetometer. Plots of $\chi_m T$ *vs.* T are shown in Figs. 3 and 4, where χ_m is the magnetic susceptibility per Ni_2Fe unit.

Complex 1. The $\chi_m T$ value at room temperature is *ca.* 3.3 cm^3 K mol^{-1} (5.14 μ_B) which increases smoothly down to *ca.* 50 K and then sharply reaching a maximum value of 12.28 cm^3 K mol^{-1} (9.91 μ_B) at 8.63 K. Below this temperature, $\chi_m T$ decreases rapidly down to 2.36 cm^3 K mol^{-1} (4.34 μ_B) at 1.5 K. The magnetic behaviour above 8.63 K suggests an intramolecular ferromagnetic interaction between adjacent iron(III) and nickel(II) through the cyanide bridges. The decrease in $\chi_M T$ below 8.6 K may be due to an intersheet antiferromagnetic interaction. Also, the magnetic susceptibility obeys the Curie–Weiss law with a positive Weiss constant $\theta = +5.9$ K, which sheds light on the presence of intramolecular ferromagnetic interaction. The maximum value of $\chi_m T$ is much larger than the spin-only value of 4.38 cm^3 K mol^{-1} (5.92 μ_B) for $S_T = 5/2$ resulting from the ferromagnetic coupling of two nickel(II) ions ($S = 1$, $g = 2.0$) and one iron(III) ion ($S = \frac{1}{2}$, $g = 2.0$), strongly suggestive of the occurrence of magnetic ordering.

Neglecting interactions between the 2-D sheets, the magnetic coupling for the compounds involves a 2-D spin Hamiltonian with at least four coupling constants, corresponding to the four different separations between adjacent iron(III) and nickel(II) ions revealed by the structure data of **1**. Since such a complex Hamiltonian cannot be used for data analysis, we used an approximate approach similar to that reported previously.[31–33]

As indicated in Fig. 1, the four Fe–CN–Ni linkages do not differ significantly from each other therefore they can be considered equivalent for simplicity. On this basis, the 2-D sheet was treated as a system of interacting 1-D chains. The uniform chains, formed by the Ni–Fe–Ni trinuclear units, can be schematised as shown below where J_t, J_c and J' stand for the exchange integrals between the S_{Fe} and S_{Ni} spins within the Ni_2Fe trimer, between the S_t effective spins of the trimers and between the chains, respectively, and were treated as equivalent.



Using this model, the susceptibility above 18 K can be approximated by eqns. (1)–(4). When allowing the g and J values to vary, we obtained the best fit to the experimental data with parameters $J_t = J_c = J' = 0.88$ cm^{-1}, $g = 2.29$ and $R = 1.1 \times 10^{-3}$ [$R = \Sigma(\chi_{obs} - \chi_{calc})^2/\chi_{obs}{}^2$] for the 76 observations (18–300 K). As shown in Fig. 3, the fit may be considered good.

$$\chi_t = \frac{Ng^2\beta^2}{4kT}\,\frac{10 + 35\exp(5J_t/kT) + 10\exp(4J_t/kT) + \exp(J_t/kT) + \exp(3J_t/kT)}{3\exp(5J_t/kT) + 2 + 2\exp(4J_t/kT) + \exp(J_t/kT) + \exp(3J_t/kT)} \tag{1}$$

$$\chi_t = \frac{Ng^2\beta^2}{3kT}\,S_t(S_t + 1) \tag{2}$$

$$\chi_{chain} = \frac{Ng^2\beta^2}{3kT}\,\frac{1 + u}{1 - u} \times S_t(S_t + 1), \text{ where } u = \coth[J_cS_t(S_t + 1)/kT] - kT/J_cS_t(S_t + 1) \tag{3}$$

$$\chi_m = \frac{\chi_{chain}}{1 - \chi_{chain}(2zJ'/Ng^2\beta^2)}, \text{ where } z = 2 \tag{4}$$

Complex 2. Complex **2** has similar magnetic behaviour to that of **1**. The magnetic susceptibility obeys the Curie–Weiss law with a positive Weiss constant $\theta = +9.8$ K. The $\chi_m T$ value of 3.51 cm^3 K mol^{-1} at room temperature is much larger than that expected for uncoupled two nickel(II) ($S = 1$) and one iron(III) ion ($S = 1/2$) (2.375 cm^3 K mol^{-1}, calculated with $g = 2.0$), probably due to an orbital contribution to the magnetic moment of the low-spin Fe^{III} ($^2T_{2g}$). The maximum $\chi_m T$ value (6.17 cm^3 K mol^{-1}, 7.03 μ_B) is larger than the spin-only value for $S_T = 5/2$ resulting from the ferromagnetic coupling of two nickel(II) and one low-spin iron(III) ion ($S = 1/2$, $g = 2.0$) and close to that (6.24 cm^3 K mol^{-1}, 7.07 μ_B) for $g = 2.39$.

To analyse the magnetic data, we assume that complex **2** has a structure similar to that of **1**. On this basis, the susceptibility above 21 K can be approximated by eqns. (1)–(4). When allowing the g and J values to vary, we obtained the best fit to the experimental data with parameters $J_t = J_c = J' = 0.92$ cm^{-1}, $g = 2.39$ and $R = 2.5 \times 10^{-3}$ for the 76 observations (21–300 K). As shown in Fig. 4, the fit may be considered fairly good.

The results ($J_t = J_c = J' > 0$) show the presence of weak ferromagnetic interaction between the nickel(II) and iron(III) ions within each sheet through the CN^- ligands. The ferromagnetic interaction can be rationalised by the strict orthogonality of the magnetic orbitals of low-spin Fe^{III} (t_{2g}^5) and Ni^{II} (e_g^2).[34] The decrease in $\chi_M T$ at low temperatures may be due to an intersheet antiferromagnetic interaction. Taking into account the structure of **1** which contains bent Ni–N≡C–Fe linkages, we can conclude that the characters of magnetic coupling are not significantly affected by the Ni–N≡C bond angles.

Acknowledgements

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