

Magnetic characteristics of two two-dimensional bimetallic assemblies, $[\text{Ni}(\text{diamine})_2]_2[\text{Fe}(\text{CN})_6]\text{NO}_3 \cdot n\text{H}_2\text{O}$ (diamine = 1,3-diaminopropane, $n = 2$; ethylenediamine, $n = 3$), with a square molecular structure

Hui-Zhong Kou,^a Wei-Ming Bu,^b Dai-Zheng Liao,^{*a} Zong-Hui Jiang,^a Shi-Ping Yan,^a Yu-Guo Fan^b and Geng-Lin Wang^a

^a Department of Chemistry, Nankai University, Tianjin 300071, P.R. China.

E-mail: chemczl@sun.nankai.edu.cn

^b Laboratory of Supramolecular and Spectroscopy, Jilin University, Changchun 130023, Jilin Province, P.R. China

Received 14th July 1998, Accepted 23rd October 1998

Two bimetallic assemblies, $[\text{Ni}(\text{diamine})_2]_2[\text{Fe}(\text{CN})_6]\text{NO}_3 \cdot n\text{H}_2\text{O}$ [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 $\text{Fe}(\text{CN})_6^{3-}$ co-ordinate to the *trans*- $[\text{Ni}(\text{tn})_2]^{2+}$ 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 $[\text{M}(\text{CN})_6]^{n-}$ ($\text{M} = \text{Cr}^{\text{III}}, \text{Mn}^{\text{III}}, \text{Fe}^{\text{III}}$ 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 $[\text{M}(\text{CN})_6]^{3-}$ ($\text{M} = \text{Cr}^{\text{III}}, \text{Mn}^{\text{III}}$, 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 $\text{Ni}^{\text{II}}\text{–Fe}^{\text{III}}$ bimetallic assemblies, e.g. pentanuclear cluster $[\text{Ni}(\text{bpm})_2]_3[\text{Fe}(\text{CN})_6]_2 \cdot 7\text{H}_2\text{O}$ [bpm = bis(pyrazol-1-yl)methane],¹³ 1-D chain complexes $[\text{Ni}(\text{en})_2]_3[\text{Fe}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ ¹⁵ and $[\text{PPh}_4][\text{Ni}(\text{pn})_2][\text{Fe}(\text{CN})_6]$ (pn = propane-1,2-diamine)¹⁷ and 2-D sheet $[\text{Ni}(\text{diamine})_2]_2[\text{Fe}(\text{CN})_6]\text{X}$ (diamine = 1,1-dimethylethylenediamine or pn; $\text{X} = \text{ClO}_4^-, \text{NO}_3^-, \text{PhCO}_2^-, \text{I}^-$ or N_3^-)^{20–22} as well as 3-D $[\text{Ni}(\text{tren})_3][\text{Fe}(\text{CN})_6]_2 \cdot 6\text{H}_2\text{O}$ [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 $[\text{Ni}(\text{diamine})_2]_2[\text{Fe}(\text{CN})_6]\text{X} \cdot n\text{H}_2\text{O}$ exhibit ferro- or meta-magnetic behaviour dependent on the difference in intersheet separations.²¹ As an extension of those studies, two 2-D complexes, $[\text{Ni}(\text{tn})_2]_2[\text{Fe}(\text{CN})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ (**1**) (tn = propane-1,3-diamine) and $[\text{Ni}(\text{en})_2]_2[\text{Fe}(\text{CN})_6]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ (**2**), were prepared. The crystal structure of **1** was determined by X-ray crystallography revealing a 2-D network extended by $\text{Fe}^{\text{III}}\text{–CN–Ni}^{\text{II}}$ linkages. Magnetic properties of the compounds are also reported.

Experimental

The physical measurements have been performed as described previously.¹⁸

Preparations

$[\text{Ni}(\text{tn})_2]_2[\text{Fe}(\text{CN})_6]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ **1.** To an aqueous solution of $[\text{Ni}(\text{tn})_3][\text{NO}_3]_2$ prepared by mixing $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 290.8 mg) and tn (3 mmol, 222.3 mg) in 20 cm^3 of water was added $\text{K}_3\text{Fe}(\text{CN})_6$ (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. $\text{C}_{18}\text{H}_{44}\text{FeN}_{15}\text{Ni}_2\text{O}_5$ requires C, 29.9; H, 6.1; N, 29.0%). IR: $\nu_{\text{max}}/\text{cm}^{-1}$ 2150, 2140 and 2060 ($\text{C}\equiv\text{N}$) 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.

$[\text{Ni}(\text{en})_2]_2[\text{Fe}(\text{CN})_6]\text{NO}_3 \cdot 3\text{H}_2\text{O}$ **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. $\text{C}_{14}\text{H}_{38}\text{FeN}_{15}\text{Ni}_2\text{O}_6$ requires C, 24.5; H, 5.6; N, 30.6%). IR: $\nu_{\text{max}}/\text{cm}^{-1}$ 2150, 2130 and 2110 ($\text{C}\equiv\text{N}$) and 1380 (N–O).

Crystal structure determination of complex **1**

Crystal data. $\text{C}_{18}\text{H}_{44}\text{FeN}_{15}\text{Ni}_2\text{O}_5$, $M = 723.95$, triclinic, space group $P1$, $a = 8.9298(8)$, $b = 9.9358(9)$, $c = 10.1319(7)$ Å, $U = 806.97(12)$ Å³, $T = 293(2)$ K, $Z = 1$, $\mu(\text{Mo–K}\alpha) = 1.651 \text{ mm}^{-1}$, 3440 reflections measured and considered unique ($R_{\text{int}} = 0.062$) used in all calculations. The final wR was 0.053. $R1(F) = 0.0466$.

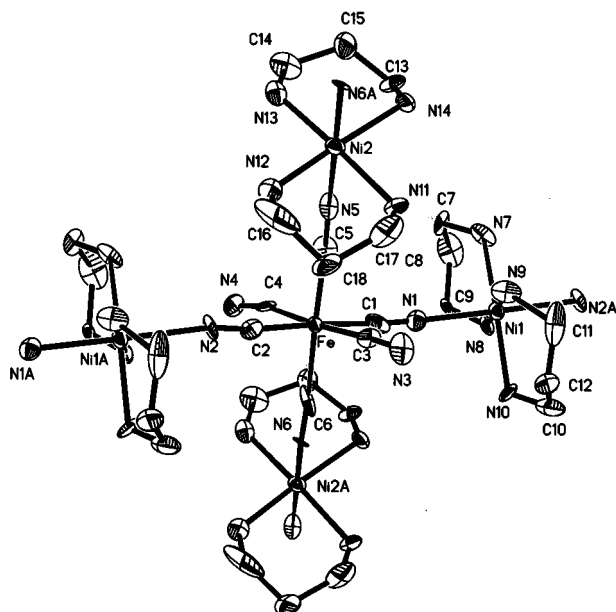


Fig. 1 An ORTEP³⁰ drawing of complex **1** with the atom numbering scheme.

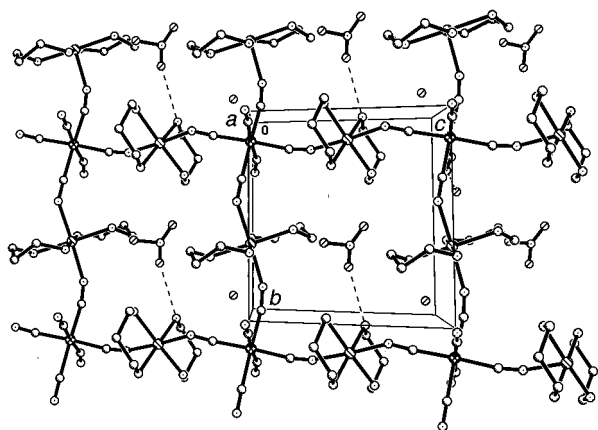


Fig. 2 Projection of the polymeric sheet-like structure along the *a* axis showing Fe_4Ni_4 squares and hydrogen bonds (---).

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 $\text{Fe}(\text{CN})_6^{3-}$ reacted with $[\text{Ni}(\text{diamine})_3][\text{NO}_3]_2$ (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 $\text{C}\equiv\text{N}$ stretching modes. The shift of $\nu(\text{C}\equiv\text{N})$ to higher wavenumber compared with that of $\text{K}_3\text{Fe}(\text{CN})_6$ (2119 cm^{-1}) suggests a lowered symmetry about the $\text{Fe}(\text{CN})_6^{3-}$ 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 ⁱⁱⁱ)	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 $\text{trans}[\text{Ni}(\text{tn})_2]^{2+}$ cations, one $\text{Fe}(\text{CN})_6^{3-}$, one NO_3^- anion and two water molecules. No atom is sited at a special equivalent position. The 2-D sheet-like $\{[\text{Ni}(\text{tn})_2]_2[\text{Fe}(\text{CN})_6]_n\}^{n+}$ 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 $\text{trans}[\text{Ni}(\text{tn})_2]^{2+}$ 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 $\text{trans}[\text{Ni}(\text{tn})_2]^{2+}$ assume a chair conformation similar to that in $[\text{Ni}(\text{tn})_2]_3[\text{Fe}^{\text{III}}(\text{CN})_6][\text{PF}_6]_2$.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 $\text{Fe}(\text{CN})_6^{3-}$ 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 $[\text{Ni}(\text{en})_2]_2[\text{Fe}(\text{CN})_6]_X$

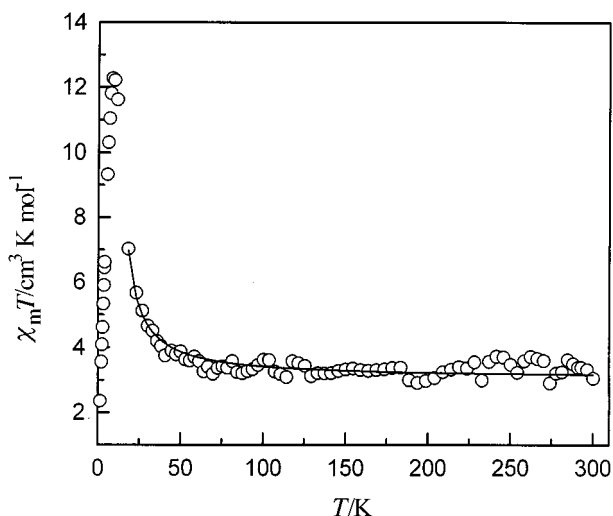


Fig. 3 Temperature dependence of $\chi_M T$ for complex 1. The solid line is the calculated curve discussed in the text.

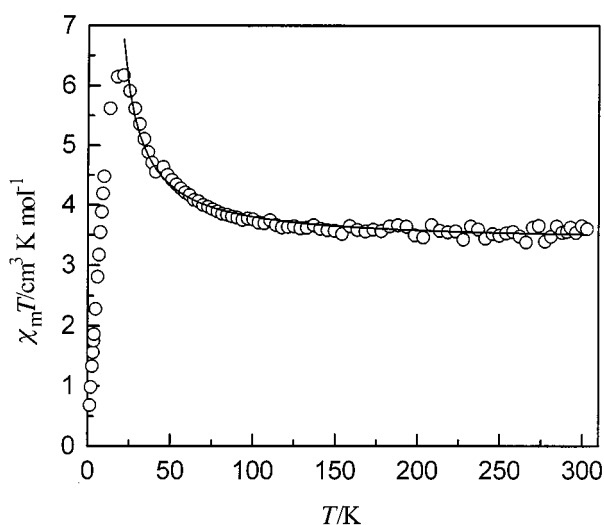


Fig. 4 Temperature dependence of $\chi_M T$ for complex 2. The solid line represents the fit discussed in the text.

($X = \text{ClO}_4^-$, 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 $[\text{Ni}(\text{en})_2]_2[\text{Fe}(\text{CN})_6]\text{NO}_3$ complex.

Magnetic properties

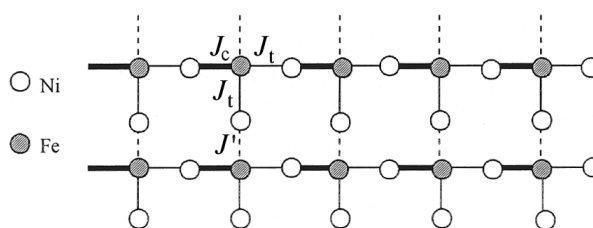
The magnetic susceptibilities of complexes 1 and 2 have been measured in the temperature range 1.5–300 K with a model CF-1 vibrating-sample magnetometer. Plots of $\chi_m T$ vs. T are

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.* $3.3 \text{ cm}^3 \text{ K mol}^{-1}$ ($5.14 \mu_B$) which increases smoothly down to *ca.* 50 K and then sharply reaching a maximum value of $12.28 \text{ cm}^3 \text{ K mol}^{-1}$ ($9.91 \mu_B$) at 8.63 K. Below this temperature, $\chi_m T$ decreases rapidly down to $2.36 \text{ cm}^3 \text{ K mol}^{-1}$ ($4.34 \mu_B$) 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 $\theta = +5.9 \text{ K}$, 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 $4.38 \text{ cm}^3 \text{ K mol}^{-1}$ ($5.92 \mu_B$) 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 $J_t = J_c = J' = 0.88 \text{ cm}^{-1}$, $g = 2.29$ and $R = 1.1 \times 10^{-3}$ [$R = \Sigma(\chi_{\text{obs}} - \chi_{\text{calc}})^2 / \chi_{\text{obs}}^2$] for the 76 observations (18–300 K). As shown in Fig. 3, the fit may be considered good.

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

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

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

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

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 $3.51 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature is much larger than that expected for uncoupled two nickel(II) ($S = 1$) and one iron(III) ion ($S = 1/2$) ($2.375 \text{ cm}^3 \text{ K mol}^{-1}$, 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 ($6.17 \text{ cm}^3 \text{ K mol}^{-1}$, $7.03 \mu_B$) 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 ($6.24 \text{ cm}^3 \text{ K mol}^{-1}$, $7.07 \mu_B$) 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 $J_t = J_c = J' = 0.92 \text{ cm}^{-1}$, $g = 2.39$ 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 $\text{Ni}-\text{N}\equiv\text{C}-\text{Fe}$ linkages, we can conclude that the characters of magnetic coupling are not significantly affected by the $\text{Ni}-\text{N}\equiv\text{C}$ bond angles.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 59772020, No. 29631040) and Natural Science Foundation of Tianjin.

References

- 1 R. Klenze, B. Kanellakopoulos, G. Trageser and H. H. Eysel, *J. Chem. Phys.*, 1980, **72**, 5819.
- 2 F. Herren, P. Fischer, A. Ludi and W. Halg, *Inorg. Chem.*, 1980, **19**, 956.
- 3 W. D. Griebler and D. Babel, *Z. Naturforsch., Teil. B*, 1982, **87**, 832.
- 4 V. Gadet, T. Mallah, I. Castro and M. Verdaguer, *J. Am. Chem. Soc.*, 1992, **114**, 9213.
- 5 V. Gadet, M. Bujoli-Doeuff, L. Force, M. Verdaguer, K. El Malkhi, A. Deroy, J. P. Besse, C. Chappert, P. Veillet, J. P. Renard and P. Beauvillain, in *Molecular Magnetic Materials*, eds. D. Gatteschi, O. Kahn, J. S. Miller and P. Palacio, *NATO ASI Ser.* 198, Kluwer, Dordrecht, 1990, p. 281.

- 6 T. Mallah, S. Thiebaut, M. Verdaguer and P. Veillet, *Science*, 1993, **262**, 1554.
- 7 W. R. Entley and G. S. Girolami, *Inorg. Chem.*, 1994, **33**, 5165.
- 8 W. R. Entley and G. S. Girolami, *Science*, 1995, **21**, 268.
- 9 S. Ferlay, T. Mallah, R. Ouaches, P. Veillet and M. Verdaguer, *Nature (London)*, 1995, **378**, 701.
- 10 O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science*, 1996, **271**, 49.
- 11 M. Verdaguer, *Science*, 1996, **272**, 698.
- 12 O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science*, 1996, **272**, 704.
- 13 K. V. Langenberg, S. R. Batten, K. J. Berry, D. C. R. Hockless, B. Moubaraki and K. S. Murray, *Inorg. Chem.*, 1997, **36**, 5006.
- 14 H. Miyasaka, H. Ieda, N. Matsumoto, N. Re, R. Crescenzi and C. Floriani, *Inorg. Chem.*, 1998, **37**, 255.
- 15 M. Ohba, N. Maruone, H. Okawa, T. Enoki and J.-M. Latour, *J. Am. Chem. Soc.*, 1994, **116**, 11566.
- 16 M. Ohba, N. Fukita and H. Okawa, *J. Chem. Soc., Dalton Trans.*, 1997, 1733.
- 17 H. Okawa and M. Ohba, *ACS Symp. Ser.*, 1996, **644**, 319.
- 18 H.-Z. Kou, D.-Z. Liao, P. Cheng, Z.-H. Jiang, S.-P. Yan, G.-L. Wang, X.-K. Yao and H.-G. Wang, *J. Chem. Soc., Dalton Trans.*, 1997, 1503.
- 19 H.-Z. Kou, H.-M. Wang, D.-Z. Liao, P. Cheng, Z.-H. Jiang, S.-P. Yan, X.-Y. Huang and G.-L. Wang, *Aust. J. Chem.*, 1998, **51**, 661.
- 20 M. Ohba, H. Okawa, T. Ito and A. Ohto, *J. Chem. Soc., Chem. Commun.*, 1995, 1545.
- 21 M. Ohba and H. Okawa, *Mol. Cryst. Liq. Cryst.*, 1996, **286**, 101.
- 22 M. Ohba, H. Okawa, N. Fukita and Y. Hashimoto, *J. Am. Chem. Soc.*, 1997, **119**, 1011.
- 23 S. Ferlay, T. Mallah, J. Vaissermann, F. Bartolome, P. Veillet and M. Verdaguer, *Chem. Commun.*, 1996, 2481.
- 24 H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo and C. Floriani, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1446.
- 25 H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo and C. Floriani, *J. Am. Chem. Soc.*, 1996, **118**, 981.
- 26 N. Re, E. Gallo, C. Floriani, H. Miyasaka and N. Matsumoto, *Inorg. Chem.*, 1996, **35**, 5964.
- 27 H. Miyasaka, N. Matsumoto, N. Re, E. Gallo and C. Floriani, *Inorg. Chem.*, 1997, **36**, 670.
- 28 M. S. El Fallah, E. Rentschler, A. Caneschi, R. Sessoli and D. Gatteschi, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1947.
- 29 N. Fukita, M. Ohba, H. Okawa, K. Matsuda and H. Iwamura, *Inorg. Chem.*, 1998, **37**, 842.
- 30 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- 31 B. Chiari, A. Cinti, O. Piovesana and P. F. Zanazzi, *Inorg. Chem.*, 1995, **34**, 2652.
- 32 M. C. Burla, B. Chiari, A. Cinti and O. Piovesana, *Mol. Cryst. Liq. Cryst.*, 1995, **273**, 211.
- 33 A. Caneschi, D. Gatteschi, M. C. Melandri, P. Rey and R. Sessoli, *Inorg. Chem.*, 1990, **29**, 4228.
- 34 O. Kahn, in *Molecular Magnetism*, VCH, Weinheim, 1993.

Paper 8/05470C