

Reactions between macrocyclic nickel(II) complexes and ferricyanide. Metamagnetic properties of a two-dimensional honeycomb assembly $[\text{NiL}^3]_3[\text{Fe}(\text{CN})_6]_2 \cdot 8\text{H}_2\text{O}$ ($\text{L}^3 = 3,10$ -dihydroxyethyl-1,3,6,8,10,12-hexaazacyclotetradecane)†

Hui-Zhong Kou,*‡^a Wei-Ming Bu,^b Song Gao,^c 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: coord@sun.nankai.edu.cn

^b Key Laboratory for Supramolecular Structure and Spectroscopy, Jilin University, Changchun 130023, P.R. China

^c State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University, Beijing 100871, P.R. China

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The synthesis, structural and magnetic properties of the 2-D bimetallic complex $[\text{NiL}^3]_3[\text{Fe}(\text{CN})_6]_2 \cdot 8\text{H}_2\text{O}$ ($\text{L}^3 = 3,10$ -dihydroxyethyl-1,3,6,8,10,12-hexaazacyclotetradecane) are presented. The structure consists of cyano-bridged neutral honeycomb-like layers. Each hexacyanoferrate(III) ion connects three nickel(II) ions using three *cis* CN^- groups and the remaining CN^- groups are terminal. The bridging cyanide ligands coordinate to the nickel ion in a *trans* fashion. Magnetic studies showed that the complex displays a metamagnetic behaviour arising from intralayer ferromagnetic coupling and interlayer antiferromagnetic interactions. A long-range magnetic ordering at $T_c = 6.0$ K was observed. In addition, the ionic complex $[\text{NiL}^4]_3[\text{Fe}(\text{CN})_6]_2 \cdot 6\text{H}_2\text{O}$ ($\text{L}^4 = 8$ -methyl-1,3,6,8,10,13,15-heptaazatricyclo-[13.1.1.1^{13,15}]octadecane) showing the absence of cyano bridging, is reported.

Introduction

It is well known that the cyanide ion can connect two metal ions as a bridging ligand. Magnetic exchange through bridging cyanide has been extensively investigated and there has been increasing interest in magnetic studies on transition metal cyanides.^{1–41} To clarify the magneto-structural correlation of cyanide-bridged systems, it is very important to determine the molecular structure since predictions from indirect measurements are risky. For example, bimetallic cyanides $[\text{M}(\text{L})]_3[\text{M}'(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}, \text{L} = \text{polydentate ligand}; \text{M}' = \text{Fe}^{\text{III}}, \text{Cr}^{\text{III}}, \text{Co}^{\text{III}}$) assume cyanide-bridged zero-,¹³ one-,^{14,21,33,34,40} two-^{19,24,29} or three-dimensional^{18,30,40b} molecular structures dependent upon the differences in steric hindrance and coordination modes of ligands L , although the complexes have similar formulae and IR spectra. We have investigated the reactions of a series of diamagnetic azamacrocyclic nickel(II) complexes with ferricyanide and found that the hexaazamacrocyclic nickel(II) complex $[\text{NiL}^1](\text{ClO}_4)_2$ yields a two-dimensional stair-shaped honeycomb-like complex $[\text{NiL}^1]_3[\text{Fe}(\text{CN})_6]_2 \cdot 9\text{H}_2\text{O}$ **1** ($\text{L}^1 = 3,10$ -dimethyl-1,3,6,8,10,12-hexaazacyclotetradecane),^{24a} whereas using a similar hexaazamacrocyclic nickel(II) complex $[\text{NiL}^2](\text{ClO}_4)_2$ ($\text{L}^2 = 3,10$ -diethyl-1,3,6,8,10,12-hexaazacyclotetradecane) instead of $[\text{NiL}^1](\text{ClO}_4)_2$ a completely different molecular network **2** is obtained⁴² (Scheme 1). Magnetic investigations indicate that there are significant differences in magnetism. In addition, a similar complex $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ with a honeycomb-like molecular structure has been reported by Colacio *et al.*²⁹ Interestingly, magnetic studies on $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ indicate a spin canted ground state. These interesting observations promp-

ted us to explore the reaction between $[\text{NiL}^3](\text{ClO}_4)_2$ ($\text{L}^3 = 3,10$ -dihydroxyethyl-1,3,6,8,10,12-hexaazacyclotetradecane)⁴³ and $[\text{Fe}(\text{CN})_6]^{3-}$. As expected, a cyanide-bridged bimetallic compound $[\text{NiL}^3]_3[\text{Fe}(\text{CN})_6]_2 \cdot 8\text{H}_2\text{O}$ **3** was obtained, and structural analysis showed that the complex is isomorphous with $[\text{NiL}^1]_3[\text{Fe}(\text{CN})_6]_2 \cdot 9\text{H}_2\text{O}$ **1**. This validates the comparison of the magnetic behaviour of the two complexes and consequently the identification of the factors that control the magnetic properties with the purpose of designing and synthesizing molecular magnetic materials. Also, an ionic Ni(II)–Fe(III) complex derived from a heptaazacyclic nickel(II) complex $[\text{NiL}^4](\text{ClO}_4)_2$ ($\text{L}^4 = 8$ -methyl-1,3,6,8,10,13,15-heptaazatricyclo-[13.1.1.1^{13,15}]octadecane)⁴⁴ and $[\text{Fe}(\text{CN})_6]^{3-}$ is briefly discussed.

Experimental

Physical measurements

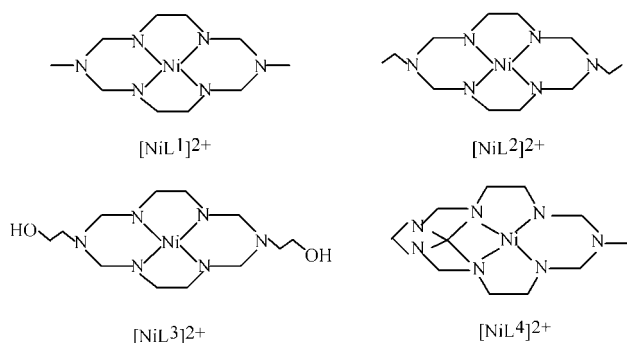
C, H, N elemental analyses were carried out with a Perkin-Elmer analyzer model 240. Electronic spectra were measured with a Perkin-Elmer Hitachi-240 spectrophotometer in water. IR spectroscopy on KBr pellets was performed on a 5DX FT-IR spectrophotometer in the region 4000–400 cm^{-1} . Variable-temperature magnetic susceptibility (1.8–290 K) in a field of 1 T, zero-field ac magnetic susceptibility (1.5–9 K) measurements and field dependence magnetization (0–0.5 T) at 1.93 K were performed on a Maglab System²⁰⁰⁰ magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's Tables).

Preparations

All reagents used in the synthesis were of analytical grade and were used without further purification. The precursors $[\text{NiL}^3](\text{ClO}_4)_2$ and $[\text{NiL}^4](\text{ClO}_4)_2$ were prepared by literature methods.^{43,44}

† Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24} \text{ J T}^{-1}$.

‡ Present address: State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University, Beijing 100871, P. R. China.



Scheme 1

[NiL³]₃[Fe(CN)₆]₂·8H₂O 3. To an aqueous solution (20 cm³) of [NiL³](ClO₄)₂ (0.3 mmol) was added K₃[Fe(CN)₆] (0.2 mmol) in water (10 cm³) at room temperature. Brown microcrystals precipitated from the resulting brown solution after 10 min which were collected by suction filtration, thoroughly washed with water and dried in air. Yield 130.8 mg, 85%. Anal. Calc. for C₄₂H₉₆Fe₂N₃₀Ni₃O₁₄: C, 34.71; H, 6.66; N, 28.92. Found: C, 34.87; H, 6.48; N, 28.95%. IR: ν_{max} /cm⁻¹ 2150s, 2110s and 2050w (C≡N).

Well-shaped dark brown crystals suitable for X-ray structure analysis were grown at room temperature by the slow diffusion of an orange acetonitrile solution of [NiL³](ClO₄)₂ and a yellow aqueous solution of K₃[Fe(CN)₆] in an H-tube.

[NiL⁴]₃[Fe(CN)₆]₂·6H₂O 4. To [NiL⁴](ClO₄)₂ (0.3 mmol) in 20 cm³ of acetonitrile was added an excess of K₃[Fe(CN)₆] until the initial precipitate dissolved (*ca.* 1 mmol) at room temperature. Orange single crystals were obtained from the resulting brown solution after one week, one of which was selected for X-ray diffraction analysis. IR: ν_{max} /cm⁻¹ 2110s (C≡N).

X-Ray structure determinations

Crystal data for 3. C₄₂H₁₀₆Fe₂N₃₀Ni₃O₁₄, *M* = 1615.33, trigonal, space group *P*3̄c1, *a* = *b* = 14.993(3), *c* = 18.450(3) Å, γ = 120°, *U* = 3591.8(12) Å³, *T* = 293(2) K, *Z* = 2, $\mu(\text{Mo-K}\alpha)$ = 1.239 mm⁻¹, 4951 reflections measured (1.57 ≤ θ ≤ 25.04°) and 2113 considered unique (*R*_{int} = 0.0345). The final *R*_w*F* was 0.0652, with conventional *R*_F 0.0456 for 154 parameters.

Crystal data for 4. C₄₈H₈₇Fe₂N₃₃Ni₃O₆, *M* = 1615.33, rhombohedral, space group *R*3̄, *a* = *b* = 31.750(5), *c* = 18.390(3) Å, γ = 120°, *U* = 9741(3) Å³, *T* = 293(2) K, *Z* = 6, $\mu(\text{Mo-K}\alpha)$ = 1.364 mm⁻¹, 3333 reflections measured (1.59 ≤ θ ≤ 27.51°) and 2599 considered unique (*R*_{int} = 0.0420). The final *R*_w*F* was 0.0611, with conventional *R*_F 0.0448 for 279 parameters.

CCDC reference number 186/2076.

See <http://www.rsc.org/suppdata/dt/b0/b003289/> for crystallographic files in .cif format.

Results

The IR spectrum of complex **3** shows two strong bands at 2150, 2110 cm⁻¹ and a weak band at 2050 cm⁻¹, which are attributed to C≡N stretching modes. The shift of $\nu(\text{C}\equiv\text{N})$ to higher wave number compared with that of K₃[Fe(CN)₆] (2119 cm⁻¹) is characteristic of formation of CN⁻ bridges, as observed for other cyano-bridged systems.¹⁻⁴¹ The non-splitting of $\nu(\text{C}\equiv\text{N})$ in **4** indicates that there is no cyano bridging which is consistent with the X-ray crystal structure results (*vide infra*).

Complexes **3** and **4** are stable in air and insoluble in most inorganic and organic solvents.

Crystal structures

The asymmetric unit of **3** is shown in Fig. 1 while projections of

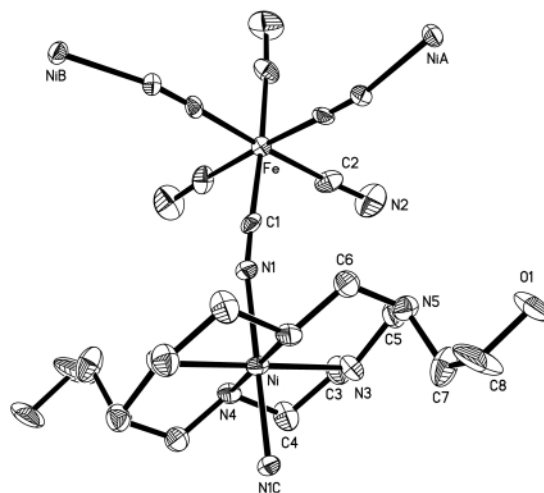


Fig. 1 A drawing of **3** with the numbering scheme of the unique atoms.

Table 1 Selected bond lengths (Å) and angles (°) for **3** and **1**^{24a}

| | 3 | 1 |
|--------------|----------|-----------|
| Fe–C(1) | 1.942(9) | 1.916(10) |
| Fe–C(2) | 1.933(9) | 1.930(10) |
| Ni–N(1) | 2.083(7) | 2.088(9) |
| Ni–N(3) | 2.106(7) | 2.094(9) |
| Ni–N(4) | 2.076(7) | 2.065(9) |
| C(1)–N(1) | 1.148(9) | 1.152(12) |
| C(2)–N(2) | 1.153(9) | 1.132(12) |
| N(1)–C(1)–Fe | 177.9(8) | 177.2(9) |
| N(2)–C(2)–Fe | 174.0(9) | 175.1(8) |
| Ni–N(1)–C(1) | 165.7(7) | 164.6(8) |

the molecular entity in the lattice along and perpendicular to the *c* axis are presented in Figs. 2(a) and (b); selected bond distances and angles are listed in Table 1.

Complex **3** is isostructural to complex **1**.^{24a} The structure consists of neutral stair-shaped layers with stoichiometry [NiL³]₃[Fe(CN)₆]₂. Each [NiL³] unit is linked to two hexacyanoferrate(III) ions in *trans* positions. Each [Fe(CN)₆]³⁻ unit uses three C₃ rotational symmetry related *cis* C≡N groups to connect with three [NiL³]²⁺, whereas the three remaining symmetry related *cis* CN⁻ groups are monodentate. The nickel(II) ion assumes a nearly octahedral geometry with the Ni–N bond distances ranging from 2.076 to 2.106 Å, and the cyanide nitrogen atoms are located in the equatorial plane, rarely observed in six-coordinate nickel(II) macrocyclic complexes (usually at axial positions) and suggests a considerably strong interaction between the cyanide nitrogen atoms and the nickel(II) ion. The average Fe–C and C≡N distances are 1.937(10) and 1.150(9) Å, and the Fe–C≡N bonds do not deviate significantly from linearity [177.9(8) and 174.0(9)°] while the Ni–N≡C bond angle is 165.7(7)°. The closest neighbour Fe...Ni distance is 5.130 Å.

The local molecular disposition leads to a honeycomb-like structure [Fig. 2(a)]. The two-dimensional layer is not planar but adopts a chair conformation [Fig. 2(b)], which is similar to that of complex **1**.^{24a} [Ni(cyclam)]₃[Cr(CN)₆]₂·20H₂O¹⁹ and [Ni(cyclam)]₃[Fe(CN)₆]₂·12H₂O.²⁹ The layers align along the *c* axis with a separation of *ca.* 9.23 Å, and the nearest interlayer metal–metal distance is 7.784 Å (Ni...Fe). The water molecules are positioned between the layers and linked to the terminal CN ligands of Fe(CN)₆³⁻, the nitrogen atom of the macrocyclic ligand L³, and the other water molecules *via* hydrogen bonding with bond distances ranging from 2.497 to 3.127 Å. The oxygen atom of L³, O(1), is also involved in hydrogen-

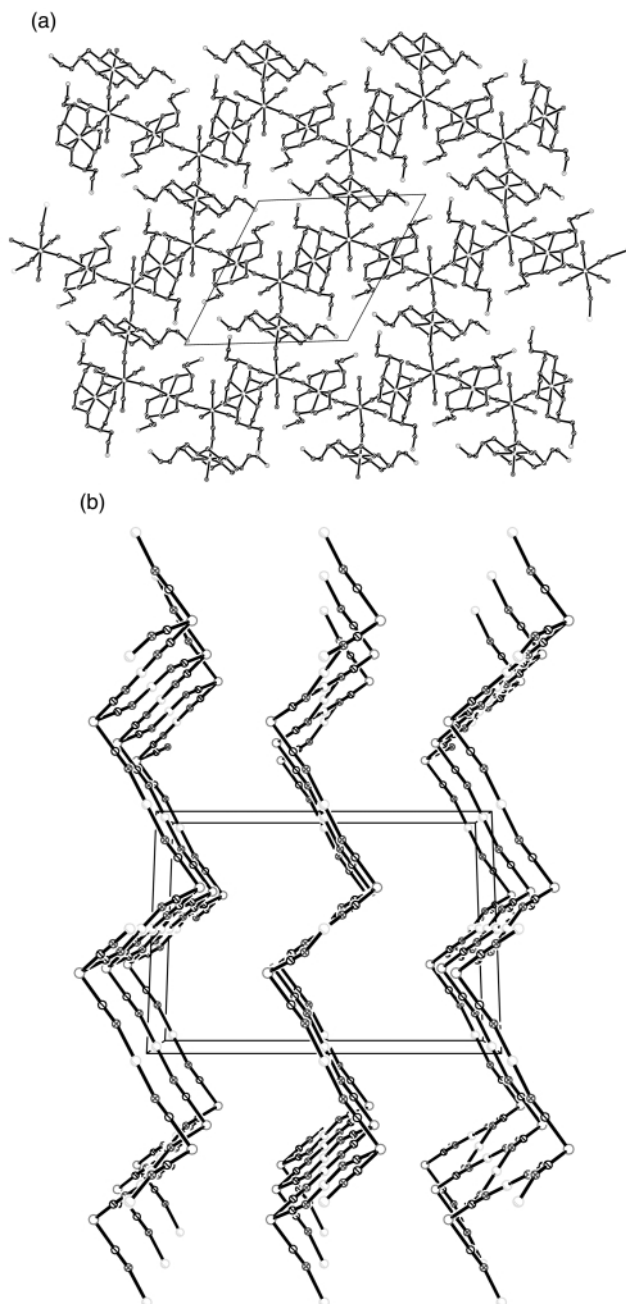


Fig. 2 (a) Projection along the *c* axis, showing the polymeric layer containing Fe_6Ni_6 hexagons of **3**. (b) Projection perpendicular to the *c* axis, showing stacking of the waved layers of **3**.

bonding, $\text{O}(1) \cdots \text{Ow}(2)$ 2.743 Å and $\text{O}(1) \cdots \text{Ow}(3)\#$ 2.879 Å (# denotes the symmetry operation $-x + y, -x, z$).

The asymmetric unit of **4** is shown in Fig. 3. The structure consists of discrete cations and anions with stoichiometry $[\text{NiL}^4]_3[\text{Fe}(\text{CN})_6]_2$. There are no significant differences in the bond distances and angles of the $[\text{NiL}^4]$ moiety between **3** and $[\text{NiL}^4](\text{ClO}_4)_2$.⁴⁴ Important bond distances and angles for **4** are included in the caption of Fig. 3.

Magnetic properties of **3**

The magnetic susceptibilities of **3** have been measured in the temperature range 1.7–290 K. A plot of $\chi_m T$ vs. *T* is shown in Fig. 4, where χ_m is the magnetic susceptibility per Ni_3Fe_2 unit. With a decrease of the temperature, $\chi_m T$ increases slowly down to ca. 30 K and then sharply reaches a maximum value of 16.8 emu K mol^{-1} ($11.6 \mu_B$) at 6.85 K. The $\chi_m T$ value (5.3 emu K mol^{-1} , $6.5 \mu_B$) at room temperature is much higher than expected for a spin-diluted $S_T = (3 \times 1) + (2 \times 1/2)$ system (3.75

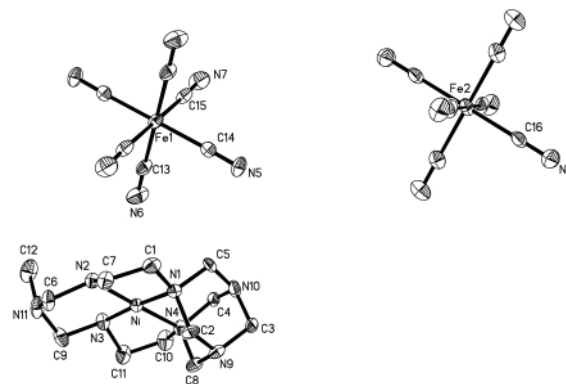


Fig. 3 Ionic structure of **4** with the numbering scheme of the unique atoms. Selected bond distances (Å) and angles (°): Ni–N(3) 1.919(9), Ni–N(1) 1.921(9), Ni–N(4) 1.928(9), Ni–N(2) 1.929(8), Fe(1)–C(13) 1.930(8), Fe(1)–C(15) 1.952(9), Fe(1)–C(14) 1.977(8), Fe(2)–C(16) 1.945(8), N(5)–C(14) 1.143(9), N(7)–C(15) 1.154(8), N(8)–C(16) 1.152(9); N(3)–Ni–N(1) 176.3(4), N(3)–Ni–N(4) 87.7(4), N(1)–Ni–N(4) 89.3(4), N(3)–Ni–N(2) 94.9(4), N(1)–Ni–N(2) 88.1(4), N(4)–Ni–N(2) 177.4(4), N(6)–C(13)–Fe(1) 177.7(11), N(5)–C(14)–Fe(1) 178.3(11), N(7)–C(15)–Fe(1) 177.4(9), N(8)–C(16)–Fe(2) 179.4(9).

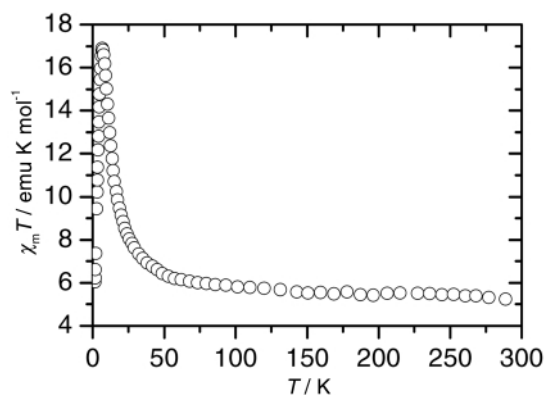


Fig. 4 Temperature dependence of $\chi_m T$ for **3**.

emu K mol^{-1}). Fixing the measured magnetic moment value of $2.37 \mu_B$ for $\text{K}_3[\text{Fe}(\text{CN})_6]$ at room temperature,⁴⁵ we can estimate the $(\chi_m T)_{\text{Ni}}$ value at 1.3 emu K mol^{-1} with a g_{Ni} value of 2.28, which is typical for nickel(II) ions in an octahedral environment. The maximum value is much larger than the spin-only value of 10.0 emu K mol^{-1} ($8.9 \mu_B$) for $S_T = 4$ resulting from the ferromagnetic coupling of three nickel(II) ions and two low-spin iron(III) ions, strongly suggestive of the occurrence of magnetic ordering. Below 6.9 K, $\chi_m T$ decreases rapidly, which indicates the presence of interlayer antiferromagnetic interactions. The magnetic susceptibility above 10 K obeys the Curie–Weiss law with a positive Weiss constant $\theta = +9.0$ K, which also proves the presence of ferromagnetic coupling within the Ni_3Fe_2 sheet of **3**. The ferromagnetic interaction between the iron(III) and nickel(II) ions is due to the strict orthogonality of the magnetic orbitals of low-spin Fe^{III} (t_{2g}^5) and Ni^{II} (e_g^2).⁴⁶

The onset of a long-range magnetic phase transition is further confirmed by the temperature dependence of ac molar magnetic susceptibility as shown in Fig. 5. Both the real and the imaginary parts of the zero field ac magnetic susceptibilities show a maximum at ca. 6.0 K for a frequency of 133 Hz, suggesting that T_c of complex **3** is ca. 6.0 K.⁴⁷

The field dependence of the magnetization (0–6 T) measured at 1.93 K is shown in Fig. 6(a) in the form of $M/N\mu_B$ (per Ni_3Fe_2 unit) vs. *H*, where *M*, *N*, μ_B and *H* are magnetization, Avogadro's number, the electron Bohr magneton and applied magnetic field, respectively. The magnetization shows a rapid saturation and reaches a value of $7.7 N\mu_B$ at 6 T which is close to the expected $S = 4$ value of $8 N\mu_B$ for the Ni_3Fe_2 system,

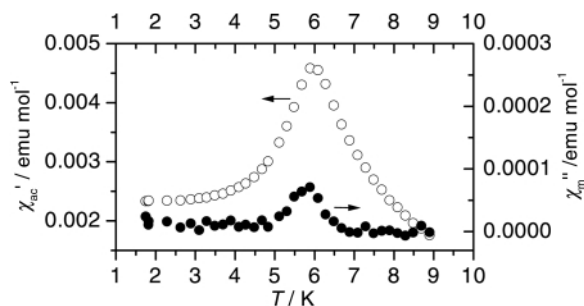


Fig. 5 Real χ' and imaginary χ'' ac magnetic susceptibility as a function of temperature taken at 133 Hz for **3**.

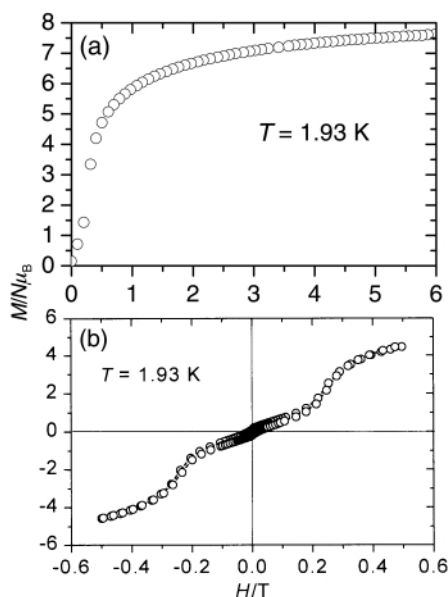


Fig. 6 Magnetization as a function of the applied magnetic field (0–6 T) (a) and hysteresis loop (b) at 1.93 K for **3**.

indicating the presence of ferromagnetic interactions between the adjacent Fe^{III} and Ni^{II} ions.

The field dependence of the magnetization at 1.93 K shown in Fig. 6(b) reveals a hysteresis loop with a coercive field of 150 Oe and a remnant magnetization of *ca.* $0.15 N\mu_{\text{B}}$, suggesting that complex **3** is a soft magnet. The magnetization shows a pronounced sigmoidal behaviour, which suggests metamagnetic behaviour. The magnetization first increases slowly with the increased field and then sharply showing a spin-flipping from an antiferromagnetic arrangement to a ferromagnetic arrangement between the layers. The critical field (the lowest field which is used to reverse the interlayer antiferromagnetic interaction) is *ca.* 900 Oe at 1.93 K.^{27,32}

Discussion

The synthetic strategy to prepare cyanide-bridged bimetallic systems can be described as the reaction of coordinately unsaturated precursors $[\text{NiL}](\text{ClO}_4)_2$ with $\text{K}_3[\text{M}(\text{CN})_6]$ ($\text{M} = \text{Cr}, \text{Fe}$). Generally speaking, this family of bimetallic complexes readily crystallizes to give large single crystals suitable for X-ray structural analysis, which is favourable for structural-magneto correlation studies. It should be pointed out that using DMF as a solvent instead of MeCN does not give single crystals of **3** suitable for X-ray structural analysis.

The reaction of the heptaazacyclic nickel(II) complex $[\text{NiL}^4](\text{ClO}_4)_2$ with $\text{K}_3[\text{Fe}(\text{CN})_6]$ yields an ionic complex **4** the absence of cyano bridges being due to the steric hindrance of the macrocyclic ligand L^4 .

Allowing $[\text{NiL}^3](\text{ClO}_4)_2$ to react with $\text{K}_3[\text{Fe}(\text{CN})_6]$ gives rise to a cyano-bridged honeycomb-like network, which is similar to that of complex **1**. Comparisons of bond distances and angles for the two similar complexes are shown in Table 1. The two complexes possess similar magnetic behaviour, which is in good agreement with their similar structure. Slight differences are, however, evident in the long-range magnetic transition temperatures (T_c), 6.0 K for **3** and 5.1 K for **1**. Since the intralayer molecular displacement and the magnitude of intralayer ferromagnetic interaction (on the basis of the θ values) are quite similar, the difference can be ascribed to small differences in the magnitude of the interlayer antiferromagnetic interactions. It is known that interlayer antiferromagnetic interactions usually result from an anti-parallel arrangement of the spins of adjacent layers and consequently T_c values are lowered.⁴⁸ This suggests that the interlayer antiferromagnetic interaction in **3** is somewhat weaker than that in **1**. The difference in the critical field (H_c) between the two complexes, 900 Oe for **3** and 1000 Oe for **1**, also adds support to the above supposition: the smaller the value of H_c the weaker is the interlayer antiferromagnetic interaction.

It is also interesting to compare the magnetic properties of **3** and $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ ²⁹ from which clear differences are apparent. The former exhibits a T_c of 6.0 K, higher than that of the latter (3.0 K for $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$). This may be accounted for by the difference in the intralayer $\text{Ni}(\text{II}) \cdots \text{Fe}(\text{III})$ ferromagnetic coupling. The structural data show that the Ni-bridging cyano nitrogen bond distance [2.123(2)–2.144(3) Å] in $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ is much larger than that (2.083 Å) in **3**. Such an elongation diminishes the magnetic coupling and results in a lower T_c value. In addition, the coercive field of **3** (150 Oe) is smaller than that of $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ (600 Oe). It is well established that the coercivity of a magnet is essentially related to the magnetic anisotropy of the spin carriers.⁴⁹ Based on the structural features of the complexes, the differences in coercivity can be understood: the nickel(II) ions assume an axially elongated octahedral geometry in $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$, whereas they are approximately octahedral in **3**. The magnetic anisotropy in $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$ leads to higher coercivity, whereas the nearly perfectly octahedral environment of the nickel(II) ions in **3** gives rise to small single ion anisotropy and consequently a small coercive field.

Acknowledgements

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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. Hälg, *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 T. Mallah, S. Thiebaut, M. Verdaguer and P. Veillet, *Science*, 1993, **262**, 1554.
- 6 S. M. Holmes and G. S. Girolami, *J. Am. Chem. Soc.*, 1999, **121**, 5593.
- 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*, 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 M. Ohba, N. Maruone, H. Okawa, T. Enoki and J.-M. Latour, *J. Am. Chem. Soc.*, 1994, **116**, 11566; M. Ohba, N. Fukita and H. Okawa, *J. Chem. Soc., Dalton Trans.*, 1997, 1733.
- 15 H. Okawa and M. Ohba, *ACS Symp. Ser.*, 1996, **644**, 319; M. Ohba, N. Usuki, N. Fukita and H. Okawa, *Inorg. Chem.*, 1998, **37**, 3349; J. Z. Zou, X. D. Hu, C. Y. Duan, Z. Xu, X. Z. You and T. C. W. Mak, *Transition Met. Chem.*, 1998, **23**, 477; E. Colacio, J. M. Dominguez-Vera, M. Ghazi, R. Kivekas, J. M. Moreno and A. Pajunen, *J. Chem. Soc., Dalton Trans.*, 2000, 505.
- 16 M. Ohba, H. Okawa, T. Ito and A. Ohto, *J. Chem. Soc., Chem. Commun.*, 1995, 1545; M. Ohba, H. Okawa, N. Fukita and Y. Hashimoto, *J. Am. Chem. Soc.*, 1997, **119**, 1011.
- 17 H.-Z. Kou, W.-M. Bu, D.-Z. Liao, P. Cheng, Z.-H. Jiang, S.-P. Yan, Y.-G. Fan and G.-L. Wang, *J. Chem. Soc., Dalton Trans.*, 1998, 4161.
- 18 M. S. El Fallah, E. Rentschler, A. Caneschi, R. Sessoli and D. Gatteschi, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1947.
- 19 S. Ferlay, T. Mallah, J. Vaissermann, F. Bartolome, P. Veillet and M. Verdaguer, *Chem. Commun.*, 1996, 2481.
- 20 H. Miyasaka, H. Ieda, N. Matsumoto, N. Re, R. Crescenzi and C. Floriani, *Inorg. Chem.*, 1998, **37**, 255.
- 21 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; T.-B. Lu, H. Xiang, X.-Y. Li, C.-Y. Su, Z.-W. Mao and L.-N. Ji, *Chem. J. Chin. Univ.*, 2000, **21**, 187.
- 22 M. Ohba and H. Okawa, *Mol. Cryst. Liq. Cryst.*, 1996, **286**, 101.
- 23 H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo and C. Floriani, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1446; H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo and C. Floriani, *J. Am. Chem. Soc.*, 1996, **118**, 981.
- 24 (a) H.-Z. Kou, S. Gao, W.-M. Bu, D.-Z. Liao, B.-Q. Ma, Z.-H. Jiang, S.-P. Yan, Y.-G. Fan and G.-L. Wang, *J. Chem. Soc., Dalton Trans.*, 1999, 2477; (b) H.-Z. Kou, S. Gao, B.-Q. Ma and D.-Z. Liao, *Chem. Commun.*, 2000, 713.
- 25 N. Re, E. Gallo, C. Floriani, H. Miyasaka and N. Matsumoto, *Inorg. Chem.*, 1996, **35**, 5964.
- 26 H. Miyasaka, N. Matsumoto, N. Re, E. Gallo and C. Floriani, *Inorg. Chem.*, 1997, **36**, 670.
- 27 N. Re, R. Crescenzi, C. Floriani, H. Miyasaka and N. Matsumoto, *Inorg. Chem.*, 1998, **37**, 2717.
- 28 E. Colacio, J. M. Dominguez-Vera, M. Ghazi, R. Kivekas, M. Klinga and J. M. Moreno, *Chem. Commun.*, 1998, 1071.
- 29 E. Colacio, J. M. Dominguez-Vera, M. Ghazi, R. Kivekas, F. Lloret, J. M. Moreno and H. Stoeckli-Evans, *Chem. Commun.*, 1999, 987.
- 30 M. Ohba, N. Usuki, N. Fukita and H. Okawa, *Angew. Chem., Int. Ed.*, 1999, **38**, 1795.
- 31 A. K. Sra, M. Andruh, O. Kahn, S. Golhen, L. Ouahab and J. V. Yakhmi, *Angew. Chem., Int. Ed.*, 1999, **38**, 2606.
- 32 N. Matsumoto, Y. Sunatsuki, H. Miyasaka, Y. Hashimoto, D. Luneau and J.-P. Tuchagues, *Angew. Chem., Int. Ed.*, 1999, **38**, 171.
- 33 M. Ferbinteanu, S. Tanase, M. Andruh, Y. Journaux, F. Cimpoesu, I. Strenger and E. Riviere, *Polyhedron*, 1999, **18**, 3019.
- 34 A. Marvillers, S. Parsons, E. Riviere, J.-P. Audiere and T. Mallah, *Chem. Commun.*, 1999, 2217.
- 35 J. Larionova, J. Sanchiz, S. Golhen, L. Ouahab and O. Kahn, *Chem. Commun.*, 1998, 953.
- 36 J. Larionova, O. Kahn, S. Golhen, L. Ouahab and R. Clerac, *J. Am. Chem. Soc.*, 1998, **120**, 13088.
- 37 J. Larionova, O. Kahn, S. Golhen, L. Ouahab and R. Clerac, *J. Am. Chem. Soc.*, 1999, **121**, 3349.
- 38 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; H.-Z. Kou, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan, Q.-J. Wu, S. Gao and G.-L. Wang, *Inorg. Chem. Commun.*, 2000, **3**, 151.
- 39 H. L. Shyu, H. H. Wei and Y. Wang, *Inorg. Chim. Acta*, 1997, **258**, 81.
- 40 (a) D. G. Fu, J. Chen, X. S. Tan, L. J. Jiang, S. W. Zhang and W. X. Tang, *Inorg. Chem.*, 1997, **36**, 220; (b) S.-W. Zhang, D.-G. Fu, W.-Y. Sun, Z. Hu, K.-B. Yu and W.-X. Tang, *Inorg. Chem.*, 2000, **39**, 1142.
- 41 S. M. Holmes and G. S. Girolami, *Mol. Cryst. Liq. Cryst. A*, 1997, **305**, 279; W. E. Buschmann, J. Ensling, P. Gütlich and J. S. Miller, *Chem. Eur. J.*, 1999, **5**, 3019.
- 42 H.-Z. Kou, S. Gao, B.-Q. Ma and D.-Z. Liao, *Chem. Commun.*, 2000, 1309.
- 43 R. W. Hay, J. M. Armstrong and M. M. Hassan, *Transition Met. Chem.*, 1992, **17**, 270; M. P. Suh, B. Y. Shim and T.-S. Yoon, *Inorg. Chem.*, 1994, **33**, 5509.
- 44 M. P. Suh, W. Shin, H. Kim and C. H. Koo, *Inorg. Chem.*, 1987, **26**, 1846.
- 45 I. Bertini, C. Luchinat, F. Mani and A. Scozzafava, *Inorg. Chem.*, 1980, **19**, 1333.
- 46 O. Kahn, in *Molecular Magnetism*, VCH, Weinheim, 1993.
- 47 A. Bohm, C. Vazquez, R. S. McLean, J. C. Calabrese, S. E. Kalm, J. L. Manson, A. J. Epstein and J. S. Miller, *Inorg. Chem.*, 1996, **35**, 3083.
- 48 B. B. Kaul, R. D. Sommer, B. C. Noll and G. T. Yee, *Inorg. Chem.*, 2000, **39**, 865.
- 49 O. Kahn, J. Larionova and L. Ouahab, *Chem. Commun.*, 1999, 945.