

Magnetic characteristics of bimetallic assemblies, $[\text{Ni}(\text{en})_2]_3[\text{M}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ ($\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$; $\text{M} = \text{Fe}$ **1**, Mn **2**, Cr **3** or Co **4**), with a one-dimensional rope-ladder chain structure †

Masaaki Ohba,* Nobuo Fukita and Hisashi Ōkawa*

Department of Chemistry, Faculty of Science Kyushu University, Hakozaki, Higashiku, Fukuoka 812, Japan

Four bimetallic assemblies, $[\text{Ni}(\text{en})_2]_3[\text{M}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ ($\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$; $\text{M} = \text{Fe}$ **1**, Mn **2**, Cr **3** or Co **4**), have been prepared in crystalline form and their magnetic properties studied. A crystal structure analysis of complex **4** revealed a one-dimensional rope-ladder chain structure extended through $\text{Co}-\text{CN}-\text{Ni}-\text{NC}-\text{Co}$ linkages. Compounds **1–3** show ferromagnetic intramolecular interaction based on the strict orthogonality of magnetic orbitals between adjacent nickel(II) and metal(III) ions. All the compounds show antiferromagnetic intermolecular interaction and hence no magnetic ordering. A polycrystalline sample of **1** was metamagnetic below 18.6 K. This is interpreted in terms of a disorder of the network containing pseudo-two- and -three-dimensional domains.

It is known that O_h symmetric hexacyanometalate ions $[\text{M}(\text{CN})_6]^{n-}$ are good building blocks for bimetallic assemblies of the Prussian Blue type^{1–12} which form a family of molecular-based magnets. We are investigating the ordered molecular systems derived from hexacyanometalate and $[\text{NiL}_2]^{2+}$ ($\text{L} = \text{ethane-1,2-diamine derivative}$) ions.^{13–17} Four-co-ordinate $[\text{NiL}_2]^{2+}$ complexes are co-ordinatively unsaturated and can accept two donor atoms to achieve six-co-ordination about the metal ion. Thus, the combination of $[\text{M}(\text{CN})_6]^{3-}$ and $[\text{NiL}_2]^{2+}$ can build up various network structures extended through $\text{M}-\text{CN}-\text{Ni}-\text{CN}$ linkages.

Previously we reported three bimetallic assemblies of different networks: $[\text{PPh}_4][\text{Ni}^{\text{II}}(\text{pn})_2][\text{Fe}^{\text{III}}(\text{CN})_6] \cdot \text{H}_2\text{O}$ with a one-dimensional zigzag chain structure,¹⁵ $[\text{Ni}^{\text{II}}(\text{en})_2]_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ with a one-dimensional rope-ladder structure^{13,15} and $[\text{NiL}_2]_2[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ [$\text{L} = 1,2\text{-diaminopropane}$ (pn) or 8 methylpropane-1,2-diamine (1,1-dmen); $\text{X}^- = \text{ClO}_4^-$, BF_4^- , PF_6^- , etc.; $n = 2\text{--}6$] with a two-dimensional sheet structure.^{14–17} They can be prepared by the reaction of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{NiL}_2]^{2+}$ in the appropriate stoichiometry, in the absence or presence of an appropriate counter ion.

The one-dimensional bimetallic assembly $[\text{PPh}_4][\text{Ni}(\text{pn})_2][\text{Fe}(\text{CN})_6] \cdot \text{H}_2\text{O}$ shows ferromagnetic interaction within the chain but no magnetic ordering in the lattice. The two-dimensional bimetallic assemblies $[\text{NiL}_2]_2[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ show magnetic ordering based on the two-dimensional network structure and are classified as ferro- or meta-magnets based on the inter-sheet separation.¹⁷ In our previous study $[\text{Ni}^{\text{II}}(\text{en})_2]_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ in a polycrystalline form, obtained by reaction of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Ni}(\text{en})_2\text{Cl}_2]$, was found to be metamagnetic.¹³ Later we noticed that a crystalline sample of the one-dimensional rope-ladder structure shows no magnetic ordering.

In order to determine the magnetic nature of the two-dimensional rope-ladder-type bimetallic assemblies in different Ni/M combinations, in this study the series $[\text{Ni}^{\text{II}}(\text{en})_2]_3[\text{M}^{\text{III}}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Fe}$ **1**, Mn **2**, Cr **3** or Co **4**) has been prepared. The crystal structure of complex **4** has been determined and found to be isomorphous with **1** having the one-dimensional rope-ladder structure. The cryomagnetic properties of these

assemblies were studied in the temperature range 4.2–290 K. Further, the origin of the metamagnet-like nature of polycrystalline **1** is considered in some detail.

Experimental

Physical measurements

Elemental analyses of carbon, hydrogen, and nitrogen were obtained at the Service Centre of Elemental Analysis of Kyushu University. Metal (iron, cobalt and nickel) analyses were made on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. Infrared spectra were measured on a JASCO IR-810 spectrophotometer using KBr discs. Magnetic susceptibilities were measured by the use of a HOXAN HSM-D SQUID susceptometer in the temperature range 4.2–100 K (applied magnetic field 100 G) and by the use of a Faraday balance in the temperature range 80–300 K (applied magnetic field 3000 G). Calibrations were made with $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ for the SQUID susceptometer and with $[\text{Ni}(\text{en})_3]\text{S}_2\text{O}_3$ for the Faraday balance. Diamagnetic corrections were made with Pascal's constants. Effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi_{\text{m}} T)^{1/2}$, where χ_{m} is the molar magnetic susceptibility corrected for diamagnetism of the constituting atoms.

Preparations

The component complexes $[\text{Ni}(\text{en})_3]\text{X}_2$ ($\text{X} = \text{Cl}^-$ or ClO_4^-) and $\text{K}_3[\text{Mn}(\text{CN})_6]$ were prepared by the literature methods.¹⁸ The salts $\text{K}_3[\text{Fe}(\text{CN})_6]$ (Wako Pure Chemical Industries Ltd.), $\text{K}_3[\text{Cr}(\text{CN})_6]$ (Mitsuwa Chemical Co.) and $\text{K}_3[\text{Co}(\text{CN})_6]$ (Nakalai Tesque Inc.) were of reagent grade and used as such.

$[\text{Ni}(\text{en})_2]_3[\text{Fe}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ **1.** The complex $[\text{Ni}(\text{en})_3]\text{X}_2$ ($\text{X} = \text{Cl}^-$ or ClO_4^-) (0.5 mmol) was dissolved in water (20 cm³). To this solution was added an aqueous solution (20 cm³) of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (110 mg, 0.33 mmol) at room temperature. The resulting brown solution was allowed to stand overnight to form black prismatic crystals. They were collected by suction filtration, washed successively with water and methanol, and dried *in vacuo* over P_2O_5 . Yield: 120 mg, 72% (Found: C, 28.9; H, 5.25; Fe, 11.0; N, 33.6; Ni, 17.5. Calc. for $\text{C}_{24}\text{H}_{52}\text{Fe}_2\text{N}_{24}\text{O}_2\text{Ni}_3$: C, 28.95; H, 5.25; Fe, 11.4; N, 33.75; Ni, 17.7%). IR (cm⁻¹, KBr disc): $\nu(\text{CN})$ 2150, 2130 and 2110.

† Supplementary data available (No. SUP 57 230, 5 pp.): variable-temperature magnetic susceptibilities. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

Non-SI units employed: $G = 10^{-4}$ T, $\mu_{\text{B}} \approx 9.27 \times 10^{-24}$ J T⁻¹.

When the synthesis was carried out using $[\text{Ni}(\text{en})_2\text{Cl}_2]$ instead of $[\text{Ni}(\text{en})_2\text{X}_2]$, a polycrystalline product **1'** was obtained.¹³ IR (cm^{-1} , KBr disc): $\nu(\text{CN})$ 2150, 2130 and 2110.

$[\text{Ni}(\text{en})_2]_3[\text{Mn}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ **2**. This compound was prepared as light brown microcrystals in a procedure similar to that for **1**, except for the use of $\text{K}_3[\text{Mn}(\text{CN})_6]$ instead of $\text{K}_3[\text{Fe}(\text{CN})_6]$. The synthesis was made at 0°C to avoid decomposition of $\text{K}_3[\text{Mn}(\text{CN})_6]$ in solution. Yield 130 mg, 78% (Found: C, 28.65; H, 5.2; Mn, 10.8; N, 33.5; Ni, 17.3. Calc. for $\text{C}_{24}\text{H}_{52}\text{Mn}_2\text{N}_{24}\text{Ni}_3\text{O}_2$: C, 29.0; H, 5.25; Mn, 11.0; N, 33.8; Ni, 17.7%). IR (cm^{-1} , KBr disc): $\nu(\text{CN})$ 2150, 2130 and 2110.

$[\text{Ni}(\text{en})_2]_3[\text{Cr}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ **3**. This compound was prepared as light purple crystals in a way similar to that of **1**, except for the use of $\text{K}_3[\text{Cr}(\text{CN})_6]$ instead of $\text{K}_3[\text{Fe}(\text{CN})_6]$. All the operations were carried out in the dark to avoid the decomposition of $\text{K}_3[\text{Cr}(\text{CN})_6]$. Yield 80 mg, 49% (Found: C, 28.45; H, 5.3; Cr, 10.8; N, 33.35; Ni, 17.5. Calc. for $\text{C}_{24}\text{H}_{52}\text{Cr}_2\text{N}_{24}\text{Ni}_3\text{O}_2$: C, 28.65; H, 5.4; Cr, 10.3; N, 33.9; Ni, 17.5%). IR (cm^{-1} , KBr disc): $\nu(\text{CN})$ 2150, 2130 and 2120.

$[\text{Ni}(\text{en})_2]_3[\text{Co}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ **4**. This compound was prepared as purple crystals in a way similar to that of **1**, except for the use of $\text{K}_3[\text{Co}(\text{CN})_6]$ instead of $\text{K}_3[\text{Fe}(\text{CN})_6]$. Yield 120 mg, 72% (Found: C, 28.6; H, 5.0; Co, 11.6; N, 33.6; Ni, 17.3. Calc. for $\text{C}_{24}\text{H}_{52}\text{Co}_2\text{N}_{24}\text{Ni}_3\text{O}_2$: C, 28.75; H, 5.25; Co, 11.8; N, 33.5; Ni, 17.6%). IR (cm^{-1} , KBr disc): $\nu(\text{CN})$ 2150, 2130 and 2120.

Crystallography

A single crystal of $[\text{Ni}(\text{en})_2]_3[\text{Co}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ **4** was mounted on a glass fibre and coated with epoxy resin. All the crystallographic measurements were carried out on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$) and a 12 kW rotating-anode generator. The data were collected at $20 \pm 1^\circ\text{C}$ using the ω - 2θ scan technique to a maximum 2θ value of 50.0° at a scan speed $16.0^\circ \text{ min}^{-1}$ (in ω). The weak reflections [$I < 10.0\sigma(I)$] were rescanned (maximum of four scans) and the counts accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident-beam collimator was 1.0 mm, the crystal to detector distance was 235 mm, and the computer-controlled detector aperture was set to $9.0 \times 13.0 \text{ mm}$ (horizontal \times vertical). The cell parameters were determined by 25 reflections in the range $29.42 \leq 2\theta \leq 29.98^\circ$. The octant measured was $+h, \pm k, \pm l$. The intensities of representative reflections were measured after every 150. Over the course of data collection the standards increased by 1.3%. A linear correction factor was applied to account for this. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.75 to 1.00. Intensity data were corrected for Lorentz-polarization effects.

Crystal data. $\text{C}_{24}\text{H}_{52}\text{Co}_2\text{N}_{24}\text{Ni}_3\text{O}_2$, $M = 1002.80$, purple crystal, dimensions $0.25 \times 0.2 \times 0.15$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.698(4)$, $b = 15.992(6)$, $c = 7.416(2) \text{ \AA}$, $\alpha = 91.63(3)$, $\beta = 106.86(3)$, $\gamma = 74.89(3)^\circ$, $U = 1061.2(7) \text{ \AA}^3$, $Z = 1$, $D_c = 1.569 \text{ g cm}^{-3}$, $F(000) = 518.00$, $\mu(\text{Mo-K}\alpha) = 21.25 \text{ cm}^{-1}$.

The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3396 observed reflections [$I > 3.00\sigma(I)$] and 287 variable parameters and converged with unweighted and weighted agreement factors of $R = \Sigma |F_o| - |F_c| / \Sigma |F_o| = 0.038$ and $R^w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma F_o^2]^{1/2} = 0.051$ with $w = [\sigma^2(F_o)]^{-1}$. Neutral atom scattering factors were taken from Cromer and

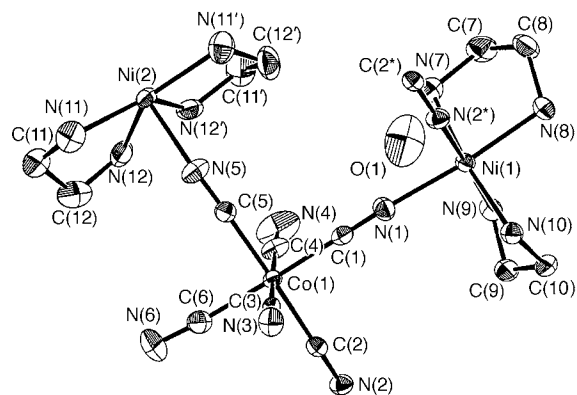
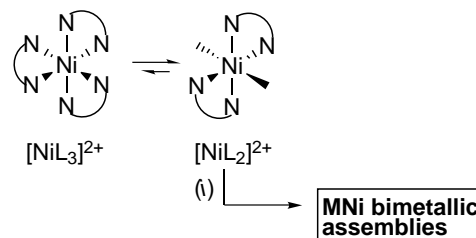


Fig. 1 An ORTEP²³ drawing of the asymmetric unit of $[\text{Ni}(\text{en})_2]_3[\text{Co}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ **4**



Scheme 1 (i) $[\text{M}(\text{CN})_6]^{3-}$, self-assembly

Waber.¹⁹ Anomalous dispersion effects were included in F_c ; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.²⁰ The values for the mass-attenuation coefficients were those of Creagh and Hubbel.²¹ All calculations were performed using the TEXSAN crystallographic software package.²²

Atomic coordinates, thermal parameters, and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/447.

Results and Discussion

The compounds **1–4** were obtained as good crystals when $[\text{M}(\text{CN})_6]^{3-}$ was treated with $[\text{Ni}(\text{en})_3]^{2+}$ instead of $[\text{Ni}(\text{en})_2\text{Cl}_2]$. In this synthesis the slow dissociation of $[\text{Ni}(\text{en})_3]^{2+}$ into $[\text{Ni}(\text{en})_2]^{2+}$ in aqueous solution leads to the growth of crystals in a self-assembling process. This crystallization method is applicable to cyanide-bridged bimetallic assemblies of different networks^{13–17} (Scheme 1).

Relevant IR spectral data for compounds **1–4** are given in the Experimental section. Each compound shows three sharp $\nu(\text{C}\equiv\text{N})$ bands in the region of $2110\text{--}2150 \text{ cm}^{-1}$. The intensity of the bands increases with decreasing frequency. The presence of three $\nu(\text{C}\equiv\text{N})$ modes and the appearance of one $\nu(\text{C}\equiv\text{N})$ mode at high frequency relative to that of $\text{K}_3[\text{M}(\text{CN})_6]$ suggest a lowered symmetry about the $[\text{M}(\text{CN})_6]^{3-}$ entity in each bimetallic assembly.

Crystal structure

A perspective view of the asymmetric unit of complex **4** with the atom numbering scheme and projections of the molecular entity in the lattice are presented in Figs. 1 and 2, respectively. Selected metal–metal separations and bond angles are listed in Table 1.

The single-crystal X-ray analysis shows that complex **4** is isomorphous with **1**.¹³ The asymmetric unit consists of one $[\text{Co}(\text{CN})_6]^{3-}$ anion, one *cis*- $[\text{Ni}(\text{en})_2]^{2+}$ cation, one-half a *trans*- $[\text{Ni}(\text{en})_2]^{2+}$ cation, and one water molecule, with the inversion centre at the Ni(2) of *trans*- $[\text{Ni}(\text{en})_2]^{2+}$ (see Fig. 1). Three cyano nitrogens [N(1), N(2), N(5)] in the meridional plane co-ordinate

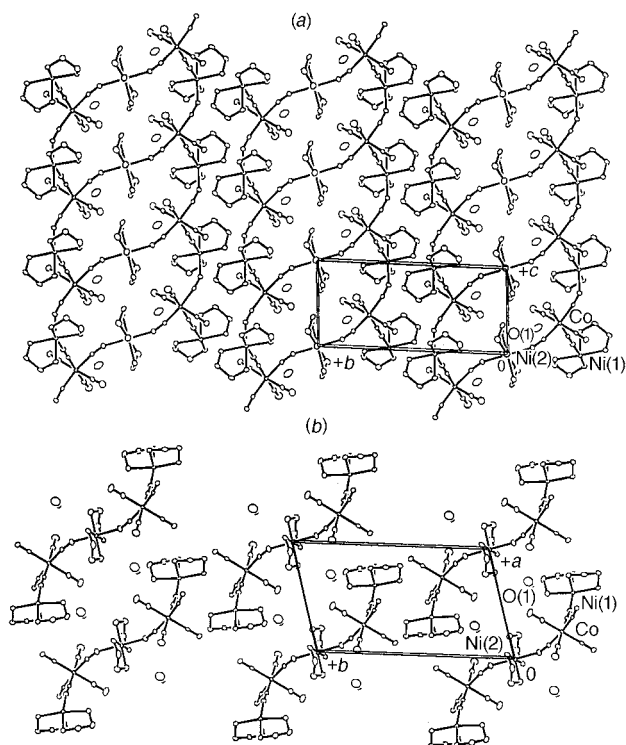


Fig. 2 Projections of the network structure of complex **4** along the *a* (a) and *c* axes (b)

Table 1 Selected separations (Å) between metal centres and bond angles (°) of complexes **1** and **4**

	1 (M = Fe)	4 (M = Co)
Intrachain separations		
Ni(1)···M	5.145	5.091
Ni(2)···M	4.993	4.942
Nearest interchain separations		
Ni(1)···M	5.375	5.357
Ni(1)···Ni(1)	6.295	6.257
Nearest intersheet separations		
M···M	9.709	9.698
Ni(1)···M	6.494	6.498
Ni(2)···M	10.412	10.350
Ni(1)···Ni(2)	7.713	7.699
Ni(2)···Ni(2)	9.709	9.698
M–C(1)–N(1)	178.2	177.6
C(1)–N(1)–Ni(1)	168.9	168.4
M–C(2)–N(2)	172.1	171.5
C(2)–N(2)–Ni(1*)	151.6	151.0
M–C(5)–N(5)	171.3	170.8
C(5)–N(5)–Ni(2)	156.2	155.6

to the adjacent nickel ions, through N(1) to Ni(1) of *cis*-[Ni(en)₂]²⁺, through N(2) to Ni(1) of another *cis*-[Ni(en)₂]²⁺, and through N(5) to Ni(2) of *trans*-[Ni(en)₂]²⁺. The bridging angles are C(1)–N(1)–Ni(1) 168.4(5), C(2)–N(2)–Ni(1*) 151.0(4) and C(5)–N(5)–Ni(2) 155.6(5)° (* indicates the symmetry operation *x*, *y*, *z* + 1). A polymeric zigzag chain is formed by the alternate array of [Co(CN)₆]³⁻ and *cis*-[Ni(en)₂]²⁺ [Co–C(1)–N(1)–Ni(1)–N(2)–C(2*)–linkage] and two zigzag chains are combined by *trans*-[Ni(en)₂]²⁺ [C(5)–N(5)–Ni(2)–N(5**)–C(5**) linkage], ** indicates the symmetry operation *-x*, *-y*, *-z*], providing a rope-ladder chain running along the *c* axis (see Fig. 2). The Co···Ni(1) and Co···Ni(2) distances are 5.091(3) and 4.942(2) Å, respectively. In the crystal the chains align along the diagonal of the *ab* plane (*n*-glide) to form

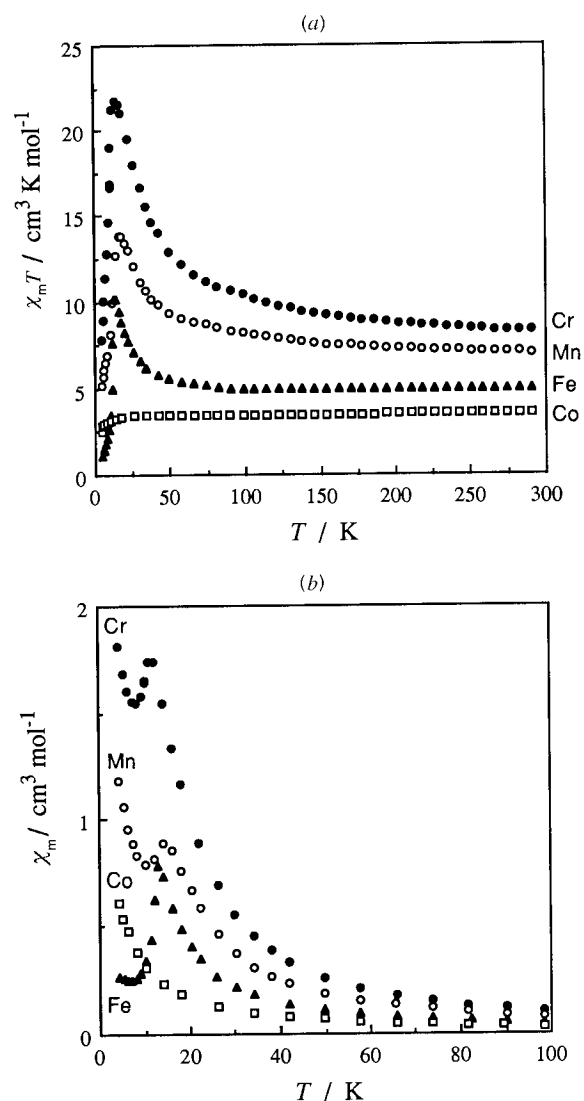


Fig. 3 The temperature dependence of $\chi_m T$ (a) and the χ_m (b) for [Ni(en)₂]₃[M(CN)₆]₂·2H₂O per Ni₃M₂ unit: M = Fe (**1**, ▲), Mn (**2**, ○), Cr (**3**, ●) or Co (**4**, □)

a pseudo two-dimensional sheet. The nearest interchain Ni(1)···Ni(1)(*-x* - 1, *-y* + 1, *-z*) and Ni(1)···Co(*-x* - 1, *-y* + 1, *-z*) separations in the sheet are 6.257 and 5.357 Å, respectively. The lattice water molecules reside between the sheets. The nearest intersheet Co···Co(*x* + 1, *y*, *z*), Ni(1)···Co(*x* - 1, *y*, *z*), Ni(2)···Co(*x* + 1, *y*, *z*), Ni(1)···Ni(2)(*x* - 1, *y*, *z*), and Ni(2)···Ni(2)(*x* + 1, *y*, *z*) separations are 9.698, 6.498, 10.350, 7.699 and 9.698 Å, respectively. The ethane-1,2-diamine in *trans*-[Ni(en)₂]²⁺ assumes two configurations, {N(11)–C(11)–C(12)–N(12)} and {N(11')–C(11')–C(12')–N(12')} (see Fig. 1), the occupancy factors of which are determined to be 0.5 and 0.5 on the basis of the peak heights. The cobalt ion has an octahedral surrounding with the Co–C bond lengths ranging from 1.889(6) to 1.916(5) Å. The mean bridging and non-bridging C–N bond distances are 1.143 and 1.141 Å, respectively. All the nickel ions assume six-coordination with the Ni–N bond lengths ranging from 2.08(1) to 2.144(4) Å. There is no significant difference in the local structure and the intersheet separations between **1** and **4** (see Table 1).

Magnetic properties

The cryomagnetic properties of complexes **1–4** have been studied in the temperature range 4.2–300 K. Plots of $\chi_m T$ vs. *T* and χ_m vs. *T* are given in Fig. 3, where χ_m is the magnetic susceptibility per Ni₃M₂ unit. For [Ni(en)₂]₃[Fe(CN)₆]₂·2H₂O a

comparative magnetic study has been made for crystalline (**1**) and polycrystalline samples (**1'**) (see Fig. 4 and SUP 57230).

Compound 1 (Ni₃Fe₂). The $\chi_m T$ value for complex **1** at room temperature is 4.95 cm³ K mol⁻¹ (6.29 μ_B) which increases with decreasing temperature to a maximum of 10.22 cm³ K mol⁻¹ (9.04 μ_B) at 14 K and then decreases below this temperature. The maximum value is close to the spin-only value of 10.0 cm³ K mol⁻¹ (8.94 μ_B) for $S_T = 4$ resulting from the ferromagnetic coupling of two low-spin iron(III) ions ($S = \frac{1}{2}$, $g = 2.00$) and three nickel(II) ions ($S = 1$, $g = 2.00$). The magnetic behaviour above 14 K suggests a ferromagnetic intramolecular interaction between adjacent Fe^{III} and Ni^{II} through the cyanide bridge. In accord with this the magnetic susceptibility obeys the Curie–Weiss law with a positive Weiss constant $\theta = +6.3$ K. The ferromagnetic interaction can be rationalized by the strict orthogonality of the magnetic orbitals of low-spin Fe^{III} [(t_{2g})¹] and Ni^{II} [(e_g)²].²⁴ The drop in $\chi_m T$ value below 14 K suggests the operation of an antiferromagnetic intermolecular interaction. However, χ_m slightly increases below 7 K, indicating that there is a non-zero magnetic moment in the lattice. This can be understood by taking into consideration the magnetic anisotropy. For the powdered sample χ_m is given by $(\chi_{\parallel} + 2\chi_{\perp})/3$ where \parallel and \perp represent the parallel and perpendicular orientation with respect to the applied magnetic field, respectively. In antiferromagnets χ_{\parallel} falls to zero as T tends to 0 K but χ_{\perp} has a non-zero value due to a temperature-independent net magnetization of the sublattice.²⁵ Thus, the residual χ_m value below 7 K may be attributed to the non-zero contribution of χ_{\perp} , and the slight increase in χ_m below 7 K suggests that local spins are canted in the intermolecular antiferromagnetic interaction and not fully cancelled in the lattice.

Compounds 2 (Ni₃Mn₂) and 3 (Ni₃Cr₂). Complexes **2** and **3** have similar magnetic behaviour to that of **1**. The maximum $\chi_m T$ value of **2** is 13.83 cm³ K mol⁻¹ (10.52 μ_B) at 16 K and that of **3** is 21.78 cm³ K mol⁻¹ (13.20 μ_B) at 14 K. These maxima are close to the spin-only value of 15.0 cm³ K mol⁻¹ (10.95 μ_B) for $S_T = 5$ and 21.0 cm³ K mol⁻¹ (12.96 μ_B) for $S_T = 6$, respectively. Compounds **2** and **3** show a ferromagnetic intramolecular interaction with positive Weiss constants $\theta = +13.8$ and $+18.4$ K, respectively, which can be explained in terms of the strict orthogonality of the magnetic orbitals of M^{III} [(t_{2g})² for Mn^{III} and (t_{2g})³ for Cr^{III}] and Ni^{II} [(e_g)²]. There is a drop in $\chi_m T$ below 14 and 16 K, respectively, due to antiferromagnetic intermolecular interaction. An increase in χ_m is seen for both compounds at low temperature, which may originate from a disorder in the network as discussed below for **1'**.

Compound 4 (Ni₃Co₂). The $\chi_m T$ value of complex **4** is 3.57 cm³ K mol⁻¹ (5.34 μ_B) at room temperature, which is within the range expected for two cobalt(III) ($S = 0$) and three nickel(II) ions ($S = 1$) (3.00–3.96 cm³ K mol⁻¹: 4.90–5.63 μ_B , calculated with $g = 2.0$ –2.3). When the temperature is lowered, the $\chi_m T$ decreases gradually until 18 K and then rapidly to 2.56 cm³ K mol⁻¹ (4.53 μ_B) at 4.3 K. The magnetic behaviour below 18 K suggests that the intermolecular (through-space) interaction is antiferromagnetic. A negative constant of $\theta = -1.8$ K was evaluated from the Curie–Weiss plot in the temperature range 90–4.3 K.

Compound 1'. The magnetic behaviour of polycrystalline **1'** differs from that of crystalline **1** (see Fig. 4). The metamagnet-like nature of **1'** has been preliminarily reported.¹³ Since the IR spectral and X-ray diffraction patterns of **1** and **1'** are essentially identical (see Fig. 5), they must have the same local structure but differ in network structure. It must be emphasized that **1** and **1'** are obtained in different ways. That is, **1** was prepared by slow crystallization from the reaction of [Fe(CN)₆]³⁻ and [Ni(en)₃]²⁺ (in aqueous solution), whereas **1'** was prepared by

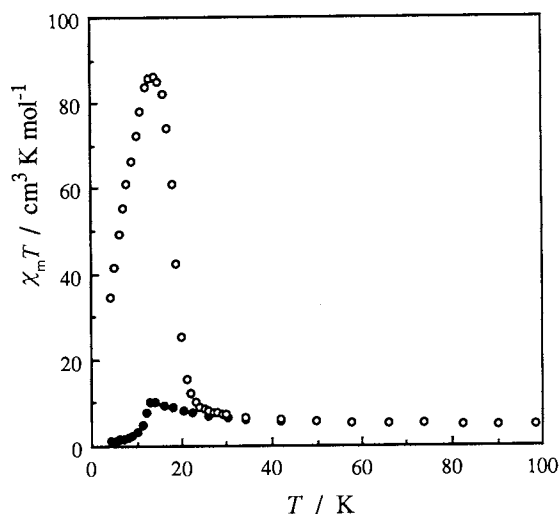


Fig. 4 The temperature dependence of the $\chi_m T$ for complexes **1** (●) and **1'** (○) per Ni₃Fe₂ unit

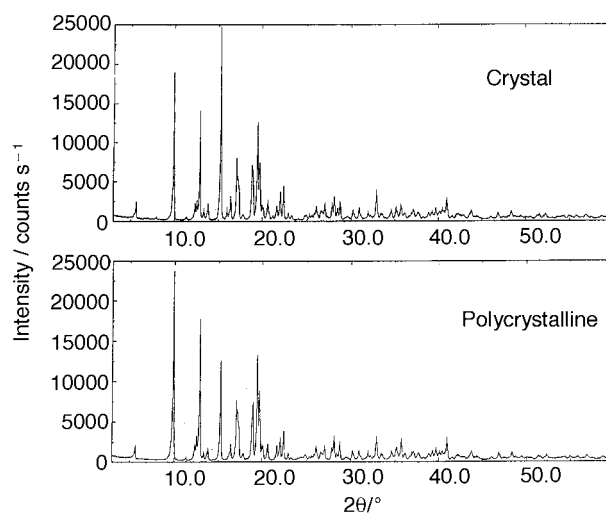


Fig. 5 Powder X-ray diffraction patterns of complexes **1** (above) and **1'** (below)

rapid precipitation in the reaction of [Fe(CN)₆]³⁻ and [Ni(en)₃Cl₂]. The rapid precipitation may result in incomplete ladder formation and interladder crossing, providing quasi-two- and -three-dimensional domains in the network. Such domains are probably the origin for the metamagnet-like nature observed for the polycrystalline sample **1'**. Furthermore, the magnetic behaviour of the polycrystalline sample varies depending upon the synthetic conditions (concentration, temperature, etc.). Polycrystalline forms of **2** and **3** were not examined in this work but a tendency to magnetic ordering due to a disorder in the network is seen in their χ_m vs. T curves [Fig. 3(b)]. Compounds **2** and **3** are available as crystals (but not single crystals). It is likely that the polycrystalline samples of them, used for magnetic studies in this work, contain more or less quasi-two- and -three-dimensional domains in their network.

Conclusion

The reaction of [Ni(en)₃]²⁺ and [M(CN)₆]³⁻ in the 3:2 molar ratio in aqueous solution formed bimetallic assemblies [Ni(en)₂]₃[M(CN)₆]₂·2H₂O (M^{III} = Fe **1**, Mn **2**, Cr **3** or Co **4**) which have a one-dimensional rope-ladder network structure. Compounds **1**–**3** show a ferromagnetic intramolecular interaction based on the strict orthogonality between magnetic

orbitals of M^{III} and Ni^{II} . No magnetic ordering occurs in all the compounds because of an antiferromagnetic intermolecular interaction. The polycrystalline form (**1'**) of **1**, prepared by rapid precipitation from the reaction of $[Ni(en)_2Cl_2]$ and $[Fe(CN)_6]^{3-}$, was found to be metamagnetic. From a comparison of X-ray powder patterns and IR spectra, the origin of the spontaneous magnetization of **1'** is attributed to the disorder in the network structure.

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 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 Material*, eds. D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio, NATO ASI Ser. 198, Kluwer, Dordrecht, 1990, p. 281.
- 6 T. Mallah, S. Thiébaud, 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. Ouachés, 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 M. Ohba, N. Maruono, H. Ōkawa, T. Enoki and J.-M. Latour, *J. Am. Chem. Soc.*, 1994, **116**, 11 566.
- 14 M. Ohba, H. Ōkawa, T. Ito and A. Ohto, *J. Chem. Soc., Chem. Commun.*, 1995, 1545.
- 15 H. Ōkawa and M. Ohba, *ACS Symp. Ser.*, 1996, **644**, 319.
- 16 M. Ohba and H. Ōkawa, *Mol. Cryst. Liq. Cryst.*, 1996, **286**, 101.
- 17 M. Ohba, N. Fukita and H. Ōkawa, *J. Am. Chem. Soc.*, 1997, **119**, 1011.
- 18 A. Werner, *Z. Anorg. Chem.*, 1899, **21**, 210.
- 19 D. T. Cromer and J. T. Waber, in *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
- 20 D. C. Creagh and W. J. McAuley, in *International Tables for Crystallography*, Kluwer, Boston, 1992, vol. C.
- 21 D. C. Creagh and J. H. Hubbel, in *International Tables for Crystallography*, Kluwer, Boston, 1992, vol. C.
- 22 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.
- 23 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- 24 O. Kahn, in *Molecular Magnetism*, VCH, Weinheim, 1993.
- 25 R. L. Carlin, in *Magnetochemistry*, Springer, Berlin, 1986.

Received 18th November 1996; Paper 6/07795A