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A New Bimetallic Ferromagnet, $[Ni(en)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$, with a Rare Rope-Ladder Chain Structure

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In the past decade there has been a growing interest in molecular-based ferromagnets derived from paramagnetic complexes.[2−8] It has been shown that hexacyanometalate ions $[M(CN)_6]^{n-}$ act as good building blocks to provide bimetallic assemblies exhibiting spontaneous magnetization.[9−12] Three types of bimetallic ferromagnets have been obtained so far: (1) $Mn^{II}Mn^{IV}(CN)_6$, (2) $CsA^{II}B^{III}(CN)_6$ (A = Mn, Co, Ni, Cu; B = Cr, Fe), and (3) $A^{II}_3[B^{III}(CN)_6]_2$ (A = Mn, Co, Ni, Cu; B = Fe, Cr). The first type is a ferrimagnet of $T_N = 48.7$ K.[9] The second type is a ferri- or ferromagnet depending upon the combination of metal ions. High magnetic phase-transition temperatures are reported for $CsA^{II}Cr^{III}(CN)_6$ (A = Mn, Ni) (T_C or $T_N = 90$ K)[10] and mixed-valent $Cs_{0.75}[Cr^{II}_{1.125}Cr^{III}(CN)6]$ ($T_C = 190$ K).[12] These two types have the "rock-salt" structure. The last type, B = Fe, is also a ferri- or ferromagnet (T_C or T_N = 9−23 K)[11] depending upon the combination of metal ions, but for mixed-valent $Cr^{II}_3[Cr^{III}(CN)_6]_2$, a very high magnetic phase-transition of 240 K is reported.[12] We describe here a new bimetallic ferromagnet, $[Ni(en)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$, derived from $[Fe(CN)_6]^{3-}$.

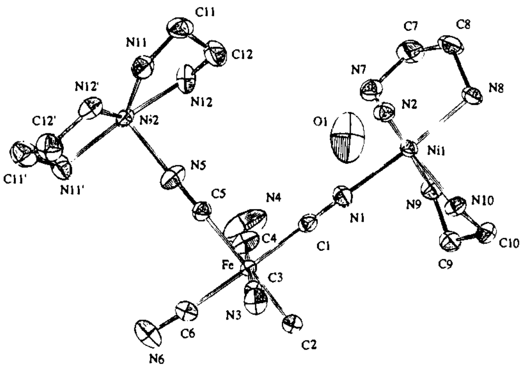

Figure 1. ORTEP drawing of the asymmetric unit showing atom labeling scheme. Selected bond lengths (Å) and bond angles (deg) are as follows: Fe−C1, 1.941(7); Fe−C2, 1.946(5); Fe−C3, 1.934(7); Fe−C4, 1.938(8); Fe−C5, 1.932(5); Fe−C6, 1.949(8); Ni1−N1, 2.079(6); Ni1−N2, 2.129(5); Ni1−N7, 2.120(6); Ni1−N8, 2.111(6); Ni1−N9, 2.127(5); Ni1−N10, 2.129(5); Ni2−N5, 2.091(6); Ni2−N11, 2.114(11); Ni2−N12, 2.097(15); Ni2−N11′, 2.105(11); Ni2−N12′, 2.097(14); C1−Fe−C2, 92.8(3); C1−Fe−C3, 86.9(3); C1−Fe−C4, 90.3(3); C1−Fe−C5, 90.3(3); C1−Fe−C6, 174.3(3); C2−Fe−C3, 95.3(3); C2−Fe−C4, 86.5(3); C2−Fe−C5, 171.1(3); C2−Fe−C6, 91.3(3); C3−Fe−C4, 176.7(3); C3−Fe−C5, 93.3(3); C3−Fe−C6, 88.8(3); C4−Fe−C5, 85.1(3); C4−Fe−C6, 93.9(3); C5−Fe−C6, 86.3(3); N1−Ni1−N2, 92.4(2); N1−Ni1−N7, 91.6(2); N1−Ni1−N8, 173.5(2); N1−Ni1−N9, 85.2(2); N1−Ni1−N10, 93.9(2); N2−Ni1−N7, 90.2(2); N2−Ni1−N8, 89.5(2); N2−Ni1−N9, 76.8(3); N2−Ni1−N10, 95.1(2); N7−Ni1−N8, 82.2(2); N7−Ni1−N9, 92.0(2); N7−Ni1−N10, 172.2(2); N8−Ni1−N9, 93.2(2); N8−Ni1−N10, 92.1(2); N9−Ni1−N10, 83.0(2); N5−Ni2−N11, 86.6(3); N5−Ni2−N12, 94.0(4); N5−Ni2−N11′, 88.9(3); N5−Ni2−N12′, 94.4(4); N5−Ni2−N5, 180.0(3); N11−Ni2−N12, 96.3(5); N11′−Ni2−N12′, 83.2(5).

The bimetallic assembly is obtained as black crystals by the reaction of $K_3[Fe_3(CN)_6]$ and *trans*-$[NiCl_2(en)_2]$ in an aqueous solution.[13] X-ray crystallography shows that the asymmetric unit consists of two $[Fe(CN)_6]^{3-}$ anions, two *cis*-$[Ni(en)_2]^{2+}$ cations, one *trans*-$[Ni(en)_2]^{2+}$ cation, and two water molecules, with the inversion center at the Ni of *trans*-$[Ni(en)_2]^{2+}$ (Figure 1).[14] Three cyano nitrogens (N1, N2, N5) in the meridional mode coordinate to the adjacent Ni ions, through N1 to Ni1 of *cis*-$[Ni(en)_2]^{2+}$, through N2 to Ni1′ of another *cis*-$[Ni(en)_2]^{2+}$, and through N5 to Ni2 of *trans*-$[Ni(en)_2]^{2+}$. A polymeric zigzag chain is formed by the alternate array of $[Fe(CN)_6]^{3-}$ and *cis*-$[Ni(en)_2]^{2+}$ ions, and two zigzag chains are combined by *trans*-$[Ni(en)_2]^{2+}$, providing a novel rope-ladder chain running along the *c* axis (Figure 2). In the crystal, the chains align along the diagonal line of the *ab* plane to form two-dimensional sheets (Figure 3). The nearest interchain Ni1⋯Ni1 and Ni1⋯Fe

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(13) IR: ν(CN) = 2110, 2130, 2150 cm^{-1}. Anal. Calcd. for $C_{24}Fe_2H_{52}N_{24}Ni_3O_2$ ($[Ni(en)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$): C, 28.93; H, 5.26; N, 33.73; Fe, 11.21; Ni, 17.67. Found: C, 29.06; H, 4.98, N, 33.40; Fe, 11.36; Ni, 18.30.

(14) Crystal data for $[Ni(en)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$ at room temperature: black prisms, triclinic, space group $P1$ with $Z = 2$, $a = 9.709(2)$ Å, $b = 16.036(5)$ Å, $c = 7.445(2)$ Å, $\alpha = 91.81(3)°$, $\beta = 106.72(2)°$, $\gamma = 74.91(2)°$, and $V = 1070(1)$ Å^3. The refinement converges with $R = 0.0478$ and $R_w = 0.0617$ for 3363 reflections with $|F_o| > 3\sigma(|F_o|)$.

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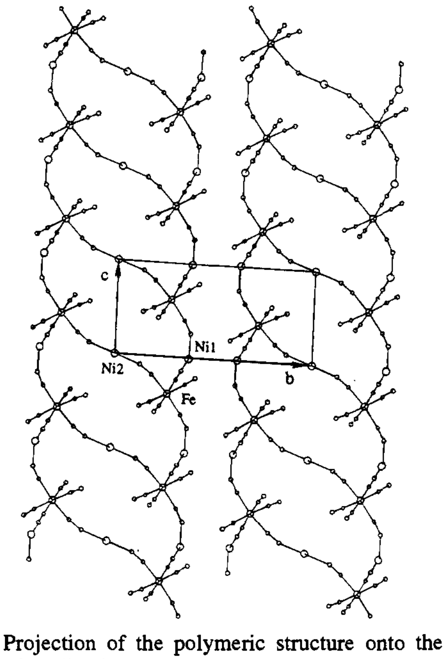

Figure 2. Projection of the polymeric structure onto the *bc* plane (omitted ethylenediamine molecules).

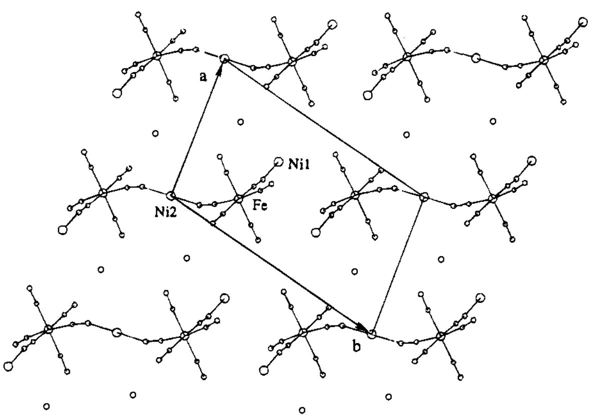

Figure 3. Projection of the polymeric structure onto the *ab* plane (omitted ethylenediamine molecules).

separations in the sheet are 5.375 and 6.295 Å, respectively. The lattice water molecules reside between the sheets. The nearest intersheet Ni1⋯Fe, Ni1⋯Ni2, and Ni1⋯Ni1 separations are 6.494, 7.713, and 9.709 Å, respectively. The ethylenediamine in *trans*-$[Ni(en)_2]^{2+}$ assumes two configurations, (N11−C11−C12−N12) and (N11′−C11′−C12′−N12′) (see Figure 1), the occupancy factors of which are determined to be 0.5 and 0.5 on the basis of the peak heights. The Fe−C bond lengths range from 1.932(5) to 1.946(5) Å. All the Ni ions assume a six-coordination, with the Ni−N bond lengths ranging from 2.079(6) to 2.114(11) Å. The Fe−Ni1 and Fe−Ni2 distances are 5.145(2) and 4.993(2) Å, respectively.

The cryomagnetic property of the complex is shown in Figure 4 in the form of a $\chi_M T$ vs T plot. At room temperature, $\chi_M T$ is equal to 4.95 cm^3 K mol^{-1} (per Fe_2Ni_3), which increases with decreasing temperature very abruptly below 20 K, up to the maximum value of 86.1 cm^3 K mol^{-1} at 14 K, and then decreases below this temperature. The magnetic behavior, except for the drop in $\chi_M T$ below 14 K, suggests an intramolecular ferromagnetic interaction between the adjacent Fe(III) and Ni(II) ions through the cyano bridge. In fact, our preliminary magnetization study at 12 K showed a tendency to saturate at 5 T with ca. 4.3 cm^3 T mol^{-1}, which corresponds to M_S ($=gN\beta S$) of 7.7 μ_B (per Fe_2Ni_3). The ferromagnetic interaction between the Fe(III) and Ni(II) ions is rationalized by the strict orthogonality of the magnetic orbitals of the low-spin Fe(III) ($(t_{2g})^1$) and Ni(II) ($(e_g)^2$).[15−18]

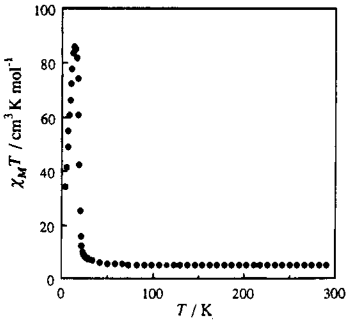

Figure 4. Plot of the temperature dependence of the $\chi_M T$ per Fe_2Ni_3.

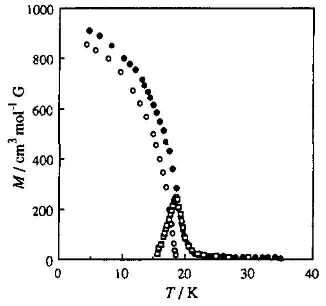

Figure 5. Plot of the temperature dependence of the magnetization M (applied field 3 G): (●) field-cooled magnetization (FCM), (○) remnant magnetization (RM), (□) zero-field-cooled magnetization (ZFCM).

The abrupt increase in magnetic moment around 20 K suggests the onset of long-range ferromagnetic ordering. To prove this, magnetizations have been measured in the range of 4.2−35 K (Figure 5). The field-cooled magnetization, measured under an applied field of 3 G, shows a rapid increase in magnetization below 20 K and tends to saturate near liquid helium temperatures. When the applied field is switched off at 4.2 K, there remains a remnant magnetization of 860 cm^3 mol^{-1} G, which upon warming vanishes at 18.6 K. The zero-field-cooled magnetization, measured by cooling the sample under zero field and warming up under 3 G, shows a maximum at 18.6 K. From these measurements, the T_C of this assembly was determined to be 18.6 K.

It is plausible that the ferromagnetic ordering is achieved within the two-dimensional sheet. The drop in $\chi_M T$ below 14 K suggests the operation of a weak antiferromagnetic interaction between the sheets that leads to a three-dimensional antiferromagnetic ordering at low temperature.

Further details will be reported together with the results on analogous bimetallic assemblies $[Ni(en)_2]_3[M(CN)_6]_2{\cdot}2H_2O$ (M = Cr, Mn).

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Supplementary Material Available: Tables of magnetic susceptibility and magnetization, atom coordinates, thermal parameters, bond lengths and bond angles, and hydrogen atom location of $[Ni(en)_2]_3[Fe(CN)_6]_2{\cdot}2H_2O$ (15 pages); listing of observed and calculated structure factors (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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