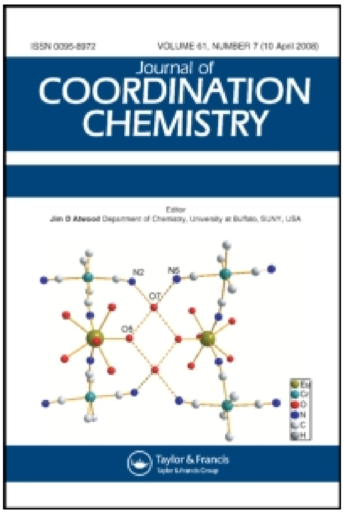

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CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF HETEROTRINUCLEAR COMPLEX, $(CUTREN)_2FE(CN)_6 \cdot 12H_2O$

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CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF HETEROTRINUCLEAR COMPLEX, (CUTREN)$_2$FE(CN)$_6$ · 12H$_2$O

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A heterotrinuclear complex, (Cutren)$_2$Fe(CN)$_6$ · 12H$_2$O, was synthesised and its crystal structure solved by direct methods. Crystal data are: $C_{18}H_{60}N_{14}Cu_2FeO_{12}$, M = 847.7, monoclinic, space group: $P2_1/c$, a = 13.568(5), b = 10.100(3), c = 13.935(6) Å, β = 95.50(4)°, V = 1901(1) Å^3, Z = 2, D_x = 1.48 gcm^{-3}, final R = 0.039 and $R\omega$ = 0.049. The crystal structure shows that the complex is composed of two (Cutren) and one hexacyanometallate Fe(CN)$_6$ subunits. Bridging cyano C(1) — N(1) is 1.148(4) Å, which is shorter than non-bridging (1.155(4) Å and 1.164(4) Å). Magnetic properties of (Cutren)$_2$Fe(CN)$_6$ indicate weak ferromagnetic exchange over the temperature range of 6.2–37K.

Keywords: heterotrinuclear; cyano bridge; crystal structure; magnetic properties

INTRODUCTION

In the past decade, there has been growing interest in molecular-based ferromagnets derived from paramagnetic complexes and some encouraging results had been obtained either with organic (*i.e.*, fullerene),[1] metal-organic,[2] metal-radical[3a] or bimetallic systems.[3b] However, the number of ferri- and ferro-magnets is still limited. Hexacyanometalate ions $[M(CN)_6]^{n-}$ (M: Fe^{3+}, Cr^{3+}, Mn^{3+}) act as good building blocks for bimetallic ferromagnets with high transition temperatures (Tc). Verdaguer and coworkers[4] obtained the series of complexes Mn^{II} Mn^{IV}

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$(CN)_6$,[5] $CsA^{II}B^{III}(CN)_6$, A: Mn, Co, Ni, Cu; B: Cr, Fe, $A_3^{II}[B^{III}(CN)_6]_2$ A: Mn, Co, Ni, Cu; B: Fe, Cr, through hexacyanometalate ions $[M(CN)_6]^{3-}$, (M: Cr^{3+}, Fe^{3+}, Mn^{3+}, which possess empty orbitals) reacting with metal ions (Ni^{2+}, Cu^{2+}, Co^{2+} and Mn^{2+}) which possess $d\sigma$ electrons. Recently, It was reported that the mixed-valence complexes $Cs_{0.75}[Cr^{II}_{1.25}Cr^{III}(CN)_6$ and $Cr^{II}[Cr^{III}(CN)_6]_2$ have a very high magnetic phase transition temperatures (Tc = 190 and 240K). Ferromagnets synthesized by hexacyanometalate ions and coordination compounds with empty *d* orbitals were reported recently and a novel chain complex $[Ni(en)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$ (Tc = 18.6K)[7] and a net complex $[Ni(pn)_2][Fe(CN)_6]\ ClO_4 \cdot 2H_2O$ (Tc = 9.0K)[8] were obtained.

In the area of the ferromagnets of high nuclearity spin clusters, Mall *et al.*[9] reacted $K_3Cr(CN)_6$ with $[Ni(tetren)]^{2+}$ and obtained a heteronuclear complex with S = 15/2 ground state and ferromagnetic exchange constant J = 16.8 cm^{-1}.

It was found that the number of *d* electrons of the central metal ion and the structure of the complex ions played very important roles in the magnetic properties. However, what role the central metal atoms play in magnetic exchange is not well understood. As a part of a research programme, we have synthesized the title complex from a hexacyanometalate ion $Fe(CN)^{4-}_6$ and $[Cutren]^{2+}$ (tren: $N(CH_2CH_2NH_2)_3$) and studied the magnetic properties of the complex.

EXPERIMENTAL

Measurements

Elemental analyses for carbon, hydrogen and nitrogen were performed on a Perkin Elmer 240C microanalyser. Variable-temperature (1.5–300K) magnetic susceptibilities of the complex $(Cutren)_2Fe(CN)_6 \cdot 12H_2O$ (7.03 mg) were obtained on a CF-1 ESM magnetic balance at 39770 G. IR spectra were obtained on a Nicolet FT-703X spectrophotometer using KBr pellets.

Preparation

The complex $Cutren(ClO_4)_2$ was prepared following the ref.[10]
$(Cutren)_2Fe(CN)_6 \cdot 12H_2O$

$Cutren(ClO_4)_2$ 0.333g, (1mmol) was dissolved in water with heating and stirring, and to the blue solution 10 cm^3 of an aqueous solution of 0.211g (0.5mmol) of $K_4Fe(CN)_6 \cdot 3H_2O$ was added, when the colour of the solution turned to violent-red. The mixture stood for a few days and the black single crystals obtained were filtered and washed with cold water and dried in air. *Anal.* Calcd. for

$(\mathrm{Cutren})_2\mathrm{Fe(CN)}_6 \cdot 12\mathrm{H_2O}(\mathrm{C_{18}H_{60}N_{14}Cu_2FeO_{12}})$ (%): C, 25.48; H, 7.08; N, 23.23. Found: C, 25.15; H, 5.78; N, 20.01. IR(cm^{-1}): 3586(sh, m), 3460(m, sh), 3392(m, sh), 3336(s), 3278(m), 2151(m), 2945(w), 2924(w), 2881(w), 2105(m, sh), 2042(vs), 1607(m), 1454(m), 1316(W), 1060(m), 994(m), 975(m), 582(m).

Crystal Structure Determination of $(\mathrm{Cutren})_2\mathrm{Fe(CN)}_6 \cdot 12\mathrm{H_2O}$

A black crystal with dimensions of 0.90 × 0.90 × 0.28 mm was mounted on an Enraf-Nonius CAD4 diffractometer for data collection at 296K using graphite-monochromated MoK_α radiation (0.71074 Å) with the ω- 2θ scan technique. The crystal was apparently unchanged during the measurements (no decay of intensities was observed). All reflections in the range of $2\theta < 50.0^\circ$ were measured for the compound. Of 3535 independent reflections collected, 2901 reflections ($I > 3\sigma(I)$) were used in the crystal structural analysis. Intensities were corrected for Lorentz and polarization factors; corrections for absorption were not applied.

Crystal data

$\mathrm{C_{18}H_{60}N_{14}Cu_2FeO_{12}}$, M = 847.7, monoclinic, space group: $P2_1/a$ = 13.568(5), b = 10.100(3), c = 13.935(6) Å, β = 95.50(4)°, V = 1901(1)Å^3, Z = 2, D_x = 1.48 gcm^{-3}, $\mu(\mathrm{Mo\text{-}K_\alpha})$ = 1.553 cm^{-1}.

The structure was solved by direct method by use of the TEXSAN program system. Hydrogen positions were located by difference Fourir syntheses. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms using 2901 reflections with $I > 3\sigma(I)$ gave a final R factor of 0.039 and R_ω, 0.049. Atomic coordinates and thermal parameters, together with observed and calculated ($\omega = 1/\sigma^2(F)$ structure factors, have been deposited with the Editor, from whom copies are available on request. The final fractional atomic coordinates are listed in Table I. Bond lengths and angles are given in Table II.

TABLE I Final Fraction atomic coordinates and equivalent thermal parameters

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
Cu	0.32839(3)	0.11071(4)	0.07519(2)	2.08(2)
Fe	1/2	1/2	0	1.94(2)
N(1)	0.4088(2)	0.2241(3)	−0.0003(2)	2.9(1)
N(2)	0.3078(2)	0.6504(3)	−0.0617(2)	3.6(1)
N(3)	0.4492(2)	0.5140(3)	0.2110(2)	3.2(1)
N(4)	0.3743(3)	0.2027(3)	0.2023(2)	3.7(1)
N(5)	0.4000(3)	−0.0812(4)	0.0874(3)	4.2(2)
N(6)	0.2143(2)	0.1123(4)	−0.0312(2)	3.1(1)

TABLE I (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
N(7)	0.2274(2)	0.0227(3)	0.1543(2)	2.7(1)
C(1)	0.4404(2)	0.3290(3)	−0.0053(2)	2.3(1)
C(2)	0.3786(2)	0.5899(3)	−0.0393(2)	2.4(1)
C(3)	0.4694(2)	0.5100(3)	0.1318(2)	2.4(1)
C(4)	0.2873(4)	0.2061(5)	0.2579(3)	4.4(2)
C(5)	0.2426(3)	0.0707(5)	0.2552(3)	4.1(2)
C(6)	0.3509(3)	−0.1559(4)	0.1595(3)	3.7(2)
C(7)	0.2424(3)	−0.1240(4)	0.1495(3)	3.8(2)
C(8)	0.1253(3)	0.0521(5)	0.0012(3)	3.5(2)
C(9)	0.1292(3)	0.0637(5)	0.1092(3)	3.7(2)
O(1)	0.2947(3)	−0.0880(3)	−0.1726(2)	4.4(1)
O(2)	0.1828(3)	0.4124(4)	0.0137(3)	5.8(2)
O(3)	−0.0001(3)	0.3407(4)	−0.0799(3)	5.8(2)
O(4)	0.0134(4)	0.3271(5)	0.2580(3)	6.8(2)
O(5)	0.1373(3)	−0.0103(4)	−0.3052(3)	5.9(2)
O(6)	−0.0987(3)	0.2774(4)	0.0838(3)	6.2(2)

TABLE II Selected distances and angles for the complex (Cutren)$_2$Fe(CN)$_6$·12H$_2$O (Å,°)

Cu—N(1)	1.958(3)	Cu—N(6)	2.038(3)
Cu—N(4)	2.044(3)	Cu—N(7)	2.044(3)
Cu—N(5)	2.166(4)	Fe—C(1)	1.907(4)
Fe—C(1)*	1.907(4)	Fe—C(2)	1.913(4)
Fe—C(3)	1.924(3)		
N(1)—Cu—N(6)	91.7(1)	N(1)—Cu—N(4)	93.4(1)
N(1)—Cu—N(7)	169.2(1)	N(1)—Cu—N(5)	107.3(1)
N(6)—Cu—N(4)	140.8(2)	N(6)—Cu—N(7)	83.9(1)
N(6)—Cu—N(5)	111.5(2)	N(4)—Cu—N(7)	84.0(1)
N(4)—Cu—N(5)	104.0(2)	N(7)—Cu—N(5)	83.5(1)
C(1)*—Fe—C(1)	180 (2)	C(1)—Fe—C(2)	93.9(1)
C(1)*—Fe—C(3)	92.6(1)	C(2)—Fe—C(3)	89.4(1)
C(1)*—Fe—C(2)	86.1(1)	C(1)—Fe—C(3)	87.4(1)
C(2)*—Fe—C(3)	90.6(1)	C(2)*—Fe—C(3)*	89.4(1)
C(3)*—Fe—C(3)	180.00		

RESULTS AND DISCUSSION

Crystal Structure

The molecular structure with atom numbering of (Cutren)$_2$Fe(CN)$_6$ is shown in Figure 1. The complex is centrosymmetric and is composed of two (Cutren) and one hexacyanometalate Fe(CN)$_6$ subunits. Fe(CN)$_6$ lies in the middle of two (Cutren) subunits. Six cyano groups coordinate to Fe(II) forming octahedral geometry, and of which two, C(1)—N(1) and C(1)*—N(1)* act bridge, with N(1) and N(1)* to two Cu atoms in (Cutren). Fe—C(1) is 1.907-(4) Å, which is slight shorter than for the other four non-bridging Fe—C bonds (1.913(4) Å

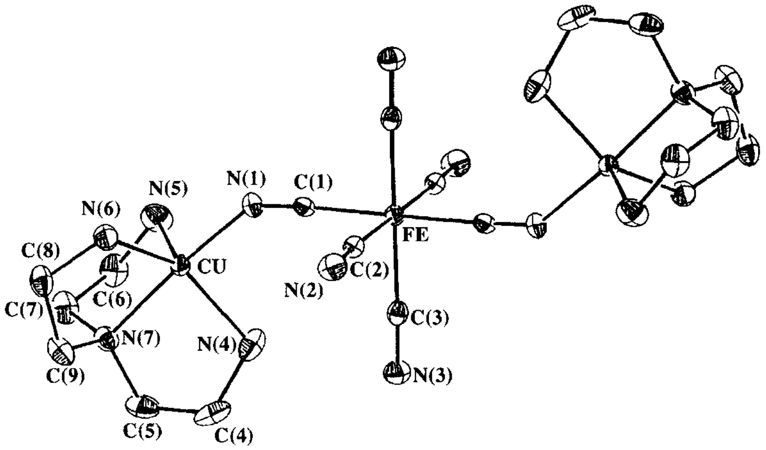

FIGURE 1 View of the structure of the title complex (ellipsoids are drawn at the 30% probability level).

and 1.924(3) Å). The bridging ligand C(1)—N(1) is 1.148(4) Å which is shorter than that of the non-bridging ligand, 1.155(4) Å and 1.164(4) Å.

Electrons in the weak antibonding orbital(5 σ) mainly belonging to the nitrogen atom of a bridging cyano ion enter the unfilled orbital of the copper(II) ion, while d-electrons of the copper(II) ions return to the π orbitals of the cyano ion. In general, cyanide is a strong σ-donor and a weak π-acceptor, so the bond strength of CN becomes greater and the bond length shorter.

Copper(II) is in a 3+2 distorted triangular bipyramid environment. The basal plane of the pyramidal is composed of three nitrogen atoms, N(4), N(5) and N(6), of the tren ligand. The apical positions are occupied by the bridgehead nitrogen atom, N(7), from tren and the nitrogen atom, N(1), from the bridging cyano ligand. Cu—N(1) is 1.958(7) Å, which is shorter than the other Cu—N bonds (2.038—2.166 Å). C(1) —N(1) —Cu is 143.6°, leading to a non-linear configuration. This is different to other cyano bridging polynuclear complexes, such as $Fe(CN)_5(\mu\text{—}CN)Fe(CN)_4NH_3$[11] in which the bond angle is 179.3°. There are twenty-four water molecules in the cell. Weak hydrogen bonds exist between water molecules and amine groups of tren.

IR Spectra

IR spectra of the complex were obtained in the range 400–4000 cm^{-1}. A very strong and broad band at 3460–3336 cm^{-1} belongs to the OH stretch of crystal water molecules and a strong band at 3295-3150 cm^{-1} belongs to stretch vibrations of the NH group. The peak at 2945-2881 cm^{-1} is assigned to $\nu_{as}(CH_2)$.

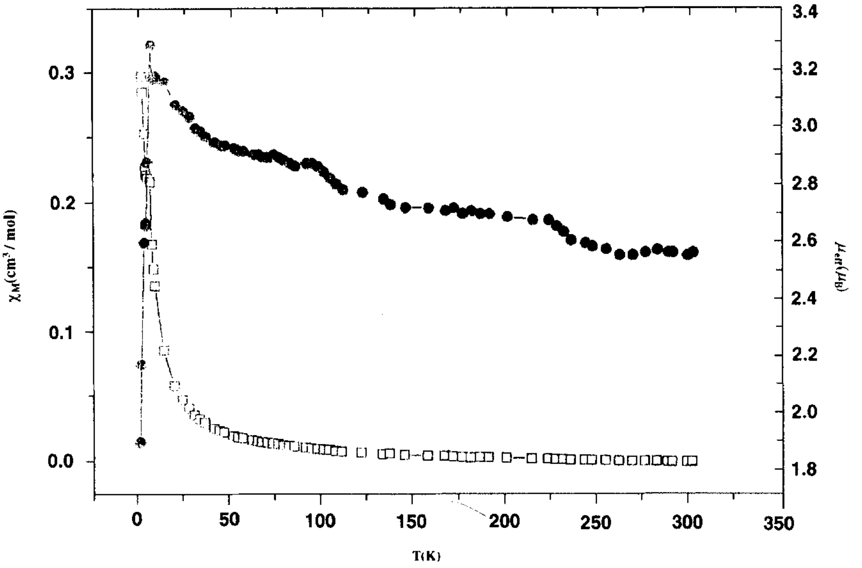

FIGURE 2 Temperature dependence of the magnetic susceptibility χ_M (□□□) and the effective magnetic moment μ_{eff} (•••) for the title complex.

A very strong band at 2042 cm^{-1} with a shoulder at 2105 cm^{-1} is assigned to ν_{as} of bridging and non-bridging cyano groups. Due to the bond strength of the bridging cyano ion is stronger, the shoulder band is assigned to it.

Magnetic Properties

The variable temperature magnetic susceptibility of the complex was measured from 1.5–300K. Plots of the magnetic susceptibility, χ_m and the effective magnetic moment (μ_{eff}) *vs* temperature are shown in Figure 2. The effective magnetic moment of the complex is 2.56μ_B at 300K and almost does not change with until the temperature is decreased to 37K(2.93μ_BK, when it increases to a maximum (3.27μ_B) at 6.2K. After that, the magnetic moment decreases rapidly to 1.88μ_B (T = 1.49K). At the present time we do not understand this magnetic behaviour and further study is under way.

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