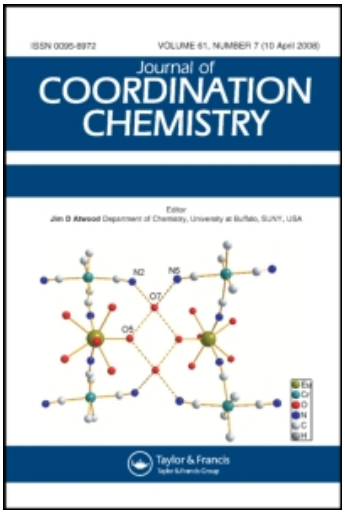

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A cyano bridged copper(ii)-iron(iii) binuclear complex, (cutren)fe(cn)$_5$no 2h$_2$o crystal structure and magnetic properties

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A CYANO BRIDGED COPPER(II)-IRON(III) BINUCLEAR COMPLEX, (Cutren)Fe(CN)$_5$NO·2H$_2$O CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES

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A heterobinuclear complex (Cutren)Fe(CN)$_5$NO·2H$_2$O (where tren = N(CH$_2$CH$_2$NH$_2$)$_3$) has been synthesized and its structure determined. The compound crystallizes in the triclinic system, space group $P\bar{1}$, a = 8.437(2), b = 10.535(4), c = 11.780(6) Å, α = 108.46(4), β = 76.75(4), γ = 109.31(2)° and Z = 2. The two metal atoms Cu(II) and Fe(III) have trigonal bipyramidal and octahedral arrangements respectively, and are bridged by a cyano group. Magnetic susceptibility data show an antiferromagnetic exchange interaction between Cu(II) and Fe(III). The exchange coupling constant (2J) and the g value were estimated to be -0.5 cm^{-1} and 2.20, respectively.

Keywords: heterobinuclear; cyanide; bridge; crystal structure; magnetic properties

INTRODUCTION

In the past decade, there has been a 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]; ferri- and ferromagnets are

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still, however, limited. The cyanide system based on the Prussian blue family $CA^{II}[B^{III}(CN)_6]$ (C = Cs^+; A = Ni, Mn, Cr; B = Cr, Fe) exhibits excellent potential for molecular design of ferri- and ferromagnets, in which the $[B^{III}(CN)_6]^{3-}$ ion acts as a multidentate complex ligand and the A^{II} ion receives the donor atoms. These cyanide compounds have rigid three-dimensional structures in which two alternate magnetic centres are bridged by the CN^- ion. Verdaguer and coworkers [4] obtained a series of complexes, $Mn^{II}Mn^{IV}(CN)_6$ [5], $CsA^{II}B^{III}(CN)_6$ (A: Mn, Co, Ni, Cu; B: Cr, Fe) and $^{II}_{3}[B^{III}(CN)_6]_2$ (A: Mn, Co, Ni, Cu; B: Fe, Cr). 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 from hexaocyanometallate ions and coordination compounds with partly filled d-orbitals were reported recently and a novel rope-ladder chain complex $[Ni(en)_2]_3[Fe(CN)_6]_2 \cdot 2H_2O$ (Tc = 18.6K) [7] and 2D-network complex $[Ni(pn)_2][Fe(CN)_6]ClO_4 \cdot 2H_2O$ (Tc = 9.0K) [8] were obtained.

It was found that the number of d-electron in the central metal ions and the structure of the coordination complexes ions plays a very important role in the magnetic properties of cyano-bridged heteronuclear complexes [9]. However, the role the central metal atoms play in magnetic exchange is not well understood. As a part of our continuing research programme [10], we synthesized the title complex from $Fe(CN)_5NO^{2-}$ and $(Cutren)^{2+}$ and have 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 (4-300K) magnetic susceptibilities were obtained on a CF-1 ESM magnetic balance at 10000 G magnetic field. IR spectra were obtained on a Nicolet FT-703X spectrometer using KBr pellets.

Preparation

The complex $Cutren(ClO_4)_2$ was prepared following the literature [10].

(Cutren)$Fe(CN)_5NO \cdot 2H_2O$

Some 0.333 g (1 mmol) of $Cutren(ClO_4)_2$ was dissolved in 20 cm^3 of water with heating and stirring, then 20 cm^3 of an aqueous solution of 0.370 g (1 mmol) of

$K_2Fe(CN)_5NO{\cdot}2H_2O$ was added. The colour of the solution turned green. After a few days, green single crystals were obtained, which were filtered and washed with cold water and dried in air. *Anal.* Calc. for $C_{11}H_{20}N_{10}O_2CuFe$(%): C, 29.77, H, 4.54; N, 31.57. Found: C, 30.59; H, 4.66; N, 29.69. IR: 3479 cm^{-1}(w), 3435(w), 3336(s), 3274(s), 3175(m), 2968(w), 2947(w), 2903(w), 2170(s), 2134(s), 1952(vs), 1606(m), 1581(m), 1466(m), 1308(w), 1100(m), 1062(s), 977(m).

X-ray Crystallographic Studies

A green crystal with dimensions of 0.70 × 0.65 × 0.50 mm was mounted on an Enraf-Nonius CAD4 diffractometer for data collection using graphite-monochromated MoK_α radiation at 296K. Of the 3253 independent reflections collected 2861 observed reflections ($I > 3\sigma(I)$) were used in the structure calculations. The structure was solved by Patterson methods followed by Fourier syntheses and refined by full-matrix least-squares with anisotropic thermal parameters for non-hydrogen atoms. All the hydrogen atoms were found in difference Fourier maps and were refined with isotropic thermal parameters. The calculations were performed on a MICRO-VAX 3100 using the TEXSAN program system. Crystallographic data are summarized in Table I. H atom positions and thermal parameters, anisotropic thermal parameter and observed and calculated structure factors are available from the authors.

RESULTS AND DISCUSSION

Crystal Structure

The molecular structure with the atom numbering of the complex (Cutren-)$Fe(CN)_5NO$ is shown in Figure 1. Final fractional atomic coordinates are given in Table II and selected bond lengths and angles in Table III. The complex is composed of Cutren and $Fe(CN)_5NO$ subunits bridged by a cyano group, C(6)-N(6). The Fe(III) ion is coordinated by five cyano groups and one NO group in octahedral geometry. Copper(II) is in a 3 + 2 distorted trigonal bipyramidal environment. The equatorial plane of the bipyramid is composed of three nitrogen atoms N(7), N(8) and N(9) of tren. Apical positions are occupied by the bridgehead nitrogen atom N(10) from tren and the nitrogen atom N(6) from the bridging cyano ligand. Fe-C(6) is 1.936(3) Å, which falls in the range of distances between carbon atoms from non-bridging cyano groups and Fe(III) ions (1.927(4)-1.944(4) Å). C(6)-N(6) is 1.145(4) Å which is a bit longer than for a non-bridging ligand (1.126(5)-1.142(5) Å). It is different to other cyano-bridging

TABLE I Crystallographic data for (Cutren)Fe(CN)$_5$NO·2H$_2$O.

Formula	$C_{11}H_{20}N_{10}O_2CuFe$
Formula weight	443.74
crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell constants	
a (Å)	8.437(2)
b (Å)	10.535(4)
c (Å)	11.780(6)
α (°)	108.46(4)
β (°)	76.75(4)
γ (°)	109.31(2)
V (Å^3)	928.1(8)
Z	2
Dc (g cm^{-3})	1.59
μ (cm^{-1})	19.57
F(000)	454
Scan speed (° min^{-1})	5.49
Scan width	0.60 + 0.35 tanθ
2θ$_{max}$ (°)	49.9
No. of collected reflections	3497
No. of independent reflections	3253
No. of observed reflections	2861 ($I > 3\sigma(I)$)
No. of refined parameters	226
R ($R\omega$)	0.037 (0.052)
S	1.64
ω	$1/\sigma^2(F)$

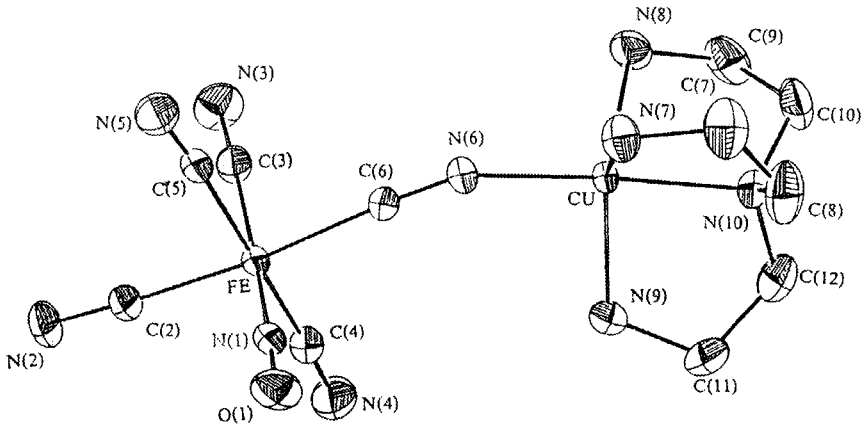

FIGURE 1 View of the structure of the title complex (ellipsoids are drawn at the 50% probability level).

TABLE II Final fractional atomic coordinates and thermal parameters.

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
Cu	0.86843(4)	0.17957(4)	0.22433(3)	2.56(2)
Fe	0.69861(5)	0.31386(4)	−0.08603(4)	2.66(2)
O(1)	0.7493(4)	0.5862(3)	0.0601(3)	5.5(1)
O(2)	0.6395(4)	0.5137(4)	0.3737(4)	7.6(2)
N(1)	0.7239(3)	0.4739(3)	0.0033(2)	3.2(1)
N(2)	0.5455(5)	0.3718(4)	−0.2707(3)	5.5(2)
N(3)	0.6711(5)	0.0251(4)	−0.2665(3)	5.6(2)
N(4)	0.3410(5)	0.1913(4)	0.0382(3)	5.3(2)
N(5)	1.0321(4)	0.4040(4)	−0.2459(3)	5.2(2)
N(6)	0.8496(4)	0.2166(3)	0.0752(3)	3.7(1)
N(7)	1.1042(4)	0.3253(3)	0.2557(3)	4.4(1)
N(8)	0.9159(5)	−0.0149(3)	0.1477(3)	4.9(1)
N(9)	0.6435(4)	0.2198(3)	0.3047(3)	4.1(1)
N(10)	0.8711(4)	0.1435(3)	0.3837(2)	3.5(1)
C(2)	0.5968(4)	0.3477(4)	−0.2010(3)	3.6(1)
C(3)	0.6794(4)	0.1309(4)	−0.1979(3)	3.6(1)
C(4)	0.4743(5)	0.2339(4)	−0.0076(3)	3.7(1)
C(5)	0.9120(5)	0.3675(4)	−0.1854(3)	3.3(1)
C(6)	0.7978(4)	0.2511(4)	0.0116(3)	3.1(1)
C(7)	1.1518(6)	0.3098(5)	0.3624(4)	6.1(2)
C(8)	1.0026(7)	0.2601(5)	0.4457(4)	6.6(2)
C(9)	0.8621(6)	−0.0864(4)	0.2432(5)	5.3(2)
C(10)	0.9114(6)	0.0101(5)	0.3589(4)	5.2(2)
C(11)	0.6173(6)	0.2255(6)	0.4330(4)	5.7(2)

heteronuclear complexes. For example, in $(Cutren)_2Fe(CN)_6 \cdot 12H_2O$ [10], of Fe-C(bridging) (1.907 Å) and the bridging cyano group C(1)-N(1) (1.148 Å) are shorter than Fe-C(non-bridging) (1.913-1.924 Å) and non-bridging cyano groups (1.155-1.164 Å). It is obvious that the electronic structure of the NO ligand and high oxidation state of iron are responsible. Cu-N(6) is 1.967(3) Å, shorter than for other Cu-N bonds (2.033(3)-2.099(2) Å). The bond angle C(6)-N(6)-Cu is 158.8(3)°, larger than that of the analogous complex $(Cutren)_2Fe(CN)_6 \cdot 12H_2O$[10](143.6°), but much smaller than in the binuclar complex $Fe(CN)_5(\mu\text{-}CN)Fe(CN)_4NH_3$ [13], in which the corresponding bond angle is 179.3°. There are four water molecules in the unit cell unit of $(Cutren)Fe(CN)_5NO$. Weak hydrogen bonds between the water molecules and amine groups of tren link the structural elements.

IR Spectra

The IR spectrum of the complex was obtained in the range of 400-4000 cm^{-1}. There are very weak bands at 3479 cm^{-1} − 3435 cm^{-1} belonging to OH groups

TABLE III Selected distances and angles for the complex (Cutren)$Fe(CN)_5NO \cdot 2H_2O$ (Å, °).

Cu-N(6)	1.967(3)	Cu-N(9)	2.033(3)
Cu-N(10)	2.036(3)	Cu-N(7)	2.099(3)
Cu-N(8)	2.093(3)	Fe-N(1)	1.654(3)
Fe-C(5)	1.927(4)	Fe-C(2)	1.934(4)
Fe-C(6)	1.936(4)	Fe-C(3)	1.939(4)
Fe-C(4)	1.944(4)	O(1)-N(1)	1.136(4)
N(2)-C(2)	1.138(5)	N(3)-C(3)	1.142(5)
N(4)-C(4)	1.140(3)	N(5)-C(5)	1.126(5)
N(6)-C(6)	1.145(4)		
N(6)-Cu-N(9)	91.2(1)	N(6)-Cu-N(8)	98.3(1)
N(6)-Cu-N(10)	175.9(1)	N(6)-Cu-N(7)	97.6(1)
N(9)-Cu-N(10)	84.7(1)	N(9)-Cu-N(8)	127.9(1)
N(9)-Cu-N(7)	123.1(1)	N(10)-Cu-N(8)	84.1(1)
N(10)-Cu-N(7)	84.9(1)	N(8)-Cu-N(7)	106.4(1)
C(5)-Fe-C(2)	86.4(1)	C(5)-Fe-C(6)	92.7(1)
C(5)-Fe-C(3)	84.4(1)	C(5)-Fe-C(4)	170.8(2)
C(2)-Fe-C(3)	84.4(1)	C(2)-Fe-C(3)	90.0(2)
C(6)-Fe-C(3)	86.2(1)	C(6)-Fe-C(4)	89.5(1)
C(3)-Fe-C(4)	86.8(2)		

of crystal water molecules and a strong band at 3274-3175 cm^{-1} due to the NH group. The peak at 2968-2903 cm^{-1} is assigned to $\nu_{as}(CH_2)$. A very strong band at 2170-2134 cm^{-1} is assigned to ν_{as} of bridging and non-bridged cyano groups [11a] and the band at 1952 cm^{-1} is the NO stretch [11b].

Magnetic Properties

The variable-temperature magnetic susceptibilities of the complex (Cutren-)$Fe(CN)_5NO$ were obtained in the temperature range 4-300 K. A plot of the magnetic susceptibility χ_M *vs* temperature, T, is shown in Figure 2. The susceptibility data were analyzed by a binuclear exchange model [12] and fitted by expression (*1*) for the magnetic susceptibility of isotropically coupled S = 1/2 ions.

$$X_M = [N\beta^2g^2(1 - \rho)]/[KT(3 + \exp(-2J/KT))] + N\beta^2g^2/(4KT) + N_\alpha \qquad (1)$$

Here, ρ is the proportion of paramagnetic impurity contained in the sample and other constants have their usual meaning. A good simulation of the magnetic susceptibility is achieved with $2J = -0.5$ cm^{-1}, $g = 2.20$, $\rho = 0.038$ and $N_\alpha = -2.7 \times 10^{-4}$ with an *R* value of 4.08×10^{-4} (*R* is the agreement factor defined as $\Sigma[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\Sigma[(\chi_M)_{obs}]^2$), as indicated in Figure 2. The large ρ value was reported in a previous reference [13]. The weak antiferromagnetic interaction, and hence the small value of the exchange parameter 2J in the title

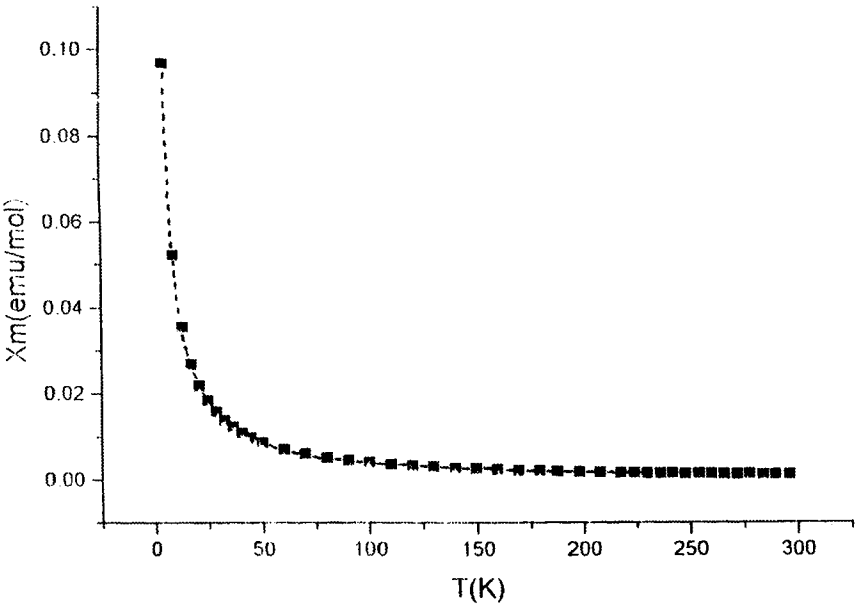

FIGURE 2 Thermal variation of χ_M for Cutren $Fe(CN)_5NO{\cdot}2H_2O$; the dashed line shows the best fit using (*1*).

complex, is rationalized by the bond angle between the two magnetic centres. The angle Cu-N(6)-C(6)(158.8(3)°) is far from linear.

Acknowledgements

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