

Crystal structure and magnetic properties of a three-dimensional complex constructed from $[\text{CuL}]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ precursors

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Abstract Self-assembly of the precursor $[\text{Cu}(\text{L})]^{2+}$ ($\text{L} = 3,10$ -dipropyl-1,3,5,8,10,12-hexaazacyclotetradecane) with hexacyanometalate $[\text{Fe}(\text{CN})_6]^{3-}$ produces a 3-D cyano-bridged Cu(II)–Fe(III) bimetallic assembly, $[\text{CuL}]_2[\text{Fe}(\text{CN})_6]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (*1*), characterized by single-crystal X-ray diffraction studies, and magnetic measurements. The crystallographic determination reveals that each hexacyanoferrate(III) ion connects four copper(II) ions using four co-planar CN^- groups which axially coordinate to the copper ion in a *trans* fashion forming *trans*- $\text{CuL}(\text{N}\equiv\text{C})_2$ moieties in (*1*). Magnetic studies reveal that (*1*) displays a ferromagnetic interaction between Cu(II) and Fe(III) through the CN linkage.

Introduction

In recent years, hybrid magnetic materials including chiral magnets [1–3] and photomagnets [4–6] have been actively studied to open a new opportunity in molecular magnetism. Out of all the classes of molecule-based magnets, a wide variety of hybrid Prussian Blue complexes have been studied for their fabrication of molecular bimetallic systems with various structures, such as heteropolynuclear, 1-D chain, 2-D layer, and 3-D network entities [7–10]. Among them, Prussian blue analogues constructed from

building blocks such as $[\text{V}(\text{CN})_6]^{4-}$ and $[\text{Cr}(\text{CN})_6]^{3-}$ exhibit some of the highest magnetic ordering temperatures [11–14]. The current record is held by $\text{KV}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$, which remains magnetic up to 376 K [13].

Since copper(II) complexes exhibit a great stereochemical plasticity, they are expected to give rise to a large variety of assembled complexes with hexacyanometalates. For example, some of us have previously reported a 3-D ferromagnet, $[\text{CuL}]_2[\text{Cr}(\text{CN})_6]\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ [15f], in which each hexacyanochromate connects four copper(II) ions using co-planar CN^- groups, which coordinate axially to the copper(II) ions in a *trans* fashion forming *trans*- $\text{CuL}(\text{N}\equiv\text{C})_2$ moieties.

In order to further explore the correlations between structure and magnetism of this system, recently, choosing $[\text{Fe}(\text{CN})_6]^{3-}$ as building block, we obtained a cyano-bridged Cu(II)–Fe(III) assembly, $[\text{CuL}]_2[\text{Fe}(\text{CN})_6]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (*1*), formed by self-assembling $[\text{Cu}(\text{L})]^{2+}$ ($\text{L} = 3,10$ -dipropyl-1,3,5,8,10,12-hexaazacyclotetradecane) and $[\text{Fe}(\text{CN})_6]^{3-}$ in a ratio of 2:1. In the present study, we present its synthesis, crystal structure and magnetic properties.

Experimental

General considerations

Elemental analyses (C, H, N) were performed on a Perkin–Elmer 240°C analyzer. Cu and Fe analyses were made on a Jarrell–Ash 1100+2000 inductively coupled plasma quantometer. Infrared spectra were measured between 4,000 and 400 cm^{-1} on a Nicolet FT-170SX Spectrometer with KBr pellets. Variable-temperature magnetic susceptibilities (1.8–300 K) in a 2 kOe field were measured with a Quantum Design MPMS-5 susceptometer. Diamagnetic

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corrections were made using Pascal's constants [16]. Effective magnetic moments were calculated using the equation $\mu_{\text{eff}} = 2.828(\chi_M \times T)^{1/2}$, where χ_M is the magnetic susceptibility per formula unit.

Synthesis of $[\text{CuL}]_2[\text{Fe}(\text{CN})_6]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (*I*)

All chemicals and solvents were reagent grade. $[\text{CuL}](\text{ClO}_4)_2$ was prepared according to the literature [17]. (*I*) was obtained as purplish-red single crystals by slow diffusion of a DMF solution (15 cm^3) of $[\text{CuL}](\text{ClO}_4)_2$ (0.15 mmol) and an aqueous solution (15 cm^3) of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (0.15 mmol) through a U-tube containing silica gel at room temperature. The resulting crystals were collected, washed with H_2O and EtOH, respectively, then dried in air. The complex is insoluble in most inorganic and organic solvents. Anal. Calc. for $\text{C}_{34}\text{H}_{69}\text{Cu}_2\text{FeN}_{18}\text{ClO}_5$: C, 39.67; H, 6.85; N, 24.49; Fe, 5.42; Cu, 12.35. Found: C, 39.77; H, 6.79; N, 24.54; Fe, 5.40; Cu, 12.43. IR: $\nu_{\text{C}\equiv\text{N}}$ / cm^{-1} 2,125, 2,140.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled in small quantities with great care.

X-ray crystallography

Diffraction data were collected at 293 K on a Siemens P4 diffractometer using graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) with the ω scan mode. The structures were solved by direct methods and refined by full matrix least-squares techniques based on F^2 [18]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized positions and refined using a riding model. All computations were carried out using the SHELXTL-PC program package. The crystallographic data and selected important bond parameters are given in Tables 1 and 2, respectively.

CCDC 621966 contains the supplementary crystallographic data for this article. These data could be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

Results and discussion

I.r. spectroscopy

The i.r. spectrum of (*I*) exhibits two sharp and strong peaks at ca. $2,125 \text{ cm}^{-1}$ and $2,140 \text{ cm}^{-1}$ in the range $2,100$ –

Table 1 Crystal data and structure refinement for (*I*)

Complex	(<i>I</i>)
Empirical formula	$\text{C}_{34}\text{H}_{69}\text{Cu}_2\text{FeN}_{18}\text{ClO}_5$
Formula weight	1028.45
Crystal size (mm)	$0.20 \times 0.20 \times 0.30$
Crystal system	Hexagonal
Space group	$P6122$ (No. 178)
<i>a</i> (Å)	14.2602(7)
<i>b</i> (Å)	14.2602(7)
<i>c</i> (Å)	41.5490(4)
α (°)	90
β (°)	90
γ (°)	120
<i>V</i> (Å ³)	7317.1(9)
<i>Z</i>	6
D_{calc} (gm cm ⁻³)	1.400
<i>F</i> (000)	3,240
$M(\text{Mo-}K_\alpha)$ (mm ⁻¹)	1.269
Reflections collected	39,580
Unique reflections	4,822
Observed reflections	4,149
<i>R</i> (int)	0.025
<i>h</i> / <i>k</i> / <i>l</i>	–17, 12/–17, 17/–46, 51
$R_1, \omega R_2$ [$I > 2\sigma(I)$]	0.0378, 0.1101
$R_1, \omega R_2$ (all data)	0.0410, 0.1107
Data/restraints/parameters	4,822/0/286
GOF on F^2	1.044
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.273, –0.243

Table 2 Selected bond distances (Å) and bond angles (°) for (*I*)

<i>Bond lengths</i>			
Cu1–N4	2.556(3)	Fe1–C2	1.951(4)
Cu1–N5	1.993(3)	Fe1–C3	1.938(4)
Cu1–N6	1.997(3)	Fe1–C4	1.940(3)
Cu1–N8	2.013(3)	N1–C1	1.147(5)
Cu1–N9	1.999(2)	N2–C2	1.120(6)
Cu1–N1-j	2.610(4)	N3–C3	1.119(6)
Fe1–C1	1.932(4)	N4–C4	1.133(4)
<i>Bond angles</i>			
Cu1–N4–C4	139.5(3)	C2–Fe1–C3	180.00(12)
C1–Fe1–C2	93.58(15)	C2–Fe1–C4	86.63(12)
C1–Fe1–C3	86.42(15)	C3–Fe1–C4	93.37(12)
C1–Fe1–C4	89.39(14)		

Symmetry transformations used to generate equivalent atoms: *j*: $x-y, 1-y, 1-z$

$2,200 \text{ cm}^{-1}$, assigned to terminal and bridging CN^- , respectively. The higher frequency band at $2,140 \text{ cm}^{-1}$ was blue-shifted from the $\nu(\text{C}\equiv\text{N})$ stretching frequency of

2,125 cm^{-1} in the free $[\text{Fe}(\text{CN})_6]^{3-}$ ion, indicating the presence of bridging cyanide in (1).

Crystal structure

The ORTEP diagram of the asymmetric unit of (1) with atom numbering scheme is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. (1) consists of four parts: one $[\text{Fe}(\text{CN})_6]^{3-}$ anion, two $[\text{CuL}]^{2+}$ cations, one ClO_4^- anion and a water molecule. Moreover, occupancies of O_3 and O_4 from water molecules are both 50%. Each $[\text{Fe}(\text{CN})_6]^{3-}$ anion coordinates with four $[\text{CuL}]^{2+}$ cations via four equatorial $\text{C}\equiv\text{N}$ groups, whereas each $[\text{CuL}]^{2+}$ anion is linked to two $[\text{Fe}(\text{CN})_6]^{3-}$ ions in *trans* conformation.

Each Cu^{II} atom is hexacoordinate: four N atoms, N(5), N(6), N(8), N(9), from the L ligand with the $\text{Cu}-\text{N}_{\text{eq}}$ bond distances in the range of 1.993(3)–2.011(3) Å occupy the four equatorial positions and two N atoms, N(4) and N1-j, from the bridging cyanide groups with the $\text{Cu}-\text{N}_{\text{ax}}$ distances of 2.553(3) and 2.612(4) Å are in the axial sites, giving an elongated octahedron around Cu^{II} atom. Due to the Jahn–Teller effects, the $\text{Cu}-\text{N}_{\text{ax}}$ distances are much longer than the $\text{Cu}-\text{N}_{\text{eq}}$ bond distances. The average values of the four $\text{Cu}-\text{N}_{\text{eq}}$ bond distances in the plane are 1.999 Å and 2 $\text{Cu}-\text{N}_{\text{ax}}$ 2.583 Å, respectively. In addition, the $\text{C}-\text{N}-\text{Cu}$ bond angles are far from linearity with the angles ranging from 138.43° to 139.45°.

As usual, each $[\text{Fe}(\text{CN})_6]^{3-}$ fragment has a (4+2) slightly elongated octahedral coordination environment caused by Jahn–Teller effects. The $\text{Fe}-\text{C}$ average bond length of the four non-bridging cyanide groups is 1.936 Å, which is slightly shorter than that of two bridging cyanide groups, 1.945 Å. According to the $\text{Fe}-\text{CN}-\text{Cu}$ linkage, $[\text{Fe}(\text{CN})_6]^{3-}$ anion ions can be divided into two types: one forms $\text{Fe}-\text{CN}-\text{Cu}$ linkages in the *bc* plane and the other in

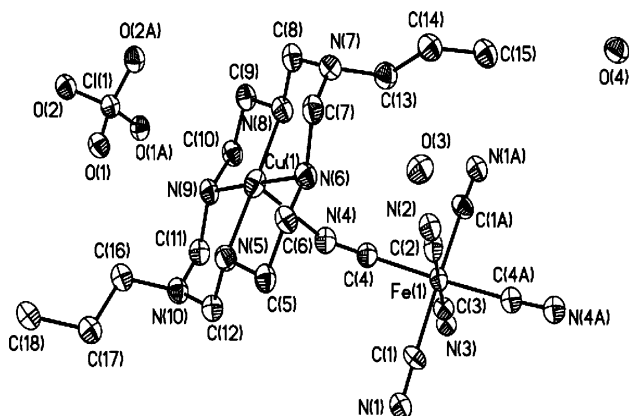


Fig. 1 ORTEP diagram of (1) showing atom numbering scheme. Perchlorate anion is omitted for clarity

the *ac* plane, which results in a novel 3-D honeycomb-like structure (Fig. 2). Moreover, there are hydrogen bonds between the water molecule oxygen and the terminal CN nitrogen [$\text{O}(3)\cdots\text{N}(2) = 2.973$ Å and $\text{O}(4)\cdots\text{N}(3) = 2.523$ Å, respectively.]

Magnetic study

The magnetic susceptibilities of (1) were measured with an applied field $H = 2$ kOe in the temperature range 1.8–300 K. The plots of $\chi_{\text{M}}T$ versus T and $1/\chi_{\text{M}}$ versus T are given in Fig. 3. At room temperature, the $\chi_{\text{M}}T$ per Cu_2Fe unit is 1.13 emu K mol^{-1} ($3.0 \mu_{\text{B}}$), which is consistent with the spin-only value expected for an uncoupled spin system (two $S_{\text{Cu}} = 1/2$, one $S_{\text{Fe}} = 1/2$) with $g = 2.0$. On lowering the temperature, the $\chi_{\text{M}}T$ value gradually increases to 1.18 emu K mol^{-1} ($3.1 \mu_{\text{B}}$) at 14 K, then decreases with further decreasing temperature to 0.87 emu K mol^{-1} ($2.63 \mu_{\text{B}}$) at 1.8 K. The plot of $1/\chi_{\text{M}}$ versus T above 10 K

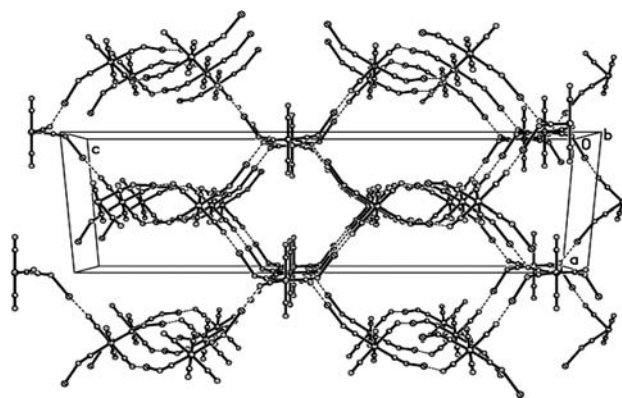


Fig. 2 Projection of the 3-D honeycomb-like structure onto the *bc* plane for (1). Non-bridged cyanides, L ligands, perchlorate anions, and water molecules are omitted for clarity

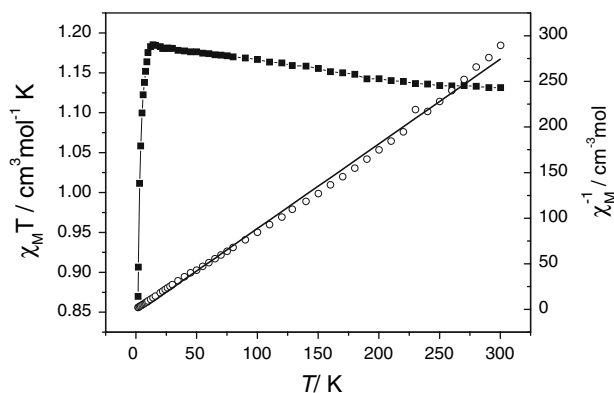


Fig. 3 Temperature dependence of $\chi_{\text{M}}T$ (■) and $1/\chi_{\text{M}}$ (○) for (1) measured at 2 kOe. The solid line represents the fit obtained by the Curie–Weiss law

obeys the Curie–Weiss law with a positive Weiss constant $\theta = +4.6$ K, which indicates the presence of a weak ferromagnetic coupling between copper(II) and iron(III) ions through a cyano bridge due to the orthogonality of the magnetic orbitals of e_g (Cu^{2+}) and t_{2g} (Fe^{3+}). The very weak magnetic interaction may be interpreted from the character of the structure of (*I*). As discussed in the structural description, the axial Cu–N_{cyanide} bond lengths are very long due to Jahn–Teller effects and the Cu–N≡C angles are far from linear. This will markedly weaken the ferromagnetic interactions through the Fe–C–N–Cu linkages. The decrease of the $\chi_M T$ below 14 K may be due to the zero-field splitting effect and/or the intermolecular antiferromagnetic interaction via hydrogen bond.

Conclusion

In summary, a 3-D cyano-bridged bimetallic assembly, $[\text{CuL}]_2[\text{Fe}(\text{CN})_6]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (*I*), has been synthesized and characterized by structural and magnetic methods. The crystallographic determination reveals that each hexacyanoferrate(III) ion connects four copper(II) ions using four co-planar CN^- groups which coordinate axially to the copper ion in a *trans* fashion forming *trans*- $\text{CuL}(\text{N}\equiv\text{C})_2$ moieties in the complex. Magnetic studies reveal that (*I*) displays a ferromagnetic interaction between Cu(II) and Fe(III) through the CN linkage.

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