Synthesis, structure and magnetic behaviour of a two-dimensional cyano-bridged complex $[\{Cu(ept)\}_3Fe(CN)_6](ClO_4)_2 \cdot 5H_2O$ [ept = *N*-(2-aminoethyl)-1,3-diaminopropane]

Zdeněk Trávníček,*[a] Zdeněk Smékal,[a] Albert Escuer[b] and Jaromír Marek[c]

[a] *Department of Inorganic and Physical Chemistry, Palacký University, Křížkovského 10, CZ-77147 Olomouc, Czech Republic. E-mail: trav@aix.upol.cz*
[b] *Departament de Química Inorgànica, Universitat de Barcelona, Av. Diagonal 647, 08028 Barcelona, Spain*
[c] *Laboratory of Biomolecular Structure and Dynamics, Masaryk University, Kotlářská 2, CZ-61137 Brno, Czech Republic*

Received (in Strasbourg, France) 27th July 2000, Accepted 10th January 2001
First published as an Advance Article on the web 19th March 2001

The bimetallic compound $[\{Cu(ept)\}_3Fe(CN)_6](ClO_4)_2 \cdot 5H_2O$ [ept = *N*-(2-aminoethyl)-1,3-diaminopropane] has been prepared from the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$, ept and $K_4[Fe(CN)_6] \cdot 3H_2O$ in water and its crystal and molecular structure has been determined. The structure consists of a two-dimensional network formed by $[\{Cu(ept)\}_3Fe(CN)_6]^{2+}$ moieties, perchlorate anions and water molecules. Every $[Fe(CN)_6]^{4-}$ anion is coordinated by six $[Cu(ept)]^{2+}$ cations through six cyano nitrogens, providing a 2D sheet structure extended by Fe–(CN)–Cu linkages. All the copper(II) ions are five-coordinated by three ept nitrogen and two cyanide nitrogen atoms in a distorted square-pyramidal arrangement. The EPR spectrum of the compound at room temperature also confirms the coordination environment of the copper(II) atoms. A magnetic susceptibility measurement of the complex was performed down to 4 K but no coupling was found among the copper atoms *via* the –(NC)–Fe–(CN)– bridges.

Cyanide-bridged bimetallic assemblies, derived from $[M(CN)_6]^{n-}$ (M = transition metal ion) and simple metal ions (for example Cu^{2+}, Ni^{2+}, Fe^{3+}), form an intensively studied family of magnetic materials.[1,2] During the last few years, much attention has been directed towards the syntheses of molecular-based magnets, especially the Prussian blue-like ones.[3,4] Moreover, Prussian blue is ferromagnetic with T_C = 5.6 K.[5] Considering that the magnetic interactions are caused by diamagnetic $[Fe(CN)_6]^{4-}$ anions, it is useful to investigate the magnetic properties of polynuclear μ-cyanido complexes derived from hexacyanoferrate(II). Since copper(II) is normally four-, five- or six-coordinate, it was anticipated that the coupling of a copper(II) amine to the $[Fe(CN)_6]^{4-}$ ion might lead to the formation of a novel family of magnetic compounds with potential control over the structure of the compound. Suzuki and Uehara[6] prepared the cyano-bridged complexes $[\{Cu(L)\}_2(CN)_2Fe(CN)_4] \cdot 4H_2O$ (L = diethylenetriamine or dipropylenetriamine) and characterized these compounds by IR and UV-vis spectroscopy. Zou *et al.*[7] synthesized the trinuclear complex $[\{Cu(tren)\}_2Fe(CN)_6]$ [tren = tris(2-aminoethyl)amine]. The molecular structure of the complex showed that it is composed of two $[Cu(tren)]^{2+}$ and one $[Fe(CN)_6]^{4-}$ subunits with two cyanide bridges between the iron(II) and copper(II) atoms. The copper(II) ion is in a distorted trigonal bipyramidal environment. The magnetic properties of $[\{Cu(tren)\}_2Fe(CN)_6]$ indicate weak ferromagnetic exchange. Therefore, we carried out the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$, ept [ept = *N*-(2-aminoethyl)-1,3-diaminopropane] and $K_4[Fe(CN)_6] \cdot 3H_2O$.

Results and discussion

The crystals of $[\{Cu(ept)\}_3Fe(CN)_6](ClO_4)_2 \cdot 5H_2O$ contain a unique two-dimensional network formed by $[\{Cu(ept)\}_3Fe(CN)_6]^{2+}$ moieties, perchlorate anions and water molecules. The asymmetric unit consists of three $[Cu(ept)]^{2+}$ cations, a $[Fe(CN)_6]^{4-}$ anion, two perchlorate anions, and five water molecules (see Fig. 1). Every $[Fe(CN)_6]^{4-}$ anion is coordinated by six $[Cu(ept)]^{2+}$ cations through six cyano nitrogens (*i.e.* all cyano groups form bridges), providing a 2D sheet structure (the geometry of which is illustrated in Fig. 2) extended by Fe–(CN)–Cu linkages. The Fe(II) ion in $[Fe(CN)_6]^{4-}$ is octahedrally coordinated by six CN^- groups. The Fe–C bond lengths lie in the range 1.884(4)–1.926(5) Å. Each of the CN^- ligands coordinates a Cu(II) ion in $[Cu(ept)]^{2+}$. All the copper(II) ions are coordinated by three ept nitrogen and two cyano nitrogen atoms in a distorted square-pyramidal arrangement. In the

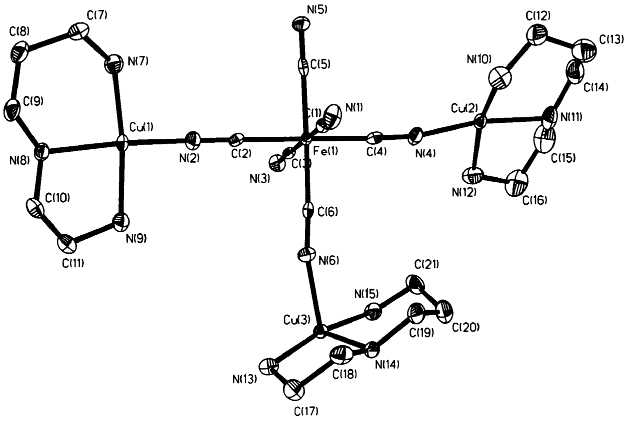

Fig. 1 The asymmetric unit of $[\{Cu(ept)\}_3Fe(CN)_6](ClO_4)_2 \cdot 5H_2O$ showing the atom labeling scheme. The perchlorate anions and water molecules are omitted for clarity.

DOI: 10.1039/b006741p

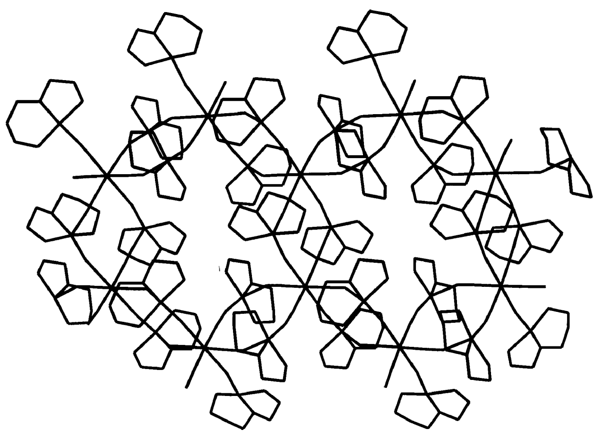

Fig. 2 View of the 2D polymeric structure of $[\{Cu(ept)\}_3Fe(CN)_6]^{2+}$.

structure, one cyano nitrogen atom and the three ept nitrogen atoms are bonded in a plane, while the second cyano nitrogen atom is situated in the apical position of the distorted square-pyramidal environment. The in-plane Cu–N bond lengths vary from 1.962(4) to 2.050(5) Å. The axial Cu–N bond lengths are significantly longer [2.165(4)–2.263(4) Å]. The bridging cyanides coordinate to the copper ions in a bent fashion with the C–N–Cu bond angles ranging from 148.5(4) to 170.3(3)°.

The IR spectrum of $[\{Cu(ept)\}_3Fe(CN)_6](ClO_4)_2 \cdot 5H_2O$ shows one strong band at 2056 cm^{-1}, which can be attributed to the C≡N stretching mode. According to the literature, the formation of the cyano bridge shifts ν(C≡N) towards higher frequency.[8] The shift of ν(C≡N) to higher wavenumber compared with that for $K_4[Fe(CN)_6] \cdot 3H_2O$ (2040 cm^{-1})[6] is consistent with the formation of C≡N bridges as revealed by the X-ray determination.

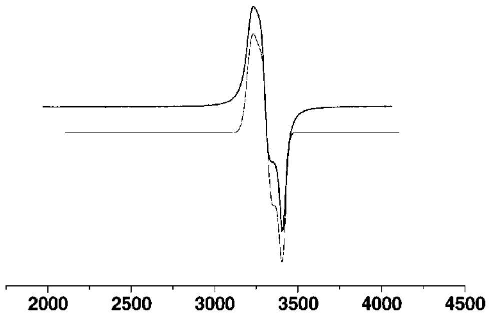

Fig. 3 EPR spectrum of $[\{Cu(ept)\}_3Fe(CN)_6](ClO_4)_2 \cdot 5H_2O$. Top: experimental spectrum; bottom: simulated spectrum with $g_1 = 2.05$, $g_2 = 2.11$, $g_3 = 2.17$.

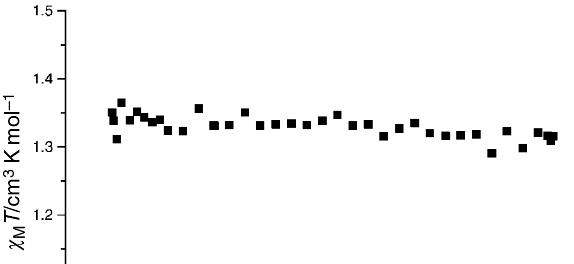

Fig. 4 The temperature dependence of $\chi_M T$ for $[\{Cu(ept)\}_3Fe(CN)_6](ClO_4)_2 \cdot 5H_2O$.

The electronic absorption spectrum of the prepared complex results probably from a superposition of the spectra of $[Fe(CN)_6]^{4-}$ and $[Cu(ept)]^{2+}$. The spectrum of $[\{Cu(ept)\}_3Fe(CN)_6](ClO_4)_2 \cdot 5H_2O$ shows two bands at 16000 and 22000 cm^{-1}. The band at 16000 cm^{-1} corresponds to the d–d transition localized on the Cu(II) ion.[9]

The EPR spectrum of the studied compound at room temperature also confirmed the feature of isolated copper(II) ions with a distorted rhombic environment (*i.e.* three signals that are quite close and partially overlapped, see Fig. 3). The spectrum may be simulated to determine three g values ($g_1 = 2.05$, $g_2 = 2.11$, $g_3 = 2.17$). The EPR spectra of $[\{Cu(ept)\}_3Fe(CN)_6](ClO_4)_2 \cdot 5H_2O$ at 77 and 4 K seem to confirm the absence of exchange interaction, which corresponds to the existence of isolated Cu(II) centres. The spectra at low temperatures maintain the same shapes and g values as the EPR spectrum at room temperature.

The magnetic properties of a powder sample of $[\{Cu(ept)\}_3Fe(CN)_6](ClO_4)_2 \cdot 5H_2O$ are represented as $\chi_M T$ *vs.* T in Fig. 4. At room temperature, the $\chi_M T$ value of the presented complex is 1.32 $cm^3\ mol^{-1}$ K. The effective magnetic moment of the complex (3.25 BM) at room temperature corresponds to three copper(II) ions with one unpaired electron. As the temperature is lowered down to 4.9 K, the value of $\chi_M T$ is nearly constant and the complex is not coupled in the studied temperature range (4.9–289.5 K). From the structure it seems that some coupling, even if weak, is possible, but this has not been observed in the temperature range studied.

Conclusions

A unique extended 2D polymeric copper(II)–iron(II) structure has been obtained from the reaction of $[Cu(ept)]^{2+}$ with the $[Fe(CN)_6]^{4-}$ anion. The assembly of the two components is achieved through the bridging mode of the CN^- ligand and is also due to the coordination properties of the copper ion. Magnetic susceptibility measurements of the complex $[\{Cu(ept)\}_3Fe(CN)_6](ClO_4)_2 \cdot 5H_2O$ were performed in the 289.5–4.9 K range but no coupling was found between the copper atoms *via* the –(NC)–Fe–(CN)– bridges. The magnetic behaviour of the 1D polymeric complex $[Cu(en)_2Fe(CN)_5NO]$ (en = ethylenediamine) reported previously shows weak antiferromagnetic exchange interaction ($J = -1.06\ cm^{-1}$),[10] while in the trinuclear complex $[\{Cu(tren)\}_2Fe(CN)_6]$ a weak ferromagnetic exchange interaction *via* the –(NC)–Fe–(CN)– bridges was found.[7] In order to obtain a correlation between magnetic properties and structures more examples of complexes of this type are needed.

Table 1 Crystallographic data for $[\{Cu(ept)\}_3Fe(CN)_6](ClO_4)_2 \cdot 5H_2O$

Formula	$C_{21}H_{55}Cl_2Cu_3FeN_{15}O_{13}$
M_r	1043.17
T/K	150(2)
λ/Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	12.8812(11)
b/Å	13.0279(12)
c/Å	14.2552(9)
α/°	78.667(7)
β/°	86.219(6)
γ/°	60.753(9)
U/Å^3	2045.3(3)
Z	2
μ/mm^{-1}	2.090
Reflections collected	8552
Independent reflections	6138 [$R_{int} = 0.0349$]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0473$, $wR_2 = 0.1185$
R indices (all data)	$R_1 = 0.0511$, $wR_2 = 0.1218$

Table 2 Selected bond lengths (Å) and angles (°) for $[\{Cu(ept)\}_3Fe(CN)_6]$ $(ClO_4)_2 \cdot 5H_2O$. Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y+1, -z+1$; #2: $-x+2, -y, -z+1$; #3: $-x+1, -y, -z+1$

Cu(1)–N(2)	1.962(4)	Cu(3)–N(14)	2.037(4)
Cu(1)–N(7)	2.014(4)	Cu(3)–N(13)	2.041(4)
Cu(1)–N(9)	2.025(4)	Cu(3)–N(6)	2.165(4)
Cu(1)–N(8)	2.035(4)	Fe(1)–C(3)	1.884(4)
Cu(1)–N(1)#1	2.204(4)	Fe(1)–C(2)	1.905(5)
Cu(2)–N(4)	1.960(4)	Fe(1)–C(6)	1.907(4)
Cu(2)–N(10)	2.000(4)	Fe(1)–C(4)	1.912(5)
Cu(2)–N(11)	2.050(4)	Fe(1)–C(1)	1.917(4)
Cu(2)–N(12)	2.050(5)	Fe(1)–C(5)	1.926(5)
Cu(2)–N(5)#2	2.263(4)	N(1)–Cu(1)#1	2.204(4)
Cu(3)–N(3)#3	1.983(4)	N(3)–Cu(3)#3	1.983(4)
Cu(3)–N(15)	2.023(4)	N(5)–Cu(2)#2	2.263(4)
N(2)–Cu(1)–N(7)	91.06(17)	N(3)#3–Cu(3)–N(13)	90.73(16)
N(2)–Cu(1)–N(9)	90.70(17)	N(15)–Cu(3)–N(13)	169.11(18)
N(7)–Cu(1)–N(9)	164.2(2)	N(14)–Cu(3)–N(13)	83.54(16)
N(2)–Cu(1)–N(8)	169.04(17)	N(3)#3–Cu(3)–N(6)	103.28(15)
N(7)–Cu(1)–N(8)	91.90(17)	N(15)–Cu(3)–N(6)	95.87(16)
N(9)–Cu(1)–N(8)	83.63(16)	N(14)–Cu(3)–N(6)	94.32(16)
N(2)–Cu(1)–N(1)#1	97.53(16)	N(13)–Cu(3)–N(6)	94.78(17)
N(7)–Cu(1)–N(1)#1	96.74(18)	C(3)–Fe(1)–C(2)	88.07(18)
N(9)–Cu(1)–N(1)#1	98.57(18)	C(3)–Fe(1)–C(6)	87.16(17)
N(8)–Cu(1)–N(1)#1	92.60(16)	C(2)–Fe(1)–C(6)	88.85(17)
N(4)–Cu(2)–N(10)	90.92(18)	C(3)–Fe(1)–C(4)	91.69(18)
N(4)–Cu(2)–N(11)	170.09(17)	C(2)–Fe(1)–C(4)	179.76(17)
N(10)–Cu(2)–N(11)	91.77(19)	C(6)–Fe(1)–C(4)	91.15(17)
N(4)–Cu(2)–N(12)	91.72(18)	C(3)–Fe(1)–C(1)	176.67(18)
N(10)–Cu(2)–N(12)	164.0(2)	C(2)–Fe(1)–C(1)	89.45(17)
N(11)–Cu(2)–N(12)	83.13(19)	C(6)–Fe(1)–C(1)	90.58(17)
N(4)–Cu(2)–N(5)#2	95.33(15)	C(4)–Fe(1)–C(1)	90.80(18)
N(10)–Cu(2)–N(5)#2	95.27(17)	C(3)–Fe(1)–C(5)	93.01(17)
N(11)–Cu(2)–N(5)#2	93.91(16)	C(2)–Fe(1)–C(5)	90.03(17)
N(12)–Cu(2)–N(5)#2	100.21(18)	C(6)–Fe(1)–C(5)	178.86(18)
N(3)#3–Cu(3)–N(15)	89.02(17)	C(4)–Fe(1)–C(5)	89.97(17)
N(3)#3–Cu(3)–N(14)	161.90(17)	C(1)–Fe(1)–C(5)	89.20(17)
N(15)–Cu(3)–N(14)	93.40(17)		

Experimental

General procedures

All chemicals were commercial products of reagent grade and used without further purification. Elemental analyses of carbon, hydrogen and nitrogen were carried out with an EA 1108 CHN analyser (Fisons Instruments). Infrared spectra were measured (in the 4000–400 cm^{-1} region) with a SPECORD IR 80 instrument using the Nujol technique. Absorption UV-vis spectra (33 000–11 000 cm^{-1}) were recorded on a SPECORD M40 instrument in Nujol. Magnetic susceptibility measurements were made on a polycrystalline sample with a conventional susceptometer, under a 1.5 T field and down to 4 K. Diamagnetic corrections were taken from Pascal's constants. The EPR spectra were recorded on a Bruker ES 200 spectrometer with X-band frequency at room temperature, 77 and 4 K, respectively.

Preparation

$[\{Cu(ept)\}_3Fe(CN)_6](ClO_4)_2 \cdot 5H_2O$. A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.62 mmol, 0.60 g) and ept (1.59 mmol, 0.20 mL) in water (30 mL) was added to a solution of $K_4[Fe(CN)_6] \cdot 3H_2O$ (0.80 mmol, 0.34 g) in water (30 mL). After standing two days, a black polycrystalline solid was filtered off, washed with water and dried in air. The yield was 0.3 g (53%). Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent from the above filtrate. Anal. found (calc. for $C_{21}H_{55}Cl_2Cu_3FeN_{15}O_{13}$): C 23.9 (24.2); H 5.7 (5.3); N 20.1 (20.1%).

X-Ray structure determination

Single crystals of $[\{Cu(ept)\}_3Fe(CN)_6](ClO_4)_2 \cdot 5H_2O$ were obtained as described above. The diffraction experiment was carried out at 150 K on a four-circle κ-axis KUMA KM-4 diffractometer equipped with an Oxford Cryostream cooler using graphite-monochromated Mo-Kα radiation. The data collection was perfomed using a CCD detector. Ω rotations performed for 4 different orientations of the diffractometer axis (φ, κ and θ) were in sequence chosen to cover practically a full 2θ hemisphere. A total of 743 frames (0.5 deg. per 40 s) were recorded. The cell parameters were determined by least-squares methods from 3000 strong reflections.

The structure was solved by direct methods.[11] All non-H atoms were refined anisotropically[12] by the full-matrix least-squares procedure with the weight: $w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 9.2985P]$ where $P = (F_o^2 + 2F_c^2)/3$. Some atoms of both ClO_4^- anions are disordered over two positions. Crystallographic data for $[\{Cu(ept)\}_3Fe(CN)_6]$-$(ClO_4)_2 \cdot 5H_2O$ are summarized in Table 1 and selected bond lengths and angles are listed in Table 2.

CCDC reference number 440/257. See http://www.rsc.org/suppdata/nj/b0/b006741p/ for crystallographic files in .cif format.

Acknowledgement

This work was supported by the Grant Agency of the Czech Republic (Grant No. 203/98/P221).

References

1 M. Ohba, H. Okawa, N. Fukita and Y. Hashimoto, *J. Am. Chem. Soc.*, 1997, **119**, 1011 and references therein.

2 S. Ferlay, T. Mallah, R. Ouahes, P. Veillet and M. Verdaguer, *Inorg. Chem.*, 1999, **38**, 229.

3 A. Bleuzen, C. Lomenech, V. Escax, F. Villain, F. Varret, C. Cartier dit Moulin and M. Verdaguer, *J. Am. Chem. Soc.*, 2000, **122**, 6648.

4 C. Cartier dit Moulin, F. Villain, A. Bleuzen, M.-A. Arrio, P. Sainctavit, C. Lomenech, V. Escax, F. Baudelet, E. Dartyge, J.-J. Gallet and M. Verdaguer, *J. Am. Chem. Soc.*, 2000, **122**, 6653.

5 F. Herren, P. Fischer, A. Ludi and W. Haly, *Inorg. Chem.*, 1980, **19**, 956.

6 M. Suzuki and A. Uehara, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 3134.

7 J. Zou, Z. Xu, X. Huang, W. L. Zhang, X. P. Shen and Y. P. Yu, *J. Coord. Chem.*, 1997, **42**, 55.

8 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn., Wiley, New York, 1978, p. 259.

9 B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd edn., Elsevier, New York, 1984, p. 554.

10 H. Z. Kou, H. M. Wang, D. Z. Liao, P. Cheng, Z. H. Jiang, S. P. Yan, X. Y. Huang and G. L. Wang, *Aust. J. Chem.*, 1998, **51**, 661.

11 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

12 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.