Supramolecular heteropolymetallic assemblies constructed from binuclear complexes and hexacyanometallate anions. Synthesis, crystal structure and magnetic properties of $[Cu_2(fsal\text{-}33)(H_2O)_2]_3[Fe(CN)_6]_2 \cdot 8\ H_2O$†

Gabriela Grasa,[a] Floriana Tuna,[a] Ruxandra Gheorghe,[b] Daniel B. Leznoff,[c] Steven J. Rettig‡[d] and Marius Andruh*[b]

[a] *Coordination Chemistry Laboratory, Institute of Physical Chemistry of the Romanian Academy, Splaiul Independentei nr. 202, 70208 Bucharest, Romania*
[b] *Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Rosie nr. 23, 70254 Bucharest, Romania. E-mail: marius.andruh@dnt.ro*
[c] *Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC, V5A 1S6, Canada*
[d] *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C, V6T 1Z1, Canada*

Received (in Montpellier, France) 18th January 2000, Accepted 30th May 2000
Published on the Web 3rd July 2000

A supramolecular heteropolymetallic system, $[Cu_2(fsal\text{-}33)(H_2O)_2]_3[Fe(CN)_6]_2 \cdot 8\ H_2O$ (**1**), was obtained by reacting $K_3[Fe(CN)_6]$ with $[Cu_2(fsal\text{-}33)(H_2O)_2](ClO_4)_2$ ($H_2fsal\text{-}33$ is the symmetric macrocyclic binucleating Schiff base ligand obtained by condensation of 2,6-diformyl-4-methylphenol with 1,3-propylenediamine). The crystallographic investigation of **1** reveals a complex three-dimensional structure based on hydrogen-bond interactions between the aqua ligands coordinated to the copper atoms, the water molecules, and the cyano groups arising from the hexacyanoferrate(III) anions. The cryomagnetic measurements reveal the strong antiferromagnetic interaction between the copper(II) ions within the binuclear cationic entity, and the temperature dependence of the $\chi_M T$ product, which is due to the first-order orbital momentum associated with low-spin Fe(III).

In recent years, hexacyanometallate anions have been extensively used as building blocks in designing heteropolymetallic systems.[1,2] The increasing interest in this chemistry is mainly justified by the search for molecule-based magnets.[3–8] Since the pioneering work of Verdaguer and co-workers on the spontaneous three-dimensional long-range magnetic ordering exhibited by the Prussian blue analogs, $[A_k[B(CN)_6]_l \cdot n\ H_2O$ and $C^IA^{II}[M(CN)_6] \cdot nH_2O$,[3] we are facing a spectacular revival of the chemistry generated by $[M(CN)_6]^{q-}$ anions. The synthesis can be seen as a self-assembly process between the anionic building blocks and: (*a*) "necked" (actually hydrated metal ions);[1,3,9] (*b*) cationic complexes containing a pre-existing ligand and potentially free coordination sites;[1,10] and (*c*) cationic organic radicals.[11] In the first two cases, a plethora of cyano-bridged heteropolymetallic complexes, ranging from discrete entities to 1-D, 2-D and 3-D systems, has been obtained. In the last case, very interesting supramolecular hydrogen-bonded assemblies with novel topologies of the spin carriers have been characterized and their magnetic properties investigated.

We have recently started a research project on the synthesis of heterometallic systems of interest in molecular magnetism, which are obtained by the self-assembly process between hexacyanometallate anions and binuclear complexes. This synthetic approach could be an alternative way to design heteropolynuclear complexes with predictable magnetic properties. The basic idea of our strategy is to combine the magnetic behavior of the binuclear assembling cation (exhibiting a ferro- or an antiferromagnetic coupling between the two metal ions) with the one of the anionic building blocks. Beyond the individual magnetic behavior, the two molecular entities may interact, either through genuine cyano bridges, or through hydrogen bonds. We report here on our first results in this chemistry, namely the synthesis, crystal structure and magnetic properties of a new hydrogen-bonded supramolecular polymetallic system, which is obtained by the self-assembly of $[Fe(CN)_6]^{3-}$ anions with $[Cu_2(fsal\text{-}33)(H_2O)_2]^{2+}$ ($H_2fsal\text{-}33$ is the symmetric macrocyclic binucleating Schiff-base ligand obtained by condensation of 2,6-diformyl-4-methylphenol with 1,3-propylenediamine).

Experimental

Syntheses

Chemicals were purchased from Aldrich and all manipulations were performed using materials as received. The binuclear complex, $[Cu_2(fsal\text{-}33)(H_2O)_2](ClO_4)_2 \cdot 2\ H_2O$, has been synthesized by a template procedure according to ref. 12. $[Cu_2(fsal\text{-}33)(H_2O)_2]_3[Fe(CN)_6]_2 \cdot 8\ H_2O$ (**1**) was obtained as follows: to a solution containing 0.229 g (0.3 mmol) $[Cu_2(fsal\text{-}33)(H_2O)_2](ClO_4)_2$ in 20 mL acetonitrile was added a solution containing 0.2 mmol $K_3[Fe(CN)_6]$ dissolved in 20 mL of a 50 : 50 isopropanol–water mixture. The resulting green microcrystalline precipitate was filtered off, washed with water and isopropanol, and finally dried *in vacuo* over P_4O_{10}. Yield:

† Dedicated to the memory of Professor Olivier Kahn (1942–1999).
‡ Dr Steven J. Rettig passed away suddenly on 27th October 1998.

Table 1 Crystal data and structure refinement

Empirical formula	$C_{84}H_{106}Cu_6Fe_2N_{24}O_{20}$
Formula weight	2264.88
Crystal system	Monoclinic
Crystal group	$P2_1/c$ (#14)
a/Å	12.3234(8)
b/Å	17.1876(12)
c/Å	22.1979(2)
α/°	90
β/°	96.0123(3)
γ/°	90
U/Å^3	4675.9(4)
Z	2
T/K	180
μ/cm^{-1}	17.20
F(000)	2328
Final R indices [$I > 3\sigma(I)$]	$R = 0.051$, $Rw = 0.038$

85%. IR data (KBr, cm^{-1}), **1**: 3385s, 2930w, 2111s, 1640vs, 1596s, 1441m, 1417m, 1376vw, 1324s, 1272w, 1242w, 1197w, 1117m, 1097w, 1073w, 973vw, 940vw, 882vw, 816s, 762m, 620m, 569w, 522w, 490w, 452m. Elem. anal.: found: C, 44.1; H, 4.9; N, 14.6%; calcd: C, 44.54; H, 4.72; N, 14.84%. Single crystals were obtained by slow diffusion, in an H-shaped tube, of two solutions, one of them containing $[Cu_2(fsal\text{-}33)(H_2O)_2](ClO_4)_2$ dissolved in acetonitrile, and the other one $K_3[Fe(CN)_6]$ dissolved in a water–isopropanol mixture. The infrared spectra were found to be identical for both the microcrystalline powder and single crystals. The cobalt(III) derivative, $[Cu_2(fsal\text{-}33)(H_2O)_2]_3[Co(CN)_6]_2 \cdot 8\ H_2O$ (**2**), has been obtained as a green powder in a similar way as compound **1**. IR data (KBr, cm^{-1}), **2**: 3396s, 2926w, 2124s, 1636vs, 1570s, 1441m, 1419m, 1376vw, 1325s, 1272w, 1241w, 1198w, 1118m, 1074w, 973vw, 942vw, 884vw, 817s, 762m, 620m, 566w, 523w, 490w, 452m. Elem. anal.: found: C, 44.6; H, 4.5; N, 15.1%; calcd: C, 44.42; H, 4.70; N, 14.80%.

Caution! Perchlorate salts are potentially explosive and should only be handled with care and in small quantities.

Physical measurements

IR spectra (KBr pellets) were recorded on a Bio-Rad FTS 135 spectrophotometer in the 4000–400 cm^{-1} region. UV-VIS spectra (diffuse reflectance technique) were recorded with a UV4 Unicam spectrophotometer. Magnetic measurements were carried out in the temperature range 1.8–300 K, on a Quantum Design MPMS-5S SQUID magnetometer.

Crystal structure determination

A green crystal of **1** having approximate dimensions of 0.20 × 0.06 × 0.03 mm was mounted on a glass fiber. All measurements were made on a Rigaku/ADSC CCD area detector with graphite monochromated Mo-Kα radiation. Cell constants were based on 18785 reflections with $2\theta = 4.0$–61° (see Table 1).

The data were collected at -93 ± 1 °C to a maximum 2θ value of 61.0°. Of the 42 584 reflections that were collected, 12 625 were unique ($R_{int} = 0.085$); equivalent reflections were merged. The structure was solved by direct methods and expanded using Fourier techniques.[13] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed in calculated (C–H = 0.98 Å) or difference map (O–H) positions. The final cycle of full-matrix least-squares refinement was based on all 12 625 unique reflections and 613 variable parameters and converged to $R_1 = 0.051$ and $Rw = 0.038$. Largest difference peak and hole: 1.47 e Å^{-3} (0.53 Å from Cu) and -2.32 e Å^{-3}. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[14]

CCDC reference number 440/193.

Results and discussion

The reaction between $K_3[Fe(CN)_6]$ and $[Cu_2(fsal\text{-}33)(H_2O)_2](ClO_4)_2 \cdot 2\ H_2O$ in a molar ratio of 1 : 1.5 leads to the heteropolymetallic system $[Cu_2(fsal\text{-}33)(H_2O)_2]_3[Fe(CN)_6]_2 \cdot 8\ H_2O$ (**1**). The infrared spectrum of **1** shows only one ν_{CN} band (2111 cm^{-1}), indicating that the cyano groups are not involved in bridging with the copper(II) ions. The broad band centered at 3385 cm^{-1} is due to the presence of both coordinated and non-coordinated water molecules.

The crystal structure of **1** consists of distinct cationic, $[Cu_2(fsal\text{-}33)(H_2O)_2]^{2+}$, and anionic, $[Fe(CN)_6]^{3-}$, units, which are held together by an extensive hydrogen-bonding network. The structure of the binuclear species in **1** is essentially identical to the one found in $[Cu_2(fsal\text{-}33)(H_2O)_2]F_2(CH_3OH)_2$.[15] There are two crystallographically nonequivalent binuclear cationic entities, {Cu(1)Cu(2)} and {Cu(3)Cu(3a)}. Within the cationic units, each copper atom exhibits a square pyramidal geometry, with a N_2O_4 macrocycle basal donor set, the aqua ligand occupying the apical position. The basal copper–ligand distances fall in the range 1.956–1.997 Å. The Cu–aqua bond lengths [Cu(1)–O(3) = 2.254(3) Å, Cu(2)–O(4) = 2.280(3) Å, Cu(3)–O(6) = 2.325(3) Å] are somewhat longer than those found in the fluoro derivative [2.2027(8) Å].[15] The two aqua ligands are disposed in a *trans* arrangement and are further connected by hydrogen bonds to the $[Fe(CN)_6]^{3-}$ ions or to the water molecules (see below). The copper–copper distances are: Cu(1)–Cu(2) = 3.120 Å and Cu(3)–Cu(3a) = 3.101 Å.

Let us have a closer look at the hydrogen-bonding interactions in the crystal structure. Two $[Fe(CN)_6]^{3-}$ anions are linked, each one through two *cis*-CN groups, to two aqua ligands arising from two different binuclear cationic species, {Cu(1)Cu(2)}, resulting in 16-membered rhombic meshes, as depicted in Fig. 1 [O(3a)···N(7a) = 2.851(5) Å; O(3a)···N(10b) = 2.869(5) Å]. These meshes are further interconnected by hydrogen bonds, which are established between cyano groups [N(9)] and the *trans*-disposed aqua ligands from a binuclear cationic unit, {Cu(3)Cu(3a)}, resulting in infinite alternate chains [O(6b)···N(9a) = 2.925(5) Å; O(6b) is the oxygen atom from the apical aqua ligand coordinated to Cu(3b), (Fig. 2)]. The three-dimensional order in the crystal is achieved by hydrogen-bond interactions between the chains and the crystallization water molecules (Fig. 3). The stability of the crystal arises from the combination of Madelung energy with the hydrogen-bond interactions.

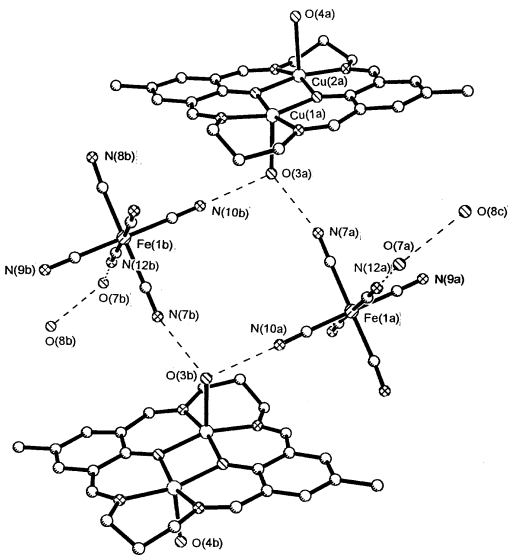

Fig. 1 View showing the hydrogen-bond interactions between two {Cu(1)Cu(2)}units and two $[Fe(CN)_6]^{3-}$ ions.

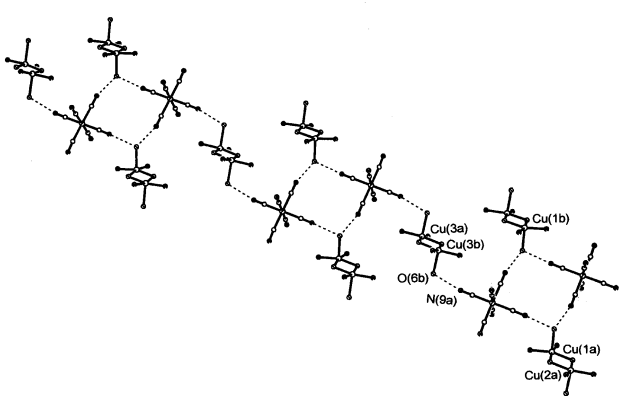

Fig. 2 Interconnection between the rhombic meshes (see text) and {Cu(3)Cu(3a)} cationic units. For clarity, the carbon atoms of the macrocyclic ligand and the crystallization water molecules have been omitted.

The electronic spectrum of **1**, recorded by the diffuse reflectance technique, shows a large band located at $\sim 15\,000$ cm^{-1} with a tail on its low energy side. This feature is characteristic of Cu(II) in a square-pyramidal environment,[16] and agrees with the crystal structure.

The magnetic properties of **1** combine the magnetic behavior of the binuclear species, $[Cu_2(fsal\text{-}33)(H_2O)_2]^{2+}$, with that of the anionic units, $[Fe(CN)_6]^{3-}$. The $\chi_M T$ *vs.* T plot for **1** is given in Fig. 4. At room temperature, the value of $\chi_M T$ (1.32 cm^3 mol^{-1} K) is much lower than the expected value for six Cu(II) and two low-spin Fe(III) uncoupled ions [~ 3.5 cm^3 mol^{-1} K, by neglecting the orbital contribution due to the low-spin Fe(III) ions, with a $^2T_{2g}$ ground term]. This low value is explained by the strong antiferromagnetic coupling of the Cu(II) ions within the binuclear entities. Upon lowering the temperature, the $\chi_M T$ curve decreases continuously, exhibiting an inflexion around 150 K. At this temperature, $\chi_M T$ is about 1.1 cm^3 mol^{-1} K, and corresponds to what is expected for two uncoupled low-spin Fe(III) ions. The further decrease of $\chi_M T$ is due to the intervention of the first-order orbital momentum associated with low-spin Fe(III), which couples with the spin momentum, and partially removes the degeneracy of the $^2T_{2g}$ state. In order to put in evidence more clearly the contribution of the iron(III) ions on the overall magnetic behavior of **1**, we have subtracted the contribution of the $\{Cu(II)_2\}$ entities, which has been obtained by measuring the magnetic properties of the similar system $[Cu_2(fsal\text{-}33)(H_2O)_2]_3[Co(CN)_6]_2 \cdot 8\ H_2O$, **2**. Compounds **1** and **2** exhibit almost identical infrared spectra. The temperature dependence of the difference $\chi_M T(\mathbf{1}) - \chi_M T(\mathbf{2})$, corresponding to the magnetic behavior of the $[Fe(CN)_6]^{3-}$ ions, is represented in Fig. 4 (curve b).

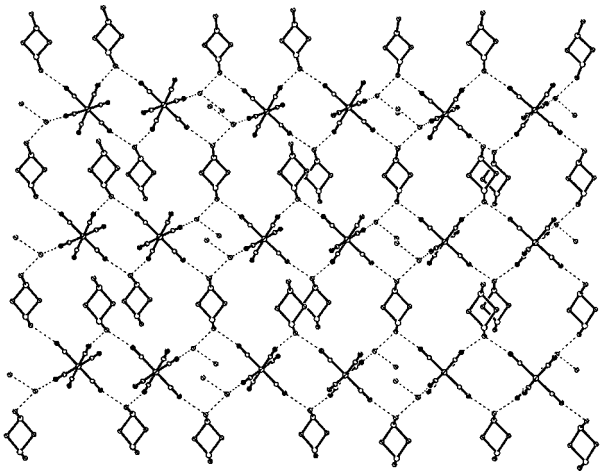

Fig. 3 Packing diagram in the *ab* plane of the crystal structure of **1**. For clarity, the carbon atoms of the macrocyclic ligands have been omitted.

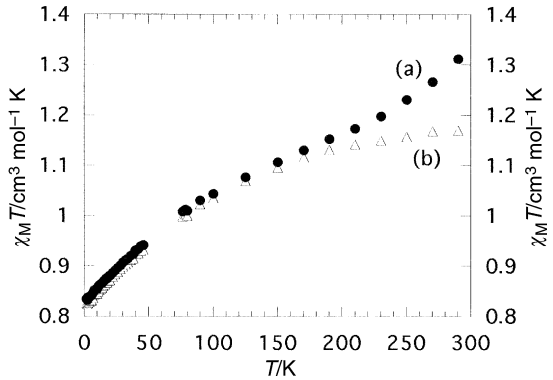

Fig. 4 Temperature dependence of (a) $\chi_M T$ for **1**, and (b) $\chi_M T(\mathbf{1}) - \chi_M T(\mathbf{2})$ (see text).

The coupling constants in the binuclear cationic units in **1** can be roughly estimated using Thompson's equation,[15] which relates the value of J (cm^{-1}) with the Cu–O(Ph)–Cu bridging angle, α:

$$-J = 31.95\alpha - 2462$$

As already mentioned, in crystal **1** there are two crystallographically nonequivalent binuclear cationic entities, {Cu(1)Cu(2)} and {Cu(3)Cu(3a)}. The values of the bridging angles are, respectively: Cu(1)–O(2)–Cu(2) = 103.23(14)° and Cu(3)–O(5)–Cu(3a) = 102.72(13)°. Accordingly, the predicted values of the Cu–Cu coupling constants in **1** are: ~ -836 and ~ -819 cm^{-1}. In the fluoro derivative, $[Cu_2(fsal\text{-}33)(H_2O)_2]F_2(CH_3OH)_2$, the value of the bridging angle is 103.65(10)°, which leads to a calculated value of ~ -849 cm^{-1}. The experimental value of the coupling constant was found to be $J = -784$ cm^{-1}.[15]

Since in the cobalt(III) derivative the anionic units are diamagnetic, we can directly determine the value of the coupling constant describing the exchange interaction between the copper(II) ions. The results of the cryomagnetic investigation of **2** are shown in the χ_M and $\chi_M T$ *vs.* T plots (Fig. 5). The room temperature value of the $\chi_M T$ product (0.18 cm^3 mol^{-1} K) indicates a very strong antiferromagnetic exchange interaction. The sharp rise in χ_M at low temperature is due to the presence of a small amount, ρ, of a paramagnetic, uncoupled Cu(II) impurity. Consequently, the experimental data were fitted using the Bleaney–Bowers equation, modified to take into account the paramagnetic impurities:

$$\chi_M T = 3(2Ng^2\beta^2/k)[3 + \exp(-J/kT)]^{-1}(1 - \rho) + \rho(Ng^2\beta^2/2k)$$

By least-squares fitting ($g = 2.1$, fixed value) we obtained $J = -834$ cm^{-1} and $\rho = 0.01$, with a reliability factor $R(\chi_M T) = 4.4 \times 10^{-4}$ $\{R = \sum[(\chi_M T)_{obs} - (\chi_M T)_{calc})]^2/$

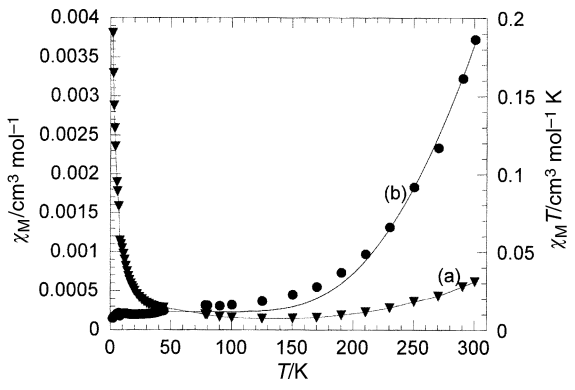

Fig. 5 (a) χ_M and (b) $\chi_M T$ *vs.* T plots for **2**.

$[\sum(\chi_M T)_{obs}]^2\}$. In the difference curve shown in Fig. 4, the contribution of the paramagnetic impurity has been subtracted.

Further work on this chemistry, including systems with genuine cyano bridges between different metal ions, is in progress and will be presented in subsequent papers.

Acknowledgements

This work was funded by the Romanian Agency of Science and Technology (Grant 4116/1999) and by NSERC of Canada (Postdoctoral fellowship to D.B.L.) We are grateful to one of the referees for useful comments on this paper.

References

1 K. R. Dunbar and R. A. Heintz, *Prog. Inorg. Chem.*, 1997, **45**, 198, references therein.
2 O. Kahn, *Adv. Inorg. Chem.*, 1995, **43**, 179.
3 V. Gadet, T. Mallah, I. Castro and M. Verdaguer, *J. Am. Chem. Soc.*, 1992, **114**, 9213.
4 T. Mallah, S. Thiebaut, M. Verdaguer and P. Veillet, *Science*, 1993, **262**, 1554.
5 W. R. Entley and G. S. Girolami, *Science*, 1995, **268**, 397.
6 M. Ohba, N. Usuki, N. Fukita and H. Okawa, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 1795.
7 S. Ferlay, T. Mallah, R. Ouahès, P. Veillet and M. Verdaguer, *Inorg. Chem.*, 1999, **38**, 229.
8 (*a*) S. Ferlay, T. Mallah, R. Ouhès, P. Veillet and M. Verdaguer, *Nature* (*London*), 1995, **378**, 701; (*b*) O. Kahn, *Nature* (*London*), 1995, **378**, 667.
9 W. R. Entley, C. R. Treadway and G. S. Girolami, *Mol. Cryst. Liq. Cryst.*, 1995, **273**, 153.
10 M. Ohba, N. Maruono, H. Okawa, T. Enoki and J. M. Latour, *J. Am. Chem. Soc.*, 1994, **116**, 11566.
11 C. Michaut, L. Ouahab, P. Bergerat, O. Kahn and A. Bousseksou, *J. Am. Chem. Soc.*, 1996, **118**, 3610.
12 R. R. Gagné, C. A. Koval, T. J. Smith and M. C. Cimolono, *J. Am. Chem. Soc.*, 1979, **101**, 4571.
13 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, *The DIRDIF-94 Program System*, Technical Report of the Crystallography Laboratory, University of Nijmegen, Nijmegen, The Netherlands, 1994.
14 *teXsan: Crystal Structure Analysis Package*, Molecular Structure Corporation, The Woodlands, TX, 1985, 1992.
15 L. K. Thompson, S. K. Mandal, S. S. Tandon, J. N. Bridson and M. K. Park, *Inorg. Chem.*, 1996, **35**, 3117.
16 B. J. Hathaway, in: *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, p. 652.