^{57}Fe Mössbauer spectroscopy predicts superstructure for $K_{0.08}[Cu^{II}(N,N'app)Cl]_2[Fe^{III}(CN)_6]\cdot 0.92H_3O\cdot 3H_2O$

Uday Mukhopadhyay,[a] C. Matthias Grunert,[b] Joachim Kusz,[c] Sergey Reiman,[b] P. Gütlich*[b] and Ivan Bernal*[a]

Received (in Cambridge, UK) 18th October 2006, Accepted 14th February 2007
First published as an Advance Article on the web 7th March 2007
DOI: 10.1039/b615130b

The compound $[Cu(N,N'app)Cl]_2[Fe(CN)_6]\cdot xH_2O$, with N,N′app being bis(*N,N′*-3-aminopropylpiperazine), was prepared and its structure determined by single crystal X-ray analysis, confirming a ratio of two copper complexes to one iron complex; ^{57}Fe Mössbauer spectra showed three quadrupole doublets typical of iron(III) low spin species which call for the presence of a superstructure.

Recently, we studied the structure and magnetic behavior of infinite one-, two- and three-dimensional arrays, where semi-planar copper–amine complexes were linked together by cyano (Cu–N–C–Fe) bonds[1,2] which acted as stereochemical linkers as well as magnetic exchange bridges between the Cu(II) and the metal hexacyanide bridges. In ref. 1 we described compounds in which the metals were Cr(III), Fe(III) and Co(III). In ref. 2 Ni(II) was used instead of Cu(II) and the hexacyanide contained Fe(III). The Cu(II) and Ni(II) described in refs. 1,2 contained, respectively, the tetramines 3,2,3-tet and 2,3,2-tet, where 3,2,3-tet = 1,5,8,12-tetraazadodecane and 2,3,2-tet = 1,4,8,11-tetraazaundecane. These ligands permit the formation of semi-planar derivatives of Cu(II) and of Ni(II) having charge-compensating axial chloride ligands which are readily displaced by the terminal nitrogens of the hexacyanides (ferro- or ferri-). Later, we decided to block access to the axial positions by the use of a piperidine in the central amine site and observe the effect of that change on the nature of the species formed, sterically, magnetically and *via* ^{57}Fe Mössbauer spectroscopy.

Also, in 2006, we reported the synthesis and structure of a compound with composition $[[Cu(N,N'app)]_2[Fe(CN)_6]\cdot 10H_2O$, with (N,N′app) being bis(*N,N′*-3-aminopropylpiperazine) which was not only novel but contained unexpected and, then unknown, quasi-planar rings of ten waters.[3] A perspective structure of the copper compound is shown in Fig. 1. This prompted us to try to prepare the ferricyanide analog. The results were not those expected, as we detail below. Parker *et al.*[4] have reported that in the presence of copper amine complexes the educt ferrocyanide oxidises to ferricyanide. They have proven this by Mössbauer spectroscopy, where the spectrum clearly shows a 1 : 1 mixture of ferro- and ferricyanide, both in the low spin state. In our study we have observed, again by Mössbauer spectroscopy, that there is no equilibration leading to a reduction of ferri- to ferrocyanide. Ferricyanide anions have exclusively been analysed in the present case.

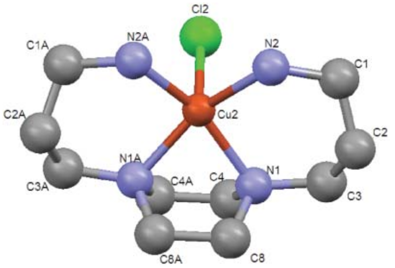

Fig. 1 The ligand N,N′app forms with Cu(II) and Cl$^-$ a cationic complex. The equivalent atoms with the additional ‘A’ letters are invoked by the mirror plane ($x,-y,z$). The hydrogen atoms are omitted.

The compound we now isolated has been characterised by single crystal X-ray diffractometry as $[Cu(N,N'app)Cl]_2[Fe(CN)_6]\cdot 4H_2O$ (Fig. 2). However, ^{57}Fe Mössbauer spectroscopy unexpectedly showed the presence of three quadrupole doublets (Fig. 3) typical of iron(III) in the low spin state located in crystallographically

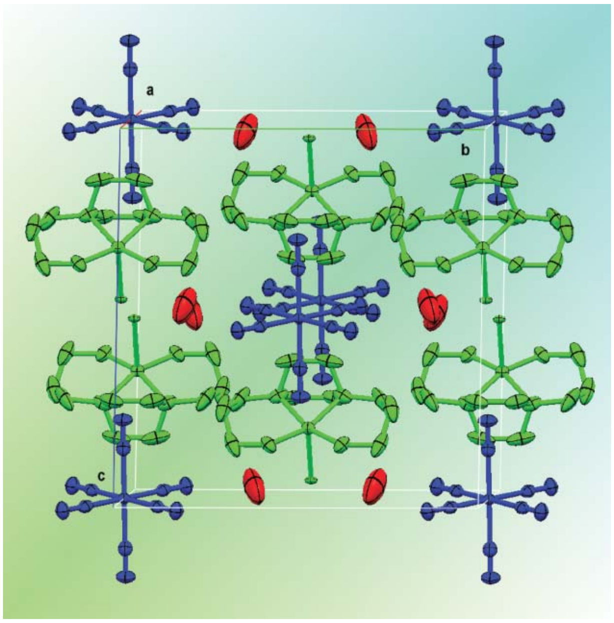

Fig. 2 View of **1** in a first model as $[Cu(N,N'app)Cl]_2[Fe(CN)_6]\cdot 2H_2O$ measured at 200 K and presented down the crystallographic *a* axis and with the use of colours to mark symmetry equivalent groups. Hydrogen atoms are omitted.[5]

---

[a] *University of Houston, Chemistry Department, Houston, TX 77204-5003, USA. E-mail: ibernal@uh.edu*
[b] *Johannes Gutenberg Universität Mainz, Institut für Anorganische Chemie und Analytische Chemie, Staudingerweg 9, D-55099 Mainz, Germany. E-mail: guetlich@uni-mainz.de*
[c] *University of Silesia, Institute of Physics, ul. Uniwersytecka 4, PL-40007 Katowice, Poland*

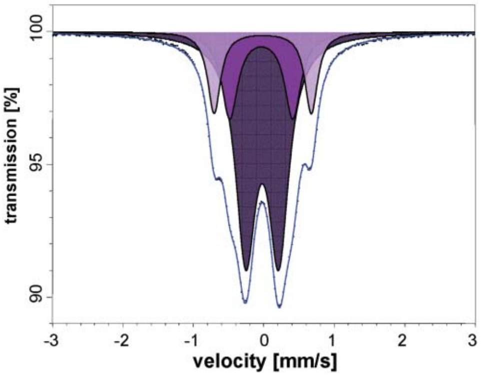

Fig. 3 The ^{57}Fe Mössbauer spectrum of **1** obtained at a temperature of 80 K can be separated into three quadrupole doublets.

inequivalent lattice sites, *i.e.* the crystal lattice has to be arranged in an unexpected superstructure. Repeated crystallographic measurements and data analysis confirm this, and according to magnetic susceptibility measurements, temperature dependent Mössbauer measurements and charge balance requirements the precise formula unit of the compound now is $K_{0.08}$[Cu(N,N′app)Cl]$_2$[Fe(CN)$_6$]·0.92H_3O·3H_2O (**1**). The superstructure includes 12 of the previously found unit cells and, therefore, contains 24 formula units of complex **1**.

Complex **1** was synthesized† by slowly adding an aqueous solution of K_3[Fe(CN)$_6$] into a solution of [Cu^{II}(N,N′app)Cl$_2$]. After a few days in the dark, the brown crystalline product was formed and collected by filtration. Single crystal diffraction was performed at 200 K. The space group of the average unit cell is *I2/m*. The unit cell contains two formula units of **1**. Cu(II) reacts with the ligand N,N′app and the chlorine ion and forms a cationic, tetragonally pyramidal complex (see Fig. 1).

The anionic iron hexacyanoferrate serves as counter ion for two copper complexes. It is not directly linked to the copper complex and is, therefore, almost of a perfect octahedral symmetry. Fig. 2 depicts in a first model the crystal packing along the *a* axis and shows further the existence of four molecules of water per formula unit, respectively eight in one unit cell. The hydrogen atoms of the ligand and the water molecules are not shown, and the atoms are colored to mark symmetry equivalent groups.

It is evident from the structural features that there are no magnetic pathways favorable for magnetic interactions between the copper and iron centers (see Fig. 2). The results from the present Mössbauer effect measurements indicate that there are three different iron lattice sites. This is in contradiction to the expectation that the hexacyanoferrate anions are not interacting with the surrounding lattice and lends support to the conclusion that a superstructure has formed, which could be confirmed by subsequent detailed structural analysis.

^{57}Fe Mössbauer spectroscopy has been employed to characterise the valence state and the molecular structure of the iron hexacyanoferrate anions in this compound. The result of the structure determination calls for symmetrical octahedral surroundings of the iron centers. In the case of hexacyanoferrate(III) the Mössbauer spectrum is expected to show a quadrupole doublet with parameter values similar to those in *e.g.*, K_3[Fe^{III}(CN)$_6$] with iron(III) in the low spin state.[6] However, the measured spectrum at 80 K, presented in Fig. 3, shows a superposition of three quadrupole doublets A, B and C with isomer shift values of −0.044(3) mm s^{-1} (A), −0.054(5) mm s^{-1} (B) and −0.036(1) mm s^{-1} (C) and quadrupole splitting values of 0.39(1) mm s^{-1} (A), 0.91(2) mm s^{-1} (B) and 1.34(2) mm s^{-1} (C). These values are typical of iron(III) low spin complexes and are very similar to the Mössbauer parameter values of hexacyanoferrate(III) compounds.[6] This assignment also fully agrees with the data from magnetic susceptibility measurements. The magnetic response at room temperature of about 1.7 cm^3·K·mol^{-1} assigns a total spin of S = $^3/_2$ and is the sum of two copper(II) centers with each S = $^1/_2$ and the iron(III) low spin complex with S = $^1/_2$. The respective area fractions of the Mössbauer resonances are 62(4)% for doublet A, 21(6)% for B and 17(3)% for C, corresponding to a population ratio of approximately 3 : 1 : 1.

The results from Mössbauer spectroscopy have stimulated us to reinvestigate the crystal structure at 90 K, 150 K, 200 K, 250 K and 300 K with a KM4 diffractometer and Oxford 600 Cryostrim Cooler.† From the temperature dependence of the mean square displacements of the thermal probability tensor U_{eq} (*T*) of the iron atom position it seemed to be clear that the iron atoms in the structure are not identical (Fig. 4), because the values of U_{eq} as a function of temperature do not extrapolate to zero at 0 K.

Therefore, a single crystal was remeasured very carefully with a KM4CCD diffractometer at 90 K and the subsequent search for satellite reflections was successful. Fig. 5 shows the reciprocal space reconstruction. There is a typical diffraction pattern with satellite reflections at 90 K which are described by wave vectors $\mathbf{q} = 1/4\mathbf{a}^* + 1/3\mathbf{c}^*$. It turned out that the structure of the compound can be interpreted on the basis of a superstructure with the space group *P2/m* and with the lattice parameters of $4a{\cdot}b{\cdot}3c$ of the expanded lattice as compared to the unit cell shown in Fig. 2. The study of the satellites in the structure determination of **1** proves the presence of a superstructure, as predicted by ^{57}Fe Mössbauer spectroscopy. The diffraction pattern at 90 K also revealed the presence of $^1/_{12}$ potassium ion in the water position. The presence of potassium was confirmed qualitatively with atomic absorption spectroscopy. It interacts with [Fe(CN)$_6$]$^{3-}$ anion *via* nitrogen to the water molecules as well as to the copper complexes *via* the chlorine atom.

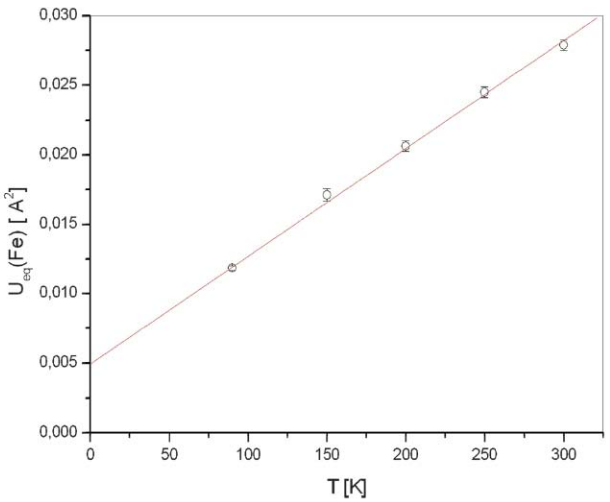

Fig. 4 Mean square thermal amplitudes U_{eq} (*T*) for the Fe atoms (circles) and their linear fit (dashed line).

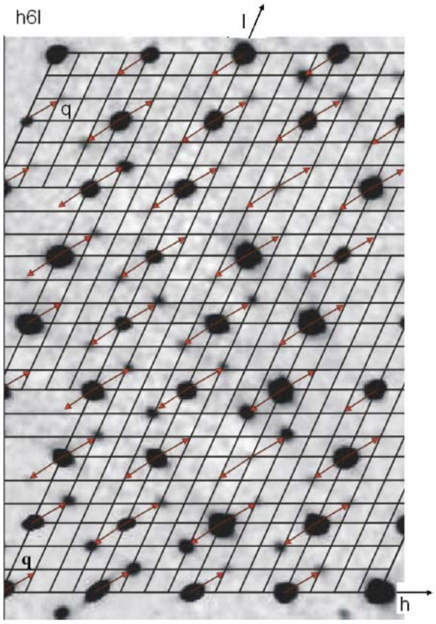

Fig. 5 A diffraction pattern of $K_{0.08}[Cu^{II}(N,N'app)Cl]_2[Fe^{III}(CN)_6]\cdot 0.92H_3O\cdot 3H_2O$ at 90 K, (*h*6*l*) layer with satellite reflections **q**.

The interactions with the large potassium atom lead to a distortion of the iron and the copper complexes (see Fig. 2). The fact that the potassium is only partially occupied in the average structure results in extremely elongated thermal ellipsoids and, therefore, the location of the atoms in the presented structure is an average over different positions of the atoms in the superstructure. To solve the complete structure including the determination of the exact positions of atoms in the superstructure, it would be necessary to repeat this experiment with synchrotron radiation to improve the resolution of the diffraction pattern. The potassium, however, is not only responsible for the formation of the superstructure. It also contributes to the charge balance in the lattice. For the full compensation of the $[Fe(CN)_6]^{3-}$ anion, part of the included water molecules is supposed to be present as H_3O^+ ions leading to the correct formula as $K_{0.08}[Cu(N,N'app)]_2[Fe(CN)_6]\cdot 0.92H_3O\cdot 3H_2O$. The presence of H_2O, H_3O^+ and K^+ is distributed in the superstructure cell such that different influences on the low spin iron(III) lattice sites become effective, which ultimately lead to the three different quadrupole doublets A, B and C in the Mössbauer spectrum. Further structural studies using synchrotron radiation are the suitable choice to confirm the population ratio 3 : 1 : 1 as derived from Mössbauer spectroscopy.

This work is part of a study of a series of related compounds. An extended report is in preparation.

Financial support of this work by Deutsche Forschungsgemeinschaft (Priority Program 1137 "Molecular Magnetism") is gratefully acknowledged. I. Bernal thanks the Robert A. Welch Foundation for support of these studies (Grant E-592) which provided postdoctoral support for U. Mukhopadhyay.

Notes and references

† Preparation of **1**: $K_3[Fe(CN)_6]$ (0.39 g, 1.2 mmol) in 20 ml water was slowly added into the aqueous solution (20 ml) of [Cu(N,N′app)Cl]Cl (0.6 g, 1.8 mmol). The clear mixture was kept in the dark for a few days. Brown well crystallised compounds were formed which were collected by filtration. These crystals were suitable for X-ray diffraction studies. The yield was 70%. Elemental analysis (%) calcd for $C_{26}H_{56.92}N_{14}O_4Cl_2Cu_2FeK_{0.08}$ (886.7 g mol^{-1}): C 35.2, H 6.47, N 22.1, found C 35.3, H 6.3, N 22.6. Crystallographic data: $C_{26}H_{52.92}N_{14}O_2Cl_2Cu_2FeK_{0.08}$, **K0.08C26H63.84N14O3.92Cl2Cu2Fe1**, $M = 892.43$, $\mu = 1.6$;

***T* = 300 K**, monoclinic, *I*2/*m*, $Z = 2$, $a = 9.7976(12)$, $b = 14.057(3)$, $c = 14.7122(16)$ Å, $\beta = 104.180(16)°$, $V = 1964.6(5)$ Å^3, number of measured/independent reflections = 3805/1909, $R_{int} = 0.022$, $R1 = 0.056/0.087$;

***T* = 250 K**, monoclinic, *I*2/*m*, $Z = 2$, $a = 9.791(2)$, $b = 14.033(5)$, $c = 14.675(2)$ Å, $\beta = 104.16(2)°$, $V = 1955.0(9)$ Å^3, number of measured/independent reflections = 3782/1828, $R_{int} = 0.021$, $R1 = 0.055/0.088$;

***T* = 200 K**, monoclinic, *I*2/*m*, $Z = 2$, $a = 9.786(2)$, $b = 13.998(5)$, $c = 14.643(2)$ Å, $\beta = 104.17(2)°$, $V = 1945.0(9)$ Å^3, number of measured/independent reflections = 3317/1661, $R_{int} = 0.022$, $R1 = 0.052/0.072$;

***T* = 150 K**, monoclinic, *I*2/*m*, $Z = 2$, $a = 9.7836(18)$, $b = 13.967(5)$, $c = 14.6155(16)$ Å, $\beta = 104.11(2)°$, $V = 1937.0(8)$ Å^3, number of measured/independent reflections = 2491/1187, $R_{int} = 0.023$, $R1 = 0.046/0.058$;

***T* = 90 K**, monoclinic, *I*2/*m*, $Z = 2$, $a = 9.8104(12)$, $b = 13.967(3)$, $c = 14.6291(16)$ Å, $\beta = 103.93(2)°$, $V = 1945.6(5)$ Å^3, number of measured/independent reflections = 19747/9683, $R_{int} = 0.034$, $R1 = 0.061/0.064$;

Crystallographic data: the average structure (without satellite reflections) of $K_{0.08}[Cu(N,N'app)Cl][Fe(CN)_6]\cdot 0.92H_3O\cdot 3H_2O$ was solved by direct methods using SHELXS-86 and refined using the SHELXL-97 program (G. Sheldrick, University of Göttingen, Germany) in space group *I*2/*m*.

The hydrogen atoms of the complex were assigned on the basis of geometric considerations and treated according to the riding model. The presence of potassium was confirmed by atomic absorption spectroscopy. The analysis revealed a very low amount of potassium which could only be proven qualitatively. We then considered the charge balance as well as the fact that the superstructure contains 12 "normal" unit cells and we arrived at the conclusion that potassium is present to 0.08 in the stoichiometry. The position of potassium was assigned near to water with the SHELXL program on the basis of highest difference Fourier peaks. The bond lengths between K1–Cl2 and K1–N3, within the error limits, are consistent with 3.284 Å and 2.870 Å, respectively. For the full compensation of the charge balance part of the included water molecules is supposed to be present as H_3O^+ ions. The exact determination of the positions of the hydrogen atoms of H_3O^+ and H_2O is not possible with conventional X-ray diffraction. Diffraction study using synchrotron radiation is the proper choice to solve the problem.

The full crystallographic data for five temperatures can be found in the supplementary material deposited at the Cambridge Crystallographic Data Centre and allocated under the deposition numbers: CCDC 622279–622283. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615130b

^{57}Fe Mössbauer spectroscopy was carried out at 80 K using a constant-acceleration conventional spectrometer with a nitrogen cryostat. The source used was ^{57}Co in a Rh-matrix with an activity of about 10 mCi and kept at room temperature. The isomer shift values are given with reference to α-iron.

1 M. K. Saha, F. Lloret and I. Bernal, *Inorg. Chem.*, 2004, **43**, 1965.
2 M. K. Saha, M. M. Moron, F. Palacio and I. Bernal, *Inorg. Chem.*, 2005, **44**, 1354.
3 U. Mukhopadhyay and I. Bernal, *Cryst. Growth Des.*, 2006, **6**, 363.
4 R. J. Parker, L. Spiccia, S. R. Batten, J. D. Cashion and G. D. Fallon, *Inorg. Chem.*, 2001, **40**, 4696.
5 At this stage we were unaware of the presence of trace amounts of potassium cations in the lattice and that the ferricyanide anions were in reality inequivalent.
6 N. N. Greenwood and T. C. Gibb, *Mössbauer Spectroscopy*, Chapman and Hall Ltd., London, 1971.