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Hydrate isomerism in $[Cu(en)_2(H_2O)_{1.935}]_2[Fe(CN)_6]\cdot 4H_2O$

Juraj Kuchár,[a]* Juraj Černák[a] and Werner Massa[b]

[a]Department of Inorganic Chemistry, P. J. Šafárik University, Moyzesova 11, SK-041 54 Košice, Slovakia, and [b]Fachbereich Chemie, Philipps Universität, Hans-Meerwein-Straße, D-35043 Marburg, Germany
Correspondence e-mail: kucharj@kosice.upjs.sk

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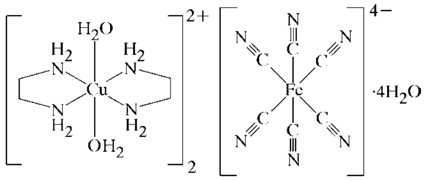
The title compound, bis[diaquabis(ethylenediamine-κ^2N,N')-copper(II)] hexacyanoiron(II) tetrahydrate, $[Cu(C_2H_8N_2)_2(H_2O)_{1.935}]_2[Fe(CN)_6]\cdot 4H_2O$, was crystallized from an aqueous reaction mixture initially containing $CuSO_4$, $K_3[Fe(CN)_6]$ and ethylenediamine (en) in a 3:2:6 molar ratio. Its structure is ionic and is built up of two crystallographically different cations, *viz*. $[Cu(en)_2(H_2O)_2]^{2+}$ and $[Cu(en)_2(H_2O)_{1.87}]^{2+}$, there being a deficiency of aqua ligands in the latter, $[Fe(CN)_6]^{4-}$ anions and disordered solvent water molecules. All the metal atoms lie on centres of inversion. The Cu atom is octahedrally coordinated by two chelate-bonded en molecules [mean Cu—N = 2.016 (2) Å] in the equatorial plane, and by axial aqua ligands, showing very long distances due to the Jahn–Teller effect [mean Cu—O = 2.611 (2) Å]. In one of the cations, significant underoccupation of the O-atom site is observed, correlated with the appearance of a non-coordinated water molecule. This is interpreted as the partial contribution of a hydrate isomer. The $[Fe(CN)_6]^{4-}$ anions form quite regular octahedra, with a mean Fe—C distance of 1.913 (2) Å. The dominant intermolecular interactions are cation–anion O—H···N hydrogen bonds and these interactions form layers parallel to (001).

Comment

Cyano complexes are often used as model compounds for studies of magneto–structural correlations (Dunbar & Heintz, 1997; Verdaguer *et al.*, 1999; Ohba & Okawa, 2000; Černák *et al.*, 2002). Previously, as part of our studies of magnetic materials, we have isolated and structurally characterized several compounds with the composition $Cu(L_N)_2Ni(CN)_4$, where L_N is a bidentate N-donor ligand (Kuchár *et al.*, 2003). Our original aim here was to extend the class of compounds studied to include another coordination polymer, in which the diamagnetic tetracyanonickelate(II) anion would be replaced by the paramagnetic cyano complex anion $[Fe(CN)_6]^{3-}$.

To date, several Cu–Fe bimetallic compounds with similar ligation of the Cu atom have been prepared and structurally characterized. Luo *et al.* (2002) synthesized and studied the compound $K[Cu(en)_2][Fe(CN)_6]$, which is built up of $[Fe(CN)_6]^{3-}$ anions, K^+ cations, and $[Cu(en)_2]^{2+}$ cations which weakly interact with the anions *via* the cyano groups [Cu—N = 2.861 (1) Å]. Using $[Fe(CN)_6]^{4-}$, Kou *et al.* (1996) studied the ferromagnetic complex $[Cu(en)]_3[Fe(CN)_6]_2\cdot 3H_2O$, which exhibits a polymeric structure. Suzuki & Uehara (1984) prepared and characterized the double complex salt $[Cu(en)_2]_2[Fe(CN)_6]\cdot nH_2O$. Moreover, Cu–Fe bimetallic compounds were found with other ligands, *e.g.* dien (diethylenetriamine; Kou *et al.*, 1997), piperazine (Kundu *et al.*, 1995) or tren [tris(2-aminoethyl)amine; Zou *et al.*, 1997]. All these exhibit polymeric structures.



(I)

Our synthesis of the title compound, (I), was carried out in aqueous solution containing, as building blocks, $[Cu(en)_2]^{2+}$ cations and $[Fe(CN)_6]^{3-}$ anions in the molar ratio 2:1. As confirmed by the crystal structure determination, compound (I), *viz*. $[Cu(en)_2(H_2O)_{1.935}]_2[Fe(CN)_6]\cdot 4H_2O$, was formed. It is clear that, during the synthesis and crystallization, reduction of $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ took place. The redox equilibrium can be complex, as Cu^{2+} cations, cyano groups and N-donor ligands were initially also present in the mixture. Moreover, the solution was in contact with air. Such systems often give rise to mixed-valence compounds (Dunaj-Jurčo *et al.*, 1988). Compound (I) was also identified by chemical analysis (see *Experimental*). The measured IR spectrum indicates the presence of the respective ligands (CN, en and H_2O) in (I).

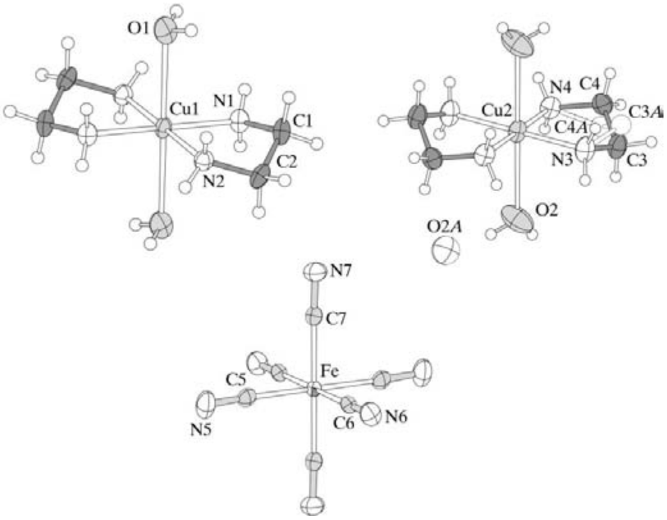


Figure 1
Plots of the two crystallographically independent cations and the anion of (I), along with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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The structure of (I) is ionic (Figs. 1 and 2). The asymmetric unit contains two crystallographically independent Cu complex cations and one $[Fe(CN)_6]^{4-}$ anion. Four solvate water molecules per formula unit are disordered over five independent sites in the space between the cations and anions, and most of their H atoms could not be located. Compound (I) is the first cyano complex containing the $[Cu(en)_2(H_2O)_2]^{2+}$ cation, although the same cation was found in, for example, $[Cu(en)_2(H_2O)_2]F_2\cdot 4H_2O$ (Emsley *et al.*, 1990).

Both Cu atoms in (I) exhibit centrosymmetric axially elongated octahedral coordination, due to the presence of the Jahn–Teller effect. The environment around both Cu atoms is very similar, with slight differences in bond lengths and angles. The four N atoms from two en ligands occupy the equatorial plane of a deformed CuN_4O_2 octahedron [mean $Cu-N_{eq}$ = 2.016 (2) Å] and water O atoms occupy the axial positions [mean $Cu-O_{ax}$ = 2.611 (2) Å]. These geometric parameters are comparable with the corresponding values in $[Cu(en)_2(H_2O)_2]F_2\cdot 4H_2O$ [$Cu-N_{eq}$ = 2.021 (2) and $Cu-O_{ax}$ = 2.572 (2) Å].

Interestingly, at atom Cu2, the H_2O ligands (O2) are only 93.4 (5)% occupied. The remaining 6.6% are in a more remote position, O2*A* [Cu2$\cdots$O2*A* = 4.29 (2) Å and O2$\cdots$O2*A* = 2.39 (1) Å]. The close distance between O2 and O2*A*, observed only in very strong symmetrical hydrogen bonds in acid systems, rules out a simultaneous occupation of both sites in this structure. Refinement of a model with a fully occupied O2 position and omitting O2*A* gives a small but significant deterioration of the refinement results: wR_2 = 0.075, R_1 = 0.030, and a residual electron density of 0.57 e Å^{-3} at the site of O2*A*. This is an example, therefore, of disorder of an elongated octahedron, *viz*. $[Cu(en)_2(H_2O)_2]^{2+}$, and its 'hydrate isomer', $[Cu(en)_2(H_2O)]^{2+}\cdot H_2O$, which has square-pyramidal coordination, or $[Cu(en)_2]^{2+}\cdot 2H_2O$, which has square-planar coordination. Both coordination geometries are well known for the Jahn–Teller-sensitive Cu^{2+} ion.

The en molecules in (I) behave as bidentate N-donor chelate-type ligands, and are in *gauche* conformations of the δ and λ types. One of them (at Cu2) shows disorder of the C atoms, with 24 (1)% occupancy of the alternative positions (Fig. 1). Such disorder is not uncommon for bis(en) complexes (Černák *et al.*, 2003). The geometric characteristics of the organic ligand are normal (Table 1) and are similar to those found in $K[Cu(en)_2][Fe(CN)_6]$ (Luo *et al.*, 2002).

The Fe central atom of (I) has an almost ideal octahedral geometry. The average Fe—C and C≡N distances are 1.913 (2) and 1.160 (3) Å, respectively, which are similar to the values found in $K_4[Fe(CN)_6]\cdot 3H_2O$ [1.925 (4) and 1.165 (1) Å, respectively; Razak *et al.*, 2000].

The coordinated water molecules, the cyano N atoms and some of the solvate water molecules are involved in O—H$\cdots$N(≡C) and O—H$\cdots$O hydrogen bonds (Table 2 and Fig. 2). Owing to severe disorder, not all of those involving solvate water can be localized clearly. As shown in Fig. 3, the dominant feature is a two-dimensional hydrogen-bonding net of Cu1 cations and $[Fe(CN)_6]^{4-}$ anions in layers parallel to the *ab* plane. Each cation is surrounded by four anions and *vice versa*. The Cu2 cations and disordered water molecules O2*A*, O4*A* and O4*B* are located between these layers (Fig. 2), and are connected by the weaker O2—H21$\cdots$N6 hydrogen bond and the disordered water molecules O4*A* and O4*B*. Possible hydrogen-bond interactions involving the NH_2 groups of the en ligands are all very weak ($D\cdots A$ > 3.0 Å, low angles) and are therefore not discussed further. The distances between the neighbouring Fe and Cu1 and Fe and Cu2 atoms are 5.380 (2) and 5.476 (2) Å, respectively.

Experimental

Single crystals of (I), in the form of dark-brown needles suitable for single-crystal X-ray diffraction, were crystallized from a solution formed by the following procedure. To a warm solution of 0.1 *M* $CuSO_4$ (30 ml, 3 mmol) was added a solution of ethylenediamine (0.39 ml, 6 mmol) in water (10 ml), followed by addition of a warm solution of 0.1 *M* $K_3[Fe(CN)_6]$ (20 ml, 2 mmol). The resulting solution was filtered and set aside for crystallization at room temperature. The first crystals appeared after 1 d. IR spectroscopy (cm^{-1}): ν(NH)

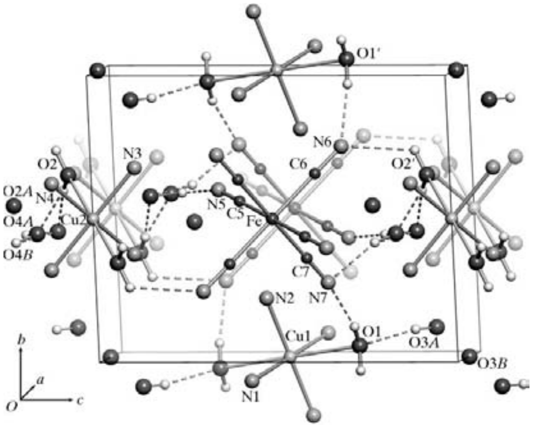

Figure 2
A packing diagram for (I). Hydrogen bonds are shown as dashed lines (for $D\cdots A < 3$ Å). For the sake of clarity, the methylene groups and the H atoms of the en ligands have been omitted. Atom O1′ is at the symmetry position (x, $1 + y$, z) and atom O2′ is at the symmetry position (x, y, $1 + z$).

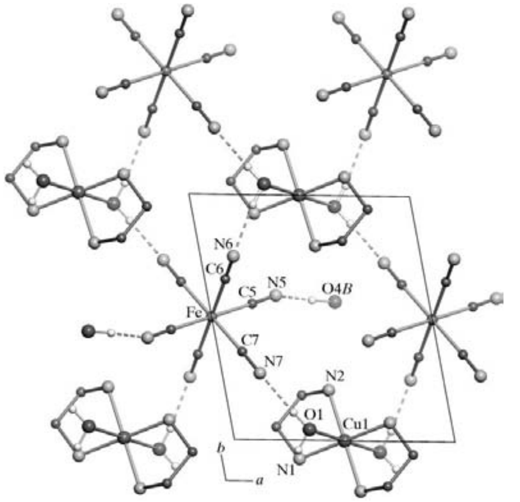

Figure 3
The two-dimensional hydrogen-bond system in (I) (dashed lines) in the (001) layers.

3309 (*vs*) and 3218 (*vs*), ν(CH) 2964 (*w*), 2945 (*w*) and 2885 (*w*), ν(CN) 2040 (*vs*), $\delta(NH_2)$ 1584 (*s*), $\delta(CH_2)$ 1452 (*m*), ν(Fe—C) 584 (*m*), δ(Fe—CN) 421 (*s*). CHN analysis (found/calculated): C 23.5/23.2, H 6.4/6.7, N 27.4/27.1%.

Crystal data

$[Cu(C_2H_8N_2)_2(H_2O)_{1.935}]_2$-$[Fe(CN)_6]\cdot 4H_2O$
$M_r = 721.07$
Triclinic, $P\overline{1}$
$a = 7.9407$ (6) Å
$b = 8.9815$ (7) Å
$c = 10.9523$ (10) Å
$\alpha = 91.072$ (10)°
$\beta = 91.061$ (10)°
$\gamma = 101.290$ (9)°
$V = 765.67$ (11) Å^3
$Z = 1$
$D_x = 1.564$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7673 reflections
$\theta = 2.7$–25.9°
$\mu = 1.90$ mm^{-1}
$T = 193$ (1) K
Needle, brown
0.38 × 0.10 × 0.06 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: multi-scan (*XPREP* in *SHELXTL*; Siemens, 1996)
$T_{min} = 0.462$, $T_{max} = 0.892$
7571 measured reflections
2774 independent reflections
2408 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 25.9°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 11$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.073$
$S = 0.99$
2774 reflections
243 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.0138 (19)	N3—C3	1.468 (4)
Cu1—N2	2.0183 (18)	C3—C4	1.499 (6)
Cu1—O1	2.6244 (19)	C4—N4	1.463 (4)
N1—C1	1.478 (3)	Fe—C6	1.911 (2)
C1—C2	1.502 (4)	Fe—C7	1.914 (2)
C2—N2	1.478 (3)	Fe—C5	1.915 (2)
Cu2—N4	2.0125 (18)	C5—N5	1.158 (3)
Cu2—N3	2.021 (2)	C6—N6	1.162 (3)
Cu2—O2	2.597 (3)	C7—N7	1.158 (3)
N1—Cu1—N2	84.34 (8)	C3—N3—Cu2	108.37 (18)
N1—Cu1—O1	94.96 (7)	N3—C3—C4	109.4 (4)
N2—Cu1—O1	89.76 (7)	N4—C4—C3	108.5 (3)
N1—C1—C2	108.17 (17)	C6—Fe—C7	90.03 (9)
N2—C2—C1	108.16 (18)	C6—Fe—C5	91.47 (9)
C2—N2—Cu1	108.47 (14)	C7—Fe—C5	90.68 (9)
N4—Cu2—N3	84.68 (8)	N5—C5—Fe	177.1 (2)
N4—Cu2—O2	90.35 (8)	N6—C6—Fe	179.0 (2)
N3—Cu2—O2	82.89 (10)	N7—C7—Fe	178.0 (2)

Table 2
Geometry of hydrogen bonds (Å, °) with $D\cdots A < 3.0$ Å.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H11$\cdots$N6^{i}	0.850 (19)	1.988 (18)	2.825 (2)	168 (3)
O1—H12$\cdots$N7	0.85 (3)	1.97 (3)	2.804 (3)	166 (3)
O2—H21$\cdots$N6^{ii}	0.85 (3)	2.56 (5)	2.947 (4)	109 (4)
O2—H22$\cdots$O4*A*	0.85 (3)	1.98 (5)	2.826 (14)	172 (4)
O2—H22$\cdots$O4*B*	0.85 (3)	1.81 (5)	2.600 (16)	154 (4)
O3*A*—H3O*A*$\cdots$O1	0.84 (3)	1.99 (3)	2.816 (4)	165 (4)

Symmetry codes: (i) $x, y - 1, z$; (ii) $x, y, z - 1$.

The H atoms of the coordinated water molecules (O1 and O2) were refined with restraints on the bond lengths (0.85 Å) and a common U_{iso}(H). The H atoms at nitrogen of the ordered en ligand (N1 and N2) were also refined with common U_{iso} values by groups. The H atoms of the CH_2 groups and all H atoms of the second disordered en ligand (N4 and N5) were treated as riding on idealized positions, with C—H distances of 0.99 Å and N—H distances of 0.92 Å. The solvate water molecules (O3 and O4) are disordered over two positions and a centre of symmetry. Only some of these H atoms could be localized. Both C atoms of the en ligand at Cu2 are disordered over two positions. The aqua ligand O2 at Cu2 is disordered over two positions, the minor component (O2*A*) having no bond to Cu and belonging to the region of solvate water (O4*A*/O4*B*). Free refinement of the site occupancies for O2*A*, O4*A* and O4*B* sums to 1.00.

Data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1999); cell refinement: *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1319). Services for accessing these data are described at the back of the journal.

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