Data collection

Siemens SMART area-detector diffractometer
ω rotation scans with narrow frames
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.53$, $T_{\max} = 0.87$
12 182 measured reflections
4394 independent reflections
3485 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 27.5°$
$h = -16 \rightarrow 25$
$k = -17 \rightarrow 15$
$l = -19 \rightarrow 19$
Intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.028$
$wR(F^2) = 0.064$
$S = 1.074$
4394 reflections
217 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.003$
$\Delta\rho_{\max} = 0.526$ e Å^{-3}
$\Delta\rho_{\min} = -0.391$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

In1—N12^{i}	2.193 (2)	In1—N21	2.289 (2)
In1—N11	2.223 (2)	In1—Cl1	2.4449 (7)
In1—O31	2.230 (2)	In1—Cl2	2.4591 (8)
N12^{i}—In1—N11	97.38 (8)	O31—In1—Cl1	89.53 (6)
N12^{i}—In1—O31	86.73 (8)	N21—In1—Cl1	94.27 (6)
N11—In1—O31	82.12 (8)	N12^{i}—In1—Cl2	96.68 (7)
N12^{i}—In1—N21	168.38 (8)	N11—In1—Cl2	93.72 (6)
N11—In1—N21	73.36 (8)	O31—In1—Cl2	174.96 (5)
O31—In1—N21	85.07 (8)	N21—In1—Cl2	91.02 (6)
N12^{i}—In1—Cl1	93.88 (6)	Cl1—In1—Cl2	93.94 (3)
N11—In1—Cl1	165.55 (6)	C32—O31—In1	128.8 (2)

Symmetry code: (i) $1 - x, -y, -z$.

Unit-cell dimensions were determined from reflections taken from three sets of 30 frames (at 0.3° steps in ω) each at 20 s exposure. Slightly more than a full hemisphere of reciprocal space was scanned by 0.3° ω steps at φ = 0, 90 and 180° with the area detector held at $2\theta = -29°$ and each frame exposed for 20 s. The crystal-to-detector distance was 4.94 cm. The absence of crystal decay was established by repeating the initial 50 frames at the end of data collection and analysing the duplicate reflections. The data were corrected empirically for absorption effects (Sheldrick, 1996) and refined by full-matrix least squares on all F^2 data using *SHELXTL* (Siemens, 1995*a*). H atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the $U_{\rm iso}$ value of their attached atom (for aromatic or other sp^2 C atoms) or 1.5 times the $U_{\rm iso}$ value of their attached atom (for all others).

Data collection: *SMART* (Siemens, 1995*b*). Cell refinement: *SAINT* (Siemens, 1995*b*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1995*a*). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1206). Services for accessing these data are described at the back of the journal.

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Dipotassium (2,2′-Bipyridyl-*N*,*N*′)-tetracyanoferrate(II) 2.5-Hydrate, $K_2[Fe(bpy)(CN)_4].2.5H_2O$

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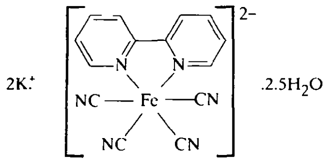
Abstract

Analysis of the title complex, $K_2[Fe(CN)_4(C_{10}H_8N_2)]$.-$2.5H_2O$, shows that the asymmetric unit contains two $[Fe(bpy)(CN)_4]^{2-}$ units, four K^+ ions and five water molecules. There is extensive hydrogen bonding within the structure and, as expected, all hydrogen-bond donors and acceptors are involved in hydrogen bonding, resulting in a complex three-dimensional network. The water molecules and K^+ ions occupy three different channels in the framework created by the packing of the $[Fe(bpy)$-$(CN)_4]^{2-}$ units.

Comment

The spectroscopic and excited-state properties of tetracyano compounds of the type $[Fe(L–L)(CN)_4]^{2-}$, where *L–L* is a polypyridyl ligand such as 2,2′-bipyridyl (bpy), 1,10-phenanthroline or bipyrimidine, have been studied in detail (Blundell *et al.*, 1989; Burgess *et al.*, 1992;

Blandamer *et al.*, 1993; Kotowsky *et al.*, 1987; Ruminski *et al.*, 1984; Brewer *et al.*, 1987, 1989; Schilt & Cresswell, 1966). Interest in these systems has arisen from efforts to describe the bonding therein, their application as probes for micellar systems (Blandamer *et al.*, 1993) and piezoelectric and thermochromic behaviour (Kotowsky *et al.*, 1987). Combination of strong σ-donating ligands with π-acceptor ligands may enable the formation of photostable iron complexes (Brewer *et al.*, 1985). However, investigations of these systems have been hampered by poor crystal quality and substantial disorder (Tullberg & Vannerburg, 1974; Lanfranconi *et al.*, 1973; Manoharan & Hamilton, 1963; Swanson *et al.*, 1974; Pierrot *et al.*, 1966; Christoph & Goedken, 1973; Buser *et al.*, 1977; Herren *et al.*, 1980; Garcia Posse *et al.*, 1984). This is not the case with $K_2[Fe(bpy)(CN)_4].2.5H_2O$, (1), which forms well defined crystals. The extensive pattern of hydrogen bonding and the electrostatic interactions promote the formation of an ordered crystal structure. Crystal engineering of metal complexes and the systematic design of metal-containing complexes based on complementary hydrogen-bonding motifs has attracted increasing attention in the last few years (Aakeröy & Seddon, 1993).



(1)

The asymmetric unit contains two $[Fe(bpy)(CN)_4]^{2-}$ units, four K^+ ions and five water molecules. The geometry of the two $[Fe(bpy)(CN)_4]^{2-}$ units is consistent and there are no significant deviations from the expected octahedral coordination of the Fe atoms within these units. The basic building block of the structure is a C—H···N hydrogen-bonded $[Fe(bpy)(CN)_4]^{2-}$ dimer and these dimers are formed into chains through further C—H···N hydrogen bonding (Table 2). The chains then form sheets through $\pi\cdots\pi$ interactions between the bipyridyl moieties of adjacent chains (3.5–3.9 Å) and these sheets pack together such that they form three different channels within the structure. The channels, which have differing sizes and shapes, zigzag through the lattice in the [001] direction and are occupied by either K^+ ions, or K^+ ions and water molecules (Fig. 2). The first type of channel (type I) is rectangular and is defined by an N atom of a cyano group at each corner. The second type of channel (type II) is hexagonal and is defined by four N atoms and two H atoms at the vertices. The third channel type (type III) is octagonal and is defined by four N atoms and four H atoms at the vertices.

Type I channels contain only K^+ ions which are located at the intersection of the diagonals of the rectangle defined by the equatorial cyano N atoms. Type II channels contain K^+ ions and water molecules in a 1:1 ratio. Finally, type III channels contain water molecules and K^+ ions in a 4:1 ratio. The channels alternate ..1,2,1,3,1,.. parallel to the *a* axis and the adjacent motif is staggered so that type I channels are aligned parallel to the *b* axis. The K^+ ions in channel type I, K1 and K2, are octahedrally coordinated by six cyano N atoms, with distances in the range 2.846 (4)–3.117 (4) Å. In channel type II, the K^+ ions, K4, are surrounded by four cyano N atoms and two symmetry-related water molecules. Two of the cyano groups have shorter K···N distances for K4 compared with K1 and K2 above, and the coordination environment of K4 is trigonally-distorted octahedral. The water molecules bridge the K4 ions and are hydrogen bonded to the cyano N atoms from two different $[Fe(bpy)(CN)_4]^{2-}$ units, adding to the stability of the two-dimensional $[Fe(bpy)(CN)_4]^{2-}$ sheets.

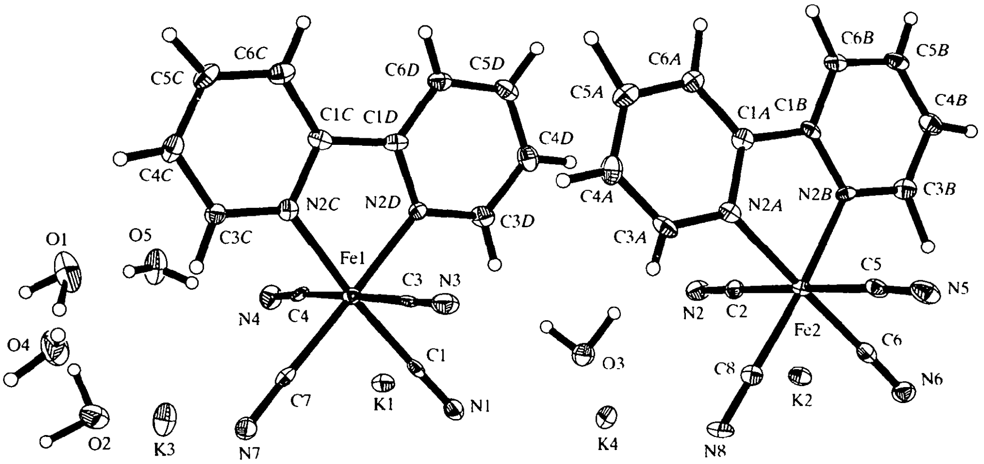


Fig. 1. The asymmetric unit for $K_2[Fe(bpy)(CN)_4].2.5H_2O$ with 50% probability ellipsoids.

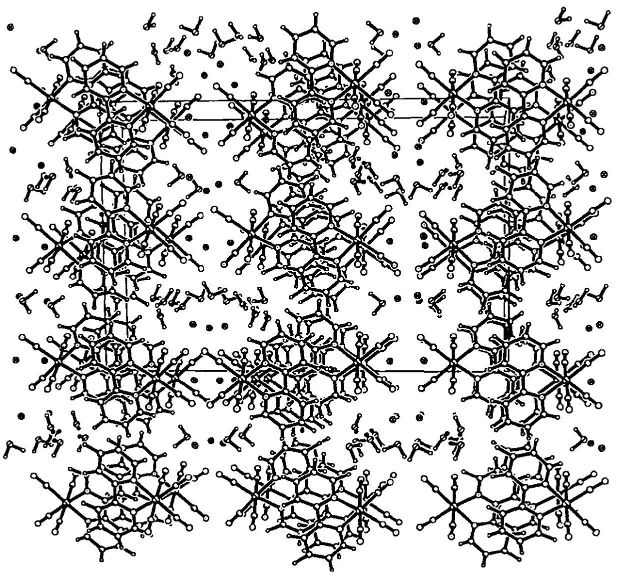


Fig. 2. Crystal packing showing the channels containing cations and water molecules. The view direction is along **c**, with **a** vertical and **b** horizontal.

Finally, the type III channels each contain a tape of hydrogen-bonded water molecules coordinated to the K3 K^+ ions. The K^+ ions are seven-coordinate, surrounded by four water molecules, at 2.825 (4)–3.234 (4) Å, and three cyano N atoms, at 2.938 (4)–3.132 (4) Å. The hydrogen-bonded tape of water molecules also forms hydrogen bonds with the cyano N atoms and again stabilizes the $[Fe(bpy)(CN)_4]^{2-}$ sheet motif.

The $[Fe(bpy)(CN)_4]^{2-}$ anions are related by an approximate non-crystallographic inversion centre at (0.25,0.36,0.75), but this does not apply to the K^+ cations and water molecules.

Experimental

$K_2[Fe(bpy)(CN)_4].2.5H_2O$, (1), was prepared from $[Fe(bpy)_2(CN)_2]$ and KCN as described by Schilt & Cresswell (1966), and recrystallized from water.

Crystal data

$K_2[Fe(CN)_4(C_{10}H_8N_2)].2.5H_2O$
$M_r = 439.35$
Monoclinic
$P2_1/c$
$a = 17.765\ (1)$ Å
$b = 26.708\ (2)$ Å
$c = 7.6153\ (9)$ Å
$\beta = 99.46\ (1)°$
$V = 3563.9\ (6)$ Å^3
$Z = 8$
$D_x = 1.638$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 5.0–12.5°$
$\mu = 1.337$ mm^{-1}
$T = 293\ (2)$ K
Block
0.58 × 0.46 × 0.21 mm
Red

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: empirical ψ scans (Sheldrick, 1990*b*)
$T_{min} = 0.617$, $T_{max} = 0.755$
6753 measured reflections
6245 independent reflections
4071 reflections with $I > 2\sigma(I)$

$R_{int} = 0.033$
$\theta_{max} = 25°$
$h = -21 \rightarrow 20$
$k = -31 \rightarrow 0$
$l = 0 \rightarrow 8$
3 standard reflections every 97 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.093$
$S = 1.121$
6241 reflections
460 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 4.5423P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.441$ e Å^{-3}
$\Delta\rho_{min} = -0.406$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

N2*A*—Fe2	2.003 (4)	K2···N8^{i}	2.899 (4)
N2*B*—Fe2	1.993 (4)	K2···N2	2.941 (4)
N2*C*—Fe1	1.987 (4)	K2···N6	3.033 (4)
N2*D*—Fe1	1.994 (4)	K2···N6^{i}	3.048 (4)
Fe1—C1	1.891 (5)	K2···N8^{ii}	3.104 (4)
Fe1—C7	1.907 (5)	K3···O2^{iii}	2.825 (4)
Fe1—C3	1.931 (5)	K3···O2	2.841 (4)
Fe1—C4	1.936 (5)	K3···N7^{i}	2.938 (4)
Fe2—C8	1.896 (5)	K3···N7	3.020 (4)
Fe2—C6	1.898 (5)	K3···N4	3.132 (4)
Fe2—C5	1.930 (5)	K3···O4	3.141 (4)
Fe2—C2	1.931 (5)	K3···O1	3.234 (4)
K1···N1^{i}	2.873 (4)	K4···O3^{iii}	2.672 (3)
K1···N3^{ii}	2.904 (4)	K4···N1	2.765 (4)
K1···N1	2.928 (4)	K4···O3	2.781 (4)
K1···N4	2.941 (4)	K4···N8^{i}	2.798 (4)
K1···N7^{i}	3.056 (4)	K4···N8	3.117 (4)
K1···N7^{ii}	3.117 (4)	K4···N2	3.156 (4)
K2···N5^{ii}	2.846 (4)		

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x, y, z - 1$; (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
O1—H11···N5^{i}	1.897 (5)	2.816 (5)	154.96 (17)
O2—H21···N6^{ii}	1.985 (5)	2.966 (5)	159.36 (15)
O2—H22···N5^{i}	2.691 (6)	3.553 (6)	145.75 (11)
O3—H32···N2	1.970 (5)	2.793 (5)	136.78 (14)
O3—H31···N3^{iii}	1.880 (5)	2.817 (5)	174.84 (16)
O4—H41···N6^{iv}	2.151 (5)	3.012 (5)	157.65 (14)
O5—H52···N4	2.004 (5)	2.829 (5)	160.57 (15)
O1—H12···O4	1.728 (6)	2.789 (6)	162.49 (17)
O2—H22···O5	2.518 (5)	3.129 (5)	119.70 (11)
O4—H42···O5^{v}	1.933 (5)	2.822 (5)	171.99 (15)
O5—H51···O1	1.954 (5)	2.842 (5)	174.22 (16)
C3*D*—H3*D*···N1	2.764 (6)	3.577 (6)	146.47 (12)
C5*B*—H5*B*···N2^{vi}	2.534 (6)	3.426 (6)	161.50 (14)
C5*C*—H5*C*···N3^{vii}	2.607 (6)	3.449 (6)	145.98 (13)
C6*C*—H6*C*···N4^{viii}	2.921 (6)	3.943 (6)	170.08 (12)
C6*D*—H6*D*···N4^{viii}	2.711 (6)	3.642 (6)	163.34 (13)
C6*A*—H6*A*···N5^{ix}	2.480 (6)	3.525 (6)	168.08 (14)
C6*B*—H6*B*···N5^{ix}	2.688 (6)	3.753 (6)	170.04 (12)

C3*B*—H3*B*···N6	2.709 (6)	3.706 (6)	142.27 (12)
C3*C*—H3*C*···N7	2.916 (6)	3.731 (6)	143.11 (11)
C3*A*—H3*A*···N8	3.030 (6)	3.614 (6)	136.54 (11)

Symmetry codes: (i) $x-1, y, z-1$; (ii) $x-1, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $x, y, z-1$; (iv) $x-1, y, z$; (v) $x, y, 1+z$; (vi) $1-x, 1-y, 1-z$; (vii) $-x, 1-y, 2-z$; (viii) $-x, 1-y, 1-z$; (ix) $1-x, 1-y, 2-z$.

H atoms were located in a difference synthesis and refined with a riding model and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(C or O).

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1210). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 606–608

Diaquachlorobis(4-pyridinioacetate-*O*)-copper(II) Perchlorate

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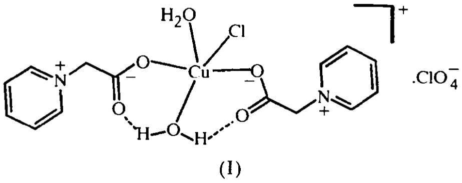
Abstract

In the title compound, $[CuCl(C_7H_7NO_2)_2(H_2O)_2]ClO_4$, the metal atom is coordinated in a distorted square-pyramidal environment with one aqua ligand [Cu—O 1.944 (4) Å], one chloride ion [Cu—Cl 2.2538 (15) Å] and two monodentate carboxylate O atoms [Cu—O 1.994 (4) and 2.004 (4) Å] in basal positions. The apical position is occupied by another aqua ligand [Cu—O 2.367 (4) Å].

Comment

Recently, we used zwitterionic betaines to prepare metal carboxylate complexes containing anionic ligands. The compounds included some dimeric copper(II) complexes in which the anionic ligands are axial (Chen & Mak, 1993; Chen *et al.*, 1997). In order to relate their magnetic properties and structures, we have synthesized several new dimeric copper(II)–carboxylate complexes containing different types of carboxylate bridge, as well as different types of axial ligand. The title complex, the mononuclear species $[CuCl(pybet)_2(H_2O)_2]ClO_4$, (I) (pybet is pyridinioacetate, $C_5H_5N^+CH_2O_2^-$), was obtained as a minor product (Chen *et al.*, 1998). We describe its crystal structure herein.



(I)

The crystals consist of discrete monomeric $[CuCl(pybet)_2(H_2O)_2]^+$ cations and perchlorate anions. The Cu^{II} atom is in a distorted square-pyramidal environment, being coordinated at the basal positions by one aqua ligand [Cu—O1*w* 1.944 (4) Å], one chloro ligand [Cu—Cl 2.2538 (15) Å] and two *trans* monodentate carboxylate ligands [Cu—O 1.994 (4) and 2.004 (4) Å],

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