Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, p. 293. Copenhagen: Munksgaard.

Marzluff, W. F. (1964). *Inorg. Chem.* **3**, 395–397.

Spek, A. L. (1994). *PLATON94. Molecular Geometry Program*. Univ. of Utrecht, The Netherlands.

Stiefel, E. I. (1977). *Prog. Inorg. Chem.* **22**, 1–223.

Taylor, R. S., Gans, P., Knowles, P. F. & Sykes, A. G. (1972). *J. Chem. Soc. Dalton Trans.* pp. 24–28.

Cs6Cl3[Fe(CN)6].H2O: a Mixed-Anion Salt

Mario V. Capparelli and Juan Murgich

Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela

Abstract

Hexacaesium trichloride hexacyanoferrate(III) monohydrate, $Cs_6Cl_3[Fe(CN)_6].H_2O$, is a novel type of compound which contains two different anions. The crystal structure consists of alternating layers, A {Cs^+, Cl^-, $[Fe(CN)_6]^{3-}$, H_2O} and B (Cs^+, Cl^-), stacked perpendicularly to the b axis. The octahedral complex ion has m point symmetry. The water molecules of solvation are disordered and form hydrogen bonds (O—H···Cl and O—H···N) within layer A. The Cs^+ ions have coordination numbers six to eight.

Comment

Potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$, has been studied extensively by different techniques because of its interesting properties, such as the existence of polytypes (Vannerberg, 1972; Figgis, Skelton & White, 1978; Murgich & Oja, 1987; Murgich, 1994), one-dimensional disorder (Murgich & Oja, 1987), the possible existence of incommensuration in the low-temperature phase (Murgich & Oja, 1987), *etc*. In addition, the crystal and magnetic structures, phase transitions and spectroscopic data of several mixed-cation salts, such as $Cs_2M[Fe(CN)_6]$ (M = Li, Na, K) have been determined (Jones, Swanson & Kubas, 1974; Fletcher & Gibb, 1977; Swanson, Lucas & Ryan, 1977; Daul *et al.*, 1988).

As a part of a study on the effects of different cations on the structure and properties of hexacyanoferrates(III), the preparation of the $Cs_3[Fe(CN)_6]$ salt was attempted, following the synthesis of Garg & Goel (1970). Microscopic examination of the resultant product showed two different types of crystals, orange–yellow prisms and yellow needles, neither of which turned out to be the target compound. A crystal structure determination of the orange–yellow prisms revealed that they were $Cs_2K[Fe(CN)_6]$, already studied by several authors (Fletcher & Gibb, 1977; Herren & Ludi, 1979; Figgis, Kucharski, Raynes & Reynolds, 1990). This paper reports the structure of the mixed salt $Cs_6Cl_3[Fe(CN)_6].H_2O$ that forms the yellow needles.

The crystal structure of the title compound contains Cs^+, Cl^- and $[Fe(CN)_6]^{3-}$ ions and disordered water molecules of solvation. Some of the Cs^+ and Cl^- ions lie on the mirror plane ($y = \frac{1}{4}$, Wyckoff c sites). Since the $N(1)C(1)FeC(2)N(2)$ axis of $[Fe(CN)_6]^{3-}$ also lies on the mirror plane, the octahedral complex has m crystallographic point symmetry.

The average values of the Fe—C (1.941 Å) and C—N (1.15 Å) bond lengths are in good agreement with the mean values of 1.937 and 1.146 Å compiled by Orpen *et al.* (1989). All four independent Fe—C distances are equal within three e.s.d.'s. The differences between the C—N bond lengths are somewhat larger (up to five e.s.d.'s), but probably not significant. The octahedral geometry of the $[Fe(CN)_6]^{3-}$ ion is moderately distorted. All of the C—Fe—C and Fe—C—N angles are within 5° of 90 or 180°, but their values depart significantly from the nominal values.

The O(1w) atom of the water molecule is close (0.68 Å) to the mirror plane and was given an occupancy of 0.5, because both of the mirror-related positions are mutually exclusive. The largest residual electron density peak (1.4 e Å^{-3}) is located on the mirror plane between the symmetry-related O(1w) atoms (the next largest peak is of a magnitude similar to that of the most negative peak).

The Cs^+ and Cl^- ions are spherical and of similar sizes, but the $[Fe(CN)_6]^{3-}$ ion has a more complex shape, with six protruding arms, which may produce voids in the crystal structure. The water molecule fills one of these voids, which is somewhat larger than the volume of the water molecule and allows disorder. The actual disorder of the solvent molecules is caused by their hydrogen bonding. One of the hydrogen bonds is to Cl(1), which lies on the mirror plane and is unique, but the other one is directed to N(4), which has two equally accessible mirror-related positions. The location of the water molecule on either side of the mirror plane is determined by this second hydrogen bond and therefore a 50–50% distribution is expected.

Each of the four Cs^+ ions is surrounded by six to eight negatively charged atoms (O, N and Cl^-). The neighbouring atoms form irregular polyhedra, with distances in the ranges 2.99–3.35 for $Cs^+ \cdots O$, 3.17–3.61 for $Cs^+ \cdots N$ and 3.41–3.75 Å for $Cs^+ \cdots Cl^-$. These values are within −6.3 to 10.7% of the sums of the respective radii [Cl^- and Cs^+ (CN = 6, 8) from

Shannon (1976); Cs^+ (CN = 7) calculated according to Pauling (1960); O and Cl from Bondi (1964)]. Most of the $Cs^+\cdots N$ distances are larger than the sum of the corresponding radii, indicating a rather weak interaction between caesium and the complex ion.

The crystal structure can be described as formed by alternating layers, A and B, stacked along [010]. Layer A ($\frac{1}{4}$) is formed by Cs(1), Cs(2), Cl(1), $[Fe(CN)_6]^{3-}$ and the water molecules, which are hydrogen bonded to Cl(1) and to the complex ion [through N(4)], while layer B ($\frac{1}{2}$) is composed of Cs(3), Cs(4) and Cl(2). If the charge of the $[Fe(CN)_6]^{3-}$ ion is assumed to be localized on the N atoms (*i.e.* a charge of $-\frac{1}{2}$ on each N), and these atoms are assigned either to layer A [N(1), N(2)] or B [N(3), N(4)], depending on their y coordinate, then the charge sum for each layer is zero.
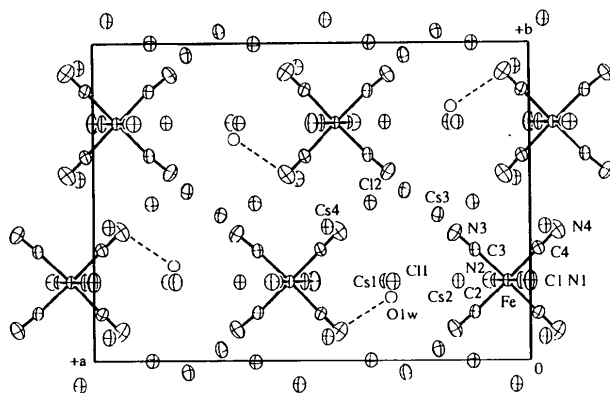

Fig. 1. The crystal structure and atom-numbering scheme of the title compound viewed down the c axis. Displacement ellipsoids are drawn at 50% probability.

Experimental

The title compound was obtained by the double decomposition of a stoichiometric mixture of $Ag_3[Fe(CN)_6]$ and CsCl (Garg & Goel, 1970). The insoluble $Ag_3[Fe(CN)_6]$ was prepared by reacting $AgNO_3$ and $K_3[Fe(CN)_6]$. It is thought that the $Cs_2K[Fe(CN)_6]$ salt obtained along with the title compound came from unreacted $K_3[Fe(CN)_6]$, which was retained by the $Ag_3[Fe(CN)_6]$ precipitate.

Crystal data

$Cs_6Cl_3[Fe(CN)_6].H_2O$	Mo $K\alpha$ radiation
$M_r = 1133.76$	$\lambda = 0.71069$ Å
Orthorhombic	Cell parameters from 25
$Pnma$	reflections
$a = 18.560\,(3)$ Å	$\theta = 15.5–19.6°$
$b = 13.335\,(4)$ Å	$\mu = 9.959$ mm^{-1}
$c = 9.677\,(3)$ Å	$T = 295\,(1)$ K
$V = 2395.0\,(9)$ Å^3	Needle
$Z = 4$	$0.30 \times 0.18 \times 0.14$ mm
$D_x = 3.144$ Mg m^{-3}	Yellow

Data collection

Rigaku AFC-7S diffractometer	2431 observed reflections
	$[I > 3\sigma(I)]$
$\omega–2\theta$ scans	$\theta_{max} = 27.50°$
Absorption correction:	$h = 0 \rightarrow 24$
refined from ΔF	$k = 0 \rightarrow 17$
(*DIFABS*; Walker &	$l = -12 \rightarrow 0$
Stuart, 1983)	3 standard reflections
$T_{min} = 0.748$, $T_{max} =$	monitored every 150
1.000	reflections
3137 measured reflections	intensity decay: 0.24%
3137 independent reflections	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.0006$
$R = 0.0243$	$\Delta\rho_{max} = 1.44$ e Å^{-3}
$wR = 0.0276$	$\Delta\rho_{min} = -0.83$ e Å^{-3}
$S = 2.188$	Extinction correction: none
2431 reflections	Atomic scattering factors
116 parameters	from *International Tables*
Weighting scheme based	*for X-ray Crystallography*
on measured e.s.d.'s	(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

U_{iso} for O(1w); $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for other atoms.

	x	y	z	U_{iso}/U_{eq}
Cs(1)	0.33360 (3)	1/4	−0.15765 (6)	0.0373 (2)
Cs(2)	0.16600 (3)	1/4	−0.53558 (6)	0.0336 (1)
Cs(3)	0.21132 (2)	0.46254 (3)	0.11326 (4)	0.0358 (1)
Cs(4)	0.46585 (2)	0.42461 (3)	0.21140 (4)	0.0374 (1)
Fe	0.05403 (5)	1/4	−0.1437 (1)	0.0221 (3)
Cl(1)	0.3150 (1)	1/4	0.2023 (3)	0.0445 (7)
Cl(2)	0.36862 (8)	0.4991 (1)	−0.0741 (2)	0.0355 (4)
N(1)	0.0000 (4)	1/4	−0.4460 (7)	0.045 (2)
N(2)	0.0945 (4)	1/4	0.1673 (8)	0.042 (2)
N(3)	0.1753 (3)	0.4023 (4)	−0.2125 (5)	0.044 (2)
N(4)	−0.0590 (3)	0.4098 (5)	−0.0740 (7)	0.060 (2)
C(1)	0.0212 (4)	1/4	−0.3336 (9)	0.033 (2)
C(2)	0.0812 (4)	1/4	0.0491 (8)	0.027 (2)
C(3)	0.1281 (3)	0.3490 (4)	−0.1867 (6)	0.028 (1)
C(4)	−0.0169 (3)	0.3524 (4)	−0.0993 (6)	0.030 (1)
O(1w)	0.3205 (5)	0.1990 (8)	0.486 (1)	0.064 (3)

Table 2. *Selected geometric parameters* (Å, °)

Fe—C(1)	1.936 (8)	N(1)—C(1)	1.16 (1)
Fe—C(2)	1.932 (8)	N(2)—C(2)	1.17 (1)
Fe—C(3)	1.950 (6)	N(3)—C(3)	1.156 (7)
Fe—C(4)	1.945 (6)	N(4)—C(4)	1.121 (7)
C(1)—Fe—C(3)	91.1 (2)	C(1)—Fe—C(2)	176.8 (3)
C(1)—Fe—C(4)	89.8 (2)	C(3)—Fe—C(4^i)	177.8 (2)
C(2)—Fe—C(3)	91.3 (2)	Fe—C(1)—N(1)	178.5 (7)
C(2)—Fe—C(4)	87.9 (2)	Fe—C(2)—N(2)	177.1 (7)
C(3)—Fe—C(3^i)	85.2 (3)	Fe—C(3)—N(3)	175.3 (5)
C(3)—Fe—C(4)	92.8 (2)	Fe—C(4)—N(4)	178.4 (6)
C(4)—Fe—C(4^i)	89.2 (3)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Table 3. *Contact distances* (Å)

Cs(1)$\cdots$O(1w)	3.25 (1)	Cs(3)$\cdots$N(3^{vii})	3.244 (5)
Cs(1)$\cdots$N(1^i)	3.248 (7)	Cs(3)$\cdots$N(4^{viii})	3.322 (6)
Cs(1)$\cdots$N(3)	3.611 (6)	Cs(3)$\cdots$Cl(1)	3.533 (2)
Cs(1)$\cdots$N(3^{ii})	3.611 (6)	Cs(3)$\cdots$Cl(2)	3.471 (2)
Cs(1)$\cdots$Cl(1)	3.500 (3)	Cs(3)$\cdots$Cl(2^{vii})	3.408 (2)
Cs(1)$\cdots$Cl(2)	3.479 (2)	Cs(4)$\cdots$N(1^i)	3.524 (5)

Cs(1)· · ·Cl(2ⁱⁱ)	3.479 (2)	Cs(4)· · ·N(2ⁱˣ)	3.535 (6)
Cs(2)· · ·O(1w)	2.99 (1)	Cs(4)· · ·N(3ᵛⁱⁱ)	3.569 (6)
Cs(2)· · ·N(1)	3.200 (7)	Cs(4)· · ·N(4ˣ)	3.544 (7)
Cs(2)· · ·N(2ⁱⁱⁱ)	3.167 (7)	Cs(4)· · ·N(4ᵛⁱⁱ)	3.489 (7)
Cs(2)· · ·Cl(1ⁱⁱⁱ)	3.752 (2)	Cs(4)· · ·Cl(1)	3.643 (2)
Cs(2)· · ·Cl(2ⁱᵛ)	3.428 (2)	Cs(4)· · ·Cl(2)	3.446 (2)
Cs(2)· · ·Cl(2ᵛ)	3.428 (2)	Cs(4)· · ·Cl(2ˣⁱ)	3.499 (2)
Cs(3)· · ·O(1wᵛⁱ)	3.35 (1)	O(1w)· · ·N(4ⁱ)	2.73 (1)*
Cs(3)· · ·N(2)	3.607 (5)	Cl(1)· · ·O(1wˣⁱⁱ)	3.10 (1)*
Cs(3)· · ·N(3)	3.321 (5)		

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

* Possible hydrogen bonds

The systematic absences ($0kl, k+l = 2n+1$; $hk0, h = 2n+1$) were consistent with space groups $Pn2_1a$ (No. 33) and $Pnma$ (No. 62); the latter was chosen on the basis of the statistical analysis of intensity distribution and confirmed by refinement. The structure was solved by direct methods (*SHELXS86*; Sheldrick, 1990). A Fourier difference map calculated after all Cs, Cl, Fe, N and C atoms were located and refined showed a residual electron density peak of $3.7 \, e \, \text{Å}^{-3}$, which was assigned to a water molecule of solvation. This O atom was refined isotropically, with an occupancy of 0.5 (see *Comment*). No satisfactory positions for the corresponding H atoms could be found.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993b). Program(s) used to solve structure: *SHELXS86*. Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

References

Bondi, A. (1964). *J. Chem. Phys.* **68**, 441–451.
Daul, C. A., Day, P., Figgis, B. N., Gudel, H. U., Herren, F., Ludi, A. & Reynolds, P. A. (1988). *Proc. R. Soc. London, Ser. A*, **419**, 205–219.
Figgis, B. N., Kucharski, E. S., Raynes, J. M. & Reynolds, P. A. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3597–3604.
Figgis, B. N., Skelton, B. W. & White, A. H. (1978). *Aust. J. Chem.* **31**, 1195–1199.
Fletcher, S. R. & Gibb, T. C. (1977). *J. Chem. Soc. Dalton Trans.* pp. 309–316.
Garg, A. N. & Goel, P. S. (1970). *J. Inorg. Nucl. Chem.* **32**, 1547–1557.
Herren, F. & Ludi, A. (1979). *Acta Cryst.* **B35**, 3129–3130.
Jones, L. H., Swanson, B. I. & Kubas, G. J. (1974). *J. Chem. Phys.* **61**, 4650–4655.

Molecular Structure Corporation (1993a). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1993b). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Murgich, J. (1994). Unpublished results.
Murgich, J. & Oja, T. (1987). *J. Chem. Soc. Dalton Trans.* pp. 1637–1640.
Orpen, G. A., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–S83.
Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 538. Ithaca: Cornell Univ. Press.
Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
Sheldrick, G. M. (1990). *Acta Cryst.* **A41**, 467–473.
Swanson, B. I., Lucas, B. C. & Ryan, R. R. (1977). *J. Chem. Phys.* **69**, 4328–4334.
Vannerberg, N. C. (1972). *Acta Chem. Scand.* **26**, 2863–2876.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Aquabis(2,2'-bipyridine)chloromanaganese(II) Perchlorate

Xiao-Ming Chen* and Kai-Liang Shi

Department of Chemistry, Zhongshan University, 135 Xingang Rd W., Guangzhou 510275, People's Republic of China

Thomas C. W. Mak and Bao-Sheng Luo

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Abstract

The crystal structure of the title compound, [MnCl(C₁₀H₈N₂)₂(H₂O)]ClO₄, contains monomeric [Mn(bpy)₂Cl(H₂O)]⁺ cations in which the Mnᴵᴵ ion is surrounded by a pair of chelating bpy ligands (bpy = 2,2'-bipyridine) [Mn—N 2.235 (3)–2.291 (3) Å], an aqua ligand [Mn—O 2.167 (3) Å] and a chloro ligand [Mn—Cl 2.447 (1) Å] in a distorted octahedral environment. Adjacent cations are linked into dimers by pairs of Cl···O hydrogen bonds [Cl···O 3.137 (3) Å].

Comment

Manganese complexes have attracted considerable interest recently because of the frequent occurrence of such metal centers in biological systems (Wieghardt,