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Structure of Ferrocenium Hexafluorophosphate

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Abstract. $[Fe(C_5H_5)_2]PF_6$, $M_r = 331·0$, monoclinic, $P2_1/c$, $a = 13·429$ (3), $b = 9·547$ (2), $c = 9·499$ (2) Å, $\beta = 93·31$ (3)°, $V = 1215·8$ (5) Å^3, $Z = 4$, $D_x = 1·808$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 14·20$ cm^{-1}, $F(000) = 660$, room temperature, $R = 0·0397$, $wR = 0·0431$ for 678 independent observed reflections. The structure consists of a PF_6^- anion in a general position and two ferrocenium cations lying on independent crystallographic inversion centres. This imposed symmetry leads to the cyclopentadienyl rings being ideally staggered (twist angle 36° from eclipsed conformation).

Introduction. Some organometallic compounds, particularly of the sandwich type, can be considered as electron reservoirs because of their multiple, relatively stable oxidation states (Astruc, 1986). These systems are able to transfer electrons stoichiometrically (Smart & Pinsky, 1980) or catalytically (Buet, Darchen & Moinet, 1979) without decomposition. The ferrocenium/ferrocene couple can be considered as one of the simplest of these systems. In this paper we report the crystal structure of ferrocenium hexafluorophosphate and compare it with the structures of other ferrocenium salts.

Experimental. Ferrocenium hexafluorophosphate was prepared according to the reported method (Smart & Pinsky, 1980) by oxidizing ferrocene with ferric chloride in water/acetone (3:1 *v*/*v*). The $[(C_5H_5)Fe]^+$ cation was precipitated with aqueous $[NH_4]PF_6$. The blue product thus obtained was recrystallized at room temperature from acetone/ethanol with the addition of a small amount of anhydrous $FeCl_3$. A dark-blue crystal, having approximate dimensions 0·12 × 0·16 × 0·22 mm, grown from a CH_2Cl_2/*n*-hexane mixture, was used for the structure determination.

Siemens AED diffractometer, Nb-filtered Mo $K\alpha$ radiation, 30 reflections ($12·6 < \theta < 15·9°$) for accurate unit-cell parameters; 1092 independent reflections with $2·5 < \theta < 24°$, $-14 \le h \le 14$, $0 \le k \le 10$, $0 \le l \le 10$ from $\theta/2\theta$ scans, 678 reflections with $I > 3\sigma(I)$ considered observed, no significant deterioration of the standard reflection (532). Lp correction applied, absorption ignored. Patterson and Fourier methods; full-matrix least-squares refinement, anisotropic parameters for non-H atoms (*SHELX*76, Sheldrick, 1976); H in calculated positions (C—H = 1·0 Å) with fixed isotropic parameters ($U = 0·09$ Å^2); $\sum w|\Delta F|^2$ minimized; final $R = 0·0397$, $wR = 0·0431$; $w = [\sigma^2(F_o) + 0·005\ F_o^2]^{-1}$; $(\Delta/\sigma)_{max} = 0·49$, final $\Delta\rho$ values < |0·24| e Å^{-3}; atomic scattering factors (anomalous dispersion of Fe and P atoms) from *Interational Tables for X-ray Crystallography* (1974); calculations performed on the Gould-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma.†

Discussion. Until 1983 all reported structures of ferrocenium ions showed an eclipsed conformation for the η^5-C_5H_5 (Cp) rings: (Cp_2Fe)(picrate) (Petterson, 1966), $(Cp_2Fe)(CCl_3CO_2H)_3$ (Schleuter & Gray, 1971), $(Cp_2Fe)(BiCl_4)$ (Mammano, Zalkin, Landers & Rheingold, 1977), $[(Cp_2Fe)_2(Sb_4Cl_{12}O)]_2.2C_6H_6$ (Rheingold, Landers, Dahlstrom & Zubieta, 1979), $(Cp_2Fe)_2(As_4Cl_{10}O_2)$ (Churchill, Landers & Rheingold, 1981), $(Cp_2Fe)(FeCl_4)$ (Paulus & Schäfer, 1978). The structure of $(Cp_2Fe)I_3$ (Bernstein & Herbstein, 1968) was so disordered that no structural details concerning the ferrocenium ion could be obtained. In contrast to these results, neutral ferrocene derivatives have normally been found with a staggered conformation. In 1983 the crystal structure of $(Cp_2Fe)_4(Bi_4Br_{16})$ (Rheingold, Uhler & Landers, 1983) was found to contain two non-equivalent ferrocenium ions, one adopting a nearly eclipsed conformation and the other, for the first time, a staggered conformation. A similar situation was found in 1986 for $(Cp_2Fe)_2[(FeCl_3)_2O]$ (Bullen, Howlin, Silver, Fitzsimmons, Sayer & Lark-

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† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52215 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters, with e.s.d.'s in parentheses, for the non*-H *atoms*

$B_{eq} = (8\pi^2/3)$ trace **U**.

	x	*y*	*z*	B_{eq}(Å^2)
Fe(1)	½	0	−½	3·4 (1)
Fe(2)	0	0	−½	3·1 (1)
P	2637 (3)	356 (4)	360 (4)	5·0 (1)
F(1)	1433 (7)	212 (10)	222 (10)	8·8 (3)
F(2)	3786 (7)	465 (14)	496 (12)	12·7 (5)
F(3)	2578 (10)	1544 (12)	1485 (11)	12·2 (5)
F(4)	2599 (9)	−778 (11)	1572 (9)	11·5 (5)
F(5)	2663 (8)	1451 (9)	−864 (9)	9·3 (4)
F(6)	2661 (8)	−853 (8)	−772 (8)	8·8 (4)
C(1)	3470 (10)	189 (20)	−5056 (19)	7·5 (7)
C(2)	3705 (11)	−1171 (20)	−5356 (16)	6·5 (5)
C(3)	4388 (14)	−1813 (18)	−4295 (22)	8·3 (7)
C(4)	4424 (14)	−703 (26)	−3192 (14)	9·4 (8)
C(5)	3874 (12)	452 (19)	−3734 (19)	7·4 (6)
C(6)	105 (19)	−442 (21)	−2881 (13)	9·8 (8)
C(7)	−541 (13)	−1394 (20)	−3616 (18)	7·5 (6)
C(8)	107 (18)	−2125 (16)	−4482 (18)	8·7 (7)
C(9)	972 (16)	−1531 (25)	−4428 (26)	9·5 (9)
C(10)	1003 (17)	−680 (35)	−3456 (23)	12·1 (12)

Table 2. *Selected bond distances* (Å) *and angles* (°)

Fe(1)—C(1)	2·061 (14)	Fe(2)—C(6)	2·053 (13)
Fe(1)—C(2)	2·079 (16)	Fe(2)—C(7)	2·034 (18)
Fe(1)—C(3)	2·046 (18)	Fe(2)—C(8)	2·090 (16)
Fe(1)—C(4)	2·037 (16)	Fe(2)—C(9)	2·013 (23)
Fe(1)—C(5)	2·031 (17)	Fe(2)—C(10)	2·039 (23)
C(1)—C(2)	1·37 (3)	C(6)—C(7)	1·41 (3)
C(1)—C(5)	1·36 (2)	C(6)—C(10)	1·37 (3)
C(2)—C(3)	1·46 (2)	C(7)—C(8)	1·42 (3)
C(3)—C(4)	1·49 (3)	C(8)—C(9)	1·29 (3)
C(4)—C(5)	1·41 (3)	C(9)—C(10)	1·23 (4)
P—F(1)	1·621 (10)	P—F(4)	1·583 (10)
P—F(2)	1·545 (10)	P—F(5)	1·566 (10)
P—F(3)	1·563 (12)	P—F(6)	1·579 (9)
C(2)—C(1)—C(5)	106 (2)	C(7)—C(6)—C(10)	103 (2)
C(1)—C(2)—C(3)	113 (2)	C(6)—C(7)—C(8)	103 (2)
C(2)—C(3)—C(4)	100 (2)	C(7)—C(8)—C(9)	110 (2)
C(3)—C(4)—C(5)	108 (1)	C(8)—C(9)—C(10)	108 (2)
C(1)—C(5)—C(4)	111 (2)	C(6)—C(10)—C(9)	115 (2)
F(1)—P—F(3)	91·6 (6)	F(2)—P—F(5)	87·3 (6)
F(1)—P—F(4)	85·8 (6)	F(2)—P—F(6)	92·7 (6)
F(1)—P—F(5)	93·5 (5)	F(3)—P—F(4)	89·7 (5)
F(1)—P—F(6)	86·7 (5)	F(3)—P—F(5)	91·6 (6)
F(2)—P—F(3)	89·1 (7)	F(4)—P—F(6)	89·9 (5)
F(2)—P—F(4)	93·4 (6)	F(5)—P—F(6)	88·9 (5)

worthy, 1986; Carty, Clare, Creighton, Metcalfe, Raper & Dawes, 1986). In the crystal structures of $(Cp_2Fe)[(TCNQ)F_4]$ and $(Cp_2Fe)_2[(TCNQ)F_4]_3$ [$(TCNQ)F_4$ = 7,7,8,8-tetracyanoperfluoro-*p*-quinodimethane] (Miller, Zhang & Reiff, 1987) the cation possesses one ordered and one essentially disordered Cp ring; the crystal structure of $(Cp_2Fe)_3$-$[(CN)_2C{=}C(CN)O]_2$ (Sullivan & Foxman, 1983) is unique in that ferrocenium ions with eclipsed conformations and ferrocene molecules with staggered conformations coexist.

We now report the crystal structure of $(Cp_2Fe)(PF_6)$ where the two non-equivalent ferrocenium cations both lie on inversion centres so that the Cp rings adopt a rigorously staggered conformation (twist angle 36°). The PF_6^- anions lie in general positions. Final atomic coordinates for the non-H atoms are listed in Table 1. Relevant bond distances and angles are given in Table 2. A view of one of the two independent ferrocenium ions is shown in Fig. 1 and a view along [001] of the packing is given in Fig. 2.

The Cp ligands are planar within ±0·07 Å, with the Fe atoms lying between them, Fe(1) at 1·660 (1) Å from the ring defined by the atoms C(1)–C(5) and Fe(2) at 1·701 (1) Å from that defined by the atoms C(6)–C(10). The average Fe—C distances are 2·051 (16) and 2·046 (16) Å for the cations containing Fe(1) and Fe(2) respectively. The average

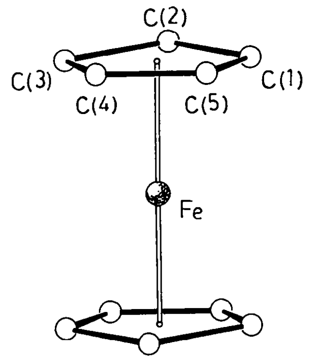

Fig. 1. View of one of the two independent ferrocenium cations.

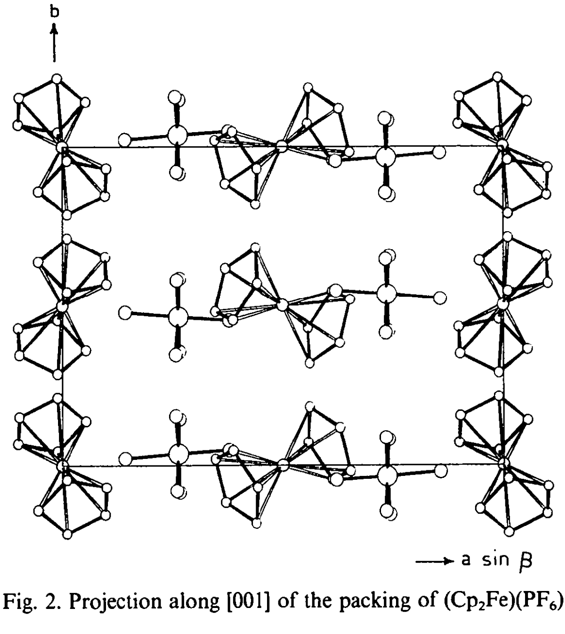

Fig. 2. Projection along [001] of the packing of $(Cp_2Fe)(PF_6)$.

Table 3. *Selected structural data for ferrocenium compounds* $(Cp_2Fe)_xL_y$

L	*x*	*y*	Fe—C (Å)	C—C (Å)	Fe—Cp (Å)	Twist^a angle (°)	Orientation^b	Dihedral angle (°)
Picrate	1	1			1·68^c		*ec*	
I_3	1	1			1·65^c		*di*	
$(CCl_3CO_2H)_3$	1	1	2·048 (5)				*ec*	
$BiCl_4$	1	1	2·08 (1)	1·40 (2)	1·70 (2)^c	1	*ec*	2
$FeCl_4$	1	1	2·07 (1)	1·43 (2)	1·68 (2)^d		*ec*	2·2
$Sb_4Cl_{12}O$	2	1			1·68^c	3·6	*ec*	5
$As_4Cl_{10}O_2$	2	1	2·067 (9)	1·380 (13)	1·702 (8)^d		*ec*	1·44
Bi_4Br_{16}	4	1	2·058 (3)	1·370 (5)	1·697 (7)^d	7·8	*ec*	6·4
			2·051 (3)	1·359 (5)	1·694 (6)^d	23·4	*st*	2
$(NC)_2C{=}C(CN)O$	3	2	2·073 (2)		1·700 (2)^c	0	*ec*	4·6
$(FeCl_3)_2O$	2	1	2·075 (2)	1·419 (9)	1·688 (5)^d	0	*ec*	
			2·084 (2)	1·431 (12)	1·690 (6)^d		*st*	
$(TCNQ)F_4{}^e$	1	1	2·09 (3)	1·44 (3)			*di*	
$(TCNQ)F_4{}^e$	2	3	2·091 (7)	1·414 (12)			*di*	
PF_6	1	1	2·051 (16)	1·42 (3)	1·660 (1)^d	36	*st*	0
			2·046 (16)	1·34 (3)	1·701 (1)^d	36	*st*	0

Notes: (*a*) Twist angle (from an eclipsed conformation).
(*b*) Orientation: *ec* = eclipsed, *di* = disordered, *st* = staggered.
(*c*) To the centroid of the Cp ring.
(*d*) Displacement from the Cp mean plane.
(*e*) The cation possesses one ordered and one disordered Cp ring, the data concern only the ordered ring.

C—C distances of 1·42 (3) and 1·34 (3) Å for the C(1)—C(5) and C(6)—C(10) rings are rather different, probably because of some degree of disorder. On the other hand a wide range for the C—C distances in ferrocenium cations has been found, as is evidenced in Table 3, in which the most important structural features of the ferrocenium salts have been collected.

It has been pointed out that the Fe—Cp and Fe—C distances in eclipsed ferrocenium cations appear to be slightly longer than those reported for ferrocene and for most ferrocene derivatives (Churchill *et al.*, 1981). From Table 3 the average Fe—Cp and Fe—C distances found in eclipsed ferrocenium ions are 1·689 and 2·069 Å respectively against 1·66 and 2·045 Å reported for ferrocene (Dunitz, Orgel & Rich, 1956). In the structure of $(Cp_2Fe)_3[(CN)_2C{=}C(CN)O]_2$ (Sullivan & Foxman, 1983), where ferrocenium ions and ferrocene coexist, the Fe—Cp and the average Fe—C distances are 1·700 (2) and 2·073 (2) Å against 1·656 (4) and 2·018 (4) Å. It has been suggested (Churchill *et al.*, 1981) that the increase in the Fe—Cp and Fe—C distances is due mainly to electronic factors as MO theory predicts, that is the oxidation step $Cp_2Fe \rightarrow Cp_2Fe^+$ removes an electron which is slightly bonding with respect to the Fe–Cp interaction (Rettig, 1973; Lauher & Hoffman, 1976; Schustorovich & Dyatkina, 1959).

The *ab initio* study on eclipsed and staggered conformations of the Cp rings of ferrocene (Bagus, Walgren & Almlof, 1976) showed that the energy was essentially the same for both conformations. In fact ferrocene in the gas phase at 413 K has an unhindered eclipsed equilibrium conformation with a barrier to rotation of only $3{\cdot}8 \pm 1{\cdot}3\ \text{kJ mol}^{-1}$ (Dunitz *et al.*, 1956; Haaland & Nilsson, 1968). Curiously, ferrocene derivatives in the solid state have normally been found in staggered conformations unless sterically forced away from this arrangement (Churchill & Wormald, 1969).

The Fe—Cp and Fe—C distances in the staggered ferrocenium ions are closely comparable to those found in the eclipsed ferrocenium ions (see Table 3), suggesting that the energy difference between eclipsed and staggered conformations is small, as is the case in ferrocene. Consequently the presence of an eclipsed or staggered conformation (or of both) in the crystals is probably the result of packing forces.

The PF_6^- anion is quite regular with an approximately octahedral arrangement and rather anisotropic thermal ellipsoids for F atoms.

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Structures of Chromium(III) Cyclam Complexes. 1. Structure of *trans*-Dicyano(1,4,8,11-tetraazacyclotetradecane)chromium(III) Perchlorate

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Abstract. $[Cr(CN)_2(C_{10}H_{24}N_4)]ClO_4$, $M_r = 403{\cdot}5$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}874\,(2)$, $b = 13{\cdot}506\,(1)$, $c = 19{\cdot}222\,(2)$ Å, $V = 1784{\cdot}6\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}50$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71073$ Å, $\mu = 7{\cdot}7$ cm^{-1}, $F(000) = 834{\cdot}97$, room temperature, $R = 0{\cdot}036$ for 4186 observed reflections. The cyclam moiety exists in a chair conformation. The equatorial nitrogen ligands and the central chromium ion are approximately coplanar. The Cr–C(cyano) vectors lie 1·3 and 1·9° respectively from the normal to the CrN_4 plane.

Introduction. The cyclam ligand has been used in the preparation of transition-metal complexes for kinetic (Ferguson & Tobe, 1970; Eriksen & Monsted, 1983), photochemical (Maguire, Crippen & Miller, 1983) and spectroscopic (Forster & Monsted, 1986) studies where it is desirable to maintain a rigid four-coordinate plane in order to investigate the properties of the two remaining ligands (*i.e.* in six-coordinate complexes).

It has been suggested that macrocyclic complexes of transition metals have similar properties to biologically important systems (Christensen, Eatough & Izatt, 1974). Cyclam structures resemble porphyrins in that both systems are cyclic tetradentate nitrogen donor ligands. A crystal structure has been reported for a copper complex where the tetrathia analogue of cyclam was used as a ligand (Glick, Gavel, Diadoarrio & Robarbacher, 1976). We report here the crystal-structure determination of the *trans*-dicyano chromium(III) complex.

The compound is of interest because it displays unusual phosphorescence behaviour in solution. It has also been described as exhibiting unusual behaviour in its visible emission spectrum (Kane-Maguire, 1983). Luminescence of the chromium(III) complex is thought to arise from the lowest component of the $^2T_{1g}$ (O_h) electronic state. Solid-state absorption and emission spectra for spin-forbidden transitions have also been measured (Flint & Gazi, 1989). However, the complete and detailed assignments of these spectra will depend on some knowledge of the crystal structure of the complex

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