

Fair, C. K. (1990). *MOLÉN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Nierlich, M., Sabatie, J. M., Keller, N., Lance, M. & Vigner, J.-D. (1994). *Acta Cryst. C50*, 52–54.

Walker, N. & Stuart, D. (1983). *Acta Cryst. A39*, 158–166.

Acta Cryst. (1994). **C50**, 1544–1545

[(5a,6,7,8,9,9a- η^6)-[1,4]Benzodioxino[2,3-*b*]pyridine)(η^5 -cyclopentadienyl)iron(II) Hexafluorophosphate

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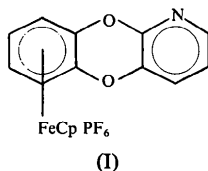
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Abstract

The structure of [(5a,6,7,8,9,9a- η^6)-[1,4]benzodioxino[2,3-*b*]pyridine)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate, [Fe(C₅H₅)(C₁₁H₇NO₂)]PF₆, has been studied. The dihedral angle between the benzene and pyridine rings of the ligand system is 177.4 (3)°; the benzene and cyclopentadienyl rings are nearly parallel [dihedral angle 1.3 (4)°]. The Fe atom is closer to the benzene ring [1.542 (4) Å] than to the cyclopentadienyl (Cp) ring [1.652 (5) Å] and it is located within the fold of the heterocyclic ligand.

Comment

The title complex (I) was synthesized following the procedure of Sutherland, Piórko, Lee, Simonsen & Lynch (1988) by the reaction of 2,3-dihydroxypyridine with (η^6 -1,2-dichlorobenzene)(η^5 -Cp)iron(II) hexafluorophosphate. Results obtained in the course of this work supplement earlier studies of the structure of tricyclic heterocycles complexed with the FeCp moiety.



In (I), the Fe atom is centred above the Cp ring while the longest Fe—C(arene) distances are found for the atoms C5a [2.116 (8) Å], C9 [2.097 (7) Å] and

C9a [2.096 (7) Å]. The central dioxin ring is symmetrical, unlike that in the FeCp complex of 2-methylidibenzodioxin (Abboud, Simonsen, Piórko & Sutherland, 1991). The distances between the Fe atom and the Cp ring plane [1.652 (5) Å] and between Fe and the coordinated arene ring plane [1.542 (4) Å] are within the range reported for FeCp complexes of arenes (Houlton, Roberts, Silver, Wells & Frampton, 1992). The planes of the coordinated benzene ring and Cp ring are nearly parallel [1.3 (4)°] and the FeCp moiety is located within the fold of the heterocyclic ligand; both these results have been reported for similar complexes (Abboud, Simonsen, Piórko & Sutherland, 1991; Abboud, Lynch, Simonsen, Piórko & Sutherland, 1990; Sutherland, Piórko, Lee, Simonsen & Lynch, 1988; Lynch, Thomas, Simonsen, Piórko & Sutherland, 1986; Simonsen, Lynch, Sutherland & Piórko, 1985). The dihedral angle between the benzene and pyridine rings of the ligand system is 177.4 (3)°, which is smaller than the angle found in 2,7,8-trinitro-1,4-benzodioxino[2,3-*b*]pyridine [174.65 (8)°; Piórko, Christie, Crook & Sampson, 1994]. (The structure of 1,4-benzodioxino[2,3-*b*]pyridine has not been reported.)

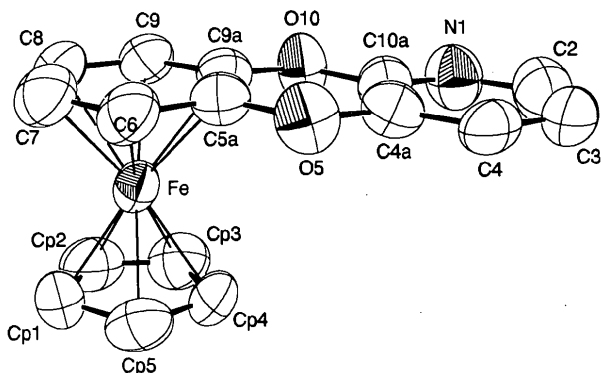


Fig. 1. Molecular structure of the cation of (I) with atom numbering. Displacement ellipsoids are at the 50% probability level.

Experimental

The complex was synthesized according to the method described by Sutherland, Piórko, Lee, Simonsen & Lynch (1988). The crystal used for data collection was grown from acetone-diethyl ether-dichloromethane solution at ca 255 K.

Crystal data

[Fe(C₅H₅)(C₁₁H₇NO₂)]PF₆

M_r = 451.08

Monoclinic

*P*2₁/*n*

a = 8.053 (3) Å

b = 13.955 (2) Å

c = 14.843 (6) Å

β = 97.12 (2)°

Mo *K* α radiation

λ = 0.7107 Å

Cell parameters from 24

reflections

θ = 28–38°

μ = 1.08 mm⁻¹

T = 290 K

Parallelepiped

$V = 1655.2 (9) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.81 \text{ Mg m}^{-3}$

$0.43 \times 0.23 \times 0.18 \text{ mm}$
 Orange

Data collection

Enraf-Nonius CAD-4
 diffractometer
 $\omega/2\theta$ scans [width (0.80 +
 $0.35\tan\theta)^\circ$]
 Absorption correction:
 empirical (ψ scans)
 $T_{\min} = 0.898$, $T_{\max} =$
 0.999
 2332 measured reflections
 2156 independent reflections

1418 observed reflections
 $[I > 2.5\sigma(I)]$
 $R_{\text{int}} = 0.019$
 $\theta_{\max} = 22.5^\circ$
 $h = -8 \rightarrow 8$
 $k = 0 \rightarrow 15$
 $l = 0 \rightarrow 15$
 3 standard reflections
 frequency: 60 min
 intensity variation: -6%

Refinement

Refinement on F^2
 $R = 0.051$
 $wR = 0.046$
 $S = 2.42$
 1418 reflections
 244 parameters
 H-atom parameters not
 refined
 $w = 1/[\sigma^2(F_o) + 0.00007F_o^2]$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.420 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.290 \text{ e \AA}^{-3}$
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV)

Fe—C8	2.076 (7)	C5a—C9a	1.408 (10)
Fe—C9	2.097 (7)	C6—C7	1.414 (13)
Fe—C9a	2.096 (7)	C7—C8	1.405 (13)
Fe—Cp1	2.034 (8)	C8—C9	1.410 (12)
Fe—Cp2	2.030 (9)	C9—C9a	1.412 (10)
Fe—Cp3	2.018 (9)	Cp1—Cp2	1.386 (16)
Fe—Cp4	2.036 (7)	Cp1—Cp5	1.409 (14)
Fe—Cp5	2.036 (7)	F4—F5	2.197 (10)
P—F1	1.578 (5)	F4—F6	2.194 (7)
P—F2	1.547 (5)	O5—C4a	1.379 (9)
P—F3	1.559 (5)	O5—C5a	1.366 (9)
P—F4	1.529 (5)	O10—C9a	1.371 (9)
P—F5	1.554 (6)	O10—C10a	1.389 (9)
P—F6	1.571 (5)	N1—C2	1.349 (13)
F2—F6	2.195 (8)	N1—C10a	1.305 (11)
F3—F5	2.146 (8)	Cp2—Cp3	1.359 (16)
F3—F6	2.193 (7)	Cp3—Cp4	1.384 (15)
C2—C3	1.367 (15)	Cp4—Cp5	1.399 (13)
C3—C4	1.396 (13)		
C4a—O5—C5a	116.6 (5)	C5a—C6—C7	119.2 (7)
C9a—O10—C10a	115.8 (5)	C6—C7—C8	121.0 (7)
C2—N1—C10a	116.4 (7)	Fe—C8—C9	71.0 (4)
N1—C2—C3	123.5 (7)	Fe—C9—C9a	70.3 (4)
C2—C3—C4	119.4 (7)	O10—C9a—C5a	122.5 (6)
C3—C4—C4a	117.3 (7)	O10—C9a—C9	116.4 (6)
O5—C4a—C4	119.1 (6)	C5a—C9a—C9	121.1 (7)
O5—C4a—C10a	122.0 (7)	O10—C10a—N1	113.9 (7)
C4—C4a—C10a	118.9 (7)	O10—C10a—C4a	121.6 (7)
O5—C5a—C6	118.2 (7)	N1—C10a—C4a	124.5 (7)
O5—C5a—C9a	121.5 (7)		

The structure was solved by direct methods. All non-H atoms were located via *E*-map inspection and were refined anisotropically. The positions of all H atoms were calculated (C—H = 1.08 Å) and given temperature factors based upon the C atoms to which they are bonded. All calculations were conducted with the PC version of the *NRCVAX* program package (Gabe, Le Page, Charland, Lee & White, 1989) implemented on IBM compatible 80486 computers.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: ST1084). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Abboud, K. A., Lynch, V. M., Simonsen, S. H., Piórko, A. & Sutherland, R. G. (1990). *Acta Cryst.* **C46**, 1018–1022.
 Abboud, K. A., Simonsen, S. H., Piórko, A. & Sutherland, R. G. (1991). *Acta Cryst.* **C47**, 1198–1202.
 Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
 Houlton, A., Roberts, R. M. G., Silver, J., Wells, A. S. & Frampton, C. S. (1992). *Acta Cryst.* **C48**, 1018–1022.
 Lynch, V. M., Thomas, S. N., Simonsen, S. H., Piórko, A. & Sutherland, R. G. (1986). *Acta Cryst.* **C42**, 1144–1148.
 Piórko, A., Christie, S., Crook, M. & Sampson, P. (1994). *J. Heterocycl. Chem.* In the press.
 Simonsen, S. H., Lynch, V. M., Sutherland, R. G. & Piórko, A. (1985). *J. Organomet. Chem.* **290**, 387–400.
 Sutherland, R. G., Piórko, A., Lee, C. C., Simonsen, S. H. & Lynch, V. M. (1988). *J. Heterocycl. Chem.* **25**, 1911–1916.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Fe	0.18775 (13)	0.98365 (6)	0.20382 (6)	4.40 (5)
P	0.8328 (3)	0.30352 (15)	0.08460 (14)	5.37 (11)
F1	0.9505 (6)	0.3914 (3)	0.0710 (3)	8.5 (3)
F2	0.9776 (6)	0.2341 (3)	0.0713 (4)	10.6 (4)
F3	0.7730 (7)	0.3010 (3)	-0.0194 (3)	10.4 (3)
F4	0.8847 (9)	0.3070 (5)	0.1872 (3)	15.4 (5)
F5	0.6844 (7)	0.3727 (4)	0.0933 (5)	12.7 (4)
F6	0.7169 (7)	0.2151 (3)	0.0969 (3)	9.6 (3)
O5	-0.1880 (6)	0.9135 (3)	0.1483 (3)	5.6 (3)
O10	0.0415 (6)	0.7805 (3)	0.2422 (3)	5.9 (3)
N1	-0.0885 (9)	0.6589 (5)	0.1613 (4)	6.4 (4)
C2	-0.2126 (13)	0.6262 (6)	0.0996 (7)	7.1 (5)
C3	-0.3281 (11)	0.6844 (7)	0.0516 (5)	6.4 (5)
C4	-0.3218 (9)	0.7831 (6)	0.0672 (5)	5.1 (4)
C4a	-0.1973 (10)	0.8166 (5)	0.1303 (5)	5.0 (4)
C5a	-0.0627 (10)	0.9428 (5)	0.2130 (5)	4.7 (4)
C6	-0.0414 (11)	1.0402 (5)	0.2279 (5)	5.9 (4)
C7	0.0882 (13)	1.0723 (6)	0.2941 (6)	6.7 (5)
C8	0.1983 (11)	1.0071 (7)	0.3425 (5)	6.6 (5)
C9	0.1801 (10)	0.9081 (6)	0.3253 (4)	5.7 (4)
C9a	0.0488 (9)	0.8769 (6)	0.2599 (5)	4.9 (4)
C10a	-0.0847 (10)	0.7512 (6)	0.1755 (5)	5.3 (4)
Cp1	0.3438 (13)	1.0720 (6)	0.1449 (6)	6.6 (5)
Cp2	0.4308 (10)	0.9925 (9)	0.1813 (6)	7.3 (5)
Cp3	0.3606 (14)	0.9110 (6)	0.1436 (7)	7.2 (5)
Cp4	0.2300 (12)	0.9369 (7)	0.0787 (6)	6.5 (5)
Cp5	0.2172 (11)	1.0369 (7)	0.0791 (5)	6.3 (5)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Fe—C5a	2.116 (8)	C4—C4a	1.367 (11)
Fe—C6	2.078 (8)	C4a—C10a	1.397 (11)
Fe—C7	2.058 (8)	C5a—C6	1.384 (11)