

Structure of (7^F-Cyclopentadienyl)(1,2,3,4,4a,10a-7^F-2-methyl-dibenzo[h,e][1,4]dioxine)iron(II) Hexafluorophosphate at 163 K

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Abstract. [C₁₈H₁₅FeO₂][PF₆]₂ (1), *M_r* = 464.13, monoclinic, *P*2₁/*c*, *a* = 7.976 (1), *b* = 8.959 (3), *c* = 24.936 (8) Å, β = 99.00 (2)°, *V* = 1760 (1) Å³, *Z* = 4, *D_x* = 1.751 g cm⁻³. *A*(Mo *Kα*) = 0.71069 Å, *JL* = 10.153 cm⁻¹, *F*(000) = 936, *T* = 163 (2) K, full-matrix least-squares refinement of (1) converged to *R* = 0.047 and *wR* = 0.044 with 3103 reflections [*I* > 3σ(*I*)] of 4065 total unique reflections. The dihedral angle between the arene rings of the dioxine ligand is 173.8 (1)°; the C—O bond distances to the coordinated ring are significantly shorter than those of the uncoordinated ring. Inclusion of electronegative

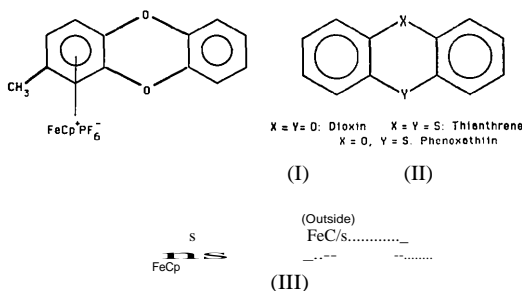
atoms (*i.e.* N) in the arene rings of thianthrenes and complexation of iron cyclopentadienyl (FeCp) to the arene rings, resulted in flattening of the dihedral angle. The effect was similar, but more pronounced, in phenoxathiins. The effect of an electron-releasing group (methyl) substituent on the arene ring of a thianthrene FeCp complex was to decrease the dihedral angle; but, inconsistently, two methyl groups (in the 2 and 7 positions) increased the angle. Dibenzodioxine and other dibenzodioxines with varying numbers of chloro substituents are planar. The dihedral angle of the title compound is 173.8°. It

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is not clear whether this is owing to the influence of the substituent methyl group, complexation, or packing forces.

Introduction. Previous studies of the synthesis, structure and reactivity of tricyclic heterocycles (II) complexed with an FeCp moiety indicated that both the location of the FeCp moiety [inside or outside of the heterocycle fold (III)] and the presence of a substituent on the heterocycle may influence the dihedral angle between the arene rings. In the thianthrene complex (Aboud, Lynch, Simonsen, Piorko & Sutherland, 1990) the FeCp moiety was located inside the fold in one molecule of the asymmetric unit and outside the fold in the other; in the 2-methylthianthrene complex (Simonsen, Lynch, Sutherland & Piorko, 1985) it was located inside the fold. However, there were significant differences in the dihedral angles of the thianthrene skeletons. This difference may result from the action of packing forces in the crystal, or it may be owing to the presence of the methyl substituent in the 2-methylthianthrene complex. To extend the investigation of the influence of the substituents and complexation with FeCp upon the geometry of the three-ring heterocyclic ligand, (I) was synthesized and its crystal structure determined.



Experimental. The title compound was synthesized by the reaction of catechol with $(\eta^6\text{-}3,4\text{-dichlorotoluene})(\eta^5\text{-Cp})\text{iron(II) hexafluorophosphate}$ following the described procedure (Sutherland, Piorko, Lee, Simonsen & Lynch, 1988). Crystals of the complex were grown from an acetone-diethyl ether-methylene chloride solution at *ca* 255 K. A needle-shaped orange-yellow crystal, 0.12 x 0.23 x 0.47 mm, was mounted and transferred to a Syntex N_1 diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation), where it was maintained in an environment of dry N_2 at 163 (2) K with a Syntex LT-1 low-temperature delivery system. Preliminary investigations revealed the crystal system to be monoclinic. 45 strong reflections, 25-33 2 θ 34.73°, were used to refine the unit-cell parameters. 8420 reflections (h , 0-10; k , -11-11; l , -32-32) were collected by the ω -scan method, 4065 unique reflections, $R_{\text{int}} = 0.023$; 2 θ range 4--55° (max.

$\sin \theta / \lambda = 0.6497 \text{ \AA}^{-1}$, low scan at 4--8° min⁻¹, depending upon intensity. Background measurements were taken at both ends of the scan with ω displaced by 1.0° from the $K\alpha_{1,2}$ peak; each measurement was made for one-half of the scan time. Intensities of four reflections (135, 14T, 148, 126) were remeasured every 96 reflections to monitor instrument stability and crystal decay; max. correction was 1.6%. Absorption corrections based on measured crystal faces (Riley & Davis, 1976) were applied; min., max. transmission coefficients 0.695, 0.874. An extinction correction was not applied. The structure was solved by the heavy-atom (Patterson) method (SHELX76; Sheldrick, 1976) which revealed the position of the Fe atom; the remainder of the atoms were located from difference Fourier maps. Refinement was carried out by full-matrix least squares in SHELX76 with anisotropic thermal parameters for the non-H atoms and isotropic thermal parameters for the H atoms. $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/(u^2 \sigma_o^2 + v^2 \sigma_c^2)$, $u(F_o) = 0.5k_i^{-1/2} [u(l)f + (0.02l)^2]^{1/2}$, $l = (|F_o| - |F_c|) / (|F_o| + |F_c|)$, $I = (|F_o| - |F_c|) / (|F_o| + |F_c|)$, k is the correction due to decay and Lp effects, and 0.02 is a factor used to downweight intense reflections and to account for instrument instability. Convergence was attained with R_{int} of 0.047 and 0.044, respectively, for 3103 reflections of intensity larger than $3\sigma(I)$; 962 reflections were considered to be unobserved. In the last cycle of refinement, 313 variables were refined to a goodness-of-fit of 2.88; the largest shift/e.s.d. did not exceed 0.08; min. and max. peaks in the difference Fourier map were -0.44 and 1.43 e \AA^{-3} , respectively. The largest residual peak was 0.88 e \AA^{-3} from the Fe atom and thus was attributed to its anisotropy. The linear absorption coefficient was calculated with values from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 55). Scattering factors for non-H atoms were taken from Cromer & Mann (1968) with anomalous-dispersion corrections from Cromer & Liberman (1970); those of H atoms were from Stewart, Davidson & Simpson (1965). The least-squares program was supplied by Cordes (1983); other programs used are cited in reference II of Gadol & Davis (1982). Positional parameters of all non-H atoms with their equivalent isotropic thermal parameters are given in Table I. Bond lengths and angles for the non-H atoms are listed in Table 2.* Fig. 1 shows the thermal-ellipsoids drawing of (I) with the atom-numbering scheme.

* Lists of structure factors, anisotropic thermal parameters, crystallographic data, bond lengths and angles including H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53854 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (*A*²) for the non-H atoms of (I)

	x	y	z	U*
Fe	0.36640 (6)	0.18949 (5)	0.16340 (2)	0.02946 (13)
P	0.08859 (13)	0.35356 (II)	-0.14762 (4)	0.0453 (3)
F1	0.0857 (4)	0.2337 (3)	-0.10150 (10)	0.0789 (11)
F2	0.0913 (3)	0.4732 (3)	-0.19467 (10)	0.0743 (10)
F3	0.2893 (3)	0.3506 (3)	-0.13868 (12)	0.0934 (12)
F4	0.0861 (4)	0.2238 (3)	-0.19089 (II)	0.0866 (12)
F5	-0.1120(3)	0.3521 (3)	-0.15857 (15)	0.1035 (14)
F6	0.0908 (6)	0.4823 (3)	-0.10641 (12)	0.127 (2)
OS	0.5741 (3)	0.0205 (2)	0.08315 (9)	0.0405 (8)
O10	0.3468 (3)	0.2486 (3)	0.03666 (9)	0.0438 (8)
C1	0.1636 (4)	0.1886 (4)	0.10051 (13)	0.0375 (10)
C2	0.1220 (4)	0.1025 (4)	0.14398 (13)	0.0366 (11)
C3	0.2361 (5)	-0.0104 (4)	0.16573 (14)	0.0399 (11)
C4	0.3871 (4)	-0.0364 (4)	0.14506 (14)	0.0372 (11)
C4a	0.4257 (4)	0.0472 (3)	0.10069 (13)	0.0338 (10)
C5a	0.6144 (4)	0.1169 (4)	0.04359 (13)	0.0350 (10)
C6	0.7705 (5)	0.0983 (4)	0.02683 (15)	0.0449 (13)
C7	0.8150 (6)	0.1907 (5)	-0.0126 (2)	0.056 (2)
C8	0.7059 (6)	0.2993 (5)	-0.0356 (2)	0.060 (2)
C9	0.5501 (6)	0.3164 (5)	-0.01920 (15)	0.0495 (13)
C9a	0.5058 (4)	0.2267 (3)	0.02068 (13)	0.0363 (11)
C10a	0.3127 (4)	0.1599 (3)	0.07832 (13)	0.0351 (10)
C11	0.4130 (5)	0.4124 (4)	0.1774 (2)	0.0416 (12)
C12	0.5670 (5)	0.3358 (4)	0.1781 (2)	0.0410 (12)
C13	0.5777 (5)	0.2272 (4)	0.2194 (2)	0.0433 (13)
C14	0.4307 (5)	0.2366 (4)	0.24391 (14)	0.0423 (12)
C15	0.3291 (5)	0.3512 (4)	0.2179 (2)	0.0423 (12)
C16	-0.0345 (5)	0.1365 (5)	0.1680 (2)	0.0512 (15)

*For anisotropic atoms, the *U* value is *U*_{eq}, calculated as $U_{eq} = (1/3)L_j U_{jj} a_j^2$.

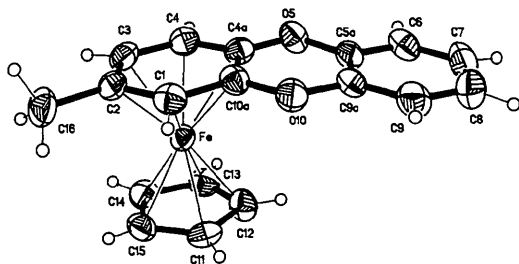


Fig. 1. Molecular structure of (1), with 50% probability ellipsoids, showing the atom-numbering scheme.

Discussion. The crystal structure of (I) was studied in a continuing effort to investigate the variation of the dihedral angles of tricyclic heterocycles by (1) replacing some of the C atoms in the terminal arene rings with more electronegative atoms (*e.g.* N), (2) placing substituents on the rings and (3) complexation of these heterocycles with FeCp. Comparison of the structures of a number of phenoxathiins, Table 3, reveals that the dihedral angle of the heterocycle flattens and approaches 180° with the inclusion of N atoms in the ring. The effect of complexation parallels the influence of electron-withdrawing substituents in the rings. However, in some cases packing effects may be more important than electronic effects.

Table 2. Bond lengths (Å) and angles (°) for the non-H atoms of (I)

	2	3	1-2	1-2-3
C1	Fe		2.069 (3)	
C2	Fe		2.085 (3)	
C3	Fe		2.075 (3)	
C4	Fe		2.087 (3)	
C4a	Fe		2.128 (3)	
C10a	Fe		2.114 (3)	
C11	Fe		2.051 (4)	
C12	Fe		2.056 (4)	
C13	Fe		2.041 (4)	
C14	Fe		2.037 (4)	
C/S	Fe		2.039 (4)	
F1	P	F2	1.576 (3)	179.38 (14)
F1	P	F3		90.9 (2)
F1	P	F4		89.83 (14)
F1	P	F5		89.5 (2)
F2	P	F3	1.592 (3)	89.2 (2)
F2	P	F4		89.56 (14)
F2	P	F5		90.5 (2)
F2	P	F6		89.28 (15)
F3	P	F4	1.581 (3)	89.3 (2)
F3	P	F5		177.7 (2)
F3	P	F6		90.7 (2)
F4	P	F5	1.584 (3)	88.4 (2)
F4	P	F6		178.8 (2)
F5	P	F6	1.580 (3)	91.5 (2)
F6	P	F1	1.543 (3)	91.3 (2)
C4a	O5	C5a	1.346 (4)	115.7 (2)
C5a	O5		1.386 (4)	
C9a	O10	C10a	1.401 (4)	115.5 (2)
C10a	O10		1.369 (4)	
C2	C1	C10a	1.412 (5)	121.0 (3)
C10a	C1		1.412 (5)	
C3	C2	C16	1.411 (5)	121.4(3)
C3	C2	C1		118.2 (3)
C16	C2	C1	1.497 (6)	120.4 (3)
C4	C3	C2	1.401 (5)	121.2 (3)
C4a	C4	C3	1.410 (5)	120.4 (3)
C10a	C4a	O5	1.409 (4)	122.6 (3)
C10a	C4a	C4		119.1 (3)
O5	C4a	C4		118.2 (3)
C6	C5a	C9a	1.385 (5)	119.9 (3)
C6	C5a	O5		117.4 (3)
C9a	C5a	O5	1.374 (4)	122.7 (3)
C7	C6	C5a	1.373 (6)	119.3 (4)
C8	C7	C6	1.370 (6)	120.7 (4)
C9	C8	C7	1.377 (7)	119.8 (4)
C9a	C9	C8	1.367 (5)	119.9 (4)
O10	C9a	C5a		121.4 (3)
O10	C9a	C9		118.2 (3)
C5a	C9a	C9		120.4 (4)
O10	C10a	C1		118.1 (3)
O10	C10a	C4a		121.7 (3)
C1	C10a	C4a		120.1 (3)
C12	C11	C15	1.405 (5)	108.3 (3)
C15	C11		1.406 (6)	
C13	C12	C11	1.408 (5)	107.4 (3)
C14	C13	C12	1.407 (6)	108.5 (3)
C15	C14	C13	1.403 (5)	107.6 (3)
C11	C15	Ci4		108.2 (3)

Electron-withdrawing groups and complexation have a similar, but smaller, effect on the dihedral angles of thianthrenes [thianthrene (127.1°) and 1-azathianthrene (130.4°), Larson, Simonsen, Martin, Smith & Puig-Torres (1984); (η⁵-cyclopentadienyl)(1)⁶-thianthrene)iron(II) hexafluorophosphate (143.1° and 136.3°), Abboud *et al.* (1990) and 1,4-diazathianthrene (138.9 and 137.0°), Larson, Simonsen, Lam, Martin, Lindsay & Smith (1985)].

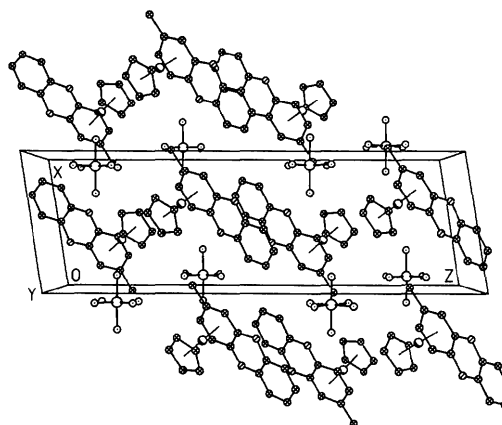
Table 3. Comparison of structures

	Dihedral angle Φ	Reference
Phenoxathiin	147.7	Kimura & Simonsen (1981).
3-Azaphenoxathiin	168.8	Caldwell, Martin, Simonsen, Inners & Willcutt (1981).
1,3-Diazaphenoxathiin	165.4	Puig-Torres, Martin, Larson & Simonsen (1984).
1,4,9-Triazaphenoxathiin	172.5	Larson, Simonsen, Martin & Smith (1985).
7-Chloro-1-azaphenoxathiin	175.3	Martin, Korp, Turley & Bernal (1978).
8-Chloro-1-azaphenoxathiin	176.8	Martin, Korp, Turley & Bernal (1978).
1-Nitrophenoxathiin	163.8	Hossain, Dwiggin, van der Helm, Gupta, Turley & Martin (1982).
(2 molecules/asymmetric unit)	145.7	
9-Nitro-1-azaphenoxathiin	178.3	Hossain, Dwiggin, van der Helm, Gupta, Turley & Martin (1982).
1-Dimethylamino-2,3-diazaphenoxathiin	174.0	Womak, Turley, Martin, Kimura & Simonsen (1981).
6,7,9-Trimethyl-4-azaphenoxathiin	180.0	Lynch, Simonsen, Martin, Puig-Torres & Smith (1984).
77 ⁵ -Cyclopentadienyl(77 ⁶ -phenoxathiin)iron(II) Hexafluorophosphate	178.6	Simonsen, Lynch, Sutherland & Piorko (1984).

Electron-releasing groups, however, do not show a similarly consistent trend. Whereas the methyl group in 2-methylthianthrene FeCp complex (Simonsen *et al.*, 1985), is believed to cause the ring to fold [dihedral angle, 127.4 (*3t*, compared to 143.1 (2)^o in the thianthrene FeCp complex], the dihedral angle in 2,7-dimethylthianthrene [136.96^o, Weakley (1982)] is larger than that of thianthrene. Thus, the two methyl groups were accompanied by ring flattening.

Uncomplexed dibenzodioxine is a planar molecule (Singh & McKinney, 1978), and dioxines with two (Boer & North, 1972), four (Boer, van Remoortere, North & Neuman, 1972) or six (Cantrell, Webb & Mabis, 1969) chloro substituents were found to be planar or nearly so. In the title compound the dihedral angle is 173.8 (*1t*), which clearly shows that the three-ring heterocycle deviates from planarity in spite of complexation to FeCp. The folding in (*1*) may be attributed to the presence of the methyl group as an electron-releasing substituent. However, it is not clear yet whether this effect is electronic in nature or due to packing forces.

The Fe atom is centered above the Cp ring; however, bonding between Fe and the arene ring is asymmetrical. The longest Fe-C distances are to C atoms adjacent to O atoms. This phenomenon is also observed in similar compounds reported by Simonsen *et al.* (1985) and Lynch, Thomas, Simonsen, Piorko & Sutherland (1986). The Fe-C4a and Fe-C10a distances are 2.128 (3) and 2.114 (3) Å, respectively, which represent the longest Fe-C distances in (*1*), indicating that the Fe atoms are not exactly centered upon the arene rings. In addition, the C-C distances of the coordinated ring are longer than the C-C distances of the

Fig. 2. The packing diagram for (*1*).

uncoordinated rings which has also been observed in similar compounds. The distances between the O atoms and the C atoms of the coordinated ring are shorter than those of the uncoordinated one; O5-C4a is 1.346 (4) whereas O5-C5a is 1.386 (4) Å; O10-C10a is 1.369 (4) compared to 1.401 (4) Å for O10-c9a. This may be due to the electron-withdrawing power of the FeCp moiety.

The distance between Fe and the Cp ring plane, 1.659 (4) Å, is longer than the distance between Fe and the coordinated arene ring planes, 1.548 (4) Å. These distances are well within the range of similar compounds (Lynch *et al.*, 1986; Simonsen *et al.*, 1985). The dihedral angle between the Cp ring plane and the coordinated arene is 2.1 (*1t*).

The PF₆ group is reasonably well behaved with the P-F bonding distance ranging between 1.543 (3) and 1.592 (3) Å. No F-P-F angle deviates from the octahedral geometry by more than 1.5^o.

The packing diagram for (*1*) is given in Fig. 2.

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