Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1095). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). **C50**, 1868–1870

(η^5-Cyclopentadienyl)[(1,2,3,4,4a,10a-η^6)-2-methylthianthrene]iron(II) Hexafluorophosphate

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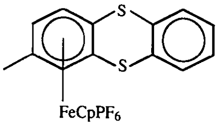
Abstract

The structure of the title compound, $[Fe(C_5H_5)(C_{13}H_{10}S_2)].PF_6$, (I), has been studied. The dihedral angle between the outer benzene rings of the ligand is 137.7 (3)°; the benzene and Cp rings are nearly parallel to each other [dihedral angle 3.5 (5)°]. The Fe atom, which is located inside the fold of the heterocyclic ligand, is closer to the benzene ring [1.548 (3) Å] than the Cp ring [1.668 (7) Å].

Comment

The title complex was synthesized following the described procedure (Sutherland, Piórko, Gill & Lee, 1982) by the reaction of 1,2-benzenedithiol with (η^6-3,4-dichlorotoluene)(η^5-Cp)iron(II) hexafluorophosphate. Crystals were grown from acetone–dichloromethane–diethyl ether solution at *ca* 255 K. Results obtained in the course of this study add to earlier data on the structure of thianthrenes and their FeCp complexes.



(I)

The Fe atom is centered above the Cp ring while the longest Fe—C distances to the arene ring are found for the quaternary C atoms [Fe—C2 = 2.111 (6), Fe—C4a = 2.111 (5) and Fe—C10a = 2.109 (5) Å]. Similar results have been noted for the isomeric 2-methylthianthrene complex (Simonsen, Lynch, Sutherland & Piórko, 1985) but not for both 'in'- and 'out'-FeCp–thianthrene complexes [FeCp moiety inside or outside the fold of the heterocyclic ligand (Abboud, Lynch, Simonsen, Piórko & Sutherland, 1990)]. The C—C distances of the coordinated rings also show a tendency to be longer than those of the uncoordinated rings. The distances between Fe and the Cp ring plane [1.668 (7) Å] and between Fe and the coordinated arene ring plane [1.548 (3) Å] are within the range reported for FeCp complexes of arenes (Zaworotko, Sturge & White, 1990; Houlton, Roberts, Silver, Wells & Frampton, 1992). The planes of the coordinated benzene ring and the Cp ring are nearly parallel [3.5 (5)°]; the dihedral angle is within the range of values reported for similar complexes.

It has been observed earlier that complexation with the FeCp moiety flattens the thianthrene (TT) molecule [the dihedral angle between the outer benzene rings of the ligand is 136.3 (2) for TT–out-FeCp and 143.1 (2)° for TT–in-FeCp (Abboud, Lynch, Simonsen, Piórko & Sutherland, 1990)]. For the isomeric 2-methyl-TT complex however, the folding was actually of the same magnitude as for TT itself [127.14 (3)° (Larson, Simonsen, Martin, Smith & Puig-Torres, 1984); for isomeric 2-MeTTFeCp, 127.4 (3)° (Simonsen, Lynch, Sutherland & Piórko, 1985)]. The dihedral angle for (I) was found to be 137.7 (3)°, which is between the values found for TT–in-FeCp and isomeric 2-MeTT-FeCp. The FeCp moiety in (I) is located inside the heterocyclic fold.

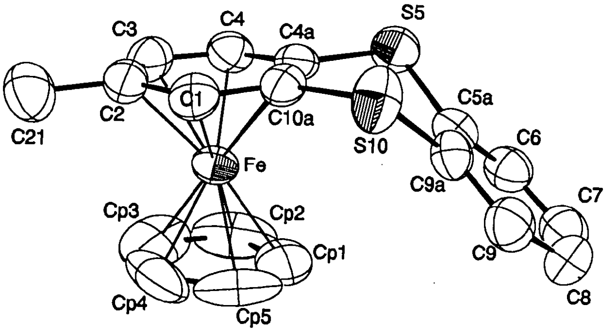


Fig. 1. Molecular structure of the cation of (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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Further studies will be required to evaluate the influence of both methyl substitution of the TT ring and FeCp complexation, as well as of packing forces, on the geometry of the TT molecule.

Experimental

Crystal data

$[Fe(C_5H_5)(C_{13}H_{10}S_2)].PF_6$
$M_r = 496.2$
Monoclinic
$P2_1/c$
$a = 9.7224\ (16)$ Å
$b = 11.335\ (3)$ Å
$c = 18.0256\ (15)$ Å
$\beta = 102.081\ (11)°$
$V = 1942\ (6)$ Å^3
$Z = 4$
$D_x = 1.70$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 24 reflections
$\theta = 17.5$–$22.5°$
$\mu = 1.12$ mm^{-1}
$T = 290$ K
Plate
0.60 × 0.25 × 0.10 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.617$, $T_{\max} = 0.999$
3628 measured reflections
3414 independent reflections

2546 observed reflections $[I > 2.5\sigma(I)]$
$R_{\rm int} = 0.020$
$\theta_{\max} = 22.5°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 60 min
intensity variation: ±2%

Refinement

Refinement on F
$R = 0.058$
$wR = 0.062$
$S = 4.67$
2546 reflections
253 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o) + 0.00003F_o^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.920$ e Å^{-3}
$\Delta\rho_{\min} = -0.650$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Fe	0.69952 (9)	0.28037 (7)	0.10904 (4)	3.80 (4)
P	0.91388 (17)	0.76922 (16)	0.07795 (9)	4.52 (7)
F1	0.9197 (4)	0.8646 (3)	0.14297 (20)	6.56 (20)
F2	0.7737 (6)	0.7202 (6)	0.0907 (3)	12.8 (4)
F3	0.9086 (6)	0.6760 (5)	0.0138 (3)	10.6 (3)
F4	1.0625 (6)	0.8073 (7)	0.0703 (4)	14.5 (5)
F5	0.8435 (9)	0.8555 (5)	0.0196 (3)	16.1 (6)
F6	0.9883 (8)	0.6831 (5)	0.1409 (3)	13.3 (4)
S5	0.60656 (18)	−0.01335 (14)	0.14914 (10)	5.21 (9)
S10	0.63785 (18)	0.17784 (16)	0.28710 (8)	5.19 (8)
C1	0.8262 (6)	0.2895 (5)	0.2175 (3)	4.2 (3)
C2	0.9120 (6)	0.3018 (5)	0.1643 (3)	4.5 (3)
C3	0.8983 (6)	0.2165 (6)	0.1052 (4)	5.0 (3)
C4	0.8028 (6)	0.1226 (5)	0.0999 (3)	4.5 (3)
C4a	0.7217 (6)	0.1084 (5)	0.1550 (3)	3.9 (3)
C5a	0.4583 (6)	0.0494 (5)	0.1770 (3)	4.2 (3)
C6	0.3260 (7)	0.0121 (5)	0.1392 (3)	4.9 (3)
C7	0.2086 (7)	0.0521 (6)	0.1631 (4)	5.4 (3)
C8	0.2216 (7)	0.1306 (6)	0.2222 (4)	5.2 (3)
C9	0.3522 (7)	0.1724 (6)	0.2577 (3)	4.8 (3)
C9a	0.4714 (6)	0.1305 (5)	0.2356 (3)	4.0 (3)
C10a	0.7333 (6)	0.1921 (5)	0.2143 (3)	3.8 (3)
C21	1.0116 (7)	0.4030 (6)	0.1665 (4)	6.0 (3)
Cp1	0.4895 (8)	0.3040 (10)	0.0657 (8)	8.3 (5)
Cp2	0.5595 (15)	0.2910 (10)	0.0082 (6)	9.2 (6)
Cp3	0.6602 (13)	0.3818 (18)	0.0142 (8)	11.4 (8)
Cp4	0.6430 (14)	0.4476 (8)	0.0767 (9)	9.6 (6)
Cp5	0.5409 (13)	0.3985 (12)	0.1065 (5)	8.4 (6)

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

Fe—C1	2.084 (5)	C2—C3	1.425 (10)
Fe—C2	2.111 (6)	C2—C21	1.497 (9)
Fe—C3	2.079 (6)	C3—C4	1.402 (9)
Fe—C4	2.075 (6)	C4—C4a	1.402 (9)
Fe—C4a	2.111 (5)	Fe—C10a	2.109 (5)
Fe—Cp1	2.045 (7)	C4a—C10a	1.416 (8)
Fe—Cp2	2.034 (7)	C5a—C6	1.390 (8)
Fe—Cp3	2.029 (8)	C5a—C9a	1.386 (8)
Fe—Cp4	2.025 (8)	C6—C7	1.378 (10)
Fe—Cp5	2.035 (7)	P—F1	1.587 (4)
C7—C8	1.373 (11)	P—F2	1.533 (5)
P—F3	1.560 (4)	C8—C9	1.380 (9)
P—F4	1.542 (5)	P—F5	1.494 (5)
C9—C9a	1.386 (9)	P—F6	1.556 (5)
Cp1—Cp2	1.36 (2)	Cp1—Cp5	1.335 (19)
Cp2—Cp3	1.41 (3)	S5—C4a	1.766 (6)
Cp3—Cp4	1.39 (3)	S5—C5a	1.771 (6)
S10—C9a	1.772 (6)	Cp4—Cp5	1.34 (2)
S10—C10a	1.766 (6)	C1—C2	1.403 (9)
C1—C10a	1.419 (8)		
C4a—S5—C5a	102.3 (3)	C9a—S10—C10a	101.7 (3)
C2—C1—C10a	120.9 (5)	C1—C2—C3	117.9 (5)
C1—C2—C21	122.1 (6)	C3—C2—C21	119.9 (6)
C2—C3—C4	121.5 (6)	C3—C4—C4a	120.1 (5)
S5—C4a—C4	119.4 (4)	S5—C4a—C10a	121.2 (4)
C4—C4a—C10a	119.4 (5)	S5—C5a—C6	117.6 (5)
S5—C5a—C9a	122.1 (4)	C6—C5a—C9a	120.2 (6)
C5a—C6—C7	119.3 (6)	C6—C7—C8	120.5 (6)
C7—C8—C9	120.6 (6)	C8—C9—C9a	119.5 (6)
S10—C9a—C5a	121.9 (5)	S10—C9a—C9	118.2 (5)
C5a—C9a—C9	119.8 (5)	S10—C10a—C1	118.0 (4)
S10—C10a—C4a	121.9 (4)	C1—C10a—C4a	120.1 (5)

A single crystal of (I) was mounted and sealed in a glass capillary and was then centred optically in the X-ray beam. The structure was solved by direct methods and refined using full-matrix least-squares techniques. Ring and methylene H atoms were placed in calculated positions (C—H = 1.08 Å) and assigned isotropic displacement factors equivalent to those calculated for the C atom to which they are bonded. Methyl H atoms were located *via* inspection of difference Fourier maps and were fixed to the attached C atom.

All calculations were conducted with the PC version of the *NRCVAX* program package (Gabe, LePage, Charland Lee & White, 1989) implemented on IBM compatible 80486 computers.

AP acknowledges the financial support of Saint Mary's University through Senate and General Research Grants.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: ST1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). **C50**, 1870–1872

Di-μ-oxo-bis{[tris(2-pyridylmethyl)amine-*N*,*N'*,*N''*,*N'''*]rhenium(IV)} Tetrakis(hexafluorophosphate) Diacetone Tetrahydrate

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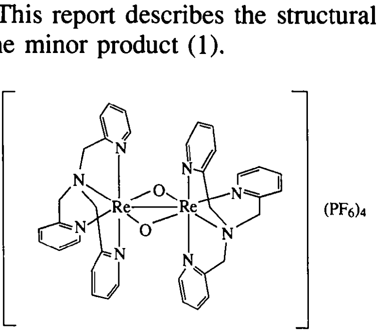
Abstract

The title compound, $[Re_2(\mu\text{-}O)_2(C_{18}H_{18}N_4)_2](PF_6)_4.2(CH_3)_2CO.4H_2O$, was structurally characterized. The structure of the complex cation consists of a binuclear unit, (tpa)Re(μ-O)$_2$Re(tpa) [tpa = tris(2-pyridylmethyl)amine], having a crystallographically imposed centre of symmetry at the midpoint of the Re$\equiv$Re triple bond. Each Re ion is in a pseudo-octahedral coordination environment comprising two bridging O atoms and four N atoms of tpa, in which the tertiary amine and one of the pyridine N atoms are *trans* to the oxo bridge. The Re$\equiv$Re distance, average Re—O distance and Re—N distances are 2.364 (1), 1.950 (6) and 2.105 (7)–2.150 (6) Å, respectively.

Comment

The reaction of $Re^VOCl_3(PPh_3)_2$ with tris(2-pyridylmethyl)amine (tpa) gave a μ-oxo Re^{III} dimer, $[Re^{III}_2(\mu\text{-}O)Cl_2(tpa)_2](PF_6)_2$, as a major product (Takahira, Umakoshi & Sasaki, 1994). An Re^{IV} dimer, $[Re_2(\mu\text{-}O)_2(tpa)_2]^{4+}$, was obtained as a minor product on one occasion during the repeated preparation of the Re^{III} dimer. Although the Re^{IV} dimer was not obtained reproducibly and in sufficient quantity to study its properties further, its structure was successfully determined. This report describes the structural characteristics of the minor product (1).



(1)

Fig. 1 shows the configuration of the complex cation with the atomic numbering scheme. The structure of the complex cation consists of a binuclear unit, (tpa)Re(μ-O)$_2$Re(tpa), having a crystallographically imposed centre of symmetry at the midpoint of the Re$\equiv$Re bond. Each Re ion is in a pseudo-octahedral coordination environment comprising two bridging O atoms and four N atoms of tpa, in which the tertiary amine and one of the pyridine N atoms are *trans* to the oxo bridge. The distance between the Re atoms [2.364 (1) Å] is comparable to those of $Ba_2[Re_2(\mu\text{-}O)_2(edta)_2].4.5H_2O$ [2.3621 (8) Å; Ikari *et al.*, 1993], $K_4[Re_2(\mu\text{-}O)_2(C_2O_4)_4].3H_2O$ [2.362 (1) Å; Lis, 1975], $[Re_2(\mu\text{-}O)_2Cl_2(tacn)_2]I_2.2H_2O$ (tacn = 1,4,7-triazacyclononane) [2.376 (2) Å; Böhm, Wieghardt, Nuber & Weiss, 1990] and $[Re_2(\mu\text{-}O)_2I_2(tacn)_2]I_2.2H_2O$ [2.381 (1) Å; Böhm, Wieghardt, Nuber & Weiss, 1991], and an Re$\equiv$Re triple bond is indicated. The average Re—O distance [1.950 (6) Å] is also comparable to that of these complexes. The bond lengths between Re and N that are *trans* to bridging O are *ca* 0.04 Å longer than those *cis* to bridging O.

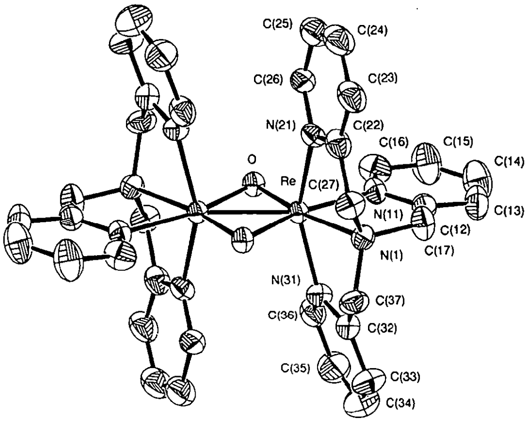


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the $[Re_2(\mu\text{-}O)_2(tpa)_2]^{4+}$ ion with the atomic numbering scheme.

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