(η^5-Cyclopentadienyl)(η^6-phenoxathiin 10,10-dioxide)iron(II) hexafluoridophosphate and phenoxathiin 10,10-dioxide

Arthur D. Hendsbee, Jason D. Masuda and Adam Piórko*

Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, Canada B3H 3C3

Correspondence e-mail: adam.piorko@smu.ca

In the structure of the title complex salt, [Fe(C$_5$H$_5$)(C$_{12}$H$_8$-O$_3$S)]PF$_6$, the coordinated cyclopentadienyl (Cp) and benzene ring planes are almost parallel, with a hinge angle between the planes of 0.8 (2)°. The hinge angle between the planes of the peripheral (coordinated and uncoordinated) benzene rings in the coordinated phenoxathiin 10,10-dioxide molecule is 169.9 (2)°, and the FeCp moiety is located inside the shallow fold of the heterocycle. The hinge angle between the benzene ring planes in the free heterocycle, C$_{12}$H$_8$O$_3$S, is 171.49 (6)°.

Comment

The title complex, (I) (Fig. 1), was obtained in an extension of work on the synthesis of polycyclic heteroaromatic systems by the double nucleophilic aromatic substitution reaction using *o*-dichlorobenzene FeCp (Cp is cyclopentadienyl) and related complexes (Sutherland *et al.*, 1982, 1988), followed by modification of the structure of the heterocycle by oxidation [see Lee, Chowdhury *et al.* (1986), and references therein]. This study continues our observations of changes that result in the structure of tricyclic heterocycles containing O and/or S atoms in the central ring of the system upon FeCp complexation and the introduction of substituents into a heterocycle structure. The free heterocycle, phenoxathiin 10,10-dioxide, (II) (Fig. 2), was obtained by oxidation of phenoxathiin with hydrogen peroxide in glacial acetic acid solution, as described by Gilman & Esmay (1952).

The asymmetric unit of (I) contains one (phenoxathiin 10,10-dioxide)FeCp cation and one hexafluoridophosphate counter-anion. The FeCp moiety is located inside the shallow fold of the heterocycle. The coordinated Cp and benzene rings are nearly coplanar, with a hinge angle of 0.8 (2)°, which is in agreement with observations for both phenoxathiin and related azaphenoxathiin FeCp complexes (Lynch *et al.*, 1986; Sutherland *et al.*, 1988). The centroid of the Cp ring, the Fe centre and the centroid of the benzene ring are nearly

collinear, with an angle 179.35 (11)° measured between the two vectors extending from the Fe atom to the centroids in the complexed rings, and this value is typical for FeCp arene complexes [see, for example, Manzur *et al.* (2000) and Fuentealba *et al.* (2007)].

(I)

(II)
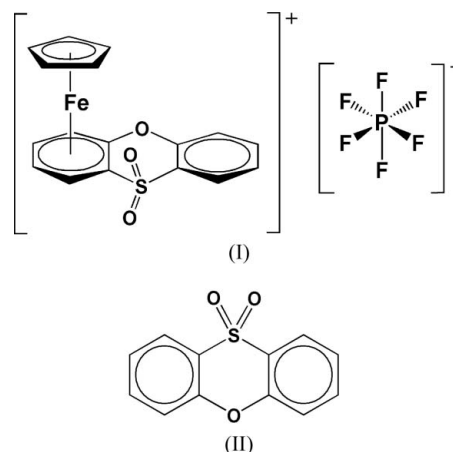
The distances from the Fe1 ion to the Cp plane and to the coordinated benzene ring plane are 1.645 (2) and 1.540 (2) Å, respectively. These values are close to those reported in the literature for similar FeCp complexes [see, for example, Lynch *et al.* (1986), Abboud *et al.* (1990), Fuentealba *et al.* (2007), Manzur *et al.* (2007) and Hendsbee *et al.* (2010)]. The distances from Fe1 to the C atoms of the coordinated benzene ring are within the range 2.048 (4)–2.113 (4) Å, with a mean of 2.082 (4) Å. The shortest Fe1—C distance is found for a quaternary C atom bonding to an SO$_2$ group, while the distance to another quaternary C atom, bonding to an O atom, appears to be the longest. These distances are within the range of reported values for FeCp complexes (Abboud *et al.*, 1990; Piórko *et al.*, 1994; Fuentealba *et al.*, 2007; Manzur *et al.*, 2007; Jenkins *et al.*, 2008). However, they differ from the data for both phenoxathiin and azaphenoxathiin complexes, in which
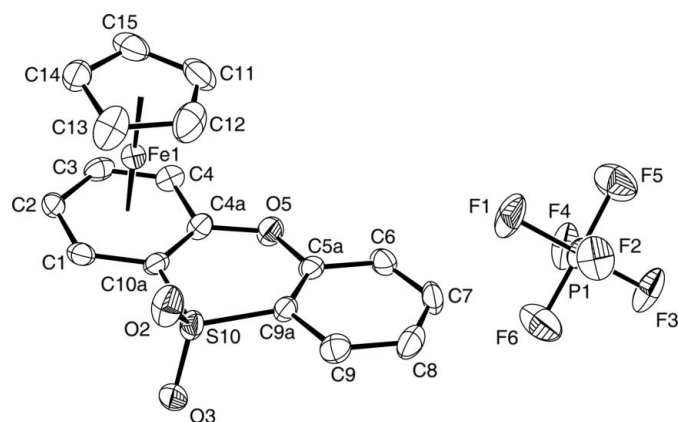

Figure 1
The cation and anion of complex (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.
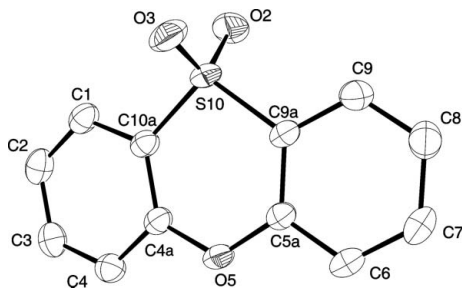
metal-organic compounds

Figure 2
The free heterocycle, (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

the two Fe—C(quaternary) distances are the longest of all six distances (Lynch *et al.*, 1986; Sutherland *et al.*, 1988).

The C—C distances in the coordinated ring of phenoxathiin 10,10-dioxide appear to be the same length as those in the uncoordinated ring, with the average distances being 1.401 (6) and 1.387 (6) Å, respectively. The C—S bonds extending from both the coordinated and uncoordinated ring C atoms to the bridging S atom are similar in length [1.757 (4) and 1.743 (4) Å, respectively]. The C—O distances, however, are quite different, as the bond extending from the bridging O atom to the C atom of the coordinated ring is significantly shorter than the C—O bond extending towards the uncoordinated ring [1.361 (5) and 1.393 (5) Å, respectively]. Both these observations agree with earlier findings for phenoxathiin and azaphenoxathiin complexes (Lynch *et al.*, 1986; Sutherland *et al.*, 1988) and for dibenzodioxin complexes (Piórko *et al.*, 1994, 1995; Hendsbee *et al.*, 2010).

The C—C bonds in the rings of the free heterocycle, phenoxathiin 10,10-dioxide, (II), have similar average lengths [1.385 (2) and 1.387 (2) Å] and are similar in length to the C—C bonds in the uncoordinated ring of complex (I). The S—C bond lengths from the bridging S atom to the benzene ring C atoms in the uncoordinated heterocycle are similar [1.7471 (16) and 1.7481 (18) Å] to those found in the complex. The C—O distances in the free heterocycle are 1.369 (2) and 1.371 (2) Å, more similar to the length of the C—O bond extending towards the coordinated ring of the FeCp complex [1.361 (5) Å] rather than that extending towards the uncoordinated ring of the FeCp complex [1.393 (5) Å].

A double nucleophilic aromatic substitution reaction yielding tricyclic heterocycle complexes may result in the formation of FeCp-in-fold, FeCp-out-of-fold or both isomeric molecules of the nonplanar tricyclic heterocycle in the solid state. Examples of all three cases may be found in the literature, and all reports provide crystallographic data supporting this statement. The earlier studies of the synthesis and structure of dibenzodioxin and thianthrene FeCp complexes suggested that only FeCp-in-fold molecules are formed in such a reaction. This conclusion was based on the results of several crystallographic studies (Simonsen *et al.*, 1985; Abboud *et al.*, 1990; Christie *et al.*, 1994; Piórko *et al.*, 1994, 1995). Recently, we reported that a double nucleophilic substitution reaction leading to the formation of (1,2,3,4,4a,10a-η)-1-methylthian-

threne FeCp hexafluoridophosphate gave rise to a mixture of both in-fold and out-of-fold isomers, as found in a crystallographic study of the reaction products (Hendsbee *et al.*, 2009). The only previously reported out-of-fold thianthrene complex was obtained, along with its in-fold isomer, in a different reaction, a photolytic demetallation of a mixture containing *cis*- and *trans*-di(η^5-Cp)(η^6,η^6-thianthrene)(iron)$_2$ bis(hexafluoridophosphate)s, which were prepared in a ligand-exchange reaction (see Abboud *et al.*, 1990).

Two phenoxathiin complexes which were obtained using a double nucleophilic substitution reaction have been reported in the literature to date. Both (phenoxathiin)FeCpPF$_6$ (Lynch *et al.*, 1986) and [(5a,6,7,8,9,9a-η)-1,4-benzoxathiino[3,2-*b*]-pyridine]FeCpPF$_6$ (Sutherland *et al.*, 1988) contain, in the solid state, only out-of-fold FeCp moieties. In both complexes, the FeCp moiety is located outside the shallow heterocycle fold, with hinge angles of 178.7 (1) and 176.8 (1)° for the phenoxathiin and azaphenoxathiin complexes, respectively. The hinge angle for the free phenoxathiin molecule was reported as 138° (Hosoya, 1966) and as 147.8° (Fitzgerald *et al.*, 1991; 223 K). This angle has yet to be reported for the uncoordinated azaphenoxathiin molecule. It appears then that FeCp complexation flattens the phenoxathiin skeleton. In this study, it was found that the FeCp moiety is located inside the phenoxathiin 10,10-dioxide fold, with a hinge angle of 169.9 (2)° between the two peripheral benzene rings. Thus, oxidation of the S atom in the central ring appears to counteract the effect of FeCp complexation, causing more pronounced folding of the heterocycle molecule and apparently converting the FeCp-out-of-fold isomer into the FeCp-in-fold one. For free phenoxathiin 10,10-dioxide, we found the hinge angle to be 171.49 (6)°, which means that when this molecule is coordinated to FeCp it is slightly more folded. This is the first confirmed example, and only the second case in which FeCp coordination appears to increase folding of the tricyclic heterocycle molecule. In the earlier case, this effect was observed in the structure of a methylthianthrene molecule carrying a methyl group in an uncoordinated benzene ring. The structure of the free heterocycle, 2-methylthianthrene, has not yet been reported, so the folding angle of a parent thianthrene molecule was used for comparison (Simonsen *et al.*, 1985). A similar effect was reported for a structurally related thioxanthene molecule, with a methylene group replacing the O atom in the central ring. Literature reports indicate that oxidation of the S atom to a dioxide results in slightly more pronounced folding of the molecule. For thioxanthene, the hinge angle was reported as 135.3 (1)° (Gillean *et al.*, 1973), while for thioxanthene 10,10-dioxide this angle was 133.9° (Chu & Chung, 1974).

We suggest that both the increased folding and the location of the FeCp moiety inside the fold may be requirements for minimizing the interaction of S-bonded O atoms with Fe in a complex. In this apparently favoured in-fold isomer, the distance from Fe to the proximal O atom will be longer than the analogous distance in the out-of-fold molecule. With a relatively small hinge angle in the starting phenoxathiin molecule, thermal flipping of this molecule during oxidation,

which results in inversion of the FeCp-out-of-fold isomer to the FeCp-in-fold isomer, appears to be possible and favoured at an elevated reaction temperature. However, this inversion process may be difficult to observe experimentally.

Experimental

The precursor (phenoxathiin)FeCp hexafluoridophosphate complex was obtained in the double nucleophilic aromatic substitution reaction of the *o*-dichlorobenzene FeCp complex with 2-mercaptophenol, as described in the literature (Sutherland *et al.*, 1982). The title complex salt was obtained in an oxidation of the precursor phenoxathiin complex using hydrogen peroxide in trifluoroacetic acid. This method, while used for oxidation of the amino group to a nitro group in similar complexes (see Lee *et al.*, 1982; Chowdhury *et al.*, 1985; Lee, Abd-El-Aziz *et al.*, 1986; Abd-El-Aziz *et al.*, 1988) and, more recently, for simultaneous oxidation of both amino and alkyl groups to nitro and carboxy groups, respectively (Abd-El-Aziz *et al.*, 1997; Abd-El-Aziz & Epp, 1995), has not been reported previously in the oxidation of sulfur-containing FeCp complexes, although it has been generally used in the oxidation of sulfur-containing heterocycles using glacial acetic acid as solvent [see, for example, oxidation of dibenzothiophene and phenoxathiin to the corresponding dioxides by Gilman & Esmay (1952)]. The reaction gave a 68% yield and a crystal suitable for X-ray analysis was obtained from an acetone–diethyl ether–dichloromethane solution at 280 (2) K. The same complex was also obtained in 63% yield in an alternative oxidation of the phenoxathiin complex with *m*-chloroperbenzoic acid, according to the procedure of Lee, Abd-El-Aziz *et al.* (1986). Phenoxathiin 10,10-dioxide, (II), was obtained by oxidation of the precursor phenoxathiin using 30% hydrogen peroxide in glacial acetic acid (Gilman & Esmay, 1952) with a total yield of 98%. A crystal suitable for X-ray analysis was obtained upon cooling the reaction mixture to room temperature. Experimental details and analytical data for both complex (I) and free heterocycle (II) are provided in the *Supplementary materials*.

Compound (I)

Crystal data

[Fe(C$_5$H$_5$)(C$_{12}$H$_8$O$_3$S)]PF$_6$	$V = 1796.6$ (8) Å^3
$M_r = 498.16$	$Z = 4$
Monoclinic, Cc	Mo $K\alpha$ radiation
$a = 10.059$ (2) Å	$\mu = 1.12$ mm^{-1}
$b = 13.618$ (3) Å	$T = 100$ K
$c = 13.544$ (4) Å	$0.30 \times 0.18 \times 0.18$ mm
$\beta = 104.446$ (2)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	10650 measured reflections
	4277 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)	3615 reflections with $I > 2\sigma(I)$
$T_{min} = 0.521$, $T_{max} = 0.746$	$R_{int} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	H-atom parameters constrained
$wR(F^2) = 0.089$	$\Delta\rho_{max} = 0.87$ e Å^{-3}
$S = 1.28$	$\Delta\rho_{min} = -0.28$ e Å^{-3}
4277 reflections	Absolute structure: Flack (1983), with 2066 Friedel pairs
262 parameters	Flack parameter: -0.037 (19)
52 restraints	

Compound (II)

Crystal data

C$_{12}$H$_8$O$_3$S	$\gamma = 93.399$ (2)°
$M_r = 232.24$	$V = 496.33$ (12) Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.2067$ (10) Å	Mo $K\alpha$ radiation
$b = 7.9568$ (11) Å	$\mu = 0.31$ mm^{-1}
$c = 8.9360$ (13) Å	$T = 150$ K
$\alpha = 102.475$ (1)°	$0.22 \times 0.20 \times 0.19$ mm
$\beta = 95.493$ (2)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	4816 measured reflections
	1746 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker; 2008)	1592 reflections with $I > 2\sigma(I)$
$T_{min} = 0.665$, $T_{max} = 0.746$	$R_{int} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	145 parameters
$wR(F^2) = 0.072$	H-atom parameters constrained
$S = 0.97$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
1746 reflections	$\Delta\rho_{min} = -0.31$ e Å^{-3}

H atoms were placed in geometrically idealized positions, with C—H = 0.95 [for all uncoordinated and coordinated aromatic C atoms in (I), and all C atoms in free heterocycle (II)] or 1.00 Å [for cyclopentadienyl C atoms in (I)], and constrained to ride on their parent C atoms, with U_{iso}(H) = 1.2U_{eq}(C). For the PF$_6^-$ counter-anion in (I), the F atoms were restrained to have the same U^{ij} components within a standard uncertainty of 0.05 Å^2. Thermal motion of the Cp ring π-bonded to the Fe atom resulted in unsatisfactory anisotropic displacement parameters for atoms C11, C12, C13 and C15. This was resolved through the use of the restraints applied to the refinement of these atoms: the U^{ij} components of these atoms were restrained to be equal within 0.004 Å^2 and their anisotropic displacement parameters were restrained to be equal within 0.002 Å^2.

For both compounds, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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