(η⁵-Cyclopentadienyl)(η⁶-phenoxathiin 10,10-dioxide)iron(II) hexafluoridophosphate and phenoxathiin 10,10-dioxide

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


Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site or institutional repository provided that this cover page is retained. Republication of this article or its storage in electronic databases other than as specified above is not permitted without prior permission in writing from the IUCr.

For further information see http://journals.iucr.org/services/authorrights.html
In the structure of the title complex salt, \([\text{Fe(C}_5\text{H}_5\text{(C}_12\text{H}_8\text{O}_3\text{S})}\text{]PF}_6\), 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, \(\text{C}_12\text{H}_8\text{O}_3\text{S}\), 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 \(\text{o-dichlorobenzene FeCp (Cp is cyclopentadienyl)}\) 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)].

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...
we reported that a double nucleophilic substitution reaction

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 uncoor-
dinated 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; Suther-
land et al., 1988) and for dibenzodioxin complexes (Piórkó 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 extending towards the uncoor-
dinated 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 litera-
ture, and all reports provide crystallographic data supporting
this statement. The earlier studies of the synthesis and struc-
ture 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; Piórkó 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-methylthia-
threne FeCp hexafluoridophosphate gave rise to a mixture of
both in-fold and out-of-fold isomers, as found in a crystal-
lographic 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(η⁵-C₅)(η⁶-thianthrene)iron₂(bis(hexafluoridophosphate)), 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)FeCpPF₆ (Lynch
et al., 1986) and [(5a,6,7,8,9a-η)-1,4-benzoxathiino[3,2-b]-
pyridine]FeCpPF₆ (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 coun-
teract the effect of FeCp complexation, causing more
pronounced folding of the heterocycle molecule and appar-
ently 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
compound 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 thi-
oxanthene, 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 mol-
cule, 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 α-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 Abd-El-Aziz et al. (1986) using 30% hydrogen peroxide in glacial acetic acid (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 obtained in 63% yield in an alternative oxidation of the ether–dichloromethane solution at room temperature. Experimental details and analytical data for both compounds (I) and free heterocycle (II) are provided in the Supplementary materials.

**Compound (I)**

**Crystal data**

\[\text{Fe(C}_5\text{H}_8\text{O}_3\text{S})\text{PF}_6\]  

\[M_1 = 498.16\]

Monoclinic, \(\text{Cc}\)

\(a = 10.059 (2)\) Å  

\(b = 13.618 (3)\) Å  

\(c = 13.544 (4)\) Å  

\(\beta = 104.446 (2)\)

**Data collection**

Bruker APEXII CCD area-detector diffractometer  

Absorption correction: multi-scan  

\(T_{\text{min}} = 0.521, T_{\text{max}} = 0.746\)

**Refinement**

\(R[F^2 > 2\sigma(F^2)] = 0.046\)  

\(wR(F^2) = 0.089\)  

\(S = 1.28\)  

4277 reflections  

262 parameters  

52 restraints

**Compound (II)**

**Crystal data**

\[\text{C}_{12}\text{H}_{23}\text{O}_5\text{S}\]  

\(M_1 = 232.24\)

Triclinic, \(\text{P}\)  

\(a = 7.2067 (10)\) Å  

\(b = 7.9568 (11)\) Å  

\(c = 8.9360 (13)\) Å  

\(\alpha = 102.475 (1)\)  

\(\beta = 93.399 (2)\)

**Data collection**

Bruker APEXII CCD area-detector diffractometer  

Absorption correction: multi-scan  

\(T_{\text{min}} = 0.665, T_{\text{max}} = 0.746\)

**Refinement**

\(R[F^2 > 2\sigma(F^2)] = 0.030\)  

\(wR(F^2) = 0.072\)  

\(S = 0.97\)  

1456 reflections  

145 parameters  

H-atom parameters constrained  

\(\Delta_{	ext{max}} = 0.33\) e Å\(^{-3}\)  

\(\Delta_{	ext{min}} = -0.31\) e Å\(^{-3}\)  

H atoms were placed in geometrically idealized positions, with C—H = 0.95 Å [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 \(U_{	ext{iso}}(\text{H}) = 1.2U_{	ext{eq}}(\text{C})\). For the \(\text{PF}_6^-\) counter-anion in (I), the F atoms were restrained to have the same \(U_{	ext{eq}}\) 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 \(U_{	ext{eq}}\) 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: SHELX97 (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.

The authors thank Saint Mary’s University for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: YP3006). Services for accessing these data are described at the back of the journal.

**References**


metal-organic compounds


