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# ($\eta^5$-Cyclopentadienyl)[(1,2,3,4,4a,-10a-$\eta$)-1-methylthianthrene]iron(II) hexafluoridophosphate acetone 0.33-solvate

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The title complex salt, [Fe(C$_5$H$_5$)(C$_{13}$H$_{10}$S$_2$)]PF$_6$·0.33C$_3$H$_6$O, obtained from an acetone–diethyl ether–dichloromethane mixture at 280 (2) K, has three cationic molecules (*A*–*C*), three hexafluoridophosphate counter-anions and one acetone solvent molecule in the asymmetric unit. Two of the three cations contain FeCp (Cp is cyclopentadienyl) inside the fold of the heterocycle. The dihedral angles between the planes of the external (complexed and uncomplexed) benzene rings in the thianthrene molecule are 146.5 (2)° for FeCp-out-of-fold molecule *A*, and 139.0 (3) and 142.5 (2)° for the two FeCp-in-fold molecules *B* and *C*, respectively. The complexed Cp and benzene rings in each molecule are almost parallel, with a dihedral angle between the planes of 0.2 (5)° for molecule *A*, 2.8 (5)° for *B*, and 2.19 (4) and 6.86 (6)° for the disordered Cp ring in *C*.

## Comment

The title compound, (I), was obtained while extending earlier studies on the synthesis of polycyclic heteroaromatic systems in a double nucleophilic aromatic substitution reaction using 1,2-dichlorobenzene FeCp complexes (Sutherland *et al.*, 1982, 1988). This study is a continuation of our earlier work on the combined influence of methyl substitution and FeCp complexation on the geometry of the thianthrene molecule. The crystal structure of (I) contains three cationic molecules (*A*–*C*) of the CpFe(1-methylthianthrene) complex, three hexafluoridophosphate counter-anions and one acetone solvent molecule in the asymmetric unit. This is the first time that the formation of both FeCp-out-of-fold and FeCp-in-fold molecules of folded tricyclic heterocycles resulting from a double nucleophilic aromatic substitution reaction have been observed. Our earlier studies of the synthesis of dibenzodioxin and thianthrene FeCp complexes using the same reaction suggested that only FeCp-in-fold molecules are formed in such a reaction, as crystals of the dibenzodioxins and thianthrenes

studied by X-ray crystallography have shown the presence of only FeCp-in-fold species (Simonsen *et al.*, 1985; Abboud *et al.*, 1990, 1991; Christie *et al.*, 1994; Piórko *et al.*, 1994, 1995). Conversely, phenoxathiin complexes obtained in a similar reaction have shown the presence of only out-of-fold molecules in the solid state, as determined from examination of their crystal structures (Lynch *et al.*, 1986; Sutherland *et al.*, 1988). The only previous case in which the presence of both FeCp-out-of-fold and in-fold molecules was observed in the solid state came from the monodemetallation of the thianthrene bis(FeCp) dication obtained in a ligand-exchange reaction from thianthrene (Abboud *et al.*, 1990). Thus, it appears that both in-fold and out-of-fold molecules may be formed in a nucleophilic aromatic substitution reaction.



(I)

**FeCp-out-of-fold**          **FeCp-in-fold**
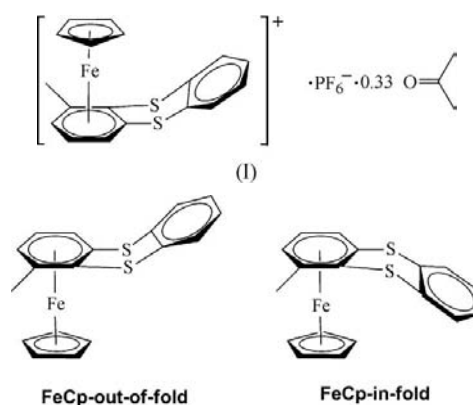
The complexed Cp and benzene rings of (I) are nearly coplanar in all three molecules, with a dihedral angle of 0.2 (5)° for molecule *A*, 2.8 (5)° for *B*, and 2.19 (4) and 6.86 (6)° for the disordered Cp ring in *C*. These values are in the range observed for other thianthrene and dibenzodioxin FeCp complexes in our previous studies (see, for example, Simonsen *et al.*, 1985; Lynch *et al.*, 1986; Abboud *et al.*, 1990, 1991; Christie *et al.*, 1994; Piórko *et al.*, 1995). The Cp–Fe–benzene ring centroid vectors are nearly collinear, with angles of 179.65 (8) and 178.42 (7)° for molecules *A* and *B*, and 178.69 (7) and 176.39 (7)° for the disordered Cp ring in *C*. These values are typically found in the literature for FeCp–arene complexes (see, for example, Manzur *et al.*, 2000; Fuentealba *et al.*, 2007).
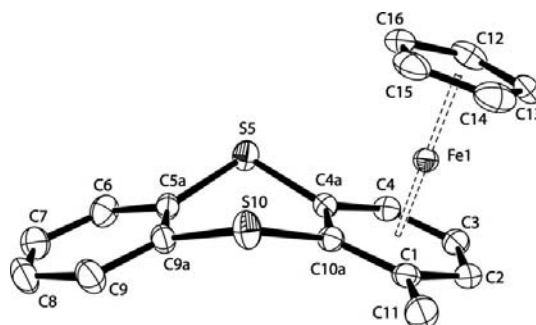


**Figure 1**
A view of the cation of (I), showing the atom-labelling scheme for molecule *A* (Fe1). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.
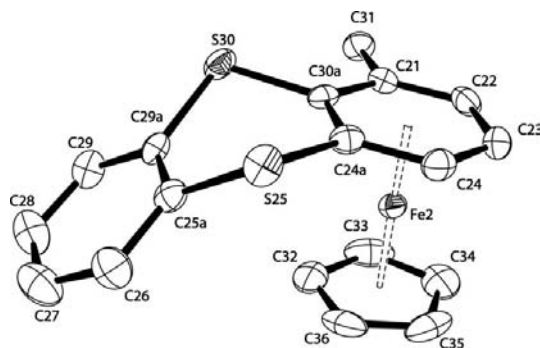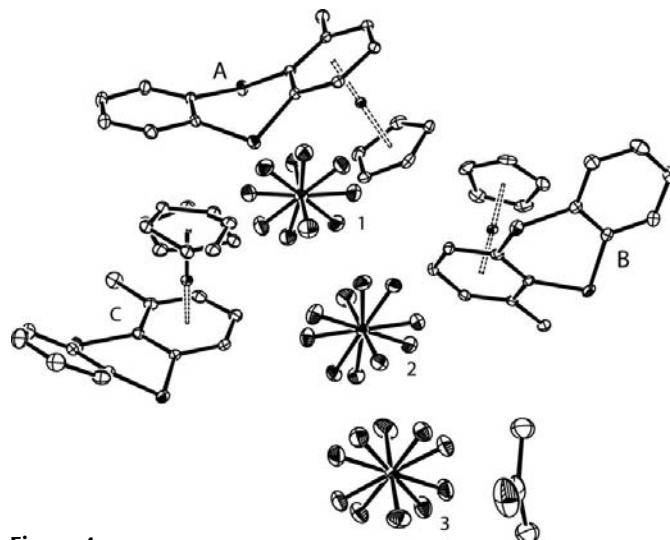
**Figure 2**
A view of the cation of (I), showing the atom-labelling scheme for molecule *B* (Fe2). H atoms have been omitted for clarity.
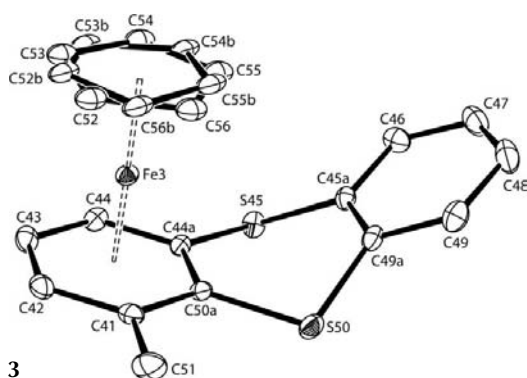


**Figure 3**
A view of the cation of (I), showing the labelling of non-H atoms of molecule *C* (Fe3) and the disorder of the Cp ring, with displacement ellipsoids drawn at 50% probability level. H atoms have been omitted for clarity.



**Figure 4**
A view of the asymmetric unit of (I), showing the positions of the three cations, *viz. A* (out-of-fold FeCp), *B* and *C*, the three hexa-fluoridophosphate anions and the acetone solvent molecule in the unit. H atoms have been omitted for clarity.

The distances from the Fe ion to the Cp plane and to the complexed benzene ring plane are 1.666 (3) and 1.537 (3) Å, respectively, in molecule *A*, 1.662 (3) and 1.551 (3) Å in *B*, and 1.648 (4)/1.538 (3) and 1.701 (4)/1.538 (3) Å in the two disorder components of the Cp ring in *C*. These values are close to those reported in the literature for similar complexes (see, for example, Lynch *et al.*, 1986; Abboud *et al.*, 1990; Piórko *et al.*, 1995; Fuentealba *et al.*, 2007; Manzur *et al.*, 2007; Jenkins *et al.*, 2008).

The Fe—C distances of the complexed benzene ring are in the range 2.073 (6)–2.121 (7) Å, with all three distances to quaternary C atoms being the longest in FeCp-in molecules *B* and *C*, while in FeCp-out molecule *A*, one of these distances is among the shorter ones. In all four thianthrene molecules studied previously, the distances from the Fe atom to the quaternary C atoms of the complexed benzene ring are longer than those to the nonquaternary C atoms, with the thianthrene FeCp-out-of-fold molecule showing the narrowest range for these distances (Simonsen *et al.*, 1985; Abboud *et al.*, 1990; Christie *et al.*, 1994). Overall, the average Fe—C distances of the complexed ring are 2.086, 2.095 and 2.088 Å for molecules *A*, *B* and *C*, respectively, and again these are within the range of reported distances for FeCp complexes (Abboud *et al.*, 1990; Piórko *et al.*, 1995; Fuentealba *et al.*, 2007; Manzur *et al.*, 2007; Jenkins *et al.*, 2008).

The C—C distances in the complexed ring of the thianthrene show a tendency to be longer than those in the uncomplexed ring, with averages of 1.410 *versus* 1.382 Å for molecule *A*, 1.409 *versus* 1.380 Å for molecule *B*, and 1.413 *versus* 1.379 Å for molecule *C*. The S—C distances to both complexed and uncomplexed ring C atoms are quite similar and in the rather narrow range 1.750 (7)–1.770 (6) Å. Both of these observations agree with our earlier findings for thianthrene and isomeric methylthianthrene FeCp complexes (Simonsen *et al.*, 1985; Abboud *et al.*, 1990; Christie *et al.*, 1994).

The dihedral angle between the two benzene rings of the thianthrene molecule has been reported to be insensitive to changes in substitution in or on one of the aromatic rings compared with thianthrene itself (for thianthrene, see: Larson *et al.*, 1984; for other alkylthianthrenes, see: Wei, 1971; Lynch *et al.*, 1984; Ogawa *et al.*, 1999; Yamamoto *et al.*, 2006). In our previous studies, we concluded that complexation of the thianthrene molecule with FeCp changes the dihedral angle between the two external benzene rings of this heterocycle. We reported that FeCp complexation of thianthrene flattens its structure and we found that the dihedral angle changes from 128.28 (7)° in thianthrene (Larson *et al.*, 1984) to 136.3 (2)° for FeCp-out-of-fold and to 143.1 (2)° for FeCp-in-fold molecules (Abboud *et al.*, 1990), and to 137.7 (3)° for the 2-methylthianthrene FeCp-in-fold molecule (Christie *et al.*, 1994). We noted, however, that this angle was slightly smaller [127.4 (3)°] for the 2-methylthianthrene molecule with FeCp complexed on the unsubstituted benzene ring (Simonsen *et al.*, 1985). In the current study, we have found that complexation does indeed flatten the heterocycle, and that the dihedral angles for molecules *A*, *B* and *C* are 146.5 (2), 139.0 (3) and 142.5 (2)°, respectively. It is surprising that, unlike in the case of thianthrene–FeCp complexes, the molecule is flattened more by an FeCp moiety located out-of-fold. Also, the

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magnitude of this influence is notable, as such a value of the dihedral angle has not been reported previously.

Our results indicate that more studies are required in order to understand the joint influence of the presence and position of a methyl substituent and FeCp complexation on the geometry of a thianthrene molecule. In addition, the presence of two distinct structures in which FeCp is located inside the thianthrene fold signifies the importance of packing forces as another factor, still difficult to evaluate, which influences the geometry of thianthrene in FeCp complexes in crystals.

## Experimental

The title complex salt was obtained as a yellow–orange powder in 78% yield following the method of Sutherland *et al.* (1982) in a reaction of benzene-1,2-dithiol with $(\eta^6\text{-}2,3\text{-dichlorotoluene})(\eta^5\text{-Cp})$-iron(II) hexafluoridophosphate. Elemental analysis calculated: C 43.57, H 3.05%; found: C 43.62, H 3.15%; $^1$H NMR (300.133 MHz, acetone-$d_6$): $\delta$ 2.86 (*s*, methyl), 4.87 (*s*, Cp), 6.49 (*t*, 1H, complexed benzene ring, $J = 6.2$ Hz), 6.57 (*d*, 1H, complexed benzene ring, $J = 6.2$ Hz), 6.91 (*d*, 1H, complexed benzene ring, $J = 6.2$ Hz), 7.63 (*m*, 2H, uncomplexed benzene ring), 7.81 (*m*, 2H, uncomplexed benzene ring); $^{13}$C NMR (75.469 MHz, acetone-$d_6$): $\delta$ 20.4 (methyl), 79.4 (Cp), 86.4, 88.0, 88.2 (C of complexed benzene ring), 104.1, 105.2, 106.0 (quaternary C of complexed benzene ring), 130.4, 130.5, 130.7, 130.9 (C of uncomplexed benzene ring), 133.3, 134.0 (quaternary C of uncomplexed benzene ring). The crystal used for data collection was grown by slow evaporation of the solvents from a solution of the complex in an acetone–diethyl ether–dichloromethane mixture at 280 (2) K; the compound was dissolved in a small volume of acetone and brought to the edge of precipitation with diethyl ether, and then a few drops of dichloromethane were added to clear the solution.

*Crystal data*

| | |
|---|---|
| [Fe(C5H5)(C13H10S2)]PF6·· 0.33C3H6O | $\beta = 75.251\ (1)^\circ$ |
| $M_r = 515.60$ | $\gamma = 84.088\ (1)^\circ$ |
| Triclinic, $P\bar{1}$ | $V = 3053.6\ (5)\ \text{Å}^3$ |
| $a = 10.5598\ (10)$ Å | $Z = 6$ |
| $b = 15.4984\ (15)$ Å | Mo $K\alpha$ radiation |
| $c = 19.4769\ (19)$ Å | $\mu = 1.08\ \text{mm}^{-1}$ |
| $\alpha = 83.508\ (1)^\circ$ | $T = 296$ K |
| | $0.46 \times 0.32 \times 0.13$ mm |

*Data collection*

| | |
|---|---|
| Bruker APEXII CCD diffractometer | 20371 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2008) $T_{\min} = 0.643$, $T_{\max} = 0.746$ | 10509 independent reflections 6357 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.041$ |

*Refinement*

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.063$ | 498 restraints |
| $wR(F^2) = 0.180$ | H-atom parameters constrained |
| $S = 1.08$ | $\Delta\rho_{\max} = 0.93$ e Å$^{-3}$ |
| 10509 reflections | $\Delta\rho_{\min} = -0.77$ e Å$^{-3}$ |
| 884 parameters | |

The H atoms were placed in geometrically idealized positions with C—H distances of 0.93 (aromatic), 0.98 (cyclopentadienyl) and 0.96 Å (idealized CH$_3$), and were constrained to ride on the parent C atom, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the C—H and aromatic H atoms and $1.5U_{\text{eq}}(\text{C})$ for the idealized methyl H atoms. The C atoms in the disordered cyclopentadienyl rings were restrained to be regular pentagons, with C—C distances of 1.42 Å and their occupancies refined to give a 68:32 ratio. For each of the disordered cyclopentadienyl rings, C-atom ellipsoids were constrained to be similar in size and shape using the SIMU and DELU commands. For all of the PF$_6$ groups, the equatorial P—F distances were restrained to be 1.55 Å and the *cis* F···F distances were restrained to be 2.19 Å. The ellipsoids of the three PF$_6$ groups were restrained to be similar in size. All three PF$_6$ groups were found to have rotational disorder and were refined to have occupancies of 59:41 (P1), 51:49 (P2) and 50:50 (P3).

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: *SHELXTL*.

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