

Bis[hydrogen 1,1'-bis(diphenylphosphinato)ferrocenium] octachloro-diantimony(III)

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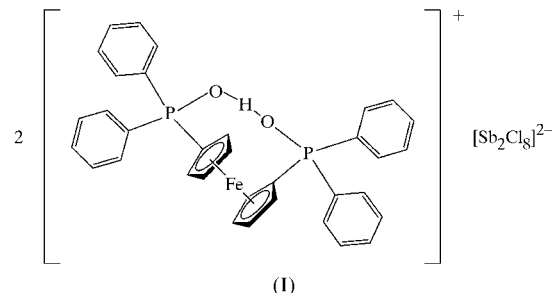
In the title compound, $[\text{Fe}(\text{C}_{34}\text{H}_{29}\text{O}_2\text{P}_2)]_2[\text{Sb}_2\text{Cl}_8]$, the discrete centrosymmetric $[\text{Sb}_2\text{Cl}_8]^{2-}$ anions are formed from two edge-shared square pyramids of Cl atoms about each Sb atom. Within the cation, the two diphenylphosphinato groups share one H atom and the ferrocene cyclopentadienyl rings are in a staggered conformation, with the average value of the twist angle being 46° . In the crystal, each $[\text{Sb}_2\text{Cl}_8]^{2-}$ anion is involved in eight C—H \cdots Cl interactions with four surrounding cations and these interactions interconnect the ions to form molecular columns along the *a* direction.

Comment

The reaction of diphenylphosphinoferrrocene (dppf) with tin tetrachloride and tin tetrabromide always leads to the formation of phosphonate–tin complexes (Yamin *et al.*, 1996; Razak *et al.*, 1998). However, the reaction of phosphorus derivatives with antimony pentachloride is more complicated due to adduct formation between the antimony species and the solvent molecules, followed by auto-ionization. As a result, different products can be obtained when a phosphorus compound is reacted with a fresh or aged solution of SbCl_5 . We have shown previously that bis(diphenylphosphino)-methane (dppm), when reacted with an aged solution of SbCl_5 , gave trichloro[methylenebis(diphenylphosphine oxide-*O*)]-antimony(III) (Razak *et al.*, 1999). After several attempts at reacting dppf with fresh SbCl_5 solution, good crystals of the title compound, (I), were obtained and subjected to an X-ray crystallographic investigation.

The C—C, Fe—C and Fe–ring centroid distances in the ferrocenium moieties are comparable with reported values (Orpen *et al.*, 1989; Razak *et al.*, 1998). The P—C bond lengths agree with the corresponding values in the structure of $\text{Ph}_2\text{PSCH}_2\text{P}(\text{S})\text{Ph}_2$ (Carmalt *et al.*, 1996), although the $\text{C}_{\text{Ph}}-\text{P}-\text{C}_{\text{Ph}}$ bond angles in (I) are up to 4° larger. The cyclopentadienyl (Cp) rings are in a staggered conformation. The

torsion angle between a Cp ring C atom, the two ring centres and the corresponding C atom on the opposite ring define the angle of twist for the Cp rings (Palenik, 1970); the average value for this twist angle is 46° . Examples of staggered and eclipsed Cp-ring conformations are given by Osborne *et al.* (1996).



The acidic H atom, H10, of the cation is shared between two O atoms. This delocalized H atom was located in difference Fourier maps, but its positional parameters were not refined. This arrangement results in dppf being positively charged. The delocalization of the H atom is supported by the observation that the two P—O bond lengths are 1.5158 (19) and 1.529 (2) Å, which are intermediate between a P—O single and double bond. These values are comparable with the value of 1.513 Å for P—O bonds with a delocalized H atom (Allen *et al.*, 1987). The O \cdots O distance of 2.411 (4) Å is

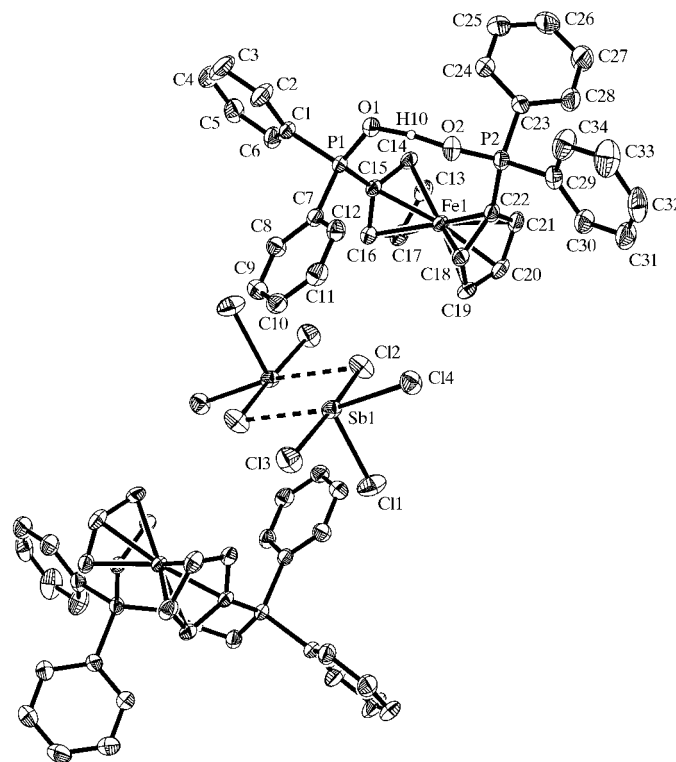


Figure 1

The structure of the title compound showing 50% probability displacement ellipsoids, the atom-numbering scheme and the shared H atom. Other H atoms have been omitted for clarity.

comparable with the values reported by Naik *et al.* (1974) [2.421 (7) Å] and Colbran *et al.* (1990) [2.375 (5) Å], who also observed an H atom being equally shared by two O atoms.

The discrete centrosymmetric $[\text{Sb}_2\text{Cl}_8]^{2-}$ anions are made up of two $[\text{SbCl}_4]^-$ units joined by two long asymmetric Cl bridges. The bridging Cl atoms complete a square-pyramidal coordination about each Sb atom and the overall anion geometry can be described as being composed of two edge-shared square pyramids. The basal plane of each square pyramid is occupied by atoms Cl2, Cl3, Cl4 and Cl2(1 - x, 1 - y, 1 - z), while the apical position is occupied by Cl1. The two longest Sb—Cl bonds (Table 1) involve Cl2 bridging between Sb1 and Sb1(1 - x, 1 - y, 1 - z), whereas the short bonds, which involve the remaining Cl atoms, are terminal. Similar Sb—Cl bond lengths involving bridging and terminal Cl atoms have been observed in related structures (Porter & Jacobson, 1970; Yamin *et al.*, 1996; Razak *et al.*, 2000).

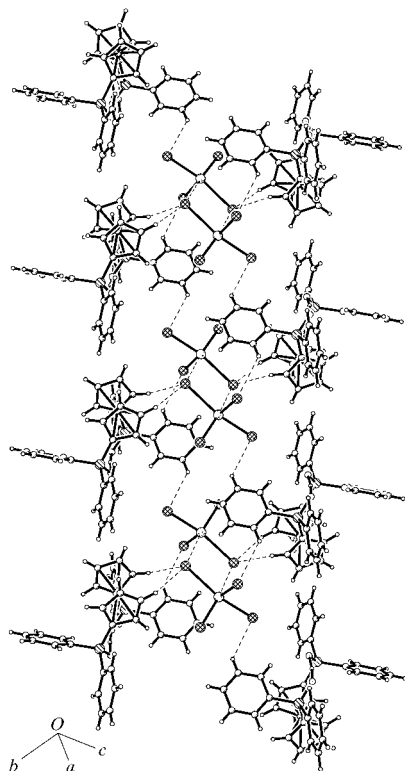


Figure 2
View of the inter-ionic interactions in (I) and the packing of the ions into columns along the *a* axis.

The discrete $[\text{Sb}_2\text{Cl}_8]^{2-}$ anions in (I) are different to the anions in the structures of $[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{SbCl}_4][\text{SbCl}_3]$ (Razak *et al.*, 2000) and $[\text{Fe}(\text{C}_5\text{H}_5)_2][\text{SbCl}_4]$ (Yamin *et al.*, 1996), in which $[\text{SbCl}_4]^-$ moieties are linked to form infinite chains. Each $[\text{Sb}_2\text{Cl}_8]^{2-}$ anion is linked by eight C—H...Cl interactions to four surrounding symmetry-related cations (Table 2). These interactions interconnect the ions to form columns along the *a* direction (Fig. 2).

Experimental

A few drops of fresh SbCl_5 were added to a solution of bis(diphenylphosphino)ferrocene (dppf, obtained from Aldrich Chemicals) in acetonitrile (50 ml). The solution was stirred for about 30 min. The solution was then filtered and left to evaporate slowly. After a few days, good quality crystals suitable for X-ray crystallographic analysis were obtained. The expected product was trichloro[bis(diphenylphosphine oxide-*O*)ferrocene]antimony(III), as in the case of bis(diphenylphosphino)methane (dppm) (Razak *et al.*, 1999), where dppm was oxidized to dppmCl_2 , thus forming SbCl_3 . In the presence of water vapour, dppmCl_2 was converted to methylenebis(diphenylphosphine oxide). This was followed by the formation of the complex with chemical binding between the Sb atom of SbCl_3 and the two O atoms of the phosphine oxide. However, in the present complex, the IR spectrum shows a more complicated nature in the region of the P—O vibration bands. A small amount of HCl is present in the solution as a result of the formation of bis(diphenylphosphine oxide-*O*)ferrocene, and this reacts with the P—O—Sb bonds to give $[\text{SbCl}_4]^-$ and the $(2\text{dppf-}O)\text{H}^+$ species.

Crystal data

$[\text{Fe}(\text{C}_{34}\text{H}_{29}\text{O}_2\text{P}_2)]_2[\text{Sb}_2\text{Cl}_8]$
 $M_r = 1701.82$
 Triclinic, $P\bar{1}$
 $a = 11.036(1) \text{ \AA}$
 $b = 12.348(1) \text{ \AA}$
 $c = 14.002(1) \text{ \AA}$
 $\alpha = 76.35(1)^\circ$
 $\beta = 77.19(1)^\circ$
 $\gamma = 70.82(1)^\circ$
 $V = 1729.5(2) \text{ \AA}^3$

$Z = 1$
 $D_x = 1.634 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 38 reflections
 $\theta = 5.3\text{--}12.5^\circ$
 $\mu = 1.63 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Block, orange
 $0.38 \times 0.36 \times 0.32 \text{ mm}$

Data collection

Siemens *P4* diffractometer
 $\theta/2\theta$ scans
 Absorption correction:
 ψ scan (Siemens, 1994)
 $T_{\min} = 0.576$, $T_{\max} = 0.623$
 7093 measured reflections
 6061 independent reflections
 5393 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -1 \rightarrow 13$
 $k = -13 \rightarrow 14$
 $l = -16 \rightarrow 16$
 3 standard reflections
 every 97 reflections
 intensity decay: $<3\%$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.076$
 $S = 1.06$
 6061 reflections
 397 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 0.4246P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.57 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

| | | | |
|----------------------|------------|--------------------------|------------|
| Sb1—Cl1 | 2.379 (1) | P1—C7 | 1.786 (3) |
| Sb1—Cl4 | 2.456 (1) | P1—C1 | 1.797 (3) |
| Sb1—Cl3 | 2.493 (1) | P2—C22 | 1.763 (3) |
| Sb1—Cl2 | 2.780 (1) | P2—C23 | 1.787 (3) |
| Sb1—Cl2 ⁱ | 2.945 (1) | P2—C29 | 1.791 (3) |
| P1—Cl5 | 1.764 (3) | | |
| Cl1—Sb1—Cl4 | 90.96 (3) | Cl1—Sb1—Cl2 ⁱ | 98.29 (3) |
| Cl1—Sb1—Cl3 | 88.79 (4) | Cl4—Sb1—Cl2 ⁱ | 169.96 (3) |
| Cl4—Sb1—Cl3 | 97.34 (3) | Cl3—Sb1—Cl2 ⁱ | 86.79 (3) |
| Cl1—Sb1—Cl2 | 88.00 (3) | Cl2—Sb1—Cl2 ⁱ | 82.64 (3) |
| Cl4—Sb1—Cl2 | 93.86 (3) | Sb1—Cl2—Sb1 ⁱ | 97.36 (3) |
| Cl3—Sb1—Cl2 | 168.40 (3) | | |

Symmetry code: (i) 1 - x, 1 - y, 1 - z.

Table 2

Hydrogen-bonding geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-------------------------------------|-------------|--------------|--------------|----------------|
| O1—H1O \cdots O2 | 1.1771 (18) | 1.2352 (19) | 2.411 (3) | 176.19 (13) |
| C19—H19A \cdots Cl2 | 0.98 | 2.76 | 3.599 (4) | 144 |
| C16—H16A \cdots Cl2 | 0.98 | 2.87 | 3.615 (3) | 133 |
| C8—H8A \cdots Cl1 ⁱ | 0.93 | 2.86 | 3.481 (4) | 125 |
| C11—H11A \cdots Cl3 ⁱⁱ | 0.93 | 2.80 | 3.484 (4) | 132 |

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, 1-y, 1-z$.

After checking their presence in a difference map, all H atoms bonded to C atoms were fixed in geometrically idealized positions and allowed to ride on their parent atoms [$C-H = 0.93$ or 0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. The H atom shared by the O atoms was held fixed in its difference-map position, with $O1-H1O = 1.1771$ (18) Å and $O2-H1O = 1.2352$ (19) Å, and $U_{iso}(H10) = 1.5U_{eq}(O1)$.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1132). Services for accessing these data are described at the back of the journal.

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