

Bis[1,1'-bis(diphenylphosphino)-ferrocenium] hexadecachlorotetra-antimony(III) ethanol solvate

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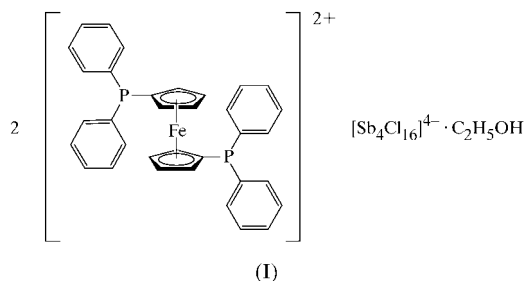
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In the title compound, $[\text{Fe}(\text{C}_{17}\text{H}_{14}\text{P})_2][\text{Sb}_4\text{Cl}_{16}] \cdot \text{C}_2\text{H}_6\text{O}$, the Fe atoms lie on inversion centres and the pairs of cyclopentadienyl rings are consequently in a fully staggered conformation. The centrosymmetric anionic clusters formed by $[\text{Sb}_4\text{Cl}_{16}]^{4-}$ are surrounded by the cations and are held together by weak $\text{C}-\text{H} \cdots \text{Cl}$ interactions. These formations stack along the a axis to form columns, and the columns are interconnected by another weak $\text{C}-\text{H} \cdots \text{Cl}$ interaction along the b axis.

Comment

Antimony trichloride is known to form adducts with phosphorus oxide derivatives, such as triphenylphosphine oxide (Golič & Milicev, 1978). It also interacts with and oxidizes ferrocene in chloroform or acetonitrile to give ferrocenium tetrachloroantimonate (Yamin *et al.*, 1996) and bis(ferrocenium) bis[tetrachloroantimonate(III)] trichloroantimony(III) (Razak *et al.*, 2000), respectively. The presence of the P atom in diphenylphosphinoferrrocene (dppf) was



thought to give a P—Sb or Sb—O—P bond formation, as in the case of dppf with SnCl_4 (Yamin *et al.*, 1996). A good quality crystal of the title compound, (I), obtained by recrystallization from ethanol, was subjected to X-ray crystallographic investigation and the results are presented here.

The asymmetric unit of (I) contains two $[\text{Fe}\{\text{C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2\}_2]^{2+}$ cations with the Fe atoms lying on inversion centres, a centrosymmetric anionic $[\text{Sb}_4\text{Cl}_{16}]^{4-}$ cluster and one ethanol molecule (Fig. 1).

The C—C, Fe—C and Fe—centroid distances in the ferrocenium moieties are comparable with the values reported by Orpen *et al.* (1989) and Razak *et al.* (1998). The Sb—Cl bond lengths range from 2.397 (2) to 2.743 (2) Å. A very similar

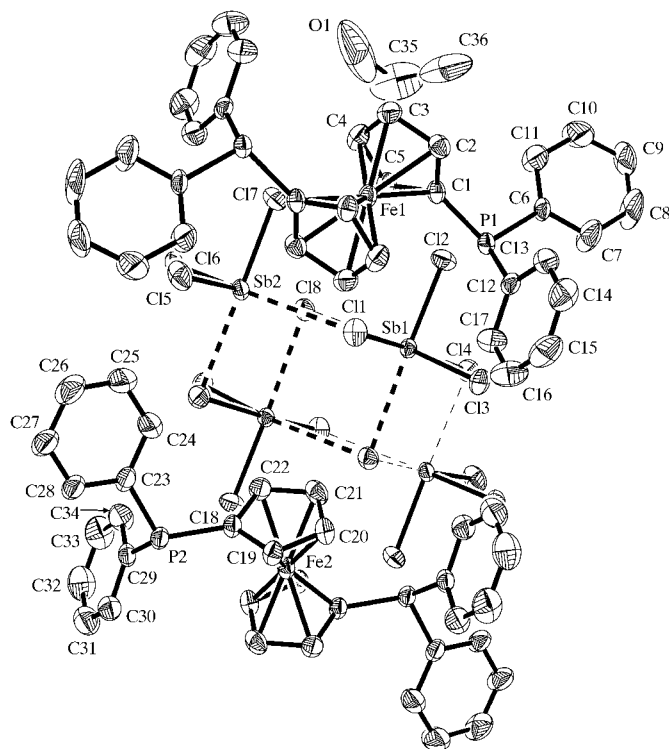


Figure 1
The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

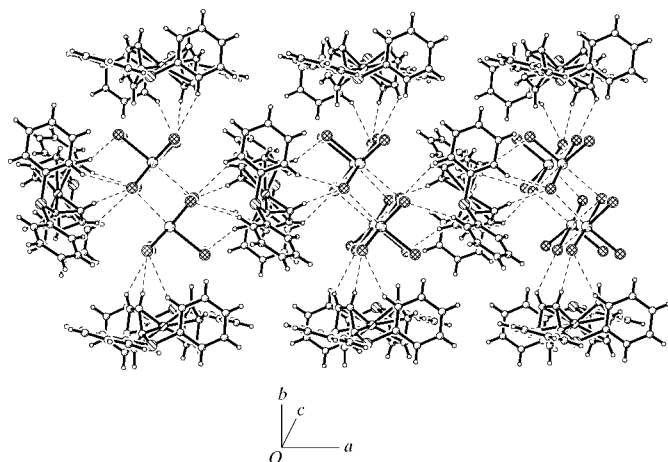


Figure 2
A view of the columns along the a axis in the packing of (I).

Sb—Cl range has also been observed in a related structure (Razak *et al.*, 2000). The longer bond lengths involving Cl1 and Cl4 are bridging, while the remaining Cl atoms are non-bridging (Porter & Jacobson, 1970; Yamin *et al.*, 1996; Razak *et al.*, 2000). The P—C bond lengths are comparable with the corresponding values in the structure reported by Carmalt *et al.* (1996), but the $C_{Ph}-P-C_{Ph}$ bond angles in (I) are larger.

The cyclopentadienyl (Cp) rings are in a staggered conformation. The torsion angle between a ring C atom, the two ring centres and the corresponding C atom on the opposite ring defines the angle of twist for the Cp rings (Palenik, 1970). The average $Cn-Cg \cdots Cg'-Cn'$ (Cg is the ring centroid) torsion angle is 36° for both cations. Examples of the staggered and eclipsed conformations of Cp rings are given by Osborne *et al.* (1996).

The coordination around Sb1 is provided by atoms Cl1, Cl3, Cl4 and Cl8 at the equatorial positions, while the apices are occupied by Cl2 and Cl8ⁱ [symmetry code: (i) $-x, 1-y, 1-z$]. The basal plane around Sb2 is formed by atoms Cl1, Cl5, Cl6 and Cl8, while the axial positions are occupied by Cl7 and Cl4ⁱ. The bond lengths and angles around the Sb atoms are in the ranges 2.397 (2)–3.329 (2) Å and 77.22 (4)–177.24 (6)°, respectively.

In the structure of (I), four $[SbCl_4]^-$ anions form a Cl1—Cl8 edge-shared octahedron, to form an anionic centrosymmetric $[Sb_4Cl_{16}]^{4-}$ cluster. Each cluster is surrounded by $[Fe\{C_5H_4P(C_6H_5)_2\}_2]^{2+}$ cations. These formations are held together by weak C—H \cdots Cl interactions and are joined continuously along the *a* axis to form columns. These columns are then interconnected along the *b* axis by other C—H \cdots Cl interactions (Table 2).

Experimental

Antimony trichloride (0.049 g, 0.22 mmol) in chloroform (5 ml) was added to a 50 ml flask containing a triphenylphosphinoferrrocene (0.121 g, 0.22 mmol) solution in chloroform. The mixture was stirred at ambient temperature for about 30 min. The solid obtained after 4 d of evaporation was recrystallized from ethanol.

Crystal data

$[Fe(C_{17}H_{14}P)_2]_2[Sb_4Cl_{16}] \cdot C_2H_6O$
 $M_r = 2208.98$
 Monoclinic, $P2_1/n$
 $a = 11.6280$ (3) Å
 $b = 15.0898$ (3) Å
 $c = 25.6100$ (6) Å
 $\beta = 90.342$ (1)°
 $V = 4493.56$ (18) Å³
 $Z = 2$

$D_x = 1.633$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 6411 reflections
 $\theta = 1.6$ – 28.4°
 $\mu = 2.08$ mm⁻¹
 $T = 293$ (2) K
 Slab, light yellow
 $0.34 \times 0.22 \times 0.20$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 $T_{min} = 0.538$, $T_{max} = 0.681$
 25 353 measured reflections

7901 independent reflections
 5408 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.084$
 $\theta_{max} = 25^\circ$
 $h = -13 \rightarrow 13$
 $k = -13 \rightarrow 17$
 $l = -30 \rightarrow 30$

Table 1

Selected geometric parameters (Å, °).

P1—C1	1.764 (6)	Sb1—Cl4	2.743 (2)
P1—C6	1.792 (6)	Sb1—Cl8 ⁱ	3.012 (2)
P1—C12	1.793 (6)	Sb1—Cl8	3.227 (2)
P2—C18	1.776 (6)	Sb2—Cl5	2.397 (2)
P2—C29	1.782 (6)	Sb2—Cl7	2.442 (2)
P2—C23	1.800 (6)	Sb2—Cl6	2.462 (2)
Sb1—Cl3	2.402 (2)	Sb2—Cl8	2.869 (2)
Sb1—Cl2	2.431 (2)	Sb2—Cl4 ⁱ	2.949 (2)
Sb1—Cl1	2.547 (2)	Sb2—Cl1	3.329 (2)
Cl1—Sb1—Cl4	174.18 (5)	Cl6—Sb2—Cl8	177.21 (5)
Cl2—Sb1—Cl8 ⁱ	177.24 (6)	Cl7—Sb2—Cl4 ⁱ	173.11 (6)
Cl3—Sb1—Cl8	170.37 (5)	Cl5—Sb2—Cl1	164.68 (5)

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

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> —H⋯ <i>A</i>
C2—H2A \cdots Cl6 ⁱ	0.98	2.85	3.829 (6)	173
Cl3—H13A \cdots Cl6 ⁱ	0.93	2.87	3.671 (7)	145
C27—H27A \cdots Cl3	0.93	2.84	3.508 (8)	130
C3—H3A \cdots Cl1 ⁱ	0.98	2.83	3.582 (7)	134
C9—H9A \cdots Cl5 ⁱⁱ	0.93	2.83	3.744 (9)	168
C19—H19A \cdots Cl2 ⁱⁱⁱ	0.98	2.87	3.564 (6)	128
C21—H21A \cdots Cl8 ^{iv}	0.98	2.83	3.582 (6)	134
C28—H28A \cdots Cl5 ⁱⁱⁱ	0.93	2.81	3.679 (7)	155
C22—H22A \cdots Cl4 ^{iv}	0.98	2.66	3.636 (6)	173

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.108$
 $S = 0.96$
 7901 reflections
 454 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0396P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.70$ e Å⁻³
 $\Delta\rho_{min} = -1.01$ e Å⁻³

After checking their presence in a difference map, all H atoms were fixed geometrically and allowed to ride on their parent atoms. The highest peak (0.70 e Å⁻³) and deepest hole (−1.01 e Å⁻³) were found near P2 (1.35 Å) and Sb1 (1.09 Å), respectively.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; 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: NA1547). Services for accessing these data are described at the back of the journal.

References

- Carmalt, C. J., Cowley, A. H., Decken, A., Lawson, Y. G. & Norman, N. C. (1996). *Acta Cryst.* **C52**, 931–933.
- Golič, L. & Milicev, S. (1978). *Acta Cryst.* **B34**, 3379–3381.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Orpen, G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–83.
- Osborne, A. G., da Silva, M. W., Hursthouse, M. B., Malik, K. M. A., Oromolla, G. & Zanello, P. (1996). *J. Organomet. Chem.* **516**, 167–176.
- Palenik, J. (1970). *Inorg. Chem.* **9**, 2424–2430.
- Porter, S. K. & Jacobson, R. A. (1970). *J. Chem. Soc. A*, pp. 1356–1359.
- Razak, I. A., Fun, H.-K., Yamin, B. M., Bashaala, A. M. A. & Chinnakali, K. (1998). *Acta Cryst.* **C54**, 912–914.
- Razak, I. A., Shanmuga Sundara Raj, S., Fun, H.-K., Yamin, B. M. & Hashim, N. (2000). *Acta Cryst.* **C56**, 664–665.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Yamin, B. M., Fun, H.-K., Sivakumar, K., Yip, B. C. & Shawkataly, O. B. (1996). *Acta Cryst.* **C52**, 1966–1968.