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Ferrocenium Tetrachloroantimonate

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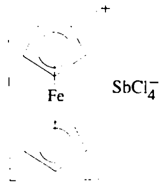
Abstract

The crystal structure of ferrocenium tetrachloroantimonate, [Fe(C$_5$H$_5$)$_2$][SbCl$_4$], has been determined at 173 K. The cyclopentadiene rings in the ferrocenium cation are in an eclipsed conformation. The Sb atom is coordinated by six Cl ions in an irregular octahedral arrangement. Two Cl$^-$ ions form halogen bridges with neighbouring Sb atoms, resulting in a polymeric chain of anions {the compound may be named *catena*-poly[ferrocinium (dichloroantimonate-di-μ-chloro)]}. The ferrocenium cations are stacked between these polymeric chains and form two-dimensional layers parallel to the *bc* plane.

Comment

Although ferrocene is readily oxidized to the ferrocenium cation by Group 15 trihalides such as PCl$_3$, AsCl$_3$, SbCl$_3$ and BiCl$_3$, the products can be quite complicated due to the presence of highly aggregated halogeno–Group 15 anions (Landers *et al.*, 1976; Mammano, Zalkin, Landers & Rheingold, 1977). Therefore, it can be generalized that the oxidation products of such reactions can have different compositions depending on the molar ratio of metal halide to ferrocene used, and also on the type of solvent. The ability of some metals to expand their coordination number during reaction could further contribute to the complexity of the product. Recrystallization of ferrocenium salts from water or organic solvents is normally very difficult and hence relatively few detailed X-ray structures of ferrocenium salts have been reported. Our literature search on ferrocenium Group 15 halides indicated that so far only the structures of ferrocenium tetrachlorobismuthate, $[\eta^5\text{-}(C_5H_5)_2Fe]_2[As_4Cl_{10}O_2]$ and $\{[\eta^5\text{-}(C_5H_5)_2Fe]_2[Sb_4Cl_{12}O]\}_2.2C_6H_6$ have been reported (Mammano *et al.*, 1977; Churchill, Landers & Rheingold, 1981; Rheingold, Landers, Dahlstrom & Zubieta, 1979). Even though a product from SbCl$_3$ with an empirical formula analogous to that of ferrocenium tetrachlorobismuthate was found, no structural details of the compound were reported (Cowell, Ledwith, White & Wood, 1970) and hence the X-ray structure analysis of the title compound, (I), was undertaken.



(I)

The structure was found to be isomorphous with that of ferrocenium tetrachlorobismuthate. The Sb atom is coordinated by six Cl$^-$ ions, forming an irregular octahedron. The Sb—Cl distances vary from 2.3888 (7) (Sb—Cl1) to 3.3202 (8) Å (Sb—Cl3′). The Sb atoms are connected by Sb—Cl—Sb′ halogen bridges *via* atoms Cl3 and Cl4, leading to a polymeric chain of anions running along the *c* axis. In this chain, the Sb coordination octahedra are found to be 'edge sharing'. Among the six Sb—Cl bonds, the four long bonds involving atoms Cl3, Cl4, Cl3′ and Cl4′ are bridging, whereas the two short bonds, Sb—Cl1 and Sb—Cl2, are non-bridging. The Sb—Cl3—Sb′ and Sb—Cl4—Sb′ angles are 92.9 (1) and 98.2 (1)°, respectively. The octahedron is considerably distorted owing to the vast differences in the relevant bond lengths and angles. The Sb—Cl distances observed in this structure show variations from those observed in pyridinium tetra-

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chloroantimonate (Porter & Jacobson, 1970), where the anion sits on a special position and hence only one short bond and two long bonds are present, *i.e.* non-bridging Sb—Cl 2.33 Å, bridging Sb—Cl 2.63 and 3.13 Å; in the title compound, only one of the non-bridging distances (Sb—Cl1) agrees with this value, whereas all the other distances are different and unique.

The cyclopentadiene rings in the ferrocenium cation are in an eclipsed conformation; the dihedral angle between the planes of these rings is 3.3 (1)°. The C—C bond distances in these rings range from 1.391 (5) (C2—C3) to 1.422 (6) Å (C1—C5), with an average value of 1.409 (6) Å. The average Fe—C distance is 2.085 (3) Å. The Fe-to-ring-centre distances are 1.7062 (4) (C1–C5) and 1.7054 (4) Å (C6–C10).

The molecular packing in the title compound is in line with other related structures such as ferrocenium tetrachlorobismuthate and pyridinium tetrachloroantimonate (Mammano *et al.*, 1977; Porter & Jacobson, 1970). In general, the Group 15 halogen anion MX_4^- forms an infinite chain of octahedra with the cations packed into the spaces between these chains. This arrangement results in two-dimensional layers of anions and cations (Fig. 2) parallel to the *bc* plane.

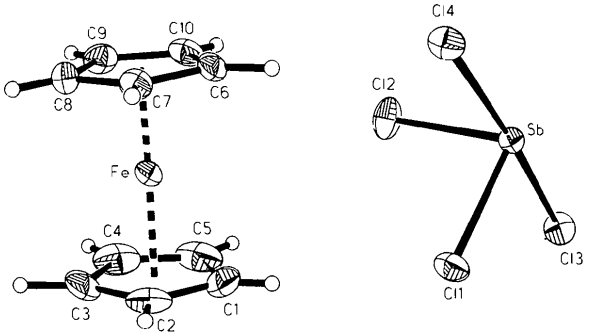

Fig. 1. Displacement ellipsoid plot (50% probability) of the title molecule with the numbering scheme.

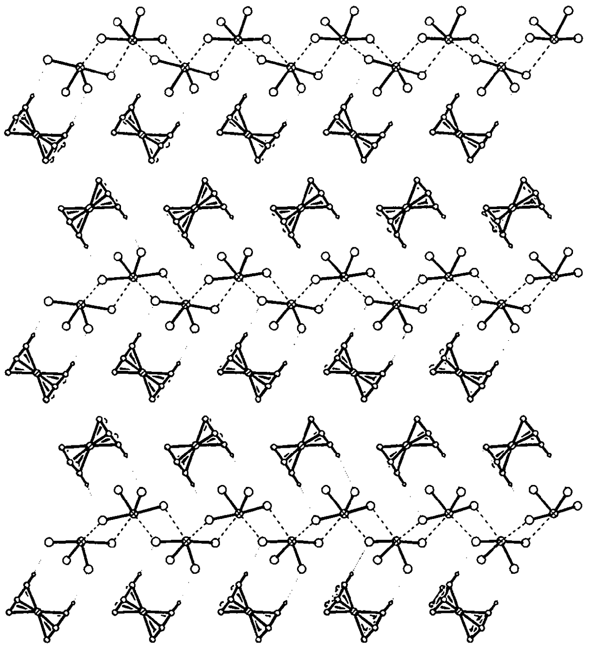

Fig. 2. A single layer of molecules viewed down the *a* axis. The Sb—Cl bridging is shown as dashed lines and the C—H···Cl hydrogen bonds are shown as dotted lines.

Experimental

The title compound was prepared by mixing equimolar amounts of ferrocene and antimony trichloride in acetonitrile. After a few days, dark blue needle-like crystals were obtained.

Crystal data

$[Fe(C_5H_5)_2][SbCl_4]$
$M_r = 449.58$
Monoclinic
$P2_1/c$
$a = 10.733\ (1)$ Å
$b = 17.017\ (2)$ Å
$c = 7.6830\ (1)$ Å
$\beta = 97.49\ (1)°$
$V = 1391.3\ (3)$ Å^3
$Z = 4$
$D_x = 2.146$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 10$–$25°$
$\mu = 3.721$ mm^{-1}
$T = 173\ (2)$ K
Needle
$0.56 \times 0.38 \times 0.28$ mm
Dark blue

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XSCANS*; Siemens, 1994)
$T_{min} = 0.802$, $T_{max} = 0.986$
4120 measured reflections
3175 independent reflections
3046 observed reflections $[I > 2\sigma(I)]$

$R_{int} = 0.0248$
$\theta_{max} = 27.49°$
$h = -13 \rightarrow 13$
$k = -22 \rightarrow 1$
$l = -1 \rightarrow 9$
3 standard reflections monitored every 100 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R(F) = 0.0248$
$wR(F^2) = 0.0624$
$S = 1.094$
3175 reflections
186 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2 + 2.3752P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$

$\Delta\rho_{max} = 0.842$ e Å^{-3}
$\Delta\rho_{min} = -0.720$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0060 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Sb	0.23245 (2)	0.30718 (1)	0.35402 (2)	0.01728 (8)
Cl1	0.36868 (7)	0.40978 (4)	0.47591 (10)	0.0277 (2)
Cl2	0.10910 (7)	0.39965 (5)	0.16334 (11)	0.0337 (2)
Cl3	0.08650 (7)	0.32835 (5)	0.59127 (10)	0.0280 (2)
Cl4	0.39272 (7)	0.29377 (4)	0.11523 (10)	0.0262 (2)
Fe	0.27396 (4)	0.59740 (2)	−0.04572 (5)	0.01836 (10)
C1	0.2915 (4)	0.6018 (2)	0.2292 (4)	0.0396 (8)
C2	0.3805 (3)	0.6514 (2)	0.1665 (4)	0.0345 (8)
C3	0.3170 (4)	0.7077 (2)	0.0576 (5)	0.0350 (8)
C4	0.1879 (4)	0.6943 (2)	0.0516 (6)	0.0429 (10)
C5	0.1705 (4)	0.6289 (3)	0.1566 (5)	0.0453 (10)
C6	0.3008 (3)	0.4828 (2)	−0.1349 (4)	0.0241 (6)
C7	0.3930 (3)	0.5340 (2)	−0.1860 (4)	0.0231 (6)
C8	0.3307 (3)	0.5934 (2)	−0.2934 (4)	0.0250 (6)
C9	0.1995 (3)	0.5788 (2)	−0.3069 (4)	0.0282 (6)
C10	0.1822 (3)	0.5105 (2)	−0.2086 (4)	0.0273 (6)

Table 2. *Selected geometric parameters (Å, °)*

Sb—Cl1	2.3888 (7)	C2—C3	1.391 (5)
Sb—Cl2	2.4226 (8)	C3—C4	1.399 (6)
Sb—Cl3	2.5788 (8)	C4—C5	1.402 (6)
Sb—Cl4	2.6832 (8)	C6—C10	1.406 (4)
Sb—Cl3$^{\rm i}$	3.3202 (8)	C6—C7	1.413 (4)
Sb—Cl4$^{\rm ii}$	3.0063 (8)	C7—C8	1.416 (4)
C1—C2	1.406 (6)	C8—C9	1.421 (4)
C1—C5	1.422 (6)	C9—C10	1.411 (5)
Cl1—Sb—Cl2	91.18 (3)	Cl4—Sb—Cl4$^{\rm ii}$	92.6 (1)
Cl1—Sb—Cl3	91.03 (3)	Cl3$^{\rm i}$—Sb—Cl4$^{\rm ii}$	101.1 (1)
Cl2—Sb—Cl3	90.13 (3)	C2—C1—C5	107.3 (3)
Cl1—Sb—Cl4	85.18 (3)	C3—C2—C1	108.6 (3)
Cl2—Sb—Cl4	89.44 (3)	C2—C3—C4	108.2 (3)
Cl3—Sb—Cl4	176.18 (2)	C3—C4—C5	108.4 (3)
Cl1—Sb—Cl3$^{\rm i}$	164.2 (1)	C4—C5—C1	107.4 (3)
Cl2—Sb—Cl3$^{\rm i}$	84.6 (1)	C10—C6—C7	108.1 (3)
Cl3—Sb—Cl3$^{\rm i}$	104.2 (1)	C6—C7—C8	107.9 (3)
Cl4—Sb—Cl3$^{\rm i}$	79.6 (1)	C7—C8—C9	107.8 (3)
Cl1—Sb—Cl4$^{\rm ii}$	83.6 (1)	C10—C9—C8	107.7 (3)
Cl2—Sb—Cl4$^{\rm ii}$	174.2 (1)	C6—C10—C9	108.5 (3)
Cl3—Sb—Cl4$^{\rm ii}$	87.4 (1)		

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

The determination of the cell parameters and intensity-data collection were carried out at 173 K. The structure was solved by heavy-atom methods and refined by a full-matrix least-squares technique. All H atoms were located from difference maps and refined isotropically.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93. Geometric calculations: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1201). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diaqua[2,6-diacetylpyridine bis(thiosemicarbazone)]manganese(II) Diperchlorate

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Abstract

The Mn atom in $[Mn(C_{11}H_{15}N_7S_2)(H_2O)_2](ClO_4)_2$ is in a distorted pentagonal bipyramidal environment with three N and two S atoms of the open-chain ligand forming the pentagonal girdle and O atoms of the water molecules occupying the apical positions. The ClO_4^- ions are involved in hydrogen bonding with the H_2O molecules and with the terminal amino groups of the ligand [3.002 (5) and 2.962 (8) Å].