Potočňák, I., Dunaj-Jurčo, M., Mikloš, D. & Jäger, L. (1996*b*). *Acta Cryst.* C**52**, 532–535.
Potočňák, I., Dunaj-Jurčo, M., Mikloš, D. & Jäger, L. (1996*c*). *Acta Cryst.* C**52**, 1653–1655.
Potočňák, I., Dunaj-Jurčo, M., Mikloš, D., Kabešová, M. & Jäger, L. (1995*a*). *Acta Cryst.* C**51**, 600–602.
Potočňák, I., Dunaj-Jurčo, M., Mikloš, D., Kabešová, M. & Jäger, L. (1995*b*). *Acta Cryst.* C**51**, 1291–1293.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Acta Cryst. (1996). C**52**, 2412–2414

Perchlorotriphenylcarbenium Hexachloroantimonate(V)

ELIES MOLINS,[a] MONTSE MAS,[a] WALDEMAR MANIUKIEWICZ,[a] MANUEL BALLESTER[a] AND JUAN CASTAÑER[b]

[a]*Institut de Ciència de Materials de Barcelona, Campus de la UAB, 08193 Bellaterra, Spain, and* [b]*Departamento de Materiales Orgánicos Halogenados, Centro de Investigación y Desarrollo, Jorge Girona, 18-26, 08034 Barcelona, Spain. E-mail: waldemar@icmab.es*

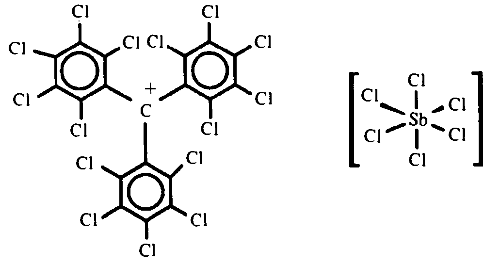
(*Received 12 January 1996; accepted 4 June 1996*)

Abstract

The title compound, $C_{19}Cl_{15}^{+}.SbCl_6^{-}$, consists of perchlorotriphenylcarbenium cations and hexachloroantimonate anions. The central Sb and C atoms occupy special positions of symmetry 32 along the *c* axis. The cation shows a symmetrical propeller conformation. Four Cl atoms of the $SbCl_6^-$ anion are disordered.

Comment

The so-called 'inert carbon-free radicals' belong mainly to the perchlorodiphenylmethyl (Ballester & Riera, 1954), perchlorotriphenylmethyl (Ballester, 1967; Ballester, Riera, Castañer, Badía & Monsó, 1971) and 9-phenylfluorenyl radical (Ballester, Castañer & Pujadas, 1971) classes. They have chemical and thermal stabilities which are higher than those of the majority of normal tetrahedral carbon compounds and materials. Such passivity is due to steric shielding of the molecular sites, where most of the radical reactivity normally resides (sites of high spin density), and to the strength of their valence bonds. Yet they are active in single-electron transfers yielding stable isolable carbenium (Ballester, Riera-Figueras & Rodríguez-Siurana, 1970) and carboanion (Ballester & De la Fuente, 1970) salts. As part of a systematic investigation of overcrowded polyhalogenated aromatic species, we report here the structural study of perchlorotriphenylcarbenium hexachloroantimonate, (I), obtained from the perchlorotriphenylmethyl radical by single-electron oxidation (Ballester *et al.*, 1982). This carbenium salt possesses a highly symmetrical structure.



(I)

The overall conformation of the perchlorotriphenylcarbenium ion (Fig. 1) is described by the angle between the mean planes of the aromatic rings [77.2 (2)°] and the angle between these planes and the plane defined by the C1 and three C2 atoms [46.1 (2)°]. The mean values of the bond lengths and angles in the pentachlorophenyl group are C—C 1.397 (7), C—Cl 1.700 (6) Å, C—C—C 119.9 (6) and C—C—Cl 119.9 (4)°. These values do not differ significantly from those found in other structures containing the carbenium cation (Miravitlles, Molins, Solans, Germain & Declercq, 1985; Veciana, Carilla, Miravitlles & Molins, 1987). The most significant difference is that in the present compound, the three perchlorophenyl groups of the cation are crystallographically equivalent, while in the cited structures, these three groups are not. In the present structure, the perchlorotriphenylcarbenium ion adopts the highest symmetrical conformation so far described. Due to the intercalated packing, the shortest intermolecular Cl···Cl interactions are between the anions and cations [Cl6···Cl7($x + \frac{1}{3}$, $y + \frac{2}{3}$, $z - \frac{1}{3}$) 3.121 (2) Å].

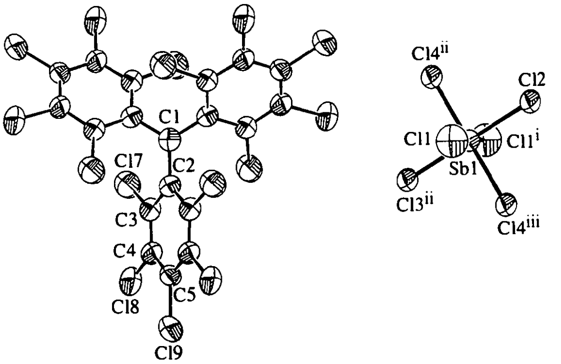


Fig. 1. The molecular structure and atomic labelling of the perchlorotriphenylcarbenium cation and hexachloroantimonate anion. Only one of the six components of the disordered $SbCl_6^-$ anion is shown [symmetry codes: (i) $y, x, -z$; (ii) $-y, x - y, z$; (iii) $-x, y - x, -z$]. Displacement ellipsoids are drawn at the 50% probability level.

Acta Crystallographica Section C
ISSN 0108-2701 © 1996

Experimental

The title salt, $(C_6Cl_5)_3C^+.SbCl_6^-$, was synthesized by reaction of the perchlorotriphenyl radical with antimony pentachloride in sulfuryl chloride, as described previously by Ballester *et al.* (1982). Dark green crystals were obtained by slow evaporation of the reaction solution at room temperature.

Crystal data

$C_{19}Cl_{15}^{+}.SbCl_6^-$
$M_r = 1094.39$
Trigonal
$R32$
$a = 11.559\,(2)$ Å
$c = 21.783\,(4)$ Å
$V = 2520.5\,(8)$ Å^3
$Z = 3$
$D_x = 2.163$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 2.23$–$30.38°$
$\mu = 2.509$ mm^{-1}
$T = 293\,(2)$ K
Rectangular
0.65 × 0.59 × 0.35 mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical using azimuthal ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.68$, $T_{\max} = 0.97$
5208 measured reflections
1715 independent reflections

1583 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0449$
$\theta_{\max} = 30.45°$
$h = -16 \rightarrow 16$
$k = -16 \rightarrow 16$
$l = 0 \rightarrow 30$
3 standard reflections monitored every 100 reflections
intensity decay: 22.7%

Refinement

Refinement on F^2
$R(F) = 0.0438$
$wR(F^2) = 0.1322$
$S = 1.025$
1715 reflections
71 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0887P)^2 + 4.8171P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.789$ e Å^{-3}
$\Delta\rho_{\min} = -1.026$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Flack parameter for absolute configuration determination = 0.48 (4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	$U_{\rm eq}$
Sb1	0	0	0	0.0474 (2)
Cl1	0	0	0.10758 (10)	0.0909 (8)
Cl2†	0.20281 (6)	0	0	0.0741 (11)
Cl3†	0.20281 (6)	0.20281 (6)	0	0.0741 (11)
Cl4†	0.11723 (14)	−0.11700 (13)	0	0.0741 (11)
Cl5†	0.16569 (11)	−0.06056 (10)	0	0.0741 (11)
Cl6†	0.16566 (11)	0.22622 (10)	0	0.0741 (11)
Cl7	0.0268 (2)	−0.1877 (2)	0.40900 (8)	0.0773 (5)
Cl8	0.2933 (2)	−0.1789 (2)	0.40882 (10)	0.0827 (5)
Cl9	0.5139 (2)	0	0.5	0.0888 (7)
C1	0	0	0.5	0.050 (2)
C2	0.1255 (6)	0	0.5	0.0498 (13)
C3	0.1450 (5)	−0.0863 (5)	0.4600 (2)	0.0541 (10)
C4	0.2652 (5)	−0.0822 (5)	0.4596 (3)	0.0571 (11)
C5	0.3680 (6)	0	0.5	0.058 (2)

† Occupancy of 0.167.

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

Sb1—Cl1	2.343 (2)	C4—C5	1.400 (7)
C1—C2	1.450 (7)	C3—Cl7	1.696 (5)
C2—C3	1.424 (6)	C4—Cl8	1.716 (6)
C3—C4	1.366 (7)	C5—Cl9	1.687 (7)
C3$^{\rm i}$—C2—C3	118.8 (6)	C2—C3—Cl7	121.9 (4)
C3—C2—C1	120.6 (3)	C4—C3—Cl7	118.3 (4)
C4—C3—C2	119.7 (5)	C3—C4—Cl8	120.2 (5)
C3—C4—C5	121.5 (5)	C5—C4—Cl8	118.3 (4)
C4$^{\rm i}$—C5—C4	118.7 (7)	C4—C5—Cl9	120.6 (3)

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

The crystal used for analysis showed an average intensity decrease of 22.7% during data collection and so the data were scaled accordingly. The space group of the carbenium salt may be $R3$, $R\bar{3}$, $R32$, $R3m$ or $R\bar{3}m$ according to the systematic absences $-h + k + l = 3n$. Subsequent structure solution and least-squares refinement indicated the correct space group to be $R32$. The disordered $SbCl_6^-$ ion was treated as an ideal octahedron with two Cl atoms on a threefold axis parallel to the c axis and four disordered Cl atoms (with an occupation factor of 0.167 and the same displacement parameters) distributed about 15° from each other in the ab plane. This model led to a relatively flat $\Delta\rho$ map. An interesting finding is that the Flack (1983) parameter has the value 0.48 (4), indicating that the crystal may be an example of an inversion twin with 50% of each component.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1995). Software used to prepare material for publication: *SHELXL*93.

The authors would like to acknowledge the Dirección General de Investigación Científica y Técnica for financial support from Grant PB93-0119.

Lists of structure factors, anisotropic displacement parameters, complete geometry and torsion angles have been deposited with the IUCr (Reference: AB1351). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Ballester, M. (1967). *Pure Appl. Chem.* **15**, 123–151.

Ballester, M., Castañer, J. & Pujadas, J. (1971). *Tetrahedron Lett.* pp. 1699–1702.

Ballester, M. & De la Fuente, G. (1970). *Tetrahedron Lett.* pp. 4509–4510.

Ballester, M. & Riera, J. (1954). *J. Am. Chem. Soc.* **86**, 4505–4505.

Ballester, M., Riera, J., Castañer, J., Badía, C. & Monsó, J. M. (1971). *J. Am. Chem. Soc.* **93**, 2215–2225.

Ballester, M., Riera, J., Castañer, J., Rodriguez, A., Rovira, C. & Veciana, J. (1982). *J. Org. Chem.* **47**, 4498–4500.

Ballester, M., Riera-Figueras, J. & Rodríguez-Siurana, A. (1970). *Tetrahedron Lett.* pp. 3615–3618.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.

Miravitlles, C., Molins, E., Solans, X., Germain, G. & Declercq, J.-P. (1985). *J. Incl. Phenom.* **3**, 27–34.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1995). *PLATON. Molecular Geometry Program.* Version of October 1995. University of Utrecht, The Netherlands.
Veciana, J., Carilla, J., Miravitlles, C. & Molins, E. (1987). *J. Chem. Soc. Chem. Commun.* **1**, 812–814.

Acta Cryst. (1996). C**52**, 2414–2416

Bis(η^5-hydropentalenyl)iron

Elies Molins,[a] Waldemar Maniukiewicz,[a] Carlos Miravitlles,[a] Montse Mas,[a] Juan M. Manriquez,[b] Ivonne Chavez,[c] Beatriz Oelckers,[d] Joan Farran[e] and José Luis Briansó[e]

[a]*Institut de Ciència de Materials de Barcelona, Campus UAB, 08193 Bellaterra, Spain,* [b]*Centro de Investigación Minera y Metalurgica, Avda. Parque A. Rabat 6500, Santiago, Chile,* [c]*Departamento de Ciencias de los Materiales, Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 307, Santiago, Chile,* [d]*Instituto de Química, Universidad Catolica de Valparaíso, Avda. Brasil 2950, Valparaíso, Chile, and* [e]*Unidad de Cristalografía, Universidad Autónoma de Barcelona, 08193 Bellaterra, Spain. E-mail: elies.molins@icmab.es*

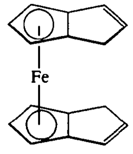
(*Received 7 February 1996; accepted 7 May 1996*)

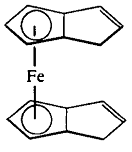
Abstract

In the structure of bis[(3a,4,5,6,6a-η)-1-hydropentalenyl]iron, [Fe(C_8H_7)$_2$], the two pentalene ligands are parallel. The molecules are packed in chains along the *a* axis and there are no significant intermolecular interactions. The compound shows disorder at the iron position with a 93.3% major and a 6.7% minor component. The structure of the predominant component has been determined. In addition, the double bond in one pentalene ligand is disordered. This confirms the results of a previous spectroscopic ^{1}H NMR study [Katz & Rosenberger (1963). *J. Am. Chem. Soc.* **85**, 2030–2031].

Comment

The title compound, (I), has been used recently as a useful building block in the synthesis of triple- and quadruple-decker pentalene complexes (Oelckers, Chávez, Manríquez & Román, 1993). The present structure is the first single crystal X-ray study of a dihydrodipentalenyl–metal complex. The only other related structure is that of (1,1′-dihydro-1,1′-bipentalenyl)iron, where the 'ferrocene' moiety is distorted due to the dimerization of the two pentalene ligands *via* 1-*endo*,1′-*endo* C—C bond formation (Churchill & Lin, 1973).


(I*a*) 93.3%


(I*b*) 6.7%

An *ORTEP* (Johnson, 1965) drawing of (I) is shown in Fig. 1. The Fe—C distances of 2.035 (2)–2.068 (2) Å are similar to those found for ferrocene (Seiler & Dunitz, 1979). The two planar five-membered rings are tilted 1.24 (11)° from being parallel and twisted *ca* 0.5 (2)° (mean) from an eclipsed conformation. The C—C distances within the π-cyclopentadienyl rings range from 1.416 (3) to 1.434 (3) Å [average 1.422 (3) Å].

In the crystal, the complex molecules are packed in chains (Fig. 2), with the intermolecular separation within a chain exceeding 3.5 Å.

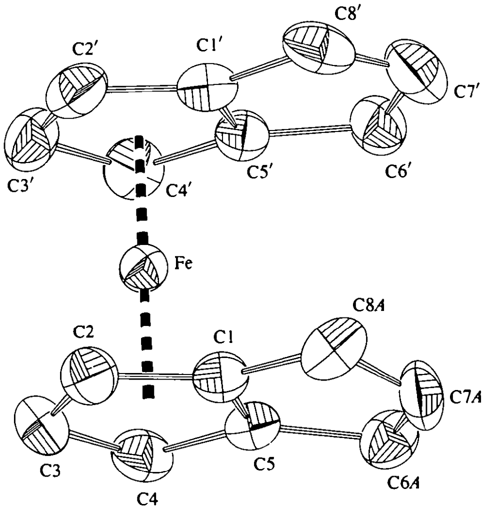


Fig. 1. View of the title structure showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted.

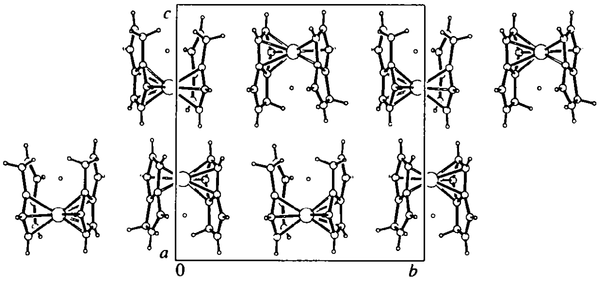


Fig. 2. Projection of the title structure down the *a* axis. The non-bonded small circles represent the positions of the Fe′ atoms.