The Crystal Structure of μ-Oxo-bis[tris(*p*-chlorophenyl)(1,1,1-trifluoro-2,4-pentanedionato-*O*,*O'*)antimony(V)]–Chloroform (1/2)

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The title compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 11\cdot961$ (2), $b = 14\cdot352$ (3), $c = 11\cdot818$ (2) Å, $\alpha = 124\cdot54$ (1), $\beta = 104\cdot36$ (1), $\gamma = 103\cdot84$ (1)° and $Z = 1$. Least-squares refinement with anisotropic thermal factors gave an R value of $0\cdot041$ for 6958 observed reflexions collected by diffractometry. The binuclear Sb^{V} complex consists of two distorted octahedra joined by an O atom which is situated at an inversion centre; the Sb–O–Sb bridge is linear and the Sb–O distance, $1\cdot943$ Å, is somewhat shorter than those in previously reported Sb–O(bridge) bonds. The remaining five sites of the octahedron around the Sb atom are occupied meridionally by two O atoms of the fluorinated β-diketonate and three C atoms of the aryl groups. The β-diketonate forms two distinct Sb–O bonds with the Sb atom: Sb–O(CF$_3$) = $2\cdot180$ (4) and Sb–O(CH$_3$) = $2\cdot417$ (3) Å.

Introduction

Recently, a new type of reaction of fluorinated β-diketones, such as 1,1,1-trifluoro-2,4-pentanedione and 1,1,1-trifluoro-4-phenyl-2,4-butanedione, coordinated to triarylantimony(V), has been found (Ebina, Uehiro, Iwamoto, Ouchi & Yoshino, 1976). The crystal structures of the two reaction products have already been determined (Ebina, Ouchi, Yoshino, Sato & Saito, 1977; Ebina, Ouchi, Yoshino, Sato & Saito, 1978). In the two products, the coordinated β-diketonate is hydrated at the C$\cdots$C group attached to the CF$_3$ group, to form a novel terdentate ligand: the β,β-dihydroxyketone dianion.

On the other hand, the IR and NMR spectra of the starting compound suggest that it is the μ-oxo dimer and that the β-diketonate is bonded to Sb in an enolate form. However, the detailed structure of the complex could not be elucidated from the spectral data.

The title compound, a starting material of the reaction, was subjected to structural analysis in order to obtain structural details for the elucidation of the reaction mechanism.

Experimental

Colourless crystals of the title compound were prepared by recrystallization from a mixture of chloroform and petroleum spirit under an anhydrous atmosphere, a vacuum-line apparatus being used to prevent the formation of the hydrated compound. The crystals are unstable in air, losing chloroform of crystallization. Preliminary cell dimensions and the space group were determined from oscillation and Weissenberg photographs. The former were refined by least-squares calculations on the basis of 2θ values of 39 higher-order reflexions ($45 < 2\theta < 50°$) measured on a diffractometer. The density was determined by flotation in an aqueous solution of potassium iodide.

Crystal data

C$_{46}$H$_{32}$Cl$_6$F$_6$O$_5$Sb$_2$.2CHCl$_3$, FW 1454$\cdot$62, triclinic, $a = 11\cdot961$ (2), $b = 14\cdot352$ (3), $c = 11\cdot818$ (2) Å, $\alpha = 124\cdot54$ (1), $\beta = 104\cdot36$ (1), $\gamma = 103\cdot84$ (1)°, $U = 1423\cdot9$ (7) Å^3, $Z = 1$, $D_m = 1\cdot72$, $D_x = 1\cdot72$ g cm^{-3}, space group $P\bar{1}$ (No. 2), μ(Mo $K\alpha$; $\lambda = 0\cdot7107$ Å) = $15\cdot63$ cm^{-1}.

The intensity data were collected on a Rigaku automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate, the ω scan ($2\theta \leq 10°$) and the θ–2θ scan technique ($10 < 2\theta \leq 60°$) being employed. Five standard reflexions were monitored every 50 reflexions. The specimen deteriorated during exposure to X-rays. Thus, two crystal specimens were used for the data collection. They were shaped into spheres (about 0$\cdot$45 and 0$\cdot$40 mm in diameter, respectively) and coated with epoxy resin. The combined data were corrected for Lorentz and polarization factors as well as for the intensity decrease of the standard reflexions. No correction was applied

for absorption or extinction. 8321 independent reflexions were measured, of which 6958 with $|F| > 3\sigma(|F|)$ were used for the structure determination and refinement.

Structure determination

The structure was solved by the heavy-atom method, the sharpened Patterson function being employed to locate the Sb atom. The positions of all other non-hydrogen atoms could be determined by successive Fourier syntheses of electron density. The structure was refined by a block-diagonal least-squares method with anisotropic thermal factors. At a later stage, the population of the solvent molecule was included in the full-matrix least-squares refinement. The positions of all the H atoms were obtained from a difference Fourier synthesis. A final refinement was carried out including the H atoms with isotropic thermal factors. In the last cycle of the calculation, all the parameter shifts were less than one-half of the corresponding standard deviations. The final R and R_w values were 0·041 and 0·058, respectively, for all the 6958 observed reflexions. The scattering factors and the corrections for anomalous scattering for Sb, C, O, F and Cl were taken from *International Tables for X-ray Crystallography* (1974). For H, the values given by Stewart, Davidson & Simpson (1965) were used. A weighting scheme [$w = 0\cdot4$ for $|F_o| < 5$, $w = 1$ for $5 \leq |F_o| \leq 16$ and $w = (16/|F_o|)^2$ for $|F_o| > 16$] was employed.

The possibility of the space group $P1$ was also considered. At the final stage of the refinements, the chemically equivalent bond lengths and angles in the two halves of the molecule differed considerably and the shape of the aryl rings was unreasonably deformed even though the R values were smaller than those based on $P\bar{1}$. Thus, the space group $P1$ was rejected.

The positional parameters with their estimated standard deviations are listed in Table 1.†

Description of the structure and discussion

The crystal consists of neutral Sb complexes and chloroform molecules. A view of the packing along c^* is presented in Fig. 1. A perspective view of the complex molecule is illustrated in Fig. 2, together with the numbering scheme. The relevant bond lengths and angles are listed in Tables 2 and 3 respectively.

† Lists of the structure factors, thermal parameters, intramolecular non-bonded distances, some calculated least-squares planes and the references of the complexes with a linear oxo bridge have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33408 (50 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^4$, *for* H $\times 10^3$)

	x	y	z
O(br)*	5000 (0)	5000 (0)	5000 (0)
Sb	4193 (0)	5495 (0)	3931 (0)
O(1)	3611 (3)	6368 (2)	3029 (3)
O(2)	5698 (3)	7753 (2)	6138 (3)
C(1)	2865 (4)	7598 (4)	2728 (6)
C(2)	3756 (4)	7511 (4)	3813 (4)
C(3)	4538 (4)	8572 (4)	5347 (5)
C(4)	5457 (4)	8637 (3)	6457 (4)
C(5)	6204 (6)	9884 (4)	8151 (5)
F(1)	3193 (4)	7359 (4)	1627 (4)
F(2)	1638 (3)	6729 (4)	1966 (5)
F(3)	2923 (5)	8739 (4)	3455 (5)
C(11)	2603 (3)	3669 (3)	1808 (4)
C(12)	2429 (4)	2577 (3)	1596 (4)
C(13)	1357 (4)	1386 (4)	286 (5)
C(14)	447 (4)	1297 (4)	−800 (4)
C(15)	593 (4)	2347 (4)	−632 (5)
C(16)	1682 (4)	3544 (4)	673 (4)
Cl(1)	−884 (1)	−195 (1)	−2442 (1)
C(21)	3169 (3)	6088 (3)	5227 (4)
C(22)	1917 (4)	5871 (4)	4494 (5)
C(23)	1221 (4)	6243 (5)	5316 (6)
C(24)	1785 (4)	6807 (4)	6860 (5)
C(25)	3021 (5)	7010 (5)	7605 (5)
C(26)	3711 (4)	6646 (4)	6787 (4)
Cl(2)	922 (2)	7282 (2)	7895 (2)
C(31)	5703 (3)	5698 (3)	3321 (4)
C(32)	7022 (4)	6457 (4)	4449 (4)
C(33)	8000 (4)	6499 (4)	4037 (5)
C(34)	7654 (4)	5756 (5)	2462 (5)
C(35)	6364 (5)	4997 (5)	1315 (5)
C(36)	5387 (4)	4974 (4)	1755 (4)
Cl(3)	8901 (1)	5779 (2)	1953 (2)
C(S)†	2374 (16)	816 (13)	7186 (25)
Cl(S)	1473 (6)	−727 (5)	5775 (8)
Cl'(S)	3354 (7)	1619 (4)	6944 (8)
Cl''(S)	3418 (9)	719 (11)	8413 (9)
H(3)	447 (4)	931 (4)	567 (5)
H(5)	705 (6)	999 (6)	870 (7)
H'(5)	572 (5)	981 (5)	869 (6)
H''(5)	639 (5)	1073 (5)	844 (6)
H(12)	298 (5)	259 (5)	220 (6)
H(13)	125 (5)	69 (5)	18 (6)
H(15)	−3 (5)	225 (5)	−139 (6)
H(16)	182 (5)	425 (5)	81 (5)
H(22)	157 (5)	548 (5)	348 (6)
H(23)	43 (5)	620 (5)	490 (6)
H(25)	341 (5)	738 (5)	863 (6)
H(26)	458 (4)	679 (4)	728 (5)
H(32)	724 (5)	690 (5)	550 (6)
H(33)	885 (5)	706 (5)	481 (6)
H(35)	611 (5)	443 (4)	20 (5)
H(36)	451 (5)	449 (5)	100 (5)
H(S)	164 (8)	112 (8)	662 (9)

* Bridge atom.
† S indicates solvent atoms.

The complex comprises two tris(*p*-chlorophenyl)-(1,1,1-trifluoro-2,4-pentanedionato)antimony(V) units joined by the O(br) atom, which is situated at a crystallographic centre of symmetry. Accordingly, the Sb—O—Sb moiety is linear. The geometry around Sb is
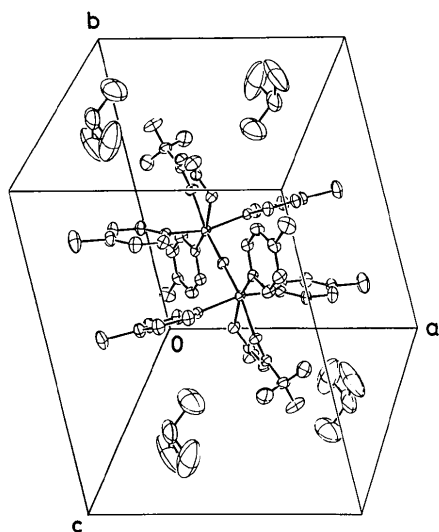
Fig. 1. The packing viewed along c^* with 30% probability thermal ellipsoids (drawn with ORTEP, Johnson, 1965).
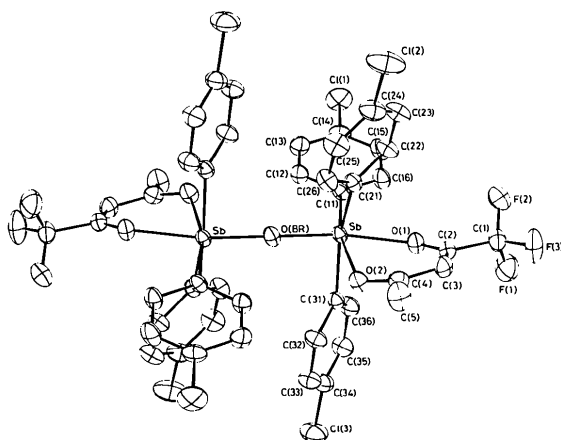

Fig. 2. A perspective view of the Sb complex with 30% probability thermal ellipsoids and the numbering scheme. H atoms are omitted.

a distorted octahedron comprising three O atoms (one from the bridge and two from the β-diketonate) and three C atoms from the aryl groups in meridional positions. The position *trans* to O(br) is occupied by O(1) of the β-diketonate, so that the CF_3 group of the β-diketonate is disposed along the apical direction of the molecule. The molecule possesses a pseudo symmetry plane (plane 1)* formed by Sb, O(br), C(11), O(1) and O(2). C(21) and C(31) deviate from plane 1 by 2·08 and −2·09 Å respectively. The aryl plane *trans* to O(2) and plane 1 are approximately coplanar, the dihedral angle being 6·0°.

* See deposition footnote.

Table 2. *Bond lengths* (Å) *with their estimated standard deviations in parentheses*

Sb—O(br)	1·943 (0)	C(11)—C(12)	1·392 (7)
Sb—O(1)	2·180 (4)	C(12)—C(13)	1·388 (5)
Sb—O(2)	2·417 (3)	C(13)—C(14)	1·380 (8)
Sb—C(11)	2·138 (3)	C(14)—C(15)	1·362 (9)
Sb—C(21)	2·126 (5)	C(15)—C(16)	1·398 (5)
Sb—C(31)	2·121 (4)	C(16)—C(11)	1·394 (7)
		C(14)—Cl(1)	1·735 (4)
O(1)—C(2)	1·282 (5)		
O(2)—C(4)	1·235 (6)	C(21)—C(22)	1·385 (6)
C(1)—C(2)	1·537 (9)	C(22)—C(23)	1·395 (8)
C(2)—C(3)	1·352 (5)	C(23)—C(24)	1·376 (9)
C(3)—C(4)	1·426 (8)	C(24)—C(25)	1·380 (8)
C(4)—C(5)	1·515 (6)	C(25)—C(26)	1·384 (8)
C(1)—F(1)	1·333 (9)	C(26)—C(21)	1·396 (6)
C(1)—F(2)	1·310 (6)	C(24)—Cl(2)	1·744 (7)
C(1)—F(3)	1·320 (8)		
		C(31)—C(32)	1·394 (5)
C(S)—Cl(S)	1·621 (14)	C(32)—C(33)	1·375 (7)
C(S)—Cl'(S)	1·637 (29)	C(33)—C(34)	1·389 (7)
C(S)—Cl"(S)	1·760 (30)	C(34)—C(35)	1·374 (7)
		C(35)—C(36)	1·393 (8)
		C(36)—C(31)	1·389 (6)
		C(34)—Cl(3)	1·741 (6)

Table 3. *Bond angles* (°) *with their estimated standard deviations in parentheses*

Sb—O(br)—Sb'	180·0 (0)	Sb—O(1)—C(2)	127·7 (3)
		Sb—O(2)—C(4)	124·8 (3)
O(br)—Sb—O(1)	169·9 (1)	F(1)—C(1)—C(2)	110·9 (5)
O(br)—Sb—O(2)	92·1 (1)	F(2)—C(1)—C(2)	111·6 (6)
O(br)—Sb—C(11)	101·1 (1)	F(3)—C(1)—C(2)	113·9 (4)
O(br)—Sb—C(21)	93·2 (1)	C(1)—C(2)—C(3)	119·3 (5)
O(br)—Sb—C(31)	90·4 (1)	C(2)—C(3)—C(4)	124·8 (5)
O(1)—Sb—O(2)	78·4 (1)	C(3)—C(4)—C(5)	118·0 (4)
O(1)—Sb—C(11)	88·6 (1)	O(1)—C(2)—C(1)	110·0 (4)
O(2)—Sb—C(21)	76·9 (1)	O(1)—C(2)—C(3)	130·7 (5)
O(2)—Sb—C(31)	80·6 (1)	O(2)—C(4)—C(3)	124·8 (4)
C(11)—Sb—C(21)	98·6 (1)	O(2)—C(4)—C(5)	117·2 (4)
C(11)—Sb—C(31)	102·7 (1)		
C(21)—Sb—C(31)	157·3 (2)	Sb—C(21)—C(22)	119·5 (3)
		C(22)—C(21)—C(26)	119·1 (4)
Sb—C(11)—C(12)	118·9 (3)	C(21)—C(22)—C(23)	120·6 (5)
C(12)—C(11)—C(16)	118·6 (4)	C(22)—C(23)—C(24)	119·1 (5)
C(11)—C(12)—C(13)	120·8 (4)	C(23)—C(24)—C(25)	121·2 (6)
C(12)—C(13)—C(14)	119·2 (5)	C(24)—C(25)—C(26)	119·4 (5)
C(13)—C(14)—C(15)	121·4 (4)	C(25)—C(26)—C(21)	120·5 (5)
C(14)—C(15)—C(16)	119·6 (5)	C(23)—C(24)—Cl(2)	119·3 (5)
C(15)—C(16)—C(11)	120·3 (5)		
C(13)—C(14)—Cl(1)	119·0 (4)	Sb—C(31)—C(32)	121·3 (3)
		C(32)—C(31)—C(36)	118·6 (4)
Cl(S)—C(S)—Cl'(S)	118·9 (16)	C(31)—C(32)—C(33)	121·2 (4)
Cl(S)—C(S)—Cl"(S)	94·7 (13)	C(32)—C(33)—C(34)	118·9 (4)
Cl'(S)—C(S)—Cl"(S)	104·5 (11)	C(33)—C(34)—C(35)	121·6 (5)
		C(34)—C(35)—C(36)	118·7 (5)
		C(35)—C(36)—C(31)	121·0 (4)
		C(33)—C(34)—Cl(3)	118·3 (3)

The fluorinated β-diketonate is coordinated to the Sb in an enolato form. The β-diketonate skeleton is approximately planar (plane 2), though the chelate ring is slightly twisted, O(1) and O(2) deviating from plane

2 by 0·08 and −0·07 Å respectively. The Sb atom is also shifted from plane 2 by 0·69 Å toward C(21), as reported for a number of acetylacetonato complexes. The large dihedral angle between planes 1 and 2 (22·7°) may be ascribed to the twisting of the β-diketonate skeleton.

The pairs of Sb—O, O—C and C—C bonds in the β-diketonate chelate ring differ significantly from each other. The Sb—O(1) distance is slightly longer than the Sb—O(acetylacetonate) bond of 2·117 (10) Å (Kroom, Hulscher & Peerdeman, 1972), whereas the Sb—O(2) bond is unusually long [its value is similar to those observed in the two hydrated compounds, 2·534 (8) and 2·568 (2) Å (Ebina et al., 1977, 1978)]. The O(1)—C(2) distance is close to the values for coordinated C ⁔ O groups of trifluoroacetylacetonate and acetylacetonate (Kroom et al., 1972; Cotton & Winquist, 1969; Lingafelter & Braun, 1966) and, on the other hand, the O(2)—C(4) distance of 1·235 (6) Å is typical for free C=O groups (International Tables for X-ray Crystallography, 1968). The C(2)—C(3) length agrees with that of a normal C=C bond within experimental error, while C(3)—C(4) is still longer than the aromatic C ⁔ C bonds. These facts suggest that the main resonance structure of the β-diketonate skeleton is O⁻—C(CF₃)=C—C(CH₃)=O, probably owing to the electron-attracting effect of the CF₃ group. The marked difference between the Sb—O(1) and Sb—O(2) bond lengths can be reasonably accounted for by this resonance structure. Cotton & Winquist (1969) reported a similar trend for the same β-diketonate skeleton in the hexameric Ni^{II} complex. However, the two Ni—O(non-bridging) distances are equal within experimental error, in contrast to this Sb complex. Further examples may be needed for a detailed discussion of this remarkable difference.

The three Sb—C bond lengths are equivalent within the error of this determination and agree with previously reported values. The Sb—C(11) bond and the Sb—C(21) and Sb—C(31) bonds make angles of about 100° because of repulsions between the bulky aryl groups, and the weak interactions between O(2) and C(21) and C(31) arising from the long Sb—O(2) distance. Consequently, two of the three aryl groups attached to two Sb atoms related by the centre of symmetry form a slightly staggered arrangement, to alleviate the repulsions between the two halves of the molecule. The two aryl groups out of plane 1 are approximately parallel to each other and to the line joining O(br) and C(11).

The geometry of the Sb—O—Sb bridge is of particular interest because this compound appears to contain the first example of a linear Sb—O—Sb bond. Only four examples of organoantimony(V) compounds involving an oxo bridge − [Ph₃Sb(N₃)]₂O (Ferguson & Ridley, 1973) and [(CH₃)₂Sb(X)]₂O (X = ClO₄, Cl and N₃) (Ferguson, March & Ridley, 1975) − have

been reported; in these the coordination around Sb is trigonal bipyramidal, and the Sb—O—Sb angle is 139·8 (4)° in the first and ranges from 126 to 129° with disordered bridging O atoms, despite the molecular symmetry of 3̄ required by the space group, in the other three cases. In the present compound, no appreciable features indicating disorder of O(br) were observed and the thermal parameters of O(br) are normal.

On the other hand, more than ten examples* of linear or nearly linear (>170°) oxo bridges have been found in other metal complexes, and the main factors giving rise to the straight oxo bridge have been regarded as intramolecular repulsions between the two halves, the degree of π-bonding character of the M—O bond, and intermolecular forces [see, for example, Davies & Gatehouse (1973) and Knox & Prout (1969)]. In this complex, the closest approach between the two octahedra* is O(2)···C(12)' at 3·374 (7) Å, which is shorter than the sum of the relevant van der Waals radii and the common C—H bond distance of 1·08 Å, the C(12)'—H(12)' bond being almost directed to O(2). This repulsion may also be reflected in the large O(br)—Sb—C(11) angle of 101·1 (1)°. It should be noted that the Sb—O(br) distance, 1·943 (0) Å, is shorter than previously reported Sb—O(bridge) bonds. This value can be explained by the partial multiple-bond character arising from the donation of electrons from two filled p_π orbitals of O(br) to the unfilled d_π orbital of Sb, since it is reasonable to presume sp hybridization of O(br) in the linear Sb—O—Sb structure. No remarkable intermolecular contacts were observed.

The bond lengths and angles of the chloroform molecule are absurd owing to the violent librational motion around its threefold axis. The final population of the solvent molecule was 0·921 (6).

* See deposition footnote.

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Structure and Activity Relationships of Platinum Complexes Related to Antitumour Activity: The Crystal and Molecular Structure of trans-Dichlorobis(cyclohexylamine)platinum(II)

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Crystals of *trans*-dichlorobis(cyclohexylamine)platinum(II), $PtCl_2(C_6H_{11}NH_2)_2$, are orthorhombic, space group *Pbcn*, with four molecules in a cell of dimensions $a = 26 \cdot 170$ (9), $b = 6 \cdot 673$ (2) and $c = 9 \cdot 002$ (4) Å. Intensity data were collected on a four-circle diffractometer with Mo $K\alpha$ radiation. The structure was solved by the heavy-atom method and refined by full-matrix least squares to a final conventional R value of $0 \cdot 041$ for 1131 observed reflections. The Pt atom configuration is square-planar with the N and Cl atoms in *trans* positions. The cyclohexyl ring assumes a chair-like conformation.

Introduction

Since the discoveries by Rosenberg, Van Camp, Trosko & Mansour (1969, and references therein), it has been shown that certain complexes of the platinum-group metals exhibit interesting biological effects. At low concentrations some are effective bactericides while others stop cell division and force bacteria to grow into long filaments. Some of these complexes are also very potent broad-spectrum antitumour agents. Indeed, it is considered that Pt^{II} complexes inhibit DNA synthesis by direct interaction with the nucleic acid (Harder & Rosenberg, 1970). In addition, it has been found that this interaction depends on hetero-

cyclic base composition (Macquet & Theophanides, 1975; Millard, Macquet & Theophanides, 1975), guanine being the preferred site of attack, at least at low complex/DNA ratios, and induces localized conformational changes in DNA (Munchausen & Rahn, 1975; Tamburro, Celotti, Furlan & Guantieri, 1977).

From a general survey seeking relationships between activity, toxicity and structure a general conclusion arose which is in agreement with that of Rosenberg, Van Camp, Trosko & Mansour (1969), namely that the complexes should be uncharged, two amines should be present, these ligands should be *cis* to one other and the complexes are most effective when the other two sites are occupied by Cl (Braddock, Connors, Jones,