

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of D. SCHWARZENBACH. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

WILLETT, R. D. & WILLETT, J. J. (1977). *Acta Cryst.* **B33**, 1639–1641.

Acta Cryst. (1978). **B34**, 1512–1515

The Crystal Structure of [4,4,4-Trifluoro-3,3-dihydroxy-1-phenyl-1-butanonato(2–)-*O,O',O''*]tris(*p*-tolyl)antimony(V)–1,2-Dichloroethane (2/1)

BY F. EBINA, A. OUCHI AND Y. YOSHINO

Department of Chemistry, College of General Education, The University of Tokyo, Komaba-3, Meguro-ku, Tokyo 153, Japan

AND S. SATO AND Y. SAITO

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan

(Received 11 October 1977; accepted 8 December 1977)

Crystals of the title compound, $C_{31}H_{28}F_3O_3Sb \cdot \frac{1}{2}C_2H_4Cl_2$, are triclinic, space group $P\bar{1}$, with $a = 11.828$ (1), $b = 13.851$ (1), $c = 10.516$ (1) Å, $\alpha = 103.65$ (1), $\beta = 113.03$ (1), $\gamma = 84.14$ (1)° and $Z = 2$. The structure has been refined by the least-squares method to an R value of 0.028 on the basis of 6159 observed reflexions collected by diffractometry. The Sb complex is monomeric and exhibits a distorted octahedral coordination. The fluorinated ligand is hydrated at the carbonyl group next to the CF_3 group, to form a terdentate ligand, 3,3-dihydroxy-1-ketone, in which three O atoms are bonded to the Sb atom in facial positions. The Sb–O(alcohol) distances are 2.050 (2) and 2.042 (2) Å, and the Sb–O(carbonyl) distance is 2.568 (2) Å. The three Sb–C bonds, 2.122 (3), 2.112 (3) and 2.127 (2) Å, make angles ranging from 101.1 (1) to 103.9 (1)° owing to the repulsions among the three bulky tolyl groups.

Introduction

It is well known that a carbonyl or an aldehyde group attached to an electron-attracting group is liable to hydration to form a *gem*-diol. A typical example is chloral hydrate. However, a metal complex with such an organic ligand had not been reported, although the carbonate ion is a common inorganic *gem*-diol ligand. Recently, the first example of a complex of this type has been found for the reaction product of a triaryl-antimony(V) compound with trifluoroacetylacetone (Ebina, Ouchi, Yoshino, Sato & Saito, 1977; Ebina, Uehiro, Iwamoto, Ouchi & Yoshino, 1976). In this compound, the β -diketone is hydrated at the carbonyl group next to the trifluoromethyl group, being converted to a 4,4-dihydroxy-2-ketone ligand in which the *gem*-diol moiety forms a four-membered chelate ring with the Sb atom.

In this paper, the structure of the related compound with hydrated benzoyltrifluoroacetone is described.

Experimental

Colourless crystals of the title compound were grown by recrystallization from a mixture of dichloroethane and petroleum spirit. They are unstable in air, losing the solvent of crystallization. Preliminary cell dimensions and the space group were determined from oscillation and Weissenberg photographs. The cell dimensions were refined by least-squares calculations on the basis of 2θ values of higher-order reflexions ($37^\circ < 2\theta < 55^\circ$) measured on a diffractometer. The density was determined by flotation in an aqueous solution of potassium iodide.

The crystal data are: $C_{31}H_{28}F_3O_3Sb \cdot \frac{1}{2}C_2H_4Cl_2$, FW 676.82, triclinic, $a = 11.828$ (1), $b = 13.851$ (1), $c = 10.516$ (1) Å, $\alpha = 103.65$ (1), $\beta = 113.03$ (1), $\gamma = 84.14$ (1)°, $U = 1540.6$ (3) Å³, $Z = 2$, $D_m = 1.45$, $D_x = 1.46$ g cm⁻³; space group $P\bar{1}$ (No. 2); $\mu(Mo K\alpha)$ ($\lambda = 0.7107$ Å) = 10.46 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 θ - 2θ scan technique being employed. A crystal specimen was shaped into a sphere approximately 0.45 mm in diameter, and sealed in a thin-walled Lindemann-glass capillary. Three standard reflexions were monitored every 50 reflexions. Their intensities decreased by about 2.5% during the data collection owing to radiation damage. Data were corrected for this effect and for Lorentz and polarization factors. No correction was applied for absorption or extinction. 7059 independent reflexions were measured up to $2\theta = 55^\circ$, of which 6159 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 used 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 the 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. Final refinement was carried out including the H atoms with isotropic thermal factors. The final R value

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

	<i>x</i>	<i>y</i>	<i>z</i>
Sb	3165 (0)	2339 (0)	2856 (0)
O(1)	1278 (2)	2838 (1)	3510 (2)
O(2)	2727 (2)	3768 (1)	2587 (2)
O(3)	1728 (2)	2439 (1)	1012 (2)
C(1)	502 (2)	3434 (2)	2968 (3)
C(2)	502 (3)	3812 (2)	1727 (3)
C(3)	1653 (2)	3474 (2)	1392 (3)
C(4)	1654 (3)	3925 (2)	202 (3)
C(5)	-465 (2)	3802 (2)	3545 (3)
C(6)	-384 (3)	3530 (2)	4772 (3)
C(7)	-1247 (3)	3875 (3)	5364 (4)
C(8)	-2195 (3)	4491 (3)	4735 (4)
C(9)	-2282 (3)	4761 (3)	3526 (4)
C(10)	-1419 (3)	4423 (3)	2926 (3)
F(1)	1634 (2)	4924 (1)	537 (2)
F(2)	2638 (2)	3660 (2)	-118 (2)
F(3)	667 (2)	3664 (2)	-991 (2)
C(11)	2621 (2)	895 (2)	2732 (3)
C(12)	3520 (3)	227 (2)	3321 (4)
C(13)	3227 (3)	-734 (2)	3230 (4)
C(14)	2030 (3)	-1059 (2)	2537 (4)
C(15)	1130 (3)	-399 (2)	1935 (3)
C(16)	1417 (2)	570 (2)	2030 (3)
C(17)	1713 (4)	-2112 (3)	2418 (5)
C(21)	4641 (2)	1998 (2)	2164 (3)
C(22)	5836 (3)	2155 (4)	3082 (4)
C(23)	6800 (3)	1878 (4)	2631 (5)

Table 1 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>
C(24)	6590 (3)	1444 (3)	1259 (4)
C(25)	5399 (4)	1276 (3)	337 (4)
C(26)	4426 (3)	1557 (3)	777 (3)
C(27)	7666 (4)	1157 (4)	784 (5)
C(31)	4038 (2)	2882 (2)	5075 (3)
C(32)	4826 (3)	3686 (2)	5606 (3)
C(33)	5428 (3)	4013 (2)	7058 (3)
C(34)	5239 (3)	3558 (3)	7994 (3)
C(35)	4416 (3)	2782 (3)	7453 (3)
C(36)	3821 (3)	2440 (2)	6006 (3)
C(37)	5920 (4)	3883 (3)	9578 (4)
C(S)*	390 (14)	-218 (10)	5311 (15)
Cl(S)	1399 (6)	943 (5)	6513 (7)
H(2)	-22 (2)	357 (2)	90 (3)
H'(2)	46 (2)	454 (2)	194 (3)
H(6)	27 (2)	309 (2)	519 (3)
H(7)	-119 (2)	369 (2)	622 (3)
H(8)	-278 (2)	472 (2)	515 (3)
H(9)	-294 (2)	520 (2)	309 (3)
H(10)	-147 (2)	462 (2)	210 (3)
H(12)	435 (2)	44 (2)	378 (3)
H(13)	385 (2)	-118 (2)	365 (3)
H(15)	31 (2)	-61 (2)	145 (3)
H(16)	80 (2)	102 (2)	162 (3)
H(17)	206 (3)	-266 (2)	179 (3)
H'(17)	93 (3)	-225 (2)	220 (3)
H''(17)	246 (3)	-247 (2)	302 (3)
H(22)	602 (3)	246 (2)	406 (3)
H(23)	762 (3)	200 (2)	329 (3)
H(25)	522 (3)	95 (2)	-65 (3)
H(26)	358 (3)	143 (2)	10 (3)
H(27)	758 (3)	51 (2)	21 (3)
H'(27)	847 (3)	101 (2)	176 (3)
H''(27)	765 (3)	168 (2)	21 (3)
H(32)	496 (2)	401 (2)	496 (3)
H(33)	599 (2)	457 (2)	743 (3)
H(35)	425 (2)	247 (2)	807 (3)
H(36)	327 (2)	190 (2)	567 (3)
H(37)	614 (3)	452 (2)	983 (3)
H'(37)	661 (3)	350 (2)	984 (3)
H''(37)	550 (3)	366 (2)	1010 (3)
H(S)	7 (4)	-69 (3)	575 (4)
H'(S)	73 (3)	-76 (3)	486 (4)

* S: solvent.

was 0.028 for all the 6159 observed reflexions. In the last cycle of the calculation, all the parameter shifts were less than one third of the corresponding standard deviations. Unit weight was given to all the reflexions. The scattering factors and anomalous-scattering corrections 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.

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

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33289 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Description of the structure and discussion

The crystal comprises the neutral Sb complexes and 1,2-dichloroethane molecules. In Fig. 1 is shown a projection of the structure along the *c* axis. A perspective view of the complex is illustrated in Fig. 2, together with the numbering scheme. The relevant bond lengths and angles are given in Tables 2 and 3 respectively. Table 4 lists computed least-squares planes of the complex with their equations and the deviations of various atoms from these planes.

The Sb complex is monomeric and the coordination around the Sb atom is a distorted octahedron. Three O atoms of the β -diketone derivative and three C atoms of the *p*-tolyl groups are bonded to Sb in facial positions. As seen in Table 4, four donor atoms, O(2), O(3), C(11) and C(31), lie on the same plane (plane 1) and the Sb atom deviates from this plane toward the C(21) atom by about 0.44 Å. If the orientation of the three aryl rings is ignored, the complex possesses a pseudo-

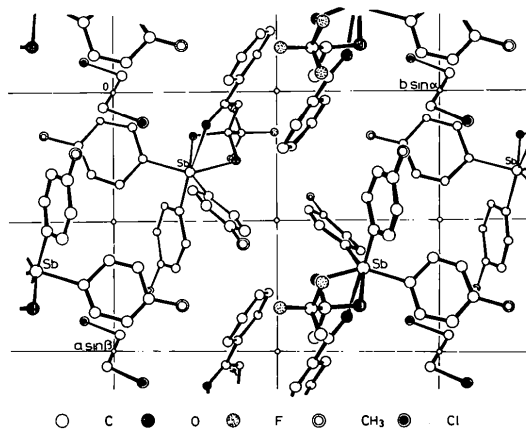


Fig. 1. A projection of the structure along the *c* axis.

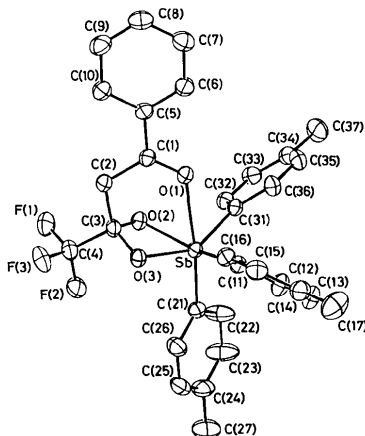


Fig. 2. A perspective view of the Sb complex with 30% probability thermal ellipsoids (drawn with ORTEP, Johnson, 1965), and the numbering scheme.

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

Sb—O(1)	2.568 (2)	C(11)—C(12)	1.388 (4)
Sb—O(2)	2.050 (2)	C(12)—C(13)	1.382 (5)
Sb—O(3)	2.042 (2)	C(13)—C(14)	1.381 (5)
Sb—C(11)	2.122 (3)	C(14)—C(15)	1.384 (4)
Sb—C(21)	2.112 (3)	C(15)—C(16)	1.390 (5)
Sb—C(31)	2.127 (2)	C(16)—C(11)	1.388 (4)
		C(14)—C(17)	1.507 (6)
O(1)—C(1)	1.228 (3)	C(21)—C(22)	1.369 (4)
O(2)—C(3)	1.404 (3)	C(22)—C(23)	1.386 (6)
O(3)—C(3)	1.398 (3)	C(23)—C(24)	1.359 (6)
C(1)—C(2)	1.517 (5)	C(24)—C(25)	1.367 (5)
C(1)—C(5)	1.488 (4)	C(25)—C(26)	1.390 (6)
C(2)—C(3)	1.537 (4)	C(26)—C(21)	1.374 (4)
C(3)—C(4)	1.526 (5)	C(24)—C(27)	1.526 (8)
C(5)—C(6)	1.393 (5)		
C(6)—C(7)	1.384 (6)	C(31)—C(32)	1.390 (4)
C(7)—C(8)	1.382 (5)	C(32)—C(33)	1.390 (4)
C(8)—C(9)	1.372 (6)	C(33)—C(34)	1.382 (6)
C(9)—C(10)	1.388 (5)	C(34)—C(35)	1.384 (5)
C(10)—C(5)	1.388 (4)	C(35)—C(36)	1.388 (4)
F(1)—C(4)	1.346 (4)	C(36)—C(31)	1.382 (5)
F(2)—C(4)	1.327 (4)	C(34)—C(37)	1.516 (4)
F(3)—C(4)	1.339 (3)		
C(S)—C(S)'	1.114 (27)	C(S)—Cl(S)	1.964 (14)

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

O(1)—Sb—O(2)	73.9 (1)	Sb—O(1)—C(1)	122.2 (2)
O(1)—Sb—O(3)	73.8 (1)	Sb—O(2)—C(3)	92.7 (1)
O(1)—Sb—C(11)	81.8 (1)	Sb—O(3)—C(3)	93.3 (1)
O(1)—Sb—C(21)	174.8 (1)	O(1)—C(1)—C(2)	121.9 (3)
O(1)—Sb—C(31)	79.7 (1)	O(1)—C(1)—C(5)	119.3 (3)
O(2)—Sb—O(3)	66.3 (1)	C(2)—C(1)—C(5)	118.8 (2)
O(2)—Sb—C(11)	150.3 (1)	C(1)—C(2)—C(3)	112.2 (2)
O(2)—Sb—C(31)	89.9 (1)	O(2)—C(3)—O(3)	105.9 (2)
O(3)—Sb—C(11)	91.0 (1)	C(2)—C(3)—C(4)	110.4 (2)
O(3)—Sb—C(31)	148.2 (1)	C(3)—C(4)—F(1)	111.9 (3)
C(11)—Sb—C(21)	101.1 (1)	C(3)—C(4)—F(2)	112.6 (3)
C(11)—Sb—C(31)	102.4 (1)	C(3)—C(4)—F(3)	112.3 (3)
C(21)—Sb—C(31)	103.9 (1)	C(1)—C(5)—C(6)	118.3 (3)
		C(6)—C(5)—C(10)	119.3 (3)
		C(5)—C(6)—C(7)	120.2 (3)
		C(6)—C(7)—C(8)	119.9 (4)
		C(7)—C(8)—C(9)	120.2 (4)
		C(8)—C(9)—C(10)	120.4 (3)
		C(9)—C(10)—C(5)	120.0 (3)
Sb—C(11)—C(12)	118.5 (2)	C(23)—C(24)—C(25)	118.1 (4)
C(12)—C(11)—C(16)	118.2 (3)	C(23)—C(24)—C(27)	120.1 (4)
C(11)—C(12)—C(13)	121.1 (3)	C(24)—C(25)—C(26)	121.3 (3)
C(12)—C(13)—C(14)	120.8 (3)	C(25)—C(26)—C(21)	120.5 (3)
C(13)—C(14)—C(15)	118.4 (3)		
C(13)—C(14)—C(17)	120.8 (3)	Sb—C(31)—C(32)	120.6 (2)
C(14)—C(15)—C(16)	121.1 (3)	C(32)—C(31)—C(36)	119.3 (3)
C(14)—C(15)—C(17)	121.1 (3)	C(31)—C(32)—C(33)	120.2 (3)
C(15)—C(16)—C(11)	120.4 (3)	C(32)—C(33)—C(34)	120.8 (3)
		C(33)—C(34)—C(35)	118.5 (3)
Sb—C(21)—C(22)	121.8 (2)	C(33)—C(34)—C(37)	121.4 (3)
C(22)—C(21)—C(26)	117.8 (3)	C(34)—C(35)—C(36)	121.3 (4)
C(21)—C(22)—C(23)	121.2 (4)	C(35)—C(36)—C(31)	119.9 (3)
C(22)—C(23)—C(24)	121.1 (3)		

symmetry plane (plane 2) consisting of Sb, C(21) and the atoms on the skeleton of the fluorinated ligand, except for O(2) and O(3). The dihedral angle between planes 1 and 2 is 83.5°.

The benzoyltrifluoroacetone precursor is hydrated at the carbonyl group attached to the trifluoromethyl group to form a terdentate ligand, 3,3-dihydroxy-1-ketone, which forms an unusual chelate ring, bicyclo-[3.1.1], with the Sb atom. The Sb—O(2) and Sb—O(3) distances are normal for an Sb—O(alcohol) bond (Shen, McEwen, La Placa, Hamilton & Wolf, 1968) and the O(2)—Sb—O(3) angle of 66.3° is acceptable for a four-membered chelate ring (Ferguson & Hawley, 1974; Raston & White, 1976). On the other hand, the Sb—O(1) distance, 2.568 (2) Å, is very long. A similar value, 2.534 (8) Å, has also been observed for the hydrated Sb complex (Ebina, Ouchi, Yoshino, Sato & Saito, 1977). These values suggest a weak coordinating ability for the carbonyl O atom to Sb.

The three Sb—C(tolyl) distances are equivalent

Table 4. *Least-squares planes and atom deviations (Å) from them*

The atoms with asterisks were used in the calculations of the least-squares planes.

Plane 1

$$-0.947X + 0.148Y + 0.284Z = -1.148$$

Sb	-0.441	C(11)*	-0.011
O(1)	2.119	C(21)	-2.553
O(2)*	0.019	C(31)*	0.012
O(3)*	-0.018		

Plane 2

$$-0.411X - 0.668Y - 0.620Z = -4.552$$

Sb*	-0.072	C(6)*	-0.049
O(1)*	0.174	C(7)*	-0.133
O(2)	1.044	C(8)*	-0.100
O(3)	-1.182	C(9)*	0.016
C(1)*	-0.149	C(10)*	0.095
C(2)*	-0.039	C(11)	-1.646
C(3)*	0.095	C(21)*	-0.261
C(4)*	0.119	C(31)	1.640
C(5)*	0.067		

within experimental error, the mean value being 2.120 (3) Å. Owing to the repulsions among the bulky tolyl groups, the three C—Sb—C bond angles are greater than 100°. Rather short interatomic contacts among the aryl groups, C(11)···C(21), C(11)···C(31) and C(21)···C(31), are 3.269 (5), 3.311 (4) and 3.337 (4) Å respectively. As seen from Fig. 1, the aryl group *trans* to O(1) exhibits a larger librational motion around the Sb—C bond than the other aryl groups, this aryl group being situated in the most loosely packed environment.

The 1,2-dichloroethane molecule has a *trans* conformation and its centre of symmetry coincides with the crystallographic inversion centre. The population of the solvent molecule was 0.427 (6) in the final refinement. The bond lengths of the molecule are absurd owing to the violent thermal vibration.

No remarkable intermolecular contact is observed.

The calculations were performed on a FACOM 230-48 computer of this Institute and on a HITAC 8800/8700 computer at the Computer Centre of the University of Tokyo. This research was aided by a Scientific Research Grant from The Ministry of Education, to which the authors' thanks are due.

References

- EBINA, F., OUCHI, A., YOSHINO, Y., SATO, S. & SAITO, Y. (1977). *Acta Cryst.* **B33**, 3252–3253.
- EBINA, F., UEHIRO, T., IWAMOTO, T., OUCHI, A. & YOSHINO, Y. (1976). *Chem. Commun.* pp. 245–246.
- FERGUSON, G. & HAWLEY, D. M. (1974). *Acta Cryst.* **B30**, 103–111.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- RASTON, C. L. & WHITE, A. H. (1976). *J. Chem. Soc. Dalton Trans.* pp. 791–794.
- SHEN, K., MCEWEN, W. E., LA PLACA, S. J., HAMILTON, W. C. & WOLF, A. P. (1968). *J. Am. Chem. Soc.* **90**, 1718–1723.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.