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The crystal and molecular structure of μ-oxobis[chlorotriphenylantimony(V)]-benzene solvate (1/2)

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Abstract

The crystal and molecular structure of μ-oxobis[chlorotriphenylantimony(V)]benzene solvate (1/2) has been determined by single-crystal X-ray diffraction techniques. The dinuclear complex, $(Ph_3SbCl)_2O$, features a bent Sb–O–Sb bridge (139.0(3)°), short Sb–O(bridge) bond distances of 1.980(6) and 1.986(6) Å, and relatively long Sb–Cl bond lengths of 2.553(2) and 2.582(3) Å. Crystals are triclinic, space group $P\bar{1}$, with unit cell parameters a 12.974(5), b 13.716(7), c 12.865(5) Å, α 110.04(4), β 97.52(3), γ 77.70(4)° with $Z = 2$. Refinement on 3314 reflections (with $I \geq 2.5\sigma(I)$] converged to final $R = 0.045$ and $R_w = 0.047$.

Introduction

The crystal structures of a number of derivatives of the general formula $(R_3SbX)_2O$ are available in the literature. For the compounds with R = Ph, both bent and linear Sb–O–Sb geometries are known. Linear Sb–O–Sb moieties have been reported for $X = OO\text{-}t\text{-}C_4H_9$ [1] and for $X = O_3SCH_2CH_2OH$ [2]; in each of these compounds the linear Sb–O–Sb geometries are crystallographically imposed. In contrast, bent Sb–O–Sb units are found for $X = N_3$, 139.8(4)° [3]; $X = OC(CN){=}C(CN)_2$, 140.0(3)° [4]; $X = O_3SPh$, 139.8(3)° [5]; and $X = O_3SCF_3$, 136.5(5)° [5]. The situation is further complicated for the trimethylantimony derivatives, $(Me_3SbX)_2O$ with X = Cl, N_3, and ClO_4 [6], in which disorder in each of the cubic crystals prevented the accurate determination of the Sb–O–Sb angles. In these $(Me_3SbX)_2O$ compounds, the crystallographically imposed symmetry dictated angles of 180°, however angles in the range 126–129° were reported on the basis of a disordered model for each of the systems [6]. The recent work of Preut et al. [2,5] on $(Ph_3SbX)_2O$ derivatives, where X is a monodentate sulphonate group, has focussed on the question as to why some $(R_3SbX)_2O$ systems possess linear Sb–O–Sb groups

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[1,2] whereas others [3,6] feature bent Sb–O–Sb units. The current interest in this field [2,5] has prompted this report of the crystal structure analysis of $(Ph_3SbCl)_2O$ (obtained as a benzene solvate) recently completed in this laboratory. The compound was obtained as well-formed, colourless crystals as a side product in an investigation of organoantimony(V) complexes and was presumably generated by the partial hydrolysis [7] of one of the starting materials Ph_3SbCl_2 [8].

Experimental

Intensity data for a crystal, coated with cyano-acrylate super glue to prevent the possible loss of solvent from the crystal lattice, were collected, at room temperature, on an Enraf–Nonius CAD4F diffractometer with Mo-K_α (graphite monochromatized) radiation, λ 0.7107 Å. The $\omega/2\theta$ scan technique was employed to measure the intensities for a total of 5949 reflections; no significant decomposition of the crystal occurred during the data collection. The data set was corrected for Lorentz and polarization effects and for absorption with the use of an analytical procedure [9]. After the amalgamation of equivalent reflections, there were 5140 reflections remaining ($R_{\text{int}} = 0.025$), of which 3314 satisfied the $I \geq 2.5\sigma(I)$ criterion of observability and were used in the subsequent analysis.

Crystal data. $C_{48}H_{42}Cl_2OSb_2$, $M = 949.2$, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a 12.974(5), b 13.716(7), c 12.865(5) Å, α 110.04(4), β 97.52(3), γ 77.70(4)°, V 2097.2 Å^3, D_x 1.503 g cm^{-3}, $Z = 2$, $F(000)$ 948, $2 \leq 2\theta \leq 44$°, μ(Mo-K_α) 14.24 cm^{-1}, max. and min. transmission factors for absorption correction 0.8377 and 0.4778, respectively.

The structure was solved from the interpretation of the Patterson synthesis and refined by a blocked-matrix least-squares procedure in which the function $\Sigma w\Delta^2$

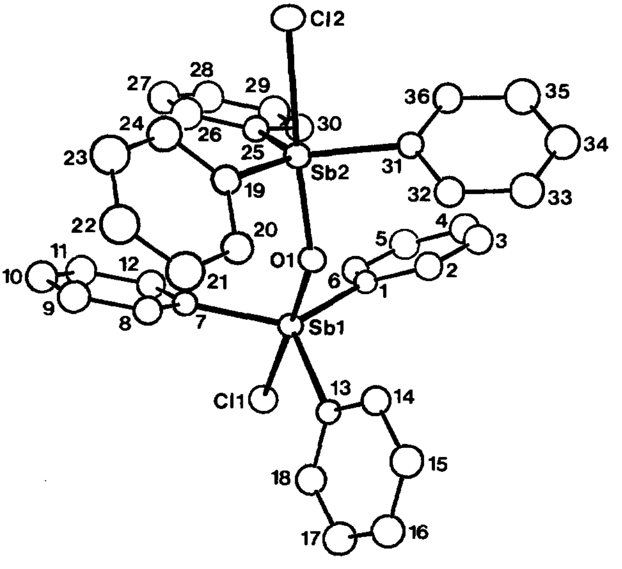

Fig. 1. The molecular structure and numbering scheme used for $(Ph_3SbCl)_2$; note that atoms otherwise not indicated are carbons.

Table 1

Fractional atomic coordinates for $(Ph_3SbCl)_2O,2C_6H_6$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sb(1)	−0.07362(4)	−0.33895(4)	0.27171(4)	C(23)	−0.3417(11)	−0.4791(11)	0.5731(14)
Sb(2)	−0.35058(4)	−0.30359(4)	0.34266(5)	C(24)	−0.3699(9)	−0.4380(9)	0.4840(10)
Cl(1)	0.0860(2)	−0.4171(2)	0.1533(2)	C(25)	−0.3520(7)	−0.4114(8)	0.1792(8)
Cl(2)	−0.5472(2)	−0.3133(2)	0.3425(2)	C(26)	−0.3540(10)	−0.5126(8)	0.1612(10)
O(1)	−0.2018(4)	−0.2830(4)	0.3571(5)	C(27)	−0.3553(11)	−0.5831(9)	0.0535(12)
C(1)	−0.1400(7)	−0.2598(7)	0.1554(7)	C(28)	−0.3546(9)	−0.5456(10)	−0.0348(10)
C(2)	−0.1921(7)	−0.1556(7)	0.1992(8)	C(29)	−0.3548(11)	−0.4447(11)	−0.0161(9)
C(3)	−0.2350(8)	−0.0987(8)	0.1314(9)	C(30)	−0.3540(9)	−0.3736(9)	0.0942(8)
C(4)	−0.2232(9)	−0.1437(10)	0.0210(10)	C(31)	−0.3996(7)	−0.1421(9)	0.3609(8)
C(5)	−0.1759(10)	−0.2466(11)	0.0220(9)	C(32)	−0.3560(8)	−0.0699(8)	0.4483(9)
C(6)	−0.1283(8)	−0.3046(9)	0.0461(8)	C(33)	−0.3828(9)	0.0364(10)	0.4597(10)
C(7)	−0.0768(7)	−0.4962(7)	0.2604(8)	C(34)	−0.4480(10)	0.0709(9)	0.3833(12)
C(8)	−0.0794(7)	−0.5143(7)	0.3595(8)	C(35)	−0.4895(10)	−0.0050(10)	0.2909(11)
C(9)	−0.0811(8)	−0.6166(8)	0.3570(10)	C(36)	−0.4690(9)	−0.1103(8)	0.2832(9)
C(10)	−0.0782(8)	−0.6967(8)	0.2586(11)	C(37)	0.6852(13)	0.1727(16)	0.1200(22)
C(11)	−0.0766(10)	−0.6779(8)	0.1627(11)	C(38)	0.6131(17)	0.1312(12)	0.0341(16)
C(12)	−0.0731(9)	−0.5773(8)	0.1620(9)	C(39)	0.5097(16)	0.1548(13)	0.0499(18)
C(13)	0.0176(7)	−0.2481(7)	0.4045(7)	C(40)	0.4787(12)	0.2196(16)	0.1503(22)
C(14)	−0.0327(8)	−0.1634(8)	0.4852(8)	C(41)	0.5507(20)	0.2600(13)	0.2390(15)
C(15)	0.0234(10)	−0.0994(8)	0.5702(9)	C(42)	0.6563(17)	0.2347(16)	0.2188(20)
C(16)	0.1327(9)	−0.1262(9)	0.5766(9)	C(43)	0.2333(15)	−0.0742(36)	0.2438(20)
C(17)	0.1851(9)	−0.2116(9)	0.4962(9)	C(44)	0.1638(33)	−0.1456(14)	0.1946(26)
C(18)	0.1265(8)	−0.2748(9)	0.4098(9)	C(45)	0.0705(20)	−0.1017(30)	0.1383(20)
C(19)	−0.3210(8)	−0.3602(8)	0.4804(8)	C(46)	0.0605(20)	−0.0021(30)	0.1420(16)
C(20)	−0.2417(8)	−0.3257(8)	0.5577(8)	C(47)	0.1337(30)	0.0454(16)	0.1880(24)
C(21)	−0.2190(10)	−0.3641(11)	0.6466(9)	C(48)	0.2107(22)	0.0171(27)	0.2356(20)
C(22)	−0.2641(12)	−0.4374(11)	0.6549(11)				

Table 2

Selected bond distances (Å) and angles (°) for $(Ph_3SbCl)_2O$

Atoms	Distance	Atoms	Distance
Sb(1)–Cl(1)	2.553(2)	Sb(2)–Cl(2)	2.582(3)
Sb(1)–O(1)	1.980(6)	Sb(2)–O(1)	1.986(6)
Sb(1)–C(1)	2.130(9)	Sb(2)–C(19)	2.13(1)
Sb(1)–C(7)	2.12(1)	Sb(2)–C(25)	2.116(8)
Sb(1)–C(13)	2.118(8)	Sb(2)–C(31)	2.109(8)
Atoms	**Angle**	**Atoms**	**Angle**
Cl(1)–Sb(1)–O(1)	177.0(2)	Cl(2)–Sb(2)–O(1)	174.0(2)
Cl(1)–Sb(1)–C(1)	87.3(2)	Cl(2)–Sb(2)–C(19)	87.9(3)
Cl(1)–Sb(1)–C(7)	86.2(3)	Cl(2)–Sb(2)–C(25)	87.3(3)
Cl(1)–Sb(1)–C(13)	91.7(2)	Cl(2)–Sb(2)–C(31)	87.6(3)
O(1)–Sb(1)–C(1)	91.7(3)	O(1)–Sb(2)–C(19)	90.3(3)
O(1)–Sb(1)–C(7)	92.3(3)	O(1)–Sb(2)–C(25)	98.6(3)
O(1)–Sb(1)–C(13)	91.3(3)	O(1)–Sb(2)–C(31)	88.6(3)
C(1)–Sb(1)–C(7)	128.0(3)	C(19)–Sb(2)–C(25)	120.0(4)
C(1)–Sb(1)–C(13)	113.1(4)	C(19)–Sb(2)–C(31)	122.5(3)
C(7)–Sb(1)–C(13)	118.6(4)	C(25)–Sb(2)–C(31)	117.0(4)
Sb(1)–O(1)–Sb(2)	139.0(3)		

was minimized [9]; where $\Delta = \| F_o | - | F_c \|$ and w was the weight applied to each reflection. The remaining non-hydrogen atoms for the $(Ph_3SbCl)_2O$ molecule were located from subsequent difference maps. A difference map calculated at this stage indicated the presence of twelve (i.e. two sets of six) residual electron density peaks consistent with two benzene molecules of solvation (one of which was found to be disordered) which were included in the model. Anisotropic thermal parameters were introduced for non-hydrogen atoms and hydrogen atoms were included in the model at their calculated positions. A weighting scheme, $w = k/[\sigma^2(F) + gF]^2$, was introduced and the refinement continued until convergence. Final $R = 0.045$, $R_w = 0.047$ for $k = 0.5$ and $g = 0.009$. The analysis of variance showed no special features which indicated that an appropriate weighting scheme had been applied.

Scattering factors (corrected for $\Delta f'$ and $\Delta f''$) for neutral Sb were from ref. 10 and the values for the remaining atoms were those incorporated in SHELX [9]. Fractional atomic coordinates are listed in Table 1 and the numbering scheme used is shown in Fig. 1 which was drawn with ORTEP [9]. Selected interatomic parameters are given in Table 2. Listings of anisotropic thermal parameters, hydrogen atoms parameters, all bond lengths and angles, and the observed and calculated structure factor tables are available from the author.

Results and discussion

The dinuclear complex, $(Ph_3SbCl)_2O$, is comprised of two Ph_3SbCl units linked via a bridging oxygen atom and features a bent Sb–O–Sb unit; angle 139.0(3)°. Both of the Sb atoms exist in a slightly distorted trigonal bipyramidal environment; the trigonal place being defined by the three phenyl groups. The apical positions are occupied by a bridging O atom and a terminal Cl atom. In the central atom geometry, the Sb atom is displaced by 0.066 Å (0.089 Å for the Sb(2) atom) out of the trigonal plane in the direction of the bridging O atom. The phenyl groups on one Sb atom are arranged so as to adopt an approximately staggered configuration relative to the other Ph_3Sb fragment. The overall geometry about each of the Sb atoms in $(Ph_3SbCl)_2O$ is in good agreement with the geometries found for related systems [1,5].

The Sb to bridging O distances, Sb–O(br), of 1.980(6) and 1.986(6) Å lie in the upper range of Sb–O(br) distances found in related structures; Table 3. There does not appear to be any correlation however, between the length of the Sb–O(br) bond distance and the angle subtended at the bridging O atom by the two Sb atoms. Thus in $(Ph_3SbO_3SPh)_2O$ [5], the bridging Sb–O distances are 1.963(5) and 1.963(4) Å with an Sb–O–Sb angle of 139.8(3)° which can be compared with an angle of 180° with a Sb–O(br) distance of 1.974(2)° in $(Ph_3SbOO\text{-}t\text{-}C_4H_9)_2O$ [1]; Table 3.

In $(Ph_3SbCl)_2O$ the Sb–Cl bond distances at 2.553(2) and 2.582(2) Å are not equal, and are longer than Sb–Cl distances found in comparable structures. In the X-ray structures of $(acac)MeSbCl_3$ [11] and in both the high- [11] and low-melting [12] point forms of $(acac)Ph_2SbCl$, the Sb–Cl distances lie in the range 2.25(1)–2.421(3) Å. The Sb–Cl distances in $(Ph_3SbCl)_2O$ are shorter however, than the minimum value of 2.622(6) Å reported for the disordered models for the $(Me_3SbX)_2O$ compounds [6]. The significant lengthening of the Sb–Cl bonds in the $(R_3SbCl)_2O$ compounds, may indicate that the Sb–Cl interactions may be only partially covalent in nature as has been noted by others [13] for related systems. The

Table 3

Selected parameters in $(Ph_3SbX)_2O$ compounds

X	Sb–O(br) (Å)	Sb–X (Å)	Sb–O–Sb (°)	Ref.
$OO\text{-}t\text{-}C_4H_9$	1.974(2)	2.088(9)	180	1
$O_3SCH_2CH_2OH$	1.936(1)	2.276(4)	180	2
N_3 [a]	1.985(3)	2.236(8)	139.8(4)	3
$OC(CN)=C(CN)_2$	1.978(8)	2.350(9)	140.0(3)	4
	1.943(7)	2.302(8)		
O_3SPh	1.963(5)	2.247(5)	139.8(3)	5
	1.963(4)	2.280(5)		
O_3SCF_3	1.980(8)	2.347(9)	136.5(5)	5
	1.94(1)	2.37(1)		
Cl	1.980(6)	2.553(2)	139.0(3)	this work
	1.986(6)	2.582(3)		

[a] Bridging oxygen atom is situated on a two-fold axis.

disparity of the Sb–Cl bond distances in $(Ph_3SbCl)_2O$ is not reflected in any differences in the associated Sb–O(br) bonds. Further, there is no clear relationship between the length of the Sb–O(br) bonds and the associated Sb–X bonds for the $(Ph_3SbX)_2O$ systems in general. As can be seen from Table 3, in $(Ph_3SbO_3SCF_3)_2O$

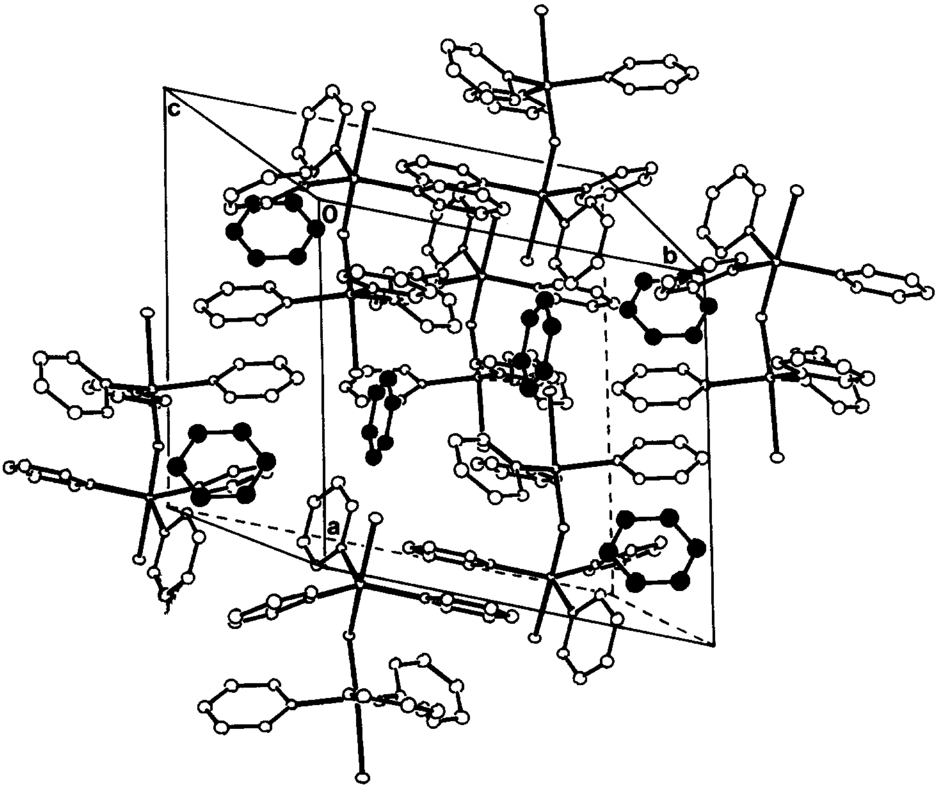

Fig. 2. The unit cell contents for $(Ph_3SbCl)_2O,2C_6H_6$.

[5] the shorter Sb–O(br) bond (1.94(1) Å) is ca. *trans* to the longer Sb–X bonds (Sb–O: 2.37(1) Å) however in the structure of $(Ph_3SbOC(CN){=}C(CN)_2)_2O$, the shorter Sb–O(br) bond of 1.943(7) Å is ca. *trans* to the shorter Sb–X bond, i.e. Sb–O: 2.302(8) Å.

Of interest in these systems is the magnitude of the Sb–O–Sb angle. In all of the complexes cited in Table 3, the normal tetrahedral angle, expected for the central O atom, has been opened up either to approximately 140° (five cases) or 180° (two cases). It has been suggested that the interaction of the lone pairs of electrons (residing on the O atom) with the unoccupied *d*-orbitals of the Sb atoms would not only shorten the Sb–O(br) bond lengths, but may provide a possible explanation for the expansion of the Sb–O–Sb angle [13]; i.e. the opening up of the Sb–O–Sb angle would allow a more efficient delocalization of π-electrons in the Sb–O–Sb moiety. While it may be expected that a linear Sb–O–Sb unit would be more ammenable for π-electron delocalization, it is noted that equally short Sb–O(br) bonds are also found in complexes with bent Sb–O–Sb bridges.

The unit cell of $(Ph_3SbCl)_2O,2C_6H_6$ is comprised of two dinuclear units and four molecules of occluded benzene; a view of the unit cell contents is shown in Fig. 2. The benzene molecules are held in the crystal lattice via normal van der Waals contacts; the closest intermolecular distances involving the solvent molecules being 2.65 Å for H(41)...H(34) and 2.40 Å for H(43)...H(33) for benzene molecules C(37)–C(42) and C(43)–C(48) respectively. Consistent with this finding is the observation that, once removed from benzene solution, the crystals rapidly decomposed, presumably owing to the loss of solvent.

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