Organometallic Chemistry

Synthesis and structure of μ-oxo-bis-[(2,5-dimethylbenzenesulfonato)tri-*p*-tolylantimony(v)]

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μ-Oxobis[(2,5-dimethylbenzenesulfonato)tri-*p*-tolylantimony(v)] was prepared by the reaction of 2,5-dimethylbenzenesulfonic acid with tri-*p*-tolylstibine in the presence of hydrogen peroxide. According to X-ray diffraction data, the linear O bridge links two Sb atoms having a trigonal bipyramidal configuration. The 2,5-dimethylbenzenesufonate group and the bridging O atom occupy the axial positions and the three tolyl substituents are equatorial. The Sb(1)—O—Sb(2) and O—Sb—O angles are 180.0(0)° and 177.2(1)°; the Sb—C(Ph)$_{eq}$, Sb—O(SO$_2$Ar), and Sb—μ-O distances are 2.090(5)—2.095(6), 2.258(3), and 1.9361(5), respectively.

Key words: μ-oxobis[(2,5-dimethylbenzenesulfonato)tri-*p*-tolylantimony(v)], synthesis, X-ray diffraction study, molecular structure.

Triphenylstibine is known[1] to undergo oxidation by hydrogen peroxide in acetic anhydride or acetic acid to give triphenylantimony diacetate. The reactions of triphenylstibine with organic and inorganic acids HX in the presence of hydrogen peroxide or tertiary alkyl hydroperoxide (molar ratio of the reactants 1 : 2 : 1) in an ethereal solution[2] afford Ph_3SbX_2 compounds in quantitative yields. Similar products are formed from triarylstibines and arenesulfonic acids under the same conditions.[3] The reaction of equimolar amounts of tri-*p*-tolylstibine, hydrogen peroxide, and 2,5-dimethylbenzenesulfonic acid results in μ-oxobis[tri-*p*-tolyl(2,5-dimethylbenzenesulfonato)antimony(v)] (**1**) in a virtually quantitative yield.

$$2\,(4\text{-}MeC_6H_4)_3Sb + 2\,HOSO_2C_6H_3Me_2\text{-}2,5 + 2\,H_2O_2 \longrightarrow$$
$$\longrightarrow [(4\text{-}MeC_6H_4)_3Sb(OSO_2C_6H_3Me_2\text{-}2,5)]_2O$$

Compounds of this type have been prepared previously from either triphenylantimony oxide and arenesulfonic acid or μ-oxobis(chlorotriphenylantimony) and arenesulfonic acid in the presence of silver oxide; how-

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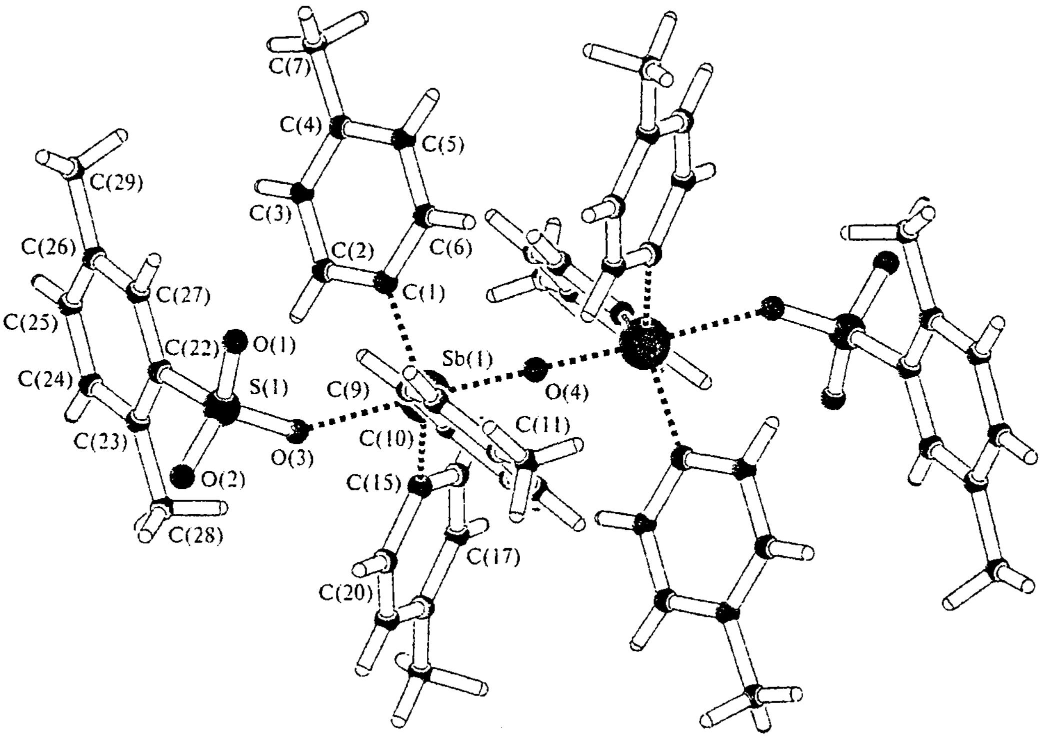

Fig. 1. Structure of molecule **1**.

ever, the yield of μ-oxobis[arenesulfonatotriphenylantimony(v)] in these reactions[4] did not exceed 84%.

Antimony compounds of the general formula (Ph$_3$SbX)$_2$O (where X is an organic or inorganic ligand) have been known[5] since 1973. In the crystal, the molecule of μ-oxobis[triphenyl(azido)antimony(v)], (Ph$_3$SbN$_3$)$_2$O (**2**), has[5] a V-shaped configuration with a Sb—O—Sb bond angle of 139.7°. At present, 12 structures of pentavalent antimony of this type are known. They include μ-oxobis[(2-hydroxyethanesulfonato)triphenylantimony(v)] (**3**),[6] μ-oxobis[(benzenesulfonato)triphenylantimony(v)] (**4**) and μ-oxobis[(trifluoromethanesulfonato)triphenylantimony(v)] (**5**),[7] nonaphenyltristiboxane-1,5-diylbis(2,4-dinitrophenylsulfonate) (**6**),[8] μ-oxobis[(chloro)triphenylantimony(v)] (**7**),[9] tetrakis-μ-oxobis[(iodo)triphenylantimony(v)] diiodide (**8**),[10] μ-oxobis[(bromo)triphenylantimony(v)] (**9**),[11] μ-oxobis[(*tert*-butylperoxy)triphenylantimony(v)] (**10**),[12] μ-oxobis[(1,1,2-tricyanoethenoxo)triphenylantimony(v)] (**11**),[13] and linear (**12**) and twisted (**13**) modifications of μ-oxobis[(iodo)triphenylantimony(v)].[14] The coordination polyhedra of the Sb atoms in these compounds are trigonal bipyramids with electronegative ligands located in the axial positions, which is the typical coordination of pentavalent antimony.

In the majority of cases, the molecules occur in a twisted V-shaped configuration (structures **2**, **4—7**, **11**, and **13**), in which the Sb—O—Sb angles lie in the 135—144° range. The molecules of compounds **3**, **8**, **10**, and **12** have linear centrosymmetric configurations; the angle at the bridging O atom is 180°. The configuration of the molecule of **9** is nearly linear: the angle at the O atom is 176.5°. It has been suggested[15] that the linear arrangement of the Sb—O—Sb atoms is possible when the terminal ligand X is strongly bound to the Sb atom. Indeed, the Sb—X distances in the linear structures are shorter than the corresponding distances in the twisted structures (for example, the Sb—I bond lengths in **12** (linear) and in **13** (twisted) are 2.954 Å and 2.995 Å, respectively). The fact that the same compound can exist as both linear and twisted species accounts for the interest in the spatial structure of this type of derivatives.

The X-ray diffraction analysis of the crystals of **1** (Fig. 1) showed that the molecule of compound **1** has a linear symmetrical structure; the bridging O atom is located in the center of symmetry; as a result, both Sb atoms are characterized by identical geometric parameters and the O(4) atom has a linear coordination (the Sb(1)—O(4)—Sb(1′) angle is 180°). The coordination environment of the Sb atoms is a trigonal bipyramid, typical of Sb^{V} compounds (the sum of C(Tol)—Sb—C(Tol) angles in the equatorial plane is 358.9°). The angle between the axial substituents (O(3)—Sb(1)—O(4)) is 177.2(1)°. The Sb(1)—O(4) distance, equal to 1.9361(5) Å, coincides with that found for linear structures (1.936 (**3**), 1.942 (**8**), and 1.944 Å (**9**)) and is much shorter than that in twisted structures (1.985 (**2**) and 1.962 Å (**4**)). The Sb(1)—O(3) distances (2.258(5) Å) are some-

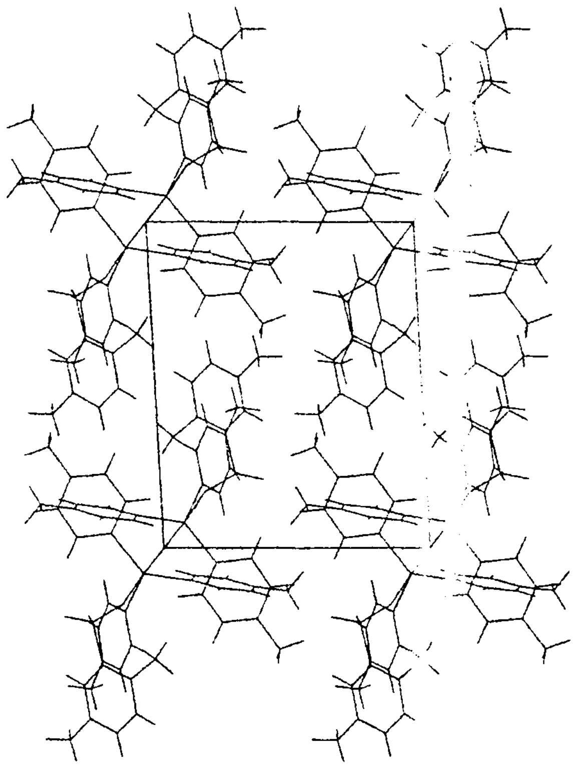

Fig. 2. Packing of the molecules of compound 1 in the crystal.

what shorter than those in structures [illegible] ([illegible]276 Å) and 5 (2.347 Å). It should be noted that the lengths of the terminal Sb—O bonds in compounds of this type vary over wide limits, from 2.089 to 2.347 Å. Shortening of the Sb—O bonds at the bridging O atom is also observed in Sb^{III} compounds; for example, the distance between the Sb and O atoms in μ-oxobis[diphenylantimony(III)][16] is 1.970 Å, which is much shorter than the sum of the covalent radii of these atoms.[17] The shortening of the bridging Sb—O bonds in Sb^{III} and Sb^{V} compounds indicates that the bond multiplicity has increased due to the interaction between the lone electron pairs of the O atom and the vacant d orbitals of the Sb atoms, as has also been noted previously.[12,18,19]

The Sb—C bond lengths in structure **1** are identical to within the experimental errors and, on the average, they are equal to 2.093(5) Å, which coincides with the value found for linear structure **3**. The Sb—C bond lengths in twisted structures are normally somewhat longer, from 2.105 to 2.130 Å.

Analysis of the intermolecular contacts in the crystal of **1** showed that the packing of molecules is determined by ordinary van der Waals interactions. Neither contacts shorter than 4.745 Å between the aromatic rings nor their parallel arrangement were found. Weak interactions of the C—H...π type between H atoms of the benzene rings and aromatic fragments may occur because intermolecular contacts with distances between H atoms and centers of the benzene rings equal to 2.82—2.86 Å are found in the structure (Fig. 2).

Table 1. Principal bond lengths (*d*) and angles (ω) in molecule **1**

Bond	*d*/Å	Angle	ω/deg
Sb(1)—O(3)	2.258(5)	O(3)—Sb(1)—O(4)	177.2(1)
Sb(1)—O(4)	1.9361(5)	O(3)—Sb(1)—C(1)	87.9(2)
Sb(1)—C(1)	2.090(5)	O(3)—Sb(1)—C(8)	89.1(2)
Sb(1)—C(8)	2.095(6)	O(3)—Sb(1)—C(15)	82.9(2)
Sb(1)—C(15)	2.094(6)	O(4)—Sb(1)—C(1)	93.1(2)
S(1)—O(1)	1.433(5)	O(4)—Sb(1)—C(8)	92.7(2)
S(1)—O(2)	1.436(5)	O(4)—Sb(1)—C(15)	94.3(2)
S(1)—O(3)	1.478(5)	C(1)—Sb(1)—C(15)	118.7(2)
S(1)—C(22)	1.774(6)	O(1)—S(1)—O(2)	116.2(3)
C(1)—C(2)	1.365(9)	O(1)—S(1)—C(22)	106.6(3)
C(1)—C(6)	1.382(8)	O(2)—S(1)—C(22)	107.6(3)
		Sb(1)—O(3)—S(1)	143.8(2)

Experimental

The IR spectra were recorded on a Hitachi 215 instrument (for Vaseline oil mulls).

μ-Oxobis[tri-*p*-tolyl-(2,5-dimethylbenzenesulfonato)antimony] (1). A 31% solution of hydrogen peroxide (0.29 mL, 2.53 mmol) was added to a mixture of tri-*p*-tolylantimony (1.00 g, 2.53 mmol), the 2,5-dimethylbenzenesulfonic acid crystal hydrate (0.56 g, 2.53 mmol), and 20 mL of ether, and the mixture was kept for 12 h at –20 °C to give a crystalline precipitate. The solvent was removed and the residue was dried to give 1.48 g (93%) of compound **1**, m.p. 246 °C. IR, ν/cm^{-1}: 1288 s, 1150 vs, 1072 s, 970 s, 950 s. Found (%): C, 58.63; H, 4.87; S, 5.22. $C_{58}H_{60}O_7S_2Sb_2$. Calculated (%): C, 59.18; H, 5.10; S, 5.44.

The X-ray diffraction analysis of the crystals of **1** was carried out on an Enraf-Nonius CAD-4 four-circle automated diffractometer with K-geometry (20 °C, Mo-Kα radiation, λ(Mo-Kα) = 0.71074 Å, graphite monochromator).

The crystals of the compound $C_{58}H_{60}O_7S_2Sb_2$ (**1**) are triclinic; at 20 °C, a = 10.324(4) Å, b = 10.781(4) Å, c = 13.428(4) Å, α = 89.44(2)°, β = 73.89(3)°, γ = 76.09(3)°, V = 1391.1(8) Å^3, d_{calc} = 1.405 g cm^{-3}, Z = 1 (the molecule occurs in a specific position in the center of symmetry). The absorption corrections were applied empirically (μ(Mo) = 11.0 cm^{-1}); nine reflections with $\chi \geq 80°$ were scanned with rotation over the ψ vector with a step of 10°. The intensities of 5961 reflections were measured; for 3507 of them, $I \geq 3\sigma$. ω/2θ scanning with $\theta \leq 29.96°$ was used. The structure was solved by the direct method using the SIR program[20] and refined first in the isotropic and then in the anisotropic approximation. The H atoms were revealed from the electron density difference series; their contributions to the structural amplitudes were taken into account in the final step of refinement with fixed positional and isotropic thermal parameters. The final discrepancy factors were as follows: R = 0.044, R_w = 0.049 over 3556 independent reflections with $F^2 \geq 3\sigma$. All the calculations were performed using the MolEN program package[21] on a DEC Alpha Station 200 computer. The intermolecular contacts in the structure were analyzed and the molecular models were drawn using the WINPL98 program package.[22] The principal bond lengths and angles in **1** are presented in Table 1.

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