

The Crystal and Molecular Structure of μ -Oxo-bis-[bromotriphenylantimony(V)], $[\text{SbBr}(\text{C}_6\text{H}_5)_3]_2\text{O}$

Akira OUCHI* and Shoichi SATO†

Department of Chemistry, College of Arts and Sciences, The University of Tokyo,
Komaba, Meguro-ku, Tokyo 153

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

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Synopsis. The crystal and molecular structure of the title complex was determined by the single-crystal X-ray diffraction method. The crystallographic data are: monoclinic, space group $P2_1/c$, $a=19.164(6)$, $b=19.020(9)$, $c=18.649(7)$ Å, $\beta=95.06(3)^\circ$, and $Z=8$ (16 metal atoms are in a unit cell). There are two crystallographically independent dimeric $[\text{SbBr}(\text{C}_6\text{H}_5)_3]_2\text{O}$ molecules, which are almost in the same form. Each antimony atom is bonded with three phenyl carbon atoms equatorially and one bromine as well as one bridging oxygen atoms axially, being in a trigonal-bipyramidal geometry. The Sb–O–Sb' angles are $170.2(7)$ and $176.6(8)^\circ$, while the Sb–O lengths are in the range of $1.931(13)$ – $1.958(13)$ Å, which are shorter than the sum of their covalent radii of the atoms: 2.15 Å.

The halogeno derivatives of organoantimony(V) have been one of the best known species since the 19th century.^{1a, 2)} They are hydrolyzed in a solution containing water into their hydroxides or oxides,^{1b)} and the decomposition is quantitative in a water-acetonitrile mixed solution, even at room temperature.³⁾

On the other hand, some intermediate compounds of the type $(\text{SbXR}_3)_2\text{O}$ (where X^- is a halide or acidate ion, and R is a hydrocarbon group) were obtained and some of their structures were elucidated: the compounds where $\text{R}=\text{C}_6\text{H}_5$, $\text{HX}=2$ -hydroxyethanesulfonic acid⁴⁾ or HN_3 ,⁵⁾ $\text{R}=\text{CH}_3$, $\text{HX}=\text{HCl}$, HClO_4 or HN_3 ,⁶⁾ and $\text{R}=p$ -chlorophenyl, $\text{HX}=1,1,1$ -trifluoro-2,4-pentanedione⁷⁾ are examples. In addition to them, this time we could obtain the title compound, in spite of the fact that dibromotriphenylantimony is hydrolyzed into $[\text{Sb}(\text{C}_6\text{H}_5)_3]\text{O}$ easily and quantitatively in the moistened acetonitrile solution at ambient temperature.

Moreover, the Sb–O–Sb' bridge of this type dimeric complex is one of the subjects of discussion. In the related compounds such as $[\text{BiClO}_4(\text{C}_6\text{H}_5)_3]_2\text{O}$,⁸⁾ $[\text{Ge}(\text{C}_6\text{H}_5)_3]_2\text{O}$,⁹⁾ and $[\text{Sn}(\text{C}_6\text{H}_5)_3]_2\text{O}$ ¹⁰⁾ the M–O–M' angles are $142.2(7)$, $135.2(2)$, and $137.3(1)^\circ$, respectively: not 109° of the sp^3 hybridization orbital angle nor 180° to separate both side metal atoms the furthest. Among the $(\text{SbXR}_3)_2\text{O}$ type dimers, $[\text{SbN}_3(\text{C}_6\text{H}_5)_3]_2\text{O}$ has an angle of $139.8(4)^\circ$,⁵⁾ however, the others were reported to have an angle of 180° , since their oxygen atom is at the center of symmetry. As the Sb–O distances of these bridges are relatively short, the oxygen atom is assumed to be disordered into several positions around it.⁶⁾ To discuss this problem more clearly, we need more structural data concerning this type dimers.

From these viewpoints, we have determined the

crystal and molecular structures of the title compound using the single crystal X-ray diffraction technique.

Experimental

Synthesis of the μ -Oxo-bis[bromotriphenylantimony(V)]. Dibromotriphenylantimony(V) (1.02 g, 2.0 mmol) was dissolved into 10 cm³ of benzene, and triethylamine (including trace of water, 0.20 g, 2.0 mmol) was added and stirred. The precipitate (triethylammonium bromide) was filtered off, and the filtrate was dried up by the rotary vacuum evaporator at about 80°C . The residue was recrystallized from acetonitrile (the title compound is relatively soluble into hot acetonitrile, while $[\text{Sb}(\text{C}_6\text{H}_5)_3]\text{O}$ is more insoluble at any temperature). Yield, 0.30 g (34%). Found: C, 48.86; H, 3.39%. Calcd for $\text{Sb}_2\text{C}_{36}\text{H}_{30}\text{OBr}_2$: C, 49.03; H, 3.43%.

Single Crystal X-Ray Structure Analysis. The crystal of the title compound (colorless), in the shape of parallelepiped ($0.30 \times 0.20 \times 0.30$ mm³) was used for the intensity measurement. Crystallographic data: $\text{Sb}_2\text{C}_{36}\text{H}_{30}\text{OBr}_2$, F. W., 881.94, monoclinic, space group $P2_1/c$, $a=19.164(6)$, $b=19.020(9)$, $c=18.649(7)$ Å, $\beta=95.06(3)^\circ$, $U=6711(5)$ Å³, $Z=8$, $D_m=1.74(3)$, $D_x=1.74$ g cm⁻³, $\mu(\text{Mo K}\alpha)=41.8$ cm⁻¹, and the final R value was 0.053.¹¹⁾ Reflections within a range of $3^\circ < 2\theta < 36^\circ$ were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.71073$ Å), the ω - 2θ scan technique being employed (scan speed, 4° min^{-1} in θ ; scan width $1.10 + 0.5 \tan \theta$). Of the 5155 independent reflections measured, 3553 $|F_o| > 3\sigma(|F_o|)$ reflections were used for the structure determination. The intensities were corrected for the Lorentz and polarization factors, but not for the absorption and extinction. The structure was solved by the heavy-atom method. Their positional and thermal parameters were refined by the least-squares method. At the final step, all non-hydrogen atoms were found: all hydrogen atoms were excluded from the structure factor calculations.

All the calculations were carried out on a HITAC M-680H computer at the Computer Center of the University of Tokyo, using the local version of the UNICS program system.¹²⁾ The atomic scattering factors were taken from Ref. 13.

Results and Discussion

The selected bond lengths and bond angles are shown in Table 1.¹⁴⁾ A perspective drawings of both dimeric complexes from different visual points, together with their numbering scheme of the atoms in Figs. 1 and 2, and the projection of the unit cell to the ac-plane in Fig. 3.

Although both kinds of the dimers are crystallographically independent, and the bridging oxygen atom is not at the center of symmetry, their general features, as well as the geometries around all anti-

Table 1. Selected Bond Lengths and Bond Angles with Their Standard Deviations in Parentheses

Bond length (<i>l</i> /Å)			
Sb(1)–Br(1)	2.707(4)	Sb(3)–Br(3)	2.716(3)
Sb(1)–O(1)	1.958(13)	Sb(3)–O(2)	1.943(14)
Sb(1)–C(1)	2.09(2)	Sb(3)–C(37)	2.091(19)
Sb(1)–C(7)	2.09(2)	Sb(3)–C(43)	2.08(2)
Sb(1)–C(13)	2.07(2)	Sb(3)–C(49)	2.14(2)
Sb(2)–Br(2)	2.722(3)	Sb(4)–Br(4)	2.693(3)
Sb(2)–O(1)	1.931(13)	Sb(4)–O(2)	1.943(13)
Sb(2)–C(19)	2.107(19)	Sb(4)–C(55)	2.112(19)
Sb(2)–C(25)	2.08(2)	Sb(4)–C(61)	2.06(2)
Sb(2)–C(31)	2.12(2)	Sb(4)–C(67)	2.09(2)
Bond angle (ϕ /°)			
Sb(1)–O(1)–Sb(2)	170.2(7)	Sb(3)–O(2)–Sb(4)	176.6(8)
Br(1)–Sb(1)–O(1)	178.8(4)	Br(3)–Sb(3)–O(2)	178.6(4)
Br(1)–Sb(1)–C(1)	88.3(6)	Br(3)–Sb(3)–C(37)	87.5(5)
O(1)–Sb(1)–C(1)	92.8(7)	O(2)–Sb(3)–C(37)	92.2(7)
C(1)–Sb(1)–C(7)	124.4(8)	C(37)–Sb(3)–C(43)	119.8(8)
C(1)–Sb(1)–C(13)	117.8(8)	C(37)–Sb(3)–C(49)	124.2(8)
C(7)–Sb(1)–C(13)	117.7(8)	C(43)–Sb(3)–C(49)	115.9(8)
Br(2)–Sb(2)–O(1)	178.8(4)	Br(4)–Sb(4)–O(2)	178.5(4)
Br(2)–Sb(2)–C(19)	88.9(5)	Br(4)–Sb(4)–C(55)	90.7(5)
O(1)–Sb(2)–C(19)	90.3(6)	O(2)–Sb(4)–C(55)	90.6(6)
C(19)–Sb(2)–C(25)	118.6(8)	C(55)–Sb(4)–C(61)	122.9(8)
C(19)–Sb(2)–C(31)	121.4(8)	C(55)–Sb(4)–C(67)	117.4(8)
C(25)–Sb(2)–C(31)	120.0(9)	C(61)–Sb(4)–C(67)	119.7(8)

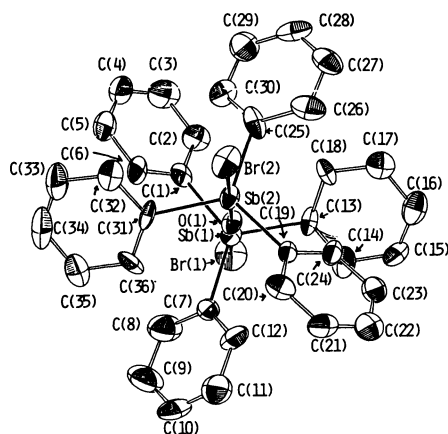


Fig. 1. A perspective drawing of the complex around the Sb(1) and Sb(2) atoms, with the numbering scheme.

mony atoms are approximately the same. Of course, there are some slight differences between them: for example, the angles Sb(1)–O(1)–Sb(2) and Sb(3)–O(2)–Sb(4) are 170.2(7) and 176.6(8)°, respectively, and the mutual dihedral angles between the three benzene ring planes around the Sb(2) atom distribute in the widest range, 49.0–70.6°.

Each antimony atom is coordinated to three phenyl-carbon atoms equatorially, and to one bromine as well as one bridging oxygen atom axially, being in a trigonal-bipyramidal geometry. The lengths of the Sb–C are in the range 2.06(2)–2.14(2) Å, which are not much different from the sum of the Pauling's covalent radii of the atoms C and O: 2.18 Å. On the other hand, the Sb–Br lengths are in the range 2.693(3)–

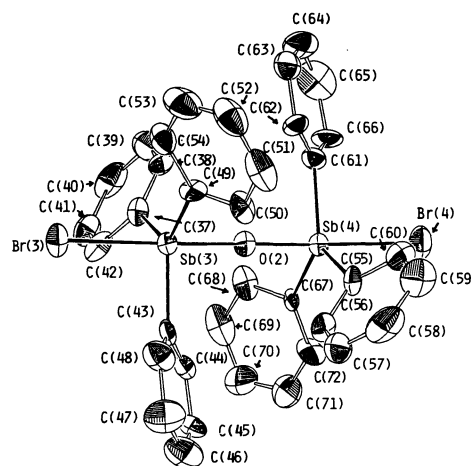


Fig. 2. A perspective drawing of the complex around the Sb(3) and Sb(4) atoms, with the numbering scheme.

2.722(3) Å, which are longer than the sum of their radii: 2.55 Å.¹⁵ The Sb–O(bridge) lengths are in the range 1.931(13)–1.958(13) Å, which are much shorter than the sum of their radii: 2.15 Å. The common Sb–O bond lengths in the monomeric organoantimony(V) compounds are not so short: for example, in methoxytetraphenylantimony(V) it is 2.061(7) Å, while in dimethoxytriphenylantimony(V) they are 2.039(8) and 2.027(8) Å,¹⁶ while in the other compounds, the bond length is sometimes longer. On the other hand, in cases of this type bridging, the bond is always very short. The Sb–O bond lengths as well as the Sb–O–Sb' bond angles of some [SbXR₃]₂O type com-

Table 2. Bond Lengths and Angles Around the Bridging Oxygen Atom of the $(\text{SbXR}_3)_2\text{O}$ ($\text{R}=\text{C}_6\text{H}_5$, CH_3) Type Compounds

Compound	Sb-O(bridge) ($\text{\AA}$)	Sb-O-Sb' ($^\circ$)	Ref.
$[\text{SbBr}(\text{C}_6\text{H}_5)_3]_2\text{O}^a$	1.944 (average)	173.4 (average)	
$[\text{Sb}(\text{HOC}_2\text{H}_4\text{SO}_3)(\text{C}_6\text{H}_5)_3]_2\text{O}$	1.936(1)	(180) ^b	4
$[\text{SbN}_3(\text{C}_6\text{H}_5)_3]_2\text{O}$	1.985(3)	139.8(4)	5
$[\text{SbCl}(\text{CH}_3)_3]_2\text{O}$	1.907(1)	(180) ^b	6
$[\text{SbN}_3(\text{CH}_3)_3]_2\text{O}$	1.872(3)	(180) ^b	6
$[\text{Sb}(\text{ClO}_4)(\text{CH}_3)_3]_2\text{O}$	1.862(2)	(180) ^b	6

a) Respective values with their standard deviations are shown in Table 1. b) The bridging oxygen atom is at the center of symmetry.

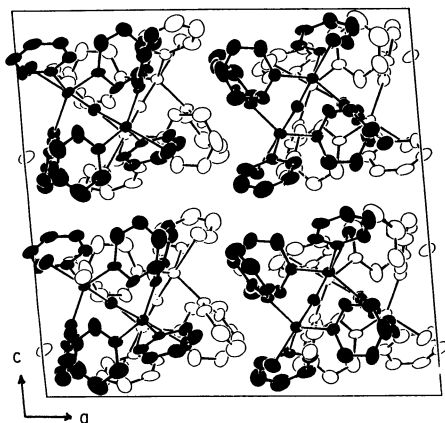


Fig. 3. A projection of the unit cell to the ac -plane. Black atoms belong to the upper, and the white atoms to the lower layers, respectively.

pounds are summarized in Table 2. As shown in this table, of the three triphenylantimony derivatives, the title compound has a bond longer than that of the sulfonato derivative, but shorter than the azido derivative. The polarizability of the bonded anion should not be the sole factor used to determine the length, because in the trimethylantimony derivatives, the Sb-O(bridge) length of the chloro derivative is longer than that of the azido derivative. Moreover, the bond lengths of the azido derivatives of the triphenyl- and trimethylantimony(V) are not the same: the former length is 0.113 $\text{\AA}$ longer than the latter. Therefore, the massive hydrocarbon groups bonded to the metal atom elongate the bridging bond length. Although the Sb-O-Sb' angles of the title compound is not much different from 180° , but as the temperature factors of the both bridging oxygen atoms, O(1) and O(2), are not very large, the disorder of the oxygen atoms proposed by Ferguson⁶⁾ may not be true in this case. One probable reason is that, although which may not be the sole reason, the mutual steric effect of such large molecules to pack them most closely in the crystal gives the bridging oxygen atom such a large angle, almost 180° , in some of this type dimers.

As shown in Figs. 1 and 2, three benzene rings around each metal atom are situated like the three

wing plates of a screw around their shaft. All the mutual dihedral angles between the three benzene ring planes bonded to each metal atom are 59.7° , on the average, and all the angles between the benzene ring planes and the respective Sb-O shafts are 54.6° on the average (in the range of 48.2 – 66.1°).

There are no bridging ligands nor hydrogen bondings between any dimeric complex molecules: the distances between any non-hydrogen atoms of the different molecules are more than 3.7 $\text{\AA}$.

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