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μ-Oxo-Bis[(Bromo)Tri-*m*-Tolylantimony]: Synthesis and Structure

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Abstract—μ-Oxo-bis[(bromo)tri-*m*-tolylantimony] was synthesized by the reaction of tri-*m*-tolylstibine with hydrobromic acid in ether in the presence of hydrogen peroxide. The complex was structurally characterized by X-ray diffraction analysis. The coordination polyhedron of the Sb atoms is a distorted trigonal bipyramid with the bromine and the bridging O atoms in the axial positions. The Sb(1)–C(Ph) distances vary from 2.085(9) to 2.111(8) Å. The Sb(1)–Br(1) and Sb(2)–Br(2) bond lengths are 2.739(2) and 2.735(2) Å, respectively; the Sb–O_{br} distances measure 1.949(1) Å.

About 20 compounds of the general formula $(Ar_3SbX)_2O$ have been structurally characterized to date [1–15]. The SbOSb fragment in these compounds may be either nearly linear or curved (the SbOSb angle ranges from 139.0° to 160.0°). Apparently, the geometry of this fragment is determined by substituents at the Sb atoms (in particular, by their steric and electron effects) or by the molecular packing in the crystal.

In this study, the molecular and crystal structures of μ-oxo-bis[(bromo)tri-*m*-tolylantimony] (**I**) with ligands more bulky than phenyl were investigated.

EXPERIMENTAL

Complex I was synthesized as follows. A 31% solution of H_2O_2 (0.15 ml, 1.38 mmol) was added to a mixture of tri-*m*-tolylantimony (1.00 g, 2.78 mmol) and aqueous 40% HBr (0.50 ml, 2.72 mmol) in 20 ml of ether. After 12 h, the colorless crystals that formed were filtered off and dried. The yield of **I** was 1.06 g (87%); mp 210°C.

For $C_{42}H_{42}OBr_2Sb_2$

anal. calcd. (%):	C, 57.17;	H, 4.35;	Br, 16.56.
Found (%):	C, 57.48;	H, 4.53;	Br, 16.04.

X-ray diffraction analysis of crystals **I** was carried out using a Siemens P3/CP four-circle diffractometer (MoK_α radiation, graphite monochromator, θ/2θ scan mode).

The crystals of **I** are triclinic: at 20°C, $a = 9.921(3)$ Å, $b = 10.259(5)$ Å, $c = 19.834(13)$ Å, $\alpha = 95.12(5)°$, $\beta = 95.08(4)°$, $\gamma = 99.39(4)°$, $V = 1973(2)$ Å^3, space group $P\bar{1}$, $\rho_{calcd} = 1.626$ g/cm^3, $\mu = 3.425$ mm^{-1}, $Z = 4$ (two independent molecules).

The structure was solved by the direct method and refined by the full-matrix least squares method in the anisotropic approximation for all non-hydrogen atoms to $R = 0.0580$, $R_w = 0.1430$, and $S = 1.016$ from 6937 reflections with $I > 2\sigma(I)$. The H atoms were located geometrically and refined in the rider model with fixed U_{iso} values.

All computations were performed with the SHELX97 programs [16] using an IBM PC.

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1. Bond lengths and angles are presented in Table 2.

RESULTS AND DISCUSSION

It is known that triarylstibine can be oxidized with hydrogen peroxide in the presence of arenesulfonic acids into μ-oxo-bis[(arenesulfonato)triarylantimony] [15]. We found that the use of hydrobromic acid instead of arenesulfonic acid does not change the reaction scheme. In this way, μ-oxo-bis[(bromo)tri-*m*-tolylantimony(V)] (**I**) was obtained from tri-*m*-tolylstibine, hydrogen peroxide, and hydrobromic acid:

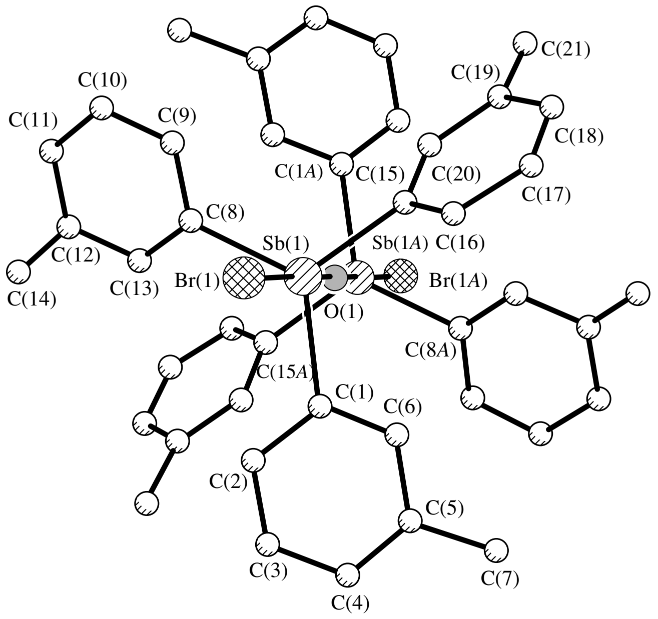
$$2(m\text{-}MeC_6H_4)_3Sb + 2HBr + 2H_2O_2 \xrightarrow[-3H_2O]{\text{ether}} [(m\text{-}MeC_6H_4)_3SbBr]_2O.$$

The structural units of crystal **I** are two types of crystallographically nonequivalent binuclear Sb(V) complexes in which two $(m\text{-}MeC_6H_4)_3SbBr$ fragments are united through the bridging O atom (figure) lying in the center of inversion.

The Sb(1) and Sb(2) atoms have a slightly distorted trigonal-bipyramidal coordination; the equatorial CSbC angles range from 115.7(3)° to 124.1(1)° for Sb(1) and from 119.8(4)° to 121.6(3)° for Sb(2), and the axial BrSbO angle is equal to 175.52(4)° and 176.30(4)°, respectively.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) for structure **I**

Atom	x	y	z	U_{equiv}, Å^2
Sb(1)	–5707(1)	1333(1)	4495(1)	34(1)
O(1)	–5000	0	5000	45(2)
Br(1)	–6688(1)	3328(1)	3880(1)	65(1)
C(1)	–3716(9)	2276(9)	4348(4)	44(2)
C(2)	–3248(13)	3620(10)	4587(6)	65(3)
C(3)	–1924(15)	4168(12)	4495(7)	85(4)
C(4)	–1112(13)	3413(13)	4141(6)	76(4)
C(5)	–1582(11)	2129(11)	3886(5)	60(3)
C(6)	–2903(10)	1538(10)	4007(4)	47(2)
C(7)	–757(13)	1320(15)	3460(7)	91(4)
C(8)	–6785(10)	1889(8)	5299(4)	44(2)
C(9)	–8218(11)	1689(12)	5220(12)	66(3)
C(10)	–8896(12)	1997(14)	5771(7)	78(4)
C(11)	–8167(14)	2509(13)	6387(7)	81(4)
C(12)	–6759(14)	2707(12)	6482(6)	70(3)
C(13)	–6084(11)	2374(10)	5922(5)	54(2)
C(14)	–5923(16)	3290(19)	7149(7)	124(7)
C(15)	–6720(9)	–66(8)	3690(4)	38(2)
C(16)	–6751(12)	218(11)	3029(5)	63(3)
C(17)	–7341(14)	–774(12)	2509(5)	83(4)
C(18)	–7910(13)	–2035(11)	2677(5)	67(3)
C(19)	–7896(10)	–2325(9)	3330(5)	51(2)
C(20)	–7281(9)	–1328(8)	3855(5)	42(2)
C(21)	–8451(12)	–3678(10)	3508(6)	71(3)
Sb(2)	–13613(1)	3983(1)	–279(1)	37(1)
O(2)	–15000	5000	0	50(2)
Br(2)	–11548(1)	2705(1)	–665(1)	65(1)
C(22)	–12868(9)	5420(9)	–910(4)	41(2)
C(23)	–13061(11)	5117(11)	–1601(5)	55(3)
C(24)	–12674(13)	6117(13)	–2011(6)	73(3)
C(25)	–12020(14)	7360(14)	–1709(7)	81(4)
C(26)	–11779(12)	7641(11)	–1026(6)	69(3)
C(27)	–12217(11)	6646(9)	–619(5)	55(3)
C(28)	–11023(20)	8984(13)	–699(10)	146(8)
C(29)	–15069(11)	2325(9)	–726(5)	54(3)
C(30)	–14810(16)	1065(11)	–704(9)	102(5)
C(31)	–15817(21)	3(12)	–994(10)	143(8)
C(32)	–17041(16)	233(13)	–1287(8)	99(5)
C(33)	–17314(13)	1511(11)	–1327(5)	65(3)
C(34)	–16302(11)	2548(10)	–1034(5)	54(3)
C(35)	–18647(13)	1730(14)	–1648(7)	91(4)
C(36)	–12731(9)	4022(8)	742(4)	40(2)
C(37)	–11368(11)	4461(10)	912(5)	55(3)
C(38)	–10843(12)	4493(12)	1579(6)	67(3)
C(39)	–11676(13)	4011(11)	2054(5)	66(3)
C(40)	–13039(12)	3553(11)	1891(5)	57(3)
C(41)	–13550(10)	3580(9)	1207(5)	47(2)
C(42)	–13961(15)	2996(15)	2392(7)	98(5)



Structure of one of the two independent dimers **I**.

The Sb–O and Sb–Br distances in the independent molecules of **I** are 1.949(1) and 2.739(2) Å for Sb(1) and 1.946(1) and 2.735(2) Å for Sb(2), which are close to the analogous Sb–O (1.930–1.965 Å) and Sb–Br distances (2.693–2.750 Å) found for similar molecules [7, 11]. The Sb–C(Ph) distances in **I** (2.085(9)–2.127(9) Å) are typical of organoantimony(V) compounds.

Table 2. Selected bond lengths and angles in structure **I**

Bond	*d*, Å	Bond	*d*, Å
Sb(1)–O(1)	1.949(1)	Sb(2)–O(2)	1.946(1)
Sb(1)–C(8)	2.085(9)	Sb(2)–C(22)	2.104(9)
Sb(1)–C(1)	2.110(9)	Sb(2)–C(29)	2.113(9)
Sb(1)–C(15)	2.111(8)	Sb(2)–C(36)	2.127(9)
Sb(1)–Br(1)	2.739(2)	Sb(2)–Br(2)	2.735(2)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)Sb(1)C(8)	91.4(2)	O(2)Sb(2)C(22)	91.6(2)
O(1)Sb(1)C(1)	92.5(2)	O(2)Sb(2)C(29)	94.0(3)
C(8)Sb(1)C(1)	124.1(4)	O(22)Sb(2)C(29)	118.0(4)
O(1)Sb(1)C(15)	93.9(2)	O(2)Sb(2)C(36)	92.4(2)
C(8)Sb(1)C(15)	119.6(4)	C(22)Sb(2)C(36)	121.6(3)
C(1)Sb(1)C(15)	115.7(3)	C(29)Sb(2)C(36)	119.8(4)
O(1)Sb(1)Br(1)	175.52(4)	O(2)Sb(2)Br(2)	176.30(4)
C(8)Sb(1)Br(1)	84.9(2)	C(22)Sb(2)Br(2)	85.6(2)
C(1)Sb(1)Br(1)	87.5(2)	C(29)Sb(2)Br(2)	89.5(3)
C(15)Sb(1)Br(1)	90.1(2)	C(36)Sb(2)Br(2)	87.1(2)

With the aim of elucidating the reasons for the broad range of the SbOSb angles in $(Ar_3SbX)_2O$ complexes, we analyzed two series of analogous compounds, namely, $(Ph_3SbX)_2O$ (where X = Cl [6, 10], Br [7, 11], and I [8, 9]) and $(Ar_3SbBr)_2O$ (where Ar = Ph [7], *o*-Tol [11], and *p*-Tol [11]). In the former series, the SbOSb angle ranges from 139° to 180°, being independent of the nature of the X atom (139.0° [6] and 173.1° [10] for Cl, 170.3° [7] for Br, and 180° [8, 9] and 144.6° [8] for I). The same situation is observed in the latter series: the SbOSb angle ranges from 161° to 180° and is independent of the Ar structure (170.3° [7] for Ph, 161.0° [11] for *o*-Tol, 180° [11] for *p*-Tol, and 180° (this study) for *m*-Tol).

Thus, the SbOSb angle in $(Ar_3SbX)_2O$ complexes depends neither on the electron-accepting properties of the X atoms nor on the presence of substituents in the aryl groups. Hence, one can assume that the SbOSb angle value in $(Ar_3SbX)_2O$ complexes is mainly influenced by the molecular packing in the crystal.

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