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μ-Oxo-Bis[(arenesulfonato)triphenylantimony]: Synthesis and Structure

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Abstract—μ-Oxo-bis[(4-methylbenzenesulfonato)triphenylantimony] (**I**) and μ-oxo-bis[(2,5-dimethylbenzenesulfonato)triphenylantimony] (**II**) were synthesized by reacting triphenylstibine Ph_3Sb with tri-*p*-tolylbismuth bis(4-methylbenzenesulfonate) and tri-*p*-tolylbismuth bis(2,5-dimethylbenzenesulfonate), respectively, in toluene in the presence of air moisture. According yo X-ray diffraction data, the antimony atoms in the compounds synthesized have a distorted trigonal bipyramidal configuration. The SbOSb angles are equal to 138.5(2)° and 180°, respectively. A bent molecule **I** contains the Sb(1)···Sb(2) (3.690(1) Å) and Sb···S(1,2) (3.521(2), 3.559(2) Å) intramolecular contacts. In a linear molecule **II**, the Sb···S distances are equal to 3.438(1) Å.

In the antimony compounds with the general formula $(Ar_3SbX)_2O$, the SbOSb fragment is known to have a linear or a bent geometry [1–15]. To determine the factors influencing the SbOSb angle, the molecular and crystal structures of μ-oxo-bis[(4-methylbenzenesulfonato)triphenylantimony] (**I**) and μ-oxo-bis[(2,5-dimethylbenzenesulfonato)triphenylantimony (**II**) were studied in this work.

EXPERIMENTAL

Synthesis of I. A mixture containing 0.50 g of tri-*p*-tolylbismuth bis(4-methylbenzenesulfonate) and 0.20 g of triphenylstibine in 30 ml of toluene was kept in a glass evacuated tube at 25°C for 72 h. Large crystals formed on the tube walls were collected, dried, and weighted; 0.15 g (88%) of μ-oxo-bis[(4-methylbenzenesulfonato)triphenylantimony] was thus obtained (mp 215°C). The solvent was removed from mother liquor, and the residue was recrystallized from water. The yield was 0.30 g (94%); (mp 220°C).

IR spectrum of I (ν, cm^{-1}): 1300m, 1265vs; 1145vs; 1100vs; 1045w, 1020m, 970vs.

Synthesis of II. Complex **II** was synthesized similarly, using the above-described procedure. The yield was 87% (mp 220°C).

IR spectrum of II (ν, cm^{-1}): 1270vs, 1150vs, 1100vs; 1060w; 1020s, 960vs.

X-ray diffraction analysis of complexes **I** and **II** was performed on a Bruker SMART-1000 CCD diffractometer. For **I**, the data were collected in sets of 606, 435, and 230 scans at φ = 0°, 90°, and 180°, respectively (ω scan mode with a step of 0.3° and 30 s per frame). For **II**, sets of 909 scans were collected at φ = 0°, 90°, 180°, and 270°; (ω scan mode with a step of 0.2° and 10 s per frame). The crystal–detector distance was 45 mm.

The structures were solved by direct methods and refined by the full-matrix least-squares method in an anisotropic approximation for all nonhydrogen atoms. The positions of the hydrogen atoms were determined geometrically and refined in the rider model.

The data collection, processing and refinement of the unit cell parameters were performed using the SMART and SAINT-*Plus* programs [16]. All calculations for the determination and refinement of the structure were performed using the SHELXTL/PC program [17].

Selected crystallographic data and the results of the structure refinement are presented in Table 1, the coordinates of atoms and their equivalent isotropic thermal parameters are given in Table 2, and selected bond lengths and angles are listed in Table 3.

RESULTS AND DISCUSSION

Triarylstibine is known to be oxidized with hydrogen peroxide in the presence of arenesulfonic acids to yield μ-oxo-bis[(arenesulfonato)triarylantimony] [15]. We established that antimony compounds of this type can be obtained in a high yield via the reaction of triphenylstibine with tri-*p*-tolylbismuth bis(arenesulfonates) in ether in the presence of air moisture:

$$2Ph_3Sb + 2p\text{-}Tol_3Bi(OSO_2Ar)_2 + H_2O$$

$$\longrightarrow (Ph_3SbOSO_2Ar)_2O + 2p\text{-}Tol_2BiOSO_2Ar$$

$$Ar = C_6H_4Me\text{-}4\ (\mathbf{I}),\ C_6H_3Me_2\text{-}2,5\ (\mathbf{II}).$$

Table 1. Crystallographic parameters and summary of data collection and refinement for the structures of μ-oxo-bis[(4-methylbenzenesulfonato)triphenylantimony] (**I**) and μ-oxo-bis[2,5-dimethylbenzenesulfonato)triphenylantimony] (**II**)

Parameter	Value	
	I	**II**
Empirical formula	$C_{50}H_{44}O_7S_2Sb_2$	$C_{52}H_{48}O_7S_2Sb_2$
M	1064.47	1092.52
T	294(2) K	295(2) K
Wave length	MoK_α (0.71073 Å)	MoK_α (0.71073 Å)
Space group	$P\bar{1}$	$P2_1/n$
a, Å	10.060(3)	14.243(2)
b, Å	13.317(4)	9.485(1)
c, Å	19.401(6)	17.554(2)
α, deg	106.882(6)	90
β, deg	97.107(7)	102.757(2)
γ, deg	106.536(5)	90
V, Å^3	2324(1)	2313.0(4)
Z	2	2
ρ(calcd), g/cm^3	1.521	1.569
μ, mm^{-1}	1.302	1.311
F(000)	1068	1100
Crystal form	Sphere (0.17 mm in diameter)	Plate (0.043 × 0.15 × 0.25 mm)
Range of data collection for θ, deg	1.69–23.31	1.67–25.02
Reflection index ranges	$-11 \le h \le 11, -14 \le k \le 14, -15 \le l \le 21$	$-16 \le h \le 16, -11 \le k \le 9, -20 \le l \le 20$
Measured reflections	10130	11785
Independent reflections	6601 (R_{int} = 0.047)	4077 (R_{int} = 0.0616)
Reflections with $I > 2\sigma(I)$	3896	2670
Refinement method	Full-matrix least-squares method for F^2	Full-matrix least-squares method for F^2
Number of refined parameters	552	288
GOOF	0.873	0.816
R-factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0474$, $wR_2 = 0.0985$	$R_1 = 0.0342$, $wR_2 = 0.0613$
R-factors for all reflections	$R_1 = 0.0940$, $wR_2 = 0.01112$	$R_1 = 0.623$, $wR_2 = 0.0669$
Residual electron density (min/max), e/Å^3	–0.947/1.354 (near Sb atoms)	–481/0.433

X-ray diffraction analysis of compounds **I** and **II** revealed that they are binuclear Sb(V) complexes, in which two Ph_3SbOSO_2Ar fragments are joined via a bridged oxygen atom (Figs. 1, 2). In complex **I**, the Sb(1)O(1)Sb(2) angle is equal to 138.5°, while in **II**, this angle is close to 180° (bridged oxygen atom is located in the inversion center of the molecule).

In complexes **I** and **II**, the Sb atoms have slightly distorted trigonal bipyramidal coordination. The equatorial CSbC angles lie in the 115.1(2)°–122.6(2)° and 116.6(1)°–124.2(1)° ranges, and the axial OSbO angles are equal to 171.4(1)°, 174.0(2)°, and 171.64(5)°, respectively.

The Sb–C(Ph) bond lengths in these complexes lie in the interval of 2.074(5)–2.123(5) Å which corresponds to the normal Sb–C(Ph) distances in organic antimony(V) compounds. The Sb–O_{term} distances in **I** and **II** are equal to 2.237(4), 2.246(4), and 2.238(2) Å, respectively, which is close to analogous Sb–O distances (2.258(5) Å) in μ-oxo-bis[2,5-dimethylbenzenesulfonato)tri-*p*-tolylantimony] [15]. The Sb–O_{br} bond lengths in compound **I** are equal to 1.979(4) and

Table 2. Coordinates of atoms (×10^4) and their equivalent isotropic thermal parameters (×10^3) in structures **I** and **II**

Atom	x	y	z	U_{eq}, Å^2	Atom	x	y	z	U_{eq}, Å^2
		I					**I**		
Sb(1)	1004.0(4)	2559.3(3)	3425.5(2)	36(1)	C(71)	3091(6)	1110(4)	5077(3)	47(2)
Sb(2)	–679(1)	3236(1)	1899(1)	40(1)	C(72)	4475(6)	1131(4)	5280(3)	48(2)
S(1)	2312(2)	792(1)	4140(1)	50(1)	C(73)	5057(7)	1342(5)	6006(3)	58(2)
S(2)	–1794(2)	2856(1)	0(1)	50(1)	C(74)	4348(7)	1549(5)	6549(3)	64(2)
O(1)	156(4)	3393(3)	2912(2)	48(1)	C(75)	2928(8)	1492(6)	6336(4)	74(2)
O(2)	2078(4)	1854(3)	4151(2)	52(1)	C(76)	2294(6)	1267(5)	5606(3)	59(2)
O(3)	3332(4)	597(4)	3712(2)	75(1)	C(77)	5013(9)	1787(7)	7345(4)	121(4)
O(4)	988(5)	–99(3)	3952(2)	68(2)	C(81)	–3080(6)	3393(5)	–329(3)	47(2)
O(5)	–1765(4)	3170(3)	795(2)	56(1)	C(82)	–4465(7)	2829(6)	–424(4)	81(3)
O(6)	–2360(4)	1664(3)	–344(2)	67(2)	C(83)	–5491(7)	3257(6)	–698(4)	100(3)
O(7)	–467(4)	3402(4)	–142(3)	84(2)	C(84)	–5087(7)	4152(6)	–890(4)	81(3)
C(11)	3042(6)	3751(4)	3677(3)	42(2)	C(85)	–3678(8)	4701(7)	–785(4)	102(3)
C(12)	3145(6)	4826(5)	3703(3)	59(2)	C(86)	–2668(7)	4319(6)	–504(4)	86(2)
C(13)	4476(7)	5632(6)	3839(4)	87(3)	C(87)	–6210(8)	4540(7)	–1231(5)	139(4)
C(14)	5669(8)	5351(7)	3953(5)	110(4)			**II**		
C(15)	5580(8)	4287(7)	3893(5)	100(3)	Sb	4778.2(1)	3980.1(2)	908.3(1)	31.09(6)
C(16)	4262(6)	3482(5)	3770(4)	72(2)	S	4781.4(6)	2458(1)	2686.4(5)	44.4(3)
C(21)	404(6)	1043(5)	2573(3)	52(2)	O(1)	5000	5000	0	44(1)
C(22)	1379(6)	687(5)	2207(3)	59(2)	O(2)	4306(1)	2757(2)	1848(1)	41(1)
C(23)	916(7)	–342(5)	1645(3)	58(2)	O(3)	5804(2)	2670(3)	2816(1)	59(1)
C(24)	–450(7)	–1012(5)	1459(3)	62(2)	O(4)	4463(2)	1118(3)	2908(1)	66(1)
C(25)	–1411(7)	–689(5)	1840(4)	71(2)	C(1)	4311(2)	3792(4)	3217(2)	37(1)
C(26)	–990(6)	324(5)	2399(3)	61(2)	C(2)	3322(2)	3853(4)	3188(2)	42(1)
C(31)	–340(5)	2647(4)	4186(3)	37(2)	C(3)	3025(2)	4948(4)	3599(2)	56(1)
C(32)	–850(6)	1775(5)	4420(3)	55(2)	C(4)	3660(3)	5939(4)	4014(2)	60(1)
C(33)	–1748(7)	1824(5)	4913(4)	75(2)	C(5)	4636(2)	5848(4)	4045(2)	49(1)
C(34)	–2116(7)	2773(6)	5141(4)	71(2)	C(6)	4954(2)	4756(4)	3637(2)	42(1)
C(35)	–1624(6)	3640(5)	4876(3)	55(2)	C(7)	2588(2)	2847(4)	2756(2)	63(1)
C(36)	–760(6)	3557(5)	4391(3)	46(2)	C(8)	5324(3)	6912(4)	4478(2)	77(2)
C(41)	–330(6)	4953(4)	2228(3)	41(2)	C(11)	5625(2)	2237(3)	740(2)	35(1)
C(42)	98(7)	5520(5)	1765(4)	59(2)	C(12)	6326(2)	2464(4)	319(2)	49(1)
C(43)	405(7)	6685(5)	1998(4)	77(3)	C(13)	6899(2)	1366(4)	178(2)	63(1)
C(44)	226(8)	7211(6)	2667(4)	89(3)	C(14)	6785(3)	64(4)	445(2)	58(1)
C(45)	–180(8)	6656(6)	3116(4)	90(3)	C(15)	6085(3)	–179(4)	861(2)	62(1)
C(46)	–525(7)	5488(5)	2897(3)	74(2)	C(16)	5508(2)	907(4)	1009(2)	50(1)
C(51)	886(6)	2707(5)	1422(3)	50(2)	C(21)	5408(2)	5535(4)	1716(2)	36(1)
C(52)	570(7)	1810(6)	788(4)	84(3)	C(22)	6377(2)	5453(4)	2091(2)	51(1)
C(53)	1620(8)	1442(6)	540(4)	109(3)	C(23)	6799(3)	6529(5)	2567(2)	69(2)
C(54)	2999(8)	1991(7)	899(4)	123(3)	C(24)	6259(3)	7660(5)	2696(2)	70(1)
C(55)	3331(7)	2884(7)	1511(4)	100(3)	C(25)	5296(3)	7757(4)	2344(2)	64(1)
C(56)	2268(6)	3258(5)	1776(3)	64(2)	C(26)	4870(2)	6686(4)	1843(2)	45(1)
C(61)	–2646(6)	2061(5)	1832(3)	52(2)	C(31)	3281(2)	4103(3)	485(2)	32(1)
C(62)	–3086(6)	2121(5)	2495(4)	66(2)	C(32)	2680(2)	4606(4)	935(2)	43(1)
C(63)	–4316(7)	1298(6)	2487(4)	84(2)	C(33)	1712(2)	4850(4)	610(2)	58(1)
C(64)	–5064(7)	421(6)	1816(5)	88(3)	C(34)	1363(2)	4527(4)	–167(2)	58(1)
C(65)	–4621(8)	394(6)	1182(4)	91(3)	C(35)	1953(2)	3998(4)	–617(2)	52(1)
C(66)	–3418(7)	1228(5)	1191(4)	62(2)	C(36)	2913(2)	3780(4)	–294(2)	42(1)

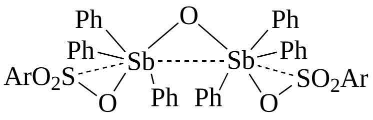
Table 3. Selected bond lengths and angles in the structures of μ-oxo-bis[(4-methylbenzenesulfonato)triphenylantimony] (**I**) and μ-oxo-bis[(2,5-dimethylbenzenesulfonato)triphenylantimony] (**II**)

Bond	*d*, Å	Angle	ω, deg
		I	
Sb(1)–Sb(2)	3.690(1)	Sb(2)O(1)Sb(1)	138.5(2)
Sb(1)–O(1)	1.979(4)	O(1)Sb(1)C(21)	99.6(2)
Sb(1)–C(21)	2.074(5)	O(1)Sb(1)C(11)	91.9(2)
Sb(1)–C(11)	2.100(5)	C(21)Sb(1)C(11)	121.8(2)
Sb(1)–C(31)	2.123(5)	O(1)Sb(1)C(31)	92.5(2)
Sb(1)–O(2)	2.237(4)	C(21)Sb(1)C(31)	115.1(2)
Sb(2)–O(1)	1.966(4)	C(11)Sb(1)C(31)	121.2(2)
Sb(2)–C(41)	2.098(5)	O(1)Sb(1)O(2)	171.4(1)
Sb(2)–C(61)	2.106(6)	C(21)Sb(1)O(2)	89.1(2)
Sb(2)–C(51)	2.110(6)	C(11)Sb(1)O(2)	83.4(2)
Sb(2)–O(5)	2.246(4)	C(31)Sb(1)O(2)	83.9(2)
S(1)–O(4)	1.430(4)	O(1)Sb(2)C(41)	90.5(2)
S(1)–O(3)	1.431(5)	O(1)Sb(2)C(61)	95.0(2)
S(1)–O(2)	1.493(4)	C(41)Sb(2)C(61)	122.6(2)
S(1)–C(71)	1.764(6)	O(1)Sb(2)C(51)	95.5(2)
S(2)–O(7)	1.428(5)	C(41)Sb(2)C(51)	116.1(2)
S(2)–O(6)	1.438(4)	C(61)Sb(2)C(51)	120.2(2)
S(2)–O(5)	1.472(4)	O(1)Sb(2)O(5)	174.0(2)
S(2)–C(81)	1.783(6)	C(41)Sb(2)O(5)	85.4(2)
		II	
Sb–O(1)	1.9494(3)	O(1)SbC(31)	91.04(8)
Sb–C(31)	2.101(3)	O(1)SbC(21)	94.67(8)
Sb–C(21)	2.105(3)	C(31)SbC(21)	116.6(1)
Sb–C(11)	2.106(3)	O(1)SbC(11)	94.2(1)
Sb–O(2)	2.238(2)	C(31)SbC(11)	124.2(1)
S–O(4)	1.432(3)	C(21)SbC(11)	118.2(1)
S–O(3)	1.437(2)	O(1)SbO(2)	171.64(5)
S–O(2)	1.505(2)	C(31)SbO(2)	80.97(9)
S–O(1)	1.788(3)	C(21)SbO(2)	91.1(1)

1.966(4) Å and coincide with analogous distances in other bent structures [5], but they are longer than those in complexes with linear structures [15]. In compound **II**, the Sb–O_{br} distances are equal to 1.949(3) Å.

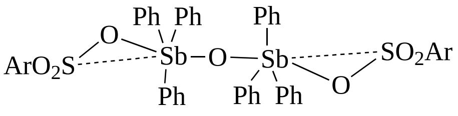
In μ-oxo-bis[(2-hydroxyethanesulfonato)triphenylantimony], the SbOSb angle is equal to 180° [4], while in $(Ph_3SbOSO_2Ph)_2O$ and $(Ph_3SbOSO_2CF_3)_2O$, analogous angles are equal to 139.8° and 136.5°, respectively [5]. The authors of [5] suggested that this difference in SbOSb angles is due to the effect of crystal packing. In complex **I**, the SbOSb angle (138.5°) slightly differs from the latter two values, while in **II**, it is close to 180°. The molecule of μ-oxo-bis[(2,5-dimethylbenzenesulfonato)tri-*p*-tolylantimony] also has linear structure [15]. One can conclude that neither the electron-accepting properties of arenesulfonate substituents nor the methyl substituents in aryl ligands at the antimony atom affect the SbOSb angle. The value of the SbOSb angle seems to be affected not only by the crystal packing effect, but also by steric factors, namely, the size of organic radical at the sulfur atom of the sulfonate fragment. However, unambiguous conclusion cannot be drawn on the basis of data available at present.

In bridged antimony compounds considered, the bent geometry of molecules suggests that its fragments approach one another such that they can interact and, consequently, decrease the total energy of the system. In this case, the nonvalent Sb··Sb interaction seems to be most probable, particularly because coordinatively unsaturated sphere of the Sb atom allows for its additional coordination [18]. Indeed, in compound **I**, the Sb··Sb distance is equal to 3.690(1) Å that is less than the twice van der Waals radius of antimony atom (4.40 Å) but greater than its twice covalent radius (2.82 Å) [19]. This fact points to an interaction between the antimony atoms in V-shape molecules of bridged antimony aryl compounds. In the molecules of the complexes synthesized, the intramolecular contacts were also observed: Sb(1)··S(1) 3.521(2) Å, Sb(2)··S(2) 3.559(2) Å in **I** and Sb··S 3.438(1) Å in **II** that are noticeably shorter than the sum of the van der Waals radii of antimony and sulfur atoms (4.05 Å [19]). One can suggest that the S··Sb··Sb··S interactions should ensure the saturation of the coordination sphere of each Sb atom in complex **I**:



(**I**)

In linear molecule of complex **II**, the absence of contact Sb··Sb is compensated by the sulfur atom of 2,5-dimethylbenzenesulfonate ligand approaching the antimony atom (the Sb··S distance is equal to 3.438(1) Å).



(**II**)

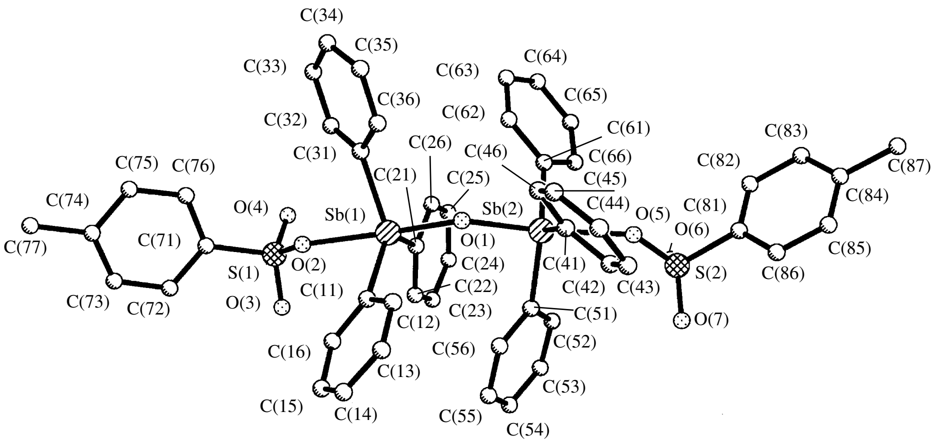


Fig. 1. The structure of complex **I**.

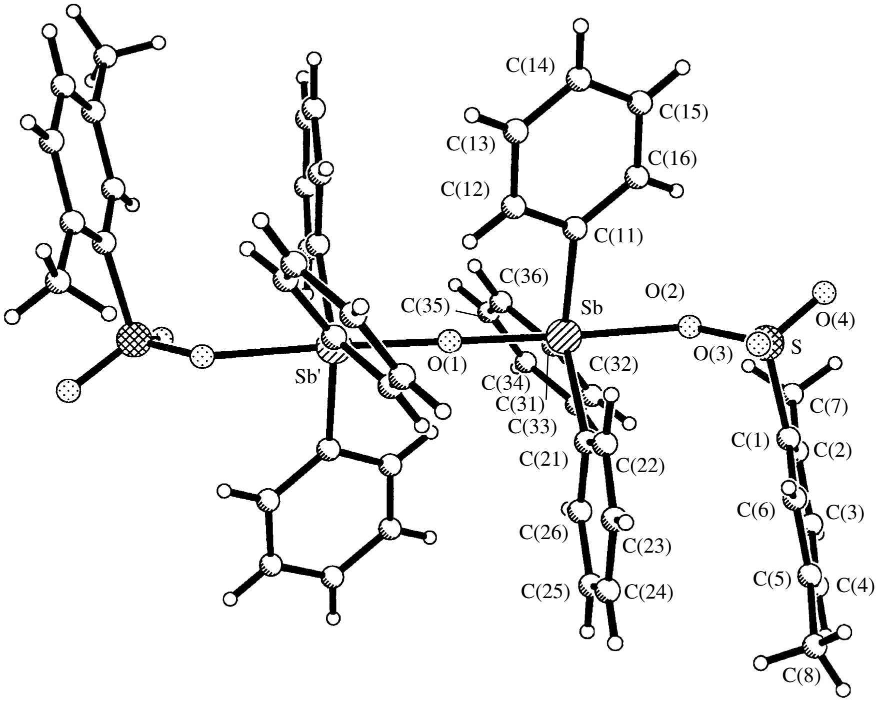


Fig. 2. The structure of complex **II**.

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