ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2023, Vol. 49, No. 1, pp. 47–55. © Pleiades Publishing, Ltd., 2023.

Oxidation of Tris(5-bromo-2-methoxyphenyl)antimony by *tert*-Butyl Hydroperoxide in the Presence of Compounds Containing an Active Hydrogen Atom

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Received November 11, 2022; revised November 15, 2022; accepted November 19, 2022

Abstract—The oxidation of tris(5-bromo-2-methoxyphenyl)antimony with *tert*-butyl hydroperoxide in diethyl ether in the presence of water, benzoic acid, 2,6-dihydroxybenzoic acid, or 2-chloro-4-fluorophenol gives tris(5-bromo-2-methoxyphenyl)antimony oxide (**I**), tris(5-bromo-2-methoxyphenyl)antimony dibenzoate (**II**), **μ**-oxo[hexakis(5-bromo-2-methoxyphenyl)-bis(2,6-dihydroxybenzoato)diantimony] (**III**), or **μ**-oxo[hexakis(5-bromo-2-methoxyphenyl)-bis(2-chloro-4-fluorophenoxo)diantimony] (**IV**), respectively. The products were identified by X-ray diffraction analysis (CCDC nos. 2070383 (**I**), 2074511 (**II**), 1970910 (**III**), 2064392 (**IV**). According to the X-ray diffraction data, the crystal of chloroform solvate **I** consists of centrosymmetric binuclear molecules containing an Sb_2O_2 ring with a tetragonal coordination of the antimony atoms (the Sb—O bond lengths are 1.961(4) and 2.041(5) Å; the Sb—C distances are 2.114(6)—2.153(6) Å). In benzene solvate **II**, the antimony atoms have a distorted trigonal-bipyramidal coordination, with carboxylate oxygen atoms being in the axial positions (Sb–O, 2.075(4); 2.105(4) Å); the carbonyl oxygen atoms are coordinated to the central metal atom (Sb···O=C, 3.023(6); 3.077(8) Å), with the Sb—C bond lengths (2.104(5)—2.112(5) Å) being markedly shorter than those in **I**. The ranges of variation of the Sb—C bond lengths in the virtually linear binuclear molecule of acetonitrile solvate **III** (SbOSb angle of 178.05(18)°) are 2.101(5)–2.106(5) and 2.100(5)–2.104(5) Å. The bond lengths between the antimony atoms and the bridging oxygen atom (1.925(4); 1.936(4) Å) are shorter than the sum of the Sb and O covalent radii and than the distances between the Sb atom and the terminal carboxyl ligand (Sb–O, 2.263(4); 2.214(4) Å). The carbonyl oxygens are coordinated to the central metal atom (Sb···O=C, 3.484(8); 3.512(9) Å) to a lesser extent than those in **II** The crystal of benzene solvate **IV** has two types of crystallographically independent angular molecules (the SbOSb angles are 163.75(18)° and 164.27(19)°); the difference between the $Sb—O_{bridge}$ (1.939(11)—1.981(13) Å) and $Sb—O_{term}$ (2.096(11)—2.208(11) Å) bond lengths is less pronounced that that in **III**.

Keywords: oxidation, tris(5-bromo-2-methoxyphenyl)antimony, *tert*-butyl hydroperoxide, water, benzoic acid, 2,6-dihydroxybenzoic acid, 2-chloro-4-fluorophenol, structure, X-ray diffraction analysis

DOI: 10.1134/S1070328422700312

Triaryl derivatives of antimony are represented by a broad range of compounds with one substituent in the aryl ligands [1, 2]. Compounds of this type with two or more substituents are less known. Among them, note tris(5-bromo-2-methoxyphenyl)antimony, which was synthesized in 2011 [3, 4]. Using oxidative addition reactions, this parent compound was converted to a number of triarylantimony dicarboxylates on treatment with carboxylic acids in the presence of an oxidant [5–9]. Tris(5-bromo-2-methoxyphenyl)antimony reacts with arenesulfonic acids in a similar way [10]; however, reactions of this type with weaker acids have not been reported so far.

In this study, we demonstrated that the oxidation of tris(5-bromo-2-methoxyphenyl)antimony with tert-butyl hydroperoxide in diethyl ether in the presence of water, benzoic acid, 2,6-dihydroxybenzoic acid, or 2-chloro-4-fluorophenol affords tris(5-bromo-2-methoxyphenyl)antimony oxide (**I**), tris(5-bromo-2-methoxyphenyl)antimony dibenzoate (**II**), **μ**-oxo-[hexakis(5-bromo-2-methoxyphenyl)-bis(2,6-dihydroxybenzoato)diantimony] (**III**), or **μ**-oxo[hexakis(5-bromo-2-methoxyphenyl)-bis(2-chloro-4-fluorophenoxy)diantimony] (**IV**), respectively. The structures of the products were determined by X-ray diffraction.

EXPERIMENTAL

Synthesis of the tris(5-bromo-2-methoxyphenyl)antimony oxide chloroform solvate (I). A mixture of tris(5-bromo-2-methoxyphenyl)antimony benzene solvate (152 mg, 0.2 mmol) [4] and a 70% aqueous solution of *tert*-butyl hydroperoxide (26 mg, 0.2 mmol) in diethyl ether (20 mL) was kept for 18 h at room temperature. The solvent was removed, and the residue was recrystallized from chloroform. The yield of the chloroform solvate of complex **I** was 140 mg (86%) (T_{dec} = 254°C).

For $C_{42}H_{38}O_8Cl_6Br_6Sb_2$

Anal. calcd., %	C, 30.92	H, 2.33
Found, %	C, 30.76	H, 2.48

IR (ν, cm^{-1}): 3055, 2995, 2933, 2835, 1566, 1525, 1496, 1469, 1435, 1375, 1284, 1265, 1249, 1207, 1178, 1143, 1091, 1051, 1018, 960, 894, 885, 877, 846, 806, 752, 744, 721, 707, 665, 642, 617, 594, 520, 489, 441.

Synthesis of tris(5-bromo-2-methoxyphenyl)antimony dibenzoate benzene solvate (II). A mixture of tris(5-bromo-2-methoxyphenyl)antimony benzene solvate (152 mg, 0.2 mmol) [4], benzoic acid (98 mg, 0.4 mmol), and a 70% aqueous solution of *tert*-butyl hydroperoxide (26 mg, 0.2 mmol) in diethyl ether (20 mL) was kept for 18 h at room temperature. The solvent was removed, and the residue was recrystallized from an *n*-octane–benzene mixture. The yield of the benzene solvate of complex **II** was 180 mg (90%) (T_{m} = 221°C).

IR (ν, cm^{-1}): 3101, 3086, 3068, 3032, 3001, 2935, 2841, 1645, 1627, 1600, 1573, 1473, 1448, 1438, 1377, 1319, 1298, 1282, 1269, 1253, 1172, 1147, 1122, 1091, 1068, 1047, 1014, 937, 887, 875, 839, 810, 715, 678, 621, 570, 522, 441, 428.

For $C_{41}H_{34}O_7Br_3Sb$

Anal. calcd., %	C, 49.20	H, 3.40
Found, %	C, 49.12	H, 3.49

Synthesis of μ-oxo-[hexakis(5-bromo-2-methoxyphenyl)-bis(2,6-dihydroxybenzoato)diantimony] acetonitrile solvate (III). A mixture of tris(5-bromo-2-methoxyphenyl)antimony benzene solvate (152 mg, 0.2 mmol) [4], 2,6-dihydroxybenzoic acid (31 mg, 0.2 mmol), and a 70% aqueous solution of *tert*-butyl hydroperoxide (26 mg, 0.2 mmol) in diethyl ether (20 mL) was kept for 18 h at room temperature. The solvent was removed, and the residue was recrystallized from an *n*-octane–acetonitrile mixture. The yield of the acetonitrile solvate of complex **III** was 140 mg (81%) (T_{m} = 185°C).

For $C_{58}H_{49}NO_{15}Br_6Sb_2$

Anal. calcd., %	C, 39.00	H, 2.67
Found, %	C, 38.96	H, 2.74

IR (ν, cm^{-1}): 3091, 3068, 3010, 2962, 2933, 2904, 2837, 2748, 1643, 1598, 1577, 1475, 1460, 1436, 1375, 1328, 1282, 1253, 1219, 1180, 1155, 1126, 1093, 1047, 1028, 1016, 883, 842, 817, 804, 777, 769, 736, 704, 673, 619, 603, 532, 470, 433.

Synthesis of μ-oxo-[hexakis(5-bromo-2-methoxyphenyl)-bis(2-chloro-4-fluorophenoxy)diantimony] benzene solvate (IV). A mixture of tris(5-bromo-2-methoxyphenyl)antimony (150 mg, 0.221 mmol), 2-chloro-4-fluorophenol (32 mg, 0.221 mmol) and a 70% aqueous solution of *tert*-butyl hydroperoxide (28 mg, 0.221 mmol) in diethyl ether (30 mL) was kept for 18 h at room temperature. After the removal of diethyl ether and the subsequent recrystallization of the solid product from an *n*-octane–benzene solvent mixture, compound **IV** was isolated as colorless crystals in 176 mg (96%) yield, T_{m} = 210°C.

For $C_{60}H_{48}O_9F_2Cl_2Br_6Sb_2$

Anal. calcd., %	C, 41.26	H, 2.75
Found, %	C, 41.11	H, 2.81

IR (ν, cm^{-1}): 3089, 3070, 3001, 2960, 2931, 2837, 1571, 1473, 1436, 1375, 1284, 1269, 1249, 1188, 1180, 1145, 1091, 1053, 1018, 906, 875, 846, 804, 783, 705, 680, 619, 576, 520, 491, 443, 428, 418.

The IR spectra of compounds **I**–**IV** were recorded on a Shimadzu IR Affinity-1S IR spectrometer for KBr pellets in the 4000–400 cm^{-1} range.

The X-ray diffraction study of the crystals of compounds **I**–**IV** was carried out on a D8 Quest Bruker diffractometer (MoK_α radiation, λ = 0,71073 Å, graphite monochromator) at 293 K. The data collection and editing and refinement of unit cell parameters were performed and the absorption corrections were applied using the SMART and SAINT-Plus software [11]. All calculations for structure determination and refinement were carried out using the SHELXL/PC [12] and OLEX2 programs [13]. The structures were solved by the direct methods and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and structure refinement details for **I**–**IV** are summarized in Table 1.

The full Tables of atom coordinates, bond lengths, and bond angles are deposited with the Cambridge Crystallographic Data Centre (nos. 2070383 (**I**), 2074511 (**II**), 1970910 (**III**), 2064392 (**IV**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Table 1. Crystallographic data and X-ray experiment and structure refinement details for **I**–**IV**

Parameter	Value			
	I	**II**	**III**	**IV**
M	815.20	1000.16	1722.94	3489.68
System	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1$
a, Å	12.07(2)	9.734(8)	12.259(8)	13.42(5)
b, Å	20.25(4)	13.863(15)	15.501(10)	17.31(6)
c, Å	13.00(2)	15.654(11)	32.54(3)	29.22(11)
α, deg	90.00	107.32(4)	90.00	90.00
β, deg	116.89(8)	90.46(3)	90.18(3)	91.7(2)
γ, deg	90.00	91.15(5)	90.00	90.00
V, Å^3	2833(9)	2016(3)	6184(8)	6784(43)
Z	4	2	4	2
ρ(calcd.), g/cm^3	1.911	1.648	1.851	1.708
μ, mm^{-1}	5.514	3.704	4.815	4.464
F(000)	1560.0	984.0	3344.0	3376.0
Crystal size, mm	0.16 × 0.13 × 0.1	0.27 × 0.27 × 0.14	0.4 × 0.36 ×0.35	0.65 × 0.27 ×0.04
Data collection range 2θ, deg	6.54–61.12	5.946–56.998	5.66–54.3	4.772–57.796
Ranges of reflection indices	$-17 \le h \le 17$, $-28 \le k \le 28$, $-16 \le l \le 18$	$-13 \le h \le 13$, $-18 \le k \le 18$, $-21 \le l \le 21$	$-13 \le h \le 15$, $-19 \le k \le 19$, $-41 \le l \le 41$	$-17 \le h \le 17$, $-22 \le k \le 23$, $-39 \le l \le 38$
Number of measured reflections	81303	102882	119381	253086
Number of unique reflections (R_{int})	8660 (0.1389)	10196 (0.0674)	13659 (0.0596)	33797 (0.1787)
Number of refinement variables	301	473	750	1439
GOOF	1.006	1.020	1.038	1.001
R-factors on $F^2>2\sigma(F^2)$	$R_1 = 0.0497$, $wR_2 = 0.0941$	$R_1 = 0.0611$, $wR_2 = 0.1537$	$R_1 = 0.0451$, $wR_2 = 0.1012$	$R_1 = 0.0654$, $wR_2 = 0.1090$
R-factors for all reflections	$R_1 = 0.1429$, $wR_2 = 0.1206$	$R_1 = 0.0885$, $wR_2 = 0.1724$	$R_1 = 0.0829$, $wR_2 = 0.1199$	$R_1 = 0.1941$, $wR_2 = 0.1381$
Residual electron density (max/min), e/Å^3	1.02/–1.54	2.88/–2.14	1.45/–1.62	0.94/–0.67

RESULTS AND DISCUSSION

Members of the Laboratory of the Chemistry of Organoelement Compounds at the South Ural State University (SUSU) have deposited more than 1000 organoelement, inorganic, and organic compounds with the Cambridge Crystallographic Data Centre [14]. Characteristic features of many antimony compounds were discussed in some publications of SUSU staff members [15–18] and foreign authors, e.g., [19–26]. Some studies addressed the oxidative addition reactions of tris(5-bromo-2-methoxyphenyl)antimony with simple carboxylic [3, 5–9] and sulfonic acids [10]; however, little was known about reactions of this type in the presence of water and other compounds containing an active hydrogen atom.

Previously, it was found that the oxidative addition of tris(5-bromo-2-methoxyphenyl)antimony to water in the presence of *tert*-butyl hydroperoxide in THF afforded the THF solvate of dimeric tris(5-bromo-2-methoxyphenyl)antimony oxide [27]. The replacement of the oxidant in a similar reaction performed in dioxane by hydrogen peroxide was accompanied by the formation of dioxane solvates of tetranuclear organoantimony derivatives [28].

We found that tris(5-bromo-2-methoxyphenyl)antimony reacts with water in the presence of *tert*-butyl hydroperoxide in diethyl ether to give triarylantimony oxide dimer, which was isolated from the reaction mixture after recrystallization from chloroform as the solvate $\{[(2\text{-MeO})(5\text{-Br})C_6H_3]_3SbO\}_2 \cdot CHCl_3$ (**I**):

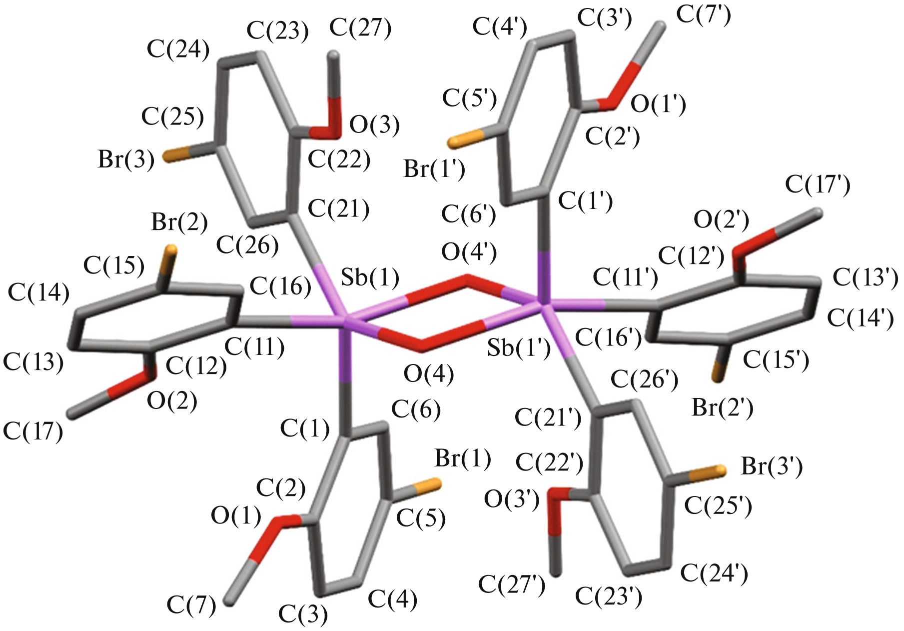

Fig. 1. Structure of the chloroform solvate of complex **I** (the hydrogen atoms and the chloroform molecule are omitted).

$$2[(2\text{-MeO})(5\text{-Br})C_6H_3]_3Sb + 2H_2O + 2t\text{-BuOOH} \rightarrow \{[(2\text{-MeO})(5\text{-Br})C_6H_3]_3SbO\}_2 + 2t\text{-BuOH}.$$

In the centrosymmetric binuclear molecules of solvate **I**, the antimony atoms have a distorted square pyramidal coordination, with the bridging oxygen atoms occupying the equatorial positions (Fig. 1).

The C(1)Sb(1)O(4) and C(1)Sb(1)O(4') angles are 93.10(18)° and 108.24(19)°; the C(1)Sb(1)C(21) and C(1)Sb(1)C(11) angles are somewhat greater (106.16(19)° and 111.6(2)°). The distance between the central metal atom and the axial carbon atom (2.114(6) Å) is shorter than similar distances to equatorial carbon atoms (2.147(6), 2.153(6) Å). The Sb_2O_2 moiety is planar, the O(4)Sb(1)O(4') angle is 77.65(19)°. The Sb(1)–O(4) and Sb(1)–O(4') bond lengths are 1.961(4) and 2.041(5) Å. The distance between the Sb(1) and Sb(1') atoms in the ring is 3.119(6) Å, which is significantly shorter than twice the van der Waals radius of antimony (4.4 Å [29]). The crystal of **I** contains short intramolecular contacts MeO···Sb (2.904(3); 3.056(5); 3.196(4) Å), which are comparable with the corresponding distances in the tris(5-bromo-2-methoxyphenyl)antimony molecule (2.985(1), 3.051(1), and 3.052(1) Å) [4]. There are no short contacts corresponding to strong intermolecular interactions in the crystal of **I**.

The replacement of water in a similar reaction by stronger benzoic acid resulted in $[(2\text{-MeO})(5\text{-Br})C_6H_3]_3Sb[OC(O)Ph]_2 \cdot PhH$ (**II**), which was isolated from the reaction mixture after recrystallization from benzene as a solvate in 78% yield.

$$[(2\text{-MeO})(5\text{-Br})C_6H_3]_3Sb + 2PhC(O)OH + t\text{-BuOOH} \rightarrow [(2\text{-MeO})(5\text{-Br})C_6H_3]_3Sb[OC(O)Ph]_2.$$

The antimony atoms in solvate **II** have trigonal-bipyramidal coordination, with the carboxylate oxygen atoms being located in the axial positions (Fig. 2). The axial angle is 174.53(14)°.

The sum of the CSbC bond angles in the equatorial plane of **II** is nearly 360° (359.8°). Like in other tris(5-bromo-2-methoxyphenyl)antimony dicarboxylates [5–9], two equatorial angles (127.5(3)° and 124.2(3)°) in **II** are greater than the ideal value (120°), while the third one is markedly smaller (108.1(2)°). Note that, as a rule, in the molecules of triarylantimony dicarboxylates [14], two equatorial angles are, conversely, smaller than the ideal value, and the third one is significantly greater. This distinction of **II** is attributable to the disruption of the *cis*-orientation of the carboxylate ligands relative to the SbC_3 group, which is typical of triarylantimony dicarboxylates. The angle between the carboxyl group planes is 45.22°. The antimony atom deviates from the equatorial plane by 0.053, the OSbC angles vary in the 83.55(19)°–91.19(19)° range. The Sb–O (2.075(4), 2.105(4) Å) and Sb–C bond lengths (2.104(5)–2.112(5) Å) are similar. The carboxylate ligands are additionally coordinated to antimony by a carbonyl oxygen atom; the Sb···O=C distances are 3.023(8) and 3.077(9) Å. In addition, molecule **II** contains short contacts Sb···OMe (3.075(8)–3.174(9) Å). In the crystal of **II**, there are weak intermolecular

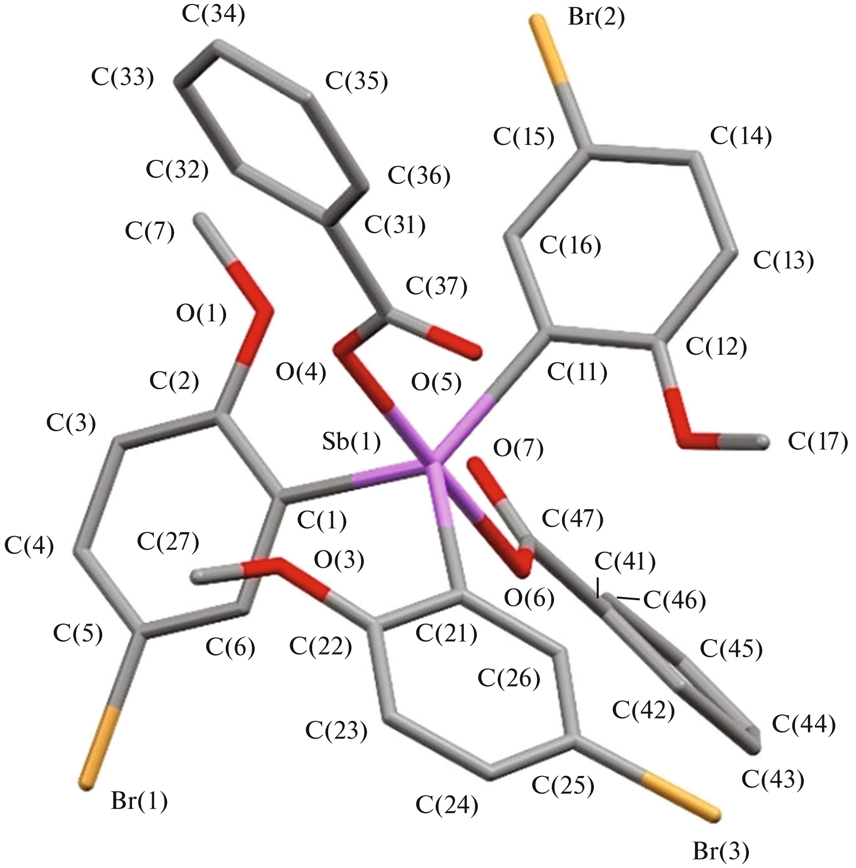

Fig. 2. Structure of the benzene solvate of complex **II** (the hydrogen atoms, disordered atoms, and the benzene molecule are omitted).

hydrogen bonds involving carboxylate oxygen atoms: $H_{Ar}\cdots O(=C)$ (2.54–2.67 Å).

The reaction of tris(5-bromo-2-methoxyphenyl)antimony with 2,6-dihydroxybenzoic acid (which is stronger than benzoic acid) carried out under similar conditions afforded a bridged binuclear antimony compound, which was isolated from the reaction mixture after recrystallization from acetonitrile as the solvate $\{[(2\text{-MeO})(5\text{-Br})C_6H_3]_3SbOC(O)C_6H_3(OH)_2\text{-}2,6]\}_2O\cdot MeCN$ (**III**). The yield of the target product markedly increased at an equimolar ratio of the starting compounds.

$$2\left[(2\text{-MeO})(5\text{-Br})C_6H_3\right]_3Sb + 2\ 2,6\text{-}(OH)_2C_6H_3C(O)OH + 2t\text{-BuOOH}$$
$$\rightarrow \left\{\left[(2\text{-MeO})(5\text{-Br})C_6H_3\right]_3SbOC(O)C_6H_3(OH)_2\text{-}2,6\right]\right\}_2O.$$

There are publications describing binuclear antimony compounds containing the Sb–O–Sb group, such as $[Ar_3SbOC(O)R]_2O$, with the carboxylate terminal ligands [18, 30–34]. According to X-ray diffraction data, the SbOSb angle in **III** is 178.05(18)° (Fig. 3).

The sums of the CSbC angles in the equatorial planes of **III** are 357.7(2)° and 359.6(2)°. The Sb atoms deviate from the $[C_3]$ plane by 0.185 and 0.073 Å, respectively, towards the bridging carbon atom. In **III**, the equatorial Sb–C bond lengths are virtually equal (2.101(5), 2.102(5), 2.106(5) and 2.100(5), 2.103(5), 2.104(5) Å), the Sb–O bond lengths with the bridged oxygen atom (1.925(4), 1.936(4) Å) are shorter than analogous bonds with terminal carboxylate ligands (2.263(4), 2.214(4) Å). The intramolecular Sb···O distances to the carbonyl oxygen atom are 3.512(4) and 3.484(4) Å. Note that in μ-oxo-bis(trifluoroacetatotriphenylantimony) [35] and μ-oxo-bis(2-chloronicotinatotriphenylantimony) [30] with angular Sb–O–Sb group and in μ-oxo-bis(chloroacetatotriphenylantimony) with linear Sb–O–Sb group [31], the average Sb–O bond

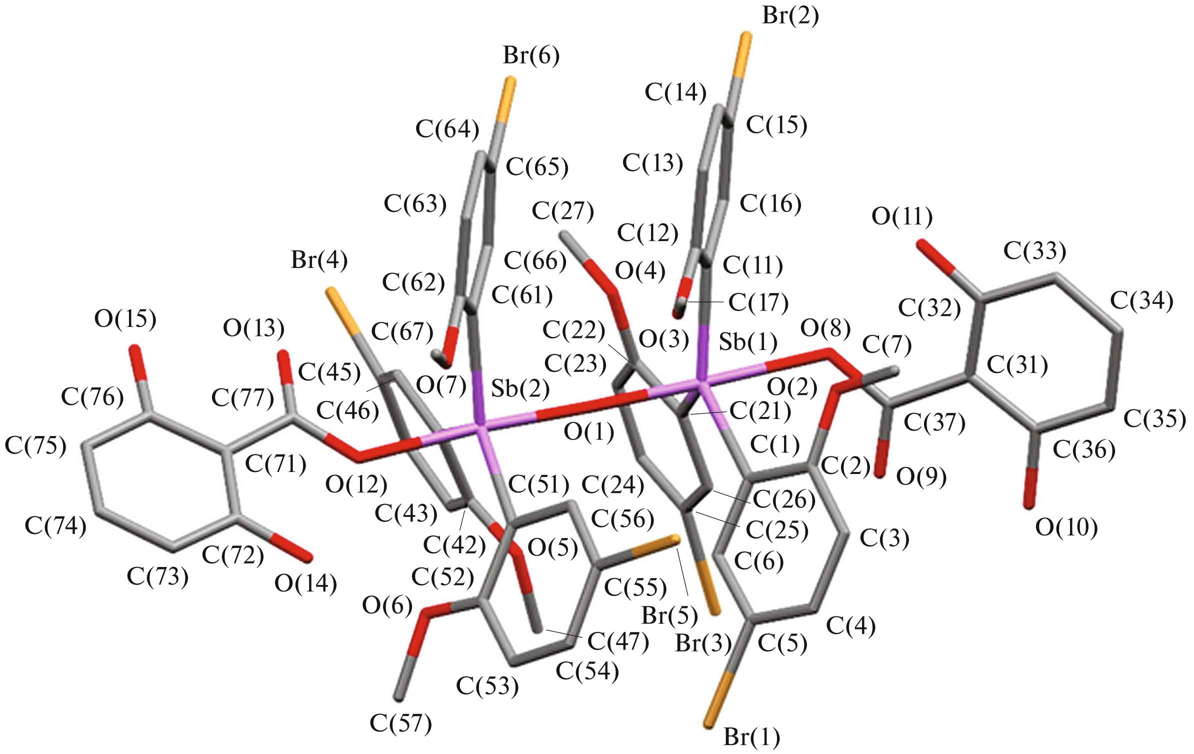

Fig. 3. Structure of the acetonitrile solvate of complex **III** (the hydrogen atoms and the acetonitrile molecule are omitted).

lengths are markedly longer (1.974(5), 2.239(5) Å; 1.955(5), 2.219(5) Å, and 1.950(4), 2.197(4) Å, respectively).

A similar reaction involving 2-chloro-4-fluorophenol was accompanied by the formation of a bridged antimony compound, which was isolated from the reaction mixture after recrystallization from an *n*-octane–benzene solvent mixture as the solvate $\{[(2\text{-MeO})(5\text{-Br})C_6H_3]_3SbOC_6H_3(Cl\text{-}2)(F\text{-}4)]\}_2O\cdot PhH$ (**IV**).

$$2[(2\text{-MeO})(5\text{-Br})C_6H_3]_3Sb + 2C_6H_3(Cl\text{-}2)(F\text{-}4)OH + 2t\text{-BuOOH}$$
$$\rightarrow \{[(2\text{-MeO})(5\text{-Br})C_6H_3]_3SbOC_6H_3(Cl\text{-}2)(F\text{-}4)]\}_2O.$$

According to X-ray diffraction data, the crystal of compound **IV** contains two types of crystallographically independent molecules **A** and **B** with slightly differing geometrical parameters (Fig. 4). The Sb coordination polyhedra are trigonal bipyramids in which the oxygen atoms of the aroxide ligands and the bridging oxygen atom occupy axial positions. The two benzene molecules are disordered over two positions with occupancies of 0.54/0.46 and 0.57/0.43.

In molecules **A** and **B** of complex **IV**, the SbOSb angles are 163.9(6)° and 164.1(6)°, respectively. Note that in the previously studied μ-oxo-bis(aroxytriarylantimony) structures, this angle varied in the 138.0°–177.7° range [14]. The sums of the CSbC angles in the equatorial plane for molecules **A** and **B** are 357.2(6)°, 360.1(6)° and 359.9(6)°, 357.0(6)°. The Sb atoms deviate from the $[C_3]$ plane towards the bridging oxygen atom by 0.001, 0.208 Å (**A**) and 0.022, 0.216 Å (**B**). In molecules **A** and **B**, the equatorial Sb–C bond lengths are almost equal, but at each antimony atom, one Sb–C bond is significantly shorter than the other two bonds (2.147(16), 2.144(16), and 2.105(16) Å at Sb(1) and 2.165(15), 2.144(15), and 2.107(15) Å at Sb(2) in (**A**); 2.188(14), 2.165(15), and 2.132(15) Å at Sb(3) and 2.169(15), 2.165(15), and 2.105(14) Å at Sb(4) in (**B**)). The Sb–O lengths to the bridging oxygen atom (1.946(11), 1.993(11) Å (**A**); 1.962(11), 1.937(11) Å (**B**)) are shorter than similar bonds with terminal aroxide ligands (2.208(11), 2.122(12) Å (**A**), 2.084(12), and 2.184(11) Å (**B**)); this is also inherent in the μ-oxo-bis(aroxotriarylantimony) molecules structurally characterized earlier [14]. The difference between the $Sb-O_{bridge}$ and $Sb-O_{term}$ bond lengths is less pronounced than for complex **III**. The formation

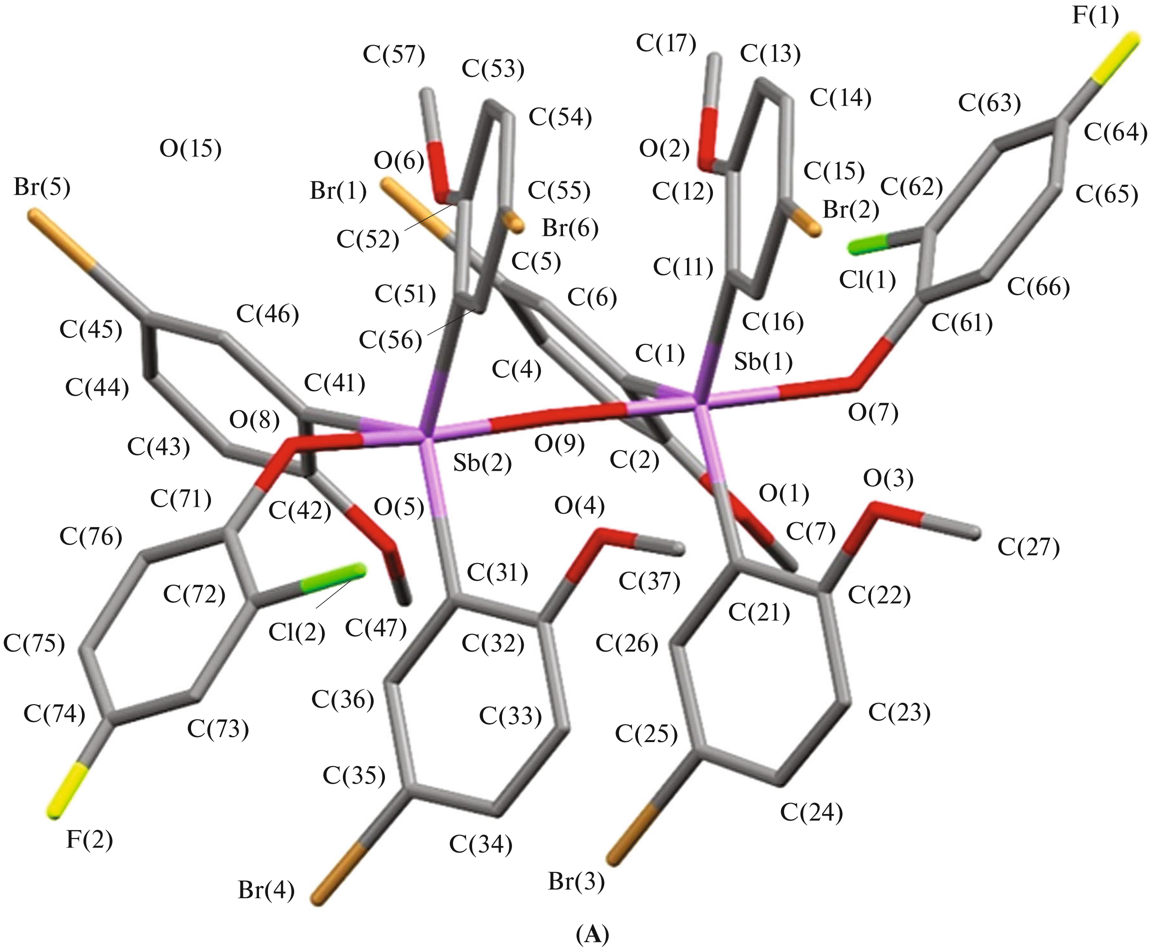

Fig. 4. Structure of the benzene solvate of complex **IV** (the hydrogen atoms, molecules **B**, and benzene molecules are omitted).

of the 3D network in the crystal of **IV** is due to the presence of weak intermolecular hydrogen bonds involving bromine atoms: $H_{Me}\cdots Br$ (3.00 Å), $H_{PhH}\cdots Br$ (2.62 Å). Also, CH···π-contacts are present in the crystal.

The IR spectra of compounds **I**–**IV** exhibit medium-intensity absorption bands for the Sb–C stretching modes at 441, 441, 433, and 428 cm^{-1}, respectively. The stretching modes of the carbon skeleton of aromatic moieties give rise to bands at 1566, 1469, and 1435 (**I**); 1573, 1473, and 1438 (**II**); 1577, 1475, and 1436 (**III**); and 1571, 1473, and 1436 cm^{-1} (**IV**). The medium-intensity bands at 3055 (**I**), 3068 (**II**), 3068 (**III**), and 3089 (**IV**) cm^{-1} correspond to the C_{Ar}–H stretching vibrations, while strong bands at 806, 752, and 744 (**I**); 810, 715, and 678 (**II**); 817, 804, and 704 (**III**); 804, 783, and 705 cm^{-1} (**IV**) refer to the out-of-plane bending vibrations of the C_{Ar}–H bonds. The stretching modes of the methyl groups occur in the IR spectra of **I**–**IV** at 2933, 2935, 2933, and 2931 cm^{-1} (asymmetric modes) and at 2835, 2841, 2837, and 2837 cm^{-1} (symmetric modes), respectively. The C_{Ar}–O–C_{Me} stretching modes are responsible for a pair of strong bands at 1051, 1018 (**I**); 1047, 1014 (**II**); 1047, 1016 (**III**); and 1053, 1018 (**IV**). The ν(C–Br) vibrations give rise to a strong band at 617 (**I**), 621 (**II**), 619 (**III**), and 619 (**IV**) cm^{-1}, while ν(C–F) mode is manifested at 1180 cm^{-1} (**IV**). The presence of the carbonyl group in **II** and **III** is evidenced by the strong C=O stretching bands at 1645 and 1643 cm^{-1}, respectively. The strong absorption bands corresponding to the ν(C_{Ar}–O) modes in the aryl (**I**–**IV**), carboxylate (**III**), and aroxide (**IV**) ligands occur at 1249 (**I**), 1253 (**II**), 1253 (**III**), and 1249 (**IV**) cm^{-1}. The ν(C–O) modes of the carboxyl group of compounds **II** and **III** are manifested at 1319 and 1282 cm^{-1}. The absence of absorption bands for free hydroxyl groups in the IR spectra indicates the formation of Sb–O bonds [36–38].

Thus, reactions of tris(5-bromo-2-methoxyphenyl)antimony with compounds containing an active hydrogen atom in the presence of *tert*-butyl hydroperoxide affords structurally different pentavalent antimony derivatives, which indicates that the nature of the acid influences the reaction pathway.

FUNDING

This work was supported by the Russian Foundation for Basic Research (project no. 20-33-90099).

CONFLICT OF INTERESTS

The authors declare that they have no conflicts of interest.

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Translated by Z. Svitanko