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Synthesis and Structural Features of Tris(5-bromo-2-methoxyphenyl)antimony Bis (cyclopropanecarboxylate)

V. V. Sharutin, O. K. Sharutina, V. S. Senchurin, and O. V. Chagarova

National Research Southern Ural State University, ul. Lenina 76, Chelyabinsk, 454080 Russia
e-mail: vvsharutin@rambler.ru

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Abstract—Reaction of tris(5-bromo-2-methoxyphenyl)antimony with cyclopropanecarboxylic acid in the presence of hydrogen peroxide (1:2:1 mol) results in tris(5-bromo-2-methoxyphenyl)antimony bis(cyclopropanecarboxylate) **I**. The structure of the resulting complex was proved by the XRD analysis.

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The coordination sphere of the antimony atom is known to be nonrigid. In the antimony(V) derivatives, whose ligands contain the heteroatoms with lone electron pairs the additional intra- and intermolecular *n*,*d*-interactions are possible [1–3].

Triarylantimony dicarboxylates are the examples of compounds that exhibit the non-valence interactions between the central atom and the carbonyl oxygen atom (Sb···O=C). The carboxylate ligands were found to be usually *cis*-oriented relative to the SbC_3 fragment. This leads to an increase in the CSbC angle in the equatorial plane from the contact side and to a distortion of the trigonal-bipyramidal coordination of the central atom [4].

We studied the reaction of tris(5-bromo-2-methoxyphenyl)antimony with cyclopropanecarboxylic acid in the presence of hydrogen peroxide giving rise to tris(5-bromo-2-me-toxyphenyl)antimony bis(cyclopropanecarboxylate) **I**. As might be expected, in the molecules of the structurally characterized reaction product the additional contacts between the methoxy groups and bromine atoms are possible along with the Sb···O=C interactions.

One of the most effective methods of triarylantimony dicarboxylates synthesis is the oxidative addition reactions [5, 6], which have been well studied for triphenyl- and tritolylantimony [7–13].

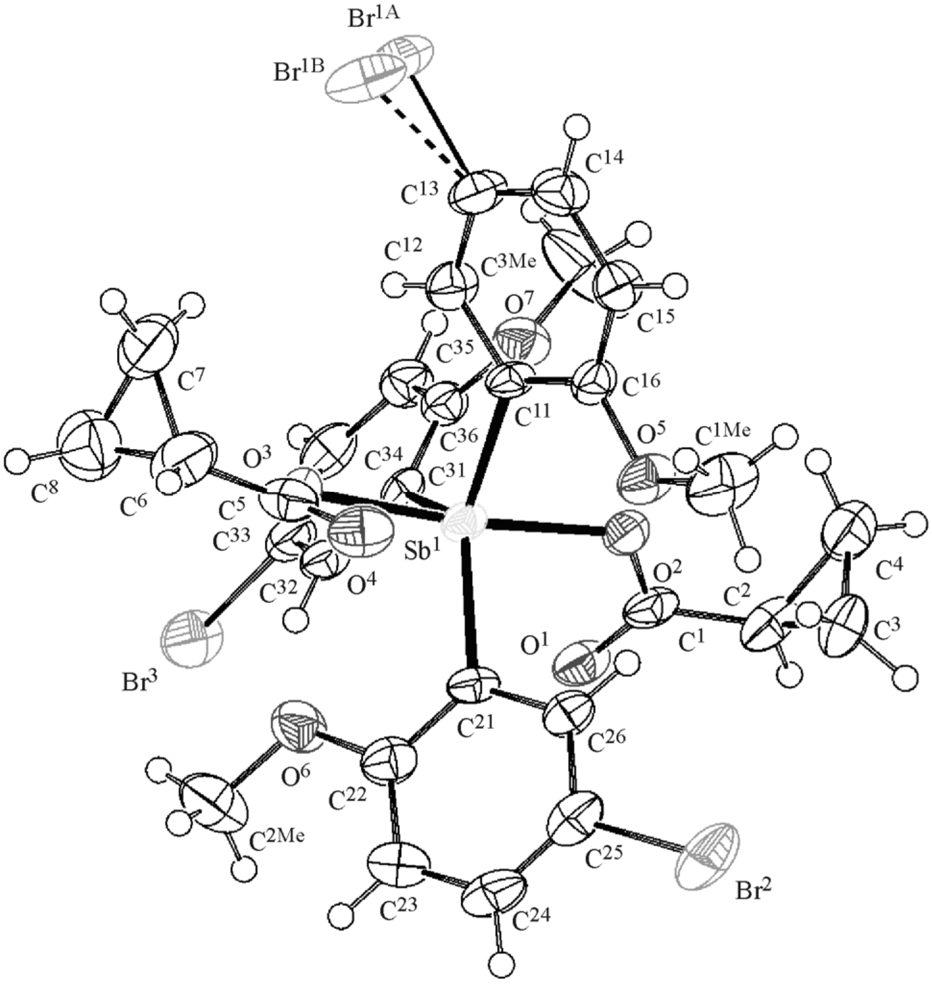
The reaction of tris(5-bromo-2-methoxyphenyl) antimony with cyclopropanecarboxylic acid in the presence of hydrogen peroxide proceeds by the usual route to form tris(5-bromo-2-methoxyphenyl)antimony bis(cyclopropanecarboxylate) in 91% yield.

Owing to the *n*-donor substituents in all five ligands of the molecule **I** surrounding the antimony atom, it is of interest to determine how the possibility of the non-valence intramolecular and intermolecular interactions is implemented in the crystal.

According to the XRD data, in the molecule of I the antimony atom has a distorted trigonal-bipyramidal coordination (see Fig.). The planes of the aryl rings have not “propeller” conformation relative to to the equatorial plane, which is energetically the most favorable, but are arranged in such a way that the torsion angles $O^2SbC^{11}C^{12}$, $O^2SbC^{21}C^{22}$, $O^2SbC^{31}C^{32}$ equal 125.62, –137.97 and 121.92°, respectively. In this case, the methoxy groups of aryl ligands C^{11}–C^{16} and C^{31}–C^{36} are oriented towards the atom O^2 and the ligand C^{21}–C^{26}, towards the atom O^3. The bromine atom Br^1 of one of the aryl ligands is disordered over two positions with a weight of 0.75/0.25.

The axial angle O^2SbO^3 is 173.59(17)°, the bond angles in the equatorial plane CSbC are 115.1(2), 120.8(2), and 124.1(2)° (Σ 360°). The carbon atoms of the aryl ligands and the antimony atom lie almost in the same plane. The angles between the axial and equatorial bonds $O^{2,3}SbC^{11,21,31}$ differ from the theoretical value of 90° [84.9(2)°–96.1 (2)°] (Table 1, 2).

The bond lengths Sb–$C^{11,21}$ are identical [2.133(5), 2.133(6) Å] and longer than the bond length Sb–C^{31}



General view of the molecule of **I** by the XRD-data.

[2.127(5) Å]. In the molecule of tris(5-bromo-2-methoxyphenyl)antimony the Sb–C distances are 2.1603(15), 2.1631(15) and 2.1569(16) Å [14]. The bond lengths Sb–$O^{2,3}$ are 2.079(4) and 2.125(4) Å. The first of them is shorter, and the second is commensurate with the length of the equatorial bonds Sb–C. In the triarylantimony dicarboxylate molecule the range of the average bond lengths Sb–O is 2.105–2.156 Å [4].

The carboxylate ligands in the molecule **I** are unsymmetrically coordinated to the antimony atom as in the other triarylantimony dicarboxylates: the distances Sb···$O^{1,4}$ are 3.076 and 2.953 Å (the average values of these distances in triarylantimony dicarboxylates are in the range of 2.664–3.219 Å [4]) . The dihedral angle between the planes of carboxy groups has an unusually large value of 123°; as a result the carbonyl oxygen atoms are placed opposite different equatorial angles: the O^1 atom is opposite the angle $C^{21}SbC^{31}$, the atom O^4 is opposite the angle $C^{11}SbC^{21}$. The angles CSbC in the equatorial plane vary in the range 120°±10° that is usual for the compounds of the general formula Ar_3SbX_2.

The similar unusual orientation of the carboxy groups was also observed in the molecules of triphenylantimony bis(trifluoroacetate) [15], bis(2-hydroxybenzoate) [16], and bis(3-niacinate) [9], where the values of the equatorial angles are also a little different.

Along with the intramolecular interactions Sb···O=C in the molecule **I** there are the Sb···OMe contacts [the distances Sb···$O^{5,6,7}$ are 3.192, 3.205, 3.067 Å, significantly shorter than the sum of van der Waals radii of the antimony and oxygen atoms (3.70 Å)]. A similar intramolecular coordination of the methoxy groups is observed in the molecule of tris(5-bromo-2-methoxyphenyl)antimony (Sb···O 2.985, 3.051, 3.052 Å [14]).

Obviously, the presence of the non-valence interactions Sb···OMe in the crystal of **I** causes the

Table 1. Crystallographic data and experimental parameters of structure **I**

Parameter	Value
Formula	$C_{29}H_{28}Br_3O_7Sb$
M	849.99
T, K	123
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	12.2430(3)
b, Å	16.5156(4)
c, Å	15.9076(4)
β, deg	105.876(2)
V, Å^3	3093.83(13)
Z	4
d_{calc}, g cm^{-3}	1.825
Radiation	CuK_α, λ 1.54184 Å
μ, mm^{-1}	11.979
F(000)	1656
Crystal size, mm	(0.117×0.102×0.075)
Theta range for data collection, deg	3.75–72.77
Index ranges	$-13 \le h \le 14$, $-18 \le k \le 19$, $-19 \le l \le 13$
Reflections collected	9615
Independent reflections	5867
R_{int}	0.0485
Refinement parameters	373
GOOF	1.013
R-Factors on $F^2 > 2\sigma(F^2)$	R_1 0.0537, wR_2 0.1291
R- Factors on all reflections	R_1 0.0665, wR_2 0.1412
Residual electron density (min/max), e Å^{-3}	–1.436/1.177

unusual orientation of the carboxylate groups and the aryl rings with respect to the equatorial plane.

In the carboxylate ligands the angles between the planes [C^3] and the carboxy groups are 91° and 93°. The carbonyl groups and the rings are *trans*-positioned with respect to the ordinary C–C bond.

According to the published data, the length of a single bond C–O in the carboxylic acids equals 1.293–1.308 Å, and the length of the double C=O bond is 1.214–1.229 Å [17]. The distance $C^1–O^1$ and $C^1–O^2$, $O^4–C^5$ and $C^5–O^3$ in the carboxylate groups are equal to 1.225(8) and 1.326(8) Å, 1.211(9) and 1.321(9) Å, respectively.

Table 2. The bond lengths (d) and bond angles (ω) in structure **I**

Bond	d, Å	Angle	ω, deg
$Sb^1–O^2$	2.079(4)	$O^2Sb^1O^3$	173.59(17)
$Sb^1–O^3$	2.125(4)	$O^2Sb^1C^{11}$	87.3(2)
$Sb^1–C^{11}$	2.133(6)	$O^2Sb^1C^{21}$	89.9(2)
$Sb^1–C^{21}$	2.133(5)	$O^2Sb^1C^{31}$	94.16(19)
$Sb^1–C^{31}$	2.127(5)	$O^3Sb^1C^{11}$	87.3(2)
$Br^{1A}–C^{13}$	1.928(7)	$O^3Sb^1C^{21}$	96.1(2)
$Br^{1B}–C^{13}$	1.951(8)	$O^3Sb^1C^{31}$	84.9(2)
$Br^2–C^{25}$	1.914(7)	$C^{21}Sb^1C^{11}$	124.1(2)
$Br^3–C^{33}$	1.903(7)	$C^{31}Sb^1C^{11}$	115.1(2)
$O^1–C^1$	1.225(8)	$C^{31}Sb^1C^{21}$	120.8(2)
$O^2–C^1$	1.326(8)	$C^1O^2Sb^1$	117.8(4)
$O^3–C^5$	1.321(9)	$C^5O^3Sb^1$	112.7(4)
$O^4–C^5$	1.211(9)	$C^{16}O^5C^{1Me}$	117.0(6)
$O^5–C^{16}$	1.366(7)	$C^{22}O^6C^{2Me}$	118.2(6)
$O^5–C^{1Me}$	1.432(8)	$C^{36}O^7C^{3Me}$	118.5(6)
$O^6–C^{22}$	1.376(8)	$O^1C^1O^2$	123.1(6)
$O^6–C^{2Me}$	1.418(9)	$Br^{1A}C^{13}Br^{1B}$	21.90(15)
$O^7–C^{36}$	1.367(8)		
$O^7–C^{3Me}$	1.387(9)		

The structural organization of the crystal is caused by weak hydrogen bonds C=O···H–C (2.34–2.40 Å), and C–Br···H–C (3.02 Å) and by π–π-interactions between the parallel aromatic rings. The methoxy oxygen atoms are not involved into the intermolecular interactions.

Thus, the features of the molecular structure of compound I are as follows: the additional coordination of the antimony atom with three oxygen atoms $O^{5,6,7}$ of the methoxy groups, along with the intramolecular interactions Sb···$O^{1,4}$=C; an unusual orientation of the carboxy groups with respect to the fragment SbC_3. The presence of the carboxy groups and the bromine atoms in the organic substituents leads to the formation of a three-dimensional structure in the crystal.

EXPERIMENTAL

The IR spectra were recorded on a 1201 FTIR-spectrometer from KBr pellets.

The XRD structural analysis was carried out on a SuperNova automatic four-circle diffractometer equipped with a two-coordinate CCD-detector using a Super Nova X-ray Source (Agilent Technologies) Cu-anode radiation (λ 1.54178 Å) at 123 K. The intensity of the reflections was measured by φ-scanning the frames (1°) to 2θ 142.16°. An extinction was taken into account analytically by cutting the crystal using a CrysAlisPro software (Agilent Technologies, Version 1.171.34.49, release 20-01-2011 CrysAlis171.NET) [18]. The structure was solved by the direct method and refined by the full least squares method in the anisotropic approximation for the non-hydrogen atoms using a SHELXTL software [19]. The hydrogen atoms were refined in the geometrically calculated positions. The main crystallographic data and structure refinement are given in Table 1, the main bond lengths and angles, in Table 2.

Synthesis of complex (I). To a mixture of 0.318 g (0.44 mmol) of $[(5\text{-Br})(2\text{-MeO})C_6H_3]_3Sb\cdot 0.5C_6H_6$ solvate and 0.076 g (0.88 mmol) of cyclopropanecarboxylic acid in 40 ml of diethyl ether was added 0.043 g (0.44 mmol) of 35% aqueous hydrogen peroxide solution. The mixture was maintained for 24 h at room temperature. The formed fine colorless powder (0.38 g) was recrystallized from a benzene–heptane mixture (3:1). Yield 0.34 g (91%), colorless crystals, mp 220°C. IR spectrum, ν, cm^{-1}: 404, 442, 488, 524, 50, 618, 678, 753, 808, 819, 887, 904, 938, 1017, 1050, 1072, 1093, 1147, 1180, 1193, 1231, 1256, 1294, 1356, 1374, 1390, 1439, 1474, 1573, 1646, 1658, 2836, 2938, 2971, 2999, 3008, 3068, 3090. Found, %: C 40.62; H 3.63. $C_{29}H_{28}Br_3O_7Sb$. Calculated, %: C 40.97; H 3.30.

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