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Synthesis of New Antimony(III) and Bismuth(III) Aryl Compounds: Crystal and Molecular Structure of Tris(5-bromo-2-methoxyphenyl)antimony

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Abstract—Tris(5-bromo-2-methoxyphenyl)antimony (**I**) (yield, 85%) and tris(5-bromo-2-methoxyphenyl)bismuth (**II**) (yield, 81%) were obtained by reacting 5-bromo-2-methoxyphenyllithium with antimony(III) chloride and bismuth(III) chloride, respectively. According to X-ray diffraction data, the antimony atom in **I** is highly coordinated. The Sb–C bonds lengths are 2.160(1) Å, 2.163(1) Å, and 2.157(2) Å; the Sb···O distances are 2.985(1) Å, 3.051(1) Å, and 3.052(1) Å. The CSbC bond angles vary in the range of 92.19(6)°–94.52(6)°. Molecules of **I** are linked via Sb(A)···Br(B) intermolecular contacts (3.742(2) Å) to form polymer chains.

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Triorganylantimony and -bismuth molecules (where the electronic configuration of the base state of the atoms is ns^2np^3) are, as a rule, trigonal bipyramids with a lone electron pair of the central atom located in the apex. However, antimony and bismuth atoms have free *d* orbitals, whose low energy gives a possibility of easily accepting electron pairs of various donor atoms to form both intra- and intermolecular additional bonds. Large atomic radii of antimony and bismuth are also in favor of this; their coordination spheres remain unsaturated after formation of three covalent bonds. Triaryl compounds of antimony and bismuth are known, which have potential coordination centers in aryl ligands (see, e.g., [1, 2]). X-ray diffraction studies have shown that, in case of the spatial accessibility of potential coordination sites, the coordination number of the central atom in these compounds increases.

In this work, aimed at further studying highly coordinated antimony and bismuth compounds, we have synthesized for the first time tris(5-bromo-2-methoxyphenyl)antimony (**I**) and tris(5-bromo-2-methoxyphenyl)bismuth (**II**) and studied the crystal and molecular structure of **I**.

EXPERIMENTAL

Synthesis of a benzene solvate of complex I. To a solution of 28.95 g (50.0 mmol) of 5-bromo-2-methoxyphenyllithium obtained by metalation of 28.05 g of *p*-bromoanisole with phenyllithium in ether, a solution of 3.65 g (16.0 mmol) of antimony(III) chloride in 20 mL of diethyl ether was added; and the mixture was stirred and kept overnight. Then, the mixture was carefully decomposed with cool water (2 mL); the solvent was removed; and the residue was recrystallized from benzene. As a result, colorless crystals of **I** were obtained. Yield, 10.42 g (85%); T_m = 198°C.

IR (cm^{-1}): 2933, 2834, 1563, 1488, 1425, 1371, 1283, 1261, 1234, 1177, 1136, 1088, 1073, 1042, 1017, 890, 826, 805, 767, 744, 615, 540, 443.

For $C_{27}H_{24}SbBr_3O_3$ anal. calcd. (%): C, 42.74; H, 3.17. Found (%): C, 42.12; H, 3.07.

The benzene solvate of **II** was obtained analogously. Yield, 81%; T_m = 203°C.

IR (cm^{-1}): 2934, 2833, 1560, 1488, 1457, 1434, 1372, 1295, 1260, 1234, 1175, 1142, 1084, 1036, 1013, 880, 829, 800, 613, 528, 434.

For $C_{27}H_{24}BiBr_3O_3$ anal. calcd. (%): C, 38.34; H, 2.84. Found (%): C, 38.06; H, 2.93.

IR spectra were recorded as KBr pellets on an FSM 1201 FT-IR spectrophotometer.

X-ray single-crystal diffraction of compound $\mathbf{I} \cdot C_6H_6$ was carried out on a Bruker-Nonius X8Apex four-circle diffractometer (CCD area detector, MoK_α radiation, λ = 0.71073 Å, graphite monochromator). The experimental intensity array was collected by φ scans of narrow frames (0.5°) to $2\theta = 50°$. The correction for absorption was applied empirically (SADABS) [3]. The structure was solved by direct methods and refined by the full-matrix least-squares in the anisotropic approximation for non-hydrogen atoms (SHELX-97) [4].

Selected crystal data and refinement parameters for structure **I** are compiled in Table 1; atomic coordinates and thermal parameters are presented in Table 2;

Table 1. Crystal data, experimental details, and refinement parameters for structure **I**

Parameter	Value
FM	718.89
T, K	100.0(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	9.00170(10)
b, Å	20.9598(3)
c, Å	13.5361(2)
β, deg	105.0430(10)
V, Å^3	2466.39(6)
Z	4
ρ_{calc}, g/cm^3	1.936
μ, mm^{-1}	6.002
F(000)	1380
Crystal shape (dimensions, mm)	Fragment (0.21 × 0.20 × 0.20)
θ range, deg	1.84–31.60
Reflection index ranges	$-13 \le h \le 12$, $-29 \le k \le 30$, $-14 \le l \le 19$
Reflections measured	6979
Independent reflections	6022
Refinement parameters	364
GOOF	1.009
Reflections with $I > 2\sigma(I)$	5844
R indices on $F^2 > 2\sigma(F^2)$	$R_1 = 0.0180$, $wR_2 = 0.0364$
R indices (all reflections)	$R_1 = 0.0259$, $wR_2 = 0.0384$
Residual electron density (min/max), e/Å^3	−0.451/0.530

Table 2. Atomic coordinates (×10^4) and equivalent isotropic thermal parameters (×10^3) in the structure of **I**

Atom	x	y	z	U_{eq}, Å^2
Sb(1)	7371.14(11)	1948.96(5)	7063.39(8)	11.87(3)
C(1A)	8929.1(18)	2747.3(7)	7199.1(12)	12.8(3)
C(2A)	9032.6(18)	3046.0(7)	6293.6(12)	15.0(3)
C(3A)	9960(2)	3579.6(8)	6314.4(13)	17.0(3)
C(4A)	10816.3(19)	3815.3(7)	7248.3(13)	16.0(3)
C(5A)	10716.9(18)	3521.2(7)	8140.9(12)	13.3(3)
C(6A)	9781.6(18)	2992.8(7)	8130.4(12)	13.3(3)
C(1AM)	8026(2)	3108.7(9)	4475.1(13)	24.3(4)
Br(1)	11881.32(19)	3845.49(7)	9424.33(12)	17.27(4)
O(1)	8185.2(15)	2765.7(6)	5412.9(8)	20.9(3)
C(1B)	9058.5(18)	1252.0(7)	6891.3(11)	12.2(3)
C(2B)	8571.2(18)	616.3(7)	6732.1(12)	14.5(3)
C(3B)	9514(2)	152.3(8)	6482.2(13)	19.8(3)
C(4B)	10982(2)	316.1(8)	6417.7(14)	21.3(4)
C(5B)	11485.7(18)	936.7(8)	6609.0(12)	17.5(3)
C(6B)	10539.1(18)	1406.8(8)	6837.3(12)	14.0(3)
C(1BM)	6446(2)	−106.1(9)	6515.1(17)	26.5(4)
Br(2)	13523.2(2)	1156.27(10)	6566.71(16)	29.11(5)
O(2)	7124.2(13)	501.2(5)	6840.6(9)	19.4(2)
C(1C)	7860.4(19)	1842.0(7)	8701.2(12)	15.3(3)
C(2C)	7129.8(19)	2282.0(8)	9199.0(13)	18.1(3)
C(3C)	7446(2)	2296.8(9)	10256.3(14)	25.2(4)
C(4C)	8503(2)	1871.1(9)	10831.8(14)	25.9(4)
C(5C)	9206(2)	1433.9(9)	10344.3(13)	21.9(4)
C(6C)	8895.0(19)	1412.7(8)	9281.3(13)	17.6(3)
C(1CM)	5527(3)	3211.8(10)	9011.8(17)	32.6(5)
Br(3)	10654.2(2)	847.99(10)	11138.43(14)	32.70(5)
O(3)	6137.3(15)	2691.6(6)	8557.1(9)	22.9(3)
C(1S)	6542(2)	88.2(9)	10080.7(17)	31.1(4)
C(2S)	5467(3)	306.9(9)	9225.5(16)	30.8(4)
C(3S)	3925(3)	219.1(9)	9148.7(15)	29.9(4)

and selected bond lengths and bond angles are shown in Table 3.

RESULTS AND DISCUSSION

Compounds **I** and **II** were obtained by the substitution reactions of 5-bromo-2-methoxyphenyllithium with antimony chloride and bismuth chloride, respectively. The high product yields (up to 85%) show the efficiency of this method for the synthesis of triarylantimony and -bismuth compounds.

$$3(5\text{-Br,2-MeOC}_6\text{H}_3)\text{Li} + \text{ECl}_3$$

$$\xrightarrow{\text{Et}_2\text{O},20°\text{C}} (5\text{-Br,2-MeOC}_6\text{H}_3)_3\text{E} + 3\text{LiCl}$$

$$\text{E} = \text{Sb(I), Bi(II)}.$$

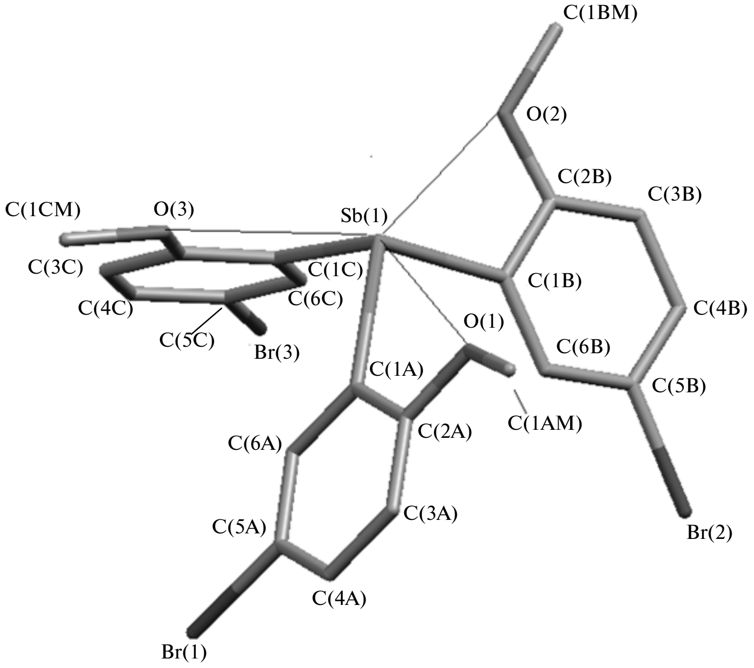

Fig. 1. Structure of tris(5-bromo-2-methoxyphenyl)antimony (benzene molecule is omitted).

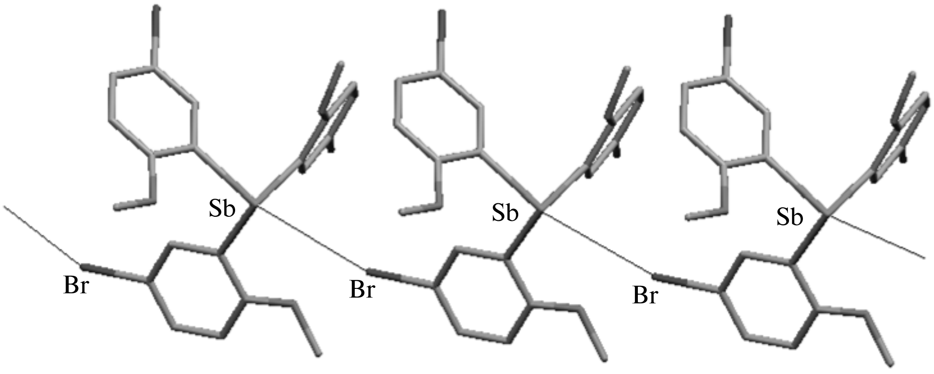

Fig. 2. Configuration of a polymer chain in crystals of tris(5-bromo-2-methoxyphenyl)antimony.

According to X-ray diffraction data, the molecule of compound **I** has a configuration of a trigonal bipyramid. The Sb–C bond lengths are 2.1603(15) Å, 2.1631(15) Å, and 2.1569(16) Å. The CSbC bond angles are 92.19(6)°, 94.23(6)°, 94.52(6)°. The oxygen atoms of the methoxy groups are coordinated to the antimony atom (Fig. 1). The intramolecular Sb···O distances (2.985(1) Å, 3.051(1) Å, and 3.052(1) Å) are 81–82% of the sum of the Van der Waals radii of antimony and oxygen atoms (3.7 Å [5]).

The presence of the intramolecular contacts is likely responsible for smaller CSbC bond angles in **I** compared to those in triphenyl- and tri-*p*-tolylantimony molecules (95.52°–97.36° [6] and 97.31° [7]), where these contacts are absent. On the contrary, in tris[2-dimethylaminomethyl)phenyl]antimony molecules where Sb···N intramolecular contacts were observed, the CSbC angles (94.67° [2]) are close to the analogous parameters of compound **I**.

Due to intermolecular Sb···Br contacts (3.742(2) Å; the sum of the Van der Waals radii of Sb and Br atoms is 4.1 Å), molecules of compound **I** form the polymer chains (Fig. 2).

Therefore, introduction of potential coordination sites into aromatic rings of molecules of compound **I** causes an increase in the coordination number of the

Table 3. Bond lengths and bond angles in the structure of **I**

Bond	*d*, Å	Angle	ω, deg
Sb(1)–C(1A)	2.1603(15)	C(1A)Sb(1)C(1B)	94.23(6)
Sb(1)–C(1B)	2.1631(15)	C(1C)Sb(1)C(1A)	92.19(6)
Sb(1)–C(1C)	2.1569(16)	C(1C)Sb(1)C(1B)	94.52(6)
C(2A)–O(1)	1.3697(19)	C(2A)O(1)C(1AM)	117.44(13)
C(5A)–Br(1)	1.9061(15)	C(2B)O(2)C(1BM)	117.73(14)
C(1AM)–O(1)	1.433(2)	C(2C)O(3)C(1CM)	117.63(14)
C(2B)–O(2)	1.3695(19)	C(4A)C(5A)Br(1)	119.57(12)
C(5B)–Br(2)	1.9061(16)	C(6A)C(5A)Br(1)	118.83(11)
C(5C)–Br(3)	1.9068(18)	C(4B)C(5B)Br(2)	119.58(13)
C(1CM)–O(3)	1.430(2)	C(6B)C(5B)Br(2)	119.08(13)

central atom and distortion of its coordination polyhedron compared to molecules in which intra- and intermolecular contacts are absent.

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