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Synthesis and Structure of Tris(4-*N,N*-dimethylaminophenyl)antimony Bis(4-methyl benzoate)

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

Blagoveshchensk State Pedagogical University, ul. Lenina 104, Blagoveshchensk, 675000 Russia
e-mail: vvsharutin@rambler.ru

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Abstract—The tris(4-*N,N*-dimethylaminophenyl)antimony bis(4-methyl benzoate) (**I**) was synthesized by the reaction of tris(4-*N,N*-dimethylaminophenyl)antimony with 4-methylbenzoic acid in ether in the presence of hydrogen peroxide. According to the X-ray diffraction data, in this molecule the antimony atom is in distorted trigonal-bipyramidal coordination (the axial angle OSbO is 176.15(4)°). The CSbC angles in the equatorial plane are 105.27(6)°, 108.01(6)°, 146.71(6)° (the sum is 359.99°). The Sb–O and Sb–C bond lengths are 2.131(1), 2.137(1) Å and 2.099(2), 2.100(1), 2.107(1) Å, respectively. The intramolecular contacts Sb···O=C are 2.826(1) and 2.928(1) Å.

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Oxidative addition reaction of the trivalent antimony phenyl and tolyl derivatives as well as the molecular structure of compounds Ar_3SbX_2 (Ar = Ph, Tol; X = Hal, NO_3, OAr, OSO_2Ar, OC(O)R, ONCRR') have been studied rather in details [1, 2]. However, the reactivity of aryl derivatives of antimony-containing functional groups in the aromatic substituents remains virtually unexplored, and only some of them have been characterized structurally [3].

In this paper we describe the synthesis of tris(4-*N,N*-dimethylaminophenyl)antimony bis(4-methylbenzoate) (**I**) and study of its crystal and molecular structure.

We found that oxidation of tris(4-*N,N*-dimethylaminophenyl)antimony with hydrogen peroxide in the presence of 4-methylbenzoic acid in ether at room temperature results in the formation of **I**:

$$(4\text{-}Me_2NC_6H_4)_3Sb + 2HOC(O)R + H_2O_2 \xrightarrow{Et_2O} (4\text{-}Me_2NC_6H_4)_3Sb[OC(O)R]_2 + 2H_2O,$$

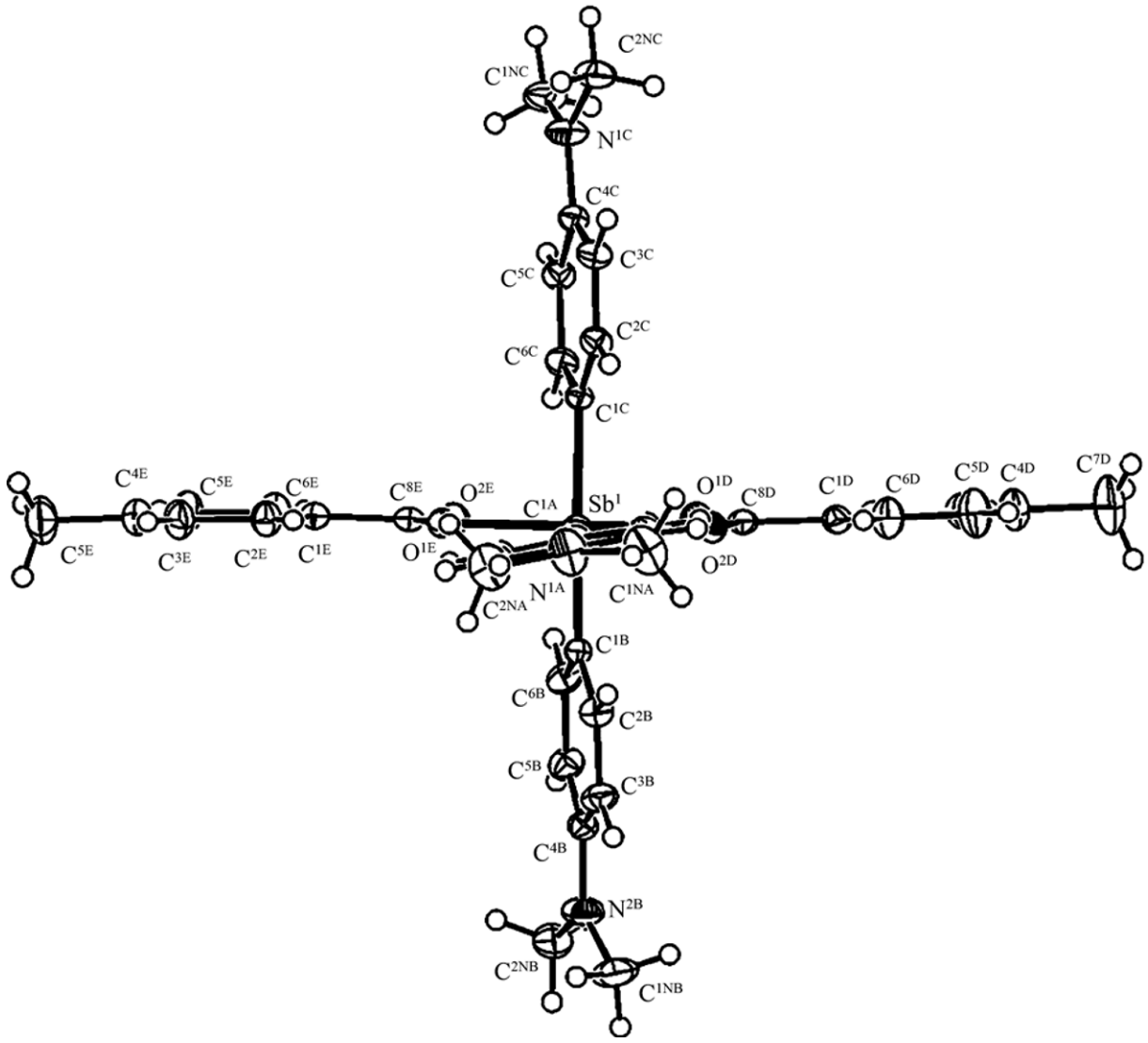
I

R = 4-MeC_6H_4.

Compound **I** is colorless crystals, readily soluble in aromatic hydrocarbons and polar organic solvents. It can be argued that the reaction of oxidative addition of the trivalent antimony organic derivatives is general in nature, since the introduction of functional groups to the aryl substituents at the antimony atom does not change the reaction scheme.

To identify the structural features of compounds **I** we studied its X-ray diffraction.

Molecule **I** has a sligthly distorted trigonal–bipyramidal configuration with oxygen atoms in axial positions and the carbon atoms of 4-*N,N*-dimethylaminophenyl groups in the equatorial plane. The axial angle OSbO is 176.15(4)°, which is close to the related axial angle in the tris(4-*N,N*-dimethylaminophenyl) antimony dibenzoate (**II**) (176.5°) [3]. The CSbC angles in the equatorial plane are 105.27(6)°, 108.01(6)°, 146.71(6)° (the sum is 359.99°). Analogous angles in **II** are 107.9°, 107.9°, and 144.1°, the difference in the CSbC equatorial angles is insignificant. The angles between axial and equatorial substituents OSbC vary in the range 88.15(5)°–92.31(5)°, which is comparable to that observed in II (88.25°–90.09°). Carboxylate and



Structure of compound **I**.

phenyl fragments of the the 4-methylbenzoate groups in **I** are coplanar. While the Sb–C bond lengths in **I** and **II** are almost identical [2.099(2), 2.100(1), 2.107(1) Å and 2.091, 2.097, 2.097 Å, respectively], the distances Sb–O [2.131(1), 2.137(1), and 2.121 Å] differ markedly. The large values of the Sb–O bond length in **I** correspond to stronger intramolecular contacts Sb···O=C [2.826(1), 2.928(1) Å] compared to the same parameters in **II** (2.987 Å). The carboxylate ligands are in *cis*-orientation relative to the SbC_3 fragment, and their intramolecular interaction causes a significant increase of the respective equatorial CSbC angle to 146.71(6)°. For the structures **I** and **II** is observed correlation between the Sb···O=C distance and the maximum equatorial angle in the triarylantimony dicarboxylates noted in [5]. In the carboxylate groups of the bond lengths C–O and C=O are respectively 1.307(2), 1.310(2) and 1.231(2), 1.232(2) Å. The OSO angles [121.96(15)° and 122.21(15)°] differ little from the theoretical value of 120°, the COSb angles are 108.8(1)° and 112.4(1)°. All values are typical of the structurally characterized triarylantimony dicarbo-xylates and close to the analogous parameters of the triphenylantimony bis(2-methylbenzoate) molecule [4]. The introduction of substituents in the aromatic group almost does not affect distortion of the central atom of coordination polyhedron.

In the IR spectrum of **I** the strong absorption bands in the region of the carbonyl groups stretching vibrations are shifted compared to corresponding

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

Parameter	Value
M	752.53
T, K	150.0(2)
Crystal system	Triclinic
Space group	P-1
a, Å	11.0171(3)
b, Å	12.7813(4)
c, Å	15.2730(5)
α, deg	100.8570(10)
β, deg	100.5410(10)
γ, deg	115.0210(10)
V, Å^3	1828.69(10)
Z	2
d_{calc}, g cm^{-3}	1.367
μ, mm^{-1}	0.776
F(000)	7988
Crystal shape (size, mm)	Chip (0.14×0.11×0.09)
Data collection area θ, deg	2.14–31.50
Intervals of reflection indices	$-16 \le h \le 13$, $-16 \le k \le 17$, $-21 \le l \le 20$
Measured reflections, total	10044
Independent reflections	8819
Number of refined variables	441
$GOOF$	1.047
R-Factors over $F^2 > 2\sigma(F^2)$	R_1 0.0255, wR_2 0.0555
R-factors over all reflections	R_1 0.0338 wR_2 0.0587
Residual electron density (min/max), e Å^{-3}	–0.340/0.627

carboxylic acid to longer wavelengths by 80–90 cm^{-1}, which indicates a decrease in the multiplicity of the C=O bond in the triarylantimony dicarboxylates.

The intermolecular hydrogen bonds of the $Me_2N\cdots H$ type in the crystals of **I** were not found.

EXPERIMENTAL

Synthesis of tris(4-*N,N*-dimethylaminophenyl) antimony bis(4-methyl benzoate) (I). To a mixture of 0.48 g (1.0 mmol) of tris(4-*N,N*-dimethylaminophenyl) antimony and 0.27 g (1.0 mmol) of 4-methylbenzoic acid in 30 ml of ether was added 0.12 ml of 30% aqueous solution of hydrogen peroxide, and the mixture was kept for 18 h at 20°C. The crystals of **I** formed were filtered off and dried. Yield 92%, mp 130°C. Found, %: C 63.87, H 5.75. $C_{40}H_{42}N_3O_4Sb$. Calculated, %: C 64.00, H 5.60.

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

Bond	d, Å	Angle	ω, deg
Sb^1–O^{2E}	2.1312(11)	$O^{2E}Sb^1O^{2D}$	176.15(4)
Sb^1–O^{2D}	2.1371(11)	$C^{1B}Sb^1O^{2E}$	92.31(5)
Sb^1–C^{1B}	2.0988(16)	$C^{1B}Sb^1O^{2D}$	90.13(5)
Sb^1–C^{1C}	2.1005(15)	$C^{1B}Sb^1C^{1C}$	146.71(6)
Sb^1–C^{1A}	2.1072(15)	$C^{1B}Sb^1C^{1A}$	105.27(6)
O^{2E}–C^{8E}	1.3067(19)	$C^{1C}Sb^1O^{2E}$	89.73(5)
O^{2D}–C^{8D}	1.3101(19)	$C^{1C}Sb^1O^{2D}$	89.88(5)
O^{1E}–C^{8E}	1.2319(19)	$C^{1C}Sb^1C^{1A}$	108.01(6)
O^{1D}–C^{8D}	1.231(2)	$C^{1A}Sb^1O^{2E}$	88.15(5)
N^{1A}–C^{4A}	1.375(2)	$C^{1A}Sb^1O^{2D}$	88.33(5)
N^{1A}–C^{2NA}	1.446(2)	$C^{8E}O^{2E}Sb^1$	112.45(10)
N^{1A}–C^{1NA}	1.440(3)	$C^{8D}O^{2D}Sb^1$	108.81(10)

IR spectrum (ν, cm^{-1}): 3072, 2881, 2802, 1581, 1508, 1435, 1334, 1221, 1199, 1182, 1131, 1075, 945, 855, 805, 777, 664, 625, 512, 417.

X-ray diffraction of the crystals of compound **I** was studied on an automatic four-circle diffractometer Bruker-Nonius X8Apex (CCD area detector, the MoK_α-radiation, λ = 0.71073 Å, graphite monochromator). Intensity of the reflections were measured by the φ-scanning of narrow (0.5°) frames to 2θ = 50°. Absorption is taken into account empirically (SADABS) [6]. The structure was solved by direct methods and refined by full-matrix anisotropic approximation for non-hydrogen atoms (SHELX-97) [7].

The main crystallographic data and structure **I** refinement are given in Table 1, the main bond lengths and angles in Table 2.

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

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