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Synthesis and Structure of Tri-*p*-tolylantimony Dibromide

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Abstract—Tri(*p*-tolyl)antimony dibromide is synthesized by the oxidation of tri(*p*-tolyl)stibine with copper bromide $CuBr_2$ in acetone. According to the X-ray diffraction analysis data, the antimony atom in tri(*p*-tolyl)antimony dibromide has the configuration of a trigonal bipyramid with axial bromine atoms. The Sb–Br and Sb–C bond lengths are 2.631(5) and 2.111(4) Å, the CSbC and BrSbBr angles are 120° and 180°, and the intramolecular Br…C(1,2) contacts are 3.374 and 3.517 Å, respectively.

INTRODUCTION

The structure of phenyl derivatives of pentavalent antimony with the general formula Ph_3SbX_2 (X is an electronegative substituent) was described in [1–4]. The majority of these compounds are characterized by trigonal-bipyramidal coordination of the central atom with the electronegative ligands in the axial positions. In triphenylantimony dichloride, the carbon and hydrogen atoms of one of the phenyl groups are close to the chlorine atoms in spite of the arising steric hindrances [3]. Similar contact is observed in the tri(*m*-tolyl)antimony dichloride, wherein the distance from the equatorial carbon atom of one of the phenyl groups to the chlorine atom (3.188 Å) [4] is also shorter than the sum of the van der Waals radii of the elements (3.5 Å) [5].

EXPERIMENTAL

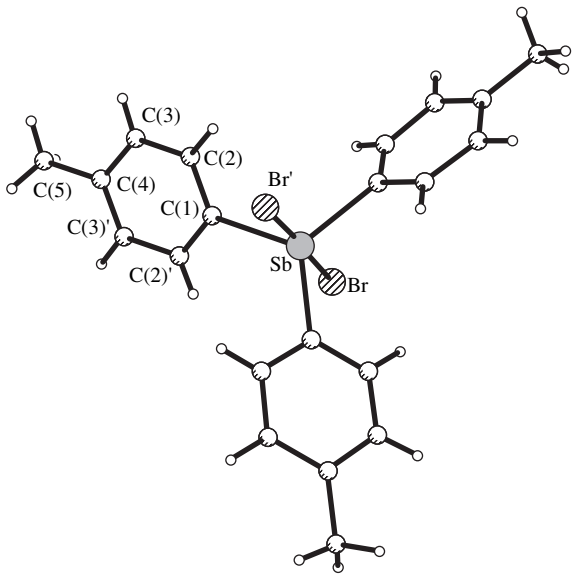
Synthesis. Tri(*p*-tolyl)antimony dibromide (**I**) was synthesized using the procedure described in [6]. A saturated solution of $CuBr_2$ (1.24 g) in acetone was added to a solution of tri-*p*-tolylantimony (1.00 g) in acetone (10 ml). The colorless precipitate of $CuBr_2$ was formed. The solvent was removed, and the residue was recrystallized from toluene. The compound was obtained in 85% yield (1.23 g), mp 233°C, which coincides with the data in [7].

X-ray diffraction analysis of compound **I** was performed for the naturally faceted single crystal on a SMART-1000 CCD diffractometer (Bruker). The data were collected in series of 606, 435, and 230 frames at the values of $\phi = 0°$, 90°, and 180°, respectively (ω scan mode with an increment of 0.3° and exposure of 10 s per frame). The X-ray absorption in the sample was corrected for by the indices of the crystal faces.

The structure was determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were calculated geometrically and included in the refinement by the "rider" model.

The data collection and processing and the refinement of the unit cell parameters were performed using the SMART and SAINT-Plus program packages [8]. All calculations for the determination and refinement of the structure were performed using the SHELXTL/PC program package [9].

The main crystallographic data and results of refinement of the structure are presented in Table 1. The coordinates of atoms and thermal parameters are presented in Table 2. The bond lengths and angles are given in Table 3.



Molecular structure of tri(*p*-tolyl)antimony dibromide (**I**).

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Table 1. Summary of data collection and refinement of the tri(*p*-tolyl)antimony dibromide structure (**I**)

Parameter	Value
Empirical formula	$C_{21}H_{21}Br_2Sb$
M	554.95
T, K	293(2)
λ, Å	MoK_α (0.71073)
System	Cubic
Space group	$P4_332$
a, Å	12.859(1)
V, Å^3	2126.4(3)
Z	4
ρ(calcd), g/cm^3	1.733
μ, mm^{-1}	5.055
F(000)	1072
Crystal shape	Cube (0.22 × 0.22 × 0.22 mm)
Range of θ, deg	2.24 – 27.97
Intervals of refractive indices	$-16 \le h \le 16$, $-16 \le k \le 16$, $-16 \le l \le 16$
Measured reflections	14055
Independent reflections	861 (R_{int} = 0.0427)
Reflections with $I > 2\sigma(I)$	761
Refinement method	Full-matrix least-squares for F^2
Refinement variables	41
GOOF	1.103
R factors for $F^2 > 2\sigma(F^2)$	R_1 = 0.0224, wR_2 = 0.0621
R factors for all reflections	R_1 = 0.0275, wR_2 = 0.0639
Molar absorption coefficient	0.0005(4)
Residual electron density (min/max), *e*/Å^3	–0.402/0.357

Table 2. Coordinates of atoms (×10^4) and equivalent isotropic thermal parameters (×10^3) in the tri(*p*-tolyl)antimony dibromide structure (**I**)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Sb	8750	3750	11250	49.6(2)
Br	9931.3(2)	4931.3(2)	10068.7(2)	75.6(2)
C(1)	8750	2589(2)	10089(2)	51.4(8)
C(2)	7829(2)	2177(3)	9737(3)	67.8(8)
C(3)	7833(3)	1439(3)	8956(3)	71(1)
C(4)	8750	1051(3)	8551(3)	61(1)
C(5)	8750	226(3)	7726(3)	84(2)

RESULTS AND DISCUSSION

The structure of tri(*p*-tolyl)antimony dibromide was studied to reveal the reasons for the indicated nonvalence interaction. According to the X-ray diffraction analysis data, the antimony atom in compound **I** has regular trigonal-bipyramidal coordination with equatorial tolyl groups and axial bromine atoms (see figure). Unlike tri(*m*-tolyl)antimony dichloride (**II**), in which the ClSbCl angle is equal to 177.2°, these atoms in molecule **I** Br'SbBr have a linear arrangement. The antimony atom lies exactly in the equatorial plane. The angles between the planes of the phenyl rings and the

Table 3. Interatomic distances and bond angles in the tri(*p*-tolyl)antimony dibromide structure (**I**)

Bond	*d*, Å	Angle	ω, deg
Sb–Br	2.6310(5)	C(1)SbC(1)'	120.0
Sb–C(1)	2.111(4)	C(1)SbBr	90.0
C(1)–C(2)	1.373(4)	BrSbBr'	180.0
C(2)–C(3)	1.382(5)	C(2)C(1)C(2)'	119.3(4)
C(3)–C(4)	1.382(4)	C(1)C(2)C(3)	120.1(3)
C(4)–C(5)	1.501(7)	C(4)C(3)C(2)	121.6(3)
		C(3)C(4)C(3)'	117.2(4)
		C(3)C(4)C(5)	121.4(2)

equatorial plane are 37.0°. The Sb–Br and Sb–C bond lengths are 2.631(5) and 2.111(4) Å, respectively. In molecule **II**, the antimony atom has a distorted trigonal-bipyramidal arrangement of the substituents: the Sb–Cl bond lengths are 2.462(1) and 2.479(1) Å, and the Sb–C bond lengths are 2.101(4), 2.112(4), and 2.116(4) Å [4]. No intramolecular contacts between the carbon atoms of the *p*-tolyl ligands and chlorine atoms are observed in tri(*p*-tolyl)antimony dichloride, whose crystal molecule occupy positions with D_3 symmetry and each plane of the aryl rings makes an angle of 37.9° with the equatorial plane [10]. Thus, the introduction of methyl substituents into the *para*-position of the aryl rings improves the symmetry of the triarylantimony dihalide molecule.

Despite the high symmetry of molecule **I**, it contains intramolecular Br··C(1) and Br··C(2) contacts equal to 3.374 and 3.517 Å, respectively, which are shorter than the sum of the van der Waals radii of these atoms (3.6 Å [5]).

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