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Structural Features of Pentaphenylantimony, Penta(*p*-tolyl)antimony, and Their Solvates with Organic Solvents

V. V. Sharutin[a], * **and M. S. Golovin**[a]

[a] *South Ural State University (National Research University), Chelyabinsk, Russia*

**e-mail: sharutin50@mail.ru*

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Abstract—The structures of pentaphenylantimony (**I**), its solvates with benzene (**II**) and dioxane (**III**), and penta(*p*-tolyl)antimony (**IV**) are solved by X-ray diffraction (XRD) (CIF files CCDC nos. 2124594, 2121835, 2124972, and 2124962, respectively). The following parameters are determined from the XRD data: crystals of Ph_5Sb (**I**): $a = 10.286(3)$, $b = 10.510(4)$, $c = 13.590(4)$ Å; $\alpha = 68.29(2)°$, $\beta = 79.364(14)°$, $\gamma = 61.272(12)°$; $V = 1196.9(7)$ Å^3; $Z = 2$; solvate $Ph_5Sb·0.5PhH$ (**II**): $a = 13.165(11)$, $b = 14.394(16)$, $c = 15.193(13)$ Å; $\alpha = 90.22(3)°$, $\beta = 113.71(2)°$, $\gamma = 94.23(5)°$; $V = 2627(4)$ Å^3; $Z = 2$; solvate $Ph_5Sb·0.5C_4H_8O_2$ (**III**): $a = 10.451(5)$, $b = 10.462(4)$, $c = 13.323(5)$ Å; $\alpha = 75.647(11)°$, $\beta = 69.648(19)°$, $\gamma = 86.300(19)°$; $V = 1322.8(9)$ Å^3; $Z = 2$; and p-Tol_5Sb (**IV**): $b = 12.084(7)$, $c = 17.009(6)$ Å; $\beta = 102.934(14)°$; $V = 2899(2)$ Å^3; $Z = 4$. The antimony atoms in solvates **II** and **III** have a distorted trigonal bipyramidal coordination.

Keywords: pentaphenylantimony, penta(*p*-tolyl)antimony, solvate, benzene, dioxane, structure, XRD

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INTRODUCTION

The structures of the pentaarylantimony compounds of the general formula Ph_5Sb were studied earlier [1–6]. However, in this work we succeeded to refine the structure of pentaphenylantimony (**I**) and to determine for the first time the structures of its solvates with benzene (**II**) and dioxane (**III**). Penta(*p*-tolyl)antimony (**IV**) and its derivatives, whose structural features were discussed in [7, 8], are also very important compounds in the chemistry of pentaaryl derivatives of antimony. The use of pentaarylantimony in organoelement synthesis was reported [9].

Molecules of all structurally characterized to date compounds of pentacoordinate antimony have a trigonal bipyramidal configuration. The exception is pentaphenylantimony, whose molecule has the structure of a distorted square pyramid (it should be mentioned that this is one of a few examples for compounds of group 15 elements). The XRD studies of $Ph_5Sb·0.5PhH$ (**I**) were carried out several times [3, 4, 6]. According to the data obtained, the Sb–C distances in molecule **I** lie in ranges of 2.05–2.23 [3], 2.128–2.225 [4], and 2.208–2.212 Å [6], and the axial bond (2.05 [3], 2.128 [4], 2.129 Å [6]) is significantly shorter than the equatorial bonds (2.12–2.23 [3], 2.202–2.225 [4], 2.208–2.212 Å [6]). The CSbC bond angles in the equatorial plane of the square pyramid are close to 90° (84°–91° [3], 86.7°–88.6° [4], and 86.80°–88.91° [6]), and their sums are 350°, 351.5°, and 351.42°, respectively. The angles between the axial and equatorial carbon atoms are 95°–109° [3], 96.4°–106.0° [4], and 96.47°–105.64° [6] and differ significantly from the theoretical value, indicating a distortion of the square pyramid toward a trigonal bipyramid. If the trigonal bipyramid is accepted to be the basic configuration of molecule **I**, then its distortion from an "ideal" would be more noticeable: the axial and equatorial angles will be 163°, 104°, 109°, and 147° [3]; 164.0°, 104.8°, 106.0°, and 149.2° [4]; and 164.26°, 104.04°, 105.64°, and 150.31° [6]. These values differ strongly from theoretical angles of 180° and 120° in a trigonal bipyramid. The calculations by the method proposed [10] indicate that the contribution of the trigonal bipyramidal structure in molecule **I** is 26.7 [3] and 24.7% [4]. The approximate symmetry of molecule **I** is C_{2v} instead of ideal C_{4v} characteristic of a square pyramid, which appears in the difference in $C_{eq}SbC_{ax}$ angles: two of them are smaller than 100°, and two other angles are larger than 100°. The "diagonal" angles in the equatorial plane also differ substantially. The planes of the phenyl rings are turned at ~25.27°, 66°, and 69° relative to the equatorial plane.

Probably, the configuration of a distorted square pyramid is advantageous over the trigonal bipyramidal configuration in the crystal of compound **I** due to a combined action of intermolecular and intramolecular forces. The role of Coulomb interactions was discussed [11] in order to explain the "anomalous" structure of pentaphenylantimony. However, the authors

[12] found from the spectral data that the square pyramidal coordination of the central atom in the molecule was retained upon the dissolution of pentaphenylantimony in dichloromethane or dibromomethane. Therefore, it can be assumed that the crystal packing exerts no decisive effect on the choice of a possible structure during the formation of a polyhedron around the central atom in pentaphenylantimony.

It was already mentioned that the trigonal bipyramidal configuration was energetically slightly preferable than the square pyramidal configuration. Therefore, it is not surprising that any factors can result in the predomination of the square pyramidal structure over the trigonal bipyramid in some cases. The difference in energy between alternative structures becomes negligible for heavy elements with a bulky valent shell. In the crystalline solvate with cyclohexane $Ph_5Sb{\cdot}0.5\mathit{cyclo}\text{-}C_6H_{12}$, the pentaphenylantimony molecule is characterized by the trigonal bipyramidal structure [5]. The authors [5] found no contacts of the cyclohexane molecule with pentaphenylantimony molecules capable of changing the coordination of the central atom. A comparatively easy loss of cyclohexane molecule by the crystal was emphasized. It was assumed that the cyclohexane content in the crystal was approximately 85% of the initial value at the final stage of the experiment. The pentaphenylantimony molecule in the crystalline solvate with tetrahydrofuran $Ph_5Sb{\cdot}0.5C_4H_8O$ [6] has also a trigonal bipyramidal structure.

The purpose of this work was to study structural features of crystals of pentaarylantimony and its solvates with benzene and dioxane.

EXPERIMENTAL

Prior to synthesis, solvents (reagent grade) were dehydrated over calcium chloride and distilled.

The synthesis of Ph_5Sb (**I**) was carried out using a published procedure [2], and *p*-Tol_5Sb (**IV**) was synthesized according to [8].

Elemental analyses to C and H were carried out on a Carlo Erba CHNS-O EA 1108 elemental analyzer. IR spectra were recorded on a Shimadzu IRAffinity-1S FT-IR spectrometer in a range of 4000–400 cm^{-1} in the KBr matrix. Melting points were measured on a Netzsch 449C Jupiter synchronous thermoanalyzer.

Synthesis of pentaphenylantimony solvate with benzene (II) was carried out by the recrystallization of pentaphenylantimony **I** from benzene. Colorless crystals with T_{decomp} = 135.5°C were obtained.

For $C_{66}H_{56}Sb_2$		
Anal. calcd., %	C, 72.46	H, 5.12
Found, %	C, 72.32	H, 5.30

IR (ν, cm^{-1}): 3059, 3035, 3011, 1572, 1476, 1429, 1298, 1258, 1182, 1055, 1018, 729, 693, 681, 642, 474, 446.

Synthesis of pentaphenylantimony solvate with dioxane (III) was carried out by the recrystallization of pentaphenylantimony **I** from dioxane. Colorless crystals with T_{decomp} = 150°C were obtained.

For $C_{32}H_{29}OSb$		
Anal. calcd., %	C, 69.65	H, 5.26
Found, %	C, 69.51	H, 5.37

IR (ν, cm^{-1}): 3059, 3038, 3007, 2961, 2849, 1572, 1475, 1431, 1252, 1121, 1055, 997, 874, 731, 696, 623, 474, 457, 446.

XRD of crystals was carried out on a D8 QUEST automated four-circle diffractometer (Bruker, MoK_α radiation, λ = 0.71073 Å, graphite monochromator). Data were collected and processed, unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-Plus programs [13]. All calculations on structure determination and refinement were performed using the SHELXL/PC [14] and OLEX2 [15] programs. The structures were solved by a direct method and refined by least squares in the anisotropic approximation for nonhydrogen atoms. The positions of hydrogen atoms were refined by the riding model ($U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$). The crystallographic data and structure refinement results are given in Table 1. The geometric characteristics of the coordination polyhedron of the antimony atom are listed in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2124594 (**I**), 2121835 (**II**), 2124972 (**III**), and 2124962 (**IV**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The recrystallization of pentaphenylantimony from acetonitrile was not accompanied by the incorporation of its molecules into the lattice. The structure of compound **I** was determined at the laboratory of the South Ural State University with a higher accuracy (R = 4.46%) than previously [1–6].

At the same time, the crystallization of pentaphenylantimony from benzene and dioxane was shown to afford pentaphenylantimony solvates with benzene $Ph_5Sb{\cdot}0.5C_6H_6$ (**II**) and dioxane $Ph_5Sb{\cdot}0.5C_4H_8O_2$ (**III**), respectively, having the trigonal bipyramidal structure. The decomposition temperatures of solvates **II** and **III** are considerably lower than the melting point of pure pentaphenylantimony, which confirms the loss of benzene and dioxane molecules, respectively, by the solvate crystals.

Table 1. Crystallographic data and experimental and structure refinement parameters for compounds **I**–**IV**

Parameter	**I**	**II**	**III**	**IV**
Empirical formula	$C_{30}H_{25}Sb$	$C_{66}H_{56}Sb_2$	$C_{32}H_{29}OSb$	$C_{35}H_{35}Sb$
FW	507.25	1092.61	551.30	577.38
T, K	293	293	293	293
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	10.286(3)	13.165(11)	10.451(5)	14.472(6)
b, Å	10.510(4)	14.394(16)	10.462(4)	12.084(7)
c, Å	13.590(4)	15.193(13)	13.323(5)	17.009(6)
α, deg	68.29(2)	90.22(3)	75.647(11)	90.00
β, deg	79.364(14)	113.71(2)	69.648(19)	102.934(14)
γ, deg	61.272(12)	94.23(5)	86.300(19)	90.00
V, $Å^3$	1196.9(7)	2627(4)	1322.8(9)	2899(2)
Z	2	2	2	4
ρ_{calc}, g/cm^3	1.407	1.381	1.384	1.323
μ, mm^{-1}	1.166	1.068	1.064	0.972
F(000)	512.0	1108.0	560.0	1184.0
Crystal size, mm	0.5 × 0.38 × 0.29	0.49 × 0.38 × 0.33	0.43 × 0.35 × 0.27	0.38 × 0.26 × 0.24
Data collection range over 2θ, deg	5.52–96.22	5.86–54.74	6.4–77.5	5.776–56.774
Ranges of reflection indices	$-21 \le h \le 21$, $-21 \le k \le 21$, $-28 \le l \le 28$	$-16 \le h \le 16$, $-18 \le k \le 18$, $-19 \le l \le 19$	$-18 \le h \le 18$, $-18 \le k \le 18$, $-23 \le l \le 23$	$-19 \le h \le 19$, $-16 \le k \le 16$, $-22 \le l \le 22$
Measured reflections	177843	61668	99009	106229
Independent reflections	22858	11757	15054	7238
R_{int}	0.0446	0.0395	0.0505	0.0296
Refinement variables	280	614	311	331
GOOF	1.067	1.015	1.036	1.081
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0440$, $wR_2 = 0.0848$	$R_1 = 0.0269$, $wR_2 = 0.0583$	$R_1 = 0.0554$, $wR_2 = 0.1038$	$R_1 = 0.0239$, $wR_2 = 0.0548$
R factors for all reflections	$R_1 = 0.0840$, $wR_2 = 0.0991$	$R_1 = 0.0433$, $wR_2 = 0.0652$	$R_1 = 0.1145$, $wR_2 = 0.1202$	$R_1 = 0.0319$, $wR_2 = 0.0599$
Residual electron density (min/max), e/$Å^3$	–0.86/1.09	–0.51/0.50	–0.58/1.04	–0.69/0.59

The crystal of compound **II** (Fig. 1) contains two crystallographically independent pentaphenylantimony molecules (**A** and **B**). The geometric characteristics for molecule **A** are the following: the Sb–C distances are 2.129(3)–2.228(3) Å; the axial bond angle CSbC is 178.41(9)°; the equatorial bond angles CSbC are 119.23(10)°, 119.60(12)°, and 121.17(10)°; and their sum is 360°. The corresponding characteristics for molecule **B** (2.131(3)–2.146(3) Å, 179.50(9)°, 118.53(10)°–121.58(11)°, and 359.99°) do not almost differ from those observed in pentaphenylantimony solvates with cyclohexane [5] and tetrahydrofuran [6].

In solvate **III** (Fig. 2), the Sb–C distances are 2.143(2)–2.244(2) Å (which are somewhat longer than the sum of covalent radii of atom-partners (2.14 Å [16]), the axial bond angle CSbC and the equatorial bond angles CSbC are 179.68(8)° and 118.55(0)°, 120.66(9)°, and 120.79(0)°, respectively, while the sum of equatorial CSbC angles is 360°. Note that no considerable intermolecular contacts are observed in the crystal of compound **III**, but the C(44)···H(24) distances (2.8 Å) are somewhat shorter than the sum of van der Waals radii of these atoms (2.9 Å [17]), indicat-

Table 2. Bond lengths and bond angles in compounds **II** and **III**

Bond	*d*, Å	Angle	ω, deg
II			
Sb(1)–C(41)	2.130(3)	C(41)Sb(1)C(11)	91.87(10)
Sb(1)–C(11)	2.227(3)	C(41)Sb(1)C(1)	119.23(10)
Sb(1)–C(1)	2.141(3)	C(41)Sb(1)C(31)	121.17(10)
Sb(1)–C(31)	2.143(3)	C(41)Sb(1)C(21)	87.55(11)
Sb(1)–C(21)	2.231(3)	C(11)Sb(1)C(21)	178.43(9)
Sb(2)–C(61)	2.231(3)	C(1)Sb(1)C(31)	119.60(12)
Sb(2)–C(81)	2.233(3)	C(61)Sb(2)C(81)	179.49(9)
Sb(2)–C(51)	2.136(3)	C(51)Sb(2)C(91)	119.88(10)
Sb(2)–C(91)	2.141(3)	C(51)Sb(2)C(71)	118.53(10)
Sb(2)–C(71)	2.146(3)	C(91)Sb(2)C(71)	121.58(11)
Symmetry transforms: ^{1} $2 - x, 2 - y, 2 - z$; ^{2} $2 - x, 1 - y, 1 - z$.			
III			
Sb(1)–C(31)	2.155(2)	C(41)Sb(1)C(11)	179.68(8)
Sb(1)–C(21)	2.145(2)	C(21)Sb(1)C(31)	120.79(9)
Sb(1)–C(1)	2.143(2)	C(1)Sb(1)C(31)	120.66(9)
Sb(1)–C(11)	2.244(2)	C(1)Sb(1)C(21)	118.55(9)
Sb(1)–C(41)	2.237(2)	C(31)Sb(1)C(41)	89.09(9)
Symmetry transforms: ^{1} $2 - x, 1 - y, -z$.			

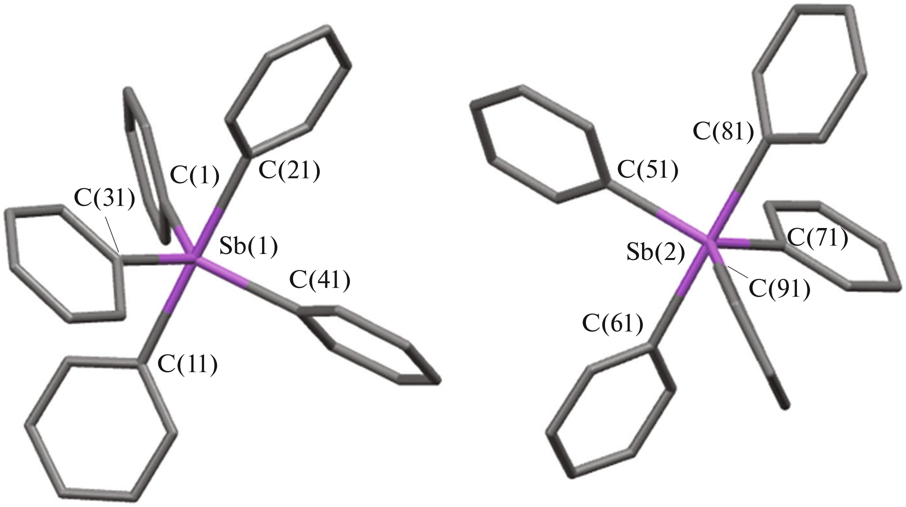

Fig. 1. Structure of compound **II** (solvate benzene molecules and hydrogen atoms are omitted).

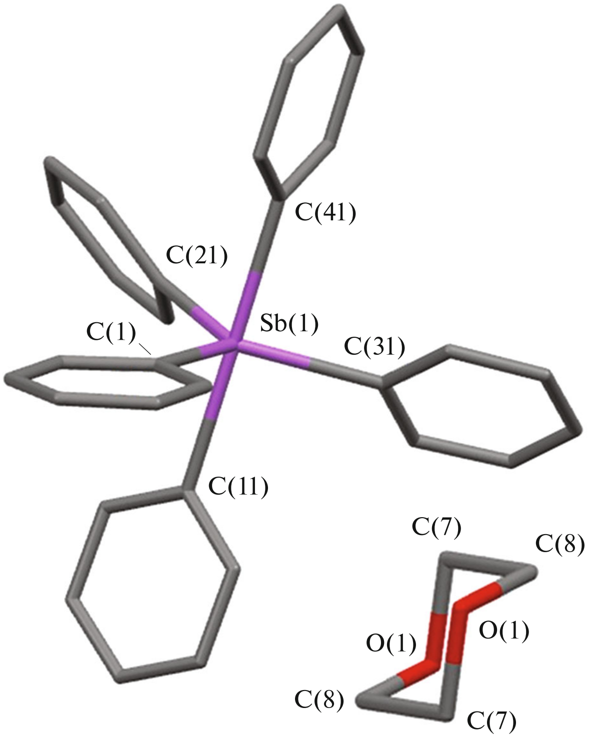

Fig. 2. Structure of compound **III** (hydrogen atoms are omitted).

ing the presence of the so-called "supporting" contacts in the crystal.

The Sb–C bond lengths (2.130(3)–2.244(2) Å) in solvates **II** and **III** are somewhat longer than analogous distances in molecules of triphenylantimony (~2.143 Å [18]), tri-*p*-tolylantimony (~2.143 Å [19]), tris(4-*N*,*N*-dimethylaminophenyl)antimony (~2.140 Å [20]), tris(5-bromo-2-methoxyphenyl)antimony (~2.160 Å [21]), and tris(2-methoxy-5-chlorophenyl)antimony (~2.169 Å [22]).

Thus, the lattice energy of the crystal and rather low changes in the packings of the molecules in the crystal for the transition of the square pyramidal to trigonal bipyramidal configuration are the determining factors in choosing coordination polyhedra by the molecules.

Note that the recrystallization of penta(*p*-tolyl)antimony **(IV)** from acetone, *o*-, *m*-, and *p*-xylenes, benzene, dioxane, and tetrahydrofuran was not accompanied by the formation of the corresponding solvates. In all cases, crystals of compound **IV** were isolated from solutions, and their structure was determined with a higher accuracy ($R = 2.4\%$) than previously [7, 8].

The IR spectra of the compounds exhibit bands characterizing the aryl ligands at the antimony atom. In addition, the IR spectrum of compound **III** contains the band at 1121 cm^{-1} assigned to the C–O vibrations in the solvate dioxane molecules [23, 24].

To conclude, the recrystallization of pentaphenylantimony from benzene and dioxane gave the corresponding pentaphenylantimony solvates ($Ph_5Sb{\cdot}0.5PhH$ and $Ph_5Sb{\cdot}0.5C_4H_8O_2$), the structures of which were determined by XRD. The antimony atoms in the solvates have the distorted trigonal bipyramidal coordination. The structures of pentaphenylantimony and penta(*p*-tolyl)antimony) were refined.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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