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Synthesis and Structure of [(μ_4-Succinato)hexadecaphenyltetraantimony] Triiodide Solvate with Benzene $[(Ph_4Sb)_2O_2CCH_2CH_2CO_2(Ph_4Sb)_2][I_3]_2 \cdot 4PhH$

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Abstract—The reaction of bis(tetraphenylantimony) succinate with iodine in benzene affords [(μ_4-succinato)hexadecaphenyltetraantimony] triiodide solvate with benzene $[(Ph_4Sb)_2O_2CCH_2CH_2CO_2(Ph_4Sb)_2][I_3]_2 \cdot 4PhH$ (**I**). The symmetrically nonequivalent Sb(1) and Sb(2) atoms in the centrosymmetric cation of compound **I** have a distorted trigonal bipyramidal coordination mode with the oxygen atoms in the axial positions (Sb(1,2)–O 2.347(4) 2.525(4) Å; Sb(1,2)–C_{equiv} 2.109(7)–2.120(7) Å, 2.082(5)–2.106(7) Å; Sb(1,2)–C_{axial} 2.158(7), 2.121(9) Å; angles OSb(1,2)C 178.8(2)°, 174.5(3)°). The geometry of the $[I_3]^-$ anions is close to linear (angle III 179.41(4)°, I–I distances 2.880(1) and 2.921(1) Å) (CIF file CCDC no. 1486690).

Keywords: bis(tetraphenylantimony) succinate, interaction, iodine, benzene

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INTRODUCTION

Compounds in which various substituents X along with organic radicals are bound to the antimony atom play an important role in the chemistry of organoantimony compounds. They serve as precursors in the syntheses of diverse antimony derivatives and are practically significant as catalysts, biologically active substances, and others. In addition, these compounds are objects of theoretical studies associated with the investigation of the structure of molecules and the character of Sb–C and Sb–X bonds. Therefore, the reactions leading to the substitution of functional groups X by other groups without a change in the number and character of organic radicals bound to the metal atom are very interesting but remain yet poorly studied. The reactions of the substitution of tetraarylantimony halides (as a rule, bromides and, more rarely, chlorides) by sodium or silver salts of carboxylic acids are widely used for the syntheses of tetraarylantimony carboxylates [1, 2]. However, the reactions of tetraarylantimony carboxylates with halogens are not described.

In this work, we studied the reaction of bis(tetraphenylantimony) succinate with iodine and determined the structure of the reaction product by X-ray diffraction analysis.

EXPERIMENTAL

Synthesis of [(μ_4-succinato)hexadecaphenyltetraantimony] triiodide solvate with benzene (I). A mixture of bis(tetraphenylantimony) succinate (0.48 g, 0.50 mmol) and iodine (0.19 g, 0.75 mmol) in benzene (10 mL) in a glass sealed tube was heated in a boiling water bath for 1 h. The mixture was cooled, and the formed precipitate was filtered off, dried, and recrystallized from a benzene–ethanol (4 : 1) mixture. The yield of the brown crystals of complex **I** was 0.52 g (72%), T_{decomp} = 155°C.

For $C_{124}H_{108}O_4I_6Sb_4$		
anal. calcd., %:	C, 51.13;	H, 3.71.
Found, %:	C, 51.06;	H, 3.87.

IR (ν, cm^{-1}): 1639, 1630, 1571, 1477, 1335, 1327, 1221, 1138, 1066, 1018, 995, 916, 845, 795, 730, 687, 665, 513, 453, 440.

The IR spectrum of compound **I** was recorded on a Shimadzu IR Affinity-1S FT-IR spectrometer in KBr pellets in a range of 4000–400 cm^{-1}.

The X-ray diffraction analysis of a crystal of compound **I** was carried out on a D8 QUEST diffractometer (Bruker) (MoK_α radiation, λ = 0.71073 Å, graphite monochromator) at 296(2) K. The data collection and editing, refinement of unit cell parameters, and

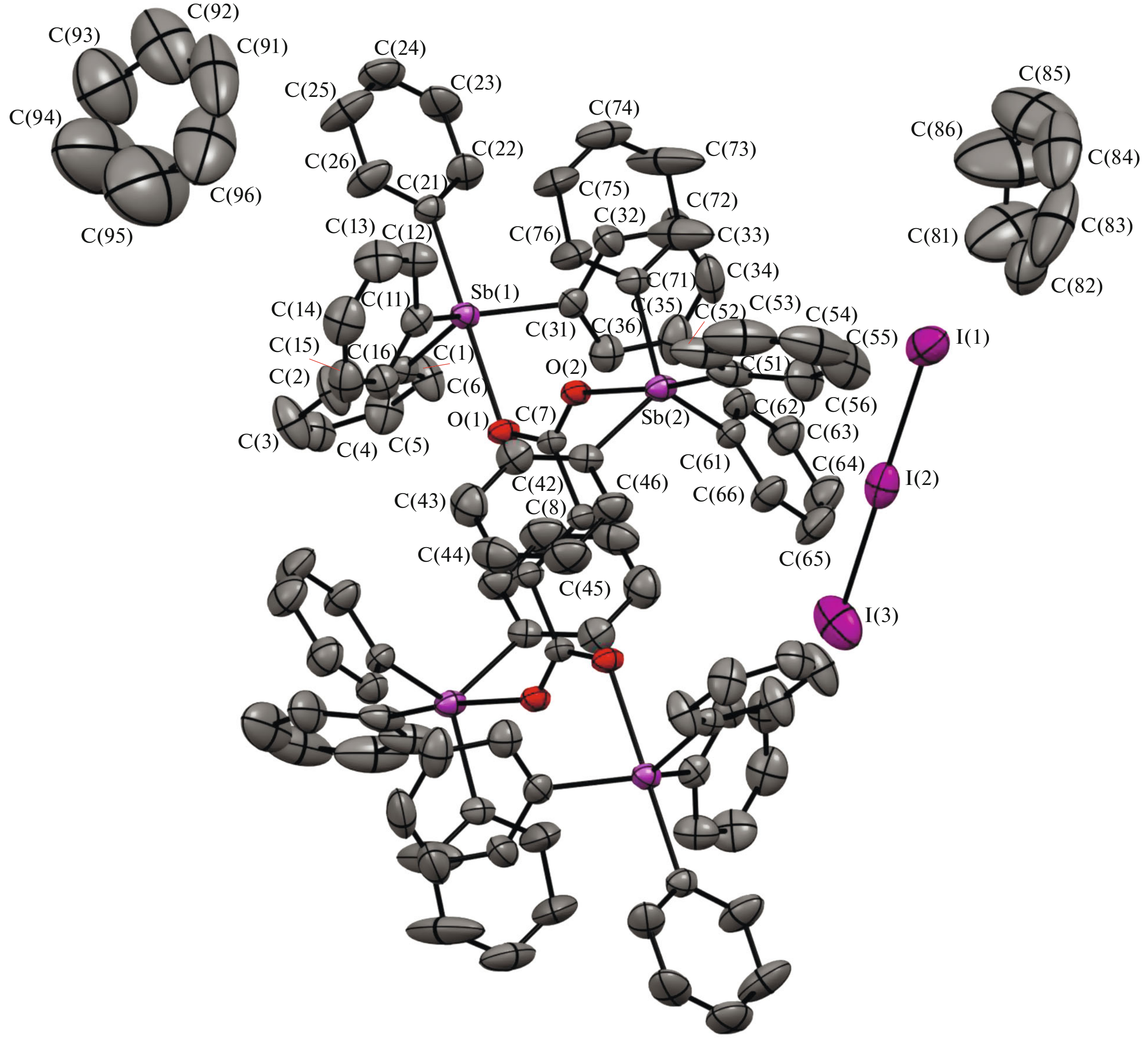
Table 1. Crystallographic data and the experimental and structure refinement parameters for compound **I**

Parameter	Value
FW	2910.50
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	14.8925(7)
b, Å	18.1041(9)
c, Å	21.7591(10)
β, deg	97.407(2)
V, Å^3	5817.6(5)
Z	2
ρ_{calcd}, g/cm^3	1.662
μ, mm^{-1}	2.561
F(000)	2812.0
Crystal size, mm	1.11 × 0.58 × 0.26
Range of data collection over 2θ, deg	6.98–50.88
Ranges of reflection indices	$-17 \le h \le 17$, $-21 \le k \le 21$, $-26 \le l \le 26$
Measured reflections (R_{int})	88635
Independent reflections	10653 (0.0391)
Number of reflections with $F^2 > 2\sigma(F^2)$	10653
Refinement variables	568
GOOF	1.059
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0536$, $wR_2 = 0.1065$
R factors for all reflections	$R_1 = 0.0765$, $wR_2 = 0.1256$
Residual electron density (min/max), e/Å^3	1.55/–1.44

applying an absorption correction were performed using the SMART and SAINT-Plus programs [3]. All calculations on structure determination and refinement were performed using the SHELXL/PC [4] and OLEX2 [5] programs. The structure was solved by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The crystallographic data and structure refinement results are presented in Table 1. Selected bond lengths and bond angles are given in Table 2. The full tables of

Table 2. Selected bond lengths (d) and bond angles (ω) in the structure of complex **I**

Bond	d, Å	Angle	ω, deg
I(1)–I(2)	2.9206(12)	C(1)Sb(1)C(31)	113.6(3)
I(2)–I(3)	2.8802(12)	C(1)Sb(1)C(11)	111.8(3)
Sb(1)–C(1)	2.113(6)	C(21)Sb(1)C(1)	96.1(2)
Sb(1)–C(31)	2.109(8)	C(21)Sb(1)C(11)	97.8(3)
Sb(1)–C(21)	2.158(7)	C(31)Sb(1)O(1)	82.3(2)
Sb(1)–C(11)	2.121(7)	C(41)Sb(2)C(51)	99.0(3)
Sb(1)–O(1)	2.347(4)	C(61)Sb(2)C(71)	117.3(3)
Sb(2)–O(2)	2.525(4)	C(61)Sb(2)C(51)	101.6(4)
Sb(2)–C(41)	2.106(7)	C(61)Sb(2)C(41)	115.9(3)
Sb(2)–C(61)	2.094(7)	C(71)Sb(2)O(2)	77.23(19)
Sb(2)–C(51)	2.122(8)	C(1)Sb(1)O(1)	83.16(19)
Sb(2)–C(71)	2.082(4)	I(3)I(2)I(1)	179.41(3)



Structure of complex **I** (hydrogen atoms are omitted).

atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1486690; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

We found that the reaction between bis(tetraphenylantimony) succinate (obtained using a described procedure [6]) and an excess of iodine in benzene afforded complex **I**

$$2Ph_4SbOC(O)CH_2CH_2C(O)OSbPh_4 + 3I_2 \xrightarrow{PhH} [(Ph_4Sb)_2O_2CCH_2CH_2CO_2(Ph_4Sb)_2][I_3]_2 \cdot 4PhH.$$

(I)

The crystal of compound **I** (figure) consists of triiodide anions, centrosymmetric (symmetry center at the middle of the C(8)–C(8a) bond) cations in which the $[Ph_4Sb]$ moieties are linked by the tetradentate bridging succinate ligand, and four molecules of solvate benzene (two types of crystallographically independent molecules). The Sb(1) and Sb(2) atoms have a distorted trigonal bipyramidal coordination mode. The axial angles C(21)Sb(1)O(1) and C(51)Sb(2)O(2) are equal to 178.8(2)° and 174.5(3)°, respectively. The equatorial CSb(1)C and CSb(2)C angles vary in the ranges 111.7(3)°–130.1(3)° and 116.0(3)°–119.1(2)°, respectively. The Sb(1) and Sb(2) atoms shift from the corresponding equatorial planes [C_3] to the axial carbon atom by 0.261 and 0.338 Å, respectively, resulting in a noticeable deviation of the angles between the axial and equatorial bonds from the theoretical value. The Sb(1)–C(21) axial bond length (2.158(7) Å) significantly exceeds the lengths of the Sb(1)–C(1, 11, 31) equatorial bonds (2.113(7), 2.120(7), and 2.109(7) Å), whereas the difference in the Sb(2)–C(51) (2.121(9) Å) and Sb(2)–C(41, 61, 71) bond lengths (2.106(7), 2.093(7), and 2.082(5) Å) is less noticeable. An increase in the strength of the Sb(2)–C atom binding compared to that of Sb(1)–C can be mentioned. The Sb(1)–O(1) and Sb(2)–O(2) distances are 2.347(4) and 2.525(4) Å, respectively. In addition, the intramolecular distance Sb(1)···O(2) (3.301(4) Å) is shorter than the sum of the van der Waals radii of antimony and oxygen (3.8 Å [7]). All presented geometric parameters characterizing the coordination polyhedra of the Sb(1) and Sb(2) atoms indicate a higher distortion of the polyhedron for the second atom. The C(7)–O(1) and C(7)–O(2) bond lengths are almost equalized (1.262(8) and 1.255(8) Å), which is usually observed for carboxylate anions. The O(1)C(7)O(2) bond angle is 122.6(6)°. The triiodide anion is nonsymmetrical, the I(1)I(2)I(3) angle is 179.41(4)°, and the I(1)–I(2) and I(2)–I(3) bond lengths are 2.921(1) and 2.880(1) Å, respectively.

Note that the succinate ligand in the centrosymmetric molecule of bis(tetraphenylantimony) succinate is also tetradentate and each carboxyl group coordinates the antimony atom by two oxygen atoms via the nonsymmetrical mode. The Sb–O(1, 2) distances (2.319(2) and 2.528(2) Å) are close to those observed in complex **I**. The coordination number of the antimony atom increases to 6, and its coordination polyhedron can be considered as a strongly distorted octahedron [6].

Monomolecular layers of [(μ_4-succinato)hexadecaphenyltetraantimony] are formed in the crystal structure of compound **I** in the direction $(1\bar{1}0)$. The binding inside the layer occurs via the weak van der Waals and π–π aromatic interactions between the symmetrically equivalent rings C(51)–C(56). The planes of the interacting fragments are parallel, the distance between them is ~3.42 Å, and the relative shift of the centers of gravity of the rings is ~2.44 Å. The triiodide anions and solvate benzene molecules are arranged between the layers of [(μ_4-succinato)hexadecaphenyltetraantimony].

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REFERENCES

1. Goel, R.G., *Can. J. Chem.*, 1969, vol. 47, no. 24, p. 4607.
2. Millington, P.L. and Sowerby, D.B., *J. Chem. Soc., Dalton Trans.*, 1992, no. 7, p. 1199.
3. *SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System*, Madison: Bruker AXS Inc., 1998.
4. *SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*, Madison: Bruker AXS Inc., 1998.
5. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., et al., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339.
6. Sharutin, V.V. and Sharutina, O.K., *Russ. J. Coord. Chem.*, 2014, vol. 40, no. 9, p. 643.
7. Batsanov, S.S., *Zh. Neorg. Khim.*, 1991, vol. 36, no. 12, p. 3015.

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