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PHYSICAL METHODS
OF INVESTIGATION

Adducts of Tetraphenylstibium Nitrate with Nitric Acid and of Tetraphenylstibium Acetate with Acetic Acid: Syntheses and Structures

V. V. Sharutin, V. S. Senchurin, O. K. Sharutina, and L. P. Panova
Blagoveshchensk State Pedagogical University, ul. Lenina 104, Blagoveshchensk, 675000 Russia

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Abstract—The reactions of tetraphenylstibium nitrate with nitric acid and of tetraphenylstibium acetate with acetic acid yield adducts $Ph_4SbONO_2 \cdot HNO_3$ (**I**) and $Ph_4SbOC(O)CH_3 \cdot CHH_3COOH$ (**II**). According to X-ray diffraction data, the antimony atom in $[Ph_4Sb]^+[O_2N–O\cdots H\cdots O–NO_2]^-$ has a tetrahedral coordination. The CSbC bond angles and Sb–C bond lengths vary within 108.04(6)°–109.75(4)° and 2.096(1)–2.098(1) Å, respectively. The anion includes the intermolecular hydrogen bond O(1)–H(1)···O(1)'': the O(1)–H(1), H(1)···O(1)'', and O(1)···O(1)'' distances are 0.91(4), 1.56(4), and 2.460(2) Å, respectively; and the OHO angle is 169(5)°. The nitrate groups are usually planar. Complex **II** also contains the intermolecular hydrogen bond with the following parameters: O(3)–H(3), 0.92 Å; H(3)···O(2), 1.68 Å; and O(3)···O(2) 2.594 Å; the O(2)H(3)O(3) angle is 172.1°. This H-bond noticeable changes the coordination polyhedron of the antimony atom compared to that in tetraphenylstibium acetate.

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Pentaarylstibium reacts with organic compounds (HX) containing an active hydrogen atom, such as alcohols, phenols, β-diketones, and carboxylic and sulfonic acids, to form, as a rule, products of the general formula Ar_4SbX; i.e., pentaarylstibium is selectively dearylated to eliminate only one aryl group [1, 2]. The addition of one mole of carboxylic acid to tetramethyl- or tetraphenylstibium acylate results in the formation of stable crystalline monomeric adducts $R_4SbOC(O)R' \cdot HOC(O)R''$ ($R = CH_3$; $R' = H$, $R'' = H$; $R' = CH_3$, $R'' = CH_3$; $R' = CH_3$, $R'' = C_6H_5$; $R'= C_6H_5$, $R''= C_6H_5$; $R = C_6H_5$, $R' = CH_3$, $R'' = CH_3$ [3]. Under severe conditions, pentaphenylstibium and tetraphenylstibium bromide are dephenylated to triphenylstibium dibromide [1].

This work studies the reaction of tetraphenylstibium nitrate with nitric acid and the structure of the resulting adduct $Ph_4SbNO_3 \cdot HNO_3$ (**I**). We also refine the earlier established [4] structure of the adduct of tetraphenylstibium acetate with acetic acid, $Ph_4SbOC(O)CH_3 \cdot HOC(O)CH_3$ (**II**). The changes in the geometric parameters of Ph_4SbX molecules caused by the additional acid molecule are analyzed.

EXPERIMENTAL

Synthesis of compound I. Tetraphenylstibium nitrate was recrystallized from 10% nitric acid. Uncolored crystals with mp = 102°C were obtained. IR, cm^{-1}: 3054, 2924, 1699, 1575, 1478, 1444, 1434, 1419, 1384, 1334, 1161, 1066, 1019, 999, 929, 800, 739, 688, 509, 463.

For $C_{2}4H_{21}O_6N_2Sb$ anal. calcd. (%): C, 51.70; H, 3.54; N, 4.97.

Found (%): C, 51.89; H, 3.78; N, 5.04.

Synthesis of compound II. Tetraphenylstibium acetate was recrystallized from 95% acetic acid. Uncolored crystals with mp = 118°C (112–113°C [4]) were obtained. IR, cm^{-1}: 3059, 2988, 2923, 1733, 1634, 1582, 1570, 1479, 1431, 1395, 1364, 1335, 1295, 1275, 1067, 1019, 997, 738, 692, 469.

For $C_{28}H_{27}O_4Sb$ anal. calcd. (%): C, 61.20; H, 4.92.

Found (%): C, 61.01; H, 4.83.

IR spectra were recorded on an FSM1201 FTIR spectrometer in KBr pellets.

Single-crystal X-ray diffraction analyses of compounds **I** and **II** were carried out on a SMART-1000 CCD diffractometer (Bruker, MoK_α radiation, graphite monochromator).

Structures **I** and **II** were determined by a 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 into the refinement in the riding model.

The data were collected and edited and the unit cell parameters were refined using the SMART and SAINT *Plus* programs [5]. All calculations on structure determination and refinement were performed according to the SHELXTL/PC programs [6].

Selected crystallographic data and the results of refinement for structures **I** and **II** are given in Table 1.

Table 1. Crystallographic data and details of the X-ray experiment and structure refinement for compounds **I** and **II**

Parameter	Value	
	I	II
FW	555.18	549.25
T, K	173(1)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P21/n$
a, Å	18.133(1)	16.288(2)
b, Å	6.519(1)	10.334(1)
c, Å	19.095(1)	17.117(2)
β, deg	93.713(1)	117.113(2)
V, Å^3	2252.4(1)	2567.1(5)
Z	4	4
ρ_{calcd}, g/cm^3	1.637	1.421
μ, mm^{-1}	1.269	1.105
$F(000)$	1112	1112
Crystal shape (size, mm)	Prism (0.35 × 0.30 × 0.15)	Prism (0.30 × 0.30 × 0.35)
θ range, deg	3.00–31.64	2.34–30.04
Intervals of reflection indices	$-26 \leq h \leq 20$, $-8 \leq k \leq 9$, $-28 \leq l \leq 28$	$-22 \leq h \leq 19$, $-11 \leq k \leq 14$, $-21 \leq l \leq 24$
Measured reflections	9046	18216
Independent reflections	3726 ($R_{int} = 0.0288$)	7156 ($R_{int} = 0.0476$)
Refinement variables	154	303
GOOF	1.039	0.869
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0219$, $wR_2 = 0.0639$	$R_1 = 0.0291$, $wR_2 = 0.0569$
R factors for all reflections	$R_1 = 0.0229$, $wR_2 = 0.0648$	$R_1 = 0.0507$, $wR_2 = 0.0616$
Residual electron density (min/max), e/Å^3	–0.643/0.637	–0.454/0.366

The coordinates of atoms and temperature factors are presented in Table 2. Selected bond lengths and bond angles are listed in Table 3.

RESULTS AND DISCUSSION

Tetraphenylstibium nitrate (light yellow crystals with mp = 186°C), synthesized from pentaphenylstibium and an equimolar amount of nitric acid in an aqueous-acetate solution, was treated with excess nitric acid. Regardless of the reaction conditions (temperature, solvent, time, acid concentration), the product was the same compound $Ph_4SbNO_3 \cdot HNO_3$ (**I**) in the form of colorless needle-like crystals with mp = 102°C. The IR spectrum of complex **I**, unlike the IR spectrum of tetraphenylstibium nitrate, contains absorption bands at 1384 cm^{-1} (vs) and 800 cm^{-1} (w), which are characteristic of the nitrate ion.

According to the X-ray diffraction data, the composition of adduct **I** can be presented by the formula $[Ph_4Sb]^+[O_2N–O\cdots H\cdots O–NO_2]^-$ (Fig. 1). The antimony atom in the $[Ph_4Sb]^+$ cation has an almost regular tetrahedral coordination. The CSbC bond angles and Sb–C bond lengths vary in intervals of 108.04(6)°–109.75(4)° and 2.096(1)–2.098(1) Å, respectively (Table 3). The anion includes the intermolecular hydrogen bond O(1)–H(1)···O(1)'': the O(1)–H(1), H(1)···O(1)'', and O(1)···O(1)'' distances are 0.91(4), 1.56(4), and 2.460(2) Å, respectively, and the OHO angle is 169(5)°. The nitrate groups are planar, and the ONO angles range from 118.05° to 124.66°. The N–O(2,3) distances in complex **I** are equal to 1.218(1) and 1.221(1)Å and correspond to the length of the delocalized double bond $N\overset{\cdots}{-}O$ (1.22 Å [7]), and the N–O(1) bond (1.316(1) Å) is substantially shorter than the ordinary bond N–O in nitric acid (1.41 Å [7]).

In a molecule of compound **III**, the antimony atom has a distorted trigonal bipyramidal coordination [8]. The $C_{ax}SbC_{eq}$, $OSbC_{eq}$, $C_{eq}SbC_{eq}$, and $OSbC_{ax}$ bond angles in molecules **a** and **b** in a crystal of compound **III** are as follows: 100.0°–100.2° (100.2°), 78.1°–81.3° (79.8°), 114.7°–119.6° (350.8°), and 178.4° and 96.3°–100.3° (98.7°), 74.5°–85.1° (81.53°), 114.4°–

Table 2. Coordinates of atoms (×10^4) and their isotropic equivalent temperature parameters (×10^3) in structures **I** and **II**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
		I		
Sb	10000	3069.4(1)	7500	17.35(2)
O(1)	7052(1)	3915(2)	5003(1)	32.5(2)
H(1)	7410(30)	2940(50)	5050(30)	42(3)
O(2)	6874(1)	6755(2)	5555(1)	43.7(3)
O(3)	7862(1)	4983(2)	5812(1)	46.0(3)
N	7274(1)	5280(2)	5479(1)	27.5(2)
C(11)	9066(1)	1180(2)	7365(1)	19.0(2)
C(12)	8899(1)	–124(2)	7914(1)	23.0(2)
C(13)	8291(1)	–1421(2)	7828(1)	26.0(2)
C(14)	7867(1)	–1446(2)	7193(1)	25.8(2)
C(15)	8039(1)	–157(2)	6648(1)	24.8(2)
C(16)	8636(1)	1182(2)	6732(1)	21.6(2)
C(21)	9902(1)	4869(2)	8401(1)	20.1(2)
C(22)	10468(1)	6211(2)	8623(1)	24.8(2)
C(23)	10390(1)	7406(2)	9217(1)	30.0(3)
C(24)	9747(1)	7260(2)	9577(1)	30.5(3)
C(25)	9189(1)	5912(2)	9356(1)	29.1(2)
C(26)	9262(1)	4703(2)	8768(1)	23.2(2)
		II		
Sb	4844.85(6)	8225.0(1)	1819.78(5)	40.27(3)
O(1)	3408(1)	7845(1)	1703(1)	56.3(3)
O(2)	3684(1)	8884(1)	2934(1)	74.0(4)
O(3)	3219(1)	9401(2)	4163(1)	94.5(5)
O(4)	3582(1)	8898(2)	5515(1)	124.3(7)
C(1)	3171(1)	8277(2)	2271(1)	63.3(5)
C(2)	2190(1)	7960(4)	2071(1)	151(1)
C(3)	3753(1)	8846(2)	4916(1)	77.1(6)
C(4)	4573(2)	8174(3)	4972(2)	130(1)
C(11)	4294(1)	7131(1)	645(1)	42.8(4)
C(12)	4640(1)	7351(2)	54(1)	56.0(5)
C(13)	4306(1)	6657(2)	–716(1)	71.8(6)
C(14)	3650(1)	5722(2)	–895(1)	70.7(6)
C(15)	3318(1)	5478(2)	–305(1)	64.8(5)
C(16)	3630(1)	6184(2)	458(1)	52.8(4)
C(21)	6164(1)	8603(2)	1844(1)	43.3(4)
C(22)	6349(1)	9771(2)	1564(1)	52.4(4)
C(23)	7143(1)	9925(2)	1465(1)	63.4(5)
C(24)	7751(1)	8924(2)	1641(1)	70.5(6)
C(25)	7573(1)	7755(2)	1919(1)	69.5(6)
C(26)	6791(1)	7596(2)	2021(1)	57.0(5)
C(31)	4419(1)	10168(2)	1692(1)	44.4(4)
C(32)	4871(1)	11035(2)	2367(1)	55.7(5)
C(33)	4607(1)	12316(2)	2258(1)	69.6(5)
C(34)	3907(1)	12727(2)	1481(1)	78.4(6)
C(35)	3465(1)	11874(2)	816(1)	79.5(6)
C(36)	3716(1)	10597(2)	912(1)	61.4(5)
C(41)	5337(1)	7157(2)	3004(1)	43.7(4)
C(42)	6143(1)	7551(2)	3721(1)	54.3(5)
C(43)	6479(1)	6849(2)	4495(1)	64.6(5)
C(44)	6033(1)	5766(2)	4550(1)	68.4(6)
C(45)	5238(1)	5370(2)	3842(1)	67.6(5)
C(46)	4883(1)	6070(2)	3066(1)	55.7(5)
H(3)	3330(12)	9240(20)	3693(12)	110

Table 3. Bond lengths (*d*) and bond angles (ω) in structures **I** and **II**

Bond	*d*, Å	Angle	ω, deg
		I	
Sb–C(11)	2.0964(10)	C(11)SbC(11)'	108.04(6)
Sb–C(11)'	2.0964(10)	C(11)SbC(21)	108.58(4)
Sb–C(21)	2.0985(10)	C(11)'SbC(21)	109.75(4)
Sb–C(21)'	2.0985(10)	C(11)SbC(21)'	109.75(4)
O(1)–N	1.3158(14)	C(11)'SbC(21)'	108.58(4)
O(1)–H(1)	0.91(4)	C(21)SbC(21)'	112.04(6)
O(2)–N	1.2179(15)	NO(1)H(1)	103(3)
O(3)–N	1.2207(14)	O(2)NO(3)	124.66(12)
C(11)–C(16)	1.3941(14)	O(2)NO(1)	117.29(11)
C(11)–C(12)	1.3986(15)	O(3)NO(1)	118.05(11)
C(12)–C(13)	1.3902(16)	C(16)C(11)C(12)	120.91(9)
C(13)–C(14)	1.3943(17)	C(16)C(11)Sb	120.53(7)
C(14)–C(15)	1.3885(17)	C(12)C(11)Sb	118.53(7)
		II	
Sb–C(31)	2.105(2)	C(31)SbC(11)	115.79(5)
Sb–C(11)	2.118(1)	C(31)SbC(41)	124.07(6)
Sb–C(41)	2.119(1)	C(11)SbC(41)	116.17(6)
Sb–C(21)	2.166(2)	C(31)SbC(21)	96.15(6)
Sb–O(1)	2.291(1)	C(11)SbC(21)	95.83(6)
O(1)–C(1)	1.279(2)	C(41)SbC(21)	97.83(5)
O(2)–C(1)	1.232(2)	C(31)SbO(1)	83.05(5)
O(3)–C(3)	1.313(2)	C(11)SbO(1)	81.47(5)
O(4)–C(3)	1.181(2)	C(41)SbO(1)	85.43(5)
C(1)–C(2)	1.509(3)	C(21)SbO(1)	176.47(4)
C(3)–C(4)	1.469(3)	O(2)C(1)O(1)	124.4(2)
C(11)–C(12)	1.383(2)	O(2)C(1)C(2)	121.5(2)
C(11)–C(16)	1.384(2)	O(1)C(1)C(2)	114.0(2)
C(12)–C(13)	1.376(2)	O(4)C(3)O(3)	121.4(2)
C(13)–C(14)	1.368(3)	O(4)C(3)C(4)	122.1(2)
C(14)–C(15)	1.370(3)	O(3)C(3)C(4)	116.6(2)

Symmetry transformations:' $-x + 2$, y, $-z + 3/2$; " $-x + 3/2$, $-y + 1/2$, $-z + 1$.

119.8° (353.3°), and 170.7° respectively (the average values of the angles or the sums of the corresponding angles are given in parentheses). The average Sb–C_{eq} bond lengths (2.108 (a) and 2.104 (b) Å) are less than the Sb–C axial bonds (2.138 and 2.134 Å, respectively). The Sb–O distances are 2.548 Å (a) and 2.493 Å (b).

The nitrate groups in both compounds **III** and **I** are planar; the angles at the nitrogen atoms do not virtually differ from a theoretical value of 120° (118.0°–121.6°, 118.0°–121.3° in **III**, **a** and **b**). The N–O bond lengths in

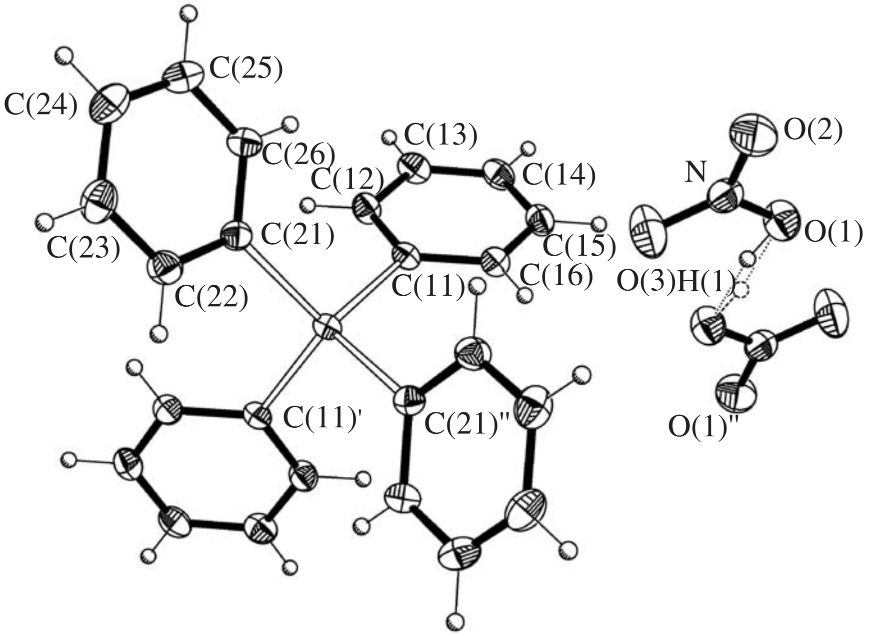

Fig. 1. Structure of complex **I**.

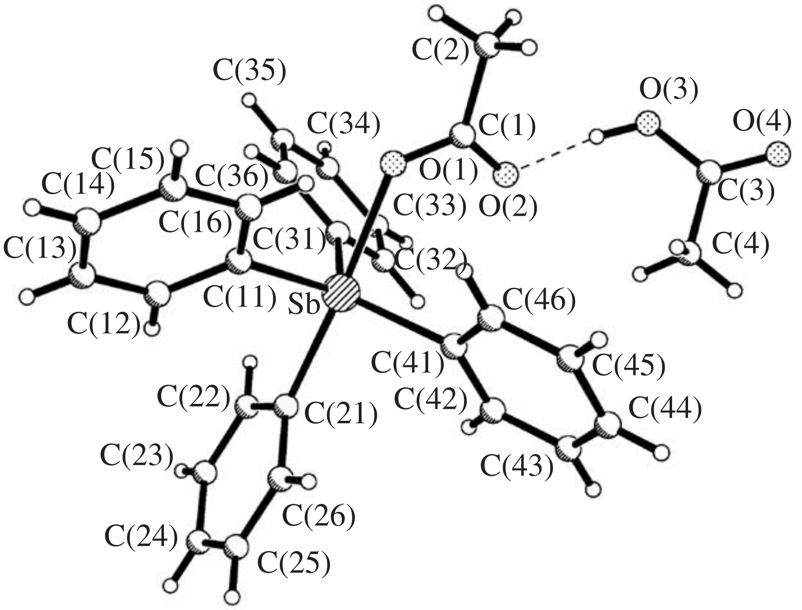

Fig. 2. Structure of complex **II**.

compound **III** (**a** and **b**) are 1.278, 1.249, 1.225 Å and 1.269, 1.241, and 1.226 Å, respectively. The longer bond is observed with the oxygen atom that is coordinated to the antimony atom. The observed values suggest the electron density distribution in the nitrate group like that in the nitrate anion.

Thus, the tendency of the central atom in compound **III** to acquire the tetrahedral coordination mode is implemented in complex **I**, because the introduction of an acid molecule enhances the efficient delocalization of the negative charge and the stability of the anion.

We refined the structure of complex **II**, in which the carbonyl oxygen atom of the acetate ligand is hydrogen-bonded to the hydroxy group of the acetic acid molecule (Fig. 2). The presence of the rather stable intermolecular hydrogen bond (O(3)–H 0.92, H···O(2)

1.68, O(3)···O(2) 2.594 Å, O(2)HO(3) angle 172.1°) noticeably changes the geometric parameters of complex **II** (Table 3) compared to the same characteristics of tetraphenylstibium acetate (**IV**). For example, the Sb–O bond (2.291 Å) in complex **II** is much longer than that in compound **IV** (2.234 Å). The Sb···O=C distance in compound **I** is 3.307 Å, whereas this distance in **IV** is 2.594 Å. On the contrary, the axial and equatorial Sb–C bonds (2.166 Å and 2.105, 2.118, and 2.119 Å) in compound **II** are much shorter than those in **IV** (2.179 Å and 2.136, 2.138, and 2.143 Å). The coordination polyhedron of the antimony atom in compound **II** is less distorted (the CSbO axial angle is 176.47°; the CSbC equatorial angles are 115.79°, 116.17°, and 124.07°) than that in compound **IV** (the corresponding angles are 170.04°, 102.15°, 102.92°, and 152.62°) because the strong intramolecular Sb···O=C interaction is absent.

In adduct **II**, the C–O distance in the acetate fragment is 1.279 Å and coincides with that in **IV**. The C=O bond in the carbonyl group in **II** (1.232 Å) is shorter than that in **IV** (1.266 Å), which correlates with a less stable Sb···O=C contact. The C(3)–O(3) and C(3)–O(4) distances in an acetic acid molecule are 1.313 and 1.181 Å, respectively.

In tetraphenylstibium carboxylates $Ph_4SbOC(O)R$, the distance between the antimony atom and carbonyl oxygen atom (which are not formally linked to each other) was found to be 2.594–3.509 Å [9–21] (the sum of the van der Waals radii of the antimony and oxygen atoms is 3.70 Å [22]), and in **IV** this value is minimum (2.594 Å) [9]. The strength of the Sb···O=C intramolecular contact, associated with the donor-acceptor interaction, is obviously due to many factors, for instance, the electron-donating ability of the oxygen atom of the carbonyl group. This ability, in turn, is caused by the nature of the organic radical R. A considerable weakening of the Sb···O=C contact in **II** compared to that in **IV** indicates that intermolecular interactions involving the carbonyl oxygen atom play an important role in the formation of compound **IV**.

Thus, the appearance of an additional acid molecule in the $Ph_4SbX \cdot HX$ adduct ($X = NO_3$ or $OC(O)CH_3$) affects the geometric parameters of the X fragments and also substantially changes the coordination polyhedron of the antimony atom.

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