Tri- and Tetraphenylantimony Propiolates: Syntheses and Structures

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Abstract—The reaction of triphenylantimony with propiolic acid in the presence of hydrogen peroxide (molar ratios 1 : 2 : 1 and 1 : 1 : 1) in diethyl ether affords triphenylantimony dipropiolate Ph₃Sb[OC(O)C=CH]₂ (I) and μ_2 -oxobis[(propiolato)triphenylantimony] [Ph₃SbOC(O)C=CH]₂O (II). Tetraphenylantimony propiolate Ph₄SbOC(O)C=CH (III) is synthesized from pentaphenylantimony and propiolic or acetylenedicarboxylic acid in toluene. According to the X-ray diffraction data, the crystals of compounds I and III include two types of crystallographically independent molecules (a and b). The antimony atoms in molecules Ia, Ib, II, IIIa, and IIIb have the trigonal—bipyramidal coordination mode with different degrees of distortion. The OSbO and OSbC axial angles are 176.8(2)° (Ia, Ib), 170.17(15)°, 178.78(14)° (II), and 173.2(5)°, 174.4(5)° (IIIa, IIIb). The CSbC equatorial angles lie in the ranges 108.2(3)°–143.1(3)° (I), 109.0(2)°–131.0(2)° (II), and 113.1(4)°–125.4(4)° (III). The SbOSb angle in II is 141.55(19)°. The Sb–C bond lengths are 2.103(8)–2.141(5) (I), 2.105(5)–2.119(5) (II), and 2.076(12)–2.166(13) Å (III). The Sb–O distances increase in a series of I, II, and III: 2.139(6)–2.156(7) (Ia, Ib); 2.206(4), 2.218(3) (II); and 2.338(10), 2.340(10) Å (III).

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INTRODUCTION

The antimony(V) phenyl derivatives containing carboxylate ligands of the type $Ph_4SbOC(O)R$ and $Ph_3Sb[OC(O)R]_2$ are studied fairly well [1, 2], whereas compounds $[Ph_3SbOC(O)R]_2O$ are investigated to a lower extent [3–6]. It is known that carboxylate ligands, as a rule, are anisobidentate. The asymmetry of the coordination mode of the same ligand in compounds of different types can strongly differ. In tetraphenylantimony acetate the Sb–O and Sb…O distances are 2.234 and 2.594 Å [7], whereas they are 2.130 and 2.780 Å in triphenylantimony diacetate [8].

The purpose of this work is the synthesis of triphenylantimony dipropiolate $Ph_3Sb[OC(O)C=CH]_2$ (I), μ_2 , μ_2 -oxobis[(propiolato)triphenylantimony] [Ph_3SbOC(O)C=CH]_2O (II), and tetraphenylantimony propiolate $Ph_4SbOC(O)C=CH$ (III) and the elucidation of regularities of the coordination mode of the carboxylate ligands, depending on the type of the compound.

EXPERIMENTAL

Synthesis of I. A 30% aqueous solution of hydrogen peroxide (0.096 g) was added to a mixture of triphenylantimony (0.30 g, 0.85 mmol) and propiolic acid (0.12 g, 1.70 mmol) in diethyl ether (15 mL), and the mixture was kept for 24 h at 20°C. The yield of colorless crystals of compound I was 0.38 g (91%); m.p. = 146° C (with decomposition). IR, v, cm⁻¹: 3274, 3067, 2360, 2189, 2106, 1640, 1576, 1542, 1480, 1436, 1292, 1185, 1164, 1070, 1021, 996, 903, 843, 773, 735, 685, 667, 631, 592, 461.

For C ₂₄ H ₁₇ O ₄ Sb		
anal. calcd., %:	C, 58.69;	Н, 3.46.
Found, %:	C, 58.53;	Н, 3.54.

Synthesis of II. A 30% aqueous solution of hydrogen peroxide (0.096 g) was added to a mixture of triphenylantimony (0.30 g, 0.85 mmol) and propiolic acid (0.06 g, 0.85 mmol) in diethyl ether (15 mL), and the mixture was kept for 24 h at 20°C. The formed finely crystalline powder was recrystallized from toluene. The yield of colorless crystals of compound II was 0.29 g (80%); m.p. = 166°C (with decomposition).

IR, v, cm⁻¹: 3274, 3053, 2106, 1640, 1576, 1480, 1435, 1386, 1292, 1185, 1071, 1021, 997, 896, 773, 734, 716, 688, 667, 631, 615, 458.

Synthesis of III. (A) A mixture of pentaphenylantimony (0.50 g, 0.99 mmol) and propiolic acid (0.07 g, 0.99 mmol) in toluene (10 mL) was heated for 1 h in a boiling water bath, then the bath and the mixture were cooled down, and the solvent was removed. The yield

Table 1.	Crystallographic	data and the	experimental	and refinement	t parameters for structures	I-III
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Demonster	Value				
Parameter	Ι	II	III		
M	491.13	860.18	998.38		
<i>Т</i> , К	296(2)	296(2)	273.15		
Crystal system	Triclinic	Monoclinic	Triclinic		
Space group	$P\overline{1}$	$P2_{1}/c$	$P\overline{1}$		
<i>a</i> , Å	8.085(6)	20.062(6)	10.2129(12)		
<i>b</i> , Å	8.155(3)	9.996(4)	10.2899(12)		
<i>c</i> , Å	17.234(9)	19.739(5)	12.7441(16)		
α, deg	100.75(4)	90.00	78.951(4)		
β, deg	99.92(5)	110.36(2)	66.758(4)		
γ, deg	102.84(4)	90.00	68.055(3)		
<i>V</i> , Å ³	1061.0(10)	3711(2)	1139.9(2)		
Ζ	2	4	2		
$\rho_{calcd}, g/cm^3$	1.537	1.539	1.454		
μ , mm ⁻¹	1.326	1.499	1.230		
<i>F</i> (000)	488.0	1704.0	500.0		
Crystal size, mm	$0.19 \times 0.14 \times 0.03$	$0.32 \times 0.22 \times 0.14$	$0.48 \times 0.16 \times 0.09$		
θ Range for data collection, deg	5.26-61.12	4.34-61.86	5.66-49.48		
Ranges of reflection indices	$-11 \le h \le 8,$	$-16 \le h \le 29,$	$-11 \le h \le 11,$		
	$-9 \le k \le 11,$	$-14 \le k \le 13,$	$-11 \le k \le 12,$		
	$-24 \le l \le 24$	$-28 \le l \le 28$	$-14 \le l \le 14$		
Measured reflections	11748	41045	61919		
Independent reflections	7629	11598	7525		
R _{int}	0.0436	0.0545	0.0513		
Refinement variables	523	442	541		
Goodness-of-fit	1.082	1.092	1.073		
<i>R</i> factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0517, wR_2 = 0.0867$	$R_1 = 0.0589, wR_2 = 0.0930$	$R_1 = 0.0237, wR_2 = 0.0548$		
<i>R</i> factors for all reflections	$R_1 = 0.0927, wR_2 = 0.0991$	$R_1 = 0.1158, wR_2 = 0.1142$	$R_1 = 0.0285, wR_2 = 0.0568$		
Residual electron density (min/max), $e/Å^3$	1.26/-1.26	1.66/-1.74	0.58/-0.39		

of colorless crystals of compound III was 0.41 g (83%); m.p. = 174° C (with decomposition).

(B) A mixture of pentaphenylantimony (0.250 g, 0.49 mmol) and acetylenedicarboxylic acid (0.056 g, 0.49 mmol) in toluene (5 mL) was heated for 1 h in a boiling water bath. Then the mixture was cooled down, and the solvent was removed. The yield of colorless crystals of compound **III** was 0.214 g (87%); m.p. = 174° C (with decomposition).

IR, v, cm⁻¹: 3277, 3053, 3010, 2990, 2917, 2591, 2361, 2178, 2091, 1967, 1885, 1819, 1621, 1575, 1562, 1477, 1433, 1377, 1333, 1301, 1187, 1158, 1070, 1057, 1020, 997, 883, 782, 737, 693, 658, 643, 601, 586, 462, 447.

For C ₂₇ H ₂₁ O ₂ Sb		
anal. calcd., %:	C, 64.96;	H, 4.21.
Found, %:	C, 64.81;	H, 4.29.

IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer (pellets with KBr).

X-ray diffraction analyses for crystals I–III were carried out on a D8 QUEST diffractometer (Bruker, Mo K_{α} radiation, $\lambda = 0.71073$ Å, graphite monochromator). Data were collected and edited, unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-Plus programs [9]. All calculations on the determination and refinement of structure I were performed using the SHELXL/PC programs [10]. The structures were determined by a direct method and refined by least squares in the anisotropic approximation for nonhydrogen atoms. The main crystallographic data and the refinement results for I–III are presented in Table 1. Selected bond lengths and bond angles are given in Table 2. The full tables of atomic coordinates, bond lengths, and bond angles for structures **I–III** were deposited with the Cambridge Crystallographic Data Centre (nos. 940655–940657; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Triphenylantimony dipropiolate (I) and μ_2 -oxobis[(propiolato)triphenylantimony] (II) were synthesized from triphenylantimony and propiolic acid in the presence of hydrogen peroxide at different molar ratios (1 : 2 : 1 and 1 : 1 : 1, respectively)

 $Ph_3Sb + 2HOC(O)C \equiv CH + H_2O_2$

$$\rightarrow$$
 Ph₃Sb[OC(O)C=CH]₂ + H₂O,

 $2Ph_3Sb + HOC(O)C \equiv CH + 2H_2O_2$

$$\rightarrow$$
 [Ph₃SbOC(O)C=CH]₂O + H₂O.

Tetraphenylantimony propiolate (III) was synthesized by the dephenylation of pentaphenylantimony with propiolic acid on heating in a toluene solution (1 h, 100° C)

 $Ph_5Sb + HOC(O)C \equiv CH$

$$Ph_4SbOC(O)C \equiv CH + PhH.$$

Product **III** is also formed by the reaction of pentaphenylantimony with acetylenedicarboxylic acid, which evidently undergoes decarboxylation under the reaction conditions

Ph₅Sb + HOC(O)C≡CC(O)OH \rightarrow III + CO₂ + PhH.

According to the X-ray diffraction data, the crystals of compounds I and III include two types of crystallographically independent molecules (a and b). The antimony atoms in molecules Ia, Ib, II, IIIa, and IIIb have the trigonal-bipyramidal coordination mode with different degrees of distortion (figure). The axial positions of molecules Ia and Ib contain the oxygen atoms of the carboxylate ligands, those of molecules II contain the oxygen atoms (bridging and carboxylate), and the axial positions of molecules IIIa and IIIb contain the carbon atom of the phenyl group and the carboxvlate oxvgen atom. The OSbO axial angles in compounds Ia and Ib coincide (176.8(2)°) and substantially differ in two fragments of molecule II 170.17(15)°, (O(2)Sb(1)O(1))O(4)Sb(2)O(1)178.78(14)°). The C_{ax}SbO angles in molecules IIIa and IIIb are similar $(174.4(5)^{\circ} \text{ and } 173.2(5)^{\circ})$ (Table 2). The substantial distortion of the O(2)Sb(1)O(1) angle in structure II can be explained by the deviation of the Sb(1)-O(2) and Sb(1)-O(1)bonds from the C(11)-C(16) phenyl axial group, whose plane almost coincides with the equatorial plane C(1)C(11)C(21) (the angle between them is only 8.92°). The O(2)Sb(1)C(11) and O(1)Sb(1)C(11) angles are 92.16(18)° and 97.40(18)°. In molecules Ia and Ib, the antimony atoms shift from the equatorial plane by 0.006 and 0.003 Å. In structure II, the Sb(1) and Sb(2) atoms are shifted to the bridging oxygen atom by 0.115 and 0.137 Å,
 Table 2. Selected bond lengths and bond angles in structures I–III

Bond	d, Å	Angle	ω, deg
		Ι	
Sb(1)–O(3)	2.156(7)	C(21)Sb(1)O(3)	89.7(3)
Sb(1)–C(21)	2.109(9)	C(21)Sb(1)O(1)	91.1(3)
Sb(1)–O(1)	2.152(7)	C(21)Sb(1)C(1)	109.4(3)
Sb(1) - C(11)	2.103(8)	O(1)Sb(1)O(3)	176.8(2)
Sb(1) - C(1)	2.138(5)	C(11)Sb(1)O(3)	91.8(3)
Sb(2) - O(5)	2.139(6)	C(11)Sb(1)C(21)	142.4(4)
Sb(2) - O(7)	2.141(6)	C(11)Sb(1)O(1)	89.5(3)
Sb(2) - C(31)	2.124(9)	C(11)Sb(1)C(1)	108.2(3)
Sb(2) - C(41)	2.112.(9) 2.118(9)	C(1)Sb(1)O(3)	88.4(2)
Sb(2) - C(51)	2.110(5) 2.141(5)	C(1)Sb(1)O(1)	88.4(2)
O(3) - C(17)	1.308(9)	O(5)Sb(2)O(7)	176.8(2)
O(3) = C(27)	1.300(9) 1.233(10)	O(5)Sb(2)O(7)	89 1(2)
O(2) - C(27)	1.233(10) 1.321(0)	O(3)Sb(2)C(51)	87.7(2)
O(3) = C(37)	1.321(9) 1.220(10)	C(21)Sb(2)C(31)	07.7(2) 00.7(3)
O(1) - C(27)	1.320(10) 1.206(0)	C(31)Sb(2)O(3)	90.7(3)
O(7) = C(47)	1.300(9) 1.220(10)	C(31)Sb(2)O(7)	89.9(3)
O(8) = C(47)	1.230(10)	C(31)SD(2)C(31)	108.7(3)
C(1/) = O(4)	1.232(9)	C(41)Sb(2)O(5)	89.7(3)
O(6) - C(5/)	1.227(9)	C(41)Sb(2)O(7)	91.8(3)
Sb(1) = O(2)	2 206(4)	O(1)Sb(1)O(2)	170 17(15)
Sb(1) = O(1)	1.975(3)	O(1)Sb(1)C(11)	97 40(18)
Sb(1) - C(1)	2.106(5)	O(1)Sb(1)C(21)	91.06(17)
Sb(1) = C(11)	2.100(5) 2.105(5)	C(1)Sb(1)C(21)	86 69(19)
Sb(1) = C(21)	2.103(5) 2.112(5)	C(1)Sb(1)C(2)	122.8(2)
Sb(2) = O(1)	1.982(3)	C(1)Sb(1)C(21)	122.0(2) 116 5(2)
Sb(2) = O(1) Sb(2) $C(41)$	1.982(3) 2.120(5)	C(11)Sb(1)C(1)	110.3(2) 110.8(2)
Sb(2) - C(41) Sb(2) C(31)	2.120(3) 2.110(5)	C(21)Sb(1)C(21)	119.0(2) 82.13(18)
SU(2) = C(31) Sb(2) $C(51)$	2.119(3) 2.100(5)	C(21)SU(1)O(2)	02.13(10) 06.44(17)
SD(2) - C(31) Sb(2) - O(4)	2.109(3)	O(1)SO(2)C(31)	90.44(17)
SU(2) = O(4)	2.218(3)	O(1)SO(2)O(4) C(21)Sb(2)C(41)	1/0./0(14)
O(2) = C01	1.280(0)	C(51)SD(2)C(41)	110.7(2)
C(61) = O(3)	1.21/(7)	C(51)Sb(2)C(41)	131.0(2)
O(4) - C(64)	1.303(6)	C(51)Sb(2)C(31)	109.03(19)
C(64) - O(5)	1.214(7)	C(51)Sb(2)O(4)	87.99(16)
Sb(1) - C(1)	2 082(11)	C(1)Sb(1)C(21)	113 1(4)
Sb(1) = C(21)	2.002(11) 2.136(10)	C(1)Sb(1)C(21)	125.1(1)
Sb(1) - C(21) Sb(1) C(31)	2.130(10) 2.076(12)	C(31)Sb(1)C(11)	123.4(+) 07 0(5)
Sb(1) - C(31) Sb(1) C(11)	2.070(12) 2.166(13)	C(31)Sb(1)C(21)	117 1(5)
Sb(1) - C(11) Sb(1) O(1)	2.100(13) 2.338(10)	C(31)Sb(1)C(21)	81.8(4)
Sb(1) = O(1) Sb(2) $O(3)$	2.338(10) 2.340(10)	C(31)Sb(1)O(1)	174 4(5)
SU(2) = O(3) Sb(2) = $O(41)$	2.340(10) 2.140(11)	C(11)Sb(1)O(1) C(41)Sb(2)O(3)	174.4(3)
SU(2) = C(41) Sb(2) $C(71)$	2.140(11) 2.151(10)	C(41)Sb(2)C(3)	124.0(4)
SU(2) = C(71) Sb(2) $C(61)$	2.131(10) 2.162(10)	C(41)Sb(2)C(71)	124.0(4)
SU(2) = C(01)	2.103(12)	C(41)SD(2)C(51)	110.4(4)
SU(2) = C(31)	2.030(11)	C(01)SD(2)U(3)	1/3.2(3)
O(2) - C(3/)	1.198(17)	C(01)SD(2)C(41)	93.4(4)
O(3) - C(77)	1.512(16)	C(01)SD(2)C(71)	98.9(S)
U(4) - C(77)	1.253(17)	C(61)SD(2)C(51)	97.0(5)
U(1) - C(37)	1.278(14)	C(51)Sb(2)C(71)	115.0(4)

respectively. In structures **IIIa** and **IIIb**, the antimony atoms deviate to the axial carbon atom by 0.255 and 0.262 Å, respectively. The sums of the angles in the equatorial plane are 360.0° (**Ia**), 359.1° (**Ib**), 358.7° (**II**), 355.6° (**IIIa**), and 355.4° (**IIIb**).

The ranges of changing the Sb– C_{eq} bond lengths and their average values are 2.103(8)–2.138(5), 2.117(8) Å (**Ia**); 2.118(9)–2.141(5), 2.128(8) Å (**Ib**); 2.105(5)–2.112(5), 2.108(5) and 2.109(5)–2.120(5), 2.116(5) Å (II); 2.076(12)–2.136(10), 2.099(11) Å (IIIa); and 2.056(11)–2.151(10), 2.116(10) Å (IIIb). The Sb– C_{ax} axial bonds (2.166(13) in IIIa and 2.163(12) Å in IIIb) are longer than the equatorial bonds.

In a series of compounds I, II, and III, the bond between the antimony atom and the oxygen atom of the Sn–O carboxylate ligand elongates: 2.156(7), 2.152(7) Å (Ia); 2.139(6), 2.141(6) Å (Ib); 2.206(4),



General view of molecules I-III.



Figure. (Contd.).

2.218(3) Å (II); and 2.338(10) (IIIa), 2.340(10) Å (IIIb).

The carboxylate ligands exhibit the anisobidentate properties. The distances between the antimony atom and the carbonyl oxygen atoms (Sb-O=C) in compounds Ia and Ib are 2.962(7), 2.976(7) Å and 2.977(6), 2.936(6) Å, respectively. In molecules IIIa and **IIIb**, the interactions of the central atom with the carbonyl oxygen atom are considerably weaker (the Sb---O=C distances are 3.373(18) and 3.384(18) Å). In molecule II, the intramolecular contacts differ (3.613(4) and 3.076(3) Å), and the Sb(1)...O(3) value is close to the sum of van der Waals radii of the Sb and O atoms (3.7 Å [11]), which is evidently due to the geometric factor: the coordination mode of the ligand could be usual for a larger O(2)Sb(1)O(1) axial angle. The asymmetry of the coordination mode of the carboxylate ligands can be estimated by the ratio d(Sb - O = C)/d(Sb - O), which is equal to 1.374, 1.379 (Ia); 1.371, 1.392 (Ib); 1.387, 1.638 (II); and 1.443 (IIIa), 1.446 (IIIb).

Note that the Sb···O=C intramolecular interactions result in the distortion of the CSbC equatorial angles compared to the theoretical value. The angle at the side of the contacts increases due to a decrease in two other angles: $142.4(4)^{\circ}$ (**Ia**), $143.1(3)^{\circ}$ (**Ib**); $122.9(2)^{\circ}$, $131.0(2)^{\circ}$ (**II**); and $125.4(4)^{\circ}$ (**IIIa**), $124.0(4)^{\circ}$ (**IIIb**). The sequence of increasing the CSbC angles in compounds **III**, **II**, and **I** is reciprocal to the sequence of the elongation of the Sb···O distance.

In the central fragment of compound II, the Sb(1,2)-O(1) bond lengths are 1.975(3) and

1.982(3) Å and the Sb(1)O(1)Sb(2) angle is 141.55(19)°. Analogous parameters have similar values in four structurally characterized complexes of μ_2 -oxobis[(carboxylato)triphenylantimony] [3–6].

A crystal of compound I includes weak intermolecular hydrogen bonds involving the acetylenic hydrogen atom C–H···O–C (H···O 2.69–2.71 Å). The three-dimensional structure of crystal II is formed by the contacts $metaH_{Ph}$ ···O=C 2.60–2.68 Å and $metaH_{Ph}$ ···O–C 2.61 Å; in addition, there is the hydrogen bond C(63)–H(63)···O(3) 2.36 Å between the acetylenic hydrogen atom and the carbonyl oxygen atom. A crystal of compound III includes the C–H···O=C contacts between the hydrogen atoms of the phenyl rings and the oxygen atoms of the carboxylate ligands (2.45–2.69 Å).

Thus, in the series of compounds $Ph_3Sb[OC(O)C=CH]_2$, $[Ph_3SbOC(O)C=CH]_2O$, and $Ph_4SbOC(O)C=CH$ the distortion of the trigonal—bipyramidal coordination mode of the central atom increases, which appears as its increasing deviation from the equatorial plane and the elongation of the Sb–O axial bonds, and the asymmetry of the coordination mode of the carboxylate ligand also increases.

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