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Bis(tetraphenylantimony) Succinate, Malate, and Tartrate: Syntheses and Structures

V. V. Sharutin* and O. K. Sharutina

National Research Southern Ural State University, Chelyabinsk, Russia

**e-mail: vvsharutin@rambler.ru*

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Abstract—The reactions of pentaphenylantimony with succinic, malic, and tartaric acids (mole ratio 2 : 1) in toluene afford bis(tetraphenylantimony) succinate (**I**), malate (**II**), and tartrate (**III**) in yields of 98, 92, and 94%, respectively. According to the X-ray diffraction analysis results, molecules **I** and **II** are centrosymmetric. In compound **II**, the hydroxy group in the acid residue is disordered over two positions. Crystal **III** includes two types of crystallographically independent molecules (**a** and **b**). The antimony atoms in compounds **I**, **II**, **IIIa**, and **IIIb** have distorted trigonal bipyramidal coordination modes. The axial angles $C_{ax}SbO_{ax}$ are 166.80(8)° (**I**); 174.8(2)° (**II**); 176.4(4)°, 177.4(3)° (**IIIa**); and 173.3(4)°, 172.7(4)° (**IIIb**). The equatorial angles $C_{eq}SbC_{eq}$ vary in the ranges 99.3(1)°–154.5(1)° (**I**); 115.2(2)°–123.3(2)° (**II**); 115.7(4)°–123.3(4)°, 115.2(5)°–125.6(5)° (**IIIa**); and 107.9(4)°–129.1(4)°, 113.7(4)°–124.8(5)° (**IIIb**). The Sb–C and Sb–O bonds are 2.138(3)–2.176(3), 2.319(2) Å (**I**); 2.111(6)–2.163(5), 2.243(4) Å (**II**); 2.072(13)–2.169(11), 2.252(7), 2.284(7) Å (**IIIa**); and 2.047(11)–2.190(11), 2.224(7), 2.256(7) Å (**IIIb**). The intramolecular distances Sb···O=C are 2.528(3) (**I**); 3.267(7) (**II**); 3.381(7), 3.436(7) (**IIIa**); and 3.351(7), 3.162(7) Å (**IIIb**). For structures **I**, **II**, and **III,** the CIF files are CCDC 929151, 941542, and 941543, respectively.

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INTRODUCTION

The syntheses and structures of tetraarylantimony carboxylates are fairly well studied [1–7]. The organoantimony derivatives of dicarboxylic acids are studied to a less extent [8–13].

It is known that the reactions of pentaarylantimony with dicarboxylic acids afford compounds of two types: acidic tetraarylantimony carboxylates or bis(tetraarylantimony) carboxylates, that is, one or two carboxy groups are involved in the reaction [8–10]. According to the X-ray diffraction data, the coordination modes of the antimony atoms differ substantially in molecules of these types. In the first case, the trigonal bipyramidal coordination of the antimony atom is strongly distorted and there is a tendency of the Ar_4Sb fragment to the transition to a tetrahedral configuration accompanied by the elongation of the distance between the antimony atoms and oxygen atoms of the carboxylate ligand exhibiting the monodentate type of binding [8–10]. In the second case, the antimony atoms have a slightly distorted trigonal bipyramidal coorination mode. The bridging carboxylate ligand demonstrates a tendency to the tetradentate mode due to intramolecular interactions Sb···O=C between the antimony atoms and the carbonyl oxygen atoms [9, 11–13]. The ligands exhibit the anisobidentate coordination mode in three structurally characterized bis(tetraarylantimony) carboxylates [9, 11, 12]. Only the oxalate ligand coordinates to the antimony atom nearly symmetrically, and the coordination mode of the antimony atoms is transformed into the octahedral one [13].

To continue the study of the organoantimony derivatives of dicarboxylic acids, we synthesized bis(tetraphenylantimony) succinate (**I**), malate (**II**), and tartrate (**III**) and established the regularities of their structures by X-ray diffraction analysis.

EXPERIMENTAL

Synthesis of compound I. A mixture of pentaphenylantimony (0.200 g, 0.394 mmol) and succinic acid (0.023 g, 0.197 mmol) in toluene (5 mL) was kept at 20°C for 48 h. The solvent was slowly removed, and the residue was recrystallized from a benzene–isopropyl alcohol (1 : 2) mixture. Colorless crystals of compound **I** with mp = 193–194°C were obtained in a yield of 0.188 g (98%).

For $C_{52}H_{44}O_4Sb_2$		
anal. calcd., %:	C, 63.93;	H, 4.51.
Found, %:	C, 63.89;	H, 4.60.

IR, ν, cm^{-1}: 3053, 2988, 2948, 1638, 1574, 1541, 1479, 1452, 1432, 1395, 1186, 1140, 1072, 1062, 1019, 997, 737, 693, 670, 655, 468, 459, 448.

The other compounds were synthesized similarly.

Compound **II** (92% yield, mp = 165–167°C).

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

Parameter	Value		
	I	**II**	**III**
M	976.38	992.41	1008.39
T, K	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$C2/c$	$P2_12_12_1$
a, Å	14.647(9)	28.484(2)	16.4932(18)
b, Å	9.468(4)	10.3704(7)	18.640(2)
c, Å	16.076(6)	17.4651(11)	28.961(3)
β, deg	99.86(4)	92.416(2)	90.00
V, Å^3	2196.5(19)	5154.4(6)	8903.6(16)
Z	4	4	8
ρ_{calcd}, g/cm^3	1.476	1.297	1.505
μ, mm^{-1}	1.274	1.091	1.263
F(000)	980.0	2016.0	4048.0
Crystal size, mm	0.53 × 0.2 × 0.06	0.62 × 0.27 × 0.08	0.41 × 0.3 × 0.08
θ Range of data collection, deg	4.14–69.18	6.2–51.3	6.04–38.48
Ranges of reflection indices	$-23 \le h \le 21$, $-14 \le k \le 15$, $-25 \le l \le 21$	$-34 \le h \le 34$, $-12 \le k \le 12$, $-21 \le l \le 20$	$-15 \le h \le 15$, $-17 \le k \le 17$, $-26 \le l \le 26$
Measured reflections	31579	44678	86492
Independent reflections (R_{int})	9319 (0.0474)	4886 (0.0438)	7437 (0.0922)
Refinement variables	262	272	485
Goodness-of-fit	1.027	1.109	1.059
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0435$, $wR_2 = 0.0790$	$R_1 = 0.0484$, $wR_2 = 0.1608$	$R_1 = 0.0604$, $wR_2 = 0.1529$
R factors for all reflections	$R_1 = 0.0897$, $wR_2 = 0.0920$	$R_1 = 0.0596$, $wR_2 = 0.1731$	$R_1 = 0.0687$, $wR_2 = 0.1606$
Residual electron density (min/max), e/A^3	1.39/–1.01	1.89/–0.64	2.28/–1.82

For $C_{52}H_{44}O_5Sb_2$

anal. calcd., %: C, 62.90; H, 4.44.

Found, %: C, 63.09; H, 4.30.

IR, ν, cm^{-1}: 3382, 3062, 2966, 2919, 1624, 1574, 1479, 1434, 1320, 1267, 1182, 1161, 1085, 1066, 1020, 997, 968, 880, 735, 692, 615, 556, 457, 446.

Compound **III** (94% yield, mp = 167–168°C (decomp.).

For $C_{52}H_{44}O_6Sb_2$

anal. calcd., %: C, 61.90; H, 4.36.

Found, %: C, 62.01; H, 4.46.

IR, ν, cm^{-1}: 3461, 3048, 1629, 1479, 1453, 1308, 1185, 1119, 1066, 1020, 996, 909, 853, 733, 692, 620, 557, 456, 423.

IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer in KBr pellets.

The X-ray diffraction analyses of crystals **I**–**III** were carried out on a D8 QuestBruker diffractometer (MoK_α radiation, λ = 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 [14]. All calculations on structure determination and refinement were performed using the SHELXL/PC programs [15]. The structures were determined by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and refinement results for structures **I**–**III** are listed in Table 1. Selected bond lengths and bond anglLes are given in Table 2. The structures of molecules **I**–**III** are shown in the figure.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 929151, 941542, and 941543 for compounds **I**, **II**, and **III**,

respectively; deposit@ccdc.cam.ac.uk; http://www.ccdc. cam.ac.uk).

RESULTS AND DISCUSSION

The reactions of pentaphenylantimony with succinic, malic, and tartaric acids (mole ratio 2 : 1) occur in a toluene solution at room temperature with the replacement of the hydrogen atoms in two carboxy groups and the formation of bis(tetraphenylantimony) carboxylates in yields close to a quantitative one:

$$2Ph_5Sb + HOC(O)-R-C(O)OH \rightarrow Ph_4SbOC(O)-R-C(O)OSbPh_4$$

$$R = CH_2CH_2 \textbf{ (I)}, CH_2CH(OH) \textbf{ (II)}, CH(OH)CH(OH) \textbf{ (III)}.$$

Molecule **I** is centrosymmetric with the inversion center at the middle of the C–C bond of the ethylene fragment. In molecule **II**, the hydroxy group is disordered over two positions. Crystal **III** includes two types of crystallographically independent molecules.

The trigonal bipyramidal coordination of the antimony atoms in structures **I–III** is distorted to different extents. The axial angles $C_{ax}SbO_{ax}$ are 166.80(8)° (**I**); 174.8(2)° (**II**); 176.4(4)°, 177.4(3)° (**IIIa**); and 173.3(4)°, 172.7(4)° (**IIIb**). The antimony atoms shift from the equatorial planes C_3 to the axial carbon atom by 0.234, 0.224, and 0.214 Å for Sb(1), 0.243 Å for Sb(2), 0.243 Å for Sb(3), and 0.174 Å for Sb(4) in compounds **I–IIIa,b**, respectively. The sums of the $C_{eq}SbC_{eq}$ angles are similar: 355.12(10)° (**I**), 356.7(2)° (**II**), 356.0(4)° and 356.0(5)° (**IIIa**), and 358.8(4)° and 358.0(5)° (**IIIb**). The Sb–C_{eq} equatorial bonds (average values 2.149(3) (**I**); 2.121(6) (**II**); 2.095(9), 2.102(11) (**IIIa**); and 2.087(11), 2.104(11) Å (**IIIb**)) are shorter than the axial Sb–C_{ax} bonds (2.176(3) (**I**); 2.164(5) (**II**); 2.164(11), 2.169(11) (**IIIa**); and 2.190(11), 2.071 (12)Å (**IIIb**)).

The main distinction in molecular geometries of compounds **I–III** is the bonding character of the carboxylate ligands with the antimony atoms. In molecule **I**, the coordination mode of the ligand is close to symmetrical one: the Sb(1)–O(1) and Sb(1)···O(2) distances are 2.319(2) and 2.528(2) Å, respectively. The carboxylate group manifests the bidentate properties, which is accompanied by a strong distortion of the axial and equatorial angles: C(7)Sb(1)C(13) 154.52(10)°, whereas C(1)Sb(1)C(13) and C(1)Sb(1)C(7) decrease to 101.26(10)° and 99.34(10)°, respectively. The C(25)–O(1) (1.277(3) Å) and C(25)–O(2) (1.252(3) Å) bond lengths indicate the redistribution of the electron density in the carboxy group. In molecule **II**, the ligand is anisobidentate: the Sb(1)–O(1) bond (2.243(4) Å) is much shorter than the intramolecular distance Sb(1)···O(2) 3.267(7) Å. The trigonal bipyramidal polyhedron of the antimony atom is slightly distorted, and the C(37)–O(1) (1.269(7) Å) and C(37)–O(2)

Table 2. Selected bond lengths and bond angles in structures **I***, **II****, and **III**

Bond	*d*, Å	Angle	ω, deg
		I	
Sb(1)–O(1)	2.319(2)	C(19)Sb(1)O(1)	166.80(8)
Sb(1)–O(2)	2.528(2)	C(1)Sb(1)O(1)	90.40(9)
Sb(1)–C(1)	2.138(3)	C(1)Sb(1)C(7)	99.34(10)
Sb(1)–C(7)	2.161(3)	C(1)Sb(1)C(13)	101.26(10)
Sb(1)–C(13)	2.147(3)	C(13)Sb(1)C(7)	154.52(10)
Sb(1)–C(19)	2.176(3)	C(1)Sb(1)C(19)	102.77(10)
O(1)–C(25)	1.277(3)	C(7)Sb(1)O(1)	81.24(8)
O(2)–C(25)	1.252(3)	C(7)Sb(1)C(19)	95.59(9)
C(26)–C(26a)	1.513(5)	C(26a)C(26)C(25)	109.3(3)
* Symmetry transforms: [a] $1-x, 1-y, 1-z$.			
		II	
Sb(1)–O(1)	2.243(4)	C(1)Sb(1)O(1)	82.98(19)
Sb(1)···O(2)	3.267(7)	C(1)Sb(1)C(11)	118.2(2)
Sb(1)–C(1)	2.116(6)	C(1)Sb(1)C(21)	94.4(2)
Sb(1)–C(11)	2.132(5)	C(11)Sb(1)O(1)	81.58(19)
Sb(1)–C(31)	2.111(6)	C(11)Sb(1)C(21)	95.8(2)
Sb(1)–C(21)	2.164(5)	C(31)Sb(1)O(1)	87.1(2)
O(1)–C(37)	1.269(7)	C(31)Sb(1)C(1)	123.3(2)
O(2)–C(37)	1.227(8)	C(31)Sb(1)C(11)	115.2(2)
C(37)–C(38)	1.509(9)	C(31)Sb(1)C(21)	98.1(2)
C(38)–C(38a)	1.463(14)	C(21)Sb(1)O(1)	174.80(18)
** Symmetry transforms: [a] $1-x, 1-y, -z$.			
		III	
Sb(1)–O(1)	2.252(7)	C(1)Sb(1)O(1)	176.4(4)
Sb(1)···O(2)	3.381(7)	C(31)Sb(1)C(11)	123.3(4)
Sb(1)–C(1)	2.164(11)	C(31)Sb(1)C(21)	115.7(4)
Sb(1)–C(11)	2.074(12)	C(21)Sb(1)C(11)	117.9(4)
Sb(1)–C(31)	2.090(9)	C(21)Sb(1)O(1)	82.5(4)
Sb(1)–C(21)	2.121(9)	C(31)Sb(1)O(1)	87.1(3)
Sb(2)–O(3)	2.284(7)	C(41)Sb(2)O(3)	177.4(3)
Sb(2)···O(4)	3.436(7)	C(71)Sb(2)C(51)	115.2(5)
Sb(2)–C(51)	2.115(12)	C(71)Sb(2)C(61)	115.2(5)
Sb(2)–C(71)	2.120(11)	C(61)Sb(2)C(51)	125.6(5)
Sb(2)–C(41)	2.169(11)	C(71)Sb(2)O(3)	82.0(4)
Sb(2)–C(61)	2.072(13)	C(61)Sb(2)O(3)	85.3(4)
Sb(3)–O(7)	2.224(7)	C(131)Sb(3)O(7)	173.3(4)
Sb(3)···O(8)	3.351(7)	C(111)Sb(3)C(101)	107.6(4)
Sb(3)–C(111)	2.093(11)	C(121)Sb(3)C(111)	119.1(5)
Sb(3)–C(131)	2.190(11)	C(121)Sb(3)C(101)	129.1(4)
Sb(3)–C(121)	2.047(11)	C(121)Sb(3)O(7)	82.9(4)
Sb(3)–C(101)	2.123(10)	C(101)Sb(3)O(7)	86.1(4)
Sb(4)–O(9)	2.256(7)	C(141)Sb(4)O(9)	172.7(4)
Sb(4)···O(10)	3.162(7)	C(151)Sb(4)C(161)	124.8(5)
Sb(4)–C(151)	2.122(11)	C(171)Sb(4)C(151)	119.5(5)
Sb(4)–C(171)	2.097(9)	C(171)Sb(4)C(161)	113.7(4)
Sb(4)–C(161)	2.092(13)	C(171)Sb(4)O(9)	81.9(3)
Sb(4)–C(141)	2.071(12)	C(161)Sb(4)O(9)	88.5(4)

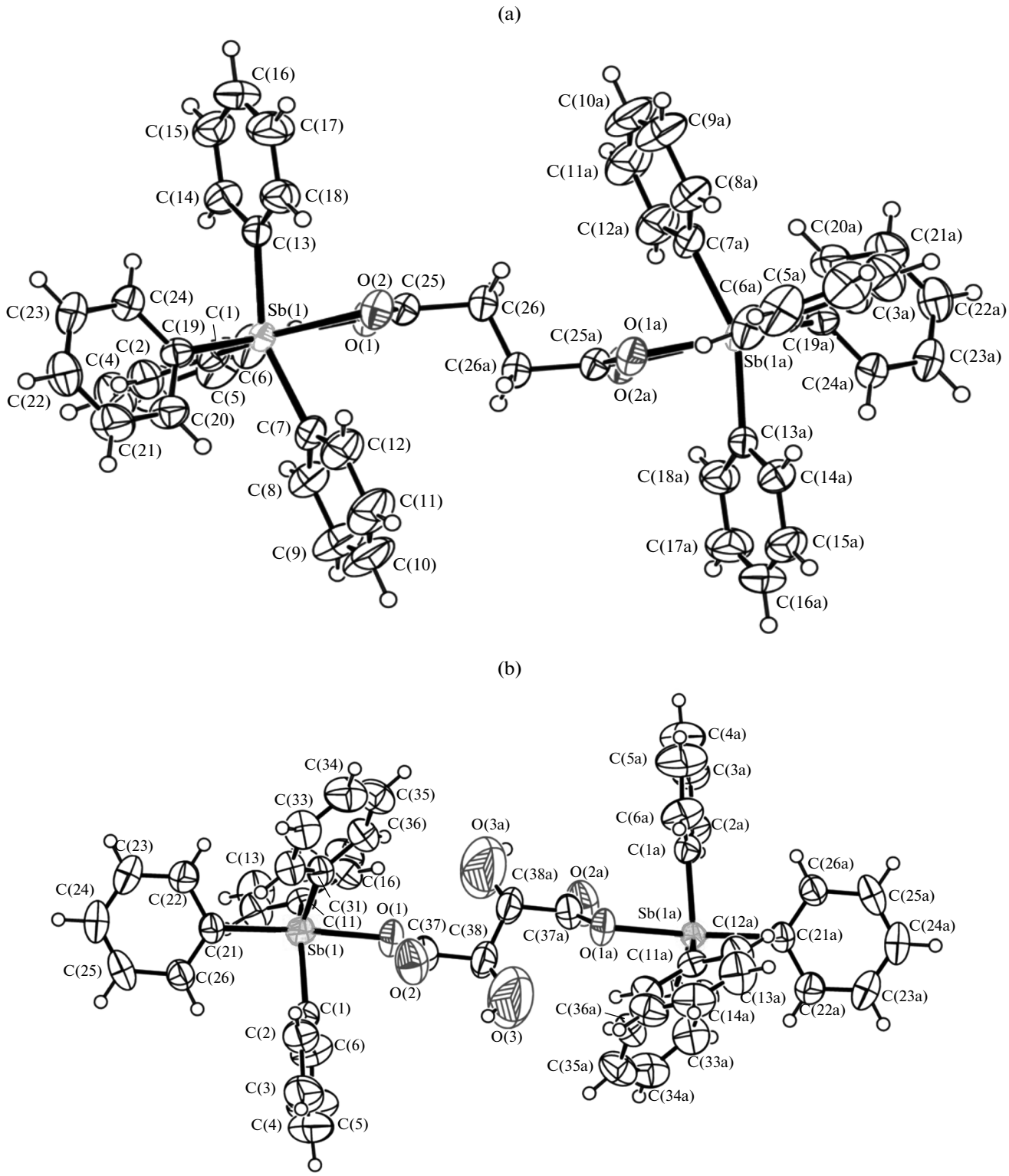

Fig. 1. Structures of molecules (a) **I**, (b) **II**, and (c) **III**.

(1.227(8) **IIIa**) bond lengths correspond to the carbon–oxygen ordinary and double bonds. In molecule **IIIa**, the Sb(1)–O(1) and Sb(2)–O(3) bonds and the Sb(1)···O(2), Sb(2)···O(4) distances (2.252(7), 2.284(7), 3.381(7), and 3.436(7) Å, respectively) considerably exceed similar values in

(c)

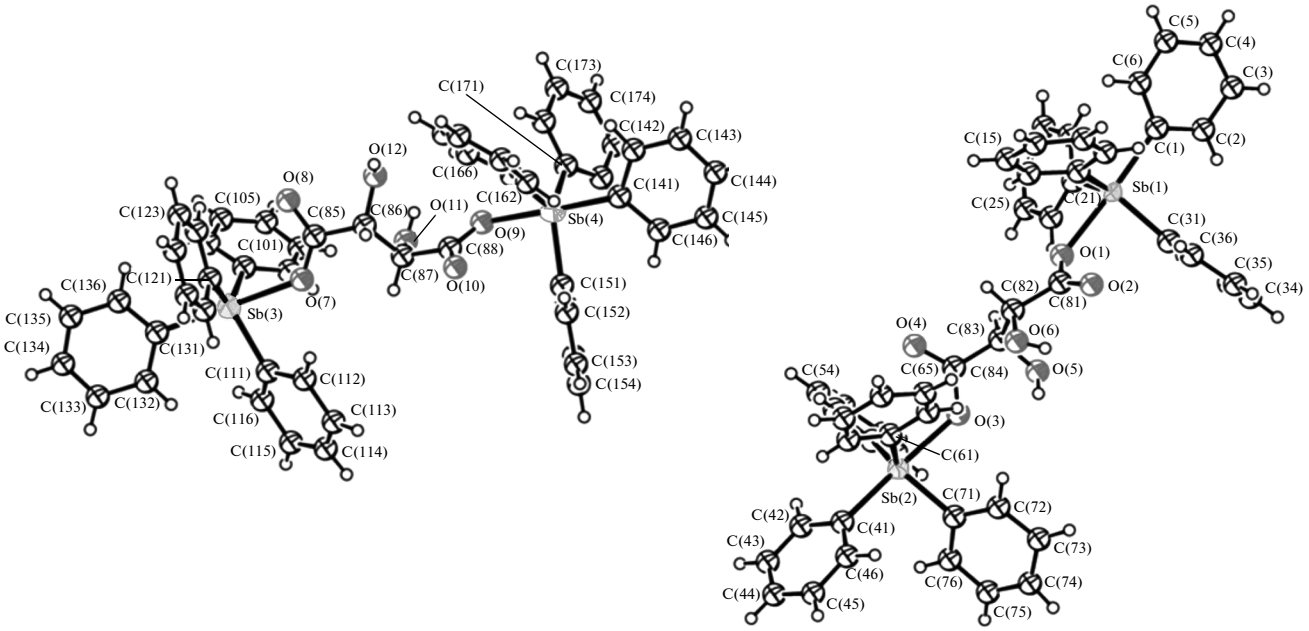

Fig. 1. (Contd.)

molecule **II**. In structure **IIIb**, the Sb(3)–O(7) 2.224(7), Sb(4)–O(9) 2.256(7) Å bonds and intermolecular contacts Sb(3)···O(8) 3.351(7), Sb(4)···O(10) 3.162(7) Å are shorter than those in molecule **IIIa**. However, a tendency to decreasing the total strength of binding of the carboxylate ligand is explicitly observed in a series of molecules **I**–**III**.

REFERENCES

1. Bone, S.P. and Sowerby, D.B., *J. Chem. Res. Synop.*, 1979, no. 3, p. 82.
2. Bone, S.P. and Sowerby, D.B., *Phosphorus, Sulfur, Silicon. Relat. Elem.,* 1989, vol. 45, nos. 1–2, p. 23.
3. Wen, L., Yin, H., Li, W., and Wang, D., *Inorg. Chim. Acta*, 2010, vol. 363, no. 4, p. 676.
4. Ma, Y., Li, J., Xuan, Z., and Liu, R., *J. Organomet. Chem.*, 2001, vol. 620, no. 2, p. 235.
5. Li, J.-S., Ma, Y., Cui, J.-R., and Wang, R.-Q., *Appl. Organomet. Chem.*, 2001, vol. 15, no. 7, p. 639.
6. Quan, L., Yin, J.C., Hong, M., and Wang, D., *J. Organomet. Chem.*, 2009, vol. 694, no. 23, p. 3708.
7. Yin, H.-D., Wen, L.-Y., Cui, J.-C., and Li, W.-K., *Polyhedron*, 2009, vol. 28, no. 14, p. 2919.
8. Sharutin, V.V., Sharutina, O.K., Mel'nikova, I.G., et al., *Izv. Akad. Nauk, Ser. Khim.*, 1996, no. 8, p. 2082.
9. Sharutin, V.V., Sharutina, O.K., Pakusina, A.P., and Belsky, V.K., *J. Organomet. Chem.*, 1997, vol. 536, p. 87.
10. Sharutin, V.V., Sharutina, O.K., Pakusina, A.P., and Bel'skii, V.K., *Russ. J. Gen. Chem.*, 1997, vol. 67, no. 9, p. 1443.
11. Sharutin, V.V., Sharutina, O.K., and Senchurin, V.S., *Russ. J. Coord. Chem.*, 2001, vol. 27, no. 9, p. 669.
12. Sharutin, V.V., Sharutina, O.K., and Bondar', E.A., *Russ. J. Gen. Chem.,* 2002, vol. 72, no. 12, p. 1920.
13. Millington, P.L. and Sowerby, D.B., *Dalton Trans.*, 1992, no. 7, p. 1199.
14. *SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System*, Madison (WI, USA): Bruker AXS Inc.,1998.
15. *SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data,* Madison (WI, USA): Bruker AXS Inc., 1998.

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