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Triarylantimony Dicaroxylates $Ar_3Sb[OC(O)R]_2$ (Ar = Ph, *p*-Tol; R = 2-C_4H_3O, 3-C_5H_4N): Synthesis and Structure

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Abstract—Bis(2-furoinate)triphenyl- and tri-*p*-tolylantimony and bis(3-niacinate)triphenylanitmony were synthesized by reacting triarylantimony (Ar_3Sb; Ar = Ph, *p*-Tol) with 2-furancarboxylic and 3-pyridinecarboxylic acids in the presence of hydrogen peroxide. According to X-ray diffraction data, Sb atoms have trigonal bipyramidal coordination polyhedra. The Sb–O distances are 2.117(4), 2.137(4) Å; 2.136(2), 2.158(2) Å, and 2.112(1), 2.101(2) Å, the Sb··O distances are 2.866(4), 2.798(4) Å; 2.816(2), 2.774(2) Å, and 3.054(2), 3.168(2) Å, respectively.

The structures of triarylantimony dicarboxylates, which were synthesized by the substitution reactions from triarylantimony dihalides [7, 8] or via the oxidative addition reactions from triarylstibine and carboxylic acid in the presence of hydrogen peroxide [9, 10] were reported in [1–7]. In all structurally characterized tripheylantimony dicarboxylates, the Sb atoms have the trigonal-byparamidal coordination polyhedra with the axial carboxylate ligands. In these complexes, the carboxylate ligands exhibit the bidentate properties: the distances between Sb atoms and the carbonyl oxygen Sb···O(=C) is less than the sum of their van der Waals radii and are equal to 2.664–3.231 Å. One more intramolecular interaction Sb···O(=C) is confirmed by the change in valence angles in the equatorial plane of molecules, the leveling of the C–O and C=O bond lengths in a carboxyl group, and by some other factors. It should be noted that the Sb···O(=C) distances are determined by the nature of the R radical in the ligand. Thus, the maximum distances (3.209 and 3.231 Å) are observed in triphenylantimony bis(trifluoroacetate) [5], while the minimum distances (2.664 Å) were established for triphenylantimony dicinnamate [6]. The bidentate nature of the carboxylate ligands is thus shown to different extent and can be estimated by asymmetry of coordination of the carboxyl group at the Sb atom. The additional coordination of the Sb atom is different in $Ph_3Sb[OC(O)C_5H_4N\text{-}2]_2$, where one carboxylate group is bound to a central atom through the oxygen atoms, while the other group is bound through the oxygen and nitrogen atoms [4], i.e., the additional potential coordinating sites in the R radical changes the coordination type of the Sb atom.

In continuation of our study of the structure of triarylantimony dicarboxylates containing heteroatoms with unshared electron pairs in the carboxylate ligands, we examined the molecular and crystal structures of triphenylantimony bis(2-furoinate) (**I**), tri-*p*-tolylantimony bis(2-furoinate) (**II**), and triphenylantimony bis(3-niacinate) (**III**).

EXPERIMENTAL

Triphenylantimony bis(2-furoinate) (I). A 42% aqueous solution of hydrogen peroxide (0.24 ml) was added to a mixture of triphenylantimony (1.00 g) and 2-furancarboxylic acid (0.62 g) in 20 ml diethyl ether at 20°C. The mixture was allowed to stand at this temperature for 12 h. Then, the solvent was removed, and the solid was recrystallized from toluene. The yield of crystals **I** was 1.61 g (99%); mp 190°C. IR (ν, cm^{-1}): 1615 vs, 1580 s, 1340 vs, 1190 vs, 1130 s, 920 s.

For $C_{28}H_{21}SbO_6$		
anal. calcd (%):	C, 58.43;	H, 3.65.
Found (%):	C, 58.11;	H, 3.86.

Tri-*p*-tolylantimony bis(2-furoinate) (II) was prepared similarly (mp 204°C, yield 98%). IR (ν, cm^{-1}): 1619 vs, 1345 s, 1180 vs, 1065 s, 1010 m, 920 m.

For $C_{31}H_{27}SbO_6$		
anal. calcd (%):	C, 60.29;	H, 4.38.
Found (%):	C, 59.74;	H, 4.56.

Triphenylantimony bis(3-niacinate) (III) (mp 145°C, yield 97%). IR (ν, cm^{-1}): 1600 vs, 1540 s, 1320 vs, 1260 s, 1130 s, 1090 s, 1010 s, 975 s.

For $C_{30}H_{23}SbO_4N_2$		
anal. calcd (%):	C, 60.30;	H, 3.85.
Found (%):	C, 60.12;	H, 3.92.

Table 1. Crystallographic data and summary of the data collection and refinement of structures **I–III**

Parameter	**I**	**II**	**III**
M	575.20	617.28	643.32
Symmetry system	Monoclinic	Triclinic	Monoclinic
T, K	296(2)	298(2)	203(1)
Space group	$P21/n$	$P\bar{1}$	$C2/c$
Unit cell parameters:			
a, Å	8.859(1)	10.275(2)	30.664(3)
b, Å	17.237(2)	11.750(2)	11.643(1)
c, Å	15.800(2)	12.877(3)	17.229(1)
α, deg.	90	83.761(4)	
β, deg.	93.491(3)	83.746(4)	110.821(2)
γ, deg.	90	64.288(3)	
V, Å^3	2408.2(5)	1389.1(5)	5749.4(8)
Z	4	2	8
ρ(calcd.), g/cm^3	1.586	1.476	1.486
μ_{Mo}, mm^{-1}	1.188	1.035	1.001
F(000)	1152	624	2600
Crystal shape (size)	Prism (0.17 × 0.13 × 0.04 mm)	Prism (0.10 × 0.17 × 0.20 mm)	Prism (0.17 × 0.17 × 0.06 mm)
θ, deg.	3.30–21.50	1.59–30.06	1.89–29.03
Index range	$-8 \le h \le 9$, $-17 \le k \le 17$, $-14 \le l \le 16$	$-14 \le h \le 14$, $-16 \le k \le 16$, $-17 \le l \le 17$	$-26 \le h \le 41$, $-15 \le k \le 15$, $-23 \le l \le 23$
Number of measured reflections	8944	19358	20478
Number of unique reflections	2755 (R_{int} = 0.0692)	7819 (R_{int} = 0.0638)	7640 (R_{int} = 0.0618)
Number of refined parameters	317	346	369
GOOF	1.023	0.784	0.999
Final *R*-factor ($I > 2\sigma(I)$)	$R_1 = 0.0385$, $wR_2 = 0.0811$	$R_1 = 0.0446$, $wR_2 = 0.0883$	$R_1 = 0.0409$, $wR_2 = 0.0855$

Tri-*p*-tolylantimony bis(3-niacinate) (IV) (mp 212°C, yield 99%). IR, ν, cm^{-1}: 1600 vs, 1550 vs, 1280 vs, 1140 s, 1080 s.

For $C_{33}H_{29}SbO_4N_2$		
anal. calcd (%):	C, 61.97;	H, 4.54.
Found (%):	C, 62.21;	H, 4.39.

X-ray diffraction analysis of crystals **I–III** was carried out on a SMART 1000 CCD diffractometer (graphite monochromator, MoK_α radiation). Data for crystals **I** and **II** were collected in sets of 906, 660, and 345 scans with φ = 0°, 90° and 180°, respectively; ω-scan mode at a step of 0.2° and exposure time of 10 s per frame (for **I**), 20 s per frame (for **II**). Data for crystals **III** were collected in sets of 906, 606, and 345 scans with φ = 0°, 88°, and 180°, respectively; ω-scan mode at a step of 0.2° and exposure time of 10 s per frame. The distance between crystal (**I–III**) and detector was 45 mm. The absorption of X-ray in the samples was accounted for by the equivalent reflections.

The structures were solved by the direct method and refined by the least-squares method in anisotropic approximation for non-hydrogen atoms. Positions of H atoms were located geometrically and included in refinement in the rider model.

The data were collected and processed and the unit cell parameters were refined with the SMART and SAINT-*Plus* programs [11]. All calculations were performed with the SHELXTL/PC program packages [12].

The crystal data and the results of refinement for **I–III** are given in Table 1. The coordinates and thermal factors of non-hydrogen atoms are listed in Table 2, while the bond lengths and angles are listed in Table 3.

Table 2. Coordinates of atoms ($\times 10^4$) and their equivalent isotropic thermal parameters ($\times 10^3$) in structures **I–III**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
		I		
Sb	9099.8(5)	1559.6(2)	7518.2(2)	34.6(2)
O(1)	7598(5)	733(2)	6943(2)	44(1)
O(2)	9286(5)	729(2)	5957(3)	49(1)
O(3)	6011(5)	–427(2)	6147(3)	47(1)
O(4)	10652(5)	2346(2)	8153(2)	39(1)
O(5)	11729(5)	2209(3)	6922(3)	53(1)
O(6)	12981(5)	3222(2)	8787(3)	50(1)
C(1)	8115(8)	469(4)	6241(4)	38(2)
C(2)	7252(7)	–126(4)	5794(4)	39(2)
C(3)	7393(7)	–463(4)	5036(4)	45(2)
C(4)	6189(9)	–984(4)	4896(5)	62(2)
C(5)	5406(9)	–943(4)	5584(5)	59(2)
C(6)	11746(8)	2462(4)	7649(4)	41(2)
C(7)	13034(7)	2905(3)	8000(4)	35(2)
C(8)	14362(8)	3075(4)	7676(4)	51(2)
C(9)	15207(8)	3511(4)	8292(5)	57(2)
C(10)	14331(9)	3592(4)	8941(5)	63(2)
C(11)	7702(7)	1607(3)	8560(4)	35(2)
C(12)	6315(8)	1256(4)	8509(5)	65(2)
C(13)	5374(9)	1318(5)	9190(5)	83(3)
C(14)	5885(9)	1720(4)	9905(5)	60(2)
C(15)	7227(9)	2060(4)	9940(4)	58(2)
C(16)	8145(8)	2011(4)	9273(4)	53(2)
C(21)	8287(7)	2466(4)	6700(4)	37(2)
C(22)	8367(8)	3205(4)	7024(4)	50(2)
C(23)	7765(8)	3822(4)	6544(5)	60(2)
C(24)	7112(9)	3698(5)	5744(5)	66(2)
C(25)	7046(9)	2976(5)	5432(5)	62(2)
C(26)	7625(8)	2350(4)	5899(4)	53(2)
C(31)	10738(7)	680(4)	7791(4)	38(2)
C(32)	10594(8)	275(4)	8540(4)	51(2)
C(33)	11632(9)	–270(4)	8791(5)	67(2)
C(34)	12821(9)	–438(4)	8323(6)	68(2)
C(35)	12971(8)	–37(4)	7579(5)	59(2)
C(36)	11946(8)	522(4)	7309(4)	50(2)
		II		
Sb	4004.4(2)	3916.1(2)	2968.8(2)	38.80(5)
O(1)	5610(2)	4570(2)	3127(1)	47.8(5)
O(2)	4854(2)	5533(2)	1580(2)	55.6(6)
O(3)	7549(2)	5546(2)	3088(2)	58.5(6)
O(4)	2408(2)	3202(2)	2889(1)	49.9(5)
O(5)	2176(2)	4384(2)	1383(2)	56.1(6)
O(6)	302(3)	2496(2)	2460(3)	108(1)

Table 2. (Contd.)

Atom	x	y	z	U_{eq}, Å^2
C(1)	5647(3)	5293(2)	2297(2)	44.4(8)
C(2)	6723(3)	5820(2)	2246(2)	43.9(7)
C(3)	7116(3)	6509(3)	1497(3)	59.7(9)
C(4)	8239(3)	6699(3)	1869(3)	65.9(9)
C(5)	8453(3)	6121(3)	2810(3)	69(1)
C(6)	1834(3)	3660(3)	1997(2)	45.6(8)
C(7)	721(3)	3271(3)	1751(2)	52.6(8)
C(8)	–23(3)	3679(3)	899(2)	70(1)
C(9)	–992(4)	3084(4)	1066(4)	172(2)
C(10)	–800(4)	2445(4)	1908(6)	179(3)
C(11)	4576(3)	2867(2)	4412(2)	40.9(7)
C(12)	5658(3)	2875(3)	4939(2)	69.1(9)
C(13)	6101(3)	2137(3)	5844(3)	72(1)
C(14)	5486(3)	1370(3)	6291(2)	50.0(8)
C(15)	4387(3)	1387(3)	5781(3)	87(1)
C(16)	3947(3)	2107(3)	4864(3)	79(1)
C(17)	6003(3)	562(3)	7283(2)	77(1)
C(21)	5339(2)	2663(2)	1836(2)	41.2(7)
C(22)	5435(3)	2962(3)	771(2)	48.2(8)
C(23)	6326(3)	2038(3)	116(2)	57.0(9)
C(24)	7134(3)	806(3)	489(2)	62(1)
C(25)	7019(3)	528(3)	1550(3)	64(1)
C(26)	6146(3)	1441(3)	2220(2)	52.5(9)
C(27)	8115(4)	–196(4)	–242(3)	104(2)
C(31)	2328(3)	5706(2)	3308(2)	43.8(7)
C(32)	1809(3)	5849(3)	4338(2)	58.4(9)
C(33)	715(3)	6989(3)	4642(3)	70(1)
C(34)	138(3)	8012(3)	3936(3)	64(1)
C(35)	665(3)	7857(3)	2901(3)	61(1)
C(36)	1739(3)	6715(3)	2579(2)	52(1)
C(37)	–1007(4)	9256(3)	4278(3)	97(2)
		III		
Sb	8270.03(5)	412.5(1)	7576.01(8)	23.99(3)
O(1)	7600(1)	97(1)	6688(1)	28.2(4)
O(2)	7384(1)	1863(1)	6911(1)	37.8(4)
O(3)	8923(1)	733(1)	8498(1)	31.5(4)
O(4)	8901(1)	–860(1)	9217(1)	40.3(4)
N(1)	6251(1)	–1033(2)	5627(1)	43.6(6)
N(2)	9939(1)	2250(2)	10442(1)	47.4(6)
C(1)	7284(1)	899(2)	6631(1)	26.7(5)
C(2)	6686(1)	–618(2)	5973(1)	35.8(6)
C(3)	6791(1)	514(2)	6220(1)	28.7(5)
C(4)	6423(1)	1272(2)	6096(1)	33.8(6)
C(5)	5973(1)	861(2)	5741(1)	43.1(7)
C(6)	5903(1)	–283(2)	5520(2)	46.1(7)

Table 2. (Contd.)

Atom	x	y	z	U_{eq}, Å^2
C(7)	9062(1)	88(2)	9171(1)	30.3(6)
C(8)	9593(1)	1733(2)	9828(2)	39.4(7)
C(9)	9431(1)	632(2)	9888(1)	32.6(6)
C(10)	9629(1)	41(2)	10631(1)	38.1(6)
C(11)	9987(1)	567(2)	11265(2)	45.8(7)
C(12)	10129(1)	1652(2)	11135(2)	48.1(8)
C(21)	8429(1)	1807(2)	6952(1)	28.1(5)
C(22)	8361(1)	1673(2)	6125(1)	43.2(7)
C(23)	8505(1)	2517(2)	5710(2)	52.9(8)
C(24)	8703(1)	3505(2)	6113(2)	46.1(7)
C(25)	8770(1)	3653(2)	6937(2)	42.0(7)
C(26)	8637(1)	2801(2)	7366(1)	35.0(6)
C(31)	7975(1)	465(2)	8505(1)	26.2(5)
C(32)	8106(1)	1312(2)	9110(1)	34.5(6)
C(33)	7914(1)	1326(2)	9722(1)	45.5(7)
C(34)	7605(1)	482(3)	9747(2)	49.7(7)
C(35)	7481(1)	–377(2)	9155(2)	45.4(7)
C(36)	7659(1)	–383(2)	8522(1)	34.7(6)
C(41)	8474(1)	–1102(2)	7140(1)	24.9(5)
C(42)	8227(1)	–2114(2)	7065(1)	29.9(5)
C(43)	8379(1)	–3091(2)	6772(1)	37.0(6)
C(44)	8759(1)	–3053(2)	6536(1)	40.0(6)
C(45)	8997(1)	–2033(2)	6591(2)	40.8(6)
C(46)	8861(1)	–1055(2)	6896(1)	34.4(6)
C(51)	10000	6527(4)	2500	66(1)
C(52)	9973(1)	5941(3)	1792(2)	72(1)
C(53)	9976(1)	4758(3)	1795(2)	69(1)
C(54)	10000	4190(5)	2500	73(2)
C(55)	10000	7828(5)	2500	133(3)

Table 3. Selected bond lengths and angles in structures **I–III**

Bond	*d*, Å	Angle	ω, deg	Bond	*d*, Å	Angle	ω, deg
I				**II**			
Sb–O(1)	2.117(4)	O(1)SbC(11)	88.7(2)	C(6)–C(7)	1.477(4)	O(4)SbO(2)	131.94(6)
Sb–C(11)	2.120(5)	O(1)SbC(31)	90.6(2)	C(7)–C(8)	1.330(4)	O(5)SbO(2)	79.99(6)
Sb–C(31)	2.125(6)	C(11)SbC(31)	107.1(2)	C(8)–C(9)	1.433(6)	C(1)O(1)Sb	108.0(2)
Sb–C(21)	2.126(6)	O(1)SbC(21)	93.1(2)	C(9)–C(10)	1.232(8)	C(1)O(2)Sb	77.7(2)
Sb–O(4)	2.137(4)	C(11)SbC(21)	104.6(2)	C(11)–C(16)	1.364(4)	C(5)O(3)C(2)	104.5(2)
Sb···O(5)	2.798(4)	C(31)SbC(21)	148.2(2)	C(11)–C(12)	1.368(4)	C(6)O(4)Sb	106.0(2)
Sb···O(2)	2.866(4)	O(1)SbO(4)	176.7(2)	C(12)–C(13)	1.367(4)	C(6)O(5)Sb	78.9(2)
O(1)–C(1)	1.307(7)	C(11)SbO(4)	90.0(2)	C(13)–C(14)	1.359(4)	C(7)O(6)C(10)	99.8(3)
O(2)–C(1)	1.239(7)	C(31)SbO(4)	86.9(2)	C(14)–C(15)	1.359(4)	O(2)C(1)O(1)	123.3(3)
O(3)–C(5)	1.347(8)	C(21)SbO(4)	90.2(2)	C(14)–C(17)	1.504(4)	O(2)C(1)C(2)	120.5(3)
O(3)–C(2)	1.365(7)	O(1)SbO(5)	129.7(1)	C(15)–C(16)	1.372(4)	O(1)C(1)C(2)	116.2(2)
O(4)–C(6)	1.307(7)	C(11)SbO(5)	141.6(2)	C(21)–C(26)	1.377(3)	C(3)C(2)O(3)	110.3(3)
O(5)–C(6)	1.229(7)	SbO(4)C(6)	106.9(4)	**III**			
O(6)–C(7)	1.362(7)	SbO(1)C(1)	110.8(4)	Sb–C(41)	2.098(2)	C(41)SbC(21)	108.33(9)
O(6)–C(10)	1.364(8)	O(4)SbO(5)	51.7(1)	Sb–C(21)	2.098(2)	C(41)SbO(3)	95.43(7)
II				Sb–O(3)	2.101(1)	C(21)SbO(3)	85.27(7)
Sb–C(11)	2.105(3)	C(11)SbC(21)	104.6(1)	Sb–C(31)	2.101(2)	C(41)SbC(31)	124.14(8)
Sb–C(21)	2.110(3)	C(11)SbC(31)	106.9(1)	Sb–O(1)	2.112(1)	C(21)SbC(31)	127.51(8)
Sb–C(31)	2.115(2)	C(21)SbC(31)	148.5(1)	Sb···O(2)	3.054(2)	O(3)SbC(31)	88.40(7)
Sb–O(1)	2.136(2)	C(11)SbO(1)	87.58(9)	Sb···O(4)	3.168(2)	C(41)SbO(1)	86.06(7)
Sb–O(4)	2.158(2)	C(21)SbO(1)	91.90(9)	O(1)–C(1)	1.324(3)	C(21)SbO(1)	96.12(7)
Sb···O(5)	2.774(2)	C(31)SbO(1)	91.03(9)	O(2)–C(1)	1.218(3)	O(3)SbO(1)	177.55(6)
Sb···O(2)	2.816(2)	C(11)SbO(4)	89.40(9)	O(3)–C(7)	1.318(3)	C(31)SbO(1)	89.15(7)
O(1)–C(1)	1.299(3)	C(21)SbO(4)	89.00(9)	O(4)–C(7)	1.223(3)	C(41)SbO(2)	132.00(6)
O(2)–C(1)	1.226(3)	C(31)SbO(4)	89.71(9)	N(1)–C(6)	1.340(3)	C(21)SbO(2)	73.55(7)
O(3)–C(5)	1.367(4)	O(1)SbO(4)	176.97(7)	N(1)–C(2)	1.342(3)	O(3)SbO(2)	131.85(5)
O(3)–C(2)	1.373(3)	C(11)SbO(5)	141.31(9)	N(2)–C(12)	1.326(3)	C(31)SbO(2)	72.74(6)
O(4)–C(6)	1.301(3)	C(21)SbO(5)	76.63(8)	N(2)–C(8)	1.344(3)	O(1)SbO(2)	47.03(5)
O(5)–C(6)	1.235(3)	C(31)SbO(5)	77.92(8)	C(1)–C(3)	1.492(3)	C(41)SbO(4)	76.19(6)
O(6)–C(7)	1.386(4)	O(1)SbO(5)	131.08(7)	C(2)–C(3)	1.388(3)	C(21)SbO(4)	129.78(6)
O(6)–C(10)	1.427(6)	O(4)SbO(5)	51.95(6)	C(3)–C(4)	1.388(3)	O(3)SbO(4)	44.99(5)
C(1)–C(2)	1.477(4)	C(11)SbO(2)	138.64(9)	C(4)–C(5)	1.381(3)	C(31)SbO(4)	68.02(6)
C(2)–C(3)	1.334(4)	C(21)SbO(2)	78.76(8)	C(5)–C(6)	1.381(4)	O(1)SbO(4)	133.86(5)
C(3)–C(4)	1.407(4)	C(31)SbO(2)	78.87(8)	C(7)–C(9)	1.488(3)	C(7)O(3)Sb	119.2(1)
C(4)–C(5)	1.314(4)	O(1)SbO(2)	51.09(6)	C(8)–C(9)	1.391(3)	C(1)O(1)Sb	115.4(1)

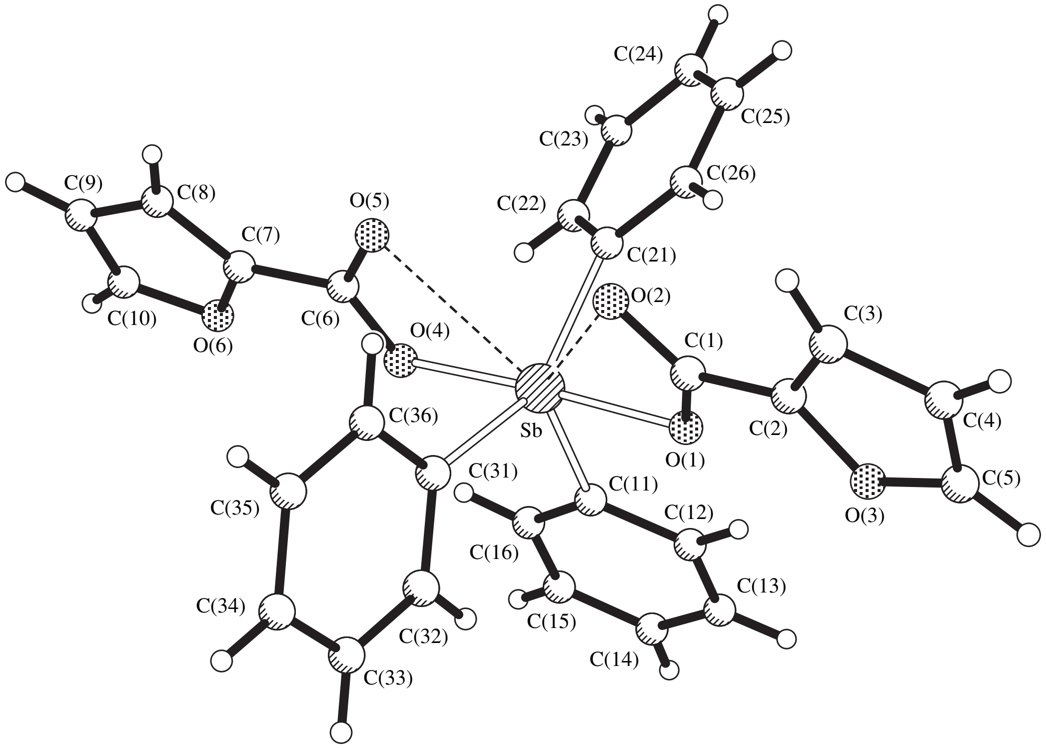

Fig. 1. Molecular structure of compound **I**.

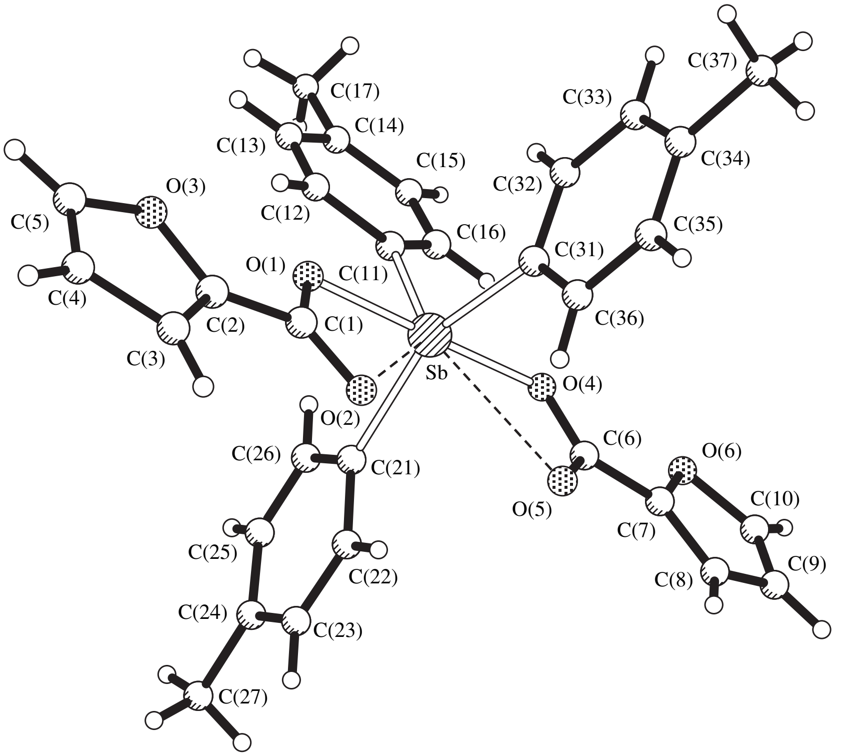

Fig. 2. Molecular structure of compound **II**.

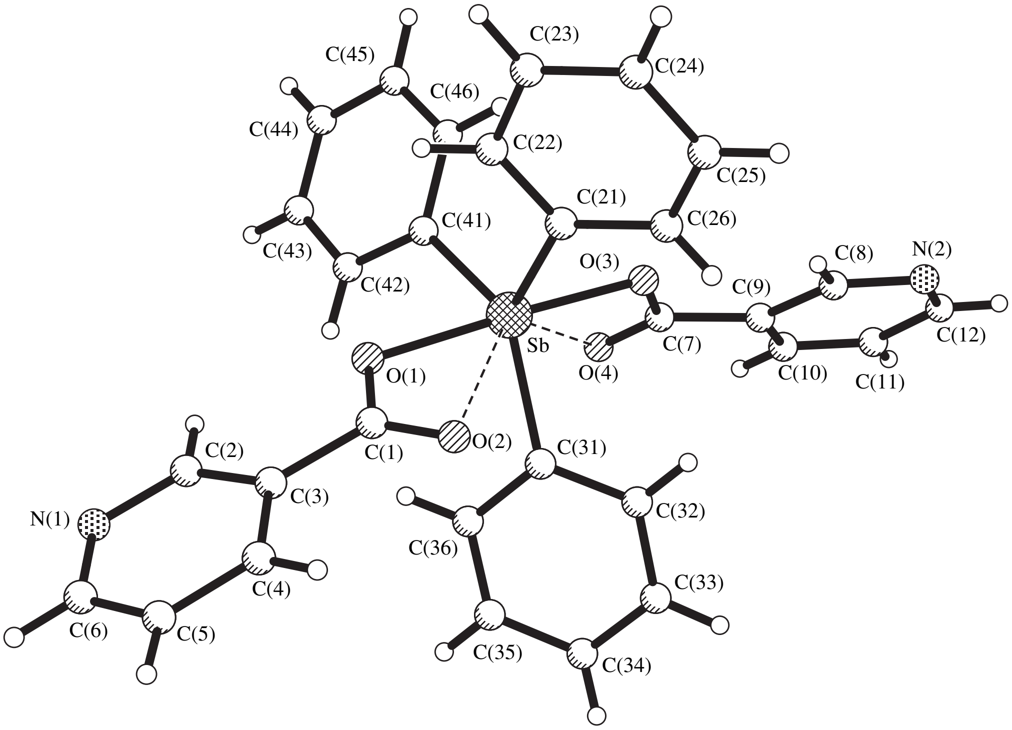

Fig. 3. Molecular structure of compound **III**.

RESULTS AND DISCUSSION

The oxidation of triarylstibine with hydrogen peroxide in the presence of carboxylic acids RCOOH, whose radical R does not contain the potential coordinating sites, results in the formation of triarylantimony dicarboxylates with the general formula $Ar_3Sb(O_2CR)_2$ [9, 10].

We established that the reaction of triarylstibine with hydrogen peroxide in the presence of the acids, such as pyrimucic and nicotinic acids, with heteroatoms in the R radical (at the molar ratio of 1 : 1 : 2) occurs in an ether with the formation of triarylantimony dicarboxylates (in the yield up to 99%).

$$Ar_3Sb + H_2O_2 + 2HOC(O)R$$

$$\longrightarrow Ar_3Sb[OC(O)R]_2 + 2H_2O$$

$$Ar = Ph, R = C_4H_3O\text{-}2\ (\mathbf{I});$$

$$Ar = p\text{-Tol}, R = C_4H_3O\text{-}2\ (\mathbf{II});$$

$$Ar = Ph, R = C_5H_4N\text{-}3\ (\mathbf{III});$$

$$Ar = p\text{-Tol}, R = C_5H_4N\text{-}3\ (\mathbf{IV}).$$

Thus, the direction of the oxidative addition reaction does not depend on the presence of the potential coordinating sites in radical R of the acid.

According to X-ray diffraction data, the Sb atoms in compounds **I**–**III** lie in the equatorial plane and have the distorted trigonal-bipyramidal coordination with the O atoms of the carboxylate ligands in the axial positions (Figs. 1–3). As it was expected, molecules **I** and **II** have almost identical geometries. The sums of angles in an equatorial plane and the axial angles OSbO for molecules **I** and **II** are equal to 359.9°, 360.9°, and 176.7°, and 177.0°, respectively. The carboxyl groups with the *cis*-orientation relative to the equatorial Ar_3Sb fragment lie in **I** and **II** almost in one plane (the dihedral angles between the planes of the carboxyl groups are 14.38° and 2.56°, respectively). The Sb atom extends from the equatorial plane in compound **I** by 0.043 Å and in **II**, by 0.023 Å. The planes of arene rings of the carboxylate ligands are almost coplanar to the planes that contain the carboxyl groups (the respective angles are equal to 5.95°, 5.14°, and 3.90°), which can bring about their conjugation. The *n*–π-conjugations are confirmed by a decrease in the C–C(OO) bond lengths (1.440(8), 1.454(8), and 1.477(4), 1.477(4) Å in **I** and **II**, respectively) as compared to their values in triarylantimony dicarboxylates that do not exhibit conjugation (1.522(6)–1.547(7) Å [7]).

The geometrical parameters of molecules **I** and **II** slightly differ in the Sb–C and Sb–O bond lengths. The Sb–C distances in **I** (2.120(5), 2.125(6), and 2.126(6) Å) are longer than in **II** (2.105(3), 2.110(3), and 2.115(2) Å), which can be explained by the introduction of the electron-donor methyl substituents into the aryl ligands of compound **II**. Similar decrease in the Sb–C bond lengths was observed in the Sb(V) tolyl derivatives as compared to their phenyl analogs [13].

The Sb–O bond lengths in complexes **I** and **II** are equal to 2.117(4), 2.137(4), and 2.136(2), 2.158(2) Å, respectively, which is comparable with the respective values in the known triphenylantimony dicarboxylates (2.095(2)-2.185(2) Å).

As distinct from $Ph_3Sb[OC(O)C_5H_4N\text{-}2]_2$ (**V**), in which the carboxylate ligands are coordinated by the Sb atom in different ways, in **I** and **II**, the O atoms of heterocycles are not bound to the Sb atom.

As the other triphenylantimony dicarboxylates, compounds **I** and **II** also contain the intramolecular contacts Sb···O(=C). The respective distances are 2.866(4), 2.798(4) and 2.816(2) and 2.774(2) Å that are comparable with the analogous distances in $Ph_3Sb[OC(O)CH_3]_2$ (2.779 Å [1]), $Ph_3Sb[OC(O)C_6H_5]_2$ (2.70 and 2.81 Å [2]), $Ph_3Sb[OC(O)C_4H_3S\text{-}2]_2$ (2.744 and 2.949 Å [3]). Since the carboxylate ligands in **I** and **II** have the *cis*-orientation with respect to the equatorial Ar_3Sb fragment, one of the equatorial angles CSbC on the side of the Sb···O(=C) contacts is noticeably increased (148.2° and 148.5° in **I** and **II**), which brings about a decrease in the other two angles (104.6°, 107.1° and 104.6°, 106.9° in **I** and **II**, respectively).

Compound **III** has almost undistorted trigonal-bipyramidal coordinaton of the Sb atom: the sum of the angles in equatorial plane and the axial angle OSbO are 359.9° and 177.5°, respectively; the Sb atom deviates from equatorial plane by 0.016 Å.

The Sb–C bonds in **III** (2.098(2)–2.101(2) Å) are shorter than in **II**, which suggests that the length of the indicated bonds is determined not only by the nature of the aryl ligands, but also of the carboxylate groups. Thus, in compound **V**, which differs from **III** only in the position of the N atom in heterocycle of the carboxylate ligand, the Sb–C distances are 2.118(3)–2.130(3) Å [4].

The lengths of the Sb–O bonds in **III** are equal to 2.112(1) and 2.101(2) Å (in **V**, these are 2.099(2) and 2.185(2) Å). Compound **III** has common coordination of ligands. However, the asymmetry of the bidentate carboxylate ligands in **III** is more pronounced than in **I** and **II**: the Sb···O=C distances are 3.054(2) and 3.168(2) Å. The structure of compound **III** is peculiar in that it has an abnormally large (for triphenylantimony dicarboxylates) dihedral angle between the planes of carboxyl groups (62.18°) such that two equatorial angles (on the side of contacts) have close values (124.1° and 127.5°), while the third angle is significantly smaller (108.3°).

The planar phenyl rings C(11)–C(16), C(21)–C(26), C(31)–C(36) in **I**–**III** are rotated about the Sb–C bonds in such a way that the intra- and intermolecular contacts are minimal (the corresponding angles are equal to 82.3°, 64.0°, 5.0° in **I**; 90.0°, 7.7°, 7.2° in **II**; 40.4°, 38.5°, 33.5° in **III**).

Thus, the above analysis of X-ray diffraction data of compounds **I**–**III** shows that the strengthening of intramolecular contacts in triarylantimony dicarboxylates results in the higher distortion of the trigonal-bipyramidal coordination of a central atom and, conversely, with weak intramolecular interactions (compound **III**), the coordination polyhedron of the Sb atom is only slightly distorted.

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