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Tetra- and Triarylantimony Fluorobenzoates: Synthesis and Structures

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Abstract—The reactions of pentaarylantimony (Ar_5Sb, where Ar = Ph or *p*-Tol) with triarylantimony bis(pentafluorobenzoate) and triarylantimony bis(3,4,5-trifluorobenzoate) in toluene afforded tetraarylantimony pentafluoro- and 3,4,5-trifluorobenzoates in up to 90% yields. The starting triarylantimony bis(pentafluorobenzoates) and bis(3,4,5-trifluorobenzoates) were prepared in ether by oxidative addition involving triarylstibine, hydrogen peroxide, and pentafluorobenzoic or 3,4,5-trifluorobenzoic acid, respectively, in up to 98% yields. Tetra-*p*-tolylantimony pentafluorobenzoate and triphenylantimony bis(pentafluorobenzoate) were structurally characterized by X-ray diffraction analysis. The coordination polyhedron of the Sb atoms is a distorted trigonal bipyramid with axial carboxy groups. In these compounds, the Sb atoms and carbonyl O atoms are linked by intramolecular contacts, which are especially pronounced in the latter complex (the Sb··O(=C) distances are 3.377(3) and 2.943(2), 3.167(2) Å, respectively).

Pentaphenylantimony Ar_5Sb is known to react with triphenylantimony diacylates $Ar_3Sb[OC(O)Ar']_2$ to give tetraphenylantimony acylates $Ar_4SbOC(O)Ar'$ [1–3]. It was shown that the presence of functional groups in the aryl ring of an acylate substituent sometimes prevents the above redistribution of aryl radicals. Thus, the reaction of triphenylantimony disalicylate with pentaphenylantimony does not yield tetraphenylantimony salicylate [2]. To elucidate the factors that determine the behavior of these reagents, we studied the reactions of Ar_5Sb (**I**) (Ar = C_6H_5 or $C_6H_4CH_3$-4) with triarylantimony diacylates $Ar_3Sb[OC(O)Ar']_2$ (**II**) (Ar' = C_6F_5, or $C_6H_2F_3$-3,4,5) and examined the molecular and crystal structures of triphenylantimony bis(pentafluorobenzoate) and tetra-*p*-tolylantimony pentafluorobenzoate.

EXPERIMENTAL

The starting acylates $Ar_3Sb(OC(O)Ar')_2$ were prepared following the Thepe method [4] using oxidative addition in ether at $T = 20°C$ for 12 h.

Triphenylantimony bis(pentafluorobenzoate) (IIa). Pentafluorobenzoic acid (1.35 g, 6.37 mmol) and 30% aqueous hydrogen peroxide (3.17 mmol, 0.36 ml) were added to a solution of triphenylstibine (1.12 g, 3.17 mmol) in 10 ml of ether. The reaction mixture was kept at 20°C for 12 h. The crystals formed were filtered off and dried.

IR (ν, cm^{-1}): 1672 vs, 1340 vs, 1260 vs, 1100 s, 1065 m, 990 vs, 920 s.

Other triarylantimony dibenzoates (**IIb**)–(**IId**) were obtained analogously. Elemental analysis data are given in Table 1.

The compounds $Ar_4SbOC(O)Ar'$ (III) were synthesized in a solution of an arene (90°C, 1 h) by the reaction

$$\underset{(\mathbf{I})}{Ar_5Sb} + \underset{(\mathbf{II})}{Ar_3Sb[OC(O)Ar']_2} \longrightarrow \underset{(\mathbf{III})}{2Ar_4SbOC(O)Ar'}$$

(Ar = (a, c) C_6H_5 and (b, d) 4-$CH_3C_6H_4$ and Ar' = (a, b) C_6F_5 and (c, d) 3,4,5-$F_3C_6H_2$).

Tetraphenylantimony pentafluorobenzoate (IIIa). A mixture of pentaphenylantimony (0.91 g, 1.79 mmol) and triphenylantimony bis(pentafluorobenzoate) (1.40 g, 1.80 mmol) was kept in 15 ml of toluene at 90°C for one hour. The solvent was removed, and the residue was recrystallized from toluene–heptane (1 : 1).

IR (ν, cm^{-1}): 1655 vs, 1335 vs, 1275 vs, 1098 s, 1060 m, 980 vs.

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Table 1. Yields, melting points, and elemental analysis data for tetra- and triarylantimony pentafluorobenzoates and 3,4,5-trifluorobenzoates

Complex	Empirical formula	Content (found/calculated), %			Yield, %	T_{mp}, °C
		C	H	F		
IIa	$C_{32}H_{15}SbO_4F_{10}$	50.13/49.55	1.65/1.93	24.22/24.52	97	173
IIb	$C_{35}H_{21}SbO_4F_{10}$	51.11/51.41	2.75/2.57	23.02/23.26	98	147
IIc	$C_{32}H_{19}SbO_4F_6$	54.19/54.62	2.83/2.70	16.08/16.22	99	236
IId	$C_{35}H_{25}SbO_4F_6$	56.12/56.38	3.49/3.36	15.14/15.30	99	171
IIIa	$C_{31}H_{20}SbO_2F_5$	57.83/58.03	3.47/3.12	14.43/14.82	69	161
IIIb	$C_{35}H_{28}SbO_2F_5$	60.06/60.26	3.84/4.02	13.29/13.63	78	150
IIIc	$C_{31}H_{22}SbO_2F_3$	61.06/61.49	3.87/3.64	9.05/9.42	97	161
IIId	$C_{35}H_{30}SbO_2F_3$	63.48/63.54	4.87/4.54	8.34/8.62	96	173

The IR spectrum and melting point of compound **IIIa** are identical to those of the substance synthesized from pentaphenylantimony and fluorobenzoic acid in [5].

Other tetraarylantimony benzoates (**IIIb**)–(**IIId**) were obtained analogously (Table 1).

IR spectra were recorded on a Hitachi-215 spectrometer (suspension in Vaseline oil between NaCl plates).

X-ray diffraction analysis of crystals **IIa** and **IIIb** was carried out on a Bruker P4 automated diffractometer (graphite monochromator, MoK_α radiation, θ/2θ scan mode).

The crystals of **IIa** are triclinic: at 20°C a = 12.1218(5) Å, b = 12.1640(5) Å, c = 12.7307(5) Å, α = 71.369(3)°, β = 62.988(3)°, γ = 60.461(3)°, V = 1443.9(1) Å^3, space group $P\bar{1}$, ρ_{calcd} = 1.783 g/cm^3, crystal size 0.5 × 0.3 × 0.2 mm, μ_{Mo} = 1.059 mm^{-1}, $2\theta < 50°$, and Z = 2. The final residuals are wR_2 = 0.0798 and R = 0.0349, S = 1.026 for all 6717 reflections and wR_2 = 0.0772 and R = 0.0303 for 6055 reflections with $F > 4\sigma(F)$.

The crystals of **IIIb** are monoclinic: at 20°C a = 11.3947(5) Å, b = 15.7868(6) Å, c = 17.6219(5) Å, β = 103.813(3)°, V = 3078.3(2) Å^3, space group $P2_1/n$, ρ_{calcd} = 1.505 g/cm^3, crystal size 0.56 × 0.45 × 0.42 mm, μ_{Mo} = 0.957 mm^{-1}, $2\theta < 50°$, and Z = 4. The final residuals are wR_2 = 0.0825 and R = 0.0347, S = 1.072 for all 5399 reflections and wR_2 = 0.0790 and R = 0.0289 for 4757 reflections with $F > 4\sigma(F)$.

Structures **IIa** and **IIIb** were solved by the direct method and refined by the least-squares method in full-matrix anisotropic approximation for all reflections with the use of the SHELXTL programs [6]. Hydrogen atoms were located geometrically.

Atomic coordinates and thermal parameters are given in Table 2. The bond lengths and angles are listed in Table 3.

RESULTS AND DISCUSSION

The aforementioned syntheses of tetraarylantimony fluorobenzoates showed that the presence of F atoms in the aryl ring of the benzoato ligand does not change the mechanism of radical redistribution in reaction (1) between pentaarylantimony and symmetrical arylantimony derivatives. Therefore, the area of application of this reaction proves to be wider than was previously assumed [7].

The X-ray diffraction analysis of triphenylantimony bis(pentafluorobenzoate) (**IIa**) revealed a distorted trigonal-bipyramidal coordination of the Sb atom with axial carboxy O atoms (Fig. 1). The sum of the CSbC angles in the equatorial plane is 359.9°, and the Sb–O distances (2.122(2) and 2.154(2) Å) are close to analogous distances in other triphenylantimony diacylates [8]. Note that the Sb–O (2.137 and 2.127 Å) and Sb–C bond lengths (2.094–2.120 Å) in triphenylantimony dibenzoate (**IIe**) [9] are virtually the same as in **IIa**.

The presence of the carboxy groups in tri- and tetraarylantimony acylates suggests an intramolecular interaction of the Sb atom with the carbonyl O atom (i.e., the CN of antimony can increase to 7 and 6, respectively) [9, 10]. In complex **IIa**, the Sb··O(=C) intramolecular contacts are 2.943(2) and 3.167(2) Å; they are substantially longer than those in **IIe** (2.699 and 2.813 Å) (the sum of the van der Waals radii of antimony and oxygen equals 3.70 Å [11]). The Sb··O(=C) interaction in **IIa** is confirmed by an increased CSbC equatorial angle (138.57(9)°) (on the contact side) and by the other two equatorial angles being respectively decreased to 109.13(9)° and 112.2(1)° relative to the perfect angle of 120°. The analogous angles in complex

Table 2. Coordinates ($\times 10^4$) and equivalent isotropic thermal parameters U_{equiv} ($\times 10^3$, Å^2) of non-hydrogen atoms in structures **IIa** and **IIIb**

Atom	*x*	*y*	*z*	U_{equiv}	Atom	*x*	*y*	*z*	U_{equiv}
IIa					**IIIb**				
Sb(1)	8483(1)	2541(1)	3121(1)	36(1)	Sb(1)	–28(1)	9623(1)	1921(1)	40(1)
O(11)	10275(2)	1914(2)	3506(2)	42(1)	O(1)	–1851(2)	9195(1)	2236(1)	52(1)
O(21)	11217(2)	2417(2)	1572(2)	57(1)	O(2)	–2993(2)	9447(2)	1038(1)	67(1)
C(11)	11276(2)	2020(2)	2552(2)	42(1)	F(1)	–3818(2)	10226(2)	2775(1)	76(1)
C(21)	12582(2)	1576(2)	2732(2)	44(1)	F(2)	–5734(2)	9786(2)	3318(1)	89(1)
C(31)	12650(3)	1820(3)	3680(3)	56(1)	F(3)	–6873(2)	8300(2)	2874(2)	103(1)
C(41)	13871(4)	1419(4)	3800(4)	75(1)	F(4)	–6156(3)	7304(2)	1817(2)	115(1)
C(51)	15059(3)	747(4)	2958(4)	79(1)	F(5)	–4234(2)	7751(2)	1261(2)	95(1)
C(61)	15025(3)	483(3)	2012(4)	72(1)	C(11)	–2839(3)	9236(2)	1716(2)	49(1)
C(71)	13810(3)	906(3)	1897(3)	55(1)	C(12)	–3947(2)	8994(2)	2013(2)	49(1)
F(31)	11516(2)	2508(2)	4494(2)	81(1)	C(13)	–4363(3)	9490(2)	2535(2)	53(1)
F(41)	13905(3)	1707(3)	4705(3)	121(1)	C(14)	–5345(3)	9271(3)	2825(2)	61(1)
F(51)	16247(3)	365(3)	3063(3)	129(1)	C(15)	–5929(3)	8536(3)	2593(2)	67(1)
F(61)	16193(2)	–181(3)	1207(3)	112(1)	C(16)	–5569(3)	8029(2)	2057(3)	72(1)
F(71)	13826(2)	617(2)	963(2)	81(1)	C(17)	–4586(3)	8262(2)	1774(2)	62(1)
O(12)	6646(2)	3103(2)	2880(2)	49(1)	C(21)	1589(2)	10041(2)	1594(2)	43(1)
O(22)	7602(2)	3309(2)	906(2)	55(1)	C(22)	2101(3)	9584(2)	1084(2)	47(1)
C(12)	6628(3)	3373(2)	1820(2)	43(1)	C(23)	3078(3)	9895(2)	834(2)	53(1)
C(22)	5238(2)	3808(2)	1793(2)	41(1)	C(24)	3599(3)	10661(2)	1091(2)	50(1)
C(32)	4032(3)	4496(3)	2649(2)	49(1)	C(25)	3090(3)	11119(2)	1597(2)	65(1)
C(42)	2789(3)	4914(3)	2577(3)	56(1)	C(26)	2103(3)	10818(2)	1842(2)	65(1)
C(52)	2683(3)	4645(3)	1669(3)	56(1)	C(27)	4653(3)	11002(3)	808(2)	70(1)
C(62)	3844(3)	3966(3)	815(3)	52(1)	C(31)	596(3)	9464(2)	3136(2)	43(1)
C(72)	5092(3)	3567(2)	880(2)	45(1)	C(32)	1143(4)	10123(2)	3586(2)	79(1)
F(32)	4060(2)	4787(2)	3558(2)	73(1)	C(33)	1520(5)	10040(3)	4386(2)	96(2)
F(42)	1658(2)	5568(3)	3431(2)	90(1)	C(34)	1367(3)	9309(3)	4760(2)	66(1)
F(52)	1475(2)	5035(2)	1617(2)	84(1)	C(35)	850(3)	8645(2)	4311(2)	65(1)
F(62)	3750(2)	3679(2)	–59(2)	77(1)	C(36)	457(3)	8717(2)	3504(2)	59(1)
F(72)	6174(2)	2885(2)	34(2)	69(1)	C(37)	1751(5)	9241(4)	5643(2)	102(2)
C(13)	7420(2)	2299(2)	4960(2)	39(1)	C(41)	–254(3)	8474(2)	1292(2)	43(1)
C(23)	6023(3)	2894(4)	5408(3)	70(1)	C(42)	484(3)	7803(2)	1603(2)	58(1)
C(33)	5328(3)	2790(4)	6633(3)	81(1)	C(43)	434(4)	7053(2)	1198(2)	66(1)
C(43)	6009(3)	2117(3)	7389(2)	59(1)	C(44)	–338(3)	6958(2)	474(2)	62(1)
C(53)	7386(3)	1521(4)	6949(2)	66(1)	C(45)	–1064(3)	7629(2)	170(2)	64(1)
C(63)	8102(3)	1619(3)	5737(2)	57(1)	C(46)	–1033(3)	8385(2)	568(2)	54(1)
C(14)	9394(2)	861(2)	2346(2)	41(1)	C(47)	–342(5)	6144(3)	23(3)	96(1)
C(24)	9072(3)	–130(3)	3075(3)	52(1)	C(51)	–959(3)	10771(2)	1613(2)	45(1)
C(34)	9671(4)	–1285(3)	2635(3)	64(1)	C(52)	–859(3)	11170(2)	934(2)	59(1)
C(44)	10581(3)	–1438(3)	1495(3)	62(1)	C(53)	–1429(3)	11933(2)	730(2)	66(1)
C(54)	10904(3)	–447(3)	774(3)	58(1)	C(54)	–2073(3)	12326(2)	1196(2)	58(1)
C(64)	10318(3)	716(3)	1181(2)	51(1)	C(55)	–2157(3)	11930(2)	1877(2)	56(1)
C(15)	8388(2)	4402(2)	2610(2)	39(1)	C(56)	–1610(3)	11152(2)	2086(2)	50(1)
C(25)	8302(3)	4932(3)	3477(3)	54(1)	C(57)	–2656(4)	13180(3)	963(3)	86(1)
C(35)	8247(4)	6145(3)	3219(3)	64(1)					
C(45)	8277(3)	6822(3)	2128(3)	61(1)					
C(55)	8365(3)	6297(3)	1268(3)	57(1)					
C(65)	8434(3)	5077(3)	1494(2)	48(1)					

Table 3. Bond lengths and angles in structures **IIa** and **IIIb**

IIa				**IIIb**			
Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Sb(1)–C(13)	2.103(2)	Sb(1)–C(15)	2.105(2)	Sb(1)–C(51)	2.104(3)	Sb(1)–C(31)	2.104(3)
Sb(1)–C(14)	2.108(2)	Sb(1)–O(12)	2.122(2)	Sb(1)–C(41)	2.110(3)	Sb(1)–C(21)	2.160(3)
Sb(1)–O(11)	2.154(2)	O(11)–C(11)	1.296(3)	Sb(1)–O(1)	2.373(2)	O(1)–C(11)	1.273(4)
O(21)–C(11)	1.206(3)	C(11)–C(21)	1.503(3)	O(2)–C(11)	1.212(4)	F(1)–C(13)	1.338(4)
C(21)–C(31)	1.376(4)	C(21)–C(71)	1.388(4)	F(2)–C(14)	1.340(4)	F(3)–C(15)	1.339(4)
C(31)–F(31)	1.338(4)	C(31)–C(41)	1.378(5)	F(4)–C(16)	1.343(4)	F(5)–C(17)	1.342(4)
C(41)–F(41)	1.329(4)	C(41)–C(51)	1.375(6)	C(11)–C(12)	1.527(4)	C(12)–C(13)	1.375(5)
C(51)–F(51)	1.336(4)	C(51)–C(61)	1.363(6)	C(12)–C(17)	1.377(5)	C(13)–C(14)	1.380(5)
C(61)–F(61)	1.338(4)	C(61)–C(71)	1.362(5)	C(14)–C(15)	1.352(5)	C(15)–C(16)	1.373(6)
C(71)–F(71)	1.333(4)	O(12)–C(12)	1.292(3)	C(16)–C(17)	1.381(5)	C(21)–C(26)	1.384(5)
O(22)–C(12)	1.213(3)	C(12)–C(22)	1.510(3)	C(21)–C(22)	1.386(4)	C(22)–C(23)	1.381(4)
C(22)–C(72)	1.386(3)	C(22)–C(32)	1.398(4)	C(23)–C(24)	1.376(5)	C(24)–C(25)	1.379(5)
C(32)–F(32)	1.332(3)	C(32)–C(42)	1.370(4)	C(24)–C(27)	1.506(4)	C(25)–C(26)	1.381(5)
C(42)–F(42)	1.348(3)	C(42)–C(52)	1.371(5)	C(31)–C(32)	1.365(5)	C(31)–C(36)	1.372(4)
C(52)–F(52)	1.326(3)	C(52)–C(62)	1.372(4)	C(32)–C(33)	1.379(5)	C(33)–C(34)	1.361(6)
C(62)–F(62)	1.332(3)	C(62)–C(72)	1.376(4)	C(34)–C(35)	1.360(5)	C(34)–C(37)	1.515(5)
C(72)–F(72)	1.336(3)	C(13)–C(23)	1.376(4)	C(35)–C(36)	1.390(5)	C(41)–C(46)	1.376(4)
C(13)–C(63)	1.376(3)	C(23)–C(33)	1.394(4)	C(41)–C(42)	1.382(4)	C(42)–C(43)	1.376(5)
C(33)–C(43)	1.352(5)	C(43)–C(53)	1.357(4)	C(43)–C(44)	1.375(5)	C(44)–C(45)	1.372(5)
C(53)–C(63)	1.384(4)	C(14)–C(24)	1.373(4)	C(44)–C(47)	1.510(5)	C(45)–C(46)	1.382(5)
C(14)–C(64)	1.396(3)	C(24)–C(34)	1.394(4)	C(51)–C(52)	1.381(4)	C(51)–C(56)	1.380(4)
C(34)–C(44)	1.369(5)	C(44)–C(54)	1.372(5)	C(52)–C(53)	1.376(5)	C(53)–C(54)	1.372(5)
C(54)–C(64)	1.384(4)	C(15)–C(65)	1.387(3)	C(54)–C(55)	1.377(5)	C(54)–C(57)	1.515(5)
C(15)–C(25)	1.389(4)	C(25)–C(35)	1.379(4)				
C(35)–C(45)	1.365(5)	C(45)–C(55)	1.374(5)				
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
C(13)Sb(1)C(14)	112.2(1)	C(13)Sb(1)C(15)	109.13(9)	C(51)Sb(1)C(41)	127.8(1)	C(51)Sb(1)C(31)	113.1(1)
C(13)Sb(1)O(12)	87.53(8)	C(15)Sb(1)C(14)	138.57(9)	C(51)Sb(1)C(21)	94.4(1)	C(31)Sb(1)C(41)	113.7(1)
C(14)Sb(1)O(12)	91.38(8)	C(15)Sb(1)O(12)	92.73(8)	C(41)Sb(1)C(21)	97.3(1)	C(31)Sb(1)C(21)	101.9(1)
C(15)Sb(1)O(11)	89.77(8)	C(13)Sb(1)O(11)	88.13(8)	C(31)Sb(1)O(1)	80.22(9)	C(51)Sb(1)O(1)	83.7(1)
O(12)Sb(1)O(11)	175.52(6)	C(14)Sb(1)O(11)	89.20(8)	C(21)Sb(1)O(1)	177.64(9)	C(41)Sb(1)O(1)	82.80(9)
O(21)C(11)O(11)	124.6(2)	C(11)O(11)Sb(1)	111.3(2)	O(2)C(11)O(1)	128.3(3)	C(11)O(1)Sb(1)	119.4(2)
O(11)C(11)C(21)	115.0(2)	O(21)C(11)C(21)	120.4(2)	O(1)C(11)C(12)	113.7(3)	O(2)C(11)C(12)	118.0(3)
C(31)C(21)C(11)	123.6(2)	C(31)C(21)C(71)	116.6(3)	C(13)C(12)C(11)	122.1(3)	C(13)C(12)C(17)	116.2(3)
F(31)C(31)C(21)	120.2(3)	C(71)C(21)C(11)	119.8(2)	F(1)C(13)C(12)	119.9(3)	C(17)C(12)C(11)	121.7(3)
C(21)C(31)C(41)	121.9(3)	F(31)C(31)C(41)	117.9(3)	C(12)C(13)C(14)	123.0(3)	F(1)C(13)C(14)	117.1(3)
F(41)C(41)C(31)	120.4(4)	F(41)C(41)C(51)	120.2(3)	F(2)C(14)C(13)	120.8(4)	F(2)C(14)C(15)	120.1(3)
F(51)C(51)C(61)	120.2(4)	C(51)C(41)C(31)	119.4(3)	F(3)C(15)C(14)	120.5(4)	C(15)C(14)C(13)	119.1(4)
C(61)C(51)C(41)	120.1(3)	F(51)C(51)C(41)	119.7(4)	C(14)C(15)C(16)	120.1(3)	F(3)C(15)C(16)	119.4(4)
F(61)C(61)C(51)	119.1(3)	F(61)C(61)C(71)	121.2(4)	F(4)C(16)C(17)	119.9(4)	F(4)C(16)C(15)	120.4(4)
F(71)C(71)C(61)	117.5(3)	C(71)C(61)C(51)	119.7(3)	F(5)C(17)C(12)	119.3(3)	C(15)C(16)C(17)	119.7(3)
C(61)C(71)C(21)	122.3(3)	F(71)C(71)C(21)	120.1(3)	C(12)C(17)C(16)	121.8(3)	F(5)C(17)C(16)	118.8(3)
O(22)C(12)O(12)	125.4(2)	C(12)O(12)Sb(1)	119.8(2)	C(26)C(21)Sb(1)	120.7(2)	C(26)C(21)C(22)	117.0(3)

Table 3. (Contd.)

IIa				**IIIb**			
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(12)C(12)C(22)	113.6(2)	O(22)C(12)C(22)	121.0(2)	C(23)C(22)C(21)	121.2(3)	C(22)C(21)Sb(1)	122.1(2)
C(72)C(22)C(12)	121.0(2)	C(72)C(22)C(32)	115.8(2)	C(23)C(24)C(25)	117.3(3)	C(24)C(23)C(22)	121.6(3)
F(32)C(32)C(42)	117.7(2)	C(32)C(22)C(12)	123.2(2)	C(25)C(24)C(27)	121.2(3)	C(23)C(24)C(27)	121.4(3)
C(42)C(32)C(22)	121.7(3)	F(32)C(32)C(22)	120.6(2)	C(25)C(26)C(21)	121.5(3)	C(24)C(25)C(26)	121.4(3)
F(42)C(42)C(52)	119.9(3)	F(42)C(42)C(32)	119.3(3)	C(32)C(31)Sb(1)	119.7(2)	C(32)C(31)C(36)	118.0(3)
F(52)C(52)C(42)	120.4(3)	C(32)C(42)C(52)	120.8(3)	C(31)C(32)C(33)	120.6(4)	C(36)C(31)Sb(1)	122.3(2)
C(42)C(52)C(62)	119.1(2)	F(52)C(52)C(62)	120.5(3)	C(35)C(34)C(33)	117.4(3)	C(34)C(33)C(32)	122.1(4)
F(62)C(62)C(72)	120.6(3)	F(62)C(62)C(52)	119.5(3)	C(33)C(34)C(37)	121.2(4)	C(35)C(34)C(37)	121.4(4)
F(72)C(72)C(62)	116.4(2)	C(52)C(62)C(72)	119.8(3)	C(31)C(36)C(35)	120.6(3)	C(34)C(35)C(36)	121.4(3)
C(62)C(72)C(22)	122.7(2)	F(72)C(72)C(22)	120.9(2)	C(46)C(41)Sb(1)	123.1(2)	C(46)C(41)C(42)	119.1(3)
C(23)C(13)Sb(1)	119.9(2)	C(23)C(13)C(63)	119.0(2)	C(43)C(42)C(41)	120.5(3)	C(42)C(41)Sb(1)	117.6(2)
C(13)C(23)C(33)	119.7(3)	C(63)C(13)Sb(1)	121.0(2)	C(45)C(44)C(43)	118.1(3)	C(44)C(43)C(42)	120.9(3)
C(33)C(43)C(53)	119.5(3)	C(43)C(33)C(23)	120.9(3)	C(43)C(44)C(47)	120.2(4)	C(45)C(44)C(47)	121.7(3)
C(13)C(63)C(53)	120.2(3)	C(43)C(53)C(63)	120.8(3)	C(41)C(46)C(45)	119.5(3)	C(44)C(45)C(46)	121.9(3)
C(24)C(14)Sb(1)	116.0(2)	C(24)C(14)C(64)	120.7(2)	C(52)C(51)Sb(1)	118.4(2)	C(52)C(51)C(56)	119.5(3)
C(14)C(24)C(34)	119.2(3)	C(64)C(14)Sb(1)	123.2(2)	C(53)C(52)C(51)	119.7(3)	C(56)C(51)Sb(1)	122.0(2)
C(34)C(44)C(54)	119.9(3)	C(44)C(34)C(24)	120.6(3)	C(53)C(54)C(55)	118.4(3)	C(54)C(53)C(52)	121.7(3)
C(54)C(64)C(14)	118.6(3)	C(44)C(54)C(64)	120.9(3)	C(55)C(54)C(57)	121.5(3)	C(53)C(54)C(57)	120.2(3)
C(65)C(15)Sb(1)	124.5(2)	C(65)C(15)C(25)	120.5(2)	C(51)C(56)C(55)	119.9(3)	C(54)C(55)C(56)	120.9(3)
C(35)C(25)C(15)	119.1(3)	C(25)C(15)Sb(1)	115.1(2)				
C(35)C(45)C(55)	120.1(3)	C(45)C(35)C(25)	120.8(3)				
C(55)C(65)C(15)	118.8(3)	C(45)C(55)C(65)	120.7(3)				

IIe are 150.0°, 104.8°, and 105.2°, which is consistent with the shorter Sb⋅⋅O(=C) distances.

The benzoato fragments containing *o*-F atoms in the aryl ring of the acyl substituent are not planar; the torsion angles between the carboxy and aryl planes are 40.3(1)° and 32.2(1)° for the O(11)–C(71) and O(12)–C(72) fragments, respectively. The corresponding torsion angles in complexes **IIa** and **IIe** are 9.4(1)° and 13.0°, respectively; i.e., their carboxy and aryl groups lie in nearly the same plane. Conformational differences in the equatorial phenyl substituents are noteworthy. In **IIa**, only one of them (C(14)–C(64)) is in the equatorial plane (the corresponding torsion angle is 7.8(1)°), while the other values are 30.9(1)° and 72.7(1)°. In **IIe**, the planes of two phenyl substituents are virtually coplanar to the equatorial plane (1.9° and 5.1°), while the third phenyl ligand is rotated through 73.2°.

The trigonal-bipyramidal configuration is significantly distorted in tetra-*p*-tolylantimony pentafluorobenzoate **IIIb** (Fig. 2). The axial angle is 177.64(9)°, while the equatorial angles range from 113.1(1)° to 127.8(1)°, their sum being equal to 354.7(1)°. The $OSbC_{eq}$ angles are less than 90° (80.2(1)° to 83.7(1)°), while the $C_{ax}SbC_{eq}$ angles are 94.4(1)° to 101.9(1)°. The Sb–C_{eq} bond lengths range from 2.104(3) to 2.110(3) Å; the Sb–C_{ax} bond is slightly longer (2.160(3) Å). The Sb–C_{eq} and Sb–C_{ax} bond lengths in tetraphenylantimony benzoate **IIIe** are 2.125–2.129 and 2.172 Å, respectively [3]; the angles with a vertex at the Sb atom are close to those in **IIIb**.

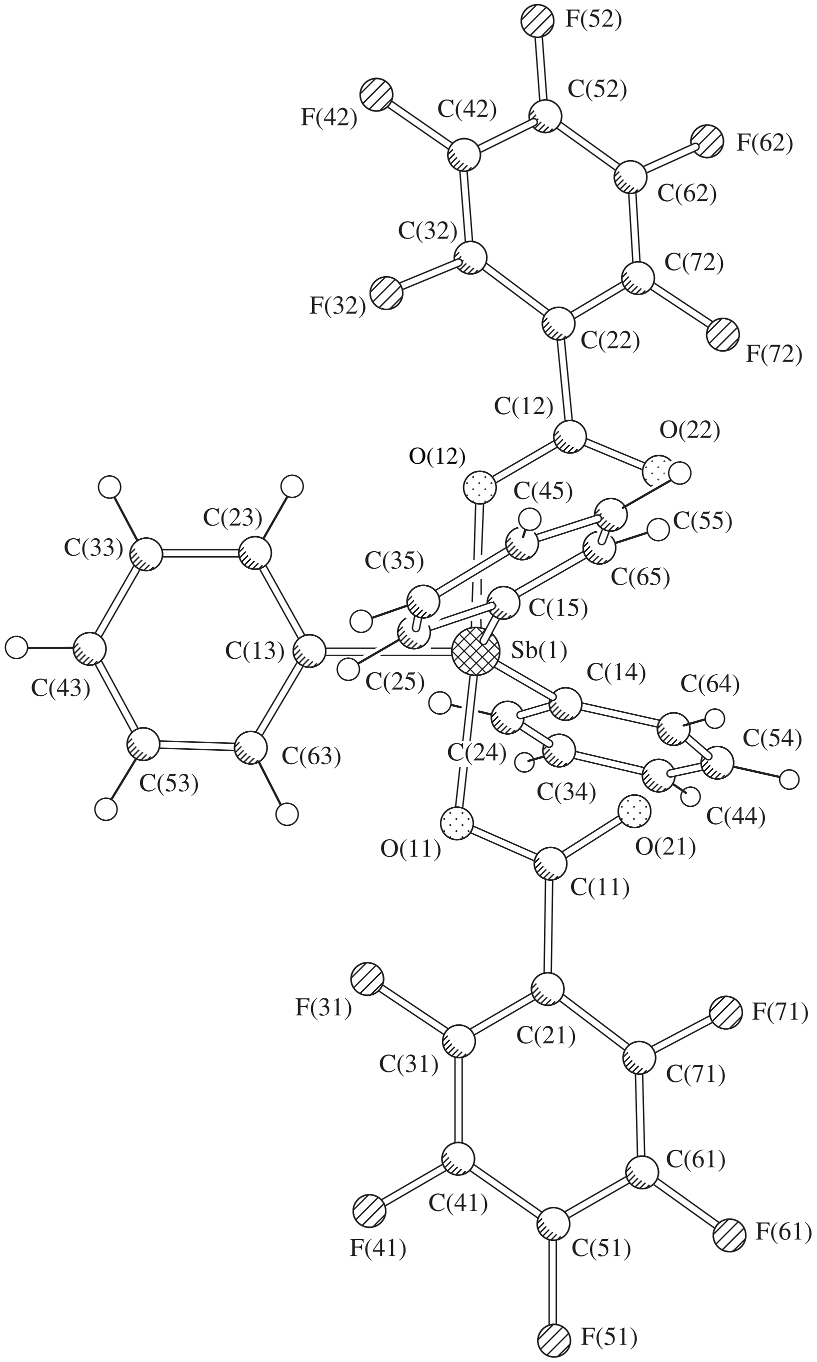

Fig. 1. General view of the molecule of triphenylantimony bis(pentafluorobenzoate) (**IIa**).

The Sb–O bond lengths in tetraarylantimony acylates **IIIb** and **IIIe** (2.373(2) and 2.243 Å, respectively) significantly exceed the sum of the covalent radii of antimony and oxygen (2.07 Å [9]), indicating that this bond is polar, especially in compound **IIIb**.

In aroxytetraphenylantimony complexes, a lone electron pair on the oxygen atom can interact with the π electron system of the arene ring [12]. The intensity of this interaction depends on the nature and arrangement of substituents in the aroxy group and determines the electron density transfer from antimony to oxygen and, therefore, the Sb–O bond length. Apparently, the Sb–O distance in tetraarylantimony acylates also depends on the apparent charge on the oxygen atom bound to antimony. The electron density on the hydroxy O atom is determined (1) by the induction effect of the CO group, (2) by the conjugation of the π electrons of the CO group with the lone electron pairs

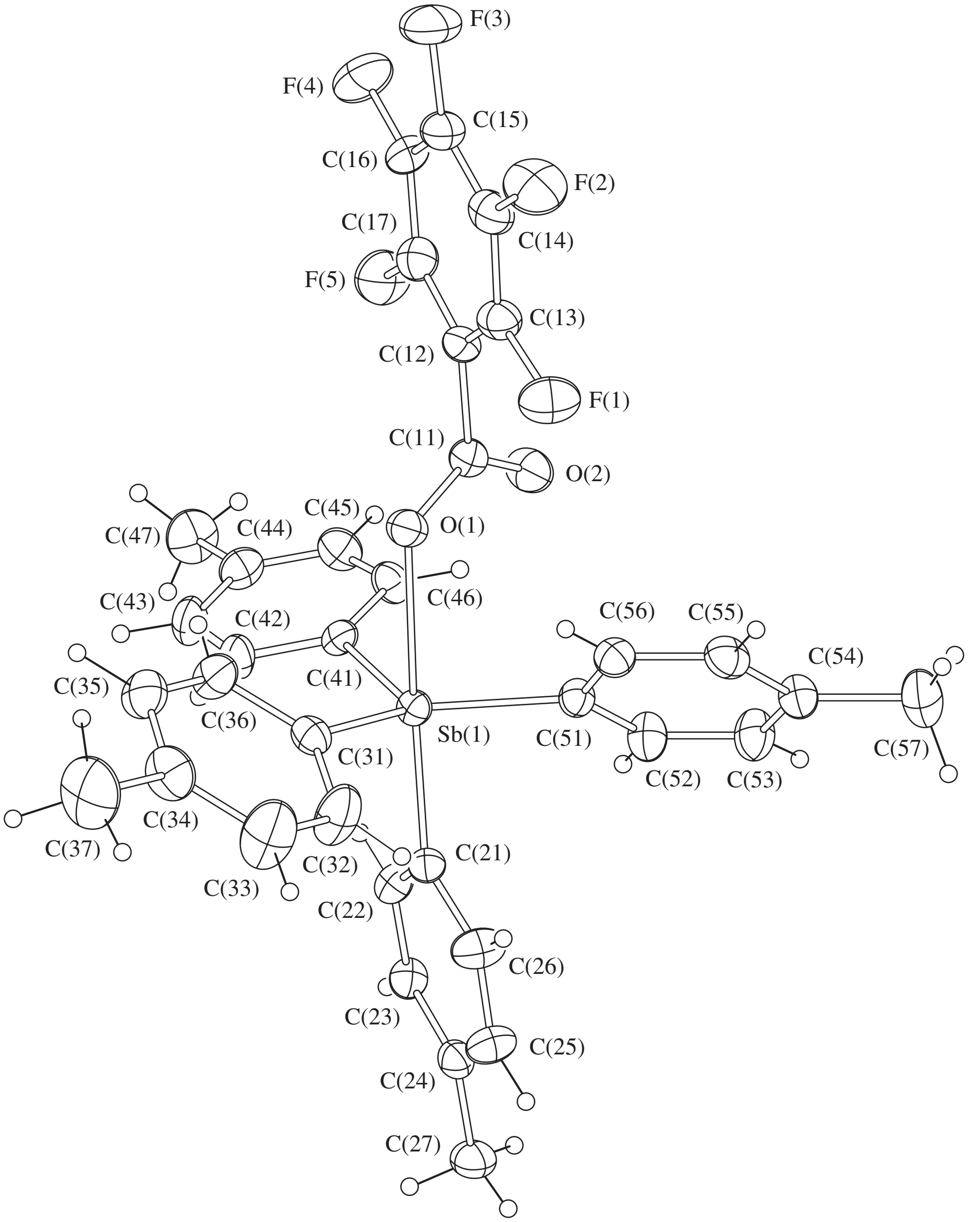

Fig. 2. General view of the molecule of tetra-*p*-tolylantimony pentafluorobenzoate (**IIIb**).

of the hydroxy O atom, and (3) by the nature and structure of the radical R. The first two factors decrease the electron density on the hydroxy O atom, while the radical R can both increase and lower the charges on the carboxy O atoms, depending on the sign and magnitude of its effects. In the fluorinated phenyl radical, which is a significantly stronger electron acceptor, the charge on the hydroxy O atom decreases. This results in an electron density transfer from the Sb atom and makes the Sb–O bond in **IIIb** longer than that in **IIIe**.

As in many other tetraphenylantimony acylates, the distance between the Sb atom and the carbonyl O atom in compound **IIIb** is shorter than the sum of their van der Waals radii (3.309(3) Å versus 3.7 Å), but it is still longer than the Sb··O(=C) distances in compound **IIa**.

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