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Synthesis and Structure of Triphenylantimony Dipropionate

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Abstract—Triphenylantimony dipropionate $Ph_3Sb[OC(O)C_2H_5]_2$ was prepared by reacting triphenylantimony dibromide with sodium salt of propionic acid in toluene at 90°C. The structure of the compound was determined by X-ray diffraction. The coordination of the Sb atom in the compound is a trigonal bipyramid with the carboxylic groups in the axial positions. The Sb(1)–C(Ph)$_{eq}$ distances vary in the 2.099(7)–2.135(6) Å range; the Sb(1)–O(1,3) distances are 2.113(5) and 2.109(5) Å, respectively. The value of the O(1)Sb(1)O(3) axial angle is 175.0(2)°.

The trigonal-bipyramidal configuration and the coordination number (C.N.) 5 are typical of the Sb atom in most antimony compounds with general formula Ph_3SbX_2 (X is an organic or inorganic ligand) [1]. However, when the ligands incorporate potential coordinating centers, they can additionally interact with the Sb atom. As a result, the coordination number of the Sb atom may be increased to 6 or 7. Thus, the shortened Sb··O distances (as compared with the sum of the van der Waals radii), which vary in the 2.70–2.95 Å range, can be observed in triphenylantimony diacetate [2], dibenzoate [3], and other diacylates [4–6], which indicates additional coordination of the Sb atom in these compounds.

In continuation of our studies on the structures of triarylantimony diacylates [3, 6], we have established the molecular and crystal structures of triphenylantimony dipropionate (**I**).

EXPERIMENTAL

Synthesis of triphenylantimony dipropionate was carried out in an evacuated glass ampule by the following procedure. 2.67 g (5.20 mmol) of triphenylantimony dibromide and 1.00 g (10.40 mmol) of sodium propionate were heated in 20 ml of toluene at 90°C for 6 h. The solution was filtered; the residue was washed with hot toluene. The filtrate was concentrated to 5 ml and cooled to –18°C. The obtained crystals were

Table 1. Atomic coordinates (×10^4) and equivalent isotropic thermal parameters (U_{equiv}) in structure **I**

Atom	x	y	z	U_{eqiv}, Å^2	Atom	x	y	z	U_{eqiv}, Å^2
Sb(1)	1190(1)	6788(1)	7863(1)	59(1)	C(11)	738(10)	5745(6)	10898(9)	90(3)
O(1)	3531(5)	6844(2)	8605(4)	74(1)	C(12)	1035(10)	5902(5)	9876(8)	81(3)
O(2)	3389(6)	5770(2)	8553(4)	72(1)	C(13)	1501(8)	6424(3)	6338(6)	65(2)
O(3)	–1147(5)	6821(2)	7109(4)	76(1)	C(14)	1763(13)	6874(5)	5598(9)	96(3)
O(4)	–1020(6)	5744(3)	7249(4)	81(2)	C(15)	2040(15)	6667(7)	4598(9)	123(4)
C(1)	1176(8)	7835(3)	7798(6)	61(2)	C(16)	2008(12)	6014(7)	4329(9)	109(4)
C(2)	2459(9)	8176(4)	8361(8)	84(2)	C(17)	1689(10)	5573(5)	5051(8)	88(3)
C(3)	2408(14)	8858(5)	8308(10)	101(3)	C(18)	1435(9)	5770(4)	6032(8)	74(2)
C(4)	1201(13)	9180(4)	7716(9)	88(3)	C(19)	4127(8)	6267(4)	8786(6)	64(2)
C(5)	–56(12)	8850(4)	7153(9)	98(3)	C(20)	5816(10)	6276(5)	9317(10)	89(3)
C(6)	–74(10)	8167(4)	7216(8)	87(3)	C(21)	6504(13)	5597(6)	9519(12)	105(4)
C(7)	822(8)	6512(4)	9411(6)	63(2)	C(22)	–1742(8)	6240(4)	6949(6)	66(2)
C(8)	296(14)	7003(6)	9988(10)	109(3)	C(23)	–3392(9)	6244(5)	6342(8)	94(3)
C(9)	8(17)	6844(8)	10984(11)	130(5)	C(24)	–4097(12)	5606(6)	6209(10)	139(4)
C(10)	214(13)	6234(8)	11416(10)	110(4)					

Table 2. Selected bond lengths and angles in structure **I**

Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
Sb(1)–O(1)	2.113(5)	C(7)Sb(1)C(13)	143.8(3)	O(1)Sb(1)C(1)	87.5(2)
Sb(1)–O(3)	2.109(5)	C(13)Sb(1)O(3)	90.1(2)	C(19)O(1)Sb(1)	111.4(4)
Sb(1)–C(1)	2.135(6)	C(7)Sb(1)O(1)	91.9(2)	C(22)O(3)Sb(1)	112.3(4)
Sb(1)–C(7)	2.099(7)	C(13)Sb(1)O(1)	91.2(2)	C(13)Sb(1)C(1)	108.6(3)
Sb(1)–C(13)	2.107(7)	O(3)Sb(1)O(1)	175.0(2)	O(3)Sb(1)C(1)	87.5(2)
O(1)–C(19)	1.292(8)	C(7)Sb(1)C(1)	107.5(3)	C(7)Sb(1)O(3)	89.9(2)
O(2)–C(19)	1.212(8)				
O(3)–C(22)	1.298(9)				
O(4)–C(22)	1.212(9)				

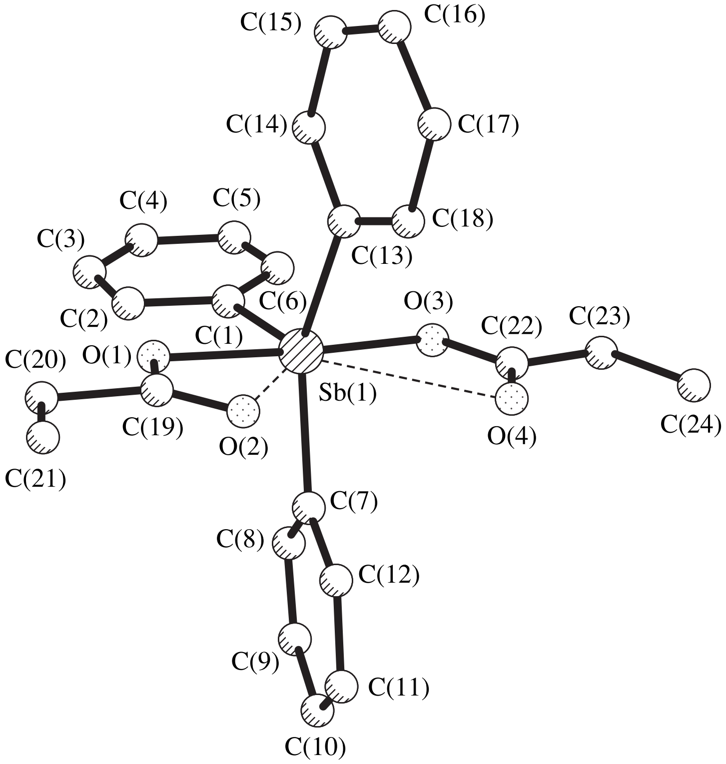
washed with petroleum ether and dried. The yield was 2.20 g (85%) of triphenylantimony dipropionate, mp 139°C (139°–140°C [7]).

X-ray diffraction analysis of crystals **I** was performed on a Siemens P3/PC four-circle diffractometer (graphite monochromator, MoK_α radiation, $\theta/2\theta$ scan mode). Crystals **I** are monoclinic: at 20°C, $a = 9.293(4)$, $b = 20.374(10)$, $c = 12.273(4)$ Å, $\beta = 106.25(3)°$, $V = 2231(2)$ Å^3, space group $P2_1/n$, $Z = 4$, and $\rho_{calc} = 1.486$ g/cm^3.

The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms to $R = 0.046$, $R_w = 0.097$, and $S = 1.09$ from 2074 reflections with $I > 2\sigma(I)$. The H atoms of the phenyl groups and the C(20) and C(21) atoms of the ethyl group were located from difference syntheses and refined isotropically. The H atoms of the ethyl group, C(23) and C(24), were placed in geometrically calculated positions and refined in the rider model with fixed U_{iso} values.

All calculations were performed with the SHELX97 programs [8] on an IBM PC.

Coordinates of the atoms and their equivalent isotropic thermal parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively.



Molecular structure of complex **I**.

RESULTS AND DISCUSSION

Compound **I** was prepared from triphenylantimony dibromide and sodium propionate in toluene at 90°C. When the reaction mixture was heated for 6 h, the reaction

$$Ph_3SbBr_2 + 2NaOC(O)C_2H_5$$
$$\longrightarrow Ph_3Sb[OC(O)C_2H_5]_2 + 2NaBr$$

was almost complete.

The X-ray diffraction analysis of **I** showed that the Sb(1) atom has a distorted trigonal-bipyramidal coordination (figure) with the O atoms of the propionate ligands in the axial positions, Sb–O 2.109(5) and 2.113(5) Å. The sum of the C(Ph)SbC(Ph) angles in the equatorial plane is 359.9°; the O(1)Sb(1)O(3) axial angle is 175.0(2)°. The C(Ph)SbC(Ph) angles between the equatorial phenyl ligands are nonequivalent, their values being 107.5(3)°, 108.5(3)°, and 143.8(3)° for the C(1)Sb(1)C(7), C(1)Sb(1)C(13), and C(7)Sb(1)C(13) angles, respectively. The Sb(1)··O(2) and Sb(1)··O(4) distances (2.867(6) and 2.906(6) Å) are shorter than the sums of the van der Waals radii of Sb and O atoms (3.60 Å [9]). Note that the value of the C(7)Sb(1)C(13) angle, 143.8(3)°, from the side of the Sb(1)··O(2) and Sb(1)··O(4) intramolecular contacts drastically exceeds the standard value of 120°. A similar situation is observed in other triphenylantimony diacylates. The Sb··O distances in $Ph_3Sb[OC(O)Ph]_2$ (**II**) [3] and $Ph_3Sb[OC(O)CH{=}CHPh]_2$ (**III**) [6] are 2.70(2), 2.81(2), and 2.664(4) Å, while the equatorial angles from the side of intramolecular contacts are 150(1)° [3] and 151.7(2)° [6], respectively. Therefore, the C.N. of the Sb atom in **I**–**III** is 7 (5 + 2).

The Sb··O(2, 4) distances in **I** (2.867 and 2.906 Å) exceed the analogous values in molecules **II** (2.81(2) and 2.70(2) Å) and **III** (2.664(4) Å). Their ratios to the length of an ordinary Sb–O bond are equal to 1.36 and 1.38 in molecule **I**, which is somewhat greater than in **II** (1.26 and 1.36) and **III** (1.23). This value, suggested in [10] as a measure of the asymmetry of the bidentate acylate ligand (this ratio is equal to unity for symmetrically coordinated bidentate acylate ligand), indicates that the asymmetry of a bidentate coordination in benzoate and cinnamate substituents develops to a lesser extent than in the propionate group. The values of the SbOC angles, which may also serve as a degree of the bidentate nature of the acylate ligands (the smaller the SbOC angle, the lower the asymmetry of the bidentate acylate group), are 108(1)° and 107(1)° in molecule **II** [3], 104.2(2)° in molecule **III** [6], and 111.4(4)° and 112.3(4)° in molecule **I**.

The propionate groups in **I** lie almost in one plane, the extension of the atoms from the plane of the C(21)C(20)C(19)O(2)O(1)Sb(1)O(3)O(4)C(22)C(23) C(24) fragment being, on average, 0.026 Å, while the dihedral angle between the carboxylic groups is 3.5°. The propionate ligands in structure **I** are *cis*-oriented about the equatorial $C(Ph)_3Sb$ fragment. A similar situation in the arrangement of the carboxylic groups is observed in other antimony diacylates [3, 6].

The Sb(1)–O(1) and Sb(1)–O(3) distances in **I** (2.113(5) and 2.109(5) Å) are close to the analogous distances in **II** (2.13(2) and 2.14(2) Å), but are shorter than in **III** (2.155(2) Å). The O(1)–C(19), O(3)–C(22) and O(2)=C(19), O(4)=C(22) distances in **I** (1.292(8), 1.298(9) and 1.212(8), 1.212(9) Å, respectively) are close to the analogous distances in carboxylic acids (1.293–1.308 Å for the C–O bonds and 1.214–1.229 Å for the C=O bonds) [11].

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