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Synthesis and Structure of Tetraphenylantimony Nicotinate

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Abstract—Tetraphenylantimony nicotinate was prepared in 91% yield by reaction of pentaphenylantimony with triphenylantimony bis(nicotinate) in toluene. Triphenylantimony bis(nicotinate), in turn, was prepared in 87% yield by oxidative addition of pyridine-3-carboxylic acid to triphenylstibine in ether in the presence of hydrogen peroxide. The structure of tetraphenylantimony nicotinate was determined by single-crystal X-ray diffraction. The Sb atom has a distorted trigonal bipyramidal coordination surrounding with the carboxy group in the axial position. The Sb–C distances are 2.118(1), 2.121(1), 2.130(1), and 2.170(1) Å, and the Sb–O distance is 2.268(1) Å. There is an intramolecular contact between the Sb atom and the carbonyl O atom [3.363(1) Å].

It is known that the antimony atoms in compounds Ar_4SbX have a trigonal bipyramidal configuration; the electronegative ligand X, as a rule, occupies one of the axial positions [1]. If ligand X contains free donor atoms potentially capable of coordination, the coordination number of antimony can increase to six, as, e.g., in tetraphenylantinomy carboxylates [2, 3]. Proceeding with structural studies of tetraphenylantimony carboxylates [4–8], we have examined in this work the molecular and crystal structure of tetraphenylantimony nicotinate (**I**), which was prepared in 91% yield by reproportionation of pentaphenyl antimony with triphenylantimony bis(nicotinate) (**II**):

$$Ph_5Pb + Ph_3Sb[OC(O)C_5H_4N]_2 \rightarrow \underset{\mathbf{I}}{2Ph_4SbOC(O)C_5H_4N}.$$

Triphenylantimony bis(nicotinate), in turn, was prepared in 87% yield by oxidative addition of pyridine-3-carboxylic acid to triphenylstibine in ether in the presence of hydrogen peroxide:

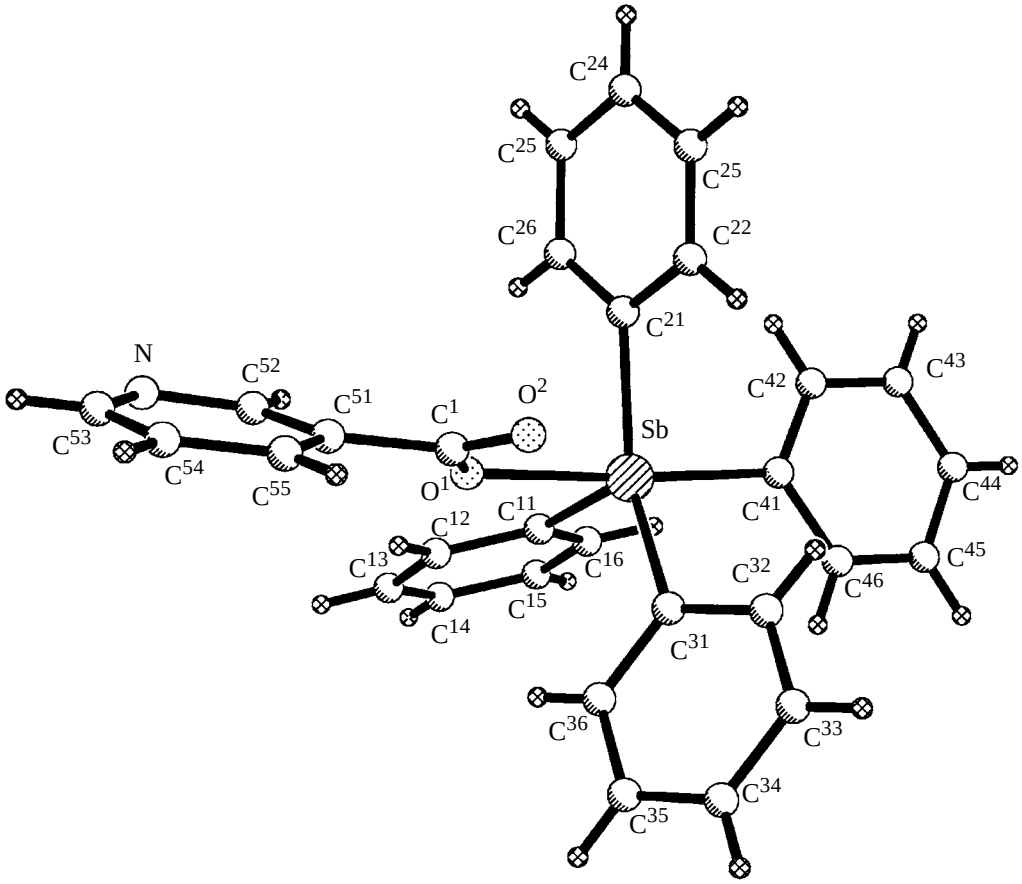
$$Ph_3Sb + 2HOC(O)C_5H_4N + H_2O_2 \longrightarrow \underset{\mathbf{II}}{Ph_3Sb[OC(O)C_5H_4N]_2} + 2H_2O.$$

The single-crystal X-ray diffraction study (see figure; Tables 1, 2) shows that the antimony atom in **I** has a trigonal bipyramidal coordination with the carboxylate oxygen atom occupying the axial position. The sum of the CSbC angles in the equatorial plane is 355.85(5)°; the axial angle CSbO is 176.78(4)°. The Sb–O bond in the molecule of **I** is somewhat longer [2.268(1) Å] than in tetraphenylantimony benzoate **III** [2.245(1) Å] [8] differing from **I** only in the nature of the aromatic ring in the carboxylate ligand. Note that an increase in the Sb–O distance in **I** compared to **III** is accompanied by a decrease in the C^1–O^1 bond length (1.279 Å, against 1.286 Å in **III**). The C^1–C^{51} distance between the carbon atoms of the carbonyl group and aromatic ring in the carboxylate ligand, 1.508(2) Å, is virtually the same as in **III** [1.507(2) Å], which suggests that in these molecules the *p* electrons of the carbonyl carbon atom are involved in conjugation with the π system of the aromatic ring to a similar extent.

In **I**, there is an intramolecular contact between the antimony and carbonyl oxygen atoms. The Sb···O(=C) distance is 3.363(1) Å, which is smaller than the sum of the van der Waals radii of Sb and O (3.70 Å [9]) but larger than the similar distance in **III** (3.309 Å); thus, in **I** both the Sb–O and Sb···O(=C) distances are longer than in **III**. The occurrence of the intramolecular contact Sb···O(=C) in **I** is confirmed by increased equatorial angle CSbC (from the side of the contact), 128.81(5)°, and decreased other equatorial angles, 115.68(5)° and 111.36(5)° (the ideal value is 120°).

EXPERIMENTAL

Single-crystal X-ray diffraction study of tetraphenylantimony nicotinate $C_{30}H_{24}NO_2Sb$ (I). The



General view of the tetraphenylantimony nicotinate (**I**) molecule.

unit cell parameters and intensities of 5403 unique reflections with $I \geq 2\sigma(I)$ were measured on a SMART CCD-1000 automatic diffractometer (MoK_α radiation, λ 0.71073 Å, 2θ/θ scanning). Monoclinic system; at 20°C, *a* 11.341(1), *b* 14.622(2), *c* 17.195(2) Å; β 104.990(2)°, *V* 2511.6(5) Å^3, *Z* 4, d_{calc} 1.461 g cm^{-3}, space group $P2_1/n$. The structure was solved by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms to *R* 0.0243, R_W 0.0543. The positions of hydrogen atoms were calculated geometrically and included in the refinement in the rider model. The perspective view of the molecule is shown in the figure. The coordinates of non-hydrogen atoms are given in Table 1, and the principal interatomic distances and bond angles in **I** are listed in Table 2. The data collection and edition, and also the refinement of unit cell paameters were performed with SMART and SAINT Plus programs [10]. All the calculations for the structure determination and refinement were performed using SHELXTL/PC programs [11].

Tetraphenylantimony nicotinate I. A mixture of 1.00 g of pentaphenylantimony, 1.18 g of triphenylantimony bis(nicotinate), and 50 ml of benzene was heated in an evacuated glass ampule for 2 h at 90–100°C. Then the reaction mixture was cooled, the solvent was removed, and the residue was recrystallized from a 1 : 3 benzene–heptane mixture. Yield of **I** 1.98 g (91%), mp 179°C.

Triphenylantimony bis(nicotinate) II. A 30% H_2O_2 solution (0.32 g) was added to a mixture of 1.00 g of triphenylstibine and 0.70 g of 3-nicotinic acid in 20 ml of ether. The mixture was allowed to stand for 12 h, after which the crystalline precipitate was filtered off and dried. Yield of **II** 1.47 g (87%), mp 187°C.

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Table 1. Coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^3$) of atoms in the structure of tetraphenylantimony nicotinate **I**

Atom	*x*	*y*	*z*	U_{eq}, Å
Sb	4618.7(1)	9795.3(1)	1999.9(1)	37.3(3)
O^1	2847(1)	9100(1)	2299(1)	48.2(3)
O^2	2371(1)	10225(1)	3059(1)	58.1(3)
N	–768(2)	7851(1)	2121(1)	70.1(5)
C^{11}	4849(1)	8501(1)	1483(1)	38.7(3)
C^{12}	4099(2)	7736(1)	1569(1)	50.5(4)
C^{13}	4333(2)	6908(1)	1251(1)	59.2(5)
C^{14}	5298(2)	6827(1)	839(1)	62.8(5)
C^{15}	6049(2)	7575(1)	753(1)	63.1(5)
C^{16}	5829(2)	8412(1)	1073(1)	49.6(4)
C^{31}	5465(1)	9792(1)	3261(1)	40.6(3)
C^{32}	5953(2)	10583(1)	3674(1)	54.0(4)
C^{33}	6515(2)	10545(1)	4493(1)	63.8(5)
C^{34}	6637(2)	9723(1)	4897(1)	62.1(5)
C^{35}	6193(2)	8936(1)	4478(1)	62.1(5)
C^{36}	5595(2)	8967(1)	3664(1)	51.0(4)
C^{41}	6237(1)	10517(1)	1675(1)	39.8(3)
C^{42}	5997(2)	11041(1)	982(1)	46.1(4)
C^{43}	7027(2)	11473(1)	753(1)	53.4(4)
C^{44}	8320(2)	11377(1)	1209(1)	56.4(4)
C^{45}	8584(2)	10857(1)	1902(1)	58.2(5)
C^{46}	7553(2)	10435(1)	2136(1)	53.1(4)
C^{21}	3082(1)	10643(1)	1308(1)	39.6(3)
C^{26}	2319(2)	10320(1)	584(1)	63.6(5)
C^{25}	1392(2)	10889(2)	78(1)	75.7(6)
C^{24}	1230(2)	11764(1)	299(1)	65.0(5)
C^{23}	1975(2)	12082(1)	1023(1)	68.2(5)
C^{22}	2904(2)	11526(1)	1527(1)	58.5(5)
C^{51}	906(1)	8949(1)	2747(1)	42.7(3)
C^{52}	332(2)	8343(1)	2145(1)	54.9(4)
C^{53}	–1300(2)	7958(1)	2743(1)	70.5(6)
C^{54}	–808(2)	8528(1)	3375(1)	68.6(5)
C^{55}	321(2)	9048(1)	3383(1)	56.2(4)
C^1	2134(1)	9486(1)	2713(1)	39.7(3)

Table 2. Bond lengths (*d*) and bond angles (ω) in the molecule of tetraphenylantimony nicotinate **I**

Bond	*d*, Å	Angle	ω, deg
$Sb–C^{31}$	2.118(1)	$C^{31}SbC^{21}$	128.81(5)
$Sb–C^{21}$	2.121(1)	$C^{31}SbC^{11}$	111.36(5)
$Sb–C^{11}$	2.130(1)	$C^{21}SbC^{11}$	115.68(5)
$Sb–C^{41}$	2.170(1)	$C^{31}SbC^{41}$	97.05(5)
$Sb–O^1$	2.268(1)	$C^{21}SbC^{41}$	95.02(5)
$O^1–C^1$	1.279(2)	$C^{11}SbC^{41}$	98.48(5)
$O^2–C^1$	1.228(2)	$C^{31}SbO^1$	84.87(5)
$C^{11}–C^{16}$	1.382(2)	$C^{21}SbO^1$	81.77(5)
$C^{11}–C^{12}$	1.391(2)	$C^{11}SbO^1$	83.17(5)
$C^{12}–C^{13}$	1.376(2)	$C^{41}SbO^1$	176.78(4)
$C^{13}–C^{14}$	1.370(2)	C^1O^1Sb	123.0(1)
$C^{14}–C^{15}$	1.371(2)	$C^{42}C^{41}Sb$	120.8(1)
$C^{15}–C^{16}$	1.384(2)	$C^{46}C^{41}Sb$	121.1(1)
$C^{31}–C^{36}$	1.381(2)	$C^{43}C^{42}C^{41}$	121.3(1)
$C^{31}–C^{32}$	1.382(2)	$C^{44}C^{43}C^{42}$	120.0(1)
$C^{32}–C^{33}$	1.379(2)	$C^{43}C^{44}C^{45}$	119.7(1)
$C^{33}–C^{34}$	1.377(3)	$C^{46}C^{45}C^{44}$	120.2(1)
$C^{34}–C^{35}$	1.372(2)	$C^{45}C^{46}C^{41}$	120.7(1)
$C^{35}–C^{36}$	1.377(2)	$C^{22}C^{21}C^{26}$	119.0(1)
$C^{41}–C^{42}$	1.384(2)	$C^{22}C^{21}Sb$	122.0(1)
$C^{41}–C^{46}$	1.392(2)	$C^{26}C^{21}Sb$	118.6(1)
$C^{42}–C^{43}$	1.380(2)	$C^{21}C^{26}C^{25}$	120.2(2)
$C^{43}–C^{44}$	1.371(2)	$C^{24}C^{25}C^{26}$	120.2(2)
$C^{44}–C^{45}$	1.380(2)	$C^{25}C^{24}C^{23}$	119.7(2)
$C^{45}–C^{46}$	1.379(2)	$C^{24}C^{23}C^{22}$	120.6(2)
$C^{21}–C^{22}$	1.371(2)	$C^{21}C^{22}C^{23}$	120.2(1)
$C^{21}–C^{26}$	1.374(2)	$C^{52}C^{51}C^{55}$	118.0(1)
$C^{26}–C^{25}$	1.391(2)	$C^{52}C^{51}C^1$	120.7(1)
$C^{25}–C^{24}$	1.358(3)	$C^{55}C^{51}C^1$	121.3(1)
$C^{24}–C^{23}$	1.365(2)	$NC^{52}C^{51}$	124.6(2)
$C^{23}–C^{22}$	1.380(2)	$C^{53}NC^{52}$	115.8(2)
$C^{51}–C^{52}$	1.375(2)	$NC^{53}C^{54}$	124.6(2)
$C^{51}–C^{55}$	1.388(2)	$C^{53}C^{54}C^{55}$	118.8(2)
$C^{51}–C^1$	1.508(2)	$C^{51}C^{55}C^{54}$	118.1(2)
$C^{52}–N$	1.337(2)	$O^2C^1O^1$	125.9(1)
$N–C^{53}$	1.333(3)	$O^2C^1C^{51}$	120.2(1)
$C^{53}–C^{54}$	1.360(3)	$O^1C^1C^{51}$	113.8(1)
$C^{54}–C^{55}$	1.391(2)		

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