Organometallic Chemistry

Synthesis and molecular structure of the complex $[Ph_3Sb(NO_3)]_2O \cdot Me_2CO$

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The reaction of silver nitrate with Ph_3SbBr_2 in an ethanol-acetone solution afforded the complex $[Ph_3Sb(NO_3)]_2O \cdot Me_2C{=}O$ (**1**). According to the data of X-ray diffraction study of crystals of **1**, molecule **1** contains a nonlinear O-bridge, which links two Sb atoms. The Sb atoms have a trigonal-bipyramidal configuration. The NO_3 group and the bridging oxygen atom are in axial positions and the three Ph substituents are in equatorial positions.

Key words: antimony complex, μ-oxobis(nitratotriphenylantimony(v)), synthesis, X-ray diffraction study, molecular structure.

In compounds of the general formula $(Ph_3SbX)_2O$ (X is an organic or inorganic ligand), the trigonal-bipyramidal configuration with electronegative substituents in axial positions is typical of Sb atoms.[1–3] For most of the complexes of this type,[3] the Sb—O—Sb angles are in the range of 135—140°. However, in some of them, as in the case of μ-oxobis(*tert*-butylperoxytriphenylantimony),[2] these atoms form an almost linear group. Previously,[4] it has been suggested that the linear configuration of the Sb—O—Sb group can occur when the terminal X ligand is strongly bound to the Sb atom, *i.e.*, in the case of the minimum Sb—X distance. However, more recently[5] it has been demonstrated that the Sb—O—Sb fragment in $(Ph_3SbI)_2O$ can exist in two forms, namely, both as the linear and the V-shaped group. The aim of this work is to study the structures of molecules containing the Sb—O—Sb group.

The antimony complex $[Ph_3Sb(NO_3)]_2O \cdot Me_2C{=}O$ (**1**) of the above-mentioned type was prepared from triphenylantimony dibromide and silver nitrate in an ethanol-acetone solution in the presence of water.

$$Ph_3SbBr_2 + 2\,AgNO_3 + H_2O \xrightarrow{Me_2CO-EtOH}$$

$$\longrightarrow \underset{\mathbf{1}}{[Ph_3Sb(NO_3)]_2O \cdot Me_2C{=}O}.$$

The compound $[(p\text{-}MeC_6H_4)_3Sb(NO_3)]_2O$ (**2**) was synthesized analogously.

The melting point (218 °C) determined for complex **1** is lower than those reported previously for $[Ph_3Sb(NO_3)]_2O$ (237—240 °C [1] and 224—225 °C [6]), which is associated with the presence of the acetone molecule of solvation in the structure of **1**.

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Table 1. Atomic coordinates (×10^4) and equivalent temperature factors (U_{eq}) in molecule **1**

Atom	*x*	*y*	*z*	$U_{eq}\cdot10^3/\text{Å}^2$
Sb(1)	5079(1)	3115(1)	2237(1)	40(1)
Sb(2)	6964(1)	2691(1)	4893(1)	41(1)
O(1)	8796(3)	2730(2)	6090(3)	57(1)
O(2)	8602(4)	1304(3)	6849(4)	87(1)
O(3)	10436(5)	2004(4)	7067(5)	134(2)
O(4)	4600(3)	3537(2)	424(2)	52(1)
O(5)	2503(4)	3123(3)	712(3)	70(1)
O(6)	3224(5)	3351(3)	−867(3)	85(1)
O(7)	5440(3)	2684(2)	3826(2)	46(1)
N(1)	9272(4)	2034(4)	6656(4)	70(1)
N(2)	3390(5)	3337(3)	74(3)	56(1)
C(1)	7025(4)	3566(3)	1786(3)	45(1)
C(2)	7384(5)	4466(3)	1596(4)	54(1)
C(3)	8680(5)	4752(4)	1331(4)	64(1)
C(4)	9610(5)	4158(4)	1247(4)	67(2)
C(5)	9267(6)	3273(5)	1428(5)	76(2)
C(6)	7960(5)	2967(4)	1693(5)	65(1)
C(7)	4545(4)	1820(3)	2164(4)	45(1)
C(8)	4928(6)	1521(4)	1343(5)	65(1)
C(9)	4580(8)	662(4)	1325(6)	86(2)
C(10)	3830(8)	115(4)	2095(6)	85(2)
C(11)	3433(7)	403(4)	2915(5)	77(2)
C(12)	3808(5)	1254(3)	2960(4)	61(1)
C(13)	3765(4)	4118(3)	2295(3)	43(1)
C(14)	3072(5)	4018(4)	3199(4)	52(1)
C(15)	2285(5)	4702(4)	3278(5)	62(1)
C(16)	2189(6)	5478(4)	2450(5)	69(2)
C(17)	2875(6)	5586(4)	1544(5)	66(1)
C(18)	3655(5)	4907(3)	1457(4)	52(1)
C(19)	8111(5)	1799(3)	4401(4)	61(1)
C(20)	9474(7)	1931(5)	4297(7)	94(2)
C(21)	10168(12)	1359(9)	3906(9)	135(4)
C(22)	9472(18)	663(11)	3662(10)	164(7)
C(23)	8135(14)	525(6)	3760(7)	123(3)
C(24)	7417(8)	1096(4)	4143(5)	79(2)
C(25)	5686(4)	2283(3)	6172(3)	45(1)
C(26)	4429(5)	1914(3)	6010(4)	58(1)
C(27)	3558(6)	1701(4)	6819(5)	73(2)
C(27)	3916(7)	1869(4)	7781(5)	75(2)
C(29)	5146(7)	2244(4)	7938(5)	76(2)
C(30)	6056(6)	2446(3)	7150(4)	60(1)
C(31)	7359(4)	4077(3)	4384(3)	42(1)
C(32)	6267(5)	4634(3)	4187(4)	54(1)
C(33)	6439(6)	5547(4)	3781(5)	66(1)
C(34)	7704(6)	5914(4)	3582(4)	64(1)
C(35)	8796(6)	5364(3)	3794(4)	62(1)
C(36)	8649(5)	4447(3)	4199(4)	53(1)

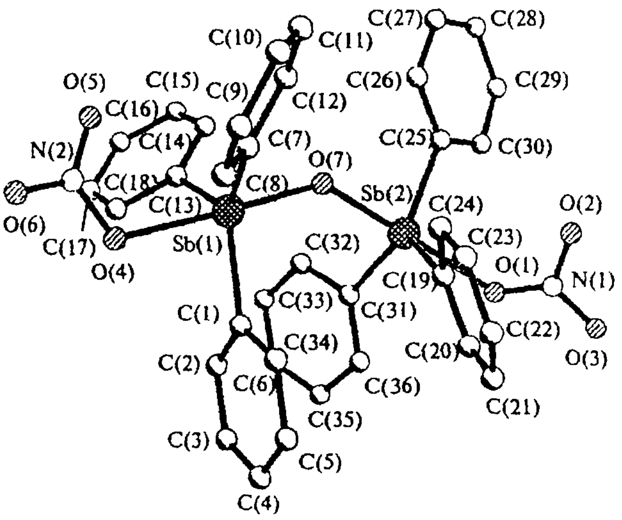

Fig. 1. Structure of complex **1**. The acetone molecule of solvation is omitted.

Table 2. Principal bond lengths (*d*) in molecule **1**

Bond	*d*/Å	Bond	*d*/Å
Sb(1)—O(7)	1.978(3)	O(2)—N(1)	1.262(6)
Sb(1)—C(1)	2.092(4)	O(3)—N(1)	1.222(6)
Sb(1)—C(7)	2.097(4)	O(4)—N(2)	1.301(5)
Sb(1)—C(13)	2.103(4)	O(5)—N(2)	1.228(5)
Sb(1)—O(4)	2.264(3)	O(6)—N(2)	1.215(5)
Sb(2)—O(7)	1.959(3)	C(1)—C(6)	1.382(7)
Sb(2)—C(31)	2.096(4)	C(1)—C(2)	1.389(6)
Sb(2)—C(25)	2.108(4)	C(2)—C(3)	1.377(7)
Sb(2)—C(19)	2.108(5)	C(3)—C(4)	1.368(8)
Sb(2)—O(1)	2.295(3)	C(4)—C(5)	1.364(9)
O(1)—N(1)	1.204(5)	C(5)—C(6)	1.395(7)

X-ray diffraction study of the crystal-solvate of **1** demonstrated that the Sb atoms (Fig. 1) have the trigonal-bipyramidal configuration typical of Sb^{V} compounds (the sum of the C(Ph)—Sb—C(Ph) angles in the equatorial plane is 357.8° and 358.6° for Sb(1) and Sb(2), respectively). The Sb(1)—O(7)—Sb(2), O(7)—Sb(2)—O(1), and O(7)—Sb(1)—O(4) angles are 137.4(2)°, 177.83(11)°, and 176.81(11)°, respectively. The Sb(1)—O(7) and Sb(2)—O(7) distances (1.978(3) and 1.959(3) Å, respectively) are substantially smaller than the Sb(1)—O(4) and Sb(2)—O(1) distances (2.264(3) and 2.295(3) Å, respectively). An analogous shortening of the Sb—O—Sb bonds has also been observed[7] in the Sb^{III} compound, namely, in oxobis(diphenylantimony). In this case, the Sb—O distance is 1.970 Å, which is substantially smaller than the sum of the covalent radii.[8] This is indicative of an increase in the multiplicity of the Sb—O bond due to interactions of the lone electron pairs of the O atom with the unoccupied d-orbitals of the Sb atom, which has been reported previously in a number of works.[2,9,10] In the structure of the crystal-solvate of **1**, the atoms of the acetone fragment are statistically disordered, which does not allow one to adequately interpret the distances and angles in this fragment. Nevertheless, the data of ^{1}H NMR and IR spectroscopy and elemental analysis indicate that the structure of complex **1** contains acetone molecules.

Table 3. Principal bond angles (ω) in molecule **1**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(7)—Sb(1)—C(1)	100.2(2)	O(7)—Sb(2)—O(1)	177.83(11)	C(3)—C(2)—C(1)	119.5(5)
O(7)—Sb(1)—C(7)	92.0(2)	C(31)—Sb(2)—O(1)	81.70(14)	C(4)—C(3)—C(2)	120.6(5)
C(1)—Sb(1)—C(7)	115.2(2)	C(25)—Sb(2)—O(1)	90.4(2)	C(5)—C(4)—C(3)	120.5(5)
C(7)—Sb(1)—C(13)	93.1(2)	C(19)—Sb(2)—O(1)	85.8(2)	C(4)—C(5)—C(6)	120.1(6)
C(1)—Sb(1)—C(13)	115.3(2)	N(1)—O(1)—Sb(2)	119.0(3)	C(1)—C(6)—C(5)	119.4(5)
C(7)—Sb(1)—C(13)	127.3(2)	N(2)—O(4)—Sb(1)	116.8(3)	C(8)—C(7)—Sb(1)	121.1(3)
O(7)—Sb(1)—O(4)	176.81(11)	Sb(2)—O(7)—Sb(1)	137.4(2)	C(12)—C(7)—Sb(1)	119.5(4)
C(1)—Sb(1)—O(4)	81.99(14)	O(1)—N(1)—O(3)	121.0(5)	C(18)—C(13)—Sb(1)	120.2(3)
C(7)—Sb(1)—O(4)	84.9(2)	O(1)—N(1)—O(2)	122.0(4)	C(14)—C(13)—Sb(1)	120.4(3)
C(13)—Sb(1)—O(4)	87.93(14)	O(3)—N(1)—O(2)	117.0(5)	C(20)—C(19)—Sb(2)	121.6(5)
O(7)—Sb(2)—C(31)	96.90(14)	O(6)—N(2)—O(5)	124.1(5)	C(24)—C(19)—Sb(2)	117.2(4)
O(7)—Sb(2)—C(25)	91.7(2)	O(6)—N(2)—O(4)	117.2(4)	C(26)—C(25)—Sb(2)	119.6(3)
C(31)—Sb(2)—C(25)	113.5(2)	O(5)—N(2)—O(4)	118.6(4)	C(30)—C(25)—Sb(2)	120.7(3)
O(7)—Sb(2)—C(19)	93.6(2)	C(6)—C(1)—C(2)	120.0(4)	C(32)—C(31)—Sb(2)	117.4(3)
C(31)—Sb(2)—C(19)	121.2(2)	C(6)—C(1)—Sb(1)	120.1(3)	C(36)—C(31)—Sb(2)	123.2(3)
C(25)—Sb(2)—C(19)	123.9(2)	C(2)—C(1)—Sb(1)	119.9(3)		

Experimental

The IR spectrum was recorded on a Hitachi-215 spectrometer (Nujol mulls). The ^1H NMR spectra were measured on a Tesla BS-567 A spectrometer (100 MHz) in $CDCl_3$ with Me_4Si as the internal standard.

μ-Oxobis(nitratotriphenylantimony) (1). A solution of silver nitrate (1.33 g, 7.80 mmol) in alcohol (30 mL) was added to a solution of triphenylantimony dibromide (2.00 g, 3.90 mmol) in acetone (20 mL). A colorless precipitate formed. The precipitate blackened upon storage in air. After washing with acetone (20 mL), the weight of the precipitate was 1.45 g. After removal of the solvent from the filtrate, compound **1** was obtained as colorless crystals in a yield of 2.50 g (76%), m.p. 218 °C. Found (%): C, 51.47; H, 3.50. $C_{39}H_{36}N_2O_8Sb_2$. Calculated (%): C, 51.77; H, 3.98. IR, ν/cm^{-1}: 1670 (C=O). ^1H NMR, δ: 2.13 (s, 6 H, Me); 7.50 (m, 30 H, Ph).

μ-Oxobis(nitratotri-*p*-tolylantimony) (2) was prepared analogously, m.p. 176 °C, yield 72%. Found (%): C, 54.05; H, 4.73; N, 2.80. $C_{42}H_{42}N_2O_7Sb_2$. Calculated (%): C, 54.19; H, 4.52; N, 3.01. ^1H NMR, δ: 2.37 (s, 18 H, Me); 7.50 (m, 24 H, Ph).

X-ray diffraction study of the crystal of **1** was carried out on an automated ENRAF-NONIUS CAD-4 diffractometer (Mo-Kα radiation, Nb filter, θ/2θ scanning technique, $2\theta_{max} = 50°$); crystal dimensions were 0.20×0.26×0.30 mm. Crystals are triclinic, $a = 9.889(2)$ Å, $b = 15.632(3)$ Å, $c = 13.026(3)$ Å, $\alpha = 72.45°$, $\beta = 95.11(2)°$, $\gamma = 92.54(2)°$, $V = 1911.9(7)$ Å^3, space group $P\bar{1}$, $d_{calc} = 1.470$ g cm^{-3}, $Z = 2$. Of a total of 4508 measured reflections, 4232 independent reflections ($R_{int} = 0.014$) with $I > 4\sigma(I)$ were used in calculations. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The positions of the H atoms were located from the difference electron density synthesis. Their positional and isotropic thermal parameters were included in the refinement. The final value of the R factor is 0.025, $wR_2 = 0.065$, GOOF = 1.101. All calculations were carried out on an IBM PC/AT computer using the SHELX-97 program package.[11] The atomic coordinates and equivalent temperature factors are given in Table 1. The principal bond lengths and bond angles are listed in Tables 2 and 3, respectively.

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