

Synthesis and structural characterization of some new triorganoantimony oxides. Molecular and crystal structure of tris(2,4,6-trimethylphenyl)antimony dihydroxide

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(Received February 9th, 1988)

Abstract

The triorganoantimony oxides prepared by oxidation of R_3Sb ($R = 4-ClC_6H_4$, $4-FC_6H_4$, $2-CH_3OC_6H_4$, $2,5-(CH_3)_2C_6H_3$) and of 9-phenyl-9-stibafluoren, $(C_6H_5)(2,2'-C_6H_4C_6H_4)Sb$, with H_2O_2 in acetone, shown by IR data to be dimeric in the solid state, and a structure with a four-membered Sb–O–Sb–O ring is proposed. The analogous oxidation of tris(2,4,6-trimethylphenyl)antimony produced a dihydroxide, the structure of which has been determined by X-ray diffraction. In this compound Sb has only a slightly distorted trigonal bipyramidal environment with OH groups in apical positions. The Sb–O(H) bond distance of 202.7(3) pm is in the normal range of covalent SbO bond distances. Intermolecular hydrogen bonding is excluded by the IR and diffraction data.

Introduction

During our investigations on triorganoantimony(V) sulphonates and carboxylates [1–3], neutralization of the appropriate triorganoantimony oxides or dihydroxides by acids proved to be the best method for synthesizing such compounds. We thus had to prepare such oxides as starting materials, and, in view of the confusion in the literature [4] on the structure of Ph_3SbO and of other triorganoantimony(V) oxides which existed when we started these studies we were faced with the question of what structure the newly prepared triorganoantimony(V) oxides would have. This problem gained further in interest when one of us [5] and others independently [6,7], found by X-ray diffraction that Ph_3SbO exists in a dimeric form and when we were able to isolate $Mes_3Sb(OH)_2$ [8] ($Mes = 2,4,6(CH_3)_3C_6H_2$), the first triarylantimony(V) dihydroxide. We were able to obtain good single crystals of the latter compound, and we report now on its structure as determined by X-ray diffraction, and present proposals on the structures of a series of new triarylantimony(V) oxides on the basis of IR data.

Experimental

IR spectra were recorded with a Perkin–Elmer PE 580B spectrophotometer fitted with KBr windows. C and H were determined microanalytically, melting points were measured in a Büchi apparatus SMP-20 (temperatures uncorrected), and molecular weights were determined osmotically.

$\text{Mes}_3\text{Sb}(\text{OH})_2$ was synthesized as described in ref. 8. H_2O_2 was used as supplied. 9-Phenyl-9-stibafluorene, $(\text{C}_6\text{H}_5)(2,2'\text{-C}_6\text{H}_4\text{C}_6\text{H}_4)\text{Sb}$ was synthesized according to ref. 9. The product was purified by column chromatography.

Preparation of triarylantimony(V) oxides

For the preparation of the compounds listed in Table 1 a solution of H_2O_2 (35% in water) in acetone (1/5 by volume) was added slowly to a suspension of Ar_3Sb in acetone with cooling in an icebath, the H_2O_2 was used in about 10% excess. When the addition was complete the ice bath was removed and the mixture was stirred for 1 h at room temperature. The precipitate was filtered off and dried. The oxidation of $(2\text{-MeOC}_6\text{H}_4)_3\text{Sb}$ had to be performed under reflux and needed 5 h. The yields were generally about 70 to 80%.

Determination of the structure of $\text{Mes}_3\text{Sb}(\text{OH})_2$

$\text{Mes}_3\text{Sb}(\text{OH})_2$ was crystallized from CHCl_3 by addition of petroleum ether (b.p. 50–60 °C). Crystal data: $\text{C}_{27}\text{H}_{35}\text{O}_2\text{Sb}$, $M = 513.3$, monoclinic, space group $C2/c$, a 1043.6(8), b 1280.0(12), c 1869.2(9) pm, β 103.5(6)°, V 2428.1 × 10⁶ pm³, $Z = 4$, D_c 1.404 Mg m⁻³, $F(000) = 1056$, $\mu(\text{Mo-K}_\alpha)$ 1.2 mm⁻¹ graphite-monochromated Mo-K_α radiation, λ 71.07 pm, crystal size ~ 0.21 × 0.16 × 0.13 mm, temperature 291(1) K, lattice parameters from least-squares fit with 25 reflexions up to 2θ 32.5°, CAD-4 diffractometer, $\omega/2\theta$ scan, scan speed 2.2–6.7° min⁻¹, six standard reflexions recorded every 2.5 h, only random deviations, 4555 reflexions measured in the range $1.5 \leq \theta \leq 25^\circ$, $-12 \leq h \leq 12$, $0 \leq k \leq 15$, $-22 \leq l \leq 22$; after averaging ($R_{\text{int.}} = 0.018$) 2130 unique reflexions, 1981 with $F \geq 3.0 \sigma(F)$. The following corrections were applied: Lorentz polarization correction and absorption correction via Ψ

Table 1

Analytical data for triarylantimony oxides

Compounds	M.p. (°C)	Analysis (found (calcd.) (%))	
		C	H
$[(2,5\text{-}(\text{CH}_3)_2\text{C}_6\text{H}_3)_3\text{SbO}]_2$ (1)	238	63.9 (63.60)	6.3 (6.00)
$[(2\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{SbO}]_2$ (2)	247	54.8 (54.93)	4.5 (4.61)
$[(4\text{-FC}_6\text{H}_4)_3\text{SbO}]_2$ (3)	175	49.0 (51.11)	2.6 (2.86)
$[(4\text{-ClC}_6\text{H}_4)_3\text{SbO}]_2$ (4)	165–167	46.2 (45.76)	2.8 (2.56)
$[(\text{C}_6\text{H}_5)(2,2'\text{-C}_6\text{H}_4\text{C}_6\text{H}_4)\text{SbO}]_2$ (5)	224	58.9 (58.90)	3.9 (3.57)

Table 2

Atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$). $U_{\text{eq}} = (1/3)(U_{11} + U_{22} + U_{33})$

	x	y	z	U_{eq}
Sb(1)	0.0	0.09564(2)	0.25	29
O(1)	0.1973(2)	0.0911(2)	0.2589(1)	43
C(11)	0.0266(3)	0.1816(2)	0.3506(2)	33
C(12)	-0.0307(3)	0.1469(2)	0.4072(2)	37
C(13)	-0.0152(3)	0.2063(3)	0.4709(2)	47
C(14)	0.0560(4)	0.2986(3)	0.4809(2)	48
C(15)	0.1104(3)	0.3316(3)	0.4246(2)	47
C(16)	0.0995(3)	0.2757(2)	0.3606(2)	38
C(17)	-0.1103(4)	0.0468(3)	0.4033(2)	49
C(18)	0.0706(6)	0.3607(4)	0.5510(3)	77
C(19)	0.1672(4)	0.3207(3)	0.3034(2)	52
C(21)	0.0	-0.0717(3)	0.25	34
C(22)	0.0887(3)	-0.1275(3)	0.3051(2)	38
C(23)	0.0861(3)	-0.2357(2)	0.3039(2)	46
C(24)	0.0	-0.2918(4)	0.25	48
C(25)	0.1909(4)	-0.0766(3)	0.3666(2)	49
C(26)	0.0	-0.4091(3)	0.25	64

scans; max./min. transmission 1.00/0.95; systematic absences: $(hkl) h + k = 2n + 1$, $(h0l) l = 2n + 1$. Space group: $C2/c$ (No. 15) and Cc (No. 9). The structure was solved via Patterson synthesis, ΔF syntheses, and full-matrix least-squares refinement with anisotropic temperature factors for all non H-atoms and a common

Table 3

Bond lengths (pm) and bond angles ($^\circ$) in $\text{Mes}_3\text{Sb}(\text{OH})_2$ with e.s.d.'s. in parentheses ^a

Sb(1)–O(1)	202.7(3)
Sb(1)–C(11)	214.1(3)
Sb(1)–C(21)	214.2(4)
O(1)–Sb(1)–C(11)	91.2(1)
O(1)–Sb(1)–C(21)	88.3(1)
O(1)–Sb(1)–C(11a) ^b	90.5(1)
O(1a)–Sb(1)–C(11)	90.5(1)
O(1a)–Sb(1)–C(21)	88.3(1)
O(1a)–Sb(1)–C(11a)	91.2(1)
Sb(1)–C(11)–C(16)	120.6(2)
Sb(1)–C(11)–C(12)	120.6(2)
Sb(1)–C(21)–C(22)	120.5(2)
C(11)–Sb(1)–C(21)	120.9(1)
C(11)–Sb(1)–C(11a)	118.2(1)
C(21)–Sb(1)–C(11a)	120.9(1)
O(1)–Sb(1)–O(1a)	176.7(1)

The C–C distances and the C–C–C angles in the aromatic groups are in the range 137.4(6) to 141.4(4) pm (mean distance: 139.1(6) pm) and 117.5(4) to 122.7(3) $^\circ$. (mean angle: 119.8(4) $^\circ$), and the C–C(methyl) distances and C–C–C(methyl) angles at the 2,4,6-trimethylphenyl groups are in the range 150.2(6) to 152.5(5) pm (mean distance: 151.6(6) pm) and 117.1(3) $^\circ$ to 124.2(3) $^\circ$ (mean angle: 120.7(4) $^\circ$).

^a Numbering of atoms according to Fig. 1. ^b (a) corresponds to the symmetry operation: $-x, y, 0.5 - z$.

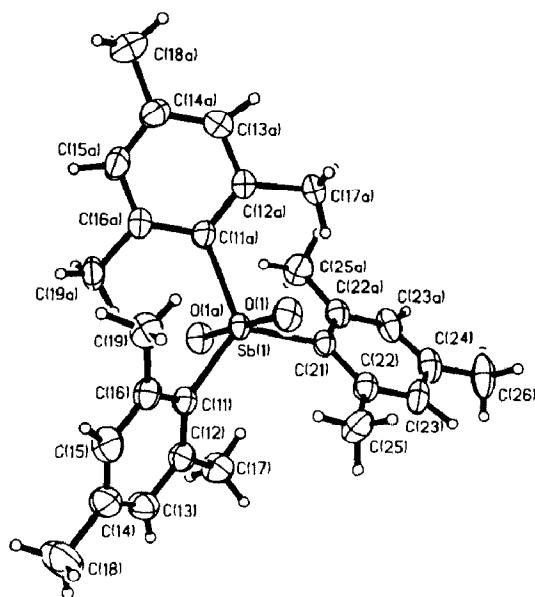


Fig. 1. General view (SHELXTL PLUS) of one molecule of $\text{Mes}_3\text{Sb}(\text{OH})_2$, showing atom numbering.

isotropic temperature factor for all H-atoms, which were placed in calculated positions (C–H 96 pm); refinement in space group $C2/c$ on F with 1981 reflexions and 139 refined parameters; weighting scheme $w = 1.0/(\sigma^2(F) + (0.0005 F^2))$, $S = 1.35$, $R(\text{unweighted}) = 0.026$, $R(\text{weighted}) = 0.028$, max. $\Delta/\sigma = 0.13$; no extinction correction; largest peak in final ΔF map = $\pm 0.4(1) 10^{-6} \text{ e pm}^{-3}$, complex neutral-atom scattering factors from ref. 10. Programs: Enraf–Nonius Structure Determination Package [11], SHELXTL PLUS; PARST [12].

Final fractional atomic coordinates and the equivalent values of the anisotropic temperature factors for the non H-atoms are listed in Table 2, and intramolecular bond distances and angles in Table 3). The molecule and the numbering scheme are shown in Fig. 1. The molecule resides on a twofold axis and so six H-positions (occupancy 0.5) were used for the H atoms at C(26) (disorder) in the final refinement cycle. Tables of thermal parameters and lists of structure factors are available from the authors.

Results and discussion

The new triorganoantimony(V) oxides listed in Table 1 have been prepared by the standard procedure [4] of oxidizing the appropriate triorganoantimony(III) compound with H_2O_2 .

Experiments to oxidize Mes_3Sb did not give the oxide Mes_3SbO but instead the dihydroxide $\text{Mes}_3\text{Sb}(\text{OH})_2$ [8]. The final proof for this composition came from a single crystal structure determination, the first X-ray structure analysis of a triorganoantimony(V) dihydroxide. $\text{Mes}_3\text{Sb}(\text{OH})_2$ proved to be monomeric in the solid state, and from Fig. 1 it follows that Sb is pentacoordinated, two OH groups being in the apical positions and three C(Mes) atoms in the equatorial plane of a trigonal bipyramid. A consideration of the axial angle O(1)–Sb(1)–O(1a) $176.7(1)^\circ$

and of the equatorial and equatorial/axial bonding angles (Table 3) with maximum deviations of 1.8 and 1.7°, respectively, from the mean values of 120.0(1) and 90.0(1)°, respectively, shows that this polyhedron around Sb is only slightly distorted. The bond distance Sb(1)–O(1) corresponds to distances in compounds with covalent Sb–O bonds, e.g. 204.8 pm in Ph₄SbOH [13], or 203.3(8) pm in Ph₃Sb(OMe)₂ [14]. Intermolecular distances exceed the appropriate sums of Van der Waals radii. This also excludes intermolecular hydrogen bonds, indicating that the OH groups are efficiently shielded by the bulky Mes ligands. The absence of hydrogen bonds can also be deduced from the fact that there is no IR band in the range of 3000 to 3500 cm⁻¹. One middle strong sharp band at 3650 cm⁻¹ can be safely assigned to the stretching frequency of a free OH group. The related Sb–O stretching frequency appears at 520 cm⁻¹ as a strong band.

The new triorganoantimony oxides R₃SbO (R = 2,5-(CH₃)₂C₆H₃ (1), 2-CH₃OC₆H₄ (2), 4-FC₆H₄ (3), 4-ClC₆H₄ (4)) and 9-phenyl-9-stibafluorene oxide (5) are white, microcrystalline solids, which are soluble in CHCl₃ and CH₃OH, but scarcely soluble in CH₃COCH₃ and water; in general, the solubilities resemble those of (Ph₃SbO)₂ [5 to 7]. Molecular weights found in benzene corresponded to values calculated for dimeric units (R₃SbO)₂ (found (calcd.): 1: 934(906), 4: 952(944)). In CHCl₃ the molecular weights of 2 and 4 were distinctly higher than calculated for monomeric species R₃SbO (2: 666(459), 4: 546(472)) and only the value obtained for 1 could be taken to correspond roughly to that of the monomer (486(453)). Similar observations have been made for (Ph₃SbO)₂ in benzene and CHCl₃ solutions [5 to 7]. It therefore is inferred that the new compounds are dimers in benzene as in the solid state (vide infra) but dissociate more or less when dissolved in CHCl₃, probably to form an equilibrium (R₃SbO)₂ ⇌ 2 R₃SbO.

In the IR spectra of the oxides 1 to 5 there are no absorptions between 3000 and 4000 cm⁻¹ which excludes the presence of OH groups. However, there are absorptions in the range between 500 and 690 cm⁻¹ that we assign to Sb–O stretching frequencies (see Table 4).

The X-ray structure determination of (Ph₃SbO)₂ has shown that the central structural unit is a planar four-membered Sb₂O₂ ring [5 to 7]. In the IR spectrum of (Ph₃SbO)₂ bands at 643 and 651 cm⁻¹ have been assigned to two ν_{as}(Sb₂O₂) by comparison with data of Ph₃SbF₂ [6]. An additional band at 664 [18] or 668 cm⁻¹ [19], respectively, which had been ascribed to ν(Sb–O) was observed both in (Ph₃SbO)₂ and Ph₃SbF₂ and was therefore no longer considered in recent work [6]. However, the IR spectra of the other halides Ph₃SbX₂ (X = Cl, Br, I) [20] and also of the products of the reactions of (Ph₃SbO)₂ with sulfonic acids [21] show no absorptions in the range of ca. 660 to 680 cm⁻¹. We therefore assume that the absorption at 670 cm⁻¹ in the spectrum of (Ph₃SbO)₂ is actually due to ν_{as}(Sb₂O₂). The two bands at 658 and 648 cm⁻¹ are also assigned to ν_{as}(Sb₂O₂) (see above, [18,19]), the absorption probably being split by coupling. Additionally, in the IR spectrum of (Ph₃SbO)₂ there is a band at 480 cm⁻¹ which we assign to δ(Sb₂O₂). An analogous band is also present in the spectrum of Ph₃SbF₂, but not in the spectra of the other halides or sulfonates. The above assignment of the band at 480 cm⁻¹ is supported by the appearance of such a band in all triorganoantimony oxides studied hitherto.

Comparison of the IR data of the trialkyl- and triaryl-antimony oxides in Table 4 reveals a remarkable similarity of the values of ν_{as}(Sb₂O₂) and of δ(Sb₂O₂). We

Table 4

Characteristic frequencies $\nu_{\text{as}}(\text{Sb}_2\text{O}_2)$ and $\delta(\text{Sb}_2\text{O}_2)$ (in cm^{-1}) of compounds of the type $(\text{R}_3\text{SbO})_2$

		$\nu_{\text{as}}(\text{Sb}_2\text{O}_2)$ (cm^{-1})	$\delta(\text{Sb}_2\text{O}_2)$ (cm^{-1})	Ref.
$[(\text{C}_6\text{H}_5)_3\text{SbO}]_2$		670, 658, 648	480	5, 6, 7
$[(\text{C}_6\text{H}_5)_2\text{SbBrO}]_2$		650	495	15
$[(2,5\text{-}(\text{CH}_3)_2\text{C}_6\text{H}_3)_3\text{SbO}]_2$	(1)	658, 629	475	this paper
$[(2\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{SbO}]_2$	(2)	657, 642	480	this paper
$[(4\text{-FC}_6\text{H}_4)_3\text{SbO}]_2$	(3)	670	475	this paper
$[(4\text{-ClC}_6\text{H}_4)_3\text{SbO}]_2$	(4)	670	470	this paper
$[(\text{C}_6\text{H}_5)(2,2'\text{-C}_6\text{H}_4\text{C}_6\text{H}_4)\text{SbO}]_2$	(5)	640, 625	500	this paper
$[(\text{CH}_3)_3\text{SbO}]_2$		645	485	16
$[(\text{C}_2\text{H}_5)_3\text{SbO}]_2$		678	478	17
$[(n\text{-C}_3\text{H}_7)_3\text{SbO}]_2$		650	450	17
$[(n\text{-C}_4\text{H}_9)_3\text{SbO}]_2$		650	450	17
$[(n\text{-C}_5\text{H}_{11})_3\text{SbO}]_2$		650	450	17

assume that in all these compounds there is the same structural central unit, namely a Sb–O–Sb–O ring, as was shown to be the case by X-ray structure determination for $(\text{Ph}_3\text{SbO})_2$ [5 to 7] and $(\text{Ph}_2\text{SbBrO})_2$ [15]. This implies that all these compounds will be dimers in the solid state. In this context it should be recalled that the dimeric nature of **1** and **4** has also been established in benzene solution (see above).

This inference is substantiated (i) by the ^{121}Sb Mössbauer spectra of low melting (= dimeric) triphenylantimony oxide [22] and of the appropriate methyl compound [23] which show very similar e^2qQ values of $-10.6(1)$ and $-11.4(6)$ mm s^{-1} , respectively and (ii) by the mass spectra of these two compounds, which show $\text{R}_3\text{Sb}_2\text{O}_2^+$ ($\text{R} = \text{Me}$ [16], Ph [24]) as the fragment of highest mass in both cases. The ion $\text{Ph}_5\text{Sb}_2\text{O}_2^+$ is also found in the mass spectrum of high melting (= polymeric) triphenylantimony oxide, but in lower abundance [25].

The appearance of $\nu_{\text{as}}(\text{Sb-O-Sb-O})$ in Sb_2O_2 ring compounds at wave numbers lower than the bands due to $\nu_{\text{as}}(\text{Sb-O-Sb})$ in μ -oxo type compounds $(\text{R}_3\text{SbX})_2\text{O}$ is noteworthy, and this shift should correlate with the different values of the Sb–O–Sb angles in $(\text{Ph}_3\text{SbO})_2$ (102.6° [5–7]) and in hexaphenyldistiboxans $(\text{Ph}_3\text{SbX})_2\text{O}$ (136 to 140° [26,27] or 180° [28]). It is known that the values of the stretching frequencies of M–O–M systems depend strongly on the M–O–M bond angle [28], and we recently noted a correlation between $\nu_{\text{as}}(\text{Sb-O-Sb})$ and the size of the Sb–O–Sb bond angle in such compounds [19]. From these considerations it can be inferred that the Sb–O–Sb angles in the dimer **5** must be still more acute. This would be caused by the rigid arrangement of the biphenyl group. By analogy with the structure of biphenyl-2,2'-diyltriphenylantimony [29], we assume that one of the two C atoms of the biphenyl unit bonded to Sb is in axial, and the second one, like C(phenyl), in an equatorial position, and it would follow that like in $(\text{Ph}_3\text{SbO})_2$ [5–7] one O atom occupies an equatorial and one an axial position.

Acknowledgement

Financial assistance by Fonds der Chemischen Industrie is gratefully acknowledged.

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