Tris[(trimethylsilyl)oxy]antimony

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Dedicated to Professor R. Schmutzler on the occasion of his 60th birthday

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Heterosiloxanes, Stibiosiloxanes, Antimonites

Tris[(trimethylsilyl)oxy]antimony ($Sb(OSiMe_3)_3$, **1**) has been prepared from $SbCl_3$ and 3 equiv. of $LiOSiMe_3$ in diethylether. According to mass spectrometric and NMR spectroscopic data, **1** appears to be a monomer in solution and in the gas phase. Dimerisation occurs, however, in the solid state as verified by an X-ray crystal structure determination. The unit cell contains three crystallographically independent monomers, two of which form one type of dimer, while the other is part of a centrosymmetrical dimer. In both types of dimers two Sb atoms are connected *via* two $OSiMe_3$ groups to form distorted Sb_2O_2-squares. Together with the remaining 4 $OSiMe_3$ groups and the two stereochemically active lone pairs, each Sb exhibits a trigonal bipyramidal coordination.

Introduction

Thin oxide films containing arsenic and antimony are becoming increasingly important for applications in semiconductor technology [1]. They can function as diffusion sources as well as insulating and passivating layers and are promising alternatives to the common P-doped oxide layers [2–4]. For this purpose, precursor compounds are being developed and investigated, which allow the deposition of thin oxide films from the gas or liquid phase. Among the most promising groups of compounds are the silyl derivatives of arsenic and stibinic acids. The high tendency of disiloxane formation is indicative of the most preferred decomposition pathway for these precursors leading to the oxides of As and Sb, respectively, which offers advantages over most common alternatives, like the alkyl esters. To date silyl arsenites and antimonites have been only poorly investigated, and little is known about the properties and structures [5]. We have therefore resumed our studies in the heterosiloxane chemistry of arsenic and antimony [6–9]. As another part of our results we present in the following the synthesis, properties and crystal structure of $Sb(OSiMe_3)_3$ and compare its structural chemistry with that of the corresponding alkyl esters [10, 11].

Results

Tris[(trimethylsilyl)oxy]antimony(III) (**1**)

Treatment of $SbCl_3$ with three equivalents of lithium trimethylsilyloxide in diethylether gives tris[(trimethylsilyl)oxy]antimony(III) in good yields (**1**, eq. (1)) [12].

$$SbCl_3 + 3\,LiOSiMe_3 \longrightarrow \underset{\mathbf{1}}{Sb(OSiMe_3)_3} + 3\,LiCl \quad (1)$$

The product can be purified by distillation and is obtained as a colorless viscous liquid, which is readily soluble in common non-protic solvents, but susceptible to hydrolysis. It has been characterized by elemental analysis and mass spectrometry, which shows the compound to be a monomer in the gas phase. NMR spectra (of benzene or toluene solutions) give only singlet resonances (for ^1H, $\{^1H\}^{13}C$ and $\{^1H\}^{29}Si$), indicating the equivalence of all the (trimethylsilyl)oxy groups in solution even at low temperature (−90 °C). Thus there is no evidence for an oligomerization of the compound in the liquid or gas phase. Such oligomers should show seperate NMR signals for terminal and bridging ligands, as *e.g.* observed for $[Al(OSiMe_3)_3]_2$ and its gallium and indium analogues [13]. For the solution state a rapid ligand scrambling can be envisaged which would equilibrate the silyloxy groups and lead to coalescence of the NMR signals.

Compound **1** solidifies at −15 °C to give colorless crystals suitable for a single crystal X-ray diffrac-

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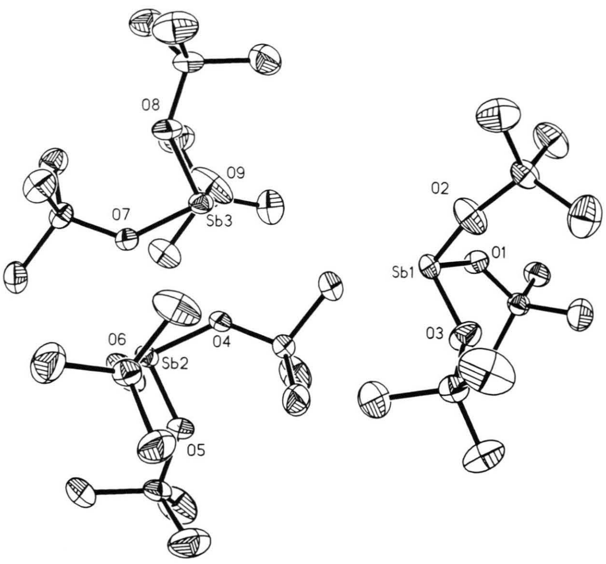


Fig. 1a. Molecular structures of the three crystallographically independent monomeric units $Sb(OSiMe_3)_3$ with numbering of the Sb and O atoms. Hydrogen atoms are omitted for clarity. (ORTEP, 50% probability ellipsoids).

tion study. Crystals of **1** are monoclinic, space group $P2_1/n$, with three crystallographically independent monomers in the unit cell. Two of these monomers form a dimer $(Me_3SiO)_2Sb(OSiMe_3)_2Sb(OSiMe_3)_2$ without crystallographic symmetry. The third one is part of a dimer with a center of inversion. Both dimers are very similar in their geometry as can be demonstrated by a superposition of the models. Therefore in the following discussion only the dimer with center of inversion is considered (Fig. 1).

Atom Sb1 has three short $Sb-OSiMe_3$ contacts (Sb1–O1: 1.954(2) Å, Sb1–O2: 1.906(3) Å, Sb1–O3: 1.946(3)) Å to what may be referred to as the silyloxy groups of the original monomeric unit, and one significantly longer one (Sb1–O1a: 2.897(2) Å) to a silyloxy group of the second monomer. Taking into account a stereochemically active lone pair at antimony(III), a trigonal bipyramidal coordination is obtained, where O1, O2 and the lone pair of electrons are in equatorial positions and O3 and O1a in apical positions. The (equatorial) distance Sb1–O2 is about 0.5 Å shorter than the (apical) distance Sb1–O3, as expected for bonding in trigonal bipyramidal structures of Main Group Metals. The distance between Sb1 and the bridging (equatorial) O1 atom is elongated on account of the coordination to a second antimony atom (Sb1a). The Sb_2O_2-parallelogram is planar (by symmetry) with Sb1–O1–Sb1a angles of 107.9(1)° and O1–Sb1–O1a angles of 72.1(1)°.

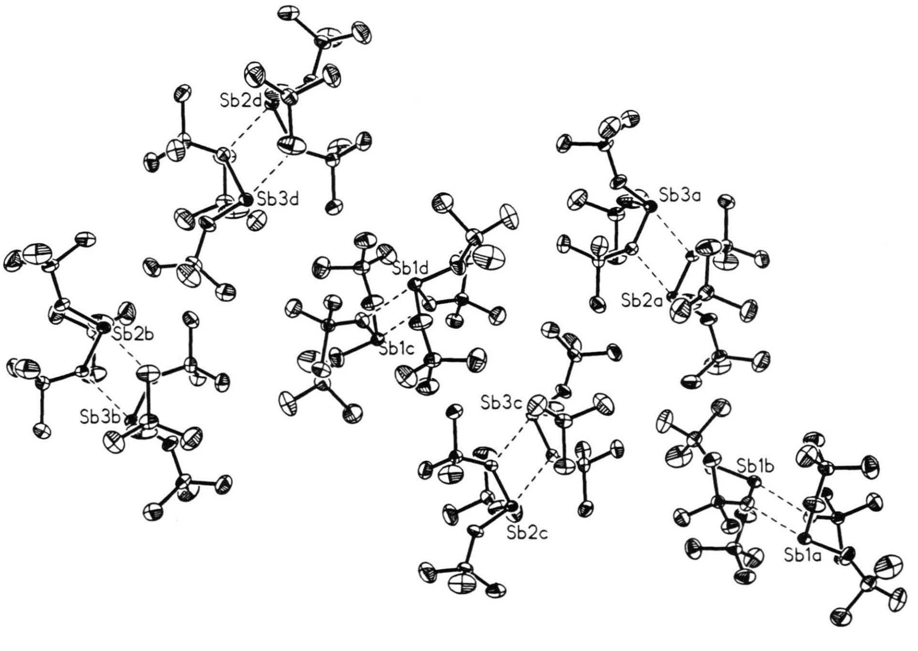


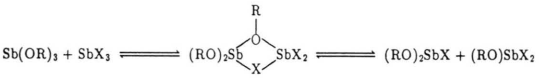
Fig. 1b. Packing of the dimers in the lattice with numbering of the Sb atoms, referring to the monomers in Fig. 1a. (Hydrogen atoms omitted, ORTEP, 50% probability ellipsoids.)

Table I. Selected distances [pm] and angles [°] of $C_9H_{27}O_3SbSi_3$ (**1**).

Sb1–O1	195.4(2)	O2–Sb1–O3	95.3(1)
Sb2–O4	194.6(3)	O6–Sb2–O5	95.0(1)
Sb3–O7	195.1(2)	O8–Sb3–O9	95.0(1)
Sb1–O2	190.6(3)	O1–Sb1–O2	97.8(1)
Sb2–O6	190.0(3)	O4–Sb2–O6	98.5(1)
Sb3–O9	189.9(3)	O7–Sb3–O9	97.1(1)
Sb1–O3	194.6(3)	O1–Sb1–O3	92.4(1)
Sb2–O5	194.4(3)	O4–Sb2–O5	92.0(1)
Sb3–O8	193.8(3)	O7–Sb3–O8	93.3(1)
Sb1–O1′	289.7(2)	O1–Sb1–O1′	72.1(1)
Sb2–O7	289.5(2)	O4–Sb2–O7	72.1(1)
Sb3–O4	291.5(2)	O4–Sb3–O7	72.1(1)
		Sb1–O1–Sb1′	107.9(1)
		Sb2–O4–Sb3	107.3(1)
		Sb2–O7–Sb3	108.0(1)

The crystal structure of compound **1** is the first example for a dimerization of an antimonous(III) acid ester. Such dimers have been proposed as intermediates of the dismutation reactions known to occur with these compounds (eq. 2), but hitherto could not been isolated [14].

(2)



X = Ci, Br, I, NR'₂, OR'

All antimonous acid esters $Sb(OR)_3$ appear to be monomers in the gas phase and – with bulky substituents – also in the liquid phase [15, 16], and thus are similar to the esters of arsenous and phosphorous acids. By contrast, oligomerization is observed if the substituents are small, and $Sb(OMe)_3$ *e. g.* has been found to have a polymeric structure [17] with a distorted octahedral coordination of 6 OMe groups at the Sb atom. The oligomerization is limited to the dimer for the title compound, probably owing largely to the steric effect of the bulky Me_3SiO groups.

Experimental

The experiments were carried out under an atmosphere of dry nitrogen. Solvents were purified, dried, and saturated with nitrogen. Glassware was oven-dried and filled with nitrogen. Instruments: NMR, JEOL JNM-GX 400 spectrometer; MS, Varian MAT 311 A; IR, Nicolet FX 354.

Table II. Positional and equivalent thermal parameters for the non-hydrogen atoms of $C_9H_{27}O_3SbSi_3$ (**1**), with e.s.d.s in parantheses.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Sb1	0.14148(2)	0.06374(1)	0.02593(1)	0.033
Sb2	0.31964(2)	0.47262(1)	−0.14441(1)	0.031
Sb3	0.38872(2)	0.25586(1)	−0.17393(1)	0.032
Si1	−0.1222(1)	0.02869(6)	0.08364(3)	0.034
Si2	0.2847(1)	−0.11181(7)	0.04765(4)	0.041
Si3	0.2793(1)	0.16758(7)	0.10004(4)	0.045
Si4	0.2332(1)	0.34859(6)	−0.07367(3)	0.035
Si5	0.2397(1)	0.61702(6)	−0.08419(3)	0.041
Si6	0.6541(1)	0.46628(7)	−0.11466(3)	0.040
Si7	0.4810(1)	0.38270(7)	−0.24307(3)	0.036
Si8	0.4918(1)	0.11249(6)	−0.23230(3)	0.039
Si9	0.0636(1)	0.26283(6)	−0.21027(4)	0.042
O1	−0.0295(2)	0.0184(1)	0.04264(7)	0.037
O2	0.2517(3)	−0.0248(2)	0.0334(1)	0.060
O3	0.1757(3)	0.1060(2)	0.07946(8)	0.056
O4	0.2906(3)	0.3732(1)	−0.11863(7)	0.035
O5	0.2521(3)	0.5274(2)	−0.09754(8)	0.058
O6	0.5044(3)	0.4859(2)	−0.1306(1)	0.068
O7	0.4157(2)	0.3557(1)	−0.19935(7)	0.034
O8	0.4807(3)	0.2012(2)	−0.21664(8)	0.048
O9	0.2130(3)	0.2373(2)	−0.1948(1)	0.075
C11	−0.1601(4)	0.1319(2)	0.0922(1)	0.047
C12	−0.2835(4)	−0.0227(2)	0.0740(1)	0.049
C13	−0.0356(5)	−0.0135(3)	0.1279(1)	0.057
C21	0.1352(5)	−0.1745(3)	0.0399(2)	0.067
C22	0.4246(5)	−0.1467(3)	0.0161(2)	0.071
C23	0.3361(5)	−0.1133(3)	0.1011(1)	0.073
C31	0.1952(5)	0.2154(3)	0.1424(2)	0.077
C32	0.3219(6)	0.2439(3)	0.0624(2)	0.080
C33	0.4318(6)	0.1191(4)	0.1173(2)	0.115
C41	0.2320(4)	0.2415(2)	−0.0725(1)	0.051
C42	0.3456(5)	0.3843(3)	−0.0335(1)	0.061
C43	0.0580(5)	0.3835(3)	−0.0672(2)	0.074
C51	0.3212(5)	0.6784(3)	−0.1228(2)	0.067
C52	0.0594(5)	0.6410(3)	−0.0800(2)	0.086
C53	0.3226(6)	0.6313(3)	−0.0350(2)	0.080
C61	0.7764(5)	0.5071(3)	−0.1502(2)	0.083
C62	0.6832(5)	0.5101(3)	−0.0648(1)	0.074
C63	0.6736(5)	0.3608(3)	−0.1121(2)	0.073
C71	0.3832(4)	0.3417(3)	−0.2859(1)	0.049
C72	0.4704(4)	0.4897(2)	−0.2447(1)	0.051
C73	0.6610(4)	0.3538(3)	−0.2450(1)	0.053
C81	0.4251(5)	0.1062(3)	−0.2845(1)	0.058
C82	0.3930(5)	0.0488(3)	−0.1987(1)	0.063
C83	0.6714(5)	0.0837(3)	−0.2311(2)	0.072
C91	0.0505(4)	0.3690(2)	−0.2108(2)	0.056
C92	−0.0624(5)	0.2226(3)	−0.1753(1)	0.062
C93	0.0341(6)	0.2243(3)	−0.2616(2)	0.079

Tris[(trimethylsilyl)oxy]antimony(III) (**1**)

Lithium trimethylsilanolate (25.3 g, 263 mmol) is dissolved in 90 ml of diethylether and treated with a solution of antimony trichloride (20.0 g, 87.7 mmol) in 40 ml of diethylether at ambient temperature. The mixture is stirred for 2 h and then filtered. After evaporation of the solvent under reduced pressure, the liquid raw product is purified by fractional distillation. The yield is 22.0 g (64.5%).

M.p.: −15 °C. – B.p.: 95 °C (6.5 Torr); 240 °C (760 Torr). – ^{1}H NMR (C_6D_6): δ = 0.21 ppm (s). – {^{1}H}−^{13}C NMR (C_6D_6): δ = 3.36 ppm (s). – {^{1}H}−^{29}Si NMR (C_6D_6): δ = 11.27 ppm (s). – MS (EI): *m/z* = 373 (1%, $(Me_3SiO)_3Sb{-}Me$). – IR (cm^{-1}): $\nu_{as}(CH_3)$ = 2956 (s), $\nu_{as}(CH_3)$ = 2898 (m), $\delta_s(CH_3)$ = 1249 (vs), ν_{as}(Si−O−Sb) = 994 (s), ν_{as}(Si−O−Sb) = 908 (vs), $\varrho(CH_3)$ = 837 (vs), $\varrho(CH_3)$ = 751 (s), $\nu_{as}(C_3Si)$ = 686 (m), $\nu_{as}(C_3Si)$ = 631 (m).

Analysis for $C_9H_{27}O_3SbSi_3$ *(389.32)*

Calcd C 27.77 H 6,99 Sb 31,27 Si 21,64%,
Found C 27.61 H 6,97 Sb 31.12 Si 21.42%.

Crystal and structure solution data for $C_9H_{27}O_3SbSi_3$ (**1**)

M_r = 389.32, monoclinic, a = 9.923(1), b = 17.418(1), c = 33.077(2) Å, β = 90.39(1)°, space group $P2_1/n$ (No. 14, Int. Tables), V = 5716.5 Å^3, Z = 12, D_c = 1.348 g cm^{-3}, T = −80 °C, μ(Mo−Kα) = 21.7 cm^{-1}, λ(Mo−K$_\alpha$) = 0.71069 Å, CAD4 diffractometer, 13568 reflections measured, 11381 unique, and 9346 observed ($F_o \geq 4\sigma(F_o)$); empirical absorption correction applied (T_{min} = 68.29%, T_{max} = 99.95%). Structure solution by direct methods, with all missing non hydrogen atoms located by successive difference Fourier synthesis; refinement of 434 parameters converged at R = 0.036 (R_w = 0.029) ($R = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/[wF_o^2]]^{1/2}$ with $w = [\sigma^2(F_o) + 0.000057\,F_o^2]^{-1}$), including hydrogen atoms in idealized, fixed positions; maximum and minimum residual electron densities in the difference Fourier map were 0.513 and −0.477 e Å^{-3}, respectively.

Details of the X-ray structure determination have been deposited at Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, and may be obtained on quoting the names of the authors, the journal citation, and the code number CSD 58306.

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