The Intriguing Structural Characteristics of the Heterosiloxane Molecule Na$_4$[Sb$_2$O(OSiMe$_3$)$_8$]

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Treatment of Sb(OSiMe$_3$)$_3$ with NaOSiMe$_3$ in the molar ratio 1:2 in hexane at ambient temperature leads to the formation of Me$_3$SiOSiMe$_3$ and a crystalline complex of the formula Na$_4$[Sb$_2$O(OSiMe$_3$)$_8$] in ca. 35% yield. The composition of the product has been confirmed by elemental analysis and negative-ion CI mass spectrometry. The single crystal X-ray structure analysis (rhombohedral, space group $R\bar{3}c$, Z = 6) resulted in a disorder model for the complex with pseudo-cubic symmetry owing to virtually random distribution of sodium and antimony atoms over the vertices of an oxygen-centered octahedron with the eight silyloxy groups capping the faces. Low solubility in non-coordinating solvents prevented solution NMR studies, but solid-state NMR investigations using cross polarization and magic-angle spinning techniques (^{13}C, ^{29}Si) allowed the assignment of a point group C_{2v} structure with the Sb^{III} atoms in *cis* position relative to the oxo center of the complex.

Heterosiloxanes containing antimony have been the subject of a first series of preparative studies in the 1950s and 1960s in the course of attempts to modify the chemical and physical properties of siloxane polymers[1−7]. Among the early prototype monomers were the simple tris(trialkylsilyl) antimonites(III) (R$_3$SiO)$_3$Sb[4−6]. More recent interest[8] in these materials is arising from potential applications as single-source precursors for the deposition (from solution or from the vapor phase) of antimony-containing silicate glasses for usage in surface technology of semiconductor devices. The situation is similar to that presently observed for the chemistry of related heterosiloxanes containing arsenic[9].

In this context we have been engaged in studies of the chemistry of sodium trialkylsilyl antimonites(III), which arise from the acceptor properties of (R$_3$SiO)$_3$Sb species towards sodium trialkylsilyloxides (trialkylsilanolates). The rich collection of halogeno complexes derived from antimony(III) trihalides already documented in the literature[10−12] clearly indicates that a large family of antimony(III) silyloxide complexes with a variety of structural features can be expected. We report in this paper on the formation and structural characterization of the title compound as one of the structurally most intriguing examples.

Preparation and Properties

Layering of a solution of sodium trimethylsilyloxide in hexane with a solution of half an equivalent of antimony(III) tris(trimethylsilyloxide) in the same solvent, at ambient temperature with the exclusion of air and moisture, affords colorless crystals within a period of 3 to 4 d in ca. 35% yield. The results of the elemental analysis of this product are compatible with a stoichiometry according to formula **1** in Eq. (1). The hexamethyldisiloxane byproduct is readily detected in the mother liquor by GC/MS analysis. In the negative-ion mass spectra (chemical ionization) the fragment [M − SiMe$_3$] is detected as the parent peak [m/z (%) = 989 (5)], followed by [M − Me$_3$SiOSiMe$_3$] [m/z (%) = 900

(13)], [(Me$_3$SiO)$_3$O$_4$Sb$_2$Na$_4$] [m/z (%) = 649 (83)], and [(Me$_3$Si)$_2$O$_3$Sb$_2$Na$_3$] [m/z (%) = 537 (100)], where m refers to the high-abundance isotopes for all elements.

$$4\ \text{NaOSiMe}_3 + 2\ \text{Sb(OSiMe}_3)_3 \longrightarrow$$
$$\text{Me}_3\text{SiOSiMe}_3 + \text{Na}_4\text{Sb}_2\text{O(OSiMe}_3)_8 \quad (1)$$
$$\mathbf{1}$$

Compound **1** is insoluble or only very sparingly soluble in benzene, toluene, hexane, chloroform, dichloromethane, and diethyl ether, but dissolves in tetrahydrofuran or diglyme with noticeable decomposition even at low temperature. Solution-NMR and -IR/Raman-vibrational spectroscopic studies were therefore impossible, and information regarding the structure of the compound had to rely on solid-state investigations.

Crystal Structure and Solid-State NMR Spectra

Compound **1** crystallizes in the rhombohedral space group $R\bar{3}c$ (Nr. 167) with six formula units in the unit cell. To a first approximation, the individual molecules in the lattice can be described as oxygen-centered octahedra of metal atoms, with the eight faces of the polyhedron capped by trimethylsilyloxy groups. Crystallographically, the unit has to be referred to as a trigonal antiprism of virtually equivalent metal atoms with a threefold inversion axis passing through two trimethylsilyloxy groups on opposite sides of the cluster and through the oxygen center [point group D_{3d}; Figure 1 (top)]. It is obviously impossible to distinguish crystallographically between sodium and antimony atoms owing to a disorder, which leads to a random distribution of the metal atoms over the various structural sites. Based on such a disorder, which takes into account the relative
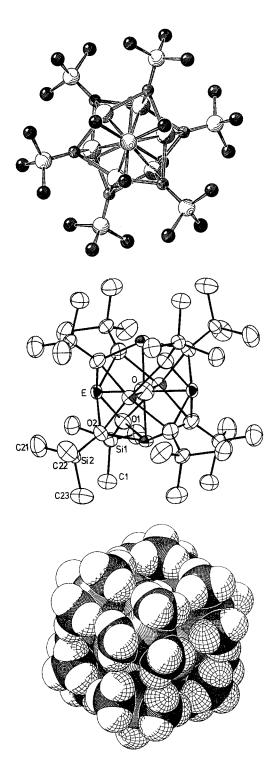
Figure 1. Top: Molecular structure of compound 1 (ORTEP; 50%-probability ellipsoids) with atomic numbering [atoms E designate disordered Na and Sb atoms (ratio 4:2) at the vertices of a pseudo-octahedron; the oxygen atoms of the eight trimethylsilyloxy groups are capping the octahedral faces, and thus are forming a cube] (see also Figure 2); hydrogen atoms are omitted for clarity; selected bond distances [Å] and angles [°]: Si1−O1 1.619(3), Si1−C1 1.857(5), Si2−O2 1.610(3), Si2−C21 1.848(5), Si2−C22 1.852(4), Si2−C23 1.858(5), E−O 2.269(2), E−O2 2.358(2), E−O2b 2.304(3), E−O2d 2.411(2); O1−Si1−C1 109.89(11), C−Si1−C' 109.0(2), O2−Si2−C21 110.36(19), O2−Si2−C22 111.00(17), O2−Si2−C23 111.6(2), C21−Si2−C22 108.1(2), C21−Si2−C23 107.8(2), C22−Si2−C23 107.8(2). − Center: Projection along the crystallographically imposed threefold axis (SCHAKAL). − Bottom: Space-filling model

abundance of Na:Sb = 2:1, the refinement of the structure results in a cube-like appearance of the cluster with the silyloxy oxygen atoms at the vertices [Figure 1 (center)]. Space-filling diagrams of this model illustrate the high apparent symmetry and the compact structure of the molecules [Figure 1 (bottom)].

The bond distances and angles in this disorder model must be taken as symmetry-constrained averages of the true values, especially as far as metal−oxygen distances and metal−oxygen−metal angles are concerned. However, the parameters for the trimethylsilyloxy groups are within the range of standard literature data available, and thus appear to be quite meaningful, largely due to the satisfactory overall quality of the refinement (see caption to Figure 1).

The disorder model obtained for the collective of cluster molecules [Figure 2 (left), with E representing a weighted average of Na and Sb (2:1)] must be resolved for the individual molecules in terms of a cis or a trans structure [Figure 2 (center, right)]. The crystals may be composed uniformly of either one of these, or of a mixture of both, randomly or following a certain stoichiometric pattern. In order to reach a decision regarding this question, solid-state NMR spectroscopic techniques were employed, which should allow us to distinguish not only between a cis and trans form, but also give a clue as to the relative representation of both forms[13].

The cis and trans form of compound 1 are of idealized point group C_{2v} or D_{4h} symmetry, respectively. These point groups render the trimethylsilyloxy groups equivalent for the trans form, but inequivalent for the cis form, with a 4:2:2 distribution for the individual sites [Figure 2 (center, right)].

The ^{29}Si-CPMAS-NMR spectrum of a polycrystalline powder of compound 1 at ambient temperature shows three resonances with the intensity ratio 2:1:1 (Figure 3). This ratio is confirmed by the pattern observed in the ^{29}Si-MAS-NMR spectrum with conventional high-power decoupling. This result is a first proof that cluster 1 is present exclusively in the cis form in the crystalline modification investigated in this study.

The ^{13}C-MAS-NMR spectrum provides further evidence for the proposed cis structure. Although the signal dispersion is much poorer (Figure 4), three resonance lines of the relative intensity 2:1:1 can again be detected, as also confirmed by a cross-polarization experiment. No further splitting of the lines is observed, which indicates quasi-free rotation of the trimethylsilyl groups about the Si−O axes in the crystal, rendering the three methyl groups at each Me₃Si unit equivalent. There is ample precedent for such rotational freedom in solid phases containing trimethylsilyl groups[14].

Quadrupolar coupling of ^{29}Si or ^{13}C to ^{23}Na (J = 3/2) and $^{121/123}$Sb (J = 5/2 and 7/2) does not seem to be responsible for the splitting observed, since much more complicated signal patterns are to be expected for multi-metal interaction with nuclei of high spin[15,16].

On the basis of these results we assign to compound 1 the cis structure represented by Figure 2 (center). This is the first example of an anionic antimony(III) oxide silyloxide cluster. Given the large variety of antimony(III) complexes with oxide, hydroxide, or halide ligands already reported in
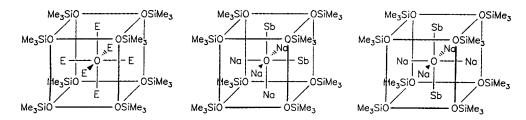
Figure 2. Schematic representations of the disordered structure (left), the *cis* (center) and the *trans* structures (right) of compound **1**
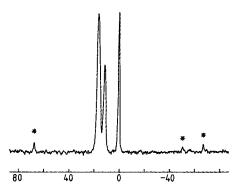

Figure 3. ²⁹Si-CPMAS-NMR spectrum (δ values) of compound **1** (59.63 MHz, 5 ms contact, 10 s recycle time); asterisks denote spinning sidebands
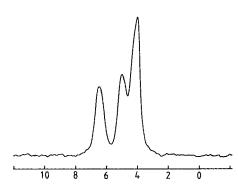

Figure 4. ¹³C-CPMAS-NMR spectrum (δ values) of compound **1** (75.47 MHz, 5 ms contact, 4 s recycle time)

the literature, a broader scope can also be envisaged in the future for the corresponding silyloxide system.

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Experimental

All experiments were carried out in dry and purified N_2. Glassware was dried and filled with N_2, and solvents were dried and saturated with N_2. The rotors for solide-state NMR measurements were packed in a glove-box and dry N_2 was used as a bearing and drive gas. Elemental analyses were performed in the Microanalytical Laboratory of this Institute. — MS: MAT 90 and MAT 311 (Varian). NMR: MSL 300P (Bruker). X-ray analysis: CAD4 four-circle diffractometer (Enraf Nonius). — Sodium trimethylsilyloxide is commercially available. Tris(trimethylsilyloxy)antimony(III) was prepared according to published methods[5,8].

Tetrasodium Diantimony(III) Oxide Octakis(trimethylsilyloxide) (**1**): Sodium trimethylsilyloxide (1.38 g, 12.3 mmol) is dissolved in hexane (12 ml) and cooled to −195°C to form a glass, and a layer of a liquid solution of tris(trimethylsilyloxy)antimony(III) (2.40 g, 6.16 mmol) in hexane (5 ml) is allowed to develop on top of this frozen phase. The mixture is slowly warmed to room temperature. A fine white powder and larger pale-brown crystals precipitate, from which the mother liquor is decanted after 4 d. Careful separation of the macrocrystalline fraction, which is washed with hexane and dried in a vacuum, gives 1.12 g (34%) of the product, which decomposes upon heating at 120°C. This crude product, which is insoluble in benzene, toluene, hexane, and diethyl ether, cannot be recrystallized. Treatment with dichloromethane, chloroform, tetrahydrofuran, or diglyme leads to noticeable decomposition. — MS (CI; neg.): m/z (%) = 989 (5) [M − SiMe₃]; 900 (13) [M − Me₃SiOSiMe₃]; 649 (83) [Na₄Sb₂O₄(OSiMe₃)₃]; 537 (100) [Na₃Sb₂O₃(OSiMe₃)₂].

$C_{24}H_{72}Na_4O_9Sb_2Si_8$ (1064.97)
Ber. C 27.07 H 6.81 Sb 22.86 Na 8.63 Si 21.10
Gef. C 26.83 H 6.78 Sb 23.02 Na 8.58 Si 20.97

Solid-State NMR Studies

²⁹Si-CPMAS NMR [59.63 MHz; rotational frequency 4 kHz; Hartmann-Hahn optimization and external shift standard: tetrakis(trimethylsilyl)silane test sample[13]; ²⁹Si pulse length 5 μs; recycle time 10 s, 250 pulses, contact pulse length 5 ms]: δ = −9.8 [s, 2 Si, {Na₃}OSiMe₃], 1.4 [s, 2 Si, {NaSb₂}OSiMe₃], 6.3 [s, 4 Si, {Na₂Sb}OSiMe₃]. The assignments of the first two signals may be reversed.

¹³C-CPMAS NMR [75.47 MHz; rotational frequency 4 kHz; Hartmann-Hahn optimization and external shift standard: adamantane test sample[13]; ¹³C pulse length 4 μs, recycle time 4 s, 300 pulses, contact pulse 5 ms]: δ = 3.39 [s, 12 C, {Na₂Sb}OSi(CH₃)₃], 4.33 [s, 6 C, {NaSb₂}OSi(CH₃)₃], 5.77 [s, 6 C, {Na₃}OSi(CH₃)₃]. The assignment of the last two resonances may be interchanged.

Crystal Structure Analysis: A crystal of the dimensions 0.35 × 0.25 × 0.25 mm was mounted in a capillary at Dry Ice temperature in Ar and investigated on the diffractometer. The compound crystallizes in the rhombohedral space group $R\bar{3}c$ (Nr. 167) with a = 12.896(1), c = 54.488(4) Å, Z = 6, V = 7748 Å³. After checks for higher symmetry, 6136 reflections (2 ≤ Θ ≤ 27°) were measured, followed by Lp and absorption corrections [empirical, Ψ Scans, min/max transmission 0.971/0.999, μ(Mo-$K_α$) = 12.8 cm⁻¹]. Of 1917 independent reflections, 1686 with F_o ≥ $4\sigma(F_o)$ were used for structure solution (SHELXS-86) and refinement (SHELX-76). The heavy-atom positions were refined by using hybrids of scattering curves for antimony (s.o.f. = 0.333) and sodium (s.o.f. = 0.666). In the anisotropic refinement the thermal displacement parameters were also tied up according to this model. A free approach confirmed the relative occupational factors. After anisotropic refinement of all non-hydrogen atoms all hydrogen atoms were included

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for compound 1; $U_{eq} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2 and U_3 are the eigenvalues of the U_{ij} matrix; e.s.d.'s in parentheses

ATOM	X/A	Y/B	Z/C	U(eq.)
Sb/Na	0.05777(4)	0.89884(4)	0.02403(1)	0.033
Si1	0.00000	1.00000	0.07919(2)	0.035
Si2	0.36425(8)	1.12762(8)	0.02675(2)	0.038
O	0.33330	0.66670	0.16670	0.061
O1	0.33330	0.66670	0.11720(6)	0.042
O2	0.4203(2)	0.8971(2)	0.14897(4)	0.045
C1	0.3176(4)	0.5241(3)	0.07588(6)	0.059
C21	0.3423(4)	1.0314(4)	0.12097(8)	0.069
C22	0.4902(4)	1.1320(4)	0.16639(7)	0.069
C23	0.5996(4)	1.0945(4)	0.12113(8)	0.071

with idealized geometry [U_{iso}(fix) = 0.05 Å^2] and with rotational positions of the methyl groups giving maximum coverage of the residual electron density. Refinement for 84 parameters converged at R (R_w) = 0.038 (0.036) with residual electron densities at +0.41/ −0.55 e/Å^3. Supplementary material for the structure determination is available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, by quoting the depository number CSD-57105, the names of the authors and the journal citation.

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