Organometallics 1993, 12, 2208–2212

Synthesis and Derivatives of Pentakis[(trimethylsilyl)oxy]antimony

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Received January 22, 1993

Pentakis[(trimethylsilyl)oxy]antimony(V) [$Sb(OSiMe_3)_5$; **1**] is prepared from $SbCl_5$ and 5 equiv of $NaOSiMe_3$ in benzene or hexane solution. According to mass spectrometric and NMR spectroscopic data, **1** appears to be a monomer. It forms a pyridine adduct pyr·$Sb(OSiMe_3)_5$ (**2**), the crystal structure of which has been determined. The mononuclear complex has octahedrally coordinated antimony atoms. With an additional equivalent of $NaOSiMe_3$, the antimonate complex $Na[Sb(OSiMe_3)_6]$ (**3**) is formed, which crystallizes as a monoglyme adduct $[Na(MeOCH_2CH_2OMe)][Sb(OSiMe_3)_6]$ (**3a**). Partial hydrolysis of **3**, or a direct synthesis using $NaOSiMe_3$ and NaOH as reagents for $SbCl_5$, leads to the crystalline dinuclear complex $Na_2[Sb_2(OH)_2(OSiMe_3)_{10}]$, the structure of which has also been determined. It features two cubes with a common Na_2O_2 face and tetracoordinated sodium and hexacoordinated antimony atoms. The hydroxy groups are in bridgehead positions. NMR data suggest that the dimers dissociate in solution to give octahedral mononuclear complexes with the silyloxy groups in fixed cis and trans positions (4:1) relative to the OH groups.

Introduction

"Heterosiloxanes" containing antimony(V) as a heteroatom center in a siloxane structure are receiving renewed attention due to their interesting properties as covalent siloxide synthons[1] and as precursors for heterosiloxane catalysts or for the deposition of antimony oxides (and mixed oxides) from the vapor phase or from solution.[2–4] For these usages, antimony siloxides are promising alternatives as compared to the corresponding antimony(V) alkoxides, hydroxides, or halides, which are either poorly characterized (OR, OH), or unsuitable (halides) because of the hydrogen halide acid invariably coproduced in hydrolysis or pyrolysis.

Parallel to current studies of the chemistry of heterosiloxanes of antimony(III),[5,6] we have therefore also been engaged recently in investigations of related antimony(V) compounds, thus resuming earlier work carried out in the 1960s.[7–10] Previous studies had focused on alkylantimony(V) siloxides, notably of the types $R'_4SbOSiR_3$ and $R'_3Sb(OSiR_3)_2$. However, species of the type $R'_2Sb(OSiR_3)_3$ and $R'Sb(OSiR_3)_4$ and simple homoleptic silyloxy compounds $Sb(OSiR_3)_5$ have not yet been described in the literature. We report here the preparation of the prototype $Sb[OSi(CH_3)_3]_5$ and its pyridine adduct, which could be structurally characterized, together with the "ate" complex sodium hexakis(trimethylsiloxy)antimonate(V), and its binuclear hydrolysis product of the formula $Na_2[Sb_2(OH)_2\{OSi(CH_3)_3\}_5]$, the crystal structure of which has also been determined.

Experimental Section

All experiments were carried out under dry nitrogen. Glassware was dried and filled with nitrogen, and solvents were purified, dried, degassed, and saturated with nitrogen. For NMR, Jeol JMN-GX 270 and JMN-GX 400 spectrometers were used. For MS, Varian MAT 90 and MAT 311 A spectrometers were used. For IR, a Nicolet 5DX (FT) spectrophotometer was used. All chemicals were commercially available.

Pentakis[(trimethylsilyl)oxy]antimony(V) (1). Antimony pentachloride (1.44 mL, 3.39 g, 11.4 mmol) is dissolved in benzene (200 mL) and treated with a solution of sodium trimethylsilanolate (6.36 g, 56.7 mmol) in benzene (100 mL) at ambient temperature. The mixture is heated for 4 h under reflux conditions to give a colloidal suspension, which is impossible to filter. However, after a freeze/thaw cycle a clear solution can be decanted from the precipitate. The filtrate is concentrated to a volume of 50 mL to give a first precipitate of the byproduct $Na[Sb(OSiMe_3)_6]$ (**3**), which is again filtered off. Compound **1** is obtained from the filtrate through evaporation of the solvent in a vacuum as a colorless oil, yield 3.56 g (55%). The product decomposes slowly at room temperature to give hexamethyldisiloxane, and silyl polyantimonates of unknown stoichiometry are present in the sample (GLC/MS).

^1H NMR (C_6D_6): $\delta = 0.35$ (s). ^{13}C NMR (C_6D_6): $\delta = 3.67$ [$J(Si,C) = 59.7$, $J(C,H) = 118.6$ Hz]. ^{29}Si NMR (C_6D_6): $\delta = 15.74$ [$J(Si,H) = 6.78$ Hz]. MS (CI): $m/z = 566.2$ [M + 1] (100, calcd for ^{121}Sb). No IR spectra were recorded because of the limited stability of the compound. Anal. Calcd for $C_{15}H_{45}O_5SbSi_5$ (567.70): C, 31,74; H, 7.99; Sb, 21.5; Si, 24.74. Found: C, 31.68; H, 7.97; Sb, 21.3; Si, 24.53.

Pentakis[(trimethylsilyl)oxy]antimony(V)–Pyridine (2). A mixture of $SbCl_5$ (1.44 mL, 3.39 g, 11.4 mmol) and hexane (200 mL) is treated at −80 °C with a solution of $NaOSiMe_3$ (6.36 g, 56.7 mmol) in hexane (50 mL). After stirring for 1 h, the reaction mixture is allowed to warm to room temperature. After addition of monoglyme (25 mL) the reaction mixture is refluxed for 6 h in order to complete the precipitation of macrocrystalline NaCl.

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0276-7333/93/2312-2208$04.00/0

After cooling, the supernatant solution is decanted and the precipitate washed with hexane (3 × 100 mL). The solvents are evaporated from the filtrates, and the residue is crystallized from a mixture of hexane and pyridine (1:1) to give colorless, deliquescent crystals, yield 3.39 g (46%).

^{1}H NMR (toluene-d_8): (25 °C) $\delta = 0.05$ (br s); (−10 °C) 0.02 (s, 36H), 0.20 (s, 9H). ^{13}C{^{1}H} NMR: (C_6D_6, 25 °C) $\delta = 3.46$ (br s), 123.7, 140.1, and 147.3 (s, *m*-, *p*-, and *o*-C in Pyr). (Toluene-d_8, −10 °C) 3.43 (s, 3C), 2.70 (s, 12C); ^{29}Si{^{1}H} NMR (C_6D_6, 25 °C): $\delta = 6.85$ (s). IR [C_6D_6 (cm^{-1})]: 2954, ν_{as}Me; 2898, ν_sMe; 1452, δ_{as}SiMe; 1247, ν_sSiMe; 941, νSiOSb, 839, and 839, ρSiMe. MS (CI): $m/z = 566.2$ [1] (100, calcd for ^{121}Sb). Anal. Calcd for $C_{20}H_{50}NO_5SbSi_5$ (646.80): C, 37.14; H, 7.79; N, 2.17; Si, 21.71. Found: C, 36.84; H, 7.75; N, 2.15; Si, 21.53.

Sodium Hexakis[(trimethylsilyl)oxy]antimonate(V) (3). $SbCl_5$ (2.88 mL, 6.78 g, 22.7 mmol) in hexane (400 mL) is treated at −80 °C with a solution of $NaOSiMe_3$ (14.24 g, 135.9 mmol) in hexane (90 mL). The mixture is stirred for 1 h and then allowed to warm to room temperature. Monoglyme (25 mL) is added, and the mixture is refluxed for 4 h and cooled to room temperature. The clear solution is decanted and the precipitate washed with hexane (2 × 100 mL). The filtrate is evaporated to dryness to leave a colorless solid, which crystallizes from hexane on slow cooling to −80 °C as a monoglyme adduct, yield 10.7 g (61%).

^{1}H NMR (C_6D_6): $\delta = 0.46$ (s). ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 4.48$ (s). ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = 27.3$ (s). IR [C_6D_6 (cm^{-1})]: 2956, ν_{as}Me; 2898, ν_sMe; 1439, δ_{as}SiMe; 1250, δ_sSiMe; 994 and 904, νSbOSi, 840 and 752, ρSiMe. MS (CI): $m/z = 679.3$ [M + 1] (1), 663.3 [M − Me] (75, ^{121}Sb). Anal. Calcd for $C_{22}H_{64}NaO_8SbSi_6$ (770.00): C, 34.32; H, 8.38; Na, 3.0; Sb, 15.8; Si, 21.89. Found: C, 34.42; H, 8.32; Na, 3.2; Sb, 16.2; Si, 21.81.

Disodium Dihydroxydecakis[(trimethylsilyl)oxy]diantimonate(V) (4). A suspension of $SbCl_5$ (1.44 mL, 3.39 g, 11.4 mmol) in hexane (200 mL) is treated at −80 °C with a suspension of $NaOSiMe_3$ (6.36 g, 56.7 mmol) and NaOH (0.46 g, 11.4 mmol) in hexane (100 mL). The mixture is stirred for 1 h and then allowed to warm to room temperature. Monoglyme (25 mL) is added, and the mixture is refluxed for 4 h. After cooling to room temperature, the solution is decanted and the precipitate washed with hexane (2 × 100 mL). Evaporation of the solvents from the solutions leaves a colorless residue consisting mainly of 3·monoglyme and 4. Fractional crystallization from lutidine at −10 °C gives 3, while 4 is obtained from the mother liquor after evaporation to dryness and recrystallization from toluene at −30 °C, yield 2.22 g (32%).

^{1}H NMR (C_6D_6): $\delta = 0.45$ (s, 9H), 0.30 (s, 36H). ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 4.20$ (s, 3C), 3.96 (s, 12C). ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = 8.01$ (s, 1Si), 5.35 (s, 4Si). IR [C_6D_6 (cm^{-1})]: 3647, νOH. MS (CI): $m/z = 566.2$ [1] (18, ^{121}Sb). Anal. Calcd for $C_{30}H_{92}Na_2O_{12}Sb_2Si_{10}$ (1215.38): C, 29.65; H, 7.63; Na, 3.7; Sb, 20.0; Si, 23.11. Found: C, 29.31; H, 7.58; Na, 3.9; Sb, 20.3; Si, 22.81.

Crystal Structure Determination. Suitable crystals of 2 (4) were sealed into glass capillaries under argon at dry ice temperature and mounted on a Syntex (CAD4) diffractometer. After a check for higher symmetry 6339 (18917) data were collected and corrected for Lorentz and *Lp* effects. Both structures were solved by direct methods (SHELXS-86) and full matrix refinement (SHELX-76). In both cases refinement was not fully satisfactory due to disorder problems and rather poor crystal quality.

2 crystallizes in the monoclinic space group $P2_1$ with one molecule in the asymmetric unit. The positions of the silicon and oxygen atoms had to be refined isotropically as a split model in two positions (site occupation factor = 0.5) to cope with the common problem of disorder in crystals with octahedral antimony environments. No hydrogen atom positions were found or calculated because of the disorder and the high thermal motion parameters of the pivot carbon atoms. No decision has been made regarding the enantiomorph, since the inverted set of positional data refined identically.

Table I. Crystal and Structure Solution Data for Compounds 2 and 4

	2	4
formula	$C_{20}H_{50}NO_5SbSi_5$	$1.5{\cdot}C_{30}H_{92}Na_2O_{12}Sb_2Si_{10}$
molecular mass	646.805	1215.400
temp (°C)	−50	−45
cryst syst	monoclinic	triclinic
space group	$P2_1$ (4)	$P\bar{1}$ (2)
a (Å)	10.318(1)	10.486(5)
b (Å)	16.838(3)	20.442(4)
c (Å)	11.189(2)	22.088(4)
α (deg)	90	93.46(1)
β (deg)	118.68(1)	93.43(3)
γ (deg)	90	90.90(3)
V (Å^3)	1705.4	4716.7
ρ_{calc} (g cm^{-3})	1.259	1.284
Z	2	2
F(000) (e)	676	1893
μ(Mo Kα) (cm^{-1})	10.0	11.0
radiation ($\lambda = 0.71069$ Å, graphite monochromator)	Mo Kα	Mo Kα
diffractometer	Syntex $P2_1$	CAD4
scan	ω	θ–θ
scan width (θ) (deg)	2–25	2–26
hkl range	±12, ±20, +13	±12, ±25, +27
measured reflections	6339	18 917
unique reflections	5975	18 416
R_{int}	0.022	0.030
obsd reflections	5355	5852
$F_o \geq$	$4\sigma(F_o)$	$6\sigma(F_o)$
refined parameters	284	430
weighting scheme	$w = l/\sigma^2(F_o)$	
weighting parameter *l*	1.5683	1.0
R	0.046	0.068
R_w	0.055	0.074
ρ_{fin} (max/min) (e Å^{-3})	+1.33/−1.05	+1.11/−1.24

4 crystallizes in the triclinic space group $P\bar{1}$ with one and a half, respectively, of two virtually identical molecules in the asymmetric unit. The half molecule is positioned such that it relates to a center of inversion. The antimony and all but two silicon atoms were refined anisotropically and the remainder atoms isotropically due to severe thermal motion without detectable disorder. Further details of the structure determination and refinement are given in Table I.

Results

Pentakis[(trimethylsilyl)oxy]antimony(V) (1) and Its Pyridine Adduct (2). Treatment of antimony(V) pentachloride with 5 equiv of sodium trimethylsilanolate in benzene at ambient temperature yields pentakis[(trimethylsilyl)oxy]antimony(V) (1) together with small amounts of sodium hexakis[(trimethylsilyl)oxy]antimonate(V) (3). Compound 3 crystallizes from the benzene (or hexane) solutions, while 1 is obtained as a colorless viscous liquid upon careful evaporation of the solvent. Attempts to distill compound 1 lead to decomposition with hexamethyldisiloxane as the only volatile material. The residue consists of amorphous poly(silyloxy)antimonates(V) of unknown composition.

$$SbCl_5 + 5NaOSiMe_3 \rightarrow 5NaCl + \underset{1}{Sb(OSiMe_3)_5} \qquad (1)$$

$$1 + Pyr \rightarrow \underset{2}{Pyr{\cdot}Sb(OSiMe_3)_5} \qquad (2)$$

Compound 1 is soluble in nonpolar solvents, but is susceptible to hydrolysis. It has been characterized by a complete elemental analysis and by its mass spectrum, which shows the compound to be a monomer. NMR

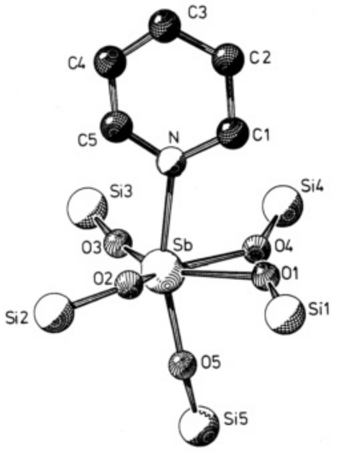

Figure 1. Molecular structure of $(Me_3SiO)_5Sb{\cdot}NC_5H_5$ (**2**) with atomic numbering. (Methyl groups are omitted, and only one position of the disordered group O4–Si4 is shown.) Selected bond distances (Å) and angles (deg): Sb–O1 2.053(4), Sb–O2 1.864(3), Sb–O3 1.916(5), Sb–O4 2.034(5), Sb–O5 1.917(3), Sb–N 2.258(3); O1–Sb–O2 89.8(2), O1–Sb–N 85.4(2), O1–Sb–O3 157.2(2), O1–Sb–O4 59.0(2) [O1–Sb–O41 81.7(2)], O1–Sb–O5 92.7(2).

spectra (of benzene or toluene solutions) give only singlet resonances (for ^{1}H, ^{13}C, and ^{29}Si), indicating the equivalence of the five (trimethylsilyl)oxy groups in solution even at low temperature (−80 °C). Thus there is no evidence for a dimerization of the compound, which would lead to terminal and bridging ligands in the oligomer, as, e.g., observed for penta(ethoxy)antimony[11,12] or for the related niobium and tantalum siloxides.[13,14]

If the preparation of compound **1** is carried out in the presence of pyridine, or if pyridine is added to the compound prepared as described above, a crystalline monoadduct (**2**) is obtained. This adduct has also been characterized by its elemental analysis and NMR spectra. In the latter, a splitting of the (trimethylsilyl)oxy resonance into two signals of intensity ratios 1:4 is observed (^{1}H, ^{13}C, ^{29}Si). These patterns are easily explained by a pseudo-octahedral structure where the hexacoordinate antimony atoms carry a pyridine donor with one *trans*- and four *cis*-[(trimethylsilyl)oxy] ligands. In the mass spectrum (chemical ionization) the cation of **1** is detected as the parent ion, indicating dissociation of the pyridine donor in the low-pressure vapor phase. In separate experiments it could be demonstrated that compound **2** in fact slowly loses pyridine in a vacuum.

The structure proposed for **2** could be confirmed by a single-crystal X-ray diffraction study. Although the results are crystallographically not fully satisfactory owing to disorder of the silyloxy groups, the octahedral environment of the antimony atom and other basic features of the structure are well established (Figure 1, Experimental Section). It is not appropriate, however, to discuss details of bond lengths and angles of this molecule at this stage.

Sodium Hexakis[(trimethylsilyl)oxy]antimonate(V) (3) and Disodium Dihydroxydecakis[(trimethylsilyl)oxy]diantimonate(V) (4). As already indicated (above), in the reaction of $SbCl_5$ with 5 eqiv of $NaOSiMe_3$ the salt-like "ate" complex **3** is also formed. This compound is the main product if 6 equiv of the silanolate are used. With monoglyme added to the hexane solvent, the product is an adduct $[Na(MeOCH_2CH_2OMe)]^+[Sb(OSiMe_3)_6]^-$. This solvate is obtained as a colorless solid,

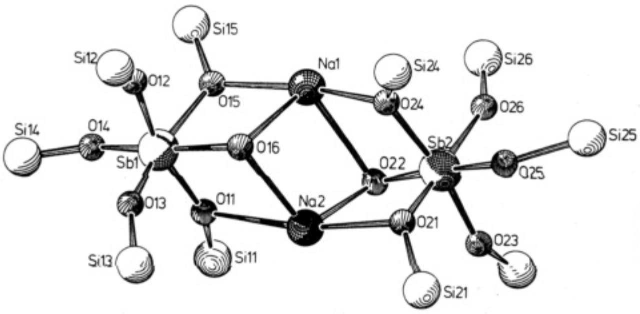

Figure 2. Molecular structure of $Na_2[Sb_2(OH)_2(OSiMe_3)_{10}]$ (**4**) with atomic numbering. (All methyl groups and the two hydrogen atoms at O16 and O22 are omitted, and only one of the two independent molecules is shown.) Selected bond distances (Å) and angles (deg): Sb1–O11 1.91(3), Sb1–O12 1.96(2), Sb1–O13 1.90(2), Sb1–O14 1.91(1), Sb1–O15 2.07(1), Sb1–O16 1.94(2); Sb2–O21 1.89(2), Sb2–O22 1.95(2), Sb2–O23 1.98(2), Sb2–O24 2.09(1), Sb2–O25 1.83(2), Sb2–O26 2.01(1); Na1–O15 2.23(2), Na1–O16 2.56(3), Na1–O22 2.45(3), Na1–O24 2.13(2); Na2–O11 2.29(3), Na2–O16 2.26(3), Na2–O21 2.58(2), Na2–O22 2.55(2); O11–Sb1–O12 172.7(9), O11–Sb1–O13 86.3(9), O11–Sb1–O14 87.8(8), O11–SB1–O15 84.5(8), O11–Sb1–O16 86(1); O21–Sb2–O22 87.8(8), O21–Sb2–O23 94.7(8), O21–Sb2–O24 87.0(8), O21–Sb2–O25 99.3(7), O21–Sb2–O26 163.0(8).

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 2[a]

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å^2
SB1	−0.07493(3)	0.01828	−0.81801(3)	0.032
Si1	0.1593(3)	−1.1363(2)	0.3941(3)	0.040
Si2	0.1641(3)	−0.8626(2)	0.3914(3)	0.049
Di3	−0.3063(4)	−0.8842(3)	−0.0636(4)	0.041[b]
Si31	−0.3085(4)	−0.8442(3)	0.0233(4)	0.044
Si4	−0.3012(4)	−1.1157(3)	−0.0628(4)	0.042[b]
Si41	−0.3076(4)	−1.1552(3)	0.0125(4)	0.045[b]
Si5	−0.2825(3)	−1.0176(2)	0.3395(3)	0.042[b]
Si51	−0.2844(4)	−0.9606(2)	0.3359(3)	0.039[b]
O1	0.0281(4)	−1.1076(3)	0.2500(4)	0.042
O2	0.0983(4)	−0.9484(3)	0.3042(3)	0.043
O3	−0.2094(5)	−0.9246(4)	0.0545(4)	0.065
O4	−0.1609(5)	−1.0911(3)	0.0940(4)	0.016[b]
O41	−0.2325(5)	−1.0703(4)	0.0376(5)	0.031[b]
O5	−0.1583(3)	−1.0025(5)	0.3025(3)	0.042
N	0.0337(3)	−0.9988(5)	0.0485(3)	0.034
C1	0.0575(5)	−1.0726(4)	0.0099(5)	0.054
C2	0.1484(4)	−0.9946(5)	−0.1295(4)	0.047
C3	0.1117(6)	−1.0687(4)	−0.0910(5)	0.064
C4	0.1275(5)	−0.9296(4)	−0.0785(5)	0.051
C5	0.0693(5)	−0.9351(4)	0.0040(5)	0.041
C11	0.1534(6)	−1.1043(5)	0.5572(5)	0.084
C12	0.3577(5)	−1.1405(4)	0.4435(5)	0.067
C13	0.1469(6)	−1.2549(4)	0.3782(5)	0.071
C21	0.1400(5)	−0.8760(4)	0.5428(5)	0.056
C22	0.3484(6)	−0.8861(5)	0.4050(6)	0.105
C23	0.0633(6)	−0.7763(4)	0.2997(5)	0.071
C31	−0.2397(6)	−0.7778(4)	−0.0675(5)	0.067
C32	−0.4899(5)	−0.9050(4)	−0.0780(5)	0.062
C33	−0.2845(5)	−0.7999(4)	0.1838(5)	0.064
C41	−0.2627(6)	−1.2307(4)	−0.0607(6)	0.080
C42	−0.5123(5)	−1.1414(4)	−0.1070(5)	0.065
C43	−0.2910(5)	−1.0676(4)	−0.2057(5)	0.061
C51	−0.2243(5)	−1.0056(6)	0.5171(4)	0.067
C52	−0.4677(5)	−0.9916(6)	0.2255(5)	0.078
C53	−0.2951(5)	−0.8616(5)	0.3259(5)	0.080

[a] $U(eq) = (U_1U_2U_3)^{1/3}$, where U_1, U_2, and U_3 are the eigenvalues of the U_{ij} matrix; esd's are given in parentheses. [b] Refined isotropically by using a split model.

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Table III. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 4[a]

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å²	atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å²
Sb1	0.3612(2)	0.2417(1)	0.0570(2)	0.041	C121	0.016(2)	0.335(1)	0.007(1)	0.077[b]
Sb2	0.3065(2)	0.4239(1)	0.2806(2)	0.035	C122	0.066(2)	0.282(1)	–0.114(1)	0.080[b]
Sb3	0.0243(2)	0.90726(9)	0.3872(2)	0.039	C123	0.242(2)	0.393(1)	–0.063(1)	0.070[b]
Na1	0.302(1)	0.3931(8)	0.1277(8)	0.062	C131	0.023(2)	0.138(1)	0.076(1)	0.066[b]
Na2	0.3645(9)	0.2691(4)	0.2036(8)	0.043	C132	0.180(2)	0.024(2)	0.073(2)	0.144[b]
Na3	0.043(1)	0.9511(4)	0.5422(7)	0.038	C133	0.054(2)	0.126(1)	–0.040(1)	0.097[b]
Si11	0.549(1)	0.1563(6)	0.1476(8)	0.082	C141	0.713(2)	0.200(1)	–0.072(1)	0.071[b]
Si12	0.1614(9)	0.3176(6)	–0.0489(7)	0.072	C142	0.448(2)	0.239(1)	–0.130(1)	0.091[b]
Si13	0.1621(6)	0.1094(3)	0.0313(5)	0.030	C143	0.472(2)	0.099(1)	–0.085(1)	0.080[b]
Si14	0.5342(6)	0.1890(4)	–0.0698(3)	0.054	C151	0.564(2)	0.448(1)	0.071(1)	0.059[b]
Si15	0.5824(9)	0.3618(7)	0.0593(9)	0.083	C152	0.614(2)	0.370(1)	–0.022(1)	0.058[b]
Si21	0.0983(9)	0.3000(5)	0.2733(6)	0.058	C153	0.710(2)	0.322(1)	0.088(1)	0.064[b]
Si23	0.4987(9)	0.3431(5)	0.3686(4)	0.048	C211	0.034(2)	0.327(2)	0.359(2)	0.121[b]
Si24	0.1347(8)	0.5172(4)	0.1784(7)	0.045	C212	0.088(2)	0.211(1)	0.238(1)	0.084[b]
Si25	0.1576(9)	0.5002(6)	0.3877(5)	0.037	C213	–0.030(2)	0.343(1)	0.206(1)	0.102[b]
Si26	0.5763(7)	0.5244(4)	0.2937(4)	0.063	C231	0.490(2)	0.253(1)	0.327(1)	0.094[b]
Si31	0.2388(8)	1.0338(5)	0.3850(6)	0.057	C232	0.626(2)	0.364(2)	0.428(2)	0.200[c]
Si32	0.192(1)	0.8202(6)	0.4839(6)	0.057	C233	0.669(2)	0.347(2)	0.318(2)	0.200[c]
Si33	–0.154(1)	0.9951(7)	0.2829(5)	0.046	C241	–0.010(2)	0.535(1)	0.214(1)	0.087[b]
Si34	–0.176(1)	0.7771(9)	0.364(1)	0.162[b]	C242	0.267(2)	0.591(1)	0.190(1)	0.064[b]
Si35	0.166(1)	0.8270(9)	0.278(1)	0.160[b]	C243	0.032(2)	0.478(2)	0.109(2)	0.173[b]
O11	0.471(2)	0.222(1)	0.125(1)	0.082[b]	C251	–0.045(2)	0.493(1)	0.396(2)	0.108[b]
O12	0.245(1)	0.2731(7)	–0.0073(7)	0.035[b]	C252	0.247(2)	0.479(1)	0.454(1)	0.090[b]
O13	0.298(1)	0.1543(9)	0.057(1)	0.069[b]	C253	0.172(2)	0.581(2)	0.390(2)	0.133[b]
O14	0.495(1)	0.2157(6)	0.0065(7)	0.026[b]	C261	0.540(2)	0.567(1)	0.383(1)	0.077[b]
O15	0.438(1)	0.3354(7)	0.0731(8)	0.035[b]	C262	0.688(2)	0.460(1)	0.270(1)	0.074[b]
O16	0.242(1)	0.271(1)	0.116(1)	0.064[b]	C263	0.610(2)	0.592(2)	0.250(2)	0.137[b]
O21	0.216(1)	0.3436(8)	0.265(1)	0.059[b]	C311	0.182(2)	1.128(1)	0.419(1)	0.050[b]
O22	0.429(1)	0.3897(8)	0.224(1)	0.040[b]	C312	0.361(2)	1.008(1)	0.441(1)	0.067[b]
O23	0.406(1)	0.3955(9)	0.3535(9)	0.058[b]	C313	0.255(2)	1.050(1)	0.301(2)	0.099[b]
O24	0.222(1)	0.4522(7)	0.1982(7)	0.040[b]	D321	0.292(2)	0.775(1)	0.424(1)	0.083[b]
C25	0.191(1)	0.4690(8)	0.3250(9)	0.061[b]	C322	0.100(2)	0.756(2)	0.508(2)	0.122[b]
O26	0.427(1)	0.5006(6)	0.2743(6)	0.039[b]	C323	0.366(2)	0.850(1)	0.522(1)	0.053[b]
O31	0.090(1)	0.9967(6)	0.3918(6)	0.024[b]	C331	–0.331(2)	0.986(2)	0.303(2)	0.165[b]
C32	0.136(1)	0.8864(7)	0.4575(8)	0.025[b]	C332	–0.105(2)	1.073(1)	0.305(1)	0.100[b]
O33	–0.090(1)	0.9208(7)	0.3188(8)	0.046[b]	C333	0.204(2)	1.038(2)	0.796(2)	0.136[b]
O34	–0.048(1)	0.8203(7)	0.3776(7)	0.045[b]	C341	–0.241(2)	0.792(1)	0.278(1)	0.082[b]
O35	0.168(1)	0.8892(9)	0.3284(9)	0.062[b]	C342	–0.314(2)	0.829(2)	0.406(2)	0.192[b]
O36	–0.093(1)	0.9582(6)	0.4507(7)	0.030[b]	C343	–0.132(2)	0.688(1)	0.373(1)	0.084[b]
C111	0.589(2)	0.094(1)	0.081(1)	0.088[b]	C351	–0.109(2)	1.120(2)	0.795(2)	0.133[b]
C112	0.551(2)	0.167(1)	0.240(1)	0.055[b]	C352	–0.082(2)	1.263(1)	0.711(1)	0.086[b]
C113	0.438(2)	0.116(1)	0.202(1)	0.073[b]	C353	0.340(2)	0.821(1)	0.268(2)	0.117[b]

[a] $U(\mathrm{eq}) = (U_1U_2U_3)^{1/3}$, where U_1, U_2, and U_3 are the eigenvalues of the U_{ij} matrix; esd's are given in parentheses. [b] Refined isotropically. [c] Refined with fixed thermal motion parameter.

which is soluble in polar organic solvents, but rapidly hydrolyzed by water or alcohols. The compound is identified by its elemental analysis and by its mass spectrum (CI) with a peak at $m/z = 679.3$ which is assigned to the solvent-free ion pair. The ^{1}H, ^{13}C, and ^{29}Si singlet signals in the NMR spectra are temperature-independent (+20 to −80 °C). This provides evidence for a regular octahedral structure of the anion in solution. Until now, no single crystal free of disorder could be grown, but X-ray diffraction data of a disordered crystal gave a preliminary solution compatible with the octahedral structure proposed on the basis of the spectroscopic data (Experimental Section).

$$\mathrm{SbCl_5 + 6NaOSiMe_3 \rightarrow 5NaCl + \underset{\mathbf{3}}{Na^+[Sb(OSiMe_3)_6]^-}} \quad (3)$$

$$\mathrm{\mathbf{3} + MeOCH_2CH_2OMe \rightarrow \underset{\mathbf{3a}}{[(MeOCH_2CH_2OMe)Na]^+[Sb(OSiMe_3)_6]^-}} \quad (4)$$

During the experiments it was noted that partially hydrolyzed samples of **3** gave well-developed crystals of a compound with one trimethylsilyl group less than required by the idealized stoichiometry. To verify this observation, the stoichiometry of the synthesis was changed accordingly, replacing 1 equiv of $NaOSiMe_3$ by NaOH:

$$\mathrm{2SbCl_5 + 10NaOSiMe_3 + 2NaOH \rightarrow 10NaCl + \underset{\mathbf{4}}{Na_2[Sb_2(OH)_2(OSiMe_3)_{10}]}} \quad (5)$$

Compound **4** shows a slightly higher solubility in organic solvents than **3** and can be separated from this byproduct in a series of careful crystallization steps. It is quite stable and undergoes hydrolysis only slowly. In its ^{1}H, ^{13}C, and ^{29}Si NMR spectra the signals are split into two singlets in the intensity ratio 4:1, indicating a structure with inequivalent bonding sites for the silanolate ligands.

Details of this structure could be determined by single-crystal X-ray diffraction. Crystals (from toluene at −30 °C) show two crystallographically independent molecular units, one of which has a crystallographic center of inversion. The unit cell thus contains 1.5 (dinuclear) units with very similar geometrical parameters. The structure of the dimers is based on face-sharing cubes, with two sodium atoms and two (hydroxy) oxygen atoms at the corners of the common face. The antimony atoms are in a distorted octahedral environment of nearest oxygen neighbors. The coordination sites of the silanolate groups are inequivalent (ratio 2:2:1). Referring to the NMR data, it thus appears plausible that the dimers are at least partially dissociated in solution into (solvated) monomers with one *trans*- and four *cis*-$OSiMe_3$ ligands relative to the OH group. However, many other mechanisms can also be proposed for the site equilibration of the silyloxy groups of 4 in solution. In the crystal, the Sb–O and Si–O distances are in the range already reported for related compounds.[15,16] Selected data are given in the caption to Figure 2. Other details are summarized in the Experimental Section and in Tables II and III or have been deposited.

Inspection of structure 4 shows that a similar dimerization is probably not favored for the symmetrical hexakis[(trimethylsilyl)oxy]antimonate (3) with its six bulky substituents. In the absence of an auxiliary chelating ligand (like monoglyme in **3a**), the structure is more saltlike, and the solubility is low in nonpolar solvents.

Acknowledgment. This work was supported by Deutsche Forschungsgemeinschaft (Leibniz-Programm) and by Fonds der Chemischen Industrie. The authors are grateful to Wacker-Chemie, Burghausen, for the donation of chemicals, to Mr. J. Riede for establishing the X-ray data sets, and to Prof. F. R. Kreissl for mass spectra.

Supplementary Material Available: Tables of atomic coordinates, thermal displacement parameters, and bond distances and angles (23 pages). Ordering information is given on any current masthead page. Details of the X-ray structure determinations have been deposited at Fachinformationszentrum Karlsruhe GmbH, D-7514 Eggenstein-Leopoldshafen, Germany, and may be obtained on quoting the names of the authors, the journal citation, and the code number CSD-57312.

OM930040U

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