Synthesis and Structure of Sodium Phenylsiloxanolate

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Two different synthetic routes for the formation of sodium phenylsiloxanolate (SPS) have been developed: (i) the cleavage of oligo(phenylsilsesquioxane), OPSSO, by NaOH in *n*-butyl alcohol and (ii) the reaction of phenyltri-*n*-butoxysilane, $PhSi(n\text{-}BuO)_3$, and NaOH in *n*-butyl alcohol in the presence of water. From both reactions, (i) and (ii), crystalline *sym-cis*-$\{(Na^+)_4[PhSi(O)O^-]_4\}\cdot 8n\text{-}BuOH$ (**A**) was the product isolated and characterized by X-ray diffraction. Reaction of SPS with Me_3SiCl resulted in the formation of the corresponding *sym-cis*-tetraphenyltetrakis(trimethylsiloxy)cyclotetrasiloxane, $[PhSi(O)OSiMe_3]_4$. Under anhydrous conditions, $PhSi(n\text{-}BuO)_3$ and NaOH reacted to give sodium phenyldi-*n*-butoxysilanolate, $PhSi(ONa)(n\text{-}BuO)_2$. Subsequent treatment with Me_3SiCl led to the formation of phenyl(trimethylsiloxy)di-*n*-butoxysilane, $PhSi(n\text{-}BuO)_2(OSiMe_3)$.

Introduction

In earlier work a series of cagelike metallasiloxanes was synthesized by an exchange reaction of sodium phenylsiloxanolate with corresponding metal chlorides.[1] These compounds are based on one or two stereoregular macrocycles $[PhSi(O)O^-]_n$ ($n = 6, 8, 12$), which surround up to six transition-metal atoms to form a cagelike structure. Notably, depending on the transition-metal chloride used, large 12-, 16-, and 24-membered siloxane rings have been generated with high selectivity. Such selectivity had not been observed before in traditional siloxane polymer chemistry[2] and should be caused by a directive effect of the transition-metal atoms on a silicon−oxygen-containing intermediate that is able to be organized around the metal center. A determination of the structure of this building block might be the key to understand the mechanism for the formation of the cyclics and the cagelike metallasiloxanes. In this paper we report the molecular structure of sodium phenylsiloxanolate, prepared by two independent synthetic routes. The structure was determined by X-ray single-crystal analysis and was confirmed by its subsequent reaction with Me_3SiCl.

Results and Discussion

Various suggestions have been made to describe the structure of sodium phenylsiloxanolate (SPS) in the solid state. On the basis of elemental analysis data[3] SPS, synthesized by alkaline cleavage of oligo(phenylsilsesquioxane) (OPSSO) in water−ethanol solution, was suggested to be a sodium monosilanolate hydrate, $[PhSi(OH)_2ONa]\cdot xH_2O$, with a variable water content. Furthermore, cryoscopic as well as analytical data indicated SPS to have the formula $Ph_4Si_4O_8Na_4\cdot 8H_2O$.[4] According to X-ray single-crystal analysis,[5] a single crystal of SPS isolated from the reaction mass obtained by alkaline cleavage of OPSSO in aqueous ethanol was identified as trisodium *sym-cis*-triphenylcyclotrisiloxanolate octahydrate, $\{(Na^+)_3[PhSi(O)O^-]_3\}\cdot 8H_2O$. Alkaline cleavage of OPSSO in boiling toluene and in the presence of DMSO yields SPS, which was reported to be a mixture of oligomeric products.[6]

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(3) Andrianov, A. A.; Zhdanov, A. A. *Dokl. Akad. Nauk SSSR* **1957**, *114*, 1005−1007.

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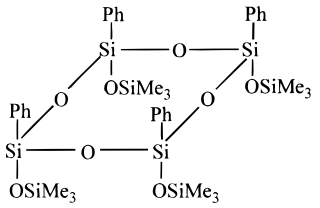
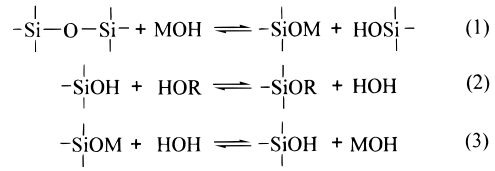


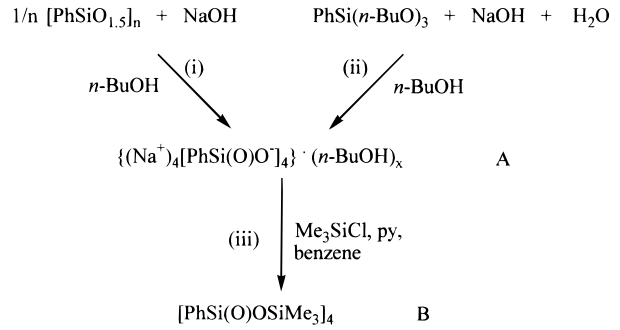
Figure 1. *sym-cis*-Tetraphenyltetrakis(trimethylsiloxy)-cyclotetrasiloxane (**B**).

Scheme 1[a]



[a] Legend: (1) cleavage of OPSSO by alkali-metal hydroxide; (2) etherification of silanol units by alcohol solvent and liberation of reaction water; (3) hydrolysis reaction of metal silanolate units with reaction water.

Scheme 2



The structure of SPS in solution still remains an open question. SPS prepared in situ by the alkaline cleavage of OPSSO in alcohol solution (usually *n*-BuOH) is the main reagent for the synthesis of cagelike metallasiloxanes. It seems likely that a silicon−oxygen-containing intermediate undergoes oligocyclization directed by the transition-metal cation, thus resulting in a selective formation of different sizes of cyclic siloxanes. This intermediate was assumed to be the partially deprotonated silanediol or -triol Ph(OR)Si(OH)ONa (R = alkyl, H)[7] formed in at least three coupled equilibrium reactions (Scheme 1; eqs 1−3).

To obtain a deeper insight into the "nature" and origin of SPS, sodium phenylsiloxanolate was prepared by two different routes: (i) the alkaline cleavage of OPSSO with NaOH in *n*-butyl alcohol and (ii) the reaction of $PhSi(n\text{-}BuO)_3$ with NaOH in *n*-butyl alcohol in the presence of water (Scheme 2). From reactions i and ii, an identical white crystalline solid, compound **A**, was obtained upon cooling of the reaction solutions to room temperature. Treatment of **A** with Me_3SiCl gave the new crystalline compound **B**. Analytical and spectroscopic data show that in both reaction routes the identical product **B** resulted (Figure 1), which was identified as *sym-cis*-tetraphenyltetrakis(trimethylsiloxy)-

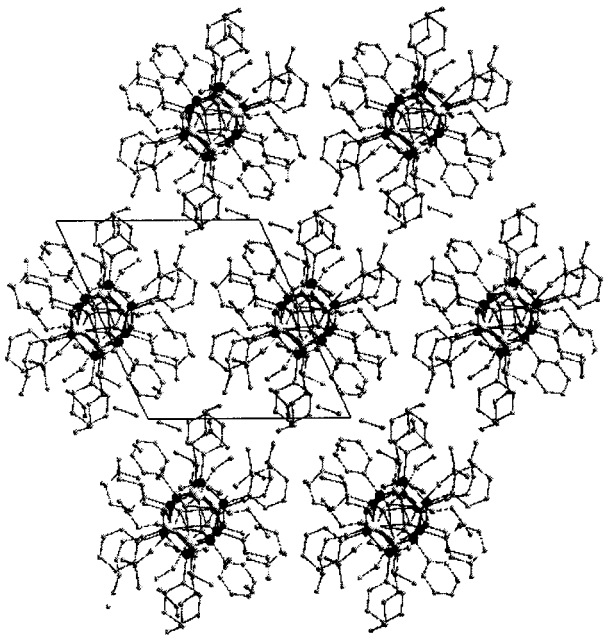
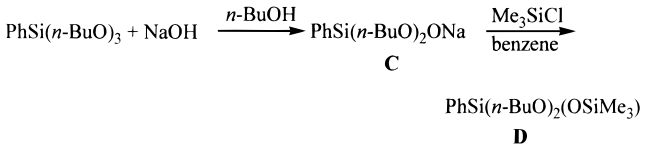


Figure 2. DIAMOND[11] plot of the crystal structure of $\{(Na^+)_4[PhSi(O)O^-]_4\}\cdot 8n\text{-BuOH}$ (**A**) viewed along [001].

Scheme 3



cyclotetrasiloxane. Compound **B** was characterized by NMR spectroscopy and cryoscopy in benzene. Spectroscopic and analytical data were in full agreement with the data reported by Makarova[8] and Feher,[9] both of whom obtained **B** from the reaction of *cis*-$[PhSi(O)OH]_4$ and Me_3SiCl. In contrast to reaction ii described in Scheme 2, phenyltri-*n*-butoxysilane and NaOH reacted under anhydrous conditions in *n*-butyl alcohol solution to give a colorless, crystalline intermediate, presumably the sodium siloxanolate **C**, which upon reaction with Me_3SiCl gave phenyl(trimethylsiloxy)di-*n*-butoxysilane (**D**) as the main reaction product (Scheme 3). A suitable single crystal of the solid compound **A** was subjected to X-ray structure analysis and identified to be $\{(Na^+)_4[PhSi(O)O^-]_4\}\cdot 8n\text{-BuOH}$ (Figure 2). In the solid state, the siloxanolate anions and the solvated cations in **A** build up chains running along [001] through the crystal. The chains with a relatively polar Si/O and Na/O backbone (Figure 3), enveloped by nonpolar phenyl substituents at the silicon atoms and butyl alcohol ligands at the sodium cations, respectively, adopt a pseudo hexagonal rod packing (Figure 2). This dense rod packing has no further cavities for additional solvent molecules but allows positional disorder of the phenyl rings on the silicon atoms and the *n*-butyl chains of the *n*-butyl alcohol molecules at room temperature. This disorder was frozen on cooling to 190 K. The absence of ionic interactions between the chains explains the observed decomposition of the crystals in which the

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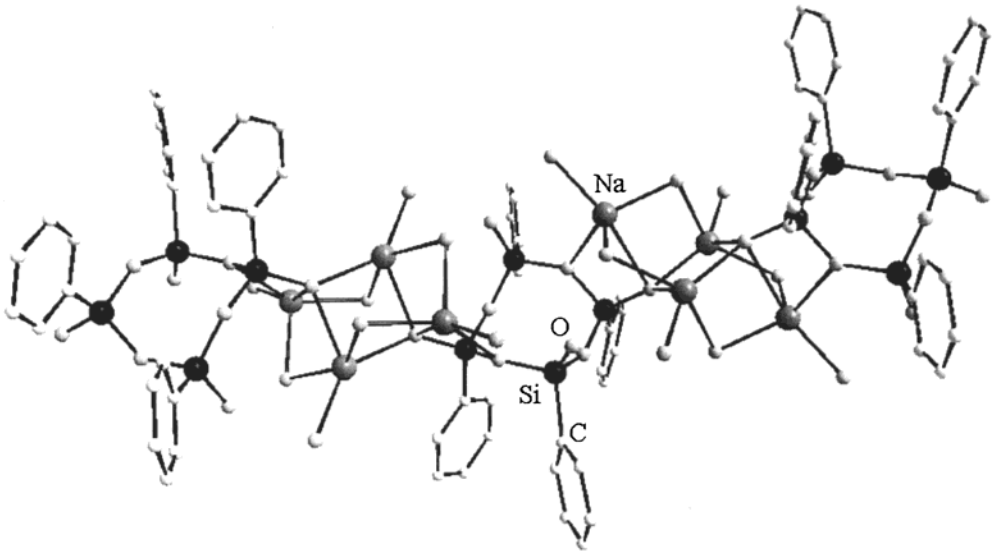

Figure 3. Chain structure of **A** with alternating Na−O step units and cyclotetrasiloxanolate rings. *n*-Butyl chains were omitted for clarity. The chains run along the *c* axis of the unit cell.

solvent molecules are lost, since *n*-butyl alcohol at the crystal surface is only weakly bonded to the sodium cations. A system of weak hydrogen bridges between the terminal siloxanolate oxygen atoms O6 and O8 and butyl alcohol molecules can be deduced from a set of eight oxygen−oxygen contacts showing distances from 2.598(5) to 2.636(5) Å. Since none of the hydrogen atoms were located on a difference Fourier map, all were calculated in idealized positions to gain a correct scaling. On the basis of the achieved level of precision of the structure determination, a detailed discussion of this structural feature is omitted.

The molecular structure of **A** (Figure 4) is best described as the tetrasodium salt of the tetraphenylcyclotetrasiloxanolate tetraanion containing two diametrically connected, crystallographically independent, edge-sharing Na_2O_8 units of pentacoordinate sodium atoms and *n*-butyl alcohol ligands. These units each have one terminal and one bridging oxygen atom of the siloxanolate ring in common (Figure 3), leaving the remaining two bridging and two terminal oxygen atoms of the cycle without coordinative contacts. All other oxygen atoms of the Na_2O_8 units, except for the symmetrically generated $O5^2$ and $O7^1$, stem from *n*-butyl alcohol solvent ligands. Crystal data are given in Table 1; selected bond distances and angles are listed in the caption of Figure 4.

The tetrasiloxanolate ring moiety adopts a slightly distorted boat conformation. With respect to the mean plane of the Si_4O_4 ring, all phenyl substituents point to the same side of that plane, and consequently, the anionic oxygen atoms point in the opposite direction. The chain structure is generated by centers of inversion of the space group $P\bar{1}$ (No. 2) (Figure 3). From that, the edge-sharing Na_2O_8 units of pentacoordinate sodium atoms are transformed into two incomplete, face-sharing Na−O heterocubane units (Figure 5). The latter exhibit two different types of sodium atoms: while sodium atom Na1 (or Na4) is coordinated by three *n*-butyl alcohol ligands, one bridging oxygen atom O3 (O1), and one terminal oxygen O7 (O5) of the *same* siloxanolate ring, the sodium Na2 (Na3) is also surrounded by three *n*-butyl alcohol molecules but is, in contrast, coordinated by two terminal oxygen atoms O7 and the symmetrically generated $O7^4$ (or O5, $O5^2$) and is thus serving as a linker between two consecutive siloxanolate rings of the chain. The two bridging oxygens O2 and O4, respectively, remain without contacts closer than 4 Å to sodium atoms. However, the terminal oxygen atoms O6 and O8, respectively, do have contacts between 3.32 and 3.50 Å to sodium atoms, expanding their coordination number to 5 + 1 and 5 + 2, respectively. Thus, the coordination number of the sodium atoms in **A** resembles that of sodium in sodium hydroxide.[10,11] Due to the overall stoichiometry, one corner of each heterocubane unit is left unoccupied.

Summary

The reaction of phenyltri-*n*-butoxysilane with NaOH in the presence of water led to the formation of the same compound as had been formed by alkaline cleavage of OPSSO. In contrast, treatment of $PhSi(n\text{-}BuO)_3$ with NaOH under anhydrous conditions did not lead to the tetrasiloxanolate ring but gave monomeric sodium phenyldi-*n*-butoxysilanolate.

Experimental Section

The ^1H and ^{29}Si NMR spectra were recorded on a Bruker DRX-500 spectrometer (500.13 MHz for ^1H, 99.36 MHz for ^{29}Si) at 20 °C and in $CDCl_3$ solution with TMS as an internal reference standard.

Preparation of Oligo(phenylsilsesquioxane) Resin (OPSSO). A solution of 132 g (0.624 mol) of phenyltrichlorosilane in 100 mL of anhydrous toluene was added dropwise with vigorous stirring to a mixture of 300 g of ice, 100 mL of water, and 150 mL of toluene. After completion of the addition, stirring was continued for 30 min at room temperature. The organic phase was separated and washed with water until neutral; then the solvent was evaporated, and the residue was dried at 130−150 °C for 4 h. The solid resin obtained ($(PhSiO_{1.5})_n$; 76.2 g, 94.5%) contains residual solvent; thus, a

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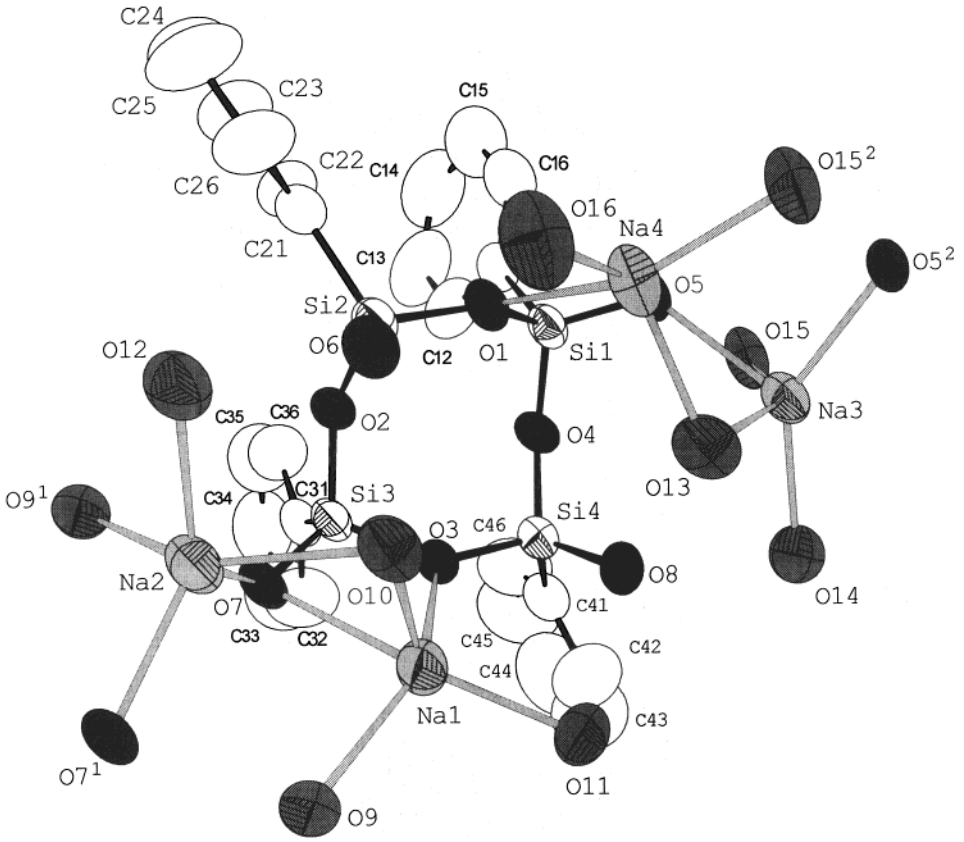

Figure 4. DIAMOND[11] representation of the molecular structure of **A** with probability envelopes at the 50% level. The Na_2O_8 units are light gray and medium gray, the siloxane oxygen atoms are dark gray, silicon atoms are shown with a colorless interior, and carbons have no octant shading. The *n*-butyl chains were omitted for clarity. Bond lengths (Å) for bridging Si−O bonds: Si1−O4 = 1.634(3), Si1−O1 = 1.644(3), Si2−O1 = 1.639(3), Si2−O2 = 1.640(3), Si3−O2 = 1.629(3), Si3−O3 = 1.647(3), Si4−O3 = 1.638(3), Si4−O4 = 1.629(3). Bond lengths (Å) for terminal Si−O bonds: Si1−O5 = 1.583(3), Si2−O6 = 1.589(3), Si3−O7 = 1.572(3), Si4−O8 = 1.593(4). Bond angles (deg) at bridging oxygen atoms: Si1−O1−Si2 = 139.9(2), Si2−O2−Si3 = 143.9(2), Si3−O3−Si4 = 139.5(2), Si4−O4−Si1 = 144.4(2). The Na−O bond lengths (Å) vary from 2.259(4) to 2.582(4). Symmetry generators are indicated by the following superscript numbers: (1) $2 - x, 1 - y, 1 - z$; (2) $2 - x, 1 - y, -z$.

determination of the Si content is required. It was found to be 20.56%.

Synthesis of SPS by Alkaline Cleavage of OPSSO and Subsequent Reaction with Me_3SiCl. In a three-necked flask with a reflux condenser topped with a $CaCl_2$ tube, 13.66 g of OPSSO (0.1 mol) was suspended in 250 mL of *n*-BuOH and then 4 g of NaOH (0.1 mol) was added with stirring. The suspension was refluxed for 1 h until a clear solution was obtained. White needlelike crystals formed on subsequent cooling to room temperature. A suitable single crystal was used for X-ray crystal structure analysis. The bulk of the crystalline material was separated by filtration and dried under reduced pressure (1 mmHg, 80 °C, 1 h), whereupon the crystalline material changed to a fine white powder. The yield of SPS was 15.4 g (84%). A 9.77 g portion of Me_3SiCl (0.09 mol) and 3.96 g (0.05 mol) of pyridine in 60 mL of benzene were placed in a flask, and 7.14 g (0.01 mol) of SPS was added in one portion. The resulting mixture was stirred under reflux for 1 h. After the mixture was cooled to room temperature, the precipitate was filtered. The benzene filtrate was washed with water and then dried over sodium sulfate. Benzene was removed in vacuo, and the residue was recrystallized from hot ethanol to give 7.40 g (87.9%) of white crystalline solid (M_r = 850 (M_r(theor) = 841.5)).

Anal. Calcd for $[C_6H_5Si(O)ONa]_4 \cdot n$-BuOH, $C_{28}H_{30}Si_4Na_4O_9$: C, 47.04; H, 4.23; Si, 15.71; Na, 12.87. Found: C, 47.87; H, 4.99; Si, 15.41; Na, 12.58.

Anal. Calcd for $[C_6H_5Si(O)OSiMe_3]_4$, $C_{36}H_{56}O_8Si_8$: C, 51.38; H, 6.71; Si, 26.70. Found: C, 52.00; H 6.78; Si 26.50. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ 0.19 (9H, s, CH_3), 7.09 (2H, t, *m*-C$_6H_5$, ^3J = 7.4 Hz), 7.26 (1H, t, *p*-C$_6H_5$, ^3J = 7.4 Hz), 7.31 (2H, d, *o*-C$_6H_5$, ^3J = 7.4 Hz). ^{29}Si{^{1}H} NMR (99.36 MHz, $CDCl_3$, TMS): δ 10.49 (O*Si*Me$_3$); −79.02 (O$_3$*Si*Ph).

Synthesis of SPS from Phenyltri-*n*-butoxysilane and Sodium Hydroxide in the Presence of an Equimolar Amount of Water. Phenyltri-*n*-butoxysilane was synthesized according to the procedure of Filler with slight modification.[12] A mixture of 5 g of PhSi(*n*-BuO)$_3$ (0.015 mol), 0.62 g of NaOH (0.015 mol), and 0.28 g of H_2O (0.015 mol) in 15 mL of *n*-butyl alcohol was refluxed for 1 h. A white crystalline material formed upon cooling to room temperature. After filtration, the solid was dried in vacuo to give 2.35 g (78%) of a white powder of composition $[C_6H_5SiO_2Na]_4 \cdot 3n$-BuOH. Anal. Calcd for $[C_6H_5Si(O)ONa]_4 \cdot 3n$-BuOH, $C_{36}H_{50}Si_4Na_4O_{11}$: C, 50.10; H, 5.84; Si, 13.02; Na, 10.66. Found: C, 49.43; H, 5.14; Si, 13.98; Na, 10.95.

Trimethylsilylation of SPS Obtained from the Procedure Described Above. At room temperature 2.35 g (0.027 mol) of SPS was added to a mixture of 40 mL of benzene, 1.17 g of Me_3SiCl (0.011 mol), and 0.64 g of pyridine (0.008 mol). The reaction mixture was refluxed for 0.5 h, cooled to room temperature, and washed with water until chloride free. The solvent was removed and the residue dried in vacuo (1 mmHg, 80 °C, 1 h). A 2.3 g amount (96%) of white solid *cis*-tetraphenyltetrakis(trimethylsiloxy)cyclotetrasiloxane (mp 80 °C, DSC) was obtained. Anal. Calcd for $[PhSi(O)(OSiMe_3)]_4$, $C_{36}H_{56}O_8Si_8$: C, 51.38; H, 6.71; Si, 26.70. Found: C, 51.82; H,

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Table 1. Crystal Data and Structure Refinement for A

empirical formula	$C_{56}H_{100}Na_4O_{16}Si_4$
fw	1233.68
temp (K)	190(2)
wavelength (Å)	0.71073
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell	
a, Å	13.933(4)
b, Å	15.692(4)
c, Å	18.945(4)
α, deg	109.11(2)
β, deg	92.44(3)
γ, deg	112.63(3)
V, Å^3	3545(2)
Z	2
ρ (g/cm^3)	1.156
μ (mm^{-1})	0.165
F(000)	1328
cryst size (mm)	0.40 × 0.40 × 0.12
scan range, deg	2.16 < *θ* < 26.07
index ranges	*h*, −17 to +16, *k*, −19 to +18, *l*, 0−23
no. of rflns collected ($F_o^2 > 2\sigma(F_o^2)$)	13 259 (after data reduction)
no. of unique rflns ($R_{int} = 0.0000$, $F_o^2 > 2\sigma(F_o^2)$)	12 733
no. of data ($F_o^2 > 2\sigma(F_o^2)$)	12 729
no. of rflns omitted	4, affected by strong extinction
refinement method	full-matrix least squares based on F^2
no. of params	722
GOF	0.902
R ($I > 2\sigma_I$)	R1 = 0.0744, wR2 = 0.1847
R (all data)	R1 = 0.1393, wR2 = 0.2152
Δe (max) (e/Å^3)	0.595

6.66; Si, 26.15. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): *δ* 0.21 (9H, s, CH_3), 7.11 (2H, t, *m*-C$_6H_5$, ^3J = 7.4 Hz), 7.28 (1H, t, *p*-C$_6H_5$, ^3J = 7.4 Hz), 7.33 (2H, d, *o*-C$_6H_5$, ^3J = 7.4 Hz). ^{29}Si{^{1}H} NMR (99.36 MHz, $CDCl_3$, TMS): *δ* 10.46 (O*Si*Me$_3$), −78.98 (O$_3$*Si*Ph).

Reaction of PhSi(*n*-BuO)$_3$ with NaOH under Anhydrous Conditions and Subsequent Reaction with Me$_3$SiCl. A mixture of 21.21 g of PhSi(*n*-BuO)$_3$ (0.0654 mol) and 2.87 g of NaOH (0.0719 mol) was stirred at room temperature in 65 mL of *n*-butyl alcohol until a clear solution was formed. Most of the *n*-butyl alcohol was removed. The residue was dissolved in 40 mL of *o*-xylene and the solution refluxed with a gradual removal of solvents (*n*-BuOH, *o*-xylene). After the mixture was cooled to room temperature, the solid product which remained was dissolved in benzene (80 mL), and 14.22 g of Me$_3$SiCl (0.138 mol) dissolved in 20 mL of benzene was added dropwise. The mixture was refluxed for 1 h. When this mixture was heated, the formation of a clear NaCl gel was observed. The latter was separated by filtration, and the solution was distilled in vacuo to yield 14.4 g (64.9%) of PhSi(OSiMe$_3$)(*n*-BuO)$_2$ (bp 101−102 °C/1 mmHg, n_d^{20} = 1.4536).

Anal. Calcd for PhSi(OSiMe$_3$)(*n*-BuO)$_2$, $C_{17}H_{32}Si_2O_3$: C, 59.94; H, 9.47; Si, 16.49; Found: C, 60.96; H, 9.59; Si, 16.70. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): *δ* 0.15 (9H, s, OSiCH_3), 0.92 (6H, t, OCH$_2$CH$_2$CH$_2$CH_3, ^3J = 7.4 Hz), 1.37−1.43 (4H, m, OCH$_2$CH$_2$CH_2CH$_3$), 1.58−1.73 (4H, m, OCH$_2$CH_2CH$_2$CH$_3$), 3.78 (4H, t, OCH_2CH$_2$CH$_2$CH$_3$, ^3J = 6.6 Hz), 7.36 (2H, t, *m*-C$_6H_5$, ^3J = 7.7 Hz), 7.43 (1H, t, *p*-C$_6H_5$, ^3J = 7.7 Hz), 7.68 (2H, d, *o*-C$_6H_5$, ^3J = 7.7 Hz). ^{29}Si{^{1}H} NMR (99.36 MHz, $CDCl_3$, TMS): *δ* 9.77 (O*Si*Me$_3$), −64.00 (O$_3$*Si*Ph).

X-ray Crystallography. On standing in their mother liquor for longer periods (72 h maximum), the crystals of product **A** redissolved. Outside their mother liquor they effloresced within a few seconds due to a rapid loss of included solvent. The temperature of 190(2) K, just above the freezing point of *n*-butyl alcohol, was chosen throughout the measurement to prevent solidification. Specimens investigated at temperatures below 180 K changed to polycrystalline material with powder-like diffracting behavior within minutes. Attempts to identify the bulk of product **A** by indexing a powder diffractogram failed due to the degradation of the solid by quick solvent loss outside its mother liquor. Diffraction experiments with crystals of **A** in their mother liquor in a rotating capillary on a Guinier camera to gain a powder diffractogram are ongoing. From a set of unstable colorless crystals suspended in polyether oil, one single-crystal sample of dimensions 0.4 × 0.4 × 0.12 mm was mounted on the goniometer (STOE IPDS, graphite monochromator, 0.8 mm collimator diameter, lead beam stop) equipped with a cold gas stream (Oxford Cryostream) at 190(2) K. A tilt angle of approximately 15° between the crystal needle axis and the X-ray beam was chosen. The data collection was performed by a *φ*-oscillation measurement, where the crystal was rotated by an increment of 1.2° for each frame. A total rotation angle of 230.4° was chosen, resulting in 192 exposures with an irradiation time of 3 min at 50 kV/40mA. After measurement, 12 733 unique reflections with a mean value of $I/\sigma(I)$ = 7.2 out of 13 742 possible reflections in the range 2.16° < *θ* < 26.07° were obtained and used for structure solution (SHELX97).[13] Atom form factors for neutral atoms were taken from the literature.[14] The crystal structure of **A** was solved by direct methods and subsequent ΔF^2 syntheses. The positions of the hydrogen atoms were calculated in idealized positions. The difference Fourier synthesis for **A** revealed additional peaks, which were interpreted as slightly disordered butyl alcohol molecules. The structure was refined by full-matrix least-squares techniques

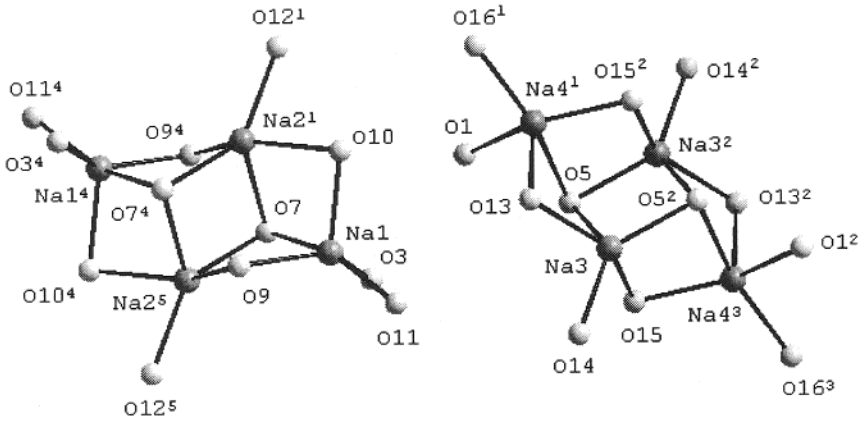

Figure 5. Two crystallographically independent, face-sharing Na−O heterocubane units. Na$_4$(*n*-BuOH)$_8$O$_4$ moieties. Symmetry generators are indicated by the following superscript numbers: (1) 1 + *x*, *y*, *z*; (2) 2 − *x*, 1 − *y*, −*z*; (3) 1 − *x*, 1 − *y*, −*z*; (4) 2 − *x*, 1 − *y*, 1 − *z*; (5) 1 − *x*, 1 − *y*, 1 − *z*.

against F^2, considering 12 729 reflections as observed. Crystal data and results of the refinement are summarized in Table 1; selected bond lengths and angles are given in the caption of Figure 4. Further details of the crystal structure analysis of **A** have been deposited (without structure factor listing) with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-140489. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (phone, +44-1223/336-033; fax, +44-1223/336-033; e-mail, deposit@ccdc.cam.ac.uk; WWW, http://www.ccdc.cam.ac.uk).

(13) Sheldrick, G. M. SHELX97-Programs for Crystal Structure Analysis (Release 97-2); Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

(14) Wilson, A. J. C., Ed. *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; Vol. C.

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Supporting Information Available: Tables of atomic coordinates, all bond distances and angles, and anisotropic thermal factors for **A**. This material is available free of charge via the Internet at http://pubs.acs.org.

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