Cyclic and Polyhedral Aluminosiloxanes with $Al_2Si_2O_4$, $Al_4Si_2O_6$, and $Al_4Si_4O_{12}$ Frameworks: X-ray Crystal Structures of $[(2,4,6\text{-}Me_3C_6H_2)N(SiMe_3)Si(OAlBu\text{-}i)(OAl(Bu\text{-}i)_2)O]_2$ and $[(2,6\text{-}Me_2C_6H_3)N(SiMe_3)SiO_3Al{\cdot}C_4H_8O_2]_4$[†]

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Reactions of (silylamino)silanetriols $RN(SiMe_3)Si(OH)_3$ (R = 2,4,6-$Me_3C_6H_2$ (**1**) and 2,6-$Me_2C_6H_3$ (**2**)) with *i*-Bu_2AlH in 1:1 molar ratio at −78 °C afford aluminosiloxanes $[RN(SiMe_3)Si(OH)O(OAlBu\text{-}i{\cdot}\text{dioxane})]_2$ (R = 2,4,6-$Me_3C_6H_2$ (**3**) and 2,6-$Me_2C_6H_3$ (**4**)) and $[RN(SiMe_3)Si(OAlBu\text{-}i)(OAl(Bu\text{-}i)_2)O]_2$ (R = 2,4,6-$Me_3C_6H_2$ (**5**) and 2,6-$Me_2C_6H_3$ (**6**)), respectively. While **3** and **4** are eight-membered $Al_2Si_2O_4$ cyclic compounds, **5** and **6** are drum-shaped aluminosiloxanes with an $Al_4Si_2O_6$ core. When the same reactions were carried out in 1:2 molar ratio of the reactants at −78 °C, only the drum-shaped polyhedral compounds **5** and **6** are isolated. The reactions between the silanetriols and *i*-Bu_2AlH in 1:1 molar ratio at 65 °C proceed quantitatively to yield the cubic aluminosiloxanes $[RN(SiMe_3)SiO_3Al{\cdot}\text{dioxane}]_4$ (R = 2,4,6-$Me_3C_6H_2$ (**7**) and 2,6-$Me_2C_6H_3$ (**8**)) with an $Al_4Si_4O_{12}$ framework. The X-ray crystal structures of **5** and **8** have been determined.

Introduction

Aluminosilicates are ubiquitous in nature, being the constituents of a wide range of naturally occurring minerals.[1,2] Although most of the aluminosilicates are built upon simple structural principles, a wide range of structural and compositional diversity is present among these compounds. For example, among zeolites which are composed of three-dimensional interconnected networks of SiO_4 and AlO_4 tetrahedra, there is a large variation in their compositions.[2] Even when the Al/O/Si composition is fixed in a series of aluminosilicates such as $M[Al_2Si_2O_8]$, different structures are found depending on the metal.[2] These large structural and compositional variations present also lead to important reactivity differences. Thus, among the catalytically important class of zeolites the reactivity of ZSM-5 is well-known, but modified zeolites such as titanium containing TS-1 or TS-2 very recently have been found to be useful catalysts for a range of organic transformations.[3−5]

Given this background, it is surprising that there have been very few attempts to prepare nonionic *soluble* analogues of these highly complex materials. Such soluble derivatives might be useful model compounds for the complex aluminosilicates, and it is also possible that they can be used as precursors to assemble, by appropriate chemistry, aluminosilicates such as zeolites via cage fusion reactions or sol−gel processes under mild conditions. The greatest obstacle in the preparation of soluble nonionic aluminosilicate analogues is the lack of suitable synthons. Feher and co-workers have reported the use of a siloxanetriol $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ for the preparation of aluminosilsesquioxanes containing a $Si_7O_{12}Al$ unit.[6−8] We have shown that stable and discrete (silylamino)silanetriols $RN(SiMe_3)Si(OH)_3$ are excellent synthons for the assembly of three-dimensional metallasilsesquioxanes.[9,10] In this paper, we report the synthesis of new polyhedral and cyclic alu-

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(1) Wells, A. F. *Structural Inorganic Chemistry*; Oxford: London, 1984; pp 998−1000.

(2) Liebau, F. *Structural Chemistry of Silicates*; Springer: Berlin, 1985; pp 244−260.

(3) (a) Bhaumik, A.; Kumar, R. *J. Chem. Soc., Chem. Commun.* **1995**, 869. (b) Zhao, D.; Goldfarb, D. *J. Chem. Soc., Chem. Commun.* **1995**, 875. (c) Gao, H.; Suo, J.; Li, S. *J. Chem. Soc., Chem. Commun.* **1995**, 835. (d) Serano, D. P.; Li, H.-X.; Davis, M. E. *J. Chem. Soc., Chem. Commun.* **1992**, 745. (e) Reddy, J. S.; Kumar, R.; Ratnasamy, P. *App. Catal.* **1990**, *58,* L1. (f) Reddy, J. S.; Kumar, R. *J. Catal.* **1991**, *130*, 440.

(4) (a) Perego, G.; Ballussi, G.; Corno, C.; Tamarasso, M.; Buonomo, F.; Esposito, A. In *Studies in Surface Science and Catalysis, New Developments in Zeolite Science and Technology*; Murakami, Y., Iijima, A., Word, J. W., Eds.; Elsevier: Amsterdam, 1986. (b) Boccuti, M. R.; Rao, K. M.; Zecchina, A.; Leofanti, G.; Petrini, G. In *Structure and Reactivity of Surfaces*; Morterra, C., Zecchina, A., Costa, G., Eds.; Elsevier: Amsterdam, 1989.

(5) (a) Joseph, R.; Ravindranathan, T.; Sudalai, A. *Tetrahedron Lett.* **1995**, *36*, 1903 and references cited therein. (b) Sheldon, R. A.; Dakka, J. *Catal. Today* **1994**, *19*, 215. (c) Sonawane, H. R.; Pol, A. V.; Moghe, P. P.; Biswas, S. S.; Sudalai, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1215. (d) Kumar, P.; Hegde, V. R.; Pandey, B.; Ravindranathan, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1553. (e) Blasco, T.; Camblor, M. A.; Corma, A.; Pérez-Pariente, J. *J. Am. Chem. Soc.* **1993**, *115*, 11806. (f) Notari, B. *Stud. Surf. Sci. Catal.* **1988**, *37*, 413.

(6) Feher, F. J.; Budzichowski, T. A.; Weller, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 7288.

(7) Feher, F. J.; Weller, K. J. *Organometallics* **1990**, *9*, 2638.

(8) Feher, F. J.; Weller, K. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 9686.

(9) Montero, M. L.; Usón, I.; Roesky, H. W. *Angew. Chem.* **1994**, *106*, 2198; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2103.

(10) (a) Winkhofer, N.; Voigt, A.; Dorn, H.; Roesky, H. W.; Steiner, A.; Stalke, D.; Reller, A. *Angew. Chem.* **1994**, *106*, 1414; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1352. (b) Montero, M. L.; Voigt, A.; Teichert, M.; Usón, I.; Roesky, H. W. *Angew. Chem.* **1995**, *107*, 2761; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2504. (c) Voigt, A.; Murugavel, R.; Chandrasekhar, V.; Winkhofer, N.; Roesky, H. W.; Schmidt, H.-G.; Usón, I. *Organometallics*, in press.

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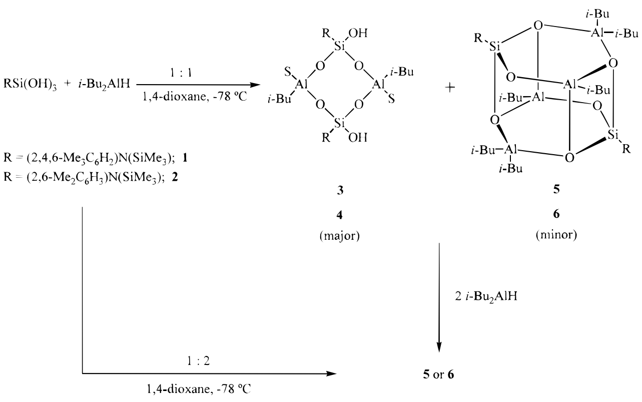
Scheme 1



minosiloxanes. The polyhedral aluminosiloxanes exist in two different cage structural forms containing a $Al_4Si_2O_6$ or $Al_4Si_4O_{12}$ framework.

Results and Discussion

Synthesis and Spectra. We have recently synthesized air-stable and lipophilic (silylamino)silanetriols $RN(SiMe_3)Si(OH)_3$ (R = 2,4,6-$Me_3C_6H_2$ (**1**) and 2,6-$Me_2C_6H_3$ (**2**)) starting from hindered primary aromatic amines as shown in eq 1.[11]

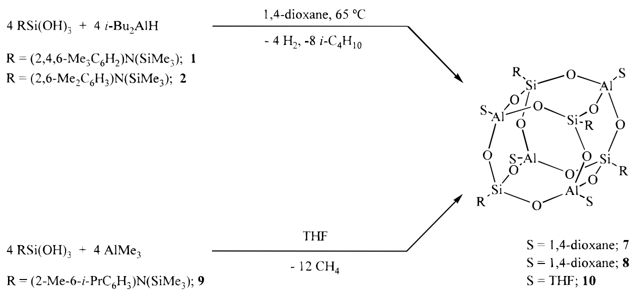
$$RNH_2 \xrightarrow[2.\ SiMe_3Cl]{1.\ n\text{-BuLi}} RN(SiMe_3)H \xrightarrow[2.\ SiCl_4]{1.\ n\text{-BuLi}} RN(SiMe_3)SiCl_3 \xrightarrow{H_2O/\text{aniline}} \underset{\mathbf{1},\ \mathbf{2}}{RN(SiMe_3)Si(OH)_3} \quad (1)$$

Addition of *i*-Bu_2AlH to solutions of silanetriols **1** and **2** in hexane and 1,4-dioxane (5:1 v/v) at −78 °C in 1:1 stoichiometry affords the mixtures of aluminosiloxanes $[RN(SiMe_3)Si(OH)O(OAlBu\text{-}i\cdot dioxane)]_2$ (R = 2,4,6-$Me_3C_6H_2$ (**3**) and 2,6-$Me_2C_6H_3$ (**4**)) and $[RN(SiMe_3)Si(OAlBu\text{-}i)(OAl(Bu\text{-}i)_2)O]_2$ (R = 2,4,6-$Me_3C_6H_2$ (**5**) and 2,6-$Me_2C_6H_3$ (**6**)) (Scheme 1). The cyclic compounds **3** and **4** could not be isolated in an analytically pure form. However, the polyhedral derivatives **5** and **6** were obtained in good purity by fractional crystallization. Compounds **5** and **6** are isolated as the only products directly from 1:2 stoichiometric reactions of silanetriols (**1** and **2**) with *i*-Bu_2AlH (Scheme 1).

We had earlier reported, in a preliminary communication, that in an analogous 1:1 reaction between *i*-Bu_2AlH and a more sterically hindered silanetriol $RN(SiMe_3)Si(OH)_3$ (R = 2,6-*i*-$Pr_2C_6H_3$) only the eight-membered Si−O−Al ring aluminosiloxane $[RN(SiMe_3)Si(OH)O(OAlBu\text{-}i\cdot THF)]_2$ with an unreacted OH group on silicon was isolated and structurally characterized.[9] However, in the present case, the replacement of the isopropyl groups by methyl groups in the ortho positions of the aryl ring is sufficient to tilt the steric balance required for the isolation of the polyhedral drum compounds **5** and **6** in minor quantities along with the eight-membered ring compounds **3** and **4**.

Treatment of the crude product mixtures of **3** and **5** or **4** and **6** with 2 equiv of *i*-Bu_2AlH in hexane at room temperature leads to the complete conversion of the cyclic aluminosiloxanes **3** and **4** to the drum compounds **5** and **6**, respectively (Scheme 1). From this observation, one can assume that the formation of **5** and **6** should have proceeded via the intermediacy of the eight-membered rings. The initially formed eight-membered rings probably further react stepwise with 2 equiv of *i*-Bu_2AlH and subsequently fold to form the resultant drum structures which contain coordinatively saturated aluminum centers.

Scheme 2



In order to probe whether other structures are possible between the reactions of these two reactants under different experimental conditions, we carried out the reactions of silanetriols **1** and **2** with *i*-Bu_2AlH in a 1:1 stoichiometry at 65 °C. The result is the complete elimination of all the isobutyl and hydride groups on aluminum with the formation of the three-dimensional aluminosiloxanes **7** and **8** (Scheme 2). In contrast, the reaction between the silanetriol $RN(SiMe_3)Si(OH)_3$ (R = 2-Me-6-*i*-PrC_6H_3 (**9**)) and $AlMe_3$ proceeds cleanly at room temperature. All the methyl groups of $AlMe_3$ react, and the cubic aluminosiloxane $[RN(SiMe_3)SiO_3Al\cdot THF]_4$ (**10**) is formed as the only product (Scheme 2). Spectroscopic examination of the isolated product did not show the presence of any cyclic or drum compounds, an observation that demonstrates the steric role played by the bulky isobutyl groups in stabilizing the cyclic and drum structures **3**-**6**.

The new aluminosiloxanes **3**-**8** and **10** are freely soluble in common organic solvents such as pentane, diethyl ether, tetrahydrofuran, and toluene.[12] While the ring and drum aluminosiloxanes **3**-**6** are air- and moisture-sensitive, the cubic aluminosiloxanes **7**, **8**, and **10** can be handled in air for short periods (ca. 1 h) without any detectable decomposition. The cyclic aluminosiloxanes **3** and **4** were not isolated in an analytically pure form, and the crude products were characterized by means of IR, mass, and NMR spectroscopy. The drum and cubic aluminosiloxanes do not melt up to ca. 200 °C and decompose without melting on further heating.

The IR spectra of **3** and **4** contain a strong broad absorption around 3400 cm^{-1} due to the free −OH group on each silicon. Peaks due to $[M - Bu]^+$ ions are observed in their EI mass spectrum. In the ^1H NMR spectra of **3** and **4**, in addition to the resonances due to aryl, $SiMe_3$, and *i*-Bu groups, two additional signals around δ 3.4 and 3.7 are observed due to the OCH_2 protons of the 1,4-dioxane molecules coordinated to the aluminum centers. Compounds **3** and **4** show two ^{29}Si NMR resonances each. The resonances due to SiO_3 silicon centers are seen around δ_{Si} −80, while those due to the $SiMe_3$ group are seen around δ_{Si} 1. These chemical shifts are characteristic of the eight-membered

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(11) Murugavel, R.; Chandrasekhar, V.; Voigt, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1995**, *14*, 5298.

(12) Quantities of 3 mmol of all the compounds can be dissolved in 10 mL of THF or diethyl ether at 25 °C.

Table 1. ^{29}Si NMR Data for Cyclic and Polyhedral Aluminosiloxanes

compd	structure	δ(SiMe$_3$), ppm	δ(SiO$_3$), ppm
$[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{SiMe}_3)\text{Si(OH)O(OAlBu-}i\cdot\text{dioxane})]_2$ (**3**)	ring	1.0	−80.0
$[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)\text{Si(OH)O(OAlBu-}i\cdot\text{dioxane})]_2$ (**4**)	ring	0.8	−79.8
$[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)\text{Si(OH)O(OAlBu-}i\cdot\text{THF})]_2$[a]	ring	1.3	−77.0
$[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{SiMe}_3)\text{Si(OAlBu-}i)(\text{OAl(Bu-}i)_2)\text{O}]_2$ (**5**)	drum	11.5	−65.5
$[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)\text{Si(OAlBu-}i)(\text{OAl(Bu-}i)_2)\text{O}]_2$ (**6**)	drum	11.8	−65.6
$[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)\text{Si(OAlBu-}i)(\text{OAl(Bu-}i)_2)\text{O}]_2$[a]	drum	12.5	−65.3
$[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{SiMe}_3)\text{SiO}_3\text{Al}\cdot\text{dioxane}]_4$ (**7**)	cube	0.8	−79.8
$[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)\text{SiO}_3\text{Al}\cdot\text{dioxane}]_4$ (**8**)	cube	0.8	−79.7
$[(2\text{-Me-6-}i\text{-PrC}_6\text{H}_3)\text{N}(\text{SiMe}_3)\text{SiO}_3\text{Al}\cdot\text{THF}]_4$ (**10**)	cube	0.7	−79.3

[a] From ref 9.

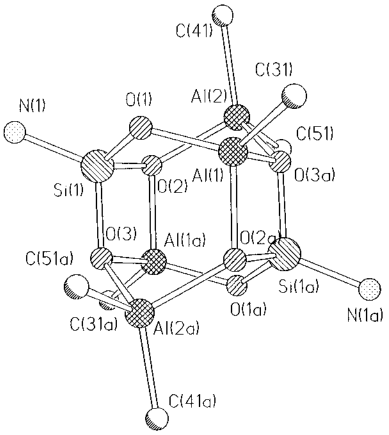

Figure 1. Core structure of **5** showing the drum polyhedron.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5[a]

Bond Lengths for Molecule 1			
Si(1)−O(1)	1.603(7)	Si(1)−N(1)	1.670(8)
Si(1)−O(2)	1.685(6)	Si(1)−O(3)	1.692(6)
Al(1)−O(1)	1.731(7)	Al(1)−O(2a)	1.879(6)
Al(1)−O(3a)	1.883(6)	Al(1)−C(31a)	1.929(10)
Al(2)−O(3a)	1.871(6)	Al(2)−O(2)	1.880(7)
Al(2)−C(51)	1.954(10)	Al(2)−C(41)	1.964(10)
Bond Angles for Molecule 1			
O(1)−Si(1)−N(1)	113.3(3)	O(1)−Si(1)−O(2)	109.5(3)
N(1)−Si(1)−O(2)	114.7(3)	O(1)−Si(1)−O(3)	110.4(3)
N(1)−Si(1)−O(3)	115.2(4)	O(2)−Si(1)−O(3)	91.9(3)
O(1)−Al(1)−O(2a)	103.8(3)	O(1)−Al(1)−O(3a)	103.9(3)
O(2a)−Al(1)−O(3a)	80.3(2)	O(1)−Al(1)−C(31a)	123.3(4)
O(2a)−Al(1)−C(31a)	120.3(4)	O(3a)−Al(1)−C(31a)	116.4(4)
O(3a)−Al(2)−O(2)	95.8(3)	O(3a)−Al(2)−C(51)	108.2(4)
O(2)−Al(2)−C(51)	108.1(4)	O(3a)−Al(2)−C(41)	109.2(4)
O(2)−Al(2)−C(41)	109.3(4)	C(51)−Al(2)−C(41)	122.9(4)
Si(1)−O(1)−Al(1)	125.1(3)	Si(1)−O(2)−Al(1a)	93.8(3)
Si(1)−O(2)−Al(2)	121.6(3)	Al(1a)−O(2)−Al(2)	117.6(3)
Si(1)−O(3)−Al(2a)	121.2(3)	Si(1)−O(3)−Al(1a)	93.5(3)
Al(2a)−O(3)−Al(1a)	117.3(3)		
Bond Lengths for Molecule 2			
Si(3)−O(4)	1.574(6)	Si(3)−O(6)	1.673(6)
Si(3)−N(2)	1.681(7)	Si(3)−O(5)	1.692(6)
Al(3)−O(4)	1.758(6)	Al(3)−O(5b)	1.868(7)
Al(3)−O(6b)	1.873(6)	Al(3)−C(81)	1.919(11)
Al(4)−O(5)	1.880(7)	Al(4)−O(6b)	1.885(6)
Al(4)−C(101)	1.951(11)	Al(4)−C(91)	1.958(9)
Bond Angles for Molecule 2			
O(4)−Si(3)−O(6)	110.5(3)	O(4)−Si(3)−N(2)	113.5(3)
O(6)−Si(3)−N(2)	114.5(4)	O(4)−Si(3)−O(5)	110.4(3)
O(6)−Si(3)−O(5)	91.3(3)	N(2)−Si(3)−O(5)	114.7(3)
O(4)−Al(3)−O(5b)	102.6(3)	O(4)−Al(3)−O(6b)	103.9(3)
O(5b)−Al(3)−O(6b)	80.1(3)	O(4)−Al(3)−C(81)	122.9(4)
O(5b)−Al(3)−C(81)	119.9(4)	O(6b)−Al(3)−C(81)	118.7(5)
O(5)−Al(4)−O(6b)	95.2(3)	O(5)−Al(4)−C(101)	109.4(4)
O(6b)−Al(4)−C(101)	108.5(4)	O(5)−Al(4)−C(91)	108.7(4)
O(6b)−Al(4)−C(91)	109.7(3)	C(101)−Al(4)−C(91)	122.0(5)
Si(3)−O(4)−Al(3)	125.2(3)	Si(3)−O(5)−Al(3b)	93.8(3)
Si(3)−O(5)−Al(4)	121.0(3)	Al(3b)−O(5)−Al(4)	118.7(3)
Si(3)−O(6)−Al(3b)	94.3(3)	Si(3)−O(6)−Al(4b)	121.4(3)
Al(3b)−O(6)−Al(4b)	117.0(3)		

[a] Positions: (a) $-x, -y+1, -z+1$; (b) $-x+1, -y, -z+2$.

cyclic aluminosiloxanes and compare well with an analogous cyclic aluminosiloxane $[\text{RN(SiMe}_3)\text{Si(OH)O(OAlBu-}i\cdot\text{THF})]_2$ (R = 2,6-i-Pr$_2$C$_6$H$_3$), whose crystal structure has been reported earlier (Table 1).[9]

In the drum compounds **5** and **6**, both the ^{29}Si resonances due to the SiO$_3$ and SiMe$_3$ groups are shifted downfield and are observed around δ_{Si} −66 and 12, respectively. These significant shifts are a likely consequence of the presence of the four-membered Si−O−Al−O rings in these compounds (*vide infra*). It is interesting to note that in the cubic structures **7**, **8**, and **10** which are composed of only eight-membered Si−O−Al rings (*vide infra*), the ^{29}Si chemical shifts again move upfield (Table 1).

X-ray Crystal Structure of 5. The molecular structure of the Al/Si/O core of **5** is shown in Figure 1. Selected structural parameters are listed in Table 2. The compound crystallizes in the triclinic space group $P\bar{1}$ with two half molecules in the asymmetric unit. The structure of **5** can be described as a cylindrical drum with the top and bottom faces of the polyhedron being made of six-membered Al$_2$SiO$_3$ rings. The side faces are composed of two such six-membered rings in addition to two four-membered AlSiO$_2$ rings. All the six-membered rings are puckered and exist in a boat conformation. The four-membered rings are planar.

There are two types of Si−O distances in the molecules. The longer distance (average 1.68 Å) is associated with the Si−O bonds in the planar four-membered ring. Similarly, there also are two types of Al−O distances, with the Al−μ_3-O distance being substantially longer (1.88 Å) than the Al−μ_2-O distances (1.74 Å). These differences also extend to the Si−O−M and O−Si−O angles. Thus, the expected tetrahedral values around silicon fall to 94.0°. Even the angles around μ_3-oxygen are smaller (91.4°). All these geometrical parameters compare well with values found in the related compound $[\text{RN(SiMe}_3)\text{Si(OAlBu-}i)(\text{OAl(Bu-}i)_2)\text{O}]_2$ (R = 2,6-i-Pr$_2$C$_6$H$_3$).[9]

X-ray Crystal Structure of 8. The molecular structure of the Al/Si/O core of **8** is shown in Figure 2. Selected structural parameters are summarized in Table 3. The molecule crystallizes in the tetragonal space group $P42_1c$ as a 1,4-dioxane solvate.[13] A cubic polyhedron can be defined with 4 silicon atoms and 4

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(13) The lattice 1,4-dioxane solvate does not show any interaction with the aluminosiloxane molecule.

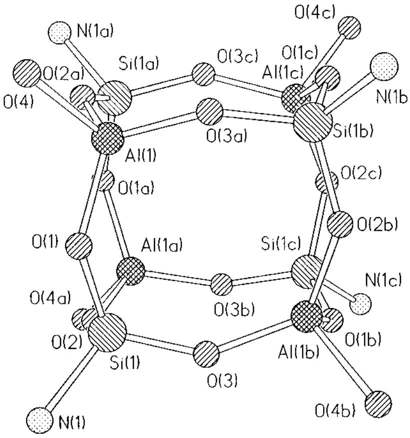

Figure 2. Core structure of **8** showing the cubic polyhedron.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 8[a]

Si(1)−O(3)	1.615(4)	Si(1)−O(2)	1.616(4)
Si(1)−O(1)	1.623(4)	Si(1)−N(1)	1.739(5)
Al(1)−O(3a)	1.703(4)	Al(1)−O(1)	1.708(4)
Al(1)−O(2b)	1.712(4)	Al(1)−O(4)	1.877(4)
O(3)−Si(1)−O(2)	111.1(3)	O(3)−Si(1)−O(1)	108.9(3)
O(2)−Si(1)−O(1)	111.7(2)	O(3)−Si(1)−N(1)	110.0(2)
O(2)−Si(1)−N(1)	106.7(2)	O(1)−Si(1)−N(1)	108.4(3)
O(3a)−Al(1)−O(1)	113.5(2)	O(3a)−Al(1)−O(2b)	117.5(2)
O(1)−Al(1)−O(2b)	115.5(2)	O(3a)−Al(1)−O(4)	102.2(2)
O(1)−Al(1)−O(4)	104.1(2)	O(2b)−Al(1)−O(4)	101.0(2)
Si(1)−O(1)−Al(1)	135.5(3)	Si(1)−O(2)−Al(1b)	140.1(3)
Si(1)−O(3)−Al(1c)	144.4(3)		

[a] Positions: (a) $y - 1, -x - 1, -z$; (b) $-x - 2, -y, z$; (c) $-y - 1, x + 1, -z$.

aluminum atoms occupying its alternate corners. The Si···Al edges of the cube are bridged by an oxygen atom in a μ_2 fashion. The cube is composed of six puckered $Al_2Si_2O_4$ eight-membered rings, each of which exists in a C_4 crownlike conformation.

The average Al−O bond length within the polyhedron (1.71(4) Å) is considerably shorter than the exocyclic Al−O bond length (1.88(4) Å). This is consistent with the bonding type differences within and outside the framework. The average Si−O bond length (1.62 Å) is shorter than the Si−O distances observed in the parent silanetriol.[11] The average Si−O−Al angle within the framework is 140.0°.

Conclusion

We have demonstrated that the (silylamino)silanetriols are excellent synthons for the preparation of soluble, neutral aluminosiloxanes with different types of Al/Si/O frameworks which might serve as model compounds for many naturally occurring insoluble, ionic aluminosilicates. Small changes in the reaction temperature or the bulkiness of the substituents on aluminum or nitrogen have allowed the isolation of aluminosiloxanes with different polyhedral structures. Further, the synthesis involves only the elimination of alkane or hydrogen during the reaction, thereby making the workup procedure very simple. We have also been recently successful in synthesizing soluble, anionic aluminosilicates using this synthetic method.[10b] Hence, this synthetic route appears to be general and may be applicable to the preparation of hitherto unknown metallasiloxanes.

Experimental Section

General Data. All experimental manipulations were carried out under an atmosphere of dinitrogen rigorously excluding air and moisture. The samples for spectral measurements were prepared in a drybox. Solvents were purified according to conventional procedures and were freshly distilled prior to use. Diisobutylaluminum hydride (1 M solution in hexanes, Aldrich) and trimethylaluminum (2 M solution in hexanes, Aldrich) were used as received. The silanetriols **1**, **2**, and **9** were prepared as described.[11] NMR spectra were recorded on a Bruker AM 200 or a Bruker AS 400 instrument, and the chemical shifts are reported with reference to TMS. The upfield shifts are negative. IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer (only the strong absorption bands are given; *vide infra*). Mass spectra were obtained on Finnigan MAT System 8230 and a Varian MAT CH5 mass spectrometer. Melting points were obtained on a HWS-SG 3000 apparatus and are uncorrected. CHN analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry at Göttingen, Germany.

Reactions of 1 and 2 with *i*-Bu_2AlH at −78 °C (1:1 Ratio). A solution of $RN(SiMe_3)Si(OH)_3$ (0.56 of **1** or 0.54 g of **2**, 2 mmol) in hexane (10 mL) and 1,4-dioxane (2 mL) was cooled to −78 °C. To this was added *i*-Bu_2AlH (2 mmol, 2 mL of 1 M solution in hexane) dropwise using a syringe. The reaction mixture was allowed to attain room temperature and stirred for 24 h. The solvent was removed *in vacuo* affording mixtures of **3** and **5** and **4** and **6**, respectively. From these mixtures the drum compounds **5** and **6** could be obtained in a pure form in small quantities (20%) by fractional crystallization at −20 °C from hexane/1,4-dioxane (4:1 v/v).

Reactions of 1 and 2 with *i*-Bu_2AlH at −78 °C (1:2 Ratio). A solution of $RN(SiMe_3)Si(OH)_3$ (0.56 of **1** or 0.54 g of **2**, 2 mmol) in hexane (10 mL) and 1,4-dioxane (4 mL) was cooled to −78 °C. To this was added *i*-Bu_2AlH (4 mmol, 2 mL of 1 M solution in hexane) dropwise using a syringe. The reaction mixture was allowed to attain room temperature and stirred for 24 h. The solvent was removed *in vacuo* affording **5** or **6** in nearly quantitative yields.

Synthesis of Cubic Aluminosiloxanes 7 and 8. Compounds **7** and **8** were synthesized in a similar manner. A solution of $RN(SiMe_3)Si(OH)_3$ (0.56 of **1** or 0.54 g of **2**, 2 mmol) in hexane (10 mL) and 1,4-dioxane (2 mL) was cooled to −78 °C. To this was added *i*-Bu_2AlH (2 mmol, 2 mL of 1 M solution in hexane) dropwise using a syringe. The reaction mixture was allowed to attain room temperature and was heated under reflux for 6 h until the gas evolution ceased. Subsequently, the solvent was removed *in vacuo* affording **7** or **8** as white solid residues in quantitative yields. The products were dried thoroughly for 24 h under high vacuum and recrystallized from hexane and dioxane at 5 °C.

Synthesis of Cubic Aluminosiloxane 10. To a solution of (2-Me-6-*i*-PrC_6H_3)$N(SiMe_3)Si(OH)_3$ (**9**) (0.6 g, 2 mmol) in hexane (10 mL) and THF (2 mL) was added $AlMe_3$ (2 mmol, 1 mL of 2 M solution in hexane) dropwise using a syringe. The evolution of CH_4 ceased within 10 min, and the reaction mixture was stirred at room temperature for another 6 h. Subsequently, the solvent was removed *in vacuo* affording **10** as white solid residue in quantitative yield. The solid was recrystallized from 10:1 v/v hexane and THF.

3. IR (Nujol): 3415, 1423, 1230, 1055, 970, 798, 680 cm^{-1}. ^1H NMR (C_6D_6): 0.01 (s, 18H, $SiMe_3$), −0.30 (d, 4H, $CH_2CH(CH_3)_2$), 0.71 (m, 2H, $CH_2CH(CH_3)_2$), 0.84 (d, 12H, $CH_2CH(CH_3)_2$), 2.14 (s, 6H, CH_3), 2.21 (s, 12H, CH_3), 3.35 (s, 8H, OCH_2), 3.68 (s, 8H, OCH_2), 6.80 (s, 4H, aromatic). ^{29}Si NMR (C_6D_6): −80.0 (SiO_3), 1.0 ($SiMe_3$). MS (EI, 70 eV): *m/e* 853 ($[M - Bu]^+$).

4. IR (Nujol): 3400, 1431, 1235, 1061, 966, 787, 678 cm^{-1}. ^1H NMR (C_6D_6): 0.03 (s, 18H, $SiMe_3$), −0.28 (d, 4H, $CH_2CH(CH_3)_2$), 0.67 (m, 2H, $CH_2CH(CH_3)_2$), 0.81 (d, 12H, $CH_2CH(CH_3)_2$), 2.20 (s, 12H, CH_3), 3.38 (s, 8H, OCH_2), 3.66 (s, 8H,

OCH_2), 6.8−7.0 (m, 6H, aromatic). ^{29}Si NMR (C_6D_6): −79.8 (SiO_3), 0.8 ($SiMe_3$). MS (EI, 70 eV): *m*/*e* 825 [M − Bu]$^+$).

5. Mp > 200 °C (dec). IR (Nujol): 1320, 1302, 1257, 1218, 1183, 1155, 1129, 1057, 1020, 960, 894, 875, 839, 797, 757, 736, 722, 681, 568, 561, 476 cm^{-1}. ^{29}Si NMR (C_6D_6): −65.5 (SiO_3), 11.5 ($SiMe_3$). MS (EI, 70 eV): *m*/*e* 957 ([M − Bu]$^+$, 100%). Anal. Calcd for $C_{48}H_{94}Al_4N_2O_6Si_4$: C, 56.8; H, 9.3; N, 2.8. Found: C, 56.2; H, 9.1; N, 3.0.

6. Mp > 200 °C (dec). IR (Nujol): 1319, 1296, 1259, 1206, 1185, 1129, 1047, 1020, 966, 949, 912, 894, 876, 839, 800, 767, 683, 559, 547, 493, 481 cm^{-1}. ^{29}Si NMR (C_6D_6): −65.6 (SiO_3), 11.8 ($SiMe_3$). MS (EI, 70 eV): *m*/*e* 929 ([M − Bu]$^+$, 100%). Anal. Calcd for $C_{46}H_{90}Al_4N_2O_6Si_4$: C, 56.0; H, 9.2; N, 2.8. Found: C, 55.7; H, 9.1; N, 2.9.

7. Mp > 220 °C (dec). IR (Nujol): 1303, 1258, 1219, 1154, 1129, 1082, 1049, 955, 894, 876, 839, 802, 756, 735, 723, 682, 638, 574, 550, 477 cm^{-1}. ^1H NMR (C_6D_6): 0.30 (s, 36H, $SiMe_3$), 2.20 (s, 12H, Me), 2.51 (s, 24H, Me), 3.34 (s, 8H, CH_2, free dioxane), 3.38 (t, 16H, CH_2), 3.64 (t, 16H, CH_2), 6.80 (s, 8H, aromatic). ^{29}Si NMR (C_6D_6): −79.8 (SiO_3), 0.8 ($SiMe_3$). Anal. Calcd for $C_{68}H_{120}Al_4N_4O_{22}Si_8$: C, 48.7; H, 7.2; N, 3.3. Found: C, 48.5; H, 7.7; N, 3.6.

8. Mp > 200 °C (dec). IR (Nujol): 1257, 1208, 1128, 1084, 1069, 1047, 966, 947, 913, 876, 839, 766, 684, 636, 613, 560, 545, 494 cm^{-1}. ^1H NMR (C_6D_6): 0.28 (s, 36H, $SiMe_3$), 2.48 (s, 24H, Me), 3.35 (s, 8H, CH_2, free dioxane), 3.38 (t, 16H, CH_2), 3.64 (t, 16H, CH_2), 6.80 (m, 12H, aromatic). ^{29}Si NMR (C_6D_6): −79.7 (SiO_3), 0.8 ($SiMe_3$). Anal. Calcd for $C_{64}H_{112}Al_4N_4O_{22}Si_8$: C, 47.4; H, 7.0; N, 3.5. Found: C, 46.7; H, 6.8; N, 3.5.

10. Mp > 250 °C (dec). IR (Nujol): 1251, 1195, 1175, 1074, 964, 910, 837, 783, 752, 610, 548 cm^{-1}. ^1H NMR (C_6D_6): 0.06 (s, 36H, $SiMe_3$), 1.20 (d, 24H, Me), 2.20 (s, 12H, Me), 3.75 (m, 4H, CH), 6.95 (m, 12H, aromatic), 1.80 (m, 8H, thf), 3.60 (m, 8H, thf). ^{29}Si NMR (C_6D_6): −79.3 (SiO_3), 0.7 ($SiMe_3$). Anal. Calcd for $C_{68}H_{120}Al_4N_4O_{16}Si_8$: C, 51.6; H, 7.6; N, 3.3. Found: C, 51.1; H, 7.8; N, 3.3.

X-ray Structure Determination of 5 and 8. Colorless single crystals suitable for X-ray diffraction studies were grown from 5:1 v/v hexane/1,4-dioxane at −20 °C for **5** and at 5 °C for **8**. A suitable crystal of each compound was mounted on a glass fiber and coated with paraffin oil. Diffraction data were collected on a Siemens-Stoe AED2 four-circle instrument (at −50 °C for **5** and at −120 °C for **8**), with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The structures were solved by direct methods using SHELXS-90[14] and refined against F^2 on all data by full-matrix least squares with SHELXL-93.[15] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model. The crystals of **5** developed cracks at −120 °C, and hence, the data collection was carried out at −50 °C. This resulted in large thermal parameters for the carbon atoms of the isobutyl groups. Other details pertaining to the data collection, structure solution, and refinement are listed in Table 4.

Table 4. Crystal Data and Structure Refinement for 5 and 8

	compd	
	5	**8**
empirical formula	$C_{48}H_{94}Al_4N_2O_6Si_4$	$C_{60}H_{104}Al_4N_4O_{20}Si_8{\cdot}C_4H_8O_2$
fw	1015.53	1622.22
temp, K	223(2)	153(2)
wavelength, Å	0.710 73	0.710 73
cryst system	triclinic	tetragonal
space group	$P\bar{1}$	$P42_1c$
a, Å	12.408(2)	18.810(2)
b, Å	12.550(3)	
c, Å	22.822(5)	12.717(2)
α, deg	82.37(3)	90
β, deg	80.85(3)	90
γ, deg	63.60(3)	90
V, Å^3	3135(1)	4500(1)
Z	2	2
D_{calcd}, g·cm^{-3}	1.076	1.197
μ, mm^{-1}	0.191	0.222
F(000)	1104	1728
cryst size, mm	0.5 × 0.4 × 0.2	1.2 × 1.0 × 1.0
θ range, deg	3.5−20.0	3.5−22.5
index range	$-11 \le h \le 11$ $-11 \le k \le 12$ $-21 \le l \le 21$	$-20 \le h \le 20$ $-1 \le k \le 20$ $0 \le l \le 13$
tot. reflcns	9266	3014
indepdt reflcns	5780	1643
refinement method	full-matrix least squares on F^2	
data/restraints/params	5740/0/601	1636/14/249
*R*1, *R*2 ($I > 2\sigma(I)$)	0.090, 0.234	0.063, 0.172
*R*1, *R*2 (all data)	0.132, 0.321	0.068, 0.190
S	1.013	1.069
largest diff peak and hole, e·Å^{-3}	0.555, −0.428	0.714, −0.411

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Supporting Information Available: Listings of crystal data, atomic coordinates and equivalent isotropic displacement parameters for all non-hydrogen atoms, hydrogen positional and thermal parameters, anisotropic displacement parameters, and bond distances and bond angles and plots (16 pages). Ordering information is given on any current masthead page.

OM950685P

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[14] Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[15] Sheldrick, G. M. SHELXL-93, program for crystal structure refinement, Göttingen, 1993.