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Octakis[(2,2,6,6-tetramethylpiperidino)methyl]octasilsesquioxane: synthesis and crystal structure analysis of a new aminoorganyl-functionalized octasilsesquioxane

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Dedicated to Professor Manfred Christl on the occasion of his 60th birthday

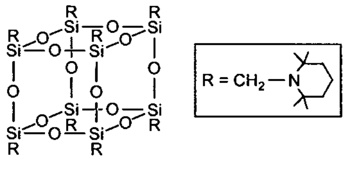
Abstract

Octakis[(2,2,6,6-tetramethylpiperidino)methyl]octasilsesquioxane (**1**), an aminoorganyl-functionalized octasilsesquioxane, was synthesized by hydrolysis of bis[ethane-1,2-diolato(2-)][(2,2,6,6-tetramethylpiperidinio)methyl]silicate (**2**). The zwitterionic pentacoordinate silicate **2** was obtained by treatment of dimethoxy(methyl)[(2,2,6,6-tetramethylpiperidino)methyl]silane (**3**) with two molar equivalents of ethane-1,2-diol. The cage-like compound **1** was structurally characterized by single-crystal X-ray diffraction and solution and solid-state NMR spectroscopy. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Octasilsesquioxane; Pentacoordinate silicon; Zwitterionic pentacoordinate silicate; Crystal structure; Solid-state NMR spectroscopy

1. Introduction

In recent years, numerous papers dealing with the synthesis, structure, and properties of silsesquioxanes have been published [1,2]. Most information is available about octakisorganyloctasilsesquioxanes, compounds of the general formula type $R_8Si_8O_{12}$ (R = organyl) with a cage-like molecular skeleton. Typically, compounds of this particular formula type are synthesized by hydrolysis of the respective trichloro(organyl)silanes (Cl_3SiR) or tri(organyloxy)organylsilanes [$(RO)_3SiR$] (R = organyl). Some years ago, we have reported on a quite different synthetic method based on the hydrolysis of a zwitterionic pentacoordinate silicate precursor [3]. Meanwhile, this method has also been extended to anionic pentacoordinate silicates [4]. We have now succeeded in synthesizing a new amino-functionalized octasilsesquioxane, octakis[(2,2,6,6-tetramethylpiperidino)methyl]octasilsesquioxane (**1**), again starting from a zwitterionic pentacoordinate silicate. We report here on the synthesis and structural characterization of **1**. The studies described in this paper were carried out as part of our systematic investigations on zwitterionic pentacoordinate silicates [5].



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2. Results and discussion

The title compound was prepared by a two-step synthesis starting from dimethoxy(methyl)[(2,2,6,6-tetramethylpiperidino)methyl]silane (**3**) [6] (Scheme 1). Treatment of **3** with two molar equivalents of ethane-1,2-diol yielded the zwitterionic pentacoordinate silicon compound bis[ethane-1,2-diolato(2-)][(2,2,6,6-tetramethylpiperidinio)methyl]silicate (**2**) [7] (86% yield; after recrystallization from toluene–petroleum ether), which upon hydrolysis gave the octasilsesquioxane **1** (43% yield; after recrystallization from toluene–ethanol).

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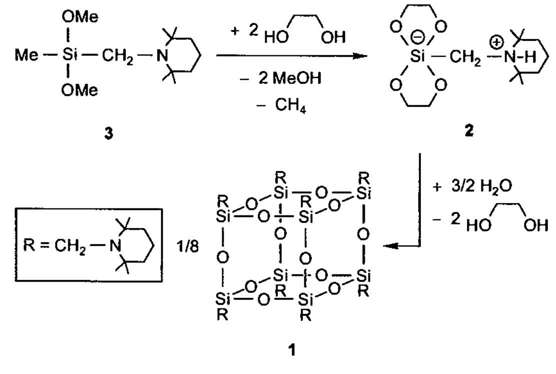
The formation of the zwitterionic pentacoordinate silicate **2** is quite remarkable. The synthesis of this compound is based on the cleavage of two Si–O bonds (formation of two molar equivalents of methanol) and one Si–C bond (formation of one molar equivalent of methane). Similar Si–C cleavage reactions have already been reported for benzene-1,2-diols, α-hydroxycarboxylic acids, salicylic acid, aceto- and benzohydroxamic acid, and benzoin [5], but not for aliphatic *vic*-diols.

The synthesis of compound **1** is quite remarkable as well. Contrary to the typical methods applied to the synthesis of octasilsesquioxanes [hydrolysis of silanes of the formula type Cl_3SiR or $(RO)_3SiR$ (R = organyl) at higher temperatures; long reaction times], compound **1** was formed under relatively mild reaction conditions: the hydrolysis of **2** was performed in dichloromethane at room temperature and the product obtained in good yield within a few hours. This example again demonstrates the synthetic potential of pentacoordinate silicates for the synthesis of silsesquioxanes.



Scheme 1.

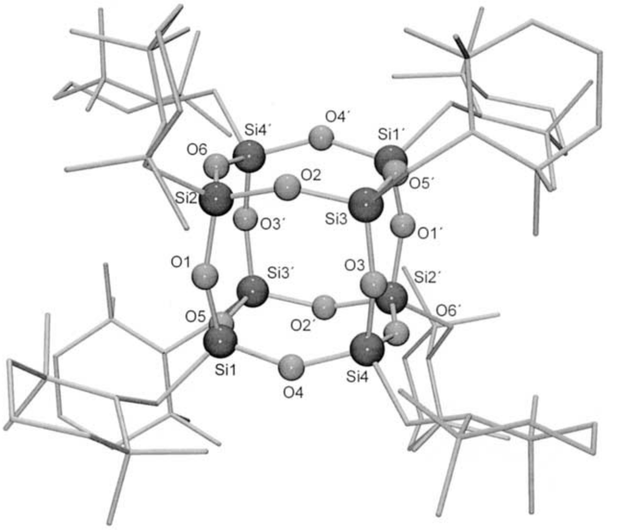


Fig. 1. Molecular structure of **1** in the crystal, showing the atomic numbering scheme of the central Si_8O_{12} skeleton. The tetramethylpiperidino groups are represented as stick models.

Table 1
Crystal data and experimental parameters for the crystal structure analysis of **1**

Empirical formula	$C_{80}H_{160}N_8O_{12}Si_8$
Formula (g mol^{-1})	1650.88
Temperature (K)	173(2)
λ (Mo–K$_\alpha$) (Å)	0.71073
Crystal system	Monoclinic
Space group (no.)	$P2_1/n$ (14)
Unit cell dimensions	
a (Å)	12.7998(11)
b (Å)	18.1310(13)
c (Å)	21.434(2)
β (°)	103.002(12)
V (Å^3)	4846.8(8)
Z	2
$D_{calc.}$ (g cm^{-3})	1.131
μ (mm^{-1})	0.167
$F(000)$	1808
Crystal dimensions (mm)	0.6 × 0.3 × 0.3
2θ range (°)	4.50–54.18
Index ranges	$-16 \leq h \leq 16$, $-23 \leq k \leq 23$, $-27 \leq l \leq 27$
Reflections collected	57 721
Independent reflections	10 229 [$R_{int} = 0.0428$]
No. of reflections used	10 229
No. of restraints	0
No. of parameters	503
S [a]	1.040
Weight parameters a/b [b]	0.0576/0.7729
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0361$ [c]; wR_2 (all data) = 0.0986 [d]
Max./min. residual electron density (e Å^{-3})	+0.294 and −0.327

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; n = no. of reflections; p = no. of parameters.

[b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

[c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[d] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

Compounds **1** and **2** were isolated as crystalline solids, and their identities were established by elemental analyses (C, H, N) and solution (^1H,^{13}C,^{29}Si) and solid-state (^{29}Si) NMR studies. In addition, the octasilsesquioxane **1** was structurally characterized by single-crystal X-ray diffraction.

Compound **1** crystallizes in the space group $P2_1/n$. The molecular structure of **1** in the crystal is depicted in Fig. 1. The crystal data and the experimental parameters used for the crystal structure analysis are summarized in Table 1 (for further details, see Section 3). Selected interatomic distances and angles of **1** are listed in Table 2.

The cage-like molecular structure of **1** is characterized by C_i symmetry. The Si-coordination polyhedra around the four crystallographically independent silicon atoms are slightly distorted tetrahedra [O–Si–O angles, 108.22(6)–109.73(6)°; O–Si–C angles, 105.75(6)–112.97(6)°]. The Si–O distances are in the range

1.6044(11)–1.6197(10) Å, and the Si–C distances amount to 1.8608(15)–1.8655(13) Å.

The solid-state ^{29}Si VACP/MAS-NMR spectrum of **1** is compatible with the molecular C_i symmetry established by the crystal structure analysis. As shown in Fig. 2, three resonance signals were observed [isotropic chemical shifts: $\delta = -70.5$, -71.3 (two-fold intensity, two non-resolved sites), and -72.4]. In solution (solvent C_6D_6) only one ^{29}Si resonance signal ($\delta = -70.8$) was observed as would be expected for a molecular structure with O_h symmetry (Fig. 2). This finding is in accordance with the results of the solution ^{1}H- and ^{13}C-NMR studies (see Section 3).

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths			
Si1–O1	1.6044(11)	O4–Si1–C1	111.57(6)
Si1–O4	1.6197(10)	O5–Si1–C1	107.47(6)
Si1–O5	1.6130(10)	O1–Si2–O2	108.84(6)
Si1–C1	1.8608(15)	O1–Si2–O6	108.50(6)
Si2–O1	1.6146(12)	O2–Si2–O6	109.34(6)
Si2–O2	1.6116(10)	O1–Si2–C21	108.20(6)
Si2–O6	1.6167(11)	O2–Si2–C21	112.02(6)
Si2–C21	1.8616(14)	O6–Si2–C21	109.86(6)
Si3–O2	1.6162(10)	O2–Si3–O3	108.38(6)
Si3–O3	1.6177(11)	O2–Si3–O5′	108.85(6)
Si3–O5′	1.6071(11)	O3–Si3–O5′	109.40(6)
Si3–C31	1.8655(13)	O2–Si3–C31	108.01(6)
Si4–O3	1.6131(11)	O3–Si3–C31	110.93(6)
Si4–O4	1.6177(10)	O5′–Si3–C31	111.19(6)
Si4–O6′	1.6135(11)	O3–Si4–O4	109.73(6)
Si4–C41	1.8638(15)	O3–Si4–O6′	108.81(6)
Bond angles			
O1–Si1–O4	108.47(6)	O4–Si4–O6′	108.22(6)
O1–Si1–O5	108.98(6)	O3–Si4–C41	112.97(6)
O4–Si1–O5	108.73(6)	O4–Si4–C41	105.75(6)
O1–Si1–C1	111.56(6)	O6′–Si4–C41	111.22(6)

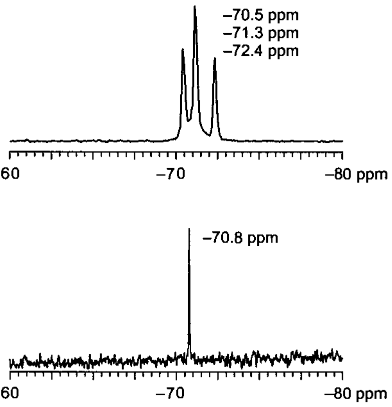


Fig. 2. ^{29}Si-NMR spectra of compound **1** in the solid state (top; VACP/MAS-NMR) and in solution (bottom; solvent C_6D_6).

3. Experimental

3.1. Syntheses

3.1.1. General procedures

All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in sealed capillaries. The ^{1}H, ^{13}C, and ^{29}Si solution NMR spectra were recorded at 22 °C on a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz), C_6D_6 was used as solvent. Chemical shifts (ppm) were determined relative to internal C_6D_5H (^{1}H, $\delta = 7.28$), internal C_6D_6 (^{13}C, $\delta = 128.0$), or external Me_4Si (^{29}Si, $\delta = 0$). Assignment of the ^{13}C-NMR data was supported by DEPT 135 experiments. Solid-state ^{29}Si VACP/MAS-NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO_2 (diameter 7 mm) containing ca. 300 mg of sample [79.5 MHz; Me_4Si as external standard ($\delta = 0$); spinning rate, 5 kHz; contact time, 5 ms; 90° ^{1}H transmitter pulse length, 3.6 μs; repetition time, 4 s].

3.1.2. Octakis[(2,2,6,6-tetramethylpiperidino)-methyl]octasilsesquioxane (**1**)

Water (40 mg, 2.22 mmol) was added to a solution of **2** (2.00 g, 6.59 mmol) in CH_2Cl_2 (10 ml) at room temperature and the reaction mixture then kept undisturbed for 2 h at the same temperature (formation of crystals at the surface and predominantly at the CH_2Cl_2–water interface). The solid was isolated by removal of the CH_2Cl_2–water system by a syringe, and water (40 mg, 2.22 mmol) was added to this liquid system (again formation of crystals at the surface and CH_2Cl_2–water interface). This procedure was repeated three times, and all solid crops obtained in the five single steps were combined and then dried in vacuo (0.01 Torr, 1 h) at 100 °C. Recrystallization of this solid crude product from toluene–EtOH [addition of EtOH (80 ml) to a solution of the solid in toluene (80 ml) at room temperature] gave compound **1** in 43% yield as a colorless crystalline product (580 mg, 351 μmol); m.p. > 350 °C. ^{1}H-NMR (C_6D_6): δ 1.37 (s, 96 H, CCH_3), 1.64–1.78 (m, 48 H, CCH_2C), 2.50 (s, 16 H, $SiCH_2N$). ^{13}C-NMR (C_6D_6): δ 17.0 ($NCC\mathit{C}H_2C$), 25.7 (br, $\mathit{C}CH_3$), 29.5 ($SiCH_2N$), 40.2 ($NC\mathit{C}H_2C$), 62.5 ($N\mathit{C}CC_3$). ^{29}Si-NMR (C_6D_6): δ -70.8. ^{29}Si VACP/MAS-NMR: δ -70.5, -71.3 (two-fold intensity), -72.4. Anal. Calc. for $C_{80}H_{160}N_8O_{12}Si_8$ (1650.9): C, 58.20, H, 9.77, N, 6.79. Found: C, 58.0, H, 9.8, N, 6.8%.

3.1.3. *Reisolation of* **2**

The volatile components of the CH_2Cl_2–water system isolated in the synthesis of **1** (see above) were removed under reduced pressure, and the resulting residue was then heated at 100 °C/0.01 Torr for 1 h in a Kugelrohr distillation apparatus operating at 15 rpm (removal of CH_2Cl_2, water, and ethane-1,2-diol) to give **2** in 28% yield (related to **2** used for the synthesis of **1**) as an almost analytically pure colorless solid (550 mg, 1.81 mmol). This product could be directly used again for the synthesis of **1** following the procedue described above [8].

3.1.4. *Bis[ethane-1,2-diolato(2-)][(2,2,6,6-tetramethylpiperidinio)methyl]silicate* **(2)**

A mixture of **3** (2.00 g, 7.71 mmol) and ethane-1,2-diol (957 mg, 15.4 mmol) was kept for 2 h at 100 °C and ambient pressure in a Kugelrohr distillation apparatus operating at 15 rpm [collection of the MeOH formed in a cooled (−78 °C) distillate receiver]. After the residue was cooled to room temperature, a crystalline product was formed. Recrystallization from toluene–petroleum ether (40–60 °C) [addition of petroleum ether (140 ml) to a solution of the solid in toluene (100 ml) at room temperature] gave compound **2** in 86% yield as a colorless crystalline solid (2.02 g, 6.66 mmol); m.p. 151 °C (dec.). The solution ^{1}H-, ^{13}C-, and ^{29}Si-NMR data (solvent $CDCl_3$) and the ^{29}Si VACP/MAS-NMR data of the product were identical with those reported in Ref. [7]. Anal. Calc. for $C_{14}H_{29}NO_4Si$ (303.5): C, 55.41, H, 9.63, N, 4.62. Found: C, 55.2, H, 9.8, N, 4.5%.

3.1.5. *Dimethoxy(methyl)[(2,2,6,6-tetramethylpiperidino)methyl]silane* **(3)**

This compound was synthesized according to Ref. [6].

3.2. *Crystal structure analysis*

A suitable single crystal of **1** was obtained directly from the reaction mixture (see preparation). The crystal was mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer [Stoe IPDS; graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å)]. The structure was solved by direct methods [9] and refined by full-matrix least-squares on F^2 with all unique reflections [10]. For the hydrogen atoms, a riding model was employed.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 167158 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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