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Synthesis and Structure of a Tetrahydroxydisilane and a Trihydroxycyclotrisiloxane with All the OH Functions in cis Position[†]

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Summary: The reaction of the tetrachlorodisilane $R_2Si_2Cl_4$ ($R = CH(SiMe_3)_2$) with a mixture of $H_2O_2/H_2O/$toluene resulted in the formation of the tetrahydroxydisilane $R_2Si_2(OH)_4$. However the corresponding tetraaminodisilane $R_2Si_2(NH_2)_4$ reacted under the same conditions to yield a trihydroxycyclotrisiloxane $(RSi(OH)O)_3$ ($R = CH(SiMe_3)_2$). The structures of both products were determined by X-ray crystallography. The latter structure is reminiscent of that of a calixarene with an inverse conic shape.

Introduction

Many silanols,[1] silandiols,[2] silantriols,[3] and the aliphatic[4] and cyclic[5] condensation products have been prepared, mostly by hydrolysis of the corresponding chlorosilanes.

We report here the preparation of the tetrahydroxydisilane **3** and the trihydroxycyclotrisiloxane **4** by the reaction of 1,2-bis[bis(trimethylsilyl)methyl]-1,1,2,2-tetrachlorodisilane, **1** (Scheme 1), and 1,2-bis[bis(trimethylsilyl)methyl]-1,1,2,2-tetraaminodisilane, **2**, respectively (Scheme 2) with hydrogen peroxide. The structures of both products were determined by X-ray crystallography. Both show new structural types in the series of silanols and siloxanes.

1,2-Bis[bis(trimethylsilyl)methyl]-1,1,2,2-tetrahydroxydisilane, **3**, consists of a disilane with each silicon containing two hydroxy groups. Compound **3** was also obtained by the reaction of **2** with water in refluxing tetrahydrofuran[6] (Scheme 1), while compound **1** shows no reaction with water. The conversion of **2** to **3** with water is due to the easy cleavage of the Si−N bonds under elimination of ammonia. Obviously the ammonia reacts with the acidic protons to yield partly the NH_4 salt of **3** in solution. Therefore we were not able to grow single crystals of **3** prepared by this procedure for a structural analysis. For this reason we developed the new method using aqueous hydrogen peroxide, which was used in the preparation of **3** as well as of **4**. In this system no salt formation is possible. 1,3,5-Tri[bis(trimethylsilyl)methyl]-1,3,5-trihydroxycyclotrisiloxane, **4**, consists of a six-membered ring with alternating silicon and oxygen atoms and a hydroxy group on each silicon atom.

Results and Discussion

Only the important physical data of compounds **3** and **4** are discussed here. The ^1H, ^{13}C, and ^{29}Si resonances of the organic ligands are in the typical range. In the ^1H NMR spectra the protons of the hydroxy groups were observed as broad singlets at 3.55 (**3**) and 5.20 ppm (**4**). The ^{29}Si NMR spectra exhibit the resonances of the hydroxy-carrying silicon atoms at −7.4 (**3**) and −21.8 ppm (**4**). The IR spectrum of compound **3** gave the absorptions of the hydroxo groups at 3361 and 850 cm^{-1}. In the IR spectrum of **4** the absorptions of the ring vibrations are tentatively assigned to 1071 and 1023 cm^{-1}. Moreover the stretching mode of the hydroxo groups is found at 3342 cm^{-1}, while the frequency of the Si−OH bending mode appears at 861 cm^{-1}.[7]

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[†] Dedicated to Professor Ionel Haiduc on the occasion of his 65th birthday.

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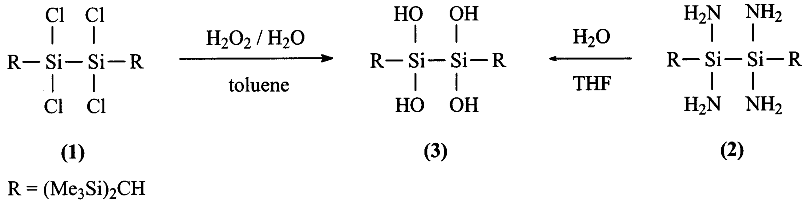
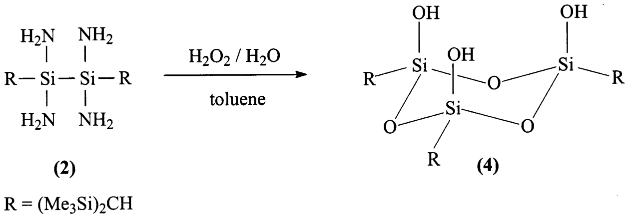
Scheme 1



Scheme 2



The single-crystal structural analysis of $3\cdot{}^1/_2CH_3OH\cdot{}^1/_8C_6H_6$ shows a $Si_2(OH)_4$ core as the central unit of the molecule. The tetrahedral coordination sphere of each silicon center is completed by a bis(trimethylsilyl)methyl group (Figure 1). The molecule exhibits an anti-clinal conformation. The Si−Si bond length is 2.398(1) Å. Similar Si−Si bond lengths are found in $R_2Si_2Cl_4$ (R = $CH(SiMe_3)_2$) (2.380(2) Å), $R_2Si_2I_4$ (R = $CH(SiMe_3)_2$) (2.423(2) Å), $R_2Si_2(NH_2)_4$ (R = $CH(SiMe_3)_2$) (av 2.3790 Å), and (R = Cp*) (2.3693(14) Å).[6] The average O−Si−O angle is 105.90°, which is comparable to the X−Si−X angle in $R_2Si_2Cl_4$ (R = $CH(SiMe_3)_2$) (av 104.08°), $R_2Si_2I_4$ (R = $CH(SiMe_3)_2$) (av 105.75°), $R_2Si_2(NH_2)_4$ (R = $CH(SiMe_3)_2$) (av 107.18°), and (R = Cp*) (av 106.23°).[6] In the crystal four molecules of **3** and two molecules of methanol are bridged by 12 hydrogen bonds (Figure 2).

Compound **4** crystallizes in the trigonal space group $P\bar{3}$. The core of the structure is a six-membered Si_3O_3 ring in a chair conformation, with O and Si atoms occupying alternating sites. To complete the tetrahedral coordination sphere, each Si atom in the ring is connected to a hydroxy group and a bis(trimethylsilyl)methyl substituent. All OH groups are oriented in the same direction with respect to the ring plane (Figure 2). This is the same arrangement as in the iso-structural $(RSi(OH)NH)_3$ (R = $(Me_3Si)_2CH$) (**5**)) recently reported.[8] Therefore compounds **4** and **5** can be considered analogues of calixarenes, however, with an inverted conic shape.[9] The endocyclic O−Si distance is 1.642 Å (Si−N: 1.704 Å (**5**)), and the angles are 105.95° for O−Si−O (N−Si−N: 104.55° (**5**)) and 130.46° for Si−O−Si (Si−N−Si: 131.25° (**5**)). The distance between the silicon in the ring and the connecting oxygen is 1.639 Å (1.673 Å (**5**)). In the crystal packing two molecules are bridged by six hydrogen bonds (Figure 3). The O−H···O distance was calculated on 1.900 Å (1.952 Å (**5**)). The O−H−O arrangement is nearly linear with an angle of 168° (173° (**5**)).

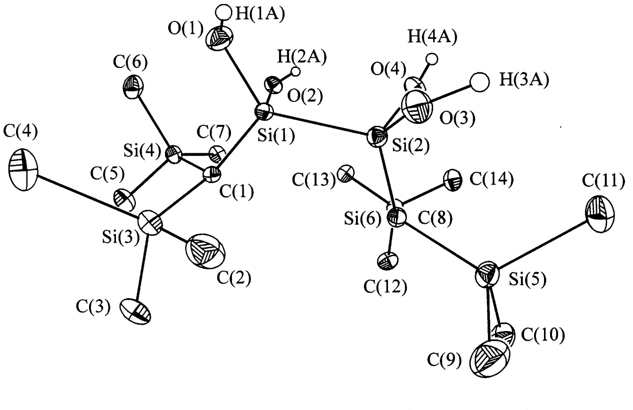


Figure 1. Molecular structure of $3\cdot{}^1/_2CH_3OH\cdot{}^1/_8C_6H_6$ in the crystal (50% thermal probability ellipsoids). Selected bond lengths (Å) and angles (deg): Si(1)−Si(2) 2.398(1), Si(1)−O(1) 1.664(3), Si(1)−O(2) 1.644(3), Si(1)−C(1) 1.858(3); O(1)−Si(1)−O(2) 104.68(15), O(1)−Si(1)−C(1) 108.64(15), O(2)−Si(1)−C(1) 108.04(15), C(1)−S1(1)−Si(2) 118.79(11).

Summary

In summary we have shown that aqueous hydrogen peroxide is an interesting reagent for the preparation of cyclic and acyclic Si−OH compounds using Si−Cl- or Si−NH_2-containing precursors to yield new types of silanols and siloxanes. Obviously the very different reaction products **3** and **4** that are formed using H_2O_2 are a result of changing the redox potential by forming HCl and NH_3, respectively, during the progress of the reactions. The redox potential of H_2O_2 changes from the alkaline (0.867 V) to the acidic (1.763 V) media.

To the best of our knowledge these properties of H_2O_2 have not been used for the preparation of organometallic compounds in aqueous solutions and are an interesting perspective for further reactions.

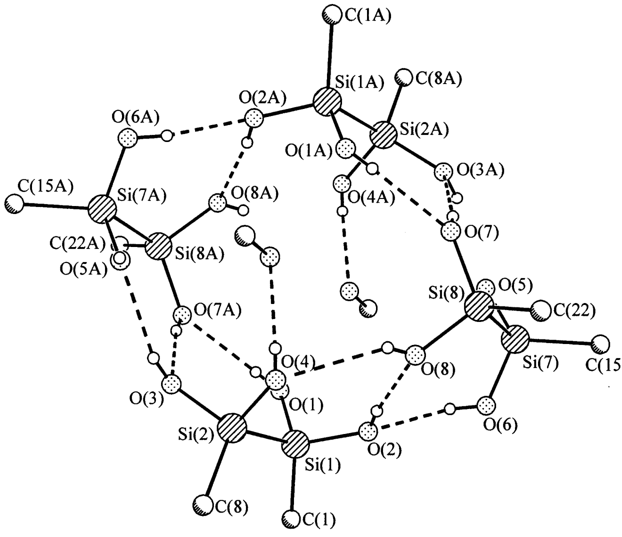


Figure 2. The structure contains four molecules of **3** and two molecules of methanol with hydrogen bridging bonds in the crystal. The organic ligands are not shown.

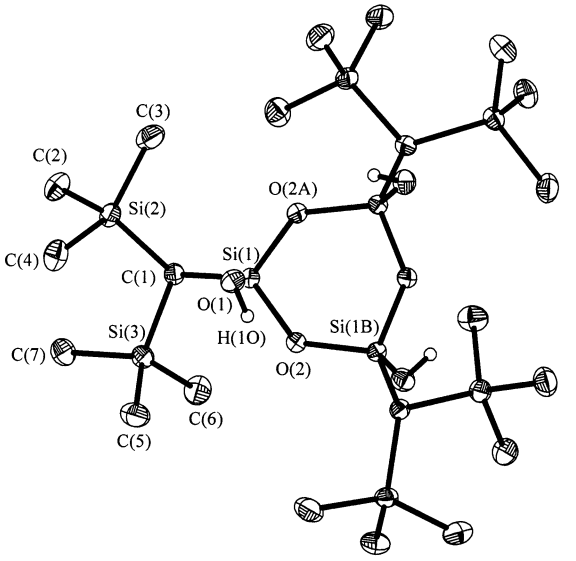


Figure 3. Molecular structure of **4** in the crystal (50% thermal probability ellipsoids). Selected bond lengths (Å) and angles (deg): Si(1)−O(1) 1.639(2), Si(1)−O(2) 1.642(2), Si(1)−C(1) 1.831(2); O(1)−Si(1)−O(2) 107.41(7), O(1)−Si(1)−C(1) 109.46(8), O(2)−S1(1)−O(2A) 105.95(9), Si(1)−O(2)−Si(1B) 130.46(9). Symmetry transformations for the equivalent atoms: A: −*y*, *x*−*y*, *z*; B: −*x*+*y*, −*x*, *z*.

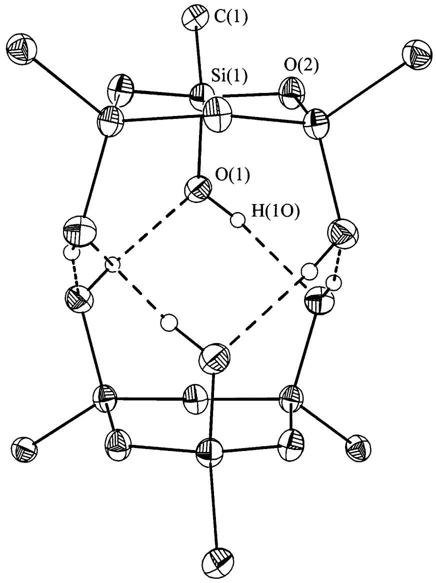


Figure 4. The structure contains two molecules of **4** without the organic ligands, but with the hydrogen bridging bonds in the crystal.

Experimental Section

Synthesis of 3 and 4. To a solution of **1** (1.00 g, 1.94 mmol) (**2**, 1.00 g, 2.28 mmol) in toluene (50 mL) was added a hydrogen peroxide solution (10 mL, 30% in water). After stirring for 72 h the mixture was filtered and the two phases were separated in a separatory funnel. The water phase was extracted three times with toluene (20 mL). The solvents of the combined organic phases were removed under vacuum. Benzene/methanol (20 mL, 9:1) (for **4** benzene, 20 mL) was added to the crude product, and after slow crystallization at room temperature **3** (0.65 g, 1.47 mmol, 76%) (**4**, 0.69 g, 1.04 mmol, 68%) was obtained as colorless crystals suitable for X-ray crystal structural analysis. For the other analytical investigations the crystals were ground and stored under vacuum for 5 h to remove the solvent molecules.

Table 1. Crystallographic Data for 3·$^1/_2$CH$_3$OH·$^1/_8$C$_6$H$_6$ and 4

empirical formula	2 $C_{14}H_{42}O_4Si_6\cdot CH_3OH\cdot {}^1/_4C_6H_6$	$C_{21}H_{60}O_6Si_9$
fw	937.60	661.50
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{3}$
unit cell dimens [Å, deg]	$a = 12.6748(13)$	$a = 13.3609(19)$
	$b = 15.7437(17)$	$b = 13.3609(19)$
	$c = 15.8571(15)$	$c = 12.508(3)$
	$\alpha = 63.077(7)$	$\alpha = 90$
	$\beta = 82.138(8)$	$\beta = 90$
	$\gamma = 79.484(8)$	$\gamma = 120$
cell volume [Å^3]	2768.6(5)	1933.7(5)
Z	2	2
density(calcd) [g/cm^3]	1.125	1.136
abs coeff [mm^{-1}]	0.319	0.338
θ range for data collection [deg]	1.54−24.71	1.76−22.19
limiting indices	$-14 \le h \le 14$	$-14 \le h \le 11$
	$-15 \le k \le 18$	$-14 \le k \le 13$
	$-18 \le l \le 18$	$-11 \le l \le 13$
no. of reflns colld	16811	3689
no. of ind reflns	8662 [$R_{int} = 0.0701$]	1610 [$R_{int} = 0.0393$]
no. of data/restraints/params	8662/3/514	1610/1/119
goodness-of-fit on F^2	$S = 1.055$	$S = 1.066$
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0551	R1 = 0.0288
	wR2 = 0.1647	wR2 = 0.0787
R indices (all data)	R1 = 0.0671	R1 = 0.0338
	wR2 = 0.1736	wR2 = 0.0806
largest diff peak and hole [e·Å^{-3}]	1.169 and −1.010	0.316 and −0.182

Characterization Data for 3. Mp: 148 °C. ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ −0.40 (s, 2 H, CH(SiMe$_3$)$_2$), 0.14 (s, 36 H, Si(CH$_3$)$_3$), 3.55 (br s, 4 H, OH). ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ 3.1 (Si(CH$_3$)$_3$), 8.7 (CH(SiMe$_3$)$_2$). ^{29}Si NMR (50 MHz, CDCl$_3$, TMS): δ −7.4 (Si(OH)$_2$), −0.6 (SiMe$_3$). IR (KBr, Nujol): $\tilde{\nu}$ 3631, 3348, 1301, 1251, 1062, 1025, 1007, 857, 845, 777, 723, 681, 551, 429 cm^{-1}. MS (EI): *m*/*e* (%) 393 (50) [M$^+$ − 2 OH − Me], 379 (45) [M$^+$ − 3 Me − H$_2$O], 203 (100) [$^1/_2$M$^+$ − H$_2$O]. Anal. Calcd for $C_{14}H_{42}O_4Si_6$ (443.00): C, 38.0; H, 9.6; Si, 38.0. Found: C, 38.0; H, 9.6; Si, 38.5.

Characterization Data for 4. Mp: 90 °C. ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ −0.53 (s, 3 H, CH(SiMe$_3$)$_2$), 0.11 (s, 54 H, Si(CH$_3$)$_3$), 5.20 (br s, 3 H, OH). ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ 1.0 (CH(SiMe$_3$)$_2$), 2.5 (Si(CH$_3$)$_3$). ^{29}Si NMR (100 MHz, CDCl$_3$, TMS): δ −21.8 (Si(OH)), −0.2 (SiMe$_3$). IR (KBr, tablet): $\tilde{\nu}$ 3668, 3342, 2956, 2901, 1550, 1404, 1252, 1071, 1023, 861, 805, 682, 552, 470, 442 cm^{-1}. MS (EI): *m*/*e* (%) 645 (2) [M$^+$ − Me], 597 (4) [M$^+$ − 3 Me − H$_2$O], 443 (32) [M$^+$ − SiCH(SiMe$_3$)$_2$ − 2 Me], 393 (100) [M$^+$ − OSiCH(SiMe$_3$)$_2$ − 2 Me − 2 OH]. Anal. Calcd for $C_{21}H_{60}O_6Si_9$ (661.47): C, 38.1; H, 9.1; Si, 38.2. Found: C, 38.3; H, 8.9; Si, 37.3.

X-ray Structure Determination of 3 and 4. The crystals were mounted on glass fibers in rapidly cooled mineral oil. Diffraction data were collected on a Stoe IPDS II at 133(2) K with graphite-monochromated Mo Kα radiation (λ = 0.71073

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Å) performing ω scans. The structure was solved by direct methods using SHELXS-97[10] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[11] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. Other details of the data collection, structure solution, and refinement are listed in Table 1.

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Supporting Information Available: Tables of crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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