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The First Niobasilsesquioxanes[§]

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Synthetic routes leading to the first polyhedral oligosilsesquioxane derivatives incorporating niobium are reported. Tetrasilanol $(c\text{-}C_6H_{11})_6Si_6O_7(OH)_4$ (**2**), for which an improved laboratory-scale synthesis is reported, cleanly reacts with $Nb(OEt)_5$ to afford the dinuclear niobasilsesquioxane $[(c\text{-}C_6H_{11})_6Si_6O_{11}\text{-}NbOEt]_2$ (**3**), which slowly converts to the tetranuclear μ-oxo species **4** in the presence of moisture. A structurally different μ-ethoxy-bridged dinuclear niobasilsesquioxane, $[(c\text{-}C_6H_{11})_7Si_7O_{12}NbOEt(\mu\text{-}OEt)]_2$ (**6**), is readily accessible from $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ (**5**) and $Nb(OEt)_5$. The molecular structures of **2**, **3**, **4**, and **6** have been determined by X-ray diffraction.

Introduction

Incompletely condensed silsesquioxanes[1] form an interesting class of Si−O cage compounds representing partial structures of the silica surface used to support heterogeneous catalysts. Metallasilsesquioxanes[2] derived from these species have been found to effectively catalyze the polymerization and epoxidation of olefins.[2d] The "Periodic Table of Metallasilsesquioxanes"[2e] already covers numerous metallic elements ranging from alkaline metals[2,3] through early[2,4] and late transition metals[2,5] to the lanthanide elements.[2,6] Surprisingly, niobium represents one of the elements for which no metallasilsesquioxane derivatives are known to date, although the first silanediolates and disiloxanediolates of niobium have already been reported by Roesky in 1994[7] and Sullivan in 1997.[8] Also known in the literature are some niobium species containing the bulky tBu_3SiO^- (= silox) ligand. Especially remarkable is the PC bond cleavage of $(silox)_3NbPMe_3$ under dihydrogen leading to $(silox)_3Nb{=}CH_2$, $(silox)_3Nb{=}PH$ or $(silox)_3NbP(H)(silox)_3Nb$, and CH_4.[9] This unusual reactivity clearly demonstrates the need for further work on niobium siloxides. Here we report a facile synthetic route to niobasilsesquioxanes starting from commercially available $Nb(OEt)_5$.

Experimental Section

General Comments. Preparation of the niobium compounds and handling of reagents were performed under an atmosphere of dry nitrogen or argon using standard Schlenk techniques or a glovebox where the O_2 and H_2O levels were usually kept below 1 ppm. All glassware was oven-dried at 140 °C for at least 24 h, assembled while hot, and cooled under high vacuum prior to use. Toluene was dried over Na/benzophenone and freshly distilled prior to use. $Nb(OEt)_5$ (Strem) was used as received; $(c\text{-}C_6H_{11})_6Si_6O_9$ (**1**) and $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ (**5**) were prepared according to literature procedures.[1] IR spectra were recorded using KBr pellets on a Perkin-Elmer FT-IR spectrometer system 2000 between 4000 and 400 cm^{-1}. ^1H (400 MHz), ^{13}C (101 MHz), and ^{29}Si (79.5 MHz) NMR spectra were recorded in THF-d_8 solutions on a Bruker DPX 400 spectrometer at 25 °C. Chemical shifts are referenced to TMS. Microanalyses of the compounds were performed using a Leco CHNS 923 apparatus. Melting/decomposition points were measured in sealed glass tubes with a Büchi B-450 digital melting point apparatus and are not corrected.

[§] Dedicated to Professor Erwin Weiss on the occasion of his 80th birthday.

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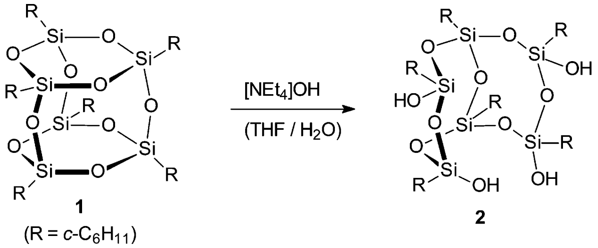
Table 1. Crystallographic Data of (c-C_6H_{11})$_6Si_6O_7(OH)_4$ (2), [(c-C_6H_{11})$_6Si_6O_{11}$NbOEt]$_2$ (3), [(c-C_6H_{11})$_6Si_6O_{11}Nb_2$(OEt)(μ-OEt)(μ-O)(THF)]$_2$ (4), and [(c-C_6H_{11})$_7Si_7O_{12}$NbOEt(μ-OEt)]$_2$ (6)

	2	**3**	**4**	**6**
formula	$C_{38}H_{75}O_{11.5}Si_6$	$C_{78}H_{142.5}Nb_2O_{24.5}Si_{12}$	$C_{52}H_{100}Nb_2O_{18}Si_6$	$C_{46}H_{87}NbO_{14}Si_7$
fw	884.52	1995.32	1367.68	1153.70
temperature (K)	183(2)	210(2)	180(2)	293(2)
cryst syst	monoclinic	tetragonal	triclinic	triclinic
space group	$P2_1/n$	$P4_2/n$	$P\bar{1}$	$P\bar{1}$
unit cell dimens (Å, deg)	$a = 12.6692(2)$ $b = 19.5522(3)$ $c = 20.8522(5)$ $\beta = 103.511(1)$	$a = 26.642(4)$ $b = 26.642(4)$ $c = 14.580(3)$	$a = 14.677(3)$ $b = 14.949(3)$ $c = 17.199(3)$ $\alpha = 104.56(3)$ $\beta = 96.05(3)$ $\gamma = 108.18(3)$	$a = 11.848(2)$ $b = 16.503(3)$ $c = 16.665(3)$ $\alpha = 100.03(3)$ $\beta = 106.87(3)$ $\gamma = 94.21(3)$
volume (Å^3)	5022.36(16)	10349(3)	3399.9(12)	3043.9(11)
Z, calcd density (g cm^{-3})	4, 1.170	4, 1.281	2, 1.336	2, 1.258
absorp coeff (mm^{-1})	0.216	0.424	0.504	0.390
F(000)	1916	4226	1444	1228
θ-range for data collection (deg)	1.95 to 27.12	2.07 to 25.95	3.52 to 30.51	3.09 to 26.83
limiting indices	$-16 \le h \le 15$, $-23 \le k \le 25$, $-24 \le l \le 26$	$-32 \le h \le 32$, $-32 \le k \le 32$, $-17 \le l \le 17$	$-20 \le h \le 20$, $-21 \le k \le 20$, $-22 \le l \le 24$	$-14 \le h \le 14$, $-19 \le k \le 20$, $-21 \le l \le 21$
no. of reflns collected/unique	31 575/11 047 [R(int) = 0.0516]	13 7493/10 097 [R(int) = 0.1178]	32 557/20 258 [R(int) = 0.0444]	35 694/12 858 [R(int) = 0.0588]
completeness to	$\theta = 27.12$, 99.6%	$\theta = 25.95$, 99.8%	$\theta = 30.51$, 97.5%	$\theta = 26.83$, 98.5%
absorp corr	none	numeric	numeric	numeric
max. and min. transmn		0.9589 and 0.8488	0.8239 and 0.7867	0.9620 and 0.9260
refinement method	full-matrix least-squares on F^2			
no. of data/restraints/params	11 047/4/511	10 097/0/556	20 258/0/722	12 858/0/865
goodness-of-fit on F^2	1.047	0.751	0.983	1.089
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0797$, $wR_2 = 0.2141$	$R_1 = 0.0395$, $wR_2 = 0.0966$	$R_1 = 0.0568$, $wR_2 = 0.1598$	$R_1 = 0.0488$, $wR_2 = 0.1027$
R indices (all data)	$R_1 = 0.1140$, $wR_2 = 0.2388$	$R_1 = 0.0905$, $wR_2 = 0.1048$	$R_1 = 0.0855$, $wR_2 = 0.1752$	$R_1 = 0.0674$, $wR_2 = 0.1095$
largest diff peak and hole (e Å^{-3})	2.940 and -0.941	0.779 and -0.315	2.985 and -1.075	0.463 and -0.653

Scheme 1



Improved Laboratory-Scale Preparation of (c-C_6H_{11})$_6Si_6O_7(OH)_4$ (2). A solution of (c-C_6H_{11})$_6Si_6O_9$ (**1**, 10.0 g, 12 mmol) and 20% aqueous NEt_4OH (11.9 g, 12 mmol) in THF (120 mL) was stirred at 25 °C for 30 min and then neutralized with dilute aqueous HCl. Evaporation of the volatiles, dissolution in Et_2O, drying over $MgSO_4$, and concentration afforded (c-C_6H_{11})$_6Si_6O_7(OH)_4$ as a white solid. Impurities of (c-C_6H_{11})$_7Si_7O_9(OH)_3$ were removed by recrystallization from pentane. Yield: 6.5 g (64%). Decomposition > 230 °C. Anal. Calc for $C_{36}H_{70}O_{11}Si_6$ (847.45 g mol^{-1}): C 51.02, H 8.33. Found: C 50.55, H 8.48. ^{1}H NMR (400 MHz, [D_8]THF, 25 °C): δ 7.29 (br s, 4H, OH), 1.73 (vbr m, 30H; CH_2, c-C_6H_{11}), 1.23 (vbr m, 30H; CH_2, c-C_6H_{11}), 0.75 (vbr m, 6H, CH, c-C_6H_{11}) ppm. ^{13}C NMR (101 MHz, [D_8]THF, 25 °C): δ 27.57, 27.48, 26.88, 26.64 (CH$_2$, c-C_6H_{11}), 23.69, 23.14 (SiCH, c-C_6H_{11}) ppm. ^{29}Si NMR (79.5 MHz, [D_8]THF, 25 °C): δ -59.4, -68.8 ppm. IR (KBr, ν (cm^{-1})): 3272 m(br), 2923 vs, 2850 s, 1448 m, 1356 vw, 1269 w, 1197 m, 1111 vs, 1038 m, 1027 m, 999 w, 913 m, 895 s, 848 m, 825 w, 757 w, 741 w, 516 m, 494 w, 461 w, 417 w.

Preparation of [(c-C_6H_{11})$_6Si_6O_{11}$NbOEt]$_2$ (3). Nb(OEt)$_5$ (0.51 g, 1.60 mmol) was added to a solution of 1.33 g (1.57 mmol) of (c-C_6H_{11})$_6Si_6O_7(OH)_4$ (**2**) in toluene (50 mL; the initially formed suspension of (c-C_6H_{11})$_6Si_6O_7(OH)_4$ was slightly heated until a clear solution had formed). The reaction mixture was stirred for 15 min, followed by refluxing for an additional 1 h. One-third of the solvent was distilled off, and cooling of the solution to 5 °C for 1 week afforded [(c-C_6H_{11})$_6Si_6O_{11}$NbOEt]$_2$ as colorless needles. Yield: 0.98 g (63.6%). Decomposition > 112 °C. IR (KBr, ν (cm^{-1})): 2975 m, 2923 s, 2850 s, 1609 w, 1558 w, 1448 m, 1379 w, 1355 w, 1268 m, 1244 m, 1195 m, 1108 vs, 1067 vs, 986 s, 924 s, 892 s, 848 m, 825 m, 807 m, 762 w, 641 w, 530 m, 514 m, 463 m, 411 m. Anal. Calc for $C_{76}H_{142}Nb_2O_{24}Si_{12}$ (1962.78 g mol^{-1}): C 46.51, H 7.29. Found: C 46.14, H 7.55. ^{1}H NMR (400 MHz, [D_8]THF, 25 °C): δ 4.35 (br s, 4H; CH_2, OC_2H_5), 2.00$-$1.50 (br m, 60H; CH_2, c-C_6H_{11}), 1.40$-$1.00 (br m, 60H; CH_2, c-C_6H_{11} + 6H, CH_3, OC_2H_5), 0.80$-$0.55 (br m, 12H, CH, c-C_6H_{11}) ppm. ^{13}C NMR (101 MHz, [D_8]THF, 25 °C): δ 74.05$-$70.01 (br, O-CH$_2$-CH$_3$), 28.89, 28.81, 28.64, 28.49, 28.40, 28.35, 28.26, 28.19, 28.09, 28.01, 27.94, 27.89, 27.82, 27.75, 27.67 (CH$_2$, c-C_6H_{11}), 25.63, 25.61, 24.94, 24.67, 24.34, 24.14(SiCH, c-C_6H_{11}), 19.29$-$17.68 (br, O-CH$_2$-CH$_3$) ppm. ^{29}Si NMR (79.5 MHz, [D_8]THF, 25 °C): δ -56.95, -61.84, -64.07, -64.91, -67.75, -68.18 ppm.

Preparation of [(c-C_6H_{11})$_7Si_7O_{12}$NbOEt(μ-OEt)]$_2$ (6). Nb(OEt)$_5$ (0.327 g, 1.027 mmol) was added to a solution of 1 g (1.03 mmol) of (c-C_6H_{11})$_7Si_7O_{12}(OH)_3$ (**5**) in toluene (50 mL; the initially formed suspension of (c-C_6H_{11})$_7Si_7O_{12}(OH)_3$ was slightly heated until a clear solution had formed). The reaction mixture was stirred for 24 h, followed by refluxing for an additional 2 h. One-third of the solvent was evaporated in vacuum, and cooling of the solution to 5 °C for 1 week afforded [(c-C_6H_{11})$_7Si_7O_{12}$NbOEt(μ-OEt)]$_2$ as colorless crystals. Yield: 0.85 g (71.5%). Decomposition > 120 °C. IR (KBr, ν (cm^{-1})): 2923 s, 2850 s, 1448 m, 1379 w, 1355 w, 1269 m, 1244 m, 1196 m, 1107 vs, 1038 m, 1026 m, 1005 s, 951 w, 914 m, 892 s, 849 m, 826 w, 742 w, 647 w, 557 w, 513 m, 469 m, 411 m. Anal. Calc for $C_{92}H_{174}Nb_2O_{28}Si_{14}$ (2307.38 g mol^{-1}): C 47.89, H 7.60. Found: C 47.34, H 7.39. ^{1}H NMR (400 MHz, [D_8]THF, 25 °C): δ 4.60$-$4.20 (br s, 8H; CH_2, OC_2H_5), 1.90$-$1.60 (br m, 70 H; CH_2, c-C_6H_{11}), 1.40$-$1.10 (br m, 70 H; CH_2, c-C_6H_{11} + 12H, CH_3, OC_2H_5), 0.80$-$0.60 (br m, 14H, CH, c-C_6H_{11}) ppm. ^{13}C NMR (101 MHz, [D_8]THF, 25 °C): δ 69.53 (br, O-CH$_2$-CH$_3$), 28.42, 28.28, 28.09, 27.74, 27.72, 27.65, 27.58 (CH$_2$, c-C_6H_{11}), 25.25, 24.25, 24.21 (SiCH, c-C_6H_{11}), 18.35 (br, O-CH$_2$-CH$_3$) ppm. ^{29}Si NMR (79.5 MHz, [D_8]THF, 25 °C): δ -67.74, -68.67, -69.47 ppm.

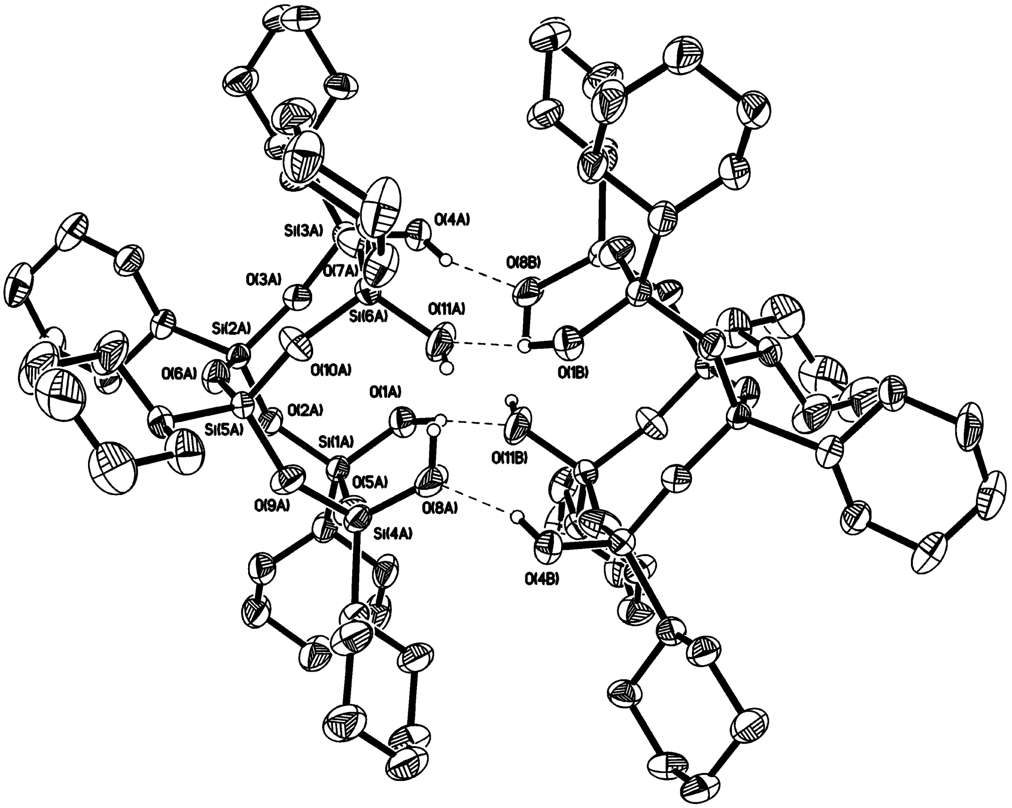
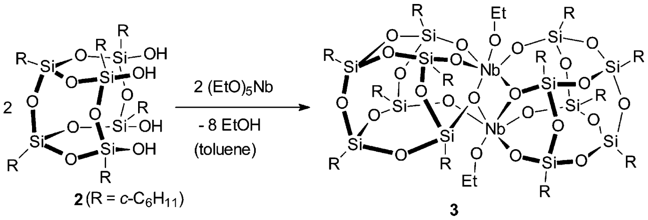


Figure 1. Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn to encompass 50% probability. Selected distances [Å] and angles [deg]: Si−O 1.607(3)−1.627(3), Si−C 1.845(4)−1.861(4), intermolecular O−O (hydrogen bonds) O1A−O11B 2.729(4), O4A−O8B 2.700(5), O8A−O4B 2.700(5), O11A−O1B 2.729(4), O−Si−O 107.70(15)−110.8(2), Si−O−Si 142.06(19)−157.1(2), O−Si−C 107.51(18)−112.86(18).

Scheme 2



Crystal Data Collection, Structure Solution, and Refinement. The intensity data of **2** were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz and polarization effects, but not for absorption effects. The data for compound **2** were collected with the Bruker COLLECT program using ω-scans. The diffraction data for the compounds **3**, **4**, and **6** were measured on a Stoe IPDS 2T diffractometer with Mo Kα radiation. The data for compounds **3**, **4**, and **6** were collected with the Stoe XAREA program using ω-scans. Numeric absorption correction was applied. The space groups were determined with the XPREP program, and the structures were solved by direct methods (SHELXS-97) and refined with all data by full-matrix least-squares methods on F^2 using SHELXL-97. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-617586 (**2**), CCDC-617587 (**3**), CCDC-617588 (**4**), and CCDC-617589 (**6**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk). Data collection parameters are given in Table 1.

Results and Discussion

One of the silsesquioxane starting materials, the tetrasilanol derivative (c-C_6H_{11})$_6Si_6O_7(OH)_4$ (**2**), is prepared by cage-opening of *closo*-(c-C_6H_{11})$_6Si_6O_9$ (**1**) in the presence of tetraethylammonium hydroxide. Compound **2** was first reported by Feher et al. and isolated in minor quantities (<0.2 g).[10] We found that the preparation of **2** according to Scheme 1 can be scaled up by a factor of about 100, leading to synthetically useful amounts of this valuable precursor.

An X-ray crystal structure determination of **2** revealed the presence of hydrogen-bonded dimers in the solid state (Figure 1). Closely related structures have been reported earlier for the corresponding tetraphenyl derivative[11] and a cyclo*heptyl*-substituted tetrasilanol, although the structure of the latter could not be fully refined due to severe disorder problems.[1d]

Commercially available niobium(V) pentaethoxide, $Nb(OEt)_5$, was found to be the reagent of choice for the straightforward preparation of niobasilsesquioxane derivatives. $Nb(OEt)_5$ cleanly reacts with **2** in a 1:1 molar ratio in toluene solution under elimination of 8 equiv of ethanol (Scheme 2). The resulting dinuclear niobasilsesquioxane derivative [(c-C_6H_{11})$_6Si_6O_{11}$-NbOEt]$_2$ (**3**) was isolated in 64% yield in the form of colorless, moderately moisture-sensitive needle-like crystals.

A ^1H NMR spectrum of **3** showed the presence of only one remaining ethoxide ligand per niobium, while the ^{29}Si NMR spectrum displayed six signals at δ −56.95, −61.84, −64.07, −64.91, −67.75, and −68.18 ppm. This pattern clearly indicated a different chemical environment for each of the six cage Si

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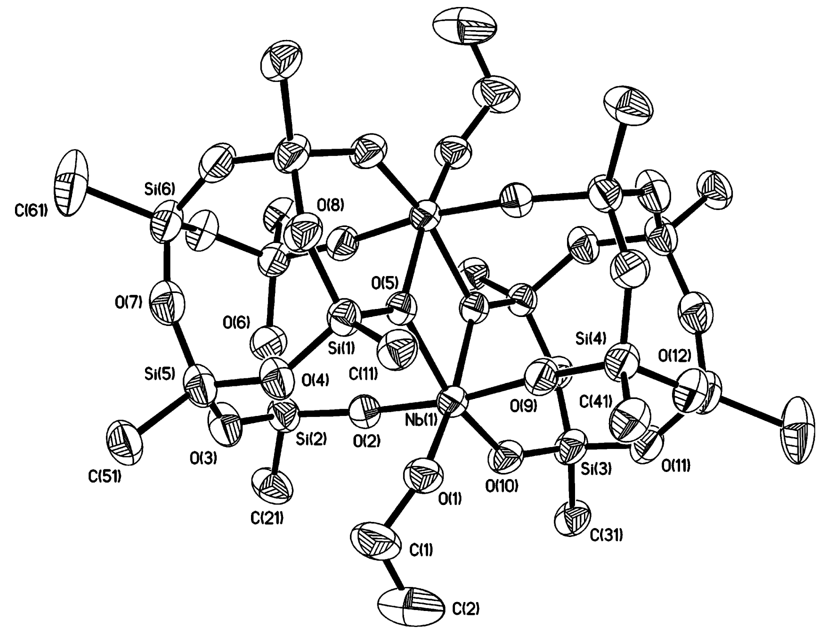


Figure 2. Perspective ORTEP view of the molecular structure of **3**. Thermal ellipsoids are drawn to encompass 50% probability. Only the *ipso*-carbon atoms of the cyclohexyl groups are shown, and the hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [deg]: Nb(1)−O(1) 1.849(3), Nb(1)−O(1) 1.890(3), Nb(1)−O(9) 1.920(3), Nb(1)−O(5) 2.161, Si−O 1.617(3)−1.659(3), Si−C 1.840(4)−1.860(4), O(9)−Nb(1)−O(10) 91.41(12), O(5)−Nb(1)−O(2) 88.01(10), O(10)−Nb(1)−O(5) 163.77(10), O(9)−Nb(1)−O(2) 172.47(11), O−Si−O 107.55(15)−110.83(16), Si−O−Si 136.12(18)−156.82(19), Nb(1)−O(10)−Si(3) 139.07(17), Nb(1)−O(9)−Si(4) 175.77(17).

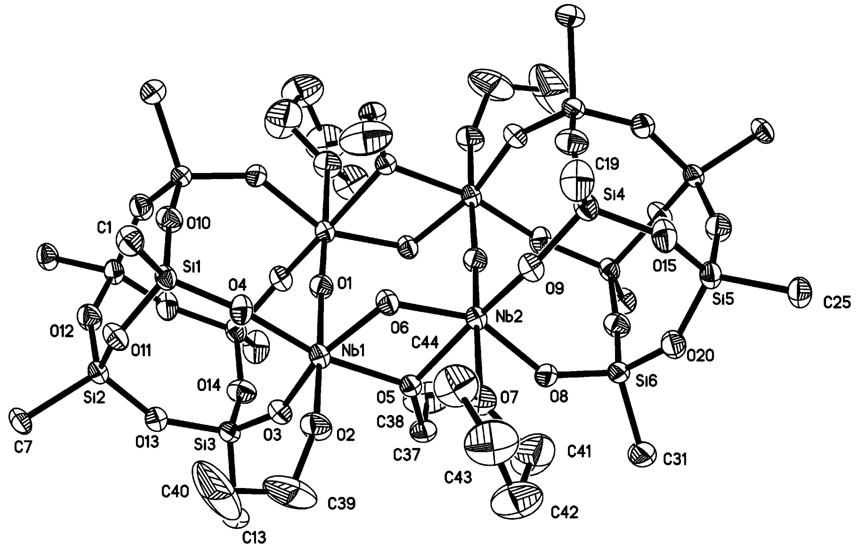


Figure 3. Perspective ORTEP view of the molecular structure of **4**. Thermal ellipsoids are drawn to encompass 50% probability. Only the *ipso*-carbon atoms of the cyclohexyl groups are shown, and the hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [deg]: Nb(1)−O(2) 1.865(2), Nb(1)−O(4) 1.899(3), Nb(1)−O(6) 1.912(2), Nb(1)−O(3) 1.947(3), Nb(1)−O(1) 2.110(2), Nb(1)−O(5) 2.110(2), Nb(1)−Nb(2) 3.2211(18), Nb(2)−O(1#) 1.775(2), Nb(2)−O(9) 1.915(3), Nb(2)−O(8) 1.941(3), Nb(2)−O(6) 1.952(2), Nb(2)−O(5) 2.113(2), Nb(2)−O(7) 2.338(3), Si−O 1.609(3)−1.629(3), O(2)−Nb(1)−O(4) 95.49(12), O(2)−Nb(1)−O(6) 96.27(11), O(4)−Nb(1)−O(6) 98.54(12), O(2)−Nb(1)−O(3) 91.12(12), O(4)−Nb(1)−O(3) 99.59(12), O(6)−Nb(1)−O(3) 159.65(11), O(2)−Nb(1)−O(1) 175.82(12), O(4)−Nb(1)−O(1) 85.75(11), O(6)−Nb(1)−O(1) 87.48(10), O(3)−Nb(1)−O(1) 84.73(10), O(2)−Nb(1)−O(5) 94.61(11), O(4)−Nb(1)−O(5) 168.09(10), O(6)−Nb(1)−O(5) 74.07(10), O(3)−Nb(1)−O(5) 86.48(11), O(1)−Nb(1)−O(5) 84.62(9), O−Si−O 108.15(15)−110.64(15).

atoms. This was verified by the X-ray diffraction analysis of **3**, which revealed the presence of a dinuclear niobasilsesquioxane. In this molecule each niobium atom adopts a highly distorted octahedral coordination geometry with the silsesquioxane tetraanions acting as bridging ligands as shown in Figure 2. Each of the two Nb atoms retains one ethoxide group as a terminal ligand.

Due to the presence of 12 cyclohexyl substituents on the outside of the molecule, compound **3** freely dissolves in THF, diethyl ether, and even toluene despite its high molecular mass of ∼2000 g/mol. Upon prolonged standing of a sample of **3** in THF-d_8 in an NMR tube, the formation of well-formed crystals was observed, which had a distinctly more compact appearance than the needle-like crystals of **3**. An X-ray structural analysis of these crystals revealed the formation of an unprecedented tetranuclear oxoniobium silsesquioxane cluster (Figure 3). In **4** two silsesquioxane cages are connected via a tricyclic $Nb_4O_4(OEt)_2$ unit, resulting in a condensed inorganic 15-ring system.

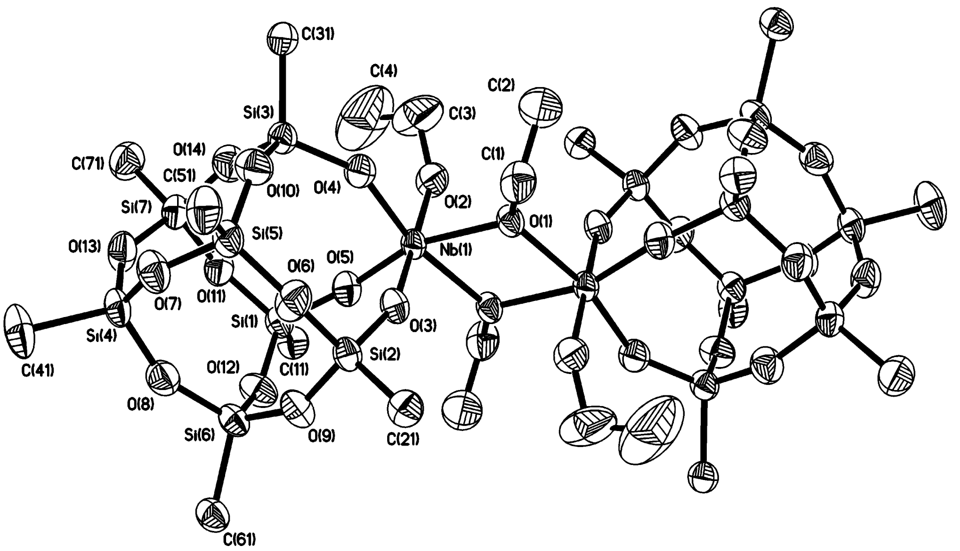
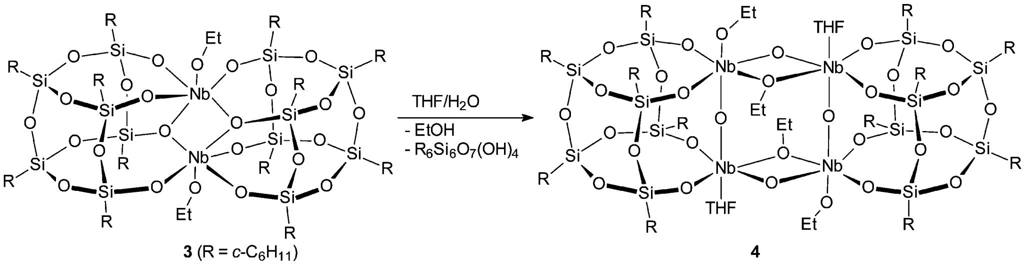
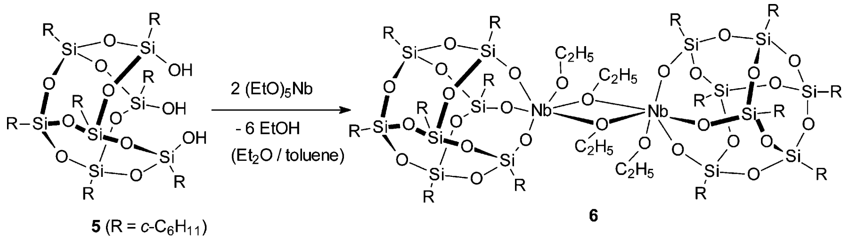


Figure 4. Perspective ORTEP view of the molecular structure of **6**. Thermal ellipsoids are drawn to encompass 50% probability. Only the *ipso*-carbon atoms of the cyclohexyl groups are shown, and the hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [deg]: Nb(1)−O(1) 2.108(2), Nb(1)−O(2−5) 1.884(2)−1.944(2), Si−O 1.610(2)−1622(2), O(2)−Nb(1)−O(5) 93.80(10), O(2)−Nb−O(4) 86.28(9), O(5)−Nb(1)−O(4) 102.28(9), O(2)−Nb(1)−O(3) 173.83(9), O(3)−Nb(1)−O(1) 70.62(8), O−Si−O 107.92(12) − 109.73(13), Si−O−Si 143.03(15)−158.15(17), Nb(1)−O−Nb(1#) 109.38(8), O(1)−Nb(1)−O(1#) 70.62(8).

Scheme 3



Scheme 4



The formation pathway leading from dinuclear **3** to tetranuclear **4** is not clear yet. However, it is reasonable to anticipate slow diffusion of moist air into the NMR sample, causing partial hydrolysis followed by condensation, as qualitatively illustrated in Scheme 3. Although this reaction could not yet be reproduced on a preparative scale, the structural result is remarkable, as it demonstrates the potential structural diversity in niobasilsesquioxane chemistry.

Apart from serendipity, structurally different niobasilsesquioxanes can also be prepared deliberately by employing the incompletely condensed trisilanol precursor **5**. Treatment of **5** with 1 equiv of Nb(OEt)$_5$ in toluene according to Scheme 4 resulted in smooth formation of the dinuclear niobasilsesquioxane $[(c\text{-}C_6H_{11})_7Si_7O_{12}NbOEt(\mu\text{-}OEt)]_2$ (**6**), which was isolated in 72% yield. The colorless crystalline solid is only slightly moisture sensitive and freely soluble in THF and toluene. In contrast to **3**, the ^{29}Si NMR spectrum of **6** shows only three resonances at δ −67.74, −68.67, and −69.47 ppm in an intensity ratio of 3:3:1.

According to an X-ray structure determination (Figure 4), compound **6** is the result of capping of the silsesquioxane cage in **5** by niobium accompanied by elimination of 3 equiv of ethanol. Subsequent dimerization occurs though two bridging ethoxide ligands to give a four-membered Nb_2O_2 ring as the central structural motif. Each niobium atom retains one terminal ethoxide ligand. These initial results show that different types of niobasilsesquioxanes are accessible in a straightforward manner using the simple, commercially available precursor Nb(OEt)$_5$. The results also indicate a high structural diversity, which should stimulate further investigations in this field.

Acknowledgment. This work was financially supported by the Otto-von-Guericke-Universität Magdeburg.

Supporting Information Available: CIF files giving X-ray structural data for **2**, **3**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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