

Discrete Oxygen Containing Oligosilane Cluster – Modelling Oxygen Defects in Silicon Nanomaterials

U. Jäger-Fiedler, M. Köckerling, H. Reinke and C. Krempner*

^a *Institut für Chemie der Universität Rostock, A.-Einstein-Str. 3a, 18059 Rostock, Germany.*

^b *Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX, 79409,*

USA. E-mail: clemens.krempner@ttu.edu

General Remarks

The manipulation of air-sensitive compounds involved standard Schlenk line and Glove box techniques. THF, THF-D₈, C₆D₆ and hydrocarbons were distilled under argon from alkali metals and stored over molecular sieves prior to use. MeSi(SiMe₃)₃ [1], MeSi(SiMe₂Cl)₃ [2] and silanetriol *l,l*-**3** [3] and ClSi[SiMe₂Si(SiMe₃)₂]₃ [4] were synthesized according to the literature procedures. The ¹H, ¹³C, ²⁹Si, ⁷Li and NMR spectra were obtained from a Bruker DPX 400 and a Bruker Avance 400 spectrometer. All measurements, unless noted otherwise, were carried out at 300 K. The ⁷Li spectra were referenced to a 0.1 M solution of LiCl in D₂O ($\delta = 0$). The ¹H DOSY NMR experiments were performed on a Bruker DRX 500 NMR instrument. UV spectroscopic measurements were performed on a Perkin Elmer Lambda 2 with quartz cells of 1.0 cm path length and spectral grade n-heptane. For UV spectroscopic measurement of the moisture sensitive lithium siloxide *l,l*-**4**, spectral grade n-heptane was distilled under argon from Na-K alloy prior to use.

Synthetic Procedures

Synthesis of MeSi[SiMe₂Si(SiMe₃)₂Me]₃ (1):

In a Schlenk flask with magnetic stirrer were placed rapidly Bu^tOK (2.134 g, 19.0 mmol) and MeSi(SiMe₃)₃ (5 g, 19.0 mmol). The flask was evaporated and refilled with argon three times, THF was added and the colored solution immediately formed was stirred overnight. After replacing the solvent by n-pentane, the resulting solution was cooled to -78°C, MeSi(SiMe₂Cl)₃ (1.868 g, 5.77 mmol) dissolved in pentane was added and stirring was continued for additional 30 min at -78°C. After the reaction mixture was allowed to warm to room temperature, water was added, the organic layer was separated and the aqueous layer was extracted twice with n-pentane. The combined organic extracts were dried over MgSO₄, filtered, the solvent was evaporated and the residue was dried in vacuum (0.01 mbar, 100°C). The solid raw product was recrystallized from acetone to give 3.9 g (86%) of MeSi[SiMe₂Si(SiMe₃)₂Me]₃ (1). The analytical data obtained were in full agreement with those reported [5].

Synthesis of HOSi[SiMe₂Si(SiMe₃)₂Me]₃ (2):

Aqueous H₂SO₄ (10%, 5 mL) was added to a stirred solution of ClSi[SiMe₂Si(SiMe₃)₂Me]₃ (200 mg, 0.25 mmol) in THF (5 mL) and the mixture was stirred for additional 3 days. Then n-pentane was added, the organic layer was separated and the aqueous layer was extracted twice with n-pentane. The combined organic extracts were dried over MgSO₄, filtered and the solvent was removed under vacuum. The solid residue was recrystallized from acetone to give 0.16 g (83%) of the title compound. ¹H NMR (C₆D₆, 400 MHz): δ 0.53 (s, SiMe₂, 18 H), 0.42 (s, SiMe, 9 H), 0.39 (s, OH, 1 H), 0.29 (s, SiMe₃, 54 H) ppm. ¹³C NMR (C₆D₆, 100.6 MHz): δ 1.4 (SiMe₂), 1.1 (SiMe₃), -10.0 (SiMe) ppm. ²⁹Si NMR (C₆D₆, 79.5 MHz): δ 15.2 (SiOH), -11.2 (SiMe₃), -32.0 (SiMe₂), -80.8 (SiMe) ppm. Anal. calc. for C₂₇H₈₂OSi₁₃ (788.051): C 41.15, H 10.49. Found C 40.89, H 10.41%.

Synthesis of MeSi[SiMe(OLi)Si(SiMe₃)₂Me]₃ (l,l-4):

6.25 mL of n-BuLi (1.6 M, 10 mmol) were added to a stirred slurry of l,l-3 (2.0 g, 2.5 mmol) and n-heptane (ca. 50 mL). The mixture was refluxed until all components were virtually dissolved. After slowly cooling the resulting hot solution to room temperature colorless

crystal began to precipitate, which were collected and dried in vacuum. Another crop of crystals could be obtained by reducing the volume of the mother liqueur to a half. Yield 1.45 g (71%). ^1H NMR (C_6D_6 , 400 MHz): δ 0.99 (s, SiMeOLi, 9 H), 0.45 (s, SiMe, 9 H), 0.40 (s, SiMe, 3 H), 0.38, 0.30 (2s, SiMe₃, 2 \times 27 H) ppm. ^{13}C NMR (C_6D_6 , 100.6 MHz): δ 11.0 (SiMeOLi), 1.4, 0.7 (SiMe₃), -9.0, -10.3 (SiMe) ppm. ^7Li NMR (toluene-D₈, 155.5 MHz): δ 0.46 (303 K), 0.45 (313 K), 0.44 (318 K), 0.43 (328 K), 0.42 (343 K), 0.40 (363 K) ppm. Anal. calc. for $\text{C}_{25}\text{H}_{75}\text{Li}_3\text{O}_3\text{Si}_{13}$ (809.80): C 37.08, H 9.34. Found C 36.91, H 9.28%.

Synthesis of *l,l*-5:

A slurry of $\text{MeSi}(\text{SiMe}_2\text{Cl})_3$ (0.12 g, 0.37 mmol), *l,l*-4 (0.3 g, 0.37 mmol) and n-heptane (10 mL) was stirred for one day at room temperature and then refluxed for ca. 10 days. After the mixture was allowed to cool to room temperature, water was added, the organic layer was separated and the aqueous layer was extracted twice with n-heptane. The combined organic extracts were dried over MgSO_4 , filtered and the solvent was removed under vacuum. The solid residue was recrystallized from acetone to give 0.15 g (38%) of *l,l*-5. Mp. 210°C. ^1H NMR (C_6D_6 , 250 MHz): δ 1.00 (s, SiMeO, 9 H), 0.52, 0.49 (2s, SiMe₂O, 2 \times 9 H), 0.42 (s, SiMe, 2 \times 9 H), 0.4, -0.10 (2s, SiMe, 2 \times 3 H), 0.37, 0.29 (2s, SiMe₃, 2 \times 27 H) ppm. ^{13}C NMR (C_6D_6 , 75.5 MHz): δ 9.0 (SiMeO), 5.7, 5.2 (SiMe₂O), 1.2, 0.9 (SiMe₃), -8.7, -10.1, -12.3 (SiMe) ppm. ^{29}Si NMR (C_6D_6 , 59.6 MHz): δ 20.0, 12.2 (SiO), -10.7, -13.1 (SiMe₃), -75.1, -79.2, -98.4 (SiMe) ppm. MS (CI, isobutene): 1006 (1) [M^+], 991 (10) [M^+ -Me], 816 (100) [M^+ -Si(SiMe₃)₂Me]. Anal. calc. for $\text{C}_{32}\text{H}_{96}\text{O}_3\text{Si}_{32}$ (1006.56): C 38.18, H 9.61. Found C 37.89, H 9.68%.

Determination of the hydrodynamic radii of **1** and *l,l*-**4**

All measurements were carried out in 2.5×10^{-3} M solutions. The viscosities of C_6D_6 ($\eta = 0.613 \text{ g s}^{-1} \text{ m}^{-1}$) at 302 K was estimated by interpolation of the data reported for C_6D_6 [6]. The hydrodynamic radii (r_H) of **1** and *l,l*-**4** were calculated graphically according to the empirically modified Stokes-Einstein equation,

$$D = \frac{kT[1 + 0.695 ((r_{\text{solv}} / r_H)^{2.234})]}{6\pi\eta r_H}$$

in which D is the diffusion coefficient, k is the Boltzmann constant, T is the temperature, r_{solv} is the van der Waals radius of the solvent ($r_{C_6D_6} = 2.70 \text{ \AA}$) [7, 8] and η is the viscosity of the solvent. Details regarding to the modified Stokes-Einstein equation can be found elsewhere [9].

Table 1. Diffusion coefficients D [$10^{-10} \times \text{m}^2 \text{s}^{-1}$]^[a] and hydrodynamic radii r_H [\AA] of **1** and *l,l*-**4**.

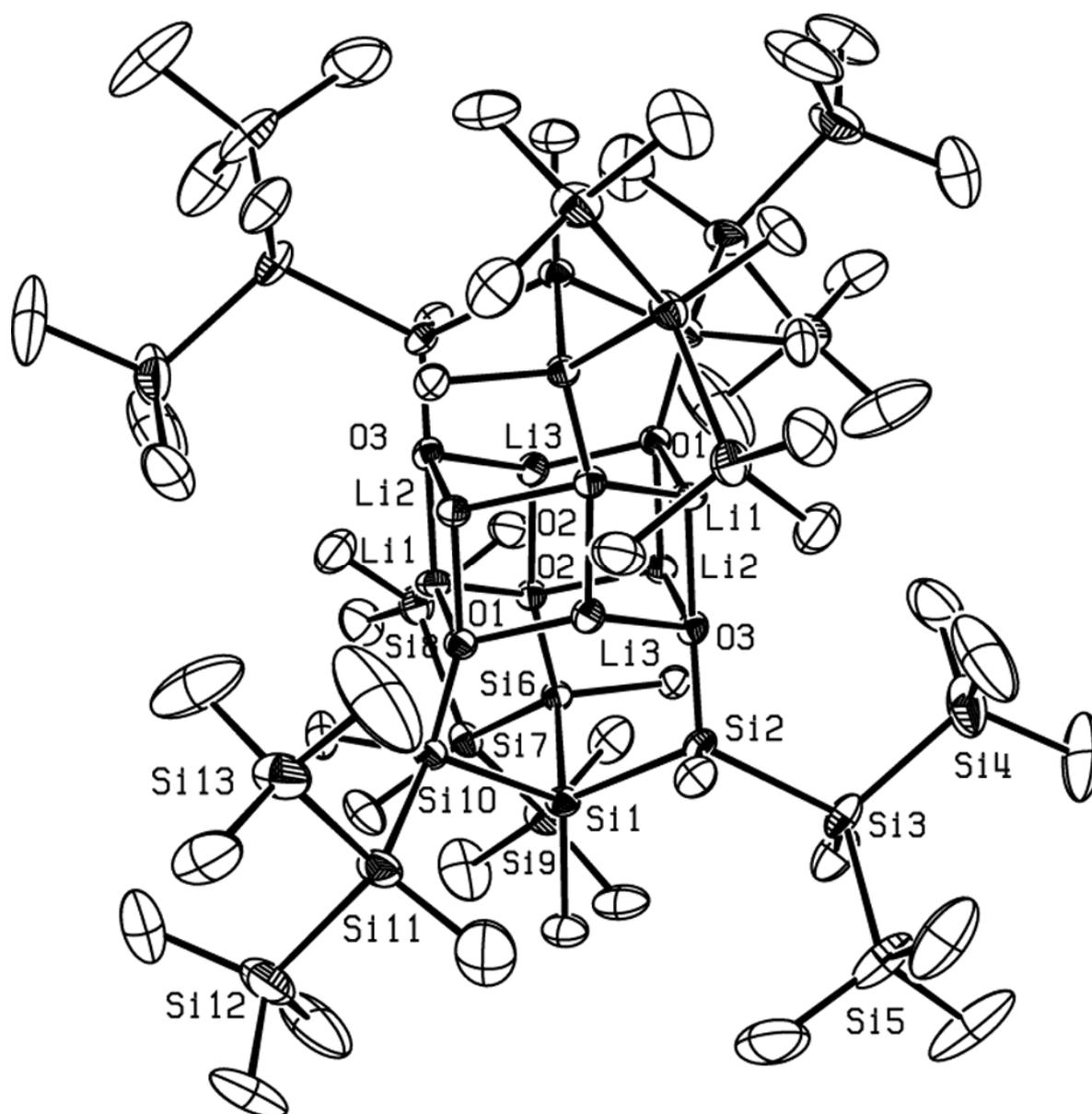
Compound	Solvent	c [mM]	T [K]	D [$\text{m}^2 \text{s}^{-1}$]	r_H [\AA]	r [\AA] ^[a]
1	C_6D_6	2.5	302	7.11	5.73	6.01
<i>l,l</i> - 4	C_6D_6	2.5	302	5.28	7.34	7.67 (dimer) 6.09 (monomer)

^[a] The volumes of **1** and *l,l*-**4** were estimated from their solid-state structures by using the software package Chem3D Ultra. From these volumes the radii were calculated by pragmatically assuming spherical shapes of the molecules.

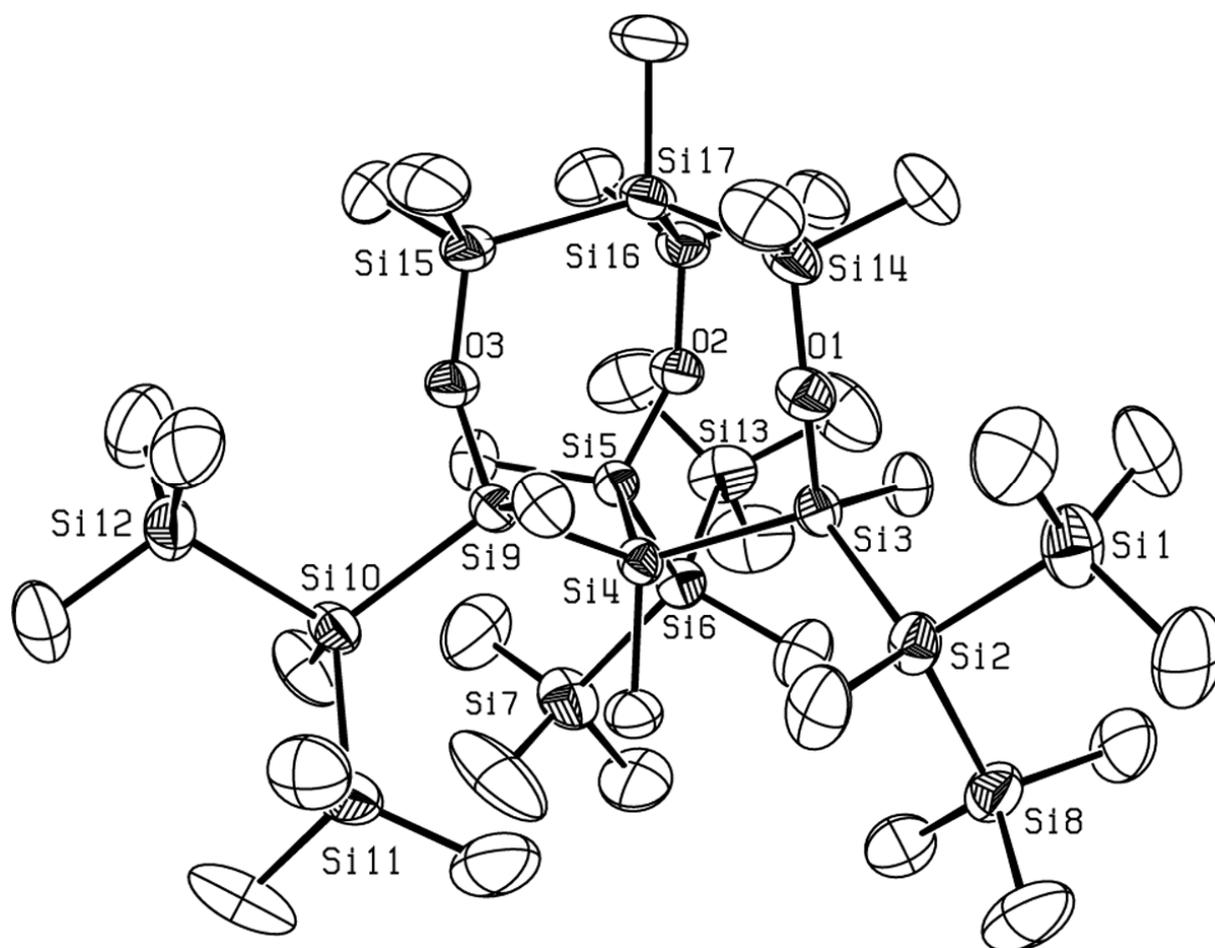
X-ray structure analyses

Transparent, colourless crystals of *l,l*-**4**, C₅₀H₁₅₀O₆Li₆Si₂₆, and *l,l*-**5**, C₃₂H₉₆O₃Si₁₇, were mounted on the tips of thin glass fibres for the single crystal X-ray diffraction measurements. Data were collected on a Bruker-Nonius Apex X8 diffractometer equipped with a CCD detector. Measurements were done using monochromatic MoK α radiation ($\lambda = 0.71073$ Å). Preliminary data of the unit cell were obtained from the reflex positions of 36 frames, measured in different directions of the reciprocal space. After completion of the data measurements the intensities were corrected for Lorentz, polarization, and absorption effects using the Bruker-Nonius software [10]. The structure solution and refinement was done with the aid of the SHELX-97 program package [11]. Structure solutions were achieved using Direct Methods. For the structure completion atom positions were derived from Difference Fourier Maps. Full-matrix least-squares refinements were used. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added on idealized positions and refined using riding models. The structure of *l,l*-**4** contains one disordered trimethylsilyl group, which was refined with two sets of atoms on split positions. Final $R1(F)$ values converged at 0.0537 for 4628 reflections with $I > 2\sigma(I)$ and $wR2(F^2) = 0.1354$ for all data (*l,l*-**4**) and $R1(F) = 0.0559$ for 9084 reflections with $I > 2\sigma(I)$ and $wR2(F^2) = 0.1883$ for all data (*l,l*-**5**).

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC-659383 for *l,l*-**4** and CCDC-642474 for *l,l*-**5**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.



Molecular structure of *l,l*-4 (thermal ellipsoids 30% probability; all hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Li1-O1 1.979(7), Li1-O2 1.886(7), Li1-Li2 2.348(9), Li1-Li3 2.337(9), Si10-O1 1.636(3), Si6-O2 1.634(2), Si2-O3 1.636(3), Li3-Li1-Li2 88.3(3), O2-Li1-O1 115.2(3), O3-Li1-O2 106.3(3), O3-Li1-O1 101.9(3), Li2-O1-Li1 75.3(3), Li3-O1-Li1 112.1(3).



Molecular structure of *l,l*-**5** (thermal ellipsoids 30% probability; all hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Si3-O1 1.655(2), Si5-O2 1.650(2), Si9-O3 1.646(2), Si14-O1 1.626(2), Si15-O3 1.634(2), Si16-O2 1.639(2), Si14-O1-Si3 152.8(1), Si16-O2-Si5 151.1(1), Si15-O3-Si9 150.0(1).

References

- [1] H. C. Marsmann, W. Raml, and E. Hengge *Zeitschrift f. Natur. B* 1980, **35B**, 1541.
- [2] U. Herzog, N. Schulze, K. Trommer, and G. Roewer *J. Organomet. Chem.* 1997, **547**, 133.
- [3] C. Krempner, U. Jäger-Fiedler, M. Köckerling, and H. Reinke *Organometallics* 2009, **28**, 382-385.
- [4] C. Krempner, and H. Reinke *Inorg. Chem. Commun.* 2006, **9**, 259.
- [5] M. Nanjo, T. Sunaga, A. Sekiguchi, and E. Horn *Inorg. Chem. Commun.* 1999, **2**, 203.
- [6] M. Holz, X. Mao, D. Seiferling, and A. Sacco *J. Chem. Phys.* 1996, **104**, 669.
- [7] A. Bondi *J. Phys. Chem.* 1964, **68**, 441.
- [8] J. T. Edwards *J. Chem. Education* 1970, **47**, 261.
- [9] C. Zuccaccia, N. G. Stahl, A. Macchioni, M.-C. Chen, J. A. Roberts, and T. J. Marks *J. Am. Chem. Soc.* 2003, **126**, 1448.
- [10] Bruker-Nonius *Inc.*, Apex-2, v. 1.6-8, Saint, v. 6.25a, SADABS – Software for the CCD detector System, Madison, WI, USA 2003.
- [11] G. M. Sheldrick, *Acta. Cryst.* 2008, *A64*, 112-122.