Notiz / Note

Synthesis and Structure of the New α-Aminosilanolate $[LiOSiMe_2(NMe_2)]_6$

Gerhard E. Herberich*, **Thomas P. Spaniol**, and **Andreas Fischer**

Institut für Anorganische Chemie, Technische Hochschule Aachen,
D-52056 Aachen, Germany

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Lithium (dimethylamino)dimethylsilanolate (**1**) is obtained from trimeric dimethylsiloxane and lithium dimethylamide in quantitative yield. In the crystal **1** is a hexamer $[LiOSiMe_2(NMe_2)]_6$ with crystallograpic C_{3i} (S_6, $\bar{3}$) symmetry. The molecule of **1** consists of a hexagonal prismatic $(LiO)_6$ core and an *N*,*O*-chelating anion.

Organolithium structural studies are currently of intense interest[1]. One α-aminosilanolate, the sterically protected tetrameric compound $[LiOSi\mathit{t}Bu_2(NMe_2)]_4$, has been described previously[2]. While working with lithium dimethylamide in THF solution we observed the formation of a new α-aminosilanolate $[LiOSiMe_2(NMe_2)]_6$ (**1**) from the amide and the silicone grease used[3]. More rationally **1** may be prepared in a simple one-pot reaction of trimeric dimethylsiloxane with lithium dimethylamide. This method should be suitable for the preparation of a wide range of α-aminosilanolates.

$$2\ (Me_2SiO)_3 + 6\ LiNMe_2 \rightarrow \underset{\mathbf{1}}{[LiOSiMe_2(NMe_2)]_6}$$

The crystal structure of **1** has been determined by X-ray diffraction. A hexameric aggregate was found with crystallographic C_{3i} (S_6, $\bar{3}$) symmetry. The core is a hexagonal prism built from lithium and oxygen atoms (Figure 1). It consists of a stack of two $(Li-O)_3$ rings with alternating long and short Li–O bond distances [203.2(4) and 185.9(4) pm] with the longer and presumably strained bond in the four-membered LiOSiN chelate ring. Li–O bonds of intermediate length [197.2(4) pm] interconnect the two $(Li-O)_3$ rings within the stack. Thus the overall structure and the Li–O bond lengths pattern conform to the ring-stacking principle[1a,1b].

Hexagonal prismatic cores have been found, for instance, for the alkoxides $(LiOCMe_2Ph)_6$[4a] and $(NaO\mathit{t}Bu)_6$ (together with a nonamer)[4b] and for the silanolate $(LiOSiMe_2Np)_6$ (Np = α-Naphthyl)[3b]; in these examples steric protection stabilizes alkalimetal ions in a three-coordinate environment. In **1** the more favourable four-coordination can be achieved by internal coordination of the anion. To the best of our knowledge $[LiOSi\mathit{t}Bu_2(NH_2)]_4$ is the only other structurally characterized lithium α-aminosilanolate[2]. In this case, the bulky tertiary butyl groups enforce a smaller ring size which results in the formation of a tetramer.

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Experimental

Reactions were carried out under nitrogen by means of conventional Schlenk techniques. – NMR: Unity-500 (^1H 500 MHz; ^{13}C 125.7 MHz; ^{29}Si 99.3 MHz), Varian.

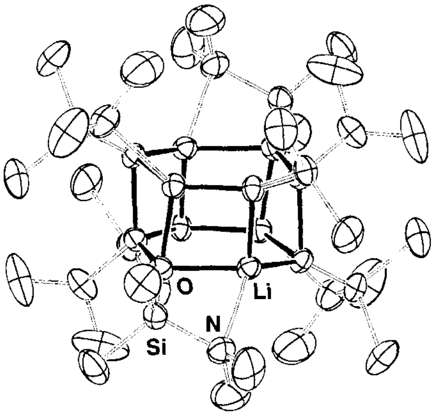

Figure 1. Molecular structure of **1**, probability of thermal ellipsoids 50%, hydrogen atoms omitted. Dashed atoms are generated from asymmetric unit by rotation C_3 (*y*, *z*, *x*), double-dashed atoms by rotation C_3^2 (*z*, *x*, *y*), and starred atoms by inversion *i* (−*x*, −*y*, −*z*). Interatomic distances: Li–O 203.2(4), Li–O′ 185.9(4), Li–O″* 197.2(4), Li–N 232.5(4), Li–Li′* 258.4(5), Li–Li′ 319.4(5), Si–O 159.7(1), Si–N 172.6(2), Si–C3 187.3(3), Si–C4 186.3(3), N–C1 148.2(5), N–C2 144.6(4) pm. Angles: O–Li–O′ 128.5(2), O–Li–O″* 93.9(2), O′–Li–O″* 99.5(2), O–Li–N 74.3(1), Li–O–Si 94.6(1), O–Si–N 105.2(1), Li–N–Si 81.5(1)°

Lithium (Dimethylamino)dimethylsilanolate (**1**): In a typical procedure, a Schlenk tube is purged with dry, oxygen-free nitrogen and charged with THF and with stoichiometric amounts of halide-free (!) lithium dimethylamide and trimeric dimethylsiloxane. The reaction mixture is stirred for 4 h; removal of the volatiles in vacuo yields 98% of a white, infusible solid, m.p. >250°C. Single crystals of **1** can be obtained by recrystallization from hexane. – ^1H NMR (500 MHz, $[D_8]THF$): $\delta = 2.41$ (s, NMe_2), -0.13 (s, $SiMe_2$). – $^{13}C\{^1H\}$ NMR ($[D_8]THF$): $\delta = 38.79$ (NMe_2), 1.04 ($SiMe_2$). – ^{29}Si NMR ($[D_8]THF$): $\delta = -16.46$. – $C_{24}H_{72}Li_6N_6O_6Si_6$ (750.8): calcd. C 38.38, H 9.66; found C 38.31, H 9.70.

Crystal Structure Determination: Colourless single crystals of **1** were obtained by crystallization from hexane. $C_{24}H_{72}Li_6N_6O_6Si_6$, molecular weight 750.8 g/mol, rhombohedral, $R\bar{3}c$ (No. 167), a = 1337.6(1) pm, $\alpha = 91.171(6)°$, $V = 2.3818(3)$ nm³, $Z = 2$, d_{calc} = 1.047 g/cm³, $\mu(Cu\text{-}K_\alpha) = 19.43$ cm⁻¹. – Diffractometer CAD4

(Enraf-Nonius), Cu-K_α radiation (graphite monochromator, $\lambda =$ 154.18 pm), crystal size $0.4 \times 0.4 \times 0.4$ mm^3, ambient temperature, ω scans ($5 < \Theta < 70°$). All data were corrected for Lorentz and polarisation effects, using the SDP system of programs[5]. Of the 3827 data collected, 3497 were unique, 1045 with intensities $I \geqslant 2\sigma(I)$ and only those were used in the structure solution and refinement. The structure was solved by direct methods using the SHELX-86 program[6] and difference fourier maps. Positions for all hydrogen atoms were found, but idealized to $C-H = 98$ pm, keeping the geometry. In the full-matrix least-squares refinement hydrogen atoms were treated as riding with isotropic thermal parameters of $B_H = 1.3 \cdot B_C$. Convergence was obtained for 73 parameters with the agreement factors $R = 0.058$ and $R_w = 0.069$, using statistical weights $w = 1/\sigma^2(F_o)$. The final difference fourier map showed a maximum of residual electron density of $0.502 \cdot 10^{-6}$ e/pm^3[7].

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