A Coordination Polymer of Bis-[2-(dimethylamino)ethanolato]dimethylsilane with a Lithium Chloride Dimer

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The reaction of lithium 2-(dimethylamino)ethanolate with Me_2SiCl_2 yielded a lithium chloride adduct of $Me_2Si(OCH_2CH_2NMe_2)_2$. Despite the application of an excess of Me_2SiCl_2, the formation of $ClMe_2SiOCH_2CH_2NMe_2$ was not observed. $[Me_2Si(OCH_2CH_2NMe_2)_2 \cdot Li_2Cl_2]$ was characterised by NMR spectroscopy and determination of its crystal structure by X-ray diffraction. In the solid state it forms endless chains consisting of Li_2Cl_2 rhombi, with the lithium atoms chelated by the O and N atom of one $OCH_2CH_2NMe_2$ substituent of $Me_2Si(OCH_2CH_2NMe_2)_2$ units.

Key words: Aggregate, Silicon, Lithium, N,O-Ligands, Crystal Structure

Introduction

In the course of our studies on the intramolecular interactions between silicon and nitrogen atoms in flexible ring systems, we have addressed various classes of compounds. These include systems capable of forming three-membered ring systems of the type SiCN [1], SiNN [2] and SiON [3], and five-membered ring systems with the atom sequences SiCCCN [4] and SiOCCN [5]. In the latter series we observed recently extreme differences between calculated gas phase structures; the Si···N distance in $Cl_3SiOCH_2CH_2NMe_2$ *e. g.* is more than 1 Å longer in the gas phase than in the crystal. These differences are much smaller in $Cl_2HSiOCH_2CH_2NMe_2$ [5]. Looking for the reasons for such large changes we tried to get hold of the analogous compound $ClMe_2SiOCH_2CH_2NMe_2$.

Results and Discussion

We had previously tried reacting $LiOCH_2CH_2NMe_2$ with H_2SiCl_2 with the intention to prepare $ClH_2SiOCH_2CH_2NMe_2$, but always obtained mixtures of $ClH_2SiOCH_2CH_2NMe_2$ and $Cl_2HSiOCH_2CH_2NMe_2$, which we were unable to separate [5]. Since these attempts to isolate pure $ClH_2SiOCH_2CH_2NMe_2$ were not successful, we aimed at synthesising the dimethyl derivative $ClMe_2SiOCH_2CH_2NMe_2$ by the reaction of $LiOCH_2CH_2NMe_2$ with Me_2SiCl_2. As a test, the reaction of $LiOCH_2CH_2NMe_2$ with Me_3SiCl was performed and led to the known $Me_3SiOCH_2CH_2NMe_2$ [6].

The reaction of Me_2SiCl_2 and $LiOCH_2CH_2NMe_2$ was performed in tetrahydrofuran at 0 °C. The product could be crystallised, but not purified by distillation. Slow cooling of the reaction solution (solvent tetrahydrofuran) to −78 °C afforded single crystals suitable for an X-ray diffraction experiment. These crystals deliquesced upon warming to ambient temperature. Attempts to achieve crystallisation from hydrocarbon solvents yielded also solid material, but this was not containing single crystals.

The ^1H NMR spectrum of the crystalline product showed it to contain the doubly substituted $Me_2Si(OCH_2CH_2NMe_2)_2$, as there are four signals with an integral ratio of 6 (0.17 ppm): 12 (2.13 ppm): 4 (2.44 ppm): 4 (3.81 ppm). Besides this the signals of tetrahydrofuran were detected. The ^{13}C NMR data were also consistent with the formula $Me_2Si(OCH_2CH_2NMe_2)_2$. A resonance at 13 ppm was detected in the ^{29}Si NMR spectrum. It has to be mentioned that $Me_2Si(OCH_2CH_2NMe_2)_2$ has been described earlier in the literature and was then made from the sodium salt $NaOCH_2CH_2NMe_2$ and Me_2SiCl_2 [7]. Also noteworthy is the fact that carbosilanes with $OCH_2CH_2NMe_2$ side-arms are nowadays popular compounds for the construction of polyfunctional molecules including extended dendrimer architectures [8].

Analysis of the X-ray diffraction data gave a result consistent with the NMR data but showing an additional component, LiCl, which was not observed by the applied NMR methods. The formula of the crystals is thus $Me_2Si(OCH_2CH_2NMe_2)_2 \cdot Li_2Cl_2 \cdot THF$ with four molecules in the unit cell. The crystals belong to the monoclinic space group *C*2/*c*. In the crystal the molecules form polymeric chains. Each Me_2-

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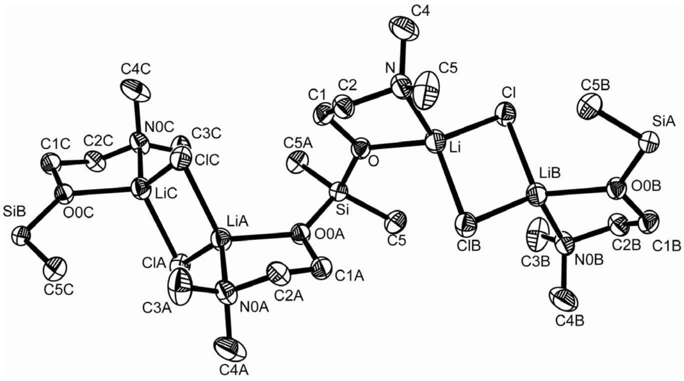


Fig. 1. Cut-out of the structure of $Me_2Si(OCH_2CH_2NMe_2)_2 \cdot Li_2Cl_2 \cdot THF$. One molecule of $Me_2Si(OCH_2CH_2NMe_2)_2$ is connected to the two adjacent ones through a Li_2Cl_2 unit on each side. The THF molecule and the hydrogen atoms are omitted for reasons of clarity.

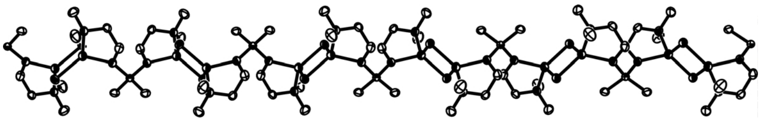
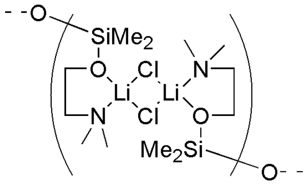


Fig. 2. Polymeric chain of $Li_2Cl_2 \cdots Me_2NCH_2CH_2OSi(Me)_2OCH_2CH_2NMe_2$ units in the crystal.



Scheme 1. Connectivity pattern in the crystal structure of $Me_2Si(OCH_2CH_2NMe_2)_2 \cdot Li_2Cl_2 \cdot THF$.

$Si(OCH_2CH_2NMe_2)_2$ unit is connected to the adjacent ones by rectangular Li_2Cl_2 units. The lithium atoms of these rectangles are chelated by the O and N atoms of $OCH_2CH_2NMe_2$ arms of two different $Me_2Si(OCH_2CH_2NMe_2)_2$ units, so that the chain consists of $Li_2Cl_2 \cdots Me_2NCH_2CH_2OSi(Me)_2OCH_2CH_2NMe_2$ units as depicted in Scheme 1 and Fig. 1. The THF molecules are not connected to the Li atoms in the structure; the closest Li···O(thf) distance is 5.47 Å.

The planes O–Li–N and Cl–LiB–ClB are almost perpendicular to one another. No interatomic distances smaller than the sum of the van-der-Waals radii between the polymeric chains shown in Fig. 2 are observed, that would indicate more than simple packing of these chains.

The LiOCCN five-membered rings adopt an envelope-like conformation with typical atomic distances and angles. As expected the angles at the silicon-substituted oxygen atoms are wide at 120.3(2)°, which is typical for such situations. The sum of angles at the oxygen atoms is 358.6°, which demonstrates that they have almost planar coordination geometry. Similar findings of a planar coordination environment of oxygen have been reported for the simple systems $(H_3Si)_2O$ [9] and H_3SiOCH_3 [10] for their interactions between two such molecules each under formation of Si···O contacts. This implies that the donating lone pair at the silylated oxygen atom has *sp*^{2} character.

Table 1. Selected bond lengths (Å) and angles (deg) of $Me_2Si(OCH_2CH_2NMe_2)_2 \cdot Li_2Cl_2 \cdot THF$.

Distance	(Å)	Angle	(deg)
Si–O	1.658(2)	C5–Si–O	104.8(1)
Si–C5	1.837(2)	Si–O–C1	120.3(2)
Cl–Li	2.301(3)	O–C1–C2	108.6(2)
Cl–LiB	2.331(4)	N–C1–C2	112.1(2)
O–C1	1.453(2)	C1–O–Li	108.7(2)
O–Li	2.025(4)	C2–N–Li	99.8(2)
C1–C2	1.505(3)	O–Li–N	86.5(2)
Li–N	2.087(4)	Li–Cl–LiB	76.6(2)
N–C2	1.467(3)	Cl–Li–ClB	103.4(1)
N–C3	1.472(3)		
N–C4	1.462(3)		

The Li_2Cl_2 ring in $Me_2Si(OCH_2CH_2NMe_2)_2 \cdot Li_2Cl_2 \cdot THF$ has two different Li···Cl distances at 2.301(3) and 2.331(4) Å, which are in the same range as the Li···Cl contacts in $[LiCl \cdot 2THF]_2$ at 2.342(3) and 2.308(3) Å [11], in $[LiCl \cdot Et_2O]_4$ at 2.35(1)–2.40(1) Å [12], and in $(TMEDA)LiClAlMe_2C(SiMe_3)PMe_2$ at 2.369(6) [13]. Even in $[{}^tBu_2AlCH_2N{}^iPr_2 \cdot LiCl]_2$ the Li–Cl distances are of similar lengths at 2.339(4) and 2.374(4), despite that there the Li_2Cl_2 rings are bonded simultaneously at the Li and Cl atoms to the difunctional Lewis acid/base ${}^tBu_2AlCH_2N{}^iPr_2$ [14]. The Li–Cl–Li angle in $Me_2Si(OCH_2CH_2NMe_2)_2 \cdot Li_2Cl_2 \cdot THF$ at 76.6(2)° and the

Cl–Li–Cl angle at 103.4(1)° are also in the range of values found in [LiCl·2THF]$_2$ [Li–Cl–Li 77.1(1)°, Cl–Li–Cl 102.9(1)°] [10], in [LiCl·Et$_2$O]$_4$ [Li–Cl–Li 77.3(3) – 81.5(4)°, Cl–Li–Cl 97.5(4) – 102.0(4)°] [11] and in [^{t}Bu$_2$AlCH$_2$N^{i}Pr$_2$·LiCl]$_2$ [80.8(1)° and Cl–Li–Cl 99.2(1)°] [14]. The Li–O and Li–N distances of 2.025(4) and 2.087(4) are again in a typical range [9 – 12] (Table 1).

The formation of $Me_2Si(OCH_2CH_2NMe_2)_2$ as an Li_2Cl_2 adduct in a reaction of one equivalent $LiOCH_2CH_2NMe_2$ with one equivalent of Me_2SiCl_2 was repeatedly observed. Changing the reaction conditions (hydrocarbon solvent, low temperature) did not change the product. Conditions for the formation of the monosubstituted product $Me_2ClSiOCH_2CH_2NMe_2$ could not be found, even if a large excess of Me_2SiCl_2 was employed. Obviously this mono-substituted silane reacts faster with the lithiated aminoethanol compared to Me_2SiCl_2. No other product could be observed.

Experimental Section

All operations were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and saturated with nitrogen by standard methods. Me_2SiCl_2 and 2-(dimethylamino)ethanol were purchased from a commercial source and used after distillation. NMR spectra were recorded on a Bruker AV 400 NMR spectrometer. Chemical shifts are reported in ppm with reference to the residual solvent signals for ^{1}H and ^{13}C NMR spectroscopy and to external $SiMe_4$ for ^{29}Si NMR spectroscopy. Elemental analyses were carried out on a VARIO E1 III CHNS instrument. IR spectra were recorded on a Midac Prospect IR spectrometer. Mass spectra were recorded on a Varian MAT 212 instrument.

Synthesis

$LiOCH_2CH_2NMe_2$ (3.3 g, 35 mmol) was dissolved in THF (30 mL). The reaction mixture was cooled to 0 °C. At this temperature Me_2SiCl_2 (4.85 g, 37.8 mmol) was slowly added. The reaction solution was stirred for two hours. The mixture was filtered through a cannula fitted with a filter. The resulting clear solution was slowly cooled to −78 °C to afford a crystalline product, which is a liquid at r. t. By recrystallisation single crystals suitable for X-ray diffraction were grown. – ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.17 (s, 6H, $^1J_{CH}$ = 118 Hz, Si(CH_3)$_2$), 2.13 (s, 12H, N(CH_3)$_2$), 2.44 (t, 6H, $^3J_{HH}$ = 6.0 Hz, NCH_2), 3.81 (t, 6H, $^3J_{HH}$ = 6.0 Hz, OCH_2). – ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = −0.8 (Si(CH$_3$)$_2$), 45.1 (N(CH$_3$)$_2$), 58.4 (NCH$_2$), 61.8 (OCH$_2$). – ^{29}Si DEPT-19.5-NMR (79.5 MHz, C_6D_6): δ = 13.

Crystal structure determination

Diffraction data for $Me_2Si(OCH_2CH_2NMe_2)_2 \cdot Li_2Cl_2 \cdot THF$ were collected with a Bruker SMART 6000 CCD diffractometer equipped with a rotating anode at 153(2) K using Goebel mirror-monochromated CuK_α radiation (λ = 1.54178 Å). A crystal was selected and prepared under perfluoropolyether and mounted in a drop of it onto the tip of a glass fibre on the goniometer head of the diffractometer. The structure was solved by Direct Methods and refined with full-matrix least-squares procedures against F^2 (SHELXTL) [15]. $C_{14}H_{34}Cl_2Li_2N_2O_3Si$, M_r = 391.30, crystal size = 0.2 × 0.2 × 0.2 mm^3, monoclinic crystal system, space group $C2/c$, a = 15.6254(6), b = 12.6124(6), c = 12.2193(5) Å, β = 110.941(3)°, V = 2249.1(2) Å^3, T = 153(2) K, Z = 4, ρ_{calc} = 1.156 g cm^{-3}, μ(CuK_α) = 3.201 mm^{-1}. 6296 scattering intensities were collected of which 2074 were independent and 1737 met the "observed" criterion [$I \geq 2\sigma(I)$]. R_1 = 0.0395, wR_2 = 0.1013 for 1737 scattering intensities with $I \geq 2\sigma(I)$, and R_1 = 0.0474, wR_2 = 0.1058 for all data. $\Delta\rho_{fin}$ = 0.34 / −0.30 e Å^{-3}.

CCDC 716817 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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