Crystal Structure of Dimeric *N*-Lithiohexamethyldisilazane Etherate, $[(Et_2O)Li\{\mu\text{-}N(SiMe_3)_2\}_2Li(OEt_2)]$ *

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The crystal structure of a 1 : 1 adduct, $Li[N(SiMe_3)_2]\cdot OEt_2$, has been determined by *X*-ray diffraction. Crystals are tetragonal, space group $P\bar{4}n2$, with a = 9.762(6), c = 17.280(9) Å, and Z = 4. The lattice contains dimeric molecules of symmetry *222* with the silazane groups functioning as the bridging ligands [Li–N 2.055(5) Å, Li–N–Li 75.1(2)°, N–Li–N 104.9(3)°]; the lithium atoms are three-co-ordinate [Li–O 1.943(6) Å, O–Li–N 127.5(1)°].

The degree of aggregation of bis(trimethylsilyl)amidolithium, $[Li\{N(SiMe_3)_2\}]$, in solution is solvent dependent and is different to that found in the solid. In aromatic hydrocarbons, molecular-weight determinations indicate dimeric units [1] while n.m.r. results are consistent with the presence of a dimer–tetramer equilibrium.[2] In contrast the species that crystallizes from these solvents is trimeric.[3,4] For potentially co-ordinating ether solvents such as tetrahydrofuran and OEt_2 the picture is not complete. In solution, n.m.r. and molecular-weight data support the existence of a monomer–dimer equilibrium whereas the degree of association (and solvation) of the crystalline species derived from such solvents is unknown. Accordingly we have undertaken a structural investigation on the complex that crystallizes from OEt_2, $Li[N(SiMe_3)_2]\cdot OEt_2$,[5] and the results are herein reported. The compound was prepared as described in ref. 2 and recrystallized from diethyl ether.†

Results and Discussion

The crystal structure determination establishes the etherate, of composition $Li[N(SiMe_3)_2]\cdot OEt_2$, to comprise discrete dimeric units with the silazane group acting as the bridging entity. There are no significant intermolecular contacts (Figure). The overall symmetry of the dimer is *222*, such that the trimethylsilyl groups are void of crystallographically imposed symmetry elements.

The presence of dimeric species compares favourably with the reported degree of association of 1.6—1.77 for $[\{Li[N(SiMe_3)_2]\}_3]$ in diethyl ether.[2] Formation of an additional covalent bond in the present compound compared to the unsolvated version is associated with a decrease in oligomerization, from a trimer [4] to a dimer. It is interesting to note that the structure of 'unsolvated' $[Li\{NCMe_2(CH_2)_3CMe_2\}]$ is a cyclic tetramer.[6]

In a related complex, the dimer of $[Li(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)(OEt_2)]$, the disposition of ligands is similar, *viz.* the anion donor atoms bridge the three-co-ordinate lithium centres.[7] A further common feature is that the bridging ligands are regarded as very bulky. The isoelectronic C-centred analogue of $^-N(SiMe_3)_2$, $^-CH(SiMe_3)_2$, has an extensive inorganic chemistry but there are no examples of it functioning as a bridging moiety. It is restricted to a two-electron donor and two lithium alkyls recently reported, $[Li\{CH(SiMe_3)_2\}(Me_2NCH_2CH_2NMe_2)]$ and $[Li\{CH(SiMe_3)_2\}\{Me_2N(CH_2)_2N(Me)(CH_2)_2NMe_2\}]$, are monomeric [8] even though lithium alkyls readily form electron-deficient bonding.

Like the phenoxide-containing complex mentioned above the arrangement of ligands about each lithium atom defines a good plane; the lithium angular geometry is defined by the unique angles, N–Li–N, 104.9(3), and N–Li–O, 127.5(1)° (Table 1). The Li–O distance of 1.943(6) Å again is similar to that found in the phenoxide structure [1.96(1) Å].[7]

The noteworthy features of the Li_2N_2 molecular core are its planarity and that the endocyclic angles [N–Li–N 104.9(3) and Li–N–Li 75.1(2)°] are substantially less than those of the unsolvated cyclotrimer [N–Li–N 147(3) and Li–N–Li 92(2)°].[4] Although polymeric $[\{Na[N(SiMe_3)_2]\}_n]$ is essentially ionic (see below) the relevant angles for comparison are 150.2(1) and 102.0(1)° respectively for N–Na–N and Na–N–Na.[9] The dramatic reduction in the N–Li–N angle in the etherate is not surprising in view of the expansion of the lithium co-ordination sphere. Variations in M–N–M angle suggest it to be a rather flexible bonding parameter for bridging silazanes in general.

The Li–N distance of 2.055(5) Å is marginally longer than that in the trimer [2.00(2) Å].[4] It has been proposed that the change in geometry about the N centre of $N(SiMe_3)_2$ is a

Table 1. Non-hydrogen atom geometries; * distances (Å) and angles (°)

(*i*) Li environment			
Li–N	2.055(5)	N–Li–O	127.5(1)
Li–O	1.943(6)	N–Li–N	104.9(3)
(*ii*) $N(SiMe_3)_2$			
		Si–N–Si	121.2(2)
N–Si	1.705(2)	Li–N–Si	120.4(2)
Si–C(1)	1.883(5)	N–Si–C(1)	115.3(2)
Si–C(2)	1.878(5)	N–Si–C(2)	111.0(2)
Si–C(3)	1.868(6)	N–Si–C(3)	112.9(2)
		C(1)–Si–C(2)	104.8(2)
		C(1)–Si–C(3)	106.2(3)
		C(2)–Si–C(3)	105.9(3)
(*iii*) Et_2O			
O–C(1)	1.436(6)	Li–O–C(1)	121.5(3)
C(1)–C(2)	1.44(1)	C(1)–O–C(1)	117.0(4)
		O–C(1)–C(2)	114.0(5)

* Li–N–Li 75.1(2)°.

* Bis[μ-bis(trimethylsilyl)amido-(diethyl ether)lithium].

Supplementary data available (No. SUP 23615, 7 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

† *Note added in proof:* preliminary results of an independent determination of the same crystal structure and further details of $[(Li\{NCMe_2(CH_2)_3CMe_2\}_4]$[6] have appeared since acceptance of this paper (M. F. Lappert, M. J. Slade, A. Singh, J. L. Atwood, R. D. Rogers, and R. Shakir, *J. Am. Chem. Soc.*, 1983, **105**, 302).

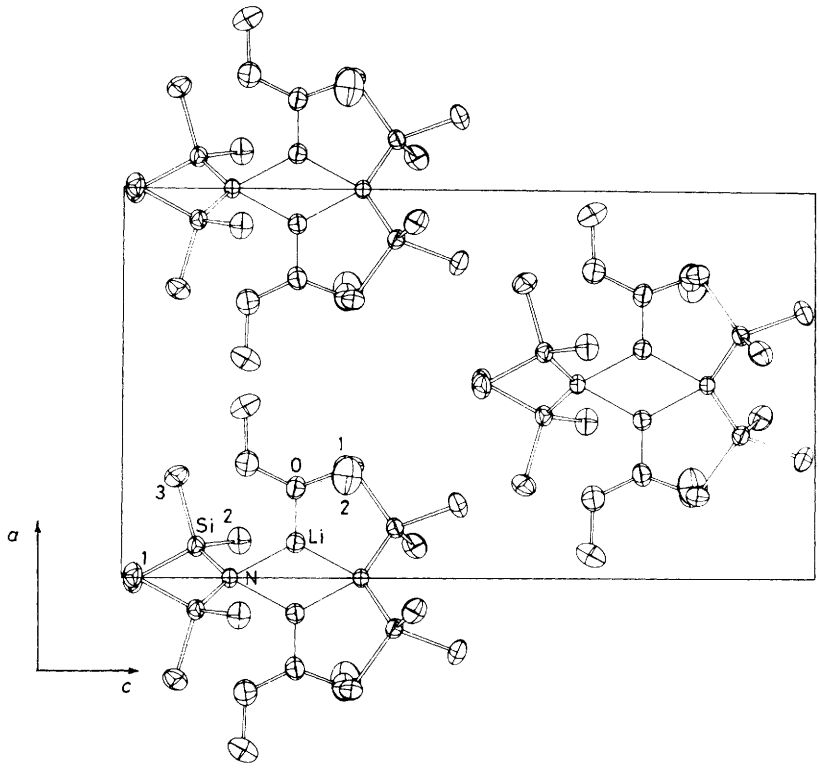

Figure. Unit-cell contents (non-hydrogen atoms) projected down *b*; 20% thermal ellipsoids are shown

Table 2. Comparison of molecular parameters for $M[N(SiMe_3)_2]$ (M = Li, Na, or K) complexes

Compound	Li···N/ Å	Si–N/ Å	Si–N–Si/°
$[\{Li[N(SiMe_3)_2](OEt_2)\}_2]$ [a]	2.055(5)	1.705(2)	121.2(2)
$[\{Li[N(SiMe_3)_2]\}_3]$ [b]	2.00(2)	1.729(4)	118.6(9)
$[\{Na[N(SiMe_3)_2]\}_n]$ [c]	2.355(3)	1.690(5)	125.6(1)
$[\{K[N(SiMe_3)_2](C_4H_8O_2)_2\}_2]$ [d]	2.70(2)	1.64(1)	136(1)

[a] This work. [b] Ref. 4. [c] Ref. 9. [d] Ref. 10.

reliable guide as to the degree of covalency for the M–N bonding.[9] If this is considered in the context of all Group 1 silazane structures thus far determined, the important details of which are set out in Table 2, the present compound, containing a relatively small Si–N–Si angle and high Si–N distance, is best considered as covalent along with the other lithium complex.[4] The reduction in Si–N distance and increase in Si–N–Si angle for the complexes of Li through to K[10] are accompanied by an increase in ionic character.[9] The short N–Si distance of 1.68 Å in $[Eu\{N(SiMe_3)_2\}_3]$ has been considered as evidence for a predominantly ionic structure.[11] Since Si–N distances provide a measure of delocalization of negative charge into $p\pi$–$d\pi$ bonding orbitals whereas Si–N–Si variations may be sterically controlled, the Si–N parameter is perhaps a more reliable criterion of the degree of ionic character. If the trend in Si–N–Si angles is disregarded, it may then be that the decrease in Si–N distance with a concomitant increase in Li–N from the trimer to the dimer represents a slight increase in ionic character. The lack of consistent correlation in Si–N *versus* Si–N–Si variations is highlighted by the complex $[Co\{N(SiMe_3)_2\}_2(PPh_3)]$ in which the Si–N distance of 1.706(9) Å is similar to the present structure [1.705(2) Å] but the Si–N–Si angles are dissimilar [125(1) *versus* 121.2(2)°].[12]

The Si–C(Me) distances and angular variations within the $N(SiMe_3)$ group are unexceptional.

Table 3. Non-hydrogen co-ordinates

Atom	*x*	*y*	*z*
Li	0.090 7(8)	0.590 7(8) *	¼
(*i*) $N(SiMe_3)_2$			
Si	0.081 1(1)	0.371 2(1)	0.107 30(6)
C(1)	−0.006 8(7)	0.311 2(6)	0.016 4(2)
C(2)	0.095 7(6)	0.213 9(5)	0.169 3(3)
C(3)	0.259 9(6)	0.416 7(6)	0.078 7(3)
N	0 *	½ *	0.155 7(2)
(*ii*) Et_2O			
O	0.231 4(3)	0.731 4(3) *	¼ *
C(1)	0.278 6(8)	0.792 8(8)	0.320 6(3)
C(2)	0.261 2(10)	0.939 2(8)	0.323 5(4)

* Parameter constrained by symmetry.

Experimental

Crystal Data.—$Li[N(SiMe_3)_2]\cdot OEt_2$. $C_{10}H_{28}LiNOSi_2$, M = 241.4, Tetragonal, space group $P\bar{4}n2$ (D_{2d}^8, no. 118), a = 9.762(6), c = 17.280(9) Å, U = 1 647(2) Å^3, Z = 4, D_c = 0.97 g cm^{-3}, $F(000)$ = 536, Monochromatic Mo-K_α radiation, λ = 0.710 69 Å, μ_{Mo} = 1.9 cm^{-1}, T = 295(1) K. Specimen: cuboid, *ca.* 0.5 mm, mounted in capillary.

Structure Determination.—A unique data set was measured to $2\theta_{max.}$ = 50°, using a Syntex $P2_1$ four-circle diffractometer

in conventional $2\theta/\theta$ scan mode, yielding 1 648 reflections; 738 of these with $I > 3\sigma(I)$ were used in the full-matrix least-squares refinement, after solution of the structure by the heavy-atom method, without absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms. Hydrogen atoms (x, y, z, U) were constrained at estimated values, U_H being set at 1.25 $\bar{U}_{iso}$. At convergence, residuals $R = 0.046$ and $R' = 0.057$. Neutral-atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[13] Computation used the *X*-RAY 76 program system[14] implemented on a Perkin–Elmer 3240 computer. Atomic co-ordinates are given in Table 3; non-hydrogen atom numbering is in the Figure.

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