Mononuclear Lithium Amides using a Crown Ether: *X*-Ray Crystal Structure of Lithium Bis(trimethylsilyl)amide·12-crown-4, [LiN(SiMe$_3$)$_2$·12-crown-4]

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The crystal structure of the crown ether–lithium bis(trimethylsilyl)amide complex, [LiN(SiMe$_3$)$_2$·12-crown-4], has been determined by *X*-ray diffraction; this represents the first structural characterization of a mononuclear lithium amide.

Lithium alkyls,[1] amides,[2] and alkoxides[3] have been widely used as precursors to other inorganic and organometallic complexes and as synthetic reagents in organic chemistry. Their importance has generated widespread interest in their structure. To date all structural studies in both the solid state and solution have shown that these three classes of compounds are associated in numbers varying between two and six.[1-3] In addition, many studies have shown that the reactivity of the reagents may be augmented by adding donor molecules[4] which increase their polarity and reduce the degree of association.[5] However, no monomeric species, which have the potential for the highest reactivity, have been isolated from these solutions.

In this paper we report the *X*-ray crystal structure† of the first mononuclear lithium amide, the complex [LiN(SiMe$_3$)$_2$·12-crown-4]. It was synthesized by the addition of one equivalent of 12-crown-4 to a hexane solution of LiN(SiMe$_3$)$_2$. Recrystallization from tetrahydrofuran–Et$_2$O–hexane gives the title compound in moderate yield. The structure of the complex is illustrated in Figure 1.

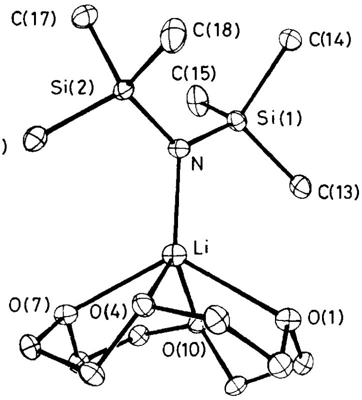

Figure 1. ORTEP plot of [LiN(SiMe$_3$)$_2$·12-crown-4].

The *X*-ray data show that the complex consists of discrete molecules with no close intermolecular interactions. The Li–N distance of 1.965(4) Å is slightly shorter than those previously reported in the dimer [{LiN(SiMe$_3$)$_2$·Et$_2$O}$_2$],[6,7] the trimer [{LiN(SiMe$_3$)$_2$}$_3$],[8] and the tetramer $[\{\mathrm{LiNCMe_2(CH_2)_3CMe_2}\}_4]$.[6] The distance suggests that the Li–N bond has considerable covalent character. Support for this view comes from the N–Si distances, 1.681(2) Å, and Si–N–Si angle of 123.5(1)°. It has been suggested[9] (mainly on the basis of an N–Si p–d π interaction) that the geometry around nitrogen in N(SiMe$_3$)$_2$ units reflects the ionic character of the M–N bond. Increasing the polarity of the metal–nitrogen interaction shortens the N–Si distance and increases the N–Si–N angle. For example, the N–Si distance in the more ionic [KN(SiMe$_3$)$_2$·2C$_4$H$_8$O$_2$][10] is 1.64 Å and the N–Si–N angle is 136(1)°. In the limiting case of a completely separate cation and anion a linear Si–N–Si unit might be expected. One of the objects of our continuing work in this laboratory is the isolation of free amide anions and their related alkyl and alkoxy analogues.

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† *Crystal data*: [LiN(SiMe$_3$)$_2$·12-crown-4], C$_{14}$H$_{34}$LiNO$_4$Si$_2$, $M = 343.53$, triclinic, space group $P\bar{1}$, $T = 140$ K, $a = 9.171(2)$, $b = 9.996(4)$, $c = 11.543(4)$ Å, $\alpha = 81.07(3)$, $\beta = 77.30(2)$, $\gamma = 80.55(3)°$, $Z = 2$, $U = 1\,010.4(6)$ Å^3, $D_c(140\ \mathrm{K}) = 1.13\ \mathrm{g\,cm^{-3}}$, Mo-$K_\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.9\ \mathrm{cm^{-1}}$, 4610 reflections, 3257 had $I > 3\sigma(I)$, $R = 0.0382$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

There are several other features of interest. For example the lithium atom is five co-ordinate with an approximately square pyramidal geometry consisting of four basal oxygen atoms and an apical nitrogen atom. This type of co-ordination is quite rare for lithium,[11] and further supports the view that main group metal ions are capable of having at least as great a variety of co-ordination numbers as the transition metal ions. In the case of lithium it is widely held that four co-ordination is preferred but co-ordination numbers varying from two[6,8] to eight[12] are now known for this metal.

A noteworthy aspect of the structure is the disparity of the Li–O distances. Two are very long with values of 2.332(4) and 2.393(3) Å, whereas the others are 2.094(4) and 2.108(4) Å, closer to the distances normally associated with lithium–diethyl ether[6,7,13,14] complexes. Longer distances are expected with higher co-ordination numbers,[15] however close examination of the data does not provide an obvious reason for the differences seen here in terms of close interatomic contacts or ring strain. Smaller variations in lithium–oxygen bond distances (average value 2.35 Å) have also been seen in structures involving the cation $[Li(12\text{-crown-}4)_2]^+$.[12] The different lithium–oxygen distances in these compounds do not show a regular pattern whereas in the title compound the distortion is symmetric.

In summary 12-crown-4 may be used to prevent association in lithium bis(trimethylsilyl)amide. Our preliminary results involving other systems indicate that this phenomenon may have considerable generality. For example, *X*-ray structural data have been obtained for the mononuclear lithium diphenylamide and di-isopropylamide analogues.[16] In addition, complete cation and anion separation has been effected in the complexes $[Li(12\text{-crown-}4)_2][PPh_2]$[12] and $[Li(12\text{-crown-}4)_2][CuPh_2]$.[15] Details of this work will be described in future publications.

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