Mixed Dimer and Mixed Trimer Complexes of *n*BuLi and a Chiral Lithium Amide

Göran Hilmersson* and Birgitta Malmros[a]

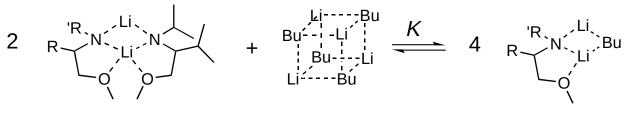
Abstract: Multinuclear and multidimensional NMR spectroscopy have shown that lithium (*S*)-*N*-isopropyl-*O*-methyl-valinol (**1**-[^{6}Li]) exists in a mixed 2:1 complex with *n*Bu[^{6}Li], (**1**-[^{6}Li])$_2$/*n*Bu[^{6}Li], in non-coordinating solvents such as hexane or toluene. A ^{6}Li,^{1}H-HOESY NMR spectrum indicates that the complex is a cyclic trimer with a large distance between the di-coordinated lithium and the carbanion of *n*Bu-[^{6}Li]. Such arrangements are present in the solid state as previously reported by Williard and Sun. The exchange of lithium atoms within the trimer is slow at $-33\,^\circ$C. The exchange barrier ($\Delta G^{\neq}$) was determined to be 14.7 kcal mol^{-1} from quantitative ^{6}Li,^{6}Li-EXSY spectra. Addition of diethyl ether results in the formation of mixed dimers of (**1**-[^{6}Li])/*n*Bu[^{6}Li], tetramers of *n*Bu[^{6}Li], and homodimers (**1**-[^{6}Li])$_2$. The apparent equilibrium constant of the mixed dimer was determined from the ^{6}Li NMR integrals as $K = 7$.

Keywords: aggregation · NMR spectroscopy · organolithium compounds

Introduction

Organolithium compounds are among the most versatile and widely used reagents in organic chemistry.[1] New applications using organolithium reagents and also modifications/improvements of known reaction conditions are steadily under development. The role of solvent in organolithium chemistry has been the subject of a number of investigations.[2] Chiral lithium amides are an important class of compounds developed for use in asymmetric synthesis.[3] They are used either as strong bases capable of enantioselective deprotonations or as chiral ligands that can modify other non-chiral organolithium reagents.[4] However, knowledge about structures and dynamics of such organolithium reagents is still in its infancy.

There are a few reports on chiral lithium amides and their mixed complexes with *n*Bu[^{6}Li] studied by multinuclear NMR spectroscopy.[5] Chiral lithium amides may exist as monomers, symmetrical solvated dimers, non-symmetrically solvated (C_2-symmetric) dimers, cyclic trimers or ladders.[5, 6] Generally, it has been found that *n*Bu[^{6}Li] and chiral lithium amides form mixed dimers in ether solvents. These dimers exist in fast equilibrium with tetrameric *n*Bu[^{6}Li] and dimeric lithium amides, see Scheme 1.



Scheme 1. Aggregates and equilibrium of chiral lithium amide dimers *n*BuLi tetramers and mixed dimers.

The apparent equilibrium constants are not only largely dependent on the structure of the amides but also on the solvent.[4] The chiral mixed dimers may be key intermediates in asymmetric alkylation of for example aldehydes in which the chiral amide induces asymmetry to the alkylating agent. A large equilibrium constant for the mixed complexes could pave the way for success in asymmetric synthesis.

Although there are some exceptions to the rule of mixed dimer formation. Aggregates with four lithiums tetrahedrally arranged have been observed.[7] We are particularly interested in the crystal structure of the chiral lithium amide (*S*)-*N*-isopropyl-*O*-methyl valinol (**1**-Li) derived from (*S*)-valinol described by Williard and Sun.[8] The structure of **1**-Li in the presence of *n*BuLi was determined with X-ray diffraction analysis as a mixed trimer, (**1**-Li)$_2$/*n*BuLi (Figure 1), and not the expected mixed dimer. Williard and Sun suggested that if such trimeric complexes are present they could be responsible for the asymmetric alkylation reactions. Closely related

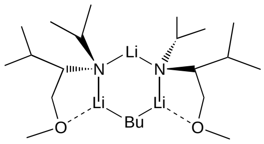


Figure 1. The mixed trimer, (**1**-Li)$_2$/*n*BuLi, crystallised from **1**-Li and *n*BuLi.

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lithium amides have been reported to yield enantioselectivities over 90% in the butylation of aldehydes.[5c, 9]

Using variable temperature NMR spectroscopy we now have studied mixtures of **1**-[^{6}Li] and *n*Bu[^{6}Li] in diethyl ether and toluene solutions.

Experimental Section

General: All glassware was dried overnight in an oven at 120 °C (syringes were dried at 50 °C in a vacuum oven) before transfer into a glove box (Mecaplex GB 80 equipped with a gas purification system that removes oxygen and moisture) containing a nitrogen atmosphere. Typical moisture content was less than 2 ppm. All manipulations of the lithium compounds were carried out in the glove box using gas-tight syringes. Ether solvents were stored and freshly distilled from Deporex (FLUKA) prior to use. Hexane and toluene were distilled and stored over molecular sieves (5 Å) in the glovebox prior to use. All NMR experiments were performed in Wilmad (5 mm) tubes fitted with a Wilmad/Omnifit Teflon valve assembly (OFV) with a silicone septum.

(*S*)-*N*-Isopropyl-*O*-methyl-valinol: The (*S*)-*N*-isopropyl-*O*-methyl-valinol was prepared according to published procedures: $LiAlH_4$ reduction of D-valine to D-valinol,[10] methylation by MeI to afford the amino methyl ether,[11] condensation with acetone to the corresponding imine and finally reduction using H_2/Pd/C in a Parr apparatus at 4 atm.[12]

Preparation of [^{6}Li]-*n*-butyllithium: This compound was prepared according to the literature.[4b]

NMR Spectroscopy: All NMR spectra were recorded using a Varian Unity 500 spectrometer equipped with three channels using a 5 mm ^{1}H, ^{13}C, ^{6}Li triple resonance probe head, built by the Nalorac Company. Measuring frequencies were 500 MHz (^{1}H), 125 MHz (^{13}C), and 73 MHz (^{6}Li). The ^{1}H and ^{13}C NMR spectra were referenced to the solvent [D_{10}]diethyl ether signals at $\delta = 1.06$ (^{1}H, $-CH_3$) and $\delta = 15.2$ (^{13}C, $-CH_3$), respectively. Lithium spectra were referenced to external 0.3 M [^{6}Li]Cl in [D_4]MeOH ($\delta = 0.0$). Probe temperatures were measured after 30 min of temperature equilibrium with a methanol NMR thermometer supplied by Varian.

2D NMR measurements: All 2D spectra were acquired using non-spinning 5 mm tube diameter samples with deuterium field-frequency locking. Spectra were processed in phase-sensitive mode with square sinebell weighting both in F_1 and F_2. For the ^{6}Li,^{1}H-HOESY[13] spectrum the following parameters were used: spectral window of 1000 Hz ($F_2 = {}^6$Li) and 8000 Hz ($F_1 = {}^1$H); 84 increments and 32 scans per increment in t_1; sinebell weighting in F_1 and F_2 for the phase sensitive spectrum; 28 μs proton 90° decoupler pulse. For the ^{6}Li,^{6}Li-EXSY spectrum the following parameters were used: spectral window of 1000 Hz (F_1 and F_2); 96 increments and 32 scans per increment in t_1; one time zero filling in F_1 and F_2; mixing time $T_m = 1$ s; no proton decoupling; absolute value data which was processed with exponential linebroadening without symmetrization.

Computational methods: Due to the considerable size of the aggregates under investigations we restricted our geometry optimizations to semi-empirical PM3 calculations.[14] The structures were reoptimized using the keyword HHon,[15] to eliminate the HH attraction that is typical for the PM3 method. All geometries were characterized as minimum by calculation of their frequencies. The calculations were performed using the Titan program package[16] on a PIII 600 MHz PC.

Results and Discussion

Investigations in non-coordinating solvents (toluene and hexane): The ^{13}C NMR spectrum of a 2:1 mixture of **1**-[^{6}Li] (0.4 M) and *n*Bu[^{6}Li] (0.2 M) in [D_8]toluene or [D_{14}]hexane at −80 °C shows only one set of signals for each carbon in **1**-[^{6}Li] and a single set of signals for each carbon in *n*Bu[^{6}Li]. The signals for *n*Bu[^{6}Li] in the presence of **1**-[^{6}Li] are shifted slightly compared with those of pure *n*Bu[^{6}Li] in toluene; this indicates that they arise from a mixed complex with **1**-[^{6}Li]. In the ^{13}C NMR spectrum obtained at −80 °C the α-carbon signal of *n*Bu[^{6}Li] is broad and unresolved in the presence of **1**-[^{6}Li].

In contrast, the ^{6}Li NMR spectrum of the toluene solution displays two signals in a 2:1 intensity ratio at $\delta = 2.24$ and $\delta = 2.73$, the smaller one significantly broader than the other (vertical spectrum in Figure 2). The corresponding [D_{14}]hexane solution of *n*Bu[^{6}Li] and **1**-[^{6}Li] display the two ^{6}Li signals at $\delta = 2.88$ and $\delta = 3.45$. The intensity ratios are concentration independent (0.05–0.4 M). Further addition of *n*Bu[^{6}Li] to the toluene solutions results in additional signals for *n*Bu[^{6}Li], identical to those observed from authentic *n*Bu[^{6}Li] in toluene. On the other hand, addition of amine **1** (< 0.2 equiv) did not result in any new signals. An interesting observation is that the NMR tube contained some precipitated crystals at −80 °C, possibly from a higher order complex of (**1**-[^{6}Li]). The single set of ^{13}C NMR signals and two ^{6}Li signals in a 1:2 ratio indicate the presence of only one specie. At lower concentrations of **1**-[^{6}Li], the signals for the various aggregates of *n*Bu[^{6}Li] in toluene predominate but the 1:2 ratio of the ^{6}Li NMR signals of the mixed complex was not affected.

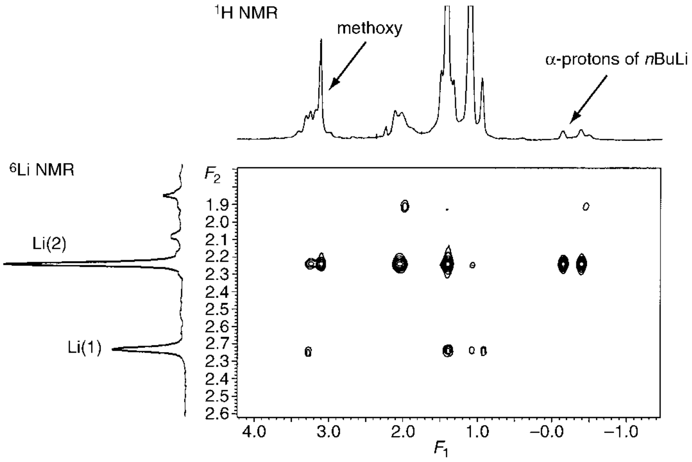


Figure 2. The ^{6}Li,^{1}H-HOESY spectrum of the mixed trimer aggregate *n*Bu[^{6}Li]/(**1**-[^{6}Li])$_2$, (0.2 M) in [D_8]toluene at −90 °C.

A ^{6}Li,^{1}H-HOESY experiment performed at −80 °C on the mixed complex also showed proximity between the two lithiums and the protons of *n*Bu[^{6}Li] and **1**-[^{6}Li]. The α-protons of *n*Bu[^{6}Li] showed no heteronuclear Overhauser effects (NOE) to the lithium which appear at $\delta = 2.73$ in the ^{6}Li NMR spectrum. This clearly indicates that this lithium is not in proximity of the α-protons of the butyl group. These NMR studies altogether show that the 2:1 mixed trimer (**1**-[^{6}Li])$_2$/*n*Bu[^{6}Li] dominates in toluene, which is a non-coordinated solvent. This complex seems to be the solution analogue of the corresponding solid-state complex of (**1**-[^{6}Li])$_2$/*n*Bu[^{6}Li] that Williard and Sun crystallized from hexane.

This complex **1**-[^{6}Li])$_2$/*n*Bu[^{6}Li] has a di-coordinated lithium nucleus, which is only coordinated by two amide anions and no internal coordinated Lewis base(s). Thus, this complex is a promising candidate for the observation of lithium interactions with aromatic solvents. So far, only computational data and a few X-ray structures are known on phenyl-lithium interactions between a solvent benzene or toluene and a lithium cation.[17]

So the question remained as to whether the trimer could be solvated by a toluene molecule, through a phenyl-lithium interaction? This was investigated by semi-empirical computational methods, in particular with the PM3 method.

Full geometry optimization at PM3 level was performed for various mixed complexes between **1**-Li and *n*BuLi and the results supported that (**1**-[^{6}Li])$_2$/*n*Bu[^{6}Li] is the favored complex in the absence of coordinating solvents. The mixed dimers (with symmetric as well as non-symmetric internal coordination) were largely non-favored compared with the mixed trimer in these calculations. A ladder-type trimer with an interaction between the α-carbon of the butyl group and the lithium was also disfavored in the PM3 calculations. Instead the cyclic trimer with one of the lithium di-coordinated was found to have the lowest energy, see Figure 3. This is also in agreement with the X-ray analysis and the 2D ^{6}Li,^{1}H-HOESY-NMR spectroscopic data above.

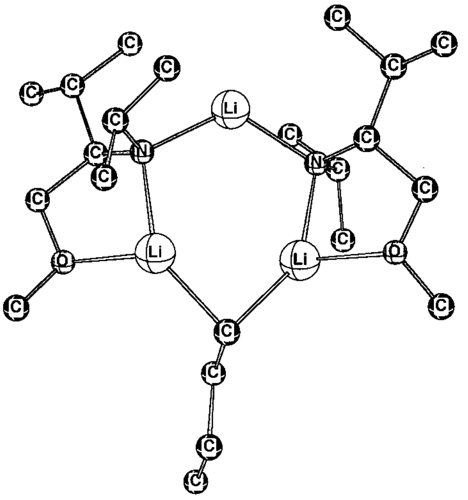


Figure 3. The geometry optimised (PM3) structure of *n*BuLi/(**1**-Li)$_2$. Hydrogens are omitted for clarity.

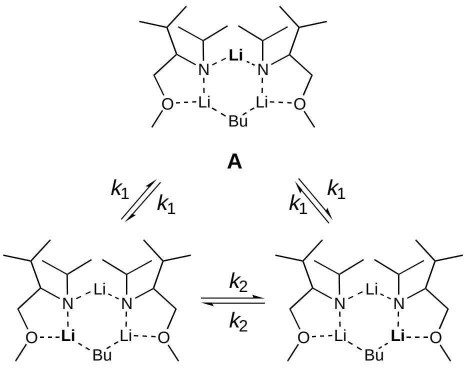
To the PM3 geometry optimized trimeric complex was added a benzene molecule as a lithium ligand, and the complex was re-optimised. There is enough space for a benzene molecule to solvate the lithium, but the structure does not correspond to an energy minimum on the potential energy surface at the PM3 level of theory. However, since PM3 may be poor in describing phenyl-lithium interactions we have also undertaken further studies using NMR on this issue.

If a toluene molecule solvates the lithium it would give different ^{6}Li NMR chemical shifts in toluene and hexane. However, only small differences were observed for the ^{6}Li signals of (**1**-[^{6}Li])$_2$/*n*Bu[^{6}Li]. An enhanced determination of a phenyl-lithium interaction should be obtained from quantitative ^{6}Li,^{1}H-distance measurements using the heteronuclear NOE build-up rates from ^{6}Li,^{1}H-HOESY spectra.[18] At short mixing times the NOE is approximately proportional to the NOE build-up rates (f), which are related to the sixth power of distance (r) according to Equation (1).

$$\frac{f(^6\mathrm{Li}-\mathrm{H}^A)}{f(^6\mathrm{Li}-\mathrm{H}^X)} = \left(\frac{r(^6\mathrm{Li}-\mathrm{H}^A)}{r(^6\mathrm{Li}-\mathrm{H}^X)}\right)^6 \qquad (1)$$

Several HOESY spectra (with mixing times of 0.4–1 s) of (**1**-[^{6}Li])$_2$/*n*Bu[^{6}Li] (0.2 M) in [D$_{14}$]hexane with 3 equivalents of non-deuterated toluene per lithium in (**1**-[^{6}Li])$_2$/*n*Bu[^{6}Li] were obtained, that is 9 equivalents of toluene per mixed trimer aggregate. The distance between the lithium and a proton on the methyl group of toluene was calculated to about 4.6 ± 1 Å based on the estimated hetero-NOE. From the magnitude of this value, we conclude that there are no phenyl-lithium interactions present in the [D$_{14}$]hexane/[D$_8$]toluene solution of (**1**-[^{6}Li])$_2$/*n*Bu[^{6}Li]. The steric requirements of the isopropyl groups of **1**-[^{6}Li] are most likely too large for an effective phenyl-lithium interaction.

The two ^{6}Li NMR signals from (**1**-[^{6}Li])$_2$/*n*Bu[^{6}Li] were found to undergo exchange. A ^{6}Li,^{6}Li-EXSY experiment performed on a solution of (**1**-[^{6}Li])$_2$/*n*Bu[^{6}Li] at $-33\,^\circ$C showed strong cross-peaks as a result of a degenerate lithium–lithium exchange. Using the D2DNMR program the observed rate constant was determined from the diagonal and cross-peak volumes.[19] We derived a $k_{\mathrm{obs}} = 0.8\ \mathrm{s}^{-1}$ for the observed exchange rate constant. The lithium atoms in (**1**-[^{6}Li])$_2$/*n*Bu[^{6}Li] may exchange according to Scheme 2. The observed exchange rate constant is the sum of the microscopic forward and reverse rate constants for the exchange of the di-coordinated lithium with the two identical methoxy coordinated lithium nuclei, A with B and A with C, respectively, that is $k_{\mathrm{obs}} = 2 \times (k_1 + k_{-1})$. Lithium exchange between the magnetically equivalent sites in B and C is not observable by NMR. The observed exchange corresponds to a microscopic rate constant $k_1 = 0.2\ \mathrm{s}^{-1}$ at $-33\,^\circ$C. Hence the activation energy ($\Delta G^{\neq}$) was calculated to 61.4 kJ mol^{-1} at $-33\,^\circ$C, a value slightly higher than expected.[20]



Scheme 2. Possible lithium exchange.

Structures in Et$_2$O: Addition of diethyl ether to the above mixed trimer in toluene at $-90\,^\circ$C resulted in large spectroscopic changes. Both ^{13}C and ^{1}H NMR showed the appearance of homodimers of the lithium amide, namely (**1**-[^{6}Li])$_2$, a mixed dimer between **1**-[^{6}Li] and *n*Bu[^{6}Li], namely *n*Bu[^{6}Li]/

(**1**-[^{6}Li]) and tetrameric *n*Bu[^{6}Li], namely (*n*Bu[^{6}Li])$_4$. The ^{13}C NMR spectrum shows two sets of signals, accordingly there are two α-carbon multiplet signals from *n*Bu[^{6}Li]. One of them, at $\delta = 10.9$, is the septet arising from the excess of tetrameric *n*Bu[^{6}Li] ($J = 5.4$ Hz) and the other, at $\delta = 11.2$, are from the mixed dimer *n*Bu[^{6}Li]/(**1**-[^{6}Li]) which splits into a distorted quintet ($J = 8.5$ Hz) as a result of the coupling to two non-equivalent lithium.

In addition, the ^{6}Li NMR spectrum of **1**-[^{6}Li] in [D$_{10}$]Et$_2$O shows five signals, two of which could be assigned to the signals from homodimers of the chiral lithium amide, (**1**-[^{6}Li])$_2\cdot$Et$_2$O, Figure 4. One of the signals of **1**-[^{6}Li])$_2\cdot$Et$_2$O is significantly broader than the other. Furthermore, tetrameric *n*Bu[^{6}Li] gives rise to one signal at $\delta = 1.9$. In addition there are two more signals at $\delta = 2.09$ and $\delta = 3.23$ (in a 1:1 ratio) arising from a mixed dimer (**1**-[^{6}Li])/*n*Bu[^{6}Li]. We conclude that in agreement with previous findings on similar lithium amides, **1**-[^{6}Li] forms mixed dimers with *n*Bu[^{6}Li] in Et$_2$O.[12]

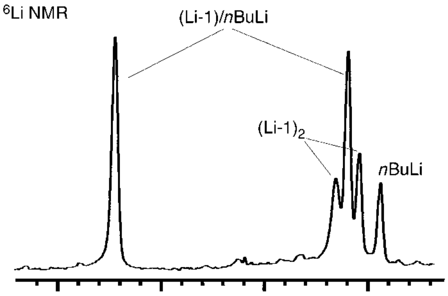


Figure 4. ^{6}Li NMR spectra of **1**-[^{6}Li] and *n*Bu[^{6}Li] in Et$_2$O at −80 °C.

The apparent equilibrium constant *K* was estimated roughly from the ^{6}Li NMR intensities to 7 in favor of the mixed dimer **1**-[^{6}Li]/*n*Bu[^{6}Li]. Figure 5 below shows the PM3 geometry optimized structure of the 1:1 mixed complex **1**-[^{6}Li]/*n*Bu[^{6}Li].

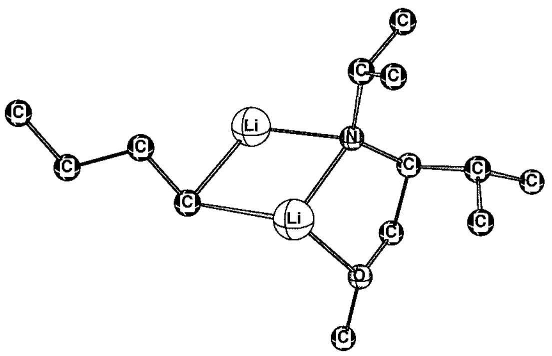


Figure 5. Geometry optimised (PM3) structure of (**1**-Li)/*n*BuLi in diethyl ether; lithium coordinating to Et$_2$O and hydrogens have been excluded for clarity.

On addition of **1** to the previous mixture the concentration of the lithium amide dimer (**1**-[^{6}Li])$_2$ increased as expected. The ^{13}C NMR spectrum shows only one set of signals, assigned to (**1**-[^{6}Li])$_2$, the ether ligand exchange is fast on the NMR time scale at −90 °C.

The two ^{6}Li NMR signals at $\delta = 2.05$ and 2.15 in a 1:1 intensity ratio were assigned to the two lithiums from the lithium amide dimer (**1**-[^{6}Li])$_2$. The signal at 2.15 is from the ether solvated lithium in (**1**-[^{6}Li])$_2$ and the signal at 2.05 is from the lithium which is internally coordinated by the two methoxy groups. The ^{6}Li,^{1}H-HOESY spectrum (**1**-[^{6}Li])$_2$ is depicted in Figure 6.

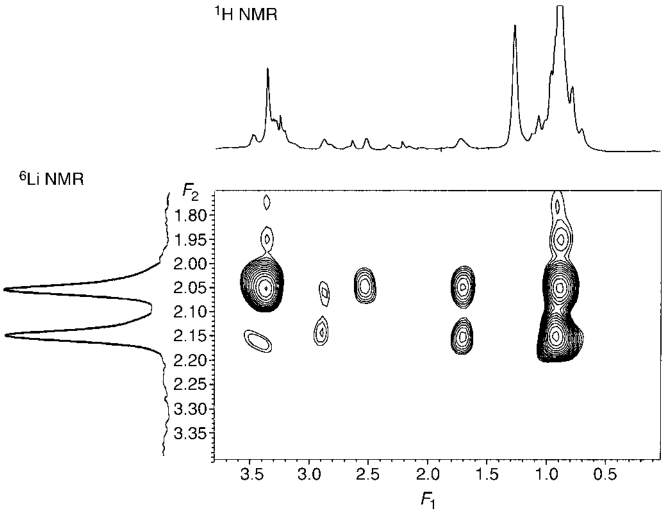


Figure 6. The ^{6}Li,^{1}H-HOESY spectrum of (**1**-[^{6}Li])$_2$, (0.3 M) in [D$_8$]toluene at −85 °C.

Only the ^{6}Li NMR resonance at $\delta = 2.05$ shows NOE (presence of a strong cross-peak) to the methoxy proton signal at 3.35. This indicates that the dimer is coordinated non-symmetrically. Addition of non-deuterated Et$_2$O followed by a new HOESY experiment resulted in a new spectrum with a strong hetero-NOE cross-peak at the trace of the ^{6}Li signal at $\delta = 2.15$ and the α-protons of Et$_2$O. This cross-peak arises as a result of the lithium–Et$_2$O interaction. The full geometry optimized (PM3) structure of the non-symmetric solvated dimer of **1**-Li, (**1**-Li)$_2$, is shown in Figure 7.

According to the calculations only one Et$_2$O molecule is coordinated to the lithium amide dimer.

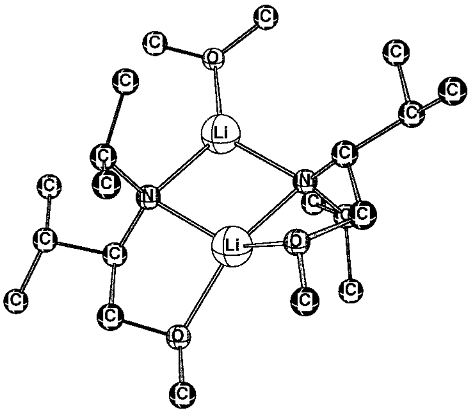


Figure 7. The geometry optimised structure of the non-symmetric dimethyl ether (DME) solvated dimer of **1**-Li, (**1**-Li)$_2\cdot$DME. Diethyl ether was replaced with dimethyl ether in the PM3 calculations. Hydrogens are omitted for clarity.

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Conclusion

With these results we have added another valid structural type to the arsenal of various different aggregation states or complexes for organolithium compounds in solution. It is particularly interesting to study the asymmetric induction that the mixed trimer can give rise to in comparison to that of the mixed dimer. Comparison of the asymmetric induction in non-coordinated and coordinated solvents is under investigation and will be published later.

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