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A sandwich complex of lithium oxide: $\{Li[Bu^nC(NBu^t)_2]\}_4{\cdot}Li_2O$

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Hydrolysis of $\{Li[Bu^nC(NBu^t)_2]\}_2$, prepared from $LiBu^n$ and Bu^tNCNBu^t in hexanes, produced the nineteen atom cluster $\{Li[Bu^nC(NBu^t)_2]\}_4{\cdot}Li_2O$; an X-ray structure determination revealed an Li_2O molecule encapsulated by two eight-membered $Li_2N_4C_2$ rings.

Novel structural and/or reaction chemistry often results from ligands that provide unusual steric and/or electronic environments at metal centres. To this end N-silylated benzamidinates $RC(NSiMe_3)_2^-$ (R = aryl)[1,2] and, more recently, dialkylamidinates $RC(NR')_2^-$ (where R and R′ are different alkyl groups) have been investigated extensively.[1b,3–5] Although a wide range of both main-group and transition-metal complexes of these chelating ligands has been characterized,[6] structural information for the lithium derivatives of these important reagents is limited to complexes in which the lithium ions are co-ordinated to Lewis bases such as RCN (R = aryl),[7] THF,[8] HMPA,[9] *N,N,N′,N′*-tetramethylethylenediamine[9] or *N,N,N′,N′,N″*-pentamethyldiethylenetriamine.[9] The complexes $[4\text{-}MeC_6H_4C(NSiMe_3)_2Li(THF)]_2$[8] and $[PhC(NPh)_2Li(HMPA)]_2$[9] form dimeric, step-shaped structures whereas chelating Lewis bases give rise to monomeric structures.[9]

We describe here the unexpected generation and crystal structure of the complex $\{Li[Bu^nC(NBu^t)_2]\}_4{\cdot}Li_2O$ **2** in which a molecule of lithium oxide is trapped between two twisted $Li_2N_4C_2$ ladders of a dimeric lithium amidinate. Compared to other complexes of Li_2O,[10–14] complex **2** exhibits some novel features that result from the unique ligand behaviour of the $Li_2N_4C_2$ ring.

Amidinates $Li[RC(NR')_2]$ are readily obtained by the nucleophilic addition of an organolithium reagent (RLi) to a carbodiimide R′NCNR′.[3,5] In this work, the addition of a 2.5 M solution of $LiBu^n$ in hexanes (3.7 mL) to a solution of 1,3-di-*tert*-butylcarbodiimide (9.22 mmol) in hexane (10 mL) under argon at 23 °C produced a transparent, pale yellow solution. Removal of volatile materials *in vacuo* gave a viscous yellow oil, which was redissolved twice in diethyl ether (≈ 5 mL). Evaporation of the solvent *in vacuo* produced $\{Li[Bu^nC(NBu^t)_2]\}_n$ **1** as a fine yellow powder (8.63 mmol, 94%).‡ Recrystallization of **1** from a saturated toluene solution (4 d at −20 °C) produced a few X-ray quality crystals with NMR parameters significantly different from those of **1**.

An X-ray structural determination revealed that the composition of these crystals is $\{Li[Bu^nC(NBu^t)_2]\}_4{\cdot}Li_2O$ **2** (Fig. 1).§ This nineteen atom cluster has a μ_6-OLi_6 core. Six-fold co-ordination of O^{2-} by metal cations in molecular compounds is rare and usually involves regular O_h symmetry.[12–14] A major difference between the structure of **2** and those of other Li_2O aggregates[11–14] is that the molecule of Li_2O is readily identified in **2** because of the relatively low symmetry of this cluster. Thus **2** may be viewed as an almost linear Li_2O molecule [Li(1)–O–Li(2) 175.8(2)°] sandwiched between two twisted $Li_2N_4C_2$ ladders. The oxygen atom is tightly co-ordinated to all six lithium atoms, but the mean Li–O distance in the Li_2O molecule [1.803(4) Å] is significantly shorter than that in the other Li–O bonds [mean value 1.869(4) Å], *cf.* 1.89(1) Å in $[(cyclo\text{-}C_5H_9)N(H)Li]_{12}{\cdot}Li_2O$,[13] 1.81–1.90(2) Å in $[Pr^i_2(Mes)SiP]_8Li_{16}{\cdot}Li_2O$[14] (Mes = $C_6H_2Me_3$-2,4,6). The distortion of the octahedral geometry of the OLi_6 unit in **2** is reflected in the Li ··· Li separations which range from 2.169(5) Å across the $Li_2N_4C_2$ rings to 3.127(5) Å {*cf.* 2.63–2.67(2) Å in $[Pr^i_2(Mes)SiP]_8Li_{16}{\cdot}Li_2O$[14]}. All six lithium atoms can be viewed as four-co-ordinate, but there is considerable variation in the Li–N bond distances. Those belonging to the Li_2O moiety are bonded *symmetrically* to two nitrogen atoms of *different* $Li_2N_4C_2$ rings [|*d*(Li–N)| 2.106(4) Å] and are also involved in a third, weaker Li ··· N interaction [2.573(4) Å]. This results in a ‘pinching in’ of the $Li_2N_4C_2$ rings as reflected from the values of |Li–O–Li| 70.9(2)° and |N–C–N| = 115.3(9)°. The other four lithium atoms are bonded *unsymmetrically* to two nitrogen atoms of *the same* $Li_2N_4C_2$ ring [|*d*(Li–N)| 2.03(2) and 2.36(2) Å]. As a result there are three four-co-ordinate and one five-co-ordinate nitrogen atom in each $Li_2N_4C_2$ ring. The mean C–N bond distances are slightly longer for the four-co-ordinate compared to the five-co-ordinate N atoms [1.346(2) *vs.* 1.329(2) Å].

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‡ **1** Mp 51–54 °C. ^1H NMR (25 °C, 200 MHz, C_6D_6): δ 0.90 (t, 3 H, $C\mathit{H}_3CH_2CH_2CH_2$), 1.32 [s + m, 20 H, $CH_3C\mathit{H}_2CH_2CH_2$ and $C(C\mathit{H}_3)_3$], 1.85 (m, 2 H, $CH_3CH_2C\mathit{H}_2CH_2$), 2.50 (m, 2 H, $CH_3CH_2CH_2C\mathit{H}_2$). ^{13}C NMR (25 °C, 50.288 MHz, C_6D_6): δ 14.1 (s, $CH_2CH_2CH_2\mathit{C}H_3$), 24.1 (s, $CH_2CH_2\mathit{C}H_2CH_3$), 33.0 (s, $CH_2\mathit{C}H_2CH_2CH_3$), 33.2 (s, $\mathit{C}H_2CH_2CH_2CH_3$), 33.7 [s, $C(\mathit{C}H_3)_3$], 51.6 [s, $\mathit{C}(CH_3)_3$], 178.4 [s, $\mathit{C}(NBu^t)_2Bu^n$]; (25 °C, 75.432 MHz, solid state): δ 14.2 (s, $CH_2CH_2CH_2\mathit{C}H_3$), 24.1 (s, $CH_2CH_2\mathit{C}H_2CH_3$), 34.1 [s br, $CH_2\mathit{C}H_2CH_2CH_3$, $\mathit{C}H_2CH_2CH_2CH_3$ and $C(\mathit{C}H_3)_3$], 51.3 [s, $\mathit{C}(CH_3)_3$], 175.3 [s, $\mathit{C}(NBu^t)_2Bu^n$]. ^7Li NMR (25 °C, 155.508 MHz, C_6D_6, relative to 1 M LiCl in D_2O): δ −0.62 (s); (25 °C, 116.54 MHz, solid state, relative to LiCl): δ 1.46 (s).

2 Mp 132–134 °C (Found: C, 69.40; H, 12.78; N, 12.51. Calc. for $C_{52}H_{108}Li_6N_8O$: C, 69.16; H, 12.05; N, 12.41%). ^1H NMR (25 °C, 200 MHz, C_6D_6): δ 0.99 (t, 3 H, $C\mathit{H}_3CH_2CH_2CH_2$), 1.46 [s + m, 20 H, $CH_3C\mathit{H}_2CH_2CH_2$ and $C(C\mathit{H}_3)_3$], 1.95 (m, 2 H, $CH_3CH_2C\mathit{H}_2CH_2$), 2.60 (m, 2 H, $CH_3CH_2CH_2C\mathit{H}_2$). ^{13}C NMR (25 °C, 50.288 MHz, C_6D_6): 15.5 (s, $CH_2CH_2CH_2\mathit{C}H_3$), 23.5 (s, $CH_2CH_2\mathit{C}H_2CH_3$), 32.9 ($CH_2\mathit{C}H_2CH_2CH_3$), 34.5 (s, $\mathit{C}H_2CH_2CH_2CH_3$), 34.6 [s, $C(\mathit{C}H_3)_3$], 51.9 [s, $\mathit{C}(CH_3)_3$], 179.6 [s, $\mathit{C}(NBu^t)_2Bu^n$]; (25 °C, 75.432 MHz, solid state): δ 14.4 (s, $CH_2CH_2CH_2\mathit{C}H_3$), 24.5 (s, $CH_2CH_2\mathit{C}H_2CH_3$), 35.5 [s br, $CH_2\mathit{C}H_2CH_2CH_3$, $\mathit{C}H_2CH_2CH_2CH_3$ and $C(\mathit{C}H_3)_3$], 52.7 [s, $\mathit{C}(CH_3)_3$], 180.6 [s, $\mathit{C}(NBu^t)_2Bu^n$]. ^7Li NMR (25 °C, 155.508 MHz, C_6D_6, relative to 1 M LiCl in D_2O): δ −0.82 (s), −1.23 (s); (25 °C, 116.54 MHz, solid state, relative to LiCl): δ 2.97 (s).

§ Crystal data: $C_{52}H_{108}Li_6N_8O$, $M = 903.10$, triclinic, space group $P\bar{1}$, $a = 10.137(3)$, $b = 14.205(4)$, $c = 21.961(6)$ Å, $\alpha = 91.7718(5)$, $\beta = 103.207(5)$, $\gamma = 101.442(5)°$, $U = 2008(1)$ Å^3, $Z = 2$, $\mu = 0.58$ cm^{-1}, $T = 213$ K, 24 534 reflections collected, 13 710 independent reflections, $R_{int} = 0.0701$. The final $R(F)$ and $wR(F^2)$ values were 0.0545 and 0.0821, respectively. CCDC reference number 186/1071. See http://www.rsc.org/suppdata/dt/1998/2603/ for crystallographic files in .cif format.

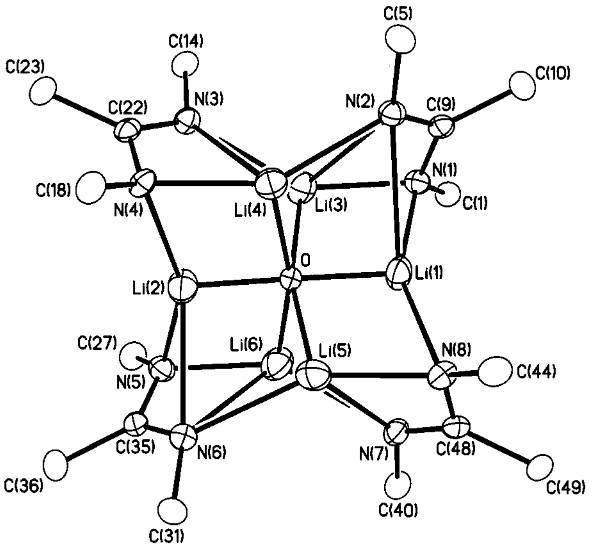


Fig. 1 Molecular structure and atomic numbering scheme for complex **2**. Thermal ellipsoids are depicted at 30% probability. For clarity only the α-carbon atoms of Bu^n and Bu^t are shown. Selected bond distances (Å) and angles (°): O–Li(1) 1.805(4), O–Li(2) 1.801(4), O–Li(3), 1.880(4), O–Li(4) 1.883(4), O–Li(5) 1.852(4), O–Li(6) 1.862(4), Li(1)–N(1) 2.082(4), Li(1)–N(2) 2.664(4), Li(1)–N(8) 2.092(4), Li(2)–N(4) 2.102(4), Li(2)–N(5) 2.148(4), Li(2)–N(6) 2.481(4), Li(3)–N(1) 2.047(4), Li(3)–N(2) 2.505(4), Li(3)–N(3) 2.293(4), Li(4)–N(2) 2.316(4), Li(4)–N(3) 2.458(4), Li(4)–N(4) 2.050(4), Li(5)–N(6) 2.390(4), Li(5)–N(7) 2.443(4), Li(5)–N(8) 2.062(4), Li(6)–N(5) 2.048(4), Li(6)–N(6) 2.514(5), Li(6)–N(7) 2.376(4); |N–C–N| 115.1 [range 114.6(2)–115.9(2)]

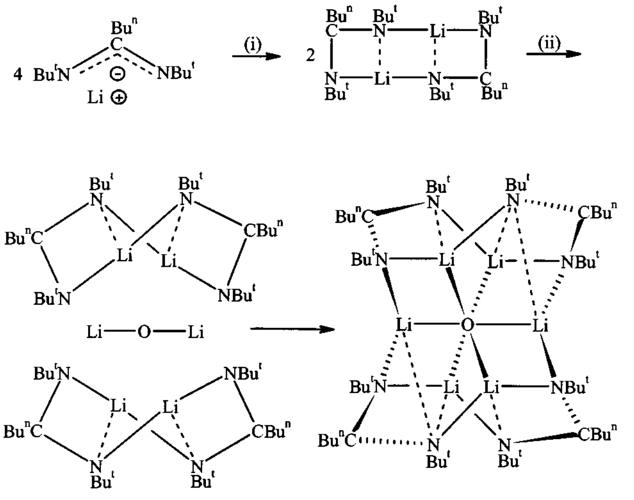
The most obvious explanation for the formation of **2** is the partial hydrolysis of **1** by trace amounts of water present in the solvent or flask used for recrystallization [reactions (1) and (2)].

$$\underset{\mathbf{1}}{\mathrm{Li[Bu^nC(NBu^t)_2]}} + \mathrm{H_2O} \longrightarrow \mathrm{LiOH} + \underset{\mathbf{3}}{\mathrm{Bu^nC(NBu^t)[N(H)Bu^t]}} \qquad (1)$$

$$5\,\mathbf{1} + \mathrm{LiOH} \longrightarrow \underset{\mathbf{2}}{\mathrm{\{Li[C(NBu^t)_2(Bu^n)]\}_4\cdot Li_2O}} + \mathbf{3} \qquad (2)$$

The adventitious presence of water has previously been identified as the source of Li_2O in aggregates with lithium amides.[12,13] To test this hypothesis a stoichiometric amount of water was added, by syringe, to a 0.46 M solution of **1** in toluene (5 mL) at 23 °C. This produced an oily white solid, which was stirred for 1 h to give an opaque yellow solution. The volume of the solution was reduced by one-half and colourless crystals of **2** were obtained in 30% yield after 3 d at −14 °C. The analytical and spectroscopic characterization of **2** were completed on this product.‡ The observation of two resonances in the ^7Li NMR spectrum (in C_6D_6) at δ −0.82 and −1.23 (the latter is of lower relative intensity) suggests a higher average symmetry (D_2) for **2** in solution compared to that observed (C_2) in the solid state. The ^7Li NMR spectrum of **1** in C_6D_6 exhibits a singlet at δ −0.62. There are significant differences in the ^{13}C NMR chemical shifts observed for **1** and **2**.‡ In particular, δ [*C*(NBu^t)$_2$(Bu^n)] provides a diagnostic distinction between **1** and **2** both in solution and, especially, in the solid state. The ^1H NMR spectrum of the mother-liquor from reaction (1) showed it to consist of a mixture of unreacted **1** and the hydrolysis product **3**. Thus hydrolysis of **1** is clearly established as a route to **2**. Further support for this conclusion is provided by the observation that the direct reaction of **1** with LiOH in toluene at 23 °C for 48 h produces **2** in 41% yield, but **2** is not formed from the treatment of **1** with Li_2O under similar conditions.

A conceptual representation of the assembly of the nineteen atom cluster **2** from two $Li_2N_4C_2$ dimers and a Li_2O molecule is shown in Scheme 1, where the source of Li_2O is LiOH produced by the hydrolysis of **1**. An alternative source of LiOH and, hence, Li_2O in the original formation of **2** is the commercial LiBu^n used for the preparation of **1**.[15] Indeed the ^7Li NMR spectrum of *fresh* LiBu^n (2.5 M in hexanes, Aldrich) in C_6D_6 exhibited a small resonance at δ −0.89 in addition to the dominant resonance at δ −0.22 (*vs.* 1 M LiCl in D_2O). The intensity of the former relative to that at δ −0.22 increased upon addition of water to the solution, but not upon addition of solid LiOH. Although the identity of the δ −0.89 species has not been established, we cannot rule out commercial LiBu^n as a source of Li_2O in the formation of **2**.



Scheme 1 Schematic representation of the formation of **2**. (i) Dimerisation; (ii) partial hydrolysis

Finally, we note that the co-ordination of Li_2O does not affect the use of **2** as a source of the chelating amidinate ligand $Bu^nC(NBu^t)_2^-$. For example, reaction of **2** (5.82 mmol) with $PhBCl_2$ (5.29 mmol) in toluene (15 mL) produces $PhB(Cl)[C(NBu^t)_2Bu^n]$ **4** in 82% Yield.¶ The four-membered ring structure of **4** has been confirmed by X-ray crystallography and full details of this structure and those of related four-co-ordinate boron complexes will be reported in a separate publication.[16]

In summary, complex **2** provides the first demonstration of the ligand behaviour of a dimeric lithium amidinate. The entrapment of other alkali-metal chalcogenides, *e.g.* Li_2S, Na_2O, by lithium amidinates is an interesting possibility that will be pursued.

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¶ Mp 76–79 °C (Found: C, 67.76; H, 9.97; N, 8.45. Calc. for $C_{19}H_{32}BClN_2$: C, 68.16; H, 9.65; N, 8.37%). ^1H NMR (25 °C, 200 MHz, C_6D_6): δ 0.73 (t, 3 H), 1.11 (m, 2 H), 1.17 (s, 18 H), 1.60 (m, 2 H), 2.14 (m, 2 H) 7.2–8.1 (m, 5 H). ^{11}B NMR (25 °C, 64.2 MHz, relative to $BF_3\cdot OEt_2$): δ 6.8 (s). EI-MS [70 eV (eV ≈ 1.602×10^{-19} J)]: *m/z* 334 (M^+, good agreement between calculated and observed isotopic distribution).

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