

A sandwich complex of lithium oxide:  $\{\text{Li}[\text{Bu}^n\text{C}(\text{NBu}^t)_2]\}_4 \cdot \text{Li}_2\text{O}$ Tristram Chivers,<sup>\*†</sup> Andrew Downard<sup>a</sup> and Glenn P. A. Yap<sup>b</sup><sup>a</sup> Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4<sup>b</sup> Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

Hydrolysis of  $\{\text{Li}[\text{Bu}^n\text{C}(\text{NBu}^t)_2]\}_2$ , prepared from  $\text{LiBu}^n$  and  $\text{Bu}^t\text{NCNBu}^t$  in hexanes, produced the nineteen atom cluster  $\{\text{Li}[\text{Bu}^n\text{C}(\text{NBu}^t)_2]\}_4 \cdot \text{Li}_2\text{O}$ ; an X-ray structure determination revealed an  $\text{Li}_2\text{O}$  molecule encapsulated by two eight-membered  $\text{Li}_2\text{N}_4\text{C}_2$  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  $\text{RC}(\text{NSiMe}_3)_2^-$  (R = aryl)<sup>1,2</sup> and, more recently, dialkylamidinates  $\text{RC}(\text{NR}')_2^-$  (where R and R' are different alkyl groups) have been investigated extensively.<sup>1b,3-5</sup> Although a wide range of both main-group and transition-metal complexes of these chelating ligands has been characterized,<sup>6</sup> 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),<sup>7</sup> THF,<sup>8</sup> HMPA,<sup>9</sup> N,N,N',N'-tetramethylethylenediamine<sup>9</sup> or N,N,N',N',N''-pentamethyldiethylenetriamine.<sup>9</sup> The complexes  $[\text{4-MeC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2\text{Li}(\text{THF})_2]_2$  and  $[\text{PhC}(\text{NPh})_2\text{Li}(\text{HMPA})_2]_2$  form dimeric, step-shaped structures whereas chelating Lewis bases give rise to monomeric structures.<sup>9</sup>

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

Amidines  $\text{Li}[\text{RC}(\text{NR}')_2]$  are readily obtained by the nucleophilic addition of an organolithium reagent (RLi) to a carbodiimide  $\text{R}'\text{NCNR}'$ .<sup>3,5</sup> In this work, the addition of a 2.5 M solution of  $\text{LiBu}^n$  in hexanes (3.7 mL) to a solution of 1,3-ditert-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 ( $\approx$  5 mL). Evaporation of the solvent *in vacuo* produced  $\{\text{Li}[\text{Bu}^n\text{C}(\text{NBu}^t)_2]\}_n$  **1** as a fine yellow powder (8.63 mmol, 94%).<sup>‡</sup> 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  $\{\text{Li}[\text{Bu}^n\text{C}(\text{NBu}^t)_2]\}_4 \cdot \text{Li}_2\text{O}$  **2** (Fig. 1).<sup>§</sup> This nineteen atom cluster has a  $\mu_6\text{-OLi}_6$  core. Six-fold co-ordination of  $\text{O}^{2-}$  by metal cations in molecular compounds is rare and usually involves regular  $\text{O}_h$  symmetry.<sup>12-14</sup> A major difference between the structure of **2** and those of other  $\text{Li}_2\text{O}$  aggregates<sup>11-14</sup> is that the molecule of  $\text{Li}_2\text{O}$  is readily identified in **2** because of the relatively low symmetry of this cluster.

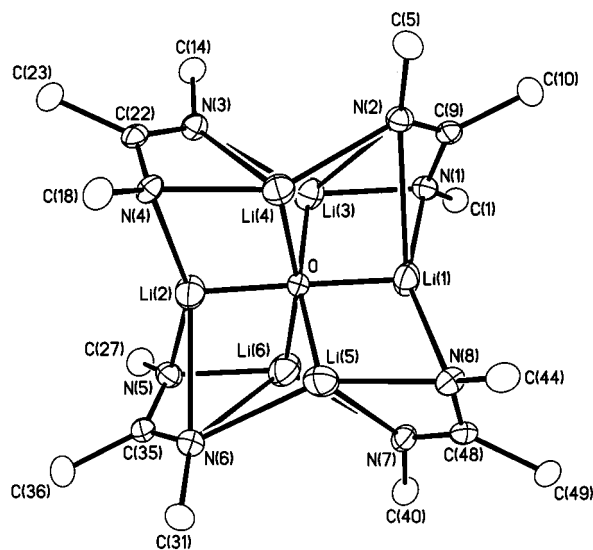
Thus **2** may be viewed as an almost linear  $\text{Li}_2\text{O}$  molecule [ $\text{Li}(1)\text{-O-Li}(2)$  175.8(2)°] sandwiched between two twisted  $\text{Li}_2\text{N}_4\text{C}_2$  ladders. The oxygen atom is tightly co-ordinated to all six lithium atoms, but the mean Li-O distance in the  $\text{Li}_2\text{O}$  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  $[(\text{cyclo-C}_5\text{H}_9)\text{N}(\text{H})\text{Li}]_{12} \cdot \text{Li}_2\text{O}$ ,<sup>13</sup> 1.81-1.90(2) Å in  $[\text{Pr}^t_2(\text{Mes})\text{-SiP}]_8\text{Li}_{16} \cdot \text{Li}_2\text{O}$ <sup>14</sup> (Mes =  $\text{C}_6\text{H}_2\text{Me}_3$ -2,4,6). The distortion of the octahedral geometry of the  $\text{OLi}_6$  unit in **2** is reflected in the  $\text{Li} \cdots \text{Li}$  separations which range from 2.169(5) Å across the  $\text{Li}_2\text{N}_4\text{C}_2$  rings to 3.127(5) Å [*cf.* 2.63-2.67(2) Å in  $[\text{Pr}^t_2(\text{Mes})\text{-SiP}]_8\text{Li}_{16} \cdot \text{Li}_2\text{O}$ <sup>14</sup>]. 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  $\text{Li}_2\text{O}$  moiety are bonded *symmetrically* to two nitrogen atoms of *different*  $\text{Li}_2\text{N}_4\text{C}_2$  rings [ $d(\text{Li-N})$ ] 2.106(4) Å] and are also involved in a third, weaker  $\text{Li} \cdots \text{N}$  interaction [2.573(4) Å]. This results in a 'pinching in' of the  $\text{Li}_2\text{N}_4\text{C}_2$  rings as reflected from the values of  $|\text{Li-O-Li}|$  70.9(2)° and  $|\text{N-C-N}|$  = 115.3(9)°. The other four lithium atoms are bonded *unsymmetrically* to two nitrogen atoms of *the same*  $\text{Li}_2\text{N}_4\text{C}_2$  ring [ $d(\text{Li-N})$ ] 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  $\text{Li}_2\text{N}_4\text{C}_2$  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].

‡ 1 Mp 51-54 °C. <sup>1</sup>H NMR (25 °C, 200 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  0.90 (t, 3 H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.32 [s + m, 20 H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$  and  $\text{C}(\text{CH}_3)_3$ ], 1.85 (m, 2 H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.50 (m, 2 H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ ). <sup>13</sup>C NMR (25 °C, 50.288 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  14.1 (s,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ ), 24.1 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 33.0 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 33.2 (s,  $\text{CH}_2\text{CH}_2\text{-CH}_2\text{CH}_3$ ), 33.7 [s,  $\text{C}(\text{CH}_3)_3$ ], 51.6 [s,  $\text{C}(\text{CH}_3)_3$ ], 178.4 [s,  $\text{C}(\text{NBu}^t)_2\text{Bu}^n$ ]; (25 °C, 75.432 MHz, solid state):  $\delta$  14.2 (s,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ ), 24.1 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 34.1 [s br,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{C}(\text{CH}_3)_3$ ], 51.3 [s,  $\text{C}(\text{CH}_3)_3$ ], 175.3 [s,  $\text{C}(\text{NBu}^t)_2\text{Bu}^n$ ]. <sup>7</sup>Li NMR (25 °C, 155.508 MHz,  $\text{C}_6\text{D}_6$ , relative to 1 M LiCl in  $\text{D}_2\text{O}$ ):  $\delta$  -0.62 (s); (25 °C, 116.54 MHz, solid state, relative to LiCl):  $\delta$  1.46 (s).

‡ 2 Mp 132-134 °C (Found: C, 69.40; H, 12.78; N, 12.51. Calc. for  $\text{C}_{52}\text{H}_{108}\text{Li}_6\text{N}_8\text{O}$ : C, 69.16; H, 12.05; N, 12.41%). <sup>1</sup>H NMR (25 °C, 200 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  0.99 (t, 3 H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.46 [s + m, 20 H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$  and  $\text{C}(\text{CH}_3)_3$ ], 1.95 (m, 2 H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.60 (m, 2 H,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ ). <sup>13</sup>C NMR (25 °C, 50.288 MHz,  $\text{C}_6\text{D}_6$ ): 15.5 (s,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ ), 23.5 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 32.9 ( $\text{CH}_2\text{CH}_2\text{-CH}_2\text{CH}_3$ ), 34.5 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 34.6 [s,  $\text{C}(\text{CH}_3)_3$ ], 51.9 [s,  $\text{C}(\text{CH}_3)_3$ ], 179.6 [s,  $\text{C}(\text{NBu}^t)_2\text{Bu}^n$ ]; (25 °C, 75.432 MHz, solid state):  $\delta$  14.4 (s,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ ), 24.5 (s,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 35.5 [s br,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{C}(\text{CH}_3)_3$ ], 52.7 [s,  $\text{C}(\text{CH}_3)_3$ ], 180.6 [s,  $\text{C}(\text{NBu}^t)_2\text{Bu}^n$ ]. <sup>7</sup>Li NMR (25 °C, 155.508 MHz,  $\text{C}_6\text{D}_6$ , relative to 1 M LiCl in  $\text{D}_2\text{O}$ ):  $\delta$  -0.82 (s), -1.23 (s); (25 °C, 116.54 MHz, solid state, relative to LiCl):  $\delta$  2.97 (s).

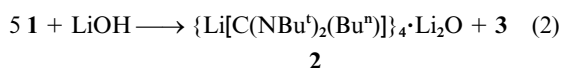
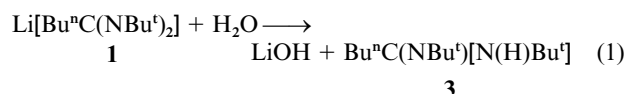
§ Crystal data:  $\text{C}_{52}\text{H}_{108}\text{Li}_6\text{N}_8\text{O}$ ,  $M = 903.10$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.137(3)$ ,  $b = 14.205(4)$ ,  $c = 21.961(6)$  Å,  $\alpha = 91.7718(5)$ ,  $\beta = 103.207(5)$ ,  $\gamma = 101.442(5)^\circ$ ,  $U = 2008(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $\mu = 0.58$  cm<sup>-1</sup>,  $T = 213$  K, 24 534 reflections collected, 13 710 independent reflections,  $R_{\text{int}} = 0.0701$ . 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.

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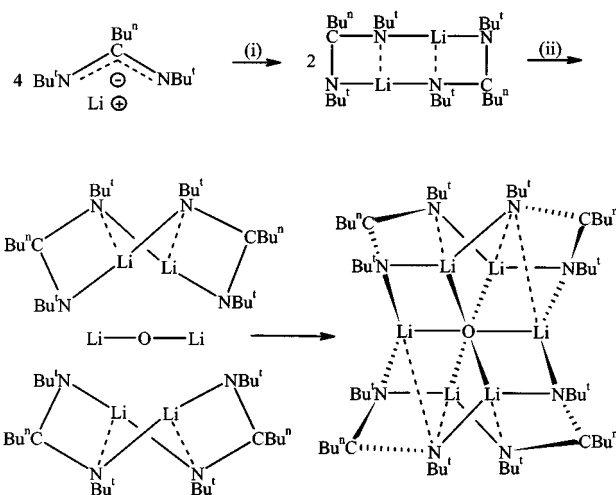
**Fig. 1** Molecular structure and atomic numbering scheme for complex **2**. Thermal ellipsoids are depicted at 30% probability. For clarity only the  $\alpha$ -carbon atoms of  $\text{Bu}^n$  and  $\text{Bu}^t$  are shown. Selected bond distances (Å) and angles ( $^\circ$ ): O–Li(1) 1.805(4), O–Li(2) 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)].



The adventitious presence of water has previously been identified as the source of  $\text{Li}_2\text{O}$  in aggregates with lithium amides.<sup>12,13</sup> 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  $^7\text{Li}$  NMR spectrum (in  $\text{C}_6\text{D}_6$ ) at  $\delta$  –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  $^7\text{Li}$  NMR spectrum of **1** in  $\text{C}_6\text{D}_6$  exhibits a singlet at  $\delta$  –0.62. There are significant differences in the  $^{13}\text{C}$  NMR chemical shifts observed for **1** and **2**.‡ In particular,  $\delta$  [ $\text{C}(\text{NBu}^t)_2$ –( $\text{Bu}^n$ )] provides a diagnostic distinction between **1** and **2** both in solution and, especially, in the solid state. The  $^1\text{H}$  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  $\text{Li}_2\text{O}$  under similar conditions.

A conceptual representation of the assembly of the nineteen atom cluster **2** from two  $\text{Li}_2\text{N}_4\text{C}_2$  dimers and a  $\text{Li}_2\text{O}$  molecule is



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

shown in Scheme 1, where the source of  $\text{Li}_2\text{O}$  is LiOH produced by the hydrolysis of **1**. An alternative source of LiOH and, hence,  $\text{Li}_2\text{O}$  in the original formation of **2** is the commercial  $\text{LiBu}^n$  used for the preparation of **1**.<sup>15</sup> Indeed the  $^7\text{Li}$  NMR spectrum of *fresh*  $\text{LiBu}^n$  (2.5 M in hexanes, Aldrich) in  $\text{C}_6\text{D}_6$  exhibited a small resonance at  $\delta$  –0.89 in addition to the dominant resonance at  $\delta$  –0.22 (vs. 1 M LiCl in  $\text{D}_2\text{O}$ ). The intensity of the former relative to that at  $\delta$  –0.22 increased upon addition of water to the solution, but not upon addition of solid LiOH. Although the identity of the  $\delta$  –0.89 species has not been established, we cannot rule out commercial  $\text{LiBu}^n$  as a source of  $\text{Li}_2\text{O}$  in the formation of **2**.

Finally, we note that the co-ordination of  $\text{Li}_2\text{O}$  does not affect the use of **2** as a source of the chelating amidinate ligand  $\text{Bu}^n\text{C}(\text{NBu}^t)_2^-$ . For example, reaction of **2** (5.82 mmol) with  $\text{PhBCl}_2$  (5.29 mmol) in toluene (15 mL) produces  $\text{PhB}(\text{Cl})[\text{C}(\text{NBu}^t)_2\text{Bu}^n]$  **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-coordinate boron complexes will be reported in a separate publication.<sup>16</sup>

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.  $\text{Li}_2\text{S}$ ,  $\text{Na}_2\text{O}$ , by lithium amidinates is an interesting possibility that will be pursued.

## Acknowledgements

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¶ Mp 76–79 °C (Found: C, 67.76; H, 9.97; N, 8.45. Calc. for  $\text{C}_{19}\text{H}_{32}\text{B}-\text{ClN}_2$ : C, 68.16; H, 9.65; N, 8.37%).  $^1\text{H}$  NMR (25 °C, 200 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  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).  $^{11}\text{B}$  NMR (25 °C, 64.2 MHz, relative to  $\text{BF}_3\cdot\text{OEt}_2$ ):  $\delta$  6.8 (s). EI-MS [70 eV ( $\text{eV} \approx 1.602 \times 10^{-19}$  J)]:  $m/z$  334 ( $M^+$ , good agreement between calculated and observed isotopic distribution).

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