# Novel octameric structure of the lithium primary amide [$\{Bu^tN(H)Li\}_8$] and its implication for the directed synthesis of heterometallic imide cages

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**The crystalline lithium primary amide derived from *tert*-butylamine, [$\{Bu^tN(H)Li\}_n$], is structurally characterised by an X-ray diffraction study and shown to be a novel octameric ($n$ = 8) ladder conformation, the cyclic, 'double-crown' nature of which implies molecules of this design could direct the synthesis of heterobimetallic (*i.e.* lithium and another metal) imide cage constructions.**

Long overshadowed by their much studied, much utilised secondary counterparts, lithiated primary amines [$\{RN(H)Li\}_n$] are themselves currently growing in stature as synthetic reagents. Two general applications have been established. First, they can effect the simple transfer of the intact amido ligand to another metal centre, *e.g.* as recently demonstrated by the reaction of lithium anilide and the rhodium(I) complex [$RhCl(PPh_3)_3$].[1] Secondly, they can be transformed into imido ($RN^{2-}$) formulations, in more complex processes, the products of which are less easy to predict. In this latter regard, the specific amide of interest here, [$\{Bu^tN(H)Li\}_n$] **1**, has recently proved its usefulness in the synthesis of the manganese dimer [$Mn(\mu\text{-}Bu^tN)(Bu^tN)_2]_2$, and the mixed lithium–tellurium cage species [$\{(Bu^tN)_3TeLi_2\}_2$.][2,3] Disclosed in this paper is the solid-state structure of **1**, as determined by two independent X-ray crystallographic studies in Brown and Newcastle Universities. An octameric ($n$ = 8) aggregate, unprecedented in both primary and secondary amides,[4] its dimensions reveal it to be a cyclic ladder molecule, the 'double-crown' shape of which implies it could potentially function as a template for designing heterometallic (*i.e.* lithium plus another metal) imide cages. Indeed, there is literature evidence to suggest that another lithium primary amide has already been used in this capacity though its suspected cyclic ladder nature had not been recognised.

When **1** is synthesised by lithiation of *tert*-butylamine in hexane solution,† its crystal structure consists of discrete octameric lithium amide molecules with solvent molecules of crystallisation (one per octamer).‡ Prepared in toluene solution, a solvent-free structure is obtained.§ In keeping with the well established aggregation principles of lithium amide chemistry,[4] and by analogy with the hexameric precedent in the secondary amide [$\{H_2C(CH_2)_5NLi\}_6$] **2**,[5] the octameric arrangement can be categorized as a cyclic ladder (Fig. 1). This description relates not only to its appearance as drawn, but also to the idea that it self-assembles by a laddering process [*i.e.* ideally, the lateral fusing of four identical $(NLi)_2$ dimeric rings, but, in practice, curving occurs to minimize van der Waals repulsions between substituents], and not by a stacking process [*i.e.* the vertical association of two identical $(NLi)_4$ tetrameric rings].[4] Dimensions within **1** fully corroborate this interpretation. To elaborate, mean bond angles within the four-membered $(NLi)_2$ rings (at N, 71.8°, at Li, 108.2°) bear a close resemblance to those in discrete lithium amide dimers (*e.g.* in the anilide [$\{PhN(H)Li{\cdot}2py\}_2$],[6] 76.7 and 103.2° respectively). In contrast, the $(NLi)_4$ ladder edges of **1** differ significantly from the $(NLi)_4$ ring in the known discrete lithium amide tetramer [$\{Me_2C(CH_2)_3CMe_2NLi\}_4$],[4] which is considerably more distorted being much wider at the Li corners (*i.e.* mean angles, 168.5° *cf.* 123.8° for **1**; at N, 101.5°, *cf.* 122.0°). Bond lengths within the ladder framework of **1** (range 2.028–2.068 Å) are more typical of solvated than solvent-free lithium amide structures,[4] which is understandable as in effect its 'interdimer' bonds [*e.g.* N(1)–Li(1′)] mimic the role of solvent–Li bonds. It is also significant that rung lengths (mean, 2.035 Å) are generally, though marginally, shorter than edge lengths (mean, 2.058 Å). Both the Li and N atoms assume three-coordinate, pyramidal geometries within the ladder (mean sum of N–Li–N angles 340.2°, mean sum of Li–N–Li angles 265.6°), though the latter carry additional $Bu^t$ and H *exo* substituents, and so are overall five-coordinate.

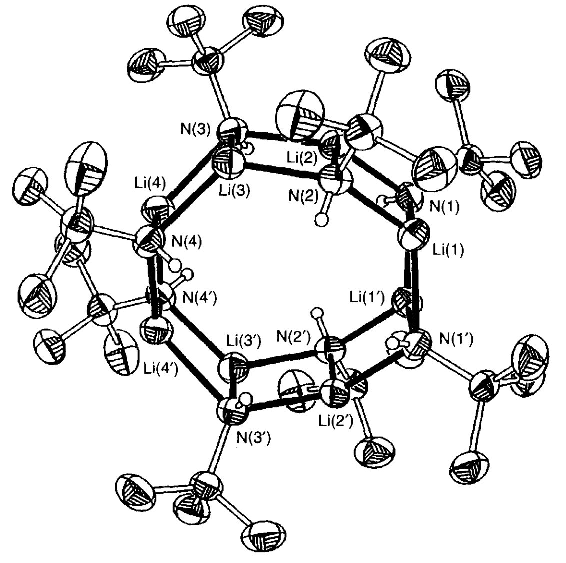


**Fig. 1** Thermal ellipsoid plot (at 40% probability level) of the molecular structure of **1** in its hexane solvate, with $Bu^t$ hydrogen atoms omitted, showing atom-labelling scheme. Selected bond lengths (Å) and angles (°): Li(1)–N(1) 2.042(5), Li(2)–N(2) 2.028(5), Li(3)–N(3) 2.035(5), Li(4)–N(4) 2.034(5), Li(1)–N(2) 2.046(5), Li(1)–N(1′) 2.046(5), Li(2)–N(1) 2.058(5), Li(2)–N(3) 2.068(5), Li(3)–N(2) 2.053(5), Li(3)–N(4) 2.050(5), Li(4)–N(3) 2.082(5), Li(4)–N(4′) 2.063(5); Li(1)–N(1)–Li(2) 72.0(2), Li(1)–N(1)–Li(1′) 71.2(2), Li(1)–N(2)–Li(2) 72.5(2), Li(2)–N(2)–Li(3) 71.8(2), Li(2)–N(3)–Li(3) 71.3(2), Li(3)–N(3)–Li(4) 71.5(2), Li(3)–N(4)–Li(4) 72.2(2), Li(4)–N(4)–Li(4′) 71.7(2), Li(2)–N(1)–Li(1′) 118.3(2), Li(1)–N(2)–Li(3) 128.0(2), Li(2)–N(3)–Li(4) 121.5(2), Li(3)–N(4)–Li(4′) 120.3(2), N(1)–Li(1)–N(1′) 108.7(2), N(1)–Li(1)–N(2) 107.7(2), N(1)–Li(2)–N(2) 107.8(2), N(2)–Li(2)–N(3) 108.2(2), N(2)–Li(3)–N(3) 108.6(2), N(3)–Li(3)–N(4) 108.7(2), N(3)–Li(4)–N(4) 107.6(2), N(4)–Li(4)–N(4′) 108.3(2), N(2)–Li(1)–N(1′) 121.6(2), N(1)–Li(2)–N(3) 127.3(3), N(2)–Li(3)–N(4) 122.0(2), N(3)–Li(4)–N(4′) 124.3(3). Symmetry operation for primed atoms: $3/2 - x, y, 1/2 - z$.

Now that lithium primary amides are receiving more attention from synthetic chemists, it is of interest to consider how such ladder structures may form imido species as noted in the introduction. One potential mode of reactivity is immediately obvious from the alternative view of **1** (Fig. 2). Clearly, with both octagonal rings (ladder edges) severely puckered, a double-crown conformation is created. By occupying the outer points of the crown (the $Li^+$ cations inhabit inner points), the $(NH^-)$ units could in theory be deprotonated by a suitable metallating reagent to generate $(N^{2-})$ units with retention of the hexadeca $N_8Li_8$ core. The additional metal cations, needed to maintain charge neutrality, could then bind to the bed of N atoms on each side of the core, *i.e.* akin to the way in which metal cations fit macrocyclic crown ether holes. Provided the metalling reagent used was not lithium based, this process would produce a mixed-metal imide cage.

This proposed structure-directed synthetic strategy may already have been (unwittingly) successfully employed in the synthesis of the recently reported mixed lithium–antimony imide $[\{(PhCH_2CH_2NLi)_3Sb(thf)\}_2]$.[7] Wright and coworkers state that its cage structure can be regarded as being constructed from a hexameric lithium amide fragment, '$(PhCH_2CH_2NLi)_6$', bicapped at the open $N_3Li_3$ faces by a pair of Sb atoms. As Scheme 1 illustrates, this synthesis exactly fits the scenario described above if the lithium amide precursor is a six-rung cyclic ladder (*cf.* **2**). The rung size of primary amide cyclic ladders will obviously vary depending on the relative steric demands of the single 'R' substituent.

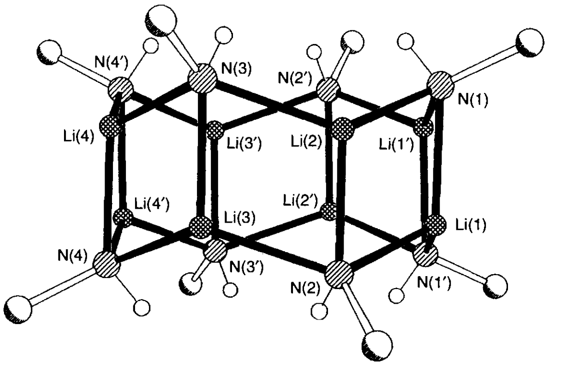
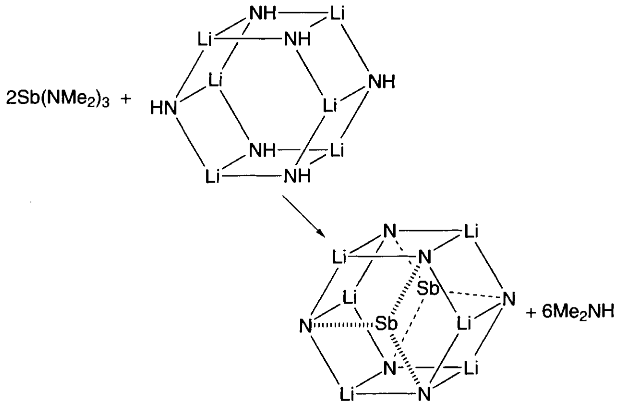


**Fig. 2** Double-crown shaped conformation of **1**. The hydrogen atoms attached to nitrogen are included; the methyl atoms of the *tert*-butyl groups are omitted.



**Scheme 1** (R groups on N atoms are omitted)

These findings raise important questions: can this cyclic ladder-directed synthesis be extended to other metal atoms, and, if so, can it be achieved selectively (*i.e.* can cyclic ladders behave like pseudo-crown ether ligands by capturing specific metal cations)? Studies are in hand to test this exciting prospect.

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## Footnotes

† The preparation was performed in a Schlenk tube under a dry argon blanket. Predistilled $Bu^tNH_2$ (10 mmol) was added dropwise to a stirred solution of $Bu^nLi$ (10mmol) in hexane at ambient temperature. A highly exothermic reaction ensued resulting in a colourless solution. Subambient cooling (to *ca.* −30 °C) of this solution produced after 24 h a crop of colourless hexagonal plates of **1**. Yield (of initial batch) 65%, decomp. from 260 °C; moisture- and oxygen-sensitive. Satisfactory C,H,Li,N analyses. $^1H$ NMR (25 °C, 400 MHz, $[^2H_6]$benzene) $\delta$ −1.53 (s, 1H, NH), 1.37 (s, 9H, $Bu^t$); $^{13}C$ NMR (25 °C, 101 MHz, $[^2H_6]$benzene) $\delta$ 38.17 (Me), 51.84 (quat-C).

‡ *Crystal data*: $\mathbf{1}\cdot C_6H_{14}$; $M_r = 718.73$, monoclinic, space group $P2/n$, $a = 12.000(8)$, $b = 12.547(7)$, $c = 18.339(12)$ Å, $\beta = 105.55(5)°$, $U = 2660(3)$ Å$^3$, $Z = 2$ (octameric molecule and hexane solvent both on $C_2$ axes), $D_c = 0.897$ g cm$^{-3}$, $F(000) = 804$, Mo-K$\alpha$ radiation, $\lambda = 0.710\,73$ Å, $\mu = 0.05$ mm$^{-1}$. The structure was determined by direct methods and refined on $F^2$ using all 3481 independent reflections measured at 160 K with a Stoe-Siemens diffractometer ($2\theta_{max} = 45°$, 8031 reflections measured in total, $R_{int} = 0.084$), with anisotropic atomic displacement parameters, isotropic amido H atoms, constrained isotropic $Bu^tH$ atoms, and two-fold disordered hexane: $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}} = 0.159$, conventional $R = 0.052$ on $F$ values for 2120 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.043$ on $F^2$ for all data and 300 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and reference number 182/235.

§ Crystallises unsolvated with four molecules in a monoclinic cell (space group $I2/a$) of volume 4675(3) Å$^3$ (measured at 160 K, $D_c = 0.904$ g cm$^{-3}$); the molecule has crystallographic $C_2$ symmetry and is essentially as described here. W. Clegg, L. Horsburgh, D. M. Lindsay and R. E. Mulvey, unpublished work.

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