

A new architecture in lithium amide chemistry: synthesis of $[(c-C_5H_9)N(H)]_{12}(O)Li_{14}$, a cage molecule containing a salt-like, distorted, face-centred cube of lithium cations

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Synthesised in the presence of trace quantities of water, which can account for its central oxo anion, the tetradecalithium title compound represents a rare three-dimensional, high-oligomeric cage arrangement in an area generally populated by pseudo-two-dimensional ring and ladder structures.

Although lithium–amide chemistry is renowned for its structural diversity, established through the determination of more than a hundred crystal structures,¹ in terms of aggregation numbers (n) it is actually rather limited. Recent reviews² intimate that most such compounds, mainly ones derived from secondary amines R^1R^2NH , have n values in the range 1–6; polymeric aggregates (with $n = \infty$) are assumed also to be common, but due to difficulties in growing suitable crystals, only one (the LDA helix³) has been confirmed by X-ray crystallographic study. Known oligomeric structures with aggregation numbers higher than six are in contrast extremely rare. Odd heptalithium and icosalithium species, obtained by lithiation of (i) a mixture of 6-methyl-2-trimethylsilylamino pyridine and 2-amino-6-methylpyridine,⁴ and (ii) 1-aminonaphthalene,⁵ respectively, are known; however, the latter is formally an imido (RN^{2-}) species. This paper introduces a new high-oligomer, indeed to our knowledge the highest so far discovered in lithium–amide chemistry, in disclosing the crystal structure of the tetradecalithium species $[(c-C_5H_9)N(H)]_{12}(O)Li_{14}$ **1**. Remarkably, **1** was synthesised in the presence of water! Normally, chemists go to considerable lengths to ensure that even minute traces of this protic acid are rigorously excluded to prevent decomposition reactions. Significantly, the synthesis of **1** is reproducible, but not under completely anhydrous conditions.

Cyclopentylamine, the parent amine, is very hygroscopic.† To make **1**, the amine must be wet, though it is still necessary to perform the procedure under argon. In a typical preparation, the amine (10 mmol) is added dropwise to a stirred, chilled solution of Bu^oLi (10 mmol in hexane). Following a vigorous reaction, a pale yellow solid forms. Heating the mixture to near boiling does not cause dissolution, nor does adding another molar equivalent of the amine. However, addition of a further molar equivalent (making 30 mmol in total) produces a cloudy pale red solution which is subsequently filtered. Slow cooling of the hot filtrate to ambient temperature affords small colourless, transparent cubic crystals of **1**.‡ Based on the consumption of alkyllithium, yields in the range 40–60% can be achieved. Significantly, noting the excess amine present in the reaction mixture, the crystals turn cloudy on isolation. Performing the same procedure with triply distilled cyclopentylamine under strictly anhydrous conditions, leads to a different product. In this preparation the yellow solution colour is maintained throughout with no sign of the red colour that marks the synthesis of **1**. Furthermore, the yellow product crystallises as needles, not cubes, in a much more difficult process than in the case of **1**, requiring subambient cooling (to ca. $-10^\circ C$). So far, only a few crystals, unsuitable for X-ray diffraction study, have been obtained. This alternative product is believed to be the

oxygen-free analogue $[(c-C_5H_9)N(H)Li]_n$, or possibly an amine solvate thereof, though this requires confirmation.

Fig. 1 shows the new structure,‡ while Fig. 2 highlights its $Li_{14}N_{12}O$ metal–heteroatom core. The cage structure is discrete, but lying between cages throughout the lattice are unresolved molecules, most probably free amine or possibly hexane (or a mixture of both). Interestingly, the fourteen Li^+ cations form a salt-like, distorted, face-centred cube. Those six occupying face positions [Li(1) and its symmetry equivalents], octahedrally surround the central oxo anion. A related $\mu_6-O Li_6$ coordination was recently reported in the double-cube structure of $[(salen)Li_2]_3 \cdot Li_2O \cdot 2tmeda \cdot H_2O$ ⁷ [$H_2salen = N,N'$ -ethylenebis(salicylideneimine)], while the mixed-metal cresylate $[(R)_7(O)LiMg_4 \cdot 4thf]$ ⁸ [$R = o-MeC_6H_4O^-$] exhibits a μ_5-O^{2-} anion encapsulated in a trigonal-bipyramidal coordination polyhedron. All the Li^+ cations in **1** have three-coordinate, pseudo-trigonal planar geometries: those in the face bind to one O and two N atoms with a strictly planar arrangement; corner ones [Li(2), Li(3) and their equivalents] bind exclusively to N atoms with a slightly pyramidal arrangement. In terms of coordination environment the twelve N atoms are all equivalent: three Li^+ cations, one face and two corner types, the α -C atom

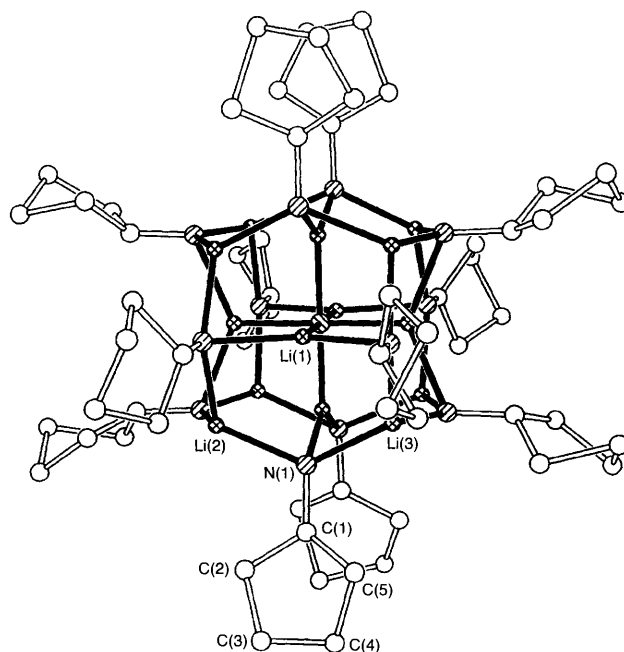


Fig. 1 Molecular structure of **1** without hydrogen atoms and minor disorder components, showing numbering scheme for key atoms. Principal distances (Å) and angles ($^\circ$): Li(1)–O(1) 1.888(10), Li(1)–N(1') 2.080(5), Li(2)–N(1) 2.062(8), Li(3)–N(1) 2.004(8), O(1)–Li(1)–N(1') 112.7(3), N(1')–Li(1)–N(1'') 134.6(5), N(1)–Li(2)–N(1') 111.7(5), N(1)–Li(3)–N(1'') 114.6(5), Li(1')–N(1)–Li(2) 80.0(5), Li(1')–N(1)–Li(3) 77.9(6), Li(2)–N(1)–Li(3) 130.8(5), all angles at O(1) 90 and 180.

of the cyclopentyl ring, and the remaining NH atom surround them. The structure is completed by the puckered five-membered organic rings, which, because of their boundary location, possess considerable steric freedom. It is not surprising, therefore, that they are twofold disordered; a problem independent of the quality of crystals. More disorder is created by the molecules of crystallisation present (see above). These factors conspire to limit the precision of the structure, thus denying an analysis of some dimensions, though, importantly, not those associated with the metal-heteroatom core. Hence, it is discernible that Li–O bond lengths, all equivalent due to the molecule's crystallographic *I* symmetry, lie within the standard deviation of those in the salen structure mentioned above [*i.e.* 1.888(10) Å in **1**, *cf.* 1.883(9) Å⁷]. This μ_6 -OLi₆ unit is strictly octahedral. Also, the range of Li–N bond lengths (2.004–2.080 Å) is similar to that observed in the related primary amide [$\{\text{PhN(H)Li}\}_6\cdot 8\text{thf}\}^9$ (*i.e.* 2.011–2.066 Å).

Regarding the analogy between **1** and lithium salts, it should be mentioned that the Li \cdots Li distances in **1** (three unique: 2.567, 2.661, 2.671 Å) are similar to that in the rock-salt structure of lithium fluoride (2.847 Å), in which the Li⁺ cations themselves form a face-centred cubic array (infinite, of course, unlike the finite unit in **1**).

Finding cases of adventitious oxygen in lithiated organics^{10,11} is not surprising given the strong oxophilicity of the small Li⁺ cation. Provided the contaminant is present in solution in a deficient amount relative to the number of moles of Li⁺, the metal's proclivity for aggregation is so great that there is always a possibility that transient Li₂O molecules will be trapped within growing lithium amide species, leading to thermodynamically stable mixed [(R₂NLi)_{*n*}·(Li₂O)_{*m*}] aggregates, rather than forming separate (R₂NLi)_{*n*} and (Li₂O) _{∞} aggregates. Snaith and coworkers make a similar point in their discussion of the salen structure,⁷ which was synthesised by the deliberate addition of water to the lithiated organic. By not drying the amine before its subsequent lithiation, in effect, **1** was synthesised in the same way. On this basis, **1** is best interpreted as a mixed dodecameric amide–monomeric oxide, [$\{(c\text{-C}_5\text{H}_9)\text{N(H)Li}\}_{12}\cdot\text{Li}_2\text{O}\}$, aggregate. However, as in the salen structure, due to symmetry considerations, the Li⁺ centres of the oxide component are indistinguishable from the remainder.

Concerning the possibility of extending this partial-decomposition strategy to other amines, it is significant that the construction of the cage of **1** relies on the amido units engaging in μ_3 -bonding interactions with the metal. This contrasts with

the usual μ -bonding modes observed when secondary (R¹R²N[−]) amido units bridge Li⁺ centres in ring structures (when μ_3 -bonding does occur, pseudo-two-dimensional ladders, not cages, form).² The implication therefore is that cage formation could be dependent on the reduced steric capacity provided by primary [R(H)N[−]] amido units though the primary factor is probably the incorporation of an oxo anion (*i.e.* a dianion). We plan to test this hypothesis on a series of primary amines.

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Footnotes

† IR data: the symmetrical and antisymmetrical NH bands of the primary amine occur at 3358 and 3281 cm^{−1}, respectively. When the amine is wet these bands are obscured by a broad band covering the range *ca.* 3500–3100 cm^{−1}.

¹H NMR spectroscopic data (400 MHz, 300 K, C₆D₅CD₃) δ −1.43 (1 H, NH), 1.16 (2 H, H^β), 2.10 (2 H, H^β), 1.72 (2 H, H^γ), 1.79 (2 H, H^γ), 3.48 (C^αH). All signals are complex multiplets. Trace quantities of the free amine could also be observed, most easily recognised by the NH₂ resonance located at δ 0.56. Mp > 320 °C; satisfactory analyses (C, H, Li, N) were obtained.

‡ Crystal data for **1**: C₆₀H₁₂₀Li₁₄N₁₂O (ignoring unresolved disordered molecules), *M* = 1122.8, cubic, space group *F*23, *a* = 20.481(2) Å, *U* = 8591.2(13) Å³, *Z* = 4, *D*_c = 0.868 g cm^{−3}, μ = 0.05 mm^{−1} (Mo- $\text{K}\alpha$, λ = 0.71073 Å), *F*(000) = 2456, *T* = 160 K. A total of 8470 reflections were measured with a Siemens SMART CCD area-detector diffractometer, giving 953 unique data with $2\theta < 45^\circ$ (*R*_{int} = 0.072). Refinement on *F*² included anisotropic displacement parameters, isotropic riding hydrogen atoms, twofold conformational disorder of cyclopentyl rings with restraints, and partially occupied sites for isotropic atoms in regions of highly disordered solvent or amine molecules. Final *R*_w = $\{\sum[w(F_o^2 - F_c^2)]^2\}^{1/2} = 0.356$ for all data, conventional *R* = 0.121 for *F* values of 709 reflections with *F*_o² > 2 σ (*F*_o²), goodness of fit = 1.132 on *F*² for all data and 110 refined parameters. Difference map features were in the range +0.30 to −0.17 e Å^{−3}. The absolute structure parameter was indeterminate. Programs: Siemens SHELXTL; SMART and SAINT for data collection and reduction, and local programs.

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 the reference number 182/43.

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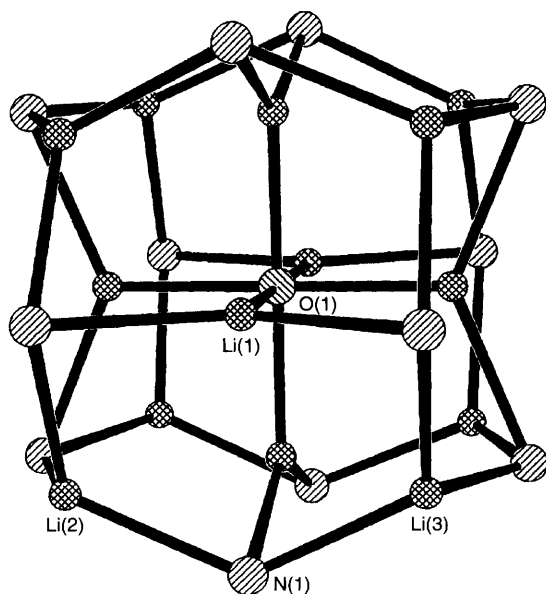


Fig. 2 Lithium-heteroatom core of **1**, in the same view direction as for Fig. 1