Lithium Anilide Complexed by pmdeta[†]: Expectation of a Simple Monomer, but in Reality an Odd Trinuclear Composition Combining Three-, Four- and Five-coordinate Lithium

Donald Barr,[a] William Clegg,[b] Lucy Cowton,[a] Lynne Horsburgh,[b] Fiona M. Mackenzie[c] and Robert E. Mulvey*[c]

[a] *The Associated Octel Company Limited, Ellesmere Port, UK L65 4HF*
[b] *Department of Chemistry, University of Newcastle, Newcastle upon Tyne, UK NE1 7RU*
[c] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK G1 1XL*

Lithium structural chemistry continues to surprise as highlighted here by the reaction of Bu^nLi, aniline and pmdeta, which by analogy with related systems, should yield a simple monomeric complex, when, in fact, an unprecedented trinuclear formulation is produced; in contrast, the corresponding Na system falls into line with predictions, in yielding a dimeric product.

Novelty is becoming ever increasingly difficult to find in lithium structural chemistry in view of the vast databank of crystal structures now known.[1] Whilst certain classes of compound remain to be investigated in quantity, primary amine derivatives among them, the principles of aggregation and solvation are so well established that the majority of new crystal structures appear predictable, and can be categorised as belonging to one or another familiar structural type. A variety of recent review articles[2] reinforce this point. However, in this paper, we report a rare exception in $[\{PhN(H)Li\}_3\cdot 2pmdeta]$ **1**, the first lithium anilide complex to be crystallographically characterised. The unexpected nature of its structure is best illustrated by considering a series of closely related pmdeta complexes of lithium and sodium. Two contrasting structural types are found within this series: a dimeric or monomeric arrangement with five- and four-coordinate metal cations respectively, having in common tridentate pmdeta ligands. Cation size dictates that sodium complexes adopt the former set-up, while lithium complexes adopt the latter, as previously established for $[(PhNa\cdot pmdeta)_2]$[3] and (PhLi·pmdeta).[4] In this work, the sodium anilide complex, $[\{PhN(H)Na\cdot pmdeta\}_2]$ **2** was found to conform to the former type. Logically we thus anticipated that the lithium congener would assume the latter monomeric type, whereas, remarkably, it prefers an unprecedented trinuclear arrangement. This structure is all the more unusual by virtue of its simultaneous exhibition of three-, four- and five-coordinate Li^+ cations.

Metal anilides **1** and **2** were synthesised starting from equimolar amounts (10 mmol scale) of freshly distilled aniline and the appropriate Bu^nM reagent (M = Li or Na) in hexane under a protective argon atmosphere. In the former case, the alkyllithium solution had to be stringently degassed beforehand. At this stage, both reactions gave cream solids, which dissolved completely on the subsequent addition of a specific amount of pmdeta. For **2**, 1 equiv. (10 mmol) was sufficient, but, significantly, 2 equiv. (20 mmol) were required for **1**. Why this excess donor solvent should be necessary is, as yet, baffling, especially as less than one equivalent ultimately appears in the isolated product **1**[‡] (Li^+ : donor ratio 3 : 2). Finally, on standing both solutions at ambient temperature for 24 h, colourless crystals of **1** and **2**[‡] were deposited.

The three lithium centres in the crystal structure of **1** (Fig. 1)[§] lie almost in a straight line [Li(1)···Li(2)···Li(3) 166.8°]. Pseudo-trigonal planar, three-coordinate Li(2) is centrally positioned and binds to three anilino N centres, but not to pmdeta. Pseudo-tetrahedral, four-coordinate Li(1) binds to only one anilino N centre, while five-coordinate Li(3) binds to two, with tridentate pmdeta ligands completing the metal coordinations in each case. The geometry of attachment of each pmdeta ligand is markedly distinct. One fits easily to the lower-coordinated Li(1), as reflected by the short N–Li bond lengths (mean 2.146 Å) and the open NLiN bond angles [N(4)–Li(1)–N(5) 85.9(2)°, N(5)–Li(1)–N(6) 85.6(2)°]. On the other hand, the approach of the second is hampered [corresponding dimensions: 2.351 Å, 78.9(2)°, 74.7(2)°], as a consequence of the higher coordination of Li(3). Of the special features of **1**, this five coordination of a pmdeta ligated Li^+ centre is the most surprising, having never been previously observed in a lithium amide, whether derived from a primary or secondary amine. Only two precedents can be found in other types of lithium compound, monomeric 3-fluoro-2-lithio-1-sulfonylbenzene·pmdeta[5] and dimeric lithium bromide·pmdeta,[6] but their anionic centres (C or Br), in forming three or two bonds, respectively, are more sterically accessible than N(2) and N(3) here, which each form four bonds (to two Li,one C, one H). The fact that one of these substituents is a H atom is probably critical, making it highly unlikely that this structural motif could be duplicated by a secondary amidolithium, RR′NLi (R,R′ ≠ H). There is a wide, but regular, variation in (anilino)N–Li bond lengths (1.961–2.188 Å), with values generally weighted in accord with the metal coordination number: the shortest and longest are formed by three-coordinate Li(2) and five-coordinate Li(3), respectively, with four-coordinate Li(1) forming a bond of intermediate length (1.976 Å). Decidedly irregular, in contrast,

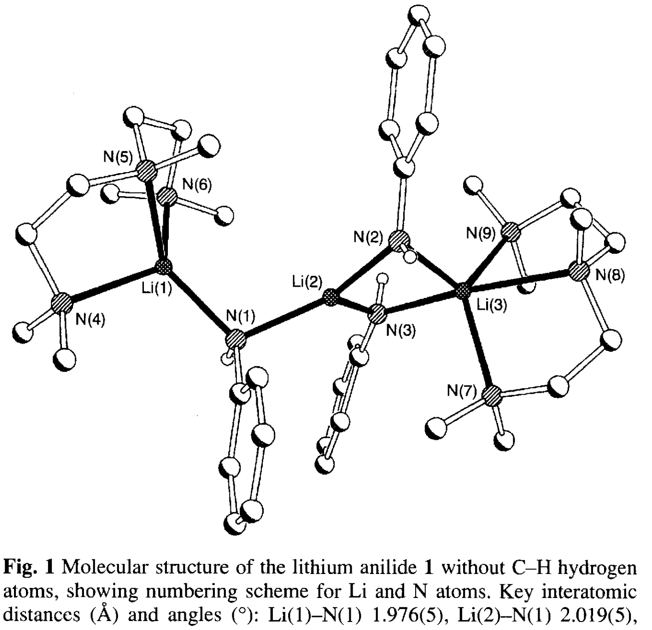

Fig. 1 Molecular structure of the lithium anilide **1** without C–H hydrogen atoms, showing numbering scheme for Li and N atoms. Key interatomic distances (Å) and angles (°): Li(1)–N(1) 1.976(5), Li(2)–N(1) 2.019(5), Li(2)–N(2) 1.973(5), Li(2)–N(3) 1.961(5), Li(3)–N(2) 2.121(5), Li(3)–N(3) 2.188(5), Li(1)–N(4) 2.122(5), Li(1)–N(5) 2.139(5), Li(1)–N(6) 2.179(5), Li(3)–N(7) 2.239(5), Li(3)–N(8) 2.338(5), Li(3)–N(9) 2.478(5); Li(1)–N(1)–Li(2) 111.7(2), Li(2)–N(2)–Li(3) 79.0(2), Li(2)–N(3)–Li(3) 77.7(2), N(1)–Li(1)–N(4) 115.6(2), N(1)–Li(1)–N(5) 137.3(2), N(1)–Li(1)–N(6) 110.2(2), N(4)–Li(1)–N(5) 85.9(2), N(4)–Li(1)–N(6) 120.1(2), N(5)–Li(1)–N(6) 85.6(2), N(1)–Li(2)–N(2) 136.8(3), N(1)–Li(2)–N(3) 118.8(2), N(2)–Li(2)–N(3) 104.3(2), N(2)–Li(3)–N(3) 92.2(2), N(2)–Li(3)–N(7) 103.8(2), N(2)–Li(3)–N(8) 106.3(2), N(2)–Li(3)–N(9) 123.3(2), N(3)–Li(3)–N(7) 104.3(2), N(3)–Li(3)–N(8) 160.0(2), N(3)–Li(3)–N(9) 89.0(2), N(7)–Li(3)–N(8) 78.9(2), N(7)–Li(3)–N(9) 130.6(2), N(8)–Li(3)–N(9) 74.7(2).

is the rhomboidal N_2Li_2 ring with endocyclic bond angles at Li deviating by over 12° [*i.e.* N(2)–Li(2)–N(3) 104.3°, N(2)–Li(3)–N(3) 92.2°], reflecting the coordinative imbalance, while those at N hardly vary at all [*i.e.* 79.0° at N(2); 77.7° at N(3)]. Acute N corners and obtuse Li corners are the norm in amidolithium N_2Li_2 rings,[2] but generally they are more symmetrical, being regular dimers having equal Li coordination numbers, *e.g.* as in $[\{(PhCH_2)_2NLi{\cdot}THF\}_2]$.[7]

In the context of the structural information gathered to date, the novel arrangement of **1** can be best thought of as being derived from a three-runged ladder, ideally represented in Fig. 2. Only one N–Li (edge) bond, as marked, would need to be cleaved from this structure to generate the basic trinuclear skeleton of **1**. So called 'broken ladders' are a recognised structural type, with the pyrrolidine derivative $[\{[H_2C(CH_2)_3NLi]_3{\cdot}pmdeta\}_2]$[8] being especially relevant. While **1** shares certain characteristics of this type, most obviously a 'deficiency' of donor molecules, its five-coordinate Li^+ cation sets it apart from any previously reported ladderoid construction.

Though, to our knowledge, **2** is only the second sodium primary amide to be crystallographically authenticated, its structure (Fig. 3)§ is for the most part predictable. The first to be reported, $2\text{-}PhOC_6H_4N(H)Na{\cdot}pmdeta$,[9] also a dimeric pmdeta complex, heralded a new ligating conformation for the tridentate base with its three N arms coplanar with Na, but **2** now establishes that this is not general for such compounds, as it favours the normal tripodal (out of plane) chelation. Even though Na^+ is much larger than Li^+, the pmdeta ligands still appear to have insufficient room to achieve a good fit, as evidenced by the twisting of the anilino rings out of the plane perpendicular to the Na···Na vector (*i.e.* angle of inclination 65°, not 90°). Looking wider afield than amides, we see that transoid, symmetrical ring-cores akin to that of **2** have become one of the most common structural hallmarks of lithium and sodium chemistry.[2] Key dimensions of **2** are listed in the legend to Fig. 3.

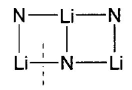

Fig. 2

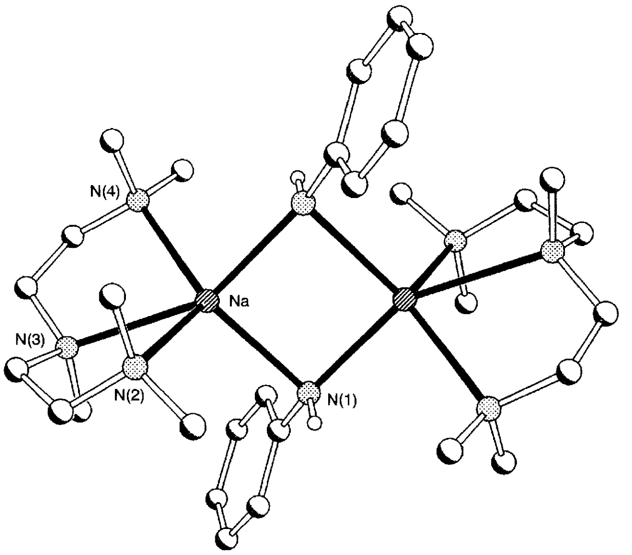

Fig. 3 Molecular structure of the sodium anilide **2** without C–H hydrogen atoms, showing numbering scheme for Na and N atoms. Key interatomic distances (Å) and angles (°): Na–N(1) 2.444(5), Na–N(1a) 2.390(5), Na–N(2) 2.548(4), Na–N(3) 2.620(4), Na–N(4) 2.581(4); Na–N(1)–Na(a) 87.4(2), N(1)–Na–N(1a) 92.6(2), N(1)–Na–N(2) 103.5(2), N(1)–Na–N(3) 113.4(2), N(1)–Na–N(4) 131.5(2), N(1a)–Na–N(2) 109.6(2), N(1a)–Na–N(3) 153.7(2), N(1a)–Na–N(4) 90.8(2), N(2)–Na–N(3) 69.77(12), N(2)–Na–N(4) 120.67(14), N(3)–Na–N(4) 69.24(13). Atoms Na(a) and N(1a) are centrosymmetrically related to Na and N(1).

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Footnotes

† pmdeta = pentamethyldiethylenetriamine, $(Me_2NCH_2CH_2)_2NMe$.

‡ Yield of **1** (not refined), 37%; mp 59–62 °C. Yield of **2** (not refined), 21%; mp 86–88 °C. Both complexes were further characterised by ^1H NMR spectroscopic studies on dissolving the crystals in C_6D_6 solution, which revealed empirical formulae consistent with the X-ray determined structures. Given that the yield of **1** was not optimised, and that its stoichiometry does not match that in the initial reaction mixture, the possibility of other products remaining in solution cannot be discounted.

§ *Crystal data* for **1**: $C_{36}H_{64}Li_3N_9$, $M = 643.8$, triclinic, space group $P\bar{1}$, $a = 10.981(5)$, $b = 12.899(4)$, $c = 14.460(7)$ Å, $\alpha = 101.42(3)$, $\beta = 92.83(3)$, $\gamma = 92.38(3)°$, $U = 2002(2)$ Å^3, $Z = 2$, $D_c = 1.068$ g cm^{-3}, $F(000) = 704$, $T = 160$ K, 9767 reflections were measured on a Stoe-Siemens diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 0.064$ mm^{-1}, $2\theta < 45°$) with ω–θ scans and on-line profile fitting. Structure solution was by direct methods, and refinement by full-matrix least-squares of F^2 for all 5239 independent reflections ($R_{int} = 0.0423$). $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}} = 0.1703$ for all data, conventional R [on F values for 3865 reflections with $F^2 > 2\sigma(F^2)$] = 0.0578, goodness of fit = 1.048 on F^2 for all data and 453 refined parameters. All non-H atoms were refined with anisotropic displacement parameters, H atoms were subjected to riding model constraints. Programs: SHEXLTL and SHELXL-93, G. M. Sheldrick, University of Göttingen.

Crystal data for **2**: $C_{30}H_{58}N_8Na_2$, $M = 576.8$, monoclinic, space group $P2_1/n$, $a = 9.7670(14)$, $b = 12.789(2)$, $c = 14.354(2)$ Å, $\beta = 91.83(2)$, $U = 1792.0(4)$ Å^3, $Z = 2$, $D_c = 1.069$ g cm^{-3}, $F(000) = 632$, $T = 160$ K, μ(Mo-Kα) = 0.086 mm^{-1}. Experimental details are as for **1** except as follows: 4064 measured reflections, 2346 independent data, $R_{int} = 0.0204$, $R_w = 0.2224$, conventional $R = 0.0750$ [for 1692 reflections with $F^2 > 2\sigma(F^2)$] goodness of fit = 1.051 on F^2 for 184 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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