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# Pentanuclear asymmetrical ladder structure of the 1,4-dimethylpiperazine solvate of lithium anilide and its implication for the unknown structure of amorphous lithium anilide

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**The weak solvating ligand 1,4-dimethylpiperazine appears to only partially disrupt the aggregation within lithium anilide, as evidenced by the structure of the title solvate: a three-dimensional polymer of solvent-linked irregularly shaped $(\mathrm{NLi})_5$ substructures, which can be interpreted as two interconnected ladders.**

Long in the shadow of their better known secondary counterparts,[1] lithiated primary amines $[\{\mathrm{RN(H)Li}\}_n]$ are now emerging as valuable and versatile chemical intermediates themselves. Their ability to function as either amido $[\mathrm{RN(H)}^-]$[2] or imido $(\mathrm{RN}^{2-})$[3] transfer agents, or sometimes as both simultaneously,[4] has proved particularly useful for the development of new heterometallic[5] and/or hetero-anionic[6] compositions. This paper focuses on one of the most important primary amides, lithium anilide. While its simple solvates with THF[7,8] or PMDETA[9] have been structurally elucidated, the pure solvent-free structure remains elusive. This situation is relatively common for lithium amides (whether primary or secondary) suspected of having polymeric constitutions (lithium anilide is thought to exist as a high oligomeric/polymeric ladder structure). Adding solvent ligands often produces smaller oligomers which can be crystallised and are therefore suitable for X-ray crystallographic study, unlike their solvent-free parent compounds which tend to be amorphous. Thus while lithium anilide is easy to prepare as a powder, so far it has not been possible to grow single crystals of it. However, keeping in mind that competition between aggregation and solvation can be delicately balanced, we have subjected it to the weak (weaker than THF or PMDETA) coordinating solvent 1,4-dimethylpiperazine (DMP) in the hope of crystallising a solvate with a structure more representative of the pure solvent-free compound, *i.e.* one in which the high (or infinite) aggregation has been only partially disrupted. As reported herein, the new solvate produced in this way, $[\{[\{\mathrm{PhN(H)Li}\}_5\cdot(\mathrm{DMP})_2]\cdot(\mathrm{C_6H_5Me})_2\cdot(\mathrm{DMP})_{0.5}\}_\infty]$ **1**, possesses a remarkable structure. Besides fulfilling the aim of revealing a sizable ladder fragment (spanning five N–Li rungs), the structure also exhibits a new tetraanilido–lithium $[\{\mathrm{PhN(H)}\}_4\mathrm{Li}]$ coordination mode, which facilitates the grafting of an additional N–Li bond onto a ladder edge. This unprecedented connectivity may provide an important clue as to the cause of the amorphous character of unsolvated lithium anilide.

The weak solvating power of DMP was reflected in the molar excess required (2.2 equivalents, 11 mmol) to dissolve a freshly prepared slurry of lithium anilide (5 mmol) in hexane–toluene solution. Cooling the resulting pale yellow solution to −30 °C for 2 days, afforded a crop of colourless crystalline **1**.† A standard inert-atmosphere protocol was used throughout this preparative and subsequent isolation procedure.

As determined by an X-ray crystallographic study,‡ the structure of **1** is made up of novel pentanuclear $(\mathrm{NLi})_5$ crossed ladder substructures (Fig. 1), linked together by bridging DMP ligands (Fig. 2) into a three-dimensional polymeric network. The crystal packing arrangement leaves spacious cavities in the structure which are filled by toluene solvent and free DMP molecules of crystallisation [2 and 0.5, respectively, per $(\mathrm{NLi})_5$ ladder]. Two essentially planar $(\mathrm{anilidoN{-}Li})_2$ rings, Li(1)N(6)Li(2)N(5) and Li(3)N(8)Li(4)N(7), joined together by Li(3)–N(6) and Li(2)–N(7) bonds, make up the main run of the ladder, the undulation of which is ‘U-shaped’ rather than ‘stepped’. These rings can be classified as *cisoid*[10] (or *syn*), because their N–H substituents lie on the same side of the $(\mathrm{NLi})_2$ plane in each case. In contrast, at the junction of these two rings the conformation is *transoid* (*anti*) and the Li(2)N(7)Li(3)N(6) ring is butterfly shaped with an N···N hinge (folding angle, 138.4°) and Li wingtips. Located within the smaller cross-run of the ladder, the remaining Li(3)N(8)Li(5)N(9) ring is also *transoid* and butterfly shaped (folding angle, 151.7°). Those Li atoms positioned at ladder ‘ends’, Li(1), Li(4) and Li(5), have three-

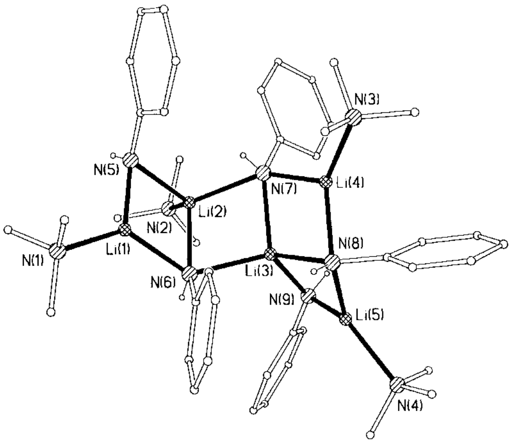

**Fig. 1** Asymmetric unit of **1** showing atom labelling. Hydrogen atoms, except for N–H, are omitted for clarity, and solvent molecules are not shown.

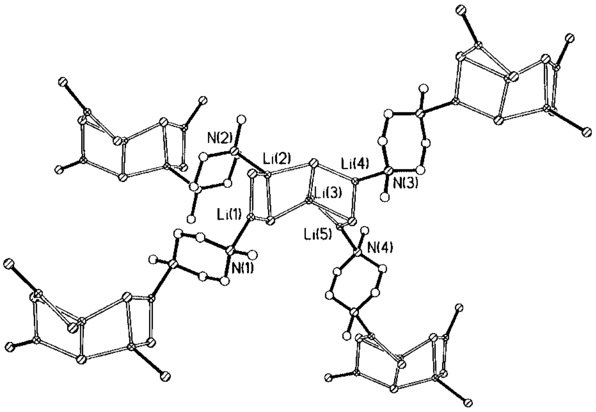

**Fig. 2** View of **1** showing the bridging of four DMP ligands to neighbouring ladder substructures of which only Li and N atoms are shown.

coordinate, distorted trigonal planar geometries, though Li(4) is slightly pyramidalised (sum of bond angles, 353.2°). Occupying an inner rung, Li(2) displays a four-coordinate distorted tetrahedral geometry [bond angles, 99.8(3)–121.6(3)°]. Each of these Li atoms binds to one N atom from a chair-shaped DMP molecule which bridges through its second N atom to a Li atom of a neighbouring $(NLi)_5$ ladder. Connecting both runs of the ladder, Li(3) is unique as its distorted tetrahedral environment [bond angles, 96.7(3)–124.0(3)°] does not include a DMP molecule, but is made up exclusively of anilido N atoms. This coordination of Li by four monodentate anions is unprecedented for an anilide (and, to the best of our knowledge, for any amide). It is also rare generally in the wider context of organolithium chemistry, but not unknown, as a $C_4Li$ coordination exists in the contact-ion pair structure of sodium tetraphenyllithate $[\{Na\cdot(TMEDA)\}_3\{LiPh_4\}]$.[11] Three anilide anions in **1** [at N(6), N(7) and N(8)] engage in $\mu_3$ bonding with Li atoms, while the other two situated in the end rungs [at N(5) and N(9)] are $\mu_2$ bonded. These end rungs, N(5)–Li(1) and N(9)–Li(5), display the shortest lengths [1.934(8) and 1.954(7) Å, respectively] in the $(NLi)_5$ ladder framework reflecting the low coordination numbers (C.N.) involved (four for N; three for Li). Similarly, the longest such bond, N(8)–Li(3) [2.208(6) Å], reflects the high C.N. involved (five for N; four for Li). The remaining N–Li ladder lengths lie in the range 2.014(8)–2.178(7) Å. There is also a correlation between the dative (DMP)N–Li bond lengths and Li C.N. [where C.N. = 3, the mean length is 2.073 Å; where C.N. = 4, the length increases to 2.176(6) Å]. Turning to angular values, despite the ladder having an irregular shape and a variety of C.N., its endocyclic bond angles subtended at N cover a narrow range [73.1(3)–77.9(3)°]. The corresponding bond angles at Li cover a wider range [96.7(3)–107.8(3)°].

Pentanuclear aggregation is extremely rare in lithium structural chemistry. A previous example was reported for the anion of the lithium ketimidolithate complex $[\{Li\cdot(HMPA)_4\}^+\text{-}\{Li_5(N{=}CPh_2)_6\cdot(HMPA)\}^-]$,[12] but in this case the $(N_6Li_5)$ substructure is of a discrete cage anion, rather than a segment of a polymeric chain. The asymmetric unit of **1** represents the first pentanuclear $Li_5$ ladder conformation. Hitherto, homoaggregated lithium amide ladders generally have regular, symmetrical structures of laterally connected $(NLi)_2$ rings, the opposite facing N–Li bonds of which become either pairs of rungs or pairs of edges. Representative examples include the tetrameric ‘concave’ ladder of the piperidide $[\{H_2C(CH_2)_4NLi\cdot HN(CH_2)_4CH_2\}_4]$,[13] the octameric cyclic ladder of $[\{Bu^tN(H)Li\}_8]$,[14] and the polymeric sinusoidal wave-shaped ladder of $[\{H_2NCH_2CH_2N(H)Li\}_\infty]$.[15] Aside from having an odd number of rungs, the ladder of **1** differs by virtue of the additional rung [N(9)–Li(5)] grafted onto the N(8)–Li(3) ‘edge’. This is a new structural development§ since ladder edges usually stand alone, or in rare cases, are solvated at Li.[16] The presence of this special feature implies that removal of the DMP ligands from **1** would allow the laddering process to extend in several directions. Viewing the $(NLi)_5$ framework as two interconnected ladders, there are four end-rungs N(5)–Li(1), N(8)–Li(4), N(9)–Li(5) and N(7)–Li(4), from which further laddering might be possible, though the kinetics of growth at each site may be different. The amorphous nature of unsolvated lithium anilide may have its origin in the availability of such irregular branching. Hence this contrasts with the situation so far found in crystalline lithium amide polymeric ladders[15,16] where the laddering process is mono-directional.

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## Notes and references

† Yield of first batch, 21%. Mp: decomp. from 290 °C. $^1H$ NMR (300 K, 400 MHz, $d_5$-pyridine) $\delta$ 2.20 (s, 3H, Me of DMP), 2.40 (s, 4H, $CH_2$ of DMP), 4.33 (s, 1H, NH), 6.49 (t, 1H, *p*-Ph), 6.89 (d, 2H, *o*-Ph) and 7.18 (t, 2H, *m*-Ph). Trace quantities of toluene are also present. $^{13}C$ NMR (300 K, 100.6 MHz, $d_5$-pyridine) $\delta$ 46.64 (Me of DMP), 55.94 ($CH_2$ of DMP), 110.58 (*p*-Ph), 116.72 (*o*-Ph), 130.03 (*m*-Ph) and 162.94 (*ipso*-Ph).

‡ *Crystal data* for **1**: $C_{59}H_{81}Li_5N_{10}$, $M$ = 965.0, triclinic, space group $P\bar{1}$, $a$ = 11.205(2), $b$ = 16.726(3), $c$ = 17.152(3) Å, $\alpha$ = 64.592(3), $\beta$ = 80.095(4), $\gamma$ = 85.225(4)°, $U$ = 2860.1(8) Å$^3$, $Z$ = 2, $D_c$ = 1.121 g cm$^{-3}$, $\mu$ = 0.065 mm$^{-1}$ (Mo-K$\alpha$, $\lambda$ = 0.71073 Å), $T$ = 160 K; $R_w$ = 0.2625 on $F^2$ values of all 9732 unique data, conventional $R$ = 0.0851 on $F$ values of 5443 reflections with $F_o^2 > 2\sigma(F_o^2)$, 683 parameters; final difference map within ±0.65 e Å$^{-3}$ except for one peak of 1.00 e Å$^{-3}$ in a disordered toluene molecule. Restraints were applied for the toluene molecules. H atoms were constrained except for free refinement of positions for N–H. CCDC 182/159. See http://www.rsc.org/suppdata/cc/a9/a909754f/ for crystallographic files in .cif format.

§ The homoaggregated ladders described herein should not be confused with heteroanionic systems which have ladder shapes, for example, as in the amidinate–hydroxide $[\{(Li[(Bu^n)C(NBu^t)_2])_2\cdot LiOH\cdot THF\}_2]$,[17] in which O–Li ‘edges’ interact with N–Li ‘rungs’.

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