Dis-assembling lithium amide ladder structures: new insight through the structure of [{[$PhCH_2N(H)Li]_2$·thf}$_\infty$], a polymer of $(NLi)_2$ planar rings connected by thf-bridged $(NLi)_2$ butterfly junctions

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One can visualise how the novel hemi-solvated polymeric ladder structure of the title compound would dis-assemble at its long, weak cisoid-$(NLi)_2$ butterfly junctions on further solvation, to release transoid-$(NLi)_2$ planar dimeric rings, the expected product of full solvation.

While our understanding of the complicated bond-making and bond-breaking processes involved in lithium amide aggregational chemistry[1,2] has deepened considerably in recent years primarily through the 'ring-laddering' principle,[3] it remains far from comprehensive. Most conspicuously, at the time of writing, there is still no example of a crystallographically characterised polymeric ladder structure of a pure (*i.e.*, donor-free) lithium amide. Mono-lithiated ethylenediamine [{$H_2NCH_2CH_2N(H)Li$}$_\infty$][4] does exist as an infinite sinusoidal wave-shaped ladder, but its NH_2 amine arms function as internal donor ligands. There is also little tangible information hitherto on the coordination chemistry taking place when coordinating solvent molecules approach a long (high oligomeric/polymeric) ladder framework. However, light has been shed on subsequent processes, specifically on the possible sequence of steps involved when lower oligomeric ladders break down to tetrasolvated $(NLi)_2$ ring dimers on gradually increasing the number of solvent ligands in the system.[5] In contrast, here, we report an unique example of a ladder structure which stays polymeric in the presence of coordinating thf molecules, in the hemi-thf complex of lithium benzylamide [{[$PhCH_2N(H)Li]_2$·thf}$_\infty$] **1**. Attention is drawn to the pattern of solvent ligation in **1**, which is without precedent in any previously reported lithium structure, amide or otherwise; and to how this extends our knowledge of the dis-assembling process in lithium amide ladder chemistry. The new structure also provides a contrast with that of the polymeric phosphide [{CyP(H)Li·thf}$_\infty$][6] which has conventional, terminal thf solvation.

Regarding the synthesis of **1**, it is a trivial matter to abstract one NH proton from benzylamine by the action of *n*-butyllithium provided a routine inert-atmosphere protocol is followed. However, obtaining a pure crystalline thf complex of the lithium benzylamide so produced is more challenging. Only pink slurries could be prepared on subjecting a 1 : 1, Bu^n-Li : $PhCH_2NH_2$ mixture with various amounts of thf (1, 2 or 6 molar equivalents). Alternatively, when excess amine was employed (*e.g.* in a 1 : 2 : 1 mixture), the known amide–amine complex [{[$PhCH_2N(H)Li]_2$·H_2NCH_2Ph}$_\infty$][7] **2** preferentially crystallised from solution. Success eventually came from a 1 : 2 : 2 mixture in hexane–toluene solution, with **1** forming as colourless crystals,† though the product was still contaminated with crystals of **2**. This product is only partially soluble in arene solvents. ^1H NMR spectra in d_6-benzene solution always show both benzylamine and thf molecules (in variable and inconsistent amounts) as well as *smaller* amounts of amide anions. Thus it can be reasoned that the polymeric ladder framework easily loses donor ligands, which escape into solution leaving behind a solid residue of unsolvated lithium benzylamide. In turn, the excess donor molecules in solution can dissolve a portion of this solid to generate a soluble, but weak oligomeric solvate (possibly a tetrasolvated dimer, see later). This notion of a weak solution complex is consistent with the fact that while lithium benzylamide is completely soluble in concentrated benzylamine or thf solutions, only polymeric solids are deposited from such solutions.

Pure unsolvated lithium benzylamide almost certainly has an infinite ladder structure with an alternating cisoid–transoid pattern of laterally fused $(NLi)_2$ rings. This deduction is based on the evidence that the same basic ladder framework is found in both **1** and **2**. But, of particular interest here, is the unique manner in which the solvent ligands in **1** attach themselves to this ladder framework. Spanning a four-rung section of the ladder, the central Li–N–Li(a)–N(a) ring is solvent free, while those adjacent to it, Li–N–Li(b)–N(b) and Li(a)–N(a)–Li(c)–N(c) are capped on one side by μ-bonding thf ligands, which alternate above and below the ladder plane (Fig. 1).‡ The first mentioned ring is transoid and strictly planar by virtue of its centrosymmetry. In contrast, the other two are cisoid and butterfly shaped (deviations from planarity ± 0.326 Å), with N···N hinges (folding angle 119.4°) and Li wingtips, due to the pull exerted by thf ligands, which lie on twofold rotation axes passing through oxygen atoms. As a result of symmetry, there are only three unique N–Li bond lengths in **1**: ladder edges are short [2.046(3) Å] and long [2.098(3) Å] within the non-solvent-bridged and solvent-bridged $(NLi)_2$ rings respectively; the ladder rungs are all equivalent and have an intermediate length [2.087(3) Å]. The O–Li bond lengths are also equivalent [2.146(4) Å] reflecting the symmetrical fit of the thf ligand over the puckered $(NLi)_2$ ring face.

Consideration of the architecture and dimensions of **1** leads to a more complete picture of the multistepped, ladder dis-

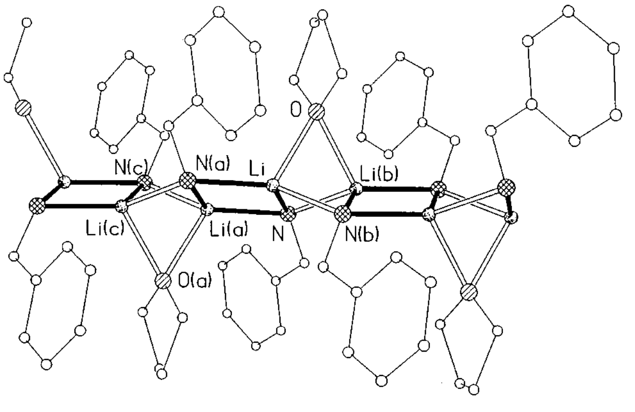
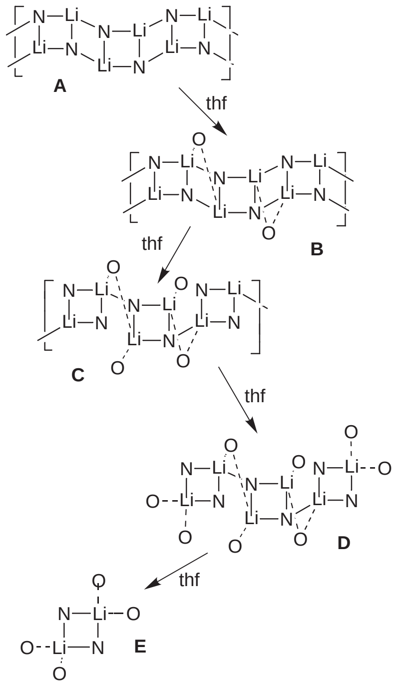


Fig. 1 Polymeric structure of **1** with atom-labelling. Hydrogen atoms are omitted for clarity. Key dimensions (Å and °): Li–N 2.087(3), Li–N(a) 2.046(3), Li–N(b) 2.098(3), Li–O 2.146(4), Li···Li(a) 2.440(6), Li···Li(b) 2.230(6), N–Li–N(a) 107.64(13), N–Li–N(b) 103.83(14), Li–N–Li(a) 72.36(13), Li–N–Li(b) 64.38(14), Li–O–Li(b) 62.60(17).



Scheme 1

assembling process than that previously outlined.[8] In particular, they provide valuable new insight into the possible early steps involved. These are included in the full sequence of steps, as we now perceive them, in Scheme 1. **A** represents the infinite ladder structure, the framework of which provides the foundation of both **1** and **2**. **B** represents the new structure **1**. This is a key structural finding as previously it was assumed that the attachment of donor ligands would automatically encourage ladder fragmentation (oligomerisation); but in **B** the polymeric arrangement is retained. Noting that lithium amide polymers are generally insoluble in arene solvents, the **A**→**B** transformation also has implications for the coordination chemistry developing at the solid–solution interface which eventually leads to the dissolution of the amide in an arene–thf mixture. The next transformation, **B**→**C**, takes place on the addition (or involvement) of more thf molecules. From the crystal structure of **1** the weakest points of the $(NLi)_\infty$ ladder framework are those bridged by the thf ligands. Logically, therefore, as the incoming thf molecules approach the metal centres in **C** (note that they all occupy identical steric environments), one of the longer, weaker N–Li edge bonds of the $(NLi)_2$ butterfly-shaped rings will cleave. This leaves the shorter, stronger bonds of the adjacent $(NLi)_2$ rings (*i.e.* those in **1** unbridged by the thf ligands) intact. The transformation **C**→**D** should not be regarded as a single step, polymer→oligomer one. It is more likely to be a fragmented process. To elaborate, as the solvation pattern in **C** develops along the polymer backbone, it will undoubtedly lead to increased steric repulsions caused by the presence of both bridging and terminal thf ligands. Hence, not the whole of **C**, but sections of it (possibly covering six N–Li rungs) will periodically break away from the remainder of the infinite ladder to form the oligomer **D**. Completing the sequence is the **D**→**E** transformation, the evidence for which is based on the structural characterisations of $[\{PhN(H)Li\}_6\cdot 8thf]$[8] and $[\{PhN(H)Li\cdot 2thf\}_2]$[9] respectively, as discussed previously. Note that the discrete $(NLi)_2$ rings in the final product **E** can be traced back to the ‘unsolvated’ $(NLi)_2$ rings in **1**, as both are planar and transoid.

In the specific case of lithium benzylamide, the tetra-thf solvated ring dimer possibly exists in solution. However, steric crowding probably destabilises it (note that the dibenzylamido analogue is only bis-solvated[10]) with respect to **1** which preferentially crystallises from solution. This crystallisation process is in effect the retro-counterpart of Scheme 1, and would be induced by collisions between dimers and concomitant cleavage of some thf ligands.

Finally, note that this ladder dis-assembling pathway should not be considered as all-embracing, as it is likely to be dependent on the particular donor solvent employed.

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Notes and references

† Yield of crystalline material, 28%. Our attempts to separate **1** and **2** have so far been unsuccessful. ^1H NMR (25 °C, 400 MHz, C_6D_6) δ −1.05 (t, NH), 0.57 (s, NH_2), 1.40 (s, CH_2, thf), 3.55 (s, OCH_2, thf, CH_2-amine), 4.27 (d, CH_2-amide), 7.07 (br m, Ph).

‡ *Crystal data*: $C_8H_{24}Li_2N_2O$, M = 298.3, orthorhombic, space group *Pbcn*, a = 22.617(5), b = 10.047(2), c = 7.594(2) Å, U = 1725.6(7) Å^3, Z = 4, D_c = 1.148 g cm^{-3}, μ = 0.53 mm^{-1} (Cu-Kα, λ = 1.54184 Å), T = 160 K; R_w = 0.1469 on F^2 values of all 1528 unique data, conventional R = 0.0509 on F values of 1151 reflections with $F_o^2 > 2\sigma(F_o^2)$, 109 parameters; final difference map within ±0.25 e Å^{-3}. CCDC 182/1165. See http://www.rsc.org/suppdata/cc/1999/511/ for crystallographic files in .cif format.

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