A 3 : 1 mixed aggregate of diphenylamidolithium with lithium chloride: crystal structure of [$(Ph_2NLi)_3LiCl\cdot3tmen$] (tmen = *N,N,N′,N′*-tetramethylethylenediamine)

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Demonstrating a new structural type in mixed aggregate chemistry, a 3 : 1 mixture of Ph_2NLi and LiCl with 3 equiv. of *N,N,N′,N′*-tetramethylethylenediamine exists in toluene and in the solid state as a Ph_2NLi/LiCl mixed 'dimer' and a $(Ph_2NLi)_2$ homodimer linked only by a Li–Cl coordinate bond, as determined by NMR spectroscopy and X-ray crystallography.

There has been growing interest in the effect of added salts in a wide variety of chemical reactons, focused by a recent treatise on the subject.[1] One of the most intensely investigated phenomena has been the effect of added lithium halides on reactions involving lithium amides.[2] Mixed aggregates have been implicated by NMR[3] and, more recently, by crystallographic,[4] and *ab initio* computational[4d,f,5] analysis. So far for mixtures of lithium amides and lithium halides, of particular importance in modern enolisation reaction methodology, there have been examples of 1 : 1 {the 5,10-dihydrophenazine derivative[4a] [$LiCl\cdot Li(NC_{12}H_8NH)\cdot4thf$] and the 2,2,6,6-tetramethylpiperidine (tmp) derivative[4d] [$LiBr\cdot Li(tmp)\cdot3thf$]} and 2 : 1 {*e.g.* [$LiCl\cdot2LDA\cdot2tmen$] and isostructural analogues[4b,c,d,f]} aggregates. For 3 : 1 amide/halide aggregates there is no prior evidence; the only structurally characterised 3 : 1 mixed aggregate has been the organolithium heterocubane [$LiBr\cdot3LiPh\cdot3thf$], a structure in which the halide occupies one corner of the cube,[6] in retrospect unsurprising in view of the isostructural homo-aggregates [$LiBr\cdot Et_2O$]$_4$ and [$LiPh\cdot Et_2O$]$_4$.[7,6] While halides and carbanions are often associated with the ring stacking motif, inclusion of amides in the aggregates precludes this structural type.[8] Halides have previousl been incorporated into ladder structures,[4] including a very recent tetralithium butterfly cluster with μ_4 bromide,[4e] but we here report an alternative way for two dimers to associate *via* a single contact.

We chose the diphenylamido system as the basis for an extensive study of mixed aggregation phenomena since it is a simple model secondary amide amenable to crystallographic study. Prior to our work, only a single structure involving Ph_2NLi had been reported, that of a monomeric 12-crown-4 complex.[9] However, a thorough NMR spectroscopic investigation of the Ph_2NLi/LiBr system was also in the literature. This revealed evidence only of mixed dimeric aggregates.[3a] As this manuscript was in preparation, a further structure report appeared involving Ph_2NLi in a large aggregate with Bu^{n}Li and dilithiated Ph_2NH.[10]

Crystals of [$(Ph_2NLi)_3LiCl\cdot3tmen$] **1** were grown from a toluene solution prepared from Ph_2NH, Ph_2NH_2Cl and Bu^{n}Li in the presence of tmen.† This hydrohalide *in situ* route has proved advantageous over 'direct' or 'ammonium salt' routes in the past for generation of crystalline mixed aggregates.[4b,d,f] Structure determination by X-ray crystallography‡ revealed the elegantly simple structure depicted in Fig. 1. Perhaps the simplest way of rationalising the molecule is to consider it as an adduct of a homodimeric amidolithium and a 1 : 1 mixed dimer. Taken in this way the mixed dimer may be compared with [$LiCl\cdot Li(NC_{12}H_8NH)\cdot4thf$] in which each lithium is four-coordinate,[4a] as in **1**, but in which the chloride was only two-coordinate. In **1** the chloride is μ_3, as it is in [$LiCl\cdot2LDAP\cdot2tmen$],[4b] but in a Y-shaped rather than a T-shaped conformation. This near-planar (sum of angles 356°) Y-shape is rare for chloride. The closest analogy structurally lies in [$(LiCl)_4(pmdeta)_3$] (pmdeta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine),[11] where the sum of angles around the three-coordinate chloride is 337°. This structure also provides the closest analogy to the two linked rhomboids of **1**. However, in [$(LiCl)_4(pmdeta)_3$] the link is supported by a bridging pmdeta ligand.[11]

A more intriguing view of the molecule might be as a frozen analogue of a postulated intermediate in the fluxion of [$LiCl\cdot2LDA\cdot2tmen$] in toluene solution.[4f] In this way, inclusion of a further amidolithium unit converts this fluxion intermediate, in which chloride acts as a fulcrum around which the other ligands rotate, into a stable geometry. The retention of the double-ring structure of **1** in solution is proven by the concentration-invariant observation of three signals in a 2 : 1 : 1 ratio in the ^{7}Li NMR spectrum in toluene. This view of an extra amidolithium unit trapping an opened 2 : 1 aggregate is also relevant to enolisation mechanisms of 2 : 1 LDA/LiCl ag-

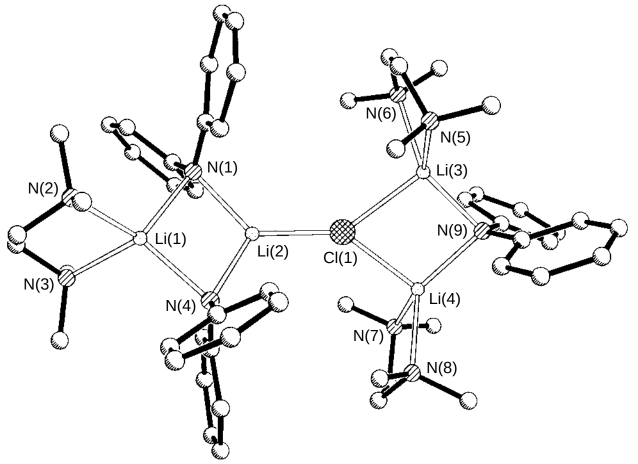
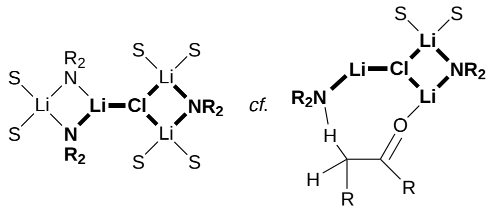


Fig. 1 Molecular structure of compound **1**. Selected bond lengths (Å) and angles (°): Cl(1)–Li(2) 2.242(6), Cl(1)–Li(3) 2.377(7), Cl(1)–Li(4) 2.378(7), Li(1)–N(4) 2.140(7), Li(1)–N(1) 2.151(8), Li(1)–N(3) 2.169(7), Li(1)–N(2) 2.220(7), Li(2)–N(4) 2.004(9), Li(2)–N(1) 2.106(8), Li(3)–N(9) 2.068(8), Li(3)–N(5) 2.130(8), Li(3)–N(6) 2.168(9), Li(4)–N(9) 2.088(7), Li(4)–N(8) 2.135(9), Li(4)–N(7) 2.165(8), Li(2)–Cl(1)–Li(3) 135.9(3), Li(2)–Cl(1)–Li(4) 144.0(3), Li(3)–Cl(1)–Ll(4) 75.8(2), N(4)–Li(1)–N(1) 98.1(3), N(4)–Li(2)–N(1) 107.5(3), N(4)–Li(2)–Cl(1) 127.5(4), N(1)–Li(2)–Cl(1) 124.9(4), N(9)–Li(3)–Cl(1) 97.7(3), N(9)–Li(4)–Cl(1) 97.1(3), Li(2)–N(1)–Li(1) 76.9(3), Li(2)–N(4)–Li(1) 77.4(3), Li(2)–N(9)–Li(4) 89.3(3).



S = Lewis base solvent
R = hydrocarbon substituent

Scheme 1

gregates in solution: it has been proposed that such aggregates react *via* scission of a Li–N bond and coordination of a ketone.[4d] This proposal is further supported by the similarities between the putative opened intermediate and the stable geometry of **1** as shown emboldened in Scheme 1.

Another interesting view of the molecule is as a 'crystallographic snapshot' of the process of amidolithium ladder fragmentation by solvation, as recently discussed by Mulvey and coworkers.[12] By variation of solvent ratio and organic substituent on amido nitrogen, a series of fragmented ladders have been structurally determined, most recently by use of the primary amide PhNHLi and limited amounts of thf.[12] Inclusion of chloride in the aggregate **1** reduces the connectivity of two dimers to its minimal limit.

The success of the Ph_2N anion as a platform for mixed aggregate studies is due in large part to its favour of asymmetric solvation in the dimeric state. One four-coordinate and one three-coordinate lithium are observed in the unmixed tmen complex of this amide, just as in **1**, and in other mixed aggregates that we have structurally characterised. Details of some of these will be found in a forthcoming full paper once their solution behaviour has been fully characterised.[13]

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Footnotes and References

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† Compound **1**, mp 151 °C, was obtained as colourless needles in a yield of 51%. A second crop produced a combined yield of 98%. Satisfactory C, H, and N analyses were obtained.

‡ *Crystal data* for **1**: $C_{54}H_{78}ClLi_4N_9$, M = 916.5, monoclinic, space group $P2_1/c$, a = 23.067(3), b = 14.879(2), c = 17.124(2) Å, β = 104.77(2)°, U = 5682.8(12) Å^3, Z = 4, D_c = 1.071 g cm^{-3}, μ = 0.896 mm^{-1} (Cu-Kα, λ = 1.541 78 Å), $F(000)$ = 1976, T = 160 K. Stoe-Siemens diffractometer, crystal size 0.57 × 0.42 × 0.30 mm, θ_{max} 67.5°, 9314 reflections measured, 9266 unique (R_{int} = 0.0772). Structure solution by direct methods, full-matrix least-squares refinement on F^2 for all data, with anisotropic displacement parameters, riding isotropic H atoms, no absorption correction. Final $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$ = 0.2627 for all data, conventional R = 0.0930 for 6115 data having $F_o^2 > 2\sigma(F_o^2)$, S = 1.032. Final difference map between +0.70 and −0.35 e Å^{-3}. Programs: SHELXTL (G. M. Sheldrick, University of Göttingen, Germany), and local programs. CCDC 182/661.

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