CHEMICAL SOCIETY REVIEWS

Synthetic and structural developments in hetero-s-block-metal chemistry: new ring-laddering, ring-stacking and other architectures

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Hetero-alkali metal organic compounds are of interest because they can exhibit superior reactivity to conventional organolithium reagents. Structurally well-defined mixed lithium–sodium and mixed lithium–sodium–potassium compositions, based on a variety of organic ligands, are surveyed here. A complicated assortment of architectures with lithium-rich, sodium-rich, or equimolar metal stoichiometries is revealed. These structures are analysed with respect to the 'ring-laddering' and 'ring-stacking' concepts used previously in the rationalisation of organolithium structures. Important homometallic structures, which have appeared since these concepts were reviewed, are also included. Finally, an intriguing new class of mixed lithium–magnesium amide, based around an oxo or peroxo core, is described.

1 Introduction

The start of hetero-alkali metal chemistry can be traced back to 1955 when Wittig reported the synthesis of 'diphenyllithium sodium',[1] an ill-defined compound of variable stoichiometry and unknown structure which outperformed normal phenyllithium in its nucleophilic reactivity towards benzophenone. This was a fundamentally important observation, its essential message being that intermetallic (mixed-metal) systems can display unique chemical behaviours (beneficial in this particular case) compared to those of their single-metal components. The same principle applies to the elements, as it is now well-established that incorporation of a few atoms of sodium into the metallic lattice structure of lithium leads to an enhancement in reactivity over that of pure lithium in reactions with organic halides. Even earlier in 1952, Gilman pioneered the synthesis of organocuprates, mixed-lithium Group 11 metal systems.[2] These reagents, typified by lithium dimethylcuprate, 'Li$^+$ (Me$_2$Cu)$^-$', provide the synthetic chemist with a valuable source of 'soft' nucleophiles, the regioselectivity of which often deviates from that of 'hard' nucleophilic alkyllithiums (*e.g.* in their action on α,β-unsaturated carbonyl compounds). The year 1967 was also highly significant for it was then that Schlosser first recognised that alkyllithium/heavier alkali metal (sodium or potassium) alkoxide combinations were in fact intermetallic reagents of exceptional deprotonating ability, thus beginning the application of the so called 'superbases' widely utilised in organic synthesis today.[3] Despite their maturity and popularity, the true nature of these mixed-metal, mixed-anion superbasic concoctions still remains to be definitely established. Of fundamental importance in asymmetric synthesis, mixed-anion aggregates of another type thought to occur when salts such as lithium halides are added to lithium enolates,[4] can profoundly affect the stereochemical outcome and efficiency of subsequent reaction steps. There is a common thread running through all of the mixed-chemical species so far mentioned: in general, little is known about their structural constitutions and, as a result, the role of the mixed-metal or mixed-anion component within the reaction mechanism is not clear. One recurring problem is that such species tend to exist as dynamic mixtures in solution, from which only homometallic components can be isolated (particularly so in the case of superbases). Furthermore, often the isolated material is amorphous, and thus not suitable for X-ray crystallographic study.

We therefore decided to take a fundamental approach to start to fill this gap in our knowledge, by setting out to synthesise inter-alkali metallic derivatives of a range of organic precursors with the aim of acquiring new, tangible, isolable products, the structures of which could be determined with certainty. These structures could serve as models for the synthetically-useful materials. The first success in this quest came in 1986 through the synthesis and X-ray crystallographic characterisation of the monolithium trisodium guanidide $\{[(Me_2N)_2C{=}N]_4LiNa_3{\cdot}(HMPA)_3\}$ [HMPA = $(Me_2N)_3P{=}O$].[5] More intermetallic lithium–sodium complexes (prepared both in our laboratory and in others) quickly followed, and a complicated assortment of structural architectures, some lithium-rich, some sodium-rich, and some with equimolar metal stoichiometries, began to emerge. To this series were also added the first examples of heterotrimetallic lithium–sodium–potassium complexes.[6] This collection of structures forms the primary basis of this review. In general, it appears that the architectural principles governing lithium amide and organolithium chemistry, the so-called 'Ring-Laddering' and 'Ring-Stacking' concepts, are also applicable to these intermetallic systems. Accordingly, therefore, they are presented in two separate groups, depending on whether their structures exhibit ladder-like or stack-like features. Also included within these groups are several important homometallic structures which have appeared since the publication of the last structural review on 'Ring-Laddering' and 'Ring-Stacking' phenomena.[5] Another section will consider special intermetallic ring systems which either exhibit no further association, or which fuse together in a manner other than laddering or stacking. Finally, attention is drawn to an intriguing new class of intermetallic (lithium–magnesium)

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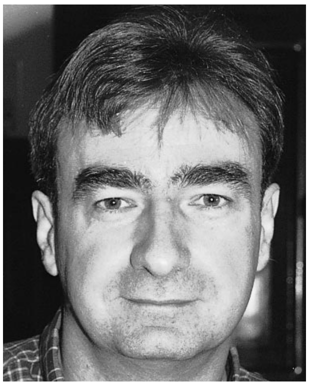


structure, the architecture of which is not solely founded on rings, but on a core atom or molecule.

2 Structures with ring-laddering connotations

As the concept of ring-laddering is associated with lithium secondary amides, it is germane to begin this section with discussion of the most important compound in this class. The history, development and commercial foundation of lithium amide chemistry essentially revolves around that of lithium diisopropylamide [LDA, (Pr^i_2NLi)]. A good advert for the merits of fundamental research, LDA was originally prepared in 1950 at the University of Pittsburgh by Hamell and Levine during a study of condensation reactions of esters,[7] but lay almost dormant for two decades before climbing to its present elevated status as one of the most applied synthetic reagents in modern chemistry. Its extraordinary deprotonating ability is kinetically—rather than thermodynamically—based, and stems from the sterically-hindered nature of its dialkylamido branches. Like all lithium amides it is air- and moisture-sensitive, but more aggressive than most in its fierce pyrophoricity. Due to the difficulty in growing suitable single crystals, the structure of LDA was not determined until 1991.[8] The first polymeric lithium amide to be crystallographically characterised, it adopts an eye-catching helical arrangement (Fig. 1) composed of near-linear NLiN units, eight of which constitute a turn of the helix. Obviously the special steric requirements of the bulky diisopropylamido groups cannot be accommodated within an infinite ladder (double-strand) framework, and hence this single-strand structure is preferred. By coiling, the strand can extend *ad infinitum* without disrupting the linearity of the NLiN units which keeps the ligand–ligand repulsions to a minimum. Though this polymer exists as a single strand, it can still form oligomeric $(NLi)_2$ rings when attacked by solvent molecules. The docking of a solvent ligand will cause the NLiN bond angle to narrow, thus setting up the ring-closing process. Such rings have been found discrete in the dimer $[(Pr^i_2N\text{-}Li{\cdot}THF)_2]$,[9] and linked together by bridging solvent ligands in the polymer $\{[(Pr^i_2NLi)_2.TMEDA]_\infty\}$.[10] Therefore it should not be assumed that the solvent-free, polymeric parent structures of solvated ring dimers necessarily possess ladder architectures, though such are likely to be common.

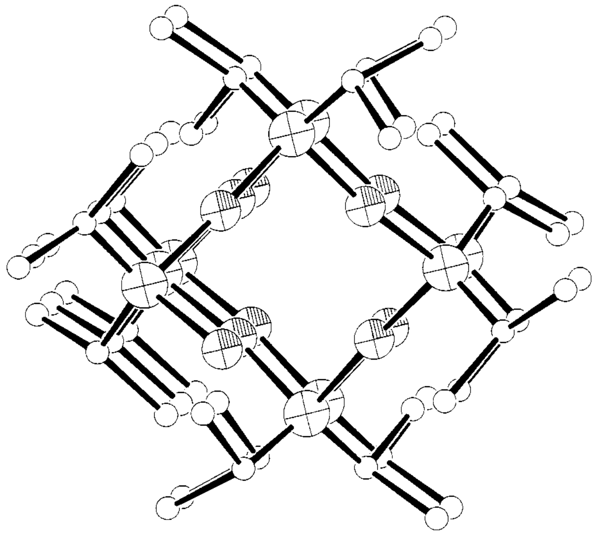


Fig. 1 Polymeric structure of $[(Pr^i_2NLi)_\infty]$. Key to crystal structure figures: metal atoms represented by shaded spheres, N and O atoms by quartered spheres, and C atoms by plain circles; for clarity H atoms and certain organic fragments are omitted.

Crystallographic confirmation of the long predicted lithium amide polymeric ladder structures finally arrived in 1998. The two examples clearly demonstrate the lateral, edge-to-edge association of $(NLi)_2$ rings on which the concept of ring-laddering is founded. Furthermore, both structures have in common –N(H)Li units formed by lithiation of primary amido $-NH_2$ functions. The extended ladder of the ethylenediamine derivative $\{[H_2NCH_2CH_2N(H)Li]_\infty\}$ reveals a sinusoidal ribbon-like appearance (Fig. 2).[11] The μ_3-N framework atoms belong to $N(H)^-$ anions, while the neutral NH_2 arms act as internal donor atoms. This internal ligation is accomplished in two distinct ways: across the framework of the ladder in the direction of the rungs (to Li1 and Li2), or along the ladder edges (to Li3 and Li4). Thus, the ladder is characterised by two types of $(NLi)_2$ ring which alternate throughout its infinite length. Another important feature of the rings is their conformational order along the framework: an alternating cisoid–transoid sequence is observed [cisoid represents the situation where the α-C atoms of both amide anions lie on the same side of the $(NLi)_2$ ring to which they are attached]. This sequence is primarily responsible for the undulation within the ladder polymer. Ring conformations were not considered in the original ring-laddering papers, but they form an essential part of the description of the new additions to the ladder family discussed here. Found in the hemi-benzylamine adduct of lithium benzylamide, $(\{[PhCH_2N(H)Li]_2{\cdot}H_2NCH_2Ph\}_\infty)$, the structure of the second polymeric ladder is even more remarkable (Fig. 3).[12] Curiously, the solvation occurs regioselectivity, along one ladder edge only, with amine ligands positioned alternatively above and below the $[(NLi)_2]_\infty$ ladder framework. This leads to an asymmetrical arrangement with four-coordinate solvated Li centres lining one edge, while three-coordinate unsolvated ones line the other. There is also a severe twisting of the ladder framework, coincident with a highly-

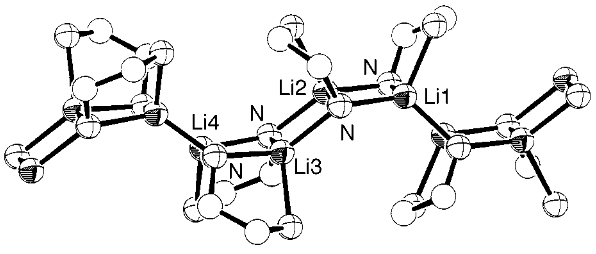


Fig. 2 Polymeric structure of $\{[H_2NCH_2CH_2N(H)Li]_\infty\}$

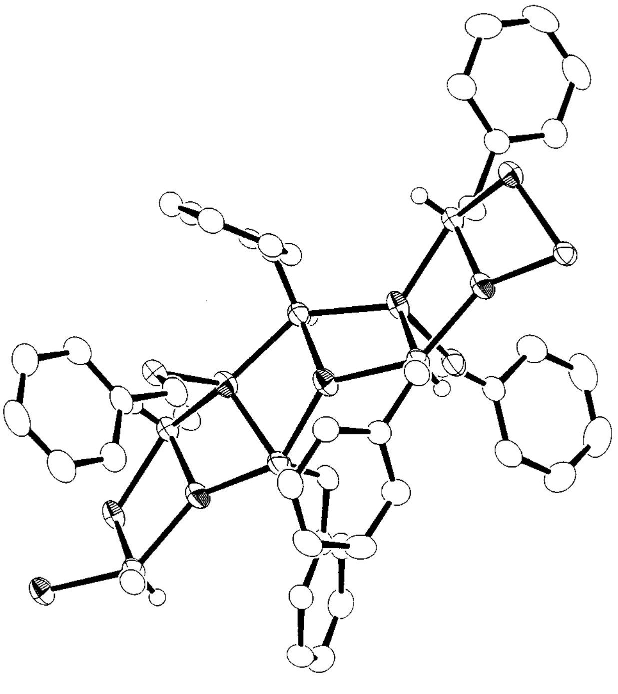
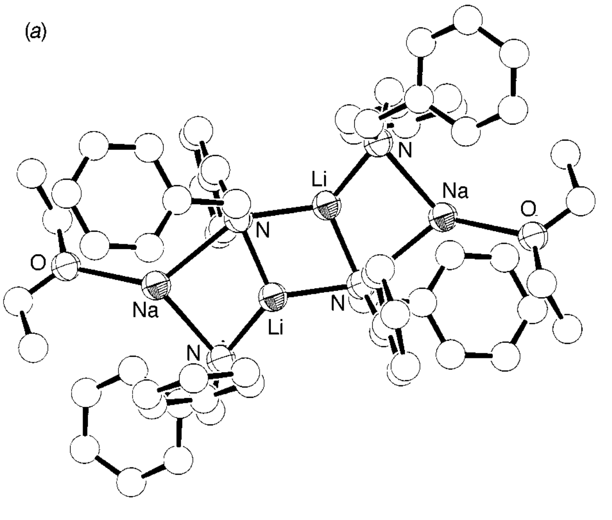


Fig. 3 Polymeric structure of $(\{[PhCH_2N(H)Li]_2{\cdot}H_2NCH_2Ph\}_\infty)$

pyramidalised Li centre. Again, as in the previous polymer, the conformational order is cisoid–transoid. Another twisted ladder polymer, but one having full rather than selective solvation, is known for the lithium primary phosphide {[Cy-P(H)Li·THF]$_\infty$}.[13] However, as yet, there is still no example of a crystallographically characterised pure, donor-free, lithium amide (or phosphide) polymeric ladder.

Turning to heterobimetallic systems, two small oligomeric ladder species (Fig. 4), having the same rung length and metal–metal stoichiometry have been synthesised. The four N-metal rungs of the dilithium disodium secondary amide ({[(PhCH$_2$)$_2$N]$_2$LiNa·OEt$_2$}$_2$) are accommodated within a stepped ladder framework.[14] In this centrosymmetric dimer, the Li$^+$ cations occupy the inner rungs, while the larger Na$^+$ cations occupy the more sterically accessible outer rungs which permit the inclusion of solvent ligands. No differentiation of the type of ring conformation (cisoid *vs.* transoid) can be made here as the two 'R' substituents on the amido N centre are equivalent. The most illuminating aspect of this structure is the μ_3-bonding role of the dibenzylamide anions located in the central (NLi)$_2$ ring. This bonding mode would be sterically prohibited in an all-lithium structure, so its existence here can be attributed to the presence of the Na$^+$ cations. This is an important finding, because modifications in chemical structure could translate into modifications in chemical reactivity. Hence, by implication, the reagent properties of the mixed lithium sodium amide could be different (superior?) to that of its pure lithium counterpart. With this in mind, it is significant that the stepped ladder structure of the former is retained in arene solution. A contrasting 'convex' construction is found for the other four-rung ladder structure of the dilithium disodium primary amide ({[Bu^{t}N(H)]$_2$LiNa·TMEDA}$_2$) (Fig. 4).[15] This alternative architecture does not alter the site preferences of the individual metal cations: the smaller ones occupy the inner rungs. Again, the end-positioned Na$^+$ cations are solvated, this time by bidentate diamine molecules. The curvature of the structure can be attributed to the transoid–cisoid–transoid conformational order within the ladder framework.



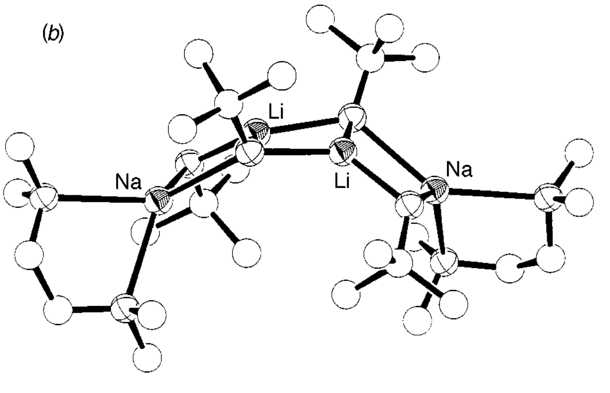


Fig. 4 (*a*)Molecular structure of [{[(PhCH$_2$)$_2$N]$_2$LiNa·OEt$_2$}$_2$]; (*b*)Molecular structure of [{[Bu^{t}N(H)]$_2$LiNa·TMEDA}$_2$]

This latter compound belongs to a remarkable family of ladder structures. When unsolvated the pure lithium amide exists as the octameric cyclic ladder {[Bu^{t}N(H)Li]$_8$} (Fig. 5).[15]

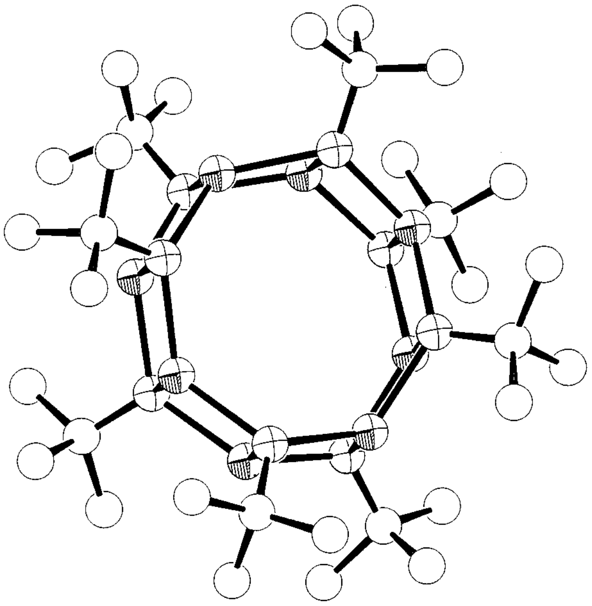


Fig. 5 Molecular structure of [{Bu^{t}N(H)Li}$_8$]

The conformational order of the eight, fused (NLi)$_2$ rings is exclusively cisoid with the small H substituents projected inwards and the large alkyl substituents projected outwards with respect to the N$_8$Li$_8$ core. It is significant that this cisoid conformation is retained within the lithium section of the dilithium disodium derivative. The third member of this family is the partially amine-solvated ({[Bu^{t}N(H)Na]$_3$·H$_2$NBu^t}$_\infty$).[15] As with the other two *tert*-butyl amide structures, it is synthesised by stoichiometric metallation of the parent amine, but additional amine was required for solubility purposes in this case. In the context of its oligomeric dilithium disodium relative, the structure of this all-sodium amide is best described as an infinite ladder of alternating, fused, convex and concave units (Fig. 6). Covering three N–Na rungs, these curved units display a cisoid conformation of amide substituents; but a switch to transoid occurs where these units fuse together. The repeating conformational order of the polymer is therefore cisoid–cisoid–transoid. Ligating every third Na$^+$ cation within the ladder framework, the *tert*-butylamine solvent molecules prevent the 'convex' units from ring-closing as in the octameric lithium amide and hence the ladder curves away in the opposite 'concave' direction. Being derived from the same primary amine, these three ladder compounds have in common a H atom still attached to the amido N centre. Thus, they constitute a convenient source of imido Bu^{t}N^{2-} ions on removal of this H atom as recently demonstrated for the lithium amide in the

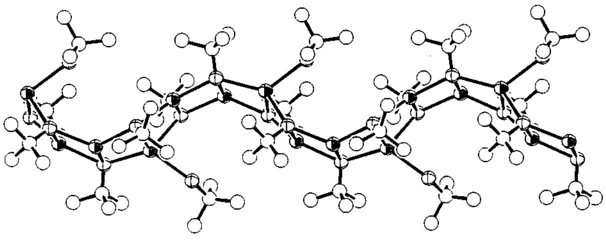


Fig. 6 Polymeric structure of ({[Bu^{t}N(H)Na]$_3$·H$_2$NBu^t}$_\infty$)

synthesis of transition metal imide complexes[16] and of novel Group 16 anions.[17]

Insight into how an infinite ladder might dis-assemble into a more synthetically useful finite oligomeric ladder has come from a structural study of the lithiation of aniline. Synthetic chemists probably perform this dis-assembling procedure unwittingly when adding donor solvent to a suspension of pure lithium amide for solubility purposes. Pure lithium anilide precipitates from hydrocarbon solution as a cream solid on treating aniline with Bu^{n}Li. The structure of the compound is unknown, but its amorphous nature is consistent with a polymeric, or high-oligomeric, ladder. Addition of a limited amount of THF gives the solvate $\{[PhN(H)Li]_6{\cdot}8THF\}$.[18] Its structure (Fig. 7) can be interpreted as a loose assembly of three dimeric $(NLi)_2$ rings held together by rare, bridging THF ligands, resulting from the partial rupturing of a ladder cut into sections of six N–Li rungs in length. As such, it represents a step on the way to fragmenting into three separate dimeric molecules. This point was later verified experimentally by the crystallographic characterisation of $\{[PhN(H)Li{\cdot}(THF)_2]_2\}$,[19] which confirms that the fragmentation process goes to completion when excess THF is available. On the basis of these structural 'snapshots', the possible sequence of steps involved in dis-assembling long ladders to their constituent solvated dimeric rings can be proposed (Scheme 1). The key step appears to be insertion of solvent molecules into inner rung sites as implied by the μ-THF ligands in $\{[PhN(H)Li]_6{\cdot}8THF\}$ (**E** in Scheme 1). Significantly, its $(NLi)_2$ rings and that in the discrete tetra-solvated dimer display a transoid conformation. This contrasts with the cisoid arrangement found in $\{[PhN(H)Li{\cdot}TMEDA]_2\}$,[20] and in two other diamine-chelated amide dimers $\{[p\text{-}CH_3C_6H_4N(H)Li{\cdot}TMEDA]_2\}$[20] and $\{[PhCH_2(Me)NNa{\cdot}TMEDA]_2\}$.[21] It is conceivable therefore that an alternative dis-assembly mechanism operates for bidentate solvent molecules such as TMEDA. One possibility is that the diamine clips off N–Li monomeric rungs, which can subsequently re-associate to a cisoid dimer (Scheme 2). More work is required to resolve this matter. Subjecting lithium anilide to the tridentate triamine PMDETA also generates a fragmented ladder structure in $\{[PhN(H)Li\}_3{\cdot}(PMDETA)_2\}$: this is based on a three-runged ladder, one N–Li rung of which has broken apart from a $(NLi)_2$ ring that is highly distorted from planarity through complexation with the bulky amine.[22]

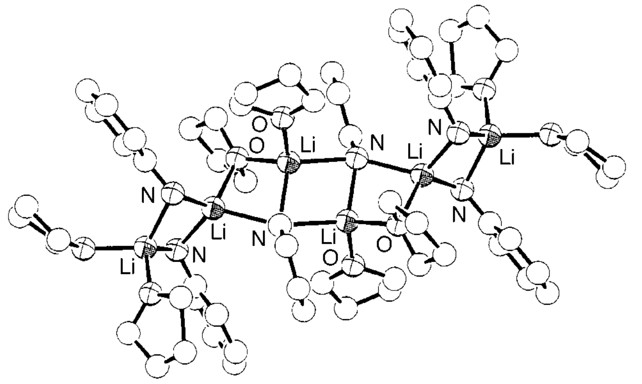
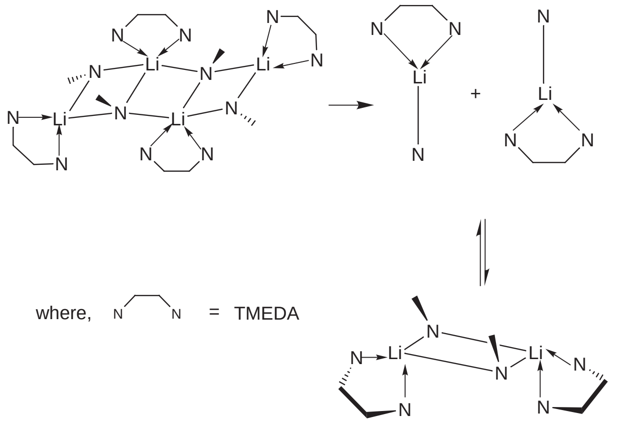


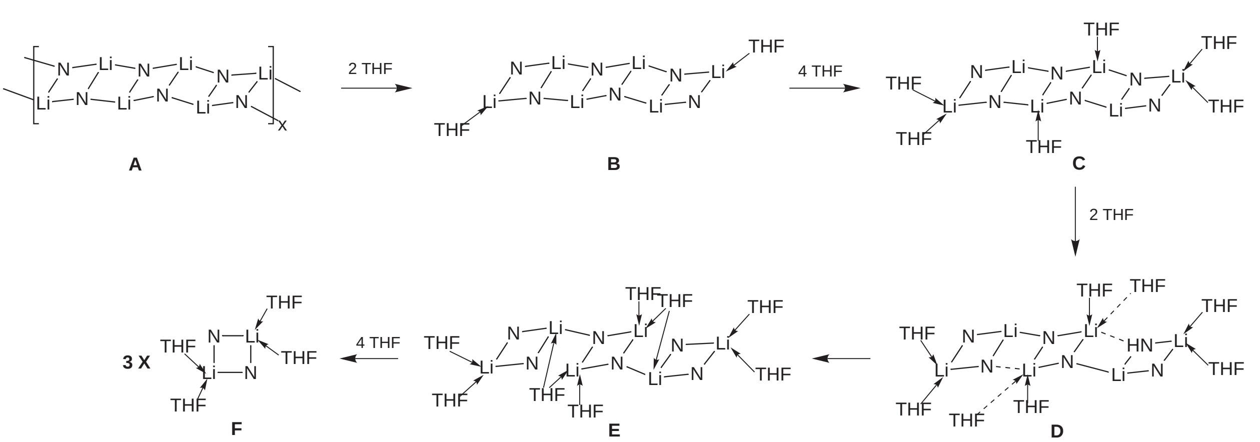
Fig. 7 Molecular structure of $\{[PhN(H)Li]_6{\cdot}8THF\}$



Scheme 2

3 Structures with ring-stacking connotations

The concept of ring-stacking sprang from the detailed analysis of the dimensions of a series of homeotypic lithium imide hexamers $[(R^1R^2C{=}Li)_6]$,[5] the precursors of which are ketimines $R^1R^2C{=}NH$. Leaving aside subtle patterns in interatomic distances between and within rings (covered fully in earlier reviews),[5,23] the basic feature of stacking is that the R substituents, or more precisely their α-atoms, lie approximately in the same plane as the $(NLi)_2$ rings to which they are attached. Rings conforming to this stereochemistry can then 'self-associate' in a face-to-face manner so that the N centres of one ring lie effectively above the Li centres of the other. Increasing the number of attractive $N^{\delta-}$–$Li^{\delta+}$ interactions, whilst restricting the Van der Waals repulsions between substituents, leads to an overall gain in stability *cf.* the discrete single ring structures. Making use of the excellent stacking characteristics of $R^1R^2C{=}N^-$ ligands, a number of stacked-ring structures have been established in the intermetallic lithium–sodium area. Here, the driving force towards formation of these stable three-dimensional cage architectures is so strong, that the reactions involved tend not to follow stoichiometric lines, *i.e.* the Li : Na ratios in the isolated intermetallic products do not match those in the initial reaction mixtures. This point is illustrated in equations (1)–(3), while (4) highlights an all-sodium example.



Scheme 1

As no other products were isolated from these reactions, the equations do not balance.

$$2(Me_2N)_2C{=}NH + Bu^nLi + Bu^nNa + 5HMPA \rightarrow \tfrac{1}{x}\{[(Me_2N)_2C{=}N]_4LiNa_3{\cdot}(HMPA)_3\} \quad (1)$$

$$2(Me_2N)_2C{=}NH + Bu^nLi + Bu^nNa \rightarrow \tfrac{1}{x}\{[(Me_2N)_2C{=}N]_6Li_4Na_2\} \quad (2)$$

$$2Bu^tC{\equiv}N + PhLi + PhNa \rightarrow \tfrac{1}{x}\{[Ph(Bu^t)C{=}N]_6Li_4Na_2\} \quad (3)$$

$$Bu^t{}_2C{=}NH + Bu^nNa \rightarrow \tfrac{1}{x}[(Bu^t{}_2C{=}NNa)_4{\cdot}(HN{=}CBu^t{}_2)_2] \quad (4)$$

These stacked-ring structures are shown in Fig. 8. The monolithium trisodium guanidide $\{[(Me_2N)_2C{=}N]_4LiNa_3{\cdot}(HMPA)_3\}$[5] adopts a distorted cubane arrangement, which is formally a double-layered stack between a heterometallic NNaNLi and a homometallic NNaNNa ring. This metal stoichiometry also appears in the aryl complex $[Ph_4LiNa_3{\cdot}(TMEDA)_3]$,[24] but its geometry is based on a tetrahedral tetraphenyllithate ion and therefore is not a stack. Triple-layered stack structures are favoured in the absence of external solvent ligands, as exemplified by the ketimide $\{[Ph(Bu^t)C{=}N]_6Li_4Na_2\}$[5] and the guanidide $\{[(Me_2N)_2C{=}N]_6Li_4Na_2\}$.[25] Their tetralithium disodium stoichiometries can be rationalised by consideration of the distinct metal sites that such $[(N\text{-metal})_2 \times 3]$ frameworks offer: two central ring, four-coordinate sites and four outer ring, three-coordinate sites. The greater coordinative needs of the larger alkali metal dictates its preference for the former sites. This apparently contrasts with the situation found in intermetallic ladder structures, where the Na^+ cations occupy the outer-rung sites. However, the outermost sites in the three-dimensional stacks are considerably less exposed than those in the two-dimensional ladders, and therefore, are less accessible to external solvent molecules; hence in the stack, the Na^+ cations are better off in the high-coordinate central ring sites. While external solvation is difficult without disrupting the triple-stack architecture, internal solvation of an outer-ring metal site can occur. This is demonstrated in the guanidide structure[25] by the Me_2N donor atoms (projecting from the central ring) intramolecularly binding to the Li^+ cations. Stack structures with protic ligands, whose compositions are apparently incompatible with the stoichiometries used in the reactions can preferentially crystallise from solution (consider eqn. 4). Representative of this type is the sodium ketimide•ketimine complex $[(Bu^t{}_2C{=}NNa)_4{\cdot}(HN{=}CBu^t{}_2)_2]$,[26] which can be regarded as a novel cubane stack of solvated and solvent-free $(NNa)_2$ rings. Here, where there is sufficient metal reagent present in solution to metallate all protic sites, kinetic factors may dominate with rates of aggregation and solvation being in competition with rates of deprotonation.

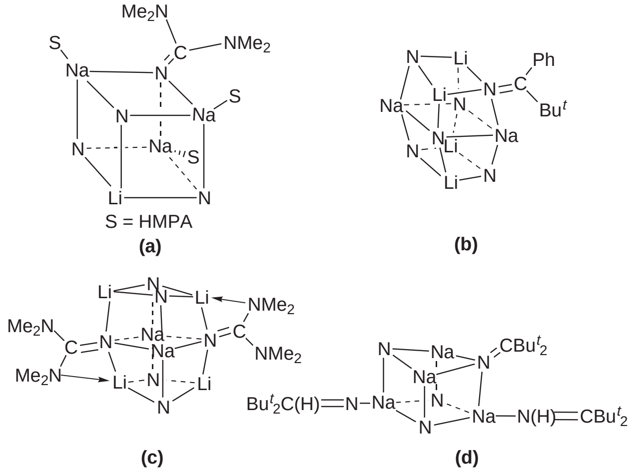


Fig. 8 Molecular structure of (a) $\{[(Me_2N)_2C{=}N]_4LiNa_3{\cdot}(HMPA)_3\}$; (b) $\{[Ph(Bu^t)C{=}N]_6Li_4Na_2\}$, (c) $\{[(Me_2N)_2C{=}N]_6Li_4Na_2\}$; and (d) $[(Bu^t{}_2C{=}NNa)_4{\cdot}(HN{=}CBu^t{}_2)_2]$

The first reported example of an intermetallic lithium sodium enolate also contains a protic ligand. Formulated as $\{[Bu^t(CH_2{=})CO]_6Li_2Na_4{\cdot}(HNPr^i{}_2)_2\}$,[27] the core of this dilithium tetrasodium composition has been interpreted as an 'open stack' structure, but with 'missing' edge bonds (Fig. 9). Prepared by deprotonation of pinacolone, its most enlightening feature with regard to the reaction mechanism is the ligation of the outer-positioned Na^+ cations by diisopropylamine molecules, *i.e.* the amine co-produced in the reaction. The existence of such coordinations at the post-enolization stage prompts the thought that the amine co-product as well as the amide reactant may have an influence on the nature and stereochemistry of the enolate product; this could be relevant to the performance of chiral amide bases as chiral catalysts in enantioselective aldol reactions.

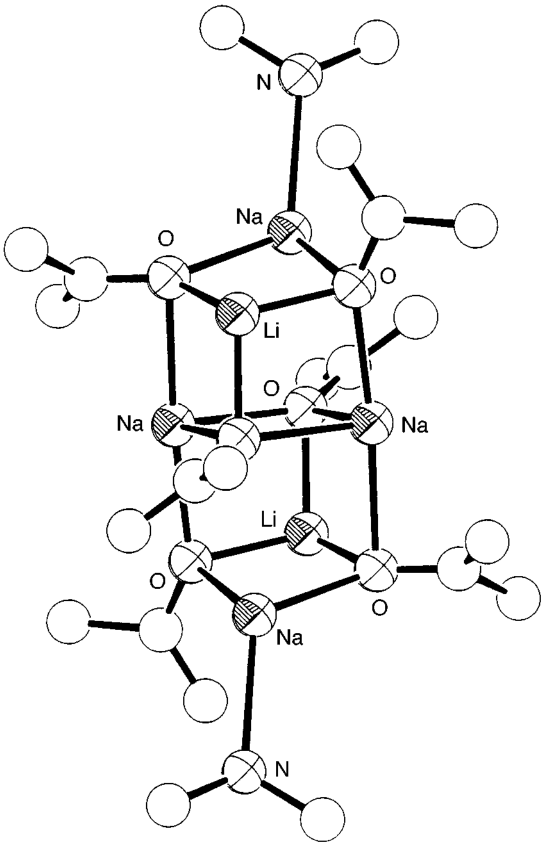


Fig. 9 Molecular structure of $\{[Bu^t(CH_2{=})CO]_6Li_2Na_4{\cdot}(HNPr^i{}_2)_2\}$

4 Other ring structures

There are many examples of discrete single-ring structures in homolithium and homosodium compounds. These prevail when further association through laddering or stacking is disallowed on steric grounds. Structures in this category are now beginning to appear in the intermetallic area. For example, a series of isostructural hexamethyldisilazide complexes of general formula $\{[(Me_3Si)_2N]_2M^1M^2{\cdot}(THF)_3\}$ (where M^1 = Li, M^2 = Na or K; M^1 = Na, M^2 = K) has been synthesised by simply mixing together the individual homometallic amides.[28] Based on asymmetric (NM^1NM^2) rings, the structures are prevented from further association by the bulk of the silylamide unit and the THF solvation. A larger octagonal ring structure (Fig. 10) is produced when toluene is metallated by a Bu^nLi–Bu^nNa mixture in the presence of TMEDA. This intermetallic benzyl complex, $[(PhCH_2)_4Li_2Na_2{\cdot}(TMEDA)_4]$,[29] contains Li^+ cations solvated by bidentate TMEDA molecules, a situation normally sterically forbidden in homometallic lithium tetramers. Why is this chelation to the smaller alkali metal allowed here? In reply, it can be attributed to the presence of the larger Na^+ cation,

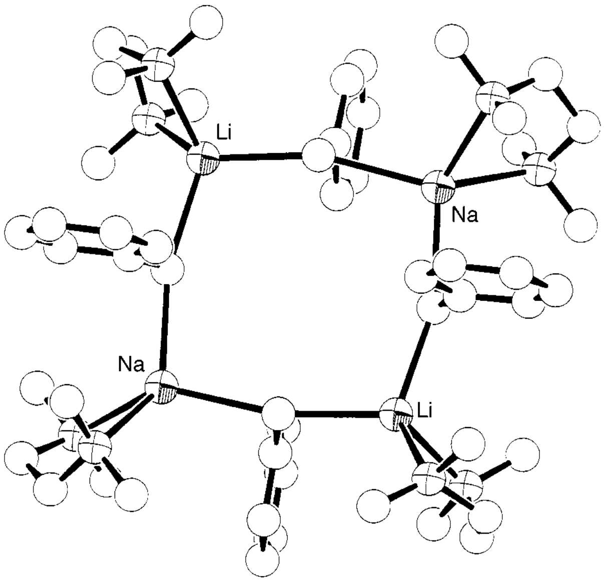


Fig. 10 Molecular structure of $[(PhCH_2)_4Li_2Na_2{\cdot}(TMEDA)_4]$

which creates more room for the ring-attached substituents, as heterometallic LiCNa triads are considerably longer than homometallic LiCLi ones. This explanation raises a fundamentally important point. *Placing Na^+ near Li^+ could open the way to realising new structures/unconventional coordination modes in organolithium compounds, which, in turn, could have a profound effect on the reactivity and selectivity of organolithium reagents.* In effect, this is reiterating the point made earlier regarding the reason for the novel μ_3-bonding mode of the dibenzylamide anions found within the stepped ladder structure of $(\{[(PhCH_2)_2N]_2LiNa{\cdot}OEt_2\}_2)$. The challenge now is therefore to incorporate Na^+ cations into a wide variety of other organolithium molecules, to provide the synthetic chemist with a new stock of chemical bases and nucleophiles which could exhibit gradations of reactivity and selectivity in comparison to the conventional sodium-free organolithium reagents.

In turning to discussion of the first trimetallic lithium–sodium–potassium complexes,[6] another way in which (element-alkali metal)$_2$ dimeric rings can join together that does not involve laddering or stacking is introduced. These complexes are accessible *via* the reaction shown in eqn. (5), starting from either lithium anilide or lithium *p*-toluidine.

$$2RN(H)Li + Bu^tONa + Bu^tOK + 2TMEDA \xrightarrow{\text{hexane}} \tfrac{1}{2}\,(\{[RN(H)]_2(Bu^tO)LiNaK{\cdot}(TMEDA)_2\}) \quad (R = Ph \text{ or } p\text{-}CH_3C_6H_4) \tag{5}$$

Containing alkoxide and amide anions, as well as the mixture of alkali metal cations, these complexes are related to the ‘superbases’ currently finding increasing use in organic synthesis. Experimental superbases typified by ‘$Bu^nLi{\cdot}Bu^tOK$’ have not as yet been structurally elucidated, leading to uncertainty in the origin of their enhanced deprotonating ability. The crystal structure of the *p*-toluidide complex is shown in Fig. 11;[20] the anilide complex is isostructural. Note that the tetrahedral Li^+ cations are buried in the core of the centrosymmetric structure, binding strongly to two O and two N atoms. Solvated by TMEDA, the Na^+ and K^+ cations are situated more towards the periphery, binding to two N and two N/two O anions, respectively. Viewing the structure as a model superbase, it is significant that the amide anions, which formally would perform the deprotonation step on a protic substrate, form one σ bond to Li^+ and two longer, weaker π bonds to Na^+ and K^+ cations. Hence the amide anions would be more easily cleaved, and, by implication, be more reactive than they would be in the pure lithium amide, where they are held tightly by three Li^+ cations (assuming a ladder arrangement as discussed in Section 2). The framework of the trimetallic structure is best regarded as a composite of two heterometallic NaNLiN rings and one homometallic $(KO)_2$ ring, which lies orthogonal to the other two (Scheme 3). These rings fuse in an unusual manner with the Li corners of the former capping the O···O diagonal of the latter in one direction, while the K corners interact with the N corners in the opposite direction. The structure is likely to be repeated for different amide–alkoxide combinations and for other anion–alkoxide combinations given the wide occurrence of four-membered ring systems in alkali metal chemistry.

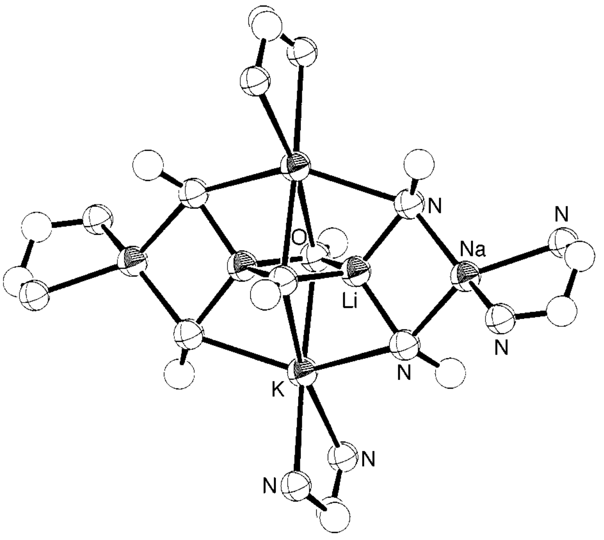
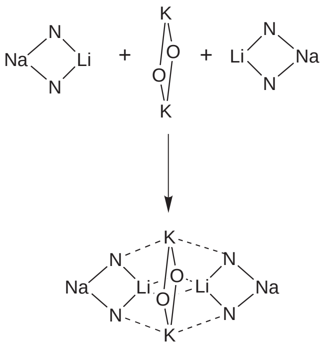


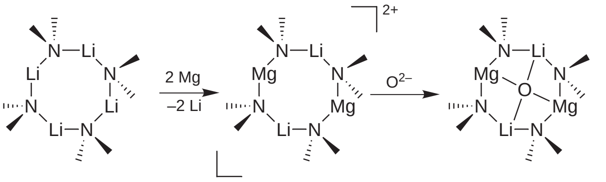
Fig. 11 Molecular structure of $(\{[p\text{-}CH_3C_6H_4N(H)]_2(Bu^tO)\text{-}LiNaK{\cdot}(TMEDA)_2\}_2)$



Scheme 3

5 Structures built around a central atom or molecule

This final section introduces a special new class of intermetallic structure designed around a central oxide or peroxide anion. In these compounds, Li^+ cations are paired with their Mg^{2+} diagonal partners from Group 2. Maintaining a common theme in this review, rings again play an important part in the construction of these molecules. Consider the textbook example of a lithium amide tetrameric ring system, namely, that of lithium 2,2,6,6-tetramethylpiperidide $\{[Me_2C(CH_2)_3C\text{-}Me_2NLi]_4\}$.[30] Two-coordinate Li^+ cations bridge pairs of amide N centres in an octagonal ring core. Substituting two Mg^{2+} cations in a transannular manner for two of the four Li^+ cations would be feasible from a steric standpoint given the similarity in ion sizes. However, valency considerations dictate that such a mixed lithium–magnesium aza cycle would carry a 2+ charge. This, in turn, begs the interesting question: would it be possible to capture small ions carrying a 2− charge in the central void of such a ring to generate a neutral entity (Scheme 4)? Recent work in our laboratory has realised this prospect. The proposed structure is exactly that adopted by the dilithium dimagnesium derivative of tetramethylpiperidine (Fig. 12),[20] which has an oxo (O^{2-}) anion at its core. Held in an unusual square planar arrangement, the oxo anion increases the metal coordination number to three. The intermediate steps in its formation have not yet been established as metallation of the precursor amine was performed *in situ* by an alkyllithium–dialkylmagnesium mixture (eqn. 6). So far only low yields of the product are



Scheme 4

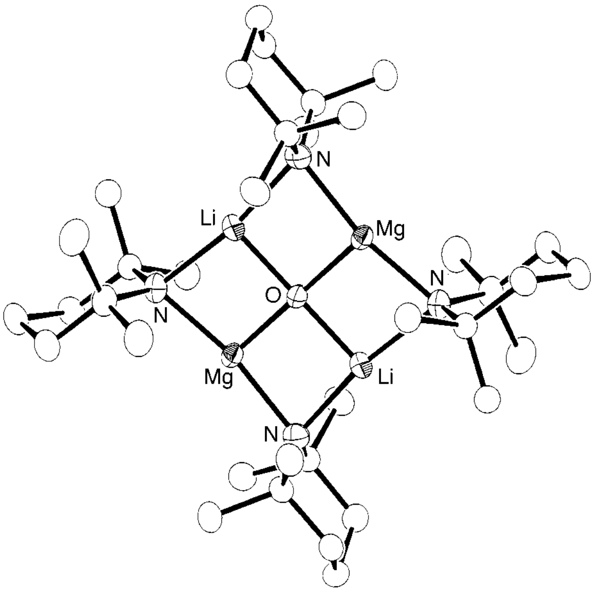


Fig. 12 Molecular structure of $\{[Me_2C(CH_2)_3CMe_2N]_4Li_2Mg_2(O)\}$

$$Bu_2Mg + Bu^nLi + 3\ Me_2C(CH_2)_3CMe_2NH \xrightarrow{\text{Limited } O_2} \tfrac{1}{x}\ \{[Me_2C(CH_2)_3CMe_2N]_4Li_2Mg_2(O)\} \qquad (6)$$

achievable by this method. However, more importantly, the same synthetic strategy has now been applied successfully, to a second amide system. Thus the complex $\{[(Me_3Si)_2N]_4Li_2Mg_2(O)\}$, a variant of lithium hexamethyldisilazide, has been synthesised.[20] It exhibits the same gross structural features as the piperidide analogue. Interestingly, peroxide molecules ($^{-}O–O^{-}$) can also be incorporated into the centre of the octagonal ring instead of oxo anions (Fig. 13): it is reasoned that this is a kinetic product stabilised by the effective shielding of the bulky silylamide groups.

These new molecules can be classified as both metal molecular oxides and intermetallic amides. As such, they could have a fascinating chemistry, which may lead to possible applications in the materials area or in chemical synthesis. Their reaction chemistry awaits to be studied and developed, as is the case with most of the intermetallic compositions mentioned in this article. New recruits to alkali metal chemistry may find this a convenient starting point for their research, stimulated by the knowledge that the use of organolithium compounds in industrial chemistry (*e.g.* in the production of polymers, pharmaceuticals, agrochemicals, flavourings and fragrances) is still rapidly growing today.[31]

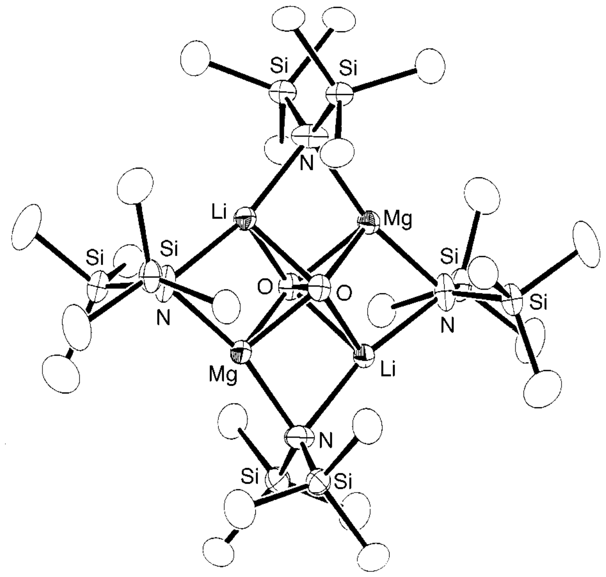


Fig. 13 Molecular structure of $\{[(Me_3Si)_2N]_4Li_2Mg_2(O_2)\}$

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