Applications of the Laddering Principle — A Two-Stage Approach to Describe Lithium Heterocarboxylates

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Dedicated to the memory of the late Dr. Ron Snaith[+]

Keywords: Lithium / Carboxylate ligands / Electrostatic interactions / Cluster compounds / Ladder polymers

Since the development of the laddering principle in the mid-1980s, it has become a useful concept for describing structural features in a wide variety of organoalkali metal (particularly organolithium) and other main-group element oligomers. Here a brief account of the laddering principle is given, and a two-stage approach to understanding structural diversity is described for several lithium heterocarboxylates. "Primary laddering" describes the initial aggregation of monomeric units, whereas "secondary laddering" deals with the assembly of these primary laddered units into larger structures. Both homo- and heteromolecular clusters can be formed by these processes. In this context, several examples are discussed, with particular emphasis on the effects of solvation and heteroatoms.

1. Introduction

Our group has been concerned for some time with novel cluster structures involving alkali metal cations and polyimido anions with a central p-block element.[1] The structures of these polycyclic systems can usually be rationalized after they are known, but the goal of accurately predicting cluster geometry remains elusive. Here we outline a two-stage approach to application of the laddering principle that has proven useful for describing a range of lithium heterocarboxylates with diverse architectures. The ideas of "primary" and "secondary" laddering are explored, and several recent examples are rationalized using this binary version of the principle as a guide. While the goal of developing a complete principle with predictive validity far exceeds the scope of this Microreview, we hope that some progress towards a better comprehension of laddered structures will be possible at its conclusion.

1.1. The Laddering Principle

The concept of laddering first appeared in the mid-1980s in seminal papers by Snaith and co-workers describing the formation of imidolithium hexamers.[2] These prototypical

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Tristram Chivers was born in Bath, England in 1940. He received his B. Sc. in chemistry from the University of Durham (U.K.) in 1961 and his Ph. D. from the same university in 1964 working with R. D. Chambers on pentafluorophenylboron chemistry. He carried out postdoctoral studies in organometallic electrochemistry with R. E. Dessy at the University of Cincinnati (1964−65) and on inorganic ring systems with N. L. Paddock at the University of British Columbia (1967−69). From 1965 to 1967 he was a Tutorial Fellow at the University of Sussex. He joined the University of Calgary in 1969 and was promoted to Professor in 1978. The focus of his research is the chemistry of the main group elements. He is a Fellow of the Royal society of Canada (1991). Recent awards include the Alcan (1987) and E. W. R. Steacie (2001) Awards of the Canadian Society for Chemistry and the Main Group Element Chemistry award of the Royal Society of Chemistry (1993).

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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compounds contained Li_6N_6 cores and were described as "stacked pairs of cyclic trimers" joined by Li−N bonds.[2a] The original laddering principle has been expanded and elucidated in the intervening years by the groups of Snaith and Mulvey, among many others. It is now known that laddering can give rise to many different cluster architectures depending on the steric and electronic environment of the centres involved, and on the presence/absence of coordinating solvent.

Laddering has been reviewed extensively,[3,4] and laddered aggregates are now well-known throughout main-group element chemistry. This is particularly true among organoalkali metal compounds, where a wide variety of clusters ranging from dimers to polymers has been found.[3] While the reasons for the occurrence of laddering as a structural motif are generally well understood, the method by which the principle of laddering should be applied, particularly in advance of structural characterization, is still a topic of ongoing investigation.

Here we will define laddering in the simplest case as the lateral association of E−M (E = group 15−17, M = group 1−2) units to form E_2M_2 rings. Such interactions are typically electrostatic in origin, occurring as a result of polarity within the E−M moiety, and can be considered as essentially ionic.[4] In addition to "open" ladders of various lengths, a variety of "closed" ladder clusters can also be constructed from the basic E_2M_2 dimeric unit (Figure 1). For many of these aggregates multiple descriptions apply; for example, an E_6M_6 hexamer might be called a closed six-rung ladder or a pair of stacked E_3M_3 rings. We will generally focus on the former view in order to stress the utility and consistency of the approach discussed here, although in some cases other descriptions may be more appropriate.

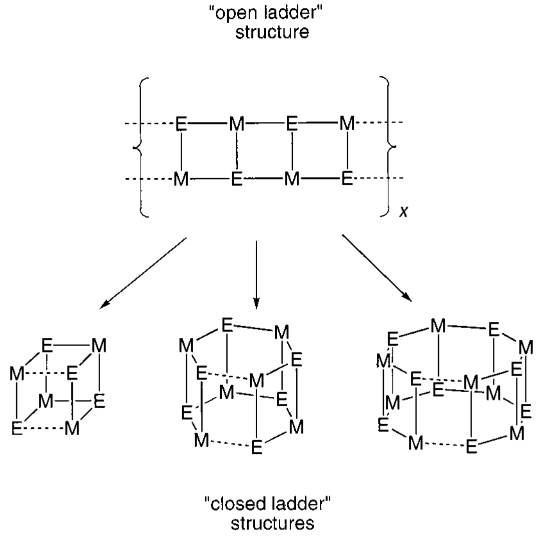


Figure 1. Open and closed E_xM_x ladder frameworks; the substituents on E have been omitted for clarity

1.2. Cisoid and Transoid Geometries

Laddered structures generally exhibit curvature, twisting, or other deviations from planarity in order to accommodate the steric demands of the substituents. The terminology to describe this effect in primary and secondary lithium amides was first introduced by Mulvey,[5] and focused on the relative orientation of substituents about the Li_2N_2 rings. We have adopted a natural extension of these terms, using *cisoid* and *transoid* to describe arrays of any three contiguous four-membered rings as well (Figure 2).[6]

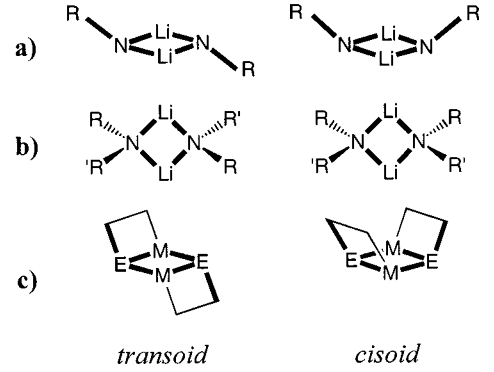


Figure 2. *Cisoid* and *transoid* orientations in: a) primary lithium amides; b) asymmetric, secondary lithium amides; c) arrays of three contiguous four-membered rings

Where laddering is limited to dimerization by bulky substituents and/or solvation, a *transoid* geometry is most often observed,[7] as would be expected on steric grounds. However, in ladders with three or more rungs there is often a preference for regions of *cisoid* geometry, either exclusively or intermixed with *transoid* regions.[5,6,8] Presumably this is because a *cisoid* geometry sometimes provides a greater separation of substituents that are two or more rungs apart than would the corresponding *transoid* arrangement. This distribution of ring conformations influences the overall topology of laddered aggregates as curving occurs to minimize van der Waals repulsions between the substituents. For example, in four-rung ladder segments, an exclusive *transoid* geometry produces a sterically crowded, repeating stair-shape, whereas an exclusive *cisoid* geometry produces a curvilinear shape (Figure 3). Since the ring conformation has a pronounced effect on the eventual outcome of laddering, any general principle describing such aggregation must take it into account.

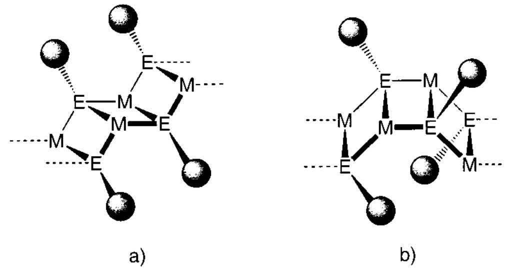


Figure 3. Alternative conformations in E_xM_x ladders with bulky substituents on E (represented by filled spheres): a) *transoid* region; b) *cisoid* region

1.3. Solvation Effects

Donor solvent molecules generally limit the oligomerization of laddered compounds in two ways: 1) by the formation of E−M bonds that are too sterically encumbered to undergo lateral association; 2) by maximizing the coordination number of the cations through solvent contacts. Solvents which are effective at limiting ladder length typically have one or more Lewis basic centres capable of forming dative bonds with cations such as lithium, sodium, magnesium, etc. Common examples include *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), pentamethyldiethylenetriamine (PMDETA), and tetrahydrofuran (THF).

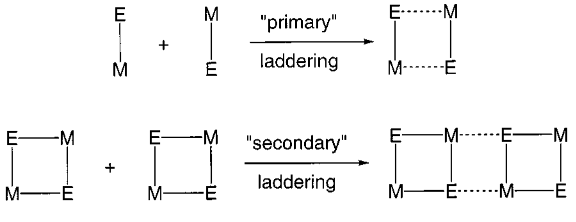
2. A Two-Stage Approach to Laddering

Snaith's original description of an imidolithium hexamer as two stacked trimers[2a] implied that the laddering principle should be somewhat hierarchical in nature. While it is true that any aggregate can be described as a collection of monomeric units, it is often more fruitful for laddered compounds to be described as being formed from slightly larger units that then associate in various ways to produce oligomers. For example, while an E_6M_6 hexamer can be thought of as six EM monomers, a more useful description might make reference to two E_3M_3 trimers associated by ring stacking, or three E_2M_2 dimers associated by laddering. In this way multiple distinct, but related, aggregation pathways may be invoked to explain the architecture of any given structure.

The purpose of this Microreview is to outline our method of describing lithium heterocarboxylates by using a two-stage approach to the laddering principle, and to show how this can be applied to other, similar, systems within the rubric of organolithium chemistry. Our methodology for rationalizing structures focuses on the use of small building blocks to construct large aggregates. As such, we have found it useful to formally separate the process of laddering into "primary" and "secondary" components as follows (Scheme 1):

Primary laddering describes the lateral association of monomeric EM fragments to produce a primary laddering unit (PLU). Such units are often homomolecular dimers, but other types of oligomers are also possible.

Secondary laddering describes the association of PLUs to form clusters. When secondary laddering does occur, the structure of the compound as a whole can often be rationalized by understanding the behaviour of PLUs as they aggregate.



Scheme 1. Homomolecular primary and secondary laddering of E_xM_x; the substituents on E have been omitted for clarity

The hierarchical nomenclature of these principles is intentional; primary laddering processes must occur before secondary, and secondary laddering cannot occur in the absence of primary. Thus, when examining a laddered system the pertinent questions to ask are:

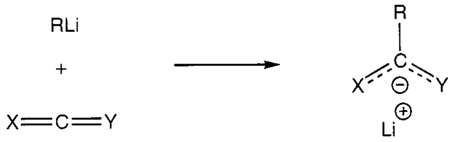
1) Will primary laddering occur?
2) If so, what is the resultant PLU?
3) Will secondary laddering of PLUs occur?
4) If so, what is the resultant structure?

We have found that by answering the four questions above a good conceptual understanding of laddered lithium heterocarboxylate structures can be gained, and we believe that this approach may be applicable to a wider variety of systems. In the cases discussed here the most common PLU is a dimer, as illustrated in Scheme 1. We note, however, that this need not be the case — primary laddering can, in theory, generate trimers, tetramers, etc., as well as dimers, and secondary laddering can occur with any combination of these PLUs. Thus, while the dimer will be given special attention in this account, it is not true that the dimers are the only PLUs of interest.

The idea of primary and secondary units of aggregation is well-established in other areas, most prominently supramolecular chemistry.[9] Indeed, although they are not typically discussed as such, many laddered compounds can be considered as supramolecules.[3a,10] In addition, Snaith's description of a hexamer as two stacked trimers[2a] is one of many examples where a two-stage approach to laddering is used without invoking the terminology suggested here. Thus, the novelty and value of this approach lies not in the concepts of primary and secondary aggregation themselves, but rather in developing an understanding of how this two-stage framework can be *systematically* and *consistently* applied in the specific context of laddering.

3. Two-Stage Laddering in Lithium Heterocarboxylates

Carboxylate anions $[RCO_2]^-$ are ubiquitous ligands, as are a number of other related "heterocarboxylates" $[RCXY]^-$ (X, Y = main group centre, e.g. xanthates $[(RO)CS_2]^-$, thiocarbamates $[(R_2N)COS]^-$, dithiocarboxylates $[RCS_2]^-$, etc.). Such systems can be understood as monomeric units in which a single unit of negative charge is delocalized throughout an XCY unit. While lithium heterocarboxylates are well-known as sources of anionic ligands in metathetical syntheses, we have investigated several lithium amidinates, oxoamidates, and thioamidates as probes to explore a two-stage approach to the laddering principle. Convenient access to these compounds is provided by the reaction between nucleophiles and heteroallenes [X=C=Y] (1). Use of this route to synthesize carboxylic acids from CO_2 is well-known.[11]

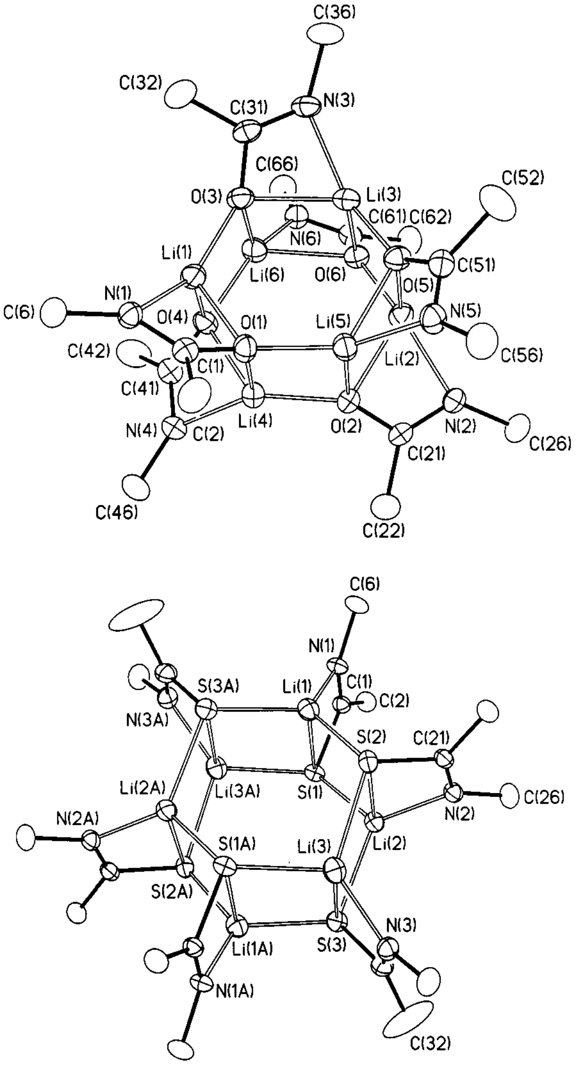


(1)

X = Y = O, carbon dioxide → carboxylate
X = Y = NR', carbodiimide → amidinate
X = NR', Y = O, isocyanate → oxoamidate
X = NR', Y = S, isothiocyanate → thioamidate

3.1. Secondary Laddering of Dimeric Primary Laddered Units

The lithium oxoamidate and thioamidate hexamers $[Li\{(nBu)CE(NtBu)\}]_6$ (**1**: E = O; **2**: E = S)[12,13] provide illustrative examples of secondary laddering employing dimeric PLUs. However, even though both structures clearly involve laddering, comparing the hexameric cores of **1** and **2** (Figure 4) highlights an interesting contrast: the two Li_6E_6 hubs are quite similar even though the ligand orientations are strikingly different.

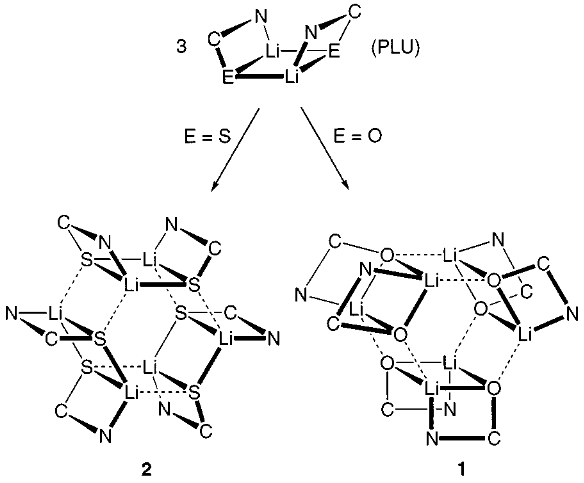


1

2

Figure 4. The cores of $[Li\{(nBu)CE(NtBu)\}]_6$ (**1**: E = O; **2**: E = S)

This phenomenon can be explained by using a two-stage approach to the laddering principle. The formation of both hexamers can be visualized as a secondary laddering (trimerization) of *cisoid*, dimeric PLUs (Scheme 2). In the case of **1**, secondary laddering occurs such that the transannular bonds of the PLU form the Li_3O_3 rings in the hexamer. In **2**, however, the transannular bonds of the PLU become the links between the two Li_3S_3 hexagonal rings of the hexameric unit. Thus, whereas **1** adopts a D_3-symmetric, trilobate conformation in the solid-state, **2** is observed to assume a D_{3d}-symmetric, paddle-wheel like shape.



Scheme 2. Secondary laddering (trimerization) of dimeric, *cisoid* PLUs producing **1** and **2**; the dashed lines indicate bonds being formed

We attribute the difference in conformations for **1** and **2** to a heteroatom-related secondary laddering effect. The shorter Li−O (compared to Li−S) distances result in steric constraints that prevent **1** from adopting the paddle-wheel conformation, which otherwise would be preferred.[12] Some credence is lent to the notion of secondary laddering of dimeric PLUs as a mechanism of assembly for **1** and **2** by the fact that **1** adopts a conformation in which the lobes of the Li_3O_3 rings are eclipsed rather than staggered. While a staggered conformation (Figure 5) would certainly be less sterically hindered, this is not the conformation actually adopted by the hexamer. We speculate that this is because it is not accessible as an aggregate of dimers, and hence cannot be generated by the primary and secondary laddering of such dimers.

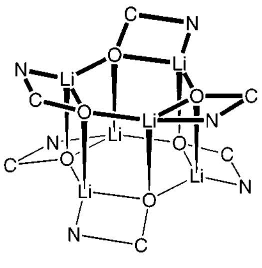
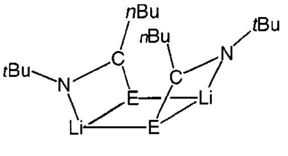
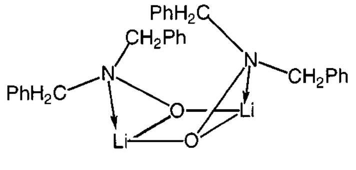


Figure 5. A possible, but unobserved, conformation for the core of $[Li\{(nBu)CO(NtBu)\}]_6$ (**1**)

A different scenario is encountered in the case of the hexameric lithiated hydroxylamine [Li{ON(CHPh)$_2$}]$_6$.[14] The situation here is somewhat similar to the ones discussed above: each lithium cation is chelated by both oxygen and nitrogen, yielding three membered [NOLi] rings. However, in the case of oxoamidates and thioamidates, the geometry at nitrogen is three-coordinate and planar (**A**), while in the lithiated hydroxylamine it is four-coordinate and pyramidal (**B**). This prevents the formation of the *cisoid* dimer **B** on steric grounds.

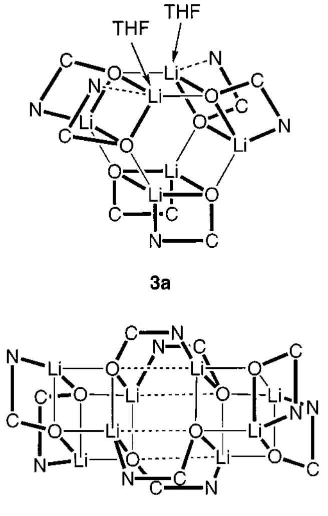


A



B

Interestingly, the architecture adopted by [Li{ON(CHPh)$_2$}]$_6$ is a Li_6O_6 hexagonal prism with staggered N(CHPh)$_2$ lobes. This arrangement probably arises due to the stacking of trimeric rings, thus it is unsurprising that the less sterically demanding staggered conformation is preferred[14] over the eclipsed conformation of **2**. We note that this observation lends support to our hypothesis that **2** forms by the secondary laddering of dimers, since ring stacking should evidently prefer the conformation depicted in Figure 5. We note also that both the solvated and unsolvated forms of the lithium oxoamidate [Li{(C_6H_5)CO(N*i*Pr)}]$_x$·*n*THF (**3a**: $x = 6$, $n = 2$; **3b**: $x = 8$, $n = 0$)[15] can be generated from *cisoid*, dimeric PLUs in a manner similar to that described for **1** and **2** (Figure 6).



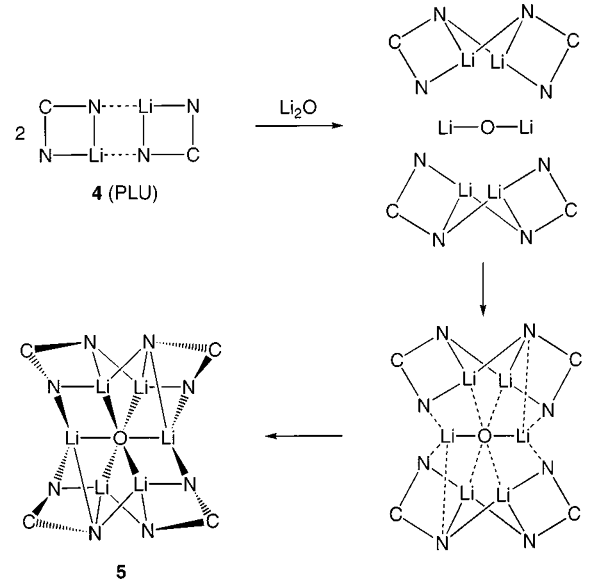
3a

3b

Figure 6. The cores of [Li{(C_6H_5)CO(N*i*Pr)}]$_x$·*n*THF (**3a**: $x = 6$, $n = 2$; **3b**: $x = 8$, $n = 0$) viewed as secondary laddered aggregates of dimeric PLUs

3.2. Heteromolecular Primary and Secondary Laddering

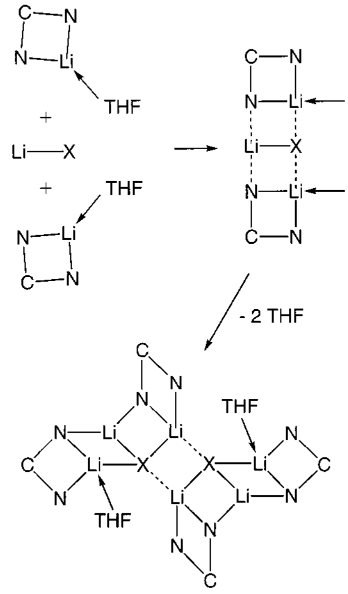
In cases where steric constraints are preclusive, dimeric homomolecular PLUs like those discussed above may be unable to associate further. Thus, while lithium oxo- and thioamidates will readily form dimeric PLUs which then undergo secondary laddering, the same is not true of the lithium amidinate Li[(*n*Bu)C(N*t*Bu)$_2$] (**4**). In this case, other, less hindered laddering units must be employed to promote secondary laddering. For example, the aggregation of **4** with Li_2O in a non-coordinating solvent yields the cluster [Li{(*n*Bu)C(N*t*Bu)$_2$}]$_4$·Li_2O (**5**).[16] In **5**, two Li[(*n*-Bu)C(N*t*Bu)$_2$] monomers associate laterally to give a homomolecular, dimeric PLU. Unlike **1** and **2**, the secondary laddering of these PLUs cannot occur due to steric hindrance. However, in the presence of an unhindered, incipient Li_2O fragment, heteromolecular secondary laddering involving three fragments takes place to give the aggregate **5** (Scheme 3).



Scheme 3. Formation of [Li{(*n*Bu)C(N*t*Bu)$_2$}]$_4$·Li_2O (**5**) by primary and heteromolecular secondary laddering; the dashed lines indicate bonds being formed

The addition of a coordinating solvent to **4** effectively appends a substituent at lithium and causes even greater steric congestion around the monomeric unit. This apparently prevents homomolecular primary laddering. However, the presence of an unhindered fragment suitable for the promotion of primary laddering can alleviate this circumstance. Thus, the addition of LiX (X = OH, Cl, Br) to a solution of **4** in THF generates the laddered complexes [(Li{(*n*Bu)C(N*t*Bu)$_2$})$_2$·LiX·THF]$_2$ (**6a**, X = OH; **6b**, X = Cl; **6c**, X = Br),[6] which arise *via* heteromolecular laddering (Scheme 4). Here two Li[(*n*Bu)C(N*t*Bu)$_2$]·THF monomers and one LiX fragment associate to produce a heteromolecular PLU, which then undergoes secondary laddering (dimerization) with concomitant loss of solvent.

The topologies of **6a−c** are clearly a consequence of the conformation adopted by the PLUs involved. Each three-rung ladder is composed of contiguous *cisoid* and *transoid* units, an arrangement which minimizes the steric congestion and imparts a gentle undulation to the structure as a



Scheme 4. Formation of $[(Li\{(nBu)C(NtBu)_2\})_2{\cdot}LiX{\cdot}THF]_2$ (**6a**, X = OH; **6b**, X = Cl; **6c**, X = Br) by heteromolecular primary and secondary laddering; the dashed lines indicate bonds being formed

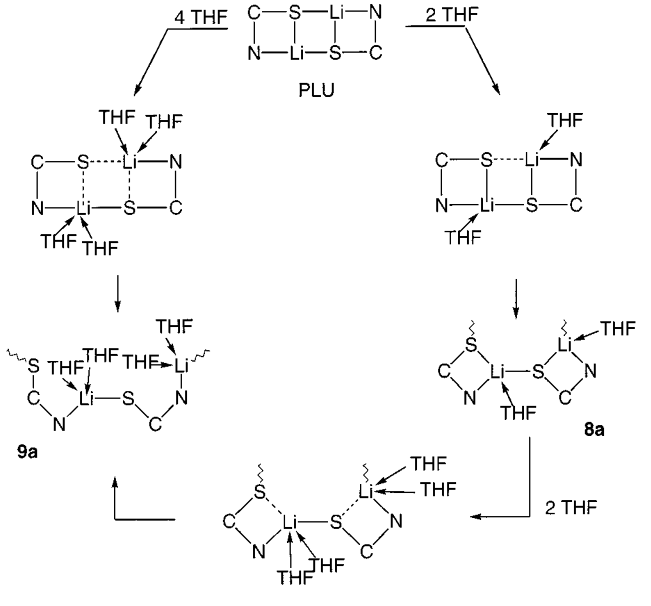
whole. Secondary laddering occurs through a *transoid* $[LiX]_2$ ring. We note that this secondary laddering process does not occur when the added fragment is LiI; in that case the heteromolecular PLU $[(Li\{(nBu)C(NtBu)_2\})_2{\cdot}LiI{\cdot}2THF]$ (**7**) forms and does not associate further, probably due to the relative weakness of Li−I bonds compared to the other lithium halides.[6] Thus, solvation is preferable as a mechanism to disperse charge in this case, and no secondary laddering occurs. We note also that **7** has the same basic topology as the PLUs proposed for **6a**−**c**.

3.3. Unladdered Structures from Primary Laddered Units

The previous examples demonstrated that various PLUs can associate through secondary laddering to produce a range of molecular architectures. However, other aggregation pathways are also possible, some of which lead to unladdered, extended arrays. While it is not immediately clear that such structures should fall in the same category as their laddered counterparts, it would certainly be useful if the laddering principle could explain not only situations where laddering *does* occur, but also situations where laddering could reasonably be expected to occur but *does not*.

For lithium thioamidates at least, this is the case: use of a two-stage approach to laddering is sufficient to explain the formation of unladdered, solvated polymers in addition to the laddered structures discussed above. Originally we reasoned that replacing the bulky butyl groups in **2** by methyl groups might afford alternative secondary laddering routes resulting in higher laddered oligomers. Accordingly, the lithium thioamidates Li[MeCS(NR)] (**8**: R = *t*Bu; **9**: R = Me) were prepared. However, the crystallographic characterization of these species revealed the unladdered, solvated polymers $[Li\{MeCS(NtBu)\}{\cdot}THF]_\infty$ (**8a**) and $[Li\{MeCS(NMe)\}{\cdot}2THF]_\infty$ (**9a**).[13]

Although the connection between structures **8a** and **9a** and the laddering principle is not obvious, both polymeric forms can in fact be derived from a common dimeric PLU, which is then broken down upon solvation by THF (Scheme 5). Significantly, the putative PLUs for **8a** and **9a** are analogous to the one which undergoes secondary laddering (trimerization) to form **2**. The degradation of laddered structures upon solvation is a well-documented phenomenon in the literature, although it is usually used to explain the disassembly of higher states of oligomerization to lower oligomers.[17] Here the opposite occurs, with solvation producing polymers by opening the Li_2S_2 and LiNCS rings of laddered dimers.



Scheme 5. Generation of $[Li\{MeCS(NR)\}{\cdot}xTHF]_\infty$ (**8a**: R = *t*Bu, *x* = 1; **9a**: R = Me, *x* = 2) from a common dimeric PLU; the dashed lines indicate bonds being broken

The polymer **8a** is produced by the solvation of both lithium centres in the dimeric PLU, leading to the rupture of one Li−S bond. The orientation adopted by **9a** is generated either from further solvation, leading to disruption of the exocyclic Li−S bonds, or directly from the dimeric PLU upon solvation of each lithium ion by two THF molecules; thus the three disparate structures **2**, **8a**, and **9a** all stem from the same primary unit. While other descriptions are certainly possible for each structure viewed independently, the use of a two-stage approach to the laddering principle affords a consistent rationale for all three structures despite their substantial differences.

The fact that **2** remains unsolvated in the solid state, even when recrystallized from THF, is of significance. We suggest that this occurs because the steric bulk of the substituents in **2** prevents solvent molecules from entering the coordination sphere of the PLU. This allows an unsolvated, oligomeric structure to form through secondary laddering. In **8a** and **9a**, smaller substituents allow solvation of the PLU; solvation effectively competes with secondary laddering as a mechanism to disperse electronic charge and solvated, unladdered polymers result.

3.4. Other Examples

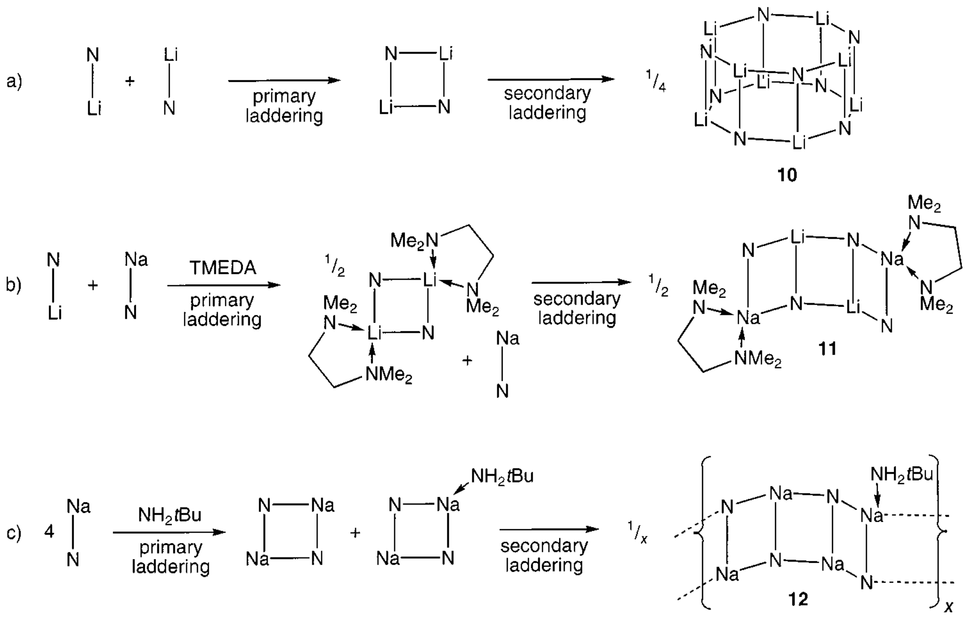
A two-step approach to laddering is also useful for understanding systems other than lithium heterocarboxylates. For example, the lithium arenethiolate $[\{Li[SC_6H_4\{(R)\text{-}CH(Me)NMe_2\}\text{-}2]\}]_6$ forms a hexamer[18] composed of three dimeric PLUs assembled in much the same manner as **2**. Likewise the laddered polymer $[PhCH_2SLi{\cdot}NC_6H_5]_\infty$ can be viewed as resulting from the secondary association of monosolvated dimers.[19]

An illustrative series of examples from alkali metal amide chemistry is provided by the lithium,[20] sodium,[5] and heterobimetallic lithium/sodium[5] derivatives of *tert*-butyl amide,[3e] all of which can be rationalized through primary and secondary laddering processes (Scheme 6). The unsolvated octamer $[Li(HN\mathit{t}Bu)]_8$ (**10**) can be viewed as a secondary aggregate of dimeric, *cisoid*, homomolecular PLUs forming a closed ladder. Primary laddering in the mixed system $[LiNa(HN\mathit{t}Bu)_2{\cdot}TMEDA]_2$ (**11**) probably forms a solvated, dimeric $[Li_2N_2]$ PLU initially, which then loses solvent upon secondary laddering with Na−N units. The final aggregate is thus centred around a *cisoid* $[Li_2N_2]$ ring, and further laddering is prevented by solvation of the outer Na−N rungs. In contrast, the solvated polymer $[\{Na(HN\mathit{t}Bu)\}_3{\cdot}NH_2\mathit{t}Bu]_\infty$ (**12**) arises from the unhindered secondary laddering of solvated and unsolvated dimeric PLUs. As in **10** the PLUs are all *cisoid*, but secondary laddering in **12** involving the solvated Na−N unit produces a *transoid* $[NaN]_2$ ring, probably due to the "steric intrusion"[5] of the solvent molecule.

Clearly, alternative descriptions are possible for each of the systems discussed here. For example, **10** could be viewed as an arrangement of eight monomers or two stacked tetramers rather than four laddered dimers. However, as was the case for the lithium heterocarboxylate structures discussed earlier, a two-stage approach to the laddering principle allows a diverse range of architectures to be understood using a single conceptual framework. While we feel that this is an important point in favour of using the two-stage approach consistently, we note that is not sufficient for every case, such as, for example, structures arising from the stacking of M_nE_n ($n > 2$) rings[14] as well as odd-numbered and/or asymmetric oligomers.[17g] Such cases are in the minority, however, and can generally be handled by using a similar two-stage approach wherein building blocks may be unladdered and further aggregation steps (tertiary, etc.) may need to be invoked. We have seen this in our own work, for example the lithium diazasulfite hexamers $[Li_2\{SO(N\mathit{t}Bu)(NR)\}]_6$ (R = *t*Bu, $SiMe_3$), derived from the aggregation of three hexagonal prisms through Li_2O_2 faces (R = *t*Bu), or the dimerization of eighteen-atom cages through Li_3O_3 faces (R = $SiMe_3$).[21]

4. Polymeric Laddered Compounds

It has been accepted for some time that organolithium species that precipitate as insoluble, amorphous solids (i.e. do not crystallize easily) are probably laddered polymers. While confirmation of this hypothesis has long been anticipated for lithium amides in particular, few "unsolvated," polymeric ladder structures have been characterized to date, and in each of these cases some form of internal solvation is present. For example, 2,3,4,5-tetramethyl-1-sodiopyrrole[22]



Scheme 6. Primary and secondary laddering processes leading to: a) $[Li\{HN\mathit{t}Bu\}]_8$ (**10**); b) $[LiNa(HN\mathit{t}Bu)_2{\cdot}TMEDA]_2$ (**11**); c) $[\{Na(HN\mathit{t}Bu)\}_3{\cdot}NH_2\mathit{t}Bu]_\infty$ (**12**)

and phenyllithium[23] both form ladder polymers wherein the lithium cations are coordinated by the aromatic substituents on neighbouring rungs. Likewise, monolithiated ethylenediamine $[Li\{HN(CH_2)_2NH_2\}]_\infty$ [8] consists of an infinite ladder wherein each lithium cation is chelated by both the amide and amine ends of the molecule. In fact, although a few truly unsolvated, laddered lithium amides are now known,[17b,20] none have proven to be polymeric. Conversely, although some alkali metal amide polymers have been characterized (notably $[LiN(iPr)_2]_\infty$ [24]), none have been found that are both laddered and unsolvated.

A recent survey[10] tallied only two examples of unsolvated organolithium polymers involving any laddered portions, $[LiOPh]_\infty$ [25] and $[LiC(OEt){=}CH_2)]_\infty$,[26] among several solvated examples and several unsolvated, finite ladders. This demonstrates two important points: 1) that solvation does not preclude polymerization, and may even encourage it in some cases (e.g. **8a** and **9a**); and 2) that unsolvated laddered compounds, whether polymeric or not, can indeed be crystallized (i.e. they are not necessarily amorphous solids). With these observations in mind, we note that the two-stage framework presented here leaves room, and provides rationale, for a number of alternative architectures; it does not point exclusively to laddered polymers for any particular class of compounds. Given the wide diversity of laddered structures now known, we feel that this is a point in favour of this approach.

5. Conclusions and Outlook

We have tried to show briefly how a two-stage approach to the laddering principle provides a useful framework for describing and understanding laddered structures, particularly among lithium heterocarboxylates. We note also an initially unanticipated feature of this approach: it can explain unladdered systems topologically related to laddered ones. Thus, as with the lithium thioamidates **2**, **8**, and **9**, widely disparate structures can be understood in terms of a single conceptual process. Furthermore, we have shown that the nature of secondary laddered structures is strongly dependent on the behaviour of PLUs with regard to steric effects, solvation, etc. This is true for both homo- and heteromolecular aggregation. While these influences on laddering processes have been noted previously,[3] the two-stage approach discussed here affords a consistent and systematic method of gauging their effect on structure.

Finally, we anticipate that the continued development of the laddering principle may have implications outside the realm of main-group element chemistry. Recently we have seen that a process much like primary and secondary laddering (involving dimeric PLUs) can be used to explain the formation of copper(I) thioamidate oligomers.[27] Although not strictly within the rubric of laddering as defined here, the behaviour of these derivatives can evidently be understood in a similar manner. A complete investigation of this phenomenon is currently underway, and may prove germane to developing a more generally applicable laddering principle.

Acknowledgments

We thank the NSERC (Canada) for financial support and the University of Calgary for a Silver Anniversary Fellowship (A. D.).

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Received February 15, 2001
[I01059]