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Recent developments in the synthetic and structural chemistry of lithium zincates

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The usefulness of lithium tri- and tetraorganozincates in chemical transformations is discussed in the context of their structures, the regiospecificity with which they effect reactions and the manner in which these differ to those resulting from the use of either homometallic reagents or of other 'ate compounds. Discussion focuses on their structural properties in solution, in the solid state, and in the gas phase by theoretical routes. The systematic reaction of lithium zincates with oxygen is considered and the question of whether certain lithium zincates should be represented instead as organolithium-organozinc co-complexes is addressed.

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Introduction

Organometallic and metallo-organic reagents that exhibit Lewis acidity by virtue of having a vacant orbital on their metal component are particularly susceptible to nucleophilic attack by alkali metal substrates and, as such, are ideally suited to the formation of so called "'ate complexes" whereby the acidic metal is usually, though not invariably, coordinatively saturated. Species formed in this way have been of particular interest to a range of synthetic chemists for some years now because they contain (at least) two types of metal ions and consequently exhibit structures and reactivities that differ from those of their homometallic precursors.[1,2] In this framework, among the most commonly employed alkali-metal-containing 'ate complexes are those of groups 12 and 13 in general and lithium aluminates in particular.[3] The present article will concentrate, however, on the most frequently utilized group 12 species of this type—lithium zincates. These compounds have formed the basis of recent reviews in both synthetic[4–7] and structural[3] veins and the aim of the present article is twofold. Firstly, it seeks to update the field of lithium zincate chemistry in general, and in so doing it will concentrate on work reported from 1998 onwards. Secondly, it will comprehensively discuss the studies into lithium zincate synthesis, manipulation and reactivity going on in our own group. In both cases the chemistry will be discussed *vis-à-vis* possible future applications in synthetic, materials and structural fields.

The article is divided into two sections: the first deals with the preparation and synthetic applications of alkali metal zincates, while the second discusses their structural properties and is itself subdivided with solution, solid state and gas phase (theoretical) investigations being presented in that order.

Dr Andrew Wheatley graduated from the University of Kent at Canterbury and did his PhD (University of Cambridge, 1995–1998) for the late Dr Ron Snaith after which he became a Research Fellow at Gonville & Caius College (1998–2002). In 1999 he was awarded the Harrison Memorial Medal by the Royal Society of Chemistry and in 2000 he was made a University Assistant Lecturer at Cambridge. In 2002 he became a Fellow of Fitzwilliam College and he was made University Lecturer in 2003. He has published extensively in the field of main group organometallic chemistry. He specializes in the elucidation of organolithium reaction intermediates and the development of alkali metal 'ate complexes and main group metal interstitial hydrides.

1 Preparations and synthetic applications

Lithium zincates can adopt two possible formulations—R_3ZnLi and R_4ZnLi_2. The generation and use of the first of these has been the subject of a recent review, with their ability to perform conjugate additions across α,β-unsaturated ketones, to react with aryl halides (halogen-zinc exchange) or with 1,1-dihalocyclopropyls (to give 1-halocyclopropylzincates capable of undergoing invertive 1,2-alkyl migration), to make allenes and α,γ-disubstituted propargylic species from propargylic substrates all having been reported.[3,4] Furthermore, the synthetic usefulness of dilithium tetraorganozincates has begun to be explored in recent years.[8] Under their influence reduction,[9] intermolecular epoxide ring-opening, halogen- and tellurium-zinc exchange, and intramolecular Michael addition, carbozincation and epoxide ring-opening processes have all been enabled.[10]

Both the nucleophilic and basic properties of zincates have been further developed over the last five years. The steric and electronic factors governing the interaction of trialkylzincates with ketones have been probed and it has been determined that the rate at which Et_3ZnLi adds to acetophenone is slowed significantly by α and orthomethyl substituents thereon, such that the relative rates of addition to acetophenone, *o*-methylacetophenone, and *tert*-butyl phenyl ketone are 1.00, 0.012, and 0.003.[11] The use of zincates as highly

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chemoselective substrates in the directed metallation of aromatic rings has seen recent developments in the context of deprotonative zincation leading to the preparation of functionalized benzyne intermediates. Reaction of tmpLi (tmp = tetramethylpiperidide) with Bu^t_2Zn has been suggested (by NMR spectroscopy) to yield a stable zincate of the type $Bu^t_2Zn(tmp)Li$ **1**, the introduction of which to various benzoates, benzamides and benzonitrile has yielded ortho-substituted derivatives upon electrophilic work-up.[12,13] Interestingly, this study has also been extended to the selective substitution of pyridines. This is worthwhile because it is an established fact that bromopyridinyllithium reaction intermediates tend to be unstable. Pyridyne formation[14] and lithium migration[15] create synthetic issues and may in large part be responsible for the complete absence of structural data on 2-lithiated pyridines.[16] Whereas the sequential reaction of 2-bromopyridine with **1** and I_2 yields 2-bromo-6-iodopyridine, employment of the alternative base $Bu^t_2Zn(da)Li$ **2** (formed by the use of lithium diisopropylamide, lda, in place of tmpLi) gives the 3-iodo analogue. In a similar vein, 3-bromopyridine is converted to the 2-iodo derivative by $\mathbf{1}/I_2$ and its 4-iodo congener by $\mathbf{2}/I_2$.[17]

2 Structural properties

2.1 Solution studies

It has been known for some time that the exchange of ^7Li between aggregates of MeLi and Me_4ZnLi_2 **3** is rapid relative to dissociation of the methyllithium tetramer to the more reactive dimer.[18] More recently, ligand-reagent complexes capable of effecting the stereoselective alkylation of carbonyl groups have been studied, with a combination of ^6Li NMR spectroscopy and $^1H,^1H$ NOESY, revealing that the stereospecifically catalysed asymmetric alkylation of simple aldehydes proceeds *via* the reorganization of the boat conformer of a lithium piperazide-dialkylzinc adduct **4**[19] to the chair form on application of the carbonyl substrate.[20]

So-called "highly coordinated" heteroleptic organozincates have been probed by a combination of Raman spectroscopy, EXAFS (see below) and NMR spectroscopy. Data suggest the existence of a Zn–R bond in the zincate Me_3ZnRLi_2 (R = CN **5**, SCN **6**), with highfield ^1H NMR signals indicating the presence of a Zn-centred dianion.[9,10,21]

2.2 Solid-state studies

Given the synthetic utility of lithium zincates, it is surprising that their structural properties have not been better elucidated. This can, however, be largely attributed to the oxophilicity of zinc-carbon bonds—an issue first commented on by Frankland and one which has plagued chemists ever since![22] While it is many years since peroxides were suggested to form by the oxygenation of diethylzinc,[22] it is only much more recently that evidence has been presented for the operation of a free radical (S_H2) mechanism in such a system.[23] Indeed, 2003 saw the first structural authentication of a zinc alkyl peroxide.[24] In spite of these difficulties, it is some time since the first full characterization of a lithium zincate—that of polymeric dilithium tetramethylzincate **7**.[25] However, more common in recent years have been crystallographic investigations of lithium triorganozincates, be they ion-separated (as often results from the presence of strongly coordinating Lewis bases) or ion-associated. The structural properties of many of these species were the subject of review in 2001.[3] More recently, 2,2,6,6-tetramethyl-1-piperidine oxide (tmpo) has been found to exhibit a variety of coordination modes towards lithium, sodium and magnesium. Whereas the nitroxide ligands can act as mono-anions, they may also adopt radical behaviour, and this is demonstrated by the ion-separated zincate $[(hmds)_3Zn]^-$ $(Li{\cdot}4tmpo)^+$ **8** (hmds = hexamethyldisilamide).[26] The lack of a sterically restrictive Lewis base, combined with the presence of an accessible, electron-rich zincate anion facilitates ion-pairing. A case in point is represented by the ability of nitrogen to bridge between group 1 and group 12 ions in $hmds(Me_3SiCH_2)_2ZnLi{\cdot}[(MeN)_3(CH)_3]$ **9**[27]—a species with a structure of a type to which we shall return. A related motif has been noted previously wherein oxygen linked the two metal centres.[3] However, more recently, this structure type has manifested itself in the non-trivial cluster $(MeCN)Cl(\mu_3,\eta^2\text{-ddbfo})_2(\mu,\eta^2\text{-ddbfo})_3ZnLi_4$ **10** (ddbfo = 2,3-dihydro-2,2-dimethyl-7-benzofuranoxide), which is based on an irregular array of edge-fused metallocycles in the solid state.[28] As part of a study into the interaction of 2-arsa-1,3-dionatolithium complexes with metal halides, mono-halide bridges between lithium and zinc have been noted in $\{As[C(O)Bu^t]_2\}_2Zn[(\mu\text{-Cl})Li{\cdot}dme]_2$ **11** (dme = dimethoxyethane).[29] Monobridged motifs are also possible in the absence of a heteroatom, and in fact the $Zn(\mu\text{-C})Li$ unit is common in ion-bonded lithium zincate chemistry.[3] Moreover, it is only fairly recently that investigations into the oxygen-scavenging properties of mixed group 1/group 2 systems[30,31,32] have been extended to incorporate the synthesis and X-ray structural characterization of $[(hmds)_2ZnMeLi]_\infty$ **12**, in which polymerization results from the ability of Zn-bonded methyl groups to bridge between the two metal types.[33] Moving to dibridged systems, N- and O-link motifs have been observed once more. Hence, the heterocubane $(Me_3PNZnBr)_4$ has been treated with $NCCH_2Li$ to yield the $Zn(\mu\text{-N})_2Li$ based phosphoraneiminate complex $[(Me_3PN)_4Zn_3(CH_2CN)_3LiBr]Li{\cdot}thf$ **13**.[34] Methyllithium has been reacted with dimethylzinc and $RSi(OH)_3$ (R = 2,6-$Pr^i_2C_6H_3NSiMe_3$) in *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (tmpda) to give the soluble zinc silicate $(RSiO_3ZnLi{\cdot}tmpda)_4$ **14**, the core of which is defined by a $Si_4O_{12}Zn_4Li_4$ polyhedron.[35] Examples have been published recently in which double halide bridges between metal centres yield four-membered ZnX_2Li rings; $(dipp)nacnacZn(\mu\text{-X})_2Li{\cdot}2OEt_2$ {dipp = 2,6-diisopropylphenyl; nacnacH = 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]pent-2-ene; X = Cl **15**,[36] I **16**[37]} has been prepared by the simple combination of X_2Zn with lithium vinamidide. A single example has lately been reported in which it can be argued that ion-association has occurred, but with the two metal centres significantly distant. Hence, the triimidosulfonate $MeS(=NBu^t)_2N(Bu^t)ZnMe_2Li{\cdot}2thf$ **17** reveals a monomer in the solid state.[38] As we shall see later, this structure, when taken with some of our own recent work, suggests that the question of whether mixed metal Zn–Li systems should be regarded as 'ate complexes or as adducts is not yet solved. The research going on in our own group has dealt mostly with the preparation and reaction of lithium triorganozincates, both in ion-separated and ion-associated contexts, and the next section deals with the first of these.

2.2.1 Ion-separated lithium zincates. The recent development of a new type of alkali metal 'ate chemistry has been reported by ourselves. The reaction of *N*-2-pyridylaniline with Me_3Al has been noted to yield dimethylaluminium(*N*-2-pyridylanilide) **18**.[39] This has then been treated with Bu^tLi to give species that X-ray crystallography suggests to be the cluster complexes $[(Bu^t_2AlMe_2)_2Li]^-\{[Ph(2\text{-}C_5H_4N)N]_6Li_8H\}^+$ **19** (isolable from toluene) and $[Ph(2\text{-}C_5H_4N)N]_6Li_7H$ **20** (from thf–toluene).[40,41] The only relatives of these main group metal compounds, proposed to incorporate interstitial hydride, are the hydride/*tert*-butoxide $(Bu^tO)_{16}Li_{33}H_{17}$ **21**[42] and the heterobimetallic species $[(Pr^i_2N)_2MgM(\mu\text{-H}){\cdot}PhMe]_2$ (M = Na **22**,[43] K **23**[44]) and $[(Bu^tCH_2O)_5Al_3H_5]Li{\cdot}OEt_2$ **24**.[45] These notwithstanding, the field is dominated by transition metal compounds.[46] Lately, a succession of complexes related to **19** and **20** have been characterized in the solid state.[47] Salient to

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the current article are attempts to achieve related hydride-encapsulation using Me_2Zn in place of Me_3Al. In the first instance, this has involved the straightforward transplantation of the group 12 organometallic substrate for its group 13 analogue. This, however, whilst yielding hydride-incorporating species has—presumably for reasons of organozincate stability—only resulted in the isolation of homometallic **20**.[47] We are presently in the course of establishing the generality with which neutral clusters of the type $\{R(2\text{-}C_5H_4N)N\}_6Li_7H$ (*cf.* **20**) form, with the employment of Me_2Zn/thf apparently being crucial.[47] However, the preparation of a lithium zincate hydride-encapsulation complex has recently been achieved by utilizing the bicyclic guanidine reagent 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH) in place of the aniline. Rather than giving the simple methylzinc(guanidinate) Me(hpp)Zn **25**, Me_2Zn reacts with hppH in toluene to yield non-trivial, chiral $Me_2(hpp)_4Zn_3$ **26** in which a molecule of $(hpp)_2Zn$ bridges two Me(hpp)Zn moieties.[48] NOESY suggests that **26** retains its trinuclear structure in hydrocarbon solution,[47] while its treatment with Bu^tLi gives an oil from which crystals deposit that ^1H NMR spectroscopy suggests contain $[hpp]^-$ and $[Bu^t]^-$ in a 2:1 ratio. X-Ray crystallography reveals this product to be $[Bu^t_2Zn]^-[(hpp)_6Li_8H]^+$ **27** (Fig. 1).[49]

The anionic tris(*tert*-butyl)zincate ion in **27** incorporates an essentially trigonal planar metal centre that in no way interacts with the $[(hpp)_6Li_8H]^+$ cluster. As with our previously described lithium aluminate analogues,[40,47] an analysis of the Fourier difference map allows tentative location of the hydride. Contrary to previous examples of hydride-encapsulating alkali metal dications,[41,47] the metallic framework in this last component of **27** is almost exactly cubic with a non-bonding Li···Li range of 2.473(14)–2.527(14) Å, suggesting μ_8-coordination of the hydride (*cf.* octahedral coordination in **19** with the extrusion of two metal centres from the cluster core). In the same way as for previous analogues, each face of the metal cube is straddled by a $[hpp]^-$ ligand and it would appear to be the symmetry demonstrated by each of these that is responsible for the regular μ_8-coordination state of the interstitial anion and which, in turn, causes the mean Li–H bonding distance (2.16 Å) to be extended relative to those in both **19** and **20** (mean: 2.015 and 2.06 Å, respectively) and also that of 2.04 Å reported in octahedral $(LiH)_\infty$.[50] The isolation and characterization of zincate **27** is rendered more interesting still by reaction of the dimethylaluminium(guanidinate) $Me_2(hpp)Al$ **28**[51] with Bu^tLi to give not a hydride-encapsulating analogue of **27**, but instead the ion-separated lithium aluminate $\{[(Bu^t_2AlMe_2)_2Li]^-\}_2[(hpp)_6Li_8]^{2+}$ **29** (Fig. 1 and Scheme 1). In the same way as for **27**, the cation incorporates an alkali metal array that is nearly cubic and each face of which is straddled by $[hpp]^-$. In this last cluster the inter-metal cube

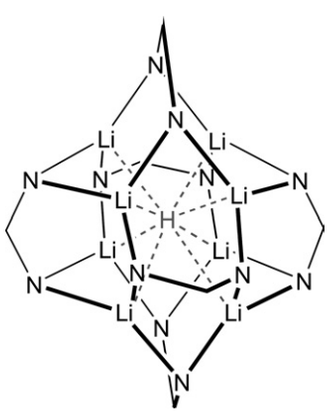
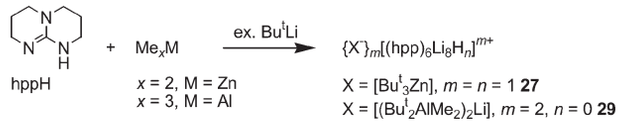


Fig. 1 Cationic component of **27** and **29** with the interstitial hydride present only in **27** shown in grey.



Scheme 1

edges are extended relative to those in **27** [Li···Li range: 2.473(14)–2.527(14) Å in **27**, 2.751(7)–2.795(7) Å in **29**] and, to compensate, the Li–N distances in **29** are shorter than those in **27**. These geometrical parameters are consistent with the absence of interstitial hydride in **29**—that is, this species incorporates the dication cluster "parent" of the hydride-encapsulating monocations noted in, for example, **19** and **27**. This observation—that main group metal polyhedra are capable of encapsulating *either* hydride *or* a vacant interstitial site—suggests that the dynamic inclusion and extrusion of H^- from such arrays may be viable and so holds out the possibility of these clusters acting as hydride (or, in the presence of H^+, hydrogen) sources. Studies into the ability of these systems to evolve hydride/hydrogen are proceeding.

2.2.2 Ion-bonded lithium zincates. It is a consistent feature of previous studies into ion-associated lithium zincates that the structural core utilizes both metal types.[3] In this context our recent work on the preparation of lithium zincate complexes that feature carboxylic amide ligands has afforded new types of alkali-metal-centred products. Such species are prepared firstly by reacting Me_2Zn with a secondary carboxylic amide, PhC(O)N(R)H (R = Me, Pr^i, Ph), to give both N- and O-stabilized PhC(O)N(R)ZnMe (R = Me **30**, Pr*i* **31**, Ph **32**)—themselves species of a type not hitherto fully characterized in organozinc chemistry.[52] Hence, while neutral carboxylic amides have externally stabilized (for example) zinc halides,[53] structures akin to those of **30**–**32** have previously only been inferred.[54] Extensive early work by Coates and coworkers dealt with structure, bonding and aggregation in a variety of divalent zinc species—alkoxy-, thio- and amino-derivatives of methylzinc, their solvates and their reactivities with acetoxime, phenylisocyanate and benzophenone all having been extensively probed.[54] In a similar vein, Noltes and Boersma have published a study on dimers based on the formulation RC(O)N(R)ZnR and their demonstration of azaenolate character.[55] However, previous examples of structurally authenticated N-zincated carboxylic amides have all been monomers in the solid state, with the metal being N- but not O-stabilized.[56]

Both **30** and **31** react with Bu^tLi to give complexes of formulation $PhC(O)N(R)Zn(Bu^t)_2Li{\cdot}2thf$ (R = Me **33**, Pr^i **34**). These species dimerize in the solid state and so yield a core $(LiO)_2$ ring that uses the carboxylic amide O-centres. Azaenolate contribution to ligand structure affords *E*-configured organic residues, implying that previous observations of *cis*-geometry in 'ate complexes had their origins in electrostatic stabilization of the alkali metal centres.[57] While our own previously reported lithium aluminate $[PhC(O)N(Ph)Al(Bu^t)Me_2Li]_2$ **35** is *Z*-configured, azaenolate characteristics therein nonetheless compare closely with those seen in **33** and **34**. Average Zn–N distances of 2.089 (**33**) and 2.184(4) (**34**) Å, with mean C–Zn–C angles of 136.89° (**33**) and 132.29(16)° (**34**) are of interest since, to the best of our knowledge, no other Bu^t_2Zn containing systems have been fully characterized. Significant geometrical variations, particularly in Zn–N distances, suggest a lack of uniformity in the manner and strength of interactions between the dialkylzinc and organolithium components of these triorganozincates—an issue of potential importance to synthetic chemists[12,13] and one to which we shall return.

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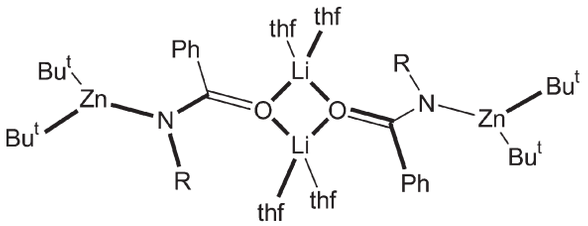
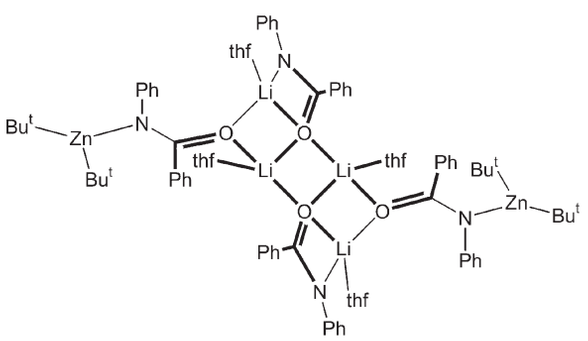


R = Me **33**, Pr^i **34**

Unlike **30** and **31**, PhC(O)N(Ph)ZnMe **32** reacts with Bu^{t}Li in a more complicated manner to give a dimer (by X-ray crystallography) based on the dinuclear formulation [PhC(O)N(Ph)Li·thf]·[PhC(O)N(Ph)Zn(Bu^t)$_2$Li·thf] **36**. Rather than featuring an isolated $(LiO)_2$ cyclic core (*cf.* **33** and **34**), **36** is based on three edge-fused rings in a boat-shaped conformation (Fig. 2), peripheral to which four thf molecules and two types of anionic ligands are coordinated. Two formally N-lithiated carboxylic amide anions use their charge centres to close 4-membered OCNLi rings. Once again, it is evidently the necessity for alkali metal stabilization that imposes N-coordination on the core metal centres and leads to the *Z*-configuration of the ligands. The second class of anions comprises zincate ions whose O-centres bridge the two types of Li^+ centres present. A combination of *E*-isomerism and coordination of the Bu$^t_2$Zn moiety prevents their N-centres from replicating the coordinative behaviour noted for the N-lithiated carboxylic amide moieties. Finally, **36** reveals a mean Zn–N distance that, at 2.161 Å, is intermediate between those observed for **33** and **34**, and a C–Zn–C angle (mean 140.85°) that is larger than those in either of these species. Overall, it is clear that Zn–N interactions in **33**, **34** and **36** [range 2.078(3)–2.184(4) Å] are significantly extended relative to those in **30**–**32** [range 2.010(4)–2.050(3) Å].



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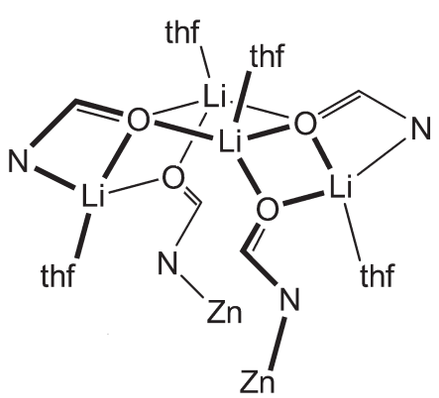

Fig. 2 The boat-shaped core of **36**.

The occurrence of Bu$^t_2$Zn moieties in **33**, **34** and **36**, and the *in situ* formation of Bu$^t_2$Zn in general, is of particular interest in light of the recent synthetic utilization of this species.[12] It also, of course, raises questions about the mechanism that operates in the present systems. The observation that **30**–**32** react with Bu^{t}Li to give PhC(O)N(R)Zn(Bu^t)$_2$Li·*n*thf rather than PhC(O)N(R)Zn(Bu^t)MeLi·*n*thf indicates the non-trivial attack of Bu^{t}Li and contrasts with our previous data on the reaction of Bu^{t}Li with related aluminium species.[58] The retention of Zn–C bonds characteristic of the substrate can, however, be achieved by the straightforward 1:1:1 reaction of PhC(O)N(R)H, Bu^{t}Li and R′$_2$Zn *in this order*. The deprotonation of PhC(O)N(R)H can be followed by treatment with Me_2Zn to yield products of the type PhC(O)N(R)ZnMe$_2$-Li·2thf (R = Me **37**, Ph **38**) or with Et_2Zn to give PhC(O)N(R)ZnEt$_2$Li·2thf (R = Pr^i **39**, Ph **40**). The structure of co-complex **36** implies the evolution of two equivalents of dialkylzinc from an as yet hypothetical tetrameric zincate precursor—a view reinforced by the observation that upon isolation from the mother liquor, **37** fumes in an inert atmosphere. While this phenomenon has prevented a full characterization of **37**, the employment of PhC(O)N(Ph)H affords the more stable crystalline product PhC(O)N(Ph)ZnMe$_2$Li·2thf **38**. In the solid state it is a dimer isostructural with those noted for **33** and **34**. The Zn–N bonds (mean 2.140 Å) lie in the range described by those in **33**, **34** and **36**. That they are relatively long for such interactions[52] is, again, suggestive of at least some instability towards Me_2Zn evolution. In the same way, the C–Zn–C angle in **38** implies a labile zinc-nitrogen interaction. At 145.06° it is significantly greater than that of 131.64(13)° noted recently in **17** [wherein Zn–N = 2.1374(17) Å].[38] Similarly, an affinity for Et_2Zn emission is implied by the geometric parameters in **39** and **40**. Hence, for example, **39** registers mean Zn–N bonds and mean C–Zn–C angles of 2.142 Å and 141.45°, respectively.

The synthesis and isolation of **37**–**40** can be taken, in conjunction with the observed instability of the first of these complexes with respect to the evident emission of Me_2Zn and the inclusion of PhC(O)NLi moieties in **36**, to suggest the lability of zinc-nitrogen bonds in these systems. However, there is no clear correlation between variations in Zn–N distance and the size of the C–Zn–C angle. Nevertheless, the general observation of long Zn–N distances (*cf.* those in **30**–**32**) and severely distorted trigonal geometry at zinc in **33**, **34**, **36** and **38**–**40** makes the issue of whether to treat these systems as lithium triorganozincates or as co-complexes of homometallic organolithium and (weakly coordinating) organozinc moieties a very real one. In essence, therefore, these data suggest the intriguing possibility that a Lewis acid (R′$_2$Zn) can act as a solvent to deaggregate a lithiated organic {in this case one of the type [PhC(O)N(R)Li·2thf]$_n$} by coordinating the *negative charge centre*. This is quite the reverse of normal solvation behaviour in organolithium chemistry where, of course, Lewis *bases* are generally employed to stabilize the positively charged metal ions. That **39** has a dimeric solid-state structure is of particular importance because the carboxylic amide PhC(O)N(Pr^i)H is one of only a very few such reagents to have undergone N-lithiation in tandem with a full structural characterization. Accordingly, it has been reported that an octameric lithiate is isolable from toluene[59] but that it undergoes deaggregation only to a hexamer in the presence of *excess* thf.[60] The implication of our own observation of dimeric **39** is that the presence of thf alone cannot explain the aggregation state. It seems that Et_2Zn is acting as a Lewis acid solvent at the formally negatively charged N-centre of the deprotonated substrate and that it participates in the formation of a labile Zn–N bond, with its presence obviating the requirement for hexameric aggregation (*cf.* ref. 60) (Scheme 2).

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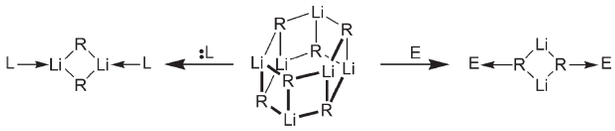
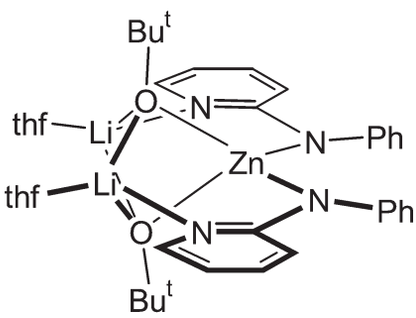


Scheme 2 Organolithium aggregates might be complexed at Li^+ by Lewis bases (:L) or at R^- by Lewis acids (E).

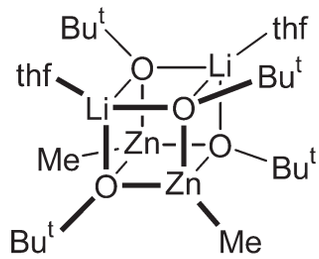
Remaining with ion-associated lithium zincates but moving now to those that incorporate formally bifunctional organic ligands, we have recently reacted Me_2Zn with a variety of *N*-2-pyridylamines, R(2-C_5H_4N)NH [R = Ph, 3,5-Xy (= 3,5-xylyl), 2,6-Xy], thence with isomers of BuLi in attempts to generate species of the type [R(2-C_5H_4N)N]$_2$ZnBuLi and, thereafter, with either dry air or molecular oxygen in order to probe whether oxygenation processes are templated in the same manner as we have recently established to be the case for certain lithium aluminates.[39,58,61] Initial results were not promising; they suggested that reaction was less controlled and more erratic than was found to be the case for group 13 systems. By way of an example, Ph(2-C_5H_4N)NH gives two isolable oxygenated products upon recrystallization from thf; the dimeric {[Ph(2-C_5H_4N)N]$_2$ZnOMeLi·thf}$_2$ **41** (which is structurally analogous to **53**, Scheme 3, below) and trigonal [Ph(2-C_5H_4N)N]$_2$Zn[(μ_3-O)Bu^t]$_2$(Li·thf)$_2$ **42**.[62] In the solid state, **41** reveals a structure that demonstrates the facility with which Zn–C interactions can undergo oxo-insertion. It has a core $(ZnO)_2$ ring in which each zinc is tetrahedral—oxygen having empirically reacted with {[Ph(2-C_5H_4N)N]$_2$ZnMe}$^-$. The group 1 centres lie exocyclic to the core, each one interacting with one methoxy O-centre and with two pyridyl N-centres.



42

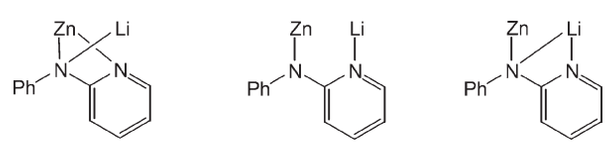
A complicated reaction mechanism involving the formation of by-products is suggested by the observation of a trace [OBu^t]$^-$ signal in the ^{1}H NMR spectrum of an isolated sample of **41**, and it transpires that its synthesis is concomitant with that of **42**. In the solid state **42** reveals a trigonal $ZnLi_2$ core, each heterometallic edge of which is spanned by an *N*-2-pyridylamide ligand and the face of which is doubly μ_3-capped by *in situ* generated [OBu^t]$^-$ ions. However, in spite of the known propensities of organolithium compounds for affording peroxide intermediates on exposure to oxygen,[63] the inter-oxygen distance [2.530(2) Å] in **42** fails to suggest the presence of a peroxide moiety here. Empirically, the distortion of a dimer of Bu^{t}OLi has occurred in tandem with the coordinative saturation of a zinc diamide molecule, meaning that **42** is best considered to represent a 1:2 [Ph(2-C_5H_4N)N]$_2$Zn:Bu^{t}OLi adduct.

Complex **43** (structurally analogous to **41**) results from the employment of 3,5-Xy(2-C_5H_4N)NH in place of Ph(2-C_5H_4N)-NH, while more sterically congested 2,6-Xy(2-C_5H_4N)NH originally yielded a significantly different post-oxygenation product, the composition and structure of which may be of importance in comprehending the mechanisms active in oxygen-capture processes inherent to systems of this type. X-Ray diffraction reveals that the systematic oxygenation of this reaction mixture gives dimeric [MeZn(OBu^t)$_2$Li·thf]$_2$ **44**. Based on an $O_4Zn_2Li_2$ pseudo-cubic core, it is notable for the retention of labile Zn–Me groups and the asymmetric *tert*-butoxy capping of both $ZnLi_2$ and Zn_2Li triangulated fragments akin to those noted in compounds **41**–**43**. Interestingly however, and very recently, we have established a link between the oxygen-capture chemistry that affords dimeric **41** and **43**, trigonal **42**, and dimeric **44**. This comes in the form of the oxygenation of a 2:1:1 mixture of 2,6-Xy(2-C_5H_4N)NH, Me_2Zn and Bu^{t}Li and the subsequent isolation and full characterization of trigonal [2,6-Xy(2-C_5H_4N)N]$_2$Zn[(μ_3-O)Bu^t]$_2$-(Li·thf)$_2$ **45** (*cf.* **42**).[47] Efforts to establish the nature of the precursor to this oxygen-capture complex are ongoing (see below).



44

The stoichiometric ratios of components in all of these oxygenated products point to non-trivial reactions and this begs the question: can lithium zincates undergo controllable oxygenation? Our inability to isolate oxo-capture precursors from 1:1:1 reaction systems has meant that, in order to probe this issue, it has been necessary to change the initial Zn:pyridylaniline ratio to 1:2. Thus, Me_2Zn has been treated with two equivalents of *N*-2-pyridylaniline to cleanly afford [Ph(2-C_5H_4N)N]$_2$Zn **46**. This has then been reacted with BuLi to give [Ph(2-C_5H_4N)N]$_2$ZnRLi·*n*thf (R = Bu^n, *n* = 2 **47**; R = Bu^t, *n* = 1 **48**) when effected in thf or [Ph(2-C_5H_4N)N]$_2$ZnBu^n Li·dme **49** if dme is used instead.[64] ^{1}H NMR spectroscopy and NOESY suggest essential retention of the heterobimetallic 'ate complex nature of **47** in [$^2H_6$]C_6H_6 solution but also indicate that in hydrocarbon solution it adopts multifarious geometries. Nonetheless, COSY demonstrates that the dominant solution species exhibits an α-methylene signal at δ 1.75 with the corresponding α-C signal at δ 29.7 by ^{13}C NMR spectroscopy. X-Ray crystallography reveals that in monomeric **47** the alkali metal centre is supported by two distinctly different inter-metal 2-pyridylanilide bridges; one ligand utilizes its formally deprotonated N-centre to interact with both metals while its pyridyl substituent stabilizes the group 12 ion to give a 4-membered NCNZn ring (mode a in Fig. 3). This means that the 2-pyridylanilide ligand exhibits the same bridging motif as the organic unit in the only other N-bridged lithium zincate to have previously been fully characterized.[27] The second organic moiety behaves in a manner akin to that noted recently by ourselves in dimeric {[R(2-C_5H_4N)N]$_2$ZnOMe-Li·thf}$_2$ [R = Ph **41**; 3,5-Xy **43**].[62] Each N-centre in this ligand interacts with only a single metal ion. Thus, the formally



a **b** **c**

Fig. 3 2-Pyridylanilide bonding modes in **47** (a and b) and in **48** (a and c).

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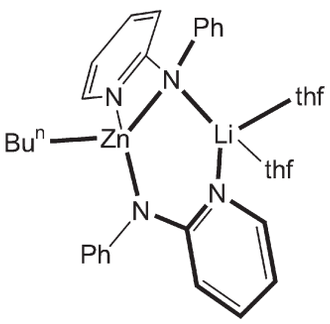
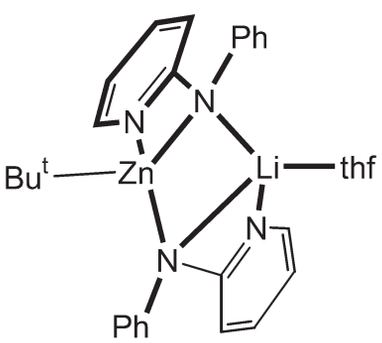
deprotonated donor site bonds to the Zn^{2+} ion while the pyridyl N-centre interacts only with the alkali metal (mode b in Fig. 3). Consequently, the solid-state structure of **47** is based on a 6-membered NZnNCNLi metallocycle. The crystal structure of $[Ph(2\text{-}C_5H_4N)N]_2ZnBu^nLi\cdot dme$ **49**[47] is precisely analogous to that of **47**, notwithstanding the replacement of bis(thf) solvation of the alkali metal centre by dme chelation.[65]



47

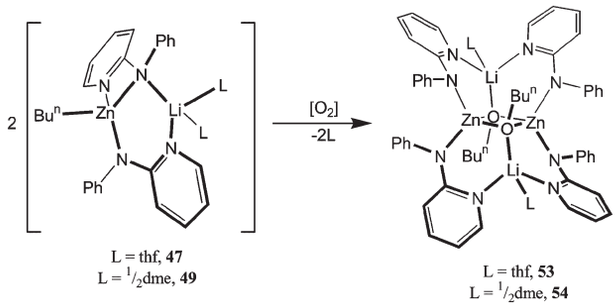
In a similar way, Bu^tLi reacts with **46** to give $[Ph(2\text{-}C_5H_4N)N]_2ZnBu^tLi\cdot thf$ **48**, the Zn–C unit of which reveals a signal at δ 33.9 by ^{13}C NMR spectroscopy. As for **47**, NOESY implies retention of the 'ate complex in $[^2H_6]C_6H_6$ solution. Mono(thf) coordination of the alkali metal centre in **48** can be explained by the X-ray crystallographic observation of three interactions between amide moieties and Li^+. One ligand bridges between the two metals utilizing its deprotonated N-centre, with further interaction between this residue and the group 1 metal involving its pyridyl N-atom and giving a CN_2Li ring (mode c in Fig. 3). The second amide ligand adopts the same behaviour as that noted in **47** (mode a, Fig. 3).[64]



48

Just as templated metal alkoxide formation has been probed for lithium aluminates $[PhC(O)N(Me)Al(Bu^t)Me_2Li]_n$ **50** {to give $[PhC(O)N(Me)Al(OMe)(Bu^t)MeLi\cdot PhC(O)N(Me)Al(OMe)(OBu^t)MeLi]_2$ **51** as the only isolable product}[61] and $[PhC(O)N(Ph)Al(Bu^t)Me_2Li]_2$ **35** {to yield $\frac{1}{2}[PhC(O)N(Ph)AlMe(OR)R'Li]_2$ (R = Bu^t, R′ = Me **52a**; R = Me, R′ = Bu^t **52b**},[61] so the exposure of **47**–**49** to O_2 gives controlled reaction and results in the isolation of well-defined, reproducible and crystalline materials. However, whereas the structure cores of **35** and **50**–**52** are controlled by Li–O bonding (to the exclusion of aluminium),[58] **47** and **49** yield zinc alkoxides analogous to methoxides **41** and **43**.

Zinc dianilide **46** reacts with Bu^nLi in thf (to give **47**) or dme (to give **49**) and thence with O_2 to make $\{[Ph(2\text{-}C_5H_4N)N]_2ZnOBu^nLi\cdot nL\}_2$ (n = 1, L = thf **53**; n = 0.5, L = dme **54**; Scheme 3). The structural relationships demonstrated here strongly suggest that in each case oxygenation proceeds by insertion into the Zn–C bond in $\{[Ph(2\text{-}C_5H_4N)N]_2ZnBu^n\}^-$. Accordingly, while ^1H NMR spectroscopy reveals retention of the 2:1 *N*-2-pyridylanilide:Bu^n ratio in **53**, a broad



Scheme 3

signal centred at δ 4.02 and a singlet at δ 64.8 (by ^1H and ^{13}C NMR spectroscopy, respectively) both indicate the formation of a Bu^nOZn moiety. Both **53** and **54** are based on C_i symmetry dimers in the solid state (Scheme 3). However, whereas the previous observation of tetrahedral metal centres in the core $(ZnO)_2$ ring in complexes of this type only implied the inclusion of oxygen into the Zn–C bond of a triorganozincate anion, comparison of the structures of **53** and **54** with those of **47** and **49** clearly establishes that the process has occurred. The motif in which a 2-pyridylanilide ligand bridges between lithium and zinc such that each N-centre bonds to only one metal ion—noted in the structures of **47** and **49**—is retained in those of **53** and **54**. The stability of the 4-membered $(ZnO)_2$ metallocycle in dimeric **41**, **43** and **53** is revealed by the behaviour of dme in **54**. Here, the sequential treatment of **46** with Bu^nLi, dme and O_2 has afforded a product in which the same dimeric configuration and $(ZnO)_2$ metallocycle are manifest. Instead of adopting chelating behaviour,[65] the preference of Li^+ for tetrahedral coordination, coupled with the presumed stability of the $(ZnO)_2$ dimer core, causes dme to bridge between alkali metal centres[65,66] in adjacent aggregates. Consequently, **54** forms polymeric chains in the solid state. The crystalline dimer units of **53** and **54** appear to be retained in hydrocarbon solution. Two distinct types of *N*-2-pyridylanilide ligand are observable in the X-ray diffraction structure with one arranged such that its pyridyl component is oriented *endo* to the $(ZnO)_2$ ring (this ligand is shown top-right and bottom-left in **53**/**54**, Scheme 3), and the other incorporating an *exo* pyridyl ring (this ligand type is shown top-left and bottom-right in **53**/**54**, Scheme 3). These orientations are consistent with the observation that each of the aromatic signals in the ^{13}C NMR spectra are split into two equally intense peaks.

Instead of giving a complex of the type $\{[Ph(2\text{-}C_5H_4N)N]_2ZnOBu^tLi\cdot thf\}_2$, the reaction of **46** with Bu^tLi and excess O_2 in thf yields previously seen trigonal **42** as the only isolable product. This suggests that the choice of R group in $\{[Ph(2\text{-}C_5H_4N)N]_2ZnR\}^-$ has a significant effect on the oxophilic properties of the anion. The $[OBu^n]^-$ moieties in **53** reside in an elongated enclosure defined by two pyridyl rings, two Ph groups and one thf (or one half of a dme in **54**) complexant (Scheme 3). The topology of these pockets can be approximated from the non-bonding distances between van der Waals extrema of the organic groups and analysis reveals that the cavities are ideal for occupation by $[OBu^n]^-$ but are too small to house $[OBu^t]^-$. Furthermore, whereas on the face of it dimeric **53** is somewhat dissimilar to trigonal **42** there is, in fact, a close conceptual relationship between the structural types represented by these compounds. This can be formally viewed in terms of the rearrangement of two Zn–O interactions and two Li–O bonds in response to the presence of either *one* or *two* equivalents of **46** (Fig. 4).

Replacement of pyridyl*aniline* ligands with the pyridyl*amines* $Bz(2\text{-}C_5H_4N)NH$ (Bz = benzyl) or $Me(2\text{-}C_5H_4N)NH$ has not allowed the isolation or characterization of crystalline

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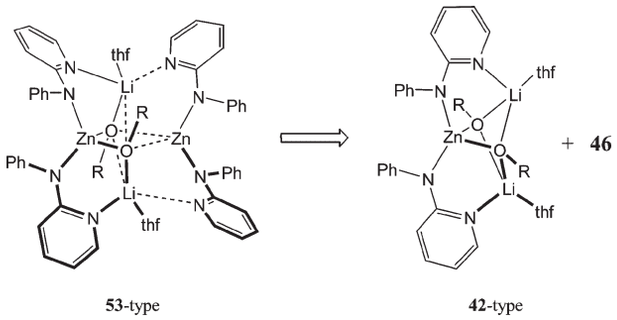
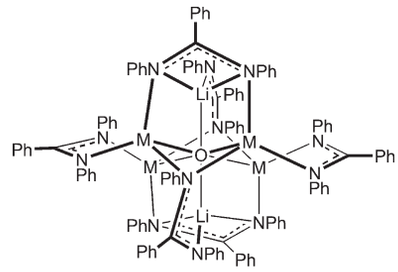
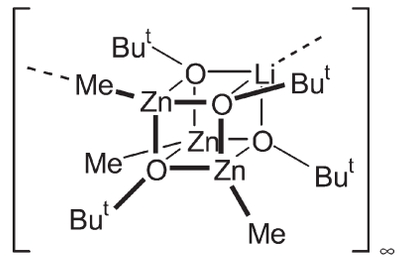


Fig. 4 The structural relationship between **42** and **53** based on the extrusion of dianilide **46** from the latter.

lithium zincates on treatment with Me_2Zn and Bu^tLi. It has, upon exposure to dried air, afforded the beryllium-acetate-type[67] oxide-encapsulation complex $[Bz(2\text{-}C_5H_4N)N]_6Zn_4(\mu_4\text{-}O)$ **55** and the distorted octahedral alkoxide oxide *fac*-$[Me(2\text{-}C_5H_4N)N]_6Zn_3(Li_3OBu^t)(\mu_6\text{-}O)$ **56**.[62] These species both empirically incorporate an $\{[R(2\text{-}C_5H_4N)N]_6Zn_3(\mu_3\text{-}O)\}^{2-}$ ligand. It acts as a tetradentate donor to Zn^{2+} in **55** and as a heptadentate donor to $[Li_3OBu^t]^{2+}$ in **56**, suggesting some flexibility in the orientations of the organic moieties. In the first of these, three zinc ions describe the base of a trigonal pyramid, each edge of which is spanned by $[Bz(2\text{-}C_5H_4N)N]^-$. . The last zinc centre occupies the cluster apex and is stabilized by the pyridyl N-centres of the remaining three ligands, each of which spans one non-bonding base-apex edge. At the cluster core is a nearly tetrahedral oxide ion that, while $Zn_4(\mu_4\text{-}O)$ tetrahedra are well-known, is unusual by virtue of its source. In contrast to related tetrahedra that have been afforded by reaction with CO_2 or H_2O,[68] the oxide source in **55** is O_2.[62] This is further suggested by an analysis of the structure of **56**, wherein the metal ions in the Li_3 face bridge $[OBu^t]^-$ and the encapsulated oxide ion. With an observed interoxygen distance of 2.685(13) Å [*cf.* 2.530(2) Å in **42**] the two group 16 centres in **56** are clearly independent. Nevertheless, efforts are ongoing to establish whether individual clusters of **56** contain both the atomic centres (albeit separated) of single oxygen molecules. The interstitial oxide itself interacts with the three zinc centres to afford a molecular $Zn_3Li_3(\mu_6\text{-}O)$ isomer. The coordination spheres of both Zn^{2+} and Li^+ ions are completed by organic ligands, three of which span Zn···Zn distances whilst the remainder circumscribe the Li_3 array but are oriented such that their NMe groups also bridge Li···Zn octahedron edges.[62]

Intimate relationships between mechanisms of organooxide formation (*e.g.*, in **53**) and oxide encapsulation (*e.g.*, in **56**) have been recently demonstrated. It is in this context that, just as **41** and **43** could be prepared by sequential reaction of the appropriate *N*-pyridylaniline in toluene with Me_2Zn, Bu^tLi and an oxygen source,[62] so the amidine substrate *N*,*N*′-diphenylbenzamidine (HAm) has undergone similar reaction to effect formation of a slurry that dissolves on addition of thf to yield the oxygenated dimer $(Am_2ZnOMeLi{\cdot}thf)_2$ **57**.[69] It has also proved possible, effecting dissolution by treatment not with a donor solvent but with further toluene, to isolate and characterize both a new heterobimetallic oxide-encapsulation cluster, **58**, and a metal alkoxide polymer, **59**, from a single reaction. The first of these products is revealed by X-ray crystallography to be $(Am_3ZnLi_2)_2(\mu_6\text{-}O)$. It is a complicated cluster with 2-fold rotational symmetry and three crystallographically independent metal sites. One is occupied by Li^+ (top and bottom in the structure illustrated) while the other two are disordered, with a mixture of lithium and zinc character. Overall, the effect is to give a M_6O^{6+} octahedral core based on a disordered Zn_2Li_2 equator with Li^+ ions in the axial positions.





59

The Li–O and Zn–O bond distances suggest that the metal centres in the M_4 plane are less strongly bonded to the encapsulated dianion than the two axial lithium ions, such that the cluster could be considered to contain a near linear $[Li_{ax}\text{–}O\text{–}Li_{ax} = 178.9(5)°]$ lithium oxide unit. The metal centres in the equatorial plane also display significantly different bonding interactions with O^{2-}, depending on how they combine with the organic periphery. These ligands adopt orientations reminiscent of those observed in hydride-encapsulation cluster **19**[40] and also in the cubic oxides R_6Li_8O (R = 4-azabenzimidazole derivative **60**;[70] PhNC(H)NPh **61**[47]). The backbones of the residues in **58** are mutually perpendicular, affording a distorted icosahedral array of inward-pointing electron pairs. The result is that an essentially spherical pattern of electron density is provided to the metal oxide core—an arrangement that is ideally suited to the positional disorder therein [Fig. 5(a)]. Of course, whereas a cubic metal arrangement (*cf.* **19**) can be uniformly coordinated by a pseudo-icosahedral periphery, an octahedral structure necessitates formally different bonding patterns for each ligand. Accordingly, three distinct modes are noted for the ligands in **58** [Fig. 5(b)].[71] In spite of the different method of oxygen-capture demonstrated here (*i.e.*, encapsulation as opposed to organooxide formation) the arrangement of metal ions in **58** means that it can be viewed, like organooxides such as **41** and **53**, as comprising triangulated $ZnLi_2$ arrays. This view argues that the amidinate

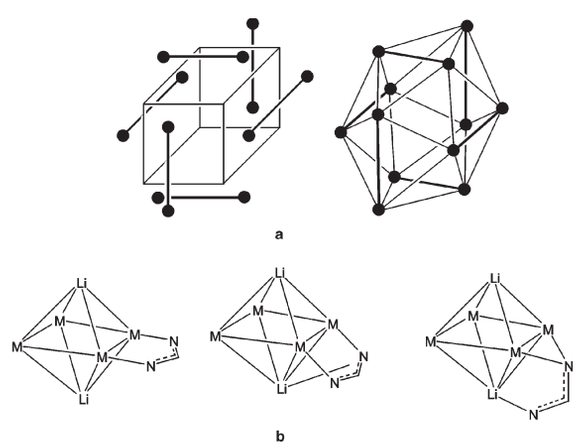


Fig. 5 (a) Icosahedral periphery of and (b) ligand bonding modes in **58**.

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ligands that chelate the M_4 plane hold the two intermetallic trigonal units together about the central oxide.

The complexity with which oxygen is scavenged by this system is further evidenced by the isolation of crystalline $\{[Me(Bu^tO)Zn]_3(Bu^tOLi)\}_\infty$ **59**. The chains noted in the solid state are based on pseudo-cubic O_4Zn_3Li clusters, themselves formed by the empirical insertion of oxygen into $(Bu^t)C–M$ bonds. Remarkable in each cuboid building block of **59** is the retention of an unreacted MeZn group. This contrasts with the majority of our data on oxygenated lithium zincates and bears comparison only with the structure of $[MeZn(OBu^t)_2$-$Li{\cdot}thf]_2$ **44**.[62] Just as the core of **58** revealed the positional interchangeability of lithium and zinc, the two Me-bonded metal centres in **59** refine crystallographically as zinc while the remaining metals refine with 50% Zn and 50% Li occupancy. The methyl group involved in polymerization occupies a crystallographic centre of symmetry midway between these metals, making it impossible to distinguish unambiguously between Zn–Me···Li and Zn···Me–Li motifs.[69] This renders **59** a species (like interstitial-hydride complexes **19**, **20** and **27**) that we hope to study by single-crystal neutron diffraction.

2.3 Theoretical studies

Little theoretical work has been done on lithium zincates to date, though we envisage commencing a variety of computational investigations shortly. However, the gas phase structures of dilithium tetraorganozincates **3**, **5** and **6** have all been probed.[10] Computed data have revealed that while the relative energies of Me_3ZnRLi_2 depend on the choice of R, it is generally the case that monoanionic *tri*organozincates are favoured over dianionic *tetra*organozincates. Moreover, it is suggested that monomeric triorganozincates will preferentially adopt R-bridged structures in which the zinc is only tricoordinate. It should be borne in mind, however, that these data conflict with related spectroscopic studies[10,12] and with the formative work of Weiss and Wolfrum that established the solid-state structure of the tetramethylzincate dianion.[25]

More recently, and in an attempt to better understand the similarities and differences between alkylcuprate and -zincate reactivity, Kohn–Sham orbital analyses of MeCu, Me_2Cu_2, $[Me_2Cu_2]^-$, Me_2Zn, $[Me_3Zn]^-$ and $[Me_4Zn]^{2-}$ have been performed using DFT methods. It has been calculated that whereas the d orbitals of the cuprate metal centres are at the same energy levels as the methyl carbon orbitals (encouraging reaction as metal-centred nucleophiles), organozincates possess high-lying methyl carbon orbitals and low-lying d orbitals. This leads to the expectation that they will act as alkyl nucleophiles.[72]

3 Concluding remarks

Whereas lithium aluminates have received much attention in the past, the relative lack of published data relating to the structural properties of lithium zincates is surprising given their established[3] and still developing[12–17] synthetic applications. The most recent of these preparative uses has allowed the generation of a variety of otherwise problematic target molecules and, in the case of **1** and **2**, data point to particular use being made of these systems in the future for selective substitution of pyridines.[17]

As has been discussed, the paucity of structural data on lithium zincates can be largely attributed to the extremely oxophilic behaviour of zinc-carbon bonds. Nevertheless, it is clear that both anaerobically prepared zincates[52,64] and the oxygenated derivatives, both of these[62,64] and also of alkylzinc species,[24] are now being increasingly well understood. Structural principles that govern anaerobically prepared zincates have now been elucidated in the context of heteroatom stabilization of each metal centre along with the importance of intermetal bridging motifs—these have been used to rationalize fully characterized examples of both oligomeric and polymeric zincates. It is also now clear that (as has been established for lithium aluminates)[58,61] controlled oxygenation of these compounds is possible, resulting in structure types (such as those exhibited by dimers **53** and **54** and trigonal adduct **42**) that can be understood in terms of precursors to oxidation (**47**–**49**).[47,62,64] It is certainly to be hoped that our increasing appreciation of the differences and similarities between anaerobically prepared and oxygenated compounds will be of significance in the fields of preparative chemistry and materials science now and in the future.

Advances have also been reported in highly unusual new areas of mixed Zn-Li chemistry. The recently developed field of alkali metal cluster interstitial hydride chemistry[40] has only very lately been successfully extended to group 12 with the isolation and full characterization of the ion-separated zincate $(Bu^t_3Zn)^-[(hpp)_6Li_8H]^+$ **27**.[49] This incorporates a hydride-containing cluster whose structural parameters bear direct comparison with those of the vacant parent cage $[(hpp)_6Li_8]^{2+}$ (synthesized as a component in the analogous lithium aluminate system). Taken together, these data hold out the possibility that lithium 'ate complexes of this type may have applications in hydride and hydrogen storage chemistry.[49] Efforts are now being instituted to probe the generality and interconvertability of hydride-containing and vacant alkali metal polyhedra. At the centre of this study, demonstrating new structure types, will be lithium zincates.

Just as developments in the structural chemistry of lithium zincates and their oxygenated derivatives promise significant new applications for these systems, so the lability of zinc-centred bonding in organozincates has yielded data suggesting that in some cases the traditional view of lithium zincates should be replaced by one in which a diorganozinc solvates an organolithium compound.[38,52] This observation and the correlation of structure with Lewis acid solvent properties will be of clear significance to chemists attempting to utilize the synthetic potential of a range of organometallic substrates.

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