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Synthesis and structural elucidation of solvent-free and solvated lithium dimethyl (HMDS) zincates†‡§

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Using a co-complexation methodology the unsolvated lithium zincate [LiZn(HMDS)Me_2] (**4**, HMDS = 1,1,1,3,3,3-hexamethyldisilazide) was prepared by reaction of an equimolar amount of LiHMDS with Me_2Zn in a non-polar toluene–hexane solvent mixture. X-Ray crystallographic studies reveal that the asymmetric unit of **4** has a dinuclear arrangement, based on a planar LiNZnC four-membered ring. As a result of intermolecular interactions between the lithium centre of one asymmetric unit and a terminal methyl group of another, **4** presents a polymeric chain array in the solid state. DFT calculations revealed that the formation of the polymer is the driving force for the success of co-complexation of LiHMDS and Me_2Zn to yield the unsolvated zincate **4**. The reaction of **4** with PMDETA (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine) afforded the new solvated zincate [(PMDETA)Li(μ-Me)Zn(HMDS)Me] (**5**). X-Ray crystallographic studies show that the asymmetric unit of **5** consists of an open, dinuclear LiCZnC arrangement rather than a closed cyclic one, in which the HMDS ligand unusually occupies a terminal position on Zn. DFT computational studies showed that the structure found for **5** was energetically preferred to the expected HMDS-bridging isomer due to the steric hindrance imposed by the tridentate PMDETA ligand. The reaction of **4** with the neutral nitrogen donors 4-*tert*-butylpyridine and *tert*-butylcyanide afforded the homometallic compounds [(^{t}Bu-pyr)Li(HMDS)] (**6**) and [(^{t}BuCN)Li(HMDS)] (**7**) respectively as a result of disproportionation reactions. Compounds **6** and **7** were characterized by NMR (^{1}H, ^{13}C and ^{7}Li) spectroscopy.

Introduction

Alkali metal zincates have been known since the epochal synthesis of $NaZnEt_3$ by Wanklyn in 1858[1] and thus represent one of the oldest classes of 'ate' compounds in history. Despite their age, this important family of organometallic compounds has been neglected for a long time by the synthetic community and it is only relatively recently that they have started to be used in many fundamental reactions in organic synthesis such as metal/halogen exchange,[2] deprotonative metallation[3] or nucleophilic addition,[4] establishing themselves as extremely versatile reagents that sometimes can surpass the performances of conventional non-ate monometallic reagents such as alkyllithium or Grignard reagents.[3] Alkali metal zincates show a greater functional group tolerance and selectivity than the latter traditional reagents, but also their reactivity can be exceptionally enhanced in comparison with neutral, kinetically retarded dialkyl zinc compounds, R_2Zn.[5] Amongst this family of bimetallic compounds, dialkyl-amido zincates, $MZn(NR_2)R'_2$ have received particular attention due to their high degrees of selectivity in aromatic deprotonation reactions.[3] Thus, pioneering work by the groups of Kondo and Uchiyama has shown that lithium di-*tert*-butyl(TMP) zincate (TMP = 2,2,6,6 tetramethylpiperidide)[6] is an effective chemoselective base for achieving direct zincation of a wide range of functionalised aromatic substrates.[7] The same researchers have also found that the selectivity of these lithium dialkyl amido zincates can be modulated and controlled by changing the specific ligands bonded to zinc.[7b,8]

Despite this new found synthetic usefulness, the number of reported structures of alkali metal zincates is relatively small as highlighted in recent reports.[9] The first structural characterization of a zincate was actually as long ago as 1968, when Weiss and Wolfrum reported the unsolvated lithium tetraalkylzincate $Li_2[ZnMe_4]$.[10] However, the structure of the first dialkyl amido zincate, [(TMTA)Li(μ-HMDS)Zn(CH_2SiMe_3)$_2$] (TMTA = 1,3,5-trimethyl-1,3,5-triazinane, HMDS = 1,1,1,3,3,3-hexamethyldisilazide)[11] was published over 25 years later by Westerhausen *et al*. Recently we have prepared and fully characterised the first examples of TMP zincates [(TMEDA)Li(μ-TMP)(μ-Bu)ZnBu] (**1**) (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine)[12] which can selectively monozincate ferrocene, and its sodium relative [(TMEDA)Na(μ-TMP)(μ-^{t}Bu)Zn^{t}Bu] (**2**),[13] which has proved to be a highly selective alkyl base towards aromatic substrates such as benzene,[13,14] naphthalene,[15] tertiary amides[16] and dimethylanilines.[17] These two synthetically useful

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† Dedicated to Professor Ken Wade on the occasion of his 75th birthday.

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TMP zincates adopt similar contacted-ion pair structures (Fig. 1) where the alkali metal and the zinc atoms are predominantly connected by an amide bridge that bonds equally strongly to both metals. In addition, both structures show a secondary (electron deficient or agostic) interaction between the alkali metal and one of the alkyl ligands on the zinc, giving rise to a four-atom LiNZnC ring for **1** and a five-atom NaNZnCC ring for **2**.[18]

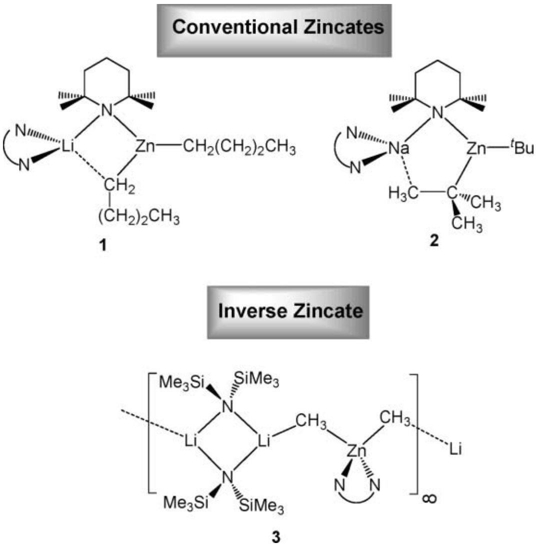
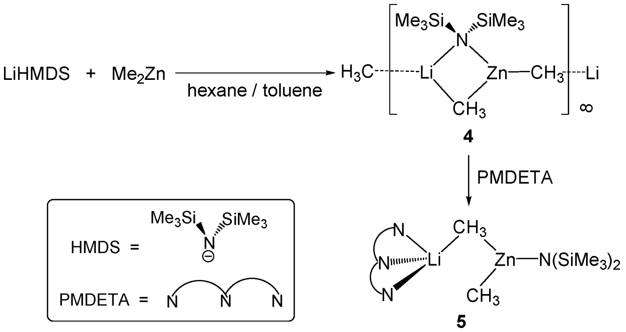


Fig. 1 Contrasting structural motifs found for different alkyl-amido zincates.

Recently we have also started to study the effects that the amide group has on the structure of these dialkyl-amido zincates.[19] Thus in a previous communication we reported the synthesis and structural characterisation of new TMEDA-solvated lithium dimethyl-amido zincates [$LiZnMe_2(NR_2)$]. For NR_2 = TMP, the dimethyl zincate [(TMEDA)Li(μ-TMP)(μ-Me)ZnMe] is isostructural to the butyl congener **1** whereas for NR_2 = HMDS a unique dilithium monozinc formulation [$Li_2(HMDS)_2Me_2Zn(TMEDA)$] (**3**) is obtained which exhibits a markedly different structural motif (Fig. 1). Unlike **1** and **2** which can be considered conventional zincates as the zinc centre is supported by three anionic ligands and the Lewis base TMEDA is bonded to the more electropositive lithium atom, in **3** there is a reversal in the usual roles of the two metals. Thus zinc is supported by only two anionic ligands but now exhibits TMEDA chelation, whereas lithium is coordinated by three anionic ligands (2 amido; 1 alkyl) and is not bonded to TMEDA. Therefore in coordination terms this compound can be described as an "inverse zincate" or a "lithiate", which in the solid state forms a polymeric zig-zag chain arrangement propagated through the Me groups. These intriguing preliminary results prompted us to carry out a systematic study of the synthesis and structures of new HMDS zincates. Herein we report the synthesis and characterisation of the unsolvated zincate [$LiZn(HMDS)Me_2$] (**4**) and its PMDETA (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine) adduct [(PMDETA)Li(μ-Me)Zn(HMDS)Me] (**5**) which is to the best of our knowledge the first dialkyl-amido zincate where the amide occupies a terminal position exclusively bonded to zinc. The reactions of **4** with other typical but monodentate nitrogen donor ligands such as 4-*tert*-butylpyridine and *tert*-butylcyanide are also reported. In addition, a theoretical DFT study has been carried out in order to shed light on the pathways involved and structures obtained for these HMDS zincates.

Results and discussion

One of the synthetic methodologies most commonly employed to prepare heteroleptic zincates is direct combination (which one could alternatively describe as ate-complex formation) of the two individual homometallic reagents.[20] This method was employed here. Thus, a commercial solution of dimethylzinc in toluene was added to a solution of freshly prepared Li(HMDS) in hexane (Scheme 1). The mixed-metal product [$LiZn(HMDS)Me_2$] (**4**) was immediately formed as indicated by the precipitation of an extremely insoluble white solid, which contrasted with the high solubility of the monometallic reagents when employed in the same solvent mixture. The new solvent-free zincate **4** was obtained as colourless crystals in an isolated yield of 81% following recrystallisation from a hexane–toluene mixture. NMR (^1H, ^{13}C and ^7Li) spectroscopic studies of **4** (see Experimental section) in a solution in deuterated benzene showed unambiguously the mixed-metal constitution of **4**. Thus, for example, its ^1H NMR spectrum contains a singlet at −0.67 ppm for the methyl groups which can be compared with the chemical shift of uncomplexed dimethylzinc in the same solvent (−0.52 ppm, Table 1). This significant but not major diference (0.15 ppm) shows that although the methyl groups are now part of a Li/Zn mixed-metal compound and possess a different chemical shift from the homometallic Me_2Zn, they retain a large amount of their original "zinc character", in other words the methyl groups are still strongly bonded to the Group 12 metal. We have found that this feature also extends to other related dialkyl-amido zincates,[12,19] emphasizing zinc's strong carbophilic character. Regarding the HMDS ligand, the ^1H NMR spectrum of **4** shows a resonance at 0.15 ppm which appears in between



Scheme 1 Co-complexation reaction to afford **4** and its subsequent chelation with PMDETA to yield **5**.

Table 1 Comparison of the ^1H chemical shifts (δ in ppm) for the methyl and HMDS ligands in zincates **4** and **5** with those of other related species in C_6D_6 solution

Compound	δ(Zn–CH_3)	δ(HMDS)
Li(HMDS)		0.12
$Zn(HMDS)_2$		0.20
[$Li_2(HMDS)_2Me_2Zn(TMEDA)$] (**3**)	−0.52	0.28
$ZnMe_2$	−0.52	
[$LiZn(HMDS)Me_2$] (**4**)	−0.67	0.15
[(PMDETA)Li(μ-Me)Zn(HMDS)Me] (**5**)	−0.53	0.50

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those for the homometallic amides Li(HMDS) (0.12 ppm) and $Zn(HMDS)_2$ (0.20 ppm). Compound **4** was also characterised by ^{13}C NMR spectroscopic studies showing resonances at 5.51 and −6.67 ppm for the HMDS and the methyl groups respectively. However this spectrum was less diagnostic of the formation of a mixed-metal compound as the chemical shifts of these signals are only marginally different from those for Li(HMDS) and Me_2Zn.

As determined by X-ray crystallography, the structure of the contacted ion pair zincate **4** was found to be based on a planar four-membered LiNZnC ring (Fig. 2), with the two metals connected through the HMDS ligand and one of the methyl groups, the remaining methyl occupying a pseudo-terminal position on zinc. Coordinatively unsaturated within this asymmetric unit, the solvent-free lithium atom attains a higher coordination number overall by forming an intermolecular interaction with the terminal methyl group of a neighbouring molecular unit, affording a polymeric chain structure (Fig. 3). A noteworthy feature is the cisoid arrangement of the HMDS group, which lie on the same side of the $Li \cdots Zn–C$ vector. A similar polymeric array has been previously reported by Mulvey and coworkers for the amido-rich zincate $[LiZn(HMDS)_2Me]$[21] and it has also recently been observed in the unsolvated TMP zincate $[LiZn(TMP)Et_2]$[7d] where the TMP groups also adopt a cisoid disposition within the chain. Unfortunately a large amount of motion between the metal sites and the terminal methyl ligand in **4** adversely affects the precision of this structure and therefore prevents discussion of any geometrical parameters.

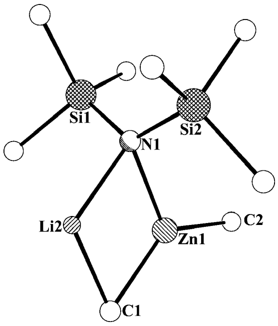


Fig. 2 Asymmetric unit of **4** with hydrogen atoms and minor disorder components omitted for clarity.

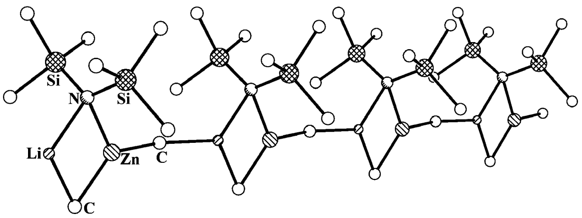
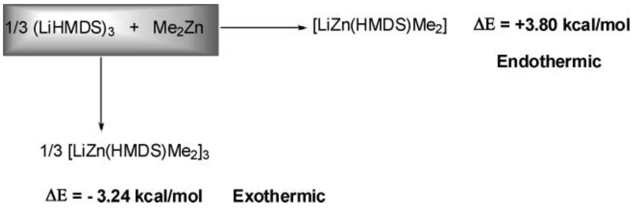


Fig. 3 Section of the extended chain structure of **4** without hydrogen atoms.

The co-complexation of LiHMDS and Me_2Zn to afford **4** in the non-polar solvent mixture toluene–hexane was rather unexpected as it contrasts with previous results in our laboratory where mixtures of M(TMP) (M = Li, Na) and another dialkylzinc compound $^tBu_2Zn$ failed to yield mixed metal compounds in the absence of a neutral Lewis base coligand such as TMEDA or THF.[19] This tendency of unsolvated zincates to dissociate into their monometallic components in the absence of a donor ligand has also been previously noticed by Westerhausen *et al.* for the putative homoleptic alkyl zincate "$[LiZn\{CH(SiMe_3)_2\}_3]$",[22] which forms stable solvent-separated zincate molecules in the presence of neutral donors such as TMEDA or TMTA but cannot be obtained in its unsolvated form.

To attempt to understand better the formation of **4** we next carried out a theoretical study of the reaction between LiHMDS and Me_2Zn. Firstly, exploratory *ab initio* calculations at the Hartree Fock (HF) level were performed using the 6-31G* basis set. The resultant optimised geometries were subject to a frequency analysis and then refined further by density functional theory (DFT) calculations utilising the B3LYP functionals and the 6-311G** basis set (Scheme 2). We modelled the reactant Li(HMDS) as a cyclic trimer since this is the arrangement that this lithium amide exhibits in the absence of any neutral donor ligand,[23] while Me_2Zn was modelled as a simple linear monomer.[24] When the product **4a** was modelled as a dinuclear monomer the co-complexation reaction was calculated to be endothermic by +3.80 kcal mol^{-1}. However, the thermodynamics of this reaction were reversed when **4** was modelled in a higher aggregation state. Thus, on modelling **4** as a dimer the reaction became exothermic with an energy gain of −1.20 kcal mol^{-1}, which increased to −3.24 kcal mol^{-1} for the corresponding trimer.[25] These theoretical results suggest that the success of co-complexation reactions of these homometallic reagents to form an unsolvated zincate is dramatically dependent on the ability of the resulting mixed-metal product to aggregate. Thus, compound **4**, as previously described, adopts a polymeric chain (of infinite aggregation) in non-polar solvents which judged on the trend seen in these calculations, would be thermodynamically extremely favoured. The same rationale can be applied to the recently reported related unsolvated TMP zincate $[LiZn(TMP)Et_2]$[7d] which also adopts a polymeric structure. In the same way these calculations can explain why co-complexation of M(TMP) (M = Li, Na) and $^tBu_2Zn$ fails in the lack of a donor solvent.[19] *tert*-Butyl groups are decidedly bulkier than methyl or ethyl groups and therefore the formation of an infinite chain by polymerisation through its quaternary carbon is much less favoured. Perhaps a polymer could be propagated by intermolecular agostic interactions between the alkali metal and the methyl group on the terminal ^tBu group as recently reported for the related lithium magnesiate $[LiMg(HMDS)_2{}^tBu]$.[26] However these interactions are much weaker and less energetically preferred than those found in **4** or in $[LiZn(TMP)Et_2]$ where the interaction between the lithium of one asymmetric unit and the alkyl group of another occurs through a more anionic carbon that bears most of the negative charge of the alkyl group.



Scheme 2 Relative energetics of modelled DFT reactions to yield **4a**.

As previously mentioned the addition of one molar equivalent of TMEDA to **4** yielded the unprecedented inverse zincate **3**

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Table 2 Key bond lengths (Å) and bond angles (°) within the structure of **5**

Zn1–C1	2.0074(14)	Zn1–C2	2.0361(15)
Zn1–N1	1.9851(10)	Li1–C2	2.335(2)
Li1 · · · C1	3.084(3)	Li–N2	2.196(2)
Li1–N3	2.132(2)	Li1–N4	2.113(2)
Si1–N1	1.6914(11)	Si2–N1	1.6904(11)
C1–Zn1–C2	132.64(6)	C1–Zn1–N1	112.68(5)
C2–Zn1–N1	114.59(6)	Li1–C2–Zn1	78.98(7)
N2–Li1–N3	84.22(8)	N3–Li1–N4	121.97(10)
N2–Li1–N4	87.12(8)	N4–Li1–C2	111.96(10)
N3–Li1–C2	125.87(11)	N2–Li1–C2	103.56(9)

where the Li/Zn roles are inverted with respect to those in conventional zincates with TMEDA unusually bound to Zn (Fig. 1).[19] We therefore decided to study the reactivity of **4** with other neutral nitrogen donors (tridentate PMDETA) and monodentate ligands (4-*tert*-butylpyridine and *tert*-butylcyanide). Starting with PMDETA, we added one molar equivalent of it to a freshly prepared suspension of **4** in a hexane–toluene mixture to afford a colourless solution that deposited colourless crystals of **5** in a near-quantitative yield (Scheme 1).

The molecular structure of **5** (Fig. 4) was successfully determined by X-ray crystallographic studies. Table 2 lists its key bond lengths and bond angles. Ion contacted zincate **5** can be considered to have an open LiCZnC arrangement rather than a closed cyclic one like that exhibited by the related dialkyl-amido zincates **1**,[12] **2**[13] and **4**. This more open structural motif is reminiscent of that previously found by Westerhausen *et al.* for the HMDS zincate [(TMTA)Li(μ-HMDS)Zn(CH_2SiMe_3)$_2$].[11] However, there is an essential difference between the latter molecule and **5**. To explain: whereas in [(TMTA)Li(μ-HMDS)Zn(CH_2SiMe_3)$_2$] the lithium and zinc centres are connected by the amide ligand, in **5** the HMDS group is terminally disposed with respect to Zn and instead one of the methyl groups, generally a much poorer bridging ligand, connects the two different metals together. To the best of our knowledge this is the first dialkyl-amido zincate where the amide ligand occupies a terminal disposition.

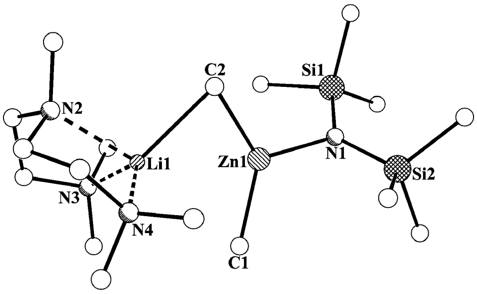

Fig. 4 Molecular structure of **5** showing selected atom labelling with dashed bonds representing the Li–N_{PMDETA} dative interactions. Hydrogen atoms are omitted for clarity.

To shed light on the formation and structure of **5** another theoretical study was carried out at the same level as that described for **4**. Thus, the modelled co-complexation reaction between Li(HMDS) and Me_2Zn in the presence of PMDETA was calculated to be exothermic by −13.64 kcal mol^{-1}. Two regioisomers of **5** were modelled (Fig. 5) where the amido ligand adopts a terminal position in **5a** or a bridging position in **5b**. In agreement with the experimental findings the most stable model structure was found to be **5a** by 5.29 kcal mol^{-1} over **5b**. The calculated bond lengths of models **5a** and **5b** are listed in Table 3 along with the relevant experimental values taken from the X-ray determination of **5** for comparison.

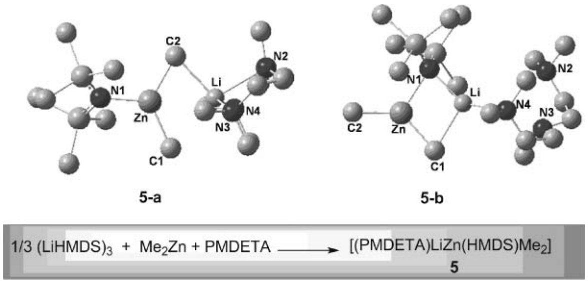

Fig. 5 Modelled structures of **5a** with terminal HMDS and **5b** with bridging HMDS.

Table 3 Comparison of the calculated bond distances (Å) for models **5a** and **5b** with those from the X-ray crystallographic data of **5**

Bond distances	**5**	**5a**	**5b**
Zn–C1	2.0074	2.067	1.981
Zn–C2	2.0361	2.042	2.057
Zn–N1	1.9851	1.975	2.143
Li–C2	2.335	2.271	
Li · · · C1	3.084	2.671	2.569
Li–N1			1.978
Li–N4	2.113	2.256	2.130
Li–N3	2.132	2.251	3.711
Li–N2	2.196	2.362	5.035

In general the bond lengths calculated for **5a** agree favourably with those found experimentally for **5** although the calculations overestimate the strength of the interaction of the lithium centre with C1 (length, 2.671 Å in **5a** *versus* 3.084 Å in **5**). As previously mentioned amide ligands are in general much better bridging ligands than alkyl groups as they have two lone pairs of electrons available to construct a bridge, whereas alkyl groups with a single lone pair give rise to electron-deficient bonds. Belying this generality, surprisingly for **5**, the HMDS-terminal isomer **5a** is energetically preferred to the HMDS-bridging one **5b**. In contrast, when the same calculations were carried out in the absence of PMDETA a reversal of the relative energies between the two possible isomers occurred with the unsymmetrical isomer [Li(μ-HMDS)(μ-Me)Zn(Me)], where HMDS bridges the two metals, being 14.01 kcal mol^{-1} lower in energy than symmetrical [Li(μ-Me)$_2$Zn(HMDS)] with its terminal amide. This illustrates the dramatic influence that the neutral Lewis base employed, in this case PMDETA, has in the ultimate preferred choice of structure for the zincate. The hapticity of the triamine coupled with its steric bulk provokes the HMDS to adopt a terminal position even when from an electronic point of view its ability to coordinate as a bridge between two metals is considerably superior to that of an alkyl group. It is also noteworthy that in **5b**, PMDETA coordinates to the lithium centre in an unsatisfactory monodentate fashion as indicated by the huge differences in calculated Li–N_{PMDETA} separation distances: Li–N4: 2.130 Å (similar to the average Li–N_{PMDETA} bond distance found in the crystal structure, 2.147 Å) whereas Li–N3 and Li–N2 are 3.711 and 5.035 Å respectively.

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Thus another aspect that must contribute to lower the energy of the reaction and in consequence to increase the stability for **5a** in comparison with **5b** is the higher coordination number of the Lewis acidic lithium centre (*i.e*, 4 *versus* 3).

These theoretical and experimental results for **5** show significant differences from the molecular structure of [(TMTA)Li(μ-HMDS)Zn(CH_2SiMe_3)$_2$].[11] As aforementioned, in this zincate HMDS acts as a bridge connecting the two metals. This can be explained in terms of the much larger steric hindrance of the alkyl groups. Although TMTA is a tridentate ligand similar to PMDETA, the CH_2SiMe_3 coligands are much bulkier than the CH_3 groups in **5**, thus the exchange of the bridging positions between HMDS and one of the CH_2SiMe_3 ligands does not imply a remarkable improvement from a steric point of view. Therefore the structure of this silylalkyl zincate is dictated by the better ability of the amide HMDS to bridge the two metals.

Considering the molecular structure of **5** in more detail, it displays a trigonal planar zincate anion made up of two methyl groups and one HMDS ligand. This complex anion connects to the lithium cation through one of the methyl groups [Li1–C2: 2.335(2) Å]. PMDETA coordinates in a tridentate fashion to lithium to complete the structure. The zinc atom has a distorted trigonal planar geometry (sum of the angles around Zn: 359.91°). This distortion is mainly located at the C1–Zn–C2 bond angle that has to expand [to 132.64(6)°] to develop the interaction between C2 and the {Li(PMDETA)}$^+$ fragment. The Zn–N_{HMDS} bond distance [1.9851(10) Å] is similar to those found in other zinc compounds with terminal HMDS ligands[27] and appreciably longer than that in the monomeric parent bis(amide) [Zn(HMDS)$_2$][28] [mean bond length 1.832 Å]. The Zn–N bond distance of **5** [1.9851(10) Å] is marginally shorter than those found for other related HMDS-based zincates where the amide is acting as a bridging ligand such as aforementioned [(TMTA)Li(μ-HMDS)Zn(CH_2SiMe_3)$_2$] [2.131(9) Å][11] and amido-rich [LiZn(μ-HMDS)$_2$Me] [2.010(3) Å].[21] In **5**, the two methyl ligands remain attached to the Zn centre, one at a slightly shorter distance than the other as indicated by the bond lengths Zn1–C2 [2.0361(15) Å] and [Zn1–C1; 2.0074(14) Å]. Predictably the shorter distance corresponds to the methyl group terminal on the Zn whereas the remaining one is for the methyl group which also binds to the lithium atom, the sharing of which explains the modest elongation of the Zn–C bond distance. Both Zn–C distances are comparable to those found in the inverse zincate **3**[19] [2.002(2) and 2.008(2) Å] and in the related dimethyl zincate [(TMEDA)Li(μ-TMP)(μ-Me)ZnMe][19] [2.032(3) and 1.995(3) Å] and slightly longer than in monomeric [(TMEDA)ZnMe_2][29] [1.989(9) and 1.974(9) Å]. In **5** the lithium atom exhibits a distorted tetrahedral environment bonded to the neutral κ^3-coordinated triamine PMDETA[30] as well as to one methyl group. This Li–Me connection [Li1–C2: 2.335(3) Å] is slightly longer than those reported for other related compounds with bridging methyl groups such as for instance the methyllithium solvates [{(−)-sparteine}$_2$$Li_2$(μ-Me)$_2$][31] [average length 2.257 Å], [(THF)$_4$$Li_4$(μ-Me)$_4$][32] [mean length 2.235 Å] but noticeably longer than the Li–C secondary (agostic) interaction found in the related zincate [(TMEDA)Li(μ-TMP)(μ-Me)ZnMe] [2.603(5) Å].[19] In addition, this Li–C2 bond distance in **5** is nearly identical to those reported for the inverse zincate **3**[19] [average length 2.375 Å] where two methyl groups are bridging lithium and zinc (Fig. 1). In contrast, no interaction is observed between the {Li(PMDETA)}$^+$ cation and the remaining methyl group in **5**, located at 3.084(3) Å from the lithium centre. This distance is too elongated even to suggest any kind of secondary agostic interaction, giving rise to an open arrangement for **5** similar to that exhibited by [(TMTA)Li(μ-HMDS)Zn(CH_2SiMe_3)$_2$][11] rather than a closed cyclic one such as those of **1** and **2**.

Compound **5** was also characterised in deuterated benzene solution using NMR (^{1}H, ^{13}C and ^{7}Li) spectroscopy (see Experimental section). The ^{1}H NMR spectrum of **5** shows a sole singlet for the methyl groups at −0.53 ppm which is indicative that **5** exhibits a different structure in benzene solution from that found in the solid state where there are two distinct methyl groups. This can be explained by considering the formation of a fully solvent-separated ion pair {(PMDETA)Li(benzene)$_x$}$^+${Zn(HMDS)Me_2}$^-$ or alternatively that at room temperature there is a fast exchange process between the terminal and bridge positions of the two methyl groups that makes both groups chemically equivalent at ambient temperature. The chemical shift of these methyl groups (−0.53, Table 1) is nearly identical to that found for free Me_2Zn in the same deuterated solvent which shows that for **5**, as for **4**, the methyl groups also maintain a great deal of their original "zinc character". On the other hand the resonance for the HMDS group is significantly further downfield (at 0.50 ppm) than the analogous signal of Zn(HMDS)$_2$ (at 0.20 ppm) or of the related unsolvated zincate **4** (at 0.15 ppm), which suggests that the coordination number (3) and charge of the zinc centre (R_3Zn^-) are different to those in linear HMDS–Zn–HMDS (corresponding values 2 and neutral R_2Zn). The ^{1}H NMR spectrum also suggests that the PMDETA ligand remains chelated to lithium in benzene solution. Thus the ^{1}H NMR spectrum of free PMDETA shows two multiplets at 2.50 and 2.37 ppm for the NCH_2 groups and two singlets at 2.19 and 2.12 ppm for the NCH_3, however, for **5** the relative positioning of these signals is reversed with the protons from the NCH_2 group becoming equivalent in the form of a singlet at 1.72 ppm whereas the resonances for the NCH_3 appear at 1.87 and 1.85 ppm. As previously observed with **4**, the ^{13}C NMR spectrum of **5** is not as diagnostic as its ^{1}H NMR counterpart as the chemical shifts of the signals are only marginally different compared to those found for the homometallic components Li(HMDS) and Me_2Zn.

The reactivity of **4** with the monodentate neutral nitrogen donor ligands 4-*tert*-butylpyridine and *tert*-butylcyanide has also been studied. In both cases the resulting solutions deposited colourless crystalline products that were analysed by ^{1}H, ^{13}C and ^{7}Li NMR spectroscopy (see Experimental section) and were identified as the homometallic Lewis acid–Lewis base complexes [(^{t}Bu-pyr)Li(HMDS)] (**6**) and [(^{t}BuCN)Li(HMDS)] (**7**). Compound **7** has been previously prepared by 1 : 1 reaction of LiHMDS with ^{t}BuCN and its crystal structure has been determined by X-ray crystallography,[33] showing a simple dimeric (LiN)$_2$ ring arrangement with bridging HMDS and terminal ^{t}BuCN. A similar dimeric structure could be expected for **6** in view of that exhibited by the closely related unsubstituted-pyridine solvate [{(pyr)Li(HMDS)}$_2$].[34] The formation of **6** and **7** as a consequence of the reaction of **4** with one molar equivalent of the relevant nitrogen donor molecule suggests disproportionation processes have occurred. Cleavage of mixed-metal compounds on the addition of a donor solvent such as pyridine has been previously

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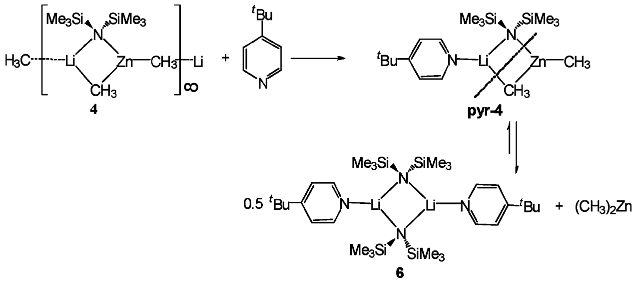
observed for the tris(amido) magnesiate [LiMg(HMDS)$_3$].[34] Its reaction with one molar equivalent of pyridine affords pyridine-solvated [(pyr)LiMg(HMDS)$_3$]; however, when an excess of 2–4 equivalents of the same donor solvent is employed the homometallic species [(pyr)Li(HMDS)] and [(pyr)$_2$Mg(HMDS)$_2$] are obtained. A plausible pathway to explain the formation of **6** by a similar cleavage process is shown in Scheme 3. Initially the reaction of ^{t}Bu-pyridine, a strong Lewis base with **4** would lead to the formation of a solvated zincate **pyr-4** which could cleave as indicated by the dashed line (Scheme 3) to afford **6** and Me$_2$Zn. The disproportionation of the putative zincate **pyr-4** into its homometallic components is probably an equilibrium reaction, the position of which greatly favours the formation of **6** and Me$_2$Zn due to the low solubility of the former in hexane solution. The same rationale can be employed to explain the formation of **7**. It is remarkable to mention that, although *tert*-butylpyridine and *tert*-butylcyanide are both well-known unsaturated molecules susceptible to nucleophilic addition, compound **4** fails to react with them in that way under the conditions studied.



Scheme 3 Plausible disproportionation pathway for the formation of **6**.

Experimental

General

All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane and toluene were dried by heating to reflux over sodium benzophenone and distilled under nitrogen prior to use. *n*BuLi and Me$_2$Zn, were purchased from Aldrich Chemicals. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ^{1}H, 150.32 MHz for ^{7}Li and 100.62 MHz for ^{13}C.

Synthesis of [LiZn(HMDS)Me$_2$] (4)

Li(HMDS) was prepared *in situ* by reaction of BuLi (2.5 mL of a 1.6 M solution in hexane, 4 mmol) and HMDS(H) (0.84 mL, 4 mmol) in hexane. Me$_2$Zn (2 mL of a 2 M solution in toluene) was then introduced. A white precipitate is formed immediately. At this stage 5 mL of toluene were added and the mixture was gently heated until all the white solid dissolved affording a transparent colourless solution. Allowing this solution to cool slowly to room temperature produced a crop of colourless crystals (0.85 g, 81%). ^{1}H NMR (400 MHz, 25 °C, C$_6$D$_6$): δ 0.14 (s, 18H, HMDS), −0.67 (s, Zn–CH$_3$, Me). ^{13}C{^{1}H} NMR (100.63 MHz, 25 °C, C$_6$D$_6$): δ 5.51 (HMDS), −6.67 (Zn–CH$_3$, Me). ^{7}Li NMR (155.50 MHz, 25 °C, C$_6$D$_6$, reference LiCl in D$_2$O at 0.00 ppm): δ 0.46.

Synthesis of [(PMDETA)Li(μ-Me)Zn(HMDS)Me] (5)

To a suspension of **4** (4 mmol) in hexane, prepared *in situ* as previously described, was added PMDETA (0.84 mL, 4 mmol). The resulting colourless solution was concentrated by removal of some solvent *in vacuo* and placed in the freezer at −26 °C. A crop of colourless crystals was deposited after 48 h (1.60 g, 92%). ^{1}H NMR (400 MHz, 25 °C, C$_6$D$_6$): δ 1.87 (s, 12H, CH$_3$, PMDETA), 1.85 (s, 3H, CH$_3$, PMDETA), 1.72 (s, 8H, CH$_2$, PMDETA), 0.50 (s, 18H, HMDS), −0.53 (s, Zn–CH$_3$, Me). ^{13}C{^{1}H} NMR (100.63 MHz, 25 °C, C$_6$D$_6$): δ 56.85 (CH$_2$, PMDETA), 53.97 (CH$_2$, PMDETA), 45.85 (CH$_3$, PMDETA), 6.69 (HMDS), −6.99 (Zn–CH$_3$, Me). ^{7}Li NMR (155.50 MHz, 25 °C, C$_6$D$_6$, reference LiCl in D$_2$O at 0.00 ppm): δ 0.67.

Synthesis of [(^{t}Bu-pyr)Li(HMDS)] (6)

To a suspension of **4** (4 mmol) in hexane, prepared *in situ* as previously described, was added *tert*-butylpyridine (0.59 mL, 4 mmol). The resulting colourless solution was concentrated by removal of some solvent *in vacuo* until it became slightly cloudy. The solution was briefly heated to ensure complete dissolution of the precipitate. A pale yellow solution was obtained. This solution was slowly cooled by leaving it in a Dewar flask filled with hot water. On reaching ambient temperature, colourless crystals of **6** were obtained (0.88 g, 72%). ^{1}H NMR (400 MHz, 25 °C, C$_6$D$_6$): δ 8.75 (d, 2H, H$_\alpha$, ^{t}Bu-pyr), 6.88 (d, 2H, H$_\beta$, ^{t}Bu-pyr), 0.91 (s, 9H, CH$_3$, ^{t}Bu-pyr), 0.53 (s, 18H, HMDS). ^{13}C{^{1}H} NMR (100.63 MHz, 25 °C, C$_6$D$_6$): δ 161.66 (Cα, ^{t}Bu-pyr), 149.74 (C$_\beta$, ^{t}Bu-pyr), 121.59 (C$_\gamma$, ^{t}Bu-pyr), 34.61 (C(CH$_3$)$_3$, ^{t}Bu-pyr), 30.08 (C(CH$_3$)$_3$, ^{t}Bu-pyr), 6.64 (HMDS). ^{7}Li NMR (155.50 MHz, 25 °C, C$_6$D$_6$, reference LiCl in D$_2$O at 0.00 ppm): δ 2.75.

Synthesis of [(^{t}BuCN)Li(HMDS)] (7)

To a suspension of **4** (4 mmol) in hexane, prepared *in situ* as previously described, was added *tert*-butylcyanide (0.44 mL, 4 mmol). The resulting colourless solution was concentrated by removal of some solvent *in vacuo* and placed in the freezer at −26 °C. A crop of colourless crystals was deposited after 48 h (0.83 g, 83%). ^{1}H NMR (400 MHz, 25 °C, C$_6$D$_6$): δ 0.71 (s, 9H, CH$_3$, ^{t}BuCN), 0.49 (s, 18H, HMDS). ^{13}C{^{1}H} NMR (100.63 MHz, 25 °C, C$_6$D$_6$): δ 27.20 (C(CH$_3$)$_3$, ^{t}BuCN), 27.16 (C(CH$_3$)$_3$, ^{t}BuCN), 6.25 (HMDS). ^{7}Li NMR (155.50 MHz, 25 °C, C$_6$D$_6$, reference LiCl in D$_2$O at 0.00 ppm): δ 1.21.

X-Ray crystallography

Crystallographic data were collected on Bruker SMART and Nonius KappaCCD diffractometers at 123 K for **4** and 150 K for **5**, with Mo-Kα radiation ($\lambda = 0.71073$ Å) and corrected semi-empirically for absorption in the case of **5**. Crystal data for **4**: C$_8$H$_{24}$LiNSi$_2$Zn, $M = 262.77$, monoclinic, space group $P2_1/n$, $a = 6.7840(3)$, $b = 13.9936(7)$, $c = 15.8133(7)$ Å, $\beta = 97.650(2)°$, $V = 1487.84(12)$ Å^3, $Z = 4$; 17703 measured data, 3239 unique ($R_{\text{int}} = 0.069$), R (on F, for $F^2 > 2\sigma$) = 0.0655, R_w (on all F^2) = 0.1347, $S = 1.239$, final difference map features within ±0.772 e Å^{-3}. Crystal data for **5**: C$_{17}$H$_{47}$LiN$_4$Si$_2$Zn, $M = 436.08$, monoclinic, space group $P2_1/c$, $a = 9.616(3)$, $b = 13.522(4)$, $c = 20.444(6)$ Å, $\beta = 100.676(4)°$, $V = 2612.2(12)$ Å^3, $Z = 4$; 22855 measured data,

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6301 unique ($R_{\text{int}} = 0.0185$), R (on F, for $F^2 > 2\sigma$) = 0.0227, R_w (on all F^2) = 0.0642, S = 1.036, final difference map features within ±0.344 e Å^{-3}.

Conclusions

The unsolvated zincate **4** has been prepared by direct combination of its two homometallic components in a non-polar solvent mixture and fully characterized in solution and in the solid state. Its crystal structure shows a dinuclear arrangement based on a planar LiNZnC ring. Due to an intermolecular interaction between the terminal methyl of one asymmetric unit and the lithium of another, **4** presents an infinite chain arrangement in the solid state. DFT calculations show that co-complexation of LiHMDS and Me_2Zn is thermodynamically favoured due to the energy gained through sequentially increasing the aggregation, consistent with the stable polymeric structure observed experimentally. When PMDETA is added to **4** the new solvated zincate is obtained which to the best of our knowledge is the first example of a dialkyl-amido zincate where the amide ligand adopts a terminal position and it is solely bonded to zinc; whereas the two metals are connected through one of the alkyl groups. DFT calculations also reveal that this arrangement is energetically preferred to the common one found in other compounds of this family, primarily due to the steric bulk of the neutral donor PMDETA which solvates and crowds lithium. The addition of other monodentate neutral donors such as *tert*-butylpyridine or *tert*-butylcyanide to **4** produces the monometallic compounds [(^{t}Bu-pyr)Li(HMDS)] (**6**) and [(^{t}BuCN)Li(HMDS)] (**7**) as the result of a disproportionation process.

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