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A hetero-alkali-metal version of the utility amide LDA: lithium–potassium diisopropylamide†

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Designed to extend the synthetically important alkali-metal diisopropylamide [N^iPr_2 ; DA] class of compounds, the first example of a hetero-alkali-metallic complex of DA has been prepared as a partial TMEDA solvate. Revealed by an X-ray crystallographic study, its structure exists as a discrete lithium-rich trinuclear Li_2KN_3 heterocycle, with TMEDA only solvating the largest of the alkali-metals, with the two-coordinate lithium atoms being close to linearity [$161.9(2)^\circ$]. A variety of NMR spectroscopic studies, including variable temperature and DOSY NMR experiments, suggests that this new form of LDA maintains its integrity in non-polar hydrocarbon solution. This complex thus represents a rare example of a KDA molecule which is soluble in non-polar medium without the need for excessive amounts of solubilizing Lewis donor being added.

Introduction

An extremely common entry point for the selective functionalisation of an organic molecule is *via* a metallated intermediate (converting an inert C–H bond into a C–C, C–N or C–O bond for example), with alkali-metals (AMs) ideally suited to this task due to the considerable polarity and thus reactivity of the resulting C–AM bond.¹ This transformation is regularly achieved by use of an alkali-metal (usually lithium) secondary amide reagent (AM–NR₂) due to their highly desirable properties of high Brønsted basicity coupled with low nucleophilicity.² For many years the principal alkali-metal amides of choice (the so-called utility amides) for the synthetic organic community have been 1,1,1,3,3,3-hexamethyldisilazide [HMDS, NR₂ = N(SiMe₃)₂], 2,2,6,6-tetramethylpiperidide [TMP, NR₂ = NC(Me)₂CH₂CH₂CH₂C(Me)₂] and, most pertinent to this study, diisopropylamide [DA, NR₂ = N(ⁱPr)₂].³ The reactivity of such reagents is influenced by a variety of factors including but not limited to temperature, bulk solvent and aggregation state; with this third factor itself being heavily influenced by the presence of any Lewis base donors [*e.g.* tetrahydrofuran (THF) or *N,N,N',N'*-tetramethylethylenediamine (TMEDA) are the most commonly encountered in this regard]. Due to the obvious structure–reactivity relationship it is therefore desirable to be fully appraised of the aggregation state of a reagent, both in the solid state and most importantly in solution where

it operates. In comparison to other bimetallic combinations (that is alkali-metal/non alkali-metal),⁴ considerably much less attention has been placed on hetero-alkali-metallic complexes despite one of the leading synthetically useful metallating agents, commonly referred to as the Lochmann–Schlosser (LiCKOR) superbases,⁵ containing both lithium (through ^tBuLi) and potassium (through ^tBuOK). Studies of hetero-alkali-metallic complexes of the utility amides have thus far been limited to a handful of papers focusing on either HMDS⁶ or TMP⁷ (Fig. 1), while O'Shea has recently utilized an *in situ* TMP–O^tBu Li–K mixture to good effect in benzylic metallation reactions.⁸ However, to the best of our knowledge, surprisingly no mixed alkali-metal complexes of DA have thus far been reported in the literature. We now start to address this vacancy in the literature by reporting a novel modification of LDA, namely the dilithium–monopotassium complex $Li_2K(DA)_3$ **1**, as its TMEDA solvate.

LDA is known to exist as a helical polymer in the solid state with near linear N–Li–N units, a turn of the helix consisting of four units of alternating Li and N atoms (Fig. 2).⁹ The addition of THF breaks up this helix into a cyclodimer, with a central N₂Li₂ ring and each lithium atom solvated by a single donor molecule.¹⁰ This arrangement (N₂Li₂ ring with three coordinate lithium atoms) is repeated in replacing THF with TMEDA, but with the ditopic ligand acting as a monodentate (non-chelating) bridging linker between the dimeric subunits to give a different type of polymeric structure.¹¹ Unsolvated or THF solvated molecular structures of the heavier alkali-metal diisopropylamides are currently unknown, however in the presence of TMEDA a discrete dimeric motif is witnessed for both Na¹² and K¹³ congeners, with the TMEDA ligating in a bidentate manner to give a tetra-coordinate metal centre.

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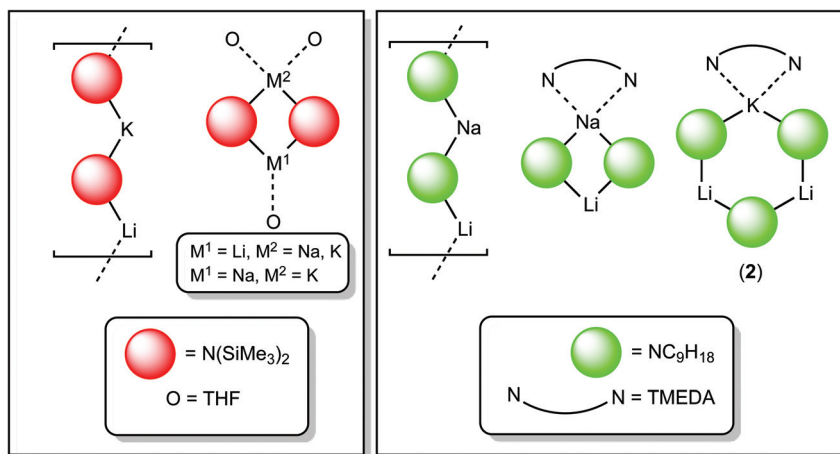


Fig. 1 Pictorial representation of known molecular structures of hetero-alkali-metallic complexes of the utility amides HMDS (left) and TMP (right).

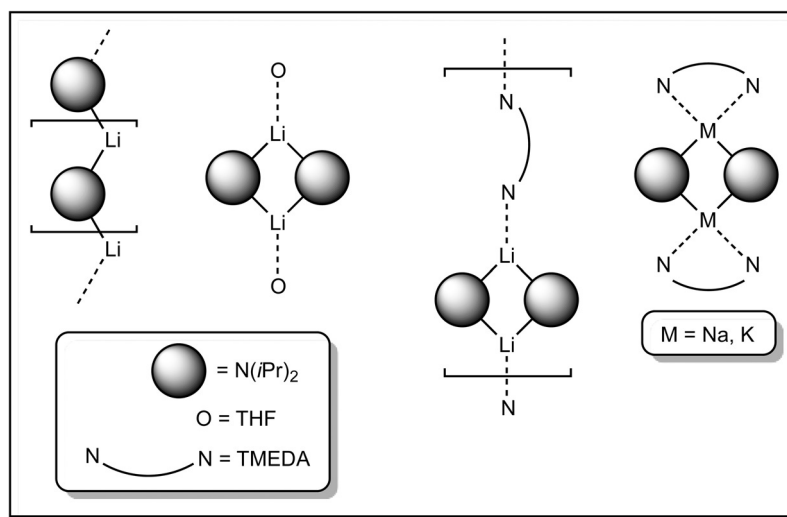
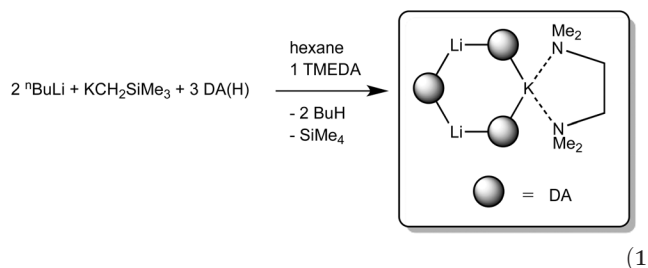


Fig. 2 Pictorial representation of known molecular structures of homometallic alkali-metal diisopropylamide complexes.

The larger potassium centre also displays three agostic contacts each of less than 3 Å in length with the methyl fragments of the diisopropyl groups for an overall coordination number of seven.



Results and discussion

The synthesis of the dilithium–monopotassium diisopropylamide complex **1** was achieved straightforwardly, mimicking the preparation of the previously prepared TMP analogue [2, TMEDA·K(μ-TMP)Li(μ-TMP)Li(μ-TMP)] by mixing ⁿBuLi and KCH₂SiMe₃ in a 2 : 1 ratio in hexane, followed by addition of three molar equivalents of DA(H) to give a pale suspension and then one molar equivalent of TMEDA to aid solubility (eqn (1)).

Cooling this solution to –32 °C overnight afforded a crop of X-ray quality colourless crystals in a 58% yield, their molecular structure (Fig. 3a) being determined *via* a single crystal diffraction experiment. This revealed **1** to exist as a discrete spirocyclic trinuclear molecule, containing a crystallographic 2-fold axis which passes through the potassium atom, the nitrogen atom of the unique DA anion (N3) and the centre of the



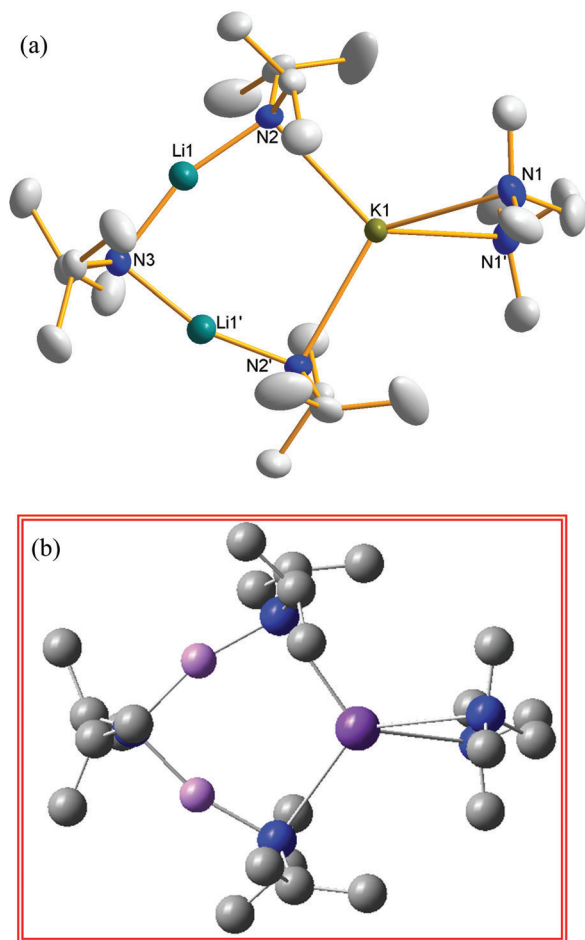


Fig. 3 (a) Molecular structure of complex **1** showing key atom labels with hydrogen atoms and minor disordered components of diisopropylamido anions omitted for clarity and ellipsoids drawn at the 50% probability level. Symmetry operation to generate equivalent atoms marked ' = -x, y, 1/2 - z. (b) Computed structure of same complex, **1_{calc}**.

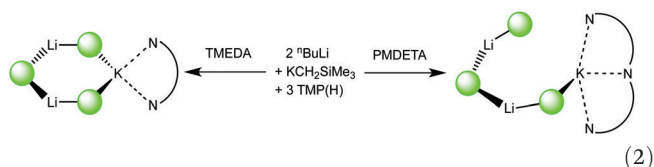
$\text{CH}_2\text{-CH}_2$ bond of TMEDA. **1** contains a central virtually planar LiLiKN ring (RMS deviation from planarity = 0.0297 \AA) lying approximately perpendicular [$70.56(4)^\circ$] to a KNCCN ring formed by the chelate coordination of TMEDA to potassium, with lithium atoms unsolvated and thus two-coordinate. This lack of solvation at lithium is perhaps unsurprising given Collum's observation that TMEDA-solvated LDA desolvates at ambient temperature even in the absence of other donor ligands.¹¹ Furthermore, X-ray quality crystals of polymeric unsolvated LDA were in fact obtained from a TMEDA-containing solution, albeit one having a substoichiometric quantity of the diamine.⁹ The overall structure of **1** can essentially be thought of as a dinuclear fragment of the LDA polymer which has trapped a monomeric fragment of $\text{KDA}\cdot\text{TMEDA}$. Note no β -hydride elimination from the N^1Pr_2 anion was witnessed unlike that recorded previously in heterometallic Mg/AM ($\text{AM} = \text{Na}, \text{K}$) complexes of this amide which had been refluxed in toluene/heptane.¹⁴ The optimized structure was modelled *via* DFT calculations and is shown in Fig. 3b for comparison, with the computed bond parameters displayed in Table 1.

Table 1 Comparison of selected bond parameters of $\text{Li}_2\text{K}(\text{amide})_3\cdot\text{TMEDA}$ (amide = DA, **1**, this work; amide = TMP, **2**, ref. 7), distances in \AA , angles in $^\circ$

	1_{calc}	1	2
K1–N1	3.056	2.907(1)	3.016(1)
K1–N2	2.772	2.869(1)	2.890(1)
Li1–N2	1.939	1.912(3)	1.950(2)
Li1–N3	1.989	1.972(3)	1.987(2)
N1–K1–N1'	62.5	64.22(4)	59.54(3)
N1–K1–N2	109.8	111.03(4)	119.54(3)
N1–K1–N2'	129.9	130.19(4)	122.62(3)
N2–K1–N2'	110.0	107.30(4)	107.05(3)
K1–N2–Li1	95.5	98.4(1)	97.9(1)
N2–Li1–N3	163.4	161.9(2)	164.2(1)
Li1–N3–Li1'	92.1	91.7(1)	88.7(1)

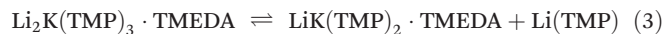
The modelled structure **1_{calc}** shows reasonably close agreement to **1** in the bond angles of the spirocyclic ring. However, the computed bond distances vary noticeably from those seen in the molecular structure, in particular **1_{calc}** predicts a shorter K-N_{DA} distance and concomitantly longer Li-N_{DA} distances. A subsequent effect of the shorter K-N_{DA} distances is the prediction that TMEDA will not be able to gain as close proximity to the potassium centre, with the predicted value of 3.056 \AA almost 0.15 \AA longer than the experimentally determined value.

On comparing the bond parameters of complex **1** with those of its TMP analogue **2**, it is noticeable that the six-membered ring of **1** has marginally shorter metal–nitrogen bond lengths. This can almost certainly be explained by the reduced steric strain imposed on this ring by the diisopropylamide anions *versus* the more sterically demanding TMP anions in **2**. This is also manifested in the $\text{K-N}_{\text{TMEDA}}$ bond lengths, with the less bulky DA groups allowing the bidentate donor to approach potassium more closely in **1** [$2.907(1) \text{ \AA}$ *versus* $3.016(1) \text{ \AA}$ in **2**]. This strain imposed by the TMP anions in **2** helps explain the previously witnessed opening of the six-membered ring on substituting TMEDA with the tridentate donor PMDETA (eqn (2)).⁷ We note here that an analogous crystalline PMDETA solvated derivative of **1** could not be obtained in this study despite numerous attempts. Other common polydentate donors such as diglyme, O ($\text{CH}_2\text{CH}_2\text{NMe}_2$)₂ and Me_6TREN [$\text{N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_3$] were also examined but failed to provide an isolable product.



Complex **1** was also investigated in the solution state for comparison with **2**, which is believed to undergo an equilibrium between the trinuclear species and a dinuclear (Li/K) species along with homometallic LiTMP according to eqn (3),⁷ probably due to the strain imposed on the ring by the bulky secondary amide molecules.





With respect to its THF solvate, much less has been reported regarding the solution behaviour of diisopropylamide complexes in non-polar solvents. Collum showed *via* ^6Li NMR spectroscopy that donor-free LDA in hexane exists as a mixture of 3–5 cyclic oligomers.¹⁵ Williard noted that the solubility of LDA in warm hydrocarbon solvents was dependent on the method of its preparation, with that prepared by reaction of lithium metal with DA(H) in ether in the presence of styrene¹⁰ being more soluble than that prepared from $^n\text{BuLi}$ and DA(H) in pentane.¹⁶ Similarly it has recently come to light that the production method of LDA is important with regards to its reactivity, since the presence of minute quantities of LiCl (on the parts per million scale) can profoundly influence the rate or regioselectivity of a reaction.¹⁷ We note at this juncture that in our hands, LDA generated *in situ* in hexane from $^n\text{BuLi}$ and DA(H) can be stirred indefinitely without precipitating yet once precipitated it is considerably more difficult to re-dissolve.

The ^1H NMR spectrum of **1** in deuterated cyclohexane solution at ambient temperature displayed only one principal set of resonances corresponding to the diisopropylamido anions at 3.06 and 1.02 ppm [Fig. 4, *cf.* DA(H) 2.86 and 0.96 ppm], with only a minute amount of DA(H) (presumably from unavoidable hydrolysis), suggesting that the two distinct DA environments within the molecular structure of the crystalline species are equivalent in NMR terms, although some form of rapid equilibrium which is faster than the NMR timescale cannot be unequivocally ruled out. A comparison with the corresponding ^1H NMR spectra of LDA both in the presence and absence of TMEDA suggested that complex **1** was not cleaving into its homometallic constituent parts (Fig. 4). It is highly unlikely that a stable TMEDA solvated LDA species would arise from cleavage of **1** given the previous observations of Collum *et al.* of the poor affinity of LDA for substoichiometric quantities of this donor. As shown in Fig. 4 and in accord with previous research, there appears to be more than one DA[−] component in a hydrocarbon solution of unsolvated LDA.

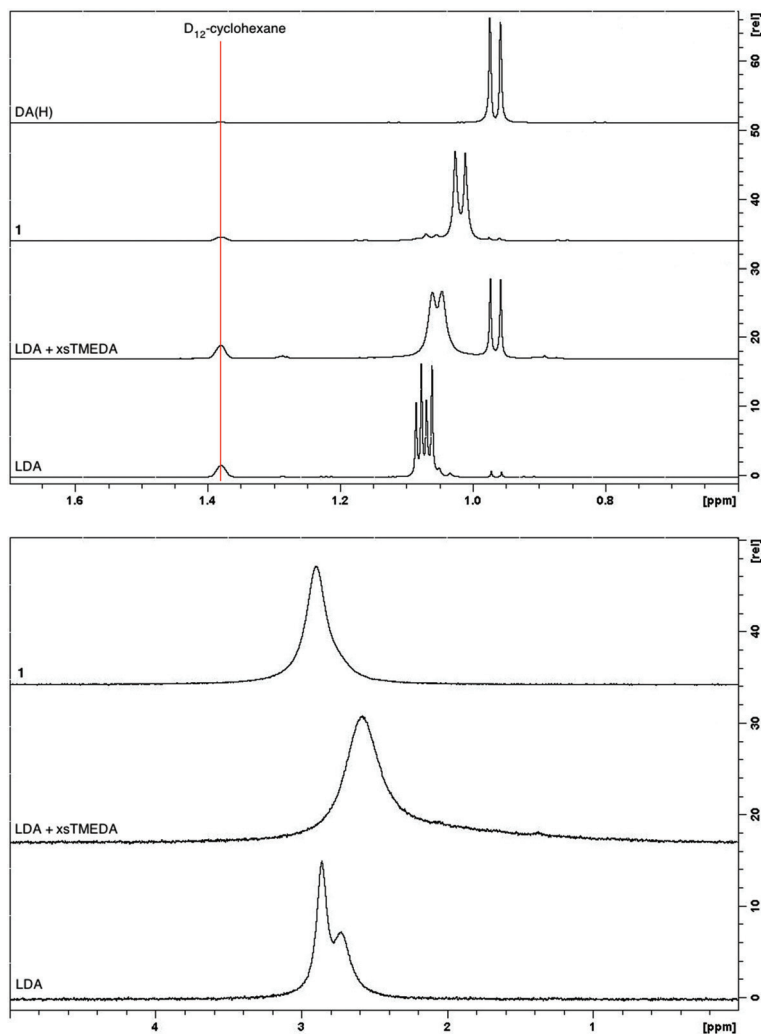


Fig. 4 Part of the ^1H (top) and the full ^7Li NMR (bottom) spectra of various N^iPr_2 containing species relevant to this study. A comparison of the ^7Li NMR spectra of **1** at both high and low concentration confirmed there was no concentration dependencies.



The ^1H NMR resonances corresponding to TMEDA appear at 2.29 and 2.19 ppm for the methylene and methyl groups respectively, very close to those of free TMEDA which appear at 2.30 and 2.14 ppm, suggesting that this bidentate donor is perhaps weakly bound or not bound at all to the potassium centre given that it is typical for TMEDA resonances to be considerably shielded when bound to an alkali-metal amide moiety.¹⁸ Furthermore, it has previously been noted that the relative positioning of the two TMEDA resonances is inverted upon coordinating to a metal¹² yet that is not the case here. We do note however that while such inversion is prevalent in C_6D_6 solutions, far less is known on alkane solutions and thus it is perhaps premature to draw any firm conclusions based on such a small sample set.

The ^7Li NMR spectrum of **1**, unlike that of **2**, displayed only a single resonance at 2.90 ppm in non-polar cyclohexane solution. Again, a comparison with LDA (both with and without TMEDA present) suggests that **1** is not simply extruding a homometallic LDA moiety in solution. Collum, Williard and co-workers have shown a TMEDA concentration dependence on the ^6Li chemical shift of LDA in hexane solution, ranging between almost 3 ppm (for no TMEDA) to slightly greater than 2 ppm (for 8.0 M TMEDA).¹¹ Corroborating our ^1H NMR spectra (*vide supra*), unsolvated LDA contains more than one lithium environment, in agreement with the findings of Collum *et al.* A low temperature ^7Li NMR spectrum of **1** (in hexane solution) was then recorded at 210 K and compared with the corresponding room temperature spectrum (Fig. 5). The latter spectrum was similar to that collected in C_6D_{12} , namely a singlet with a very small shoulder on the upfield side. Lower temperature affected the chemical shift of the resonance (and resolved the shoulder marginally better) but despite some broadening, the resonance did not split.

An interesting feature worthy of mentioning here is the excellent solubility of **1** in this aliphatic hydrocarbon solvent,

which is in contrast to the poor solubility of homometallic KDA complexes. This hints at the prospect of utilising **1** as a soluble source of KDA in organic reactions which are to be carried out in such a medium.

This heterometallic species was also studied in solution *via* DOSY spectroscopy (Fig. 6) in an attempt to glean more information on its solution state constitution.¹⁹

This technique, which is gaining in popularity for identifying solution structures of both homo-²⁰ and heterometallic alkali-metal complexes,²¹ can separate components according to their diffusion coefficient (and therefore indirectly to their size – akin to NMR chromatography). This revealed that the principal diisopropylamido-anion containing species has a molecular weight (MW_{DOSY}) of approximately 382, noticeably less than the molecular weight of the crystalline sample ($\text{MW} = 469.7$). However, as can clearly be seen in Fig. 6, the TMEDA component ($\text{MW}_{\text{DOSY}} = 242$) does not have the same molecular

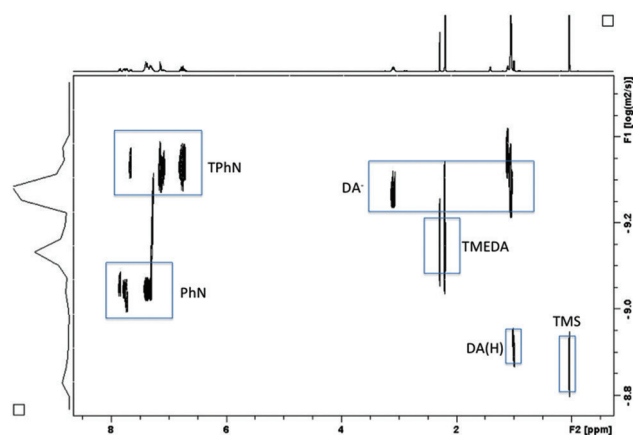


Fig. 6 DOSY NMR spectrum of complex **1** in C_6D_{12} at 27 °C in the presence of the standards of decreasing molecular weight tetraphenyl-naphthalene (TPhN), phenyl-naphthalene (PhN) and tetramethylsilane (TMS).

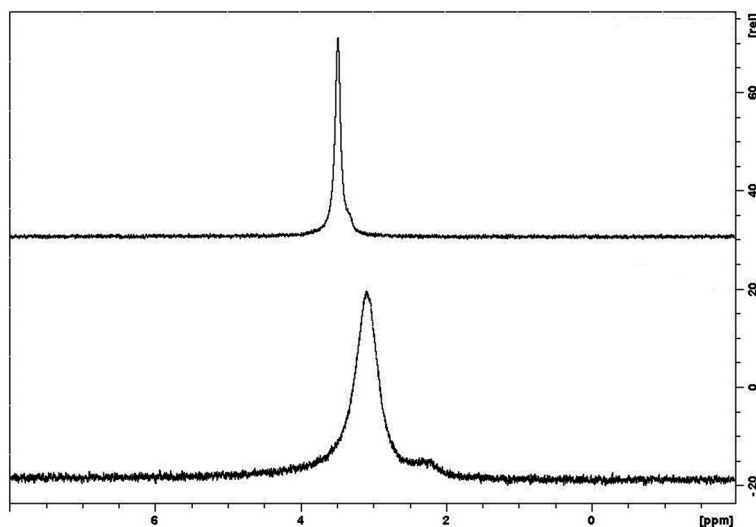
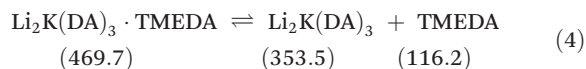


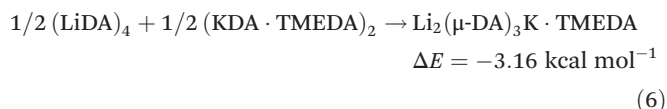
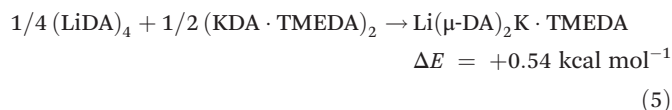
Fig. 5 ^7Li NMR spectra of **1** in hexane solution recorded at 300 K (top) and 210 K (bottom).



weight as the DA⁻ component. If TMEDA were completely dissociated from **1** in solution it should have a MW_{DOSY} equal to its true MW (116). This difference appears consistent with a rapid coordination–decoordination event occurring in solution with MW_{DOSY} giving a value intermediate between that of free and bound TMEDA and explains why MW_{DOSY} of the DA anions is intermediate between that of solvated and unsolvated Li₂K(DA)₃ (eqn (4)). This phenomenon has been observed previously in the solution behaviour of the related solvated amide species [Li(TMP)·THF]₂.^{20c}



We note here that varying the Li : K ratio (for example 1 : 1, or with an excess of K) within the reaction mixture did not result in a different complex being prepared. To probe this observation further, we compared the formally 1 : 1 reaction with the stoichiometrically precise 2 : 1 reaction (matching that in the formula of **1**) *via* DFT calculations according to eqn (5) and (6) respectively. In each case we commenced with a cyclo-tetramer of LDA as the lithium starting material²² and dimeric TMEDA-solvated KDA¹³ as the potassium starting material/Lewis donor source.



These calculations supported our assertion that the lithium rich constitution **1** is the energetically preferred product as the 1 : 1 reaction yielding a dinuclear product was calculated as being moderately endothermic (by +0.54 kcal mol⁻¹) while the 2 : 1 reaction yielding a trinuclear product was exothermic by a more substantial value of -3.16 kcal mol⁻¹.

Experimental section

General experimental

All reactions and manipulations were carried out under a protective argon atmosphere using either standard high vacuum Schlenk techniques or an MBraun glove box fitted with an inert gas recirculation and purification system. Bulk solvents were dried over Na/benzophenone and freshly distilled prior to use. ⁿBuLi was purchased from Aldrich and used as received. DA(H) and TMEDA were distilled over CaH₂ and stored over 4 Å molecular sieves. KCH₂SiMe₃ was prepared by the previously described literature method.²³

NMR spectra were collected on a Bruker AV400 MHz spectrometer operating at 400.13 MHz for ¹H, 155.47 MHz for ⁷Li and 100.62 MHz for ¹³C. All ¹³C NMR spectra were proton decoupled.

Synthesis of complex 1

ⁿBuLi (2 mL, 1.6 M in hexanes, 3.2 mmol) was added *via* syringe to a stirred suspension of KCH₂SiMe₃ (202 mg, 1.6 mmol) in hexane (5 mL) to give a homogeneous solution. After 5 min, DA(H) (0.67 mL, 4.8 mmol) was introduced *via* syringe producing another suspension. TMEDA was slowly added dropwise with stirring until a second homogeneous solution was obtained. Cooling this solution overnight at -32 °C yielded a crop of colourless crystals suitable for X-ray analysis (yield: 438 mg, 58%).

¹H NMR (D₁₂-cyclohexane, 300 K): 3.06 (sept, 6H, ²J_{H-H} = 6 Hz, CH(CH₃)₂), 2.29 (s, 4H, TMEDA CH₂), 2.19 (s, 12H, TMEDA CH₃), 1.02 (d, 36H, ²J_{H-H} = 6 Hz, CH(CH₃)₂) ppm.

¹³C NMR (D₁₂-cyclohexane, 300 K): 58.4 (TMEDA CH₂), 51.2 (CH(CH₃)₂), 46.2 (TMEDA CH₃), 28.2 (CH(CH₃)₂) ppm.

⁷Li NMR (D₁₂-cyclohexane, 300 K): 2.90 ppm.

Crystallographic data were collected at 123(2) K on an Oxford Diffraction Instrument using MoK_α (λ = 0.71073 Å) radiation.²⁴ Structure was solved using SHELXS-97 and refined to convergence against F² against all independent reflections by the full-matrix least-squares method using the SHELXL-97 program.²⁵ The isopropyl arms of the unique DA anion were modelled as being disordered over two sites in a 81 : 19 ratio, as was one of the methyl arms of the other DA anion. CCDC 901793 contains the supplementary crystallographic data for this paper.

Theoretical calculations were carried out using the Gaussian 03 package.²⁶ Geometry optimization was undertaken at the HF/6-31G*²⁷ level, followed by a frequency analysis. The geometry was then refined by further calculation at the B3LYP^{28/}6-311G**²⁹ level. The structural parameters reported were taken from the DFT calculations, whereas the total energy abstracted from the DFT calculations was adjusted by inclusion of the zero-point energy value from the HF calculation modified by the factor 0.91.

Conclusions

A hetero-alkali-metallic complex of the utility amide diisopropylamide, surprisingly the first example of its kind, has been prepared and characterized in the solid state and solution. The molecular structure shows the complex to be a lithium rich trinuclear cycle of formula Li₂K(DA)₃·TMEDA, with two coordinate lithium centres and TMEDA chelated potassium. Theoretical calculations suggest the 2 : 1 Li : K ratio witnessed in the final product is inevitable even when the ratio of starting materials is varied. Unlike the closely related TMP complex Li₂K(TMP)₃·TMEDA, complex **1** appears to maintain its metal-amide integrity in (non-polar) hydrocarbon media, though TMEDA appears to be involved in a decoordination–coordination event. This makes such a complex promising as a source of the highly reactive yet poorly soluble KDA, and also represents a well-defined LDA complex given the complexities described previously for this homometallic reagent in solution. The pursuit of alternative hetero-alkali-metallic complexes and



the use of this complex as a potential selective reagent for organic transformations will now be pursued in our research laboratory.

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