

Synthesis and structural characterisation of ‘solvent-free’ lithium–calcium hexamethyldisilazide, $[\text{Li}\{\mu\text{-N}(\text{SiMe}_3)_2\}_2\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}]$, exhibiting a double ration of agostic $\text{H}_3\text{C}\cdots\text{Li}$ and $\text{H}_3\text{C}\cdots\text{Ca}$ intramolecular interactions

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Received 10 October 2001; accepted 19 November 2001

Abstract

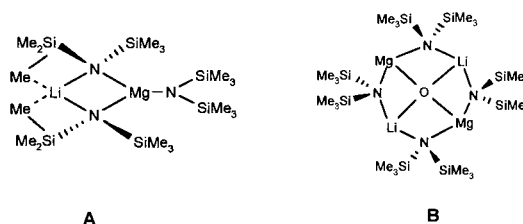
Addition of lithium hexamethyldisilazide to an equimolar amount of calcium bis(hexamethyldisilazide) in toluene gave ‘solvent-free’, $[\text{Li}\{\mu\text{-N}(\text{SiMe}_3)_2\}_2\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}]$ (**1**). An X-ray study reveals a dinuclear arrangement based on a planar LiNCaN four-membered ring: both metals engage in additional $\text{H}_3\text{C}\cdots\text{M}$ (where $\text{M} = \text{Li}, \text{Ca}$) interactions with the $\mu\text{-N}(\text{SiMe}_3)_2$ substituents resulting in a distorted tetrahedral geometry at lithium and a distorted trigonal-bipyramidal geometry at calcium. This contrasts with the previously reported mixed Li-Mg analogue, $[\text{Li}\{\mu\text{-N}(\text{SiMe}_3)_2\}_2\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}]$, where only the lithium centre engages in such intramolecular agostic $\text{H}_3\text{C}\cdots\text{Li}$ interactions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Agostic; Amide; Calcium; Heterometallic; Intramolecular interactions

1. Introduction

Our research group has recently been interested in the preparation and characterisation of mixed-metal Li-Mg amide complexes [1], which may have differing chemistries to their homometallic counterparts. A highlight of this research thus far has been the synthesis of the heterometallic hexamethyldisilazide, $[\text{Li}\{\mu\text{-N}(\text{SiMe}_3)_2\}_2\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}]$ (**A**) [2], a mixed-metal analogue of the commercially important reagent, $[\text{LiN}(\text{SiMe}_3)_2]$ [3]. Surprisingly, repetition of the preparation of **A** resulted in the crystallisation of an oxygen-contaminated derivative, $[\text{Li}_2\text{Mg}_2\{\text{N}(\text{SiMe}_3)_2\}_4(\text{O})_x(\text{O}_2)_y]$ (**B**), which structurally is made up of an eight-membered $[\{\text{LiNMgN}\}_2]^{2+}$ cationic ring with either oxide (O^{2-}) or peroxide (O_2^{2-}) dianions at its core. Further work has uncovered a whole family of these compounds, namely, $[\text{M}^{\text{I}}\text{M}^{\text{II}}\{\text{N}(\text{SiMe}_3)_2\}_4(\text{O})_x(\text{O}_2)_y]$ where $\text{M}^{\text{I}} = \text{Na}$ [4] or K [5] and $\text{M}^{\text{II}} = \text{Mg}$ or Zn [6] and

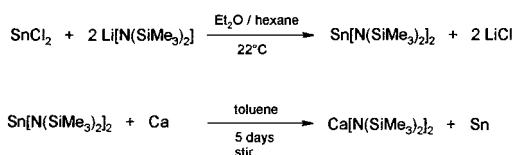
$[\text{Li}_2\text{Mg}_2\{\text{TMP}\}_4(\text{O})]$ [4] where $\text{TMP} = 2,2,6,6$ -tetramethylpiperidine. These compounds have since been coined ‘inverse-crown ethers’ [7] since their arrangements of Lewis acidic/basic sites have been reversed relative to those of conventional crown-ether complexes [8].



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The aim of this present study was to investigate the possibility of extending the family of inverse-crown ether complexes by replacing magnesium with its heavier congener, calcium. We attempted this preparation in a similar manner to the Li/Mg analogue [2]. However the reaction yielded only the unsolvated heterobimetallic species, **1**, with no inverse-crown ether complex evident from the reaction mixtures. Recently, Davies [9] published the structure of the THF-solvated dinuclear



Scheme 1.

derivative, $[\text{THF} \cdot \text{Li}\{\mu\text{-N}(\text{SiMe}_3)_2\}_2\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}]$ (**2**), which was found to crystallise as an impure mixture containing modest quantities of donor-solvated starting materials (i.e. homometallic compounds). Herein, we report the synthesis and X-ray characterisation of the ‘THF-free’, analogue, **1**, which has been produced in high purity as gauged from ^1H -NMR spectroscopic studies.

2. Results and discussion

Heterometallic **1** was prepared by the simple mixing of its homometallic amide precursors in toluene solution. The calcium amide, $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$, was prepared beforehand as a reddish-brown crystalline solid by the metathetical procedure described by Westershausen and co-workers [10] (Scheme 1).

In order to maximise yields of $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ it was necessary to crystallise it from the less polar solvent hexane at -25°C in which it has a greatly reduced solubility compared to that in toluene. The crystalline material was then isolated by cooling the reaction vessel in dry ice, removing the mother liquor by syringe, then evacuating the Schlenk tube directly and placing it in the glove box. The synthesis of compound **1** was then straightforward, involving the simple mixing of equimolar quantities of $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ and $[\text{LiN}(\text{SiMe}_3)_2]$ in toluene solution. This notwithstanding, problems arose when attempting to isolate compound **1** from solution as it was found to be

extremely soluble at room temperature, which explains why a rather low isolated yield of 18% was obtained. The filtrate was cooled to 5°C to give a solid, identified from its ^1H -NMR spectrum as **1**; however, the mass of solid was not recorded.

The melting point of compound **1** was found to be higher than that of its homometallic precursors, i.e. $129\text{--}134^\circ\text{C}$ cf. $[\text{LiN}(\text{SiMe}_3)_2]$, $78\text{--}80^\circ\text{C}$; $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$, 120°C (dec.). Infra-red spectroscopic studies of compound **1** revealed several bands characteristic of the HMDS [where HMDS = $\text{N}(\text{SiMe}_3)_2$] ligand, e.g. the sharp symmetric CH_3 deformation at 1245 cm^{-1} ; the asymmetric NSi_2 stretch at 1040 cm^{-1} ; and the asymmetric SiC_3 stretch at 658 cm^{-1} . Both $\{\delta_s(\text{CH}_3)\}$ and $\{\nu_{\text{as}}(\text{SiC}_3)\}$ bands are found to be in good agreement with those recorded in $[\text{LiN}(\text{SiMe}_3)_2]$, i.e. at 1245 and 663 cm^{-1} , respectively. Unfortunately, here it was not possible to distinguish between bridging and terminal HMDS groups in compound **1**, which was possible in the IR-characterisation of $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$, i.e. two bands at 1248 and 1240 cm^{-1} for $\{\delta_s(\text{CH}_3)\}$ [10]. By exposing **1** to air, hydrolysis occurred, resulting in the formation of sharp bands at 3643 , 3677 and 3378 cm^{-1} , corresponding to $\text{Ca}(\text{OH})_2$, LiOH and N-H (from regenerated amine), respectively.

Table 1 displays the ^1H - and ^{13}C -NMR spectroscopic data in toluene- d_8 for compound **1** and for comparison the corresponding data on $[\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ [10], $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ and the mixed Li/Mg analogue, $[\text{Li}\{\mu\text{-N}(\text{SiMe}_3)_2\}_2\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}]$. The ^1H -NMR data shows that, in general, the methyl resonances of the bridging amide groups $[\mu\text{-N}(\text{SiMe}_3)_2]$ lie at lower frequencies than the terminal ones, except in the case of homometallic $[\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ where the opposite is true, i.e. $\delta_b = 0.45$ cf. $\delta_t = 0.38$. Interestingly, it is observed that the chemical shift difference ($\Delta\delta$) of both Group 2 homometallic amides are identical to that of their corresponding heterometallic analogues (either

Table 1
 ^1H - and ^{13}C -NMR chemical shift (in ppm) data for alkaline-earth and mixed lithium-alkaline earth HMDS complexes

	$[\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ ^a	$[\text{LiMg}\{\text{N}(\text{SiMe}_3)_2\}_3]$ ^b	$[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ ^a	$[\text{LiCa}\{\text{N}(\text{SiMe}_3)_2\}_3]$
^1H -NMR				
Temperature (K)	302	300	210	300
$\delta_b(\text{SiMe}_3)$	0.45	0.21	0.21	0.16
$\delta_t(\text{SiMe}_3)$	0.38	0.28	0.33	0.28
$\Delta\delta$	0.07	-0.07	-0.12	-0.12
$^{13}\text{C}\{^1\text{H}\}$ -NMR				
Temperature (K)	302	300	302	300
$\delta_b(\text{SiMe}_3)$	8.12	5.53	6.94	5.16
$\delta_t(\text{SiMe}_3)$	7.14	7.05	6.48	6.06
$\Delta\delta$	0.98	-1.52	0.46	-0.90

Where br = bridging, t = terminal, $\Delta\delta = |\delta_b - \delta_t|$.

^a Data from Ref. [10].

^b Data from Ref. [2].

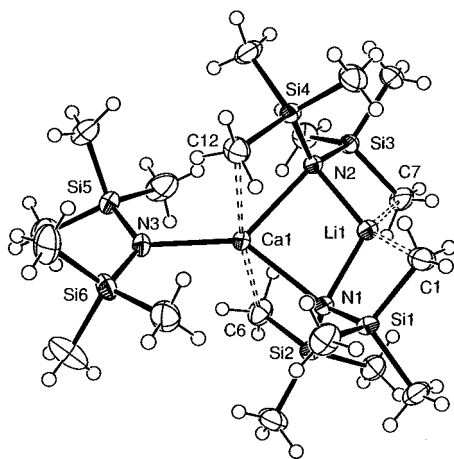


Fig. 1. Molecular structure of $[\text{Li}\{\mu\text{-N}(\text{SiMe}_3)_2\}_2\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}]$.

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths			
Ca(1)–N(1)	2.414(1)	Ca(1)–N(2)	2.426(1)
Ca(1)–N(3)	2.288(1)	Ca(1)⋯C(6)	2.831(2)
Ca(1)⋯C(12)	2.859(2)	Li(1)–N(1)	2.007(3)
Li(1)–N(2)	2.005(3)	Li(1)⋯C(1)	2.368(4)
Li(1)⋯C(7)	2.413(4)		
Bond angles			
N(1)–Ca(1)–N(2)	86.57(4)	N(1)–Ca(1)–N(3)	138.63(5)
N(2)–Ca(1)–N(3)	134.80(5)	N(2)–Ca(1)–C(12)	66.51(5)
N(3)–Ca(1)–C(6)	96.83(6)	C(6)–Ca(1)–C(12)	170.81(6)
N(1)–Li(1)–N(2)	111.6(1)	N(2)–Li(1)–C(1)	128.8(2)
N(1)–Li(1)–C(1)	82.7(1)		

0.07 or 0.12 ppm). From the table it can also be deduced that under the conditions studied the dinuclear molecular structures of the heterometallic compounds remain intact in solution, as they possess different chemical shifts to that of their homometallic precursors. In the $^{13}\text{C}\{^1\text{H}\}$ -NMR data the bridging amide resonances lie at higher frequencies than the terminal ones in the homometallic compounds, but the situation is reversed in the heterometallic analogues. This reversal can be attributed to the strong polarising power of the small alkali metal which has a greater bearing on the electronic structure of the compound.

The crystal structure of compound **1** (Fig. 1) reveals a dinuclear arrangement, the central feature of which is a four-membered $\overline{\text{LiNCaN}}$ planar ring (sum of endocyclic angles 359.96°). Within the structure there are three $[\text{N}(\text{SiMe}_3)_2]$ amide anions, two of which bridge both metal centres with the third bound in a terminal fashion at the larger calcium ion. With respect to nitrogen, the lithium centre occupies a two-coordinate bent geometry [$111.6(1)^\circ$], while the calcium centre occupies a three-coordinate distorted trigonal-planar geometry (a selection of bond distances and angles are shown in Table 2). The same N_3LiCa motif is found in

the structure of the aforementioned THF-solvated analogue, **2** [9] (however, in this case the lithium coordination number is raised to three due to the docking of an external donor molecule in THF). The Li–N bond distances in **1** are significantly shorter than those present in **2**, i.e. mean 2.006 \AA in **1** cf. mean 2.104 \AA in **2**, which can be attributed to the THF molecule in **2** donating electron density to the lithium centre hence lengthening its nitrogen contacts. In trimeric $[\text{LiN}(\text{SiMe}_3)_2]_3$ [11] the mean Li–N distances are the same within experimental error as those in **1**, i.e. mean 2.005 \AA . The endocyclic N–Li–N [$111.6(1)^\circ$] angle in **1** is slightly more obtuse than that in **2** [107.23°] indicating that the introduction of a THF molecule in **2** results in only a modest angular reorganisation about lithium. Turning to calcium, the bridging Ca–N distances in both **1** and **2** are significantly longer than their corresponding terminal Ca–N distances, i.e. Ca–N(br) in **1**, mean 2.420 \AA , in **2**, mean 2.40 \AA cf. Ca–N(t) in both **1** and **2** are identical at 2.288 \AA . The Ca–N(br) distances in compounds **1** and **2** are shorter (by 0.09 \AA) than those present in homometallic $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}]_2$ [12]. This can be explained in terms of the size differential between lithium and calcium, e.g. ionic radii: Li, 0.76 \AA ; Ca, 1.00 \AA , [13], resulting in a concomitant angular distortion about the nitrogen centres, i.e. mean Li–N–Ca angle in **1**, 80.9° ; in **2**, 81.4° , cf. the mean Ca–N–Ca angle in homonuclear $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}]_2$, 90.7° . In contrast, the endocyclic angles at calcium are relatively unaffected by the incorporation of lithium, i.e. N–Ca–N: in **1**, 86.57° ; in **2**, 89.95° ; and in $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}]_2$, mean 89.2° .

Perhaps the most interesting feature of compound **1** is the presence of short intramolecular contacts between the methyl groups of the bridging amide units with both lithium and calcium. This type of interaction, commonly referred to as agostic, is being increasingly found in structural organolithium chemistry, especially where the organic ligand possesses highly polarised functionalities such as the $\text{Si}^\delta+\text{CH}_3^\delta-$ [14,15] ones present here. There are two short $\text{H}_3\text{C}\cdots\text{Li}$ contacts present in compound **1**, i.e. $\text{Li}\cdots\text{C}(1)$, $2.368(4) \text{ \AA}$ and $\text{Li}\cdots\text{C}(7)$, $2.413(4) \text{ \AA}$ (mean 2.39 \AA), which are comparable in length to those found in the Li/Mg analogue (mean 2.31 \AA), but are considerably shorter than the closest $\text{H}_3\text{C}\cdots\text{Li}$ contact present in compound **2** [3.054 \AA]. In **2** the presence of the coordinated THF molecule at lithium increases the steric congestion and provides additional electronic stabilisation, thus $\text{H}_3\text{C}\cdots\text{Li}$ interactions are no longer necessary, hence the methyl groups pivot away from the lithium centre resulting in the shortest $\text{H}_3\text{C}\cdots\text{Li}$ distance (non-bonding) elongating by 0.66 \AA . Turning to calcium, there are two short $\text{H}_3\text{C}\cdots\text{Ca}$ contacts in **1** which belong to the bridging methyl groups, i.e. $\text{Ca}\cdots\text{C}(6)$, $2.831(2) \text{ \AA}$ and $\text{Ca}\cdots\text{C}(12)$, $2.859(2) \text{ \AA}$ [mean 2.85 \AA], which are com-

parable to the shortest contact present in **2**, i.e. 2.912 Å (note that this contact was not mentioned in the report of this structure [9]). It is noteworthy that the dimeric, homometallic amide, $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$, possesses only one short bridging $\text{H}_3\text{C}\cdots\text{Ca}$ contact at 2.855 Å: other distances for this calcium amide lie over a large range, i.e. 3.113–5.480 Å. The aforementioned short bridging $\text{H}_3\text{C}\cdots\text{Ca}$ contacts in **1** are found to be considerably shorter than the intermolecular $\text{H}_3\text{C}\cdots\text{Ca}$ contacts found in $[\text{CaCp}^*\text{AlMe}_3\cdot\text{THF}]_2$ [16], i.e. mean 2.98 Å. Formal Ca–C σ -bonds are as expected, shorter than the above aforementioned intramolecular contacts, e.g. in monomeric $\text{Ca}[\text{C}(\text{SiMe}_3)_3]_2$ [17], their length is 2.459(9) Å in solvated $\text{Ca}[\text{CH}(\text{SiMe}_3)_2]_2\cdot 2\text{C}_4\text{H}_8\text{O}_2$ [18], it is 2.483 Å.

While it is difficult to quantify the importance or otherwise of the $\text{H}_3\text{C}\cdots\text{Li}$ and $\text{H}_3\text{C}\cdots\text{Ca}$ interactions (there is currently much debate on the nature of agostic interactions from theoretical chemists [15]) towards the overall stability of compound **1**, they may have a profound influence on its good solubility properties in hydrocarbon solvent by ensuring that the polar bonds are covered up by a lipophilic shell. Furthermore, it is conceivable that this extra stabilisation hinders the possibility of converting the mixed Li–Ca tris(amide) into an inverse-crown ether. Inspection of the corresponding $\text{H}_3\text{C}\cdots\text{Mg}$ distances in $[\text{Li}\{\mu\text{-N}(\text{SiMe}_3)_2\}_2\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}]$ reveals that the closest contact is 2.830 Å, which, taking into account the smaller radius of magnesium, is perhaps too long to be considered an agostic interaction. Hence, the lack of any agostic stabilisation may be one contributory factor behind the apparent ease with which the $[\text{LiMg}\{\text{N}(\text{SiMe}_3)_2\}_3]$ system forms an inverse-crown ether.

3. Experimental

Reactions were performed under a protective Ar atmosphere using standard Schlenk-line techniques. C, H, N analyses were determined in a Perkin–Elmer 2400 elemental analyser; lithium analysis was carried out by atomic absorption on a PU 9100 Philips spectrometer. Infra-red spectroscopic measurements were carried out in a Nicolet Avatar 360 FTIR spectrometer. ^1H - (400 MHz)/ ^{13}C - (100 MHz)/ ^7Li (155 MHz)-NMR analyses were carried out in a Bruker DPX 400 MHz NMR spectrometer.

To a toluene solution of $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (5 mmol, 1.8 g) was added an equimolar quantity of $[\text{Li}\{\text{N}(\text{SiMe}_3)_2\}]$ (5 mmol, 0.84 g). The resultant yellow solution was stirred for 1 h at room temperature then filtered through a pad of Celite. The filtrate was then placed in the refrigerator at 4 °C for 24 h, to give colourless crystals, identified as the title compound **1**.

Yield 0.48 g, 18.1% (first batch). M.p. 129–134 °C. ^1H -NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 400 MHz, 300 K): 0.28 (s, 18H, t-N(SiMe_3)₂), 0.16 (s, 36H, br-N(SiMe_3)₂). ^{13}C -NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 100 MHz, 300 K): 6.06 (s, t-N(SiMe_3)₂), 5.16 (s, br-N(SiMe_3)₂). ^7Li -NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 155 MHz, 300 K): 1.19 (s). Anal. Calc. for $\text{C}_{18}\text{H}_{54}\text{N}_3\text{CaLiSi}_6$: C, 40.9; H, 10.2; Li, 1.3; N, 8.0. Found: C, 40.6; H, 10.1; Li, 1.3; N, 7.8%. IR spectrum (Nujol mull, KBr): 1245 (vs) $\{\delta_s(\text{CH}_3)\}$, 1177 (w), 1040 (m) $\{v_{\text{as}}(\text{NSi}_2)\}$, 982 (s), 932 (w), 873 (m), 826 (br), 721 (s), 658 (s) $\{v_{\text{as}}(\text{SiC}_3)\}$.

4. X-ray crystallography

A colourless prism of approximate size $0.65 \times 0.45 \times 0.25$ mm was mounted using the oil-drop method. Measurements were made on a Rigaku AFC7S diffractometer at 123 K with Mo–K α radiation ($\lambda = 0.71069$ Å) using ω – 2θ scans. Found triclinic, $P\bar{1}$ $a = 8.911(3)$, $b = 11.765(2)$, $c = 16.471(4)$ Å, $\alpha = 96.52(2)$, $\beta = 95.56(2)$, $\gamma = 102.35(2)^\circ$, $V = 1662.7(8)$ Å³, $Z = 2$. A total of 9208 reflections were collected and corrected for absorption by the ψ -scan method; 8667 were unique ($R_{\text{int}} = 0.0469$) of which 7414 observed ($I > 2\sigma(I)$) were used in the final refinement to convergence on F [19]. All non-H atoms were treated anisotropically and all H atoms isotropically to give $R = 0.0393$ (obs. data only) and $R_w = 0.0574$ (all data).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 171308 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

We thank the EPSRC for their generous sponsorship of this research through grant award no. GR/M78113.

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