DALTON
FULL PAPER

New homo- and hetero-alkali metal alkoxide cages; crystal structures of $[Me_2N(CH_2)_2OLi]_8$ and $[\{Me_2N(CH_2)_2O\}_{12}Li_8K_6]O$

Philip C. Andrews,*[a] Jonathan G. MacLellan,[b] Robert E. Mulvey[b] and Peter J. Nichols[a]

[a] *School of Chemistry, Monash University, Clayton, Melbourne, Vic. 3800, Australia.*
E-mail: p.andrews@sci.monash.edu.au
[b] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK G1 1XL*

Received 29th November 2001, Accepted 12th February 2002
First published as an Advance Article on the web 25th March 2002

The reaction of *N*,*N*′-dimethylaminoethanol (DMAEH), $(Me)_2N(CH_2)_2OH$, with ${}^nBuLi$ and ${}^nBuLi/{}^nBuK$ respectively results in the formation of the homo- and hetero-metallic alkoxides $[Me_2N(CH_2)_2OLi]_8$, **1**, and $[\{Me_2N(CH_2)_2O\}_{12}Li_8K_6]O$, **2**, rather than mixed alkyl–alkoxide species. From single crystal X-ray diffraction studies the two complexes are shown to be highly aggregated cage structures. Complex **1** (monoclinic, *C*2/*c*) adopts a rare octameric structure constructed from a ring stacked hexamer fused with a $(LiO)_2$ dimer creating a sixteen vertex Li–O cluster. Complex **2**, which crystallises (rhombohedral, $R\bar{3}$) with thf and cyclohexane molecules in the lattice, forms a highly symmetrical, almost spherical, cage with an unprecedented Li : K ratio of 8 : 6.

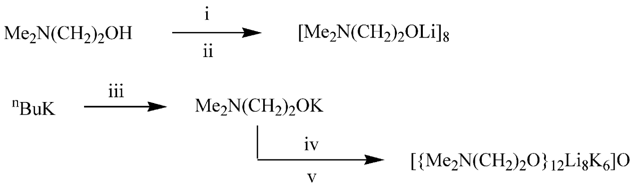
Introduction

Metal alkoxides have been intensively studied and, in recent years, have received increasing attention due to their role as precursors in thin film metal oxide production *via* sol–gel and CVD processes, and as such are of interest in the ceramics and electronics industries.[1,2] However, another important reason for studying metal alkoxides is that mixtures of organolithium compounds (*e.g.* alkyls, amides or enolates) and alkali metal alkoxides have provided extremely useful tools for both synthetic organic and polymer chemists.[3,4] These mixed anion species, commonly referred to as 'superbases', owe their popularity to their exceptionally high deprotonating ability combined with increased selectivity, and in some circumstances stability, when compared with their homometallic mono-anionic counterparts. The involvement of the alkoxide has remained an area of great debate and contention. One reason for the difficulty in identifying the reactive species or providing an explanation for observed increased reactivity has been the inability to obtain crystals of suitable quality for single crystal X-ray diffraction studies. Most systems have proved either insoluble or have yielded microcrystalline products or only one component of the mixture.[5,6] A few model compounds[7] and one proven superbase[8] have been structurally characterised providing support for the hypothesis of mixed aggregate formation. These also indicate the pronounced tendency for lithium–oxygen (alkoxide) bond formation and how this can dictate, to a large extent, the structures produced.

In order to further establish the intrinsic relationship of structure and reactivity in superbases we have turned our attention to those containing only one type of metal. It has been established that lithium alkoxides mixed with organolithium species can have varying effects on reactivity and selectivity; they can lead to no overall change, can actually cause a reduction,[4] or can lead to significant improvements.[9] We feel an understanding of this phenomenon could provide valuable insight in to these mysterious species. Caubère has investigated many homometallic systems[9] and one which caught our interest was that involving a 1 : 1 mixture of lithium dimethylaminoethanolate (LiDMAE) and ${}^nBuLi$ which has been shown to deprotonate 2-substituted pyridines in the unusual C-6 position.[10] By studying the structures formed in this system and comparing them to the known structure of $[\{LiO^tBu\}_4\{{}^nBuLi\}_4]$,[11] which does not act as a superbase, we hoped to begin to answer some interesting questions. We also extended this system to include a study of more usual mixed-metal systems by introducing a potassium alkoxide. From initial investigations we have, as yet, been unable to isolate crystals of an alkyl–alkoxide complex, however, we have isolated and determined the solid state structures of two novel alkali metal alkoxide cages. The first is an octameric cage, $[Me_2N(CH_2)_2OLi]_8$, **1**, and the second an octalithium-hexapotassium oxo-alkoxide cage, $[\{Me_2N(CH_2)_2O\}_{12}Li_8K_6]O$, **2**, both of which to the best of our knowledge adopt previously unseen structural motifs for internally coordinated alkali metal alkoxides.[12]

Results and discussion

The synthetic routes to **1** and **2** are shown in Scheme 1. Addition of thf to the hexane solutions was necessary to solubilise the reaction components with crystals of the alkoxides being obtained on slow cooling of the solutions to ambient temperature from approx. 60 °C. ${}^1H$ and ${}^{13}C$ NMR on isolated crystals in d_6-benzene indicated that the only anion present was $Me_2N(CH_2)_2O^-$, for which the chemical shifts are not unexpected or unusual. In both complexes all the observable proton signals move downfield from those observed in the d_6-benzene solution of the 'free' alcohol (OCH_2 δ 3.51; NCH_2 2.21; NMe_2 1.99). Thus, the triplets for OCH_2 in **1** and **2** are found at δ 4.08 and 4.06, those for the NCH_2 signals at δ 2.44 and 2.51 and the Me signals at δ 2.31 and 2.27 respectively. Despite the presence of K^+, and the bimetallic coordination of O(alkoxide) in **2**, there is no significant effect on the chemical shifts relative to those observed in the homometallic complex **1**.



Scheme 1 Synthesis of **1** and **2**. i = ${}^nBuLi$, 0 °C, hexane; ii = thf; iii = DMAEH, cyclohexane, 0 °C; iv = ${}^nBuLi$, hexane; v = thf.

DOI: 10.1039/b110708a

It was noted though that there were solvent molecules present in the crystals of **2** but not in **1**, and this knowledge of the ratios of the $Me_2N(CH_2)_2O^-$ anion to that of thf and cyclohexane obtained from the ^1H NMR of **2** was crucial in solving the X-ray diffraction data.

Complex **1** crystallises in the space group *C*2/*c* with four molecules in the unit cell. It has an asymmetric octameric structure which can be envisaged as a ring stacked hexamer (a common motif for lithium organic derivatives)[13] with two neighbouring Li–O 'rungs' cleaved to allow inclusion of an additional $(LiO)_2$ dimeric ring, Fig. 1(a). This creates a sixteen vertex Li–O cage overall with six four-membered and four six-membered rings. Selected bond lengths and angles are given in Table 1. Each O has a four-coordinate distorted tetrahedral geometry, bonding to three Li atoms in addition to the alkoxide C atom. O(2) and O(4) have Li–O bond lengths in the narrow range 1.925(2)–1.939(2) Å while O(1) and O(3) each have a short bond (1.894(2) and 1.899(2) Å) and a long one (1.990(2) and 1.994(2) Å). Each Li also has a four-coordinate distorted tetrahedral geometry bonding to three O atoms and one N atom with Li–N bond lengths of 2.189(2) Å for Li(1)–N(3*), 2.157 (2) Å for Li(2)–N(2), 2.186(3) Å for Li(3)–N(1*), and 2.114(2) Å for Li(4)–N(4*) (* denotes symmetry generated atom, #1). The $Me_2N(CH_2)_2O^-$ anions arrange themselves around the cage so as to leave the six-membered rings relatively open or uncovered by the ligand. The easiest way to understand the construction of the cage is to simply look at the arrangement of the LiDMAE fragments in the asymmetric unit, the most important aspects of which are presented in Fig. 1(b). The six-membered $(LiO)_3$ ring results from two internally coordinated LiDMAE molecules, *i.e.* those with Li(1)–O(3) and Li(2)–O(2) at the base of the five-membered ring, being joined by a bridging O anion, O(1), and a bridging Li cation, Li(3). These, in turn, belong to LiDMAE units whose associated O and Li ions are found in the second, symmetry generated, six-membered ring and thus form bonds which can be described as 'rungs'. This bonding arrangement is also observed for the Li and O atoms, Li(4) and O(4), which form the basis of the LiDMAE 'dimer' which attaches to the hexameric cage. This attachment opens two 'rungs' in the hexameric cage and forces the closest 'internally' coordinated LiDMAE units to sit almost perpendicular to the ring plane. Within the Li(1)–O(1)–Li(2)–O(2)–Li(3)–O(3) six-membered ring (and its symmetry equivalent) O–Li–O bond angles are all very similar at 120.9(1)°, 121.9(1)° and 120.4(1)° for Li(1), Li(2) and Li(3) respectively. However, the Li–O–Li angles show greater variation at 118.4(1)°, 109.5(1)° and 110.4(1)° for O(1), O(2) and O(3) respectively. In the other type of six-membered ring; Li(1)–O(1)–Li(3*)–O(3*)–Li(4*)–O(4) (and its symmetry equivalent) O–Li–O angles are again very similar at 121.8(1)° at Li(1), 121.5(1)° at Li(3*) and 120.3(1)° at Li(4*). Li–O–Li angles again have one wider angle of 119.1(1)° at O(3*), with O(1) and O(4) at 108.6(1)° and 109.5(1)° respectively. All six of the four-membered rings are planar with summed bond angles ranging from 359.04–359.16°. The Li–O–Li angles are the more acute averaging 80.7° whilst the O–Li–O angles are greater at an average of 98.9°. In containing only one organic group, alkoxides have reduced steric crowding when compared with other common anions such as alkyls and amides and, therefore, have a greater tendency to form more highly aggregated three-dimensional structures. As such, it is not uncommon for lithium alkoxides to be found as tetramers or hexamers, though they are most commonly found as dimers.[14] However, **1** is only the second example of an octamer. The first, formed from the reaction of neopentanol with $(Me_3Si)_2NLi$, appeared only very recently and has the same $(LiO)_8$ cage structure at it's core.[15] The high aggregations states which are observed for both **1** and **2** are even more surprising given the alkoxide anion contains an 'internal' donor atom (N:) which normally acts to reduce the state of aggregation.

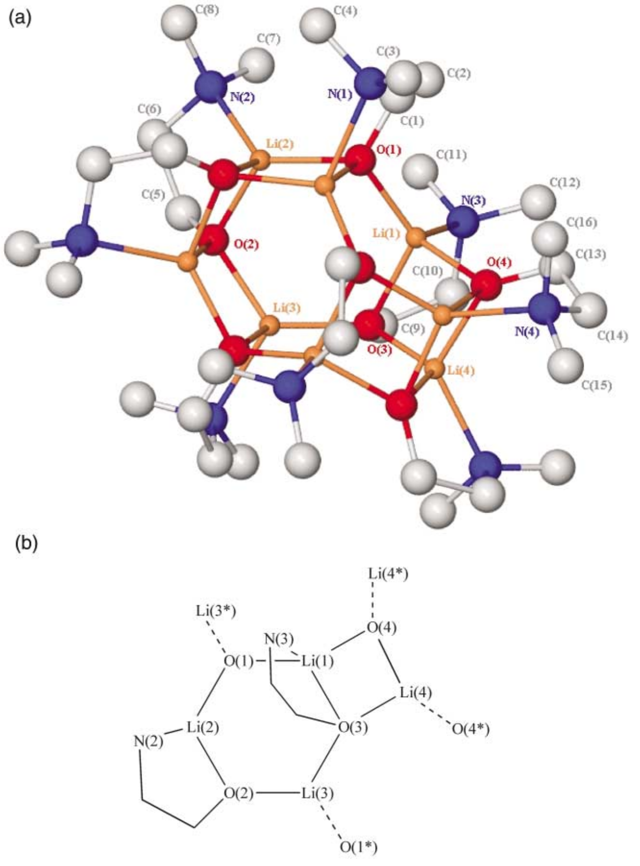


Fig. 1 Crystal structure of $[Me_2N(CH_2)_2OLi]_8$, **1**. (a) Partial representation of the asymmetric unit of **1** with connections (---) to its symmetry equivalent.

Unsolvated, or only partially solvated, alkali metal amides on the other hand, as a consequence of containing an sp^2 N, tend to give rise to two-dimensional ladder structures.[13,16] One favourable comparison in this context is with lithium *tert*-butylamide, $[^tBuN(H)Li]_8$, which is a cyclo-octamer with an isotactic arrangement of ^tBu substituents.[17] This high degree of aggregation for a lithium amide stems from the negligible steric influence of the amido H and the structure adopts a more conventional eight rung cyclic ladder.

Complex **2**·2thf·2/3cyclohexane crystallises in the space group $R\bar{3}$ with three molecules in the unit cell and to the best of our knowledge is the first example of a lithium–potassium compound with an 8Li : 6K stoichiometry. Fig. 2a depicts the asymmetric unit of **2**, though, as shown in Fig. 2b the central feature of **2** is a 27-vertex Li/K oxo-alkoxo cage. Fig. 2c shows how this highly symmetrical, near spherical, structure is built on several interconnecting homo-ionic polyhedra. The centre, or inner core, comprises an eight-coordinate O^{2-} anion which is immediately surrounded by eight Li cations, each occupying a corner of a near perfect cube. Selected bond lengths and angles are given in Table 2. Distances to the central O atom (O3) are 2.526(7) Å for Li(1) and 2.55(1) Å for Li(2). Each square face of the cube has almost ideal right-angles for Li···Li···Li with a range of 89.1(3)–90.7(3)°. Surrounding the Li cube is a dodecahedron of O atoms spaced 1.94 Å from each Li. Eight O atoms form the corners of a cuboid with dimensions (*i.e.* O–O distances) of 3.36 × 3.35 × 4.75 Å. This cuboid is outside the Li cube and twisted to the side such that each Li lies half way along the puckered edges of the O cuboid. All four of the larger faces are then capped by the remaining four O anions to complete the dodecahedron. The smaller 3.36 × 3.35 Å faces are left open. The four outer, or capping, O atoms lie above the centre of an edge on the Li cube. The six K cations then form an elongated rhomboid weaved between the oxygen dodeca-

Table 1 Selected bond lengths (Å) and angles (°) for **1**. Symmetry operator: #1 = $-x, y, -z + 1/2$

O(3)–Li(4)	1.899(2)	N(1)–Li(3)#1	2.186(3)
O(3)–Li(3)	1.906(2)	Li(3)–O(2)	1.931(2)
O(3)–Li(1)	1.994(2)	Li(3)–O(1)#1	1.990(2)
O(4)–Li(1)	1.925(2)	Li(3)–N(1)#1	2.186(3)
O(4)–Li(4)	1.929(2)	N(2)–Li(2)	2.157(2)
O(4)–Li(4)#1	1.935(2)	O(2)–Li(2)#1	1.938(2)
Li(1)–O(1)	1.903(2)	O(2)–Li(2)	1.939(2)
Li(1)–N(3)	2.189(2)	Li(2)–O(2)#1	1.938(2)
O(1)–Li(2)	1.894(2)	Li(4)–O(4)#1	1.935(2)
O(1)–Li(3)#1	1.990(2)	Li(4)–N(4)#1	2.114(2)
N(4)–Li(4)#1	2.114(2)		
Li(4)–O(3)–Li(3)	119.11(10)	O(1)#1–Li(3)–N(1)#1	87.15(9)
Li(4)–O(3)–Li(1)	80.55(9)	Li(3)–O(2)–Li(2)#1	81.09(10)
Li(3)–O(3)–Li(1)	110.41(10)	Li(3)–O(2)–Li(2)	109.52(10)
Li(1)–O(4)–Li(4)	81.58(10)	Li(2)#1–O(2)–Li(2)	81.20(10)
Li(1)–O(4)–Li(4)#1	109.47(10)	O(1)–Li(2)–O(2)#1	100.39(10)
Li(4)–O(4)–Li(4)#1	80.14(11)	O(1)–Li(2)–O(2)	121.88(12)
O(1)–Li(1)–O(4)	121.80(12)	O(2)#1–Li(2)–O(2)	98.32(10)
O(1)–Li(1)–O(3)	120.90(11)	O(1)–Li(2)–N(2)	122.51(11)
O(4)–Li(1)–O(3)	97.19(10)	O(2)#1–Li(2)–N(2)	122.31(11)
Li(2)–O(1)–Li(1)	118.41(11)	O(2)–Li(2)–N(2)	90.25(10)
Li(2)–O(1)–Li(3)#1	80.67(9)	O(3)–Li(4)–O(4)	100.30(10)
Li(1)–O(1)–Li(3)#1	108.61(10)	O(3)–Li(4)–O(4)#1	120.29(12)
O(3)–Li(3)–O(2)	120.36(12)	O(4)–Li(4)–O(4)#1	99.44(10)
O(3)–Li(3)–O(1)#1	121.47(12)	O(3)–Li(4)–N(4)#1	123.08(12)
O(2)–Li(3)–O(1)#1	97.31(10)	O(4)–Li(4)–N(4)#1	122.61(11)
O(3)–Li(3)–N(1)#1	114.48(11)	O(4)#1–Li(4)–N(4)#1	89.79(9)
O(2)–Li(3)–N(1)#1	110.53(10)		

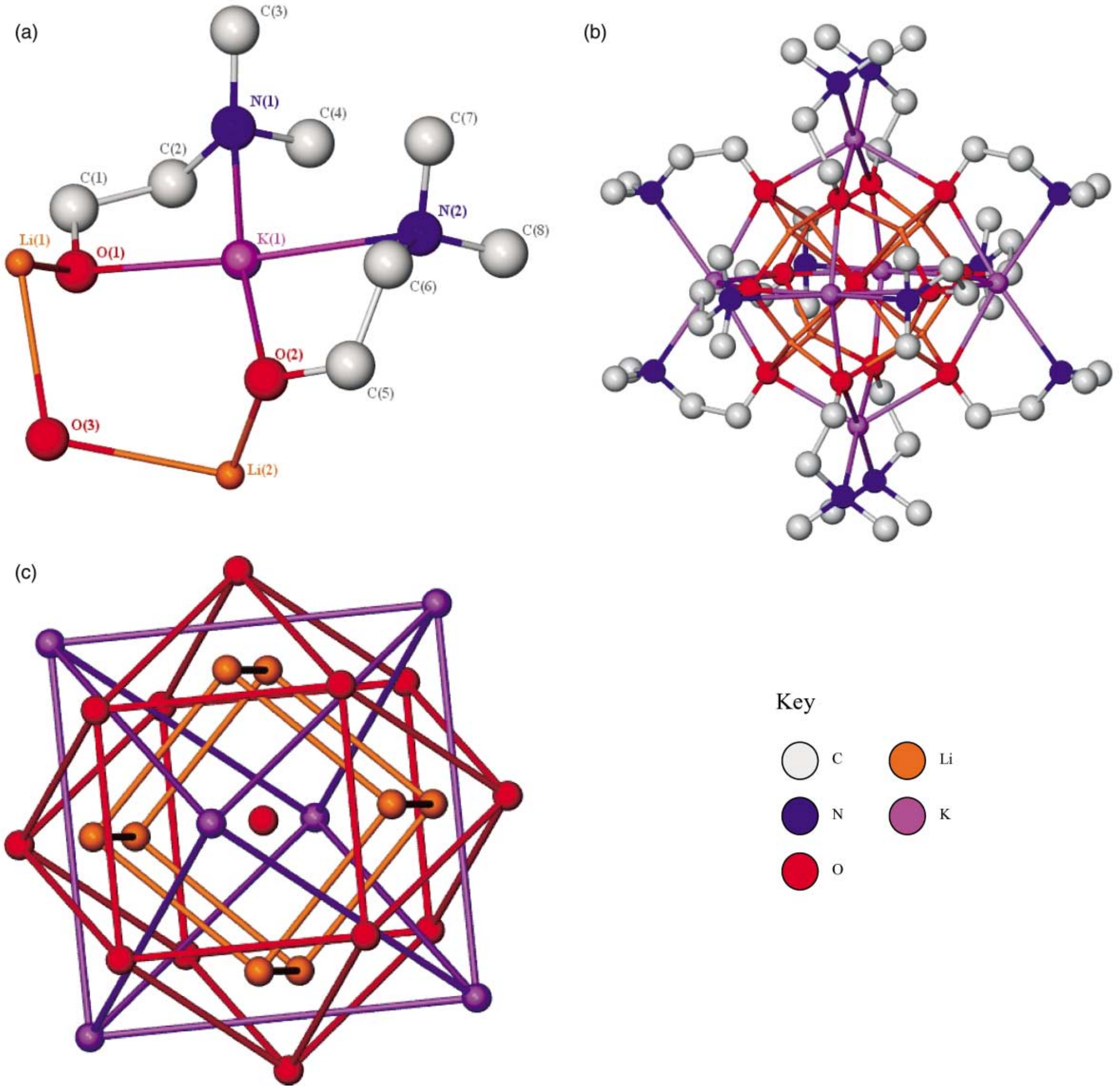


Fig. 2 (a) Asymmetric building block of [$\{Me_2N(CH_2)_2O\}_{12}Li_8K_6$]O, **2**. (b) Crystal structure of [$\{Me_2N(CH_2)_2O\}_{12}Li_8K_6$]O, **2**. (c) Representation of [$\{Me_2N(CH_2)_2O\}_{12}Li_8K_6$]O, **2**, inner core revealing the positonal relationships of the Li cube, O dodecamer and K rhomboid.

Table 2 Selected bond lengths (Å) and angles (°) for **2**. Symmetry operators: #1 = $x - y + 1, x + 1, -z$; #2 = $-x + y - 1, -x + 1, z$

K(1)–O(2)	2.727(3)	Li(1)–O(1)	1.937(7)
K(1)–O(1)	2.731(3)	Li(2)–O(2)	1.941(3)
K(1)–N(2)	2.848(5)	Li(1)–O(3)	2.526(7)
K(1)–N(1)	2.850(4)	Li(2)–O(3)	2.554(12)
O(1)–K(1)–O(1)#1	75.51(6)	O(1)–Li(1)–O(1)#1	119.7(3)
O(1)–K(1)–O(2)#2	75.90(8)	O(1)–Li(1)–O(3)	96.3(3)
O(2)–K(1)–O(1)	120.38(9)	Li(2)–O(2)–Li(1)#1	97.6(4)
O(2)–K(1)–O(2)#2	75.46(11)	Li(2)–O(2)–K(1)	80.32(11)
O(1)–Li(1)–O(3)	96.3(3)	Li(1)–O(3)–Li(2)	109.12(14)
O(2)–Li(2)–O(3)	95.7(4)	Li(2)–O(3)–Li(1)#1	70.88(14)
N(2)–K(1)–N(1)	109.43(14)		

hedron. Four K cations, which form the central square of the bipyramidal shape of the rhomboid, lie inside the four outlying O atoms whilst the two 'apical' K centres are outside the boundaries of the O cuboid situated above the centre of the smaller open face. The K cations possess six-coordinate distorted octahedral geometries bonding to four O(alkoxo) atoms with bond distances ranging from 2.727(3) Å to 2.738(3) Å, and to two N atoms with an average bond distance of 2.85 Å. In the crystal each ethylene backbone is disordered over two sites with C(2) and C(6) each having 50% occupancy. Each cluster packs with disordered solvent molecules loosely bound in the lattice with six thf and two cyclohexane molecules for every three clusters. The thf molecules are non-bonding with the closest M–O distance being over 6 Å.

We believe this structure is unique for alkali metal alkoxides, however, some comparisons with related structures can be made. One previous mixed-lithium potassium oxide/alkoxide complex $[(\mathrm{Bu^tO})_8\cdot\mathrm{Li_8K_2}\cdot(\mathrm{tmeda})_2]\mathrm{O}$, **3**,[18] and one mixed-lithium rubidium peroxide/alkoxide $[(\mathrm{Bu^tO})_9\cdot\mathrm{Li_7Rb_4}\cdot(\mathrm{tmeda})_2]\mathrm{O_2}$, **4**,[19] have been prepared and structurally authenticated, both show some similar structural features to **2**. All three compounds result from incomplete metal–metal exchange reactions *i.e.* a portion of the heavier alkali metal alkoxides (K in **2** and **3** and Rb in **4**) remain in the product. Both **3** and **4** were prepared from the reaction of the homometallic *tert*-butoxide (K, or Rb respectively) and lithium *tert*-butyl amide. As in **2** an $\mathrm{O^{2-}}$ core surrounded by eight Li and eight O atoms is present in **3**, however, it is comprised of two highly puckered $(\mathrm{LiO})_4$ stacked rings and, in order to balance the charge, eight $\mathrm{Bu^tO^-}$ anions and two tmeda solvated K cations are included on either side of this cage. In slight contrast **4** contains a peroxide $\mathrm{O_2}^{2-}$ core with the surrounding cage possessing two-fold rotation symmetry about an axis bisecting the O–O peroxide bond. Along this axis is the one unique Li atom with the remaining six Li atoms comprising the three others and their symmetry generated equivalents. On either side of this central core are two $(\mathrm{Rb{-}O})_2$ dimers with each Rb coordinated by one N of a bridging tmeda molecule, which links the cage into infinite sheets. The Li–O(alkoxide) distances in **2**, **3** and **4** are essentially identical (1.94 Å, 1.95 Å and 1.93 Å respectively) but show significantly different Li–O(oxide) distances, 2.54 Å for **2** but only 2.05 Å for **3** and 2.10 Å to the peroxide in **4**. The K–O(alkoxide) distances are slightly shorter in **2** at 2.74 Å as compared with 2.80 Å in **3**, with K–N distances to the chelating DMAE or tmeda at 2.85 Å and 2.89 Å for **2** and **3** respectively.

The source of the oxygen dianion is at present unclear, however, we suspect it most likely arises from adventitious moisture carried into the reaction mixture by incomplete drying of the alcohol. It's formation has proved to be completely reproducible though we have found it is fully dependent on the presence of traces of moisture in the DMAE. The formation of $\mathrm{O^{2-}}$ is necessary both to allow a charge balance for the unusual K : Li ratio and, we believe, to act as a template for the highly symmetrical structure. A recent review has highlighted the oxygen scavenging behaviour of alkali metal complexes and the importance of oxygen anions in determining structural outcomes.[21] The incomplete transmetallation reaction which leads to **2** must leave behind mixed-anion species in solution {ROM and ^{n}BuM (M = Li and K)}, which are calculated to be the most stable aggregates.[22] However, we have, as yet, been unable to isolate any other crystalline species, and any 'free' ^{n}BuK will react quickly with any residual thf present.

Another key architectural point in **2**, **3**, and **4** is the occupation of the inner metal core positions exclusively by the smaller Li cation, a structural arrangement which has been previously noted[7a] There are two likely reasons. Firstly Li forms more kinetically stable M–O bonds than the heavier alkali metals and Li–O contacts are maximised in the inner core. Secondly, short Li–O bonds mean that structural stability is enhanced by having more tightly bound atom arrangements in the core centre. This size difference of the Li cation in comparison with Na, K and Rb (ionic radii; 0.76, 1.02, 1.38 and 1.52 Å respectively)[23] means that the heavier alkali metals form longer M–O bonds, and are therefore suited to more exterior positions. While in general it would be assumed that the most kinetically stable complex would be the homometallic lithium alkoxide and that complete transmetallation would occur this has been calculated as being unfavourable,[22] and it is also often counteracted by the reduced solubility of the heterometallic complex, leading to precipitation, which then chemically acts against complete transmetallation.

Conclusion

In examining mixed anion alkali metal complexes involving *N*,*N'*-dimethylaminoethanol we have demonstrated that in these systems it is the alkali metal alkoxide cages which are the energetically preferred species formed in the solid state. These cage compounds highlight the tendency for high states of aggregation for the alkoxides even in the presence of internal coordinating donor atoms and in **2**, at least, the preference of inner core positions for Li over that of the other metals. The inclusion of oxo anions in alkali metal chemistry, whether intentional or not, has become commonplace and in some cases despite all attempts to avoid it is seemingly inevitable.[24] Metal oxide/alkoxides have attracted special attention[25] as they represent a structural link between molecular metal alkoxides and macromolecular metal oxides.

Experimental

Preparation of 1, [LiDMAE]$_8$

Following a standard air sensitive protocol, *N*,*N'*-dimethylaminoethanol (10 mmol, 1.00 ml) in hexane was cooled to 0 °C in a Schlenk flask. ^{n}BuLi (10 mmol, 6.25 ml of a 1.6 M hexane solution) was added dropwise. An exothermic reaction ensued depositing a fine white precipitate in a light yellow solution. 2–3 ml of THF was added and the mixture heated until a transparent light yellow solution was achieved. This was cooled slowly to room temperature yielding small colourless crystals of **1**. Yield 0.8 g (84%). Mp 251–252 °C. Elemental analysis for $\mathrm{C_{32}H_{80}N_8O_8Li_8}$, Found (calc.): C, 50.27 (50.53); H, 10.42 (10.6); N, 14.59 (14.74)%. ^{1}H NMR (300 MHz, d$_6$-benzene, 300 K): δ 4.08 (t, 2H, OCH$_2$), 2.44 (t, 2H, NCH$_2$), 2.31 (s, 6H, CH$_3$). ^{13}C NMR (75 MHz, d$_6$-benzene, 300 K): δ 67.5 (OCH$_2$), 62.5 (NCH$_2$), 45.3 (CH$_3$).

Preparation of 2, [{DMAE}$_{12}$Li$_8$K$_6$]O

^{n}BuK (10 mmol, 0.96 g) was suspended in cyclohexane (5 ml) and cooled to 0 °C. To this *N*,*N'*-dimethylaminoethanol (10 mmol, 1.00 ml) was added dropwise resulting in a light brown/yellow solution. This mixture was left to stir overnight before the dropwise addition of ^{n}BuLi (10 mmol, 6.25 ml of a 1.6 M hexane solution) resulting in the immediate precipitation of a dark brown solid. Addition of 5 ml THF and vigorous heating resulted in a dark brown clear solution which was cooled slowly to room temperature yielding small colourless prismatic crystals of **2**·2thf·2/3cyclohexane. Yield 0.34 g (28% based on DMAE). Mp 270–272 °C. Satisfactory microanalysis could not be obtained, most likely due to solvent loss. ^{1}H NMR (300 MHz, d$_6$-benzene, 300 K): 4.06 (t, 2H, OCH_2), δ 3.57 (t, 2H, thf), 2.51 (t, 2H, NCH_2), 2.27 (s, 6H, CH_3) 1.38 (t, 2H, thf), 1.12 (br s, 2H, cyclohexane). ^{13}C NMR (75 MHz, d$_6$-benzene, 300 K): δ 66.8 (OCH_2), 60.5 (NCH_2), 44.2 (CH_3). Proton assignments of solvent molecules are relative only within, and not between, each molecule. Actual ratios are 12 : 2 : 3 for $Me_2N(CH_2)_2O^-$: thf : cyclohexane. Solvent molecules were not observed in the ^{13}C spectrum.

Crystallographic data

1. $C_{16}H_{40}N_4O_4Li_4$, M = 760.56, monoclinic, $C2/c$, a = 18.571(4), b = 13.243(3), c = 19.467(4) Å, β = 95.30(3)°, V = 4767.1(16) Å^3, D_c = 1.060 g cm^{-3}, Z = 4, T = 123(2) K. $F(000)$ = 1664, $\mu_{MoK\alpha}$ = 0.72 cm^{-1}, $2\theta_{max}$ = 56.6°, GooF = 1.077. The structure was determined from 5885 unique reflections (34585 measured, R_{int} = 0.0679); $wR2$ = 0.1447 for all F^2 values, conventional R = 0.0483. All H atoms were placed in calculated positions.

2·2thf·2/3cyclohexane. $C_{60}H_{144}N_{12}O_{15}Li_8K_6$, M = 1564, rhombohedral, $R\bar{3}$, a = 14.895(2), b = 14.895(2), c = 36.505(7) Å, γ = 120°, V = 7014(2) Å^3, D_c = 1.1107 g cm^{-3}, Z = 3, T = 293(2) K, $F(000)$ = 2526, $\mu_{MoK\alpha}$ = 0.34 cm^{-1}, $2\theta_{max}$ = 56.54°, GooF = 0.97. The structure was determined from 3848 unique reflections (26025 measured, R_{int} = 0.0774); $wR2$ = 0.2385 for all F^2 values, conventional R = 0.0844. H atoms were not placed on thf and cyclohexane molecules and were omitted from least squares refinements. The disordered thf has three-fold disorder through the oxygen atom while the cyclohexane is derived from a carbon atom on a special position with six-fold symmetry which is not actually disordered. The populations for the atoms in thf and cyclohexane were as indicated by NMR and required by symmetry.

All data were collected on an Enraf Nonius KappaCCD (λ_o = 0.71073 Å) with crystals mounted on a fibre under oil.

CCDC reference numbers 175465 and 175466.

See http://www.rsc.org/suppdata/dt/b1/b110708a/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank Monash University, the Australian Research Council and the EPSRC (U.K.) for financial support.

References

1 D. C. Bradley, *Chem. Rev.*, 1989, **89**, 1317.
2 W. A. Herrmann, N. W. Huber and O. Runte, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2187.
3 M. Schlosser, *J. Organomet. Chem.*, 1967, **8**, 9.
4 L. Lochmann, *Eur. J. Inorg. Chem.*, 2000, 115.
5 M. Schlosser and S. Strunk, *Tetrahedron Lett.*, 1984, **25**, 741.
6 L. Lochmann, J. Pospisil and D. Lim, *Tetrahedron Lett.*, 1966, **2**, 257.
7 (*a*) A. Streitweiser and S. Harder, *Angew. Chem.*, 1993, **32**, 1066; A. Streitweiser and S. Harder, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1066; (*b*) R. E. Mulvey, F. M. MacKenzie, W. Clegg and L. Horsburgh, *J. Am. Chem. Soc.*, 1996, **118**, 4721; (*c*) A. R. Kennedy, J. G. MacLellan, R. E. Mulvey and A. Robertson, *J. Chem Soc., Dalt. Trans.*, 2000, 4112.
8 A. R. Kennedy, J. G. MacLellan and R. E. Mulvey, *Angew. Chem., Int. Ed.*, 2001, **40**, 3245.
9 P. Caubère, *Chem. Rev.*, 1993, **93**, 2317.
10 P. Gros, Y. Fort and P. Caubère, *J. Chem. Soc., Perkin Trans. 1*, 1997, 3071.
11 M. Marsch, K. Harms, L. Lochmann and G. Boche, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 308.
12 3D Search and Research Using the Cambridge Structural Database, F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 1; F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 31 . Search conducted 1/10/2001.
13 R. E. Mulvey, *Chem. Soc. Rev.*, 1998, **27**, 339; R. E. Mulvey, *Chem. Soc. Rev.*, 1991, **20**, 167; M. A. Beswick and D. S. Wright, *Comprehensive Organometallic Chemistry II*, eds. E. W. Abels, F. G. A. Stone and G. Wilkinson, Pergamon Press, New York, 1995, ch. 1; K. Gregory, P. v. R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47.
14 F. Pauer and P. P. Power, *Lithium Chemistry*, eds. A.-M. Schade and P. v. R. Schleyer, John Wiley & Sons, New York, 1995, pp. 299–314.
15 T. J. Boyle, T. M. Alam, K P. Peters and M. A. Rodriguez, *Inorg. Chem.*, 2001, **40**, 6281.
16 A. Downard and T. Chivers, *Eur. J. Inorg. Chem.*, 2001, 2193.
17 N. D. R. Barnett, W. Clegg, L. Horsburgh, D. M. Lindsay, Q.-Y. Liu, F. M. Mackenzie, R. E. Mulvey and P. G. Williard, *Chem. Commun.*, 1996, 2321.
18 F. M. MacKenzie, R. E. Mulvey, W. Clegg and L. Horsburgh, *Polyhedron*, 1998, **17**, 993.
19 W. Clegg, A. M. Drummond, R. E. Mulvey and S. T. Liddle, *Chem. Commun.*, 1998, 2391.
20 R. Pi, W. Bauer, B. Brix, C. Schade and P. v. R. Schleyer, *J. Organomet. Chem.*, 1986, **306**, C1.
21 A. E. H. Wheatley, *Chem. Soc. Rev.*, 2001, 265.
22 T. Kremer, S. Harder, M. Junge and P. v. R. Schleyer, *Organometallics*, 1996, **15**, 585.
23 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
24 R. E. Mulvey, *Chem. Commun.*, 2001, 1049.
25 R. C. Mehrotra and A. Singh, *Chem. Soc. Rev.*, 1996, **25**, 1.