

# A novel heterometallic alkoxide: lithium–potassium *tert*-butoxide [(Bu<sup>t</sup>O)<sub>8</sub>Li<sub>4</sub>K<sub>4</sub>]

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Synthesised from its homonuclear components in the presence of the Lewis base TMEDA, the title heteronuclear alkoxide crystallises in an unsolvated TMEDA-free form; its novel breastplate-like Li<sub>4</sub>K<sub>4</sub>O<sub>8</sub> cage structure, which undergoes an exchange process in arene solution as determined by dynamic NMR spectroscopic studies, displays a planar K<sub>4</sub> arrangement in marked contrast to the tetrahedral K<sub>4</sub> arrangement found in homonuclear [(Bu<sup>t</sup>OK)<sub>4</sub>].

The chemistry of metal alkoxides has gained greater significance in recent years primarily because of the demand for technologically important oxide materials: metal alkoxides serve as excellent precursors to oxide-based electronic and ceramic materials by sol–gel and MOCVD processes.<sup>1,2</sup> Group 1 alkoxides command additional attention due to their role in two-component ‘superbases’,<sup>3</sup> epitomised by ‘BuLi·Bu<sup>t</sup>OK’, which are utilised widely in synthetic chemistry. As part of our continuing development of hetero-s-block metal chemistry, we have a particular interest in synthesising alkoxides that contain a mixture of Group 1 metals. Having recently reported the octalithium–dipotassium mixed oxide–alkoxide [(Bu<sup>t</sup>OLi)<sub>6</sub>(Bu<sup>t</sup>OK)<sub>2</sub>(Li<sub>2</sub>O)·2TMEDA],<sup>4</sup> the cage structure of which is built around an O<sup>2-</sup> core, we subsequently directed our efforts towards synthesising a pure, oxide-free, analogue. These studies have afforded the new solvent-free heterometallic tetralithium–tetrapotassium alkoxide, [(Bu<sup>t</sup>O)<sub>8</sub>Li<sub>4</sub>K<sub>4</sub>], **1**. Herein we report its synthesis, novel molecular structure, and dynamic NMR spectral data in arene solution.

Whilst many bimetallic alkoxides containing an alkali metal in combination with a less electropositive (p- or d-block) metal have been synthesised by direct reaction of the component homonuclear alkoxides,<sup>5</sup> this strategy has not been used previously as an entry into mixed alkali metal alkoxides. We have found it to be successful here for the synthesis of **1**. To elaborate, in a Schlenk tube under an argon atmosphere, a mixture of Bu<sup>t</sup>OLi (4 mmol) and Bu<sup>t</sup>OK (2 mmol) in toluene (5 ml) solution was heated to 70–80 °C for 20 min. On cooling to room temperature, the solution was treated with dried TMEDA (4 mmol) and stirred for 2 h. All solvent was then removed *in vacuo* to leave an oily pale yellow residue. Almost complete dissolution was achieved by the subsequent addition of hexane (5 ml). After filtering, the resulting solution was cooled to –26 °C for 48 h, at which time colourless crystals of **1** were obtained (yield, based on consumption of Bu<sup>t</sup>OK, 65%). These crystals can be distinguished from their homonuclear components by a simple melting point analysis (*i.e.*, 242 °C, *cf.*, Bu<sup>t</sup>OLi, decomp. > 250 °C;<sup>6</sup> Bu<sup>t</sup>OK, 256–258 °C<sup>7</sup>). The synthesis of **1** proved reproducible on changing the Bu<sup>t</sup>OLi: Bu<sup>t</sup>OK reaction stoichiometry to 1:1 to match that found in the crystal. It is noteworthy that no TMEDA is present in **1** even though it was available in the reaction mixture. This contrasts with the situation encountered in the aforementioned [(Bu<sup>t</sup>OLi)<sub>6</sub>(Bu<sup>t</sup>OK)<sub>2</sub>(Li<sub>2</sub>O)·2TMEDA], and its rubidium relative [(Bu<sup>t</sup>OLi)<sub>5</sub>(Bu<sup>t</sup>ORb)<sub>4</sub>(Li<sub>2</sub>O<sub>2</sub>)·2TMEDA]<sub>∞</sub>.<sup>8</sup> The compositions and structures of these solvates are presumably largely dictated by the templating action of their core dianion, O<sup>2-</sup> or

O<sub>2</sub><sup>2-</sup>. An alternative structure building principle must operate in the absence of such templates; hence it is no surprise that the metal stoichiometry in **1** (4Li:4K) is very different to that in the mixed-anion alkoxides (8Li:2K or 7Li:4Rb). Why such oxygen-based contaminants, and different ones at that, appear in the TMEDA solvates but not in **1** when the same routine ‘inert-atmosphere’ conditions were used in all three cases is not clear at present. Less efficient drying and degassing, leading to adventitious moisture or oxygen participation, is an obvious possibility, but more complex chemistry may be at work. In this regard, it is germane to note that the formation of another heterometallic oxo-alkoxide of potassium, [(Pr<sup>i</sup>O)<sub>10</sub>(O)K<sub>4</sub>Zr<sub>2</sub>],<sup>9</sup> is thought to involve C–O bond scission from Pr<sup>i</sup>OM units.

Possessing exact crystallographic C<sub>s</sub> (*m*) symmetry, the molecular structure of **1**<sup>†</sup> (Fig. 1) displays a distinctive breastplate-like, sixteen vertex Li<sub>4</sub>K<sub>4</sub>O<sub>8</sub> core (Fig. 2). The crystallographic mirror plane runs through Li(1), Li(2), O(1), O(2), O(3), O(4) in the body of the cage, and C(1), C(4), C(7),

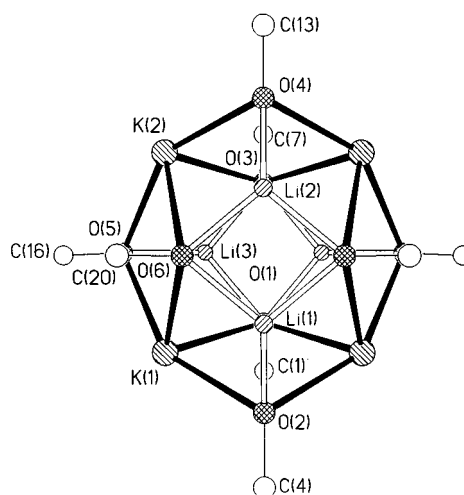


Fig. 1 Molecular structure of **1** with unique atoms labelled (not methyl C). Hydrogen atoms and methyl C atoms have been omitted for clarity. Bonds to K are filled, to Li hollow, to C single line.

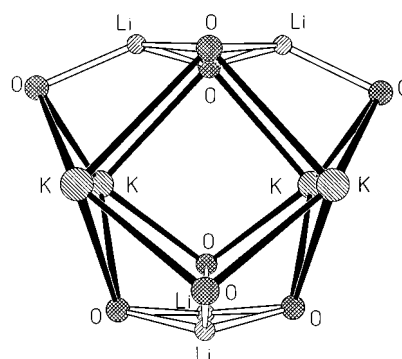


Fig. 2 Sixteen-vertex O<sub>8</sub>Li<sub>4</sub>K<sub>4</sub> ‘breastplate’ core of **1**.

C(10) outside the body. The molecular symmetry is essentially  $D_{2d}$  ( $42m$ ), with Fig. 1 viewed along the  $S_4$  axis. There are 14 MOMO faces: 8(LiOKO), 4(KO)<sub>2</sub> and 2(LiO)<sub>2</sub> types. The Li(3)O(1)Li(3A)O(3) 'neck' and Li(1)O(6)Li(2)O(6A) 'waist' rings lie almost orthogonal to each other. A plane of 4K<sup>+</sup> cations occupies the 'midriff' position. These large cations form the apex of tetragonal pyramidal KO<sub>4</sub> coordination polyhedra. The smaller Li<sup>+</sup> cations form the apex of trigonal pyramidal LiO<sub>3</sub> coordination polyhedra. Half of the O centres [O(2)O(4), O(5)O(5A)] coordinate to 3 metal cations (1Li/2K), while the other half [O(1)O(3), O(6)O(6A)] coordinate to 4 metal cations (2Li/2K). The alkyl foliage completes the structure.

Intriguingly, whilst **1** is formally a 1:1 stoichiometric composite of lithium *tert*-butoxide and potassium *tert*-butoxide, it has a unique structure not made from contiguous fragments of the homonuclear structures [(Bu<sup>o</sup>OLi)<sub>6</sub>]<sup>10</sup> and [(Bu<sup>o</sup>OK)<sub>4</sub>].<sup>7</sup> From a comparison with the homonuclear structures the major reorganisation behind the heterometallic construction has taken place at the 'softer' K<sup>+</sup> centres. First, together they make up a K<sub>4</sub> plane. Second, they occupy the higher (four) coordinate sites which are organised asymmetrically in two short and two long K–O bonds (mean values: 2.463 Å and 2.815 Å, respectively). This contrasts markedly with the tetrahedral K<sub>4</sub> arrangement and symmetrical μ<sub>3</sub>–K–O bonding (mean length, 2.623 Å) found in the cubane [(Bu<sup>o</sup>OK)<sub>4</sub>]. Furthermore, there are no planar (KO)<sub>n</sub> rings in **1** like those observed in other cocomplexes of potassium *tert*-butoxide such as [(cyNLi)<sub>3</sub>Sb]<sub>2</sub>(Bu<sup>o</sup>OK)<sub>3</sub>·*x*-(toluene)<sup>11</sup> or [[PhN(H)]<sub>2</sub>(Bu<sup>o</sup>Li)NaK·(TMEDA)<sub>2</sub>]<sub>2</sub>.<sup>12</sup> There has been only one previous report of a planar K<sub>4</sub> substructure in the aforementioned [(Pr<sup>o</sup>O)<sub>10</sub>(O)K<sub>4</sub>Zr<sub>2</sub>],<sup>9</sup> but this is not strictly analogous as here the four cations are fixed in place by an O<sup>2-</sup> ligand at its centre. Contrary to the situation for K<sup>+</sup>, the Li<sup>+</sup> cations have not had to compromise from their optimum μ<sub>3</sub>-bonding role adopted in [(Bu<sup>o</sup>OLi)<sub>6</sub>] in forming heterometallic **1** [range of Li–O bond lengths, 1.815(3)–1.919(3) Å]. This reflects the 'harder', more strongly polarising character of the smaller alkali metal. Given the strength of Li–O bonding it is perhaps surprising that a larger fragment of [(Bu<sup>o</sup>OLi)<sub>6</sub>] has not been retained in **1**, *cf.* the tetrameric unit in [(Bu<sup>o</sup>Li·Bu<sup>o</sup>OLi)<sub>4</sub>]<sup>13</sup> and the hexameric unit in [(Bu<sup>o</sup>OLi)<sub>10</sub>(LiOH)<sub>6</sub>].<sup>14</sup> The fact that **1** formally contains only dimeric (Bu<sup>o</sup>OLi)<sub>2</sub> fragments suggests that the Lewis base TMEDA may be involved in the mechanism of the reaction without appearing in the final product. Another factor in the construction of **1** is the coordinative flexibility of the alkoxide ligands. Exclusively μ<sub>3</sub>-bonded in the homonuclear precursors, they exhibit both μ<sub>3</sub>- and μ<sub>4</sub>-bonding modes here. Following the expected trend, the μ<sub>4</sub>-O centres form longer bonds (mean: to Li, 1.915 Å; to K, 2.875 Å) than their μ<sub>3</sub>-O counterparts (mean: to Li, 1.811 Å; to K, 2.643 Å).

The <sup>1</sup>H NMR (400 MHz) spectrum of **1** in [<sup>2</sup>H<sub>8</sub>]toluene solution at 295 K reveals two singlet resonances (at 1.25 and 1.31 ppm) in a 1:1 ratio. Assuming the sixteen-vertex cage structure is retained these resonances can be assigned to the two distinct types (μ<sub>3</sub>- or μ<sub>4</sub>-bonded) of butoxide ligand present (there are four of each type). This receives support from the corresponding <sup>13</sup>C NMR (100.6 MHz) spectrum which shows a pair of CH<sub>3</sub> (36.09 and 36.55 ppm) and a pair of (CH<sub>3</sub>)<sub>3</sub>C resonances (66.79 and 67.11 ppm). A variable-temperature <sup>1</sup>H NMR study reveals only one resonance at elevated temperatures with coalescence occurring at 312(±1) K, while the two resonances remain distinct but progressively broaden at lower temperatures down to 183 K. This data is consistent with the exchange of Bu<sup>o</sup>O<sup>-</sup> ligands between three-coordinate and four-

coordinate sites. From the limiting chemical shift difference of 27(±2) Hz, a rate constant *k* of 60 s<sup>-1</sup> can be estimated<sup>15</sup> for the uncoupled exchanging protons: this corresponds to a free energy of activation, Δ*G*<sup>‡</sup>, of 65.9 kJ mol<sup>-1</sup>. The variable-temperature spectra also contain trace amounts of an unknown protic impurity (having chemical shifts of 1.54 and 1.50 ppm at 273 K) which is not involved in the dynamic process.

Perhaps the most interesting aspect of **1** is its remarkable structural similarity to a series of heterobimetallic Group 15–Group 1 or Group 11 imido cage species (*e.g.*, [(As<sub>2</sub>(N-Cy)<sub>4</sub>]<sub>2</sub>Na<sub>4</sub>)];<sup>16</sup> this development, which will be elaborated upon in a full account of this work, may have its origin in the isoelectronic relationship between RO<sup>-</sup> and RN<sup>2-</sup>.

Finally, in view of the relationship of Bu<sup>o</sup>OK to the superbasic reagent 'BuLi·Bu<sup>o</sup>OK' as alluded to earlier, it will be of future interest to probe the interaction of BuLi with the new heterometallic alkoxide.

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## Notes and references

† Crystal data for **1**: C<sub>32</sub>H<sub>72</sub>K<sub>4</sub>Li<sub>4</sub>O<sub>8</sub>, *M* = 769.1, monoclinic, space group *P*2<sub>1</sub>/*m*, *a* = 11.5194(6), *b* = 17.1506(10), *c* = 13.0058(7) Å, β = 110.166(2)°, *U* = 2412.0(2) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.059 g cm<sup>-3</sup>, μ = 0.41 mm<sup>-1</sup> (Mo-Kα, λ = 0.71073 Å), *T* = 160 K; *R* (*F*<sup>2</sup> > 2σ) = 0.0324, *R<sub>w</sub>* (*F*<sup>2</sup>, all data) = 0.0880, for 4372 unique data (10325 measured, *R<sub>int</sub>* = 0.0192, 2θ < 50°, CCD diffractometer) and 266 refined parameters, including three-fold disorder of the C(7) *tert*-butyl group. Programs: standard Bruker AXS control and integration software and SHELXTL. CCDC 182/1324. See <http://www.rsc.org/suppdata/cc/1999/1569/> for crystallographic files in .cif format.

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