Synthesis and structure of the novel heptalithiumtetrarubidium mixed alkoxide peroxide [{$(\mathrm{Bu^tOLi})_5(\mathrm{Bu^tORb})_4(\mathrm{Li_2O_2})\cdot 2\mathrm{tmeda}\}_\infty$]: twenty-two vertex cage molecules linked by Rb–TMEDA–Rb bridges

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Made by a metal–metal partial exchange reaction involving lithium *tert*-butylamide, rubidium *tert*-butoxide and TMEDA, the title compound represents the first mixed lithium–rubidium organoelement species of its type.

Recent times have witnessed a revival of interest in metal alkoxides. Considerable attention has been paid to them as precursors for the deposition of metal oxides used in the electronics and ceramics industries.[1] Within preparative chemistry, they are best known for their role in two-component superbasic mixtures, typified by '$\mathrm{BuLi\cdot KOBu^t}$', which often succeed where orthodox alkyllithium reagents fail in difficult proton abstraction applications.[2] Also, the stereochemical rigidity of the $\mathrm{Bu^tO^-}$ ligand frequently aids the crystallisation process, thus permitting the gathering of valuable structural information from X-ray crystallographic studies. Recent important crystal structures in this category of $[(\mathrm{C_6H_{11}O^-})_4(\mathrm{Bu^tO^-})_4(\mathrm{Li^+})_4(\mathrm{K^+})_4(\mathrm{KOH})\cdot 5\mathrm{THF}]$,[3] $[(\mathrm{Bu^tOLi})_{10}(\mathrm{LiOH})_6]$,[4] $[\{[\mathrm{PhN(H)}]_2(\mathrm{Bu^tO})\mathrm{LiNaK}\cdot 2\mathrm{TMEDA}\}_2]$,[5] and $[\{(\mathrm{cyNLi})_3\mathrm{Sb}\}(\mathrm{Bu^tOK})_3\cdot x\mathrm{PhMe}]$,[6] respectively give insight into the nature of alkoxide–enolate interactions, the intermediates involved in the hydrolytic degradation of lithium alkoxides, the architecture of an amide–alkoxide model superbase, and the assembling of large polyamidoantimony anionic cage complexes. In earlier work we reported the crystal structure of an octalithium dipotassium mixed oxide alkoxide, which can be formally represented as $[(\mathrm{Bu^tOLi})_6(\mathrm{Bu^tOK})_2(\mathrm{Li_2O})\cdot 2\mathrm{TMEDA}]$ **1**.[7] This was prepared by a permutational metal–metal exchange reaction [eqn. (1)], which was incomplete in the sense that a proportion of the potassium *tert*-butoxide reactant molecules remains in the product as part of **1**. We pondered whether this same synthetic strategy applied to rubidium *tert*-butoxide could generate a mixed lithium–rubidium compound, in the knowledge that hitherto no such compound exists in the Cambridge Crystallographic Database.[8] The dearth of studies in organorubidium chemistry generally, flagged in a recent review,[9] provided another incentive for pursuing this topic. As revealed herein, our goal has been realised through the synthesis and crystallographic characterisation of the heptalithiumtetrarubidium mixed alkoxide peroxide $[\{(\mathrm{Bu^tOLi})_5(\mathrm{Bu^tORb})_4(\mathrm{Li_2O_2})\cdot 2\mathrm{TMEDA}\}_\infty]$ **2**, the composition, structure, and bonding of which are unprecedented.

$$\mathrm{Bu^tN(H)Li} + \mathrm{Bu^tOK} \xrightarrow{\mathrm{TMEDA}} 1/x[(\mathrm{Bu^tOLi})_6(\mathrm{Bu^tOK})_2(\mathrm{Li_2O})\bullet 2\mathrm{TMEDA}] + \text{other products} \qquad (1)$$

Standard inert-atmospheric (argon) Schlenk techniques were employed throughout the preparative procedure. Rubidium *tert*-butoxide was pre-prepared as a white powder by a literature method,[10] and subsequently suspended in hexane. To this was added an equimolar amount of $\mathrm{Bu^tN(H)Li}$ (in hexane), prepared *in situ* beforehand by lithiation of *tert*-butylamine. The resulting mixture was heated to reflux for 1.5 h, then filtered to remove fine solids leaving a transparent brown solution. Addition of TMEDA (1 mol equivalent) caused the solution to darken. Refrigerating the solution at *ca.* 4 °C for 48 h afforded colourless crystals of **2** [eqn. (2)]. Based on consumption of butoxide molecules the yield obtained was 51%. Satisfactory C, H, Li, N, Rb analyses were obtained. No other product could be crystallised despite prolonged cooling of the solution remaining following removal of **2** (analogous to the situation found with **1**). This is perhaps not surprising since the leftover solutions in containing a mixture of amide (mainly) and butoxide molecules can be likened to a type of superbase, which is a class of compound notoriously difficult to crystallise.

$$\mathrm{Bu^tN(H)Li} + \mathrm{Bu^tORb} \xrightarrow{\mathrm{TMEDA}} 1/x[\{(\mathrm{Bu^tOLi})_5(\mathrm{Bu^tORb})_4(\mathrm{Li_2O_2})\bullet 2\mathrm{TMEDA}\}_\infty] + \text{other products} \qquad (2)$$

The structure of **2** (Fig. 1)† consists of polynuclear $(\mathrm{Bu^tO})_9(\mathrm{O_2})\mathrm{Li_7Rb_4}$ cages (Fig. 2) which link together *via* Rb–TMEDA–Rb bridges. As Fig. 3 shows, this produces polymeric sheets, arranged in layers such that the cages in one sheet run orthogonal to those in the next sheet. The cage possesses exact twofold rotation symmetry about the O(5)···Li(2) axis which bisects the peroxide O(6)–O(6A) bond; the $\mathrm{Bu^t}$ group on O(5) is disordered over two orientations. Thus there are three pairs of Li

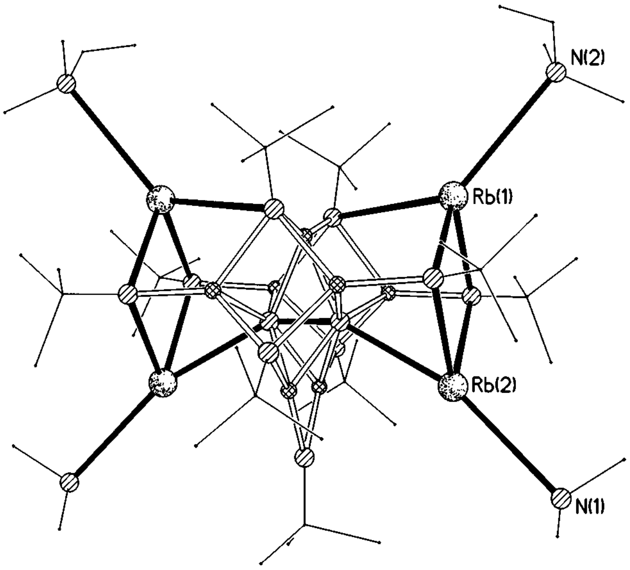

Fig. 1 Double asymmetric unit of **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Rb(1)–N(2) 3.267(7), Rb(2)–N(1) 3.126(7), Rb(1)–O(1) 2.743(5), Rb(1)–O(2) 2.748(5), Rb(1)–O(4) 3.393(5), Rb(2)–O(6) 2.749(4), Rb(2)–O(1) 2.841(5), Rb(2)–O(2) 2.851(5), Li(1)–O(1) 1.873(12), Li(1)–O(3A) 1.944(12), Li(1)–O(4) 2.038(13), Li(1)–O(6) 2.333(11), Li(2)–O(4) 1.844(6), Li(2)–O(6) 1.937(17), Li(3)–O(2) 1.907(13), Li(3)–O(3) 1.934(13), Li(3)–O(4A) 2.101(14), Li(3)–O(6) 2.278(13), Li(4)–O(5) 1.830(14), Li(4)–O(3) 1.876(13), Li(4)–O(6) 1.968(12), Li(4)–O(6A) 1.971(13).

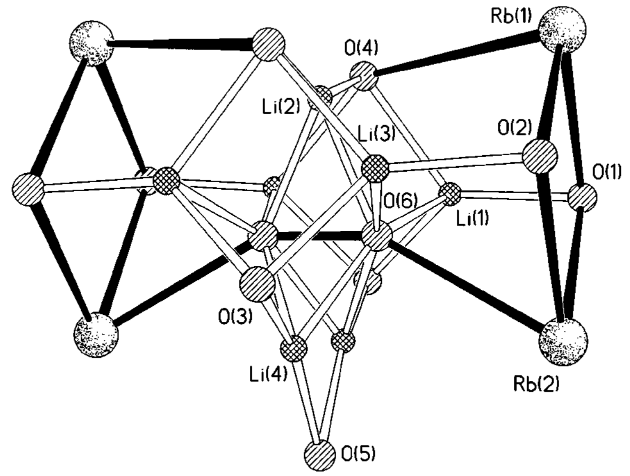

Fig. 2 Twenty-two $O_{11}Li_7Rb_4$ vertex cage core of **2**, with atom labelling.

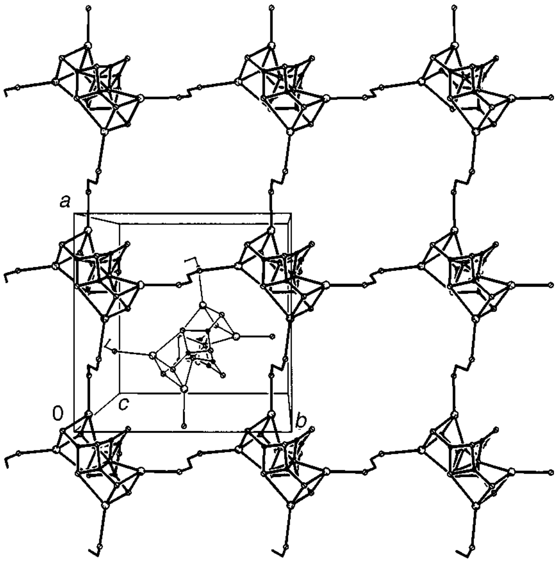

Fig. 3 View showing layer arrangement of polymeric **2**, without Bu^t and TMEDA methyl groups. For clarity, only one cage unit is shown in the further layer.

centres [Li(1), Li(3), Li(4) and their symmetry equivalents] and a unique Li(2), each in a distorted tetrahedral environment; two pairs of distorted tetrahedral Rb centres [Rb(1), Rb(2) with their equivalents]; three pairs of four-coordinate [O(1), O(2), O(3)] and one pair of five-coordinate [O(4)] butoxide O centres and a unique three-coordinate O(5); and a single peroxo unit [O(6)–O(6A)]. The (butoxide) O–Li bond lengths span a wide range [1.830–2.101 Å] reflecting the various coordination numbers involved. This compares with a range of 1.856–2.063 in **1**. Excluding the long O(4)–Rb(1) contact [length 3.393(Å)], the (butoxide) O–Rb bond lengths in **2** have a mean value (2.796 Å) close to that in the [(Bu^{t}ORb)$_4$] cubane (2.757 Å).[10] To the best of our knowledge, **2** provides the first example of Rb–TMEDA–Rb bridging (mean N–Rb bond length, 3.197 Å), though bridges of this type have long been known for lithium, *e.g.* in [{(MeLi)$_4$·2TMEDA}$_\infty$][11] and [{(Bu^{n}Li)$_4$·TMEDA}$_\infty$].[12] The peroxo O(6)–O(6A) molecule in **2** is side-on coordinated by Li(2), Li(4) and Li(4A) (mean length, 1.958 Å) forming three OOLi triangles. A similar arrangement exists within the peroxide fragment of the triple-anion structure of [{(Me$_3$SiOLi)$_4$·Li$_2$O$_2$·(Me$_3$Si)$_2$NLi}·2THF] [mean peroxo O–Li bond length, 2.002 Å],[13] which coincidentally also contains seven Li centres. Additional end-on coordinations of O(6) and O(6A) in **2** occurs *via* Li(1), Li(3) and Rb(2) (mean lengths: O–Li 2.306 Å, O–Rb 2.749 Å). The O–O bond itself measures 1.541(9) Å, in good agreement with that (1.557 Å) in the aforementioned triple-anion structure. Here the presence of the peroxide molecule demonstrates again the strong oxophilic nature of metal alkoxides, which in **1** manifests itself in the form of oxo (O^{2-}) ions. Peroxide incorporation has also been reported in the barium diketonate [(thd)$_{10}$(O$_2$)(H$_2$O)$_6$Ba$_6$] (thd = 2,2,6,6-tetramethylheptane-3,5-dionate),[14] while both peroxo and oxo ions appear in the mixed lithium–magnesium amide [{(Me$_3$Si)$_2$N}$_4$Li$_2$Mg$_2$(O$_2$)$_x$(O)$_y$].[15] Obviously the mode of formation of such anions is complex and as such, is not yet understood.

Recorded in [^{2}H$_8$]toluene solution at 300 K, the ^{1}H NMR (400 MHz) spectrum of **2** exhibits two broad Bu^{t}O resonances centred at 1.25 and 1.44 ppm in an approximate ratio of 5 : 4. The former resonance can be tentatively assigned to the five cage Bu^{t}O$^-$ ligands bound only to Li centres (provided the long O–Rb contacts are disregarded). Significantly, pure Bu^{t}OLi comes at a near-identical chemical shift (1.26 ppm). Likewise, the latter resonance can be assigned to the four cage Bu^{t}O$^-$ ligands bound to mixed Li/Rb centres. Interestingly, the order and chemical shifts of the TMEDA resonances (CH$_2$, 2.32 ppm; Me, 2.11 ppm) are characteristic of uncoordinated molecules. Hence the implication is that the Li$_7$Rb$_4$ cage remains intact, but that the Rb–TMEDA–Rb bridges linking them together in the solid state, cleave in solution. This could explain why **2** is soluble in arene solvents.

In conclusion, we have demonstrated that a metal–metal partial exchange methodology between a rubidium alkoxide and a lithium amide can successfully yield a mixed lithium–rubidium crystalline product, the first of its type. Future work will examine whether the presence of amide ligands is essential for the crystallisation of such novel compositions; or are they accessible by simply mixing together the appropriate homometallic alkoxides?

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Notes and references

† *Crystal data* for **2**: $C_{48}H_{113}Li_7N_4O_{11}Rb_4$, M = 1312.9, tetragonal, $P4_12_12$, $a = b =$ 14. 7025(14), c = 35.956(4) Å, V = 7772.4(14) Å^3, Z = 4, T = 160 K. The structure was determined from 6844 unique reflections (46913 measured, $\theta \leqslant 25°$, $R_{\text{int}} = 0.106$) and refined[16] to $wR2 = 0.168$ on all F^2 values, conventional $R = 0.058$ for F values of 5001 reflections with $F_o^2 > 2\sigma(F_o^2)$; 349 parameters, including an absolute structure parameter[17] of 0.002(15); final difference map between +1.00 and −0.41 e Å^{-3}. CCDC 182/1042.

1 D. C. Bradley, *Chem. Rev.*, 1989, **89**, 1317.
2 A. Mordini, in *Advances in Carbanion Chemistry*, ed. V. Snieckus, JAI Press, London, 1992, vol. 1, p. 1.
3 P. G. Williard and G. J. MacEwan, *J. Am. Chem. Soc.*, 1989, **111**, 7671.
4 C. Lambert, F. Hampel, P. v. R. Schleyer, M. G. Davidson and R. Snaith, *J. Organomet. Chem.*, 1995, **487**, 139.
5 F. M. Mackenzie, R. E. Mulvey, W. Clegg and L. Horsburgh, *J. Am. Chem. Soc.*, 1996, **118**, 4721.
6 D. Barr, A. J. Edwards, M. A. Paver, P. R. Raithby, M.-A. Rennie, C. A. Russell and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1012.
7 F. M. Mackenzie, R. E. Mulvey, W. Clegg and L. Horsburgh, *Polyhedron*, 1998, **17**, 993.
8 F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 31.
9 R. Snaith, in *Specialist Periodical Reports, Organometallic Chemistry*, the Royal Society of Chemistry, Cambridge, 1998, vol. 26, p. 1.
10 M. H. Chisholm, S. R. Drake, A. A. Naiini and W. E. Streib, *Polyhedron*, 1991, **10**, 337.
11 H. Köster, D. Thoennes and E. Weiss, *J. Organomet. Chem.*, 1978, **160**, 1.
12 N. D. R. Barnett, R. E. Mulvey, W. Clegg and P. A. O'Neil, *J. Am. Chem. Soc.*, 1993, **115**, 1573.
13 C. Drost, C. Jäger, S. Freitag, U. Klingebiel, M. Noltemeyer and G. M. Sheldrick, *Chem. Ber.*, 1994, **127**, 845.
14 A. Drozdov and S. Troyanov, *Polyhedron*, 1996, **15**, 1747.
15 A. R. Kennedy, R. E. Mulvey and R. B. Rowlings, *J. Am. Chem. Soc.*, 1998, **120**, 7816.
16 G. M. Sheldrick, SHELXTL user manual, version 5, Bruker AXS Inc., Madison, WI, 1998.
17 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.

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