Synthesis and X-ray structures of tetralithium derivatives of *tert*-butylcalix[4]arene containing unique Li–O cores based on a square-pyramidal geometry

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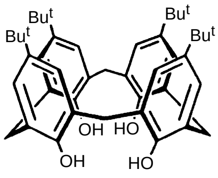
Tetralithiation of *tert*-butylcalix[4]arene in the presence of hmpa (hexamethylphosphoramide) results in the isolation of either a monomeric complex in which LiOH is incorporated into an Li_5O_5 core based on an isolated square pyramid of Li atoms, or a dimeric LiOH-free species containing an Li_8O_8 core in which the same structural motif is maintained by edge-sharing of two square pyramids of Li atoms.

Both underivatised and partially O-alkylated calixarenes have attracted much attention as phenolic ligands for both transition and p-block metals. The flexible orientation of the coordinating phenolic oxygen atoms, coupled with the potential for multimetallations has recently led to reports of some fascinating and unique structures.[1,2] Although the interaction of alkali metals with neutral lower-rim-modified calixarenes is well known,[1] the isolation and characterisation of homometallic phenoxy-bound alkali-metal derivatives of calixarenes is restricted to only one Cs-[3] and one Na-containing[4] example. Floriani *et al.* have very recently reported the syntheses and X-ray structures of some mixed alkali-metal–transition metal–calixarene complexes[5] although in these cases solvation of the alkali metal is exclusively in the cavity of the calixarene. In the light of these considerations and also in view of the unusual structural chemistry that has recently been found to result from multilithiations of organic molecules[6] we felt it was timely to consider the simple metallation of calixarenes with s-block metals. We herein report our preliminary results concerning the simple reaction of Bu^nLi with *tert*-butylcalix[4]arene H_4L (below) which has resulted in the isolation and X-ray structural characterisation of two related tetralithiated calixarenes.



H_4L

Reaction of H_4L in toluene solution with 4 equiv. of Bu^nLi in the presence of an excess of hexamethylphosphoramide hmpa (used as received, without pre-drying, *vide infra*) resulted in the formation of a fine white precipitate suspended in a pale yellow solution. Dissolution of this solid by warming to 100 °C and then cooling to room temp. afforded a crop of colourless, air-sensitive crystals. Preliminary characterisation by IR (in particular a strong sharp O–H stretch at 3612 cm^{-1}) and ^1H NMR spectroscopies, and then an X-ray crystal structure† revealed the isolated product to be $Li_4L\cdot LiOH\cdot 4hmpa$ **1**. In the solid state (Fig. 1) the molecule lies on a crystallographic twofold axis. The four coplanar Li atoms which formally metallate the calixarene lie below the plane defined by the O atoms of the calixarene's lower rim. Each of the Li atoms is coordinated to a neutral hmpa molecule. Together, the four hmpa ligands create a lower rim cavity of similar dimensions to that defined by the four aryl groups of the calixarene on the opposite side of the macrocycle, which itself retains a normal cone configuration. In spite of their similar proportions the two cavities are electronically very different. The bottom of the upper cavity is anionic (O^- lined) while the lower one is cationic (Li^+ lined) in nature, which facilitates the complementary binding of a Li^+ cation [Li(3) bound to all four phenolic oxygen atoms] and an OH^- anion [O(99), μ_4-bridged to the four coplanar Li atoms]. An additional feature of the structure of **1** is that both the normal upper rim cavity and the novel lower rim cavity (defined by the hmpa ligands) act as hosts for guest toluene molecules (not shown in the figure), emphasising their similar dimensions. Thus overall, the structure of **1** may be viewed as resulting from the incorporation of LiOH into a Li_4L moiety; Li(3)···O(99) [2.25(1) Å] is longer than other Li–O bonds within the core of **1** [1.92(1)–2.089(4) Å] though an interaction between the two is still probable.

The incorporation of LiOH and Li_2O into organolithium compounds, whether deliberately or serendipitously, has been reported before,[7] and in order to probe the source of the LiOH unexpectedly incorporated into **1**, and to obtain an LiOH free complex, similar reactions were carried out using a freshly dried (over activated 13X molecular sieve) sample of hmpa. Analysis of the resulting crystalline solid, again ultimately by X-ray crystallography,† revealed the composition of complex **2** to be $(Li_4L\cdot 2hmpa)_2$. In the solid state **2** is dimeric, is free from LiOH, and has only two rather than four hmpa molecules per calixarene (Fig. 2). The crystallographic asymmetric unit consists of two independent but geometrically and chemically similar Li_4O_4 'monomeric' units which then give centrosymmetric 'dimeric' aggregates. Within the Li_8O_8 core there are

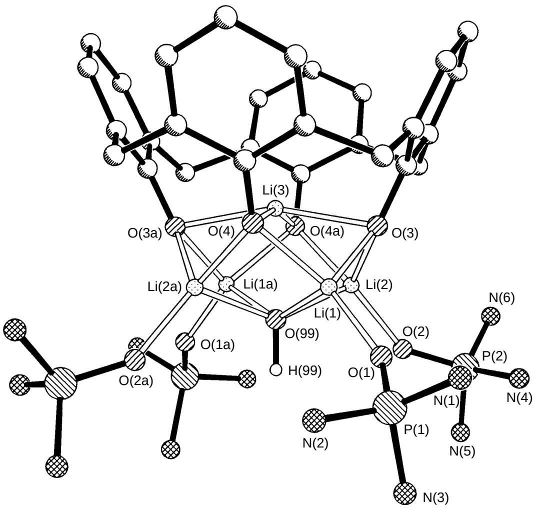


Fig. 1 Molecular structure of **1**; for clarity, all hydrogen atoms, calixarene Bu^t groups, hmpa methyl groups and lattice solvent are omitted

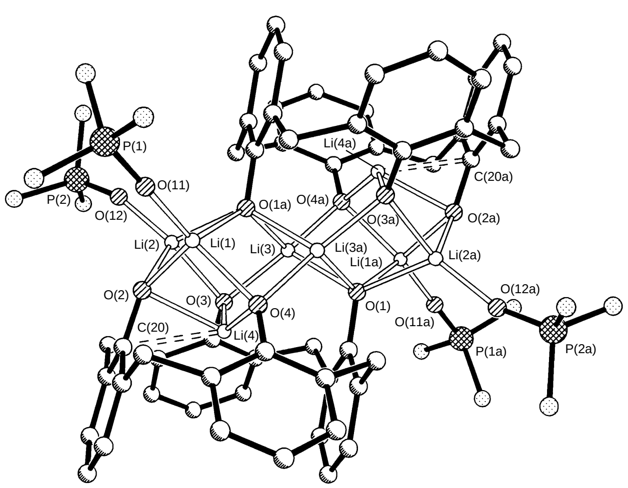


Fig. 2 Molecular structure of **2** (only one of two crystallographically independent but chemically similar molecules is shown). For clarity, all hydrogen atoms, calixarene Bu^t groups, hmpa methyl groups and lattice solvent are omitted.

three distinct lithium environments: two Li atoms [Li(1) and Li(2)] are complexed by hmpa and retain a similar environment to that found for the four coplanar Li atoms of **1**; Li(3) is uncomplexed by hmpa and bridges the two calixarenes; and Li(4) lies within the calixarene cavity. One oxygen atom [O(1)] fulfils the μ_4-capping role played by O(99) in **2**, resulting in a distortion of the original cone conformation of the calixarene. Thus, Li(4) is bound to only three O atoms which prompts an interaction with the π-system of one of the calixarene aryl groups [Li(4)–C(20) 2.31(1) Å]. The distance between O(1) and Li(4a) (> 2.8 Å) is considerably longer than the corresponding Li$\cdots$O separation found in **1**. Other Li–O distances within the core of **2** [1.91(1)–2.11(1) Å] are comparable to those found in **1**. Thus, despite being free of LiOH, in **2** the same general structural features are present as in **1**: a Li$^+$ cation lies in the O lined cavity of the calixarene and an O$^-$ anion caps four Li atoms. The ^{1}H NMR spectrum of **2** suggests that the complex retains a distorted cone configuration in solution: three resonances assigned to Bu^t groups (relative integrals 2 : 1 : 1) and three corresponding Ar–H resonances are observed, which is consistent with the asymmetry of the calixarene seen in the solid state, and contrasts with the equivalence of Bu^t groups (and Ar–H protons) in the ^{1}H NMR spectrum of **1**.

In the light of the structures of **1** and **2**, one can envisage the latter as being suited to act as a carrier for inorganic salts by binding the ion-separated components of the salt in two complementary cavities, resulting in a complex for which **1** is a model. In contrast to the work described by Floriani,[5] in which the shape of the calixarene cavity was modified using Nb or Ta in order to accommodate alkali-metal cations, the structures of **1** and **2** suggest that significant deviation from the normal cone configuration is unnecessary in order to bind lithium within the cavity.

Although **2** can be reproducibly prepared using dried hmpa, the synthesis of **1** has not to date been reproduced, even though spectroscopic evidence suggests that its crystal structure is representative of the bulk product obtained. The source of LiOH incorporated in **1** remains an open question. Although the use of ‘wet’ hmpa is consistent with the product obtained, it is possible that LiOH present in the sample of Bu^{n}Li used,[7c] or contamination from another source was responsible. We are currently investigating the incorporation, by controlled and reproducible means, of s-block metal salts (including LiOH) into lithiated calixarene derivatives.

Also of note in these structures are the geometries of the Li_5O_5 and Li_8O_8 cores of **2** and **3**. Both are best viewed as derived from a square-pyramidal structural motif (Fig. 3). In **2** all five faces of an isolated square pyramid of lithium atoms are capped by oxygen atoms [four μ_3 and one μ_4, Fig. 3(*a*)]. In **2**, the same motif persists, though here two square pyramids of lithium share one edge and the inner triangular face of each is uncapped leaving the eight oxygen atoms to cap the other eight faces [six μ_3 and two μ_4, Fig. 3(*a*)]. To our knowledge, these are the first observations of such a structural motif in organolithium chemistry, though pentanuclear organolithium species of any geometry are extremely rare.[8] The arrangement of a square plane of lithium atoms capped by a μ_4 oxygen atom is, however, reminiscent of an isolated fragment of the polymeric layered structure of LiOMe.[9]

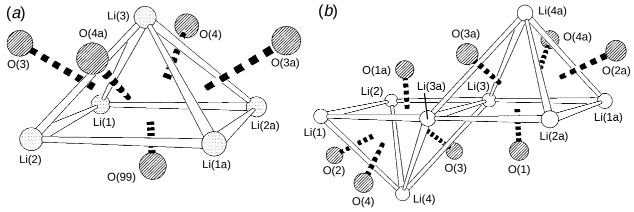


Fig. 3 Li–O cores of (*a*) **1** and (*b*) **2**; connections between lithium atoms are not intended to imply bonding interactions

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Footnotes and References

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† *Crystal data*: **2**: colourless crystals of $C_{68}H_{125}Li_5N_{12}O_9P_4 : 3.9 C_5H_5CH_3 \cdot 0.1H_2O$, orthorhombic, space group *Pbca*, M = 1771.28, a = 18.380(3), b = 28.436(6), c = 19.724(3) Å, U = 10309(3) Å^3, Z = 4. Data collection at T = 150 K, $wR(F^2$, all data) = 0.2484, $R(F$, obs. data) = 0.0887.

3: colourless crystals of $C_{136}H_{200}Li_8N_{12}O_{12}P_4$ triclinic, space group $P\bar{1}$ (no. 2), M = 2374.48 a = 15.435(2), b = 16.891(2), c = 30.674(3) Å, α = 95.66(1), β = 90.68(1), γ = 116.71(4), U = 7094(1), Z = 2. Data collection at T = 150 K, $wR(F^2$, all data) = 0.4154, $R(F$, obs. data) = 0.1322.

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