Synthesis and Structural Analysis of the Polymetallated Alkali Calixarenes $[M_4(p\text{-}tert\text{-butylcalix[4]arene-4H})(thf)_x]_2 \cdot n\,THF$ (M = Li, K; $n = 6$ or 1; $x = 4$ or 5) and $[Li_2(p\text{-}tert\text{-butylcalix[4]arene-2H})(H_2O)(\mu\text{-}H_2O)(thf)] \cdot 3\,THF$

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Abstract: To study the structures and reactivities of alkali metallated intermediates of calix[4]arenes, three compounds were isolated: $[Li_4(p\text{-}tert\text{-butylcalix[4]arene-4H})(thf)_4]_2 \cdot 6\,THF$ (**1**), $[Li_2(p\text{-}tert\text{-butylcalix[4]arene-2H})(H_2O)(\mu\text{-}H_2O)(thf)] \cdot 3\,THF$ (**2**), and $[K_4(p\text{-}tert\text{-butylcalix[4]arene-4H})(thf)_5]_2 \cdot THF$ (**3**). The structure of **1** is shown to be dependent on the coordinating solvent. Partial hydrolysis of **1** leads to the formation of **2**. The potassium compound **3** features a different structure to that of **1**, due to a higher coordination number as well as stronger cation – π-bonding interactions.

Keywords: calixarenes · cluster compounds · lithium · O ligands · structure elucidation

Introduction

Calix[4]arenes are well-known valuable building blocks in supramolecular chemistry, because selective functionalisation at the upper and/or lower rim is possible.[1] Their chemistry is also of interest concerning their potential in building inclusion-based network koilates.[2] Water-soluble calixarene derivatives have also been studied in the context of alkali-metal-containing organic clays.[3] The hard acid character of the lower-rim-substituted calixarenes has been exploited to design polytopic receptors for the complexation of transition and lanthanide metals either for extraction purposes, nuclear waste management, catalysis, coordination chemistry or for the design of efficient luminescent and/or magnetic devices.[4–6] For most of these syntheses, the alkali-metallated intermediate in solution is used to substitute lithium, sodium or potassium afterwards by a transition-metal or lanthanide ion.[7, 8] However, little is known about the structures of such intermediate species, and the very few examples that have been isolated to date show interesting structural motives.[9–11] The low number of examples in the literature is probably due to the fact that these compounds do not easily crystallise, they are fragile towards hydrolysis and their structure seems to be very much dependent on the presence, size and quantity of further donor ligands, stabilising the lithiated or otherwise metallated compound. The simple calixarenes with phenolic groups on their lower rim can bind to metal ions through the deprotonated phenolate ligand. With oxygen as donor atoms, this is a hard donor ligand, which is expected to show a preference for hard metal ions, that is, alkali metal ions in our case.

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Results and Discussion

When calix[4]arene is treated with LiO*t*Bu in THF at room temperature, colourless single crystals of $[Li_8(calix[4]arene\text{-}4H)_2(thf)_8] \cdot 6\,THF$ (**1**) are obtained. Compound **1** crystallises in the monoclinic space group $P2_1/n$ (no. 14) with two molecules per unit cell. The molecular unit of **1** consists of two face-sharing Li_4O_4 heterocubanes with an inversion centre in the geometrical middle of the central Li2-O3-Li2′-O3′-ring (Figure 1). Half of the oxygen atoms O2, O3 and O4 stem from the first calixarene, the other three O2′, O3′ and O4′ from the second calixarene ligand. Four lithium atoms, Li1, Li2 and their symmetry equivalents, lie between the two calixarene molecules, whereas Li3 points into the cavity of the deprotonated ligand and is bonded in an *endo* fashion. Its tetrahedral coordination sphere is completed by the oxygen atom O5 of a THF molecule that fits into the cavity of the calixarene. Li4 is bonded in an *exo* fashion to only one oxygen atom of a calixarene ligand and to three other oxygen atoms (O6, O7 and O8) of terminally bound THF molecules.

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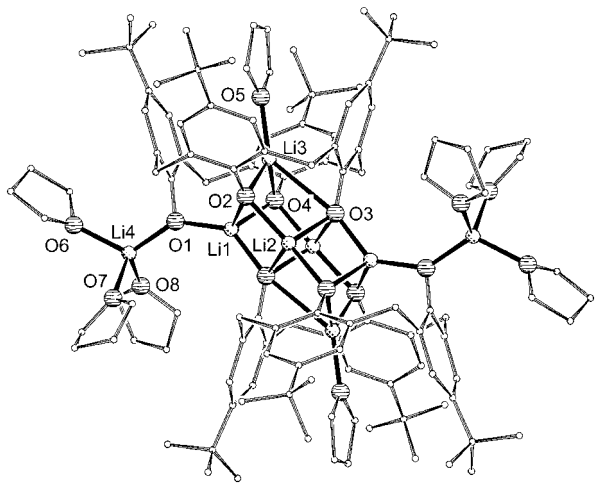
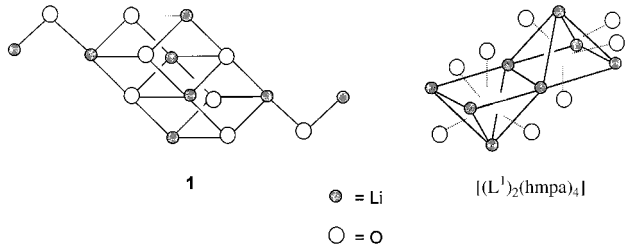


Figure 1. Molecular structure of **1**, H atoms omitted for clarity.

Two oxygen atoms of the calixarene ligand O2 and O4 act as μ_3-bridging ligand on three lithium atoms of the heterocubane system with Li–O distances of 1.933(5) to 2.001(5) Å. One oxygen atom, O3, can be considered as μ_4-bridging donor atom with three short Li–O bonds of 1.870(5) – 1.949(5) Å and one longer Li3–O3 distance of 2.775(6) Å. This arrangement gives a coordination number of four to all six lithium atoms in the diheterocubane unit. Oxygen atom O1 acts as μ_2-bridging atom towards Li4 and Li1 with bond lengths of 1.831(6) and 1.827(5) Å, respectively. The valence bond sums of the three lithium cations Li1, Li2 and Li4 are all larger than 1, whereas the one for Li3 is 0.9, which is rather low.[12] Indeed, weak interactions (2.578(5), 2.458(6) and 2.614(5) Å) of Li3 with the carbon atoms at the base of three aromatic rings (C17, C28 and C39, respectively) can be discussed, leading to a valence bond sum of 1.22 for Li3, a value comparable to the valence bond sums of the three other lithium cations in **1**.[13] This leads to four differently coordinated lithium atoms: 1) Li1 is coordinated by three oxygen atoms of the first, and one oxygen atom of the second ligand; 2) Li2 is coordinated by two oxygen atoms of the first and two oxygen atoms of the second calixarene; 3) Li3 is coordinated *endo* to the cavity by three oxygen atoms of one calixarene ligand and one THF molecule and 4) Li4 is coordinated by three THF molecules and one oxygen atom, bonded *exo*, of a calixarene ligand. Six non-coordinating THF molecules are arranged around the core of the molecule, and do not interact further with the molecule of **1**. Thermogravimetric analysis differentiates the two types of THF molecules (loss of six non-coordinating THF molecules at 212 °C). The preservation of the cone conformation of the two divergent calixarene cavities in THF is also evidenced by the ^{1}H NMR spectroscopy.

Whereas **1** is a dimeric structure, *p-tert*-butylcalix[4]arene (L^1) can also form a monomeric lithiated species, $[(L^1)Li_4(LiOH)(hmpa)_4]$, in the presence of LiOH and HMPA (hexamethylphosphoramide).[9] In this case, all four oxygen atoms of the calixarene are lithiated by one lithium ion each, forming a Li_4O_4 square antiprism. An OH^- group bridges the four lithium atoms, which lie in one plane; this structural motive is known in the literature.[14] A fifth lithium atom is found in the calixarene cavity, bonded *endo*. The lithium ions of the square antiprism are complexed by HMPA in order to complete their coordination sphere. In the same solvent, but in absence of LiOH, the dimer $[(L^1)_2Li_8(hmpa)_4]$ is observed.[9] At first sight, the eight THF molecules in **1** have been formally replaced by four HMPA molecules. However, not only the ligand is different, but the complete structure of the lithiated calixarene has changed, contrary to what is stated for a compound identical to **1** described very recently by Floriani et al.[15] Instead of the fused heterocubane structure of **1**, the structure of $[(L^1)_2Li_8(hmpa)_4]$ is derived from the square antiprisms of $[(L^1)Li_4(LiOH)(hmpa)_4]$, in which two such antiprisms are fused through one edge. The lithium skeleton of $[(L^1)_2Li_8(hmpa)_4]$ can be described as two edge-sharing square pyramids, oriented one pointing upwards, the other downwards (Scheme 1).[9] Both structures, **1** and $[(L^1)_2Li_8(hmpa)_4]$, have an inversion centre in the geometric middle of the molecule.



Scheme 1. Comparison of the arrangement of Li and O atoms of the central core in **1** and $[(L^1)_2(hmpa)_4]$.

The apical lithium ions of $[(L^1)_2Li_8(HMPA)_4]$, bonded *endo* to the calixarene, are three-coordinate, as the solvent and HMPA ligand are too large to enter the upper rim cavity of the calixarene. This leads to a distortion in the ligand, as one carbon atom of a benzyl ring features a rather short Li–C distance, indicating weak interactions. Thus, only the border lithium atoms of the cluster core are coordinated by one of the four HMPA ligands. In **1**, however, the THF molecules can enter the calixarene cavity and coordinate the *endo*-bound lithium ion. They also complete of the coordination sphere of Li4, whereas HMPA would be too sterically demanding in the same case. Thus, the size of the ligand, on one hand the smaller THF and on the other the larger HMPA, determines the overall structure of the alkali-metal cluster formed by the lithiated calixarene.

Compound **1** is the first example of a lithiated calixarene with a fused cubane structure; however, this structure is known for other cluster compounds. Thus, open calixarenes, that is, linked aryloxide groups derived from the Koebner trimer H_3L^2 [L^2 = 2,6-bis(3-*tert*-butyl-5-methyl-2-hydroxybenzyl)-4-methyl phenol or 2,6-bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)-4-methyl phenol] can be metallated with the alkali metals lithium and sodium. Depending on the solvent used during synthesis of the metallated species, $[Li_3L^2(thf)_4]$ or dimeric $[\{Li_3L^2(thf)\}_2]$ can be obtained when recrystallised from THF.[16] The THF molecules in the latter compound can also be replaced by dichloromethane. For the sodium derivatives, an acetone adduct of the dimer is known in

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addition to the dichloromethane variant. All dimeric structures, be it with lithium or sodium, feature the fused heterocubane structure with one metal cation in the *endo* position of the pseudocavity formed by the open, three-membered aryloxide chains.[16] For **1** and $[\{Li_3L^2(thf)\}_2]$, similar bond lengths and angles in the heterocubane are observed (see Supporting Information).

Further studies concerning the ability of calix[4]arenes L^1 to form monomeric lithiated derivatives, and the reactivity of **1** towards hydrolysis, lead to the formation of a partially hydrolysed compound identified as the monomeric species $[Li_2(L\text{-}2H)(H_2O)(\mu\text{-}H_2O)(thf)]\cdot 3\,THF$ (**2**). Colourless single crystals of **2** were obtained from slow evaporation in air of a solution of the dimeric lithiated compound **1** in THF. The crystal structure of **2** is quite remarkable because partial hydrolysis of the fully deprotonated and lithiated dimeric compound **1** could also have lead to the formation of dimeric species such as those already known in the literature for the zinc derivative of L^1, $[Zn_2(L^1\text{-}2H)_2]$.[17] This is probably due to the stronger complexation of water to lithium than zinc.

Compound **2** crystallises in the triclinic space group $P\bar{1}$ with two molecules per unit cell. The molecular unit of **2** consists of a doubly deprotonated *p-tert*-butylcalix[4]arene (Figure 2).

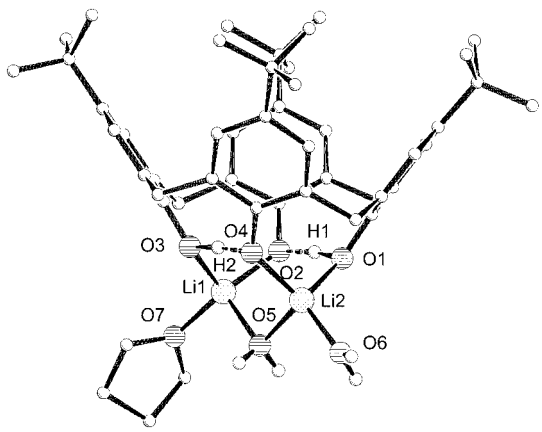

Figure 2. Molecular structure of **2**, part of the H atoms omitted for clarity.

Two remaining lithium atoms Li1 and Li2 still bind to the "lower rim" of the calixarene cavity with Li1–O bonds of 1.886(4)–1.923(4) Å (Li1–O3 and Li1–O2) and Li2–O bonds of 1.902(4)–1.954(4) Å (Li2–O4 and Li2–O1), featuring a bis-bidentate coordination mode for the calixarene. The coordination sphere of Li1 is completed with the oxygen atom O7 of a THF molecule and the oxygen atom O5 of a water molecule. The latter is a μ_2-bridging ligand and also connects bonds to Li2, whose coordination sphere is completed by the oxygen O6 of a second water molecule in terminal position. This leads to near-tetrahedral geometry for the lithium ions. The bridging water molecule with the lithium ions has elongated O–Li bonds (with 1.982(4) for Li1 and 2.019(4) Å for Li2) compared with the those that are found for water or THF bound in a terminal fashion (1.927(4) Å for H_2O and 1.973(4) Å for THF).

This leads to two different coordination environments of lithium atoms: 1) Li1 bound to two oxygen atoms of the calixarene, one THF ligand and one bridging water molecule and 2) Li2 bound to two oxygen atoms of the calixarene and the oxygen atoms of the two water molecules (one bridging and one terminal). Both lithium atoms have valence bond sums of 1.2.[12] In $[D_8]$THF, the ^{7}Li spectrum is composed of two broad signals, indicative of the nonequivalence of both lithium atoms in **2**. The ^{1}H NMR spectrum of **2** exhibits a pair of doublets in the $-CH_2$ region ($\delta = 3.1-4.3$ ppm), indicative of the cone conformation for the calixarene in THF.[1] In the case of calix[4]arene, this cone shape is usually retained upon metallation, indicating that the solid-state structure is maintained in solution. Unfortunately the distinction between the phenolate/phenol groups is not apparent in THF on the NMR timescale. In the solid state, the two remaining phenolic protons H1 and H2 could be localised in the structure, and form intramolecular hydrogen bonds between O1 and O2, and O3 and O4, respectively, leading to angles ranging from 171.36–172.79° for O1-H1-O2 and O3-H2-O4. Nevertheless, by comparing the H–O bond lengths , H1 belongs to O1, and H2 to O3, (1.154(5) and 1.162(5) Å, respectively), whereas the H1–O2 and H2–O4 bond lenghts are longer (1.300(5) and 1.269(5) Å, respectively). The presence of hydroxyl groups and water is confirmed by IR spectroscopy revealing two bands of note in the OH region. The first one at 3604 cm^{-1} is narrow and can be assigned to the remaining phenolic groups; the broader band at 3439 cm^{-1} is attributed to coordination of the water molecules. While solvent molecules are required to fill the coordination sphere of the cations, no further free THF molecules are complexed in the cavity of calixarene, as frequently noticed for similar compounds.[10, 17–19] Three non-coordinating THF molecules are arranged in the unit cell with no further interaction with the molecule of **2**. Other monomeric dilithiated species were previously observed from the reaction of the parent macrocycle with LiH to afford a rather similar monomeric compound, $[\{Li(CH_3OH)\}_2(\mu\text{-}H_2O)][p\text{-}tert\text{-butylcalix[4]arene}]\cdot 2\,H_2O\cdot 3\,CH_3OH$[10] with a solid-state structure that exhibits a higher symmetry than **2**. Nonetheless, comparable trends are evident in the metrical parameters for the latter and **2**, with Li–O distances ranging from 1.87(4) to 1.98(4) Å and the angle Li-O-Li of the bridging water molecule (102(1) vs 101.34(14)° in **2**. The coordination sphere of the lithium atoms is completed by the binding of two methanol molecules with similar Li–O bond lengths (1.90(2) and 1.96(2) Å). More recently, comparable structural geometries for the crystal structures of the lithium adducts $[Li_2(LH_2)(thf)_2(H_2O)_2]\cdot 2\,THF$, in which L represents the S-substituted homologue, *p-tert*-butyltetrathiacalix[4]arene, have come to our attention.[19] The authors aimed to conclude that the formation of monomers or small oligomers of the Group 1 elements complexes could only occur with the sulphur-substituted calixarene, but our present results demonstrate that the lithium complexes of the methylene-bridged analogue can also form monomeric adducts. In both crystal structures the same mixed-solvent component is observed (composed of THF and water, playing different roles), but in the first case, the inclusion of a free THF molecule is allowed by the larger size of the cavity in the thiacalixarene. The latter exhibits comparable bond lengths to **2**, that is, Li–O(calix) bond lengths in the range 1.945(3)–1.993(4) Å and bonds

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from Li1 and Li2 to terminal THF and water molecules of 1.986(3) and 1.926(4) Å respectively; however, the Li–O bonds to the bridging water molecule are slightly longer in the sulfur derivative (2.060(4) and 2.065(3) Å).

Formation of comparable dimeric compounds $[\{M_2L\}_2]$ with heavier Group I metals was found to be achieved by metallation of a doubly O-substituted derivative, the 1,3-dimethyl ether *p-tert*-butylcalix[4]arene H_2L, with sodium hydride in THF leading to a tetranuclear dimeric crystal structure with both *exo* and *endo*-binding of Na^+, as we previously noticed for the lithium ions in compound **1**.[20] More recently, direct reaction of the bulk metal with the parent calixarene homologue, in the presence of naphthalene, lead to the species "$[(MO)_4(p\text{-}t\text{Bu-calix}[4])]\cdot 2\,THF$" (M = Na, K) in THF. These compounds crystallise in the form of pyridine- or THF-solvated centrosymmetric dimers.[15] Hence, to complete our family of calixarenes complexes with larger alkali metal ions by our synthetic pathway, reaction of *p-tert*-butylcalix[4]arene L^1 with KO*t*Bu, performed in THF, affords colourless single crystals of the dimeric metallocalixarene species $[K_4(\text{calix}[4]\text{arene-4H})(thf)_5]_2\cdot THF$ (**3**). This centrosymmetric solid-state structure exhibits potassium ions coordinated in four different geometrical environments. Compound **3** crystallises in the orthorhombic space group *Pbca* (no. 61) with four molecules per unit cell. In a similar way to the lithiated compound **1**, molecular units of **3** are composed of two fully deprotonated *p-tert*-butylcalix[4]arene tetraanions fused at the lower rim by six bridging potassium cations arranged in a "sandwich" between the two calixarene moieties. The cavity of each calixarene is further filled with a fourth type of potassium ion, as in the previously described dimeric compound **1**; however, in this case there is no THF coordination to the potassium ion (Figure 3).

Owing to the larger ionic radius and the softer character of potassium compared to lithium, compounds **1** and **3** are not isostructural. The cluster core of **1** consists of two fused heterocubanes and one lithium ion linked on each side, whereas in the compound **3**, the heterocubane structure is not maintained, and the outer cation K4 is linked differently. The potassium ion K1 in **3**, which is bound *endo* to the calixarene, is pushed further up into the calixarene cavity than Li3 in **1**.

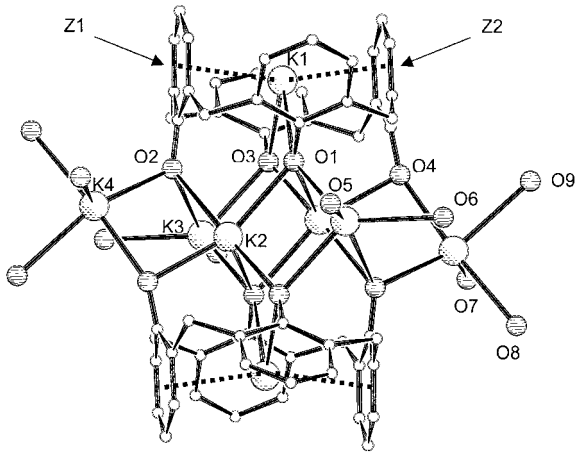

Figure 3. Molecular structure of **3**, *t*Bu- and THF groups omitted for clarity.

Thus, the core structure in **3** consists of two fused open heterocubanes, the distance K1–O2 (>3.8 Å) being too long for a strong bonding interaction. The K1 ion is complexed by two oxygen atoms of the calixarene, that is, O1 at 2.881(3) and O3 at 2.685(3) Å. With these two bonds, K1 reaches a valence bond sum of 0.4,[12] indicating that further coordination must exist. Indeed, to complete its coordination sphere, strong π donation occurs from the two phenyl rings linked to O2 (C8–C13) and O4 (C22–C27) toward the cation K1 (C–K: 3.005(4)–3.180(4) Å) as well as from C1 and C20, the basal carbon atoms of the phenyl rings linked to O1 and O3, respectively, at a distance of 2.931(5) and 2.991(5) Å, respectively. The average planes through the two phenyl rings attached to O1 and O3 form an angle of 83.8(1)°, whereas the ones attached to O2 and O4 are almost parallel to each other with an angle of 4.21(4)°. The centres of these phenyl rings Z1 (C8–C13) and Z2 (C22–C27) are at distances of 2.799 and 2.780 Å from K1, respectively. This is in the same range as the K1–O bonds, but shorter by 0.05 Å than the equivalent distances reported for theoretical calculations of $[K(C_6H_6)_2]^+$.[21] In the solid state, only longer K^+–aryl(centroid) (aryl = aromatic six-membered ring) distances of 3.07–3.39 Å have been reported.[16, 22] Even in the cyclopentadienyl compound KCp, in which the potassium ion is sandwiched between two Cp rings of a zigzag chain structure and interacts with two more Cp rings of the neighbouring chain,[21] the K–Cp(centroid) distances are still longer (2.816 Å) than in **3**. The Z1-K-Z2 angle in **3** is not quite linear with 167.49°, whereas in KCp the analogue angle is 140°.[23] Thus, the valence bond sum for K1 amounts to 1.6 when the K1–C contacts <3.075 Å are taken into account in addition to the K1–O bonds.[12] For the other potassium ions K2, K3 and K4, bond valence sums of 1.1, 1.1 and 1.0, respectively, are obtained (the K3–C1 bond being taken into account 3.053(5) Å). The potassium ions K2, K3 and K4 possess in principle a coordination sphere of five oxygen atoms in the form of more or less distorted square pyramids. K2 is only complexed by oxygen atoms provided by the two calix[4]arene ligands, and the K2–O bond lengths lie between 2.494(3) and 2.765(3) Å. Three oxygen atoms of the calix[4]arene ligands and the oxygen atoms of the terminally bound THF molecules complex K3 with K3–O(calix[4]arenes) bond lengths between 2.650(3) and 2.909(3) Å, and K3–O(thf) bond lengths of 2.801(5) (O5) and 2.777(5) (O6) Å. The last cation K4 is linked to one oxygen atom of each calix[4]arene ligand with bond lengths of 2.656(3) and 2.531(3) Å to O2 and O4, respectively, and three terminally bonded THF molecules, with bond lengths from 2.716(5) to 2.794(7) Å; as expected these bonds are longer for neutral ligands relative to the charged oxygen anions of the calix[4]arene ligand. Normally, the potassium ion tends to a coordination number of six, but here it exhibits coordination number of five; however very weak interactions between one oxygen atom (O6) and the potassium ion K4 (>2.9 Å) are observed to give a pseudo-octahedral coordination (Figure 4).

Compound **3** resembles very much the structure of $[\{\text{calix}[4]\text{-}(O)_4K\}_2(\mu\text{-}K)_6(thf)_{10}]$.[15] However, the latter crystallises in the triclinic space group $P\bar{1}$ with four free THF molecules per molecular unit, whereas **3** crystallises in the orthorhombic

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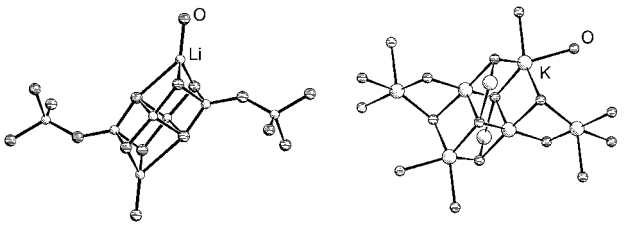

Figure 4. Left: Li_8O_{16} cluster core of **1**. Right: K_8O_{18} cluster core of **3**.

space group *Pbca* with one THF molecule per molecule, and with better standard deviations with respect to bond lengths and angles. The bond lengths concerning the potassium atoms K1 and K1′ are 0.03–0.06 Å shorter than in the literature compound, even though the crystals of **3** were measured at a higher temperature (200 K compared to 143 K for the literature compound). The sodium compound was also identified to have a similar structure to **3**, but with pyridine ligands instead of THF.[15]

In both structures **1** and **3**, all four metal ions M1, M2, M3 and M4 (M = Li, K) of the asymmetric unit have each a different environment of oxygen atoms. The inversion centre in each structure is situated in the middle of a central M_2O_2 ring. The larger cation K^+ requires a higher coordination number than the smaller lithium ion. The cluster core of **3** contains 18 oxygen atoms compared to 16 oxygen atoms in **1**. A fundamental difference between **1** and **3** is the *endo* coordination of the THF molecule in **1**; this is absent in **3**. This is due to the small diameter of the calix[4]arene cavity in **3** of approximately 5 × 8.5 Å, the distance between the two almost parallel phenyl rings linked to O2 and O4 being about 5.5 Å, the other two phenyl rings are ~9 Å apart. In **1**, the two almost parallel phenyl rings are ~7 Å apart, whereas the other two are, similarly to **3**, at a distance of 9 Å in average. The strong interactions of two phenyl rings with the potassium ion K1 in **3**, relative to the weak ones with Li3 in **1**, can be a model for the high selectivity of potassium channels in living organisms. These interactions were shown to belong to cation–π interactions in general, and to be very strong for **3**. In detail, the selectivity of the benzene ring in the gas phase was shown to be highest for Li^+ and lowest for Rb^+, whereas in aqueous media, K^+ is always preferred leading to the formation of a sandwich compound. Similar interactions were attributed to the potassium selective channels of *Drosophila*.[24]

In the search for an analogy between clusters of Group 1 and 11 metal ions, we note that several chlorogold(I) complexes with either phosphinitocalixresorcinarenes[25] or calix[4]arene derived phosphates[26] have been previously described. In the first class of compounds, the tetranuclear complex crystal structure contains three AuCl units around the upper rim of the bowl with the fourth folded inside the cavity. The second class exhibits only one Au^I ion, doubly coordinated with the motive P-Au-Cl, but no crystal structures are available for this. For Ag^+, only complexes with a single metal ion are known, the metal ion being bonded either *exo* or *endo* to the cavity of the calixarene ligand.[27] Nuclearity is found to be increased with copper compounds. Hence a one-dimensional Cu^+ derivative with four Cu^+ cations per Ph_2P-substituted calix[8]arene with a Cu_2Cl_2 unit bridging the two ligands—its structure however being far from comparable to our alkali metal derivatives,[28]—has already been characterised, and more recently the square, phenoxo- and sulfur-bridged cluster of four Cu^{II} ion sandwiched between two fully deprotonated *p-tert*-butyltetrathiacalix[4]-arenes.[29] To the best of our knowledge, cluster compounds of higher nuclearity than four have not been characterised yet for the Group 11 elements. We are currently investigating how other donor ligands than THF can influence the structure of our compounds and the differences in reactivity of different structured metallated calixarenes.

Conclusion

Three unique and new structures of alkali-metallated calix-[4]arenes are presented, and for compound **1**, the influence of the solvent and at the same time coordinating donor ligand on the solid-state structure is reported. Given these results, it can be expected that depending on the donor ligand and its concentration, other structures might be obtained also for **2** and **3**. Compound **2** is obtained from **1** by partial hydrolysis. The potassium compound shows the shortest K–aryl(centroid) distances ever reported, revealing the excellent complexation properties of calixarene ligands for potassium and their model role for biological potassium channels. More investigations are currently under way to elucidate the mechanism of formation of other derived compounds, for instance the transition metal coordination compounds.

Experimental Section

All reactions, except the synthesis of L^1, were carried out under nitrogen atmosphere. Lithium and potassium *tert*-butoxides 1M/THF were purchased from Fluka. Solvent was dried over sodium/benzophenone and freshly distilled under nitrogen. *p-tert*-butylcalix[4]arene was prepared according to the literature procedure.[30] The NMR spectra were recorded on a Varian Gemini 300 spectrometer, the chemical shifts are relative to TMS as an internal standard. The IR spectra of compound were recorded with a Perkin–Elmer, Spectrum One FT-IR spectrometer on CsI plates in nujol.

Compound 1: LiO*t*Bu (1 mL, 1 mmol, $c = 1$M in THF) was added to a white suspension of *p-tert*-butylcalix[4]arene (0.142 g, 0.192 mmol) in THF (10 mL), and yielded a clear orange solution after 30 min of stirring at room temperature. After concentration, the yellow solution was allowed to stand at room temperature. Colourless single crystals suitable for X-ray analysis grew from the solution at room temperature in a few days. Yield: 0.11g/2354.69 g mol^{-1} = 4.67.10^{-5} mol, 48%; ^{1}H NMR (300 MHz, [D$_8$]THF, 293 K): $\delta = 1.16$ (s, 72H; CH_3), 1.78 (m 32H; CH_2 thf), 3.11 (d, $J = 12$ Hz, 8H; CH_2), 3.62 (m 32H; CH_2O thf), 4.33 (d, $J = 12.3$ Hz, 8H; CH_2), 6.78 (s, 4H; ArH), 6.87 ppm (s, 12H; ArH); ^{7}Li NMR (116 MHz, [D$_8$]THF, 293 K): $\delta = 1.5$ (brs), 4.1 (s), 5.3 ppm (brs); ^{13}C NMR (75 MHz, [D$_8$]THF, 293 K): $\delta = 25.53$ (CH_2 thf), 31.42 (CH_3), 32.87 (CH_2), 34.96 (CMe_3), 67.57 (CH_2O thf), 126.12, 131.82, 132.75 ppm (ArH); elemental analysis calcd (%) for $C_{144}H_{216}O_{22}Li_8$: C 73.45, H 9.24; found: C 71.17, H 8.31. Further satisfying microanalysis could not be obtained for **1**, **2** or **3**, as a result of rapid decomposition (loss of solvent) upon exposition to air and moisture, as well as high reactivity of these compounds. IR (Nujol): $\tilde{\nu} = 3604$ (s), 2921 (nujol), 1750 (w), 1604 (m), 1483 (s), 1456 (nujol), 1391 (w), 1376 (nujol), 1358 (m), 1313 (s), 1277 (s), 1208 (s), 1131 (m), 1046 (s), 912 (m), 872 (s), 821 (s), 797 (s), 738 (s), 722 (nujol), 652 (m), 616 (m), 508 (m), 448 (m), 413 cm^{-1} (m); m.p. (decomp) ~210 °C; DTA/TG: loss of 6 molecules THF

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at 212 °C. Apparently, only the free, uncoordinated THF is lost, corresponding to the decomposition observed during fusion point measurements. No further loss was observed at higher temperature up to 400 °C. Single-crystal data for **1**: $C_{144}H_{216}O_{22}Li_8$, $M = 2354.7\ g\,mol^{-1}$, monoclinic, space group $P2_1/n$, $a = 18.449(4)$, $b = 17.790(4)$, $c = 22.070(4)$ Å, $V = 6670(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.172\ Mg\,m^{-3}$, $F(000) = 2560$, $T = 203$ K, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.076\ mm^{-1}$, $4° < 2\theta < 51.66°$, 42070 reflections collected of which 12717 unique and observed, $R(int) = 0.0755$, 796 parameters refined, GOOF(on F^2) = 1.026, $R1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.0866$, $wR2 = 0.2309$ for $I > 2\sigma(I)$ and $R1 = 0.1209$, $wR2 = 0.2610$ for all data.

Compound 2: Colourless single crystals of **2**, suitable for X-ray analysis, grew from slow evaporation on air of a solution of **1** in THF at room temperature in a few weeks in an approximate yield of 50 %. ^{1}H NMR (300 MHz, [D$_8$]THF, 293 K): $\delta = 1.17$ (s, 36 H; CH$_3$), 1.75 (m, 4 H; CH$_2$ thf), 2.47 (br s, H$_2$O), 3.11 (d, $J = 14$ Hz, 4 H; CH$_2$), 3.60 (m, 4 H; CH$_2$O thf), 4.27 (d, $J = 14.3$ Hz, 4 H; CH$_2$), 6.86 ppm (s, 8 H; ArH); ^{7}Li NMR (116 MHz, [D$_8$]THF, 293 K): $\delta = 4.14$, 5.06, 5.45 ppm (br s); m.p. (decomp) 220 °C (becomes greenish); IR (Nujol): $\tilde{\nu} = 3604$ (s), 3439 (s), 2923 (nujol), 2768 (w), 2284 (w), 1692 (m), 1600 (m), 1485 (m), 1456 (nujol), 1412 (m), 1376 (nujol), 1357 (m), 1288 (m), 1203 (m), 1072 (s), 910 (s), 821 (m), 735 (w), 730 (nujol), 672 (m), 560 (w), 493 (w), 284 cm^{-1} (w). Single-crystal data for **2**: $C_{60}H_{90}O_{10}Li_2$, $M = 985.20\ g\,mol^{-1}$, triclinic, space group $P\bar{1}$ (Nr. 2), $a = 12.030(2)$, $b = 13.457(3)$, $c = 19.788(4)$ Å, $\alpha = 109.59(3)$, $\beta = 104.81(3)$, $\gamma = 91.78(3)°$ $V = 2893.8(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.131\ Mg\,m^{-3}$, $F(000) = 1072$, $T = 200$ K, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.074\ mm^{-1}$, $3.24° < 2\theta < 59.1°$, 54573 reflections collected of which 16074 unique and observed, $R(int) = 0.0731$, 673 parameters refined, GOOF(on F^2) = 1.076, $R1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.0692$, $wR2 = 0.1824$ for $I > 2\sigma(I)$ and $R1 = 0.1180$, $wR2 = 0.2616$ for all data.

Compound 3: KO*t*Bu (1 mL, 1 mmol, $c = 1$ M in THF) was added to a white suspension of *p-tert*-butylcalix[4]arene (0.14 g, 0.216 mmol) in THF (20 mL) and yielded a colourless solution. A milky pale yellow solution was obtained after stirring one hour at room temperature. This solution was allowed to stand at room temperature. Colourless single crystals suitable for X-ray analysis grew from the solution at room temperature in a few days (50 %). M.p. (decomp) 130 °C; DTA/TG: loss of only half of the THF molecules. ^{1}H NMR (300 MHz, [D$_8$]THF, 293 K): $\delta = 1.15$ (s, 72 H; CH$_3$), 1.77 (m, 40 H; CH$_2$ thf), 2.78 (d, $J = 12.6$ Hz, 8 H; CH$_2$), 3.62 (m, 40 H; CH$_2$O thf), 4.30 (d, $J = 12.6$ Hz, 8 H; CH$_2$), 6.80 ppm (s, 16 H; ArH). Single-crystal data for **3**: $C_{132}H_{192}O_{19}K_8$, $M = 2395.66\ g\,mol^{-1}$, orthorhombic, space group *Pbca*, $a = 23.220(5)$, $b = 22.690(5)$, $c = 26.860(5)$ Å, $V = 14152(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.124\ Mg\,m^{-3}$, $F(000) = 5152$, $T = 203$ K, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.301\ mm^{-1}$, $3.5° < 2\theta < 58.64°$, 122699 reflections collected of which 18377 unique and observed, $R(int) = 0.1416$, 739 parameters refined, GOOF(on F^2) = 1.535, $R1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.1074$, $wR2 = 0.2517$ for $I > 2\sigma(I)$ and $R1 = 0.1776$, $wR2 = 0.2838$ for all data.

Crystals of **1**, **2** and **3** were measured on a STOE IPDS diffractometer at 203 K. The data collections for **1** and **2** were best for crystals of 0.4 × 0.4 × 0.2 mm and 0.4 × 0.4 × 0.4 mm in size, respectively. The structures were solved with direct methods and refined by full matrix least squares on F^2 with the SHELX-97 package.[31] Slight disorder was generally observed for the *t*Bu group and the THF molecules. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms. The higher R factors are mainly due to the amount of free solvent and disorder in the coordinating solvent molecules. CCDC-168603 (**1**), CCDC-183985 (**2**) and CCDC-183986 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Awknowledgemnets

The Swiss National Foundation and the University of Geneva financed this work. I am grateful to Prof. A. F. Williams and Prof. C. Piguet for their generous support.

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Received: April 26, 2002
Revised: October 7, 2002 [F4048]

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