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Alkali metal salts of oxyanions of *p*-tert-butylcalix[4]arene

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The reaction of a ten-fold excess of NaH with *p*-tert-butylcalix[4]arene in THF results in the mono-oxyanion, $[Na(MeOH)(H_2O)_2][$*p*-tert-butylcalix[4]arene$]\cdot H_2O\cdot MeOH$, 1. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.982(5)$, $b = 19.236(8)$, $c = 21.763(8)$ Å, $\beta = 94.77(4)°$, and $D_c = 0.97$ g cm^{-3} for $Z = 4$. Refinement based on 2722 observed reflections led to a final R value of 0.099. The similar reaction of LiH with *p*-tert-butylcalix[4]arene affords as the only product the di-oxyanion, $[(Li(MeOH))_2(\mu\text{-}H_2O)][$*p*-tert-butylcalix[4]arene$]\cdot 2H_2O\cdot 3MeOH$, 2. The compound crystallizes in $P2_1/n$ with $a = 12.420(6)$, $b = 21.656(9)$, $c = 21.172(9)$ Å, $\beta = 108.14(5)°$, and $D_c = 1.08$ g cm^{-3} for $Z = 4$. Refinement based on 2215 observed reflections led to a final R value of 0.13. The calix[4]arene cavity in both 1 and 2 contains a methanol molecule. The failure to generate tri- or tetra-oxyanions is rationalized on the basis of electrostatic considerations.

INTRODUCTION

Unlike the crown ethers, alkali metal coordination by *p*-tert-butylcalix[4]arene has been limited to only a few reports[1] and there has been one structural investigation of the methyl ether derivative.[2,3] Transition metal complexes have been prepared by the reaction of an active metal complex with the protons of the basal –OH groups of the calixarene.[4] However, the lack of water solubility of the parent calix[4]arene has limited its metal ion complexation chemistry. In order to expand the range of available metal complexes it seemed reasonable to prepare alkali metal salts of the oxyanion of *p*-tert-butylcalix[4]arene. In this paper we present the synthesis and structure of Li^+ and Na^+ derivatives, plus preliminary information on a K^+-containing moiety.

EXPERIMENTAL SECTION

Preparation of $[Na(MeOH)(H_2O)_2][$*p*-tert-butylcalix[4]arene$]\cdot H_2O\cdot MeOH$, 1

To a suspension of *p*-tert-butylcalix[4]arene (3.0 g, 4.6 mmol) in tetrahydrofuran (100 mL), sodium hydride (1.8 g, 45 mmol, 60% dispersion in mineral oil) was added and the mixture was stirred for 1 h under an atmosphere of N_2. The remaining NaH was decomposed by addition of methanol, after which the solvent was evaporated under reduced pressure. The resulting residue was redissolved in methanol. No attempt was made to exclude atmospheric moisture from this point on. Insoluble material was filtered. The methanol fraction was evaporated again to produce a pale yellow powder which was recrystallized from methanol to give colorless crystals (yield: 1.87 g, 52%).

Preparation of $[(Li(MeOH))_2(\mu\text{-}H_2O)][$*p*-tert-butylcalix[4]arene$]\cdot 2H_2O\cdot 3MeOH$, 2

To a suspension of *p*-tert-butylcalix[4]arene (500 mg, 0.77 mmol) in tetrahydrofuran (10 mL), lithium hydride (61 mg, 7.7 mmol) was added. The reaction mixture was stirred and methanol (2 mL) was added over 30 min under an N_2 atmosphere. The reaction mixture was stirred for an additional 2 h. No attempt was made to exclude atmospheric moisture from this point on. After evaporation, the resulting residue was dissolved in methanol. Insoluble material was filtered, and the methanol fraction was evaporated slowly at room temperature to give colorless crystals (yield: 480 mg, 88%).

Preparation of the potassium salt of the oxyanion of *p*-tert-butylcalix[4] arene, 3

To a suspension of *p*-tert-butylcalix[4]arene (1.00 g, 1.54 mmol) in tetrahydrofuran (30 mL), potassium hydride (1.76 g, 15.4 mmol, 35% dispersion in mineral oil) was added and the reaction mixture was stirred for 1 h under an N_2 atmosphere. The remaining KH was decomposed by addition of methanol, after which the solvent was evaporated under reduced pressure. No attempt was made to exclude atmospheric moisture from this point on. The resulting residue was

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redissolved in methanol. Insoluble material was removed by filtration, and the methanol fraction was evaporated slowly at room temperature to give colorless crystals (yield: 910 mg, 78%).

X-ray structure determination for $[Na(MeOH)(H_2O)_2][p$-tert-butylcalix[4]arene]$\cdot H_2O\cdot MeOH$, 1

The clear, colorless single crystals quickly decomposed by loss of included MeOH or H_2O, and they were therefore sealed in thin-walled glass capillaries with a drop of mother liquor. Even with this precaution, some decomposition (10%) was noted during data collection. A summary of crystal data, data collection, and structure refinement is presented in Table 1. Data was collected in the usual manner[5] and the structure was determined by application of SHELX-86.[6] Refinement proceeded smoothly in $P2_1/n$ and all non-hydrogen atoms were treated with anisotropic thermal parameters, except for the MeOH and H_2O guest molecules. The latter was disordered over three positions (0.33:0.33: 0.33). Problems associated with the refinement of the guests were probably the cause of the relatively high *R* value. The hydrogen atoms bonded to the ring carbon atoms were placed in calculated positions, but those associated with the butyl groups, the MeOH, and the H_2O molecules could not be located. Final positional parameters are given in Table 2.

X-ray structure determination for $[(Li(MeOH))_2(\mu$-$H_2O)][p$-tert-butylcalix[4]arene]$\cdot 2H_2O\cdot 3MeOH$, 2

Crystal handling was as for **1**, except that the crystals were even more sensitive (the data crystal completely decomposed during data collection). Parameters

Table 1 Crystal data

Compound	**1**	**2**	**3**
Space group	$P2_1/n$	$P2_1/n$	$P1$
Cell dimensions			
a (Å)	12.982(5)	12.420(6)	21.236(4)
b (Å)	19.236(8)	21.656(9)	22.712(2)
c (Å)	21.763(8)	21.172(9)	24.808(3)
α (deg)	90	90	65.11(1)
β (deg)	94.77(4)	108.14(5)	72.67(1)
γ (deg)	90	90	75.13(1)
V (Å^3)	5416	5412	10241
Z	4	4	*
D_c (g cm^{-3})	0.97	1.08	–
Observed reflections	2722	2215	9900
R	0.099	0.130	–

1 = $[Na(MeOH)(H_2O)_2](p$-tert-butyocalix[4]arene)$\cdot H_2O\cdot MeOH$;
2 = $[(Li(MeOH))_2(\mu$-$H_2O)](p$-tert-butylcalix[4]arene)$\cdot 2H_2O\cdot 3MeOH$; **3** = potassium salt of an oxyanion of *p*-tert-butylcalix[4]arene.

* The assumption of a reasonable density leads to the conclusion that *Z* = 8, which in turn means that there are four calix[4]arene moieties in the asymmetric unit.

Table 2 Final fractional co-ordinates for $[Na(MeOH)(H_2O)_2][p$-tert-butylcalix[4]arene]$\cdot H_2O\cdot MeOH$, **1**

Atom	*x/a*	*y/b*	*z/c*
Na(1)	0.1881(5)	0.9282(3)	−0.0018(3)
O(11)	0.1063(6)	0.8173(4)	−0.0147(3)
O(21)	−0.0826(7)	0.8499(4)	−0.0517(4)
O(31)	−0.0448(6)	0.9337(4)	−0.1304(3)
O(41)	0.1518(6)	0.9127(4)	−0.1138(4)
C(11)	0.118(1)	0.7508(7)	−0.0380(5)
C(12)	0.2039(9)	0.7358(6)	−0.0695(5)
C(13)	0.2157(9)	0.6689(6)	−0.0906(5)
C(14)	0.144(1)	0.6153(6)	−0.0812(5)
Ct(11)	0.163(1)	0.5411(7)	−0.1049(7)
Ct(12)	0.180(2)	0.543(1)	−0.175(1)
T(12)	0.071(3)	0.528(2)	−0.163(2)
Ct(13)	0.273(2)	0.513(2)	−0.068(2)
T(13)	0.275(4)	0.526(2)	−0.117(2)
Ct(14)	0.067(3)	0.496(2)	−0.103(2)
T(14)	0.137(2)	0.488(1)	−0.058(1)
C(15)	0.059(1)	0.6330(6)	−0.0512(5)
C(16)	0.452(9)	0.6988(7)	−0.0295(5)
C(17)	−0.0519(9)	0.7157(7)	0.0048(5)
C(21)	−0.156(1)	0.7998(7)	−0.0658(5)
C(22)	−0.144(1)	0.7335(7)	−0.0398(5)
C(23)	−0.216(1)	0.6849(7)	−0.0536(6)
C(24)	−0.302(1)	0.6955(7)	−0.0952(7)
Ct(21)	−0.384(1)	0.6406(9)	−0.109(1)
Ct(22)	−0.470(2)	0.660(1)	−0.156(1)
Ct(23)	−0.321(4)	0.584(3)	−0.157(2)
T(23)	−0.354(3)	0.571(2)	−0.099(2)
Ct(24)	−0.438(3)	0.625(2)	−0.050(1)
C(25)	−0.311(1)	0.7619(8)	−0.1207(6)
C(26)	−0.240(1)	0.8140(7)	−0.1073(6)
C(27)	−0.2531(9)	0.8853(6)	−0.1367(6)
C(31)	−0.091(1)	0.9174(6)	−0.1869(6)
C(32)	−0.193(1)	0.8927(6)	−0.1929(6)
C(33)	−0.238(1)	0.8745(7)	−0.2503(7)
C(34)	−0.187(1)	0.8801(7)	−0.3049(6)
Ct(31)	−0.240(1)	0.8558(8)	−0.3683(7)
Ct(32)	−0.335(2)	0.906(1)	−0.3829(8)
Ct(33)	−0.166(2)	0.866(1)	−0.4183(7)
Ct(34)	−0.280(2)	0.781(1)	−0.3616(8)
C(35)	−0.086(1)	0.9068(6)	−0.2982(6)
C(36)	−0.38(1)	0.9251(6)	−0.2408(6)
C(37)	0.073(1)	0.9520(7)	−0.2345(6)
C(41)	0.1823(9)	0.8749(7)	−0,1624(6)
C(42)	0.1485(9)	0.8946(7)	−0.2229(6)
C(43)	0.182(1)	0.8565(7)	−0.2702(6)
C(44)	0.250(1)	0.8010(8)	−0.2627(7)
Ct(41)	0.291(2)	0.758(1)	−0.3159(7)
Ct(42)	0.240(2)	0.782(1)	−0.3788(7)
Ct(43)	0.287(2)	0.683(1)	−0.3031(9)
Ct(44)	0.414(2)	0.775(1)	−0.3175(9)
C(45)	0.2822(9)	0.7827(7)	−0.2016(6)
C(46)	0.2485(9)	0.8181(6)	−0.1513(6)
C(47)	0.2793(9)	0.7909(6)	−0.872(5)
Meo(1)	0.93(1)	0.9404(6)	0.876(5)
Mec(1)	0.078(2)	0.889(1)	0.133(1)
Meo(2)	−0.019(2)	0.726(1)	−0.2009(9)
Mec(2)	−0.077(3)	0.720(2)	−0.240(2)
W(1)	0.152(1)	1.0457(1)	−0.0237(6)
W(2)	0.345(1)	0.915(1)	0.049(1)
W(3)	0.378(2)	0.910(1)	0.199(1)
W(4)	0.064(4)	0.473(3)	0.648(3)
W(5)	0.431(4)	0.138(3)	−0.005(2)

Table 3 Final fractional co-ordinates for $[(\mathrm{Li(MeOH)})_2[\mu\text{-}\mathrm{H_2O}]]$ [*p*-tert-butylcalix[4]arene]$\cdot 2H_2O\cdot 3MeOH$, **2**

Atom	*x/a*	*y/b*	*z/c*
Li(1)	0.057(4)	0.4508(9)	0.878(1)
Li(2)	0.153(4)	0.550(1)	0.984(1)
Ct(11)	−0.318(3)	0.6112(8)	0.6192(8)
Ct(12)	−0.372(3)	0.5593(8)	0.5738(8)
Ct(13)	−0.225(3)	0.6344(8)	0.5803(9)
Ct(14)	−0.397(3)	0.6619(9)	0.6267(9)
O(11)	−0.070(1)	0.5100(3)	0.8580(4)
C(11)	−0.129(2)	0.5359(5)	0.8001(5)
C(12)	−0.111(2)	0.5125(5)	0.7424(5)
C(13)	−0.169(2)	0.5391(5)	0.6861(6)
C(14)	−0.245(2)	0.5859(6)	0.6842(6)
C(15)	−0.261(2)	0.6073(5)	0.7429(6)
C(16)	−0.194(2)	0.5838(5)	0.8017(5)
C(17)	−0.212(2)	0.6125(5)	0.8649(6)
Ct(21)	−0.107(2)	0.8357(7)	0.8577(7)
Ct(22)	−0.159(3)	0.866(1)	0.906(1)
Ct(23)	−0.150(3)	0.8373(8)	0.7921(9)
Ct(24)	0.030(4)	0.874(1)	0.873(1)
O(21)	0.003(1)	0.5859(3)	0.9447(4)
C(21)	−0.018(2)	0.6470(5)	0.9249(5)
C(22)	−0.126(2)	0.6611(5)	0.8879(6)
C(23)	−0.155(2)	0.7204(5)	0.8660(6)
C(24)	−0.071(2)	0.7670(5)	0.8834(6)
C(25)	0.039(2)	0.7510(5)	0.9205(6)
C(26)	0.068(2)	0.6916(5)	0.9419(6)
C(27)	0.185(2)	0.6795(5)	0.9776(6)
Ct(31)	0.454(3)	0.7802(8)	0.846(1)
Ct(22)	0.466(3)	0.771(1)	0.784(1)
Ct(33)	0.458(3)	0.824(1)	0.893(1)
Ct(34)	0.326(4)	0.823(2)	0.810(2)
O(31)	0.242(1)	0.5618(4)	0.9283(4)
C(31)	0.279(2)	0.6146(5)	0.9057(6)
C(32)	0.264(2)	0.6713(6)	0.9328(6)
C(33)	0.310(2)	0.7245(6)	0.9108(7)
C(34)	0.366(2)	0.7207(7)	0.8639(7)
C(35)	0.390(2)	0.6642(6)	0.8389(6)
C(36)	0.342(2)	0.6112(6)	0.8594(6)
C(37)	0.367(2)	0.5487(6)	0.8302(6)
Ct(41)	0.231(3)	0.5475(8)	0.5860(8)
Ct(42)	0.191(3)	0.4898(9)	0.550(1)
Ct(43)	0.315(4)	0.600(2)	0.589(2)
Ct(44)	0.083(3)	0.584(1)	0.552(1)
O(41)	0.169(1)	0.4874(3)	0.8432(4)
C(41)	0.173(2)	0.5034(6)	0.7816(6)
C(42)	0.276(2)	0.5324(6)	0.7753(6)
C(43)	0.277(2)	0.5487(6)	0.7106(6)
C(44)	0.187(2)	0.5339(6)	0.6575(6)
C(45)	0.091(2)	0.5050(6)	0.6660(6)
C(46)	0.078(2)	0.4905(6)	0.7308(6)
C(47)	−0.022(2)	0.4636(6)	0.7360(6)
Meo(1)	0.031(2)	0.3617(5)	0.8671(5)
Mec(1)	−0.084(3)	0.333(1)	0.857(1)
Meo(2)	0.212(2)	0.5487(4)	1.0785(4)
Mec(2)	0.309(3)	0.5621(8)	1.1132(9)
Meo(3)	0.057(2)	0.6769(9)	0.761(1)
Mec(3)	0.073(3)	0.662(1)	0.707(1)
Meo(4)	0.687(2)	0.5953(7)	1.0158(8)
Mec(4)	0.577(4)	0.580(1)	0.981(2)
Meo(5)	0.826(2)	0.7188(7)	0.0947(8)
Mec(5)	0.808(3)	0.7432(9)	0.026(1)
W(1)	0.115(1)	0.4575(3)	0.9711(4)
W(2)	0.426(2)	0.2554(8)	0.8852(8)
W(3)	0.653(3)	0.610(1)	0.148(1)

associated with the data collection and structure solution are presented in Table 1. Due to the paucity of observed data, all atoms were treated with isotropic thermal parameters. Hydrogen atoms were as for **1**. Final fractional co-ordinates are given in Table 3.

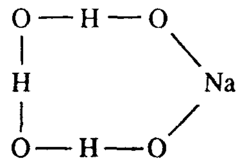
Crystal data and attempted X-ray structure determination for the potassium salt of the oxyanion of *p*-tert-butylcalix[4]arene

Crystals of the potassium salt are also very sensitive. The extraordinary size of the unit cell affords the inference of four oxyanions in the asymmetric unit. The validity of the choice of unit cells was checked for three different crystals from three different recrystallizations. Although the scattering was strong for the data collection crystal at low angles, no data could be obtained at high scattering angles. The solution of this X-ray structural problem is currently beyond our reach, but efforts to learn about this large calix[4]arene assembly are continuing.

RESULTS AND DISCUSSION

The reaction of NaH with *p*-tert-butylcalix[4]arene in THF proceeds slowly because of the lack of a solvent in which both reactants have good solubility. However, it is interesting to note that the only product of the reaction was the mono-oxyanion, even though a ten-fold excess of NaH was used. For the LiH reaction, a di-oxyanion was realized with a similar excess of hydride reagent. Tri- and tetra-oxyanions may exist, but they were not obtained from methanol using these conditions. However, the failure to generate the higher oxyanions may also be rationalized on the basis of structural arguments presented below.

The structure of the sodium salt of the mono-oxyanion, **1** (Fig 1), features a bidentate coordination mode for the calixarene. This means that three protons are distributed among the four oxygen atoms at the base of the calixarene. The fact that these hydrogen atoms are still involved in bridging as in Scheme I is evidenced by the O...O approaches of 2.43–2.58 Å compared with the 2.92 Å between O(11) and O(41). The remainder of the sodium ion coordination sphere is filled out with one methanol and two water molecules.[7] The ^{1}H-NMR spectrum exhibits a pair of



Scheme I

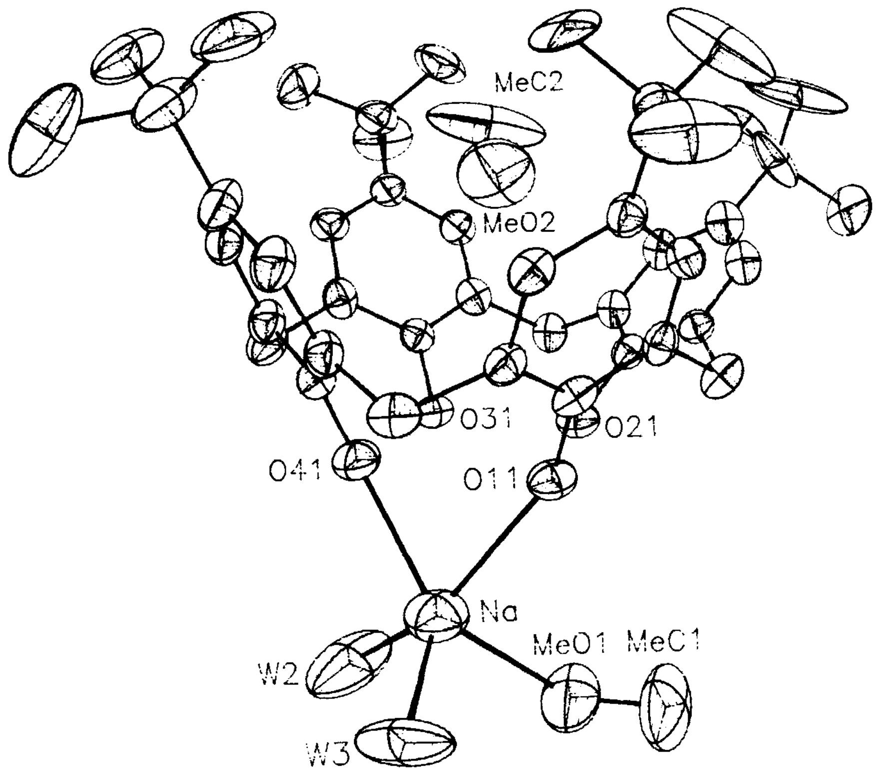


Figure 1 Structure of [Na(MeOH)(H_2O)$_2$][*p*-tert-butylcalix[4]arene]·MeOH.

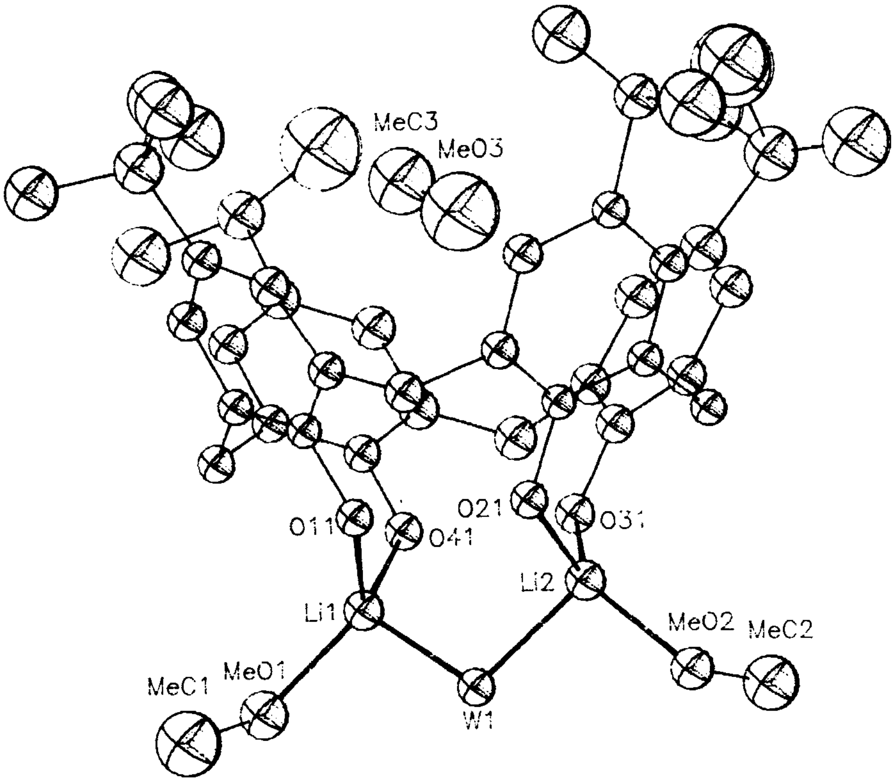
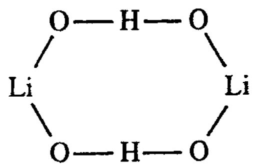


Figure 2 Structure of [(Li(MeOH))$_2$(μ-H_2O)][*p*-tert-butylcalix[4]arene]·MeOH. Important metrical parameters: Li(1)–O(11),1.98(4) Å; Li(1)–O(41), 1.93(4) Å; Li(1)–W(1), 1.89(2) Å; Li(1)–MeO(1), 1.96(2) Å; Li(2)–O(21), 1.94(4) Å; Li(2)–O(31), 1.87(4) Å; Li(2)–W(1), 2.06(2) Å; Li(2)–MeO(2), 1.90(2) Å; Li(1)–W(1)–Li(2), 102(1)°.



Scheme II

doublets in the $-CH_2-$ region (δ 3.0 to 4.5), indicative of the cone conformation for the calixarene in $CDCl_3$ solution.[8,9]

The structure of the lithium salt of the di-oxyanion, **2** (Fig 2), also shows bidentate coordination of each cation. The remaining two protons still participate in O...O bridging, as in Scheme II. The hydrogen bonded O...O separations are 2.38 and 2.42 Å, compared with 3.12 and 3.16 Å between the oxygen atoms bridged by the lithium ions. The two lithium ions are further bridged by a water molecule, and the remainder of the near-tetrahedral geometry is filled out with one methanol molecule per lithium ion. The cone conformation in $CDCl_3$ solution is also evidenced by the ^{1}H-NMR spectrum.

It is unfortunate that there is no solid state evidence for the structure of the KH reaction product. The ^{1}H-NMR spectrum of the crystalline product dissolved in $CDCl_3$ shows two resonances in the aromatic region in the ratio 1:2, two for the tert-butyl groups in the ratio 1:2, and no resonances in the $-CH_2-$ region (indicating slow conformational exchange). Both the crystal data and the solution data are consistent with the formation of a complex aggregate.

Two features of the above structures deserve mention with regard to the existence of tri- or tetra-oxyanions of *p*-tert-butylcalix[4]arene. First, in order to place four negatively charged oxides at the base of a calix[4]arene a bridging situation must exist. This is accomplished by protons in the neutral calixarene, by three protons and one sodium ion for the mono-oxyanion, and by two protons and two lithium ions for the di-oxyanion. In the latter case, the position of the cations relative to each other is also of concern. It seems more likely that higher oxyanions will be realized for divalent or trivalent metal ions, but not for Group I ions.

The second point concerns the importance of solvent. In each of the above structures, solvent molecules are needed to fill the coordination sphere of the cations. This is not necessarily the case for transition metal ions.[4]

The O...O hydrogen bonded distances in the di-oxyanion deserve discussion. In the parent calix[4]-arene the separation of 2.670(9) Å[10] is indicative of strong intramolecular hydrogen bonding. In the mono-oxyanion the two hydrogen bonded O...O distances adjacent to the sodium ion bridge are near normal at 2.58 Å, but the one opposite is quite short at 2.43 Å.[11] In the di-oxyanion the separations of 2.38 and 2.42 Å may also be regarded as indicative of very strong hydrogen bonding.[12] Indeed, 2.38(1) Å is the shortest O...O reported for any structure containing $H_5O_2^+$.[13] Further there is an electronic similarity between these $[RO-H-OR]^-$ units and the strongly hydrogen bonded $[F-H-F]^-$ and $[Cl-H-Cl]^-$ anions.[14] It follows that the hydrogen atoms involved in such strong hydrogen bonds may be difficult to displace with alkali metal ions.

In both **1** and **2** the calix[4]arene cavity is filled with an ill-defined methanol molecule. The oxygen atom is believed to be the one deeper in the cavity based on an analysis of thermal parameters for the sodium-containing structure, **1**. That for the lithium-containing one, **2**, displays an even more poorly resolved methanol guest, and the atom deeper in the cavity is assigned as oxygen by analogy with the structure of **1**.

The new oxyanions have moderate solubility in water or water/methanol. It is expected that a wide range of transition metal complexes of the oxyanions of *p*-tert-butylcalix[4]arene will now be available.

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