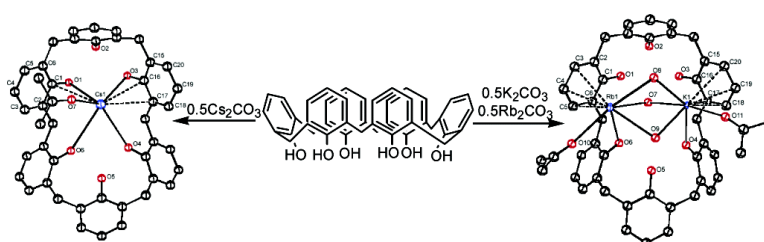


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Synthesis, Structures, and Conformational Characteristics of Calixarene Monoanions and Dianions

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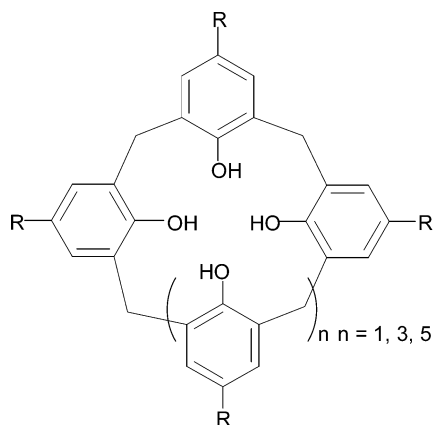
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Abstract: The synthesis, complete characterization, and solid state structural and solution conformation determination of calix[*n*]arenes (*n* = 4, 6, 8) is reported. A complete series of X-ray structures of the alkali metal salts of calix[4]arene (**HC4**) illustrate the great influence of the alkali metal ion on the solid state structure of calixanions (e.g., the Li salt of monoanionic **HC4** is a monomer; the Na salt of monoanionic **HC4** forms a dimer; and the K, Rb, and Cs salts exist in polymeric forms). Solution NMR spectra of alkali metal salts of monoanionic calix[4]arenes indicate that they have the cone conformation in solution. Variable-temperature NMR spectra of salts **HC4**·M (M = Li, Na, K, Rb, Cs) show that they possess similar coalescence temperatures, all higher than that of **HC4**. Due to steric hindrance from *tert*-butyl groups in the *para* position of *p*-*tert*-butylcalix[4]arene (**Bu^tC4**), the alkali metal salts of monoanionic **Bu^tC4** exist in monomeric or dimeric form in the solid state. Calix[6]arene (**HC6**) and *p*-*tert*-butylcalix[6]arene (**Bu^tC6**) were treated with a 2:1 molar ratio of M₂CO₃ (M = K, Rb, Cs) or a 1:1 molar ratio of MOC(CH₃)₃ (M = Li, Na) to give calix[6]arene monoanions, but calix[6]arenes react in a 1:1 molar ratio with M₂CO₃ (M = K, Rb, Cs) to afford calix[6]arene dianions. Calix[8]arene (**HC8**) and *p*-*tert*-butylcalix[8]arene (**Bu^tC8**) have similar reactivity. The alkali metal salts of monoanionic calix[6]arenes are more conformationally flexible than the alkali metal salts of dianionic calix[6]arenes, which has been shown by their solution NMR spectra. X-ray crystal structures of **HC6**·Li and **HC6**·Cs indicate that the size of the alkali metal has some influence on the conformation of calixanions; for example, **HC6**·Li has a cone-like conformation, and **HC6**·Cs has a 1,2,3-alternate conformation. The calix[6]arene dianions show roughly the same structural architecture, and the salts tend to form polymeric chains. For most calixarene salts cation- π arene interactions were observed.

Introduction

Calixarenes and their derivatives, illustrated by the examples in Figure 1, have been the focus of considerable attention since the report of tractable synthetic routes to the parent macrocycles.^{1–3} Calixarenes are intrinsically interesting due to their complexing abilities, conformational flexibility, and reactivity, and their chemistry has been applied in areas as diverse as catalysis, enzyme mimics, host-guest chemistry, selective ion transport, and sensors.^{4,5}

Deprotonated calixarene derivatives, “calixanions”, have recently attracted great interest in a number of fields. The extensive organic and organometallic chemistry of calixarene



HC4: *n* = 1, R = H **Bu^tC4:** *n* = 1, R = C(CH₃)₃
HC6: *n* = 3, R = H **Bu^tC6:** *n* = 3, R = C(CH₃)₃
HC8: *n* = 5, R = H **Bu^tC8:** *n* = 5, R = C(CH₃)₃

Figure 1. Calix[4,6,8]arenes.

derivatives, for example, has stimulated great interest in calixanions as precursors to functionalized complexes.^{4–9}

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Certain isolated calixanions have been shown to have interesting layered solid state structures, similar to clays.^{10,11} Also, the discovery that the parent calixarenes effect the transport of alkali metal ions in water/organic solvent/water membrane systems has led to particular interest in mono-deprotonated calixanions.¹²

Calixanions can vary in terms of ring size, conformation, the nature of the cation, and the degree of deprotonation. Although these changes may seem minor, the properties and reactivity of calixanions are very sensitive to each variable. For example:

- *Ion transport:* calix[4]arene anions are significantly less effective than calix[6] or calix[8]arenes, and for all three ring sizes the ion transport of Cs⁺ is highly favored compared to that of other alkali metal ions.^{4,13}

- *Cation complexation:* it has also been shown that in the 1,3-alternate and the partial cone conformations calix[4]arene selectively binds K⁺ ions, while in its cone conformation it preferentially binds Na⁺ ions.^{14,15} Rubidium ions were shown to preferentially stabilize ambiphilic calix[4]arene derivatives on an air–water interface, compared to other alkali metal cations.¹⁶

- *Conformations and structures of calixanions:* the solution conformations and the solid state structures of various calixanions have been shown to be sensitive to the identity of the cation.¹⁷

- *Synthesis:* the identity of the base has a large effect on the course of the reactions,¹⁸ possibly due to a template affect.^{17,19–21}

- *Degree of deprotonation:* this affects reactivity and nature of products.

Despite their importance, relatively little detailed characterization for alkali metal ion complexes of the partially deprotonated calixarenes has been reported. There are scattered reports of individual calixanion structures and solution conformational analyses, including those from our groups.^{12,32–35} A systematic investigation of the syntheses, complete characterization, and

solid state structural and solution conformation determination of calix[*n*]arene monoanions has not previously been undertaken.

In this paper we describe the characteristics of the alkali metal salts of calix[*n*]arene and *p*-*tert*-butylcalix[*n*]arene monoanions for *n* = 4, 6, and 8 and of the dianions for *n* = 6 and provide a useful catalog of the properties related to the identity of the cation, the ring size, and the degree of ionization.

Background

Among the calix[*n*]arene anions described in this article, those for *n* = 4 have the most representation in the literature. The synthesis and crystal structure of the Cs⁺ complex of the monoanion of **Bu^tC4** (**Bu^tC4**·Cs·MeCN)³¹ has been reported by Harrowfield et al. Hamada et al. reported the synthesis and structure of the sodium salt of the same monoanion.²⁹ Although the potassium salt was also reported,²⁹ its crystal structure was only recently solved.³⁰ While this article was under review, Thuéry et al. reported the structures of **HC4**·Na and **HC4**·Cs (pyridine and acetone complexes)³⁴ and Fromm et al. reported the structures of **Bu^tC4**·4Li, **Bu^tC4**·4K, and **Bu^tC4**·2Li.³⁵

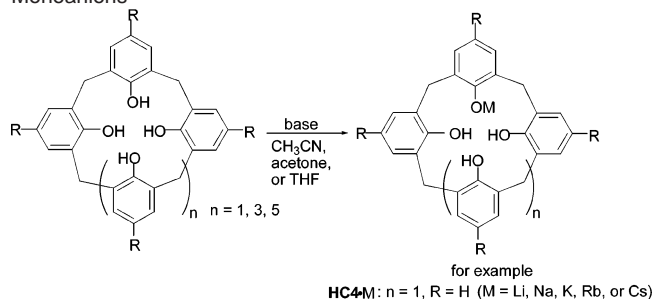
Lithium salts of deprotonated calixarenes have been synthesized for spectroscopic studies by Zundel and co-workers but not characterized.³⁶ Previous work by Gutsche and co-workers¹³ and later by Nam et al.²² included NMR conformational studies of the lithium salts of calix[4]arene anions, but without isolation. Abidi et al. reported the addition of alkali metal salts to the ammonium salt of **Bu^tC4**, but without isolation of products, for experimental and theoretical studies on the complexation of **Bu^tC4** anion with alkali metal cations in polar, nonaqueous solvents.³⁷ Wipff and co-workers have extended their computational studies to investigate alkali metal calixanions in multiple environments.^{3,38–40}

Structures of various complex salts of the monoanion have been reported,^{27,32,37} and an ammonium salt of calix[4]arene was structurally characterized by Nachtigall et al.²⁸ Amine–calix[4]arene interactions have been studied by various authors.^{5,41,42}

The following structures of alkali metal salts of triply and fully deprotonated **Bu^tC4** have been reported: two Li⁺ com-

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Scheme 1. Synthesis of Alkali Metal Salts of Calixarene Monoanions

plexes of fully deprotonated **Bu^tC4**⁴³ (**Bu^tC4**·5Li·(OH)·4(hmpa) and **2Bu^tC4**·8Li·4(hmpa)) and **2Bu^tC4**·6Li·2(NH₃),⁴⁴ and a recent contribution by Guillemot et al. deals with the alkali and alkaline-earth metalated forms of fully deprotonated **Bu^tC4** and the 1,3-diether of **Bu^tC4**.⁴⁵

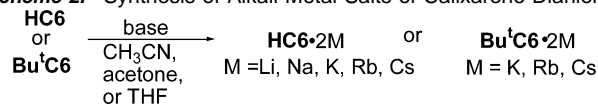
No crystal structures of monoanionic calix[6] or calix[8]arenes have been reported. The dipotassium complexes of calix[6]-arenes **HC6**·2K·5(MeOH), **Bu^tC6**·2K·4(MeOH), and **HC6**·2K·5(H₂O) have been prepared by Murayama and Aoki.²⁴ These complexes were synthesized by the reaction of calix[6]arenes with a large excess of KOH in a mixture of methanol and water. The dipotassium complexes of **Bu^tC8** were studied by Clague et al.²³

Synthesis

Calix[4]arene (HC4) and p-tert-Butylcalix[4]arene (Bu^tC4). Alkali metal salts of monoanionic calixarenes can be made by very simple procedures (Scheme 1). However, it is important to choose the correct bases. Initially, we chose LiH, NaH, and KH to make the corresponding salts of monoanionic calixarenes, as these bases are often used for the preparation of ethers and esters of calix[4]arenes^{4,5,8,18} and for the preparation of the salts **Bu^tC4**·M ($M = \text{Li, Na, K}$),²⁹ but it was found that it is difficult to isolate the salts in good purity and yield. The alkali metal hydrides are very air-sensitive, and it is difficult to accurately weigh them due to their very low molecular weights. Likewise, use of the strong base BuLi, as described by both Gutsche et al.¹³ and Nam et al.,²² proved impractical for the isolation of pure monosubstituted salts.

These results are not surprising; theoretically a weaker base should be preferred. The acidity of the phenolic OH groups, which is important for all selective deprotonations, is determined by the system of intramolecular hydrogen bonds. Shinkai et al. were the first to report pK_a determinations of water-soluble calixarene derivatives, establishing that the pK_{a1} value of calix[4]arenes is generally much lower than pK_{a2} .^{46,47} Thus, weak bases should be able to deprotonate one phenolic residue while leaving the others untouched.

We have found that the base M_2CO_3 (as used by Harrowfield and co-workers for $M = \text{Cs}$)³¹ is a good choice for making calixarene monoanions. We obtained complexes **HC4**·M

Scheme 2. Synthesis of Alkali Metal Salts of Calixarene Dianions

($M = \text{Na, K, Rb, Cs}$) and **Bu^tC4**·M ($M = \text{K, Rb, Cs}$) in 64–88% yields.

The reactions of calixarenes with Li_2CO_3 or Na_2CO_3 are occasionally unsuccessful, possibly because the solubility of Li_2CO_3 and Na_2CO_3 is low. No reaction occurs, for example, when **Bu^tC4** is treated with Li_2CO_3 or Na_2CO_3 . In these cases the monoanions can be made by the reactions of calixarenes with the base $MOC(CH_3)_3$ ($M = \text{Li, Na}$); see compounds **HC4**·Li, **Bu^tC4**·Li, and **Bu^tC4**·Na.

Calix[6]arene (HC6) and p-tert-Butylcalix[6]arene (Bu^tC6). Although treatment of calix[4]arenes with M_2CO_3 led to monoanions, the same strategy led to the formation of dianions for calix[6]arenes and calix[8]arenes. This phenomenon is readily explained. When Gutsche et al. treated DMSO solutions of calix[6]arenes with acetates and carbonates of first- or second-group elements, the trianions were obtained, indicating that the pK_1 , pK_2 , and pK_3 values of calix[6]arenes must be lower than the pK_a of acetic (4.75) or carbonic acids ($pK_1 = 6.35$, and $pK_2 = 10.40$).⁴⁸ Thus, when **HC6** and **Bu^tC6** are treated in a 1:1 molar ratio of M_2CO_3 , the dianions of calix[6]arenes should be obtained.

Experimentally, when **HC6** was treated with M_2CO_3 ($M = \text{K, Rb, Cs}$) in a 1:1 molar ratio, the resulting salts were the dianionic species **HC6**·2M ($M = \text{K, Rb, Cs}$), obtained in good yield (67–93%) (Scheme 2). Similarly, treatment of **Bu^tC6** with K_2CO_3 , Rb_2CO_3 , or Cs_2CO_3 in a 1:1 molar ratio gave the dianions **Bu^tC6**·2M ($M = \text{K, Rb, Cs}$).

When **HC6** or **Bu^tC6** was treated in a 2:1 molar ratio with K_2CO_3 , Rb_2CO_3 , or Cs_2CO_3 the mono-deprotonated product **HC6**·M ($M = \text{K, Rb, Cs}$) or **Bu^tC6**·M ($M = \text{K, Rb, Cs}$) was obtained in good yield (71–97%). The reaction of **HC6** with both K_2CO_3 and Rb_2CO_3 (2 **HC6**:1 K_2CO_3 :1 Rb_2CO_3) was carried out. Rather than a mixture of **HC6**·2K and **HC6**·2Rb, the bimetallic product **HC6**·KRb was obtained.

Calix[8]arene (HC8) and p-tert-Butylcalix[8]arene (Bu^tC8). It was found that monoanions of calix[8]arenes can be obtained by deprotonation with the strong base $MOSi(CH_3)_3$ ($M = \text{Li, Na, K}$) or MOH ($M = \text{Rb, Cs}$). The reactions generally give high yields.

NMR Studies

The NMR spectral patterns of calixarenes provide a useful measure of conformational identity, and the temperature dependence of the methylene protons allows an assessment of the rates of conformational inversion. For the monoanions, the ¹H NMR spectra of each series of calixarene salts at room temperature are very similar. The chemical shifts of the aromatic protons in the salts **HC4**·M ($M = \text{Li, Na, K, Rb, Cs}$) shift upfield to 6.9 and 6.4 ppm in acetone-*d*₆ (the chemical shifts of the aromatic protons in **HC4** are 7.14 and 6.8 ppm). In the ¹³C NMR spectra the signals at about 34 ppm are assigned to the ArCH₂Ar groups. ¹H NMR spectra of dianionic **HC6** and **Bu^tC6** (Figure 2) permit the solution state structures to be assigned as

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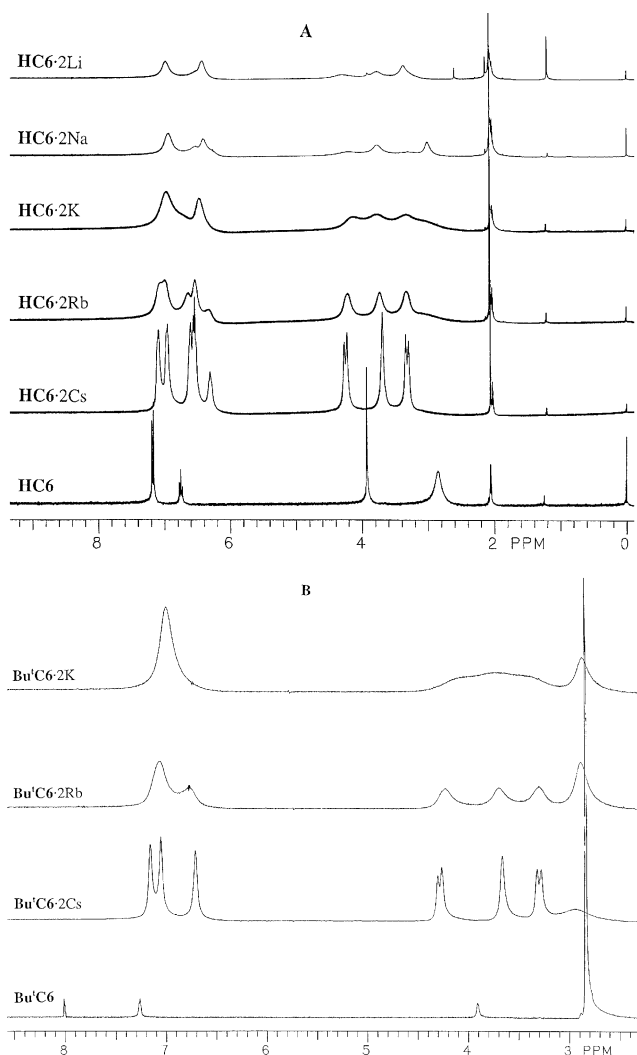


Figure 2. ^1H NMR spectra of **HC6** and **Bu^tC6** and alkali metal salts of dianionic **HC6** and **Bu^tC6** at 293 K in acetone- d_6 : (A) (for **HC6**), (B) (for **Bu^tC6**).

a 1,2,3-alternate conformation, consistent with the solid state structures (vide infra).

Conformational Studies. Temperature-dependent ^1H NMR studies for the salts **HC4**·*M* (*M* = Li, Na, K, Rb, Cs), **HC6**·Li, **HC6**·Cs, **HC6**·2*M* (*M* = K, Rb, Cs), and **Bu^tC6**·2*M* (*M* = K, Rb, Cs) were carried out, their coalescence temperatures were obtained, and the energies for conformational interconversion ΔG^\ddagger were calculated (Table 1).⁴⁹

Three factors appear to influence inversion energies: level of deprotonation, ring size, and the nature of the cation.

Deprotonation. The room-temperature ^1H NMR spectrum of **HC4** exhibits a broad peak for the methylene groups that bridge the arene units (ArCH₂Ar groups), indicating that the two types of protons of the cone conformer are exchanging environments fairly rapidly on the NMR time scale, but the ^1H NMR spectra of the salts **HC4**·*M* (*M* = Li, Na, K, Rb, Cs) give a pair of broad peaks at 4.4 and 3.2 ppm, respectively. The calixanions are likewise in a cone conformation, but inversion is less rapid than in the parent molecule. Indeed, in

Table 1. Coalescence Temperatures (at 300 MHz) and Free Energies of Activation for the Conformational Inversion of Calixarenes and Calixarene Anions

compd	T_d °C	$\Delta\nu$ /Hz	ΔG^\ddagger (kcal mol ⁻¹)	conformation(s)	solvent
HC4 ⁴	-5.0	171	13.1	cone	CD ₃ COCD ₃
HC4 ·Li	47	232	14.8	cone	CD ₃ COCD ₃
HC4 ·Cs	37	324	14.2	cone	CD ₃ CN
Bu^tC4 ⁴	52	225	15.7	cone	CDCl ₃
HC6 ⁴	-49		9.5		CD ₃ COCD ₃
HC6 ·2K	35	274	14.1	1,2,3-alternate	CD ₃ COCD ₃
HC6 ·2Cs	47	279	14.6	1,2,3-alternate	CD ₃ CN
Bu^tC6 ⁴	-40		11.0		CD ₃ COCD ₃
Bu^tC6 ·2K	10	266	13.0	1,2,3-alternate	CD ₃ COCD ₃
Bu^tC6 ·2Rb	43	253	14.7	1,2,3-alternate	CD ₃ COCD ₃
Bu^tC6 ·2Cs	63	293	15.4	1,2,3-alternate	CD ₃ CN

all cases the coalescence temperature of the anion is higher than that of its parent calixarene. Consistent with previous studies, this is caused by directed electrostatic interactions between the cation and the anionic phenolate oxygens.⁴

Ring Size. **HC4** monoanions have a slower rate of conformational inversion than **HC6** monoanions, due to more effective hydrogen bonding between phenol groups. In acetone- d_6 solution all **HC6** monoanions show the methylene resonance as a sharp singlet at room temperature, resolving to several broad peaks at low temperature. Sharp peaks are not observed even at 183 K. **HC4** monoanions, on the other hand, show a pair of sharp doublets at 243 K or higher, indicating a more rigid conformation.

Cation. Both solvent polarity and the cation influence the rate of conformational inversion of **Bu^tC4** salts. In the nonpolar solvent chloroform, we find that Na and Cs salts (methylenes are sharp doublets at room temperature) are more conformationally rigid than the K and Rb salts (methylenes are broad). In the polar solvent acetone, however, the conformational interconversion of all the salts **Bu^tC4**·*M* is slow on the NMR time scale (methylenes are sharp doublets). The dependence of the conformational rigidity on the cation in nonpolar solvent may be due to inefficient solvation of the cation, leading to strong calixanion–cation interaction. In acetone the cation–solvent interaction dominates.

For **HC6** dianions, the cations have a strong influence on coalescence temperatures. For **RC6**·2*Cs* (*R* = H, Bu^t) a pair of doublets and one singlet in the ^1H NMR spectra are assigned to the methylene groups, while **RC6**·2*M* (*M* = K, Rb) show very broad peaks for the methylene groups. This means that the conformation of **RC6**·2*Cs* in acetone is more rigid than those of the dirubidium and dipotassium salts. In general, the complexes are conformationally rigid, and the greater the size of the alkali metal, the more rigid is the conformation.

X-ray Structures of Calixanions

The X-ray structures of **HC4**·Li, **HC4**·Na, **HC4**·Rb, **HC4**·Cs, **Bu^tC4**·Rb, **Bu^tC4**·2Li, **HC6**·Li, **HC6**·Cs, **HC6**·2*M* (*M* = K, Rb, Cs), and **HC6**·KRb were obtained. These include the first reported rubidium-calixarene complexes, the first calix[6]-arene monoanion structures, and the first mixed-alkali metal calixarene anion. We will discuss selected characteristics of these and previously reported calixanion salts.

All calix[4]arene structures exhibit the cone conformation, as does the lithium salt of **HC6**. All other **HC6**·*M* and **HC6**·2*M* calixarenes are in a flattened 1,2,3-alternate conformation.

(49) For the calix[6] dianionic structures, the NMR spectra are consistent with a 1,2,3-alternate conformation in solution, leading to a pattern of one pair of doublets and one singlet in the methylene region. The coalescence temperature of the pair of doublets was used for ΔG calculations.

Table 2. Selected M–O and M–C Distances of Alkali Metal Salts of Calixanions

compound	M–O (OAr)/Å	M–O (solvate)/Å	M–C/Å ^a	ref
HC4 ·Li·2H ₂ O·Me ₂ CO	1.924(2)	1.930(3)–1.950(3)		<i>b</i>
Bu^tC4 ·2Li·2MeOH·H ₂ O (monomer)	1.87(4)–1.98(4)	1.89(2)–2.06(2)		29
Bu^tC4 ·2Li·2Me ₂ CO (dimer)	1.923(11)–1.975(11)	1.938(13)–1.999(12)	2.535(12)	<i>b</i>
Bu^tC4 ·4Li·LiOH·4HMPA	1.92(1)–2.089(4)			43
HC6 ·Li·3Me ₂ CO	1.931(10)	1.873(11)–1.895(12)		<i>b</i>
(HC4 ·Na) ₂ ·3Me ₂ CO	2.305(6)–2.359(6)	2.217(6)–2.441(7)		<i>b</i>
(HC4 ·Na) ₂ ·3Me ₂ CO	2.284(5)–2.337(5)	2.206(6)–2.394(5)		34
Bu^tC4 ·4Na·Py ₄	2.227(10)–2.550(8)			45
Bu^tC4 ·2Me·2Na	2.129(4)–2.538(4)		2.792(3)–2.900(5)	50
HC4 ·K·1.5H ₂ O·THF	2.743(3)–2.893(2)	2.656(4)–2.845(3)	3.286(3)–3.515(3)	30
Bu^tC4 ·K·4THF (monomer)	3.042(13)–3.160(12)	2.648(13)–2.728(11)		30
Bu^tC4 ·K·2THF·H ₂ O (dimer)	2.737(2)–2.935(2)	2.694(2)–2.733(2)		30
Bu^tC4 ·4K·3THF	2.544(9)–2.861(5)	2.744(11)–2.749(9)		45
HC6 ·2K·2Me ₂ CO	2.805(2)–3.056(3)	2.699(3)–2.981(3)	3.214(3)–3.713(3)	<i>b</i>
HC6 ·2K·5MeOH	2.64(1)–2.94(1)	2.74(1)–2.91(1)	3.28(2)–3.96(2)	24
HC6 ·2K·5H ₂ O	2.944(5)	2.713(5)–2.746(6)	3.168(6)–3.582(6)	24
Bu^tC6 ·2K·4MeOH	2.68(2)–3.05(2)	2.58(3)–2.89(3)	3.30(3)–4.00(3)	24
Bu^tC8 ·2K·4.67EtOH·1.339(EtO) ₂ CO	2.7205(19)–2.949(2)	2.616(4)–2.825(4)		23
HC4 ·Rb·THF	2.943(3)	2.770(17)	3.349(3)–3.579(3)	<i>b</i>
Bu^tC4 ·Rb·4THF	3.124(2)	2.796(2)		<i>b</i>
HC6 ·2Rb·2Me ₂ CO	2.986(2)–2.999(3)	2.835(4)–3.095(4)	3.304(4)–3.731(4)	<i>b</i>
HC6 ·KRb·2Me ₂ CO	2.786(3) (K–O), 3.008(2) (Rb–O)	2.863(3)–3.029(3) (Rb–O), 2.658(3)–2.773(K–O)	3.154(3)–3.417(3) (K–C), 3.314(3)–3.688(3) (Rb–C)	<i>b</i>
HC4 ·Cs·Me ₂ CO	3.100(3)	2.959(3)	3.599(3)–3.840(3)	<i>b</i>
HC4 ·Cs·Py	3.169(12)–3.704(16)		3.53(1)–4.17(1)	34
HC4 ·Cs·H ₂ O	3.065(5)–3.673(5)	2.97(3)	3.530(7) (shortest distance)	34
Bu^tC4 ·Cs·MeCN			3.545(3)–3.961(3)	31
HC6 ·Cs·Me ₂ CO	3.073(12)–3.535(15)	2.99(2)	3.416(15)–3.886(16)	<i>b</i>
HC6 ·2Cs·2Me ₂ CO	2.975(12)–3.000(8)	2.853(10)–3.093(9)	3.301(13)–3.728(13)	<i>b</i>

^a Distances for cation– π arene interactions. ^b This work.

Bond distances and angles fall within normal parameters, as can be seen from Table 2.

Metal–Oxygen versus Metal–Carbon (π -cation) Interactions. The calix[4]arene series allow us to examine the relative affinities of each metal for interaction with the phenolic oxygens on the calixarene lower rim versus π -cation interactions with the arene rings within the cavity. A combination of these effects determines the following structure types:

1. *Endo/exo polymers.* These are found for Cs (see Supporting Information and Thuéry's report³⁴) and Rb (Figure 3), both cations with high affinity for π -electrons and apparently less affinity for O-bridging interactions. Thus mononuclear metal cores are linked to one calixarene unit in an *endo* fashion by π -cation interactions, while a second calixarene unit donates an oxygen to bind a neighboring ring to the same metal in an *exo* coordination mode. A two-dimensional sheet polymeric structure is governed by similar Cs–O and Cs–arene interactions in CsO-2,6-*i*-Pr₂C₆H₃.⁵¹

2. *Polymer of dimers.* In the case of the dimeric **HC4**·K complex (previously reported by us³⁰) the π -cation interactions lead to connections between dimeric units to form a polymeric chain in the solid state. Evidently in the case of potassium, the formation of a dinuclear water-bridged core is more favorable than the *endo/exo* polymeric interaction seen with the softer cations.

3. *Discrete dimeric units.* The **HC4**·Na dimer (Figure 4) is similar to that of the **HC4**·K dimer;³⁰ however, no π -cation interactions are observed for the smaller cation. Dimeric structures are also observed for **Bu^tC4**·2Li and **Bu^tC4**·K. For

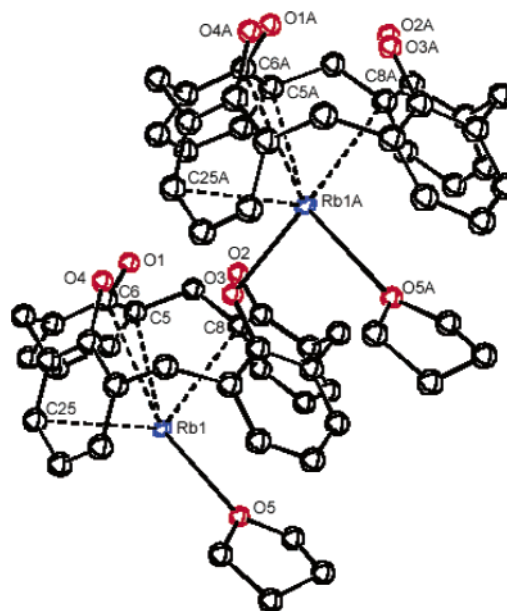


Figure 3. Crystal structure of **HC4**·Rb·THF. All H atoms are omitted for clarity. Selected bond distances (Å): Rb(1A)–O(3) 2.943(3), Rb(1)–O(5) 2.770(17), Rb(1)–C(6) 3.349(3) (shortest).

the **Bu^tC4**·M series this is the largest unit observed, indicating that the bulk of the Bu^t groups in the *para* position blocks both types of polymeric interaction.

4. *Discrete monomeric units.* **HC4**·Li (Figure 5) exhibits a monomeric structure with a single calixarene–lithium interaction through a phenolic oxygen. **Bu^tC4**·M for M = Na,³⁴ K,³⁰ Rb (Figure 6) and **Bu^tC4**·2Li²⁹ also exhibit monomeric structures, but with multiple M–calixarene interactions. The energy difference between mono- and dimeric forms is apparently slight,

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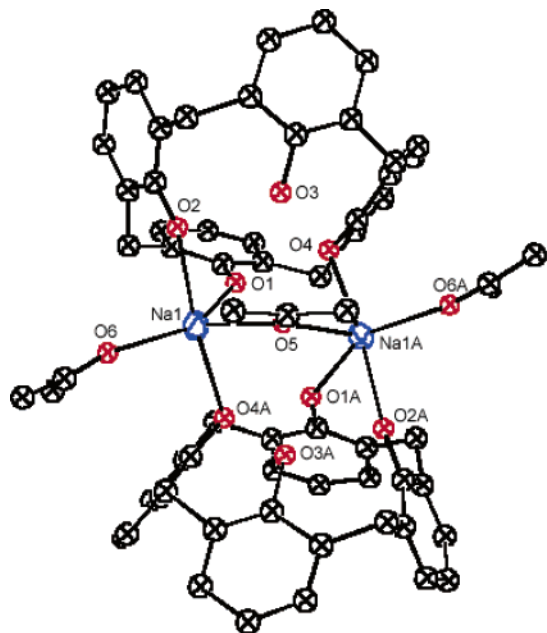


Figure 4. Crystal structure of $(\text{HC4}\cdot\text{Na})_2\cdot\text{Me}_2\text{CO}$. All H atoms are omitted for clarity. Selected bond distances (Å): Na(1)–O(1) 2.305(6), Na(1)–O(2) 2.359(6), Na(1)–O(4A) 2.306(5), Na(1)–O(5) 2.221(7), Na(1)–O(6) 2.217(6), Na(1)–Na(1A) 3.923.

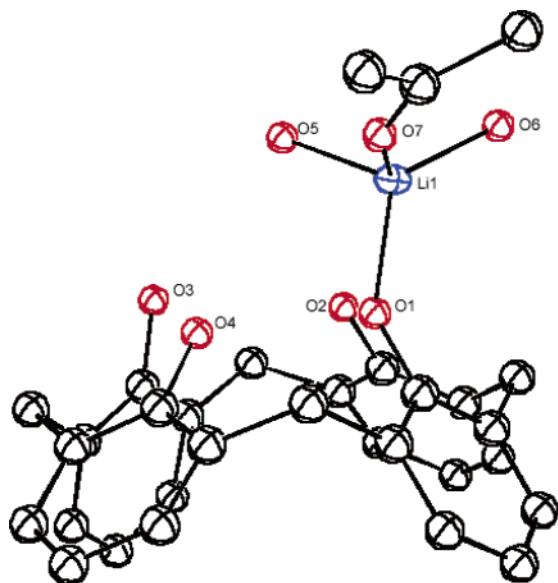


Figure 5. Crystal structure of $\text{HC4}\cdot\text{Li}\cdot 2\text{H}_2\text{O}\cdot\text{Me}_2\text{CO}$. All H atoms are omitted for clarity. Selected bond distances (Å): Li–O(1) 1.924(2), Li–O(5) 1.950(3), Li–O(6) 1.930(3), Li–O(7) 1.949(3).

as in two cases both forms have been structurally characterized for the same stoichiometry.

It is interesting to note the point at which the structure type changes in each series. The presence of *para* Bu^t groups on the calixarene decreases the accessibility of an *endo* metal for external interactions with solvent or another calixarene unit.³⁸ Thus, in the case of $\text{Bu}^t\text{C4}\cdot\text{M}$ the metal is forced to “choose” between an *exo* and *endo* interaction. Calculations for alkali metal complexes of calix[4]arenes show that all the larger cations K⁺, Rb⁺, and Cs⁺ are expected to enter the calix[4]-arene cavities,^{38–40,52} but we find that the *endo* interaction

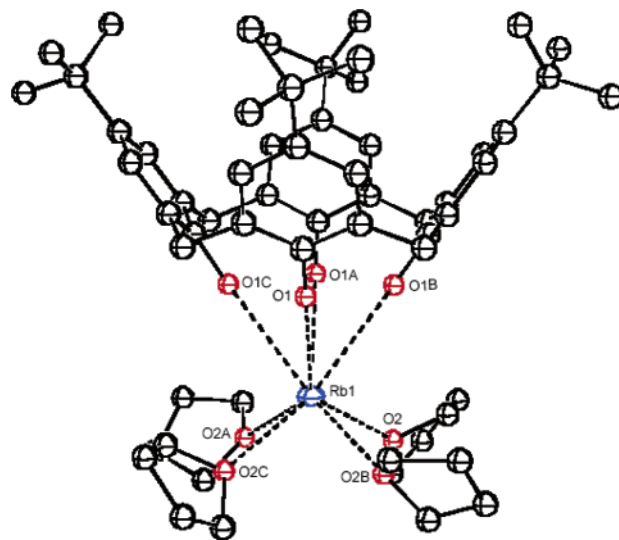


Figure 6. Crystal structure of $\text{Bu}^t\text{C4}\cdot\text{Rb}\cdot 4\text{THF}$. All H atoms are omitted for clarity. Selected bond distances (Å): Rb–O(1) 3.124(2), Rb–O(2) 2.796(2).

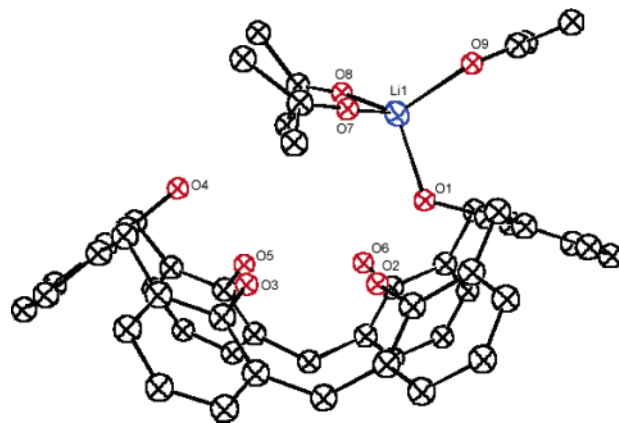


Figure 7. Crystal structure of $\text{HC6}\cdot\text{Li}\cdot 3\text{Me}_2\text{CO}$. All H atoms, and one CHCl_3 molecule in the lattice, are omitted for clarity. Selected bond distances (Å): Li–O(1) 1.931(10), Li–O(7) 1.892(11), Li–O(8) 1.873(11), Li–O(9) 1.895(12).

predominates only in the case of Cs⁺. For $\text{HC4}\cdot\text{M}$ both Cs and Rb exhibit *endo* interactions.

Core Structures. Lithium. Li aryloxides have a rich coordination chemistry^{53–55} with a predilection toward multinuclear clusters and Li–O–Li bridges. The mononuclear cores observed in $\text{HC4}\cdot\text{Li}$ (Figure 5) and $\text{HC6}\cdot\text{Li}$ (Figure 7) are unusual. In both cases the Li has a tetrahedral geometry with one bond to a phenolic calixarene oxygen and the other three to terminal solvent molecules.

The Li/O core structures seen in other lithium salts of calixarenes^{29,43,45} are more typical. Molecule $\text{Bu}^t\text{C4}\cdot 2\text{Li}$ (Figure 8), for example, comprises two doubly deprotonated $\text{Bu}^t\text{C4}$ dianions fused at the lower rim by four bridging lithium cations, each of which possesses the expected near-tetrahedral coordination geometry. In the Li/O core, the lithium cations are coordinated to phenolic OH groups, to anionic phenolate O atoms, and to O atoms from acetone in the crystal unit. The

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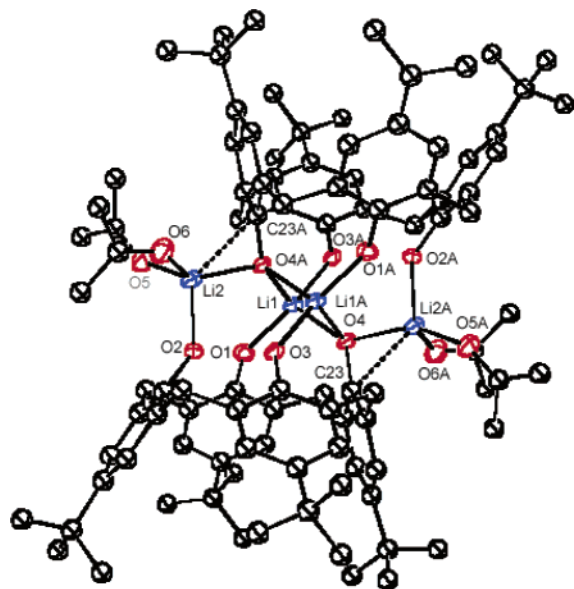


Figure 8. Crystal structure of $\text{Bu}^4\text{C}_4 \cdot 2\text{Li} \cdot 2\text{Me}_2\text{CO}$. All H atoms and lattice solvent (2 H_2O , 2 acetone molecules) are omitted for clarity. Selected bond distances (\AA): Li(1)–O(1) 1.925(11), Li(1)–O(3A) 1.947(11), Li(1)–O(4) 1.975(11), Li(1)–Li(1A) 2.39(2), Li(1)–Li(2) 3.400(14), Li(1)–Li(2A) 3.392(15), Li(2)–O(2) 1.923(11), Li(2)–O(5) 1.938(13), Li(2)–O(6) 1.999(12), Li(2)–O(4A) 1.983(11), Li(2)–C(23A) 2.535(12).

cations Li(2) and Li(2A) exhibit both Li–O binding and Li– π -ring interactions.

Sodium. The sodium atoms in both $\text{HC}_4 \cdot \text{Na}^{34}$ and $\text{Bu}^4\text{C}_4 \cdot \text{Na}^{29}$ are five-coordinate, with approximate trigonal bipyramidal geometry. This geometry is also found around some of the sodium atoms in the core cluster of Floriani's $\text{Bu}^4\text{C}_4 \cdot 4\text{Na}$,⁴⁵ but the other sodium atoms retain either tetrahedral or distorted square pyramidal coordination geometries. π -Arene interaction is observed only in the case of $\text{Bu}^4\text{C}_4 \cdot 4\text{Na}$.⁴⁵

Potassium, Rubidium, and Cesium. These metals display six-, seven-, and eight-coordinate geometries in their calixarene complexes, as is typical for their aryloxide complexes.⁵⁴ π -Cation interaction becomes progressively more important for these metals, causing the formation of polymeric structures (discussed above) and strong internal M–arene π bonds (see Table 2).

In the crystal structure of $\text{HC}_6 \cdot 2\text{K}$ (Figure 9), for example, K(1) is coordinated to five O atoms and to the π -arene in a reasonably symmetrical fashion. K(2) interacts more strongly with three carbon atoms of the phenyl ring (K(2)–C = 3.258(3)–3.431(3) \AA) than with the other three carbon atoms (K(2)–C = 3.554(3)–3.713(3) \AA). K(2) is coordinated to six O atoms with the extra one coming from interaction with O(4) on an adjacent molecule (not shown in Figure 9). These units form infinite one-dimensional chains.

In $\text{HC}_6 \cdot \text{Cs}$ (Figure 10) the cation Cs^+ is coordinated to one phenolate O atom, three phenolic O atoms, and an O atom from solvate acetone. Asymmetric cation– π interactions were also found in this system.

In $\text{Bu}^4\text{C}_4 \cdot \text{M}$ (M = K,³⁰ Rb) the *exo* M^+ is symmetrically coordinated to one phenolate and three phenol groups and to four THF molecules. No π -cation interactions are seen. In the solid state the molecule lies on a crystallographic 4-fold axis, and the geometry around the cation is that of a square antiprism with four sites occupied by THF molecules.³⁰

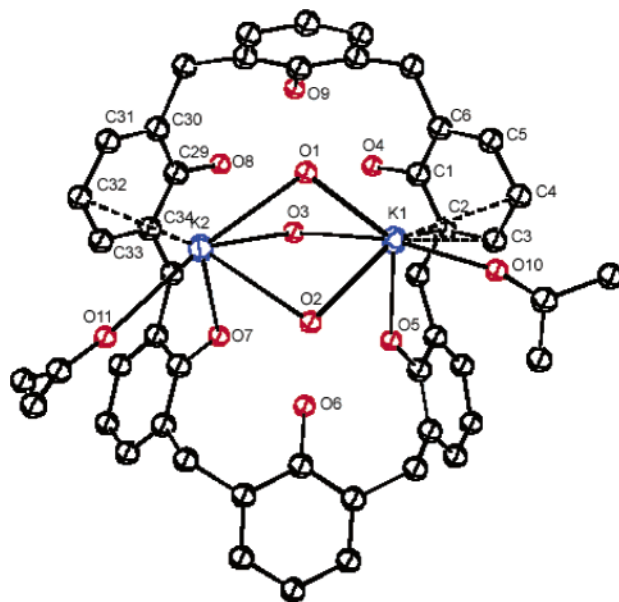


Figure 9. Crystal structure of $\text{HC}_6 \cdot 2\text{K} \cdot 2\text{Me}_2\text{CO}$. All H atoms, and CHCl_3 and hexane in the lattice, are omitted for clarity. Selected bond distances (\AA): K(1)–O(1) 2.735(3), K(1)–O(2) 2.699(3), K(1)–O(3) 2.717(3), K(1)–O(5) 2.805(2), K(1)–O(10) 2.784(3), K(2)–O(1) 2.865(3), K(2)–O(2) 2.852(3), K(2)–O(3) 2.981(3), K(2)–O(7) 2.925(2), K(2)–O(11) 2.790(3), K(2)–O(4A) 3.056(3), K(1)–C(3) 3.214(3) (shortest), K(1)–K(2) 4.1764(11), K(1)–O(1)–K(2) 96.44(9).

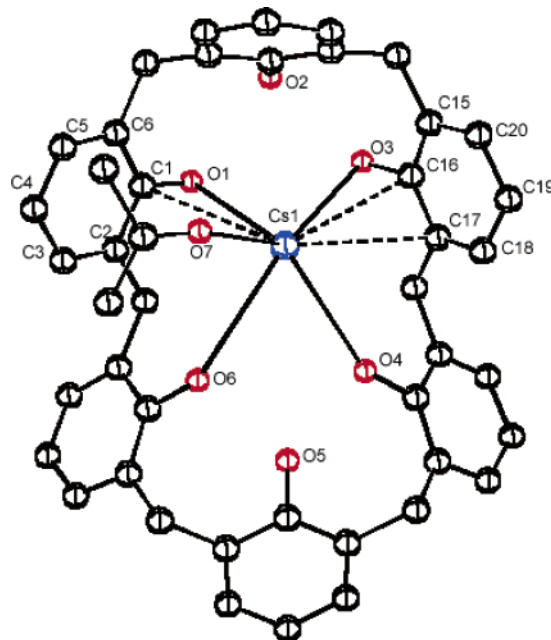


Figure 10. Crystal structure of $\text{HC}_6 \cdot \text{Cs} \cdot \text{Me}_2\text{CO}$. All of the H atoms and 2 lattice H_2O molecules are omitted for clarity. Selected bond distances (\AA): Cs–O(1) 3.44(2), Cs–O(3) 3.535(15), Cs–O(4) 3.073(12), Cs–O(6) 3.243(14), Cs–O(7) 2.99(2), Cs–C(16) 3.416(15) (shortest).

The unique $\text{Bu}^4\text{C}_4 \cdot \text{Cs}^{31}$ is the only *endo* structure reported in the solid state for which no M–O interactions are observed.

Location of Phenolate Ions. In some cases the positions of the phenolic hydrogens have been located in the crystal structures, while in other cases the positions may be inferred by comparison of O–O distances and/or M–O bond lengths. When there is a single M–O coordination site (e.g., $\text{HC}_4 \cdot \text{Li}$, $\text{HC}_6 \cdot \text{Li}$), that site is usually the phenolate oxygen. In some cases, the phenolate anion can be most stabilized by H-bonding

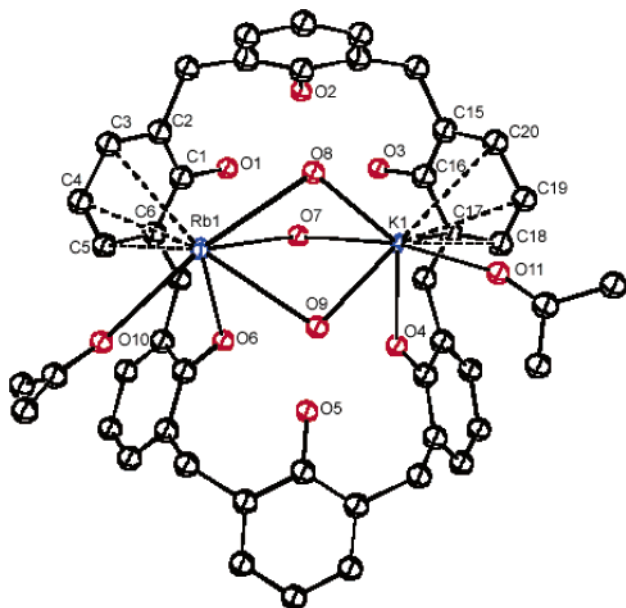


Figure 11. Crystal structure of **HC6·KRb·2Me₂CO**. All H atoms are omitted for clarity. Selected bond distances (Å): K–O(4) 2.786(3), K–O(7) 2.727(3), K–O(8) 2.685(3), K–O(9) 2.658(3), K–O(11) 2.773(3), K–C(18) 3.154(3) (shortest), Rb–O(6) 3.008(2), Rb–O(7) 3.029(3), Rb–O(8) 2.993(3), Rb–O(9) 2.999(4), Rb–O(10) 2.863(3), Rb–C(4) 3.314(3) (shortest), K–Rb 4.217(calc), K–O(9)–Rb 96.22(11).

to neighboring phenolic hydrogens and is not bound directly to the metal. This is exemplified in **HC6·KRb** (Figure 11), where the deprotonation positions are found to be O(2) and O(5), while the metals are coordinated to O(6) and O(4). Each deprotonated oxygen is surrounded by two phenols that each donate a hydrogen to maximize H-bonding interactions.

Selectivity. It is well established that cation selectivity of calixarene anions is highly dependent on experimental conditions.³⁸ It is therefore not surprising that in the three cases where a calixanion has been crystallized from a solution containing more than one cation, three different results have been observed. Aoki crystallized pure (by elemental analysis) **HC6·2K** dianion from a K/Na solution,²⁴ but we found no selectivity when crystallizing the same dianion from a K/Rb solution. Indeed, we obtained the first reported example of a mixed alkali metal complex, **HC6·KRb**.⁵⁶ Thuèry et al. recently isolated **HC4·Cs** crystals from a solution containing Na⁺, but yield and purity were not reported.³⁴

Conclusion

We have reported the high-yield syntheses and complete characterization for a comprehensive series of calix[*n*]arene monoanions and dianions. The syntheses consist of the simple addition of base to the parent calixarene, but the choices of base, stoichiometry, and solvent are very important.

NMR investigation of these calixanions has revealed that calix[4]arene anions are exclusively in the cone conformation in solution, and calix[6]arene anions are in either cone-like or 1,2,3-alternate conformations, consistent with their solid state structures. The degree of flexibility toward ring inversion is

(56) Although the satisfactory elemental analysis cannot distinguish between the pure mixed-cation species versus a 1:1 ratio of the two single-cation species, NMR spectra are consistent with a single mixed-cation species in solution.

dependent on the level of deprotonation, the ring size, and the identity of the cation(s).

We have illustrated the variety of structural types available to alkali metal salts of calixarenes in the solid state. These include two types of polymer, *viz.* calixarene-capped dimer and monomeric units. Both the *endo* and the *exo* forms can be isolated in the solid state, and both the ring size and identity of the cation play roles in determining which is the most stable form. Alkali metal cation– π arene interactions can be observed for most alkali metals, and these interactions become progressively more important as the size of the alkali metal increases.

Experimental Section⁵⁷

General Procedure for Making Calixanion with Strong Bases.

To a solution (or suspension) of 1 mmol of calix[*n*]arene (*n* = 4, 6, 8) in 20 mL of THF (or MeCN) was added 1 mmol of MOC(CH₃)₃ (M = Li, Na for **HC4**, **Bu^tC4**, **HC6**, and **Bu^tC6**) or MOSi(CH₃)₃ (M = Li, Na, or K for **HC8** and **Bu^tC8**). The mixture was stirred for 6 h at room temperature under nitrogen. The solvent was removed under reduced pressure, and the crude product was washed with 30 mL of hexane to produce a light yellow or white solid. All single crystals were obtained by slow evaporation of solvents or by pentane diffusion into a THF solution.

A solvent effect was noted in the formation of the lithium salt **Bu^tC4·Li**. Although **Bu^tC4·Li** was readily obtainable from the reaction of **Bu^tC4** with LiOC(CH₃)₃ in THF, the reaction of **Bu^tC4** with LiOC(CH₃)₃ in CH₃CN–acetone or in CH₃CN–THF yielded the dianion **Bu^tC4·2Li**. In contrast, **Bu^tC4** was treated with NaOC(CH₃)₃ in CH₃CN–THF to afford **Bu^tC4·Na** in high yield as a white solid.

For calix[6]arene, the reaction of **HC6** with Li₂CO₃ affords mono-deprotonated **HC6·Li** in low yield (35%), but if LiOC(CH₃)₃ is used, the yield is significantly improved (75%). **HC6** reacts with either 2:1 or 1:1 molar ratio of Na₂CO₃ to give the product **HC6·Na**. Compound **Bu^tC6** reacts with LiOC(CH₃)₃ or NaOC(CH₃)₃ (1:1 ratio) to give **Bu^tC6·Li** or **Bu^tC6·Na** in high yield (78% and 94%).

General Procedure for Making Calixanions with Weak Bases (using calix[4]arenes as the sample). To a suspension of 1 mmol of **HC4** or **Bu^tC4** in 25 mL of MeCN (or Me₂CO) was added 1 mmol of M₂CO₃ (M = Na, K, Rb, and Cs). The mixture was stirred at 50–55 °C for 12 h. The resulting suspension was vacuum filtered to afford a colorless solution, and the solvent was evaporated to dryness to give crude product. The crude product was purified by washing with 30 mL of hexane and recrystallized by slow evaporation of solvents from Me₂CO–CHCl₃–hexane (1:1:2) solution or Me₂CO–hexane (1:2) solution. Crystals of the salts **HC4·M** (M = Na, K, Rb, Cs) and **Bu^tC4·M** (M = K, Rb, Cs) suitable for X-ray analysis were grown by pentane diffusion into their THF solution or by slow evaporation of solvents from Me₂CO–CHCl₃–hexane (1:1:2) solution.

Yields are summarized in Figure 12. As the spectra for different alkali metal salts of the same monoanions were very similar, only representative NMR data are listed in Tables 2 and 3. The full listing of NMR, IR, and analytical data is given in the Supporting Information.

Solubility and Air-Sensitivity of Calixanions. The salts **HC4·M** (M = Na, K, Rb, Cs) and **Bu^tC4·Cs** are of limited solubility in most

(57) General information: Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. THF was freshly distilled from Na/benzophenone. The melting points of all compounds were taken in sealed and evacuated capillary tubes on a Mel-Temp apparatus (Laboratory Devices, Cambridge, MA) using a 400 °C thermometer calibrated against a thermocouple. The melting points are uncorrected. A melting temperature preceded by a “>” sign indicates that the compound starts to decompose at that temperature but appears to actually melt at some higher temperature. ¹H NMR and ¹³C NMR spectra were recorded on a Varian XL-300 spectrometer at 300 and 75 MHz, respectively. Analytical samples were dried in a drying pistol under vacuum for at least 24 h. Microanalyses were performed by Desert Laboratories, Tucson, AZ. IR spectra were obtained with an Infinity GoldTM FTIR spectrometer. Vacuum filtrations used Fisherbrand grade Q8 filter paper.

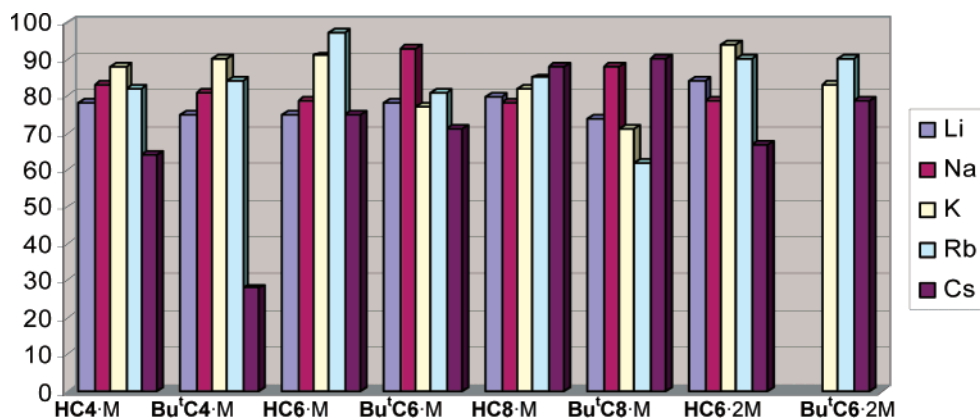


Figure 12. Yields of calixanions. The yield for **Bu'C4**·Cs is from ref 29.

Table 3. Representative ^1H NMR and ^{13}C NMR of the Alkali Metal Salts of Monoanionic HC4, **Bu'C4**, HC6, **Bu'C6**, HC8, and **Bu'C8** in Acetone- d_6

compound	$\delta_{\text{H}}/\text{ppm}$			$\delta_{\text{C}}/\text{ppm}$
	ArH	ArCH ₂ Ar	C(CH ₃) ₃	
HC4	7.17(d), 6.70(t)	3.92(s)		150.3, 130.2, 129.9, 122.7, 31.9
HC4 ·Na	6.88(d), 6.35(t)	4.40(s), 3.22(s)		156.0, 131.8, 128.6, 118.7, 34.0
Bu'C4	7.12(s)	4.45(d), 3.40(d)	1.21(s)	<i>a</i>
Bu'C4 ·Na	6.97(s)	4.37(d), 3.19(d)	1.14(s)	153.6, 140.7, 131.1, 125.3, 34.8, 34.3, 32.1
HC6	7.22(d), 6.82(t)	3.95(s)		152.1, 130.1, 129.8, 121.7, 32.8
HC6 ·Na	7.04(d), 6.57(t)	3.87(s)		155.1, 130.6, 129.1, 119.5, 34.0
Bu'C6	7.27(s)	3.92(s)	1.24(s)	<i>a</i>
Bu'C6 ·Na	7.11(s)	3.86(s)	1.22(s)	152.7, 141.3, 129.9, 125.7, 34.4(d), 32.0
HC8 ^b	6.92(d), 6.68(t)	3.89(s)		152.9, 128.9, 128.8, 120.6, 31.7
HC8 ·Na ^b	6.85(d), 6.61(t)	3.84(s)		153.0, 129.1, 128.5, 120.1, 32.0
Bu'C8 ^b	7.21(s)	4.41(d), 3.52(d)	1.29(s)	147.0, 145.1, 129.1, 125.9, 34.4, 32.7, 31.8
Bu'C8 ·Na ^b	7.07(s)	3.81(s)	1.23(s)	147.0, 142.0, 127.0, 124.0, 32.2, 30.9

^a No ^{13}C NMR spectra available, because the solubility of **Bu'C4** and **Bu'C6** is so low that ^{13}C NMR spectra could not be obtained. ^b The NMR data were obtained from DMSO- d_6 solution.

Table 4. ^1H NMR and ^{13}C NMR of the Alkali Metal Salts of Dianionic **Bu'C4**, HC6, and **Bu'C6** in Acetone- d_6

compound	$\delta_{\text{H}}/\text{ppm}$			$\delta_{\text{C}}/\text{ppm}$ ^a
	ArH	ArCH ₂ Ar	C(CH ₃) ₃	
HC6	7.22(d), 6.82(t)	3.95(s)		152.1, 130.1, 129.8, 121.7, 32.8
HC6 ·2Li	6.97–6.38(br)	4.28–3.19(br)		<i>a</i>
HC6 ·2Na	7.01–6.41(br)	4.30–3.12(br)		162.4, 150.5, 130.0, 128.4, 35.1 ^a
HC6 ·2K	6.97–6.39(br)	4.16–3.24(br)		<i>a</i>
HC6 ·2Rb	7.06–6.32(m)	4.21(s), 3.73(s), 3.32(s)		161.8, 136.7, 135.3, 125.1, 121.7, 41.5 ^a
HC6 ·2Cs	7.10(d), 6.96(d), 6.54(t), 6.30(t)	4.24(d), 3.69(s), 3.31(d)		161.0, 155.8, 130.3, 129.3, 128.7, 116.7, 115.2, 35.0, 33.9, 32.1
HC6 ·KRb	7.06–6.23 (br)	4.20–3.32 (br)		<i>a</i>
Bu'C6	7.27(s)	3.92(s)	1.24(s)	<i>a</i>
Bu'C6 ·2K	6.99(s)	4.10–3.35(br)	1.20(s)	<i>a</i>
Bu'C6 ·2Rb	7.18–6.96(br)	4.22(s), 3.67(s), 3.29(s)	1.19(s)	<i>a</i>
Bu'C6 ·2Cs	7.15(s), 7.05(s), 6.70(s)	4.27(d), 3.66(s), 3.29(d)	1.19(s)	<i>a</i>
Bu'C4 ·2Li	7.05 (s), 6.90 (s),	4.47(br), 4.33 (d), 3.30 (d), 3.23 (s), 3.14(d)	1.15(s)	152.3, 150.5, 142.0, 130.8, 125.6, 34.4, 32.0

^a It was very difficult with most of the calix[6]arene dianions to obtain the ^{13}C NMR spectra in CD_3COCD_3 , CD_3CN , or $\text{CDCl}_3/\text{CD}_3\text{COCD}_3$ (4:1). Rather than the expected spectra, only two broad peaks at 130 and 125 ppm were observed in the aromatic region. All NMR signals for the methylene carbons were observed.

solvents, but they dissolve readily in THF and acetone. Salt **HC4**·Li is very soluble in THF but less soluble in acetone. Salts **7–9 Bu'C4**·M (M = Li, Na, K, Rb) are appreciably soluble in chloroform, acetone, and THF but have very limited solubility in other solvents. Salts **HC6**·2M (M = Li, Na, K, Rb, Cs), **HC6**·KRb, and **Bu'C6**·2M (M = K, Rb, Cs) have high solubility in THF, acetone, and acetonitrile, but less solubility in chloroform. The alkali metal salts of monoanionic calix[6]arenes have good solubility in acetone and THF and less solubility in chloroform and acetonitrile. The alkali metal salts of monoanionic calix[8]arenes have high solubility in THF and DMSO and less solubility in acetone, acetonitrile, and chloroform.

Air-Stability. Most of these salts are air-stable, so it is easy to purify them by recrystallization. But their crystals readily lose solvent molecules to become powder. The salts **Bu'C4**·Li and **Bu'C4**·Na, though, were initially obtained as light yellow or off-white solids. When they were recrystallized in air after several days, yellow X-ray quality crystals were obtained, but they were starting material. Crystallization in the drybox was necessary to obtain X-ray quality crystals of the desired products.

VT-NMR Studies. Temperature-dependent ^1H NMR spectra were recorded on a Varian XL-300 spectrometer at 300 MHz, and the coolant was liquid nitrogen. The rate constants (k_c in s^{-1}) for conformational

Table 5. Crystallographic Data and Summary of Data Collection and Structure Refinement

	HC4•Li	HC4•Na	HC4•Rb	HC4•Cs	Bu ¹ C4•Rb	HC6•Li
formula	C ₃₁ H ₃₃ LiO ₇	C ₆₅ H ₆₄ Na ₂ O ₁₁	C ₃₂ H ₃₁ O ₅ Rb	C ₃₁ H ₂₉ CsO ₅	C ₆₄ H ₆₅ O ₉ Rb ₁	C ₅₂ H ₅₄ Cl ₃ LiO ₉
fw	524.51	1067.14	581.04	614.45	1093.87	936.24
cryst syst	monoclinic	orthorhombic	orthorhombic	monoclinic	tetragonal	monoclinic
space group	<i>P2₁/c</i>	<i>Fdd2</i>	<i>Pna2₁</i>	<i>P2₁/c</i>	<i>P4/n</i>	<i>P2₁/c</i>
<i>T</i> , K	213	273(2)	100(2)	173(2)	128(2)	213(2)
<i>a</i> , Å	10.7535(5)	29.155(4)	18.1392(7)	7.4016(7)	13.0013(6)	12.0435(8)
<i>b</i> , Å	14.7011(7)	37.198(4)	18.9515(7)	19.4783(17)	13.0013(6)	18.8487(12)
<i>c</i> , Å	18.2911(9)	10.5835(14)	7.4377(17)	18.4508(15)	18.2767(12)	22.2687(14)
α, deg	90	90	90	90	90	90
β, deg	106.9860(10)	90	90	97.882(2)	90	104.4370(10)
γ, deg	90	90	90	90	90	90
<i>V</i> , Å ³	2765.5(2)	11478(2)	2556.82(17)	2634.9(4)	3089.4(3)	4895.5(5)
<i>Z</i>	4	8	4	4	2	4
<i>d</i> _{calcd.} , g•cm ⁻³	1.260	1.235	1.509	1.549	1.176	1.270
μ, cm ⁻¹	0.88	0.096	1.979	1.445	0.85	0.242
2θ limits, deg	50.0	46.66	56.5	52.0	56.6	45.0
<i>N</i> measd	14 288	14 856	16 078	14 834	19 742	20 515
<i>N</i> ind	4863	4124	4839	5156	3726	6395
no. of params	485	366	471	334	157	598
<i>R</i>	0.0324	0.1016	0.0318	0.0367	0.0606	0.0811
<i>R</i> _w	0.0853	0.2087	0.0676	0.1171	0.1583	0.2366
GOF	1.02	1.203	0.96	1.015	1.009	0.98

	HC6•Cs	HC6•2K	HC6•2Rb	HC6•2Cs	HC6•KRb	Bu ¹ C4•2Li	Bu ¹ C4•CH ₃
formula	C ₄₅ H ₄₅ CsO ₉	C ₅₆ H ₅₆ K ₂ O ₁₂	C ₅₆ H ₆₅ O ₁₂ Rb ₂	C ₅₂ H ₅₉ Cl ₃ Cs ₂ O ₁₂	C ₅₇ H ₇₂ K ₁ O ₁₂ Rb ₁	C ₅₆ H ₇₈ Li ₂ O ₁₀	C ₃₀ H ₂₇ Cl ₃ O ₄
fw	862.72	984.26	1077.00	1248.16	1073.72	925.06	557.87
cryst syst	orthorhombic	monoclinic	monoclinic	Monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>Pbca</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>T</i> , K	213(2)	213(2)	213(2)	213(2)	100	293(2)	300
<i>a</i> , Å	15.693(2)	14.6363(12)	14.3918(8)	14.414(1)	14.5123(8)	13.668(3)	14.2184(10)
<i>b</i> , Å	20.271(3)	24.9037(19)	25.2018(15)	25.354(2)	24.7889(13)	22.379(5)	11.3149(8)
<i>c</i> , Å	24.076(3)	15.0403(12)	15.1928(9)	15.192(1)	14.8909(8)	20.881(4)	16.9918(12)
α, deg	90	90	90	90	90	90	90
β, deg	90	108.0120(10)	107.4530(10)	107.7150(10)	107.9540(10)	100.354(4)	94.4050(10)
γ, deg	90	90	90	90	90	90	90
<i>V</i> , Å ³	7695(2)	5213.5(7)	5256.7(5)	5288.9(7)	5096.1(5)	6283(2)	2725.6(3)
<i>Z</i>	8	4	4	4	4	4	4
<i>d</i> _{calcd.} , g•cm ⁻³	1.496	1.254	1.361	1.568	1.399	0.978	1.360
μ, cm ⁻¹	1.026	0.242	1.921	1.590	1.118	0.065	0.371
2θ limits, deg	43.0	45.0	45.0	45.0	56.6	42.0	45.0
<i>N</i> measd	27 569	21 918	21 996	22 070	32 715	21 748	11264
<i>N</i> indep	4400	6814	6874	6919	11 905	6735	3558
no. of params	509	652	655	607	592	642	338
<i>R</i>	0.1037	0.0506	0.0359	0.1040	0.0644	0.1052	0.0873
<i>R</i> _w	0.2285	0.1362	0.0891	0.3307	0.1607	0.2777	0.2650
GOF	1.074	1.04	1.01	1.30	0.89	1.088	1.05

interconversion at the coalescence temperature were calculated from the equation $k_c = 2.22(\Delta\nu^2 + J_{AB}^2)^{1/2}$.^{58–60} The free energy barrier to conformational interconversion in kcal•mol⁻¹ was calculated from the equation $\Delta G^\ddagger = 4.58T_c(10.32 + \log T_c/k_c)/1000$. Assuming an accuracy of ± 5 °C for the value of T_c , an accuracy of ± 15 Hz for the value of $\Delta\nu$, and an accuracy of ± 2 Hz for the value of J_{AB} , it is estimated that the values should be accurate to ± 0.4 kcal•mol⁻¹. The value of $\Delta\nu$ was taken as the average difference in Hz between the centers of the pairs of methylene doublets undergoing coalescence (observed at a sufficiently low temperature that peaks are sharp).

General X-ray Crystal Structure Information. Data for HC4•Na, HC4•Rb, HC4•Cs, Bu¹C4•Rb, and HC6•KRb were collected on a Bruker SMART APEX CCD diffractometer using Mo K α radiation, and SADABS absorption corrections were applied; those for HC4•Li, HC6•Li, HC6•Cs, HC6•2K, HC6•2Rb, HC6•2Cs, and Bu¹C4•2Li were collected on a Bruker SMARTTM 1000 CCD-based diffractometer using Mo K α radiation. Because the crystals cracked when cooled, data collection for HC4•Na was carried out at room temperature. The large anisotropic thermal parameters found in HC4•Na indicate that

HC4 and acetone moieties coordinated to the Na atom are very flexible. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on reflection intensities (I^2). All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms on the O atoms were located on the F-map and refined with isotropic thermal parameters. Positions of other H atoms were calculated. In the crystal structures of Bu¹C4•Rb and HC6•KRb disordered solvate molecules (THF molecule in Bu¹C4•Rb, acetone and hexane molecules in HC6•KRb) were treated by the program SQUEEZE.⁶¹ Corrections of the X-ray data for Bu¹C4•Rb and HC6•KRb by SQUEEZE (96 and 324 electron/cell, respectively) were close to the required values (80 and 328 electron/cell, respectively). The program ORTEP32 was used to generate the X-ray structural diagrams pictured in this article.⁶²

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Supporting Information Available: Detailed experimental section, ^1H NMR spectra of calixarene monoanions, VT NMR spectra of calix[6]arene dianions, **HC6**•Li, and **HC6**•Cs, X-ray crystal structures of **HC4**•Cs, **HC6**•2Cs, **HC6**•2Rb, **HC4**•Me,

HC4•Li, **HC4**•Na, **HC4**•Rb, **Bu**⁴**C4**•2Li, **HC6**•Li, and **HC6**•Cs, tables of NMR data, elemental analysis data, IR data, melting points of all compounds; X-ray crystallographic data in CIF format. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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