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Synthesis and crystal structures of mono-potassium salts of calix[4]arene and *p-tert*-butylcalix[4]arene

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Abstract—The mono-potassium salts obtained by the action of K_2CO_3 on calix[4]arene and *p-tert*-butylcalix[4]arene are found to possess very similar solid-state dimer structures that differ only in the presence of a cation–π interaction in the former. The mono-potassium salt obtained by the action of $KOSiMe_3$ on *p-tert*-butylcalix[4]arene, on the other hand, is found to possess a monomeric structure. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Calixarenes and their derivatives have been the focus of considerable attention since the report of tractable synthetic routes to the parent macrocycles.[1] Interest in these compounds derives from their ease of synthesis, their conformational characteristics, and their potential for functionalization and subsequent use in a variety of ways that include catalysis, selective ion binding, and chemical sensors.[2] The early demonstration that the parent calixarenes can effect the transport of alkali metal ions in water/organic solvent/water membrane systems in strongly basic solution has stimulated considerable interest in anionic calixarene derivatives (‘calixanions’).[3] The phenol functionalities on the lower rim of calixarenes enable them to form neutral complexes with cations through proton loss, and several of these phenoxy-bound alkali metal[4–11] and ammonium[12–17] calixanions have been isolated and structurally characterized. Calixanions have also been utilized as intermediates in the synthesis of organic[18–24] and metallated derivatives,[25,26] usually without isolation.

Despite the utility of these complexes, relatively few structural data for alkali metal ion complexes of parent calixarenes have appeared in the literature.[8–11] Of particular note is the recent work of Floriani and co-workers[27] in which the X-ray crystallographic structures of the tetra-salts of *p-tert*-butylcalix[4]arene (**H4L2**) with Li^+, Na^+, and K^+ are reported. Our interest, on the other hand, lies with the mono-salts of the calixarenes for which the X-ray crystallographic structures of the Li^+, Na^+, and Cs^+ salts[8,11] but not the K^+ salt[8] have been obtained. The potassium salts of calixarenes, though, hold special significance because of their structural similarity to biological potassium channels which have been postulated to utilize cation–π interactions in the selective transport of K^+.[9] The present paper, therefore, is directed to the synthesis and solid-state structure of a mono-potassium salt of calix[4]arene (**H4L1**) and two mono-potassium salts of *p-tert*-butylcalix[4]arene (**H4L2**). It provides the first solid-state structural comparison of calixanion salts that differ only in their *p*-substituents.

2. Results and discussion

2.1. Potassium salt of calix[4]arene

A mono-potassium salt (**1**) was obtained by the action of K_2CO_3 on calix[4]arene (**K4L1**). As shown in Figs. 1 and 2, there are two different structural units (designated as α and β) present in the crystal structure of **1**, based on the centrosymmetric $K(\mu\text{-}OH_2)_2K$ fragment containing two bridging water molecules. In the crystal structure these units associate to form infinite one-dimensional chains. There are also two solvate THF molecules, not shown in the figures, that form O(THF)···H–O (H_2O) hydrogen bonds with the hydrogen atoms of the terminal and the bridging H_2O molecules (Table 1). The H atoms attached to the phenoxy moieties and the water molecules were found from the real F-map, and the others were calculated. Each calix[4]arene unit possesses a regular cone conformation in the solid state. Compound **1** consists of two calix[4]arene monoanions connected at the lower rims by two bridging

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Keywords: calixarenes; potassium and compounds; X-ray crystal structures; macrocycles.

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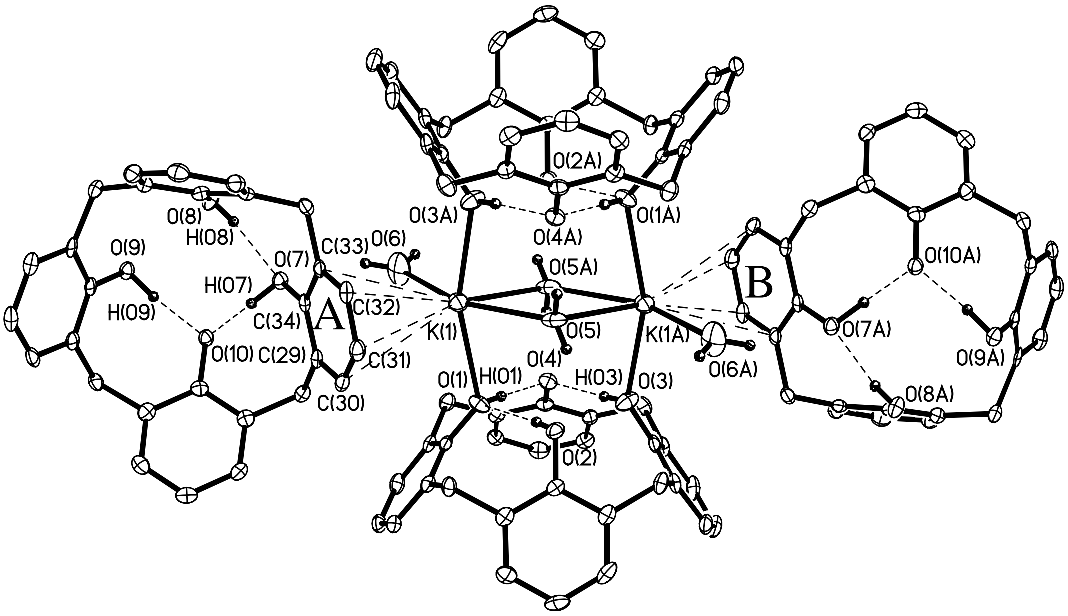

Figure 1. Structural unit α in the crystal structure of **1**. Most of the H atoms are omitted for clarity. Selected bond distances (Å): K(1)–O(1) 2.802(3), K(1)–O(3A) 2.743(3), K(1)–O(5) 2.843(3), K(1)–O(5A) 2.800(3), K(1)–O(6) 2.656(4), K(1)–C(30) 3.494(3), K(1)–C(31) 3.296(3), K(1)–C(32) 3.286(3), K(1)–C(33) 3.515(3).

potassium cations (K(1) and K(1A) in Fig. 1, K(2) and K(2A) in Fig. 2).

In the structure shown in Fig. 1 each bridging potassium is coordinated to two O atoms from bridging H_2O and two from terminal H_2O molecules, and they also engage in a cation–π interaction to an aryl ring of a neighboring calixarene (part of the unit shown in Fig. 2). The potassium–calixarene oxygen distances are K(1)–O(1)=2.802(3) Å, and K(1)–O(3)=2.743(3) Å. The calixarene phenolate atom appears to H-bond with neighboring phenol hydrogens rather than coordinating to the potassium cation.

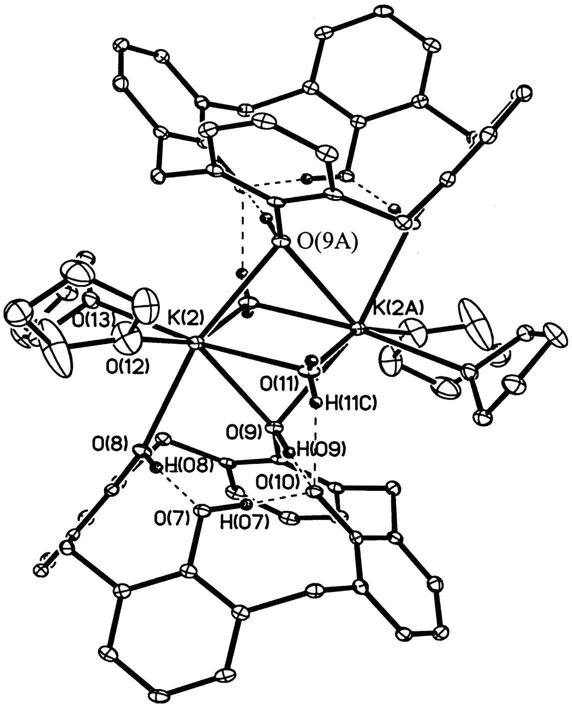

Figure 2. Structural unit β in the crystal structure of **1**. Most of the H atoms are omitted for clarity. Selected bond distances (Å): K(2)–O(8) 2.712(2), K(2)–O(9) 2.809(2), K(2A)–O(9) 2.893(2), K(2)–O(11) 2.729(3), K(2)–O(11a) 2.845(3), K(2)–C(12) 2.688(3), K(2)–C(13) 2.663(3).

Fig. 2 shows structural unit β in the crystal structure of **1**. Each bridging potassium is coordinated to two O atoms from THF, two O atoms from H_2O, and three phenolic O atoms. The unit is centrosymmetric; only the two THF molecules at the K(2) atom are symmetrically independent. The potassium ions are asymmetrically coordinated to the calixarene phenol atoms (K(2)–O(8)=2.712(2) Å, K(2)–O(9)=2.809(2) Å, K(2)–O(9A)=2.893(2) Å), in qualitative agreement with theoretical predictions.[28,29] Again, the phenolate atom O(10), which is furthest from the bridging K^+ ions, is coordinated not to the potassium atom K(2), but instead engages in H-bonding with both proximal phenol groups and one bridging water molecule. This is consistent with the structures of the di-potassium complexes of *p-tert*-butylcalix[8]arene[10] and calix[6]arenes.[9] The ranges of

Table 1. Geometrical parameters of the O–H···O hydrogen bonds in **1** and **2**

Compound **1**	O–H (Å)	H···O (Å)	O···O (Å)	O–H···O (°)
O(1)–H(01)···O(4)	0.87(5)	1.64(5)	2.506(3)	171(5)
O(2)–H(02)···O(1)	0.68(5)	2.11(6)	2.786(4)	174(6)
O(3)–H(03)···O(4)	0.77(5)	1.77(6)	2.534(4)	171(6)
O(7)–H(07)···O(10)	0.96(6)	1.52(6)	2.480(3)	177(6)
O(8)–H(08)···O(7)	0.77(6)	1.88(6)	2.646(3)	172(6)
O(9)–H(09)···O(10)	0.92(5)	1.67(5)	2.577(3)	171(4)
O(11)–H(11c)···O(10)	0.71(5)	2.14(5)	2.806(4)	156(5)
O(6)–H(06a)···O(14)(THF)	0.81(4)	1.96(5)	2.734(4)	161(4)
O(11)–H(11b)···O(15)(THF)	0.75(5)	2.09(5)	2.814(4)	164(4)
Compound **2**				
O(2)–H(20)···O(1)	0.88(4)	1.74(5)	2.610(3)	178(4)
O(1)–H(40)···O(4)	1.20(4)	1.24(4)	2.440(3)	175(4)
O(3)–H(30)···O(4)	0.84(4)	1.77(4)	2.603(3)	173(5)

Table 2. Structural data for selected potassium complexes

Compound	K–O distance (Å)	K–K distance (Å)	References
1	2.663(3)–2.893(2) (Unit α) 2.656(4)–2.84393) (Unit β)	3.4672(14) (Unit α) 4.5289(16) (Unit β)	
2	2.694(2)–2.953(2)	4.2003(11)	
3	2.648(13)–3.160(12)		
K_2**H_4L3**·5MeOH[a]	2.746(6)–2.944(5)	4.273(7)	9
K_2**H_4L4**·4MeOH[b]	2.64(1)–2.94(1)	4.31(1)	9
K_2**H_4L3**·5H_2O[a]	2.68(2)–3.05(2)	3.789(3)	9
K_2**H_6L5**·5MeOH[c]	2.616(4)–2.949(2)	4.424(2)	10
K complex of calix[4]arene crown-ether	2.85(1)–3.15(1)		31
K complex of calix[4]tube[d]	2.759(6)–2.809(6)		32
K complex of amide derivative of calix[4]	2.56(1)–2.71(2)		33

[a] **H_6L3** stands for *p*-H-calix[6]arene.

[b] **H_6L4** stands for *p*-*tert*-butylcalix[6]arene.

[c] **H_8L5** stands for *p*-*tert*-butylcalix[8]arene.

[d] Calix[4]tube is defined as two calix[4]arene moieties linked via four ethylene units to provide a rigid arrangement of eight oxygen donor atoms for metal complexation. See reference 32.

K–O bond lengths of **1–3** are typical of potassium complexes of calixarenes and their derivatives and are comparable to the K–O distances in the published structures shown in Table 2. The distances of separation of K–K in **1** and **2** are very close to those of the di-potassium complexes of calix[6]arenes[9] and *p*-*tert*-butylcalix[8]arene.[10]

The existence of the K^+–π interaction has been shown to be the origin of the unusually large association constants, both in the solution and the solid state, for K^+ ions with the 1,3-alternate conformer of calix[4]arenes or the partial cone conformer of calix[4]arene crown ethers.[9] As shown in Fig. 1, in the potassium complex **1** the cations interact with aromatic rings A and B in an η^4 fashion, via C(30), C(31), C(32), and C(33).

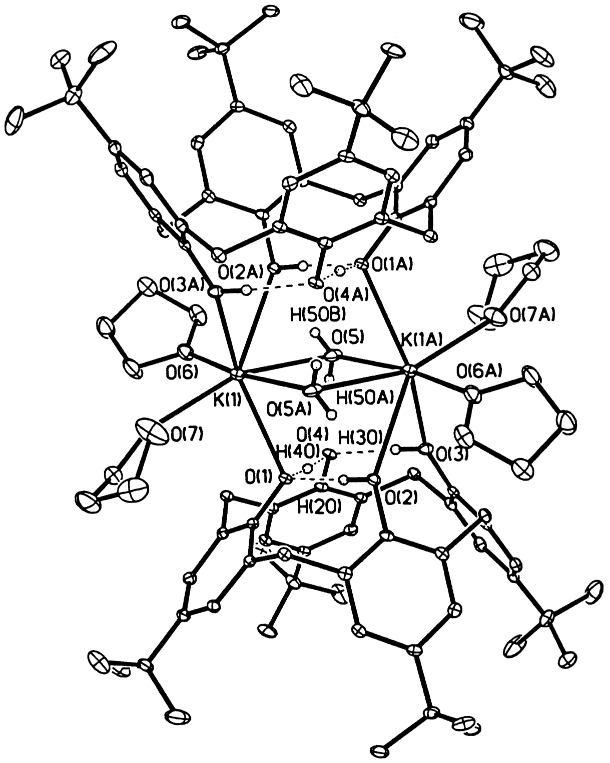

Figure 3. The crystal structure of **2**, with most of the H atoms omitted for clarity. Selected bond distances (Å): K(1)–O(1) 2.856(2), K(1)–O(2A) 2.836(2), K(1)–O(3A) 2.755(2), K(1)–O(5) 2.935(2), K(1)–O(5A) 2.737(2), K(1)–C(6) 2.733(2), K(1)–C(7) 2.694(2).

The potassium-aryl ring carbon η^4-distances (K(1)–C=3.286(3)–3.515(3) Å) (see Fig. 1) are very similar to those reported in the literature for the K complexes of calix[4] crown ether (K–C=3.27–3.52 Å)[31] and for the di-potassium complexes of calix[6]arenes (K–C=3.32–3.96 Å).[9]

2.2. Potassium salts of *p*-*tert*-butylcalix[4]arene

A mono-potassium salt (**2**) was obtained by the action of K_2CO_3 on *p*-*tert*-butylcalix[4]arene (**H_4L2**). Its solid state structure, as shown in Fig. 3, is very similar to the structural unit β of the mono-potassium salt of calix[4]arene (**1**) (see Fig. 2). The solid state structure of **2** also is a centrosymmetric dinuclear complex with bridging H_2O molecules connecting two K atoms, and four terminal THF molecules that are bonded to the K atoms. The coordination mode of calix[4]arene in **2** is different from that in unit β of **1**. In **2** there are no μ^2-bridging O atoms connecting the two K atoms as observed in **1**. The K(1)–O(1), K(1)–O(2A), and K(1)–O(3A) distances (2.856(2), 2.836(2), and 2.755(2) Å, respectively) are similar to those in **1**.

As in **1** the calixarene phenolate atom in **2** does not involve coordination of the K atom. The O(1)···O(4) distance, 2.440(3) Å, is shorter than two other distances (O(1)···O(2) 2.610(3) and O(3)···O(4) 2.603(3) Å) indicating the presence of strong O–H···O hydrogen bonding. The O(1)···H(40)···O(4) H-bond is almost symmetrical (O(1)···H(40) 1.20(4) Å, O(4)···H(40) 1.24 Å) in contrast to the other H-bonds (Table 1).

The separation between K(1) and K(1A) is 4.2003(11) Å, and in contrast with the salt from **1** there is no cation–π interaction. Presumably the steric bulk of the *tert*-butyl groups inhibits the close approach of the neighboring dimeric units.

Another mono-potassium salt (**3**) was obtained by the action of $KOSiMe_3$ on *p*-*tert*-butylcalix[4]arene (H_4L2). As shown in Figs. 4 and 5, its solid state structure is very different from that of the mono-potassium salts **1** and **2**. The *exo* potassium

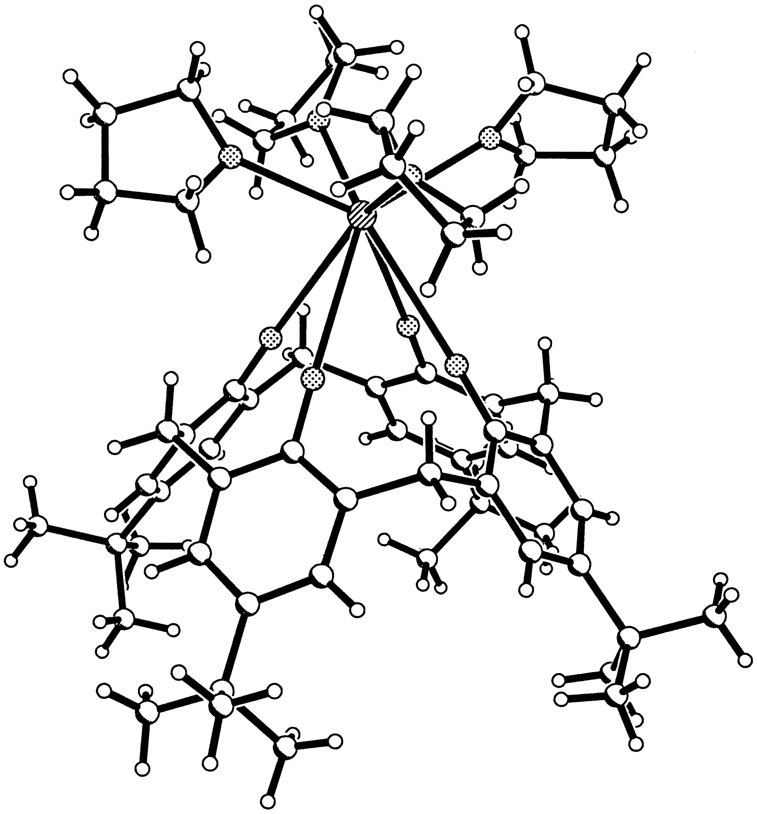

Figure 4. The crystal structure of **3**. Selected bond distances (Å): K(1)–O(1) 3.108(5), K(1)–O(2) 2.684(5).

cation is coordinated to one phenolate and three phenol groups (K–O distances are 3.153(3), 3.042(13) (phenolate), 3.109(12) and 3.160(12) Å), and to four THF molecules. The refinement reduced the *R* value to 0.077, but a 180 Å^3 void remains in the asymmetric unit. Although numerous peaks were observed in this volume, none were larger than 0.22 e Å^{-3}. The complex possesses pseudo four-fold symmetry, and the geometry around the potassium ion is that of a square antiprism with four sites occupied by THF molecules (as seen in the top view in Fig. 5).

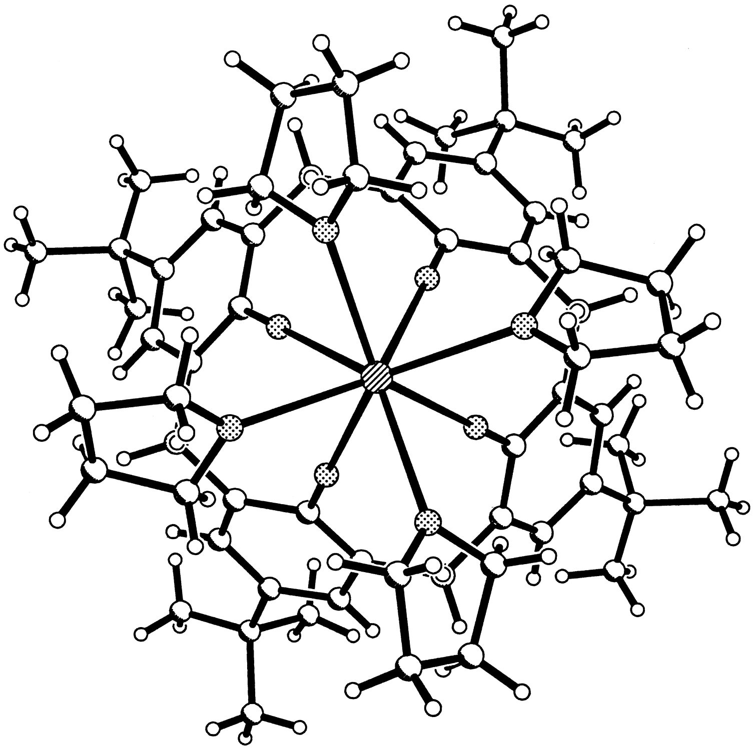

Figure 5. The crystal structure of **3**; top view showing the square antiprismatic coordination about the potassium ion.

Wipff et al. have performed MD and FEP simulations on *p-tert*-butylcalix[4]arene monoanion and its alkali metal ion complexes in the gas phase and in water, acetonitrile and chloroform solutions.[28,29] They found that the cation is located outside the cone near the oxygen atoms on the lower rim of the calix (*exo* complex), and the calculated K–O distance range is 2.9–3.3 Å in the polar solvent. The K–O distances in the solid state structure of **3** are very similar to those in the calculated structures. However, the K–O distances of **2** in the solid state are shorter than the calculated distances. The binding mode of **2** and **3** is also consistent with that of Wipff's calculations.

3. Conclusion

The reactions of calix[4]arene and *p-tert*-butylcalix[4]arene with 1 equiv. of weak base K_2CO_3 yield the mono-potassium salts **1** and **2** which possess very similar solid state structures and exist in a dimeric form. The major difference between the two is that there is no cation–π interaction when the *para*-positions of calix[4]arene are occupied by *tert*-butyl groups, probably due to the steric bulk of the *tert*-butyl groups. The mono potassium salt obtained from *p-tert*-butylcalix[4]arene and 1 equiv. of the strong base $KOSiMe_3$, on the other hand, possesses a different structure in the solid state and exists as a monomer rather than a dimer. It also differs from the other two structures in lacking a water molecule in the crystal, this perhaps being a determining factor in its crystal structure.

4. Experimental[30]

4.1. Data for compounds

4.1.1. Mono-potassium salt of calix[4]arene. Reaction of calix[4]arene (**H_4L1**) with 1 equiv. of K_2CO_3 in acetone or acetonitrile at 55°C afforded, after work-up and recrystallization from THF–hexane, the mono-potassium salt (**KH_3L1**·2THF·H_2O)$_2$ (**1**) as a white powder in 88% yield: mp 369–370°C. IR (KBr) 3418, 2925, 1702, 1592, 1448, 1258, 758 cm^{-1}. ^{1}H NMR (300 MHz, acetone-d$_6$) δ=3.20 (4H, s, ArCH$_2$Ar), 4.43 (4H, s, ArCH$_2$Ar), 6.33 (4H, q, *J*=7.7 Hz, ArH), 6.88 (8H, t, *J*=7.6 Hz, ArH). ^{13}C NMR (75 MHz, acetone-d$_6$) δ=34.1 (ArCH$_2$Ar), 118.4, 128.5, 131.9, 156.4 (Ar). Found: C, 69.99; H, 5.21%. Calcd for $C_{28}H_{25}O_5$: C, 69.98; H, 5.24%.

4.1.2. Mono-potassium salt of *p-tert*-butylcalix[4]arene using a weak base. In like fashion, the reaction of *p-tert*-butylcalix[4]arene (**H_4L2**) with 1 equiv. of K_2CO_3 in anhydrous acetonitrile or freshly distilled THF at 55°C was carried out. After work-up, a white solid was obtained that was recrystallized from THF–hexane to give the mono-potassium salt (K**H_3L2**·3THF·H_2O)$_2$ (**2**) in 83% yield: mp 298–300°C. IR (KBr) 3420, 3182, 2963, 1610, 1481, 1392, 1362, 1302, 1205, 873 cm^{-1}. ^{1}H NMR (300 MHz, acetone-d$_6$) δ=1.13 (36H, s, C(CH$_3$)$_3$), 3.16 (4H, d, *J*=12.4 Hz, ArCH$_2$Ar), 4.42 (4H, d, *J*=12.2 Hz, ArCH$_2$Ar), 6.95 (8H, s, ArH). ^{13}C NMR (75 MHz, acetone-d$_6$) δ=32.1, 34.2, and 34.8 (C(CH$_3$)$_3$ and ArCH$_2$Ar), 125.2, 131.3, 140.3, 154.0 (Ar). Found: C, 74.62; H, 7.81%. Calcd for $C_{44}H_{57}O_5$: C, 74.96; H, 8.15%.

4.1.3. Mono-potassium salt of *p-tert*-butylcalix[4]arene using a strong base. Treatment of *p-tert*-butylcalix[4]arene with 1 equiv. of the strong base $KOSiMe_3$ in THF at rt in the dry-box, produced the mono-potassium salt **KH_3L2**·4THF (**3**) in 90% yield as a white powder with IR and NMR spectral characteristics identical with those of the mono-potassium salt described above.

4.2. X-Ray crystallography

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 186392–186394. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Crystals of **1** suitable for an X-ray determination were obtained by diffusion of pentane into the solution of **1** in THF at room temperature. The crystals, which easily lose THF in air, dissolve readily in acetone, acetonitrile and THF, and to a limited extent in chloroform.

Crystal data. $2C_{28}H_{23}KO_4\cdot 4C_4H_8O\cdot 3H_2O$, *M*=1267.59, monoclinic, space group $P2_1/n$(#14), *a*=16.6174(8) Å, *b*=22.7304(11) Å, *c*=17.0517(8) Å, β=97.784(1)°, *V*=6381.4(5) Å^3, *Z*=4, *T*=100(1) K, D_c=1.319 g cm^{-3}, crystal sizes 0.20×0.15×0.10 mm^3, Mo Kα, μ=0.217 mm^{-1}. Intensities were collected on a Bruker SMART APEX CCD diffractometer at 100(1) K (Mo Kα radiation, 40 890 reflections (15 040 unique, R_{int}=0.0441) with θ_{max}=28.28° and 850 variables. SADABS absorption corrections were applied. Structure was solved using direct methods and completed by subsequent difference Fourier syntheses and refined by full matrix least-squares procedures on reflection intensities (F^2). All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms at the O atoms were located on the F-map and refined with isotropic thermal parameters. Positions of other H atoms were calculated. The final *R* factors [$I>2\sigma(I)$]: *R*1=0.0884, *wR*2=0.1839, GoF=1.211. Max/min residual density peaks are +0.56/−0.62 e Å^{-3}. All software and sources scattering factors are contained in the SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI).

Crystals of **2** suitable for X-ray determination were obtained by diffusion of pentane into the solution of **2** in THF in the dry-box at room temperature. The crystals readily lose THF.

Crystal data. $C_{44}H_{55}KO_4\cdot 3C_4H_8O\cdot H_2O$, *M*=921.31, monoclinic, space group $P2_1/c$, *a*=12.7691(6) Å, *b*=21.2740(10) Å, *c*=20.1141(9) Å, β=103.984(1)°, *V*=5302.1(4) Å^3, *Z*=4, *T*=100(1) K, D_c=1.154 g cm^{-3}, crystal sizes 0.25×0.20×0.10 mm^3, Mo Kα, μ=0.150 mm^{-1}. Intensities were collected on a Bruker SMART APEX CCD diffractometer at 100(1) K (Mo Kα radiation, 33 657 reflections (12 473 unique, R_{int}=0.0351) with θ_{max}=28.30° and 561 variables). SADABS absorption corrections were applied. Structure was solved using direct methods and completed by subsequent difference Fourier syntheses and refined by full matrix least-squares procedures on reflection intensities (F^2). All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms at the O atoms were located on the F-map and refined with isotropic thermal parameters. Positions of other H atoms were calculated. The disordered THF solvent molecule was treated by SQUEEZE program.[34] Corrections of X-ray data for **2** by SQUEEZE, 156 e cell^{-1}, were close to required value, 160 e cell^{-1}. The final R factors [$I>2\sigma(I)$]: $R1=0.0799$, $wR2=0.1995$, GoF=1.138. Max/min residual density peaks are $+0.95/-0.34$ e Å^{-3}. All software and sources scattering factors are contained in the SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI).

Crystals of **3** suitable for X-ray determination were obtained by diffusion of pentane into the solution of **3** in THF in the dry-box at room temperature. The crystals readily lose THF. Compounds **2** and **3** are both very soluble in chloroform, acetone, and THF.

Crystal data. $C_{44}H_{55}KO_4\cdot 4C_4H_8O$, $M=975.40$, tetragonal, space group $P4/n$, $a=b=13.000(1)$ Å, $c=18.424(3)$ Å, $V=3116.5(6)$ Å^3, $Z=2$, $T=213(2)$ K, $D_c=1.040$ g cm^{-3}, crystal sizes $0.31\times0.23\times0.13$ mm^3, Mo Kα, $\mu=0.13$ mm^{-1}. The crystals decomposed rapidly upon removal from the mother liquor. A drop of oil was added to the mother liquor and the crystals were removed in the droplet of oil. A crystal was attached to a glass fiber with epoxy cement and then removed from the oil. The oil drop was carefully removed leaving a thin film, and the crystal was placed immediately in a nitrogen stream at −60°C. Intensities were collected on a Bruker SMART™ 1000 CCD-based diffractometer at 213(2) K (Mo Kα radiation, 13 034 reflections (7723 unique, $R_{\text{int}}=0.0710$) with $\theta_{\max}=22.50°$ and 669 variables. SADABS absorption corrections were applied. Structure was solved using direct methods and completed by subsequent difference Fourier syntheses and refined by full matrix least-squares procedures on reflection intensities (F^2). All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms at the O atoms were located on the F-map and refined with isotropic thermal parameters. Positions of other H atoms were calculated. The calixarene moiety of the structure was solved using space group $P4/n$ in order to optimize bond distance and angle data. The disordered solvent in the crystal, however, lowers the actual symmetry to P/n. The final R factors [$I>2\sigma(I)$]: $R1=0.0794$, $wR2=0.2288$, GoF=0.885. Max/min residual density peaks are $+0.52/-0.21$ e Å^{-3}. The structure was checked using PLATON. The frames were integrated with the SAINT software package using a narrow-frame algorithm, and the structure solved and refined using the SHELXTL program package.

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