Systematic Structural Coordination Chemistry of *p-tert*-Butyltetrathiacalix[4]arene: 1. Group 1 Elements and Congeners

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Determinations of the crystal structures of complexes of the alkali metal ions with, in the case of Li, the dianion and, in the cases Na−Cs, the monoanion of *p-tert*-butyltetrathiacalix[4]arene have shown that both the sulfur atoms which form part of the macrocyclic ring, as well as the pendent phenolic/phenoxide oxygen donor atoms, are involved in coordination to these metals. Although the Li and Na complex structures are similar to those of the corresponding complexes of *p-tert*-butylcalix[4]arene, there is no similarity in the structures of the Cs complexes, with the present structure showing no evidence of polyhapto $Cs^+-\pi$ interactions. Instead, the complex crystallizes as a ligand-bridged (S-, O-donor) aggregate of three Cs ions, solvent molecules, and four calixarenes, somewhat like the Rb complex, though here four Rb ions are present, and higher in aggregation than the K^+ complex, where two K^+ ions are sandwiched between two calixarene moieties. The triethylammonium complex of the thiacalixarene monoanion, though formally analogous in that it involves a monocation, has a simpler structure than any of the alkali metal derivatives, based formally on proton coordination (H-bonding). However, interestingly, it can be isolated in both solvated (dmf, dmso) and unsolvated forms, as indeed can the “free”, *p-tert*-butyltetrathiacalix[4]arene ligand itself.

Introduction

A major reason for the intense interest in the chemistry of the calixarenes sparked by the publication of the first rational syntheses some 20 years ago[1] has been the utility of these polyphenols and their derivatives as metal-ion complexing agents.[2−4] Undoubtedly the very recent publication[5] of new syntheses, which now make the calixarenes, in terms at least of ring size, one of the most varied of all families of macrocycles, will lead to further extension of such work. Of the many variations that have already been played on the basic calixarene structure to enhance and control metal-ion binding, one of the simplest and most interesting has been that of the substitution of sulfur for the bridging methylene groups, as in the recently and readily synthesized *p-tert*-butyltetrathiacalix[4]arene (LH_4).[6] Initial spectroscopic measurements were interpreted as providing evidence that the thiaether units of LH_4 take part in metal-ion coordination,[6,7] leading to the suggestion that this may explain the stronger interaction with transition metals than is observed with *p-tert*-butylcalix[4]arene, and prompting our interest in systematically studying the coordination chemistry of the thiacalixarene. There are already indications that this chemistry may be of particular interest,[7−9] and our continuing studies of the structural chemistry of a wide variety of complexes provide substantial further evidence for this contention. Structural proof of the involvement of sulfur coordination to transition metals is already available.[8,9] Here, we describe our structural studies of group 1 element complexes, considering both the proton and ammonium species to be members of this group, though the alkali metals Li−Cs are those of primary interest.

Alkali metal ion coordination chemistry involving the calixarenes has been very strongly focused on the use of neutral calixarene derivatives as extraction agents, the employment of “calixcrowns” as selective extractants for radioactive cesium being a significant example of a practical application.[10] However, some of the earliest work exploring the potential of the calixarenes in the separation of the alkali metals was based on

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membrane transport employing phenolic calixarenes under basic conditions where at least partial deprotonation occurred,[11] and on further studies of this kind leading to the development of various concepts important in enhancing understanding of the nature of calixarene coordination chemistry in general.[12] The characterization of alkali metal ion complexes of the phenoxide anions derived from the "parent" calixarenes by structure determinations of the crystalline solids has been limited by both synthetic and crystallographic difficulties; for *p-tert*-butylcalix[4]arene, in particular, full X-ray structure determinations are known only for the di-[13] and tetralithium,[14] monosodium,[13] and monocesium[15] derivatives. Some solution equilibrium data are available for the whole series.[1,4,16] Interestingly, the sodium and cesium structures establish two very different coordination modes, sodium being bound to phenol(ate) oxygen atoms, in contrast to cesium which is included within the calixarene, presumably through interactions with the π electrons of the aromatic rings.[15] Cation$-\pi$ interactions, well-known in metallocene systems,[17] are increasingly recognized as pervasive[18] and may well be of some significance in explaining the cesium ion selectivity of calixcrowns.[10,19] Nonetheless, they are expected to be weak for weakly polarizing cations such as those derived from the alkali metals,[20] so that a marked dependence on subtle features of structural change might be anticipated, particularly where the introduction of sulfur offers an alternative "soft" donor potentially capable of interacting with softer cations. The effect of small dimensional differences in the published structures of *p-tert*-butylcalix[4]arene[21] and LH_4,[22] as well as the effect of the introduction of sulfur itself, on the nature of their alkali metal ion complexes were therefore issues we sought to explore. The results obtained are of interest in this regard as well as providing a definition of calixarene coordination chemistry within the broad context of phenoxide ion binding to the alkali and other metals, another topic to which we have recently made contributions.[23]

Experimental Section

In most instances, the following preparations were developed in order to obtain crystals best suited for structure determinations by single-crystal X-ray studies and not necessarily to optimize yields of the complexes, though these were generally satisfactory. LH_4 (*p-tert*-butyltetrathiacalix[4]arene) was prepared as described in the literature[6] and purified by recrystallization as its chloroform solvate. All commercial reagents were used as received, with the exception of dichloromethane, chloroform, and toluene, which were dried and distilled immediately prior to use.

Preparation of LH_4 (Unsolvated). This material was inadvertently obtained from an early experiment, intended to produce the As(III) complex of the calixarene, in which LH_4 was reacted with As_2O_3 in dmf. The oxide proved resistant to dissolution, even in the boiling solvent, but, on addition of triethylamine and continued heating, a clear solution was eventually obtained. Large, colorless tablets deposited on cooling of this solution to room temperature, but the structure determination showed them to be the unsolvated ligand, devoid of arsenic.

Preparation of $LH_4\cdot$Pyridine. This material was obtained by slow evaporation, at ambient temperature, of $LH_4\cdot CHCl_3$ (0.5 g) in pyridine (10 mL).

Preparation of $[HN(C_2H_5)_3](LH_3)$. Triethylamine (0.15 mL) was added to a slurry of $LH_4\cdot CHCl_3$ (50 mg) in dmf (0.5 mL), leading to rapid formation of a colorless solution. On standing at room temperature, colorless, platelike crystals suitable for an X-ray structure determination were deposited after several days. For elemental analysis, the crystals (24 mg) were collected, washed with ether, and dried in air. Anal. Calcd for $C_{40}H_{48}O_4S_4\cdot N(C_2H_5)_3$: C, 67.19; H, 7.72; N, 1.70; S, 15.60. Found: C, 67.0; H, 7.8; N, 1.5; S, 15.4.

Preparation of $[HN(C_2H_5)_3](LH_3\cdot dmf)$. This material was first isolated (and structurally characterized) as the product, in the form of rodlike crystals, from an attempt to form the lithium complex by addition of $LiClO_4$ to a solution of the calixarene with triethylamine in dmf. Seemingly, the only difference in conditions relative to the preceding above experiment was that the liquid phase consisted of similar amounts of triethylamine and dmf, whereas here the volume ratio was 1:16.

Preparation of $[HN(C_2H_5)_3](LH_3\cdot dmso)$. This material was first isolated (and structurally characterized) as the product from an attempt to form the magnesium complex by addition of $Mg(ClO_4)_2$ to a solution of the calixarene with triethylamine in dmso. For elemental analysis, the crystals were collected, washed with hexane, and dried in air. Anal. Calcd for $[C_{40}H_{48}O_4S_4][N(C_2H_5)_3]\cdot 1.25$dmso: C, 63.32; H, 7.72; N, 1.52; S, 18.30. Found: C, 63.3; H, 7.2; N, 1.4; S, 18.3.

Preparation of $[Li_2(LH_2)(thf)_2(H_2O)_2]\cdot 2thf$. $LiClO_4\cdot 3H_2O$ (38 mg) was stirred with thf (5 mL) until dissolution was complete (~10 min). $LH_4\cdot CHCl_3$ (100 mg) and triethylamine (~0.1 mL) were added, and the mixture was stirred well to form a clear, colorless solution. Slow evaporation of the solvent resulted in the deposition of colorless crystals suitable for X-ray structure determination. For elemental analysis, the crystals (43 mg) were collected, washed with thf, and dried in air. Anal. Calcd for $[(C_{40}H_{46}O_4S_4)Li_2(OC_4H_8)_2(OH_2)_2]\cdot 2(OC_4H_8)$: C, 63.61; H, 7.82; S, 12.13. Found: C, 63.5; H, 7.5; S, 11.9.

Preparation of $[Na(LH_3)(thf)_2(H_2O)]\cdot 2thf$. $LH_4\cdot CHCl_3$ (200 mg) and triethylamine (~0.15 mL) were added to a solution of NaO_3SCF_3 (45 mg) in thf (10 mL), and the mixture was stirred well to give a colorless solution. Again, slow evaporation of the solvent led to deposition of crystals suitable for an X-ray structure determination, the complex appearing to be somewhat less soluble than the Li compound. The precipitate (145 mg) was ultimately collected, washed

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with thf, and dried in air. Anal. Calcd for $(C_{40}H_{47}O_4S_4)Na{\cdot}4thf{\cdot}2H_2O$: C, 63.01; H, 7.84. Found: C, 63.2; H, 7.9.

Preparation of $[K_2(LH_3)_2(H_2O)_2(O(C_2H_5)_2)_2]{\cdot}2CH_3OH$. Aqueous KOH (1 M, 0.75 mL) was added to a slurry of $LH_4{\cdot}CHCl_3$ (500 mg) in methanol (10 mL) and the mixture stirred vigorously for 5 h. The insoluble material was filtered, washed with methanol, and then dissolved in diethyl ether. Slow evaporation of this solution over several days led to the deposition of colorless crystals suitable for an X-ray structure determination. The analysis suggests that drying the crystals in air prior to elemental analysis led to the apparent replacement of the ether, as modeled in the structure determination, by atmospheric water. This was confirmed by subsequent ^1H NMR measurements. Anal. Calcd for $(C_{40}H_{47}O_4S_4)_2K_2{\cdot}4H_2O{\cdot}2CH_3OH$: C, 59.53; H, 6.70; S, 15.50. Found: C, 59.4; H, 6.1; S, 15.5.

Preparation of $[Rb_4(LH_3)_4(H_2O)(dmf)_{11}]$. A 50% aqueous solution of RbOH (0.1 mL) was added to a slurry of $LH_4{\cdot}CHCl_3$ (360 mg) in dmf (3 mL), and the mixture was heated on a steam bath until all the solid dissolved. The platelike crystals which deposited at room temperature after 12 h were not suitable for an X-ray structure determination. These initial crystals were removed by filtration and crystals suitable for structure determination obtained by vapor diffusion of ether into the mother liquor. Anal. Calcd for $(C_{40}H_{47}O_4S_4)_4Rb_4{\cdot}H_2O{\cdot}11dmf$: C, 57.32; H, 6.65; N, 3.81; S, 12.68. Found: C, 57.0; H, 6.2; N, 3.5; S, 12.6.

Preparation of $[Cs_3(LH_3)_3(LH_4)(dmf)_7(H_2O)_4]$. Solutions of $CsClO_4$ (180 mg) in dmf (3 mL) and $LH_4{\cdot}CHCl_3$ (500 mg) in (5 mL) containing triethylamine (0.5 mL) were mixed at room temperature. After 4 days, the fluffy white precipitate (260 mg) was filtered out and the filtrate allowed stand for an additional week, during which time larger crystals (154 mg) suitable for an X-ray structure determination were deposited. For elemental analysis, the crystals were collected at the pump, washed with ether, and dried in air, perhaps leading to the loss of water relative to the composition indicated by the structure determination. Anal. Calcd for $[Cs_3(LH_3)_3(LH_4)(dmf)_7(H_2O)_2]$: C, 56.80; H, 6.37; N, 2.56; S, 13.40. Found: C, 57.0; H, 6.4; N, 2.4; S, 13.0.

Structure Determinations. Full spheres of ω-scan area detector data (Bruker CCD instrument; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; $2\theta_{max} = 58°$) were measured at ca. 153 K, yielding $N_{t(otal)}$ reflections, merging after "empirical"/multiscan absorption correction (proprietary software: SMART/SAINT/SADABS/XPREP) to N unique (R_{int} quoted), N_o with $F > 4\sigma(F)$ being considered "observed" and used in the full-matrix least-squares refinements (non-hydrogen thermal parameter forms anisotropic; $(x, y, z, U_{iso})_H$ refined). Conventional residuals R, R_w (weights: $(\sigma^2(F) + 0.0004\sigma^4F^2)^{-1}$) are quoted on $|F|$. Neutral atom complex scattering factors were employed, computation using the XTAL 3.6 program system.[24] Pertinent results are given in the figures and tables and below, Table 1 summarizing the crystallographic data for all 11 structures determined. Details of individual variations in procedure/idiosyncrasies/abnormalities/difficulties are provided as Supporting Information.

Atom Numbering. Within each phenyl ring, carbon atoms are designated C((*ll′m*) 1−6) where *l*, *l′* = molecule, ligand number as appropriate, *m* = ring number (1−4). The oxygen atoms O(*n*l) are appended at C(*n*1) and the S(*n*) atoms at C(*n*6). The *tert*-butyl carbon atoms are C(41−44).

Discussion

Structure Determinations. As noted above, systematic single-crystal X-ray studies of metal/calixarene complexes are limited, in our experience largely because of the difficulty obtaining suitably crystalline materials and even then because of the commonly very complicated nature of the crystal lattices. The complexes may be difficult to crystallize, demanding ad hoc trial and error approaches using various (mixed) solvent

Table 1. Crystal Data, Details of Data Collection, and Structure Refinement for **1**−**11**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
empirical formula	$C_{40}H_{48}O_4S_4$	$C_{41}H_{49}Cl_3O_4S_4$	$C_{45}H_{53}NO_4S_4$	$C_{46}H_{63}NO_4S_4$	$C_{49}H_{70}N_2O_5S_4$	$C_{48}H_{69}NO_5S_5$	$C_{56}H_{82}Li_2O_{10}S_4$	$C_{56}H_{81}NaO_9S_4$	$C_{90}H_{124}K_2O_{13}S_8$	$C_{193}H_{267}N_{11}O_{28}Rb_4S_{16}$	$C_{181}H_{246}C_{s3}N_7O_{27}S_{16}$
M	721.1	840.5	800.2	822.3	895.4	900.41	1057.4	1049.5	1748.7	4044.2	3863.8
cryst syst	monoclinic	tetragonal	tetragonal	triclinic	triclinic	monoclinic	triclinic	monoclinic	orthorhombic	triclinic	orthorhombic
space group	$P2_1/c$ (14)	*P*4/*ncc* (130)	*P*4/*n* (85)	$P\bar{1}$(2)	$P\bar{1}$(2)	$P2_1/n$ (14)	$P\bar{1}$(2)	$P2_1/c$(2)	*Pbcn* (60)	$P\bar{1}$(2)	*Pccn* (56)
a (Å)	9.4579(8)	15.824(7)	13.095(2)	12.062(3)	11.564(2)	14.460(1)	12.019(1)	13.259(2)	17.141(1)	12.241(2)	28.391(2)
b (Å)	31.247(3)	15.824(7)	13.095(2)	13.240(3)	13.540(2)	16.153(2)	13.662(2)	22.178(4)	17.837(1)	21.684(3)	31.018(3)
c (Å)	13.772(2)	17.383(9)	12.887(2)	16.225(4)	17.513(2)	21.147(2)	19.499(2)	20.527(4)	31.983(2)	21.685(3)	22.302(3)
α (deg)	90	90	90	106.402(3)	76.458(2)	90	69.605(2)	90	90	110.308(2)	90
β (deg)	108.497(2)	90	90	100.973(3)	85.406(2)	96.025(2)	76.401(2)	105.500(3)	90	103.140(2)	90
γ (deg)	90	90	90	110.412(3)	67.599(2)	90	88.831(2)	90	90	93.445(2)	90
V (Å^3)	3860	4353	2210	2206	2646	4912	2910	5817	9779	5196	19639
D_c (g cm^{-3})	1.24_1	1.28_2	1.20_2	1.23_8	1.20_6	1.21_7	1.20_6	1.19_8	1.18_8	1.29_2	1.30_7
Z	4	4	2	2	2	4	2	4	4	1	4
cryst size (mm)	0.22 × 0.21 × 0.20	1.20 × 1.00 × 0.50	0.35 × 0.35 × 0.22	0.40 × 0.34 × 0.14	0.40 × 0.35 × 0.20	0.55 × 0.40 × 0.12	0.45 × 0.40 × 0.25	0.45 × 0.40 × 0.20	0.40 × 0.34 × 0.30	0.40 × 0.12 × 0.10	0.44 × 0.11 × 0.10
F(000)	1536	1768	852	884	964	1936	1136	2256	3736	2120	8072
μ (Mo Kα) (cm^{-1})	2.8	4.4	2.6	2.6	2.4	2.8	2.2	1.1	3.2	11.6	7.9
$T_{min,max}$	-	0.66, 0.81	-	-	0.84, 0.93	0.80,0.94	0.83, 0.93	-	0.68, 0.93	0.64, 0.93	0.82,0.92
N_{tot}	42367	8795	25540	25220	28252	72516	33597	63310	51805	61872	220984
N	9824	1926	2865	10668	11873	18864	14147	13666	11771	25767	25824
R_{int}	0.064	0.11	0.058	0.061	0.016	0.024	0.015	0.047	0.041	0.042	0.034
N_o	7347	817	2261	6922, $F > 4\sigma(F)$	9350	13681, $F > 4\sigma(F)$	12259	9874	9581	12067	15638
n_ν	704	136	209	532	803	846	933	792	585	1230	1168
R	0.045	0.073	0.047	0.089	0.041	0.031	0.042	0.074	0.080	0.081	0.058
R_w	0.055	0.088	0.054	0.10	0.051	0.029	0.052	0.086	0.086	0.082	0.063
$\lvert\Delta\rho_{max}\rvert$ (e Å^{-3})	0.60	0.51(3)	0.51(2)	1.10(4)	0.48(3)	0.73	0.8(2)	1.01(2)	0.88(3)	1.12(6)	1.62(7)

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systems opportunistically, as is frequently the case with other large or macromolecular systems.[25] Like the latter, they may be difficult to handle by virtue of the ease with which cocrystallized solvent, included or not, may be lost, a factor which is also a problem in relating microanalyses and the results of other (physical) studies on bulk materials to the composition of a single crystal indicated by a structure solution. All these vicissitudes carry over into the structure determination process itself where, over and above the usual crystallographic difficulties which may be encountered such as twinning, long primitive cell dimensions, etc., disorder may be evident in calixarene substituents such as, as here, *tert*-butyl, which is frequently rotationally disordered, in included solvents, in the phenoxide hydrogen atoms, and, again as here, within multiple metal arrays in a core at the center of the inwardly directed calixarene cones, where, in a manner similar to that found in many carbonyl cluster compounds,[26] an ordered molecular periphery is dictated by crystal packing but within it the core entities may be distributed over a variety of sites. These latter factors mitigate against the achievement of precision in associated X-ray studies, an attribute not frequently of critical concern in many macromolecular studies but of particular relevance to situations such as the present, where phenolic/acidic hydrogen atom distributions, among phenoxide and other potentially competitive basic species, may be crucial in defining explicitly the nature of the compound. These considerations apply even more strongly in complexes formed with these metals where multiple valence states may be prevalent, since, if these are difficult of access by other methods, putative charge distributions may in the end be a key defining factor of precise stoichiometry. Many of these considerations must be borne in mind in considering the results of the present structural studies, which we have already extended to complexes with transition, lanthanide, actinide, and other main group metals.

Structural Chemistry. The formation of solid state inclusion complexes by calixarenes is one of the more familiar aspects of their chemistry.[1,27] Some close parallels in the behavior of methylene- and sulfur-bridged calix[4]arenes have been revealed by the structural characterization[22] of adducts of *p-tert*-butyltetrathiacalix[4]arene and tetrathiacalix[4]arene, where it has been shown that adducted solvent is included within the calix in the former but not in the latter, where "self-inclusion" (see ahead; Figure 1a) may occur instead (as in the relatively small number of calix[4]arene adducts known[28]). There are, however, differences apparent when particular adduct species are considered in that neither dichloromethane nor chloroform has been characterized as a guest in solid adducts of unsubstituted *p-tert*-butylcalix[4]arene. This may be a consequence of a significant difference in the cavity dimensions for the two calixarenes, the sizes as measured (e.g.) by the mean side lengths for the S_4 and $(CH_2)_4$ bridging unit "squares" in a range of compounds we have directly studied being 5.51(2) and 5.08(1) Å, respectively, so that the thiacalixarene might be expected to accommodate larger guests. The present work (Table 2; Figure 1b) provides a superior determination of the structure of the chloroform adduct (for which minimal data have been previously reported[22]) which crystallizes in a cell derivative of that of the dichloromethane adduct (tetragonal, $P4/n$, $Z = 4$, $a = 15.704(3)$ Å, $c = 8.604(2)$ Å, $V = 2121$ Å^3 at 294 K) but with a doubled c axis (tetragonal, $P4/ncc$, $Z = 4$, $a = 15.824(7)$ Å, $c = 17.383(9)$ Å, $V = 4353$ Å^3 at $\sim$295 K). The molecule is again disposed about a crystallographic *4*-axis, alternate molecules stacked in a slightly staggered array, displaced alternately from the planes of the *4/mm* archetype, as the cell projection shows, with the included solvent offset from the axis and appropriately disordered; the phenolic hydrogen atoms are ordered. The present work also extends the series of structurally characterized inclusion complexes of *p-tert*-butyltetrathiacalix[4]arene to the 1:1 pyridine adduct (Figure 1c). This is similar to but different from the other adducts; the crystal is tetragonal, $P4/n$, $Z = 4$, as in the dichloromethane adduct and with a similar cell volume (2210 Å^3 at $\sim$153 K), but not isomorphous, a being 13.095(2) Å, c 12.887(2) Å. Again, the molecule is disposed about a crystallographic *4*-axis, one quarter comprising the asymmetric unit, with the pyridine included and disordered about the *4*-axis which passes through its molecular N···C(4) axis. The phenolic hydrogen atoms are again ordered, and each is directed toward a neighboring oxygen atom, suggesting the presence of the same "lower rim", hydrogen-bonded array found in many calix[4]arene derivatives and considered to be a prime factor causing these compounds to adopt a "cone" conformation.[1] The pyridine ring is modeled with the nitrogen directed into the calixarene cavity, opposite to the orientation postulated in some other calixarene/pyridine adducts,[29,30] though there is reason to expect that the energy difference between orientational isomers of this kind should be small.[21] Given that "thermal motion" is high and that there are various forms of disorder in the structure, we do not regard this assignment as overly secure.

Significantly, when the *p-tert*-butyltetrathiacalix[4]arene is crystallized from *N*,*N′*-dimethylformamide, it is obtained in an unsolvated form (Figure 1a). The array in the crystal, in which one molecule forms the asymmetric unit, is of lower crystallographic symmetry than the solvates, presumably a consequence of the fact that the basic unit of the structure is now not a single molecule but a centrosymmetric, dimeric pair, $[LH_4]_2$. This association, similar to that observed in the methylene-bridged calixarene series for *p-tert*-butylcalix[5]arene,[31] is sometimes referred to as "self-inclusion", an rather inappropriate term indicative of inclusion of a molecule by itself (as does occur in some systems[32]), rather than the mutual interaction of two, for which we propose the terminology "*hermaphrodite pair*", one of the (ordered) *tert*-butyl substituents (24) of each molecule being included in the cavity of the other, the contacts between the *tert*-butyl (24) hydrogen and the inversion-related calixarene phenyl carbon being 3 Å or greater. The unsolvated thiacalixarene retains the cone conformation found in its solvated forms,[22] cyclic hydrogen bonding between all four phenolic groups being associated with this conformation, as in the methylene-bridged series,[1] though the phenolic hydrogen atoms (defined by refinement) are disordered, each with two components directed toward their two adjacent phenoxide oxygen

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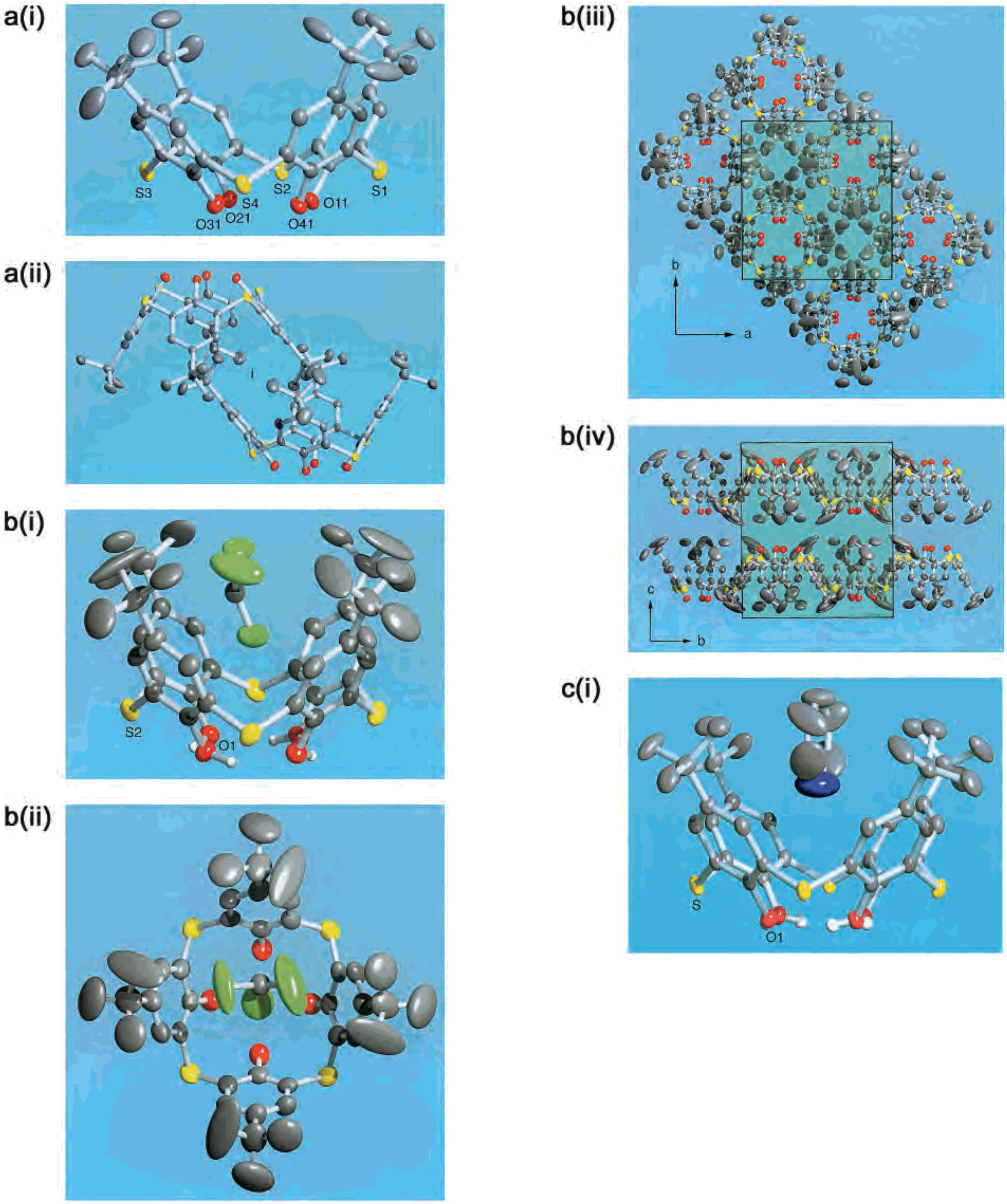

Figure 1. Projections of the ligand LH_4 (disordered solvent atoms removed for clarity). (a) Unsolvated: (i) approximately normal to that axis; (ii) showing in the latter the interaction of an inversion-related molecular pair, $(LH_4)_2$ (Here and in subsequent figures, 50% thermal ellipsoids are shown for the non-hydrogen atoms for the ca. 153 K determinations, and conventional atom colors of gray (C), red (O), and yellow (S) are used). (b) Chloroform solvated: (i) approximately normal to the putative *4*-axis; (ii) down its putative *4*-axis; (iii) the unit cell contents, projected down *a*, showing the stacking of the $[LH_4{\cdot}CHCl_3]$ aggregates in layers (solvent molecules omitted); (iv) the cell down *c*, showing the staggering of alternate molecules in each stack (solvent molecules omitted). (c) Pyridine solvated: (i) as before.

neighbors. The larger size of the thiacalixarene is reflected in O···O separations (Table 2) which are 0.1−0.2 Å greater than in the simple calixarene analogues, though these differences are smaller than that between the sides of the S_4 and $(CH_2)_4$ squares, meaning that the walls of the cone are inclined slightly more acutely to the mean O_4 plane. Considering such hydrogen bonding as proton coordination, phenolic calix[4]arenes can be regarded as (multiply) bidentate chelates for the smallest of the group 1 cations, H^+, a perspective which provides a useful basis for comparison of some aspects of the structures of complexes of the other group 1 elements.

The charge:size ratio for the series H^+, Li^+, Na^+, K^+, Rb^+, and Cs^+ must decrease in this order, and, on this basis, the stability of their complexes with calixarene anions would be expected to decrease, as indeed has been observed for the monoanion of *p-tert*-butylcalix[4]arene in acetonitrile solvent.[16] These measurements did, however, provide evidence that Li^+, at least, could compete sufficiently well with H^+ to form 2:1

Table 2. Ligand Descriptors[a]

(a) Interplanar Dihedral Angles: "1−4" are the C_6 Aromatic Planes

compd/ligand	O_4/1	O_4/2	O_4/3	O_4/4	1/2	1/4	2/3	3/4	1/3	2/4
LH_4	53.37(7)	48.10(7)	45.47(7)	57.11(8)	69.87(8)	67.84(8)	58.81(8)	70.60(8)	81.16(8)	74.80(8)
$LH_4 \cdot CHCl_3$	58.8(2)				62.5(2)				74.4(2)	
$LH_4 \cdot py$	56.56(5)				72.92(6)				69.32(7)	
$(Et_3NH)(LH_3)$										
300 K	42.5(2)	46.5(2)	61.5(2)	51.2(2)	59.9(2)	64.7(2)	71.6(2)	68.5(2)	76.1(2)	82.3(2)
153 K	42.2(2)	43.1(2)	62.1(2)	54.8(2)	58.4(2)	66.4(2)	70.8(2)	69.7(2)	75.8(2)	82.2(2)
$(Et_3NH)(LH_3)$										
dmf	74.35(5)	57.17(5)	38.13(5)	47.56(5)	68.37(6)	68.52(6)	67.50(6)	58.18(6)	67.52(6)	75.42(6)
dmso	22.2(4)	57.45(4)	75.72(4)	56.26(4)	61.37(4)	56.26(4)	79.18(4)	80.95(4)	82.12(4)	66.48(4)
$Li(LH_2)$	54.64(5)	58.99(5)	55.87(5)	48.97(5)	69.97(6)	70.57(6)	69.51(6)	64.15(6)	69.51(6)	72.04(6)
$Na(LH_3)$	45.2(1)	67.2(1)	57.4(1)	41.0(1)	67.8(1)	65.1(1)	79.6(1)	62.0(1)	77.7(1)	71.9(1)
$K_2(LH_3)_2$										
300 K	61.2(1)	41.2(1)	37.8(1)	53.9(1)	63.0(2)	74.4(2)	59.8(2)	59.3(2)	81.1(2)	85.2(2)
153 K	59.6(1)	39.2(1)	38.4(1)	53.3(1)	61.9(1)	72.8(1)	58.6(1);	59.3(1)	82.1(1)	87.8(2)
$Rb_4(LH_3)_4$(etc.)										
L1	58.4(2)	58.8(2)	43.3(2)	42.1(2)	75.4(2)	78.5(2)	63.0(2)	64.3(2)	78.5(2)	79.3(2)
L2	40.4(2)	70.2(2)	62.0(2)	47.8(2)	66.5(3)	69.3(3)	85.1(3)	63.8(3)	78.0(3)	62.3(3)
$Cs_3(LH_3)_4H$(etc.)										
L1	61.0(1)	48.7(1)	52.2(2)	53.8(2)	72.8(1)	73.5(1)	65.4(1)	68.9(1)	66.8(1)	77.5(1)
L2	79.3(1)	41.7(1)	34.7(1)	60.5(1)	78.7(1)	83.5(1)	55.6(1)	65.6(1)	66.1(1)	78.0(1)

(b) Phenolic O⋯O Distances (Å)

ligand/complex	1⋯2	2⋯3	3⋯4	4⋯1	1⋯3	2⋯4
LH_4	2.759(3)	2.668(3)	2.771(3)	2.749(3)	3.856(3)	3.885(3)
$LH_4 \cdot CHCl_3$	2.848(6)				4.028(6)	
$LH_4 \cdot py$	2.788(2)				3.943(2)	
$(Et_3NH)(LH_3)$						
300 K	2.562(7)	2.783(6)	2.897(7)	2.587(6)	3.986(6)	3.643(8)
153 K	2.557(6)	2.755(6)	2.926(7)	2.605(6)	4.002(5)	3.636(7)
$(Et_3NH)(LH_3)$						
dmf	2.889(2)	2.625(2)	2.513(2)	2.955(2)	3.917(2)	3.833(2)
dmso	2.589(1)	2.898(1)	3.091(2)	2.456(1)	3.956(2)	3.819(2)
$Li_2(LH_2)$(etc.)	2.452(2)	3.221(2)	2.430(2)	3.160(2)	3.951(2)	4.081(2)
$Na(LH_3)$(etc.)	2.748(3)	3.019(4)	2.546(3)	2.581(3)	3.679(3)	4.003(3)
$K_2(LH_3)_2$(etc.)						
300 K	2.691(5)	2.502(5)	2.551(5)	2.916(5)	3.875(5)	3.645(5)
153 K	2.682(4)	2.470(4)	2.561(4)	2.882(4)	3.835(4)	3.641(4)
$Rb_4(LH_3)_4$(etc.)						
L1	2.937(8)	2.628(7)	2.473(7)	2.585(7)	3.721(7)	3.777(7)
L2	2.630(6)	3.151(8)	2.575(5)	2.533(8)	3.781(6)	3.899(8)
$Cs_3(LH_3)_4H$(etc.)						
L1	2.598(4)	2.775(5)	2.646(5)	2.762(4)	3.896(5)	3.723(4))
L2	2.902(4)	2.488(4)	2.595(4)	3.098(4)	4.072(4)	3.726(4)

[a] In LH_4, the protonic hydrogen atoms are disordered and directed toward the phenolic oxygen to either side; in the chloroform and pyridine solvates, although directed similarly, they are ordered in one direction about the O_4 cycle. In $(Et_3NH)(LH_3)$ (153 K), they were located and refined on O(21,41) only, both being directed toward O(11) which, interacting with NH (N,H⋯O(11) 2.722(6), 1.7 Å (est.)) is presumabled deprotonated. In $(Et_3NH)(LH_3)$ dmf solvate, O(21) is deprotonated, the hydrogens on O(11,31,41) being directed toward O(21,21,31), respectively (H(11)⋯O(11,21) 0.81(3), 2.22(4); H(31)⋯O(21,31) 1.33(5), 1.30(5); H(41)⋯O(31,41) 1.33(3), 1.20(3) Å); here NH approaches O(41) (N, H⋯O(41) 2.841(2), 1.96(2) Å). In the dmso counterpart, O(11) is deprotonated, the hydrogens on O(2′,3′,4′) being directed toward O(11,21,11), respectively (H(21)⋯O(11,21) 1.75(3), 0.85(3); H(31)⋯O(21,31) 2.22(2), 0.76(2); H(41)⋯O(11,41) 1.42(2), 1.04(3) Å); here NH approaches O(21) (N,H⋯O(41) 2.746(2), 1.81(2) Å).

as well as 1:1 (M:L) species (and it has long been known[1] that, by the use of reagents such as *n*-butyllithium, complete substitution of H^+ by Li^+ can be achieved). This interaction, stronger than for the other alkali metal cations, may assist in understanding the isolation of the (structurally characterized[13]) 2:1 lithium complex of *p-tert*-butylcalix[4]arene under conditions similar to those which provide only the 1:1 complex with sodium. In any case, a similar 2:1 complex has been presently obtained from the thiacalixarene (Figure 2; Table 3). This complex, credibly described by virtue of meaningful refinement of all hydrogen atoms excepting those associated with the disordered *tert*-butyl substituent, provides a good example of the adventitious circumstances which may result in the formation of crystals of quality adequate for X-ray work. The complex may be represented by the composition $[\{(thf)(LH_2)\}Li_2(thf)(OH_2)_2] \cdot 2thf$ and contains a mixed but well-defined solvent component, there being three different roles for the thf and two for the water within this aggregate, which makes up the asymmetric unit of the structure. The structure shows the calixarene to behave as a bidentate ligand only toward each Li^+ individually, with the metal atoms achieving four-coordination through a bridging water molecule and unidentate water or tetrahydrofuran, so that the complex is less symmetrical than its *p-tert*-butylcalix[4]arene analogue, in which there is again a bridging water molecule but the terminal unidentate ligands are both methanol. In both cases, a solvent molecule, now tetrahydrofuran rather than methanol, is included in the calix, which also retains the cone conformation. The inclusion of tetrahydrofuran is novel for a calix[4]arene, again consistent with a greater cone capacity of the thia species. Binding to lithium causes the separations of the chelating pairs of oxygen atoms involved to increase from 2.74(3) Å (mean) in the proton

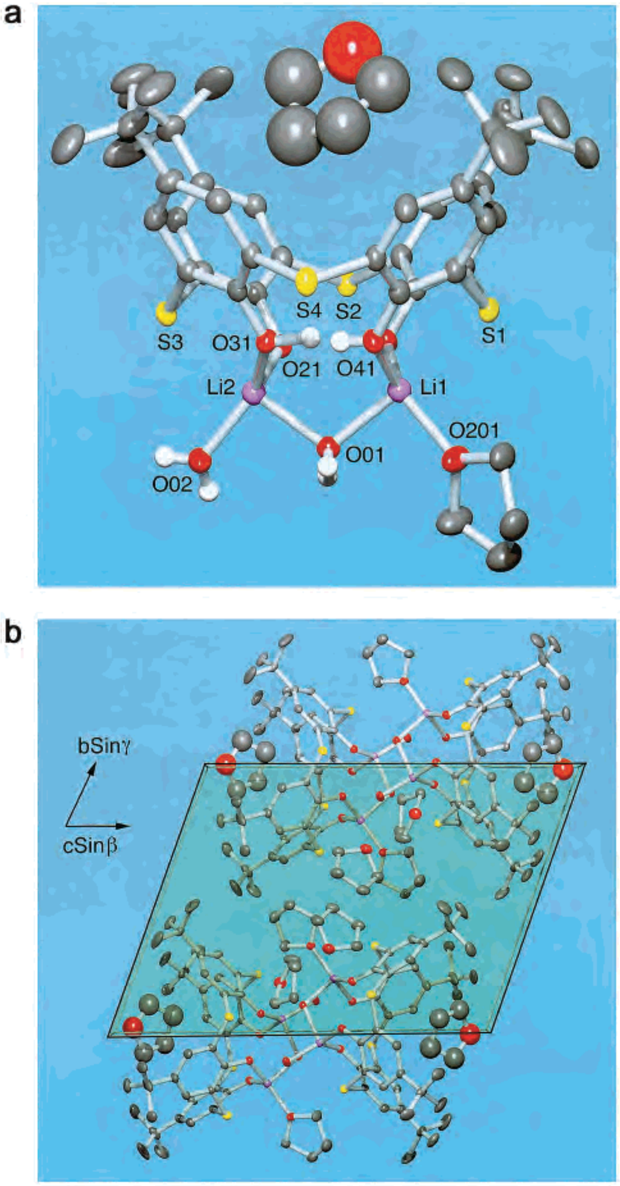

Figure 2. (a) Projections of the lithium adduct ("lattice" solvent molecules omitted here) as the "molecular" aggregate [{(thf)(LH_2)}-$Li_2(OH_2)_2$(thf)], approximately normal to the putative *4*-axis. (b) Unit cell contents projected down *a*.

Table 3. Lithium Environments[a]

Li(1)

atom	*r*	O(4)	O(01)	O(201)
O(11)	1.967(3)	107.8(1)	97.0(1)	132.8(2)
O(41)	1.945(3)		99.2(2)	115.3(2)
O(01)	2.060(4)			94.4(1)
O(201)	1.986(3)			

Li(2)

atom	*r*	O(31)	O(01)	O(02)
O(21)	1.993(4)	108.8(2)	96.2(1)	118.9(2)
O(31)	1.968(3)		97.5(1)	128.4(2)
O(01)	2.065(3)			95.9(1)
O(02)	1.926(4)			

[a] In this and subsequent similar tables, *r* is the metal−ligand atom distance (Å), other entries being the angles subtended at the metal atom (degrees) by the relevant atoms at the head of the row and column. Li(1,2) lie 1.072(2), 1.049(3) Å out of the O(n1)$_4$ plane ($\chi^2 = 831$; deviations σ (O(n1) ($n = 1-4$)) −0.022(2), 0.020(2), −0.022(2), 0.023(2) Å); Li(1) lies 0.008(4), 0.073(4) Å out of aromatic C_6 planes, 1, 4 respectively, Li(2) 0.213(4), 0.093(4) Å out of planes 2, 3. Angles (deg) Li−O−C at O(11−41) are 126.1(1), 124.5(1), 127.5(1), 127.8(2); Li(1)−O(01)−Li(2) is 108.2(1). Li(1)···S(1), Li(2)···S(3) are 2.660(4), 2.645(2) Å. C(n1)−O(n1) ($n = 1-4$) are 1.344(2), 1.345(2), 1.334(2), 1.326(2) Å, cf. 1.359(3), 1.359(3), 1.357(3), 1.363(3) Å in LH_4 (unsolvated), 1.366(7) (LH_4·$CHCl_3$), 1.360(2) Å, LH_4·py). Protons reside on O(11,31), directed toward O(21,41) respectively (H(11)···O(11,21) 1.08(4), 1.38(4) Å, H···O···H 169(3)°; H(31)···O(31,41) 1.04(4), 1.42(4) Å, H···O···H 161(3)°); other strong hydrogen bonds are found from the water molecules H(01a)···O(401)(thf) 1.85(3) (associated O(01)···O(401) 2.706(2)), H(01b)···O(21)($-x$, $2 - y$, $1 - z$) 2.17(2) (2.996(2)), H(02a)···O(11) ($-x$, $2 - y$, $1 - z$) 2.12(3) (2.881(2)), H(02b)···O(301)(thf) ($1 - x$, $2 - y$, $1 - z$) 1.97(3) (2.772(2) Å).

complex ("free" calixarene) to 3.221(2) and 3.160(2) Å, the separations of the pairs chelating the remaining protons decreasing concomitantly to 2.430(2) and 2.452(2) Å, corresponding to rather strong hydrogen bonds.[33] This may explain why the geometric parameters, Li−O and C−O distances, and the Li−O−C angle, appear to be insensitive criteria for distinguishing the formally phenolic and phenoxide donors making up the chelate unit about Li. The two lithium atoms bridged by a water molecule have Li−O(H_2) longer than Li−O(LH_2) by ~0.1 Å, the array [(H_2O)Li_2(LH_2)] being of putative *2*-symmetry. Remarkably, this symmetry is broken by the fourth coordination sites of the two lithium ions being occupied unsymmetrically, that of Li(2) by water and that of Li(1) by thf(2). The associated Li−O distances are rather disparate, with Li(2)−O(02) the shorter (1.926(4) Å) and Li(1)−O(201)(thf) the longer (1.986(3) Å). As well as the other thf molecule included within the calixarene cavity, two additional molecules of thf are found in lattice sites: thf(4) the oxygen of which is hydrogen bonded to the bridging water molecule and thf(3) similarly hydrogen bonded to the other coordinated water molecule. It is of interest that both Li and phenolic protons are chelated into similar boat conformations, Li/H and S at the prows (Figure 2), Li···S lying within an essentially tetrahedral angle in the coordination sphere (see below). As can be appreciated from the unit cell projection (Figure 2b), hydrogen bonds associated with the two water ligands link neighboring molecules into inversion-generated dimers about (0, 1, $^1/_2$) (etc.) and these then into translation generated strings parallel to *a* about (x, 0, $^1/_2$) (etc.), the most hydrophilic/polar regions of the structure, while the thf molecules, free and coordinated, occupy a tunnel about (x, $^1/_2$, $^1/_2$), the hydrocarbon substituents and thf faces of the calix cones confronting as sheets across the $z = 0$ plane.

The seeming tetrahedral four-coordination observed for both Li atoms in the complex is similar to that seen in various simpler aryloxides[23b] and indicates that the calixarene cannot be a particularly powerful ligand for Li, since binding of all four calixarene oxygen atoms in, say (with water), a square pyramidal arrangement as observed in lithium picrate monohydrate[34] might have been considered a possibility. Formally, adjacent oxygen atoms might be considered to define a chelating unit of relatively large "bite" well suited to binding a small metal such as Li,[35,36] suggesting that the reason that the two metals are bound to opposite rather than adjacent edges of the calixarene-O_4 polygon may be a consequence of the ease of distortion of the calixarene

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Table 4. Sodium Environment[a]

atom	*r*	O(31)	O(101)	O(201)	O(01/01′)	S(3)
O(21)	2.370(3)	79.57(9)	94.6(1)	155.2(2)	107.0(2)/94.8(2)	67.65(8)
O(31)	2.346(3)		166.0(2)	92.2(1)	88.1(2)/109.5(2)	68.28(8)
O(101)	2.294(4)			87.9(1)	105.8(2)/83.5(2)	97.8(1)
O(201)	2.300(4)				95.9(2)/110.0(2)	87.6(1)
O(01)	2.267(8)				26.7(3)	156.2(2)
O(01′)	2.311(7)					162.5(2)
S(3)	2.949(2)					

[a] Na lies 0.081(7), 0.617(7) out of aromatic C_6 planes 2, 3, respectively. Na−O(*n*1)−C(*n*1) ($n = 2, 3$) (deg) are 132.7(2), 129.7(2). S(3)···Na−O(21,31,101,201,01,01′)) (deg) are 67.65(8), 68.28(8), 97.8(1), 87.6(1), 156.2(2), 162.5(2). Na lies 1.525(3) Å out of the $(O(n1))_4$ plane (χ^2 627; deviations δ O(1−4) −0.044(3), 0.036(3), −0.035(3), 0.037(3) Å). O(41) is the deprotonoted phenoxide; hydrogens on O(11,21,31) are directed toward O(41,11,41) respectively: H(11)···O(11,41) 0.66(4), 1.96(4); H(21)···O(21,11) 0.79(4), 2.05(4); H(31)···O(31,41) 0.79(4), 1.77(4) Å. O(01)···O(01′) is 1.06(1) Å. C(*n*1−O(*n*1) ($n = 1-4$) are 1.359(4), 1.359(5), 1.343(4), 1.329(4) Å. O(01,01′)···O(41) ($-x$, $1-y$, $2-z$) are 2.771(8), 2.789(7); O(01′)···O(01) ($-x$, $1-y$, $2-z$), O(301) ($-x$, $^1/_2+y$, $^1/_2-z$) 2.86(1), 2.905(9) Å. O(01)···O(01) ($-x$, $1-y$, $2-z$) is 2.08(1) Å.

toward a structure of C_{2v} symmetry.[1] This conformational mobility may, of course, also be seen, as in the case of the much more complicated ligand "beauvericin",[37] as the origin of a lack of selectivity in metal ion binding, since a readily achieved tilting of the phenyl rings can produce large variations in the spatial separation of donor groups. The structures described support this conclusion. A final note on the Li structure which is relevant to the detection of interactions with S in complexes of the other alkali metals is that as noted above there is indeed a rather remote approach of S to Li, suggestive of the incipience of this interaction here. Accepting a true coordination, the coordination geometry about Li would then be better described as a highly distorted trigonal bipyramidal LiO_4S unit. However, the lack of serious associated angular distortion militates against such a description (see above). Nonetheless, its consideration does raise the interesting prospect of an unrecognized "agostic" Li···H interaction occurring in the complex of the methylene-bridged calixarene.

The sodium complex of the thiacalixarene, crystallized from tetrahydrofuran as with the lithium compound, is, in continuing parallel with the *p-tert*-butylcalix[4]arene system,[13] only a 1:1 species, with the calixarene a bidentate ligand to the metal (Figure 3; Table 4), the overall stoichiometry being $[\{(thf)(LH_3)\}Na(thf)(OH_2)]\cdot 2thf$ for the asymmetric unit of the cell as given. The crystals are again formally the product of a mixed solvent system, though this may be consequent on the absorption of moisture by the initial solution during the prolonged standing required for crystal growth. Unlike the Li complex, there are now alternatives for the metal and proton locations and it would appear that the chelation of the sodium is better described as occurring by way of two phenol hydroxyl units rather than through one phenol and a phenoxide. The separation of the oxygen atoms chelating the sodium is slightly diminished (3.020(3) Å) in comparison to the Li system, leaving other pairwise separations of 2.748(3), 2.581(3), and 2.546(3) Å, consistent with all three involving relatively strong proton chelation. Despite the fact that sodium is known to be capable of joint coordination to all four phenolic oxygen atoms of a calix[4]arene,[30,38] this is observed neither here nor in the 1:1 sodium complex of *p-tert*-butylcalix[4]arene,[13] nor in a related disodium derivative of *p-tert*-butylcalix[4]arene dimethyl ether[39] in which cation−π interactions, however, appear to be important. Since they are only found when hydrogen is *not* present at oxygen, it may be that the structures of the simple complexes reflect the dominance of proton chelation effects. Although the mere bidentate function of the calixarene toward sodium would not seem to require that it retain a cone conformation, the observation that it does provides further support for this conclusion. The protons associated with the adjacent phenolic group oxygen atoms, O(21,31), chelating sodium, are directed toward adjacent O(41,11), O(11) being modeled as protonated, with its proton directed toward unprotonated O(41). In keeping with its phenoxide status, the associated C−O distance of the latter is somewhat the shortest in the present array (1.329(4) Å), the other O(*n*1)−C(*n*1) ($n = 1-3$) distances ranging from 1.342(4) to 1.359(5) Å. Two of the thf molecules (#1, 2(disordered)) occupy cis coordination sites about Na, each trans to a phenolic oxygen donor atom. The sodium complex exists as a dimer in the solid state with two molecules being joined by H-bonding between O(41) and the water of the other molecule and also between opposing water molecules. Perhaps the extensive hydrogen and metal bonding associated with O(41) explains why it is in the phenoxide form.

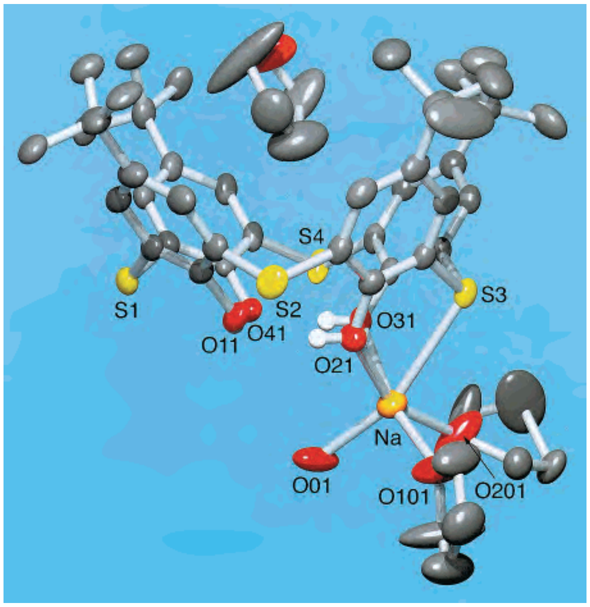

Figure 3. Projection of the sodium adduct as the molecular aggregate $[\{(thf)(LH_3)\}Na(OH_2)(thf)_2]$, approximately normal to the putative *4*-axis.

Superficially, the sodium coordination environment appears closely similar in its complexes with both *p-tert*-butylcalix[4]arene[13] and *p-tert*-butyltetrathiacalix[4]arene, the coordination number of 5 (considering O-donors only) being low in comparison to what has been observed in various simpler aryloxide

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(37) Dobler, M. *The Ionophores and Their Structures*; Wiley: New York, 1981; Chapter 6.

(38) Bott, S. G.; Coleman, A. W.; Atwood, J. L. *J. Am Chem. Soc.* **1986**, *108*, 1709.

(39) Dubberley, S. R.; Blake, A. J.; Mountford, P. *Chem. Commun.* **1997**, 1603.

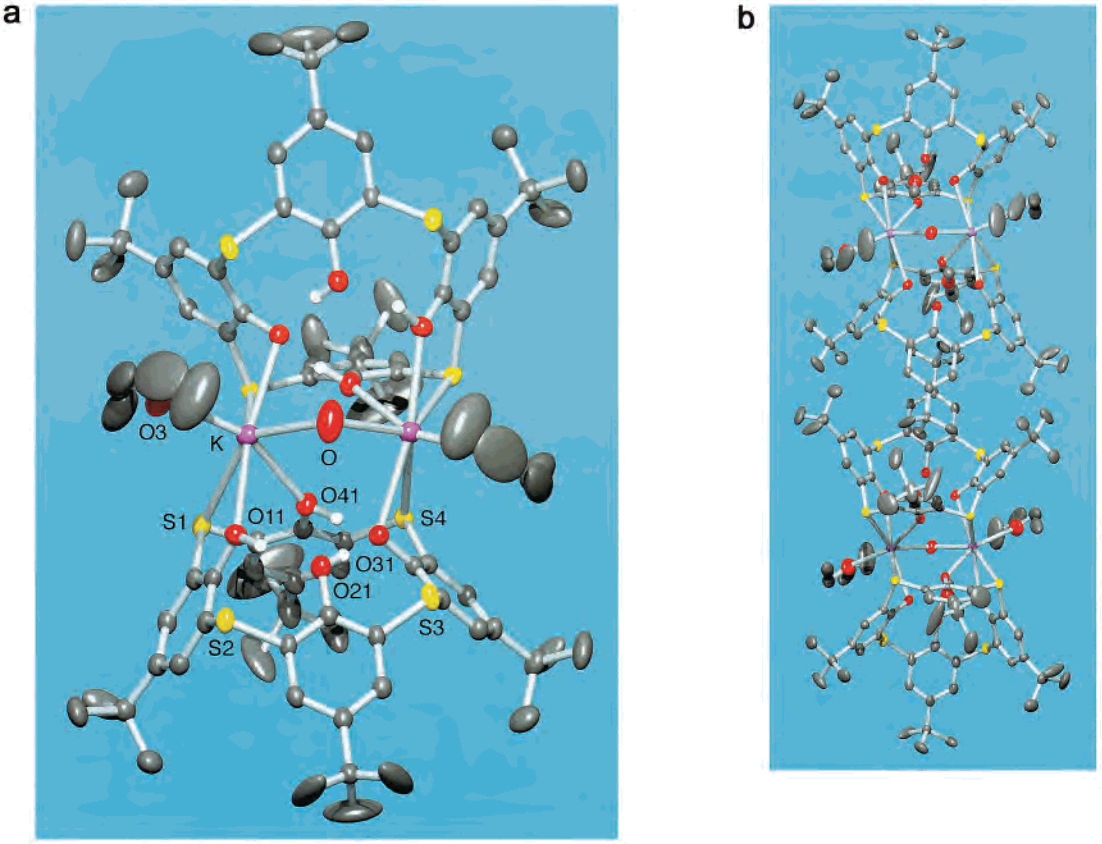

Figure 4. (a) Projection of the binuclear potassium adduct, $[(LH_3)_2(K(OEt_2)_2(OH_2))_2]$ (ca. 153 K), down the crystallographic *2*-axis. (b) The same, interlocking with its inversion image to give a linear polymer parallel to *c* (vertical in the page).

Table 5. Potassium Environment[a]

atom	*r*	O(41)	O(3)	O(0)	O(31′)	S(1)	S(4′)
O(11)	2.721(3) (2.711(3))	64.59(9) (65.2(1))	101.4(1) (97.1(2))	91.42(7) (91.30(9))	168.0(1) (168.4(1))	59.00(7) (58.77(8))	123.56(7) (126.90(9))
O(41)	2.672(3) (2.698(4))		156.2(1) (156.0(2))	84.8(1) (84.6(1))	106.46(9) (108.4(1))	58.88(7) (58.29(8))	73.13(7) (76.52(8))
O(3)	2.713(5) (2.758(7))			115.9(1) (113.3(2))	89.7(1) (91.6(2))	97.6(1) (99.1(2))	103.0(1) (105.0(2))
O(0)	2.783(3) (2.818(5))				79.42(7) (78.12(8))	139.73(6) (138.78(8))	120.78(8) (121.1(1))
O(31′)	2.797(3) (2.786(5))					124.62(7) (127.45(8))	57.09(6) (57.27(7))
S(1)	3.335(1) (3.351(2))						67.82(3) (70.29(4))
S(4′)	3.348(1) (3.464(2))						

[a] Values for the 300 K determination are given in parentheses following those for the 153 K study. Primed atoms are generated by the 2-fold axis $(-x, y, {}^3/_2 - z)$. K lies 1.991(3) (2.010(4) Å) out of the $(O(n1))_4$ plane (χ^2 213 (232); deviations δ O(n1) ($n = 1-4$) are 0.026(4), −0.029(4), 0.026(3)), −0.026(4) (0.032(4), −0.032(4), 0.031(4), −0.031(4) Å). K−O(n1)−C(n1) (n = 1, 4, 3′) are 136.2(2), 132.5(3), 108.0(2) (137.1(3), 132.9(3), 107.3(2)), with K−O(0)−K′ 103.4(2)° (101.9(2)°). O(0) contacts O(01, O(01) $(-x, y, 1^1/_2 - z)$ at 2.787(6) with O(01)···O(21) at 2.772(6) Å; the other component of the methanolic O(01) has no close contacts.

complexes,[23,34] where six-coordination predominates, though it is not an exceptional situation.[40] However, closer consideration of the thiacalixarene complex structure shows one thiaether S atom S(3) is in the vicinity of Na at what may be taken as an interactive distance (2.949(2) Å) in a void in the coordination sphere and occupying a site approximately trans to the coordinated water molecule which is disordered equally over two closely disposed (O(01)−Na−O(01′) 26.7(3)°) sites, so that the sodium may be considered to have approximately octahedral NaO_5S coordination. As with the dilithium compound, the complex serves to "coordinate" a molecule of tetrahydrofuran by inclusion of it within the calixarene cone. In both cases, the included molecule is disordered but modeled with the oxygen atom directed "out", consistent with methylene-CH/π interactions being associated with the inclusion.[41] The third thf of the stoichiometric unit occupies a lattice site.

Although possibly in part a consequence of the use of a different preparative medium, the structure of the 1:1 complex of potassium with the thiacalixarene (Figure 4; Table 5) defines a new motif involving a binuclear calixarene "sandwich" (i.e.,

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(40) Poonia, N. S.; Bajaj, A. V. *Chem. Rev.* **1979**, *79*, 389.

(41) Nishio, M.; Hirota, M.; Umezawa, Y. In *The CH/π Interaction: Evidence, Nature and Consequences*; Marchand, A. P., Ed.; Methods in Stereochemical Analysis, No. 11; Wiley-VCH: New York, 1998.

a 2:2 complex), a unit which is well-known in methylene–calixarene complexes[1,14,39] and which we and others have found to be characteristic of complexes of both d- and f-block metals with the thiacalixarene.[8,9,42] Within the present series of group 1 derivatives, the structure provides further evidence of a change in coordination proclivities in that the potassium now interacts with more than one sulfur atom, the high coordination numbers typical of potassium in simpler aryloxides[23] being attained here by weak interactions (K–S 3.480(1), 3.335(1) Å) with two sulfur atoms from different calixarene moieties in addition to those with five oxygen atoms. As with sodium, there are precedents[3] to justify the expectation that potassium might bind to all four oxygen atoms of a single calixarene, but although three oxygen atoms of a given calixarene molecule interact with potassium, this is because dimer formation allows a given potassium atom bound to two oxygen atoms of one calixarene to bind to one oxygen atom of a second calixarene. This and the retention of the cone conformation again suggest the continuing importance of (residual) proton chelation. The binuclear structure of the complex, one half of the binuclear aggregate (modeled as $[(LH_3)_2K_2(OH_2)(O(C_2H_5)_2)_2]\cdot 2CH_3OH$) being crystallographically independent and comprising the asymmetric unit of the structure, is fortified by water ligand bridging, but a surprising feature is that ether appears to be preferred as an O-donor ligand over methanol also present in the lattice. This may in part be a consequence of intermolecular CH/CH dispersion interactions, as the ethyl groups of the ether ligands are disposed in lattice cavities delineated by the *p-tert*-butylphenyl walls of adjacent calixarenes. Viewed down *a*, the 2-fold symmetric nature of the binuclear molecule is apparent, with stacked columns parallel to *c* forming in alternating directions in the *bc* plane, essentially by the accommodation of ethyl arms of one molecule between slightly inclined *tert*-butylphenyl groups of the different calixarene entities of the next molecule. The two oxygen atoms of one calixarene which chelate a potassium are 2.882(4) Å apart, closer again than in the equivalent units of the Li and Na complexes. The oxygen atom bound to the other potassium is only 2.561(4) Å from oxygen bound to the first and 2.682(4) Å from the oxygen seemingly not involved in appreciable interaction with the metal. The remaining O···O separation, involving this last, "uncoordinated" oxygen and one involved in the chelate ring to potassium, is the shortest of all at 2.470(4) Å. Proton coordination in the system is complicated by interactions outside the phenolic units involving both the bridging water molecule and the disordered lattice methanol. Thus, one component of the latter serves to bridge the uncoordinated phenol unit and the bridging water, and its involvement in such proton coordination may be another reason why it is not bound to potassium. The calices, although devoid of solvent, interlock by way of inversion-related *tert*-butyl groups of adjacent dimers, arranged in a string along *c*, in the manner of the unsolvated ligand and triethylammonium salt of the ligand, so that in this case the aggregation gives rise to a loose one-dimensional polymer, as shown in Figure 4b.

There are many parallels in the simple chemistry of the potassium and ammonium ions, and even in the presence of an anion as chemically complicated as 2,4,6-trinitrophenoxide (picrate), isostructural crystals are formed.[23,34] Although we have not prepared an $[NH_4]^+$ derivative of *p-tert*-butyltetrathiacalix[4]arene, and anticipate that this will be difficult to do because of the similar basicity of ammonia and the calixarene anion and the volatility of the former, it is possible to very readily isolate "salts" of the calixarene with triethylamine (as it is with most calixarenes[1]), and we have structurally characterized the 1:1 species obtained in solvated (with dmf and dmso) and unsolvated forms (Figure 5). Note that our unintended isolation of the unsolvated thiacalixarene after heating a solution formed from the calixarene and triethylamine in dimethylformamide shows that proton transfer equilibrium between the two species is readily reversed by allowing the base to volatilize. In this sense the $[NHEt_3]^+$ complex does mimic the properties expected of the $[NH_4]^+$ species. However, the only obvious similarities between the $[NHEt_3]^+$ and potassium complexes is that both contain the calixarene in its cone conformation, though even in this, quite marked differences can be seen in regard to the oxygen array and its involvement in proton chelation, and in anion association (see below). In the unsolvated compound (Figure 5a), a conventional view would be that the triethylammonium cation is associated with the calixarene anion through a hydrogen bond to just one of the four oxygens, specifically, that considered to have been deprotonated. The N···O separation is relatively short (2.722(6) Å), and the distances from this oxygen to its two nearest calixarene-O neighbors are shorter still (2.605(6) and 2.557(6) Å). The other two adjacent-oxygen separations are longer (2.926(7) and 2.755(6) Å) but still lie within the range conventionally considered to indicate hydrogen bonding.[33] Without precise and reliable information on the actual hydrogen atom locations, these data are open to various interpretations, one being that the predominant proton locations are those shown in Figure 5a. At present, however, little more can be said other than that, as in the true metal complexes, identification of the site of any negative charge on the calixarene structure is far from straightforward.

As in the unsolvated form of the calixarene itself and the potassium complex, occupation of the calixarene cavity in the solid state is achieved by the formation of "hermaphrodite pairs", Figure 5a showing clearly interlocking pairs of the stoichiometric units. Thus, the centrosymmetric $[(Et_3NH)(LH_3)_2(HNEt_3)]$ aggregate is the basic structural unit. For both this and the potassium adducts, preliminary room temperature studies were undertaken; we record them briefly (Tables 1 and 2; Supporting Information) since, although essentially similar to the low-temperature studies, they show significant, albeit minor responses in ligand conformation to the change in temperature or particular specimen, most notably in such parameters as the pitch of the ligand planes.

The structures of the dimethylformamide and dimethyl sulfoxide adducts of the triethylammonium complex (Figure 5b) are quite like that of the unsolvated form despite the effective dissociation of the dimer by solvent inclusion. The solvent guests are included well within the cup, lying to one side and approximately parallel to a phenyl ring in the projection shown. In the dmf adduct, the three carbon atoms of the guest all lie within 4 Å (3.466(2) Å for the formyl carbon; 3.552(3) and 3.997(3) Å for the methyl group carbons) of different aromatic carbon atoms, suggesting a form of stacking interaction[23a,34] instead of or in addition to CH/π interactions.[41] Perhaps because of the presence of the guest, proton coordination is rather different from that in the unsolvated compound. The single (triethylammonium)-N···O separation is somewhat longer (2.841(2) Å), and the separations of this oxygen atom from its two adjacent calixarene neighbors are now the longest (2.955(2) Å) and shortest (2.513(2) Å) of the array, with the two remaining separations being 2.889(2) and 2.625(2) Å. Refined proton locations are shown in Figure 5b. The structure of the dmso adduct is broadly similar to that of dmf, the orientation of the

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(42) White, A. H., et al. To be published.

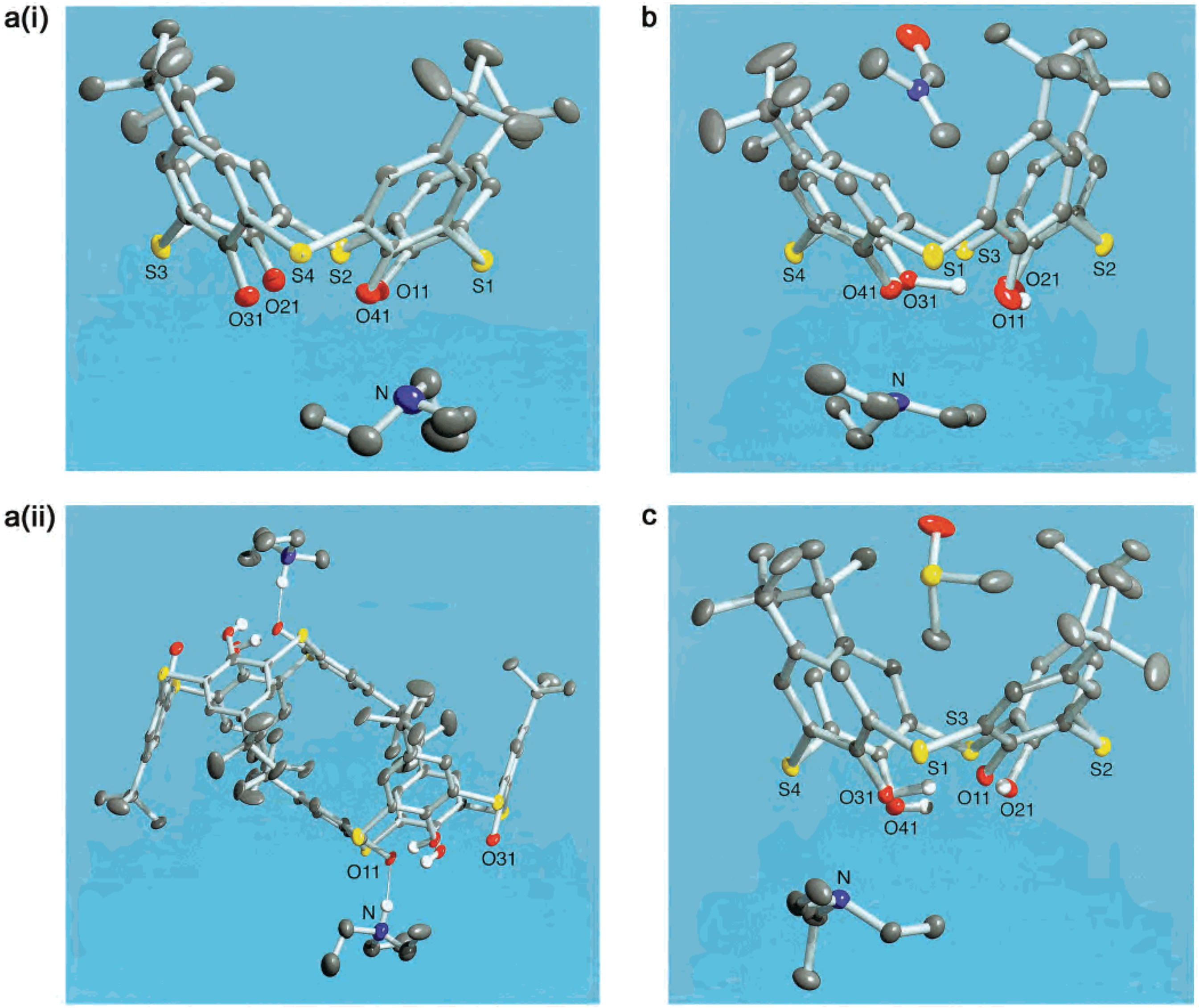

Figure 5. Projections of the triethylammonium salt [Et_3NH][LH_3]. (a) Unsolvated (ca. 153 K): (i) approximately normal to the putative *4*-axis; (ii) similarly, showing the interaction of an inversion-related anion pair in a manner similar to that of LH_4 (unsolvated) (cf. Figure 1ai), together with the interaction with the accompanying pair of hydrogen-bonded cations, [$(Et_3NH)(LH_3)_2(HNEt_3)$]. (b) As the dmf solvate. (c) As the dmso solvate.

included molecule again being consistent with possible $CH_3-\pi$ interactions, perhaps assisted here by $S\cdots\pi$ attraction, the dmso sulfur being ~4 Å from the centroid of the nearest aromatic ring. The "oxygen out" orientation of the dmso is opposite to that observed in the dmso inclusion adduct of neutral *p-tert*-butylcalix[4]arene,[43] suggesting some influence of the presumably larger dipole in the thiacalixarene monoanion. Throughout the three salts, considerable variations are observed in respect of the tilt of the aromatic ring planes vis-à-vis the O_4 core (as datum). While these correlate with $O\cdots O$ distances to adjacent rings, the association with other parameters, e.g., protonation pattern, manner of cation contact or inclusion, etc., is less secure, although it may be significant that the solvent-included arrays are the most distorted.

In simple aryloxide systems,[23,34] the coordination chemistry of rubidium is usually much more similar to that of cesium than that of potassium, and there is indeed a significant difference between the structures of the potassium and rubidium (Figure 6; Table 6) complexes of *p*-*tert*-butyltetrathiacalix[4]arene while there are closer similarities in the structures of the Rb and Cs (see ahead) structures. Again, a caution must be noted regarding the change of preparative/crystallization medium from ether (K) to dimethylformamide (Rb), but this does not detract from the remarkable nature of the tetranuclear, 4:4 Rb complex obtained. Aside from certain disordered *tert*-butyl substituents, this cluster consists of well-ordered entities, ostensibly nicely packed but with the phenoxide aggregate, encapsulated within a hydrocarbon "micelle", defining a unit with ambiguous stereochemical if not stoichiometric possibilities within the pairs of symmetry-related calixarenes. Two crystallographically independent ligands and their inversion-related congeners make up a centrosymmetric whole, ligand 2 including dmf 1. Within this, three nonlinear rubidium moieties, necessarily a noncentrosymmetric grouping, are disposed. The site of Rb(1) is fully occupied, the atom being chelated by an adjacent pair of phenolic/phenoxy oxygen atoms (ligand phenolic hydrogen atoms are not defined and, indeed, given the disorder among the other cations, may also be disordered) O(111,121) from ligand 1 only. The remainder of the coordination sphere of Rb(1) is made up of the oxygen atoms from four dmf moieties, dmf(2,3,5,6). Note that the construct of what constitutes a significant metal−ligand interaction

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(43) Furphy, B. M.; Harrowfield, J. M.; Ogden, M. I.; Skelton, B. W.; White, A. H.; Wilner, F. R. *J. Chem. Soc., Dalton Trans.* **1989**, 2217−2221.

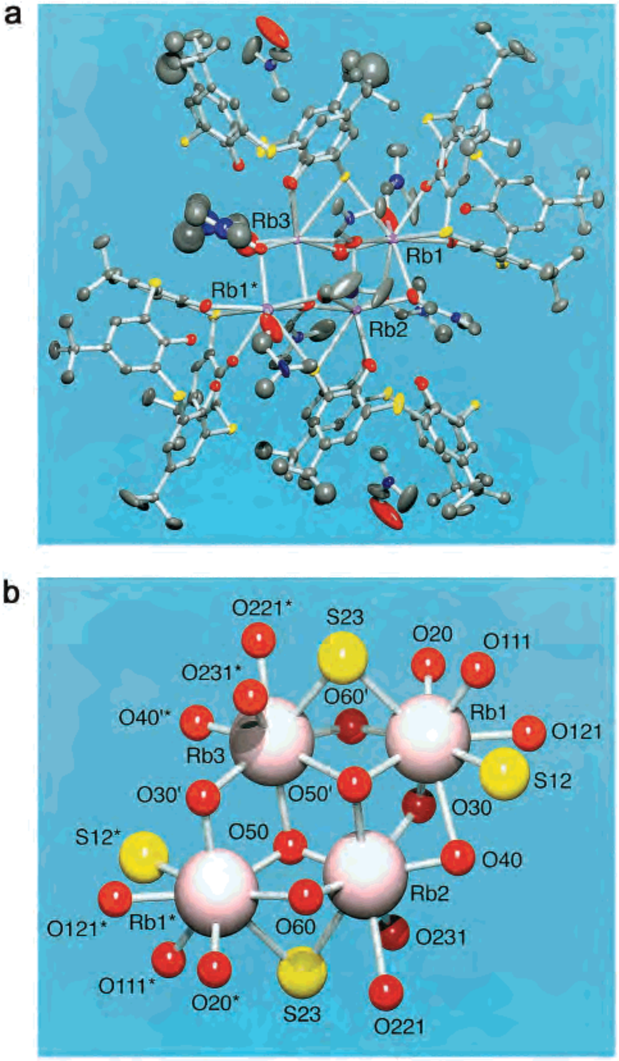

Figure 6. Projections of the rubidium adduct (a) showing the total aggregate of ligands but with a unique component of the disordered ("centrosymmetric") core deconvoluted; (b) showing the core in isolation.

becomes generally more diffuse, the larger the metal; extended contacts which may also be of interest or relevance are noted in the footnotes to the tables. Dmf molecules 2−6 are disordered, 3−6 being found in affiliation with disordered Rb(2,3), so that those oxygen atoms which interact with Rb(1), O(3,5,6), are distributed over two sets of sites, presumably dependent upon the presence or absence of the other associated Rb atom(s) in their proximity. Dmf(2), though modeled as disordered, has a disordered array of other component atoms distributed around the ordered, coordinated oxygen. It should also be noted that "disordered" dmf(6) appears half-weighted in its occupancy in refinement, the alternative O(6′) component being modeled as a half-water molecule, somewhat questionably in a complex otherwise fully solvated by dmf, i.e., the stoichiometry of the complex unit is taken to be $Rb_4(LH_3)_4(dmf)_{11}(H_2O)$ rather than $Rb_4(LH_3)_4(dmf)_{12} = [Rb_2(LH_3)_2(dmf)_6]_2$ but plausibly so in view of the difficulty of accommodating dmf 6 and its symmetry-related image simultaneously, and in the apparently critical role herein and elsewhere played by traces of alternative solvent and similar species in assisting or promoting crystallization. More precisely, the complex is modeled as $[\{(LH_3)_2(dmf)_2\}(LH_3)_2Rb_4(OH_2)(dmf)_9]$, so that the total aggregate, albeit with a disordered core, comprises a discrete "molecule".

The relative roles of the metal, on the one hand, as a template for the aggregation of the cluster of ligands, and the packing of the ligands as creating capsules for the containment of solvated metal on the other, are ambivalent. Despite their advantage of offering sites suitable for oligodentate coordination made up of neighboring sulfur and phenolic/phenoxy oxygen atoms, we find here and in the subsequently described cesium complex that relatively small proportions of the coordination spheres are made up of these components, and even then they are frequently unidentate. Indeed, where available, intentionally or otherwise, as noted above, water appears to be a major player, bridging metal atoms into aggregates, possibly more appropriate for interaction with the large ligands and the filling of the capsule they generate, and as a basis for further structural development.

The roles of Rb(2,3) in the rubidium complex are best appreciated by examination of a tentatively deconvoluted core, as in Figure 6b, corresponding to one possible combination of disordered fragments and associated environments/constructions within the constant pair of ordered Rb(1) and associated ligand aggregates, accommodated by the disordered oxygen atoms of the latter. An immediately striking feature is the fact that the oligomerization of the Rb−calixarene units is not a consequence of nor at the least associated with phenoxide-O bridging between the metals. Such bridging is very much a characteristic of alkoxide and aryloxide complexes in general[44] and specifically of all previously known polynuclear metallocalixarenes with the exception of trialkylaluminum derivatives.[45] It is also not associated with the kind of ligand bridging through independent donor atoms as described above for the potassium complex. There are certain similarities with the potassium species in the high coordination numbers of the Rb atoms and the indications of some weak sulfur−metal interactions (which may involve bridging), but further differences in the presence of included solvent in two of the calixarene cups.

Although the (mono)cesium complex of *p-tert*-butyltetrathiacalix[4]arene is quite different in its structure (Figure 7; Table 7) from its (mono)sodium analogue, this is not in the sense found in the methylene−calixarene series, where Cs is found inside the calixarene cup.[15] Instead, Cs forms a subfamily with K and Rb in that a small, oxygen-ligand-bridged cluster is enclosed within a cluster of cone-form calixarene units to create an externally lipophilic globule. The similarity of the Cs structure to that of Rb is much closer than to that of K, and indeed the Cs structure can be considered basically as that of Rb but with one molecule of proton complex replacing one Rb complex unit, so that the ratio Cs:calixarene becomes 3:4. The three cesium atoms comprise an ordered pair of 2×Cs(1), with Cs(2) disordered over a pair of half-weighted sites, the two components being generated by a crystallographic *2*-axis through the aggregate. The resultant odd number of metal atoms is in conflict with the necessarily even number of ligands, implying that despite their orderliness (only one *tert*-butyl group is disordered here), they are not unaffected by the statistics which will bear on their protonation pattern (crystallographically unresolved), although the participation of solvent-derived moieties here in this mixed solvate is not precluded.

The aggregate is shown in projection in Figure 7a, the crystallographic *2*-axis lying normal to the page, midway between the two Cs atoms (Cs(1)···Cs(1) 4.6119(5) Å). Cs(1) is associated with both of the independent ligands of the

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(44) Mehrotra, R. C.; Singh, A. *Prog. Inorg. Chem.* **1997**, *46*, 239.
(45) Bott, S. G.; Coleman, A. W.; Atwood, J. L. *J. Inclusion Phenom.* **1986**, *5*, 747.

Table 6. Rubidium Environments[a]

Rb(1)[b]

atom	*r*	O(121)	O(20)	O(30), O(30′)	*O(50)*	*O(60), O(60′)*
O(111)	2.845(5)	61.1(1)	85.1(2)	154.1(2), 135.6(2)	107.2(2)	135.6(3), 132.3(3)
O(121)	2.929(4)		83.8(2)	95.3(2), 83.7(2)	140.5(2)	141.3(3), 131.1(3)
O(20)	2.806(8)			87.5(4), 119.3(4)	134.9(2)	67.1(3), 57.1(3)
O(30)	2.78(1)			34.8(4)	95.5(3)	61.7(3), 60.0(3)
O(30′)	2.74(1)				82.2(3)	88.9(4), 90.9(4)
O(50)	2.968(7)					75.0(3), 85.9(3)
O(60)	3.09(1)					10.9(4)
O(60′)	3.04(1)					

Rb(2)[c]

atom	*r*	S(23)	O(30), O(30′)	O(40)	O(50), *O(50)*	O(60)
O(231)	2.654(6)	58.3(1)	75.4(3), 79.0(3)	90.1(3)	95.2(3), 161.5(2)	129.4(3)
S(23)	3.394(2)		124.0(2), 137.2(32)	136.4(3)	69.2(2), 138.2(1)	75.0(3)
O(30)	3.17(2)		31.2(3)	65.5(4)	87.0(3), 86.3(3)	154.5(4)
O(30′)	2.53(1)			34.4(5)	117.8(3), 83.9(3)	144.1(4)
O(40)	2.77(1)				149.7(4), 79.5(3)	114.5(4)
O(50)	2.595(5)				86.6(2)	84.7(3)
O(50)	3.060(7)					69.1(3)
O(60)	2.88(1)					

Rb(3)[d]

atom	*r*	O(231)	O(30′)	O(40), O(40′)	O(60), O(60′)	*O(50)*
O(221)	2.797(6)	63.4(2)	113.0(3)	101.9(3), 74.8(5)	94.5(3), 89.6(3)	166.5(2)
O(231)	3.167(6)		65.0(3)	82.8(3), 108.2(5)	130.0(3), 128.4(3)	130.1(2)
O(30′)	2.96(1)			32.4(4), 83.7(5)	152.3(4), 157.3(4)	77.3(3)
O(40)	2.61(1)			51.5(6)	147.3(5), 148.3(4)	82.1(3)
O(40′)	2.79(2)				107.8(6), 105.3(5)	98.5(5)
O(60)	2.34(1)				5.0(4)	76.1(4)
O(60′)	2.88(1)					80.7(3)
O(50)	3.054(7)					

[a] Italicized atoms are inversion related. [b] Also: Rb(1)···S(12,*23′*) 3.443(2), 3.600(2) Å. Rb(1)···Rb(2,*2′*) are 4.118(2), 4.342(2) Å. Rb(1)−O(*mn*1)−C(*mn*1) (*mn* = 11, 12) 133.5(4), 133.6(4)° respectively; Rb(1)−O(*n*0)−C(*n*0) (*n* = 2, 3, 3′, *5*, *6*, *6′*) 117.8(9), 123(1), 120(1), 94.7(7), 116(1), 154(2)°. Rb(1)−O(30,30′)−Rb(2) 87.4(4), 102.7(4); Rb(1)−O(30′)−Rb(3) 104.0(4); Rb(1)−*O(50)*−Rb(*2*,2′,3) 102.4(2), 86.2(2), 96.5(2); Rb(1)−*O(60)*−Rb(*2*,*3*) 93.2(4), 111.3(5); Rb(1)−*O(60′)*−*Rb(3)* 99.2(4)°. (Simultaneous occupancy of O(30,30′) appears improbable, as is also the case with O(60,60′) (pair separations: 1.65(2), 0.58(2) Å respectively; see text).) [c] Also: Rb(2)···Rb(3) is 1.021(2) Å; Rb(2)···O(221,60′) 3.319(6), 3.43(2) Å. Rb(2)−O(231)−C(231) 131.3(4)°. Rb(2)−O(*n*0)−C(*n*0) (*n* = 3, 3′, 4, 5, *5*, 6) 111(1), 132(1), 122(1), 132.9(7), 131.6(7), 149(1)°. Rb(2)−O(30′)−Rb(3) 19.5(1); Rb(2)−O(40)−Rb(3) 21.57(9); Rb(2)−*O(50)*−Rb(*2′*,*3′*) 93.43(2), 106.9(2); Rb(2)−O(60)−Rb(3) 19.2(1)°. [d] Also: Rb(3)···S(23) 3.585(2) Å. Rb(3)···O(50) is 3.381(6) Å. Rb(3)−O(*mn*1)−C(*mn*1) (*mn* = 22, 23) 140.8(4), 137.0(4)°. Rb(3)−O(*n*0)−C(*n*0) (*n* = 3′, 4, 4′, *5*, 6, 6′) 119(1), 104(1), 130(2), 114.4(7), 129(1), 107(2)°. Rb(2)−O(231)−Rb(3) 17.52(6)°. (Simultaneous occupancy of O(40,40′) also appears improbable (pair separation: 2.35(3) Å).)

asymmetric unit, ligand 2 chelating through a pair of adjacent phenolic/phenoxy oxygen atoms O(211,241), together with the associated sulfur, S(21), and ligand 1 as unidentate (O(111)) (S(12) at 3.733(1) Å). The remaining coordination sites are occupied by the oxygen atoms of dmf molecules 3, 4 (O(30,40)), which bridge to the symmetry-related Cs(1); dmf(3) is disordered, pendent from its ordered O(30), while the totality of dmf(4) is disordered. Site occupancies of both are 0.5, that of dmf(3) by virtue of its proximity to the symmetry axis and that of dmf(4) by virtue of its association with Cs(2). Water molecule oxygen atom O(01) also bridges Cs(1,1′), also interacting with the occupied fragment of Cs(2); occupancies of O(01,02) are concerted with the presence or absence of Cs(2), being 0.5. The coordination sphere of Cs(2) is sparse, comprising ligand 1 as tridentate through O(121,131), S(13) (at 3.792(2) Å), ligand 2 as unidentate through O(221) and bridging O(01,02) as mentioned above. The dmf molecules 1 and 2 lie within the cavities of ligands 1 and 2, fully ordered except for the oxygen of dmf(1), which is distributed over two sites. The lattice holds dmf(5) and water molecules 3 and 4, equally distributed over two sites.

As noted above, close similarities between Rb and Cs have generally been found in structures of various aryloxides,[23,34] another feature of the analysis of the latter, a difficulty in precisely defining the coordination sphere of the metal, being also encountered here. Within the core of the aggregate, Cs(2), waters O(01,02), and dmfs 3,4 are modeled with site occupancies 0.5 in consequence of refinement behavior, disordered dmf 3 pivoting about its oxygen. Simultaneous occupation of the rotation image of dmf 4 with the parent Cs(2), O(02), and dmf 4 entities is incompatible, and it seems strange that it is not displaced by a further cesium at that site also. If a limiting distance for bonding is taken as 4 Å, for example, Cs−O separations ranging from 3 to 3.5 Å and Cs−S separations ranging from 3.5 to 3.8 Å give rise to uncertainly assigned coordination numbers of 9 and 7 for the two inequivalent Cs atoms, both with very irregular coordination geometry. Considering the impossibility of the O(40) dmf components jointly being involved in the coordination sphere, also true of the O(01,01′) components, the coordination environment of Cs(1) is neither unreasonable nor unduly crowded, while that of Cs(2) is remarkably, but not necessarily unusually or impossibly, sparse. Since in the complex [Cs(*p*-*tert*-butylcalix[4]arene − H)(CH_3CN)], the mean Cs−aromatic carbon separation is 3.57 Å, the significantly greater dimensions of the thiacalixarene may mean that multiple interactions at this distance are no longer sustainable so that binding to donor sites outside the calixarene cavity is preferred, especially, perhaps, when the calixarene itself

Table 7. Cesium Environments[a]

Cs(1)[b]

atom	*r*	O(211)	O(241)	S(21)	O(30)	O(40), O(40′)		O(01), O(01′)		O(02)
O(111)	3.050(3)	67.80(7)	124.90(7)	84.12(6)	153.77(9)	77.0(2),	79.5(2)	134.9(1),	105.3(1)	62.6(2)
O(211)	3.201(3)		58.96(7)	53.44(5)	132.47(5)	104.7(1),	87.8(1)	86.5(1),	167.5(1)	54.1(1)
O(241)	3.090(3)			53.83(5)	80.15(7)	128.0(2),	110.2(2)	56.7(1),	129.6(1)	94.5(1)
S(21)	3.509(1)				120.66(9)	155.8(1),	141.3(1)	110.2(1),	138.0(1)	107.0(1)
O(30)	3.014(4)					80.9(2),	84.5(2)	48.8(1),	51.2(1)	112.4(2)
O(40)	3.277(9)						19.8(2)	74.6(2),	63.0(8)	50.6(2)
O(40′)	3.066(9)							62.4(2),	80.5(2)	34.6(2)
O(01)	3.597(7)								92.1(2)	72.2(2)
O(01′)	3.382(7)									113.7(2)
O(02)	3.339(8)									

Cs(2)[c]

atom	*r*	O(01)	O(02)	O(121′)	O(131′)
O(221)	3.217(3)	84.5(1)	76.8(2)	162.51(8)	141.00(9)
O(01)	3.195(8)		82.1(2)	87.4(1)	133.7(1)
O(02)	3.034(8)			117.3(2)	97.7(2)
O(121′)	3.176(3)				51.38(9)
O(131′)	3.226(4)				

[a] Primed atoms are related by the crystallographic *2*-axis ($^1/_2 - x$, $^1/_2 - y$, z). [b] Also: Cs(1)···S(12) 3.733(1) Å. (Simultaneous occupancy of the pairs of components O(10,10′) O(40,40′) is improbable, as is also true of O(40) and O(02) (separations 1.48(2), 1.11(1), 1.92(1) Å respectively.) [c] Also: Cs(2)···S(13) 3.792(2); Cs(2)···O(40) 3.414(9) Å. Cs(1)−O(*mn*1)−C(*mn*1) (*mn* = 11, 21, 24) are 113.2(2), 135.0(2), 127.2(2)°; Cs(2)−O(*mn*1)−C(*mn*1) (*mn* = 22, 12′, 13′) are 124.4(2), 131.4(2), 136.6(3)°. Cs(1)−O(01)−Cs(2,1′), Cs(2)−O(01)−Cs(1′) are 97.7(2), 82.7(1), 97.1(2); Cs(1)−O(02)−Cs(2) 106.9(2)°.

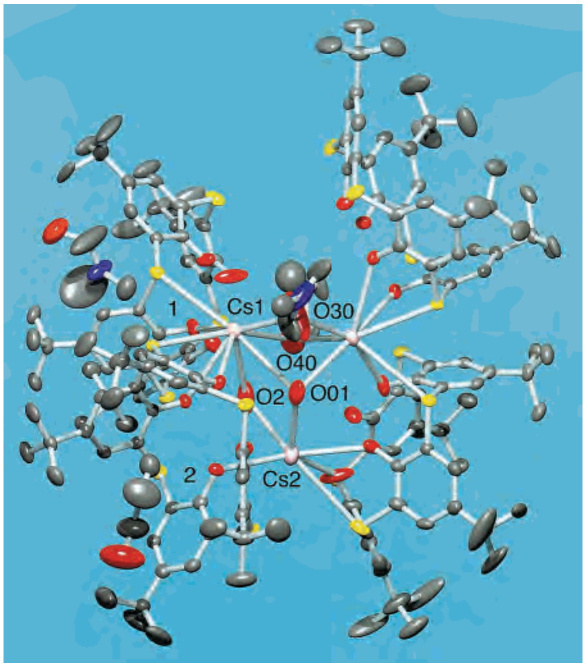

Figure 7. Projection of the cesium adduct, down the crystallographic *2*-axis. Water molecule oxygen atoms O(01,02) and Cs(2) are modeled with site occupancy 0.5, as are dmf 3 and dmf 4, the former disordered about the fully occupied oxygen as pivot. The rotation image of dmf 4 is incompatible with simultaneous occupancy by Cs(2), O(02), and itself; one deconvoluted component of the core of the aggregate is shown.

provides extra sites (S donors) of this kind. It should be noted that evidence for M−π interactions, where M is any of the alkali metals, has been noted in structures of simple aryloxides[23,34,45] and in aryloxide adducts of calixarene complexes.[47]

Conclusions

As aryloxide ligands, the calixarenes must be expected to be unusual in that their macrocyclic structure restricts, to varying extents depending on the ring size of the calixarene, the spatial array of the alkoxo donor groups and thus the coordination geometry of any bound Lewis acid, and must also limit both the form and degree of oligomerization of their complexes. The present results show indeed that the group 1 element complexes of *p-tert*-butyltetrathiacalix[4]arene exist as monomers or rather small oligomers by comparison with the polymeric forms observed for simpler aryloxide ligands,[23,34] a consequence, perhaps, of the segregation of polar groups and lipophilic groups when the calixarene is in the cone conformation, as is the case for the structures reported here. Thus, the present results alone show that calixarenes may well deserve the sobriquet "cluster keepers",[9] and we will show in subsequent description of the structures of transition and other metal complexes of the thiacalixarene in particular that a remarkable variety of novel simple metal clusters can be isolated in this way. The present work also illustrates a rather subtle feature of the coordination chemistry of the calixarenes in that the involvement of their phenyl rings as donor centers for metal ion binding may be rather sensitive to the macrocycle size. Whether this would be true only for "internal" coordination (inclusion) as known for Cs^+ [15,48] or could also apply for "external" coordination, such as has been structurally characterized for Ru(II),[49] Rh(I),[49] Ir(I),[49] Ag(I),[50] and Cr(0),[51] and suggested for Tl(I),[52] is impossible

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to say presently, although it is clear that at least Cr(0) binding to *p*-*tert*-butylcalix[4]arene is associated with quite dramatic conformational changes.

For *p*-*tert*-butyltetrathiacalix[4]arene, a somewhat unexpected feature of its bonding to the alkali metals is the involvement of at least weak bridging-sulfur atom interactions with all the metal ions. While they may be relatively weak compared to such interactions involving transition metal ions,[8,9] they presumably play some role in determining the differences between *p*-*tert*-butylcalix[4]arene and *p*-*tert*-butylthiacalix[4]arene reflected in the structures presently characterized. The specific comparison of *p*-*tert*-butylcalix[4]arene and *p*-*tert*-butyltetrathiacalix[4]arene, as both their proton and metal ion complexes, shows that their inclusion chemistry is rather different, presumably as a result of their differences in cavity size, and the presently reported structures provide evidence that a guest such as dimethylformamide may be involved in attractive interactions other than just the $CH_3-\pi$ forces commonly viewed as controlling the inclusion chemistry of methylene calixarenes.[41]

In any discussion, such as the present, of solid state structures, it must of course be recognized that the forces controlling the assembly and form of the complete, crystalline lattice must play some role in determining the features excised as “molecular”, and our assumption that the features of alkali metal ion binding by phenolic calixarenes can be largely related to local influences is simply that. In regard to possible applications of *p*-*tert*-butyltetrathiacalix[4]arene in alkali metal separation, the present structural information is of some value, though it is doubly qualified by the facts that it is information relating to the solid state and that kinetic factors are often dominant in separation procedures. Perhaps most significant of the present results is the observation that the oligomeric Cs complex of *p*-*tert*-butyltetrathiacalix[4]arene does not involve Cs^+ as an included species, implying that if Cs^+/π interactions are to be exploited as a factor engendering selectivity in alkali metal separations, the spatial dimensions of the complexing agent may be of critical importance.

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Supporting Information Available: Eleven crystallographic files, in CIF format. Materials describing particular variations in procedure for individual structure solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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