Alkali-metal Ion Complexes of the Calixarenes. Part 1. Caesium Bonding in Calix[4]arene Systems†

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A crystal structure determination on the monocaesium derivative of bis(homooxa)-*p*-*tert*-butylcalix[4]-arene (L^2), $[Cs(L^2 - H)(OH_2)_3]\cdot xH_2O$ ($x \approx 3$) [orthorhombic, *Pmnb*, a = 26.666(5), b = 15.928(4), c = 11.499(9) Å, Z = 4, R = 0.071 for 1500 'observed' reflections] showed that the caesium may be considered to be involved in polyhapto interactions with carbon atoms in two of the four phenyl rings as well as co-ordination to two phenolic oxygens, the ether oxygen and three water molecules. The nature of the polyhapto aromatic interactions seems to be similar to that of those previously observed as the exclusive mode of calixarene binding in the caesium complex of the monoanion of *p*-*tert*-butylcalix[4]arene. Both complexes can be described as cation inclusion compounds, and the retention of this solid-state structure in some solvents is associated with very low-field ^{133}Cs nuclear magnetic resonances. On the basis of ^{133}Cs NMR spectra, it can be concluded that a series of calix[4]arenes bridged at the upper rim by an aliphatic chain $-(CH_2)_n-$ also forms inclusion complexes with Cs^+ for n = 7–10, in accord with Cs^+ transport studies previously reported for a similar series.

Considerable study has been made of the interaction of calixarenes with alkali-metal ions because of both the marked influence ('template effect') of the nature of the alkali metal on the product distribution in calixarene synthesis,[1] and the selectivity shown by particular calixarenes in alkali-metal ion co-ordination.[1–4] Despite this interest, remarkably little information is available concerning the exact mode of this interaction for the parent (phenolic) calixarenes although several structures are known for derivatives of calixarenes where the phenoxide groups have been alkylated with chains providing additional donor atoms,[5] and it is difficult to decide upon any precedents which may be useful guidelines as to anticipated co-ordination modes. Structural studies to date of various metal complexes of calixarenes have shown aryloxide-*O* lone-pair donor bonding to be dominant,[1,5,6] but despite the apparent success of theoretical models of alkali metal-ion complexation[7] based upon the assumption of conventional[8] co-ordination or 'electrostatic' bonding, there is ample structural evidence for complexes of both neutral (crown ether)[9] and anionic ligands[10,11] containing aromatic groups that polyhapto interactions with these aromatic groups may well be as important generally as those with O-donor moieties. In the particular case of the Cs^+ complex of the monoanion of *p*-*tert*-butylcalix[4]arene, we have recently shown[12] in fact that the solid-state structure may be rationalised in terms of Cs^+ inclusion *via* polyhapto aromatic bonding alone. Hence, for the calixarenes, even if not for other ligands, there remains a need for detailed characterisation of their co-ordination to the alkali metals.

Although single-crystal X-ray structure determination offers the most obvious means of obtaining very detailed information on co-ordinate bonding, it is dependent upon the synthesis and crystallisation of appropriate compounds, and our experience has been that while the synthesis of alkali-metal ion salts of the common calixarenes is relatively straightforward, their conversion to optimally crystalline materials suitable for X-ray diffraction studies is much less so. Caesium salts have, however, proven to be relatively amenable to the latter aim, and one focus of the present work is the structural characterisation of the caesium complex of bis(homooxa)-*p*-*tert*-butylcalix[4]arene,‡ a species in which the metal ion displays an interesting combination of co-ordinate interactions. As another index of caesium ion co-ordination environment, ^{133}Cs nuclear magnetic resonance is a valuable complement to structural crystallography, being of particular value in measurements of stability of complexes in solution,[8] and we also report herein magnetic resonance studies on Cs^+ complexes of both *p*-*tert*-butylcalix[4]arene and its bis(homooxa) derivative as well as for a series of upper-rim-bridged calix[4]arenes[13a] similar to that previously studied in respect of caesium transport through lipophilic membranes.[13b]

Experimental

Instrumentation.—300 MHz ^{1}H spectra and 39.37 MHz ^{133}Cs NMR spectra were recorded on a Bruker AM300 spectrometer at 293 K. Deuteriochloroform was degassed before use and samples were prepared in 10 mm tubes under a dry argon atmosphere. Caesium-133 shifts were referenced to (external) 0.5 mol dm^{-3} CsBr in D_2O. Proton chemical shifts were referenced to the solvent signal ($CDCl_3$, residual H, δ 7.26).

The two-dimensional ^{133}Cs–^{1}H heteronuclear Overhauser effect (HOESY) spectra were recorded on ≈0.01 mol dm^{-3} solutions in $CDCl_3$ at 297 K; mixing time, τ_m = 1.85 s; spectral width, 1736 Hz (f_2, ^{133}Cs) and 1497 Hz (f_1, ^{1}H); 1024 data

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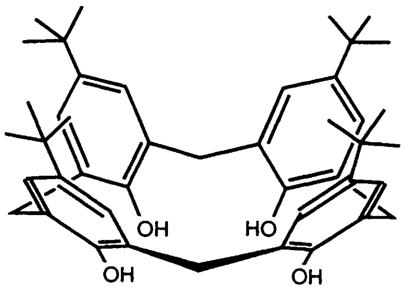
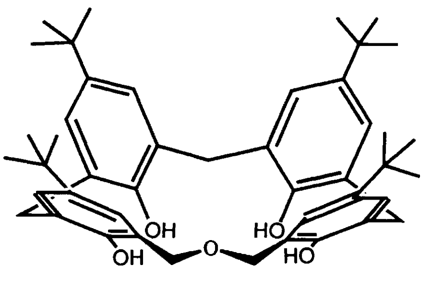
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

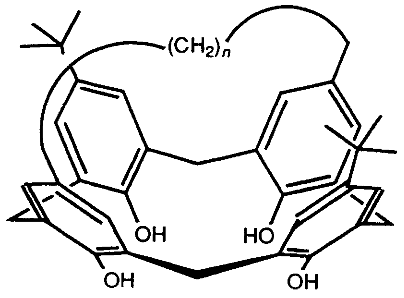
‡ Bis(homooxa)-*p*-*tert*-butylcalix[4]arene = 7,13,19,25-tetra-*tert*-butyl-27,28,29,30-tetrahydroxy-2,3-dihomo-3-oxacalix[4]arene.



L^1



L^2



n	
5	L^3
6	L^4
7	L^5
8	L^6
9	L^7
10	L^8
16	L^9

points in t_2, 32 increments in t_1, with zero filling to 128 data points; relaxation delay, 0.85 s; overall measuring time, 18 h. Spin–lattice relaxation times were estimated by the inversion-recovery method.

Synthesis.—The ligands L^1 (*p*-*tert*-butylcalix[4]arene) and L^2 bis(homooxa)-*p*-*tert*-butylcalix[4]arene) were prepared and isolated as in the literature.[2,14] The upper-rim-bridged calix-[4]arene compounds L^3–L^9 were prepared as described in previous work.[13]

[Cs(L^2 − H)(OH_2)]. Caesium carbonate (0.5 g) was added to a slurry of L^2 (1.0 g) in acetonitrile (15 cm^3) and the mixture heated at reflux for 1 h, then filtered and allowed to cool. Colourless, air-stable crystals precipitated slowly from the filtrate. Yield: 0.40 g (31%) (Found: C, 65.40; H, 7.15; Cs, 18.6 for material subjected to desiccation, resulting in obvious efflorescence, over silica gel for 24 h. Calc. for $C_{45}H_{57}CsO_5$: C, 65.20; H, 7.15: Cs, 16.05%).

Table 1 Non-hydrogen positional parameters

Atom	*x*	*y*	*z*
Cs	1/4	0.56534(8)	0.3084(1)
O(1)	0.2972(3)	0.3365(5)	0.2437(7)
C(11)	0.3181(4)	0.3761(6)	0.3269(8)
C(12)	0.2992(4)	0.3770(7)	0.440(1)
C(13)	0.3203(4)	0.4260(7)	0.531(1)
C(14)	0.3642(3)	0.4712(6)	0.519(1)
C(141)	0.3880(2)	0.5197(4)	0.6190(6)
C(142)[a]	0.3930(6)	0.460(2)	0.724(3)
C(143)[a]	0.3524(8)	0.596(1)	0.656(1)
C(144)[a]	0.4354(9)	0.551(1)	0.586(2)
C(142′)[a,b]	0.3690(9)	0.493(1)	0.722(4)
C(143′)[a]	0.3790(7)	0.602(3)	0.606(2)
C(144′)[a]	0.448(1)	0.504(1)	0.618(2)
C(15)	0.3857(4)	0.4650(6)	0.417(1)
C(16)	0.3651(4)	0.4206(6)	0.3175(9)
C(1)	1/4	0.3271(9)	0.470(1)
O(2)	0.3020(2)	0.4618(4)	0.0773(7)
C(21)	0.3407(4)	0.5150(6)	0.0732(9)
C(22)	0.3873(4)	0.4980(7)	0.1333(9)
C(23)	0.4272(4)	0.5556(6)	0.1290(9)
C(24)	0.4247(4)	0.6287(6)	0.0718(9)
C(241)	0.4692(4)	0.6908(7)	0.064(1)
C(242)	0.4804(7)	0.722(1)	0.177(1)
C(243)	0.4584(6)	0.7703(9)	−0.009(2)
C(244)	0.5125(6)	0.649(1)	0.015(2)
C(25)	0.3788(4)	0.6452(7)	0.0131(9)
C(26)	0.3392(3)	0.5907(6)	0.0176(9)
C(2)	0.3906(4)	0.4153(6)	0.204(1)
C(3)	0.2935(4)	0.6094(7)	−0.060(1)
O(3)	1/4	0.6087(6)	0.0108(8)
O(01)	0.3393(4)	0.6811(5)	0.3022(8)
O(02)	1/4	0.719(3)	0.545(3)
O(03)	0.312(1)	0.795(2)	0.600(3)
O(04)	1/4	0.375(2)	−0.202(2)

[a] Site occupancy factor = 0.5. [b] Refined isotropically.

Caesium complexes of the *para*-bridged calixarenes (L^3–L^9) were prepared as follows: A slurry of L^n (25 mg) in acetonitrile (10 cm^3) was heated at reflux for 1 h in the presence of an excess of Cs_2CO_3 or CsF, the mixture filtered, and the filtrate evaporated to dryness. The residue was then dissolved directly in $CDCl_3$ for NMR measurements. In the case of L^1 and L^2, the spectra obtained in this way were the same as those for the isolated crystalline complexes.

Structure Determination.—A unique diffractometer data set (2θ–θ scan mode; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; $2\theta_{max} = 50°$) was measured at $\approx$295 K on a capillary-mounted specimen. 3221 Independent reflections were obtained, 1500 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement without absorption correction after solution of the structure by the heavy-atom method. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values where possible. Conventional residuals on $|F|$ at convergence were $R = 0.071$, $R' = 0.071$ [statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$]. Neutral atom complex scattering factors were used;[15] computation used the XTAL 3.0 program system[16] implemented by S. R. Hall. Pertinent results are given in Figs. 1 and 2 and Table 1.

Crystal data. $[Cs(C_{45}H_{57}O_5)(OH_2)_3]\cdot xH_2O$ ($x \approx 3$), $M \approx$ 919.0. Orthorhombic, space group *Pmnb* [D_{2h}^{16}, no. 62 (variant)], $a = 26.666(5)$, $b = 15.928(4)$, $c = 11.499(9)$ Å, $U =$ 4884 Å^3, D_c ($Z = 4$) $\approx$ 1.25 g cm^{-3}, $F(000) \approx 1928$, $\mu_{Mo} \approx 8$ cm^{-1}, specimen, cuboid $\approx$ 0.2 mm^3 (capillary).

Abnormal features/variations in procedure. The compound was recrystallised from acetonitrile, and the presence of water was unexpected. The caesium atom is located on a crystallographic mirror plane; its interactions with the ligand oxygens

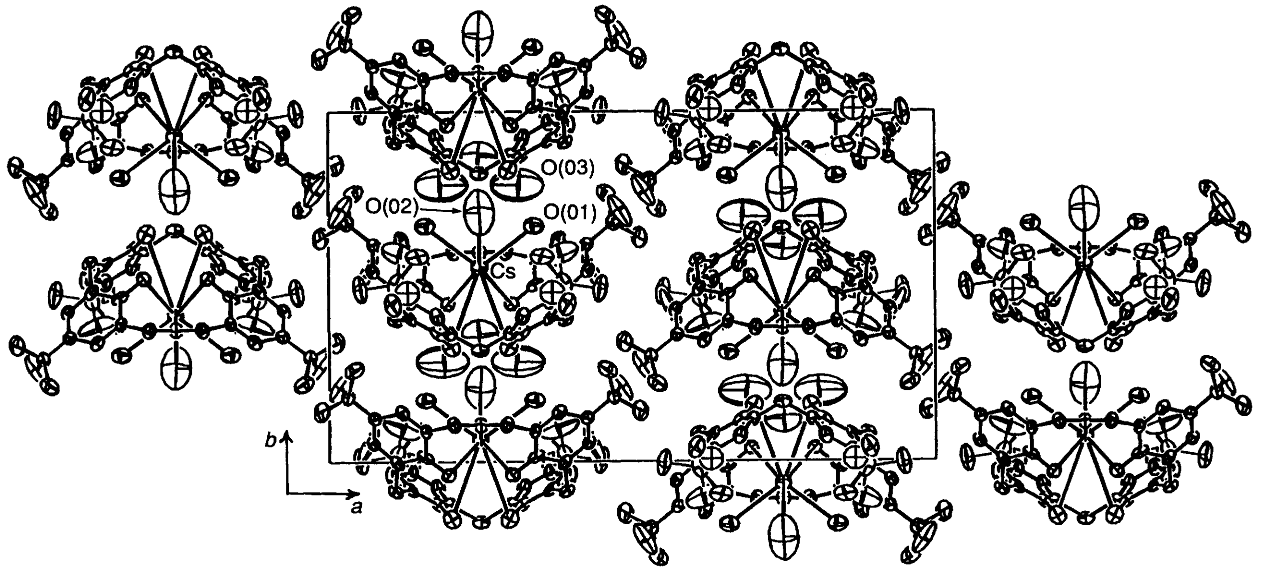


Fig. 1 Unit-cell contents projected down *c*, showing key atom labelling; 20% thermal ellipsoids are shown for the non-hydrogen atoms

are clearly defined, leaving a considerable gap in the co-ordination sphere opposite in which substantial difference map residues at reasonable interaction distances were observed. These were initially modelled as three oxygen atoms; the behaviour of the pair of symmetry-related O(01) in respect of geometry, thermal motion and residues is nicely compatible with this assignment, and indeed, in spite of the relatively poor precision of the determination in respect of disorder and other ill defined solvent, it was possible to observe difference map residues plausibly assignable to pairs of associated hydrogen atoms. The residue modelled by O(02) on the mirror plane is more contentious; it is very broad and diffuse with no well defined components which can be modelled as disordered fragments or for that matter the component atoms of acetonitrile or other possibilities. Its thermal motion tensor, shown in the cell diagram, has its major axis in the mirror plane of the complex, occupying the considerable void between the pair of water molecules O(1) and the polyhapto aromatic rings 1. No associated hydrogen atoms could be resolved. On the calixarene ligand, the *tert*-butyl substituent on ring 1 is disordered over two well defined sets of sites with occupancy factors assigned on the basis of refinement behaviour as 0.5. The other *tert*-butyl group on ring 2 is well behaved. Substantial lattice voids are found in the vicinity of O(2), with further broad and diffuse residues well removed from that atom; these were also modelled as (mirror-related) oxygen atoms O(03), O(04) with very high thermal motion, but a site occupancy assigned as unity on the basis of refinement behaviour.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and complete bond lengths and angles.

Results and Discussion

Description of the Structure.—In gross terms, the conformation of bis(homooxa)-*p*-tert-butylcalix[4]arene monoanion found in its Cs^+ complex is similar to those of the tetra- and tri-anionic forms found in the uranyl[17] and europium(III)[18] ion complexes, respectively, and indeed to the conformation of the unco-ordinated, neutral ligand.[17] Thus, despite its inherent conformational lability,[19] the ligand appears to show a preference for a cone conformation markedly flattened with regard to the two phenolic groups flanking the CH_2OCH_2 link. In the Cs^+ complex presently described, this allows the cation to be included within the cone and to interact with the two aromatic rings ('1') opposite those flanking the ether unit in a polyhapto manner, here with *m* rather than *4* symmetry, but otherwise similar to that observed in the *p-tert*-butylcalix[4]arene complex.[11] In that compound, Cs . . . C(arene) range between 3.545(3) and 4.121(4) Å, the shortest and longest contacts corresponding to C(1) and C(4), respectively. Here, a similar range of distances is found [3.53(1)–4.17(1) Å], with the extreme values again corresponding to C(1) and C(4), the phenolic and *tert*-butyl substituted positions. With the centroid of the C_6 ring 1 calculated at (0.3421, 0.4226, 0.4251), the Cs–centroid distance is 3.61 Å, *cf.* the value of 3.57 Å found for the *tert*-butylcalix[4]arene complex.

The larger, more open and more unsymmetrical cone of the present compound also allows what appear to be legitimately describable as co-ordinative or electrostatic interactions with the phenolic oxygen atom substituents of the other two rings and the ether oxygen [Cs–O(2), 3.422(7), Cs–O(3) 3.49(1) Å]. In addition, the 'open' side of the cone appears to be of dimensions sufficient to allow further co-ordinate interactions with up to three solvent molecules, at least two of which are water [Cs–O(01), 3.928(8) Å]. In the caesium complex of *p-tert*-butylcalix[4]arene monoanion,[12] the pitch of the cone is quite steep, the dihedral angle between the phenolic O_4 plane and the four equivalent phenyl rings being 57.4(1)° [*cf.* 54.6(2)° in the dimethyl sulfoxide inclusion complex[20]]. Here, the pitch of the polyhapto rings 1 is somewhat steeper, the dihedral angle being 68.7(3)°, while the O-co-ordinated rings 2 lie much flatter, with dihedral angles of 25.4(3)°. The ether oxygen O(3) is inverted to co-ordinate with the caesium, lying 1.07(1) Å above the phenolic O_4 plane, on the same side as the caesium.

Thus, the present structure simultaneously reveals several modes for stabilisation of the caesium cation, and comparison with the structure determined for the *p-tert*-butylcalix[4]arene complex indicates that the differences in energy for such interaction modes may well be comparable to torsional energy barriers in these calixarene systems. While the low ionisation energy of caesium may mean that unusually weak interactions can be effective in stabilising the cation, and hence that conclusions drawn from studies of caesium alone may well not be valid for the alkali metals as a group, the present data are nonetheless consistent with more general studies of alkali-metal ion complex structures[9–11] in indicating that both the σ and π donor capacities of any binding agent should be taken into account in considering its binding.

Solution Magnetic Resonance Studies.—Complexes of Cs^+ with calixarenes show appreciable solubility in only a rather

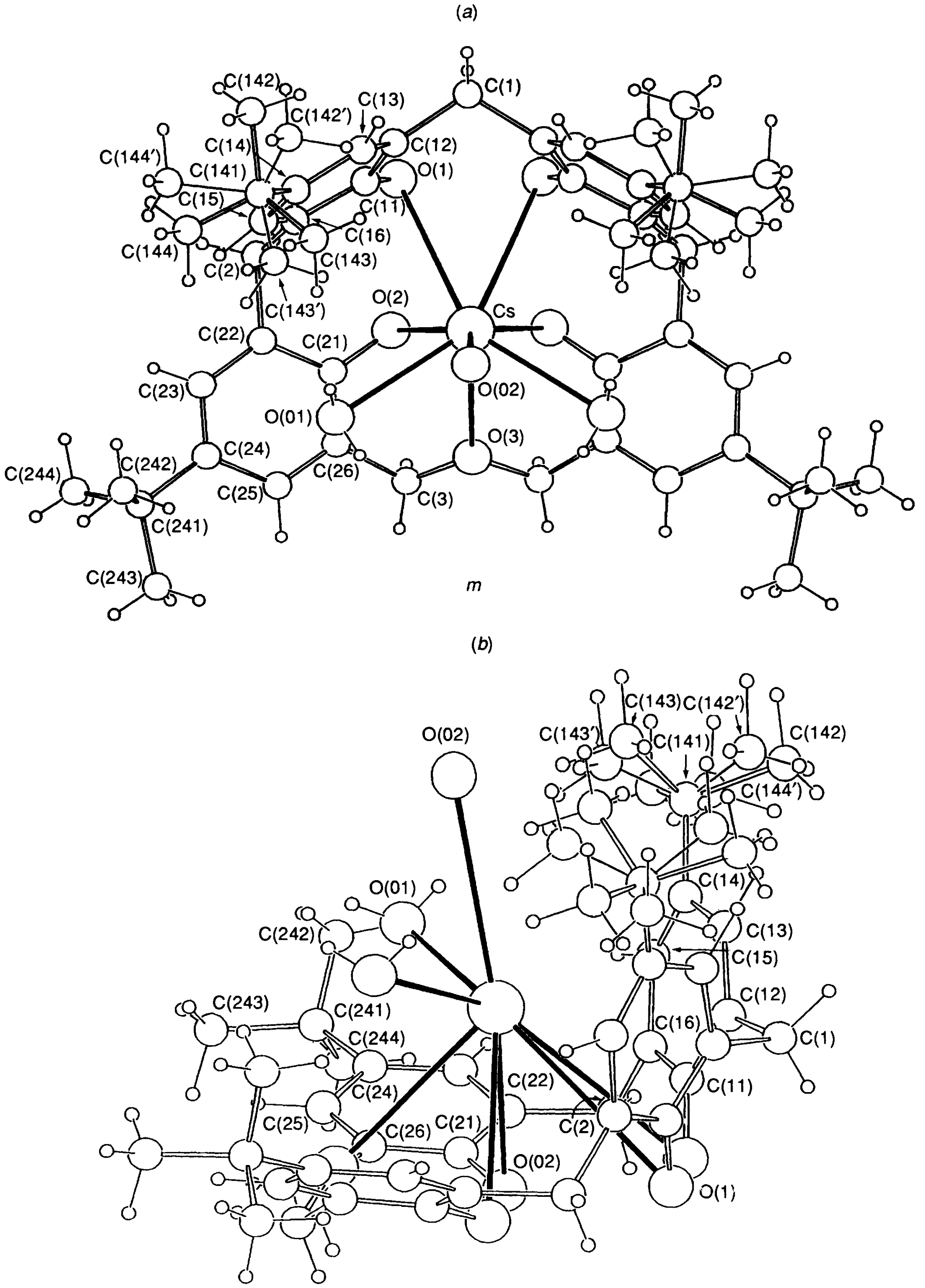


Fig. 2 The Cs–ligand complex array viewed through (*a*) and side-on (*b*) to the cup (for thermal ellipsoids, see Fig. 1). The Cs–O vectors (not necessarily *bonds*) are shown as solid lines. Non-hydrogen labelling is given

limited range of solvents, and our work has been restricted almost entirely to the use of acetone and chloroform only. Nonetheless, a strong solvent dependence of spectroscopic properties has been revealed. Thus, although ^{133}Cs spin–lattice relaxation times for acetone (T_1 = 1.43 s), acetonitrile (T_1 = 4.06 s) and chloroform (T_1 = 0.81 s) all seemed compatible with the detection of ^{133}Cs–^{1}H Overhauser effects, only in chloroform were detectable cross-peaks observed (Fig. 3) in the ^{133}Cs–^{1}H HOESY spectrum of [Cs(L′ − H)]. The cross-peaks correspond to interactions between the caesium ion and the aromatic and *tert*-butyl protons of the calixarene, protons which in fact are closest to the caesium in the crystalline solid.[1] We interpret these results as indicating that the solid-state structure is preserved in chloroform solution, but that in acetone (and acetonitrile) the better cation-solvating ability of the solvent leads to removal of the caesium from the calixarene cavity and possibly to the formation of a solvent-separated ion pair. Consistent with this, ^{1}H spectra show that the ligand in the complex is conformationally much less mobile (relative to the uncomplexed calixarene) in chloroform than it is in acetone.

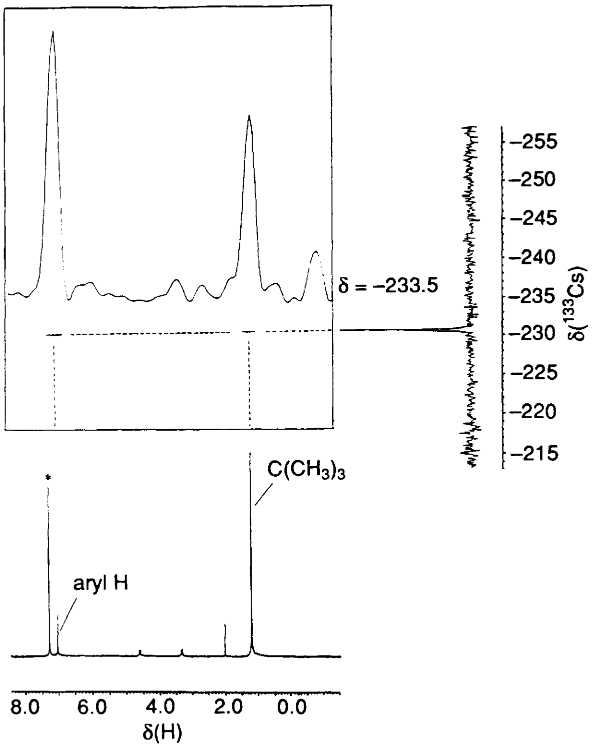


Fig. 3 The ^{133}Cs–^{1}H HOESY spectrum of [Cs(L′ − H)]·MeCN, 0.01 mol dm^{-3} solution in CDCl$_3$. The ^{133}Cs spectrum is shown on the vertical axis, the ^{1}H spectrum on the horizontal. Inset: f_1 cross section at δ (^{133}Cs) −233.5

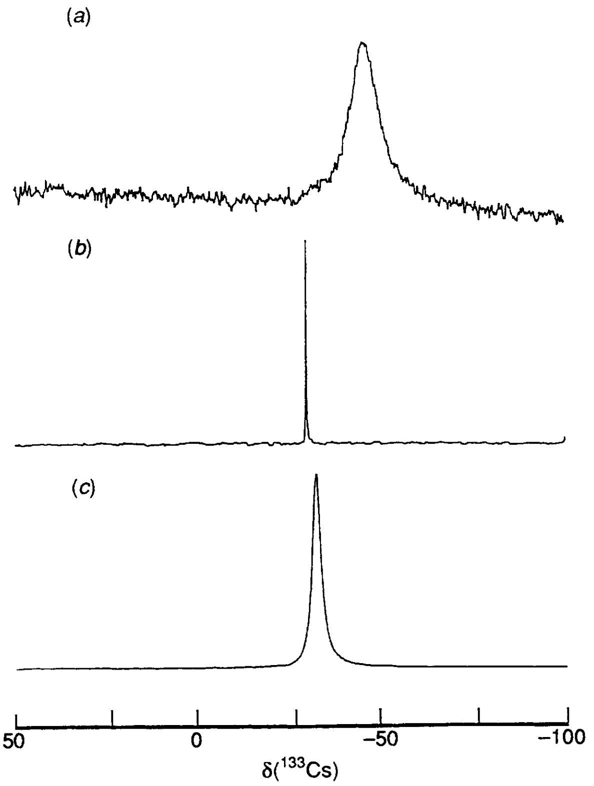


Fig. 4 Caesium-133 NMR spectra of (*a*) [Cs(L′ − H)]·MeCN, (*b*) Cs(CF$_3$SO$_3$) and (*c*) a mixture of the two, in acetone, 0.01 mol dm^{-3} solutions at 293 K

Further, the ^{133}Cs resonance for the complex in acetone is broad, little shifted from that of Cs(CF$_3$SO$_3$) [and provides only a single (broad) resonance when mixed with Cs(CF$_3$SO$_3$)] (Fig. 4), while the resonance for the complex in chloroform is sharp and shifted 170 ppm upfield of the resonance for [Cs(dibenzo-18-crown-6)]BPh$_4$ (dibenzo-18-crown-6 = 6,7,9,10,17,18,20,21-octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecine) and 200 ppm upfield of that for the caesium salt of *p*-*tert*-butylphenol (Fig. 5) (though the nature of the latter species in chloroform is, of course, problematical).

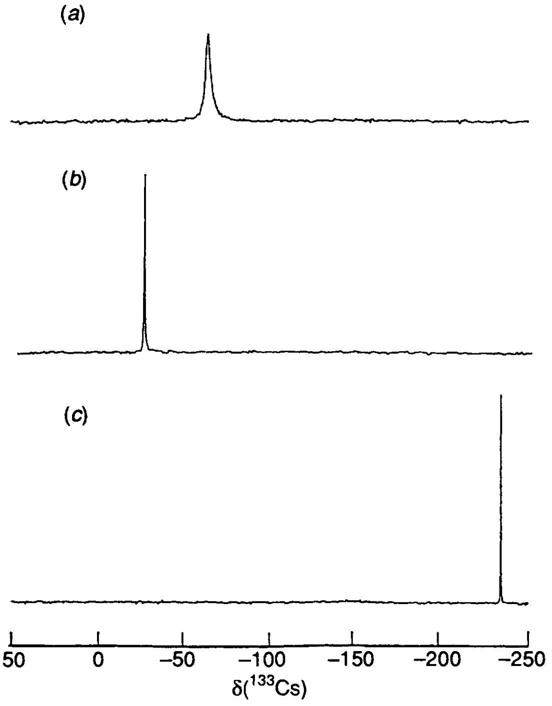


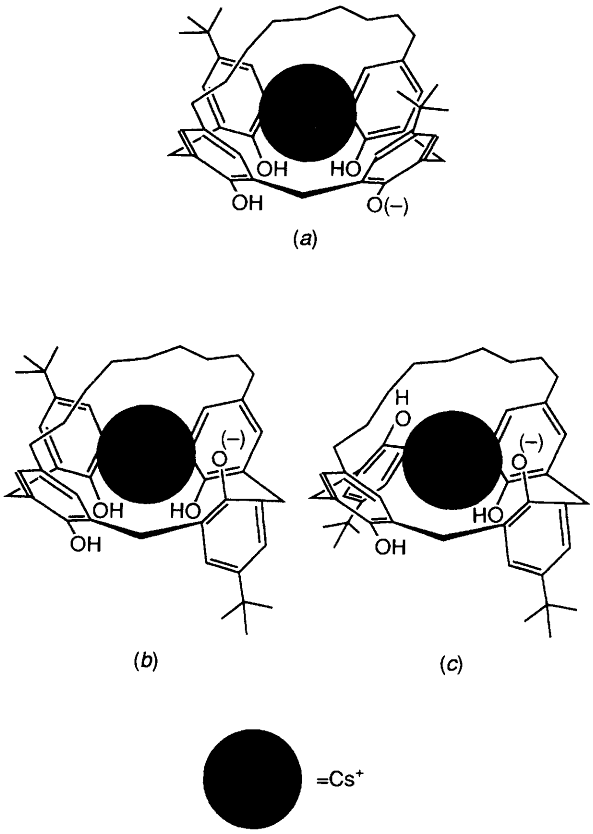
Fig. 5 Caesium-133 NMR spectra of (*a*) [Cs(dibenzo-18-crown-6)]BPh$_4$, (*b*) Cs(OC$_6$H$_4$Bu^t-*p*) and (*c*) [Cs(L′ − H)]·MeCN in CDCl$_3$ at 293 K

Table 2 Caesium-133 resonances in Cs$^+$ complexes of calix[4]arene monoanions in CDCl$_3$ at 293 K

Calix[4]arene	δ (^{133}Cs)			
L^1				−234
L^3	+90 (br)			
L^4	+91 (br)			
L^5		−37 (br)		−161
L^6				−190
L^7	+90 (br)	−39	−153	−209
L^8			−158	−217
L^9	+91 (br)			

Unfortunately, the solubility of the caesium complex of bis(homooxa)-*p*-tert-butylcalix[4]arene in chloroform is low, so that ^{133}Cs spectra in this solvent showed rather poor signal : noise ratios. The single resonance detected was of similar breadth and chemical shift to that of [Cs(dibenzo-18-crown-6)]BPh$_4$, and the same was true for better quality spectra obtained in acetone solvent, but no facile interpretation of these apparent similarities in average Cs environments can be made. The ^{1}H spectrum at 298 K in chloroform is completely consistent with the solid-state structure being maintained in this solvent, and the ligand rigidity (coalescence temperature for the methylene resonances is > 50 °C) is much greater than that of the free ligand.[19]

Chloroform solubilities of the caesium complexes of the bridged calix[4]arenes L^3–L^9 differed considerably, but all were sufficient for ^{133}Cs resonances to be detected (Table 2). In several cases, more than one resonance was detected, with the



(*a*)

(*b*) (*c*)

Fig. 6 Possible modes of caesium ion inclusion by an upper-rim-bridged calix[4]arene. The negative charge on the calixarene anion is shown arbitrarily localised on a phenolic oxygen. (*a*) Cone conformation, (*b*) partial cone conformation, (*c*) 1,3-alternate conformation

large chemical shift differences indicating that the caesium ion could be found in very different environments. It is conceivable that these different resonances may reflect the presence of various oligomers of the complex in a weakly polar solvent like chloroform but the relatively slow interconversion implied by the observation of distinct ^{133}Cs resonances indicates that such oligomerisation would have to involve more than simple substitution on Cs^+, and for the Cs^+ salt of *p-tert*-butylphenol, which might well be expected to oligomerise as a means of increasing the co-ordination number of caesium, only a single resonance is observed. On the basis of the facts that ether-oxygen co-ordination is generally associated with downfield shifts,[8] and that polyhapto-aromatic binding is reflected in large upfield shifts,[12] we suggest in fact that the extreme resonances may be associated with *exo*-calyx O-binding and *endo*-calyx polyhapto aromatic binding of Cs^+. As with the simple calix[4]arenes, those with the longer upper-rim bridges in particular may adopt both partial cone and 1,3-alternate conformations as well as the cone, and since different conformations may influence the relative contributions of *exo*- and *endo*-calyx types of interaction (Fig. 6), it is possible that resonances with intermediate chemical shifts may be assigned to species involving different combinations. The presently reported structure of the complex of the bis(homooxa)calix[4]arene indicates that 'mixed' co-ordinate bonding is effective, and ionophoric activity has recently been demonstrated for a calix[4]arene in the 1,3-alternate conformation.[21] More subtle differences (such as the degree of cone 'pinching') within species considered to have the same gross conformation may also influence chemical shifts significantly, since the extreme upfield ^{133}Cs peak shifts from δ −161 to −217 as n varies from 7 to 10, yet still does not attain the position (δ −234) observed for the complex of *p-tert*-butylcalix[4]arene itself.

The series of upper-rim bridged calixarenes presently studied differs from that used in the ion transport work in that *tert*-butyl groups replace the methyl groups found as *para* substituents on the unbridged phenolic units of the original compounds. While this may give rise to some differences in conformational preferences, the overall results of the two studies seem very largely consistent provided, of course, that selectivity in Cs^+ inclusion is the overriding factor determining rates of transport in the undoubtedly highly complicated system of a membrane separating two aqueous phases. Certainly, the presence of a short (n = 5 or 6) upper-rim bridge seems to prevent Cs^+ inclusion as well as inhibit Cs^+ transport, and although longer bridges are not invariably associated with the formation of a single included species, the most effective ion transport is obtained with the bridge (n = 8) which also results in only a single Cs^+ complex being detectable. That a resonance indicative of inclusion is not detected for the ligand with n = 16 and transport rates are lower for n = 12 and 14 ligands may reflect the fact that 'self-inclusion' of such long alkyl chains may prevent inclusion of Cs^+. Certainly it is possible for long alkyl chains to fold down within the cavity of a calixarene in its cone conformation, but the number of conformational energy minima which may be found [using a molecular-mechanics program (a modified version of MM2) incorporated into the software package Chem 3D Plus, Cambridge Scientific Computing] for these systems is large, and we are not able to state that self-inclusion is the most strongly preferred state.

Acknowledgements

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