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Complexation of the caesium cation by the host *p-tert*-butylcalix[6]arene hexaacetamide

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The complexation of the caesium cation by a *p-tert*-butylcalix[6]arene hexaacetamide derivative (5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40-hexakis(*N*,*N*-diaethylaminocarbonyl)methoxycalix[6]arene) (**I**) in a binary mixture of deuterated chloroform and acetonitrile was studied by ^{1}H, ^{133}Cs NMR spectroscopy and X-ray crystallography. Different complexes between Cs^+ and **I** with Cs^+ : **I** stoichiometries ranging from 1 to 3 are formed in solution. The 3 : 1 complex is only observed below 250 K, in the presence of excess of Cs^+. The structure of the 2 : 1 complex in solution is similar to the distorted partial cone crystal structure in the solid state. The two caesium cations are coordinated to carbonyl and phenolic oxygens, with a short distance of 4.16 Å between them. The dissociation of the 2 : 1 complex follows a dissociative mechanism with $\Delta H^{\neq}$ = 58 kJ mol^{-1} and $\Delta S^{\neq}$ = −2 J K^{-1} mol^{-1}. The activation parameters indicate that the dissociative process is kinetically governed by the successive flipping of two aromatic rings leading to a 1,2,3 alternate conformation of a 1 : 1 complex, similar to the crystal structure of the uncomplexed calix[6]arene hexaacetamide.

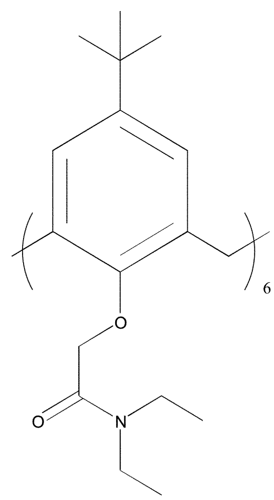
Introduction

Calix[*n*]arenes are macrocyclic phenol–formaldehyde condensation oligomers which continue to receive widespread attention due to their versatile molecular recognition properties towards neutral, cationic and anionic guests,[1–6] and their propensity to act as molecular building blocks for the design of large supramolecular assemblies.[7,8] The recognition properties can be fine-tuned through modifications at the phenolic oxygens (lower rim) and at the *para* positions (upper rim). The thermodynamics of the alkali metal cation complexation by calixarenes, especially calix[4]arenes, has been quite extensively studied.[4,5,9,10] However, the studies of the kinetics and mechanisms of the alkali metal cation complexation by calixarenes are rather scarce and, so far, limited to calix[4]arenes.[11–18]

Compared to calix[4]arenes, calix[*n* > 4]arenes have greater conformational freedom[19–23] and the ability to form complexes with alkali metal cations with stoichiometries higher than 1 : 1.[24]

Therefore we decided to study the kinetics and mechanisms of formation of caesium cation complexes with a calix[6]arene derivative, substituted by acetamide groups on the lower rim, 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40-hexakis(*N*,*N*-diaethylaminocarbonyl)methoxycalix[6]arene, **I** (Scheme 1), in the binary mixture of deuterated chloroform and deuterated acetonitrile. The solvent system was chosen for solubility reasons, and in order to compare directly the results with previous data on similar calix[4]arene systems.[17,25] It has been shown that, in this solvent system, the caesium triiodide ion pair is dissociated, at least to a very large extent.[16] In the case of the corresponding calix[4]arene tetraacetamide derivative, a 1 : 1 complex is formed with Cs^+ as a major species, with the presence of small amounts of a 2 : 1 Cs^+–calix[4]arene complex.[17] The decomplexation of the 1 : 1 complex follows a dissociative mechanism, with no participation of the 2 : 1 complex in a potential competitive associative exchange mechanism.[13,17]

In this work, it is shown that the calix[6]arene hexaacetamide derivative, **I**, forms four different complexes with caesium, with Cs^+ : calixarene stoichiometries ranging from 1 : 1 to 3 : 1. The structure of the 2 : 1 complex in solution is similar to its distorted partial cone crystal structure. It is suggested that the major 1 : 1 complex adopts in solution a 1,2,3 alternate structure similar to the crystal structure of the uncomplexed calixarene. The mechanism of exchange between the 2 : 1 and the 1 : 1 complexes is dissociative. The activation parameters suggest that the dissociative process is kinetically governed by the successive flipping of two aromatic rings.



I
Scheme 1

Experimental

The *p-tert*-butylcalix[6]arene hexaacetamide, **I**, 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40-hexakis(*N*,*N*-diaethylaminocarbonyl)methoxycalix[6]arene, was synthesized from the hexahydroxy calix[6]arene derivative (Aldrich >95%) following the procedure of Ungaro *et al.*[26,27]

Deuterated acetonitrile (99.8%) and deuterated chloroform (99.8%) were purchased from Cambridge Isotope Laboratories. All measurements were made in a binary mixture of deuterated chloroform and deuterated acetonitrile (1 : 1 by volume). CsI_3 was used as the caesium source. CsI_3 was dried under vacuum overnight prior to use.

NMR Measurements

The ^{1}H and ^{133}Cs NMR spectra were recorded on a Bruker AMX 500 NMR spectrometer operating at 500.14 and 65.59 MHz, respectively. The ^{1}H NMR and ^{133}Cs NMR spectra were referenced to chloroform (7.24 ppm) and 10 mM CsCl in 20% D_2O (0 ppm at 300 K), respectively.

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Table 1 Crystallographic collection and refinement parameters for the 2 : 1 Cs^+ : **I** complex and for **I**

	$(Cs_2I)^{2+}$ complex (**II**)	**I**
Empirical formula	$C_{104}H_{154}Cl_4Cs_2I_6N_6O_{12}$	$C_{104}H_{158}N_6O_{14}$
M_r	2849.35	1716.36
T/K	203(2)	203(2)
λ/Å	0.71073	0.71073
Space group	$P2_1/c$	$P2_1/n$
a/Å	28.633(8)	14.518(9)
b/Å	18.160(5)	14.424(8)
c/Å	24.970(7)	24.461(9)
β/°	106.254(5)	91.35(7)
V/Å^3	12465(6)	5121(5)
D_c/Mg m^{-3}	1.518	1.113
Z	4	2
μ/mm^{-1}	2.209	0.073
Reflections collected/unique	13585/11635	12256/7330
R_{int}	0.0793	0.0519
Goodness-of-fit	1.047	1.176
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0743$, $wR2 = 0.2404$	$R1 = 0.0747$, $wR2 = 0.2363$
R indices (all data)	$R1 = 0.0933$, $wR2 = 0.2570$	$R1 = 0.0983$, $wR2 = 0.2511$

^{133}Cs NMR spectra: The parameters were chosen to obtain quantitative spectra. A 90° pulse of 14 µs, an acquisition time of 0.015 to 2 s, a sweep width of 20 kHz, a relaxation delay of 0.5 to 4 s were used, and 24 to 32 k scans accumulated per spectrum.

T_1: ^{133}Cs NMR longitudinal relaxation times of the 2 : 1 Cs^+ : **1** complex were obtained by the inversion recovery method. The T_1 values at 238, 251, 266, 278, 308 and 321 K were 10.9, 10, 11.1, 15.4, 26.4 and 29.3 ms, respectively.

X-Ray crystallography

Crystals suitable for X-ray diffraction of uncomplexed **I** and of the 2 : 1 Cs^+ : **I** complex **II** were respectively obtained through slow evaporation from MeOH and from a CH_2Cl_2–n-Heptane mixture using a layer technique.

Suitable crystals were selected, mounted on thin, glass fibers using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90 and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.

Systematic absences in the diffraction data-sets and unit-cell parameters were consistent with space groups $P2_1/n$ for **I** and $P2_1/c$ for **II**. The structures were solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2.

Two cocrystallized solvent molecules were located in the asymmetric unit, methanol in the case of **I** and dichloromethane in the case of **II**. Generally, all non-hydrogen atoms were refined with anisotropic displacement coefficients. The quality of the data for **II** did not allow anisotropic refinements for all the non-H atoms. Nevertheless, the chemical connectivity remains demonstrated. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library with the latest used version being v.6.12 (G. M. Sheldrick, Bruker AXS, Madison, WI, 2001). Crystallographic data are reported in Table 1.

CCDC reference numbers 215682 and 215683.

See http://www.rsc.org/suppdata/dt/b3/b307897n/ for crystallographic data in CIF or other electronic format.

Results and discussion

The ^{133}Cs NMR spectra recorded at 238 K of 31.64 mM CsI_3 in a binary mixture of deuterated chloroform and deuterated acetonitrile (1 : 1 by volume), in the absence (Fig. 1(a)) and presence of variable amounts of **I** (Fig. 1(b)–(h)) are shown in Fig. 1. A total of five different ^{133}Cs NMR signals are observed over the range of R = [**I**]/[Cs^+] from 0 to 1. In the absence of **I**, the signal of solvated Cs^+ at 52 ppm is observed as expected.[17] Upon addition of **I** two peaks at 72 ppm (major) and 58 ppm (minor) superimpose on the spectra of solvated Cs^+ for R = [**I**]/[Cs^+] <0.5. For R >0.5, the signal of solvated Cs^+ disappears, two additional signals at 43 ppm (minor) and −64 ppm (major) appear, while the resonances at 72 and 58 ppm lose intensity.

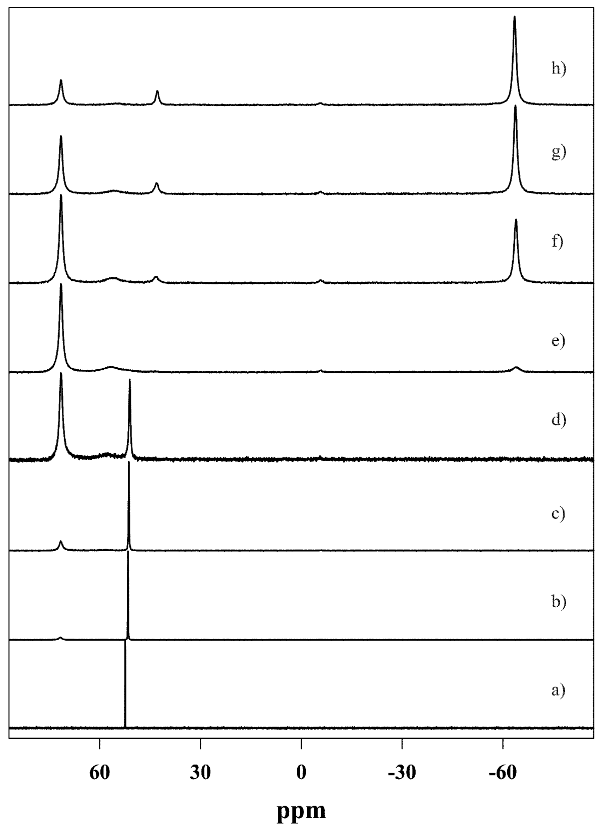


Fig. 1 ^{133}Cs NMR spectra (238 K) of solutions containing CsI_3 (31.64 mM) and **I** at concentrations of (a) 0, (b) 5.07, (c) 8.09, (d) 12.33, (e) 17.25, (f) 22.24, (g) 26.78 and (h) 30.94 mM.

The major signals at 72 and −64 ppm are attributed, respectively, to a 2 : 1 and a 1 : 1 Cs^+ : **I** complexes. Since the ratio of the integrals of the signals at 43 and −64 ppm remains constant upon variation of R (it is equal to 0.13), the minor signal at 43 ppm is attributed to a second complex of 1 : 1 stoichiometry. Finally, the minor species observed at 58 ppm is attributed to a 3 : 1 complex, present only at low R values, and at low temperatures (see below).

An analysis of the peak integration data leads to the calculation of the cumulative equilibrium constants for the formation of the 2 : 1 and 3 : 1 complexes. They are $K_{2:1} = 1.86 \times 10^5$ M^{-2} and $K_{3:1} = 1.21 \times 10^7$ M^{-3} at 238 K. The stepwise formation constant $K_{3:1}/K_{2:1}$ is 65 M^{-1}. This value is an order of magnitude lower than the square root of $K_{2:1}$, 430 M^{-1}, which shows, at first approximation, that the cation binding process is anticooperative. This is expected both from entropic and enthalpic reasons, and was observed previously in the case of the stepwise formation of 2 : 1 and 3 : 1 complexes of Na^+ with a calix[8]arene octaester derivative.[24]

Fig. 2 shows the aromatic part of the ^1H NMR spectra of variable amounts of **I** in the presence (Fig. 2(a)–(g)) and absence (Fig. 2(h)) of 31.64 mM CsI_3 at 238 K. For $R = [\mathbf{I}]/[Cs^+]$ <0.5, the spectra display six peaks of equal integrals at 7.39, 7.36, 7.08, 7.06, 6.98 and 6.79 ppm in the aromatic region, and four peaks with a 1 : 1 : 2 : 2 integral ratio at respectively, 1.10, 1.02, 0.96 and 0.82 ppm in the *tert*-butyl region. Due to extensive overlap, the methylene region is of little diagnostic value. These signals are ascribed to the 2 : 1 complex corresponding to the major signal at 72 ppm in the ^{133}Cs NMR spectra. For $[\mathbf{I}]/[Cs^+]$ >0.5 broad peaks at 6.51 ppm in the aromatic region and 0.74 ppm in the *tert*-butyl region appear, indicating conformational exchanges involving the 1 : 1 Cs^+ : **I** complexes formed with different conformers of **I**. The ^1H NMR spectra of free **I** (Fig. 2(h)) is dominated by conformational interconversions as evidenced by the presence of broad lines which can not be attributed to specific conformers. Essentially, the ^1H NMR spectra (Fig. 2) recorded under the same molar and temperature conditions as the ^{133}Cs NMR spectra (Fig. 1) confirm the formation of two major species, a 1 : 1 and a 2 : 1 Cs^+ : Calix[6]arene complexes.

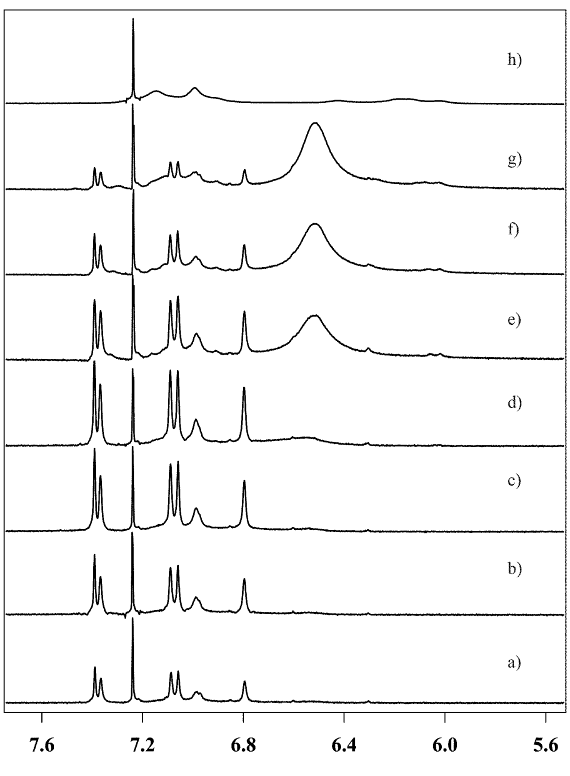


Fig. 2 ^1H NMR spectra (238 K) of solutions containing various amounts of **I** in the presence (a–g) and absence (h) of CsI_3 (31.64 mM): (a) 5.07, (b) 8.09, (c) 12.33, (d) 17.25, (e) 22.24, (f) 26.78 and (g, h) 30.94 mM.

The temperature dependence of the ^{133}Cs NMR spectra of 73.5 mM CsI_3 and 34.1 mM **I** ($R = 0.464$) is shown on Fig. 3. Under these conditions, three species, the solvated Cs^+, and the 2 : 1 and 3 : 1 complexes are present at 238 K in measurable

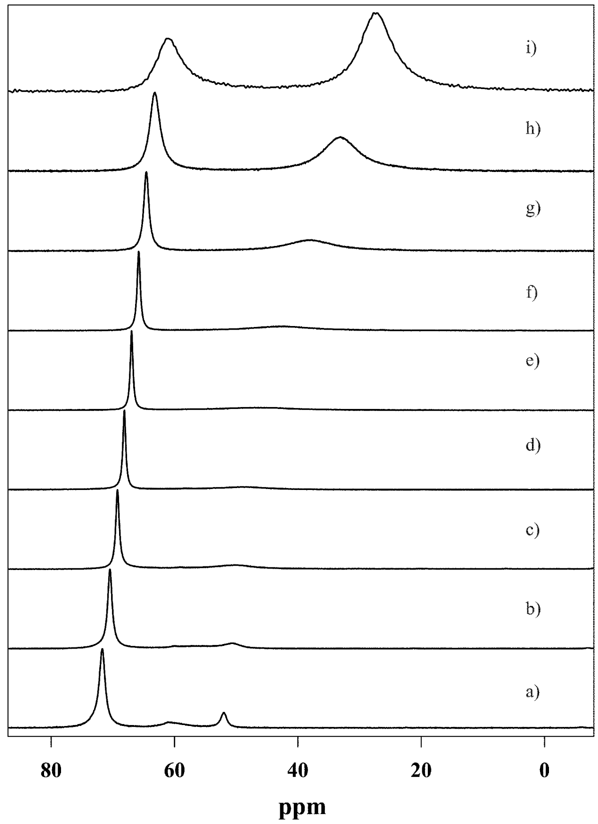


Fig. 3 ^{133}Cs NMR spectra of solutions containing CsI_3 (73.49 mM) and **I** (34.11 mM) at various temperatures: (a) 238, (b) 246, (c) 255, (d) 265, (e) 274, (f) 283, (g) 292, (h) 300 and (i) 314 K.

amounts. The ^{133}Cs NMR linewidths of solvated Cs^+ and of the 3 : 1 complex increase strongly with increasing temperature. They are lost in the baseline around 265 K. A further increase in temperature results in the appearance of a broad line near 40 ppm at 283 K, which narrows and shifts towards lower frequencies with further increase of the temperature. This is in contrast to the behaviour of the 2 : 1 complex, whose line width has a minimum at ~274 K. The shift towards lower frequencies of the low frequency signal is much more pronounced than in the case of the 2 : 1 complex, indicating a moderately fast exchange between solvated Cs^+ and the major 1 : 1 complex, whose chemical shift is −64 ppm at 238 K, and for which it is expected that the concentration will increase with increasing temperature. This interpretation of the temperature behaviour of the ^{133}Cs NMR spectra is supported by the dependence of the chemical shift of the low frequency signal on the $R = [\mathbf{I}]/[Cs^+]$ ratio. An increased shift towards lower frequencies is observed for an increase of the R ratios. The chemical shifts are, respectively, 33 ppm (Fig. 3(h)), 25 ppm and −58 ppm for R = 0.46, 0.71 and 0.99 at 300 K. The value of −58 ppm for the ratio 0.99 is close to the value of −64 ppm attributed to the 1 : 1 complex at 238 K. The intensity ratios between the two peaks follow the same trend than the chemical shifts, in agreement with the interpretation. These results confirm (i) that the 3 : 1 complex can be observed only at low temperatures, below 250 K, (ii) that the 1 : 1 complex is thermodynamically favored when temperature increases, and (iii) that the exchange between the solvated Cs^+ and the 1 : 1 complex is at least an order of magnitude faster than the exchange processes involving the 2 : 1 complex with the 1 : 1 complex and with the solvated caesium cation.

Fig. 4 shows the temperature dependence of the ^1H NMR spectra of 73.5 mM CsI_3 and 34.1 mM **I** ($R = 0.464$) in the same range of temperatures as in Fig. 3, from 238 to 314 K. At 238 K, the six signals with equal integrals are observed as on Fig. 2. They are attributed to the 2 : 1 complex. At 255 K, a broad

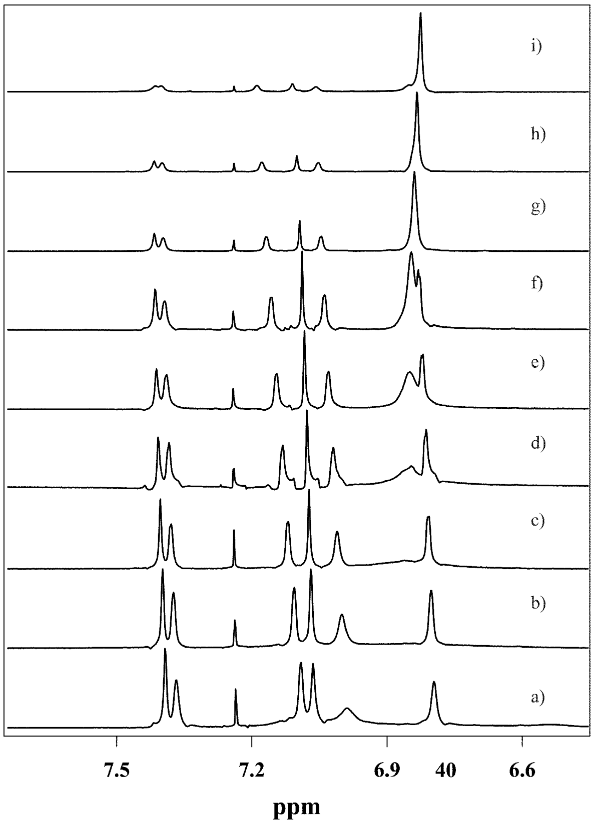
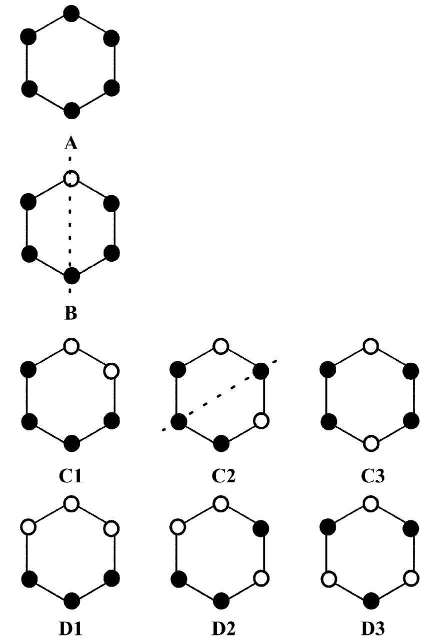


Fig. 4 ^{1}H NMR spectra of solutions containing CsI_3 (73.49 mM) and **I** (34.11 mM) at various temperatures: (a) 238, (b) 246, (c) 255, (d) 265, (e) 274, (f) 283, (g) 292, (h) 300 and (i) 314 K.

signal begins to appear at 6.86 ppm. It is assigned to the major 1 : 1 complex corresponding to the broad, low frequency, ^{133}Cs signal observed under identical concentrations and temperature conditions (Fig. 3). Increasing further the temperature results in a narrowing and a slight low frequency shift of this signal. In parallel with the increasing appearance of the single ^{1}H signal attributed to the major 1 : 1 complex, the six signals of equal intensity attributed to the 2 : 1 complex decrease in intensity. This is similar to the intensity variations observed for the $^{133}Cs^{+}$ species on Fig. 3. This corroborates the interpretation that the lower frequency resonance in the ^{133}Cs NMR spectra contains contributions from the solvated Cs^{+} and the 1 : 1 complexes with the shift given by the weighted mean of all contributions.

The structure in solution of the 2 : 1 complex can be deduced from the ^{1}H NMR spectra. Assuming only idealized "up" (full circles) and "down" (empty circles) orientations of the *tert*-butyl groups with respect to the best plane containing the six bridging methylene groups, eight different conformations, shown in Scheme 2, are possible. As mentioned above, the ^{1}H NMR spectrum of the 2 : 1 complex is characterized by six peaks with equal integrals in the aromatic and four peaks in a 1 : 1 : 2 : 2 ratio in the *tert*-butyl region. Based on the symmetry of the possible conformers of **I** only the conformers **B** and **C2** (Scheme 2), both having one symmetry plane (dotted lines in Scheme 2) as symmetry element, can account for the observed ^{1}H NMR spectra of the 2 : 1 complex. In the solid state the 2 : 1 complex adopts a distorted partial cone conformation (see below), close to the idealized conformer B of Scheme 2. Moreover, the value of the ^{133}Cs NMR chemical shift observed for the 2 : 1 complex (72 ppm at 238 K) is in agreement with such a structure, in which the two caesium cations are coordinated by phenolic and carbonyl oxygen at the lower rim of the calixarene. This shift is comparable to the shift of 68 ppm observed in the case of the 1 : 1 caesium–calix[4]arene tetraacetamide complex.[17] A correlation between the ^{133}Cs chemical shifts and the mean Cs–O distance has been shown for a series of



Scheme 2

macrocyclic compounds.[28] Downfield shifts are observed for shorter Cs–O distances.[28] The average of the 15 Cs–O distances in the crystal structure of the 2 : 1 complex (see below) is 3.1 ± 0.2 Å. On the basis of the correlation,[28] this value corresponds to an isotropic ^{133}Cs chemical shift in the range of 70–90 ppm, in excellent agreement with the experimental value for the 2 : 1 complex. Since the two coordination sites of the caesium cations in the solid state 2 : 1 complex are not equivalent, the observation of one ^{133}Cs NMR signal for the two Cs^{+} in solution indicates a rapid intramolecular exchange between the two sites. The crystal structure of the 1 : 1 complex of **I** with Sr^{2+} shows that the metal cation is also exclusively coordinated by the phenolic and amide oxygen atoms, in that case by five of the six phenolic units of the calixarene.[29,30]

In the case of the 1 : 1 complex, the observation of one signal only in the ^{1}H NMR spectrum indicates either a perfect, symmetrical, cone conformation, or a rapid exchange between two or more conformations, resulting in a single, averaged, ^{1}H NMR signal. The ^{133}Cs NMR chemical shift, −64 ppm at 238 K, suggests an alternate conformation, with hapto coordination of the caesium to aromatic rings. In the case of the *endo* caesium complex of *p-tert*-butylcalix[4]arene monophenolate, a ^{133}Cs NMR chemical shift of −235 ppm was reported.[31] The ^{133}Cs MAS spectrum of the caesium complex with *p-tert*-butyl calix[4]arene in the solid state contains two lines at 218 and at −200 ppm, which have been attributed respectively to an *exo* and an *endo* complex.[32] Theoretical[33,34] and experimental[35–37] studies have recently demonstrated the importance of the arene group as a donor, and as a coordination site, for the alkali metal cations. In the case of the tetramethoxy derivative of *p-tert*-butylcalix[4]arene, two 1 : 1 complexes of the caesium cation coexist, observed at −49 and −100 ppm on the ^{133}Cs NMR spectra.[16] They were attributed respectively to the 1,3 alternate and the partial cone conformers.[16] The theoretical results have indicated that the caesium cation is coordinated to 2 O and 2 arene groups in the 1,3 alternate conformer complex, and to 1 O and 3 arene groups in the partial cone conformer complex.[33] The chemical shift of −64 ppm observed for the 1 : 1 complex in this study, suggests the participation of arene groups in the coordination shell of the caesium cation,[38] coupled with longer Cs–O average distances[28] resulting from poorer fit of caesium in the complexation cavity than in the case of the 2 : 1 complex. This interpretation is consistent also with the observation of ^{133}Cs chemical shifts in the range of −13 to −14 ppm and of −57 to

−60 ppm, respectively, for 2 : 1 and 1 : 1 complexes of two 1,3-calix[4]arene bis(crown ethers) derivatives, fixed in a 1,3 alternate conformation.[39,40] The crystal structure of **I** was determined (see below) to be of the **D1** type (Scheme 2). It is suggested that the structure in solution of the 1 : 1 Cs^+ : **I** complex is close to the **D1** structure, with the caesium cation coordinated to aromatic rings and to a number of phenolic and/or carbonyl oxygens. There are two such coordination sites in the complex, the caesium cation exchanging very rapidly between them, as indicated by the ^{1}H NMR spectra. This fast intramolecular exchange is similar to what was observed in the case of a 1,2,3 alternate isomer of a bis-crown-4-calix[6]arene.[41]

As mentioned above, the linewidth of the ^{133}Cs NMR signal of the 2 : 1 complex increases with temperature above 265 K. Therefore, the rate constants for the dissociation of the 2 : 1 complex can be determined for T >265 K by a complete band-shape analysis. This analysis was done using the DNMR5 software.[42] The enthalpy and entropy of activation are respectively $\Delta H^{\neq} = 58$ kJ mol^{-1} and $\Delta S^{\neq} = -2$ J K^{-1} mol^{-1}). These activation parameters describe the dissociation of the 2 : 1 complex to a 1 : 1 complex. The exchange follows a dissociative mechanism, *i.e.* $(Cs_2\mathbf{I})^{2+} \longrightarrow (Cs\mathbf{1})^+ + Cs^+$, since the obtained rate constants were independent of the molar composition of the solution. The activation parameters are comparable to those observed for the conformational exchange between the 1,3 alternate and partial cone Cs^+ complexes of the corresponding calix[4]arene tetramethoxy derivative.[16] An activation enthalpy in the order of magnitude of 60 kJ mol^{-1} and an entropy of activation close to zero are characteristic of conformational processes involving the flipping of one aromatic ring in the case of the calix[4]arene methoxy derivative in the same solvent.[14] It is plausible that the dissociation process of the 2 : 1 complex is governed by the successive flipping of two aromatic rings transforming the **B** calix[6]arene conformation of the 2 : 1 complex in the proposed **D1** conformation of the 1 : 1 complex (Scheme 2). These results also demonstrate the relative inertness of the 2 : 1 complex compared to the 3 : 1 and 1 : 1 complexes.

Crystals of the 2 : 1 Cs^+ : **I** complex were obtained from CH_2Cl_2–*n*-heptane using a layer technique (Table 1). In the solid state the calixarene–Cs^+ complex adopts a distorted partial cone conformation, similar to the idealized structure **B** of Scheme 2, Fig. 5) All amide groups are tilted inwards the calixarene cavity, but to different extents, with one phenyl ring (A) almost lying in the plane defined by the bridging methylene groups. The dihedral angles of the phenyl rings to the bridging methylene mean plane provide the best structural assessment with angles of 174° (A), 106° (B), 139° (C), 123° (D), 100° (E) and 122° (F). The separation of adjacent phenolic oxygens

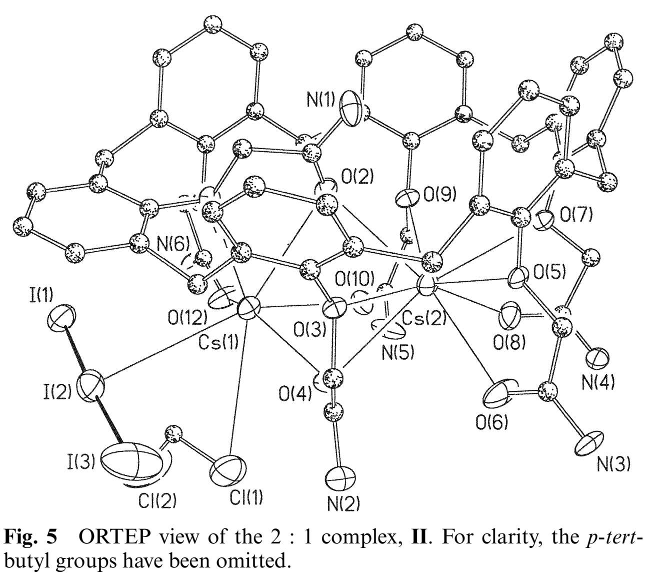


Fig. 5 ORTEP view of the 2 : 1 complex, **II**. For clarity, the *p-tert*-butyl groups have been omitted.

varies between 3.01 and 4.79 Å, highlighting the distorted partial cone conformation.

The two caesium cations are bound to the phenolic and carbonyl oxygens at the lower rim of the calixarene as in the case of alkali metal complexes with calix[5]arene ketones,[43] whereas the nitrogen atoms of the amide groups are not involved in the cation binding. The amide group (A), which is most tilted inwards the cavity of the calix[6]arene, acts as a bridge between the two Cs^+, which are separated by 4.16 Å. In a $[Cs_2(18\text{-crown-}6)]^{2+}$ cation, the distance between the two Cs^+ cations was reported[44] to be 3.92 Å, a distance only slightly longer than the sum of the ionic radii, 3.56 Å. Typically, the distance reported so far between two caesium cations separated by 18-crown-6 is in the range 3.84–4.66 Å.[45] Similarly to what is the case for the crown ether complexes, the Cs^+–calixarene interactions through the carbonyl and the phenolic oxygens are able to overcome the electrostatic repulsion between the two caesium cations located at the short distance of 4.16 Å.

The distance between the Cs^+ and the phenolic oxygens is larger than between the Cs^+ and carbonyl oxygens involved in the binding to the same cation. Distances between Cs^+ and the carbonyl and phenolic oxygens are in the range of 2.92–3.26 and 3.02–3.44 Å, respectively, with an average of 3.1 ± 0.2 Å.

Crystals of **I** were obtained from methanol (Table 1). Three adjacent amide groups are *cis*, but the inversion symmetry places the other *cis* amide groups in the *anti* position on the opposite site of the macroring, a structure similar to structure **D1** of Scheme 2, Fig. 6) A similar crystal structure was obtained by Arnaud-Neu *et al.* in the case of the hexaethylcalix[6]arene hexaacetate.[46] The conformation is best described by the dihedral angles that the three phenolic rings A (98°), B (310°) and C (231°) make with the plane of the macrocyclic ring methylene groups. Thus the A and C ring have their phenol oxygens oriented towards the center of the calixarene cavity. Adjacent phenolic oxygens are separated by 5.25 Å (A–B) and 5.65 Å (B–C).

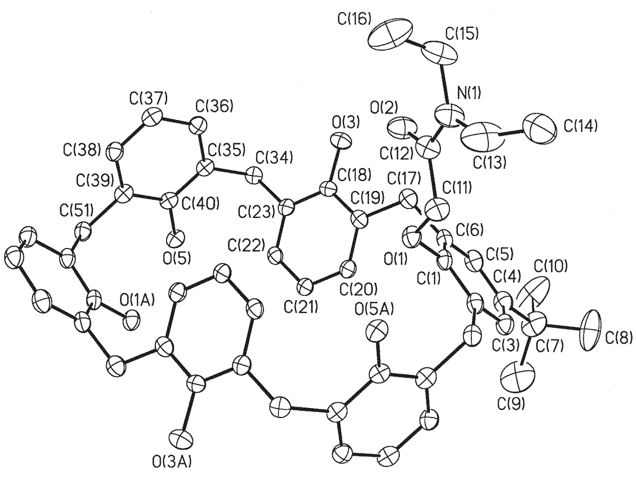


Fig. 6 ORTEP view of **I**. For clarity, the *p-tert*-butyl and the acetamido groups have been indicated on one aromatic ring only, and omitted on the five other aromatic rings.

The caesium coordination chemistry of **I** in solution is remarkably complex. Peaks for four different complexes are observed in the ^{133}Cs NMR spectra at 238 K, in a binary mixture of acetonitrile and chloroform. They are attributed to complexes of stoichiometries Cs^+ : calix[6]arene n : 1, with n = 1–3. The 3 : 1 complex is observed only at low temperatures (below 250 K), and high concentration ratios of Cs^+ over calixarene. Two 1 : 1 complexes coexist at 238 K for Cs^+ over calixarene ratios above 0.5. Their formation is favored at higher temperatures. The 2 : 1 complex, one of the two major species, is more kinetically stable than the other complexes. The exchange between the solvated Cs^+ and the 1 : 1 complexes is at least an order of magnitude faster than the exchange processes involving the 2 : 1 complex. The structure of the 2 : 1 complex in solution is similar to its crystal structure, in which the calixarene adopts a distorted partial cone conformation. It is suggested that the structure of the major 1 : 1 complex is similar to the crystal structure of the uncomplexed calixarene, adopting a 1,2,3 alternate conformation. The ^{133}Cs NMR chemical shifts are an indication that the arene groups are involved in the coordination of caesium in the major 1 : 1 complex. The activation parameters of the dissociation process of the 2 : 1 complex suggest that the dissociation is governed by the successive flipping of two aromatic rings transforming the partial cone calix[6]arene conformation of the 2 : 1 complex in the proposed 1,2,3 alternate conformation of the 1 : 1 complex.

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