Kinetics and Mechanisms of Complexation of the Cesium Cation by 5,11,17,23-Tetra-*p*-*tert*-butyl-25,26,27,28-tetramethoxycalix[4]arene in Solution

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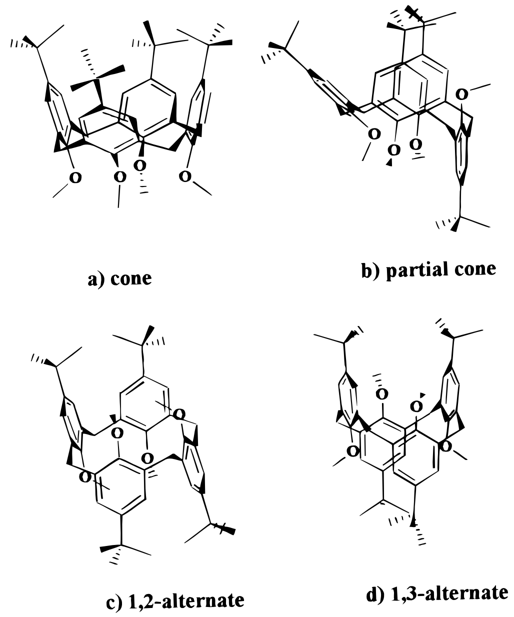
The kinetics and mechanism of the cesium cation complexation by 5,11,17,23-tetra-*p*-*tert*-butyl- 25,26,27,28-tetramethoxycalix[4]arene (**1**) were studied in a 1:1 (v/v) mixture of deuterated chloroform and deuterated acetonitrile using ^{1}H NMR, ^{133}Cs NMR, and 2D-EXSY ^{133}Cs NMR spectroscopy. The results show the formation of 1:1 complexes with the partial cone (pc) and 1,3-alternate (alt,3) conformer of **1**. In the latter case, Cs^+ is bound asymmetrically to one of the two metal binding sites, composed of two phenolic oxygen and two phenyl groups. The equilibrium association constants are respectively 194 and 33 M^{-1} at 236 K. In the case of the pc complex $\Delta H = -14 \pm 1$ kJ/mol and $\Delta S = -12 \pm 4$ J/(mol K), while for the alt,3 complex $\Delta H = -11 \pm 1$ kJ/mol and $\Delta S = -11 \pm 7$ J/(mol K). The preferred complexation pathway of Cs^+ by **1** follows the complexation by the pc conformer, which can undergo a conformational exchange to the alt,3 conformer, from which Cs^+ cannot escape directly with a measurable rate. The activation parameters for the complex formation between solvated Cs^+ and the pc conformer and for the exchange between the alt,3 and the pc complexes are $\Delta H^* = 38 \pm 2$ kJ/mol and $\Delta S^* = -66 \pm 6$ J/(mol K), and $\Delta H^* = 61 \pm 5$ kJ/mol and $\Delta S^* = -9 \pm 15$ J/(mol K), respectively. ^{1}H NMR spectroscopy shows that the exchange of Cs^+ between the two binding sites of the alt,3 complex proceeds through an interconversion to the pc complex and not through an internal tunneling process of Cs^+.

Introduction

The cyclic oligomers of phenolic units linked through the ortho position, called calixarenes, associate their skeleton simplicity with versatile recognition properties both of ions and neutral molecules.[1−4] The understanding of the factors and mechanisms responsible for the selective host−guest complexation in solution necessitates thermodynamic and kinetic studies of the complexation and dissociation processes.[5] While several thermodynamic studies on the complexation processes of calixarenes have appeared in the past few years,[6−16] kinetic and mechanistic studies are more scarce.[17−20]

It has been shown recently, using rigidified calix[4]arenes, that the complexation properties depend not only on the nature of the donor groups but also on their stereochemical arrangement, which is determined by the conformation of the calixarene.[21,22] Depending upon the relative orientation of the para and phenolic sites, the tetramer can adopt four different conformations: cone (c), partial cone (pc), 1,2-alternate (alt,2), and 1,3-alternate (alt,3),[23] shown in Chart 1. These conformers display selective properties of complexation of alkali metal cations. The cone conformer of calix[4]arenes shows usually the highest affinity for Na^+, whereas the partial cone and 1,3-alternate conformers show the best selectivity for K^+ and Cs^+.[21,22,24−29] Among the possible structural variations, 5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27,28-tetramethoxycalix[4]arene (**1**) is particularly interesting, since the four conformers are present simultaneously in solution and can be detected on the ^{1}H NMR spectrum.[17,30] The conformational interconversion of **1** and the kinetics and mechanisms of the sodium cation complexation have been determined recently, showing that Na^+ is exclusively complexed by the cone conformer of **1**.[17,19]

CHART 1



a) cone

b) partial cone

c) 1,2-alternate

d) 1,3-alternate

In this paper, the complexation of the cesium cation by calix[4]arene **1** is studied by ^{133}Cs and ^{1}H NMR in a binary mixture of acetonitrile and chloroform. It is shown that the cesium cation is selectively complexed by the partial cone conformer of **1**. The 1,3-alternate complex coexists with the pc but is thermodynamically disfavored. The pc complex is kinetically more labile than the alt,3, and the decomplexation route for the alt,3 complex involves first a conformational interconversion to the pc complex.

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Experimental Section

Chemicals and Solutions. 5,11,17,23-Tetra-*p*-*tert*-butyl-25,26,27,28-tetramethoxycalix[4]arene was synthesized from the tetrahydroxy derivative (Aldrich, 99%), following the procedure of Gutsche et al.[23] Cesium triiodide (Johnson Matthey 99%) was used as the cesium cation source. CsI_3 was dried under vacuum overnight prior to use. CsSCN was synthesized from NH_4SCN (Aldrich) and CsOH (Aldrich, 99%, 50 wt % solution) and recrystallized from a 50:50 methanol/acetonitrile mixture. CsSCN was dried under vacuum for $1^1/_2$ days prior to use.

All measurements were made in binary mixtures of chloroform and acetonitrile (1:1 by volume). Deuterated acetonitrile (99.8%) and deuterated chloroform (99.8%) were purchased from Cambridge Isotope Laboratories. The solvents were dried over 4 Å molecular sieves before use.

NMR Measurements. The ^1H and ^{133}Cs NMR spectra were recorded on a Bruker AMX-500 NMR spectrometer at 500.14 and 65.59 MHz, respectively. ^1H NMR spectra are referenced to chloroform (7.24 ppm) and the ^{133}Cs spectra to 0.01M CsCl in 20% D_2O.

1D ^{133}Cs Spectra. The parameters were chosen to obtain quantitative spectra. A relaxation delay time of 2.5 s ($>5T_1$), a 90° pulse (14 μs), an acquisition time of 0.03−0.1 s, and a sweep width of 20 kHz were used and 256−2048 scans accumulated per spectrum.

T_1:T_1 was determined by the inversion−recovery technique. A 90° pulse of 14 μs and 10 delay times and a relaxation delay of at least 2.5 s ($>5T_1$) were used. The data were fitted to the equation $I(\tau) = M_0(1 - ke^{\tau/T_1})$ and T_1, M_0, and k determined by a nonlinear regression analysis. The T_1's were determined at 250, 264, 274, 283, and 300 K. They were found to be respectively 197, 212, 255, 320, and 603 ms (solvated $^{133}Cs^+$ at 52 ppm), 34, 63, 99, 204, and 666 ms (1,3-alternate−$^{133}Cs^+$ complex at −49 ppm), and 139, 219, 273, 331, and 645 ms (partial cone−$^{133}Cs^+$ complex at −100 ppm).

2D-EXSY Spectroscopy. The parameters were chosen to obtain quantitative spectra. A standard NOESY pulse sequence was used for these experiments.[31−33] A relaxation delay of $5T_1$, a 90° pulse of 14 μs, a sweep width of 20 kHz, an acquisition time of 0.03−0.1 s, and 96−128 scans of 512 points by 128 slices were used, resulting in a measuring time of 4−8 h per spectrum. Mixing times (τ_m) ranging from 500 μs to 0.35 s were used. Spectra were recorded at 250, 269, and 283 K. At each temperature at least five spectra with different τ_m values were recorded.

Data Treatment. *1D ^{133}Cs Spectra.* The line widths, intensities, and chemical shifts were determined by fitting each peak with a Lorentzian line shape using the Simplex optimization procedure. The integrals were calculated analytically using these line widths and the intensities.

2D-EXSY Spectra. The 2D spectra were symmetrized and all peaks integrated using standard Bruker software. Each cross-peak intensity was referenced against the total intensity of the auto-peaks. No corrections for the differences in T_1 were applied. The resulting normalized cross-peak intensities were then plotted against τ_m and the rate constants extracted using the initial rate method. At low exchange rates there is a linear relationship between the cross-peak intensities and τ_m:[34] $I_{i\to j} = k_{i\to j}p_i\tau_m$. For faster exchange an equation of the form $I(\tau_m) = a(1 - e^{b\tau_m})$ was fitted to the data and $k_{i\to j} = ab/p_i$. Both the $I_{j\to i}$ and $I_{i\to j}$ integrals were used for the determination of $k_{i\to j}$, giving an idea of the errors associated with the determination of $k_{i\to j}$.

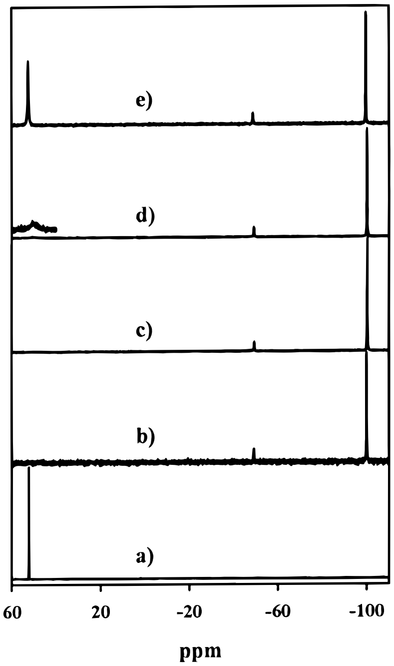


Figure 1. ^{133}Cs NMR spectra of various amounts of CsI_3 at 236 K in the absence (a) and in the presence (b−e) of 35.5 mM tetramethoxycalix[4]arene (**1**). [CsI_3] = 70.0 (a), 10.3 (b), 19.5 (c), 27.6 (d), and 70.1 mM (e).

Results and Discussion

Figure 1 shows the ^{133}Cs NMR spectra of variable amounts of CsI_3 at 236 K in the presence of 35.5 mM **1** in the binary mixture 1:1 chloroform/acetonitrile. For [CsI_3] < [**1**] two resonances are observed at −49 and −100 ppm. For [CsI_3] > [**1**], a third resonance is observed at 52 ppm. Exactly the same behavior was observed when CsSCN was used instead of CsI_3. The observed chemical shifts, both for the uncomplexed and the complexed cesium cations, were identical for both counter-anions. Moreover, a concentration study in the range of 5−100 mM of the chemical shifts of CsI_3 in the binary mixture 1:1 chloroform/acetonitrile shows that the line widths remain essentially independent of the concentration (between 1 and 2 Hz in the whole range of concentrations) and that the ^{133}Cs NMR signal varies by 5 ppm. Given the total chemical shift range of the $^{133}Cs^+$ cation, which is more than 300 ppm,[35] this variation is small, indicating a minor amount, if any, of contact ion pair formation. The chemical shift of 9.7 mM $^{133}Cs^+$ at 300 K is almost identical in the cases of acetonitrile and of the binary mixture 1:1 acetonitrile/$CHCl_3$ (1 ppm difference). This indicates that the primary solvation shell of Cs^+ in the binary mixture is made exclusively of acetonitrile molecules, which does not favor contact ion pair formation. All of these results suggest that, in the concentration range of this study, the contact ion pair eventually formed between Cs^+ and I_3^-, is dissociated, at least to a very large extent.

The resonance at 52 ppm corresponds to the solvated cesium cation, which is confirmed by the spectrum of 70 mM CsI_3 in the absence of **1** (Figure 1a). The resonances at −49 and −100 ppm are assigned to complexes formed between Cs^+ and two different conformers of **1**. Figure 2 shows the *tert*-butyl region of the ^1H NMR spectra of 35.5 mM **1** as a function of [CsI_3] at 236 K. The peaks corresponding to the free conformers and the two complexes of **1** were assigned as described below and are indicated in Figure 2 as cone (c), partial cone (pc), 1,3 alternate (alt,3), 1,2 alternate (alt,2), 1,3 alternate complex (alt,3Cs^+), and partial cone complex (pcc). Upon addition of

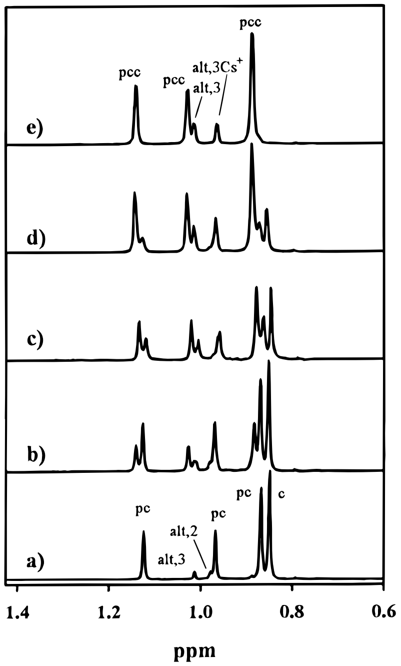


Figure 2. ^{1}H NMR spectra of 35.5 mM tetramethoxycalix[4]arene (**1**) in the absence (a) and in the presence (b−e) of various amounts of CsI_3: 10.3 (b), 19.5 (c), 27.6 (d), and 70.1 mM (e).

TABLE 1: ^{1}H NMR Chemical Shifts and Relative Intensities for the 1,3 Alternate and Partial Cone Complex between 1 and CsI_3 at 236 K

region	pc	1,3 alternate
tert-butyl	1.14, 1.03, 0.89 (1:1:2)	1.03, 0.97 (1:1)
methoxy	3.35, 3.0, 2.24 (2:1:1)	3.45, 3.25 (1:1)
aromatic	7.16, 6.96, 6.83, 6.68 (1:1:1:1)	6.88, 6.86 (1:1)

Cs^+, new peaks at 1.14, 1.03, 1.02, 0.97, and 0.89 ppm superimpose on the ^{1}H NMR spectrum of **1**, whose resonances do not shift. When an excess of Cs^+ is added to **1**, only the new resonances are seen (Figure 2e). It is apparent in Figure 2e that two different complexes are formed. The major species is characterized by three peaks at 1.14, 1.03, and 0.89 ppm in the ratio 1:1:2. This pattern fits the spectra of the pc conformer.[30] Two additional signals of equal intensity are present at 1.02 and 0.97 ppm. These features are assigned to a nonsymmetrical complex between Cs^+ and the 1,3 alternate conformer of **1**, which has two binding sites in slow exchange, while the uncomplexed 1,3 alternate conformer of **1** displays one peak in each of the *tert*-butyl, methoxy, and aromatic regions. On the basis of the observation of these two peaks of equal intensity, the possibility of complexes formed with the 1,2 alternate or cone conformers (Chart 1a,c) can be ruled out. A symmetrical 1,2 alternate complex would have only one peak in the *tert*-butyl and two doublets in the aromatic region. An nonsymmetrical 1,2 alternate complex would double the peaks in each region. A cone complex requires only one peak in each region. Therefore, the formation of a 1,3 alternate complex is the most plausible hypothesis which corresponds to the observed ^{1}H NMR spectrum. Moreover, in addition to the signals corresponding to the complexed partial cone, two peaks of equal intensity are also observed in the methoxy and aromatic regions, at 3.25 and 3.45 ppm and at 6.86 and 6.88 ppm, respectively. The ^{1}H NMR chemical shifts attributed to the individual complexes are given in Table 1. On the basis of the ^{1}H NMR spectra, the resonances at −49 and −100 ppm in the ^{133}Cs NMR spectra are therefore respectively assigned to complexes formed between Cs^+ and the 1,3 alternate conformer (Chart 1d) and the partial cone conformer (Chart 1b). The ratio of the integration of the two ^{133}Cs peaks at −49 and −100 ppm corresponds to the ratio of the integrals of the peaks attributed respectively to the 1,3 alternate and the partial cone complexes on the ^{1}H NMR spectrum.

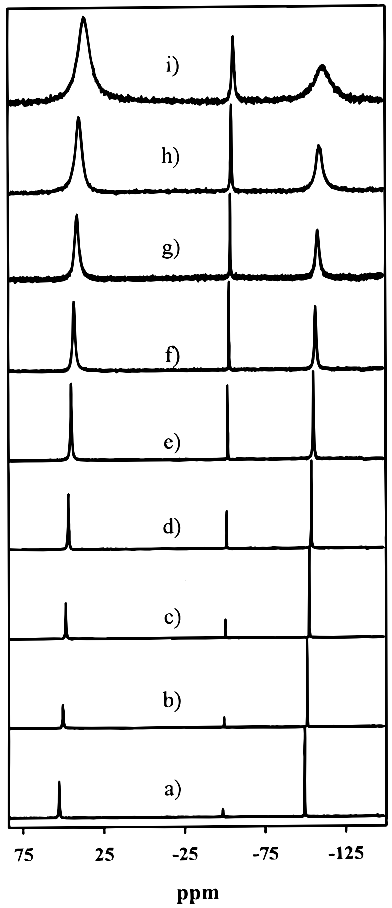


Figure 3. ^{133}Cs NMR spectra of CsI_3 80.4 mM, in the presence of 43.3 mM tetramethoxycalix[4]arene (**1**). The spectra were recorded at various temperatures: 236 (a), 246 (b), 254 (c), 264 (d), 274 (e), 283 (f), 292 (g), 300 (h), and 314 K (i).

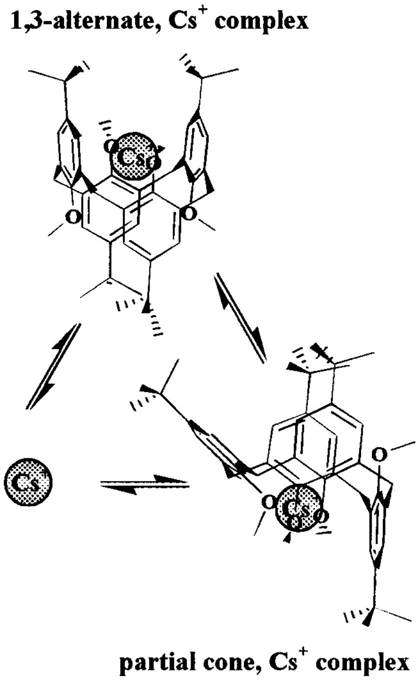
The temperature dependence of the ^{133}Cs NMR spectra of 80.4 mM Cs^+ and 43.3 mM **1** is shown in Figure 3. These spectra allow the determination of the concentration of the individual species and the calculation of the equilibrium constants for the complex formation using the integrals and the total concentration of Cs^+ and **1**. The equilibrium constants for complex formation and the corresponding thermodynamic parameters are given in Table 2. ^{1}H NMR and the ^{133}Cs NMR are in agreement and confirm that only complexes having a 1:1 stoichiometry are formed. At 236 K, the equilibrium constants for the alt,3 and pc complex formations are 33 M^{-1} with $\Delta H = -11 \pm 1$ kJ/mol and $\Delta S = -11 \pm 7$ J/(mol K) and 194 M^{-1} with $\Delta H = -14 \pm 1$ kJ/mol and $\Delta S = -12 \pm 4$ J/(mol K), respectively. The entropic variations are identical in the error limits. They are negative as expected for a complexation process. The selectivity of the complexation process between the alt,3 and the pc conformers is enthalpy-driven. This can be interpreted by the larger number of oxygen donor atoms (3) involved in the complexation by pc, compared to only two oxygens in the case of alt,3. In the latter case, however, cation−para interactions between the Cs^+ and the two aromatic rings play also a stabilizing effect on the Cs^+ encapsulation.[21,28,29,36,37] In agreement with these results, in a study of alkali metal picrates extraction by various rigidly fixed conformers of calix-

TABLE 2: Stability Constant for the Alt,3 and pc Complex at Various Temperatures

	T (K)	$K_{\mathrm{alt,3}}$ (M^{-1})	K_{pc} (M^{-1})	$K_{\mathrm{pc}}/K_{\mathrm{alt,3}}$
	236^a	33	194	5.9
	246^a	42	227	5.4
	254^a	30	142	4.7
	264^a	35	155	4.5
	274^a	33	139	4.3
	283^a	25	97	3.9
	292^a	21	80	3.9
	300^a	19	71	3.7
	314^a	14	51	3.7
ΔH^b (kJ/mol)		-11 ± 1	-14 ± 1	
ΔS^b (J/(mol K))		-11 ± 7	-12 ± 4	
	236^c	23.1	134.3	5.8

^{a} 80.4 mM CsI$_3$, 43.3 mM **1**. ^{b} Calculated without using data at 236 and 254 K. ^{c} 70.1 mM CsI$_3$, 35.5 mM **1**.

SCHEME 1



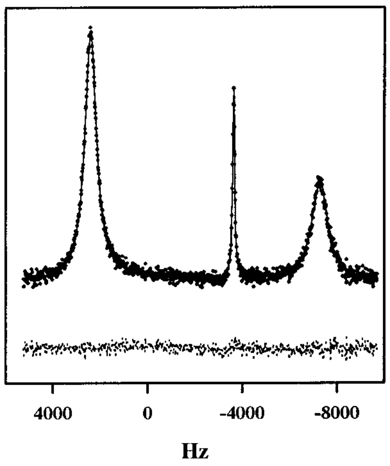


Figure 4. ^{133}Cs NMR spectra of [**1**] = 43.3 mM, [CsI$_3$] = 80.4 mM at 314 K showing the measured spectrum, the fit (solid line) from DNMR5, and the difference.

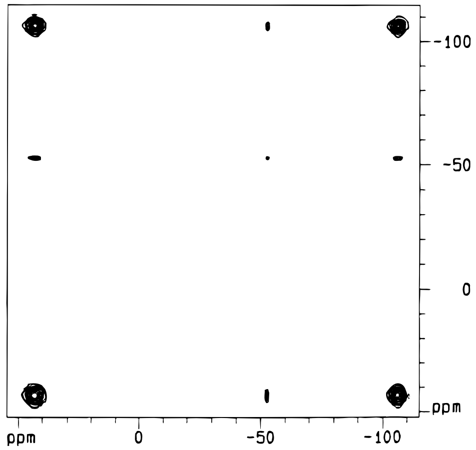


Figure 5. ^{133}Cs 2D-EXSY spectrum of [**1**] = 43.3 mM, [CsI$_3$] = 80.4 mM at 283 K: mixing time (τ_m) = 0.1 s.

[4]arene propyloxy derivatives, Ikeda and Shinkai[21] have found a strong selectivity of Cs$^+$ toward the alt,3 and the pc derivatives.

Figure 3 shows that the line width of all peaks increases with increasing temperatures for $T > 260$ K, indicating an exchange of Cs$^+$ between different sites. In this system, consisting of solvated Cs$^+$ and of two Cs$^+$ complexes, three exchange processes should be considered, as shown in Scheme 1.

At 314 K, the spectra can be analyzed by a full line shape analysis using the DNMR5 software.[38] The rate constant for the exchange between the solvated Cs$^+$ cation and the alt,3 conformer is negligibly small compared to the other two exchange processes and cannot be determined by the full line shape analysis. The rate constants for the exchanges between the solvated Cs$^+$ cation and the pc conformer, as well as the exchange between the Cs$^+$ complexes of the alt,3 and pc conformers could be determined by the full line shape analysis at 314 K. The experimental spectrum and the calculated spectrum obtained from the DNMR5 analysis are shown in Figure 4, illustrating the excellent agreement between the calculated and the experimental spectra. The rate constants at 314 K are respectively 960 ± 90 and 190 ± 50 s^{-1} for the exchanges between solvated Cs$^+$ and the pc complex and for the exchange between the alt,3 and the pc complexes.

Below 314 K, a line shape analysis was not possible and the rate constants were measured by ^{133}Cs 2D-EXSY spectroscopy. A typical EXSY spectrum, obtained at 283 K, is shown in Figure 5. Cross-peaks between all sites are observed. The cross-peaks between the alt,3 and pc complex and between the solvated Cs$^+$ and the alt,3 complex always appear simultaneously. Figure 6 gives the cross-peak volumes as a function of the mixing time, τ_m, for all three exchanges. The rate constants were determined for the three processes. At 283 K the rate constant for the exchange between the solvated cesium cation and the pc,Cs$^+$ complex is 200 s^{-1}. The rate constants for the exchange between the alt,3 and the pc complex and between the alt,3 complex and the solvated cation are 18 and 19 s^{-1}, respectively.

As mentioned above, cross-peaks between all sites are observed, indicating an exchange of Cs$^+$ between all sites. At first, this seems to contradict the results obtained by the full line shape analysis at 314 K. However, if the same Cs$^+$ cation occupies all sites within the mixing time, cross-peaks between non-directly exchanging sites will appear in the 2D-EXSY spectrum.[34] These cross-peaks can be easily recognized by the fact that the rate constants derived from them match the rate constant of the slowest direct process. The rate constants for the exchange between the alt,3,Cs$^+$ and the pc,Cs$^+$ complexes and between the alt,3,Cs$^+$ complex and the solvated cation are identical within the precision of the experimental measurement.

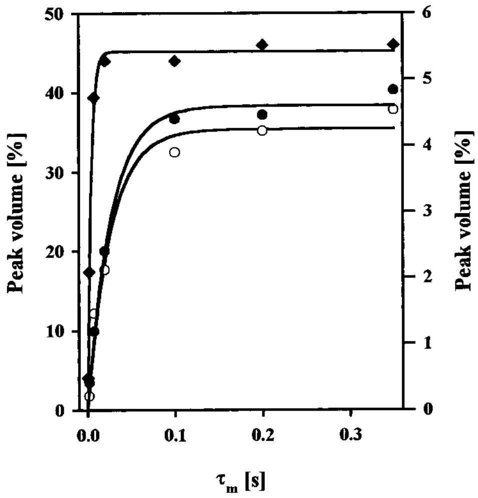


Figure 6. Cross-peak volumes of the ^{133}Cs 2D-EXSY as a function of the mixing times (τ_m) at 283 K: [**1**] = 43.3 mM and [CsI_3] = 80.4 mM. The left *Y* axis corresponds to the exchange between the solvated Cs^+ and partial cone complexed Cs^+ (◆). The right axis corresponds to the exchanges between the free and the 1,3 alternate complexed Cs^+ (●) and between the partial cone and 1,3 alternate complexed Cs^+ (○).

SCHEME 2

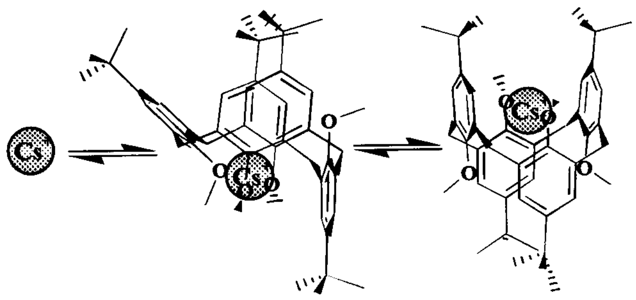


TABLE 3: Activation Parameters for Various Exchange Processes in a 1:1 Mixture of $CDCl_3$ and CD_3CN

exchange	ΔH^* (kJ/mol)	$\Delta S^{*\,d}$ (J/(mol K))	k_{314} (s^{-1})
Cs^+_{solv}−pc,Cs^+	38 ± 2	−66 ± 6	960[a]
alt,3,Cs^+−Cs^+_{solv}	59 ± 4	−13 ± 12	210[b]
alt,3,Cs^+−pc, Cs^+	61 ± 5	−9 ± 15	190[a]
pc−alt,3[c]	62 ± 9	−3 ± 30	220[b]

[a] Directly measured at 314 K. [b] Calculated from ΔH^* and ΔS^*. [c] Data from ref 17. [d] T = 300 K.

This confirms that a linear model, given in Scheme 2, accounts for the exchange pathways. This was also suggested by the line shape analysis at 314 K.

The activation parameters for the exchange processes are given in Table 3. The complexation of the solvated cesium cation by the partial cone conformer is characterized by ΔH^* and ΔS^*, respectively, of 38 ± 2 kJ/mol and −66 ± 6 J/(mol K). The entropy of activation is comparable to the one obtained for the case of the complexation of Na^+ by the cone conformer,[19] corresponding mainly to losses of translational entropies for the cation and the ligand, partly compensated by some desolvation of the cation. The activation parameters for the complexation by the alt,3 conformer is very different, with a much larger enthalpy of activation (59 ± 4 kJ/mol), and an entropy of activation (−13 ± 12 J/(mol K)) close to zero. It is remarkable that these data are almost identical with the activation parameters ($\Delta H^* = 61 \pm 5$ kJ/mol and $\Delta S^* = -9 \pm 15$ J/(mol K)) for the exchange between the two complexes, suggesting that the processes for the alt,3 complexation and for the Cs^+ exchange between the two complexes are identical. In fact, this is confirmed by the activation parameter values of the conformational exchange between the alt,3 and the pc conformer in the case of the uncomplexed calixarene **1**. An activation enthalpy in the order of magnitude of 60 kJ/mol and an entropy of activation close to zero are characteristic of conformational processes for this calixarene derivative.[17] These considerations show very clearly that the complexation of Cs^+ by the calixarene **1** is exclusively done by the pc conformer, which provides a set of three methoxy groups oriented in a favorable way for the Cs^+ complexation. Then, the complex can undergo a conformational exchange to the alt,3 conformer, from which the Cs^+ cation cannot escape directly, at least with a measurable rate constant compared to the other decomplexation route, the one passing through the pc conformer. This mechanism of complexation and exchange is shown in Scheme 2. The rate constants given in Table 3 at 314 K are a clear illustration of this scheme: while the complexation of Cs^+ by the pc conformer has a rate constant of 960 s^{-1}, the two other processes are much slower, in the order of magnitude of 200 s^{-1}, identical to the rate constant for the conformational exchange in the absence of complexation.

The alt,3 conformer complex is thermodynamically less stable than the pc complex, which can be rationalized by an interaction of cesium with two aromatic rings that is weaker than with one methoxy group. However, when incorporated in the cage of the alt,3 conformer, the steric interactions are too large to allow a fast decomplexation, which is done by a conformational interconversion to the pc, followed by faster decomplexation of this latter complex.

Since the ^{1}H NMR permits differentiation of the two sides of the complexed alt,3 conformer, giving two signals at 1.02 and 0.97 ppm (Figure 2), it is possible to test the hypothesis of an internal tunneling process, by which the Cs^+ cation would visit both sides of the alt,3 complex by an internal process. The two *tert*-butyl ^{1}H NMR signals coalesce around 300 K and the aromatics around 280 K. This corresponds to rate constants on the order of 60 and 15 s^{-1}, respectively. These values are also the rate constants for the conformational interconversion between the uncomplexed or complexed pc and alt,3 conformers, respectively, 70 and 12 s^{-1}. These data strongly suggest that the exchange of Cs^+ between the two sides of the alt,3 conformer does not follow here a tunneling process, contrary to what has been reported in the case of the silver cation with propoxycalixarene derivatives.[21] The exchange is done more rapidly by an interconversion to the pc complex, followed by its decomplexation. In the case of the silver tunneling, the Ag^+ cation (126 pm) has cationic radii smaller than the Cs^+ cation (167 pm), and the calixarene substitutions by propoxy groups instead of the methoxy groups of this study provides a much larger barrier for the conformational interconversions and for the direct decomplexation process.

In conclusion, the cesium cation is selectively complexed by the partial cone conformer of **1**. The 1,3 alternate complex coexists with the partial cone complex but is thermodynamically disfavored. The pc complex is kinetically more labile than the alt,3, and the decomplexation route for the alt,3 complex involves first a conformational interconversion to the pc complex.

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