Complexation of the Sodium Cation by a Calix[4]arene Tetraester in Solution. Formation of a 2:1 Calixarene:Sodium Complex

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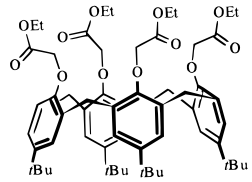
The complexation of the sodium cation by a calix[4]arene tetraester, 5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27,28-tetrakis((ethoxycarbonyl)methoxy)calix[4]arene (**1**) was studied by ^{1}H and ^{23}Na NMR in a 50:50 v:v mixture of deuteriated acetonitrile and deuteriated chloroform. A 1:1 complex was formed, in very slow exchange, both on the ^{1}H and on the ^{23}Na NMR time scales, with solvated calixarene and sodium cation, respectively. From ^{1}H NMR 2D exchange spectroscopy experiments and ^{23}Na NMR line width analysis, an upper limit of the rate constant for the dissociation of the 1:1 complex was estimated to be 3 Hz. A 2:1 calixarene:sodium complex in fast exchange with the 1:1 complex was evidenced by ^{23}Na NMR. The characteristic ^{23}Na NMR line widths of the 1:1 and of the 2:1 complexes, determined at several temperatures, were linearly related, with a slope of 1.8 ± 0.2. This corresponds to a reorientational correlation time, characteristic of the ^{23}Na quadrupolar relaxation, twice as large in the case of the 2:1 complex than in the case of the 1:1 complex. The standard enthalpy and the standard entropy of formation of the 2:1 complex could be estimated: $\Delta H° = -16 \pm 5$ kJ mol^{-1} and $\Delta S° = -28 \pm 17$ J K^{-1} mol^{-1}. It is speculated that this complex could be an intermediate in the pathway of the exchange of sodium cations between 1:1 complexes in solution.

Introduction

Calixarenes, cyclic oligomers of phenolic units linked through the ortho positions, are a fascinating class of macrocycles, because of their skeleton simplicity associated with versatile recognition properties both of metallic or organic ions and of neutral molecules.[1−4] The elucidation of the factors and of the mechanisms responsible for selective host−guest complexation in solution necessitates thermodynamic and kinetic studies of the complexation and dissociation processes.[5] Several rigorous thermodynamic studies on the complexation processes of calixarenes have appeared in the last few years.[6−10] Kinetic and mechanistic studies are more scarce.[11−15]

Among the large diversity of calixarene derivatives, the calix[4]arene esters are particularly interesting (Scheme 1). Their synthesis results in a conformer distribution remarkably affected by the metal cation present, sodium leading quantitatively to the cone conformer.[16] An intriguing solvent-dependent photochemical dissociation of their sodium salt was recently reported.[17] Their cone conformations are fixed in solution,[18,19] and they contain both hydrophobic and hydrophilic regions. The cryptand-like hydrophilic region, consisting of a cavity made of oxygen atoms from the original phenols and of the carbonyl oxygens, is particularly well adapted for the complexation of alkali metal cations,[19] while the hydrophobic cavity, made of the aromatic rings, can include neutral molecular guests, such as acetonitrile.[20,21] In previous papers, the kinetics of the conformational processes[11] and of the sodium cation complexation[12] of the tetramethoxy derivative of calix[4]arene were reported.[11,12] While the hydrophilic part of the cone conformation of the tetramethoxy derivative is analogous to a crown ether, it is reminiscent of the cryptand cavity in the case of the tetraester derivative.

SCHEME 1



In this paper, the complexation of the sodium cation by the calix[4]arene **1** is studied by ^{1}H and ^{23}Na NMR in a mixture of acetonitrile and chloroform to permit comparison with previously studied systems.[12] The exchange kinetics of the sodium cation complexed by **1** are too slow to be determined by this method. A 2:1 calixarene:sodium complex in fast exchange with the 1:1 complex was evidenced by ^{23}Na NMR. This complex could be an intermediate in the pathway of the exchange of sodium cations between 1:1 complexes in solution.

Experimental Section

5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27,28-tetrakis((ethoxycarbonyl)methoxy)calix[4]arene (**1**) and sodium tetraphenyl borate were purchased from Aldrich with purities, respectively, of 97% and +99.5%. The calixarene was used without further purification. Sodium tetraphenylborate was dried in an oven at 100 °C for at least one day.

^{1}H and ^{23}Na NMR spectra were recorded on a Bruker AMX 500 spectrometer operating at 500.13 and 132.30 MHz, respectively. Five millimeter NMR tubes sealed with parafilm were used. The solvent was a 50:50 mixture of deuteriated chloroform and deuteriated acetonitrile (1:1 by volume). Acetonitrile-d_3 (99.6%) was purchased from Aldrich and chloroform-*d* (99.8%) from Cambridge Isotope Laboratories. Both solvents were dried over 4 Å molecular sieves.

The ^{1}H NMR spectra were recorded with a 90° pulse width of 6.3 μs. The chloroform signal in CD_3CN was used as internal reference for the ^{1}H chemical shifts (7.46 ppm), based on a value of 1.93 ppm for the chemical shift of acetonitrile-d_3 at 27 °C. The acquisition time and the delay between two pulses

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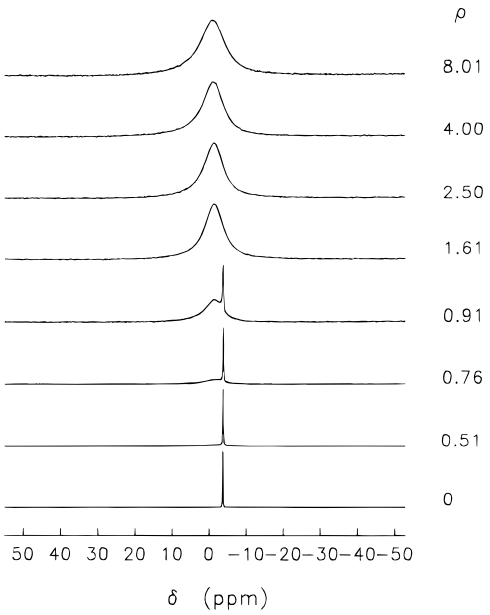

Figure 1. ^{23}Na NMR spectra of 20 mM $NaBPh_4$ in the presence of various amounts of **1** at 300 K ($\rho = [\mathbf{1}]_{tot}/[NaBPh_4]_{tot}$).

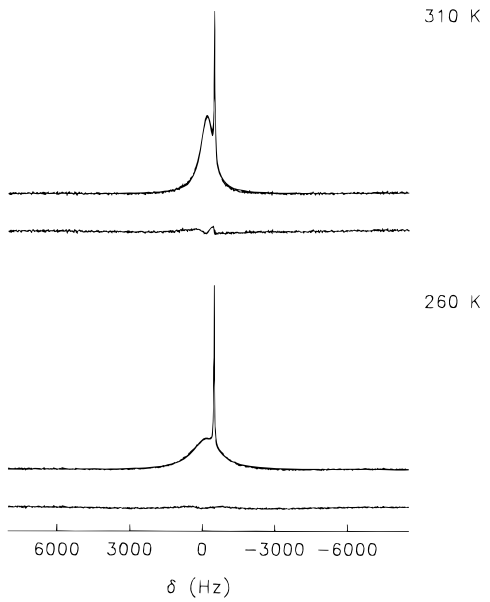

Figure 2. ^{23}Na NMR spectra of 20 mM $NaBPh_4$, in the presence of **1** at 310 and 260 K, showing the measured spectrum, (the fit from DNMR5 ($k = 0$)), and the difference between the experimental and the calculated spectra.

were 4.65 and 1 s, respectively. Typically, the number of scans was 150. A standard NOESY pulse sequence was used for the 2D exchange spectroscopy (2D EXSY) experiments.[11,12,22−24] The NMR parameters were delay time, 2 s; 90° pulse, 6.1 μs; sweep width, 3.6 kHz; acquisition time, 0.141 s; and eight scans of 1024 points by 104 slices and a mixing time (τ_m) of 0.10 s.

A 90° pulse of 10 μs was used in the case of the ^{23}Na NMR spectra. All chemical shifts were referenced against the 2.00 $\times 10^{-2}$ M stock solution of $NaBPh_4$ in 50:50 v:v $CDCl_3$:CD_3CN, used throughout this study, at 300 K. The chemical shift of this stock solution is −3.71 ppm referenced to a 1.0 $\times 10^{-2}$ M NaCl solution in 10% D_2O. The acquisition times ranged from 16.4 to 143 ms, corresponding to sweep widths of 31.3−14.3 kHz. The relaxation delay time was 0.1 s ($>5T_1$ in all cases). The longitudinal relaxation times were measured by the inversion recovery pulse sequence. Typically, the number of scans was 3000−20 000.

The temperature calibration was done with a thermocouple inserted in a nonspinning tube containing chloroform or water. The temperature was estimated to be reliable at ±0.5 K.

Results

Figure 1 shows the ^{23}Na NMR spectra of a 2.00 $\times 10^{-2}$ M solution of sodium tetraphenylborate ($NaBPh_4$) at 300 K, in a mixture of 50:50 v:v $CDCl_3$:CD_3CN, in the absence and in the presence of increasing quantities of **1**. In the presence of **1**, a broad line, attributed to a 1:1 complex Na^+−**1**, is observed about 2.5 ppm downfield from the signal of the solvated sodium at −3.71 ppm. The relative intensity of the broad signal increases with an increase of ρ, defined as $\rho = [\mathbf{1}]_{tot}/[NaBPh_4]_{tot}$, while the signal of the solvated sodium remains narrow. For values of ρ larger than 1, a single broad peak is observed. The ^{23}Na NMR spectra of the solutions corresponding to the ρ values indicated on Figure 1 were systematically recorded at temperatures of 240, 250, 260, 275, 300, and 310 K. In all the cases, similar evolutions were observed, characteristic of a very slow exchange of the sodium cation between the uncomplexed and complexed sites on the ^{23}Na NMR time scale. All the spectra of solutions with $\rho < 1$ were submitted to a full line shape analysis, using the DNMR5 software.[25] The fact that the two sites are in very slow exchange was confirmed by the necessity of using a rate constant of zero in the full line shape analysis. Two examples of this analysis are shown on Figure 2, for $\rho = 0.91$, at 260 and 310 K. The populations, the line widths, and the chemical shifts of the two sites could be obtained in all the cases. The line widths and the chemical shifts of the spectra corresponding to $\rho > 1$ were obtained after fitting the spectra to a Lorentzian line.

The populations of the two sites, p_A and p_B, confirm the formation of a 1:1 complex with a large equilibrium constant of formation ($K_f > 10^5$). In the limits of the experimental error, the chemical shifts of solvated sodium remain constant, while a small, but systematic, variation of the chemical shifts of the complexed sodium is observed. For example, the chemical shift of Na^+−**1**, obtained for $\rho = 0.26$, is −1.67 ppm at 310 K. It shifts regularly to a value of −1.02 ppm for $\rho = 8.0$. The nonconstancy of the NMR parameters of the signal of the complexed sodium is striking if one considers the line width variations. Figure 3 shows the variation of the ^{23}Na NMR line widths $(\nu_{1/2})_B$ obtained for the complexed species as a function of the total concentration of **1**, at the various temperatures used in this study. The line widths increase regularly. For example, at 260 K, $(\nu_{1/2})_B$ is 897 Hz for $\rho = 0.26$. It broadens to 1800 Hz in the case of $\rho = 8.01$. As shown in Figure 3, the curves obtained are characteristic of an equilibrium between two or more species. It was checked that this observed broadening is not due to a chemical exchange contribution. Since, in the limits of the moderately fast exchange, the observed line width contains a field-dependent exchange component,[26,27] some spectra were recorded at a different frequency (79.30 MHz) for comparison. In the limits of the experimental error, the line widths were identical at 132.30 and at 79.30 MHz, ruling out a contribution from chemical exchange on the observed line width. For example, $(\nu_{1/2})_B$ was measured to be 937 Hz at 79.30 MHz and 902 Hz at 132.3 MHz, in the case of $\rho = 4.0$ at 300 K. Consequently, the observed line width results from a fast averaging of at least two signals. Moreover, as shown in Figure 4 for several ρ values, $(\nu_{1/2})_B$ is linearly related to the inverse temperature. This experimental observation also precludes a chemical exchange contribution to $(\nu_{1/2})_B$.

On the basis of the variations shown in Figure 3, the most plausible model, and the most simple, is to take a 2:1 complex

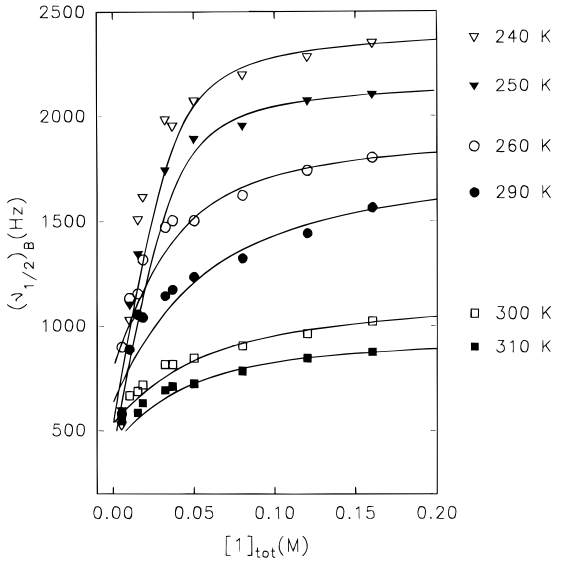

Figure 3. ^{23}Na NMR line widths of the complexed species $(\nu_{1/2})_B$ as a function of the total concentration of **1** at various temperatures. The data points are experimental, and the solid lines are calculated on the basis of eq 4.

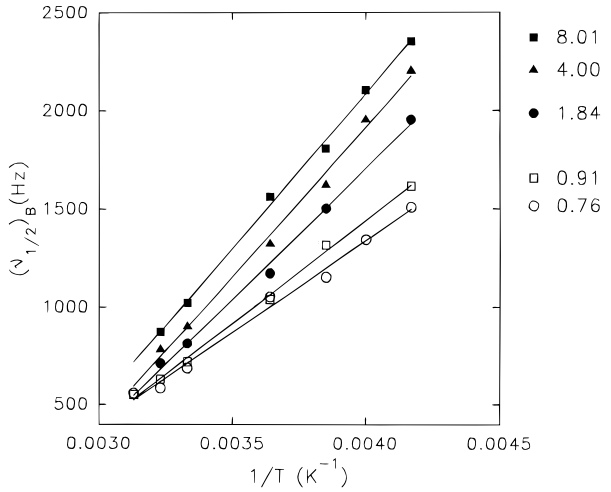

Figure 4. ^{23}Na NMR line widths of the complexed species $(\nu_{1/2})_B$ as a function of $1/T$ for a series of ρ values.

into consideration a $(\mathbf{1})_2$−Na^+ species. The observed line width $(\nu_{1/2})_B$ is then given by eq 1, where p_I and p_{II} are, respectively, the populations of the 1:1 and of the 2:1 complexes, characterized, respectively, by line widths $(\nu_{1/2})_I$ and $(\nu_{1/2})_{II}$.

$$(\nu_{1/2})_B = p_I(\nu_{1/2})_I + p_{II}(\nu_{1/2})_{II} \quad (1)$$

Equations 2 and 3 account for the experimental ^{23}Na NMR observations.

$$Na^+ + C \rightleftarrows (C, Na)^+ \quad (2)$$

$$(C, Na)^+ + C^* \rightleftarrows (C, Na, C^*)^+ \quad (3)$$

The equilibrium of eq 2, corresponding to the formation of the 1:1 complex, is very slow on the ^{23}Na NMR time scale, while the equilibrium of eq 3 is very fast. The two calixarene molecules involved in the 2:1 complex are chemically different and are identified C and C*. This point will be addressed below in the section on ^{1}H NMR and will be discussed in the Discussion section. At each temperature, the stability constant for the formation of the 2:1 complex (eq 3) K_2, the populations p_I and p_{II} (eq 1), as well as $(\nu_{1/2})_I$ and $(\nu_{1/2})_{II}$ (eq 1) could be determined from eq 4. It was assumed that the dilutions were high enough to neglect the ionic factors γ_i and to use concentrations instead of activities. The derivation of eq 4 is given in the Supporting Information. with

TABLE 1: Stability Constant K_2 and ^{23}Na NMR Line Withs of the 1:1 ($(\nu_{1/2})_I$) and 2:1 ($(\nu_{1/2})_{II}$) Complexes at Various Temperatures

T (K)	$(\nu_{1/2})_I$ (Hz)	$(\nu_{1/2})_{II}$ (Hz)	ln K_2
240	1400 ± 300	2420 ± 30	4.7 ± 0.5
250	1200 ± 300	2170 ± 20	4.7 ± 0.6
260	1190 ± 90	1940 ± 50	3.6 ± 0.4
275	930 ± 80	1800 ± 100	3.0 ± 0.5
300	690 ± 30	1170 ± 50	2.9 ± 0.4
310	590 ± 30	960 ± 20	3.2 ± 0.3

$$\rho[Na^+]_{tot} = \frac{(1-\Delta)}{\Delta K_2} + \alpha(2-\Delta) \quad (4)$$

$$\Delta = \frac{(\nu_{1/2})_{obs} - (\nu_{1/2})_{II}}{(\nu_{1/2})_I - (\nu_{1/2})_{II}}$$

and with

$$\alpha = [Na^+]_{tot}/(1+p) \quad \text{and} \quad p = p_A/p_B$$

The unknown parameters were determined from eq 4 by nonlinear regression analysis. They are given in Table 1. In Figure 3, the points are experimental and the solid lines are calculated according to the values given in Table 1. The standard enthalpy and the standard entropy of formation of the 2:1 complex could be estimated from the temperature variation of K_2. The values obtained are $\Delta H° = -16 \pm 5$ kJ mol^{-1} and $\Delta S° = -28 \pm 17$ J K^{-1} mol^{-1}. A large error is associated with these data, since they result from values of K_2 themselves obtained with a large error from the nonlinear regression analysis.

Despite the regular variation of the ^{23}Na NMR chemical shifts with ρ, a similar regression analysis was not done on the chemical shifts since their total variation is less than one ppm, in contrast with the total variation of the line widths which permits an accurate analysis. However, the plot of the observed chemical shift as a function of the population of the 1:1 complex, calculated from the line widths data, is linear, giving an estimate of the chemical shifts characteristic of each species, respectively, of −1.5 and −0.6 ppm at 300 K for the 1:1 and the 2:1 complexes.

Figure 5 shows the ^{1}H NMR spectra, in the region 3.0−5.0 ppm, of various amounts of **1** in a mixture 1:1 v:v of CD_3CN-$CDCl_3$ at 300 K, in the presence of a 20 mM solution of $NaBPh_4$. The assignment of the ^{1}H NMR peaks of **1** was done according to the literature.[6,7,18,19] Singlets were observed at 1.04, 4.70, and 6.86 ppm, corresponding to the *tert*-butyl groups on the upper rim, to the methoxy groups, and to the aromatic protons, respectively. The pair of doublets observed at 3.16 and 4.74 ppm is an AB system associated to the methylene bridging groups. The quadruplet at 4.13 ppm and the triplet at 1.21 ppm correspond to the ethyl ester group. As indicated by the ^{1}H NMR spectrum, **1** is in a cone conformation.[19] Upon the addition of Na^+ new signals appear, also characterized by a cone pattern. They can be attributed to complexed **1**. Their intensity increases with the relative amount of Na^+, and they are the only ones observed when sodium is in excess ($\rho < 1$). This is comparable with previously reported results in the literature.[13,19] The ^{1}H NMR chemical shifs depend slightly upon the relative amounts of calixarene over Na^+. Typically, they

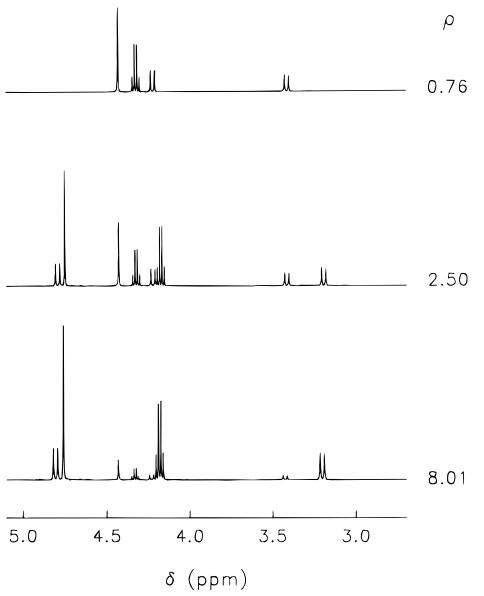

Figure 5. ^{1}H NMR spectra of various amounts of **1** in the presence ($\rho = 0.76$, 2.50, and 8.01) of a 20 mM solution of $NaBPh_4$ at 300 K ($\rho = [\mathbf{1}]_{tot}/[NaBPh_4]_{tot}$).

vary by amounts in the range from 0.01 to 0.03 ppm. Even if too small to permit a quantitative analysis, these variations are in agreement with the chemical model given in eq 2 and 3 and are discussed below (eq 5).

An EXSY experiment was carried out on $\rho = 2.5$ at 300 K with a mixing time of 100 ms. No cross peak linking the signals of complexed and uncomplexed **1** could be detected. Since the longitudinal relaxation times of **1** are in the range 0.20−0.30 s, an *upper* limit of the rate constant for the exchange of calixarene between the two sites in eq 2 can be estimated to be in the Hz range.[22]

Discussion

The thermodynamic parameters of complexation of the sodium cation by **1** have been determined in acetonitrile.[20] The equilibrium constant of formation of the complex (K_f) is 6.3×10^5 at 298 K. It is reasonable to assume that in the 50:50 mixture of acetonitrile and chloroform used in this study, K_f will be at least equal to the value in pure acetonitrile. This is borne out by the ^{23}Na NMR titration shown in Figure 1, where the signal corresponding to uncomplexed sodium disappears for ρ values larger than 1.0, since, for values of K_f larger than 10^5, the complexation appears quantitative by NMR.[28]

The crystal structure of a 1:1 clathrate **1**:CH_3CN has been solved,[21] showing that an acetonitrile molecule is included in the calixarene cavity along the 4-fold axis with the methyl group inside the cavity.[21] It is then reasonable to assume that, in solution, the cavity is also occupied by an acetonitrile molecule. Toluene, with the methyl group pointing toward the cavity, has been shown to be included in the cavity of a calixarene complexing a sodium cation.[29] On that basis, one could expect the tetraphenylborate counteranion to accompany the sodium cation, with one of its phenyl rings included in the calixarene cavity. The fact that no interaction between **1** and the tetraphenylborate anion could be detected by ^{1}H NMR, despite the potential π interactions between the phenyl groups and the methyl groups of the *tert*-butyl moiety, could be due to an unfavorable competition with the highly concentrated acetonitrile solvent for the occupation of the receptor cavity. Moreover, de Namor *et al.*[30] have shown that, in acetonitrile, the perchlorate anion is not associated with the sodium cation complexed by a butylcalix[4]arene tetraester. Like perchlorate, tetraphenylborate is a self-stabilizing anion, known for its weak propensity to form ion pairs in a variety of nonaqueous solvents,[31,32] including acetonitrile.[31] This is particularly true in the case of the low concentrations used in this study (typically 20 mM).

The exchange of the sodium cation between its complexed and uncomplexed states is very slow on the ^{23}Na NMR time scale, below a detectable limit. Since $\pi(\nu_{1/2})_{obs} = (T_2^{-1} + k)$,[27] and since no significant broadening is observed on the signal of solvated sodium (the sharper peak) and assuming that a detectable broadening would be 10% of the observed signal, an approximate upper limit of 3 Hz can be assigned to the exchange rate constant at 300 K. This is confirmed by the absence of detectable cross peaks on the ^{1}H 2D EXSY spectrum. This upper limit is slower than the rate measured previously by Jin and Ichikawa[13] in the case of the same calixarene derivative presumably because of the presence of a more donating solvent, methanol, and of a more associating anion, thiocyanate. In this case, both the solvent and the anion should favor the expected dissociative mechanism responsible for the cation exchange and should strongly increase the exchange rate constant.[5]

The increase of the ^{23}Na NMR line width of the complexed sodium with an increase of the calixarene concentration can be rationalized by the following model (eq 5).

$$(C, Na)^+ + C^* \rightleftarrows ((C, Na)^+, C^*) \quad \text{(fast)} \qquad (5a)$$

$$((C, Na)^+, C^*) \rightleftarrows ((C^*, Na)^+, C) \quad \text{(very slow)} \qquad (5b)$$

$$((C^*, Na)^+, C) \rightleftarrows (C^*, Na)^+ + C \quad \text{(fast)} \qquad (5c)$$

A fast equilibrium is established between the complex and an additional calixarene molecule (eqs 5a and 5c). This is observed on the ^{23}Na NMR spectra of the complexed species. The line widths of the 1:1 and of the 2:1 complexes could be calculated on the basis of eq 3 (Table 1). The relaxation of ^{23}Na, purely quadrupolar, is given by Equation 6,[33,34]

$$T_q^{-1} = \pi\nu_{1/2} = (2\pi^2/5)(e^2qQ/h)^2\tau_q \qquad (6)$$

where $\nu_{1/2}$ is the line width at one-half the height of the Lorentzian signal, (e^2qQ/h) is the quadrupolar coupling constant, q is the electric field gradient at the quadrupolar nucleus site, Q is the quadrupole moment, and τ_q is the correlation time associated to the quadrupolar relaxation. Since τ_q is proportional to the volume of the reorientating entity through the Debye−Stokes−Einstein equation,[35] one can further test the model given in eqs 5a−c: the quadrupolar relaxation rate of the 2:1 complex should be roughly twice as large as the quadrupolar relaxation rate of the 1:1 complex since the volume is roughly doubled, while the efg should remain constant, since the sodium cation remains in the calixarene hydrophilic cavity. Figure 6 gives a plot of the calculated line widths of the 2:1 complex versus the calculated line widths of the 1:1 complex at several temperatures. Indeed, in agreement with eq 6 and the model of eq 5, the plot is linear with a slope of 1.8 ± 0.2.

The thermodynamic values for the formation of the 2:1 adduct from the 1:1 complex were estimated by ^{23}Na NMR as $\Delta H° = -16 \pm 5$ kJ mol^{-1} and $\Delta S° = -28 \pm 17$ J K^{-1} molmol^{-1}. The association of a second calixarene molecule with the sodium complex is driven by enthalpy, since, quite expectedly, the corresponding entropy is negative.

One can only speculate on the structure of such a 2:1 complex. The latter should not be visualized as a "classical", symmetrical, sandwich complex, similar to 2:1 complexes of crown ethers

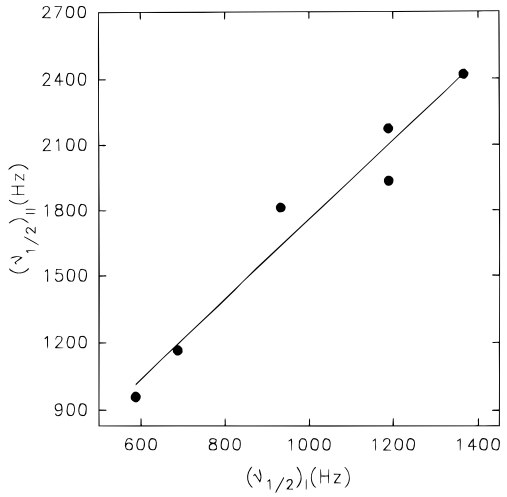

Figure 6. ^{23}Na NMR line widths of the 2:1 complex as a function of the ^{23}Na NMR line widths of the 1:1 complex calculated at several temperatures from a regression analysis based on eqs 3 and 4.

with alkali metal cations, for example, since such a structure would then provide a fast way for the exchange of calixarene molecules in the coordination shell of the sodium cation. This is not observed by ^{1}H NMR. Rather, one could visualize this 2:1 complex as an outer-sphere association of the hydrophilic part of a second calixarene molecule with a sodium cation encaged in the 1:1 complex with the 1:1 complex retaining most of its structural integrity. The exchange of the sodium cation from the complexation cavity of one calixarene to the other should then involve a dissociation process similar to the expected dissociative process for the 1:1 complex, with rate constants in the same order of magnitude, the exchange being very slow in this case. At this stage, one cannot exclude the possibility of two calixarene molecules encapsulating one single molecule of the acetonitrile guest, similar to what has been shown in the crystalline state in the case of anisole.[36]

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Supporting Information Available: Derivation of eq 4 (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) Gutsche, C. D. *Acc. Chem. Res.* **1983**, *16*, 161.
(2) Gutsche, C. D. *In Calixarenes*; Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge, 1989.
(3) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713.
(4) Takeshita, M.; Shinkai, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1088.
(5) Detellier, C. Complexation Mechanisms. In *Comprehensive Supramolecular Chemistry*; Gokel, G., Ed.; Elsevier Science: Oxford, 1996; Vol. 1, Chapter 9, pp 357−375.
(6) Arnaud-Neu, F.; Barrett, G.; Cremin, S.; Deasy, M.; Ferguson, G.; Harris, S. J.; Lough, A. J.; Guerra, L.; McKervey, M. A.; Schwing-Weill, M. J.; Schwinte, P. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1119.
(7) de Namor, A. F. D.; Gil, E.; Tanco, M. A. L.; Tanaka, D. A. P.; Salazar, L. E. P.; Schulz, R. A.; Wang, J. *J. Phys. Chem.* **1995**, *99*, 16781.
(8) de Namor, A. F. D.; Gil, E.; Tanco, M. A. L.; Tanaka, D. A. P.; Salazar, L. E. P.; Schulz, R. A.; Wang, J. *J. Phys. Chem.* **1995**, *99*, 16776.
(9) Arnaud-Neu, F.; Barrett, G.; Fanni, S.; Marrs, D.; McGregor, W.; McKervey, M. A.; Schwing-Weill, M.-J.; Vetrogon, V.; Wechsler, S. *J. Chem. Soc., Perkin Trans. 2* **1995**, 453.
(10) de Namor, A. F. D. *Pure Appl. Chem.* **1993**, *65*, 193.
(11) Blixt, J.; Detellier, C. *J. Am. Chem. Soc.* **1994**, *116*, 11957.
(12) Blixt, J.; Detellier, C. *J. Am. Chem. Soc.* **1995**, *117*, 8536.
(13) Jin, T.; Ichikawa, K. *J. Phys. Chem.* **1991**, *95*, 2601.
(14) Dijkstra, P. J; Brunink, J. A. J; Bugge, K.-E.; Reinhoudt, D. N.; Harkema, S.; Ungaro, R.; Ugozzoli, F.; Ghidini, E. *J. Am. Chem. Soc.* **1989**, *111*, 7567.
(15) Bakker, W. I. I.; Haas, M.; Khoobeattie, C.; Ostaszewski, R.; Franken, S. M.; Denhertog, H. J.; Verboom, W.; Dezeeuw, D.; Harkema, S.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1994**, *116*, 123.
(16) Iwamoto, K.; Shinkai, S. *J. Org. Chem.* **1992**, *57*, 7066.
(17) Barrett, G.; Corry, D.; Creaven, B. S.; Johnston, B.; McKervey, M. A.; Rooney, A. *J. Chem. Soc., Chem. Commun.* **1995**, 363.
(18) Yamada, A.; Murase, T.; Kikukawa, K.; Arimura, T.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 2* **1991**, 793.
(19) Arduini, A.; Pochini, A.; Reverberi, S.; Ungaro, R.; Andreetti, G. D.; Ugozzoli, F. *Tetrahedron* **1986**, *42*, 2089.
(20) de Namor, A. F. D.; de Sueros, N. A.; McKervey, M. A.; Barrett, G.; Arnaud Neu, F.; Schwing-Weill, M. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1546.
(21) McKervey, M. A.; Seward, E. M.; Ferguson, G.; Ruhl, B. L. *J. Org. Chem.* **1986**, *51*, 3581.
(22) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935.
(23) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.
(24) Ernst, R. R., Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon Press: Oxford, 1987.
(25) Stephenson, D. S.; Binsh, G. *QCPE* **1978**, *11*, 365.
(26) Delville, A.; Stöver, H. D. H.; Detellier, C. *J. Am. Chem. Soc.* **1987**, *109*, 7293.
(27) Detellier, C. Reaction Kinetics and Exchange. In *Practical Spectroscopy Series*; Popov, A. I., Hallenga, K., Eds.; Marcel Dekker: New York, 1990; Vol. 11, p 521.
(28) Stöver, H. D. H.; Delville, A.; Detellier, C. *J. Am. Chem. Soc.* **1985**, *107*, 4167.
(29) Bott, S. G.; Coleman, A. W.; Atwood, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 1709.
(30) de Namor, A. F. D.; Cabaleiro, M. C.; Vuano, B. M.; Salomon, M.; Pieroni, O. I.; Tanaka, D. A. P.; Ng, C. Y.; Tanco, M. A. L.; Rodriguez, N. M.; Garcia, J. D. C.; Casal, A. R. *Pure Appl. Chem.* **1994**, *66*, 435.
(31) Erlich, R. H.; Popov, A. I. *J. Am. Chem. Soc.* **1971**, *93*, 5620.
(32) Greenberg, M. S.; Bodner, R. L.; Popov, A. I. *J. Phys. Chem.* **1973**, *77*, 2449.
(33) Detellier, C. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2, (Chemically and Biochemically Important Elements) p 105.
(34) Detellier, C., Graves, H. P.; Brière, K. M. Alkali Metal NMR Studies of Synthetic and Natural Ionophore Complexes. In *Isotopes in the Physical and Biomedical Science*; Buncel, E., Jones, J. R., Eds.; Elsevier: Amsterdam, 1991; Vol. 2, Chapter 4, p 159.
(35) Bisnaire, M.; Detellier, C.; Nadon, D. *Can. J. Chem.* **1982**, *60*, 3071.
(36) Ungaro, R.; Pochini, A.; Andreetti, G. D.; Domiano, P. *J. Chem. Soc., Perkin Trans. 2* **1985**, 197.