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Complexation of the Sodium Cation by a Calix[8]arene Derivative: Formation of 2:1 and 3:1 Na$^+$-Calixarene Complexes in Solution

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The complex formation between sodium tetraphenylborate and Octaethyl-*p-tert*-Butylcalix[8]arene Octaacetate has been studied in a 1:1 binary mixture of deuterated chloroform and deuterated acetonitrile by ^{23}Na NMR spectroscopy. The formation of complexes with 2:1 and 3:1 calix[8]arene/Na$^+$ stoichiometries is reported. The dissociation equilibrium constant is $9.3*10^{-8}$ M^2 for the 2:1 complex. It is $3.2*10^{-3}$ M for the dissociation of the 3:1 complex to form the 2:1 complex.

Keywords: Calixarenes, ^{23}Na NMR, complexes, complex formation, solution, cation recognition

INTRODUCTION

Calix[*n*]arenes are macrocyclic phenol-formaldehyde condensation oligomers which got widespread attention due to their versatile recognition properties towards neutral, cationic and anionic guests [1-7]. The selectivity of the complexation properties can be controlled by the size of the calixarene and by substitutions at the phenolic oxygen (lower rim) [8-16]. The thermodynamics of the complexation of cations by lower rim modified calixarenes, particularly alkali metal cations by calix[4]arenes, was recently reviewed by McKervey *et al.* [17]. Complexes between alkali metal cations and neutral calix[4]arenes have usually a 1:1 stoichiometry. The stoichiometry of alkali metal cation complexes with calix[6]arene and calix[8]arenes is not well known, and in most studies the formation of 1:1 complexes was generally assumed, the formation of higher stoichiometries complexes not being explicitly taken in consideration [8, 9, 11, 18-21].

Recently the kinetics and mechanisms of the alkali metal cation complexation by calix[4]arenes and their conformational interconversion in binary mixtures of chloroform and acetonitrile were studied by Detellier *et al.* [22-26]. Extension of these studies to larger calixarenes requires a precise knowledge of the complexes formed and of their stoichiometry. This prompted us to determine the stoichiometry of the complexes formed between a calix[8]arene and

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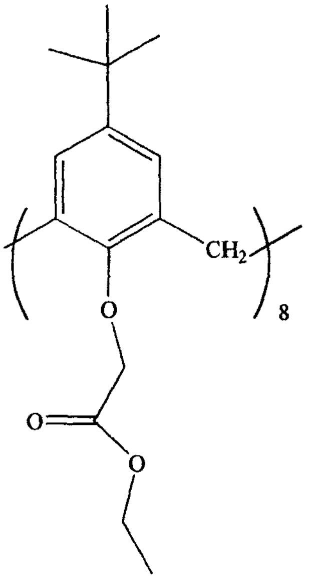
the sodium cation using ^{23}Na NMR chemical shifts and line widths.

In this paper, the complexation of the sodium cation by Octaethyl-*p*-*tert*-Butycalix[8]arene Octaacetate (**1**) (Scheme I) was studied in a 1:1 binary mixture of deuterated acetonitrile and deuterated chloroform by ^{23}Na NMR spectroscopy. It is shown that **1** and Na$^+$ form two predominant complexes having 2:1 and 3:1 stoichiometries.



SCHEME I

RESULTS AND DISCUSSION

Figure 1 shows the ^{23}Na NMR spectra of variable amounts of **1** (from 0 to 22.3 mM) in the presence of 22 mM sodium tetraphenylborate (NaB(Ph)$_4$) in the binary mixture chloroform:acetonitrile (1:1 by volume) at 300 K. In all solutions only one peak of Lorentzian lineshape can be observed. The line width increases with increasing concentrations of **1** and the chemical shift is slightly shifted towards higher frequencies. These variations indicate a fast exchange of Na$^+$ between at least two species, solvated and bound Na$^+$.

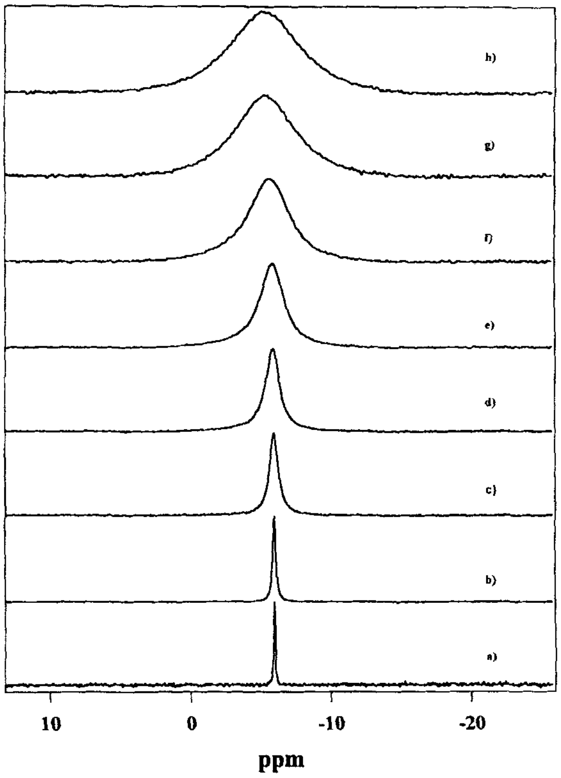


FIGURE 1 ^{23}Na NMR spectra of 22 mM sodium tetraphenylborate in the absence (a) and the presence (b-h) of various amounts of Octaethyl-*p*-*tert*-Butylcalix[8]arene Octaacetate at 300 K. a) 0, b) 0.9, c) 2.8, d) 4.7, e) 6.5, f) 8.6, g) 11.3 and h) 22.3 mM.

The ^{1}H NMR spectra show that the tetraphenylborate anion resonances at 7.06, 6.74 and 6.58 ppm are invariant upon the addition of **1**, excluding the possibility of interactions between the tetraphenylborate and **1** or its sodium complexes. This is in agreement with previous observations in the same solvent system [26]. Moreover, a concentration study in the range 4.7 – 45.3 mM of the chemical shift and of the line width of NaB(Ph)$_4$ in the binary mixture of this study show that these two parameters remain essentially independent of the Na$^+$ concentration.

The line width variation is shown on the top part of Figure 2, as a function of the concentrations of **1**. For [**1**]/[Na$^+$] < 0.3 the line width is roughly proportional to the concentration of **1**.

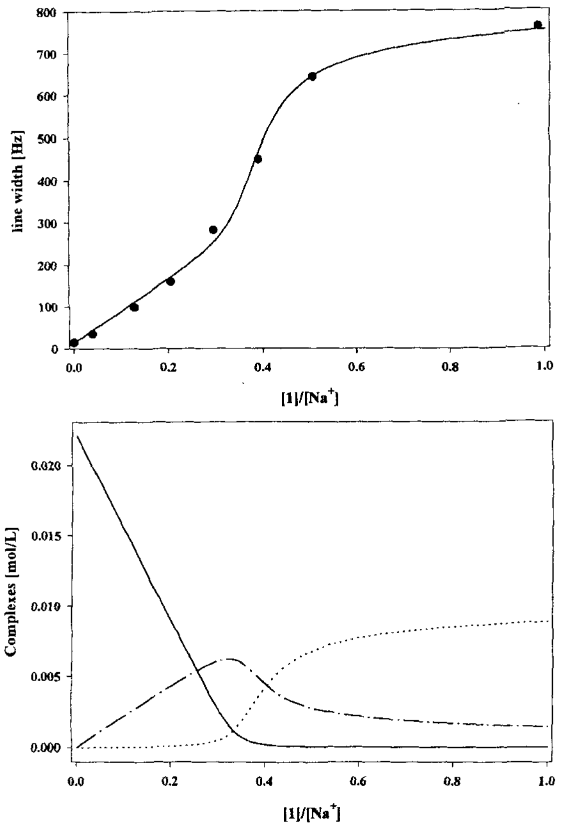


FIGURE 2 ^{23}Na NMR line width of 22 mM Na^+ in the presence of various amounts of calix[8]arene (**1**). Top: • measured line width. The solid line is calculated on the basis of the formation of 2:1 and 3:1 complexes using Eqs. (3–7). Bottom: Concentration profiles calculated from Eqs. (3–7). -solvated Na^+,... 2:1 complex and -•- 3:1 complex.

For $0.3 < [\mathbf{1}]/[Na^+] < 0.5$ a steeper increase of the line width is observed and reaches saturation for larger $[\mathbf{1}]/[Na^+]$.

Obviously, the observed curvature cannot be interpreted assuming the formation of one complex only [27–29]. If one type of complex only was formed, one could not observe the presence of an inflection point of the graph. The solid line is the best fit obtained, assuming the formation of 2:1 and 3:1 complexes, as described in the experimental part (Eqs. 3–7). The agreement between the experimental and the calculated line widths is very good. Other models were tested, in particular the simultaneous formation of 1:1 and 2:1 complexes, as well as the formation of 2:1 and 4:1 complexes. In none of these cases, any agreement could be found between the calculated and the experimental data (see below).

The 2:1 and 3:1 complexes have dissociation equilibrium constants of $9.3{*}10^{-8}\,M^2$ and $3.2{*}10^{-3}\,M$ and are characterized by line widths of 840 and 140 Hz respectively (Tab. I). The large difference between the line width characterizing the two complexes is indicative of a major difference in the nature of the sodium coordination shell. A value of 14 Hz for the line width of solvated sodium indicates that the coordination shell is symmetrical, with exclusively acetonitrile ligands. Upon complexation, some of the acetonitrile ligands are replaced by acetate groups, which creates a dissymmetric electronic distribution around the quadrupolar cation, increases the electric field gradient and, consequently, the quadrupolar coupling constant and the observed line width [27,30,31]. Interestingly, the line width is much larger in the case of the 2:1 than the 3:1 complex, suggesting a low symmetry in the case of the 2:1 complex. The ^1H NMR spectra recorded at various $[\mathbf{1}]/[Na^+]$ ratios, show a single broad signal for each type of calixarene protons at 300 K, indicative of relatively fast exchange between several species and/or conformations.

The value of the equilibrium constant for the formation of the 1:1 complex could not be obtained from the data. The value for the 2:1 complex is for a cumulative constant, corresponding to the fixation process of two sodium cations. Its value, $1.1{*}10^7\,M^{-2}$, is larger than the square of the value of the equilibrium constant corresponding to the fixation of the third sodium cation, $3.1{*}10^2\,M^{-1}$, showing, at first approx-

TABLE I ^{23}Na NMR chemical shifts and line widths and dissociation constants for the solvated Na^+, 2:1 and 3:1 complexes at 300 K

	$Na^+_{,solvated}$	2:1	3:1	$K_2[M^2]$	$K_3[M]$
δ [ppm]	-6.3	-5.5	-6.1	$1.3{*}10^{-9}$	$3.6{*}10^{-4}$
$\nu_{1/2}$[Hz]	14.4	840	140	$9.3{*}10^{-8}$	$3.2{*}10^{-3}$

imation, that the cation binding is slightly anticooperative. This is expected both from entropic and enthalpic (electrostatic repulsions) reasons.

The calculated concentration profile, shown at the bottom of Figure 2, shows that up to [1]/[Na$^+$] < 0.3, the 3:1 complex is almost exclusively formed and for [1]/[Na$^+$] > 0.3, a conversion from the 3:1 to the 2:1 complex takes place. This conversion is however not complete in the [1]/[Na$^+$] range studied.

The formation of 2:1 complexes between Na$^+$ and **1** is in agreement with results from Shinkai *et al.* [32] based on mass spectrometry. However, in that work, simultaneous formation of 1:1 and 2:1 complexes was observed, with no evidence for higher stoichiometry complexes. This is probably due to the exclusive use of [1]/[Na$^+$] = 0.5 in their study. A strong dependence upon the nature of the counter-anion was observed, with the formation of the 2:1 complex being favored in the case of iodide compared to the more associating chloride anion. In the present study, the non associating tetraphenylborate anion was used, leading to the formation of 2:1 and 3:1 complexes, with no evidence for the formation of 1:1 complexes.

The ^{23}Na chemical shift are shown as function of added **1** on top of Figure 3. The solid line is the best fit obtained assuming the formation of 2:1 and 3:1 complexes, on the basis of Eqs. (3–7). The agreement between the calculated and the experimental chemical shifts is good. The chemical shifts are −5.5 and −6.1 ppm for the 2:1 and 3:1 complexes respectively (Tab. I). The broadness of the line and the small variation of the chemical shifts result in larger errors for the calculated parameters than in the case of the line widths. However, the calculated concentration profile, shown in the bottom part of Figure 3, is in excellent agreement with the similar profile obtained from the line widths (Fig. 2). This is convincingly shown on Figure 4. The concentrations of the solvated Na$^+$, 2:1 and 3:1 complexes determined from the line widths are plotted as a function of the same species population calculated from the chemical shifts. The concentrations calculated from the ^{23}Na line widths are proportional to the concentrations calculated from the ^{23}Na chemical shifts with zero intercept and a slope of 1. Despite the small chemical shift changes upon addition of **1** to Na$^+$, and the broadness of the lines, the chemical shift results are in excellent agreement with the results obtained from the line widths. This is in strong support of the correctness of the proposed model based upon the formation of 2:1 and 3:1 complexes.

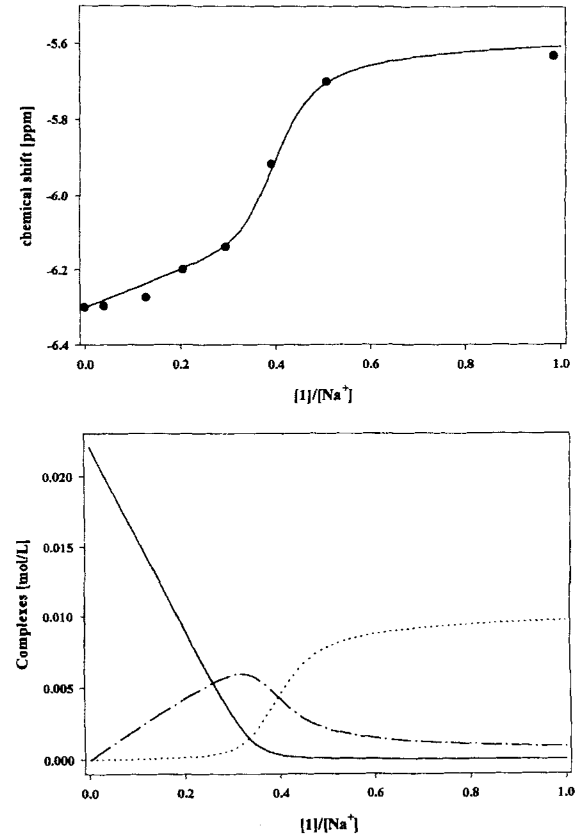


FIGURE 3 ^{23}Na NMR chemical shift of 22 mM Na$^+$ in the presence of various amounts of calix[8]arene (1). Top: ● measured chemical shift. The solid line is calculated on the basis of the formation of 2:1 and 3:1 complexes using Eqs. (3–7); Bottom: Concentration profiles calculated from Eqs. (3–7). -solvated Na$^+$,...2:1 complex and -•- 3:1 complex.

Figure 5 shows the concentrations calculated from the ^{23}Na chemical shifts and the ^{23}Na line

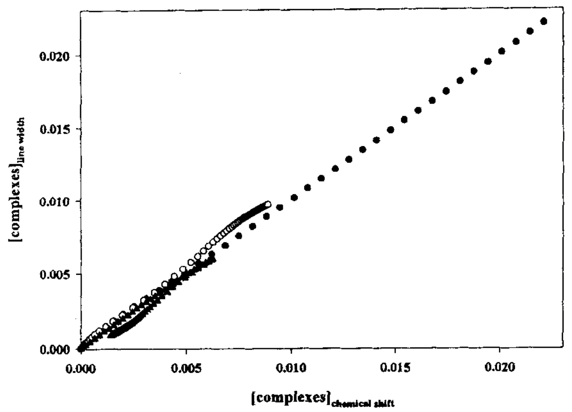


FIGURE 4 Concentration of the 2:1 and 3:1 complexes determined from the chemical shift *versus* the concentration determined from the line width, from Eqs. (3–7). ● solvated Na$^+$, ○ 2:1 complex, ▲ 3:1 complex.

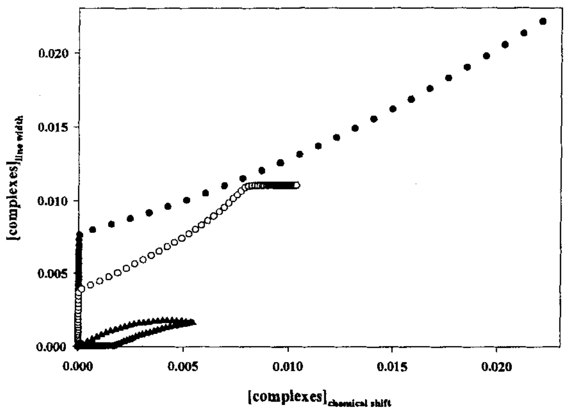


FIGURE 5 Concentration of the 2:1 and 4:1 complexes determined from the chemical shift *versus* the concentration determined from the line width (hypothesis of the 2:1 and 4:1 model). ● solvated Na$^+$, ○ 2:1 complex, ▲ 4:1 complex.

width assuming the formation of 2:1 and 4:1 complexes. In this case, the concentrations calculated from the line width are no longer proportional to the concentrations calculated from the chemical shifts. Similar absences of correlation could be obtained for the other tested models.

In this work, the formation of 2:1 and 3:1 Na$^+$ complexes with a large calix[8]arene derivative was demonstrated. We are now working on the definition of the structure of these complexes as well as on their mechanisms of formation and dissociation in solution. In comparison with crown ethers, on the basis of the findings of this study, one can expect the predominance of associative exchange mechanisms in solutions of relatively low donicity, and in the presence of poorly associating counterions [25, 30, 31].

EXPERIMENTAL

Octaethyl *p-tert*-Butylcalix[8]arene Octaacetate was synthesized from the 4-*tert*-Butylcalix[8]arene derivative (Aldrich 99%), purified and characterized, following the procedure of Arnaud-Neu *et al.* [21]. Sodium tetraphenylborate (Aldrich 99.5%) was used as sodium cation source. The sodium tetraphenylborate was recrystallised from chloroform/ethanol (50/50) and dried at RT under vacuum for one day prior to use.

All measurements were made in a binary mixture of deuterated chloroform and deuterated 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 activated 4 Å molecular sieves before use.

NMR MEASUREMENTS

The ^{1}H- and ^{23}Na-NMR spectra were recorded on a Bruker AMX-500 NMR spectrometer at 500.14 and 132.29 MHz respectively. The ^{1}H NMR and the ^{23}Na NMR spectra were referenced to chloroform (7.24 ppm) and 0.1 M NaCl in H_2O (0 ppm) respectively.

^{23}Na-NMR Spectra

The parameters were chosen to obtain quantitative spectra. A relaxation delay of 0.05 s, 90° pulse (9 µs), acquisition time 0.03–0.1 s, sweep width 8 kHz and 64 to 16 k FID's were accumulated per spectrum. The free induction decay was Fourier transformed without line broadening.

Data Treatment

All peaks have a Lorentzian line shape. The line width, intensities and chemical shifts were determined by fitting each peak with one Lorentzian.

The complex formation between Na^+(M) and the octaethyl-*p*-*tert*-Butylcalix[8]arene Octaacetate (C) was analyzed under the hypothesis of various models. More specifically, the formations of 1:1 and 2:1, 2:1 and 3:1 and 2:1 and 4:1 complexes were considered. The complex formation equilibria between the calixarene C and the metal cation M, forming 2:1 and 3:1 complexes are described by the following equations:

$$K_2 = \frac{[\mathrm{C}][\mathrm{M}]^2}{[\mathrm{CM}_2]} \tag{1}$$

$$K_3 = \frac{[\mathrm{CM}_2][\mathrm{M}]}{[\mathrm{CM}_3]} = \frac{[\mathrm{C}][\mathrm{M}]^3}{[\mathrm{CM}_3]K_2} \tag{2}$$

Solving these coupled complex formation equilibria for M yields:

$$[\mathrm{M}]^4 + [\mathrm{M}]^3(3[\mathrm{C}]_t - [\mathrm{M}]_t K_3) + [\mathrm{M}]^2 K_3(2[\mathrm{C}]_t - [\mathrm{M}]_t) + [\mathrm{M}]K_2K_3 - [\mathrm{M}]_t K_2 K_3 = 0 \tag{3}$$

K_2 and K_3 are the dissociation constants and $[\mathrm{C}]_t = [\mathrm{C}] + [\mathrm{CM}_2] + [\mathrm{CM}_3]$ the total calixarene concentration and $[\mathrm{M}]_t = [\mathrm{M}] + 2[\mathrm{CM}_2] + 3[\mathrm{CM}_3]$ the total sodium cation concentration. The concentration of the free calixarene and the 2:1 and 3:1 complexes are given respectively by

$$[\mathrm{C}] = \frac{[\mathrm{C}]_t K_2 K_3}{K_2K_3 + [\mathrm{M}]^2 K_3 + [\mathrm{M}]^3} \tag{4}$$

$$[\mathrm{CM}_2] = \frac{[\mathrm{C}][\mathrm{M}]^2}{K_2} \tag{5}$$

$$[\mathrm{CM}_3] = \frac{[\mathrm{C}][\mathrm{M}]^3}{K_2K_3} \tag{6}$$

Expressions similar to Eqs. (3–6) are obtained for the model of formation of 1:1 and 2:1 and of 2:1 and 4:1 complexes.

The solvated sodium and complexed sodium cations are in a fast exchange at 300 K and the ^{23}Na NMR chemical shifts and line widths are the weighted average of all contributions.

$$\sigma_{\mathrm{obs}} = p_{\mathrm{solv}}\sigma_{\mathrm{solv}} + p_{2:1}\sigma_{2:1} + p_{3:1}\sigma_{3:1} \tag{7}$$

where σ_x are the chemical shifts or line widths and p_x the mole fractions of the different species. σ_{solv} was measured in the absence of **1**. The line width and chemical shift are respectively 14 Hz and −6.3 ppm, K_2, K_3, $\sigma_{2:1}$ and $\sigma_{3:1}$ were determined by fitting Eq. (7) to the experimental ^{23}Na chemical shifts and line widths.

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