

Interaction of Cesium Ions with Calix[4]arene-bis(*t*-octylbenzo-18-crown-6): NMR and Theoretical Study

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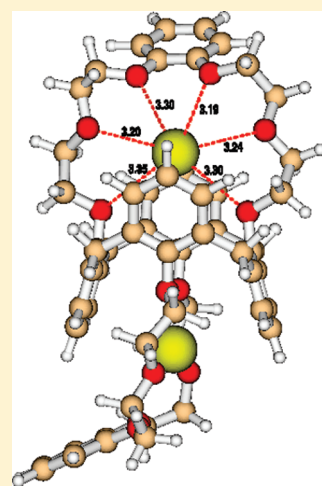
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S Supporting Information

ABSTRACT: Using ^1H , ^{13}C , and ^{133}Cs NMR spectra, it is shown that calix[4]arene-bis(*t*-octylbenzo-18-crown-6) (L) forms complexes with one ($\text{L}\cdot\text{Cs}^+$) and two ($\text{L}\cdot 2\text{Cs}^+$) Cs^+ ions offered by cesium bis(1,2-dicarbollide) cobaltate (CsDCC) in nitrobenzene- d_5 . The ions interact with all six oxygen atoms in the crown-ether ring and the π electrons of the calixarene aromatic moieties. According to extraction technique, the stability constant of the first complex is $\log \beta_{\text{nb}}(\text{L}\cdot\text{Cs}^+) = 8.8 \pm 0.1$. According to ^{133}Cs NMR spectra, the value of the equilibrium constant of the second complex is $\log K_{\text{nb}}^{(2)}(\text{L}\cdot 2\text{Cs}^+) = 6.3 \pm 0.2$, i.e., its stabilization constant is $\log \beta_{\text{nb}}(\text{L}\cdot 2\text{Cs}^+) = 15.1 \pm 0.3$. Self-diffusion measurements by ^1H pulsed-field gradient (PFG) NMR combined with density functional theory (DFT) calculations suggest that one DCC^- ion is tightly associated with $\text{L}\cdot\text{Cs}^+$, decreasing its positive charge and consequently stabilizing the second complex, $\text{L}\cdot 2\text{Cs}^+$. Using a saturation-transfer ^{133}Cs NMR technique, the correlation times τ_{ex} of chemical exchange between $\text{L}\cdot\text{Cs}^+$ and $\text{L}\cdot 2\text{Cs}^+$ as well as between $\text{L}\cdot 2\text{Cs}^+$ and free Cs^+ ions were determined as 33.6 and 29.2 ms, respectively.



1. INTRODUCTION

Among various chemical compounds that can bind metal cations in a complex soluble in organic solvents, those based on calixarenes or crown ethers have proven to be particularly successful in strong, highly specific binding and extraction. Recently, interesting compounds combining both structural motives, i.e. having variously modified crowns attached to calixarenes, have been prepared and studied.^{1–18} As in the previous simpler cases, the structure can be tailored to selectively bind a narrow spectrum of ions or even one kind of cation according to its size. This makes such compounds practically attractive e.g. as extraction agents in processing nuclear waste or rare element ore. However, their interactions with the appropriate metal cation raise interesting theoretical questions, too. Take the case of an alternate 1,3-calix[4]arene bis(crown ether) with or without a benzo- or naphtho-group embedded in the crown ring:^{13,15} (i) Does the coordinated metal cation interact solely with the lone pairs of the crown oxygen atoms, or is there any contribution of the π electron to the coordination bond? (ii) How different in conformational structure are the possible complexes with one and two metal ions, and how stable is the latter considering the strong electrostatic repulsion of the ions? (iii) Given the usually high stability of the complex with the

appropriate cation, how fast is the exchange of the ions between different molecules? (iv) What is the ion-pairing behavior of the calixarene–metal complexes with counter-anions? Some hints of the answers to these questions can already be found in the literature.^{14,20} In the calix[4]arene-crown-6 family, which appears to be selective to cesium cations, crystal structures of the Cs^+ complexes indicate^{1,9–12} significant contribution of the π electrons to the bonding besides that of the six ethereal oxygen atoms of the crown moiety. The solution ^{133}Cs NMR study¹⁵ of Cs^+ interaction with 1,3-calix[4]arene bis(naphtho-18-crown-6) shows that the complex with two ions is formed in high yield in a methanol–chloroform mixture, and that the exchange between the $\text{L}\cdot\text{Cs}^+$ and $\text{L}\cdot 2\text{Cs}^+$ complexes (L being the calixarene-crown ligand) must be rather slow. As the SCN^- were used as counterions in this study, the high stability of the $\text{L}\cdot 2\text{Cs}^+$ complex could be explained by ion pairing, which surely lowers the electrostatic repulsion between the bound Cs^+ ions. This appears to be corroborated by the crystal structure, which, however, does not give unequivocal information about the behavior in solution.

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In order to clarify these interesting questions, we studied the interaction of Cs^+ with a similar ligand, namely, calix[4]arene-bis(*t*-octylbenzo-18-crown-6) (further symbolized as **L**). This compound has the advantage of good solubility in organic solvents while retaining^{13,14} the high coordination affinity to Cs^+ . As the source of Cs^+ ions, we used in the NMR studies cesium bis(1,2-dicarbolide) cobaltate (**CsDCC**), a compound known to be fully ionized in appropriate media due to the spread of negative charge over its large anion.¹⁹ Nitrobenzene-*d*₅ (NB), chosen as a reaction medium, favors the ionization of **CsDCC** due to its relatively high dielectric constant and ability to solvate the Cs ions.

2. EXPERIMENTAL SECTION

2.1. Materials and Samples. Calix[4]arene-bis(*t*-octylbenzo-18-crown-6) (**L**) was obtained from IBC Advanced Technologies, American Fork, UT, USA. **CsDCC** was prepared in the Institute of Nuclear Research, Řež, Czech Republic, according to the procedure by Hawthorne et al.¹⁹ NB was purchased from

Sigma-Aldrich and used as obtained. Cesium iodide was purchased from Fluka. The radionuclide $^{137}\text{Cs}^+$ purchased from Technaveksport, Russia was of standard radiochemical purity.

The samples for NMR were prepared by mixing 0.3 mL of 0.02 mol/L solution of **L** in NB with appropriate amounts of 0.04 mol/L solution of **CsDCC** in NB and neat NB so that the final concentration of **L** was 0.01 mol/L in all cases.

2.2. Extraction Experiments. The experiments were carried out in 10 mL glass test tubes with polyethylene stoppers: 2 mL of an aqueous solution of CsI in the concentration range 2×10^{-4} to 1×10^{-3} mol/L and microamounts of $^{137}\text{Cs}^+$ were added to 2 mL of an NB solution of **L**, the concentration of which varied from 1×10^{-3} to 5×10^{-3} mol/L (in all experiments, the initial concentration of **L** in NB, $C_{\text{L}}^{\text{in,nb}}$, was always higher than the initial concentration of CsI in water, $C_{\text{CsI}}^{\text{in,aq}}$). The test tubes filled with the solution were shaken for 2 h at 25 ± 1 °C using a laboratory shaker. After that, the phases were separated by centrifugation. Then, 1 mL samples were taken from each phase, and their γ activities ($^{137\text{m}}\text{Ba}$ daughter of ^{137}Cs) were measured using a well-type NaI(Tl) scintillation detector connected to a γ -analyzer NK350 (Gamma, Budapest, Hungary). The equilibrium distribution ratios of cesium, D_{Cs} , were determined as the ratios of the measured levels of radioactivity of $^{137}\text{Cs}^+$ in the NB and aqueous samples.

2.3. NMR spectra. ^1H and ^{13}C NMR spectra were measured at 600.2 and 150.9 MHz, respectively, with a Bruker Avance III 600 NMR spectrometer; 64 and 128 kpoints were measured, respectively. The ^{13}C NMR measurements were performed using ^1H – ^{13}C DEPT45 sequence (collecting 3000 scans). 2D ^1H COSY and NOESY and ^1H – ^{13}C HSQC and HMBC spectra of

Scheme 1. Saturation–Recovery Sequence for Measuring Chemical Exchange

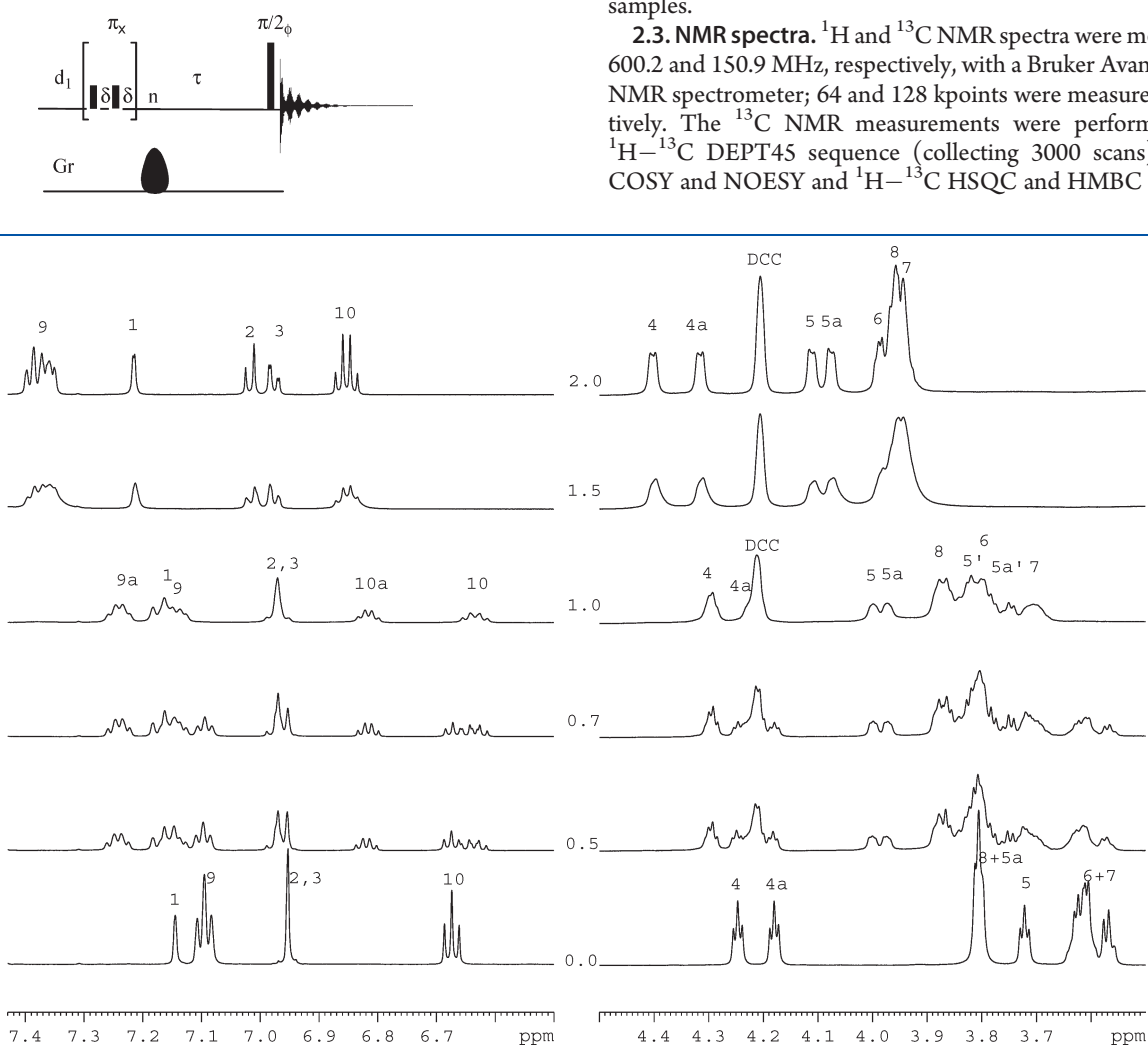


Figure 1. ^1H NMR spectra (relevant parts) of the NB solutions of **L** (0.01 mol/L) with the added **CsDCC** (molar ratios $\lambda = \text{CsDCC}/\text{L}$ are indicated) at 300 K.

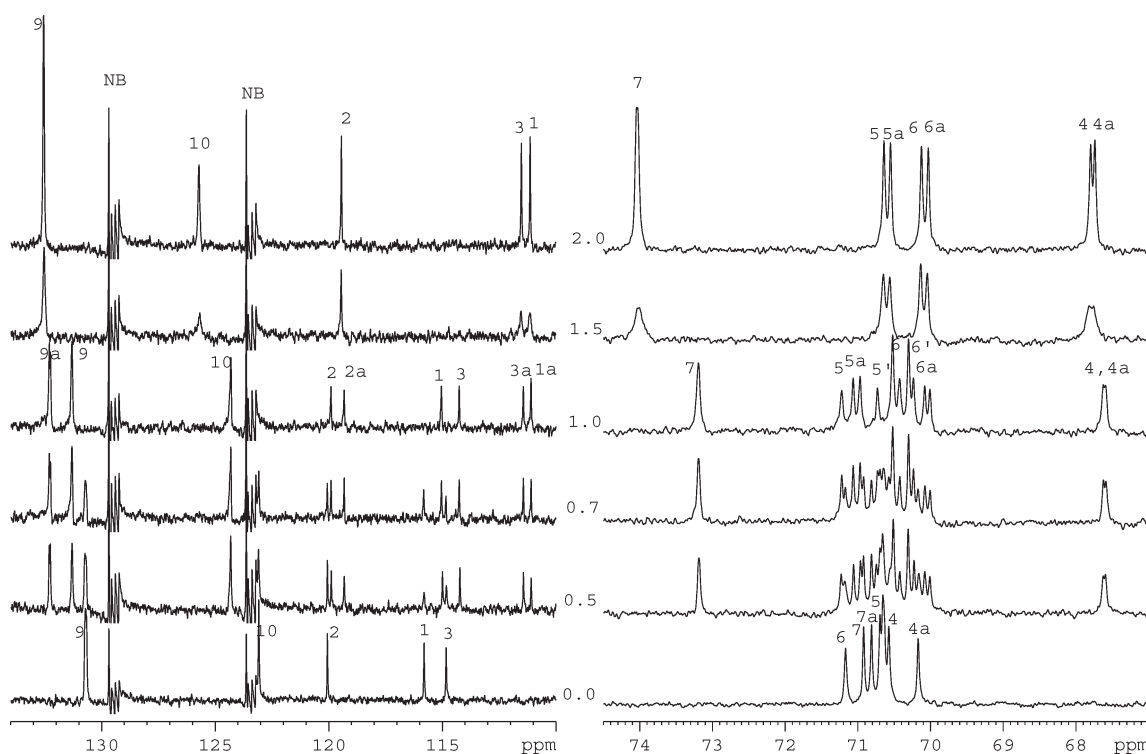


Figure 2. ^{13}C DEPT45 NMR spectra (relevant parts) of the NB solutions of **L** (0.01 mol/L) with the added CsDCC (molar ratios $\lambda = \text{CsDCC}/\text{L}$ are indicated) at 300 K.

the solutions of **L** and its 1:1 and 1:2 mol/mol mixtures with CsDCC were measured with 1028 points in F2 and 256 points in F1 domains, respectively, collecting 16, 80, 80, and 160 scans for each increment in COSY, NOESY, HSQC, and HMBC, respectively. Sine-bell weighting functions in both domains were applied before Fourier transform. Pulsed-field gradient (PFG) diffusion experiments were done on the ^1H resonance using the stimulated echo sequence²¹ with bipolar gradient pulses. Sixteen points were measured (16 scans each) with the gradient linearly increasing from 4 to 190 G/cm. The gradient pulse length was 2 ms, and the diffusion delay was 400 ms. ^{133}Cs NMR spectra were measured at 39.37 MHz with an upgraded Bruker Avance 300 AC spectrometer. Single pulse spectra were measured with a 80 ppm spectral window, mostly with 0.75 s repetition time, collecting 3200 scans in order to warrant precision of the integral intensities. Longitudinal relaxation times were measured with the usual inversion–recovery sequence measuring 16 points, each collecting 240 scans. The chemical exchange rate of ^{133}Cs between different sites was measured using the special saturation–recovery sequence shown in Scheme 1. Here, after relaxation delay d_1 , the magnetization at one site is selectively inverted by a DANTE sequence, with n being 10 in our case and the delay δ between $\pi/20$ pulses (1.13 μs) being 57 μs (the resulting selectivity of the pulse train was 500 Hz). Immediately after inversion, the possibly remaining transverse polarization is destroyed by a 1 ms spoiling gradient pulse. The inversion is followed by the incremented delay τ (48 increments spaced by 1 ms were used in the present case), and the sequence is ended by a hard $\pi/2$ pulse (for the phase φ , usual circling is sufficient).

2.4. Quantum Chemistry Calculations. Molecular orbital calculations were performed using the GAUSSIAN 03 suite of programs.²² Molecular geometry was fully optimized at the

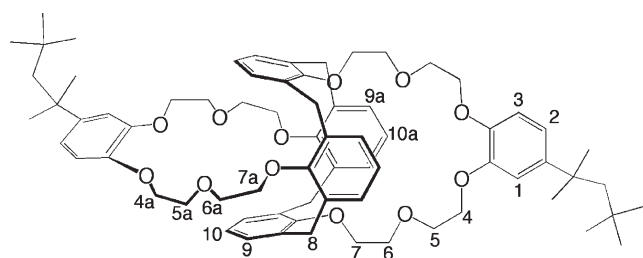
B3LYP level of the density functional theory (DFT) with the 6-31G(d) and LanL2DZ (for Cs) basis sets. The optimization was unrestrained, vibrational frequencies were used in all cases except the largest complexes to characterize the stationary points as minima. Several local configurations near the achieved energy minimum were examined. We believe the achieved energy minimum to be the global one.

3. RESULTS AND DISCUSSION

In some contrast to the studies of similar (but not identical) systems cited in the Introduction, we present here a concerted approach using all the techniques offered by NMR (including the fully interpreted ^1H , ^{13}C , and ^{133}Cs NMR spectra, PFG NMR and saturation-transfer NMR) and high-precision quantum-mechanical DFT calculations, and targeted on the problems of the modes of the cesium binding to the ligand, the stability constants of both possible complexes, and last but not least the exchange dynamics of these complexes in solution.

3.1. NMR Examination of the Interactions of Cs^+ with Calix[4]arene-bis(*t*-octylbenzo-18-crown-6) (L**).** Figure 1 shows ^1H NMR spectra of **L** and its mixtures with CsDCC, and Figure 2 shows relevant parts of ^{13}C DEPT45 NMR spectra of the same mixtures in NB (DEPT45 spectra were used instead of single-pulse ^{13}C NMR for sensitivity reasons, but also because the NB signals interfere with aromatic signals of **L**). The signal assignment in both Figures was done on the basis of 2D COSY, NOESY, HSQC, and HMBC spectra, which are shown in the Supporting Information. It corresponds to Scheme 2 where the protons have the same numbers as the carbons to which they are attached.

The ^1H NMR spectrum of **L** in Figure 1 (bottom spectrum) shows that the original molecule is not as symmetric as one

Scheme 2. The Structure of L and the Numbering of Relevant Atoms


would expect from Scheme 2: although all four aromatic moieties of the calixarene part are equivalent, the crown-ether rings are not as seen mostly from the signals 4, 4a, 5, and 5a. The nonequivalency is not large and is, without doubt, conformational. As the Cs^+ ion interacts with one of the binding sites (at $\lambda \leq 1.0$), most signals of this part of the molecule exhibit a downfield shift. This is true not only of the crown- CH_2 protons 4, 5, 6, and 7, but also for the calixarene protons 9 and 10. Thus it is clear that the Cs^+ ion interacts not only with all six of the crown-ether oxygen atoms in the binding site, lowering thus the electron density at the attached CH_2 groups, but with high probability also interacts with the π electrons¹⁴ of the two calixarene aromatic rings. All signals are slightly broadened at $\lambda > 0$, but those of free L are retained up to $\lambda = 1.0$, i.e. there is only a relatively slow exchange between free and bound L. Nonetheless, the signals of the free part of the molecule are shifted, too; some of them (e.g., 5) are even doubled, thus indicating asymmetry due to conformation change and may be other interactions of the whole molecule (see below). At $\lambda > 1.0$, there is further shift of all the signals and the spectrum gradually simplifies. These changes show that (i) a second Cs^+ ion is incorporated into the complex, and (ii) there is slow but perceptible exchange between $\text{L} \cdot \text{Cs}^+$ and $\text{L} \cdot 2\text{Cs}^+$ complexes (further examination of this exchange will be reported below). At $\lambda = 2.0$, the signals of both crown moieties are downfield shifted even in comparison with those of the bound one at $\lambda = 1.0$. Evidently, the deshielding effect of the bound ion reaches to some extent the whole molecule of L. It is also probable that the electrostatic repulsion of the two bound Cs^+ ions exerts some tension on the whole complex, thus somewhat changing its conformation. It is of mild interest that protons 2 and 3 become slightly nonequivalent, whereas the signal 9 is strongly downfield shifted, and the corresponding protons are almost equivalent, which shows that also the calixarene part undergoes conformational change in the $\text{L} \cdot 2\text{Cs}^+$ complex.

^{13}C NMR spectra offer complementary information. Whereas proton signals of 4 and 7 undergo only a slight shift between L and $\text{L} \cdot \text{Cs}^+$, the shifts of corresponding carbon signals are much more apparent and counterintuitive in the case of 4. There is no difference of the shifts of either 4 or 7 between the coordinated and uncoordinated part of L, suggesting that they are caused by relative orientations of the nearby aromatic rings. This possibility is supported by the correlated shifts of their signals (1, 3 and 9, 10). At $\lambda = 1.5$, the signals are perceptibly broadened by slow exchange. At $\lambda = 2.0$, we have a relatively simple spectrum, suggesting equivalence of the calixarene aromatic rings as well as the two remaining aromatic moieties and a near-equivalence of the two crown rings. Excess of Cs^+ over $\lambda = 2.0$ does not change the spectrum, which suggests a high equilibrium constant even for the $\text{L} \cdot 2\text{Cs}^+$ complex.

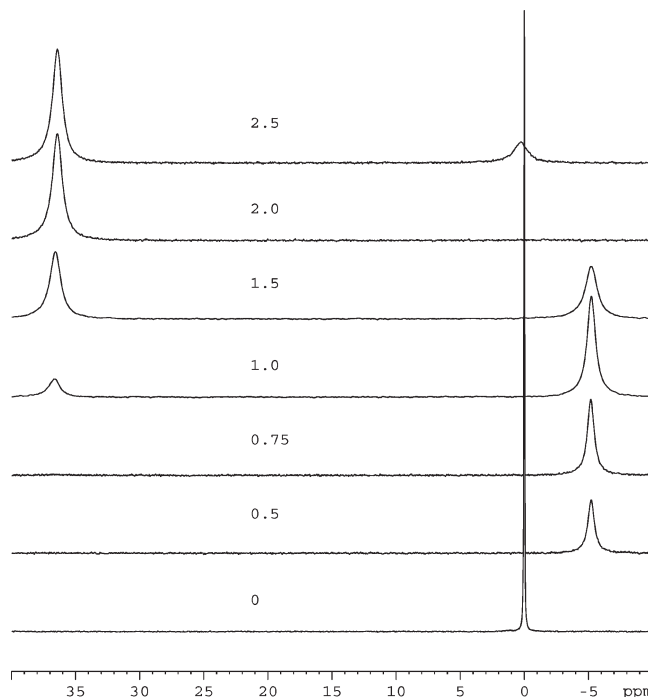


Figure 3. ^{133}Cs NMR spectra of CsDCC (bottom) and its mixtures with L (molar ratios λ of Cs^+ to 0.01 mol/L of L are indicated) in NB at 300 K.

The clearest information about the transfer between $\text{L} \cdot \text{Cs}^+$ and $\text{L} \cdot 2\text{Cs}^+$ can be obtained from ^{133}Cs NMR spectra, some of which are shown in Figure 3. As expected, coordination of the Cs^+ ion up to $\lambda = 1.0$ leads to an upfield shift of the ^{133}Cs signal as the electron density in the outer orbitals of the ion is partially filled by the interacting atoms of L. However, the coexistence of two Cs ions in $\text{L} \cdot 2\text{Cs}^+$ leads to mutual deshielding and consequently to a huge downfield shift of about 37 ppm (relatively to the free Cs ion).

As seen in Figure 3, the ^{133}Cs signals corresponding to $\text{L} \cdot \text{Cs}^+$ and $\text{L} \cdot 2\text{Cs}^+$ do not change positions with respect to λ , but are broader in the region 0.9 to 1.5. Hence, chemical exchange of Cs^+ between the two complexes takes place, but it must be relatively slow (see the corresponding paragraph below) and does not influence the signal intensities.

It has to be added that chemical exchange is not the sole reason of signal broadening in our case. ^{133}Cs is a nucleus with 7/2 spin, and although its quadrupole moment is only $-3 \times 10^{-27} \text{ m}^2$, the rate of its quadrupolar relaxation is exceedingly sensitive to the symmetry of the electric field around the nucleus. The free Cs^+ ion has at least six NB molecules in the primary solvation sphere with the 12 oxygen atoms placed in nearly spherical symmetry. Consequently, the longitudinal as well as transverse relaxation time is relatively long ($T_1 \approx T_2 = 1.22 \text{ s}$), and the signal of CsDCC in NB is narrow. In the complex, even the longitudinal relaxation time (unaffected by chemical exchange) is much shorter (15.8 ms in $\text{L} \cdot \text{Cs}^+$ and 16.6 ms in $\text{L} \cdot 2\text{Cs}^+$, respectively). This large change can serve as a further evidence that the Cs^+ ion is bound. The transverse relaxation time is even shorter (9.68 ms in $\text{L} \cdot \text{Cs}^+$ and 9.40 ms in $\text{L} \cdot 2\text{Cs}^+$, respectively), thus showing that chemical exchange adds to the signal width.

The interesting feature of the spectra in Figure 3 is the appearance of a small amount of $\text{L} \cdot 2\text{Cs}^+$ even at $\lambda = 1.0 \text{ mol/mol}$,

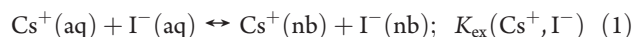
Table 1. Experimental Values of D_{Cs} and the Calculated Values of $\log K_{ex}(L \cdot Cs^+, I^-)$

$C_{CsI}^{in,aq}$ [mol/L]	$C_L^{in,nb}$ [mol/L]	D_{Cs}	$\log K_{ex}(L \cdot Cs^+, I^-)$
2×10^{-4}	1×10^{-3}	0.85	2.9
4×10^{-4}	2×10^{-3}	1.39	3.0
6×10^{-4}	3×10^{-3}	1.50	2.9
8×10^{-4}	4×10^{-3}	1.80	3.0
1×10^{-3}	5×10^{-3}	1.71	2.8

indicating that its stabilization constant is comparable with that of $L \cdot Cs^+$. This possibility is quite counterintuitive as the electrostatic repulsion of both ions in $L \cdot 2Cs^+$ (calculated to be 47.2 kcal/mol for bare ions in the corresponding distance) should strongly destabilize the complex. Vicens et al.¹⁵ made analogous observation with a molecule chemically similar to **L** but with a less ionized cesium salt and in a less polar medium. To clear the situation in our case, we determined the stabilization constants as reported in the following paragraph.

3.2. Determination of the Equilibrium Constants. If the equilibrium constant is higher than $10^4 L \cdot mol^{-1}$, NMR is able to determine only its lower bound, not its absolute value. Therefore we used extraction experiments for the determination of the stabilization constant of the first complex, $L \cdot Cs^+$.

3.2.1. Extraction Experiments. Following the notation of our previous works,^{23–26} the two-phase water–CsI–NB extraction system can be described by the equilibrium

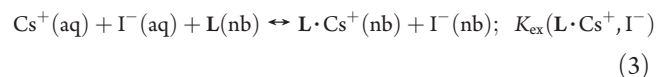


where $K_{ex}(Cs^+, I^-)$ means the corresponding extraction constant, and the abbreviations aq and nb mean the aqueous and NB phases, respectively. One can write²³

$$\log K_{ex}(Cs^+, I^-) = \log K_{Cs^+}^i + \log K_{I^-}^i \quad (2)$$

where the constants on the right side are the respective individual extraction constants for Cs^+ and I^- in the water–NB system. From the known²² values $\log K_{Cs^+}^i = -2.7$ and $\log K_{I^-}^i = -3.2$, eq 2 gives $\log K_{ex}(Cs^+, I^-) = -5.9$.

The two-phase water–CsI–NB–**L** extraction system can be described^{27,28} by the equilibrium



where the equilibrium constant is

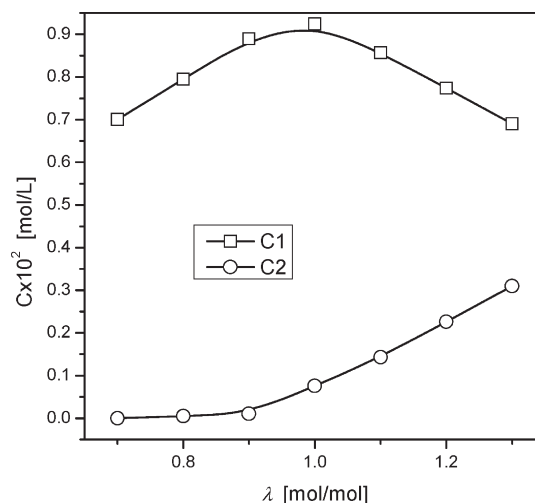
$$K_{ex}(L \cdot Cs^+, I^-) = \frac{[L \cdot Cs^+]_{nb} [I^-]_{nb}}{[Cs^+]_{aq} [I^-]_{aq} [L]_{nb}} \quad (4)$$

Equation 4 is valid because **L** is a considerably hydrophobic ligand¹⁴ practically present in the NB phase only.

Taking into account the condition of electroneutrality in the organic and aqueous phases and the mass balances of **L** and CsI at equal volumes of both phases, eq 4 can be reformulated using the distribution ratio of cesium $D_{Cs} = [L \cdot Cs^+]_{nb} / [Cs^+]_{aq}$ as

$$K_{ex}(L \cdot Cs^+, I^-) = D_{Cs}^2 \left[C_L^{in,nb} - \frac{D_{Cs}}{1 + D_{Cs}} C_{CsI}^{in,aq} \right]^{-1} \quad (5)$$

where $C_L^{in,nb}$ is the initial concentration of **L** in NB, and, analogously, $C_{CsI}^{in,aq}$ is the initial concentration of CsI in the aqueous phase. The measured D_{Cs} as the ratio of γ activities of

**Figure 4.** Concentrations of $L \cdot Cs^+$ (C_1) and $L \cdot 2Cs^+$ (C_2) as obtained by ^{133}Cs NMR for different values of $\lambda = [Cs^+]_0/[L]_0$ (NB, 298 K).

the NB and aqueous phases are given in Table 1. From there, the value of $\log K_{ex}(L \cdot Cs^+, I^-) = 2.9 \pm 0.1$ is determined.

Considering now the stabilization constant $\beta_{nb}(L \cdot Cs^+)$ corresponding to the equilibrium

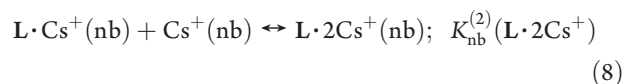


the following relation holds:^{27,28}

$$\log \beta_{nb}(L \cdot Cs^+) = \log K_{ex}(L \cdot Cs^+, I^-) - \log K_{ex}(Cs^+, I^-) \quad (7)$$

Using the values given above, eq 7 gives $\log \beta_{nb}(L \cdot Cs^+) = 8.8 \pm 0.1$ for NB at 298 K. This value is similar to those obtained in NB by Wintergerst et al.³⁰ (8.23 from Cl^- and 8.57 from Br^-) but strongly differs from that obtained¹⁴ by Moyer et al. (12.3 ± 0.2) in 1,2-dichloroethane saturated with water. As the stability of any complex of an ion depends on the competition between coordination abilities of the ligand and the solvent, one can expect much higher values of β obtained in a low-polarity and nonsolvating media such as 1,2-dichloroethane. Even less meaningful would be the comparison with the β values obtained by Arnaud et al.⁶ for a different ligand, quite different anion, and medium with very different solvating properties such as methanol.

3.2.2. NMR Determination of the Second Stabilization Constant. It is quite easy to determine the values of $[L \cdot Cs^+]$ and $[L \cdot 2Cs^+]$ from the ^{133}Cs NMR spectra as the signals of the two complexes and free Cs^+ ions are separate (cf. Figure 3). Figure 4 shows them for seven values of λ . Assuming the equilibrium



we used the program²⁹ LEGATROP for determining the corresponding equilibrium constant. Figure 4 shows the fitting curves corresponding to $\log K_{nb}^{(2)}(L \cdot 2Cs^+) = 6.3 \pm 0.2$. Thus for the formal equilibrium



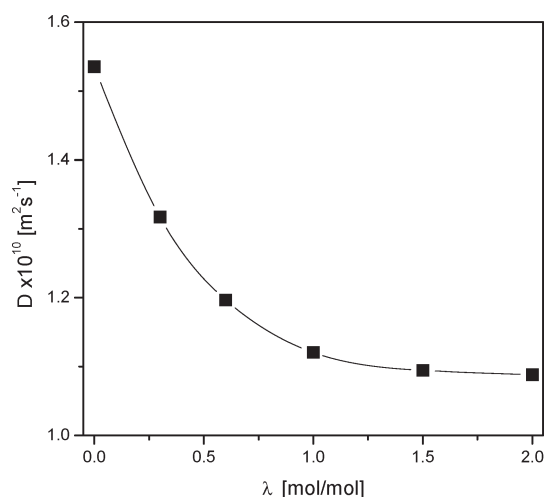


Figure 5. The values of self-diffusion coefficients D_s of **L** under varying value of λ (NB, 298 K).

it must hold

$$\log \beta_{\text{nb}}(\text{L} \cdot 2\text{Cs}^+) = \log \beta_{\text{nb}}(\text{L} \cdot \text{Cs}^+) + \log K_{\text{nb}}^{(2)}(\text{L} \cdot 2\text{Cs}^+) \quad (10)$$

giving $\log \beta_{\text{nb}}(\text{L} \cdot 2\text{Cs}^+) = 15.1 \pm 0.3$.

3.3. PFG NMR Self-Diffusion Measurements. The value of $K_{\text{nb}}^{(2)}(\text{L} \cdot 2\text{Cs}^+)$ determined in the preceding paragraph is surprisingly high (if lower than $\beta_{\text{nb}}(\text{L} \cdot \text{Cs}^+)$) considering the inevitable electrostatic repulsion of the two Cs^+ ions (calculated to be 47.24 kcal/mol for bare ions). Our aim in measuring self-diffusion coefficients of **L** in various stages of its coordination with Cs^+ was to get a clue of a possible stabilization mechanism of $\text{L} \cdot 2\text{Cs}^+$. As it is well-known, the safest way to measure the self-diffusion coefficient D_s by PFG NMR is to measure the signal intensity at gradually increased field gradient. Under such conditions,

$$I(g)/I_0 = \exp[-D_s \gamma^2 g^2 \delta^2 (\Delta - \delta/3)] \quad (11)$$

where γ is the gyromagnetic ratio of the given nucleus, g is the field gradient, δ the length of the gradient pulse, and Δ is the diffusion delay. Taking ideally the Stokes–Einstein expression for D_s , we can derive the hydrodynamic radius of the diffusing species from eq 12:

$$R_H = kT/(6\pi\eta_v D_s) \quad (12)$$

where k is the Boltzmann constant, T is the absolute temperature, and η_v is the viscosity.

Figure 5 shows the experimental diffusion coefficients obtained by measuring the intensities of the *t*-butyl signals of **L** under various values of λ . As seen, D_s is decreased (and thus R_H increased) by a factor almost 1.4 at $\lambda = 1.0$, compared to free **L**, but does not decrease perceptibly under higher values of λ . Hence the increase in R_H cannot be caused by the coordination of Cs^+ . This can be expected as the ion is embedded in the molecule of **L** and cannot substantially increase its volume.

The most natural explanation of this observation is that $\text{L} \cdot \text{Cs}^+$ forms a tightly bound ion pair with the DCC^- anion. This is rather surprising if we consider that Cs^+ and DCC^- ions are free under the absence of **L** as already explained in section 3.1. Moreover, the present results show that only one molecule of

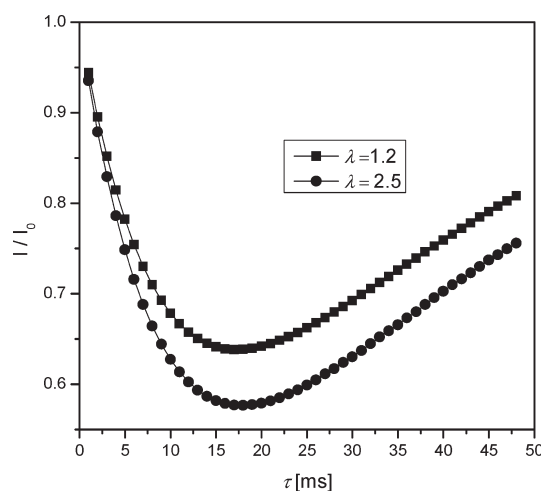


Figure 6. Relative intensities of the ^{133}Cs signal of $\text{L} \cdot 2\text{Cs}^+$ under selective inversion of the signal of $\text{L} \cdot \text{Cs}^+$ ($\lambda = 1.2$) and Cs^+ ($\lambda = 2.5$) (NB, 298 K).

DCC^- is tightly bound even to $\text{L} \cdot 2\text{Cs}^+$, which is somewhat surprising, too. Nonetheless, DFT calculations (section 3.5.) confirm this conclusion.

3.4. Investigation of Chemical Exchange. ^1H , ^{13}C , and ^{133}Cs NMR, indicate that there is slow but perceptible exchange between individual species, in particular between $\text{L} \cdot \text{Cs}^+$ and $\text{L} \cdot 2\text{Cs}^+$ and between $\text{L} \cdot 2\text{Cs}^+$ and free Cs^+ ions. This qualitative observation, somewhat surprising if one considers the high stabilization constants of the complexes, rests on the broadening of some signals which, in principle, could be due to other causes, e.g., increased relaxation rate. Therefore, direct and quantitative measurement of the respective exchange rates is called for. This, however, is not without some difficulties. The usual techniques based on the dependence of transverse relaxation rate on the distance of pulses in CPMG sequence^{31,32} or of $T_{1\rho}$ on spin-lock field intensity³³ fail because of too slow exchange. The popular derivation of exchange rate simply from T_2 or the half-width of the appropriate signal also fails because of the interference of fast quadrupolar relaxation. Therefore, we have chosen the saturation transfer technique mostly used in the nuclear Overhauser effect measurements.³⁴ The most appropriate for this technique are the ^{133}Cs NMR spectra where the signals of the exchanging species are well separated. In our somewhat modified approach, after selective inversion of the magnetization of one spin, say **S**, there follows an incremented delay τ and the sequence is ended by a hard $\pi/2$ pulse. As the selective inversion of the signal by a shaped pulse is difficult because of fast quadrupolar relaxation (cf. Section 3.1.), we used the so-called DANTE sequence, i.e., a train of fractional hard pulses (see Experimental Section) with the 500 Hz selectivity. The gradient pulse is applied in order to spoil possible remains of transverse polarization.

If we have two exchanging spins, the inverted **S** and the measured **I**, the spin dynamics is described by the Solomon equations

$$dI_z/dt = -\rho_I I_z + \sigma S_z \quad (13a)$$

$$dS_z/dt = \sigma I_z - \rho_S S_z \quad (13b)$$

where $\rho_I = R_{II} + \sigma$, with R_{II} being the longitudinal relaxation rate of the spin **I**, and σ is the rate of chemical exchange between the

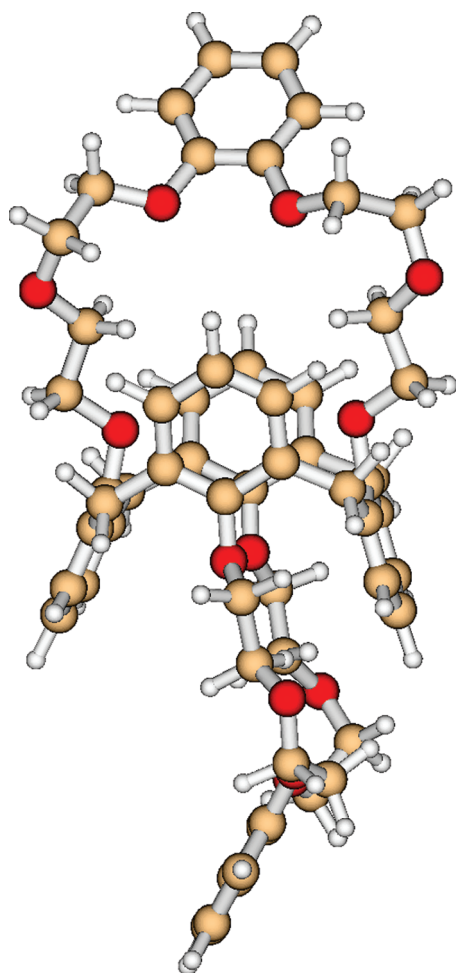


Figure 7. Optimized structure of L (B3LYP/6-31G(d)).

sites S and I. As R_{1I} and R_{1S} are practically identical, we can write $\rho_I = \rho_S = \rho$.

Under our arrangement, the intensity of the signal of I is then (cf.³⁴):

$$I/I_0 = 1 + e^{-(\rho - \sigma)\tau} - e^{-(\rho + \sigma)\tau} \quad (14)$$

where I_0 is the intensity of the signal I without selective inversion of S.

Figure 6 shows 48 relative intensities of the ^{133}Cs signal of $\text{L} \cdot 2\text{Cs}^+$ under selective inversion of the signal of $\text{L} \cdot \text{Cs}^+$ ($\lambda = 1.2$) and Cs^+ ($\lambda = 2.5$) measured at 1 ms interval. The curves correspond to the fittings of σ to the experimental intensities using eq 14. The respective values obtained were 29.72 and 34.27 s^{-1} , i.e., the corresponding exchange correlations times τ_{ex} are 33.6 and 29.2 ms, respectively. Thus the exchange is not fast, as already assumed from the shape of the NMR spectra, but it is much faster than one could expect from the high stabilization constants of both complexes. Presumably, some mediation of exchange by cooperative interaction of the Cs^+ ions with the solvent molecules must be operative.

3.5. Quantum Chemical Calculations. In the following, *t*-octyl groups were omitted from the structures of L in order to save some operation memory. We believe that this omission has a negligible effect on the conclusions made. The molecular geometry of individual structures was fully optimized at the B3LYP level of DFT with the 6-31G(d) LanL2DZ (for Cs) basis sets. No restraint

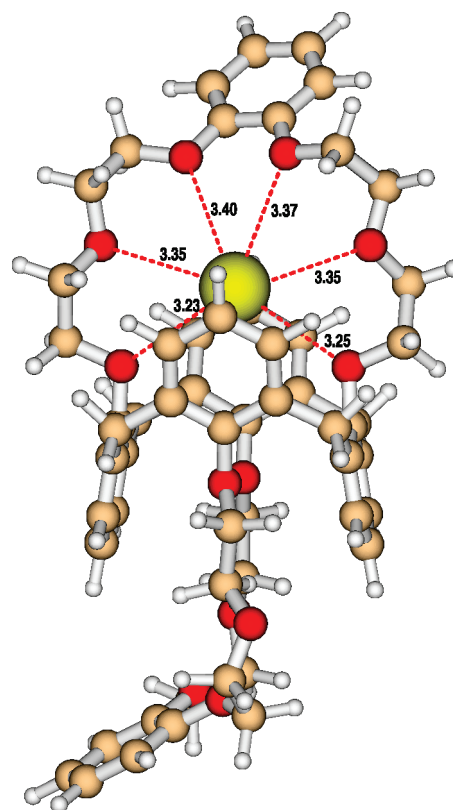


Figure 8. Optimized structure of $\text{L} \cdot \text{Cs}^+$ (B3LYP/6-31G(d))/LanL2DZ).

was applied during the optimization. Also, the calculations were made in vacuo, but the interaction of NB molecules with the complexes was inspected by separate calculations.

Figure 7 shows the optimized structure of L. In accord with ^1H and ^{13}C NMR spectra, the structure has no real symmetry although the crown-ether rings are equivalent so that no of them is preferred in taking up the Cs^+ ion.

Figure 8 shows the structure of the first complex, $\text{L} \cdot \text{Cs}^+$. As the molecular geometry suggests, the cesium-binding crown-ether ring undergoes conformation change, in accord with NMR. All its six oxygen atoms are roughly in the same distances from the ion, i.e., they take an equal part in the coordination bonding. Moreover, the ion sits in a position where it surely interacts with the π systems of two aromatic rings of the calixarene system. This is in accord both with our NMR spectra as well as the solid-state X-ray structure of the complex.¹⁴

Figure 9 shows the optimized structure of the second complex, $\text{L} \cdot 2\text{Cs}^+$.

The situation of the coordinating groups is similar to that in the previous case, only a slight asymmetry of the oxygen atoms attached to carbons 3 and 4 is introduced. This is in accord with both ^{13}C and ^1H NMR spectra. However, as shown in Table 1 (where the individual items in the given process symbolize the independently optimized structures), this structure is not very stable because of the strong electrostatic repulsion of the Cs^+ ions (process 2 compared to 1). However, $\text{L} \cdot \text{Cs}^+$ is shown to coordinate readily with the counterion DCC^- (process 3 or 4), and the adduct then accepts another Cs^+ ion to $\text{L} \cdot 2\text{Cs}^+ \cdot \text{DCC}^-$ with fairly good energy gain (process 5). The structure of this complex is depicted in Figure 10.

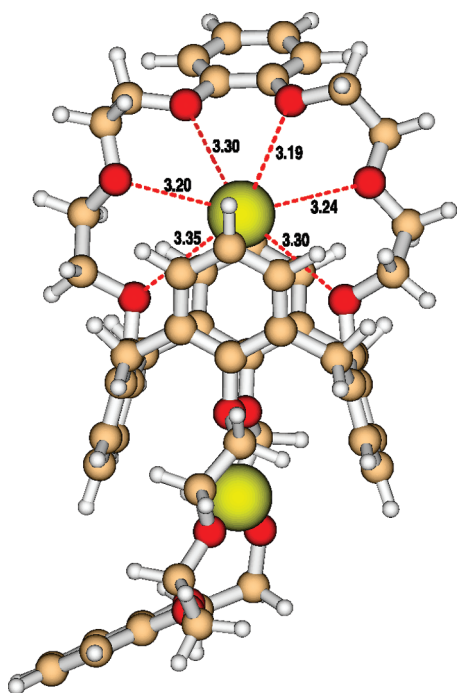


Figure 9. Optimized structure of $L \cdot 2Cs^+$ (B3LYP/6-31G(d)/LanL2DZ).

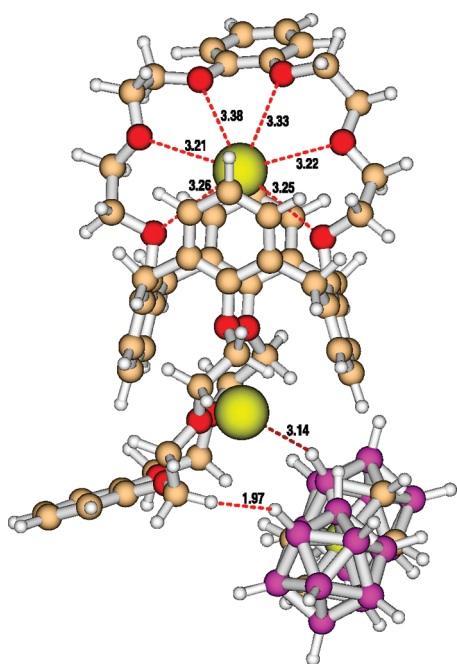


Figure 10. Optimized structure of $L \cdot 2Cs^+ \cdot DCC^-$ (B3LYP/6-31G(d)/LanL2DZ).

The ability of **L** to accept two Cs^+ ions (under an appropriate Cs^+/L ratio) is in accord with NMR spectra and the determination of the second equilibrium constant. The coordination of $L \cdot Cs^+$ with DCC^- ion has been suggested by PFG NMR (although NMR is unable to see signals of the anion). It is in seeming contradiction with the full ionization of $CsDCC$ documented by the ^{133}Cs NMR spectrum. One has to bear in mind, however, that Cs^+ is fully solvated by NB in that case, which is

Table 2. Coordination Processes and the Corresponding Calculated Energy Changes ΔE

no.	coordination process	ΔE [kcal/mol]
1	$L + Cs^+ \rightarrow L \cdot Cs^+$	−56.9
2	$L \cdot Cs^+ + Cs^+ \rightarrow L \cdot 2Cs^+$	−4.8
3	$L \cdot Cs^+ + DCC^- \rightarrow L \cdot Cs^+ \cdot DCC^-$	−47.1
4	$L + Cs^+ + DCC^- \rightarrow L \cdot Cs^+ \cdot DCC^-$	−104.1
5	$L \cdot Cs^+ \cdot DCC^- + Cs^+ \rightarrow L \cdot 2Cs^+ \cdot DCC^-$	−96.1
6	$L + Cs^+ + 2 DCC^- \rightarrow L \cdot Cs^+ \cdot 2DCC^-$	−110.4
7	$L \cdot Cs^+ \cdot 2DCC^- + Cs^+ \rightarrow L \cdot 2Cs^+ \cdot 2DCC^-$	−86.9
8	$L \cdot Cs^+ \cdot DCC^- + Cs^+ + DCC^- \rightarrow L \cdot 2Cs^+ \cdot 2DCC^-$	−93.2
9	$L \cdot 2Cs^+ \cdot DCC^- + DCC^- \rightarrow L \cdot 2Cs^+ \cdot 2DCC^-$	+2.9

Table 3. Solvation Processes and the Corresponding Calculated Energy Changes ΔE

no.	coordination process	ΔE [kcal/mol]
1	$L \cdot Cs^+ + NB \rightarrow L \cdot Cs^+ \cdot NB$	−11.4
2	$L \cdot Cs^+ \cdot NB + Cs^+ \rightarrow L \cdot 2Cs^+ \cdot NB$	−9.0
3	$L \cdot Cs^+ \cdot 4NB + Cs^+ \rightarrow L \cdot 2Cs^+ \cdot 4NB$	−25.4
4	$L \cdot Cs^+ \cdot 8NB + Cs^+ \rightarrow L \cdot 2Cs^+ \cdot 8NB$	−41.4

apparently sufficient for ionization in spite of the weak solvation of DCC^- . In $L \cdot Cs^+$, the cation is tightly held by the groups of **L** but it is not fully covered like in $Cs^+ \cdot 6NB$ (NB being abbreviation of NB). However, this is not the only reason for the binding of the anion to the complex. As Figure 10 shows, additional interactions exist between B–H protons of DCC^- and CH_2 protons of **L**, which add to the overall bonding.

Table 2 also shows that binding of the second DCC^- anion to $L \cdot 2Cs^+ \cdot DCC^-$ is not very probable. This is in full accord with the observations of PFG NMR where the diffusion coefficient (and thus the hydrodynamic radius) of the complex does not perceptibly change after introducing a second Cs^+ ion into the complex.

All the above calculations were done in vacuo, i.e., without respect to the medium. We are fully aware that the alternative way of alleviating the electrostatic repulsion and thus stabilizing the $L \cdot 2Cs^+$ is the interaction with solvating NB molecules. Table 3 shows some results of the corresponding calculations. Evidently, solvation of the complex by at least eight NB molecules could be the weaker alternative of the complex stabilization.

Concluding this part, one can say that the structures obtained here with high-precision quantum mechanical calculations are mostly geometrically analogous to those obtained for chemically similar ligands and complexes analyzed by much less precise computational methods,^{5,7,9,11} although some slight differences exist in the overall conformation of the comparable molecular parts. No comparable quantitative data of the formation energy of the complexes and solvates were given in the literature, however.

4. CONCLUSIONS

Using 1H , ^{13}C , and ^{133}Cs NMR spectra, it was shown that **L** forms complexes with one ($L \cdot Cs^+$) and two ($L \cdot 2Cs^+$) cesium ions offered by $CsDCC$ in NB. According to 1H and ^{13}C spectra, the ions interact preferentially with all six oxygen atoms in the

crown-ether ring as well as with the π electrons of the calixarene aromatic moieties. These conclusions are in full accord with the corresponding DFT calculations. Using the extraction technique, the stabilization constant of the first-stage complex was determined, $\log \beta_{\text{nb}}(\text{L} \cdot \text{Cs}^+) = 8.8 \pm 0.1$. For the consecutive equilibrium constant of the second-stage complex ($\text{L} \cdot 2\text{Cs}^+$), ^{133}Cs NMR spectra were applied, using seven different Cs^+/L molar ratios and fitting the obtained signal intensities using the program LEGATROP. The value $\log K_{\text{nb}}^{(2)}(\text{L} \cdot 2\text{Cs}^+) = 6.3 \pm 0.2$ was obtained, thus leading to the stabilization constant of the second complex $\log \beta_{\text{nb}}(\text{L} \cdot \text{Cs}^+) = 15.1 \pm 0.3$.

Self-diffusion measurements made by ^1H PFG NMR showed that the hydrodynamic radius of **L** increases by a factor 1.4 when the $\text{L} \cdot \text{Cs}^+$ complex is formed, but does not further increase when the second Cs^+ ion enters the complex. DFT calculations suggest that one DCC^- ion is tightly bound to $\text{L} \cdot \text{Cs}^+$, whereas the binding of the second DCC^- to $\text{L} \cdot 2\text{Cs}^+ \cdot \text{DCC}^-$ is not very favored, which is a natural explanation of these results. The binding of DCC^- to $\text{L} \cdot \text{Cs}^+$ decreases its positive charge and consequently stabilizes the second complex, $\text{L} \cdot 2\text{Cs}^+$.

DFT calculations suggest that solvation of $\text{L} \cdot \text{Cs}^+$ by at least eight NB molecules could have an analogous if not milder effect. In reality, the second complex $\text{L} \cdot 2\text{Cs}^+$ is probably stabilized both by pairing with the DCC^- ion and the solvation by NB.

Using a saturation-transfer NMR technique, we have demonstrated the chemical exchange of Cs^+ between $\text{L} \cdot \text{Cs}^+$ and $\text{L} \cdot 2\text{Cs}^+$ as well as between $\text{L} \cdot 2\text{Cs}^+$ and free Cs^+ ions, with the respective correlation times τ_{ex} being 33.6 and 29.2 ms, i.e., comparable to the relaxation time of the bound Cs^+ . Although relatively slow, this exchange is much faster than expected from the stabilization constants of the complexes. Thus some cooperation with the solvating NB molecules has to be expected.

■ ASSOCIATED CONTENT

S Supporting Information. ^1H COSY, ^1H NOESY, and ^1H - ^{13}C HSQC spectra of **L**, **L**/ CsDCC 1:1, and **L**/ CsDCC 1:2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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