

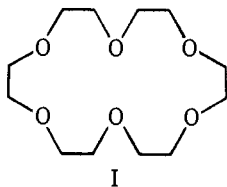
Cesium-133 Nuclear Magnetic Resonance Study of the Complexation of Cesium Tetrphenylborate by 18-Crown-6 in Pyridine Solutions

Elizabeth Mei, James L. Dye, and Alexander I. Popov*

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824. Received February 11, 1977

Abstract: Cesium-133 nuclear magnetic resonance was used as a probe of the interaction of Cs^+ with the macrocyclic polyether 18-crown-6 (18C6) in pyridine solutions. A study of the ^{133}Cs chemical shift as a function of crown/ Cs^+ mole ratio showed that the complexation reaction occurs in two steps—formation of a stable 1:1 complex ($K_1 \sim 10^6$ at 298 K) followed by the addition of a second ligand molecule to form a sandwich compound, $\text{Cs}^+(\text{18C6})_2$ ($K_2 = 44 \pm 2$ at 298 K). The thermodynamic functions for the second step are: $(\Delta G^\circ_2)_{298} = -2.58 \pm 0.02 \text{ kcal mol}^{-1}$, $\Delta H^\circ_2 = -5.8 \pm 0.2 \text{ kcal mol}^{-1}$, and $\Delta S^\circ_2 = -10.7 \pm 0.6 \text{ cal mol}^{-1} \text{ deg}^{-1}$. Line-shape analysis of the ^{133}Cs resonance at various temperatures gave rate parameters for the decomplexation of the 1:1 complex as follows: $\Delta H^\ddagger = 7.8 \pm 0.1 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -14.3 \pm 0.4 \text{ cal mol}^{-1} \text{ deg}^{-1}$ and $(\Delta G^\ddagger)_{298} = 12.02 \pm 0.02 \text{ kcal mol}^{-1}$.

The complexation reaction between cesium tetrphenylborate (CsTPB) and 18-crown-6 (18C6) macrocyclic polyether (I) has been studied by cesium-133 NMR in several solvents.



Preliminary results of this investigation have been described in a previous publication.¹

It was found that the variation of cesium-133 chemical shift as a function of 18C6/ Cs^+ mole ratio in pyridine solution had some interesting features. As the ligand concentration increased the cesium-133 resonance shifted downfield. It reached minimum value at 1:1 mole ratio and further addition of 18C6 resulted in an *upfield* shift. It seemed reasonable to assume that the data indicated a two-step reaction, i.e., formation of a 1:1 crown complex followed by the addition of a second molecule of the ligand to give a "sandwich" 2:1 complex. It was of interest to us to study this reaction in detail and to determine the thermodynamic and kinetic parameters.

Experimental Section

Cesium tetrphenylborate was prepared by reacting sodium tetrphenylborate with cesium chloride in tetrahydrofuran solution. Flame emission spectra showed that the contamination with Na^+ was <0.01%. Macrocyclic polyether 18C6 (obtained from PCR, Inc.) was purified by forming solid addition compound with acetonitrile and then removing CH_3CN under vacuum.

Pyridine (Fisher) was purified by vacuum distillation as described previously.² Karl Fischer titration indicated that the water content of the purified solvent was <100 ppm. Cesium tetrphenylborate-18-crown-6 solutions were prepared by distilling purified solvent on a vacuum line into sample tubes containing known amounts of solutes.

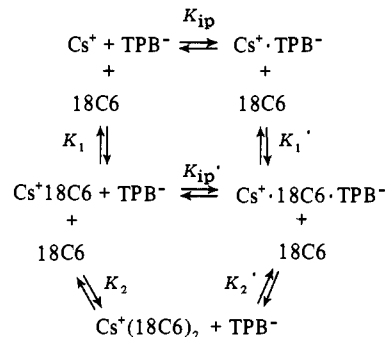
The NMR spectrometer and the measurement techniques were described in a previous publication.¹ In this study, however, it was necessary to measure ^{133}Cs chemical shifts as a function of temperature. Since it appeared that the resonance frequency of the reference would vary with temperature, an insulated reference tube was constructed (Figure 1). A 0.5 M cesium bromide solution was sealed in a 5 mm precision Wilmad NMR tube. The latter was sealed concentrically into a 10-mm Wilmad NMR tube; the space between the two tubes was evacuated to 10^{-6} Torr and sealed off. The temperature variation of the chemical shift of the insulated reference sample vs. an identical, but uninsulated reference sample, is given in Figure 2. It is seen that the use of the insulated reference tube makes it possible

to determine the true temperature dependence of the chemical shifts.

Results and Discussion

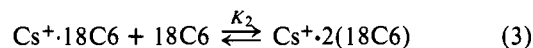
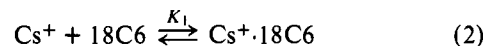
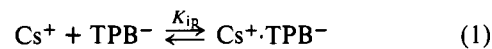
A. Equilibrium Studies. Since pyridine has a relatively low dielectric constant of 12.4, ionic association should readily take place in this medium. Indeed, the Cs^+TPB^- ion pair formation constant in this solvent was found to be 307 ± 24 at 25 °C.³ A priori we should also consider the possibility of ion pair formation involving complexed cesium cations. Consequently, in a solution containing CsTPB and 18C6, the equilibria shown in Scheme I are possible. It seems unlikely that the "sandwich"

Scheme I



complex cation would form ion pairs, since it is effectively insulated by the two ligands. Therefore, this ion pairing reaction was left out of the general scheme.

In order to establish the actual equilibria present we studied the concentration dependence of the ^{133}Cs chemical shift for solutions of CsTPB and of $\text{Cs}^+ \cdot 18\text{C6}$. The results, shown in Figure 3, indicate the absence of the species $18\text{C6} \cdot \text{Cs}^+ \cdot \text{TPB}^-$, since the chemical shift of the 1:1 complex is independent of concentration. Consequently, the above reaction scheme can be reduced to three reactions.



Since at high temperatures the exchange between the four Cs^+ sites is fast on the NMR time scale, only one population-averaged resonance will be observed. The frequency of this

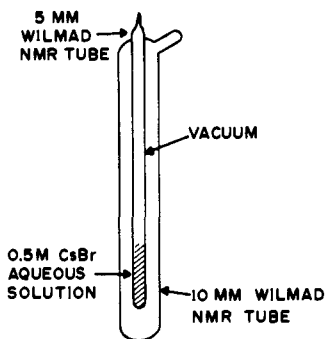


Figure 1. Insulated ^{133}Cs reference solution.

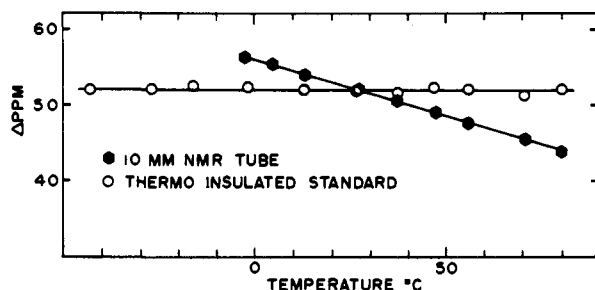


Figure 2. Comparison of ^{133}Cs chemical shift of 0.1 M CsBr aqueous solution vs. insulated reference solution.

resonance is given by,

$$\delta_{\text{obsd}} = \delta_f X_f + \delta_{\text{ip}} X_{\text{ip}} + \delta_1 X_1 + \delta_2 X_2 \quad (4)$$

where X_f , X_{ip} , X_1 , and X_2 indicate respectively the relative populations of the species $\text{Cs}^+_{\text{solv}}$, Cs^+TPB^- , $\text{Cs}^+\cdot 18\text{C}6$, and $\text{Cs}^+\cdot 2(18\text{C}6)$, while δ_f , δ_{ip} , δ_1 , and δ_2 are the corresponding chemical shifts for these species.

The total concentrations of the salt C_M^t and of the crown, C_L^t are ($L \equiv 18\text{C}6$)

$$C_M^t = [\text{Cs}^+] + [\text{Cs}^+\cdot\text{TPB}^-] + [\text{Cs}^+\text{L}] + [\text{Cs}^+\text{L}_2] \quad (5)$$

and

$$C_L^t = [L] + [\text{Cs}^+\text{L}] + 2[\text{Cs}^+\text{L}_2] \quad (6)$$

By combining eq 5 and 6 with the expressions for the concentration equilibrium constants we obtain

$$[\text{Cs}^+] = C_M^t \{1 + K_{\text{ip}}[\text{TPB}^-] + K_1[L] + K_1K_2[L]^2\} \quad (7)$$

and

$$[L]^2(2K_1K_2[\text{Cs}^+]) + [L](1 + K_1[\text{Cs}^+]) - C_L^t = 0 \quad (8)$$

From which we get

$$[L] = \frac{-(1 + K_1[\text{Cs}^+]) + \{(1 + K_1[\text{Cs}^+])^2 + 8K_1K_2C_L^t[\text{Cs}^+]\}^{1/2}}{4K_1K_2[\text{Cs}^+]} \quad (9)$$

The relative population of the cesium species are given by the equations

$$X_1 = K_1[\text{Cs}^+][L]/C_M^t \quad (10)$$

$$X_2 = K_1K_2[\text{Cs}^+][L]^2/C_M^t \quad (11)$$

$$X_f = [\text{Cs}^+]/C_M^t \quad (12)$$

$$X_{\text{ip}} = [\text{Cs}^+\text{TPB}^-]/C_M^t = K_{\text{ip}}[\text{Cs}^+][\text{TPB}^-]/C_M^t \quad (13)$$

The inclusion of activity coefficients for the ion pairing equilibrium calculated from the Debye-Hückel theory would

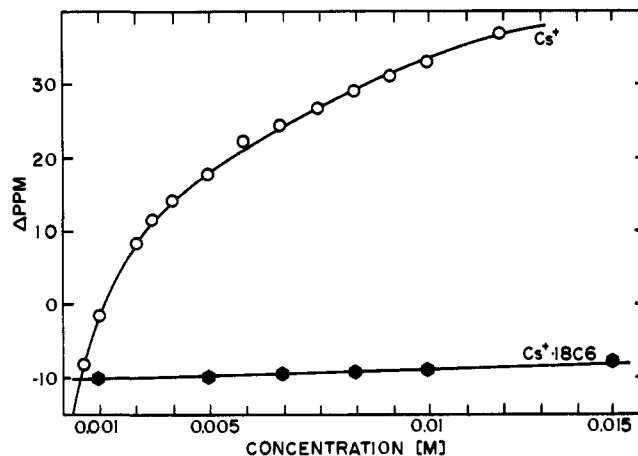


Figure 3. Cesium-133 chemical shift vs. concentration of uncomplexed Cs^+ and of $\text{Cs}^+\cdot 18\text{C}6$ complex cation.

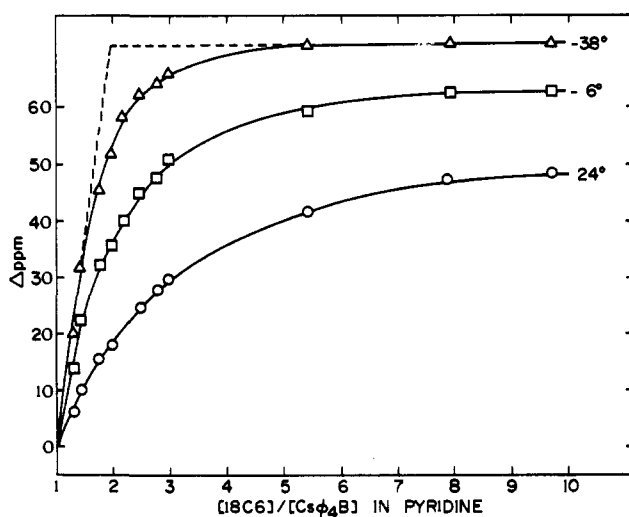


Figure 4. Cesium-133 chemical shift vs. $18\text{C}6/\text{Cs}^+$ mole ratio after the formation of the 1:1 complex.

have been a relatively simple procedure. However, as shown later, K_1 is so large that only its order of magnitude can be obtained from the NMR data. Thus the concentration of ion pairs in solutions containing $18\text{C}6$ in excess of 1:1 mole ratio is very small and the activity correction should be negligible. Complexation reactions involve addition of a neutral ligand to an ion and should not be affected by activity corrections in reasonably dilute solutions.

The set of equations was solved by an iteration technique.⁴ Starting with an initial estimate of the free cesium ion concentration, the first value of $[L]$ was obtained from eq 9 and used to calculate a more accurate estimate of $[\text{Cs}^+]$ from eq 7. This procedure was repeated until convergence occurred. Then the final values of $[L]$ and $[\text{Cs}^+]$ were used to calculate relative mole fractions from eq 10–13. The values of K_1 and K_2 were then obtained by fitting the calculated δ_{obsd} values to the values obtained experimentally. Each nonlinear least-squares iteration used updated and internally consistent values of $[L]$ and of $[\text{Cs}^+]$.

Cesium-133 chemical shifts at various ligand/ Cs^+ mole ratios were studied as a function of temperature. The results are illustrated in Figures 4 and 5. Figure 4 shows the variation in the ^{133}Cs chemical shift after the formation of the 1:1 complex. It is clearly seen that the stability of the $\text{Cs}^+(18\text{C}6)_2$ complex increases with decreasing temperature and, that the stoichiometry of the second complex is $\text{Cs}^+(18\text{C}6)_2$.

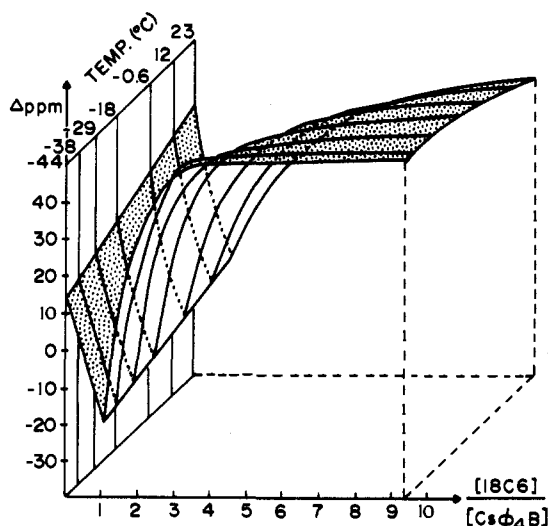


Figure 5. A three-dimensional plot of the ^{133}Cs chemical shift vs. mole ratio and temperature ($^{\circ}\text{C}$) for solutions of CsTPB and 18C6 in pyridine. The concentration of CsTPB was 0.01 M.

Figure 5 gives a three-dimensional view of the chemical shift behavior at various temperatures. It is seen that in all cases we have a very sharp break and a change in the direction of the chemical shift at the 1:1 mole ratio. The nearly linear variation of δ_{obsd} with the ligand/ Cs^+ mole ratio up to 1:1 prevented direct determination of K_1 by a least-squares technique. Therefore, in order to obtain at least an approximate value of K_1 , a simulation technique was used; this approach considered K_1 as a constant in the program and varied K_2 , δ_1 , and δ_2 to obtain the best least-squares fit of the data. Then K_1 was changed and the process was repeated. Decreasing K_1 eventually increased the residual and caused "rounding off" of the break at the 1:1 mole ratio and a poor fit in this region. In this way a lower limit for K_1 was obtained. The results are given in Table I and indicate that at all temperatures K_1 is much larger than K_2 . A typical fit is shown in Figure 6. On the basis of these results, we assumed that at 1:1 ligand/ Cs^+ mole ratio, essentially all Cs^+ ions are complexed by 18C6. Thus we can obtain the values of K_2 and of δ_2 from the chemical shifts ob-

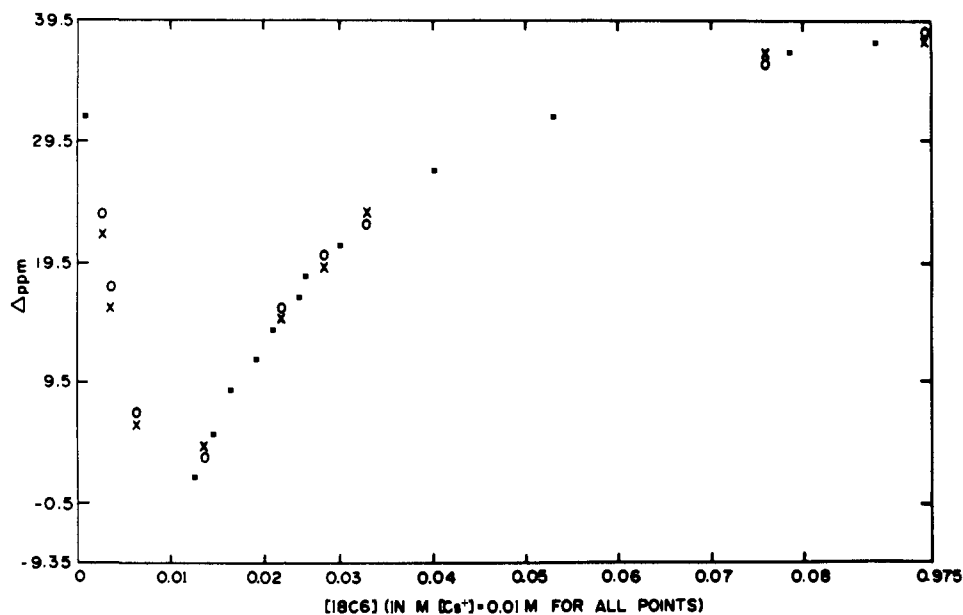


Figure 6. Computer fit of the chemical shift mole ratio data to eq 4-13.

Table I. Limiting Chemical Shift of the $\text{Cs}^+\cdot 2(18\text{C}6)$ Complex and the Thermodynamic Parameters for the Reaction $\text{Cs}^+\cdot 18\text{C}6 + 18\text{C}6 \rightleftharpoons \text{Cs}^+(18\text{C}6)_2$ in Pyridine^a

Temp, K	K_1 (min), M^{-1}	K_2 , M^{-1}	δ_2 , ppm
297	10^5	79 ± 2	47.8
285	10^6	121 ± 5	49.4
272	10^6	218 ± 14	49.9
255	10^6	432 ± 58	51.4
244	10^6	623 ± 35	51.9
235	5×10^6	1173 ± 160	51.2

^a $(\Delta G^{\circ}_2)_{298} = -2.58 \pm 0.02 \text{ kcal mol}^{-1}$; $\Delta H^{\circ}_2 = -5.8 \pm 0.2 \text{ kcal mol}^{-1}$; $\Delta S^{\circ}_2 = -10.7 \pm 0.6 \text{ cal mol}^{-1} \text{ deg}^{-1}$.

Table II. Temperature Dependence of the Exchange Time in Pyridine^a and the Corresponding Relaxation Rates in the Absence of Exchange^{b,d}

Temp, $^{\circ}\text{C}$	τ , ms	$1/T_{2A}$, s^{-1}	$1/T_{2B}$, s^{-1}
-47	4.7 (0.7) ^c	12 (4) ^c	41 (7) ^c
-38	2.6 (0.5)	7 (2)	22 (6)
-32	1.4 (0.2)	7 (2)	15 (5)
-26	1.0 (0.2)	5 (1)	10 (2)
-15	0.4 (0.1)	3 (1)	5 (1)
-7	0.4 (0.1)	8 (2)	8 (2)
9	0.14 (0.03)	5 (2)	5 (2)
23	0.06 (0.01)	3 (1)	7 (2)

^a 0.01 M CsTPB + 0.005 M 18C6. ^b A = Cs^+ , B = $\text{Cs}^+\cdot 18\text{C}6$. $1/T_{2A}$ and $1/T_{2B}$ have been corrected for field inhomogeneities. ^c Standard deviation. ^d $E_a = 8.3 \pm 0.1 \text{ kcal mol}^{-1}$; $(\Delta G^{\ddagger})_{298} = 12.02 \pm 0.02 \text{ kcal mol}^{-1}$; $\Delta H^{\ddagger} = 7.8 \pm 0.1 \text{ kcal mol}^{-1}$; $\Delta S^{\ddagger} = -14.3 \pm 0.4 \text{ cal mol}^{-1} \text{ deg}^{-1}$.

tained for solution with $18\text{C}6/\text{Cs}^+ > 1$. The results are listed in Table II.

A plot of $\ln K_2$ vs. $1/T$ is shown in Figure 7 and the enthalpy, entropy, and free energy of the complexation reaction are given in Table I. The complex is enthalpy stabilized, but entropy destabilized. Similar behavior has been observed by Kauffmann et al.⁵ for sodium, potassium, and rubidium complexes with cryptand C222 in aqueous and in 95% methanol/ H_2O

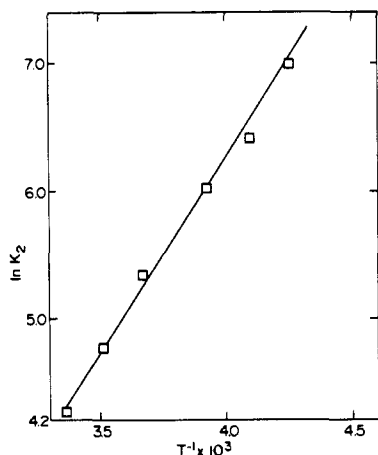
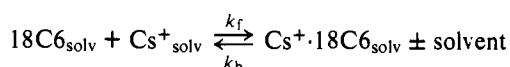


Figure 7. Plot of $\ln K_2$ vs. $10^3/T$ for the reaction $\text{Cs}^+\cdot 18\text{C}6 \rightleftharpoons \text{Cs}^+\cdot 2(18\text{C}6)$ in pyridine.

solutions. In aqueous solutions ΔS of complexation was found to be -7 , -14.1 , and -19.8 eu for Na^+ , K^+ , and Rb^+ , respectively. The negative entropy change was attributed to a rearrangement of water structure upon formation of a structure-making cation $\text{C}222\text{M}^+$. Similar enthalpy stabilization and entropy destabilization of complexes were also observed by Izatt et al.⁶ for alkali complexes of dicyclohexyl-18-crown-6 in aqueous solutions.

It is not clear why the complexation reaction results in a decrease of entropy, since by comparison to water, pyridine is not a structured solvent. It may be caused by a conformational change of the ligand or by a change in the solvation state of the ligand upon complexation.

Kinetic Studies. In solutions with the mole ratio (18C6/ Cs^+) between 0 and 1, the complexation reaction can be written as



The rate of the first-order reverse reaction (decomplexation) can be deduced from the ^{133}Cs resonance line-shape analysis as a function of temperature. The general case of exchange of a nucleus between two sites with different relaxation times is described by the modified Bloch equations⁷ and has been discussed in detail in previous publications.⁸

Solutions with a mole ratio of $18\text{C}6/\text{Cs}^+ = 0.5$ were used. Since K_1 is large (Table I), an equal population of the two sites is present. The line widths of the signal for the free cesium ion (A) and the complexed cesium ion (B) were determined in a separate experiment by fitting the absorption line shape with a Lorentzian function. The results are given in Table II together with the exchange times obtained by fitting the line shape with the Bloch equations modified for exchange. The temperature range used was large enough to give spectra varying from two peaks at low temperatures to one exchange-averaged peak at high temperatures. The position of the exchange-averaged peak was midway between those of Cs^+ and of $\text{Cs}^+\cdot 18\text{C}6$ at the corresponding temperature.

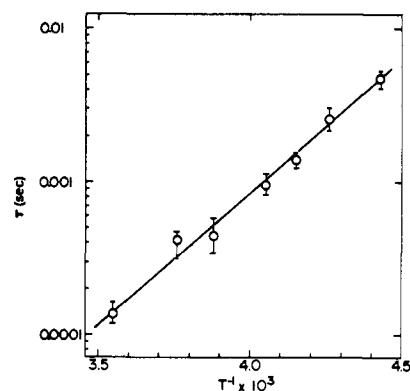


Figure 8. Arrhenius plot of exchange rate of Cs^+ in pyridine.

Because of low concentration and large chemical shifts, the signal-to-noise ratio was poor, especially in the temperature region of coalescence (-20 to -35 °C). Nevertheless, a least-squares plot of the data by the general two-site exchange equations gave the straight line semilog Arrhenius plot of τ (decomplexation rate) vs. $10^3/T$ shown in Figure 8. The rate parameters for the decomplexation reaction are given in Table II.

Shchori et al.⁹ showed that there is considerable difference in the activation energy value for the decomplexation reaction between dicyclohexyl-18C6 and dibenzo-18C6 complexes. In the first case, the activation energy for Na^+ complex in methanol or DMF is $8.3 \text{ kcal mol}^{-1}$ (as obtained here), while with the aromatic substituent the activation energy has a higher value of $12.6 \text{ kcal mol}^{-1}$. These authors ascribe the difference in the activation energy value to the difference in the steric configuration of the two ligands.

In our case, the activation energy value may be due to several origins, ligand effect, cation effect, and solvent effect. It should be noted that the Cs^+ ion is much larger than either Na^+ or K^+ and, therefore, it should be more difficult to get it in and out of the 18C6 cavity.

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