Cesium-133 Nuclear Magnetic Resonance Study of Complexation by Cryptand C222 in Various Solvents: Evidence for Exclusive and Inclusive Complexes

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Abstract: The chemical shift of the ^{133}Cs resonance was studied as a function of the mole ratio of cryptand C222 to Cs^+ at various temperatures in six solvents, pyridine, acetone, propylene carbonate, *N,N*-dimethylformamide, acetonitrile, and dimethyl sulfoxide. The variation of the chemical shift with the mole ratio was used to determine the apparent complexation constants at temperatures high enough to yield a single, exchange-narrowed line. At lower temperatures, complete line-shape analysis was used to determine apparent exchange rates. The limiting chemical shift at high C222/Cs^+ mole ratios was found to be strongly dependent upon both solvent and temperature but converged to a solvent-independent value of −245 ± 5 ppm (downfield) at low temperatures. The behavior of the chemical shift and the variation of the line shape and apparent activation energy with temperature suggests the presence of two types of 1:1 complexes in solution, an exclusive complex in which the ion may interact with the solvent, and an inclusive complex which has a solvent-independent chemical shift. The temperature dependence of both the thermodynamic and the rate parameters is consistent with this model.

Introduction

The diameter of the cesium ion (3.3 Å) is greater than the cavity size of cryptand C222.[1] However, x-ray studies of the Cs^+–C222 complex show that in the solid state, the cesium ion is located in the center of the cavity[2] (inclusive complex). Since the Cs^+ ion forms complexes in solution, not only with C222 but also with cryptands C221 and C211,[3] both of which have cavity sizes even smaller than that of C222, it seems likely that exclusive complexes can form, in which the Cs^+ ion is not completely within the cavity.

Alkali metal NMR measurements have been found useful for the study of the thermodynamics and kinetics of complexation.[4] These studies show that when cavity and ion sizes are conducive to the formation of inclusive complexes, the cationic chemical shifts are nearly independent of solvent and temperature. The observation that the chemical shifts of the Cs^+–C222 complex are strongly temperature and solvent dependent[5] prompted us to make a systematic study of this effect.

Experimental Section

Cryptand 222 from E. M. Laboratoreis was recrystallized from *n*-hexane (Fisher) and vacuum sublimed. The melting point of the snow-white sublimate was 68 ± 1 °C. Solvent purification and the preparation of cesium tetraphenylborate have been previously described.[5]

The NMR measurements were made by the pulsed Fourier-transform method at 7.87 MHz. The ^{133}Cs chemical shifts are referred to an infinitely dilute aqueous CsI solution at 25 °C. The reported chemical shifts were corrected for the bulk diamagnetic susceptibility of the solvent and follow a convention which assigns a positive value of the shift to upfield (diamagnetic) shifts. In order to provide an absolute reference at all temperatures, a vacuum-jacketed NMR tube containing 0.5 M aqueous CsBr was used.[5] All of the data were analyzed by using a generalized nonlinear least-squares program, KINFIT,[6] with appropriate equations.

Results

Six solvents were used in this study. They are pyridine, acetone, propylene carbonate (PC), *N,N*-dimethylformamide (DMF), acetonitrile (MeCN), and dimethyl sulfoxide (DMSO). The limiting chemical shifts at large mole ratios (C222/Cs^+) at 25 °C were found to be very solvent dependent. The values (ppm) are: pyridine (−224), acetone (−203), PC (−194), DMF (−156), MeCN (−210), and DMSO (−144). By contrast, as shown in Figure 1, the nmr spectra obtained at low temperatures for mole ratio (C222/Cs^+) = 0.5 show a nearly solvent-independent peak for the $Cs^+\cdot$C222 species and a second peak for the free Cs^+ ion which has the same chemical shift as that obtained in the absence of C222. (DMSO is not suitable for low-temperature studies because it freezes at 18.5 °C.)

In order to study this behavior in more detail, extensive chemical shift-mole ratio studies were made of the cesium tetraphenylborate (CsTPB)–cryptand 222 system in acetone, PC, and DMF solutions over a wide temperature range. The results are shown in Figures 2–4. It is seen (Figure 5) that, while the chemical shifts are very solvent dependent at room temperature, they converge to a solvent-independent value of −245 ± 5 ppm at low temperatures. Essentially the same value was obtained for the $Cs^+\cdot$C222 complex in five solvents at low temperatures (Figure 1). These results suggest the presence of an inclusive complex at low temperatures and increasing concentrations of an exclusive complex as the temperature is increased.

If two types of 1:1 complexes are present according to

$$Cs^+ + C \underset{}{\overset{K_1}{\rightleftarrows}} \underset{\text{(exclusive)}}{(Cs^+C)_{ex}} \overset{K_2}{\rightleftarrows} \underset{\text{(inclusive)}}{(Cs^+C)_{in}} \qquad (1)$$

then, at a given temperature, the ratio

$$\frac{(Cs^+C)_{ex} + (Cs^+C)_{in}}{(Cs^+)(C)} = K \qquad (2)$$

is a constant, related to the individual equilibrium constants by

$$K = K_1(1 + K_2) \qquad (3)$$

The values of this apparent equilibrium constant and the limiting chemical shift at each temperature, determined by a least-squares fit of the chemical shift vs. mole ratio, are given in Table I for solutions in acetone, PC, and DMF. A semilog plot of K vs. $1/T$ is shown in Figure 6.

The NMR line shapes as a function of temperature for solutions with mole ratio (C222/Cs^+) = 0.5 are shown in Figures 7–9. A characteristic exchange pattern is observed. If step 2 (eq 1) is fast compared with step 1, then the two-site exchange equations are valid. Although, as discussed below, this is probably not valid for solutions in acetone and PC at low temperatures, the complete line shapes were fitted by the two-site Bloch equations, modified for exchange. A nonlinear

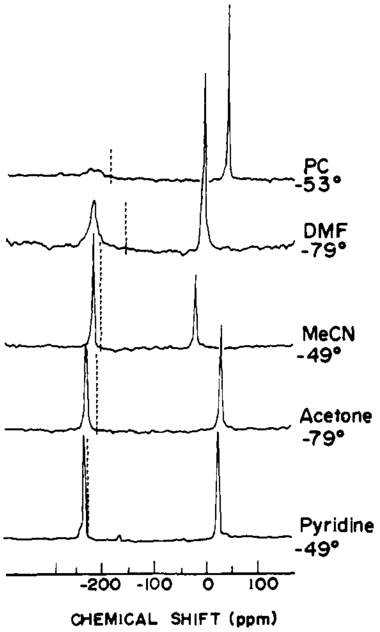

Figure 1. Cesium-133 NMR spectra at low temperatures of $Cs^+ \cdot C222$ (left peaks) and Cs^+ (right peaks) in solutions containing cesium tetraphenylborate and one-half the equivalent amount of cryptand-2,2,2. The dotted lines give the limiting chemical shifts at room temperatures ($[C222]/[Cs^+] \gg 1$).

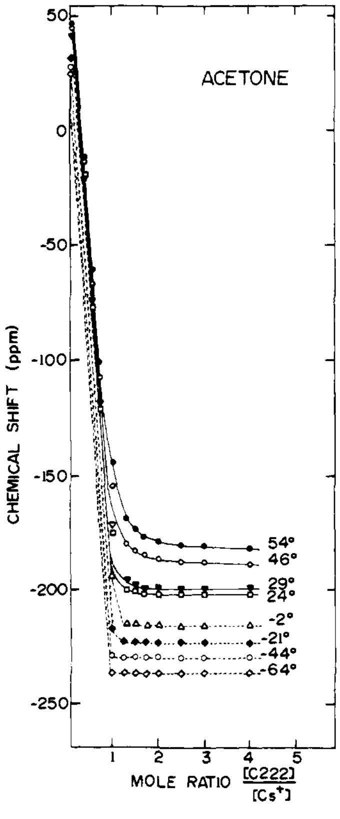

Figure 2. Cesium-133 chemical shift vs. mole ratio, $[C222]/[Cs^+]$, in acetone solutions at various temperatures.

least-squares program was used.[11] Semilog plots of τ vs. $1/T$ for the three solvents are given in Figure 10.

Discussion

The remarkably large paramagnetic shift, -245 ± 5 ppm, for Cs^+ trapped in the C222 cryptand contrasts with shifts ranging from +50 ppm for $Cs^+ \cdot 2(18C6)$, +8 to −20 ppm for $Cs^+ \cdot (18C6)$, −20 to −40 ppm for $Cs^+ \cdot (DCC)$, and −50 to −80 ppm for $Cs^+ \cdot (C222B)$. The variability for a given complex is caused by solvent effects. The abbreviations 18C6, DCC, and C222B refer to 18-crown-6, dicyclohexyl-18-crown-6, and monobenzo-2,2,2-cryptand, respectively. The origin of these shifts, which are all strongly paramagnetic compared to gaseous Cs^+,[7] is electron donation from the solvent and/or the complexing agent into p and d orbitals of the ion. When the interaction is free to relax to an optimum ion–ligand distance then one might expect to correlate the magnitude of the

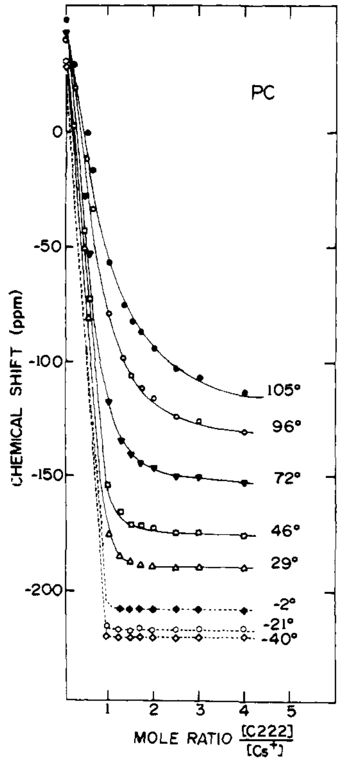

Figure 3. Cesium-133 chemical shift vs. mole ratio, $[C222]/[Cs^+]$, in propylene carbonate solutions at various temperatures.

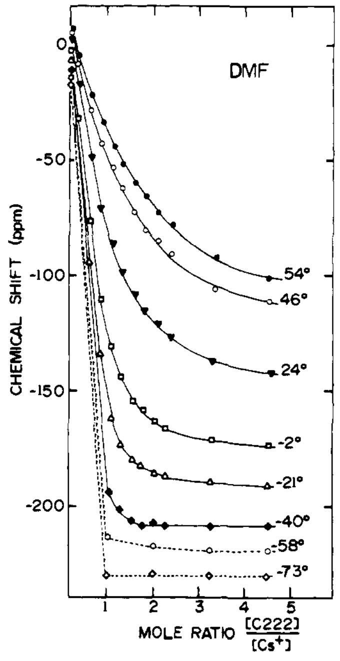

Figure 4. Cesium-133 chemical shift vs. mole ratio, $[C222]/[Cs^+]$, in *N,N*-dimethylformamide solutions at various temperatures.

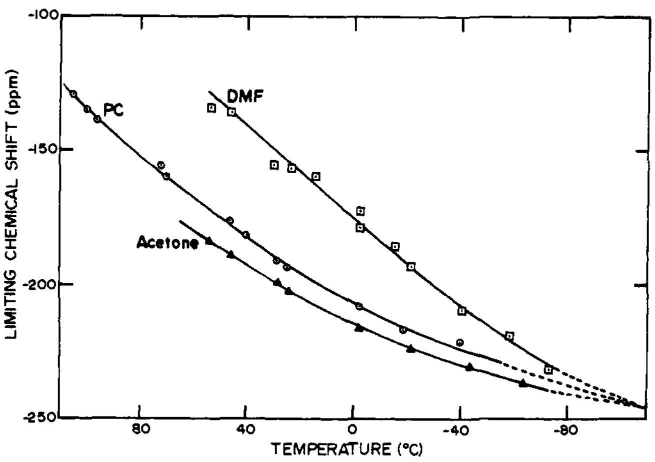

Figure 5. Limiting cesium-133 chemical shift at high mole ratios, [C222]/[Cs^+], vs. temperature for solutions in acetone, propylene carbonate, and *N,N*-dimethylformamide.

Table I. Limiting Chemical Shifts and Apparent Formation Constants of the $Cs^+{\cdot}C222$ Complex in Acetone, Propylene Carbonate, and *N,N*-Dimethylformamide at Various Temperatures

Temp, °C	Limiting chemical shift,[a] ppm	Apparent formation constant, M^{-1}
	Acetone	
54	−184	$1.9 \pm 0.2 \times 10^3$[b]
46	−189	$3.8 \pm 0.3 \times 10^3$
29	−200	$1.8 \pm 1.1 \times 10^4$
24	−203	$1.8 \pm 0.5 \times 10^4$
	Propylene Carbonate	
105	−129	$1.7 \pm 0.1 \times 10^2$
100[c]	−136	$2.6 \pm 0.2 \times 10^2$
96	−139	$3.6 \pm 0.3 \times 10^2$
72	−156	$1.0 \pm 0.1 \times 10^3$
70[c]	−160	$8.6 \pm 0.4 \times 10^2$
46	−177	$4.0 \pm 0.9 \times 10^3$
40[c]	−182	$4.1 \pm 0.3 \times 10^3$
29	−191	$6.7 \pm 0.4 \times 10^3$
25[c]	−194	$1.0 \pm 0.1 \times 10^4$
	N,N-Dimethylformamide	
54	−134	$4.43 \pm 0.05 \times 10^1$
46	−136	$7.0 \pm 0.6 \times 10^1$
25[c]	−155	$1.56 \pm 0.06 \times 10^2$
24	−156	$1.48 \pm 0.02 \times 10^2$
−2	−178	$5.12 \pm 0.06 \times 10^2$
−2[c]	−172	$6.9 \pm 0.3 \times 10^2$
−15[c]	−186	$9.2 \pm 0.9 \times 10^2$
−21	−194	$1.11 \pm 0.08 \times 10^2$
−40	−209	$6 \pm 2 \times 10^3$

[a] Estimated precision ±1 ppm; estimated accuracy ±3 ppm. [b] Standard deviation estimates given based upon the least-squares fit of chemical shift vs. mole ratio. [c] 0.01 M cesium tetraphenylborate used; all others are 0.02 M solutions.

paramagnetic shift with the strength of the interactions, i.e., electron-pair donation. However, when the electron-pair donors are rigidly interconnected, a large paramagnetic shift can occur because of strong overlap of the electron pairs with the cation orbitals even when the individual electron pair-cation interaction may be on the repulsive side of the binding curve. According to this picture, the large chemical shift for Cs^+ inside of a C222 cavity is caused by the "tightness" of the fit. The net binding energy can be relatively small even though the lone-pair donation by individual cryptand oxygens is large.

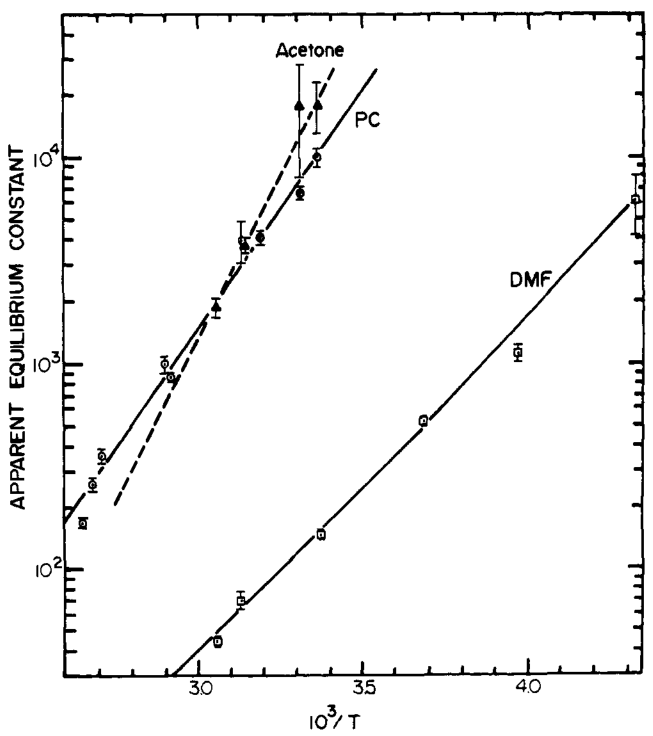

Figure 6. Semilog plot of the apparent equilibrium constant, $K = [Cs^+C222]_{total}/([Cs^+]{\cdot}[C222])$, vs. $10^3/T$ for solutions in acetone, propylene carbonate, and *N,N*-dimethylformamide. The lines through the data were calculated from the thermodynamic parameters given in Table III.

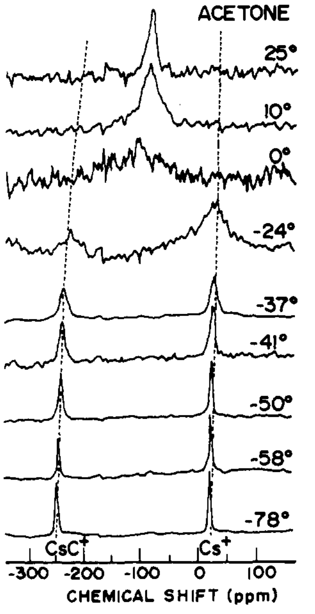

Figure 7. Cesium-133 NMR spectra at various temperatures for a mixture of 0.02 M CsTPB and 0.01 M cryptand-2,2,2 in acetone. The dashed lines give the positions of the $Cs^+{\cdot}C222$ complex and the Cs^+ ion at the corresponding temperatures.

The variation of the chemical shift with solvent and temperature and the common limiting value at low temperatures strongly suggest the presence of at least two types of 1:1 complexes. The chemical shift of Cs^+ in an external complex should be considerably less negative than that for the inclusive complex because much of the repulsive overlap has been relieved. Most of the observed variation of the chemical shift with solvent and temperature would then reflect changes in the

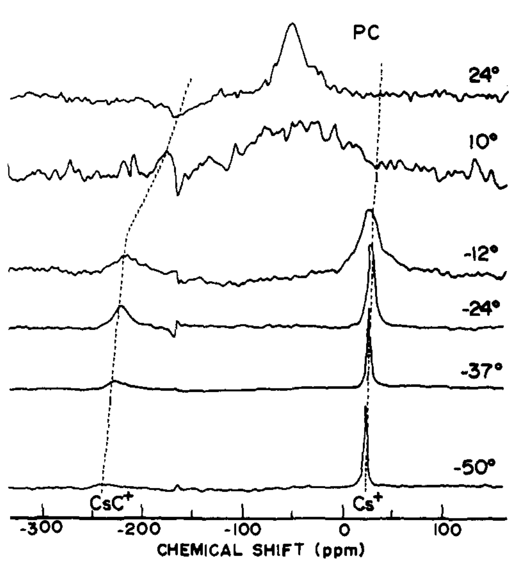

Figure 8. Cesium-133 NMR spectra at various temperatures for a mixture of 0.02 M CsTPB and 0.01 M cryptand-2,2,2 in propylene carbonate. The dashed lines give the positions of the Cs^+•C222 complex and the Cs^+ ion at the corresponding temperatures.

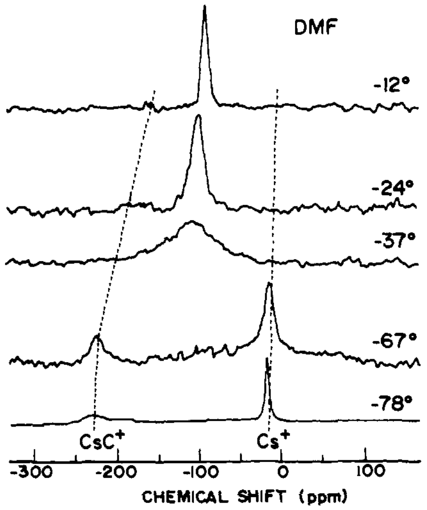

Figure 9. Cesium-133 NMR spectra at various temperatures for a mixture of 0.02 M CsTPB and 0.01 M cryptand-2,2,2 in *N,N*-dimethylformamide. The dashed lines give the positions of the Cs^+•C222 complex and the Cs^+ ion at the corresponding temperatures.

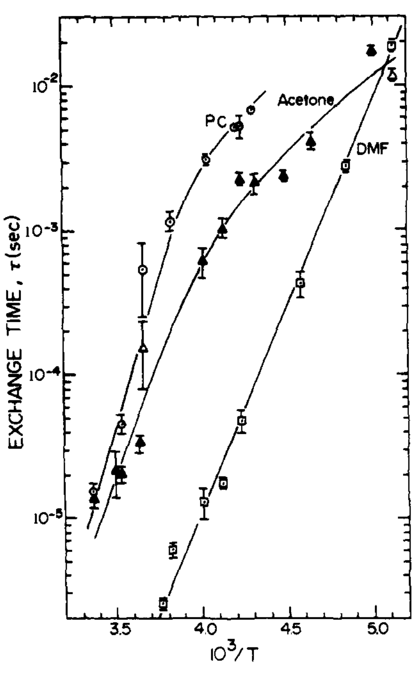

Figure 10. Variation of the exchange time, τ, obtained from a two-site fit of the complete NMR line shape as a function of temperature for three solvents.

Table II. The Effect of Various Choices for the Chemical Shift of the Exclusive Cs^+-C222 Complex on ΔH_2, the Enthalpy Change for Formation of the Inclusive Complex from the Exclusive Complex

Solvent	δ_{ex}, ppm	$\Delta H_2°$, kcal mol^{-1}
Acetone	6.4	-2.5 ± 0.1
	-53.6	-2.7 ± 0.1
Propylene carbonate	8.1	-2.9 ± 0.1
	28.0	-2.8 ± 0.1
	-52.6	-3.3 ± 0.2
N,N-Dimethylformamide	-3.4	-2.6 ± 0.1
	-51.8	-2.8 ± 0.1

relative populations of the exclusive and inclusive complexes.

Equation 3, which is valid when both complexes are present, predicts that a plot of log K vs. $1/T$ would *not* be a straight line unless either $K_2 \ll 1$ or $|\Delta H_2°| \ll |\Delta H_1°|$. However, the data given in Table I *do* give straight-line plots as shown in Figure 6. Therefore the complexation constants do not provide evidence for more than one complex. Such evidence is, however, provided by the rate data shown in Figure 10. For solutions in both acetone and PC the Arrhenius plots show marked curvature at low temperatures while a straight line is observed for solutions in DMF. Inspection of Figures 7-9 shows that for acetone and PC solutions, the line shape has reached nearly the slow-exchange limit at −37° and −24°, respectively, while for solutions in DMF, the slow-exchange limit is at −67° or below. Therefore we might expect that the line shape is dominated by process 1 (eq 3) for DMF solutions over the entire temperature range. However, for solutions in acetone and PC any slowing down of the exclusive-to-inclusive exchange rate at low temperatures would profoundly affect the line shape in the slow-exchange region. Indeed, at low temperatures, especially for solutions in PC, the Cs^+•C222 resonance broadens markedly as the temperature is lowered, suggesting that process 2 (eq 3) is becoming slow enough to affect the line width. If this is indeed the case, then treatment of the line shape with a two-site equation is not valid and the τ values which result from such a treatment will be too low.

The fact that the two peaks occur at chemical shifts characteristic of the inclusive complex and the Cs^+ ion, respectively, and that only a single peak is observed at high C222/Cs^+ mole ratios proves that the initial complexation step has a larger characteristic lifetime, τ, than the isomerization step. Because of curvature in the Arrhenius plots for solutions in acetone and PC and the likelihood that the two-site line shape equations are not valid, we can obtain the activation parameters only for solutions in DMF. The results are: $\Delta H_0^{\ddagger} = 12.9 \pm 0.3$ kcal mol^{-1} and $\Delta S_0^{\ddagger} = +17 \pm 1$ cal mol^{-1} deg^{-1} for the release of Cs^+ from C222. These are comparable to the values $\Delta H_0^{\ddagger} = 14.3 \pm 0.6$ kcal mol^{-1}, $\Delta S_0^{\ddagger} = +15 \pm 2$ cal mol^{-1} deg^{-1} for the release of Cs^+ from C222B in PC.[8]

The most direct effect of the exclusive-inclusive process appears to be the large difference in chemical shift. At high mole ratios of cryptand to Cs^+ only equilibrium 2 is important and we can relate the limiting chemical shift δ_{obs} to the relative mole fraction of exclusive and inclusive complexes, X_{ex} and X_{in}, respectively, through

$$\delta_{obs} = \delta_{ex}X_{ex} + \delta_{in}X_{in} \tag{4}$$

Table III. Thermodynamic Parameters ($\Delta H_1°$ and $\Delta S_1°$) for the Formation of the Exclusive Complex, $Cs^+ \cdot C222$, and for Its Conversion ($\Delta H_2°$ and $\Delta S_2°$) to the Inclusive Complex in Acetone, Propylene Carbonate, and *N,N*-Dimethylformamide

Solvent	$\Delta H_1°$, kcal mol^{-1}	$\Delta S_1°$, cal mol^{-1} deg^{-1}	$\Delta H_2°$, kcal mol^{-1}	$\Delta S_2°$, cal mol^{-1} deg^{-1}
Acetone	(−12.9)[a]	(−26.8)[a]	−2.5	−5.6
Propylene carbonate[b]	−8.6	−13.7	−2.9	−7.0
N,N-Dimethylformamide[b]	−5.7	−11.2	−2.6	−7.6

[a] The limited temperature range and small number of points (see Figure 6) obtained for acetone solutions provide only these crude estimates of $\Delta H_1°$ and $\Delta S_1°$. [b] Estimated uncertainties in the $\Delta H°$ and $\Delta S°$ values are ±0.4 kcal mol^{-1} and ±1.5 cal mol^{-1} deg^{-1}, respectively, for solutions in PC and DMF.

which yields

$$K_2 = \frac{\delta_{obs} - \delta_{ex}}{\delta_{in} - \delta_{ex}} \qquad (5)$$

Since $\delta_{in} = -245$ ppm, independent of solvent, if we knew δ_{ex}, K_2 could be calculated at each temperature. Since

$$\Delta G_2° = -RT \ln K_2 = \Delta H_2° - T\Delta S_2° \qquad (6)$$

and we can expect $\Delta H_2°$ and $\Delta S_2°$ to be reasonably constant, an attempt was made to adjust three parameters, δ_{ex}, $\Delta H_2°$, and $\Delta S_2°$ to fit the data. However, it was found that $\Delta H_2°$, δ_{ex}, and $\Delta S_2°$ are so strongly "coupled" that they could not be independently determined. To test whether the proposed model was reasonable, the value of δ_{ex} was fixed at either of two values; the chemical shift of the $Cs^+ \cdot 18C6$ complex or that of the $Cs^+ \cdot C222B$ complex in the same solvent. For the solvent PC an additional value of δ_{ex}, 20 ppm higher than that of the 18C6 complex, was also tested. The results are given in Table II. It can be seen that for any reasonable choice of δ_{ex}, $\Delta H_2°$ is small and not too dependent upon the choice. This is fortunate since it might be expected that δ_{ex} depends not only upon solvent but upon temperature as well. Simulation of the expected variation of δ_{obs} with temperature over the range −100 to 500 °C with the values of δ_{ex}, $\Delta H_2°$, and $\Delta S_2°$ used for fitting the data showed that we had sampled only the low-temperature portion of the curve and that experiments to obtain δ_{ex} directly from the observed chemical shifts would require temperatures far above those which are accessible to experiment.

By assuming that δ_{ex} is the same as the chemical shift of the 18-crown-6 complex of Cs^+ it was possible to obtain values of K_2 as a function of temperature. From these values and the apparent constant K from Table I, K_1 could also be calculated as a function of temperature. In this way, the values of $\Delta H_1°$, $\Delta S_1°$, $\Delta H_2°$, and $\Delta S_2°$ given in Table III were obtained.

The small value of $\Delta H_2°$ compared with $\Delta H_1°$ accounts for the absence of noticeable curvature in semilog plots of K vs. $1/T$ shown in Figure 6. The lines through the data were calculated by using the thermodynamic values given in Table III. The calculations included the effects of both exclusive and inclusive complex formation.

As expected, $\Delta H_2°$ and $\Delta S_2°$ are essentially independent of solvent while $\Delta H_1°$ and $\Delta S_1°$ are solvent dependent. Most of the loss of primary solvation would be expected to occur during formation of the exclusive complex.

All of the results reported here are consistent with the presence in solution of two types of 1:1 complexes, an exclusive complex whose binding energy, activation energy, and chemical shift are similar to those of complexes between the Cs^+ ion and the monobenzo-2,2,2-cryptand, and an inclusive complex whose binding energy is only slightly greater than that of the exclusive complex but whose chemical shift is much more negative. There is no evidence for formation of 2:1 "sandwich-type" complexes with either C222 or C222B, probably because even in the exclusive complex the cesium ion is partially enclosed in the cavity. By contrast, the crown ethers have a strong tendency to form 2:1 complexes in these solvents.[9]

It is interesting that the activation entropy, $\Delta S^{\ddagger}$, for the release of Cs^+ from C222 in DMF has a value (+15 cal mol^{-1} deg^{-1}) which is nearly as large as the overall entropy change for the release of Cs^+ from the inclusive complex (+20 cal mol^{-1} deg^{-1}). This suggests that the activated complex resembles the final state (the solvated cesium ion and the free cryptand) rather than the initial state (the complexed cesium ion). Similar conclusions were reached for lithium and sodium cryptates.[10,11] The origin of such a large positive entropy change is uncertain. The fact that $\Delta S^{\ddagger}$ for the corresponding release of Cs^+ from crown complexes has the opposite sign suggests that configurational entropy changes may play an important role. However, effects caused by solvation of the cation and the complexing agent and changes in the solvent structure complicate any interpretation of the overall entropy change.

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References and Notes

(1) J.-M. Lehn, *Struct. Bonding*, **16**, 1 (1973).
(2) D. Moras, B. Metz, and R. Weiss, *Acta Cryst.*, **B29**, 388 (1973).
(3) J.-M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc.*, **97**, 6700 (1975).
(4) A. I. Popov, in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, Inc., New York, N.Y., Vol. 2, Chapter 13, 1976.
(5) E. Mei, J. L. Dye, and A. I. Popov, *J. Am. Chem. Soc.*, **99**, 5308 (1977), and references listed therein.
(6) V. A. Nicely and J. L. Dye, *J. Chem. Educ.*, **48**, 443 (1971).
(7) J. D. Halliday, R. E. Richards, and R. R. Sharp, *Proc. Roy. Soc. London, Ser A*, **313**, 45 (1969).
(8) E. Mei, A. I. Popov, and J. L. Dye, *J. Phys. Chem.*, **81**, 1677 (1977).
(9) E. Mei, J. L. Dye, and A. I. Popov, *J. Am. Chem. Soc.*, **98**, 1619 (1976).
(10) Y. M. Cahen, J. L. Dye, and A. I. Popov, *J. Phys. Chem.*, **79**, 1292 (1975).
(11) J. M. Ceraso, P. B. Smith, J. S. Landers, and J. L. Dye, *J. Phys. Chem.*, **81**, 760 (1977).