

A Study of the Inclusive and Exclusive Cesium Cryptates in Nonaqueous Solvents by ^{133}Cs NMR

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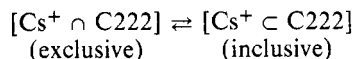
Abstract: Cesium ion complexes with cryptands C222, C322, and C222B were studied by ^{133}Cs NMR in several nonaqueous solvents in the +63 to -110 °C temperature range. The results indicate that only an *inclusive* complex is formed at all temperatures with C322 whose cavity size is commensurate with that of the cation. The smaller cavity and higher rigidity of C222B allow only the formation of the *exclusive* complex while in the intermediate case of cryptand C222 temperature- and solvent-dependent *exclusive* \rightleftharpoons *inclusive* equilibrium is observed. In polar solvents the equilibrium is essentially completely displaced toward the inclusive complex at ~ -100 °C, but in tetrahydrofuran solutions the formation of the inclusive complex is hindered by the strong cation-anion interaction. Addition of water in low concentration, in this case, gives both complexes and the exchange between the two cationic sites is slow enough at -100 °C to give separate ^{133}Cs signals for the two complexes.

Introduction

Diazapolyoxamacrobicyclic ligands (cryptands) have a somewhat flexible skeleton^{2,3} and can form stable complexes with alkali cations even in some cases where the nominal ligand cavity size is slightly smaller than the diameter of the cation. Thus, for example, X-ray studies of a solid cesium ion-cryptand C222 complex showed that the cation is situated in the center of the cavity,⁴ although the cationic radius is 1.65 Å while that of the cavity is about 1.4 Å.⁵

On the other hand, our recent studies of the Cs^+ -C222 complex in various solvents by ^{133}Cs NMR have indicated coexistence at room temperature of two types of complexes,^{6,7} an *inclusive* complex such as described above and an *exclusive* complex in which the cation is partially enclosed in the cavity of the ligand.⁸ In the latter case, the cation is still partially solvated and the ^{133}Cs chemical shift of the complexed cation is solvent dependent.

The equilibrium



is temperature dependent and shifts to the right with decreasing temperature. At ~ -100 °C the ^{133}Cs resonance becomes independent of the solvent,^{6,7} showing that in the inclusive complex the cation is very effectively insulated from the medium.

It is interesting to note that a recent crystallographic study of the K^+ -C221 complex showed that the cation protrudes out of the ligand cavity.⁹ Here again, the cation is somewhat larger than the cavity of the cryptand.

It was of interest to continue the studies of the equilibria between the two forms of the complexes and to establish more thoroughly the influence of the solvent and temperature on these equilibria. As before,^{6,7} we used ^{133}Cs NMR as the probe for the immediate chemical environment of the cesium ion.

Experimental Section

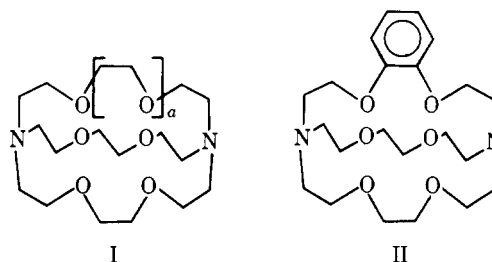
Instrumentation. Cesium-133 resonance was observed at 7.8709 MHz and a field of 1.41 T in the pulsed Fourier-transform mode. Measurements were carried out on a DA-60 Varian spectrometer equipped with a wide band probe,¹⁰ using 15-mm nonspinning tubes. All chemical shifts are referenced to an infinitely dilute aqueous solution of cesium bromide. The shifts have been corrected for the difference in the bulk diamagnetic susceptibilities of the solvents. In contrast to the previous publications of two of the authors (A.I.P. and J.L.D.), in this paper we designate paramagnetic (downfield) shifts as *positive*.

Proton magnetic resonance was observed on a Bruker WH-180 spectrometer. The measurements were carried out in the Fourier

transform mode at 4.228 T and at a frequency of 180 MHz in 10-mm tubes.

Reagents. Cryptand C222 (I, with $a = 1$) was obtained from E. M. Laboratories. It was purified by two recrystallizations from hexane followed by a vacuum sublimation at ~ 90 °C.

Cryptands C322 (I, $a = 2$) and C222B (II) were synthesized as



described earlier.¹¹⁻¹³ Cryptand C322 was purified by vacuum distillation at ~ 150 – 175 °C. The monobenzo derivative, C222B, was purified by dissolving it in hot toluene and passing the solution through an alumina column which was then eluted with toluene containing 2% methanol. The solvent was evaporated and the residue dried for several hours under vacuum. Both C222B and C322 are oils at room temperature.

Cesium thiocyanate and cesium octanoate were commercial products. Both compounds were dried under vacuum before use.

Methanol and deuterated methanol were purified by distillation over magnesium turnings. Tetrahydrofuran was dried over calcium hydride and then distilled from Na-K alloy. Nitropropane was distilled from phosphorus pentoxide, then further dried with freshly activated molecular sieves, followed by another distillation.

Results and Discussion

Studies in Methanol Solutions. The variation of the ^{133}Cs chemical shift with temperature in methanol solution is shown in Figure 1. Measurements were carried out on a 0.05 M solution of CsSCN . An external reference (0.5 M aqueous CsBr at ambient temperature) was used, but the chemical shifts were corrected to the infinitely dilute cesium salt solution as described in the Experimental Section.

Downfield ^{133}Cs shifts with increasing salt concentration have been observed previously as a result of contact ion pair formation.¹⁴ However, one would expect that the increase in the dielectric constant upon lowering the temperature will favor ion-pair dissociation¹⁵ so that in this case the paramagnetic shift indicates an increase in the solvent-cation interaction at lower temperatures.

When an excess of cryptand C322 is added to a 0.05 M solution of cesium thiocyanate in methanol, a narrow ^{133}Cs resonance signal is observed at +22.1 ppm. The frequency of the resonance is *independent of temperature* in the 25 to -95

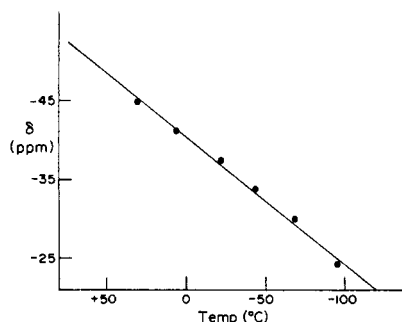


Figure 1. Temperature dependence of the cesium-133 chemical shift of a 0.05 M solution of CsSCN in methanol.

°C temperature range. Since $\log K_f$ of the C322-Cs⁺ complex is >6 ,¹⁶ the solution must contain essentially all of the cesium ion in the complexed form. The constancy of the chemical shift with temperature indicates the constancy of the chemical environment. In other words, the cation is completely enclosed in the cavity of the ligand, and, in contrast to the C222-Cs⁺ system, only the *inclusive* complex exists in the solution at all temperatures. These results are not unexpected since the cavity size of the C322 cryptand is larger than the size of the cesium ion (3.6 vs. 3.38 Å). Also, in this case the ¹³³Cs chemical resonance is at a relatively high field compared with the C222-Cs⁺ inclusive complex, since the overlap between the lone-pair orbitals of the ligand and the outer p orbitals of the cation is much smaller than in the case of the tight-fitting C222-Cs⁺ cryptate.^{6,7}

The cesium-133 resonance of a methanol solution 0.05 M in C322 and 0.10 M in CsSCN was observed as a function of temperature. As shown in Figure 2, the resonance is exchange broadened at 30 °C. The coalescence temperature is 26 ± 2 °C. The analysis of the spectra gives the following results: decomplexation rate constant (25 °C) $k = 1090 \pm 20 \text{ s}^{-1}$; $\Delta G^\ddagger = 13.3 \pm 0.1 \text{ kcal mol}^{-1}$.

The cesium-133 chemical shift of a 1:1 mixture of cesium thiocyanate and cryptand C222 was studied in methanol solution between +63 and -108 °C. The concentrations of the ligand and of the salt were both 0.05 M. The results are shown in Figure 3. Only a single resonance was observed at all temperatures. It is seen that the resonance shifts downfield with decreasing temperature but below -100 °C it reaches a constant value of $+244 \pm 3 \text{ ppm}$. The same limiting value was previously observed for the 1:1 C222:Cs⁺ mixtures in acetone, propylene carbonate, and *N,N*-dimethylformamide solutions.⁶

Since the formation constant of the C222-Cs⁺ complex in methanol is $10^{4.4}$, the concentration of the uncomplexed Cs⁺ ion must be negligible.¹⁶ The variation of the ¹³³Cs chemical shift with temperature, therefore, is attributed to an equilibrium between the exclusive and the inclusive forms of the complex. Below -100 °C the complex is entirely in the inclusive form and the cesium-133 chemical shift becomes independent of the solvent. The magnitude of the paramagnetic shift indicates a strong overlap between the orbitals of the donor atoms and the outer p orbital of the cesium ion. Such strong overlap is consistent with a tightly fitting ion inside a "stretched" cavity of the inclusive complex. In a "loose" exclusive complex the overlap is much weaker and the ¹³³Cs resonance is much further upfield.

¹H NMR Studies. Proton magnetic resonance spectra of the cryptand protons were obtained for a 1:1 mixture of C222-CsSCN in methanol-*d*₄ solutions. At room temperature the spectrum consists of a singlet for the OCH₂CH₂O protons at 0.31 ppm (with respect to the CHD₂ proton of incompletely deuterated methanol) and an AA'XX' "triplet" at 0.23 ppm for the OCH₂CH₂N protons and at -0.74 ppm for the NCH₂

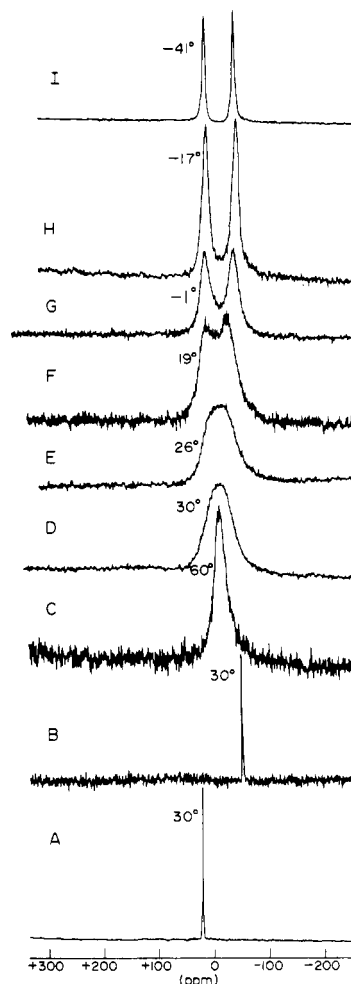


Figure 2. Cesium-133 spectra of (A) a solution containing CsSCN and an excess of C322; (B) uncomplexed Cs⁺ in methanol; (C-I) a methanol solution 0.05 M in C322 and 0.10 M in CsSCN at various temperatures.

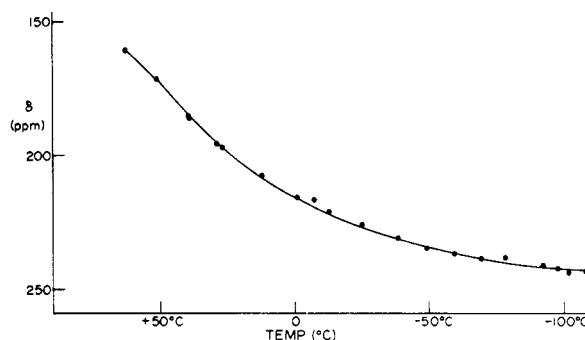


Figure 3. Cesium-133 chemical shift of a methanol solution 0.05 M in C222 and 0.05 M in CsSCN as a function of temperature.

protons (Figure 4). The same pattern was previously reported by Lehn et al.^{12,17} The spectrum represents a rapid exchange between all conformations of the ligand.

The resonance of the NCH₂ protons was studied as a function of temperature. At -102 °C the resonance is split into two signals, each corresponding to a single proton (Figure 4C). The ligand in the complex (all in the inclusive form at this temperature) must be frozen in one configuration in which the two protons are in different environments. It seems reasonable to assume that one proton is pointing inside the cavity and is influenced by the cation as well as by the neighboring nuclei of the ligand. The second proton is directed outside the cavity and is influenced by the solvent. The kinetic data follow: coales-

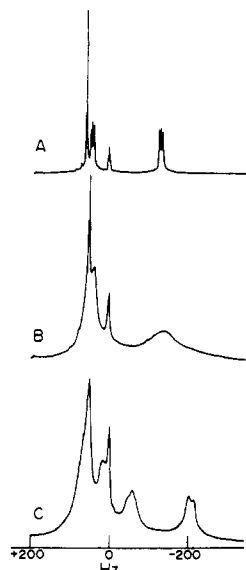


Figure 4. ^1H NMR of 0.05 M CsSCN and 0.05 M C222 in methanol: (A) room temperature; (B) -76°C ; (C) -102°C .

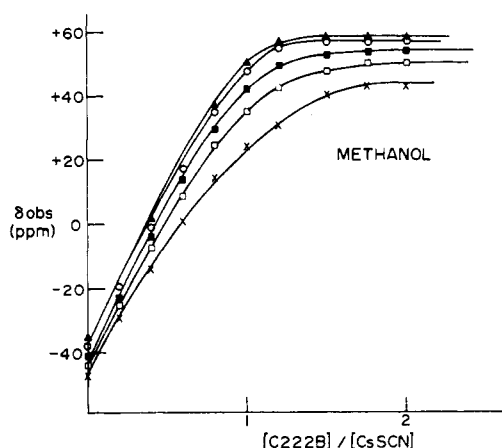


Figure 5. Cesium-133 chemical shift as a function of C222B/ Cs^+ mole ratio in methanol solution: X, $+55^\circ\text{C}$; \square , $+30^\circ\text{C}$; \blacksquare , $+12^\circ\text{C}$; \circ , -9°C ; Δ , -20°C . This solution was 0.05 M in CsSCN.

cence temperature $-79 \pm 4^\circ\text{C}$ (Figure 4B), $k_c \geq 355\text{ s}^{-1}$, and $\Delta G^\ddagger = 9.0 \pm 0.1\text{ kcal}$. Similar results were obtained for a 1:1 C222-KSCN mixture in methanol- d_4 solution which is expected to contain only the $[\text{K}^+ \subset \text{C222}]$ cryptate.

Cesium Ion Complex with Monobenzo C222. Monobenzo C222 (C222B, II) has a somewhat smaller cavity size than the unsubstituted ligand. The ligand is less readily deformed than C222 and, therefore, it should be even less capable of forming an inclusive complex with the large Cs^+ ion.

The cesium-133 resonance of a 1:1 mixture of CsSCN and C222B shifts downfield with decreasing temperature. In contrast to the C222- Cs^+ system, however, the resonance shifts downfield only from +21 to +60.5 ppm in going from $+63$ to -100°C . At the same time, below -20°C the band broadens, attains maximum width at -60°C , and then begins to narrow. Below -90°C a weak signal appeared at -26 ppm . This resonance frequency is identical with that of the Cs^+ ion solvated by methanol. Thus it appears that the complex is relatively weak so that, in contrast to the C222 and C322 complexes, the C222B- Cs^+ complex is appreciably dissociated in solutions with stoichiometric ratios of the ligand and the salt. Above -56°C the exchange is fast, but at -90°C it slows down sufficiently to separate the individual signals for the two Cs^+ sites.

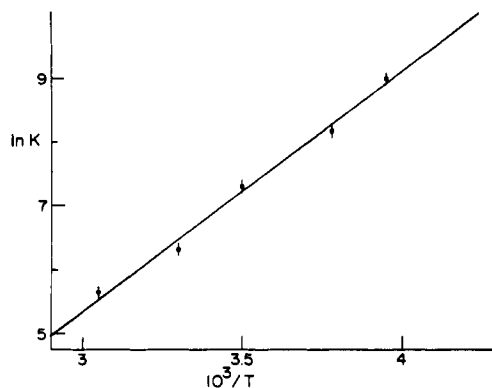


Figure 6. Plot of $\ln K_f$ vs. $1/T$ for the C222B- Cs^+ complex in methanol.

The cavity of the C222B is slightly smaller and more difficult to deform than that of C222 since one of the C-C bonds of one of the chains is replaced by an aromatic linkage.⁵ An inclusive complex would have an even larger overlap between the lone-pair orbitals of the ligand and the outer p orbital of the cesium ion than the overlap in the case of the C222- Cs^+ complex, i.e., the chemical shift should be *downfield* from +244 ppm. The fact that the limiting chemical shift for the complexed Cs^+ ion at low temperatures is at +60.5 ppm reveals that the complex must be of the *exclusive* type.

Cesium-133 chemical shifts were determined at several temperatures as a function of the C222B/CsSCN mole ratio. The results are shown in Figure 5. The analysis of these data by previously described techniques^{6,7} gives the values of the formation constant. The enthalpy and the entropy of complexation were determined from the temperature dependence of the complexation constant (Figure 6). The values are $\log K_{f(298)} = 2.9 \pm 0.1$, $\Delta G_c^\circ = -3.9 \pm 0.1\text{ kcal mol}^{-1}$, $\Delta S_c^\circ = 9.9 \pm 0.1\text{ eu}$, $\Delta H_c^\circ = -0.97 \pm 0.05\text{ kcal mol}^{-1}$. A value of $\log K_f$ of 3.2 was found using a cation selective electrode.^{5,18}

It is seen that the Cs^+ -C222B complex is both enthalpy and entropy stabilized, the entropy stabilization being dominant. In contrast, the complexation of the Cs^+ ion in several non-aqueous solvents by C222,⁶ by 18-crown-6,¹⁹ or by dibenzo-30-crown-10²⁰ is enthalpy stabilized but entropy destabilized. In these latter cases we assumed that the overall decrease in the entropy of the system upon complexation is related to a decrease in the conformational entropy of the ligand which is quite flexible in the free state but is locked into a rigid conformation upon complexation. It was indicated above, however, that cryptand C222B already has a more rigid structure and the conformational entropy change upon complexation should be smaller, so that the entropy increase caused by the desolvation of the cation dominates.

Studies in Nitropropane Solutions. Nitropropane is a polar solvent ($\mu = 3.59\text{ D}$, $D = 23.24$ at 20°C) but, by analogy with nitromethane, it should have a poor solvating ability. Since 1-nitropropane melts at -104°C compared to -29°C for nitromethane, it is a more useful solvent for studies at low temperatures.

The poor solvating abilities of this solvent are clearly demonstrated by its inability to dissolve either cesium thiocyanate or cesium octanoate in any appreciable amount. Solubilization of both salts can be achieved, however, by the addition of C222. Solutions up to 0.01 M in Cs^+ -C222 could easily be prepared by the addition of a stoichiometric amount of C222 to a suspension of the cesium salt in the solvent.

At room temperature the ^{133}Cs resonance of a solution containing a twofold excess of C222 appeared at $\sim +200\text{ ppm}$. As the temperature was lowered, the resonance shifted downfield and appeared to reach a limiting value of $\sim +235\text{ ppm}$ at -100°C , which should be close to the limiting shift.

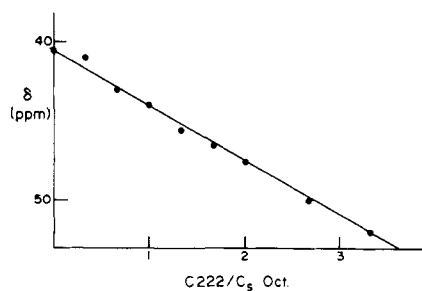


Figure 7. Variation in the ^{133}Cs chemical shift as a function of $\text{C222}/\text{Cs}^+$ octanoate at room temperature.

The paramagnetic shift of +200 ppm at room temperature indicated that most of the complex is present in the inclusive form. The low-temperature shift is ~ 10 ppm upfield from the limiting shift of the inclusive complex in other solvents.

Studies in Tetrahydrofuran Solutions. The cesium-133 chemical shift was studied in tetrahydrofuran solutions of 0.05 M cesium octanoate between +30 and -20°C . Only a very slight downfield shift with decreasing temperature was observed (+44 to +49 ppm). Below -20°C the salt was largely insoluble in THF. Just as in the case of 1-nitropropane solutions, the solubility of the salt is enhanced by the addition of C222.

The linear variation in the ^{133}Cs chemical shift with $\text{C222}/\text{Cs}^+$ mole ratio (Figure 7) even up to $\text{C222}/\text{Cs}^+ = 3$ (compare to Figure 5) shows that only a weak complex is formed. These results are not too surprising in view of the very low dielectric constant of this solvent. The salt must exist largely as tight ion pairs and the strong cation-anion interaction would compete with complexation. The chemical shifts indicate that in the +30 to -20°C temperature range the complex exists primarily in the exclusive form. It is likely that the complexed cesium ion forms an ion pair with the octanoate anion.

Interesting results were obtained upon progressive addition of water to a THF solution which was 0.02 M in C222 and 0.01 M in CsOct. As seen in Figure 8 the addition of water first induces a shift in the paramagnetic direction. When the concentration of water is ~ 4 M, the shift reverses directions and becomes diamagnetic. Addition of an equivalent volume of THF to the original solution shifts the resonance only by ~ 2 ppm, indicating that the observed effect is not caused by dilution. In pure water, at room temperature, the ^{133}Cs resonance of a 0.01 M CsOct solution is at -1.5 ppm and it is not affected by the addition of C222. These data agree with the previously reported results which indicate that the $\text{Cs}^+\text{-C222}$ complex is very weak in aqueous solutions.¹⁶

It seems reasonable to assume, therefore, that the initial addition of water results in the solvation of the octanoate anion by hydrogen bonding, thus weakening $\text{Cs}^+\text{-Oct}^-$ interaction. Consequently the equilibrium in the solution shifts toward the formation of the inclusive cesium cryptate as indicated by the paramagnetic shift. At higher water concentrations the cesium ion-water interaction begins to predominate and the C222-Cs^+ complex begins to dissociate; as a result the cesium-133 resonance shifts back to a higher field.

When a small amount of water is added to a 2:1 C222/CsOct solution (water/CsOct ~ 5), a single sharp signal at +54 ppm is obtained at room temperature. The signal broadens and shifts to a lower field as the temperature is lowered. A very broad resonance around 70 ppm is obtained at -89°C (Figure 9). Further lowering of temperature to -102°C splits the resonance into two well-separated resonances, one at +240 ppm and the other at +70 ppm. The frequencies of these two signals correspond to those expected for the Cs^+ ion in the inclusive and the exclusive forms of the C222-Cs^+ complex.

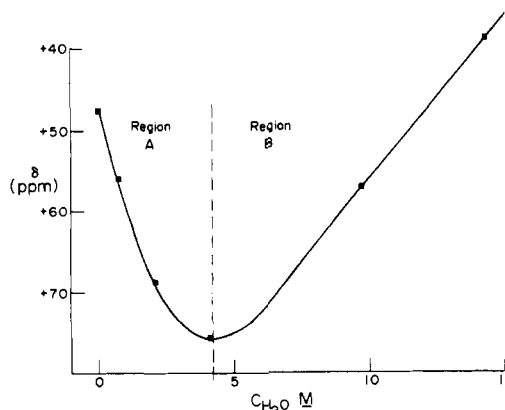


Figure 8. Variation in the ^{133}Cs chemical shift of a $\text{C222}/\text{Cs}^+$ octanoate = 2 solution in tetrahydrofuran upon addition of water.

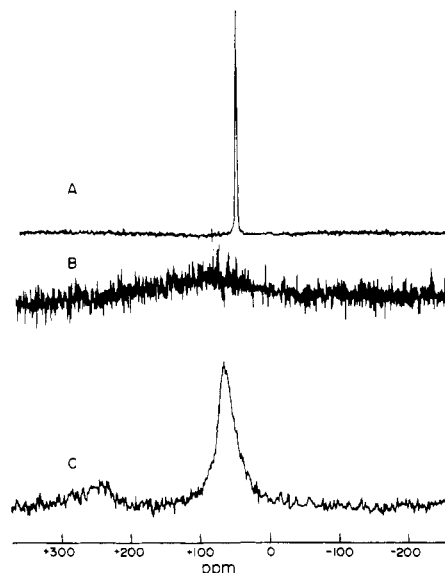


Figure 9. Cesium-133 signals of a $\text{C222}/\text{Cs}^+$ octanoate = 2 solution in THF containing a small amount of water (water/CsOct ~ 5): (A) room temperature; (B) -89°C ; (C) -102°C .

At higher water concentrations the solution freezes out before splitting of the Cs^+ resonance can be observed. However, the averaged Cs^+ signal shifts strongly downfield as the temperature is lowered, for instance, from +60 to +206 ppm between +30 and -75°C when water/CsOct ~ 18 . This indicates that lowering the temperature shifts the complex toward the inclusive form in agreement with earlier data. Thus the above results present new and convincing evidence for the existence of two forms of cesium cryptate in solutions.

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- of inclusion, the inclusive complex may be written as $[\text{Cs}^+ \subset \text{C222}]$. Since in the exclusive complex the cation penetrates *partially* into the ligand cavity, it may be represented by the intersection sign, i.e., $[\text{Cs}^+ \cap \text{C222}]$.
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Electrochemical Studies of Europium and Ytterbium Cryptate Formation in Aqueous Solution. Effects of Varying the Metal Oxidation State upon Cryptate Thermodynamics and Kinetics

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Abstract: The thermodynamics and kinetics of complexation of europium and ytterbium in both trivalent and divalent oxidation states with (2.2.1) and (2.2.2) cryptands have been monitored in aqueous media using electrochemical methods. All these cryptates were found to be electrochemically reversible and substitutionally inert on the time scale of cyclic voltammetry. The thermodynamic stabilities of the trivalent lanthanide cryptates were found to be substantially less than those of the corresponding divalent cryptates, arising from a large enthalpic destabilization outweighing a smaller entropic stabilization. These differences can be understood in terms of the marked dependence of the hydration thermodynamics of the uncomplexed cations upon their charge, and are compatible with the observed complexation thermodynamics for alkaline-earth and alkali-metal cryptates having similar ionic radii. The rates of both cryptate formation and dissociation were found to decrease markedly as the cation charge increased from one to three for cations of approximately constant size. These rate differences and also their enthalpic and entropic components are compatible with the increased changes in cation hydration that are anticipated for cryptate substitution as the cation charge increases. Marked acid catalyses were observed upon the dissociation kinetics of lanthanide cryptates which were ascribed to the need for the cryptate to undergo a conformational change prior to or during release of the cation. The trivalent lanthanide cryptates were also found to associate strongly with fluoride and hydroxide anions to an extent comparable to the aquated cations.

Introduction

A number of polyoxadiazamacrobicyclic ligands ("cryptands") originally synthesized by Lehn and co-workers have been shown to encapsulate alkali and alkaline-earth cations to form coordination compounds ("cryptates") that often exhibit high thermodynamic and kinetic stability in aqueous as well as nonaqueous media.^{1,2} This thermodynamic stability has been shown to be extremely sensitive not only to the relative sizes of the unsolvated cation and the cryptate cavity but also to the cation charge. Thus alkaline-earth cryptates generally are somewhat more stable than those for alkali-metal cations having similar ionic radii.³ Corresponding variations have also been observed in the kinetic stability of these cryptates so that a number of alkaline-earth cryptates can be classified as "substitutionally inert" complexes.⁴ These results suggest that tripositive lanthanide ions might also form thermodynamically stable and substitutionally inert cryptates with cryptands having appropriate cavity radii. Since the ionic radii of tripositive lanthanides (0.85–1.05 Å⁵) are similar to the radii of Ca²⁺ and Na⁺ which form stable complexes with (2.2.2) and particularly (2.2.1) cryptands,⁶ these ligands might be anticipated to form stable complexes with lanthanides. Indeed, a number of such lanthanide cryptates have been isolated as solids from anhydrous organic solvents.^{7,8}

Some electrochemical properties of Eu(III) cryptates in aqueous solution have been summarized in a preliminary

communication.⁷ We have found that Eu^{III}(2.2.1), Yb^{III}(2.2.1), Eu^{III}(2_B.2.1),⁹ and Eu^{III}(2.2.2) cryptates can be reduced electrochemically to the corresponding Eu(II) and Yb(II) complexes in a reversible manner. Aside from the implications to the redox chemistry of lanthanides,¹⁰ this property enables the thermodynamics and kinetics of cryptate formation to be monitored conveniently using electrochemical methods. Using this approach, we have observed that both Eu(III) and Eu(II) do indeed form substitutionally inert (2.2.1) and (2.2.2) cryptates. However, much more unexpected is the observation that the formation constants for Eu^{III}(2.2.2) and Eu^{III}(2.2.1) are about 10⁷ and 10³ smaller than for the corresponding Eu(II) cryptates.⁷ In addition, these Eu(III) cryptates were found to have a surprisingly strong tendency to complex small anions.⁷ In the present paper, results are presented of a detailed study of the thermodynamic and kinetic aspects of europium and ytterbium cryptate formation in aqueous media using electrochemical techniques. When compared with the corresponding data for alkali and alkaline-earth cryptates, these data provide some interesting insights into the effects of varying the cationic charge upon cryptate stability.

Experimental Section

Materials. Solid samples of Eu(2.2.1)Cl₃, Eu(2.2.2)Cl₃, Eu(2.2.1)(NO₃)₃, Eu(2.2.2)(NO₃)₃, Yb(2.2.1)Cl₃, and Eu(2_B.2.1)Cl₃ were prepared as described elsewhere.^{7,8a} Solutions of the aquated