of inclusion, the inclusive complex may be written as [$Cs^+ \subset$ C222]. Since in the exclusive complex the cation penetrates *partially* into the ligand cavity, it may be represented by the intersection sign, i.e., [$Cs^+ \cap$ 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 Å[5]) are similar to the radii of Ca^{2+} 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 10^7 and 10^3 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)Cl_3, Eu(2.2.2)Cl_3, Eu(2.2.1)$(NO_3)_3$, Eu(2.2.2)$(NO_3)_3$, Yb(2.2.1)Cl_3, and Eu(2_B.2.1)Cl_3 were prepared as described elsewhere.[7,8a] Solutions of the aquated

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Table I. Thermodynamics of Some Europium and Ytterbium Cryptate Redox Couples in Noncomplexing Media at 25 °C

redox couple	electrolyte	$-E_f$,[a] mV vs. SCE	$\Delta S°_{rc}$,[b] cal deg^{-1} mol^{-1}	$(\Delta G°_{III} - \Delta G°_{II})$,[c] kcal mol^{-1}	$(\Delta H°_{III} - \Delta H°_{II})$,[d] kcal mol^{-1}	$(\Delta S°_{III} - \Delta S°_{II})$,[e] cal deg^{-1} mol^{-1}
$Eu_{aq}^{3+/2+}$	0.1M NapTS (pH 3)	626[f]	48[f]			
$Eu(2.2.1)^{3+/2+}$	0.1M Et_4NClO_4	425		4.6	10.7	20.5
	0.1M $NaClO_4$	425				
	0.5M $NaClO_4$ (pH 2-7)	435	27.5			
$Eu(2.2.2)^{3+/2+}$	0.1M Et_4NClO_4	205		9.7	17.7	27
	0.5M $NaClO_4$	215	21			
$Eu(2_B.2.1)^{3+/2+}$	0.5M $NaClO_4$	370		5.9		
$Yb_{aq}^{3+/2+}$	0.1M KPF_6 (pH 5)	1423[f]	48[f]			
$Yb(2.2.1)^{3+/2+}$	0.1M Et_4NClO_4	1105		7.4	11.9	15
	0.5M $NaClO_4$	1110	33			

[a] Formal potential of redox couple, obtained from average of cathodic and anodic peak potentials of reversible cyclic voltammogram.[13] [b] Reaction entropy of redox couple: determined using nonisothermal cell arrangement.[11] [c] Difference between free energies of complexation of corresponding trivalent and divalent cryptates, obtained from E_f values using eq 1. [d] Obtained from $(\Delta H°_{III} - \Delta H°_{II}) = (\Delta G°_{III} - \Delta G°_{II}) + T(\Delta S°_{III} - \Delta S°_{II})$. [e] Obtained from $\Delta S°_{rc}$ using eq 2. [f] Data taken from ref 11.

cation Eu^{3+} were obtained by dissolving Eu_2O_3 in a slight excess of perchloric acid. The divalent aquo cation Eu^{2+} was prepared by cathodically electrolyzing Eu^{3+} using a stirred mercury pool electrode at −800 mV vs. SCE. Solutions of Eu^{2+} were found to be stable in perchlorate media over extended periods of time (~10 h) when oxygen was rigorously excluded. For ligand equilibration experiments with Eu^{2+} over longer periods of time, the solution was kept over a stirred mercury pool held at −800 mV in order to electroreduce any Eu^{3+} formed by homogeneous oxidation of Eu^{2+} by impurities. Identical electrochemical behavior was obtained for solutions of europium cryptates prepared from the solid cryptates and by mixing Eu^{2+} and the appropriate cryptand together in situ. The cryptands (2.2.1) and (2.2.2) were obtained from P.C.R., Inc. Analytical grade reagents were normally used without further purification. Water was purified using a Milli-Q purification system (Millipore Corp.).

Apparatus. Conventional two-compartment glass cells (solution volume 5-10 mL) were employed for the electrochemical measurements, with a glass frit ("very fine" grade, Corning, Inc.) separating the working and reference compartments. Bulk electrolyses were performed with cells containing a separate compartment for the platinum gauze counterelectrode. The working compartments of these cells were surrounded by a jacket through which was circulated water from a Braun Melsungen circulating thermostat. This enabled the temperature of the cell solution to be controlled to ±0.05 °C. Measurements of reaction entropies $\Delta S°_{rc}$ for cryptate redox couples employed a nonisothermal cell arrangement that is described in ref 11. Both hanging mercury drop electrodes (HMDE, Metrohm Model E410, Brinkmann Instruments) and dropping mercury electrodes (DME) were used. The latter had flow rates in the range 1.5-2.0 mg s^{-1} and the drop life was mechanically controlled to be 1, 2, or 5 s.

Cyclic voltammograms and dc polarograms were obtained using a PAR 174A polarographic analyzer (Princeton Applied Research Corp.) coupled with a Hewlett-Packard HP 7045A X-Y recorder. Constant-potential electrolyses were performed using either a PAR 174A or a PAR 173 potentiostat. All solutions were deoxygenated by bubbling with prepurified nitrogen which had passed through a V(II) solution. All electrode potentials are quoted vs. a saturated (KCl) calomel electrode (SCE), although an SCE filled with saturated NaCl was used for measurements in perchlorate media to avoid precipitation of $KClO_4$ in the liquid junction. Determinations of the thermodynamics of association between Eu(III) cryptates and fluoride anions employed an Orion Model 94-09A fluoride ion selective electrode.

Results

As noted previously,[7] the encapsulation of Eu^{3+} to form $Eu(2.2.1)^{3+}$ and $Eu(2.2.2)^{3+}$ cryptates produces substantial changes in the electrochemistry of the Eu(III)/(II) couple. Thus the cathodic-anodic cyclic voltammograms obtained for $Eu(2.2.1)^{3+}$ and $Eu(2.2.2)^{3+}$ in perchlorate electrolytes at an HMDE exhibited cathodic and anodic peaks that were independent of sweep rate with potential separations close to the value (57 mV) expected for reversible redox couples.[7] In contrast, the $Eu^{3+/2+}$ couple exhibits highly irreversible cyclic voltammograms in perchlorate media which result from the small electrochemical exchange rates for this couple.[12] Additionally, the formal potentials E_f for $Eu(2.2.1)^{3+/2+}$ and $Eu(2.2.2)^{3+/2+}$ obtained from the mean of the cathodic and anodic peak potentials[13] were found to be markedly more positive than for $Eu_{aq}^{3+/2+}$.[7] Similar behavior was also observed for $Eu(2_B.2.1)^{3+/2+}$ and $Yb(2.2.1)^{3+/2+}$ redox couples. These results are summarized in Table I, along with data for $Eu(2_B.2.1)^{3+/2+}$, $Yb(2.2.1)^{3+/2+}$, and the corresponding aquo couples. (The data for $Eu^{3+/2+}$ and $Yb^{3+/2+}$ were taken from ref 11.) Identical cyclic voltammograms with peak separations of about 60 mV were obtained for the cryptate couples in the absence and presence of added cryptand over the range of sweep rates 50-500 mV s^{-1} and for supporting electrolytes containing sodium, barium, or tetraethylammonium cations which have widely differing abilities to compete for the cryptand.[3] This indicates that both the trivalent and divalent cryptates are substitutionally inert on the cyclic voltammetric time scale, and the rate constant for electrochemical exchange k_{el} is large ($k_{el} > 5 \times 10^{-2}$ cm s^{-1} [14]). Since the difference in formal potentials ΔE_f between the complexed and uncomplexed one-electron redox couples can be related directly to the difference in the free energy driving force for these processes, we can write

$$\Delta E_f = (2.303RT/F)\log(K_{II}/K_{III}) = (\Delta G°_{III} - \Delta G°_{II})/F \quad (1)$$

where $\Delta G°_{III}$ and $\Delta G°_{II}$ are the free energies of complexation for the trivalent and divalent species, respectively, and K_{III} and K_{II} are the corresponding stability constants. The resulting values of $(\Delta G°_{III} - \Delta G°_{II})$ are listed in Table I.

It is seen that the stabilities of the trivalent cryptates are consistently and substantially smaller than for the corresponding divalent cryptates, i.e., the values of $(\Delta G°_{III} - \Delta G°_{II})$ are large and positive. In order to unravel the factors responsible for this behavior, it is desirable to evaluate the enthalpic and entropic contributions to $(\Delta G°_{III} - \Delta G°_{II})$. This can be achieved by determining the reaction entropies $\Delta S°_{rc}$ for the various redox couples. We have discussed elsewhere the measurement and significance of $\Delta S°_{rc}$;[11] it is essentially equal to the difference $(\bar{S}°_{red} - \bar{S}°_{ox})$ between the partial molal entropies of the reduced and oxidized halves of the redox couple. The values of $\Delta S°_{rc}$ are also given in Table I. These values can be used to determine the difference in the entropies of complexation between the trivalent and divalent species $(\Delta S°_{III} - \Delta S°_{II})$ from

$$\Delta S°_{III} - \Delta S°_{II} = (\Delta S°_{rc})_{aq} - (\Delta S°_{rc})_{crypt} \quad (2)$$

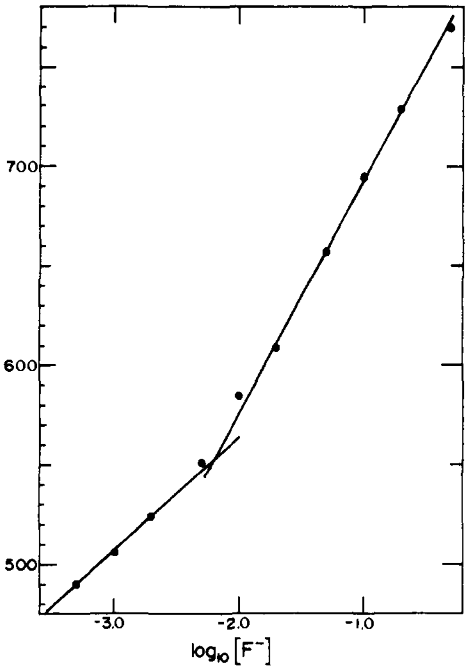

Figure 1. Plot of formal potential for $Eu(2.2.1)^{3+/2+}$ couple E^F_f in the presence of fluoride anions vs. the logarithm of the fluoride concentration, log $[F^-]$. Ionic strength held constant at 0.5 with sodium perchlorate.

where $(\Delta S°_{rc})_{aq}$ and $(\Delta S°_{rc})_{crypt}$ are the reaction entropies for the corresponding aquo and cryptate redox couples, respectively.[15] Inspection of Table I reveals that the values of $(\Delta S°_{III} - \Delta S°_{II})$ are also positive, so that the large positive values of $(\Delta G°_{III} - \Delta G°_{II})$ are associated with still larger values of the corresponding enthalpic terms $(\Delta H°_{III} - \Delta H°_{II})$.

It is clearly desirable to obtain absolute values of these thermodynamic complexation parameters for either the trivalent or divalent cryptates. Since both the nitrogens on the (2.2.1) and (2.2.2) cryptands have a strong tendency to be protonated, the required stability constants could in principle be determined by the pH-titration method used by Lehn and Sauvage.[3] For the present systems, a slightly more direct method can be employed since the concentration ratios of lanthanide cryptate to free lanthanide [LnC]/[Ln] in equilibrated solutions containing a stoichiometric excess of the cryptand can be directly determined from the magnitude of the reversible voltammetric peaks for the $LnC^{3+/2+}$ couple combined with the known total lanthanide concentration. These ratios [LnC]/[Ln] determined as a function of pH yield the required cryptate stability constants when coupled with the known pK_a values for the free cryptands.[3]

Attempts to determine K_{III} for either $Eu(2.2.1)^{3+}$ or $Eu(2.2.2)^{3+}$ in this manner failed for two reasons. First, the rate constant for ligand exchange with $Eu(2.2.1)^{3+}$ is extremely small (vide infra), so that equilibrium times of the order of a few months would be required.[16] Second, neither complex is sufficiently stable to form significantly at pH values below those where precipitation of Eu(III) as $Eu(OH)_3$ occurs (pH ~7). Nonetheless, approximate values of K_{II} for the divalent cryptates $Eu(2.2.1)^{2+}$ and $Eu(2.2.2)^{2+}$ could be obtained using the above procedure since Eu^{2+} is stable over the pH range (ca. 5-9) required for the pH titration. The ligand exchange rate for $Eu(2.2.2)^{2+}$ is rather small (half-life for aquation $\tau_{1/2} \sim 6$ h at 25 °C), which necessitated long equilibrium times ($\gtrsim 1$ day). Coupled with the sensitivity of Eu^{2+} to air oxidation, this difficulty limited somewhat the accuracy of the resulting stability constants and precluded determination of K_{II} for $Yb(2.2.1)^{2+}$. The values of K_{II} obtained in 0.1 M Et_4NClO_4 at 25 °C are $2 \pm 1 \times 10^9$ M^{-1} for $Eu(2.2.1)^{2+}$ and $3 \pm 2 \times 10^{10}$ M^{-1} for $Eu(2.2.2)^{2+}$. Unfortunately, the reproducibility of these values was not sufficient to allow useful estimates of $\Delta H°_{II}$ and $\Delta S°_{II}$ to be obtained from the temperature dependence of K_{II}.

We have previously noted that the trivalent cryptates exhibit a surprisingly strong tendency to associate with fluoride and hydroxide ions.[7] Thus the addition of F^- or OH^- ions to $NaClO_4$ at a constant ionic strength results in shifts in the formal potentials of the lanthanide cryptate couples to markedly more negative potentials.[7] Significant potential shifts to more negative values were also observed upon the addition of oxalate, phthalate, and phosphate anions, although small or negligible effects were observed with sulfate, chloride, azide, and nitrate anions up to concentrations around 0.1 M. The magnitude of these potential shifts ΔE^x_f was found to be linearly dependent upon log [X], where [X] is the concentration of fluoride or hydroxide anions. Some typical results are shown in Figure 1, which is a plot of $-E^F_f$ vs. log $[F^-]$ at $\mu = 0.5$ for the $Eu(2.2.1)^{3+/2+}$ couple. Two linear regions are obtained, with slopes of 57 and 116 mV. (Virtually identical slopes were observed if the logarithm of the fluoride activity, obtained using a fluoride ion selective electrode, was plotted instead of log $[F^-]$.) This behavior is expected if $Eu(2.2.1)^{3+}$ and possibly also $Eu(2.2.1)^{2+}$ associate with fluoride anions to form substitutionally labile complexes. Then we can write[17]

$$-\Delta E^x_f = (2.303RT/F)\{\log \beta_{MX_p} - \log \beta_{MX_q} + (p - q) \log [X]\} \quad (3)$$

or

$$-\Delta E^x_f = (2.303RT/F)\{\log \beta_{MX_p} + p \log [X]\} \quad (4)$$

where β_{MX_p} and β_{MX_q} are the (cumulative) stability constants of the oxidized and reduced complexes having the stoichiometry p and q, respectively. Equation 3 will apply when both the oxidized and reduced species form stable complexes with X, and eq 4 when only the oxidized species undergoes complexation under the conditions of the experiment.[18] To decide between these two possibilities for the present systems, absolute values of β_{MX_p} were determined for the association of trivalent cryptates with F^- and OH^- by means of potentiometric titrations using a fluoride ion selective electrode and a pH electrode, respectively. The values of β_{MX_p} were found to agree consistently with the values determined using eq 4. It was therefore deduced that only the trivalent cryptates significantly associate with F^- and OH^- under the experimental conditions employed ($[F^-]$, $[OH^-] \sim 10^{-3}$-0.5 M). Consequently, from eq 4 the two linear regions seen in Figure 1 with slopes of 57 and 116 mV correspond to $Eu(2.2.1)^{3+}$-F^- stoichiometries of 1:1 and 1:2, respectively, with cumulative stability constants β_1 and β_2 equal to 2×10^4 M^{-1} and 3×10^6 M^{-2}. Large values of β_1 and β_2 were also deduced for the association between $Eu(2.2.1)^{3+}$ and OH^-. Although $Eu(2.2.2)^{3+}$ was also found to associate strongly with OH^-, quantitative studies were precluded by a very rapid base-catalyzed cryptate dissociation observed for this system. A summary of β_1 and β_2 values determined for the trivalent cryptates with F^- and OH^- is given in Table II, along with the corresponding data for Eu^{3+} and Yb^{3+} taken from the literature.

Since both the trivalent and divalent lanthanide cryptates are substitutionally inert on the time scale of cyclic voltammetry, this technique can be used to monitor the kinetics of ligand exchange. In principle the kinetics of either complexation or dissociation could be monitored. However, in practice it is only feasible to monitor the latter processes in this manner because the rates of complexation are typically rapid, and in any case the trivalent cryptates cannot be produced in aqueous media from the cryptand and the metal cation owing to hydrolysis of the latter species at the pH values (>8) where the

Table II. Cumulative Formation Constants for Association between Europium and Ytterbium Cryptates and Fluoride and Hydroxide Ions

cation–anion pair	medium	β_1, M^{-1} [a]	β_2, M^{-2} [b]
$Eu(2.2.1)^{3+}$–F^-	0.5M $NaClO_4$–NaF	2×10^4 [c]	3×10^6 [c]
$Eu(2.2.1)^{3+}$–OH^-	0.5M $NaClO_4$–NaOH	3×10^5 [c]	7×10^6 [c]
$Eu(2.2.2)^{3+}$–F^-	0.5M $NaClO_4$–NaF	3×10^4 [c]	7×10^6 [c]
$Yb(2.2.1)^{3+}$–F^-	0.5M $NaClO_4$–NaF		3×10^6 [c]
$Eu_{aq}{}^{3+}$–F^-	0.5M $NaClO_4$–NaF	2.5×10^3 [d]	3×10^6 [d]
$Eu_{aq}{}^{3+}$–OH^-	0.3M $NaClO_4$–NaOH	$\sim 5 \times 10^5$ [e]	
$Yb_{aq}{}^{3+}$–F^-	0.5M $NaClO_4$–NaF	4×10^3 [f]	

[a] Formation constant for 1:1 complex. [b] Formation constant for 1:2 complex. [c] Determined from shift in formal potential $\Delta E^x{}_f$ upon addition of complexing anion X using eq 4, and by potentiometric titration (see text). [d] From A. Aziz and S. J. Lyle, *Anal. Chim. Acta*, **47**, 49 (1969). [e] Calculated from $pK_a = 8.3$, given in U. K. Frolova, V. N. Kumok, and V. V. Serebrennikov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **9**, 176 (1966). [f] B. N. Ivanov-Emin, V. A. Zaitseva, and A. M. Egorov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **13**, 1368 (1968).

Table III. Rate Constants and Activation Parameters for Dissociation of Europium and Ytterbium Cryptates at 25 °C

cryptate	medium	k_d,[a] s^{-1}	$\Delta H^{\ddagger}{}_d$,[b] kcal mol^{-1}	$\Delta S^{\ddagger}{}_d$,[c] cal deg^{-1} mol^{-1}
$Eu(2.2.1)^{3+}$	0.5 M $NaClO_4$ (pH ~ 7)	4.1×10^{-7}		
	0.5 M $NaClO_4$ (pH 2.5)	3.0×10^{-7}	18.9[d]	−25.5[d]
	0.1 M Et_4NClO_4 (pH 2.5)	4.0×10^{-7}	19.2[d]	−23.5[d]
$Eu(2.2.1)^{2+}$	0.1 M Et_4NClO_4 (pH 2.5)	2.0×10^{-4}	15.1[e]	−25.0[e]
$Eu(2.2.2)^{3+}$	0.1 M Et_4NClO_4 (pH ~ 7)	1.1×10^{-3}	13.8[e]	−26.0[e]
$Eu(2.2.2)^{2+}$	0.5 M Et_4NClO_4 + 0.033 M $Ba(NO_3)_2$	3.0×10^{-5}	18.8[d]	−16.0[d]
$Yb(2.2.1)^{3+}$	0.5 M $NaClO_4$	1.3×10^{-6}	22.3[d]	−10.5[d]

[a] First-order rate constant for cryptate dissociation at 25 °C, obtained at pH values where the acid-independent pathway dominates, i.e., where $k'_d \approx k_d$ (eq 5). [b] Enthalpy of activation for cryptate dissociation, determined from $\Delta H^{\ddagger} = -R\text{d} \ln k_d/\text{d}(1/T) - RT$. [c] Entropy of activation for cryptate dissociation, determined from $\Delta S^{\ddagger} = \Delta H^{\ddagger}/T + R \ln k_B T/h - R \ln k_d$, where k_B is the Boltzmann constant and h is Planck's constant. [d] Determined over the temperature range 25–60 °C. [e] Determined over the temperature range 5–35 °C.

Table IV. Acid Catalysis of Europium Cryptate Dissociation at 25 °C

cryptate	medium	k_d,[a] s^{-1}	k_{H^+},[b] M^{-1} s^{-1}	k_{H^+}/k_d, M^{-1}
$Eu(2.2.1)^{3+}$	1 M $LiClO_4$/ $HClO_4$	3×10^{-7}	$\sim 1 \times 10^{-6}$	~3
$Eu(2.2.1)^{2+}$	1 M $LiClO_4$/ $HClO_4$	1×10^{-4}	2.5×10^{-3}	40
$Eu(2.2.2)^{3+}$	0.1 M $LiClO_4$/ $HClO_4$	1×10^{-3}	0.2	200
$Eu(2.2.2)^{2+}$	0.1 M $LiClO_4$/ $HClO_4$	$\sim 5 \times 10^{-5}$	7.5×10^{-3}	~150

[a] First-order rate constant for acid-independent aquation pathway, obtained from intercept of plot of k'_d vs. $[H^+]$ (eq 5). [b] Second-order rate constant, determined from slope of plot of k'_d vs. $[H^+]$ (eq 5).

cryptand is significantly deprotonated.

Table III summarizes rate constants and activation parameters for the dissociation of five europium and ytterbium cryptates. The progress of the dissociation reactions was followed by periodically monitoring the cathodic or anodic voltammetric peak heights for the trivalent and divalent cryptates, respectively. Conditions were arranged in each case so that the reactions went essentially to completion. Initially, strongly acidic solutions were employed to achieve this end. However, for some reactions it was found that the apparent first-order rate constants for dissociation k'_d increased significantly as the pH was lowered. This pH dependence was determined to be in accordance with the rate law

$$k'_d = k_d + k_{H^+}[H^+] \quad (5)$$

Similar behavior has been noted previously for the dissociation kinetics of univalent and divalent cryptates in aqueous media.[19] The derived values of k_d and k_{H^+} are given for the dissociation kinetics of four europium cryptates in Table IV. The values of k_d given in Table III were obtained under conditions where the acid-dependent term in eq 5 is unimportant, i.e., where $k_d \approx k'_d$. For some reactions, this condition could only be achieved by working in neutral media where the cryptand released by the dissociation reaction could prevent aquation of the remaining cryptate. In such cases the presence of such back-(complexation) reactions was prevented by adding a small stoichiometric excess of a metal cation such as Ba^{2+} that will strongly complex the released cryptand.[3] Unlike protons, these complexing agents were not found to have any significant effect upon k'_d.

The presence of significant concentrations of OH^- and F^- was also found to have a marked accelerating effect upon the dissociation rates of the trivalent lanthanide cryptates. For example, the addition of 50 mM OH^- or F^- to 0.5 M $NaClO_4$ reduced $\tau_{1/2}$ for the aquation of $Eu(2.2.1)^{3+}$ at 25 °C from 27 days to 22 min and 2.8 days, respectively.

Discussion

Effects of Varying the Cation Charge upon Cryptate Thermodynamics. In view of the substantial differences in the complexation thermodynamics between corresponding divalent and trivalent lanthanide cryptates (Table I), it is of interest to compare these results with the thermodynamic parameters for other divalent cations of comparable size, as well as for univalent cations. Table V summarizes values of the free energies ($\Delta G°_c$), enthalpies ($\Delta H°_c$), and entropies ($\Delta S°_c$) of complexation for alkali and alkaline-earth cations with (2.2.1) and (2.2.2) cryptands as well as for the lanthanides considered here and the post-transition-metal cation Pb^{2+}. The values of $\Delta G°_c$ given for Eu^{2+} and Eu^{3+} cryptates were obtained from the measured values of K_{II} for the divalent complexes together with the corresponding values of ($\Delta G°_{III} - \Delta G°_{II}$) given in Table I. Also listed in Table V are estimates of the ionic radius of each cation. These values were obtained using the method of Goldschmidt but are from the more recent compilation of Shannon and Prewitt[5] and are estimated for a coordination number of six. Although there are a number of scales of ionic radii which differ to a greater or lesser degree,[20] there is reason to believe that the scale used here provides a reasonable approximation (±0.1 Å) to at least the relative radii of the bare ions in aqueous solution[21] as well as the effective cation radii within the cryptate cavities. The use of larger coordination

Table V. Free Energies, Enthalpies, and Entropies of Complexation of Various Metal Cations with (2.2.1) and (2.2.2) Cryptands at 25 °C

		(2.2.1) cryptand			(2.2.2) cryptand		
cation	r_c,[a] Å	$-\Delta G°_c$, kcal mol^{-1}	$-\Delta H°_c$, kcal mol^{-1}	$\Delta S°_c$, cal deg^{-1} mol^{-1}	$\Delta G°_c$, kcal mol^{-1}	$-\Delta H°_c$, kcal mol^{-1}	$\Delta S°_c$, cal deg^{-1} mol^{-1}
Li$^+$	0.59	3.4[b,c]	0.0[c]	11.4[c]	1.7[i]	1.4[i]	1[i]
Na$^+$	1.02	7.2[c]	5.4[c]	6.2[c]	5.3[b,c]	7.4[c]	−7[c]
K$^+$	1.38	5.4[b,c]	6.8[c]	−4.7[c]	7.2[c]	11.4[c]	−14[c]
Rb$^+$	1.49	3.5[b,c]	5.4[c]	−6.5[c]	5.9[b,c]	11.8[c]	−19.8[c]
Cs$^+$	1.70				2.0[i]	5.2[i]	−11[i]
Ca^{2+}	1.00	9.5[b,c]	2.9[c]	22[c]	6.0[b,c]	0.2[c]	19.5[c]
Sr^{2+}	1.16	10.0[b,c]	6.1[c]	13.1[c]	10.9[b,c]	10.3[c]	2[c]
Ba^{2+}	1.36	8.6[b,c]	6.3[c]	7.7[c]	12.9[b,c]	14.1[c]	−4.0[c]
Pb^{2+}	1.18				16.9[j]	13.8[j]	10.1[j]
Eu^{2+}	1.17	12.7[d]	(8.8)[h]	(13)[f]	14.3[d]	(13.7)[h]	(2)[f]
Eu^{3+}	0.95	8.1[e]	(−1.9)[h]	(33.5)[g]	4.6[e]	(−4.0)[h]	(29)[g]

[a] Ionic radius for metal cation, taken from compilation in ref 5 for coordination number six (see text). [b] From ref 3; determined at ionic strength $\mu = 0.05$. [c] From ref 22; $\mu \sim 0.05$. [d] Present work; from experimental value of K_{11} (see text). [e] Present work; from ΔG°_c for corresponding Eu(II) cryptate combined with value of $(\Delta G^\circ_{\rm III} - \Delta G^\circ_{\rm II})$ given in Table I; $\mu = 0.1$. [f] Estimated value; ΔS°_c assumed to be equal to ΔS°_c for corresponding Sr(II) cryptate (see text). [g] From ΔS°_c given for corresponding Eu(II) cryptate combined with value of $(\Delta S^\circ_{\rm III} - \Delta S^\circ_{\rm II})$ given in Table I; $\mu \sim 0.5$. [h] From corresponding values of ΔG°_c and ΔS°_c. [i] M. H. Abraham, A. F. Danil de Namor, and W. H. Lee, Extended Abstracts, 29th Meeting, I.S.E., Budapest, Hungary, 1978. [j] G. Anderegg, *Helv. Chim. Acta*, **58**, 1218 (1975).

numbers such as eight that may be appropriate for the larger cations considered here increases the absolute values of the ionic radii by ca. 0.1–0.15 Å, but the differences between the values remain relatively unchanged providing that the coordination numbers do not greatly depend upon the cation size.[5]

The large variations in $\Delta G°_c$ and particularly in the enthalpic and entropic components $\Delta H°_c$ and $\Delta S°_c$ seen between different cations of groups 1 and 2 have been discussed by Lehn and co-workers.[3,22] The markedly increasing values of $-\Delta G°_c$ seen as the ionic radii of the cations approach the radius of the cryptate cavity (ca. 1.1 and 1.4 Å for (2.2.1) and (2.2.2) cryptates, respectively[3]) are probably due in part to steric factors associated with the fit of the cation into the relatively inflexible cryptate cavity.[3] However, these variations in $-\Delta G°_c$ consist of marked alterations in $\Delta S°_c$ as well as $\Delta H°_c$. This indicates that an important factor determining the sensitivity of cryptate stability to cation size is the partial desolvation of the cation that is required in order for cryptate formation to be accomplished.[22] Thus the large increases in $-\Delta H°_c$ and $-\Delta S°_c$ that generally occur as the cation radius increases for a given cationic charge (Table V) undoubtedly stem in part from the decreasingly negative hydration enthalpy and decreasingly negative hydration entropy of the aquated cations under these circumstances.[22] Such influences also appear to be paramount in determining the dependence of cryptate thermodynamics upon the cation charge. Thus the pairs of cations Na$^+$ and Ca^{2+} and K$^+$ and Ba^{2+} have similar ionic radii, and yet the divalent cations exhibit markedly less favorable values of $-\Delta H°_c$ for formation of either (2.2.1) or (2.2.2) cryptates. These differences are nevertheless counteracted by markedly more favorable values of $\Delta S°_c$ so that $-\Delta G°_c$ is typically larger for the divalent compared with the univalent cations. The variations in $\Delta H°_c$ are in harmony with the markedly more negative hydration enthalpies for divalent cations compared with those for univalent cations of similar size.[22,23] Although increasing the cationic charge will result in increasingly favorable ion–dipole interactions with the cryptate ether moieties, these interactions are expected to be relatively less favorable compared with those involving the solvent molecules on account of the smaller dipole moment of dimethyl ether vs. water.[22] These factors therefore result in a net increase in $\Delta H°_c$ as the cationic charge increases. The more positive values of $\Delta S°_c$ for the divalent cryptates undoubtedly result from the more negative hydration entropies of the divalent vs. univalent cations. These stem from a greater degree of "solvent ordering" (or less "solvent disordering") in the vicinity of the former cations[23] which is markedly diminished or removed upon cryptate formation.[22]

The differences in both cation size and charge between Eu^{3+} and Eu^{2+} are therefore both expected to play important roles in determining the relative stabilities of their (2.2.1) and (2.2.2) cryptates. Thus Eu^{3+} has a noticeably smaller ionic radius (0.95 Å) than Eu^{2+} (1.17 Å), which, along with the increase in the cationic charge, contributes toward a markedly more negative hydration enthalpy for the former cation.[23] These two factors taken together appear to account nicely for the relatively more positive values of $\Delta H°_c$ and $\Delta S°_c$ seen for Eu(III) vs. Eu(II) cryptate formation (Table I). The larger value of $(\Delta H°_{\rm III} - \Delta H°_{\rm II})$ seen for Eu(2.2.2)$^{3+/2+}$ (17.7 kcal mol^{-1}) compared with Eu(2.2.1)$^{3+/2+}$ (10.7 kcal mol^{-1}) could be anticipated on the basis of the greater sensitivity of $\Delta H°_c$ to the cation size seen for (2.2.2) compared to (2.2.1) cryptates with cations of comparable size to Eu^{3+} and Eu^{2+} (Table V). For example, $\Delta H°_c$ for Ca(2.2.2)$^{2+}$ is 10.2 kcal mol^{-1} less negative than for Sr(2.2.2)$^{2+}$, whereas $\Delta H°_c$ for Ca(2.2.1)$^{2+}$ is ca. 4 kcal mol^{-1} less negative than for Sr(2.2.1)$^{2+}$. One reason for the behavioral difference between (2.2.2) and (2.2.1) cryptates may be the greater size mismatch between these cations and the cavity formed by the former ligand.

The similar effects seen for the complexation thermodynamics of the other lanthanide couples Eu(2B.2.1)$^{3+/2+}$ and Yb(2.2.1)$^{3+/2+}$ (Table I) also support these arguments. The relative instability of Yb(2.2.1)$^{3+}$ vs. Yb(2.2.1)$^{2+}$, arising again from a marked enthalpic destabilization outweighing a smaller entropic stabilization, is expected in view of the smaller ionic radius of Yb^{3+} (0.86 Å[5,24]) compared to Yb^{2+}(0.93 Å[24]).

Table V also lists the absolute values of $\Delta G°_c$ for Eu(2.2.1)$^{2+}$ and Eu(2.2.2)$^{2+}$ obtained from the experimental values of $K_{\rm II}$, along with $\Delta G°_c$ for the corresponding Eu(III) cryptates obtained by combining this information with the data in Table I. Although the ionic radii of Sr^{2+} and Eu^{2+} are very similar, it is seen that the values of $-\Delta G°_c$ for the latter cation are significantly larger with both (2.2.1) and (2.2.2) cryptands (by 2.7 and 3.4 kcal mol^{-1}, respectively). These differences may arise from weak covalent bonding between the oxygen and nitrogen atoms of the cryptand with the unfilled 4f orbitals on Eu^{2+}. Although the chemistry of divalent lanthanide ions closely resembles that for the corresponding alkaline-earth

Table VI. Rate Constants and Activation Parameters for Formation and Dissociation of Some Cryptates at 25 °C

cation	r_c,[a] Å	k_d,[b] s^{-1}	$\Delta H^{\ddagger}_d$,[c] kcal mol^{-1}	$\Delta S^{\ddagger}_d$,[d] cal deg^{-1} mol^{-1}	k_c,[e] M^{-1} s^{-1}	$\Delta H^{\ddagger}_c$,[f] kcal mol^{-1}	$\Delta S^{\ddagger}_c$,[g] cal deg^{-1} mol^{-1}
A. (2.2.1) Cryptates							
Na^+	1.02	$15.5^{h,i}$	12.3	−11.7	$4 \times 10^{6\ h,i}$	6.9	−5.5
K^+	1.38	$2 \times 10^{3\ j}$			$3 \times 10^{7\ j}$		
Ca^{2+}	1.00	$6.5 \times 10^{-4\ h,i}$	13.4	−28.2	$5.8 \times 10^{3\ h,i}$	10.5	−6.2
		$2.2 \times 10^{-3\ k}$	15.1	−20	$1.6 \times 10^{4\ k}$	13.8	7
Sr^{2+}	1.16	$1.45 \times 10^{-3\ h,i}$	14.6	−22.5	$3.2 \times 10^{4\ h,i}$	8.5	−9.4
Ba^{2+}	1.36	$6.4 \times 10^{-2\ h,i}$	15.0	−13.8	$1.3 \times 10^{5\ h,i}$	8.7	−6.1
Eu^{2+}	1.17	$2.0 \times 10^{-4\ l}$	15.1	−25	$4 \times 10^{5\ m}$	(6.3)	(−12)
Eu^{3+}	0.95	$4.1 \times 10^{-7\ l}$	19.2	−23.5	0.35^{m}	(21.1)	(10)
Yb^{3+}	0.86	$1.3 \times 10^{-6\ l}$	22.3	−10.7			
B. (2.2.2) Cryptates							
Na^+	1.02	147^{n}	14.5	16.1	$1.9 \times 10^{6\ n}$	8.7	−0.5
K^+	1.38	$7.8^{h,i}$	20.3	13.9	$3.0 \times 10^{6\ h,i}$	9.3	2.4
		9^{j}			$2 \times 10^{6\ j}$		
Ca^{2+}	1.00	0.185^{h}	10.8	−25.8	$6.9 \times 10^{3\ h}$	10.6	−5.6
		0.26^{k}	8.4	−33	$7.3 \times 10^{3\ k}$	7.9	−14
Sr^{2+}	1.16	$7.1 \times 10^{-5\ h}$	18.9	−14.1	$1.3 \times 10^{4\ h}$	8.3	−11.9
		$1.0 \times 10^{-4\ k}$	17.7	−17	$1.0 \times 10^{4\ k}$	7.4	−15
		$1 \times 10^{-4\ o}$			$6 \times 10^{3\ o}$		
Ba^{2+}	1.36	$1.8 \times 10^{-5\ h,i}$	21.0	−9.8	$9 \times 10^{4\ h,i}$	6.7	−13.5
		$2.2 \times 10^{-5\ k}$	20.9	−9	$7 \times 10^{4\ k}$	6.8	−13
Eu^{2+}	1.17	$3.0 \times 10^{-5\ l}$	18.8	−16	$9.5 \times 10^{5\ m}$	(5.1)	(−14)
Eu^{3+}	0.95	$1.1 \times 10^{-3\ l}$	13.8	−26	2.5^{m}	(17.8)	(3)

[a] Crystallographic ionic radius, from Table V. [b] Rate constant for cryptate dissociation, acid-independent pathway. [c] Activation enthalpy for dissociation. [d] Activation entropy for dissociation. [e] Rate constant for cryptate formation. [f] Activation enthalpy for cryptate formation. [g] Activation entropy for cryptate formation. [h] B. G. Cox and H. Schneider, to be published; determined at ionic strength $\mu = 10^{-3}$–10^{-2}. [i] Reference 19. [j] K. Henco, B. Tümmler, and G. Maass, *Angew. Chem., Int. Ed. Engl.*, **16**, 538 (1977). [k] Reference 29. [l] This work, from Table III. [m] This work, from dissociation kinetics combined with thermodynamic data given in Table V. [n] J. M. Ceraso, P. B. Smith, J. S. Landers, and J. L. Dye, *J. Phys. Chem.*, **81**, 760 (1977). [o] Reference 1.

cations having similar ionic radii,[25] the stability constant of the Eu^{2+}-EDTA complex is also somewhat larger than for the Sr^{2+}-EDTA complex.[26] It is interesting to note that Pb^{2+}, which has an ionic radius close to those for Sr^{2+} and Eu^{2+} (Table V), exhibits a value of $-\Delta G°_c$ for (2.2.2) cryptate formation which is markedly larger than for Sr^{2+} (Table V). This difference can also be attributed to the influence of covalent bonding.

Although absolute values of $\Delta H°_c$ and $\Delta S°_c$ were not determined for the lanthanide cryptates, rough estimates are included in Table V for comparison purposes. These were obtained by assuming that $\Delta S°_c$ for $Eu(2.2.1)^{2+}$ and $Eu(2.2.2)^{2+}$ are approximately equal to those for $Sr(2.2.1)^{2+}$ and $Sr(2.2.2)^{2+}$, and then obtaining $\Delta H°_c$ by combining these estimates of $\Delta S°_c$ with the experimental values of $\Delta G°_c$. Although this procedure may be questionable, it is supported by the similar activation entropies observed for the dissociation of corresponding Sr^{2+} and Eu^{2+} cryptates (vide infra).

Association of Lanthanide Cryptates with Small Anions. It has often been asserted that cryptates provide an unusually effective way of shielding the encapsulated ions from the surrounding solvent. However, the strong ion association found between the tripositive cryptates and F^- and OH^- is a striking example of the limitations of this argument. Particularly unexpected is the finding that both the first and second cumulative association constants β_1 and β_2 are comparable to or even larger than the values for the corresponding aquo lanthanide cations (Table II). It therefore appears that one or two anions are able to approach closely or even contact Eu^{3+} or Yb^{3+} despite the encapsulation of the cations within the cryptate cavity. Inspection of molecular models reveals that such small anions could indeed fit between the polyether strands of the cryptate, although a significant distortion of the symmetrical endo, endo form is required in order for two anions to contact the encapsulated cation. Bearing in mind that the measured association constants reflect the ability of the anion to compete with water molecules for sites adjacent to the metal cation, it is plausible that the surprising stability of the cryptate-anion complexes arises simply from the markedly weaker solvation of the encapsulated compared with the aquated metal cation. An alternative way of rationalizing the experimental results is to regard the surrounding cryptate as providing a region of saturated dielectric and therefore of low dielectic constant which will enhance the Coulombic attraction between the encapsulated cation and the incoming anions. It is not clear if the cation–anion associates involve direct cation–anion contact or solvent-separated ior pairs. It therefore may not be necessary for the complexing anions to be buried between the cryptate polyether strands in order to achieve strongly favorable interactions with the metal ion.

Effects of Varying the Cation Charge upon Cryptate Substitution Kinetics. The kinetic parameters for the dissociation of lanthanide cryptates summarized in Table III exhibit some surprising features. Most prominently, the rate constant k_d for dissociation of $Eu(2.2.1)^{3+}$ is almost three orders of magnitude smaller than for the corresponding divalent cryptate $Eu(2.2.1)^{2+}$ despite the substantially lower thermodynamic stability of the former complex (Table I). Even the enormously larger driving force for the dissociation of $Eu(2.2.2)^{3+}$ compared with $Eu(2.2.1)^{2+}$ $[(\Delta G°_{III} - \Delta G°_{II}) = 9.7$ kcal mol^{-1}, Table I] results in values of k_d that are only ca. 30-fold larger for the former cryptate. As in the case of the corresponding thermodynamic parameters, some insight into the factors responsible for this behavior can be obtained by comparing the rate constants and activation parameters for Eu(III) and Eu(II) cryptate dissociation and formation with corresponding data for cryptates of alkali and alkaline-earth cations having similar ionic radii. Table VI contains such data for (2.2.1) and (2.2.2) cryptates. The values of k_c for the europium cryptates were obtained by combining the values of k_d given in Table III with the values of $\Delta G°_c$ listed in Table I. Approximate estimates of the corresponding activation parameters $\Delta H^{\ddagger}_c$ and $\Delta S^{\ddagger}_c$ are listed in Table VI; these were similarly obtained using the estimates of $\Delta H°_c$ and $\Delta S°_c$ given in Table V.

Inspection of Table VI reveals the importance of the charge as well as the size of the cation in determining the kinetics of cryptate substitution. Thus for the series of cations Na^+, Ca^{2+}, Eu^{3+}, which have comparable radii, both k_d and k_c fall dramatically as the cation charge increases. For example, $Eu(2.2.1)^{3+}$ exhibits values of k_c and k_d that are ca. 10^7-fold smaller than for $Na(2.2.1)^+$ and ca. 10^4-fold smaller than for $Ca(2.2.1)^{2+}$ (Table VIA). Since Eu^{2+} and Sr^{2+} have very similar ionic radii and also exhibit comparable kinetic parameters with both (2.2.1) and (2.2.2) cryptands (Table VI), it is likely that these behavioral differences between Eu^{3+} and the lower charged cations result chiefly from the influences of ionic rather than covalent bonding.

The first possibility to be considered in interpreting such variations in the complexation kinetics is that they may be connected with the rates of substitution of water molecules in the coordination sphere of the cations. However, the "characteristic rates" of water substitution[27] for tripositive lanthanides and heavier alkaline-earth and alkali-metal cations are all extremely fast (10^7–10^8, 10^8–10^9, and ca. 10^9 s^{-1}, respectively[27]). It has been suggested[28] that the rate constants k_c for complexation of cryptands with alkali and alkaline-earth cations that are markedly below these water substitution rates may be due partly to the need for the complexing cation to bind with the endo, endo form[1] of the cryptand, whereas the exo, exo conformation could be the predominant form in solution.[1] However, since the 10^6- to 10^7-fold difference in k_c between Na^+ and Eu^{3+}, for example, is much greater than the corresponding variation in water substitution rates, it is likely that an additional factor is chiefly responsible at least for the large energy barriers required for complexation of multicharged cations. It is plausible that an important component of these energy barriers arises from the inability of the rigid ligand to achieve a smooth stepwise replacement of water molecules in the metal coordination sphere by the cryptand coordinating groups, so that the loss of solvating water molecules may not be immediately compensated by the formation of cation–cryptand bonds.[1,29]

As noted previously,[1,28,29] the large changes in cryptate thermodynamic stability induced by variations in the radii of univalent or divalent cations (Table V) are chiefly reflected in k_d rather than k_c (Tables VI), suggesting that the transition states more closely resemble the separated cation and cryptand rather than the cryptate.[1,28-30] This latter result can be reconciled with the larger sensitivity of k_c to cation charge by noting that the hydration energies of simple cations are much more sensitive to ionic charge than to size.[23] Therefore any partial desolvation of the cation required to reach the transition state from the separated reactants is expected to result in a greater dependence of the activation barrier on the charge rather than the size of the cation.

Further insight into the factors influencing these reactivity patterns can be obtained by inspecting the corresponding activation parameters (Table VI). By and large, the marked variations in ΔS°_c seen for the univalent and divalent cryptates as the cation size and charge varies (Table V) are primarily reflected in the activation entropies for the dissociation reactions $\Delta S^{\ddagger}_d$. The majority of the activation entropies for complexation $\Delta S^{\ddagger}_c$ are small and negative (ca. -5 to -10 eu). Since an activation entropy of ca. -10 to -15 eu is predicted on statistical grounds from the loss of translational entropy ΔS_t attending such association reactions,[31] the values of $\Delta S^{\ddagger}_c$ support the above contention that no drastic changes in the solvent structure surrounding the cation are required in order to form the transition state from the separated reactants.

In contrast, however, the large differences in ΔS°_c between $Eu(2.2.1)^{3+}$ and $Eu(2.2.1)^{2+}$, and between $Eu(2.2.2)^{3+}$ and $Eu(2.2.2)^{2+}$, are chiefly reflected in $\Delta S^{\ddagger}_c$ rather than $\Delta S^{\ddagger}_d$ (Table VI). Consequently, the markedly smaller values of k_c for the Eu(III) cryptates compared to Eu(II) and other divalent cryptates arise from substantially larger enthalpic barriers $\Delta H^{\ddagger}_c$ (Table VI). The differences in activation entropy suggest that the solvent surrounding the Eu^{3+} cation in the transition state is substantially less "ordered" than around the uncomplexed cation. Indeed, the ionic entropy $\bar{S}^\circ$ of Eu^{3+} is large and negative,[32] reflecting its large solvent "structure-making" ability.[33,34] A good deal of this extensive hydration shell may be required to be removed in order to form the transition state, resulting in the observed large positive values of $\Delta H^{\ddagger}_c$ as well as $\Delta S^{\ddagger}_c$.

It has been pointed out that the significant acid catalyses observed for the dissociation of a number of metal cryptates suggest that it is often necessary to alter the cryptate conformation from the stable endo, endo form to one where at least one of the two bridgehead nitrogens has its lone pair pointing outward (exo, endo or exo, exo conformation) prior to or within the transition state.[19] The significant acid catalyses of the dissociation of the Eu(III) and Eu(II) cryptates (Table IV) indicates that such a mechanism is also applicable to these systems. Inasmuch as any clear trends can be discerned in the ratios k_{H^+}/k_d of the rate constants for the acid-catalyzed and uncatalyzed pathways, it appears from the data in Table IV and ref 19 that k_{H^+}/k_d increases as the charge/radius ratio of the cation increases and as the thermodynamic (or kinetic) stability of the cryptate decreases. The ratio k_{H^+}/k_d also is generally larger for (2.2.2) compared with (2.2.1) cryptates. The role of the proton in accelerating the dissociation reaction may be to aid the endo, endo to exo, endo conformational change by forming an incipient nitrogen–proton bond as the nitrogen–metal bond is broken, or it may simply provide a more favorable dissociation pathway once this conformational change has occurred.[19] The smaller or undetectable acid catalysis seen for the more stable cryptates may arise from the greater difficulty of accomplishing this conformation change due to their tendency to be less flexible than cryptates having cavities that are markedly larger than the encapsulated cations.

The very marked acceleration of the dissociation rates of trivalent lanthanide cryptates by OH^- or F^- is not surprising in view of the strong binding of these anions to the cryptates. These anions could lower the energy barrier to dissociation by distorting the cryptate conformation so as to enlarge the space between the polyether strands through which the encapsulated cation can pass. Additionally, the bound anions will act to lower the effective charge of the assembly, thus reducing the extent of the solvation changes which must occur in order for the cation to be removed from the cryptate cavity. It is interesting to note that these substantial accelerations of the cryptate dissociation rates occur in spite of the thermodynamic *stabilization* of the cryptates by both fluoride and hydroxide (Table II).

Conclusions

The foregoing discussion demonstrates that the observed sensitivity of the thermodynamic and kinetic stability of lanthanide cryptates to the metal oxidation state in aqueous media can be nicely accounted for in terms of the same hydration factors that appear to be responsible for the pronounced selectivity toward cation size and charge of alkali and alkaline-earth cryptates. Thus the large differences in the thermodynamic and kinetic stability of trivalent vs. divalent lanthanide cryptates are due to large and opposing influences of enthalpic and entropic factors, which are compatible with the notion that the cations are at least partially desolvated within the cryptate cavity. The most striking result is that the trivalent europium and ytterbium cryptates are remarkably substitutionally inert in a range of neutral and acidic electrolytes despite their relative thermodynamic instability. This finding has a number of implications, including the use of lanthanide cryptates as cationic tracers in biological systems,[8a] as T_1 relaxation[38] and chemical-shift reagents in NMR spectroscopy,[7] and as redox reagents in studies of electron-transfer kinetics.[10] The large differences in formal potential of the cryptate couples compared with the corresponding aquo couples, arising from the sensitivity of the complexation thermodynamics to the metal oxidation state, suggest that it should be possible to design macrobicyclic ligands that selectivity stabilize given oxidation states and therefore yield large yet controllable changes in the redox thermodynamics. Experiments to explore these possibilities further are currently in progress in our laboratory.

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(14) See, for example, D. T. Sawyer and J. L. Roberts, Jr., "Experimental Electrochemistry for Chemists", Wiley, New York, 1974, Chapter 7.
(15) Although the determination of absolute values of $\Delta S°_{rc}$ requires at least one extrathermodynamic assumption to be made,[11] this uncertainty will cancel when *differences* in $\Delta S°_{rc}$ are being considered, as in eq 2.
(16) It should be noted that the time taken to attain true equilibrium will be determined by the ligand exchange rate (i.e., the first-order rate constant for dissociation of the complex) irrespective of whether the complex is allowed to aquate spontaneously or the free metal ion is allowed to complex with added ligand.
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(18) Equation 4 is a form of the well-known Lingane equation;[17] it should be carefully distinguished from eq 1 since the former relation will apply when only the oxidized species is complexed to form substitutionally labile complexes.
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(35) These partial molal entropies have been converted to the "absolute" scale which assumes the most probable value of $\bar{S}°_{H^+} = -5.5$ eu, rather than the "conventional" scale where it is assumed that $\bar{S}°_{H^+} = 0$.[10,37]
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Formation of 1-Silacyclopenta-2,4-diene through Recoil Silicon Atom Reactions

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Abstract: [^{31}Si]-1-Silacyclopenta-2,4-diene was prepared through the reactions of recoil silicon-31 atoms with butadiene. Its identification was verified by the fact that it was catalytically hydrogenated to [^{31}Si]-1-silacyclopent-3-ene. [^{31}Si]-1-Silacyclopenta-2,4-diene is sensitive to γ-ray irradiation. It is also thermally unstable at a temperature higher than 100 °C. Possible mechanisms for its formation are considered.

The synthesis of silacyclopentadienes has been a long-term challenge to chemists during the past 2 decades. The successful preparation and characterization of such compounds were reported as early as 1961 and labeled as the first example of an aromatic system containing the silicon atom.[1-4] However, some reinvestigation in the same laboratory found that such syntheses cannot be experimentally duplicated.[5] Over the years, attempts to prepare this type of compound have been

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