the addition of all types of electrolyte salts. This effect may be reconciled with solvent-separated ion pairs for some ions and contact pairs for others. We assume that the $CH_3N(CH_2CH_2OH)_3^+$ cations prefer the same hydrophilic solvation region as the $M(H_2O)_6^{n+}$ ions that cause a bathochromic shift in the LMCT band. Those ions in the hydrophilic region near the CN^- ligands, which are sufficiently polarizing of the lone pair of a coordinated CN^- ligand to form a good bond, may make a contact ion pair, $[(H_2O)_5MNCFe(CN)_4L]^{n-2}$. As the polarizing power (Z/r) decreases, one anticipates that at some point the sixth hydration energy is substantially more exothermic than bonding to the CN^- ligand. Only a solvent-separated ion pair $[M(H_2O)_6,(CN)_5FeL]^{n-2}$ should be produced. This is apparently the observed result in the case of Ba^{2+}.

A nearly constant spectral maximum of 666 nm from 0.10 to 0.64 M $BaCl_2$ is observed. Above 0.64 M the salt $Ba[(CN)_5Fe(dmapy)]$ precipitates, precluding use of higher molar values of Ba^{2+}. Very slight systematic increases on the long-wavelength side of the LMCT transition of $(CN)_5Fe(dmapy)^{2-}$ do appear on the spectra with increasing $[Ba^{2+}]$, indicative of electrostatic interaction between Ba^{2+} and $(CN)_5Fe(dmapy)^{2-}$. These results suggest that if the $Fe^{III}{-}C{\equiv}N{:}{\cdots}M^{n+}$ distance becomes very large (cationic radius of Ba^{2+} = 1.98 Å vs. 1.12 Å for Sr^{2+})[18] there is insufficient exothermicity to allow formation of the contact ion pair. Outer-sphere association constants also decrease with the increasing distance of separation for like charge-type pairs. K_{IP} for Ba^{2+} should be smaller than those for the other ions of Table I. Therefore, a smaller fraction of $(CN)_5FeL^{2-}$ will be converted to the ion pair. The net result is that ions of quantum level $n = 6$ are no longer efficient in producing a substantial stabilization of the excited state; the energy separation of the ground and excited states remains reasonably constant over a wide concentration range, even in the presence of solvent-separated ion pairs with $Ba(H_2O)_6^{2+}$ or $CH_3N(CH_2CH_2OH)_3^+$.

Within the inherent limitations imposed by changing activities with changing total electrolyte salt concentration, we believe that the correlation between the shifts per mole relative to Li^+ for the LMCT bands and the hydration energies (also normalized to Li^+) of the smaller ions is quite excellent. The hydration energy of an ion follows the relationship $\Delta H_{hyd} = -167Z^2/r_{eff}$; therefore, it is a function of its charge to effective radius, Z/r.[16] By virtue of higher charge and smaller radius, one anticipates Li^+ to be the most efficient in producing a shift in the LMCT spectra for monovalent ions, Mg^{2+} for divalent ions, and Al^{3+}, ionic radius 0.51 Å, to be greater than Sc^{3+}, ionic radius 0.81 Å.[18] Experimentally, the smallest ion of each charge type does produce the greatest shift per mole of the LMCT transition while the sensitivity to charge, Z, shows +3 > +2 > +1 on the shift. However, the result with $Ba(H_2O)_6^{2+}$ shows that a knowledge of the last hydration energy of each ion is required for a detailed understanding.

The experiments of Sutton and Taube on the influence of X^- anions on the spectrum of $(NH_3)_5Ru^{III}(4\text{-}NH_2py)^{3+}$ were not carried out as a function of concentration; the shift produced by 5 M salts on the LMCT band of this complex were reported together with those of 3.0 M Na_2SO_4 and 3.4 M CF_3SO_3H. The smallest ion, F^-, produced the largest shift of 30 nm at 5.0 M. If linearity in concentration is assumed, this gives a 6 nm/mol of F^- to be compared with 7.75 nm/mol of Li^+ for the related $[Li^+,(CN)_5Fe(dmapy)^{2-}]$ ion pair. Therefore, the net effect of the ion pair on the LMCT transition is quite similar for monovalent counterions in each case. However, about 9 times the influence of monovalent Li^+ is achieved by its replacement with Al^{3+} after correction for the competitive equilibrium forming $[Al(H_2O)_6^{3+},Cl^-]$.

Experimental Section

Electrolyte Salts. The electrolyte salts used in this study were obtained from several commercial sources: (Aldrich) LiCl; (Alfa) $ScCl_3{\cdot}6H_2O$; (Baker) KCl, $CaCl_2{\cdot}2H_2O$, $BaCl_2{\cdot}2H_2O$; (Fisher) $AlCl_3{\cdot}6H_2O$; (Mallinckrodt) NaCl, $SrCl_2{\cdot}6H_2O$; (MCB) $MgCl_2{\cdot}6H_2O$. These analytical grade reagents were used without further purification. $CH_3N(C_2H_4OH)_3I$ was prepared by alkylation of triethanolamine. A 0.10-mol sample of triethanolamine (Fisher) was reacted with 0.13 mol of CH_3I (Aldrich) in ethanol (200 mL) at reflux for 1 h. The salt is filtered off after cooling and recrystallized from ethanol.

$Na_2[Fe(CN)_5L]$ Complexes. The ligands benzimidazole and 4-(dimethylamino)pyridine were obtained from Eastman and Aldrich, respectively. These ligands were used without further purification. Preparation of the complexes has been reported previously.[1,2]

Spectra. The ultraviolet-visible spectra were recorded with a Varian-Cary 118C spectrophotometer in the case of the $Fe(CN)_5(bzimH)^{2-}$ complex and with a Hewlett-Packard 8450A spectrophotometer for the $Fe(CN)_5(dmapy)^{2-}$ complex.[21] The λ_{max} values of spectra taken on the HP-8450A were determined by the instrument's PEAK-FIND function. All spectra were obtained at room temperature in quartz or glass cells.

The solutions on which the spectra were recorded were prepared by dissolving a freshly weighed sample of $Na_2[Fe(CN)_5L]$ in a 10.0-mL volumetric flask with water. Aliquots of this solution were then added to other 10.0-mL volumetric flasks containing the proper amounts of the predissolved electrolyte salt for final dilution. Spectra were taken as soon as possible after preparation of the solutions in order to minimize the effects of ligand dissociation. For the $(CN)_5Fe(bzimH)^{2-}$ series an excess of bzimH at 5.0×10^{-3} M (10-fold excess) was added to suppress the problem of ligand dissociation. In the case of Al^{3+} all samples were prepared with 0.01 M HCl to suppress hydrolysis of the Al^{3+}. The aliquot of $Fe(CN)_5(dmapy)^{2-}$ solution was added to each acidified sample immediately before recording its spectrum.

Acknowledgment. We gratefully acknowledge the National Science Foundation, Grant No. CHE802183, for support of this work.

Registry No. $(CN)_5Fe(dmapy)^{2-}$, 91209-30-2; $(CN)_5Fe(bzimH)^{2-}$, 91209-20-0; Li^+, 17341-24-1; Na^+, 17341-25-2; K^+, 24203-36-9; Mg^{2+}, 22537-22-0; Ca^{2+}, 14127-61-8; Sr^{2+}, 22537-39-9; Ba^{2+}, 22541-12-4; Al^{3+}, 22537-23-1; Sc^{3+}, 22537-29-7; tetramethylammonium cation, 51-92-3; tetraethylammonium cation, 66-40-0.

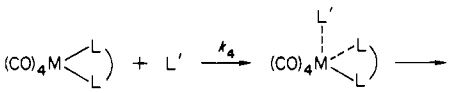
Contribution from the Institute for Physical
and Theoretical Chemistry, University of Frankfurt,
6000 Frankfurt am Main, FRG,
and Department of Chemistry, North Texas
State University, Denton, Texas 76203-5068

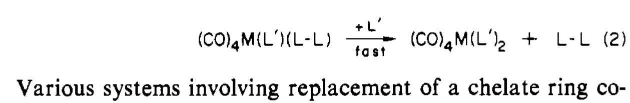
Volumes of Activation and Mechanistic Assignment for Chelate Ring Replacement at Tetracarbonylchromiun(0) Centers

H.-T. Macholdt,[1a] R. van Eldik,*[1a] and G. R. Dobson[1b]

Received July 2, 1985

Mechanistic studies at chelate ring replacement reactions of tetracarbonylmetal(0) centers, in general, have revealed two possible pathways.[2] The first involves unimolecular ring opening (eq 1), and the second, concerted ring opening under the influence of the incoming nucleophile L′ (eq 2).





Various systems involving replacement of a chelate ring coordinated through sulfur have been interpreted in terms of these

---

(1) (a) Univeristy of Frankfurt. (b) North Texas State University.
(2) Halverson, D. E.; Reisner, G. M.; Dobson, G. R.; Bernal, I.; Mulcachy, T. L. *Inorg. Chem.* **1982**, *21*, 4285 and references cited therein.

0020-1669/86/1325-1914$01.50/0

Table I. Effect of Pressure on k_{obsd} for the Reaction[a]

$$(CO)_4Cr(\widehat{SS}) + P(OC_2H_5)_3 \rightarrow (CO)_4Cr(P(OC_2H_5)_3)_2 + \widehat{SS}$$

$\widehat{SS}$	temp, °C	press., MPa	$10^4 k_{obsd}$,[b] s^{-1}	$\Delta V^{\ddagger}_{exptl}$,[c] $cm^3\ mol^{-1}$
dto[d]	54.8	0.1	3.11 ± 0.15	$+14.7 \pm 0.7$
		5	2.88 ± 0.25	
		50	2.22 ± 0.16	
		100	1.70 ± 0.10	
		150	1.35 ± 0.09	
BTE[e]	45.0	0.1	8.17 ± 0.30	$+14.0 \pm 0.6$
		2	7.59 ± 0.53	
		50	5.95 ± 0.44	
		100	4.64 ± 0.34	
		150	3.53 ± 0.09	

[a] Solvent = 1,2-dichloroethane; $[P(OC_2H_5)_3] = 0.5$ M. [b] Mean value of at least three kinetic runs. [c] Calculated from a least-squares fit of ln k_{obsd} vs. pressure. [d] Reaction was followed at 420 nm. [e] Reaction was followed at 425 nm.

two pathways.[2] For the dissociative mechanism outlined in (1), under pseudo-first-order conditions and with assumed steady-state concentrations of the five-coordinate intermediate, $k_{obsd} = k_1k_3[L']/(k_2 + k_3[L'])$. This expression simplifies to $k_{obsd} = k_1k_3[L']/k_2$ for systems in which ring closure (governed by k_2) is significantly faster than the reaction with L′ (governed by $k_3[L']$). In this treatment the formation of the ring-opened intermediate is a non-rate-determining preequilibration such that $k_{obsd} = k_3K[L']$, where $K = k_1/k_2$. For the associative mechanism outlined in (2), $k_{obsd} = k_4[L']$ under pseudo-first-order conditions. It follows that both pathways result in similar rate expressions, viz. a linear dependence of k_{obsd} on [L′], under the cited conditions. This significantly complicates the mechanistic assignment, and conventional kinetic parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) are used to distinguish between the mechanisms in (1) and (2). Unfortunately, $\Delta S^{\ddagger}$ is not a strong mechanistic discriminator and leads to equivocal assignments.[2]

Our earlier activities in the application of high-pressure kinetic techniques to the elucidation of inorganic reaction mechanisms[3-10] have demonstrated the mechanistic discrimination ability of volume of activation data. Especially in systems where the reactant and product species are uncharged, i.e., where solvational changes are not expected to influence significantly the volume of activation, the experimental data directly reflect intrinsic volume changes during the activation process. We have therefore studied the pressure dependence of the substitution reactions of $(CO)_4Cr(BTE)$ and $(CO)_4Cr(dto)$ (BTE = 1,2-bis(*tert*-butylthio)ethane and dto = 3,6-dithiaoctane) with $P(OC_2H_5)_3$, for which negative and positive entropies of activation, respectively, have been reported.[2,11]

Experimental Section

The complexes $Cr(CO)_4(BTE)$ and $Cr(CO)_4(dto)$ were prepared[1b] according to the procedures outlined before.[2,11] The chelate ring replacement by $P(OC_2H_5)_3$ was followed spectrophotometrically in 1,2-dichloroethane by using a thermostated (±0.2 °C) high-pressure cell[12] and a Zeiss PMQ II spectrophotometer operating in a double-beam mode. The reactions were followed to completion, and the corresponding first-order plots of ln $(A_\infty - A_t)$ vs. t were linear for at least 3 half-lives of the reaction.

Table II. Activation Parameters for the Reaction[a]

$$(CO)_4Cr(\widehat{SS}) + P(OC_2H_5)_3 \rightarrow (CO)_4Cr(P(OC_2H_5)_3)_2 + \widehat{SS}$$

$\widehat{SS}$	$\Delta H^{\ddagger}$,[b] kJ mol^{-1}	$\Delta S^{\ddagger}$,[b] J $K^{-1}\ mol^{-1}$	$\Delta V^{\ddagger}_{exptl}$, $cm^3\ mol^{-1}$ (temp, °C)
dto	117 ± 3	56 ± 10	$+14.7 \pm 0.7$ (55)
BTE	92 ± 1	-7 ± 4	$+14.0 \pm 0.6$ (45)

[a] Solvent = 1,2-dichloroethane. [b] Data reported in ref 14 for the second-order rate constant, i.e. $k_{obsd}/[P(OC_2H_5)_3]$.

Results and Discussion

The chelate ring replacement reactions were studied under pseudo-first-order conditions in the presence of excess $P(OC_2H_5)_3$. The experimental conditions were selected according to the kinetic data reported at ambient pressure,[2,11] for which the observed rate constant (k_{obsd}) depends linearly on the entering nucleophile concentration. Values of k_{obsd} as a function of pressure are summarized in Table I. The fairly large error limits on k_{obsd} are due to small fluctuations in temperature over the long reaction periods. Plots of ln k_{obsd} vs. pressure are linear within the experimental error limits, and the volume of activation ($\Delta V^{\ddagger}$) was estimated from the slopes of such plots, viz. $(\partial \ln k/\partial P)_T = -\Delta V^{\ddagger}/RT$.[4] Extrapolation of the rate data in Table I to ambient pressure results in values for k_{obsd} that are in close agreement with those reported previously.[2,11,13] The activation parameters for the investigated reactions are summarized in Table II.

A remarkable feature of the data in Table I is the very similar volume of activation obtained for both systems in spite of the different values of $\Delta S^{\ddagger}$ in Table II. These results permit a definite assignment of the intimate nature of the chelate replacement mechanism. The large positive values of $\Delta V^{\ddagger}$ rule out the possibility of an associative mechanism as given in (2). Furthermore, these values are in good agreement with those expected for the dissociative mechanism given in (1). According to the rate expression, $k_{obsd} = k_3K[P(OC_2H_5)_3]$, it follows that $\Delta V^{\ddagger}_{exptl} = \Delta V^{\ddagger}(k_3) + \Delta \bar{V}(K)$. The k_3 reaction step involves bond formation such that $\Delta V^{\ddagger}(k_3)$ is expected to be negative, from which it follows that $\Delta \bar{V}(K)$ must have a large positive value. This is in agreement with the suggested ring-opening preequilibration and underlines the dissociative nature of the substitution process. Alternatively, $\Delta V^{\ddagger}_{exptl}$ can be analyzed in terms of contributions arising from the effect of pressure on k_1, k_2, and k_3; viz., $\Delta V^{\ddagger}_{exptl} = \Delta V^{\ddagger}(k_1) + \Delta V^{\ddagger}(k_3) - \Delta V^{\ddagger}(k_2)$. Since both the k_2 and k_3 steps involve bond formation, their contributions are expected to be negative and are probably of the same size. In such a case $\Delta V^{\ddagger}_{exptl} \approx \Delta V^{\ddagger}(k_1)$, which is in line with the dissociative nature of the k_1 step. Furthermore, it is even possible that $\Delta V^{\ddagger}(k_3)$ could be more negative than $\Delta V^{\ddagger}(k_2)$ since recently observed[15] values of $\Delta S^{\ddagger}$ for such reactions involving the $(\eta^1\text{-DTO})W(CO)_4$ and $(\eta^1\text{-DTN})W(CO)_4$ species, where DTO = 2,2,7,7-tetramethyl-3,6-dithiaoctane and DTN = 2,2,8,8-tetramethyl-3,7-dithianonane, exhibit such a trend. Although the dto and BTE ligands do differ in size, values for $\Delta V^{\ddagger}_{exptl}$ are very similar. This indicates that the chelate size probably influences $\Delta V^{\ddagger}(k_1)$ and $\Delta V^{\ddagger}(k_2)$ in such a way that there is no overall effect on $\Delta V^{\ddagger}_{exptl}$.

These results clearly demonstrate that $\Delta V^{\ddagger}$ is a more revealing mechanistic discriminator than $\Delta S^{\ddagger}$, for which quite different values have been reported (see Table II). It must be kept in mind that the estimation of $\Delta S^{\ddagger}$ is subject to large error limits since it is extrapolated from a ln (k/T) vs. $1/T$ plot at $1/T \rightarrow 0$, whereas $\Delta V^{\ddagger}$ results from a slope of a ln k vs. p plot. Furthermore, the interpretation of $\Delta S^{\ddagger}$ is in general more complicated than that of $\Delta V^{\ddagger}$.

Volumes of activation have also recently been measured for ligand replacement reactions on *cis*-$Mo(CO)_4(py)_2$ complexes (py

---

(3) van Eldik, R.; Palmer, D. A.; Kelm, H. *Inorg. Chem.* **1979**, *18*, 572.
(4) van Eldik, R.; Kelm, H. *Rev. Phys. Chem. Jpn.* **1980**, *50*, 185.
(5) van Eldik, R. *Inorg. Chem.* **1982**, *21*, 2501.
(6) Doss, R.; van Eldik, R. *Inorg. Chem.* **1982**, *21*, 4108.
(7) van Eldik, R. *Inorg. Chem.* **1983**, *22*, 353.
(8) Breet, E. L. J.; van Eldik, R. *Inorg. Chem.* **1984**, *23*, 1865.
(9) Kitamura, Y.; van Eldik, R.; Kelm, H. *Inorg. Chem.* **1984**, *23*, 2038.
(10) Sisley, M. J.; Rindermann, W.; van Eldik, R.; Swaddle, T. W. *J. Am. Chem. Soc.* **1984**, *106*, 7432.
(11) Dobson, G. R.; Al-Saigh, Z. Y.; Binzet, N. S. *J. Coord. Chem.* **1981**, *11*, 159.
(12) Fleischmann, F. K.; Conze, E. G.; Stranks, D. R.; Kelm, H. *Rev. Sci. Instrum.* **1974**, *45*, 1427.
(13) The values of k_{obsd} quoted for the reaction of $Cr(CO)_4(dto)$ with $P(OC_2H_5)_3$ in ref 11 are too large by a factor of exactly 10: Dobson, G. R., private communication, 1984; also see ref 14.
(14) Dobson, G. R.; Binzet, C. S.; Cortes, J. E. *J. Coord. Chem.*, in press.
(15) Dobson, G. R.; Dobson, C. B.; Mansour, S. E. *Inorg. Chem.* **1985**, *24*, 2179.

= pyridine)[16,17] by bidentate nitrogen donor ligands such as dab (biacetyl bis(phenylimine)) and bpy (bipyridine). These reactions proceed according to a dissociative mechanism similar to the one outlined in (1), and typical $\Delta V^{\ddagger}$ values of +4 cm^3 mol^{-1} were found. These values are significantly smaller than those found for related chromium(0) complexes in this study, which could be due to the larger metal center responding differently to the ligand dissociation (or ring-opening) reaction. A similar trend was also reported by Brower and Chen[18] for the dissocition of CO from $Cr(CO)_6$ and $Mo(CO)_6$, for which $\Delta V^{\ddagger}$ is +15 ± 1 and +10 ± 1 cm^3 mol^{-1}, respectively. These authors,[18] however, interpret this trend as due to an increase in reactivity along the series. Alternatively, these differences may partly be due to the solvent dependence of the substitution process.

In our earlier study[17] we pointed out that since the substitution rate constant of *cis*-$Mo(CO)_4(py)_2$ increases with increasing polarity of the solvent, this could result in an acceleration of the reaction at elevated pressure, since solvent polarity in general increases with increasing pressure.[19] From the solvent dependence data, we could conclude[17] that this acceleration would result in a $\Delta V^{\ddagger}$ value of approximately −5 cm^3 mol^{-1} and that the measured $\Delta V^{\ddagger}$ value was in fact 5 cm^3 mol^{-1} too small. For the present systems the rate constant for the substitution of the BTE complex by $P(OEt)_3$ decreases with increasing polarity of the solvent, viz. 2.8×10^{-3} (toluene), 2.2×10^{-3} (chlorobenzene) and 1.8×10^{-3} M^{-1} s^{-1} (1,2-dichloroethane) at 46 °C. From a comparison of the dielectric constants of these solvents at ambient pressure and at 100 MPa,[20] it is easy to predict that an increase in the polarity of 1,2-dichloroethane with increasing pressure will retard the substitution process, according to the quoted rate data,[21] equivalent to a $\Delta V^{\ddagger}$ of +3.8 cm^3 mol^{-1}. This means that the reported $\Delta V^{\ddagger}$ values in Table I are in fact too large and should be reduced to approximately +10 cm^3 mol^{-1} to account for this effect. It follows that the corrected $\Delta V^{\ddagger}$'s are indeed very similar for the Cr and Mo systems and that the resulting $\Delta V^{\ddagger}$ value of +10 cm^3 mol^{-1} must be typical for such dissociatively activated substitution processes on neutral complexes.

Summarizing, we conclude that the volume of activation can be a powerful tool for the elucidation of substitution mechanisms of organometallic complexes, especially in light of the general interest in the mechanism of such reactions[22–24] and the assignment of mechanisms in the case of two-term rate laws[25–28] and deviating activation parameters (viz. $\Delta S^{\ddagger}$).[14,29]

Acknowledgments. R.v.E. gratefully acknowledges financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Max-Buchner-Forschungsstiftung. G.R.D. acknowledges financial support of the Robert A. Welch Foundation and the experimental assistance of Jose E. Cortes.

Registry No. $(CO)_4Cr(BTE)$, 21948-40-3; $(CO)_4Cr(dto)$, 61411-30-1; $P(OC_2H_5)_3$, 122-52-1.

---

(16) Macholdt, H.-T.; Elias, H. *Inorg. Chem.* **1984**, *23*, 4315.
(17) Macholdt, H.-T.; van Eldik, R. *Transition Met. Chem. (Weinheim, Ger.)* **1985**, *10*, 323.
(18) Brower, K. R.; Chen, T. *Inorg. Chem.* **1973**, *12*, 2198.
(19) Isaacs, N. S. *Liquid Phase High Pressure Chemistry*; Wiley: 1981; p 99, data for toluene at 30 °C.
(20) ϵ = 2.36 (toluene), 5.20 (chlorobenzene), and 9.22 (1,2-dichloroethane) at ambient pressure and 2.47, 5.56, and 10.67, respectively, at 100 MPa and 50 °C.[19]
(21) From the rate data it follows that $k = 3.06 \times 10^{-3} - 1.37 \times 10^{-4}$ M^{-1} s^{-1}.
(22) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557.
(23) Basolo, F. *Coord. Chem. Rev.* **1982**, *43*, 7.
(24) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113.
(25) Douglas, B.; McDaniel, D. H.; Alexander, J. J. *Concept and Models of Inorganic Chemistry*; Wiley: New York, 1983.
(26) Darensbourg, D. J.; Ewen, J. A. *Inorg. Chem.* **1981**, *20*, 4168.
(27) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *Organometallics* **1982**, *1*, 1033.
(28) Dobson, G. R.; Binzet, N. S. *J. Coord. Chem.* **1984**, *13*, 153.
(29) Faber, G. C.; Dobson, G. R. *Inorg. Chem.* **1968**, *7*, 584.

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Solvent-Dependent Redox Thermodynamics as a Probe of Solvent Shielding in Lanthanide Cryptates

Jila Tabib, Joseph T. Hupp,[†] and Michael J. Weaver*

Received November 19, 1985

We have been interested for some time in the redox properties of lanthanide cryptates (polyoxa diaza macrobicyclic complexes[1]). The Eu(III) cryptates are known to exhibit reversible reductive electrochemistry.[2,3] and are relatively facile one-electron-transfer reagents.[4] Similar electrochemical behavior has been noted for an ytterbium cryptate.[2] Europium(II) and -(III) cryptates are also attracting attention on account of their luminescence properties[5,6] and the attendant photophysics and photochemistry.[7]

A significant point of interest in both redox and spectroscopic studies is the extent to which an encapsulating cryptand is able to isolate the lanthanide cation from specific interactions with the surrounding solvent. The ability to achieve such isolation appears to be a major factor in obtaining long lifetimes for emissive excited states.[6b,8] Such "solvent shielding" is clearly also important in lanthanide redox processes. Thus we have shown, for example, that encrypting europium cations yields very large increases in Eu(III/II) self-exchange rates in aqueous media.[4]

Given the importance of solvent shielding, it is clearly desirable to establish quantitative measures of the extent of its occurrence. One method has been developed that enables estimates of the number of water molecules bound directly to lanthanide ions to be obtained from the deuterium solvent isotope effect on the luminescence lifetimes.[8] This approach has recently been employed to estimate the extent of solvent shielding for encrypted Eu(III).[6b] While relatively direct, the method is limited to aqueous environments. It would clearly be desirable to have available methods that are applicable in a range of solvents and for different metal ions.

Toward these ends, we briefly report here some pertinent redox thermodynamic data for europium, ytterbium, and samarium cryptates as a function of the solvent in comparison with corresponding data for the fully solvated ("solvento") redox couples. The results bear directly on the question of solvent shielding brought about by cryptand encapsulation.

Experimental Section

The various europium, ytterbium, and samarium cryptates were normally prepared[9] in situ by mixing a ca. millimolar solution of the lanthanide in the divalent form in the required solvent with a slight excess of the appropriate polyoxa diaza macrobicyclic ("cryptand") ligand (2.2.1) or (2.2.2).[10] The cryptands were obtained from PCR Inc. The lanthanide starting materials were the trivalent salts $Eu(ClO_4)_3{\cdot}6H_2O$, $Yb(ClO_4)_3{\cdot}6H_2O$ (Alfa Inorganics), and $Sm(ClO_4)_3{\cdot}nH_2O$ (Research Organic/Inorganic), which were dried in a vacuum oven at 100 °C. Tetraethylammonium perchlorate (Eastman) was used as a supporting electrolyte. Lanthanide reduction to the divalent form was accomplished electrochemically at a stirred mercury pool. Some solid lanthanide(III) cryptate samples (from Dr. O. A. Gansow) were also employed as solutes, with identical electrochemical results.

Formal potentials, E_f, were obtained as a function of the solvent by using cyclic voltammetry. Experimental details are given in ref 2 and 11. Reversible or near-reversible cyclic voltammograms were usually obtained at either platinum or hanging-mercury-drop electrodes at slow sweep rates (100–500 mV s^{-1}), enabling E_f to be approximated from the mean of the cathodic and anodic peak potentials. Reaction entropies,[12] ΔS_{rc}°, were obtained from the temperature dependence of E_f by using a nonisothermal cell arrangement as outlined in ref 11.

Results and Discussion

Table I summarizes formal potentials (vs. the ferrocenium–ferrocene couple in the same media) and reaction entropies for $Eu^{3+/2+}$, $Eu(2.2.1)^{3+/2+}$, and $Eu(2.2.2)^{3+/2+}$ in aqueous media and

---

[†] Department of Chemistry, The University of North Carolina, Chapel Hill, NC 27514.