

= pyridine)<sup>16,17</sup> 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  $+4 \text{ cm}^3 \text{ mol}^{-1}$  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<sup>18</sup> for the dissociation of CO from  $\text{Cr}(\text{CO})_6$  and  $\text{Mo}(\text{CO})_6$ , for which  $\Delta V^\ddagger$  is  $+15 \pm 1$  and  $+10 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$ , respectively. These authors,<sup>18</sup> 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<sup>17</sup> we pointed out that since the substitution rate constant of *cis*- $\text{Mo}(\text{CO})_4(\text{py})_2$  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.<sup>19</sup> From the solvent dependence data, we could conclude<sup>17</sup> that this acceleration would result in a  $\Delta V^\ddagger$  value of approximately  $-5 \text{ cm}^3 \text{ mol}^{-1}$  and that the measured  $\Delta V^\ddagger$  value was in fact  $5 \text{ cm}^3 \text{ mol}^{-1}$  too small. For the present systems the rate constant for the substitution of the BTE complex by  $\text{P}(\text{OEt})_3$  decreases with increasing polarity of the solvent, viz.  $2.8 \times 10^{-3}$  (toluene),  $2.2 \times 10^{-3}$  (chlorobenzene) and  $1.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  (1,2-dichloroethane) at 46 °C. From a comparison of the dielectric constants of these solvents at ambient pressure and at 100 MPa,<sup>20</sup> 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,<sup>21</sup> equivalent to a  $\Delta V^\ddagger$  of  $+3.8 \text{ cm}^3 \text{ mol}^{-1}$ . This means that the reported  $\Delta V^\ddagger$  values in Table I are in fact too large and should be reduced to approximately  $+10 \text{ cm}^3 \text{ mol}^{-1}$  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  $+10 \text{ cm}^3 \text{ mol}^{-1}$  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<sup>22-24</sup> and the assignment of mechanisms in the case of two-term rate laws<sup>25-28</sup> and deviating activation parameters (viz.  $\Delta S^\ddagger$ ).<sup>14,29</sup>

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**Registry No.**  $(\text{CO})_4\text{Cr}(\text{BTE})$ , 21948-40-3;  $(\text{CO})_4\text{Cr}(\text{dto})$ , 61411-30-1;  $\text{P}(\text{OC}_2\text{H}_5)_3$ , 122-52-1.

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

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

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.<sup>6b,8</sup> 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.<sup>4</sup>

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.<sup>8</sup> This approach has recently been employed to estimate the extent of solvent shielding for encrypted Eu(III).<sup>6b</sup> 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<sup>9</sup> 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).<sup>10</sup> The cryptands were obtained from PCR Inc. The lanthanide starting materials were the trivalent salts  $\text{Eu}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Yb}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  (Alfa Inorganics), and  $\text{Sm}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$  (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  $\text{mV s}^{-1}$ ), enabling  $E_f$  to be approximated from the mean of the cathodic and anodic peak potentials. Reaction entropies,<sup>12</sup>  $\Delta S_{rc}^\ddagger$ , were obtained from the temperature dependence of  $E_f$  by using a nonisothermal cell arrangement as outlined in ref 11.

## Results and Discussion

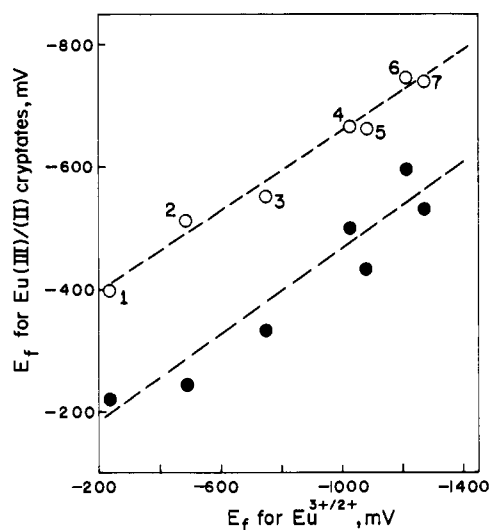
Table I summarizes formal potentials (vs. the ferrocenium-ferrocene couple in the same media) and reaction entropies for  $\text{Eu}^{3+/2+}$ ,  $\text{Eu}(2.2.1)^{3+/2+}$ , and  $\text{Eu}(2.2.2)^{3+/2+}$  in aqueous media and

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**Table I.** Formal Potentials,  $E_f$  (mV), and Reaction Entropies,  $\Delta S_{rc}^\circ$  (cal/(deg mol)), for Europium(III/II) Solvento and Cryptate Redox Couples in Various Solvents at 25 °C

solvent	DN <sup>a</sup>	AN <sup>b</sup>	Eu <sup>3+/2+</sup>		Eu-(2.2.1) <sup>3+/2+</sup> <sup>c</sup>		Eu-(2.2.2) <sup>3+/2+</sup> <sup>c</sup>	
			$-E_f^c$	$\Delta S_{rc}^\circ$ <sup>d</sup>	$-E_f^c$	$\Delta S_{rc}^\circ$ <sup>d</sup>	$-E_f^c$	$\Delta S_{rc}^\circ$ <sup>d</sup>
acetonitrile	14.1	19.3	215		392	155	222	85
propylene carbonate	15.1	18.3	488		511	140	243	135
water	18	55	748	200	550	115	330	90
formamide	24	40	1025	90	666	80	502	90
DMF <sup>f</sup>	26.6	16	1080	235	660	145	427	120
NMF <sup>g</sup>	27	31	1210	110	745	95	596	80
Me <sub>2</sub> SO <sup>h</sup>	29.8	19.3	1280	190	739	130	533	85

<sup>a</sup>Solvent "donor number" from ref 13. <sup>b</sup>Solvent "acceptor number" from ref 13. <sup>c</sup>Formal potential in given solvent containing 0.1 M tetraethylammonium perchlorate, with respect to ferrocenium-ferrocene under the same conditions. <sup>d</sup>Reaction entropy of redox couple determined from the temperature dependence of  $E_f$  by using a nonisothermal arrangement.<sup>11,12</sup> <sup>e</sup>See footnote 10 for cryptand terminology. <sup>f</sup>DMF = *N,N*-dimethylformamide. <sup>g</sup>NMF = *N*-methylformamide. <sup>h</sup>Me<sub>2</sub>SO = dimethyl sulfoxide.

**Figure 1.** Formal potentials for Eu(221)<sup>3+/2+</sup> (○) and Eu(222)<sup>3+/2+</sup> (●) vs. formal potentials for Eu(III/II) solvent couples. Key to solvents: (1) acetonitrile; (2) propylene carbonate; (3) water; (4) formamide; (5) dimethylformamide; (6) *N*-methylformamide; (7) dimethyl sulfoxide.

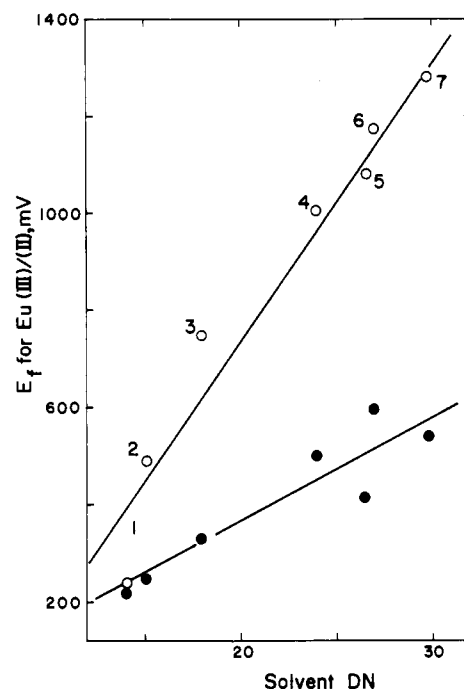
six nonaqueous solvents. The latter solvents were chosen so to yield reasonable variations in the solvent basicity and acidity, as

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**Table II.** Sensitivities of Formal Potentials of Lanthanide(III/II) Solvento and Cryptate Couples to the Solvent

redox couple	$-dE_f/d(DN)$ , <sup>a</sup> mV DN <sup>-1</sup>	$dE_f(M-cryptand)/dE_f(M-solvento)$ <sup>b</sup>
Eu <sup>3+/2+</sup>	67 ± 7	
Eu(2.2.1) <sup>3+/2+</sup>	20 ± 3	0.32 ± 0.02
Eu(2.2.2) <sup>3+/2+</sup>	22 ± 4	0.35 ± 0.05
Yb <sup>3+/2+</sup>	56 ± 7	
Yb(2.2.1) <sup>3+/2+</sup>	22 ± 3	0.39 ± 0.02
Yb(2.2.2) <sup>3+/2+</sup>	19 ± 4	0.31 ± 0.05
Sm <sup>3+/2+</sup>	67 ± 4	
Sm(2.2.1) <sup>3+/2+</sup>	22 ± 3	0.32 ± 0.04
Sm(2.2.2) <sup>3+/2+</sup>	19 ± 3	0.29 ± 0.04

<sup>a</sup>Average dependence of formal potential for redox couple indicated (vs. ferrocenium-ferrocene) upon donor number, DN, for solvents listed in Table I. Plus-minus limits given refer to one standard deviation. <sup>b</sup>Relative dependence of formal potential (vs. ferrocenium-ferrocene) for corresponding lanthanide solvento and cryptate redox couples brought about by varying the solvent. Plus-minus limits given refer to one standard deviation.

**Figure 2.** Formal potentials for Eu(222)<sup>3+/2+</sup> (●) and Eu(III/II) solvent (○) couples vs. solvent donor number, DN. Key to the solvents is as in Figure 1.

estimated approximately by the so-called donor numbers (DN) and acceptor numbers (AN)<sup>13</sup> (Table I). It is seen that the solvent dependence of  $E_f$  for the nonencrypted (solvento) couples are substantially larger than for the cryptate redox couples. To illustrate this, plots of  $E_f$  values for Eu(2.2.1)<sup>3+/2+</sup> and Eu(2.2.2)<sup>3+/2+</sup> against the corresponding values for solvento Eu<sup>3+/2+</sup> are shown in Figure 1. Reasonably linear correlations are obtained with slopes,  $[dE_f(M-cryptand)/dE_f(M-solvento)]$ , equal to about 0.35 in both cases. Similarly linear correlations and slopes are obtained with the corresponding Yb(III/II) and Sm(III/II) couples, as summarized in Table II.

The solvent dependence of  $E_f$  for each redox couple can also be correlated with scales of solvent basicity. This is exemplified in Figure 2, which consists of  $E_f$  values for Eu<sup>3+/2+</sup> (open circles) and Eu(2.2.2)<sup>3+/2+</sup> (closed circles) plotted against the solvent donor number. The  $E_f$ -DN slope for the latter couple is about threefold

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less than for the former. Similar linear correlations have been observed previously for d-block transition-metal couples containing substitutionally inert ammine ligands.<sup>14,15</sup> They arise from the more electropositive oxidized form of the redox couple being stabilized to a greater extent by solvent donor interactions than the reduced form.<sup>14</sup> Similar results were obtained for the corresponding Yb(III/II) and Sm(III/II) couples; the data for all these systems are summarized in Table II as "donor selectivities",<sup>15</sup>  $[-dE_f/d(DN)]$ .

The simplest interpretation of these data, expressed as a decrease in either  $(-dE_f/d(DN))$  or  $[dE_f(M\text{-cryptand})/dE_f(M\text{-solvento})]$  (Table II), is that the number of directly coordinated solvent molecules is about threefold smaller for the metal cryptates than for the nonencrypted cations. This presumes that the donor selectivity is proportional to the number of such "inner shell" solvent molecules. Evidence for a related effect has been obtained for mixed polypyridine-ammine couples, where the donor selectivity increases linearly with the number of ammine ligands.<sup>15</sup> Although these latter couples are coordinatively saturated and substitutionally inert, the solvent can interact specifically with the polar ammine ligands. Note that the cryptand ligands, like the polypyridines, contain no polar sites suitable for specific solute-solvent interactions. The number of inner-shell water molecules,  $n$ , coordinated to Eu(III) in aqueous media has been determined to be  $8.3 \pm 0.2$  from X-ray diffraction data<sup>16</sup> and estimated to be about 9 on the basis of luminescence decay measurements.<sup>8a,17</sup> The latter method applied to Eu(2.2.1)<sup>3+</sup> yielded  $n = 3.2$ .<sup>6b</sup> The present results are nicely consistent with this latter finding since they indicate that both the (2.2.1) and (2.2.2) cryptates allow about one-third as many solvent molecules to coordinate to the lanthanide cation as obtained in the absence of such solvent shielding. This finding is consistent with structural considerations in that the macrobicyclic structure of these cryptates leaves three gaps between the polyether strands with which solvent coordination to the metal is sterically possible.<sup>18</sup> The conclusion that the (2.2.1) cryptate provides only fractional (ca. 60-80%) shielding of Eu(III) from direct coordination by water can therefore now be generalized on the basis of our electrochemical data to europium, ytterbium, and samarium complexes with (2.2.2) as well as (2.2.1) cryptates and to several nonaqueous solvents in addition to water.

It is also of interest to examine the effect of metal encryption on the reaction entropies, especially in view of our recent assessment of solvent and ligand effects upon  $\Delta S_{rc}^\circ$  for simple octahedral redox couples.<sup>19</sup> (The reaction entropy equals the difference of ionic entropies between the reduced and oxidized forms of the redox couple.) Inspection of the  $\Delta S_{rc}^\circ$  values for the Eu(III/II) couples in Table I shows that while they tend to be smaller for the cryptate compared with the solvent couples, the extent of this decrease is strongly dependent on the particular solvent. In addition, plots of  $\Delta S_{rc}^\circ$  against the solvent acceptor number, AN (Table I), found previously to be linear for a number of octahedral redox couples,<sup>19</sup> are markedly nonlinear for the present systems. Very similar solvent-dependent  $\Delta S_{rc}^\circ$  values were also obtained for the Yb(III/II) and Sm(III/II) couples. Especially discrepant in this regard are the relatively large  $\Delta S_{rc}^\circ$  values observed for the Eu(III/II) cryptates and especially Eu<sup>3+/2+</sup> in water, in contrast to the small values expected on the basis of the  $\Delta S_{rc}^\circ$ -AN correlation in ref 19. This has been noted previously for other aquo couples and ascribed to the influence of specific aquo ligand-solvent effects.<sup>19</sup>

This more complex influence of encryption upon the reaction entropies and the absence of straightforward solvent shielding

effects are almost undoubtedly due to the preponderant effect of solvent-solvent, and longer range ion-solvent, interactions upon the ionic entropies.<sup>19</sup> The solvent-dependent formal potentials (i.e., the ionic free energies), on the other hand, appear to be influenced primarily by short-range charge-solvent interactions so that the simple manifestation of solvent shielding upon encryption with regard to this latter parameter is readily understandable.

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**Registry No.** DMF, 68-12-2; NMF, 123-39-7; Me<sub>2</sub>SO, 67-68-5; acetonitrile, 75-05-8; propylene carbonate, 2453-03-4; formamide, 75-12-7.

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### Magnetic Susceptibility of Paraquat Hexabromodicuprate(II): Comparison of the Magnetochemistry of Copper(II) Chloride and Copper(II) Bromide Salts

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In the past decade, the magnetic properties of a large number of copper(II) halide salts have been investigated.<sup>1,2</sup> These include symmetrical bibriged systems,<sup>3</sup> asymmetrical bibriged systems,<sup>4</sup> tribridged systems,<sup>5</sup> and asymmetrical monobridged systems.<sup>5</sup> In examining these results when  $|J/k|$  is relatively large ( $|J/k| \geq 10$  K;  $\mathcal{H} = -2JS_1S_2$ ), a number of systematics are apparent. First, it is observed that if the exchange interaction is ferromagnetic, the magnitude of the coupling is nearly the same for the bromide and chloride salts. However, if the coupling is antiferromagnetic, the magnitude for the bromide salts is several times larger than for the chlorides. Second, in systems where the spin anisotropy is known, the two types of salts have opposite anisotropies; e.g., if the chloride has a small Ising anisotropy, the bromide will have a  $xy$  anisotropy and vice versa.

In this paper a magnetic susceptibility study of (paraquat)-Cu<sub>2</sub>Br<sub>6</sub> is reported, and the results are compared with those for the corresponding chloride salt. Next, the results of a reinvestigation of the magnetic susceptibilities of CuCl<sub>2</sub> and CuBr<sub>2</sub> are given. Finally, the role that the excitation energies for the ligand-to-metal charge-transfer states and the magnitude of the ligand spin-orbit coupling play in determining the behavior indicated above are discussed.

#### Experimental Section

(paraquat)Cu<sub>2</sub>Br<sub>6</sub> was prepared, following the procedure used for the corresponding chloride salts,<sup>6</sup> by dissolving stoichiometric amounts of paraquat and CuBr<sub>2</sub> in a moderately dilute aqueous HBr solution and crystallizing by slow evaporation at room temperature.

Magnetic measurements on CuBr<sub>2</sub> and (paraquat)Cu<sub>2</sub>Br<sub>6</sub> in the temperature range 78-300 K were performed at Washington State University on a PAR vibrating-sample magnetometer.<sup>7</sup> Measurements on

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