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The Nonadiabaticity Question for Europium(III/II): Outer-Sphere Reactivities of Europium(III/II) Cryptates

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The one-electron reduction kinetics of the europium cryptates $Eu(2.2.1)^{3+}$ and $Eu(2.2.2)^{3+}$ by the aquo ions V_{aq}^{2+} and Eu_{aq}^{2+} and the oxidation kinetics of $Eu(2.2.1)^{2+}$ by $Co(NH_3)_6^{3+}$ have been studied by using a polarographic technique in order to examine the effects of encapsulating europium within cryptate cavities upon the reactivity of the Eu(III/II) couple. At 25 °C and an ionic strength $\mu = 0.1$, the second-order rate constants ($M^{-1}\ s^{-1}$) for acid-independent pathways are as follows: $Eu(2.2.1)^{3+}$–V_{aq}^{2+}, 0.5; $Eu(2.2.1)^{3+}$–Eu_{aq}^{2+}, ca. 0.2; $Eu(2.2.2)^{3+}$–V_{aq}^{2+}, 1.5; $Eu(2.2.2)^{3+}$–Eu_{aq}^{2+}, 1.4; $Co(NH_3)_6^{3+}$–$Eu(2.2.1)^{2+}$, 0.055. By comparison of these kinetic data with those for similar reactions involving the $Eu_{aq}^{3+/2+}$ couple, the rate constant for Eu(III/II) self-exchange, k_{ex}, is estimated to increase by factors of ca. 1×10^7 and 2×10^4 upon encapsulation of europium in (2.2.1) and (2.2.2) cryptate cavities, respectively. Estimates of k_{ex} equal to ca. 10, 4×10^{-2}, and $5 \times 10^{-6}\ M^{-1}\ s^{-1}$ ($\mu = 0.1$) for $Eu(2.2.1)^{3+/2+}$, $Eu(2.2.2)^{3+/2+}$, and $Eu_{aq}^{3+/2+}$, respectively, are obtained from the Marcus cross relation. The increases in k_{ex} resulting from cryptate encapsulation suggest that nonadiabaticity is not primarily responsible for the extremely low reactivity of $Eu_{aq}^{3+/2+}$. The values of k_{ex} are shown to be roughly consistent with the Franck–Condon barriers estimated from structural data.

Introduction

Homogeneous redox reactions involving the europium(III/II) redox couple in aqueous media have long been known to exhibit extremely small rate constants. Thus, Meier and Garner found the rate constant for outer-sphere $Eu_{aq}^{3+/2+}$ self-exchange (where "aq" denotes aquo ligands) to be immeasurably slow, $\lesssim 1 \times 10^{-4}\ M^{-1}\ s^{-1}$, at high ionic strengths and ambient temperatures.[2] Application of the usual Marcus cross relation to rate and equilibrium data for suitable cross-reactions also yields values of the rate constant k_{ex} for $Eu_{aq}^{3+/2+}$ self-exchange of $\lesssim 1 \times 10^{-4}\ M^{-1}\ s^{-1}$.[3-5] A similarly large electron-transfer barrier is also observed for $Eu_{aq}^{3+/2+}$ at the mercury–aqueous interface.[6]

Interpretation of such self-exchange data can be made by using the general formulation

$$k_{ex} = \kappa_{el} A_n \exp(-w_r/RT) \exp(-\Delta G_{int}^*/RT) \qquad (1)$$

where κ_{el} is the electronic transmission coefficient, A_n is a nuclear frequency factor, w_r is the work required to form the encounter complex from the separated reactants, and ΔG_{int}^* is the intrinsic free energy barrier, i.e. the energy required to alter the nuclear configuration of the reactants and surrounding solvent within the encounter complex. The intrinsic barrier consists of an inner-shell component ΔG_{is}^* arising from changes in the metal–ligand bond distances and an outer-shell component ΔG_{os}^* associated with changes in polarization of the surrounding solvent. The small values of k_{ex} obtained for $Eu_{aq}^{3+/2+}$ are surprising on this basis since they are roughly comparable to the values of k_{ex} for other redox couples, for example $Cr_{aq}^{3+/2+}$ and $Co(en)_3^{3+/2+}$ (en = ethylenediamine),[3,4] for which large values of ΔG_{is}^* are expected on account of the extensive changes in the metal–ligand bond distance required for electron transfer.[7] The small rate constants for $Eu_{aq}^{3+/2+}$ reactions have often been attributed to nonadiabatic pathways, i.e. to values of the electron-tunneling probability, κ_{el}, that are very much less than unity.[8,9] This might be anticipated from the especially weak orbital overlap expected for electron-transfer reactions involving f orbitals.[5,8]

However, the available evidence for nonadiabaticity is inconclusive. It would be expected that highly nonadiabatic pathways would be accompanied by correspondingly small values of the Arrhenius preexponential factor or, equivalently, by abnormally negative entropies of activation. Although few detailed analyses have been undertaken,[3,4,6] the available evidence indicates that the activation entropies of homogeneous reactions involving $Eu_{aq}^{3+/2+}$ are not noticeably smaller than those involving d-block transition-metal couples[4] (vide infra).

One method of exploring the factors influencing metal ion reactivity is to examine the effects of altering the ligand environment. Such ligand effects have been largely unexplored for Eu(III/II) on account of the relative instability and substitution lability of lanthanide complexes. However, we have recently shown[10] that both Eu(III) and Eu(II) form thermodynamically stable and substitutionally inert complexes with the polyoxadiazamacrobicyclic ("cryptand") ligands (2.2.1) and (2.2.2).[11] These ligands provide a stereochemically rigid case ("cryptate"), shielding the metal ion from the surrounding environment.[12] Cryptate encapsulation may be expected to yield marked changes in the metal ion reactivity in two chief ways. If the inner-shell barrier ΔG_{is}^* is large for $Eu_{aq}^{3+/2+}$, then cryptate formation is expected to yield substantial increases in k_{ex} through decreases in ΔG_{is}^*. On the other hand, if ΔG_{is}^* is small and nonadiabaticity provides a major part of the electron-transfer barrier, decreases in k_{ex} may well occur as a result of weaker electronic coupling (i.e. smaller values of κ_{el}; eq 1) brought about by cryptate encapsulation. Information on the relative importance of κ_{el} and ΔG_{int}^* to the overall electron-transfer barrier could therefore be obtained from examining the effect of cryptate formation upon k_{ex}.

In this paper, kinetic data are presented for the reduction of $Eu(2.2.1)^{3+}$ and $Eu(2.2.2)^{3+}$ by V_{aq}^{2+} and Eu_{aq}^{2+} and the

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(1) Taken in part from: Yee, E. L. Ph.D. Thesis, Michigan State University, 1980.

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(6) Weaver, M. J. *J. Phys. Chem.* **1980**, *84*, 568.

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(8) Taube, H. *Adv. Chem. Ser.* **1977**, *No. 162*, 127.

(9) Balzani, V.; Scandola, F.; Orlandi, G.; Sabbatini, N.; Indelli, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 3370.

(10) (a) Yee, E. L.; Gansow, O. A.; Weaver, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2278. (b) Gansow, O. A.; Kausar, A. R.; Triplett, K. M.; Weaver, M. J.; Yee, E. L. *Ibid.* **1977**, *99*, 7087.

(11) This cryptand symbolism was originally due to Lehn;[12] the numerals within the parentheses refer to the number of oxygen atoms on the polyether strands that join the nitrogen bridgeheads. Thus, (2.2.1) = 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosene and (2.2.2) = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

(12) (a) Lehn, J.-M. *Struct. Bonding (Berlin)* **1973**, *16*, 1. (b) *Acc. Chem. Res.* **1978**, *11*, 49.

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Table I. Rate Constants and Formal Equilibrium Constants for Reactions Involving Europium Cryptates in Aqueous Solution at 25 °C

oxidant	reductant	μ, M	k_{12},[a] M^{-1} s^{-1}	k_H,[b] s^{-1}	K_{12}[c]
$Eu(2.2.1)^{3+}$	V_{aq}^{2+}	0.10[d]	0.5 ± 0.05		7.0
$Eu(2.2.1)^{3+}$	Eu_{aq}^{2+}	0.10[e]	ca. 0.2	0.4 ± 0.02	2.4×10^3
$Co(NH_3)_6^{3+}$	$Eu(2.2.1)^{2+}$	0.066[e,f]	0.043 ± 0.004		
		0.10	0.055[g]		
$Eu(2.2.2)^{3+}$	V_{aq}^{2+}	0.10[e]	1.5 ± 0.2		3.7×10^4
$Eu(2.2.2)^{3+}$	Eu_{aq}^{2+}	0.10[e]	1.4 ± 0.2	0.016 ± 0.004	1.3×10^7

[a] Second-order rate constant for acid-independent pathway. [b] Rate constant for inverse acid-dependent pathway. [c] Formal equilibrium constants for indicated reactions at listed ionic strength, obtained from formal potentials for constituent redox couples given in ref 10a and 18. [d] Containing 20 mM tetraethylammonium perchlorate and 1-50 mM HCl; ionic strength maintained with KPF_6. [e] Containing 20 mM tetraethylammonium or tetrabutylammonium perchlorate and 1-50 mM $HClO_4$; ionic strength maintained with $LiClO_4$. [f] Experiments conducted at lower ionic strength due to limited solubility of $Co(NH_3)_6(ClO_4)_3$. [g] Obtained from listed rate constant at ionic strength $\mu = 0.066$ by using eq 2 (see text).

oxidation of $Eu(2.2.1)^{2+}$ by $Co(NH_3)_6^{3+}$. These reactions were chosen since they have suitable small driving forces with structurally simple coreactants, enabling values of k_{ex} for outer-sphere self-exchange of $Eu(2.2.1)^{3+/2+}$ and $Eu(2.2.2)^{3+/2+}$ to be derived with some confidence from the Marcus cross relationship.[3,4] These values of k_{ex} are compared with corresponding results obtained from cross-reactions involving $Eu_{aq}^{3+/2+}$ and shown to be roughly consistent with the reactivities predicted by assuming that ΔG_{is}^* provides the major contribution to the electron-transfer barrier.

Experimental Section

Solid samples of the chloride and nitrate salts of $Eu(2.2.1)^{3+}$ and $Eu(2.2.2)^{3+}$ were supplied by Dr. O. A. Gansow. The synthesis involved refluxing Eu^{3+} with an excess of the appropriate cryptand in a nonaqueous solvent such as acetonitrile and precipitating by the addition of ethyl ether.[10b,13] These complexes are difficult to prepare by direct mixing of Eu^{3+} and cryptand in aqueous solution since they have insufficient thermodynamic stability in the acidic media (pH $\lesssim 6$) necessary to suppress Eu_{aq}^{3+} hydrolysis.[10a] Nevertheless, aqueous solutions of $Eu(2.2.1)^{2+}$ and $Eu(2.2.2)^{2+}$ were prepared by cathodically electrolyzing solutions of Eu_{aq}^{3+} to Eu_{aq}^{2+} in perchlorate media at a stirred mercury pool held at ca. -1200 mV vs. SCE and then adding a slight excess of the appropriate cryptand. The cryptands (2.2.1) and (2.2.2) were obtained from PCR Inc. The Eu_{aq}^{3+} solutions were prepared by dissolving Eu_2O_3 in a stoichiometric quantity of perchloric acid. These divalent cryptates could readily be converted to the corresponding trivalent cryptates by electrooxidation at a stirred mercury pool held at a potential about 150 mV positive of the formal potential, E_f, for the appropriate Eu(III/II) couple ($E_f = -425$ and -210 mV vs. the saturated calomel electrode (SCE) for $Eu(2.2.1)^{3+/2+}$ and $Eu(2.2.2)^{3+/2+}$, respectively[10a]). Trivalent cryptates synthesized in this fashion display behavior identical with that of solutions prepared from the solid samples. Solutions of V_{aq}^{2+} were synthesized by dissolving V_2O_5 in perchloric acid and cathodically electrolyzing the resulting solution of VO_2^+ at -1100 mV vs. SCE at a stirred mecury pool. Solid $[Co(NH_3)_6](ClO_4)_3$ was prepared by a standard literature method[14] and recrystallized from aqueous perchloric acid. Samples of tetraethylammonium and tetrabutylammonium perchlorate (Eastman or G. F. Smith, Co.) were recrystallized from water. The water was purified by means of a Milli-Q purification system (Millipore Corp.).

Rate parameters for the reactions studied here, $Eu(2.2.1)^{3+}$-V_{aq}^{2+}, $Eu(2.2.1)^{3+}$-Eu_{aq}^{2+}, $Co(NH_3)_6^{3+}$-$Eu(2.2.1)^{2+}$, $Eu(2.2.2)^{3+}$-V_{aq}^{2+}, and $Eu(2.2.2)^{3+}$-Eu_{aq}^{2+} were obtained by using a polarographic method as follows.[1] These reactions are sufficiently slow to yield half-lives of at least ca. 5 min, allowing the reaction kinetics to be determined by periodic evaluation of the reactant concentrations. Dc polarography offers a more sensitive technique than spectrophotometry for this purpose for reactants such as lanthanides that lack strong visible or near-UV adsorption bands; the former method can accurately evaluate reactant concentrations down to ca. 5×10^{-5} M. The straightforward application of the polarographic method requires that only one of the two redox couples involved in the homogeneous redox reaction be electroactive at a given electrode potential so to avoid contributions to the measured current from both couples. This will not be fulfilled if both couples are electrochemically reversible (i.e. have large standard rate constants) since there will be no potential where neither the oxidized nor the reduced form of both redox partners contributes to the polarographic current. Although the aquo and ammine reactants used here are not entirely reversible, in many electrolytes the polarographic current for the reduction or oxidation of the cryptate reactant included a contribution from the coreactant (or coproduct). This difficulty was circumvented by employing supporting electrolytes containing 20-50 mM tetraethylammonium or tetrabutylammonium perchlorate, the ionic strength being maintained with lithium perchlorate and the acidity controlled with perchloric acid. We have found that the electrochemical rate constants for cationic aquo and ammine reactants at the mercury-aqueous interface are sufficiently diminished in the presence of tetralkylammonium cations as a consequence of strong specific-cation adsorption so that these reactants are electroinactive over a wide potential range.[1,15] In contrast, both $Eu(2.2.1)^{3+/2+}$ and $Eu(2.2.2)^{3+/2+}$ remain electrochemically reversible under these conditions.

Consequently, the progress of each reaction was monitored from the decrease in the diffusion-limited polarographic current for the reduction (or oxidation) of the europium cryptate reaction at a suitable electrode potential (usually ca. -200 to -800 mV vs. SCE) where the cryptate reaction is diffusion controlled and yet the coreactant or coproduct is electroinactive. In order to facilitate data analysis, pseudo-first-order conditions were employed by using initial cryptate concentrations around 1 mM with the non-cryptate reactant present in at least a 10-fold excess. The half-lives were arranged in most cases to be sufficiently short so that aquation of the europium crypstates[10a] proceeded to an insignificant extent; where necessary, an appropriate correction was applied to the observed kinetics. The derived rate constants for the $Eu(2.2.1)^{3+}$-V_{aq}^{2+}, $Eu(2.2.2)^{3+}$-V_{aq}^{2+}, and $Co(NH_3)_6^{3+}$-$Eu(2.2.1)^{2+}$ reactions were generally reproducible to within 5-10% as determined from the average deviation of 4-10 kinetic runs for each reaction. For the first-named reaction, the ionic strength was maintained by using potassium hexafluorophosphate rather than lithium perchlorate since marked deviations from second-order kinetics were seen in the latter medium.[16] Somewhat lower precision, ca. ±50%, was obtained for the $Eu(2.2.1)^{3+}$-Eu_{aq}^{2+} and $Eu(2.2.2)^{3+}$-Eu_{aq}^{2+} reactions. Similarly irreproducible behavior has also been observed for other redox reactions involving a pair of lanthanide reactants.[8,17] Further details of the electrochemical measurements are given in ref 10a. All solutions were deoxygenated by bubbling with nitrogen, and all kinetic measurements were made at 25 ± 0.1 °C.

Results

Table I summarizes rate constants for the five reactions involving $Eu(2.2.1)^{3+/2+}$ and $Eu(2.2.2)^{3+/2+}$ for which reliable kinetic data could be obtained. At a given ionic strength and pH, the rate was found to be first order in each reactant, yielding second-order rate constants k_{12}'. Essentially identical

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(13) Pruett, D. J. Ph.D. Thesis, Michigan State University, 1978.

(14) "Handbook of Preparative Inorganic Chemistry", 2nd ed.; Brauer, G., Ed; Academic Press: New York, 1965; Vol. 2, 1531.

(15) Yee, E. L.; Wilson, M.; Weaver, M. J., unpublished results.

(16) The cause of this problem is unclear; although ClO_4^- slowly oxidizes V_{aq}^{2+} to V_{aq}^{3+},[5] the rate of this reaction appears to be insufficient to affect significantly the results.[1]

(17) Espenson, J. H., private communication, 1978; also quoted in ref 8.

(18) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131.

rate constants were obtained for most reactions in perchlorate and hexafluorophosphate media, although spurious results were obtained for the $Eu(2.2.1)^{3+}$–V_{aq}^{2+} reaction in the former medium. For this reaction it was also necessary to take into account the reverse reaction when extracting values of k_{12}' on account of its small equilibrium constant ($K_{12} = 7$). The dependence of k_{12}' upon acid concentration in the range 1–50 mM at a constant ionic strength was approximately consistent with the relation $k_{12}' = k_{12} + k_H/[H^+]$ for the $Eu(2.2.1)^{3+}$–Eu_{aq}^{2+} and $Eu(2.2.2)^{3+}$–Eu_{aq}^{2+} reactions so that values of both k_{12} and k_H are reported for these processes in Table I. The other reactions did not show any significant dependence of k_{12}' on $[H^+]$ for acid concentrations in the range 1–50 mM. None of the formal potentials for the redox couples used here exhibited an acid dependence in this region. Reactions that exhibit an inverse-acid dependence often are accelerated by the presence of complexing anions. However, the reactions in the present study did not display any discernible rate increases upon the addition of chloride ions at a constant total ionic strength, even up to chloride concentrations of 50–100 mM.

Most kinetic measurements were conducted at an ionic strength μ of 0.1, although the $Co(NH_3)_6^{3+}$–$Eu(2.2.1)^{2+}$ reaction was studied at $\mu = 0.066$ due to the limited solubility of the cobalt complex in concentrated perchlorate media. The rate constants for this reaction were corrected to $\mu = 0.1$ by using the expression[19]

$$\log k_{12} = \log k_0 + \frac{2AZ_AZ_B\mu^{1/2}}{1 + B\mathring{a}\mu^{1/2}} \tag{2}$$

where k_0 is the value of k_{12} at $\mu = 0$, Z_A and Z_B are the charge numbers of the reactants, $\mathring{a}$ is the internuclear separation in the encounter complex,[20] and A and B are the Debye–Hückel parameters.

Values of the acid-independent rate constants for self-exchange of the europium cryptates, k_{11}, were calculated from the k_{12} values in Table I by means of the Marcus cross relation[22]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \tag{3}$$

where k_{22} is the rate constant for self-exchange of the co-reacting redox couple, K_{12} is the equilibrium constant for the cross-reaction, and f_{12} is given by $\log f_{12} = (\log K_{12})^2/[4 \log (k_{11}k_{12}/A_n^2)]$. The frequency factor A_n was taken as 1×10^{12} M^{-1} s^{-1}.[23] The values of K_{12} are also given in Table I; they were obtained from the appropriate formal potentials measured at comparable ionic strengths.[10a,18] The values of k_{22} used for these calculations are 2×10^{-3} M^{-1} s^{-1} for $V_{aq}^{3+/2+}$ and 5×10^{-6} M^{-1} s^{-1} for $Eu_{aq}^{3+/2+}$. The former was estimated for $\mu = 0.1$ from the value measured at $\mu = 2$ (1.5×10^{-2} M^{-1} s^{-1} [24]) by using eq 2 with $\mathring{a} = 8$ Å. The latter is the average of several estimates, again corrected to $\mu = 0.1$, obtained from cross-reactions having suitably small driving forces[4] (Table II). The resulting values of k_{11} for $Eu(2.2.1)^{3+/2+}$ and $Eu(2.2.2)^{3+/2+}$ are given in Table II.

Table II. Derived Rate Constants k_{11} (M^{-1} s^{-1}) for Self-Exchange of Europium(III/II) Redox Couples at 25 °C and $\mu = 0.1$

redox couple	k_{11} [a]	cross-reaction used to calculate k_{11}
$Eu(2.2.1)^{3+/2+}$	13 [b,c]	$Eu(2.2.1)^{3+}$–V_{aq}^{2+}
	7 [b,d]	$Co(NH_3)_6^{3+}$–$Eu(2.2.1)^{2+}$
	~4 [b,e,h]	$Eu(2.2.1)^{3+}$–Eu_{aq}^{2+}
$Eu(2.2.2)^{3+/2+}$	4×10^{-2} [b,c]	$Eu(2.2.2)^{3+}$–V_{aq}^{2+}
	~4×10^{-2} [b,e,h]	$Eu(2.2.2)^{3+}$–Eu_{aq}^{2+}
$Eu_{aq}^{3+/2+}$	2×10^{-6} [f]	V_{aq}^{3+}–Eu_{aq}^{2+}
	~5×10^{-5} [f]	$Co(en)_3^{3+}$–Eu_{aq}^{2+} [g]
	4×10^{-6} [f]	$Ru(NH_3)_6^{3+}$–Eu_{aq}^{2+}

[a] Obtained from eq 3. [b] From data taken in part from Table I. [c] Assuming that k_{22} for $V_{aq}^{3+/2+}$ equals 2×10^{-3} M^{-1} s^{-1} (see text). [d] Obtained from eq 4 by using data for $Co(NH_3)_6^{3+}$–$Eu(2.2.1)^{2+}$ and $Co(NH_3)_6^{3+}$–$Ru(NH_3)_6^{2+}$ cross-reactions (see text). [e] Assuming that k_{22} for $Eu_{aq}^{3+/2+}$ equals 5×10^{-6} M^{-1} s^{-1} (see text). [f] From k_{12}, k_{22}, and K_{12} values quoted in Tables I and II in ref 3, corrected to $\mu = 0.1$ by using eq 2. [g] en = ethylenediamine. [h] Estimates of k_{11} from Eu(III)–Eu(II) cross-reactions are more uncertain on account of relatively poor reproducibility and acid dependence of the cross-reaction kinetics (see text).

The $Co(NH_3)_6^{3+}$–$Eu(2.2.1)^{2+}$ cross-reaction cannot be used to obtain k_{11} for $Eu(2.2.1)^{3+/2+}$ in this manner because the self-exchange rate constant and formal potential for $Co(NH_3)_6^{3+/2+}$ are unknown.[25] However, k_{11} can still be obtained by combining k_{12}, the rate constant for the $Co(NH_3)_6^{3+}$–$Eu(2.2.1)^{2+}$ reaction, with k_{23}, the corresponding quantity for a cross-reaction between $Co(NH_3)_6^{3+}$ and another reductant such as $Ru(NH_3)_6^{2+}$ for which the self-exchange rate constant, k_{33}, is known. Providing that the driving forces for the cross-reactions are small (or comparable) such that $f_{12} = f_{23}$, a ratio of the cross relations (eq 3) for such a pair of cross-reactions yields[27]

$$k_{11} = k_{12}^2k_{33}/k_{23}^2K_{13} \tag{4}$$

where K_{13} is the equilibrium constant for the $Ru(NH_3)_6^{3+}$–$Eu(2.2.1)^{2+}$ cross-reaction. Substituting into eq 4 the literature values of k_{33}, 3×10^3 M^{-1} s^{-1}, for $Ru(NH_3)_6^{3+/2+}$ self-exchange determined at $\mu = 0.1$[28] and k_{23}, 0.01 M^{-1} s^{-1}, for Eu_{aq}^{2+}–$Ru(NH_3)_6^{3+}$ corrected to $\mu = 0.1$ (eq 2) with $\mathring{a} = 7$ Å,[29] along with $k_{12} = 0.055$ M^{-1} s^{-1} ($\mu = 0.1$; Table I) and $K_{13} = 1.4 \times 10^4$ from the relevant formal potentials,[10a,18] yields a value of k_{11} for $Eu(2.2.1)^{3+/2+}$ of 7 M^{-1} s^{-1} (Table II).

The three resulting estimates of k_{11} for $Eu(2.2.1)^{3+/2+}$ and the two estimates of k_{11} for $Eu(2.2.2)^{3+/2+}$ summarized in Table II are in reasonable agreement, particularly in view of the uncertainties in the applicability of eq 3 and 4.[4] The average values are ca. 10 and 4×10^{-2} M^{-1} s^{-1} for $Eu(2.2.1)^{3+/2+}$ and $Eu(2.2.2)^{3+/2+}$, respectively. Quantitative comparisons with the estimates of k_{11} for $Eu_{aq}^{3+/2+}$, also given in Table II, may seem fraught with uncertainties, given the underlying assumptions. However, the presence of estimates of k_{11} for all three Eu(III/II) couples with a common co-reacting couple, $V_{aq}^{3+/2+}$, enables at least relative values of k_{11} to be derived with greater confidence since any systematic breakdowns in eq 4 are liable to largely cancel (vide infra).

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(19) Perlmutter-Hayman, B. *Prog. React. Kinet.* **1971**, *6*, 239.

(20) The value of $\mathring{a}$ was assumed to equal the sum of the reactant radii. These were taken as 5.3 Å for $Eu(2.2.1)^{2+}$ from the sum of the ligand thickness and cavity radius[12] and 3.5 Å for $Co(NH_3)_6^{3+}$ from the crystallographic radii of hexaammines.[21]

(21) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

(22) Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853.

(23) Values of A_n close to 1×10^{11} M^{-1} s^{-1} are usually chosen on the basis of the conventional collision model.[21] Somewhat larger frequency factors (ca. 10^{12} M^{-1} s^{-1}) are derived by using an "encounter preequilibrium model",[7,21] which is probably more appropriate for solution-phase reactants. However, such differences in the values of A_n chosen have a negligible influence on the values of k_{11} obtained from eq 3 for the present reactions that have small or moderate driving forces ($K_{12} \lesssim 10^7$) such that $f_{12} \approx 1$.[4]

(24) Krishnamurthy, K. V.; Wahl, A. C. *J. Am. Chem. Soc.* **1958**, *80*, 5921.

(25) Contrary to common belief, $Co(NH_3)_6^{2+}$ is present to an electrochemically undetectable extent in ammoniacal Co(II) solutions even up to 12 M NH_3,[26] so that meaningful values of neither the formal potential nor the self-exchange rate constant for $Co(NH_3)_6^{3+/2+}$ can be obtained in aqueous media by using conventional means. Therefore, the recent estimate of the latter (Geselowitz, D.; Taube, H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*) should be regarded as only a lower limit.

(26) Barr, S. W. Ph.D. Thesis, Michigan State University, 1981.

(27) Toppen, T. L.; Linck, R. G. *Inorg. Chem.* **1971**, *10*, 2369.

(28) Meyer, T. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 2369.

(29) Endicott, J. F.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1686.

From Table II the required ratio of self-exchange rate constants for the europium cryptates to that for $Eu_{aq}^{3+/2+}$, k_{EuC}/k_{Eu}, are thereby found to be ca. 1×10^7 and 2×10^4 for $Eu(2.2.1)^{3+/2+}$ and $Eu(2.2.2)^{3+/2+}$, respectively.

Discussion

The above results indicate that striking increases in k_{ex}, and hence decreases in the overall electron-transfer barrier[30] to Eu(III/II) exchange, occur upon encapsulation of the metal redox center within (2.2.2) and especially (2.2.1) cryptate cavities. On the basis of eq 1, the observed rate enhancements may arise from increases in the electronic transmission coefficient κ_{el} and/or from decreases in the components of ΔG_{int}^* associated with inner-shell vibrations, ΔG_{is}^*, and outer-shell solvent reorganization, ΔG_{os}^*. From the assumption that $A_n = 1 \times 10^{12}\ M^{-1}\ s^{-1}$,[23] the electron-transfer barrier to Eu(III/II) exchange is deduced to be almost halved by encapsulation into (2.2.1). Indeed, the value of k_{ex} for $Eu(2.2.1)^{3+/2+}$, ca. 10 $M^{-1}\ s^{-1}$, is comparable with those for some redox couples having small inner-shell barriers, for example $Ru(NH_3)_6^{3+/2+}$ for which $k_{ex} = 3 \times 10^3\ M^{-1}\ s^{-1}$ at $\mu = 0.1$.[21,28]

Quantitative calculations of ΔG_{is}^* for $Eu(2.2.1)^{3+/2+}$, $Eu(2.2.2)^{3+/2+}$, and $Eu_{aq}^{3+/2+}$ are precluded due to the lack of information on the changes in inner-shell structure induced by electron transfer. Nevertheless, the observed reactivity differences are roughly consistent with the differences in ΔG_{is}^* anticipated from structural considerations as follows.

The normal (2.2.1) cavity radius, ca. 1.1 Å,[12a] provides a reasonable fit for both Eu^{3+} and Eu^{2+}, which have ionic radii of ca. 1.07 and 1.25 Å, respectively,[31,32] whereas the normal (2.2.2) cavity radius of ca. 1.4 Å[12a,33] is noticeably too large for Eu^{3+}. The ligand conformational changes anticipated for electron transfer are therefore anticipated to be less extensive for the $Eu(2.2.1)^{3+/2+}$ couple, especially since the smaller (2.2.1) ligand should be less flexible than (2.2.2). Indeed, crystallographic structure determinations for various lanthanide(III) (2.2.2) cryptates, including $Eu(2.2.2)^{3+}$,[34] indicate that the cryptate ligand is distorted via decreases in the torsion angles of the polyether strands in order to yield smaller cavity radii that are closer to the size of the encapsulated lanthanide.[34b] Although the crystal structure for $Eu(2.2.2)^{2+}$ is not available, the ligand distortions are expected to be less severe on the basis of the known structures of $Ca(2.2.2)^{2+}$ and $Pb(2.2.2)^{2+}$,[35-37] so that the ligand conformation in $Eu(2.2.2)^{3+}$ should be significantly different from that in $Eu(2.2.2)^{2+}$. Consequently, $Eu(2.2.2)^{3+/2+}$ should exhibit a somewhat larger value of ΔG_{is}^* compared with that for $Eu(2.2.1)^{3+/2+}$, in harmony with the ca. 250-fold larger value of k_{ex} for the latter couple (Table II).

For $Eu_{aq}^{3+/2+}$ self-exchange, ΔG_{is}^* will arise chiefly as a result of the difference, Δa, in the Eu^{3+}–OH_2 and Eu^{2+}–OH_2 bond distances. Calculation of ΔG_{is}^* requires information both on Δa and the average symmetrical stretching frequency of these bonds, ν_{in}, neither of which have been determined directly. However, an approximate estimate of Δa can be obtained from the difference in ionic radii for Eu^{3+} and Eu^{2+} estimated from oxide crystallographic data. It has been shown that such ionic radii parallel closely the metal–oxygen bond distances for a variety of aquo complexes.[38] Inspection of the compilations due to Shannon and Prewitt[31] yields Δa for $Eu^{3+/2+}$ equal to 0.18 Å for a coordination number $n = 8$. A coordination number equal to 8.3 (±0.2) has been determined for $Eu(OH_2)_n^{3+}$ in concentrated aqueous solution from X-ray diffraction data.[39] The coordination number for $Eu(OH_2)_n^{2+}$ is unknown; it may be slightly larger than for $Eu(OH_2)_n^{3+}$ in view of the larger radius for Eu^{2+}. With $n = 8$ for Eu^{3+} and $n = 9$ for Eu^{2+}, it is deduced[31b] that $\Delta a = 0.23$ Å. The value $\Delta a \approx 0.2$ Å is therefore considered to be a reasonable estimate for $Eu_{aq}^{3+/2+}$.[40]

Insufficient vibrational spectroscopic data for metal aquo complexes exist to enable a quantitative estimate of ν_{in} for $Eu_{aq}^{3+/2+}$ to be made. Nevertheless, recent studies for tripositive and dipositive aquo species[41] have shown that M–OH_2 stretching frequencies are sensitive primarily to the metal charge rather than its size and the bonding type, although the frequencies tend to decrease with increasing metal ion size. In view of the available data[41] an estimate of ν_{in} for $Eu_{aq}^{3+/2+}$ of at least ca. 300 cm^{-1} seems reasonable.[42] Inserting these values of Δa, ν_{in}, and $n = 8$ into the usual expression[7] $\Delta G_{is}^* = n\pi^2 c^2 m \nu_{in}^2 (\Delta a)^2$, where c is the velocity of light and m is the ligand mass, yields $\Delta G_{is}^* \approx 12$ kcal mol^{-1}. In addition, ΔG_{is}^* for $Eu_{aq}^{3+/2+}$ may well contain a contribution arising from the likely increase in the number of coordinated water molecules when Eu_{aq}^{3+} is reduced to Eu_{aq}^{2+}.[9] This may amount to ca. 3–4 kcal mol^{-1},[43] yielding a total value of ΔG_{is}^* of ca. 15–16 kcal mol^{-1}. Assuming that $A_n = 1 \times 10^{12}\ M^{-1}\ s^{-1}$ and noting that w_r is calculated to be about 2.3 kcal mol^{-1} at $\mu = 0.1$,[44] taking k_{ex} for $Eu_{aq}^{3+/2+}$ to be $1 \times 10^{-5}\ M^{-1}\ s^{-1}$ ($\mu = 0.1$; Table II) yields from eq 1 a value of ΔG_{int}^* equal to 21 kcal mol^{-1} if κ_{el} is set equal to unity. From the usual dielectric continuum expression,[45] the outer-shell barrier ΔG_{os}^* is calculated to be 5.5 kcal mol^{-1} with the reactant radius taken as 4 Å. The difference between these values of ΔG_{int}^* and ΔG_{os}^* yields an inner-shell barrier ΔG_{is}^* equal to 15.5 kcal mol^{-1}, in reasonable agreement with the above estimate of ΔG_{is}^* based on structural considerations.

It therefore does not appear to be necessary to invoke the presence of very strongly nonadiabatic pathways (such as the assertion that $\kappa_{el} \lesssim 10^{-10}$ in ref 9) in order to account for the small values of k_{ex} observed for $Eu_{aq}^{3+/2+}$ self-exchange. Surprisingly, the likelihood that $Eu_{aq}^{3+/2+}$ reactions involve a substantial inner-shell barrier seems to have gone largely unnoticed. The presence of a large inner-shell barrier also

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(30) The term "electron-transfer barrier" used here includes the possible "electronic" component associated with nonadiabatic electron transfer (i.e. $\kappa_{el} << 1$) as well as the nuclear component associated with inner- and outer-shell structural rearrangements that comprise the intrinsic barrier ΔG_{int}^* (eq 1).

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(32) Both these estimates of r_c refer to a metal coordination number of 8.[31]

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(37) Pb^{2+} and Ca^{2+} are chosen here since they have ionic radii that are comparable to that for Eu^{2+}.[31]

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(40) On the basis of the constancy of the difference in the oxide radii and the M–OH_2 bond distances to within ca. 0.03 Å for 14 divalent and trivalent cations,[38] this estimate of Δa is considered to be reliable to roughly the same uncertainty.

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(42) Further support for this estimate of ν_{in} for $Eu_{aq}^{3+/2+}$ is obtained from the Eu^{3+}–O stretching frequency of ca. 350 cm^{-1} determined for $Eu(OH)_3$: Mullica, D. F.; Milligan, W. O.; Beall, G. W. *J. Inorg. Nucl. Chem.* **1979**, *41*, 525.

(43) The estimated magnitude of this contribution given in ref 9 should be doubled since a *pair* of europium ions are required to be activated for $Eu_{aq}^{3+/2+}$ self-exchange.

(44) Based on the Debye–Hückel model;[21] w_r may also contain another unfavorable component arising from solvent ordering in the multicharged encounter complex.[4]

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accounts for the enormous increase in k_{ex}, ca. (1×10^7)- and (3×10^4)-fold, arising from encapsulation into the (2.2.1) and (2.2.2) cryptates, respectively. While one cannot expect the cryptates to be entirely inflexible when bound to Eu(III) or Eu(II), they clearly present a much more rigid ligand environment than provided by the aquo ligands in $Eu_{aq}^{3+/2+}$, thereby yielding smaller ligand reorganization barriers. In addition, these rate enhancements may arise in part from a diminution of ΔG_{os}^*. Indeed, moderate decreases (ca. 2 kcal mol^{-1}) in ΔG_{os}^* are anticipated on the basis of the dielectric continuum model[45] from the increase in the effective ionic size attending cryptate formation.

One argument that has been made for nonadiabaticity of $Eu_{aq}^{3+/2+}$ reactions is that the value of k_{ex} for $Fe_{aq}^{3+/2+}$ is ca. 10^5-fold larger than that for $Eu_{aq}^{3+/2+}$, even though the inner- and outer-shell barriers for the former couple have been anticipated to be smaller on account of its larger size.[8] However, this argument becomes less persuasive upon examination of the relevant ionic radii. A value of Δa for $Fe^{3+/2+}$ of 0.14 Å is extracted from ionic radii data,[31] which is in agreement with that for $Fe_{aq}^{3+/2+}$ determined from both X-ray crystallographic[46] and solution EXAFS[7] data but is substantially smaller than the above estimate of Δa for $Eu^{3+/2+}$ ($\sim$0.2 Å). In addition, values of k_{ex} for $Fe_{aq}^{3+/2+}$ that are much closer to those for $Eu_{aq}^{3+/2+}$, ca. 10^{-4} M^{-1} s^{-1} ($\mu = 0.1$), are obtained from the kinetics of a variety of cross-reactions that are known to follow outer-sphere pathways.[47]

If the nonadiabaticity provided the major contribution to the electron-transfer barrier to $Eu_{aq}^{3+/2+}$ self-exchange, this effect would lead instead to smaller values of k_{ex} for Eu(2.2.1)$^{3+/2+}$ and Eu(2.2.2)$^{3+/2+}$ than for $Eu_{aq}^{3+/2+}$. Both (2.2.2) and (2.2.1) cryptates include gaps between the polyether strands that may enable coordination of water molecules to the central metal ion.[34,48] However, it seems very unlikely that the aquo or ammine ligands of the coreactants studied here, V_{aq}^{2+}, Eu_{aq}^{2+}, and $Co(NH_3)_6^{3+}$, would be able to displace such coordinated water and approach the encapsulated europium cation more closely than to the corresponding aquo cation. Consequently, κ_{el} is liable to be no larger for reactions involving Eu(III/II) cryptate couples than for those involving $Eu_{aq}^{3+/2+}$.

Nevertheless, the presence of nonadiabatic pathways for reactions involving Eu(III/II) redox couples are certainly not ruled out by the present results. Recent ab initio calculations indicate that outer-sphere pathways for $Fe_{aq}^{3+/2+}$ self-exchange can be mildly nonadiabatic ($\kappa_{el} \sim 10^{-1}$) even at internuclear separations within the usual ligand contact distance of 6.9 Å.[49] Given that the radial extension of the 4f orbitals involved in Eu(III/II) electron transfer is smaller than for 3d orbitals,[50] some degree of nonadiabaticity for these processes seems likely.[51] Even though eq 3 was originally derived from an adiabatic model,[22] it may still apply to nonadiabatic processes if κ_{el} for the cross-reaction equals the geometric mean of those for the component self-exchange reaction, providing κ_{el} is not too small.[3,52] To a first approximation, such a relation is not unexpected.[52] Therefore, the approximate consistency of the values of k_{ex} for the Eu(III/II) couples obtained from cross-reactions involving both one and two europium ions (Table II) is not inconsistent with smaller values of κ_{el} for the latter processes. The relative irreproducibility of the kinetics of the Eu(2.2.1)$^{3+}$–Eu_{aq}^{2+} and Eu(2.2.2)$^{3+}$–Eu_{aq}^{2+} reactions may also be rationalized on this basis.[8,17]

The inverse acid-dependent pathways observed for these two processes (Table I) may also be related to reaction nonadiabaticity. Such pathways are often observed between reactants such as aquo complexes containing replaceable protons and are usually attributed to hydroxo-bridged transition states.[53] Such a transition-state geometry would be expected to aid the electronic coupling between the redox center and could be especially felicitous if the competing acid-independent (presumably outer-sphere) route is nonadiabatic. However, although complexation between Eu(2.2.1)$^{3+}$ and OH^- can be detected,[10a] the pK_a for Eu(2.2.1)$^{3+}$ (8.5) is much larger than for other trivalent reactants, e.g. V_{aq}^{3+} (ca. 3), that exhibit comparable acid-dependent terms in the rate law.[24] It is therefore speculated that the presence of detectable acid-dependent pathways for the Eu(2.2.1)$^{3+}$–Eu_{aq}^{3+} and Eu(2.2.2)$^{3+}$–Eu_{aq}^{2+} reactions may result from the increase in κ_{el} afforded by hydroxo "bridging". The absence of detectable catalysis from added chloride ions is consistent with the lack of significant complexation between Cl^- and the europium cryptates under these conditions.[10a]

As noted above, Balzani et al.[9] have recently presented detailed arguments claiming that the large apparent intrinsic barrier to $Eu_{aq}^{3+/2+}$ self-exchange is instead due chiefly to nonadiabaticity. Their conclusion was derived primarily from an examination of the driving force dependence of the rate constants of cross-reactions involving Eu_{aq}^{2+} oxidations. The driving force dependence was noted to be substantially milder than that predicted by conventional theoretical models and was attributed to small values of κ_{el} ($\lesssim 10^{-6}$) for the cross-reactions, yielding $\kappa_{el} < 10^{-10}$ for $Eu_{aq}^{3+/2+}$ self-exchange.[9] From an analysis of the driving force dependence of rate constants for Eu^{3+} reduction by polypyridine complexes, Sutin has recently deduced that $\kappa_{el} \gtrsim 10^{-6}$ for $Eu^{3+/2+}$ self-exchange.[52] Such analyses assume that any discrepancies between the observed driving force dependence and the theoretical predictions are due entirely to nonadiabaticity. However, other complicating factors include anharmonicity and non-Coulombic work terms.[4,54] We have recently demonstrated that deviations between theory and experiment very similar to those seen for Eu_{aq}^{2+} oxidation also occur for analogous reactions involving Cr_{aq}^{2+}, V_{aq}^{2+}, and Ru_{aq}^{2+} oxidation and for the electrochemical oxidation of Cr_{aq}^{2+}, V_{aq}^{2+}, and Eu_{aq}^{2+} as a function of electrochemical driving force.[54] Moreover, neither the electrochemical[55] nor homogeneous reduction kinetics[9] of Eu_{aq}^{3+} exhibit the marked deviations from the theoretical driving force dependence that would be expected if the deviations for Eu_{aq}^{2+} oxidation were due to strongly nonadiabatic pathways.[56] Therefore, the driving force analyses do not appear to provide any conclusive evidence that reactions involving $Eu_{aq}^{3+/2+}$ are especially nonadiabatic.

Examination of activation parameters for reactions involving $Eu_{aq}^{3+/2+}$ also fails to reveal evidence for the abnormally negative activation entropies that would be expected for highly nonadiabatic pathways.[4] One approach is to evaluate the entropy of activation for $Eu_{aq}^{3+/2+}$ self-exchange, ΔS_{11}^*, from

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(56) Thus, strongly nonadiabatic pathways (i.e. $\kappa_{el} << 1$) would be expected to yield a smaller dependence of the rate constant upon the driving force than expected under highly exoergic conditions. Functionally indistinguishable behavior is expected for reactions involving formation of a thermodynamically unstable precursor intermediate, i.e. with an unfavorable work term.[4] The same rate-driving force dependence is predicted on this basis for both reductive and oxidative conditions.

a knowledge of that for a cross-reaction, $\Delta S_{12}^{\ddagger}$, with a coreactant having a known activation entropy for self-exchange, $\Delta S_{22}^{\ddagger}$, together with the entropic driving force, ΔS_{12}°. This procedure is most straightforward for cross-reactions having small driving forces (e.g. $K_{12} \lesssim 10^4$) so that $f_{12} \approx 1$ (eq 3), whereupon these quantities are related simply by[4]

$$\Delta S_{12}^{\ddagger} = 0.5(\Delta S_{11}^{\ddagger} + \Delta S_{22}^{\ddagger}) + 0.5\Delta S_{12}^{\circ} \qquad (5)$$

Although experimental activation parameters for such reactions involving $Eu_{aq}^{3+/2+}$ are sparse, one example is Eu_{aq}^{2+} oxidation by V_{aq}^{3+}. Inserting the experimental values $\Delta S_{12}^{\ddagger} = -30$ cal deg^{-1} mol^{-1},[5,57] $\Delta S_{22}^{\ddagger}$($V_{aq}^{3+/2+}$ self-exchange) = -25 cal deg^{-1} mol^{-1},[24,57] and $\Delta S_{12}^{\circ} = -11$ cal deg^{-1} mol^{-1} [58] into eq 5 yields a value of $\Delta S_{11}^{\ddagger}$ = $Eu_{aq}^{3+/2+}$ self-exchange of -25.5 cal deg^{-1} mol^{-1}. Although such negative activation entropies are consistent with nonadiabatic pathways, this value of $\Delta S_{11}^{\ddagger}$ for $Eu_{aq}^{3+/2+}$ is similar not only to that for $V_{aq}^{3+/2+}$ but also to those for a number of other aquo and amine couples for which strongly nonadiabatic pathways are unlikely.[4] The observed activation entropies are more likely to be a reflection of the solvent ordering attending the formation of the highly charged encounter complex.[4,8]

The electrochemical reactivities of Eu(III/II) are also in harmony with the above conclusions. Thus, the $Eu_{aq}^{3+/2+}$ couple exhibits a small rate constant for electrochemical exchange at mercury electrodes, $k^{e}_{ex} = 8 \times 10^{-5}$ cm s^{-1} (corrected for work terms), which is consistent with the rate constants for homogeneous $Eu_{aq}^{3+/2+}$ reactions on the basis of the Marcus model.[6,47] In addition, the electrochemical reactivity of $Eu_{aq}^{3+/2+}$ compared to those for other aquo couples is quantitatively consistent with the reactivities of these couples in homogeneous solution.[47] This consistency also extends to activation parameters.[6,54] Large increases in k^{e}_{ex} for Eu(III/II) also occur upon cryptate formation: values of k^{e}_{ex} of ca. 1 cm s^{-1} have been determined for both Eu(2.2.1)$^{3+/2+}$ and Eu(2.2.2)$^{3+/2+}$.[59]

The kinetic effects of encapsulating Eu(III/II) within cryptate cavities has a similarity with the ca. 10^5-fold larger self-exchange rate constant for Co(sep)$^{3+/2+}$ (sep = sepulchrate[60]) compared with that for $Co(en)_3^{3+/2+}$.[60] The sepulchrate differs structurally from the tris(ethylenediamine) complex in that the ethylenediamine ligands have been "capped" to form a three-dimensional cage, similar to the cryptates.[60] Although the origins of the reactivity differences between Co(sep)$^{3+/2+}$ and $Co(en)_3^{3+/2+}$ were initially obscured by apparently similar Co–N bond length differences, Δa, in the two couples,[60a] it now appears that the enhanced reactivity of the former couple is chiefly due to a smaller value of Δa and hence ΔG_{is}^{*}.[7]

Taken together, the available evidence therefore suggests that the low reactivities of $Eu_{aq}^{3+/2+}$ observed in a variety of homogeneous and also heterogeneous environments are predominantly due to large Franck–Condon barriers associated with an increase in the europium–oxygen bond distance and possibly also to an increase in the number of coordinated aquo ligands required to form Eu_{aq}^{2+} from Eu_{aq}^{3+}. It is clearly desirable to obtain further information on the structural and vibrational properties of lanthanide complexes. Especially in conjunction with theoretical estimates of κ_{el}, such information should allow the factors responsible for the reactivities of $Eu_{aq}^{3+/2+}$ and other f-electron redox couples to be quantitatively assessed.

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Registry No. V, 7440-62-2; Eu, 7440-53-1; $Co(NH_3)_6^{3+}$, 14695-95-5.

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(57) Experimental activation entropies $\Delta S^{\ddagger}$ are conventionally evaluated by assuming that the preexponential factor equals kT/h.[21] Strictly speaking, the actual preexponential factor in eq 1, $\kappa_{el}A_n$, should be used instead so that the derived activation entropy refers to the entropy of activation within the encounter complex, ΔS^{*}. Values of A_n close to 1×10^{11} M^{-1} s^{-1} have been conventionally employed on the basis of a simple collisional model;[21] if κ_{el} is taken as unity, this yields $\Delta S^{*} \approx \Delta S^{\ddagger}$ + 10 cal deg^{-1} mol^{-1}.[4] However, using a model for A_n based on activation within an encounter complex typically yields[7,21] $A_n \sim 2 \times 10^{12}$ M^{-1} s^{-1}, leading to $\Delta S^{*} \approx \Delta S^{\ddagger}$ + 2 cal deg^{-1} mol^{-1}.[4]

(58) ΔS_{12}° obtained from the difference in reaction entropies ΔS_{rc}° for $V_{aq}^{3+/2+}$ and $Eu_{aq}^{3+/2+}$ given in ref 18.

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Synthesis, Characterization, and Properties of Manganese Complexes of Macrobicyclic Lacunar Ligands and Their Reactions with Dioxygen Species

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Manganese(II) and -(III) complexes of macrobicyclic ligand systems containing a persistent void in the vicinity of one axial ligation site have been prepared. Synthesis from the appropriate ligand salt is only satisfactorily achieved by using manganese(III) reagents while the manganese(II) complexes are generated by electrochemical reduction of those complexes. Both the +2 and +3 oxidation states are high spin and 5-coordinate, displaying typical magnetic susceptibilities. The manganese(II) complexes react irreversibly with dioxygen to generate the corresponding manganese(III) complex and reduced dioxygen. Depending on solvent, this reduced dioxygen will deprotonate the ligand itself. The manganese(III) complexes display efficient but slow catalase activity while showing no corresponding oxygenation activity toward phenolic substrates.

Introduction

The interaction of manganese complexes with many of the species, in various oxidation states, derived from dioxygen has been extensively investigated and is of both biological[1,2] and industrial[3] importance. For example, with dioxygen itself, reversible binding has been claimed for a number of manganese(II) complexes, with ligands ranging from porphyrins[4] and

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