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Photoinduced Electron-Transfer Reactions of Poly(pyridine)ruthenium(II) Complexes with Europium(III/II) Cryptates

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Rate constants for electron-transfer reactions between poly(pyridine)ruthenium(II) ($\mathrm{RuL_3}^{2+}$) excited states and the europium cryptates $[\mathrm{Eu}\subset 2.2.1]^{3+}$ and $[\mathrm{Eu}\subset 2.2.1]^{2+}$ have been measured in aqueous solution by luminescence quenching techniques. The rate constants for a few electron-transfer back-reactions between the photogenerated $\mathrm{RuL_3}^{3+}$ and $[\mathrm{Eu}\subset 2.2.1]^{2+}$ or $\mathrm{RuL_3}^{+}$ and $[\mathrm{Eu}\subset 2.2.1]^{3+}$ species have also been measured by flash photolysis experiments. The results obtained have been elaborated and discussed on the basis of current electron-transfer theories. Comparison of the results obtained with those previously available for the $\mathrm{Eu_{aq}}^{3+}$ and $\mathrm{Eu_{aq}}^{2+}$ ions shows that cryptation decreases the intrinsic barrier and/or increases the adiabaticity coefficient of the electron-transfer reaction. A plot of the rate constants vs. the free energy changes of the electron-transfer processes shows that the data concerning $[\mathrm{Eu}\subset 2.2.1]^{3+}$ reduction do not correlate with those concerning $[\mathrm{Eu}\subset 2.2.1]^{2+}$ oxidation. Possible reasons for this asymmetric behavior include (i) different shapes of the potential energy wells for $[\mathrm{Eu}\subset 2.2.1]^{3+}$ and $[\mathrm{Eu}\subset 2.2.1]^{2+}$, (ii) different work terms for the formation of the precursor complex, and (iii) different distances of closest approach of $[\mathrm{Eu}\subset 2.2.1]^{3+}$ and $[\mathrm{Eu}\subset 2.2.1]^{2+}$ with the hydrophobic $\mathrm{RuL_3}^{n+}$ reaction partners.

Introduction

Photoinduced electron-transfer reactions are currently the object of extensive studies.[2] The reasons for this widespread interest include the use of these reactions in energy conversion processes[3] and the possibility to investigate fundamental but still unclear aspects of electron-transfer theories.[4-7]

The homogeneous outer-sphere electron-transfer reactions of the europium(III/II) redox couple have long been known to exhibit some peculiar kinetic features,[4,8-11] which have often been interpreted as consequences of a nonadiabatic behavior. Most of the available data on this couple concern the aquo ions, which are not free of complications even in the case of other metal ions.[10,12] Gansow et al.[13] have shown that Eu^{3+} and Eu^{2+} can be encapsulated into the 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane and 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane cryptands (Lehn's[14] 2.2.2 and 2.2.1 cryptands) to yield fairly stable complexes that exhibit a reversible electrochemical behavior. Luminescence investigations carried out in our laboratories[15] have shown that encapsulation of Eu^{3+} in the 2.2.1 cryptand cage does not completely shield the metal ion from interaction with solvent water, since three water molecules are still coordinated to Eu^{3+} through the cryptand holes. From a study of the reduction kinetics of $[\mathrm{Eu}\subset 2.2.1]^{3+}$ and $[\mathrm{Eu}\subset 2.2.2]^{3+}$ by the aquo ions $\mathrm{V_{aq}}^{2+}$ and $\mathrm{Eu_{aq}}^{2+}$ and the oxidation kinetics of $[\mathrm{Eu}\subset 2.2.1]^{2+}$ by $\mathrm{Co(NH_3)_6}^{3+}$, Weaver and co-workers[5] have recently suggested that both the cryptate and the aquo $\mathrm{Eu}^{3+/2+}$ couples probably exhibit an adiabatic behavior.

In an attempt to elucidate the factors influencing the kinetic behavior of the Eu(III/II) couple, we have measured the rate constants of the electron-transfer reactions of poly(pyridine)ruthenium(II) ($\mathrm{RuL_3}^{2+}$) excited states with $[\mathrm{Eu}\subset 2.2.1]^{3+}$ and $[\mathrm{Eu}\subset 2.2.1]^{2+}$

$$\mathrm{RuL_3}^{2+} + h\nu \rightarrow {}^*\mathrm{RuL_3}^{2+} \tag{1}$$

$${}^*\mathrm{RuL_3}^{2+} + [\mathrm{Eu}\subset 2.2.1]^{3+} \rightarrow \mathrm{RuL_3}^{3+} + [\mathrm{Eu}\subset 2.2.1]^{2+} \tag{2}$$

$${}^*\mathrm{RuL_3}^{2+} + [\mathrm{Eu}\subset 2.2.1]^{2+} \rightarrow \mathrm{RuL_3}^{+} + [\mathrm{Eu}\subset 2.2.1]^{3+} \tag{3}$$

as well as the rate constants of some electron-transfer back-reactions between the photogenerated $\mathrm{RuL_3}^{3+}$ and $[\mathrm{Eu}\subset 2.2.1]^{2+}$ or $\mathrm{RuL_3}^{+}$ and $[\mathrm{Eu}\subset 2.2.1]^{3+}$ species

$$\mathrm{RuL_3}^{3+} + [\mathrm{Eu}\subset 2.2.1]^{2+} \rightarrow \mathrm{RuL_3}^{2+} + [\mathrm{Eu}\subset 2.2.1]^{3+} \tag{4}$$

$$\mathrm{RuL_3}^{+} + [\mathrm{Eu}\subset 2.2.1]^{3+} \rightarrow \mathrm{RuL_3}^{2+} + [\mathrm{Eu}\subset 2.2.1]^{2+} \tag{5}$$

The results obtained have been elaborated and discussed in terms of the current electron-transfer theories.

Experimental Section

Materials. The 2.2.1 cryptand was obtained from Merck and purified from hexane just before use. The $[\mathrm{Eu}\subset 2.2.1]^{3+}$ cryptate was prepared by slight modification of the procedure indicated by Gansow et al.[13] The $[\mathrm{Eu}\subset 2.2.1]^{2+}$ cryptate was prepared by adding a stoichiometric amount of the ligand to a Eu^{2+} solution.[13,16] The $\mathrm{RuL_3}^{2+}$ complexes (L = 2,2′-bipyridine, 4,4′-dichloro-2,2′-bipyridine, 4-nitro-2,2′-bipyridine, 3,3′-dimethyl-2,2′-bipyridine, 5,6-dimethylphenanthroline, 3,4,7,8-tetramethylphenanthroline, 6,7-dihydro-5,8-dimethyldibenzo[*b,j*][1,10]-phenanthroline (abbreviated as DMCH), isobiquinoline, biquinoline) were available from previous studies.[17,18]

Quenching Rate Constants. Quenching rate constants were determined from Stern–Volmer plots of emission lifetime data. The measurements were performed by using a modified Applied Photophysics single-photon time-correlation apparatus as described previously.[16] The samples were excited at 430–450 nm by a thyratron-gated flash lamp filled with deuterium. All the experiments were carried out at room temperature (~295 K) in dearated aqueous solutions containing 1 M KCl.

Flash Photolysis. The experiments were performed with a frequency-doubled JK neodymium YAG System 2000 laser (25 ns, 530~nm

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Table I. Experimental Rate Constants[a]

Eu complex	redox partner	$\Delta G°$,[b] eV	k_{exptl}, $M^{-1}\,s^{-1}$
$[\mathrm{Eu}\subset 2.2.1]^{3+}$	$^*Ru(bpy)_2(4,4'\text{-}Cl_2\text{-}bpy)^{2+}$	−0.56	5.6×10^6
	$^*Ru(bpy)_2(4\text{-}NO_2\text{-}bpy)^{2+}$	−0.57	2.1×10^7
	$^*Ru(bpy)_2((CH_3)_2\text{-}bpy)^{2+}$	−0.68	3.3×10^7
	$^*Ru(bpy)_3^{2+}$	−0.69	4.9×10^7
	$^*Ru(bpy)((CH_3)_2\text{-}bpy)_2^{2+}$	−0.74	7.1×10^7
	$^*Ru((CH_3)_2\text{-}bpy)_3^{2+}$	−0.75	5.6×10^7
	$^*Ru(5,6\text{-}(CH_3)_2\text{-}phen)_3^{2+}$	−0.75	6.0×10^7
	$^*Ru(3,4,7,8\text{-}(CH_3)_4\text{-}phen)_3^{2+}$	−0.95	3.4×10^7
	$Ru(bpy)_2(DMCH)^+$	−0.75	5.9×10^7
	$Ru(bpy)_3^+$	−1.10	7.0×10^8
$[\mathrm{Eu}\subset 2.2.1]^{2+}$	$^*Ru((CH_3)_2bpy)_3^{2+}$	−0.87	1.3×10^9
	$^*Ru(bpy)(isobiq)_2^{2+}$	−0.94	1.3×10^9
	$^*Ru(bpy)_2(DMCH)^{2+}$	−0.97	1.0×10^9
	$^*Ru(bpy)_2(isobiq)^{2+}$	−0.97	1.2×10^9
	$^*Ru(bpy)_3^{2+}$	−1.03	1.3×10^9
	$^*Ru(bpy)(biq)_2^{2+}$	−1.12	1.7×10^9
	$^*Ru(bpy)_2(4\text{-}NO_2\text{-}bpy)^{2+}$	−1.81	2.3×10^9
	$Ru(bpy)_3^{3+}$	−1.51	1.3×10^9

[a] Aqueous solutions, 1 M KCl, ~295 K. [b] Calculated from the potential of the $[\mathrm{Eu}\subset 2.2.1]^{3+/2+}$ couple[13] and the potentials of the $RuL_3^{3+}/{}^*RuL_3^{2+}$, $RuL_3^{3+/2+}$, ${}^*RuL_3^{2+}/RuL_3^+$, and $RuL_3^{2+/+}$ couples[17,18] (see Appendix).

pulse). The light from the laser was filtered to remove the original 1.06 μm component and then focused to give an elliptical beam about 0.9-cm wide and 0.2-cm high at the front surface of the cell. The absorption was monitored at right angles to the excitation beam on the front volume of the irradiated solution (0.2-cm depth). The laser excitation intensity at 530 nm was about 10^2 einstein $cm^{-2}\,s^{-1}$. Disappearance of RuL_3^+ and recovery of RuL_3^{2+} were monitored at 500[19] and 454 nm, respectively, by a Hamamatsu R 955 photomultiplier in combination with a Bausch & Lomb high-intensity monochromator and narrow band interference filters. Transient signals were acquired and reduced by using a Tektronix R7912 transient digitizer equipped with a Tektronix 7A26 vertical amplifier and interfaced to a Z80-based Cromemco microcomputer. All the experiments were performed at room temperature (~295 K) in aqueous solutions and 1 M KCl ionic strength. The solutions were freshly prepared and degassed before each experiment. The rate constants for oxidation of RuL_3^+ by $[\mathrm{Eu}\subset 2.2.1]^{3+}$ and reduction of RuL_3^{3+} by $[\mathrm{Eu}\subset 2.2.1]^{2+}$ were determined under pseudo-first-order conditions in the presence of excess cryptate. The quantum yield of formation of $Ru(bpy)_3^+$ was obtained by a direct comparison, in the same absorption and quenching conditions, of the transient spectral changes at 500 nm[19] produced in the reaction of $Ru(bpy)_3^{2+}$ with $[\mathrm{Eu}\subset 2.2.1]^{2+}$ with those produced in the reaction of $Ru(bpy)_3^{2+}$ with Eu_{aq}^{2+}, for which a unitary yield is given for $Ru(bpy)_3^+$ production.[19]

Kinetic Analysis. The kinetic parameters (vide infra) were obtained from a best-fit fitting procedure on the free energy dependence of the corrected rate constants by using a Simplex algorithm.[20]

Results

Quenching Rate Constants. The quenching of the emission lifetime of the excited states of the poly(pyridine)ruthenium(II) complexes by the Eu cryptates gave good linear relationships (intercept of unity) when $\tau°/\tau$ was plotted against quencher concentration (RuL_3^{2+}, (0.1–1) × 10^{-4} M; $[\mathrm{Eu}\subset 2.2.1]^{3+}$, (0.1–1) × 10^{-1} M; $[\mathrm{Eu}\subset 2.2.1]^{2+}$, (0.1–1) × 10^{-2} M). The slope of such a plot is the so-called Stern–Volmer constant, k_{SV}, which is related to the bimolecular quenching constant by the equation $k_q = k_{SV}/\tau°$, where $\tau°$ is the excited-state lifetime in the absence of quencher. The values of k_q so obtained are reported in Table I as k_{exptl}, together with the values of the driving force for the electron-transfer-quenching reaction, $\Delta G°$ (see Discussion). The error on k_q is estimated to be ±10%.

Flash Photolysis. In a few selected cases flash photolysis experiments were performed. Flash photolysis of $Ru(bpy)_3^{2+}$ solutions containing $[\mathrm{Eu}\subset 2.2.1]^{3+}$ caused a quenching of the ${}^*Ru(bpy)_3^{2+}$ emission and a decrease of $Ru(bpy)_3^{2+}$ absorption in the 450-nm region in the submicrosecond time scale. As shown in the Discussion, the quenching reaction occurs via an electron-transfer mechanism (eq 2) which leads to $Ru(bpy)_3^{3+}$ and $[\mathrm{Eu}\subset 2.2.1]^{2+}$. Since these products do not exhibit sufficiently intense absorption bands, their electron-transfer back-reaction (eq 4) was followed from the recovery of the 450-nm $Ru(bpy)_3^{2+}$ absorption in the millisecond time scale. The second-order rate constants determined for the latter process, k_b, are shown in Table I as k_{exptl}, together with the values of the driving force for the reaction. For solutions containing $Ru(bpy)_3^{2+}$ or $Ru(bpy)_2(DMCH)^{2+}$ and $[\mathrm{Eu}\subset 2.2.1]^{2+}$, flash photolysis experiments showed that the quenching of the luminescence emission and the bleaching at 450 nm were accompanied by an increase in absorption at 500 nm, as expected for the formation of $Ru(bpy)_3^+$ or $Ru(bpy)_2(DMCH)^+$ (eq 3). On the millisecond time scale, the 500-nm absorption decreased and the 450-nm absorption was regenerated as expected from eq 5. The second-order rate constants and the free energy changes of the corresponding reactions are also shown in Table I. The error on the second-order rate constants measured by flash photolysis is estimated to be ±50%. For the reaction of ${}^*Ru(bpy)_3^{2+}$ with $[\mathrm{Eu}\subset 2.2.1]^{2+}$ the quantum yield of formation of $Ru(bpy)_3^+$ was measured to be 0.1 ± 0.05. Analogous experiments with the other Ru(II) complexes could not be performed because the extinction coefficient of the reduced form is not known.

Discussion

Quenching Mechanism. In fluid solution the quenching of an excited state may be take place by several distinct mechanisms,[17,21] the most important of which are (i) electronic energy transfer, (ii) electron transfer, (iii) a chemical reaction involving atom transfer, (iv) exciplex formation, (v) spin-catalyzed deactivation, and (vi) the external heavy-atom effect. In the specific case of the quenching of ${}^*RuL_3^{2+}$ by $[\mathrm{Eu}\subset 2.2.1]^{3+}$ or $[\mathrm{Eu}\subset 2.2.1]^{2+}$, spin-catalyzed deactivation and the external heavy-atom effect can readily be excluded because of the strong spin–orbit coupling already present in the Ru complex. Atom transfer can be excluded because the ligands that constitute the coordination sphere of the species involved are quite inert. Exciplex formation can be excluded because of the strong repulsion between complexes having a charge of the same sign and because of the use of a polar solvent. The spectroscopic energy of the luminescence excited state of the RuL_3^{2+} complexes is 17 400 cm^{-1}.[17,18] Energy transfer, therefore, is strongly endoergonic for $[\mathrm{Eu}\subset 2.2.1]^{2+}$, whose lowest excited state lies above 22 000 cm^{-1},[16] and at best very slightly endoergonic for $[\mathrm{Eu}\subset 2.2.1]^{3+}$, whose lowest excited state lies at 17 000 cm^{-1}.[15] Since energy transfer to rare-earth metal compounds is slow even when it is strongly exoergonic (presumably because of nonadiabatic reasons),[22] we must conclude that our results cannot be explained by an energy-transfer quenching mechanism. We thus remain with electron transfer as the only possible quenching mechanism for our systems (eq 3 and 4) in agreement with the conclusion drawn for the quenching by Eu^{3+}_{aq}[23] and Eu^{2+}_{aq}.[11] The occurrence of an electron-transfer quenching is also in agreement with theoretical expectations (i.e., with the strong exoergonicity of the process, see Table I and Figure 2), as well as with the transient spectral changes observed in flash photolysis experiments. The lower than unity quantum yield of formation of $Ru(bpy)_3^+$ (0.1 ± 0.05) is in fair agreement with the value expected (0.15–0.30) on the basis of the fast electron-transfer back-reaction.

Kinetic Treatment. Having established that the quenching reactions (eq 2 and 3) take place by an electron-transfer mechanism, we can now discuss our data on the basis of current electron-transfer theories.[2,24] A useful approach is to correlate the bimolecular rate constants to the free energy changes of the reactions, in order to elucidate the role played by nuclear and

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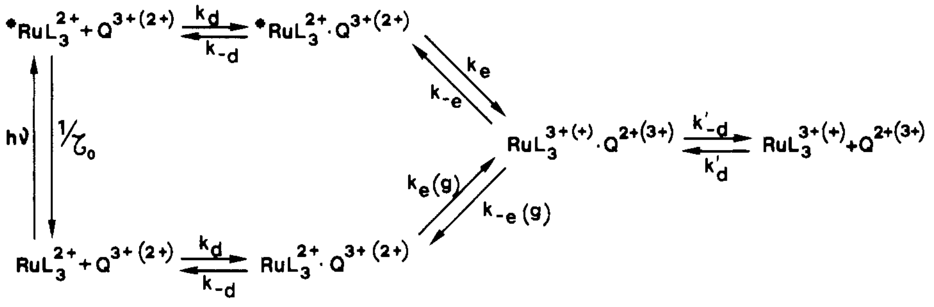

Figure 1. Kinetic scheme for the photoinduced electron-transfer reactions.

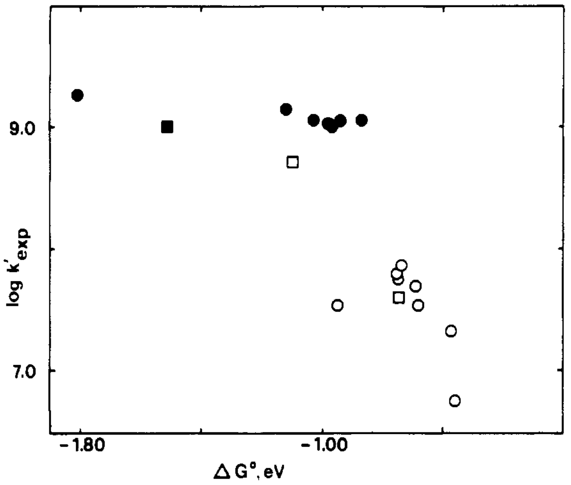

Figure 2. Diagram showing the variation of log k'_{exptl} as a function of ΔG° (Table I) for reactions 2 (○), 3 (●), 4 (■), and 5 (□).

electronic factors.[2a] The photoinduced electron-transfer processes occurring in our systems may be represented by means of the detailed kinetic scheme shown in Figure 1.[2a,25] In this scheme, RuL_3 stands for the poly(pyridine)ruthenium complexes and Q for the europium cryptates. The bimolecular quenching constant k_q can be expressed by eq 6 and the rate constant for the electron-transfer back-reaction, k_b, by eq 7 which reduce to eq 8 and

$$k_q = \frac{k_d}{1 + (k_{-d}/k_e) + (k_{-d}k_{-e}/k_{-e}(g)k_e)} \qquad (6)$$

$$k_b = \frac{k'_d}{1 + (k'_{-d}/k_{-e}(g)) + (k'_{-d}k_e(g)/k_{-d}k_{-e}(g))} \qquad (7)$$

9 when, as it happens in our case, $k_e \gg k_{-e}$, $k_e \ll k_{-d}$ and $k_{-e}(g)$

$$k_q = \frac{k_d}{k_{-d}}k_e \qquad (8)$$

$$k_b = \frac{k'_d}{k'_{-d}}k_{-e}(g) \qquad (9)$$

$\gg k_e(g)$, $k_{-e}(g) \ll k'_{-d}$. In eq 8 and 9, the diffusion (k_d, k'_d) and dissociation (k_{-d}, k'_{-d}) rate constants can be evaluated in the usual way (see Appendix). The rate constant for the electron-transfer step in the encounter (k_e in eq 8 and $k_{-e}(g)$ in eq 9) may be expressed by eq 10,[24] where κ is the adiabacitity coefficient, and

$$k = \frac{k_B T}{h}\kappa \exp(\Delta G^\ddagger/RT) \qquad (10)$$

$\Delta G^\ddagger$ is the free energy of activation. The last quantity can be expressed by eq 11,[26] where $\Delta G^\ddagger(0)$ is the so-called intrinsic barrier and ΔGs is the standard free energy change of the electron-transfer step. The experimental rate constants (k_{exptl}, Table I) for quenching and electron back-transfer have been homogenized as far as the diffusion parameters are concerned, to 3+ and 2+ reactants, $r = 12.3$ Å, and $\mu = 1$ M (see Appendix) and the values so obtained, k'_{exptl}, have been plotted in Figure 2. For a homogeneous series of reactions (i.e., when, beside the diffusion parameters, $\Delta G^\ddagger(0)$ and κ are also constant)[2a,28] k'_{exptl} is only a function of the free energy change, and the analysis of the log k'_{exptl} vs. ΔG° plot can yield some pieces of information on the role played by the electronic and nuclear factors in determining the reaction rate.[2a] To do that, one must first chose appropriate values for the diffusion parameters and the free energy changes, using available experimental data and/or current expressions (see Appendix). Then, the $\Delta G^\ddagger(0)$ and κ values that best fit the log k'_{exptl} vs. ΔG° plot may be obtained.

$$\Delta G = \Delta G^\circ + \frac{\Delta G^\ddagger(0)}{\ln 2}\left(\ln\left\{1 + \exp\left[\frac{-\Delta G^\circ(\ln 2)}{\Delta G^\ddagger(0)}\right]\right\}\right) \qquad (11)$$

Kinetic Parameters of the Electron-Transfer Reactions. Figure 2 shows that the rate constants for the quenching reactions increase with increasing exoergonicity of the electron-transfer-quenching process, in agreement with previous results and theoretical expectations.[2a,23,29] However, a noticeable scattering in the points is observed. A comparison of the data obtained in this paper with those previously reported[4] for the analogous reactions involving Eu^{3+}_{aq} and Eu^{2+}_{aq} shows that encapsulation of europium into the 2.2.1 cryptand increases the self-exchange rate constant, in qualitative agreement with the conclusions drawn by Weaver and co-workers.[5] (vide infra).

Figure 2 also shows that the rate constants obtained for reactions 2–5 do not lie on a single log k'_{exptl} vs. ΔG° curve, as would be expected for a homogeneous series of reactions.[2a,28] Such a behavior is not new since Creutz[11] had already observed that the reactions of Eu^{2+}_{aq} with $*RuL_3^{2+}$ exhibit a free energy dependence different from that for the reactions of Eu^{3+}_{aq} with RuL_3^{+}. The observed lack of homogeneity may be caused by a nonhomogeneous character of the ruthenium and/or europium reaction partners. As far as the ruthenium complexes are concerned, it can be noted that reactions 2 and 5 involve a ligand-localized π^* orbital while reactions 3 and 4 involve a metal-localized $\pi(t_{2g})$ orbital. Simple considerations suggest that orbital overlap with the reaction partner is more effective for an outer π^* orbital than for an inner $\pi(t_{2g})$ metal orbital. As a consequence, the two types of reactions could exhibit a different degree of nonadiabaticity.[7,10,23,30,31] Recently, Sutin and co-workers[7] have shown that the reaction between RuL_3^{3+} and Co(sepulchrate)$^{2+}$, which is analogous to reaction 4, is 10^3–10^4 times less adiabatic than the

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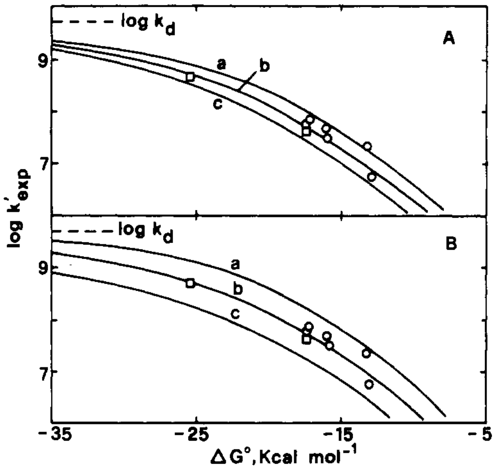

Figure 3. Best fitting curves for the data concerning $[\mathrm{Eu}\subset 2.2.1]^{3+}$ reduction (reactions 2 and 5): (A) curves obtained with $\kappa = 1 \times 10^{-3}$ and $\Delta G^*(0) = 8.5$ (curve a), 9.5 (curve b), or 10.5 (curve c) kcal mol^{-1}; (B) curves obtained with $\Delta G^*(0) = 9.5$ kcal mol^{-1} and $\kappa = 1 \times 10^{-2}$ (curve a), 1×10^{-3} (curve b), or 1×10^{-4} (curve c).

reaction between $^*\mathrm{RuL}_3^{2+}$ and Co(sepulchrate)$^{3+}$, which is analogous to reaction 2. Nonadiabaticity is also apparent in other electron-transfer processes that involve the $\pi(t_{2g})$ ruthenium orbitals.[32] In principle, there is no reason why this effect should not be shown by our systems. However, looking at Figure 2, one can see that "correction" for this type of nonhomogeneity would not improve the fitting of the points to a single log k'_{exptl} vs. $\Delta G°$ curve. It is also apparent that to improve the fitting one should either raise and/or move to the right the points that refer to $[\mathrm{Eu}\subset 2.2.1]^{3+}$ reduction (i.e., those concerning reactions 2 and 5), or lower and/or move to the left the points that refer to $[\mathrm{Eu}\subset 2.2.1]^{2+}$ oxidation (reaction 3 and 4). Since the $[\mathrm{Eu}\subset 2.2.1]^{3+/2+}$ couple exhibits a reversible electrochemical behavior,[13] it seems fair to assume that the $\Delta G°$ values are correctly defined. The explanation for the observed results has thus to be found in subtle kinetic differences between $[\mathrm{Eu}\subset 2.2.1]^{3+}$ and $[\mathrm{Eu}\subset 2.2.1]^{2+}$ that overcome the kinetic differences introduced by the different localization of the relevant orbital in the ruthenium complexes. Regardless of possible explanations, the results indicate that the data concerning $[\mathrm{Eu}\subset 2.2.1]^{3+}$ reduction must be analyzed separately from those concerning $[\mathrm{Eu}\subset 2.2.2]^{2+}$ oxidation.

Figure 3 shows that the data concerning $[\mathrm{Eu}\subset 2.2.1]^{3+}$ reduction fit reasonably well[33] a log k'_{exptl} vs. $\Delta G°$ curve, which corresponds to $\Delta G^*(0) = 9.5 \pm 1.0$ kcal mol^{-1} and $\kappa = 1 \times 10^{-3\pm1}$. Thus, it appears that we are dealing with a case of nonadiabatic behavior. In such cases, any further elaboration of the data of the cross-reaction to arrive at intrinsic parameters of the corresponding self-exchange reactions poses unsolved problems. Nevertheless, it may be interesting to go on with the equations[35,36]

$$\Delta G^*(0) = \frac{\Delta G^*(0)_{\mathrm{Ru}} + \Delta G^*(0)_{\mathrm{Eu}}}{2} \qquad (12)$$

$$\kappa = (\kappa_{\mathrm{Ru}}\kappa_{\mathrm{Eu}})^{1/2} \qquad (13)$$

taking the values $\Delta G^*(0)_{\mathrm{Ru}} = 4.2$ kcal mol^{-1} [2b] and $\kappa_{\mathrm{Ru}} = 1$[7] for the self-exchange $^*\mathrm{Ru}l_3^{2+}/\mathrm{RuL}_3^{3+}$ reaction. This procedure leads to the values $\Delta G^*(0)_{\mathrm{Eu}} \sim 15$ kcal mol^{-1} and $\kappa_{\mathrm{Eu}} \sim 10^{-6}$ for the intrinsic barrier and the adiabaticity coefficient of the $[\mathrm{Eu}\subset 2.2.1]^{3+}/[\mathrm{Eu}\subset 2.2.1]^{2+}$ self-exchange reaction.[38] With use of a frequency factor of 6×10^{12} s^{-1}, the rate constant of this self-exchange reaction is $\sim 5 \times 10^{-5}$ M^{-1} s^{-1}, a value much smaller than that (10 M^{-1} s^{-1}) estimated by Weaver et al.[5] from the kinetics of $[\mathrm{Eu}\subset 2.2.1]^{3+}$ reduction by $\mathrm{Eu}^{2+}_{\mathrm{aq}}$ or $\mathrm{V}^{2+}_{\mathrm{aq}}$. These results may be taken as a further demonstration[2b,2d,39–41] that eq 12 and 13 are not adequate to factor out the parameters of a nonadiabatic cross-reaction into intrinsic parameters. While we are waiting for a more satisfying interpretation of the relationships between cross and self-exchange reaction parameters, the use of eq 12 and 13 in a critical way is still useful to arrive at a better understanding of the factors that govern electron-transfer rates.

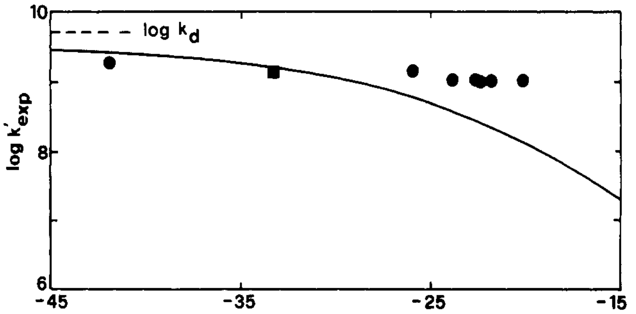

Figure 4. Comparison of the experimental data concerning $[\mathrm{Eu}\subset 2.2.1]^{2+}$ oxidation with the best fitting curve obtained for $[\mathrm{Eu}\subset 2.2.1]^{3+}$ reduction ($\Delta G^*(0) = 9.5$ kcal mol^{-1}, $\kappa = 1 \times 10^{-3}$).

The data concerning $[\mathrm{Eu}\subset 2.2.1]^{2+}$ oxidation are difficult to analyze because they fall in a region where there is a very small dependence on the free energy change. From Figure 4 it is clear, however, that they do not fit the best fitting curve obtained for $[\mathrm{Eu}\subset 2.2.1]^{3+}$ reduction and would fit even worse a curve that took into account the nonadiabatic behavior of the ruthenium complexes when they act as oxidants[7,32] (vide supra).

The results obtained clearly indicate that $[\mathrm{Eu}\subset 2.2.1]^{3+}$ and $[\mathrm{Eu}\subset 2.2.1]^{2+}$ do not behave as homogeneous[28] redox partners in their reactions with RuL_3^{n+} species.[42] It is not easy to explain which is the reason for this peculiar behavior of the Eu^{3+} and Eu^{2+} cryptates, and what we can do at this point is only to present some speculations. The nonhomogeneity of the two members of a redox couple may be due to several factors. First, the shapes of the free energy wells for the oxidative and reductive forms of the couple may be different, leading to different rate constant vs. $\Delta G°$ profiles. Unfortunately, the relevant experimental data (vibrational frequencies and nuclear displacements) are not available for the Eu cryptates so that the importance of this factor cannot be evaluated. Second, if only the oxidized species of an A^+/A couple is involved in some types of association with an X^- species, the reduction step actually involves the $\mathrm{AX}/\mathrm{AX}^-$ couple whereas the oxidation step involves the A^+/A couple. In such a case, the free energy change, intrinsic barrier, and adiabaticity coefficient would be different for the oxidation and reduction reactions.[43] This explanation does not seem to apply to the europium compounds because even the "free" Eu^{3+} ion does not give rise to inner-sphere ion pairs in

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(32) Sandrini, D.; Maestri, M.; Belser, P.; von Zelewsky, A.; Balzani, V. *J. Phys. Chem.* **1985**, *89*, 3675.

(33) An exception is the quenching of Ru(3,4,7,8-$(\mathrm{CH}_3)_4$phen)$_3^{2+}$ complex for which $\Delta G°$ is large, which proceeds more slowly than predicted (Table I). This relatively slow quenching rate, which is also observed for the quenching with Co(sep)$^{3+}$,[7,34] may be due to an extra nonadiabatic character related to the shielding effect of methyl substituents. An analogous effect was observed in the quenching of $^*\mathrm{RuL}_3^{2+}$ complexes by amines.[32]

(34) Scandola, F., private communication.

(35) Sutin, N. In *Bioinorganic Chemistry*; Eichorn, G. L., Ed.; American Elsevier: New York, 1973; Vol. 2, Chapter 9, p 611.

(36) Equation 13 has also been very recently derived by German.[37]

(37) German, E. D. *J. Chem. Soc., Faraday Trans. 1*, **1985**, 1153.

(38) It should be noted that the values obtained for the self-exchange reactions from eq 12 and 13 also depend on the reliability of the self-exchange values of the reaction partner.

(39) Brunschwig, B.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 7568.

(40) Sutin, N.; Brunschwig, B. S. In *Mechanistic Aspects of Inorganic Reactions*; Rorabacher, D. B., Endicott, J. F., Eds.; ACS Symposium Series 198; American Chemical Society: Washington, DC, 1982; p 105.

(41) Endicott, J. F.; Ramasami, T.; Gaswick, D. C.; Tamilarasan, R.; Heeg, M. J.; Brubaker, G. R.; Pyke, S. C. *J. Am. Chem. Soc.* **1983**, *105*, 5301.

(42) This behavior is quite similar to that found by Weaver et al. (Tyma, B. D.; Weaver, M. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *111*, 195. Weaver, M. J.; Hupp, J. T. *ACS Symp. Ser.* **1982**, *No. 198*, 181. Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1984**, *88*, 6128) for the driving force dependence of electrochemical parameters for metal–aquo redox couples.

(43) Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 213; Hoselton, M. A.; Drago, R. S.; Wilson, L. J.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6967.

aqueous solution.[4] A more subtle version of this second case, however, could be that in which, although there is not net change in the coordination number of the two species, the distance of closest approach to the reaction partner is different for the oxidized and reduced species because of solvation problems. This is particularly likely to occur in reactions involving hydrophilic and hydrophobic partners, as previously pointed out by Sutin and co-workers.[10,39,40] A difference in the distance of closing approach causes changes in the work terms, in the value of the outer-sphere activation barrier, and, for reactions that are in the nonadiabatic regime, also in the value of the adiabaticity coefficient κ.[24,44] The different kinetic behavior of $[\mathrm{Eu}\subset 2.2.1]^{3+}$ and $[\mathrm{Eu}\subset 2.2.1]^{2+}$ in their reactions with Ru–polypyridine complexes may perhaps be explained on this basis. Spectroscopic experiments have clearly shown that the Eu^{3+} ion enclosed into the 2.2.1 cryptand still binds three water molecules through the cryptand holes.[15] Such molecules can be replaced by F^- ions, but not by Cl^- or other anions.[13,45] This means that even when encapsulated into the cryptand Eu^{3+} maintains some "structure-making" ability on the solvent molecules, which likely precludes a close approach of the hydrophobic $\mathrm{RuL}_3{}^{n+}$ complexes. Although nothing is known as far as the interaction between $[\mathrm{Eu}\subset 2.2.1]^{2+}$ and water is concerned, it must be much smaller because of the smaller electric charge and larger size of Eu^{2+}.[46] This would favor a closer approach of $[\mathrm{Eu}\subset 2.2.1]^{2+}$ to the hydrophobic reaction partner. Since the electron-transfer reactions of europium, involving the strongly shielded f orbitals, are likely in the nonadiabatic regime,[40] differences in the distance of closest approach with the reaction partner are expected to cause, besides a change in the work terms and in the outer-sphere barrier, also a change in adiabaticity.

It should be noted that a difference in the distance of closest approach for the oxidized or reduced form of the $[\mathrm{Eu}\subset 2.2.1]^{3+/2+}$ couple is less likely when the reaction partner is hydrophilic. This could reconcile our data with those obtained by Weaver et al.[5] for the reactons of $[\mathrm{Eu}\subset 2.2.1]^{3+}$ or $[\mathrm{Eu}\subset 2.2.1]^{2+}$ with hydrophilic ions, which lead to approximately the same value for the $[\mathrm{Eu}\subset 2.2.1]^{3+}/[\mathrm{Eu}\subset 2.2.1]^{2+}$ self-exchange reaction.

Regardless of the reason why $[\mathrm{Eu}\subset 2.2.1]^{3+}$ and $[\mathrm{Eu}\subset 2.2.1]^{2+}$ do not behave as homogeneous redox partners in their reactions with $\mathrm{RuL}_3{}^{n+}$ complexes, the results obtained in this paper, as well as those previously reported for the $\mathrm{Eu}^{3+}{}_{\mathrm{aq}}/\mathrm{Eu}^{2+}{}_{\mathrm{aq}}$ couple,[4] show that extreme care must be exercized in drawing self-exchange rate constants from experimental cross-reaction rate constants (and vice versa), because the kinetic behavior of a species, mainly in the nonadiabatic regime, may be affected by very subtle factors.

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Appendix

Rate Constants. The diffusion and dissociation rate constants, k_d and $k_{-\mathrm{d}}$, are obtained from eq A1 and A2,[4] where η is the

$$k_\mathrm{d} = \frac{8RT}{3000\eta}\,\frac{w_\mathrm{r}/RT}{e^{w_\mathrm{r}/RT} - 1} \tag{A1}$$

$$k_{-\mathrm{d}} = \frac{2kT}{\pi r^3 \eta}\,\frac{w_\mathrm{r}/RT}{1 - e^{-w_\mathrm{r}/RT}} \tag{A2}$$

viscosity and w_r is given, according to the Debye–Hückel theory, by

$$w_\mathrm{r} = \frac{Z_\mathrm{D} Z_\mathrm{A} N e^2}{\epsilon r(1 + Ar\mu^{1/2})}$$

where $Z_\mathrm{D}Z_\mathrm{A}$ are the electric charges of the two reactants, e is the electron charge, ϵ is the dielectric constant, A is $(8\pi N^2 e^2/1000\epsilon RT)^{1/2}$, r is the encounter distance, and μ is the ionic strength.

The encounter distance r is obtained as the sum of the europium cryptate radius, 5.3 Å[5], and the ruthenium complex radius, 7 Å.[32] Equation 3a of ref 4 has been used to homogenize bimolecular electron-transfer rate constants that differ in charge product, $Z_\mathrm{D}Z_\mathrm{A}$.

Nuclear Frequency. In eq 10, the effective nuclear frequency ν_n, which destroys the activated complex configuration, should be used.[24] Since both inner- and outer-sphere frequencies are involved in our case, the universal frequency $k_\mathrm{B}T/h$ has been used as an average frequency.

Free Energy Change. The free energy change for the electron-transfer process within the encounter was obtained from eq A3, where $E°_\mathrm{Ru}$ and $E°_\mathrm{Eu}$ stand for the standard redox potentials

$$\Delta G° = -[E°_\mathrm{Ru} - E°_\mathrm{Eu} + w_\mathrm{p}(r) - w_\mathrm{R}(r)] \tag{A3}$$

of the appropriate ruthenium and europium couples.

For the $\mathrm{RuL}_3{}^{3+}/\mathrm{RuL}_3{}^{2+}$ and $\mathrm{RuL}_3{}^{3+}/{}^*\mathrm{RuL}_3{}^{2+}$ potentials, the literature values[18,23] reported for acetonitrile solutions vs. SCE have been used for $\mathrm{H_2O}$ solutions vs. NHE, because it is known that for the $\mathrm{Ru(bpy)_3}^{3+}/\mathrm{Ru(bpy)_3}^{2+}$ couple the same numerical values are obtained under such conditions.[18,23] For the $\mathrm{RuL}_3{}^{2+}/\mathrm{RuL}_3{}^{+}$ and ${}^*\mathrm{RuL}_3{}^{2+}/\mathrm{RuL}_3{}^{+}$ couples, the literature values for acetonitrile solutions were corrected for the junction potentials (+0.07 V).[47]

Registry No. $\mathrm{Ru(bpy)_3}^{2+}$, 15158-62-0; $\mathrm{Ru(4,4'\text{-}Cl_2\text{-}bpy)_3}^{2+}$, 75777-79-6; $\mathrm{Ru(4\text{-}NO_2\text{-}bpy)_3}^{2+}$, 73891-47-1; $\mathrm{Ru(3,3'\text{-}(CH_3)_2\text{-}bpy)_3}^{2+}$, 32881-03-1; $\mathrm{Ru(5,6\text{-}(CH_3)_2\text{-}phen)_3}^{2+}$, 14975-40-7; $\mathrm{Ru(3,4,7,8\text{-}(CH_3)_4\text{-}phen)_3}^{2+}$, 64894-64-0; $\mathrm{Ru(DMCH)_3}^{2+}$, 75778-26-6; $\mathrm{Ru(biq)_3}^{2+}$, 60451-55-0; $\mathrm{Ru(isobiq)_3}^{2+}$, 82762-29-6; $[\mathrm{Eu}\subset 2.2.1]^{3+}$, 73587-32-3; $[\mathrm{Eu}\subset 2.2.1]^{2+}$, 65013-29-8.

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(44) Marcus, R. A. *Int. J. Chem. Kinet.* **1981**, *13*, 873.

(45) Unpublished results from this laboratory.

(46) A more hydrophilic character of $[\mathrm{Eu}\subset 2.2.1]^{3+}$ is supported by the substantial positive reaction entropy of the $[\mathrm{Eu}\subset 2.2.1]^{3+/2+}$ couple.[13b]

(47) Creutz, C.; Sutin, N. *Inorg. Chem.* **1976**, *15*, 496.