

hydrogen bonds consistent with two more water molecules being bound to the noncyclic ligand. Most significantly, however, in all cases we have found a favorable entropy contribution to the macrocyclic effect. In order for Margerum's original hypothesis to be viable a negative entropy contribution must be expected since it is highly improbable that the relative gain in configurational entropy of the noncyclic ligand on decomplexation could outweigh the loss in translational entropy associated with two extra water molecules being bound to the noncyclic ligand. The present results confirm our view that this original hypothesis is no longer tenable and the equality of the macrocyclic enthalpies of the Cu(II) and octahedral Ni(II) complexes with [14]aneN₄ and 2,3,2-tet is to some extent fortuitous, both macrocyclic complexes benefiting from similar increases in M-N interaction over their noncyclic counterparts.

In conclusion, the most significant consequence of this study is to bring the interpretation of the macrocyclic effect for Ni(II) within the same framework as that already established for other metal complexes and to reemphasize that this effect has its origins in both enthalpic and entropic terms.

Acknowledgment. We thank the Italian CNR for financial support and the Royal Society for the award of a European Fellowship to R.M.C.

Registry No. [Ni[14]aneN₄(H₂O)₂]²⁺(octahedral), 64616-26-8; [Ni[14]aneN₄]²⁺(square-planar), 46365-93-9; [Ni(2,3,2-tet)(H₂O)₂]²⁺(octahedral), 23236-28-4; [Ni(2,3,2-tet)]²⁺(square-planar), 25669-75-4.

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Mechanism of the Quenching of the Emission of Substituted Poly(pyridine)ruthenium(II) Complexes by Europium(II)

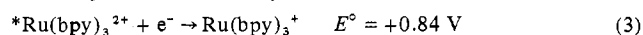
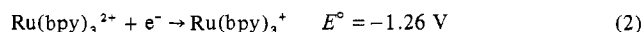
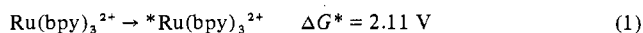
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Received July 8, 1977

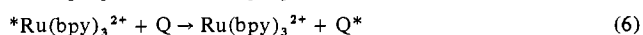
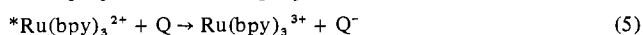
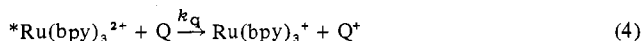
The emission from the charge-transfer excited states of poly(pyridine)ruthenium(II) complexes (RuL₃²⁺, L = a 2,2'-bipyridine or 1,10-phenanthroline derivative) is quenched by aqueous europium(II) at rate constants ranging from 1.5 × 10⁶ to 1.0 × 10⁸ M⁻¹ s⁻¹ (25 °C, 0.5 M ionic strength) depending on the identity of L. The quenching gives rise to the electron-transfer products RuL₃⁺ and Eu(III) which undergo back-reaction to form RuL₃²⁺ and Eu(II) at rate constants ranging from 2 to 6 × 10⁷ M⁻¹ s⁻¹. Energy-transfer and electron-transfer mechanisms are considered for the Eu(II) quenching process and the free energy dependences observed in europium outer-sphere electron-transfer reactions are reviewed.

Introduction

The emitting state of tris(2,2'-bipyridine)ruthenium(II) (*Ru(bpy)₃²⁺) is a stronger oxidant than the ground-state molecule by ~2.1 V as a consequence of its excitation energy (eq 1-3).^{1,2} Since the excited state is a rather strong oxidant,



its emission may be quenched by reducing agents according to eq 4; oxidative (eq 5)³⁻⁵ and energy transfer (eq 6)^{3,6}



mechanisms also provide pathways for the emission quenching.

Evidence for reductive quenching according to eq 4 has been provided by studies of the emission quenching by such diverse reductants as Ru(NH₃)₆²⁺,¹ S₂O₄²⁻,¹ Eu_{aq}²⁺,^{1,2} Os(CN)₆⁴⁻,⁷ and Fe(CN)₅L³⁻,⁸ and by organic amines.⁹ More direct evidence for the operation of this pathway has been provided by flash-photolysis studies of the Eu_{aq}²⁺ and the organic amine⁹ systems in which the low oxidation state Ru(bpy)₃⁺ was observed spectrally. The present study extends the use of Eu_{aq}²⁺ as a quencher to other poly(pyridine)ruthenium(II) complexes. The results of cyclic voltammetric, steady-state emission quenching, and flash-photolysis experiments with these complexes are reported below.

Experimental Section

Materials. Tris(2,2'-bipyridine)ruthenium(II) chloride (Ru(bpy)₃Cl₂) purchased from G. F. Smith was recrystallized from hot water at least twice before use. This was necessary in order to remove an insoluble dark brown impurity present in some lots. The other RuL₃²⁺ complexes used (L = 4,4'-(CH₃)₂bpy, 4,4'-dimethyl-2,2'-

bipyridine; L = phen, 1,10-phenanthroline; L = 4,7-(CH₃)₂phen, 4,7-dimethyl-1,10-phenanthroline; L = 5-Cl-phen, 5-chloro-1,10-phenanthroline) were from samples prepared by Mrs. M. Chou.³ Europium trichloride (Alfa-Ventron, 99.9%) was reduced to europium(II) by amalgamated zinc. The tetrapropylammonium hexafluorophosphate was prepared as described elsewhere.³ Argon was used as blanket gas in all the studies.

Cyclic Voltammetry. A Princeton Applied Research Corp. system consisting of a Model 173 potentiostat and a Model 175 universal programmer was employed in the cyclic voltammetry measurements. Millimolar solutions of the poly(pyridine)ruthenium(II) complexes as perchlorate or chloride salts were prepared in acetonitrile which was 0.1 M in tetrapropylammonium hexafluorophosphate. Before use the acetonitrile was passed through a column of acid (pH 4.5) alumina which had been heated at 350 °C overnight. Both working and auxiliary electrodes were platinum; the reference electrode was an aqueous saturated calomel situated in a Luggin capillary. The measurements were made under an argon stream.

Quenching Rate Constants. Most emission quenching rate constants (eq 4) were obtained from steady-state emission intensity measurements using a Perkin-Elmer Model MPF-4 fluorescence spectrophotometer equipped with a 150-W xenon lamp and a cell compartment thermostated at 25 °C. The solutions used in these measurements were typically 5 × 10⁻⁶ M in RuL₃²⁺, 0.05 M HCl, and 0.01–0.09 M in Eu(II) with an ionic strength of 0.5 M using sodium chloride as supporting electrolyte. Excitation was accomplished at 450–530 nm; emission was monitored at ~610 nm. The emission intensity ratios obtained were not found to be sensitive to incident light intensity, but since net photochemistry was a complication at high light intensities, the measurements were generally made at low incident intensities. The incident light intensity was varied by placing neutral density filters in the excitation beam.

For Ru[4,4'-(CH₃)₂bpy]₃²⁺ the Eu²⁺ quenching rate constant was obtained from lifetime measurements. A frequency-doubled neodymium laser³ having a ~25-ns pulse width was used to excite thermostated solutions ~5 × 10⁻⁵ M in ruthenium complex and 0–0.1 M in Eu(II) (μ = 0.5 M, NaCl). The light emitted from the sample at 90° to the excitation pulse was monitored at 630 nm. The emission lifetimes obtained in the presence and absence of europium(II) were used to determine the quenching rate constant. The same technique was used in determining the activation parameters for the quenching of Ru(bpy)₃²⁺ by Eu(II).

Flash Photolysis Experiments. Spectral and kinetics studies of RuL₃⁺ were made by a flash-photolysis technique. Solutions 0.3–3.0 × 10⁻⁴ M in RuL₃²⁺, ~0.1 M in europium(II), and 0.5 M in ionic strength were prepared in a 1 × 1 cm "microcell" having 0.4 and 1.0 cm path lengths. The cell was sealed with a rubber septum cap. The solution was excited (along the 1-cm path length) by a ~25-ns pulse from a frequency-doubled neodymium laser.³ The light from the laser was filtered to remove the original 1.06 μ component, and the remainder was focused to give an elliptical beam about 0.30 cm wide and 0.75 cm high at the front surface of the sample cell. The monitoring light source and optics were situated at 90° to the excitation beam, and the sample cell was masked so that only the front 0.4 cm of the solution was observed; the path length along the monitoring beam was 0.4 cm. Excitation intensities ranged from 10 to 10³ einstein cm⁻² s⁻¹ and the excitation light was always in excess over RuL₃²⁺ in the portion of the solution monitored.¹⁰

The rate constants for oxidation of RuL₃⁺ by Eu(III) and of Ru(bpy)₃⁺ by Ru(NH₃)₆³⁺ were determined under pseudo-first-order conditions. Aliquots of a concentrated, deaerated solution of the oxidant were added to the sample cell containing RuL₃²⁺ and quencher, the solutions were flashed, and the kinetics of the decay of RuL₃⁺ was monitored in the range 490–510 nm. Plots of log |A_t - A_∞| vs. time were constructed from these data and the values of k_{obsd} (the pseudo-first-order rate constant) obtained for the decay were plotted against the concentration of oxidant.

For Ru(bpy)₃²⁺, the yield (φ₀) of excited state produced by the laser flash was estimated in the following manner. A solution 1.5 × 10⁻³ M in Fe(NH₄)(SO₄)₂ in 0.5 M H₂SO₄ containing the desired Ru(bpy)₃²⁺ concentration was flashed. The bleaching of absorbance at 490 nm was monitored and the absorbance change (ΔA) observed within 1–2 μs after the laser flash was determined. The fraction of the Ru(bpy)₃²⁺ converted to Ru(bpy)₃³⁺ in the experiment was determined by comparing the absorbance of the Ru(bpy)₃²⁺ (A_{II}) solution used with that of a Ru(bpy)₃³⁺ (A_{III}) solution of the same

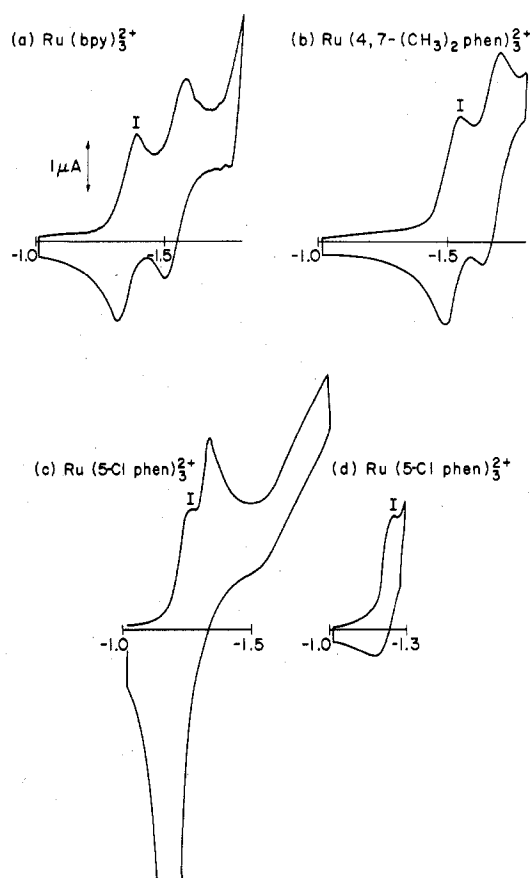


Figure 1. Cyclic voltammograms for 10⁻³ M (RuL₃)(ClO₄)₂ in acetonitrile 0.1 M in tetra-*n*-propylammonium hexafluorophosphate at 200 mV s⁻¹ sweep. Potentials are referred to aqueous SCE.

Table I. Cyclic Voltammetric Peak Potentials for Poly(pyridine)ruthenium(II) Complexes in 0.1 M Tetra-*n*-propylammonium Hexafluorophosphate-Acetonitrile Solutions at a Platinum Electrode at 200 mV s⁻¹ Sweep

Complex	E _p , V, vs. SCE	ΔE _p	E _{1/2} , V, vs. SCE
Ru(bpy) ₃ ²⁺	-1.38	0.060	-1.35
Ru(4,7-(CH ₃) ₂ phen) ₃ ²⁺	-1.55	0.064	-1.52
Ru(5-Cl-phen) ₃ ²⁺	-1.26	.. ^a	(-1.22) ^b

^a Irreversible; see Figure 1. ^b Estimated value; see text.

ruthenium concentration using the flash-photolysis monitoring optics (i.e., same wavelength, slit widths, and sample cell). This yield of Ru(bpy)₃³⁺ was finally corrected for the fraction quenched at the finite Fe³⁺ concentration used and the yield of Ru(bpy)₃³⁺ from the Fe³⁺ quenching (φ_{Fe³⁺}) according to eq 7.

$$\phi_0 = \frac{\Delta A}{A_{III} - A_{II}} \left(\frac{1 + K_{SV} [Fe^{3+}]}{K_{SV} [Fe^{3+}]} \right) \frac{1}{\phi_{Fe^{3+}}} \quad (7)$$

Results

The results of the cyclic voltammetric experiments at a 200 mV s⁻¹ sweep are shown in Figure 1 and summarized in Table I. In the potential range used RuL₃²⁺ is successively reduced to RuL₃⁺ (peak marked I in Figure 1), RuL₃⁰, and RuL₃⁻.¹¹ Only data for the first reduction wave, RuL₃²⁺ + e⁻ = RuL₃⁺, are given in the table. For Ru(bpy)₃²⁺ and Ru(4,7-(CH₃)₂phen)₃²⁺ the values obtained for ΔE_p indicate that the RuL₃²⁺/RuL₃⁺ couples are reversible.¹² The Ru(5-Cl-phen)₃²⁺/Ru(5-Cl-phen)₃⁺ couple is not reversible and the E_{1/2} value given in the table was obtained by assuming that ΔE_p for this couple would be the same as that for the bipyridine complex if the Ru(5-Cl-phen)₃⁺ produced in the cathodic portion of the sweep were not destroyed by rapid chemical side

Table II. Europium(II) Stern-Volmer and Quenching Rate Constants, Emission Maxima and Excited-State Reduction Potentials for Poly(pyridine)ruthenium(II) (RuL_3^{2+}) Complexes, and Rate Constants for Reaction of RuL_3^+ with Europium(III) at 25 °C and 0.5 M Ionic Strength

Ligand	$K_{\text{SV}}, \text{M}^{-1}$	$\lambda_{\text{em}}, \text{nm}$	$*E_{2+,+}^{\circ}, \text{V}$	$10^{-7}k_{\text{q}}, \text{M}^{-1} \text{s}^{-1}$	$E_{1/2}, \text{V}$	$10^{-7}k_{\text{Eu(III)}}, \text{M}^{-1} \text{s}^{-1}$
$(\text{CH}_3)_2\text{bpy}$	0.4	633	0.69	0.15	-1.44	4.5
bpy	17.0	613, 627	0.84	2.8	-1.35	2.7
4,7- $(\text{CH}_3)_2\text{phen}$	12.1	613, 626	0.67	0.70	-1.52	5.7
phen	45.3	605, 625	0.79	4.9 ± 0.5	-1.43	5.2
5-Cl-phen	98.5	605, 625	1.00	10	-1.22	1.6 ± 0.2

^a Data taken from ref 3. ^b Vs. hydrogen in water. ^c For the RuL_3^{2+} - RuL_3^+ couple vs. aqueous SCE in acetonitrile.

reactions. This assumption is supported by the fact that the $E_{1/2}$ value estimated in this way lies within 10 mV of the potential at which $E = 0.857E_{\text{p,c}}^{12}$ and by the following observations. With $\text{Ru}(5\text{-Cl-phen})_3^{2+}$ a desorption spike was observed in the anodic sweep when the cathodic sweep was carried to -2.0 V vs. SCE (Figure 1c). If the range of the cathodic sweep was limited to -1.3 V, however, there was no evidence for desorption, but the anodic peak current was very small (Figure 1d). In the cathodic sweeps to -2.0 V, RuL_3^+ , RuL_3^0 , and RuL_3^- are generated successively in three one-electron processes. The above behavior indicates that while RuL_3^0 or RuL_3^- ($L = 5\text{-Cl-phen}$) adsorbs on platinum, RuL_3^+ does not. The small anodic peak current for $\text{Ru}(5\text{-Cl-phen})_3^+$ very likely arises because rapid reaction of this species with itself destroys the $\text{Ru}(5\text{-Cl-phen})_3^+$ near the electrode. This interpretation is consistent with the flash-photolysis results (vide infra) which suggest that in water two $\text{Ru}(5\text{-Cl-phen})_3^+$ species undergo reaction at diffusion-controlled rates.

In Table II are presented Stern-Volmer constants and quenching rate constants for the various RuL_3^{2+} complexes with Eu(II). Data obtained from either steady-state emission intensity or lifetime measurements were treated according to the Stern-Volmer equation

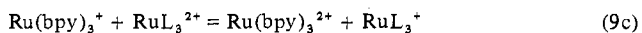
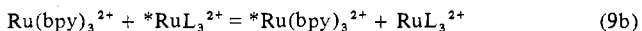
$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{\text{SV}}[\text{Q}] \quad (8)$$

where I_0 and τ_0 are the emission intensity and lifetime, respectively, in the absence of quencher, I and τ are the emission intensity and lifetime in the presence of quencher, and K_{SV} is the Stern-Volmer constant, $K_{\text{SV}} = k_{\text{q}}\tau_0$. The lifetime values used are reported in ref 3. The positions of the $*\text{RuL}_3^{2+}$ corrected emission maxima from ref 3, $E_{1/2}$ values for the $\text{RuL}_3^{2+}/\text{RuL}_3^+$ couples in acetonitrile, and rate constants for the thermal back-reaction of RuL_3^+ with Eu(III) are summarized as well.

The reduction potentials for the reduction of the excited state to RuL_3^+ (eq 9a) given in the table were calculated using



$*E_{2+,+} = +0.84 \text{ V}^1$ for the 2,2'-bipyridine complex (in water, vs. H_2) and adding $*\Delta G^\circ$ for this couple to the sum of the ΔG° values for reactions 9b and 9c.³ The values of ΔG° for



reaction 9b were assumed to be equal to the differences in the positions of the (corrected) emission maxima of $*\text{Ru}(\text{bpy})_3^{2+}$ and $*\text{RuL}_3^{2+}$.³ For $L = 2,2'-(\text{CH}_3)_2\text{bpy}$ the free energy change for reaction 9c (ΔG_c°) was calculated from the polarographic data of Saji and Aoyagui who report half-potentials of -1.25 and -1.34 V for $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(2,2'-(\text{CH}_3)_2\text{bpy})_3^{2+}$, respectively, in 0.1 M tetrabutylammonium perchlorate-*N,N*-dimethylformamide.¹³ For $L = \text{phen}$, ΔG_c° was calculated from the cyclic voltammetric data of Tokel-Takvoryan, Hemingway, and Bard¹¹ who report E_p values of -1.332 and -1.41 V for $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{phen})_3^{2+}$, respectively, in 0.1 M tetrabutylammonium fluoroborate. For $L = 4,7-$

Table III. Temperature Dependence of the Eu(II) Quenching of the $\text{Ru}(\text{bpy})_3^{2+}$ Emission at $\mu = 0.5 \text{ M}$ (NaCl)

$T, \text{°C}$	$\tau_0, \mu\text{s}$	$10^{-7}k_{\text{q}}, \text{M}^{-1} \text{s}^{-1}$
39 ± 2	0.48 ± 0.02	2.2 ± 0.2
24.4 ± 0.5	0.62 ± 0.02	2.8 ± 0.1
10 ± 1	0.70 ± 0.02	2.8 ± 0.1

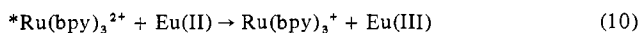
$(\text{CH}_3)_2\text{phen}$ the difference in half-potentials (Table I) between $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}[4,7-(\text{CH}_3)_2\text{phen}]_3^{2+}$ was used to estimate ΔG_c° . Since the $\text{Ru}(5\text{-Cl-phen})_3^{2+}/^+$ couple is not reversible, the difference in cathodic peak potentials for $\text{Ru}(5\text{-Cl-phen})_3^{2+}$ and $\text{Ru}(\text{bpy})_3^{2+}$ was used to calculate ΔG_c° .

In Table III values of τ_0 and k_{q} for Eu(II) quenching of $*\text{Ru}(\text{bpy})_3^{2+}$ at several temperatures are summarized. The activation parameters obtained for the quenching process are $\Delta H^\ddagger = -2.2 \pm 1.1 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -32 \pm 4 \text{ cal deg}^{-1} \text{ mol}^{-1}$, and $\Delta G^\ddagger_{298} = 7.3 \text{ kcal mol}^{-1}$. In Figure 2 the 500-nm absorbance change obtained from reaction of $*\text{Ru}(\text{bpy})_3^{2+}$ with Eu(II) is plotted as a function of the relative incident excitation intensity.

In the absence of added europium(III), $\text{Ru}(5\text{-Cl-phen})_3^+$ was observed to undergo exceedingly rapid decomposition to produce a dark insoluble product via second-order equal concentration kinetics (i.e., plots of $(A_\infty - A)^{-1}$ vs. time are linear). At 490 nm the value of k/ϵ was found to be $(2.3 \pm 0.6) \times 10^6 \text{ cm s}^{-1}$ ($25 \pm 1 \text{ °C}$, $\mu = 0.5 \text{ M}$). Since $\Delta\epsilon$ is not likely to be less than $10^3 \text{ M}^{-1} \text{ cm}^{-1}$, the rate constant must be at least $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. As determined at 500 nm, the rate constant for oxidation of $\text{Ru}(\text{bpy})_3^+$ by $\text{Ru}(\text{NH}_3)_6^{3+}$ is $(4.7 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C and 0.5 M ionic strength. The rate constant for the oxidation of $\text{Ru}(\text{bpy})_3^+$ by O_2 is $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; this was determined by using $\text{Fe}(\text{CN})_6^{4-}$ as quencher to produce $\text{Ru}(\text{bpy})_3^+$ in the presence of oxygen. As determined at 500 nm, the relative yields of $\text{Ru}(\text{bpy})_3^+$ produced by various quenchers are as follows: Eu(II), 1.0; $\text{Ru}(\text{NH}_3)_6^{2+}$, 0.1; $\text{Fe}(\text{CN})_6^{4-}$, 0.05; $\text{S}_2\text{O}_4^{2-}$, 0.04; no added quencher, 0.02. Detailed observations of the latter system will be reported elsewhere.¹⁰

Discussion

Quenching by Europium(II). Quenching of the emission of the $*\text{RuL}_3^{2+}$ complexes is observed in the presence of Eu(II). With $\text{Ru}(\text{bpy})_3^{2+}$ the absorbance changes produced in the solution as a result of the quenching provided evidence that net electron transfer had occurred (eq 10).² In previous work



the assumption that each quenching act gave rise to one $\text{Ru}(\text{bpy})_3^+$ yielded $\epsilon_{490} (1.4 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for $\text{Ru}(\text{bpy})_3^+$.² Recently Anderson, Salmon, Meyer, and Young directly measured the absorption spectrum of electrochemically generated $\text{Ru}(\text{bpy})_3^+$ in acetonitrile and reported $\epsilon_{490} 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.⁹ Thus, if the spectrum of $\text{Ru}(\text{bpy})_3^+$ is the same in water and acetonitrile, the quantum yield of $\text{Ru}(\text{bpy})_3^+$ from Eu(II) quenching of $*\text{Ru}(\text{bpy})_3^{2+}$ is unity within experimental error. Furthermore the light intensity dependence shown in Figure 2 indicates that $\text{Ru}(\text{bpy})_3^+$ is formed from $\text{Ru}(\text{bpy})_3^{2+}$ by a one-photon process.

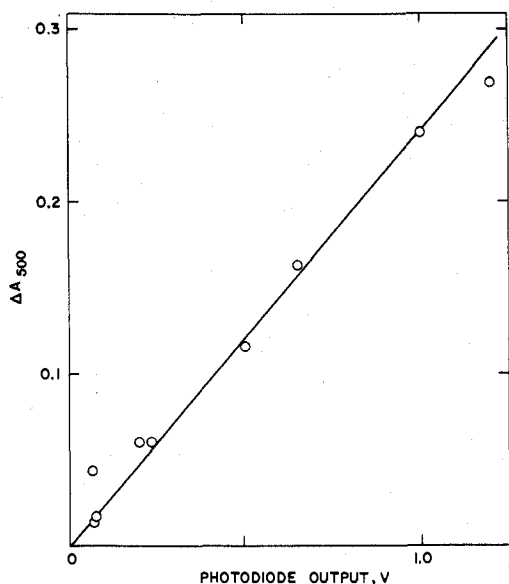
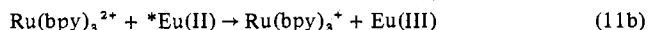
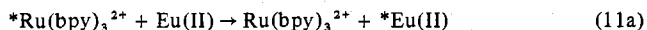


Figure 2. The 500-nm absorbance increase obtained on flashing a solution 1.2×10^{-4} M in $\text{Ru}(\text{bpy})_3^{2+}$ and 0.086 M in $\text{Eu}(\text{II})$ (0.05 M H^+ , $\mu = 0.5$ M, NaCl) as a function of relative laser light intensity.

In this system the electron-transfer products $\text{Ru}(\text{bpy})_3^+$ and $\text{Eu}(\text{III})$ could be formed in either of two ways. They may result from reductive quenching of the excited state (eq 4) or they may result from secondary reaction (eq 11b) following energy-transfer quenching (eq 11a). In the latter case



electronically excited europium(II) generated by energy transfer from $*\text{Ru}(\text{bpy})_3^{2+}$ would have to reduce ground-state $\text{Ru}(\text{bpy})_3^{2+}$ to give the observed electron-transfer products. The lower excited states of $\text{Eu}(\text{II})$ have been investigated by emission studies on solids. Recently Sommerdijk and Brill observed 4f–4f line emission and 5d–4f band emission from Eu^{2+} incorporated in halide lattices.¹⁴ Although the wavelength of the narrow 4f–4f emission is quite insensitive to the environment of the Eu^{2+} ion and generally occurs at 360–365 nm, the position of the broad 5d–4f emission is influenced by both the nature of the lattice and temperature and may range from 360 to 610 nm depending on these conditions. Although emission is not observed from aqueous $\text{Eu}(\text{II})$ solutions, it seems likely that the 4f excited states which are not sensitive to environment lie at ~ 360 nm. Since $*\text{Ru}(\text{bpy})_3^{2+}$ emission is maximal at ~ 630 nm, energy transfer to the 4f $\text{Eu}(\text{II})$ excited states is not energetically feasible. On the other hand it is more difficult to absolutely rule out energy transfer from $*\text{Ru}(\text{bpy})_3^{2+}$ to the $\text{Eu}(\text{II})$ 5d states. As the energy of the latter states is so environment sensitive, it is conceivable that they may lie at sufficiently low energy for moderately endothermic or even exothermic energy transfer. If the $\text{Eu}(\text{II})$ 5d states ($*\text{Eu}(\text{II})$) do lie at ~ 630 nm, they are sufficiently strong reductants ($\text{Eu}(\text{III}) + e^- = *\text{Eu}(\text{II})$, $*E^\circ \sim -2.4$ V) to reduce ground-state $\text{Ru}(\text{bpy})_3^{2+}$ to $\text{Ru}(\text{bpy})_3^+$ ($E^\circ_{2+,+} \sim -1.3$ V). There is one further aspect to consider in an energy-transfer model for the $\text{Eu}(\text{II})$ quenching. The yield of electron-transfer products from $\text{Eu}(\text{II})$ quenching of $*\text{Ru}(\text{bpy})_3^{2+}$ is near 100%. Furthermore $\text{Ru}(\text{bpy})_3^+$ is found to appear in parallel with $*\text{Ru}(\text{bpy})_3^{2+}$ disappearance.² Thus the reduction of $\text{Ru}(\text{bpy})_3^{2+}$ by $*\text{Eu}(\text{II})$ must be very rapid and possibly diffusion-controlled. A rapid rate constant for this reaction is also within the realm of possibility as the $*\text{Eu}(\text{II})$ is such a strong reducing agent. To summarize the above considerations, there is no positive evidence for energy-transfer

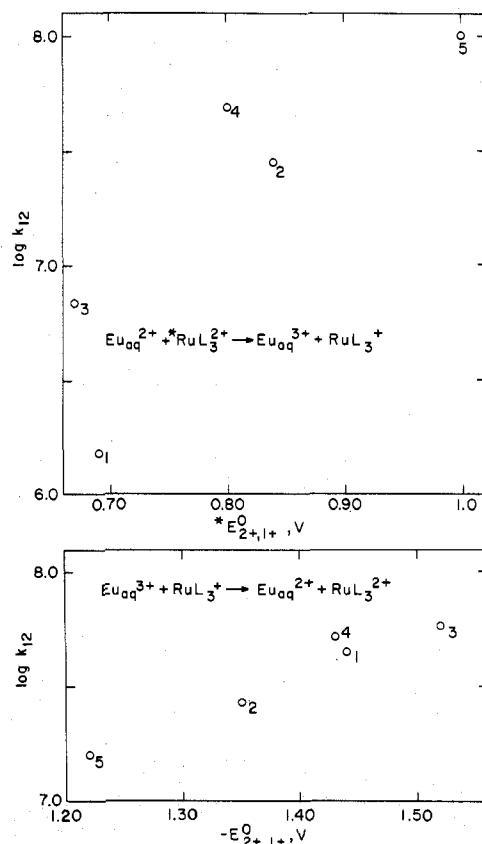


Figure 3. (Top) Logarithm of the rate constant for quenching of $*\text{RuL}_3^{2+}$ by europium(II) vs. the $*\text{RuL}_3^{2+}$ – RuL_3^+ reduction potential (in water vs. hydrogen). (Bottom) Logarithm of the rate constant for the reaction of RuL_3^+ with europium(III) vs. the RuL_3^{2+} – RuL_3^+ potential (in acetonitrile vs. SCE).

quenching in the $\text{Eu}(\text{II})$ – $\text{Ru}(\text{bpy})_3^{2+}$ system. No sensitized emission is observed from $\text{Eu}(\text{II})$ —but $\text{Eu}(\text{II})$ does not emit in water. The positions of the lowest $\text{Eu}(\text{II})$ excited states are not even known in water, but consequently their involvement cannot be ruled out. Finally, the flash-photolysis yield of $\text{Ru}(\text{bpy})_3^+$ is not incompatible with the reactivity expected for these $\text{Eu}(\text{II})$ excited states. Thus the possibility that electron-transfer products observed in $\text{Eu}(\text{II})$ – $\text{Ru}(\text{bpy})_3^{2+}$ flash photolysis arise from energy transfer followed by reduction of ground-state $\text{Ru}(\text{bpy})_3^{2+}$ by $*\text{Eu}(\text{II})$ cannot be eliminated on the basis of observations of this system alone. In an effort to discriminate between the two quenching mechanisms—reductive quenching and energy-transfer quenching—we turn next to other kinds of evidence.

Sutin has devised a rather powerful method for distinguishing between oxidative quenching and energy-transfer quenching of $*\text{Ru}(\text{bpy})_3^{2+}$.³ The quenching of $*\text{RuL}_3^{2+}$ was studied as a function of the RuL_3^{3+} – $*\text{RuL}_3^{2+}$ reduction potential. With $\text{Eu}(\text{III})$ as quencher a plot of $\log k_q$ vs. the excited-state potential was linear with a slope of 0.5 as is expected from the Marcus equation (eq 12)¹⁵ if the quenching

$$\log k_{12} = 0.5 \log (k_{11}k_{22}K_{12}f_{12}) \quad (12)$$

$$\log f_{12} = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/Z^2)}$$

proceeds by an outer-sphere electron-transfer reaction. (In eq 12 k_{12} and K_{12} are the rate constant and equilibrium constant for the electron-transfer reaction, k_{11} and k_{22} are the self-exchange rates for the oxidizing and reducing couples, and Z is a collision frequency taken as $10^{11} \text{ M}^{-1} \text{ s}^{-1}$.) By contrast, with $\text{Cr}(\text{III})$ as quencher the quenching rate constants are insensitive to the redox properties of $*\text{RuL}_3^{2+}$ as is expected

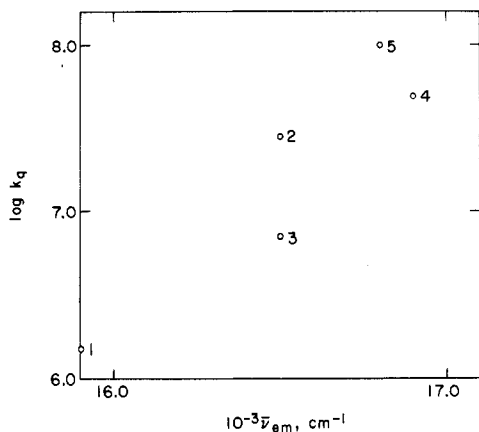


Figure 4. The logarithm of the rate constant for quenching of $*RuL_3^{2+}$ by europium(II) vs. the reciprocal of the corrected emission maximum for $*RuL_3^{2+}$ taken from ref 3.

for energy-transfer quenching. As the $*RuL_3^{2+}/RuL_3^+$ potentials also vary with L, the same method should be applicable to the Eu(II) quenching of $Ru(bpy)_3^{2+}$. In the top of Figure 3, $\log k_q$ for the quenching of $*RuL_3^{2+}$ by Eu(II) is plotted against the potential calculated for the $*RuL_3^{2+}-RuL_3^+$ couple. There it is evident that although the five points do not fall on a single line, there is definitely a correlation between the reduction potential of the excited state and the rate constant for quenching by europium(II). The lack of collinearity could arise from several sources—most likely from errors in the estimate of the excited state potentials or from differences in the self-exchange rates of the various $*RuL_3^{2+}-RuL_3^+$ couples.

Although the quenching rate patterns thus seem in accord with a reductive quenching mechanism, it is noteworthy that the rate patterns are also in accord with an energy-transfer mechanism. In Figure 4 the logarithm of the quenching rate constant is plotted against $\bar{\nu}_{em}$, the reciprocal of the corrected emission maximum given in Table II. Evidently the quenching rate constants increase as the excited-state energy of RuL_3^{2+} . In terms of an energy-transfer model this pattern indicates that energy transfer from $*RuL_3^{2+}$ to Eu(II) is endothermic.¹⁶ However, since the activation energy of $*Ru(bpy)_3^{2+}$ quenching is actually observed to be *negative*, it seems more likely that the behavior seen in Figure 4 is a coincidence. A negative value for ΔH^\ddagger is not consistent with endothermic energy transfer.

The absolute agreement between the observed quenching rate constants and the predictions of Marcus theory are considered next. The self-exchange rates for the $*Ru(bpy)_3^{2+}-Ru(bpy)_3^+$ and the $Eu_{aq}^{3+}-Eu_{aq}^{2+}$ couples have been estimated to be $5 \times 10^8 M^{-1} s^{-1}$ ⁸ and $3 \times 10^{-5} M^{-1} s^{-1}$,¹⁷ respectively. The Eu(III)–Eu(II) potential has been reported as -0.43 ¹⁷ and -0.38 ¹⁸ V in 1 M KCl and 1 M LiClO₄, respectively. The former value is more appropriate for the present work which was done in 0.5 M NaCl. Using the above value, $+0.84$ V as $*E^\circ_{2+,+}$ for the 2,2'-bipyridine complex, and eq 12, the rate constant for electron transfer from Eu(II) to $*Ru(bpy)_3^{2+}$ is calculated to be $4 \times 10^9 M^{-1} s^{-1}$ which is about 150 times greater than the observed value $2.8 \times 10^7 M^{-1} s^{-1}$. Although Marcus calculations often succeed in predicting values within a factor of 10 of the observed outer-sphere rate constants, it has recently been noted that certain reactions of aquo ions give very poor agreement with the theory at large driving force. In fact for reactions in which V_{aq}^{2+} , Cr_{aq}^{2+} , or Eu_{aq}^{2+} is the reducing agent the observed rate constant is often 100–300 times slower than the calculated value for reactions having $\log K_{12}$ 15–20.¹⁷ Thus since $\log K_{12}$ is 21.5 for the Eu(II)– $*Ru(bpy)_3^{2+}$ reaction, the fact that the observed rate constant is 150 times smaller than the calculated value for

electron transfer is actually consistent with a reductive quenching mechanism.

Finally the activation parameters for the quenching, $\Delta H^\ddagger = -2.2 \pm 1.1$ kcal mol⁻¹ and $\Delta S^\ddagger = -32 \pm 4$ cal deg⁻¹ mol⁻¹, may be discussed in terms of an electron-transfer mechanism. As there are no ΔH° and ΔS° data available for the Eu(III)–Eu(II) and $*RuL_3^{2+}-RuL_3^+$ couples, the observed parameters cannot be directly compared with those predicted from the Marcus cross relations.²⁰ It may, however, be noted that the observed values are quite similar to those found for Eu(II) reductions of ground-state complexes. For the Eu(II) reductions of $Co(phen)_3^{3+}$ and $Ru(NH_3)_5py^{3+}$ in 1.0 M $CF_3SO_3^-$ and ClO_4^- , respectively, the values $\Delta H^\ddagger = 1.8$ and 0.0 kcal mol⁻¹ and $\Delta S^\ddagger = -35$ and -37 cal deg⁻¹ mol⁻¹ have been obtained.¹⁷ These systems are not the best models since they involve +3 and +2 ions while the quenching reactions feature +2 and +2 ions, but these activation parameters do point out that large negative ΔS^\ddagger values are associated with Eu(II) reductions. The negative value of ΔH^\ddagger obtained for the quenching is to be expected if ΔH° for oxidation of Eu(II) to Eu(III) is highly negative.²⁰ Negative values of ΔH^\ddagger have been obtained in the reduction of $Ru(bpy)_3^{3+}$ by Fe_{aq}^{2+} ²¹ and found in accord with the predictions of Marcus theory.²⁰ Thus the observed activation parameters add strong support to an electron-transfer model for the quenching process.

Eu(III)– RuL_3^+ Reactions. The logarithms of the rate constants for the oxidation of RuL_3^+ by Eu(III) are plotted against $E^\circ_{2+,+}$ (vs. SCE in acetonitrile) in the lower portion of Figure 3. The five points are roughly collinear and there is an increase in rate with increasing driving force as anticipated from eq 12. Remarkably enough, if $10^8 M^{-1} s^{-1}$ is taken as an estimate of the RuL_3^{2+}/RuL_3^+ self-exchange rate,³ the observed rate constants for all five systems lie within a factor of 3 of the values calculated from eq 12. This gives rise to an unusual situation. For these “back-reactions” $\log K_{12}$ ranges from 11.9 to 14.1. For other europium reactions in this free energy range the discrepancy between observed and calculated rate constants is much larger with the observed rate constants generally being about a factor of 30 slower than those obtained from the Marcus equation.¹⁷ In addition although all the observed Eu(III)– RuL_3^+ rate constants are within a factor of 3 of the calculated values, the deviation from theory is systematic. At lower free energy the observed rate constants are larger than predicted; at larger driving force they are smaller than predicted. Thus the slope for the data presented in Figure 3b is only 0.12 while that predicted by eq 12 is 0.26 (after *f* corrections). By contrast the quenching reactions were at least 100 times too slow but the slope of the Marcus plot for those data (0.26) was actually slightly larger than predicted from eq 12 (0.21). It is not obvious how such observations can be rationalized or even reconciled with each other. The quenching and back-reactions involve different orbitals on the RuL_3^{n+} species. Reductive quenching involves a ruthenium t_{2g} acceptor orbital while the thermal back-reactions involve a ligand π^* donor orbital. Perhaps poor overlap of the Eu(II) 4f orbital with the $*RuL_3^{2+}$ d orbital gives rise to nonadiabatic behavior¹⁷ in the reductive quenching (and other reactions of Eu_{aq}^{2+} with metal complexes¹⁷) while the Eu(III)– $*RuL_3^{2+}$ (oxidative quenching involving the $*RuL_3^{2+} \pi^*$ orbital³) and Eu(III)– RuL_3^+ reactions are “well-behaved” as a consequence of good orbital overlap. Unhappily such a simple model will not account for the incorrect driving force dependence of the Eu(III)– RuL_3^+ reactions. A quantitative rationalization of the observed behavior must await the results and insights of other studies.

Acknowledgment. This work was performed at the Brookhaven National Laboratory under contract with the U.S. Energy Research and Development Administration and

supported by its Division of Basic Energy Sciences. The author gratefully acknowledges the assistance of Drs. W. D. K. Clark and G. Brown in the cyclic voltammetric studies and invaluable discussions with Dr. N. Sutin.

Registry No. Ru(4,4'-(CH₃)₂bpy)₃²⁺, 32881-03-1; Ru(bpy)₃²⁺, 15158-62-0; Ru(4,7-(CH₃)₂phen)₃²⁺, 24414-00-4; Ru(phen)₃²⁺, 22873-66-1; Ru(5-Cl-phen)₃²⁺, 47860-47-9; Ru(4,4'-(CH₃)₂bpy)₃³⁺, 65605-26-7; Ru(bpy)₃³⁺, 56977-24-3; Ru(4,7-(CH₃)₂phen)₃³⁺, 65545-47-3; Ru(phen)₃³⁺, 65545-46-2; Ru(5-Cl-phen)₃³⁺, 65545-45-1; Eu(II), 16910-54-6; Eu(III), 22541-18-0.

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Photoreaction Quantum Yields for the Cobalt(III) Complexes Co(NH₃)₅(PhCN)³⁺ and Co(NH₃)₅(CH₃CN)³⁺ 1

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Received September 14, 1977

The nature and quantum yield of the photoreactions which take place on irradiation of aqueous Co(NH₃)₅(CH₃CN)³⁺ and Co(NH₃)₅(PhCN)³⁺ have been examined. Excitation at 254 nm corresponds to direct charge-transfer to metal excitation of Co(NH₃)₅acn³⁺ (acn = acetonitrile) and to intraligand (IL) π-π* excitation of Co(NH₃)₅bzn³⁺ (bzn = benzonitrile). In both cases photoreduction to Co²⁺ is the predominant reaction but the former complex is the considerably more active. Thus, it is argued that the IL ππ* state can undergo internal conversion to give a redox-active CTTM state but also may have independent pathways for deactivation perhaps including internal conversion to the lower energy ligand field states. At 313-nm excitation the relative redox activity is reversed, suggesting that the IL ππ* states of Co(NH₃)₅bzn³⁺ provide a more facile channel for populating the CTTM states than do the LF states of Co(NH₃)₅acn³⁺ produced at this wavelength. Lastly 365- and 460-nm photolyses which correspond to LF excitation in both cases lead principally to aquation of the coordinated organonitriles despite the higher position on the spectrochemical series of these ligands compared to NH₃. At 460 nm the quantum yields for RCN aquation (0.010 mol/einstein) greatly exceed those for ammonia aquation from the same complex (<0.001 mol/einstein) or from Co(NH₃)₆³⁺ (0.0005 mol/einstein). In this context, the patterns for ligand photoaquation from various M(NH₃)₅L³⁺ and M(NH₃)₅X²⁺ (M = Co(III), Rh(III), Ir(III); L = RCN, H₂O; X = Cl⁻, Br⁻, I⁻) are compared and discussed qualitatively in terms of metal-ligand bonding in ligand field excited states.

Introduction

Previous studies³⁻⁶ in this laboratory have been concerned with the quantitative photochemistry of various heavier group 8 metal ammine complexes of the general formula M(NH₃)₅Lⁿ⁺. Ligands L which have proved especially interesting have been π-unsaturated, nitrogen-donor organic ligands such as the organonitriles (RCN) and the aromatic nitrogen heterocycles (e.g., pyridine). The use of substituents at positions on L remote from the coordination site allows one to examine series of complexes displaying wide variations in the ligand properties (i.e., σ-donor ability, π-acceptor/π-donor character, etc.) yet having the same stereochemical environment at the coordination site. Such perturbations of ligand properties not only may lead to systematic variations of metal-ligand bonding in the ground and excited states but also in some cases can be used to tune excited-state energies.^{3a,d} Another advantage is that these organic ligands generally carry no ionic charge, thus minimizing this contribution to the complexity of comparing the relative ligand photosubstitution pathways of L and of NH₃.

The organonitriles display some unusual aspects as ligands. Despite the poor σ-donor ability suggested by its low Brønsted

basicity, acetonitrile forms a wide variety of complexes.^{7,8} In addition, spectroscopic series based on the positions of ligand field (LF) bands in the absorption spectra of various d⁶ complexes^{8,9} show acetonitrile to have a ligand field strength comparable to or greater than that of ammonia. It has been argued that the strength of the metal-acetonitrile interactions must include significant π-bonding contributions. For example, π back-bonding to acetonitrile is clearly evident in lower valent metal complexes such as those of ruthenium(II)¹⁰ and can be invoked^{4a} to explain the relatively strong-field spectroscopic behavior of rhodium(III) pentaammine complexes Rh(NH₃)₅RCN³⁺. Similar rationalizations have been introduced¹¹ to explain the observation that while gas-phase binding energies between saturated ligands and the cyclopentadienylnickel cation (CpNi⁺) display a linear correlation with the gas-phase proton affinities, acetonitrile displays a much higher metal binding energy than would be predicted according to its proton affinity.

In the present work, we have studied the pentaamminecobalt(III) complexes of acetonitrile and benzonitrile with the goal of examining the generality of the photochemical properties of analogous organonitrile complexes for different