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Enantioselectivities in Electron-Transfer and Excited State Quenching Reactions of a Chiral Ruthenium Complex Possessing a Helical Structure

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The outer-sphere electron-transfer reactions between diastereomers of Ru(menbpy)$_3^{\bullet+}$ (menbpy = 4,4′-di-{(1*R*,2*S*,5*R*)-(−)-menthoxycarbonyl}-2,2′-bipyridine) and enantiomers of Co(acac)$_3$ and Co(edta)$^-$ have been studied by pulse radiolysis. Δ-Ru(menbpy)$_3^{\bullet+}$ rapidly reduces Co(acac)$_3$ in 85% EtOH/H$_2$O (1 mM NaH$_2$PO$_4$) with second-order rate constants of $(2.1 \pm 0.1) \times 10^7$ and $(7.8 \pm 0.2) \times 10^6$ M^{-1} s^{-1} for the Δ- and Λ-Co(acac)$_3$ enantiomers, respectively, and an enantioselectivity factor $(k_{et}^{\Delta}/k_{et}^{\Lambda})$ of 2.7. Λ-Ru(menbpy)$_3^{\bullet+}$ preferentially reduces Λ-Co(acac)$_3$ with an enantioselectivity factor $(k_{et}^{\Delta}/k_{et}^{\Lambda})$ of 0.8. Activation volume data ($\Delta V^{\ddagger}$) suggest that the association between the Δ−Δ isomers in the encounter complex allows closer interaction of the metal centers than between the other isomer combinations. The value of $k_{et}^{\Delta}/k_{et}^{\Lambda}$ for the reaction of Δ- and Λ-Co(edta)$^-$ with Δ-Ru(menbpy)$_3^{\bullet+}$ is 1.2. Electron-transfer reactions of seven racemic Ru(L)$_3^{\bullet+}$ (L = substituted phenanthroline) complexes with Co(acac)$_3$ were also studied and gave rate constants of $\approx 1.5 \times 10^9$ M^{-1} s^{-1}. The quenching of photoexcited *Ru(menbpy)$_3^{2+}$ by Co(acac)$_3$ and Co(edta)$^-$ exhibits small stereoselectivity: For Co(acac)$_3$ in 95 and 85% EtOH/H$_2$O the enantioselectivity factor is 1.2 and 1.1, respectively, barely outside the experimental error. For all other cases the selectivity was unity within the experimental error of the measurement. The quenching rate constants were $\approx 1 \times 10^8$ and 1.1×10^9 M^{-1} s^{-1} for Co(acac)$_3$ and Co(edta)$^-$, respectively. Quenching reactions of seven racemic ruthenium(II) phenanthroline complexes with Co(acac)$_3$ were also studied and found to be faster than those of Ru(menbpy)$_3^{2+}$ by only a factor of ≈3 despite an increase in the driving force of ≈0.5 eV for electron-transfer quenching. The quenching of *Ru(menbpy)$_3^{2+}$ by Co(acac)$_3$ is dominated by an energy-transfer mechanism. This conclusion is supported by the magnitude of the quenching rate constants compared with the rate constants for reduction by Ru(menbpy)$_3^{\bullet+}$, the effect of driving-force changes on the quenching rate constant, the low quantum yield of Co(II) products observed in the CW photolysis, and the lack of long-lived products observed in the flash photolysis experiments. The factors responsible for the selectivity exhibited in the CW photolysis studies of Ru(menbpy)$_3^{2+}$ with Co(acac)$_3$ are discussed.

Introduction

Enantioselective chemical reactions are of long-standing interest. Many of these reactions can be understood in terms of strong interactions between the reactants that can result in very large enantioselectivity factors. However, for reactions that involve weak interactions between reactants, such as outer-sphere electron or energy transfer between optically active isomers of coordination complexes, much smaller enantioselectivity factors are expected. In line with these expectations, only very modest enantioselectivity factors ($k^{\Delta}/k^{\Lambda} = 1 \pm 0.2$) have been observed for such electron-transfer reactions.[1−7] Recently, a number of observations have challenged these expectations. Energy-transfer reactions between lanthanide(III) complexes and a series of ruthenium(II) or cobalt(III) complexes have shown quenching rates that differ by up to a factor of 4 between enantiomers.[8−12]

Enantioselectivity factors as large as 92 have been reported in the photocatalytic reduction of Co(acac)$_3$ (acac = acetylacetonate) by a chiral ruthenium(II) complex Δ-Ru(menbpy)$_3^{2+}$ (menbpy = 4,4′-di{(1*R*,2*S*,5*R*)-(−)-menthoxycarbonyl}-2,2′-bipyridine),[13−18] shown in Figure 1.

Photocatalytic reactions consist of a series of elementary steps, e.g., formation of an encounter complex between the photoexcited sensitizer and quencher, electron and/or energy transfer within the encounter complex, back electron transfer, charge separation, and catalyst regeneration. While a mechanism has been proposed for the Ru(menbpy)$_3^{2+}$ based photocatalytic system, it has not been experimentally validated nor have the enantioselectivity of the individual steps been measured.

Preliminary reports on the steady-state quenching of the excited-state emission of *Ru(menbpy)$_3^{2+}$ by Co(acac)$_3$ have shown significant enantioselectivity;[14,19] however, the effect is much smaller than that observed in the catalytic system. Thus

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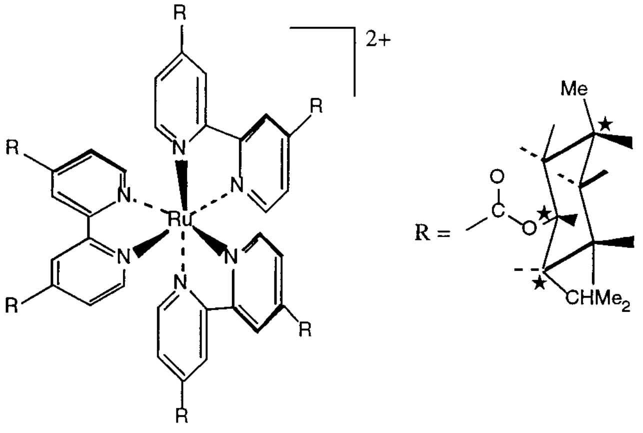
TABLE 1: Quantum Yields, Redox Potentials,[a] Quenching Rate Constants for the Reaction of $^*Ru(phen)_3^{2+}$ Derivatives with $Co(acac)_3$ in 50% EtOH/H_2O and Electron-Transfer Rate Constants for the Reaction of $Ru(phen)_3^{\bullet+}$ Derivatives with $Co(acac)_3$

phen derivative[b]	quantum yield[c]	$E^{3+/2+}$, V vs NHE[a]	$E^{2+/\bullet+}$, V vs NHE[a]	$E^{3+/*2+}$, V vs NHE[a]	$10^{-8}\,k_q$,[c,d] $M^{-1}\,s^{-1}$	$10^{-9}\,k_{et}$,[e] $M^{-1}\,s^{-1}$
3,5,6,8-tmp		+1.09	−1.52	−1.04	4.9	1.66 ± 0.03
4,7-dmp	0.059	+1.09	−1.47[g]	−1.01	6.6	1.75 ± 0.02
5,6-dmp	0.10	+1.20	−1.40	−0.93	4.8	1.42 ± 0.03
5-mp	0.041	+1.23	−1.38	−0.90	4.8	1.62 ± 0.03
phen	0.025	+1.26	−1.36	−0.87	4.4	1.42 ± 0.09
5-Cl-phen	0.039	+1.36	−1.20	−0.77	3.7	1.29 ± 0.03
5-Br-phen	0.038	+1.37	−1.4	−0.76	4.5	1.66 ± 0.01

[a] All potentials are measured in acetonitrile and corrected to water, see text and ref 24. [b] Abbreviations: dmp, dimethylphenanthroline; mp, methylphenanthroline; tmp, tetramethylphenanthroline. [c] 1.0 mM NaH_2PO_4. [d] Standard deviations for the quenching rate constants are 2−5% between independently prepared samples. [e] 1.0 mM NaOH.



Δ-$Ru(menbpy)_3^{2+}$

Figure 1. Structure of $Ru(menbpy)_3^{2+}$ (menbpy = 4,4′-di{(1*R*,2*S*,5*R*)-(−)-menthoxycarbonyl}-2,2′-bipyridine).

the quenching of excited $Ru(menbpy)_3^{2+}$ by $Co(acac)_3$ occurs with much less stereoselectivity than the overall photoreduction of $Co(acac)_3$. This suggests that the extremely large enantioselectivity of the photoreduction is not solely due to differences in the quenching rate constants for the isomers.

To obtain more detailed information on the quenching mechanism and the factors that control enantioselectivity, a pulse radiolysis/flash photolysis study of the electron-transfer reactions of optically resolved $Ru(menbpy)_3^{2+}$ complexes was undertaken. In this paper, we report studies of the reactions of $Ru(menbpy)_3^{\bullet+}$ and photoexcited $^*Ru(menbpy)_3^{2+}$ with enantiomers of $Co(acac)_3$ and $Co(edta)^-$, including the observation of large differences in the rates of stereoselective thermal electron transfer between transition-metal complexes. Evidence is also presented that the quenching of $^*Ru(menbpy)_3^{2+}$ by $Co(acac)_3$ or $Co(edta)^-$ proceeds primarily by energy transfer.

Experimental Section

Materials. 4,4′-Di{(1*R*,2*S*,5*R*)-(−)-menthoxycarbonyl}-2,2′-bipyridine (menbpy) was synthesized from menthol and 4,4′-dicarboxy-2,2′-bipyridine by an acid chloride method.[20] Anal. Calcd (%) for $C_{32}H_{44}N_2O_4$: H: 8.52, C: 73.81, N: 5.38. Found (%) H: 8.51, C: 73.79, N: 5.29. Δ-$Ru(menbpy)_3Cl_2$ was synthesized from $RuCl_3{\cdot}nH_2O$ and optically pure menbpy in ethanol, as previously reported.[14] The diastereomers, designated as Δ and Λ according to the orientations of the bipyridine ligands, were separated by silica gel column chromatography (eluant: chloroform/MeOH 95:5 v/v). Δ-$Ru(menbpy)_3Cl_2$ was obtained from the first fraction[14] and Λ-$Ru(menbpy)_3Cl_2$ was obtained from the second fraction (yield 20% for Δ-$Ru(menbpy)_3Cl_2$ and 2% for Λ-$Ru(menbpy)_3Cl_2$). Molar circular dichroism ($\Delta\epsilon$) values for Δ-$Ru(menbpy)_3^{2+}$ are 30.6 and −23.6 $mol^{-1}\,dm^3\,cm^{-1}$ at 435 and 485 nm, respectively, in 95% EtOH/H_2O, and those for Λ-$Ru(menbpy)_3^{2+}$ are −29 and +20 $mol^{-1}\,dm^3\,cm^{-1}$ at 435 and 487 nm, respectively in 95% EtOH/H_2O.[21−23]

$Ru(phen)_3(ClO_4)_2$ and its derivatives were prepared as reported previously.[24] Δ-$Co(acac)_3$ and Λ-$Co(acac)_3$ were prepared, as reported previously.[25] Their optical purity was confirmed from CD spectra; for Δ-Co(acac) in 95% EtOH/H_2O, $\Delta\epsilon$ values are +2.99 and −8.58 $mol^{-1}\,dm^3\,cm^{-1}$ at 645 and 570 nm, respectively (literature values:[25] +2.88 and −8.11 $mol^{-1}\,dm^3\,cm^{-1}$ at 647 and 574 nm, respectively, in EtOH); for Λ-$Co(acac)_3$ in 95% EtOH/H_2O: −3.22 and +8.23 $mol^{-1}\,dm^3\,cm^{-1}$ at 645 and 570, respectively (literature values:[26] −2.3 and +6.1 $mol^{-1}\,dm^3\,cm^{-1}$ at 650 and 575 nm, respectively, in isopentane/ethyl ether). Δ- and Λ-$Co(edta)^-$ were prepared as reported previously.[27,28] Their optical purities were confirmed by CD spectra; for Δ-$Co(edta)^-$ in water, −1.91 and +0.82 $mol^{-1}\,dm^3\,cm^{-1}$ at 586 and 504 nm, respectively (literature values:[29] in water, −1.79 and +0.83 $mol^{-1}\,dm^3\,cm^{-1}$ at 575 and 500 nm, respectively); for Λ-$Co(edta)^-$ in water, +1.79 and −0.86 $mol^{-1}\,dm^3\,cm^{-1}$ at 585 and 502 nm, respectively (literature values:[30] +1.71 $mol^{-1}\,dm^3\,cm^{-1}$ at 588 nm in H_2O).

Sample Preparation. Since $Ru(menbpy)_3Cl_2$ is only sparingly soluble in water, 85% EtOH/H_2O (v/v) [pure or with 0.2 mM pH 7 phosphate buffer ($[NaH_2PO_4] = [Na_2HPO_4]$) or with 1.0 and 5.0 mM NaH_2PO_4 (pH ≈ 5.7)] or 50% EtOH/H_2O [pure or with 0.2 or 1 mM pH 7 phosphate buffer media] was used in the experiments. In the pressure experiments, 60% EtOH/H_2O with 0.2 or 1.0 mM phosphate media was used due to the compressibility of solutions with higher EtOH concentrations.

Pulse Radiolysis. Electron pulse radiolysis was carried out with the 2 MeV Van de Graaff accelerator at Brookhaven National Laboratory using a PC-controlled CAMAC-based data acquisition and control system. Transient UV−vis spectral measurements under high pressure were made with a quartz pillbox cell using a high-pressure vessel.[31,32]

Laser Flash Photolysis. Laser flash photolysis was carried out with 355 nm laser pulses from a Continuum Surelite I-10 laser system (6 ns pulse width). The emission of the ruthenium(II) complex was monitored with a PMT and the output recorded on a Hewlett-Packard 54510A digital oscilloscope. The data were analyzed using nonlinear least-squares fitting routines written in MATLAB.

Cyclic Voltammetry. Redox potentials were obtained by cyclic voltammetry using a BAS 100B electrochemical analyzer at a scan rate of 100 mV s^{-1}. The electrochemical cell used a glassy carbon working electrode, a SCE reference, and a platinum counter electrode. The acetonitrile solutions contained 1 mM ruthenium(II) complex and 0.1 M tetrapropylammonium perchlorate as electrolyte.

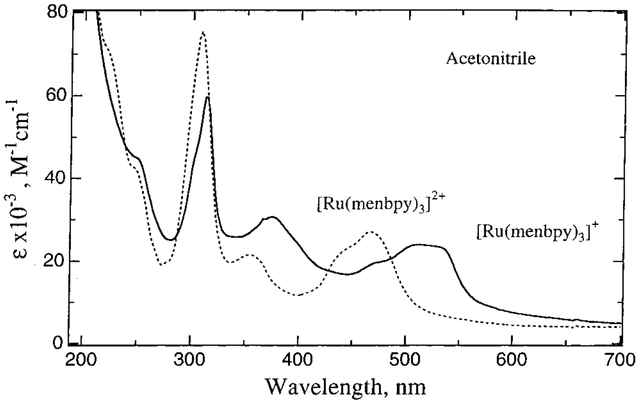


Figure 2. Absorption spectrum of $Ru(menbpy)_3^{2+}$ and $Ru(menbpy)_3^{+}$ produced by Na−Hg reduction in acetonitrile.

Spectroscopy. Circular Dichroism spectra were measured with either a JASCO-J500C or J720 circular dichroism spectropolarimeter at 25 °C. The CD instrument was standardized using ammonium d-10-camphorsulfonate.[33] UV−vis spectra were recorded with a Hewlett-Packard 8452A spectrophotometer.

Quantum Yield Measurements. Quantum yields for the photoreduction of the Co(III) complex were measured as Φ_{obsd} = [moles of photoreduced Co(III) complex]/[Einsteins of photon absorbed by the Ru complex]. In the present experiments $[Co(acac)_3]$ = 2.4 mM, $[Ru(menbpy)_3^{2+}]$ = 32 μM, and λ_{ex} = 436 nm. In this solution the $Co(acac)_3$ absorbs about half of the actinic light. The incident light intensity was measured by ferrioxalate actinometry.[34]

Results

Electrochemistry. Cyclic voltammetry of the complex yielded values for $E°$ of 1.55 V vs SCE for $Ru(menbpy)_3^{3+/2+}$ and −0.90 V vs SCE for $Ru(menbpy)_3^{2+/+}$ in acetonitrile. The $E°$ values in water vs NHE are estimated to be close to the values obtained in acetonitrile vs SCE. This is because the ferricenium/ferrocene redox potential shifts by 0.25 V (vs SCE) on going from acetonitrile to water while the SCE potential in water is 0.24 V.[35,36] The reduction potentials for $Ru(menbpy)_3^{3+/*2+}$ and $Ru(menbpy)_3^{*2+/+}$ are estimated as −0.45[13] and +1.10 V, respectively. The reduction potentials for $Co(acac)_3$ and $Co(edta)^-$ were determined previously to be −0.34[37] and +0.13[38] V vs SCE in CH_3CN, respectively. Reduction potentials of the substituted ruthenium phenanthroline complexes ($RuL_3^{3+/2+}$ and $RuL_3^{2+/+}$) were measured in CH_3CN (Table 1) and confirmed previously published values.[24,39] The values for $RuL_3^{2+/+}$, where L = 5-methylphenanthroline, 5,6-dimethylphenanthroline, and 5-bromophenanthroline, are close to those estimated previously.[39]

Pulse Radiolysis. The spectra of $Ru(menbpy)_3^{2+}$ and $Ru(menbpy)_3^{\bullet+}$ (prepared by Na−Hg reduction in sealed glassware) in acetonitrile are shown in Figure 2. In the pulse radiolysis experiments, Δ-$Ru(menbpy)_3^{2+}$ was reduced by the ethanol radical $CH_3C^{\bullet}HOH$ formed by the reaction of $H^{\bullet}$ and $OH^{\bullet}$ with ethanol in N_2O-saturated solution. The dose-corrected absorbance changes from the pulse-radiolysis experiments in N_2O-saturated $EtOH/H_2O$ agree well with the difference spectrum in acetonitrile, indicating the formation of the ligand-centered radical $Ru(menbpy)_3^{\bullet+}$ (Figure 3). Although the $CH_3C^{\bullet}HOH$ radical does not reduce $Ru(bpy)_3^{2+}$ at pH 7 ($E° \approx -1.3$ V vs NHE),[40−42] the reduction potential of $Ru(menbpy)_3^{2+/+}$ is significantly more positive, −0.90 V vs NHE in water. $CH_3C^{\bullet}HOH$ (−1.25 V at pH 7)[43] reduces $Ru(menbpy)_3^{2+}$ with a rate constant of (8.2 ± 0.5) × 10^8 M^{-1} s^{-1}. Radiolytic reduction of the Λ-$Ru(menbpy)_3^{2+}$ isomer yields an absorption spectrum that is the same as that of Δ-$Ru(menbpy)_3^{\bullet+}$.

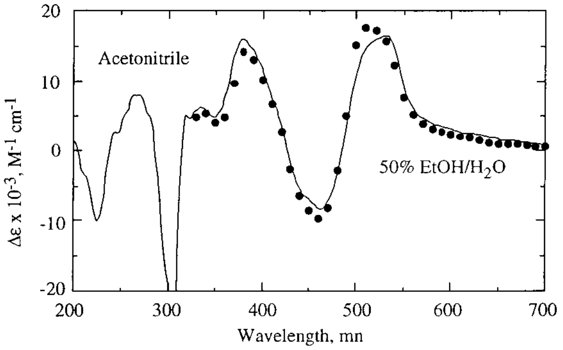


Figure 3. Difference absorption spectrum generated by pulse radiolysis of $Ru(menbpy)_3^{2+}$ (10 μM in N_2O-saturated 50% $EtOH/H_2O$ 1 mM NaH_2PO_4) (dotted line) and difference spectrum calculated from Figure 2 (solid line).

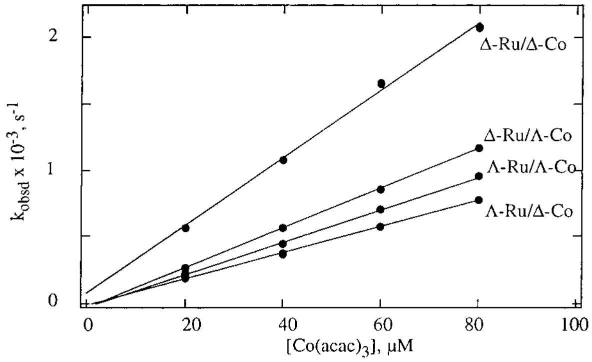


Figure 4. Observed rate constant vs concentration of $Co(acac)_3$ for the electron transfer from Δ- or Λ-$Ru(menbpy)_3^{2+}$ to Δ or Λ-$Co(acac)_3$ in 85% $EtOH/H_2O$ by pulse radiolysis.

Δ-$Ru(menbpy)_3^{\bullet+}$, generated by the pulse radiolysis, rapidly reduces $Co(acac)_3$ in 85% $EtOH/H_2O$ (1 mM NaH_2PO_4) with second-order rate constants (k_{et}) of (2.1 ± 0.1) × 10^7 and (0.78 ± 0.02) × 10^7 M^{-1} s^{-1} for the Δ- and Λ-$Co(acac)_3$ isomers, respectively (Figure 4 and Table 2). Thus Δ-$Co(acac)_3$ is preferentially reduced with an enantioselectivity factor ($k_{et}^{\Delta}/k_{et}^{\Lambda}$) of 2.7. With increasing phosphate concentration in either 85% or 50% $EtOH/H_2O$ the second-order rate constant for reduction of $Co(acac)_3$ varies by only a very small amount. The Λ-$Ru(menbpy)_3^{\bullet+}$ complex favors reduction of the Λ-$Co(acac)_3$ isomer, with an enantioselectivity factor of 0.8 (1/1.25) in 85% $EtOH/H_2O$.

The temperature dependence of the rate constants was studied and gave linear Eyring plots of log(k_{et}/T) vs T^{-1}. The pressure dependence of the rate constants for the Δ-ruthenium isomer is shown in Figure 5. The derived activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$) are summarized in Table 3.

The rate constants for the reaction of Δ-$Ru(menbpy)_3^{\bullet+}$ with the two optical isomers of $Co(edta)^-$ are also reported in Table 2. The enantioselectivity is much smaller. The reactions of $Co(acac)_3$ with seven derivatives of $Ru(phen)_3^{2+}$ were also studied (Table 1) in order to compare rate constants with those of $Ru(menbpy)_3^{\bullet+}$.

Photochemistry. The emission quantum yield for $Ru(menbpy)_3^{2+}$ was determined by comparing the integrated emission intensity of $Ru(menbpy)_3^{2+}$ in 50% $EtOH/H_2O$ (0.5 mM phosphate) with that of $Ru(bpy)_3^{2+}$ in H_2O (with a known

TABLE 2: Rate Constants for the Electron Transfer between $Ru(menbpy)_3^{\bullet +}$ and Cobalt(III) Complexes

Ru isomer	Co(III) complex	solvent, % EtOH	[Phos],[a] mM	$10^{-7}k^{\Delta}$, M^{-1} s^{-1}	$10^{-7}k^{\Lambda}$, M^{-1} s^{-1}	selectivity (k^{Δ}/k^{Λ})
Δ	$Co(acac)_3$	85	0	2.3 ± 0.05	1.11 ± 0.03	2.1
			0.2	2.6 ± 0.1	1.5 ± 0.1	1.7
			1.0[b]	2.1 ± 0.1	0.78 ± 0.02	2.7
			5.0[b]	2.6 ± 0.2	0.87 ± 0.01	2.9
		50	0.2	2.5 ± 0.1	1.3 ± 0.1	1.9
			1.0	1.7 ± 0.1	0.81 ± 0.02	2.1
Λ	$Co(acac)_3$	85	0.2	0.99 ± 0.02	1.23 ± 0.03	0.8
Δ	$Co(edta)^-$	50	1.0	2.3 ± 0.2	2.0 ± 0.1	1.2

[a] [Phos] = $[Na_2HPO_4] + [NaH_2PO_4]$, $[Na_2HPO_4] = [NaH_2PO_4]$. [b] [Phos] = $[NaH_2PO_4]$.

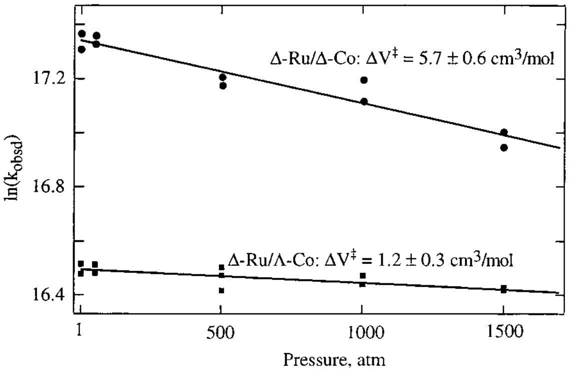


Figure 5. Pressure effects on electron transfer from Δ-$Ru(menbpy)_3^{2+}$ to Δ/Λ-$Co(acac)_3$ in 60% $EtOH/H_2O$ studied by pulse radiolysis.

emission quantum yield of 0.042[44,45]). The emission quantum yield of $Ru(menbpy)_3^{2+}$ is 0.052 at 25 °C. The lifetimes of the long-lived excited state of $Ru(menbpy)_3^{2+}$ in 95, 85, and 50% $EtOH/H_2O$ are given in Table 4. The lifetime of $Ru(menbpy)_3^{2+}$ has been reported as 1.46[16] and 1.55[22] μs in EtOH, close to the value of 1.57 μs we observe in 85% $EtOH/H_2O$. The lifetime of $Ru(menbpy)_3^{2+}$ is independent of isomer and is slightly affected by temperature and phosphate concentration, as shown in Figures 6 and 7, respectively. The activation parameters for the decay of the long-lived excited state of either isomer (Δ or Λ) of $Ru(menbpy)_3^{2+}$ are $\Delta H^{\ddagger} = -0.1 \pm 0.1$ kcal/mol and $\Delta S^{\ddagger} = -32.5 \pm 0.3$ eu in 85% $EtOH/H_2O$ (no phosphate) between 5 and 45 °C. The lifetime decreases by about 20% when the phosphate concentration is increased from 0 to 0.2 mM. The lifetime increases with EtOH concentration from 1.3 to 1.8 μs in 50−95% $EtOH/H_2O$.

The excited state of Δ-$Ru(menbpy)_3^{2+}$ is quenched by $Co(acac)_3$ with rate constants (k_q) of 9.0×10^7 and 7.7×10^7 M^{-1} s^{-1} for Δ- and Λ-$Co(acac)_3$, respectively, in 95% $EtOH/H_2O$ (enantioselectivity factor 1.2). In 85% $EtOH/H_2O$ the enantioselectivity factor decreased to 1.1 (barely larger than our experimental error). The rate constant for the quenching of Λ-$Ru(menbpy)_3^{2+}$ by either Δ- or Λ-$Co(acac)_3$ is $(8.7 \pm 0.1) \times 10^7$ M^{-1} s^{-1}; see Table 4. The enantioselectivity factor for Δ-$Ru(menbpy)_3^{2+}$ is 1.2, while the Λ isomer shows no enantioselectivity. As shown in Figure 8, activation parameters for the quenching of *Δ-$Ru(menbpy)_3^{2+}$ by Δ-$Co(acac)_3$ are $\Delta H^{\ddagger} = 2.0 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -15.5 \pm 0.5$ eu in 85% $EtOH/H_2O$ (no phosphate), while the parameters for the reactions of all the other isomers (Δ-$Ru(menbpy)_3^{2+}$ with Λ-$Co(acac)_3$ or Λ-$Ru(menbpy)_3^{2+}$ with Δ- or Λ-$Co(acac)_3$ are $\Delta H^{\ddagger} = 1.5 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -17 \pm 1$ eu (85% $EtOH/H_2O$ no phosphate). The quenching rate constants decrease by a factor of 2, and the enantioselectivity factor increases with increasing EtOH concentration from 50 to 95%.

Note that the quenching rate constants are 1 order of magnitude greater than those for the reduction of $Co(acac)_3$ by $Ru(menbpy)_3^{\bullet +}$ (k_{et}) (Table 2). Transient absorbance measurements showed no evidence of any transient species that persists after the disappearance of the ruthenium excited state. The rate constants for the quenching of the excited state of Δ-$Ru(menbpy)_3^{2+}$ by the two isomers of $Co(edta)^-$ are also given in Table 4 and indicate no enantioselectivity.

The quantum yield of Co(II) from the quenching of $Ru(menbpy)_3^{2+}$ by $Co(acac)_3$ (2.41 mM) in 85% $EtOH/H_2O$ with 0.2 mM phosphate gave $\Phi_{obsd} = 0.13\%$. Not all of the excited ruthenium complex is quenched by the $Co(acac)_3$, thus Φ_{obsd} was corrected for the fraction of *$Ru(menbpy)_3^{2+}$ quenched by the cobalt complex using

$$\Phi_{Co(II)} = \Phi_{obsd}\left[\frac{k_0 + k_q[Co(II)]}{k_q[Co(II)]}\right] \qquad (1)$$

where k_q is the second-order rate constant for the quenching reaction, $k_o = 1/\tau_o$, τ_o is the lifetime of the *$Ru(menbpy)_3^{2+}$ with no quencher present and $\Phi_{Co(II)}$ is the percentage of the quenching events that yield Co(II) products. This correction gives $\Phi_{Co(II)} = 0.6\%$.

The quenching of the excited states of seven derivatives of $Ru(phen)_3^{2+}$ by $Co(acac)_3$, Table 1, was studied to more fully understand the quenching mechanism. Transient absorbance measurements indicated that the only observable transient species was the ruthenium(II) excited state. The emission quantum yields in 50% $EtOH/H_2O$ are also given in Table 1. The rate constant for the quenching of the excited state of Δ-$Ru(menbpy)_3^{2+}$ by $acac^-$ in 0.3 M NaOH is 1.8×10^7 M^{-1} s^{-1}.

Discussion

The $Ru(menbpy)_3^{\bullet +}$ spectrum obtained by Na−Hg reduction (Figure 2) is essentially the same as that of $Ru(bpy)_3^{\bullet +}$, which contains a bpy-centered radical.[46,47] Thus $Ru(menbpy)_3^{\bullet +}$ can also be characterized as a Ru(II) center with a menbpy anion radical; the extra electron occupies a π* orbital of the ligand. This is not surprising since the one-electron reduction of menbpy occurs more easily than the reduction of bpy due to the electron-withdrawing −COOR groups.

The dose-corrected transient-absorption difference spectrum generated by pulse radiolysis is consistent with that calculated from the measured spectra of $Ru(menbpy)_3^{\bullet +}$ and $Ru(menbpy)_3^{2+}$ in CH_3CN (Figure 3). The reaction observed in the pulse radiolysis experiments after the initial reduction of $Ru(menbpy)_3^{2+}$ is the oxidation of $Ru(menbpy)_3^{\bullet +}$ by either $Co(acac)_3$ or $Co(edta)^-$ to produce $Ru(menbpy)_3^{2+}$ and the reduced cobalt complex. The reduced $Co(acac)_3^-$ will react further by losing $acac^-$ ligands to produce an equilibrium mixture of $Co(acac)_2$/$Co(acac)_3^-$ complexes. The enantioselectivity factor of 2.7 for electron transfer in the Δ-$Ru(menbpy)_3^{\bullet +}$/$Co(acac)_3$ case is dramatic.

TABLE 3: Activation Parameters ($\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta V^\ddagger$) for the Reaction between $Ru(menbpy)_3^{\bullet +}$ and $Co(acac)_3$

$Ru(menbpy)_3^{\bullet +}$ isomer	$Co(acac)_3$ isomer	$10^{-7}k,^a$ M^{-1} s^{-1}	$\Delta H^\ddagger,^a$ kcal mol^{-1}	$\Delta S^\ddagger,^a$ cal mol^{-1} K^{-1}	$\Delta V^\ddagger,^b$ cm^3 mol^{-1}
Δ	Δ	2.4 ± 0.1^d	3.1 ± 0.2^d	-14.6 ± 0.8^d	$+5.7 \pm 0.6^c$
	Λ	0.78 ± 0.02^d	3.6 ± 0.1^d	-14.2 ± 0.4^d	$+1.1 \pm 0.3^c$
Λ	Δ	0.89 ± 0.06^d	3.6 ± 0.2^d	-14.4 ± 0.8^d	-1.3 ± 0.1^d
	Λ	1.23 ± 0.03^d	3.4 ± 0.2^d	-14.4 ± 0.5^d	-0.7 ± 0.6^d

[a] In 85% EtOH/H_2O. [b] In 60% EtOH/H_2O. [c] 1.0 mM NaH_2PO_4. [d] 0.2 mM phosphate, $[Na_2HPO_4] = [NaH_2PO_4]$.

TABLE 4: Lifetimes of the Long-Lived Excited State of $Ru(menbpy)_3^{2+}$ and the Quenching of $^*Ru(menbpy)_3^{2+}$ by Cobalt(III) Complexes

Ru isomer	Co(III) complex	solvent, % EtOH	[Phos],[a] mM	$10^{-7}k^\Delta,^b$ M^{-1}, s^{-1}	$10^{-7}k^\Lambda,^b$ M^{-1}, s^{-1}	selectivity (k^Δ/k^Λ)	lifetime,[b] μs
Δ	$Co(acac)_3$	95	0	9.0	7.7	1.2	1.82
		85	0	9.5	8.6	1.1	1.57
			0.2	10.2	9.4	1.1	1.24
		50	0	17.9	16.6	1.1	1.31
			1.0	19.9	19.0	1	1.15
Λ	$Co(acac)_3$	85	0	8.5	8.8	1	1.57
			0.2	9.3	9.3	1	1.28
racemic	$Co(acac)_3$	50	1.0	21 (racemic)			1.23
Δ	$Co(edta)^-$	50	1.0	118	114		1.15
racemic	$Co(edta)^-$	50	1.0	128 (racemic)			1.28

[a] $[Phos] = [Na_2HPO_4] + [NaH_2PO_4]$, $[Na_2HPO_4] = [NaH_2PO_4]$. [b] Standard deviations for the quenching rate constants and lifetimes are 2−5% between independently prepared samples.

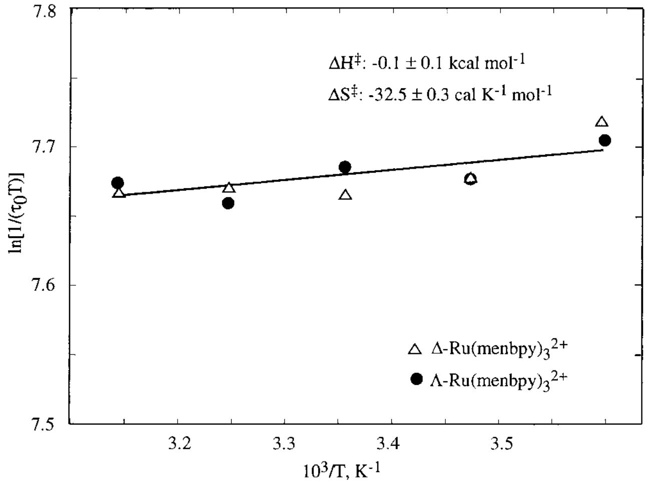


Figure 6. Temperature effects on the lifetime of the long-lived excited state of Δ- and Λ-$Ru(menbpy)_3^{2+}$ in 85% EtOH/H_2O.

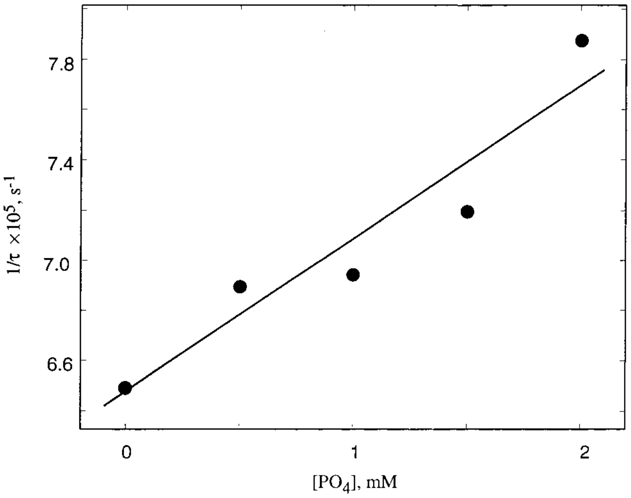


Figure 7. Effect of changes in phosphate concentration on the long-lived excited state of $Ru(menbpy)_3^{2+}$ in 85% EtOH/H_2O.

The outer-sphere electron-transfer reactions can be understood[48−50] in terms of the mechanism shown below:

$$Ru(menbpy)_3^{\bullet +} + Co(acac)_3 \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} Ru(menbpy)_3^{\bullet +}|Co(acac)_3$$

$$Ru(menbpy)_3^{\bullet +}|Co(acac)_3 \xrightarrow{k_{et}} Ru(menbpy)_3^{2+}|Co(acac)_3^-$$

$$Ru(menbpy)_3^{2+}|Co(acac)_3^- \rightleftarrows Ru(menbpy)_3^{2+} + Co(acac)_3^-$$

$$Co(acac)_3^- \rightleftarrows Co(acac)_2 + acac^-$$

where the observed first-order rate constant for the above mechanism when $Co(acac)_3$ is in large excess is given by

$$k_{obsd} = \frac{k_d}{k_{-d} + k_{et}} k_{et}[Co(acac)_3] \qquad (2)$$

where k_d, k_{-d}, and k_{et} are the diffusion-controlled rate of approach of the two reactants, the rate of dissociation of the precursor complex, and the electron-transfer rate constant, respectively. k_d is a function of the charge and size of the two reactants but is not expected to be sensitive to optical isomer. Likewise $\Delta G°$, the overall free-energy change, should not be sensitive to optical isomer. Enantioselectivity can result from differences in either k_{-d} or k_{et}. Differences in the precursor complex, such as tighter binding of one isomer, will modify k_{-d}, and possibly the driving force for the electron-transfer step. Since k_{et} is sensitive to both the distance between the redox centers and the driving force of the electron-transfer step,[48,50] k_{et} would also be expected to change. Thus both steps may contribute to the observed enantioselectivity. Since there are no hydrogen bonds between the redox partners in the precursor complex and the $Co(acac)_3$ has no net charge, the selectivity must be steric in origin, with the solvent and counterion playing a role.

$Ru(menbpy)_3^{2+}$ has two types of chiral centers: the optically active carbon centers of the menthyl groups on the ligands, and the metal center, due to the helical orientation of the bipyridine ligands around the metal (Δ/Λ). Since enantiomerically pure menbpy was used to synthesize the complexes, all the ligands have a single configuration. However, the metal centers of the Δ- and Λ-$Ru(menbpy)_3^{2+}$ isomers have opposite configurations,

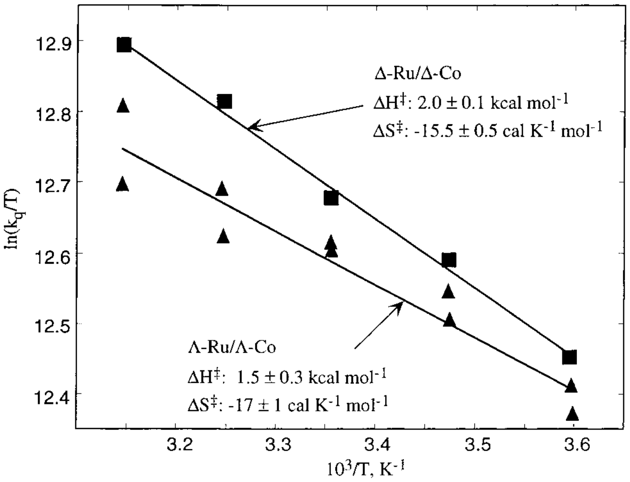


Figure 8. Temperature effects on the quenching of the long-lived excited state of $Ru(menbpy)_3^{2+}$ by $Co(acac)_3$ in 85% $EtOH/H_2O$.

as demonstrated by the CD spectra in the MLCT (450 nm) region. Accordingly, the Δ- and Λ-$Ru(menbpy)_3^{2+}$ isomers are diastereomers not enantiomers.

The Δ-$Ru(menbpy)_3^{\bullet+}$ complex preferentially reduces Δ-$Co(acac)_3$, while Λ-$Ru(menbpy)_3^{\bullet+}$ preferentially reduces Λ-$Co(acac)_3$. If the enantioselectivity were due to the menthyl groups alone, one would expect both Δ- and Λ-$Ru(menbpy)_3^{2+}$ to preferentially reduce the same $Co(acac)_3$ isomer. Alternatively, if only the metal center of the $Ru(menbpy)_3^{2+}$ complex is important, one would expect the $\Delta-\Delta$ rate constant to be the same as the $\Lambda-\Lambda$ rate constant. The fact that this does not happen suggests that the stereoselectivity is influenced by both the helicity at the metal center and the menthyl groups. Reactions of $^*Ru(bpy)_3^{2+}$ type complexes with cobalt complexes have shown both $\Delta-\Delta$ and $\Delta-\Lambda$ enantioselectivity,[2,3,7,51] and it is not known what factors control the selectivity. However, the large selectivity observed here is unusual for an outer-sphere electron-transfer reaction.

There are no remarkable differences in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ among the four combinations of reactants (Table 3). The data in Table 3 indicate that the activation volume is small and negative for the reaction of Λ-$Ru(menbpy)_3^{\bullet+}$ with either Δ- or Λ-$Co(acac)_3$. In a slightly different medium the reaction for Δ-$Ru(menbpy)_3^{\bullet+}$ with Δ-$Co(acac)_3$ is significantly more positive, 5.7 $cm^3\ mol^{-1}$, than that for Δ-$Ru(menbpy)_3^{\bullet+}$ with Λ-$Co(acac)_3$. Thus only the reaction between the $\Delta-\Delta$ isomers exhibits a significant pressure dependence.

The overall reaction volume for an electron-transfer reaction consists of intrinsic and solvational volume changes. The increase in charge for the reactions considered will result in an increase in electrostriction. The volume change associated with changes in electrostriction has been shown to correlate with the difference in the sum of the squares of the charges on the reactants and products.[52] For the $Ru(menbpy)_3^{\bullet+}$ reduction of $Co(acac)_3$ one estimates[52,53] an overall volume change of -16 $cm^3\ mol^{-1}$. For a number of Co(II/III) complexes the intrinsic volume increase found for the reduction of Co(III) to Co(II) is approximately 14 $cm^3\ mol^{-1}$.[54] For the ruthenium complex the metal−ligand bond lengths do not change significantly since the participating electron resides primarily on the ligand and one expects a volume change that is close to zero. Thus one might expect the intrinsic volume increase of the cobalt complex to approximately cancel the volume decrease from electrostriction and result in very small volumes of activation for these reactions, as observed.

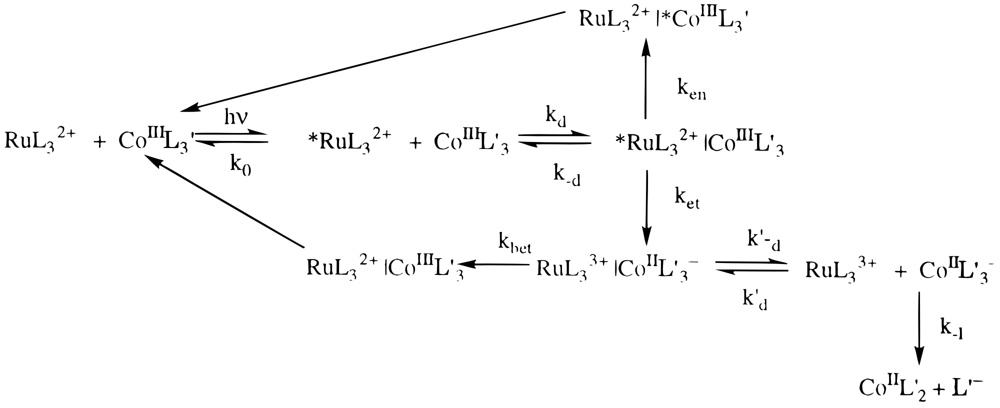
One explanation for the significantly positive $\Delta V^\ddagger$ value for the $\Delta-\Delta$ reaction is that the Δ-metal complexes allow a closer interaction in the precursor complex that requires the partial expulsion of a solvent molecule between the metal centers. The decrease in the distance between the metal centers results in an increase in the metal−metal coupling (as well as a small decrease in the outer shell reorganization energy) that increases the rate constant for the electron-transfer step. The fact that the $\Lambda-\Lambda$ reaction does not show this effect is evidence that the chiral menthyl groups also play an important role in the steric interactions between the metal complexes.

Quenching Reactions. For Δ/Λ-$Co(acac)_3$ in 95 and 85% $EtOH/H_2O$ the rate constants for excited-state quenching show an enantioselectivity factor of 1.2 and 1.1, respectively. For Δ/Λ-$Co(acac)_3$ and Δ/Λ-$Co(edta)^-$ in 50% $EtOH/H_2O$, the quenching rates for the two isomers are the same within experimental error. The enantioselectivity exhibited by Δ/Λ-$Co(acac)_3$ (or Δ/Λ-$Co(edta)^-$) determined in the present study is somewhat smaller than the value of 1.28 previously obtained[14] from steady-state emission measurements in 90% $EtOH/H_2O$. As for the electron-transfer reactions discussed above, the enantioselectivity of the quenching reaction increases with EtOH content, but the effect is small. Transient absorption measurements on the quenching of the excited ruthenium complex show no long-lived products, which suggests that the quenching does not produce any $Ru(menbpy)_3^{3+}$ or reduced cobalt, $Co(acac)_3^-$ or $Co(acac)_2$.

The mechanism of $^*Ru(menbpy)_3^{2+}$ quenching by $Co(acac)_3$ can operate by either energy or electron transfer. Electron-transfer quenching should be sensitive to changes in driving force. The reduction potentials of $Ru(menbpy)_3^{n+}$ are -0.90, $+1.55$, and -0.45 V for $E^{0(2+/+)}$, $E^{0(3+/2+)}$, and $E^{0(3+/*2+)}$, respectively,[16−18] and the reduction potential of $Co(acac)_3$ is ≈ -0.34 V.[37] Thus, the free-energy changes, $\Delta G°$, for the thermal electron-transfer reaction between $Ru(menbpy)_3^{\bullet+}$ and $Co(acac)_3$ and the photochemical electron-transfer reaction between $^*Ru(menbpy)_3^{2+}$ and $Co(acac)_3$ are -0.56 and -0.11 eV, respectively. The relative rates of the $Ru(menbpy)_3^{\bullet+}$ and $^*Ru(menbpy)_3^{2+}$ reactions are surprising in light of these $\Delta G°$ values; despite the much larger driving force for the $Ru(menbpy)_3^{\bullet+}$ reaction, the quenching of the *Ru(II) excited state is 1 order of magnitude faster. The electronic coupling, H_{ab}, is assumed to be similar for the two electron-transfer reactions since the transferring electron for either reaction comes from a ligand π^* orbital. This suggests that the primary quenching mechanism cannot be electron transfer, which is supported by the absence of any long-lived electron-transfer products of the quenching reaction.

The data for the substituted ruthenium phenanthroline complexes, $Ru(phen')_3^{n+}$, also support the conclusion that excited-state quenching of $Ru(menbpy)_3^{2+}$ by $Co(acac)_3$ operates primarily by energy transfer. In general, the rates for both the thermal electron-transfer reaction of $RuL_3^{\bullet+}$ and the quenching reaction of $^*RuL_3^{2+}$ are faster for the substituted ruthenium phenanthroline complexes than for the $Ru(menbpy)_3^{2+}$ complex, as can be seen in Table 1. The driving force is ≈0.5 eV more favorable for both reactions of the substituted ruthenium phenanthroline complexes as well. The rate constant for the reduction by $RuL_3^{\bullet+}$ increases by about 100 (to the diffusion limit), while the quenching rate constant increases by only a factor of 3! Moreover, for the substituted phenanthrolines complexes studied here, the excited-state quenching rate constant is essentially invariant as the driving force for the electron transfer changes by 0.3 eV. Thus the quenching reaction of both the $Ru(menbpy)_3^{2+}$ and the $Ru(phen')_3^{2+}$ are less sensitive to

SCHEME 1



driving force than expected for an electron-transfer reaction where the driving force is substantially smaller than the reorganization energy.

The quenching reaction of Ru(bpy)$_3^{2+}$ by Co(acac)$_3$ as a function of poly(vinyl sulfate) concentration has been studied by Meyerstein et al.[55] They observe electron-transfer products for high concentrations of PVS but at lower concentrations only trace amounts of products can be observed. They explain their results in terms of Scheme 1 where both energy transfer and electron transfer proceed in parallel. They estimate that approximately half the quenching of *Ru(bpy)$_3^{2+}$ occurs by energy transfer in aqueous solution. The lack of any significant amount of electron-transfer products is ascribed to the fast "back" reaction, k_{bet}, of the Ru(III) and Co(II) products within the solvent cage to re-form the ground-state reactants before the products can separate.

From Scheme 1 the quenching rate constant is given by

$$k_q = \frac{k_d}{k_{-d} + k_{en} + k_{et}}(k_{en} + k_{et}) \qquad (3)$$

The energy-transfer rate constant, k_{en}, is not expected to be sensitive to the driving force of the electron-transfer reaction. When k_{en} is the same size or larger than k_{et} the quenching rate constant, k_q, will be insensitive to the driving force of the electron-transfer reaction. Thus it is not surprising that the quenching rate is insensitive to the driving force for the electron-transfer reaction, as observed in the present study. We conclude that for the substituted phenanthroline complexes, both energy and electron transfer proceed in parallel with the energy-transfer pathway predominating under our conditions.

For *Ru(menbpy)$_3^{2+}$ the driving force for electron-transfer quenching to form Ru(menbpy)$_3^{3+}$ is much less favorable than for the substituted phenanthroline complexes. One would expect that the rate of electron transfer would be much slower, while the energy-transfer rate would remain the same. This would allow the energy-transfer pathway to dominate, $k_{en} \gg k_{et}$, the quenching of *Ru(menbpy)$_3^{2+}$ by Co(acac)$_3$.

The enantioselectivity of the quenching reactions could be due to differences in $k_{en}{}^{\Delta}$ and $k_{en}{}^{\Lambda}$ for the two isomers. Another possibility is that the energy-transfer rate constants are equal and the enantioselectivity is due to differences in the electron-transfer rate constants, $k_{et}{}^{\Delta}$ and $k_{et}{}^{\Lambda}$. If the electron-transfer rate constants for quenching of the excited Ru(menbpy)$_3^{2+}$ by Δ- or Λ-Co(acac)^3 differ by a factor of 3, similar to that found for the reaction of the Ru(menbpy)$_3^{\bullet+}$ complex with Co(acac)$_3^-$, then only 5% of the quenching would need to occur by electron transfer to have an enantioselectivity factor of 1.1. With higher rates of enantioselectivity for the electron-transfer reaction less of the quenching would need to occur by electron transfer to achieve the same overall enantioselectivity of the quenching. Given the small enantioselectivity observed in the quenching reaction and the high value observed for the Ru(menbpy)$_3^{\bullet+}$ reaction the latter explanation seems likely.

Energy-transfer quenching can occur by either a dipole−dipole (Förster) or electron-exchange (Dexter) mechanism.[56−58] The former operates at significantly longer distances than the latter. In both cases the rate of energy-transfer quenching is dependent on the spectral overlap of the emission of the donor and the absorbance of the acceptor; however, the specific transitions of the acceptor are different in the two mechanisms. For Förster energy transfer the acceptor undergoes a dipole-allowed transition while for the electron-exchange mechanism the overall spin of the reactants is preserved. Since the long-lived excited state of the Ru(menbpy)$_3^{2+}$ is formally a triplet, the Förster and Dexter mechanisms, respectively, are shown below:

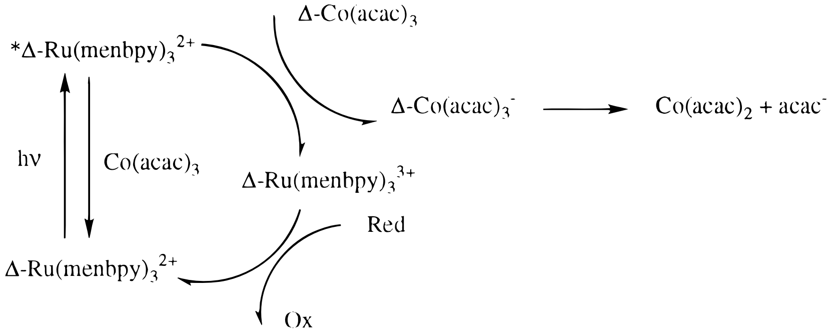
$$^3[\mathrm{Ru(menbpy)_3}]^{2+}{*} + \mathrm{Co(acac)_3} \rightarrow [\mathrm{Ru(menbpy)_3}]^{2+} + {}^1\mathrm{Co(acac)}_3^*$$

$$^3[\mathrm{Ru(menbpy)_3}]^{2+}{*} + \mathrm{Co(acac)_3} \rightarrow [\mathrm{Ru(menbpy)_3}]^{2+} + {}^3\mathrm{Co(acac)}_3^*$$

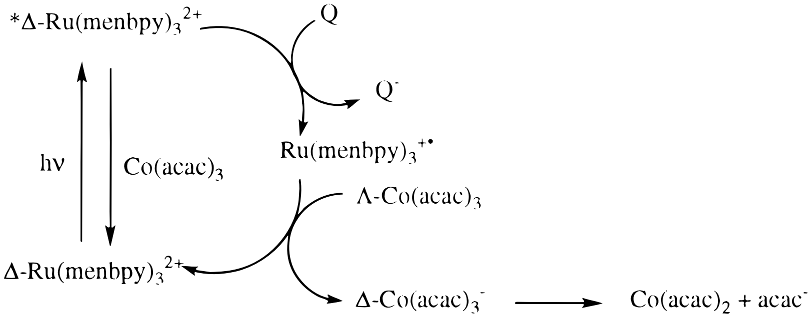
The ruthenium emission at 620 nm overlaps the weak d−d absorption of the Co(acac)$_3$ at 590 nm. This absorption is assigned to the singlet d−d excitation, $^1A_{1g} \rightarrow {}^1T_{1g}$. The $^1A_{1g} \rightarrow {}^3T_{1g}$, and $^1A_{1g} \rightarrow {}^3T_{2g}$ transitions are not observed but are certainly at lower energy than the singlet. The Tanabe−Sugano diagram suggests that the triplet absorptions would be at >700 nm.[59−61] Thus energy transfer is energetically possible.

The calculated[57,62−64] first-order rate constant for Förster energy transfer from *Ru(menbpy)$_3^{2+}$ to Co(acac)$_3$ (ϕ_D is 0.052 and $r = 7$ Å[65]) is $\approx 5 \times 10^7$ s^{-1}. The bimolecular rate constant is given by $k_{en}^{(2)} = Kk_{en}$, where K is the formation constant of the precursor complex and is estimated to be ≈ 0.4 M^{-1}.[48] Thus $k_{en}^{(2)} \approx 2 \times 10^7$ M^{-1} s^{-1}. The calculated Förster rate constant for Co(edta)$^-$ is $\approx 3 \times 10^7$ s^{-1} with a K of ≈ 4 M^{-1} (in 50% EtOH/H$_2$O),[48] giving $k_{en}^{(2)} \approx 1 \times 10^8$ M^{-1} s^{-1}. The rates are about 1 order of magnitude smaller than the observed rates even for a distance as short as 7 Å. The calculated rate constant for Förster quenching of the excited state of RuL$_3^{2+}$ by Co(acac)$_3$ is $\approx 10^7$ M^{-1} s^{-1}.[48,66] The calculated rates are about 1 order of magnitude smaller than the observed rates and do not parallel the observed ones. The above argues that a Förster energy-

SCHEME 2



SCHEME 3



transfer mechanism is unlikely for the quenching of any of the ruthenium complexes by $Co(acac)_3$ or $Co(edta)^-$.

The Dexter formalism for electron-exchange energy transfer gives a first-order rate constant that is proportional to[58]

$$k_{\text{en}} \propto \hbar P^2 \exp(-2r/L)\int F_{\text{D}}(\nu)\,\epsilon'_{\text{A}}(\nu)\,\mathrm{d}\nu \qquad (5)$$

where r is the distance between the donor and acceptor centers, P and L are constants that depend of the reaction, and F_{D} and ϵ' are the normalized ruthenium emission and cobalt absorption coefficients, respectively. The formalism shows that the rate constant decreases exponentially with distance and so is important only at short distances when the complexes are in contact. The overlap between the emission of the ruthenium and the cobalt triplet absorption will be significant especially since both the absorption and emission are normalized in the electron-exchange overlap integral. However, no absolute rates can be calculated. Despite this limitation we conclude that the energy-transfer quenching of the long-lived excited state of $Ru(menbpy)_3{}^{2+}$ by $Co(acac)_3$ probably proceeds by an electron-exchange (Dexter) type of mechanism.

Quantum Yield and Stereoselectivity of the $Co(acac)_3$ Photoreduction. The quantum yield of Co(II) from the quenching of $Ru(menbpy)_3{}^{2+}$ by $Co(acac)_3$ is less than 1%. The quantum yield for Co(II) products, $\Phi_{\text{Co(II)}}$, is given by[67]

$$\Phi_{\text{Co(II)}} = \left[\frac{k_{\text{et}}}{k_{\text{et}} + k_{\text{en}}}\right]\left[\frac{k'_{-\text{d}}k'_{-1}/(k'_{-1} + k'_{\text{d}}[\text{RuL}_3{}^{3+}])}{k_{\text{bet}} + k'_{-\text{d}}k'_{-1}/(k'_{-1} + k'_{\text{d}}[\text{RuL}_3{}^{3+}])}\right] \qquad (6)$$

where the various rate constants are defined in Scheme 1. As shown by eq 6, the quantum yield is a complex expression that depends on the rate constants for both the electron- and energy-transfer quenching reactions as well as the rate of dissociation of the successor complex and the rate of ligand loss from the Co(II) product. The quantum yield given in eq 6 is a product of two terms: the fraction of the quenching that occurs by electron transfer multiplied by the fraction of the electron-transfer products that escape the solvent cage and dissociate before they can back react. For the quenching of $^*Ru(menbpy)_3{}^{2+}$ the first term is small since energy-transfer quenching will dominate the quenching reaction. The second term is known[55] to be small for the quenching of $Ru(bpy)_3{}^{2+}$ by $Co(acac)_3$. The loss of an $acac^-$ ligand by $Co(acac)_3{}^-$ is acid-catalyzed, where the initial step is the opening of one Co−O bond to form a unidentate $acac^-$; this step is followed by protonation and loss of Hacac. The rate constant for ligand loss[68] is $k'_{-1} \approx 10^9[\text{H}^+]$ s^{-1}. For our solutions with phosphate buffer $[\text{H}^+] \approx 10^{-7}$ M, ligand loss is slow. k_{bet} is expected to be fast since the driving force for this reaction is significantly larger than for the quenching reaction. The rate constants k_{d} and $k_{-\text{d}}$ are estimated to be $\approx 10^{10}$ M^{-1} s^{-1} and $\approx 10^{10}$ s^{-1}, respectively, and the concentration of Ru^{3+} produced by the laser flash is $\approx 10^{-6}$ M. Thus the second term is estimated to be $\ll 1$. Therefore, it is not surprising that the quantum yield is so small.

The question of enantioselectivity in the CW photolysis of $Co(acac)_3$/Δ-$Ru(menbpy)_3{}^{2+}$ is intriguing. In these reactions a solution of Δ-$Ru(menbpy)_3{}^{2+}$ and rac-$Co(acac)_3$ undergoes photolysis. During the photolysis Co(II) is produced and the $Co(acac)_3$ becomes optically active, with an excess of the Λ isomer. This suggests that the Δ isomer of $Co(acac)_3$ is reduced preferentially and Scheme 2 has been proposed as the mechanism of the catalytic reaction where Red is ethanol.[13,16]

Despite the very modest stereoselectivity for the energy-transfer quenching, the electron-transfer quenching, although only a small percentage of the total quenching, could be more stereoselective, as discussed above. Since only the electron-transfer quenching results in net photochemistry, this pathway will determine the enantioselectivity of the photolysis reaction. Alternatively, the enantioselectivity could be due to differences in the rates of energy transfer, of back electron transfer and/or of dissociation of the $Ru(menbpy)_3{}^{2+}|Co(acac)_3{}^-$ successor complex (see k_{bet} and $k_{-\text{d}}$ in Scheme 1) rather than to differences in the rate of electron-transfer quenching. Finally, the possibility that the Ru(III) species stereospecifically oxidizes $Co(acac)_3{}^-$ has also been suggested.[22]

Another possibility is that of reductive quenching of the *Ru(II) as shown in Scheme 3. This mechanism uses the high enantioselectivity of the Ru(menbpy)$_3^{\bullet+}$ reaction and the very favorable reduction potential for the Ru$^{*2+/+}$ couple. One possibility for Q is free acac$^-$, which has been implicated[55] in the reduction of Ru(bpy)$_3^{3+}$ in the quenching of Ru(bpy)$_3^{2+}$ by Co(acac)$_3$. We have also shown that acac$^-$ quenches *Ru(menbpy)$_3^{2+}$ and yields a small bleach in the absorbance spectrum at 450 nm that decays on a millisecond time scale. This suggests that the bleaching by acac$^-$ yields a Ru(menbpy)$_3^{\bullet+}$ product that slowly back reacts. There are trace amounts of free ligand, as an impurity, in most preparations of Co(acac)$_3$, which will provide acac$^-$ at the start of the reaction. Interestingly, some of the photolysis studies[14,16] show an induction period in the formation of optically active Co(acac)$_3$ during which acac$^-$ could build up. Other studies[13] have shown that excess Hacac increases the enantioselectivity of the photolysis of either Co(III) or Co(II).

Conclusions

Co(acac)$_3$ is stereoselectively reduced by Δ-Ru(menbpy)$_3^{\bullet+}$ with extremely high stereoselectivity of 2.7 in 85% EtOH/H$_2$O. The reaction shows strong $\Delta-\Delta$ and weaker $\Lambda-\Lambda$ preference. Activation parameters suggest that the binding between the $\Delta-\Delta$ isomers allows closer interaction than between all other isomer combinations studied here.

The quenching of photoexcited *Ru(menbpy)$_3^{2+}$ exhibits much smaller stereoselectivity (1.2 in 95% EtOH/H$_2$O). The quenching reaction is assigned to be primarily a Dexter type of electron-exchange energy-transfer mechanism. This is supported by the magnitude of the rate constants observed when compared with the reactions of Ru(menbpy)$_3^{\bullet+}$, the effect of changes in driving force on the quenching rate constants, the low quantum yield of Co(II) products observed in the CW photolysis, and the lack of long-lived products observed in the flash photolysis experiments. The selectivity is much smaller than for the thermal reduction of Co(acac)$_3$ by Δ-Ru(menbpy)$_3^{\bullet+}$. The selectivity exhibited in CW photolysis studies of this reaction is not necessarily due to enantioselective electron-transfer quenching of Ru(menbpy)$_3^{2+}$ and various mechanisms to explain the CW photolysis results are considered.

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(53) For the Ru(menbpy) $_3{}^{\bullet+}$ reduction of Co(acac) $_3$: $\Delta z^2 = 2^2 + (-1)^2 - 1^2 - 0 = 4$. A slope of -4 cm^3 mol^{-1} per unit charge squared has been reported[52] for the correlation of volume change with Δz^2. Thus a volume change of approximately -16 cm^3 mol^{-1} due to electrostriction is expected

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(59) Co(acac)$_3$ is diamagnetic, but the acac$^-$ ligand does not have a strong ligand field. Using the standard Tanabe−Sugano diagrams for a Co(III) d^6 system[60,61] the Dq/B value must be >2 (or the complex would be paramagnetic) and probably <3 (due ot the weak ligand field of acac$^-$). The $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption is at 590 nm (17 000 cm^{-1}), which gives the energy of the $^1A_{1g} \rightarrow {}^3T_{2g}$ transition as between 700 and 800 nm (12 000 and 14 500 cm^{-1}).

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(62) The first-order rate constant for Förster energy transfer is given by:[57]

$$k_{en} = \frac{9000\ \ln(10)\kappa^2\phi_D}{128\pi^5\eta^4 N\tau_D r^6}\int F_D(\nu)\ \epsilon_A(\nu)\ \frac{d\nu}{\nu^4}$$

where ν is the wavenumber variable (cm^{-1}), $F_D(\nu)$ is the normalized emission spectrum of the ruthenium excited state (cm), $\epsilon_A(\nu)$ is the molar extinction coefficient for the acceptor transition (M^{-1} cm^{-1}), η is the refractive index of the solvent (1.36[63]), κ is the orientation factor ($\sqrt{2/3}$), ϕ_D is the emission quantum yield of the ruthenium, τ_D is the lifetime of the ruthenium excited state (s), N is Avogadro's number, and r is the distance between the donor and acceptor centers (cm).

(63) The refractive index of 95% EtOH is estimated to be 1.35.[64]

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(65) Molecular modeling of the Ru(menbpy)$_3{}^{2+}$|Co(acac)$_3$ complex using Cerius2 software from MSI gives a metal to metal distance of ≈7.4 Å.

(66) The Förster rates calculated for the excited state of the substituted phenanthroline Ru(II) complexes with Co(acac)$_3$ are $\approx 1.5 \times 10^7$ s^{-1} (r = 7 Å); one would expect that the distance between the ruthenium and Co for the substituted bpys and phens would be shorter than that for the menbpy. However, for a decrease of r to 6.5 Å the calculated rate only increases by 1.5. The bimolecular rate constant is given by $k_{en}^{(2)} = Kk_{en}$, where K is estimated[48] as ≈0.4 M^{-1}. Thus the bimolecular rate constant for the quenching of the long-lived excited state is $k_{en}{}^{(2)} \approx 10^7$ M^{-1} s^{-1}.

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