High Enantioselectivity in the Electron Transfer Reaction between a Ru(II) Complex of Menbpy Anion Radical, $[Ru(menbpy)_3]^+$ [menbpy = 4,4'-di{(1*R*,2*S*,5*R*)-(–)-menthoxycarbonyl}-2,2'-bipyridine] and $[Co(acac)_3]$: A Pulse Radiolysis Study

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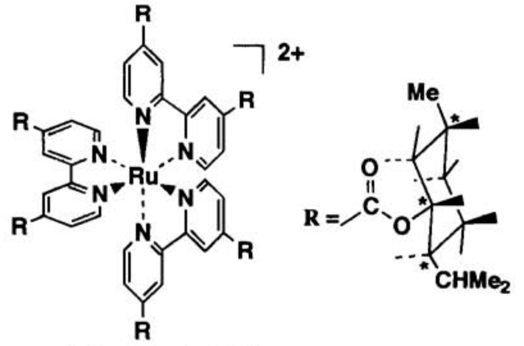
One-electron reduction of $[Ru(menbpy)_3]^{2+}$ [menbpy = 4,4'- di{(1*R*,2*S*,5*R*)- (–)- menthoxycarbonyl}- 2,2'-bipyridine] by pulse radiolysis produces a Ru(II) complex of a menbpy-centered anion radical, which reduces Δ-$[Co(acac)_3]$ more rapidly than Λ-$[Co(acac)_3]$ with an enantioselectivity of 2.7 in 85% $EtOH/H_2O$.

Outer-sphere electron-transfer reactions between coordination complexes generally display only very small differences in rates between enantiomers (≤ 20%).[1,2] Interesting preliminary reports[3] on the quenching of the long-lived excited state of a helical-shaped Ru(II) complex, $^*[Ru(menbpy)_3]^{2+}$, by $[Co(acac)_3]$ have shown significant enantioselective effects.[4] In order to gain new insight into the enantioselectivity and quenching reactions of $[Ru(menbpy)_3]^{2+}$, we have undertaken a study of the electron-transfer reactions of reduced Δ-$[Ru(menbpy)_3]^{2+}$ by use of pulse-radiolysis. We report here the first observation of large differences in the rates of stereoselective thermal electron transfer between Δ-$[Co(acac)_3]$ and the Ru(II) complex of the ligand centered radical, Δ-$[Ru(menbpy)_3]^{+}$.[5] New results are also presented on the time resolved emission quenching of the $^*[Ru(menbpy)_3]^{2+}$. These results yield a new and different interpretation of the mechanism of the quenching reaction of $^*[Ru(menbpy)_3]^{2+}$ by $[Co(acac)_3]$.



Δ-$[Ru(menbpy)_3]^{2+}$

Scheme 1.

Optically pure Δ-$[Ru(menbpy)_3]^{2+}$ and Δ- and Λ-$[Co(acac)_3]$ were prepared using reported methods.[3,6] Electron pulse-radiolysis transient absorption experiments were performed with $EtOH/H_2O$ solutions containing 20 μM Δ-$[Ru(menbpy)_3]^{2+}$, 10-60 μM Δ- or Λ-$[Co(acac)_3]$ and 0.2 mM phosphate buffer (pH ~7) using the 2 MeV Van de Graaff accelerator at Brookhaven National Laboratory. Since $[Ru(menbpy)_3]^{2+}$ is only sparingly soluble in water, an 85% $EtOH/H_2O$ medium was used 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• and OH• with ethanol in N_2O-saturated solution.

The dose-corrected absorbance changes from the pulse-radiolysis experiments in N_2O-saturated $EtOH/H_2O$ (open circles in Figure 1) agree well with the difference spectrum in acetonitrile prepared by Na-Hg reduction (solid line in Figure 1), indicating the formation of the ligand-centered radical, $[Ru(menbpy)_3]^{+}$. Although the $CH_3C^{\bullet}HOH$ radical does not reduce $[Ru(bpy)_3]^{2+}$ at pH 7 ($E^{\circ} \approx -1.3$ V vs NHE),[7] the reduction potential of $[Ru(menbpy)_3]^{2+/+}$ is significantly more

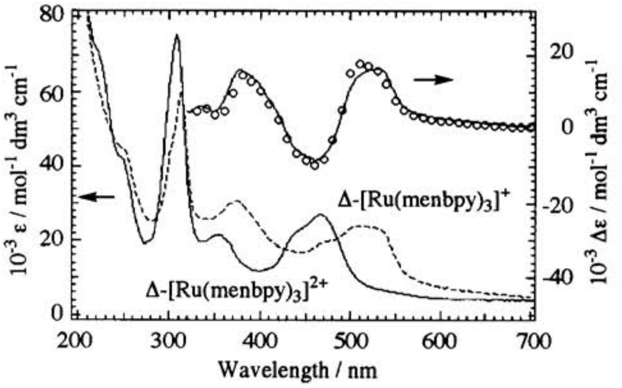


Figure 1. UV-vis absorption spectra of $[Ru(menbpy)_3]^{2+}$ (solid line) and $[Ru(menbpy)_3]^{+}$ (dotted line) in acetonitrile; and the dose-corrected difference spectrum from the reduction of $[Ru(menbpy)_3]^{2+}$ by $CH_3C^{\bullet}HOH$ (circles), compared with the difference spectrum ($[Ru(menbpy)_3]^{+}$–$[Ru(menbpy)_3]^{2+}$) in acetonitrile (upper solid line).

Table 1. Driving force and rate constants for reaction between $[Ru(menbpy)_3]^{2+}$ and $[Co(acac)_3]$ in 85% $EtOH/H_2O$ at 25 °C

Δ-Ru complex	ΔE° V	$10^{-7}k(\Delta)$ $M^{-1}\ s^{-1}$	$10^{-7}k(\Lambda)$ $M^{-1}\ s^{-1}$	$k(\Delta)/k(\Lambda)$
$[Ru(menbpy)_3]^{+}$	0.6[a]	2.1± 0.1[b]	0.78 ± 0.02[c]	2.7 ± 0.2
$^*[Ru(menbpy)_3]^{2+}$	0.1[a]	9.5 ± 0.4[b]	8.5 ± 0.3[c]	1.1 ± 0.05

[a] The reduction potential of $[Co(acac)_3]$ was previously determined to be –0.34 V vs SCE in acetonitrile.[10] [b] By pulse radiolysis using solutions containing 1.0 mM NaH_2PO_4. [c] By transient emission spectroscopy using solutions containing 0.5 mM NaH_2PO_4 and 0.5 mM Na_2HPO_4.

positive, –0.90 V (vs NHE),[8] and $CH_3C^{\bullet}HOH$ (–1.25 V)[9] reduces $[Ru(menbpy)_3]^{2+}$ with a rate constant of (8.2 ± 0.5) x $10^8\,M^{-1}\,s^{-1}$. The rate constants for the reduction of Δ- and Λ-$[Co(acac)_3]$ by Δ-$[Ru(menbpy)_3]^+$ are presented in Table 1. The enantioselectivity factor of 2.7 for electron transfer from Δ-$[Ru(menbpy)_3]^+$ to Δ- or Λ-$[Co(acac)_3]$ is dramatic. Differences in orientation and/or internuclear distances in the precursor and successor complexes can effect both their equilibrium constants and the parameters that control the rate of electron-transfer within the precursor complex. Since there are no hydrogen bonds between the redox partners, the selectivity may steric in origin.

Results for the quenching of the charge-transfer excited state of Δ-$[Ru(menbpy)_3]^{2+}$ by Δ- or Λ-$[Co(acac)_3]$ are given in Table 1 for comparison with the thermal electron-transfer rate constants. The enantioselectivity of 1.1 determined in this study by transient photoemission measurements on Δ-$^*[Ru(menbpy)_3]^{2+}$ is barely outside of experimental error and is smaller than those previously measured by CW photoemission methods in 90% $EtOH/H_2O$.[3c,g] Transient absorption measurements on the quenching of the excited ruthenium complex show no long-lived products.

The relative rates of the $[Ru(menbpy)_3]^+$ and $^*[Ru(menbpy)_3]^{2+}$ reactions are surprising: the quenching of the *Ru(II) excited state is an order of magnitude faster despite the much larger driving force for the $[Ru(menbpy)_3]^+$ reaction (0.6 V and 0.1 V for the $[Ru(menbpy)_3]^+/[Co(acac)_3]$ and $^*[Ru(menbpy)_3]^{2+}/[Co(acac)_3]$ systems, respectively, as shown in Table 1). In both cases the electron transferred would be from a ligand π^* orbital, indicating that the steric effects should be similar. Our result suggests that the predominant quenching mechanism is not electron transfer but energy transfer. This result is further supported by the failure to detect any long-lived electron-transfer products in the quenching reaction. Steric selectivity may also be responsible for the factor of 1.1 favoring energy transfer from Δ-$^*[Ru(menbpy)_3]^{2+}$ to Δ-$[Co(acac)_3]$, although the possibility of better interaction between the transition dipoles in the Δ and Δ case is an interesting alternative. Examination of pressure and solvent effects on the electron transfer between Δ-$[Ru(menbpy)_3]^+$ and Δ- or Λ-$[Co(acac)_3]$ and experiments with Λ-$[Ru(menbpy)_3]^{2+}$ are currently underway.

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References and Notes

1 A. G. Lappin and R. Marusak, *Coord. Chem. Rev.*, **109**, 125 (1991) and references therein.

2 a) G. B. Porter and R. H. Sparks *J. Chem. Soc., Chem. Commun.*, **1979**, 1094. b) G. B. Porter and R. H. Sparks, *J. Photochem.*, **13**, 123 (1980). c) S. Sakaki, T. Satoh, and K. Ohkubo, *New J. Chem.*, **10**, 145 (1986). d) K. Ohkubo and Y. Arikawa, *J. Mol. Catal.*, **33**, 65 (1985). e) Y. Kaizu, T. Mori, and H. Kobayashi, *J. Phys. Chem.*, **89**, 332 (1985). f) M. Kato, T. Sasagawa, Y. Ishihara, S. Yamada, S. Fujitani, and M. Kimura, *J. Chem. Soc., Dalton Trans.*, **1994**, 583. g) M. Wörner, G. Greiner, and H. Rau, *J. Phys. Chem.*, **99**, 14161 (1995).

3 a) K. Ohkubo, T. Hamada, T. Inaoka, and H. Ishida, *Inorg. Chem.*, **28**, 2021 (1989). b) K. Ohkubo, H. Ishida, T. Hamada, and T. Inaoka, *Chem. Lett.*, **1989**, 1545. c) K. Ohkubo, T. Hamada, and H. Ishida, *J. Chem. Soc., Chem. Commun.*, **1993**, 1423. d) K. Ohkubo, T. Hamada, H. Ishida, M. Fukushima, M. Watanabe, and H. Kobayashi, *J. Chem. Soc., Dalton Trans.*, **1994**, 239. e) K. Ohkubo, T. Hamada, and M. Fukushima, *J. Mol. Catal.*, **89**, L5 (1994). f) K. Ohkubo, M. Fukushima, H. Ohta, and S. Usui, *J. Photochem. Photobiol. A Chem.*, **98**, 137 (1996). g) T. Hamada, Thesis, Kumamoto University (1993).

4 The photocatalytic reduction of $[Co(acac)_3]$ by $[Ru(membpy)_3]^{2+}$ requires a multistep mechanism that may involve: photoactivation and deactivation, encounter complex formation, charge-transfer, energy-transfer, back electron transfer, successor complex dissociation, and ligand loss from the cobalt(III) product. The electron-transfer reaction studied here are less complicated in that excited state decay and energy transfer considerations are obviated.

5 One-electron reduction of $[Ru(menbpy)_3]^{2+}$ yields a Ru(II) complex with a menbpy anion radical ligand, $[Ru^{II}(menbpy)_2(menbpy^{-\bullet})]^+$.

6 A. F. Drake, J. M. Gould, S. F. Mason, C. Rosini, and F. Woodley, *Polyhedron*, **2**, 537 (1983).

7 M. Venturi, S. Emmi, P. G. Fuochi, and Q. G. Mulazzani, *J. Phys. Chem.*, **84**, 2160 (1980).

8 a) The estimated $E°$ values vs. NHE in water (–0.90 V and 1.55 V for $[Ru(menbpy)_3]^{2+/+}$ and $[Ru(menbpy)_3]^{3+/2+}$, respectively) are estimated equal to the measured values in acetonitrile vs SCE. This is because the ferricinium/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 vs NHE.[8b,c] b) S. Sahami and M. J. Weaver, *J. Electroanal. Chem.*, **122**, 155 (1981). c) S. Sahami and M. J. Weaver, *J. Electroanal. Chem.*, **122**, 171 (1981).

9 H. A. Schwarz and R. W. Dodson, *J. Phys. Chem.*, **93**, 409 (1989).

10 H. Ogino and K. Ogino, *Inorg. Chem.*, **22**, 2208 (1983).