

case of high-spin  $Fe^{II}TPP$  the  $d_{z^2}$  is half filled, while the low-spin form has an empty  $d_{z^2}$  and thus improved  $\sigma$  acceptor properties. The low-spin configuration also has improved metal  $d\pi$  donor properties owing to the filled  $d_{xz,yz}$  orbitals, which is important for  $\pi$  acceptor ligands like carbon monoxide. Formation of a high- or low-spin five-coordinate complex depends on a trade-off between the promotion energy for producing the low-spin state and the resulting improved  $d\sigma$  acceptor and  $d\pi$  donor properties. A low-spin five-coordinate complex will result only when covalent  $\sigma$  and  $\pi$  bonding are dominant characteristics of the ligand, as is the case for CO. Apparently the covalent bonding from single nitrogen or oxygen donor is generally insufficient to promote formation of a diamagnetic complex.

The diamagnetism of  $FeTPP(CO)$  is one more example of an emerging general rule that diatomic molecule adducts of planar metal complexes are low spin. Some examples of this behavior are [ $S = 0$ :  $MnTPPNO$ ,  $FeTPP(Cl)(NO)$ ,<sup>2</sup>  $FeTPP(NO)_2$ ,<sup>2</sup>  $CoTPP(NO)$ ,  $FeTPP(CO)$ ,  $FeTPP(CO)_2$ ,  $S = 1/2$ :  $CrTPP(NO)$ ,  $MnTPP(NO)(Cl)$ ,<sup>3,4</sup>  $CoTPP(CO)$ ,  $FeTPP(NO)$ ,<sup>2,5</sup>  $CoTPP(O_2)$ ]. This generality probably results from the necessity of a filled  $d_{xz,yz}$  in order to provide maximum metal–diatomic ligand  $d\pi$  bonding. The only published exceptions to this generality which appear authentic are  $MnTPP(O_2)$  ( $S = 3/2$ )<sup>19</sup> and  $CrTPP(O_2)$  ( $S = 1$ ).<sup>20</sup> These complexes deserve more complete characterization, for an unusual form of metal–diatomic molecule bonding may be present.

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## Kinetics and Mechanism of the Quenching of the Emission of Substituted Polypyridineruthenium(II) Complexes. Reactions of $RuL_3^+$ , $*RuL_3^{2+}$ , and $RuL_3^{3+}$ with the Copper(I)–Copper(II) Couple

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**Abstract:** The series of complexes  $RuL_3^{2+}$ , where L is a bipyridine or phenanthroline derivative, has been used to study the mechanism of the quenching of the luminescent excited state of  $RuL_3^{2+}$  by copper(II) ions in aqueous solution. The quenching rate constants were obtained from emission intensity measurements. A pulsed dye laser was used to generate the electron-transfer products  $RuL_3^{3+}$  and copper(I) and the rate constants for the reactions of these products to re-form  $RuL_3^{2+}$  and copper(II) were measured. Rate constants for the quenching of some  $OsL_3^{2+}$  complexes were also determined. The rate constants for the reaction of copper(II) with  $RuL_3^+$ , generated by pulse radiolysis, were measured and compared with the rate constants for the reaction of copper(II) with  $*RuL_3^{2+}$ . On the basis of these results and spectroscopic considerations it is concluded that the quenching of  $*RuL_3^{2+}$  by copper(II) proceeds by an electron-transfer mechanism. The free-energy dependence of the quenching reactions is smaller than expected for an electron-transfer mechanism and possible reasons for this behavior are discussed. The quantum yields for the formation of separated electron-transfer products are analyzed in terms of the electron-transfer rates within the primary cages and the rates of the thermal back reactions.

## Introduction

The predominant process occurring when  $Ru(bpy)_3^{2+}$  absorbs visible or ultraviolet light is the formation of a relatively long lived, charge transfer to ligand excited state.<sup>1</sup> This excited state decays to the ground state, in part, by the emission of

radiation. The quenching of this emission by added substrates has been the subject of a large number of studies.<sup>2,3</sup> These studies have shown that the quenching may proceed by an energy transfer mechanism or by oxidation or reduction of the complex. An added reason for the current interest in the re-

actions of the  $\text{Ru}(\text{bpy})_3^{2+}$  excited states is that these systems provide useful models for the study of solar energy conversion and storage.<sup>4</sup>

An earlier study has shown that the series of luminescent polypyridineruthenium(II) complexes  $\text{RuL}_3^{2+}$ , where L is a bipyridine or phenanthroline derivative, can be used to ascertain the relative importance of electron-transfer and energy-transfer quenching pathways.<sup>5</sup> Since the absorption and emission spectra of the polypyridine complexes are very similar, their rates of energy-transfer quenching by a given substrate are nearly identical. On the other hand, the redox potentials of the complexes vary with the nature of the ligands and consequently their rates of electron-transfer quenching by a given substrate are expected to vary with the driving force for the reactions. This criterion has been used to assign an energy-transfer mechanism to the quenching of  $\text{RuL}_3^{2+}$  emission by chromium(III) and an electron-transfer mechanism to the quenching by europium(III).<sup>5</sup>

In the present paper we report the results of a study of the quenching of the emission of the  $\text{RuL}_3^{2+}$  complexes by copper(II) and the reactions of  $\text{RuL}_3^{3+}$  and copper(I) produced in flash photolysis experiments. The quenching reactions showed some unusual features and for this reason the reaction of copper(II) with  $\text{RuL}_3^{3+}$  generated by pulse radiolysis was also studied.

### Experimental Section

**Materials.** The polypyridineruthenium(II) complexes were prepared and purified as described previously.<sup>5</sup> Solutions containing the ruthenium(II) complex and copper(II) ions (Baker Analyzed  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in 0.5 M sulfuric acid, perchloric acid, or lithium sulfate were freshly prepared using triply distilled water. The solutions for the emission intensity and flash photolysis experiments were deaerated by argon bubbling in 1-cm<sup>2</sup> serum-capped cells and, to maintain anaerobic conditions, the caps were sealed with wax.

**Emission Intensity Measurements.** The emission from the polypyridineruthenium(II) complexes was measured on a Perkin-Elmer Model MPF-4 fluorescence spectrophotometer equipped with a 150-W xenon lamp. Solutions containing  $\text{Cu}_{\text{aq}}^{2+}$  and the ruthenium(II) complex were excited at the absorbance maximum of the complex around 450 nm. The emission intensities were monitored at the (uncorrected) wavelength of maximum emission (around 600 nm in the energy mode). No correction for the  $\text{Cu}_{\text{aq}}^{2+}$  absorbance was necessary at these wavelengths.

**Flash Photolysis Measurements.** The absorbance changes at  $\sim 450$  nm resulting upon flash photolysis of deaerated solutions 0.01–0.06 M in  $\text{Cu}_{\text{aq}}^{2+}$  and  $\sim 10^{-5}$  M in ruthenium(II) complex were studied using a Phase-R Model DL-1100 dye laser. The active dye was coumarin I ( $1.5 \times 10^{-5}$  M in ethanol), the excitation wavelength was 440–480 nm (the untuned broad-band output of the laser), the laser pulse width (full width at half-height) was  $\sim 0.6 \mu\text{s}$ , and the excitation intensity was 0.4–0.8 einstein  $\text{cm}^{-2} \text{s}^{-1}$ .

The probe beam source (positioned at 90° to the laser exciting beam) was a 30-W tungsten lamp filtered to remove light below 350 nm. The probe beam passed through a Bausch and Lomb grating monochromator situated immediately after the sample and was detected with a photomultiplier (RCA 1P28) and preamplifier having a combined bandwidth of 30 MHz. The signals from the preamplifier were stored in a Biomation Model 8100 transient recorder, displayed on an oscilloscope, and photographed.

The changes in the intensity of the transmitted beam following the laser pulse were measured from the photographs and converted to absorbance changes. For the equal concentration second-order kinetics expected for the thermal electron-transfer reaction involving  $\text{RuL}_3^{3+}$  and  $\text{Cu}_{\text{aq}}^{2+}$  a plot of the inverse absorbance change at time  $t$  against time

$$\frac{1}{\Delta A_t} = \frac{1}{\Delta A_0} + \frac{k_t t}{\epsilon_{\text{ex}}} \quad (1)$$

should yield a straight line with slope equal to  $k_t/\epsilon_{\text{ex}}$  and intercept equal to the inverse of the absorbance change at  $t = 0$ . In eq 1  $k_t$  is the second-order rate constant for the thermal electron-transfer reaction, and  $\epsilon_{\text{ex}}$  is the experimental molar absorptivity. The value of the latter

is defined for the given experimental conditions of geometry, monochromator slit width, and photomultiplier sensitivity used and was determined from the known ruthenium concentration and the intensity of the light transmitted by the sample relative to that transmitted by water. Plots according to eq 1 were linear for at least 2 half-lives.

**Relative Yield Determinations.** The relative yields of  $\text{RuL}_3^{3+}$  produced in the flash photolysis using  $\text{Cu}_{\text{aq}}^{2+}$  as quencher compared to that using  $\text{Fe}_{\text{aq}}^{3+}$  as quencher were determined as follows. Solutions containing the  $\text{RuL}_3^{2+}$ - $\text{Cu}_{\text{aq}}^{2+}$  or  $\text{RuL}_3^{2+}$ - $\text{Fe}_{\text{aq}}^{3+}$  system were alternately irradiated with laser pulses generated under identical conditions. This procedure minimized errors arising from variations in the laser energy. The  $\text{Cu}_{\text{aq}}^{2+}$  and  $\text{Fe}_{\text{aq}}^{3+}$  concentrations of the solutions were adjusted so that the quenching efficiencies of the two ions were identical. Moreover, relatively high concentrations of the two ions were used so that the quenching efficiencies were also high, thereby reducing errors arising from uncertainties in the concentrations and Stern-Volmer constants. The  $\text{RuL}_3^{2+}$  concentration was the same in both solutions.

Two procedures were used to determine the amount of  $\text{RuL}_3^{3+}$  produced by the laser flash excitation. In the first method the absorbance change at  $t = 0$  was obtained from the intercept of the computer fit of the kinetic data to eq 1. The second method involved a linear extrapolation of the intensity-time data on the photographs to zero time. An extrapolation to time zero was necessary because the duration of the scattered laser pulse was long enough to distort the intensity readings during the first 1–2  $\mu\text{s}$  of the traces. Rather than extrapolating the complete second-order curve to zero time (as was done in the computer fits), the oscilloscope sweep rate was expanded to cover 6–10  $\mu\text{s}$  of reaction after the laser pulse. On these expanded sweeps a linear extrapolation of the intensity-time data could be used to obtain the intensity and thus the  $\text{RuL}_3^{2+}$  concentration at zero time. The relative yields calculated by either of these two methods gave consistent results in a number of test cases. Because of the simplicity of the latter method, direct linear extrapolations from the "short time" photographs were generally used to obtain the zero-time absorbance changes.

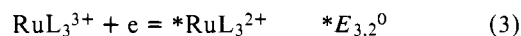
**Pulse Radiolysis Experiments.** The pulse radiolysis equipment which has been previously described was used to generate pulses of 2-MeV electrons.<sup>6</sup> The width of the pulses was 1–2  $\mu\text{s}$ . A 150-W quartz-iodine lamp was the source of the analyzing light. The optical path length was 6.1 cm (three passes through a 2-cm cell). The  $2 \times 2 \times 0.8$  cm quartz cell was first flushed with argon. It was then completely filled with an argon-saturated solution and stoppered. Solutions containing  $2\text{--}6 \times 10^{-5}$  M  $\text{RuL}_3^{2+}$ , 0.5 M *tert*-butyl alcohol, and varying amounts of  $\text{Cu}_{\text{aq}}^{2+}$  (added as  $\text{Cu}(\text{ClO}_4)_2$ ) were buffered to pH 6.6 using sodium cacodylate and  $\text{HClO}_4$ .

### Results

Stern-Volmer constants,  $K_{\text{SV}}$ , were obtained from slopes of plots of the emission intensity ratios as a function of  $\text{Cu}_{\text{aq}}^{2+}$  concentration.

$$I_0/I = 1 + K_{\text{SV}}[\text{Cu}^{2+}] \quad (2)$$

The values of these constants in 0.5 M sulfuric acid at 25 °C and the second-order quenching rate constants calculated from  $k_q = K_{\text{SV}}/\tau_0$  are presented in Table I. The results of some measurements in 0.5 M perchloric acid and 0.5 M lithium sulfate are also included in this table. The reduction potentials for the formation of the emitting states of the ruthenium(II) complexes



and the lifetimes of the emitting states shown in Table I have been reported previously.<sup>5</sup> The activation parameters for the quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  emission by copper(II) calculated from the data in Table I are  $\Delta H^\ddagger = 2.3 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -15 \text{ cal deg}^{-1} \text{ mol}^{-1}$ . Table I also contains data on the quenching of  $\text{OsL}_3^{2+}$  complexes.

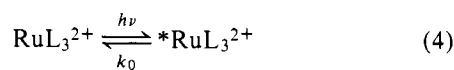
The absorbance changes following the flash photolysis of  $\text{RuL}_3^{2+}$  solutions containing  $\text{Cu}_{\text{aq}}^{2+}$  occurred in two stages. The first stage took place during the laser pulse ( $\sim 1 \mu\text{s}$ ) and was a decrease in absorbance at 450 nm. The second stage occurred in 5–300  $\mu\text{s}$  (depending on the nature of the ruthen-

**Table I.** Stern-Volmer and Rate Constants for the Quenching of Ruthenium(II) (RuL<sub>3</sub><sup>2+</sup>) and Osmium(II) (OsL<sub>3</sub><sup>2+</sup>) Emission by Copper(II) Ions in 0.5 M Sulfuric Acid at 25 °C

Ligands, L	*E <sub>3,2</sub> <sup>0</sup> , V <sup>a</sup>	τ <sub>0</sub> , μs <sup>a</sup>	K <sub>SV</sub> , M <sup>-1</sup>	10 <sup>-7</sup> k <sub>q</sub> , M <sup>-1</sup> s <sup>-1</sup>
Ruthenium Complexes				
4,4'-(CH <sub>3</sub> ) <sub>2</sub> bpy	-0.94	0.33	32	9.7
bpy	-0.84	0.54 <sup>b,d</sup>	39 <sup>b</sup>	7.2 <sup>b</sup>
		0.60	37	6.2
		0.65 <sup>c,d</sup>	35 <sup>c</sup>	5.4 <sup>c</sup>
		0.60	40 <sup>e</sup>	6.6 <sup>e</sup>
3,4,7,8-(CH <sub>3</sub> ) <sub>4</sub> phen	-1.11	1.39	143	10.0
			123 <sup>f</sup>	8.8 <sup>f</sup>
4,7-(CH <sub>3</sub> ) <sub>2</sub> phen	-1.01	1.74	150	8.6
5,6-(CH <sub>3</sub> ) <sub>2</sub> phen	-0.93	1.81	138	7.6
5-(CH <sub>3</sub> )phen	-0.90	1.33	80	6.0
5-(C <sub>6</sub> H <sub>5</sub> )phen	-0.87	1.29	74	5.7
phen	-0.87	0.92	69	7.5
5-Cl(phen)	-0.77	0.94	38	4.0
5-Br(phen)	-0.76	1.04	44	4.2
Osmium Complexes				
bpy	-0.96 <sup>i</sup>	0.019 <sup>g</sup>	~4	~20
5,6-(CH <sub>3</sub> ) <sub>2</sub> phen	-1.03 <sup>i</sup>	0.063 <sup>h</sup>	13	21

<sup>a</sup> Reference 5. <sup>b</sup> At 34.8 °C. <sup>c</sup> At 16.9 °C. <sup>d</sup> Lifetimes interpolated from the data reported in ref 1b. <sup>e</sup> In 0.5 M perchloric acid. <sup>f</sup> In 0.5 M lithium sulfate. <sup>g</sup> Reference 4c. <sup>h</sup> C. Creutz, unpublished observations. <sup>i</sup> G. M. Brown, unpublished observations.

ium complex) and corresponded to the return of the absorbance to its original value. These absorbance changes are consistent with the reactions



The decrease in absorbance at 450 nm is indicative of the loss of RuL<sub>3</sub><sup>2+</sup> as is required by the above mechanism. The weak absorbance of RuL<sub>3</sub><sup>3+</sup> precluded direct spectrophotometric detection of this species. The second-order rate constants, *k<sub>t</sub>*, for the reaction of RuL<sub>3</sub><sup>3+</sup> with Cu<sub>aq</sub><sup>+</sup> were determined from the slow absorbance change using eq 1 and are presented in Table II. In contrast to the quenching rates, the rate of reaction of Ru(bpy)<sub>3</sub><sup>3+</sup> with Cu<sub>aq</sub><sup>+</sup> decreases upon replacing sulfate by perchlorate ions. No evidence of irreversible photochemical decomposition was observed even after 20 flashes on a given solution. Similar time-dependent absorbance changes were also seen with the OsL<sub>3</sub><sup>2+</sup> systems.

Reactions 4-6 predict that significant steady-state concentrations of RuL<sub>3</sub><sup>3+</sup> should be produced under suitable conditions. Appreciable (~15%) steady-state concentrations were indeed produced when a solution containing 4.7 × 10<sup>-6</sup> M Ru(3,4,7,8-(CH<sub>3</sub>)<sub>4</sub>phen)<sub>3</sub><sup>2+</sup>, 0.005 M Cu<sub>aq</sub><sup>2+</sup>, ~10<sup>-6</sup> M Fe<sub>aq</sub><sup>3+</sup>, and 0.5 M lithium sulfate (pH 4.6) was irradiated at relatively low incident light intensity. Under these conditions less than 1% of the quenching is attributable to the added Fe<sub>aq</sub><sup>3+</sup>. The steady-state concentration of RuL<sub>3</sub><sup>3+</sup> was negligible when the 0.5 M lithium sulfate was replaced by 0.5 M sulfuric acid and was also negligible in the absence of added Fe<sub>aq</sub><sup>3+</sup>. This result is consistent with the acid dependence of the reaction of Cu<sub>aq</sub><sup>+</sup> with Fe<sub>aq</sub><sup>3+</sup>.<sup>7</sup> At pH 4.6 this reaction is very rapid and competes effectively with the oxidation of Cu<sub>aq</sub><sup>+</sup> by RuL<sub>3</sub><sup>3+</sup>. Since the Fe<sub>aq</sub><sup>2+</sup>-RuL<sub>3</sub><sup>3+</sup> reaction is appreciably slower (*k* = 6 × 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup> in 0.5 M sulfuric acid at 25 °C) than the reaction of Cu<sub>aq</sub><sup>+</sup> with RuL<sub>3</sub><sup>3+</sup> (6 × 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>,

**Table II.** Yield of Polypyridineruthenium(III) (RuL<sub>3</sub><sup>3+</sup>) and Rate Constants for the Reaction of RuL<sub>3</sub><sup>3+</sup> with Copper(I) Ions in 0.5 M Sulfuric Acid at 25 °C as Measured by the Flash-Photolysis Method

Ligands, L	E <sub>3,2</sub> <sup>0</sup> , V <sup>a</sup>	<i>k<sub>t</sub></i> , M <sup>-1</sup> s <sup>-1</sup>	Yield
4,4'-(CH <sub>3</sub> ) <sub>2</sub> bpy	1.10	8.7 × 10 <sup>7</sup>	0.94
bpy	1.26	9.7 × 10 <sup>8</sup>	0.56
		4.3 × 10 <sup>8</sup> <sup>b</sup>	0.68 <sup>b</sup>
		(3 ± 1) × 10 <sup>8</sup> <sup>c</sup>	0.76 <sup>c</sup>
		1 × 10 <sup>8</sup> <sup>d,e</sup>	1.0 <sup>d,e</sup>
3,4,7,8-(CH <sub>3</sub> ) <sub>4</sub> phen	1.02	6.0 × 10 <sup>7</sup>	0.95
4,7-(CH <sub>3</sub> ) <sub>2</sub> phen	1.09	1.4 × 10 <sup>8</sup>	0.96
5,6-(CH <sub>3</sub> ) <sub>2</sub> phen	1.20	5.4 × 10 <sup>8</sup>	0.79
5-(CH <sub>3</sub> )phen	1.23	1.0 × 10 <sup>9</sup>	0.74
5-(C <sub>6</sub> H <sub>5</sub> )phen	1.26	1.1 × 10 <sup>9</sup>	0.51
phen	1.26	1.2 × 10 <sup>9</sup>	0.54
5-Cl(phen)	1.36	2.7 × 10 <sup>9</sup>	0.31
5-Br(phen)	1.37	2.3 × 10 <sup>9</sup>	0.30

<sup>a</sup> Reference 5. <sup>b</sup> In 0.5 M perchloric acid. <sup>c</sup> In 2.4 M perchloric acid. <sup>d</sup> Ionic strength 1.9 M (1 M HClO<sub>4</sub> + 0.3 M Ca(ClO<sub>4</sub>)<sub>2</sub>). <sup>e</sup> Reference 3f.

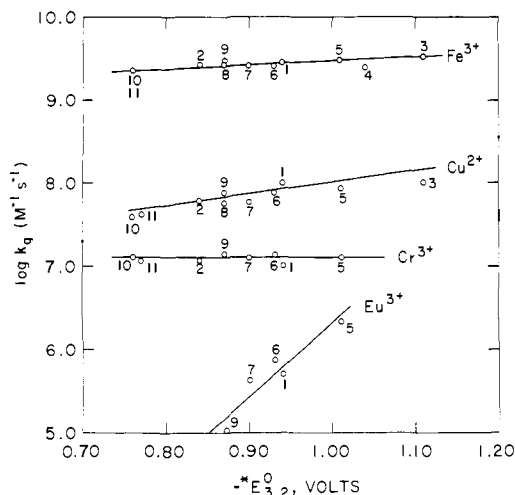
Table II) the steady-state concentration of RuL<sub>3</sub><sup>3+</sup> in the illuminated solution will increase. On the other hand, at low pH the reaction of Cu<sub>aq</sub><sup>+</sup> with Fe<sub>aq</sub><sup>3+</sup> is relatively slow (*k* = 4.8 × 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup> in 0.5 M perchloric acid) and consequently the steady-state concentration of RuL<sub>3</sub><sup>3+</sup> remains negligible at low pH. Similar considerations obtain in the absence of added Fe<sub>aq</sub><sup>3+</sup>.

The relative yields *Y* of RuL<sub>3</sub><sup>3+</sup> produced in the flash photolysis using Cu<sub>aq</sub><sup>2+</sup> as quencher compared to that using Fe<sub>aq</sub><sup>3+</sup> as quencher are also collected in Table II. Since the absolute yield of RuL<sub>3</sub><sup>3+</sup> produced in the Fe<sub>aq</sub><sup>3+</sup> quenching is close to 100%, the *Y* values in Table II provide good estimates of the absolute RuL<sub>3</sub><sup>3+</sup> yields in the Cu<sub>aq</sub><sup>2+</sup> quenching. The yields, like the rates, show a medium effect; the ruthenium(III) yields from the bipyridine complex tend to be higher in a perchlorate than a sulfate medium and approach 1.0 at high perchlorate concentrations.

Pulse radiolysis of solutions containing RuL<sub>3</sub><sup>2+</sup> produces an increase in absorbance at 510 nm.<sup>3b</sup> In the presence of Cu<sub>aq</sub><sup>2+</sup> the decay of this absorbance is exponential and the lifetime for the decay decreases linearly with increasing Cu<sub>aq</sub><sup>2+</sup> concentration. Under the experimental conditions used primary OH and e<sub>aq</sub><sup>-</sup> quickly react with *tert*-butyl alcohol and RuL<sub>3</sub><sup>2+</sup>, respectively. Reaction between e<sub>aq</sub><sup>-</sup> and Cu<sub>aq</sub><sup>2+</sup> to form Cu<sub>aq</sub><sup>+</sup> will not measurably affect the observed kinetics since Cu<sub>aq</sub><sup>+</sup> will not reduce either RuL<sub>3</sub><sup>3+</sup> or RuL<sub>3</sub><sup>2+</sup>. Under the conditions used the reaction of e<sub>aq</sub><sup>-</sup> with Cu<sub>aq</sub><sup>2+</sup> could decrease the Cu<sub>aq</sub><sup>2+</sup> concentration by only a few percent. Second-order rate constants for the reaction of RuL<sub>3</sub><sup>3+</sup> with Cu<sub>aq</sub><sup>2+</sup> were determined from the slopes of inverse lifetime vs. Cu<sub>aq</sub><sup>2+</sup> concentration plots. These results are listed in Table III.

## Discussion

A previous study has shown that the dependence of the quenching rate constants on the excited state potentials of the ruthenium(II) complexes can be used to distinguish between energy-transfer and electron-transfer quenching mechanisms.<sup>5</sup> In Figure 1 the potential dependence of the quenching rate constants measured in this work is compared with the potential dependence found for other systems. It will be seen that the variation of the copper(II) rates with the excited state potentials is less marked than the variation of the europium(III) rates but is larger than the variation of the chromium(III) rates. An electron-transfer mechanism has been assigned to



**Figure 1.** Plot of the logarithm of the rate constant for quenching by  $\text{Eu}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$  vs. the excited state potential of the  $\text{RuL}_3^{2+}$  complexes: 1, L = 4,4'-( $\text{CH}_3$ )<sub>2</sub>bpy; 2, L = bpy; 3, L = 3,4,7,8-( $\text{CH}_3$ )<sub>4</sub>phen; 4, L = 3,5,6,8-( $\text{CH}_3$ )<sub>4</sub>phen; 5, L = 4,7-( $\text{CH}_3$ )<sub>2</sub>phen; 6, L = 5,6-( $\text{CH}_3$ )<sub>2</sub>phen; 7, L = 5-( $\text{CH}_3$ )phen; 8, L = 5-( $\text{C}_6\text{H}_5$ )phen; 9, L = phen; 10, L = 5-Br(phen); 11, L = 5-Cl(phen).

**Table III.** Rate Constants for the Reaction of  $\text{RuL}_3^{2+}$  with Copper(II) Ions at 25 °C<sup>a</sup>

Ligands, L	$E_{2,1}^{0, b, c}$ V vs. SCE	$10^{-8}k$ , $\text{M}^{-1} \text{s}^{-1}$
4,4'-( $\text{CH}_3$ ) <sub>2</sub> bpy	-1.44	3.7
bpy	-1.35	3.9 5.2 <sup>d</sup> 3.4 <sup>e, f</sup>
phen	-1.43	4.7
5-Cl(phen)	-1.22	2.6

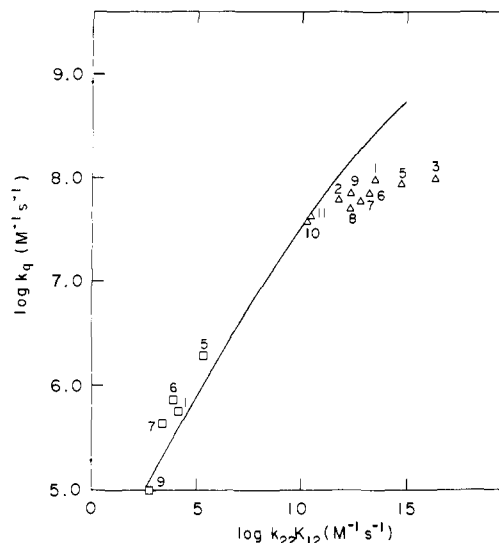
<sup>a</sup> Cacodylate buffer, pH 6.6, 0.5 M *tert*-butyl alcohol, ionic strength  $\sim 0.04$  M. <sup>b</sup> In acetonitrile containing 0.1 M tetra-*n*-propylammonium hexafluorophosphate, the potentials vs. the normal hydrogen electrode are expected to be 0.07 V more positive, ref 3a. <sup>c</sup> C. Creutz, submitted for publication. <sup>d</sup> In 0.5 M  $\text{NaClO}_4$ . <sup>e</sup> At pH 6-7, maximum ionic strength  $\sim 1.8 \times 10^{-4}$  M. <sup>f</sup> Reference 3f.

the former reactions and an energy-transfer mechanism to the latter.<sup>5</sup> (The rates of the iron(III) reactions, which involve an electron-transfer mechanism, are close to the diffusion-controlled limit.) This comparison suggests that the copper(II) reactions proceed by an electron-transfer mechanism. The potential dependence of the copper(II) quenching rates is, however, small and the plots in Figure 1 suggest that the dependence is weaker than expected for "normal" electron-transfer quenching. This is perhaps more readily apparent from Figure 2, where the quenching rate constants for the europium(III) and copper(II) reactions are plotted as a function of the driving force for electron transfer corrected for differences in the self-exchange rates of the aquo ions. This plot is suggested by the Marcus equations<sup>8</sup>

$$\log k_{12} = 0.50 \log k_{11} + 0.50 \log (k_{22}K_{12}f_{12}) \quad (7a)$$

$$\log f_{12} = (\log K_{12})^2 / 4 \log (k_{11}k_{22}/Z^2) \quad (7b)$$

where  $k_{11}$  and  $k_{22}$  refer to the exchange reactions and  $k_{12}$  and  $K_{12}$  to the cross reaction. Equation 7 predicts an increase in the electron-transfer rate constant  $k_{12}$  with increasing  $k_{22}K_{12}f_{12}$ . This trend should continue until the diffusion-limited rate is reached at high driving force. The reduction potentials and exchange rates used in applying eq 7 to the europium(III) and copper(II) quenching data are  $-0.43$  and  $+0.15$  V, and  $3 \times 10^{-5}$  and  $1 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ , for the  $\text{Eu}_{\text{aq}}^{2+}$



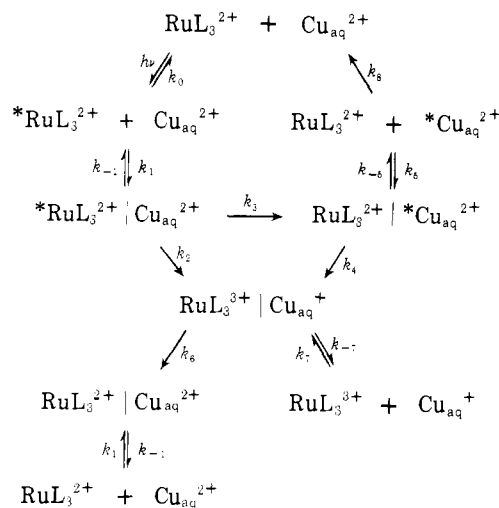
**Figure 2.** Plot of the logarithm of the quenching constants vs. the logarithm of the product of the exchange rate constant of the quencher and the equilibrium constant for the quenching reaction: squares, quenching by  $\text{Eu}^{3+}$ ; triangles, quenching by  $\text{Cu}^{2+}$ ; ruthenium complexes numbered according to the caption for Figure 1.

+  $\text{Eu}_{\text{aq}}^{3+}$  and  $\text{Cu}_{\text{aq}}^{2+}$  couples, respectively.<sup>9-12</sup> The plot in Figure 2 does indeed confirm that the dependence of the copper(II) quenching rates on the driving force for electron transfer is smaller than expected.

One explanation for the relatively small change in the copper(II) quenching rates is that the quenching proceeds by parallel energy-transfer and electron-transfer pathways. Energy transfer from  $^*\text{RuL}_3^{2+}$  (emission maximum around 600 nm) to  $\text{Cu}_{\text{aq}}^{2+}$  (absorption maximum at 800 nm) is energetically possible. The  $(t_{2g})^5(e_g)^4$  excited state of  $\text{Cu}_{\text{aq}}^{2+}$  lies about  $12\,500 \text{ cm}^{-1}$  or  $\sim 1.55 \text{ eV}$  above the  $(t_{2g})^6(e_g)^3$  ground state. This excited state would be a powerful oxidant ( $E^0 \sim +1.70 \text{ V}$ )<sup>13</sup> and could oxidize  $\text{RuL}_3^{2+}$  to form  $\text{RuL}_3^{3+}$  and  $\text{Cu}_{\text{aq}}^{+}$ . An energy-transfer mechanism leading to electron-transfer products cannot thus be excluded on thermodynamic grounds. However, such an energy-transfer mechanism can be excluded on the basis of kinetic arguments.

A detailed mechanism for the copper(II) quenching of the emission of the polypyridine ruthenium complexes is presented in Scheme I.<sup>14</sup> In this scheme, species denoted as  $\text{A}|\text{B}$  represent solvated precursor or successor complexes with  $|$  indicating that no chemical bonds have been made or broken.

#### Scheme I



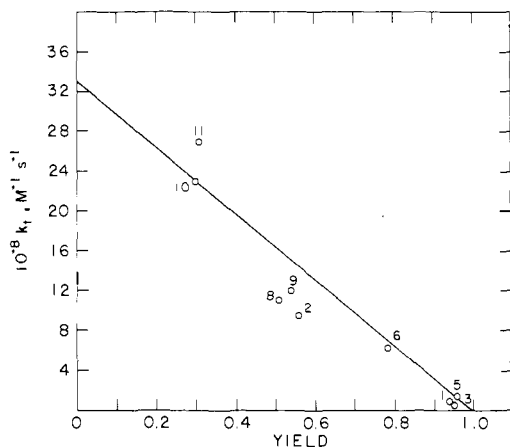


Figure 3. Plot of the rate constant for the reaction of  $\text{Cu}^+$  with  $\text{RuL}_3^{3+}$  vs. the yield of electron transfer products formed in the quenching reaction in 0.5 M sulfuric acid at 25 °C: ruthenium complexes numbered according to the caption for Figure 1.

In terms of Scheme I the yield of separated electron-transfer products is given by

$$Y = \frac{k_{-7}}{k_6 + k_{-7}} \left[ \frac{k_2}{k_2 + k_3} + \frac{k_3}{k_2 + k_3} \left( \frac{k_4}{k_4 + k_{-5}} \right) \right] \quad (8a)$$

$$= \alpha \left( \frac{k_{-7}}{k_6 + k_{-7}} \right) \quad (8b)$$

The second term in this expression allows for the formation of electron-transfer products in the energy-transfer pathway. According to Scheme I the rate constant for the thermal back-reaction of  $\text{RuL}_3^{3+}$  and copper(I) is given by eq 9. This equation can be combined with eq 8 to give eq 10.

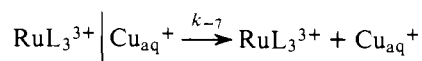
$$k_t = \frac{k_6 k_7}{k_6 + k_{-7}} \quad (9)$$

$$k_t = k_7 \left( 1 - \frac{Y}{\alpha} \right) \quad (10)$$

Equation 10 predicts that a plot of  $k_t$  vs.  $Y$  should be a straight line with intercept  $k_7$  and with a ratio of intercept to slope equal to  $-\alpha$ . This plot is shown in Figure 3. The value of  $k_7$ , the diffusion-limited rate constant, calculated from this plot is  $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , in excellent agreement with the experimental value for systems of this type.<sup>15a</sup> The value of  $\alpha$  calculated from the plot is unity within experimental error. This is an important result since it means that every quenching act, whether electron transfer or energy transfer, leads to electron transfer products: the yield of separated electron transfer products is less than unity because of competition of the reverse electron transfer



with the diffusional separation of the electron-transfer products<sup>15b</sup>



Returning to the expression for  $\alpha$  (eq 8) there are three cases of interest. It is apparent that  $\alpha$  can be equal to unity in the two limiting cases of electron-transfer quenching ( $k_2 \gg k_3$ ) and energy-transfer quenching leading to electron-transfer products with unit probability ( $k_3 \gg k_2$  and  $k_4 \gg k_{-5}$ ). For competitive energy and electron-transfer quenching ( $k_2 \sim k_3$ ) the only requirement is that  $k_4 \gg k_{-5}$ . According to the above analysis, when energy transfer is either faster than or comparable to electron-transfer quenching, energy transfer only leads to electron-transfer products if oxidation of  $\text{RuL}_3^{2+}$  by the

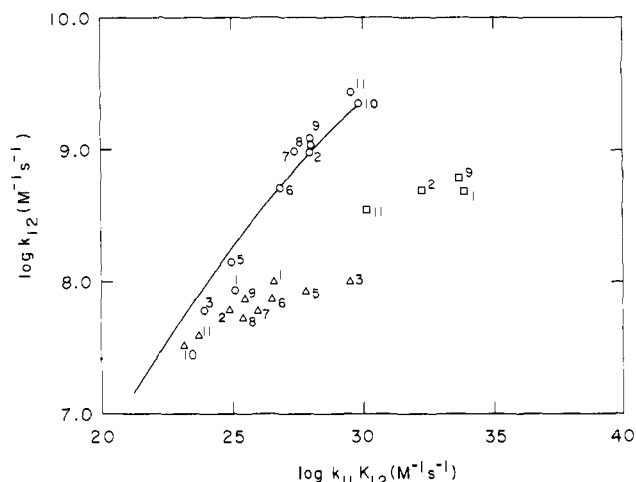


Figure 4. Plot of the logarithm of the rate constant for electron transfer vs. the logarithm of the product of the exchange rate constant of the ruthenium complex and the equilibrium constant for the reaction: circles,  $\text{Cu}^+ + \text{RuL}_3^{3+}$ ; triangles,  $^*\text{RuL}_3^{2+} + \text{Cu}^{2+}$ ; squares  $\text{RuL}_3^{3+} + \text{Cu}^{2+}$ ; ruthenium complexes numbered according to the caption for Figure 1.

excited copper(II) occurs before these species diffuse from the cage in which they were formed ( $k_4 \gg k_{-5}$ ).<sup>16</sup> The latter requires that electron transfer between  $\text{RuL}_3^{2+}$  and  $^*\text{Cu}_{\text{aq}}^{2+}$  be diffusion controlled. Because of the relatively small driving force for this electron transfer, for example,  $\Delta E^0 < 0.45 \text{ V}$  for  $\text{L} = \text{bpy}$ , a very rapid  $\text{Cu}_{\text{aq}}^+ + ^*\text{Cu}_{\text{aq}}^{2+}$  exchange rate ( $> 2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , eq 7) is required for a diffusion-controlled reaction of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $^*\text{Cu}_{\text{aq}}^{2+}$ . Although the exchange of the excited copper(II) could be rapid in view of the similar tetrahedral configurations expected for  $\text{Cu}_{\text{aq}}^+$  and  $^*\text{Cu}_{\text{aq}}^{2+}$  and because a  $t_{2g}$  electron is transferred in the exchange, the calculated lower limit of  $2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  is several orders of magnitude faster than measured aquo ion exchange rates. For this reason we conclude that it is unlikely that  $k_4 \gg k_{-5}$  and therefore that energy transfer cannot account for the observed electron-transfer products. For the same reason parallel energy and electron-transfer quenching pathways are also excluded. Finally, the conclusion that electron-transfer quenching obtains is consistent with the relatively rapid rates observed for copper(II) quenching of the  $\text{OsL}_3^{2+}$  complexes (Table I): because of energetic considerations the rates of the  $\text{OsL}_3^{2+}$  reactions are not expected to be faster than the  $\text{RuL}_3^{2+}$  rates if energy transfer is involved.

Having ruled out an energy-transfer quenching mechanism we return to the question of the small free-energy dependence of the copper(II) quenching rates. In this connection it is of interest to know whether electron-transfer reactions involving the  $\text{Cu}_{\text{aq}}^+ - \text{Cu}_{\text{aq}}^{2+}$  couple generally show small driving force dependences. Some information on this point can be obtained from the free-energy dependence of the  $\text{RuL}_3^{3+} + \text{Cu}_{\text{aq}}^+$  back-reactions. For this purpose eq 9 can be rearranged to give

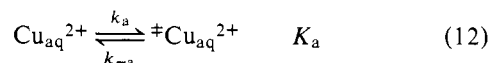
$$k_t = \frac{(k_6 k_7 / k_{-7}) k_7}{(k_6 k_7 / k_{-7}) + k_7} \quad (11a)$$

$$= \frac{k_{\text{act}} k_{\text{diff}}}{k_{\text{act}} + k_{\text{diff}}} \quad (11b)$$

in which  $k_{\text{diff}} = k_7$ , the diffusion-limited rate constant, is  $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{\text{act}} = k_6 k_7 / k_{-7}$ , the activation-controlled rate constant, can be calculated from eq 7. In Figure 4 the experimental rate constants (circles) are compared with the values calculated from eq 7 and 11 (solid line). The agreement of observed and calculated rates is remarkably good, indicating that the reactions of  $\text{RuL}_3^{3+}$  and  $\text{Cu}_{\text{aq}}^+$  and, by microscopic

reversibility, the reactions of  $\text{RuL}_3^{2+}$  and  $\text{Cu}_{\text{aq}}^{2+}$  show a normal free-energy dependence. This establishes that electron-transfer reactions involving the  $\text{Cu}_{\text{aq}}^+ - \text{Cu}_{\text{aq}}^{2+}$  couple and the polypyridineruthenium complexes do not necessarily show weak driving force dependences.

A third explanation for the small free-energy dependence of the copper(II) quenching rates is that, although the mechanism involves electron transfer, the actual quenching is not done by the bulk copper(II) species but by a form of copper(II),  $\ddagger\text{Cu}_{\text{aq}}^{2+}$ , which is normally present in low concentration but which is in very rapid equilibrium with the bulk copper(II) species:



If  $K_a \approx 0.03$  and the quenching by  $\ddagger\text{Cu}^{2+}$  is close to the diffusion-controlled limit, then (provided  $k_{-a} > k_1[\ddagger\text{Cu}^{2+}]$  and  $k_2 > k_{-a}$ , Scheme I) the observed quenching rates will level off at  $K_a k_{\text{diff}}$  or  $\approx 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . In other words, under these conditions rate saturation below the normal diffusion-controlled limit will be observed. However, we are not aware of direct evidence for the existence of  $\ddagger\text{Cu}_{\text{aq}}^{2+}$ . This species is not simply a sulfate complex of copper(II) since the quenching rate constants (Table I) are not sensitive to the replacement of a sulfate by a perchlorate medium. It could perhaps be a Jahn-Teller distorted form of  $\text{Cu}_{\text{aq}}^{2+}$ . Evidence against the existence of a species with the properties of  $\ddagger\text{Cu}_{\text{aq}}^{2+}$  is provided by the reactions of  $\text{RuL}_3^+$  with  $\text{Cu}_{\text{aq}}^{2+}$ : the rate constants for these reactions (Table III) are larger than the apparent saturation value of  $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . This is also apparent from Figure 4, where the logarithms of the rate constants for the  $\text{RuL}_3^+ + \text{Cu}_{\text{aq}}^{2+}$  reactions<sup>17</sup> are plotted as a function of  $\log k_{11}K_{12}$  (squares).<sup>18</sup> This figure also contains the data for the  $\text{*RuL}_3^{2+} + \text{Cu}_{\text{aq}}^{2+}$  quenching reactions (triangles). Evidently the rate constants for the reactions of  $\text{*RuL}_3^{2+}$  and  $\text{RuL}_3^+$  with  $\text{Cu}_{\text{aq}}^{2+}$  are reasonably consistent with each other (particularly considering the smaller charge product for the latter pair of reactants) and both series of reactions show a smaller free-energy dependence than the reactions of  $\text{RuL}_3^{3+}$  with  $\text{Cu}_{\text{aq}}^+$ . The two former reactions have in common at least one feature not shared by the  $\text{RuL}_3^{3+}$  reactions, namely, the transfer of a  $\pi^*$  electron in the oxidation-reduction step. Although this difference could be responsible for the different free-energy dependences of the  $\text{RuL}_3^+$ ,  $\text{*RuL}_3^{2+}$ , and  $\text{RuL}_3^{3+}$  reactions, the detailed nature of this effect is not obvious. Moreover, the reactions of europium(III) with  $\text{*RuL}_3^{2+}$  (which also involve the transfer of a  $\pi^*$  electron) show a normal free-energy dependence.

Finally, in addition to the reactions of  $\text{*RuL}_3^{2+}$  and  $\text{RuL}_3^+$  with copper(II), there are a number of other very exothermic reactions which also show a free-energy dependence smaller than that predicted by eq 7.<sup>11,19</sup> Indeed there is increasing evidence that eq 7 tends to overestimate the rates of reactions with large driving forces.<sup>11</sup> The origin of this effect presumably lies in the detailed shapes of the potential energy surfaces, in departures from adiabaticity and in nuclear tunneling and other quantum mechanical contributions. Although these factors are not fully understood at this time, the study of very exothermic electron-transfer reactions could provide important information about the reasons for the breakdown of the simple

Marcus model at large driving forces.<sup>20</sup>

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- (16) The lifetime of excited copper(II) is too short for the (diffusion-controlled) reaction of  $\text{RuL}_3^{2+}$  and  $\text{*Cu}^{2+}$  to occur.
- (17) The rate constants were corrected to ionic strength 0.5 M using the factor 1.3 determined for the  $\text{Ru}(\text{bpy})_3^+ + \text{Cu}^{2+}$  reaction (Table III).
- (18) A value of  $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  was used for the rate constant of the  $\text{RuL}_3^+ + \text{RuL}_3^{2+}$  exchange.<sup>5</sup> No correction for the different charge products in these reactions has been made. For this reason the rate constants for the  $\text{RuL}_3^+ - \text{Cu}^{2+}$  reaction might be expected to lie slightly above the line defined by the  $\text{*RuL}_3^{2+} - \text{Cu}^{2+}$  reactions.
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