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Mechanism of the Quenching of the Phosphorescence of Tris(2,2'-bipyridine)ruthenium(II) by Some Cobalt(III) and Ruthenium(III) Complexes

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The quenching of the $Ru(bipy)_3^{2+}$ phosphorescence by $Co(NH_3)_5X^{3+}$ ($X = Br^-$, Cl^-, H_2O, and NH_3) and by $Ru(NH_3)_5X^{3+}$ ($X = Cl^-$ and NH_3) complexes has been studied by a spectrofluorimetric technique. Stern-Volmer constants were determined and the kinetics of the quenching reactions investigated in 0.5 *M* sulfuric acid at 25°. Some measurements were also performed in 50% 2-propanol. The $Co(NH_3)_5X^{3+}$ quenched rates increase in the order $NH_3 < H_2O < Cl^- < Br^-$ with the latter reaction being diffusion controlled. In the absence of 2-propanol the ratio k_2/k_Q, where k_2 is the second-order rate constant for the formation of $Ru(bipy)_3^{3+}$ and k_Q is the second-order quenching rate constant, was close to unity for all of the cobalt(III) complexes studied. This ratio was somewhat lower for $Co(NH_3)_5Cl^{2+}$ in 50% 2-propanol. The $Ru(NH_3)_5X^{3+}$ complexes quenched much more efficiently than the corresponding $Co(NH_3)_5X^{3+}$ complexes; however, in contrast to the cobalt(III) reactions, the ruthenium(III) reactions were not accompanied by the net oxidation of $Ru(bipy)_3^{2+}$. The results are discussed in terms of an electron transfer quenching mechanism, and a value of 0.9 V is estimated for the oxidation potential of $^3Ru(bipy)_3^{2+}$.

Introduction

The tris(2,2'-bipyridine)ruthenium(II) ion is finding increasing application as a sensitizer in photochemical studies of cobalt(III) complexes.[1-5] The photosensitized reduction of a given cobalt(III) complex is readily apparent from the decrease in the emission from the low-lying triplet charge transfer state of the ruthenium(II) and the concurrent formation of Co^{2+}. There is a controversy, however, regarding the mechanism of these photoinduced oxidation-reduction reactions; Gafney and Adamson[1] have proposed an electron transfer mechanism, while Natarajan and Endicott[3,4] have proposed a mechanism involving triplet-to-triplet energy transfer followed by the intramolecular oxidation of one of the ligands of the cobalt(III) substrate. In this paper we discuss these proposals and, for purposes of comparison with the cobalt(III) results, we also present quenching constants for some ruthenium(III) complexes.

Experimental Section

Materials. The cobalt(III) complexes were synthesized and purified using published procedures.[6-8] Commercial $[Ru(NH_3)_6]Cl_3$ was purified using literature methods,[9] while $[(NH_3)_5RuCl]Cl_2$ was prepared from the hexaammine and purified by recrystallization from dilute hydrochloric acid.[10] The perchlorate salts of the complexes were prepared from the chloride salts by the addition of sodium perchlorate acidified with perchloric acid. Commercial $[Ru(bipy)_3]Cl_2 \cdot 6H_2O$ was used without further purification; preliminary experiments indicated no difference between the kinetic properties of the commercial sample and one which had been recrystallized. Solutions $0.2-1.0 \times 10^{-5}$ *M* in $Ru(bipy)_3^{2+}$ and 0.5 *M* in sulfuric acid (Merck Analytical Grade) were prepared with double distilled water or with 50% v/v spectral quality 2-propanol and were deaerated by nitrogen bubbling immediately prior to use.

Procedure. Emission intensity measurements were made on a Perkin-Elmer Model MPF-3 fluorescence spectrophotometer equipped with a 150-W xenon lamp. Incident light intensities were measured using ferrioxalate actinometry.[11] Excitation wavelengths in the region 385-460 nm were used and the phosphorescence was monitored at 610 nm; the bandwidth of the excitation wavelengths was generally 2-10 nm. In the presence of the cobalt(III) complexes, the phosphorescence intensity began to decrease immediately on opening the excitation shutter.[12] As a consequence, the initial emission intensities in these systems were obtained by extrapolation to the beginning of the measurement. The extrapolated emission intensities were corrected for absorption of the incident light by the cobalt(III) complexes by use of the equation[2]

$$\left(\frac{I_0}{I}\right)_{\text{corr}} = \left(\frac{I_0}{I}\right)_{\text{app}} \left[\frac{1 - 10^{-(A_D + A_Q)}}{1 - 10^{-A_D}}\right] \frac{A_D}{A_D + A_Q} \qquad (1)$$

where $(I_0/I)_{\text{app}}$ is the observed ratio of emission intensity from an unquenched sample to that from a quenched one, and A_D and A_Q are the absorbances per centimeter of the donor and quencher, respectively, at the exciting wavelength (1-cm² cells were used for the measurements). The corrections, which were generally less than 10%, were largest for $Co(NH_3)_6^{3+}$ and negligible for the ruthenium(III) complexes. Absorption by the quenchers at the emitting wavelengths was also negligible at the concentrations used. All of the measurements were performed in 0.5 *M* sulfuric acid at 25°.

Results

The emission intensity measurements gave excellent Stern-Volmer plots (eq 2 and Figure 1). The quenching constants

$$(I_0/I)_{\text{corr}} = 1 + K_{\text{sv}}[Q] \qquad (2)$$

calculated from these plots are summarized in Table I. This table also includes some values reported by Gafney and Adamson.[1] These workers performed measurements both in an acetate buffer and in 0.5 *M* H_2SO_4 but did not specify which medium was used for the determination of the quenching constants. Comparison with our results suggests that their measurements were made in a medium of relatively low ionic strength, presumably the acetate buffer.

Table I also contains values of the second-order rate con-

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(1) H. D. Gafney and A. W. Adamson, *J. Amer. Chem. Soc.*, **94**, 8238 (1972).

(2) J. N. Demas and A. W. Adamson, *J. Amer. Chem. Soc.*, **95**, 5159 (1973).

(3) P. Natarajan and J. F. Endicott, *J. Phys. Chem.*, **77**, 971 (1973).

(4) P. Natarajan and J. F. Endicott, *J. Phys. Chem.*, **77**, 1823 (1973).

(5) F. Bolletta, M. Maestri, L. Moggi, and V. Balzani, *J. Amer. Chem. Soc.*, **95**, 7864 (1973).

(6) D. Sebera and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1785 (1961).

(7) W. A. Hymes, L. K. Yanowski, and M. Shiller, *J. Amer. Chem. Soc.*, **60**, 3053 (1938).

(8) F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1953).

(9) J. R. Pladziewicz, T. J. Meyer, J. A. Broomhead, and H. Taube, *Inorg. Chem.*, **12**, 639 (1973).

(10) L. H. Vogt, J. T. Katz, and S. E. Wiberly, *Inorg. Chem.*, **4**, 1157 (1965).

(11) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(12) In preliminary experiments, the emission intensity did not start to decrease immediately but exhibited a short induction period. This induction period was found to be due to traces of a reducing agent, probably sulfur dioxide, in the commercial sulfuric acid used. The Merck analytical grade sulfuric acid did not contain interfering reducing agents.

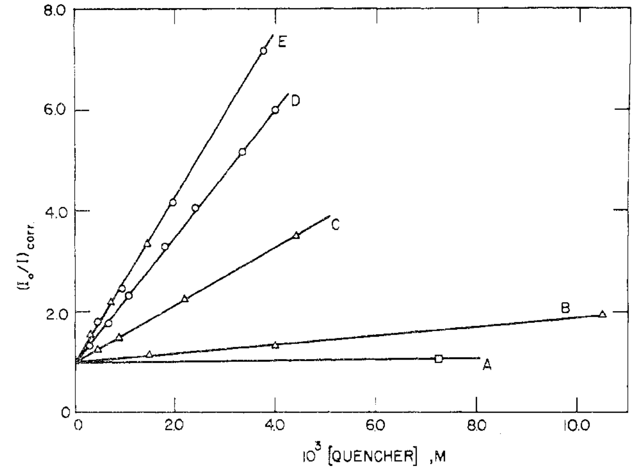

Figure 1. Stern-Volmer plots for quenching of the $Ru(bipy)_3^{2+}$ emission by $Co(NH_3)_5X^{3+}$ complexes in 0.5 *M* sulfuric acid at 25°: (A) $Co(NH_3)_6^{3+}$; (B) $Co(NH_3)_5H_2O^{3+}$; (C) $Co(NH_3)_5Cl^{2+}$; (D) $Ru(NH_3)_6^{3+}$; (E) △ $Co(NH_3)_5Br^{2+}$ and ○ $Ru(NH_3)_5Cl^{2+}$.

Table I. Stern-Volmer Constants for the Quenching of $^3Ru(bipy)_3^{2+}$ Emission by Cobalt(III) and Ruthenium(III) Complexes in 0.5 *M* Sulfuric Acid at 25°

Complex	[2-propanol], % v/v	K_{sv}, M^{-1}	$10^{-9}k_Q$,[a] M^{-1} sec^{-1}
$Co(NH_3)_6^{3+}$	0	8 ± 6	~0.01
$Co(NH_3)_5H_2O^{3+}$	0	$9.2 \pm 0.8 \times 10^1$	0.15
$Co(NH_3)_5Cl^{2+}$	0	$5.6 \pm 0.4 \times 10^2$	0.93
	0	100[b]	
	50	$4.0 \pm 0.5 \times 10^2$	0.46
$Co(NH_3)_5Br^{2+}$	0	$1.5 \pm 0.1 \times 10^3$	2.5
	0	225[b]	
	50	$1.0 \pm 0.1 \times 10^3$	1.1
$Ru(NH_3)_6^{3+}$	0	$1.25 \pm 0.06 \times 10^3$	2.1
$Ru(NH_3)_5Cl^{2+}$	0	$1.60 \pm 0.08 \times 10^3$	2.7

[a] Calculated from eq 3. [b] Reference 1.

stants for the quenching reactions. These rate constants were calculated from

$$k_Q = K_{sv}/\tau_0 \tag{3}$$

where τ_0, the unquenched lifetime of the triplet state, is $6.0 \pm 0.2 \times 10^{-7}$ sec in the absence of 2-propanol.[13] Also included in Table I are the quenching constants for $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ in 50% v/v 2-propanol. We have found the phosphorescence quantum yield of (unquenched) $Ru(bipy)_3^{2+}$ to be 50% higher in 50% v/v 2-propanol than in water implying (provided that the intrinsic radiative lifetime ($1/k_r$) of $Ru(bipy)_3^{2+}$ is similar in these two media) a triplet state lifetime of $1.5 \times 6.0 \times 10^{-7} = 9.0 \times 10^{-7}$ sec in the mixed solvent. A direct determination of this lifetime by single photon counting techniques gives $\tau_0 = 8.7 \pm 0.3 \times 10^{-7}$ sec,[13] in excellent agreement with the value estimated from the emission intensity measurements (showing that the assumption about k_r is essentially correct). The former value was used to calculate the second-order rate constants reported for the mixed solvent in Table I.

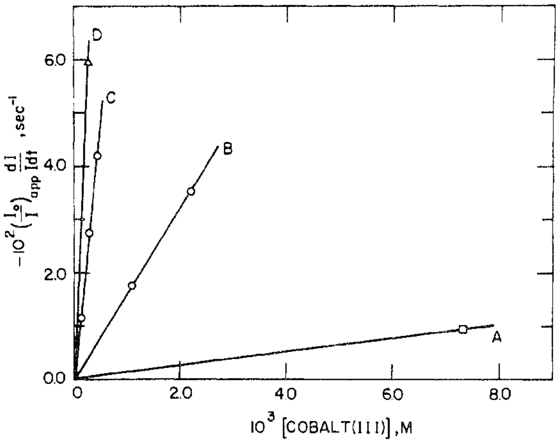

Figure 2. Apparent rates of oxidation of $Ru(bipy)_3^{2+}$ as a function of the concentration of the cobalt(III) quencher in 0.5 *M* sulfuric acid at 25°. Excitation wavelength = 430 nm, incident light intensity = 0.6×10^{-8} einstein cm^{-2} sec^{-1}: (A) $Co(NH_3)_6^{3+}$; (B) $Co(NH_3)_5H_2O^{3+}$; (C) $Co(NH_3)_5Cl^{2+}$; (D) $Co(NH_3)_5Br^{2+}$.

Table II. Composite Rate Constants for the Quenching of $^3Ru(bipy)_3^{2+}$ Emission by Cobalt(III) in 0.5 *M* Sulfuric Acid at 25°[a]

Complex	[2-propanol], % v/v	k_{comp},[b] M^{-1} sec^{-1}	k_{comp}/K_{sv},[b] sec^{-1}
$Co(NH_3)_6^{3+}$	0	1.31 ± 0.11	~0.16
$Co(NH_3)_5H_2O^{3+}$	0	16 ± 1	0.17 ± 0.03
$Co(NH_3)_5Cl^{2+}$	0	94 ± 8	0.17 ± 0.03
	50	33 ± 3	0.08 ± 0.02
$Co(NH_3)_5Br^{2+}$	0	245 ± 15	0.16 ± 0.02
	50	128 ± 12	0.13 ± 0.03

[a] Excitation wavelength = 430 nm, $I_{in} = 0.61 \times 10^{-8}$ einstein cm^{-2} sec^{-1}. [b] The composite rate constant is $-(1/[Co(III)])[I_0/I]_{app}(dI/Idt)$.

The emission intensities in the presence of the cobalt(III) complexes were not constant but decreased as a function of time. In common with previous workers, we find that this decrease is due to the photochemical oxidation of $Ru(bipy)_3^{2+}$ to $Ru(bipy)_3^{3+}$. Thus, the absorbances of the solutions at 455 nm (an absorbance maximum of $Ru(bipy)_3^{2+}$, ϵ 14,000) decreased upon irradiation but could be restored to their initial values by the addition of sodium oxalate (which reduces $Ru(bipy)_3^{3+}$ to $Ru(bipy)_3^{2+}$). The rate of the photochemical oxidation increased with increasing cobalt(III) concentration and with the incident light intensity. The initial rates of oxidation, as reflected in the initial slopes of the emission intensity *vs.* time curves, are plotted in Figure 2 as a function of the cobalt(III) concentrations and in Figure 3 as a function of the incident light intensity. The slopes of the plots in Figure 2 are presented in Table II.

The absorption spectrum of $[Ru(NH_3)_6](ClO_4)_2$, measured on a Cary 17 spectrophotometer, is shown in Figure 4. No *net* photoinduced oxidation of $Ru(bipy)_3^{2+}$ occurred with the ruthenium(III) quenchers on the time scale of our observations.

Discussion

The data in Table I show that the rate constants for the quenching of $^3Ru(bipy)_3^{2+}$ phosphorescence by the $Co(NH_3)_5X^{3+}$ complexes increase in the order $NH_3 < H_2O < Cl^- < Br^-$, with the rate constant for $Co(NH_3)_5Br^{2+}$ quenching being diffusion controlled, or at least very close to the diffusion-controlled limit. It is evident from Table II that the rates of the photoinduced oxidation of $Ru(bipy)_3^{2+}$ by the $Co(NH_3)_5X^{3+}$ complexes also increase in the order $NH_3 < H_2O < Cl^- < Br^-$. This is also the order obtaining in typi-

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[13] J. Barker and N. Sutin, unpublished observations; the emission lifetime of 6.0×10^{-7} sec in H_2O at 25° was measured by single photon counting techniques. This value may be compared with $\tau_0 = 6.6 \times 10^{-7}$ sec at an unspecified temperature reported in ref 2 and $\tau_0 = 6.2 \times 10^{-7}$ sec at ~21° calculated from the data reported in ref 14.

[14] J. N. Demas, D. Diemente, and E. W. Harris, *J. Amer. Chem. Soc.*, 95, 6864 (1973).

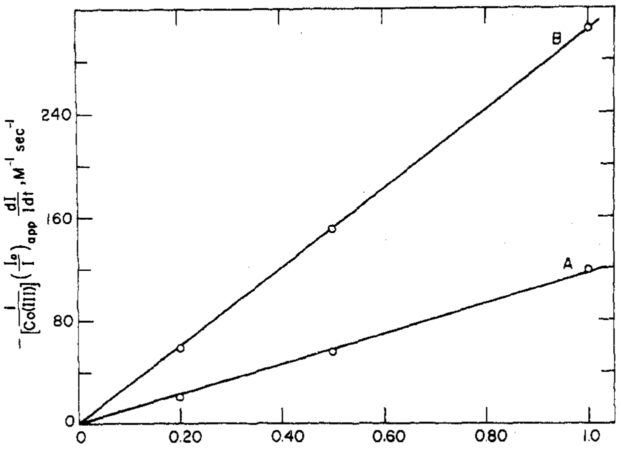

Figure 3. Composite rate constant for the oxidation of $\text{Ru(bipy)}_3{}^{2+}$ as a function of the incident light intensity in 0.5 *M* sulfuric acid at 25°. The light intensity was varied by the use of neutral density filters. Excitation wavelength = 430 nm, unfiltered incident light intensity ~0.8×10^{-8} einstein cm^{-2} sec^{-1}: (A) $\text{Co(NH}_3)_5\text{Cl}^{2+}$; (B) $\text{Co(NH}_3)_5\text{Br}^{2+}$.

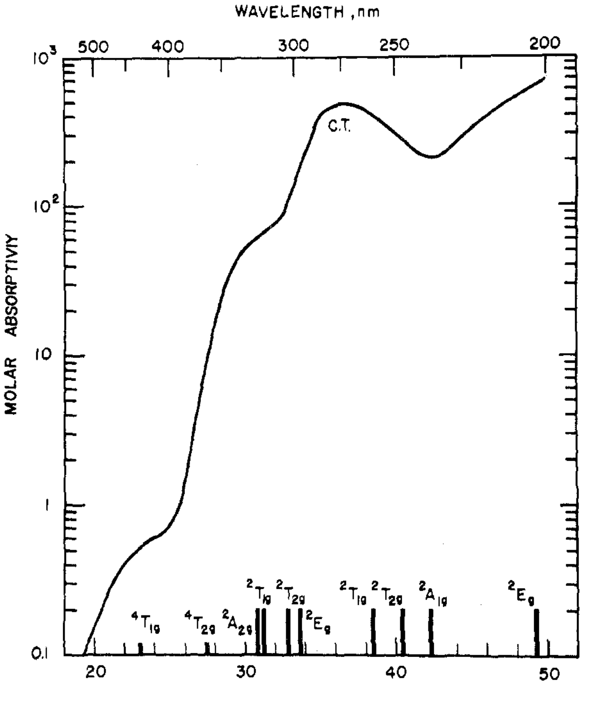

Figure 4. Absorption spectrum of $[\text{Ru(NH}_3)_6](\text{ClO}_4)_3$ in water. Measurements were made on a Cary 17 spectrophotometer using cells of 1- and 5-cm path lengths.

cal outer-sphere reductions of $\text{Co(NH}_3)_5\text{X}^{3+}$.[15] The simplest explanation of these observations is that the phosphorescence quenching proceeds by an electron transfer mechanism of the type proposed by Gafney and Adamson.[1] Consider the following general quenching scheme.

$$\text{Ru(bipy)}_3{}^{2+} \xrightarrow{h\nu} {}^3\text{Ru(bipy)}_3{}^{2+} \tag{4}$$

$${}^3\text{Ru(bipy)}_3{}^{2+} \xrightarrow{k_r} \text{Ru(bipy)}_3{}^{2+} + h\nu' \tag{5a}$$

$${}^3\text{Ru(bipy)}_3{}^{2+} \xrightarrow{k_{nr}} \text{Ru(bipy)}_3{}^{2+} + \text{heat} \tag{5b}$$

$${}^3\text{Ru(bipy)}_3{}^{2+} + \text{Co(III)} \xrightarrow{k_2} \text{Ru(bipy)}_3{}^{3+} + \text{Co}^{2+} \tag{6}$$

$${}^3\text{Ru(bipy)}_3{}^{2+} + \text{Co(III)} \xrightarrow{k_3} \text{Ru(bipy)}_3{}^{2+} + {}^3\text{Co(III)} \tag{7}$$

This scheme shows ${}^3\text{Ru(bipy)}_3{}^{2+}$ being produced with unit efficiency in the first step. Although there is evidence that the quantum efficiency of this step is indeed unity,[16] the above scheme does not require that it be so. We also assume for the time being that the ^{3}Co(III) produced in the last step does not directly or indirectly bring about any further oxidation of $\text{Ru(bipy)}_3{}^{2+}$. In terms of this scheme the steady state concentration of ${}^3\text{Ru(bipy)}_3{}^{2+}$ is given by

$$[{}^3\text{Ru(II)}] = \frac{10^3 I_{\text{in}}[1 - 10^{-(A_D + A_Q)}]A_D}{\{k_1 + k_Q[\text{Co(III)}]\}[A_D + A_Q]l} \tag{8}$$

where $k_1 = k_r + k_{nr} = 1/\tau_0$, $k_Q = k_2 + k_3$, I_{in} is the incident light intensity (einsteins cm^{-2} sec^{-1}),[17] and l is the pathlength of the cell (1 cm). The rate of oxidation of $\text{Ru(bipy)}_3{}^{2+}$ is given by

$$-\text{d}[\text{Ru(II)}]/\text{d}t = k_2[{}^3\text{Ru(II)}][\text{Co(III)}] \tag{9}$$

Substitution of eq 1, 2, and 8 into 9 gives

$$-\frac{\text{d}[\text{Ru(II)}]}{\text{d}t} = \left(\frac{I}{I_0}\right)_{\text{app}} k_2\tau_0 B I_{\text{in}}[\text{Co(III)}][\text{Ru(bipy)}_3{}^{2+}] \tag{10}$$

provided A_D is small. In the above expression $B = 2.30 \times 10^3\epsilon_D$. Since the rate of oxidation is also given by

$$\frac{\text{d}[\text{Ru(II)}]}{[\text{Ru(II)}]\,\text{d}t} = \frac{\text{d}[{}^3\text{Ru(II)}]}{[{}^3\text{Ru(II)}]\,\text{d}t} = \frac{\text{d}I}{I\text{d}t} \tag{11}$$

where I is the emission intensity in the presence of the cobalt(III) quencher, it follows that

$$-\left(\frac{I_0}{I}\right)_{\text{app}}\frac{\text{d}I}{I\text{d}t} = k_2\tau_0 B I_{\text{in}}[\text{Co(III)}] \tag{12}$$

where the term on the left will be referred to as the apparent rate of oxidation of $\text{Ru(bipy)}_3{}^{2+}$. Equation 12 correctly predicts the observed linear relationship between the apparent rate and the cobalt(III) concentration at constant incident light intensity (Figure 2) as well as the observed linear relationship between the apparent rate and the light intensity at constant cobalt(III) concentration (Figure 3). Direct substitution in eq 12 of the $\text{Co(NH}_3)_5\text{Cl}^{2+}$ data determined at a known light intensity gives $k_2 = 7.4 \pm 0.9 \times 10^8$ M^{-1} sec^{-1} for quenching by this complex. Finally, substitution for τ_0 in eq 3, and rearranging, gives eq 13. In other

$$-\frac{1}{K_{\text{sv}}[\text{Co(III)}]}\left(\frac{I_0}{I}\right)_{\text{app}}\frac{\text{d}I}{I\text{d}t} = \frac{k_2}{k_Q}BI_{\text{in}} \tag{13}$$

words, the above mechanism also predicts that the apparent rates of oxidation divided by the products of the Stern-Volmer constants and the cobalt(III) concentrations should be proportional to k_2/k_Q. Values of the left side of eq 13 are presented in Table II. Since BI_{in} was constant under the conditions used to obtain the data in Figure 2, the results show

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(15) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, p 481.

(16) J. N. Demas and C. A. Crosby, *J. Amer. Chem. Soc.*, 93, 2841 (1971).

(17) The area of the incident beam is required in the calculation of I_{in}; this was determined from the area of a slit positioned immediately in front of the cell. A small correction was made for the divergence of the incident beam.

that, with the possible exceptions of $Co(NH_3)_6{}^{3+}$ in water and of $Co(NH_3)_5Cl^{2+}$ in 50% 2-propanol, *the values of k_2/k_Q are approximately constant for all of the cobalt(III) complexes studied.* It should be noted that this conclusion is independent of the value of τ_0. In the case of $Co(NH_3)_6{}^{3+}$ an accurate K_{sv} could not be determined from eq 2 because I_0/I for this complex is not very different from unity; the propanol results will be discussed later.

The independent determinations of k_2 and k_Q show that $k_2/k_Q = 0.86 \pm 0.15$ for $Co(NH_3)_5Cl^{2+}$ in 0.5 *M* sulfuric acid. This result (which is independent of the value of τ_0), together with the finding of similar k_2/k_Q values for all of the cobalt(III) complexes studied, establishes that (in the absence of 2-propanol) the cobalt(III) quenched reactions all produce $Ru(bipy)_3{}^{3+}$ in close to 100% yield. The simplest explanation of this result is that $k_2 \gg k_3$ and thus that the quenching proceeds predominantly by means of an electron transfer mechanism. However, an energy transfer mechanism has also been proposed, and this will be considered next.

Energy Transfer Mechanism. A mechanism for quenching by $Co(HEDTA)X^-$ complexes involving triplet-to-triplet energy transfer has been proposed by Natarajan and Endicott.[3,4] Their interpretation requires that $k_3 \gg k_2$ and consequently that $Ru(bipy)_3{}^{3+}$ and Co^{2+} be formed with close to unit efficiency in the subsequent reactions of the triplet state cobalt(III). In the case of $Co(NH_3)_5Br^{2+}$ these reactions take the form

$$^3Co(NH_3)_5Br^{2+} \rightarrow Co^{2+} + 5NH_4{}^+ + Br \qquad (14)$$

$$Br + Br^- \rightleftharpoons Br_2{}^- \qquad (15)$$

$$Br_2{}^- + Ru(bipy)_3{}^{2+} \rightarrow Ru(bipy)_3{}^{3+} + 2Br^- \qquad (16)$$

In support of the above mechanism, Natarajan and Endicott[3,4] showed that Br and $Br_2{}^-$ (produced by the flash photolysis of $Co(NH_3)_5Br^{2+}$ in the absence and presence of added bromide, respectively)[18] both oxidize $Ru(bipy)_3{}^{2+}$ very rapidly.[19] They also showed that the yield of $Ru(bipy)_3{}^{3+}$ was decreased by 58% and the yield of Co^{2+} increased by 85% when the sensitization was performed in 50% 2-propanol. The latter observation was interpreted in terms of the scavenging of the bromine atoms by 2-propanol to form the 2-hydroxy-2-propyl radical which then reacts with $Co(NH_3)_5Br^{2+}$ (eq 17 and 18). We find the above mechanism unsatisfactory on

$$Br + (CH_3)_2CHOH \rightarrow H^+ + Br^- + (CH_3)_2COH \qquad (17)$$

$$(CH_3)_2COH + Co(NH_3)_5Br^{2+} \rightarrow (CH_3)_2CO + Br^- + Co^{2+} \qquad (18)$$

the following grounds. Since the low-lying ligand field states of $Co(NH_3)_5X^{3+}$ complexes are relatively unreactive,[20] Natarajan and Endicott invoked the formation of highly reactive charge transfer triplet states to account for the oxidation–reduction reactions accompanying the phosphorescence quenching. The energy of the lowest CTTM triplet states of $Co(NH_3)_5X^{3+}$ is expected to decrease as X^- becomes more easily oxidized. On this basis, the overlap of the $Ru(bipy)_3{}^{2+}$ emission and the ^{3}CTTM absorption bands of the $Co(NH_3)$-X^{3+} complexes are expected to increase in the order $NH_3 < H_2O < Cl^- < Br^-$, which is the reactivity order observed in the photosensitization. An important question which needs to be answered, however, is whether the energies of the CTTM triplet states are low enough for overlap of the CTTM absorption band with the triplet $Ru(bipy)_3{}^{2+}$ emission band to be significant. It has been estimated that the lowest CTTM triplet state and the lowest LF triplet state in $Co(NH_3)_5Br^{2+}$ have comparable energies of about 12.0 kK.[4,21] This estimate implies that energy transfer to form the CTTM triplet state would be possible for $Co(NH_3)_5Br^{2+}$ since the emission from $^3Ru(bipy)_3{}^{2+}$ occurs at 16.4 kK. However, the above estimate also implies a ^{1}CT – ^{3}CT separation of about 20.0 kK since the maximum for the first ^{1}CT transition in $Co(NH_3)_5Br^{2+}$ occurs at 32.0 kK.[22] This conclusion seems unreasonable to us in view of the fact that the ^{1}LF – ^{3}LF separation in $Co(NH_3)_5Br^{2+}$ is only 7.4 kK,[22] and the singlet-triplet separation (which is approximately equal to twice the exchange integral)[23] is expected to be larger for the ligand field transitions than for the charge transfer transitions.[24] We note, for example, that the metal-to-ligand ^{1}CT – ^{3}CT separation in $Ru(bipy)_3{}^{2+}$ is only about 4.0 kK, and although the ligand-to-metal ^{1}CT – ^{3}CT separation in $Co(NH_3)_5Br^{2+}$ is probably larger than this value, it is still likely to be ≤7.4 kK. Accordingly, we estimate that the maximum for the ^{3}CT transition in $Co(NH_3)_5Br^{2+}$ lies above $32.0 - 7.0 = 25.0$ kK and that the ^{3}CT maxima for the other $Co(NH_3)_5X^{3+}$ complexes studied lie at even higher energies. Since the $Ru(bipy)_3{}^{2+}$ emission is essentially zero above 19.2 kK (below 520 nm), we conclude that the energies of the lowest ^{3}CT states in the $Co(NH_3)_5X^{3+}$ complexes are too high for energy transfer to these states to occur by mechanisms requiring efficient overlap of the emission band of the donor with the absorption band of the acceptor.[25-28]

In addition to the question of the probability of energy transfer to the ^{3}CT states of the $Co(NH_3)_5X^{3+}$ complexes, the energy transfer mechanism also requires that oxidizing radicals be produced from the ^{3}CT states with close to unit efficiency and that these radicals react quantitatively with $Ru(bipy)_3{}^{2+}$. It is difficult to conceive of both of these con-

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(18) J. K. Thomas, *Advan. Radiat. Chem.*, 1, 103 (1960).

(19) On the other hand, Gafney and Adamson find that the radicals produced in the photodecomposition of $Co(NH_3)_5Br^{2+}$ at 395 nm in the absence of added bromide are reducing toward $Ru(bipy)_3{}^{3+}$ rather than oxidizing toward $Ru(bipy)_3{}^{2+}$: A. Adamson, personal communication.

(20) V. Balzani and V. Carasitti, "The Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970, Chapter 11.

(21) P. Natarajan and J. F. Endicott, *J. Amer. Chem. Soc.*, 95, 2470 (1973).

(22) C. K. Jorgensen, *Advan. Chem. Phys.*, 5, 33 (1963).

(23) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice Hall, Englewood Cliffs, N. J., 1969, Chapter 3.

(24) Note that the relevant orbitals are centered on two different atoms in the CTTM transition but are on the same atom (the metal center) in the LF transition.

(25) Note that the triple-to-triplet transfer rate decreases rapidly as soon as the energy of the acceptor triplet exceeds that of the donor triplet. See, for example, J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N. Y., 1970, Chapter 11.

(26) Although we have been discussing the emission from $Ru(bipy)_3{}^{2+}$ as if it arose from a single charge transfer state of triplet multiplicity, recent studies[27] have interpreted the luminescence as arising from a manifold of three closely spaced electronic states (A_1, E, and A_2 in D_3 symmetry) with spin–orbit coupling so large as to render almost meaningless a singlet and triplet classification.

(27) R. W. Harrigan, G. D. Hager, and G. A. Crosby, *Chem. Phys. Lett.*, 21, 487 (1973).

(28) It might be argued that transition energies are "vertical" Franck–Condon energies and that the ^{3}CT states could be populated *via* the excited ligand field states of the cobalt(III) complexes. There is perhaps some evidence for the formation of the ^{3}CT state (which is expected to yield Co^{2+}) when the ligand field states of cobalt(III)–ammine complexes are excited. Thus excitation of the ligand field bands of these complexes frequently produces Co^{2+} in very small yield ($\leqslant 10^{-2}$) (ref 4, 15, 16; see also A. W. Adamson and A. H. Sporer, *J. Amer. Chem. Soc.*, 80, 3865 (1958); A. W. Adamson, *Discuss. Faraday Soc.*, 29, 163 (1960)). The origin of these low Co^{2+} yields is not understood, but one possible explanation is an inefficient intersystem crossing to a ^{3}CT state (J. F. Endicott, personal communication).

ditions being satisfied in all of the $Co(NH_3)_5X^{3+}$ reactions studied. As far as the first condition is concerned, it should be noted that the quantum yields for the formation of Co^{2+} in the redox decomposition of the ^1CT states of the $Co(NH_3)_5X^{3+}$ complexes are generally less than 0.3.[20] The main evidence for the formation of oxidizing radicals in the quenching reactions is the $Co(NH_3)_5Br^{2+}$ experiments in 50% 2-propanol mentioned earlier. However, we question the interpretation of these experiments since the formation of oxidizing radicals is not required by our data in 2-propanol (Table II). Like Natarajan and Endicott, we find that the yield of $Ru(bipy)_3{}^{3+}$ in the $Co(NH_3)_5Br^{2+}$ quenched reaction is about a factor of 2 lower in 50% 2-propanol than in water; however, we find that K_{sv} is also decreased by almost the same factor. The decreased yield of $Ru(bipy)_3{}^{3+}$ in 50% 2-propanol can thus be accounted for on the basis of the slower rate of diffusion of the two positively charged reactants ($Ru(bipy)_3{}^{2+}$ and $Co(NH_3)_5Br^{2+}$) without invoking competitive radical reactions in the mixed medium. Ironically, the yield of $Ru(bipy)_3{}^{3+}$ in the $Co(NH_3)_5Cl^{2+}$ quenched reaction does appear to be somewhat lower in the mixed solvent than expected. Evidently the mixed solvent system is quite complicated and warrants further study.[29]

Quenching by Ruthenium(III) Complexes. Further information about the quenching mechanism can be obtained from a consideration of the $Ru(NH_3)_5X^{3+}$ reactions. The data in Table I show that the ruthenium(III) complexes used in this work quench the $^3Ru(bipy)_3{}^{2+}$ emission much more efficiently (the rates are probably diffusion controlled) than do the corresponding $Co(NH_3)_5X^{3+}$ complexes. We interpret the quenching by $Ru(NH_3)_6{}^{3+}$ (and ($Ru(NH_3)_5Cl^{2+}$) in terms of an electron transfer mechanism, eq 19, followed by the very

$$^3Ru(bipy)_3{}^{2+} + Ru(NH_3)_6{}^{3+} \rightarrow Ru(bipy)_3{}^{3+} + Ru(NH_3)_6{}^{2+} \qquad (19)$$

rapid transfer of an electron between the products to re-form the reactants in their ground electronic states, eq 20. This

$$Ru(bipy)_3{}^{3+} + Ru(NH_3)_6{}^{2+} \rightarrow Ru(bipy)_3{}^{2+} + Ru(NH_3)_6{}^{3+} \qquad (20)$$

mechanism accounts for our observation of no net chemical change in the irradiated solutions. Moreover, in view of the facility with which $Ru(bipy)_3{}^{3+}$ undergoes reduction, the products of reaction 19 probably react with one another to some degree before diffusing out of the solvent cage in which they are produced. $Co(NH_3)_6{}^{2+}$, by contrast, is very substitution labile[30,31] and not readily oxidized and presumably dissociates before its reoxidation can occur.

The greater quenching efficiency of the ruthenium(III) complexes compared to the corresponding cobalt(III) complexes can be rationalized on the basis of elementary electron transfer theory.[32] The energy barriers obtaining in electron transfer reactions are composed of "thermodynamic" and "intrinsic" parts. The former barriers are related to the equilibrium constants or driving forces for the reactions, while the latter are reflected in the electron exchange rate constants of the participating couples. A given electron transfer reaction may be slow because of the magnitude of one or of both of these barriers. $Co(NH_3)_6{}^{3+}$ reactions tend to be slow because of the heights of their intrinsic barriers; thus the rate constant for the $Co(NH_3)_6{}^{2+}$-$Co(NH_3)_6{}^{3+}$ electron exchange is $\leqslant 10^{-9}\ M^{-1}\ sec^{-1}$ at 65°.[33] On the other hand, the electron exchange rate constant for the $Ru(NH_3)_6{}^{2+}$-$Ru(NH_3)_6{}^{3+}$ reaction is $8.2 \times 10^2\ M^{-1}\ sec^{-1}$ [34], and, as a consequence, electron transfer reactions of $Ru(NH_3)_6{}^{3+}$ generally tend to be 10^6 times faster than those of $Co(NH_3)_6{}^{3+}$.[35]

Our observation of efficient quenching by $Ru(NH_3)_6{}^{3+}$ is in line with the above considerations and shows that the explanation advanced by Gafney and Adamson[1] for the low rate of the $Co(NH_3)_6{}^{3+}$ quenched reaction cannot be correct. These workers proposed that the small value of K_{sv} for the $Co(NH_3)_6{}^{3+}$ reaction was due to an unfavorable driving force for the electron transfer reaction. However, the reduction potentials of the $Co(NH_3)_6{}^{3+}$ and $Ru(NH_3)_6{}^{3+}$ couples are similar (each 0.1 V)[36,34] and yet $Ru(NH_3)_6{}^{3+}$ quenches very efficiently. We conclude, instead, that the slow rate of the $Co(NH_3)_6{}^{3+}$ quenched reaction is due to its unfavorable intrinsic barrier, rather than to an unfavorable driving force for its electron transfer reaction with $^3Ru(bipy)_3{}^{2+}$.

The measured rate constants for quenching by $Ru(NH_3)_6{}^{3+}$ and $Co(NH_3)_6{}^{3+}$ may be compared with the electron transfer rate constants calculated from the Marcus theory.[32,37] In order to do this it is necessary to know the reduction potential for the couple

$$Ru(bipy)_3{}^{3+} + e \rightleftharpoons {}^3Ru(bipy)_3{}^{2+} \qquad (21)$$

This potential may be estimated from the spectroscopic data. The energy difference between triplet and ground state $Ru(bipy)_3{}^{2+}$ is essentially equal to the singlet-triplet transition energy. The 0-0 band corresponds to the energy difference of these states in their thermal equilibrium levels, and this energy can be estimated by taking the average of the maxima of the singlet-triplet absorption (18.2 kK) and emission (16.4 kK) bands of $Ru(bipy)_3{}^{2+}$.[16] This procedure gives 17.3 kK or 2.15 eV for the 0-0 transition energy. For the entropy difference between triplet and singlet $Ru(bipy)_3{}^{2+}$ only that part associated with the change in spin multiplicity (k ln 3) can be calculated, giving 2.12 eV for the free energy difference between these states. Using the value 1.24 V for the reduction potential of $Ru(bipy)_3{}^{3+}$,[38] a value of −0.88 V is calculated for reaction 21. The latter value is considerably more negative than a previous estimate of E^0.[1,39] The electron transfer rates may now be estimated by use of the Marcus relation

$$k_{12} = \sqrt{k_{11}k_{22}K_{12}f}$$
$$\log f = (\log K_{12})^2/(4 \log (k_{11}k_{22}/Z^2)) \qquad (22)$$

where the symbols have their usual significance.[32,37] Substitution of $k_{11} = 8.2 \times 10^2\ M^{-1}\ sec^{-1}$ for the $Ru(NH_3)_6{}^{2+}$-$Ru(NH_3)_6{}^{3+}$ exchange rate constant[34] and $k_{22} \geqslant 2 \times 10^9\ M^{-1}\ sec^{-1}$ for the $^3Ru(bipy)_3{}^{2+}$-$Ru(bipy)_3{}^{3+}$ exchange rate constant (assumed to be diffusion controlled, by analogy with the $Fe(phen)_3{}^{2+}$-$Fe(phen)_3{}^{3+}$ reaction[40]) gives $k_{12} \geqslant 8 \times$

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[29] Natarajan and Endicott also report an 85% increase in the yield of Co^{2+} when the photosensitization is carried out in the mixed solvent at 4°. Although we cannot account for this observation, it should be noted that solvent effects are complex and reflect a delicate balance between lifetimes, cage effects, and the probabilities of energy transfer and electron transfer processes. It should also be noted that the concentration of $Ru(bipy)_3{}^{2+}$ used by the earlier workers was 50 times higher than that used in our study.

[30] The loss of the first three ammonia ligands from $Co(NH_3)_6{}^{2+}$ occurs in less than 2 μsec.[31]

[31] M. Simic and J. Lilie, *J. Amer. Chem. Soc.*, 96, 291 (1974).

[32] N. Sutin, *Accounts Chem. Res.*, 2, 321 (1969).

[33] D. R. Stranks, *Discuss. Faraday Soc.*, 29, 73 (1960).

[34] T. J. Meyer and H. Taube, *Inorg. Chem.*, 7, 2369 (1968).

[35] J. A. Stritar and H. Taube, *Inorg. Chem.*, 8, 2281 (1969).

[36] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1952.

[37] R. A. Marcus, *Annu. Rev. Phys. Chem.*, 15, 155 (1964).

[38] F. E. Lytle and D. M. Hercules, *Photochem. Photobiol.*, 13, 123 (1971).

[39] An E° value of about −1 V is quoted in ref 38.

[40] I. Ruff and M. Zimonyi, *Electrochim. Acta*, 18, 515 (1973).

$10^{10}\ M^{-1}\ \text{sec}^{-1}$ for the $^3\text{Ru(bipy)}_3{}^{2+}$-$\text{Ru(NH}_3)_6{}^{3+}$ reaction. This estimate of the rate constant for the $^3\text{Ru(bipy)}_3{}^{2+}$-$\text{Ru(NH}_3)_6{}^{3+}$ electron transfer reaction is consistent with the observed diffusion-controlled quenching rate. A similar calculation[41] for the $^3\text{Ru(bipy)}_3{}^{2+}$-$\text{Co(NH}_3)_6{}^{3+}$ reactions gives $k_{12} \geq 9 \times 10^6\ M^{-1}\ \text{sec}^{-1}$, in good agreement with the observed value of $\sim 1 \times 10^7\ M^{-1}\ \text{sec}^{-1}$. The $\text{Co(NH}_3)_6{}^{3+}$ and $\text{Ru(NH}_3)_6{}^{3+}$ quenching rates are thus entirely consistent with electron transfer mechanisms.

Further evidence for an electron transfer (eq 19) rather than energy transfer (eq 23) mechanism for the $\text{Ru(NH}_3)_6{}^{3+}$

$$^3\text{Ru(bipy)}_3{}^{2+} + {}^2\text{Ru(NH}_3)_6{}^{3+} \rightarrow {}^1\text{Ru(bipy)}_3{}^{2+} + {}^4\text{Ru(NH}_3)_6{}^{3+} \quad (23)$$

quenched reaction comes from a consideration of the absorption spectrum of $\text{Ru(NH}_3)_6{}^{3+}$. As is shown in the Appendix, the quartet ligand field and charge transfer bands of $\text{Ru(NH}_3)_6{}^{3+}$ lie at much higher energies than do the corresponding triplet bands of $\text{Co(NH}_3)_6{}^{3+}$. It may therefore be concluded with some confidence that the $\text{Ru(NH}_3)_6{}^{3+}$ (and probably also the $\text{Ru(NH}_3)_5\text{X}^{3+}$) quenched reaction proceeds by means of an electron transfer mechanism.[43]

General Conclusions. Although we have interpreted the quenching of $^3\text{Ru(bipy)}_3{}^{2+}$ emission by the cobalt(III) and ruthenium(III) complexes in terms of an electron transfer mechanism, there is good evidence that quenching by some other complexes proceeds by means of an energy transfer mechanism. For example, the quenching of the $\text{Ru(bipy)}_3{}^{2+}$ phosphorescence by *trans*-$\text{Cr(en)}_2\text{(NCS)}_2{}^+$ is accompanied by the sensitized emission of the quencher.[5] The operation of an energy transfer mechanism in these systems is not surprising in view of the generally sluggish rates of chromium(III) electron transfer reactions.[44,45]

Based on this and previous studies, it is possible to distinguish four types of quenching reactions depending upon whether the mechanism involves energy or electron transfer and whether the quenching reaction is accompanied by a net chemical change.

Type I(a): Electron transfer accompanied by no net chemical change. Examples: $\text{Ru(NH}_3)_6{}^{3+}$ (this work) and probably $\text{Fe(C}_2\text{O}_4)_2{}^-$ (ref 2).

Type I(b): Electron transfer accompanied by a net chemical change. Examples: $\text{Co(NH}_3)_5\text{X}^{3+}$ complexes and $\text{Co(C}_2\text{O}_4)_3{}^{3-}$ (this work and ref 1 and 2).

Type II(a): Energy transfer accompanied by no net chemical change. Examples: $\text{Cr(en)}_2\text{XY}^+$ (ref 5).

Type II(b): Energy transfer accompanied by a net chemical change. Examples: $\text{PtCl}_4{}^{2-}$ (aquation, ref 46), $\text{Cr(C}_2\text{O}_4)_3{}^{3-}$ (racemization, ref 2), and perhaps Co(HEDTA)X^- (redox decomposition, ref 4).

It may not always be easy or possible to distinguish between these types of reactions and the distinction between types I(a) and I(b) is to some extent arbitrary, depending upon the time scale of the measurement and the relative rates of electron transfer and ligand loss. However, we have attempted to show that comparisons of the reactivity patterns observed in the quenching reactions with those obtaining in ordinary thermal (dark) electron transfer reactions may prove useful in elucidating detailed quenching mechanisms.

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Appendix

In order to make sure that no very low intensity absorption bands in the visible were overlooked, we have analyzed the spectrum of $\text{Ru(NH}_3)_6{}^{3+}$ in terms of Tanabe and Sugano diagrams.[47] Extrapolation for the Racah parameter B, based on the values $B = 0.49$ kK for ruthenium(III) in a LiCl-KCl melt[48] and $B = 0.56$ kK for $\text{Ru(C}_2\text{O}_4)_3{}^{3-}$,[49] together with the general trends in the nephelauxetic series,[22] gave an approximate value of $B = 0.58$ kK for $\text{Ru(NH}_3)_6{}^{3+}$. The ligand field splitting $10Dq$ was next calculated using the second-order expression for this transition[22] with the aid of the following two assumptions: the shoulder at 23 kK with the low molar absorptivity is the first forbidden transition $^2\text{T}_{2g} \rightarrow {}^4\text{T}_{1g}$, and $C = 4B$. This procedure gives $10Dq = 34.0$ kK, which is very close to the value of 34.1 kK found for $\text{Rh(NH}_3)_6{}^{3+}$.[22] This result is reasonable in view of the general similarity in the $10Dq$ values of ruthenium(III) and rhodium(III) complexes. For example, $10Dq$ is 28.7 and 26.4 kK for the tris oxalato complexes of these two ions, respectively, and 18.7 and 19.3 for their hexachloride complexes in a LiCl-KCl melt.[48,50]

Using the above values of B and $10Dq$, the positions of the other ligand field transitions in $\text{Ru(NH}_3)_6{}^{3+}$ were estimated using second-order perturbation energy expressions calculated from the Tanabe and Sugano determinants. The calculated positions of the ligand field transitions are shown in Figure 4. Although the spectrum is governed by a strong absorption which we assign as a ligand-to-metal charge transfer transition, most of the calculated ligand field transitions do correspond to shoulders in the observed spectrum. Finally, the $^2\text{T}_{2g} \rightarrow {}^4\text{CT}$ band is expected to have a molar absorptivity approximately one hundredth that of the allowed charge transfer band and should easily be detected if it were located at wavelengths beyond 380 nm.

Registry No. $\text{Ru(bipy)}_3{}^{2+}$, 15158-62-0; $\text{Co(NH}_3)_6{}^{3+}$, 14695-95-5; $\text{Co(NH}_3)_5\text{H}_2\text{O}^{3+}$, 14403-82-8; $\text{Co(NH}_3)_5\text{Cl}^{2+}$, 14970-14-0; $\text{Co(NH}_3)_5\text{Br}^{2+}$, 14970-15-1; $\text{Ru(NH}_3)_6{}^{3+}$, 18943-33-4; $\text{Ru(NH}_3)_5\text{Cl}^{2+}$, 21560-19-0.

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(41) In this calculation we have used $k_{11} = 10^{-9}\ M^{-1}\ \text{sec}^{-1}$, which is the upper limit for the $\text{Co(NH}_3)_6{}^{2+}$-$\text{Co(NH}_3)_6{}^{3+}$ exchange rate constant at 65°. This k_{11} value gives good agreement with experiment in other comparisons involving the hexaammine couple.[42] It should also be noted that $\log K_{12} << 2 \log Z^2/k_1k_2$ and thus that the reactions being compared are not so exothermic as to place them in the "inverted" or nonadiabatic (nuclear tunneling) region.

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(43) After the work described here had been submitted for publication, we learned that direct evidence for reactions 19 and 20 has been obtained by a flash photolysis technique: C. R. Bock, T. J. Meyer, and D. G. Whitten, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, No. INOR-99.

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