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# Photostudies of Copper(I) Systems. 7. Studies of Bimolecular Reactions Involving Cobalt(III) Complexes, Chromium(III) Complexes, or O<sub>2</sub> following the Excitation of [Cu(dmp)<sub>2</sub>]<sup>+</sup>

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Received June 9, 1980

Photoinduced electron-transfer reactions involving the bis(2,9-dimethyl-1,10-phenanthroline)copper(I) complex, [Cu(dmp)<sub>2</sub>]<sup>+</sup>, and a variety of Co(III) complexes have been investigated. For concentrations of Co(III) in the millimolar range the quantum yields for the loss of Cu(I) are typically of the order of 10<sup>-3</sup>, but the yields are sensitive to the nature of the Co(III) complex and to solvent, increasing with solvent polarity. The results can be interpreted in terms of a model in which the reactive species is a charge-transfer excited state of [Cu(dmp)<sub>2</sub>]<sup>+</sup>. For aqueous solutions of [Co(en)<sub>2</sub>bpy]<sup>3+</sup>, *trans*-[Co(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub>]<sup>+</sup>, and *cis*-[Co(IDA)<sub>2</sub>]<sup>-</sup>, the dependence of the quantum yield on Co(III) concentration is described in detail. With extrapolation to infinite Co(III) concentrations, the apparent limiting quantum yields for the three systems are found to be 0.014, 0.005, and 0.14, respectively. Either a static or a dynamic quenching mechanism, or both, may occur. If in fact the excited state undergoes diffusional encounters with the cobalt substrates in solution, the second-order rate constants for electron transfer must be very similar for the three Co(III) systems described above and must approach the diffusion limit. On the other hand, much smaller rate constants would be required for related cobalt systems, e.g., [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>. The back-reaction from the successor complex to electron transfer is believed to be a major source of inefficiency for these reactions. Indications are that the reduction potential of the cobalt complex may be the most significant factor in determining the rate of the back-reaction. Several attempts to detect energy-transfer reactivity are reported, but none are successful. In the presence of molecular oxygen, φ<sub>-Cu(I)</sub>, the quantum yield for the photoinduced loss of Cu(I), is 7 × 10<sup>-5</sup> (pH 5). Indirect evidence for the formation of superoxide is presented.

## Introduction

Studies of the photoinduced redox reactions of metal complexes comprise a topical area of research, and as our basic understanding of the dynamics of these type reactions increases, efforts to utilize such systems in photocatalysis and photoinduced fuel formation processes are being reported.<sup>1</sup> Stimulated by a report of Demas and Adamson,<sup>2</sup> a great deal of study has been devoted to photoexcited [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (bpy denotes 2,2'-bipyridine), the electron-transfer quenching of which has by now been firmly established.<sup>3</sup> Analogous investigations involving complexes of less precious metals are also being pursued.<sup>4-7</sup>

Our interest has focused on Cu(I) complexes, and we have reported observing photoinduced electron-transfer reactions in alcohol-water solutions containing the bis(2,9-dimethyl-1,10-phenanthroline)copper(I) ion (hereafter denoted [Cu(dmp)<sub>2</sub>]<sup>+</sup>).<sup>6,7</sup> We have suggested that the reducing species generated upon irradiation may be a metal-to-ligand charge-transfer (CT) excited state<sup>7</sup> of [Cu(dmp)<sub>2</sub>]<sup>+</sup>, although the complex is virtually nonemissive in these media at room temperature.<sup>8,9</sup> However, CT emission is observed in alcohol

Table I. Quantum Yields

Co(III) complex <sup>a</sup>	[Co(III)], mM	10 <sup>3</sup> φ <sub>-Cu(I)</sub>	solvent
<i>trans</i> -[Co(IDA) <sub>2</sub> ] <sup>-</sup>	5.0	5.5 <sup>b</sup>	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
	1.5	1.8	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
<i>cis</i> -[Co(IDA) <sub>2</sub> ] <sup>-</sup>	4.7	5.5	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
	5.0	5.6 <sup>b</sup>	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
<i>trans</i> -[Co(NH <sub>3</sub> ) <sub>4</sub> (CN) <sub>2</sub> ] <sup>+</sup>	9.4	11.0	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
	5.0	0.39 <sup>b,c</sup>	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
		0.56	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
	10.0	0.58 <sup>b,d</sup>	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
		0.96	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
[Co(EDTA)] <sup>-</sup>	4.0	4.49 <sup>b</sup>	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
	10.0	8.15 <sup>b</sup>	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
[Co(en) <sub>2</sub> bpy] <sup>3+</sup>	5.0	2.6	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
	8.0	2.8	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
			C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
Co(acac) <sub>3</sub>	5.0	3.0	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
[Co(en) <sub>2</sub> phen] <sup>3+</sup>	5.0	3.0	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
β-Co(ala) <sub>3</sub>	5.0	<0.1	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
[Co(NH <sub>3</sub> ) <sub>5</sub> py] <sup>3+</sup>	5.0	<0.1	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	5.0	<0.1	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
[Co(en) <sub>3</sub> ] <sup>3+</sup>	5.0	<i>e</i>	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
[Co(NH <sub>3</sub> ) <sub>5</sub> Cl] <sup>2+</sup>	5.0	<i>e</i>	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
[Co(NH <sub>3</sub> ) <sub>5</sub> N <sub>3</sub> ] <sup>2+</sup>	5.0	<i>e</i>	C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O
<i>cis</i> -[Co(IDA) <sub>2</sub> ] <sup>-</sup>	1.0	3.7	H <sub>2</sub> O
	1.5	5.1	H <sub>2</sub> O
	5.0	15.0	H <sub>2</sub> O
	5.0	17.0	H <sub>2</sub> O
	5.0	17.0	H <sub>2</sub> O
	5.0	17.0	H <sub>2</sub> O
[Co(NH <sub>3</sub> ) <sub>5</sub> (CN)] <sup>2+</sup>	5.0	0.46	H <sub>2</sub> O
<i>trans</i> -[Co(NH <sub>3</sub> ) <sub>4</sub> (CN) <sub>2</sub> ] <sup>+</sup>	2.0	0.51	H <sub>2</sub> O
	3.0	0.78	H <sub>2</sub> O
	5.0	1.2	H <sub>2</sub> O
	7.0	1.5	H <sub>2</sub> O
	10.0	1.8	H <sub>2</sub> O
[Co(en) <sub>2</sub> bpy] <sup>3+</sup>	2.0	3.0	H <sub>2</sub> O
	4.0	4.4	H <sub>2</sub> O
	8.0	7.5	H <sub>2</sub> O
	10.0	7.5	H <sub>2</sub> O
			H <sub>2</sub> O

<sup>a</sup> Ligand abbreviations: IDA<sup>2-</sup>, iminodiacetate; EDTA<sup>4-</sup>, ethylenediaminetetraacetate; acac, acetylacetonate; en, ethylenediamine; phen, 1,10-phenanthroline; ala, alaninate; py, pyridine.

<sup>b</sup> Data from ref 7. <sup>c</sup> Average of four trials. <sup>d</sup> Average of two trials. <sup>e</sup> Not measured because of a competing thermal reaction.

glasses at 77K<sup>10</sup> and in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature.<sup>11</sup> Moreover, electron-transfer quenching of the emission has been

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observed in  $\text{CH}_2\text{Cl}_2$ .<sup>11</sup> Thus evidence is mounting that, at least under some conditions,  $[\text{Cu}(\text{dmp})_2]^+$  exhibits excited-state chemistry analogous to that of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and related systems. In order to further probe the photochemical properties of  $[\text{Cu}(\text{dmp})_2]^+$  in solution, we have now carried out additional studies involving several different Co(III) and Cr(III) complexes and molecular oxygen as substrates. We have also examined the effect of solvent on these reactions, and our results are reported herein.

## Experimental Section

**Materials.**  $[\text{Cu}(\text{dmp})_2]\text{Cl}\cdot 2\text{H}_2\text{O}$  and  $[\text{Cu}(\text{dmp})_2]\text{BF}_4$  were prepared as before;<sup>7</sup> the latter was dried over  $\text{P}_2\text{O}_5$  under vacuum. Literature methods were used to prepare  $\text{K}[\text{cis-Co}(\text{IDA})_2]\cdot 2.5\text{H}_2\text{O}$ ,<sup>12</sup>  $[\text{Co}(\text{N}(\text{H}_3)_5\text{CN})\text{Cl}_2]$ ,<sup>13</sup>  $[\text{trans-Co}(\text{NH}_3)_4(\text{CN})_2]\text{Cl}\cdot 1.5\text{H}_2\text{O}$ ,<sup>14</sup>  $[\text{Co}(\text{en})_2\text{bpy}]\text{Cl}_3$ ,<sup>15</sup>  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ,<sup>16</sup>  $[\text{Co}(\text{NH}_3)_5\text{py}]\text{Cl}_3$ ,<sup>17</sup>  $[\text{Co}(\text{NH}_3)_5\text{N}_3]\text{Cl}_2$ ,<sup>18</sup>  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ ,<sup>19</sup>  $\text{Co}(\text{acac})_3$ ,<sup>20</sup> and  $\text{K}[\text{trans-Cr}(\text{NH}_3)_2(\text{NCS})_4]$ .<sup>21</sup> (See Table I for an explanation of abbreviations.) The spin trap DMPO, 5,5-dimethyl-1-pyrroline *N*-oxide, was purified by filtering a solution of 1 part DMPO (Aldrich) and 10 parts water with decolorizing charcoal. The resulting aqueous solution was divided into small portions and kept frozen until use. The reported superoxide trap HTMP (4-hydroxy-2,2,6,6-tetramethyl-*N*-bromopiperidine) was prepared from 4-hydroxy-2,2,6,6-tetramethylpiperidine by the literature method.<sup>22</sup> All other materials were reagent grade quality.

**Solutions.** The 30:70 v/v ethanol-water solvent was 0.01 M in sodium acetate and 0.01 M in acetic acid. The ionic strength was adjusted to  $\mu = 0.1$  with NaCl, LiCl, or  $\text{LiNO}_3$ . The aqueous solutions were buffered with either acetate or succinate, and  $\text{Na}_2\text{SO}_4$  was used to adjust the ionic strength to  $\mu = 0.1$ . (The copper complex was insufficiently soluble with other electrolytes.) For the nonaqueous studies the electrolyte was  $[(n\text{-Bu})_4\text{N}]\text{PF}_6$ , and the copper was added as  $[\text{Cu}(\text{dmp})_2]\text{BF}_4$ . All irradiated solutions were freshly prepared, were thermostated at 25 °C, and were deoxygenated with an Ar stream (except those concerned with  $\text{O}_2$  effects). The  $[\text{Cu}(\text{dmp})_2]^+$  concentration was generally 0.1 or 0.2 mM. An excess of dmp equal to 6 times the concentration of copper was added to ensure full complexation of copper. In the trapping experiments the DMPO concentration was 0.05 M or the HTMP concentration was 0.1 mM.

**Apparatus.** The photolysis apparatus used has been described previously.<sup>7</sup> Absorption measurements were carried out with a Cary 17-D or a McPherson EU-707D spectrophotometer. The emission studies were carried out with use of a Perkin-Elmer MPF-44A fluorescence spectrometer. The EPR spectra were obtained with a Varian E-109 spectrometer in conjunction with a 750-W slide projector as the light source. The pH was measured with an Orion Model 601A digital ionalyzer.

**Methods of Procedure.** Light intensities were measured by ferrioxalate actinometry.<sup>23</sup> The loss of Cu(I) was followed spectrophotometrically at 454 nm (ethanol-water,  $\epsilon = 7525 \text{ M}^{-1} \text{ cm}^{-1}$ ; water (pH 5),  $\epsilon = 7700 \text{ M}^{-1} \text{ cm}^{-1}$ ). The Co(II) concentration was measured by the method of Kitson;<sup>24</sup>  $\text{SCN}^-$  levels were measured spectrophotometrically with  $\text{Fe}^{3+}$  with use of a working curve. Ammonia levels were monitored by the Bertholet method.<sup>25</sup> Quantum yields for the

Table II. Analyses of  $\phi^{-1}$  vs.  $[\text{Co(III)}]^{-1}$  Plots<sup>a</sup>

Co(III) complex	slope <sup>b</sup>	intercept <sup>b</sup>	$\phi_{\text{lim}}^b$
<i>cis</i> - $[\text{Co}(\text{IDA})_2]^-$ <sup>c</sup>	0.28 (0.01)	7.1 (2.8)	0.14 (0.06)
$[\text{Co}(\text{en})_2\text{bpy}]^{3+}$ <sup>c</sup>	0.57 (0.03)	69.4 (5.9)	0.014 (0.001)
<i>trans</i> - $[\text{Co}(\text{NH}_3)_4(\text{CN})_2]^+$	3.32 (0.18)	202.8 (33.7)	0.005 (0.001)

<sup>a</sup> Solvent was water at pH 5. <sup>b</sup> Marginal standard deviations obtained from the least-squares analyses are reported within the parentheses. The weighting method used is described in ref 7.

<sup>c</sup> Based on combined data from studies involving oxygenated and deoxygenated solutions.

Table III. Solvent Effect on the Quantum Yield

Co(III) complex <sup>a</sup>	$10^3\phi\text{-Cu(I)}$		
	$\text{H}_2\text{O}$	30% ethanol	nonaqueous
<i>cis</i> - $[\text{Co}(\text{IDA})_2]^-$	16.3 <sup>b</sup>	6 <sup>c</sup>	4 ( $\text{CH}_3\text{OH}$ ) <0.1 ( $\text{Me}_2\text{SO}$ )
$[\text{Co}(\text{en})_2\text{bpy}]^{3+}$ $[\text{Co}(\text{EDTA})]^-$	6	3 5 <sup>c</sup>	<0.1 ( $\text{CH}_3\text{OH}$ ) <0.1 ( $\text{Me}_2\text{SO}$ )
<i>trans</i> - $[\text{Co}(\text{NH}_3)_4(\text{CN})_2]^+$ $\text{Co}(\text{acac})_3$	1.2	0.4 <sup>c,d</sup> 3	<0.1 ( $\text{Me}_2\text{SO}$ ) <0.1 ( $\text{CH}_2\text{Cl}_2$ )

<sup>a</sup> The concentration of Co(III) is 5 mM in all cases. <sup>b</sup> Average of three trials. <sup>c</sup> Value from ref 7. <sup>d</sup> Average of four trials.

loss of Cu(I) were calculated as previously described.<sup>7</sup>

## Results

The absorbance of a deoxygenated solution of  $[\text{Cu}(\text{dmp})_2]^+$  was very stable both in the light and the dark, but a slow decrease was observed when the solution was exposed to oxygen and light. In aqueous solution  $[\text{Cu}(\text{dmp})_2]^+$  was less stable at low pHs while at higher pH values a thermal back-reaction was observed for some of the Co(III) substrates. So that complications were minimized, all aqueous measurements were carried out at pH 5. Photochemical studies were not carried out with  $[\text{Co}(\text{en})_3]^{3+}$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ , and  $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$  because these complexes were reduced by  $[\text{Cu}(\text{dmp})_2]^+$  in the dark.

Most of the Co(III) complexes employed did not react with  $[\text{Cu}(\text{dmp})_2]^+$  at room temperature in the absence of light but did react upon exciting the copper complex, and the efficiency of reaction was a sensitive function of the ligands bound to Co(III). Compare, for example, the yields reported in Table I for different Co(III) complexes at a given concentration, e.g., 5 mM. Upon photolysis the yield of Co(II) increased with the concentration of Co(III) added, and plots of the reciprocal of the quantum yield of the reaction vs. the reciprocal of the Co(III) concentration gave straight lines, the least-squares analyses of which are presented in Table II. From these plots we could extrapolate to infinite concentration of Co(III) and estimate limiting quantum yields for the reactions which are also reported in Table II. Although solubility problems prevented us from making detailed comparisons, the data in Table III reveal a marked solvent effect on the quantum efficiency of reaction.

We also checked for other types of photochemistry. In the case of *trans*- $[\text{Co}(\text{NH}_3)_4(\text{CN})_2]^+$  we measured the concentration of  $\text{NH}_3$  present in solution after photolysis. The yields were low and, within experimental error, were those that would be predicted on the basis of the amount of Co(II) (a labile metal center) formed in the photoredox reaction. When  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  was the substrate, ammonia aequation was not detected, and competition studies showed that the presence of  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  had no measurable effect on the amount of Cu(I) lost with *cis*- $[\text{Co}(\text{IDA})_2]^-$  as the substrate. When a solution of  $[\text{Cu}(\text{dmp})_2]^+$  and *trans*- $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$  in dimethylformamide was irradiated at 454 nm,  $\text{SCN}^-$  was

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Table IV. Oxygen Effects<sup>a</sup>

Co(III) complex	[Co(III)], mM	10 <sup>3</sup> φ-Cu(I)	
		1 atm Ar	1 atm O <sub>2</sub>
<i>cis</i> -[Co(IDA) <sub>2</sub> ] <sup>-</sup>	1.0	3.2 <sup>b</sup>	3.6
	2.0	6.8 <sup>c</sup>	6.7
	5.0	16.33 <sup>d</sup>	16.0
[Co(en) <sub>2</sub> bpy] <sup>3+</sup>	2.0	3.0	2.8
	4.0	4.4	4.5
	8.0	7.5	7.3
	10.0	7.5	8.1
	10.0	7.5	8.1
<i>trans</i> -[Co(NH <sub>3</sub> ) <sub>4</sub> (CN) <sub>2</sub> ] <sup>+</sup>	2.0	0.51	1.0
	3.0	0.78	1.3
	5.0	1.2	2.0
	7.0	1.5	2.2
	10.0	1.8	2.5

<sup>a</sup> Solvent is H<sub>2</sub>O at pH 5. <sup>b</sup> Average of two values. <sup>c</sup> Estimated from the least-squares fit reported in Table II. <sup>d</sup> Average of three values.

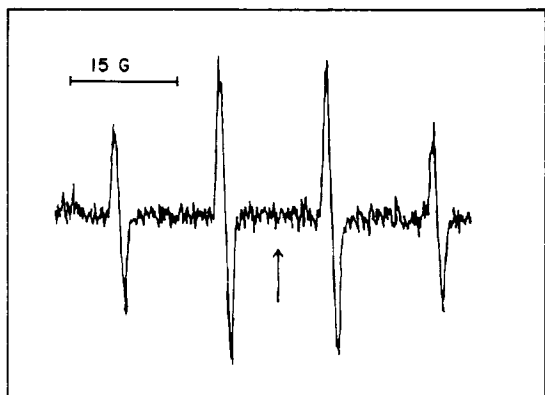


Figure 1. EPR spectrum of an aqueous [Cu(dmp)<sub>2</sub>]<sup>+</sup> solution which has been irradiated in the presence of O<sub>2</sub> and DMPO. The marker indicates the field corresponding to *g* = 2.

liberated from Cr(III), but, within experimental error, all of the thiocyanate detected could be attributed to the *direct* excitation of the Cr(III) complex at 454 nm. We also attempted to find if [Cu(dmp)<sub>2</sub>]<sup>+</sup> would sensitize luminescence from [Cr(CN)<sub>6</sub>]<sup>3-</sup>, but we were unable to find a solvent in which the complexes were cosoluble.

The quantum yield for the loss of [Cu(dmp)<sub>2</sub>]<sup>+</sup> in water at pH 5 under 1 atm of O<sub>2</sub> was found to be 7 × 10<sup>-5</sup>. As seen in Table IV, the presence of O<sub>2</sub> had no significant effect on the quantum yield of the reaction involving [Cu(dmp)<sub>2</sub>]<sup>+</sup> and either *cis*-[Co(IDA)<sub>2</sub>]<sup>-</sup> or [Co(en)<sub>2</sub>bpy]<sup>3+</sup>. However, in the case of *trans*-[Co(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub>]<sup>+</sup> the quantum yields for the loss of [Cu(dmp)<sub>2</sub>]<sup>+</sup> were significantly larger in the presence of O<sub>2</sub>, and the increases were much too large to be attributed to the direct photoreaction involving [Cu(dmp)<sub>2</sub>]<sup>+</sup> and oxygen. Interestingly, in these solutions analyses showed that the increase in the yield of Co(II) was about 60% less than the increase in the yield of Cu(II).

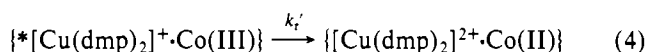
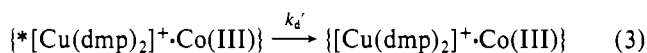
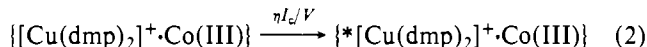
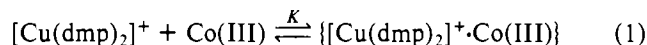
When an aqueous solution of [Cu(dmp)<sub>2</sub>]<sup>+</sup> was irradiated in an EPR cavity in the presence of O<sub>2</sub> and the spin trap DMPO, the signal presented in Figure 1 was observed. The signal (*A*<sub>H</sub> ≈ *A*<sub>N</sub> ≈ 15 G) is characteristic of the adduct of the OH radical with DMPO.<sup>26</sup> Attempts to intercept the superoxide radical with the trap HTMB failed because the trap apparently reacted with [Cu(dmp)<sub>2</sub>]<sup>+</sup> in the dark.

## Discussion

Photoexcited species are usually short lived, and sophisticated instrumentation is needed to monitor the transient species in real time. Alternatively, a steady-state property, e.g.,

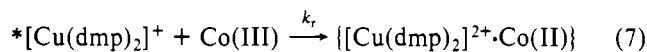
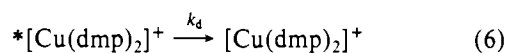
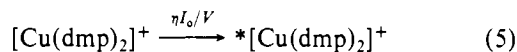
photoemission, can be monitored under conditions of continuous irradiation. A less direct, but still powerful, method of study involves chemically intercepting transients produced upon irradiation. The chemical quenching method suffers the disadvantage that any reactive species—not just an excited state—may be intercepted; nevertheless, this method has proved most useful in our studies.

**Reactions with Co(III) Substrates.** The net reaction observed upon irradiating [Cu(dmp)<sub>2</sub>]<sup>+</sup> under argon in the presence of a number of Co(III) complexes is electron transfer with the formation of Cu(II) and Co(II) in 1:1 stoichiometry. The reducing agent generated upon irradiation cannot be identified unambiguously, but in view of the emission and emission quenching results obtained for CH<sub>2</sub>Cl<sub>2</sub> solutions of [Cu(dmp)<sub>2</sub>]<sup>+</sup>,<sup>11</sup> it is reasonable to suppose that the reductant is a CT excited state of the complex. If so, two limiting schemes can be envisaged for the reactions. The first is a static mechanism in which electron transfer occurs within a precursor complex existing between the ground-state reagents before excitation occurs. Since electron transfer must compete with radiationless decay of the excited state, this mechanism is described by eq 1–4 where the braces denote complex for-

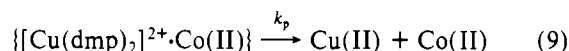
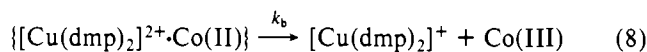


mation, e.g., { [Cu(dmp)<sub>2</sub>]<sup>2+</sup> · Co(II) } is the successor complex that exists in a solvent cage immediately after electron transfer. *I*<sub>c</sub> denotes the number of photons per second which are absorbed by the precursor complex, *V* is the photolyte volume, *η* is the quantum efficiency with which the reactive excited state is formed from the Franck-Condon state reached upon excitation, and Co(III) denotes a generic oxidizing substrate.

Alternatively, electron-transfer quenching may occur by a dynamic mechanism involving a diffusional encounter of the CT excited-state <sup>\*</sup>[Cu(dmp)<sub>2</sub>]<sup>+</sup> and a cobalt acceptor. Equations 5–7 describe this mechanism where *I*<sub>0</sub> denotes the



number of photons per second absorbed by copper. The successor complex is common to both schemes, and it can either revert to [Cu(dmp)<sub>2</sub>]<sup>+</sup> and Co(III) or proceed to give the redox products; hence either mechanistic scheme can be completed with eq 8 and 9. We have ignored other possible



competing processes, e.g., energy transfer from <sup>\*</sup>[Cu(dmp)<sub>2</sub>]<sup>+</sup> to Co(III) and the reverse of eq 9.

On the assumption that the molar absorptivities of the precursor complex and [Cu(dmp)<sub>2</sub>]<sup>+</sup> are the same and that Co(III) is present in large excess

$$I_c = \frac{K[\text{Co}(\text{III})]}{1 + K[\text{Co}(\text{III})]} I_0 \quad (10)$$

where [Co(III)] denotes the concentration of the Co(III) species. From eq 10 and a steady-state treatment of the static

(26) Finkelstein, E.; Rosen, G. M.; Rauckman, E. J. *Arch. Biochem. Biophys.* 1980, 200, 1.

mechanism, eq 11 results; eq 12 results from a steady-state treatment of the dynamic reaction mechanism.

$$\frac{1}{\phi_{\text{-Cu(I)}}} = \eta^{-1} \frac{k_p + k_b}{k_p} \frac{k_r' + k_d'}{k_r'} \left( \frac{1}{K[\text{Co(III)}]} + 1 \right) \quad (11)$$

$$\frac{1}{\phi_{\text{-Cu(I)}}} = \eta^{-1} \frac{k_p + k_b}{k_p} \left( \frac{k_d}{k_r} \frac{1}{[\text{Co(III)}]} + 1 \right) \quad (12)$$

At present we are unable to unambiguously choose between the two limiting mechanisms. Both are consistent with the linear plots of reciprocal quantum yield vs. reciprocal cobalt concentration; however, there are problems in explaining all of our observations using either mechanism. A difficulty with the static mechanism is that there is no spectral evidence in support of a precursor complex. Moreover, because of the variation in charge and types of ligands involved with the Co(III) systems, it is not obvious that precursor complexes should be important. In fact with the assumption that eq 11 is valid, analysis of the slopes and intercepts from Table II predicts that *K* increases from *cis*-[Co(IDA)<sub>2</sub>]<sup>-</sup> to *trans*-[Co(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub>]<sup>+</sup> to [Co(en)<sub>2</sub>bpy]<sup>3+</sup>, completely counter to expectations based on simple electrostatics.<sup>27</sup> On the other hand, if a diffusional mechanism is operative, it is difficult to understand why the presence of O<sub>2</sub> does not affect the quantum yields of reduction in the cases of [Co(en)<sub>2</sub>bpy]<sup>3+</sup> and *cis*-[Co(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub>]<sup>+</sup> (see Table IV).<sup>28</sup> On the basis of the reduction potential anticipated for the CT state,<sup>11</sup> O<sub>2</sub> would be expected to quench the excited state at a diffusion-controlled rate.<sup>29</sup> The issue is further confused by the fact that irradiating [Cu(dmp)<sub>2</sub>]<sup>+</sup> in the presence of O<sub>2</sub> does result in oxidation of copper, although the quantum yield is low. Perhaps both the static (possibly even "accidental" static quenching<sup>30</sup>) and the dynamic quenching mechanisms play a role. Despite the fact that the mechanism has not been definitively established, it is convenient for the purposes of this discussion to assume that dynamic quenching of a CT state is operative. In point of fact, most of the sources of inefficiency which are described below are likely to pertain whatever the type of mechanism involved.

As can be seen from eq 12, the dynamic quenching scheme predicts that the quantum yield is determined by three factors at low Co(III) concentrations: (1) the relative magnitude of the rate constant for electron transfer compared to that for decay of \*[Cu(dmp)<sub>2</sub>]<sup>+</sup> to the ground state (*k<sub>r</sub>'*/*k<sub>d</sub>'*), (2) the efficiency with which the successor complex decays to give Cu(II) and Co(II) as opposed to reactants (*k<sub>p</sub>*/*k<sub>p</sub>* + *k<sub>b</sub>*), and (3) the value of  $\eta$ . At very high Co(III) concentrations, when *k<sub>r</sub>'*[Co(III)]  $\gg$  *k<sub>d</sub>'*, the yield reaches a limiting value that depends only on factors 2 and 3.

When different Co(III) systems are compared, the relevant factors to consider are *k<sub>r</sub>'*/*k<sub>d</sub>'* and *k<sub>p</sub>*/*k<sub>p</sub>* + *k<sub>b</sub>*. Several effects influence the relative values of *k<sub>r</sub>'*. In the case of an outer-sphere electron-transfer mechanism these include the self-exchange rate constant of the Co(III) complex, the charge of the Co(III) complex, the reduction potential of the Co(III) complex, and the solvent. Where a potential bridging ligand is present, e.g., in *trans*-[Co(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub>]<sup>+</sup>, an inner-sphere mechanism would also be possible; however, if the redox active species is the CT state of [Cu(dmp)<sub>2</sub>]<sup>+</sup> with its reactive electron density in a ligand  $\pi^*$  orbital, an outer-sphere

Table V. Reduction Potentials

complex	<i>E</i> <sub>1/2</sub> (vs. SHE), V	complex	<i>E</i> <sub>1/2</sub> (vs. SHE), V
[Co(NH <sub>3</sub> ) <sub>5</sub> Cl] <sup>2+</sup>	0.53 <sup>a</sup>	[Co(en) <sub>2</sub> bpy] <sup>3+</sup>	-0.14 <sup>d</sup>
[Co(EDTA)] <sup>-</sup>	0.38 <sup>b</sup>	[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	-0.25 <sup>e</sup>
<i>cis</i> -[Co(IDA) <sub>2</sub> ] <sup>-</sup>	0.36 <sup>c</sup>	<i>trans</i> -[Co(NH <sub>3</sub> ) <sub>4</sub> (CN) <sub>2</sub> ] <sup>+</sup>	-0.35 <sup>d</sup>

<sup>a</sup> Vlček, A. A. *Discuss. Faraday Soc.* 1958, 26, 164. <sup>b</sup> Hin-Fat, L.; Higginson, W. C. E. *J. Chem. Soc. A* 1967, 298. <sup>c</sup> Rader, R. A.; McMillin, D. R. *Inorg. Chem.* 1979, 18, 545. <sup>d</sup> Estimated by polarography. <sup>e</sup> Kolthoff, I. M.; Lingane, J. J. "Polarography", 2nd ed.; Interscience: New York, 1952; Vol. 2, p 482.

mechanism seems more likely.

Assuming the validity of eq 12, it is possible to estimate the relative *k<sub>r</sub>'* values for [Co(en)<sub>2</sub>bpy]<sup>3+</sup>, *trans*-[Co(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub>]<sup>+</sup>, and *cis*-[Co(IDA)<sub>2</sub>]<sup>-</sup> from the results in Table II. The relative *k<sub>r</sub>'* values are calculated to be 4.8:2.4:1, respectively; i.e., the *k<sub>r</sub>'* values are predicted to be comparable for all three systems. It is tempting to speculate that the similarity in values may arise because electron-transfer quenching occurs at a nearly diffusion-controlled rate in each case, as indeed has been found to be the case in emission quenching studies of \*[Cu(dmp)<sub>2</sub>]<sup>+</sup> by Co(acac)<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>.<sup>11</sup> It can also be noted in this regard that based on those emission studies, we have estimated the reduction potential of the excited copper complex to be  $\sim$ -1.2 V vs. SHE, so that a large driving force for electron transfer may be expected in every case. On the other hand, from this perspective it is difficult to rationalize the fact that other Co(III) complexes, e.g., [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> and [Co(NH<sub>3</sub>)<sub>5</sub>py]<sup>3+</sup>, give no measurable photoredox reaction under comparable reaction conditions, even though similar driving forces are involved (see Table V). Besides the driving force, theory suggests that the self-exchange rate constants are important factors in determining the rate of outer-sphere electron-transfer reactions.<sup>31</sup> Conceivably, the strong variation in self-exchange rate constants which is observed among cobalt complexes<sup>32</sup> could result in a significant variation in *k<sub>r</sub>'* values. Unfortunately, the self-exchange rates germane to this discussion are unknown. Some of the differences in reactivity of the cobalt complexes are probably established *after* the *k<sub>r</sub>'* step, and these are best considered from the point of view of the limiting quantum yields.

Comparing the limiting quantum yields associated with the three Co(III) complexes is, however, a more complicated matter. According to eq 12, the limiting yields are given by the expression

$$\phi_{\text{lim}} = \eta \frac{k_p}{k_p + k_b}$$

Since eq 8 represents an electron-transfer step, *k<sub>b</sub>* is affected by the same factors as *k<sub>r</sub>'*; moreover, an inner-sphere mechanism may well be operative for these reactions. Further ambiguity arises because *k<sub>p</sub>*, the rate constant for the decay of the successor complex to products, represents a complex quantity that may be a function of pH, subtle electronic factors, etc. From the data in Table II, we would predict that the relative values of *k<sub>p</sub>*/*k<sub>p</sub>* + *k<sub>b</sub>* for the complexes [Co(en)<sub>2</sub>bpy]<sup>3+</sup>, *trans*-[Co(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub>]<sup>+</sup>, and *cis*-[Co(IDA)<sub>2</sub>]<sup>-</sup> are 2.8:1:28.0. That significant inefficiencies can arise from a back-reaction involving a successor complex has previously been postulated for photoreactions of the [Ru(bpy)<sub>3</sub>]<sup>2+</sup> system.<sup>33,34</sup> (Direct comparisons of the latter results with ours are not possible since different Co(III) complexes studied at

(27) It is of course possible that eq 1 does not accurately describe the associative equilibria which occur. For example, triple ion associates might have some importance.

(28) One of the reviewers astutely raised this point.

(29) A similar difficulty arises in any mechanism which involves diffusional encounters of a transient reductant which is produced upon irradiation, regardless of the nature of the transient—excited state or other.

(30) Wagner, P. J.; Kochevar, I. *J. Am. Chem.* 1968, 90, 2232.

(31) Marcus, R. A. *Annu. Rev. Phys. Chem.* 1964, 15, 155.

(32) Pennington, D. E. *ACS Monogr.* 1978, 174, Chapter 3.

(33) Fisher, P.; Finkenberger, E.; Huang, S. M.; Gafney, H. D. *J. Phys. Chem.* 1978, 82, 526.

(34) Böttcher, W.; Haim, A. *J. Am. Chem. Soc.* 1980, 102, 1564.

different pHs are involved.) Given the complexity of the quantity  $k_p/(k_p + k_b)$ , a detailed analysis is precluded, but some interesting observations can be made. One is that  $k_p/(k_p + k_b)$  increases with the degree of chelation at cobalt, a result which suggests that hydrolysis of the Co(II) product is *not* rate limiting in the  $k_p$  step. If it were, one might expect that increasing chelation would retard the  $k_p$  step, thereby rendering the  $k_b$  step more competitive. A second point is that charge effects in the successor complex would appear to play a secondary role since, from simple electrostatics, we expect that separation of the products should be least facile when *cis*-[Co(IDA)<sub>2</sub>]<sup>-</sup> is involved; yet, the IDA<sup>2-</sup> complex gives the highest ratio of  $k_p/(k_p + k_b)$ . The  $k_p/(k_p + k_b)$  ratios seem to correlate most regularly with the driving force of the back-reaction, which would in fact be expected to influence the  $k_b$  step. As can be seen from Table V, the Co(II) complexes are expected to be increasingly reducing in character in going from the IDA<sup>2-</sup> system to the bpy system to the CN<sup>-</sup> system. Incidentally, all three complexes are capable of reducing the [Cu(dmp)<sub>2</sub>]<sup>2+</sup> system which has a reduction potential of  $\sim 0.7$  V vs. SHE.<sup>35</sup>

All systems considered, it appears that both the  $k_r$  value and the  $k_p/(k_p + k_b)$  ratio are important factors in determining the yield for a given Co(III) substrate. Whereas the former is presumably a sensitive function of the self-exchange rate, the latter seems to depend upon the reduction potential of the cobalt complex. It is also appropriate to remark that the quantum yields may reflect additional competing processes which we have not yet identified, e.g., an energy-transfer step.<sup>36</sup>

Another point is that part of the inefficiency reflected in the limiting quantum yields of Table II may be connected with an  $\eta$  value of less than unity for the copper complex. This could obtain if, for example, the photoreaction stems from the triplet CT state and this state is not populated with unit efficiency. In fact based on P-type delayed fluorescence studies, Wehry and Sundararajan have estimated that intersystem crossing occurs within the complex with an efficiency of 0.26.<sup>8</sup>

Before leaving this section we may consider the effect that solvent has on the quantum yields; see Table III. Solvent can affect electron-transfer rates; hence,  $k_r$ ,  $k_b$ , or both can be influenced. In addition the  $k_p$  step may be solvent dependent, and in fact, the decrease in the quantum yield for Co(acac)<sub>3</sub> in going from the ethanol-water solvent to CH<sub>2</sub>Cl<sub>2</sub> may in large part be explained by the inability of CH<sub>2</sub>Cl<sub>2</sub> to solvolyze the Co(II) product. Yet another consideration is the possibility that the lifetime of the excited state, and hence the  $k_d$  step, may be sensitive to solvent.<sup>11</sup> The only trend evident is that, qualitatively at least, more polar solvents seem to give rise to higher quantum yields.

#### Attempts To Find Evidence for an Energy-Transfer Process.

If energy transfer is competitive with electron transfer for the Co(III) substrates, a further inefficiency factor involved in determining  $\phi_{\text{lim}}$  is  $k_r/(k_r + k_{\text{ET}})$ , where  $k_{\text{ET}}$  is the rate constant for the energy-transfer process.<sup>7</sup> One way to detect energy transfer would be to characterize a sensitized reaction of the Co(III) acceptor, e.g., ammonia aqutation from *trans*-[Co(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub>]<sup>+</sup>.<sup>37</sup> We have attempted this experiment, but our results are inconclusive. The quantum yield for ammonia release from the excited complex is only  $\sim 2 \times 10^{-3}$ . Thus even if the quantum yield for energy transfer were  $10^{-2}$ , the quantum yield for sensitized ammonia aqutation would be

$\sim 10^{-5}$ , making it difficult to quantify the ammonia in excess of that expected from the production of Co(II) by electron transfer and that expected from the direct excitation of the Co(III) center. Seeking a Co(III) center which exhibits a higher quantum yield for ligand aqutation, we have carried out experiments with [Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub>]<sup>2+</sup> and [Co(NH<sub>3</sub>)<sub>5</sub>NCPH]<sup>3+</sup> which feature quantum yields of ligand aqutation of  $\phi_{\text{N}_3} = 0.1$ <sup>38</sup> and  $\phi_{\text{NCPH}} = 0.01$ ,<sup>39</sup> respectively. Unfortunately, the azide complex reacts with [Cu(dmp)<sub>2</sub>]<sup>+</sup> in the dark, and the benzonitrile complex reacts fairly efficiently by electron transfer to give Co(II).

In an attempt to avoid competitive electron transfer, we have sought to establish the viability of an energy-transfer step by using Cr(III) substrates, which are in general far less oxidizing. However, attempts involving *trans*-[Cr(NH<sub>3</sub>)<sub>2</sub>(NCS)<sub>4</sub>]<sup>-</sup> and [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> have given negative results. When the Cr(III) concentration is 5 mM, we estimate that  $\phi_{\text{ET}}$ , the quantum yield for energy transfer, is 0.01 or less. The doublet state of [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> has an energy of  $\sim 1.5 \mu\text{m}^{-1}$ , and that of *trans*-[Cr(NH<sub>3</sub>)<sub>2</sub>(NCS)<sub>4</sub>]<sup>-</sup> has an energy of  $\sim 1.3 \mu\text{m}^{-1}$ .<sup>40</sup> On the basis of the absorption and emission maxima in CH<sub>2</sub>Cl<sub>2</sub> a crude estimate of the zero-zero energy of the excited state of [Cu(dmp)<sub>2</sub>]<sup>+</sup> is  $1.7\text{--}1.8 \mu\text{m}^{-1}$ ;<sup>11</sup> hence energy transfer is likely to be exoergic for both chromium complexes. Even so, the inefficiency of energy transfer in these systems may not be surprising in view of the short lifetime which is likely for \*[Cu(dmp)<sub>2</sub>]<sup>+</sup>. (The lifetime is  $54 \times 10^{-9}$  s in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C.<sup>11</sup>) To be efficient at reasonable Cr(III) concentrations,  $k_{\text{ET}}$  would presumably have to approach the diffusion limit, and energy transfer often occurs at a significantly slower rate when complex ions are involved.<sup>3e,41</sup> These findings have usually been attributed to Franck-Condon restrictions<sup>41,42</sup> and problems of orbital overlap in the collision complex.<sup>41,43</sup> The latter effect is particularly evident when metal-centered excited states are involved.

**Studies of Reactions Involving Molecular Oxygen.** The low quantum yield for the loss of Cu(I) upon irradiating [Cu(dmp)<sub>2</sub>]<sup>+</sup> in the presence of oxygen ( $\phi = 7 \times 10^{-5}$ ) suggests that an inefficient net oxidation process occurs. In accord with studies of [Ru(bpy)<sub>3</sub>]<sup>2+</sup><sup>44,45</sup> the photoreaction between \*[Cu(dmp)<sub>2</sub>]<sup>+</sup> and O<sub>2</sub> can be expected to involve electron transfer and the formation of superoxide. Given the reducing character of O<sub>2</sub><sup>-</sup>, we can also anticipate that back electron transfer to regenerate [Cu(dmp)<sub>2</sub>]<sup>+</sup> and O<sub>2</sub> is favorable, limiting the quantum yield of reaction. That net photochemistry is observed must be due to another competing reaction, presumably the disproportionation of superoxide into H<sub>2</sub>O<sub>2</sub> (or H<sub>2</sub>O) and O<sub>2</sub>. Indirect support for the contention that superoxide does form comes from the spin trapping studies in which the hydroxyl radical was detected, since according to the literature, the presence of copper ions and superoxide ions can lead to the formation of the hydroxyl radical.<sup>46,47</sup>

(35) Rader, R. A.; McMillin, D. R., unpublished results.

(36) Another possibility is that intersystem crossing within the Co(II) successor may be slow compared to back electron transfer.<sup>33</sup> If so, the potentials in Table V are not directly relevant to the  $k_b$  step.

(37) Actually, the observation of ammonia aqutation would not unequivocally establish that energy transfer occurs; for example, partial aqutation of cobalt could occur in the successor complex prior to back electron transfer.

(38) Ferraudi, G.; Endicott, J. F. *J. Chem. Soc., Chem. Commun.* **1973**, 674.

(39) Zanella, A. W.; Ford, K. H.; Ford, P. C. *Inorg. Chem.* **1978**, *17*, 1051.

(40) Forster, L. S. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; Chapter 1.

(41) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152.

(42) (a) That charge-transfer excited states of Cu(I) are subject to appreciable distortions follows from the large Stokes shifts observed<sup>10,11</sup> and the fact that multiple emissions are sometimes observed.<sup>42b</sup> (b) Buckner, M. T.; Matthews, T. G.; Lytle, F. E.; McMillin, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 5846.

(43) (a) Porter, G.; Wright, M. R. *Discuss. Faraday Soc.* **1959**, *27*, 7. (b) Balzani, V.; Indelli, M. T.; Maestri, M.; Sandrini, D.; Scandola, F. *J. Phys. Chem.* **1980**, *84*, 852.

(44) Winterle, J. S.; Kligler, D. S.; Hammond, G. S. *J. Am. Chem. Soc.* **1976**, *98*, 3719.

(45) Brunschwig, B.; Sutin, N. *J. Am. Chem. Soc.* **1978**, *100*, 7568.

(46) Sugiura, Y. *Biochem. Biophys. Res. Commun.* **1979**, *90*, 375.

(47) Lawrence, G. D.; Sawyer, D. T. *Biochemistry* **1979**, *18*, 3045.

In principle, the formation of superoxide could explain the oxygen effect on  $\phi_{-Cu(I)}$  for *trans*-[Co(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub>]<sup>+</sup> (see Table IV). Because of its reducing character, superoxide could act as an electron carrier,<sup>48</sup> or "relay", providing another route to the reduction of Co(III). However, the rate constants for the reduction of Co(III) by superoxide are not large, typically being <10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>.<sup>49</sup> Another possibility is that in the case of the cyano complex, O<sub>2</sub> may scavenge a transient Co(II) species which is capable of back-reacting with Cu(II).

### Conclusions

The reduction of a variety of Co(III) complexes and molecular oxygen has been observed upon irradiating [Cu(dmp)<sub>2</sub>]<sup>+</sup> in solution. The results are consistent with the idea that a strongly reducing CT excited state of [Cu(dmp)<sub>2</sub>]<sup>+</sup>

survives to undergo reaction. In general, rather low quantum efficiencies are observed, and several possible sources of inefficiency have been identified. So far and despite several attempts, energy-transfer reactivity has not been detected, perhaps because the rate of energy transfer is not competitive with that of excited-state relaxation. Many important questions about the mechanism of these reactions remain. Flash photolysis studies may provide some of the answers.

**Acknowledgment.** We gratefully acknowledge the Atlantic Richfield Foundation which has helped fund our work through a contribution to the Research Corp. We are also indebted to Rosemary A. Rader who provided some electrochemical measurements and to Philip S. Low for the loan of a spectrofluorimeter.

**Registry No.** [Cu(dmp)<sub>2</sub>]<sup>+</sup>, 21710-12-3; *cis*-[Co(IDA)<sub>2</sub>]<sup>-</sup>, 21718-59-2; *trans*-[Co(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub>]<sup>+</sup>, 34902-82-4; [Co(en)<sub>2</sub>bpy]<sup>3+</sup>, 48185-94-0; Co(acac)<sub>3</sub>, 21679-46-9; [Co(en)<sub>2</sub>phen]<sup>3+</sup>, 47247-88-1; β-Co(ala)<sub>3</sub>, 55448-50-5; [Co(NH<sub>3</sub>)<sub>5</sub>py]<sup>3+</sup>, 31011-67-3; [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, 14695-95-5; [Co(NH<sub>3</sub>)<sub>5</sub>(CN)]<sup>2+</sup>, 19529-81-8; O<sub>2</sub>, 7782-44-7.

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## Stereochemistry of Equatorial Aquation in the Ligand Field Photolysis of *trans*-Dicyanotetraamminechromium(III)

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Received June 12, 1980

The photolysis of *trans*-Cr(NH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub><sup>+</sup> in acidic aqueous solution at 10 °C results in NH<sub>3</sub> aquation with a wavelength-independent quantum yield of 0.24 throughout the ligand field absorption region. No cyanide is photoreleased ( $\phi < 0.005$ ), while the dark reaction is one of exclusive CN<sup>-</sup> loss. The photolabilization pattern is discussed in terms of the equatorial antibonding properties of the lowest quartet excited state, <sup>4</sup>B<sub>2g</sub>, and is compared with the predictions of the available photolysis models. By ion-exchange separations and subsequent thermal aquation, the photoproduct Cr(NH<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)(CN)<sub>2</sub><sup>+</sup> is demonstrated to consist of a mixture of 1,6-CN-2-H<sub>2</sub>O and 1,2-CN-6-H<sub>2</sub>O isomers, in a ca. 2:1 proportion. Equatorial photoaquation is concluded to be partially stereoretentive and partially stereomobile. The consistency of the product nature and distribution with the plausible excited-state mechanisms is examined.

### Introduction

Among the various aspects of chromium(III) photosubstitutions, the stereochemistry has long been a point of major interest.<sup>1</sup> The complexes investigated from this point of view are of the general types CrN<sub>3</sub>X<sup>2+</sup> and *trans*-CrN<sub>4</sub>XY<sup>2+</sup>,<sup>8-20</sup>

where N stands for ammonia or amines and X and Y are acido groups. In most of these systems the main photoreaction following ligand field (LF) excitation is displacement of the axial ligands and occurs with complete *trans* → *cis* isomerization. Moreover, photosubstitution is efficient only if such a rearrangement is not prevented.<sup>11,14</sup>

Much less stereochemical information exists on equatorial photosolvation. So far, only two species have been found to undergo preferential cleavage of the equatorial Cr-N bonds: *trans*-Cr(en)<sub>2</sub>F<sub>2</sub><sup>+</sup><sup>10,18</sup> and *trans*-Cr(en)<sub>2</sub>(CN)<sub>2</sub><sup>+</sup>, reported<sup>21</sup> after completion of this work. Photoproduct identification has been attempted for the former<sup>10,18</sup> but not for the latter.<sup>21</sup> In

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