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Studies of Photoinduced Electron Transfer from Bis(2,9-dimethyl-1,10-phenanthroline)copper(I)

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Photostudies of the bis(2,9-dimethyl-1,10-phenanthroline)copper(I) ion, $Cu(dmp)_2^+$, in solution in the presence of several different Co(III) complexes are described. Upon irradiating into the low-lying metal-to-ligand charge-transfer band of $Cu(dmp)_2^+$ a reduction of Co(III) is observed in each case, and the yield of Co(II) is markedly dependent on the nature of the Co(III) center. The results are consistent with a model in which the electron-transfer reactions occur by bimolecular processes involving a thermally equilibrated metal-to-ligand charge-transfer excited state of the copper complex. The wavelength dependence of the quantum yield for the redox process is presented for the case of the *trans*-bis(iminodiacetato)cobaltate(III) complex, and somewhat smaller quantum yields are observed upon irradiating into a higher energy band of the copper complex.

Recently, the photochemistry of Cu(I) systems has been a subject of increasing interest,[1-4] especially systems exhibiting photoredox chemistry.[1-3] Our interest has centered upon systems for which the lowest energy electronic excited state is a metal-to-ligand charge-transfer (MLCT) state.[1] Such systems absorb strongly in the visible region, and by analogy with related Ru(II) systems,[5-9] the photoexcited molecules might be expected to evidence marked reducing and/or oxidizing ability. Our current aims are to characterize the photoreactivity patterns of Cu(I) systems and to delineate the factors which influence the energies and lifetimes of the states which are generated by visible irradiation. Such systems could conceivably find application in the conversion of visible light into other forms of energy.

Previously we reported that exciting into the MLCT state of bis(2,9-dimethyl-1,10-phenanthroline)copper(I), $Cu(dmp)_2^+$, when dissolved in solution with *cis*-bis(iminodiacetato)cobaltate(III), *cis*-$Co(IDA)_2^-$, resulted in electron transfer from Cu(I) to Co(III).[1] In this report we present more detailed studies involving the more soluble *trans*-$Co(IDA)_2^-$ system as well as the results of studies involving several other Co(III) systems.

Experimental Section

Materials. The preparation of $[Cu(dmp)_2]NO_3{\cdot}2.5H_2O$ was effected by a route analogous to the one used previously[1] and was recrystallized from ethanol/water. The purple salt K[*cis*-Co(IDA)$_2$]$\cdot 2.5H_2O$ was prepared by a literature method.[10] The brown salt K[*trans*-Co(IDA)$_2$]$\cdot 1.5H_2O$ was obtained from the corresponding cis complex as follows. The cis complex was dissolved in water and warmed to ~80 °C in the presence of activated charcoal. After filtering and cooling of the system, a mixture of the two isomers, which was largely the trans, precipitated. The trans isomer was isolated in a pure form by recrystallizing the mixture two or three times from warm water. The [*trans*-Co(NH$_3$)$_4$(CN)$_2$]Cl$\cdot 1.5H_2O$ complex,[11] the K[*trans*-Co(MIDA)$_2$]$\cdot 0.5H_2O$ complex,[12] where $MIDA^{2-}$ denotes the methyliminodiacetate ligand, and the Na[Co(EDTA)]$\cdot 3H_2O$ complex,[13] where $EDTA^{4-}$ denotes the ethylenediaminetetracetate ligand, were each prepared by literature methods. All other materials were reagent grade quality. The solvent employed for the photolysis experiments was a 30:70 v/v mixture of ethanol–water which was a buffer solution of 0.01 M lithium acetate and 0.01 M acetic acid. The ionic strength was maintained at $\mu = 0.1$ by the addition of $LiNO_3$, LiCl, or NaCl.

Apparatus. The light source was a 1000-W Xe arc lamp operated in an Oriel 6141 lamp housing with an Oriel 6242 power supply. The output was collimated, passed through a water filter and, when necessary, a Corning long-wave-pass filter, and then focused onto the entrance slit of an Oriel 7241 monochromator (band-pass ≈ 13 nm) for wavelength selection. The photolyte was irradiated in a spectrophotometer cell and was stirred with a small magnetic stir bar. The cell holder was thermostated at 20 °C with a Tri-R Instruments Model B-30 circulating water bath. Absorption measurements in the visible region were made with a McPherson EU-707D spectrophotomer which included an EU-700-56 programmable filter assembly to minimize stray light. The measurements in the rear-IR region were made with a Cary 14 spectrophotometer.

Photolysis Studies. For anaerobic studies the cells were purged with argon gas prior to irradiation. The incident light intensity was determined by ferrioxalate actinometry;[14] care was taken to ensure that the solutions used for the analysis of the ferrous ion had not decomposed.[15]

In most cases the loss of Cu(I) was followed by the absorbance loss in the region of the intense MLCT transition of $Cu(dmp)_2^+$. The appearance of Co(II) was monitored by the method of Kitson.[16] The *trans*-$Co(IDA)_2^-$ complex was found to undergo a slow reaction with the thiocyanate ion, and the reaction appeared to be catalyzed by Cu(I). Therefore, following irradiation, the solutions which contained *trans*-$Co(IDA)_2^-$ were treated with a small amount of sodium ascorbate to convert the Cu(II) present back to $Cu(dmp)_2^+$ and then extracted with chloroform to remove $Cu(dmp)_2^+$. The resulting aqueous layer was then analyzed for Co(II).

A complication that can occur with aminocarboxylate complexes of Co(III), e.g., Co(EDTA),[-17,18] is a chelate-ring opening which involves the displacement of a carboxylate group from the first coordination sphere of the metal. We have no evidence that this effect occurs for the IDA^{2-} or the $MIDA^{2-}$ systems, and in no case did the absorbance of a solution of a Co(III) complex change appreciably on standing. These results suggest that if significant amounts of such species are formed in solution, their chemistry is likely to parallel that of the fully chelated systems. In any case, to be consistent, freshly prepared solutions of the complexes were used for all of the experiments reported herein.

Calculations. The quantum yield for the loss of $Cu(dmp)_2^+$ was calculated from the change in absorbance of $Cu(dmp)_2^+$, denoted A_{Cu}, with time. The rate of change of A_{Cu} is given by the following separable, differential equation where A_x denotes the absorbance of the other species present, ϵ is the molar absorptivity of $Cu(dmp)_2^+$ at the wavelength of interest, l is the path length, I_0 is the incident light intensity, and V is the volume of the photolyte solution. The

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$$\frac{-\mathrm{d}A_{\mathrm{Cu}}}{\mathrm{d}t} = \frac{\epsilon l I_0 \Phi_{-\mathrm{Cu(I)}}}{V} \frac{A_{\mathrm{Cu}}}{A_{\mathrm{Cu}} + A_{\mathrm{x}}} (1 - 10^{-A_{\mathrm{Cu}}} 10^{-A_{\mathrm{x}}})$$

quantum yields at λ 454 nm and λ 495 nm were determined by numerically integrating the absorbance function over the absorbance change observed upon irradiating for a time t, and dividing by t to obtain $\Phi_{-\mathrm{Cu(I)}}\ \epsilon l I_0/V$ from which we calculated $\Phi_{-\mathrm{Cu(I)}}$. At these wavelengths the change in A_{x} was negligible and, accordingly, A_{x} was taken to be constant. At λ 365 nm, however, we could not assume that A_{x} was constant. The $\mathrm{Cu(dmp)_2}^{2+}$ formed, for example, exhibits appreciable absorbance at this wavelength. Therefore to analyze the data we determined the average absorbance $\bar{A}_{\mathrm{Cu}}$ of $\mathrm{Cu(dmp)_2}^+$ at λ 365 nm during time t from $\bar{A}_{\mathrm{Cu}}$ at λ 454 nm and the ratio of ϵ_{365} to ϵ_{454} for $\mathrm{Cu(dmp)_2}^+$ which is 0.341. We also determined the average absorbance of the photolyte solution $\bar{A}_{\mathrm{T}}$ at λ 365 nm during time t and then calculated $\Phi_{-\mathrm{Cu(I)}}$ by dividing the number of $\mathrm{Cu(dmp)_2}^+$ ions lost in time t, computed from the absorbance change at λ 454 nm, by the number of photons absorbed in that time interval. The latter was estimated from $I_0(\bar{A}_{\mathrm{Cu}}/\bar{A}_{\mathrm{T}})(1 - 10^{-\bar{A}_{\mathrm{T}}})t$.

The least-squares analyses of the Stern–Volmer plots, vide infra, were calculated using a CDC 6500 computer. To simplify the notation for this discussion, we will denote the *i*th *measured* quantum yield for the loss of $\mathrm{Cu(dmp)_2}^+$ as Φ_i^{exptl}. The symbol Φ_i will denote the calculated value or the best estimate of the quantum yield associated with the Co(III) concentration used in the *i*th trial. In our analyses, the weight assigned to the square of the *i*th residual $(\Phi_i^{-1} - (\Phi_i^{\mathrm{exptl}})^{-1})^2$ was $(\Phi_i^{\mathrm{exptl}})^2$. The weights assigned reflect our estimates of the relative variances of the Φ_i^{-1}. To obtain these estimates, we assumed that the *relative* precision of the Φ_i^{exptl} is constant and used the general relationship that σ_f^2, the variance of a quantity f, which is a function of a variable x having a variance σ_x^2, is given by

$$\sigma_f^2 = \left(\frac{\mathrm{d}f}{\mathrm{d}x}\right)^2 \sigma_x^2$$

Results

When solutions containing $\mathrm{Cu(dmp)_2}^+$ and any of the Co(III) complexes were kept in the dark at room temperature, their absorbances were stable for long periods of time, although a very slow decrease in absorbance at 454 nm was observed in the case of *trans*-$\mathrm{Co(MIDA)_2}^-$. In each case, however, upon irradiation of a solution with visible light a smooth decrease of absorbance in the region of 454 nm was observed, and the rate of the decrease in absorbance increased with increasing concentration of the cobalt complex. On the time scale of our experiments we detected no photochemistry when a solution containing only $\mathrm{Cu(dmp)_2}^+$ was irradiated with visible light. The only reaction we observed upon irradiating the Co(III) solutions was the release of ammonia in the case of *trans*-$\mathrm{Co(NH_3)_4(CN)_2}^+$. No new absorption features were observed in solutions which contained both $\mathrm{Cu(dmp)_2}^+$ and a Co(III) complex. Over the wavelength range between 350 and ~1300 nm the absorbance of a solution containing $\mathrm{Cu(dmp)_2}^+$ and *either* IDA^{2-} complex was found to be, within experimental error, a superposition of the spectra of the two components.

The measured quantum yields for the photoinduced loss of $\mathrm{Cu(dmp)_2}^+$ are presented in Table I and were calculated assuming that only the photons absorbed by $\mathrm{Cu(dmp)_2}^+$ were effective.[19] The same quantum yield was obtained for the solution that was 3 mM in *trans*-$\mathrm{Co(IDA)_2}^-$ under conditions in which the solution was purged with O_2 prior to irradiation as was obtained when the solution was deoxygenated with an Ar purge before irradiation. Also reported in Table I are stoichiometric ratios comparing the amount of Cu(I) lost with the amount of Co(II) formed in several photolysis experiments. In Figures 1 and 2 Stern–Volmer plots of data from Table I are presented. The slopes and intercepts of the (best-fit) plots are presented in Table II.

Table I. Quantum Yields

Co(III) complex	wave-length/ nm	[Co-(III)]/ mM	$10^3 \times \Phi_{-\mathrm{Cu(I)}}$	[Cu(II)]/ [Co(II)]
trans-$\mathrm{Co(IDA)_2}^-$	454	2	2.24	0.98
		3	3.34	0.93
		5	5.51	
		10	9.30	1.02
			10.2	
			13.1	
		15	15.8	
		20	19.4	
	495	5	5.71	1.07
		10	8.61	
	365	2	1.67	
		3	2.60	
		5	3.84	1.00
			4.14	
			4.13	
		7	5.60	
		10	9.39	
		20	15.7	
cis-$\mathrm{Co(IDA)_2}^-$ [a]	454	3	3.40	
		4	4.36	
		5	5.58	
		7	7.66	
		9	9.45	
trans-$\mathrm{[Co(NH_3)_4(CN)_2]^+}$	454	3	0.24	
		4	0.32	
		5	0.28	
			0.38	
			0.44	
			0.47	0.97
		8	0.54	
		10	0.64	
			0.52	
trans-$\mathrm{Co(MIDA)_2}^-$	454	3	5.73	
		5	8.12	
$\mathrm{Co(EDTA)^-}$	454	4	4.49	0.98
		10	8.15	

[a] The $\Phi_{-\mathrm{Cu(I)}}$ reported herein differ somewhat from those reported in ref 1, presumably, because of problems in the previous actinometry measurements.[15]

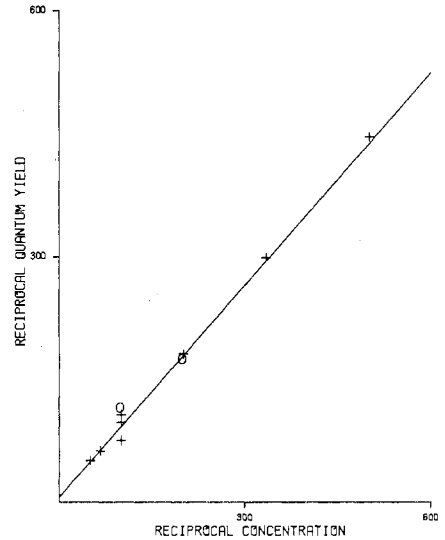

Figure 1. The best-fit Stern–Volmer plot of $(\Phi_{-\mathrm{Cu(I)}})^{-1}$ vs. [*trans*-$\mathrm{Co(IDA)_2}^-]^{-1}$ which was computed using the data (+) collected from photolysis experiments at 454 nm. For comparison the data (○) collected for experiments at 495 nm are also plotted.

Except for the experiments involving $\mathrm{Co(EDTA)^-}$, the absorbance of a solution was stable following irradiation if the solution was stored in the dark, and, for low conversions, the back-reaction was sufficiently slow in the case of $\mathrm{Co(EDTA)^-}$ that it did not affect the estimation of the quantum yields. In control experiments, solutions of Cu(II) containing 2 equiv of the dmp ligand and solutions of Co(II) containing 2 equiv of the IDA^{2-} ligand were mixed and monitored for the for-

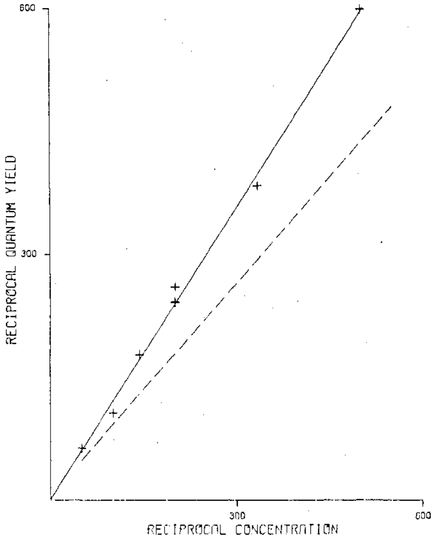

Figure 2. The best-fit Stern–Volmer plot (—) of $(\Phi_{-\mathrm{Cu(I)}})^{-1}$ vs. $[trans\text{-Co(IDA)}_2^-]^{-1}$ which was computed using the data (+) collected from experiments at 365 nm. For comparison the Stern–Volmer plot (- - -) computed for the 454 nm data is also presented.

Table II. Stern–Volmer Analyses

Co(III) complex	irradn wavelength, nm	slope[a]	intercept[a]
cis-$\mathrm{Co(IDA)_2^-}$	454	0.86 (0.02)	9.36 (3.31)
trans-$\mathrm{Co(IDA)_2^-}$	454	0.86 (0.07)	6.13 (6.44)
trans-$\mathrm{Co(IDA)_2^-}$	365	1.19 (0.05)	1.58 (5.65)
trans-$\mathrm{Co(NH_3)_4(CN)_2^+}$	454	9.77 (2.25)	718 (376)

[a] The marginal standard deviations associated with each estimate are reported within the parentheses.

mation of $\mathrm{Cu(dmp)_2^+}$. When the concentrations were ~50 mM, significant formation of $\mathrm{Cu(dmp)_2^+}$ was observed over a period of several minutes. As the concentrations of either Cu(II) or Co(II) were decreased, however, the rate of formation of $\mathrm{Cu(dmp)_2^+}$ was observed to decrease, and the absorbance profile indicated that the reaction was complex and did not reflect a simple second-order reaction. When relatively low concentrations of reagents were used, e.g., [Cu(II)] ≈ 0.05 mM, and [Co(II)] ≈ 1 mM, the formation of appreciable quantities of $\mathrm{Cu(dmp)_2^+}$ required several hours.

Discussion

Thermal Chemistry. That the electron-transfer reactions are very slow or nonexistent in the dark is consistent with the reduction potentials, presented in Table III, which have been reported for these systems. In fact the potentials predict that Co(II) should react with Cu(II) to give Cu(I) and Co(III). However, this effect was only observed in the case of $\mathrm{Co(EDTA)^-}$. For the $\mathrm{Co(IDA)_2^-}$ systems the control experiments confirmed that the back-reactions would be negligible given the low concentrations of Co(II) and Cu(II) that formed during photolysis (~0.02 mM). In all probability, the reason that the back-reactions are unimportant is that the labile Cu(II) and Co(II) systems are involved in a number of competing equilibria in the irradiated solutions. In the case of $\mathrm{IDA^{2-}}$, for example, the following complications probably retard the back-reaction: (i) the formation of the $\mathrm{Co(IDA)_2^{2-}}$ complex is incomplete because of competing equilibria involving $\mathrm{IDA^{2-}}$ and the proton or Cu(II), and (ii) the formation of $\mathrm{Cu(dmp)_2^{2+}}$ is incomplete because of a competing equilibrium involving $\mathrm{IDA^{2-}}$ and Cu(II).

Photostudies at 454 nm. Two limiting mechanisms can be envisaged for the photoinduced reactions: (i) a dynamic mechanism involving diffusional encounters of a species derived from photoexcited $\mathrm{Cu(dmp)_2^+}$ and a Co(III) species or (ii) a static mechanism involving an outer-sphere associate of $\mathrm{Cu(dmp)_2^+}$. The former mechanism is the more likely for several reasons.[20] One is that the *trans*-$\mathrm{Co(NH_3)_4(CN)_2^+}$ species is cationic and unlikely to form an outer-sphere associate with $\mathrm{Cu(dmp)_2^+}$. Moreover, in systems which involved anionic Co(III) systems no spectral evidence of associates could be found. The $\mathrm{IDA^{2-}}$ systems should be representative, and absorption spectra of solutions containing $\mathrm{Cu(dmp)_2^+}$ and either Co(III) isomer were simply composites of the corresponding solutions containing only $\mathrm{Cu(dmp)_2^+}$ and only the Co(III) complex. In any event, insofar as electrostatic interactions would be responsible for outer-sphere association, one would expect the formation constant of the associate to be small given the polar nature of the solvent employed and the relatively high ionic strength of our solutions. It should also be noted that a reaction scheme involving both a static component and a dynamic component appears to be unlikely because of the lack of curvature in our Stern–Volmer plots.[21,22]

Table III. Reduction Potentials

Complex	$E°$, V vs. SHE
$\mathrm{Cu(dmp)_2^+}$	0.62[a]
	0.64[b,c]
$\mathrm{Co(EDTA)^-}$	0.38[d]
trans-$\mathrm{Co(IDA)_2^-}$	0.29[e]
cis-$\mathrm{Co(IDA)_2^-}$	0.40[e]

[a] C. J. Hawkins and D. D. Perrin, *J. Chem. Soc.*, 2996 (1963). [b] P. Thomas, H. Spindler, D. Rehorek, and O. Gurtler, *Z. Chem.*, **13**, 225 (1973). [c] G. S. Patterson and R. H. Holm, *Bioinorg. Chem.*, 4, 257 (1975). [d] L. Hin-Fat and W. C. E. Higginson, *J. Chem. Soc. A*, 298 (1967). [e] P. Gouzerh, *J. Chim. Phys. Phys.-Chim. Biol.*, 68, 758 (1971).

The nature of the reactive species derived from photoexcited $\mathrm{Cu(dmp)_2^+}$ has not been unequivocally established. However, the simplest and most obvious possibility would be a thermally equilibrated MLCT state of the complex.[20] (The singlet state or the triplet state or both could be active.) Alternatively, thermal equilibration could lead to a completely distinct species, e.g. a Cu(I) complex with a different coordination environment or possibly a Cu(I) complex involving a covalently hydrated phenanthroline ligand.[23] In principle a species like one of the latter could still carry electronic excitation, but all that would be required is that the new species must have an appreciably more negative reduction potential than the parent ion.

If the reactive species is a thermally equilibrated excited state of $\mathrm{Cu(dmp)_2^+}$ (thexi state of Cu(I)), the electron transfer could occur directly from the thexi state of Cu(I) to Co(III). Alternatively, the thexi state of Cu(I) could transfer *energy* to Co(III) and a thexi state of Co(III) could oxidize Cu(I) in a succeeding reaction. (If the reaction occurs within a single encounter, it may not be possible, operationally, to distinguish between the latter process and the direct electron-transfer process.) Consistent with the latter mechanism, Langford has suggested that excited states of Co(III) can give rise to electron-transfer phenomena under some conditions.[24] However, the fact that the direct excitation of Co(III) did not appear to enhance the efficiency of the photoreaction, vide infra, suggests that the mechanism involving an oxidation by a thexi state of Co(III) is not operative or is at most a minor contributor to the reaction.[25]

Another alternative is that energy transfer from the thexi state of $\mathrm{Cu(dmp)_2^+}$ to Co(III) could induce an intramolecular redox decomposition of the Co(III) complex, producing radicals that *could* then oxidize $\mathrm{Cu(dmp)_2^+}$. This pathway is unlikely because of the fact that 1:1 stoichiometry was observed for the formation of Co(II) and the loss of Cu(I).

Moreover, the radicals formed in the intramolecular redox decomposition of the Co(III) systems are likely to be strongly *reducing* species[26] rather than oxidizing species. It is important to note, however, that although the energy-transfer process apparently does not lead to significant production of Co(II), an energy-transfer process could nevertheless obtain.

Thus the reaction probably involves direct electron transfer from a species derived from photoexcited $\mathrm{Cu(dmp)_2^+}$ to Co(III). As seen below this kind of mechanism would be consistent with the linear Stern–Volmer plot that we obtained for the $\mathrm{IDA^{2-}}$ systems and for the *trans*-$\mathrm{Co(NH_3)_4(CN)_2^+}$ system. Extrapolating the Stern–Volmer plots for *cis*- and *trans*-$\mathrm{Co(IDA)_2^-}$ and for *trans*-$\mathrm{Co(NH_3)_4(CN)_2^+}$ for irradiation at 454 nm predicts limiting quantum yields of 0.11, 0.16, and 0.0014, respectively, as can be calculated from the intercepts presented in Table II. In each case and particularly in the case of the *trans*-$\mathrm{Co(NH_3)_4(CN)_2^+}$ system, the electron-transfer process appears to be significantly less than 100% efficient, even at limiting concentration of Co(III). Our limiting yields may be compared with the yields of ~0.5 that have previously been reported for *intramolecular* photoinduced electron transfer from Cu(I) to Co(III), although the Cu(I) moieties involved in the intramolecular studies were very different from $\mathrm{Cu(dmp)_2^+}$.[2]

Several possible sources of inefficiency exist. One likely source involves a back-electron transfer. For example, although the back-reaction to regenerate $\mathrm{Cu(dmp)_2^+}$ and *cis*- or *trans*-$\mathrm{Co(IDA)_2^-}$ was observed to occur at a negligible rate in solutions at thermal equilibrium, the back-reaction could well be more probable in the successor complex that exists in a solvent cage immediately after the reduction of Co(III). One reason is the fact that excess thermal energy would be present to help surmount any activation barriers that might be involved. Another reason is that during the lifetime of the successor complex the Co(II) and Cu(II) ions would probably retain the coordination environments of the Co(III) and Cu(I) precursors; i.e., ligand redistribution reactions, etc., would likely not have had time to occur. Other sources of inefficiency could arise in the internal conversion and the intersystem crossing processes that may be involved in the formation of the redox-active species derived from $\mathrm{Cu(dmp)_2^+}$, which we denote $\mathrm{{}^*Cu(dmp)_2^+}$. For the discussion that follows we will assume that the production of $\mathrm{{}^*Cu(dmp)_2^+}$ occurs with a fractional efficiency η, where $0 < \eta \leq 1$. Yet another source of inefficiency arises if energy transfer to give excited states of the Co(III) systems, denoted *Co(III), competes with the electron-transfer process.[27] If energy transfer occurs, and does not lead to redox chemistry, as proposed above, the result will be that the yield of redox products will be decreased by an amount that depends upon the relative rates of the energy-transfer and electron-transfer processes, vide infra.

A minimal kinetic scheme which is consistent with the data in Table I and which includes the effects described above is presented in eq 1–6 where Co(III) represents a Co(III)

$$\mathrm{Cu(dmp)_2^+} \xrightarrow{\eta I_0/V} \mathrm{{}^*Cu(dmp)_2^+} \qquad (1)$$

$$\mathrm{{}^*Cu(dmp)_2^+} \xrightarrow{k_d} \mathrm{Cu(dmp)_2^+} \qquad (2)$$

$$\mathrm{{}^*Cu(dmp)_2^+ + Co(III)} \xrightarrow{k_{ET}} \mathrm{Cu(dmp)_2^+ + {}^*Co(III)} \qquad (3)$$

$$\mathrm{{}^*Cu(dmp)_2^+ + Co(III)} \xrightarrow{k_r} \{\mathrm{Cu(dmp)_2^{2+}\cdot Co^{II}}\} \qquad (4)$$

$$\{\mathrm{Cu(dmp)_2^{2+}\cdot Co^{II}}\} \xrightarrow{k_p} \text{redox products} \qquad (5)$$

$$\{\mathrm{Cu(dmp)_2^{2+}\cdot Co^{II}}\} \xrightarrow{k_b} \mathrm{Cu(dmp)_2^+ + Co(III)} \qquad (6)$$

complex and $\{\mathrm{Cu(dmp)_2^{2+}\cdot Co^{II}}\}$ denotes the successor complex formed after the electron-transfer step. Assuming steady-state concentrations of $\mathrm{{}^*Cu(dmp)_2^+}$ and $\{\mathrm{Cu(dmp)_2^{2+}\cdot Co^{II}}\}$ are achieved, we arrive at eq 7, which predicts a limiting value of $\eta[k_p/(k_p + k_b)][k_r/(k_r + k_{ET})]$ for $\Phi_{-\mathrm{Cu(I)}}$.

$$\frac{1}{\Phi_{-\mathrm{Cu(I)}}} = \eta^{-1}\left(\frac{k_p + k_b}{k_p}\right)\left[\frac{k_d}{k_r}\,\frac{1}{[\mathrm{Co(III)}]} + \frac{(k_{ET} + k_r)}{k_r}\right] \qquad (7)$$

From the results presented in Table I it is evident that the quantum efficiency of the electron-transfer reaction is sensitive to the nature of the Co(III) complex involved and is even sensitive to substituent effects in the aminocarboxylate systems. Factors that could affect the relative yields include the possibility that the relative efficiencies of the back-reactions within the respective successor complexes may vary and the possibility that the solvent environments of the Co(III) systems could differ in the mixed solvent employed. The reduction potentials of the Co(III) systems also vary (see Table III) and, as discussed below, may affect the relative reaction efficiencies in a very complex fashion. Therefore small variations in the quantum efficiencies are not easily interpreted. However, it is clear that for a given Co(III) concentration, the quantum yields of the *trans*-$\mathrm{Co(NH_3)_4(CN)_2^+}$ system are markedly lower than those of the other systems in Table I. In part this could reflect the fact that, in solution, collisions of a cationic Co(III) species with a short-lived, presumably cationic species derived from $\mathrm{Cu(dmp)_2^+}$ are less frequent than those with anionic Co(III) systems. (The proposal that the reducing species generated is short-lived is supported by the fact that the quantum yields that we have measured are relatively low and the fact that $\mathrm{O_2}$ has no effect on the reaction involving *trans*-$\mathrm{Co(IDA)_2^-}$.)

We suggest, however, that, more importantly than the collision frequencies, the reason that the redox yields are low for the *trans*-$\mathrm{Co(NH_3)_4(CN)_2^+}$ system may be that energy transfer is more competitive with respect to electron transfer for this system. Admittedly, the factors determining k_r and k_{ET} are complex and are not completely understood. Nevertheless, there are reasons to suspect that k_r would be small for the *trans*-$\mathrm{Co(NH_3)_4(CN)_2^+}$ by comparison with the values expected for the aminocarboxylate systems. In principle the electron-transfer reactions could occur by an inner-sphere mechanism in which a ligand, e.g., $\mathrm{CN^-}$, would bridge between the copper and cobalt centers. If, however, as seems most probable, a thermally equilibrated MLCT state of $\mathrm{Cu(dmp)_2^+}$ is the reducing agent, the outer-sphere mechanism would appear to be more likely. The reason is that, formally at least, the reducing center would not be the copper center but would be a reduced ligand moiety. Assuming the reductions occur by means of outer-sphere processes, the relative rates of the electron-transfer processes will depend on the rates of the respective self-exchange reactions and the values of the respective reduction potentials of the different Co(III) systems. Unfortunately, the relevant self-exchange rates are not all available, and the reduction potentials that have been reported, Table III, may be confused by adsorption effects.[28] On the basis of considerations of related systems, some inferences can be made, however.

According to the Marcus theory,[29] the rate constant for an outer-sphere electron transfer from A to B is approximately proportional to $(k_A k_B K_{AB})^{1/2}$ where k_A is the self-exchange rate constant associated with A, k_B is the self-exchange rate constant associated with B, and K_{AB} is the equilibrium constant for the redox reaction. In Table IV the self-exchange rate constants for two Co(III) systems having features in common with our reagents are presented. Clearly, the ammonia complex has an extremely unfavorable self-exchange rate constant. To the extent that the *trans*-$\mathrm{Co(NH_3)_4(CN)_2^+}$ system parallels the hexaammine system, it would also be

Table IV. Self-Exchange Rate Constants[a]

reaction	k, M^{-1} s^{-1} (25 °C)
$Co(NH_3)_6{}^{3+}$ + $Co(NH_3)_6{}^{2+}$	$<10^{-9}$
$Co(EDTA)^-$ + $Co(EDTA)^{2-}$	1.4×10^{-4}

[a] W. L. Jolly, "The Principles of Inorganic Chemistry", McGraw-Hill, New York, N.Y., 1976, p 337.

expected to have an unfavorable self-exchange rate constant and, consequently, a comparatively small value for k_r in eq 4. In addition the reduction potential of the *trans*-$Co(NH_3)_4(CN)_2{}^+$ system would be expected to be the most negative of the Co(III) systems employed and would lead to the smallest equilibrium constant K. Either or both of these factors could result in a kinetically unfavorable electron-transfer process and increased importance for the energy-transfer process described by eq 3. The proof for the importance of the energy-transfer process would obtain if sensitized photochemistry or emission from *Co(III) could be observed. Unfortunately the quantum yields for ligand substitution reactions of ammine complexes of Co(III) are extremely small and emission from such systems has not been detected.[30] We attempted to establish quantitatively to what extent the sensitized release of NH_3 from *trans*-$Co(NH_3)_4(CN)_2{}^+$ occurred but were unable to achieve the precision in the ammonia analysis[32] which was needed. The experiments were complicated by the fact that the quantum yield for the loss of NH_3 (estimated to be $\sim 2 \times 10^{-4}$, consistent with the values reported in ref 30) was small and the fact that four ammonia molecules were released each time a Co(II) species was formed in solution by the electron-transfer process. Another complication was that the Co(III) system absorbs at 454 nm and therefore a correction was needed for the "direct" photoreaction of the Co(III) complex. The upshot was that the calculation of the yield for the sensitized loss of NH_3 involved the difference of relatively large numbers and no reliable conclusions could be drawn. We may note in passing that the proposal that energy transfer from photoexcited $Cu(dmp)_2{}^+$ is possible has precedent, since Wehry has reported observing energy transfer from photoexcited $Cu(dmp)_2{}^+$ to a series of luminescent dyes.[31]

An alternative explanation for the low redox yield in the case of the *trans*-$Co(NH_3)_4(CN)_2{}^+$ system may also be considered. This model presumes that the back-reaction within the successor complex, eq 6, is most important for the *trans*-$Co(NH_3)_4(CN)_2{}^+$ system and leads to a low redox yield. In support of this model we note that if the reduction potential is most negative for this Co(III) system, then the driving force for the (thermal) back-reaction would be greatest in this case. However, because of the chelate effect and the Coulombic forces involved, we might expect that the successor complex would be *longer-lived* in the case of the aminocarboxylate systems, which may suggest that in fact the back-reaction would be more significant for the aminocarboxylate systems. A further drawback to this model is that if the back-reaction is an outer-sphere process, the self-exchange rate constant associated with the ammine complex is likely to limit the effectiveness of the back-reaction. All things considered, we favor the model which involves a competition between the energy-transfer process and the electron-transfer process to explain the low limiting yields in the case of the *trans*-$Co(NH_3)_4(CN)_2{}^+$ system.

Photostudies at 495 and 365 nm. The quantum yields measured for irradiation at 495 nm are in good agreement with the values obtained at 454 nm, as can be seen in Figure 1. The $\Phi_{-Cu(I)}$ measured at 495 nm were calculated assuming that only the photons absorbed by $Cu(dmp)_2{}^+$ would be effective, and the agreement between the calculated quantum yields supports this hypothesis. The implication is that the same redox-active species is obtained by exciting $Cu(dmp)_2{}^+$ at 454 or 495 nm, which is reasonable since the same, broad absorption band is involved at both wavelengths.

On the other hand, for a given concentration of Co(III), the $\Phi_{-Cu(I)}$ obtained upon irradiation at 365 nm were less than those obtained at the longer wavelengths. However, the 1:1 stoichiometry between the formation of Co(II) and Cu(II) was retained. One explanation for the decrease in the quantum yields at 365 nm could be that the relaxation to ground-state $Cu(dmp)_2{}^+$ has increased probability, relative to the conversion to the redox active species, for the higher energy excitation. Another possibility is that a different reducing species is generated from $Cu(dmp)_2{}^+$ on exciting at 365 nm than is generated on exciting at longer wavelengths.

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Note Added in Proof. After this paper was in press a report of a flash photolysis study of aqueous $Cu(dmp)_2{}^+$ solutions appeared (G. Ferraudi, *Inorg. Chem.*, **17**, 1370 (1978)) which proposed that a reduced ligand moiety is formed upon irradiating $Cu(dmp)_2{}^+$ and which inferred that the reduced ligand moiety could function as a reductant. However, the facts that emission is observed under our conditions[20] and that energy transfer has been observed from photoexcited $Cu(dmp)_2{}^+$[31] support our suggestion that an excited-state species may serve as a reductant in these solutions. Further studies to clarify this issue are in progress.

Registry No. $Cu(dmp)_2{}^+$, 21710-12-3; *trans*-$Co(IDA)_2{}^-$, 33848-79-2; *cis*-$Co(IDA)_2{}^-$, 21718-59-2; *trans*-$[Co(NH_3)_4(CN)_2]^+$, 34902-82-4; *trans*-$Co(MIDA)_2{}^-$, 66758-42-7; $Co(EDTA)^-$, 15136-66-0.

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Luminescence Quenching of Tris(2,2′-bipyridine) Complexes of Chromium(III), Ruthenium(II), and Osmium(II) by Cyanide Complexes

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Luminescence quenching of excited $Cr(bpy)_3^{3+}$, $Ru(bpy)_3^{2+}$, and $Os(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) by cyanide complexes has been investigated. Discrimination between energy and (reductive or oxidative) electron-transfer quenching has been obtained on the basis of correlations between the quenching rate constants and the spectroscopic and thermodynamic quantities involved in the processes. For each excited complex the quenching takes place by energy transfer with $Cr(CN)_6^{3-}$; by reductive electron transfer with $Mo(CN)_8^{4-}$, $Fe(CN)_6^{4-}$, and $Ru(CN)_6^{4-}$; and by oxidative electron transfer with $Fe(CN)_6^{3-}$ and $Co(CN)_6^{3-}$. $Ni(CN)_4^{2-}$ apparently quenches $*Cr(bpy)_3^{3+}$ via reductive electron transfer, $*Ru(bpy)_3^{2+}$ via energy transfer, and $*Os(bpy)_3^{2+}$ via oxidative electron transfer.

Introduction

Energy and electron transfer are two efficient quenching mechanisms of electronically excited states of coordination compounds.[2,3] As electron transfer can occur with either reduction (reductive quenching) or oxidation (oxidative quenching) of the excited state, the three expected mechanisms can be schematized as follows:

$$*A + B \xrightarrow{k_{\mathrm{en.t.}}} A + *B \qquad (1)$$

$$*A + B \xrightarrow{k_{\mathrm{Red}}} A^- + B^+ \qquad (2)$$

$$*A + B \xrightarrow{k_{\mathrm{Ox}}} A^+ + B^- \qquad (3)$$

Energy transfer (reaction 1) has been studied for several years,[2,3] while electron transfer has received attention only recently[4-6] owing to its relevance to the energy conversion problem.[7,8]

Discrimination between energy and electron-transfer quenching is often difficult for both practical and theoretical reasons.[2,4] Correlations between the quenching rate constants and the thermodynamic quantities involved in the quenching processes can provide useful information about the nature of the operative quenching mechanism. In the present work we report a systematic study of the bimolecular quenching of the luminescent excited state of $Cr(bpy)_3^{3+}$, $Ru(bpy)_3^{2+}$, and $Os(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) by cyanide complexes. These systems were chosen in order to explore a wide range of excited-state energies and redox potentials, i.e., of the spectroscopic and thermodynamic quantities involved in reactions 1–3. Some of the results reported here have been the object of a preliminary communication.[9]

Experimental Section

Materials. $[Cr(bpy)_3](ClO_4)_3\cdot{}^1/_2H_2O$,[10] $[Ru(bpy)_3]Cl_2\cdot 6H_2O$,[11] and $[Os(bpy)_3](ClO_4)_2\cdot H_2O$[12] were prepared and purified following published procedures. Emission[13] and absorption[14] spectra of the three complexes agreed well with the literature values. Pure samples of the cyanide complexes were available from previous investigations.[9] All other chemicals were of reagent grade quality.

Apparatus. Absorption spectra were recorded with a Perkin-Elmer 323 double-beam spectrophotometer. The emission intensity and the luminescence spectra were measured with a Perkin-Elmer MPF-3 spectrofluorimeter equipped with a 15-W xenon lamp and a Hamamatsu R 446 phototube. Emission lifetimes were determined by means of a modified Applied Photophysics apparatus which is based on the single-photon counting technique. The light source was a thyratron-gated air flash lamp (repetition rate 18 kHz); the pulses had a full-width at half-height of 3.0 ns. Both exciting (337 or 380 nm) and emitted beams were filtered by means of grating monochromators. The performance of the single-photon counting equipment was checked by measuring the emission lifetime of rhodamine B; the value of 3.3 ns measured with this apparatus is in good agreement with the literature value of 3.2 ns.[15]

Procedure. All of the experiments were carried out at room temperature (~20 °C), in air-equilibrated aqueous solution. Measurements were taken on freshly prepared samples in red light using doubly distilled water. $M(bpy)_3^{z+}$ concentration was about 10^{-4} M; the quencher concentration was in the range 10^{-6}–10^{-2} M, and the ionic strength was adjusted to 0.50 M with NaCl. Emission and lifetime experiments were performed using the right-angle geometry at the wavelength corresponding to the emission maximum (728, 610, and 730 nm for $Cr(bpy)_3^{3+}$, $Ru(bpy)_3^{2+}$, and $Os(bpy)_3^{2+}$, respectively). When necessary, the emission intensities were corrected for absorption of the incident light by the quenchers; this correction was never higher than 10%. In all cases, absorption by the quenchers at the emitting wavelength was negligible. For each quenching experiment the absorption spectrum of the sample was essentially equal to the sum of the $M(bpy)_3^{z+}$ and quencher spectra.

Results

Under our experimental conditions, the excited-state lifetimes were 51 μs for $*Cr(bpy)_3^{3+}$,[16] 0.40 μs for $*Ru(bpy)_3^{2+}$, and 0.021 μs for $*Os(bpy)_3^{2+}$. For all but one of the $M(bpy)_3^{z+}$–quencher couples, linear Stern–Volmer plots were obtained from steady-state emission intensity measurements. Lifetime measurements confirmed that no static quenching was present. For the $Os(bpy)_3^{2+}$–$Fe(CN)_6^{3-}$ couple, the intensity Stern–Volmer plot was not linear; a linear plot was obtained with lifetime measurements. The Stern–Volmer quenching constants obtained from the linear plots were divided by the excited-state lifetime in order to get the bimolecular quenching constant, k_q. The k_q values are collected in Table I.

Discussion

The k_q values alone provide no information about the nature of the quenching mechanism. However, inferences on the quenching mechanism can be obtained from relationships between the bimolecular quenching constant and the thermodynamic quantities which determine the driving force of the various processes. Such thermodynamic quantities are (i)

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