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Comparative Photochemistry of Carbon Monoxide Labilization from Macrocyclic Iron(II) Complexes

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The comparative photochemistry of Fe(TIM)XY and Fe(C$_{18}$H$_{18}$N$_6$)XY complexes (TIM and C$_{18}$H$_{18}$N$_6$ are planar quadridentate macrocyclic diimine ligands, and X and Y are acetonitrile, carbon monoxide, chloride, and bromide) is reported. The quantum yield for CO loss from the mixed-ligand acetonitrile–carbon monoxide complexes is 0.60 when the macrocycle is TIM and 0.49 when the macrocycle is C$_{18}$H$_{18}$N$_6$. The quantum yield for CO loss from the mixed-ligand halo–carbon monoxide complexes is 0.76 when the macrocycle is TIM but less than 10^{-2} when the macrocycle is C$_{18}$H$_{18}$N$_6$. These results strongly support an interpretation based on reactivity from ligand field excited states. The interpretation of the reactivity and the ligand which is labilized is discussed.

Six-coordinate low-spin d^6 complexes of iron(II) with the planar quadridentate macrocyclic ligand TIM (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) and a variety of axial ligands including carbon monoxide are photoactive.[1] The primary photochemical reaction is axial ligand loss with quantum yields ranging from 0.8 for [Fe(TIM)(CH$_3$CN)CO]$^{2+}$ to less than 10^{-4} for [Fe(TIM)(imid)$_2$]$^{2+}$.[1] The electronic absorption spectra of the complexes are dominated by a charge-transfer transition from the degenerate d$_{xz}$ and d$_{yz}$ orbitals on the iron to the π-antibonding orbitals on TIM. The energy of this metal to ligand charge transfer (MTLCT) is sensitive to the axial ligands and ranges from 22 000 cm^{-1} when the ligands are carbon monoxides to 14 300 cm^{-1} when the ligands are ammonias.[1,2] As the axial ligands are varied from good π acceptors to poor π acceptors, the d$_{xz}$ and d$_{yz}$ orbitals rise in energy and the MTLCT energy correspondingly decreases.

The trends in the photoreactivities for the iron(II)–TIM complexes could be interpreted in terms of either ligand field reactivity or charge-transfer excited-state reactivity.[1] According to the former interpretation, the reactivity is caused by the bonding changes upon populating a d–d excited state[3] and the low reactivity occurs when a photoinactive charge-transfer excited state is lower in energy than the d–d states. According to the latter interpretation, the iron is formally oxidized in the MTLCT excited state resulting in decreased π back-bonding and labilization of carbonyl ligands but increased σ donation and stabilization of strong σ donor and anionic ligands.

In order to differentiate between the two explanations of the photoreactivity, iron(II) complexes of the macrocyclic ligand C$_{18}$H$_{18}$N$_6$ were chosen for study.[4] Because its delocalization is greater than that of TIM, its MTLCT bands are
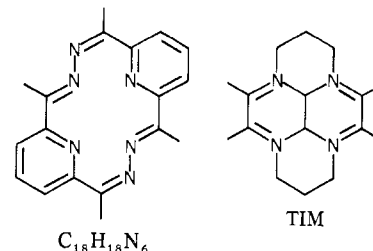
C$_{18}$H$_{18}$N$_6$ TIM

lower in energy than those of analogous TIM complexes. This lowering could cause the MTLCT state which is higher in energy than a ligand field state in TIM to drop lower in energy than the ligand field state in the C$_{18}$H$_{18}$N$_6$ complex. If the photoreactivity were substantially diminished, the ligand field interpretation would be favored. If the reactivity were essentially unchanged, the charge transfer state interpretation would be favored. We report here the comparative photochemical studies of TIM and C$_{18}$H$_{18}$N$_6$ complexes of iron(II).

Experimental Section

Synthesis. [Fe(TIM)Cl](PF$_6$) and [Fe(TIM)Cl(CO)](PF$_6$) were synthesized according to the method of Fey.[5] [Fe(C$_{18}$H$_{18}$N$_6$)CH$_3$CN(CO)](PF$_6$)$_2$ was prepared according to the method of Goedken et al.[4] Satisfactory elemental analyses were obtained for the above compounds.

[Fe(C$_{18}$H$_{18}$N$_6$)Br(CO)](PF$_6$) was prepared by modification of the method of Goedken et al.[4] The procedure reported for the chloro analogue was followed with one variation: a higher concentration of NH$_4$PF$_6$ was required to induce crystallization. The best yields were obtained with 0.2 g of NH$_4$PF$_6$ dissolved in 2 mL of methanol for each 0.5 g of precursor complex. Samples prepared in this manner

Table I. Comparison of the Low-Energy MTLCT Band Maxima (cm^{-1}) for Fe(II)-TIM and Fe(II)-C$_{18}$H$_{18}$N$_6$ Complexes

Complex	TIM	C$_{18}$H$_{18}$N$_6$	Δ^a
Bis(acetonitrile)	18 200	14 300	3900
MeCN–CO	23 200	19 300	3900
Cl–CO	21 600	18 200	3400

^{a} Energy difference between TIM and C$_{18}$H$_{18}$N$_6$ band maxima.

Table II. Quantum Yields for CO Loss

Compd	Solvent	Quantum yield^a
Fe(TIM)Cl(CO)	Acetone	0.76 ± 0.07
Fe(C$_{18}$H$_{18}$N$_6$)Cl(CO)	Acetone	<10^{-2}
Fe(C$_{18}$H$_{18}$N$_6$)Br(CO)	Acetone	<10^{-2}
Fe(TIM)(CH$_3$CN)(CO)	Acetonitrile	0.60 ± 0.06
Fe(C$_{18}$H$_{18}$N$_6$)CH$_3$CN(CO)	Acetonitrile	0.49 ± 0.02

^{a} Irradiated into the MTLCT band.

exhibited high elemental analysis for the percentage of bromide present (approximately 4% too high). The percentage of bromide in the sample could be lowered to within 2% of the theoretical value by recrystallization. Recrystallization was performed by dissolving the crude complex in a minimal amount of 2,2,2-trifluoroethanol with the addition of between 0.2 and 1.0 g of NH$_4$PF$_6$ dissolved in 2 mL of methanol. Any residue was removed by filtration. Carbon monoxide was bubbled through the solution for 10–15 min before the slow addition of diethyl ether (one drop every 5 s). A violet powder was obtained. The infrared spectrum of the recrystallized product showed the presence of a coordinated carbon monoxide ($\bar{\nu}$ 2050 cm^{-1}) and a one-to-one correspondence of bands in the 1700–600-cm^{-1} fingerprint region for the C$_{18}$H$_{18}$N$_6$ macrocyclic ligand compared to those of [Fe(C$_{18}$H$_{18}$N$_6$)CH$_3$CN(CO)](PF$_6$)$_2$. The samples could never be completely separated from coprecipitated [Fe(C$_{18}$H$_{18}$N$_6$)Br(CO)]Br. Anal. Calcd for [Fe(C$_{18}$H$_{18}$N$_6$)Br(CO)]PF$_6$: C, 36.39; H, 2.89; Br, 12.74. Bromine analysis before recrystallization: 16.36%. Analysis after recrystallization: C, 33.57; H, 3.37; Br, 15.37.

Photochemical Procedures. The photochemical procedures were identical with those reported previously with one exception. The 475-nm band-pass filter required for this study was constructed using a series of Corning 5-60 and Dirac 460-nm cuton filters and a Dirac 520 cutoff glass filter in conjunction with a 1-cm solution filter of K$_2$CrO$_4$ (0.1% w/v in water). Reinecke actinometry was used to determine the flux.[6]

Results

Spectroscopy. The visible electronic absorption spectrum of the Fe(II)–C$_{18}$H$_{18}$N$_6$ complexes is dominated by the intense CT peak characteristic of ferrous α-diimine complexes.[7–10] The two pyridine moieties increase the degree of conjugation in the ligand, lowering the energy of the π^* system of the ligand and thus moving the MTLCT transition to lower energies relative to that in TIM complexes.[4,11] The MTLCT transition energies of the C$_{18}$H$_{18}$N$_6$ complexes were lowered by roughly 3.5 × 10^3 cm^{-1} compared to those of the corresponding TIM complexes (Table I). Because the enhanced conjugation in C$_{18}$H$_{18}$N$_6$ should increase the interaction between the metal's d$_{xz}$ and d$_{yz}$ orbitals and the π^* system of the ligand, the ligand field transition d$_{xz}$, d$_{yz}$ → d$_{z^2}$ should occur at higher energy in the C$_{18}$H$_{18}$N$_6$ complexes compared to that of the TIM complexes.[11]

Photochemistry. The photochemistry of [Fe(TIM)-CH$_3$CN(CO)]$^{2+}$, [Fe(C$_{18}$H$_{18}$N$_6$)CH$_3$CN(CO)]$^{2+}$, [Fe(TIM)Cl(CO)]$^{2+}$, and [Fe(C$_{18}$H$_{18}$N$_6$)Br(CO)]$^+$ was studied by irradiating the low-energy MTLCT bands. In each case the complex was photoactive (Table II). Losses of carbon monoxide and coordinated acetonitrile were the observed photoreactions.

[Fe(TIM)Cl(CO)]$^+$. The photoreaction of [Fe(TIM)Cl-(CO)]$^+$ in acetone produced one photoproduct. Isosbestic points were found at 497 and 416 nm. The main MTLCT band at 426 nm of [Fe(TIM)Cl(CO)]$^+$ decreased in intensity as bands at 568 and 493 nm appeared and increased in in-

tensity. The spectrum of the photoproduct was identical with that of an independently prepared sample of [Fe(TIM)Cl]$^+$. The quantum yield for formation of [Fe(TIM)Cl]$^+$ was 0.76 ± 0.07.

[Fe(C$_{18}$H$_{18}$N$_6$)CH$_3$CN(CO)]$^{2+}$. The photochemistry of [Fe(C$_{18}$H$_{18}$N$_6$)CH$_3$CN(CO)]$^{2+}$ was quantitatively studied in acetonitrile. Upon irradiation into its low-energy MTLCT band at 513 nm, the intensity of the 513-nm band decreased and new bands at 700 and 793 nm developed as the photolysis proceeded. Isosbestic points were observed at 380 and 583 nm. The peaks at 700 and 793 nm are indicative of the bis(acetonitrile) complex as confirmed by comparison to peaks of an independently prepared sample of [Fe(C$_{18}$H$_{18}$N$_6$)(C-H$_3$CN)$_2$](PF$_6$)$_2$. The quantum yield for the photosolvation of carbon monoxide was 0.49 ± 0.02.

[Fe(C$_{18}$H$_{18}$N$_6$)Br(CO)]$^+$. The photoreactions of [Fe-(C$_{18}$H$_{18}$N$_6$)Br(CO)]$^+$ were studied qualitatively in 2,2,2-trifluoroethanol and acetone. The electronic absorption spectra of [Fe(C$_{18}$H$_{18}$N$_6$)Br(CO)]$^+$ in both solvents showed a decrease in the 550-nm MTLCT band characteristic of the complex, the development of a new band at 710 nm, and isosbestic points at 650 and 513 nm as the photolysis progressed. The IR spectra showed a decrease in the intensity of the carbonyl stretch accompanying the decrease in the intensity of the MTLCT peak at 550 nm.

The 710-nm band which developed during photolysis is observed as a transient species when bromide ion is added to a 2,2,2-trifluoroethanol or acetone solution of [Fe-(C$_{18}$H$_{18}$N$_6$)(CH$_3$CN)$_2$]$^{2+}$. Upon continued addition of excess bromide ion to the solution, the 710-nm band appears, grows in intensity with time, and then decreases with time as the solution turns brown, the color of [Fe(C$_{18}$H$_{18}$N$_6$)Br$_2$]. The growth and subsequent disappearance of the 710-nm band during the formation of [Fe(C$_{18}$H$_{18}$N$_6$)Br$_2$] from [Fe-(C$_{18}$H$_{18}$N$_6$)(CH$_3$CH)$_2$]$^{2+}$ is interpreted as evidence for [Fe(C$_{18}$H$_{18}$N$_6$)Br]$^+$. On this basis, the band at 710 nm is assigned to the MTLCT of the [Fe(C$_{18}$H$_{18}$N$_6$)Br]$^+$ species.

Quantitative photochemical studies were carried out in acetone. A 531-nm band-pass filter system was employed to irradiate [Fe(C$_{18}$H$_{18}$N$_6$)Br(CO)]$^+$ in its MTLCT band. Isosbestic points were again observed at 513 and 650 nm (Figure 1). The quantum yield for photolabilization of carbon monoxide from [Fe(C$_{18}$H$_{18}$N$_6$)Br(CO)]$^+$ was 0.0073 ± 0.002.

In order to further investigate the low photoreactivity of the halo–carbonyl complexes, Fe(C$_{18}$H$_{18}$N$_6$)Cl(CO) was studied. No isosbestic points were observed. A disappearance quantum yield was determined from the decrease of the MTLCT peak during photolysis into that band. The calculated quantum yield was 0.0077 ± 0.002, the same order of magnitude as that of the bromo complex. Because of the large uncertainties in the quantum yields, only the order of magnitude value, 10^{-2}, will be discussed.

Discussion

The photoreactivity patterns of the ferrous TIM and C$_{18}$H$_{18}$N$_6$ complexes are consistent with the state energy level diagram in Figure 2. In the CH$_3$CN–CO mixed-ligand complexes, a ligand field excited state is lower in energy than the MTLCT state. The quantum yields for loss of CO are similar for the TIM and C$_{18}$H$_{18}$N$_6$ complexes, 0.60[1] and 0.49, respectively. In contrast, for the halo–CO mixed-ligand complexes, the ligand field state is lowest in the TIM complex but the MTLCT is lowest in the C$_{18}$H$_{18}$N$_6$ complex. The quantum yields for CO loss for these two complexes are 0.76 and 10^{-2}, respectively. According to the ligand field interpretation, the ligand field excited state is photoactive leading to axial ligand labilization while the charge-transfer excited state is at least 2 orders of magnitude less photoreactive. On the basis of the similarities of the quantum yields of the
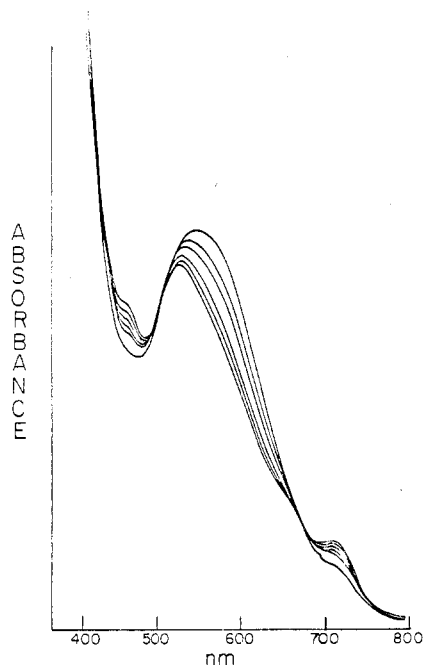
Michael J. Incorvia and Jeffrey I. Zink

Figure 1. Electronic absorption spectral changes during photolysis of [Fe($C_{18}H_{18}N_6$)Br(CO)]PF$_6$ in acetone illustrating the decrease of the 550-nm band, the increase of the 710-nm band, and isosbestic points at 513 and 650 nm.

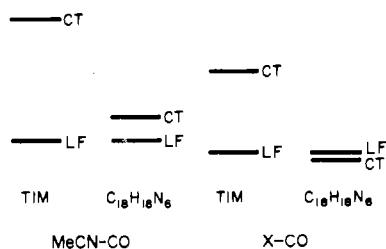**Figure 2.** State diagram proposed to explain the photoreactivity trends of TIM and $C_{18}H_{18}N_6$ complexes of iron(II).

CH$_3$CN–CO complexes, there do not appear to be more efficient radiationless deactivation pathways for $C_{18}H_{18}N_6$. Similar interpretations for d^6 complexes with closely spaced ligand field and charge-transfer excited states have been reported for ruthenium(II)[12] and tungsten(0)[13] complexes.

The energies of the ligand field states are difficult to determine with confidence. The difficulties arise partly because the presence of the intense MTLCT band obscures the much weaker ligand field bands and partly because the carbonyl complexes studied here are thermally labile. Thermal solvation products which have lost CO have MTLCT bands in the region in which ligand field bands are expected. Although the absorption spectra of the complexes were studied at high concentrations and with long path length cells, weak absorptions cannot be assigned to ligand field transitions. As a typical illustration of these problems, [Fe(TIM)CH$_3$CN-(CO)]$^{2+}$ has a weak absorption at 550 nm. This band persists in a scrupulously purified sample in noncoordinating solvents such as nitromethane.[14] However, the precursor to this compound, the bis(acetonitrile) complex, has its charge-transfer band at 550 nm. Although the ligand field transition may be assigned to the 550-nm absorption, the possibility of impurity absorptions cannot be ruled out.

In order to determine the plausibility of the existence of ligand field bands at the energies suggested by Figure 2, the energies were approximated semiquantitatively using iron(II) complexes of the saturated tetradentate ligand *meso*-5,5,7,-12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane

([14]ane-N$_4$) with CH$_3$CN, Cl$^-$, and CN$^-$ as axial ligands.[15] No charge-transfer excited state occurs in the visible region of the spectrum because the ligand is saturated. Because Dq for macrocyclic ligands increases with the degree of conjugation,[11] the ligand field state energies approximated using [14]ane-N$_4$ are probably lower limits. Another required assumption is that CN$^-$ approximates CO in the spectrochemical series. This assumption is reasonable because no tetragonal splitting of the octrahedral T$_{1g}$ band of Fe(CN)$_6^{4-}$ occurs in Fe(CN)$_5$CO^{3-}.[16] Using these assumptions, the ligand field band energy is calculated to be between approximately 17×10^3 and 19×10^3 cm^{-1} for the TIM and $C_{18}H_{18}N_6$ complexes. On the basis of these approximations, the existence of ligand field bands in the energy region suggested by Figure 2 is plausible.

The interpretation of the photoactivity in terms of ligand field excited states is further supported by an analysis of the ligands which are photolabilized. The lowest energy ligand field transition (d$_{xz}$ or d$_{yz}$ → d$_{z^2}$ in the one-electron picture)[17] removes an electron from the degenerate d$_{xz}$, d$_{yz}$ pair and populates the d$_{z^2}$ orbital. The depopulated orbital is π bonding when the ligand is a π acceptor such as CO and is π antibonding when the ligand is a π donor such as Cl$^-$. Thus, in the halo–CO complexes, depopulation of the d$_{xz}$ or d$_{yz}$ orbitals should labilize CO and strengthen the metal–halide bond. This predicted reactivity pattern is the only one which is observed. In the case of the acetonitrile–CO complexes where both ligands are π acceptors but CO is the stronger of the two, CO should be labilized to a greater extent than acetonitrile. In acetonitrile solution, CO is labilized. However, in acetone solution, acetonitrile is labilized to a much greater extent. Because the labilization is not as selective between acetonitrile and CO as it is between a halide and CO, the coordinating properties of the entering ligand become important in the photoreactions of the former complexes. The quantum yields for both systems are high: 0.6 in acetonitrile and 0.8 in acetone.[18] Because of the solvent dependence, the comparisons of photoreactions between analogous TIM and $C_{18}H_{18}N_6$ complexes were always carried out in the same solvents.

The photoreaction quantum yields of the analogous TIM and $C_{18}H_{18}N_6$ complexes are consistent only with the interpretation based on ligand field photoreactivity. The previously reported comparisons of photoreaction quantum yields within a series of TIM complexes with varying axial ligands are also consistent with charge-transfer excited-state photoreactivity.[1] The ligand field interpretation was favored because the observed labilization of acetonitrile was easily understood in terms of d orbital antibonding (vide supra) but not readily understood in terms of a formally oxidized iron(III) excited-state intermediate.

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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)$_2$]·1.5H$_2$O 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·1.5H$_2$O complex,[11] the K[*trans*-Co(MIDA)$_2$]·0.5H$_2$O complex,[12] where MIDA^{2-} denotes the methyliminodiacetate ligand, and the Na[Co(EDTA)]·3H$_2$O 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 cheiate-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