Photochemical Reduction of Bis-(2,9-dimethyl-1,10-phenanthroline)copper(II)

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Summary Bis-(2,9-dimethyl-1,10-phenanthroline)copper-(II) undergoes photoreduction in acidic aqueous media; an apparent correlation of photochemical efficiency with the spectral location of a charge-transfer excited state is reported.

WHILE photochemical oxidation–reduction processes in co-ordination compounds have received considerable attention,[1] few investigations concerning complexes of metals other than Co^{3+} have appeared. We report photochemical reduction of bis-(2,9-dimethyl-1,10-phenanthroline)copper-(II), $Cu(dmp)_2OH_2^{2+}$.

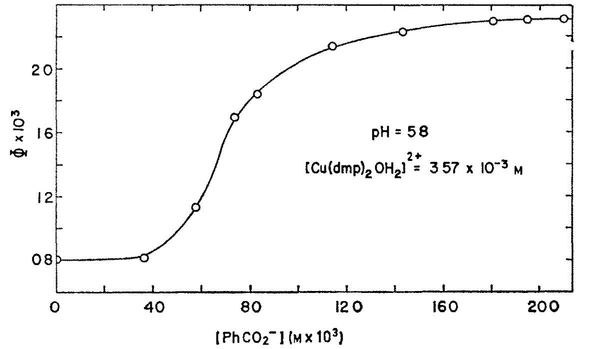

FIGURE 1. *Variation of quantum yield for* $Cu(dmp)_2^+$ *formation with benzoate concentration.*

Dissolution of salts $[Cu(dmp)_2X]X$ ($X = Cl^-$ or Br^-) in aqueous media (pH = 5·8, adjusted with concentrated $HClO_4$) is followed by rapid thermal release of the co-ordinated anion, forming an aquo-complex, presumably $Cu(dmp)_2OH_2^{2+}$.[2] Photolysis of $Cu(dmp)_2OH_2^{2+}$ leads to formation of the well-known red complex $Cu(dmp)_2^+$, together with a decrease in pH. Alteration of the anion has no significant effect upon observed quantum yields of photoreduction.

It is postulated that this photoreduction proceeds *via* simple homolytic cleavage of the co-ordinated water molecule:

$$Cu(dmp)_2OH_2^{2+} \xrightarrow[h\nu]{} Cu(dmp)_2^+ + H^+ + OH \quad (1)$$

In the presence of benzoate, a well-known scavenger of hydroxyl radicals, photolysis of $Cu(dmp)_2OH_2^{2+}$ leads to formation of salicylate, as indicated by formation of its characteristic red complex[3] with Fe^{3+}. As seen in Figure 1, the quantum yield for formation of $Cu(dmp)_2^+$ is enhanced in the presence of small quantities of benzoate, eventually reaching a limiting value at higher scavenger concentrations.

The quantum yield for appearance of $Cu(dmp)_2^+$ has been determined as a function of incident frequency, using incident power values of $(1{\cdot}05 \pm 0{\cdot}10) \times 10^{14}$ photons sec^{-1}. The results are indicated in Figure 2, along with the electronic absorption spectra of $Cu(dmp)_2OH_2^{2+}$ and $Cu(dmp)_2^+$. A very sharp decrease of Φ is noted at approximately 27,700 cm^{-1}. In an assignment of the electronic absorption spectrum of bis-(2,9-dimethylphenanthroline) chelates of Cu^{2+}, Williams[4] postulated the existence of a $\pi \rightarrow d$ (ligand → metal) charge-transfer band at 28,600 cm^{-1}. Hence, there is an extremely close correlation between photoreduction activity of $Cu(dmp)_2OH_2^{2+}$ and the assigned position of the lowest spin-allowed charge-transfer excited

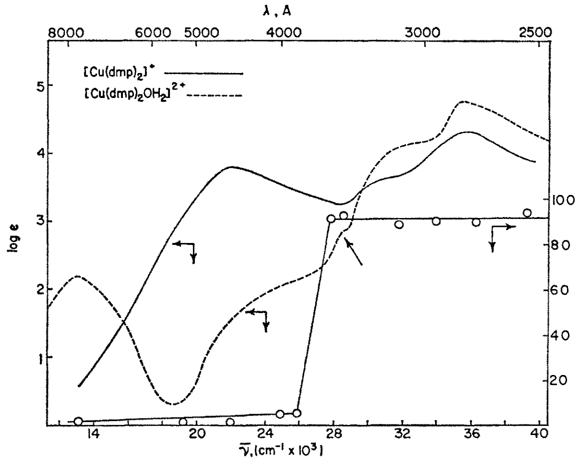

FIGURE 2. *Variation of* Φ *for* $Cu(dmp)_2^+$ *formation with incident frequency (right ordinate); electronic spectra of* $Cu(dmp)_2OH_2^{2+}$ *and* $Cu(dmp)_2^+$ *(left ordinate). Charge-transfer band in* $Cu(dmp)_2OH_2^{2+}$ *indicated by arrow.*

state. That Φ is essentially constant at all frequencies greater than 27,700 cm^{-1} may indicate that the charge-transfer state is indeed reactive, with internal conversion thereto from higher (π,π^*) intraligand states being highly efficient. It is also noteworthy that excitation in the $d \rightarrow d$ absorption region (12,000—17,000 cm^{-1}) does not effect detectable photoreduction of $Cu(dmp)_2OH_2^{2+}$. This result strongly implies that internal conversion from the lowest spin-allowed charge-transfer state into lower-lying doublet ligand-field excited states is not rapid with respect to the photoreduction process.

$Cu(dmp)_2^+$ is resistant to photochemical oxidation under all experimental conditions. The Cu–(dmp) system is thus analogous to $Fe(phen)_3^{3+}$–$Fe(phen)_3^{2+}$, wherein the former undergoes photochemical reduction[5] but the latter is resistant to photo-oxidation.

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