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The Photoinduced Oxidation of Axial and Macrocyclic Ligands in a Copper(II) Complex

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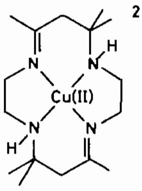
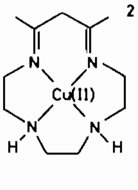
We have recently reported that ultraviolet irradiations of Cu([14]dieneN$_4$)$^{2+}$ (I) and Cu([13]AtH)$^{2+}$ (II) induce ligand hydrolysis and redox processes [1, 2].** These photoreactions have been attributed to photoactive charge-transfer metal to ligand states, CTTL, which involve isolated imino functions of the macrocycles [1]. Moreover, the charge-transfer ligand to metal states, CTTM, seem to be photoinert in these complexes.

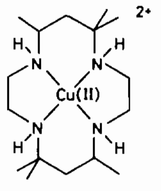
Macrocyclic ligands with coordinated amino groups, namely as in complexes of tet-a and tet-b (III)†, cannot produce CTTL states at accessible energies. Therefore, these compounds can be conveniently used for an investigation of the CTTM reactivity. Our results show, for the first time, that two distinct photoredox processes are involved in the photochemistries of the tet-a and tet-b complexes [3].



(I)



(II)



(III)

Sample solutions were deaerated by vacuum or with streams of argon. Flash and continuous wave photolyses were carried out with apparatusses described previously [1, 2]. Pulses of polychromatic light (λ ⩾ 220 nm) with a lifetime of 30 μsec were obtained for stored electrical energies between 60 and 250 Joule/pulse.

The 254 nm irradiation of Cu(tet-a)$^{2+}$ in aqueous deaerated solutions induces the oxidation of the macrocycle, eqn. 1. Two reaction intermediates, half lifetimes $t_{1/2} = 2.0 \times 10^{-4}$ sec and $t_{1/2} = 8.5 \times 10^{-2}$ sec, were observed in flash photolysis, Fig. 1a. These metastable species have been assigned as complexes with open cycles. The shortest lived intermediate, SL in eqn. 1, exhibited the chemical reactivity expected for an open cycle Cu(I)–ligand radical species. Product yields, determined in scavenging studies with methanol or isopropanol, support the assignments indicated above, Fig. 1b. Moreover, these yields show that a primary Cu(I)–ligand radical, PR in eqn. 1, is formed with an efficiency $\phi \sim 8 \times 10^{-3}$ for 254 nm photolyses.

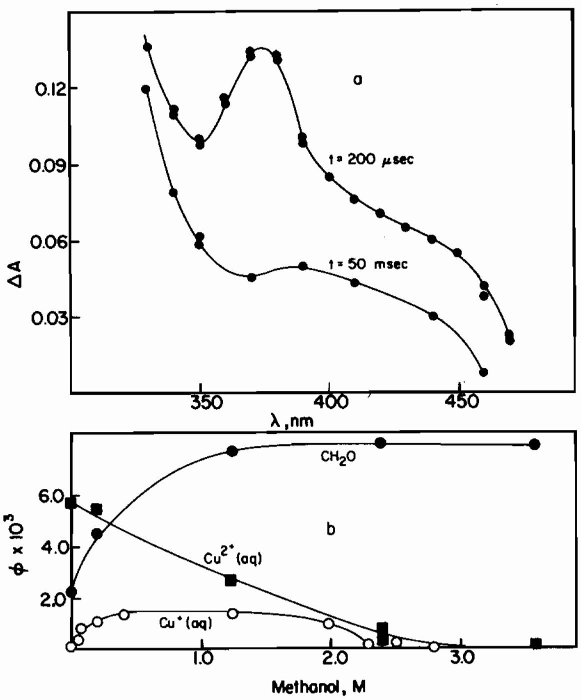


Fig. 1. (a) Transient spectrum observed in flash photolysis of Cu(tet-a)$^{2+}$ in aqueous deaerated solutions. Curves determined at 200 μsec and 50 msec reaction times. Irradiations with 250 Joule/pulse. (b) Typical distribution of product yields obtained in photolyses of Cu(tet-a)$^{2+}$ in aqueous deaerated solutions, where, methanol was used as a scavenger of the reaction intermediates.

An additional photochemical process was detected when oxidizable ligands were coordinated in axial positions, namely Cl$^-$ in Cu(tet-a)Cl$^+$. Indeed, a yield $\phi \sim 6 \times 10^{-3}$ was determined for the photooxidation of coordinated chloride. (Solutions made with 10^{-2} *M* NaCl in methanol). A similar behavior was exhibited by Cu(tet-b)X$_2$ (X: Br$^-$, H_2O, CH_3OH).

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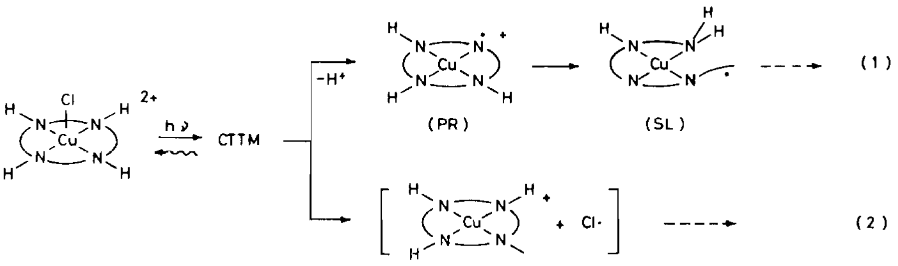
**Abbreviations: [14]dieneN$_4$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11,-diene; [13]-AtH = 11,13-dimethyl-1,4.7.10-tetraazacyclotrideca-10,12-diene; tet-a and tet-b = 5,7.7.12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

†The primary PR species is believed to have a very short life for detection in flash photolysis.



The photoreactivity of the tet-a and tet-b complexes can be originated in one or two different-charge transfer ligand to metal states. However, changes of the absorption spectra, induced by coordination of axial ligands, indicate the presence of two distinct charge-transfer states, namely $\mathrm{CTTM}_{(\mathrm{N}\rightarrow\mathrm{Cu})}$ and $\mathrm{CTTM}_{(\mathrm{Cl}^-\rightarrow\mathrm{Cu})}$.

Acknowledgments

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References

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3 For other studies on the photochemistry of copper(II) complexes see: S. Sundarajan and E. L. Wehry, *J. Phys. Chem., 76,* 1528 (1972); G. Ferraudi, *Inorg. Chem., 17,* 2506 (1978); H. D. Gafney and R. L. Linvedt, *J. Am. Chem. Soc., 92,* 1623 (1971); J. I. Morimoto and B. A. DeGraaf, *J. Phys. Chem., 79,* 326 (1975); *ibid., 76,* 1387 (1972); J. Sýkora, I. Giannini and F. D. Camassei, *J. Chem. Comm.,* 207 (1978); and references therein.