PHOTOCHEMISTRY OF COPPER(II) MACROCYCLIC COMPLEXES: THE CHARGE TRANSFER PHOTOCHEMISTRY OF 2,12-DIMETHYL-3,7,11,17-TETRAAZABICYCLO[11,3,1]HEPTADECA-1(17),2,11,13,15-PENTAENECOPPER(II)

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Summary

The photochemical properties of $Cu(CR)^{2+}$ ($CR \equiv$ 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11,3,1]heptadeca-1(17),2,11,13,15-pentaene) were investigated by continuous and flash photolysis. UV photolyses induce two reactions: the hydrolysis of the macrocyclic ligand and redox reactions that reduce the metal center to copper(I). These photoreactions are regarded as being caused by the population of ligand-to-metal and metal-to-ligand charge transfer states. A proposed mechanism is compared with mechanisms for the photochemical transformations of related macrocyclic complexes.

1. Introduction

The photochemical properties of complexes with simple macrocycles have recently been investigated [1 - 12]. UV photolysis of the copper(II) macrocyclic complexes with coordinated imino groups, such as $Cu(Me_2[13]diene-N_4)^{2+}$ (I) [3] and $Cu(Me_6[14]diene-N_4)^{2+}$ (II) [2] (Fig. 1), induce either hydrolysis of the macrocyclic ligand or redox reactions if appropriate hydrogen donors are used for intercepting reactive intermediates. These reactions have been associated with chemical transformations originating in metal-to-ligand charge transfer states (charge transfer to ligand (CTTL)) capable of forming reactive intermediates which behave as bases or oxidants when facing appropriate reactants [2, 3]:
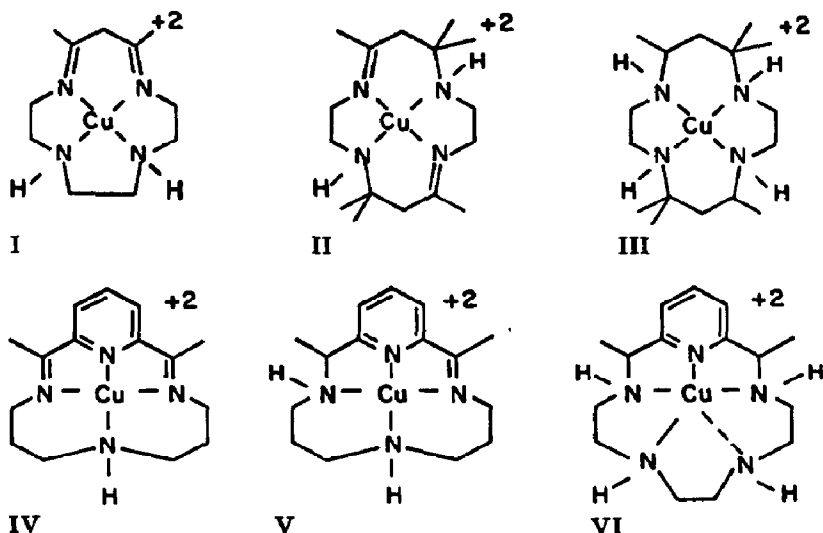

$$(1)$$

$$(2)$$
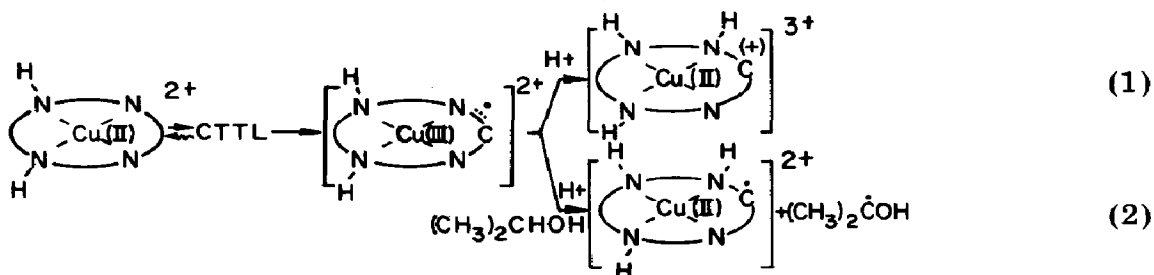
Fig. 1. Structures of the copper(II) macrocyclic complexes.

In addition, copper(II) complexes with saturated tetraaza macrocylic ligands such as $Cu(Me_6[14]ane-N_4)^{2+}$ (III) [4] undergo complex redox transformations in UV irradiations. Ligand-to-metal charge transfer states (charge transfer to metal (CTTM)) which involve the electronic density of the macrocycle (CTTM$_2$) or the axial ligand X (CTTM$_1$) are believed to participate in the photochemical transformation of these complexes:

$$(3)$$

$$(4)$$
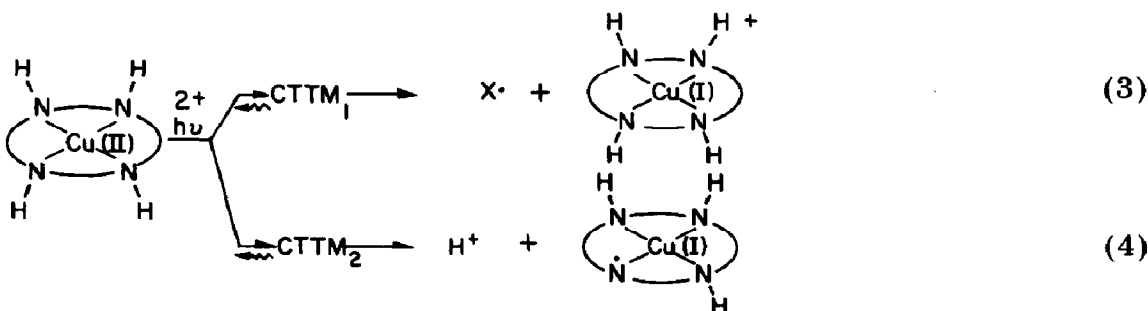
$Cu(CR)^{2+}$ (IV) (CR $\equiv$ 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11,3,1]-heptadeca-1(17),2,11,13,15-pentaene) has the type of structure that places electronic transitions with metal-to-ligand and ligand-to-metal charge transfer character within the UV region. However, it has been noticed before that the low reactivity of $Cu(CR)^{2+}$ in UV irradiations departs from the photoreactivity exhibited by other macrocyclic complexes [1]. The nature of the photochemical processes and the reasons for the low photoreactivity of $Cu(CR)^{2+}$ have been investigated in this work.

2. Experimental details

2.1. Materials

The copper(II) macrocycles $[Cu(CR)](ClO_4)_2 \cdot H_2O$ (**IV**), $[Cu(CRH)](ClO_4)_2$ (**V**) and $[Cu([15]pyane-N_5)](ClO_4)_2$ (**VI**) were synthesized according to procedures described elsewhere [13 - 16]. These compounds were recrystallized several times by adding solid $NaClO_4$ or concentrated $HClO_4$ to their aqueous acidic solutions. The UV–visible spectra of the purified compounds agreed well with published data [13 - 16].

Other chemicals were analytical grade and were used without further purification.

2.2. Analytical procedures

The total concentration of copper(I), namely copper(I) macrocyclic complexes and Cu^+(aq), was determined by means of the reaction with Fe^{3+}(aq) [2]. The equivalent concentration of iron(II) formed in the reduction of iron(III) by copper(I) species was determined with 1,10-phenanthroline. Concentrations of Cu^+(aq) were measured using 2,9-dimethyl-1,10-phenanthroline [17]. The 2,9-dimethyl-1,10-phenanthroline–ascorbic acid method [17] or ion specific electrodes were used for the quantitative analysis of Cu^{2+}(aq). Diacetylpyridine was analyzed spectrophotometrically after liberating the solutions of copper cations by ion exchange chromatography.

The transfer of deaerated solutions, namely both the irradiated solutions and solutions of the reactants, was carried out using gas-tight syringes.

2.3. Photochemical procedures

Continuous photolysis at 254 nm was carried out using General Electric G4T4 low pressure mercury lamps. A Rayonet minireactor fitted with a 300 nm Rayonet discharge lamp was used for the 300 nm photolysis. The light intensity for 254 or 300 nm photolysis was determined using potassium tris(oxalato)ferrate(III) [18]. Concentrations of the photolytes were adjusted in order to absorb 99.99% or more of the incident light. These solutions were deaerated using argon streams for at least 20 min before the irradiation, and the homogeneity was maintained by stirring the liquids with magnetic bars during the irradiation.

Two FP-8-100C flash lamps (Xenon Corporation) were fired in series at energies between 250 and 40 J pulse^{-1} in flash photolysis. A lifetime of 30 μs was measured for the light pulse under these conditions; hence the data points for both the kinetics and the spectra were regarded as significant for times equal to or longer than 50 μs. The raw data, which were stored in a binary base in a waveform recorder, were processed in a Digital PDP-8L computer for the derivation of rate constants or spectral information.

2.4. Electrochemical procedures

The reduction of the complexes was carried out using a potentiostat built in our laboratory. A two-electrode electrochemical cell was provided

with an appropriate optical cell as a detachable side-arm in order to determine the spectrum of the electrolyzed solutions under anaerobic conditions.
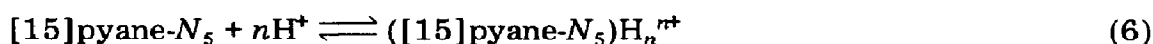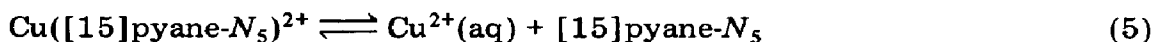
2.5. Pulse radiolysis

The apparatus and procedures used in the irradiation of the complexes have been described elsewhere [19]. Reductions with e_{aq}^- were carried out in solutions of the complexes which were deaerated using nitrogen streams. The reaction media had pHs of 4 or above and contained various concentrations of 1,1-dimethylethanol, *e.g.* concentrations in the range 2.0 M $>$ $[(CH_3)_3COH] > 0.1$ M were used to intercept the HO· radical. The reductions using 2-hydroxyisopropyl radicals were investigated at a pH of about 4 in N_2O-saturated solutions containing various concentrations of 2-propanol $(0.1$ M $< [2\text{-propanol}] < 1.0$ M).

3. Results

3.1. Thermal stability of the macrocyclic complexes

The 14-member ring complexes $Cu(CR)^{2+}$ and $Cu(CRH)^{2+}$ exhibited considerable thermal stability in acid media. Indeed no spectral changes were observed in the spectra of deaerated acidic solutions $(10^{-4}$ M $< [HClO_4]$ < 1.0 M) when they were maintained in the dark over extended periods, *e.g.* $t < 8$ h. This behavior is in agreement with previous reports on the slow acid hydrolysis experienced by 14-member ring macrocyclic complexes [3, 20, 21]. The 15-member ring macrocycle $Cu([15]\text{pyane-}N_5)^{2+}$ dissociates to $Cu^{2+}(aq)$ and a free macrocycle at various rates:

$$Cu([15]\text{pyane-}N_5)^{2+} \rightleftharpoons Cu^{2+}(aq) + [15]\text{pyane-}N_5 \tag{5}$$

$$[15]\text{pyane-}N_5 + nH^+ \rightleftharpoons ([15]\text{pyane-}N_5)H_n^{n+} \tag{6}$$

The rate (Fig. 2) and extent of the dissociation depend on the concentration of the acid. Therefore the photochemical studies of $Cu([15]\text{pyane-}N_5)^{2+}$ were limited to solutions with pH greater than 2 in order to avoid those photochemical complications which can originate from photolysis and/or secondary reactions of the dissociation products.

3.2. Continuous photolysis

Steady state irradiations $(\lambda_{excit} = 254$ nm) of $Cu(CR)^{2+}$ in deaerated acidic solutions produced $Cu^{2+}(aq)$ and diacetylpyridine in a 1:1 stoichiometry. Copper(I) products, namely $Cu^+(aq)$ or $Cu(CR)^+$, were not produced in significant concentrations when irradiations were limited to short periods, *e.g.* $t < 15$ min with $I_0 \approx 10^{-4}$ einstein l^{-1} min^{-1}. However, these products were generated in large concentrations when $Cu(CR)^{2+}$ was irradiated in solutions where 2-propanol was present in various concentrations (Fig. 3 and Table 1). The complex dependence of the product concentration on the irradiation time and the $Cu(CR)^{2+}$ concentration suggests that the secondary

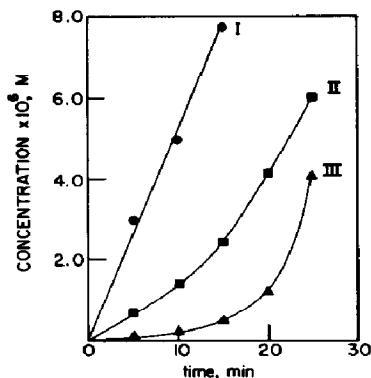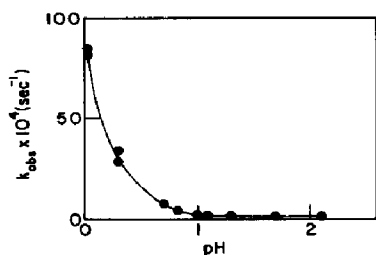Fig. 2. Acid hydrolysis of $Cu([15]pyane-N_5)^{2+}$: dependence of the rate constant for the hydrolytic demetallation on pH. The values of the rate constant were obtained by spectrophotometry and from measurements of the $Cu^{2+}(aq)$ concentration.

Fig. 3. Continuous photolysis of $Cu(CR)^{2+}$ in deaerated 0.25 M 2-propanol: dependence of the concentration of the photolysis products on the irradiation time (curve I, total copper(I); curve II, $Cu^{2+}(aq)$; curve III, $Cu^{+}(aq)$). The excitations were performed at 254 nm with $I_0 = 2.7 \times 10^{-4}$ einstein l^{-1} min^{-1}.

TABLE 1

Quantum yields for photoreactions of copper(II) macrocyclic complexes

λ_{excit} (nm)	$I_0 \times 10^4$ (einstein l^{-1} min^{-1})	$\phi \times 10^4$ [a] for the following species			Medium conditions[b]	
		$Cu(I)_{total}$	$Cu^{+}(aq)$	$Cu^{2+}(aq)$	[HClO$_4$] (M)	[2-propanol] (M)
Cu(CR)$^{2+}$						
254	2.7	17	2.5	4.2	10^{-1}	2.0
		27	2.5	3.6	10^{-2}	2.0
		10	1.9	3.0	10^{-3}	2.0
		2.0	—c	—c	10^{-4}	2.0
				1.5	0.0	0.0
				2.5	10^{-4}	0.0
				2.9	10^{-3}	0.0
				3.6[d]	10^{-2}	0.0
				4.2	10^{-1}	0.0
				5.3	1.0	0.0
300	3.1	2.0			10^{-2}	2.0
Cu(CRH)$^{2+}$						
254	2.7			0.45	10^{-2}	
		4.0	—c	—c	10^{-2}	6.5
Cu([15]pyane-N$_5$)$^{2+}$						
254	2.7	1.5	0.76	3.3	4.0×10^{-3}	0.0
		6.5	—c		4.0×10^{-3}	0.25
		8.7	—c		4.0×10^{-3}	0.75
		10.0	—c		4.0×10^{-3}	2.0
		10.1	—c		4.0×10^{-3}	6.5
300	3.8	5.1			4.0×10^{-3}	2.0

[a] Errors for quantum yields are 10% or less.
[b] Solutions deaerated using argon streams.
[c] $\phi < 10^{-5}$.
[d] A quantum yield ϕ of about 3.5×10^{-4} was obtained for 2,6-diacetylpyridine.

photolysis of Cu(CR)$^+$ has a considerable influence on the nature of the products (Fig. 3). Such a secondary photolysis and the large reactivity of the copper(I) products toward their reoxidation by oxygen and disproportionation to copper(0) and copper(II) species made the determination of accurate quantum yields an extremely difficult task. The severity of these problems in the determination of the quantum yields was reduced by using extreme precautions in the deaeration of the solutions (see Section 2) and by limiting to less than 1% the photochemical conversions of the copper(II) complexes to products.

Quantum yields were determined under various medium conditions (Table 1). The yields of Cu(CR)$^+$ and Cu$^+$(aq) increase with 2-propanol concentration (Fig. 4) in a manner that can be related to the reactivity of some of the precursors of the products, e.g. a copper(I) ligand radical species. The participation of the reducing radicals, e.g. (CH$_3$)$_2$ĊOH, in the 254 nm photolysis of Cu(CR)$^{2+}$ solutions containing 2-propanol was detected by using Cu^{2+}(aq) ([Cu^{2+}(aq)] $\leqslant 10^{-3}$ M) as a scavenger. Such scavenging of the 2-hydroxyisopropyl radicals produced a twofold increase in the copper(I) yield with respect to the yield determined in the absence of Cu^{2+}(aq). Moreover, the product yields, e.g. the yields of Cu(CR)$^+$ and Cu^{2+}(aq), exhibited a pronounced dependence on acid concentration (Table 1).

Photolyses (λ_{excit} = 254 nm) of Cu(CR)$^{2+}$ in deaerated solutions with pH 6 failed to produce Cu^{2+}(aq), Cu$^+$(aq) or Cu(CR)$^+$. However, spectral changes which indicate the formation of a new copper(II) macrocycle were observed. The sensitivity of this product to acid hydrolysis suggests that it has an open macrocycle [2, 3].

The 254 nm photochemistry of the Cu(CRH)$^{2+}$ and Cu([15]pyane-N_5)$^{2+}$ is qualitatively similar to that described above for Cu(CR)$^{2+}$. Indeed, UV photolyses of these complexes produced Cu$^+$(aq) and CuL$^+$ (L $\equiv$ CRH or [15]pyane-N_5) in solutions where 2-propanol is used to scavenge the intermediates (Table 1).

3.3. Time-resolved studies

Flash photolysis of Cu(CR)$^{2+}$ in deaerated solutions (220 nm $\leqslant \lambda_{excit} \leqslant$ 320 nm) failed to produce spectral transformations. However, such transformations were detected in flash irradiations of Cu(CR)$^{2+}$ in deaerated acidic solutions containing various concentrations of 2-propanol, namely [HClO$_4$] $\leqslant 10^{-2}$ M and [2-propanol] $\leqslant$ 3.0 M. The spectrum of the species generated in flash photolysis was attributed to Cu(CR)$^+$ (Fig. 5) since it compares very well with the spectrum generated when Cu(CR)$^{2+}$ is reduced in electrochemical experiments or in pulse radiolysis by either e$_{aq}^-$ or (CH$_3$)$_2$ĊOH. The Cu(CR)$^+$ produced by both flash photolysis and electrolysis exhibited considerable stability in solutions with low acid concentrations, e.g. [HClO$_4$] $\leqslant 10^{-2}$ M. (This behavior is in good agreement with previous reports of the stability of Cu(CR)$^+$ [14].) Indeed the rate of disappearance of Cu(CR)$^+$ shows a first-order dependence on the concentration of Cu(CR)$^+$
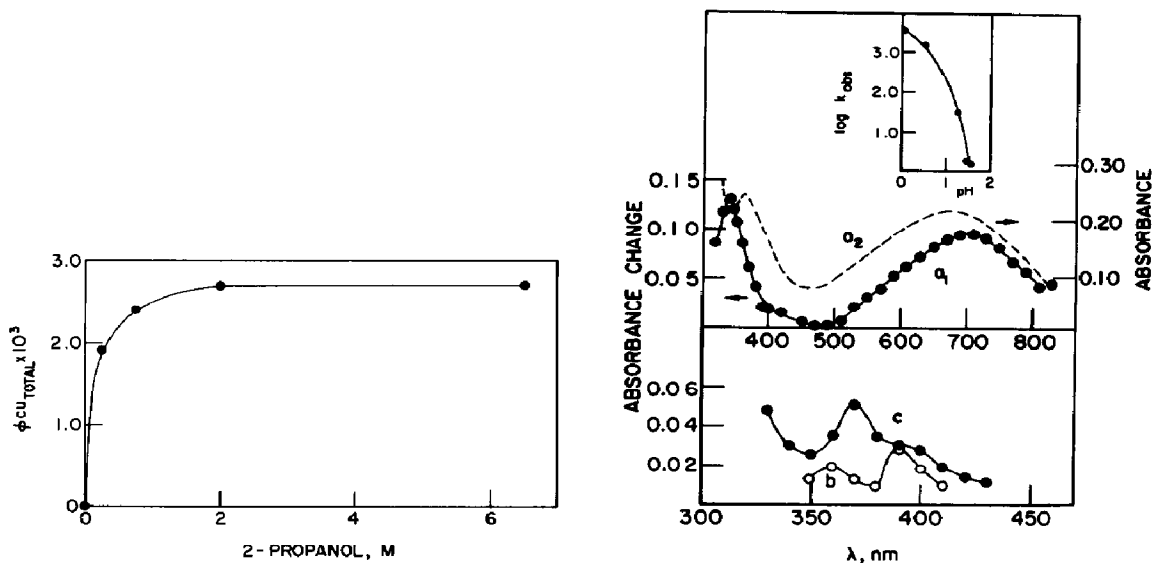
Fig. 4. Interception of reactive intermediates generated in the UV photolysis of $Cu(CR)^{2+}$: dependence of the quantum yield for the total copper(I) (i.e. copper(I) macrocycle and $Cu^{+}(aq)$) on the 2-propanol concentration. The irradiations of $Cu(CR)^{2+}$ were performed in deaerated acidic solutions ([$HClO_4$] = 10^{-2} M) at 254 nm with $I_0 = 10^{-4}$ einstein l^{-1} min^{-1}.

Fig. 5. Copper(I) species generated in UV photolyses of copper(II) macrocycles: spectra of $Cu(CR)^{+}$ (curve a_1), $Cu(CRH)^{+}$ (curve b) and $Cu([15]pyane-N_5)^{+}$ (curve c) generated in flash photolyses of the corresponding copper(II) macrocyles in deaerated 2.0 M 2-propanol and of $Cu(CR)^{2+}$ (curve a_2) generated by electrolysis of the corresponding copper(II) macrocycle in deaerated methanol. The inset shows the dependence of the rate constant for the disappearance of $Cu(CR)^{+}$ on the acid concentration.

and a more complex dependence on acid concentration (Fig. 5). This behavior can be related to the demetallation of $Cu(CR)^{+}$.

Flash photolysis of $Cu([15]pyane-N_5)^{2+}$ or $Cu(CRH)^{2+}$ in deaerated acidic solutions containing various concentrations of 2-propanol ([2-propanol] $\geqslant$ 0.1 M) produced one-electron-reduced species, namely $Cu([15]-pyane-N_5)^{+}$ or $Cu(CRH)^{+}$ (Fig. 5). The photochemical formation of the $Cu([15]pyane-N_5)^{+}$ takes place in two steps; one is too fast for the time resolution of our apparatus and the other has a half-life $t_{1/2}$ of about 3 ms. The rate of the slow step exhibited a first-order dependence on the concentration of $Cu([15]pyane-N_5)^{2+}$ and on the flash-generated concentration of $Cu([15]pyane-N_5)^{+}$. Such a step has been associated with the reaction of the 2-hydroxyisopropyl radical $(CH_3)_2\dot{C}OH$ with excess $Cu([15]pyane-N_5)^{2+}$.
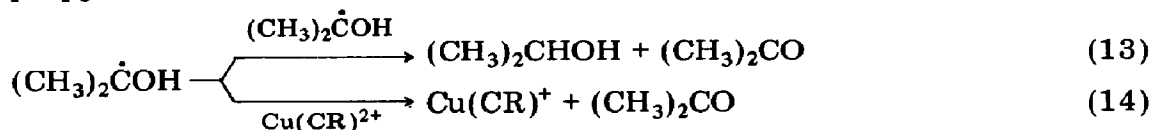
4. Discussion

Our results on the photochemical formation of $Cu(CR)^{+}$ show that this product is formed in processes which are close to the primary process.

Moreover, such a formation of the products suggests that the photochemistry of $Cu(CR)^{2+}$ must be associated in part with a population of ligand-to-metal charge transfer (CTTM) states. Such states probably involve the π electronic density of the pyridine group since amino-to-copper(II) charge transfer states must have higher energies than those expected for π-pyridine-to-copper(II) CTTM states [1]. This proposition of a photochemistry originated in CTTM states cannot describe by itself the distinctive dependence of the Cu^{2+}(aq) yield on acid concentration. The dependence on acid concentration is in good agreement with a photoinduced hydrolysis of the macrocyclic ligand in the form described for the UV photolysis of $Cu(Me_6[14]diene-N_4)^{2+}$ [2], and, as the photoinduced hydrolysis of $Cu(Me_6[14]diene-N_4)^{2+}$ was assumed to be caused by the population of CTTL states, the photochemistry of $Cu(CR)^{2+}$ can be regarded as resulting from the population of similar states. Henceforth, we suggest that the observed $Cu(CR)^{2+}$ photochemistry must be determined by the population of two different charge transfer states, namely CTTM and CTTL. Such a proposition is in agreement with the structure of the macrocyclic ligand which combines, in a qualitative sense, the necessary structural elements for undergoing the photochemical transformation of the $Me_6[14]ane-N_4$ and $Me_6[14]diene-N_4$ complexes. In this regard, the following mechanism accounts for our experimental observations:



(7)

(8)

(9)

(10)

(11)

(12)
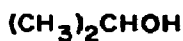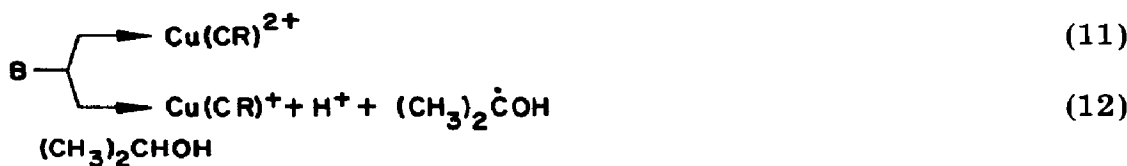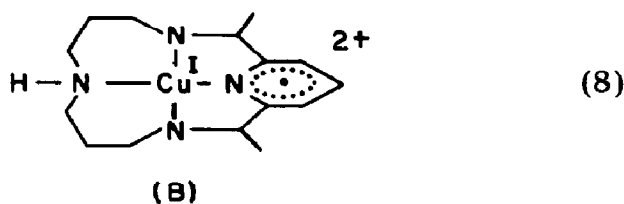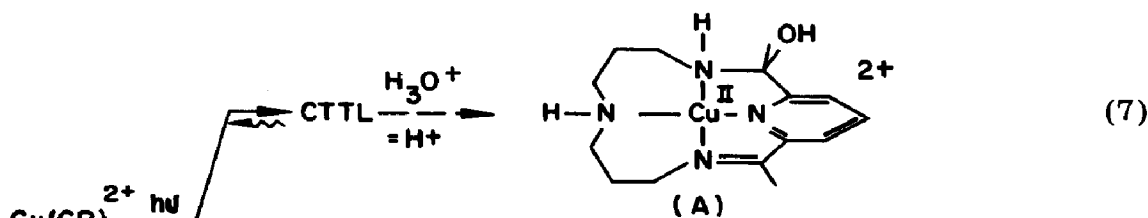
The carbinolamine product A could be the product observed in the photolyses at pH 6. However, the thermal instability of the carbinolamines toward their conversion to imino and ketonamine products suggests that the detected product is more likely to be a ketonamine derivative. A similar compound has previously been isolated in the photochemistry of $Cu(Me_6-[14]diene-N_4)^{2+}$ [2].

The formation of $Cu(CR)^+$ is attributed to the scavenging of a short-lived copper(I) ligand radical B by 2-propanol (eqn. (12)). Some of the $Cu(CR)^+$ may also be produced when $Cu(CR)^{2+}$ is reduced by 2-hydroxyiso-propyl radicals:

$$(CH_3)_2\dot{C}OH \left\langle \begin{array}{l} \xrightarrow{(CH_3)_2\dot{C}OH} (CH_3)_2CHOH + (CH_3)_2CO \qquad (13) \\ \xrightarrow{Cu(CR)^{2+}} Cu(CR)^+ + (CH_3)_2CO \qquad (14) \end{array} \right.$$

The reduction of $Cu(CR)^{2+}$ by $(CH_3)_2\dot{C}OH$ (eqn. (14)) does not make large contributions to the production of $Cu(CR)^+$ in flash photolysis since large radical concentrations favor the disproportionation reaction (13). (The photochemistries of $Cu(CRH)^{2+}$, $Cu([15]pyane-N_5)^{2+}$ and $Cu(CR)^{2+}$ are similar in that the major contribution to the product formation appears to come from CTTM states. Moreover, the contributions from redox reactions like reaction (13) are more important in the formation of products from $Cu(CRH)^{2+}$ and $Cu([15]pyane-N_5)^{2+}$.) Contributions from reaction (14) to the product formation are expected to be important in continuous photolysis. Moreover, the increase in the copper(I) yield when $Cu^{2+}(aq)$ is used as a radical scavenger can be attributed to competition between the reduction of $Cu^{2+}(aq)$ by $(CH_3)_2\dot{C}OH$

$$(CH_3)_2\dot{C}OH + Cu^{2+}(aq) \longrightarrow Cu^+(aq) + (CH_3)_2CO \qquad (15)$$
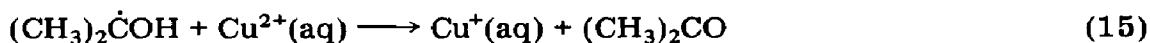
and reactions (13) and (14). (The reaction of hydroxyalkyl radicals has been investigated previously (see ref. 1 and references cited therein and ref. 22).)

It can be concluded now that the photochemistry of $Cu(CR)^{2+}$ induced in CTTL states has much less importance than in other copper(II) macrocycles, e.g. $Cu(Me_2[13]diene-N_4)^{2+}$ and $Cu(Me_6[14]diene-N_4)^{2+}$. Such a reduced significance of the photochemistry induced in CTTL states (eqn. (7)) is believed to be caused by a decrease in the reactivity of the excited state owing to an efficient delocalization of the charge through the π system of the ligand. The same argument can be extended to the CTTM states in order to explain the low yields of the other photochemical process (eqn. (8)). It should also be noticed that the charge delocalization must stabilize the intermediate B and cause a decrease in the value of its oxidation potential. Such a change could favor reaction (11) in its competition with reaction (12).

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