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PHOTOCHEMICAL PROPERTIES OF COPPER COMPLEXES

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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
teta = meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
tetb = racemic-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
transtetramine = teta or tetb
EDTA = ethylenediaminetetraacetic acid
NTA = nitrilotriacetic acid
en = ethylenediamine
dien = diethylenetriamine
trien = triethylenetetramine
CT = charge transfer
CTTM = charge transfer to metal
CTTL = charge transfer to ligand
CTTS = charge transfer to solvent
Mal = malonate
dmp = 2,9-dimethyl-1,10-phenanthroline
phen = 1,10-phenanthroline
acac = acetylacetone

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PTS = sulfophthalocyanine
dmg = dimethylglyoxime
PPh_3 = triphenylphosphine
IDA = iminodiacetic acid
NBD = norbornadiene
OAc = acetate
sym-Me_2en = *N*,*N*′-dimethylethylenediamine
asym-Me_2en = *N*,*N*-dimethylethylenediamine
sym-Et_2en = *N*,*N*′-diethylethylenediamine
asym-Et_2en = *N*,*N*-diethylethylenediamine
pn = 1,2-diaminopropane
1,3-Dap = 1,3-diaminopropane
meten = *N*-methylethylenediamine
eten = *N*-ethylethylenediamine
enta = ethylenediaminetriacetic acid
dipy = 2,2′-dipyrdine
$H_{-3}G_3a$ = triglycinamide without three ionizable hydrogens
$H_{-3}G_4$ = tetraglycine without three ionizable hydrogens
$H_{-3}G_5$ = pentaglycine without three ionizable hydrogens
$H_{-3}G_6$ = hexaglycine without three ionizable hydrogens
$H_{-3}FGGa$ = L-phenylalanylglycylglycinamide without three ionizable protons
$H_{-3}PGGa$ = L-prolylglycylcinamide without three ionizable hydrogens
H_{-4}-N-fG_4 = *N*-formylpentaglycine without four ionizable hydrogens
H_{-4}-N-fG_3a = *N*-formyltriglycinamide without four ionizable hydrogens
H_{-3}-N-fG_3 = *N*-formyltriglycine without three ionizable hydrogens

A. INTRODUCTION

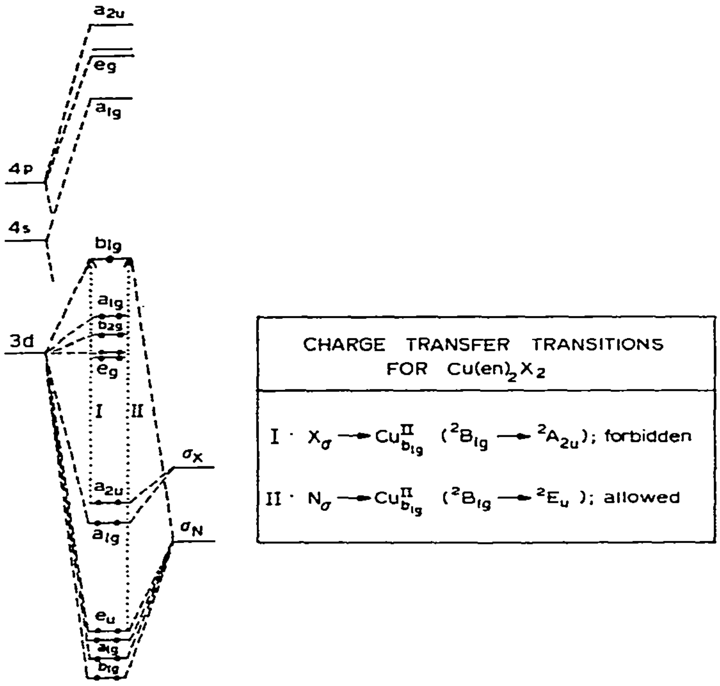
The chemistry of the copper complexes has been an active field of research for a very long time. Such studies have covered different areas and have been related, for example, with structural problems in copper compounds, catalytic activity and biochemical systems.

In this review we have tried to present some of the principal features that are associated with the redox reactivity of the copper(I), copper(II) and copper(III) complexes. The emphasis is on the photochemistry of these species. However, such closely related subjects as their charge transfer spectroscopy and their thermal redox reactivity cannot be ignored and some of the most relevant features of these subjects have also been reviewed here.

B. CHARGE TRANSFER SPECTRA

The charge transfer spectra of copper(II) complexes has been attributed to the population of charge transfer to metal, CTTM, and/or charge transfer to ligand, CTTL, states. Also, intraligand transitions, namely between ligand centered orbitals, can overlap with charge transfer transitions.

A systematic investigation of the charge transfer spectra of copper(II) complexes with substituted ethylenediamines (I), has been carried out by several groups [1—4]. Yokoi and Isobe have compared structural information obtained from charge transfer and EPR spectra of the copper(II) complexes. The EPR data have shown that σ bonding becomes more covalent with an increasing number of alkyl substituents in coordinated nitrogens. Moreover, charge transfer bands shift to longer wavelengths as the σ bonding becomes more covalent. These shifts of the charge transfer bands follow variations of the ligand electron donating tendencies. Indeed, Yokoi and Isobe found a linear correlation between the ionization potential of the ligand and the energy of the charge transfer maximum (see below). The intense ultraviolet absorptions in ethylenediamine complexes have been assigned by Kennedy and Lever as a ${}^2B_{1g} \rightarrow {}^2E_u$ charge transfer transition in a D_{4h} symmetry [2]. The splitting of the ${}^2E_u$ in D_{2h} or C_{2h} symmetries has been related to the broadening and/or the separation into two bands of the lower energy charge transfer band, see Fig. 1. Charge transfer transitions from orbitals localized in axial ligands namely ${}^2B_{1g} \rightarrow {}^2A_{1g}$ or ${}^2B_{1g} \rightarrow {}^2A_{2u}$, are symmetry forbidden in D_{4h}, see Fig. 1. Therefore, low intensities have been assigned to related transi-



CHARGE TRANSFER TRANSITIONS FOR $Cu(en)_2X_2$

I · $X_\sigma \rightarrow Cu^{II}_{b_{1g}}$ (${}^2B_{1g} \rightarrow {}^2A_{2u}$); forbidden

II · $N_\sigma \rightarrow Cu^{II}_{b_{1g}}$ (${}^2B_{1g} \rightarrow {}^2E_u$); allowed

Fig. 1. Molecular orbital diagram for $Cu(en)_2X_2$ complexes after Lever et al. Both a D_{4h} and an insignificant π copper—ligand overlap have been assumed for this scheme. Inset shows two types of charge transfer transitions from axial and equatorial ligands.

tions in complexes of *N*-substituted ethylenediamines with a D_{2h} or C_{2h} symmetry. Also, Lever and co-workers have established a linear correlation between the position of the charge transfer transitions and the metal—nitrogen stretching frequencies. This behavior has been justified in terms of the strong vibronic nature of the charge transfer transitions. Moreover, the comparison of spectroscopic and thermodynamic properties has suggested that in-plane and axial ligands compete for the copper(II) electron density. This conclusion agrees with recent reports on the photochemical properties of copper(II)-tetraaza macrocyclic complexes (see below).

In a different approach, the positions of the charge transfer bands have been correlated with the electron density donating tendencies of the ligand. Conversely the electron donating tendency of the ligand can be related to the electron affinity of the radical formed by charge transfer oxidation of the ligand. Orgel [5] and Jϕrgensen [6] have indicated that the energy of a charge transfer transition E_{CT}, is given by eqn. 1, where, I is the ionization potential of the donor and ξ is the electron affinity of the acceptor. Other contributions,

$$E_{CT} = (I - \xi) + \alpha \tag{1}$$

namely changes in the nuclear equilibrium configuration, ΔQ, reorganization of the solvation sphere, ΔS, and change of interelectronic repulsion, Δ(SPE), can be included in α for vertical, Franck—Condon allowed, and non-vertical, Franck—Condon forbidden, transitions. In this regard, eqn. 1 can be reorganized to eqn. 2 for vertical or non-vertical ligand to metal charge transfer transition.

$$E_{CTTM} = \epsilon_x - (I_0 + \Delta_i) + \Delta Q + \Delta S + \Delta(\mathrm{SPE}) + \ldots \tag{2}$$

Equation 2 suggests that the energy of the transition must exhibit a strong dependence on the electron affinity of the radical, ϵ_x, formed in the charge transfer oxidation of the ligand [7]. In this regard one can expect a linear relationship between E_{CTTM} and ϵ_x. However, the other contributions to E_{CTTM} in eqn. 2 can induce deviations from this linearity. It is possible that for some compounds a compensation between terms of eqn. 2 can reduce or eliminate such a dependence on ϵ_x. One further contribution in eqn. 2 is the difference in the energy, Δ_i, of the metal orbital with respect to the energy in the gaseous ion. Such a term corrects the ionization potential of the gaseous ion, I_0. The dependence of E_{CTTM} on ϵ_x is shown in Fig. 2, where values of E_{CTTM} have been corrected for Δ_i. The values of E_{CTTM} correspond to charge transfer transitions from ligand orbitals with σ symmetry. It is clear from Fig. 2 that the energy of the maxima for these transitions increases steadily with increasing values of the electron affinity ϵ_x.

The charge transfer spectra of copper(II) complexes can also be described in terms of the optical electronegativities, χ. A definition of χ was given by Jϕrgensen as a part of the procedure for the evaluation of charge transfer transition energies [1,8—10]. In this regard, the position of the maximum

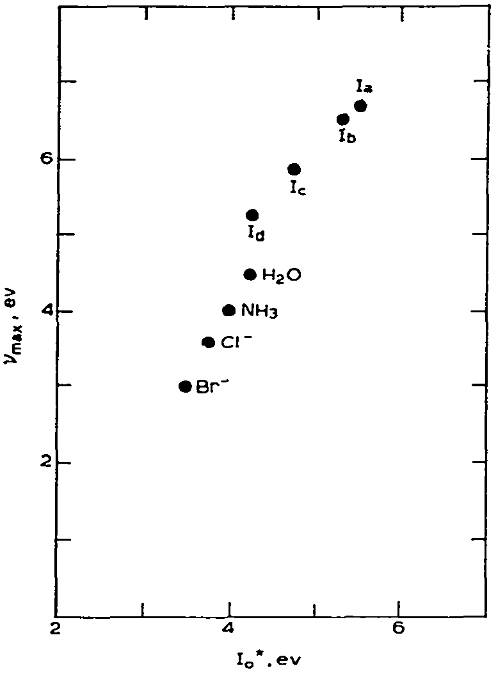


Fig. 2. Relationships between the energy of the maximum for charge transfer transitions and the corrected ionization potential of the ligand, I_0^*. (Corrections for crystal field stabilization according to: C.J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill, New York, 1962; B.N. Figgis, Introduction to Ligand Fields, Wiley, London, 1966 and J.S. Griffith, The theory of Transition Metal Ions, Cambridge University Press, 1961). The charge transfers correspond to ligand (σ) → Cu(II) transitions. The ethylenediamine ligands I_a—I_d are the following species: I_a; ethylenediamine, I_b; *meso*-2,3-diaminobutane, I_c; *N,N'*-diethylenediamine, I_d; *N,N*-dimethylenediamine.

absorption of a charge transfer transition, in cm^{-1}, is given by eqn. 3.

$$\nu_{ob} = 30 \times 10^3(\chi_x - \chi_{Cu}) + \Delta + \Delta(SPE) \tag{3}$$

The optical electronegativities for metals are normally expressed for the spherically perturbed shell. Under such an approximation χ_M corresponds to population of the t_{2g} orbitals in O_h symmetry or an orbital e in T_d, Table 1. Contributions to ν_{ob}, originating in the population of metal orbitals with different symmetries, are introduced by means of the term Δ. Moreover, differences in the interelectronic repulsions of the ground and excited state electronic configurations are considered by means of the spin-pairing energy term, Δ(SPE). This contribution has been expressed in terms of the spin, s, and orbital, l, quantum numbers for a configuration l^q (q = number of electrons), eqn. 4 [11].

$$(SPE) = [\langle S(S+1)\rangle - S(S+1)]D$$

TABLE 1

Optical electronegativities for selected ligands and copper ions

	χ	Orbital assignment [a]	Ref.
Ligand			
Cl^-	3.12	orbital with σ character	13
	2.89	orbital with π character	13
	3.0	average	12, 13
Br^-	3.99	orbital with σ character	13
	2.76	orbital with π character	13
	2.80	average	12, 13
I^-	2.87	orbital with σ character	13
	2.60	orbital with π character	13
	2.5	average	12, 13
SCN^-	2.7	average	11
$SeCN^-$	2.6	average	11
$—CO_2^-$ (e.g.: acetate, malonate oxalate, EDTA)	~3.10	average	13, 14
NH_3	3.28	orbital with σ character	13, 14
N → (e.g.: amine ligands as teta; tetb; ethylenediamines)	2.98	orbital with σ character	14
C=N (isolated imino groups, e.g: $Cu([14]dieneN_4)^{2+}$ and $Cu([14]dieneN_4)^{3+}$	3.02	orbital with π character	14
C=N (isolated imino groups, e.g: $Cu(13\text{-}AtH)^{2+}$; $Cu([14]\text{-}dieneN_4)^{2+}$)	0.4—0.3	orbital with π^* character	14
4-Methylpyridine *N*-oxide	0.8	orbital with π^* character	11
2-Picoline *N*-oxide	0.8	orbital with π^* character	11
4-Nitropyridine *N*-oxide	0.9	orbital with π^* character	11
Metal			
Copper(III) (planar or distorted octahedral)	2.74—2.8		14
Copper(II) (planar or distorted octahedral)	2.2—2.0		11, 12, 14
Copper(II) (tetrahedral)	2.5—2.2		12, 14
Copper(I) [b] (planar or octahedral)	~1.6 ~1.8	for $CTTM_{L \rightarrow Cu(I)}$ [b] for $CTTM_{d \rightarrow L}$	14

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[a] Character of the orbital involved in the electronic transition. Average indicates unresolved transitions involving σ and π or an average of them.

[b] *s* or *p* orbitals of Cu(I) must be populated in this transition.

where

$$\langle S(S+1)\rangle = \frac{q(q+2)}{4} - \frac{(2l+2)}{2(4l+1)} \tag{4}$$

The spin-pairing parameter, D, is approximately seven times the Racah parameter, $D \sim 7B$, for d electrons. In addition $\Delta(\mathrm{SPE})$ in eqn. 3 is the difference of the spin-pairing energies of the ground and excited state configurations. This term makes a contribution, $\Delta(\mathrm{SPE}) = -2/3\ D$, for charge transfer ligand to metal transitions in copper(II) complexes. Optical electronegativities between 2.2 and 3.4 have been reported for Cu(II) in a tetrahedral field [11,12]. Smaller values, $\chi_{\mathrm{Cu}} \sim 2.2$—$2.0$ were obtained for copper(II) ions in a planar or a distorted octahedral configuration. These calculations can be improved by using optical electronegativities for σ and π orbitals of the ligands, Table 1. The use of the different optical electronegativities for a given ligand has been justified in studies of the charge transfer spectra in cobalt(III) complexes [13]. Figure 3 shows the agreement between observed an calculated frequencies.

Equation 3 can also be used for metal to ligand charge transfer transitions. For these transitions the positions of the metal and ligand optical electronegativities are reversed and Δ measures the destabilization of the donor orbital for metal ions in field of a given symmetry [11]. The spin-pairing energy for a

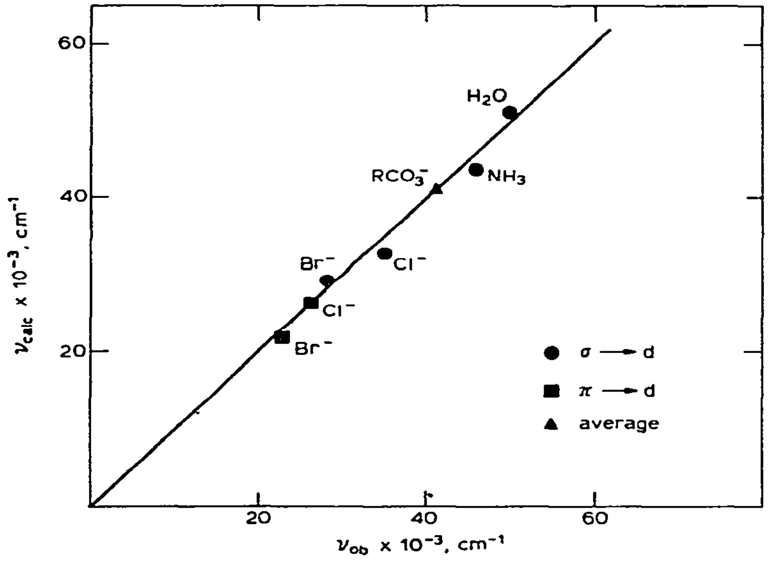
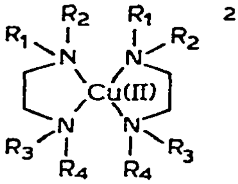
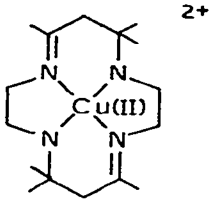
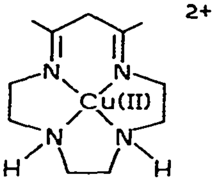


Fig. 3. Correspondence between observed and calculated frequencies for ligand to metal charge transfer transitions in copper(II) complexes. Frequencies calculated according to Jørgensen's optical electronegativities, eqn. 3. For an explanation of the orbital assigned optical electronegativities see Table 1 and elsewhere in the text.

metal to ligand charge transfer transition, where the Cu(II) changes formally to Cu(III), is —2/3 *D* (high spin Cu(III)) or —4/3 *D* (low spin Cu(III) [11,14]. Equation 3 shows that charge transfer copper to ligand transitions will be accessible only for ligands with empty orbitals and optical electronegativities smaller than 2. Lever and co-workers have obtained optical electronegativities for charge transfer to ligand transitions in a number of Cu(II)-pyridine-*N*-oxide complexes [11]. The value for various ligands are, as expected, smaller than 2, see Table 1. These transitions probably involve the population of antibonding π^* orbitals of the ligand. Optical electronegativities with values between 0.4 and 0.3 have been obtained for antibonding π^* orbitals of isolated imino groups, namely for [14]dieneN_4 (II) and [13]AtH (III) complexes of copper(II), Table 1 [14].


(I)


(II)


(III)

$R_1 = R_2 = R_3 = R_4 = H$ (en)
$R_1 = R_3 = H$; $R_2 = R_4 = CH_3$ (sym-Me$_2$en)
$R_1 = R_2 = CH_3$; $R_2 = R_4 = H$ (asym-Me$_2$en)
$R_1 = R_3 = H$; $R_2 = R_4 = C_2H_5$ (sym-Et$_2$en)
$R_1 = R_2 = C_2H_5$; $R_2 = R_4 = H$ (asym-Et$_2$en)

It is clear that CTTM and CTTL transitions can overlap in the spectrum of copper(II) complex, Table 2. One example of this behavior is found in the charge transfer spectrum of Cu([14]dieneN_4)$^{2+}$. Indeed, Endicott and co-workers have assigned the intense ultraviolet band, $\lambda_m \sim 260$ nm, to two charge transfer transitions, ligand to metal and metal to ligand, at nearly the same energy [15].

The large reducing tendency of copper(I) displaces the charge transfer to ligand transitions toward smaller energies than in copper(II). This, however, requires the presence of accessible empty orbitals in the ligand. Examples of these absorptions can be observed in the spectra of copper(I) complexes with polypyridine ligands, Table 3. In addition, light emissions from charge transfer to ligand states and ligand centered states have been reported for polypyridine complexes of copper(I) [16]. The large Stokes shift between CTTL absorption and emission suggests the existence of a large difference in the nuclear configuration between ground and excited states. This has been related with the electronic distribution of the metal center in the charge transfer state. Since the metal ion must resemble a d^9 or Cu(II) center, one can expect strong Jahn—Teller distortions with respect to the nuclear configuration of the ground state.

TABLE 2

Ultraviolet spectra of selected copper(II) complexes

Complex	$\lambda_{max}(\log \epsilon)$ [b]			Solvent [a]	Ref.
$Cu^{2+}(aq)$		~200			3
$CuCl_4^{2-}$	377(3.08);	283(4.00);	$239(3.30)_{sh}$		21, 23, 24
	417;	312;	239	solid	21
$CuBr_4^{2-}$	411;	350;	300	EtOH	22—24
$Cu(N_3)_x^{(2-x)-}$		360—380			25—27
$Cu(NH_3)_4^{2+}$		215(3.00)		0.5 M NH_3 + 0.5 M NH_4^+ in H_2O	3
$Cu(en)_2^{2+}$		228(3.78)			1
$Cu(pn)_2^{2+}$		230(3.81)			1
$Cu(1,3\text{-}Dap)_2^{2+}$		247(3.81)			1
$Cu(meten)_2^{2+}$		262(3.77)			1
$Cu(eten)_2^{2+}$	242(3.49);	265(3.40)			1
$Cu(tet\ a)^{2+}$	273(3.97);	<200(>4.00)		CH_3CN	18
	272(3.92);	<200(>4.00)			15
$Cu([14]dieneN_4)^{2+}$	262(3.87);	192(4.20)		CH_3CN	18
		260(3.73)			15, 18
$Cu(13\text{-}AtH)^{2+}$	$300(2.40)_{sh}$;	254(3.67)			28
Cu(Malonate)		240(3.49)			29
$Cu(Malonate)_2^{2-}$		250(3.81)			29
$Cu(enta)^{2-}$		270			30, 31
$Cu(dmp)_2^{2+}$	$357(3.00)_{sh}$;	$313(4.00)_{sh}$;	278(4.69)		32, 33

[a] Solutions in H_2O unless specially stated.
[b] Wavelengths in nm.

TABLE 3

Ultraviolet spectra of selected copper(I) complexes

Complex	$\lambda_{max}(\log \epsilon)$ [b]			Solvent [a]	Ref.
$Cu^{+}(aq)$		~200			33, 34
$CuCl_2^-$		271(3.63)			24, 35, 36
$CuBr_2^-$		276(3.93)			24, 35
$Cu(dipy)_2^+$		435			37
$Cu(phen)_2^+$		435			37
$Cu(dmp)_2^+$	454(3.60);	313(3.90);	278(4.69)		32, 37
$Cu(teta)^+$	395(4.16);	335(4.10)		CH_3CN	18
$Cu([14]dieneN_4)^+$	425(4.18);	375(4.08);	275(3.83)	CH_3CN	18
$Cu(NBD)^+$	$300(2.92)_{sh}$	248(3.80)		EtOH	38
	300(2.94)	253(3.90)		$CHCl_3$	38
		255(3.76)		THF	38

[a] Solutions in H_2O unless specially stated.
[b] Wavelengths in nm.

Other intense absorptions in the spectra of copper(I) complexes present the character of charge transfer to solvent transitions, CTTS. Such absorptions are observed in the ultraviolet spectra of complexes with halide and pseudohalide ligands, Table 3. The energy of the charge transfer to solvent transitions is predicted by several models. Equation 5, based on Mulliken's charge transfer theory gives the energy for the maximum of a CTTS transition.

$$h\nu_{\max} = I_{\mathrm{x}-} - \epsilon_{\mathrm{H_2O}} + \frac{\sigma^2}{I_{\mathrm{x}-} \epsilon_{\mathrm{H_2O}}} \frac{1}{r_i^2} \qquad (5)$$

The σ parameter is an overlap term which depends upon the overlap integral and polarization terms [17]. $I_{\mathrm{x}-}$ is the ionization potential of the donor ion and $\epsilon_{\mathrm{H_2O}}$ the electron affinity of the solvent acceptor orbital. The positions of the CTTS absorptions, $\nu \sim 36$ Kk, give an ionization potential, $I \sim 70$ kcal mol^{-1}, for copper(I) complexes.

Since the *d*-shells are saturated in copper(I) complexes, they are not available for charge transfer ligand to copper transitions. However, some CTTM transitions which populate metal *s* or *p* orbitals might be placed at accessible energies. Such transitions might overlap with CTTS and CTTL. This is particularly true for copper(I) complexes, where, Coulombic factors in CTTS or orbital restrictions in CTTL can increase the energy of these transitions. Indeed, it is possible to attribute the high energy absorptions in copper(I)-polyamines to charge transfer to copper transitions, Table 3.

Intense absorptions are observed in the spectra of copper(III) complexes with tetragonal or pseudooctahedral symmetries, Table 4. These absorptions are very likely charge transfer to metal transitions which can involve either or both axial or equatorial ligands in complexes with macrocyclic ligands [18]. Indeed, photochemical studies of Ni(III) macrocycles reveal that both the axially coordinated CH_3CN and the equatorial macrocycle are oxidized in independent charge transfer processes (see below). In this regard, the absorption bands at 425 nm in Cu(transtetramine)$^{3+}$ and 395 nm in Cu([14]-dieneN$_4$)$^{3+}$ both in acetonitrile solutions, can be regarded as ligand to metal charge transfer transitions that involve π electrons of the weakly coordinated acetonitrile [18]. Also the transition at 375 nm in Cu(transtetramine)$^{3+}$ can be assigned as a CTTM transition that involves the σ electron density of the amino groups. The optical electronegativity of the transtetramine macrocycle, $\chi = 2.98$, gives an optical electronegativity, $\chi \sim 2.74$, for copper(III) [14]. The value of the Cu(III) optical electronegativity suggests that the band with $\lambda_{\max} = 335$ nm in Cu([14]dienN$_4$)$^{3+}$ can be assigned as a charge transfer ligand to metal that involves π electrons of the imino group. The π imino orbital will have an optical electronegativity, $\chi_{\mathrm{C=N}} = 3.02$, according to absorptions reported for Cu([14]dieneN$_4$)$^{2+}$, Table 2, and $\chi_{\mathrm{C=N}} = 3.07$, from the absorptions reported for Cu([14]dieneN$_4$)$^{3+}$ [14].

The absorption bands with $\lambda_{\max} \sim 360$ nm in the spectra of Cu(III)—peptide complexes have also been assigned as ligand to metal charge transfer transitions by Margerum et al. [19,20]. Deprotonation of the peptide ligands

TABLE 4

Ultraviolet spectra of copper(III) complexes

Complex	$\lambda_{max}(\log \epsilon)$ [b]	Conditions [a]	Ref.
$Cu^{3+}(aq)$	295(3.76)	pH 5.7	39, 40
$Cu(NH_3)_x^{3+}$	290(3.75)	pH 11.1; 0.2 M NH_3	41
$Cu(en)_x^{3+}$	300(3.32)	pH 6.0	41
	300(3.40)	pH 11.3	41
$Cu(glycine)_x^{(2-x)}$	310(3.89)	pH 7.5	41
$Cu(H_{-3}G_3a)^-$	365(3.86); 250	pH 6—9	19
	300; 525	~pH 13	19
$Cu(H_{-3}G_4)^{2-}$	250; 365	pH 6—9	19
	325; 525	~pH 13	19
$Cu(H_{-3}G_5)^{2-}$	248; 367	pH 6—9	19
	300; 520	pH 13	19
$Cu(H_{-3}G_6)^{2-}$	367; 250	pH 6—9	19
	320; 515	~pH 13	19
$Cu(H_{-3}FGGa)^-$	355; 250	pH 6—9	19
$Cu(H_{-3}PGGa)^-$	365; 250	pH 6—9	19
	285; 600	~pH 13	19
$Cu(H_{-4}\text{-N-f}G_4)^{3-}$	357; 250	pH 10	19
$Cu(H_{-4}\text{-N-f}G_3a)^{2-}$	345	pH 9.4	19
$Cu(H_{-3}\text{-N-f}G_3)^{2-}$	365	pH 9.4	19
$Cu(teta)^{3+}$	425(4.18); 375(4.08); 275(3.83)	in CH_3CN	18
$Cu([14]dieneN_4)^{3+}$	395(4.16); 335(4.10)	in CH_3CN	18

[a] Solutions in H_2O unless specially stated.

[b] Wavelengths in nm.

induces a shift of the absorptions toward smaller photon energies. These modifications in the spectra have been associated with variations of the ligand optical electronegativity and changes in crystal field stabilization.

C. REDOX REACTIVITY OF COPPER COMPLEXES

Copper complexes can participate in a large number of redox reactions. Many of these reactions are significant in photoredox mechanisms, where, primarily generated copper(I) or copper(III) species undergo further transformations. Indeed, if the primary species of a photochemical reaction are radicals and copper(I) complexes, one can expect radical—copper(I) and radical—copper(II) reactions in further stages of the mechanism (see below). Examples of this behavior can be found in reactions of carbon-centered radicals with either copper(I) and copper(II) species. The mechanism of the reaction, of carbon-centered radicals with Cu(II) proposed by Jenkins and Kochi [42], involves the formation of copper—alkyl intermediates, eqns. 6—12.

$$R^{\cdot} + CuX_2 \rightleftharpoons RCuX_2 \qquad (6)$$

$$RCuX_2 \rightarrow R(-H) + XH + Cu^{I}X \qquad (7)$$

(oxidative elimination)

$$RCuX_2 \rightleftharpoons [RCuX^+, X^-] \tag{8}$$

$$\downarrow$$

$$[RCuX^+] \tag{9}$$

$$\xrightarrow{SH} RS + Cu^IX + H^+ \tag{10}$$

(*oxidative solvolysis*)

$$RCuX_2 \rightleftharpoons [R^+, CuX_2^-] \tag{11}$$

$$\rightarrow RX + Cu^IX \tag{12}$$

Copper(II)—alkyl intermediates have been observed by flash photolysis and pulse radiolysis, see e.g. Fig. 4 [43,44]. Moreover, the reactivity of carbon centered radicals with copper(II) and the decay of the copper(II)—alkyl intermediates, Table 5, suggest that the copper(II)—alkyl bond must have a marked covalent character [44].

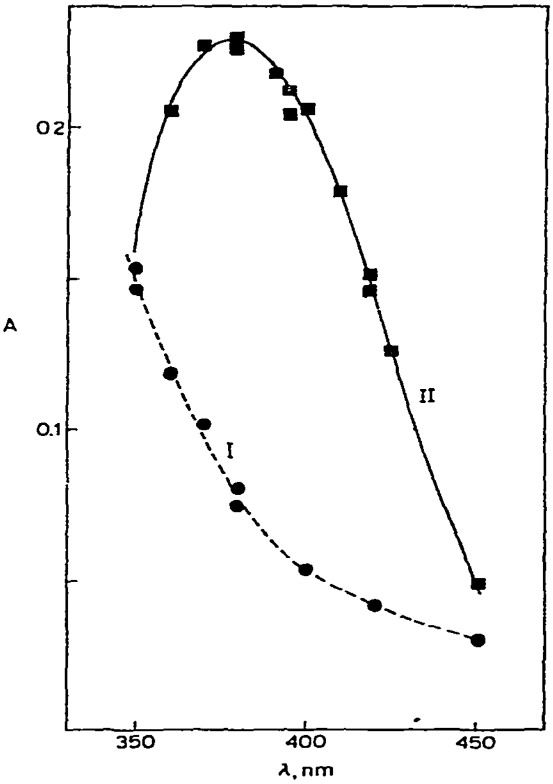


Fig. 4. Transient spectra generated in reactions of $CH_3^{\cdot}$ radicals with Cu^{2+}(aq) (I) and Cu^+-(aq) (II). These metastable species were assigned as $CuCH_3^{2+}$ (I) and $CuCH_3^+$ (II) alkyl—copper complexes.

TABLE 5

Rate constants for reactions of radicals with copper complexes

Reaction	k (M^{-1} sec^{-1})	Conditions [a]	Ref.
$Cl_2^- + Cu^{2+}(aq)$	$<1.5 \times 10^8$		67
$Cl_2^- + CuCl_4^{2-}$	1.7×10^8	CH_3CN; $[Cu(II)]/[Cl^-] = 1/8$	68, 69
$Cl_2^- + Cu(tet\ a)^{2+}$	6.5×10^8	pH 2; $I = 0.02$	70
$Cl_2^- + Cu([14]dieneN_4)^{2+}$	1.5×10^9	pH 1	54
	3.2×10^8	pH 2; $I = 0.02$	70
$Br_2^- + Cu(tet\ a)^{2+}$	2×10^7	pH 6; $I = 0.02$	70
$Br_2^- + Cu([14]dieneN_4)^{2+}$	1×10^7	pH 6; $I = 0.02$	70
$OH + Cu^{2+}(aq)$	3.1×10^8	pH 5.7;	39, 40
	($k_- = 2.8 \times 10^4$ sec^{-1}) [b]	pH 3.65	40
	($k_- = 4.2 \times 10^4$ sec^{-1}) [b]	pH 3.50	40
$OH + Cu([14]dieneN_4)^{2+}$	1.0×10^{10}		54
$OH + Cu(en)_2^{2+}$	3.0×10^9	pH 6.5	41
	8.0×10^9	pH 11.2	41
$OH + Cu(glycine)_2$	1.5×10^9	pH 6.1	41
$OH + Cu(\alpha\text{-alanine})_2$	1.4×10^9	pH 6.3	41
$OH + Cu(\beta\text{-alanine})_2$	1.2×10^9	pH 5.8	41
$OH + Cu(nta)^-$	2.6×10^9	pH 4—9	41
$OH + Cu(edta)^{2-}$	3.0×10^9	pH 4—9	41
$\dot{C}H_2OH + Cu^{2+}(aq)$	1.9×10^8		45, 71
	1.1×10^8		72
$\dot{C}H_2O^- + Cu([14]dieneN_4)^{2+}$	9.0×10^8	pH 12.0	46
$\dot{C}H_2OH + Cu([14]dieneN_4)^{2+}$	2.2×10^4	MeOH	73
$CH_3\dot{C}HOH + Cu^{2+}(aq)$	7.4×10^7		71
$(CH_3)_2\dot{C}OH + Cu^{2+}(aq)$	5.2×10^7		71
	4.5×10^7		72
$(CH_3)_2\dot{C}O^- + Cu([14]dieneN_4)^{2+}$	9.0×10^8	pH 12	46
$\dot{C}H_2(CH_3)COH + Cu^{2+}(aq)$	3.2×10^6		71
$\dot{C}H_3 + Cu^{2+}(aq)$	7.4×10^5		44
$\dot{C}H_2CO_2^- + Cu^{2+}(aq)$	7.0×10^8		43
$O_2^- + Cu^{2+}(aq)$	8.0×10^9	pH 6	50
	2.7×10^9	pH 7.8	50
$HO_2 + Cu^{2+}(aq)$	1.0×10^8	pH 2.0	50
$O_2^{\cdot -} + Cu(HCO_2)^+$	1.7×10^9		52
$O_2^{\cdot -} + Cu(HCO_2)_2$	3.0×10^8		52
$O_2^{\cdot -} + Cu(HCO_2)_3^{2-}$	8.0×10^9		52
$O_2^{\cdot -} + Cu(NH_3)^{2+}$	2.2×10^9	pH 7.0—8.5	52
$O_2^{\cdot -} + Cu(NH_3)_2^{2+}$	2.2×10^9	pH 7.0—8.5	52
$O_2^{\cdot -} + Cu(NH_3)_3^{2+}$	1.0×10^9	pH 7.0—8.5	52
$O_2^{\cdot -} + Cu(NH_3)_4^{2+}$	$\sim 2.0 \times 10^8$	pH 7.0—8.5	52
$O_2^{\cdot -} + Cu(glycine)_2$	2.1×10^6	pH 7.9	52
$\dot{N}H_2 + Cu(NH_3)_4^{2+}$	1.3×10^8	pH 11.1	41
$e_{aq}^- + Cu([14]dieneN_4)^{2+}$	5.0×10^{10}	pH 6—10	46
$CO_2^{\cdot -} + Cu([14]dieneN_4)^{2+}$	2.3×10^9	pH 7	46
$H + Cu([14]dieneN_4)^{2+}$	$>5 \times 10^9$	pH 1	46

[a] Aqueous solutions unless specially stated.

[b] Rate constants for the reverse reaction, namely formation of Cu^{2+} and $HO\cdot$ [40].

Carbon centered radicals can also react with copper(I) complexes producing either or both the oxidation and reduction of the cuprous species, eqns. 13—15.

$$(CH_3)_2\dot{C}OH + Cu^+(aq) \rightarrow CuC(CH_3)_2OH^+ \qquad (13)$$

$$CuC(CH_3)_2OH^+ \rightarrow Cu^0 + (CH_3)_2CO \qquad (14)$$

$$CuC(CH_3)_2OH^+ \rightarrow Cu^{2+} + (CH_3)_2CHOH \qquad (15)$$

Metallic copper is not formed with β-hydroxyalkyl radicals, e.g. with $\dot{C}H_2C(CH_3)_2OH$ as is indicated in eqn. 16 [45].

$$Cu^+ + \dot{C}H_2C(CH_3)_2OH \rightarrow CH_2{=}C(CH_3)_2 + Cu^{2+} + HO^- \qquad (16)$$

Also, metastable copper—alkyl species have been observed as intermediates in photochemical reactions [44].

The reactivity of copper(I) and copper(II) species with carbon centered radicals can be used as an example of the modification of the reaction course by one of the products. If copper(I) is photogenerated in a primary step, the value of the copper(I) yield will be determined by the radical reactions with copper(II) and copper(I). This behavior is illustrated for a labile complex in the reaction scheme, eqns. 17—21. Furthermore, one can observe modifications, induced by the radical—metal ion reaction, of the yield and nature of the reaction products. The yields in Table 6 show the dramatic changes, induced by $Cu^{2+}(aq)$ ions in the photolysis products of the $Co(NH_3)_5OCOCH_3^{2+}$ photodecomposition.

$$Cu^{II}L \rightleftharpoons Cu^{II} + L \qquad (17)$$

$$Cu^{II}L \xrightarrow{h\nu} Cu^{I} + R\cdot \qquad (18)$$

$$Cu^{I} + R\cdot \rightarrow Cu^{II} + \text{products} \qquad (19)$$

$$\{Cu^{II} \text{ or } Cu^{II}L\} + R\cdot \rightarrow Cu^{I} + \text{products} \qquad (20)$$

$$R\cdot + R\cdot \rightarrow \text{disproportionation or dimerization products} \qquad (21)$$

Although, the examples indicated above show that carbon centered radicals react with copper by forming copper—alkyl derivatives, a number of reactions have been reported where no intermediates have been observed. For example, a number of hydroxyalkyl radicals have been reported to reduce $Cu([14]dieneN_4)^{2+}$, Table 5, but no alkyl-intermediates have been reported [46,47]. However, it is possible that the metastable alkyl—copper species disappears with a rate larger than its formation, namely as in eqns. 22 and 23, preventing its observation in pulsed techniques.

$$Cu([14]dieneN_4)^{2+} + R\cdot \xrightarrow{k_1} R{-}Cu([14]dieneN_4)^{2+} \qquad (22)$$

$$R{-}Cu([14]dieneN_4)^{2+} \xrightarrow[k > 10^6\ \text{sec}^{-1}]{} Cu([14]dieneN_4)^{+} + \ldots \qquad (23)$$

TABLE 6

Influence of the methyl radical—copper(II) reactions on the photodecomposition of Co-$(NH_3)_5OCOCH_3^{2+}$ [a,b]

Product	Yields (ϕ) [b]	
	$[Cu^{2+}(aq)] = 0$	$[Cu^{2+}(aq)] = 1.0 \times 10^{-3}$ M
CH_3OH		0.073 ± 0.008
CH_4	0.095 ± 0.005	0.014 ± 0.004
C_2H_6	0.032 ± 0.003	~0.002
$Co^{2+}(aq)$	0.13 ± 0.03	0.11 ± 0.03

[a] Values from ref. 44.

[b] Yields determined for 254 nm ($I_0 = 8.0 \times 10^{-5}$ Einstein/L. min) irradiations of aqueous acidic (10^{-2} M $HClO_4$) solutions of $Co(NH_3)_5OCOCH_3^{2+}$.

Also, other radicals can react by complexation to copper(I) or copper(II) ions, namely by an inner sphere mechanism. One example of this behavior is found in the reaction of hydrogen atoms with Cu(I) [48]. Formation of a copper hydride has been observed by flash photolysis, Table 5. The same intermediate can be generated in heterolytic processes between dihydrogen and Cu(I), eqns. 24—26, in the autocatalytic reduction of Cu(II) [49].

$$Cu^{2+} + H_2 \rightarrow CuH^+ + H^+ \qquad (24)$$

$$CuH^+ + Cu^{2+} \rightarrow 2\,Cu^+ + H^+ \qquad (25)$$

$$2\,Cu^+ \rightarrow Cu^0 + Cu^{2+} \qquad (26)$$

Reactions of hydroperoxyradicals with $Cu^{2+}(aq)$ proceed via complexation, eqns. 27 and 28 [50,51]. The effect of Cu(I) on the reaction has been explained as a reoxidation of Cu(I) by $HO_2\cdot$, eqn. 29.

$$Cu^{2+}(aq) + HO_2\cdot \rightarrow CuO_2H^{2+} \qquad (27)$$

$$CuO_2H^{2+} \rightarrow Cu^+(aq) + H^+ + O_2 \qquad (28)$$

$$Cu^+(aq) + HO_2\cdot \rightarrow Cu^{2+}(aq) + H_2O_2 \qquad (29)$$

The same type of reaction can be observed between O_2^- and copper(II) complexes with ammonia and aminoacids, Table 5 [52,53]. The rate constant of the reaction between simple copper(II) complexes and O_2^- decreases in parallel with the decrease in the number of coordination sites that are available, Table 5. This observation is in agreement with the proposition of an inner sphere mechanism for the redox reaction.

The reactivity of copper(II) complexes with other radicals, eg.: OH; Cl_2^-;

Br_2^-, has been investigated. Reactions of OH with $Cu^{2+}(aq)$ produce $Cu^{3+}(aq)$ which undergoes hydrolysis at a low pH, eqns. 30 and 31.

$$Cu^{2+}(aq) + OH \rightarrow Cu^{3+}(aq) \qquad (30)$$

$$Cu^{3+}(aq) \rightarrow CuOH^{+} + H^{+} \qquad (31)$$

$k = (0.9 \pm 0.1) \times 10^{-3}$

The hydroxo species has been claimed to be responsible for the decomposition of water in neutral solutions, eqn. 32. The decomposition in acidic solutions can involve the reverse of reaction 30, namely the formation of OH radicals, eqn. 33.

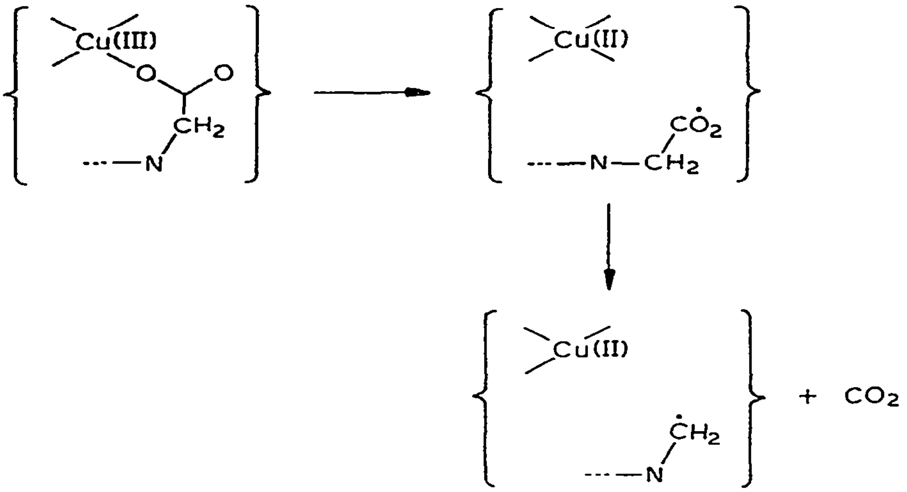
$$2\ CuOH^{2+} \rightarrow 2\ Cu^{2+} + H_2O_2 \qquad (32)$$

$$Cu^{3+}(aq) \rightarrow Cu^{2+} + HO\cdot \qquad (33)$$

Studies of the oxidation of copper(II) species by OH have been extended by Meyerstein to amino and aminoacid complexes [40,41]. The most characteristic feature in the spectra of the intermediates is an absorption band around 300 nm with $\epsilon_{max} \sim 3 \times 10^3$—$5 \times 10^3\ M^{-1}\ cm^{-1}$. Such species were assigned as Cu(III) complexes. However, Whitburn and Laurence assigned related intermediates, generated in the oxidation of $Cu([14]dieneN_4)^{2+}$ (II), as Cu(II)—ligand radical complexes [54]. The discrepancy between assignments arises in the differences between the spectra of the intermediates in aqueous solutions and Cu(II) complexes in acetonitrile, see e.g. compounds in Table 4. It is worthwhile to point out that the comparison of the spectrum in different solvents is not straightforward and Laurence has recognized that some chemical properties of the intermediates, namely the oxidation of Cl^-, can be more likely attributed to a Cu(III) complex. The assigned Cu(II)—ligand radical, generated from $Cu([14]dieneN_4)^{2+}$, exhibited a half-lifetime $t_{1/2} > 1$ s in the absence of oxidizable substrates. Such stability can only be explained if the nitrogen centered radical has a strong π bonding interaction with the copper(II) center. However, orbitals with a π symmetry are filled with electrons in Cu(II). Hence, such a π interaction must yield a significant reduction in the electronic density of the metal center.

Also, the intermediates formed by oxidation of copper(II) complexes with $EDTA^{4-}$ and NTA^{3-} with radicals have been assigned as metastable copper-(III) complexes [55]. The decomposition of these species has been related with an intramolecular oxidation of the carboxylate group. These processes must be followed by a rapid decarboxylation of the radical, eqns. 34 and 35.

The redox reactivity of copper(I) complexes with complexes of other metal ions has received some attention [56,57]. These electron transfer reactions have rate constants which extend over a wide range of values, Table 7. The mechanism of the electron transfer between cobalt(III) complexes, Table 7, and $Cu^{+}(aq)$ has been tentatively assigned as inner sphere. In this regard, the wide spread in the rates has been attributed to this type of mechanism and to

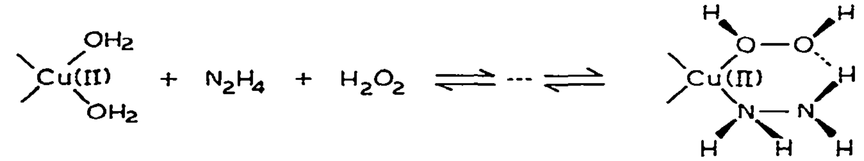


(34)

(35)

the high rate of H_2O exchange for a d^{10} ion. However, the available information seems to be too limited for a definitive proof of the mechanism's nature. More studies of this subject would be desirable.

Copper complexes or copper ions can induce reactions within the coordination sphere with or without the intervention of another reagent. In a number of processes the metal species is available for refunctioning and continuing the cycle in a catalytic fashion. Although this behavior can be extended to many kinds of metal—ligand processes, a few examples of the redox reactions are reviewed below. The decomposition of hydrogen peroxide, alone and with the intervention of another reactant, can be catalyzed by copper complexes. The catalytic activity is largely determined by the existance of water coordinated to copper(II). Such observation has been associated with the tendency of copper(II) to function by complexing the H_2O_2 and the added substrate [58]. This type of mechanism is shown in eqns. 36—39.



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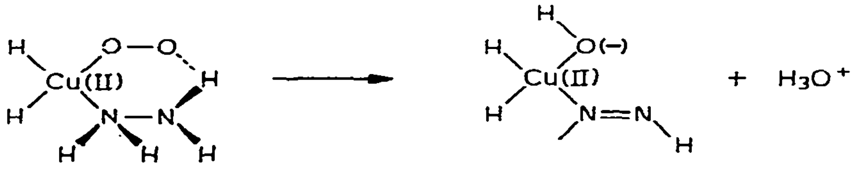
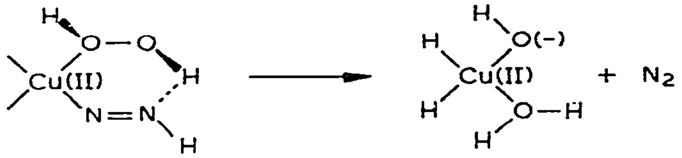


(37)

Indeed, the catalytic activity decrease in the order $Cu(en)(H_2O)_2^{2+} > Cu(dien)OH_2^{+} > Cu(trien)^{2+}$ as it is expected from the previous mechanism, eqns.

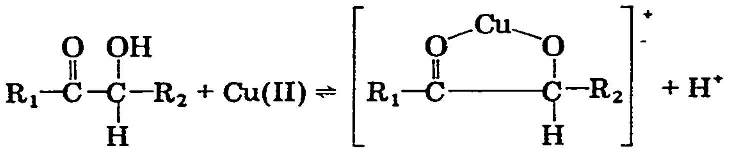
(38)



(39)

36—39. It is worthwhile to note that hydroperoxy radicals, also eqns. 27—29, and Table 5, react by an inner sphere mechanism.

The oxidation of ketoenols by copper complexes has been extensively used in organic chemistry. A number of studies have dealt with acetoin, benzoin, sugars such as sucrose and galactose and α-hydroxycarbonyl compounds such as α-hydroxyacetophenone [59—63]. The general mechanism of these oxidations seems to involve the formation of a ketoenol—copper(II) complex, eqn. 40. This complexation reaction is considered to be rapid in relation to the proton transfer to a base, eqns. 41 and 42.



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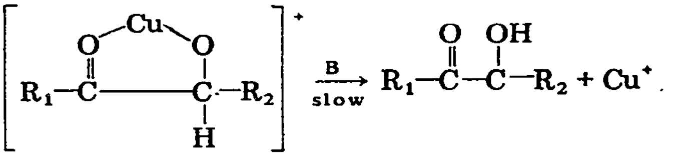
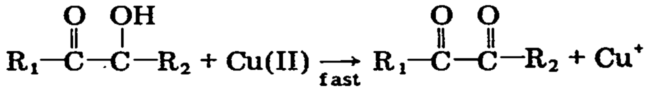


(41)



$$R_1-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-R_2 + Cu(II) \xrightarrow[\text{fast}]{} R_1-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-R_2 + Cu^+ \qquad (42)$$

The rate determining step, eqn. 41, is too complex for a single step. It is possible to represent this reaction, eqn. 41, as a process where the first-step is an acid—base dissociation. Such an acid—base process must be followed by an intramolecular electron transfer. The reoxidation of Cu(I) by dioxygen will return Cu(II) to the cycle. The copper(II)-induced oxygenolysis of *o*-benzoquinones, catechols and phenols has been reported. Extensive studies have been carried out on the nature and role of the active copper species [64].

The oxidation of the organic ligand might be induced by a metastable oxidation state of the metal center. One example of this chemical activity is the

TABLE 7

Redox reactivity of copper complexes

Reactants	k (M^{-1} sec^{-1})	Conditions	Ref.
(a) Copper(I) reactions			
$Cu^+(aq)$ + *trans*-$Co(en)_2Cl_2^+$	$>1.0 \times 10^7$		57
$Cu^+(aq)$ + *cis*-$Co(en)_2Cl_2^+$	2.13×10^4		57
$Cu^+(aq)$ + *trans*-$Co(NH_3)_4(OH)_2CN^+$	0.47		57
$Cu^+(aq) + Co(en)_3^{3+}$	$\leq 4.0 \times 10^{-4}$		57
$Cu^+(aq) + Co(NH_3)_5Cl^{2+}$	4.8×10^4		57
$Cu^+(aq) + Co(NH_3)_5N_3^{2+}$	1.5×10^3		57
$Cu^+(aq) + Co(NH_3)_5Br^{2+}$	4.5×10^4		56, 57
$Cu^+(aq) + Co(NH_3)_5OH^{2+}$	3.8×10^2		57
$Cu^+(aq) + Co(NH_3)_5OH_2^{3+}$	1.0×10^{-3}		57
$Cu^+(aq) + Co(NH_3)_5NCS^{2+}$	ca. 1—3		57
$Cu^+(aq) + Co(NH_3)_5F^{2+}$	1.1		57
$Cu^+(aq) + Co(NH_3)_5CN^{2+}$	3.3×10^{-3}		57
$Cu([14]dieneN_4)^+ + Co(bipy)_3^{3+}$	1.2×10^7		46
$Cu([14]dieneN_4)^+ + Cr(bipy)_3^{3+}$	3.7×10^6		46
$Cu([14]dieneN_4)^+ + Fe(bipy)_3^{3+}$	$<10^3$		46
$Cu([14]dieneN_4)^+ + Ru(NH_3)_6^{3+}$	7.2×10^4		46
$Cu([14]dieneN_4)^+ + Ru(NH_3)_5NO^{3+}$	$<10^3$		46
$Cu([14]dieneN_4)^+ + Co(en)_3^{3+}$	$<10^3$		46
$Cu([14]dieneN_4)^+ + Co(NH_3)_6^{3+}$	$<10^3$		46
$Cu([14]dieneN_4)^+ + Co([14]dieneN_4)(OH)_2OH^{2+}$	$<10^3$		46
$Cu([14]diene_4)^+$ + Co(1,3,8,10-tetra-	$<10^3$		46
$eneN_4)(OH)_2^+$	$<10^3$		46
$Cu([14]dieneN_4)^+ + O_2$	2.6×10^7		46
$Cu([14]dieneN_4)^+ + N_2O$	1.7×10^6		46
$Cu([14]dieneN_4)^+ + CH_3I$	3.1×10^6		46
$Cu([14]dieneN_4)^+$ + *p*-benzoquinone	2.6×10^9		46
$Cu([14]dieneN_4)^+$ + 9,10-anthraquinone-2,6-disulfonate	4.3×10^9		46
$Cu([14]dieneN_4)^+$ + 9,10-anthraquinone-quinone-2,6-sulfonate	1.1×10^9		46
(b) Copper(III) reactions			
$Cu^{3+}(aq) + NO_2^-$	5.9×10^8	pH 3.65	40
	4.5×10^7	pH 5.2	40
$Cu^{3+}(aq) + CH_3OH$	2.8×10^7	pH 3.65	40
	$<1 \times 10^6$	pH 5.4	40
$Cu^{3+}(aq) + H_2O_2$	6.5×10^6	pH 3.65	40
	6.5×10^5	pH 5.2	40

copper catalyzed oxidation of mercaptoacetate by hexacyanoferrate(III) [65]. A mixed valence complex, formed in a rapid equilibrium eqn. 43, produces a metastable Cu(II) complex, eqn. 44. The decomposition of the

Cu(II)-mercaptan takes place in a non-rate-determining step [65]. A similar

$$\mathrm{Fe(CN)_6^{3-} + Cu^{I}(SL)_n \rightarrow (CN)_5Fe{-}CN{-}Cu(SL)_n} \qquad (43)$$

$$\mathrm{(CN)_5Fe{-}CN{-}Cu(SL)_n \rightarrow Fe(CN)_6^{4-} + Cu^{II}(SL)_n} \qquad (44)$$

mechanism can be operative in the catalyzed reaction between oxalate ion and peroxodisulfate [66]. Reactions of $\mathrm{SO_4^{\cdot-}}$ with copper(II)—oxalate complexes, $\mathrm{CuC_2O_4}$ and $\mathrm{Cu(C_2O_4)_2^{2-}}$ can generate a metastable Cu(III) complex with a rate larger than the rate of reaction between $\mathrm{SO_2^{\cdot-}}$ and free $\mathrm{C_2O_4^{2-}}$. The decomposition of the copper(III) species produces $\mathrm{CO_2^{\cdot-}}$ radicals. Such radicals can decompose more $\mathrm{S_2O_8^{2-}}$ in a chain reaction, eqns. 45—52. In addition,

$$\mathrm{S_2O_8^{-2} \rightarrow 2\ SO_4^{-}\ (slow)} \qquad (45)$$

$$\mathrm{Cu^{II}Ox_n^{2(1-n)} + SO_4^{-} \rightarrow Cu^{III}Ox_n^{(3-2n)} + SO_4^{2-}} \qquad (46)$$

(Ox = oxalate, $n = 1; 2$) →

$$\mathrm{Cu^{III}Ox_n^{(3-2n)} \rightarrow Cu^{II}Ox_{n-1}^{(5-2n)} + CO_2 + CO_2^{\cdot-}} \qquad (47)$$

$$\mathrm{CO_2^{\cdot-} + O_2 \rightarrow O_2CO_2^{-}} \qquad (48)$$

$$\mathrm{CO_2^{\cdot-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{\cdot-} + CO_2} \qquad (49)$$

$$\mathrm{O_2CO_2^{\cdot-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{\cdot-} + CO_2 + O_2} \qquad (50)$$

$$\mathrm{CO_2^{\cdot-} + SO_4^{\cdot-} \rightarrow SO_4^{2-} + CO_2} \qquad (51)$$

$$\mathrm{O_2CO_2^{-} + SO_4^{\cdot-} \rightarrow SO_4^{2-} + CO_2 + O_2} \qquad (52)$$

the catalytic activity of copper in this reaction must be attributed to Cu(II) and Cu(I) species under the conditions of low oxalic and high copper concentrations.

D. PHOTOCHEMICAL PROPERTIES OF COPPER COMPLEXES

(i) Charge transfer photochemistry of copper(II) complexes

(a) The charge transfer to metal photochemistry

The photochemical properties of a number of complexes reveal that they undergo a photodissociation into a Cu(I) species and ligand radicals. Such a behavior can be associated with the population of CTTM states. Some of these systems are reviewed below.

(b) Halide complexes

The $\mathrm{CuCl_x^{(2-x)}}$ and $\mathrm{CuBr_x^{(2-x)}}$, $x = 1$—4, have been used for photooxidations and photohalogenations of a number of organic substrates [74]. Although the complexes are usually reduced to cuprous halides, the transformations of the organic substrates depend on their nature. Primary and secondary alcohols, methanol and ethanol are oxidized to aldehydes, while *t*-butyl alcohol, n-butyronitrile and tetrahydrofuran are transformed to haloderivatives. These transformations have been attributed to reactions of the organic substrate with radicals, chlorine or bromine, which are formed in photochemical processes, eqns. 53—55.

$$\mathrm{CuCl}_x^{(2-x)} \overset{h\nu}{\rightleftharpoons} \mathrm{CTTM} \rightarrow \mathrm{CuCl}_{x-1}^{(2-x)} + \mathrm{Cl}\cdot \qquad (53)$$

$$\mathrm{Cl}\cdot + \mathrm{Cl}^- \rightleftharpoons \mathrm{Cl}_2^- \qquad (54)$$

$$\mathrm{Cl}\cdot(\mathrm{Cl}_2^-) + \text{scavenger} \rightarrow \text{chlorination or oxidation} \qquad (55)$$

The rate constants of the reaction of Cl_2^- and Br_2^- with methanol and ethanol are very small ($k = 3.5 \times 10^3\ \mathrm{M}^{-1}\ \mathrm{sec}^{-1}$ for $\mathrm{Cl}_2^- + \mathrm{CH_3OH}$ [75] and $k = 4.5 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{sec}^{-1}$ for $\mathrm{Cl}_2^- + \mathrm{CH_3CH_2OH}$ [75]). However, the small steady state concentration of Cl_2^- in continuous wave photolysis might result in some direct reaction between alcohol and Cl_2^-. In addition, another mechanism can be opperative as a consequence of the accessibility of the tripositive oxidation state of copper under given conditions.

A study of the transient spectra in the photochemistry of CuCl_4^{2-} in acetonitrile has established that chlorine radicals are formed in the primary process [68,69]. It is interesting that in $\mathrm{CH_3CN}$ the rate of the Cl_2^- disappearance exhibited a first order dependence in complex concentration. Such a behavior has been used as evidence against the reaction of the radical with solvent molecules and justify a direct reaction between Cl_2^- and Cu(II) species. That acetonitrile and acetic acid are inert to chlorine atoms was also reported by other researchers. In addition, the disappearance of Cl_2^- has suggested that this radical reacts with CuCl_4^{2-} forming a Cu(III) species. In this regard, the absence of a stable Cu(III) reaction product could be attributed to back electron transfer between Cu(III) and Cu(I) complexes, the solvent and/or other reducing primary species in these solutions. (Notice that $\mathrm{CH_3CN}$ and/or Cl^- have been claimed to be the reductants.)

It is worthwhile to point out that the photoredox behavior, reported above for chlorocupric and bromocupric complexes, is in agreement with assignments of the high intensity bands to CTTM transitions, Table 2.

(c) Carboxylate complexes

The photochemistry of the mono(acetate)cuprate(II), $\mathrm{CuOCOCH_3^+}$ has been investigated by continuous wave and flash photolysis [44]. The primary process can be described as a photodissociation in Cu(I) and acetate or methyl radicals, eqns. 56 and 57. These processes are followed by radical—

$$\mathrm{CuOCOCH_3^+} \overset{h\nu}{\rightleftharpoons} \mathrm{CTTM} \begin{cases} \rightarrow [\mathrm{Cu^+}, \mathrm{CH_3^{\bullet}}] + \mathrm{CO_2} & (56) \\ \rightarrow [\mathrm{Cu^+}, \mathrm{CH_3\dot{C}O_2}] & (57) \end{cases}$$

copper(II) and radical—radical reactions, eqns. 58—66.

$$[\mathrm{Cu^+, CH_3\dot{C}O_2}] \rightarrow \begin{cases} \mathrm{CuOCOCH_3^+} & (58)\\ \mathrm{Cu_{aq}^+ + CH_3^{\bullet} + CO_2} & (59)\\ \mathrm{CuCH_3^+ + CO_2} & (60)\end{cases}$$

$$[\mathrm{Cu^+, CH_3^{\bullet}}] \rightarrow \begin{cases} \mathrm{CuCH_3^+} & (61)\\ \mathrm{Cu_{aq}^+ + CH_3^{\bullet}} & (62)\end{cases}$$

$$\mathrm{CuCH_3^+ + H^+ \rightarrow Cu^{2+} + CH_4} \qquad (63)$$

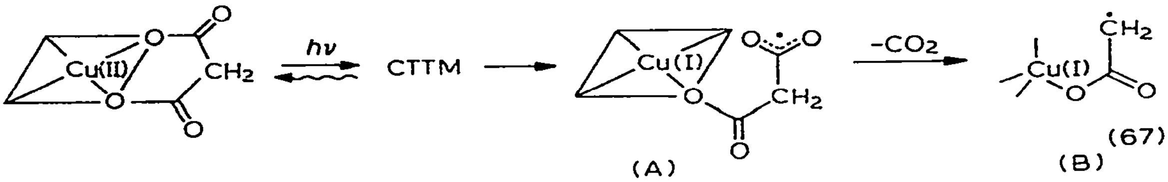
$$\mathrm{CH_3^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_6} \qquad (64)$$

$$\mathrm{CH_3^{\bullet} + CuOCOCH_3^+} \rightarrow \begin{cases} \mathrm{Cu^+ + CH_3OCOCH_3} & (65)\\ \mathrm{Cu^+ + CH_3OH + CH_3CO_2H} & (66)\end{cases}$$

A reaction intermediate, observed in flash photolysis, has been assigned as a methyl—copper derivative formed in reactions 60 and/or 61. This metastable species undergoes an acid induced decomposition, eqn. 63, with a rate constant, $k = 6.2 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$. In addition, the small yield of Cu(I), $\phi_{\mathrm{Cu(I)}} < 0.003$, has shown that reactions 59, 62, 65 and 66 do not have major significance in this mechanism, see Table 6.

The photochemical reactivity of $\mathrm{CuOCOCH_3^+}$ can be attributed to CTTM states. In this regard, the carbon dioxide yield, $\phi_{\mathrm{CO_2}} \sim 0.10$ for $\lambda_{\mathrm{excit}} = 254$ nm, can be a measure of the primary efficiency of the reaction.

The photochemistries of the mono- and di(malonate) complexes of copper(II), CuMal and $\mathrm{Cu(Mal)_2^{2-}}$, are comparable with that of $\mathrm{CuOCOCH_3^+}$. Morimoto and DeGraaf have reported that ultraviolet irradiations of the malonate complexes produced decarboxylation of the ligand [29,76]. Copper(I) was not formed as a stable reaction product. Yields of $\mathrm{CO_2}$ determined for irradiations at 254 nm, were $\phi_{\mathrm{CO_2}} \sim 0.08$ for CuMal and $\phi_{\mathrm{CO_2}} \sim 0.07$ for $\mathrm{Cu(Mal)_2^{2-}}$. These quantum efficiencies are nearly the same as those measured for $\mathrm{CuOCOCH_3^+}$. The intermediates of the reaction have been investigated by flash photolysis. The results of continuous wave and flash photolysis were explained by means of the mechanism described in eqns. 67—69. Flash irradiations revealed transient absorbances, maxima at 370—390 nm, which have been assigned to metastable copper complexes. These species can be either a Cu(I)—ligand radical, (B) in eqn. 67, or a Cu(II)—alkyl derivative, (C) in eqn. 69. The proposed formation of alkyl—copper intermediates in photolysis of $\mathrm{CuOCOCH_3^+}$ and the observation of related species in pulse radiolysis and flash photolysis seems to give further support to intermediate (B) in eqn. 69. If one accepts that reaction 68 is the main reaction path, the same reaction mechanism will apply for $\mathrm{CuOCOCH_3^+}$, $\mathrm{Cu(Mal)_2^{2-}}$ and Cu-$\mathrm{(Oxalate)_2^{2-}}$.



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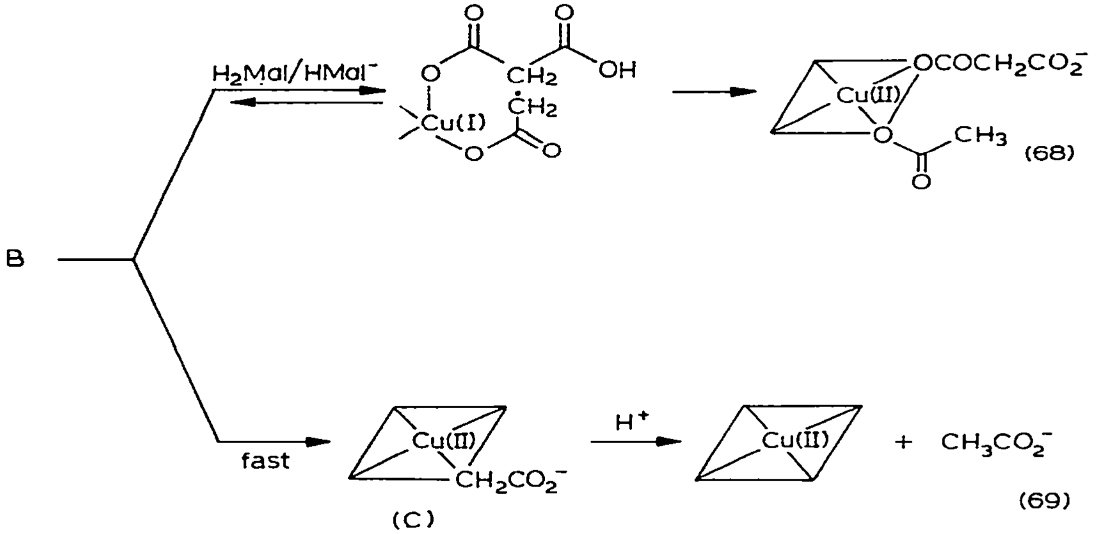


(68)

(69)

The small yields for photodecarboxylation of the malonate complexes have been attributed to an efficient depopulation of the photoactive state. Both radiationless depopulation of the reactive state and photoaquation have been offered as alternative paths for the dissipation of the energy. However, the small yield can be, in part, a consequence of a back electron transfer reaction which transforms the primary Cu(I)—ligand radical, (A) in eqn. 67, into the original malonate complex. This back electron transfer can be effective for excitations with photon energies close to the threshold energy for photochemistry if there is no thermal equilibration of the excited state or (A) in eqn. 67.

It is not surprising that both $Cu(EDTA)^{2-}$ and Cu(II)—formate complexes are insensitive to visible irradiations [78] (excitations in the region of the *d*—*d* transitions). However, it is interesting that $Cu(EDTA)_2^{2-}$ is photoinert for excitation wavelengths greater than or equal to 214 nm [79]. Such a behavior has been attributed to a very rapid non-radiative electronic relaxation of the CTTM state.

Copper(II)—aminoacid complexes were investigated as initiators for vinyl polymerization [80,81]. These studies revealed that free radicals are generated by ultraviolet irradiation of $Cu(glutamate)_2^{2-}$. More recently other studies have shown that distinct intermediates are generated in flash irradiations of $Cu(glutamate)_2^{2-}$, $Cu(\beta\text{-alanine})_2$ and $Cu(glycine)_2$. These intermediates exhibited the spectral features of copper—alkyl derivatives, Fig. 4 [81]. These transient species seem to be generated by a complex mechanism.

(d) Phenanthroline complexes

The photochemistry of $Cu(dmp)_2X$, $X = H_2O$ and CH_3OH, has been investigated by Sundarajan and Wehry [32]. Ultraviolet irradiations of $Cu(dmp)_2OH_2^{2+}$ in aqueous solutions induce the reduction of the metal center and an equivalent destruction of dmp. This transformation has been attributed to the photogeneration of hydroxyl radicals in the primary process, eqn. 70.

$$Cu(dmp)_2OH_2^{2+} \overset{h\nu}{\rightleftarrows} CTTM \rightarrow Cu(dmp)_2^+ + HO + H^+ \tag{70}$$

The consumption of the ligand has been attributed to the reactions between hydroxyl radicals and dmp. However, the inverse dependence of the copper(I) yield on the light intensity and $Cu(dmp)_2OH_2^{2+}$ concentration suggests a more complex mechanism. Sundarajan and Wehry attributed this behavior to the direct interaction of OH radicals with $Cu(dmp)_2OH_2^{2+}$.

Photolyses of $Cu(dmp)_2CH_3OH^{2+}$ in methanol do not destroy the dmp ligand. The products of the photoreaction are $Cu(dmp)_2^+$ and formaldehyde. Therefore, the photochemistry of $Cu(dmp)_2CH_3OH^{2+}$ has been described as a primary photooxidation of coordinated methanol, eqn. 70 [32]. Secondary thermal reactions of the Cu(I) product and the methoxy radicals were considered in the reaction mechanism, eqns. 71—78.

$$Cu(dmp)_2CH_3OH^{2+} \overset{h\nu}{\rightleftarrows} CTTM \rightarrow Cu(dmp)_2^+ + CH_3OH^+ \tag{71}$$

$$Cu(dmp)_2^+ \rightarrow Cu(dmp)^+ + dmp \tag{72}$$

$$CH_3OH^+ + CH_3OH \rightarrow CH_3O\cdot + CH_3OH_2^+ \tag{73}$$

$$CH_3OH^+ + CH_3OH \rightarrow \dot{C}H_2OH + CH_3OH_2^+ \tag{74}$$

$$CH_3O\cdot + CH_3OH \rightarrow CH_3OH + \dot{C}H_2OH \tag{75}$$

$$\dot{C}H_2OH + Cu(dmp)_2CH_3OH^{2+} \rightarrow CH_2O + Cu(dmp)_2^+ + H^+ \tag{76}$$

$$CH_3O\cdot + X^- \rightarrow CH_3O^- + \dot{X} \tag{77}$$

$(X^-: Cl^-; Br^-; I^-)$

$$X\cdot + Cu(dmp)_2^+ \rightarrow X^- + Cu(dmp)_2CH_3OH^{2+} \tag{78}$$

The reaction of $CH_3O\cdot$ with X^-, eqn. 77, must reduce the value of copper(I) yield to zero for very high halide concentrations. Sundarajan and Wehry found that the yields at high halide concentrations have half of the value of the yield measured at a zero halide concentration. This departure from the predicted behavior has not been explained.

Limiting yields for $Cu(dmp)_2OH_2^{2+}$, $\phi_L = 1.1 \times 10^{-3}$ and, $Cu(dmp)_2CH_3OH^{2+}$,

$\phi_L = 0.1$, were obtained for excitations at frequencies above 28 000 cm^{-1}. In addition, the first intense absorption band in the absorption spectrum has been assigned to a charge-transfer transition with $dmp_{(\pi)} \rightarrow Cu^{II}(d)$ character. Therefore, it seems that the electron donor ligand, dmp, in the charge-transfer transition does not participate in the photochemical primary process, eqns. 70 and 71. Sundarajan and Wehry had given two possible justifications for this behavior. First, these authors argued that the ligand to metal charge transfer transition would involve electron transfer from a molecular orbital extending over all ligands, including H_2O and dmp. However, in order that such a molecular orbital be meaningful requires orbitals of H_2O with energies close to those of the π orbitals of dmp. If this is the case, it is also possible to think in terms of two different charge transfer states, $CTTM_{(H_2O \rightarrow Cu(II))}$ and $CTTM_{(dmp \rightarrow Cu(II))}$, with nearly the same energies, namely degenerate or nearly degenerate states. The charge transfer transition that populates the $CTTM_{(H_2O \rightarrow Cu(II))}$ state must be orbitally forbidden and therefore low in intensity. The second alternative, proposed by Sundarajan and Wehry, is the secondary oxidation of solvation or coordinated solvent by the excited state. The oxidation of the solvent in the solvation sphere, namely as in eqn. 79, has been reported for the photochemistry of cobalt(III) complexes.

$$Cu(dmp)_2CH_3OH^{2+} \overset{h\nu}{\rightleftarrows} CTTM_{(dmp \rightarrow Cu(II)} \rightarrow [Cu(dmp)_2CH_3OH^{+}]CH_3\dot{O}H^{+} \quad (79)$$

However, it seems that the photooxidation of the bulk solvent must require larger energies than those for the population of $CTTM_{(H_2O \rightarrow Cu(II))}$ or $CTTM_{(CH_3OH \rightarrow Cu(II))}$. The oxidation of the coordinated solvent has been described as a "thermal oxidation of coordinated solvent" by means of eqns. 80 and 81 [32]. However, Sundarajan and Wehry did not define the nature of

$$Cu(dmp)_2CH_3OH^{2+} \xrightarrow{h\nu} Cu^{I}(d\dot{m}p)(dmp)CH_3OH^{2+} \quad (80)$$

$$Cu^{I}(d\dot{m}p)(dmp)CH_3OH^{2+} \rightarrow Cu(dmp)_2(C\dot{H}_3OH)^{2+} \quad (81)$$

the products in eqns. 80 and 81 and, therefore, their structural differences of a $CTTM_{(dmp \rightarrow Cu(II))}$ state and a $CTTM_{(CH_3OH \rightarrow Cu(II))}$ respectively.

The $Cu(phen)_2^{2+}$ complex was reported to be photoinert in aqueous or methanolic solutions for excitations at frequencies smaller than 50 000 cm^{-1}. The differences between the photochemical behavior of $Cu(dmp)_2X^{2+}$ and $Cu(phen)_2X_2^{2+}$, X = H_2O and CH_3OH, have been attributed to the structures of these complexes. The redox potentials of $Cu(dmp)_2^{2+}$ and $Cu(phen)_2^{2+}$ are almost the same. Indeed, the oxidation of water is endoergic by 213 kJ mol^{-1} if the oxidant is $Cu(dmp)_2^{2+}$ and 250 kJ mol^{-1} if the oxidant is $Cu(phen)_2^{2+}$.

(e) Polyamine complexes

The ultraviolet irradiation of $Cu(en)_2^{2+}$ produces CO_2 and NH_3 [77]. These products probably originate in secondary redox reactions of a primary copper(I)—ligand radical. The primary species can be formed in $CTTM_{(N \rightarrow Cu(II))}$ states. The irradiation and/or thermal decomposition of other species e.g.: en, has been raised as a possibility by Balzani and Carassitti [78]. In this regard, the photochemistry of $Cu(en)_2^{2+}$ has to be reviewed.

The photochemistries of teta and tetb complexes have been recently investigated [47,82]. The primary process has been characterized as a reduction of the metal center and oxidation of the macrocycle, eqn. 82. Back electron transfer in the primary Cu(I)—ligand radical competes with reorganization into a new Cu(II)—ligand radical and scavenging processes, eqns. 85 and 86. Figure 5 shows a typical distribution of product yields with scavenger concentrations. These results and transient spectra, determined by flash photolysis, Fig. 5, have indicated the Cu(I)—ligand radical nature of the intermediates, namely as in eqns. 84—86.

The Cu(I)—ligand radical, produced in eqn. 85, undergoes further decomposition and can also be scavenged by low concentrations of alcohols.

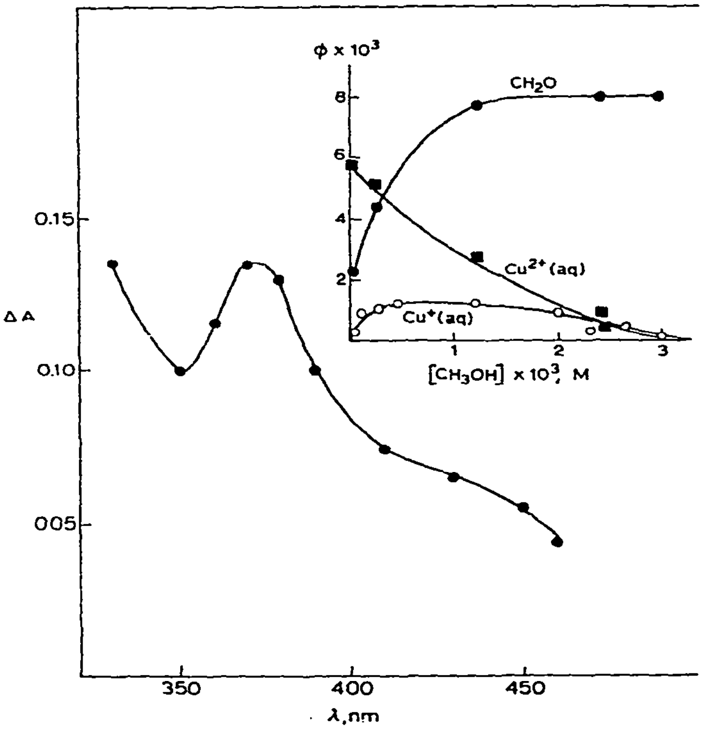
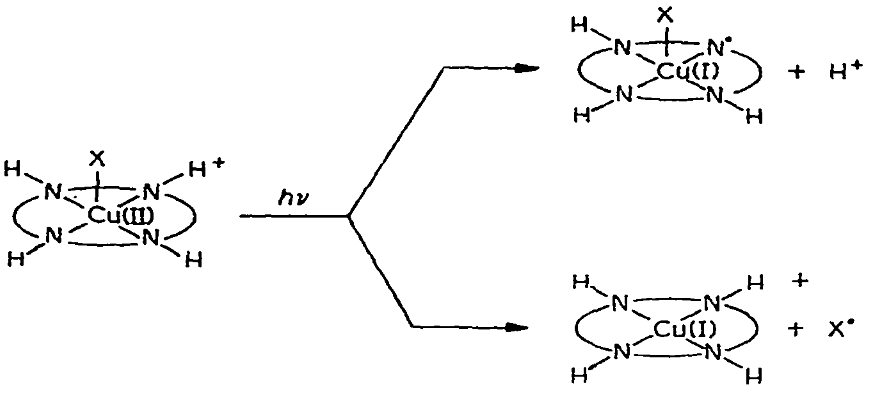


Fig. 5. Transient spectrum and product yields obtained in irradiations of acidic aqueous solutions of Cu(tet a)$^{2+}$. Spectrum determined 50 μs after an irradiation of 30 μs with polychromatic light. The absorptions at 370 nm corresponds to a short lived intermediate assigned as Cu(teta)$^{3+}$. The inset shows the distribution of open-cycle, Cu^{2+}(aq) and Cu^{+}(aq), and formaldehyde product yields for various concentrations of the scavenger methanol. Excitations at 254 nm.



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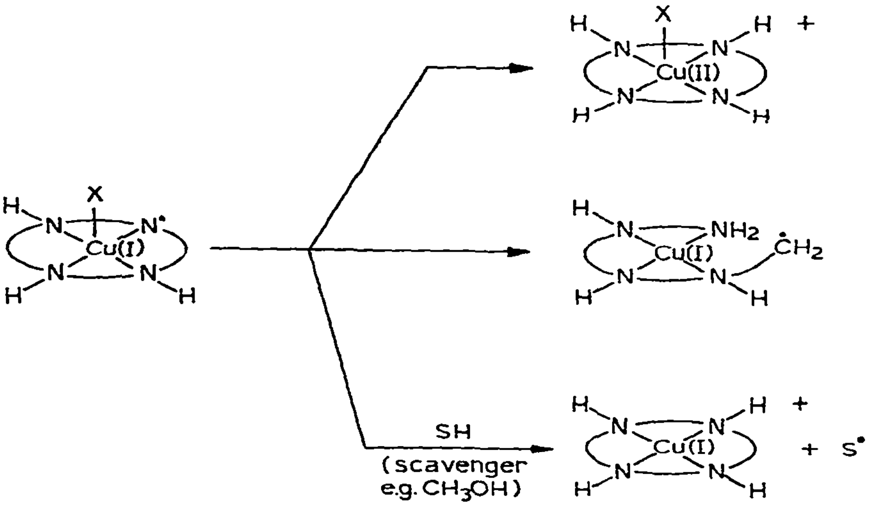

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(86)

The photoreactivity indicated above for tet a and tet b complexes is observed for excitation in a band with charge transfer amino to copper(II) character, CTTM$_{(N \to Cu(II))}$ in eqn. 82. The coordination of oxidizable ligands, namely Cl^- or Br^-, in axial positions produces modifications of the absorption spectrum. Part of the modifications in the ultraviolet region can be the result of new charge transfer transitions, namely CTTM$_{(X^- \to Cu(II))}$ with X^-: Cl^-, Br^-, in addition to CTTM$_{(N \to Cu(II))}$. The presence of new charge transfer transitions is supported by the photooxidation of Cl^- or Br^-. Such processes were observed as a new photochemical reaction of the Cu(tet a) X^+ and Cu(tet b) X^+, X: Cl^-, Br^-, in addition to the photooxidation of the macrocycle ligand, eqn. 83.

(f) Diketonate complexes

The ultraviolet irradiation of copper(II)—diketonate complexes generate copper(0) [83,84]. Products of the ligand or solvent oxidation have not been reported. The formation of Cu(0) was explained by a primary photoreduction of the metal center to Cu(I) followed by reduction to Cu(0) as it is indicated in eqns. 87—89.

$$\mathrm{CuL_2} \overset{h\nu}{\rightleftarrows} [\mathrm{CuLL\cdot}]^* \tag{87}$$

(L: 1,3-diketonate)

$$[\mathrm{CuLL\cdot}]^* \rightarrow \mathrm{CuL} + \mathrm{L\cdot} \tag{88}$$

$$\mathrm{CuL} \rightarrow \mathrm{Cu(0)} + \mathrm{L\cdot} \tag{89}$$

It is possible that ligand radicals, formed in reactions 88 and 89, are scavenged by solvent ethanol. Moreover Cu(0) can originate in a disproportionation process, eqn. 90, instead of the ligand oxidation, eqn. 89.

$$2\ \mathrm{CuL} \rightarrow \mathrm{CuL_2} + \mathrm{Cu(0)} \tag{90}$$

The disproportionation, eqn. 90, is consistent with an induction period for the formation of Cu(0). Such a period would be required for a build up of a steady-state concentration of CuL. Lintvedt et al., have provided some evidence of the CuL participation as a reaction intermediate. These authors have also reported that the photochemical reaction is reversed in the dark. Such a behavior has been attributed to the acidic-complexing properties of the free 1,3-diketonates.

The threshold for the photochemistry of copper(II)-1,3-diketonates seems to be ~38.5 Kk. This energy corresponds to excitation at wavelengths of a band with CTTM character. In addition the yield of the photoreduction is in almost a linear relationship with the reduction potential of the ligand, Table 8. However, the energy of the charge transfer transitions, $\lambda_{max} \sim 250$ nm, is independent of the ligand reduction potential, Table 8. These results, namely the dependence of λ_{max} and ϕ on $\epsilon_{1/2}$ as shown in Table 8, have no explana-

TABLE 8

Selected redox, spectroscopic and photochemical properties of copper(II)-β-diketonate complexes

Ligand	$\epsilon_{1/2}$ [a]	λ (log ϵ) [b]	ϕ [c]
$CF_3COCH_2COCF_3$	+0.03	310(3.7); 246(4.19) 305; 245(4.26); 201(4.19)	0.36
$CF_3COCH_2COCH_3$	−0.17	318; 244(4.11)	0.28
$CH_3COCH_2COCH_3$	−0.50	333(3.6); 244(3.99)	0.18

[a] Half wave potentials for the reduction of the complexes in dioxane [113].
[b] Ultraviolet absorptions of the complexes [114,115]. Wavelengths in nm.
[c] Quantum yields for photodecomposition. Excitations at 254 nm [83,84].

tion in terms of the mechanism described above or the models for the charge transfer spectrum. This indicates that more experimental information must be required for a better understanding of the copper(II)-1,3-diketonate photochemistry.

The photochemical reduction of the bis(acetylacetonato) copper(II) was recently sensitized by some ketones [85]. No sensitization was observed when the sensitizers were aromatic hydrocarbons or fluorenone. The authors proposed a mechanism based on an electron transfer within an encounter complex, eqns. 91—95.

$$\mathrm{Cu(acac)_2 + S^* \rightarrow \underset{\text{encounter complex}}{[Cu(acac)_2; S^*]}} \qquad (91)$$

$$\mathrm{[Cu(acac)_2; S^*] \rightarrow \underset{\text{solvated ion pair}}{[Cu(acac)_2^{+\cdot}; S^{-\cdot}]}} \qquad (92)$$

$$\mathrm{[Cu(acac)_2^{+\cdot}; S^{-\cdot}] \rightarrow Cu(acac)_2^{+\cdot} + S^{\cdot-}} \qquad (93)$$

$$\mathrm{Cu(acac)_2^{+\cdot} \rightarrow Cu(acac)^+ +} \qquad (94)$$

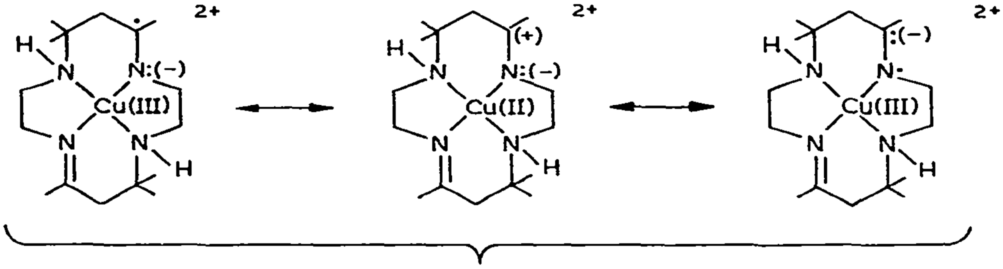
$$\mathrm{Cu(acac)^+ + S^{\cdot-} \rightarrow Cu(acac) + S} \qquad (95)$$

It has also been claimed that the photosensitized path leads to products with a better efficiency than the yield obtained in direct excitations.

(g) The charge transfer to ligand photochemistry

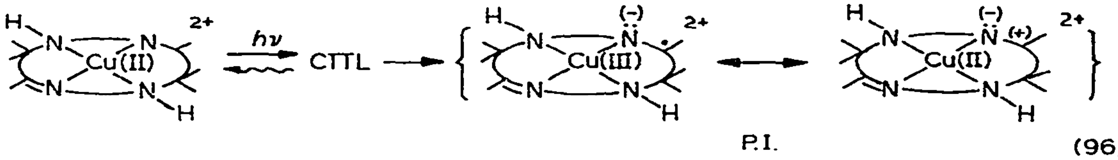
The tripositive oxidation state of copper gains stability by coordination of the metal to given ligands. Such stabilization brings the charge transfer to ligand states, CTTL, within accessible photon energies, namely less than 583 kJ mol^{-1}. Absorptions with charge transfer to ligand character have been reported, e.g., in the spectra of macrocyclic complexes of copper(II), Table 2. It is possible that CTTL transitions, in addition to CTTM and inner ligand, are present in the spectra of other copper(II) complexes.

The photochemical reactivity of the CTTL states in copper(II) complexes has been investigated for Cu([14]dieneN$_4$)$^{2+}$ (II) and Cu(13-AtH)$^{2+}$ (III) [73,86]. A primary species, P.I. (IV), with both acid—base and redox properties has been assigned as a product of the charge transfer irradiation of Cu([14]dieneN$_4$)$^{2+}$, eqn. 96. In this regard the intermediate has been described



P.I.(IV)

as a copper—ligand radical with an oxidized metal center and increased electron density on the ligand. In aqueous solutions the P.I. is protonated and undergoes hydrolysis, eqns. 97—100. Reactions of P.I. in pure methanol produce a partial hydrogenation of the ligand, eqns. 101—104. Indeed, the scavenging with hydrogen ions and methanol has suggested that such a species survives no more than a few collisions [73].



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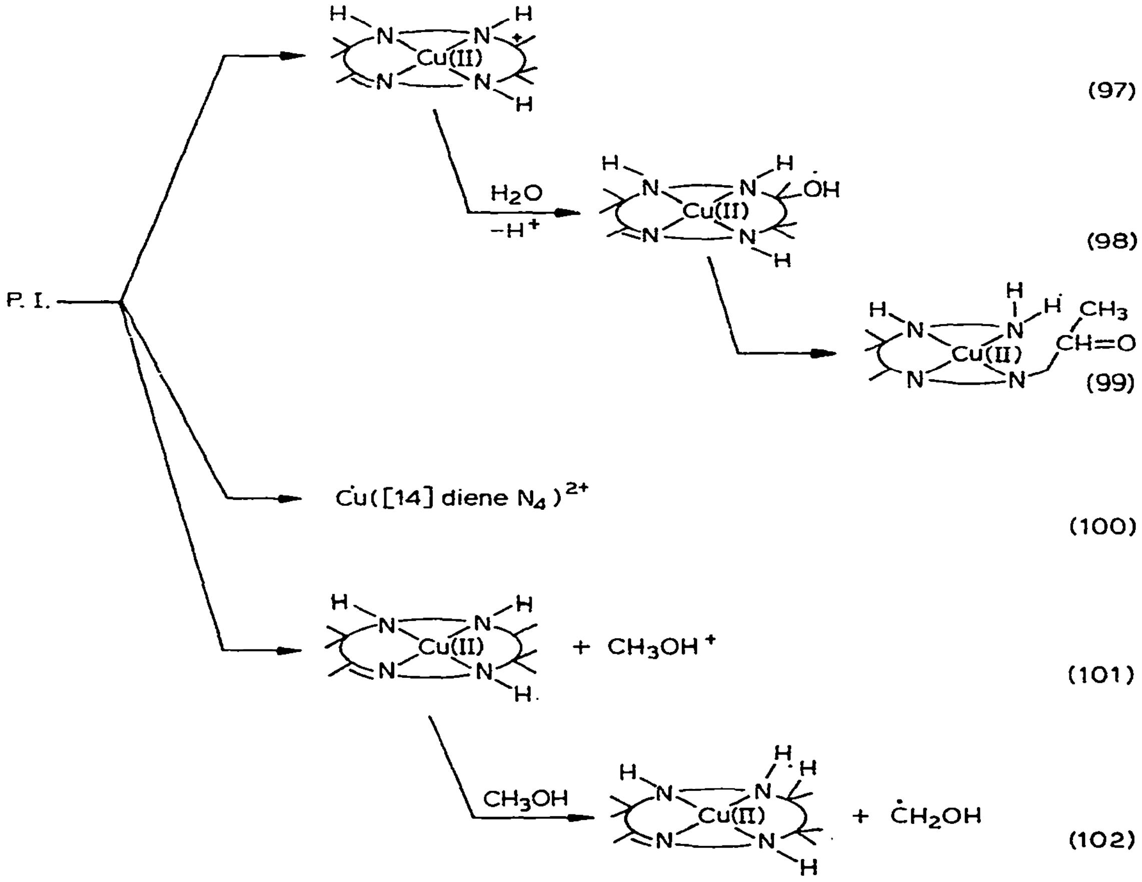


(97)

(98)

(99)

(100)

(101)

(102)

$$CH_3OH^+ + CH_3OH \rightarrow CH_3OH + H^+ + \dot{C}H_2OH \quad (103)$$

$$\dot{C}H_2OH + Cu([14]dieneN_4)^{2+} \rightarrow CH_2O + Cu([14]dieneN_4)^+ + H^+ \quad (104)$$

The photochemistry of Cu(13-AtH)$^{2+}$ presents similar features [86]. However, the primary intermediate, P.I., of Cu(13-AtH)$^{2+}$ behaves as a good oxidant and can be scavenged by alcohols in water—alcohol mixtures. The threshold for photochemical reactivity in Cu(13-AtH)$^{2+}$ is reached at photon energies smaller than for Cu([14]dieneN$_4$)$^{2+}$, Fig. 6. The limiting quantum yield for Cu(13-AtH)$^{2+}$ is larger than for Cu([14]dieneN$_4$)$^{2+}$, Fig. 6. The differences between the photochemistries of Cu(13-AtH)$^{2+}$ and Cu([14]dieneN$_4$)$^{2+}$ have been attributed to distinct properties of the photoreactive CTTL states [86]. Such properties have been related to the influence of the macrocycle in the stabilization of the tripositive oxidation state of copper and in the determination of Franck—Condon contributions [73,86].

A notable absence of photochemical reactivity has been found in copper(II) complexes, where, the electron density of the metal participates in a π system with aromatic character, namely Cu(13-At)$^{+}$ (V) and Cu(14-pydieneN$_4$)$^{2+}$ (VI) [47]. The behavior of these compounds can probably be related with a decrease of the CTTL reactivity when the ligand-transferred

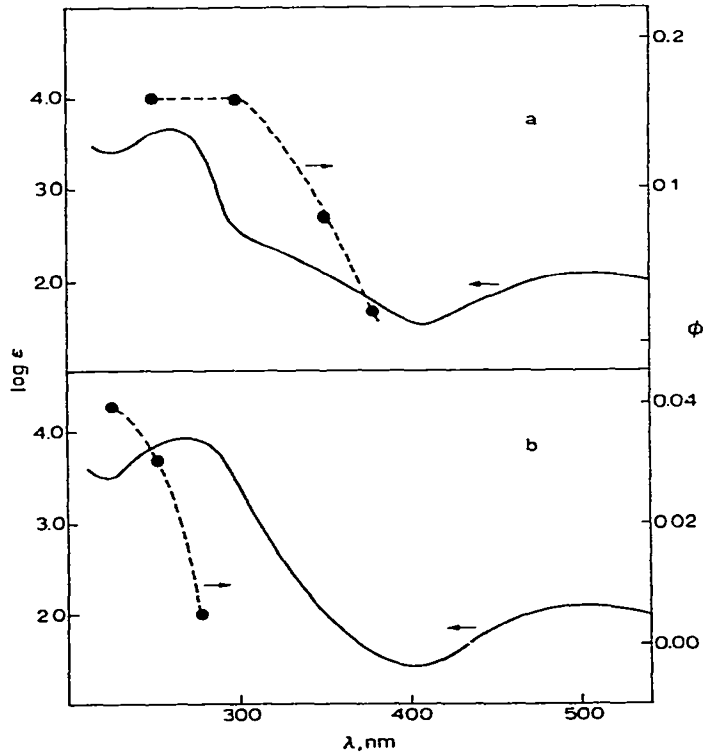
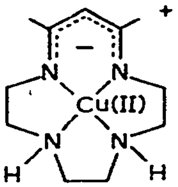
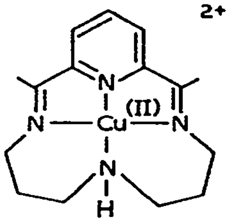


Fig. 6. Action and absorption spectra of Cu([14]dieneN$_4$)$^{2+}$ (a) and Cu(13-AtH)$^{2+}$ (b). Complexes irradiated in: (a) Cu([14]dieneN$_4$)$^{2+}$; deaerated methanolic solutions, (b) Cu(13-AtH)$^{2+}$; deaerated aqueous acidic solutions.



(V)

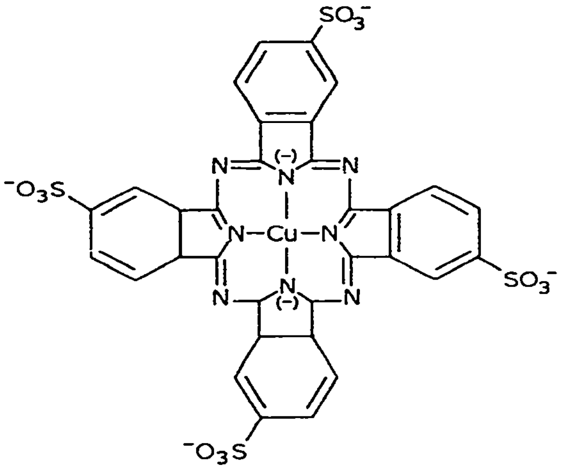


(VI)

charge is distributed through a π-system with aromatic character. In addition, the relaxation rate of the photoactive state can be dramatically increased in these types of aromatic structures.

(h) Photochemistry induced in inner ligand states

Although the visible and ultraviolet spectra of copper(II) complexes is largely composed of charge transfer transitions, the participation of ligand centered states must be considered. One example of this behavior, the photochemistry of copper(II) sulfophthalocyanine (VII), was recently reported [87,88].



VII

The ultraviolet irradiation of the dimeric copper(II) sulfophthalocyanine, $[Cu(PTS)]_2^{8-}$, produces a photodissociation in Cu(II)—ligand radicals which either recombine or participate in redox reactions with scavengers, namely alcohols or dioxygen, eqns. 105 and 106 [87]. The oxidized Cu(II)—ligand

$$[Cu(PTS)]_2^{8-} + h\nu \rightarrow [Cu(P\dot{T}S)]^{5-} + [Cu(P\dot{T}S)]^{3-} \qquad (105)$$

$$[Cu(P\dot{T}S)]^{5-} + [Cu(P\dot{T}S)]^{3-} \rightarrow [\dot{C}u(PTS)]_2^{8-} \qquad (106)$$

radicals can abstract hydrogen from 2-propanol. This reaction produces an isomer, $Cu(PTSH)^{3-}$, of the $Cu(PTS)^{4-}$ which undergoes a deprotonation assisted by dimerization, eqns. 107—110 [87]. Conversely, the reduced

$$Cu(P\dot{T}S)^{3-} + (CH_3)_3COCH \rightarrow Cu(PTSH)^{3-} + (CH_3)_2\dot{C}OH \qquad (107)$$

$$2(CH_3)_2\dot{C}OH \rightarrow (CH_3)_2CO + (CH_3)_2CHOH \qquad (108)$$

$$2\ Cu(PTSH)^{3-} \rightarrow [Cu(PTS)]_2^{8-} + 2\ H^+ \qquad (109)$$

$$Cu(PTSH)^{3-} + Cu(PTS)^{4-} \rightarrow [Cu(PTS)]_2^{8-} + H^+ \qquad (110)$$

Cu(II)—ligand radical interacts with dioxygen forming a new intermediate, $[Cu(PTS)(O_2)]^{5-}$, capable of a reaction with the oxidized Cu(II)—ligand radical, eqns. 111 and 112 and Fig. 7.

$$Cu(P\dot{T}S)^{5-} + O_2 \rightarrow [Cu(PTS)(\dot{O}_2)]^{5-} \qquad (111)$$

$$[Cu(PTS)(\dot{O}_2)]^{5-} + Cu(P\dot{T}S)^{3-} \rightarrow [Cu(PTS)]_2^{8-} + O_2 \qquad (112)$$

The photochemical reactivity of the monomeric copper(II) sulfophthalo-

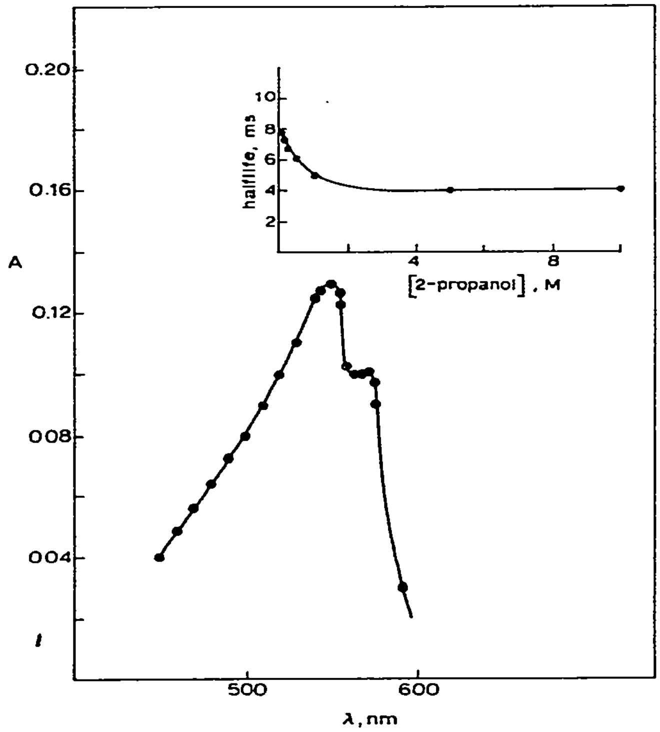


Fig. 7. Transient spectrum of $Cu(P\dot{T}S)^{3-}$ and $Cu(P\dot{T}S)^{5-}$ generated in flash irradiations of deaerated aqueous solutions of $[Cu(PTS)]_2^{8-}$. Spectrum obtained 50 μs after the irradiation. The inset shows the dependence of the half life-time of the intermediates in the concentration of the scavenger, 2-propanol.

cyanine is in agreement with population of an excited state which is more oxidizing than the ground state [87]. Indeed, it has been reported that this state is capable of hydrogen abstraction from 2-propanol, eqns. 113 and 114 [87,88].

$$\mathrm{Cu(PTS)^{4-}} \overset{h\nu}{\rightleftarrows} {}^{*}[\mathrm{Cu(PTS)^{4-}}]^{*} \qquad (113)$$

$$^{*}[\mathrm{Cu(PTS)^{4-}}] + \mathrm{(CH_3)_2CHOH} \rightarrow \mathrm{Cu(P\dot{T}S)^{5-}} + \mathrm{(CH_3)_2\dot{C}OH} \qquad (114)$$

It is worthwhile noting that the photoredox reactions of the dimeric and monomeric copper(II) sulfophthalocyanine fail to change the oxidation state of the metal center [87]. This behavior is different from the photoprocesses exhibited by cobalt(II) sulfophthalocyanine where the photodissociation of the dimer and mixed dimers produce Co(I) and Co(III) species [88]. In this regard one must conclude that the participation of the metal orbitals in the excited state of the copper(II) sulfophthalocyanine is not very large. This is probably reflected in the large stability of the Cu(II)—ligand radical species with respect to the Cu(I) and Cu(III) complexes. The nature of the photoreactive excited state has been described as a possible charge transfer state between units of the dimer or a state localized in one unit of the dimer with strong oxidizing character. The last possibility gains support from the observed photoredox behavior of the monomeric species.

The photochemistries of complexes of Cu(II) with Schiff bases might also have origin in ligand centered states. Indeed, the irradiation of the $\mathrm{Cu(dmg)_2}$ induces a redox decomposition of the complex. Copper(I) and $\mathrm{NO_2^-}$ in a 2 : 1 ratio were the products of the photoreaction. Flash photolysis experiments suggest that NO might be a precursor of metastable nitroxide complexes which generate the final $\mathrm{NO_2^-}$ product. The photochemistry of the $\mathrm{Cu(dmg)_2}$ is very important for excitations in a region where the free ligand has strong absorptions. However, the photoreactivity is characteristic of a charge transfer state. This observation suggests that a reactive CT state is more efficiently populated from a ligand centered state than from direct absorption of light in charge-transfer bands [89]. The existence of a photoreactive ligand centered state is also possible.

(ii) Charge transfer photochemistry of copper(I) complexes

(a) Charge transfer to solvent

The ultraviolet irradiation of copper(I) complexes with halides and pseudohalides induces the photogeneration of solvated electrons [28,36,90,91]. One example of this behavior is found in the photochemistry of $\mathrm{CuCl_3^{2-}}$. The generation of solvated electrons has been demonstrated by scavenging with $\mathrm{N_2O}$ or acetone and direct observation by flash photolysis. The primary generated electrons are intercepted by hydrogen ions in the absence of other scavengers. Such a reactivity is illustrated in eqns. 115 and 116.

$$\mathrm{CuCl_3^{2-}} \overset{h\nu}{\rightleftharpoons} \mathrm{CTTS} \rightarrow \mathrm{CuCl_3^-} + e^-_{aq} \qquad (115)$$

$$e^-_{aq} + \mathrm{H^+} \rightarrow \mathrm{H\cdot} \qquad (116)$$

The production of a secondary copper(II)—hydride, detected by flash photolysis, is formed when hydrogen atoms, Fig. 8, react with excess $\mathrm{CuCl_3^{2-}}$, eqns. 115—122 [28]. In addition, the formation of hydrogen has been attributed to the acid decomposition of the hydride, eqn. 119. Other transients, observed after the decomposition of the intermediate hydride, were assigned as mixed valence species, namely $\mathrm{Cu_2Cl_6^{3-}}$ and/or $\mathrm{Cu_2Cl_5^{2-}}$, as indicated in eqns. 120—122 [92].

$$\mathrm{H\cdot} + \mathrm{H\cdot} \rightarrow \mathrm{H_2} \qquad (117)$$

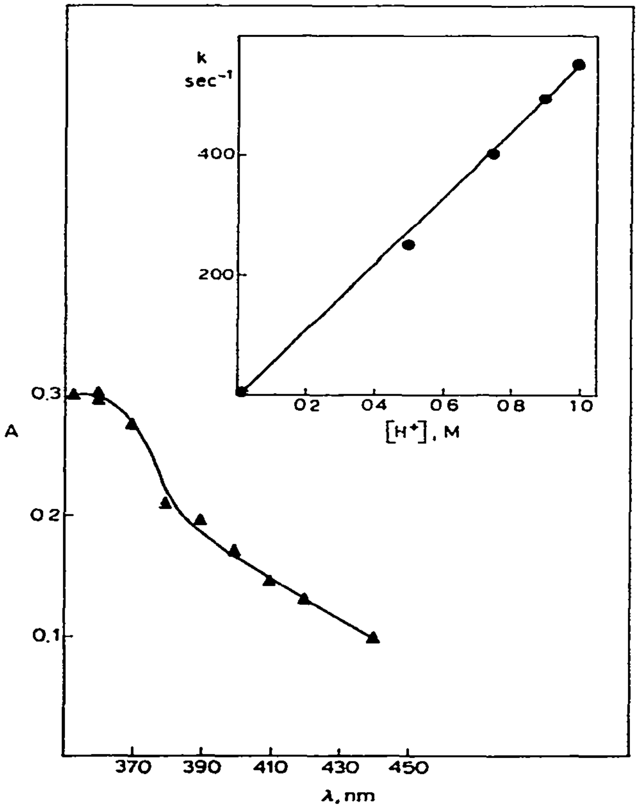


Fig. 8. Spectrum of the metastable copper—hydride, $\mathrm{HCuCl_3^{2-}}$, determined 500 μs after the flash irradiation of cuprous chloride. The inset shows the dependence of the rate constant for the decay of the copper—hydride on acid concentration.

$$H\cdot + CuCl_3^{2-} \rightarrow HCuCl_3^{2-} \quad (118)$$

$$H^+ + HCuCl_3^{2-} \rightarrow H_2 + CuCl_3^- \quad (119)$$

$$CuCl_2^- + Cl^- \rightarrow CuCl_3 \quad (120)$$

$$CuCl_2 + CuCl_3^{2-} \rightarrow Cu_2Cl_5^{2-} \quad (121)$$

$$CuCl_3^- + CuCl_3^{2-} \rightarrow Cu_2Cl_6^{3-} \quad (122)$$

The photochemical behavior of $CuBr_3^{2-}$ is comparable with that of $CuCl_3^{2-}$. Indeed, the photodissociation in solvated electrons has also been proved by flash photolysis and continuous wave photolysis [28].

It is possible to find photoactive CTTS states in copper(I) complexes with ligands different from the halides and pseudohalides. However, one must take into consideration the competitive population, either by direct absorption of light or by internal conversion, of intraligand and/or CTTL states.

(b) Charge transfer to ligand

A large number of copper(I) complexes exhibit intense optical absorptions that can be assigned to charge transfer to ligand transitions, Table 3. These CTTL states are able to induce distinct reactions in other substrates that are present in solutions of the Cu(I) complexes.

(c) Electron transfer reactions

Electron transfer reactions, induced in CTTL states, have been claimed for a number of Cu(I) complexes. Both intermolecular electron transfer between a CTTL state of a Cu(I) complex and a ground state Co(III) complex and intramolecular in a Cu(I)—Co(III) dinuclear complex have been reported.

McMillin et al. reported that the irradiation of bis(2,9-dimethyl-1,10-phenanthroline)copper(I) $Cu(dmp)_2^+$, can induce the reduction of cobalt(III) complexes as is shown in eqn. 123 [93,94].

$$Cu(dmp)_2^+ + Co^{III}L \xrightarrow{h\nu} Cu(dmp)_2^{2+} + Co^{II}L \quad (123)$$

These reactions have been explained in terms of an excited state mechanism, eqns. 124—129 [93]. The value of the ratio $k_d/(k_r + k_{ET})$, shown in Table 9, presents a large dependence on the nature of the cobalt(III) complex and excitation wavelength. Such a dependence on excitation energy suggests that more than one state participates in the electron transfer reaction. The participation of more than one state would be in agreement with various components detected in the emission of $Cu(phen)(PPh_3)_2^+$ [16]. However, $Cu(dmp)_2^+$ emmision spectrum exhibited a single band with $\lambda_{max} \sim 740$ nm in CH_2Cl_2 at room temperature [16b,47]. Such emission has a half lifetime $t_{1/2} \sim 64$ ns and a yield $\phi \sim 10^{-4}$ in CH_2Cl_2. The addition of methanol, ethanol or acetonitrile to CH_2Cl_2 quenches the emission [16b,47]. Also, aqueous solutions of $Cu(dmp)_2^+$ exhibited negligible emission [16b].

TABLE 9

Photoinduced electron transfer reactions of $Cu(dmp)_2^+$. Results from Stern—Volmer plots

Co(III)—acceptor	λ_{exc} [b]	Slope	Intercept	$k_d/(k_{ET} + k_r)$	$(k_{ET} + k_r)$ [a]
cis-$Co(IDA)_2^-$	454	0.86	9.36	0.092	1.2×10^9
trans-$Co(IDA)_2^-$	454	0.86	6.13	0.14	7.7×10^7
trans-$Co(IDA)_2^-$	365	1.19	1.58	0.075	1.4×10^8
trans-$Co(NH_3)_4(CN)_2^+$	454	9.77	[illegible].2 × 10^2	0.014	7.7×10^8

[a] The values in this column were obtained with $k_d \sim 1.1 \times 10^7$ sec^{-1}. Such a rate constant for the relaxation corresponds to $t_{1/2} \sim 64 \times 10^{-9}$ s for the reactive excited state. In this regard, the values of this column *can be used as an upper limit* of the constants.

[b] Excitations of $Cu(dmp)_2^+$ in aqueous deaerated solutions.

$$Cu(dmp)_2^+ + h\nu \rightarrow {}^*Cu(dmp)_2^+ \tag{124}$$

$$^*Cu(dmp)_2^+ \xrightarrow{k_d} Cu(dmp)_2^+ \tag{125}$$

$$^*Cu(dmp)_2^+ + Co(III) \xrightarrow{k_{ET}} Cu(dmp)_2^+ + {}^*Co(III) \tag{126}$$

$$^*Cu(dmp)_2^+ + Co(III) \xrightarrow{k_r} \{Cu(dmp)_2^{2+}, Co(II)\} \tag{127}$$

$$\{Cu(dmp)_2^{2+}, Co(II)\} \xrightarrow{k_p} \text{redox products} \tag{128}$$

$$\{Cu(dmp)_2^{2+}, Co(II)\} \xrightarrow{k_b} Cu(dmp)_2^+ + Co(III) \tag{129}$$

It would be of special interest to determine the reasons for the quenching of the emission by the solvent. Indeed, if this quenching involves a state which is precursor of the emissive state, the emission lifetime would not be affected. Although, the emissive state would be produced in small yields as a consequence of the solvent quenching, the electron transfer to cobalt(III) complexes, Table 9, would still be a feasible process. Parameters for the electron transfer quenching of the excited state are indicated in Table 9, where the lifetime of the excited state has been assumed to be 64 ns, namely $k_d \sim$ 1,1 × 10^7 sec^{-1}. The presence of high energy photoreactive states in Cu-$(dmp)_2^+$, namely in the near ultraviolet region, can explain the observed photogeneration of radicals.

Cuprous ions form adducts with organic acids containing unsaturated carbon—carbon bonds and with their pentaaminecobalt(III) or pentaaquochromium(III) complexes [34]. The mixed dimers exhibited a 1 : 1 stoichiometry. The coordination in these species has been described in terms of the Dewar—Chatt π-complexation model.

The thermal electron transfer, namely eqn. 130, has been found to be extremely slow, $t_{1/2} > 5$ years. However, the redox reactions are induced by

$$Co(NH_3)_5OCOL^{2+} + Cu^+ + 6\ H^+ \rightarrow Co^{2+} + Cu^{2+} + 5\ NH_4^+ + LCO_2H \qquad (130)$$

irradiation of the mixed valence complexes at wavelengths of some characteristic absorptions. Such absorptions, Table 10, are different from those of the Cu(I); $Co^{III}(NH_3)_5$ and $Cr^{III}(NH_3)_5$ chromophores and have been attributed to charge transfer metal to ligand transitions. This assignment is consistent with the correlation between half-wave potentials for reduction of the organic ligand and the energies of the transitions, see Table 10.

The mechanism of the photoinduced electron transfer either superexchange or radical ion, in systems with π-conjugation between metal centers has not been established yet. The photoinduced electron transfer process can occur in systems without π-conjugation between metal centers. These reactions may take place by a mechanism which involves intermolecular electron transfer by means of a ligand—radical complex, eqns. 131 and 132.

$$Co(NH_3)_5OCOLCu^{3+} + h\nu \rightarrow Co(NH_3)_5OCOL^{\cdot +} + Cu^{2+} \qquad (131)$$

$$Co(NH_3)_5OCOL^{\cdot +} + Co(NH_3)_5OCOL^{2+} \xrightarrow{H^+} Co(NH_3)_5OCOL^{2+} + Co^{2+} + 5\ NH_4^+ + LO_2H \qquad (132)$$

The observation of long lived Co(III)—ligand radicals lends some support to this possibility [95—97]. An alternative proposal involves the direct overlap of cobalt acceptor and ligand radical anion π^*-donor orbitals.

TABLE 10

Properties of cobalt(II)—copper(I), $Co^{III}(NH_3)_5$—organic acid—Cu^I, mixed valence complexes [a]

Bridge (organic acid)	λ_{max}(nm)		$K_f(T)$ [d]	$\epsilon_{1/2}$
	Bridge [b]	Mixed valence complexes [c]		
Fumarate	358; 270	348; 270	15(5); 4.4(23); 1.5(40)	—1.69
Maleate	340; 260	343; 265	40(23)	—1.82
Acrylate	318	305		—2.14
Cinnamate	345	340		—2.46
Propiolate	303	285		—2.36
Vinylacetate	280	280		<—3.05
Allylacetate	276	280		<—3.05

[a] Values from ref. 34.

[b] Absorptions of the organic acid functioning as a bridge.

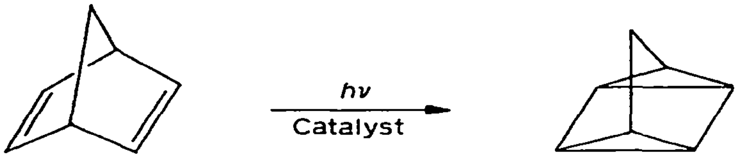
[c] Mixed valence absorptions in Cu(I)—Co(III) mixed valence complexes.

[d] Equilibrium constants for Co(III)—Cu(I) mixed dimer formation. Temperatures, in °C, given in parenthesis

[e] Half wave reduction potentials of the methyl esters.

(d) Photocatalytic reactions

A number of photochemical processes have been reported where copper(I) compounds catalyze these reactions. One example, that has been recently investigated, is the copper(I) photoassisted valence isomerization of norbornadiene, eqn. 133 [38,98]. The addition of cuprous salts, namely CuCl, CuBr, CuI or CuOAc, to norbornadiene solutions produce 1 : 1, eqn. 134, and 1 : 2, eqn. 135, complexes.



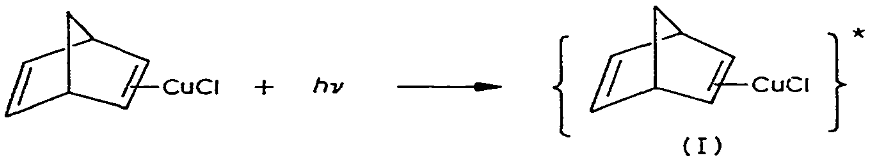
(133)

$$\mathrm{CuCl + NBD \rightarrow ClCu{-}NBD} \qquad (134)$$

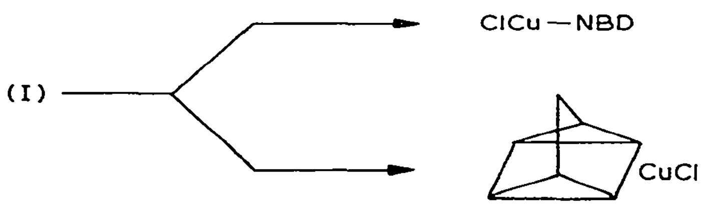
$$\mathrm{ClCu{-}NBD + NBD \rightarrow ClCu{-}(BD)_2} \qquad (135)$$

The bonding of NBD to Cu(I) in these species has been described in terms of the π-model of Chatt and Dewar. In addition, the new absorptions, observed in the spectra of these compounds, have been assigned to charge transfer transitions. These Cu(I)—NBD adducts seem to be photoactive species in the valence photoisomerization. In this regard, the absence of any dependence of both the quantum yield and the spectrum on CuCl concentration has been attributed to the existence of a single species, namely ClCu—NBD, in these solutions.

A general mechanism for the photoassisted isomerization has been proposed by Schwendiman and Kutal [38]. In the first step the photoactive species is formed upon the rapid mixing of the reagents, i.e.: eqns. 134 and 135. The second step occurs when Cu(I)—NBD species are irradiated at wavelengths of the charge transfer transitions, eqns. 136—138. Step 3 takes into



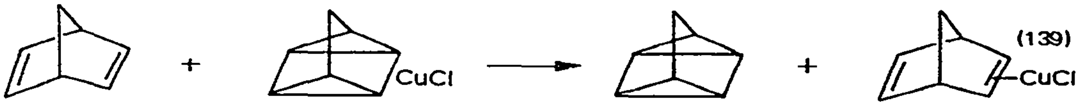
(136)



(137)

(138)

consideration the regeneration of the catalyst, eqn. 139.



(139)

Excited states, namely singlet or triplet, charge transfer or ligand centered π—π^* states, can be considered as the precursor (I), eqn. 136 of the quadricyclene product. Indeed, ligand centered π—π^* states might be populated by relaxation of the charge transfer states. The mechanism of quadricyclene formation, eqn. 138, will involve a reduction of the double bond character between C_1—C_2 and C_3—C_4 and an enhancement of this character between C_1—C_3 and C_2—C_4 in the excited state. Alternatively, another possible precursor is a carbonium ion, eqns. 140 and 141.

(140)

(141)

In addition to cuprous halides, the photoinduced valence isomerization of NBD has been obtained when Cu[HB(pz)$_3$]CO (HB(pz)$_3^-$ = hydrotris(1-pyrazolyl)borate) was the reaction catalyst [99]. The photocatalytic activity of this compound has been associated with photochemical properties of an adduct with norbornadiene. Such an adduct seems to be formed by displacement of coordinated carbon monoxide in a labile equilibrium, eqn. 142.

(142)

This NBD complex exhibits NBD—Cu(I) charge transfer absorptions which are similar to charge transfer absorptions observed in the spectrum of ClCu—NBD. In addition, there are no significant differences between the mechanisms of the ClCu—NBD and [HB(pz)$_3$]Cu—NBD photoinduced isomerization.

The valence isomerization of norbornadiene does not require the ground state coordination of the copper(I) complex to NBD. Phosphine complexes, namely Cu(PH$_3$)$_2$BH$_4$, are believed to catalyze by a mechanism different from that of the CuX salts, see above. Grutsch and Kutal have suggested the interaction of a photoexcited copper(I) with NBD as an alternative mechanism,

$$Cu(PH_3)_2BH_4 \overset{h\nu}{\rightleftarrows} [Cu(PH_3)BH_4)]^* \qquad (143)$$

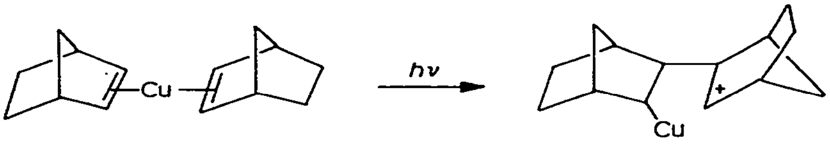
$$\downarrow NBD$$

$$[Cu(PH_3)BH_4^*, NBD] \qquad (144)$$

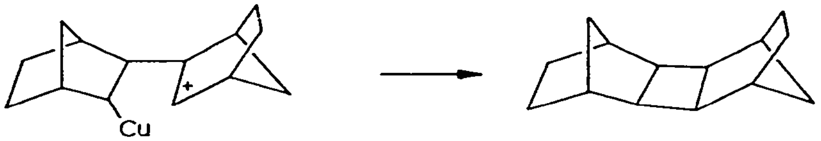
$$[Cu(PH_3)_2BH_4^*, NBD] \rightarrow \text{quadricyclene} \qquad (145)$$

eqns. 143—145 [100]. Such a proposition contemplates the possibilities of exciplex formation and energy transfer.

Many other olefin—copper(I) complexes have been used for the photoinduction of olefin reactions [101—111]. Kochi and co-workers have attributed the photodimerization of norbornene, from a 2 : 1 olefin—copper complex, to a carbonium ion intermediate, eqns. 146 and 147 [101—103].

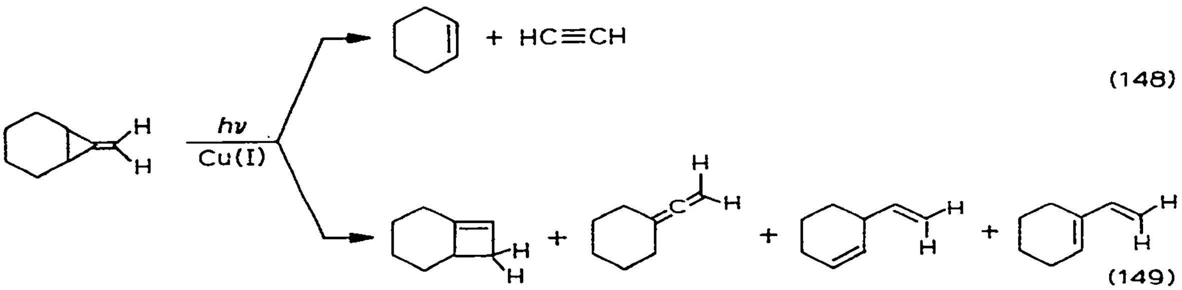


(146)



(147)

This type of reactivity has been successfully used by Salomon et al. With a number of different olefins [111]. Both photorearrangement and photofragmentation have been copper-catalyzed, e.g. as in eqn. 148, 149.



(148)

(149)

Differences have been found between the products of the photoreactions promoted by copper(I) species and those promoted by triplet sensitizers. This behavior suggests that copper(I) is able to induce photochemical reactions in a manner other than triplet sensitization.

(iii) Charge transfer photochemistry of copper(III) complexes

The photochemical decomposition of copper(III) peptide complexes has been recently reported by Margerum et al. [112]. Decarboxylation of the ligand and reduction of the metal center, $\phi = 0.18$ at $\lambda_{excit} = 468$ nm, have been observed in that photoprocess. Such observations suggest that low lying CTTM states are photoactive in these copper(III) species. This is in good agreement with assignments of the bands in the spectra of copper(III) complexes with peptide and macrocyclic ligands.

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