configurations is neglected, and the radiative lifetime of the metal-localized state is treated as a constant. The effects of movement of the $d\pi^*$ configuration relative to the dd^* configuration are incorporated in the ΔE factor in eq 2. Justification of the approach lies in the fact that two distinct $d\pi^*$ and $\pi\pi^*$ emissions are not simulataneously observed, indicating that as these configurations approach one another, they interact strongly to yield delocalized-molecular states, which are sufficiently split to prevent thermal back-population of the upper level. On the other hand, the observation of simultaneous thermally equilibrated delocalized-molecular and metal-localized emissions indicates that these states can approach each other closely without being split by mixing of the $d\pi^*$ and/or $\pi\pi^*$ configurations with the dd^* configuration.

This contrast in the degree of mixing of $d\pi^*$ and $\pi\pi^*$ configurations as opposed to $d\pi^*$ with dd^* configurations probably stems from geometric considerations. Promotion of an electron from either a nonbonding d orbital or ligand π orbital to a ligand π^* orbital appears to lead to only a small excited-state distortion as evidenced by the highly structured low-temperature emissions observed in these complexes. Promotion from a nonbonding d orbital to an antibonding d orbital leads to a large geometric distortion as evidenced by the broad red-shifted metal-localized emission. The mixing of $d\pi^*$ and $\pi\pi^*$ configurations with similar geometries should be substantially larger than that of $d\pi^*$ and dd^* configurations with very different geometries.

Summary and Conclusions. Luminescence Tuning and Its Applications

The present study provides evidence that inversion of metal-localized and delocalized-molecular states does occur when electron-withdrawing phenyl substituents are placed on the bpy or phen ligands in complexes of the type $IrCl_2(B)(B')^+$. This evidence is found in the values of lifetimes, emission yields, and τ/Q as well as in shapes of emission spectra in room-temperature fluid solutions.

The photophysical data resulting from this study have several significant implications with regard to the photochemistry of these complexes. Since inversion of delocalized-molecular and metal-centered states has been shown to occur, a significant change in photochemical properties (photochemical tuning) is anticipated. For example, the photochemical properties of $IrCl_2(4,7\text{-Phphen})_2$, which has a lowest energy delocalized-molecular state, may be quite different than those of $IrCl_2(phen)_2^+$, which has a low-energy metal-centered state. Furthermore, the availability of room-temperature lifetime data may render determination of photochemical rate constants feasible. This type of quantitative rate constant data has not been readily measurable in previous studies of photochemical tuning due to the absence of measurable room-temperature emissions.

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Registry No. $IrCl_2(phen)_2^+$, 17992-95-9; $IrCl_2(bpy)_2^+$, 47514-19-2; $IrCl_2(bpy\text{-}d_8)_2^+$, 75110-37-1; $IrCl_2(5,6\text{-Mephen})_2^+$, 53822-52-9; $IrCl_2(bpy)(5,6\text{-Mephen})^+$, 77320-95-7; $IrCl_2(4,7\text{-Phphen})_2^+$, 77320-96-8; $IrCl_2(4,4'\text{-Phbpy})_2^+$, 77320-97-9.

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Photochemistry of Copper(II) Complexes with Macrocyclic Amine Ligands

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The photochemical properties of $Cu(dl\text{-}Me_6[14]aneN_4)^{2+}$ and $Cu(rac\text{-}Me_6[14]aneN_4)^{2+}$ in the presence and absence of axially coordinated ligands have been investigated by continuous and flash irradiations. Flash photolysis of the complexes in deaerated aqueous solutions revealed the presence of copper–ligand radical complexes with closed- and open-cycle ligands. Flash photolysis of methanolic solutions of the complexes, in the presence of halides and pseudohalides, shows Cu(III) macrocyclic intermediates. The experimental observations can be explained in terms of two primary photoprocesses with origins in distinctive charge transfer to metal states. These states have been assigned as amino to copper(II) charge-transfer state and acido to copper(II) charge-transfer state.

Introduction

The photochemical properties of amino complexes of copper(II) have not been investigated in detail.[1] A report on the photochemistry of $Cu(en)_2^{2+}$ shows that ultraviolet irradiations induce the redox decomposition of the complex with formation of CO_2 and NH_3.[2] However, the irradiation and/or thermal decomposition of other species in solution complicate the interpretation of the results.[1,2] Some of the difficulties, introduced by the lability of $Cu(en)_2^{2+}$, can be resolved by using complexes of macrocyclic tetraamines, e.g., $dl\text{-}Me_6[14]aneN_4$ (I) and $rac\text{-}Me_6[14]aneN_4$ (II).[3] Moreover, these complexes, namely, $Cu(en)_2^{2+}$ and $Cu(macrocycle)^{2+}$, can be regarded as structuraly related species. Such a relationship makes it possible to extend the spectral assignments of the copper(II) ethylenediamines to the charge-transfer spectra of the macrocyclic amino complexes.[4,5]

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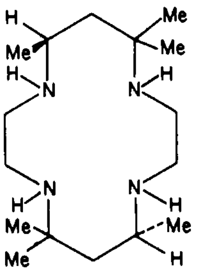
[1] For review on the subject see: Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: New York. Ferraudi, G.; Muralidharan, S. *Coord. Chem. Rev.*, in press.

[2] Shagisultanova, G. A.; Il'yukevich, L. A. *Zh. Neorg. Khim.* **1966**, *11*, 945.

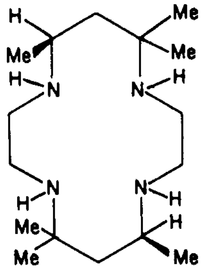
[3] Ligand abbreviations: $dl\text{-}Me_6[14]aneN_4$, *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; $rac\text{-}Me_6[14]aneN_4$, *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; $Me_6[14]dieneN_4$, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetra-4,11-diene.

[4] Yokoi, H.; Isobe, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2187.

0020-1669/81/1320-2306$01.25/0



(I) dl-Me$_6$ [14] aneN4



(II) rac-Me$_6$ [14] aneN4

The photochemical properties of the copper(II) macrocycles have been investigated in this work by continuous wave and flash photolysis. Our results support the presence of two photoreactive charge-transfer states that involve the amino and axially coordinated acido ligands, respectively.

Experimental Section

Photochemical Procedures. Continuous wave irradiations were carried out with a high-pressure xenon lamp, 300-Vix UV Eimac illuminator, coupled with a high-intensity monochromator, and collimating lenses. Details of this irradiation were previously described.[6,7] Relative values of light intensity were measured with a photocell–microvoltmeter. The absolute values were determined with tris(oxalato)ferrate(III)[8] or with bromopentaamminecobalt(III).[9]

The concentrations of the photolytes were adjusted in order to absorb more than 99.99% of the incident light. Solutions of the complexes were deaerated by vacuum or with streams of Ar. The homogeneity of the reaction medium was maintained by stirring the solutions with magnetic bars.

The apparatus used for flash irradiations was previously described.[10] Nevertheless, some of the basic features will be indicated here. Two FP-8-100C Xenon Corp. flash lamps were fired in series at energies adjusted to values between 250 and 40 J/pulse. A lifetime of 30 μs was measured for the flash pulse under these conditions. Hence, points for either kinetics or spectra determinations were regarded significant for times equal to or longer than 50 μs. The waveform recorder, a Biomation 805, was interfaced to a Digital PDP-8L processor. The raw data, stored in a digital form in the waveform recorder, was processed in the PDP-8L in order to obtain either rate constants or spectral information (the 8K Fortran programs and technical details of the entire apparatus will be described elsewhere). Solutions were irradiated at preselected wavelengths by using appropriate cut-off filters. Streams of Ar were used for the deaeration of the solutions.

Cobalt(III) complexes, namely, $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, and $Co(NH_3)_5OCOCH_3{}^{2+}$, were used for the generation of radicals, e.g., Cl_2^-, Br_2^-, and $CH_3\cdot$. Deaerated acidic solutions of the cobalt(III) complexes were flash irradiated at wavelengths of the charge-transfer transitions. The procedures used for these photolyses were previously reported (see ref 9 and references therein).

Electrochemical Procedures. The apparatus used for cyclic voltammetry was described elsewhere.[10] A 0.1 M KCl salt bridge separated the reference calomel electrode, third electrode, from the auxiliary and working electrodes. The auxiliary and working electrodes, made of platinum wire and platinum gauze, respectively, were specially treated in order to eliminate irreversible waves from impurities. These electrodes were oxidized with chromic acid and reduced with ferrous ammonium sulfate according to a procedure reported by Busch et al.[11] Moreover, traces of metallic copper, deposited during the determination of the cyclic voltammogram, were removed with 1:1 HNO_3. Solutions used in the electrochemical experiments were deaerated with streams of Ar. Customary calibrations of the apparatus were carried out with hexacyanoferrate(III) or benzoquinone.

Table I. Half-Wave Potentials for the Cu(I)/Cu(II) Couples and the Ligand Field Strength for Cu(*rac*-Me$_6$[14]aneN$_4$)$^{2+}$ with Various Axial Ligands

conditions	half-wave potential,[a] V	10^3D_z,[b] cm^{-1}	$D_z{}^c/D_e$
CH_3CN	−0.83	12.0	0.8
F^- (0.01 M)	−0.84	10.02	0.66
Cl^- (0.01 M)	−0.80	11.14	0.73
Br^- (0.01 M)	−0.93	8.46	0.55
I^- (0.0075 M)	−1.04	7.29	0.48
py (0.1 M)	−0.86	13.9	0.91
N_3^- (0.01 M)	−0.80	11.47	0.75
SCN^- (0.01 M)	−0.87	11.47	0.75
NO_2^- (0.01 M)	−0.67	16.71	1.09
CN^- (0.01 M)	−0.51	18.93	1.24

[a] With respect to SCE. [b] Ligand field stabilization parameters. Values obtained by procedures in: Figgis, B. N. "Introduction to Ligand Fields"; Wiley: London, 1966. Ballhausen, C. J. "Introduction to Ligand Field Theory"; McGraw-Hill: New York, 1962. [c] Ratio of the axial, D_z, to equatorial, D_e, ligand field stabilization parameters; see also footnote *b*.

Table II. Quantum Yields for Photoreactions of Cu(II) Macrocyclic Complexes in Methanolic Solutions

$10^3\phi_{CH_2O}$	$10^3\phi_{Cu(I)}$	conditions[a]
	Cu(*dl*-Me$_6$[14]aneN$_4$)$^{2+}$	
6.3		
6.3	11.3	5.0×10^{-3} M NaCl
7.7		7.5×10^{-3} M NaCl
15	28.7	10×10^{-3} M NaCl
11		50×10^{-3} M NaCl
9.1		100×10^{-3} M NaCl
6.9		10×10^{-3} M KBr
	Cu(*rac*-Me$_6$[14]aneN$_4$)$^{2+}$	
9.0		
22.6		1.0×10^{-3} M NaCl
19.5		5.0×10^{-3} M NaCl
17.4		10×10^{-3} M NaCl
10.9		50×10^{-3} M NaCl
8.7		100×10^{-3} M NaCl
14.5		5.0×10^{-3} M NaCl, 5.0×10^{-3} M HCl
11.3		1.0×10^{-3} M NaCl
10.0		10.0×10^{-3} M HCl

[a] $\lambda_{excit} = 254$ nm; $I_0 = 1.2 \times 10^{-4}$ einstein/(L·min). Vacuum deaerated solutions.

Analytical Procedures. Formaldehyde and other volatile compounds, namely, the solvent methanol or water, were separated from the copper complexes by vacuum distillation. Chromotropic acid was used for the determination of the isolated formaldehyde.[12] Free Cu^{2+}(aq) was investigated with iodide or with 2,9-dimethyl-1,10-phenanthrolineascorbic acid.[13] Free Cu^+(aq) was investigated with 2,9-dimethyl-1,10-phenanthroline.[13] The quantitative reaction of the copper(I) macrocycles with ferric ions was used for the analysis of these complexes. An excess of vacuum deaerated 0.01 M ferric nitrate was mixed with a given volume of the irradiated solution. The liquids were handled in a gas-tight apparatus. The concentration of Fe(II), equivalent to the total concentration of copper(I), was determined with 1,10-phenanthroline.[13] Solutions of the copper(II) complexes maintained in the dark were used for the preparation of blanks.

Materials. The copper(II) macrocycles, namely, [Cu(*dl*-Me$_6$[14]aneN$_4$)]$(ClO_4)_2$ and [Cu(*rac*-Me$_6$[14]aneN$_4$)]$(ClO_4)_2$, were synthesized according to procedures indicated elsewhere.[14-16] These

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(5) Kennedy, B. P.; Lever, A. B. P. *J. Am. Chem. Soc.* **1973**, *95*, 6907.
(6) Ferraudi, G. *Inorg. Chem.* **1979**, *18*, 1005.
(7) Ferraudi, G.; Srisankar, E. V. *Inorg. Chem.* **1978**, *17*, 3164.
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(14) Tait, A. M.; Busch, D. H. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 491.
(15) Curtis, W. F.; Hay, R. W. *Chem. Commun.* **1966**, 524.
(16) Curtis, N. F. *J. Chem. Soc.* **1964**, 2644.

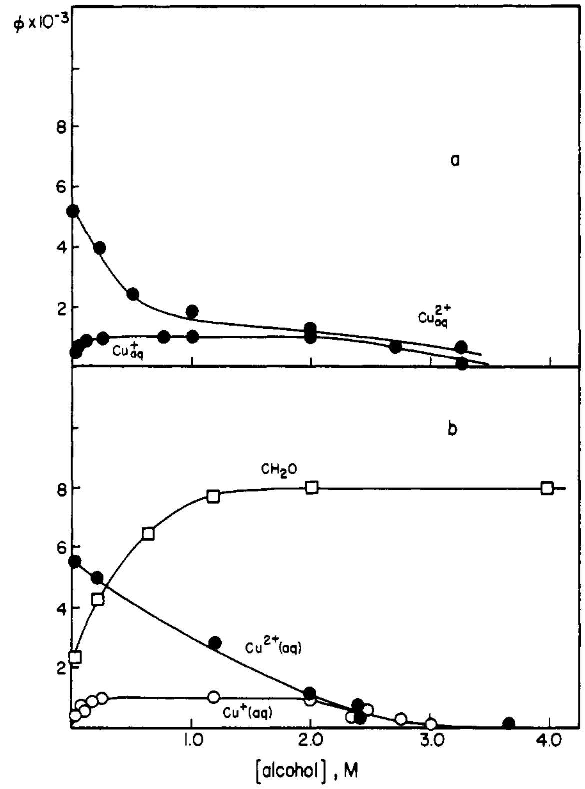

Figure 1. Distribution of product yields, obtained in photolyses of $Cu(dl\text{-}Me_6[14]aneN_4)^{2+}$ in aqueous deaerated solutions, with various concentrations of scavengers: (a) 2-propanol; (b) methanol (excitation at 254 nm, $I_0 = 2.5 \times 10^{-4}$ einstein/(L·min)).

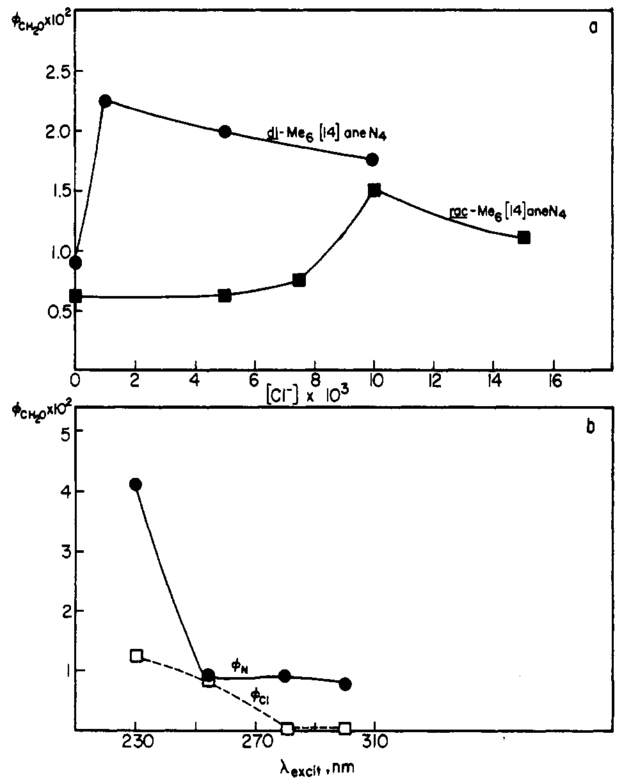

Figure 2. (a) Dependence of the limiting yield of formaldehyde on chloride ion concentration and (b) action spectrum for the oxidations of the macrocycle ligand, ϕ_N, and the axial chloride ligand, ϕ_{Cl}, in photolyses of $Cu(dl\text{-}Me_6[14]aneN_4)^{2+}$. These yields were calculated from the limiting values of ϕ_{CH_2O}, $\phi_{Cu(II)}$, and $\phi_{Cu(I)}$ with appropriate stoichiometric relationships.

compounds were recrystallized twice by adding solid $NaClO_4$ to their aqueous solutions. The UV–vis spectra agreed with previous reports.

Spectral quality methanol and acetonitrile were used without further purification. The rest of the chemicals were reagent grade. The solid compounds were dried under vacuum before the preparation of the solutions used in electrochemical or photochemical experiments.

Results

Nature of the Species in Solutions. The formation of a number of adducts between copper(II) macrocycles and various anions has been previously reported.[17-20] Also, the formation of pentacoordinated species in aqueous solutions was established.[20] This behavior can be extended to the copper(II) macrocycles investigated in this work. Indeed, the UV–vis spectra of the copper(II) complexes in methanol exhibited a large sensitivity to the concentration and nature of the anion X^-, namely, $X^- = Cl^-$, Br^-, I^-, or SCN^-, in solution.[21] Also, the half-wave potential of the Cu(I)/Cu(II) couples is determined by the anion X^- that is present in the solution of the complexes (Table I).[21] Such a dependence can be expressed as a linear function of the combined ligand field strengths of the anion X^-, D_z, and the macrocycle, D_e, as it has been predicted by Rock's relationship for a pentacoordinated copper(II) complex.[22]

Continuous Photolysis. Ultraviolet irradiations of the copper(II) macrocycles in deaerated aqueous solutions, 10^{-1}–10^{-4} M in $HClO_4$, induce the photodegradation of the complexes. The products of the photoreactions were identified as Cu^+(aq), Cu^{2+}(aq), and species originating in the photooxidation of the macrocycle ligand, e.g., formaldehyde and amines.

The yields of the photoproducts exhibited a large dependence on the concentration of radical scavengers, namely, methanol or isopropyl alcohol. Indeed, the dependence of the product yields on scavenger concentration is shown in Figure 1 for photolyses of $Cu(dl\text{-}Me_6[14]aneN_4)^{2+}$. The yield of Cu^+(aq), $\phi_{Cu(I)}$, increases with alcohol concentration until it reaches a constant figure. However, concentrations of alcohol larger than 2.0 M produces a decrease in the value of $\phi_{Cu(I)}$. In addition the yields of formaldehyde, ϕ_{CH_2O}, and Cu^{2+}(aq), $\phi_{Cu(II)}$, increase to a constant value, $\phi_{CH_2O} \approx 8.0 \times 10^{-3}$, and decreases to zero, $\phi_{Cu(II)} \leq 10^{-5}$, with alcohol concentrations (Figure 1). Such dependences of $\phi_{Cu(I)}$, $\phi_{Cu(II)}$, and ϕ_{CH_2O} on scavenger concentration reveal that the scavengers intercept several intermediates (see below).

The 254-nm irradiations of the macrocyclic complexes in 100% methanol fail to induce the photooxidative degradation that is described above. Copper(I) macrocycles, e.g., $Cu(rac\text{-}Me_6[14]aneN_4)^+$ and formaldehyde, were characterized as photolysis products. Neither free Cu(II), $\phi_{Cu(II)}$, $\leq 10^{-5}$, nor free Cu(I), $\phi_{Cu(I)} \leq 10^{-5}$, were detected in these experiments. Secondary photolysis, coupled to the large instability of the copper(I) macrocycles, demanded that irradiations be limited to very small conversions. Indeed, the formation of metallic copper was observed in solutions that were irradiated for extended periods.

The presence of halides or pseudohalides in methanolic solutions of the copper(II) complexes affects the distribution of the photolysis products. Figure 2a shows the variation of the formaldehyde yield with chloride concentration for 254-nm photolyses of $Cu(dl\text{-}Me_6[14]aneN_4)^{2+}$ and $Cu(rac\text{-}Me_6[14]$-

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(17) Duggan, D. M.; Jungst, R. G.; Mann, K. R.; Stucky, G. D.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1974**, *96*, 3443.

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(21) We have observed complexities in the dependence of the spectra and cyclic voltammograms on the concentration of halides or pseudohalides. Such a behavior has been interpreted in terms of complex equilibria that involve minor concentrations of different copper(II) adducts.

(22) Rock, P. A. *Inorg. Chem.* **1968**, *7*, 837.

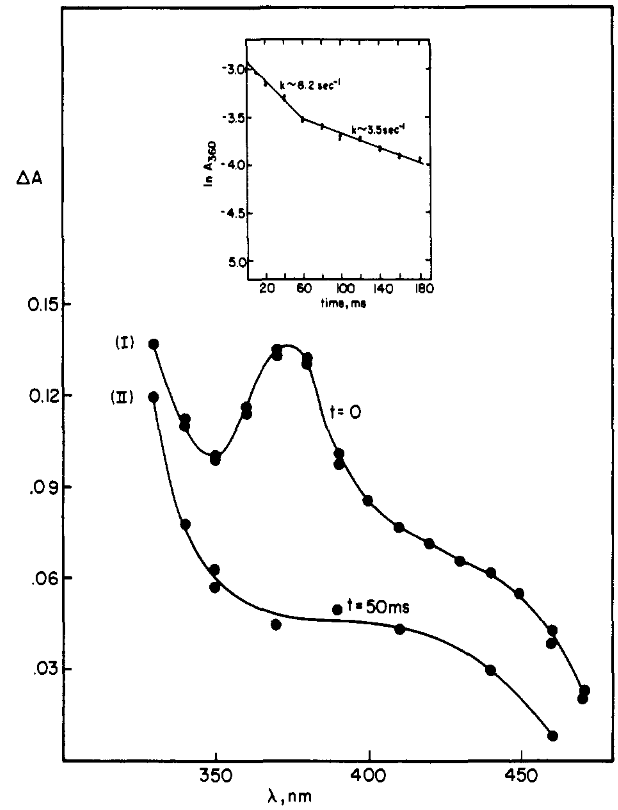

Figure 3. Transient spectrum in flash photolysis of Cu(*dl*-Me_6-[14]aneN_4)$^{2+}$ in aqueous deaerated solutions. The inset shows the decay of the transient absorbances at long reaction times (excitation at $\lambda_{excit} \geq 220$ nm with 250 J/flash pulses).

ane)$^{2+}$. Such a variation of the product distribution can be explained in terms of an increase in the concentration of the pentacoordinated species Cu(macrocycle)Cl^+ with chloride ion concentration. In addition, the pentacoordination introduces marked differences in the action spectrum (see Figure 2). These differences have been related to secondary processes (see below) with origin in two different primary photoreactions, namely, the photooxidation of the axial and macrocycle ligands in pentacoordinated species (Figure 2b and Table II).

Flash Photolysis. Flash photolysis, $\lambda_{excit} \geq 210$ nm, of Cu(*dl*-Me_6[14]aneN_4)$^{2+}$ in deaerated aqueous acidic solutions produces transient absorptions with $\lambda_{max} \approx 360$ nm, (Figure 3). The time resolved spectrum (Figure 3) reveals the presence of two different reaction intermediates at reaction times shorter than 50 ms. One intermediate, $\lambda_{max} \approx 360$ and $t_{1/2}$ ~200 μs, is shorter lived than the second one, $\lambda_{max} < 330$ nm and $t_{1/2} \approx 30$ ms. The decay of the short-lived, SL, and long-lived, LL, intermediates exhibited first-order dependences in transient concentration and a zero order in hydrogen ion concentration. A radical nature, namely, copper(I) or copper(II)–ligand radical, was attributed to these species. Indeed, the long-lived species, LL, can be scavenged by 2-propanol, 1.0×10^{-5}M ≤ [2-propanol] ≤ 1.0 10^{-2} M, with a rate constant of $k = 5.0 \times 10^5$ M^{-1} s^{-1} (Figure 4). The interception of the short-lived species, SL, requires a high concentration of the scavenger, namely, [2-propanol] ≥ 2.0 M or [methanol] ≥ 2.5 M.

The decay of the LL intermediate, in the absence of scavengers, leaves residual absorbances which can be observed at reaction times longer than 50 ms (see inset in Figure 3). Such absorbances disappear by a process with a large dependence on the acid concentration (Figure 5). Methanol or 2-propanol have no effect on the rate of the decay at concentrations smaller than those required for the scavenging of LL. This reactivity suggests that the transient absorptions can be assigned as copper(II) complexes with an open-cycle ligand.

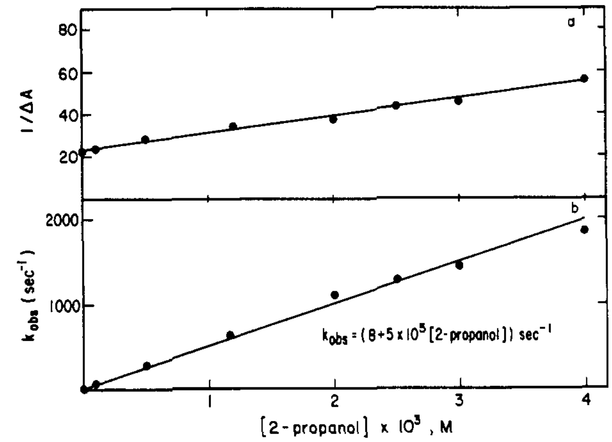

Figure 4. Scavenging of the long-lived species, LL, by 2-propanol. Dependence of (a) reciprocal of the transient absorbance and (b) decay rate constant on scavenger concentration (excitations at $\lambda_{excit} \geq 220$ nm with 250 J/pulse).

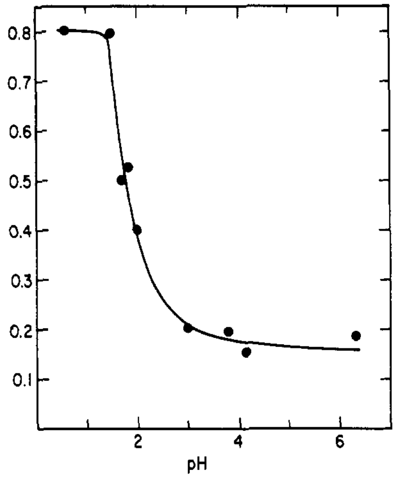

Figure 5. Dependence on acid concentration of the rate constant(s) for the final reaction stage(s). Flash irradiations of Cu(*dl*-Me_6-[14]aneN_4)$^{2+}$ in deaerated aqueous solutions (excitations at $\lambda_{excit} \geq 220$ nm with 300 J/pulse).

Flash irradiations of the copper(II) macrocycle were carried out in deaerated methanolic solutions containing given concentrations of halides or pseudohalides, namely, Cl^-, Br^-, or SCN^-. Such irradiations produced long-lived transients whose absorption spectra, $\lambda_{max} \approx 380$ nm, agree with spectra already reported for copper(III) macrocyclic complexes (Figure 6).[23] Moreover, flash irradiations of the copper(II) complexes in 0.01 M SCN^-—solvent methanol—produce transient absorbances, $\lambda_{max} \approx 480$ nm, characteristic of the $(SCN)_2^-$ radical. In this regard, the formation of copper(III) intermediates was attributed to secondary reactions between oxidizing radicals, e.g., Cl_2^- and copper(II) macrocycles. The rate of the 380-nm absorbance growth, characteristic of the copper(III) formation, reveals that the disproportionation of the halide radical competes with the oxidation of the copper(II) macrocycle. Figure 6 shows the decrease of the half-lifetime for the absorbance growth with increasing concentrations of Cu(*dl*-Me_6[14]-aneN_4)$^{2+}$. The disappearance of the copper(III) species can be observed in a long-time scale, namely, $t_{1/2} \geq 2$ s.

The production of copper(III) complexes was investigated by generating the oxidizing radicals, e.g., Cl_2^-, Br_2^-, or CH_3·, in flash irradiations of cobalt(III) complexes.[24] Reactions

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[23] Olson, D. C.; Vasielevskis, J. *Inorg. Chem.* **1971**, *10*, 463.

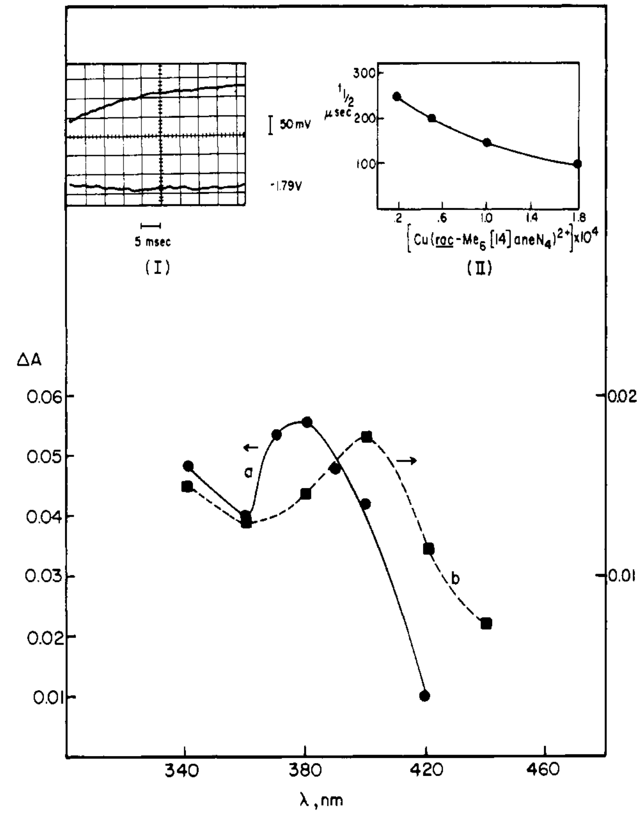


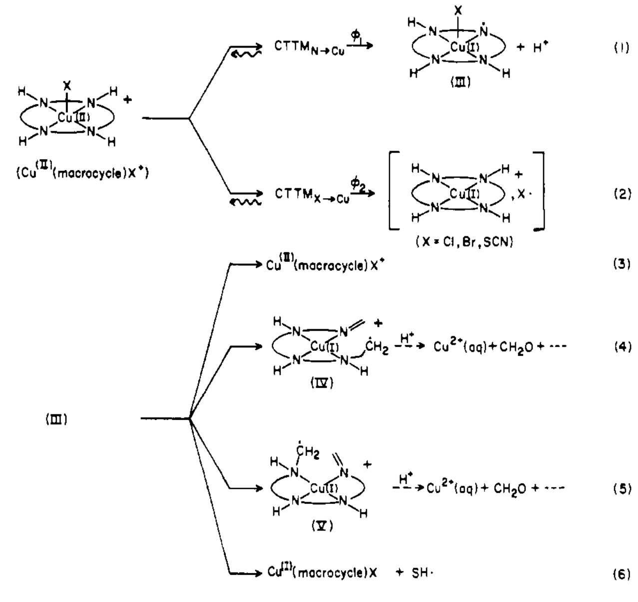
Figure 6. Transient spectra generated in reactions of free radicals with Cu(*rac*-Me_6[14]aneN_4)$^{2+}$. Transients generated with (a) Cl_2^- radicals in methanol and (b) $CH_3\cdot$ in acetonitrile. The insets show (I) the transient growth of the 380-nm absorbance in the reaction with Cl_2^- and (II) the dependence of the half-lifetime on the complex concentration.

Table III. Reaction of Methyl Radicals with Cu(*rac*-Me_6[14]aneN_4)$^{2+}$ in CH_3CN-H_2O Mixtures

medium[a]	ΔA_0[b]	$t_{1/2}$, s
10.0% H_2O	0.0326	0.20
17.0% H_2O	0.0308	0.23
29.0% H_2O	0.0204	0.22
35.0% H_2O	0.0110	0.23

[a] Solutions were 10^{-2} M in $HClO_4$. [b] Yield of Cu(*rac*-Me_6[14]aneN_4)$^{3+}$ measured at 380 nm. Irradiations of Co$(NH_3)_5$-$OCOCH_3^{2+}$ with 250 J/pulse. $\lambda_{excit} \geqslant 240$ nm.

of these radicals with Cu(*rac*-Me_6[14]aneN_4)$^{2+}$ in either acetonitrile or methanolic solutions produced transient copper(III) species (Figure 6). These copper(III) transients exhibited the same properties of those generated in flash irradiations of the copper(II) macrocycles (see above). Small concentrations of water reduce the yield of the copper(III) products with $\lambda_{max} \approx 380$ nm (Table III) and produce new species with $\lambda_{max} < 320$ nm.[25]



$$\text{(IV) and/or (V)} + SH_2 \xrightarrow[-SH\cdot]{} Cu^{(I)}L \dashrightarrow Cu^+(aq) + \text{amines} \qquad (7)$$

(L: open cycle amine)

$$Cu^{(III)}(\text{macrocycle})X^+ + SH\cdot \longrightarrow Cu^{(II)}(\text{macrocycle})^+ + S + H^+ + X^- \qquad (8)$$

$$SH\cdot + SH\cdot \longrightarrow SH_2 + S \text{ and/or } (SH)_2 \qquad (9)$$

Discussion

Ultraviolet irradiations of the copper(II) tetraaza macrocycles induce the reduction of copper(II) to copper(I). The other products of the photochemical reaction, namely, formaldehyde and amines, signal that the photooxidation involves the macrocycle ligand (eq 1). In addition, the influence of the scavenger, methanol or 2-propanol, on the distribution of the reaction products (Figure 1) shows the participation of several scavengeable intermediates with open and closed macrocycles (eq 3–6). Very short-lived copper(I)–ligand radicals with closed macrocycles, e.g., III, can undergo a transformation back to the parent copper(II) complex (eq 3) or a degradation into copper(I)–ligand radicals with open macrocycles, (eq 4 and 5). It is also possible for the radical intermediate with a closed macrocycle to react with alcohols (SH_2 in eq 6) in competition with ligand degradation (eq 4 and 5). Such a reaction with alcohols is justified by the formation of copper(I) macrocycles, e.g., Cu(*dl*-Me_6[14]aneN_4)$^+$, in continuous photolyses. Copper(I)–ligand radicals with open macrocycles can be regarded as precursors of the Cu^+(aq) and Cu^{2+}(aq) products. Therefore, the yield distribution of Cu^+(aq), Cu^{2+}(aq), and Cu(macrocycle)$^+$ in Figure 1 must be determined by the competition between the processes eq 3–9.

The transient transformations observed in flash photolysis reveal the formation of the intermediates described above. Some of the observed transients exhibited an acid assisted decay (Figure 5). These species can be assigned as copper(II) intermediates with open macrocycles. Such copper(II)–tetraaza complexes are expected to undergo the acid assisted hydrolysis that has been observed with other copper(II) tetraamines.[26-28] The alcohol scavengable transients, namely, as in Figures 3 and 4, can be attributed to copper(I)–ligand radicals with open macrocycles (eq 4 and 5). These species are expected to be longer lived than the copper(I) precursor with a closed macrocycle (species III in eq 1) and scavengeable by small alcohol concentrations than intermediate III.

The observed photogeneration of copper(III) complexes in methanolic solutions can be attributed to secondary reactions between oxidant radicals, namely, Cl_2^-, Br_2^-, or $(SCN)_2^-$ and excess copper(II) complexes. These oxidant radicals are

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(24) Blanks, prepared without copper(II) complexes, were used for tests of the reactivity of the Cl_2^-, Br_2^-, or $CH_3\cdot$ radicals in nonaqueous solutions.

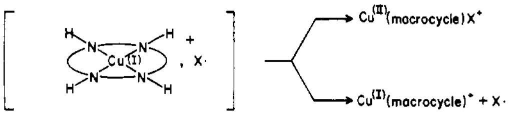
(25) The reactivity of Cu(*dl*-Me_6[14]aneN_4)$^{2+}$ with Br_2^- and Cl_2^-, in aqueous solutions, was investigated by: Whitburn, K. D.; Laurence, G. S. *J. Chem. Soc. Dalton Trans.* **1979**, 334. These authors attribute the long-lived absorbances, $t_{1/2} \gtrsim 2$ s and $\lambda_{max} \gtrsim 320$ nm, to a copper(II)–ligand radical. However, they also pointed that some properties of the transient species correspond to a copper(III) complex.

(26) Cabines, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 2155.

(27) Curtis, N. F. *J. Chem. Soc., Dalton Trans.* **1972**, 1358.

(28) Ferraudi, G.; Endicott, J. F. *Inorg. Chem.* **1977**, *16*, 2762.

generated under experimental conditions where the photolytes are mainly in the form of pentacoordinated species ($Cu(macrocycle)X^+$ with X = Cl^-, Br^-, or SCN^-). Hence, the photoreactivity of these complexes can be described by means of two primary photoprocesses. One process is the reduction of the complex to $Cu(macrocycle)^+$ with the simultaneous oxidation of the acido ligand X^- (eq 2), and the other is the photooxidation of the macrocycle ligand (eq 1). Moreover the secondary formation and decay of the copper(III) macrocycles is described in eq 2 and 10–14.



(10)

(11)

$$X\cdot + X^- \rightleftharpoons X_2^- \qquad (12)$$

$$2X_2^- \longrightarrow X_2 + 2X^- \qquad (13)$$

$$(X\cdot)\ X_2^- + Cu^{(II)}(macrocycle)X^+ \longrightarrow Cu^{(III)}(macrocycle)X_2^+ \dashrightarrow \text{products} \qquad (14)$$

The photooxidations of the acido and macrocycle ligands, in two distinct photoprocesses, have different threshold energies, namely, $E_{th}^{Cl} \approx 102$ kcal and $E_{th}^{N} \leq 92$ kcal. These energies and the action spectra (Figure 2) suggest that the two photoprocesses have different precursors, namely, two different charge-transfer to metal states. The photooxidation of the macrocycle ligand must be attributed to the population of a charge-transfer ligand to metal state that involves the electronic density of the tetraaza macrocycle, e.g., $CTTM_{N\rightarrow Cu}$ in eq 1. In addition, the photooxidation of the acido ligand is more likely the result of the population of an acido to copper(II) charge-transfer state, namely, a $CTTM_{X\rightarrow Cu}$ in eq 2. The presence of these states $CTTM_{N\rightarrow Cu}$ and $CTTM_{X\rightarrow Cu}$ can be justified by means of the optical electronegativities.[29] Indeed, the position of the charge-transfer maxima in the spectra of the copper(II) polyamine complexes yield an optical electronegativity $X \simeq 2.98$ for nitrogen orbitals with σ symmetry.[30] The value of the optical electronegativity for an amino ligand is close to the optical electronegativities of halides and pseudohalides.[30] This suggests that vertical transitions, $CTTM_{N\rightarrow Cu}$ and $CTTM_{X\rightarrow Cu}$, must occur at similar energies. However, the charge-transfer transitions that involve the electronic density of the axially coordinated ligand are orbitally forbidden and must have a low intensity. Changes in the charge-transfer spectra, induced by pentacoordination, can be the result of the introduction of new, low-intensity, charge-transfer transitions and modifications of the overall ligand field strength.[31]

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Registry No. Cu(*dl*-Me_6[14]aneN_4)$^{2+}$, 24830-76-0; Cu(*rac*-Me_6[14]aneN_4)$^{2+}$, 53447-11-3; Cu(*rac*-Me_6[14]aneN_4)(CH_3CN)$^{2+}$, 77357-89-2; Cu(*rac*-Me_6[14]aneN_4)F^+, 72477-18-0; Cu(*rac*-Me_6[14]aneN_4)Cl^+, 66139-47-7; Cu(*rac*-Me_6[14]aneN_4)Br^+, 66139-48-8; Cu(*rac*-Me_6[14]aneN_4)I^+, 70024-13-4; Cu(*rac*-Me_6[14]aneN_4)py^{2+}, 77357-90-5; Cu(*rac*-Me_6[14]aneN_4)N_3^+, 73384-35-7; Cu(*rac*-Me_6[14]aneN_4)SCN^+, 73384-34-6; Cu(*rac*-Me_6[14]aneN_4)NO_2^+, 73384-33-5; Cu(*rac*-Me_6[14]aneN_4)CN^+, 47249-07-0.

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[29] Notice that similar assignments have been made by Lever et al. in the charge-transfer spectrum of copper(II) ethylenediamines.[5]

[30] For a definition and tabulations of optical electronegativities see: Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: "Concepts in Inorganic Photochemistry"; Adamson, A., Fleischauer, P. D., Eds.; Wiley: 1975; Chapter 3.

[31] Such modifications of the overall ligand field strength are suggested by the dependence of the dd-band positions and of the half-wave potentials on axial ligand.

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Determination of the Self-Exchange Electron-Transfer Rate Constant for a Copper(III/II) Tripeptide Complex by ^1H NMR Line Broadening

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The electron-transfer self-exchange rate constant k_{11} between the +3 and +2 oxidation states of the copper complex of tri-α-aminoisobutyric acid has been determined by ^1H NMR line broadening. At 298 K $k_{11} = 5.5 \times 10^4$ M^{-1} s^{-1} with $\Delta H^* = +7.0$ kcal mol^{-1} and $\Delta S^* = -13$ cal deg^{-1} mol^{-1}. Cross reactions between copper tri- and tetrapeptide complexes indicate that this value of k_{11} is appropriate for many Cu(III)/Cu(II) oligopeptide redox couples. Chloride and hydroxide ions do not accelerate the Cu(III)/Cu(II) electron-transfer processes, which suggests an outer-sphere mechanism, although bridging by an axially bound water molecule is a possibility. Cross reactions with $IrCl_6^{3-,2-}$ appear to proceed via inner-sphere pathways.

Introduction

The Marcus correlation equation[1]

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \qquad (1)$$

where

$$\log f = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)] \qquad (2)$$

has been used extensively to interpret the kinetics of a variety of electron-transfer reactions.[2,3] Values of the self-exchange rate constants k_{11} and k_{22} are usually difficult to measure directly due to lack of experimental observables or the necessity for rapid separation techniques. Often when values of k_{11} for new redox systems cannot be measured directly, k_{11} is calculated, with use of eq 1, by measuring cross-reaction rate constants, k_{12}, for reactions involving redox couples where k_{22} is known. This procedure can result in large errors. Even for

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[1] Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853; *J. Chem. Phys.* **1965**, *43*, 679.

[2] Linck, R. G. *Surv. Prog. Chem.* **1976**, *7*, 89.

[3] Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

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