

- (10) O. Crichton, M. Poliakoff, A. J. Rest, and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1321 (1973).
- (11) M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A*, 2939 (1971).
- (12) O. Crichton, Ph.D. Thesis, University of Cambridge, 1975.
- (13) K. N. Rao, C. J. Humphreys, and D. H. Rank, "Wavelength Standards in the Infrared", Academic Press, New York, N.Y., 1966.
- (14) M. M. Rochkind, *Science*, **160**, 196 (1968).
- (15) J. D. Black and P. S. Braterman, *J. Am. Chem. Soc.*, **97**, 2908 (1975).
- (16) M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A*, 2939 (1971).
- (17) W. A. Guillroy and C. E. Hunter, *J. Chem. Phys.*, **50**, 3516 (1969).
- (18) B. A. Frenz, J. K. Enemark, and J. A. Ibers, *Inorg. Chem.*, **8**, 1288 (1969).
- (19) L. H. Jones, R. S. McDowell, M. Goldblatt, and B. I. Swanson, *J. Chem. Phys.*, **57**, 2050 (1972).
- (20) It is possible that the other NO stretch band is buried under the nitric oxide bands. In that case, more than one band is also expected for the CO stretching whereas we see only one band in that region.
- (21) L. H. Jones, R. S. McDowell, and B. I. Swanson, *J. Chem. Phys.*, **58**, 3757 (1973).
- (22) M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1351 (1973); B. I. Swanson, L. H. Jones, and R. R. Ryan, *J. Mol. Spectrosc.*, **45**, 324 (1973).
- (23) Blank runs were performed with 1% NO in argon matrix and 1% NO + 1% CO in argon matrix under the same conditions. None of the bands described above were seen. Photolysis and annealing resulted in broadening of the carbon monoxide band and changes in the relative intensities of monomer and dimer bands of NO. That all the new bands discussed above belong only to coordinated CO and NO chromium complexes is also evidenced by the fact that isotopic shifts for CO and NO stretching frequencies in these complexes are less than the isotopic shifts for uncoordinated CO and NO ligands. For example, a shift of 72.9 cm⁻¹ is observed in going from Cr(NO)₄ to Cr(¹⁵N¹⁸O)₄, whereas for free nitric oxide it is 82 cm⁻¹ (for the monomer) and 81.7 cm⁻¹ (for the dimer). Photolysis experiments were also repeated employing methane as the matrix gas. A higher yield of Cr(CO)_x (x = 3, 5) species obtained in the methane matrices resulted in easy conversion of Cr(CO)₆ to Cr(NO)₄ (ν_{NO} 1720.4 cm⁻¹). While the same intermediate bands are observed in CH₄ matrices as are observed in argon matrices, bands observed in methane matrices are quite broad.
- (24) B. I. Swanson and S. K. Satija, submitted for publication in *J. Am. Chem. Soc.*
- (25) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975).
- (26) O. Crichton and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 202, 208 (1978).
- (27) O. Crichton and A. J. Rest, *J. Chem. Soc., Chem. Commun.*, 407 (1973).
- (28) O. Crichton and A. J. Rest, *J. Chem. Soc., Dalton Trans.*, 986 (1977).

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Photochemistry of Macrocyclic Copper(II) Complexes. Photoinduced Redox Reactions of Cu[13-AtH]²⁺¹

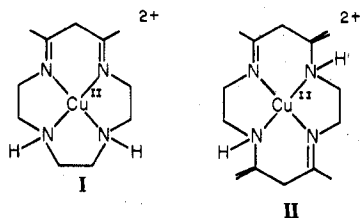
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The photochemical reactivity of the Cu[13-AtH]²⁺ complex is noticeable only for ultraviolet irradiations (254–370 nm). Photolyses, carried out in the presence of various alcohols, produced aldehydes or ketones. Two Cu(II) macrocyclic complexes, one characterized as Cu[Me₂[13]monoeneN₄]²⁺, were products of the reaction. The dependence of the quantum yields on experimental variables (acid concentration, scavenger concentration, light intensity, excitation wavelength) is explained in terms of a proposed reaction mechanism. The primary product, a Cu(III) cation–ligand radical, was postulated by a comparison with the behavior already reported for Cu[[14]dieneN₄]²⁺.

Introduction

Although the study of the macrocyclic complexes of various metal ions has been a very active field of research, the photochemistry of these compounds has not been explored until recently.^{2–9} The chemical properties already reported for these complexes show that they present some potentially interesting features for photochemical studies. Modifications in the structure of the tetraaza macrocyclic ligand, for example, in the degree of unsaturation or in the ring size, have a marked influence on the relative stability of accessible oxidation states for a given metal ion.¹⁰ Further, restrictions for rearrangement of the ligand configuration and the ability of the ligand to produce steric hindrance in reactive positions change with each ligand. Therefore, the chemical reactivity of the metal ion can be modified by these means.^{11–13} In this regard, if the various structural effects which have influence on the properties of the compounds in their ground states are somehow reflected in the behavior of the excited states, a largely tunable photochemical reactivity could be expected.^{14,15} Results obtained on the photochemistry of Cu[13-AtH]²⁺ (I) are reported here and compared with previous results of Cu[[14]dieneN₄]²⁺ (II).



Experimental Section

Photochemical Procedures. Ultraviolet photolyses were carried out in a Rayonet merry-go-round reactor using Rayonet lamps with spectral distributions appropriate to the experiment. A superpressure mercury point source combined with an Oriel 7242 monochromator was used for excitations at various wavelengths (300, 370, and 500 nm). The light intensity was found between 3×10^{-4} and 8×10^{-4} einstein/(L min) for the experimental arrangements indicated above. Ferrioxalate was used as a primary actinometric reference.¹⁶ The light was frequently tested with Co(NH₃)₅Br²⁺.¹⁷

Quantum yields were obtained using already reported procedures.^{2,17} Solutions used for such determinations absorbed more than 99.9% of the incident light (optical density ≥ 3 at the wavelength of excitation). Product concentrations were obtained at various periods of the irradiation. The slopes of the curves of the product concentration vs. time, extrapolated at zero time, were used for quantum yield calculations.

Solutions were deaerated with solvent-saturated nitrogen streams or with vacuum.² Photolyses were also carried out in presence of oxygen using solutions equilibrated under 1 atm of gas.

Flash photolyses were carried out in an instrumental setup built in this laboratory. Two FP-8-100C Xenon Corp. flash lamps were fired in series at voltages between 10 and 3 kV. The capacitor bank was formed with one, two, or three 5-μF capacitors connected in parallel. Pulses with a lifetime of 30 μs were obtained for energies below 300 J/flash. Optical detection was used in this system. The light beam used for such a purpose was obtained from a 300-W Xenon Eimac lamp coupled with collimating lenses and filters. The light was directed through the sample cell and into an optical baffle and a monochromator. A 20 cm optical path sample cell was used for observation of the transients. Cutoff filters were used in order to irradiate in preselected regions.¹⁸

The deaeration of the solutions used in flash photolysis was carried out by three freeze-thaw cycles, followed by saturation with Ar at 1 atm in a gastight apparatus.² The procedures used in the determination of the kinetic and spectroscopic properties of the transients were described in detail elsewhere.^{2,18} Rate constants were obtained as an average from more than five determinations.

Radiolytic Procedures. Pulse radiolysis was performed with 10-MeV LINAC electrons in solutions deaerated with nitrogen. The experimental setup will be described elsewhere.²⁰ Steady-state γ irradiations were performed in a 4.8×10^{17} eV g⁻¹ min⁻¹ cobalt-60 source. The amount of material converted to product in the irradiation (less than 20% conversion) was calculated from the spectra of the solutions.

Analytical Procedures. The small amount of products, obtained during the determination of the quantum yields and in steady-state γ irradiations, was isolated by chromatographic methods.

Ion-exchange separations of the copper complexes were performed in a 10 cm long and 0.5 cm wide column filled with chromatographic grade Rexyn 101 (Na). Liquids were maintained in the column at a positive pressure of 1500 g/cm² and flowed at a rate of 0.01 cm³/s. The resin was successively washed with 50 cm³ of 5 M HCl, 100 cm³ of distilled water, and 50 cm³ of 2 M NaClO₄ before the chromatographic separations. The material, absorbed from 1 cm³ of irradiated solution, was eluted with 20 cm³ of 10⁻², 2.5 \times 10⁻², 5.0 \times 10⁻², 10⁻¹, 5 \times 10⁻¹, and 2 M NaClO₄, and the liquids were collected in 3-cm³ samples.

Extinctions for the reaction products were estimated from the spectra of the samples isolated by chromatography, and the amount of Cu(II) was found in each of them after the destruction of the complexes with hot nitric and hydrochloric acids.

Quantitative analyses of the aldehydes or acetone were performed following their separation from the copper complexes. Samples of irradiated solutions (\sim 3 cm³) were absorbed in 1 cm³ of resin, treated as indicated above, and eluted with 9 cm³ of distilled water. Formaldehyde was analyzed by the chromotropic acid procedure¹⁹ while acetaldehyde and acetone were gas chromatographically analyzed.²⁰ Each product analysis was paired with parallel determinations made with solutions kept in the dark but handled otherwise by the same procedures.

Cu²⁺(aq) was also investigated with I⁻ in irradiated samples. Photolyzed solutions (3.0 cm³) were mixed with 1.0 cm³ of 0.1 M I⁻, and the final volume was adjusted to 5 cm³ with 10⁻¹ M HClO₄. The amount of I₃⁻ was estimated from the absorbance developed at 400 nm. Calibration curves were obtained for various concentrations of Cu(II) in the presence of Cu[13-AtH]²⁺.

Copper(I) products were investigated with Fe³⁺. The method has been described in detail elsewhere.²

The decomposition products of Cu[Me₂[13]monoene.N]²⁺ in hot 0.2 M HCl were studied as follows. Steam distillation was used to remove 3-penten-2-one from the reaction mixture. Such a product was analyzed by means of infrared spectra and the 2,4-dinitrophenylhydrazones. Comparisons were made with the commercial product and its corresponding derivative. Triethylenetetramine was converted into trienH₄CuCl₆ and characterized by means of IR spectra.²¹ The amount of Cu²⁺ liberated in these experiments was measured using the bathocuproine method.²² The same procedures were used with decomposition products of Cu[13-AtH]²⁺.

Materials. Literature procedures were used for the synthesis of [Cu[13-AtH]](PF₆)₂ and [Cu[13-At]]NO₃·H₂O.²³ [Cu[13-At]]NO₃ was recrystallized three times from solutions with pH 10 by addition of NaClO₄. The perchlorate salt, [Cu[13-At]]ClO₄·H₂O, was dried under vacuum for 24 h. Anal. Calcd: Cu, 16.18; C, 33.80; N, 14.27; H, 5.90. Found: Cu, 16.23; C, 33.76; N, 14.31; H, 5.92. The spectral properties of these compounds agreed with previous reports.²³

1,4,8,11-Tetraaza-2,4,4'-trimethylcyclotrideca-2-enecopper(II) tetrachlorozincate(II) was prepared by the method of House and Curtis.²⁴ This compound was dissolved in the minimum possible amount of warm water and reprecipitated with NaClO₄. Two further recrystallizations with NaClO₄ were carried out in order to transform any residual chlorozincate. The compound was dried under vacuum for 24 h. Anal. Calcd: Cu, 13.02; C, 11.50; N, 29.64; H, 4.79. Found: Cu, 13.08; C, 11.54; N, 29.68; H, 4.77.

1,5,8,11-Tetraaza-2,4-dimethylcyclotrideca-2-enecopper(II) Perchlorate (III). In 70 cm³ of 5 \times 10⁻² M HClO₄ containing 3 M 2-propanol was dissolved 0.8 g of [Cu[13-At]]ClO₄·H₂O. The resulting solution was deaerated with three freeze-thaw cycles and irradiated

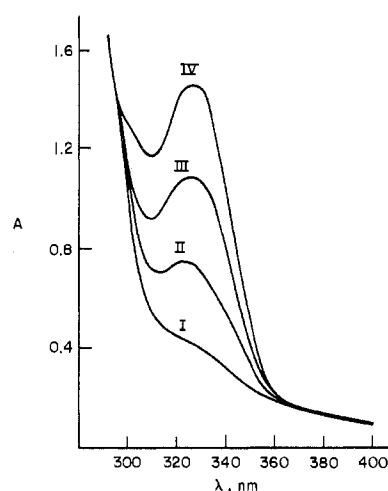


Figure 1. Absorption spectra of Cu[13-AtH]²⁺ in 0.2 M HClO₄ and 2 M 2-propanol irradiated at 254 nm ($J_0 = 8.2 \times 10^{-4}$ einstein/(L min)): I, 0 min; II, 15 min; III, 30 min; IV, 45 min.

at 254 nm ($J_0 \approx 4 \times 10^{-4}$ einstein/(L min)) for 3 h. Such a procedure was repeated four more times with fresh solutions (4.0 g of [Cu[13-At]]ClO₄·H₂O was the total amount processed). The volume of the irradiated solution was reduced to \sim 100 cm³ in a rotatory evaporator. Some crystallization was observed at the end of the evaporation. Dark blue crystals of the product separated by cooling in an ice bath. The compound was recrystallized from 10⁻² M HClO₄ and dried at 60 °C under vacuum for 24 h; yield 8% (over 4.0 g). Anal. Calcd: Cu, 13.47; C, 27.90; N, 11.87; H, 4.75. Found: Cu, 13.53; C, 27.97; N, 11.92; H, 4.70.

Spectroquality alcohols were used without further purification. Other materials used were reagent grade and they were handled without extra purifications.

Apparatus. Visible and ultraviolet spectra were recorded with a Cary 14 spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer 421, and pH measurements were performed with a Chemtrix pH meter.

Results

(A) Continuous Photolysis. (1) Products. Photolyses of Cu[13-AtH]²⁺ were carried out in deaerated acidic ($10^{-3} \leq [\text{HClO}_4] \leq 0.2$ M) aqueous solutions at various wavelengths (254–500 nm). Such irradiations produced almost no net chemical transformation. Only very small concentrations of Cu²⁺(aq) ($\phi \leq 10^{-5}$) were produced for ultraviolet excitations ($\lambda < 400$ nm). Further, the spectra of the irradiated solutions and blanks kept in the dark presented negligible differences. However, the copper complex became photoreactive in solutions containing alcohols (2-propanol, methanol, ethanol). New absorptions at 328 nm were observed in the spectra of irradiated samples for 254-nm photolyses of 1.0×10^{-3} M Cu[13-AtH]²⁺ in solutions containing 2-propanol ($3.0 \geq [2\text{-propanol}] \geq 10^{-1}$ M) and 0.2 M HClO₄ (see Figure 1). Two new copper complexes were detected in irradiated solutions using ion-exchange chromatography (see Figure 2). The first one, with absorptions at 260 and 328 nm, was eluted with 2.5×10^{-2} M NaClO₄ at pH 2–3. This species was followed in succession by untransformed Cu[13-AtH]²⁺ and a photolysis product, maximum absorption at 260 nm, when the elution was carried out with 5×10^{-2} and 10⁻¹ M NaClO₄ (see analytical procedures).

Both products exhibited a large stability toward the characteristic acid hydrolysis (i.e., in 0.1 M HClO₄) of the Cu(II) complexes with open cycle ligands.^{25,26} Furthermore, reactions with 0.05–0.1 M I⁻ were not observed.

The product, crystallized from the reaction mixture (see materials), exhibited the same ultraviolet spectra of the species with a maximum absorption at 260 nm (see above).²⁷ The infrared spectra show both absorptions, $-\text{N}=\text{C}-$ (1650–1690

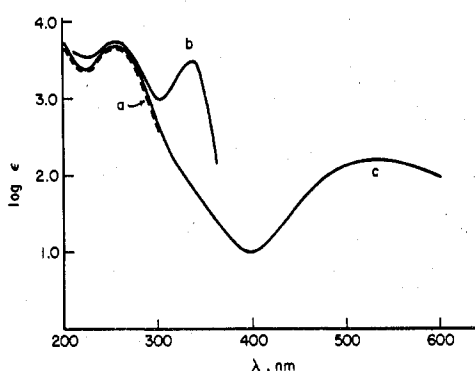


Figure 2. Absorption spectra of the products isolated by ion-exchange chromatography (a and b) and spectrum of $[\text{Cu}[\text{Me}_2[13]\text{-monoeneN}_4]](\text{ClO}_4)_2$ (c).

Table I. NH and N=C Bands for Selected 13-Member Ring Macrocyclic Complexes of Cu(II)^a

| Compd | N-H str, cm^{-1} | N=C str, cm^{-1} |
|--|---------------------------|---------------------------|
| $[\text{Cu}[\text{Me}_3[13]\text{-monoeneN}_4]](\text{ZnCl}_4)$ | 3100 ^b | 1670 ^b |
| | 3070 ^c | 1658 ^c |
| $[\text{Cu}[\text{Me}_3[13]\text{-monoeneN}_4]](\text{ClO}_4)_2$ | 3110 ^b | 1680 ^b |
| $[\text{Cu}[\text{Me}_2[13]\text{-monoeneN}_4]](\text{ClO}_4)_2$ | 3090 ^b | 1670 ^b |
| $[\text{Cu}[13\text{-AtH}]](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ | 3300 ^b | 1645 ^{b,c} |
| | 3299, 3317 ^c | |

^a Values taken using KBr disks. ^b This work. ^c Reference 24.

cm^{-1}) and N—H (3100–3200 cm^{-1}), reported for monoimine and 1,4-diimine complexes of Cu(II) (Table I). Although the compound is resistant to acid hydrolysis, it is decomposed in hot 0.1 M HCl. Such a reaction produced 3-penten-2-one and Cu(II) in a 1:1 molar ratio. A parallel determination, carried out with $[\text{Cu}[13\text{-AtH}]]^{2+}$, did not produce 3-penten-2-one. However, a product, characterized as acetylacetone, was distilled from the reaction mixture. These results are in complete agreement with cyclic structure III, being a salt of

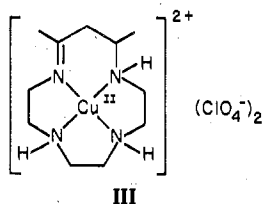


Table II. Limit Product Yields for $[\text{Cu}[13\text{-AtH}]]^{2+}$

| λ , nm | $10^4 I_0$, einstein/ (L min) | ϕ^L ^b | | | Conditions ^a |
|----------------|--------------------------------------|-----------------------|-------------------|-------------------|--|
| | | CuM ^c | CuT ^d | K ^e | |
| 254 | 8.3 | 0.16 ± 0.03 | 0.11 ± 0.02 | 0.07 ± 0.01 | [2-propanol] ≥ 0.7 M |
| | | 0.18 ± 0.04 | 0.062 ± 0.004 | 0.11 ± 0.01 | [HClO ₄] ≥ 0.1 M |
| | | 0.15 ± 0.02 | 0.051 ± 0.003 | 0.094 ± 0.005 | [EtOH] ≥ 2 M |
| | | 0.17 ± 0.03 | 0.013 ± 0.002 | <i>f</i> | [HClO ₄] ≥ 0.1 M |
| 300 | 6.5 | 0.17 ± 0.03 | 0.10 ± 0.03 | 0.10 ± 0.04 | [<i>tert</i> -butyl alcohol] ≥ 6 M |
| | | 0.15 ± 0.04 | 0.063 ± 0.004 | 0.11 ± 0.03 | [HClO ₄] ≥ 0.1 M |
| | | 0.080 ± 0.004 | 0.050 ± 0.006 | 0.03 ± 0.009 | [2-propanol] ≥ 0.7 M |
| 350 | 3.7 | 0.080 ± 0.004 | 0.050 ± 0.006 | 0.03 ± 0.009 | [HClO ₄] ≥ 0.1 M |
| | | 0.022 ± 0.004 | 0.012 ± 0.006 | <i>f</i> | [2-propanol] ≥ 0.7 M |
| 370 | 7.2 | 0.022 ± 0.004 | 0.012 ± 0.006 | <i>f</i> | [HClO ₄] ≥ 0.1 M |

^a Conditions required for obtaining of limit product yields. ^b Limit values were obtained as an average of 5–8 determinations in the range of conditions indicated in the table. ^c Yields for $[\text{Cu}[\text{Me}_2[13]\text{-monoeneN}_4]]^{2+}$. ^d Yields for the product with absorptions at 260 and 328 nm (Figure 2). ^e Yields for carbonylic products: formaldehyde, acetaldehyde, and acetone, respectively. ^f Not determined.

the 11,13-dimethyl-1,4,7,11-tetraazacyclotrideca-10-ene-copper(II) ion, $[\text{Cu}[\text{Me}_2[13]\text{-monoeneN}_4]]^{2+}$. Besides, the spectral properties of this compound agreed well with those reported by Curtis for a closely related macrocyclic complex (see ref 24, Table I and Figure 2).

The isolation of the species with absorptions at 260 and 328 nm from the crystallization liquids of the $[\text{Cu}[\text{Me}_2[13]\text{-monoeneN}_4]]^{2+}$ was not successfully achieved.²⁷ Both the large solubility, compared with that of $[\text{Cu}[13\text{-AtH}]]^{2+}$, and the limited efficiency obtained for the photochemical conversion into products (see below) seem to be the major problems for a good separation. In fact, solid samples, obtained by addition of solid NaClO_4 or by partial evaporation of the solvent, were contaminated with $[\text{Cu}[13\text{-AtH}]](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. Although this prevents the assignment of a definitive structure, its stability in acidic medium shows that it is a Cu(II) complex with a macrocyclic ligand. Furthermore, the intense ultraviolet absorption at 328 nm suggests that ligand oxidation takes place during the photochemical process. Such a possibility gains further support in light of the product yields measured under various conditions (see below).

Aldehydes (CH_2O , CH_3CHO) or acetone, produced by oxidation of the alcohols, were found in irradiated solutions.

(2) Quantum Yields. Irradiations of $[\text{Cu}[13\text{-AtH}]]^{2+}$ were carried out in acidic (0.2–0.002 M HClO_4) deaerated solutions containing various concentrations of 2-propanol ([2-propanol] ≤ 3 M) at 254 nm. Quantum yields of the species with a maximum absorption at 328 nm increased with 2-propanol (Figure 3a) and hydrogen ion concentration up to a limit value ϕ^L_{CuT} (Figure 3b). Photolyses carried out using various scavenger alcohols (methanol, ethanol, *tert*-butyl alcohol) presented the same qualitative features indicated above. Furthermore, a large dependence on the nature of the scavenger was observed for the efficiency ϕ^L_{CuT} (see Table II). No such behavior was exhibited by the limit yield ϕ^L_{CuM} of the $[\text{Cu}[\text{Me}_2[13]\text{-monoeneN}_4]]^{2+}$ product (see Table II). Besides, the stoichiometric relationship between products, indicated through the limit yields, is shown in eq 1, where ϕ^L_{K}

$$0.16 \pm 0.05 = \phi^L_{\text{CuM}} = \phi^L_{\text{K}} + \phi^L_{\text{CuT}} = 0.16 \pm 0.08 \quad (1)$$

is the yield of aldehydes or acetone and ϕ^L_{CuM} is the yield of $[\text{Cu}[\text{Me}_2[13]\text{-monoeneN}_4]]^{2+}$.

Yields for the Cu(II) products and formaldehyde were obtained in acidic solutions (0.2 M HClO_4) containing methanol in concentrations below those required for a limiting yield (see Table II). The reciprocals of these yields, ϕ_{CuT}^{-1}

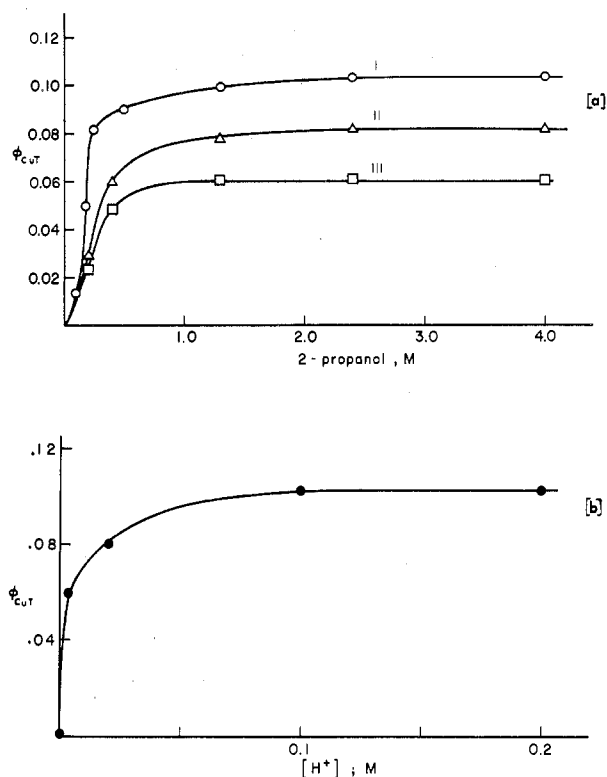


Figure 3. Variations of the yield of the oxidation product, absorptions at 260 and 328 nm, with (a) 2-propanol concentration in (I) 0.2 M HClO₄, (II) 0.02 M HClO₄, and (III) 0.004 M HClO₄ and with (b) acid concentration; [2-propanol] = 2.0 M for excitations at 254 nm ($I_0 = 6.8 \times 10^{-4}$ einstein/(L min)).

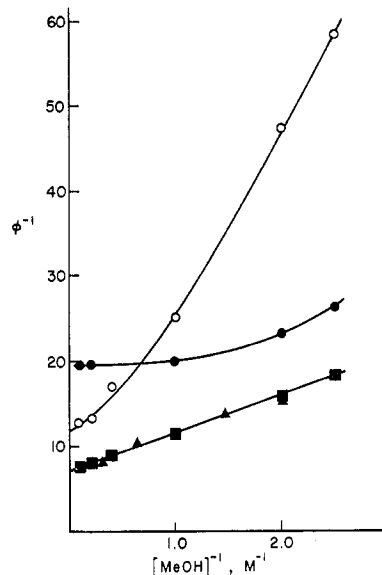


Figure 4. Dependence of the reciprocal of the yields on $[MeOH]^{-1}$ in 0.1 M HClO₄ solutions for excitations at 254 nm ($I_0 = 8.3 \times 10^{-4}$ einstein/(L min)): ○, ϕ_K ; ●, ϕ_{CuT} ; ▲, Cu[Me₂[13]monoeneN₄]²⁺; ■, $\phi_{CuT} + \phi_K$.

and ϕ_K^{-1} , presented a nonlinear dependence on the reciprocal of the methanol concentration (Figure 4). However, a good straight line relationship was obtained for the sum of the efficiencies $\phi_{CuT} + \phi_K$ as well as the monoimine yield ϕ_{CuM} in this kind of representation (Figure 4).

The photochemical behavior of Cu[13-AtH]²⁺ is more complex for photolyses at longer wavelengths (300, 350, 370 nm), presenting a nonlinear dependence of the concentration of the product with time (Figure 5). Such deviations from zero-order kinetics were found smaller for larger concentrations

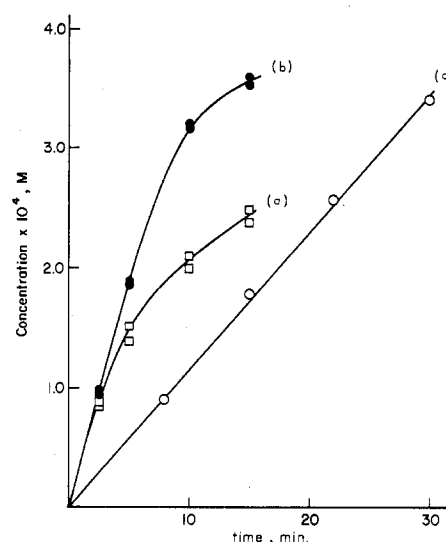


Figure 5. Departures from zero order in photolyses at 370 nm ($I_0 = 7.2 \times 10^{-4}$ einstein/(L min)) for (a) 7.5×10^{-3} M Cu[13-AtH]²⁺ and (b) 2.2×10^{-2} M Cu[13-AtH]²⁺ compared with excitations at 254 nm ($I_0 = 8.3 \times 10^{-4}$ einstein/(L min)) for (c) 5.0×10^{-3} M Cu[13-AtH]²⁺. Solutions were also 0.2 M in HClO₄ and 3 M in 2-propanol.

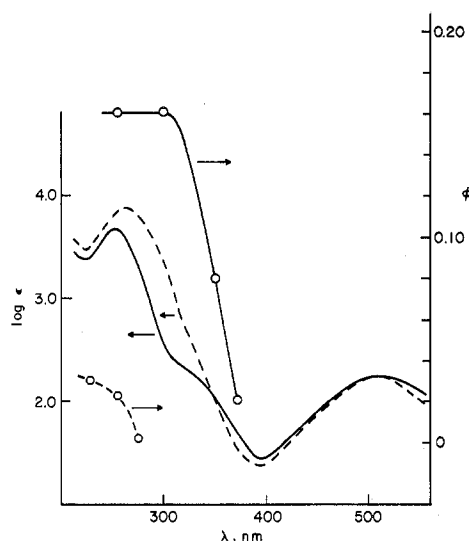


Figure 6. Absorption-spectrum and quantum-yield dependence on excitation wavelength for Cu[13-AtH]²⁺, —, and Cu[[14]dieneN₄]²⁺, ---. Quantum yields for Cu[[14]dieneN₄]²⁺ are as indicated in ref 2.

of the substrate (Figure 5). This behavior suggests that departures from a zero order are a consequence of an increasing absorption of the light by the photolysis products.

Excitations at 300 or 350 nm produced a chemical process having the same features of the reaction induced with light of 254 nm. Besides, the only change detected for photolyses at 370 nm was a smaller efficiency (see Table II and Figure 6). Equation 1 holds, within experimental error, for excitations at these wavelengths.

Variations of quantum yields with substrate concentration or light intensity were not very reliable for excitations at 300–370 nm as a consequence of the complex photochemistry indicated above. The limit yield ϕ_{CuT}^1 showed no dependence on the substrate concentration ($10^{-3} \leq [Cu[13-AtH]^{2+}] \leq 8 \times 10^{-3}$ M) or light intensity ($5 \times 10^{-4} \geq I_0 \geq 10^{-5}$ einstein/(L min)) for irradiations at 254 nm. However, the yield ϕ_{CuT} , obtained in solutions containing 0.3 M 2-propanol, experienced some small variation with substrate concentration: $\phi_{CuT} =$

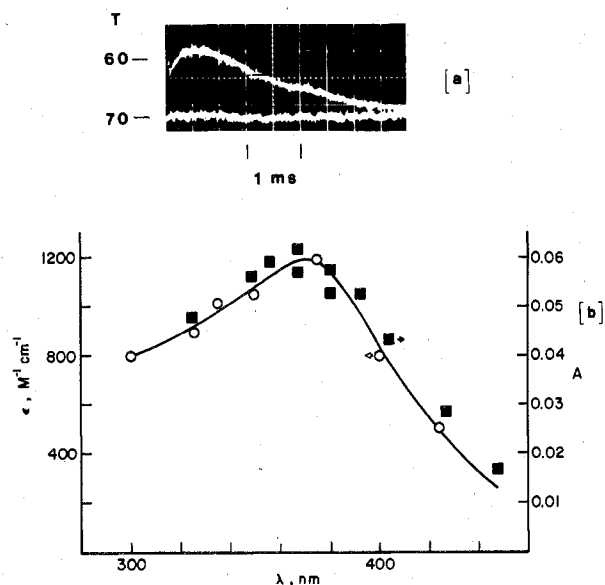


Figure 7. Intermediates generated in flash photolysis and pulse radiolysis of $\text{Cu}[13\text{-AtH}]^{2+}$. (a) Oscillographic trace obtained in flash photolysis of 10^{-4} M $\text{Cu}[13\text{-AtH}]^{2+}$ in 0.1 M HClO_4 . Reaction followed at 370 nm in deaerated solutions. (b) Spectra of the intermediate obtained in flash photolysis, ■ (see part (a) for conditions), and in pulse radiolysis, ○ ($[\text{Cu}[13\text{-AtH}]^{2+}] = 4 \times 10^{-5}$ M; 50% 2-propanol; 0.02 M HClO_4).

0.070 ± 0.004 for 10^{-3} M $\text{Cu}[13\text{-AtH}]^{2+}$ and $\phi_{\text{CuT}} = 0.56 \pm 0.007$ for 8×10^{-3} M $\text{Cu}[13\text{-AtH}]^{2+}$.

(B) Flash Photolysis. Flash irradiation of deaerated acidic solutions ($10^{-2} \leq [\text{HClO}_4] \leq 0.1$ M) of $\text{Cu}[13\text{-AtH}]^{2+}$ produced no observable transients (350–600 nm). However, the rapid buildup and slow decay of transient absorptions were observed in deaerated solutions containing 2-propanol in concentrations larger than 0.7 M, Figure 7a. The intermediate exhibited a maximum absorbance at ~ 380 nm, Figure 7b. The decay process obeyed first-order kinetics in transient concentration ($k = (1.0 \pm 0.3) \times 10^3 \text{ s}^{-1}$).

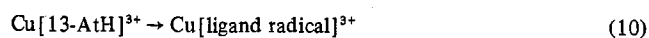
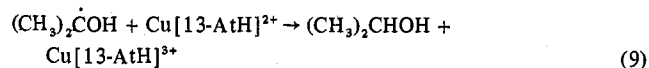
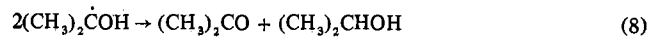
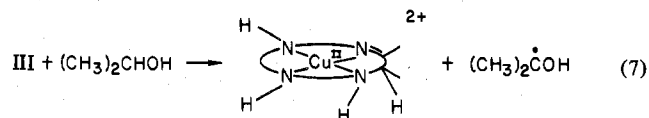
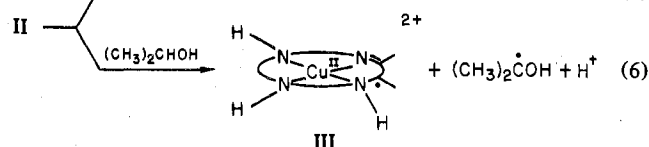
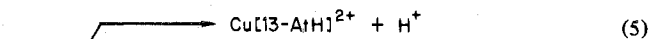
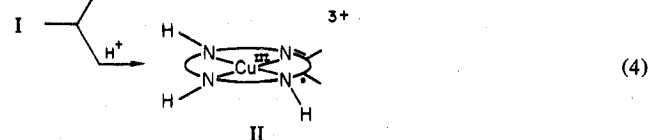
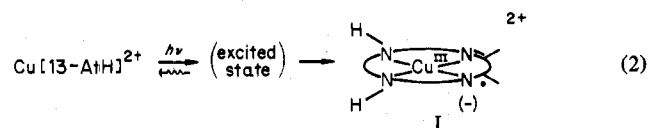
(C) Radiolytic Experiments. Reactions of alcohol radicals with the substrate were investigated by means of γ radiolysis and pulse radiolysis. Solutions of $\text{Cu}[13\text{-AtH}]^{2+}$ in 50% 2-propanol and 0.2 M HClO_4 , deaerated with nitrogen streams, were radiolyzed for periods of time between 10 and 20 min (conversions $\leq 20\%$). The product was, in more than a 90% yield, the same copper complex, with absorptions at 328 and 260 nm, produced also in photochemical irradiations. Some minor decomposition of the substrate was observed for radiolyses of $\text{Cu}[13\text{-AtH}]^{2+}$ in 0.2 M HClO_4 for ~ 3 -h irradiations.

A precursor of the product formed by a pseudo-first-order process ($k \approx 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) was detected by pulse radiolyses of $\text{Cu}[13\text{-AtH}]^{2+}$ in deaerated aqueous alcoholic medium (50% 2-propanol; 0.2 M HClO_4). The intermediate, $\lambda_{\text{max}} \sim 320$ nm and $\epsilon \sim 1000 \text{ M}^{-1} \text{ cm}^{-1}$ (see Figure 7), decay with $t_{1/2} \approx 1$ ms. Similar experiments carried out with $\text{Cu}[13\text{-AtH}]^{2+}$ in 0.2 M HClO_4 produced negligible transient absorptions in the 300–600-nm spectral region.

Discussion

The stoichiometric relationship between products, indicated in eq 1 and in Table I, shows that different precursors must be involved in the formation of the two reaction products (see below). The oxidation of the solvent as a primary process, in the sense proposed by Wehry et al.,³⁰ can be safely excluded as a possibility in this system since the absence of photochemical reactivity at $\text{pH} \geq 3$, the nature and stoichiometry of the products, and the selectivity with respect to the scavengers do not agree with this proposition. Such properties

show that $\text{Cu}[13\text{-AtH}]^{2+}$ and $\text{Cu}[[14]\text{dieneN}_4]^{2+}$ have a rather similar photochemical behavior. In this regard the formation of a copper(III)-radical intermediate, as indicated in eq 2,



might be proposed by comparison with $\text{Cu}[[14]\text{dieneN}_4]^{2+}$.² However, modifications in the nature of the intermediate, produced in the primary process, are required in order to account for the almost negligible yield of the hydrolytic pathway and the smaller concentrations of alcohols required for reactions with this species.

The steps (4)–(7) are a feasible pathway for the formation of $\text{Cu}[\text{Me}_2[13]\text{monoeneN}_4]^{2+}$ product. The results obtained in continuous radiolysis, pulse radiolyses, and flash photolysis demonstrate that alcohol radicals are able to react with $\text{Cu}[13\text{-AtH}]^{2+}$ producing an oxidized species. Further, the intermediate might be assigned as either a Cu(II) cation-ligand radical or a Cu(III) transient. The transformation of Cu(III) macrocycles into Cu(II) complexes with a larger ligand unsaturation, reported by Olson and Vasilekis,³¹ suggests that this transient is more likely a Cu(III) species. In fact the first-order dependence in transient concentration exhibited by the kinetics of the decay process suggests that reaction 10 is the rate-determining step of the stages (10) and (11) observed in flash photolysis.

A mathematical treatment of the reaction sequence (2)–(11) assuming steady state³² shows that square-root contributions are introduced in the quantum yield expressions of the oxidation product and the carbonylic product as indicated in eq 12 and 13. The abbreviations used in eq 12–14 are $[\text{A}] = [\text{Cu}[13\text{-AtH}]^{2+}]$, $[\text{SH}] = [\text{scavenger}]$, and k_i ($i = 2$ –11) is the rate constant of eq i . The expression $(\phi_{\text{CuT}} + \phi_{\text{K}})^{-1}$ is predicted to be linear in the reciprocal of the scavenger concentration (see eq 14) because of the cancellation produced in the addition of the eq 12 and 13. Besides, a linear dependence for the reciprocal of the $\text{Cu}[\text{Me}_2[13]\text{monoeneN}_4]^{2+}$ yield is expected in this representation (eq 14). The de-

$$\phi_K = \frac{1}{I} \left(\frac{k_9[A]^2}{8k_8} - \frac{k_9[A]}{2} \left(\frac{k_9^2[A]^2}{16k_8^2} + \frac{\phi I k_4 k_6 [H][SH]}{k_8(k_3 + k_4[H])(k_5 + k_6[SH])} \right)^{1/2} + \frac{\phi I k_4 k_6 [H][SH]}{(k_3 + k_4[H])(k_5 + k_6[SH])} \right) \quad (12)$$

$$\phi_{CuT} = \frac{1}{I} \left(\frac{k_9^2[A]^2}{8k_8} + \frac{k_9[A]}{2} \left(\frac{k_9^2[A]^2}{16k_8^2} + \frac{\phi I k_4 k_6 [H][SH]}{k_8(k_3 + k_4[H])(k_5 + k_6[SH])} \right)^{1/2} \right) \quad (13)$$

$$\phi_{CuM} = \phi \frac{k_4 k_6 [H][SH]}{(k_3 + k_4[H])(k_5 + k_6[SH])} = \phi_{CuT} + \phi_K \quad (14)$$

pendence of the products' yields on scavenger concentration (Figures 3 and 4) is in agreement with eq 12-14. This can be used as a further proof of the proposed reaction mechanism. An analysis of the quantum yields by means of eq 12-14 shows that the ratio k_3/k_4 is almost constant for various alcohols while k_5/k_6 seems to have some relationship with the oxidation potential of the alcohol radical (Table III).

The limit of eq 14 for high hydrogen ion and scavenger concentrations might be equated to the primary process quantum yield (see eq 15) according to the proposed mech-

$$\phi_{CuM}^L = \phi = \phi_{CuT}^L + \phi_{LK}^L \quad (15)$$

anism. The limit yields, $\phi_{CuM}^L = \phi$, obtained for $Cu[13-AtH]^{2+}$ at various excitation wavelengths, are shown in Figure 6. Contrasting features between the photochemical processes of the $Cu[13-AtH]^{2+}$ and $Cu[[14]dieneN_4]^{2+}$, namely, the larger efficiency ($\phi \approx 0.16$) and the lower threshold energy for photochemical reactivity ($E_{th} \approx 73$ kcal/mol) of the $Cu[13-AtH]^{2+}$ complex, can be seen in Figure 6. Ligand-centered excited states have been assigned at a very high energy, larger than those of the charge-transfer states, in the $Cu[[14]dieneN_4]^{2+}$ ^{34,35} system and one might expect the same situation with $Cu[13-AtH]^{2+}$ since it also has isolated imino groups. In this regard, the distinct photochemical behavior presented by these species should not be a consequence of the population of the inner ligand excited states. The nature of the photochemical reactions induced in these compounds suggests that the photoreactive state is a doublet charge transfer to ligand state, ²CTTL, as it is shown in Figure 8. The differences in threshold energies ($\Delta E_{th} \approx 25$ kcal/mol) can be related in such a case with smaller energy requirements for the formation of the oxidized metal center inside of the 13-member ring ligand. The stabilization of the upper oxidation state, through the optimization of the dimensions of the metal center and the hole provided by the macrocyclic ligand, has been proved to be important for ground-state Ni(II) complexes.¹⁰ However, the magnitude of the change in the redox potential ($E \approx 7$ kcal/mol) seems to be too small for the total change in ΔE_{th} , and some other effects might be regarded important contributions to this difference. In fact, a more distorted nuclear configuration for the thermally equilibrated excited state, with respect to ground state, is expected in $Cu[[14]dieneN_4]^{2+}$ than in $Cu[13-AtH]^{2+}$ because of the contraction of the metal center and the respective size of the ligand rings. This may have influence on the threshold energy if the change in nuclear configuration of the system for the excited-state transformation into the intermediate (I) costs some amount of reorganizational work. The primary process yield of the $Cu[13-AtH]^{2+}$ system ($\phi \approx 0.1$) is larger

Table III. Ratio of the Rate Constants for Competitive Reactions 3 and 4 and Reactions 5 and 6 with Different Alcohols

| Scavenger | k_3/k_4 | k_5/k_6 | ϵ_{00}^a V R· + e ⁻ → RH |
|------------|----------------------|-----------|--|
| Methanol | 6.0×10^{-3} | 0.5 | 1.29 |
| Ethanol | 5.5×10^{-3} | 0.2 | 0.95 |
| 2-Propanol | 6.7×10^{-3} | 0.07 | 0.80 ^b |

^a See ref 15. ^b Estimated by procedures indicated in ref 15.

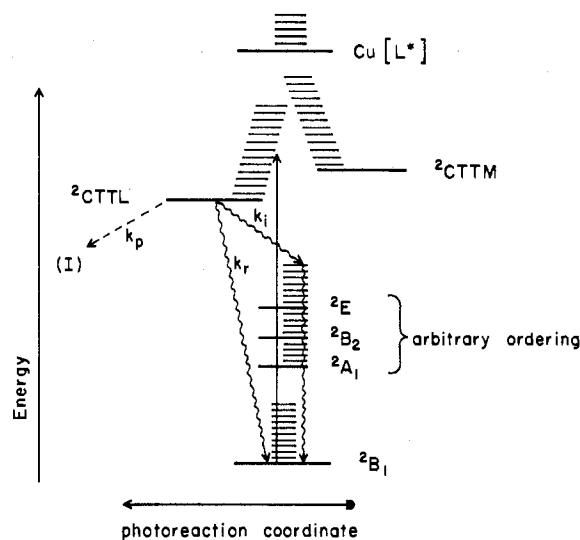


Figure 8. Kinetic scheme for the principal events in the photochemistry of $Cu^{II}L$ (L = macrocyclic ligand) complexes. The various states in the doublet charge transfer to ligand (²CTTL) and doublet charge transfer to metal (²CTTM) manifolds, respectively, have been represented by a single level for simplicity.

than in the $Cu[[14]dieneN_4]^{2+}$ system ($\phi \approx 0.03$); see Figure 5. Such a number may indicate that the excited state of $Cu[13-AtH]^{2+}$ has either a larger reactivity or lifetime than in $Cu[[14]dieneN_4]^{2+}$. Distinct contributions of the low-lying metal-centered excited states on the relaxation of the photoactive state for these complexes are not expected to be important. In fact, the relaxation of the ²CTTL state toward a metal-centered state (k_i in Figure 8) is a two-electron transition which should have a smaller probability than the direct relaxation toward the ground state.

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Registry No. $Cu[13-AtH]^{2+}$, 46472-97-3; $[Cu[Me_3[13]monoeneN_4]](ZnCl_4)$, 66240-35-5; $[Cu[Me_3[13]monoeneN_4]](ClO_4)_2$, 66240-36-6; $[Cu[Me_2[13]monoeneN_4]](ClO_4)_2$, 66240-38-8; $[Cu[13-AtH]](PF_6)_2$, 36083-71-3.

References and Notes

- (1) Ligand abbreviations: [13-AtH], 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene; $[Me_2[13]monoeneN_4]$, 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10-ene; $[Me_3[13]monoeneN_4]$, 11,13,13'-trimethyl-1,4,7,10-tetraazacyclotrideca-10-ene; $[14]dieneN_4$, 5,7,7',12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.
- (2) G. Ferraudi and J. F. Endicott, *Inorg. Chem.*, **16**, 2762 (1977).
- (3) D. W. Reichgott and N. Rose, *J. Am. Chem. Soc.*, **99**, 1813 (1977).
- (4) D. V. Stynes, *J. Am. Chem. Soc.*, **96**, 5942 (1974).
- (5) T. E. King, C. Yong, L. Yung, and Y. L. Chiang, *J. Biol. Chem.*, **250**, 6218 (1975).
- (6) Ch. Y. Mok and J. F. Endicott, *J. Am. Chem. Soc.*, **99**, 1276 (1977).
- (7) S. D. Mallone and J. F. Endicott, *J. Phys. Chem.*, **76**, 2223 (1972).
- (8) C. Kotal and A. Adamson, *Inorg. Chem.*, **12**, 1990 (1973).
- (9) D. P. Fisher, V. Piermattie, and J. C. Dabrowiak, *J. Am. Chem. Soc.*, **99**, 2813 (1977).
- (10) F. U. Lovechio, E. S. Gore, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 3109 (1974).

- (11) M. C. Weiss, B. Bursten, S.-M. Peng, and V. L. Goedken, *J. Am. Chem. Soc.*, **98**, 8021 (1976).
- (12) J. Keruohan and J. F. Endicott, *Inorg. Chem.*, **9**, 1504 (1970).
- (13) J. F. Endicott, J. Lilie, J. M. Kuszaj, B. S. Ramaswamy, W. G. Schmonsees, M. G. Simic, M. Glick, and D. P. Rillema, *J. Am. Chem. Soc.*, **99**, 429 (1977).
- (14) J. F. Endicott, G. Ferraudi, and J. Barber, Jr., *J. Phys. Chem.*, **79**, 630 (1975).
- (15) J. F. Endicott in "Concepts in Inorganic Photochemistry", A. W. Adamson and P. D. Fleishauer, Ed., Wiley, New York, N.Y., 1975.
- (16) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
- (17) G. Ferraudi, J. F. Endicott, and J. Barber, *J. Am. Chem. Soc.*, **97**, 6406 (1975).
- (18) G. Ferraudi and J. F. Endicott, *Inorg. Chem.*, **12**, 2389 (1973), and references therein.
- (19) W. Wolfrom, *Methods Carbohydr. Chem.*, **1** (1962).
- (20) W. V. Sherman, *J. Phys. Chem.*, **71**, 1695 (1967).
- (21) H. B. Jonassen, J. B. Crumpler, and T. D. O'Brien, *J. Am. Chem. Soc.*, **67**, 1709 (1945).
- (22) J. Fries, "Analysis of Traces", E. Merk, Darmstadt, 1971.
- (23) J. G. Martin, R. M. Wei, and S. Cummings, *Inorg. Chem.*, **11**, 475 (1972).
- (24) D. A. House and N. F. Curtis, *J. Am. Chem. Soc.*, **84**, 3248 (1962).
- (25) D. K. Cabbines and D. W. Margerum, *J. Am. Chem. Soc.*, **92**, 2155 (1970).
- (26) N. F. Curtis, *J. Chem. Soc., Dalton Trans.*, 1358 (1972).
- (27) Appropriate synthetic routes were not found for the photolysis products. Chemical reduction (BH_4^- ; H_2/Ni) of either $\text{Cu}[13\text{-At}]^+$ or $\text{Cu}[13\text{-AtH}]^{2+}$ produces metallic copper. Besides, chemical oxidants^{28,29} either produce no reaction (Ph_3CBF_4) or give a complex mixture of products (Br_2).
- (28) C. Hipp, L. F. Lindoy, and D. H. Busch, *Inorg. Chem.*, **11**, 1988 (1972).
- (29) T. D. Truex and R. H. Holm, *J. Am. Chem. Soc.*, **94**, 4529 (1972).
- (30) S. Sundarajan and E. L. Wehry, *J. Phys. Chem.*, **76**, 1528 (1972).
- (31) D. C. Olson and J. Vasileskis, *Inorg. Chem.*, **10**, 463 (1971).
- (32) Steady-state treatment was applied to Cu(III) and radical species according to A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms", Wiley, New York, N.Y., 1961.
- (33) J. F. Endicott, J. M. Plamer, and E. Papaconstantinou, *Inorg. Chem.*, **8**, 1516 (1969).
- (34) For a review of the photochemical properties and absorption spectra of organic compounds with imino groups see A. Padwa, *Chem. Rev.*, **77**, 37 (1977).

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Photochemistry of the Ruthenium(II)-Saturated Amine Complexes $\text{Ru}(\text{NH}_3)_6^{2+}$, $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$, and $\text{Ru}(\text{en})_3^{2+}$ in Aqueous Solution

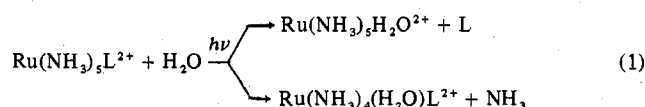
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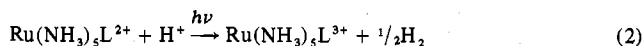
Photolysis of $\text{Ru}(\text{NH}_3)_6^{2+}$ in aqueous solution leads to products which can be attributed to two independent, primary photoreactions: aquation of coordinated ammonia and oxidation of Ru(II) to Ru(III) with concomitant formation of H_2 . At longer irradiation wavelengths (313–405 nm), which correspond to ligand field absorption bands, photoaquation predominates and gives wavelength-independent quantum yields ($\Phi_{\text{aq}} = 0.26 \pm 0.1$ mol/einstein). Wavelength-independent photooxidation ($\Phi_{\text{ox}} \sim 0.03$) is also seen in this region, and it is argued that the latter pathway is the result of the back-population from a common LF state into a higher energy charge transfer to solvent state. For $\lambda_{\text{irr}} < 313$ nm, a sharp increase in Φ_{ox} and simultaneous decrease in Φ_{aq} is noted. At these wavelengths excitation corresponds to direct absorption into a band attributed to a CTTS transition. For 254-nm photolysis Φ_{ox} is found to be 0.36 and the ratio $\Phi_{\text{ox}}/\Phi_{\text{H}_2}$ is ~ 2 . Quantum yield effects of $[\text{H}^+]$ and 2-propanol are interpreted in terms of the reaction of the CTTS excited state with H^+ to give Ru(III) plus a hydrogen atom, a species which may lead to the oxidation of a second Ru(II) complex or may be trapped by 2-propanol when the latter is present. Qualitatively, the photolysis behaviors of aqueous $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ and $\text{Ru}(\text{en})_3^{2+}$ are similar but several significant differences are evident. No photoaquation of NH_3 is seen for $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$, and photolabilization, if present, must be confined to the spectrally undetectable exchange of solvent and coordinated H_2O . For $\text{Ru}(\text{en})_3^{2+}$ the photoaquation pathway for the longer λ_{irr} is wavelength dependent indicating that a higher energy state is particularly photoactive toward ligand labilization. The photochemical technique is employed to synthesize the monodentate ethylenediaminium complex ions $\text{Ru}(\text{en})_2(\text{enH})\text{Cl}^{3+}$ and $\text{Ru}(\text{en})_2(\text{Hen})(\text{H}_2\text{O})^{3+}$, and their properties are described.

Introduction

Earlier studies have demonstrated a wide variety of photochemical reactivities for ruthenium(II) complexes^{3–8} with the pentaammine complexes $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}$ receiving particular attention in this laboratory.^{3–6} When L is a π -unsaturated ligand such as pyridine, acetonitrile, or dinitrogen, the spectra display intense metal-to-ligand charge-transfer (MLCT) absorptions.⁹ In some cases, irradiation produces photochemistry consistent with the formulation of the MLCT states as an oxidized metal center coordinated to a radical ion ligand $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\text{L}^-)]^{2+}$, examples being the photoexchange¹⁰ between the solvent and the pyridine hydrogens of $\text{Ru}(\text{NH}_3)_5\text{py}^{2+}$ and the electron-transfer photochromism seen for the pyrazine complex $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$ in the presence of cupric ion.^{4b} However, more common reaction modes in aqueous solutions are ligand photoaquation (eq 1) or oxidation of



Ru(II) to Ru(III) with simultaneous H_2 formation (eq 2).



These pathways have been attributed to the population of ligand field (LF) excited states^{4–6,10} and of charge transfer to solvent (CTTS) excited states,⁶ respectively. Such arguments suffer major ambiguity given the fact that the intense MLCT and internal ligand (IL) bands of the π -unsaturated L's generally obscure the spectral regions where the LF and CTTS absorptions are expected. Consequently, it was deemed necessary to examine the spectral and photochemical properties of Ru(II) complexes having only saturated ligands. Here are reported the photochemistries of $\text{Ru}(\text{NH}_3)_6^{2+}$, $\text{Ru}(\text{en})_3^{2+}$, and $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ in aqueous solution; elsewhere,¹¹ are described spectral properties of $\text{Ru}(\text{NH}_3)_6^{2+}$ and $\text{Ru}(\text{en})_3^{2+}$.

Experimental Section

Materials. Hexaammineruthenium(II) chloride, $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_2$, was synthesized by the procedure of Lever and Powell.¹² Purification was carried out as follows. A 0.5-g portion of $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_2$ (1.8×10^{-3} mol), 0.7 g of ammonium chloride, and 0.1 g of zinc powder