be anticipated as a product of the reaction between the oxo complexes and CO_2.

However, the mechanism leading to the production of *trans*-$O_2W(CO)_4$ in CO_2- or N_2O-doped matrices is quite different from that in O_2-doped matrices. Photooxidation by O_2 gives rise to *trans*-$O_2W(CO)_4$ in which both the oxygen atoms originate in the *same* O_2 molecule: in the experiments described here, each oxygen atom must originate in a *different* CO_2 or N_2O molecule and production of *trans*-$O_2W(CO)_4$ proceeds, we believe, via oxotungsten tetracarbonyl, B.

The observation that CO_2 is reduced to CO is of importance in relation to the fixation of the former molecule via industrial or atmospheric processes.

Acknowledgment. We thank the SERC for supporting this research and for funding a studentship for M.J.A.

Registry No. $W(CO)_6$, 14040-11-0; $Cr(CO)_6$, 13007-92-6; $OW(^{12}CO)_4$, 94136-88-6; $OW(^{13}CO)_4$, 94136-89-7; *trans*-$O_2W(^{12}CO)_4$, 91444-05-2; *trans*-$O_2W(^{13}CO)_4$, 94136-90-0; $OCr(CO)_4$, 94136-91-1; *trans*-$O_2Cr(CO)_4$, 94136-92-2; WO_3, 1314-35-8; CrO_2, 12018-01-8; N_2O, 10024-97-2; CO_2, 124-38-9; Ar, 7440-37-1; methane, 74-82-8.

Contribution from the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, Department of Chemistry, The University of North Carolina at Charlotte, Charlotte, North Carolina 28223, and Naval Research Laboratory, Washington, D.C.

Photochemistry of (2,3,9,10-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)copper(II): Participation of Copper(II) Hydrides

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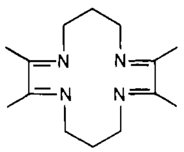
The photochemistry in acidic methanol and the relevant thermochemistry of (2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)copper(II) (ligand abbreviations are 2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4 or L in this work) have been investigated. UV photolysis results in the rapid formation of a transient identified as Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^+$. A minor fraction of the transient is produced in $t < 10$ ns and a major fraction in the microsecond time domain via a second-order process ($k = (5.7 \pm 0.3) \times 10^7$ M^{-1} s^{-1}) that involves the reaction of solvent radicals ($\cdot CH_2OH$) with the copper(II) macrocycle. In perchlorate media, $[ClO_4^-] > 10^{-3}$ M, a first-order isomerization followed in milliseconds ($k = (2.0 \pm 0.3) \times 10^3$ s^{-1}). Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^{2+}$ then undergoes slow decay by competitive pathways to produce H_2 and Cu_{solv}^+. The product quantum yields ($10^{-3} < \phi_{Cu^+_{solv}} < 10^{-2}$; $10^{-4} < \phi_{H_2} < 10^{-3}$) depend on light intensity, acid concentration, and the concentration of the copper(II) macrocycle. The production of hydrogen is postulated to occur via a copper(II) macrocycle in acid solution. The thermal properties relevant to an interpretation of the photochemistry were as follows: (1) There is a dependence on solvent of $E_{1/2}$ for the $Cu^{II}L/Cu^{I}L$ couple (varies from -0.02 V in CH_2Cl_2 to -0.62 V vs. SCE in H_2O) and the CuL^{2+} electronic absorption spectrum. (2) The $E_{1/2}$ value for the ligand reduction at ~ -1.4 V vs. SCE shifts positively in acidic media until it overlaps the metal(II/I) couple. (3) The spectral properties of Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^+$ generated by coulometric reduction ($n = 1.01$) at -0.60 V vs. SCE in acetonitrile are $\lambda_{max} = 746$ nm with $\epsilon \approx 8 \times 10^3$ M^{-1} s^{-1}.

Introduction

The photochemistry of copper(II) macrocycles is largely determined by electronic and structural features of the macrocyclic ligands that control the accessibility of various charge-transfer states. Complexes in which potentials for the $Cu^{III/II}$ and (macrocycle)/(macrocycle)$^{-}\cdot$ couples are sufficiently close have reactive charge transfer to ligand states, CTTL, that induce solvolytic and redox reactions.[1,2] For the copper(II) complexes with CTTL states placed at very high energies, the photoreactivity is limited to various ligand to metal charge-transfer states, CTTM, that induce the oxidation of the macrocyclic and ligands in the axial positions.[3] In some copper(II) complexes both the CTTL and CTTM states can be populated by UV light and simultaneous photoreactivity from both states is observed.[4]

The formation of reaction products takes place by mechanisms that involve several steps.[1-6] The copper(II) macrocycles, usually generated in the primary photochemical processes described above or in secondary reactions between radicals and excess copper(II) complex, are unstable in acidic solutions. It has been shown that solvolysis competes with hydride-mediated redox transformations.[5,6] Since the reactivity of the copper(I) species is tied to structural parameters such as the flexibility of the ligand, it is of interest to determine the properties of the copper(I) intermediates with rigid macrocycles. Therefore, the macrocycle effect on the photochemical reactivity of the copper(II) complex and the reactivity of chemical intermediates have been investigated in this work by using 2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4, which has a more rigid framework than previously investigated ligands.[1-3]



2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4

Experimental Section

Materials. All chemicals used in the investigations and preparations were reagent grade, unless otherwise noted. Water was triply distilled over potassium permanganate. Acetonitrile and methylene chloride were stored 48 h over 4-Å molecular sieves before use. Tetrabutylammonium hexafluorophosphate (TBAH) and tetraethylammonium perchlorate (TEAP) were purchased from Southwestern Analytical, Austin, TX. TEAP was dried overnight at 70 °C under vacuum prior to use. Anhydrous $NaClO_4$ was purchased from G. F. Smith. Argon was scrubbed of oxygen impurities either by passage over BTS catalyst or through scrubbing towers containing ~ 0.2 M Cr^{2+} in 0.2 M $HClO_4$.

[†] University of Notre Dame.
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Preparation of Compounds. [Cu(2,3,9,10-Me$_4$-[14]-1,3,8,10-tetraeneN$_4$)](ClO$_4$)$_2$. The compound was prepared by a modification of the one published by Fabbrizzi et al.[7] A solution of 0.12 mol of propanediamine in 300 cm^3 of CH$_3$OH was cooled to <5 °C. The temperature conditions were maintained during the addition of 0.12 mol of HClO$_4$ (70%) followed by 0.12 mol of biacetyl in 100 cm^3 of CH$_3$OH. The resulting solution was allowed to warm to room temperature, and a slurry of 0.06 mol of Cu(C$_2$H$_3$O$_2$)$_2$·H$_2$O in 1000 mL of CH$_3$OH was slowly added. After the addition was complete, the solution was stirred magnetically for 1 h and then reduced in volume (rotary evaporator) until an oil remained. Addition of ~30 cm^3 of CH$_3$OH to the oil resulted in crystallization of the desired product. The compound was removed by vacuum filtration, and additional product was obtained by the addition of a saturated aqueous NaClO$_4$ solution to the filtrate. (*Caution!* Perchlorates are potentially explosive substances.) Both products were recrystallized from CH$_3$OH or a 1:2 ethanol–acetone solution; yield 20%. Anal. Calcd for CuC$_{14}$H$_{24}$N$_4$Cl$_2$O$_8$: C, 32.92; H, 4.74; N, 10.97. Found: C, 33.65; H, 5.41; N, 10.65.

[ICu(2,3,9,10-Me$_4$-[14]-1,3,8,10-tetraeneN$_4$)]ClO$_4$. The compound was prepared by the procedure of Coltrain and Jackels.[8] A 0.4-g sample of [Cu(2,3,9,10-Me$_4$-[14]-1,3,8,10-tetraeneN$_4$e](ClO$_4$)$_2$ and 0.3 g of NaI were added to 100 cm^3 of CH$_3$OH. The volume of the solution was reduced by rotary evaporation to ~10 cm^3 and filtered by vacuum to remove 0.3 g of product. The compound was washed with hot ethanol and then air-dried; yield 80%. Anal. Calcd for CuC$_{14}$H$_{24}$N$_4$IClO$_4$: C, 31.24; H, 4.94; N, 10.41. Found: C, 30.90; H, 4.21; N, 10.00.

Physical Measurements. Elemental analyses were carried out by Integral Microanalytical Laboratories, Raleigh, NC. Electronic absorption spectra were obtained in water, methanol, and acetonitrile in matched quartz cells and recorded with a Cary 14 or Cary 219 instrument. Electrochemical properties were determined in water, acetonitrile, methanol, and methylene chloride. Solution concentrations of the metal complexes were 1.0 × 10^{-3} M. Cyclic voltammograms were obtained with the PAR 173 potentiostat and the PAR 175 programmer and recorded with a Houston Omnigraphic Model 2000 x-y recorder or the IBM Model 165 x-y recorder. The measurements were made at a Bioanalytical Systems Pt or glassy-carbon (GC) working disk electrode vs. a saturated calomel electrode (SCE). The disk electrodes were polished sequentially with 3-, 1-, and 0.25-μm diamond polishing compound followed by ultrasound cleaning in distilled water and the appropriate solvent before use. The polishing was effected with a Buehler/Ltd. apparatus and ultrasonic cleaning with a Branson B-24 unit. Coulometry was effected with the PAR 173 potentiostat, the PAR 176 coulometer, and a PAR 370 cell system or a homemade cell consisting of a central compartment separated from the reference and auxiliary electrodes by glass frits. Coulometric reduction of copper(II) to copper(I) for spectral determinations of the reduced complex was carried out in a Vacuum Atmospheres Co. Dri-Lab. The Dri-Lab was used for solution preparation of the copper(I) complex due to its oxygen sensitivity.

Photochemical Procedures. Low-pressure Hg and Cd spectral lamps were used, in conjunction with fused silica optics, for continuous photolysis at 254 and 229 nm, respectively. Argon was used for deaeration of the solutions prior to irradiation. Solutions were magnetically stirred to insure homogeniety during the irradiation. Light intensities were measured with Parker's actinometer.[9]

Flash photochemical experiments were carried out with equipment described elsewhere.[10,11] For spectral determinations of kinetics that required observations at times longer than 30 μs, the photolyte was irradiated with two xenon flash lamps fired in series at various energies (40–250 J/pulse). A neodymium yag laser flash photolysis setup (250 nm) was used for experiments in the nanosecond time domain. The output from a RC-4840 photomultiplier tube was digitized by a Biomation 805, and 100 data points were processed with a Varian PDP 11/55 computer system. The computer analyzed data associated with absorption changes due to transients and subsequent decay kinetics. Each point for a transient spectrum was an average of 5–10 experimental results. Rate constants were obtained from least-squares treatments; 100 data points derived from an average of 5–10 traces were used in the treatments.

Analytical Procedures. Free copper(I), Cu$_{solv}^+$, concentrations were determined with 2,9-dimethyl-1,10-phenanthroline.[12] The concentration of Cu(2,3,9,10-Me$_4$-[14]-1,3,8,10-tetraeneN$_4$)$^+$ was determined by oxidation with either Co(NH$_3$)$_6^{3+}$ or Fe^{3+} in order to produce the equivalent concentrations of Co^{2+} or Fe^{2+}, respectively. The Co^{2+} concentration was determined by the SCN$^-$ method;[13] the Fe^{2+} concentration was determined by the 1,10-phenanthroline procedure.[12] The concentration of Cu$_{solv}^{2+}$ was determined by the 2,9-dimethyl-1,10-phenanthroline–ascorbic acid procedure.[12] Formaldehyde was identified by a procedure reported elsewhere.[3] Hydrogen was analyzed by gas chromatographic methods. A Hewlett-Packard gas chromatograph containing a molecular sieve column and argon carrier gas was used for these determinations. Quantitative gas transfers were effected with a vacuum line and Toepler pump system.

Table I. Visible–UV Spectral Parameters and Half-Wave Potentials for Cu(2,3,9,10-Me$_4$-[14]-1,3,8,10-tetraeneN$_4$)$^{n+}$

compd^a	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	$E_{1/2}$, V (δ, mV)^b	medium
[CuL](ClO$_4$)$_2$	537 (119), 218 (1.8 × 10^4)	−0.36 (65), −1.43 (85)^c	CH$_3$CN^d
	535 (91), 220 (1.6 × 10^4)	−0.62 (57)^e	H$_2$O^d
	535 (93), 220 (2.0 × 10^4)		H$_2$O^f
		−0.43 (56)^e	CH$_3$OH^g
		−0.20 (68), −1.42 (95)^c	CH$_2$Cl$_2$^{h}
[ICuL](ClO$_4$)	625 (174), 393 (3.5 × 10^3)	+0.30 (75),^{i,j} +0.60 (80)^j	
	245 (1.6 × 10^4), 212 (2.5 × 10^4)	−0.39 (65), −1.43 (72)^c	CH$_3$CN^d
		0.35 (70), −1.41 (70)^c	CH$_2$Cl$_2$^{h,k}

^{a} L = 2,3,9,10-Me$_4$[14]-1,3,8,10-tetraeneN$_4$. ^{b} $E_{1/2}$ values determined from ($E_{p_{ox}}$ + $E_{p_{red}}$)/2 vs. SCE at a GC working electrode; except as indicated, $E_{1/2}$ ±0.01 V. δ is the separation between $E_{p_{ox}}$ and $E_{p_{red}}$ determined from the intercept of plots of ΔE_p vs. (sweep rate)$^{1/2}$. Solution concentrations were 1.0 × 10^{-3} M and degassed with argon, T = 22 °C. ^{c} Quasi-reversible. ^{d} Electrolyte was 0.10 M TEAP, spectral parameters in pure H$_2$O. ^{e} Irreversible. ^{f} Spectral parameters in 0.12 M HClO$_4$/NaClO$_4$ solutions of variable pH, 1–7. ^{g} Electrolyte was 0.1 M NaClO$_4$. ^{h} Electrolyte was 0.1 M TBAH. ^{i} ΔE_p is very sweep rate dependent, indicating only quasi-reversible behavior for this couple. ^{j} Pt working electrode. ^{k} Oxidations of the compound in CH$_2$Cl$_2$ were irreversible.

Results

Thermal Properties. The thermal properties of Cu(2,3,9,10-Me$_4$-[14]-1,3,8,10-tetraeneN$_4$)$^{2+}$ investigated in this study are summarized in Table I. The spectral characteristics consist of a d–d transition of low absorption coefficient located in the visible region and an intense band maximizing near 220 nm, i.e. where CT transitions are expected for this compound. The position of the band maxima is slightly red shifted (~2 nm), and the absorption coefficients are slightly lower in water compared to those in acetonitrile. In neutral or acidic solutions containing perchlorate ion, the band maxima remain fixed but the absorption coefficients increase compared to spectra in water. The spectra in acidic solutions (10^{-6} M ≤ [H$^+$] ≤ 10^{-1} M) remain constant over several days, indicating that the complex is stable to acid hydrolysis.

The redox properties have been investigated by cyclic voltammetry in various solvents. Two one-electron reductions have been observed: the first reduction is reversible by electrochemical standards[14] ($i_c/i_a \approx 1$; ΔE_p = 56–68 mV), and the second reduction, placed at more negative potential, is only quasi-reversible ($i_c/i_a > 1$) and is located on the edge of an irreversible process. Oxidations of Cu(2,3,9,10-Me$_4$-[14]-1,3,8,10-tetraeneN$_4$)$^{2+}$ have not been observed over the range from 0 to +2.0 V vs. SCE. The one-electron nature of the first reduction was verified by coulometry (n = 1.01). The spectrum of this one-electron-reduced species in acetonitrile shows an intense absorption at $\lambda_{max} \approx 746$

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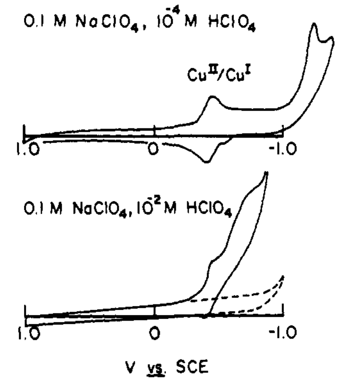

Figure 1. Cyclic voltammograms for the reduction of Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^{2+}$ in methanolic media. The dashed line shows a blank obtained in the absence of the Cu(II) complex.

nm ($\epsilon \approx 8 \times 10^3$ M^{-1} cm^{-1}). The species present in solution has been assigned as Cu^I(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^+$ by analogy to reported properties of other similar systems.[9,15]

The data in Table I indicate that Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^{2+}$ coordinates anions and probably solvent molecules in the open coordination site(s). The potential for the CuL^{2+}/CuL^+ couple depends on the nature of the medium and takes values over the range of −0.20 to −0.62 V vs. SCE. Furthermore, the iodo complex exhibits spectral and redox properties quite different from those of Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^{2+}$, although the second reduction appears to occur at similar potentials in all cases. By comparison with other macrocyclic copper(II) complexes, the redox process in this region has been attributed to ligand reduction.[3]

Figure 1 illustrates that the quasi-reversible wave for reduction of Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^{2+}$ in methanol shifts from $E_{1/2} \approx -1.4$ V vs. SCE toward more positive values as the $[H^+]$ is increased and eventually overlaps the wave for the CuL^{2+}/CuL^+ couple. The electrochemical background of the acidic electrolyte solution indicates that the shift in potential of the second reduction wave is due to the complex, not hydrogen evolution from the electrode.

Continuous Photolysis. The ultraviolet photolyses of Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^{2+}$ in acidic 10^{-6} M $\leq$ [$HClO_4$] $\leq$ 10^{-5} M deaerated methanol induce the reduction of the complex. In solutions of low acid concentration, [$HClO_4$] $\leq$ 10^{-5} M, Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^+$ is detected spectrophotometrically. However, in solutions of higher acid concentration, [$HClO_4$] $\geq$ 10^{-5} M, the copper(I) complex is too reactive for detection in continuous photolysis. The other product found in these photolyses are hydrogen, formaldehyde, and free copper(I), Cu_{solv}^+. Curves of product concentration vs. irradiation time depart from a zero-order dependence on complex concentration shortly after the conversion to products reached a few percent, a behavior that can be associated with photolysis of the long-lived copper(I) macrocycle. In order to avoid secondary photolysis, quantum yields have to be determined by limiting the conversion to <2%.

Quantum yields for formation of hydrogen and Cu_{solv}^+ are given in Table II. Quantum yields of hydrogen, in either 254- or 229-nm photolyses, have values smaller or equal to the yields of Cu_{solv}^+ under similar experimental conditions. Moreover, the dependence of the product yields on Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^{2+}$ concentration, acid concentration, and light intensity is complex. Increasing the light intensity at 229 nm increases the quantum yield of H_2 but leaves the quantum yields of Cu_{solv}^+ unaffected. Increasing the concentration of Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^{2+}$ causes a decrease in the H_2 yields but leaves the quantum yields of Cu_{solv}^+ unchanged. Decreasing the acid concentration affects both H_2 and Cu_{solv}^+ yields in different ways. The yields of Cu_{solv}^+ increase; the yields of H_2 first undergo a decrease and then an increase.

Table II. Product Yields for UV Photolysis of Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^{2+}$

λ_{excit}, nm	$10^6 I_0$, einstein dm^{-3} s^{-1}	$10^4\phi$		medium[a]
		Cu_{solv}^+	H_2	
254	8.3	10 ± 1	1.0 ± 0.2	[$HClO_4$] = 0.05 M
	8.3	5.8 ± 0.3	1.6 ± 0.2	[$HClO_4$] = 0.1 M
229	1.8	18 ± 2	6.1 ± 0.2	[$HClO_4$] = 0.1 M
		17 ± 3	3.0 ± 0.1	[$HClO_4$] = 0.1 M, [Cu(II)] = 4.0×10^{-4} M
		17 ± 3	1.0 ± 0.1	[$HClO_4$] = 0.1 M, [Cu(II)] = 2.5×10^{-3} M
		19 ± 3	0.80 ± 0.05	[$HClO_4$] = 0.1 M, [Cu(II)] = 5.0×10^{-3} M
		92 ± 3	1.3 ± 0.1	[$HClO_4$] = 10^{-2} M
		100 ± 3	2.2 ± 0.1	[$HClO_4$] = 10^{-3} M
		100 ± 3	2.2 ± 0.1	[$HClO_4$] = 10^{-4} M
	0.76	19 ± 3	4.9 ± 0.2	[$HClO_4$] = 0.1 M
	4.30	19 ± 2	6.2 ± 0.2	[$HClO_4$] = 0.1 M

[a] Solutions in methanol with [$NaClO_4$] + [$HClO_4$] = 0.1 M. The concentration of the copper(II) complex is 1.5×10^{-4} M unless stated.

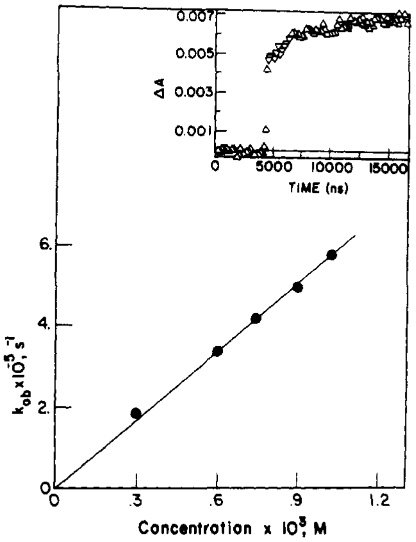

Figure 2. Dependence of the rate constant for the formation of copper(I) species on the concentration of Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^{2+}$. The inset shows a typical trace for the formation of such species, λ_{obsd} = 640 nm, in laser flash experiments, λ_{excit} = 250 nm. (Notice the prompt growth of the absorbance followed by a slow growth.)

Flash Photolysis. As illustrated in Figure 2, the 250-nm flash irradiation of Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^{2+}$ in deaerated acidic methanol produces changes starting in a nanosecond time domain. The formation of the transient takes place, in part, at times shorter than the resolution of the laser flash photolysis apparatus (see fast rise in the inset to Figure 2). A considerable fraction of the transient is formed, however, in a slower reaction that depends upon the concentration of copper(II) macrocycle and obeys a second-order rate law with $k = (5.7 \pm 0.3) \times 10^7$ M^{-1} s^{-1}, Figure 2.

The properties of the transient are illustrated in Figure 3. These data have been collected by normal flash photolysis techniques. The transient absorption spectrum can clearly be associated with formation of Cu(2,3,9,10-Me_4-[14]-1,3,8,10-tetraeneN_4)$^+$. In solutions with various concentrations of ClO_4^-, e.g. from 0.1 to 10^{-3} M, the spectrum (open circles) generated in the time domain of microseconds undergoes a transformation in the millisecond time scale (inset) to give a similar but less intense and sharper spectrum (filled circles). The latter is the same as the transient spectrum obtained at low concentrations of perchlorate ion and

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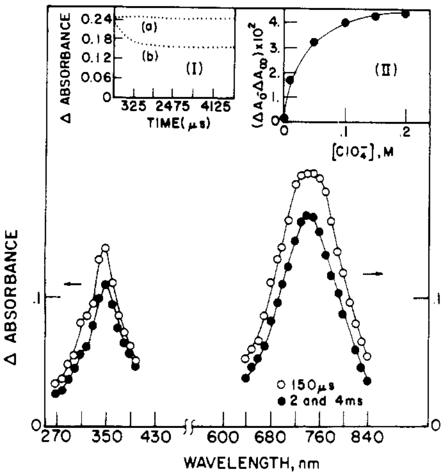

Figure 3. Difference spectra determined in flash photolysis of Cu-$(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4)^{2+}$ in methanolic solutions with 0.1 M $HClO_4$. Inset I shows two typical traces obtained in experiments with solutions where (a) $[ClO_4] \leq 10^{-3}$ M and (b) $[ClO_4] = 0.1$ M. Inset II shows the dependence of the transient's yield, $\Delta A_0 - \Delta A_\infty$, on the concentration of ClO_4^-.

more closely resembles the spectrum of the copper(I) macrocycle obtained in the electrochemical experiments. The rate of the spectral transformation obeys a first-order rate law, $k = (2.0 \pm 0.3) \times 10^3$ s^{-1}. The rate of this process is independent of the copper(II) complex concentration, acid concentration, and flash energy.

The disappearance of the copper(I) complex occurs with a half-life longer than milliseconds and shows a complex dependence on acid concentration as illustrated in Figure 4. The disappearance approaches a first-order rate law at perchloric acid concentrations greater than 6×10^{-2} M but is more complex in solutions of lower acid concentration, $[HClO_4] \leq 3 \times 10^{-3}$ M, where the disappearance of $Cu(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4)^+$ involves several steps.[16]

Discussion

Formation of $Cu(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4)^+$. Electrochemical results suggest that solvent molecules such as methanol occupy the vacant coordination sites of the copper(II) macrocycle precursor, and results on the photochemistry of this compound suggest that the primary photochemical act involves oxidation of weakly coordinated methanol[17] and the simultaneous reduction of the metal center. The $\cdot CH_2OH$ and/or $\cdot CH_2O^-$ radicals produced then react with $Cu(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4)^{2+}$ to form additional copper(I) macrocycle in the microsecond time domain. For similar reactions in aqueous solutions, it has been proposed that subsequent isomerization toward more stable, tetrahedral-like, configurations occurs.[5,6] Such a proposition stands in contrast with our observations on the photochemistry of $Cu(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4)^{2+}$ at low ClO_4^- concentrations. Flash photolysis in the nanosecond to millisecond time domains failed to reveal spectral transformations that could be associated with an isomerization process, and the copper(I) species was identified as the stable isomeric form. For large concentrations of ClO_4^-, however, the spectral transformations observed for several milliseconds are caused by an isomerization process that cannot be considered similar to the planar–tetrahedral isomerization proposed for flexible macrocycles.[5,6] Although molecular models reveal that $Cu(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4)^{2+}$ can experience distortions from planarity into a flat tetrahedron, these distortions should be more restricted than those observed in $Cu(Me_4[14]\text{-}1\text{-bora-}2,14\text{-di-}$

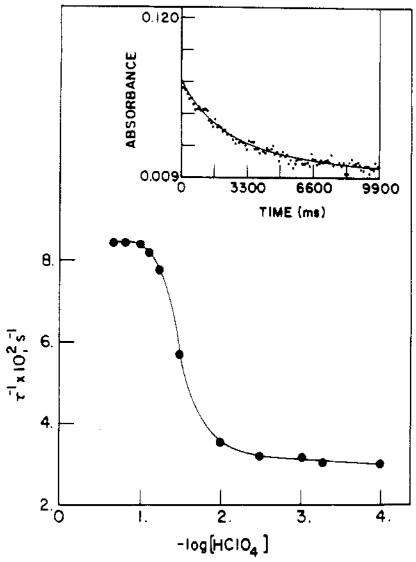

Figure 4. Dependence of the $Cu(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4)^+$ half-life on acid concentration. The inset shows the disappearance of this species, $\lambda_{obsd} = 360$ nm, in methanolic solutions with $[HClO_4] = 10^{-3}$ M and $[NaClO_4] = 0.1$ M.

$\text{oxa-}3,5,10,12\text{-tetraene}N_4)$.[18] Furthermore, the dependence of the isomerization on perchlorate concentration can be related to the formation of ion pairs[19] with a formation constant of $K \approx 30$ M^{-1}. Thus, a possible mechanism for the generation of the copper(I) is described by eq 1–6, where L = $2,3,9,10\text{-}Me_4\text{-}$

$$CuL^{2+} + ClO_4^- \rightleftarrows [CuL^{2+},ClO_4^-] \quad (1)$$

$$CuL^{2+} \xrightarrow[CH_3OH]{h\nu,\ \phi_1} CuL_d^+ + \cdot CH_2OH + H^+ \quad (2)$$

$$[CuL^{2+},ClO_4^-] \xrightarrow[CH_3OH]{h\nu,\ \phi_2} CuL_p^+ + \cdot CH_2OH + H^+\ ClO_4^- \quad (3)$$

$$CuL^{2+} + \cdot CH_2OH \rightarrow CuL_d^+ + CH_2O + H^+ \quad (4)$$

$$[CuL^{2+},ClO_4^-] + \cdot CH_2OH \rightarrow CuL_p^+ + ClO_4^- + CH_2O + H^+ \quad (5)$$

$$CuL_p^+ \rightarrow CuL_d^+ \quad (6)$$

$[14]\text{-}1,3,8,10\text{-tetraene}N_4$ and the subscripts p and d denote planar and distorted planar configurations of the macrocycle. Thus, the transformation of the transient spectrum obtained in the microsecond time scale to the one found in the millisecond time domain can be attributed to the isomerization in eq 6.

Disappearance of $Cu(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4)^+$. The loss of the copper(I) macrocycle is a complex process that involves solvolytic and redox transformations of the copper(I) species by two acid-dependent paths. Product yields show that

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(16) Although several steps can be observed in the decay of the copper(I) macrocycle, the overlap of the spectra associated with these steps makes it too difficult to unravel each stepwise process.

(17) The initial radical formed is probably $CH_3O\cdot$, which then undergoes a rapid conversion to $\cdot CH_2OH$ and/or $\cdot CH_2O^-$ in methanol.

(18) The coordination geometry of $Cu(Me_4[14]\text{-}1\text{-bora-}2,14\text{-dioxa-}3,5,10,12\text{-tetraene}N_4)^+$ is best described as a distorted square plane.[15] The small tetrahedral distortion results in dihedral angles 23 and 27° for the two sets of planes defined by copper and two adjacent atoms; angles 0 or 90° are expected for pure planar or tetrahedral structures. Such a distortion imposed upon the macrocycle by the tendency to form tetrahedral structures should be much more difficult for the less flexible $Cu(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4)$ ligand.

(19) The formation of ion pairs between copper(II) macrocycles and various anions has been previously observed due to their effect on the spectra[20] and photochemistry[1] of complexes.

(20) Endicott, J. F.; Palmer, J. M.; Papaconstantinou, E. *Inorg. Chem.* **1969**, *8*, 1516.

(21) Olsen, D. C.; Vasielevskis, J. *Inorg. Chem.* **1971**, *10*, 463.

(22) Rillema, D. P.; Endicott, J.; Papaconstantinou, E. *Inorg. Chem.* **1971**, *10*, 1739.

(23) Kumar, K.; Rotzinger, F. P.; Endicott, J. *J. Am. Chem. Soc.* **1983**, *105*, 7064.

solvolysis of $Cu(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4)^+$ is more important than redox transformations. Indeed, 35% of the copper(I) complex produces hydrogen in 0.10 M $HClO_4$ and only 1% in 0.050 M $HClO_4$. The generation of hydrogen points to the formation of hydride intermediates since $Cu(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4{}^+$ is too weak a reductant for an exoergonic reduction of H^+ in solutions within the range of acid concentrations used in this work, $10^{-6}\ M \leq [HClO_4^-] \leq 10^{-1}\ M$. Transient spectra determined at reaction times longer than 1 s in solutions with $[HClO_4] \leq 3.0 \times 10^{-3}$ M can be attributed to a hydride species. However, possible overlap of spectra associated with the hydrido complex and solvolysis products of $Cu(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4)$ render assignments dubious.

The formation of hydrides by copper(I) complexes has been reported before[6,7] and explained in terms of the two-electron process given in eq 7. This reaction requires an appropriate

$$Cu^IL_p + H_2O\ (H_3O^+) \rightarrow Cu^{III}L(H^-) + HO^-\ (H_2O) \qquad (7)$$

balance between the redox potentials of the $Cu^{III}L/Cu^{II}L$, $Cu^{II}L/Cu^IL_p$, and H_2/H^- couples and the free energy of complexation of copper(III) by hydride ions in order to be exoergonic (Appendix). The values of the redox potentials of the complexes and the weak tendency of copper(III) macrocycles to coordinate a fifth ligand indicate that $Cu(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4)_d{}^+$ probably does not undergo hydride formation directly. Rather, it is possible that the hydride is formed after a further reduction of the copper(I) complex to a copper(I)–ligand radical species. Indeed, the change in potential for reduction of the macrocycle with acid concentration as given in Figure 1 is in agreeement with this possibility. Thus, another mechanism for the formation of a reactive hydride is given by eq 8 and 9. The

$$Cu^IL + Cu^IL + H^+ \rightleftarrows Cu^{II}L^{2+} + Cu^I(LH\cdot)^+ \qquad (8)$$

$$Cu^I(LH\cdot) \rightarrow Cu^{II}L(H^-) \qquad (9)$$

postulated formation of the copper(II) hydride in eq 9 is plausible given the tendency of copper(II) macrocycles to form five-coordinated species and the well-known stability of copper(II) hydrides. In this context, it should be noted that the solvent radicals $\cdot CH_2OH$ or $\cdot CH_2O^-$ should be thermodynamically able to produce the copper(I)–ligand radical. Although this reaction has not been observed in flash photolysis, it is possible for this reaction to make contributions in steady-state reactions where there are relatively large concentrations of $Cu(2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4)^+$.

Conclusions

It must be concluded that hydrides can be very common intermediates in the photochemical[24] and thermal[5,6] redox reactions of copper(II) macrocycles. The intramolecular two-electron-transfer reaction, eq 7, and the disproportionation process, eq 8 and 9, seem to provide alternative paths leading to the hydride formation. Moreover, the disproportionation of the copper(I) macrocycles, eq 8 and 9, can be regarded as a path where restrictions imposed by the rigidity of the macrocycle are minimized.

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Appendix

The free energy associated with the transformation of $Cu^IL_p{}^+$ in $Cu^{III}L(H^-)^{2+}$, eq 7, can be expressed in terms of several elementary processes, eq 10–15. So the standard free energy for

$$CuL_p{}^+ \rightleftarrows CuL_d{}^+ \quad -\Delta G^\circ{}_{isom} \qquad (10)$$

$$CuL^{2+} + e^- \rightleftarrows CuL_d{}^+ \quad \mathcal{F}\epsilon^\circ{}_{II/I} \qquad (11)$$

$$CuL^{3+} + e^- \rightleftarrows CuL^{2+} \quad -\mathcal{F}\epsilon^\circ{}_{III/II} \qquad (12)$$

$$H^+ + e^- \rightleftarrows {}^1/{}_2H_2 \quad \Delta G^\circ{}_{H^+/H} = 0.0 \qquad (13)$$

$$^1/_2H_2 + e^- \rightleftarrows H^- \quad -\mathcal{F}\epsilon^\circ{}_{H/H^-} \qquad (14)$$

$$Cu^{III}L^{3+} + H^- \rightleftarrows Cu^{III}L(H^-)^{2+} \quad \Delta G^\circ{}_{comp} \qquad (15)$$

eq 7, ΔG°, is given in eq 16 as a combination of the redox potentials, ϵ°, the complexation free energy, $\Delta G^\circ{}_{comp}$, and the isomerization free energy, $\Delta G^\circ{}_{isom}$.

$$\begin{aligned} \Delta G^\circ &= \Delta G^\circ{}_{comp} + \Delta G^\circ{}_{isom} + \Delta G^\circ{}_{et} \\ \Delta G^\circ{}_{et} &= -\mathcal{F}(\epsilon^\circ{}_{H/H^-} - \epsilon^\circ{}_{II/I} - \epsilon^\circ{}_{III/II}) \end{aligned} \qquad (16)$$

The values obtained for ϵ° in this work and reported elsewhere[3,20–23] show that $\Delta G^\circ{}_{et}$ makes extremely large endothermic contributions, namely $\Delta G^\circ{}_{et} \geq 300$ KJ mol^{-1}, which must be compensated by exothermic contributions from $\Delta G^\circ{}_{comp}$ and $\Delta G^\circ{}_{isom}$ in order to make the overall reaction, eq 7, exothermic. Since copper(III) macrocycles have small equilibrium constants for the coordination of anions in axial positions, the term $\Delta G^\circ{}_{comp}$ is expected to be more positive than −10 kJ mol^{-1}. Moreover, the rigidity of the $2,3,9,10\text{-}Me_4\text{-}[14]\text{-}1,3,8,10\text{-tetraene}N_4$ macrocycle must restrict the reorganization of the ligand around the copper(I) with consequent reduction in the contribution that the isomerization, eq 10, makes to the exothermicity of the reaction.

Registry No. $[Cu(2,3,9,10\text{-}Me_4\text{-}[14]1,3,8,10\text{-tetraene}N_4)]^{2+}$, 71170-97-3; $[Cu(2,3,9,10\text{-}Me_4\text{-}[14]1,3,8,10\text{-tetraene}N_4)]^+$, 80502-51-8; Cu^+, 17493-86-6; hydrogen, 1333-74-0; formaldehyde, 50-00-0; perchloric acid, 7601-90-3.

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(24) The generation of hydrogen has also been detected in photolyses of copper(II) complexes of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene and *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.