On the Nature and Mechanism of Decomposition of Monovalent Copper Complexes with Tetra-aza Macrocyclic Ligands in Aqueous Solutions. A Pulse Radiolytic Study

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Some properties of four monovalent copper complexes with tetra-azamacrocyclic ligands (L) are reported. For all four complexes the same sequence of rearrangement and ligand loss (five reactions) is observed. The rates of rearrangement and ligand loss increase with increasing size of the macrocycle and by using 1,4,8,11-tetra-azacyclotetradecane in place of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane. The introduction of two non-conjugated double bonds has little effect on the rates of reaction but affects considerably the spectra of the $[CuL]^+$ complexes.

RECENTLY we have reported[1] that the reduction (1) of the copper(II) complex with 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L^1) in aqueous solution is followed by a series of reactions, (2), (3) and/or (4); $[Cu^{I}L^{1}]$(tetrahedral) denotes a tetrahedral or a distorted tetrahedral configuration of the monovalent complex. These reactions are followed in acidic solutions[1] by reaction (5). It seemed of interest to study the effect of structural changes in the macrocyclic ligand on these reactions. We wish to report here results with three analogous complexes: copper(II) with *C*-racemic 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (L^2); copper(II) with 1,4,8,11-tetra-azacyclotetradecane (L^3); and copper(II) with 2,2,4,11,11,13-hexamethyl-1,5,10,14-tetra-azacyclo-octadeca-4,13-diene (L^4).

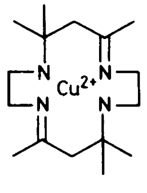
$$[Cu^{II}L^{1}](\text{planar}) + CO_2^{\bullet -} \xrightarrow{k_1} [Cu^{I}L^{1}](\text{planar}) + CO_2 \quad (1)$$

$$[Cu^{I}L^{1}](\text{planar}) + H_2O/H_3O^+ \underset{}{\overset{k_2}{\rightleftharpoons}} [Cu^{III}L^{1}\text{-}H] + OH^-/H_2O \quad (2)$$

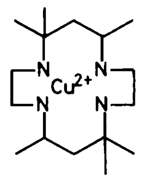
$$[Cu^{I}L^{1}](\text{planar}) \overset{k_3}{\rightleftharpoons} [Cu^{I}L^{1}](\text{tetrahedral}) \quad (3)$$

$$[Cu^{III}L^{1}\text{-}H] \rightleftharpoons [Cu^{I}L^{1}](\text{tetrahedral}) + H_3O^+ \quad (4)$$

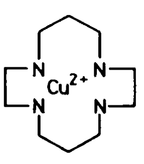
$$[Cu^{III}L^{1}\text{-}H]\ \{\text{or } [Cu^{I}L^{1}](\text{tetrahedral})\} + H_3O^+ \xrightarrow{k_5} Cu^+ + H_2L^{12+} \quad (5)$$



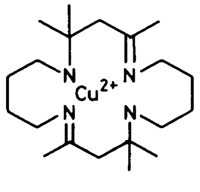
$[Cu^{II}L^{1}]$



$[Cu^{II}L^{2}]$



$[Cu^{II}L^{3}]$



$[Cu^{II}L^{4}]$

We hoped also to study the effect of the macrocyclic ligands on the properties of Cu^{II}–R (ref. 2) and Cu^{III}–R (ref. 3), where R is an aliphatic residue, *i.e.* CH_2OH and $CH_2CO_2^-$. However, no such intermediates were observed for complexes with L^1 and L^2 and though the results indicate that such intermediates are formed with CuL^3 their yields or molar absorption coefficients are small and we could not study their properties in detail.

EXPERIMENTAL

Materials.—The complexes $[CuL^2][ClO_4]_2$ and $[CuL^3][ClO_4]_2$ were prepared by heating a solution of the free ligand (Strem Chemicals Inc.) and $Cu[ClO_4]_2$ in methanol to 60 °C for several hours. The precipitate formed was recystallized from acidic ($HClO_4$) aqueous solutions. $[CuL^4][ClO_4]_2$ was prepared as described in the literature[4] by a modified Curtis' method. An acetone solution of $[Cu\{H_2N(CH_2)_4NH_2\}_2][ClO_4]_2$ was stirred at room temperature for 3 or 4 d, in the presence of active aluminium oxide without which the product was not obtained. The purple precipitate formed was filtered off and separated from the aluminium oxide by dissolving in water and recrystallization. All other chemicals were AnalaR grade and were used without further purification. No attempt to keep a constant ionic strength was made, however most experiments were carried out at 0.1 mol dm^{-3} sodium formate. Solutions were prepared using triply distilled water. The N_2O and Ar used were bubbled through two washing bottles containing VSO_4 in dilute H_2SO_4 over Zn amalgam followed by a washing bottle containing triply distilled water; thus traces of oxygen were eliminated.

Irradiation.—The linear electron accelerator at the Hebrew University of Jerusalem was used to produce electron pulses of 0.1—1.5 μs, at 200 mA and 5 MeV.† The dose per pulse was 1—30 Gy. N_2O saturated $K_4[Fe(CN)_6]$ solutions were used for dosimetry.[5] The irradiation cell

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† Throughout this paper: 1 eV = 1.602×10^{-19} J; 1 rad = 10^{-2} Gy = 10^{-2} J kg^{-1}.

was 4 cm long; the analyzing light passed three times through the cell. The experimental set-up in Jerusalem and the method used for evaluating the results were identical to that described earlier.[1]

Preparation of Free Radicals.—The radiation chemistry of water and dilute aqueous solutions can be summed up by equation (6).[5] The yields of these primary products, which

$$H_2O \xrightarrow{\gamma, e^-} e^-(aq), H^\bullet, OH^\bullet, H_2O_2, H_2, H_3O^+(aq) \quad (6)$$

are homogeneously distributed in the solution within less than 10 ns, are $G_{e^-(aq)} = G_{OH} = 2.65$, $G_H = 0.60$, $G_{H_2O_2} = 0.75$, $G_{H_2} = 0.45$ in units of molecules per 100 eV absorbed in the solution.[5] In solutions containing high concentrations of solutes the radical yield is larger whereas the yield of H_2 and H_2O_2 is smaller.[5]

In N_2O saturated solutions reactions (7) and (8) have to be considered.[6] Thus in neutral and alkaline N_2O saturated solution the free radicals present are $OH^\bullet$ and $H^\bullet$, the latter contributing *ca.* 10% of the free radical concentration.

Reactions with $CO_2^{\bullet -}$. In N_2O saturated solutions containing 0.1 mol dm^{-3} NaO_2CH reaction (9) occurs, thus converting all the primary free radicals into $CO_2^{\bullet -}$ free radicals.

At pH > 7.0 the last reaction is not observed and the product formed in the third reaction is stable for at least a few minutes.

When Ar saturated solutions containing 2×10^{-4} mol dm^{-3} $[CuL^2][ClO_4]_2$, 0.1 mol dm^3 NaO_2CH, and 5×10^{-5} mol dm^{-3} fumaric acid at pH 4.5 are irradiated the kinetics observed are identical to those observed in the absence of fumarate. However a residual absorbance at 350 nm is observed in these solutions after reaction (5) is over. This residual absorbance is attributed to $HO_2CCH\underset{Cu^+}{=}CHCO_2H$ formed in reaction (10).[9]

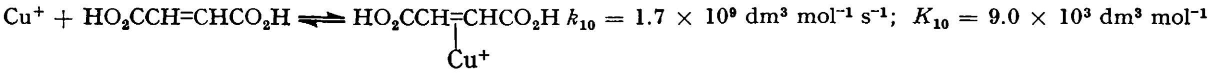
When Ar saturated solutions containing 0.1 mol dm^{-3} $(CH_3)_3COH$ and 1×10^{-4} mol dm^{-3} $[CuL^2][ClO_4]_2$ were irradiated the same intermediates and kinetics, excluding reaction (1), were observed but their yield was *ca.* 50% of that observed in the formate solutions. In identical solutions, but N_2O saturated, none of these intermediates was observed.

When N_2O saturated solutions containing 0.1 mol dm^{-3} CH_3OH and 8×10^{-4} mol dm^{-3} $[CuL^2][ClO_4]_2$ at 5 < pH < 10 were irradiated the same intermediates and kinetics as in the formate-containing solutions were observed. However

$$e^-(aq) + N_2O \xrightarrow{H_2O} OH^\bullet + N_2 + OH^- \quad k = 8.7 \times 10^9 \text{ dm}^3 \text{ mol}^{1} \text{ s}^{-1} \text{ (ref. 6)} \quad (7)$$

$$e^-(aq) + H_3O^+ \longrightarrow H^\bullet \quad k = 2.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (ref. 6)} \quad (8)$$

$$OH^\bullet/H^\bullet + HCO_2^- \longrightarrow CO_2^{\bullet -} + H_2O/H_2 \quad k_{OH^\bullet + HCO_2^-} = 3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (ref. 7)} \quad (9)$$
$$k_{H^\bullet + HCO_2^-} = 1.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (ref. 8)}$$


$$Cu^+ + HO_2CCH{=}CHCO_2H \rightleftharpoons HO_2CCH\underset{Cu^+}{=}CHCO_2H \quad k_{10} = 1.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}; \; K_{10} = 9.0 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \quad (10)$$

RESULTS

$[Cu^IL^2]$.—When Ar or N_2O saturated solutions containing 0.1 mol dm^{-3} NaO_2CH and (2—30) $\times 10^{-5}$ mol dm^{-3} $[CuL^2][ClO_4]_2$ are irradiated the formation of short-lived transients with relatively weak absorption bands in the near-u.v. (Figure 1) is observed. It should be noted that the ordinate in Figure 1 gives the changes in the molar absorption coefficients ($\Delta\varepsilon$) and thus the maxima of the absorption bands observed are at $\lambda < 330$ nm. (We could not extend our study to shorter wavelengths due to the absorption of $[CuL^2]^{2+}$).

The formation of the first transient in N_2O saturated solutions obeys a pseudo-first-order rate law, $k_1(L^2) = (2.5 \pm 0.5) \times 10^9$ dm^3 mol^{-1} s^{-1}.*

The second reaction observed which causes a decrease in the absorption over the whole wavelength range studied obeyed a first-order rate law, the rate increasing somewhat with $[H_3O^+]$. This observation is in accord with expectation for reaction (2). We find $k_2(L^2) = (2.8 \pm 0.4) \times 10^4$ s^{-1} at pH 6.0.

The third reaction observed obeys a first-order rate law, the rate being independent of complex or buffer concentration, pH, dose per pulse, or wavelength; $k_3(L^2) = (7.5 \pm 0.5) \times 10^2$ s^{-1}.

At pH < 5.5 a fourth reaction is observed which obeys a pseudo-first-order rate law, the rate being independent of complex or buffer concentration, pulse intensity, or wavelength but being proportional to $[H_3O^+]$; $k_5(L^2) = (1.6 \pm 0.4) \times 10^6$ dm^3 mol^{-1} s^{-1}.

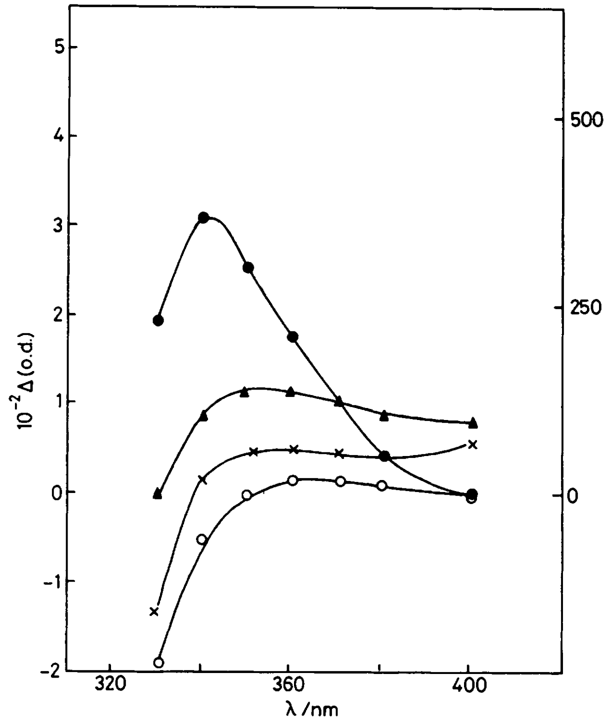


FIGURE 1 Difference spectra of transients observed in Ar saturated solutions containing 2×10^{-4} mol dm^{-3} $[CuL^2][ClO_4]_2$, 0.1 mol dm^{-3} NaO_2CH, and 1×10^{-3} mol dm^{-3} phosphate at pH 4.9 ± 0.1; pulse intensity 1.5×10^3 rad: 1 μs (▲), 50 μs (×), 5 ms (●), and 50 ms after pulse (○) (o.d. = optical density)

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* The justification for ascribing the four consecutive reactions observed for these complexes to reactions (1), (2), (3) or (4), and (5) is given in the Discussion section.

their yield was only *ca.* 50% of that in the formate solutions even when relatively small pulses were used, indicating that $^{\bullet}CH_2OH$ radicals react relatively slowly with $[CuL^2]^{2+}$.

$[Cu^IL^3]$.—When Ar or N_2O saturated solutions containing 0.1 mol dm^{-3} NaO_2CH and 1×10^{-3} mol dm^{-3} phosphate buffer and (2—40) $\times 10^{-5}$ mol dm^{-3} $[Cu^{II}L^3][ClO_4]_2$ are irradiated, similar results to those observed in the solutions containing $[CuL^2]^{2+}$ are observed. Typical spectra of the intermediates are shown in Figure 2. The peaks at *ca.* 340 nm for the first intermediate and at 335 nm for the third one seem to be real as $[CuL^3]^{2+}$ has a considerable absorbance only at $\lambda < 325$ nm. The rates of reaction observed here are $k_1(L^3) = (3 \pm 0.6) \times 10^9$ dm^3 mol^{-1} s^{-1}; $k_2 = (5.4 \pm 0.5) \times 10^4$ s^{-1}; and $k_3 = (3 \pm 1) \times 10^3$ s^{-1}. The intermediate formed in the latter reaction at pH > 8 seems to be stable for several seconds and then a precipitate is formed probably due to disproportionation of the $[CuL^3]^+$ complex in parallel to ethylenediaminecopper(I) complexes. At pH < 8 a fourth reaction is observed with $k = 26 \pm 4$ s^{-1}; 58 ± 10 s^{-1}, and $(1.4 \pm 0.3) \times 10^3$ s^{-1} at pH 7.2, 6.1, and 5.1 respectively. At lower pH's this reaction has a rate greater than or equal to that of reaction (3) and we could not measure it. From these results we estimate k_5 *ca.* 1×10^8 dm^3 mol^{-1} s^{-1}. The results seem to suggest that below the pK_a of the free ligand, water can also react as an acid in this reaction.

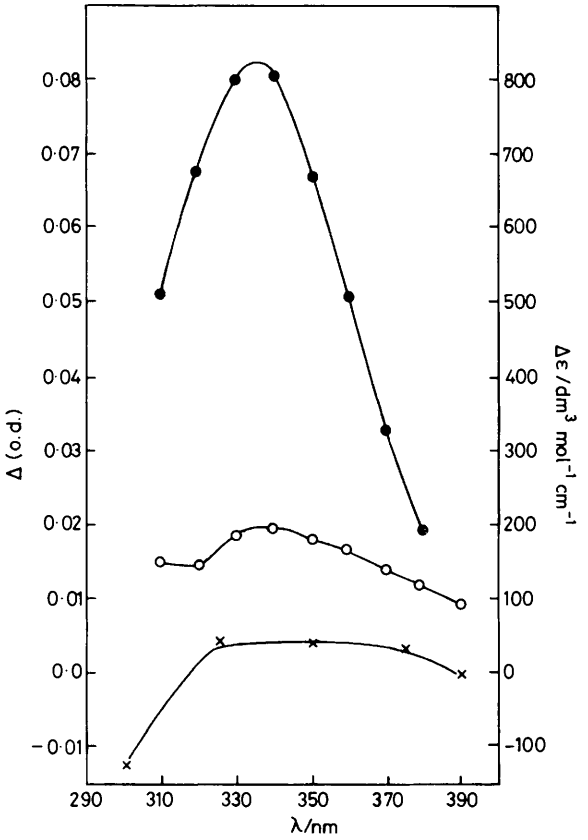


FIGURE 2 Difference spectra of transients observed in Ar saturated solutions containing 2×10^{-4} mol dm^{-3} $[CuL^3][ClO_4]_2$, 0.1 mol dm^{-3} NaO_2CH, and 1×10^{-3} mol dm^{-3} phosphate; pulse intensity 1.5×10^3 rad: 1 μs after pulse at pH 4.6 (○), 60 μs after pulse at pH 9.0 (×), and 1 ms after pulse at pH 4.6 (●)

When Ar saturated solutions containing 2×10^{-4} mol dm^{-3} $[CuL^3][ClO_4]_2$, 0.1 mol dm^{-3} NaO_2CH, and 5×10^{-5} mol dm^{-3} $HO_2CCH{=}CHCO_2H$ are irradiated, the kinetics of reaction observed differ considerably from those in the absence of fumarate.

Irradiation of N_2O saturated solutions containing (3—10) $\times 10^{-4}$ mol dm^{-3} $[CuL^3]^{2+}$ and 0.1 mol dm^{-3} $(CH_3)_3COH$ resulted in the immediate formation of a transient absorbing around 400 nm. The absorption coefficient of this transient was low and the kinetics were complex and were not studied in detail. The result suggests, however, the formation of $[Cu^{II}L^3\{CH_2C(CH_3)_2OH\}]$ and/or $[Cu^{III}L^3\{CH_2C(CH_3)_2OH\}]$ in parallel with observations with the aquacopper cations.[2,3]

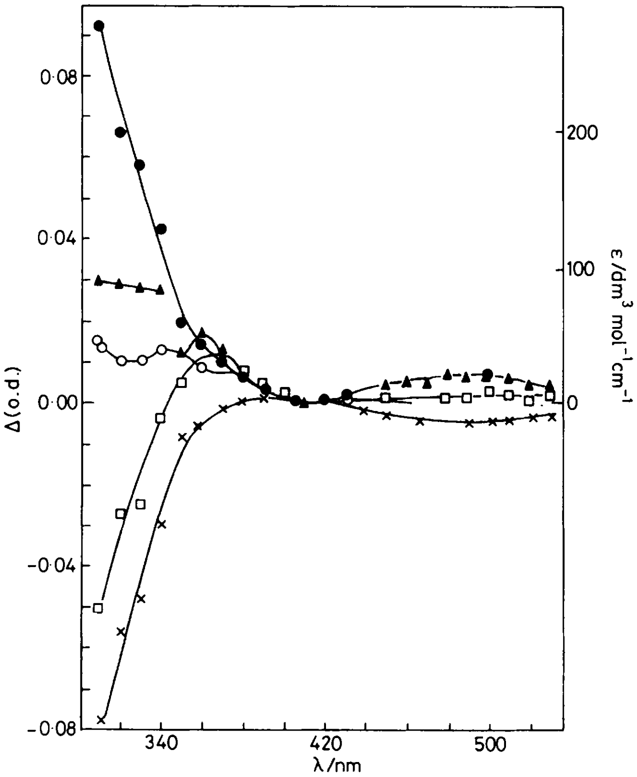


FIGURE 3 Spectra of transients observed in Ar saturated solutions containing 2×10^{-5} mol dm^{-3} $[CuL^4][ClO_4]_2$, and 0.1 mol dm^{-3} NaO_2CH at pH 7.2: immediately after pulse (○) (left ordinate), 280 μs after pulse (□) (left ordinate), 280 μs after pulse (●) (right ordinate), 6 ms after pulse (×) (left ordinate), and 6 ms after pulse (▲) (right ordinate)

$[Cu^IL^4]$.—When N_2O or Ar saturated solutions containing (5—100) $\times 10^{-6}$ mol dm^{-3} $[CuL^4][ClO_4]_2$ and 0.1 mol dm^{-3} NaO_2CH in the pH range 6—11 (below pH 6.0 the complex is unstable) are irradiated, similar results to those observed in the former two systems are observed. Typical spectra of the intermediates are shown in Figure 3. For this complex, $k_1(L^4) = (5.0 \pm 1.0) \times 10^7$ dm^3 mol^{-1} s^{-1} was determined. Due to the low rate of reaction (1) and the high rate for reaction (3) of this complex, k_3 $(L^4) = (3.6 \pm 0.6) \times 10^4$ s^{-1}, we were unable to measure k_2 (L^4). {In order to measure k_2, high concentrations of $[CuL^4]^{2+}$ are required; however, under these conditions we have to work at $\lambda > 350$ nm, due to the absorbance of the complex, and there the changes in the absorption coefficients are too small to obtain an accurate measurement of k_2 (L^4).} The product of reaction (3) is unstable in the whole pH range studied, the rate of the last reaction observed being 2 × 10^2, 4 × 10^2, 6 × 10^2, 8 × 10^2, and 1.3 × 10^3 s^{-1} at pH 11.0, 10.0, 9.0, 7.0, and 6.1 respectively. Clearly this reaction is ' acid ' catalysed and k_5 (L^4) *ca.* 6 × 10^8 dm^3 mol^{-1} s^{-1} can be estimated from the last two results. Evidently this is only an estimate due to the competing reaction with water (below). The slight

$$[Cu^IL^4] \text{ (tetrahedral)} + 2H_2O \rightarrow Cu^+ + H_2L^{42+} + 2OH^-$$

dependence of the rate of this reaction on pH might be due to the fact that the p*K* of the secondary amino-groups of the ligand are in this pH range. The addition of fumarate resulted in complicated kinetics also in this system.

Specific rates of reactions observed for the complexes

Complex	$k_1/dm^3\ mol^{-1}\ s^{-1}$	k_2/s^{-1}	k_3/s^{-1}	$k_5/dm^3\ mol^{-1}\ s^{-1}$
$[CuL^2][ClO_4]_2$	$(2.5 \pm 0.5) \times 10^9$	$(2.8 \pm 0.4) \times 10^4$ [a]	$(7.5 \pm 0.5) \times 10^2$ [a]	$(1.6 \pm 0.4) \times 10^6$
$[CuL^3][ClO_4]_2$	$(3 \pm 0.6) \times 10^9$	$(5.4 \pm 0.5) \times 10^4$ [b]	$(3 \pm 1) \times 10^3$ [c]	*ca.* 2 × 10^8 [a]
$[CuL^4][ClO_4]_2$	$(5 \pm 1) \times 10^7$	*d*	$(3.6 \pm 0.6) \times 10^4$	*ca.* 6 × 10^8 [e]
$[CuL^1][ClO_4]_2$ [f]	2.3 × 10^9	$(1.5 \pm 0.2) \times 10^5$	$(5.0 \pm 1.0) \times 10^2$	$(6 \pm 1) \times 10^6$ [g]

[a] Measured in Ar saturated solutions, containing 0.1 mol dm^{-3} CH_3OH at pH 6.0. [b] Measured in Ar saturated solutions, containing 0.1 mol dm^{-3} formate at pH 5.1. [c] As for *b*, but at pH 6.1. [d] Too fast to be measured, see text. [e] Rough estimate, see text. [f] Results from Ref. 2. [g] Measured in the pH range 4.0—5.0.

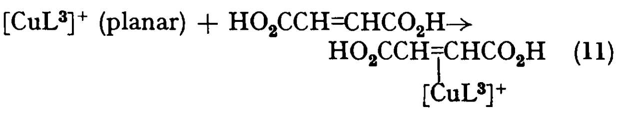
DISCUSSION

The results obtained in this study indicate that the reaction sequence following the reduction of $[CuL]^{2+}$ to $[CuL]^+$ is similar for the four ligands studied. Three reactions following the reduction are observed for all the complexes and these reactions obey similar rate laws. Thus the first reaction obeys a first-order rate law and its rate depends slightly on pH. This reaction causes a decrease in the absorption of $[Cu^IL]$ for L^1, L^2, and L^3. (For L^4 the spectrum could not be measured, see above.) The second reaction obeys a first-order rate law and causes an increase of absorption for all complexes studied. The last reaction observed obeys a second-order rate law: first order in $[Cu^IL]$ and in $[H_3O^+]$. The final products seem to be Cu^+ and H_2L^{2+}. For $[Cu^IL^1]$ and $[Cu^IL^2]$ the formation of Cu^+ is proven by the formation of the $d \rightarrow \pi$ complex $\underset{Cu^+}{HO_2CCH{=}CHCO_2H}$, reaction (10). For $[Cu^IL^3]$ and $[Cu^IL^4]$ this experiment cannot be carried out (see above), however, the precipitate formed in slightly alkaline solutions containing the third intermediate in the $[CuL^3]$ system suggests that this is a $[Cu^IL^3]$ complex which disproportionates. The acid-catalysed reaction of this intermediate can therefore also be assigned to a ligand loss. Thus we conclude that reactions (1)—(5) which were shown to occur for $[CuL^1]^{2+}$ take place also for the other complexes studied. We can therefore analyse the effect of the ligand structure on the specific rates of these reactions and on the spectra of the intermediates observed. The kinetic data are summarized in the Table.

A comparison of the properties of $[CuL^1]^+$ and $[CuL^2]^+$ indicates that saturation of the two double bonds has little effect on the rates of reaction observed. The rate of formation of the hydride (k_2) and the rate of ligand loss seem to be slightly lower but the effect is too small to merit an explanation. It should be noted that the absorption bands of the transients have been shifted considerably towards the u.v. and the absorption coefficients seem to be lower, though the maxima of the bands could not be determined. These observations are in accord with the notion that the absorption band of $[CuL^1]^+$ is due to charge transfer from copper to a ligand π^* orbital.

A comparison of $[CuL^2]^+$ and $[CuL^3]^+$ shows that both complexes have similar absorption bands. However, both the rearrangement reaction (3) and the ligand-loss reactions are considerably faster for $[CuL^3]^+$. This observation is in accord with the known fact that complexes of L^3 are less rigid than those of L^2.

It should also be pointed out that the results indicate that $[CuL^3]^+$ (tetrahedral) disproportionates while $[CuL^2]^+$ does not. This suggests that in $[CuL^3]^+$ two copper atoms may approach each other significantly more than in $[CuL^2]^+$. Furthermore, the results suggest that reaction (11) takes place whereas the corresponding



$$[CuL^3]^+ \text{ (planar)} + HO_2CCH{=}CHCO_2H \rightarrow \underset{[CuL^3]^+}{HO_2CCH{=}CHCO_2H} \quad (11)$$

reaction for $[CuL^1]^+$ and $[CuL^2]^+$ does not occur, in agreement with the less sterically hindered structure of $[CuL^3]^+$.

A comparison of $[CuL^1]^+$ with $[CuL^4]^+$ indicates that the larger ring size in $[CuL^4]^+$ enhances considerably the rates of reactions (3) and (5) as expected due to loss of rigidity of the complex. The shift of the peak of absorption to the u.v. when going from $[CuL^1]^+$ (tetrahedral) to $[CuL^4]^+$ (tetrahedral) suggests that the copper in the latter complex is a weaker reducing agent, again in agreement with expectation [4] as the larger ring is expected better to accommodate the monovalent copper and to enable a better interaction of the *d* orbitals with the π^* orbitals of the ligand. However, we note surprisingly that k_1 (L^4) is considerably lower than k_1 for the other complexes. This is unexpected if $[CuL^4]^{2+}$ is the strongest oxidant, as expected from the results in alcohol solutions [4] and from the known effects of ring size on the electrochemistry of macrocyclic complexes in aprotic media. One might speculate that the larger ring size enables a better hydration of the planar $[CuL^4]^{2+}$ complex and thus stabilizes it.

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