Oxidation of (5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)copper(II) by Radicals produced by Flash Photolysis and Reactions of the Oxidized Copper Complex

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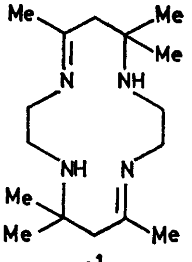
The title complex, $[CuL^1]^{2+}$, is oxidized in aqueous solution by OH and $[Cl_2]^-$ radicals generated by flash photolysis. The oxidation by OH radicals is initiated by H-atom abstraction from the ligand (k 1.5×10^{10} dm^3 mol^{-1} s^{-1}). The spectrum of the transient oxidized copper complex is more characteristic of a copper(II)–ligand-radical species than of a copper(III) macrocyclic complex. The oxidized complex is itself a powerful oxidant, oxidizing Cl^- to Cl_2 (k 1.5×10^3 dm^3 mol^{-1} s^{-1}), $[N_3]^-$ to N_2 (k 2.5×10^4 dm^3 mol^{-1} s^{-1}), and H_2O_2 to HO_2 (k 7.0×10^2 dm^3 mol^{-1} s^{-1}) as well as HO_2 and $[O_2]^-$ radicals. The oxidized $[CuL^1]^{2+}$ species is probably an intermediate in the decay of $[CuL^1]^{3+}$ in acetonitrile.

THE formation of transient copper(III) complexes of nitrogen-donor ligands by the hydroxyl-radical oxidation of the corresponding copper(II) complexes was observed by Meyerstein.[1] The spectra of the presumed copper(III) complexes were largely independent of the ligands (NH_3, ethylenediamine, glycine, *etc.*) and the complexes decayed by complex paths at pH >5. The copper(III) complexes of the macrocyclic ligands 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L^1) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (L^2) produced by electrochemical oxidation in acetonitrile[2] decay more slowly than the copper(III) complexes produced by OH oxidation in water, but much more rapidly than the corresponding nickel(III) complexes in acetonitrile.[3] The nickel(III) complexes decompose readily only in more basic solvents.[4]



L^1

Following a study of tetra-aza macrocyclic nickel(III) complexes produced in aqueous solution by the radical oxidation of the nickel(II) complexes,[5] we have now examined the oxidation of a corresponding copper(II) complex, $[CuL^1]^{2+}$. For the nickel(III)-diene complex, $[NiL^1]^{3+}$, intramolecular electron-transfer and protonation reactions lead to the stabilization of a nickel(II)-diene-radical species as the pH is increased. The larger reduction potential of Cu^{3+} compared with Ni^{3+} suggested that intramolecular ligand oxidation to form a copper(II)-ligand-radical species would be more probable for the copper(III) complex. We find that at pH $\geqslant 1$ only one oxidized copper(II)-diene species can be observed following radical oxidation. The oxidized complex itself oxidizes Cl^- ion, $[N_3]^-$ ion, and hydrogen peroxide, and is probably a copper(II)-diene-radical species.

EXPERIMENTAL

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene bis(hydrogen perchlorate), $L^1 \cdot 2HClO_4$, was prepared by the direct reaction of ethylenediamine and acetone in the presence of anhydrous $Mg[ClO_4]_2$.[5] The copper(II) complex, $[CuL^1][ClO_4]_2$, was prepared by the reaction of copper(II) carbonate with an excess of the ligand in water–methanol and purified by crystallization.[6] All other materials were of AnalaR grade and solutions were made up in triply distilled water.

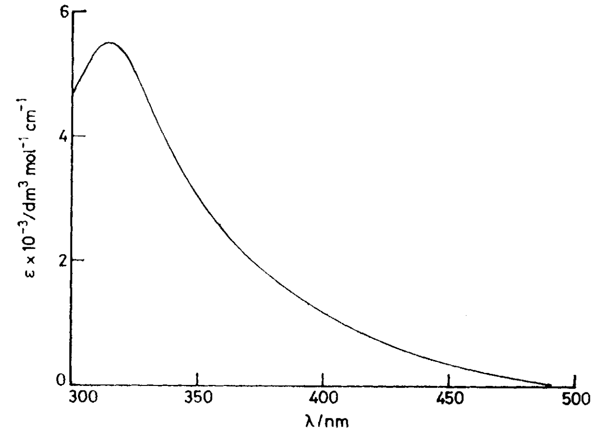


FIGURE 1 Spectrum of transient species formed by OH or $[Cl_2^-]$ radical oxidation of $[CuL^1]^{2+}$ at pH 1 and pH 5. The spectra were taken 20 μs after the initiation of the oxidation by OH radicals and 100 μs after the initiation of oxidation by $[Cl_2]^-$ radical ions

The procedures for the flash-photolysis experiments have been described.[5,7] Hydroxyl radicals were generated by flash photolysis of solutions of H_2O_2 (10^{-3}—10^{-2} mol dm^{-3}) and halogen radical ions by photolysis of the appropriate $[Co(NH_3)_5X]^{2+}$ complex ion (X = Cl or Br) in the presence of the halide ion. We have previously shown that reactions of these radicals with the free ligand are much slower than the reactions with the metal complexes, and do not interfere.[5] All the experiments were carried out at room temperature (22 ± 3 °C).

RESULTS AND DISCUSSION

Radical Oxidation.—In the presence of $[CuL^1]^{2+}$ (5×10^{-5} mol dm^{-3}), OH radicals reacted rapidly to generate a transient absorbance (Figure 1) with $\lambda_{max.} =$ 315 nm ($\varepsilon_{max.}$ 5.5×10^3 dm^3 mol^{-1} cm^{-1}). The transient yield and spectrum were independent of the acid concentration (pH 1—5). The spectrum of Figure 1 differs considerably from that of the copper(III)–diene complex prepared electrochemically in acetonitrile [2] which has two absorption maxima at 335 and 395 nm and resembles that of the nickel(III)–diene complex $[NiL^1]^{3+}$.[3,5] The transient produced by the OH radical oxidation of $[NiL^1]^{2+}$ has the same spectrum at pH 1 as $[NiL^1]^{3+}$ in acetonitrile.[5] The aquated-electron reduction of the copper(II)-diene complex in water produces the same copper(I)–diene complex as electrochemical reduction in acetonitrile.[8] The single broad absorption of Figure 1 is similar to the absorption of other copper(III) complexes generated in aqueous solution by OH radical reactions, for which $\lambda_{max.}$ lies between 290 and 320 nm, with absorption coefficients of 4 000—8 000 $dm^3\ mol^{-1}\ cm^{-1}$.[1]

The rate of the reaction between OH radicals and $[CuL^1]^{2+}$ was determined by using H_2O_2 as a competitor for the OH radicals and measuring the yields of the oxidized copper complex as a function of the concentration of $[CuL^1]^{2+}$. The rate constant, $(1.5 \pm 0.3) \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$, was independent of acid (pH 1—5) and is the same as the acid-independent rate constants for the OH oxidation of $[NiL^1]^{2+}$ and other nickel(II) tetra-aza macrocyclic complexes.[5] No changes took place in the spectrum of the oxidized copper–diene complex during the decay of the transient in the range pH 1—5. Because of the difference between the spectrum of the transient and that of $[CuL^1]^{3+}$ in acetonitrile and the lack of subsequent spectral changes, we suggest that the initial product observed in the radical oxidation of $[CuL^1]^{2+}$ may be a copper(II)–diene-radical species rather than $[CuL^1]^{3+}$. The initial step in the OH oxidation of $[NiL^1]^{2+}$ is H-atom abstraction from the ligand, which is followed by pH-dependent reactions which form $[NiL^1]^{3+}$ (pH <3) or a nickel(II)–diene-radical species (pH >3).[5] A reaction sequence similar to that proposed [5] for the OH reaction with $[NiL^1]^{2+}$ accounts for our observations for the $[CuL^1]^{2+}$ complex. The rate constant measured in the competition experiments is that of reaction (1). The rate constant is close to those for H-atom abstraction reactions of OH radicals with aliphatic amines at $-CH_3$ or $-CH_2$ sites.[9] Reaction (2) is the acid-catalyzed conversion of the initial copper(II)–ligand-radical species to the complex $[CuL^1]^{3+}$. Reaction (3) is similar to the acid-catalyzed interconversions of alkylamino-radicals and α-aminoalkyl radicals observed for aliphatic amines [10] and is included on the assumption that one form of the copper(II)–diene-radical complex, like that of the nickel(II)–diene-radical complex, is that in which the unpaired electron is located on a nitrogen atom. The independent existence of the Ni^{II}–L^2-radical in which the unpaired electron is localized on a nitrogen atom has been demonstrated by e.s.r. measurements.[4] If the overall equilibrium position of reactions (2) and (3) lies towards the copper(II)–diene-radical form in the pH range of our observations, only one transient species would be seen. For $[NiL^1]^{2+}$ the rate and equilibrium constants for the reactions equivalent to (2) and (3) are such that $[NiL^1]^{3+}$ predominates as the initial product at pH <3. Copper(III) is a more strongly oxidizing metal centre than Ni^{III},[2] and would favour the formation of the copper(II)–diene-radical species. The low basicity of the solvent accounts for the observation of $[CuL^1]^{3+}$ in acetonitrile where reaction (2) will lie towards the copper(III) species after electrochemical oxidation. Nickel(III) complexes of 14-membered macrocyclic complexes are more stable in acetonotrile than water for this reason.

$$OH + [Cu^{II}(diene)] \longrightarrow [Cu^{II}(diene\ \dot{C})] + H_2O \qquad (1)$$

$$[Cu^{II}(diene\ \dot{C})] + H^+ \rightleftharpoons [Cu^{III}(diene)] \qquad (2)$$

$$[Cu^{II}(diene\ \dot{C})] \xrightleftharpoons{H^+} [Cu^{II}(diene\ \dot{N})] \qquad (3)$$

The oxidation of $[CuL^1]^{2+}$ by $[Cl_2]^-$ radical ions leads to the same transient spectrum as oxidation by OH radicals; $[Br_2]^-$ radical ions do not react with $[CuL^1]^{2+}$ presumably because their reduction potential (1.77 V) [11] is not sufficiently high. The rate of the reaction between $[Cl_2]^-$ and $[CuL^1]^{2+}$ was relatively slow and the pseudo-first-order rate constant for the disappearance of $[Cl_2]^-$ could be measured as a function of the concentration of $[CuL^1]^{2+}$. The rate constant found from the gradient of the linear plot of the pseudo-first-order rate constant against $[CuL^1]$ was $(1.5 \pm 0.2) \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ at pH 1. This reaction is much slower than the oxidation of $[NiL^1]^{2+}$ by $[Cl_2]^-$ radicals for which the rate constant is $1.0 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$.[5] A direct electron-transfer reaction between $[Cl_2]^-$ and $[CuL^1]^{2+}$, producing $[CuL^1]^{3+}$ initially, would not necessarily result in our observing a transient product different from that seen following oxidation by OH radicals because $[CuL^1]^{3+}$ would transform to the copper(II)–diene-radical species [reactions (2) and (3)] within the time of the reaction with $[Cl_2]^-$ radicals. The slower rate of reaction for $[CuL^1]^{2+}$ compared with that for $[NiL^1]^{2+}$ is due to the smaller $\Delta G^{\ominus}$ for the reaction ($E^{\ominus}$ for $[CuL^1]^{3+}$ is *ca.* 0.25 V greater than for $[NiL^1]^{2+}$) and it is of interest that we were not able to observe any reaction between $Cu^{2+}(aq)$ and $[Cl_2]^-$ in the course of studies of the oxidation of aquametal ions by halogen radical anions.[11,12] Direct formation of a copper(II)–diene-radical species from the reaction between $[CuL^1]^{2+}$ and $[Cl_2]^-$ is unlikely because $[Cl_2]^-$ radical ions are much less effective H-atom abstraction reagents than OH radicals.

$$[Cl_2]^- + [CuL^1]^{2+} \longrightarrow [CuL^1]^{3+} + 2Cl^- \qquad (4)$$

The decay of the copper(II)–diene-radical or $[CuL^1]^{3+}$ species in the absence of reactive substrates was not followed because it was relatively slow ($t_{\frac{1}{2}}$ >0.1 s). In all the experiments, oxidizable substrates such as H_2O_2 or Cl^- were present in order to generate the radicals used to oxidize the $[CuL^1]^{2+}$ complex. Copper(III)–amino-acid complexes decay by reactions which involve ligand oxidation.[1] In acetonitrile the decay of $[CuL^1]^{3+}$ produces H^+ ion and the decay of the $[CuL^2]^{3+}$ complex in acetonitrile results in the introduction of the –N=C–

group into the ligand.[2] Reaction (2) will release H^+ in the decay of $[CuL^1]^{3+}$, and the copper(II)-diene-radical species will lead to the formation of the –N=C– function on further oxidation, just as in the case of nickel(II)-diene-radical species.

Nature of the Oxidized Species.—The differences between the transient spectra produced by radical oxidation of $[CuL^1]^{2+}$ and $[NiL^1]^{2+}$ have already been discussed. The similarity of the transient spectrum of Figure 1 to the spectra of the transients produced by OH radical oxidation of the copper(II) complexes of ethylenediamine, glycine, and amino-acids [1] and the very small differences in the transient spectra for these different ligands suggests that for all these copper(II) complexes the products observed following radical oxidation may be copper(II)-ligand-radical species. The high pH at which the ethylenediamine and other complexes were oxidized (pH 7—11) [1] would favour the formation of copper(II)-ligand-radical species rather than copper(III) complexes. The decay processes of the oxidized copper(II) complexes observed by Meyerstein involved ligand oxidation by the copper(II) centre, and the primary step in these reactions must be the formation of a ligand-radical species. The spectra of radicals formed from aliphatic amines by H-atom abstraction [9] are also similar to that of Figure 1 and to the transients observed by Meyerstein. A similar transient absorption observed in the flash photolysis of $[CuL^1]^{2+}$ in acid was attributed to a copper(II)-ligand-radical species.[13]

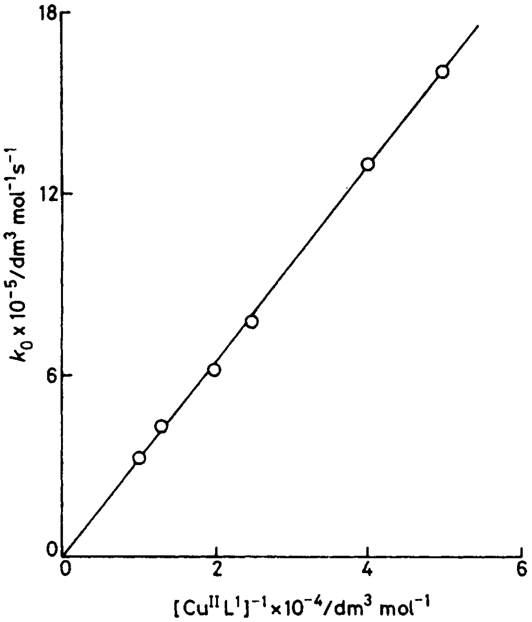


FIGURE 2 Dependence of the observed second-order rate constant for the oxidation of Cl^- by the $[CuL^1]^{3+}$ species on the concentration of $[CuL^1]^{2+}$ at 0.1 mol dm^{-3} Cl^-, 0.1 mol dm^{-3} H^+, 22 ± 2 °C

Reactions of Oxidized $[CuL^1]^{2+}$ *Species.*—Copper(III) has a reduction potential of *ca.* 2.0 V in acetonitrile,[2] and the oxidized $[CuL^1]^{2+}$ species is a powerful oxidant, reacting with Cl^-, H_2O_2, and peroxy-radicals.

In the presence of chloride ions (0.1—0.3 mol dm^{-3}) the transient decayed by a reaction which was second order in the concentration of the transient and first order in the concentration of chloride ion. The reaction was retarded by $[CuL^1]^{2+}$, Figure 2. (5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-1,4,8,11-tetraene)nickel(III), $[NiL^3]^{3+}$, the strongest oxidant of the three nickel(III) macrocyclic complexes previously studied, also oxidizes Cl^- to Cl_2.[5] The first-order dependence on $[Cl^-]$ and the retardation by $[CuL^1]^{2+}$ are typical of oxidations of halide ions by metal ions in which halogen radical anions are produced as intermediates. Reactions

$$[CuL^1]^{3+} + Cl^- \rightleftharpoons [CuL^1(Cl)]^{2+} \qquad (5)$$

$$[CuL^1(Cl)]^{2+} + Cl^- \rightleftharpoons [CuL^1]^{2+} + [Cl_2]^- \qquad (6)$$

$$[CuL^1]^{3+} + [Cl_2]^- \longrightarrow [CuL^1]^{2+} + Cl_2 \qquad (7)$$

(5)—(7) lead to the rate expression (8) under steady-state conditions if K_5 is large enough that the predominant

$$\frac{-d[Cu^{III}]}{dt} = \frac{2k_6k_7[Cu^{III}]^2[Cl^-]}{k_{-6}[Cu^{II}] + k_7[Cu^{III}]} \qquad (8)$$

reactive species is $[CuL^1(Cl)]^{2+}$ or the copper(II)-diene-radical equivalent.* For situations in which $k_{-6}[CuL^1] \gg k_7[Cu^{III}L^1]$ the observed second-order rate constant, k_0, is given by $k_0 = 2k_6k_7[Cl^-]/k_{-6}[Cu^{II}L^1]$. The concentration of $[CuL^1]^{2+}$ was always at least 25 times greater than the concentration of the oxidized species and k_{-6} was 1.5 × 10^8 dm^3 mol^{-1} s^{-1}, so that the inequality was fulfilled and the observed rate constant corresponded to k_0. From the dependence of k_0 on $[Cl^-]$ and on $1/[Cu^{II}L^1]$, Figure 2, we obtain a value of 115 ± 20 dm^3 mol^{-1} s^{-1} for k_6k_7/k_{-6}, and 5 × 10^{10} dm^6 mol^{-2} s^{-2} for the product k_6k_7. Values of k_6 and k_7 cannot be separately determined from these experiments. If we now use the value of 2.0 V (in acetonitrile) for the standard reduction potential of $[CuL^1]^{3+}$, K_6 has a value of 10^{-5}, so that k_6 = 1.5 × 10^3 dm^3 mol^{-1} s^{-1} and k_7 = 3.3 × 10^7 dm^3 mol^{-1} s^{-1}. If the reactive species is the copper(II)-diene-radical rather than $[CuL^1]^{3+}$ the value of $E^\ominus$ will be lower, leading to a smaller value for k_6 and a larger value for k_7. However, the $E^\ominus$ value must lie within *ca.* 0.2 V of 2.0 V, because the maximum possible value for k_6 will be the diffusion-controlled rate, *ca.* 10^{10} dm^3 mol^{-1} s^{-1} which is no more than three orders of magnitude greater than that estimated above. The retardation by $[CuL^1]^{2+}$ would not be observed if k_7 were very much larger than k_{-6} (1.8 × 10^8 dm^3 mol^{-1} s^{-1}), and we believe the estimated values for k_6 and k_7 are close to the true values.

The oxidized $[CuL^1]^{2+}$ species reacted with hydrogen peroxide (9) and the pseudo-first-order rate constants for the reaction were a linear function of $[H_2O_2]$. The rate constant for the reaction at pH 1 is (7.0 ± 1.0) × 10^2 dm^3 mol^{-1} s^{-1}, close to the rate constant for the

$$H_2O_2 + [CuL^1]^{3+} \longrightarrow [CuL^1]^{2+} + H^+ + HO_2 \qquad (9)$$

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* Although the nature of the oxidized $[CuL^1]^{2+}$ species is uncertain, it is convenient for the purposes of writing rate expressions and reactions to use the form $[CuL^1]^{3+}$.

oxidation of H_2O_2 by $[NiL^1]^{3+}$. No retardation by $[CuL^1]^{2+}$ was observed for this reaction and it may be assumed that HO_2 does not oxidize $[CuL^1]^{2+}$. The oxidized $[CuL^1]^{2+}$ species also reacted with HO_2 and $[O_2]^-$ radicals, but the absolute rate constants for the reactions could not be measured because of the difficulties of establishing the concentrations of both the

$$HO_2 + [CuL^1]^{3+} \longrightarrow [CuL^1]^{2+} + H^+ + O_2 \quad (10)$$

$$[O_2]^- + [CuL^1]^{3+} \longrightarrow [CuL^1]^{2+} + O_2 \quad (11)$$

peroxy-radicals and the oxidized $[CuL^1]^{2+}$ species in solutions in which both were produced simultaneously. The relative rates for the reactions with $[O_2]^-$ and HO_2 are 25 : 1, similar to the values for the nickel(III) oxidations of peroxy-radicals.[5]

When azide ion (8×10^{-4}—4×10^{-3} mol dm^{-3}) was present in solutions containing Cl^- (0.1 mol dm^{-3}), H^+ (0.1 mol dm^{-3}), and the oxidized $[CuL^1]^{2+}$ species, the decay of the transient copper species changed from second order to first. The first-order rate constant was a linear function of azide-ion concentration and the second-order rate constant for the oxidation of $[N_3]^-$ ion was $(2.5 \pm 0.3) \times 10^4$ dm^3 mol^{-1} s^{-1}. The rate was not dependent on the concentration of $[CuL^1]^{2+}$ and the rate constant applies to the initial step in the oxidation;

$$[CuL^1]^{3+} + [N^3]^- \longrightarrow [CuL^1]^{2+} + N_2 + N^\bullet \quad (12)$$

k_{12} is higher than k_6 for the oxidation of Cl^- ion due to the smaller standard reduction potential for azide ion.

The oxidation reactions of the transient copper diene complex are perhaps more typical of an oxidized metal centre than of a copper(II)–ligand-radical species, although oxidation of H_2O_2, HO_2, and $[O_2]^-$ by both $[NiL^1]^{3+}$ and nickel(II)–diene–radical species has been observed. The oxidation of Cl^- is mechanistically more straightforward if the oxidant is $[CuL^1]^{3+}$ than if it is the copper(II)–diene-radical complex. In view of the importance of the Cu^{II}—Cu^{III} couple in a number of catalytic oxidations, further studies of the relationship between copper(III) complexes and copper(II)–ligand-radical species are desirable.

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