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# THE EFFECT OF LIGAND STRUCTURE ON SPECTRAL CHARACTERISTICS AND KINETICS OF REDOX REACTIONS OF COPPER(II) AND COPPER(III) COMPLEXES WITH MACROCYCLIC LIGANDS CONTAINING AMIDE GROUPS

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Spectral characteristics of macrocyclic copper(II) and copper(III) complexes with 13- and 14-membered tetraaza ligands containing two amine and two deprotonated amide groups ( $\text{CuL}$ ) have been studied. It was shown that, unlike copper(II) complexes, the spectral properties of copper(III) compounds are more sensitive to such ligand structure parameters as ring size and the presence of benzyl substituents. Rate constants and activation parameters for oxidation of  $\text{Cu}^{\text{II}}\text{L}$  by peroxodisulfate and decomposition reactions of  $\text{Cu}^{\text{III}}\text{L}$  in aqueous solutions at pH 5 were also measured. Activation parameters were shown to be dependent on ligand structure and the tendencies of their changes are opposite in these two types of reactions. Decomposition of copper(III) compounds proceeds probably through protonation of the amide group in acidic media and through deprotonation of amine group in alkaline media. The copper(III) complex with a benzyl-substituted 13-membered ligand was found to be most kinetically stable among all compounds studied. Possible reaction mechanisms are discussed.

**Keywords:** Copper(II,III), macrocycles, complexes, redox behaviour, kinetics

## INTRODUCTION

The stabilization of high oxidation states of 3d transition metals, in particular of copper(III), is of great current interest. This is due to the fact that such compounds can serve as models for some enzymes such as galactose oxidase,<sup>1</sup> and may be used as effective oxidants and redox catalysts.<sup>2</sup> However, it is necessary to bear in mind that thermodynamic stabilization of the high oxidation state (*i.e.* lowering the  $\text{M(III)L}/\text{M(II)L}$  couple potential) prevents its use as an effective oxidant. More attractive in this sense would be compounds possessing high redox potentials along with high kinetic stability (under kinetic stabilization we assume the inhibition of metal ion reduction *via* electron transfer from the coordinated ligand).

Among copper(III)-stabilizing ligands, noncyclic tri- and tetrapeptides have been most widely studied.<sup>2</sup> The macrocyclic tetrapeptide complex  $[\text{Cu(III)L}]^-$ , where  $\text{H}_4\text{L}$  is cyclo- $\beta$ -alanyl-glycyl- $\beta$ -alanyl-glycyl, has also been the subject of detailed investigations.<sup>3</sup> The data obtained show that an increase in the number of deprotonated amide groups in the macrocycle causes a thermodynamic stabilization of copper(III).<sup>4</sup> On the other hand, saturated tetraaza macrocycles containing only secondary amine donors, do not stabilize copper(III), but are good nickel(III)-stabilizing ligands.<sup>5</sup>

From this point of view, macrocyclic ligands containing both secondary amine and amide donor groups may be of interest. Although the redox potentials for such

copper complexes with these ligands are available in the literature,<sup>4</sup> kinetic characteristics of their redox reactions are absent.

In this work, copper complexes with macrocyclic ligands  $H_2L^1$ – $H_2L^4$  (Fig. 1) were chosen to investigate the effects of ligand structure (ring size and presence of substituents) on their spectral properties, and kinetics of copper(II) oxidation by peroxodisulfate ions and decomposition of copper(III) complexes formed.

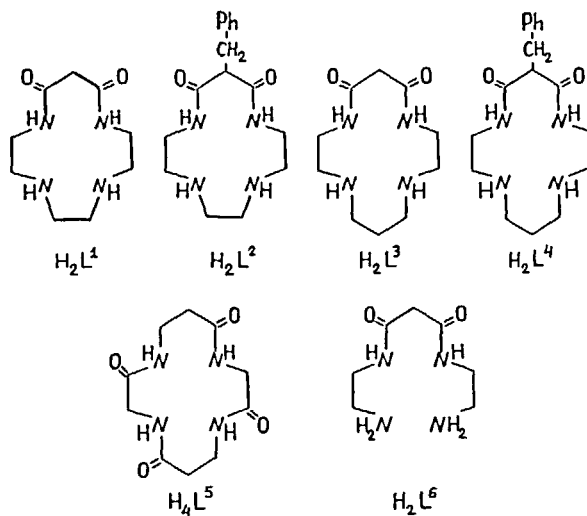


FIGURE 1 The structure of the tetraaza ligands containing amide groups used in the study.

## EXPERIMENTAL

### Reagents

All reagents used were of reagent grade. Potassium peroxodisulfate was recrystallized twice from water prior to use.

### Syntheses

Ligands  $H_2L^1$ ,  $H_2L^3$  and  $H_2L^4$  and their copper(II) complexes were prepared according to literature methods.<sup>6–8</sup> Ligand  $H_2L^2$  was prepared by condensation of benzylmalonic acid diethyl ester with 1,8-diamino-3,6-diazaoctane in a manner analogous to the preparation of  $H_2L^4$  (yield 15%). *Anal.*: Calcd. for  $C_{16}H_{24}N_4O_2$ : C, 63.2; H, 7.9; N, 18.4%. Found: C, 63.0; H, 7.7; N, 18.1%. Spectral characteristics: IR,  $cm^{-1}$  (KBr discs): 3280 s (N–H); 1655 vs (C=O, amide); 1530 s (C=C, arom.); 750 s, 694 s (C–H, arom.). PMR ( $CDCl_3$ ): 7.23s(5H); 6.9m(2H); 3.5–3.0m(7H); 2.8–2.5m(8H); 1.63s(2H). Attempts to isolate  $CuL^2$  as a solid were unsuccessful and solutions were prepared *in situ* by mixing equimolar quantities of the ligand and  $Cu(ClO_4)_2 \cdot 6H_2O$ , followed by adjustment of pH to 7 with NaOH.

### Instrumentation

Electronic spectra were recorded on Specord M-40 and Specord UV-VIS (Karl Zeiss, Jena) spectrophotometers. The infrared spectra were obtained in KBr discs using a Specord 75-IR (Karl Zeiss, Jena) spectrometer. A CXP-90 (Bruker) spectrometer was used to examine the proton NMR of the ligands. ESR spectra were obtained with an E-9 (Varian) ESR system, with MnO magnetically diluted with MgO as a standard. Cyclic voltammetry was performed with the use of a three-electrode system consisting of platinum working and auxiliary electrodes and saturated calomel reference electrode. Voltammograms were generated with a PA-3 analyser (Laboratorni pristroje, Praha). An OP-213 (Radelkis, Budapest) pH-meter was used for pH measurements (pH was adjusted with HClO<sub>4</sub>, NaOH or buffers).

### Kinetic measurements

Kinetic measurements were carried out spectrophotometrically in a thermostatted ( $\pm 0.1^\circ\text{C}$ ) quartz cell (1 cm). Solutions of reagents were thermostatted before measurement for about 15 min. Solutions of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were prepared immediately before use. In most cases an excess of copper complex with respect to peroxodisulfate was used to stabilize pH conditions and to avoid complications connected with other side reactions. The formation of copper(III) complexes and their disappearance was followed at 28 000 or 30 000 cm<sup>-1</sup>, where absorption of the initial copper(II) complexes is negligible. Decomposition of copper(III) complexes in acidic media was measured at the absorption maxima in the UV region (see below). All measurements unless otherwise stated were carried out at ionic strength I = 0.1 M (NaClO<sub>4</sub>). The observed rate constants were measured with a precision of about 10%. Accuracy of activation parameter measurement is about 5 kJ/mol for  $\Delta H^\ddagger$  and 10 J/K mol for  $\Delta S^\ddagger$ .

### Determination of copper(III) extinction coefficients

Values of  $\epsilon_{\text{max}}$  for copper(III) complexes were determined as follows: 0.5 cm<sup>3</sup> of  $5 \times 10^{-3}$  M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution was added to 1 cm<sup>3</sup> of  $2.5 \times 10^{-3}$  M CuL solution and after some time (90s to 10 min., depending on complex) 0.5 cm<sup>3</sup> of  $4 \times 10^{-2}$  M HClO<sub>4</sub> was added. After recording the absorption, 0.5 cm<sup>3</sup> of  $1.2 \times 10^{-4}$  M K<sub>4</sub>Fe(CN)<sub>6</sub> solution was added and absorption was measured again. This procedure was repeated several times. Extinction coefficients were calculated from the absorption drop after addition of K<sub>4</sub>Fe(CN)<sub>6</sub> solution with an accuracy of about 5%.

## RESULTS AND DISCUSSION

### Properties of copper(II) complexes

Interaction of copper(II) ions with dioxomacrocyclic ligands proceeds according to (1) to yield neutral complexes.<sup>4</sup>



The mechanism of this reaction includes coordination of the copper(II) ion to secondary amine nitrogen atoms and a subsequent deprotonation of amide groups.<sup>9</sup>

The equilibrium (*I*) strongly depends on pH and is almost completely shifted to the right at pH > 6 for CuL<sup>1</sup><sup>10</sup> and at pH > 5.5 for CuL<sup>3</sup>.<sup>11</sup> The spectral characteristics of the copper(II) macrocyclic complexes are given in Table I.

TABLE I  
Spectral characteristics of the copper(II) complexes.

Complex	$\nu_{\text{C-O}}, \text{cm}^{-1}$	Absorption maxima, <sup>a</sup> $\text{cm}^{-1}$	
CuL <sup>1</sup>	1580	19200(100)	40800(5400)
CuL <sup>2</sup>		19400(84)	40700(4800)
CuL <sup>3</sup>	1575	19800(91)	41900(7600)
CuL <sup>4</sup>	1570	20200(64)	41200(7200)

<sup>a</sup> Aqueous solution; extinction coefficients ( $\text{M}^{-1} \text{cm}^{-1}$ ) are given in parentheses.

The position of the low energy d-d absorption band in the electronic spectra is typical of tetragonal copper(II) complexes. Its location is close<sup>12,13</sup> to that in complexes with ligands having similar structure (19400  $\text{cm}^{-1}$  for CuL<sup>6</sup> and 20500  $\text{cm}^{-1}$  for  $[\text{CuL}^5]^{2-}$ ) and of secondary amine macrocycles<sup>4</sup> (18200  $\text{cm}^{-1}$  for  $\text{Cu}([\text{13}] \text{janeN}_4)^{2+}$  and 19800  $\text{cm}^{-1}$  for  $\text{Cu}([\text{14}] \text{janeN}_4)^{2+}$ ). The data presented show that the deprotonated amide group has little effect on the d-d transition energy, as compared to the amine group. The most prominent difference is observed between the spectra of CuL<sup>1</sup> and  $\text{Cu}([\text{13}] \text{janeN}_4)^{2+}$ . It is known that the most suitable macrocycles for Cu(II) ions are 14-membered ligands.<sup>6</sup> Apparently, in complexes with 13-membered ligands, the coordination polyhedron of the metal ion has some distortion from planarity, and this distortion is less in the case of CuL<sup>1</sup>. This causes an increase in the ligand field strength of  $[\text{L}^1]^{2-}$  as compared to  $[\text{13}] \text{janeN}_4$ .

ESR data (Table II) support the fact that ligand structure has little effect on spectral characteristics of the copper(II) complexes.

TABLE II  
ESR spectral parameters for the copper(II) complexes.

Complex	Frozen solution in H <sub>2</sub> O, 123K				Solution, 298K		
	$g_{\parallel}$	$g_{\perp}$	$10^4 A_{\parallel}, \text{cm}^{-1}$	$g_{\text{calc}}^a$	$g_{\text{iso}}$	$10^4 A_{\text{iso}}, \text{cm}^{-1}$	$\alpha^2$
CuL <sup>1</sup>	2.179	2.044	222	2.089	2.090	91.3	0.85
CuL <sup>2</sup>	2.153	2.051	225	2.085	2.087	91.3	0.84
CuL <sup>3</sup>	2.180	2.061	230	2.100	2.094	92.6	0.88
CuL <sup>4</sup>	2.153	2.060	232	2.091	2.088	97.6	0.86
$[\text{CuL}^5]^{2-}$ <sup>b</sup>	2.145	2.065	230	2.092	2.092	85.4	0.85 <sup>d</sup>
$\text{Cu}([\text{14}] \text{jane})^c$	2.194	2.052	206				0.83 <sup>d</sup>

<sup>a</sup>  $g_{\text{calc}} = 2/3 g_{\parallel} + 1/3 g_{\perp}$ . <sup>b</sup> From Ref. 13. <sup>c</sup> From Ref. 14 for solution in DMF. <sup>d</sup> Calculated.

In aqueous solution at ambient temperature a typical copper(II) spectrum is observed with splitting into four components. ESR spectra of frozen aqueous solutions are characteristic of tetragonally distorted copper(II) compounds with tetraaza ligands. In this case spectral parameters are more sensitive to ligand structure—somewhat higher  $g_{\parallel}$ -values in CuL<sup>1</sup> and CuL<sup>3</sup> in comparison with CuL<sup>2</sup>

d  $\text{CuL}^4$ , and somewhat lower values of  $g_{\perp}$  in complexes with 13-membered ligands compared to 14-membered ones have been observed. These data can reflect differences in stereochemistry of copper(II) complexes in connection with ligand structure, in particular steric hindrance created by hydrophobic benzyl substituents or axial coordination of water molecules to the metal centre. It should also be noted that a good agreement between  $g_{\text{iso}}$ , obtained from room temperature ESR spectra and  $g_{\text{calc}}$ , calculated from anisotropic spectra, is obtained.

It was somewhat surprising that the value of  $\alpha^2$  (covalence parameter) does not change substantially when amine donor atoms are replaced by amide ones. The  $\alpha^2$  value for  $[\text{CuL}^5]^{2-}$ , containing four amide groups, is practically the same as for all other complexes, including  $\text{Cu}([\text{14}] \text{aneN}_4)^{2+}$ , containing four secondary amine groups. Small differences in d-d transition energies and extinction coefficients in the electronic spectra of the copper(II) complexes also indicate, in our opinion, negligible difference between  $\text{Cu-N}_{\text{amine}}$  and  $\text{Cu-N}_{\text{amide}}$  bond covalence.

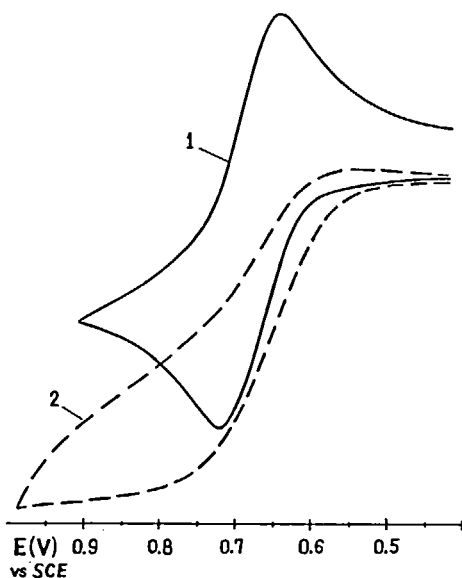


FIGURE 2 Cyclic voltammograms of copper complexes in aqueous solution (pH 7): 1- $\text{CuL}^3$ ; 2- $\text{CuL}^3$  in phosphate buffer (pH 6.86).  $[\text{CuL}] = 7.5 \times 10^{-3}$  M, sweep rate; 50 mV/s.

Cyclic voltammograms of the complexes studied (Table III, Fig. 2) were measured under conditions used for kinetic measurements. It follows from Table III that oxidation of copper(II) complexes in aqueous solution is quasi-reversible (peak separation  $\Delta E = 80$ – $130$  mV and anodic to cathodic current ratio near 1). Benzyl substituents in the macrocyclic ligands have practically no effect on the  $E_{1/2}$  value. Lower  $E_{1/2}$  values for complexes with 13-membered ligands as compared to 14-membered ones (*i.e.* thermodynamic stabilization of copper(III) in the first case) are due to the better fit of the 13-membered ring to the copper(III) ion.<sup>4,6</sup>

TABLE III  
Electrochemical data for the copper(II) complexes.<sup>a</sup>

Complex	$E_{1,2}(\pm 5)$ , mV	$\Delta E(\pm 10)$ , mV
CuL <sup>1</sup>	590	125
CuL <sup>2</sup>	600	120
CuL <sup>3</sup>	685	80
CuL <sup>4</sup>	680	90
[CuL <sup>5</sup> ] <sup>2-</sup> <sup>b</sup>	230	85

<sup>a</sup> At room temperature; sweep rate 50 mV/s. <sup>b</sup> From Ref. 4.

The presence of certain buffers in solution has a drastic effect on the electrochemical behaviour of the copper complexes. The voltammogram of CuL<sup>3</sup> in phosphate buffer (pH = 6.86) has no distinct peaks (Fig. 2). These data show a destabilizing effect of certain buffers on copper(III) compounds in good agreement with the results of kinetic measurements (see below).

#### *Spectral characteristics of the copper(III) complexes*

Copper(III) complexes with the amide macrocyclic ligands can be generated in solution electrochemically or by using such oxidants as H<sub>2</sub>O<sub>2</sub>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, IrCl<sub>6</sub><sup>2-</sup>.<sup>15,16</sup> However, their spectral properties have not been described in detail, except for [CuL<sup>5</sup>]<sup>-3</sup>. In our study, potassium peroxodisulfate was used as an oxidant, since both it and products of its reduction do not absorb in the visible and near UV region, and its reactions with copper(II) complexes are slow enough to study them by conventional spectrophotometric techniques.

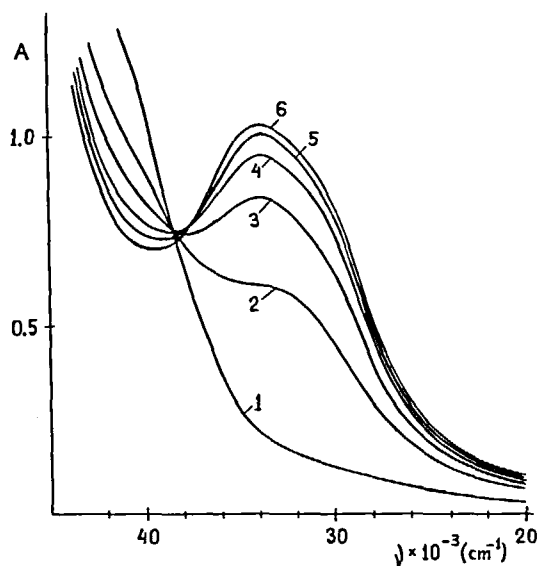


FIGURE 3 Spectral changes observed during oxidation of CuL<sup>3</sup> by peroxodisulfate. Concentrations: [CuL<sup>3</sup>] = 1.25 × 10<sup>-4</sup> M, [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] = 1.5 × 10<sup>-3</sup> M. Time intervals: 4 min.

After addition of oxidant to solutions of the copper(II) complexes an intensive absorption band appears in the near UV and visible spectral region (Fig. 3). The presence in solution of starting copper(II) complex prevents accurate determination of the position and extinction coefficient of this band. To overcome this complication, the fact was used that copper(II) complexes with ligands under consideration undergo rapid decomposition in acids (acidic dissociation constant at room temperature for  $\text{CuL}^3$  equals  $1.15 \times 10^7 \text{ M}^{-2} \text{ s}^{-1}$ <sup>17</sup>). Copper(III) complexes are much more stable under these conditions (see below). Extinction coefficients of UV absorption bands were determined as described in the Experimental Section by titration with  $\text{K}_4\text{Fe}(\text{CN})_6$ . Reaction of ferrocyanide with peroxodisulfate can be neglected, since the interaction of  $\text{Fe}(\text{CN})_6^{4-}$  with copper(III) complexes is very fast ( $k \sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$ <sup>18</sup>). This is also supported by the fact that the  $\epsilon$  value obtained was independent of the peroxodisulfate concentration used to generate copper(III).

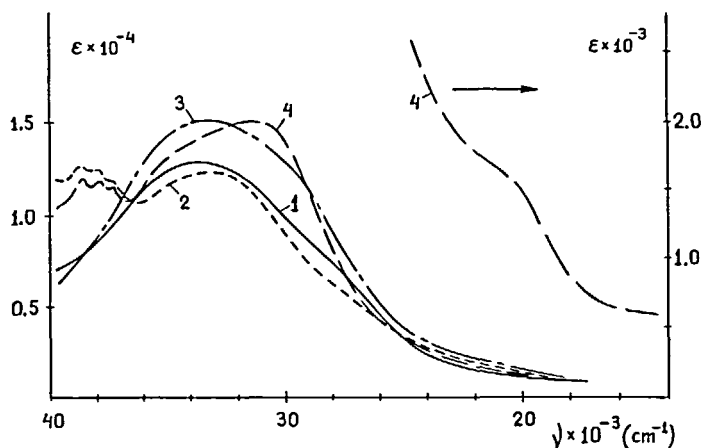


FIGURE 4 Absorption spectra of the macrocyclic copper(III) complexes: 1- $[\text{CuL}^1]^+$ ; 2- $[\text{CuL}^2]^+$ ; 3- $[\text{CuL}^3]^+$ ; 4- $[\text{CuL}^4]^+$ .

All complexes prepared have an intense absorption band in the far UV region ( $\nu > 40\,000 \text{ cm}^{-1}$ , Fig. 4). Complexes with benzyl substituted ligands also have absorption bands at about  $38\,000 \text{ cm}^{-1}$  due to aromatic ring  $\pi$ -electron excitation (the same bands are also observed in the spectra of the free ligands  $\text{H}_2\text{L}^2$  and  $\text{H}_2\text{L}^4$ ). In the region  $35\,000$ – $27\,000 \text{ cm}^{-1}$  there are several overlapping absorption bands, which are probably due to charge transfer from nitrogen atoms to the copper(III) ion. For complexes with noncyclic peptides, CT bands have been observed at  $39\,000 \text{ cm}^{-1}$  ( $\epsilon \sim 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) for  $\sigma$ -, and at  $27\,000 \text{ cm}^{-1}$  ( $\epsilon \sim 8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) for  $\pi$ -type charge transfer.<sup>19</sup> It was somewhat unexpected that the presence of benzyl substituents leads to substantial intensity redistribution in these bands, especially distinct for complexes with 14-membered ligands. This can be assigned, in our opinion, to the influence of benzyl substituents on the  $\pi$ -type CT band position.

The spectra of the copper(III) compounds have in the visible region a shoulder superimposed on strong CT bands. The intensity of this band can be estimated to be about  $200 \text{ M}^{-1} \text{ cm}^{-1}$  with a position of about  $20\,000 \text{ cm}^{-1}$  for 14 membered and  $21\,000 \text{ cm}^{-1}$  for 13-membered ligand complexes (Fig. 4). We assume that this band can be assigned to the d-d transition of the low-spin copper(III) ion, the tendency in absorption maximum shift being the same as for isoelectronic nickel(II) complexes.<sup>20</sup>



*Oxidation kinetics of copper(II) complexes by peroxodisulfate*

Despite the availability of a large number of papers concerning properties of copper(III) complexes, kinetic investigations of copper(II) to copper(III) oxidations are few. Only the oxidation of some peptide complexes by  $\text{IrCl}_6^{2-}$  and several cross reactions between peptide complexes appear to have been studied.<sup>21,22</sup> Figure 3 demonstrates spectral changes occurring during oxidation of  $\text{CuL}^3$  by peroxodisulfate. It is seen that an isosbestic point in the spectra is maintained only at initial stages and disappears as the reaction proceeds further.

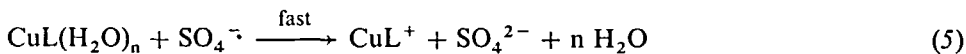
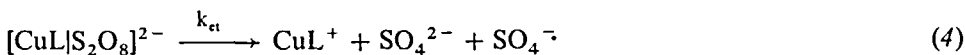
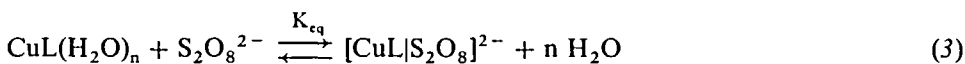
Reaction pathway depends strongly on solution composition. When buffer is present in solution (e.g. phosphate), we do not observe any measurable amount of copper(III) complex. The same effect is found for acetate- and TRIS-buffers. This is due, in our opinion, to the interaction of (buffer) weak acid anions with the copper(III) complexes thus leading to their decomposition. Addition of other salts ( $\text{NaClO}_4$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ) in concentrations up to 0.4 M has practically no effect on the kinetics of copper(III) formation.

To elucidate the stoichiometry of the oxidation we have measured absorption spectra after completion of oxidation of  $\text{CuL}^3$  and decomposition of the copper(III) complex formed at different reagent concentration ratios. Intensity of the d-d absorption band in the spectra of reaction products diminishes and additional absorption at about  $26\,000\text{ cm}^{-1}$  appears, but even at a reagent ratio of  $[\text{K}_2\text{S}_2\text{O}_8]/[\text{CuL}^3] = 1/2$  the absorption drop does not exceed 15%. Increase of this ratio leads to a bathochromic shift of the absorption maximum and to a further increase of absorption in the near UV region. The data obtained show that spectral characteristics of the product of copper(III) reduction are similar to those of the starting complex. The products can probably be oxidized further by peroxodisulfate, and this prevents determination of reaction stoichiometry.

Rate constants for oxidations were calculated from the initially linear regions of kinetic curves using the calculated  $\epsilon$  values for the copper(III) complexes. The  $\text{Cu(III)L}^+$  formation rate was found to be first-order in both reagents, (2).

$$d[\text{CuL}^+]/dt = k_{\text{eff}} [\text{CuL}][\text{S}_2\text{O}_8^{2-}] \quad (2)$$

In our opinion, the following scheme, similar to that proposed for the oxidation of nickel complexes,<sup>5</sup> can be used to describe the oxidation of the copper compounds.



Equation (2) is in agreement with the proposed scheme (3)–(5) if the rate limiting step is (4) and the value of  $K_{\text{eq}}$  is not too high. Reaction rates are practically independent of ionic strength, which fact is also in agreement with this mechanism. Rate constants and activation parameters are given in Table IV.

Comparison of  $k_{\text{eff}}$  and  $E_{1/2}$  values shows that complexes of 13-membered ligands, having lower redox potentials, oxidize slower. This may reflect a considerable

contribution of factors not immediately connected with the electron transfer step, *e.g.*  $K_{eq}$ , since

$$k_{eff} = K_{eq} k_{et} \quad (6)$$

TABLE IV

Rate constants and activation parameters for copper(II) complex oxidation by peroxodisulfate (298K).

Complex	$k_{eff}$ , $M^{-1} s^{-1}$	$\Delta H^\ddagger$ , kJ/mol	$\Delta S^\ddagger$ , J/K mol
CuL <sup>1</sup>	$1.0 \times 10^{-1}$	52	-88
CuL <sup>2</sup>	$5.9 \times 10^{-2}$	57	-77
CuL <sup>3</sup>	$2.3 \times 10^{-1}$	40	-122
CuL <sup>4</sup>	$3.4 \times 10^{-1}$	43	-108

It is seen from Table IV that although differences in the rate constants are not large, there are distinct variations in activation parameters. For complexes with 13-membered ligands, the values of  $\Delta H^\ddagger$  are considerably higher and  $\Delta S^\ddagger$  values less negative than for complexes with 14-membered ligands. This may reflect differences in copper(II) stereochemistry in both types of complexes.

The data presented allow us to elucidate the effect of benzyl substituents on activation parameters. Somewhat higher  $\Delta H^\ddagger$  and less negative  $\Delta S^\ddagger$  values for complexes CuL<sup>2</sup> and CuL<sup>4</sup> as compared with CuL<sup>1</sup> and CuL<sup>3</sup>, respectively, may be due to steric hindrance in the axial position of the copper(II) ion of the bulky benzyl groups.

#### Decomposition of the copper(III) complexes

Copper(III) complexes formed in the oxidations are relatively unstable and decompose *via* intramolecular redox reactions. Most data available concerning such reactions refer to noncyclic peptide complexes.<sup>2,23,24</sup> Decomposition of the macrocyclic complex [CuL<sup>5</sup>]<sup>-</sup> has also been studied in detail.<sup>4</sup>

Our experiments have shown that copper(III) complexes with ligands H<sub>2</sub>L<sup>1</sup>-H<sub>2</sub>L<sup>4</sup> are most stable in neutral solution. Both increase and decrease of pH enhances the decomposition rate.

#### Decomposition at pH 5

Oxidation of copper(II) complexes by peroxodisulfate is accompanied by a pH drop (pH of the solution after completion of oxidation stabilizes near a value of 5 when excess complex is used). Kinetic curves for decomposition were linear (log A vs time), indicating first-order behaviour for the copper(III) complex, (7).

$$-d[CuL^+]/dt = k_d[CuL^+] \quad (7)$$

TABLE V

Rate constants and activation parameters for decomposition of CuL<sup>+</sup> at pH 5 (298K).

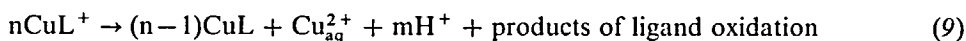
Complex	$k_d$ , s <sup>-1</sup>	$\Delta H^\ddagger$ , kJ/mol	$\Delta S^\ddagger$ , J/K mol
[CuL <sup>1</sup> ] <sup>+</sup>	$1.6 \times 10^{-4}$	60	-117
[CuL <sup>2</sup> ] <sup>+</sup>	$7.3 \times 10^{-5}$	55	-139
[CuL <sup>3</sup> ] <sup>+</sup>	$2.1 \times 10^{-4}$	61	-111
[CuL <sup>4</sup> ] <sup>+</sup>	$3.1 \times 10^{-4}$	55	-127

Analysis of data presented in Table 5 shows little effect of ring size on activation parameters, but the effect of benzyl substituents is more considerable. Decompositions of  $[\text{CuL}^2]^+$  and  $[\text{CuL}^4]^+$  are characterized by somewhat lower  $\Delta H^\ddagger$  and more negative  $\Delta S^\ddagger$  values. It should be noted that the trends in activation parameters in this case are opposite to those observed for the oxidations (*cf.* Table IV). More negative  $\Delta S^\ddagger$  values for complexes with benzyl-substituted ligands can probably be explained by steric factors and, in particular, by the influence of the substituents on the coordination of water molecules, which must occur when copper(III) is reduced to copper(II). Axial complexation in the  $\text{Cu(III)L} \rightarrow \text{Cu(II)L}$  redox transition is supported by the data.<sup>6</sup>

The mechanism of reduction may be described by (8)



where  $L'$  is the oxidized form of the ligand containing a new double bond, or by complete oxidation of the ligand molecule upon decomposition of the macrocyclic complex, (9).



The former possibility seems to be the more probable.

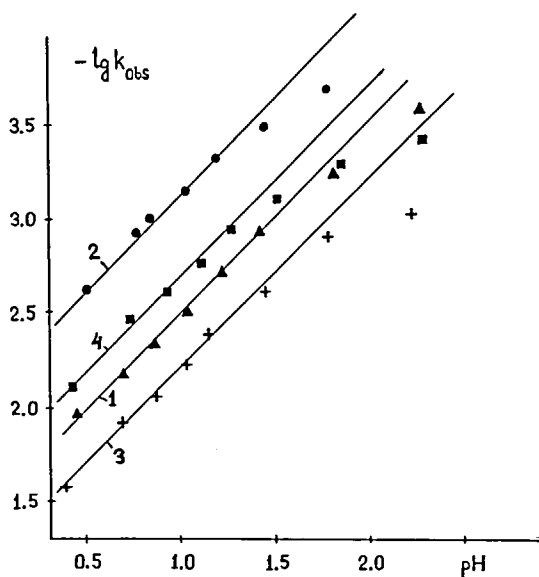


FIGURE 5 A plot of  $k_{\text{obs}}$  vs pH for the decomposition of the copper(III) complexes: 1- $[\text{CuL}^1]^+$ ; 2- $[\text{CuL}^2]^+$ ; 3- $[\text{CuL}^3]^+$ ; 4- $[\text{CuL}^4]^+$ .

#### Decomposition in acidic solutions

As was previously noted, addition of acid to the solution containing both copper(II) and copper(III) complexes causes rapid decomposition of the former, so that the absorption of the solution is due solely to the copper(III) complex. The pH

dependence of the observed decomposition rate constants,  $k_{\text{obs}}$  (Fig. 5), shows that (10) holds in the pH region 0.3–1.5.

$$k_{\text{obs}} = k_{\text{obs}}^{\text{H}} [\text{H}^+] \quad (10)$$

At higher pH values, deviations from linearity are observed. In the linear region the data obtained can probably be explained by the following scheme.



Considerable differences between kinetic parameters of these reactions (Table VI) and decomposition reactions at pH 5 (Table V) support a change of reaction mechanism.

TABLE VI  
Rate constants and activation parameters<sup>a</sup> for decomposition reactions in acid (HClO<sub>4</sub>, 298K).

Complex	$k_{\text{obs}}^{\text{H}}, \text{M}^{-1} \text{s}^{-1}$	$\Delta H^{\ddagger}, \text{kJ/mol}$	$\Delta S^{\ddagger}, \text{J/K mol}$
[CuL <sup>1</sup> ] <sup>+</sup>	$3.0 \times 10^{-2}$	67	-49
[CuL <sup>2</sup> ] <sup>+</sup>	$6.0 \times 10^{-3}$	78	-24
[CuL <sup>3</sup> ] <sup>+</sup>	$5.3 \times 10^{-2}$	71	-31
[CuL <sup>4</sup> ] <sup>+</sup>	$1.7 \times 10^{-2}$	69	-47

<sup>a</sup> Measured at pH = 1.2.

It follows from these data that both macrocyclic ring size and substituents have an effect on the stability of the copper(III) complexes in acidic medium. Complexes of 13-membered ligands are more stable (as at pH 5) and the presence of benzyl groups in the macrocycle leads to an enhanced kinetic stability of the copper(III) complex. Analysis of activation parameters is difficult in this case, but considerably less negative activation entropies as compared with the other reactions studied should be emphasized.

#### *Decomposition in alkaline solutions*

Addition of alkali to solutions of the copper(III) complexes causes rapid decomposition. In the case of complexes with 13-membered ligands (but not 14-membered ligands), formation of a red intermediate, which disappears within a few seconds, was observed. Such an intermediate is possibly a copper(III) complex with the ligand having a deprotonated amine donor atom. The pK of this deprotonation was estimated to be about 13. The possibility of amine group deprotonation in copper(III) complexes has been described in the literature and is considered to occur in the first stages of decomposition in alkaline media.<sup>25</sup>

Our study shows that macrocyclic ring size, the presence of benzyl substituents and amide groups have little effect on spectral characteristics of copper(II) macrocyclic complexes, although redox potential is determined primarily by the number of deprotonated amide groups and, to a lesser extent, by the size of the macrocycle. Spectra of copper(III) complexes are more sensitive to ligand structure. Correlation

between the structure of the ligands and kinetic parameters of redox reaction can be made in the case of oxidations of the copper(II) complexes by peroxodisulfate and decomposition of the copper(III) complexes in neutral solution. In the latter case a more negative value of activation entropy in complexes with benzyl-substituted ligands acts as a kinetic stabilizing factor. The relatively high stability in acidic medium of the macrocyclic copper(III) complexes studied, along with high redox potentials, suggests their applicability as effective oxidants for various substrates.

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