

Redox Behaviour of Copper(II) Tetrathia Macrocylic Complexes

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Abstract

Electrochemical redox properties of copper(II) complexes with quadridentate macrocyclic ligands [12]aneS₄, [13]aneS₄ and iso[14]aneS₄ have been investigated. The cyclic voltammetry at a platinum electrode in acetonitrile shows in all cases a quasi-reversible CuL^{2+/+} electrode reaction with a half-wave potential of 0.96–1.15 V versus SHE. The reversibility of the redox process was confirmed also coulometrically. The size of the cavity in the 14-membered ring as well as its conformation flexibility permits a tetrahedral environment and leads to the stabilization of the oxidation state of Cu(I) more than in the 12- and 13-membered ring systems. All three copper(II) complexes undergo autoreduction in acetonitrile solution. The reaction is of the first order with respect to the copper complex with the rate constant $(1.9\text{--}3.2) \times 10^{-5} \text{ s}^{-1}$. Due to the change of the polyhedron structure the activation energy of Cu(iso[14]aneS₄)²⁺ autoreduction is higher than that of complexes with smaller rings. The formal potentials as well as the process of autoreduction of copper(II) tetrathia macrocyclic complexes model the reactivity of 'blue' copper proteins.

Introduction

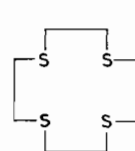
Copper(II) complexes with thiaether polydentate ligands are studied as analogues of active centres of 'blue' copper proteins in order to elucidate the nature of their unusual behaviour. The spectral [1–3], thermodynamic [2, 3] and redox [4] properties of copper(II) tetrathia macrocyclic complexes depict these compounds as the most suitable structural models for the type 1 copper sites among a variety of other sulphur-containing complexes.

The possibility of functional modelling of 'blue' copper proteins using copper(II) tetrathia macrocyclic complexes has not yet been studied thoroughly [5]. One of the main difficulties is the choice of a solvent which would dissolve both the copper com-

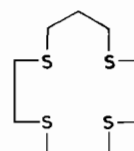
plexes and biosubstrates. Polythia macrocyclic complexes are poorly soluble in many solvents and, moreover, also interact with some of them, e.g. alcohols and water. Acetonitrile which dissolves both CuL²⁺ and many biosubstrates proved to be the most suitable medium for this purpose. However, there are no literature data on the redox potentials of the CuL^{2+/+} couples in this solvent which are required for various correlations. Besides this, in acetonitrile solution the polythia macrocyclic complexes undergo autoreduction [5], the mechanism and kinetics of which have not yet been investigated. Reaction (1) should be taken into account in the study of biomimetic reactions with the participation of these complexes.



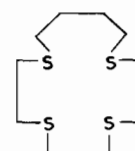
The aim of the present paper is to determine the redox potentials of CuL^{2+/+} couples and to study the kinetics of autoreduction for copper(II) complexes with ligands [12]aneS₄, [13]aneS₄ and iso[14]aneS₄.



[12]aneS₄, L1



[13]aneS₄, L2



iso[14]aneS₄, L3

Experimental

The CuL(ClO₄)₂ complexes were synthesized as reported previously [1, 5]. The voltammetric measurements were performed by using the Polarographic Analyzer PA 2 (Laboratorní přístroje, Prague). A three-electrode system was used: a platinum disc electrode (surface area 1.15 mm²) sealed in soft glass as a working electrode, a large-surface platinum electrode as an auxiliary electrode

and a calomel electrode with aqueous 4 M LiCl and with the salt bridge filled with 0.1 M LiClO₄ as a reference electrode. Voltammograms were recorded at a scan rate of 0.1 V/s. The supporting electrolyte was 0.1 M LiClO₄ and the inert gas argon saturated by acetonitrile vapours.

Coulometric measurements as well as preparatory electrolysis were performed with the coulometric analyzer OH-404 (Radelkis, Budapest). The working electrode consisted of a double circular platinum net placed parallel to a fritte separating the anodic from the cathodic compartment of the electrolytic cell. The extensive graphite electrode was used as an auxiliary electrode. The reference electrode was the same as in voltammetric measurements.

The kinetic measurements were made spectrophotometrically monitoring the decrease in absorbance at $\lambda_{\max} = 660$ nm [5] corresponding to copper(II) tetrathia macrocyclic complexes. The absorption of copper(I) complexes at this wavelength is negligible. The spectrometer Specord UV-Vis (Zeiss, Jena) was employed. Measuring cell (5 cm) was thermostated (± 0.1 °C) by an external water bath. ESR spectra were obtained with a Varian E 9 apparatus in the X-band of radiofrequency field. The measurements were carried out in very thin capillaries with 10^{-3} M complex acetonitrile solution at room temperature. For calibration the DPPH (diphenylpicrylhydrazyl) radical was used as standard.

Results and Discussion

Electrochemical Studies

The cyclic voltammograms of the complexes under study show one cathodic peak ($E_{p,c}$) with an anodic counter-peak ($E_{p,a}$). The potential separation between the peaks (ΔE_p) is 90–180 mV and the peak current ratio $i_{p,a}/i_{p,c}$ in all cases is near to one. It suggests a quasi-reversible character of the electrode reaction



The quasi-reversibility of the redox process was also confirmed coulometrically. So, the bulk-phase electrolytical CuL²⁺ reduction and CuL⁺ reoxidation consumes the charge corresponding to the charge number of electrochemical reaction $z = 0.96$.

Table 1 lists half-wave potentials determined from the cyclic voltammograms according to eqn. (3).

$$E_{1/2} = (E_{p,a} + E_{p,c})/2 \quad (3)$$

Our data for CuL1²⁺ and CuL2²⁺ are somewhat more positive than those obtained for the same compounds in 80% methanol–20% water medium [4]; the redox potential of CuL3²⁺ has not been published yet. The potential shift is common for Cu(II)/Cu(I) couples owing to the Cu(I) oxidation state stabilization in

TABLE 1. Redox potentials for CuL²⁺ complexes^a

Complex	$E_{p,c}$	$E_{p,a}$	ΔE_p	$E_{1/2}$
CuL1 ²⁺	0.70	0.79	0.09	0.74
CuL2 ²⁺	0.67	0.76	0.09	0.71
CuL3 ²⁺	0.80	0.98	0.18	0.89

^a0.1 M LiClO₄ in acetonitrile as a supporting electrolyte, 25 °C, platinum electrode used as a working electrode, E in V vs. 4 M SCE, ΔE_p values for the scan rate of 0.1 V s⁻¹, $E_{1/2} = (E_{p,c} + E_{p,a})/2$, for the ferrocenium/ferrocene couple $E_{1/2} = 0.40$ V and $\Delta E_p = 0.07$ V under the same conditions.

acetonitrile. Solvatochromism was also observed as a result of the effect of solvent donor properties on our complexes [5].

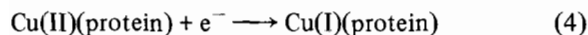
So in acetonitrile, like in the methanolic medium [4] it was also confirmed that the $E_{1/2}$ values obtained for complexes with a S₄ donor set are the most positive ones among the known copper(II) macrocyclic complexes. Such redox potentials may account for the coordination of μ -acceptor thiaether atoms to copper(II). A decrease in the number of coordinated thiaether atoms in the coordination unit diminishes the $E_{1/2}$ value. According to their redox potentials the copper(II) complexes form the series CuS₄²⁺ > CuN₂S₂²⁺ > CuN₄²⁺ [4, 6–8].

The value of the redox potential is chiefly stimulated by the single occupied molecular orbital (SOMO) energy [9]. The SOMO energy for the coordination sphere of CuS₄²⁺ is lower than that for CuN₄²⁺ which determines the high positive redox potentials of copper(II) tetrathia macrocyclic complexes. The SOMO energy for the CuN₂S₂²⁺ chromophore seems to occupy the intermediate position between those for CuS₄²⁺ and CuN₄²⁺.

The redox potentials of copper molecules with ligands L1 and L2 are nearly the same. Molecular models indicate that these macrocyclic ligands do not allow the realization of a tetrahedral environment advantageous for copper(I). An increase in the size of the cavity in L3 and its high conformation flexibility permit a tetrahedral geometry to be realized. Hence, the valent state Cu(I) in the CuL3 complex will be more stabilized than in complexes with 12- and 13-membered macrorings. As a result, the redox potential of the CuL3^{2+/+} couple is shifted into a more positive region when compared with other complexes under study or with the 14-membered macrocycle with the 5,6,5,6 sequence of chelate rings [4]. So, the size of the macrocycle cavity is the main factor determining the parameters of the characteristic spectral intense band [2, 5] and the value of formal potential.

The $E_{1/2}$ values determined for CuS₄²⁺ complexes are near to those of 'blue' copper proteins [10]. The

positive redox potentials determine the high reactivity of these metalloproteins, their oxidative and electrotransport functions *in vivo*. Due to the high values of redox potential these copper proteins are able to undergo autoreduction in solution [10].



However, the kinetics and mechanism of such reactions have not yet been studied because of the complexity of natural substances. It was shown earlier [5] that the copper(II) tetrathia macrocylic complexes have a tendency to autoreduction in acetonitrile solution.

The Kinetics of Autoreduction

As a result of autoreduction of copper(II) complexes (eqn. (1)) corresponding copper(I) complexes are formed. The bulk-phase electrooxidation performed after the autoreduction yields again the complex species CuL^{2+} as evidenced from the specific electronic spectra of these compounds. Thus the autoreduction does not lead to appreciable destruction of the macrocycle. The same results were obtained both under aerobic and anaerobic conditions which confirms the CuL^+ stability towards oxidation by atmospheric oxygen within the period of experiment.

The kinetic data obtained for three different initial concentrations of copper(II) complexes indicate that the reaction rate may be expressed by the first order rate equation

$$-\frac{d[\text{CuL}^{2+}]}{dt} = k_{\text{obs}}[\text{CuL}^{2+}] \quad (5)$$

The linearity of the integral form of eqn. (5) was found fulfilled for a consumption of the initial complex by 70%. The k_{obs} values calculated from the slope of the $\ln A$ versus time dependence are given in Table 2.

The activation energies, E_a , were obtained from the temperature dependence of k_{obs} within the interval 20–60 °C (Table 2). For CuL1^{2+} and CuL2^{2+} the E_a values are about the same within the interval of experimental error. The activation energy for reaction of CuL3^{2+} is much higher. In view of the

TABLE 2. Kinetic data for autoreduction of CuL^{2+} complexes in acetonitrile^a

Complex	$10^5 \times k_{\text{obs}}$ (s^{-1})	E_a (kcal mol^{-1})
CuL1^{2+}	3.2	9.6
CuL2^{2+}	1.9	10.4
CuL3^{2+}	3.2	17.0

^aRate constants k_{obs} at 25.0 °C.

differences in $E_{1/2}$ values we also attributed this behaviour to the different stabilizing ability of ligands to the formation of copper(I) tetrahedral complexes. Therefore, in the course of reaction (1) in 12- and 13-membered macrocylic complexes the chelate unit is not essentially affected and the contribution of conformation changes to E_a is small. The size of the L3 cavity favours the formation of a tetrahedral environment of CuS_4^+ . In this case during reaction (1) the coordination polyhedron geometry of CuL^{2+} changes dramatically which results in a considerable increase in E_a^{conf} and hence in the total activation energy, E_a .

The ESR spectra of all CuL^{2+} complexes in acetonitrile at room temperature exhibit the sharp signal near $g = 2.001$ (Fig. 1). A similar picture was obtained in the reaction of the copper(II) complex with 1,5-dithiacyclooctane [11] where this signal was attributed to the ligand cation-radical, L^+ . Such a cation-radical is produced in the course of the ligand inner-sphere oxidation by Cu(II). In analogy with ref. 11 we consider the signal with $g = 2.001$ as evidence of the presence of the tetrathia macrocylic cation free-radical. Additional confirmation of such a ligand radical was obtained from ESR spectra of free [12]ane S_4 in concentrated sulphuric acid. Here we have obtained a similar signal evidently generated in the oxidation of the macrocycle by sulphuric acid. The existence of a free-ligand radical in Cu(II) polythia macrocycle systems was also considered by Rorabacher *et al.* [12], however, no signal was evidently observed in the frozen methanol medium.

The present and the literature data indicate the presence of a redox equilibrium in the reaction mixture.

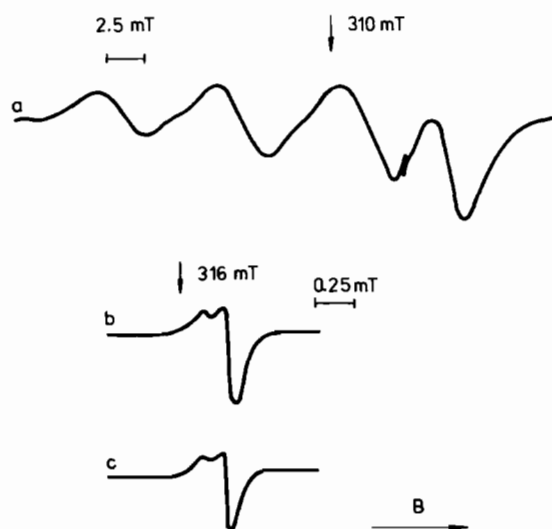
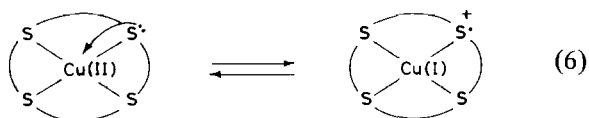


Fig. 1. ESR spectrum of CuL1^{2+} in acetonitrile (a, b) and free [12]ane S_4 in conc. H_2SO_4 (c), 298 K.



The inner-sphere electron transfer from the macrocycle thiaether donor atom to copper(II) is, probably, the rate determining step of the overall reaction (1). The cation-radical undergoes various chemical conversions to give copper(I) complexes which were obtained by this way also as solids $\text{CuL}(\text{ClO}_4)$. Identification of other reaction products is in progress at present.

Thus the physicochemical properties of copper(II) tetrathia macrocyclic complexes resemble those of 'blue' copper proteins. In addition they model the reactivity of these proteins in autoreduction reactions. The high reactivity of copper(II) polythia macrocyclic complexes towards different bioreductants seems to be due to the formation of cation-radical complexes. The unusual properties and high reactivity of 'blue' copper proteins may be accounted for in the same way.

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