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Electrochemical Study of N,N'-ethylenebis(thioacetylacetoniminato)copper(II) Complex in Non-aqueous Solvents

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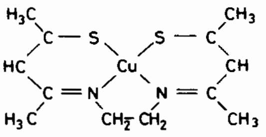
The voltammetric method was used for studying the course of oxidation and reduction of N,N'-ethylenebis(thioacetylacetoniminato)copper(II) complex (CuN_2S_2) *in a number of non-aqueous solvents, with a platinum electrode. The complex* CuN_2S_2 *undergoes reversible one-electron oxidation in all the solvents approximately at the potentials of +1.07 V* vs. $E_{1/2}$ *of the redox system BBCr(I)–BBCr(0). Reduction process was only studied in five non-aqueous solvents and an effect of the dielectric constant of the solvent on the measured potential of this process was observed.*

Introduction

Since metal complexes with Schiff bases were found to be suitable model compounds of biological systems, they attract increasing attention. The biological importance of transition metals in electron transfer reactions initiated an intensive study of the redox behaviour of transition metal chelates, especially of those in which sulphur and nitrogen atoms have a donor function [1].

This paper deals with the redox behaviour of the Cu(II) complex with the tetradentate N_2S_2 Schiff base-N,N'-ethylenebis(thioacetylacetoniminato)copper(II) (I) in a series of non-aqueous solvents.



(I)

This compound was found [2] to form a neutral monomeric complex, essentially keeping its square-planar geometry, so that axial coordination sites can be occupied by a solvent.

The aim of this study was to determine how changes of bonding properties in axial sites caused by changing the solvent influence both the electrochemical and the chemical reactivity of the given complex.

Experimental

N,N'-ethylenebis(thioacetylacetoniminato)copper(II) complex was prepared according to the method published in literature [3] and recrystallized from a mixture of water–acetone. Bis(biphenyl)chromium(I) iodide BBCrI was synthesized using an already described method [4].

The solvents used, *viz.* nitromethane (NM), acetonitrile (AN), propanediol-1,2-carbonate (PDC), acetone (AC), methanol (MeOH), N-methylformamide (NMF), N,N'-dimethylacetamide (DMA), dimethylsulphoxide (DMSO) and hexamethylphosphoric triamide (HMTP) were purified by standard procedures [5].

Voltammetric measurements were carried out by means of a polarographic analyzer Model 174 A in three-electrode arrangement. For working and auxiliary electrodes platinum wires were used while a saturated water silver/silver chloride electrode served as reference electrode. The reference electrode was separated from the solution being measured by a bridge filled with a solution of the solvent and the supporting electrolyte, thus protecting the measured solution from contamination with water. The measurements were made in nitrogen atmosphere with a depolarizer concentration of 10^{-3} *M* in 0.1 *M* tetrabutylammonium perchlorate (TBAP) solution of the corresponding solvent. The scan rate was mainly kept 50 mV s^{-1} but in some cases it was 100 and 200 mV s^{-1}. All experiments were done at the temperature of 25 °C and the values measured were expressed *vs.* $E_{1/2}$ of the redox system BBCr(I)–BBCr(0) [6, 7].

Results and Discussion

The total redox behaviour of the complex was found to be consistent with the scheme

$$CuN_2S_2^+ \xrightleftharpoons{e^-} CuN_2S_2 \xrightleftharpoons{e^-} CuN_2S_2^-$$

TABLE I. Potentials of Oxidation of CuN_2S_2 in the BBCr(I)–BBCr(0) Scale.

Solvent	$E_{1/2}{}^{a}$ (V)	DN^{c}	AN^{c}
NM	1.084	2.7	20.5
AN	1.089	14.1	18.9
PDC	1.097	15.1	18.3
AC	1.052	17.0	12.5
MeOH	1.046	19.0	41.3
NMF	1.056^{b}	–	32.1
DMA	1.070	27.8	13.6
DMSO	1.064	29.8	19.3
HMPT	1.051	38.8	10.6

$^{a}E_{1/2} = (E_{p,a} + E_{p,c})/2$. $^{b}E_{1/2} = E_{p,a} - 0.029$. ^{c}DN = donor number, AN = acceptor number [12].

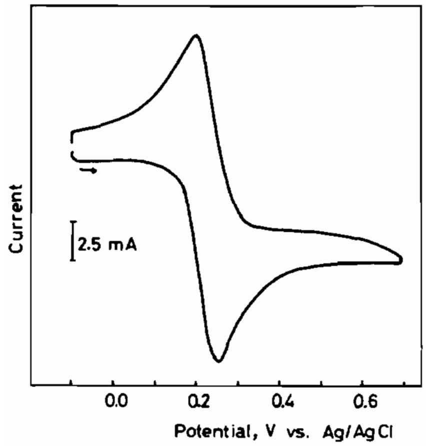


Fig. 1. Cyclic voltammogram of oxidation of CuN_2S_2 in nitromethane at the scan rate of 50 mV s^{-1}.

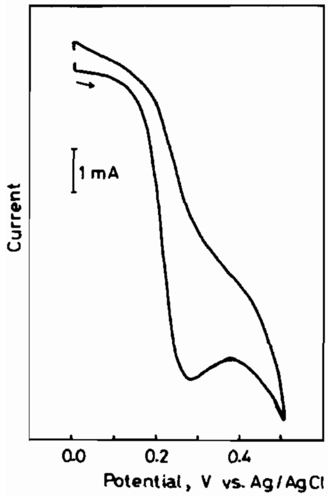


Fig. 2. Cyclic voltammogram of oxidation of CuN_2S_2 in N-methylformamide at the scan rate of 50 mV s^{-1}.

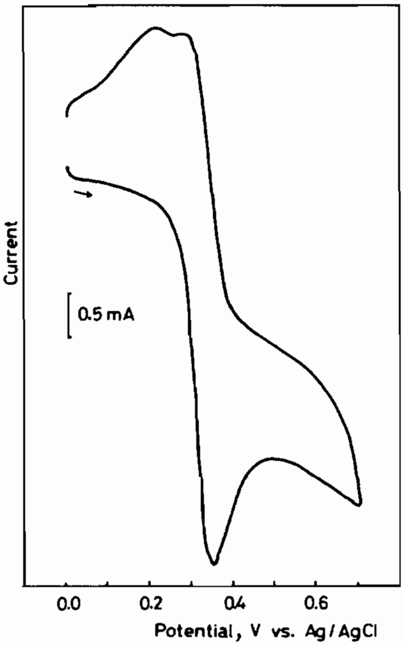


Fig. 3. Cyclic voltammogram of oxidation of CuN_2S_2 in N,N'-dimethylacetamide at the scan rate of 50 mV s^{-1}.

where CuN_2S_2 is N,N'-ethylenebis(thioacetylacetoniminato)copper(II) complex. A typical cyclic voltammogram of CuN_2S_2 oxidation in nitromethane is shown in Fig. 1. The neutral complex CuN_2S_2 undergoes oxidation in the non-aqueous solvents studied at the nearly constant potential of $E_{1/2}$ +1.07 V (Table I). The voltammogram of electrooxidation of CuN_2S_2 showed in all the solvents (except NMR, DMA and DMSO) a one oxidation peak on the ascending part of the voltage and connected with it a one reduction peak on the descending part of the voltage. No reduction peak that would correspond to the oxidation peak was observed for NMF, neither for greater scan rates (Fig. 2). In DMA on the reduction part still another peak was observed in addition to the reduction of $CuN_2S_2^{+}$ (Fig. 3). In DMSO were observed two peaks each in the oxidation and the reduction part of the voltammogram, from which that with the more positive potential value corresponded to the complex under investigation (Fig. 4).

The separation of the peaks between the anodic $E_{p/a}$ and the cathodic $E_{p/c}$ peak potentials were in the range of 60–80 mV at the scan rate of 50 mV s^{-1}. The ratio of the cathodic and the anodic peak current $i_{p/c}/i_{p/a}$ was for this scan rate near to one. In cases with lower values an increase of this ratio was observed with increasing v. The difference of $E_p - E_{p/2}$ corresponded to a reversible separation indicating a one-electron diffusion controlled oxidation.

Comparison of the oxidation and reduction results of some transition metal complexes with

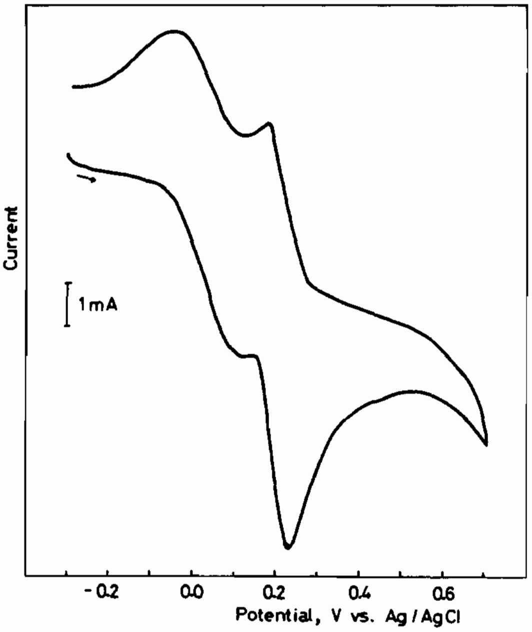


Fig. 4. Cyclic voltammogram of oxidation of CuN_2S_2 in dimethylsulphoxide at the scan rate of 50 mV s^{-1}.

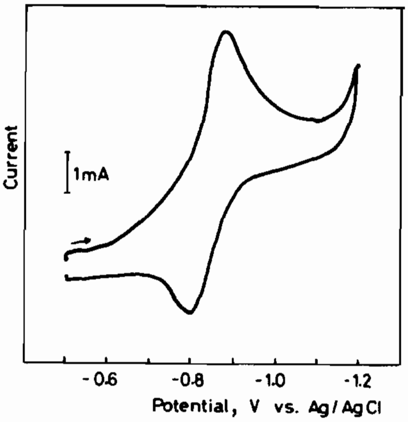


Fig. 5. Cyclic voltammogram of reduction of CuN_2S_2 in N,N′-dimethylacetamide at the scan rate of 50 mV s^{-1}.

N,N′-ethylenebis(thioacetylacetoniminato) and those of the ligand itself [10] leads to the conclusion that the molecular orbitals participating in the redox processes exhibit mostly the character of the metal. The fact that the oxidation process is not influenced by the solvent present can be connected with the results obtained by quantum-chemical computations [11] of the studied complex, according to which the unpaired electron of the studied complex is mostly localized on the Cu atom, however, in the complex plane. If at the oxidation process this electron becomes extracted, the solvent entering the coordination sphere of the complex (axial sites) should have a negligible effect on that process.

TABLE II. Potentials of Reduction of CuN_2S_2 in the BBCr(I)–BBCr(0) Scale and Dielectric Constants of the Solvents.

solvent	$E_{1/2}{}^a$ (V)	ϵ
NMF	–0.249	182.4
PDC	–0.374	65.0
DMSO	–0.388	46.7
AN	–0.414	36.0
HMPT	–0.446	29.6

$^a E_{1/2} = (E_{p,c} + E_{p,a})/2$.

The reduction of CuN_2S_2 was studied in a smaller number of solvents than the oxidation. Figure 5 shows the cyclic voltammogram of the reduction of CuN_2S_2 in N,N′-dimethylacetamide. The possibility of studying the reduction process in a given solvent was limited by its electrochemically feasible region. The reduction of CuN_2S_2 was not reversible to such an extent as its oxidation. It occurred in the potential range of –0.45––0.29 V and was dependent on the dielectric properties of the solvents (Table II). The difference $E_p - E_{p/2}$ was 70 ± 6 mV, indicating a quasi-reversible electrode reaction, the rate of which is controlled by electron transfer [8]. For this difference the relation is valid [8; 9]

$$E_p - E_{p/2} = 0.048/\alpha n_a, \qquad (1)$$

where α denotes the charge transfer coefficient and n_a is the number of electrons at the rate-determining step. Using the experimental value of $E_p - E_{p/2}$ = 70 mV the value of 0.69 is obtained for αn_a. In a reversible electrode reaction for which the diffusion coefficients of the oxidized and the reduced form are the same, $E_{1/2}$ may be identified with the standard electrode potential E° which has a thermodynamical significance. For the irreversible reaction, however, $E_{1/2}$ is not consistent with E°:

$$E_{1/2} = E^\circ - \frac{RT}{\alpha n_a F} \ln \frac{\pi^{1/2} D^{1/2} (\alpha n_a F v/RT)^{1/2}}{k_s} \qquad (2)$$

and becomes a function of αn_a, of the scan rate v and of the heterogeneous rate constant k_s [8]. Though no thermodynamic significance can be assigned to the reduction potential of CuN_2S_2, the results obtained on the changes of $E_{1/2}$ with changing the dielectric constant ϵ of the solvent should be valid, if the value of αn_a was constant in each of the solvents studied. This was the case observed.

Solvents with different donor, acceptor and also dielectric properties were selected for the study, in order to find out which property of the solvent coordinated in axial site will show the most prominent effect on the electrode reaction. Though no significant changes of the potentials $E_{1/2}$ with changing solvent were observed for electrooxidation, it was not the case for electroreduction, where on increasing the dielectric constant of the solvent the potential of the reduction process was shifted to more positive values (Table II). Based on this finding it may be suggested that changes of the Gibbs free energy necessary for the reduction of a given complex in different solvents are given by the changes of the Gibbs free energy necessary for charging the monoanion $CuN_2S_2^-$ in one solvent with respect to another. Therefore the difference of the Gibbs free energy necessary for charging the $CuN_2S_2^-$ ion in a solvent with the dielectric constant ϵ_2 compared with another solvent with the dielectric constant ϵ_1 is according to the Born theory:

$$\Delta G = \frac{N_A n^2 e^2}{2r}\left(\frac{1}{\epsilon_2} - \frac{1}{\epsilon_1}\right) \qquad (3)$$

n is the charge of the ion, e is the elementary charge and r is the radius of the ion. The corresponding change of the half-wave potential is then given by the expression

$$\Delta E_{1/2} = -\frac{\Delta G}{nF} \approx -\frac{7.19}{r}\,\Delta\left(\frac{1}{\epsilon}\right) \qquad (4)$$

From the dependence of $1/\epsilon$ *vs.* $E_{1/2}$ of the reduction of CuN_2S_2 the value of $\Delta E_{1/2}(\Delta)1(\epsilon)$ was determined to be -6.52, from which the value of 0.11 nm was calculated for the radius of the $CuN_2S_2^-$ complex. The obtained value shows good agreement with the theoretical value of the covalent copper radius, 0.1176 nm, confirming the solvent interaction with the studied complex in axial positions.

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