

Comparison of redox properties of copper and cobalt Schiff base complexes

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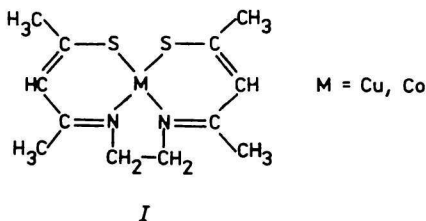
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The voltammetric method was used for studying the course of oxidation of *N,N'*-ethylenebis(thioacetylacetoniminato)copper(II) complex (CuN_2S_2) and *N,N'*-ethylenebis(thioacetylacetoniminato)cobalt(II) complex (CoN_2S_2) in a number of nonaqueous solvents at a platinum electrode. The complex CuN_2S_2 undergoes reversible one-electron oxidation in all the solvents at the almost constant potentials. The oxidation of CoN_2S_2 can be described as a quasi-reversible one-electron process and the solvent dependence of its $E_{1/2}$ values was shown to be roughly indirectly related to the donor properties of the solvents used.

Циклическая вольтамметрия была применена для исследования хода окисления комплексов *N,N'*-этиленбис(тиоацетилацетониминато)меди(II) (CuN_2S_2) и *N,N'*-этиленбис(тиоацетилацетониминато)кобальта(II) (CoN_2S_2) в ряду неводных растворителей на платиновом электроде. Во всех изученных растворителях комплекс CuN_2S_2 окисляется обратимо в одноэлектронном процессе при почти постоянном потенциале. Окисление комплекса CoN_2S_2 является также одноэлектронным, однако, квазиобратимым процессом и оказалось, что значение $E_{1/2}$ приблизительно обратно пропорционально донорным свойствам использованных растворителей.

Since metal complexes with Schiff bases were found to be suitable model compounds of biological systems, they attract increasing attention in chemistry of coordination compounds. The biological importance of transition metals in electron transfer reactions has stimulated extensive studies of the redox behaviour of transition metal chelates, especially those containing nitrogen and sulfur donors. This paper deals with the redox behaviour of the complexes (I) in a variety of nonaqueous solvents.

These compounds have been previously shown [1, 2] to form neutral monomeric complexes with a distorted square-planar geometry and with unoccupied axial sites



suitable for a solvent coordination. The purpose of this investigation was to find out how changes in axial ligand complexation affect the electrochemical oxidation of the above complexes.

Experimental

N,N'-ethylenebis(thioacetetylacetoniminato)copper(II) complex and *N,N'*-ethylenebis(thioacetetylacetoniminato)cobalt(II) complex were prepared according to a procedure described in literature [3]. Bis(biphenyl)chromium(I) iodide (BBCr(I)) was synthesized as reported elsewhere [4]. The solvents used were purified by standard procedures [5].

Voltammetric measurements were carried out with a polarographic analyzer, Model 174 A, and with a polarograph OH 105 (Radelkis, Budapest) in three-electrode arrangement. For working and auxiliary electrodes platinum wires were used while an aqueous saturated silver/silver chloride electrode and an aqueous saturated calomel electrode served as reference electrodes. 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. All the experiments were carried out under an atmosphere of nitrogen or argon with a depolarizer concentration of 10^{-3} M in 0.1 M tetrabutylammonium perchlorate (CuN_2S_2) or in 0.05 M tetrabutylammonium perchlorate (CoN_2S_2) at 25°C. The measured values of the half-wave potentials were expressed vs. $E_{1/2}$ of the redox system BBCr(I)—BBCr(0) [6, 7].

Results and discussion

The overall redox behaviour of the complexes is consistent with the scheme



The half-wave potentials ($E_{1/2}$) for CuN_2S_2 and CoN_2S_2 complexes are summarized in Table 1.

The neutral complex CuN_2S_2 undergoes oxidation in the nonaqueous solvents studied at the nearly constant potential [9]. The course of oxidation of CoN_2S_2 was influenced in contrast to CuN_2S_2 by the solvent present. The more basic properties of the solvent, the more negative the redox potential values for oxidation of CoN_2S_2 were measured.

Table 1

Half-wave potentials of the oxidation of CuN_2S_2 ($E_{1/2}^{\text{Cu}}$) and CoN_2S_2 ($E_{1/2}^{\text{Co}}$) on the $\text{BBCr(I)}-\text{BBCr(0)}$ scale and the donor properties of the solvents (DN) [8]

Solvent	$E_{1/2}^{\text{Cu}}/\text{V}^a$	$E_{1/2}^{\text{Co}}/\text{V}^a$	DN
DM	—	1.08	0.0
NM	1.08	—	2.7
AN	1.09	0.84	14.1
PDC	1.10	—	15.1
AC	1.05	0.96	17.0
MeOH	1.05	0.81	19.0
NMF	1.06	—	—
DMA	1.07	—	27.8
DMSO	1.06	0.76	29.8
HMPT	1.05	—	38.8

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

DM — dichloromethane, NM — nitromethane, AN — acetonitrile, PDC — propanediol-1,2-carbonate, AC — acetone, MeOH — methanol, NMF — *N*-methylformamide, DMA — *N,N'*-dimethylacetamide, DMSO — dimethyl sulfoxide, HMPT — hexamethylphosphoric triamide.

The comparison of the oxidation $E_{1/2}$ of some transition metal complexes with *N,N'*-ethylenebis(thioacetylacetonimine) and that of the ligand itself [10] leads to the conclusion that in the redox process participating molecular orbital is predominantly metal in character but with some ligand contribution. The fact that the oxidation process is not influenced by the solvent may be in connection with the results obtained by quantum chemical computations of the complex studied [11] according to which the unpaired electron of this complex is presumably localized on the Cu atom in the complex plane (the d_{xy} orbital). This is "isolated" from the surroundings by the π -orbital system of the ligand, hence the d orbital cannot be practically influenced by the electronic system of the solvent molecules. If at the oxidation process the unpaired electron becomes extracted, the axial interaction of the solvent should have a negligible effect on the investigated process, which was the case observed.

A correlation was found between the half-wave potential for oxidation of CoN_2S_2 and the donicity (basicity) of the ligand coordinated in the axial sites. The MO calculations showed [11] that the redox orbital has been metal-based as well, however, the unpaired electron is mainly localized out of the complex plane (the d_{yz} orbital). When ligand enters the axial position of the CoN_2S_2 complex (the z axis of coordinate system) the ligand electronic system comes into interactions with d orbitals of the central atom localized out of the complex plane (the d_{xz} , d_{yz} , d_z^2 orbitals), and consequently causes their destabilization [12]. The stronger is the axial interaction, *i.e.* the more basic properties possess the molecules interacting

with the complex, the larger is the electron density on the central atom. The increasing basicity of the ligated solvent causes the shift of the half-wave potential for oxidation of CoN_2S_2 to the more negative values.

The above results indicate that despite the similarity between the structures of the complexes studied, the axial influences were remarkably different. The symmetry of the molecular orbitals with an unpaired electron seems to be in the studied case decisive for the observed redox behaviour of both complexes.

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