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Dedicated to professor Gh. Marcu at his 80th anniversary

VOLTAMPEROMETRIC DATA ON THE BIOLOGICAL ACTIVE SYSTEMS CU(II), PD(II) AND NI(II) – SALICYLIC ALDEHIDE THIOSEMICARBAZONE

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ABSTRACT. The voltamperometric behavior of the systems Cu(II), Ni(II) and Pd(II) – thiosemicabazone of salicylic aldehyde (TSCSA) has been investigated on glassy carbon electrodes (cyclic voltametry) in DMF/$LiClO_4$ 0,2 M medium, using computer aided electrochemical systems BAS 100W and AUTOLAB – ECOCHEMIE.

In the case of all complexes can be seen that the peak related with the sulphur oxidation was moved towards positive higher values, which confirm the involving of sulphur in the coordination. From the point of view of the donor – acceptor interaction between metallic ion and sulphur atom as donor, it can be affirmed that, in these conditions, the Cu(II) complex is more stable than the Ni(II) and Pd(II) complexes. This conclusion is in accordance with the especial affinity of the Cu(II) ion against sulphur.

Based on the shifts of reduction potentials of the metals, ΔЄ = 215 mV for Cu complex, ΔЄ = 162 mV for Ni complex and ΔЄ = 180 mV for Pd complex, various degrees of interaction have been identified. They are qualitatively correlated with the stability of the complexes.

Key words: thiosemicarbazones, metal complexes, cyclic voltammetry.

Introduction

Thiosemicarbazones and related compounds, as well as their metal complexes have been the subject of great interest of many researchers, the first of all because they are active from the biological point of view, some having antitumoral activity. The statement is supported by a large number of papers, some of them in the last years [1,2]. Because in the human body there are redox processes it is important to have the information about the electrochemical behavior of the systems metal ions, Cu(II), Pd(II) and Ni(II) - thiosemicabazone of salicylic aldehyde in solution. Apart from their diverse chemical and structural characteristics, the significance of these compounds, especially related to thiosemicarbazones and theirs metal complexes, the relation between structure and biological activity has

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been covered in papers by West et al.[3,4]. The complexes have been prepared using the interaction of Ni(II) and Cu(II) sulphates, respectively $[PdCl_4]^{2-}$ with the thiosemicarbazone of salicylic aldehide (TSCSA) in aqueous solutions of ethylic alcohol, in echimolar amounts, resulting 1/1 type ligand thiosemicarbazone metal complexes [5].

In order to characterize the redox processes of these systems, which may occur on the ligands and complexes, as well as to compare the stability of the complexes and the coordinating ligand position involved in complex formation in solution, electrochemical investigations are usually performed, in suitable solvents. Although the thiosemicarbazone – based ligands were investigated by electrochemical methods [6,7], for the system (TSCSA) – Me(II) there are not the data in the literature.

The investigations have been made in organic media (DMF, THF, AC), in the presence of several supporting electrolytes, usually at glassy carbon electrode. The most important conclusion of these voltamperometric determinations was the complexity of the electrochemical answer, involving both the redox processes on the level of ligand moiety and metal ion [8].

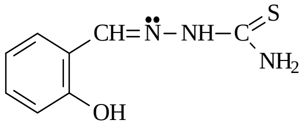
Experimental

The tests were performed in a classical cell having three electrodes. All the samples were deaerated 20-30 minutes before each test. Because of low solubility of the complex in the protic medium, the non aqueous medium of DMF was chosen.

Cyclic voltammograms were recorded in a dried cell purged with argon. DMF used as electrolyte solvent was purified according to standard procedures [9]. $LiClO_4$ dried in an oil pump vacuum at 100^oC was added as supporting electrolyte at a concentration of 0.2 M. Compounds under investigation were added at 1 mM concentration. The working electrode (GC, Hg and Pt) and platinum wire counter-electrode were used. An Ag/Ag^+, AgCl electrode, in a separate compartment served as reference electrode. CVs were recorded both in negative and positive-going direction at the starting potentials, at different scan rate using a Autolab potentiostat (Ecochemie) equipped with PGSTAT 12 soft. All experiments were run at room temperature (22^oC).

Results and discussion

The ligand (TSCSA), produced from the condensing salicylic aldehide with thioureea (TU), has basically three electroactive positions: hydroxyl oxygen, the sulphur from the remaining thiourea and the azometin grouping. From these, the last two unsaturated groups can be reduced and the OH can be easily oxidized.



The electronic interaction between datively bonded ligand (TSCSA) and divalent metal ions has been studied with cyclic voltammetry and polarography, both in reduction and oxidation potential range.

Typical CVs of complexation in Cu(II)-TSCSA system, in DMF, in negative – going direction are displayed in Fig. 1.

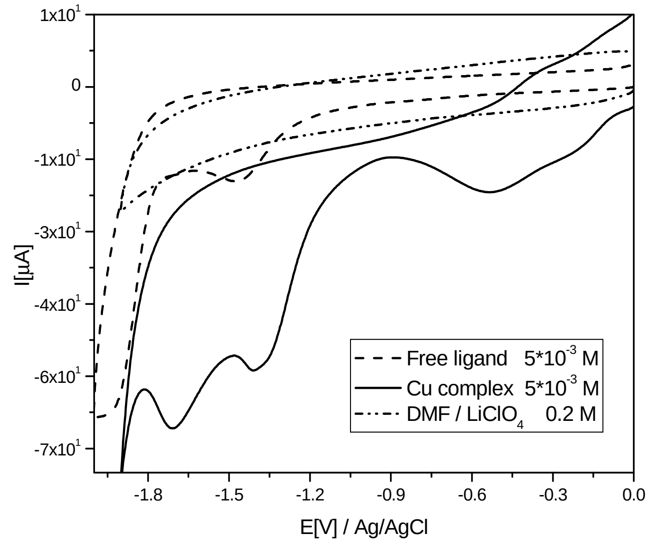
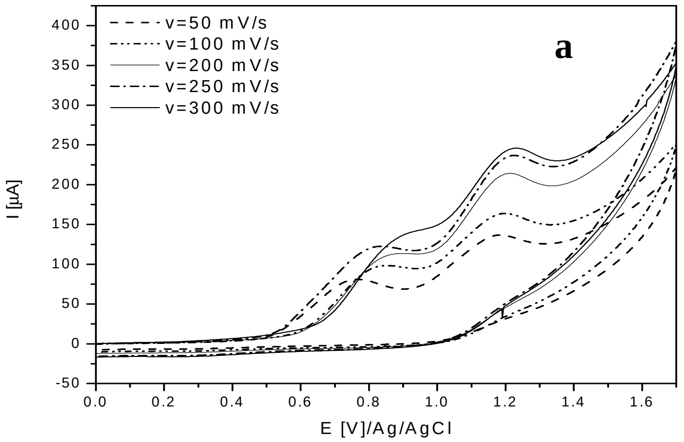


Figure 1. Comparison between the electrochemical behavior of (TSCSA) and Cu (II) complex in negative – going direction.

In DMF medium, on glassy carbon, the ligand presents two oxidation peaks, the first in the 700-850 mV range *vs* Ag/AgCl,KCl, which can be related to phenolic group [10, 11], Fig.2a.



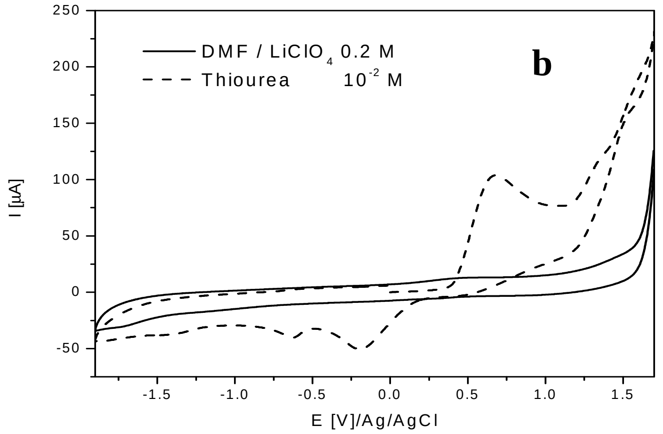


Figure 2. CVs for the oxidation of ligand and (TU) on GC electrode in DMF/
0.2 M $LiClO_4$ for :
a – oxidation of 10^{-3} M (TSCSA)
b – oxidation of 10^{-3} M (TU)

and the second in the high and positive range (>1 V *vs* Ag/AgCl) which is specific to π carbon-sulphur oxidation; this last peak's attribution was confirmed by the voltamperometric response of (TU), Fig 2b.

To spot the entail the complexation of metal ions, respectively the processes of reduction of the azometin group of ligand, it was followed in the same parameters the voltamperometric response of the components and of the system in an extended range of negative voltages, allowed by the use of non-aqueous electrolyte, ($Є_0$= - 0.4 V/ Ag/AgCl, KCl and $Є_f$=-2.2V/).

The irreversible reduction of azometin group in (TSCAS) might occur at the negative electrode potential, to $Є_{-C=N-}$> - 1.8 V/ Ag/AgCl, KCl, Fig.3.

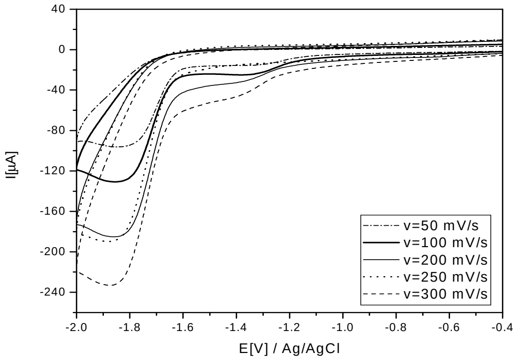
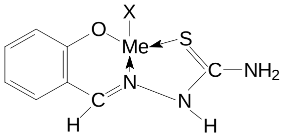


Figure 3. Reduction of azometin group in (TSCAS).

By comparing VCs of the free ligands (TSCSA) and TU, and for the complexed metalic ions can be seen differences of the peak voltages and for the peak currents because of complexation, Table 1.

According to other authors, confirmed for related compounds in solid state [8], usually thiosemicarbazones act such tridentate ligand (O, S, N):



Me: Ni(II), Cu(II), Pd(II)

but in some cases, M=Ru(II),Os(II) the phenolic oxygen is not included in the coordination [14] and the dimer structures have been demonstrated for Tl complexes with related ligands.

Table 1.

The influence of complexation on the peak potentials in DMF [V/ Ag/AgCl, KCl].

Compound	Oxidation		Reduction	
	Є$_{OH}$	Є$_{C=S}$	- Є$_{-CH=N-}$	- Є$_{Me(II)}$
TSCAS	0.81	1.09	1.47;1.82	-
Cu (II) - TSCAS	0.86	1.43	1.40; 2.12	0.40; 1.20
Cu(II)	-	-	-	0.30
Ni (II) - TSCAS	0.91	1.18	1.53; 2.02	1.53
Ni(II)	-	-	-	1.28
Pd(II) - TSCAS	0.98	1.28	1.46; 1.98	1.55
Pd(II)	-	-	-	0.55;1.30

Comparing our data in DMF for ligand and complexes, Table 1, we can see that the redox properties of the linkages involving donor atoms were stabilized by complexation, Table 2. These facts are valuable both for OH and C=S, when the oxidation potential is displaced to more positive values. For CH=N, the second reduction step could be easier, at lower negative potentials. We consider that the displacement of peaks potentials is due to the complexation and the value of the shift is in relation with the stability of the complex.

Table 2.

Displacement [mV] of the peak potentials of donors and metal ions, by complexation in DMF/0.2M $LiClO_4$.

Me(II)	Donor group	Δε* [mV]	Δε** [mV]
Cu(II)	–OH	50	215
	=S	340	
	–N=CH–	- 300	
Ni(II)	–OH	100	162
	=S	90	
	–N=CH–	- 200	
Pd(II)	–OH	170	180
	=S	190	
	–N=CH–	- 160	

* Average of 3 determinations.

** For complexed metal ions comparing to metal ion coordinated only with perchlorate.

The explanation of the shifts of oxidation potentials of donors after complexation is easier for the oxidable groups (OH and =S): the density of electrons after complexation becomes lower, so the oxidation becomes more difficult. For the azometin reducible group, the π character of double bond diminishes by complexation, the linkage becomes weaker and its reduction is possible to smaller negative potentials.

Taking the reduction potential of metal ions complexes coordinated with perchlorate anion, even in dissolved state, results in a negative shift, by complexation with (TSCSA), Table 2, corresponding to the stability of the complexes.

Conclusions

The following qualitative remarks were deducted on complexation interactions:

- Powerful engaging of the sulphur donor atom and azometin group in complexation with Cu(II) ions, more comparing to Ni(II) and Pd(II).

- Participation of the hydroxyl oxygen in complexation with Ni(II) and Pd(II) more than for Cu(II).

- Engaging of the π electrons of the azometin linkage in complexation in the following order:

Cu(II) > Ni(II) > Pd(II)

- According to shift of the reduction potentials of metals ions, the relative stability of the complexes is:

Cu(II) >Pd(II) > Ni(II)

Based on the information reported here, future experiments will be realized to establish the quantitative data on the stabilization of these metal ions through complexation.

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