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ELECTROCHEMICAL STUDY OF NEW DIPYRIDINE CYSTEINE COMPLEXES

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S-a realizat un studiu electrochimic prin voltametrie ciclica si voltametrie cu impulsuri de potential pentru trei noi complecsi de Ni si Zn cu dipiridina si cisteina.

An electrochemical study of three new Ni and Zn dipyridine cysteine complexes was performed by cyclic and differential pulse voltammetry.

Keywords: Dipyridine cysteine, nickel, zinc, cyclic voltammetry, differential pulse voltammetry

1. Introduction

The research in the field of biomolecules is very important as they play a key role in basic life processes. Due to the complexity of their structure, properties and functions, the researchers imagined simple molecular models for the active site of metalloenzymes [1].

The nickel enzymes are fewer than the greater number of enzymes containing iron or zinc. The formal oxidation state is difficult to determine, for nickel sites in proteins, owing to the charge delocalization. However, simple model complexes are useful to establish the effect of different ligand types [2].

The Ni(II) ions are characterized by higher affinity toward nitrogenous-based ligands than the Zn(II) ions [3-8] and this explains the requirement for Ni(II) ions, instead of the more common Zn(II) in hydrolytic enzymes.

The aminoacid cysteine is the most frequently occurring ligand of nickel in the active centre of nickel containing enzymes. Sulfur coordination is an important feature in metalloenzymes and the covalency and soft environment are possible prerequisites for efficient charge transfer.

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Aromatic diimines, such as 2,2’-dipyridine, provide a ligand-ligand charge-transfer (LLCT) absorption with particularly large solvatochromic shifts of complexes [9]. A wide variety of thiolates and dithiolates are known to coordinate the transition metals and several of these have been utilized for square-planar mixed-ligand systems.

This paper deals with the characterization of two new types of complexes [M(dpy)$(Cys)_2$] and [M(dpy)$(MeCys)_2$], (where M = Ni and Zn) that may be considered as simple models for an active site of a nickel enzyme.

2. Experimental

Acetonitrile (Rathburn, HPLC grade) and tetra-*n*-butylammonium perchlorate (TBAP) from Fluka were used as received for solvent and supporting electrolyte, respectively. The investigated complexes: Ni(dpy)$(cys)_2$ (1); Ni(dpy)$(cysMe)_2$ (2) and Zn(dpy)$(cys)_2$ (3), where dpy is dipyridine, cys is cysteine and cysMe is cysteine methylic ester, were obtained by specific chemical reactions [10], while $Ni(dpy)_2$ (4) was from Fluka.

Structure and physical characteristics of these complexes were confirmed by FT-IR data and measurements of electrical conductivity [5].

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were conducted in a conventional three-electrode cell under argon atmosphere at 20^{o}C using a PGSTAT 12 AUTOLAB potentiostat.

The working electrode was a glassy carbon disk (2-mm diameter) polished with 200 µm diamond paste. An Ag/10mM $AgNO_3$ in CH_3CN+ 0.1 M TBAP system was used as reference electrode. All the elctrode potentials were referred to the value of ferrocene/ferricinium (Fc/Fc^+) potential, which was 0.07 V in our experimental conditions.

CV curves have been obtained at the scan rate of 0.1 V/s. DPV curves were recorded at 10mV/s with a pulse height of 25mV and a step time of 0.2 s. The experiments have been usually performed at room temperature (20^{o}C).

3. Results and Discussion

The properties of three new dipyridine cysteine complexes: Ni(dpy)$(cys)_2$ (**1**); Ni(dpy)$(cysMe)_2$ (**2**) and Zn(dpy)$(cys)_2$ (**3**) have been compared with those of the known complex $Ni(dpy)_2$ (**4**), which has been studied in the same conditions as **1**-**3**. The electrochemical behavior of these complexes was studied in acetonitrile as solvent with 0.1 M TBAP as supporting electrolyte.

As Figures 1-3 show, the DPV study for each new compound at different concentrations (0.5 – 3 mM) enabled the measurement of anodic and cathodic peak potentials and currents, while the CV study, which was performed at different concentrations and potential ranges, enabled the characterization of each electrochemical step. As the concentration increases, as the peak current values increase in CV and DPV experiments. However, the poor solubility in acetonitrile of the complexes leads to difficulties to get linear variations of the peak currents *vs* concentration.

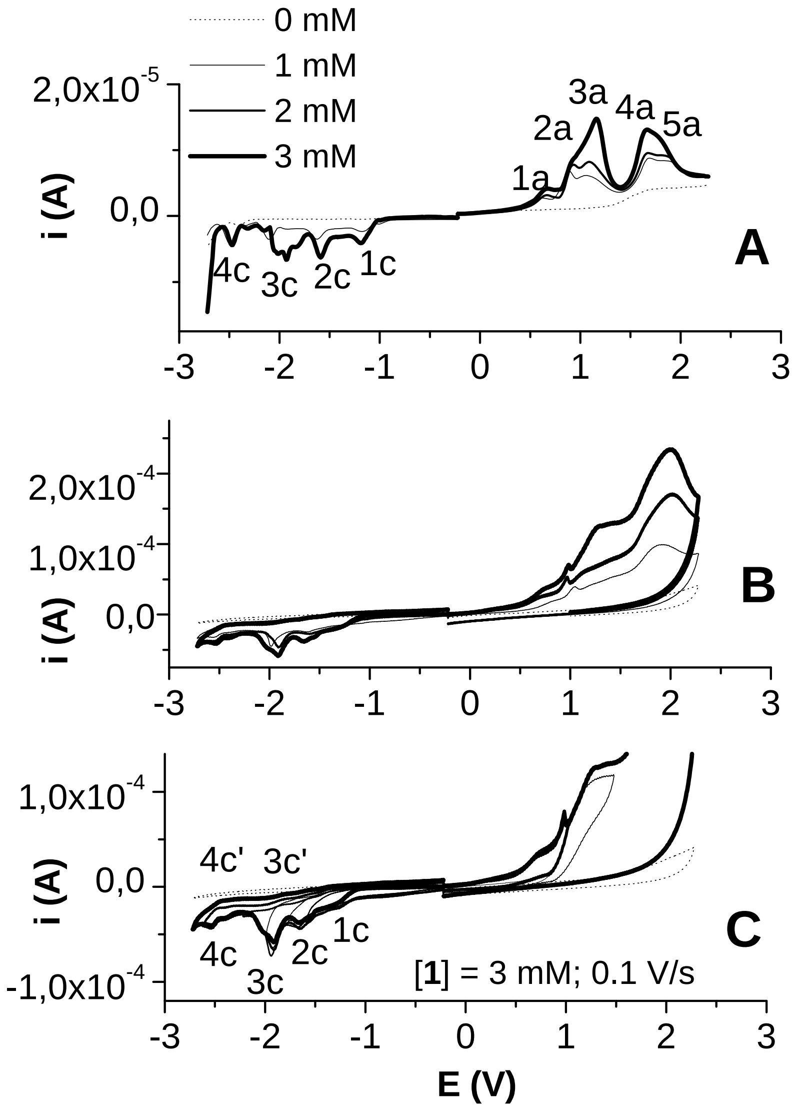

Fig. 1. DPV (A) and CV (B, C) at (0.1 V/s) curves for Ni(dpy)(cys)$_2$ **1** at different concentrations and scan ranges in 0.1 M TBAP, CH_3CN; glassy carbon disk electrode (2 mm in diameter).

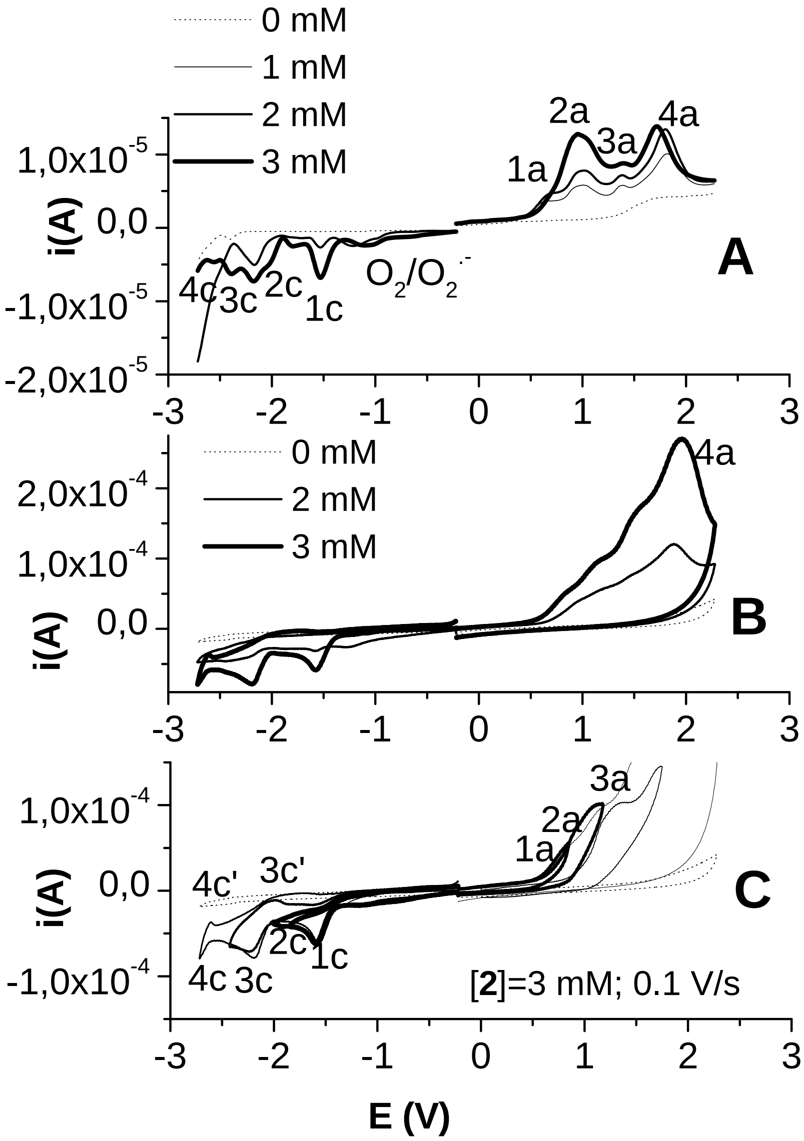

Fig. 2. DPV (A) and CV (B, C) at 0.1 V/s curves for Ni(dpy)(cysMe)$_2$ **2** at different concentrations and scan ranges in 0.1 M TBAP, CH$_3$CN; glassy carbon disk electrode (2 mm in diameter).

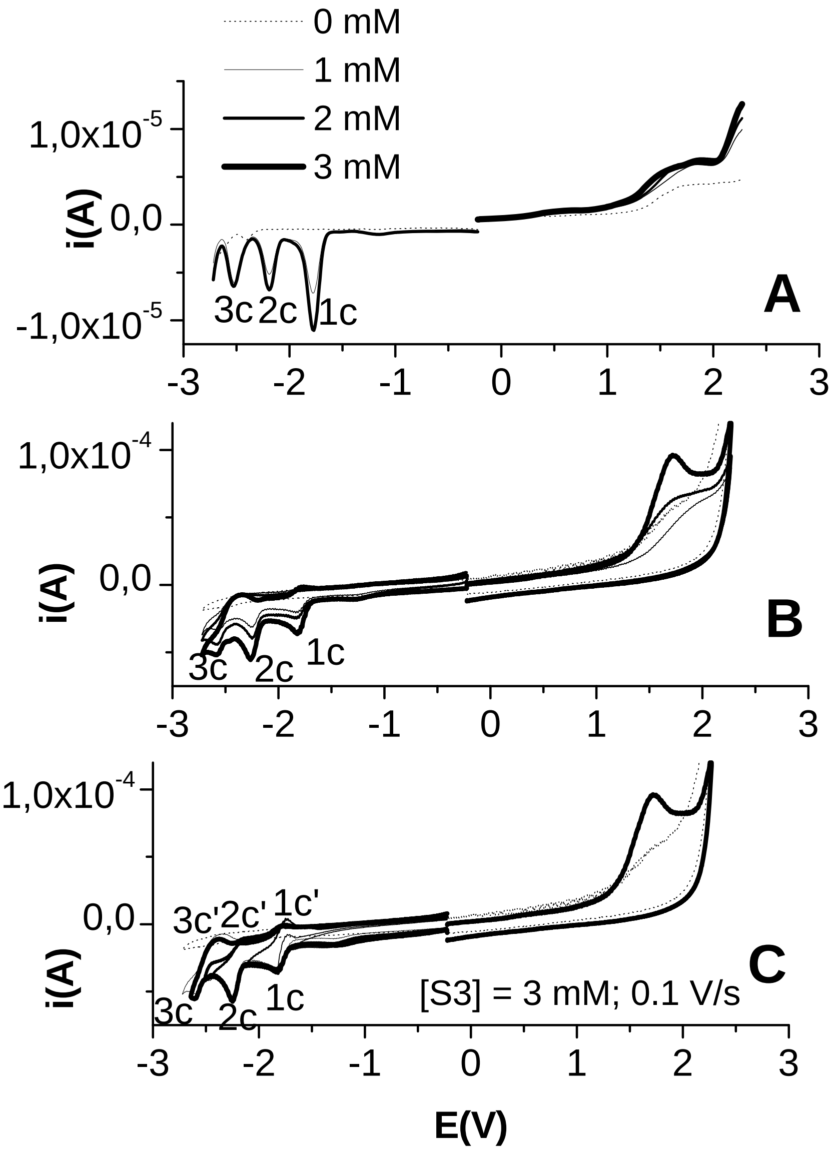

Fig. 3. DPV (A) and CV (B, C) at 0.1 V/s curves for Zn(dpy)(cys)$_2$ **3** at different concentrations and scan ranges in 0.1 M TBAP, CH$_3$CN; glassy carbon disk electrode (2 mm in diameter).

Both anodic and cathodic curves are represented in these figures, where as the background is represented with a dotted line. The redox processes are best identified as peak potentials by DPV method which enables the establishing of the real number of electrochemical processes.

The compound **1** (Fig.1) shows in DPV five anodic processes (1a – 5a) and four cathodic processes (1c – 4c). These processes are partially seen by CV method, too. By studying the influence of the scan range we notice that all the anodic processes are irreversible. The cathodic processes 1c and 2c are irreversible while 3c and 4 c are quite reversible, having small counter peaks (denoted with ') which appear in the reverse scans, 3c' and 4c', respectively.

The compound **2** shows four anodic irreversible processes and four cathodic processes. Regarding the degree of irreversibility, the cathodic processes 1c and 2c are irreversible, while 3c and 4c are quasireversible processes (small counter peaks appear in the return scans 3c', 4c').

The compound **3** has shown no anodic processes, although it presents three cathodic reversible processes 1c-3c; each of them having a cathodic counter peak in the reverse scans 1c'-3c'.

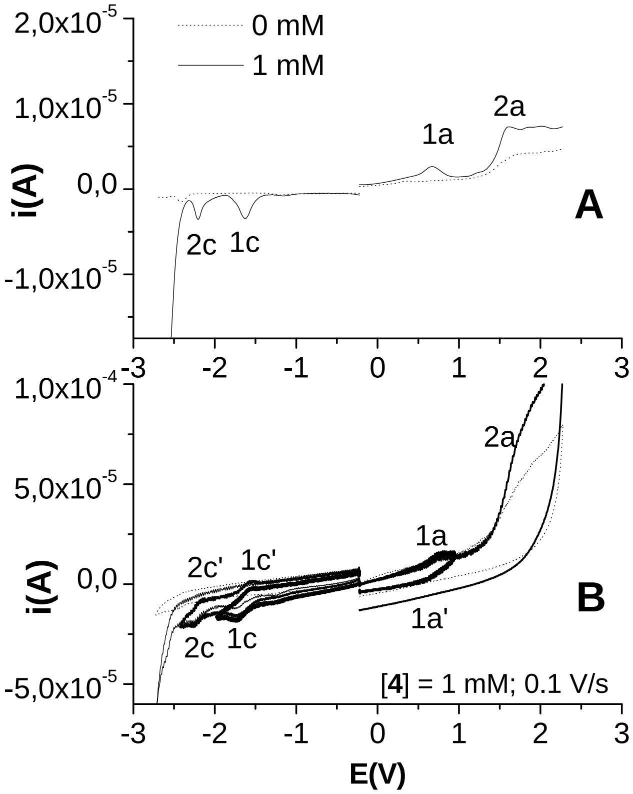

Fig. 4. DPV curves (A) and CV curves at 0.1 V/s on different scan ranges (B) for Ni(dpy)$_2$ **4** at the concentration of 1 mM in 0.1 M TBAP, CH_3CN; glassy carbon disk electrode (2 mm in diameter).

Figure 4 presents the characterization of Ni(dpy)$_2$ complex (compound **4**). It shows two anodic and two cathodic processes 1a, 2a, 1c, 2c. The anodic process 1a is a reversible process (it presents a counter peak 1a' in the reverse scan), while 2a is an irreversible process. The cathodic processes 1c and 2c are reversible processes (having counter peaks 1c', 2c' in the reverse scans).

In order to perform a comparison between substrates the electrochemical characteristics of the new investigated complexes have been compared with the ones belonging to the known complex **4**, [Ni(dpy)$_2$]. The comparison between the CV and DPV curves of the two complexes is given as example in Figure 5.

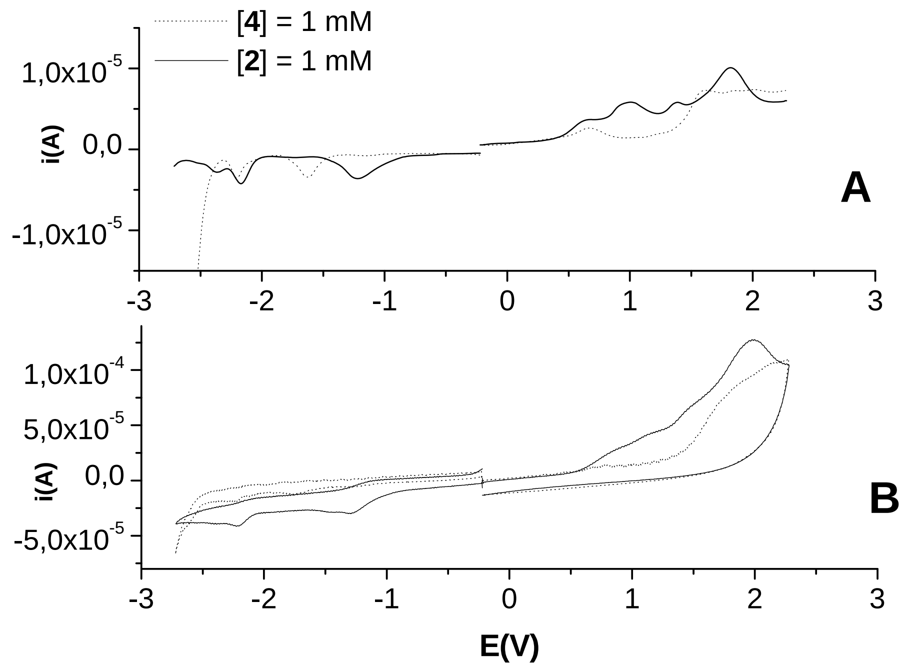

Fig. 5. The comparison between the DPV (A) and CV(B) curves for **2**, [Ni(dpy)(cysMe)$_2$] and **4**, [Ni(dpy)$_2$]; the same experimental conditions as in Figs. 2 and 4.

Looking at the cathodic domain, it is observed from Fig. 5 that **4** presents two redox couples (corresponding to: dpy/dpy$^{\cdot -}$; dpy$^{\cdot -}$/ dpy^{2-}) and a sharp branch for the reduction of the metal (Ni^{2+}/Ni^0), while **2** presents three redox couples; for this compound the couple Ni $^{2+}$/Ni^0 is not seen until a very negative value of the elctrode potential -3V, and consequently the metal is harder to be reduced in this complex than in **4**. In the anodic domain **4** shows two peaks, while **2** shows four peaks. The results obtained by CV and DPV (Fig. 5) are in agreement concerning the number of processes. By replacing dpy with cysMe, the reduction potential of Ni complexes shifts towards less negative values, and the oxidation potential shifts towards less positive values. Thus, from the comparison between **1**, [Ni(dpy)(cys)$_2$] and **4**, [Ni(dpy)$_2$], it results that the increase of the ligands number makes the complex more oxidisable and the metal becomes more difficult to be reduced.

The comparison between **1** and **2** sugests that the replacing cys with cysMe does not lead to significant changes of oxidant or reductant character of complexes.

From the comparison between **1** and **3**, we can see that the ligands are easier to be reduced in Ni complexes than in Zn complexes. The ligand is easier to be oxidized in Ni complex whereas it is stable in Zn complex.

4. Conclusions

Investigation of the electrochemical properties of some dipyridine cysteine complexes by cyclic and differential pulse voltammetry shows that these electrochemical properties vary according to the number and nature of the ligands. By replacing dipyridine with cysteine, as ligand, the Ni and Zn complexes become more oxidizable and reductible.

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