

CYCLIC VOLTAMMETRY STUDY OF [Cu(sal)(Me₂bipy)]ClO₄

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abstract: The complex [Cu(sal)(Me₂bipy)]ClO₄ was investigated by using cyclic voltammetry technique that allows to get information about electrochemical mechanism of redox behaviour of the compound during cyclic voltammetry experiment

Intoduction

The complex [Cu(sal)(Me₂bipy)]ClO₄ was investigated by using cyclic voltammetry technique. This complex belongs to a series of mononuclear Cu(II)-complexes investigated by the authors [1,2] by means of electrochemical techniques, especially CV and DPV [1,2], and spectral techniques, especially UV-Viz [1], in order to understand their behaviour during cyclic voltammetry experiments. This enables us to study the dinuclear Cu(II)-complexes or even multinuclear complexes. The multi-metal center complexes are frequent in nature as multi-metal center proteins and enzymes [3,4]. Among these are many with homo- and heterodinuclear centers. In many cases these molecular systems have two or more redox centers in close proximity and they could interact with one another or not. The CV experiments could find if the interaction exists or not in multinuclear complexes, in other words, if the two redox centers "feel" each other or not [5÷8].

Experimental Part

The electrochemical measurements were performed using a Volta LabTM 32 system, having an IMT102 electrochemical interface and a DEA 332 33V/2A potentiostat model. A three-electrode single-compartment electrochemical cell was used. The working electrode was a platinum disc of 2 mm diameter, the reference electrode was in fact a pseudo-reference electrode of Ag wire and the counter electrode was a platinum wire long enough. All the measurements were carried out in DMSO solvent with 0.1 M Bu₄NClO₄ as indifferent electrolyte. The electrolyte solutions were carefully deaerated with dry argon. The bubbling was stopped during the measurements in order to obtain semiinfinite linear conditions for diffusion process of the electroactive species. The electroactive species was [Cu(sal)(Me₂bipy)]ClO₄ in two different concentrations 1 mM and 2.3 mM.

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Results and Discussions

We have been studied the cyclic voltammetric behaviour of $[\text{Cu}(\text{sal})(\text{Me}_2\text{bipy})]\text{ClO}_4$ mononuclear complex having the structural formula given in Fig. 1:

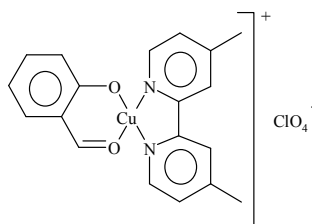


Fig. 1: The structural formula of the $[\text{Cu}(\text{sal})(\text{Me}_2\text{bipy})]\text{ClO}_4$ complex.

The complex has been studied in the potential range $+1.000\text{ V}$ to -1.000 V (referred to the pseudo-reference electrode used) and the single cyclic voltammograms obtained for the used sweep rates are given in Fig. 2. In the left the potential was swept starting from $+1.000\text{ V}$ first cathodically and then anodically and in the right starting from 0.000 V first anodically, then cathodically and finally anodically again. It is obvious that the two series of cyclic voltammograms look the same and that the anodic sweep of the potential starting from 0.000 V to $+1.000\text{ V}$ does not generate any anodic peak, due to the fact that there is no Red species into the solution. To appear the anodic peak it is necessary to firstly reduce the Ox species. After a certain value of the sweep rate a limiting contour of the cyclic voltammogram is obtained both for the first cathodic peak and also for the cathodic return of the potential applied in the -1.000 V and 0.000 V region. A comparable behaviour was noticed for 2.3 mM $[\text{Cu}(\text{sal})(\text{Me}_2\text{bipy})]\text{ClO}_4$.

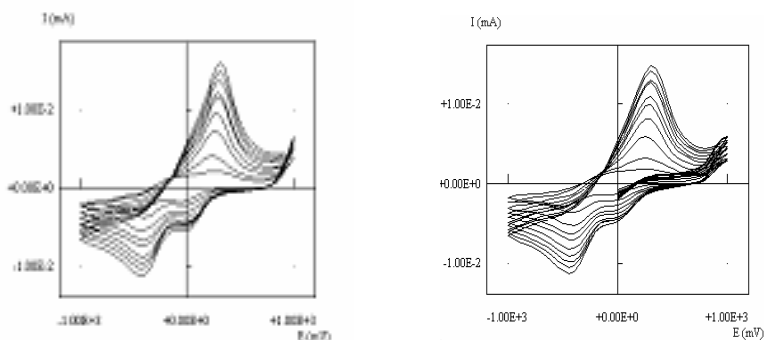


Fig. 2: The cyclic voltammograms at $\nu=50, 100, 200, 300, 400, 500, 600, 700$ and 800 mV/s for 1 mM $[\text{Cu}(\text{sal})(\text{Me}_2\text{bipy})]\text{ClO}_4$. The potential range is $+1000 \rightarrow -1000 \rightarrow +1000\text{ mV}$ (for the voltammograms in the left) and $0 \rightarrow +1000 \rightarrow -1000 \rightarrow +1000\text{ mV}$ (for the voltammograms in the right)

The typical cyclic voltammogram has, on the direct (cathodic) scan, two very well-defined cathodic waves with a first cathodic peak situated at less negative cathodic potentials and with a second cathodic peak situated at more negative cathodic potentials. When the sweep rate increases the first cathodic peak becomes less and less negative, while the second more and more negative. On the reverse (anodic) scan there is a shoulder less influenced by the sweep rate increase, and a well-defined anodic peak which is counterpeak of the first

cathodic peak. As concern the counterpeak of the first cathodic peak, it shifts positively with increasing sweep rate. With increasing concentration of the electroactive complex the first cathodic peak increases slowly in comparison with the second cathodic peak. The first anodic peak (the counterpeak of the first cathodic peak) increases too. On the other hand for the concentrations investigated, with increasing sweep rate, the voltammograms become closer and closer, tending to a limiting contour in the region of the first cathodic peak and also in the anodic shoulder region.

The voltammograms show, on one hand, the relative limitation of the current in the region of the first cathodic wave (that means that the first reduction of Cu(II) to Cu(I), responsible for the appearance of the first cathodic peak, does not increase even if the concentration of the electroactive Cu(II)-complex increases), and, on the other hand, they show how with increasing concentration of the electroactive Cu(II)-complex the shoulder remains a shoulder and the appeared anodic peak is, in fact, higher than expected, being probably a sum of two different anodic peaks, the former due to the oxidation of the Cu(I)-complex to the Cu(II)-complex and the latter to the oxidation of the Cu-atoms formed by the decomplexation reaction of the product of the second cathodic peak (i.e., Cu(0)-complex in which the Cu(0) is unable to keep the ligands in the coordination sphere). From Fig. 2 it is obvious that the anodic peak currents are greater than the cathodic peak currents of the first cathodic peak. Plotting the current peak versus square root of the sweep rate for the two cathodic peaks one obtains the graphs in Fig. 3, which are straight lines.

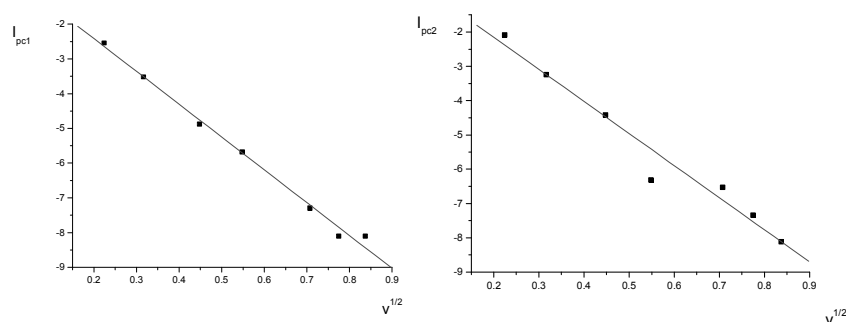
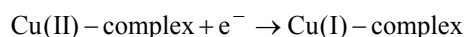


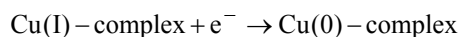
Fig. 3: The I_{pc1} vs. $v^{1/2}$ and respectively I_{pc2} vs. $v^{1/2}$ dependences for 1 mM [Cu(sal)(Me₂bipy)]ClO₄.

Taking into account the cyclic voltammetric behaviour of the complex one can propose the following mechanism of electrode and chemical reactions:

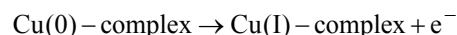
- The first cathodic peak can be assigned to the cathodic reduction of the Cu(II)–complex to the Cu(I)–complex in a quasireversible mechanism (there is a negative shift of the cathodic peak potential with increasing sweep rate):



- The second cathodic peak can be assigned to the cathodic reduction of the Cu(I)–complex to the Cu(0)–complex also in a quasireversible mechanism (there is also a negative shift of the cathodic peak potential with increasing sweep rate):

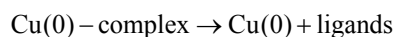


- The anodic shoulder (the counterpeak of the second cathodic peak) can be assigned to the anodic oxidation of the to Cu(I)-complex :



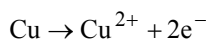
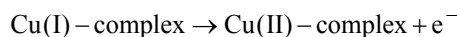
but its very small height is due to the very low concentration of the Cu(0)-complex in OHP, which very soon after its formation, participates to a decomplexation reaction.

- The decomplexation reaction is a chemical reaction occurring because the Cu(0) atom is unable to keep the ligands in a coordination arrangement:



This chemical reaction is fast enough to decrease the height of the corresponding anodic shoulder in which Cu(0)-complex is involved. The effect of the increasing sweep rate for a given concentration is unimportant at least in the sweep rate range utilized in the experiment.

- The very prominent anodic peak (which is the counterpeak of the first cathodic peak) is probably due not only to the anodic oxidation of the Cu(I)-complex to Cu(II)-complex but also to the anodic oxidation of the Cu-atoms formed by the chemical reaction:



(there is also a positive shift of the anodic peak potential with increasing sweep rate and, in addition the peak is enough large.

So that on may conclude that the mechanism of the single cyclic voltammetry behaviour of the Cu(II)-complex is described by an EECE mechanism.

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