

CYCLIC VOLTAMMETRY STUDY OF [Cu(acac)(2,2'-bipym)]ClO₄

D. Mich and C. Mihailciuc*

abstract: The complex [Cu(acac)(2,2'-bipym)]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(acac)(2,2'-bipym)]ClO₄ was investigated by using cyclic voltammetry technique. This complex belongs to a series of mononuclear Cu(II)-complexes investigated by the authors [1] by means of electrochemical techniques, especially CV and DPV, and UV-Viz spectral technique at different electrode potentials applied to the working electrode, in order to understand their behaviour during cyclic voltammetry experiments. The multi-metal center complexes are frequent in nature as multi-metal center proteins and enzymes [2,3]. 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 the case of homo- or hetero- multinuclear complexes, in other words if the two redox centers "feel" each other or not [4÷7].

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. The electroactive species was [Cu(acac)(2,2'-bipym)]ClO₄ in three different concentrations, 1 mM, 2 mM and 4 mM.

* University of Bucharest, Department of Physical Chemistry, Bd. Regina Elisabeta, 4-12
030018, Bucharest, Romania

Results and Discussions

We have been studied the cyclic voltammetric behaviour of $[\text{Cu}(\text{acac})(2,2'\text{-bipym})]\text{ClO}_4$ mononuclear complex having the structural formula given in Fig. 1.

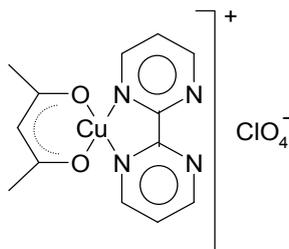


Fig. 1 The structural formula of the $[\text{Cu}(\text{acac})(2,2'\text{-bipym})]\text{ClO}_4$ complex.

The complex has been studied in the potential range $+1.000\text{ V}$ to -1.000 V and the single cyclic voltammograms obtained for the used sweep rates are given in Fig. 2.

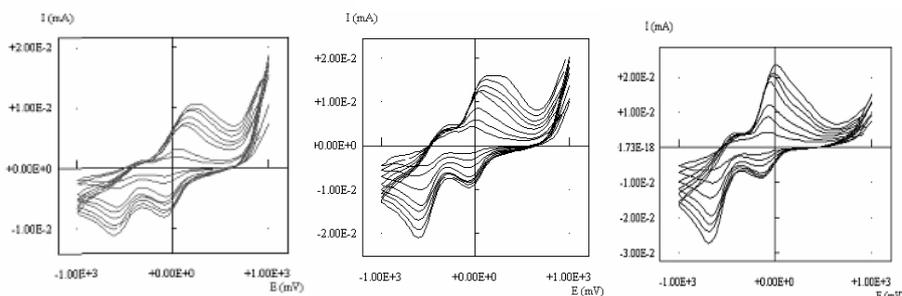


Fig. 2 The cyclic voltammograms at $v=50, 100, 200, 300, 400, 500$ and 600 mV/s for $1\text{ mM}, 2\text{ mM}$ and 4 mM $[\text{Cu}(\text{acac})(2,2'\text{-bipym})]\text{ClO}_4$.

The typical cyclic voltammogram has, on the direct (cathodic) scan, two 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 both of them become more and more negative, cathodic. On the reverse (anodic) scan there is a shoulder which becomes a genuine counterpeak of the second cathodic peak, and then a genuine counterpeak of the first cathodic peak. As concern the counterpeak of the second cathodic peak, it shifts negatively with the increasing sweep rate while the counterpeak of the first cathodic peak 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 while the anodic counterpeak of the second cathodic peak increases slowly. On the other hand for the second and third concentration investigated, with increasing sweep rate the voltammograms become closer and closer, tending to a limiting contour in the region of the first cathodic peak. In Fig. 3 one can see three voltammograms obtained at $v=200\text{ mV/s}$ for the three mentioned concentrations. They 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 $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$, 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 turns in a genuine peak and the anodic response has, in fact, two different waves, two different peaks. Obviously, the first anodic peak shifts negatively with increasing concentration. For the three investigated concentrations, one can notice that the second anodic peak becomes also limited (even with increasing sweep rate, for a given concentration, a limiting contour in the case of the second anodic peak could be observed).

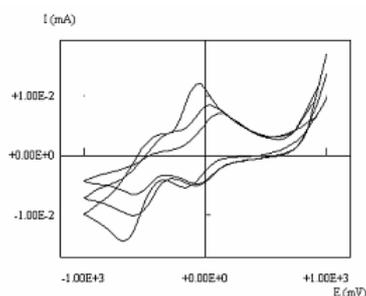


Fig. 3 The cyclic voltammograms at $v=200$ mV/s for 1 mM, 2 mM and 4 mM [Cu(acac)(2,2'-bipym)]ClO₄.

Plotting the current peak versus concentration one get the straight lines in Fig. 4.

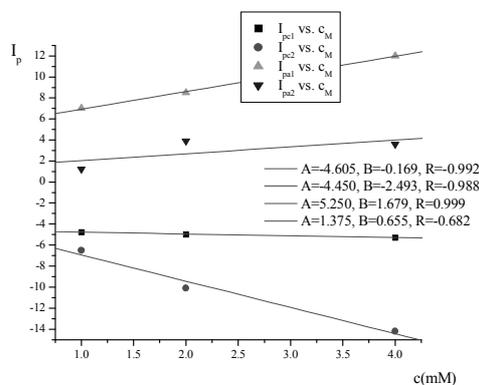


Fig. 4 The dependences I_p vs. c at $v=200$ mV/s for 1, 2 and 4 mM Cu(II)-complex.

One can observe that the slope for I_{pc1} vs. c and I_{pa2} vs. c plots are indeed very small indicating a sort of limitation of these two peak currents. The same concluding observation can be made for $v=300$ mV/s and so on.

Plotting the current peak versus square root of the sweep rate for the two cathodic peaks one obtains the graphs in Fig. 5, which are straight lines.

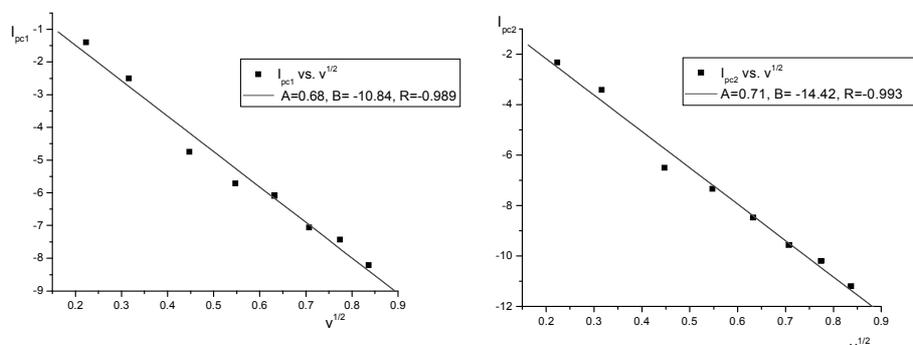
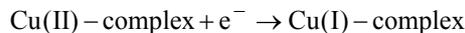


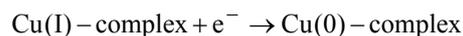
Fig. 5 The I_{pc1} vs. $v^{1/2}$ and respectively I_{pc2} vs. $v^{1/2}$ dependences for 1 mM [Cu(acac)(2,2'-bipym)]ClO₄.

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

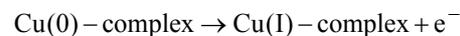
- The first cathodic peak can be assigned to the cathodic reduction of the Cu(II)–complex to the Cu(I)–complex in a quasireversible mechanism (there is a negative shift of the cathodic peak potential with increasing sweep rate):



- 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):

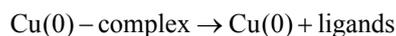


- The anodic shoulder/anodic peak (the counterpeak of the second cathodic peak) can be assigned to the anodic oxidation of the Cu(0)–complex, if this one could exist for very short time, to Cu(I)–complex :



but its very small height is due to the very low concentration of the Cu(0)–complex which very soon after its formation participates to a decomplexation reaction. The increasing concentration of Cu(II)–complex has as result the increase of this anodic shoulder/peak.

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



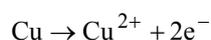
This chemical reaction is fast enough in order to decrease the height of the corresponding anodic shoulder/peak in which Cu(0)–complex is involved. The effect of the increasing

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 – adatoms formed by the chemical reaction: (there is also a positive shift of the anodic peak potential with increasing sweep rate):



but also to the anodic oxidation of the Cu – adatoms 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 one may conclude that the mechanism of the single cyclic voltammetry behaviour of the Cu(II)–complex is described by an EEC mechanism. Concerning the limiting contour observed in the regions of the first cathodic peak and the second cathodic peak for 2 mM and 4 mM concentrations in Cu(II)–complex we did not find an explanation until now.

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