

ELECTROCHEMICAL AND SPECTRAL STUDIES OF [Cu(acac)(phen)(H₂O)]ClO₄

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abstract: The complex [Cu(acac)(phen)(H₂O)]ClO₄ was investigated by using both cyclic and differential pulse voltammetry and coupled electrochemical and “in-situ” absorption spectral techniques. The electrochemical studies allow to obtain information about the electrochemical mechanism of redox behaviour in cyclic voltammetry experiments.

Introduction

The complex [Cu(acac)(phen)(H₂O)]ClO₄ was investigated by using both cyclic and differential pulse voltammetry and coupled electrochemical and “in-situ” absorption spectral techniques. This complex belongs to a series of mononuclear Cu(II)-complexes which will be investigated by electrochemical techniques, especially CV, DPV and RDE in order to get information about their behaviour enabling us to study the dinuclear Cu(II)-complexes or even multinuclear complexes. These multi-metal center complexes are frequent in nature as multi-metal center proteins and enzymes. 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. The CV experiments could find if the interaction exists or not in the case of homo- or hetero-multinuclear complexes [1-6].

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, 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

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measurements were carried out in acetonitrile (MeCN) solvent with 0,1 M tetrabutylammonium tetrafluoroborat 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 vis-spectra were recorded on a Specord-UV-Vis Carl Zeiss Jena spectrometer during the electrolysis at established electrode potential.

The electroactive species was $[\text{Cu}(\text{acac})(\text{phen})(\text{H}_2\text{O})]\text{ClO}_4$ in two different concentrations, 2 mM and 6 mM.

Results and discussions

We have been studied the cyclic voltammetric and pulse voltammetry behaviour of $[\text{Cu}(\text{acac})(\text{phen})(\text{H}_2\text{O})]\text{ClO}_4$ mononuclear complex having the structural formula given in Figure 1:

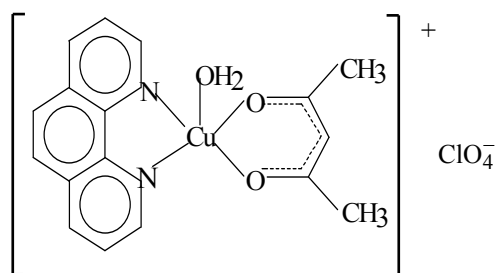


Fig. 1 The structural formula of the $[\text{Cu}(\text{acac})(\text{phen})(\text{H}_2\text{O})]\text{ClO}_4$ complex.

The complex has been studied in the potential range +0.1 V to -1.75 V and the single cyclic voltammogram obtained for several sweep rates are given in Figure 2.

These typical cyclic voltammograms show either a quasireversible behaviour or an EC mechanism. The typical cyclic voltammogram has a single cathodic wave with a cathodic peak situated in the -0,729 V to -0,863 V range. As it is shown in Table 1, the cathodic peak potential shifts toward negative potentials with increasing sweep rate. The height of the peak increases too with increasing sweep rate but the dependence between the peak current and the square root of the sweep rate, shown in Figure 3, is not linear. The ratio of the peak current to the square root of the sweep rate decreases as the sweep rate increases.

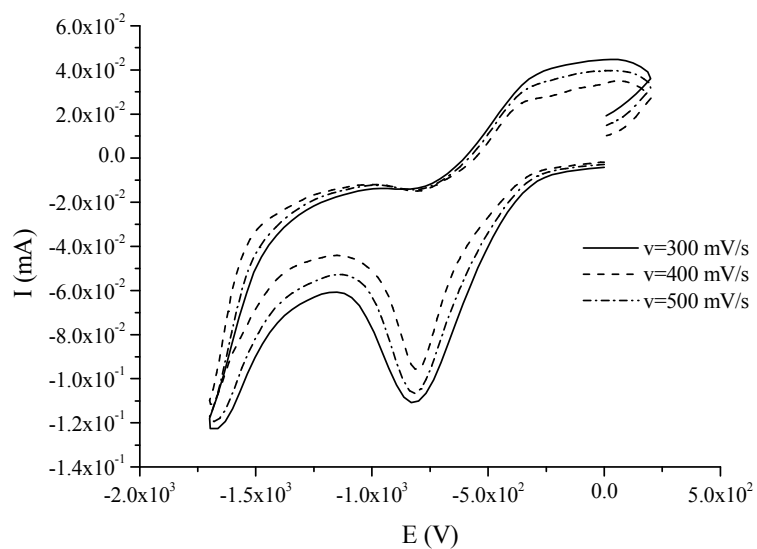


Fig. 2. The cyclic voltammograms at three indicated sweep rates for 6 mM $[\text{Cu}(\text{acac})(\text{phen})(\text{H}_2\text{O})]\text{ClO}_4$.

Table 1. The cathodic shift of the cathodic peak potential with the increasing sweep rate.

v (mV/s)	50	100	200	300	400	500
E_{cp} (V)	-0.729	-0.757	-0.803	-0.823	-0.850	-0.863

Fig. 3. The I_{cp} vs. $v^{1/2}$ dependence for 6 mM $[\text{Cu}(\text{acac})(\text{phen})(\text{H}_2\text{O})]\text{ClO}_4$.

This behaviour is common to the EC mechanism. This cathodic wave has been assigned to two-electron reduction of the mononuclear complex of copper II (step E). If the uncharged metal appears into the complex than a comproportionation reaction between this uncharged metal complex and the initial complex could take place being, in fact, thermodynamically favorable (step C). Therefore, for a single cyclic potential scan, the mechanism could be EC. The diagnostic test is fulfilled.

The next step was to investigate the multi-cycle voltammetry behaviour of the complex, Figure 4. The main noticeable features are:

- 1.-the first cycle is similar to that of the single cyclic voltammetry experiment;
- 2.-for the following cycles, as the cathodic scan continues there are two one-electron cathodic waves: the former situated at less negative peak potential and the latter situated at more negative peak potential;
- 3.-the former peak decreases rapidly after the second negative going scan and then disappears; we have assigned this cathodic wave to one-electron reduction of the initial complex;
- 4.-the latter peak increases on the third and subsequent scans; we have assigned this wave to one-electron reduction of the complex obtained after the first one-electron reduction;
- 5.-starting with the fifth cycle a limit contour is obtained;
- 6.-as seen, the wave between the two vanished; the current in the interpeak region dropped or being between is covered by the net interpeak reduction peak;

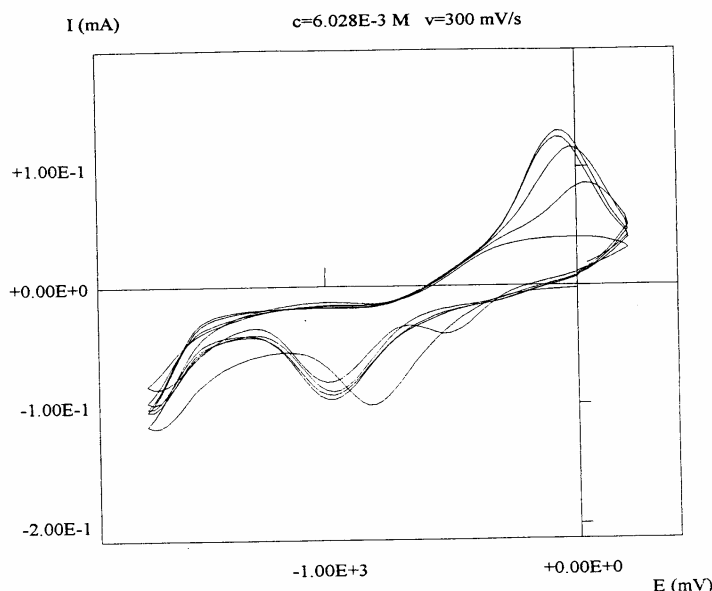


Fig. 4. The multi-cyclic voltammogram at $v=300$ mV/s for 6 mM $[\text{Cu}(\text{acac})(\text{phen})(\text{H}_2\text{O})]\text{ClO}_4$ in CH_3CN .

7.-in order to explain the decrease of the first wave it is necessary to consider both the comproportionation reaction and the fact that the diffusion layer extends as far as possible into solution while the scan is continued;

8.-at the same time this first peak becomes more negative and after the second scan its height decreases drastically and then remains constant;

9.-the increase of the second cathodic peak is owed both to the comproportionation reaction and the extension of the diffusion layer for the complex; it shows relative stability both on the potential axis and on the current axis.

Therefore the mechanism described here is ECE.

The assignment of the first cathodic peak on the second cycle of a multi-cycle voltammogram was made by scanning the potential in a sequence of two cyclic voltammetry experiments: a single cycle voltammetry followed immediately by a multi-cycle voltammetry: 1. the single scan in the +0.100V to -1.400V range in order to obtain the peak belonging to a single CV or to the first cycle in a multi CV; 2. -the multi-scan on the +0.100V to -0.900V range in order to obtain only the first peak belonging to the second and subsequent scans. The anodic wave at about -0.100-0.000V is the counterpeak of this first cathodic peak.

In addition to this, it is the visible spectral study.

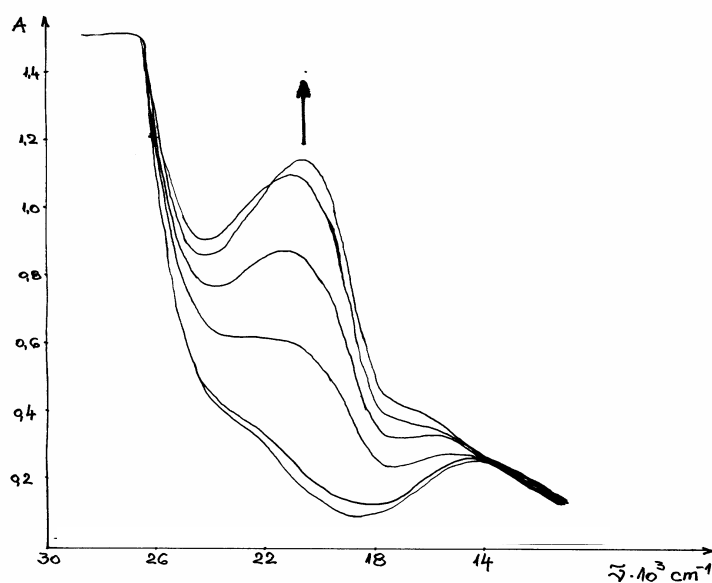


Fig. 5. The evolution of the absorption curves at an WE potential of $-0.900 V$ versus the RE, for $6 mM [Cu(acac)(phen)(H_2O)]ClO_4$ in CH_3CN .

Keeping the WE potential at -0.900V vs the RE potential (in the region of the cathodic two-electron wave) one obtains the evolution of the absorption curves shown in Figure 5. The evolution is determined by the increasing concentration of the product obtained by the electrolysis at the constant controlled potential. An absorption band at 427 nm is developed. Keeping the WE potential at $+0.100\text{V}$ vs the RE potential (in the region of the anodic wave) one obtains the evolution of the absorption curves shown in Figure 5.

The evolution is determined by the decreasing concentration of the product previously obtained by electrolysis. The absorption band at 427 nm starts to decrease because of the oxidation of the chemical product previously formed by reaction.

A DPV experiment on the solution shows the existence of three cathodic peaks with the first and the third more intense (see Figure 6).

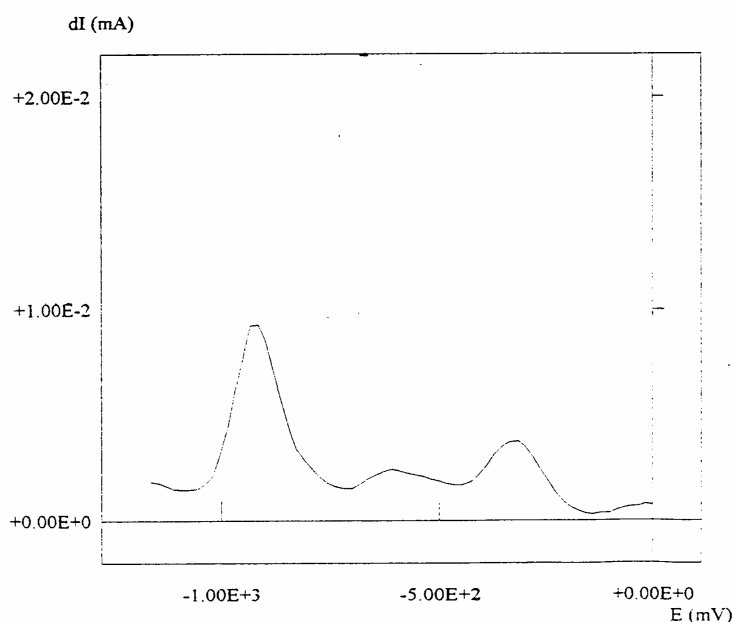


Fig. 6. The DPV voltammograms at $v=20\text{ mV/s}$ for 6 mM $[\text{Cu}(\text{acac})(\text{phen})(\text{H}_2\text{O})]\text{ClO}_4$.

These two peaks are developed at -0.350V and -0.940V which are very closely to the peak potentials obtained for CV at $50\text{ mV}\cdot\text{s}^{-1}$ (which is the nearest CV-sweep rate to the DPV-sweep rate).

REFERENCES

1. Urbach, F. L., in H. Siegel (Ed), **Metal ion in biological systems**, Vol. 13, Dekker, New York and Basel, 1981, 73.
2. Solomon, E. I., **Binuclear copper active site**, in T. G. Spiro (Ed), Copper proteins, Wiley-Interscience, New York, 1981, Chap. 2.
3. Dooley, D. M., Scott, R. A., Elinghaus, E., Solomon, E. I. and Gray, H. B., *Proc.Natl. Acad. Sci., U. S. A.*, **75**, 3019, 1978.
4. Spira, D. J., Winkler, M. E. and Solomon, E. I., *Biochim. Biophys. Res. Commun.*, **107**, 721, 1982.
5. LuBien, C., Winkler, M. E., Thamann, T. J., Scott, R. A., Co, M. S., Hodgson, K. O. and Solomon, E. I., *J. Am. Chem. Soc.*, **103**, 7014, 1981.
6. Winkler, M. E., Spira, D. J., LuBien, C., Thamann, T. J. and Solomon, E. I., *Biochim. Biophys. Res. Commun.*, **107**, 727, 1982.