STUDIA UBB CHEMIA, LVI, 2, 2011 (p. 29 - 37)

THE ELECTROCHEMICAL BEHAVIOR OF [$CU_2(DH)_4$ γ,γ-BIPY] BY CYCLIC AND ADSORPTIVE STRIPPING VOLTAMMETRY

TATIANA CAZAC[a], EDUARD COROPCEANU[a],
ROBERT SĂNDULESCU[b], LILIA CROITOR[c]

ABSTRACT. The electrochemical behavior of the [$Cu_2(DH)_4\gamma,\gamma$-bipy], (where DH is the monoanion of α,α'-dimethylglyoxime and γ,γ-bipy represents 4,4'-dipyridyl) was investigated for the first time by cyclic voltammetry and stripping cathodic voltammetry on the mercury drop electrode. The influence of some experimental parameters (pH, scan rate, concentration and electrolytic medium) on the electrochemical behavior of the complex has been examined as well. It has been established that the electrochemical reduction of [$Cu_2(DH)_4\gamma,\gamma$-bipy] is an adsorption controlled and irreversible process. The linear dependence of cathodic peak current and the concentration of [$Cu_2(DH)_4\gamma,\gamma$-bipy] has been elucidated.

Keywords: *cooper complexes, α,α'- dimethylglyoxime, 4,4'-dipyridyl, stripping voltammetry, cyclic voltammetry*

INTRODUCTION

The highly sensitive methods which allow determining the very low substance concentrations till trace level play a distinct role in solving the problems of state and dynamics evaluation of pollution, as well as in highlighting the main pollution sources of air, natural waters, rivers and soil. Investigation of the new adsorptive accumulation agents of chemical species, especially heavy metals and elaboration on its basis of the new adsorptive voltammetric methods with cathodic stripping (AdSCV) constitute the main protocol, by which the above-mentioned results can be obtained, thus presenting both theoretical and practical interest.

---

[a] *Institute of Chemistry, Academy of Sciences of the Republic of Moldova, 3 Academy Street, MD-2028, Chişinău, cazac_t@yahoo.com*

[b] *"Iuliu Haţieganu" University, Faculty of Pharmacy, Analytical Chemistry Dept., 4 Pasteur Street, 400349, Cluj-Napoca, Romania*

[c] *Institute of Applied Physics, Academy of Sciences of the Republic of Moldova, 5 Academy Street, MD-2028,Chişinău*

The elaboration of analytical dosage methods for biologically active organic compounds remains one of the contemporary problems of great interest for numerous research teams in the field of environment protection. Application of the adsorptive voltammetry with cathodic stripping from the arsenal of electrochemical methods allows preconcentration of the analytes's traces and furthermore, their quantification. Dioximes were used to determine cobalt traces in the analysis of extrapure metals. α-Benzyldioxime was employed by Bobrowski and Bond [1] to determine cobalt traces in the presence of high concentrations of zinc and their results have showen that even 10^6 – 10^7 times greater zinc concentrations tolerated the cobalt determination.

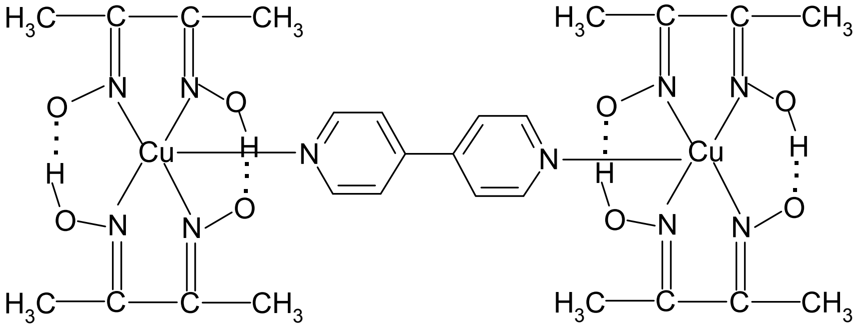
High sensitivity of the method with cathodic stripping in the case of α,α'-dimethylglyoxime for nickel and cobalt determination has been used in many investigations. Using a large range of voltammetric techniques, Dragic et al. [2] showed that the reduction process of the nickel dimethylglyoximate in ammonia solutions takes place with a consumption of 16 or 18 electrons. Feng et al. [3] have studied in detail the mechanism of the same process at pH 9 and optimised the experimental conditions for determination.

Donat et al. [4] have proposed the cobalt and nickel dosage at picomolar level in the presence of 1,2-cyclohexandiondioxime by differential pulse voltammetry. The greatest sensitivity was reached when the concentration of accumulation agent was 10^{-4} M, pH 7.6 and the adsorption potential -0.60 V. The selective feature of the process permits the use of a 15 minutes period of adsorption, which ensures the determination of 6 pM and 0.45 nM concentrations for cobalt and nickel, respectively.

It is well-known that dimeric compounds at dimethylglioxime containing different ligands show interesting biological activities [5] . Thus, deepening the knowledge in this field represents a perspective direction at investigations.

The current study is dedicated to study of the electrochemical behaviour of $[Cu_2(DH)_4\gamma,\gamma\text{-bipy}]$ in order to elucidate the optimal experimental conditions for its quantitative determination by cathodic stripping voltammetry.

The structure of the complex is depicted as follows:



RESULTS AND DISCUSSIONS

In IR (nujol) spectrum of the complex we attributed the absorption bands of valence and deformation oscillations as follows: $\nu_{as}(CH_3)$ 2945 cm^{-1}, ν(C=N) 1563 cm^{-1}, $\delta_{as}(CH_3)$ 1424 cm^{-1}, $\delta_s(CH_3)$ 1359 cm^{-1}, ν_{as}(N-O) 1219 cm^{-1}, ν_s(N-O) 1087 cm^{-1}, γ(OH) 977 cm^{-1}, δ(CNO) 742 cm^{-1}, ν_{as}(Cu-N) 484 cm^{-1}, which proves the coordination of two dioxime radicals in trans position. The signals at 3030 and 1603 cm^{-1} were attributed to the pyridine ring of the bridge ligand.

The absorption band at 230 nm obtained in **the UV-Visible spectrum** characterizes the charge transfer from the metal to the chelate ring and corresponds to the $Cu(DH)_2$ group. The band at 275 nm indicates on the presence of coordinated 4,4'-bipyridyl.

The detailed results on elemental analysis, IR and UV-visible spectral data have been recently reported in a previous paper [7].

The voltammetric investigation of the [$Cu_2(DH)_4\gamma,\gamma$-bipy] complex illustrates its property of adsorption and reduction on mercury drop electrod surface. The voltammogram of the investigated reagent showed that the mentioned reduction takes place at -0.28 V and respectively, -1.20 V potentials (Figure 1,curve 1). It was noticed that the addition of copper ions does not increase the analytical signal. By contrary, the addition of the studied complex solution produced an increase of the reduction current, which varies proportionally with the concentration. This fact, determined us to conclude that the reduction process involved the ligand from the complex, and consists in the reduction of $[Cu(HD)_2]^0$ to $[Cu(D)_2]^{2-}{}_{ads}$ and not Cu^{2+} to Cu^0.

After the investigation of the electrochemical behaviour of [$Cu_2(DH)_4\gamma,\gamma$-bipy] by cyclic voltrammetry (Figure 2) the same well-defined reduction peak at -0.28V potential has been put into evidence. This served as a conclusive indication about the irreversible nature of the process that takes place on the electrode. It was established that after the adsorption processthe anion $[Cu_2(DH)_2]^{2-}$ is reduced on mercury drop. The cyclic voltammograms for copper dimethylglioxymate present a single reduction peak at -0.24V and γ,γ-bipy at -0.95V, respectively, the nature of the processes being dominated by diffusion. The complex formation with the two components strongly facilitates the adsorbtion of copper dimethylglioxymate on mercury drop surface.

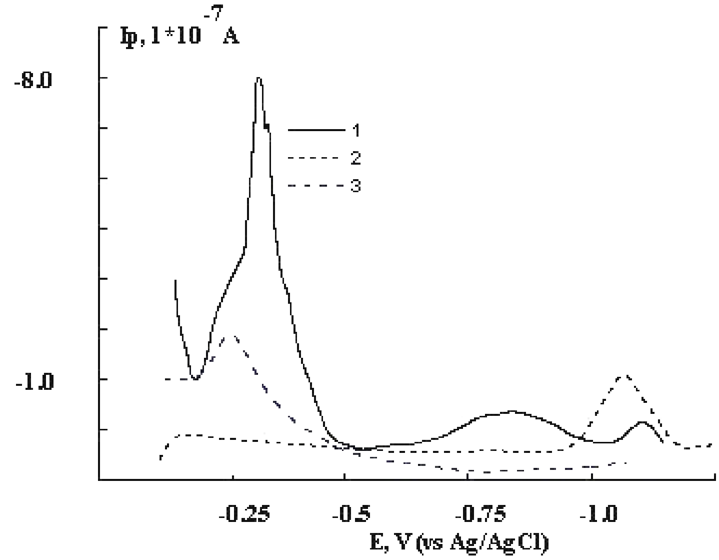


Figure 1. Square wave voltammogram of: 1- [$Cu_2(DH)_4$ γ,γ-bipy] $5\cdot10^{-5}$M in 0.1M KCl, 2- γ,γ-bipy $5\cdot10^{-5}$M in 0.1M KCl, 3- DMG $5\cdot10^{-5}$M in 0.1M KCl, pH 5.2 (E_{in} -100mV, E_{fin} -1260mV, $t_{el.}$ 10s, step.dur. -0.2s, step.apl. 10 mV, puls ampl. -50mV)

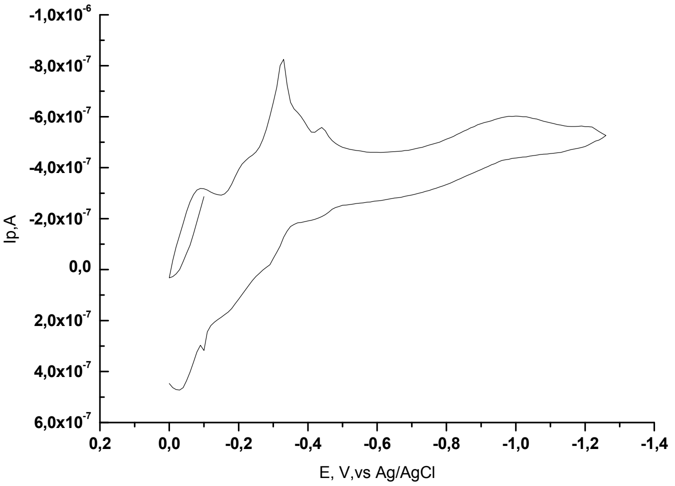


Figure 2. Cyclic voltammogram of [$Cu_2(DH)_4$γ,γ-bipy] $5\cdot10^{-5}$ M in 0.1M KCl, pH 5.2 (WE – HMDE; RE – Ag/AgCl,(3 M KCl); AuxE Pt wire; E_{in} 0 mV, E_{fin} -1260mV, $t_{el.}$ 10s, step.dur. 0.2s, step.apl. 10 mV, puls ampl. -50mV; 20°C)

The slope of the regression line, in lgI$_p$/lgv coordinates, determined from the investigation of the influence of the scan speed (v) on the peak current (I$_p$), representing the speed coefficient "X", was found to be 0.83 and 0.46 for the first and the second reduction reactions, respectively (Figure 3). The value of the experimentally obtained speed coefficient for the reduction peak at -0.28 V characterizes the electrode electrochemical processes followed by the adsorption of depolarizer on the surface of the mercury electrode (y$_1$), while in the case of the drop at -1.15V a diffusion process (y$_2$) is clearly distinguished.

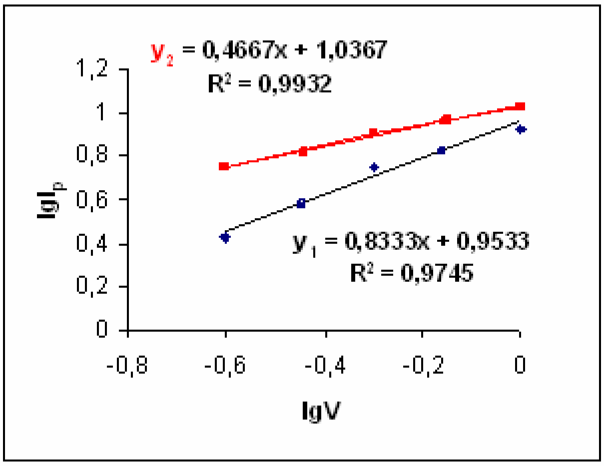


Figure 3. The slope of the regression line in lgI$_p$/lg V coordinates ([Cu$_2$(DH)$_4$ γ,γ-bipy] 5·10^{-5} M in 0.1M KCl, pH 5.2; WE - DME; RE - Ag/AgCl,(3 M KCl); AuxE - Pt wire; 20^{o} C).

The nature of the peak has been estimated from the value of the Semerano coefficient: when the slope lgI/lgV has a value close to 1, the adsorption process occurs, when it is less than 0.5, a kinetic process is involved and a value between 0.5 and 0.7 indicates on a diffusion process, accompanied by adsorption [6].

In order to demonstrate the origin of the reduction peak at -0.28 V, the voltammograms in the solutions for each separate compound of the complex were recorded. As a result, it has been concluded that this peak belongs to α,α'-dimethylglyoxime. Another points to be mentioned regard the diffusion character of the process on the surface of the mercury drop in comparison with the fact that complexation with 4,4'-bipyridyl facilitates the adsorption of α,α'-dimethylglyoxime on the drop of mercury.

An additional indication on the adsorbtive nature of the above-described process is proved by the variation curves of the current, according to the applied potential on the electrode (Figure 4). These curves demonstrate that in solution containing $[Cu_2(DH)_4\gamma,\gamma\text{-bipy}]$, the dropping time is smaller (Figure 4, curve 2) if compared to control sample of 0.1M KCl solution (curve 1).

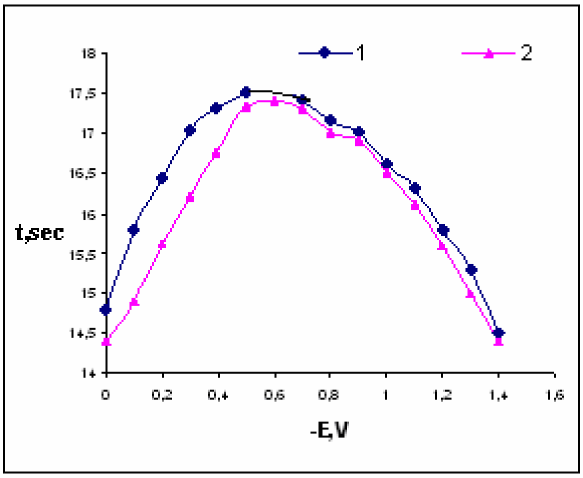
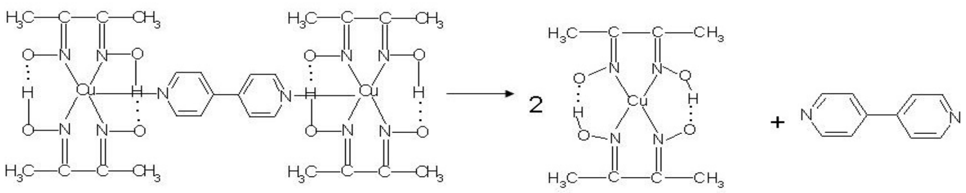


Figure 4. The variation of dropping time according to the applied potential on the electrode in solution: 1) KCl 0,1 M; 2) KCl 0,1 M + $[Cu_2(DH)_4\gamma,\gamma\text{-bipy}]$ $5\cdot10^{-5}$ M (WE - DME; RE - SCE; AuxE - Pt wire; scan rate 1 V s^{-1}; 20° C).

This phenomenon points again on the adsorption of the depolarizing compound at the surface of the mercury drop. Obviously, the ascending branch of curve 2 (Figure 4) characterizes the stronger adsorption on the mercury drop that can occur due to the presence of an electrochemically active particle of anionic nature [8-10]. This can be represented by the following equations of reactions:



$$[Cu(HD)_2]^0 + 2H^+ + 4e \rightarrow [Cu(D)_2]^{2-}_{ads} + 2H_2$$
$$2H^+ + 2e \rightarrow H_2$$

The fact that the process on the electrode is controlled by the concentration of hydrogen ions is also certified by the investigation of the dependence of the current and the reduction potential by the pH value of the solution. In the pH area from 1.0 to 4.5 a variation of the current and the reduction potential is distinguished. At higher pH values than 4.5 the reduction potential of the reagent moves from -0.28 to -0.48 value (Figure 5).

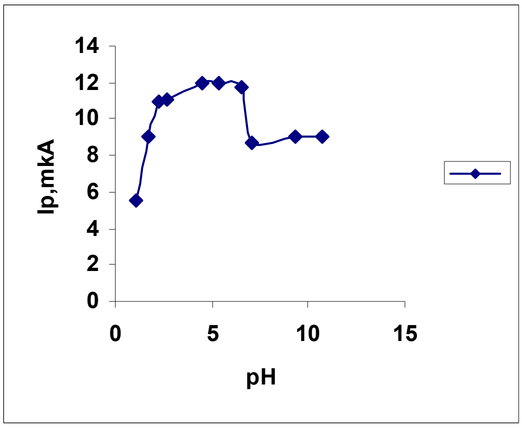


Figure 5. The dependence of the reduction current (Ip) by the pH (E_{in} -100mV, E_{fin} -1260mV, $t_{el.}$ 10s, step.dur. -0.2s, step.apl. 10 mV, puls ampl. 50mV)

The presence in solution of Zn(II), Co(II), Cr(VI), Ni(II), Mn(II), V(V), Al(III), Pb(II), Cd(II) species does not alter the value of the reduction curent of [$Cu_2(DH)_4$γ,γ-bipy] in the cases when the ratio between complex and interferent cation does not exceed 1:10. The presence of I^-, Br^-, SCN^-, CH_3COO^- anions in solution, in ratio A^- : complex of 10:1 does not influence on the value of the reduction current (Table 1).

Table 1. The influence of interferents on reduction current and potential of [$Cu_2(DH)_4$γ,γ-bipy]

Interferent	Ip, nA	E, V vs (Ag/AgCl)
[$Cu_2(DH)_4$γ,γ-bipy]	780.0	-0.28
Zn(II)	780.00	-0.30
Co(II)	783.08	-0.29
Cr(VI)	779.62	-0.28
Ni(II)	783.00	-0.28
Mn(II)	783.08	-0.28
V(V)	779.98	-0.30
Al(III)	785.56	-0.28

Interferent	Ip, nA	E, V vs (Ag/AgCl)
Pb(II)	778.32	-0.26
Cd(II)	782.34	-0.26
I^-	791.00	-0.28
Br^-	787.96	-0.28
SCN^-	783.28	-0.28
CH_3COO^-	786.65	-0.28

CONCLUSIONS

For the first time the electrochemical behavior of $[Cu_2(DH)_4\ \gamma,\gamma$-bipy] by cyclic and adsorptive stripping voltammetry has been investigated. The reduction of $[Cu_2(DH)_4\gamma,\gamma$-bipy] complex on the surface of the drop mercury electrode is an irreversible, adsorbtion-controlled process. A well-defined reduction peak at -0.28V characterize this process. The influence of pH, complex concentration, accumulation time, applied potential and interferent ions has been studied in detail. Consequently, the optimal experimental conditions have been developed.

The reduction current Ip shows a linear relationship with $[Cu_2(DH)_4\gamma,\gamma$-bipy] concentration in the range 10^{-6}M - 10^{-5}M.

EXPERIMENTAL

Apparatus and materials

Elemental analyses were performed on an Elementar Analysen systeme GmbH Vario El III. The IR spectra were obtained in nujol on a FT IR Spectrum-100 Perkin Elmer spectrometer in the range 400-4000 cm^{-1}. Absorption spectra were recorded on a UV-VIS Lambda 25 Perkin Elmer spectrometer.

The voltammetric investigations were performed with a Polarograph POL 150 (France), in a cell with three electrodes, the working electrode was the hanging mercury drop electrode (HMDE), a counter electrode of platinum and Ag/AgCl as a reference electrode.

The values of pH were measured with a pH-meter CONSORT C931 (Belgium).

The stock solutions were prepared by dissolving the weighted sample of $[Cu_2(DH)_4\ \gamma,\gamma$-bipy], KCl, KI, KSCN, nitrates of Zn(II), Co(II), Cr(VI), Ni(II), Mn(II), Al(III), Pb(II), Cd(II), $NaVO_3$ (SIGMA-ALDRICH, 50 mg), sodium acetate (Chimiopar), hydrochloric acid and sodium hydroxyde (PAM Corporation) in bidistilled water (Fistrum International Ltd). Working solutions were prepared by diluting the initial solutions and deaerated by nitrogen flow for 5 minutes. The accumulation of depolarizer on the electrode surface was performed in conditions of stirring the solutions.

Synthesis of [Cu$_2$(DH)$_4$(γ,γ-bipy)]: To a solution formed from Cu(CH$_3$COO)$_2$·H$_2$O (Sigma-Aldrich, 200 mg, 0.001 mol) and 20 ml water α,α'-dimethylglyoxime (Sigma-Aldrich, 230 mg, 0.002 mol) dissolved in 25 ml methanol was added and 4,4'-dipyridyl (Sigma-Aldrich, 40 mg, 0,0005 mol) dissolved in 10 ml of methanol, subsequently. The reaction mixture was refluxed for 10 minutes. The dark brown solution was filtered and left for slow evaporation at room temperature. Dark brown crystals were obtained. Yield: ~30 %. Calculated for $C_{26}H_{36}Cu_2N_{10}O_8$: C, 41.97%; H, 4.88%; N, 18.83%. Found: C, 41.42%; H, 4.67%; N, 18.69%.

ACKNOWLEDGMENT

T.C. thanks the **Eugen Ionescu foundation** for granting a postdoctoral scholarship (2009-2010).

REFERENCES

1. A. Bobrowski, A.M. Bond, *Pol. Electroanalysis*, **1991**, *3(3),* 157.
2. V.V. Dragic, A.P. *Anal. Chem.*, **1996**, *68*, 829.
3. Ma Feng, J. Daniel, L. Renman, *Anal. Chem.*, **1997**, *69*, 1782.
4. J.R. Donat, K.W. Bruland, *Analytical Chemistry*, **1988**, *60(3)*, 240.
5. E.B. Coropceanu, A. Deseatnic, M. Stratan, A Rija, O. Bologa, J. Tiurin, S. Labliuc, S. Clapco, I. Bulhac, *Chem. Journ. of Moldova*, **2008**, *3(2)*, 70.
6. V.I. Gorohovskaia, M. Gorohovski, "Handbook of oscilopolarography". High School Publ., Moskow, **1973**.
7. E.B. Coropceanu, L. Croitor, B. Wicher, M. Gdaniec, M.S. Fonari, *Inorganica Chimica Acta*, **2009**, *362*, 2151.
8. T.A. Criucova, S.I. Sineacova, T.V. Arefieva, Plarografic analysis, Moskow, **1959**.
9. F. Vydra, K. Stulic and E. Julacova. "Electrochemical Stripping Analysis". Halsted Press, New York, **1976**.
10. R. Kalvoda, *Pure Appl. Chem.,* **1987**, *59*, 715.