Journal of Fundamental and Applied Sciences

ISSN 1112-9867

Available online at http://www.jfas.info

Research Article

SYNTHESIS, ELECTROCHEMICAL AND HETEROGENEOUS ELECTROCATALYTIC BEHAVIORS OF A NOVEL NON SYMMETRICAL COPPER(II) COMPLEX

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Received: 23 October 2018 / Accepted: 22 December 2018 / Published online: 01 January 2019

ABSTRACT

We describe in this paper the synthesis of new unsymmetrical tetradentate copper(II) Schiff base complex, prepared from tridentate Schiff base ligand (**HL**) and pyridine molecule. This new copper complex was identified by various physicochemical characteristics such as elemental analysis (EA), FT-IR, UV-Vis, XPS analysis and thermogravimetry (TG/DTG). The electrochemical behavior of the copper(II) complex was investigated by cyclic voltammetry in N,N-dimethylformamide (DMF). These experiments have been allowed to obtain new conducting polymeric films, prepared by successive cycling at the suitable potentials. These polymeric films containing metallic centers were studied to evaluate their electrocatalytical performances in which copper (II) ions were used as electrocatalysts in the heterogeneous conditions for the electroreduction of 1,4-dibromobutane.

Keywords: Copper(II) Schiff base complex, Thermogravimetry, Cyclic voltammetry, Modified electrodes, Heterogeneous electroreduction.

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doi: http://dx.doi.org/10.4314/jfas.v11i1.31

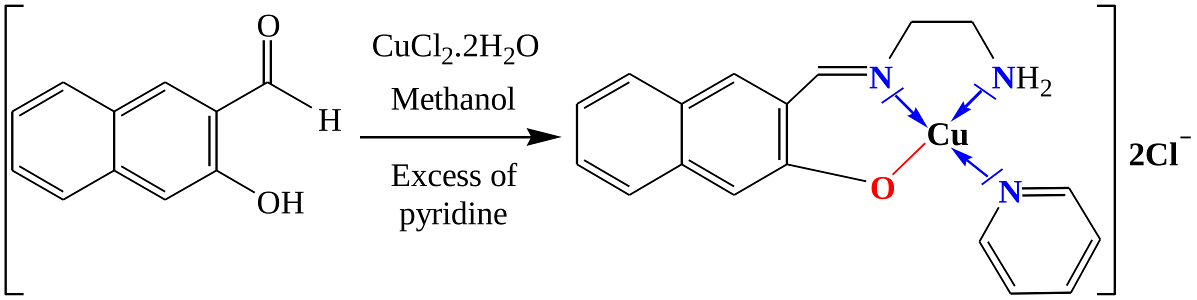
1. INTRODUCTION

Schiff bases are currently used as ligands to synthesize an infinite number of chelating agents either with their own forms or as compounds of coordination chemistry. All of these both classes of compounds are of a great interest due to their significant multiples uses very useful in several domains such as, catalysis [1], electrocatalysis [2] with other important applications like sensors for detecting of biomolecules using modified electrodes [3,4] and diverse biological activities [5,6]. Furthermore, Schiff base metal complexes have numerous biological applications since, a great deal has been focused on the study of their bioability as bactericidals in many important biological activities, such as fungicidal [7], anticancer [8-10], antitumor [11-13] and also as antimicrobial agent [14]. On the other hand, these compounds showed also other interesting properties such as ability to reversibly bind to dioxygen (O_2), electrocatalytic activity in hydrogenation of olefins with noble metals [15], electropolymerisation [16], photochromic properties [17] electrocatalytic reduction of alkyl halides [18] and electrooxidation of alcohols [19].

In general, Schiff bases ligands are easily formed by the condensation of aldehydes or ketones with amines [20]. In recent years, a particular attention has been dedicated to the mixed ligands complexes containing nitrogen and oxygen donors. In this case, the copper is actually known as an essential transition metal species that playing relevant roles in several metabolic biological functions. For this reason, it is, in principle, capable to encourage chemical processes that are associated with transition metals early mentioned such as in the catalytic oxidation reactions [21]. So, this is a continuing interest using copper complexes containing mixed ligands, because of the presence of hard nitrogen and oxygen donor atoms in the backbone of these ligands [22].

Herein, we report the synthesis of new class of tridentate Schiff base complexes as non symmetrical compounds since the compounds initially desired were the tetradentate Schiff base complexes. Being convinced that the target tridentate complexes are as well of very attractive interest with their geometry without symmetry as the classical tetradentate Schiff base complexes [23]. So, in spite of this study which have not focused the enantiomeric excess, but it limits only its main objective to the electrocatalytical reactions such as the reduction of organic halides like 1,4-dibromobutane. This work is a continuation of various studies recently undertaken with Peters's group on the electrocatalytic reduction of organic halides either in their aliphatic or aromatic forms [24]. The electroreduction reactions of these halides seem to be very interesting of the fundamental or industrial point of view. Among the more interesting goals of these applications, we can note the mechanistic studies exploring all the intermediates involved in the electroduction reaction [25]. This is considered as the main objective feeding the theoretical purposes of the organic electrochemistry.

Based on the previous considerations, we report here the synthesis of newly synthesized copper Schiff base complex, derived from template reaction implicating the 2-hydroxy-1-naphthaldehyde, 1,2-diaminoethane, pyridine (Py) and copper chloride salt in one pot (See scheme 1). The resulting complex has been characterized using elemental analysis, spectroscopic techniques, thermogravimetric analysis (TG/DTG), and cyclic voltammetry measurements. The electropolymerization of this monomer was also performed by cyclic voltammetry. In addition, the prepared polymer films electrochemically deposited onto ITO and FTO substrates were characterized by atomic force microscopy (AFM). Interestingly, these modified electrodes inspired us to explore the electrocatalytic behavior of this copper complex towards the electroreduction of 1,4- dibromobutane to 1-bromobutane and also probably to the butane.



Scheme 1. Schematic representation leading to the formation of the Schiff base copper(II) complex

2. RESULTS AND DISCUSSION

A precondition of this study is the preparation of the new mixed ligands copper complex. The tridentate Schiff base ligand with pyridine compound react with copper transition metal ions and form stable complex that is of significant electrocatalytical applications. The Schiff base ligand (HL) is prepared by the reaction of 2-hydroxynaphtaldehyde on 1,2-diaminoethane in methanol. By mixing a solution of HL with a methanolic solution of copper chloride salt and an excess of pyridine, the non symmetrical copper(II) complex, Cu(L)(Py)(2Cl^-), is obtained. This complex is stable in air and moisture. Its solubility is usually good in the coordinating solvents such as acetonitrile, DMF and DMSO.

2.1. Spectrophotometric characterizations

2.1.1. FT-IR spectrum

The spectral characterization of the prepared non symmetrical copper complex was performed by assignment of most important infrared wave numbers. Therefore, the FT-IR spectrum of Cu(L)(Py)(2Cl^-) complex shows two absorption bands at 3487 and 3433 cm^{-1} that can be attributed to the (NH_2) vibrations [27]. A strong and sharp absorption band appeared at 1620 cm^{-1} indicates iminic (C=N) linkage formation as functional group of Schiff base which is in accordance with all the complexes usually described in the literature [28]. The observed bands in the regions 439–520 and 624–670 cm^{-1}, respectively, were assigned to the M–N and M–O absorption bands [29] which further support the coordination of the phenolic oxygen and azomethine nitrogen atoms to the copper ion.

2.1.2. Electronic spectrum

The formation of the copper (II) complex was also evidenced by UV-Vis spectrum. The electronic spectrum of Cu(L)(Py)(2Cl^-), recorded in DMSO solution, displays its most important features between 300 and 390 nm. The intense absorption band observed at 314 nm may be ascribed to intra-ligand transitions (π–π*), due to the aromatic and azomethine π-systems [30]. The weak band observed at 389 nm can be attributed to the ligand-metal charge transfer transition (LMCT) [31]. Regarding the weak d–d transitions were observed in the visible region around 610 nm. These transitions express that the copper atom is well coordinated to the mixed Schiff base and pyridine ligands [32].

2.2. Thermal behavior (TG/DTG)

The thermal behavior of Cu(II)-Schiff base complex has been studied and its stepwise thermal degradation was also evidenced. The TG/DTG plots of Schiff base Cu(II) complex were recorded starting at room temperature from 25 to 1000 °C with the heat flow rate of 10 °C/min. This experiment was performed under argon atmosphere as it can be seen in Fig. 1. So, the copper complex seems to be stable up to 145 °C. Beyond this temperature, its decomposition begins to be produced at 145°C showing four steps. The first one occurs between 145 and 190 °C range with a weak DTG peak, noted at 189 °C. The resulting weight loss was estimated at (Obs. = 15.8%, Calc. = 16.1%). This weight loss was explained by the elimination of water molecules (5 H_2O). For the second step, occurred in the temperatures ranging from 200 to 225 °C showing a strong DTG peak at 217 °C exhibiting a mass loss of 12.4 % whereas the calculated percentage is of 12.7 %. This is assigned to the elimination of chlorine atoms as molecular chlorine (Cl_2). As for the third step, it was observed at the temperatures range 225-280 °C displaying a neat weight loss of 13.9% (calc. 14.1%) which has been consistent with the elimination of pyridine molecule (C_5H_5N). Regarding the last step, illustrated by a DTA peak and seen at 520 °C, this peak was observed between 280 and 570 °C and it corresponds to the total decomposition of the organic species since, the remaining product beyond 520 °C as temperature can be identified as copper oxide (CuO) as reported in the literature [33].

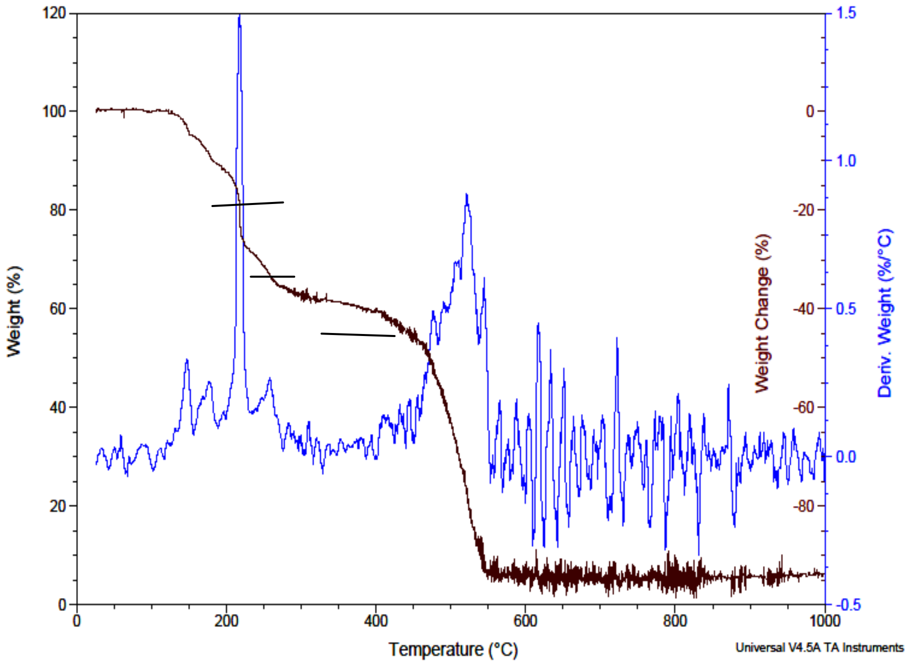
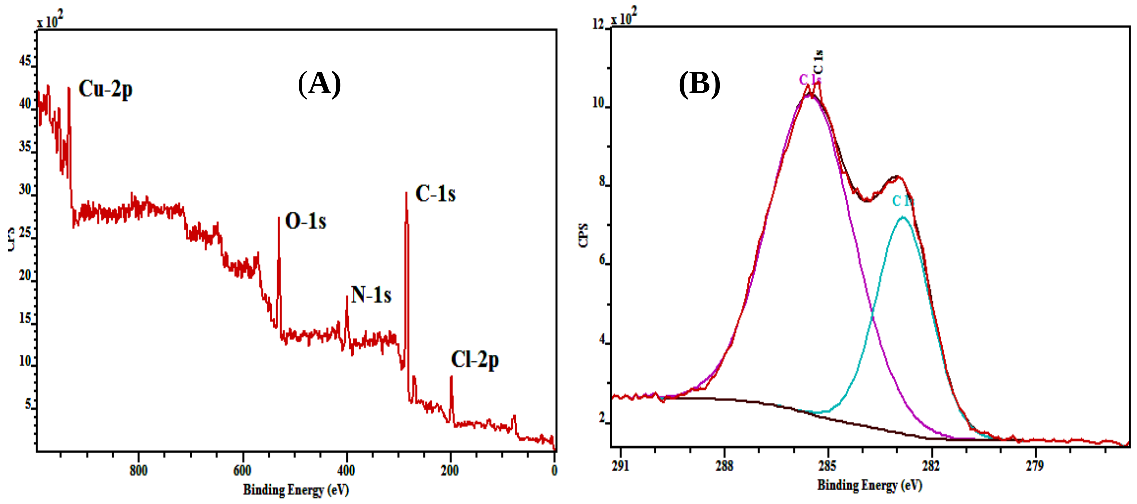


Fig.1. TG/DTG thermograms of the studied copper (II) complex

2.2. X-ray photoelectron spectroscopy (XPS)

The XPS wide scan data for Cu(L)(Py)(2Cl$^-$) copper-Schiff base complex in its solid state is presented in Fig. 2A. The XPS survey and deconvoluted spectra of Cu(L)(Py)(2Cl$^-$) Schiff base complex revealed that the presence of carbon (C-1s), nitrogen (N-1s), oxygen (O-1s), chlorine (Cl-2p) and copper (Cu-2p) [34,35]. The main C 1s peak can be deconvoluted into two main components as depicted in Fig. 2B. The position of the peak at 282,8 eV that contribute to carbon atoms (C=C) in the aromatic rings. The formation of azomethine imine is verified by the presence of carbon attached to nitrogen at 285,5 eV [35]. The N-1s (Fig. 2C) peak presents two main components which are due to NH and N=C at around 397 and 399 eV, respectively [36]. In the survey spectra of chemical solid of Cu(L)(Py)(2Cl$^-$), there are the peaks of O-1s region seen at 529 eV and 531.4 eV which are attributable to the oxygen atoms of hydroxyl as phenoxy groups Fig. 2D. Furthermore, the peak of chlorine (Cl 2p) shown in Fig. 2E is directly bonded to copper metal, deconvoluted by doublet peaks at 195 eV is ascribed to Cl 2p$_{3/2}$ and 200 eV for Cl 2p$_{1/2}$ [37]. For the Fig. 2F showing the spectrum presenting two main peaks which are usually attributed to Cu-2/p$_3$ and Cu- 2p$_{1/2}$ at 938 and 957 eV, respectively. In the same region, two other satellite peaks were also observed around 946 and 966 eV in the higher binding energy compared with main peak [22].



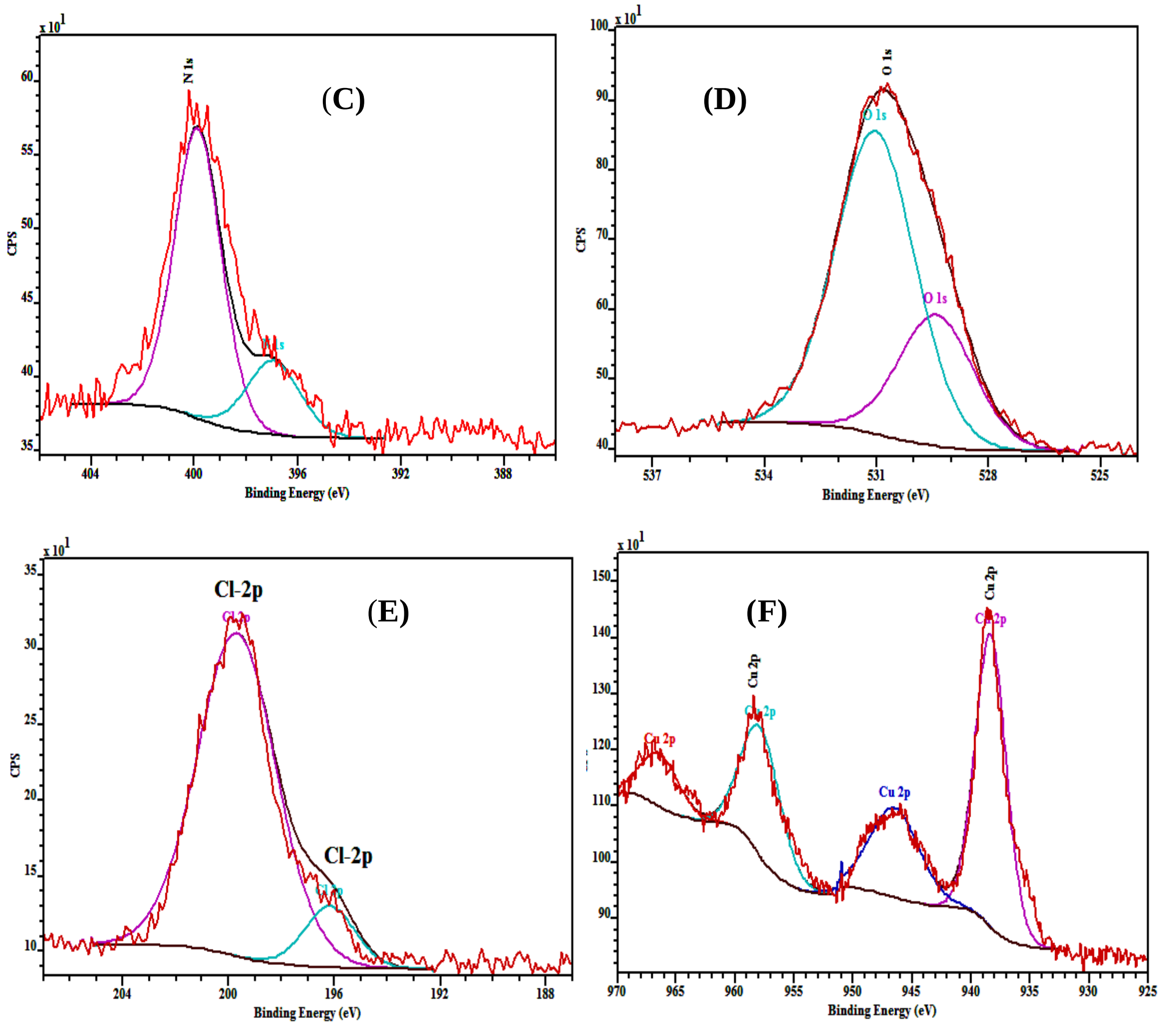


Fig.2. General XPS spectrum of Cu(L)(Py)(2Cl$^-$) Schiff base complex (A); C-1s (B); N-1s (C); O-1s (D); Cl-2p (E) and Cu 2p (F) X-ray photoelectron spectra of Cu(L)(Py)(2Cl$^-$) Schiff base complex

2.4. Electrochemical characterization

2.4.1. Cyclic voltammetry

The redox behavior of the Cu(L)(Py)(2Cl$^-$) 10^{-3} M was studied by cyclic voltammetry in DMF solutions containing 10^{-1} M of TBABF$_4$ using 100 mVs^{-1} as scan rate after bubbling for more than 15 minutes under nitrogen atmosphere.

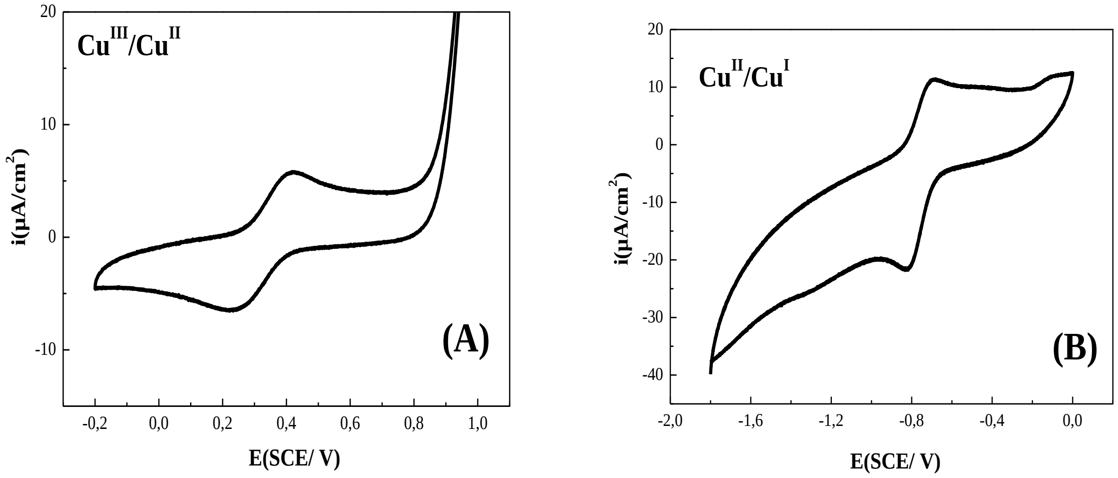


Fig.3. Cyclic voltammograms recorded with 1mM of Cu(L)(Py)(2Cl$^-$) in DMF solutions containing 0.1 M TBABF$_4$ using 100 mV s^{-1} as scan rate going from: (A) -0.2 to +1.0 and (B) +0 to -1.8 V/SCE

The cyclic voltammogram, recorded in the range between -0.2 and +1.0 V (Fig. 3, curve A), shows Cu^{III}/Cu^{II} redox couple at E$_{1/2}$= 0.34 V/SCE. The peak-to-peak separation (ΔEp) was found to be equal to 160 mV, while the theoretical value of ΔEp for one-electron process is equal or slightly superior to 60 mV [38]. This great difference between the theoretical and the experimental values would be due to a quasi-reversible behavior of the Cu^{III}/Cu^{II} redox couple. As a consequence, this indicates a relative slow redox transition and/or electron exchange process at the interface between the electrode and copper redox centers [38], which implies that these electrochemical processes are mainly diffusion-controlled. At negative potential response, the cyclic voltamogram of this copper(II) complex showed also another quasi-reversible redox system at E$_{1/2}$ equal to -0.87 V/SCE with peak-to-peak separation (ΔEp = 100 mV). This couple may be referred to the Cu^{II}/Cu^{I} redox couple as it can be seen in Fig. 3 (curve B).

2.4.2. Modified glassy carbon electrode

Fig. 4 shows the evolution of the cyclic voltammograms of Cu(L)(Py)(2Cl$^-$) complex, recorded in DMF solutions with a glassy carbon electrode (Ø 3 mm) using 100 mV s^{-1} as scan rate . During the repeated potential scans between 0.0 and 1.2 V (curve A), the anodic oxidation shows a neat decrease of the peak current indicating probably the passivation of the electrode surface. The electropolymerization of Cu(L)(Py)(2Cl$^-$) was also performed by repetitive cycling of the potential between +0.0 and −1.8 V. The buildup of the electropolymerized poly-[Cu(L)(Py)(2Cl$^-$)] films was confirmed by continuous increasing of the peak current with repeated cycling. This electrochemical process produces an electroactive film of poly-[Cu(L)(Py)(2Cl$^-$)] on glassy carbon electrode surface as illustrated by Fig. 4 (curve B).

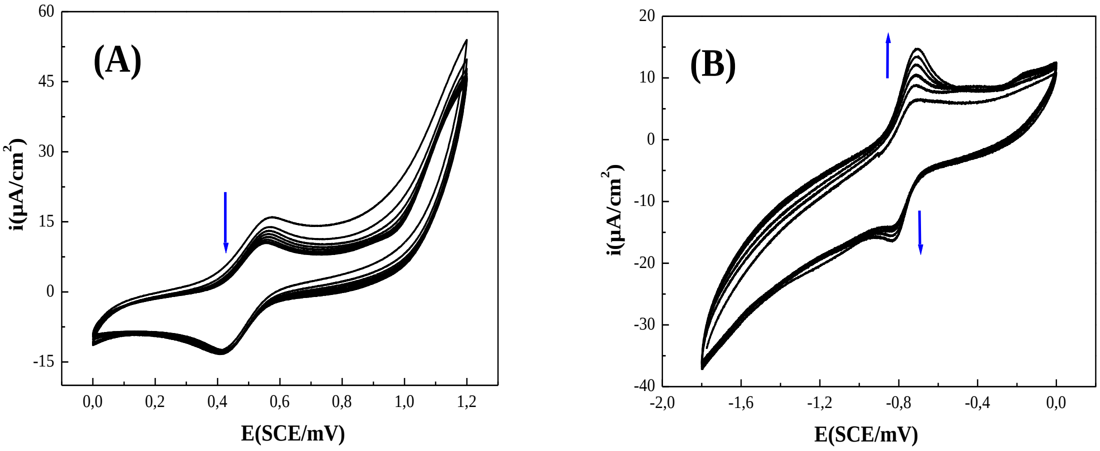
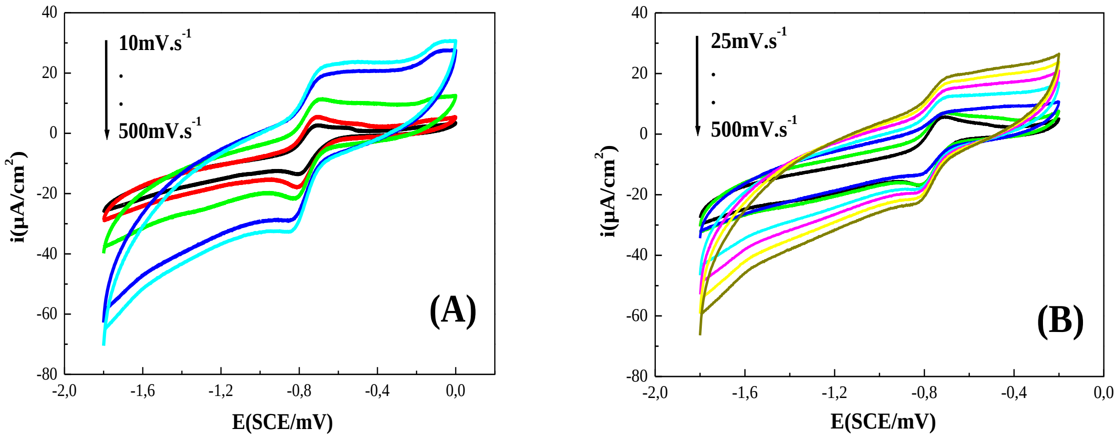
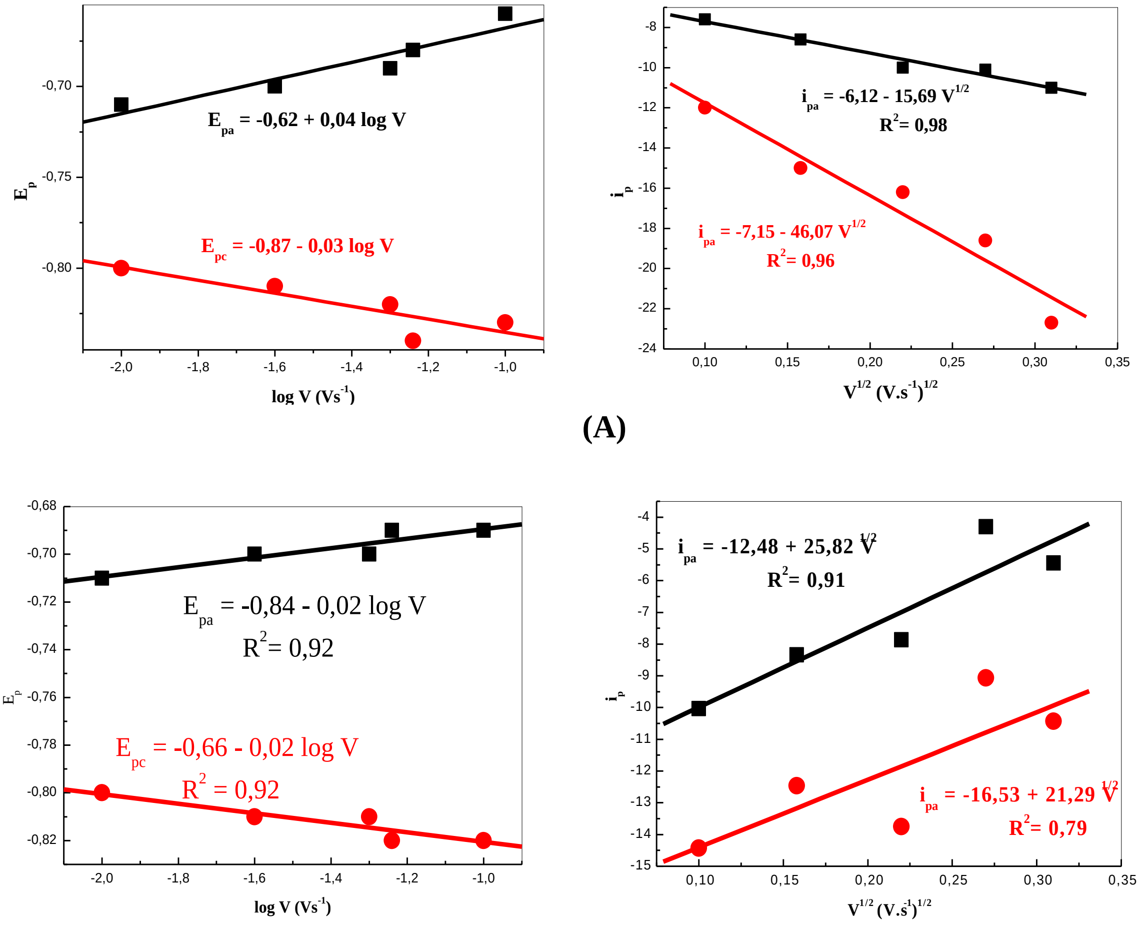


Fig.4. Poly-[Cu(L)(Py)(2Cl$^-$)] films obtained on GC electrode in DMF solutions containing 0.1 M TBABF$_4$ and 10^{-3} M of Cu(L)(Py)(2Cl$^-$) copper complex by cycling from 0.0 to +1.2 (A) and then from 0 to -1.8 V/SCE (B) using 100 mV s^{-1} as scan rate

After electrodeposition of poly-[Cu(L)(Py)(2Cl$^-$)] films on the surface of GC electrode. This modified electrode was copiously rinsed with bi-distilled water, acetone and then with DMF. When this electrode is then leached from its undesirable species (mineral and organic), it is immediately transferred into another fresh electrolytic DMF solution no containing monomer. This modified electrode (ME) was identified by the electrochemical characteristics of polymer using cyclic voltammetry technique. The results obtained proved the presence of the copper complex in the polymeric matrices. Similarly, poly-[Cu(L)(Py)(2Cl$^-$)] films are as well electrodeposited on the optically transparent electrodes like those of indium tin oxide (ITO) and fluorine tin oxide (FTO). These experiments were exactly carried out in the same experimental conditions using DMF solutions 10^{-1} M TBABF$_4$ and 10^{-3} M of the studied copper complex Cu(L)(Py)(2Cl$^-$). The buildup of the poly-[Cu(L)(Py)(2Cl$^-$)] films were characterized in these two cases by a neat continuous increase in the i_{pa} and i_{pc} peak currents, obtained for each one of the repeated cycling producing the electrodeposition of the conductive polymer film on ITO and FTO surfaces [39].

In this context, we have investigated the scan rate dependency towards Cu^{II}/Cu^{I} redox couple operating in the both homogeneous and heterogeneous phases. Thus, a wide range of scan rates was explored starting from 10 to 500 mV s^{-1} (See Fig. 5A and B) [40]. The two recorded voltammograms of the unmodified and the modified electrodes show clearly the continuous increasing of the intensities of i_{pa}, i_{pc} peaks with increasing the scan rate accompanied also with a shifting of anodic and cathodic peak potentials to the positive and negative values, respectively. Indeed, this shifting is also accompanied with enlarging of peak-to-peak separations (ΔE_P). The obtained ΔE_P values are relatively very far to be compared to 60 mV, commonly taken as theoretical standard for a Nernstian system diffusion controlled as reported in the literature [38]. In addition, the i_{pa}/i_{pc} ratios are systematically different than unity. These results suggest that this redox system is not Nernstian but a quasi reversible. The linear dependency of i_{pa}, i_{pc} peak current with the square root of the scan rate ($v^{1/2}$) Fig. 5 (curve C) can be attributed to an electron transfer controlled by diffusion. On the other hand, the E_{pa}, E_{pc} peak potentials are proportional to the logarithm of the scan rate (Log$v$) as it can be seen in Fig. 5 (curve D) expressing probably a slow charge transfer process.





(A)

(B)

Fig.5. Cyclic voltammograms, recorded from DMF solutions 1 mM of Cu(L)(Py)(2Cl$^-$) complex on GC electrode and 0.1 M TBABF$_4$ with various scan rates going from 0.0 to -1.8 V/SCE for Cu(L)(Py)(2Cl$^-$) (A) and then, from -0.2 to -1.8 V/SCE for poly-[Cu(L)(Py)(2Cl$^-$)] (B). With Anodic and cathodic potentials (*Epa/Epc*) versus Log*v* and Anodic and cathodic peak currents (*Ipa/Ipc*) versus square root of the scan rate (*v1/2*)

2.5. Atomic force microscopy

The morphological states of FTO and ITO films were investigated by atomic force microscopy (AFM). From the obtained micrographs presented in Fig. 6, it can be noticeably observed that there is an important increase in roughness and film thickness values by increasing the number of voltammetric scans. Accordingly, it becomes clear from the typical 3-D AFM micrograph (See Fig. 6) that the nucleation is produced with different forms and sizes at the electrode surface.

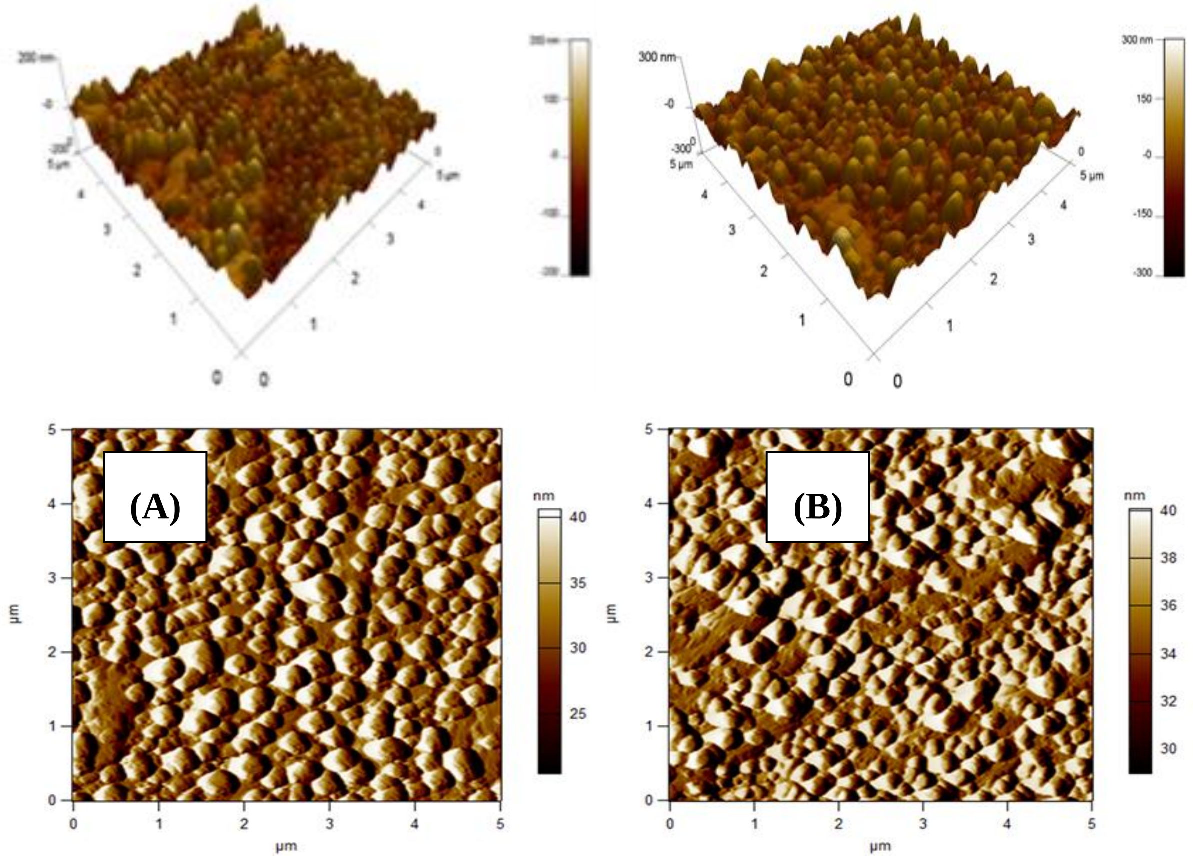


Fig.6. AFM images obtained for the polymerized films from poly-[Cu(L)(Py)(2Cl$^-$)] at: 50 cycles; on ITO (A) and FTO (B) electrodes

2.6. Electroreduction of 1,4-dibromobutane

Cyclic voltammograms of 1,4-dibromobutane on glassy carbon electrode modified with a polymerized copper complex films poly-[Cu(L)(Py)(2Cl$^-$)] recorded at 100 mVs^{-1} for the electroreduction in DMF solutions containing 0.1 M TBABF$_4$ are presented in Fig. 7A. In addition to this, the reduction of 1,4-dibromobutane alkyl halide has also been investigated in the same experimental conditions.

Cyclic voltammogram of poly-[Cu(L)(Py)(2Cl$^-$)] acquired with GC-electrode in DMF solution shows redox system of Cu^{II}/Cu^{I} at −0.807 V/SCE. After addition of 1,4-dibromobutane to this solution, a significant enhancement of (ip_c) peak current accompanied with a total disappearance of (ip_a) and the shifting of the reduction wave potential corresponding to 70 mV as gain of potential. This behavior suggests firstly that all electrocatalytic sites are totally involved in the chemical step and secondly, the gain in potential (ΔE) is also indicative for an electrocatalytic process. Cyclic voltammograms, obtained with glassy carbon electrode modified by a polymerized film of poly-[Cu(L)(Py)(2Cl$^-$)] film with using different concentrations of the alkyl halide as illustrated in Fig. 7. These voltammetric curves confirmed the presence of an important electrocatalytic effect when the modified electrodes are implicated in the heterogeneous catalysis.

Fig. 7B demonstrates that the effect of scan rate towards the electroreduction of 1,4-dibromobutane is very sensible auguring of a high efficiency for the reduction of the tested dibrominated hydrocarbon. The linear dependency of both anodic and cathodic peak currents (*ipa*, *ipc*) with the square root of the scan rate ($v^{1/2}$) and the anodic and cathodic peak potentials (*Epa, Epc)* are proportional to the logarithm of the scan rate (Log *v*) were also presented (See Fig. 7 curves C and D). As has been discussed previously, this behavior was probably attributed to a slow charge transfer process, mainly diffusion-controlled.

Therefore, these cyclovoltammograms were recorded in the presence of 3µM of 1,4-dibromobutane using the poly-[Cu(L)(Py)(2Cl$^-$)] film as modified electrode. It can be clearly seen that there is an increase in the peak currents ip_a and ip_c of the redox system Cu^{II}/Cu^{I} accompanying the increase of the scan rates. This figure showed that the increase of the scan rate induces a shift of 1,4-dibromobutane reduction potentials. These potential values were shifted to the more cathodic potential values suggesting that this electrocatalytic behavior is in good accordance with a slow electrochemical process for an heterogeneous reduction reaction of 1,4-dibromobutane using poly-[Cu(L)(Py)(2Cl$^-$)] films as modified electrode [41].

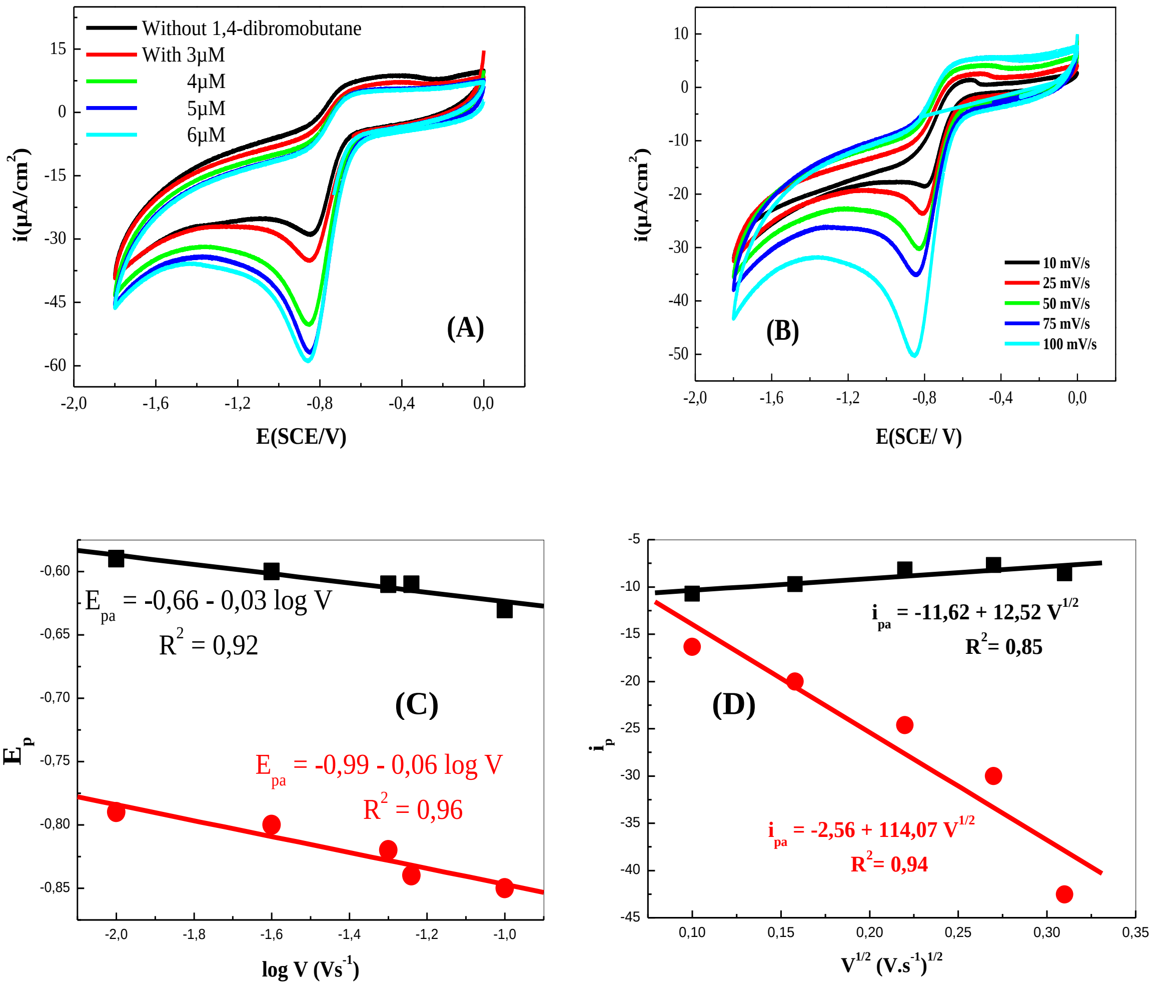


Fig.7. (A) Cyclovoltammograms of poly-[Cu(L)(Py)(2Cl$^-$)] as working electrode and 0.1 M TBABF$_4$ with various scan rates going from 0.0 to -1.8 V/SCE at scan rate 100 mVs^{-1} using different concentrations of 1,4-dibromobutane: 3µM, 4µM, 5µM and 6µM; (B) Cyclic voltammograms of poly-[Cu(L)(Py)(2Cl$^-$)], recorded from 3µM solutions of 1,4-dibromobutane using different scan rates. (C) Anodic and cathodic potentials (*Epa/Epc*) versus Log*v*; (D) Anodic and cathodic peak currents (*Ipa/Ipc*) versus square root of the scan rate (*v1/2*).

3. EXPERIMENTAL

3.1. Physical measurements

All solvents and chemical used in this study were of reagent grade and were purchased from Aldrich and Fluka. These chemicals were also used as received without any further purification. The solvents were dried before use with the appropriate drying reagents according the methods described in the literature. FT-IR spectra were recorded on Perkin and Elmer 1000-FT-IR Spectrometer using KBr disks, while the electronic spectra (UV-Vis) were obtained on a Unicam UV-300 Spectrophotometer for which a path length cell is of 1 cm.

Electrochemical experiments were carried out on a voltalab 40, Potentiostat galvanostat controlled by microcomputer. Thus, the cyclic voltammograms were recorded in DMF solutions containing 0.1 M tetra-n-butylammonium tetrafluoroborate ($TBABF_4$) and 0.001 M of copper complex. The working electrode was either a disc of glassy carbon (diam. 3 mm) or semi-transparent electrodes of indium tin oxide (ITO) and fluorine tin oxide (FTO). As for the counter electrode, it was always a platinum wire. All potentials are systematically referenced to the saturated solutions of calomel electrode (SCE).

The X-ray photoelectron spectroscopy (XPS) measurements were carried out in a MULTILAB 2000 (THERMO VG) spectrometer, equipped with an Al Ka X-ray source (1486.6 eV). Survey and high resolution spectra were recorded in constant pass energy mode 100 and 20 eV, respectively. The CASAXPS program with a Gaussian–Lorentzian mix function and Shirley's background subtraction was employed to deconvolute the XP spectra. The C1s peak at 284.6 eV was used to correct charging effects.

Thermal analysis (TG and DTG) were obtained in a nitrogen atmosphere using a TGA Perkin Elmer thermal analyzer. The heating rate was set at 10 °C min^{-1} and the weight loss was measured from ambient temperature up to 1000 °C.

3.2. Synthesis of copper complex Cu(L)(Py)($2Cl^-$)

Synthesis of copper (II) complex was carried out via template method according the literature [26] as obviously shown in Scheme 1. So, this complex was obtained by mixing stochiometric quantities of 2-hydroxynaphtaldehyde 0.172 g (1 mmol) with 0.060 g (1 mmol) of 1,2-diaminoethane in methanolic solution (10 ml). To this mixture, was added an excess of pyridine (2 mmol, 158 mg) and then copper chloride dihydrated 0.206 g (1 mmol) were similarly dissolved in the same solvent (6 ml). After two hours of reaction, a blue precipitate was formed and then recovered by filtration. The solid obtained was purified by successive cleaning steeps using cooled methanol, diethyl ether to leach all traces of amine and finally dried over $CaCl_2$ giving 65% of yield. Anal. Calc. for $[Cu(L)(Py)(2Cl^-)](CH_3CN)(5H_2O)$: C: 43.05; H: 5.60; N: 10.04. Found: C: 43.00; H: 5.09; N: 10.70%.

4. CONCLUSION

In this work, it can be concluded that a new non symmetrical copper (II) Schiff base complex was synthesized and characterized using routine spectroscopic methods. This compound is obtained from a tridentate Schiff base and pyridine as mixed ligands with an acceptable yield. Its coordination process was effectively evidenced by FT-IR, UV-Vis spectrophotometry techniques and cyclic voltammetry. The cyclic voltammograms of this copper complex demonstrate the presence of two redox couples as Cu^{III}/Cu^{II} and Cu^{II}/Cu^{I}.

It was also shown that it is possible to elaborate the poly-$[Cu(L)(Py)(2Cl^-)]$ films by electropolymerization technique on various working electrode surfaces such as glassy carbon, indium thin oxide (ITO) and fluorine-doped tin oxide (FTO). These new materials of electrode were characterized by cyclic voltammetry while the morphological states of these electrodeposited films were explored by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The modified electrode of glassy carbon (GC) obtained was tested towards the electrocatalytic activity in the reduction of dihalogenoalkanes like 1,4-dibromobutane. This electrocatalytical reduction was found to be very efficient towards the dibromohydrocarbons.

5. REFERENCES

[1] Drago R.S. and Balkus Jr K.J. Cobalt (II)-facilitated transport of dioxygen in a polystyrene membrane. Inorg. Chem. 1986, 25, pp 716-718.

[2] Adhikari A., Radhakrishnan S. and Patil R. Influence of dopant ions on properties of conducting polypyrrole and its electrocatalytic activity towards methanol oxidation. Synth. Met. 2009, 159, pp 1682-1688.

[3] Bedioui F., Devynck J., Bied-Charreton C. Electropolymerized manganese porphyrin films as catalytic electrode materials for biomimetic oxidations with molecular oxygen. J. Mol. Catal. A-Chem. 1996,113, pp 3-11.

[4] Ourari A., Ketfi B., Zerroual L. Elaboration of modified poly(NiII-DHS) films as electrodes by the electropolymerization of Ni(II)-[5,5′-dihydroxysalen] onto indium tin oxide surface and study of their electrocatalytic behavior toward aliphatic alcohols. Arab. J. Chem., 2017, 10, pp 914-921.

[5] Saraviaa L.P.H., Anandhakumara S., Parussuloa A.L.A., Matias T.A., Caldeira da Silva C.C., Kowaltowski A.J., Araki K., Bertotti M. Development of a tetraphenylporphyrin cobalt(II) modified glassy carbon electrode to monitor oxygen consumption in biological samples. J. Electroanal. Chem. 2016, 775, pp 72-76.

[6] Palmer M.H., Christen D. An ab initio study of the structure, tautomerism and molecular properties of the C- and N-amino-1,2,4-triazoles. J. Mol. Struct. 2004, 705, pp 177-187.

[7] Bagihalli G.B., Avaji P.G., Patil, Badami P.S. Synthesis, spectral characterization, in vitro antibacterial, antifungal and cytotoxic activities of Co(II), Ni(II) and Cu(II) complexes with 1,2,4-triazole Schiff bases. Eur. J. Med. Chem. 2008, 43, pp 2639-49.

[8] Emam S.M., El Sayed I.E.T., Ayad M.I., Hathout H.M. Synthesis, characterization and anticancer activity of new Schiff bases bearing neocryptolepine. J. Mol. Struc. 2017, 1146, pp 600-619.

[9] Ariyaeifar M., Rudbari H.A., Sahihi M., Kazemi Z., Kajani A.A., Zali-Boeini H., Kordestani N., Bruno G., Gharaghani S. Chiral halogenated Schiff base compounds: green synthesis, anticancer activity and DNA-binding study. J. Mol. Struc. 2018, 1161, pp 497-511.

[10] Zhao F., Wang W., Lu W., Xu L., Yang S., Cai X-M., Zhou M., Lei M., Ma M., Xu H-J., Cao F., High anticancer potency on tumor cells of dehydroabietylamine Schiff-base derivatives and a copper(II) complex. Eur. J. Med. Chem. 2018, 146, pp 451-459.

[11] Amer S., El-Wakiel N., El-Ghamry H. Synthesis, spectral, antitumor and antimicrobial studies on Cu(II) complexes of purine and triazole Schiff base derivatives. J. Mol. Struc. 2013, 1049, pp 326-335.

[12] Gabr M.T., El-Gohary N.S., El-Bendary E.R., El-Kerdawy M.M., Ni N. Synthesis, in vitro antitumor activity and molecular modeling studies of a new series of benzothiazole Schiff bases. Chin. Chem. Lett. 2016, 27, pp 380-386.

[13] Hu G.Q., Wu X.K., Wang G.Q., Duan N.N., Wen X.Y., Huang W.L. Synthesis and

antitumor and antibacterial evaluation of fluoro-quinolone derivatives (III): Mono- and bis-Schiff-bases. Chin. Chem. Lett. 2012, 23, pp 515-517.

[14] Ibrahim M.Y., Mohd Hashim N., Mariod A.A., Mohan S., Abdulla M.A., Abdelwahab S.I., Arbab I.A. “α-mangostin from Garcinia mangostana Linn: An updated review of its pharmaceutical properties. Arab. J. Chem. 2016, 9, pp 317-329.

[15] Olie G.H., Olive S. “The Chemistry of the Catalyzes Hydrogenation of Carbon Monoxide”. Springer, Berlin, 1984.

[16] Ourari A., Aggoun D. Synthesis and spectral analysis of N‑substituted pyrrole salicylaldehyde derivatives‑electropolymerization of a new nickel(II)‑Schiff base complex derived from 6‑[3′‑N‑pyrrolpropoxy]‑2‑hydroxyacetophenone and 1,2‑diaminoethane. J. Iran. Chem. Soc. 2015, 12, pp 1893-1904.

[17] Margerum J.D., Mller L.J. “Photochromism”. Wiley Interscience, New York,1971, pp 569.

[18] Guyon A.L., Klein L.J., Goken D.M., Peters D.G. Catalytic Reduction of 1-Bromooctane by Nickel(I) SalenElectrogenerated at a Mercury Cathode in Dimethylformamide. J. Electroanal. Chem. 2002, 526, pp 134-138.

[19] Golikand A.N., Raoof J., Baghayeri M., Asgari M., and Irannejad L. Nickel Electrode Modified by N,Nbis (Salicylidene)Phenylenediamine (Salophen) as a Catalyst for Methanol Oxidation in Alkaline Medium. Russ. J. Electrochem. 2009, 45, pp 192-198.

[20] Aslantas M., Kendi E., Demir N., Sabik A.E., Tumer M. and Kertmen M. Synthesis, spectroscopic, structural characterization, electrochemical and antimicrobial activity studies of the Schiff base ligand and its transition metal complexes. Spectrochim. Acta, Part A 2009, 74, pp 617-624.

[21] Brégeault J-M. Transition-metal complexes for liquid-phase catalytic oxidation: some aspects of industrial reactions and of emerging technologies. Dalton Trans. 2003, 0, pp 3289-3302.

[22] Ourari A., Derafa W. and Aggoun D. A novel copper (II) complex with an unsymmetrical tridentate-Schiff base: synthesis, crystal structure, electrochemical, morphological and electrocatalytic behaviors toward electroreduction of alkyl and aryl halides. RSC Adv. 2015, 5,

pp 82894-82905.

[23] Pfeiffer P., Breith E., Lübbe E., and Tsumaki T. Tricyclische orthokondensierte Nebenvalenzringe. Justus Liebigs Ann. Chem. 1933, 503, pp 84-130.

[24] (A) Mubarak M.S., Peters D.G. Addition to Activated Olefins of Radicals Formed from Reaction ofAlkyl Halides with Electrogenerated Nickel(I) Salen. J. Saudi Chem. Soc. 1999, 3, pp 135-146; (B) Semones M.A., Peters D.G. Production of Ethylene Oxide via Catalytic Reduction of 2-Bromo-and 2-Iodoethanol by Cobalt(I) Cyclam and Nickel(I) Cyclam Electrogenerated at Carbon Cathodes. J. Electrochem. Soc. 2000, 147, pp 260-265; (C) Fang D.M., Peters D.G., Mubarak M.S. Catalytic Reduction of 6-Bromo-1-hexene by Nickel(I)SalenElectrogenerated at Glassy Carbon Cathodes in Acetonitrile. J. Electrochem. Soc. 2001, 148, pp E464-E467; (D) Sweeny B.K., Peters D.G. Cyclic Voltammetric Study of the Catalytic Behavior of Nickel(I)SalenElectrogenerated at a Glassy Carbon Electrode in an Ionic Liquid (1-Butyl-3-methylimidazo-lium Tetrafluoroborate, $BMIM^+BF_4^-$). Electrochem. Commun. 2001, 3, pp 712-715.

[25] Grimshaw J. Electrochemical Reactions and Mechanisms in Organic Chemistry. Elsevier, 2000.

[26] Costes J.P. Bulletin de la Société Chimique de France 1986, 1, pp 78.

[27] Nakamoto K. Infrared and Raman Spectra of Inorganic and Coordination Compounds. John Wiley & Sons, Inc., New Jersey, 6th edn, 2009.

[28] (A) Nakamoto K. Infrared and raman spectra of inorganic and coordination compounds, part B: applications in coordination, organometallic, and bioinorganic chemistry. Wiley, New York, 1997; (B) Montazerozohori M., Khani S., Tavakol H., Hojjati A., Kazemi M. Synthesis, spectroscopic and thermal studies of some IIB group complexes with a new N_2-Schiff base ligand. Spectrochim. Acta, Part A 2011, 81, pp 122-127.

[29] Samanta B., Chakraborty J., Choudhury C.R., Dey S.K., Dey D.K., Batten S.R., Jensen P., Yap G.P.A. and Mitra S. New Cu(II) complexes with polydentate chelating Schiff base ligands: synthesis, structures, characterizations and biochemical activity studies. Struct. Chem. 2007, 18, pp 33-41.

[30] Lu X.-H., Xia Q.-H., Zhan H.J., Yuan H.X., Ye C.P., Su K.X. and Xu G. Synthesis,

characterization and catalytic property of tetradentate Schiff-base complexes for the epoxidation of styrene. J. Mol. Catal. A: Chem. 2006, 250, pp 62-69.

[31] Bouzerafa B., Ourari A., Aggoun D., Ruiz-Rosas R., Ouennoughi Y., Morallon E. Novel nickel(II) and manganese(III) complexes with bidentate Schiff-base ligand: synthesis, spectral, thermogravimetry, electrochemical and electrocatalytical properties. Res. Chem. Intermed. 2016, 42, pp 4839-4858.

[32] Ourari A., Aggoun D., Ouahab L. A novel copper(II)-Schiff base complex containing pyrrole ring: Synthesis, characterization and its modified electrodes applied in oxidation of aliphatic alcohols. Inorg. Chem. Commun. 2013, 33, pp 118-124.

[33] Bouzerafa B., Aggoun D., Ouennoughi Y., Ourari A., Ruiz-Rosas R., Morallon E., Mubarak M.S. Synthesis, spectral characterization and study of thermal behavior kinetics by thermogravimetric analysis of metal complexes derived from salicylaldehyde and alkylamine. J. Mol. Struct. 2017, 1142, pp 48-57.

[34] Ji R., Yu K., Lou L-L., Zhang C., Han Y., Pan S., Liu S. Chiral Mn(III) salen complexes immobilized directly on pyrolytic waste tire char for asymmetric epoxidation of unfunctionalized olefins. Inorg. Chem. Commun. 2012, 25, pp 65-69.

[35] Tourabi M., Nohair K., Traisnel M., Jama C. and Bentiss F. Electrochemical and XPS studies of the corrosion inhibition of carbon steel in hydrochloric acid pickling solutions by 3, 5-bis (2- thienylmethyl)-4-amino-1, 2, 4-triazole. Corrosion Science 2013,75, pp 123-133.

[36] Li P., Lin J.Y., Tan K.L. and Lee J.Y. Electrochemical impedance and X-ray photoelectron spectroscopic studies of the inhibition of mild steel corrosion in acids by cyclohexylamine. Electrochim. Acta 1997, 42, pp 605-615.

[37] Ourari A., Zoubeidi C., Derafa W., Bouacida S., Merazig H., Morallon E. A novel Nickel (II) complex obtained from 2-[(3-Bromo-propylimino)-methyl]-phenol as ligand: Synthesis, structural characterization, electrochemical and electrocatalytical investigations. Res. Chem. Intermed., 2016. doi: 10.1007/s11164-016-2817.

[38] Kianfar A.H., Ramazani S., Hashemi Fath R. and Roushani M. Synthesis, spectroscopy, electrochemistry and thermogravimetry of copper(II) tridentate Schiff base complexes, theoretical study of the structures ofcompounds and kinetic study of the tautomerism reactions

by ab initio calculations. Spectrochim. Acta, Part A 2013, 105, pp 374-382.

[39] Bhattacharya D., Samide M.J. and Peters D.G. Catalytic reduction of cyclohexane-carbonyl chloride withelectrogenerated nickel(I) salen in acetonitrile. J. Electroanal. Chem. 1998, 441, pp 103-107.

[40] Lundquist Jr J.T. and Nicholson R.S. Theory of the potential step-linear scan electrolysis method with a comparison of rate constants determined electrochemically and by classical methods. J. Electroanal. Chem. 1968, 16, pp 445-456.

[41] Raess P.W., Mubarak M.S., Ischay M.A., Foley M.P., Jennermann T.B., Raghavachari K. and Peters D.G. Catalytic reduction of 1-iodooctane by nickel(I) salen electrogenerated at carbon cathodes in dimethylformamide: effects of added proton donors and a mechanism involving both metal- and ligand-centered one electron reduction of nickel(II) salen. J. Electroanal. Chem. 2007, 603, pp 124-134.

How to cite this article:
Bounab N, Ourari A, Derafa W, Aggoun D. Synthesis, electrochemical and heterogeneous electrocatalytic behaviors of a novel non symmetrical copper(ii) complex. J. Fundam. Appl. Sci., 2019, *11(1), 492-512.*