



Synthesis, characterization and electrochemical behavior of new transition metal complexes derivatives of 4-hydroxy-6-methyl-3-[(2E)-3-(4-(dimethylamino) phenyl) prop-2-enoyl]-2H-pyran-2-one

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Abstract

The reaction of Ni (II) acetate, Co (II) chloride and copper (II) nitrate with 4-hydroxy-6-methyl-3-[(2E)-3-(4-(dimethylamino) phenyl)prop-2-enoyl]-2H-pyran-2-one leads to the synthesis of new complexes Ni(HL)₂, Cu(HL)₂(H₂O) and Co(HL)₂(NH₃)₄. The molecular structures of the synthesized compounds were elucidated by various physicochemical properties such as the UV-Vis, FT-IR, and elemental analysis. Electrochemical behavior of the complexes of (Cu, Ni) has been investigated by cyclic voltammetry on glassy carbon electrode in DMF at 100 mV/s scan rate. This study indicate that the reduction process corresponding to Cu^{II}/Cu^I is electrochemically quasi-reversible in complex of copper, and irreversible reduction process for Ni^{II}/Ni^I.

1. Introduction

Chalcones are promising compounds in drug preparation because of their broad spectrum of antitumor, antibacterial and anti-inflammatory activities [1]. Chalcones are the immediate precursors in the biosynthesis of flavonoids, and their structure differs considerably from the others members of the flavonoid family, since chalcones are open-chain analogs in contrast to the other family's members. Chalcones are abundantly present in nature starting from ferns to higher plants [2], and they are usually synthesized via the Claisen-Schmidt condensation, using base in a polar solvent [3].

Chalcones possess conjugated double bonds and a completely delocalized π -electron system on both benzene rings. Molecules possessing such system have relatively low redox potentials and have a greater probability of undergoing electron transfer reactions [4].

Therefore, synthesis and characterization of such unsaturated carbonyl systems and their metal complexes have tremendous importance. It is well known that dehydroacetic acid and its derivatives like chalcones have a strong ability to form metal complexes that play a prominent role in modern coordination chemistry. These compounds possessing novel structure features, interesting spectral and magnetic properties have been the subject of intensive research due to their importance in biological [5], analytical agriculture [6], antimalarial [7], and anticancer properties [8].

Recently, we are particularly interested to the synthesis of α,β -unsaturated compounds derived from DHA and 4-(N,Ndimethyl amino) benzaldehyde [9]. As a continuation of our work, we report herein the synthesis and characterization of new nickel(II), copper(II) and cobalt(II) metal complexes according to the procedure described in the literature [10]

The electrochemical techniques are so advanced in the field of analysis of drugs is due to their simplicity, low cost and relatively short analysis time when compared to the other techniques. The use of carbon based

electrodes, especially glassy carbon electrode, for electro-analytical measurements has increased in recent years because of their applicability to the determination of substances that undergo redox reactions, a matter of great importance in the field of clinical and pharmaceutical analysis. Redox properties of drugs can give insights into its metabolic fate or their in vivo redox processes or pharmaceutical activity [11-12].

2. Material and Methods

2.1. Physical measurements

All chemicals used were procured from the Sigma-Aldrich and E-Merck chemical companies. The solvents were dried before use with the appropriate drying reagents. The FT-IR spectra ($4000\text{--}400\text{ cm}^{-1}$) of all products were recorded as KBr disks using FT-IR-4000 (Shimadzu) spectrophotometer. While the electronic spectra of the ligand and its metal complexes were measured on a UV PROB SCHIMADZU 1700 spectrophotometer in the range of 200–800 nm. Elemental analysis was carried out by Std.meth.0803-CHNS method. Melting points of synthesized product are determined by Manual instructions Fusion Point M-560 (BUCHI) apparatus. The purity of the compounds was checked by TLC on pre-coated SiO_2 gel (HF254, 200 mesh) aluminum plates (E Merck) and visualized in UV chamber.

2.2. Electrochemical measurements

The electrochemical properties of the monometallic complex were investigated. A solution containing 0.1M of Tetrabutylammonium hexafluorophosphate (TBAP) was used as a supporting electrolyte on a glassy carbon (GC) and platinum (Pt) working electrodes (WE) in DMF at room temperature. A scan rate of 100 mV s^{-1} was fixed for all the voltammograms. All solutions were deoxygenated by passing a stream of pre-purified N_2 into the solution for at least 10 min prior to recording the voltammograms.

2.3. Synthesis of the metal complexes

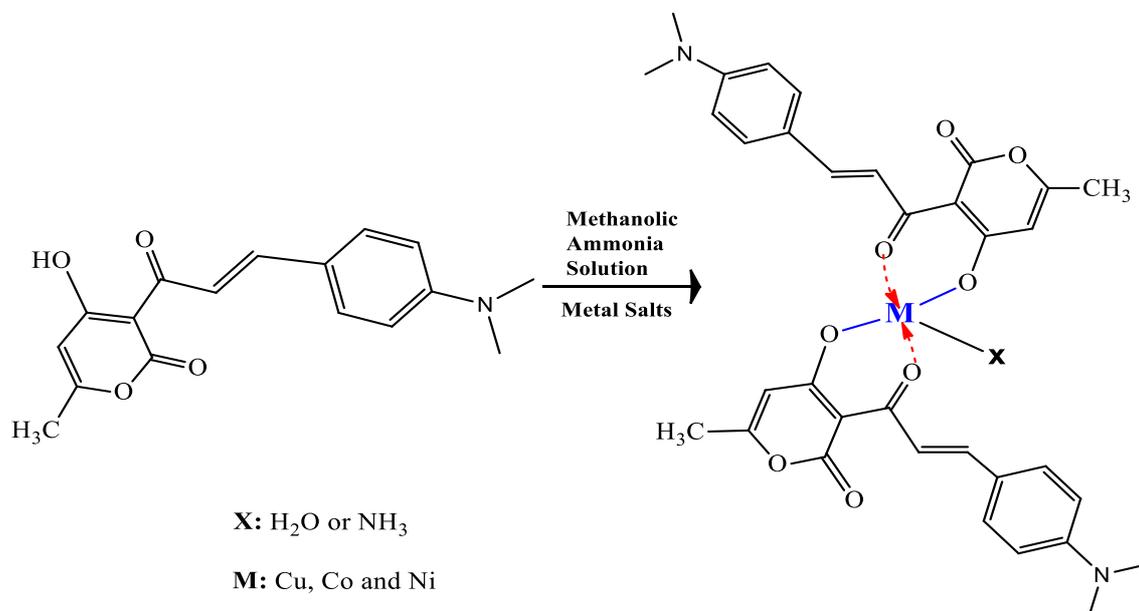
A series of divalent transition metal complexes of chalcone derivatives were synthesized according to the following general procedure. An methanolic solution (15ml) of the metal salt $\text{C}_4\text{H}_6\text{O}_4\text{Ni}\cdot 4\text{H}_2\text{O}$ (0.0621g; 2.5 mmol), $\text{Cu}(\text{NO}_3)_2\cdot 2.5\text{ H}_2\text{O}$ (0.0621g; 2.5 mmol) or $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (0.05946g; 2.5 mmol) was added gradually in small amounts to a chloroform solution of ligand HL (5mmol). The pH of the solution was maintained between 7 and 8 by adding alcoholic ammonia solution. The reaction mixture was refluxed for about 2-3 h and then cooled to room temperature. The metal complex separated out was filtered off washed successively with ethanol, ether. The purity of synthesized compounds was confirmed by TLC and elemental analysis. C, N and H analysis were carried out micro analytically. The complexes were obtained as solids in different yields. They are insoluble in acetone, ethanol and chloroform, but their considerable solubility has been noticed in acetonitrile, DMF and DMSO. The structures of the synthesized compounds were confirmed by analytical and spectral data (IR, ESR UV-Vis).

3. Results and discussion

Analytical data indicated that the condensation of dehydroacetic acid and *p*-N,N-dimethyl amino benzaldehyde occurred in 1:1 ratio to form the 4-hydroxy-6-methyl-3-[(2*E*)-3-(4-(dimethylamino) phenyl)prop-2-enoyl]-2*H*-pyran-2-one. The characterization of the ligand was published [9]. All the complexes are analytically pure, stable in air at room temperature for longer time and possess good keeping qualities. They are non hygroscopic solids. The ligand and its complexes are soluble in common organic solvents. The different properties of synthesized complexes are summarized in the (Table .1). The elemental analyses are good agreement with expected stoichiometry of complexes which indicate that the metal to ligand ratio in all complexes is 1:2. (Scheme.1)

3.1. UV-Vis Spectrum

The UV-Vis spectra were registered in methanol and the field between 200 and 800 nm. At a concentration of 10^{-5} M of solution of synthesized complexes present bands between ($\lambda=300$ and $\lambda=320$) nm assigned with the transitions $\pi\text{-}\pi^*$ of the grouping (-CH=CH-), of another bands located between $\lambda=320$ nm and $\lambda=395$ nm due to the transitions $n\text{-}\pi^*$ of ($>\text{C}=\text{O}$) [13]. The transitions which appear with $\lambda>400$ nm are probably assigned to the transfer of charge ligand-metal (TCLM) [14]. After complexation, light modifications in of the curves spectra of the complexes were noted. We note changes in the pace of the spectrum of the complexes of copper towards the big wavelengths that involve a bathochromic effect allotted to an interaction of transfer of intermolecular charge Transitions [15]. LMCT might not be detected in the most of the complexes probably for two reasons is their weak coefficients of molar extinction or the width of their bands. The table .2 summarizes the found results.



Scheme. 1: reaction of synthesis complexes

Table 1: The synthesized complexes properties.

	Color	Empirical formula	yield (%)	R _f	Elemental analysis ^(b)				m.p ^(a) (°C)
					C	H	N	O	
HL (H₂O)	bordeau	C ₁₇ H ₁₇ O ₄ N	80	0.8	68.65 (68.22)	5.76 (5.98)	20.59 (21.40)	4.72 (4.68)	222
Cu. (HL)₂ (H₂O)	red	C ₃₄ H ₃₂ N ₂ Cu O ₈	66	0.46	61.71 (61.86)	5.71 (4.89)	3.79 (4.24)	18.71 (19.39)	236
Ni.(HL)₂	Orange	C ₃₄ H ₃₂ NiN ₂ O ₈	50	0.35	62 (62.32)	4.7 (4.9)	4.0 (4.27)	19.80 (19.53)	260
Co.(HL)₂ (NH₃)₄	Orange	C ₃₄ H ₃₂ CoN ₂ O ₈ . 4NH ₃	45	0.85	56.50 (56.43)	7.03 (6.13)	11.56 (11.61)	14.31 (17.69)	270

(a): decomposition, (b): calculated

3.2. Infrared spectroscopy

The absorption IR spectra of the ligand and their complexes of Cu(II), Co(II) and Ni(II) were registered in the field 400- 4000 cm⁻¹ (table.3).

Table. 2: Absorption bands relating to the ligand HL and their complexes.

Compounds	λ _{max} (nm)	(10 ² ε, M ⁻¹ cm ⁻¹)
Ligand HL	332	22.8
	417	76.2
Cu (HL)₂	329	14.1
	409	33.1
	488	10.1
Co (HL)₂	308	10
	364	77
	446	64.8
Ni (HL)₂	329	28.1
	415	124.7
	510	1.2

Table. 3: values of the absorption bands in cm^{-1} of the IR spectrum of the complexes of HL

	ν (cm^{-1})						
	(OH)	(C=O) lactone	(C-H)	(C=O-C=C) α , β unsaturated	(C=C)	(C=O) coord.	(M-O)
HL	3400	1690	2986	1650	1570	-	-
Cu (HL)₂	3400	1695	2997	1635	1608	1278	758 631
Co (HL)₂	3296	1694	2931	1630	1604	1375	776 545
Ni (HL)₂	3250	1695	2950	1620	1600	1255	590 550

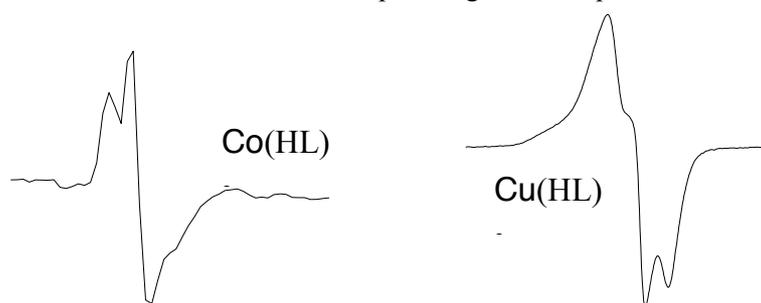
The analysis by infrared spectroscopy of the ligand and its complexes we allows to withdraw the various significant absorption bands related to groups implied in the formation of the complexes like the alcohol function (OH), the aromatic (C = C) and olefinic (C = C) , lactone (C = O) and (C = O) of the acetyl grouping. After a comparative study of the results obtained between the ligand and its complexes, it appears clearly that the absorption bands which correspond to the vibration $\nu(\text{C}=\text{O})$ underwent a displacement towards lowest number of waves which implies the participation of the free doublet of the oxygen of the acetyl grouping in coordination in metal. This displacement was 20 cm^{-1} for the complexes of HL. The appearance of a new band in the interval $1250\text{-}1275 \text{ cm}^{-1}$ characteristic of bond (C=O) coordination we affirm the preceding estimate [16]. The coordination of the metal ions with the donor sites of the ligands is confirmed by the appearance of the absorption bands $545\text{-}785 \text{ cm}^{-1}$ allotted to the frequency of the bond (M-O). The appearance of the absorption bands of the hydroxyl groupings in the all spectra of infrared.

The latter that appear in the interval $3200\text{-}3400 \text{ cm}^{-1}$ in the spectra of the complexes are due to the presence of the hydrogen bonds of water and ammonia related to the structure of complexes [17-18]

3.3. ESR Spectroscopy:

In the (figure.1) we give typical spectra of the ESR signal of the complexes of the ligand irradiated to 25 KGy. They correspond to derive from resonant absorption for the magnetic field. The (Figure.1) shows the ESR spectrum of the both complexes of Cu (II) and Co (II) of the HL.

The spectrum show the presence of paramagnetic species, which differ appreciably according to the cation, implemented. The complex of Cu(II) of the ligand HL is paramagnetic with three peaks as appears in scheme III.1 which present broad lines ($\Delta H_{pp} = 1.900 \cdot 10^5$, $2.3200 \cdot 10^5$ and $2.0300 \cdot 10^5 \text{ G}$) and asymmetric which the values of g ($g = 2.2403$, 2.0280 and 1.926) are relatively close to that of the free electron ($g = 2,0023$). The complex of CoHL is paramagnetic too (Figure.1) having three centers which peak $g_1 = 1.9970$ and ($\Delta H_{pp} = 15.1560 \cdot 10^3 \text{ G}$). The electronic paramagnetic resonance spectrum reveal that the complexes that have peaks whose values g close with that to the free electron are paramagnetic compounds.

**Figure.1.** ESR spectrum of copper and cobalt complexes at 110K.

3.4. Study of the electrochemical behavior of the complexes

The cyclic voltammetry is the most largely technique used to acquire qualitative information on the electrochemical reactions. It profits from a fast site of the potentials redox of the active species. In this work, we studied the electrochemical properties of two α,β -unsaturated ligand and their complexes of nickel, coppers by calling upon the cyclic voltamperometry. This study was carried out in an organic medium DMF, in the presence of the electrolyte support (TBAP) 0.1M on an work electrode of vitreous carbon (CV, $\phi = 3 \text{ mm}$), the reference electrode are with calomel saturated (ECS) and electrode counters it's a platinum wire (Pt).

3.4.1. Electrochemical behavior of ligand HL

The voltammograms of ligand HL (Figure.2) are registered on a tension field going of -2000 and +1600 mV/ECS for HL at a scanning rate $v=100$ mV/s. The ligand HL presents also two waves of oxidations at 562 mV/ECS probably allotted to the oxidation of the chalcone group and the second wave to +1077 mV/ECS, which is allotted to the oxidation of the hydroxyl function. The cathodic wave that might be allotted to the reduction of the chalcone function [19] locates towards -864 mV/ECS.

3.4.2. Electrochemical behavior of the complexes

After the study of the electrochemical behavior of both ligands in a completely organic medium (DMF-TBAP) 0.1M, we proceeded to the study of the electrochemical behavior of our complexes $\text{Ni}(\text{HL})_2$, $\text{Cu}(\text{HL})_2$ and this under the same conditions. The (Figure.3) given here after represents the voltamperogram of the nickel complexe registered between -2000 and +1600 mV/ECS for $\text{Ni}(\text{HL})_2$ at a scanning rate $V=100$ mV/s. In the case of $\text{Ni}(\text{HL})_2$, we observe during going scan two localized nonreversible peaks of oxidation in $E_{pa1} = +740$ mV and $E_{pa2} = +980$ mV.

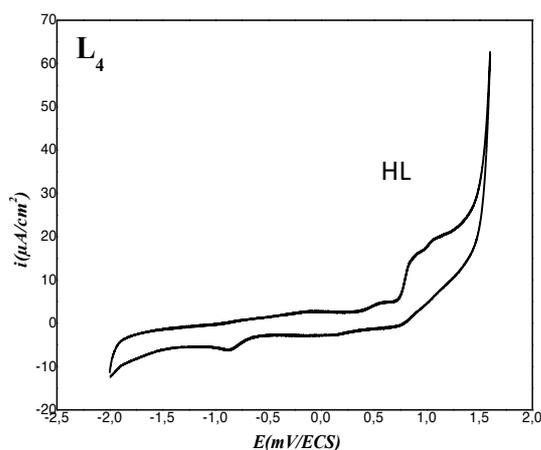


Figure.2. Voltamperograms of the ligand HL registered between -2000 and 1600 mV/ECS in DMF-TBAP 0.1M, $v=100$ mV/s

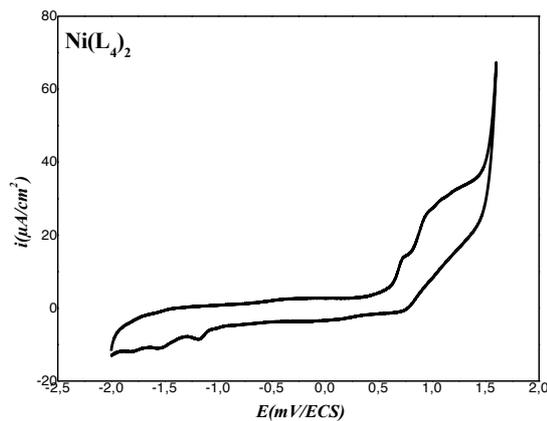


Figure.3. Voltamperograms of the complex registered in DMF-TBAP 0.1M, $v=100$ mV/s

These waves irreversible are allotted respectively to the oxidation of Ni(III)/Ni(II) [20] and the oxidation of the ligand. On the other hand with return scan, we note only one wave of irreversible cathodic reduction also that it we observe in $E_{pc1} = -1190$ mV which probably allotted to the reduction of the species Ni(II) in Ni(I). The (Figure.4) presents the evolution of the currents of the system peaks Ni(II)/Ni(I) for the both nickel complexes according to the scanning rate.

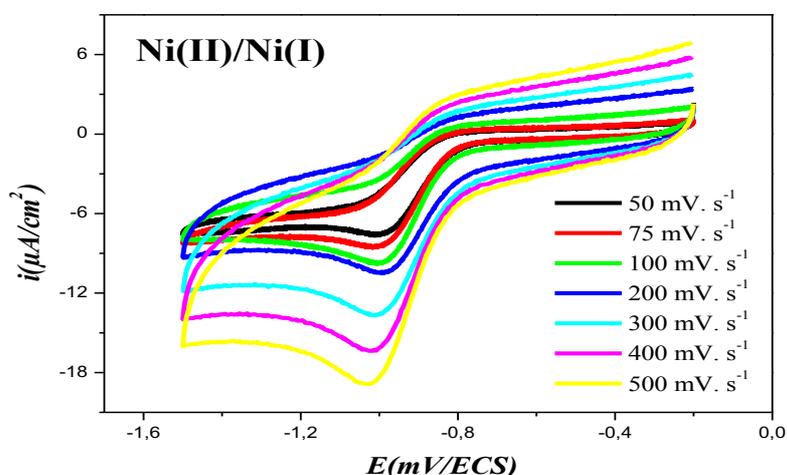


Figure 4. Evolution of the currents of the complex peaks $\text{Ni}(\text{HL})_2$ according to the scanning rate for the system Ni(II)/Ni(I)

It also shows an increase in the intensity of the peaks as the scanning rate increases. The values of the electrochemical parameters characteristic of the voltamogram corresponding to oxidation and reduction of the couple Ni(II)/Ni(I) [21] which were registered according to the scanning rate in the field of going potential between -200 to -1500 mV/ECS for Ni(HL)₂ are gathered in table.4. The voltamperogrammes of the copper complex given below were registered between -1600 and +1200 mV/ECS for Cu(HL)₂ at a scanning rate of 100 mV/s. The voltamogram of Cu(HL)₂ represented in the (Figure 5) shows three waves of oxidation. First is located at Epa1= -810 mV/ECS which characterizes the reoxydation of Cu(I) in Cu(II), Epa2= 485 mV/ECS shows the oxidation of the Cu(II) ions in Cu(III) and Epa3= 890 mV/ECS was allotted to oxidation ligand. With regard to return scan, we note the presence of peak of reduction located at Epc= -1060 mV/ECS. It may be allotted then to the reduction of the species Cu (II) in Cu(I) [22].

Table .4: Principal sizes controlled by the system Ni(II)/Ni(I).

v(mV/s)	v ^{1/2} (mV/s) ^{1/2}	log(v)	-Ipc(mA)	-Epc (V/ECS)
50	7.07	1.69	7.55	1008
75	8.66	1.87	8.57	1006
100	10	2	9.73	1004
200	14.14	2.30	11.64	1008
300	17.32	2.47	13.72	1015
400	20	2.60	16.32	1020
500	22.36	2.69	19.28	1026

The Figure 6 and the table 5 represents the voltamograms corresponding to oxidation and the reduction of the couple Cu(II)/Cu(I) which was registered between -400 and -1500mV/ECS for the complex Cu(HL)₂ (B) at various scanning rates.

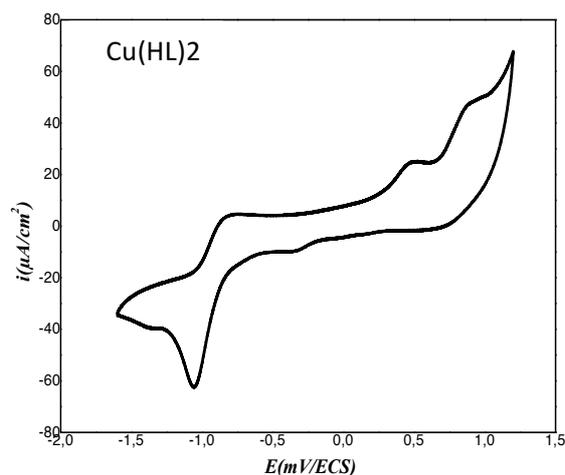


Figure.5. Voltammograms cyclic of the both copper complexes (10⁻³ M) registered on a vitreous carbon electrode (φ=3mm) in DMF solution containing 0,1 M TBAP at a scanning rate of 100 mV/s.

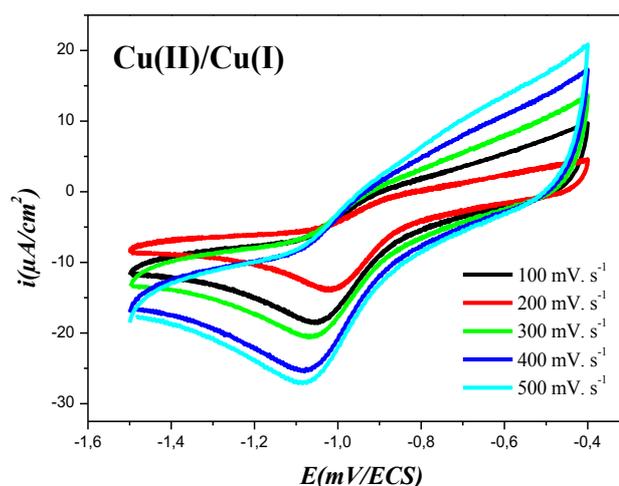


Figure 6. Evolution of the currents of the complex peaks of Cu(HL)₂ according to the scanning rate for the system Cu(II)/Cu(I)

Table .5: Principal sizes controlled by the system Cu(II)/Cu(I).

v(mV/s)	v ^{1/2} (mV/s) ^{1/2}	log(v)	-Ipc(mA)	-Epc (V/ECS)
100	10	2	14.22	1017
200	14.14	2.30	18.51	1051
300	17.32	2.47	20.90	1068
400	20	2.60	25.38	1080
500	22.36	2.69	27.21	1086

Conclusion

In summary, we have successfully synthesized and characterized a new series of metallic complexes (copper, cobalt and Nickel). The results from FT-IR, UV-Vis and elemental analysis are in good agreement with the molecular structure. HL and their metal complexes have also been characterized by an electrochemical technique which is cyclic voltammetry in an organic medium (DMF). The graphical representation of the different cyclic Voltammograms of the different redox couples of the different systems mentioned in this study represents oxidation peaks and reduction for each pair.

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