

## Synthesis, Characterization, Electrochemical and Electrocatalytic Study of New Tetradentate Nickel(II)-Schiff Base Complex Derived from 1,2-Diaminoethane and 5-(N,N-Methylphenylaminomethyl)-2-Hydroxyacetophenone

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### Abstract

The tetradentate Schiff base ligand **1c** was synthesized through the reaction of 5-(N,N-methylphenylaminomethyl)-2-hydroxyacetophenone (**1b**) with stoichiometric amount of 1,2-diaminoethane in absolute ethanol. Compound **1b** was prepared by reacting 5-chloromethyl-2-hydroxyacetophenone (**1a**) with N-methylaniline, in presence of sodium hydrogenocarbonate (NaHCO<sub>3</sub>) in tetrahydrofuran. Compound **1a**, on the other hand, was synthesized through a reaction between a mixture of hydrochloric acid and formaldehyde with 2-hydroxyacetophenone. Heating a mixture of the Schiff base **1c** and a stoichiometric amount of tetrahydrated nickel acetate in absolute ethanol at 50 °C under nitrogen atmosphere afforded the expected tetradentate Ni(II)-Schiff base complex **1d**. The synthesized compounds **1a-1d** were characterized by different spectroscopic methods such as FT-IR, UV-Vis, <sup>1</sup>H, <sup>13</sup>C NMR, and mass spectrometry. Cyclic voltammetry was employed to investigate the redox behavior of compounds **1c** and **1d**. The electrocatalytical properties toward oxidation of methanol and reduction of alkyl halides have been examined.

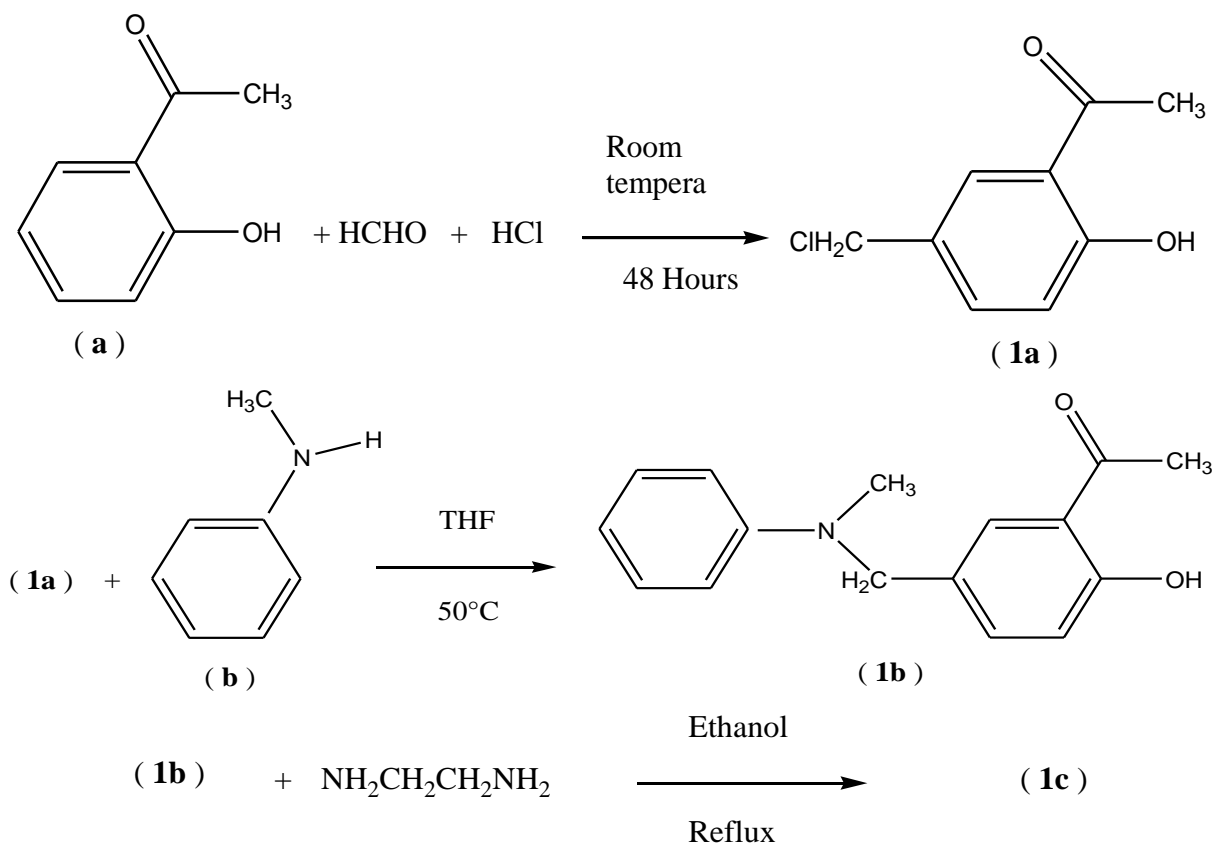
**Key words:** Chloromethylation reaction, Methylaniline, 2-hydroxyacetophenone, Tetradentate Schiff base, Nickel(II)-Schiff base complex, Cyclic voltammetry.

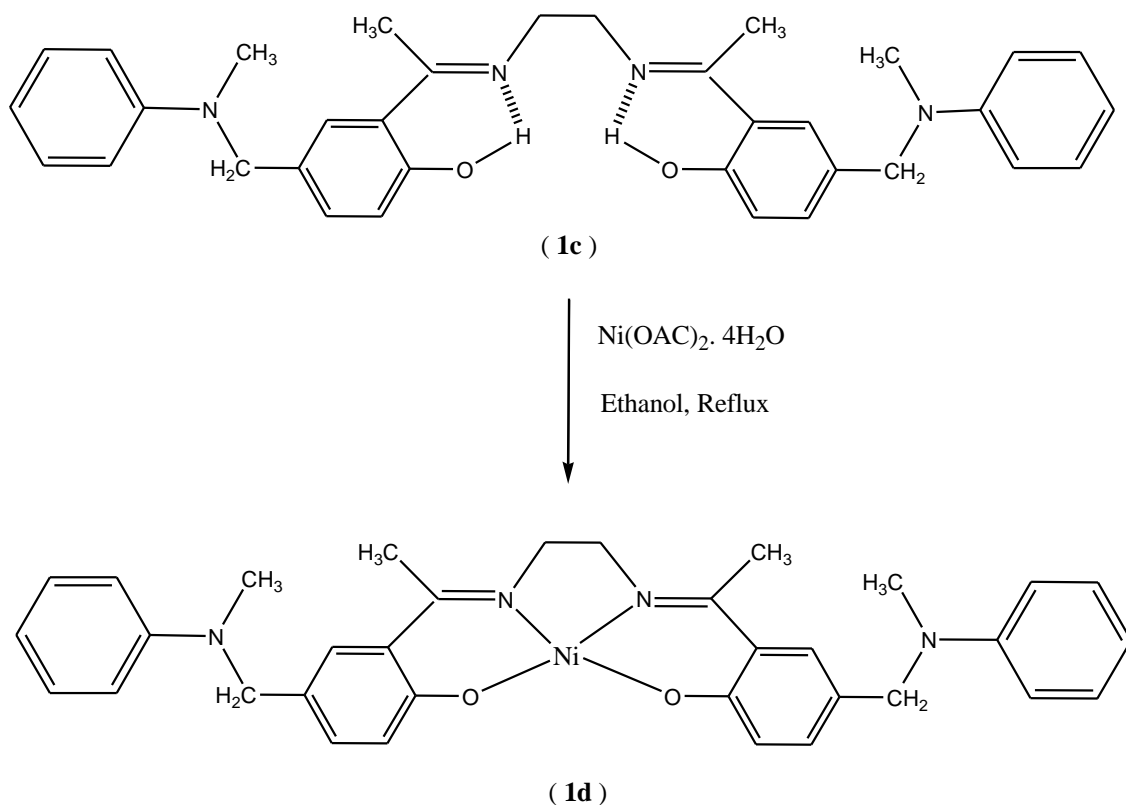
### 1. Introduction

There has been considerable effort in recent years to prepare new Schiff bases (imines) similar in their structures to porphyrins; these compounds are well known as good ligands to coordinate metal ions [1]. Their transition metal complexes were found to be useful as antibacterial [2,3], anticancer [4], in pharmacological area as efficient drugs [5], excellent catalysts in catalysis [6], electrocatalysis [7-9] and as sensors [10]. The symmetrical Schiff bases particularly those tetradentates with four donor heteroatoms as (NNOO), have been extensively studied in the literature [11] due to their ability to stabilize many different metals in various oxidation states. Moreover, Schiff base complexes are efficient as electrode modifiers for anodic oxidation or cathodic reduction [12-14]. In addition, these Schiff base

complexes could be used in several applications, such as the modification of monomers (Pyrrole, Thiophene, Aniline etc...) to form, *via* anodic oxidation, polymers used to make modified electrodes. These new complex species will appear in polymer matrices as pendant functional groups, covalently grafted. The applications of these materials are very important for electrocatalysis or mainly electroanalysis. Thus, electropolymerization is an effective way for modification of the electrode surface by depositing redox entities such as metallic complexes. Such modification of an electrode by symmetric nickel(II)-Schiff base containing an aniline molecular residue was first investigated by Murray and coworkers [15]. This approach for modification of electrodes using electropolymerizable units such as pyrrole and aniline are now in progress in our laboratory. These electropolymerizable moieties were essentially chosen for their moderate oxidation potential values, operating about 1 V/(Ag/Ag<sup>+</sup>, 10<sup>-1</sup> M) and permitting to avoid the destruction of the pendant functional groups.

In a continuation of our recent work [16-18], we herein, describe the synthesis, characterization and electrochemical behavior of new tetradentate nickel(II)-Schiff base complex bearing aniline moiety. To the best of our knowledge the four salicylaldehyde derivatives and the tetradentate Schiff base ligand and its nickel(II) complex are not known in the literature. The reactions involved in the synthesis of these new compounds are illustrated in Scheme 1.





Scheme 1: Reaction ways leading to the formation of ligand (H<sub>2</sub>L) and its nickel complex (Ni(II)-L).

## 2. Experimental

### 2.1. Physical measurements

All reagents were obtained from commercial sources and were used as received without further purification. The purity of the synthesized compounds was checked by TLC using glass plates, precoated with silica gel (60F, Merck). Melting points were determined in open capillary tubes on a Koffler Bench, type WME melting point apparatus and were uncorrected. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a Bruker 400 MHz spectrometer with CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts are expressed in δ units and coupling constants are given in Hertz. High resolution mass spectra (HRMS) were acquired by electrospray ionization (ESI) technique with the aid of Bruker APEX-2 instrument.

FT-IR spectra were recorded as KBr disks on a Perkins-Elmer 1000 FTIR Spectrophotometer while the UV-visible spectra were obtained on a UNICAM UV-300 spectrophotometer with DMF solutions (1cm, cell). Cyclic voltammetry experiments were carried out in an undivided Metrohm cell of 5 cm<sup>3</sup> using voltalab 40 (potentiostat/galvanostat) PGZ 301. A planar, circular glassy carbon (GC) electrode (3 mm diameter) was employed as working electrode and a platinum wire as auxiliary (counter) electrode. All potentials are quoted with respect to the saturated calomel electrode (SCE). Tetra-n-butylammonium tetrafluoroborate (TBABF<sub>4</sub>)

was used as supporting electrolyte and acetonitrile as solvents in all of the electrochemical experiments.

## 2.2. Synthesis of starting materials

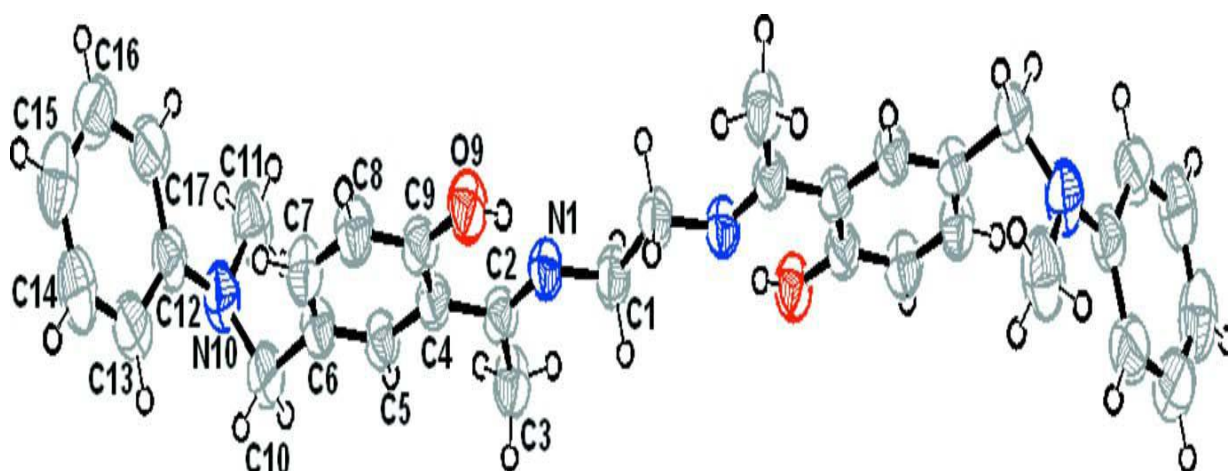
### Compound **1a**: 5-Chloromethyl-2-hydroxyacetophenone (**1a**)

The title compound was synthesized according to a procedure described by Wulff et al. [19] which involves adding 17 g (0.125 mol) of 2-hydroxyacetophenone, in small portions under stirring, to a mixture of 75 ml of concentrated hydrochloric acid containing 6.75 g (0.225 mol) of paraformaldehyde. The reaction mixture was maintained at room temperature under stirring for 48 hours until a precipitate is formed. The solid product was collected by suction filtration, washed with a solution of sodium hydrogen carbonate (NaHCO<sub>3</sub>, 0.5 %), then with water until neutrality, dried under vacuum and then recrystallized from a mixture of toluene and petroleum ether. Yield 18.5 g (80 %) of white crystals; m.p = 100 °C and its purity was checked by TLC using silica gel plates and a mixture of dichloromethane/ethanol (9.5/0.5, v/v) as eluent. UV-vis:  $\lambda_{\max(n)}$  (nm),  $\epsilon_{\max(n)}$  [M<sup>-1</sup>.cm<sup>-1</sup>]:  $\lambda_{\max(1)}$  (265),  $\epsilon_{\max(1)}$  [603];  $\lambda_{\max(2)}$  (327),  $\epsilon_{\max(2)}$  [1139]. IR (KBr):  $\nu_x$  (cm<sup>-1</sup>):  $\nu_{C-OH}$  (3426),  $\nu_{C-H(aliph.)}$  (2951-3013),  $\nu_{C=O}$  (1640),  $\nu_{CH_2-Cl}$  (1255),  $\nu_{C-Cl}$  (819). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_H$ (ppm) = 12.33 (s, 1H, OH), 7.37 (mm, 3H), 4.69 (s, 2H), 2.66 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta_C$ (ppm) = 204.3, 161.1, 137.3, 132.3, 128.9, 120.8, 118.6, 46.3, 28.4. HRMS (ESI)  $m/z$ : Calculated for C<sub>9</sub>H<sub>9</sub>ClO<sub>2</sub> [M]<sup>+</sup> 184.093; found 207.01833

### 5-(*N,N*-Methylphenylaminomethyl)-2-hydroxyacetophenone (**1b**)

This compound was prepared by the following general procedure: A mixture of 13 g (0.07 mol) of **1a** and 5.58 g (0.0775 mol) of NaHCO<sub>3</sub> in 20 ml of THF was placed in a three-necked flask surmounted by a condenser. To this mixture was added, drop wise, 7.5 g (0.07 mol) of *N*-methylaniline, dissolved in 10 ml of THF. The mixture was then heated to 50 °C and was maintained at this temperature under stirring and nitrogen atmosphere for at least 2 hours. The suspension containing NaCl was filtered, washed with diethyl ether and the solvents were removed under reduced pressure. The pale yellow solid product obtained was recrystallized from a mixture of toluene and petroleum ether to yield **1b**. Its purity was checked by TLC using silica gel plates using a mixture of dichloromethane/pentane (7/3, v/v) as eluent. Yield 9.5 g (46 %); m.p = 82 °C. UV-vis:  $\lambda_{\max(n)}$  (nm),  $\epsilon_{\max(n)}$  [M<sup>-1</sup>.cm<sup>-1</sup>]:  $\lambda_{\max(1)}$  (270),  $\epsilon_{\max(1)}$  [1500];  $\lambda_{\max(2)}$  (307),  $\epsilon_{\max(2)}$  [1231];  $\lambda_{\max(3)}$  (343),  $\epsilon_{\max(3)}$  [1065]. IR (KBr):  $\nu_x$  (cm<sup>-1</sup>):  $\nu_{C-OH}$ (3425),  $\nu_{C-H(aliph.)}$  (2827-3048),  $\nu_{C=O}$ (1641) :  $\nu_{CH_2-N}$ (1306),  $\nu_{N-CH_3}$ (512). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_H$ (ppm) = 12.15 (s, 1H, OH), 7.14 (m, 8H), 4.45 (s, 2H), 2.97(s, 3H), 2.54 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta_C$ (ppm) = 204.6 (CO), 161.7 (CO), 150.0, 135.5, 129.5, 128.9, 119.8, 118.9, 117.4, 113.1, 56.4, 38.6, 28.8. HRMS (ESI)  $m/z$ : calculated for C<sub>16</sub>H<sub>17</sub>NO<sub>2</sub> [M]<sup>+</sup> 255.0 ; found 255.000

This title compound is a tetradentate Schiff base ligand and a suitable single-crystal was formed by slow evaporation from a solvent mixture EtOH/CH<sub>2</sub>Cl<sub>2</sub> (8/2, v/v). The molecular geometry of **1b** (Figure 1) with displacement ellipsoids drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radii. Only the non-H atoms of the asymmetric unit are labelled.



**Fig.1.** ORTEP diagrams of **1b**

### 2.3. Preparation of *N,N*-Bis[5- (*N,N*-methylphenylaminomethyl)methylsalicylidyne]-1,2-diaminoethane (**1c**) and its nickel complex (**1d**).

The Schiff base **1c** was synthesized according a literature procedure [15] with slight modification. To a solution of 7 g (27.45 mmol) of 5-(*N,N*-methylphenylaminomethyl)-2-hydroxyacetophenone (**1b**) in 30 ml of absolute ethanol in a 100 ml three-necked flask surmounted with a condenser was slowly added a solution of 0.823 g (13.72 mmol) of ethylenediamine in 20 ml absolute ethanol of absolute ethanol. This mixture was heated to 50 °C under stirring and nitrogen atmosphere for two hours. The precipitate obtained was filtered, washed with diethyl ether and dried under reduced pressure to afford compound **1c** as a yellow solid. Yield 4.26 g (58 %); m.p = 156 °C. Its purity was checked by silica gel TLC plates using dichloromethane/ethyl acetate (8/2, v/v) as eluent. UV-vis:  $\lambda_{\max(n)}$  (nm),  $\epsilon_{\max(n)}$  [ $M^{-1}.cm^{-1}$ ]:  $\lambda_{\max(1)}$  (272),  $\epsilon_{\max(1)}$  [2950];  $\lambda_{\max(2)}$  (311),  $\epsilon_{\max(2)}$  [2050];  $\lambda_{\max(3)}$  (392),  $\epsilon_{\max(3)}$  [989]. IR (KBr):  $\nu_x$  ( $cm^{-1}$ ):  $\nu_{C-OH}$ (3416),  $\nu_{C-H(aliph.)}$  (2922),  $\nu_{C=N}$ (1616):  $\nu_{CH_2-N}$ (1295),  $\nu_{N-CH_3}$ (488).  $^1H$  NMR ( $CDCl_3$ ):  $\delta_H(ppm)$  = 14.15 (s, 2H, OH), 7.02 (m, 16H), 4.42 (s, 4H), 3.93 (s, 4H), 2.93 (s, 6H), 2.29 (s, 6H).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta_C(ppm)$  = 172.8 (CO), 162.4 (CO), 150.2, 131.6, 129.4, 127.6, 126.7, 119.5, 118.8, 117.0, 113.1, 56.4, 50.5, 38.4, 15.0. HRMS (ESI)  $m/z$ : Calcd for  $C_{34}H_{38}N_4O_2$  [ $M$ ]<sup>+</sup> 534.200 ; found 557.2 .

Similarly, 200 mg (0.374 mmol) of the ligand ( $H_2L$ ) (**1c**) was dissolved in 10 ml of absolute ethanol and placed in a 50 ml three-necked flask surmounted by a condenser. An ethanolic solution (10 ml) of 93 mg (374 mmol) of tetrahydrated nickel acetate ( $Ni(II)(CH_3COO)_2.4H_2O$ ) was added, drop wise, to the solution of the ligand ( $H_2L$ ). The mixture was then heated to reflux, under stirring and nitrogen atmosphere for twenty hours. After cooling to room temperature, the volume of solution was reduced to half of its original volume and was then left in a refrigerator overnight. The brown precipitate was collected by filtration, washed with ethanol and dried under reduced pressure for several hours to yield 138 mg (63 %) of the complex **1d**. M.p. was over 250 °C. UV-vis:  $\lambda_{\max(n)}$  (nm),  $\epsilon_{\max(n)}$  [ $M^{-1}.cm^{-1}$ ]:  $\lambda_{\max(1)}$  (269),  $\epsilon_{\max(1)}$  [2800];  $\lambda_{\max(2)}$  (309),  $\epsilon_{\max(2)}$  [1110];  $\lambda_{\max(3)}$  (413),  $\epsilon_{\max(3)}$  [443];  $\lambda_{\max(4)}$  (449),  $\epsilon_{\max(4)}$  [180]. IR (KBr):  $\nu_x$  ( $cm^{-1}$ ):  $\nu_{C-H(aliph.)}$  (3163-3280),  $\nu_{C=N}$ (1589),  $\nu_{CH_2-N}$ (1306),  $\nu_{C-O}$ (1328),  $\nu_{Ni-O}$ (521).  $\nu_{Ni-N}$ (498).  $^1H$  NMR ( $CDCl_3$ ):  $\delta_H(ppm)$  = 6.86 (m, 16H), 4.25 (s, 4H),



3.35 (s, 4H), 2.84 (s, 6H), 2.01 (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{C}}(\text{ppm}) = 168.2, 163.4, 150.1, 131.6, 129.1, 126.7, 124.2, 122.8, 121.1, 116.7, 112.8, 56.4, 54.6, 38.1, 18.1$ . HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{34}\text{H}_{36}\text{N}_4\text{NiO}_2$ :  $[\text{M}]^+ 591.37$  found 591.225. Anal. Calculated for  $\text{C}_{34}\text{H}_{36}\text{N}_4\text{NiO}_2$ : C, 64.99 ; H, 6.37 ; N, 8.92, found: C, 64.47 ; H, 6.21 ; N, 8.84.

### 3. Results and discussion

#### Chemistry

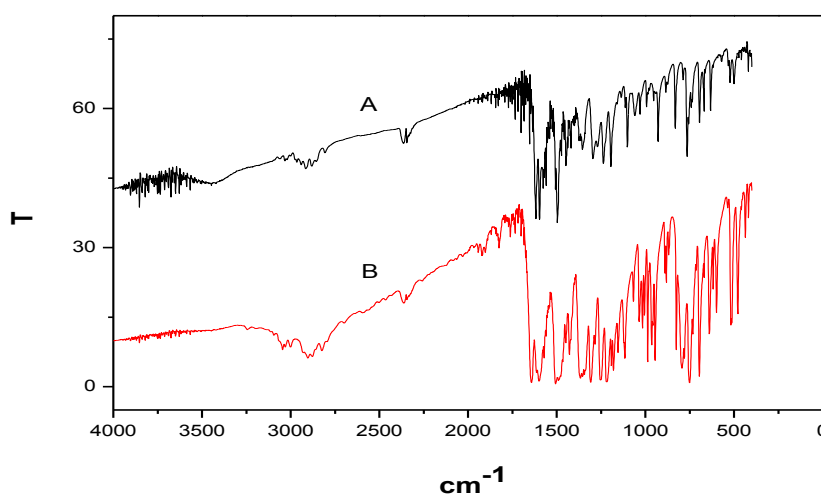
The synthesis of compounds (**1a-c**) was carried out through known chemical reactions as shown in Scheme 1. Compound **1a** was prepared according to published procedures that basically involved a reaction between 2-hydroxyacetophenone, paraformaldehyde and hydrochloric acid. Compound **1b**, on the other hand, was prepared *via* an alkylation of N-methylaniline with compound **1a**. Reaction of compound **1b** with ethylenediamine afforded the Schiff base tetradentate ligand **1c** which upon treatment with Ni(II) acetate yielded **1d**. The structures of the prepared compounds were confirmed by different spectroscopic techniques such as UV-vis, IR, NMR, and mass spectral data.

$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of the all prepared compounds are in total agreement with the suggested structures. The  $^1\text{H}$  NMR spectra of compounds **1a**, **1b** and **1c** showed signals corresponding to methylene, aromatic and OH protons. DEPT experiments were employed to differentiate between secondary and quaternary carbons from primary and tertiary carbons. Moreover, the infrared spectra of the prepared compounds showed absorption bands characteristic of C=O groups in addition to other absorptions correlated to the assigned structures. Mass spectral data of the synthesized compounds are also in total agreement with the assigned structures and showed the expected molecular ions,  $\text{M}^+$  as suggested by their molecular formulas. Additionally, elemental analysis of the nickel complex (**1d**) showed that two molecules of water are involved in the crystallographic lattice. Details of some spectral data are given below.

#### FT-IR Spectra

All the synthesized compounds show a broad absorption band in the  $3300\text{--}3800\text{ cm}^{-1}$  region assigned to the intramolecularly hydrogen bonded O–H stretching vibration due to the presence of hydroxyl group (intramolecular hydrogen bonding) in their molecular structures except with the nickel complex (**1d**) where its IR spectrum shows stretching absorption bands at about  $3450\text{ cm}^{-1}$  suggesting the presence of water molecules (water lattice) and binding absorption at  $1600\text{ cm}^{-1}$ . These bands were confirmed by elemental analysis which indicates that each molecule of the nickel complex is associated with two molecules of water [21b]. The absorption bands observed at  $1640$  and  $1641\text{ cm}^{-1}$  attributed to the C=O stretching vibrations for compounds **1a** and **1b**, respectively, whereas the stretching vibrations of the  $\text{CH}_2\text{--Cl}$  was observed at  $819\text{ cm}^{-1}$ ; this band is absent in the spectrum of **1b** which has an absorption band at  $1306\text{ cm}^{-1}$  due to the newly formed  $\text{CH}_2\text{--N}$  group [22]. The significant shift of the carbonyl group frequency to lower energy for both **1a** and **1b** compared to that of acetophenone absorbs at  $1720\text{ cm}^{-1}$  could be attributed to the stronger dipole-dipole interactions between the phenolic proton and the considered carbonyl group. This could also explain the significant displacement of the chemical shift of phenolic proton ( $\delta_{\text{Ar-OH}}$ ) from 7.54 (phenol) to about 12–15 ppm for 2-hydroxyacetophenone and its analogues; this behaviour is well discussed in  $^1\text{H}$  NMR literature for similar structures [21, 23].

As for the tetradentate Schiff base ligand **1c** and its Ni(II) complex **1d**, the characteristic frequencies of azomethine group ( $\nu_{C=N}$ ) presents an obvious shift to lower wavenumbers (1616 - 1610  $\text{cm}^{-1}$ ). This bathochromic effect could be explained by the increase in the electronic delocalization through the metal centre newly coordinated in the Ni(II)-complex [21,24]. Moreover, the ( $\nu_{C-O}$ ) absorption band shifts to higher wavenumbers (1275 - 1295  $\text{cm}^{-1}$ ). These two facts are due to coordination of metal ion through the oxygen atoms of ionised hydroxyl groups and nitrogen atoms of azomethine groups [25]. The coordination of nickel metal to the NNOO quadridentate is also illustrated by the absorption bands of  $\nu_{N-Ni}$  (498  $\text{cm}^{-1}$ ) and  $\nu_{O-Ni}$  (521  $\text{cm}^{-1}$ ) [26].



**Fig.2.** FT-IR spectra of ligand (A) and its nickel complex (B).

### Electronic spectra

Typical absorption bands of aromatic components were observed for **1a** and **1b**. Compound **1a** shows two absorption bands at 265 and 327 nm while three bands at 270, 307 and 337 nm (shoulder) appear for **1b**. In both cases, the first two bands correspond to transitions of phenyl ring [27]. The third one of compound **1b** was assigned to  $n \rightarrow \pi^*$  transition [28]. As for the other two compounds, the ligand **1c** and its nickel complex **1d**, the former displayed three bands at 250, 309 (337 shoulder) and 414 nm while the latter exhibited four bands where the first three ones are similar to those of the ligand. As for the fourth appearing at 449 nm, it was assigned to the soret band [28] suggesting that the nickel metal was effectively coordinated to the ligand as was previously shown by IR-data [25].

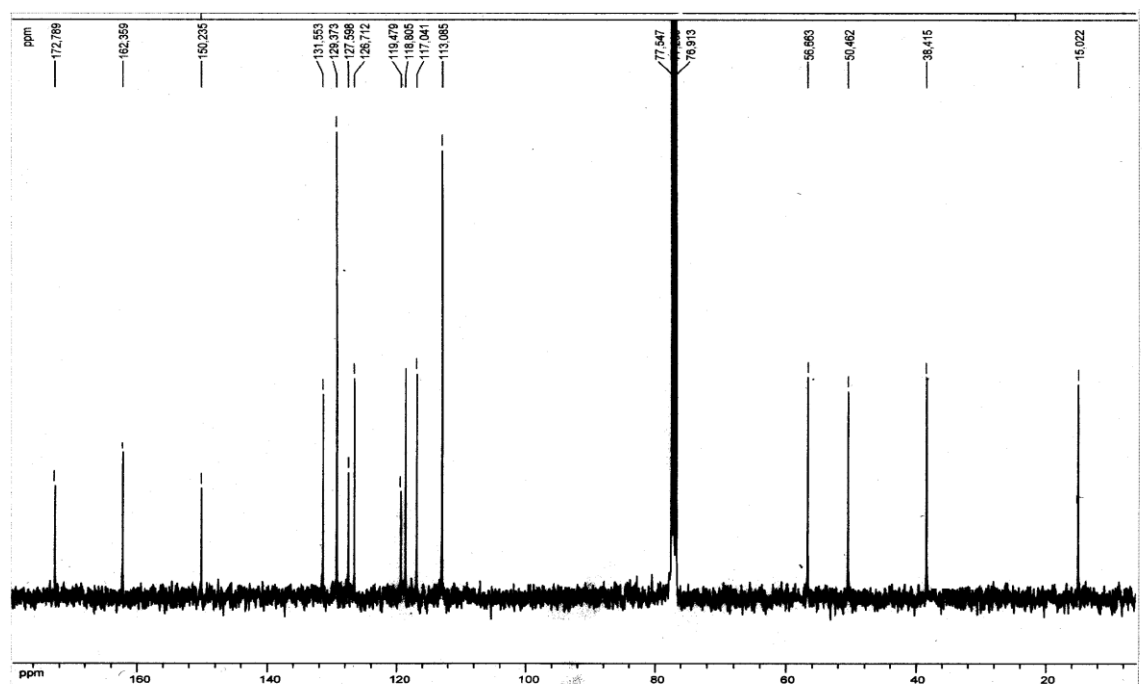
### <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR Spectra Of The Prepared Compounds, I.E. 5-Chloromethyl-2-Hydroxyacetophenone **1a**, 5-(N,N-Methylphenylaminomethyl)-2-Hydroxyacetophenone **1b**, N,N-Bis[5- (N,N-Methylphenylaminomethyl)Methylsalicylidyne]-1,2-Diaminoethane **1c** And N,N-Bis[5- (N,N-Methylphenylaminomethyl)Methylsalicylidyne]-1,2-Diaminoethane-Nickel **1d** Are In Good Agreement With Their Assigned Structures. Spectra Of **1a**, **1b**, And **1c** Reveal A Downfield Singlet Signal In The Range 14.15 – 12.15) Due To The Phenolic

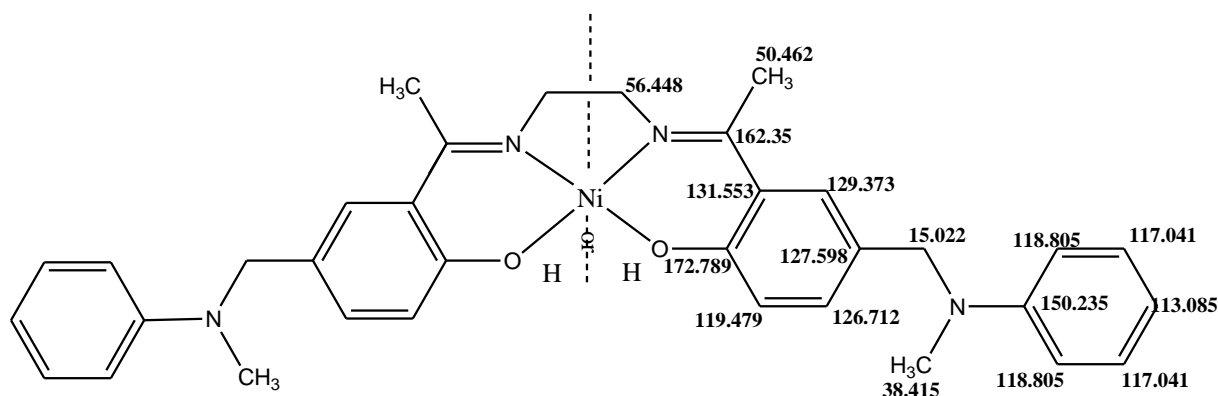
Protons [21,23]. This Deshielding Of Chemical Shifts Is Ascribed To The Formation Of Intramolecular Hydrogen Bonding [23,29a]. The Aromatic Protons Of The Four Compounds Appear As Complex Multiplets Between  $\delta$  6.864 And 7.370 Ppm. It Can Be Noted That The Singlet Of Methylene Group (CH<sub>2</sub>-Cl And CH<sub>2</sub>-N) Shifts From  $\delta$  4.690 In **1b** To 4.450 Ppm For Compound **1a**. This Shift Is Due To The Difference In Electronegativity Between Chlorine And Nitrogen Atoms. The Protons Of Both Methyl Groups, Grafted On Imine Function (N=C(CH<sub>3</sub>), Resonate As Singlet, Almost At The Same Chemical Shifts, 2.932 **1c** And 2.837 Ppm **1d**. The Phenolic Protons Signals Are Not Observed For The Nickel Complex **1d** Suggesting That Both Phenoxy Groups Bind With The Nickel Ion As Monoanions.

### <sup>13</sup>C NMR spectra

The <sup>13</sup>C NMR spectra of compounds **1a** and **1b** show peaks associated with the different types of carbons of the considered structures. Carbon atoms resonating at  $\delta$  = 204.6-150 ppm are due to those of carbonyl, phenoxy and anilinic groups. Aromatic carbon atoms resonate at  $\delta$  = 137.0–113.1 ppm range. For the spectrum of **1c**, the aliphatic carbon atoms appear at  $\delta$  = 56.4–26.8 ppm. The <sup>13</sup>C NMR spectra of **1c** and the nickel complex **1d** are similar to those of **1b** since their molecular structures are symmetrical and derived from the compound **1b** and ethylenediamine. Subsequently, the carbon atoms associated with phenoxy groups are more downfield and appear at  $\delta$  = 172.789 and 168.225 ppm, respectively. The carbon atoms of azomethine groups were observed at  $\delta$  = 163.434 for **1d** and 162.359 for **1c**. The aromatic and aliphatic carbon atoms resonate almost at the same chemical shifts of the same carbons in compounds **1a** and **1b**. These results are in good agreement with the spectra of similar compounds described in the literature [23,26].



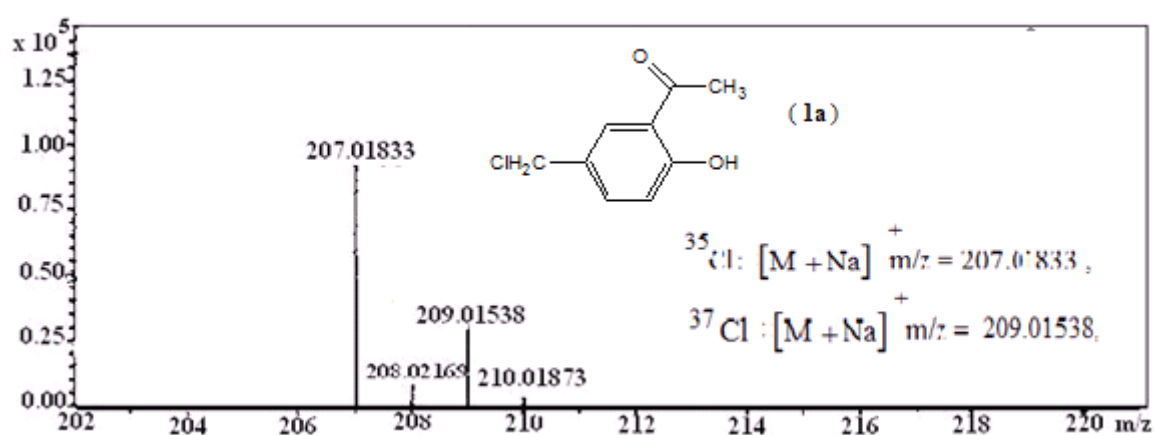


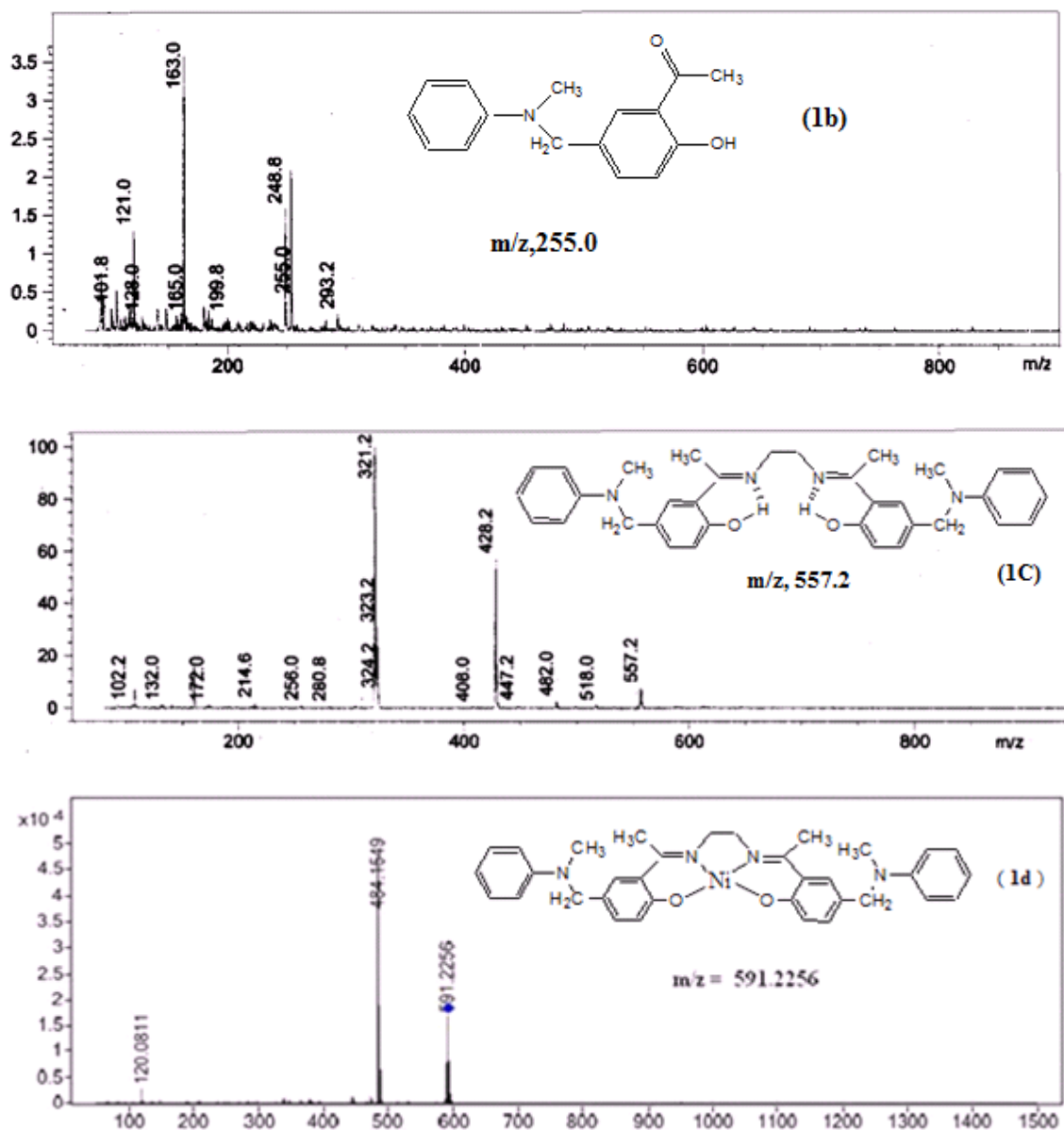


**Fig.3.**  $^{13}\text{C}$  NMR spectrum of the Schiff base ligand (**1c**) and its assignment [26].

### Mass spectra

Mass spectra of compounds **1a** and **1b** displayed the molecular ion peaks  $[\text{M} + \text{Na}]^+$  which supports their assigned structures. The phenolic groups of these compounds react with sodium hydroxide (NaOH) to afford their salts of sodium phenates which are thermodynamically highly stabilized as molecular peaks. In addition, it is worth mentioning that the protonated species are also observed affording the expected mass corresponding to the suggested molecular structure. The mass spectra of the synthesized compounds **1a-1d** are illustrated by the following Figure 4.





**Fig. 4.** Mass spectra of compounds **1a-1d**.

As for the mass spectra of the ligand **1c** and its nickel(II)-complex **1d**, they show the molecular peaks  $[M]^+$  with mass ratio  $m/z$  corresponding exactly to the proposed molecular structure for **1c** and **1d**. For the ligand **1c**, its molecular peak is associated to sodium ion  $[M+Na]^+$   $m/z$  557.2. By the same manner, when the nickel(II)-complex **1d** is introduced in the ionization chamber, a molecular peak ( $M^+$ ) corresponding to the mass ratio of  $m/z$  591.23 appeared.

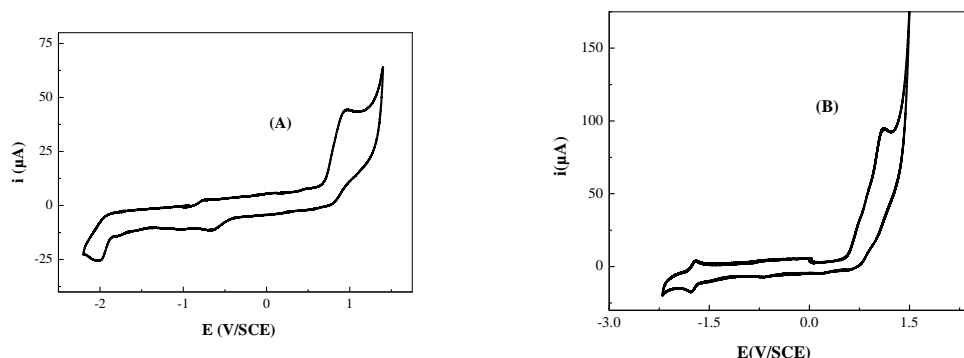
### *Cyclic voltammetric behavior of **1c** and **1d** in oxygen-free dimethylsulfoxide*

#### *Ligand **1c***

Fig. 5 (curve A) shows a cyclic voltammogram, recorded with a glassy carbon electrode at  $100 \text{ mV.s}^{-1}$  for a  $1.0 \text{ mM}$  solution of **1c** in oxygen-free dimethylsulfoxide (DMSO) containing  $0.10 \text{ M}$  TBAP as a supporting electrolyte. Two anodic waves peak potentials of  $-0.738$  and  $+0.958 \text{ V/SCE}$  were observed, which presumably correspond to the oxidation of the anilinic entities, and the amino group respectively. The second wave seems to be irreversible. However, when the scan was reversed, two cathodic waves were observed having peak potentials  $-0.652$  and  $-2.005 \text{ V/SCE}$  which could be attributed to the reduction wave of the oxidation product of the anilinic entities and the amino groups respectively.

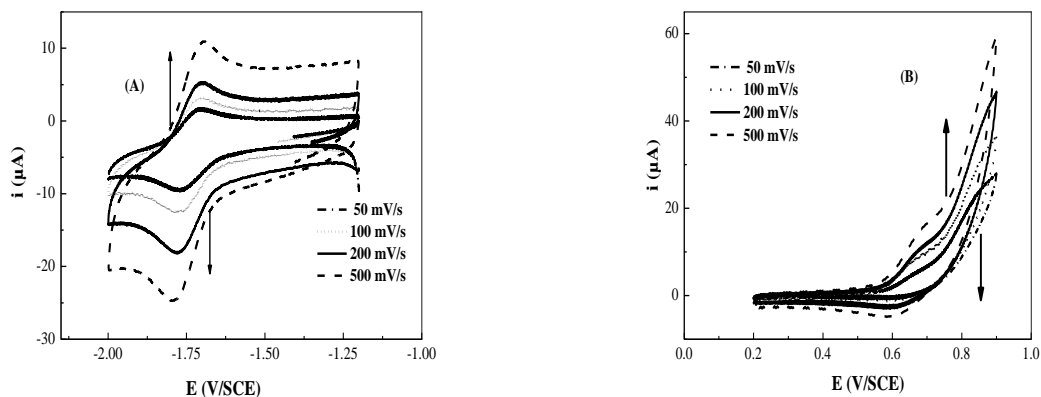
#### *Ni(II)-Complex **1d***

Fig.5 (curve B) displays a cyclic voltammograms recorded with a glassy carbon electrode at a scan rate of  $100 \text{ mV.s}^{-1}$  for DMSO solution containing  $0.10 \text{ M}$  TBAP as a supporting electrolyte and  $1 \text{ mM}$  of **1d**. Four anodic waves peak potentials of  $-1.711$ ,  $0.732$ ,  $+0.779$  and  $1.090 \text{ V/SCE}$  were observed. Thus, these peak potentials are attributed to the oxidation of Ni(I) to Ni(II) [15], the anilinic entities, Ni(II) to Ni(III), and anilinic compounds [15], respectively. In addition, three reduction waves with peak potentials at  $+0.77$ ,  $-0.663$ , and  $-1.767 \text{ V/SCE}$  also observed which are assigned to the reduction of Ni(III) to Ni(II), the anilinic species produced, and Ni(II) to Ni(I), respectively.

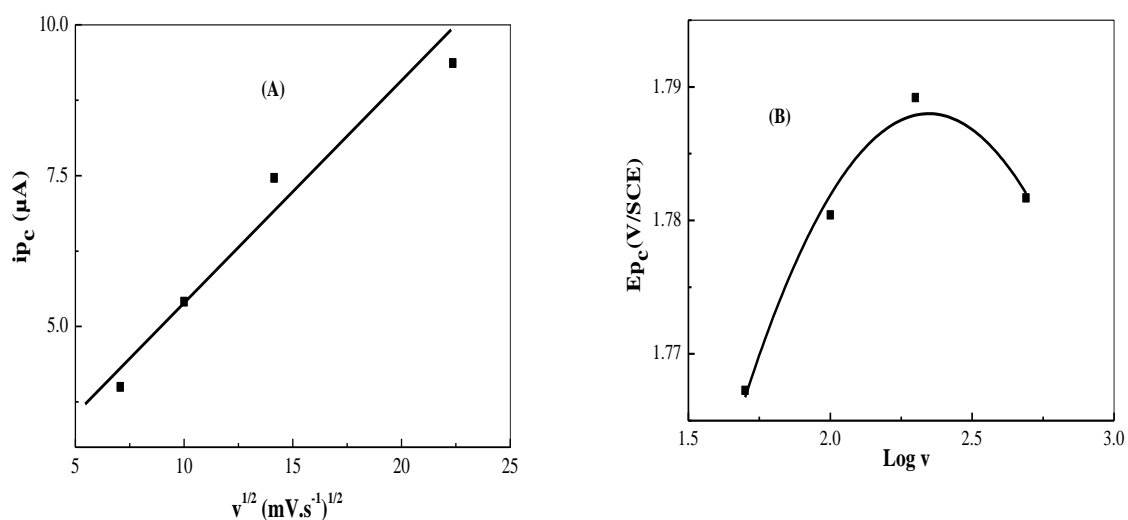


**Fig. 5.** Cyclic voltammogram recorded with a glassy carbon disk electrode ( $\varnothing 3 \text{ mm}$ ) in DMSO containing  $0.10 \text{ M}$  TBAP at a scan rate of  $100 \text{ mV.s}^{-1}$  for a solution  $10^{-3} \text{ M}$  of **1c** (curve A) and **1d** (curve B).

Fig. 6 (Curve A) Presents the effect of the peak currents ( $i_{pa}$  and  $i_{pc}$ ) versus scan rate for the redox systems of Ni(II)/Ni(I) and Ni(III)/Ni(II). The former indicates that is diffusion controlled according Nicholson's theory [30] whereas in the latter, of such behavior is rather not reversible since the Nicholson's rules are not satisfied as illustrated by the following Fig. 6 (Curve B).



**Fig. 6.** Cyclic voltammograms recorded with a glassy carbon disk electrode (Ø 3 mm) in DMSO solutions containing 1 mM of complex **1d**, 0.10 M TBAP at various scan rates ( $v$ ) under  $N_2$ . Scan rates from inner to outer: 50, 100, 200, 500  $mV.s^{-1}$ ; Ni(II)/Ni(I) (Curve A); Ni(III)/Ni(II) (Curve B).



**Fig. 7.** (Curve A) Evolution of cathodic current  $i_{pc}$  versus square root of scan rate ( $v$ ) for redox system Ni(II)/Ni(I).

(Curve B) Graphical representation of potential values  $E_{pc}$  versus  $\log v$  (Logarithm of different scan rates) for redox system Ni(II)/Ni(I).

**Table.1.** Cyclic voltammetry data<sup>a</sup> for the complex Ni(II)/Ni(I).

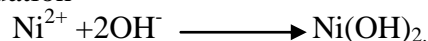
$V$ ( $mV.s^{-1}$ )	$V^{1/2}$ ( $mV.s^{-1}$ ) <sup>1/2</sup>	$LogV$	$I_{p_a}$ ( $\mu A$ )	$I_{p_c}$ ( $\mu A$ )	$E_{p_a}$ ( $mV$ )	$E_{p_c}$ ( $mV$ )	$E_{1/2}$ ( $mV$ )	$\Delta E$ ( $mV$ )	$I_{p_a}/I_{p_c}$
50	7.071	1.699	3.683	3.999	1714.31	1767.27	1740.79	52.96	0.920
75	8.660	1.875	4.696	4.378	1715.40	1770.34	1742.87	54.94	1.070
100	10.000	2.000	5.145	5.409	1712.30	1784.02	1743.16	61.72	0.950
200	14.140	2.300	6.347	7.463	1710.25	1789.18	1752.71	84.93	0.850
300	17.320	2.477	9.218	11.313	1706.10	1781.80	1743.95	75.71	0.828
400	20.000	2.602	9.364	11.130	1703.94	1796.45	1750.19	92.51	0.840
500	22.360	2.699	10.225	9.366	1701.67	1781.68	1741.67	80.01	1.090

<sup>a</sup> Working electrode: glassy carbon electrode; reference electrode: SCE electrode; supporting electrolyte: TBAP (0.1 M);  $E_{1/2} = 0.5 (E_{p_a} + E_{p_c})$ , where  $E_{p_a}$  and  $E_{p_c}$  are anodic and cathodic potentials respectively.

#### 4. Catalysis studies

##### *Oxydation of methanol*

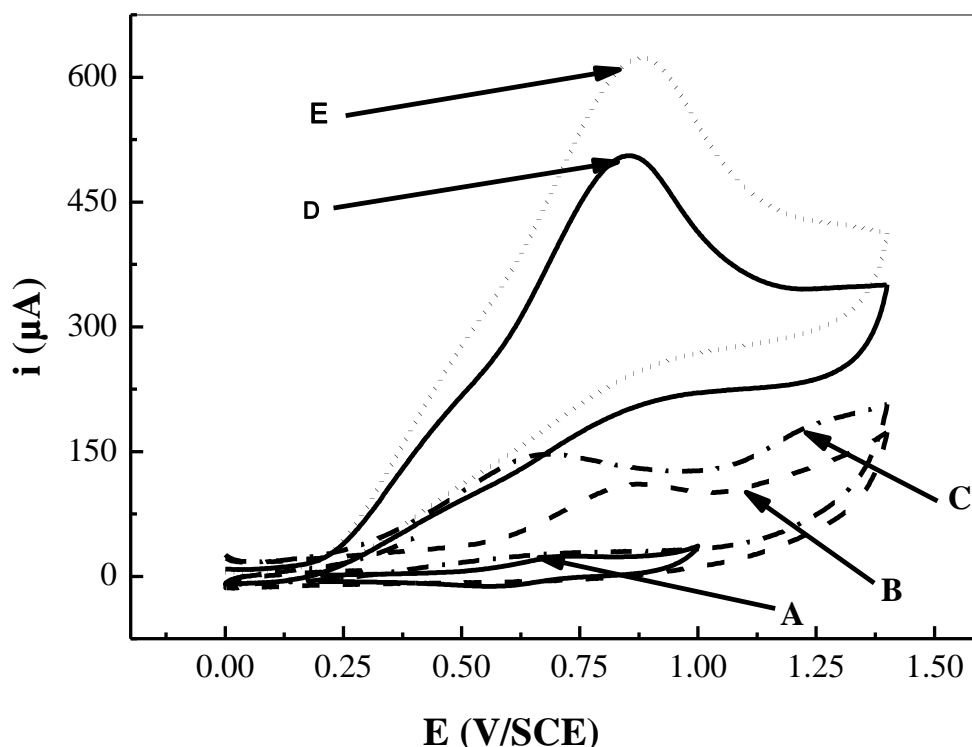
Methanol and ethanol are short aliphatic chain alcohols which can oxidize on electrodes modified containing nickel ions under alkaline medium. This environment promotes the formation of nickel hydroxide that initiates the oxidation reaction of alcohols according to the following equation



In this context, our objective is to achieve the electrochemical oxidation of alcohols in solution for the complex of copper and nickel in a medium alkaline 0.1 M NaOH.

In this paper, we realized the oxidation of methanol by cyclic voltammetry in a DMSO solution, 0.1 M of NaOH and glassy carbon working electrode. The specific results for a scan of potential ranging from 0.00 to 1400 mV/ECS are represented in the following figure:

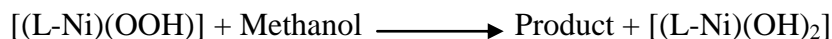




**Fig.8.** Registration of the cyclic voltammograms with glassy carbon electrode immersed in DMSO solutions containing 1.0 mM Ni(II)-L, 0.10 M t-Bu<sub>4</sub>NBF<sub>4</sub> and 0.1 M NaOH using various concentrations of methanol, **A** :0.00 M, **B** :0.2 M, **C** :0.3 M, **D** :0.7 M, **E** :1.00 M with 100 mV.s<sup>-1</sup> as scan rate.

The electrochemical response of Ni(II)-L in the absence of methanol is represented in the Figure 8 (curve **A**) shows only the characteristic Ni(II) /Ni (III) redox couple around 0.600 mV/SCE. The addition of 0.10 M of methanol in the catalytic conditions gave no obvious effect on the electrochemical response while at 0.2 (curve **B**) exhibit only one oxidation wave at about 0.850 V/SCE. This peak current ( $I_{pa}^I$ ) is relatively more intense than that of the redox Ni(II) /Ni(III) system (curve **A**) and is also accompanied by the total disappearance  $I_{pc}^I$  suggesting an electrocatalytic current. At more higher concentrations (**C**, **D** and **E**) of methanol a second oxidation wave was observed at more anodic potentials and then, the both oxidation waves shift to the lower potential values as is clearly illustrated by the Fig.8 (curves **C**, **D** and **E**). This electrocatalytic behavior is in good agreement with the literature [31] seeing that, when the catalytic current is more intense, we observed the gradual disappearance of the wave of reduction ( $I_{pc}^I$ ) (**B**,**C**,**D**,**E**) at the expense of this oxidation. This shows that Ox nickel species undergo a chemical reaction making it non-reversible reaction. It can be said therefore that the Ni(II)-L located on the surface of the electrode acts as a catalyst to the oxidation of methanol in 0.1 M NaOH solution and, according to a mechanism EC in which the reactions are given below:

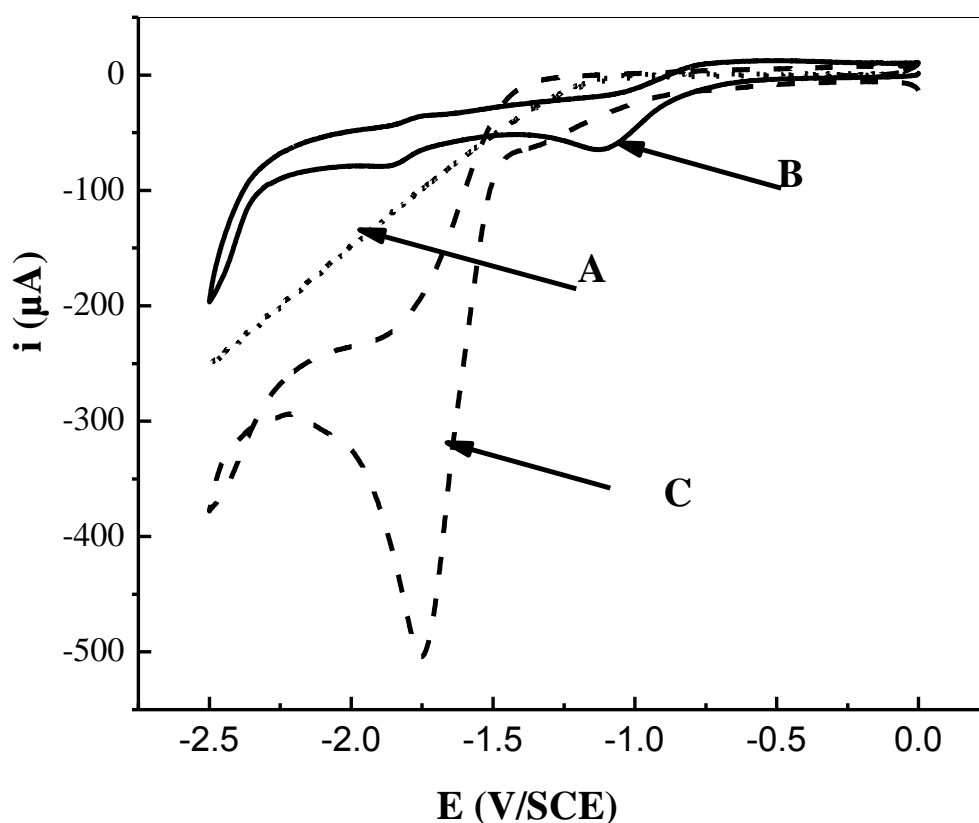




### *Reduction of alkyls halides*

- Reduction of bromide ethyl ethanoate*

Similarly, the figure 9 recorded between 0.0 and - 2500 mV/SCE on glassy carbon in organic medium (DMSO/t-Bu<sub>4</sub>NBF<sub>4</sub>, 0.1 mol.l<sup>-1</sup>) at 100 mV.s<sup>-1</sup> and 1.0 mM of complex Ni (II)-L note also the appearance of a catalytic power which increases in the presence of the alkyl halide in the reaction medium. This result confirms the catalytic effect of the complex of nickel on the electroreduction of ethyl bromoethanoate.



**Fig.9.** Cyclic voltammograms recorded obtained with a glassy carbon disk electrode (3-mm-diameter) in DMSO solutions containing 0.10 M t-Bu<sub>4</sub>NBF<sub>4</sub> at a scan rate of 100 mV.s<sup>-1</sup>: (A): 1.0 mM bromide ethyl ethanoate (B) :1.0 mM Ni(II)-L; (C):1.0 mM Ni(II)-L and 1.0 mM bromide ethyl ethanoate.

## 5. Conclusion

In this work, we have synthesized and characterized four novel compounds, one among them, was a Schiff base ligand **1c** containing in its molecular structure an anilinic moiety which could be used as an electropolymerizable monomer to build modified electrodes. The nickel(II) complex **1d** of this monomer was also synthesized and characterized and its cyclic

voltammetry behavior has been investigated. The films of this nickel complex were also found to be effective catalysts in the electro-oxidation of methanol and electro-reduction of alkyl halides. This new monomer may also be extended to the synthesis of other transition metal complexes which could be advantageously exploited as solid phase (modified electrodes) in heterogeneous catalysis, electrocatalysis, analysis, sensors and biosensors. This work is now in progress in our laboratory.

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