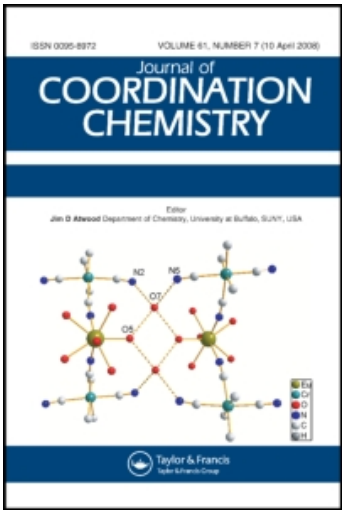
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK




**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# Synthesis and characterization of a Schiff base derived from 2-aminobenzylamine and its Cu(II) complex: electropolymerization of the complex on a platinum electrode

Cahıt Demetgül[a]; Dıdem Deletıoğlu[a]; Fılız Karaca[b]; Süleyman Yalçinkaya[a]; Mahır Tımur[a]; Selahattın Serın[b]
[a] Department of Chemistry, Faculty of Science and Letters, Mustafa Kemal University, Hatay 31040, Turkey [b] Department of Chemistry, Faculty of Science and Letters, Çukurova University, Adana 01330, Turkey

First published on: 25 June 2010

**To cite this Article** Demetgül, Cahıt , Deletıoğlu, Dıdem , Karaca, Fılız , Yalçinkaya, Süleyman , Tımur, Mahır and Serın, Selahattın(2010) 'Synthesis and characterization of a Schiff base derived from 2-aminobenzylamine and its Cu(II) complex: electropolymerization of the complex on a platinum electrode', Journal of Coordination Chemistry, 63: 12, 2181 — 2191, First published on: 25 June 2010 (iFirst)
**To link to this Article: DOI:** 10.1080/00958972.2010.496852
**URL:** http://dx.doi.org/10.1080/00958972.2010.496852

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

*Journal of Coordination Chemistry*
Vol. 63, No. 12, 20 June 2010, 2181–2191

Taylor & Francis
Taylor & Francis Group

# Synthesis and characterization of a Schiff base derived from 2-aminobenzylamine and its Cu(II) complex: electropolymerization of the complex on a platinum electrode

CAHİT DEMETGÜL*†, DİDEM DELETİOĞLU†, FİLİZ KARACA‡, SÜLEYMAN YALÇINKAYA†, MAHİR TİMUR† and SELAHATTİN SERİN‡

†Department of Chemistry, Faculty of Science and Letters, Mustafa Kemal University, Hatay 31040, Turkey
‡Department of Chemistry, Faculty of Science and Letters, Çukurova University, Adana 01330, Turkey

Downloaded At: 07:19 23 January 2011

(*Received 30 December 2009; in final form 23 March 2010*)

A precursor ($H_3A$) was synthesized by the mono condensation of 2-aminobenzylamine with salicylaldehyde and then a tetradentade Schiff-base ligand ($H_2L$) prepared by using $H_3A$ and 3-methoxysalicylaldehyde. The copper(II) complex of this new ligand was prepared and characterized by elemental analysis, electronic absorption, Fourier transform infrared (FT-IR), and magnetic susceptibility. For the ligand, $^1$H- and $^{13}$C-NMR and liquid chromatography mass spectrometry (LC–MS) spectra were obtained. The tetradentate ligand is coordinated to Cu(II) through the phenolic oxygen and azomethine nitrogen. The use of this metal complex in the preparation of a modified electrode is also described. CuL was electropolymerized on a platinum electrode surface in a 0.1 mol dm$^{-3}$ solution of lithium perchlorate in acetonitrile by cyclic voltammetry between 0 and 1.6 V *versus* Ag/Ag$^+$. Electrochemical properties of the electroactive polymeric film have been investigated and a surface confined polymerization mechanism was proposed.

*Keywords*: 2-Aminobenzylamine; Schiff base; Copper(II) complex; Electropolymerization; Modified electrode

## 1. Introduction

Schiff bases derived from substituted salicylaldehydes and various aromatic amines are common polydentate ligands in coordination chemistry, coordinating in deprotonated or neutral forms [1, 2]. Transition metal(II) complexes derived from tetradentate Schiff bases form stable compounds where the coordination takes place through the $N_2O_2$ donor set [3]. Complexes of Schiff bases containing O, N donors are of particular interest [4] because of unusual configuration, structural lability, and sensitivity to molecular environments [5]. Thus, Schiff-base complexes have been among the most widely studied coordination compounds and are becoming increasingly important

*Corresponding author. Email: cdemetgul@hotmail.com

*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.496852

as analytical, biochemical, and antimicrobial reagents [6]. These compounds also find catalytic applications ranging from asymmetric epoxidation [7], solid phase extraction of metal ions [8], polymerization [9, 10], and for the preparation of ion selective electrodes [11, 12].

Conducting polymers containing complexed transition metals are increasing [13], especially because metal centers can be electrically connected *via* the polymer skeleton. Preparation and characterization of metal salen-based electroactive polymers is an active field due to their potential application as electrocatalysts, chemical sensors, or optical devices. The incorporation of metal salen complexes into a polymeric system offers some advantages in the possibility of thickness control, good membrane-forming properties, amperometric measurements in aqueous media, and easy preparation of the modified electrodes. There has been interest in chemically modified solid electrodes, including those coated with anodically polymerized films of metal salen complexes [14–17]. A recent study is the electrochemical preparation involving electrocatalytic oxidation of sulfite on a platinum electrode with Cu(II)-salen polymer film [18].

We report the synthesis and characterization of a Schiff base from 2-aminobenzylamine and its Cu(II) complex. The characterization was done by elemental analysis, atomic absorption spectroscopy (AAS), liquid chromatography mass spectrometry (LC–MS), Fourier transform infrared (FT-IR), ultraviolet visible (UV-Vis), $^{1}$H-NMR, and $^{13}$C-NMR. The new Cu(II) complex was electropolymerized on platinum electrode in a 0.1 mol dm$^{-3}$ solution of lithium perchlorate in acetonitrile by cyclic voltammetry (CV) between 0 and 1.6 V *versus* Ag/Ag$^{+}$.

Downloaded At: 07:19 23 January 2011

## 2. Experimental

### 2.1. *Instrumentation*

All melting points were measured in sealed tubes using an electrothermal digital melting point apparatus (Gallenkamp) and are uncorrected. Vibrational properties were studied on a Perkin Elmer RX-1 FT-IR spectrometer from 4000 to 400 cm$^{-1}$ as KBr pellets. The ultraviolet visible (UV-Vis) spectra were measured using a Perkin Elmer Lambda 25 UV-Vis spectrometer. $^{1}$H-NMR and $^{13}$C-NMR spectra of the Schiff base were recorded at 25°C on a resolution Fourier transform Bruker Biospin 300 MHz spectrometer with tetramethylsilane as an internal standard. Chemical shifts were reported in ppm relative to the solvent peak. Elemental microanalysis of C, H, and N were performed with a LECO-CHNS-932 elemental analyser. Mass spectra were recorded on a LC–MS-APIES AGILENT model 1100 MSD. Metal analysis was carried out by AAS Perkin Elmer 3100 in solutions prepared by decomposing the complex in aqua regia and then digesting in concentrated HCl. Magnetic measurement was carried out with a Sherwood magnetic susceptibility balance (Model MK1) with $CuSO_4 \cdot 5H_2O$ as the calibrant.

All electrochemical studies were conducted at ambient conditions using a CHI 606 model electrochemical analyzer under computer control. The electrochemical cell consisted of a standard three-electrode system; the counter and working electrodes were a platinum sheet (with 2 cm$^{2}$ surface area), and Ag/Ag$^{+}$ electrode was used as the reference. Photographs of non-modified platinum and [CuL] polymer film modified platinum electrodes were taken by a Sony digital camera.

Downloaded At: 07:19 23 January 2011

### 2.2. *Materials*

All starting compounds and solvents for synthesis were purchased from Fluka and Merck. Solvents and reagents were of technical grade and were purified and dried by distillation from appropriate desiccant when necessary. Concentration of solutions after reactions and extractions were achieved using a rotary evaporator at reduced pressure. Analytical and preparative thin layer chromatography (TLC) was performed on silica gel HF-254 (Merck).

### 2.3. *Synthesis of Schiff bases $H_3A$ and $H_2L$*

The precursor ($H_3A$) was prepared according to the modified method described [19, 20] by mono condensation of 2-aminobenzylamine with salicylaldehyde. A two-neck flask equipped with magnetic stirrer, water condenser, and dropping funnel was charged with a dilute solution of the 2-aminobenzylamine (30 mmol) in absolute ethanol (80 $cm^3$). The solution was cooled (−5°C) with stirring, and ethanol solution (40 $cm^3$) of salicylaldehyde (25 mmol) was added dropwise over 30 min. The reaction mixture was stirred for an additional 5 h at the same temperature. The resulting solution was evaporated under vacuum to remove the solvent and excess unreacted aminobenzylamine was extracted by benzene. The structure of $H_3A$ is given in figure 1.

**$H_3A$:** Color: yellow, yield (70%), m.p. 116°C. LC–MS (*m*/*e*): 226.25 g $mol^{-1}$. ($C_{14}H_{14}N_2O$) Found % (Calcd %) C: 74.34 (74.32), H: 6.20 (6.24), N: 12.39 (12.38). FT-IR (KBr, $cm^{-1}$): 3463 $\nu$(OH), 3374–3221 $\nu(NH_2)$, 3024 $\nu$(Ar–H), 2878 $\nu(CH_2)$, 1630 $\nu$(CH=N), and 1278 $\nu$(C–OH). UV-Vis ($\lambda_{max}$, nm, EtOH): 319, 273. $^1$H-NMR ($CDCl_3$ as solvent, $\delta$ in ppm): 13.15 (s, OH), 8.60 (CH=N), 7.40–6.50 (Ar–H), 4.75 ($CH_2$), and 3.70 ($NH_2$). $^{13}$C-NMR ($CDCl_3$ as solvent, $\delta$ in ppm): 163 (CH=N), 161 (C–OH), 145 (C–$NH_2$), 133–115 (Ar), and 59 (–$CH_2$–).

$H_2L$ was synthesized according to the literature [21]. An ethanol solution (20 $cm^3$) of 3-methoxysalicylaldehyde (20 mmol) and 50 $cm^3$ precursor ($H_3A$) (20 mmol) were mixed and refluxed for 4 h. Then, the reaction mixture was cooled to room temperature and allowed to precipitate. After filtering, the residue was washed several times with ethanol and dried in vacuum. The ligand has a honey-like form. The composition of the ligand was confirmed by elemental analysis, FT-IR, UV-Vis, LC–MS, $^1$H-NMR, and $^{13}$C-NMR spectra. The structure of $H_2L$ is given in figure 2.

**$H_2L$:** Yield (85%), color: orange, LC–MS (*m*/*e*): 360.18 g $mol^{-1}$. ($C_{22}H_{20}N_2O_3$) Found % (Calcd %): C: 73.32 (73.30), H: 5.59 (5.63), N: 7.77 (7.75). FT-IR (KBr, $cm^{-1}$): 3447 $\nu$(OH), 3056 $\nu$(Ar–H), 2834 $\nu(CH_2)$, 1630; 1615 $\nu$(CH=N) and 1275; 1254 $\nu$(C–OH).

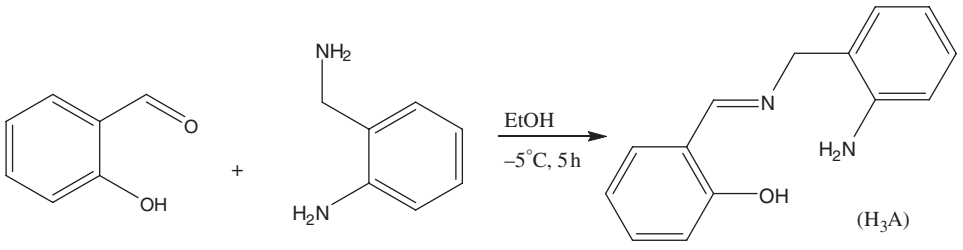



Figure 1. Synthesis of $H_3A$.

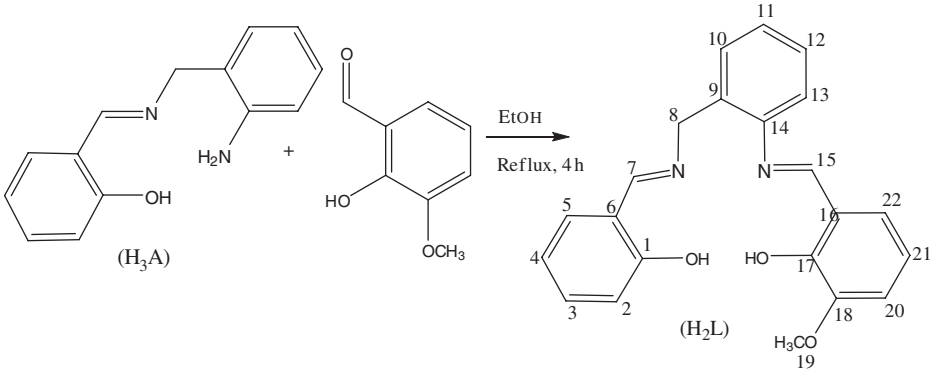



Figure 2. Synthesis of $H_2L$.

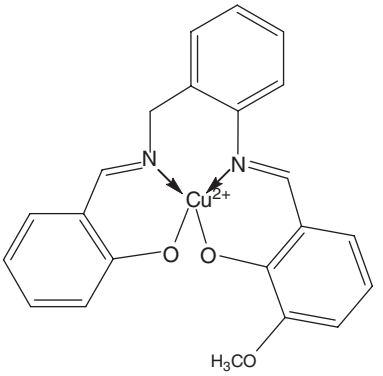


Figure 3. The proposed structure of [CuL].

Downloaded At: 07:19 23 January 2011

UV-Vis ($\lambda_{max}$, nm, EtOH): 320, 270. $^1$H-NMR ($CDCl_3$ as solvent, $\delta$ in ppm): 13.60–13.00 (br, 2H, OH), 8.90 (s, 1H, CH=N–$CH_2$–); 8.65 (s, 1H, CH=N–Ar); 7.50–6.70 (Ar–H), 4.90 (s, 2H, $CH_2$), 3.83–3.74 (d, 3H, $OCH_3$). $^{13}$C-NMR ($CDCl_3$ as solvent, $\delta$ in ppm): 163 (C-7), 162 (C-15), 161.5 (C-1), 151.5 (C-14), 151.0 (C-17), 149.5 (C-18), 133.0 (C-3), 132.0 (C-5), 129.5 (C-9), 128.5 (C-10), 127.2 (C-11), 127.1 (C-12), 124.2 (C-6), 123.8 (C-22), 119.0 (C-4), 118.5 (C-13), 117.2 (C-16), 117.0 (C-2), 116.0 (C-21), 115.0 (C-20), 61 (C-8), and 56 (C-19).

## 2.4. *Synthesis of CuL*

Cu(II) acetate (4 mmol) was dissolved in 20 cm$^3$ methanol and added dropwise to a stirred warm solution of the ligand (4 mmol) in 20 cm$^3$ methanol. The resulting solution was stirred for 2 h. The solid was first filtered, then washed with methanol and diethyl ether, and finally dried in vacuum (figure 3).

**CuL:** Yield (50%), color: green, m.p. $>250^\circ$C. $\mu_{eff}$: 1.78 BM. ($C_{22}H_{18}CuN_2O_3$) Found % (Calcd %): C: 62.59 (62.62), H: 4.36 (4.30), N: 6.62 (6.64), Cu: 15.10 (15.06).

IR (KBr, $cm^{-1}$): 3050 $\nu$(Ar–H), 2828 $\nu(CH_2)$, 1611; 1599 $\nu$(CH=N), 1244; 1214 $\nu$(C–O), 543 $\nu$(Cu–O) and 485 $cm^{-1}$ $\nu$(Cu–N). UV-Vis ($\lambda_{max}$, nm, MeOH): 286, 388, 423 (as a shoulder), and 620.

### 2.5. *Electropolymerization procedure of CuL*

Electrochemical synthesis of the polymeric film was carried out using CV [16]. Poly[CuL] film was deposited by cycling the potential of the working electrode between 0.0 and 1.6 V at 100 mV $s^{-1}$ in 10 polymerization cycles, immersed in an acetonitrile ($CH_3CN$) solution containing 5 mmol $dm^{-3}$ of CuL and 0.1 mol $dm^{-3}$ lithium perchlarate ($LiClO_4$) under nitrogen. After polymerization, the modified electrode was first rinsed with $CH_3CN$ and then twice with distilled water.

## 3. Results and discussion

The elemental analyses are in good agreement with the suggested compositions of the ligand and its metal complex. The ligand is formed in nearly quantitative yield. The yield of the complex is lower perhaps due to steric hindrance around the coordination center [22]. The ligand and its metal complex are soluble in common organic solvents such as MeOH, $CH_3CN$, and THF.

Magnetic measurement of the complex was recorded at room temperature and the effective magnetic moment ($\mu_{eff}$) was 1.78 BM, confirming tetrahedral geometry [19, 23]. A similar complex [Cu(salabza)] prepared from the Schiff base from 2-aminobenzylamine, also has tetrahedral geometry [23]. Elemental analysis (CuL) supports the tetrahedral geometry of [CuL] in this study.

Mass spectra of $H_3A$ and $H_2L$ show peaks at $m/e$ 227 and 361, respectively, attributed to the molecular ion peaks $[M]^+$.

Electronic spectra of $H_3A$, $H_2L$, and [CuL] have been measured in EtOH. The aromatic bands of the compounds in the 270–286 nm range are attributed to benzene $\pi$–$\pi^*$ transitions. Bands in the 320–423 nm range are assigned to imine n–$\pi^*$ transitions. In the spectrum of the complex, bands of the azomethine $\pi$–$\pi^*$ transition are shifted to lower frequencies indicating that the imine nitrogen is involved in the coordination to copper [21]. In addition, the band observed at 620 nm can be assigned to d–d transition of the metal ion [19, 24].

### 3.1. *FT-IR spectra*

FT-IR spectral data are given in table S1 in "Supplementary material." In the spectrum of $H_3A$, bands at 3374–3221 $cm^{-1}$ can be attributed to primary amine vibrations. Therefore, the presence of primary amine group in $H_3A$ prove the mono condensation of 2-aminobenzylamine with salicylaldehyde. The single sharp peak at 1630 $cm^{-1}$ assigned to the CH=N vibration also indicates mono condensation. Disappearance of bands at 3374–3221 $cm^{-1}$ and the presence of a new band at 1615 $cm^{-1}$ (for CH=N) in the spectrum of $H_2L$ proves the condensation of aldehyde of 3-methoxysalicylaldeheyde with amine of $H_3A$. $H_2L$ has two different azomethine groups, Ar–N=CH– and –$CH_2$–N=CH–, observed at 1615 and 1630 $cm^{-1}$, respectively [25, 26].

Downloaded At: 07:19 23 January 2011

In the spectrum of Cu(II) complex of $H_2L$, the O–H modes are no longer observed, denoting that protons are displaced by the metal ion leading to M–O bonding. In addition, the CH=N bands of $H_2L$ shift from 1630 and 1615 $cm^{-1}$ to 1611 and 1599 $cm^{-1}$ after complex formation because of the involvement of nitrogen in coordination [2, 27]. New peaks were observed with low intensity in the FT-IR spectrum of Cu(II) complex at 543 and 485 $cm^{-1}$ assigned to metal–O and metal–N stretching, respectively [27, 28].

For all compounds weak bands observed at 2878–2834 $cm^{-1}$ are assigned to $-CH_2-$ group vibration. The FT-IR spectra of compounds are provided in "Supplementary material."

### 3.2. *$^1$H- and $^{13}$C-NMR spectra*

The $^1$H- and $^{13}$C-NMR spectra of $H_3A$ were recorded in $CDCl_3$ and the spectra of $H_2L$ in DMSO-$d_6$ and $CDCl_3$, respectively. The $^1$H- and $^{13}$C-NMR spectral data of $H_3A$ and $H_2L$ are given in table S2 in "Supplementary material". In the $^1$H-NMR spectrum of $H_3A$, singlets at 8.60 and 3.70 ppm can be attributed to CH=N and $NH_2$, respectively. The singlet at 13.15 ppm is assigned to OH proton of $H_3A$, whereas broad signals in the 13.60–13.00 ppm range are attributed to OH protons, due to different phenolic moieties in the structure of $H_2L$. A new resonance at 3.83–3.74 ppm may be assigned to methoxy. There are two different azomethine groups $-CH_2-N=CH-$ and Ar–N=CH–. The proton of the first is at 8.65 ppm and the other 8.90 ppm, for the ligand [26]. Multiplets in the 7.50–6.70 ppm range can be attributed to protons of benzene rings of both $H_3A$ and $H_2L$. Also, the $-CH_2-$ protons of these compounds are observed at 4.70–4.90 ppm. The $^1$H-NMR spectra of $H_3A$ and $H_2L$ are provided in "Supplementary material".

More detailed information about the structures of the new Schiff bases ($H_3A$ and $H_2L$) is provided by the $^{13}$C-NMR spectral data, which confirm the results of the $^1$H-NMR spectra. The carbons of $CH=N-CH_2-$ are at 163 and 59 ppm, respectively [26]. In the $^{13}$C-NMR spectrum of $H_2L$, two new signals at 162 and 56 ppm are assigned to CH=N and $OCH_3$ carbons, respectively. Carbons of benzene rings are observed at 161.6–115 ppm.

### 3.3. *Electrochemical characterization of the monomer*

Cyclic voltammograms of CuL are shown in figure 4 for different solvent media. In acetonitrile + $LiClO_4$ on the positive scan, one well-defined oxidation peak and two reduction peaks are found, whereas in dichloromethane + $LiClO_4$ no peak can be observed. Therefore, the electrochemical data obtained in acetonitrile of the complex using $LiClO_4$ as a supporting electrolyte are collected.

The ratio of cathodic to anodic peak currents at various scan rates was almost unity (figure 5). The reduction and oxidation peak currents for entrapped $Cu^{2+}/Cu^{3+}$ linearly increase with potential scan rates between 5 and 200 $mV\,s^{-1}$ (figure 5). Linear correlation of the peak current with scan rate shows that the system is similar to a surface-controlled process. These results suggest that all the electroactive Cu(II) in the film has been converted in Cu(III) during the reverse scan. Additionally, the difference in potential between the anodic peak and the cathodic peak was practically constant over the range of scan rates; such behavior may be due to a good interaction between the electrode and the site of activation of the polymer (metallic cation) [29].

Downloaded At: 07:19 23 January 2011

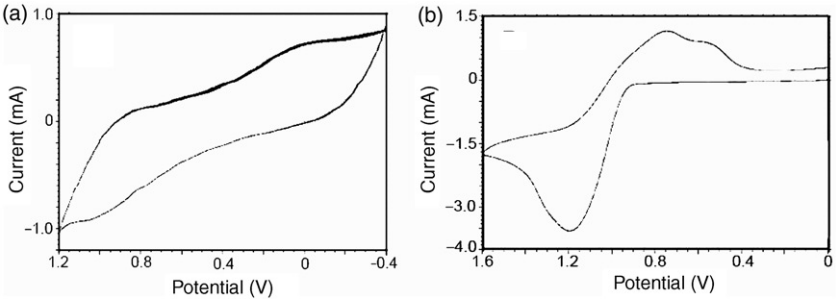



Figure 4. CV of [CuL] monomer (*ca* 5 mmol dm$^{-3}$) in dichloromethane + $LiClO_4$ (a) and in acetonitrile + $LiClO_4$ (b) on Pt at scan rate 100 mV s$^{-1}$. Potentials are referred to Ag/Ag$^+$.

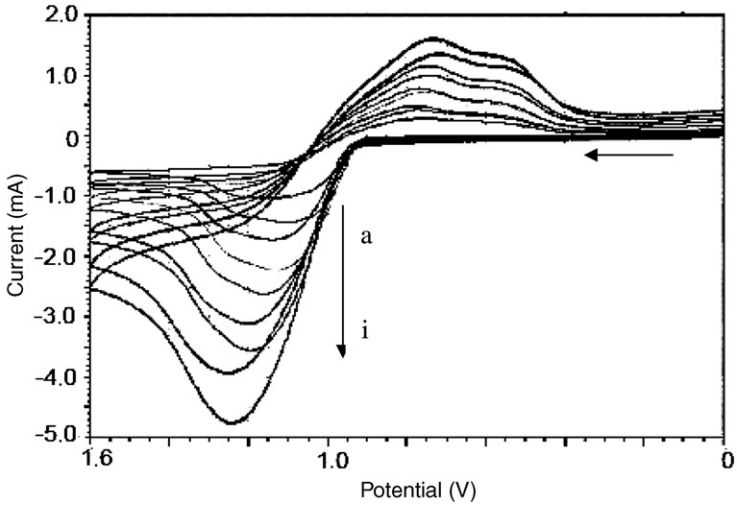



Figure 5. CV of [CuL] (*ca* 5 mmol dm$^{-3}$) in acetonitrile + $LiClO_4$ on Pt sheet electrode at various scan rates (mV s$^{-1}$): (a) 5; (b) 10; (c) 20; (d) 30; (e) 50; (f) 80; (g) 100; (h) 150; and (i) 200. Potentials are referred to Ag/Ag$^+$.

The peak current changes linearly with scan rate ($v$) according to equation $I_p = Av^x$. The $x$ values 1.0 and 0.5 are expected for adsorption and diffusion controlled reaction, respectively. For 5 mmol dm$^{-3}$ [CuL] monomer, the regression of log($I_p$) *versus* log($v$) gave a slope of 0.4 (figure 6), indicating that the reduction current had contributions from diffusion current [30, 31].

### 3.4. *Electropolymerization of CuL*

Cyclic voltammograms in 0.1 mol dm$^{-3}$ $LiClO_4/CH_3CN$ of CuL are very similar to those observed for solutions of nickel complexes with the same ligands (figure 7) [15, 16]. They are typical of irreversible systems, showing a continuous increase in current intensity with the number of scan cycles, reflecting the accumulative electrosynthesis of an electroactive polymer.

Downloaded At: 07:19 23 January 2011

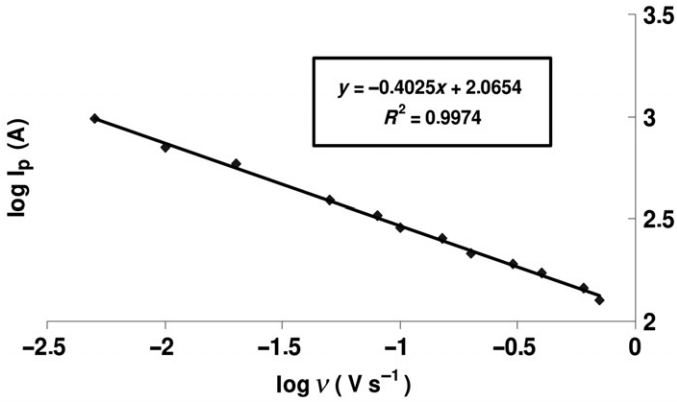



Figure 6. Logarithm of anodic peak current as a function of logarithm of scan rate in the range 5–700 mV $s^{-1}$.

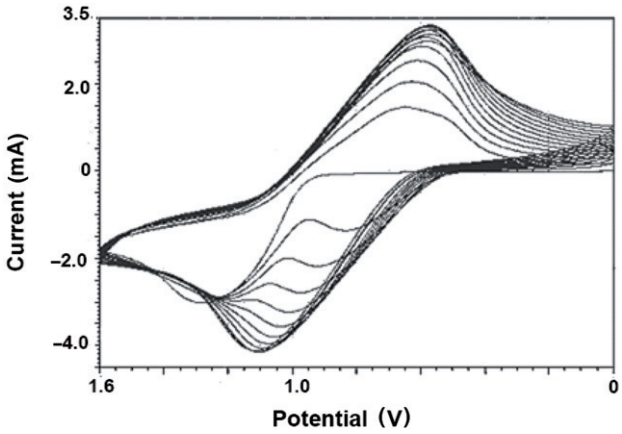



Figure 7. Series of sequential cyclic voltammograms for anodic polymerization of 1 mmol $dm^{-3}$ [CuL]/0.1 mol $dm^{-3}$ $LiClO_4/CH_3CN$ at a Pt sheet electrode, between 0.0 and 1.6 V for 12 polymerization scans ($\nu = 0.100$ V $s^{-1}$).

The first scan is different from the subsequent ones and shows one well-defined anodic peak at 1.21 V, and the cathodic process consists of low intensity wave at 0.73 V for CuL. After the first cycle, a new anodic broad peak appears at *ca* 0.83 V. Together with the wave at 0.73 V, they grow continuously with the number of polymerization cycles. For poly[CuL], the peak at 0.73 V shifts slightly toward more negative potential, and the new peak at 0.83 V shifts slightly toward more positive potential after each consecutive cycle.

Peak current intensities at $\nu = 0.1$ V $s^{-1}$ during polymerization cease to increase after about 12 polymerization scans for poly[CuL], and then slowly start to decrease. Visual inspection of the working electrode after cycling in monomer solution shows a green insoluble film on the Pt surface (Supplementary material).

Consecutively increasing currents for both anodic and cathodic peaks demonstrate that [CuL] films are continuously deposited on the electrode surface with increasing

Downloaded At: 07:19 23 January 2011

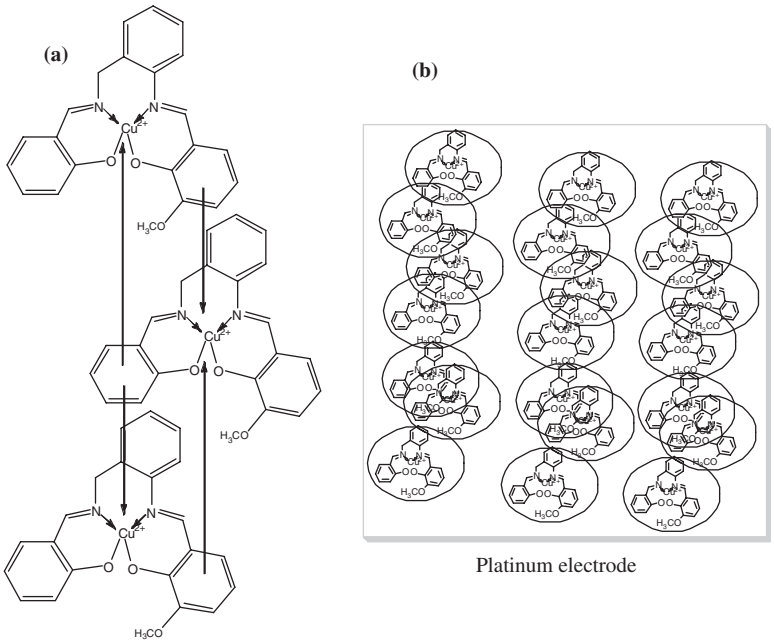



Figure 8. Scheme of electropolymerization mechanism of [CuL] on platinum electrode (a) and platinum electrode modified by nanostructured poly-[CuL] film (b).

Downloaded At: 07:19 23 January 2011

number of potential scans. In each successive cycle of polymerization of the complex, the cathodic/anodic peaks (0.73 and 0.83 V *vs.* $Ag/Ag^{+}$) corresponding to the redox process between $Cu^{2+}$ and $Cu^{3+}$ shifted for more positive potentials. The mechanism of the electrooxidative polymerization of the copper complex still remains unclear. However, according to previously reported data on the anodic oxidation of metal salen complexes [18], the polymerization occurs for a potential peak of about 1.09 V *versus* saturated calomel electrode (SCE), which corresponds to electron transfer from predominantly ligand-centered orbitals [32]. Visual inspection of the electrode surface showed the deposition of a green film; as this film was not dissolved upon subsequent anodic or cathodic scans, we have concluded that the product of oxidation of [CuL] is also a polymeric material (figure 8) [18].

Electrochemistry of the poly[CuL]-Pt and bare Pt in 0.1 mol dm$^{-3}$ $LiClO_4/CH_3CN$ are shown in figure 9. The surface CVs of the poly[CuL] films, carried out in a monomer-free acetonitrile + 0.1 mol L$^{-1}$ $LiClO_4$ solution, demonstrate that the deposited film at the surface has one anodic and one cathodic peak, although bare Pt electrode is electroinactive, from 0 to +2.0 V. This implies that the film is electroactive against positive scans up to 2.0 V.

The method of Sharp *et al.* [33] was used to roughly estimate the surface coverage of the electrode by background-corrected electric charge (Q). According to this method, the relation between the peak current and the surface coverage is given as

$$I_{pa} = \frac{n^2 F^2 A \Gamma v}{4\mathrm{RT}} \tag{1}$$

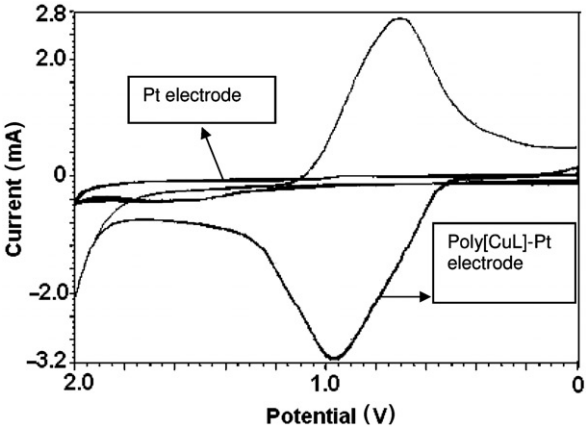



Figure 9. Cyclic voltammograms of bare Pt electrode and poly[CuL] on Pt electrode as working electrode in 0.1 mol dm$^{-3}$ $LiClO_4/CH_3CN$. Potentials are referred to $Ag/Ag^+$.

Downloaded At: 07:19 23 January 2011

where $n$ represents the number of electrons involved in the redox pair, $A$ is the area of the electrode (0.2 cm$^2$), $\Gamma$ is the surface coverage (mol cm$^{-2}$), $\nu$ is the scan rate (V s$^{-1}$), and $R$ is the gas constant (8.314 VCK$^{-1}$ mol$^{-1}$); and other symbols have their usual significance. The calculated surface coverage is based on depositions carried out with three separate electrodes and the values are not very much different from each other. The average surface coverage was found to be $4.6 \times 10^{-9}$ mol cm$^{-2}$. To obtain an ultra thin membrane bound to the electrode surface, 12 cycles of potential scans were performed during the electropolymerization.

## 4. Conclusion

Synthesis and characterization of a new Schiff base and its complex with Cu(II) suggest that the tetradentate ligand coordinates to Cu(II) through the phenolic oxygen and azomethine nitrogen. Use of this metal complex in the preparation of a modified electrode is also described. The unsymmetrical Cu(II) complex was electropolymerized on a platinum electrode surface and electrochemical properties of this nanostructured polymeric film have been investigated. In view of its stability, low working potential, simplicity, and low cost of construction, the polymer [CuL] film shows promising characteristics for investigation as sensor for the analysis of real samples, containing fine particles, deep color, or high viscosity. This new electrode may find application in catalytic reduction and oxidation reactions due to the unsymmetrical geometry of [CuL].

## Acknowledgments

The authors are grateful to the Science Research Fund of the Çukurova University in Turkey for supporting this study (project no. FEF2009YL-3) and to the Department of Chemistry of Mustafa Kemal University for allowing the use of its laboratory facilities.

## References


[1] R.H. Holm, G.W. Everett, A. Chakravorty. *Prog. Inorg. Chem.*, **7**, 83 (1966).
[2] M. Tümer, H. Köksal, S. Serin. *Transition Met. Chem.*, **24**, 13 (1999).
[3] A.D. Garnovskii, I.S. Vasilchenko, D.A. Garnovskii, B.I. Kharisov. *J. Coord. Chem.*, **62**, 151 (2009).
[4] Z.L. You, H.L. Zhu. *Anorg. Allg. Chem.*, **630**, 2754 (2004).
[5] A. Gölcü, M. Tümer, H. Demirelli, R.A. Wheatley. *Inorg. Chim. Acta*, **358**, 1785 (2005).
[6] M. Tümer, H. Köksal, M.K. Şener, S. Serin. *Transition Met. Chem.*, **24**, 414 (1999).
[7] E.G. Samsel, K. Srinivasan, J. Kochi. *J. Am. Chem. Soc.*, **107**, 7606 (1985).
[8] M. Shamsipur, A.R. Ghiasvand, H. Sharghi, H. Naeimi. *Anal. Chim. Acta*, **408**, 271 (2000).
[9] J. Satio, M. Mitani, S. Matsui, J. Mohri, S. Kojoh, N. Kashiwa, T. Fujita. *Angew. Chem. Int. Ed.*, **40**, 2918 (2001).
[10] R.K. O'Reilly, V.C. Gibson, A.J.P. White, D.J. Williams. *J. Am. Chem. Soc.*, **125**, 450 (2003).
[11] M. Shamsipur, S. Sadeghi, H. Naeimi, H. Sharghi. *Polish J. Chem.*, **74**, 231 (2000).
[12] A.R. Khorrami, H. Naeimi, A.R. Fakhari. *Talanta*, **64**, 13 (2004).
[13] R.P. Kingsborough, T.M. Swager. In *Progress in Inorganic Chemistry*, K.D. Karlin (Ed.), Vol. 48, pp. 123–231, Wiley, New York (1999).
[14] C.E. Dahm, D.G. Peters. *J. Electroanal. Chem.*, **406**, 119 (1996).
[15] M. Vilas-Boas, C. Freire, B. Castro, A.R. Hillman. *J. Phys. Chem.*, **B102**, 8533 (1998).
[16] M. Martins, M. Vilas-Boas, B. Castro, A.R. Hillmanan, C. Freire. *Electrochim. Acta*, **51**, 304 (2005).
[17] L. Mao, K. Yamamoto, W. Zhou, L. Jin. *Electroanalysis*, **12**, 72 (2000).
[18] T.R.L. Dadamos, M.F.S. Teixeira. *Electrochim. Acta*, **54**, 4552 (2009).
[19] M. Tümer, D. Ekinci, F. Tümer, A. Bulut. *Spectrochim. Acta, Part A*, **67**, 916 (2007).
[20] D.M. Boghaei, M. Lashanizadegan. *Synth. React. Inorg. Met.-Org. Chem.*, **30**, 1393 (2000).
[21] C. Çelik, M. Tümer, S. Serin. *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 1839 (2002).
[22] M. Tümer, B. Erdoğan, S. Serin, M.Y. Nutku. *Synth. React. Inorg. Met.-Org. Chem.*, **28**, 529 (1998).
[23] M. Sasaki, K. Manseki, H. Horiuchi, M. Kumagai, M. Sakamoto, H. Sakiyama, Y. Nishida, M. Sakai, Y. Sadaoka, M. Ohba, H. Okawa. *J. Chem. Soc., Dalton Trans.*, 259 (2000).
[24] P.S. Subramanian, E. Suresh, P. Dastidar. *Polyhedron*, **23**, 2515 (2004).
[25] M. Vazquez, M.R. Bermejo, M. Fondo, A.M. Garcia-Deibe, J. Sanmartin, R. Pedrido, L. Sorace, D. Gatteschi. *Eur. J. Inorg. Chem.*, 1128 (2003).
[26] C. Demetgül, M. Karakaplan, S. Serin, M. Diğrak. *J. Coord. Chem.*, **62**, 3544 (2009).
[27] C. Demetgül, M. Karakaplan, S. Serin. *Des. Monomers Polym.*, **11**, 565 (2008).
[28] H. Köksal, M. Dolaz, M. Tümer, S. Serin. *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 1141 (1997).
[29] A.J. Bard, L.R. Faulkner. *Electrochemical Methods: Fundamentals and Applications*, 2nd Edn, Wiley, New York (2001).
[30] A. Sevcik. *Czech. Chem. Commun.*, **20**, 327 (1948).
[31] N. Menek, Y. Karaman. *Dyes Pigm.*, **68**, 101 (2006).
[32] S.V. Vasil'eva, I.A. Chepurnaya, S.A. Logvinov, P.V. Gaman'kov, A.M. Timonov. *Russ. J. Electrochem.*, **39**, 310 (2003).
[33] M. Sharp, M. Petersson, K. Edstrom. *J. Electroanal. Chem.*, **95**, 123 (1979).


Downloaded At: 07:19 23 January 2011