Journal of Natural Sciences Research www.iiste.org
ISSN 2224-3186 (Paper) ISSN 2225-0921 (Online)
Vol.8, No.19, 2018

Synthesis, Spectroscopic, Structural Characterization, Conductivity and Electrochemical Studies of a Schiff Base Ligand and Its Copper Complexes

Atinafu Abayneh Sisay Tadesse* MahduThomas*
Hawassa University, College of Natural and Computational Sciences, Department of Chemistry, P.O.Box 05, Hawassa, Ethiopia

Abstract

Electrochemical behaviors of a Schiff base ligand (L) derived from Glyoxal and 4-aminoantipyrine and its chloride and nitrate Cu(II) complexes were carried out by cyclic voltametric studies. The ligand (L) has been characterized by IR, NMR and electronic spectral studies. Cu(II) complexes of a Schiff base ligand from4-aminoantpyrine and glyoxal having the composition $[CuL_1]x_2$ where x = Cl^- or NO_3^- have been prepared and characterized by elemental analysis, electrical conductivity in non- aqueous solvent, infrared and electronic, as well as cyclic voltammetric studies. L acts as a neutral tetra-dentate ligand coordinating through both the carbonyl oxygen and azomethine nitrogen. On both the complexes both the anions are not coordinated. A square planar geometry is assigned for complexes. The electrochemical studies of ligand show a typical cyclic voltammogram for an irreversible process. While copper(II) complexes show the typical cyclic voltammograms for quasi reversible process.

Keywords: Schiff base ligand, Schiff base copper(II) complexes, cyclic voltammetry

1.. Introduction

A large number of Schiff bases and their complexes have been studied for their interesting and important properties, e.g; their ability to reversibly bind oxygen [1], catalytic activity in hydrogenation of olefins and transfer of an amino group [2], photochromic properties [3], and complexing ability towards some toxic metals [4]. The high affinity for the chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes.

Schiff bases are condensation products of primary amines and carbonyl compounds and they were discovered by a German chemist, Nobel Prize winner, Hugo Schiff in 1864 [5]. In the recent decades, Schiff bases have attracted tremendous interests due to their unique properties and extensive applications in many scientific areas, e.g. anticancer[6] and antibacterial [7], biosensor [8], catalysis[2], analytical chemistry [9] and corrosion prevention[10].

Structurally, Schiff base (also known as imine or azomethine) is an analogue of a ketone or aldehyde in which the carbonyl group (C=O) has been replaced by an imine or azomethine group. Schiff bases are compounds having a formula RR'C=NR'' where R is an aryl group, R' is a hydrogen atom and R'' is either an alkyl or aryl group. However, usually compounds where R'' is an alkyl or aryl group and R' is an alkyl or aromatic group are also counted as Schiff bases. Schiff base ligands are essential in the field of coordination chemistry, especially in the development of complexes of Schiff bases because these compounds are potentially capable of forming stable complexes with metal ions [11].

During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors [12]. This may be attributed to their stability, biological activity and potential applications in many fields such as oxidation catalysis, electrochemistry, etc. In this study, the synthesis of a Schiff base ligand (L) and its Cu(II) complexes were reported. Their spectral properties and electrochemical behavior were investigated.

2. Experimental Part

2.1 Instrumental measurements

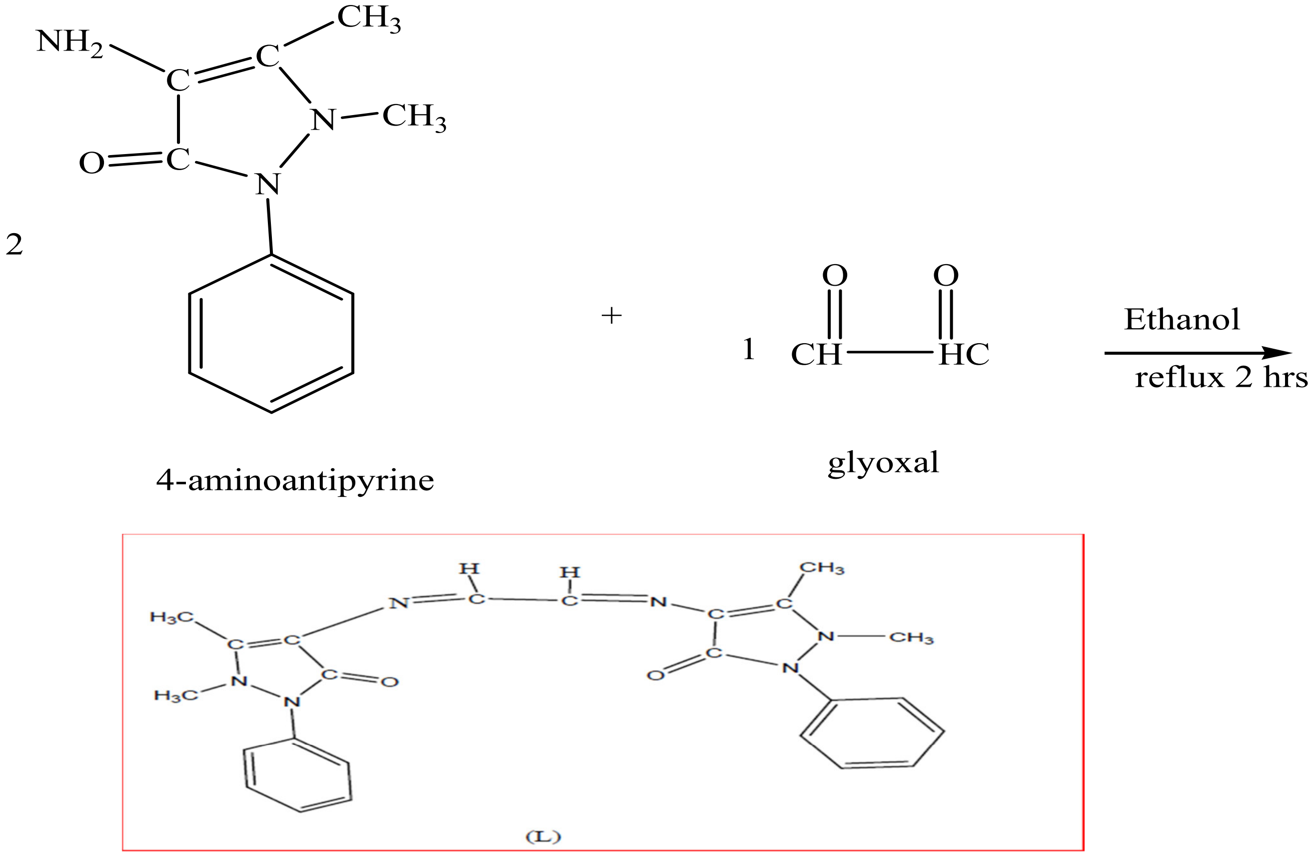
IR spectra were recorded on a PERKIN ELMER SPECTRUM 65 FT-IR spectrometer on KBr pellet in the wave number range of 4000– 400 cm^{-1}. Electronic spectral studies were conducted on a GENESY's UV-Visible spectrometer in the wavelength 200–800 nm. Nuclear Magnetic Resonance (NMR) analysis was recorded on a Brukeravance 400MHz spectrometer with tetramethylsilane as internal standard and DMSO-d^6 as solvent. FAAS(Buck scientific, model 210 VGP AAS, USA). Molar conductivity was measured with a SX713 model conductivity meter, using prepared solution of the complex in acetonitrile. All the electrochemical experiments were carried out using a computerized electrochemical analyzer (BAS CV-50W) with a conventional three electrode system at room temperature. Studying the electrochemical activity was conducted using a standard three-electrode cell. The electrodes consisted of a glassy carbon electrode (diameter = 3 mm) as working electrode, Ag/AgCl/ quasi reference electrode as the reference electrode, and a platinum wire as counter electrode. 10^{-4} M concentration of the ligand and copper(II) complexes were dissolved in DMF and electrochemical grade Tetra butyl ammonium hexafluoro phosphate (0.01 mol/dm^3) was employed as the supportingelectrolyte.

2.2 Chemicals

Cupric chloride dihydrate ($CuCl_2.2H_2O$) (Sigma-Aldrich), Na_2CO_3 (Sigma-Alderich), $CuCO_3$, $CuCl_2$, and $Cu(NO_3)_2$ were freshly prepared from Cupric chloride dihydrate ($CuCl_2.2H_2O$) and Na_2CO_3. HCl (BDH), HNO_3 (BDH), Methanol (BDH), DMF (Sigma-Aldrich), Tetrabutylammoniumhexafluorophosphate (Fluka), Ethyl acetate (Sigma-Alderich), Acetonitrile (BDH) and Diethyl ether (Sigma-Alderich), are analytical grade reagents and were used without further purification. Ethanol was distilled before use. Glyoxal (Aldrich Chem. Co. USA), 4-Aminoantipyrine (Sigma Chem. Co USA) were also used without any further purification.

2.3 Preparation of the Schiff Base

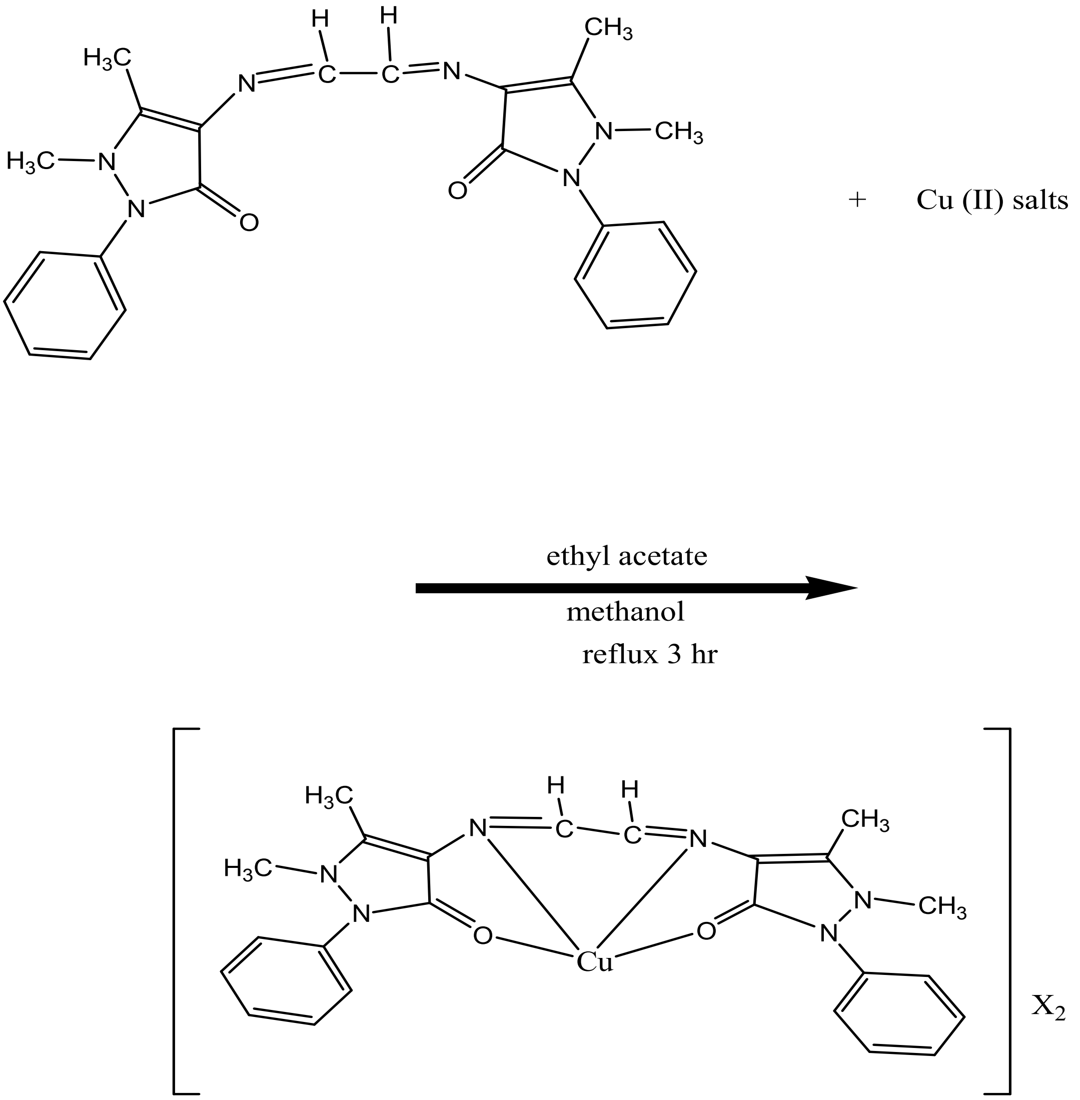
The Schiff base ligand was prepared by the condensation of the 4-Aminoantpyrine 0.44715 g (2.2mmol) with 0.057 ml (1mmol) Glyoxal in absolute ethanolic solution. The resulting mixture was then refluxed for 2hrs. The yellow precipitate formed was filtered and recrystalized from ethanol to give yellow needles.



Scheme 1 Structure of Schiff base ligand derived from glyoxal and 4-aminoantipyrine

2.4 Preparation of the Schiff base copper(II) complexes

Cupric chloride 0.170 g (1 mmole) and copper nitrate 0.18756 g (1 mmole) were dissolved in methanol 5ml and added in toa refluxing solution of Schiff base 0.4280 g (1 mmole) in ethyl acetate. The reaction mixtures were refluxed for 3 hrs. The complexes were separated as brown solid is cooled, filtered and repeatedly washed with hot ethyl acetate to remove excess ligand if any. It is then dried in a vaccum in a desiccator over P_2O_5.



Where X= Cl or NO_3

Scheme 2. Structure of copper (II) complexes

2.5 Electrochemical studies

Electrochemical cyclic voltammetry measurements were performed at room temperature in 3-electrode cell by using a glassy carbon electrode with 0.071 cm^2 surface area as a working electrode, while a platinum wire served as the counter electrode and a Ag/AgCl quasi reference electrode as the reference electrode. The electrochemical studies were conducted with DMF solution of all the ligand and complexes (1×10^{-4} M) and tetrabutylammoniumhexafloro- phosphate (0.01 M) as supporting electrolyte. Measurements were made over a potential range between 0 V to +1.6 V for Schiff base ligand (L) and copper (II) nitrate complexes and 0 V to 0.9 V for copper(II) chloride complex with a scan rate of 0.1 V/ s.

3 Results and Discussion

3.1 Proton NMR spectra of ligand (L)

^{1}H NMR of the ligand in DMSO-d^6 solution shows that it is NMR active and the data depicted in the Figure 6 below adequately supports the facts drawn on the basis of UV-Vis and IR spectral data. The ^{1}H NMR spectrum of the free ligand showed a singlet at 9.25 ppm due to the imine protons, multiplet in the range 7.1–8.0 ppm due to the aromatic protons, signals appearing at 3.10-3.50 δ correspond to methyl protons near to hetro-cyclic atoms and signals at 2.8 - 2.10 δ correspond to methyl protons [13].

Table 1. Chemical shift data of ligand

Compound	Chemical shift (δ, ppm)	Assignment
L	9.25	CH=N– imine protons
	7.8-7.1	Phenyl ring protons
	3.5-3.1	Protons near to hetro-atoms
	2.8-2.1	Methyl protons

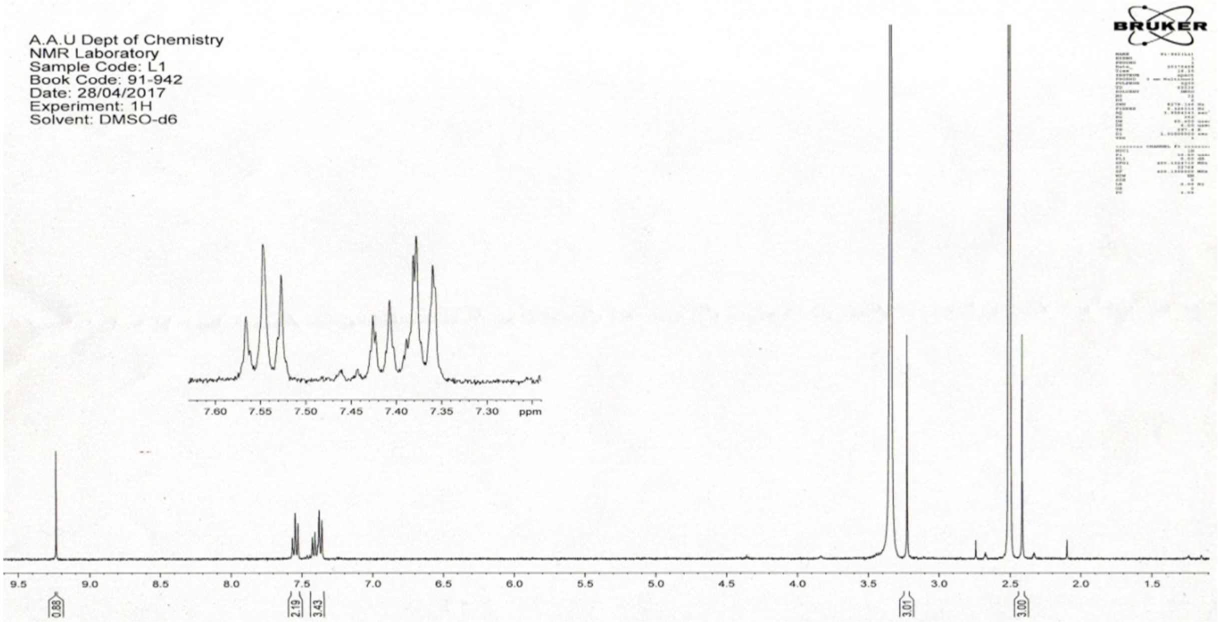


Figure 1. Proton NMR spectra

3.2 Appearance and solubility of the complexes

The Copper(II) complexes are brown solids. They are soluble in acetonitrile, dimethyl formamide, ethanol, and methanol, but insoluble in ethyl acetate.

3.3 Elemental analysis and electrical conductance

Table 2. Elemental analyses and electrical conductance data of copper(II) complexes

Compound	M.Wt	Color	%Cu (calcd.)	% Cu (Found)	Molar conductance ($\Omega^{-1}Cm^2mol^{-1}$)
$[CuL_1]Cl_2$	562.5	Brown	(11.28)	(11.2)	240
$[CuL_1](NO_3)_2$	615.5	Dark brown	(10.35)	(10.32)	235

The molar conductance values of the chloride and nitrate complexes of L_1 (10^{-3} M solution) in acetonitrile, fall in the range expected for 1:2 electrolytes[14]. Thus the complexes may be formulated as $[CuL_1Cl_2]$and $[CuL_1 (NO_3)_2]$ (where X = NO_3^- or Cl^-)

3.4 Infrared spectra of ligand and its copper complexes

The important infrared spectral bands of L and its copper complexes with the tentative assignments are presented in Table 3.

Table 3 Important infrared spectra bands (cm^{-1}) of ligand and its copper complexes

Compound	ν (C=O)	ν (C=N)	ν (M-N)	ν (M-O)	V_2 (ionic nitrate)
Ligand (L)	1659	1563	-	-	-
$[Cu(L)_1] Cl_2$	1635	1584	502	590	
$[Cu(L)_1] (NO_3)_2$	1620	1584	520	573	1374

The infrared spectrum of L exhibits two strong bands at 1659 and 1653 cm^{-1} corresponding to the stretching vibrations of the carbonyl groups of the ligand also exhibits a strong band at 1563 cm^{-1} due to the C=N stretching vibration [15]. The infrared band at 1659 cm^{-1} characteristic of the $\nu_{C=O}$ is shifted to 1635 cm^{-1} in the chloride complex and 1620 in nitrate complex indicating that the coordination of both carbonyl oxygen to the central metal ion. Also the band at 1563 cm^{-1} corresponds to C =N stretching is shifted to 1584cm^{-1} in chloride and nitrate complex indicating the coordination of both azomethinenitrogens to the central metal ion. A strong peak at 1374 cm^{-1} which is corresponds to the ν_2 out ofplane deformation of the nitrate is also seen in the nitrate complex which is concordancewith the conductance data [15].Further the ν_{Cu-O} and ν_{Cu-N} stretching vibrations are observed at about 520 and 502 cm^{-1} respectively in both complexes.

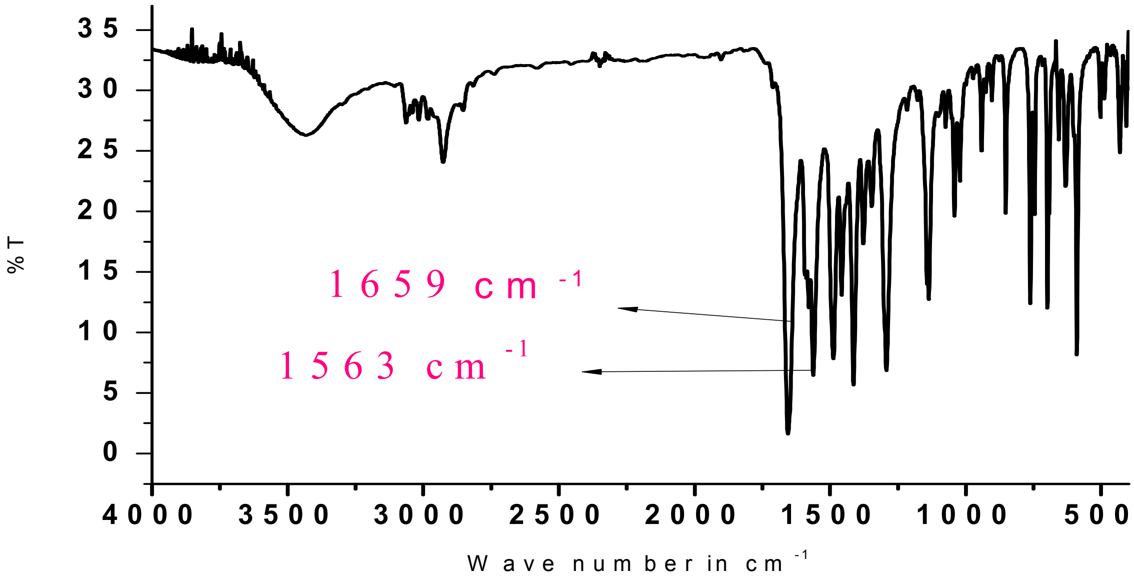


Figure 2. IR spectra of ligand(L)

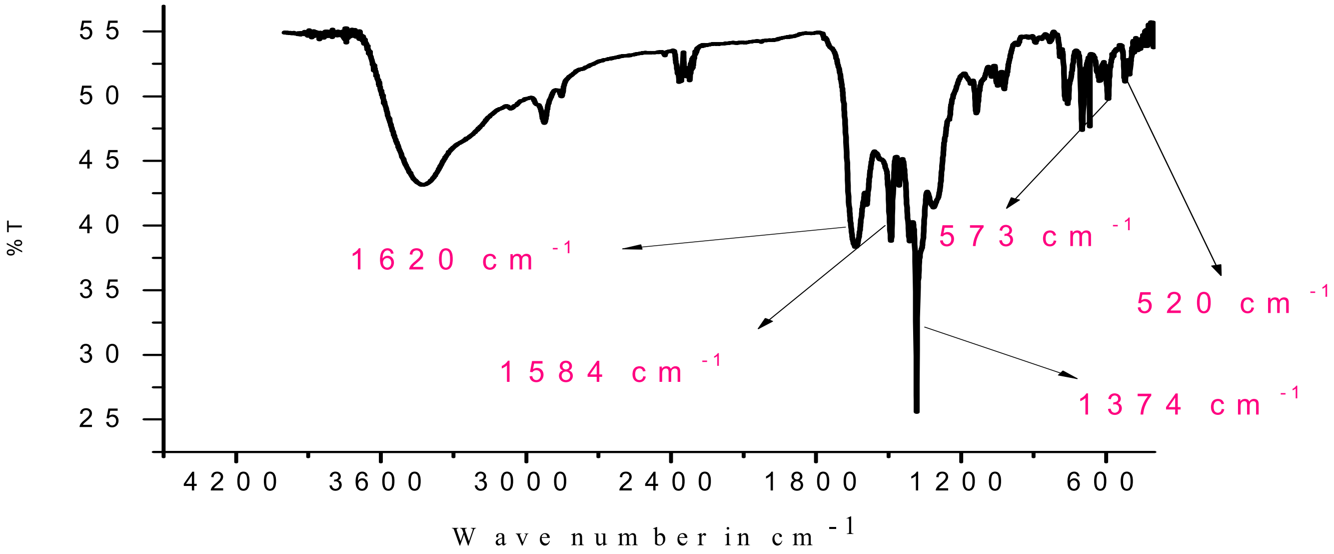


Figure 3. IR spectrum of chloride complex

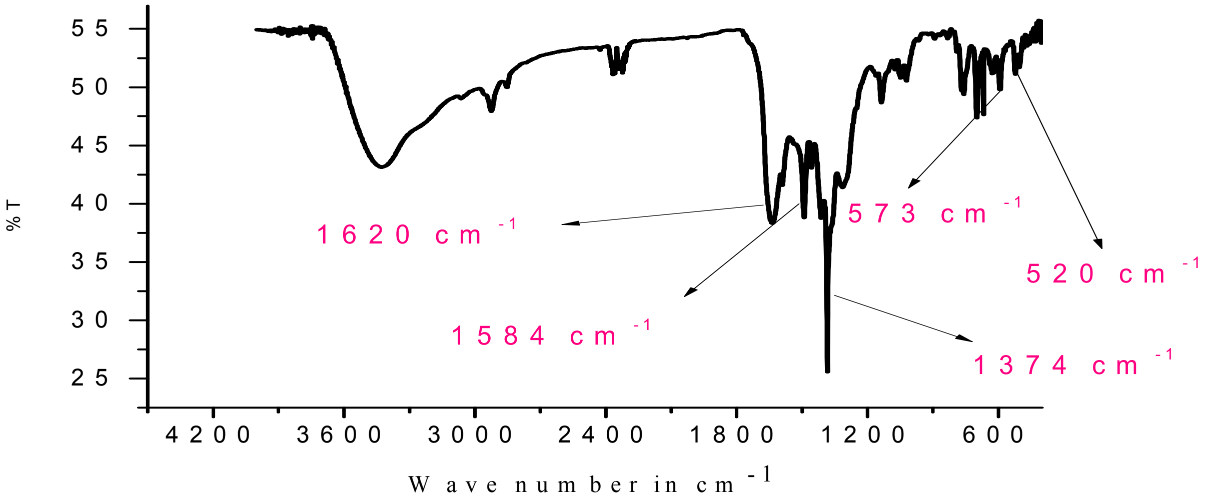


Figure 4. IR spectrum of Nitrate complex

3.5. Electronic spectral studies

The electronic spectral bands of L and its copper complexes with tentative assignments are presented in Tables 4.

Table 4. Electronic spectra data of ligand and copper(II) complexes

Compounds	Abs. max. cm^{-1}	Tentative assignment
Ligand (L)	39525 26881	π→π* n→π*
[CuL$_1$] Cl$_2$	45248 39840 27322	π→π* π→π* n→π*
[CuL$_1$](NO$_3$)$_2$	40000 26178 21739	π→π* n→π* d-d transition

The electronic spectra of L shows two band maxima at 26881 and 39525 cm^{-1} corresponding to n→π* and π→π* transitions respectively [16]. In copper(II) complexes, both the n→π* and π→π* bands are found to be blue shifted and appeared in the region 26178 -27322 cm^{-1} and 39840-45248 cm^{-1} respectively compared to that of L. The spectra of nitrate complex exhibit a band at 21739 cm^{-1} corresponding to the d-d transition consistent with square planar copper(II) complexes. The electronic spectra of chloride complex shows three band maxima at 45248 and 39840 cm^{-1} for π→π* and 27322 cm^{-1} corresponding to n→π* transitions respectively. In chloride complex, the d-d transition cannot be visible because it may be masked by the strong MLCT [16].

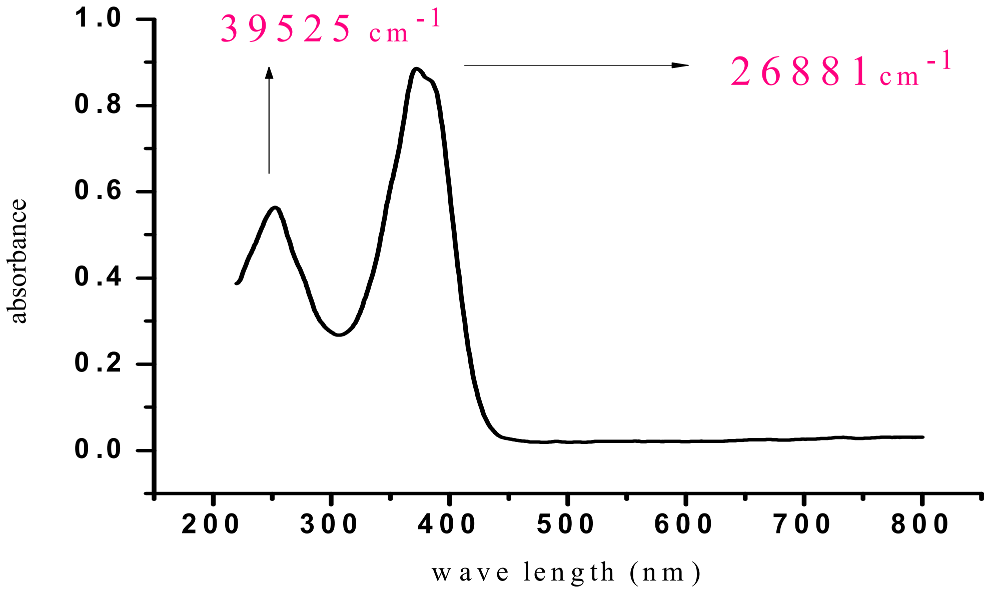


Figure 5 UV-Vis spectrum of ligand

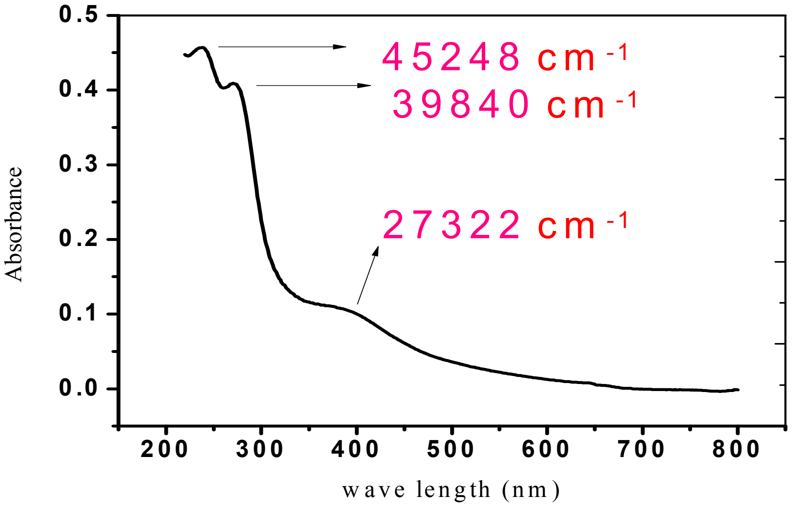


Figure 6. UV-Vis spectrum of chloride complex

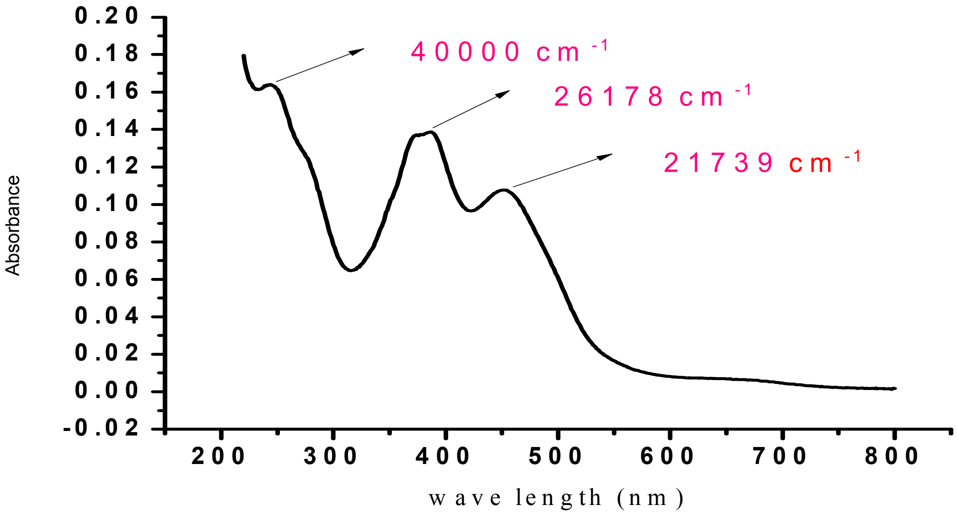
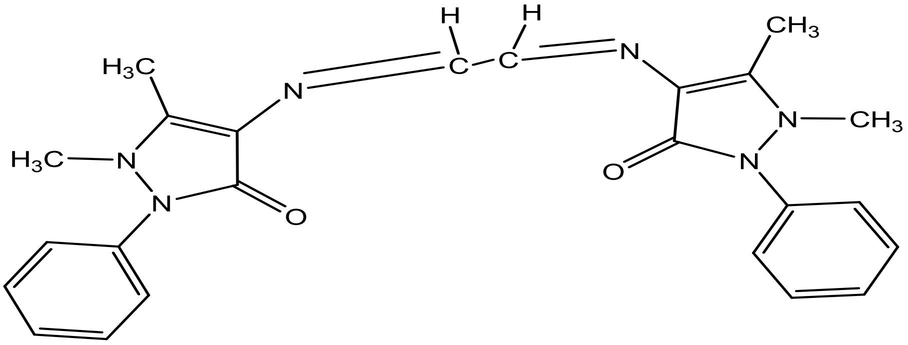
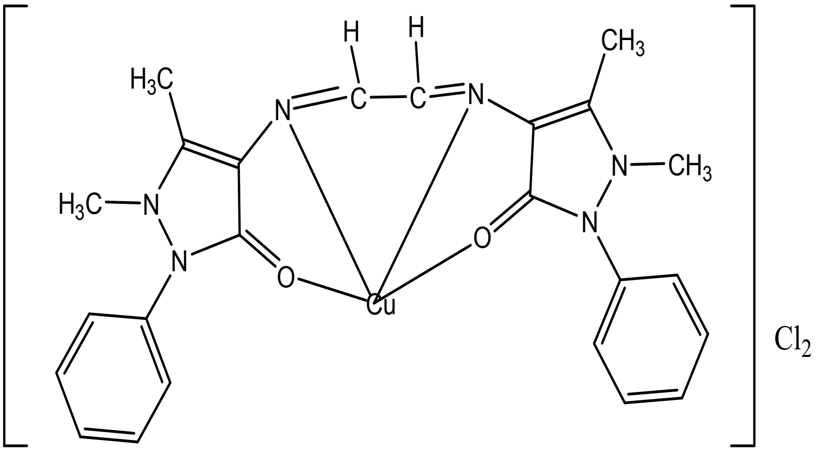


Figure 7. UV-Vis spectrum of nitrate complex

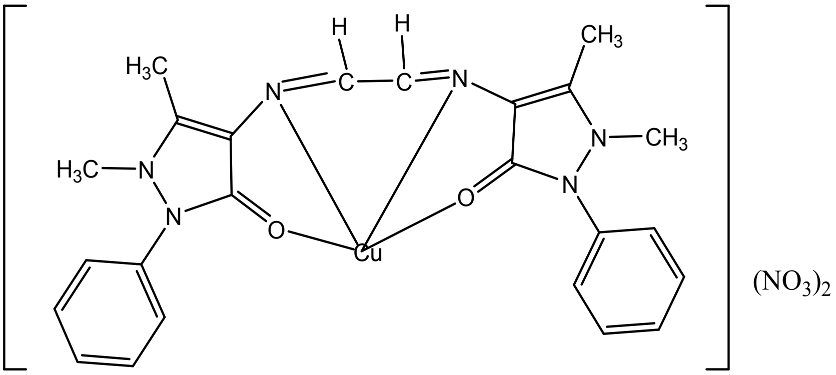
Based on the above studies the following tentative structures can be proposed for the ligand and complexes.



Scheme 3. Proposed structure of the ligand derived from glyoxal and 4-aminoantipyrine



Scheme 4. Proposed structures of chloride complex



Scheme 5 .Proposed structure of Nitrate complex

3.6 Cyclic voltammetry

The ligand (L) and copper (II) complexes were subjected to cyclic voltammetric studies with a view to examine its electrochemical behaviour. A glassy carbon electrode was used as working electrode, Ag/AgCl quasi reference electrode as reference electrode and platinum wire as auxiliary electrode. The electrochemical studies were conducted with DMF solution of all the ligand and complexes (1 × 10^{-4} M) and tetrabutylammoniumhexafloro- phosphate (0.01 M) as supporting electrolyte. Measurements were made over a potential range between 0 V to +1.6 V for Schiff base ligand (L) and copper (II) nitrate complexes and 0 V to 0.9 V for copper (II) chloride complex with a scan rate of 0.1 V/ s.

Table 5. Voltammetric data for ligand and complexes in DMF solution containing 0.01 M Tetrabutylammoniumhexafluorophosphate. Scan rate (v) =100 mV/s.

Table 5. Voltammetric data of ligand and Cu(II) complexes

	Scan rate (mV/s).	I_{pc}(μA)	I_{pa}(μA)	i_{pa}/i_{pc}	E_{pc}(mV)	E_{pa}(mV)	ΔEp(mV)
A	100	0.04			-	819	819
B	100	59.2	86.2	1.456	326	712	386
C	100	8.9	20.4	2.29	389	1064	675

The CV of the Schiff base ligand (L) which exhibited one irreversible oxidation peak as a result of a large peak separation value (ΔEp = 819 mV) at 0.100 V/ s scan rate. A cyclic voltammogram of Cu(II) chloride complex displays a reduction peak at Epc= -326 mV with an associated oxidation peak at Epa= 712 mV at a scan rate of 100 mV/s. The peak separation of this couple (ΔEp) is 386 mV. The ratio of anodic to cathodic peak height was greater than one. However, the peak current increases with the increase of the square root of the scan rates. This establishes the electrode process as diffusion controlled [17]. The copper nitrate complex exhibited two quasi-reversible peaks. The representative CV of copper nitrate complex is shown in Figure 10. A cyclic voltammogram of nitrate displays two reduction peaks. On the first positive potential sweep, the complex shows an anodic oxidation peaks at Epa(I) = 695 mV and Epa(II) = 1064 mV. The complementary reduction peaks on the negative potential sweep appear at Epc(I) = 134 mV and Epc(II) = 389 mV: corresponding to the Cu(II)/Cu(I). The value of ΔEp is 561 mV and 675 mV for first and second redox couples respectively and increases with scan rate giving evidence for quasi-reversible nature associated with one electron reduction. The ratio of the anodic to cathodic peak current (Ipa/Ipc) is deviates from one. From these observations it is concluded that the redox process is diffusion controlled.

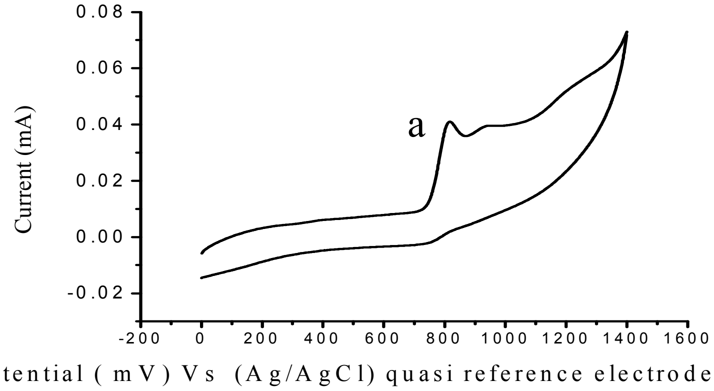


Figure 8. Cyclic voltammogram of 1x10^{-4} M of Schiff base ligand at glassy carbon electrode in DMF solution containing 0.01 M Tetrabutylammoniumhexafluorophosphate. Scan rate (v) = 100 mV/s.

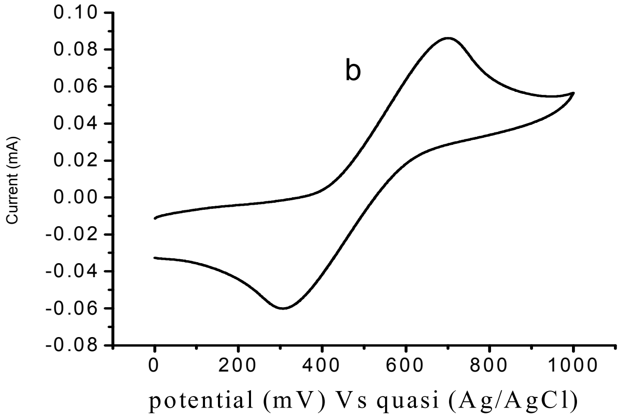


Figure 9. Cyclic voltammogram of 1x10^{-4} M of Cu(II) chloride complex at glassy carbon electrode in DMF solution containing 0.01 M Tetrabutylammoniumhexafluorophosphate. Scan rate (v) = 100 mV/s.

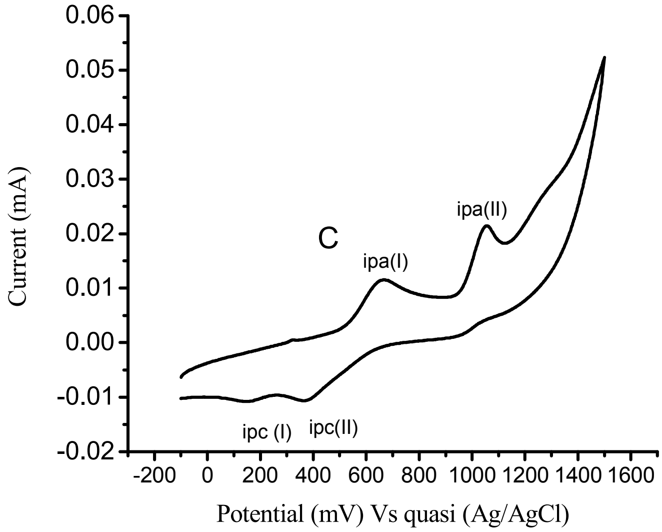


Figure 10. Cyclic voltammogram of 1x10^{-4} M of Cu(II) nitrate complex at glassy carbon electrode in DMF solution containing 0.01 M Tetra butyl ammonium hexafluoro phosphate. Scan rate (v) = 100 mV/s.

3.7 Effect of scan rate

The effect of scan rate could be shown by recorded the CV at concentration of 1×10^{-4} M of Schiff base ligand.Schiff base ligand L shows the typical cyclic voltammogram for an irreversible process. The most obvious indication is the absence of a cathodic reduction signal. Furthermore the oxidation signals significantly shift to more positive potentials with faster scan rates.

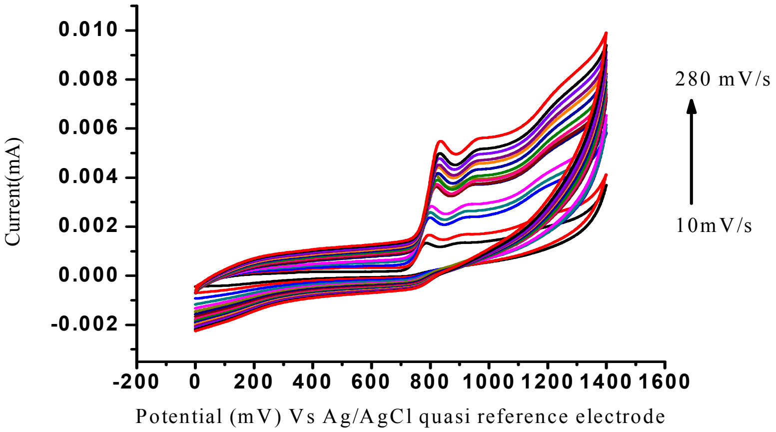


Figure 11. Cyclic voltammograms of schiff base ligand on glassy carbon electrodes in 0.01 M tetrabutylammonium hexaflorophosphate at different scan rates (mV/s): 10-280 mV/s.

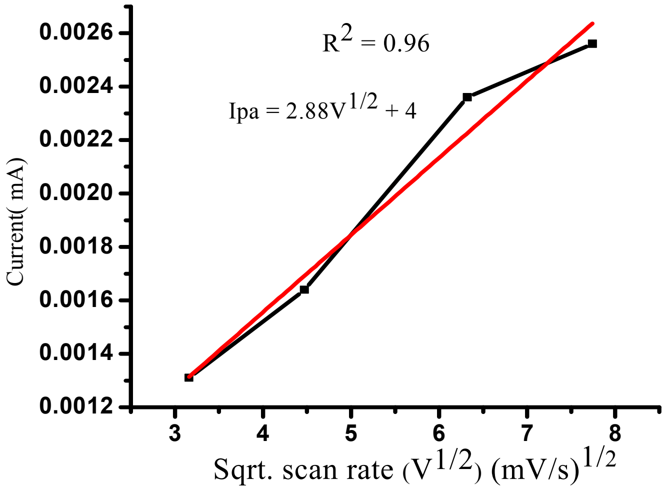


Figure 12. Plot of anodic peak current of Schiff base ligand L as a function of square root of scan rate.

1×10^{-4} Mconcentrations of copper(II) complexes show the typical cyclic voltammograms forquasi reversible process. The cyclic voltammogram will take longer to record as the scan rate is decreased. At a slow scan rate, the diffusion layer will grow much further from the electrode as compared to a fast scan. This leads to a concentration gradient to the electrode surface that is much lower as compared to a fast scan.The peak heights of the anodic signal and the cathodic signal are not completely equal anymore. However, the most obvious indication that the process is not completely reversible anymore is the separation of anodic and cathodic peak potential. The difference of the peak potentials is significantly bigger than 59 mV and the separation of the two signals increases with faster scan rates [18]. Therefore the reaction of copper(II) complexes at higher scan rates can be considered to be quasireversible.

For both chloride and nitrate complexes the graph of i_{pc} and i_{pa} against $v^{1/2}$ gave a linear plot with R^2 greater than 0.98. This indicates that the i_{pc} and i_{pa} were directly proportional to the square root of the scan rate. From the graph, it also shows that as the scan rate increases, the peak current also increases.

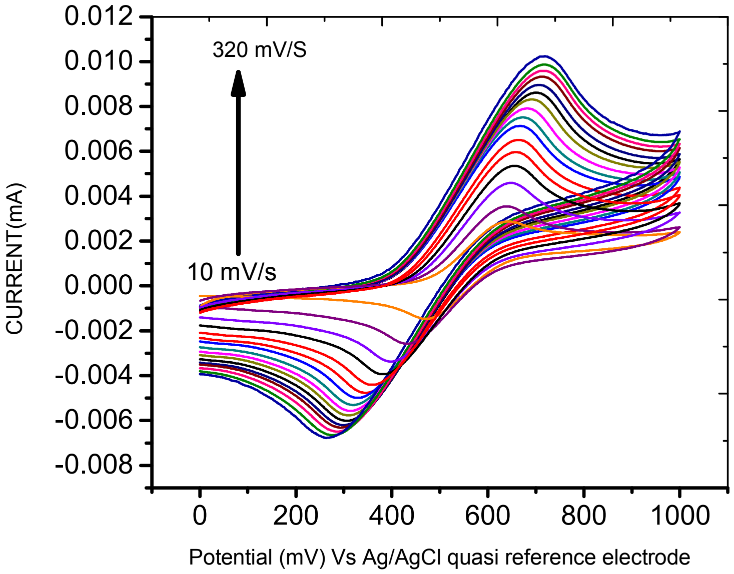


Figure 13. Cyclic voltammograms of chloride complex on glassy carbon electrodes in 0.01 M tetrabutylammoniumhexaflorophosphate at different scan rates (mV/s): 10-320 mV/s.

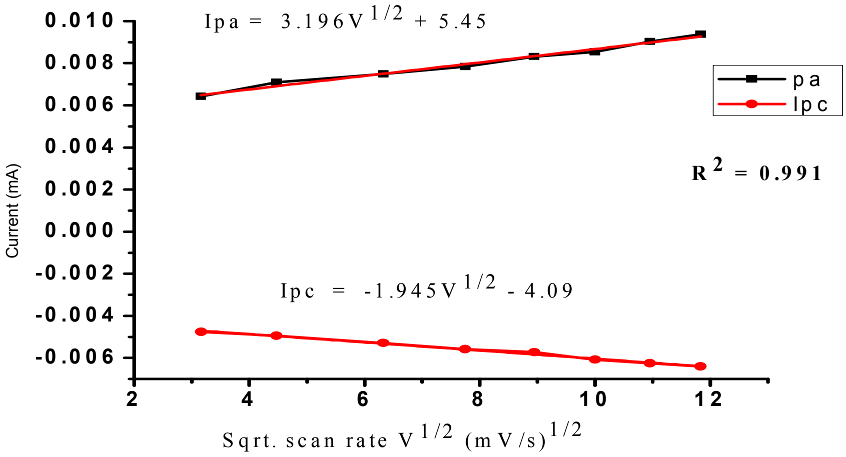


Figure 14. Plot of anodic peak current and cathodic peak current of chloride complex as a function of square root of scan rate**.**

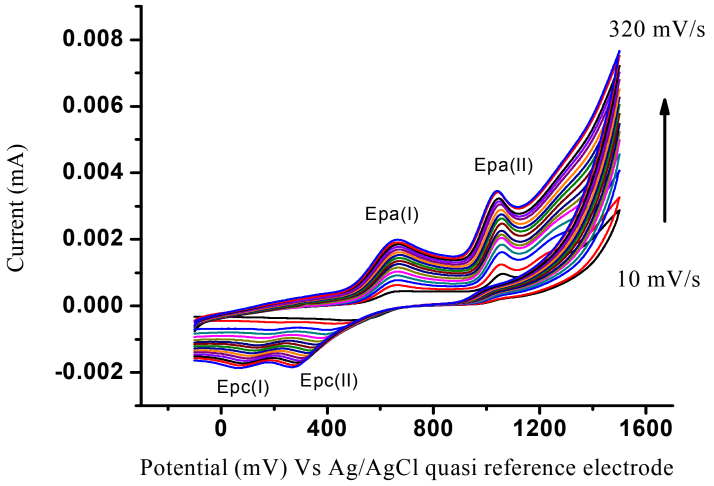


Figure 15. Cyclic voltammograms of nitrate complex on glassy carbon electrodes in 0.01 M tetra-butylammoniumhexaflorophosphate at different scan rates (mV/s): 10-320 mV/s

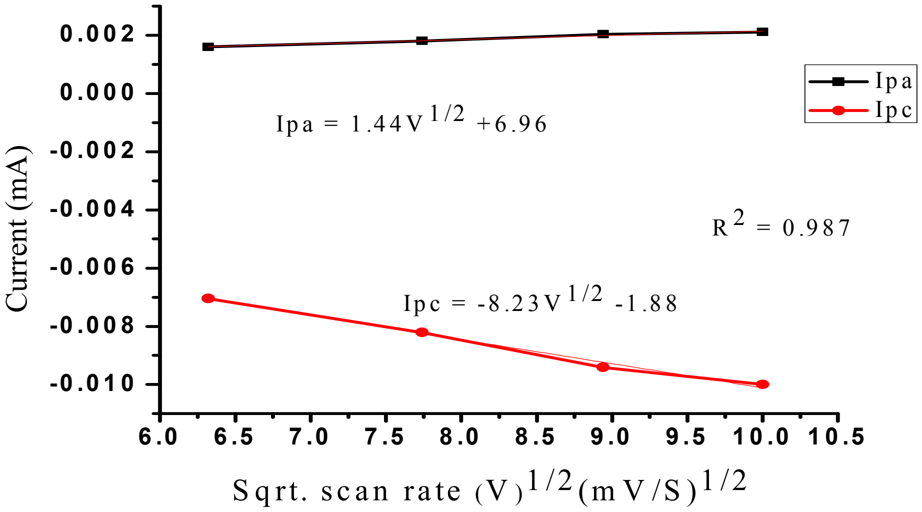


Figure 16. Plot of anodic peak current (I_{pa}(II) and cathodic peak current (I_{pc}(II) of nitrate complex as a function of square root of scan rate.

4 Summary and conclusion

The work incorporated in this work deals with the synthesis, characterisation and electrochemical studies on the Schiff base ligand (L) derived from glyoxal and 4-aminoantipyrine and its nitrate and chloride complexes. The ligand (L) has been characterised by NMR, IR and UV spectra and the corresponding chloride and nitrate complexes by elemental analyses, molar conductance in non-aqueous solvents, infrared and electronic spectra.

The complexes of L have the general formulae $[Cu(L)_1]X_2$ (where X = Cl^- or NO_3^-). The ligand L acts a neutral tetradentate ligand, coordinating through both the carbonyl oxygens and both the azomethine nitrogens in the complexes. Both counter anions remain ionic in the complexes. Electronic spectral studies suggest a square planar geometry around the Cu(II) ion in both the complexes.

The electrochemical studies of ligand show a typical cyclic voltammogram for an irreversible process. The most obvious indication is the absence of a cathodic reduction signal. Furthermore the oxidation signals significantly shift to more positive potentials with faster scan rates. Copper(II) complexes show the typical cyclic voltammograms for quasi reversible process. The cyclic voltammogram will take longer to record as the scan rate is decreased. At a slow scan rate, the diffusion layer will grow much further from the electrode as compared to a fast scan. This leads to a concentration gradient to the electrode surface that is much lower as compared to a fast scan. The peak heights of the anodic signal and the cathodic signal are not completely equal anymore. However, the most obvious indication that the process is not completely reversible anymore is the separation of anodic and cathodic peak potential. The difference of the peak potentials is significantly bigger than 59 mV and the separation of the two signals increases with faster scan rates. Therefore the reaction of copper(II) complexes at higher scan rates can be considered to be quasi-reversible

Reference

[1]. M. Li, H. Jiao.; H. Zhang.; S. Jiao.*Int. J. Electrochem. Sci*. 10, 8797, **2015**.
[2]. R. Ahmadzadeh.; M.Azarkish.; T. Sedaghat.*J. Mex. Chem. Soc*.58, 173, **2014**.
[3]. R. Katwal.;H. Kaur.; B. K. Kapur.*Sci.Revs. Chem. Commun*. 3, 1, **2013**.
[4]. P. G. Cozzi.*Chem.Soc.Rev*.33.410*,* **2004**.
[5]. H. Schiff.*Ann. Suppl*. 3, 343, **1864**.
[6]. A. Ourari.; Y. Ouennoughi.; D. Aggoun.; M. S. Mubarak.; E. M. Pasciak.;
D. G. Peters.*Inorg. Chem. Commun*. 33, 118, **2013**.
[7]. V.M. Jiménez-Pérez.; B.M. Muñoz-Flores.; J..A. Gómez.;L. D. Rangel.;R. C.Navarro.;N.Waksman.; R. R.Durón.*Int. J. Electrochem.Sci*. 9, 7431, **2014**.
[8]. K. Shikama.*Chem. Rev*. 98, 1357, **1998**.
[9]. A. Pradhan .; A. K. Koshal.*J. Environ. Res. Develop*. 9, 5, **2015**.
[10].M. Shabbir.; Z. Akhter.; I.Ahmad.;S..Ahmed.;V.McKee.; H. Ismail.; B.Mirza.*Polyhedron*.124, 171, **2017**.
[11]. M. M. H. Khalil.; E. H. Ismail.; G. G. Mohamed.; E. M. Zayed.; A.Badr,*J. Inorg. Chem*. 2, 13, **2012**.
[12]. W. A. Zoub.*Int. J. Org. Chem*. 3, 73, **2013**.
[13]. R. M. Silverstein.*Spectroscopic identification of organic compounds*, 7th ed.; John Wiley, State University of New York, **2005**.
[14]. W. J. Geary.*Coord. Chem. Rev*. **7**, 81, **1971**.
[15]. K. Nakamoto."*Infrared and Raman Spectra of Inorganic and Coordination Compounds*," Wiley, New York, **1986**.
[16]. A. B. P. Lever."*Inorganic Electronic Spectroscopy*", 2nd ed., Elsevier, Amsterdam, **1984**.
[17]. Harris, D. A. *Quantitative Chemical Analysis*, 4th ed.; W. H. Freeman and Company: New York, **1995**.
[18]. A. J. Bard.; L. R. Faulkner.*Electrochemical Methods: Fundamentals andApplications*, 2nd ed.; United States of America, **2000**.