International Journal of Academic Research and Development
ISSN: 2455-4197
Impact Factor: RJIF 5.22
www.academicsjournal.com
Volume 3; Issue 4; July 2018; Page No. 135-140

Synthesis and characterization of macro cyclic mononuclear Schiff base complexes of nickel and copper complexes

P Rajalakshmi[1], S Shamala[2]
[1] Research Scholar, Department of Chemistry, PRIST University, Puducherry, Tamil Nadu, India
[2] Assistant Professor, Department of Chemistry, PRIST University, Puducherry, Tamil Nadu, India

---

Abstract

The chemistry of macro cyclic complexes has occupied a central role in the development of coordination chemistry. The metal complexes containing synthetic macro cyclic Gilligan have attracted a great deal of attention towards more biological system. They have been synthesized and characterized by UV, IR, EPR cyclic voltammetry spectral techniques. The synthesis and characterization of a series of 2-((4-methoxyphenylimino methyl)-4, 6-dichlorophenol and thiocyanate as macro cyclic mono nuclear Schiff base complexes by template method with the corresponding metal salts like Ni(II) and Cu(II).

Keywords: potassium thiocyanate IR spectra, electronic absorption spectra

---

1. Introduction

The metal complexes containing synthetic macro cyclic Gilligan have attracted a great deal of attention because they can be used as models for more intricate biological system: anthropomorphically (globetrotting, globulin, chrome, chlorophyll), Corinne (vitamin B12) and antibiotics (Aureomycin, nonacceptance). The synthetic chemist have long been attracted to the design, synthesis of macro cyclic brigands and their metal complexes.

Metal ions play a vital role in a vast number of widely differing biological processes.

1.1 Schiff Base

Schiff based was first reported by Hugo Schiff in 1864 [1]. Schiff base can be prepared by condensing carbon compounds and amines in different conditions and in different solvents with the elimination of water molecules. The presence of a dehydrating agent normally favors the formation of Schiff base. Though the Schiff base are stable solids, care should be taken in the purification steps as it undergoes degradation. Choreographic purification of Schiff bases on silica gel is not recommended as they undergo hydrolysis.

Presence of a lone pair of electrons in Sp2 hybridized orbital of nitrogen atom of the something group is considerable chemical importance and imparts excellent calculating ability especially when used in combination with one or more donor atoms close to the something group. Examples of a few compounds are given in Figure.1. This calculating ability of the Schiff bases combined with the case of preparation and flexibility in varying the chemical environment about the C=N group makes it an interesting Gilligan in coordination chemistry.

2. Aim and scope of the present investigation

A variety of Schiff base macrocyclic complexes were found to have immense applications in various fields. In the present investigation, the researcher as synthesized a series of mononuclear macrocyclic Schiff base complexes derived from the condensation of 2((4-methoxyphenylimino)methyl)-4,6-dichlorophenol (DAMP) and Potassium thiocyanate (KSCN) and Potassium Thiocyanate (KSCN) with the corresponding metal salts like Nickel(II) and Copper(II).

In this results of our studies on the synthesis and characterization of two new macrocyclic mononuclear transition metal complexes derived from the above and their applications in antimicrobial activities are presented.

Aim and objectives

The aim of this research work will be directed towards the synthesis and characterization of macrocyclic mononuclear Schiff base complexes of Ni(II) and Cu(II) with high thermal stability, adequate balance of hydrophilicity/lipophilicity and low toxicity that could be tested for antimicrobial activities.

The research objectives are,

☎ ♓ ✆ To synthesis and characterize a series of 2-((4-methoxyphenylimino methyl)- 4,6-dichlorophenol and thiocyante as macrocyclic mononuclear Schiff base complexes by template method with the corresponding metal salts like Ni(II) and Cu(II). Whereas, the metal ions are used as the templating agents.

☎ ♓ ♓ ✆ To establish the structure of the metal complexes and analyze their spectral characterization.

☎ ♓ ♓ ♓ ✆ To screen the synthesized macrocyclic mononuclear Schiff base complexes as potential antibacterial agents.

3. Experimental techniques

In this chapter, the chemicals used, purification of solvents, preparation of macrocyclic Schiff base complexes analytical procedures and instrumental techniques employed in the determination of stoicheiometry of the complexes prepared are presented.

Chemicals

Ethanol (S.D. Fine chemicals)
Potassium thiocyanate (Nice Chemicals)
Cuppric (II) chloride (fisher scientific)
Nickel (II) chloride (fisher scientific)
Liquor ammonia (BDH)
Glacial acetic acid
3,5- chlorosalicylaldehyde(Aldrich)
p-anisidine (AVRA)

Synthesis of macrocyclic schiff base complexes

Template synthesis of Copper(II)

Complexes Complex-1

The template condensation of 2((4-methoxyphenylimino) methyl)-4, 6- dichlorophenol 0.295g dissolved in 20ml of hot ethanolic solution in a 100ml beaker and KSCN 0.19g dissolved in 20ml of Ethanol added over a solution slowly with constant stirring, finally add a 0.1709 cuppric chloride dissolved in 20ml of ethanol in the same mixture slowly with constant stirring. The reaction mixture was refluxed for 4 hours. The brown precipitate formed was filtered, washed with ethanol then dried in vacuum. Yield 75%.

A similar procedure was followed for the synthesis of other Ni(II) complex.

The data pertaining to the preparation of copper(II) and nickel(II) are given in,

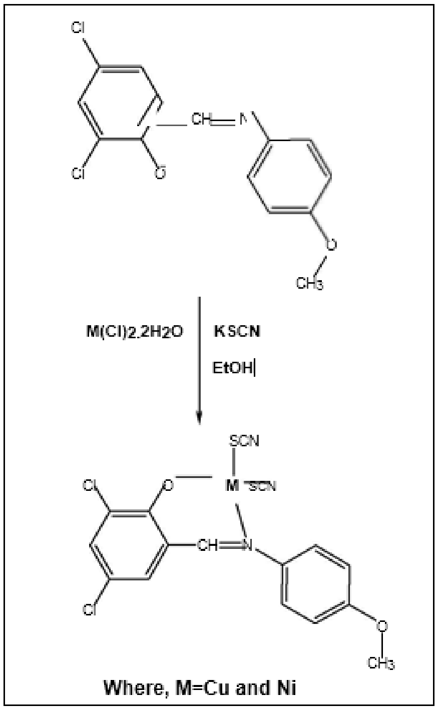

Fig 1: Template synthesis Macrocyclic mononuclear Cu(II) and Ni(II) complexes

Table 1: Template Synthesis Data for Macrocyclic Monouclear Cu(II) and Ni(II) Complexes

Complex	Metal (mg)	Compound (g)		Time of refluxion (hours)	Yield (mg)
		2-((4-methoxyphenylimino) Methyl)-4,6- dichlorophenol- DAMP (0.295)	Potassium		
	Cu(II)		Thiocynate		
[Cu(DAMP)(SCN)2]	170		(KSCN)	4	650
			(0.19)		
		2-((4-methoxyphenylimino) Methyl)-4,6- dichlorophenol- DAMP (0.295)	Potassium		
			Thiocynate		
	Ni(II)		(KSCN)		
[Ni(DAMP)(SCN)2]	237			4	720
			(0.19)		

Chemical methods for the characterization of complexes

Synthesis of Ligand 2-((4-Methoxyphenylino)Methyl)-4,6-Dichlorophenol(DAMP).

1.91g of 3,5-dichlorosalicylaldehyde was dissolved in 20ml of ethanol, then 1.23g of p- anisidine was dissolved in 20 ml of ethanol and mixed together and stirred well. Then it was stirred in magnetic stirrer for 2 hours, then added 2 drops of glacial acetic acid again run for 2 hours. It was then filtered, dried and weighed. Yield 75%. The prepared ligand 2-((4-methoxyphenylino)methyl)-4,6-dichlorophenol(DAMP).

Preparation of Copper (ii) complex

0.170g of Copper (II) Chloride was dissolved in Ethanol and 0.295g of 2-((4- methoxyphenylimino)methyl)-4,6-dichlorophenol (DAMP) was dissolved in 20ml of ethanol and mixed together, and stirred for few minutes, then ethanolic solution is added. 0.19g of potassium thiocyante was slowly to for mixture and mixture stirred for two hours. Then few 2 drops liquor ammonia is added and stirring was continues. The precipitate was black in colour. It was then filtered washed, dried a and then weighed. Yield 73%. The prepared ligand was 2-((4- methoxyphenylino)methyl)-4,6-dichlorophenol(DAMP).

Preparation of Nickel(ii) complex

0.237g of Nickel(II) Chloride was dissolved in Ethanol and 0.295g of 2-((4- methoxyphenylimino)methyl)-4,6-dichlorophenol(DAMP) was dissolved in 20ml of ethanol and mixture together and stirred for few minutes, then ethanolic solution is added. 0.19g of potassium thiocyante was slowly to for mixture and mixture stirred for two hours. Then few 2 drops liquor ammonia is added and stirring was continues. The precipitate was brown in colour. It was then filtered washed, dried and then weighed. Yield 75%. The prepared ligand was 2-((4- methoxyphenylino)methyl)-4,6-dichlorophenol(DAMP).

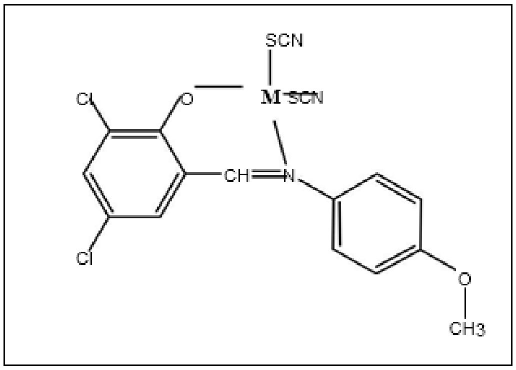

Fig 2: The structure of mononuclear Nickel and Copper complexes

4. Results and discussion

Characterisation of Cu(ii) and Ni(ii) complexes

Elemental analysis

The results of elemental analysis of Cu(II) and Ni(II) complexes were tabulated in Table.2. The structures are identified by elemental analysis. The analytical data are indicative of stoicheiometry of the complexes. The elemental content of the present complexes were compared with the formulation which is expected to give rise to a neutral complex. The difference between the two values was found to be greater than acceptable limits of experimental errors. The molecular weights of the complexes were determine by Rast method. The observed molecular weights employ well with the complex being formulated to contain two metal ions and the ligand molecules with the requisite number f counter ions. All the complexes provide proper C, H, N and Cu and Ni results, which were in good agreement with those calculated for the suggested formulae.

Molar conductance

Conductivity measurements were carried out in 10-3 mol dm-3 DMF solutions at 25°c.

The molar conductance value for the copper(II) and nickel(II) complexes are electrolytic in nature. The room temperature molar conductivity values of the complexes are given in table. 2.

Table 2: Analytical data of macrocyclic mononuclear Cu(II) and Ni(II) Schiff base Complexes

S. No	Molecular formula	Colour	Elemental Analysis[Found(Calcd)] in %				^m (ohm-1 Cm2 mol-1)
			C	H	N	M	
1.	[Cu(DAMP)(SCN)2]	black	44.90	4.41	7.85	11.88	81.2
			(44.99)	(4.52)	(7.96)	(11.97)	
2.	[Ni(DAMP)(SCN)2]	brown	45.31	4.18	7.93	11.07	67.6
			(45.41)	(4.27)	(8.03)	(11.17)	

Infrared spectral studies

Copper Complex

IR spectra of the samples are recorded in KBr medium in 400-4000cm-1 range to identify coordination sites of ligands, formation and strength of metal-ligand bonds in the complexes, and to study the bonding vibrational modes of ligand in metal complexes. The IR spectra of the complexes and ligands have a diagnostic importance to determine the structure of the compounds. The IR spectra of complexes compared with those of ligands indicated that the (C=N) stretching vibration band at region about 1503 -1750cm-1 is shifted to lower frequencies in most complexes as excepted. In contrast there are many complexes shifted to higher frequencies, which indicated that the ligands coordinated to the metal ions through nitrogen atom of the imine group.

In general the observed IR bands of Schiff's bases and their complexes are in conformity with the previously reported results [2, 3].

The presence of sharp band corresponding to the remaining hydroxyl group at 3400cm-1 but it is obscured by the presence of water molecules bands. This was appeared for the most complexes and a very broad band at about 3225-3382 cm-1 region, which is associated with coordinated or solvent water molecules. The other bands appeared at 982-1295 cm-1 region assigned to the (C— O), which are shifted to a higher frequency after complexation with central metal ions, compared to the free ligands in which was noted at 1249-1329cm-1. In addition the four bands at 537-720, 537-461, 2143-2173 and 2836-2995 cm-1 is attributed to the (M—O), (M—N), (S-C=N) and (-CH3) respectively [4,5].

The IR spectra of [Cu(DAMP)(SCN)2] complex exhibit a medium band at 1503 cm-1 which is assigned to the (C=N) stretching, because this band is shifted to lower frequency by 36cm-1 compared to free ligand, indicating that the ligand coordinated to the metal ion through nitrogen atom of the imine group and probably dianionic form. The broad band around 3382 cm- 1 indicating the presence of coordinated or lattice water in the complex. The spectrum reversals a weak band at 3225 cm-1 which is attributed to (C—O) vibration, again this band is shifted to higher value compared to the free ligand due to formation (C—O—M) bond. In addition three new bands in the regions 537 and 461 cm-1 were emerge, which are probably due to the formation of (Cu— O) and (Cu—N) bond respectively [6].

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. In order to study the binding modes of the ligand to metal in complexes, the IR spectrum of the free ligand should be compared with the corresponding metal complexes. IR spectra of the samples are recorded in KBr medium in 400-4000cm-1 range to identify coordination sites of ligands, formation and strength of metal-ligand bonds in the complexes, and to study the bonding vibrational modes of ligand in metal complexes. The IR spectra of the complexes and ligands have a diagnostic importance to determine the structure of the compounds [7]. Infrared spectra of copper (II) complex is shows in Fig.3,

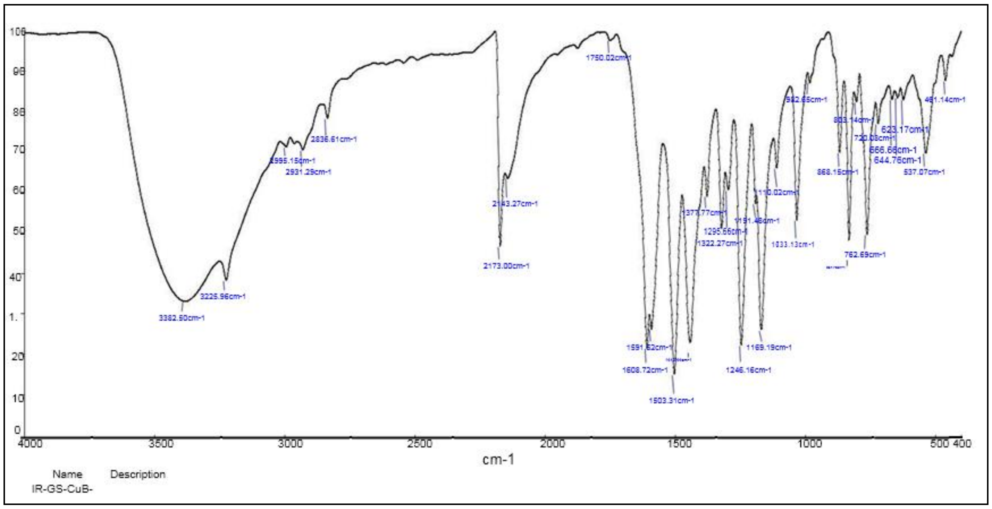

Fig 3: Infrared spectra of copper (II) complexes

Complex

The IR spectra of complexes compared with those of ligands indicated that the (C=N) stretching vibration band at region about 1515- 1679 cm-1 is shifted to lower frequencies in most complexes as excepted. In contrast there are many complexes shifted to higher frequencies, which indicated that the ligands coordinated to the metal ions through nitrogen atom of the imine group. In general the observed IR bands of Schiff's bases and their complexes are in conformity with the previously reported results [2, 3].

The presence of sharp band corresponding to the remaining hydroxyl group at 3400cm-1 but it is obscured by the presence of water molecules bands. This was appeared for the most complexes and a very broad band at about 3053-3448 cm-1 region, which is associated with coordinated or solvent water molecules. The other bands appeared at 987-1223 cm-1 region assigned to the (C— O), which are shifted to a higher frequency after complexation with central metal ions, compared to the free ligands in which was noted at 1280-1320 cm-1. In addition the four bands at 778-645, 482-429, 1833-1973 and 2926-3053cm-1 is attributed to the (M—O), (M—N) (S-C=N) and (-CH3) respectively [4, 5]. The IR spectra of [Cu(Damp)(SCN)2] complex exhibit a medium band at 1515 cm-1 which is assigned to the (C=N) stretching, because this band is shifted to lower frequency by 36cm-1 compared to free ligand, indicating that the ligand coordinated to the metal ion through nitrogen atom of the imine group and probably dianionic form. The broad band around 3382 cm- 1 indicating the presence of coordinated or lattice water in the complex. The spectrum reversals a weak band at 987-1223 cm-1 which is attributed to (C—O) vibration, again this band is shifted to higher value compared to the free ligand due to formation (C—O—M) bond. In addition three new bands in the regions 719-488 and 645-629cm-1 were emerge, which are probably due to the formation of (Ni— O) and (Ni—N) bond respectively [6].

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. In order to study the binding modes of the ligand to metal in complexes, the IR spectrum of the free ligand should be compared with the corresponding metal complexe [7]. Infrared spectra of nickel(II) complex as shows in Fig 4.

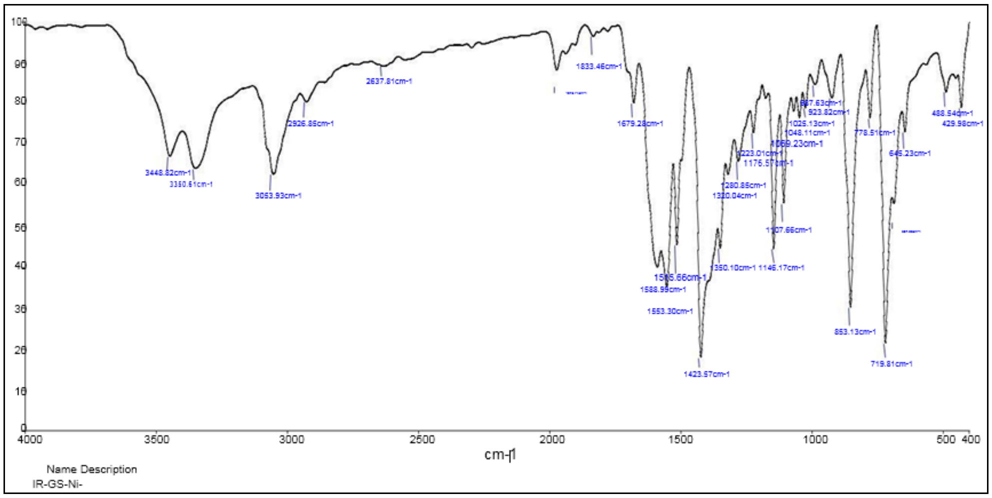

Fig 4: Infrared spectra of Nickel (II) complexes

Electronic absorption spectra

The electronic spectrum gives information on the electronic environment of the metal. The splitting of d orbital and in turn the structure expected for the complexes. It gives information on the various electronic excitations obtained for the complexes [8].

The electronic spectra of the ligand record in DMF solution. This show bands in the range of 200-800 nm region and the data presented.

The electronic absorption spectra and magnetic moment values ares often very helpful in the evaluation of results provided by other methods of structural investigation. Information about geometry of the complexes around the Cu(II) and Ni(II) ions was obtained from electronic spectra.

The electronic absorption spectra of the Schiff base ligands and its complexes were recorded at room temperature using (DMF) as solvents [9].

The absorption spectrum of the Cu(II) and Ni(II) complexes Fig.16. shows as intense band center at 265-390nm attributed to π→π*and n→π* transition of the imine group. Another intense band in 400nm shows the higher energy spectra of the complexes was related to n→π* transition of benzene ring.

The copper (II) complex show a 265-390nm broad band assign 2B1g→2A1g, transition, which consistent with proposed geometry of the complex in square planar geometry. These lower frequencies conforming the coordination of the ligand moiety to the metal. The electronic spectra of copper (II) complex is shown in Fig. 5.

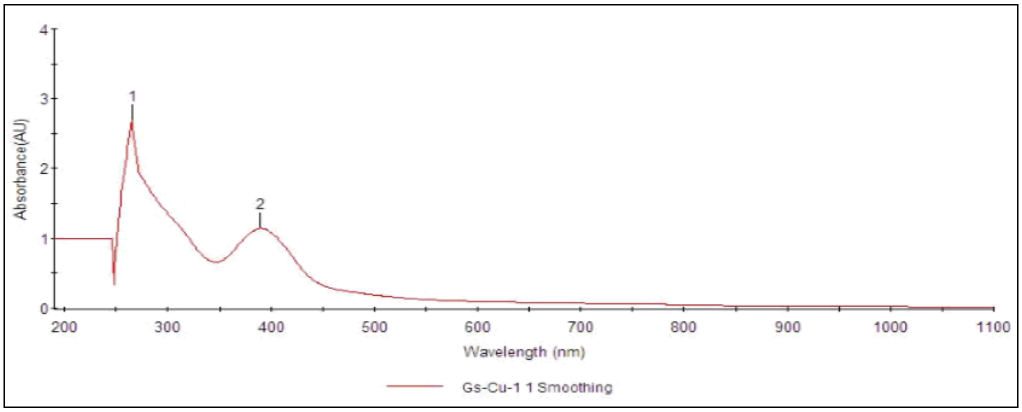

Fig 5: Electronic Spectra of Copper(II) complex

The Ni(II) complex shows two bands a 400 nm broad band which assigned to 3A2g→2T2g transition shows a square planar geometry. Another band 410nm ligand to metal transition corresponding to 1A1g→1B1g transition, respectively which is in consistent with that square planar geometry. The electronic spectra of nickel (II) complex is shown in Fig. 6.

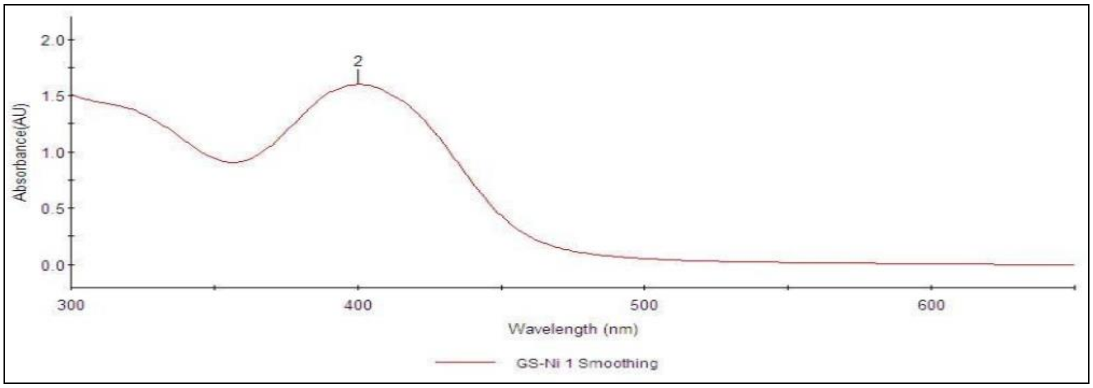

Fig 6: Electronic Spectra of Nickel(II) complex

The Electronic Spectra of Macrocyclic Mononuclear Complexes is given in Table.3

Table 3: Electronic spectral data of macrocyclic mononuclear Copper(ii), Nickel(ii) schiff base complexes

S. No	Complexes	Absorption in (nm)	
		π→π*	n→π*
1.	[Cu(DAMP)(SCN)2]	265	390
2.	[Ni(DAMP)(SCN)2]	_	400

EPR- spectra analysis

The X-band EPR spectrum of the copper(II) complex was recorded at room temperature. Fig. 7 shows solid state EPR spectrum of the mononuclear copper(II) complex [Cu(DAMP)(SCN)2].

The EPR spectrum of Cu (II) complex shows four lines with nuclear hyperfine spin 3/2 due to hyperfine splitting. The observed gII values were less than 2.3 indicating considerable covalent character in the M–L bonds.

The gII values of Cu (II) are 2.26 and $g^{\perp}$ value is2.02, indicating distorted tetrahedral geometry. The absence of the half-field signal at 1600G, corresponding to ΔMs = ± 2 transition, ruled out Cu–Cu interaction in the complex. The hyperfine AII splitting falls in the range of 150 x 10–4 cm–1, indicated that an electron interacted with only one copper nucleus. The relation gII> $g^{\perp}$ is typical of d9 copper(II) complex in a ground state doublet with the unpaired electron in the d 2 y2 orbital. The order gII>$g^{\perp}$, and EPR parameters coincide with the related systems suggesting distorted tetrahedral geometry [10].

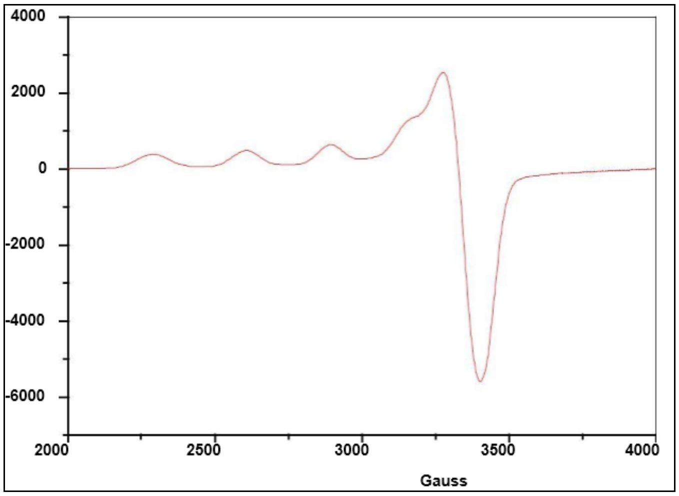

Fig 7: EPR spectrum Copper(II) Complex

Electrochemical properties of the complexes

Table 5: The electrochemical data of mononuclear complexes

No.	Complexes	Reduction	Oxidation
		E1 pa(V)	E1 pc(V)
1	[Ni(NAL)2(SCN)2]	-0.80	1.15
2	[Cu(NAL)2(SCN)2]	-0.95	-

5. Conclusion

A new series of mononuclear copper (II) and Nickel (II) Schiff base complexes have been synthesized by UV, IR, EPR, Cyclic voltametry spectral techniques and characterized. Copper (II) and Nickel (II) complexes have distorble square-planar geometry around the central metal atom.The synthesized macro cyclic mononuclear copper (II) and Nickel (II) complexes showed good antimicrobial activities the antibacterial.

Absorption studies revealed that both Copper and Nickel complexes have π→π* and n→π * transition of important CH=N, C- O and-CH3 functional groups. EPR spectrum of Copper(II) complexes shows for lines with hyperfine splitting have 3/2 values. The gII values of Cu(II) is 2.26 and $g^{\perp}$ value is 2.02 indicating disordered tetrahedral geometry. The gII > $g^{\perp}$ and the EPR parameters coincide with related systems suggesting the distorted tetrahedral geometry.

6. Reference

1. Kumar DS, Alexander V. Inorg. Chem. Acta. 1995; 238:71.
2. Raman II N, Ravichandran S, Thangaraja C. Copper(II), cobalt(II), nickel and zinc (II) complexes of schiff base derived from benzil-2,4-dinitrophenylhydrazone with aniline. Journal of the Chemical Society, Indian Academic Scociety. 2004; 4:116-215.
3. Vigato PA, Tamburini. Coordination Chemistry Reviews. 2004; 248:1717-2128.
4. Huheey JE. Inorganic chemistry, 4th ed. New York: Harper Collins College Publishes, 1993.
5. Ikotun AA, Ojo Y, Obafemi CA, Egharevba GO. African Journal of Pure and Applied Chemistry. 2011; 5:97.
6. Sharma AL, Singh IO, Singh MA, Singh HR, Kadam RM, Bhide MK, *et al.*, Trans. Met. Chem. 2001; 26:532.
7. Azevedo F, Carrondo CT, Caseto B, Convery M, Domingues D, Freire C, *et al.* Santos, Inorg. Chim. Acta. 1994; 219:43.
8. Agarwal RC, Singh NK, Singh RP. Inorg. Chem. 1981; 20:2791.
9. Mondal N, Dey DK, Mitra S, Abdul Malik KM. Synthesis and structural.
10. Geary WJ. Coord. Chem. Rev. 1971; 7:81.