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SPECTROSCOPIC CHARACTERISATION AND SYNTHESIS OF Cu(II) AND Ni(II) COMPLEXES WITH NITROGEN AND SULPHUR DONOR BIDENTATE SCHIFF'S BASE LIGAND

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ABSTRACT: The complexes of Cu(II) and Ni(II) having the general composition ML_2X_2 (where L= 2-benzoylpyridine thiosemicarbazone, M=Ni(II),Cu(II), and X=Cl^-, NO_3^-,SO_4^{2-}, OAc^-) have been synthesised and were characterised by IR, elemental analysis, magnetic susceptibility, UV-Vis, conductivity, mass spectrometry and EPR spectral studies. The IR spectral data indicates that the ligand behave as a bidentate ligand and coordinated to the metal ion through its nitrogen and sulphur donor atoms. The ligand is highly soluble in water. On the basis of molar conductance value which was determined by using DMSO as solvent it can be concluded that all the complexes were non electrolytic in nature. The value of magnetic moment indicates that all the complexes are of high spin type. On the basis of spectral studies an octahedral geometry has been proposed for Ni(II) complexes while tetragonal geometry was proposed for Cu(II) complexes..

INTRODUCTION: Through the years Schiff's base ligands and their transition metal complexes fascinates the scientist for their immense important biological activities including antitumour, antibacterial, antifungal, anticarcinogenic properties [1-5]. The presence of nitrogen and sulphur donor atoms in ligand enables them to coordinates with metal ions [6] and forms a series of complexes which are studied not only for their biological activities but they are also studied for their potential in therapeutic uses [7].

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Transition metal complexes are widely used for the construction of molecular material which are well known for their conducting and magnetic properties and can be applied in material chemistry, supramolecular and biochemistry [8-11].

Metal complexes of thiosemicarbazone were found to possess pronounced anticarcinogenic properties against a wide range of transplanted neoplasm [12]. Nickel complexes are well known for their anticarcinogenic, antibacterial and antifungal properties [13]. Copper complexes also have their importance not only in development and performance of cardiovascular and nervous system but also in development and performance of immune and reproductive system [14]. In this paper we report the synthesis and characterization of copper(II) and nickel(II) complexes with above mentioned ligand (**Fig.1**)

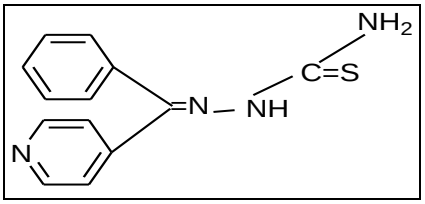

FIG. 1: STRUCTURE OF LIGAND

Experimental Section: All reagents were commercially available and used without further purification purchased from sigma Aldrich and metal salts were purchased from E. Merck. Solvents were spectroscopic pure from SRL/BDH.

Preparation of ligand: Thiosemicarbazide (0.91g, 0.01mol) was dissolved in minimum quantity of ethanol. To this solution hot ethanolic solution of 2-benzoylpyridine was added very slowly with constant stirring. The resulting solution was refluxed at 78-80ºC for 8hrs.and the pH was adjusted to approximately 4-5 by using acetic acid. On cooling bright yellow coloured crystals were separate out. These crystals were washed out several times with cold ethanol. The ligand is highly soluble in water.

Preparation of transition metal complexes: Hot aqueous solution (20 ml) of corresponding metal salts (0.01mol) were mixed with hot aqueous solution of the ligand (0.01mol) with constant stirring and refluxed for 7-8 hrs. at 65-70^{o}C. On cooling the contents, the coloured precipitates were separated out in each case. It was filtered, washed with ethanol and ether. The resultant mixture was dried over P_4O_{10}.

Analytical and physical measurement: Elemental (CHN) analysis was carried out on a Perkin Elmer sercise-II-2400. IR was recorded using a Thermo scientific Nicolet 6700 FT-IR on KBr disc in the wave number ranged 4000-400cm^{-1}. Mass spectrum was recorded using Bruker microtop-QII. ^{1}H NMR spectra were recorded on Bruker Advanced DPX-300 spectrometer using DMSO-d_6 as a solvent and TMS as an internal solvent. Electronic spectral studies were conducted on a perkin elmer-lambda 25, UV spectrophotometer.

The EPR spectra were recorded in solid as polycrystalline sample at room temperature on E_4-EPR spectrometer using DPPH as g marker.

RESULT AND DISCUSSION: All the nickel and copper complexes were synthesised by condensation reaction between ligand and corresponding metal salts. For Ni(II) and Cu(II) complexes were synthesised at 6-7pH range. The synthesised complexes were coloured and stable at room temperature and were found soluble in DMSO and DMF. The molar conductivity value lies in the range from 3.6-11.8 (ohm^{-1} cm^{2} mol^{-1}) which indicates their non electrolytic nature and indicates that complexes have stoichiometry of the type $[ML_2X_2]$ where M = Cu(II), Ni(II), L= ligand and X= Cl^-, NO_3^-,SO_4^{2-}, and OAc^- which is further supported by elemental analysis values. The physical and analytical data together of synthesised complexes is listed in **Table 1**.

^{1}H NMR of ligand: ^{1}H NMR of ligand was done in DMSO on 44-300 MHz NMR (**Fig**.**1a**). The aromatic proton appears as set of singlet, doublet and multiplet in the range 7.40-8.78ppm. The singlet for NH proton appears at 9.32ppm while two NH_2 protons resonates as a multiplet at 7.34-7.38 ppm. The NH_2 and NH protons are confirmed by their D_2O spectra. All the protons are found in their expected region.

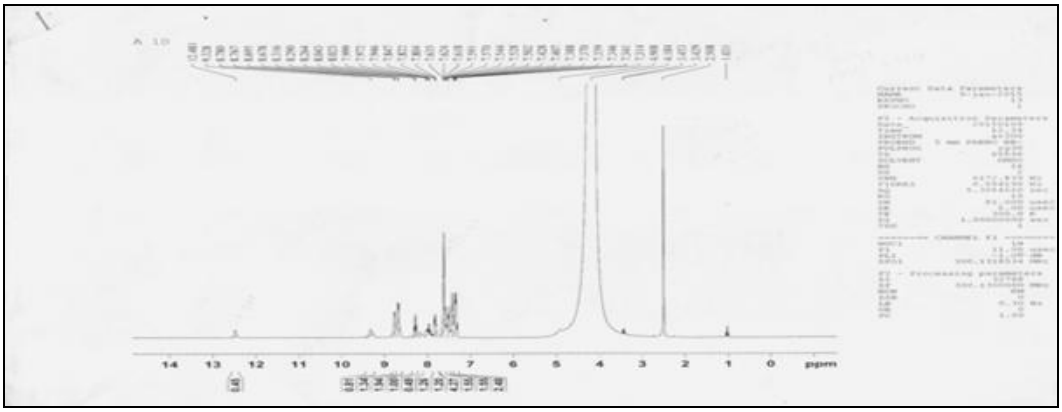

FIG. 1(A): NMR OF LIGAND

TABLE 1: ELEMENTAL ANALYSIS, COLOUR AND FORMULA OF COPPER AND NICKEL COMPLEXES

.	Colour	Found	Calc.	%
		C	H	N
$[CuL_2Cl_2]$	Dark green	48.32	4.021	17.43
		(48.25)	(4.19)	(17.32)
$[CuL_2(SO_4)_2]$	Dark green	40.32	3.56	14.92
		(40.65)	(3.38)	(14.59)
$[CuL_2(NO_3)_2]$	Dark green	44.78	3.65	20.45
		(44.60)	(3.72)	(20.01)
$[CuL_2(OAc)_2]$	Dark green	51.84	4.23	16.53
		(51.91)	(4.61)	(16.14)
$[NiL_2Cl_2]$	Buff colour	48.32	4.59	17.88
		(48.61)	(4.05)	(17.45)
$[NiL_2(SO4)_2]$	Buff colour	42.98	3.76	15.56
		(42.70)	(3.56)	(15.32)
$[NiL_{2(}OAc)_2]$	Buff colour	52.34	4.72	16.58
		(52.27)	(4.65)	(16.26)

Magnetic moment:

The magnetic moment of complexes under study was recorded at Gouy Chapman's balance using $CuSO_4.5H_2O$ as a calibarent. At room temperature the Cu(II) complexes show magnetic moment in the range 1.41-1.53 B.M. corresponding to one unpaired electron and magnetic moment of Ni(II) complexes lies between 2.9-3.1 B.M. (**Table 3**). In octahedral complexes of nickel the magnetic moment value that lies between 2.9-3.1 B.M. is temperature independent. Since complexes under study shows paramagnetic behaviour, therefore, only high spin configurations are possible.

Mass spectra:

Mass gives the important information regarding the proposed formula of the synthesised compound. Mass spectrum of ligand (**Fig. 1b**) shows a molecular ion peak at m/z=255amu corresponding to species $[C_{13}H_{11}N_4S]^+$. The peak at m/z= 255 amu indicates M-1 peak. This value favours the proposed formula of the ligand. The mass spectrum of the complex $[CuC_{26}H_{23}S_2N_8Cl_2]^+$ shows a molecular ion peak at m/z = 645.6 amu which justifies the proposed formula.

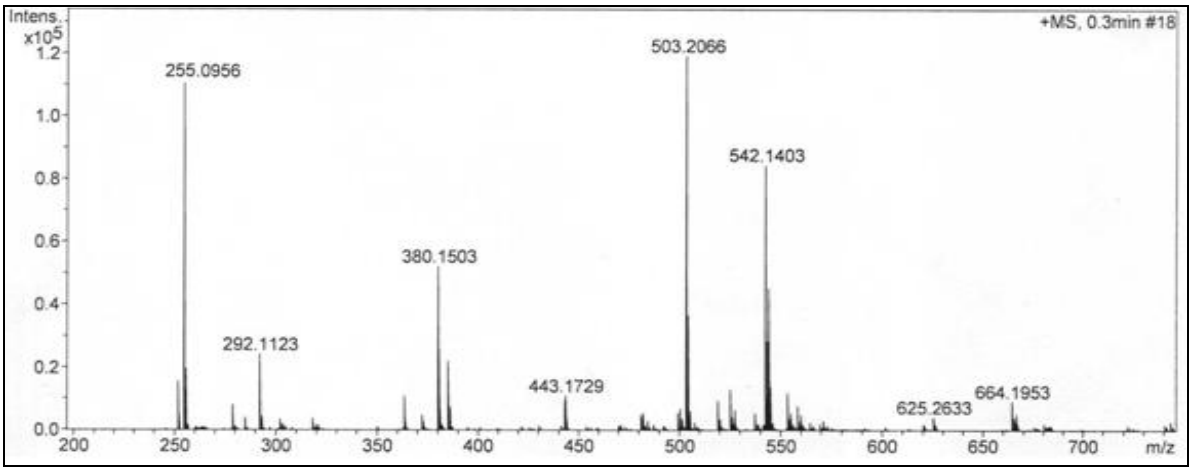

FIG. 1b: MASS SPECTRUM OF LIGAND

IR Spectra: In IR spectra of ligand a band at 1608 cm^{-1} corresponds to $\nu(C=N)_{azomethine}$ group. On complex formation (**Fig. 2a** and **2b)** position of this band is shifted towards lower side which shows the coordination of azomethine group. This is further supported by appearance of new band in the region from 414- 432 for ν(M-N). A band appeared at 781 is due to ν(C=S) group. On complex formation the position of this band is shifted towards lower side which indicates the involvement of sulphur atom in complex formation. Thus it can be concluded that the ligand act as bidentate coordinates through nitrogen atom of ν(C=N) group and sulphur atom of ν(C=S) group.

IR Bands due to anion: In the IR spectra of the nitrato complexes of copper three bands appear at 1436 cm^{-1} (v_1), 1349 cm^{-1} (v_2), 1269 cm^{-1} (v_5) and the difference between $v_5$and v_1 is 166 cm^{-1} suggests that nitrate group is attached to central metal ion in unidentate manner [15]. In IR spectra of sulphato complexes three bands appear at 1142 cm^{-1} (v_1), 1004 cm^{-1} (v_2) and 955 cm^{-1} (v_3) suggests unidentate behaviour of sulphate group. The IR spectra of acetato complexes shows v(C=O) at 1423 cm^{-1} and v(C-O) band at 1265 cm^{-1} and the difference between these two bands is 157 cm^{-1} shows that acetate group is attached to central metal ion in unidentate fashion. The nickel sulphato complexes shows three bands at 1149 cm^{-1},1099 cm^{-1}, 964 cm^{-1} shows that sulphate group is attached to central metal ion in unidentate manner[16]. The acetato complexes shows vC_{As}=O at 1530cm^{-1} and vC_{sym}-O at 1212cm^{-1}, the value of Δv= 219 cm^{-1} indicates unidentate behaviour of acetate group [17]. The values of IR are indicated in **Table 2**.

TABLE 2: IR SPECTRAL DATA OF COPPER AND NICKEL COMPLEXES

Compound	v(C=N)	v(C=S)	v(M-N)
Ligand	1618	781	
$[CuL_2Cl_2]$	1598	751	427
$[CuL_2(OAc)_2]$	1595	744	419
$[CuL_2(SO_4)_2]$	1594	742	414
$[CuL_2(NO_3)_2]$	1598	736	432
$[NiL_2Cl_2]$	1608	754	453
$[NiL_2(SO4)_2]$	1605	752	451
$[NiL2(OAc)_2]$	1594	739	436

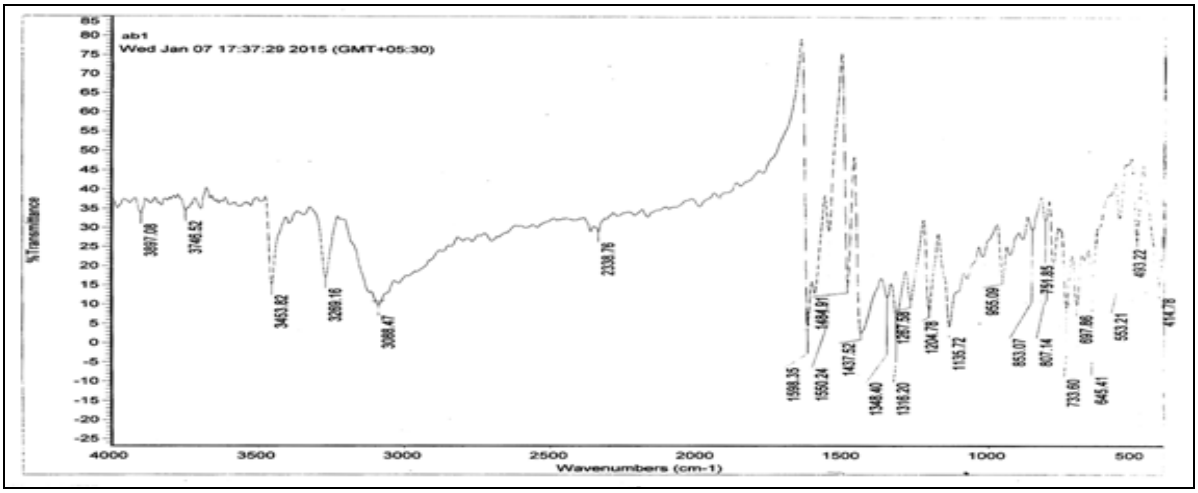

FIG. 2a: IR SPECTRUM OF $[Cu(L_2)Cl_2]$

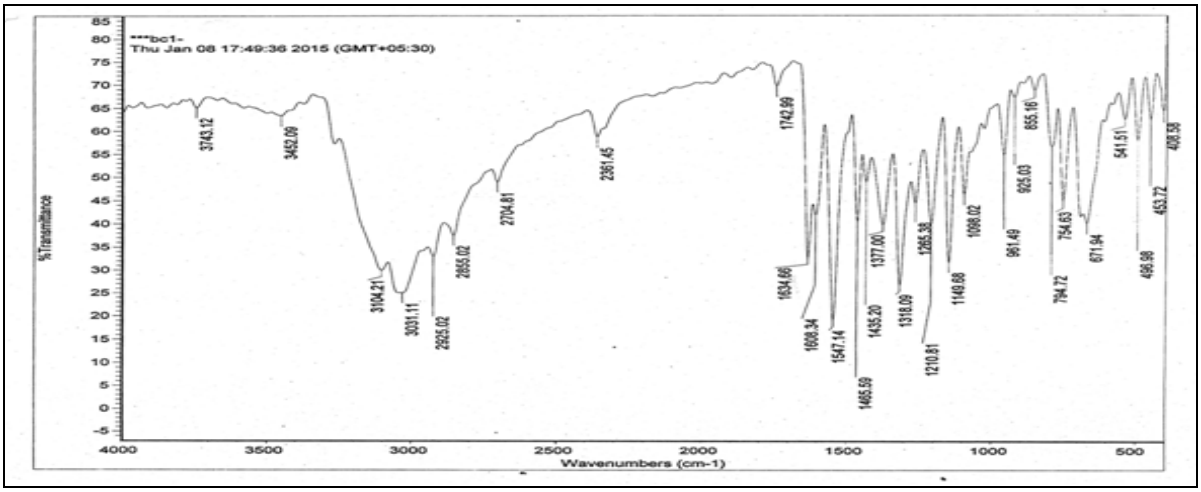

FIG. 2b: IR SPECTRUM OF $[Ni(L_2)Cl_2]$

Electronic spectra: Electronic spectra of Cu(II) (**Fig. 3a and 3b**) complexes displays absorption band in the region 16,426-16,421cm^{-1}(v_2) , 23,689-23,742 cm^{-1} (v_3), 33,012 -33,096(v_4), 39,224(v_5) [18] . These bands corresponds to these transitions: $^2B_{1g} \rightarrow {}^2B_{2g}$ ($d_{x2-y2} \rightarrow d_{zy}$)($v_2$) and $^2B_{1g} \rightarrow {}^2Eg(d_{x2-y2} \rightarrow d_{zy}d_{yz})$($v_3$) which supports the tetragonal geometry and the other bands are due to charge transfer. Electronic spectra of Ni(II) complexes represents bands in the region 10,548-12,252 cm^{-1}(v_1), 13,228 - 19,843 cm^{-1} (v_2), 23043 - 23,678 cm^{-1}(v_3) [19, 20]. These bands may be assigned to have following transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}$ (F)(v_1), $3A_{2g}(F) \rightarrow {}^3T_{1g}$ (F) (v_2), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$($v_3$) respectively and other bands may be due to charge transfer. Ligand field parameters are calculated and listed in **Table 3.**

TABLE 3: MAGNETIC MOMENT AND ELECTRONIC SPECTRAL BANDS OF COPPER AND NICKEL COMPLEXES

Complexes	λ max	μ_{eff}	Dq	B	β	LFSE
$[CuL_2Cl_2]$	16,416, 23,742, 33096, 39224	1.43	-	-	-	-
$[CuL_2OAc)_2]$	16,375, 23,689, 33,069	1.53	-	-	-	-
$[CuL_2(SO_4)_2]$	16,421, 23,700, 30,025	1.41	-	-	-	-
$[CuL_2(NO_3)_2]$	16,416, 23698, 33012	1.46	-	-	-	-
$[NiL_2Cl_2]$	10,548, 13,228, 23,678,28,735,31535	2.93	1054.88	350.70	0.337	151.54
$[NiL_2SO_4]$	12,252,19,843, 23043, 30,224, 39,062	2.96	1225.20	408.67	0.393	175.87
$[NiL_2OAc_2]$	12,473,22936,22,938,31,000,\ 38,645	3.01	1247.3	563.74	0.542	179.03

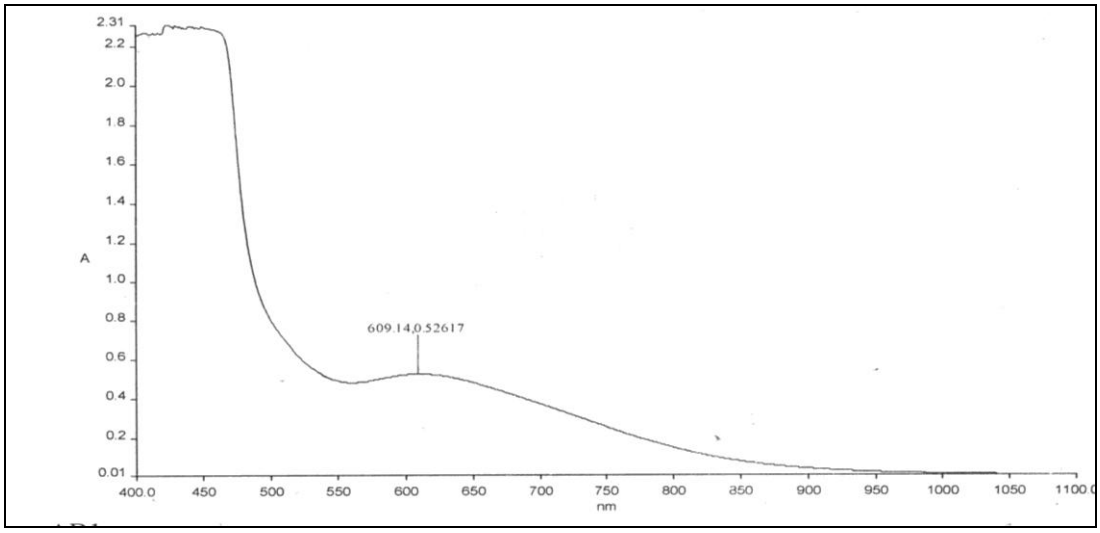

FIG. 3A: UV SPECTRUM OF $[Cu(L_2)Cl_2]$

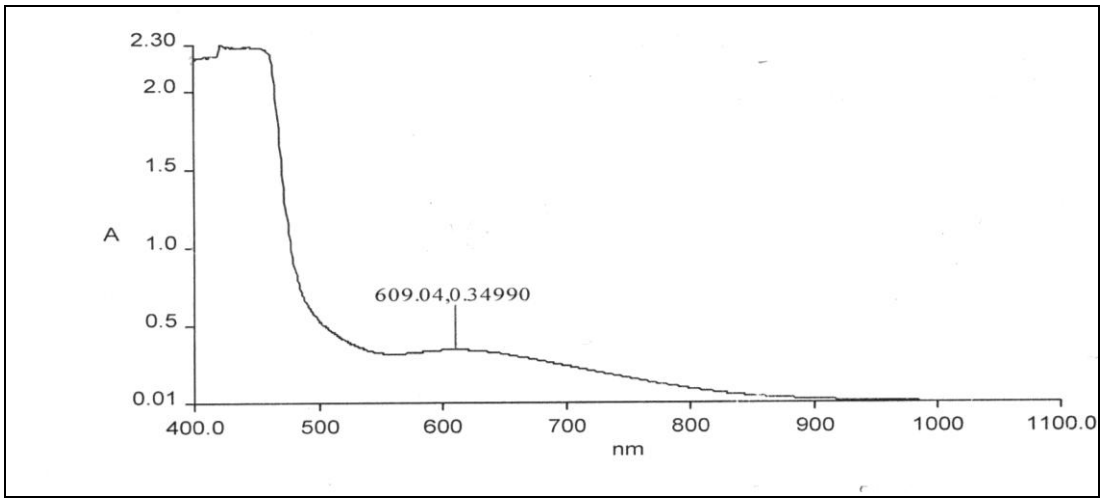

FIG. 3B: UV SPECTRUM OF $[Cu(L_2)(NO_3)_2]$

EPR Spectra: The EPR spectra of the complexes (**Fig. 4a)** under study recorded as polycrystalline sample at room temperature. The g values obtained from the EPR spectra are recorded in **Table 4**. In all the complexes $g\| > g\perp > g_e$ which further supports the distorted octahedral geometry [21]. According to Hathway and Billing [22] expression i.e. $G= (g\| -2)/ (g\perp -2)$ if the value of G is greater than 4 than exchange interaction is negligible and if it is less than 4 than there is a considerable exchange interaction is inicated in solid complexes. The calculated value of G follows the order $SO_4^{2-} > NO_3^- > Cl^- > OAc^-$. The lower value of G for acetate indicates that acetate has large exchange interaction than chloride, sulphate and nitrate. Similarly chloride has large exchange interaction than nitrate and nitrate has large exchange interaction than sulphate ion.

TABLE 4: EPR SPECTRAL DATA OF Cu(II) COMPLEXES

Complexes	g‖	g⊥	g_{iso}	G
$[Cu(L_2)Cl_2]$	2.0687	2.0344	2.0458	1.997
$[Cu(L_{2)}(OAc)_2]$	2.0996	2.0839	2.0891	1.186
$[Cu(L_{2)}(SO_4)_2]$	2.1231	2.0318	2.0622	3.804
$[Cu(L_2)(NO_3)_2]$	2.0347	2.0347	2.0144	2.4265

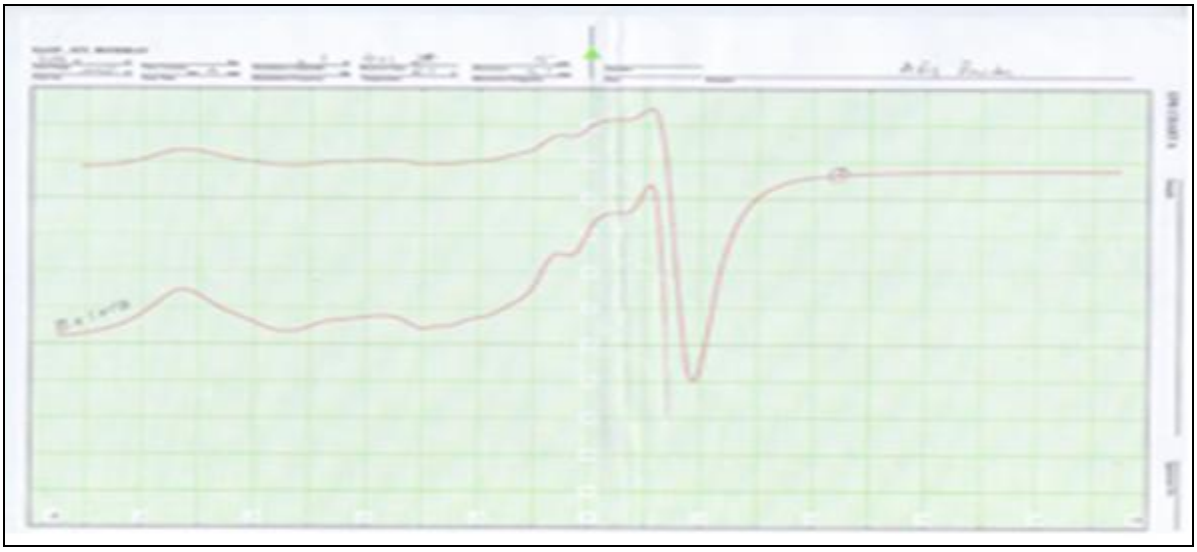

FIG. 4a: EPR SPECTRUM OF COPPER

According to above spectral studies the proposed structure of the complex is

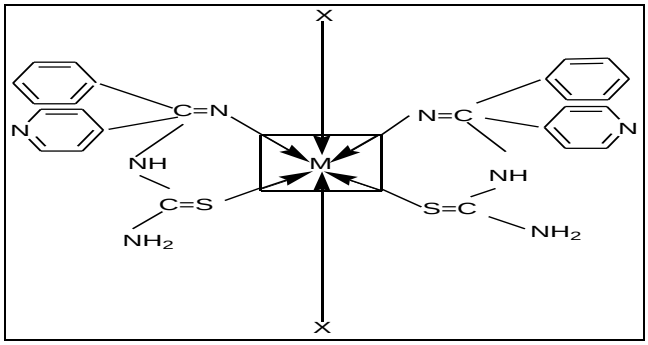

FIG. 4b:

CONCLUSION: The synthesised ligands and complexes were characterised by elemental analysis, IR spectroscopy, mass spectroscopy, UV-Vis, ^1H NMR spectroscopy and EPR spectral studies. The proposed study of complexes indicates octahedral geometry for nickel complexes and tetragonal geometry for copper complexes. Ligand was found to be bidentate which coordinates to metal through azomethine group as v(C=N) and through sulphur as v(C=S) group.

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