

SYNTHESIS AND SPECTRAL CHARACTERIZATION OF COPPER(II) COMPLEXES OF 2- BENZOYLPYRIDINE N(4)--PHENYLTHIOSEMICARBAZONE

4.1. Introduction

Copper is the third most abundant transition element in biological systems. It is bound to proteins in the body either as metalloproteins or as enzymes. The +II oxidation state is the most stable and the most important state for copper [1]. The d^9 configuration makes Cu(II) subject to Jahn-Teller distortion if placed in an environment of cubic i.e. regular octahedral or tetrahedral symmetry and this has a profound effect on all its stereochemistry [2]. Generally copper(II) forms octahedral complexes, with the weakening of two axial bonds or square planar complexes. Cu(II) also forms five coordinated complexes having square pyramidal or trigonal bipyramidal structures.

Spectral and structural investigations of a series of biologically active copper(II) complexes of thiosemicarbazones have been reported earlier. Thiosemicarbazones belong to a large group of thiourea derivatives, the biological activities - of which are functions of the parent aldehyde or ketone [3, 4]. Thiosemicarbazones are compounds with versatile structural features [5, 6] and they can coordinate to the metal either as a neutral ligand or as a deprotonated anion through the N, N, S or O, N, S donor atoms [7]. There were numerous reports on the structural and biological studies of copper(II) complexes of 2-formyl, and 2-acetylpyridine thiosemicarbazones [8, 9, 10]. D. X. West reported the structural and antifungal activities of copper(II) complexes of 2-benzoylpyridine N(4)-substituted thiosemicarbazones [11]. Recently there are reports on the

antifungal and antibacterial activities of the metal complexes of *N*(4)-phenyl 2-benzoylpyridine thiosemicarbazone [12]. Structural studies and spectral characteristics of 4-benzoylpyridine thiosemicarbazone and *N*(4)-phenyl 4-benzoylpyridine thiosemicarbazone are also reported [13]. In a review of the coordination chemistry of copper [14], there are reports on the copper(II) complexes of pyridine 2-carbaldehyde thiosemicarbazone [15], 6-methylpyridine-2-aldehyde thiosemicarbazone [16] and methyl-2-pyridyl ketone thiosemicarbazone [17].

This Chapter describes the synthesis, conductance, magnetic and spectral studies and antimicrobial activities of copper(II) complexes of 2-benzoylpyridine *N*(4)-phenylthiosemicarbazone (HL^2).

4.2. Experimental

4.2.1. Materials

Details regarding the synthesis of HL^2 is described in Chapter 2. Various copper(II) salts (GR) were used as obtained. Copper perchlorate hexahydrate was prepared by treating copper carbonate with perchloric acid, followed by evaporation and crystallization.

4.2.2. Synthesis of complexes

$[CuL^2Cl] \cdot CH_3OH$ (7)

$CuCl_2 \cdot 2H_2O$ (2 mmol, 0.341 g) in 20 ml ethanol and HL^2 (2 mmol, 0.664 g) in 20 ml hot ethanol were mixed and refluxed for 5 hrs. On cooling, blue colored solids separated, which were filtered, washed with hot water, hot ethanol and ether and dried over P_4O_{10} *in vacuo*.

$[CuL^2Br] \cdot 2H_2O$ (8)

CuBr₂ (2 mmol, 0.446 g) dissolved in a mixture of hot methanol and ethanol (40 ml) and HL² (2 mmol, 0.664 g) dissolved in 40 ml hot methanol were mixed and refluxed for 4 hrs. The blue solids separated were filtered, washed with hot water, hot ethanol and ether and dried over P₄O₁₀ *in vacuo*.

 $[CuL^2NO_3] \cdot H_2O$ (9)

To a hot solution of HL² (2 mmol, 0.664 g) in 40 ml methanol, Cu(NO₃)₂·3H₂O (2 mmol, 0.482 g) in 20 ml methanol was added and refluxed for 5 hrs. The blue colored solids formed were filtered, washed with hot water, hot ethanol and ether and then dried over P₄O₁₀ *in vacuo*.

 $[CuL^2NCS] \cdot 2H_2O$ (10)

A mixture of Cu(CH₃COO)₂·H₂O (2 mmol, 0.398 g) in 20 ml methanol and HL² (2 mmol, 0.664 g) in 40 ml methanol were refluxed for 2 hrs. To the refluxing solution, a solution of potassium thiocyanate (2 mmol, 0.198 g) in 10 ml methanol was added and again refluxed for 4 hrs. The blue colored crystals, separated on keeping for a few days, were filtered, washed with hot ethanol, hot water and ether and then dried over P₄O₁₀ *in vacuo*.

 $[CuL^2N_3]$ (11)

Solutions of Cu(CH₃COO)₂·H₂O (2 mmol, 0.3998 g) in 20 ml methanol and HL² (2 mmol, 0.664 g) in 40 ml methanol were mixed and refluxed for 2 hrs. Then a solution of sodium azide (2 mmol, 0.130 g) was added to the refluxing solution and again refluxed for 2 hrs. The green solids, which separated, were filtered, washed with hot water, hot ethanol, and ether and dried over P₄O₁₀ *in vacuo*.

$[CuL^2(HL^2)](ClO_4)$ (12)

Copper perchlorate (2 mmol, 0.414 g) in 20 ml methanol and HL^2 (2 mmol, 0.664 g) in 40 ml methanol were refluxed for 5 hrs. The dark blue solids, which separated, were filtered, washed with water, hot methanol, ether and dried over P_4O_{10} *in vacuo*.

4.2.3. Analytical methods

The details regarding the various analytical methods were discussed in the previous Chapter.

4.3. Results and discussion

4.3.1. Analytical measurements

The colors, stoichiometries, elemental analyses, and magnetic moments of the Cu(II) complexes are given in Table 4.1. All the Cu(II) complexes prepared are either blue or green in color. They are insoluble in polar solvents and soluble in dimethyl formamide and chloroform.

The molar conductances of the complexes were measured using 10^{-3} M solution in DMF. The molar conductance values of the compounds 1, 2, 3, 4 and 5 are found to be less than $20 \text{ ohm}^{-1}\text{mol}^{-1}\text{cm}^{-1}$, showing that they are nonconductors [18] which indicate that the anion and the ligand are coordinated to the central Cu(II). But the molar conductance value of compound 12 is $72 \text{ ohm}^{-1}\text{mol}^{-1}\text{cm}^{-1}$ and this is consistent with the value of 1:1 electrolyte as suggested by the formula.

The magnetic moments of the complexes are calculated from the magnetic susceptibility measurements and the values are found to be in the range 1.5-1.9 B.M. The values of magnetic moment close to the spin only value of 1.7

B.M.. indicate the presence of one unpaired electron as expected for Cu(II) complexes.

Table 4.1 Analytical data

Compound	Empirical formula	Color	Found (Calculated) (%)			μ (B.M.) at 300K
			C	H	N	
[CuL ² Cl]·CH ₃ OH (7)	C ₂₀ H ₁₉ N ₄ SOClCu	Blue	51.45 (51.95)	4.01 (4.12)	12.16 (12.12)	1.54
[CuL ² Br]·2H ₂ O (8)	C ₁₉ H ₁₉ N ₄ SBrO ₂ Cu	Blue	44.79 (44.66)	3.42 (3.72)	10.60 (10.97)	1.67
[CuL ² NO ₃]·H ₂ O (9)	C ₁₉ H ₁₇ N ₅ SO ₂ Cu	Blue	48.61 (48.04)	3.31 (3.58)	14.87 (14.75)	1.84
[CuL ² NCS]·2H ₂ O (10)	C ₂₀ H ₁₉ N ₅ S ₂ O ₂ Cu	Blue	49.72 (49.12)	3.22 (3.88)	14.57 (14.32)	1.85
[CuL ² N ₃] (11)	C ₁₉ H ₁₅ N ₇ SCu	Green	51.23 (51.06)	3.44 (3.36)	22.41 (21.94)	1.47
[Cu(HL ²)L ²](ClO ₄) (12)	C ₃₈ H ₃₁ N ₈ S ₂ OCICu	Dark blue	54.80 (55.20)	3.38 (3.75)	13.94 (13.55)	1.91

4.3.2 IR spectra

The tentative assignments of the significant IR spectral bands of HL², and their copper(II) complexes are presented in Table 4.2. The $\nu(\text{C}=\text{N})$ band of the thiosemicarbazone at 1591 cm^{-1} is found to be shifted in energy in the spectra of the complexes indicating coordination *via* the azomethine nitrogen. This is confirmed by the bands in the range $440\text{--}475\text{ cm}^{-1}$ which have been assigned to the $\nu(\text{Cu-N})$ band [19]. In all the complexes a strong band is found at *ca.* 1596 cm^{-1} which may be due to the formation of the newly formed $^2\text{N}=\text{C}$ bond. This indicates that the ligand enolizes and coordinates in the thiolate form. A strong band found at 1102 cm^{-1} in the spectrum of HL² is assigned to the $\nu(\text{N-N})$ band of the thiosemicarbazone. The increase in the frequency of this band in the spectra of the complexes, due to the increase in the bond strength, again confirms the coordination *via* the azomethine nitrogen.

In the uncomplexed thiosemicarbazone, the two bands, which appear at frequencies 1369 and 835 cm^{-1} , have been assigned to $\nu(\text{C}=\text{S})$. In the complexes these two bands are found to be shifted to lower frequencies in the ranges $1280\text{--}1335\text{ cm}^{-1}$ and $745\text{--}788\text{ cm}^{-1}$ respectively. This negative shift of the $\nu(\text{C}=\text{S})$ band in the complexes indicates the coordination *via* the thiolate sulfur atom. Strong bands observed in the region $340\text{--}355\text{ cm}^{-1}$ have been assigned to the $\nu(\text{Cu-S})$ band [20].

In all the copper complexes a strong band is observed in the region $266\text{--}280\text{ cm}^{-1}$. This is consistent with the $\nu(\text{Cu-N of pyridine})$ as suggested by Clark and Williams [21].

Based on the above spectral evidences, it is confirmed that the ligand HL² like HL¹ is tridentate, coordinating *via* the azomethine nitrogen, pyridyl nitrogen and thione / thiolate sulfur.

In the chloro complex the strong band observed at 349 cm^{-1} has been assigned to the $\nu(\text{Cu-Cl})$ bond. The $\nu(\text{Cu-Br})$ frequency is observed at 255 cm^{-1} in the bromo complex. The $\nu(\text{Cu-Cl})$ and $\nu(\text{Cu-Br})$ bands are consistent with the terminal chloro and bromo ligands. The ratio of $\nu(\text{Cu-Br})/\nu(\text{Cu-Cl})$ is 0.73 and is consistent with the usual values obtained for the complexes of the first row transition metals [19,22].

The structures and vibrational spectra of a large number of nitrate complexes have been reviewed by Addison *et al.* [23,24]. X-ray analyses show that the NO_3^- ion coordinates to a metal as a unidentate, chelating bidentate and bridging bidentate ligand of various structures. It is rather difficult to differentiate these structures by vibrational spectroscopy since the symmetry of the nitrate ion differs very little among them. Even so, vibrational spectroscopy is still useful in distinguishing unidentate and bidentate ligands.

In the nitrate complex, of HL^2 , the three bands observed at 1431, 1302 and 1014 cm^{-1} correspond to the $\nu_a(\text{NO}_2)$, $\nu_s(\text{NO}_2)$ and $\nu(\text{NO})$ modes of the nitrate group. The separation of the two highest frequency bands is 129 cm^{-1} , which indicate the presence of a terminally bonded monodentate nitrate group [19]. Besides, in the far IR spectrum of the complex, the band observed at 271 cm^{-1} can be assigned to $\nu(\text{Cu-ONO}_2)$ in consistence with the bands at $253\text{-}280\text{ cm}^{-1}$, reported earlier for Cu-ONO_2 in metal complexes [25].

In the azido complex **11**, the strong band observed at 2046 cm^{-1} is assigned to ν_a of the azide group indicative of azide coordination [26]. In thiocyanato complex **10**, a very strong band at 2098 cm^{-1} , a medium band at 869 cm^{-1} and a strong band at 480 cm^{-1} are assigned to $\nu(\text{CN})$, $\nu(\text{CS})$, and $\nu(\text{NCS})$ modes of the NCS group respectively. The intensity and position of these bands indicate the unidentate coordination of the thiocyanate group through the nitrogen. [27,28].

Table 4.2. IR spectral assignments of Cu(II) complexes of HL²

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu(\text{C}-\text{S})$	$\rho(\text{py})$	$\nu(\text{Cu}-\text{N})$	$\nu(\text{Cu}-\text{Npy})$	$\nu(\text{Cu}-\text{S})$	(Cu-X)
HL ²	1591s	1102s	1369s, 835s	622m	--	--	--	--
[CuL ² Cl]·CH ₃ O	1554s	1123s	1318s, 784s	632w	460m	272s	349s	349s
[CuL ² Br]·2H ₂ O	1536s	1128s	1316s, 754s	640m	451s	296s	344s	255s
[CuL ² NO ₃]·H ₂ O	1545s	1128m	1280s, 788s	644s	446s	272s	345s	271s
[CuL ² NCS]2H ₂ O	1534s	1124m	1314m, 748s	629s	452m	276s	346m	--
[CuL ² N ₃]	1529s	1123s	1322s, 788s	647m	463s	274s	352m	--
[CuL ² (HL ²)](ClO ₄)	1554s 1601s	1123s	1318s, 785s	644m	455s	278s	351s	--

For the perchlorate complex **12**, the bonding of the neutral ligand needs to be considered because the perchlorate group is not coordinated to the metal ion. The perchlorate complex contains a single broad band at 1123 cm^{-1} and an unsplit band at 644 cm^{-1} , indicating the presence of ionic perchlorate. The bands at 1123 and 644 cm^{-1} can be assigned to $\nu_3(\text{ClO}_4)$ and $\nu_4(\text{ClO}_4)$. The presence of these bands and the absence of a band near 930 cm^{-1} assignable to $\nu_1(\text{ClO}_4)$ suggest ionic perchlorate [29]. The IR spectrum of the compound **12** contains a strong band at 785 cm^{-1} which has been assigned to $\nu(\text{C-S})$ indicating coordination *via* the thiolate sulfur. In addition to this band, the spectrum also contains a band at 830 cm^{-1} indicating the presence of the ligand in the thione form.

According to Stefov *et al* [30] coordinated water should exhibit frequencies at 825 , 575 and 500 cm^{-1} . The absence of spectral bands in these regions in the spectra of compounds **8**, **9** and **10** indicate that the water molecules in these complexes are not coordinated but are present as lattice water.

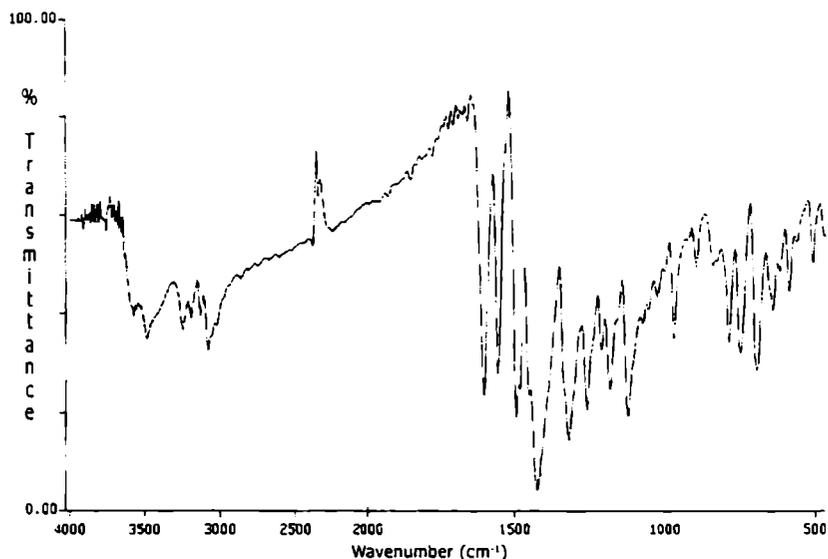


Fig.4.1. IR spectrum of $[\text{CuL}_2\text{Cl}]\cdot\text{CH}_3\text{OH}$

546.3
MAR

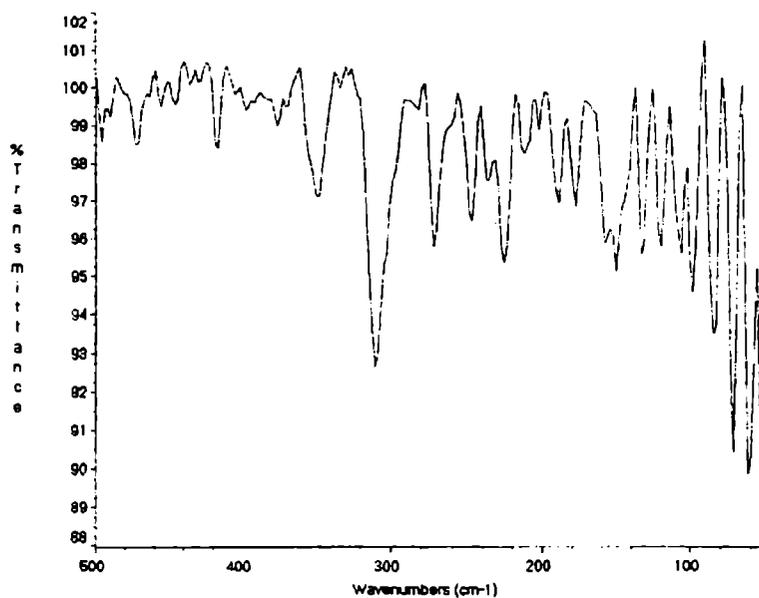


Fig.4.2. Far IR spectrum of $[\text{CuL}^2\text{Cl}]\cdot\text{CH}_3\text{OH}$

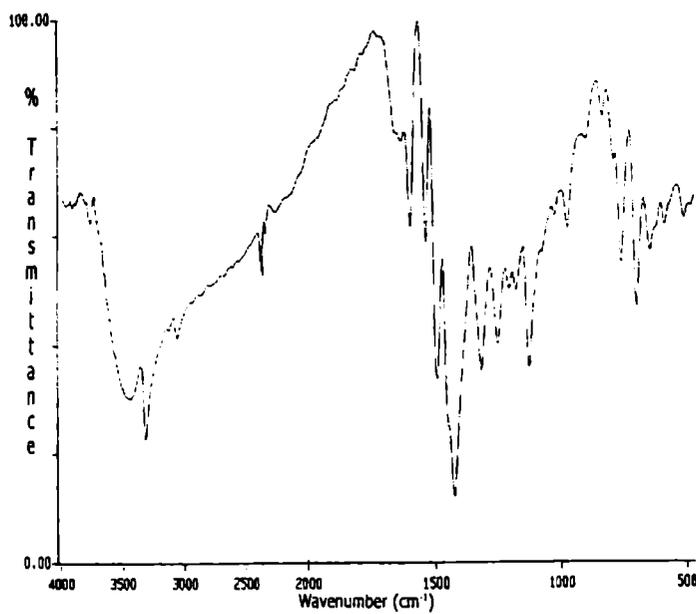
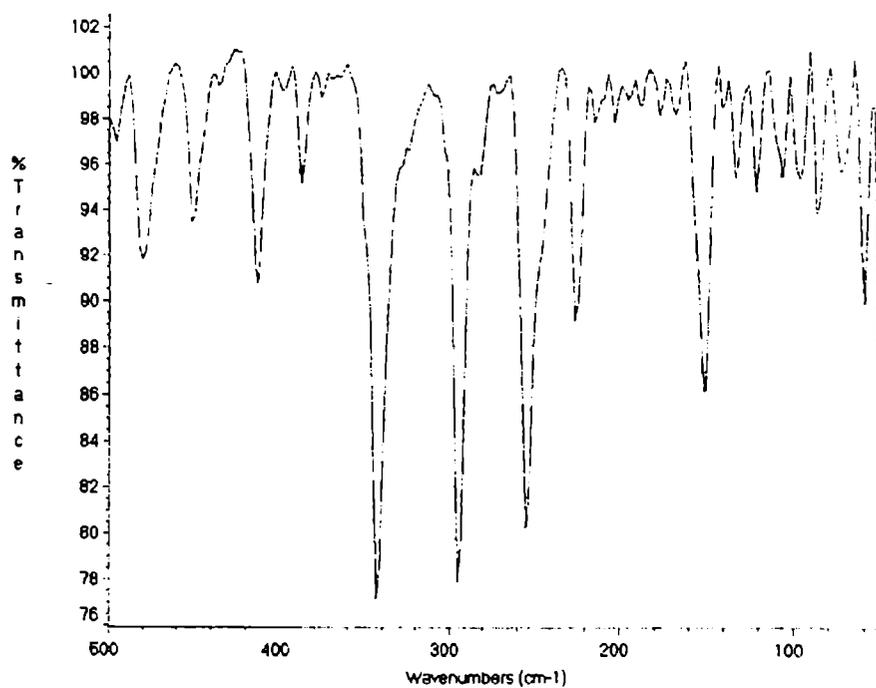
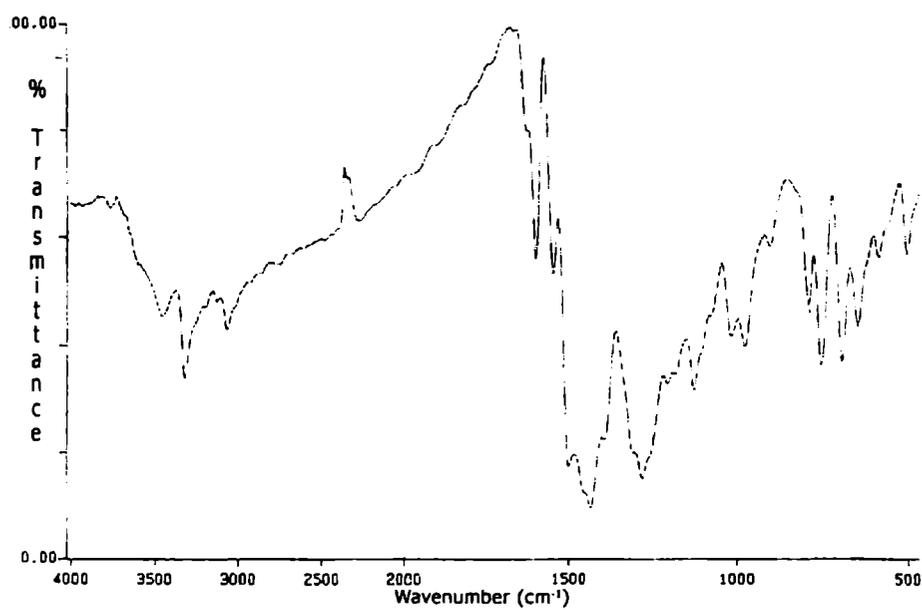
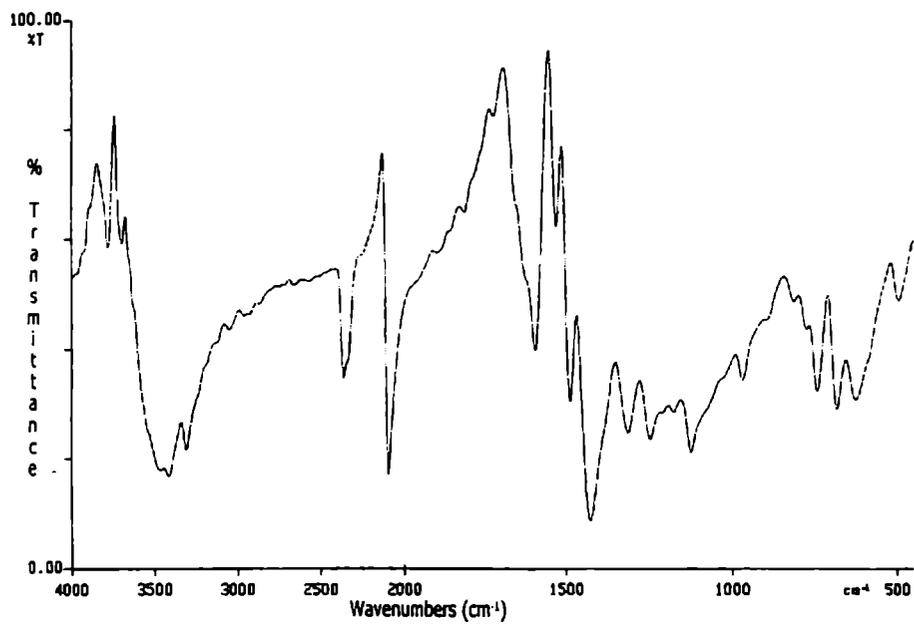
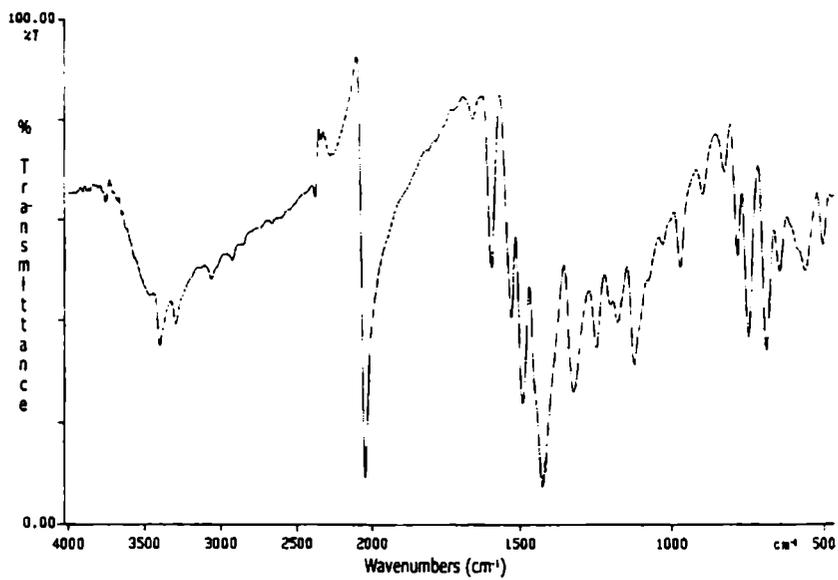


Fig.4.3. IR spectrum of $[\text{CuL}^2\text{Br}]\cdot 2\text{H}_2\text{O}$

Fig.4.4. Far IR spectrum of $[\text{CuL}^2\text{Br}] \cdot 2\text{H}_2\text{O}$ Fig.4.5. IR spectrum of $[\text{CuL}^2\text{NO}_3] \cdot \text{H}_2\text{O}$

Fig.4.6. IR spectrum of $[\text{CuL}^2\text{NCS}] \cdot 2\text{H}_2\text{O}$ Fig.4.7. IR spectrum of $[\text{CuL}^2\text{N}_3]$

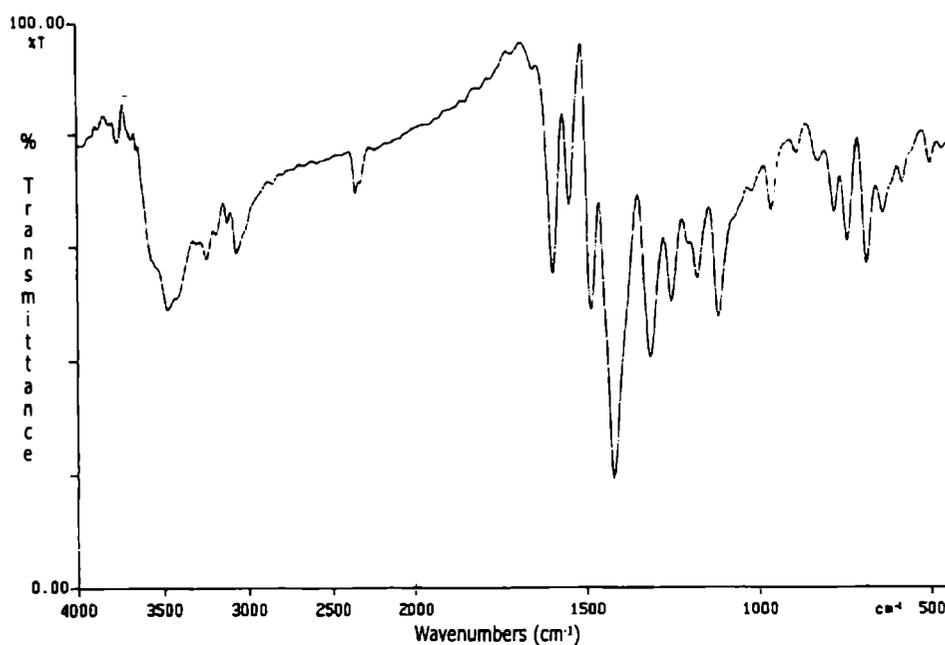


Fig.4.8. IR spectrum of $[\text{Cu}(\text{HL}^2)\text{L}^2]\text{ClO}_4$

4.3.3. Electronic spectra

The blue or green color of all the Cu(II) complexes is due to the absorption of energy in the 600 to 900 nm region of the spectrum. The energies of the electronic transitions for the thiosemicarbazone HL^2 and its Cu(II) complexes (solid state and DMF solution) are listed in Table 4.3. The solid-state electronic spectrum of the thiosemicarbazone HL^2 consists of a broad band at *ca.* 345 nm which is the $n \rightarrow \pi^*$ band of the thioamide function. Another $n \rightarrow \pi^*$ band of the pyridine ring is present at 286 nm [31]. The $n \rightarrow \pi^*$ transition of the ligand at 345 nm is shifted in energy in solution which is probably due to the hydrogen bonding taking place between the thiosemicarbazone moiety and the solvent molecules. The molar absorptivities for $n \rightarrow \pi^*$ transition are $>10^4$, which is

consistent with the values of the previously studied heterocyclic thiosemicarbazones [32].

In the solid state electronic spectra of the Cu(II) complexes, an absorption band due to the $n \rightarrow \pi^*$ transition of the thiosemicarbazone appears in the range 307-330 nm. The broad bands observed in the range 410-425 nm are assigned to the S \rightarrow Cu and Py \rightarrow Cu charge-transfer bands. In the chloro complex the shoulder observed at 318 nm is assigned to the Cl \rightarrow Cu charge-transfer transition [31,33].

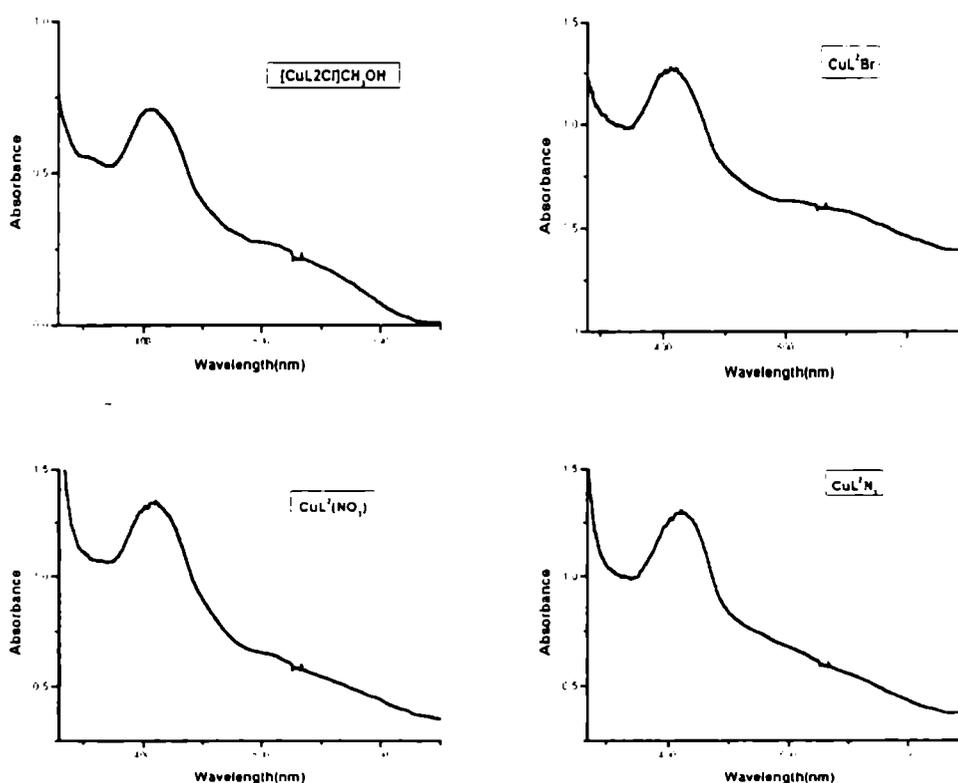
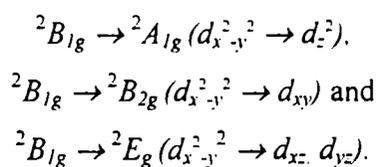


Fig.4.9. Electronic spectra of compounds 7, 8, 9 and 11

The solid-state spectra of all the Cu(II) complexes have a broad band in the region 526-610 nm. This is consistent with the broad structured band for the square planar complexes in the range 500-770 nm [34]. All the complexes exhibit a $d \rightarrow d$ band, whose maximum of absorption lie in the visible region ≈ 590 nm, as weak shoulders. Such a feature is expected for a square planar complex in accordance with the earlier reports [35]. For the square planar complexes with $d_{x^2-y^2}^2$ ground state, three spin allowed transitions are possible *viz.*,



It is difficult to resolve it into three bands [36]. The four lower orbitals are often so close in energy that individual transfer from there to the upper d level cannot be distinguished and hence the appearance of a single absorption band. It is observed that the spectra of the complexes are dominated by intense intraligand and charge transfer bands. These intense bands cause the low energy bands to appear as weak shoulders.

Table 4.3 Electronic spectral assignments (nm) of HL² and its Cu(II) complexes loge in parentheses (Lmol⁻¹cm⁻¹)

Compound	Mode	<i>d</i> → <i>d</i>	L→M	<i>n</i> → <i>π</i> *	<i>π</i> → <i>π</i> *
HL ²	Solid DMF	--	--	340, 335 (4.13),	268 262
[CuL ² Cl]·CH ₃ OH (7)	Solid DMF	610 573 (2.60)	414, 318sh 437 (4.14)	313 362 (3.83)	255 256 (4.41)
[CuL ² Br]·2H ₂ O (8)	Solid DMF	591 553 (2.41)	413 453 (4.27)	330 353 (4.61)	271sh 274sh(4.15)
[CuL ² NO ₃]·H ₂ O (9)	Solid DMF	607 624 (2.43)	417 407 (4.27)	326 311 (4.32)	282 260sh(4.25)
[CuL ² NCS]·2H ₂ O (10)	Solid DMF	561sh 625 (2.5)	423 443 (4.33)	307 311 (4.25)	279 277 (4.16)
[CuL ² N ₃] (11)	Solid DMF	590sh 528 (2.41)	422 442 (3.81)	323 352 (4.71)	277 280sh(4.15)
[CuL ² (HL ²)](ClO ₄) (12)	Solid DMF	535sh 584sh(2.34)	413 440 (4.35)	309 352 (4.21)	267sh 270sh(4.01)

4.3.4. Electron paramagnetic resonance spectra

The EPR spectra of the complexes in the polycrystalline sample at 298 K in solution at 298 and 77 K were recorded in the X band, using 100 KHz field modulation and the *g* factors were quoted relative to the standard marker TCNE (*g* = 2.0277). The EPR parameters of the copper(II) complexes obtained for the polycrystalline state at 298 K and in DMF at 298 and 77 K are presented in Table 4.4.

The copper(II) ion with a d^9 configuration, has an effective spin of $S = 1/2$ and is associated with a spin angular momentum $m_s = \pm 1/2$, leading to a doubly degenerate spin state in the absence of a magnetic field. In a magnetic field, this degeneracy is lifted and the energy difference between these states is given by $E = h\nu = g\beta H$ where h is Planck's constant, ν is the frequency, g is the Lande splitting factor (equal to 2.0023 for the free electron), β is the Bohr Magneton and H is the magnetic field. In the case of a $3d^9$ copper(II) ion the appropriate spin Hamiltonian assuming a B_{1g} ground state is given by [37].

$$\hat{H} = \beta [g_z H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] + A I_z S_z + B (I_x S_x + I_y S_y)$$

The EPR spectra of compound **11** in the polycrystalline state (298 K) show only one broad signal at $g = 2.07$. The spectra of the compounds **8**, **9** and **10** show typical axial spectra with well-defined g_{\parallel} and g_{\perp} values at ≈ 2.21 and 2.05 respectively. The spectra are often broad because of the broadening resulting from the fast spin-lattice relaxation time and exchange coupling. The spectra of compounds **7** and **12** give three g values *viz* g_1 , g_2 and g_3 , which indicate rhombic distortions in their geometry.

The geometric parameter G , which is a measure of the exchange interaction between the copper centres in the polycrystalline compound, is calculated using the equation:

$$G = (g_{\parallel} - 2.0023) / (g_{\perp} - 2.0023), \text{ for rhombic spectra, } g_{\perp} = (g_1 + g_2) / 2$$

If $G > 4$, exchange interaction is negligible and if it is less than 4, considerable exchange interaction is indicated in the solid complex [38,39]. In all the copper(II) complexes $g_{\parallel} > g_{\perp} > 2.0023$ and G value within the range 2.5-3.5 is consistent with a $d_{x^2-y^2}$ ground state.

The solution spectra of all the complexes were recorded in DMF at 298 and 77 K. In the EPR spectra of the complexes in DMF, at 298 K, four hyperfine lines are observed which arises from the coupling of copper nuclei (^{65}Cu , $I=3/2$) with the

odd electron. The spectrum of compound **7** at 77 K is a typical axial spectrum with well-resolved four hyperfine lines, no superhyperfine lines are observed in the spectrum. The spectrum of compound **8**, is isotropic without any hyperfine lines due to poor glass formation. The spectrum of compound **12** is a typical rhombic spectrum without any hyperfine and superhyperfine lines.

It was reported that the g_{\parallel} values less than 2.3 indicate considerable covalent character to the M-L bond and greater than 2.3 indicate ionic character. The g_{\parallel} values of the complexes are found to be less than 2.3, which indicate considerable covalent character to the M-L bond [40,41].

The EPR parameters g_{\parallel} , g_{\perp} , g_{av} , $A_{\parallel}(\text{Cu})$ and $A_{\perp}(\text{Cu})$ and the energies of $d-d$ transition were used to evaluate the bonding parameters α^2 , β^2 and γ^2 , which may be regarded as measures of the covalency of the in-plane σ bonds, in-plane π bonds, and out-of-plane π bonds respectively (the mathematical expressions are given in Chapter 3.).

In all the copper(II) complexes, it is observed that $K_{\parallel} < K_{\perp}$ which indicates the presence of significant in-plane π bonding. This is further confirmed by the bonding parameters α^2 , β^2 , and γ^2 which are less than 1.0, expected for 100% ionic character of the bonds, and decrease on increasing the covalent character of the bonding. This observation supports the argument that there is significant in-plane π bonding and in-plane σ bonding in the copper(II) complexes of HL².

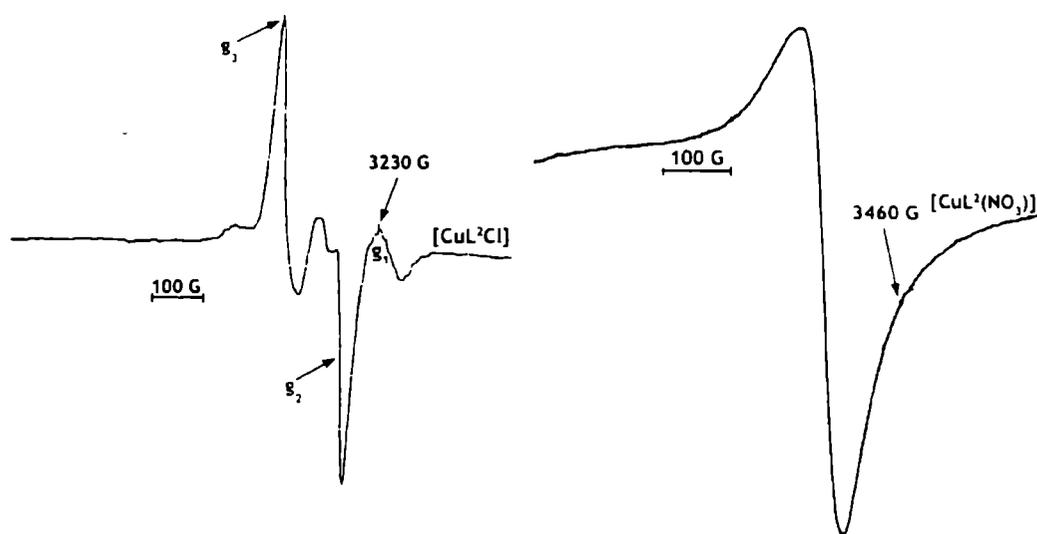


Fig.4.10. EPR spectra of compounds 7 and 9 in the polycrystalline at 298 K

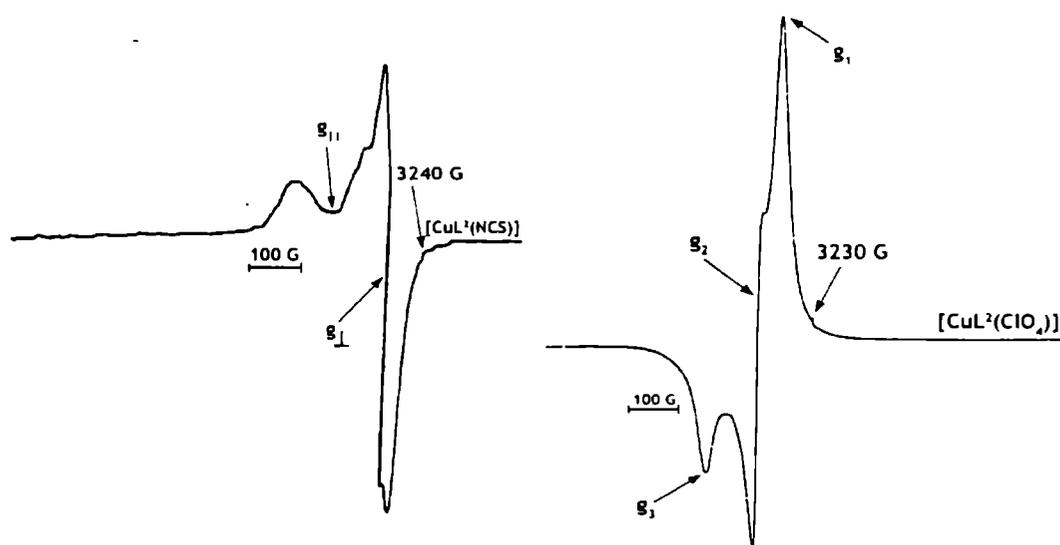


Fig. 4.11. EPR spectra of compounds 10 and 12 in the polycrystalline state at 298 K

Table 4.4 EPR parameters of the Cu(II) complexes of HL²

Compound	Solid (298 K)		DMF solution (298 K)		DMF solution (77 K)			
	$g_1/g_2/g_3$	g_{av}	g_{iso}	A_{iso}	$g_1/g_2/g_3$	g_{av}	$A_{ }$	G_{av}
[CuL ² Cl]·CH ₃ OH (7)	g_1 1.9991 g_2 2.0434 g_3 2.1230	2.0552	2.0698	84.13	$g_{ }$ 2.1500 -- g_{\perp} 2.0510	2.0840	158.91	3.03
[CuL ² Br]·2H ₂ O (8)	$g_{ }$ 2.2348 g_{\perp} 2.0898	2.1381	2.0749	112.13	g_{iso} 2.072	--	--	--
[CuL ² NO ₃]·2H ₂ O (9)	$g_{ }$ 2.213 -- g_{\perp} 2.0960	2.135	2.0560	84.00	g_1 1.971 g_2 2.0498 g_3 2.1274	2.0494	154.23	2.457
[CuL ² NCS]·H ₂ O (10)	$g_{ }$ 2.1168 -- g_{\perp} 2.0433	2.0678	2.1618	85.10	g_1 2.0593 g_2 2.169 g_3 2.2913	2.1732	175.73	2.685
[CuL ² N ₃] (11)			2.0750	102.90	g_1 1.972 g_2 2.065 g_3 2.2052	2.0809	163.58	3.20
[CuL ² (HL ²)]ClO ₄ (12)	g_1 2.0306 g_2 2.0649 g_3 2.1274	2.0743	2.0886	79.45	g_1 2.0301 g_2 2.0498 g_3 2.1274	2.0691	168.26	2.69

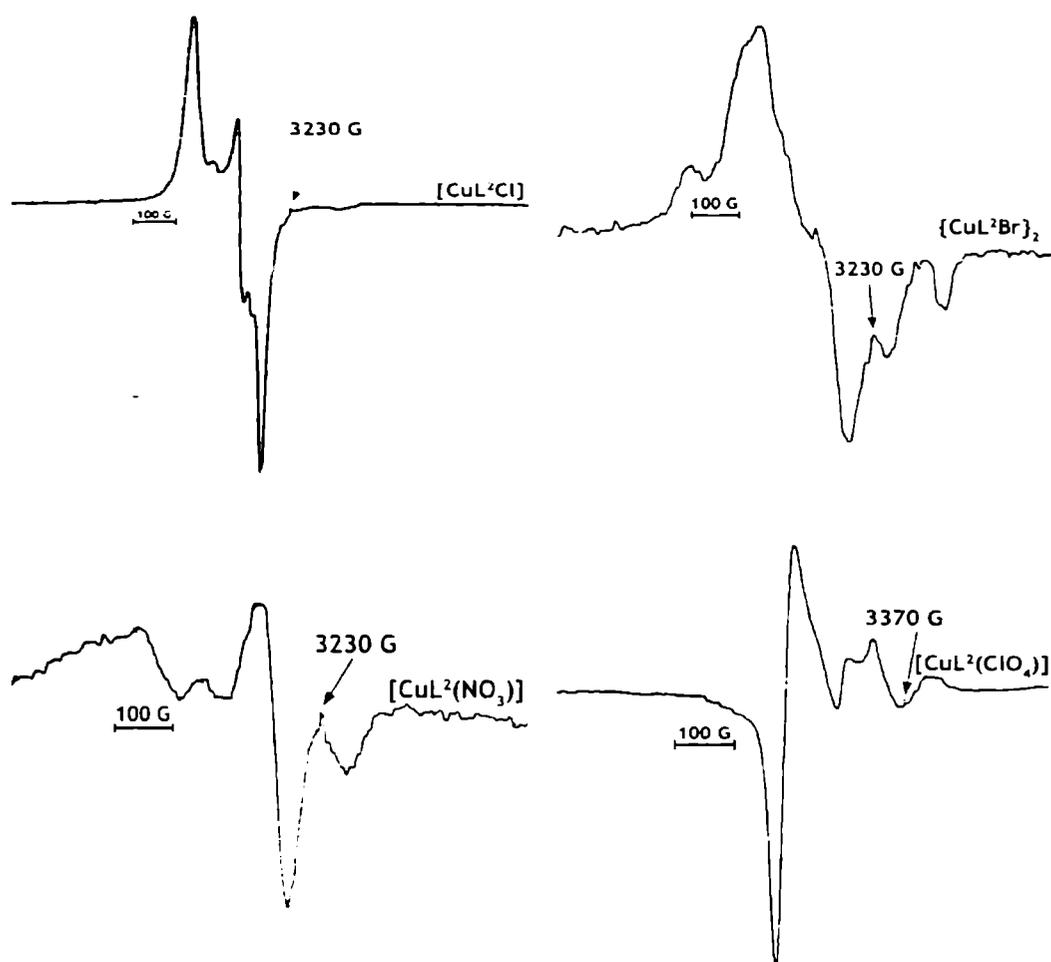


Fig.4.12. EPR spectra of compounds 7, 8, 9 and 12 in DMF at 298 K

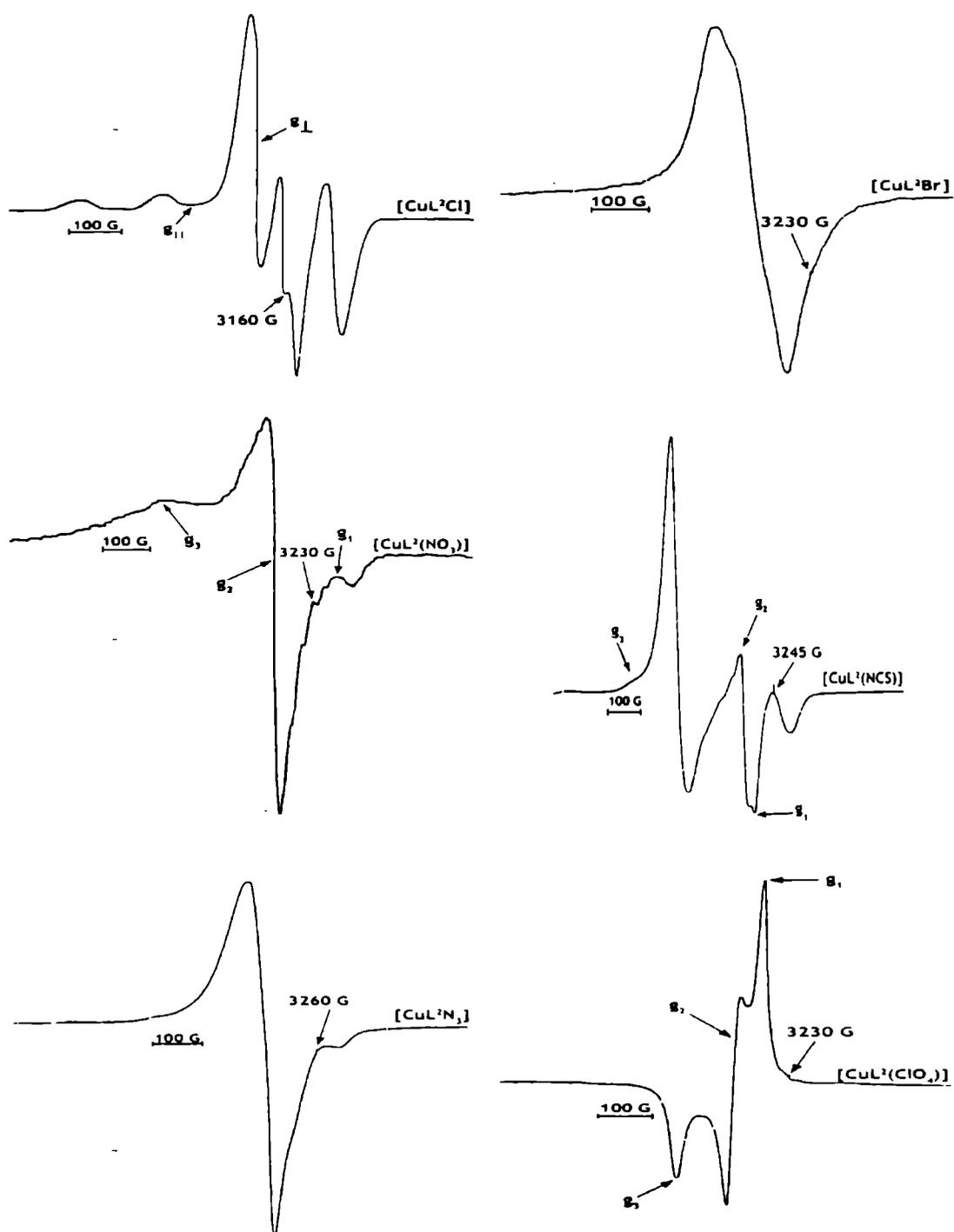


Fig. 4.13 EPR spectra of compounds 7, 8, 9, 10, 11 and 12 in DMF at 77 K.

Table.4.5 Bonding parameters and orbital reduction parameters of Cu(II) complexes of HL²

Compound	α^2	β^2	γ^2	K_{\parallel}	K_{\perp}	K_t	f
[CuL ² Cl]·CH ₃ OH	0.6392	0.9877	0.9976	0.6315	0.6333	0.3168	133.4
[CuL ² Br]·2H ₂ O	0.6423	0.9505	0.9582	0.6105	0.6155	0.4359	134.19
[CuL ² NO ₃]·H ₂ O	0.6479	0.9101	0.9793	0.5897	0.6345	0.3025	126.4
[CuL ² NCS]·H ₂ O	0.660	0.8440	0.9224	0.5570	0.608	0.3532	130.38
[CuL ² N ₃]	0.6741	0.9980	0.9877	0.6741	0.6677	0.3526	132.16
[CuL ² (HL ²)](ClO ₄)	0.6484	0.9162	1.005	0.5941	0.65190	0.3132	126.44

4.4. Antimicrobial activity

The ligand HL² and its five Cu(II) complexes were tested for their antimicrobial activity. The effectiveness of an antimicrobial agent in sensitivity testing is based on the size of the zones of inhibition. The diameter of the zone is measured to the nearest millimeter. Test substances which produce the zone of inhibition with diameters 9 mm or more are regarded as positive. i.e. having antimicrobial activity; while those cases where the diameter is below 9 mm, the bacteria are resistant to the sample tested and the sample is said to have no antimicrobial activity. Two Gram positive bacteria and three Gram negative bacteria were used as test organisms.

1. *Staphylococcus aureus* (Gram positive)
2. *Bacillus sp* (Gram positive)
3. *Escherichia coli* (Gram negative)
4. *Salmonella paratyphi* (Gram negative)
5. *Vibrio cholerae O1* (Gram negative)

The MIC (minimum inhibitory concentration), expressed in micro litres, of the compounds was also determined using the disc diffusion method and is given in

Table 4.6 The antimicrobial activity of the complexes using the disc diffusion method

Compound	Conc. (Conc/Disc in μg)	Activity Inhibition zone.				
		<i>Bacillus</i> sp	<i>Vibrio</i> <i>cholerae</i> 01	<i>Escherichia</i> <i>coli</i>	<i>Staphylococcus</i> <i>aureus</i>	<i>Salmonella</i> <i>paratyphi</i>
HL^2	50 μg	--	--	--	+ 12mm	--
$[\text{CuL}^2\text{Cl}]\cdot\text{CH}_3\text{OH}$ (7)	50 μg	--	+ 9 mm	--	--	--
$[\text{CuL}^2\text{Br}]\cdot 2\text{H}_2\text{O}$ (8)	50 μg	--	+ 10mm	--	--	--
$[\text{CuL}^2\text{NCS}]\cdot\text{H}_2\text{O}$ (10)	50 μg	--	+ 10 mm	--	--	--
$[\text{CuL}^2\text{N}_3]$ (11)	50 μg	--	+ 10 mm	--	--	+ 9 mm
$[\text{CuL}^2(\text{HL}^2)](\text{ClO}_4)$ (12)	50 μg	--	+ 9 mm	--	--	--

Table 4.6. Fig 4.14. shows the study of antimicrobial property by the disc diffusion method.

It is observed that the ligand HL^2 was active against *Staphylococcus aureus* while it was inactive against the other four test organisms. But all its Cu(II) complexes are found to be inactive against this particular bacteria. Out of the five Cu(II) complexes, four complexes are found to be active against only one type of microorganism under study, i.e. *Vibrio cholerae O1*. The complex $[CuL^2N_3]$ was found to be active against *Vibrio cholerae* and *Salmonella paratyphi*. The ligand and the Cu(II) complexes are found to be inactive against *Bacillus sp* and *Escherichia coli*.

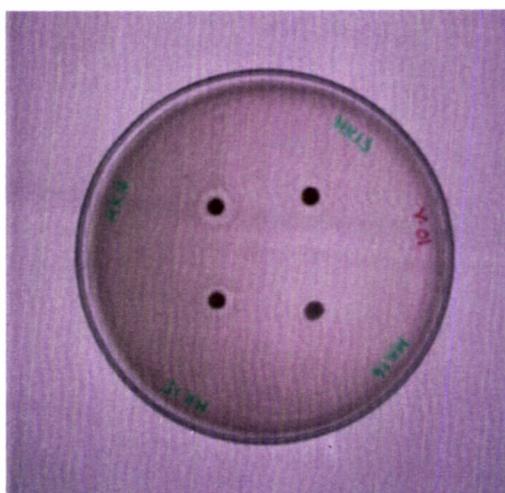


Fig.4.14. Zone of inhibition of compounds 7, 8, 9 and 10 against *Vibrio cholerae O1*

Table 4.7 MIC of HL² and its Cu(II) complexes

Compound	MIC in μl			
	<i>Bacillus</i> <i>sp</i>	<i>Vibrio</i> <i>cholerae</i> <i>O1</i>	<i>Salmonella</i> <i>paratyphi</i>	<i>Staphylococcus</i> <i>aureus</i>
HL ²	--	--	--	4
[CuL ² Cl]CH ₃ OH (7)	--	5	--	--
[CuL ² Br]·2H ₂ O (8)	--	5	--	--
[CuL ² NCS]·H ₂ O (10)	--	5	--	--
[CuL ² N ₃] (11)	--	5	4	--
[CuL ² (HL ²)](ClO ₄) (12)	--	5	--	--

References

1. J.D. Lee. Concise Inorganic Chemistry, 4thed., Oxford University Press 1991.
2. F.A. Cotton, G. Wilkinson, C.A. Murillo, Advanced Inorganic Chemistry, 6th ed., Wiley, New York, 1999.
3. S. Padhye, G.B. Kauffman, Coord. Chem. Rev. 63 (1985) 127.
4. E. Lukevics, D. Jansone, K. Rubina, E. Abele, S. Germane, L. Leite, M. Shymanska, J. Popelis, Eur.J.Med.Chem. 30 (1995) 983.
5. A. Usman, I.A. Razak, S. Chantrapomma, H.K. Fun, V. Philip, A. Sreekanth, M.R.P. Kurup, Acta Crystallogr, C 58 (2002) 652.
6. D.X. West, G.A. Bain, R.J. Butcher, J.P. Jainski, Y. Li, R.Y. Pozdniakiv, J. Valdes-Martinez, R.A. Toscano, Polyhedron 15 (1996) 665.
7. M.B. Ferrari, G. Fava. C. Pelizzi, P. Tarasani, J. Chem. Soc., Dalton Trans. (1992) 2153.
8. M.E. Hossain, M.N. Alam, J. Begum, M. Akbar Ali, M. Nazimuddin, F.E. Smith, R.C. Hynes, Inorg. Chim. Acta 249 (1996) 207.
9. A.E. Liberta, D.X. West, Biometals 5 (1992) 121.
10. D.X. West, A.M. Stark. G.A. Bain, A.E. Liberta, Transition Met. Chem. 21 (1996) 289.
11. D.X. West, J.S. Ives, J. Krejci, M.M. Salberg, T.L. Zumbahlen, G.A. Bain. A.E. Liberta, Polyhedron 14 (1995) 2189.
12. H. Beraldo, W. Nacif. A. Rebolledo, R. Costa, J.D. Ardisson, XIth Brazilian Meeting on Inorg. Chem. (2002).
13. H. Beraldo, A.M. Barreto, R.P. Vieira, A.P. Rebolledo. N.L. Speziali, C.B. Piheiro, G. Chapuis, J. Mol. Struct. 645 (2003) 213.
14. D.R. Smith, Coord. Chem. Rev. 172 (1998) 457.

15. J. Garcia-Tojal, J. Garcia-Jaca, R. Cortes, T. Rojo, M.K. Urriaga, M.I. Arriortua, *Inorg. Chim. Acta* 249 (1996) 25.
16. M.A. Ali, K.K. Dey, M. Nazimuddin, F.E. Smith, R.J. Butcher, J.P. Jasinski, J.M. Jasinski, *Polyhedron* 15 (1996) 3331.
17. P. Souza, A.I. Matesanz, V. Fernandez, *J.Chem. soc., Dalton Trans.* (1996) 3011.
18. W.J. Geary, *Coord. Chem. Rev.* 7 (1971) 81.
19. K. Nakamoto, *Infrared and Raman spectra of Inorganic and Coordination Compounds*, 5th ed. Wiley, New York, 1997.
20. D.X. West, N.M. Kozub, G.A. Bain, *Transition Met. Chem.* 21 (1996) 52.
21. R.J. Clark, C.S. Williams. *Inorg. Chem.* 4 (1965) 350.
22. S.K. Jain, B.S. Garg, Y.K. Bhoon, *Spectrochim. Acta* 42A (1986) 959.
23. M.R. Rosenthal, *J. Chem. Edu.* 50 (1973) 331.
24. C.C. Addison, N. Logan, S.C. Wallwork, D. Barner, *Rev. Chem. Soc.* 25 (1971) 289.
25. S.K. Jain, B.S. Garg, Y.K. Bhoon, *Spectrochim. Acta* 42 (1986) 701.
26. D.X. West, G. Ertem, R.M. Makeever. *Transition Met. Chem.* 10 (1985) 41.
27. A. Sreekanth, M.R.P. Kurup, *Polyhedron* 22 (2003) 3321.
28. R.A. Bailey, S.L. Kozak, T.W. Michelson, W.N. Mills. *Coord. Chem. Rev.* 6 (1971) 407.
29. B.S. Garg, M.R.P. Kurup, S.K. Jain, Y.K. Bhoon, *Transition Met. Chem.* 13 (1988) 309.
30. V. Stefov, V.M. Petrusevski, B. Soptrajanov, *J. Mol. Struct.* 293 (1993) 97.
31. D.X. West, N.M. Kozub, G.A. Bain, *Transition Met. Chem.* 21 (1996) 52.
32. D.X. West, S.I. Dietrich, I. Thientanavanich, C.A. Brown, *Transition Met. Chem.* 19 (1994) 195.
33. D.X. West, C.S. Carlson, C.P. Galloway, A.E. Liberta, C.R. Daniel, *Transition Met. Chem.* 15 (1990) 91.

34. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier Science, New York, 1984.
35. B. Harikumar, M.R.P. Kurup, T.N. Jayaprakash, *Transition Met. Chem.* 22 (1997) 507.
36. D.N Sathyanarayana, *Electronic Absorption Spectroscopy and Related Techniques*, Universities Press, Hyderabad, 2001.
37. D. Kivelson, R. Neiman, *J. Chem. Phys.* 35 (1961) 149.
38. I.M. Proctor, B.J. Hathaway, P. Nicholis, *J. Chem. Soc.*(1968) 1678.
39. B.J. Hathaway, D.E. Billing, *Coord. Chem. Rev.* 5 (1970) 1949.
40. A.H. Maki, B.R. McGrahey, *J. Chem. Phys.* 28 (1958) 35.
41. P. Bindu, M.R.P. Kurup, T.R. Satyakeerty, *Polyhedron* 18 (1998) 321.