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Studies of Schiff Base Metal Complexes Derived from Carbonyl Oximes and Sulphanilic Acid

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Mumbai, Maharashtra, India**Abstract:**

The synthesis and spectroscopic studies of some Cu (II) complexes with poly dentate Schiff bases are reported here. These Schiff bases were derived by condensing carbonyl oximes-like isonitrosoacetophenone, α -benzyl monoxime, isonitroso acetyl acetone with amines like sulphanilic acid. The characterization of the complexes was done on the basis of elemental analysis, molar conductivity, spectral IR, electronic thermal analysis and electron spin resonance spectra. On the basis of this analysis it was concluded that Cu (II) complexes exhibit paramagnetic square planar binuclear geometry with $M_2L_2Cl_2$ stoichiometry. The metal complexes have been screened for their antibacterial activity.

Keywords: Cu (II) complexes, Schiff bases, Structural analysis, ESR studies, Thermal Studies, Antibacterial studies

1. Introduction

Progress in the field of Coordination chemistry has received considerable significance because of its importance in chemical industry and life itself. Schiff bases contain azomethine ($>C=N$) group as functional group and hence act as an effective ligand. Transition metal complexes of Schiff bases have witnessed a great deal of interest in the recent years because of their chemical, pharmacological¹⁻³ and analytical applications⁴. In addition, the presence of nitrogen and oxygen donor atoms in the complexes act as stereospecific catalyst for many reactions like oxidation,⁵reduction,⁶ hydrolysis and possess antibacterial activity⁷. In this paper, the synthesis, Spectral studies, ESR, Thermal, and Antibacterial of some Cu(II) complexes with polydentate Schiff base ligands are reported.

2. Material & Methods

All chemicals used were of A. R. grade purchased from S. D. Fine chemicals (Mumbai) & used without further purification. Distilled solvents were used throughout the experiments.

Metal content was determined in the laboratory by the reported methods⁸ C, H and N analysis were performed at the IIT Mumbai. The infra-red spectra of the ligands and of their metal complexes were recorded in KBr pellets in the 4000-400 cm^{-1} region using a FTIR spectrum one supplied by Perkin Elmer instrument. The electronic spectra were recorded on Beckman Spectrophotometer, diffuse reflectance spectra of solid complexes taken on Carl-Zeiss VSU -2P spectrophotometer. The ¹H NMR spectra were recorded on a VXR-300S Varian Super Nuclear Magnetic Resonance spectrophotometer using TMS as an internal standard. ESR Spectra recorded on a Variance-Line-112 using TCNE as standard. TGA analysis was carried out using a Shimadzu DT-30 recording thermal analyzer in an inert atmosphere of nitrogen, from room temperature to 900^oc.

Antimicrobial studies: The in vitro biological screening effects of the investigated compounds were tested against the bacteria Escherichia coli, Staphylococcus, B. cereus, Bacillus subtilis were studied on laboratory grown cultures. Stock solutions were prepared by dissolving the compounds in DMSO and serial dilutions of the compounds were prepared in sterile distilled water to determine the minimum inhibition concentration (MIC). The nutrient agar medium was poured into Petri plates. A suspension of the tested microorganism (0.5 ml) was spread over the solid nutrient agar plates with the help of a spreader. Different dilutions of the stock solutions were applied on the 10 mm diameter sterile disc. After evaporating the solvent, the discs were placed on the inoculated plates. The Petri plates were placed at low temperature for two hours to allow the diffusion of the chemical and then incubated at a suitable optimum temperature for 30 – 36 hrs. The diameter of the inhibition zones was measured in millimeters.

2.1 Synthesis of 1-phenyl 1-hydroimino ethylideneiminobenzene 4-sulphonicacid (HPEIBSA) of Cu(II) complex. [L₁]

The Metal complexes of Schiff base were synthesized *in situ* condensing ethanolic solution of 0.01 mol of carbonyl oximes, namely HINAP⁹, with 0.01 mol of aqueous solution of sulphanilic acid and metal salt in 1:1:1 stoichiometric ratio and pH of the solution was raised to ~8 with 0.1 N NaOH solution when solid complexes were obtained, they were digested on water bath for about half an hour

and filtered, washed with hot water repeatedly followed by 50% alcohol and dried in vacuum. 2.2 Synthesis of 1,2-diphenyl 1-hydroxyimino ethylideneiminobenzene 4-sulphonic acid (HBEIBSA) Of Cu(II) complex. [L₂] An alcoholic solution of α -benzilmonoxime⁹ was mixed with aqueous solution of sulphanic acid and metal chloride solution in 1:1:1 molar proportions. The pH of the solution was raised 8 with dilute alkali solution when chelates separated out, the solids left overnight and filtered next day, they washed thoroughly with hot water, 50% alcohol and dried in vacuum.

2.3 Synthesis of 1-acetyl 2-methyl 1-hydroxyimino ethylideneimino benzene 4-sulphonic acid (HAMEIBSA) complex of Cu(II). [L₃] An alcoholic solution of isonitrosoacetylacetone⁹ was mixed with aqueous solution of sulphanic acid and aqueous alcoholic metal chloride in 1:1:1 molar proportion. The pH of the solution was raised to 8.0 with dilute alkali solution when solid chelate was obtained. They were digested on water bath for about half an hour and kept overnight. They were filtered on next day, washed several times with hot water followed by 50% alcohol and dried in vacuum.

3. Results & Discussion

All the metal complexes are intensely coloured. They are thermally quite stable, as shown by their high decomposition temperatures, which indicate strong metal to ligand bonding solids. The complexes are insoluble in water, ethanol, methanol, chloroform, carbon tetrachloride etc. but soluble in DMF and DMSO. The complexes dissolve in alkali like sodium hydroxide giving colour, indicating the presence of a free oxime group, suggesting oximino proton is not replaced during complexation. The elemental analysis shows 1:1 ligand metal stoichiometry for all the complexes. The analytical data along with some physical properties of the ligand and metal complexes are reported in Table 1.

The molar conductivities of 1×10^{-3} mhos $\text{cm}^2 \text{mol}^{-1}$ solutions of the complexes in nitro benzene indicate their non-electrolytic nature.¹⁰

The elemental analysis suggests 1:1 (metal: ligand) stoichiometry for all the metal complexes. They are formulated as $\text{M}_2\text{L}_2\text{Cl}_2$. Here L represents HPEIBSA, HBEIBSA and HAMEIBSA.

Complex	Colour	M.P. °C	Elemental Analysis % found % Calculated						Λ^{M} [$\text{S cm}^2 \text{mol}^{-1}$]	$\mu \text{ eff}$
			M	C	H	N	S	Cl		
$\text{Cu}_2(\text{L}_1)_2\text{Cl}_2$	Dark Green	220	16.5	40.8	3.42	6.39	7.39	7.49	0.182	1.73
			(15.93)	(41.8)	(2.7)	(6.97)	(7.9)	(8.71)		
$\text{Cu}_2(\text{L}_2)_2\text{Cl}_2$	Green	155	13	50	3	5.2	6	7.2	0.142	1.73
			(13.30)	(50.25)	(3.97)	(5.8)	(6.7)	(7.32)		
$\text{Cu}_2(\text{L}_3)_2\text{Cl}_2$	Brown	220	15.8	34.27	2.5	7.2	8	9	0.135	1.72
			(16.65)	(34.59)	(2.88)	(7.33)	(8.38)	(9.17)		

Table 1: Physical and Analytical Data of the metal complexes

The infrared spectra of the free carbonyl oximes were compared with those of their Cu(II) complexes to determine the bonding mode of the ligands to the metal in the complexes. The strong C=O stretching vibrations, in HINAP is absent in the spectra of the metal complexes corresponding ligands. The observations confirm the successful replacement of carbonyl oxygen by imino nitrogen during Schiff base formation prior to the *in situ* formation of the complexes.

The spectra of the parent carbonyl oximes show strong and broad absorption band in the region 3300 cm^{-1} , which is due to ν O-H band due to =NOH. The FT-IR spectra of the metal complexes reveal a band in the region 3246-3398 cm^{-1} attributed to O-H stretching may be concluded that sulphonic group is deprotonated on the basis of pK values of $-\text{SO}_3$ vibrations of free =NOH group. It is also corroborated by PMR spectra of complexes. It group, The N-O stretching vibrations in the spectra of complexes are in the range of 883-1024 cm^{-1} indicating a shift bonding through deprotonated free oxime. The coordination of azomethine nitrogen is confirmed by the presence of bands in the 1590-1598 cm^{-1} region in the ligand which underwent a shift to a lower frequency after complexation¹¹. All complexes show extra bands in the 515-618 cm^{-1} and 413-492 cm^{-1} region assigned to $\nu(\text{M-N})$ ¹² and $\nu(\text{M-O})$ ¹³ stretching vibrations. The medium or weak intensity bands at 355-380 cm^{-1} is due to terminal M-Cl. This data is in good agreement with literature values¹⁴. Thus these Schiff bases behave as multi-dentate ligand coordinating through the deprotonated sulphonic group and azomethine nitrogen. The presence of an ionised $-\text{SO}_3^-$ is indicated by 1120-1160 cm^{-1} . Selected IR bands for the ligands and their metal complexes are represented in Fig. 1 along with the IR spectral data (cm^{-1}) in Table 2.

Complex	ν O-H	ν C=N azomethine	ν C=N oximino	ν N-O	ν M-N	ν M-O
$\text{Cu}_2(\text{L}_1)_2\text{Cl}_2$	3374	1595	1566	894	541	492
$\text{Cu}_2(\text{L}_2)_2\text{Cl}_2$	3374	1596	1579	922	552	437
$\text{Cu}_2(\text{L}_3)_2\text{Cl}_2$	3270	1594	1558	1004	520	480

Table 2: I.R. Spectral data of Cu (II) complexes (cm^{-1})

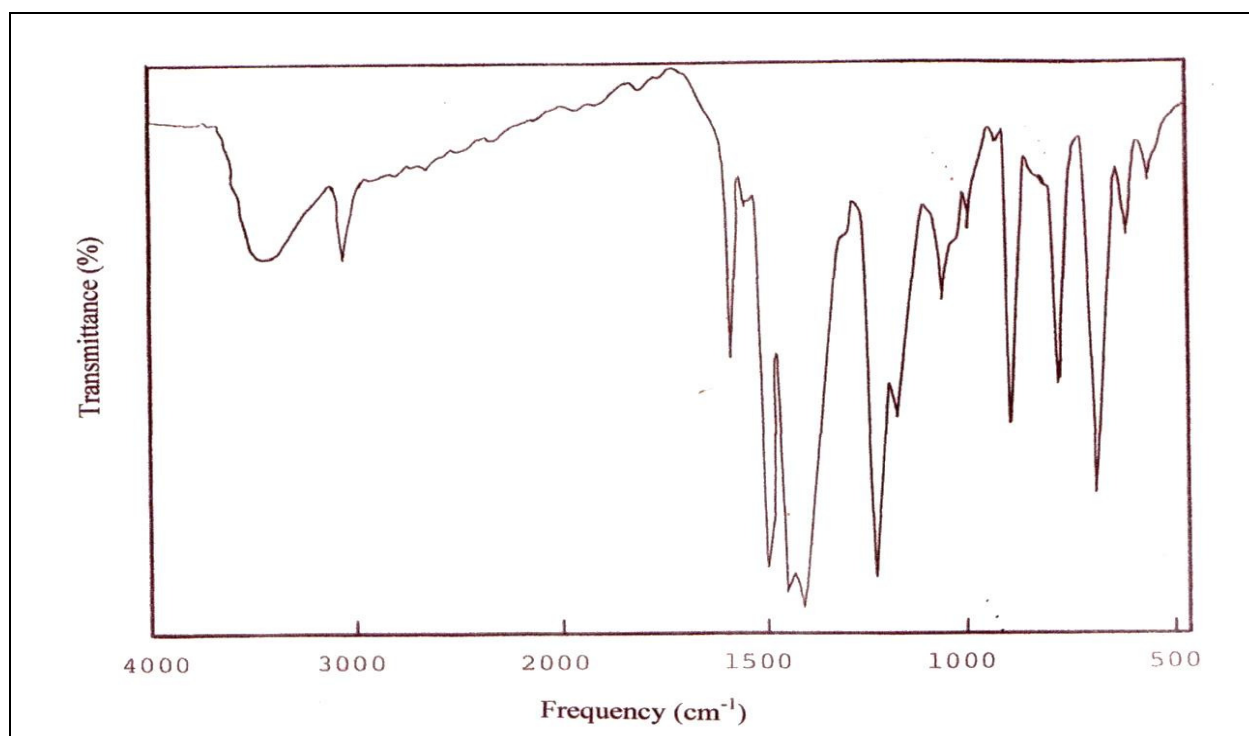


Figure 1: Infrared absorption Spectrum of $\text{Cu}_2(\text{HPEIBSA})_2\text{Cl}_2$

The metal complexes indicate that oximino proton of HINAP observed at 11.4δ in dioxan or at 9.06δ in CDCl_3 is shifted to $12-12.6\delta$ this positive shift indicates the proton of the $=\text{NOH}$ is not replaced.

Magnetic moments of the complexes are very close to 1.73 B.M corresponding to the presence of an unpaired electron expected for a d^9 system and are in the range normally found for $\text{Cu}(\text{II})$ complexes.¹⁵

The normal magnetic moments observe for $\text{Cu}(\text{II})$ complexes suggest absence of any appreciable $\text{Cu}-\text{Cu}$ interaction at least at room temperature and indicate that the complexes are magnetically dilute and nearly square planar. Electronic absorption spectra of $\text{Cu}(\text{II})$ complexes Fig. 2 show charge transfer transition bands in the range $23,180-27,770\text{cm}^{-1}$. The electronic spectral properties of the $\text{Cu}(\text{II})$ complexes are just as variable as the stereo chemical environments.¹⁵⁻¹⁶

The diffuse reflectance spectra of three solid(II) complexes Fig. 3 show a broad band in the region $14,285-15,625\text{cm}^{-1}$ with distinct maximum around $14,285\text{cm}^{-1}$. The position and shape of the unsymmetrical absorption band suggest that it may be ascribed to crystal field transitions and may envelope at least two or possibly three d-d transitions in a distorted octahedral or nearly planar environment.

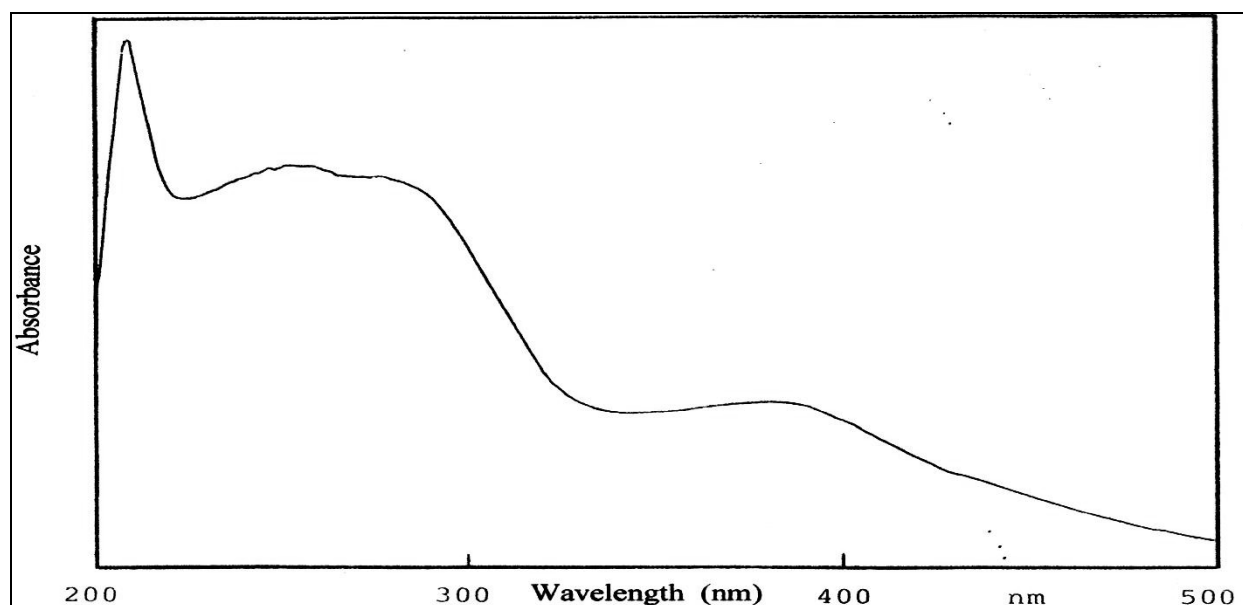


Figure 2: Electronic absorption spectrum of $\text{Cu}_2(\text{HPEIBSA})_2\text{Cl}_2$

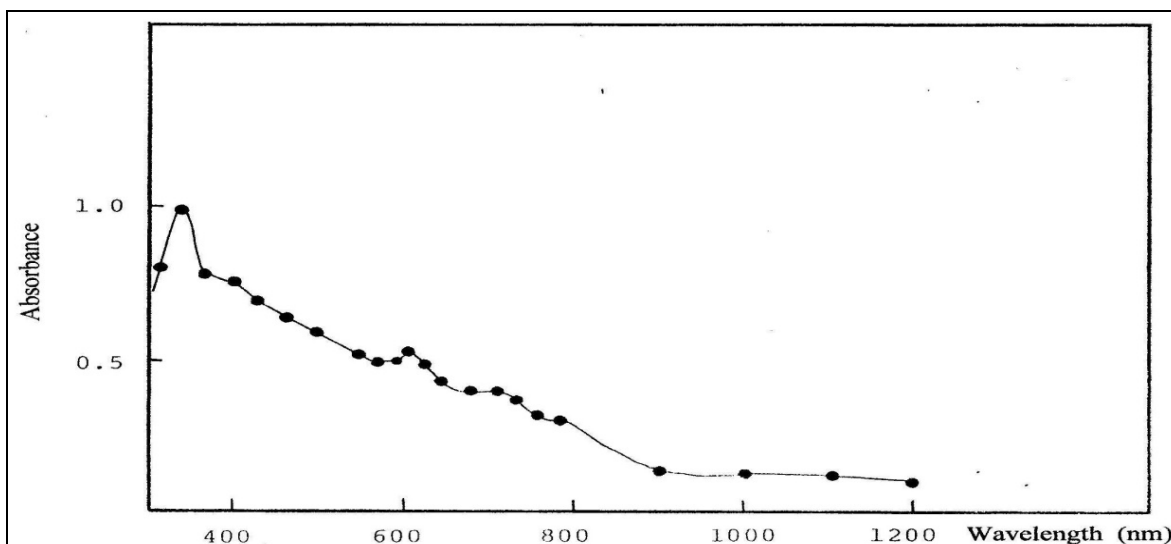


Figure 3: Diffuse reflectance spectrum of $Cu_2(HPEIBSA)_2Cl_2$

The ESR spectra of the Cu(II) complexes under present study at room temperature are poorly resolved and do not show very well defined hyperfine structure. This may be due to low crystallinity of the complexes.¹⁷

The complex $Cu_2(HPEIBSA)_2Cl_2$ in solid state at room temperature as well as at liquid nitrogen temperature Fig. 4 does not show any hyper fine structure. In fact, it shows somewhat unusual shape and exhibits single isotropic signal centred at $g=2.076$ corresponding to $\Delta Ms = +/- 1$. At liquid nitrogen temperature, the ESR spectral curve also seems to show another transition corresponding to $\Delta Ms = +/- 2$ appearing around half magnetic field (1500G). This observation appears to suggest weak anti ferromagnetic interaction between the paramagnetic centres. This may also explain the observed value of paramagnetic moment and binuclear nature of the complex.

The complex $Cu_2(HBEIBSA)_2Cl_2$ shows only isotropic spectrum with g values being 2.058 and 2.064 at room temperature as well as liquid nitrogen temperature respectively.

The complex $Cu_2(HAMEIBSA)_2Cl_2$ shows expected hyperfine structure due to interaction with Cu(II) nucleus. The nature of the spectrum suggests axial symmetry with elongated tetragonal structure¹⁸ in the solid state as only two g values $g_{||}$ and g_{\perp} . The lowest $g_{||}$ value less than 2.3 suggest that metal ligand bonding in this complex may be basically covalent, the lowest g_{\perp} is; less than 2.1 in present case suggesting tetragonal distorted or nearly planar stereochemistry¹⁸. The axial symmetry parameter G values are greater than 4 indicating there is very small interaction between the two copper centres at room temperature as shown in Table 3.

$g_{ }$	g_{\perp}	g_{av}	$A_{ }$	A_{\perp}	A_{av}	G
2.225	2.052	2.110	110 G	40.0 G	63.33 G	4.33

Table 3: ESR Spectral Parameter for Cu(II) Complex

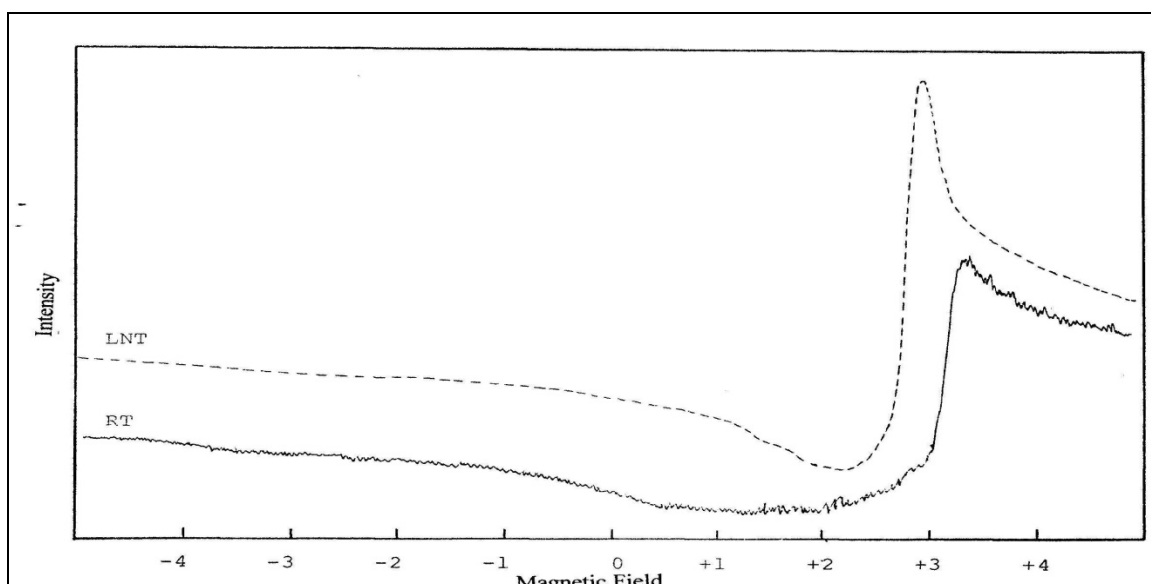


Figure 4: ESR Spectrum of $Cu_2(HPEIBSA)_2Cl_2$

Thermal studies indicate that they undergo thermal decompositions in two stages as shown in Fig. 5; the first stage of decomposition is observed around 200°C and is accompanied by about 7.00 % loss in weight which corresponds to loss of a chlorine molecules above this temperature they continuously lose weight till a temperature of about 480°C is reached. The observed weight loss is about 49% which attributed to loss of the organic moiety as shown in Table 4 & 5.

Ligand/complexes	Temperature range [C ⁰]	% weight loss	
		observed	Calculated
Cl ₂	~190	7	7.42
Cl ₂ +4(C ₆ H ₅)+2(C=NOH)	~480	49	48.64

Table 4: Thermal Decomposition Data for and Metal Complex Cu₂(HBEISA)₂Cl₂

Ligand/complexes	Temperature range [C ⁰]	% weight Loss	
		observed	Calculated
2CH ₃ +2(COCH ₃)	~180	15	15.2
Cl ₂ +4(CH ₃)+2(C=NOH) 2(COCH ₃)	~220	36	35.7
do + 2SO ₂	~400	54	52.5

Table 5: Thermal Decomposition Data for and Metal Complexes Cu₂(HAMEIBSA)₂Cl₂

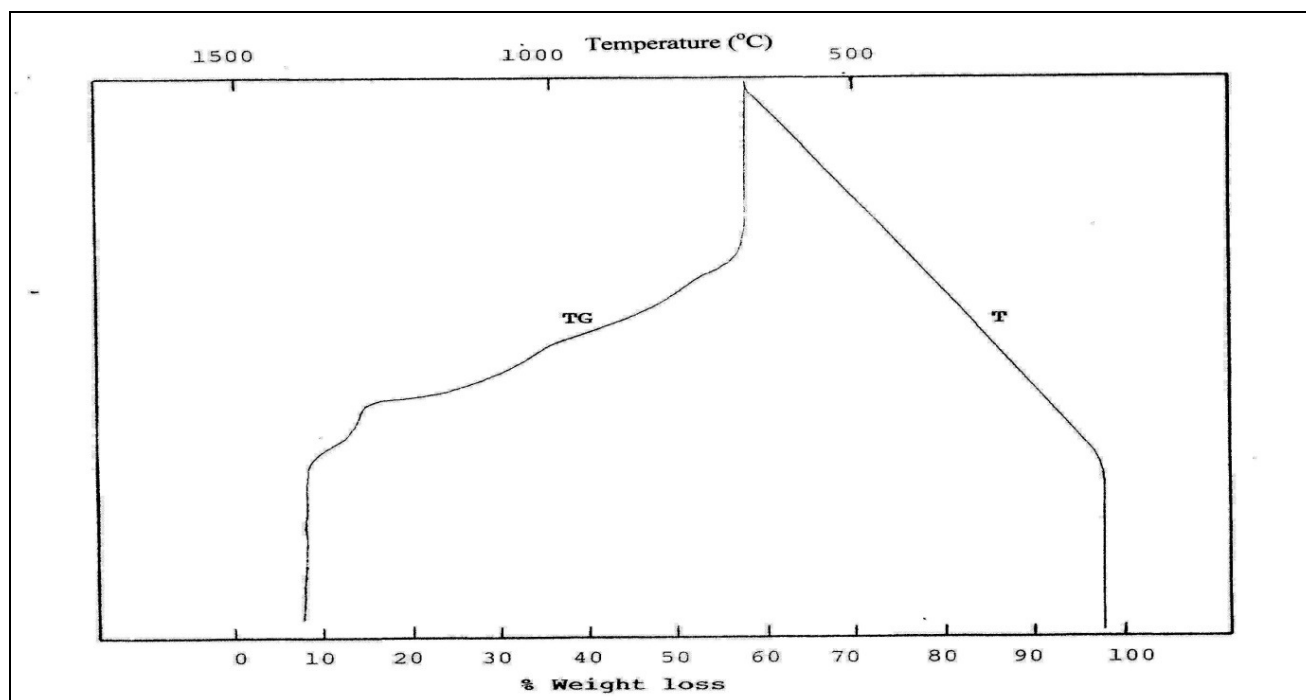


Figure 5: Thermogram of Cu₂(HAMEIBSA)₂Cl₂

Under antimicrobial studies Escherichia coli, Staphylococcus, B. cereus, Bacillus subtilis were studied on laboratory grown cultures; these yielded kind of information which is of value in guiding and understanding their therapeutic use. The concentration required to inhibit various organisms and the effects of environmental conditions on their activity are of paramount importance. The complexes show moderate activity against (10-18 mm) against the above mentioned bacteria as shown in the table given below. This shows that besides the complex formation, the nature of the metal ion has important role in the inhibition of the pathogenic activity of the bacteria. HPEIBSA, HBEISA, and HAMEIBSA respectively.

COMPOUND	B. subtilis(mm)	B. cereus(mm)	S. aureus(mm)	E. coli(mm)
Cu ₂ (HPEIBSA) ₂ Cl ₂	16	14	18	12
Cu ₂ (HBEIBSA) ₂ Cl ₂	18	10	11.5	17

Table 6: Agar cup method for the antibacterial activity of the Cu(II) complexes in (DMF).

4. Conclusions

The Schiff base and their Cu (II) complexes were characterized by elemental analysis, conductance measurements, IR, ESR, UV-VIS spectra, Thermal studies. On the basis of above data Cu(II) complexes derived from Schiff bases appear to behave as Paramagnetic moment and binuclear nature of the complex, ligand coordinating through the deprotonated sulphonic and azomethine nitrogen in Cu(II) complexes and exhibit square planar structure as shown in Fig. 6.

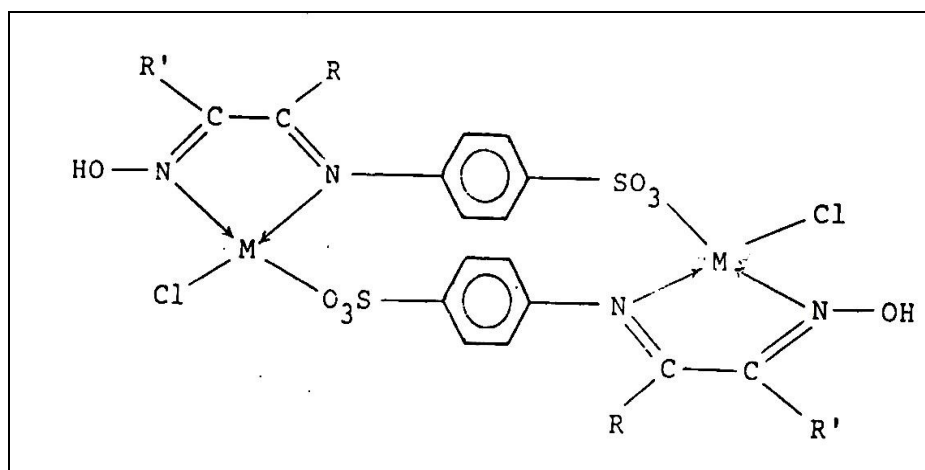


Figure 6: The proposed structure of Cu(II) complexes
 $R = C_6H_5, CH_3$ $R' = H, C_6H_5, COCH_3$ $M = Cu(II)$

5. Acknowledgement

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6. References

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Annexure

Complex	Colour	M.P. °C	M	C	H	N	S	Cl	λ_{M} [S cm ² mol ⁻¹]	μ eff
Cu ₂ (L ₁) ₂ Cl ₂	Dark Green	220	16.5	40.8	3.42	6.39	7.39	7.49	0.182	1.73
			(15.93)	(41.8)	(2.7)	(6.97)	(7.9)	(8.71)		
Cu ₂ (L ₂) ₂ Cl ₂	Green	155	13	50	3	5.2	6	7.2	0.142	1.73
			(13,30)	(50.25)	(3.97)	(5.8)	(6.7)	(7.32)		
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			(16.65)	(34.59)	(2.88)	(7.33)	(8.38)	(9.17)		

Table 1: Physical and Analytical Data of the metal complexes