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# Synthesis, Spectral and Thermal Characterization of Cu(II) Complexes Containing Schiff Base Ligands and Their Antibacterial Activity Study

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**Abstract:** Four complexes of Cu(II) ions containing Schiff base ligands, L<sup>1</sup>(C<sub>20</sub>H<sub>14</sub>O<sub>4</sub>N<sub>4</sub>) [N,N'-Bis-(2-nitro-benzylidene)-benzene-1,2-diamine] derived from condensation reaction of o-phenylenediamine and 2-nitrobenzaldehyde, L<sup>2</sup>(C<sub>8</sub>H<sub>8</sub>N<sub>3</sub>SCl)[2-(2-chlorobenzylidene) hydrazinecarbothioamide] derived from condensation reaction of thiosemicarbazide and o-chlorobenzaldehyde and L<sup>3</sup>(C<sub>9</sub>H<sub>11</sub>N<sub>3</sub>OS) [2-(4-methoxybenzylidene)-hydrazinecarbothioamide, derived from the condensation reaction of anisaldehyde and thiosemicarbazide respectively. The synthesized ligands and their metal complexes were isolated in solid state from the reaction medium and characterized by molar conductivity measurement, magnetic susceptibility, infrared, electronic spectral, thermal analysis and some physical measurements. The overall reactions were monitored by TLC analysis.

**Keywords:** Schiff Base, Copper Complexes, Antibacterial, Carbazide

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## 1. Introduction

Chelating ligands are widely used for the preparation of metal complexes with promising properties. Among these ligands, Schiff bases containing nitrogen and phenolic oxygen donor atoms are of considerable interest due to their potential application in catalysis, drug design, painting, medicine and material science [1-3]. Metals have played an important role in biological systems over the decades. Many are much significant to our diets in varying quantities, although people have only recently understand their important. Incorporating metal ions into a biological system may be carried out for therapeutic or diagnostic purposes, although these purposes overlap in many cases. Metals not only provide path for synthesis, but they also introduce functionalities that enhance drugs action. Transition metal complexes of these ligands display varying configurations, structural diversity and sensitivity to molecular

environments. Copper exposés considerable biochemical function either as an essential trace metal or as a constituent of various exogenously ordered compounds in humans. In its first role it is bound to ceruloplasmin, albumin, and other proteins, while in its latter it is bound to ligands of various types forming complexes that interact with biomolecules, mainly proteins and nucleic acids. The multidimensional role of copper in biological systems is proven by several studies. In particular the involvement of copper in human diseases has been described from a medicinal-chemical and a biochemical view focusing on the molecular physiology of Cu transport [4-6]. Current interest in Cu complexes is stemming from their potential use as antimicrobial, antiviral, anti-inflammatory, antitumor agents, enzyme inhibitors, or chemical nucleases. Markedly, the biochemical action of Cu complexes with non-steroidal anti-inflammatory drugs (NSAIDs) has been studied [7]. Numerous Cu(II) complexes of NSAIDs showing enhanced anti-inflammatory and

antiulcerogenic activity, as well as reduced gastrointestinal toxicity compared to the uncomplexed drug, have been prepared and structurally characterized [7-10]. Recently we have synthesized some metal complexes containing Schiff bases and investigated their biological application [1, 8-12]. On the continuation of this work we here in report the three Cu(II) ion complexes of three different Schiff base ligands and their antibacterial activity study.

## 2. Material and Methods

### 2.1. Reagents and Chemicals

All the reagents used were of Analar grade or chemically pure grade. All metal (II) salts were used as nitrate and chloride. The solvents such as Ethanol, methanol, chloroform, Diethyl ether, petroleum ether, DMSO (dimethyl sulfoxide) and acetonitrile were purified by distillation procedure.

### 2.2. Physical Measurement

The melting point or the decomposition temperature of all the prepared ligand and metal complexes were observed in an electro thermal melting point apparatus model No. AZ6512. It was however, not possible to measure the melting points beyond 3000C. Vibrational spectra (IR) were recorded with SHIMADZU-8400, FTIR spectrophotometer, (Japan), in the range 4000-400  $\text{cm}^{-1}$  with a KBr disc as reference. UV-Visible spectra of the complexes in methanol (0.0005 molar) were recorded in the region 200-800 nm on a Thermolectron Nicolet evolution 300 UV-Visible spectrophotometer. The Sherwood Scientific Magnetic Susceptibility Balance that following the Gouy method were used to measure the magnetic moment of the solid complexes. The electrical conductance measurements were made at room temperature in freshly prepared solution (10-3 M) in DMSO and Methanol using a WPACM35 conductivity meter and a dip-cell with a platinum electrode. The purity of the ligand and metal complexes was tested by Thin Layer Chromatography (TLC).

## 3. Experimental

### 3.1. Synthesis of Schiff Base Ligand $\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_4$ ( $L^1$ ) *N,N*-Bis (2-nitro-benzylidene)-benzene-1,2-diamine

To a stirring solution of o-phenylenediamine (1.08 gm, 10 mmol) dissolved in 20mL of ethanol with water, a solution of 2-nitrobenzaldehyde (3.02mL, 20mmol) in 10mL ethanol was added drop wise. After sometime 2ml of glacial acetic acid was added with the reaction mixture and the solution was refluxed for 5-6 h and allowed to cool overnight in room temperature as shown in figure 1. The golden product was filtered washed several times with ethanol and finally with diethyl ether and dried in vacuum over anhydrous  $\text{CaCl}_2$ . The reaction was monitored by TLC using petroleum ether, ethyl acetate, toluene and methanol solvents. The product was found to be soluble in methanol, DMF and DMSO. It provided 62% yield at 34°C.

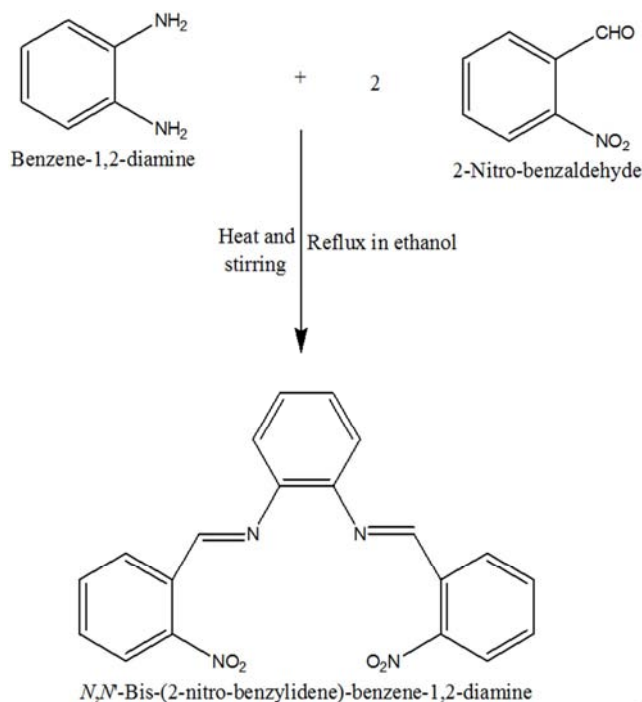


Figure 1. Synthesis route of Schiff base ligand ( $L^1$ ).

### 3.2. Synthesis of Schiff Base Ligand $\text{C}_8\text{H}_8\text{N}_3\text{SCl}$ ( $L^2$ ), *E*-(2-(2-chlorobenzylidene)hydrazinecarbothioamide

To a stirring solution of thiosemicarbazide (0.91 g, 10mmol) dissolved in 30mL of ethanol with water and a solution of o-chlorobenzaldehyde (1.12ml, 10mmol) in 15ml ethanol was added drop wise and refluxed for 5 h and allowed to cool overnight as shown in figure 2. The white product was filtered washed several times with ethanol and finally with diethyl ether and dried in vacuum over anhydrous  $\text{CaCl}_2$ . The reaction was monitored by TLC using petroleum ether, ethyl acetate, toluene and methanol solvents. The product was found to be soluble in DMF and DMSO. It provided 92% yield at 34°C.

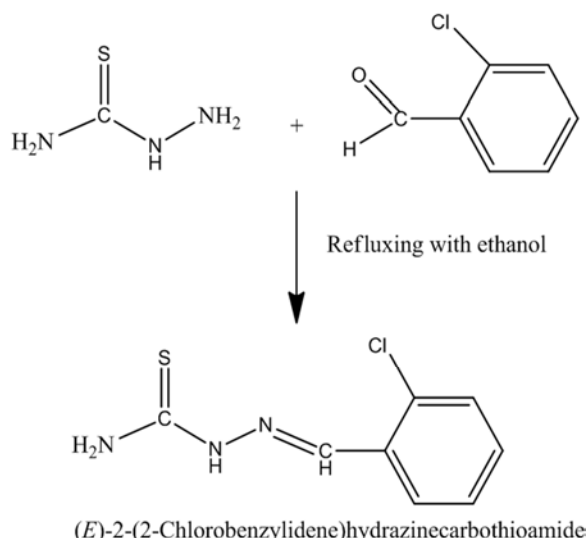


Figure 2. Synthesis route of Schiff base ligand ( $L^2$ ).

### 3.3. Synthesis of Schiff Base Ligand $C_9H_{11}ON_3S$ ( $L^3$ ), 2-(4-chlorobenzylidene) Hydrazinecarbothioamide

To a stirring solution of thiosemicarbazide (0.91g, 10 mmol) dissolved in 20mL of ethanol, a solution of p-anisaldehyde (1.22mL, 10mmol) in 10mL ethanol was added drop wise. After sometime 2ml of conc.  $H_2SO_4$  was added with the reaction mixture and the solution was refluxed for 5 h and allowed to cool overnight in room temperature as shown in figure 3. The white product was filtered washed several times with ethanol and finally with diethyl ether and dried in vacuum over anhydrous  $CaCl_2$ . The reaction was monitored by TLC using petroleum ether, ethyl acetate, toluene and methanol solvents. The product was found to be soluble in DMF and DMSO. It provided 80% yield.

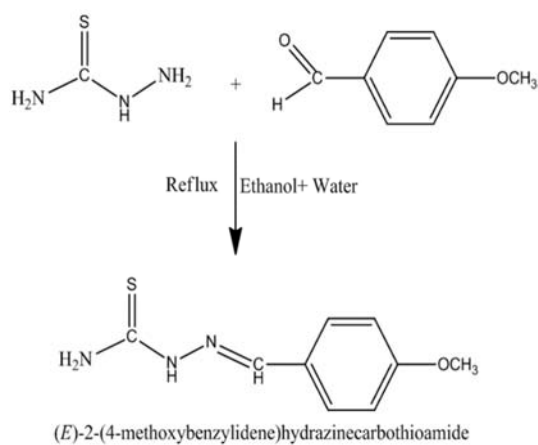


Figure 3. Synthesis route of Schiff base ligand ( $L^3$ ).

### 3.4. Synthesis of Metal Complexes Containing Schiff Base Ligand ( $L^1$ )

The complex was prepared in 1: 2 molar ratios (metal: ligand). Methanolic solution (20 mL) of Cu(II) nitrate trihydrate (0.241g, 1mmol) was taken in a two necked round bottom flask and kept on magnetic stirring. A methanolic solution (20 mL) of prepared Schiff base ligand ( $L^3$ ) (0.740g, 2mmol) was added drop wise and stirred with heating for 4-5h. On cooling, precipitate was formed which was filtered, washed with ethanol, acetone, and diethyl ether and dried in vacuum desiccators over anhydrous  $CaCl_2$ . The reaction was monitored by TLC using different solvents. The complex was soluble in DMSO with heat. The Schiff base and proposed structure of complex were shown in figure 4.

### 3.5. Synthesis of $[CuC_8H_8N_3SCl]$ Complex Containing Schiff Base Ligand ( $L^2$ )

The complex was prepared in 1: 2 molar ratio (metal: ligand). Methanolic solution (20 mL) of Cu(II) nitrate trihydrate (0.241g, 1mmol) was taken in a two necked round bottom flask and kept on magnetic stirring. A methanolic solution (20 mL) of prepared Schiff base ligand ( $L^2$ ) (0.42g, 2mmol) was added drop wise and stirred with heating for 4-5h. On cooling, precipitate was formed which was filtered, washed with ethanol, acetone, and diethyl ether and dried in

vacuum desiccators over anhydrous  $CaCl_2$ . The reaction was monitored by TLC using different solvents. The complex was soluble in DMSO with heat. The Schiff base and proposed structure of complex were shown in figure 5.

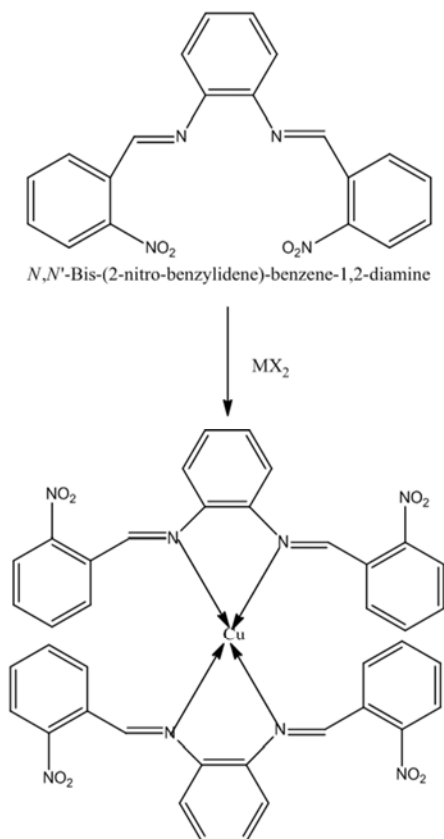


Figure 4. Synthesis pathway of metal complex containing Schiff base ligand ( $L^1$ ).

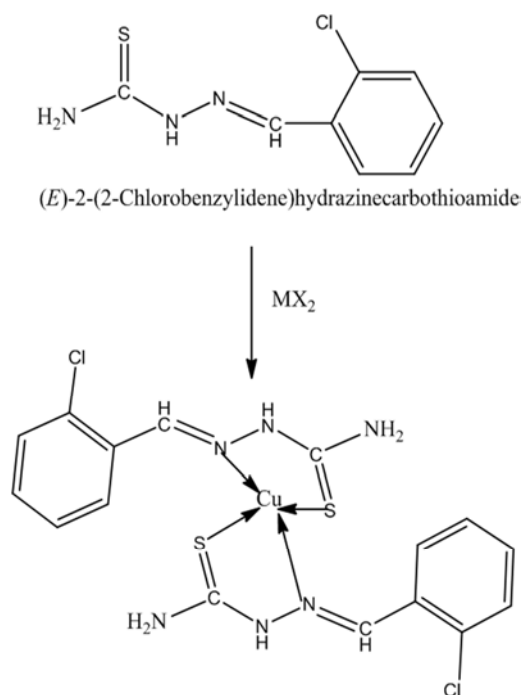
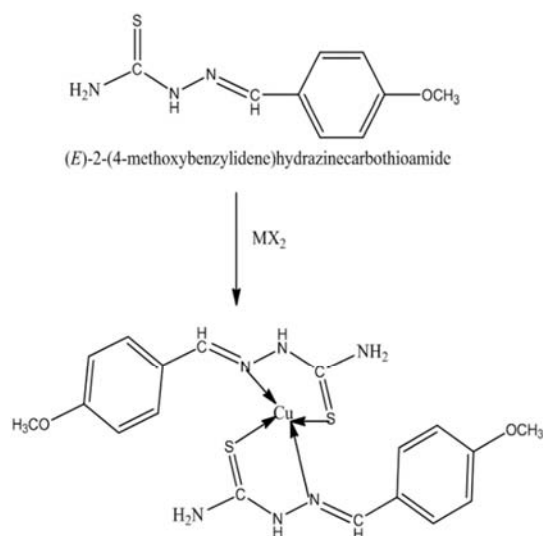


Figure 5. Synthesis pathway of  $[CuC_8H_8N_3SCl]$  complex.

### 3.6. Synthesis of Metal Complex $[C_9H_{11}ON_3SCu]$ Containing Schiff Base Ligand ( $L^3$ )



**Figure 6.** Synthesis of metal complex  $[C_9H_{11}ON_3SCu]$  containing Schiff base ligand ( $L^3$ ).

The complex was prepared in 1: 2 molar ratio (metal: ligand). Methanolic solution (20 mL) of Cu(II) nitrate

trihydrate (0.241g, 1mmol) was taken in a two necked round bottom flask and kept on magnetic stirring. A methanolic solution (20 mL) of prepared Schiff base ligand ( $L^3$ ) (0.418g, 2mmol) was added drop wise and stirred with heating for 4-5h. On cooling, precipitate was formed which was filtered, washed with ethanol, acetone, and diethyl ether and dried in vacuum desiccators over anhydrous  $CaCl_2$ . The reaction was monitored by TLC using different solvents. The complex was soluble in DMSO with heat. The Schiff base and proposed structure of complex were shown in figure 6.

## 4. Results and Discussion

### 4.1. Physical Properties

Some physical properties of the Schiff base ligand and its metal complexes such as melting point, color, pH, conductivity and activation energy are shown in table 1. The complexes are intensely colored, powder solids, which decomposes above  $300^\circ C$ . Molar conductance values of the complexes in aqueous solution and in DMSO ( $10^{-3}M$ ) showed low values (7-9  $\mu S/cm$ ) indicating them to be non-electrolyte shown in Table 1.

**Table 1.** Physical characteristics and analytical data of ligands and complexes.

Compound/Empirical Formula	Formula Weight	Color	Yield (%)	Melting Point / Decomposition temp.( $^\circ C$ )	Activation Energy, E kJ/mol	Conductivity $\mu S/cm$
Ligand( $L^1$ ) $C_{20}H_{14}O_4N_4$	374	Golden	62%	$265^\circ C - 270^\circ C$	16.05	
$[Cu C_{40}H_{28}O_8N_8]$	812.25	Light lemon	81%	$210^\circ C - 215^\circ C$	16.39	6
Ligand( $L^2$ ) $C_8H_8N_3SCL$	213	White	92%	$285^\circ C - 290^\circ C$	14.82	
$[CuC_{16}H_{16}N_6S_2Cl_2]$	508.44	Apple green	74%	$250^\circ C - 255^\circ C$	26.85	7
Ligand( $L^3$ ) $C_9H_{11}ON_3S$	209	White	80%	$145^\circ C - 150^\circ C$	15.78	
$[CuC_{18}H_{22}O_2N_6S_2]$	500.08	Van dyk brown	86%	$165^\circ C - 170^\circ C$	17.23	8

### 4.2. IR Spectral Analysis

At first the complexes heat six hours and KBr overnight in the oven. Then the complexes and KBr grind with a pestle in a mortar. Infrared spectra disc were recorded as KBr with a SHIMADZU-8400, FTIR spectrophotometer, Japan, from  $4000-200\text{ cm}^{-1}$ .

#### 4.2.1. IR Spectra of Schiff Base Ligand ( $L^1$ ) and It's $[CuC_{40}H_{28}O_8N_8]$ Complex

The spectrum of ligand showed a strong absorption band at

$1616\text{ cm}^{-1}$  due to the azomethine  $\nu(C=N)$  and  $3435\text{ cm}^{-1}$  due to  $\nu(OH)$  stretching frequency respectively in the free ligand indicating that the condensation has taken place between the CHO moiety of salicylaldehyde and  $-NH_2$  moiety of thiosemicarbazide [8]. These bands are shifted to lower frequency on complexation with Cu(II) ions (Figure 7). New vibrations at 579 which are not present in the free Schiff base are attributed to the existence of  $\nu(M-N)$  (table 2). The appearance of these vibrations confirmed the involvement of nitrogen atoms in chelation [9-10].

**Table 2.** FTIR spectral data of the ligand ( $L^1$ ) and it's  $[CuC_{40}H_{28}O_8N_8]$  complex.

Ligand/Metal Complexes	IR/ $\text{cm}^{-1}$				
	$\nu(O-H)$	$\nu(C=N)$	$\nu(C-O)$	$\nu(M-O)$	$\nu(M-N)$
$C_{20}H_{14}O_4N_4$	3435	1625	1493	-	-
$[Cu C_{40}H_{28}O_8N_8]$	3427	1610	1446	579	435

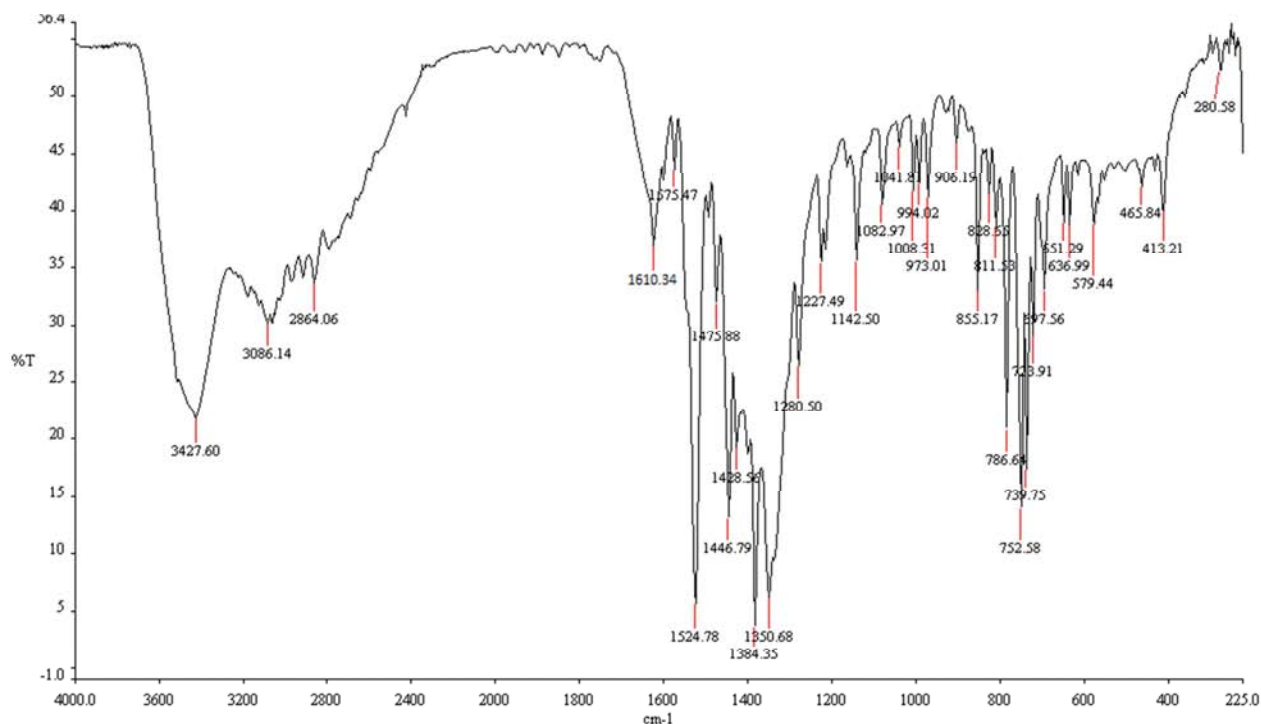


Figure 7. IR spectra of Schiff Base ligand  $[CuC_{40}H_{28}O_8N_8]$  complex.

#### 4.2.2. IR Spectra of Schiff Base Ligand ( $L^2$ ) and It's $[CuC_{16}H_{16}N_6S_2Cl_2] \cdot H_2O$ Complex

The spectrum of ligand showed a strong absorption band at  $1611\text{ cm}^{-1}$  due to the azomethine  $\nu(C=N)$  stretching frequency of the free ligand indicating that the condensation have taken place between the CHO moiety of o-chlorobenzaldehyde and  $-NH_2$  moiety of thiosemicarbazide. The IR spectra of the free ligand showed two bands at  $3416\text{ cm}^{-1}$  and  $3249\text{ cm}^{-1}$  may be attributed to the free  $-NH_2$  and  $\nu(N-H)$  groups respectively. These bands remains in the

same region in complex spectra, suggesting nonparticipation in coordination of one terminal  $-NH_2$  group in thiosemicarbazone. The band observed at  $3416\text{ cm}^{-1}$  was assigned to the  $\nu(O-H)$  of hydroxyl group. The strong band  $756\text{ cm}^{-1}$  for  $\nu(C=S)$  indicated that  $C=S$  bond was present in the Schiff base ligand. New vibrations at  $523\text{ cm}^{-1}$  and  $456\text{ cm}^{-1}$  (table 3) which are not present in the free Schiff base are attributed to the existence of  $\nu(M-N)$  and  $\nu(M-S)$  respectively [10-13].

Table 3. FTIR spectral data of the ligand ( $L^1$ ) and it's  $[CuC_{40}H_{28}O_8N_8]$  complex.

Ligand/Metal Complexes	IR/ $\text{cm}^{-1}$			
	$\nu(C=OH)$	$\nu(C=N)$	$\nu(M-N)$	$\nu(M-S)$
$C_8H_8N_3SCl$ ( $L^2$ )	3416	1611	-	-
$[CuC_{16}H_{16}N_6S_2Cl_2]$	3420	1609	523	456

#### 4.2.3. IR Spectra of Schiff Base Ligand ( $L^3$ ) and It's $[CuC_{18}H_{22}O_2N_6S_2] \cdot H_2O$ Complex

The peaks obtained at  $3405\text{ cm}^{-1}$  and  $3290\text{ cm}^{-1}$  may be assigned to symmetric and asymmetric ( $-N-H$ ) stretching frequency of primary amino group. The broad peak obtained between  $3282$  and  $2829\text{ cm}^{-1}$  may be assigned to overlapping of peaks of hydrogen bonded  $\nu(N-H)$  and aromatic  $C-H$  stretching frequency. The bands obtained between  $1186\text{ cm}^{-1}$  and  $1245\text{ cm}^{-1}$  in ligand were due to  $\nu(-OCH_3)$  groups. The

peaks observed at  $1606\text{ cm}^{-1}$  and  $834\text{ cm}^{-1}$  may be assigned to  $\nu(C=N)$  and  $\nu(C=S)$ . The bands at  $1606\text{ cm}^{-1}$  and  $834\text{ cm}^{-1}$  assigned to  $\nu(C=N)$  and  $\nu(C=S)$  modes and these bands shifted towards lower frequency in the spectra of Cu(II) complex, which indicated that coordination takes place through nitrogen of  $\nu(C=N)$  group and sulphur of  $\nu(C=S)$  group. At lower frequency the complex exhibited new bands at  $540$  and  $397\text{ cm}^{-1}$  (table 4) which further supported the coordination site  $\nu(M-N)$  and  $\nu(M-S)$  vibrations [14-16].

Table 4. FTIR spectral data of the ligand and ( $L^3$ ) and it's  $[CuC_{18}H_{22}O_2N_6S_2] \cdot H_2O$  complex.

Ligand/Metal Complexes	IR/ $\text{cm}^{-1}$			
	$\nu(C=N)$	$\nu(C=S)$	$\nu(M-N)$	$\nu(M-S)$
$C_9H_{11}ON_3S$ ( $L^3$ )	1606	834	-	-
$[CuC_{18}H_{22}O_2N_6S_2]$	1572	819	523	395

### 4.3. UV-Visible Spectral Analysis

The UV-Vis absorption spectra of the ligand and its complex was recorded after dissolving into DMSO solvent at room temperature. The electronic spectral data of Schiff bases metal complexes was shown in table 5. The electronic spectrum of the free Schiff base ligand ( $L^1$ ) display bands at 292 nm which is assigned to charge transfer transition. The electronic spectral data of complex  $[Cu C_{40}H_{28}O_8N_8]$  reveal band at 300 nm which is also attributed to charge transfer transition.

The electronic spectrum of the free Schiff base ligand ( $L^2$ ) display bands at 263 nm and 332 nm which have been assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition of imine moiety respectively. In the case of metal complexes  $[CuC_{16}H_{16}N_6S_2Cl_2]$ , the bands are shifted to longer wavelength with increasing the intensity. Such a shift may be attributed to the donation of lone pair electron present in the nitrogen atom of the Schiff base metal ions. The absorption band observed at 270 nm corresponding to  $\pi \rightarrow \pi^*$  transition of aromatic chromophore. The absorption band observed at 304 nm correspond to  $n \rightarrow \pi^*$  transition of imine moiety. New band appeared at 401 nm corresponding to metal-ligand charge transfer transition (figure 8) [16-18]. However, taking into account the spectrum and the magnetic moment value, the configuration of the Cu(II) ion, square planner could be assumed for its complex.

The UV-Vis band observed for ligand ( $L^3$ ) exhibits electronic transitions with strong band at 329 nm, was assigned to charge transfer transition. In Cu(II) complex of ( $L^3$ ) a shoulder is observed at 340 nm that can be assigned to ligand to metal charge transfer transitions (LMCT) [19-21].

However, taking into account the spectrum and the magnetic moment value, the configuration of the Cu(II) ion, square planner could be assumed for its complex.

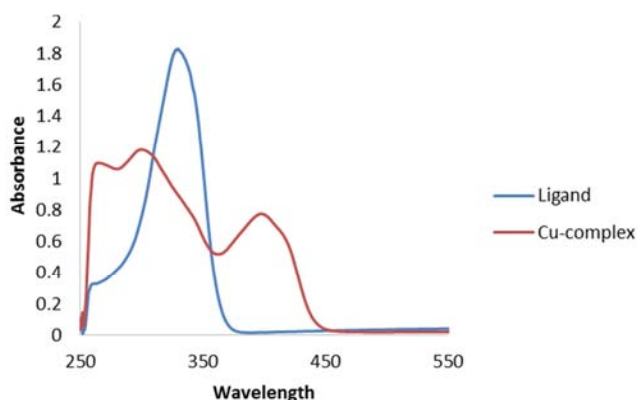


Figure 8. Electronic Spectra of Ligand ( $L^3$ )[ $C_8H_8N_3SCl$ ] and its Cu-complex.

### 4.4. Thermogravimetric Analysis

The thermal decomposition analysis of solid Cu(II) metal complex was carried out under nitrogen atmosphere and heating rate was suitably controlled at  $30^\circ C \text{ min}^{-1}$  and the weight loss was measured from the ambient temperature up to  $800^\circ C$ . The data from TGA and DTG clearly indicated that the decomposition of the complexes proceed in three or four steps. There were some minor steps and asymmetry of TGA/DTG curves also observed. The weight losses for each complex were calculated within the corresponding temperature ranges. The different thermodynamic parameters are listed in Table 6.

Table 5. Magnetic moments and electronic spectral data for metal complexes.

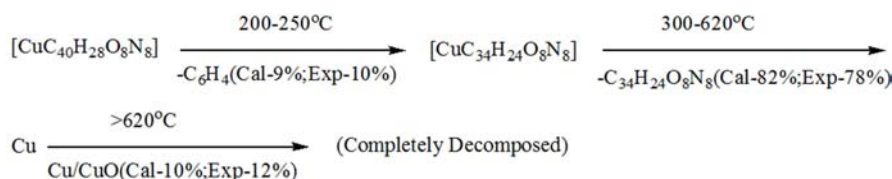
Compound	$\lambda_{\text{max}}$ n. m	Wave Number $\text{cm}^{-1}$	$\mu_{\text{eff}}$ /B. M	Assignment
[Cu $C_{40}H_{28}O_8N_8$ ]	300	33333	1.27	C. T (M $\rightarrow$ L)
	270	37037		$\pi \rightarrow \pi^*$
[Cu $C_{16}H_{16}N_6S_2Cl_2$ ]	304	32894	0.80	$n \rightarrow \pi^*$
	401	24937		C. T (M $\rightarrow$ L)
[Cu $C_{18}H_{22}O_2N_6S_2$ ]	340	29411	0.78	C. T (M $\rightarrow$ L)

#### 4.4.1. For [Cu $C_{40}H_{28}O_8N_8$ ] Complex

The decomposition of Cu(II) complex was occurred in three main steps (Figure 9). The data from the TGA and DTG curve clearly showed that the metal complex was stable up to  $200^\circ C$ , indicating absence of hydrated and coordinated water. At first step the part of ligand ( $-C_6H_4$ ) were decomposed at temperature  $200-250^\circ C$  (calculated 9.35%, experimental 10.00%). In 2<sup>nd</sup> step the decomposition

of ( $-C_{34}H_{24}O_8N_8$ ) moiety was take place at temperature  $300-620^\circ C$  (calculated 82.0%, experimental 78.65 %). Finally the complex was completely decomposed and removed as Cu/CuO (calculated 9.79%, experimental 12.00%) at above  $>620^\circ C$  [10, 12].

The probable fragment figure for the complex is shown below:



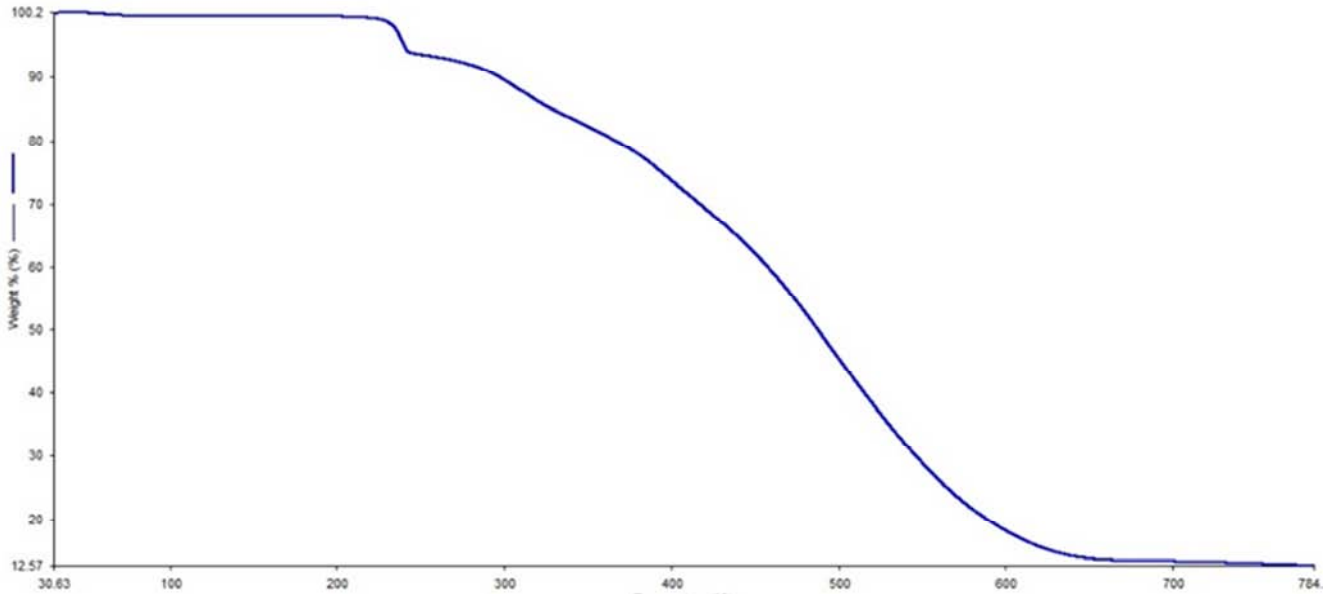


Figure 9. TGA curve of  $[\text{CuC}_{40}\text{H}_{28}\text{O}_8\text{N}_8]$  Complex.

#### 4.4.2. For $[\text{CuC}_{16}\text{H}_{16}\text{N}_6\text{S}_2\text{Cl}_2]$ Complex

The Cu(II) Complex was decomposed in main three or four steps (Figure 10). The TGA and DTG curve showed that complex was decomposed at 1<sup>st</sup> steps in the temperature range 180-220°C (calculated 4.98 %, experimental 5.05% weight) which can be attributed to the elimination of one hydrated water molecules. In 2<sup>nd</sup> step the decomposition of  $(-\text{C}_8\text{H}_8\text{N}_3)$  moiety was take place at

temperature 250-550°C (calculated 32.0%, experimental 37.0 %). The ligand part  $(\text{C}_8\text{H}_8\text{N}_3\text{S}_2^-)$  were decomposed at the 3<sup>rd</sup> step at temperature range 550-650°C (calculated 46.29%, experimental 40.10 %) and finally the complex was completely decomposed and removed as Cu/CuO (calculated 18.04%, experimental 18.25%) [1, 22].

The probable fragment figure for the complex is shown below:

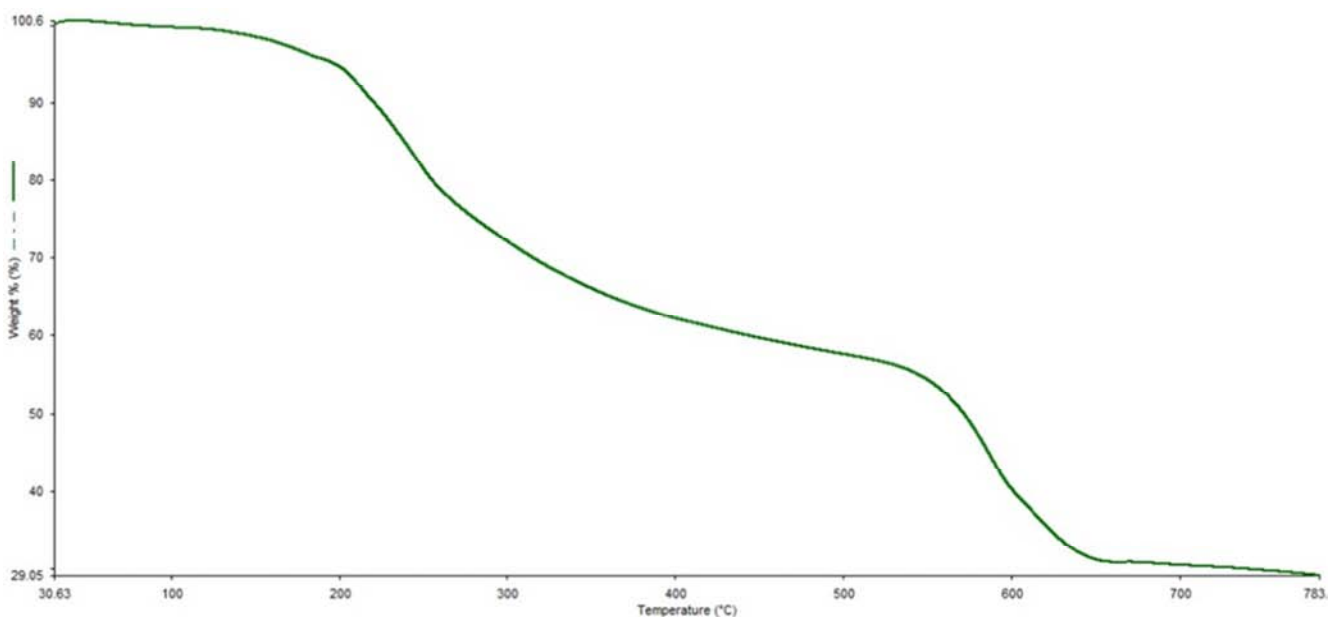
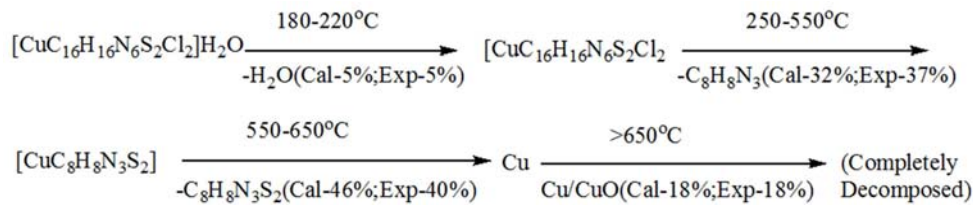


Figure 10. TGA curve of  $[\text{CuC}_{16}\text{H}_{16}\text{N}_6\text{S}_2\text{Cl}_2]$  Complex.

Table 6. Thermal data of Cu(II) complexes.

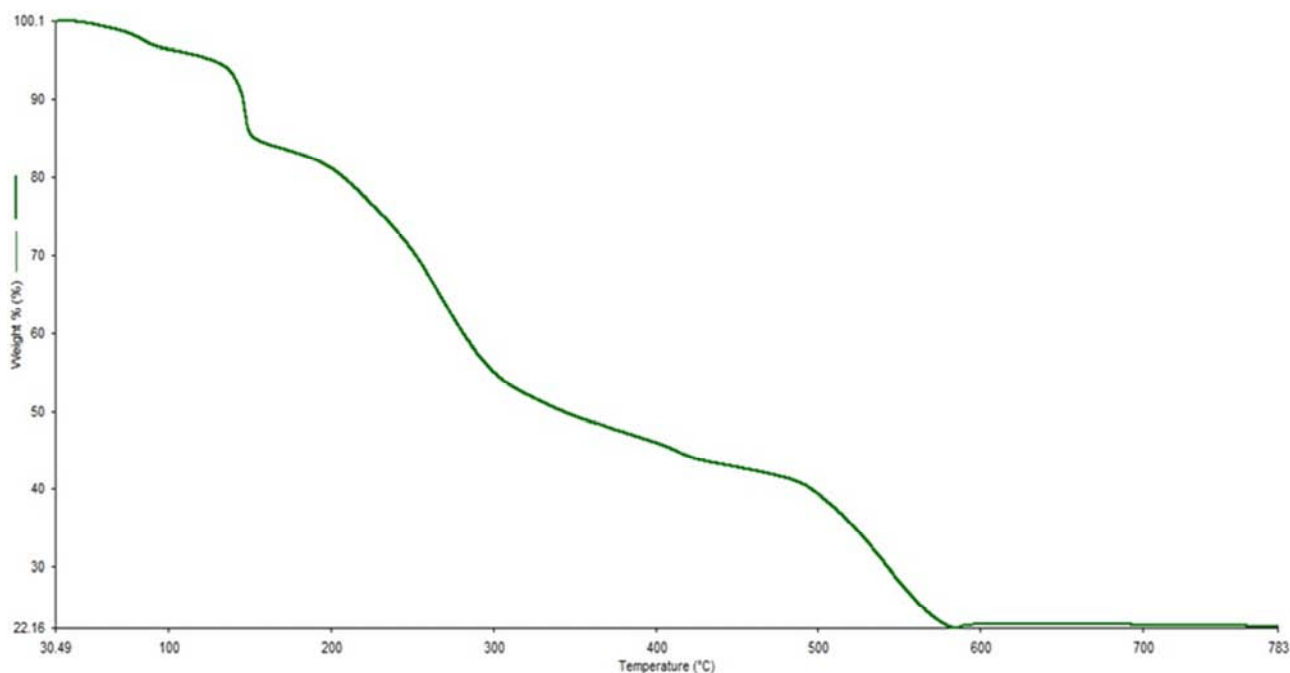
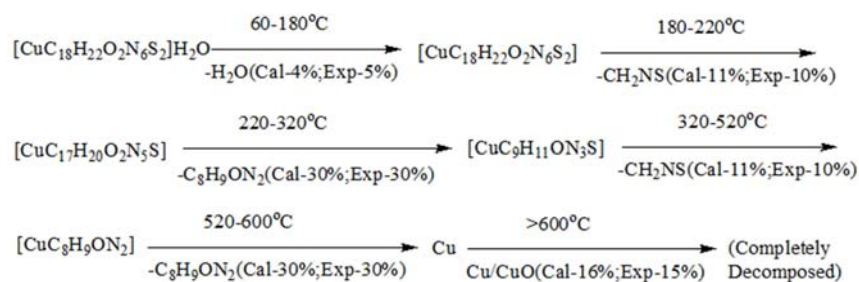
Complexes	Steps	Temperature Range/°C	TG mass loss% calc./found	Assignments
[CuC <sub>40</sub> H <sub>28</sub> O <sub>8</sub> N <sub>8</sub> ]	1 <sup>st</sup>	200-250	9.35/10.00	C <sub>6</sub> H <sub>4</sub>
	2 <sup>nd</sup>	300-620	82.00/78.85	C <sub>34</sub> H <sub>24</sub> O <sub>8</sub> N <sub>8</sub>
	3 <sup>rd</sup>	>620	9.79/12.00	Cu/CuO
[CuC <sub>16</sub> H <sub>16</sub> N <sub>6</sub> S <sub>2</sub> Cl <sub>2</sub> ]	1 <sup>st</sup>	180-220	4.98/5.05	H <sub>2</sub> O
	2 <sup>nd</sup>	250-550	32.0/37.0	C <sub>8</sub> H <sub>8</sub> N <sub>3</sub>
	3 <sup>rd</sup>	550-650	46.29/40.10	C <sub>8</sub> H <sub>8</sub> N <sub>3</sub> S <sub>2</sub> <sup>-</sup>
	4 <sup>th</sup>	>650	18.04/18.25	Cu/CuO
[CuC <sub>18</sub> H <sub>22</sub> O <sub>2</sub> N <sub>6</sub> S <sub>2</sub> ]	1 <sup>st</sup>	60-180	4.0/5.0	H <sub>2</sub> O
	2 <sup>nd</sup>	180-220	11.0/10.0	CH <sub>2</sub> NS
	3 <sup>rd</sup>	220-320	30.0/30.10	C <sub>8</sub> H <sub>9</sub> ON <sub>2</sub> <sup>-</sup>
	4 <sup>th</sup>	320-520	11.0/10.0	CH <sub>2</sub> NS
	5 <sup>th</sup>	520-600	30.0/30.10	C <sub>8</sub> H <sub>9</sub> ON <sub>2</sub> <sup>-</sup>
	6 <sup>th</sup>	>600	16.0/15.0	Cu/CuO

#### 4.4.3. For [CuC<sub>18</sub>H<sub>22</sub>O<sub>2</sub>N<sub>6</sub>S<sub>2</sub>] Complex

The Cu(II) Complex was decomposed in main three or four steps (Figure 11). The TGA and DTG curve showed that complex was decomposed at 1<sup>st</sup> steps in the temperature range 60-180°C (calculated 4.0 %, experimental 5.0% weight) which can be attributed to the elimination of one hydrated water molecules. In 2<sup>nd</sup> step the decomposition of (-CH<sub>2</sub>NS-) moiety was take place at temperature 180-220°C (calculated 11.0%, experimental 10.0 %). The ligand part (C<sub>8</sub>H<sub>9</sub>ON<sub>2</sub><sup>-</sup>) were decomposed at the 3<sup>rd</sup> step at temperature

range 220-320°C (calculated 30.0%, experimental 30.10 %). In the 4<sup>th</sup> step the ligand part of (-CH<sub>2</sub>NS-) was decomposed at temperature 320-520°C (calculated 11.0%, experimental 10.0%). The ligand part (C<sub>8</sub>H<sub>9</sub>ON<sub>2</sub><sup>-</sup>) was further decomposed at temperature at 520-600°C (calculated 30.0%, experimental 30.10) and finally the complex was completely decomposed and removed as Cu/Cu (calculated 16.0%, experimental 15.0%) [12, 22-23].

The probable fragment figure for the complex is shown below:

Figure 11. TGA curve of [CuC<sub>18</sub>H<sub>22</sub>O<sub>2</sub>N<sub>6</sub>S<sub>2</sub>] complex.



#### 4.5. Antibacterial Activities

The prime objective of performing the antibacterial screening is to determine the susceptibility of the pathogenic microorganism. The free Schiff base ligand and their metal complexes were screened for their antibacterial activity against strains the *Bacillus cereus* ATCC25923, *Escherichia coli* ATCC 25922, *Shigella sonnei*, *Shigella boydii*, *Enterobacter*, *Salmonella typhinum* of 4500. The compounds

were tested at a concentration of 50 µg/ 0.01 mL in DMSO solution using the paper disc diffusion method [8, 10, 23-25]. The susceptibility zones were measured in diameter (mm) and the result were listed in table 7. The susceptibility zones were the clear zones around the discs killing the bacteria. All the Schiff base and metal complexes were individually exhibited varying degrees of inhibitory effects on the growth of tested bacterial species (table 7).

Table 7. Antibacterial screening activity of Schiff base and metal complexes.

Tested Bacteria	Diameter of zone inhibition (mm) of tested compounds			
	$C_{20}H_{14}O_4N_4$	$[CuC_{40}H_{28}O_8N_8]$	$C_8H_8N_3SCl$	$[CuC_{16}H_{16}N_6S_2Cl_2] \cdot H_2O$
<i>Bacillus cereus</i>	11	14	13	15
<i>Bacillus subtilis</i>	8	11	10	12
<i>E. coli</i>	10	12	11	13
<i>Shigellasonnei</i>	8	11	11	15
<i>Shigellaboydii</i>	10	13	10	14
<i>Enerobacter</i>	9	13	10	15
<i>Salmonella typhinum</i>	11	13	10	12
DMSO control	-	-	-	-

Table 7. Continued.

Tested Bacteria	Diameter of zone inhibition (mm) of tested compounds		Kanamycin (30µg/disc)
	$C_9H_{11}ON_3S$	$[CuC_{18}H_{22}O_2N_6S_2] \cdot H_2O$	
<i>Bacillus cereus</i>	10	13	20
<i>Bacillus subtilis</i>	9	14	25
<i>E. coli</i>	10	12	25
<i>Shigellasonnei</i>	10	13	22
<i>Shigellaboydii</i>	09	14	22
<i>Enerobacter</i>	10	14	24
<i>Salmonella typhinum</i>	12	15	25
DMSO control	-	-	30

## 5. Conclusions

In this paper we have explored the synthesis and coordination chemistry of Cu(II) complexes containing Schiff base ligands  $L^1(C_{20}H_{14}O_4N_4)$ ,  $L^2(C_8H_8N_3SCl)$  and  $L^3(C_9H_{11}N_3OS)$ . IR spectral analysis indicated that N and O atoms are coordinated to central metal atom. Magnetic moment, UV-Visible and thermogravimetric analysis were proposed  $[CuC_{40}H_{28}O_8N_8]$ ,  $[CuC_{16}H_{16}N_6S_2Cl_2] \cdot H_2O$ ,  $[CuC_{18}H_{22}O_2N_6S_2] \cdot H_2O$  complexes have square planar geometry (Figures 6-8). Thermal analysis (TGA) data showed the possible degradation pathway of the complexes and also indicated that most of the complexes were thermally stable. Biological activity revealed that the ligand and its metal complexes have moderate to strong antibacterial activity as compared to the standard antibiotic (Kanamycin). The Cu(II) complexes showed more antibacterial activity than their respective synthesized Schiff base ligand.

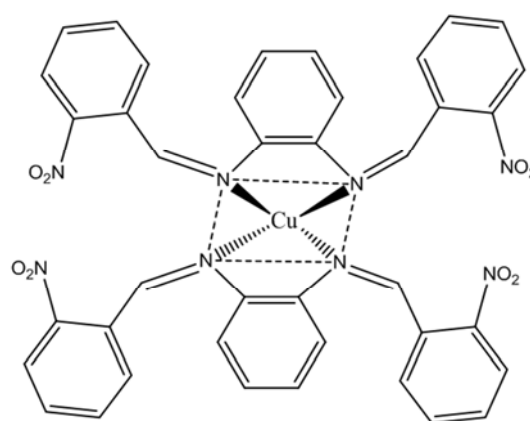


Figure 12. Proposed Structure of  $[CuC_{40}H_{28}O_8N_8]$  complex.

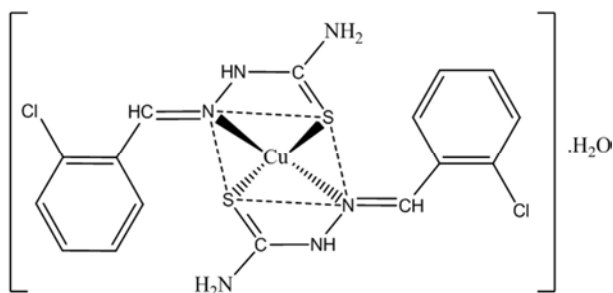


Figure 13. Proposed Structure of  $[CuC_{16}H_{16}N_6S_2Cl_2] \cdot H_2O$  complex.

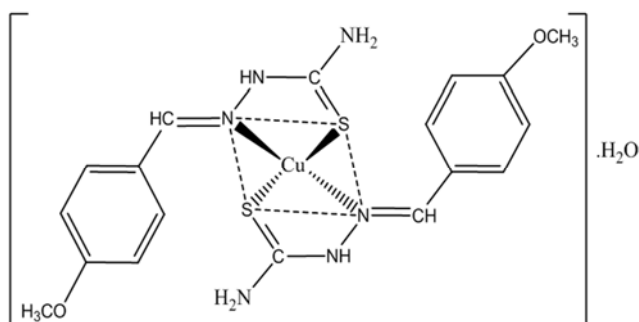


Figure 14. Proposed Structure of  $[CuC_{18}H_{22}O_2N_2] \cdot H_2O$  complex.

## Conflict of Interest

The authors have no conflict of interest to publish the article.

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