

## Synthesis, Characterization, DFT of Novel, Symmetrical, N/O-donor Tetradentate Schiff's base, Its Co(II), Ni(II), Cu(II), Zn(II) Complexes and Their in-vitro Human Pathogenic Antibacterial Activity

Satish Chand<sup>1</sup>, Monika Tyagi<sup>2</sup>, Prateek Tyagi<sup>2</sup>, Sulekh Chandra<sup>2\*</sup> and Deepansh Sharma<sup>3</sup>

<sup>1</sup>Department of Chemistry, Hans Raj College, University of Delhi, Malka Ganj, New Delhi-110007, India.

<sup>2</sup>Department of Chemistry, Zakir Husain Delhi College, University of Delhi, JLN-Marg, New Delhi-110002, India.

<sup>3</sup>Amity Institute of Microbial Technology, Amity University, Rajasthan-303002, India.

A NOVEL tetradentate Schiff's base ligand Bis(furfural)-1,8-naphthalenediimine (**L**) was synthesized and characterized by physical, analytical and spectral data. Complexes of Co(II), Ni(II), Cu(II) and Zn(II) of general composition  $MLX_2$  [ $L = C_{20}H_{14}N_2O_2$  and  $X = Cl^-$ ,  $NO_3^-$  and  $OAc^-$ ] have been synthesized in 1:1 molar ratio of metal to ligand. The elemental analysis, molar conductance measurements, magnetic susceptibility measurements, Mass, IR, UV-Visible, NMR and EPR spectral studies of the compounds led to the conclusion that the ligand acts in a tetradentate manner in Co(II), Ni(II) and Cu(II) complexes, while in bidentate fashion in Zn(II) complex. Octahedral geometry was assigned to Co(II) and Ni(II) complexes, Tetragonal geometry for Cu(II) complexes and tetrahedral geometry for Zn(II) complexes of the Schiff's base ligand. The thermal studies suggested that the complexes are more stable as compared to ligand and absence of coordinated water molecules in metal complexes. The geometries of Schiff's base and metal complexes were optimized with respect to the energy taking the 6-31+g(d,p) basis set in Gaussian 09W programme in gaseous phase. The antibacterial studies of the compounds were examined against the human pathogenic, Gram negative bacteria i.e. *Escherichia coli*, *Yersinia enterocolitica*, *Klebsiella pneumoniae*, and *Salmonella typhi* and Gram positive bacteria i.e. *Listeria monocytogenes* and *Enterococcus faecalis*.

**Keywords:** Co(II), Ni(II), Cu(II) and Zn(II) complexes, Schiff's base, Spectral characterization, DFT, Antibacterial studies.

### Introduction

In chemistry, the area of transition metal complexes of Schiff's bases and their coordination chemistry is very broad and important. Schiff's bases, the condensation products of primary amines and carbonyl compounds (i.e. aldehydes or ketones), having azomethine group (-CH=N-), are very important biologically [1]. Schiff's base ligand's transition metal complexes have different types of uses e.g. analytical, chemical, industrial, biological and clinical etc. [2-14]. Schiff's bases and their metal complexes are also used for catalyzing different reactions viz. oxidation, reduction etc. [15, 16], as corrosion inhibitor [17, 18] and as sensors [19, 20]. Chemistry of tetradentate

ligands is of great interest nowadays because of their biological activities e.g. antitumor, anticancer, antibacterial, antifungal, antitubercular, antiviral, antimalarial, antidiabetic [21-29] and DNA-binding [30, 31]. Biological activities of Schiff's base ligands are most probably due to the presence of oxygen, nitrogen atoms and different polar groups on side chains for interaction with different biomolecules while those of metal complexes is due to the additional different metal atoms and different anions which again enhance the attachment. Tetradentate Schiff's base can coordinate to metal as neutral molecule or after deprotonation as anionic ligands and can adopt various different coordination modes.

\*Corresponding author e-mail: schandra\_00@yahoo.com

Tel.: +91-11-22911267; +91-9811226273; Fax: +91-11-23215906

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Taking into consideration the above facts, Co(II), Ni(II), Cu(II) and Zn(II) complexes of Schiff base derived from condensation of 1,8-diaminonaphthalene and furfural, were synthesized. The synthesized Schiff's base and their metal complexes were characterized using various spectral techniques and evaluated for their antibacterial activities against human pathogenic bacteria i.e. *Listeria monocytogenes*, *Escherichia coli*, *Yersinia enterocolitica*, *Klebsiella pneumoniae*, *Enterococcus faecalis* and *Salmonella typhi*.

### Experimental

#### Materials and methods

All the chemicals used were of Analytical Reagent grade and received from Sigma-Aldrich and Thomas Baker. Metal salts were purchased from E. Merck and were used as received. Furfural was purified by distillation.

1,8-diaminonaphthalene was dissolved in methanol, filtered and that filtrate was used for Schiff's base synthesis.

#### Synthesis of ligand (L)

1,8-diaminonaphthalene (1.58 g, 0.01mol) was dissolved in 40 mL MeOH, filtered and then purified furfural (1.92 g, 0.02mol) was added to the filtrate. Dilute HCl was added drop wise to the above solution to maintain pH 5-6 and refluxed at 65-70°C for 2 hours. On cooling the reaction mixture, orange product was solidified. It was filtered, washed with ice-cold methanol and dried under vacuum over anhyd.  $\text{CaCl}_2$ . Yield 86%, mp 184°-186°C. The completion of the reaction was checked by Thin Layer Chromatography (TLC). TLC was performed on silica gel (Merck TLC plate) using the solvent system hexane: ethylacetate (4:1) as eluent. Scheme of synthesis of ligand is given in Fig. 1.

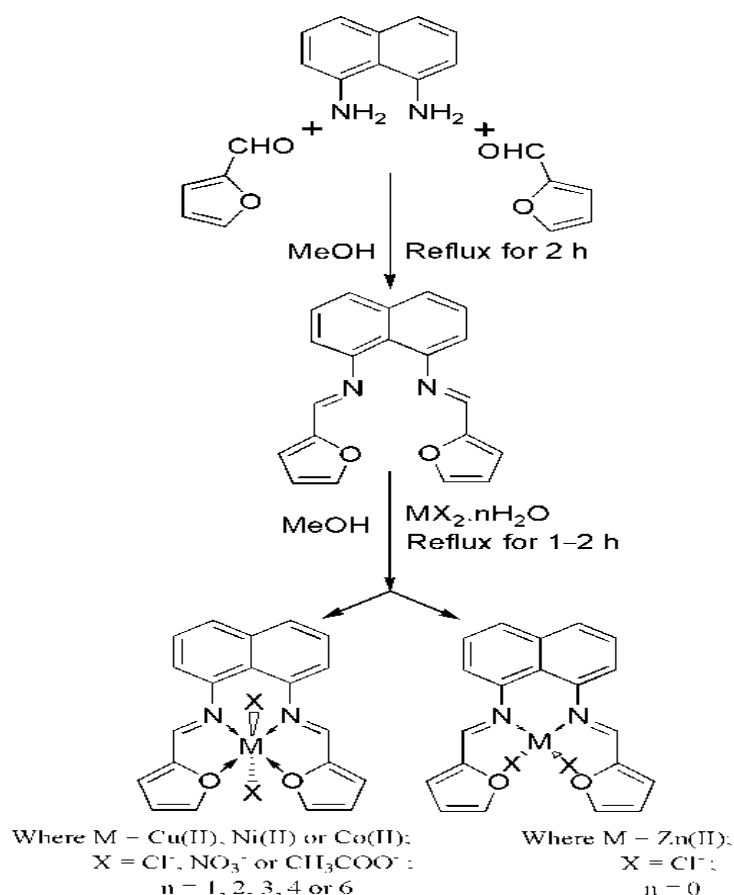


Fig. 1. Synthesis of Schiff's base ligand (L) and its metal complexes.

(10E, 11E)-N<sup>1</sup>,N<sup>8</sup>-bis ((furan-2-yl) methylene) naphthalene-1,8-diamine (L)

Yield: 86%; Colour: orange-brown; m.p.: 184-186°C; C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: Anal. Found: C, 76.38; H, 4.47; N, 8.88%; Calc.: C, 76.42; H, 4.49; N, 8.91; UV-Vis. (CHCl<sub>3</sub>, nm): 241 (π→π\*), 349 (n→π\*); IR (KBr, cm<sup>-1</sup>): ν̄(HC=N), 1594, ν̄(=C-H, Ar), 3119, 3048, ν̄(C=C in aromatic ring), 1460, *oop* bend (=C-H, Ar), 815, 747, ν̄(C-C)1011. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ, ppm): 9.672 (s, 2H, -CH=N-), 7.701 (m, 2H, Ar), 7.263-7.258 (m, 6H, Ar), 6.616-6.609 (m, 4H, Ar); Mass spectrum (ESI, m/z): [M]<sup>+</sup> = 314.

#### Synthesis of metal complexes

Methanolic solution of metal salt i.e. nitrate, chloride or acetate (25 mL, 2mmol) was mixed with a methanolic solution of the ligand (25 mL, 2 mmol). Ammonia was added to maintain pH 6-7 and the reaction mixture was stirred at room temperature for 1-2 hour. Volume of the reaction mixture was reduced to approximately half by heating on water bath. On keeping the reaction mixture overnight, the coloured product was separated out, which was filtered, washed with ice-cold methanol, ether and dried under vacuum over anhy. CaCl<sub>2</sub>. Scheme of synthesis of metal complexes is given in Fig. 1.

**Complex 1: [CoLCl<sub>2</sub>]:** Yield: 78%; Colour: sea-green; m.p.: >270°C; C<sub>20</sub>H<sub>14</sub>Cl<sub>2</sub>CoN<sub>2</sub>O<sub>2</sub>: Anal. Found: C, 54.05; H, 3.16; N, 6.29; Co, 13.30%; Calc.: C, 54.08; H, 3.18; N, 6.31; Co, 13.27%; IR (KBr, cm<sup>-1</sup>): ν̄(C=N) 1631, ν̄(C-H)Ar 3111, ν̄(M-N) 428, ν̄(M-O) 534, ν̄(M-Cl) 313; Molar Conductance (Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) in DMSO: 3.1; Mass spectrum (ESI, m/z): [M]<sup>+</sup> = 444.

**Complex 2: [CoL(NO<sub>3</sub>)<sub>2</sub>]:** Yield: 72%; Colour: sea-green; m.p.: >270°C; C<sub>20</sub>H<sub>14</sub>CoN<sub>4</sub>O<sub>8</sub>: Anal. Found: C, 48.26; H, 2.79; N, 11.22; Co, 11.87%; Calc.: C, 48.31; H, 2.84; N, 11.27; Co, 11.85; IR (KBr, cm<sup>-1</sup>): ν̄(C=N) 1621, ν̄(C-H)Ar 3125, 3054, ν̄(M-N) 430, ν̄(M-O) 542, ν̄(NO<sub>3</sub><sup>-</sup>) 1427(ν<sub>3</sub>), 1331(ν<sub>1</sub>), 1015(ν<sub>2</sub>); Molar Conductance (Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) in DMSO: 8.4; Mass spectrum (ESI, m/z): [M]<sup>+</sup> = 497.

**Complex 3: [CoL(OAc)<sub>2</sub>]:** Yield: 69%; Colour: sea-green; m.p.: >270°C; m.p.: 184-186°C; C<sub>24</sub>H<sub>20</sub>CoN<sub>2</sub>O<sub>6</sub>: Anal. Found: C, 58.64; H, 4.11; N, 5.65; Co, 11.92%; Calc.: C, 58.67; H, 4.10; N, 5.70; Co, 11.99; IR (KBr, cm<sup>-1</sup>): ν̄(C=N) 1632, ν̄(C-H)Ar 3047, ν̄(M-N) 425, ν̄(M-O)

533, ν̄(OAc) 1420, 1250; Molar Conductance (Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) in DMSO: 7.3; Mass spectrum (ESI, m/z): [M]<sup>+</sup> = 491.

**Complex 4: [NiLCl<sub>2</sub>]:** Yield: 71%; Colour: yellowish-brown; m.p.: >270°C; C<sub>20</sub>H<sub>14</sub>Cl<sub>2</sub>NiN<sub>2</sub>O<sub>2</sub>: Anal. Found: C, 54.02; H, 3.13; N, 6.26; Ni, 13.23%; Calc.: C, 54.11; H, 3.18; N, 6.31; Ni, 13.22%; IR (KBr, cm<sup>-1</sup>): ν̄(C=N) 1613, ν̄(C-H)Ar 3126, 3055, ν̄(M-N) 444, ν̄(M-O) 539, ν̄(M-Cl) 317; Molar Conductance (Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) in DMSO: 11.7; Mass spectrum (ESI, m/z): [M]<sup>+</sup> = 443.

**Complex 5: [CuLCl<sub>2</sub>]:** Yield: 76%; Colour: Blackish green; m.p.: >270°C; C<sub>20</sub>H<sub>14</sub>Cl<sub>2</sub>CuN<sub>2</sub>O<sub>2</sub>: Anal. Found: C, 53.50; H, 3.17; N, 6.19; Cu, 14.10%; Calc.: C, 53.52; H, 3.14; N, 6.24; Cu, 14.16%; IR (KBr, cm<sup>-1</sup>): ν̄(C=N) 1620, ν̄(C-H)Ar 3058, ν̄(M-N) 411, ν̄(M-O) 510, ν̄(M-Cl) 304; Molar Conductance (Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) in DMSO: 3.9; Mass spectrum (ESI, m/z): [M]<sup>+</sup> = 448.

**Complex 6: [CuL(NO<sub>3</sub>)<sub>2</sub>]:** Yield: 64%; Colour: Blackish green; m.p.: >270°C; C<sub>20</sub>H<sub>14</sub>CuN<sub>4</sub>O<sub>8</sub>: Anal. Found: C, 47.81; H, 2.78; N, 11.15; Cu, 12.63%; Calc.: C, 47.86; H, 2.81; N, 11.16; Cu, 12.63%; IR (KBr, cm<sup>-1</sup>): ν̄(C=N) 1621, ν̄(C-H)Ar 3037, ν̄(M-N) 443, ν̄(M-O) 516, ν̄(NO<sub>3</sub><sup>-</sup>) 1417(ν<sub>5</sub>), 1327(ν<sub>1</sub>), 1012(ν<sub>2</sub>); Molar Conductance (Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) in DMSO: 6.4; Mass spectrum (ESI, m/z): [M]<sup>+</sup> = 501.

**Complex 7: [CuL(OAc)<sub>2</sub>]:** Yield: 73%; Colour: Blueish green; m.p.: >270°C; C<sub>24</sub>H<sub>20</sub>CuN<sub>2</sub>O<sub>6</sub>: Anal. Found: C, 58.11; H, 4.00; N, 5.61; Cu, 12.76%; Calc.: C, 58.12; H, 4.06; N, 5.65; Cu, 12.81%; IR (KBr, cm<sup>-1</sup>): ν̄(C=N) 1627, ν̄(C-H)Ar 3042, ν̄(M-N) 436, ν̄(M-O) 521, ν̄(OAc) 1426, 1242; Molar Conductance (Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) in DMSO: 5.6; Mass spectrum (ESI, m/z): [M]<sup>+</sup> = 495.

**Complex 8: [ZnLCl<sub>2</sub>]:** Yield: 63%; Colour: sea-green; m.p.: >270°C; C<sub>20</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Zn: Anal. Found: C, 53.24; H, 3.10; N, 6.15; Zn, 14.48%; Calc.: C, 53.31; H, 3.13; N, 6.22; Zn, 14.51%; IR (KBr, cm<sup>-1</sup>): ν̄(C=N) 1604, ν̄(C-H)Ar 3132, ν̄(M-N) 442, ν̄(M-Cl) 306; Molar Conductance (Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) in DMSO: 9.8; <sup>1</sup>H NMR (δ, ppm in DMSO-d<sub>6</sub>): 9.982 (s, 2H, -CH=N-), 7.704-6.610 (m, 12H, Ar); Mass spectrum (ESI, m/z): [M]<sup>+</sup> = 450.

### Analysis

The carbon, hydrogen and nitrogen were analyzed on FLASH EA 1112 series CHNS/O Analyzer (Thermo Finnigan, Italy). Molar conductance was measured on CM82T conductivity bridge (ELICO, India). Magnetic susceptibilities were measured at room temperature on Gouy balance using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as callibrant. Electron Impact Mass spectra were recorded on JEOL, JMS – DX-303 Mass spectrometer. IR spectra (KBr) were recorded on FT-IR Perkin Elmer spectrophotometer. NMR spectra were recorded with a model JEOL, ECX-400P spectrometer operating at 400 MHz using  $\text{CDCl}_3$  as a solvent and TMS as internal standard. The electronic spectra were recorded in DMSO on Hitachi U-3900H spectrophotometer. Thermogravimetric analysis (TGA) was done in nitrogen atmosphere (30 ml/min) with the heating rate of  $10^\circ\text{C}/\text{min}$  using Shimadzu TGA-50H thermal analyzer. EPR spectra of Cu(II) and Co(II) complexes were recorded as polycrystalline sample at room temperature and low temperature on US-Varian EPR spectrometer using the tetracyanoethylene (TCNE) as the g-marker.

### Density Functional Theory (DFT) studies

The optimization of geometries of Schiff's base and its metal complexes was carried out with respect to energy using DFT method taking 6-31+g(d,p) basis set and B3LYP three parameter density functional using the Gaussian 09W suite [32].

### Biological screening

The antibacterial activity of ligand and its metal complexes was screened against six human pathogenic bacteria i.e. *L. monocytogenes*, *E. coli*, *Y. enterocolitica*, *K. pneumoniae*, *E. faecalis* and *S. typhi*, using paper-disc plate method [33]. Ciprofloxacin was used as standard drug and DMSO was used as solvent. 1000 ppm concentration solutions of compounds were prepared in DMSO. Whatman No. 1 paper discs with a diameter 5 mm were soaked in the above solutions. These paper discs were placed on nutrient agar medium already seeded with the pathogens in petri dishes and incubated in BOD incubator at  $37^\circ\text{C}$  for 24 hour. The diameter of radial inhibition zones was measured in mm. This process was repeated three times and average

values of inhibition zones were calculated for the activity result.

## Results and Discussion

The complexes were synthesized by reacting ligand with the metal ions in 1:1 Molar ratio in methanolic solution.

### Microanalysis and molar conductance

The synthesized ligand was solid and orange in colour. Metal complexes were soluble in DMF and DMSO. Metal complexes showed molar conductance in DMSO in the range  $3.1\text{--}11.7 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  indicating their non-electrolytic nature [34]. Thus the complexes may be formulated as  $[\text{MLX}_2]$  [where M = Co(II), Ni(II), Cu(II) and Zn(II); X =  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{OAc}^-$ ].

### Mass spectra

The ESI mass spectrum of ligand showed a molecular ion peak at  $m/z = 314$  amu corresponding to species  $[\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2]^+$  which confirms the proposed formula. The base peak was observed at  $m/z = 233$  amu. It also showed peaks at 166, 180, 220, 240 amu corresponding to rest various fragments. The intensities of these peaks represent the stabilities of the fragments. Mass spectrum of the ligand is depicted in Fig. 2 and proposed mass fragmentation of ligand is shown in Fig. 3. Mass spectra of copper and zinc complexes are given in Fig. 4 and Fig. 5 respectively.

### $^1\text{H}$ NMR spectra

The  $^1\text{H}$  NMR spectrum of the ligand was recorded in  $\text{CDCl}_3$  solvent, at 400 MHz. One singlet peak was appeared at  $\delta$  9.672 ppm, which confirmed the synthesis of ligand and was assigned to two azomethine protons ( $\text{CH}=\text{N}$ ). A multiplet in the region  $\delta$  7.263–7.258 ppm was assigned to six aromatic protons and another multiplet in the region  $\delta$  6.616–6.609 ppm was assigned to four aromatic protons. In  $^1\text{H}$ NMR of Zn(II) complex of the ligand, a deshielded singlet due to two azomethine protons was found at  $\delta$  9.982 ppm, rest of the peaks were found unaffected, which indicated the coordination of Zinc metal ion with the azomethine nitrogens.  $^1\text{H}$  NMR spectra of the ligand and zinc complex are shown in Fig. 6 and 7.

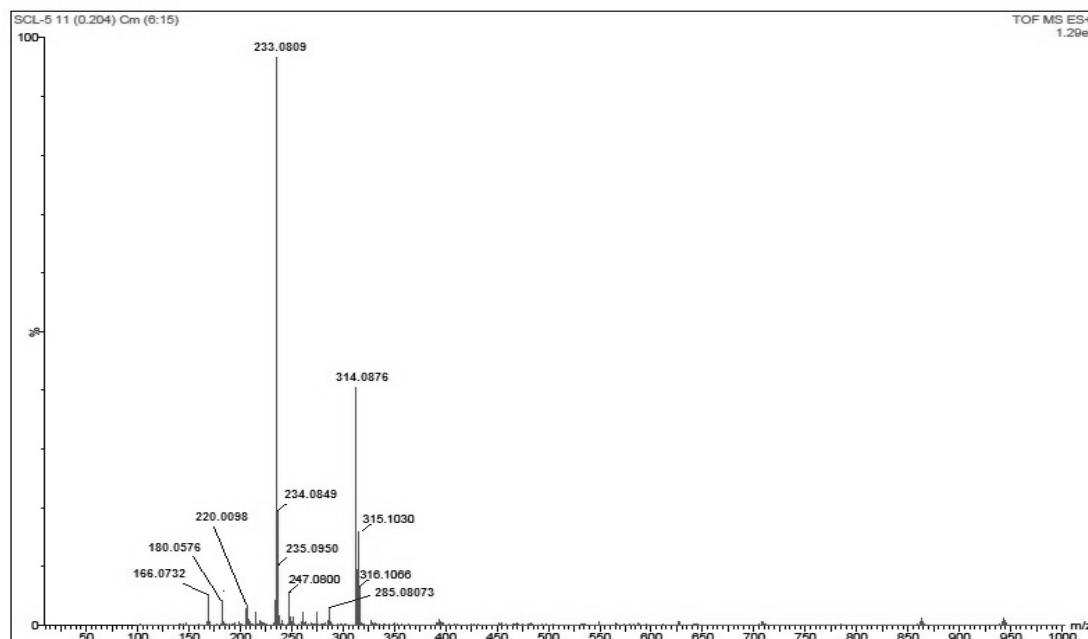


Fig. 2. Mass spectrum of the Schiff's base ligand (L).

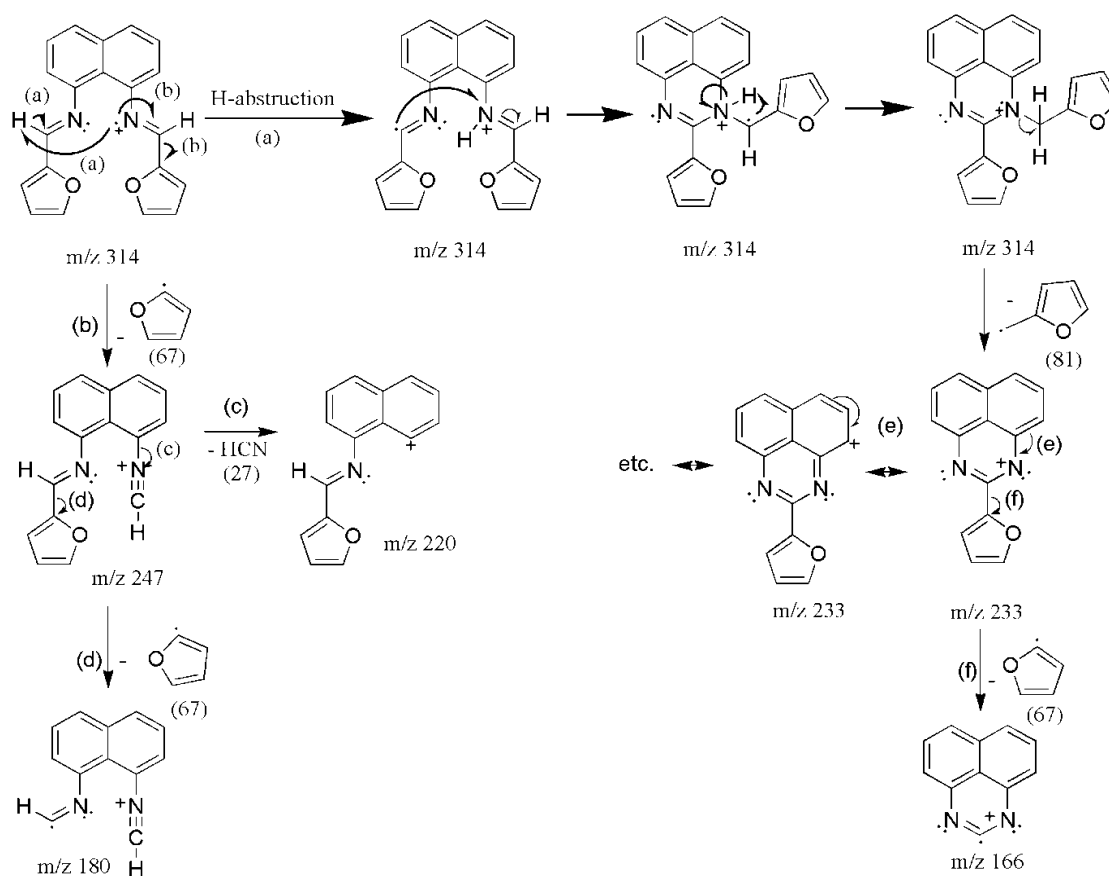


Fig. 3. Mass fragmentation of the Schiff's base ligand (L).

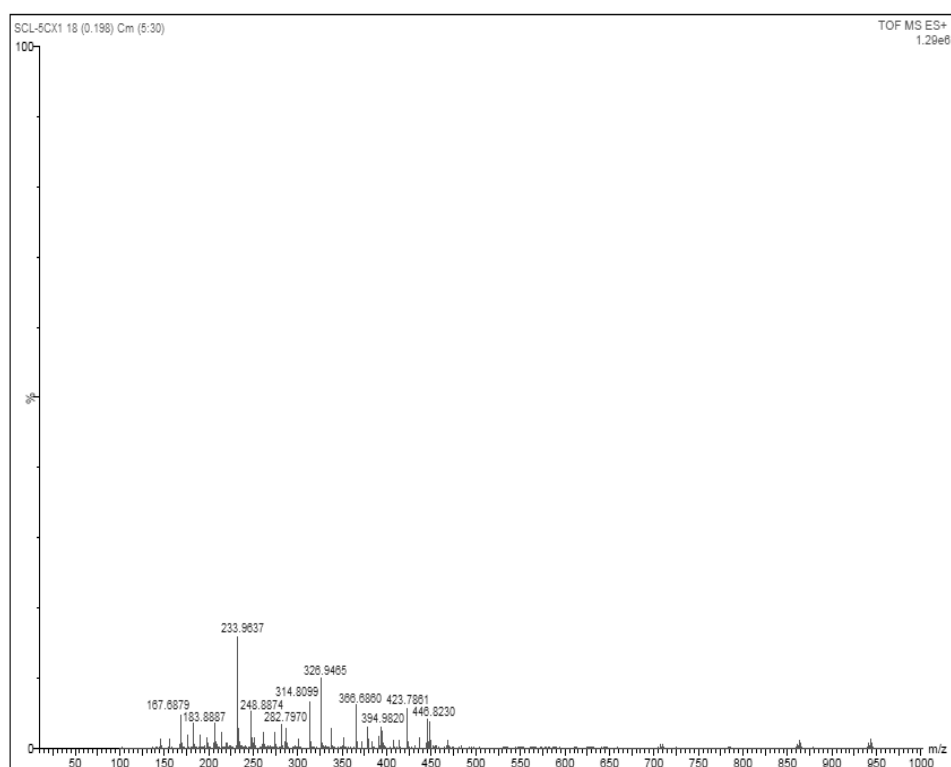


Fig. 4. Mass spectrum of the Copper complex i.e.  $[CuLCl_2]$ .

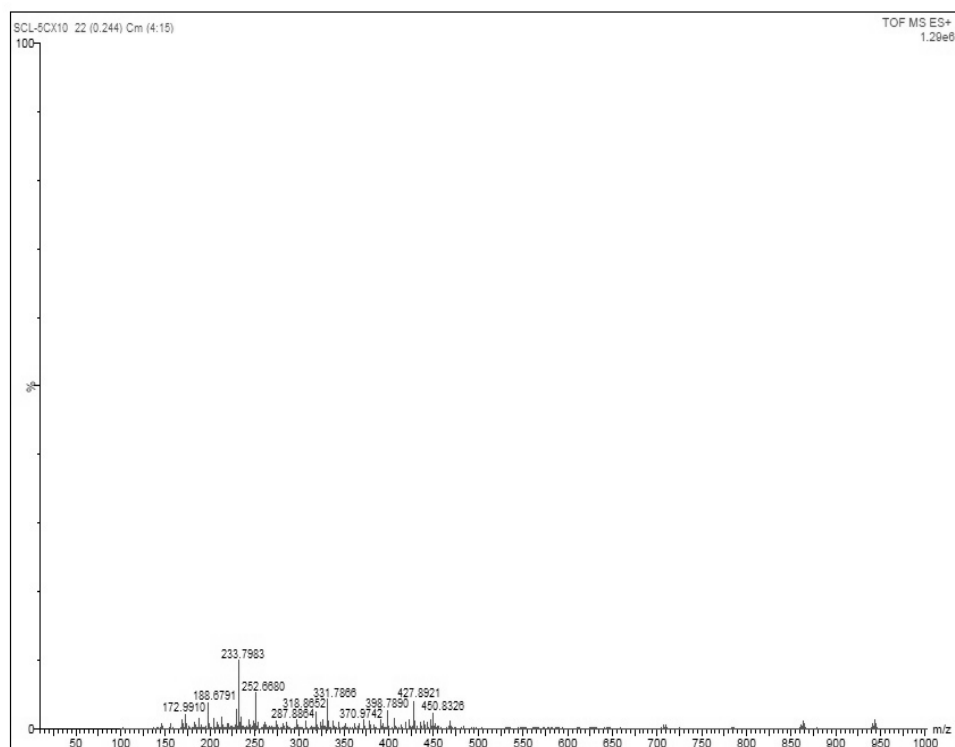
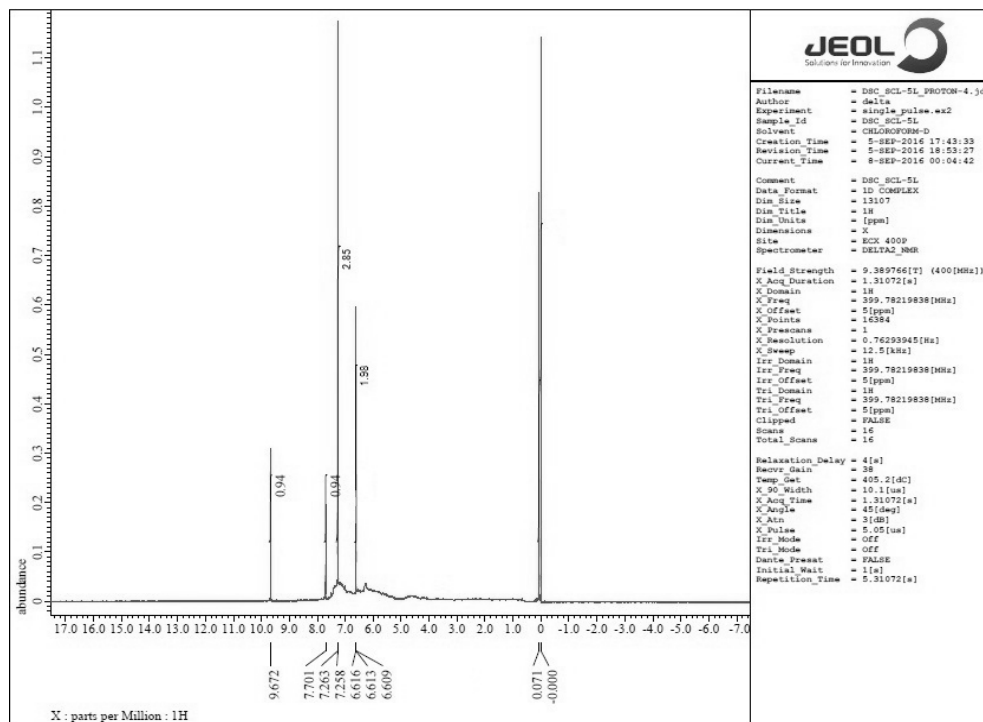
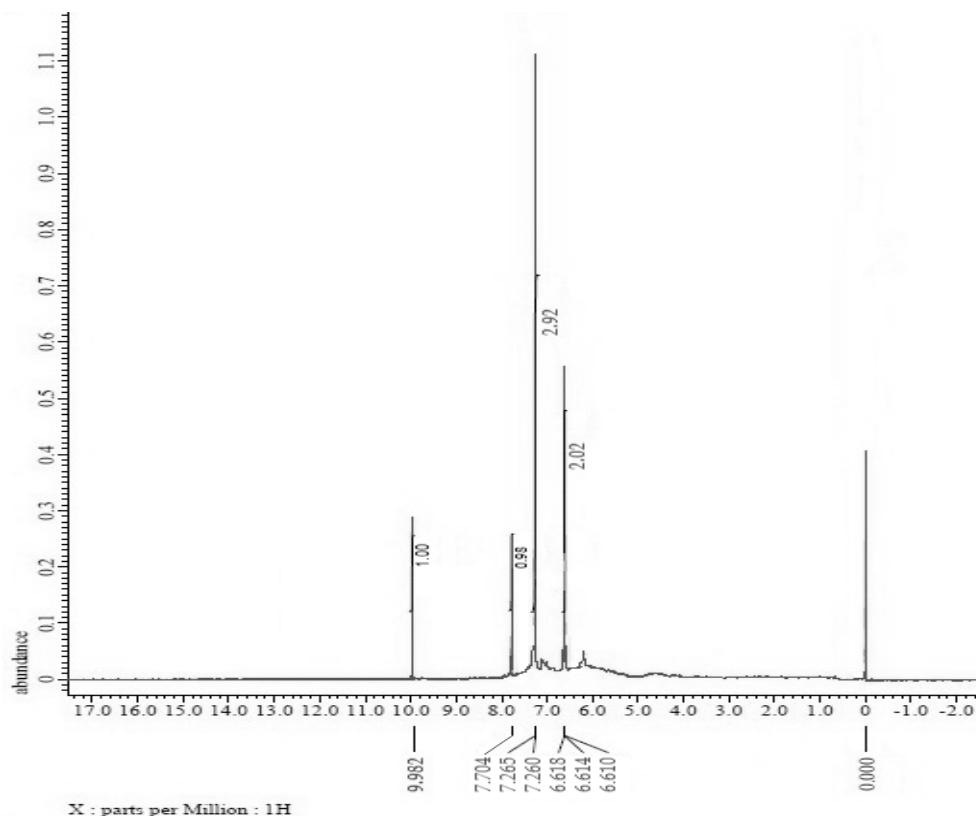


Fig. 5. Mass spectrum of the Zinc complex i.e.  $[ZnLCl_2]$ .

Fig. 6.  $^1\text{H}$  NMR spectrum of the Schiff's base ligand .Fig. 7.  $^1\text{H}$  NMR spectrum of the  $[\text{ZnLCl}]$ .

### IR spectra

A pair of bands was present in the IR spectrum of 1,8-diaminonaphthalene at 3358  $\text{cm}^{-1}$  and 3388  $\text{cm}^{-1}$  corresponding to  $\bar{\nu}(\text{NH}_2)$  which was absent in IR spectra of Schiff's base ligand as well as in all the metal complexes. A strong band at near 1670  $\text{cm}^{-1}$  due to  $\bar{\nu}(>\text{C}=\text{O})$  disappeared in the IR spectra of ligand as well as in that of all the metal complexes, indicating the absence of  $-\text{CHO}$  of furfural. A new strong band was appeared at 1594  $\text{cm}^{-1}$  that confirmed the formation of Schiff's base and was due to  $\bar{\nu}(\text{C}=\text{N})$  of azomethine group. Band near 3119  $\text{cm}^{-1}$  and 3048  $\text{cm}^{-1}$  are due to  $\bar{\nu}(\text{C}-\text{H})$  in aromatic rings. Bands near 1460  $\text{cm}^{-1}$  are due  $\bar{\nu}(\text{C}=\text{C})$  in aromatic ring. Bands near 815  $\text{cm}^{-1}$  and 747  $\text{cm}^{-1}$  are due to out of plane (*oop*) C-H bending in aromatic rings. Band at 1011  $\text{cm}^{-1}$  is due to  $\bar{\nu}(\text{C}-\text{C})$ . The position of strong  $\bar{\nu}(\text{C}=\text{N})$  band of the azomethine appeared at 1594  $\text{cm}^{-1}$  is shifted toward lower side or higher side after complexation, which confirms the coordination via the azomethine nitrogen [35, 36]. The presence of a new band corresponding to  $\bar{\nu}(\text{M}-\text{N})$  bond in the range of 411–444  $\text{cm}^{-1}$  in metal complexes support this too [37]. One more band was observed in the range of 510–542  $\text{cm}^{-1}$  due to  $\bar{\nu}(\text{M}-\text{O})$  bond in the metal complexes except Zn(II) complex. One band at 1011  $\text{cm}^{-1}$  due to furan ring C-O-C stretching was found shifted to 998–1005 in IR spectra of metal complexes, except that of Zinc complex, which indicates the coordination of metal ions with oxygen of furan ring, except

Zn(II) complex. Thus, it may be concluded that the ligand behaves as tetradentate chelating agent, coordinating through azomethine nitrogen and furan ring oxygen in Co(II), Ni(II) and Cu(II) complexes, while as bidentate ligand in Zn(II) complex coordinating only through azomethine nitrogen [37]. The presence of a band at 355–330  $\text{cm}^{-1}$  is due to  $\bar{\nu}(\text{M}-\text{Cl})$  [38]. Nitrate complexes showed bands at 1427–1417 ( $\bar{\nu}_3$ ), 1331–1327 ( $\bar{\nu}_1$ ) and 1015–1012 ( $\bar{\nu}_2$ )  $\text{cm}^{-1}$  in the IR spectra due to NO stretching. The value of  $\Delta\bar{\nu}$ , i.e. ( $\bar{\nu}_3 - \bar{\nu}_1$ ) was found to be 90–96  $\text{cm}^{-1}$  which suggested that both the  $\text{NO}_3^-$  groups are coordinated to the central metal ion in unidentate fashion [39, 40]. Acetato complexes showed bands at 1426–1420  $\text{cm}^{-1}$  and 1250–1242  $\text{cm}^{-1}$  due to  $\bar{\nu}_{\text{as}}(\text{OAc})$  and  $\bar{\nu}_{\text{s}}(\text{OAc})$  stretching vibrations respectively. The value of  $\Delta\bar{\nu}$ , i.e. 170–184 indicated the unidentate nature of coordination of  $^- \text{OAc}$  group with metal ion [40]. IR spectrum of the ligand is given in Figure 8.

### Magnetic moments

The magnetic moments of Co(II) complexes were found in the range 4.86–5.02 BM corresponding to three unpaired electrons. It was found 2.92 B.M. for Ni(II) complex due to two unpaired electrons. While for Cu(II) complexes, magnetic moments were found in the range 1.82–1.86 B.M. which correspond to one unpaired electron [41]. The observed magnetic moments of Co(II), Ni(II) and Cu(II) complexes are given in Table 1.

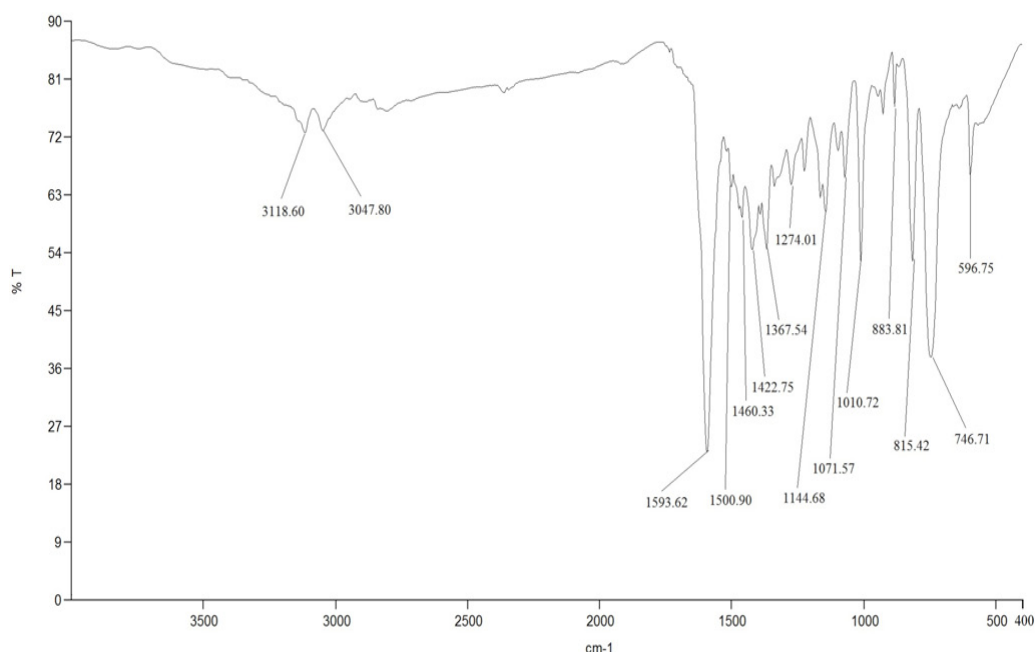


Fig. 8. IR spectrum of the Schiff's base ligand (L).



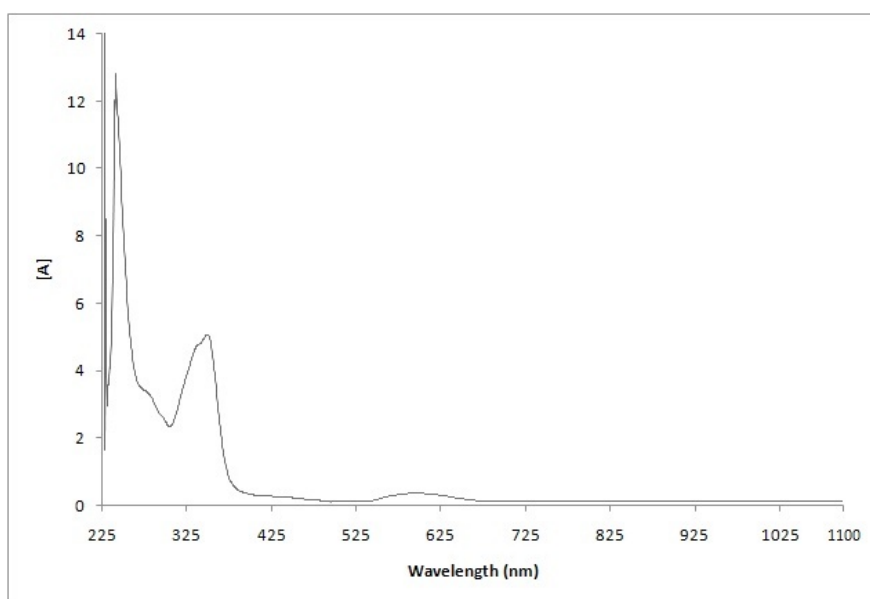
**TABLE 1. Magnetic moment (B.M.), electronic spectral bands (cm<sup>-1</sup>) and ligand field parameters of the metal complexes.**

Complexes	$\mu_{\text{eff}}$ (BM)	$1/\lambda_{\text{max}}$ (cm <sup>-1</sup> )	Dq (cm <sup>-1</sup> )	B (cm <sup>-1</sup> )	$\beta$	LFSE (kJ mol <sup>-1</sup> )
CoLCl <sub>2</sub>	4.86	10030, 20202	1003	678	0.70	96
CoL(NO <sub>3</sub> ) <sub>2</sub>	5.02	9901, 20161	990	684	0.70	95
CoL(OAc) <sub>2</sub>	4.93	10246, 21186	1025	730	0.75	98
NiLCl <sub>2</sub>	2.92	11261, 15823, 25126	1126	478	0.46	162
CuLCl <sub>2</sub>	1.83	16680	-	-	-	-
CuL(NO <sub>3</sub> ) <sub>2</sub>	1.86	17355	-	-	-	-
CuL(OAc) <sub>2</sub>	1.82	16842	-	-	-	-

*Electronic spectra*

Electronic spectra of Cu(II) complexes exhibit one broad absorption band in the range 16,680–17355 cm<sup>-1</sup>. This band may be assigned to the <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>B<sub>2g</sub> transition, corresponding to an elongated tetragonal geometry [42]. Electronic spectrum of Ni(II) complex shows three d–d transition bands at 11253, 15820 and 25124 cm<sup>-1</sup>. These bands correspond to <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub>, <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(F) and <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(P) transitions respectively [43]. An octahedral geometry

has been assigned to the Ni(II) complex. Two bands, found in the UV-visible spectra of Co(II) complexes in the range 9892–10026 cm<sup>-1</sup> and 20144–21360 cm<sup>-1</sup> were assigned to <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(F) and <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P) while the third band was calculated in the range 19801–20496 cm<sup>-1</sup> which was assigned to <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>A<sub>2g</sub> [44], which suggests the octahedral geometry around Co(II) centre. UV-Visible spectra of [CuLCl<sub>2</sub>] is given in Fig. 9.

**Fig. 9. UV–Visible spectrum of [CuLCl<sub>2</sub>].**

### Electron spin resonance spectra

ESR spectra of the Cu(II) complexes were recorded, at room temperature as polycrystalline solid samples, on the X-band at 9.1 GHz under the magnetic field set 3000 G in the scan range 2000 G while ESR spectra of Co(II) were recorded at lower temperature (Liquid nitrogen temperature). The analysis of spectra of Cu(II) complexes gave  $g_{\parallel}$  2.24205–2.48166 and  $g_{\perp}$  2.07069–2.12482. The trend  $g_{\parallel} > g_{\perp} > 2.0023$  was observed for the Cu(II) complexes, indicates that the unpaired electron is localized in the  $dx^2-y^2$  orbital of the Cu(II) ion and the spectral figures are characteristic for the axial symmetry. Elongated tetragonal geometry is thus confirmed for the Cu(II) complexes [45].  $G$

$= (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$ , which measures the exchange interaction between the metal centres in a polycrystalline solid has been calculated. According to Hathaway and Billing [46], if  $G > 4$ , the exchange interaction is negligible, but if  $G < 4$ , a considerable exchange interaction in the solid complexes would be found. The Cu(II) complexes gave the 'G' values (Table 2) in the range 3.51–3.91, which is less than 4, indicating exchange interaction in the solid complexes. In case of Co(II) complexes,  $g_{\parallel}$  was found 2.03186–2.04464 and  $g_{\perp}$  was 2.00678–2.01299 following the same trend i.e.  $g_{\parallel} > g_{\perp} > 2.0023$  indicating the octahedral geometry. ESR spectrum of  $[\text{CuLCl}_2]$  is given in Fig. 10.

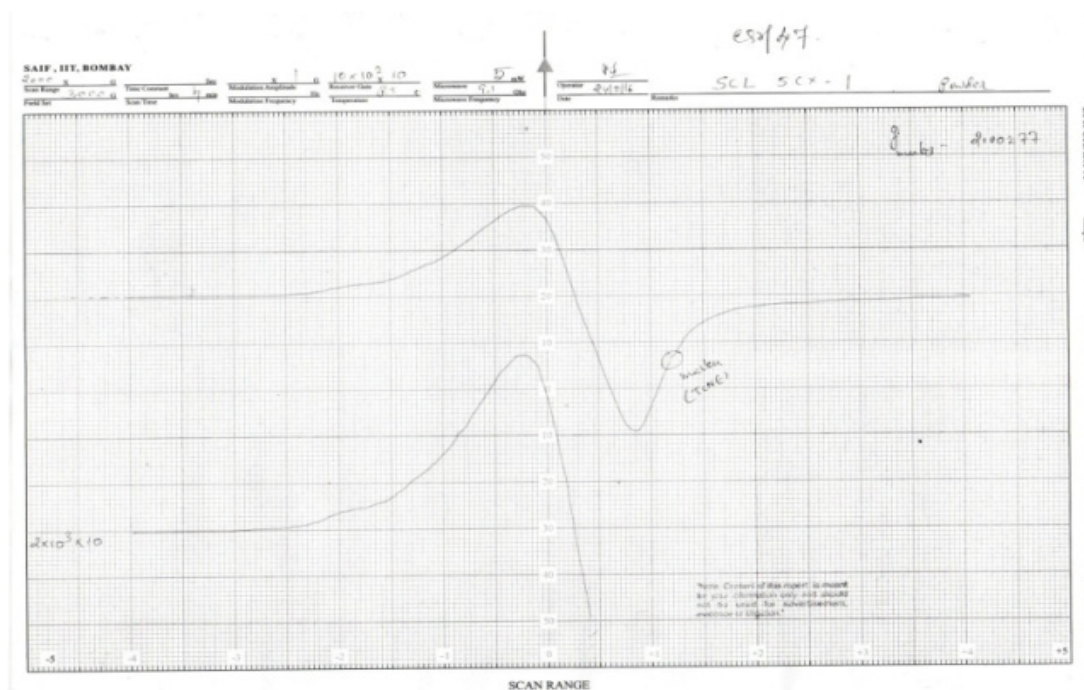


Fig. 10 . ESR spectrum of  $[\text{CuLCl}_2]$

TABLE 2. ESR spectral data of the metal complexes.

Complexes	$g_{\parallel}$	$g_{\perp}$	$g_{\text{iso}}$	G
$\text{CoLCl}_2$	2.03186	2.00678	2.01514	-
$\text{CoL}(\text{NO}_3)_2$	2.03186	2.01299	2.01928	-
$\text{CoL}(\text{OAc})_2$	2.04464	2.00988	2.01721	-
$\text{CuLCl}_2$	2.48166	2.12482	2.24377	3.91
$\text{CuL}(\text{NO}_3)_2$	2.35578	2.09740	2.18353	3.72
$\text{CuL}(\text{OAc})_2$	2.24205	2.07069	2.12781	3.51

### Thermal analysis

Schiff's base and its metal complexes were studied by thermogravimetric analysis from room temperature to 800 °C in nitrogen atmosphere at the heating rate of 10 °C/min. The TG curves were drawn as % weight loss vs. temperature and presented in Fig. 11.

The temperature ranges and percentage weight losses of the decomposition reactions are given in **Table 3** together with evolved moiety, theoretical and found percentage weight losses. The weight losses are analyzed, the percent or amount of weight loss at any temperature ranges of the degradation processes were determined. The overall loss of weight from the TG curves is 82.29% for [CuLCl<sub>2</sub>], 84.29% for [CuL(NO<sub>3</sub>)<sub>2</sub>],

83.97% for [CuLOAc<sub>2</sub>], 83.04% for [CoLCl<sub>2</sub>], 85.29% for [CoL(NO<sub>3</sub>)<sub>2</sub>], 84.69% for [CoLOAc<sub>2</sub>], 83.07% for [NiLCl<sub>2</sub>] and 82.26% for [ZnLCl<sub>2</sub>]. Schiff's base shows one degradation step while all the complexes show two degradation steps corresponding to weight loss. The first small degradation step in the complexes [CuLCl<sub>2</sub>], [CoLCl<sub>2</sub>], [NiLCl<sub>2</sub>] and [ZnLCl<sub>2</sub>] occurring between 160 °C and 380 °C may be due to loss of chlorine molecule (Cl<sub>2</sub>) and the second decomposition step in the range of 300–800 °C, corresponds to the loss of organic moiety. There was no weight loss near 100°C which indicated the absence of water molecule coordinated with metal ions in complexes. Complexes are found thermally more stable in comparison to the free Schiff's base.

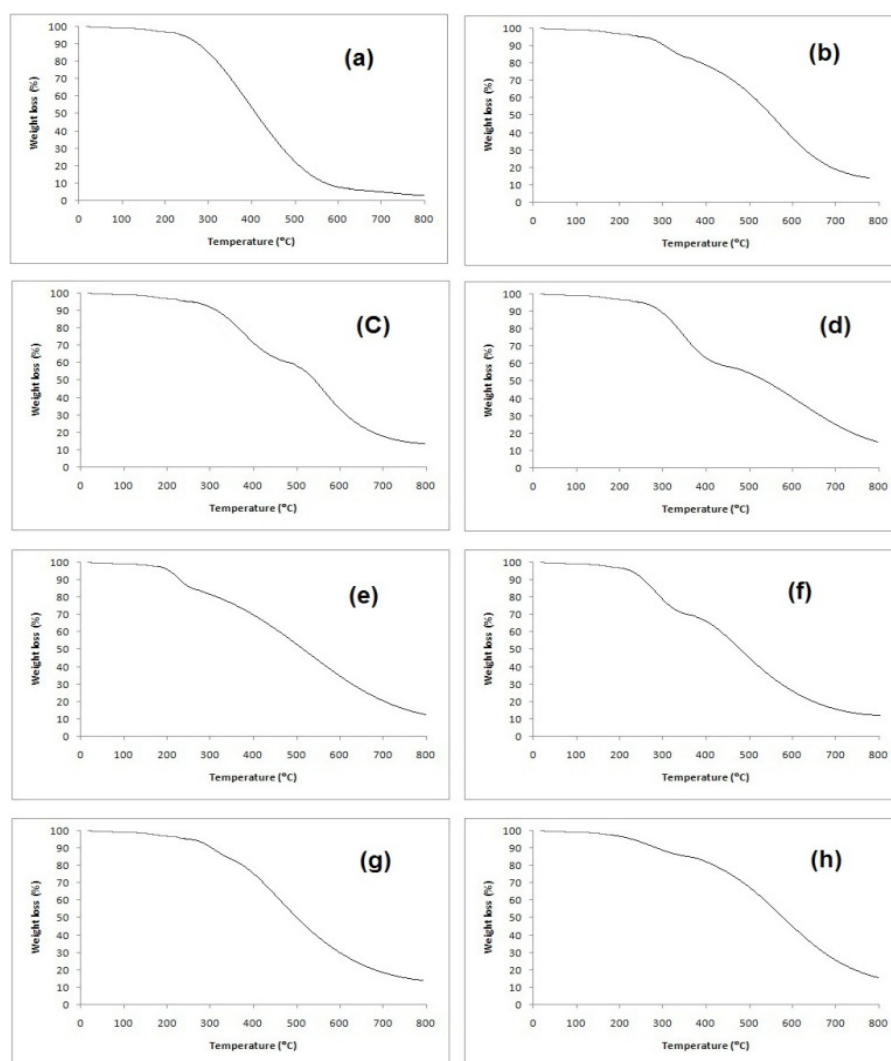


Fig. 11. TGA curves of (a) ligand (L), (b) [CuLCl<sub>2</sub>], (c) [CuL(NO<sub>3</sub>)<sub>2</sub>], (d) [CuLOAc<sub>2</sub>], (e) [CoLCl<sub>2</sub>], (f) [CoLOAc<sub>2</sub>], (g) [NiLCl<sub>2</sub>] and (h) [ZnLCl<sub>2</sub>] complexes in nitrogen atmosphere.

TABLE 3. Thermal analysis data of the Schiff's base ligand and its metal complexes.

Compounds	Stages	Temp. range (°C)	Weight loss (%)		Decomposition Species	Residual Species
			Calc.	Found		
Ligand (L)	1 <sup>st</sup>	200-600	91.17	90.82		-
C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	2 <sup>nd</sup>	600-800	8.83	6.65		-
[CoLCl <sub>2</sub> ]	1 <sup>st</sup>	160-300	15.99	16.08	Cl <sub>2</sub>	-
	2 <sup>nd</sup>	300-800	67.13	66.96	C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O (Organic moiety)	CoO
[CoL(NO <sub>3</sub> ) <sub>2</sub> ]	1 <sup>st</sup>	200-450	53.52	54.03	C <sub>10</sub> H <sub>6</sub> N <sub>2</sub> O <sub>7</sub> (Organic moiety)	-
	2 <sup>nd</sup>	450-800	31.40	31.26	C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> (Organic moiety)	CoO
[CoL(OAc) <sub>2</sub> ]	1 <sup>st</sup>	200-350	28.11	28.54	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub> (Organic moiety)	-
	2 <sup>nd</sup>	350-800	56.63	56.15	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> (Organic moiety)	CoO
[NiLCl <sub>2</sub> ]	1 <sup>st</sup>	250-350	16.03	16.17	Cl <sub>2</sub>	-
	2 <sup>nd</sup>	350-800	67.11	66.90	C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O (Organic moiety)	NiO
[CuLCl <sub>2</sub> ]	1 <sup>st</sup>	200-350	15.85	16.01	Cl <sub>2</sub>	-
	2 <sup>nd</sup>	350-800	66.40	66.28	C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O (Organic moiety)	CuO
[CuL(NO <sub>3</sub> ) <sub>2</sub> ]	1 <sup>st</sup>	250-500	40.52	40.39	C <sub>5</sub> H <sub>3</sub> N <sub>2</sub> O <sub>7</sub> (Organic moiety)	-
	2 <sup>nd</sup>	500-800	43.66	43.90	C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> (Organic moiety)	CuO
[CuL(OAc) <sub>2</sub> ]	1 <sup>st</sup>	240-430	39.80	40.02	C <sub>9</sub> H <sub>9</sub> O <sub>5</sub> (Organic moiety)	-
	2 <sup>nd</sup>	430-800	44.13	43.95	C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> (Organic moiety)	CuO
[ZnLCl <sub>2</sub> ]	1 <sup>st</sup>	240-380	15.78	15.92	Cl <sub>2</sub>	-
	2 <sup>nd</sup>	380-800	66.13	66.34	C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O (Organic moiety)	ZnO

#### Density Functional Theory (DFT) analysis

Geometry of ligand and its metal complexes were optimized using B3LYP three functional parameters with 6-31+g(d,p) basis set as incorporated in the Gaussian 09W programme in gaseous phase. [CuLCl<sub>2</sub>], [CuLOAc<sub>2</sub>] and [CuL(NO<sub>3</sub>)<sub>2</sub>] complexes have octahedral geometry with slight distortion. The two axial positions are occupied by chloride ions/oxygen of acetate or nitrate ions, while the equatorial positions are occupied by nitrogen and oxygen atoms of the ligand. The two equatorial Cu-N distances are 2.14 Å, 1.86 Å; 2.12 Å, 1.85 Å and 2.12 Å, 1.84 Å in [CuLCl<sub>2</sub>], [CuLOAc<sub>2</sub>] and [CuL(NO<sub>3</sub>)<sub>2</sub>] complexes, respectively. The two equatorial Cu-O distances are 2.02 Å, 2.09 Å; 2.11 Å, 2.08 Å and 2.04 Å, 2.07 Å in [CuLCl<sub>2</sub>], [CuLOAc<sub>2</sub>] and [CuL(NO<sub>3</sub>)<sub>2</sub>] complexes, respectively. The axial Cu-Cl bond distances in [CuLCl<sub>2</sub>] complex are 2.15 Å and 2.24 Å. The axial Cu-O bond distances in [CuOAc<sub>2</sub>] and [CuL(NO<sub>3</sub>)<sub>2</sub>] complexes are 2.02 Å, 2.05 Å and 1.84, 1.84, respectively. The

bond angles in the coordination sphere of Cu(II) complexes are found approximately near to the perpendicular value. In [CuLCl<sub>2</sub>] complex, N<sub>17</sub>-Cu-N<sub>18</sub>, N<sub>18</sub>-Cu-O<sub>33</sub>, O<sub>25</sub>-Cu-O<sub>33</sub> and N<sub>17</sub>-Cu-O<sub>25</sub> bond angles are 89.51°, 84.57°, 107.01° and 79.20°, respectively. In [CuLOAc<sub>2</sub>] complex, N<sub>17</sub>-Cu-N<sub>18</sub>, N<sub>18</sub>-Cu-O<sub>33</sub>, O<sub>25</sub>-Cu-O<sub>33</sub> and N<sub>17</sub>-Cu-O<sub>25</sub> bond angles are 83.60°, 86.12°, 110.78° and 76.15°, respectively. While in [CuL(NO<sub>3</sub>)<sub>2</sub>] complex N<sub>17</sub>-Cu-N<sub>18</sub>, N<sub>18</sub>-Cu-O<sub>33</sub>, O<sub>25</sub>-Cu-O<sub>33</sub> and N<sub>17</sub>-Cu-O<sub>25</sub> bond angles are 85.76°, 83.20°, 109.17° and 78.70°, respectively. The bond angle Cl-Cu-Cl is found 165.53. The bond angles O<sub>(NO<sub>3</sub>)</sub>-Cu-O<sub>(NO<sub>3</sub>)</sub> and O<sub>(OAc)</sub>-Cu-O<sub>(OAc)</sub> are 174.37° and 178.40° in [CuL(NO<sub>3</sub>)<sub>2</sub>] and [CuLOAc<sub>2</sub>], respectively, which are very close to linear value i.e. 180°. The Cu-Cl bond lengthens to 2.24 Å in [CuLCl<sub>2</sub>] complex, similarly Cu-O<sub>(NO<sub>3</sub>)</sub> and Cu-O<sub>(OAc)</sub> bond lengthens to 1.84 Å and 2.05 Å in CuL(NO<sub>3</sub>)<sub>2</sub> and CuLOAc<sub>2</sub> complexes, respectively, which results in distortion from regular octahedral geometry.

The two equatorial Co-N distances are 1.92 Å, 1.79 Å; 1.86 Å, 1.81 Å and 1.98 Å, 1.85 Å while two equatorial Co-O distances are 2.01 Å, 2.23 Å; 2.05 Å, 2.12 Å and 2.09 Å, 2.24 Å in [CoLCl<sub>2</sub>], [CoLOAc<sub>2</sub>] and [CoL(NO<sub>3</sub>)<sub>2</sub>] complexes, respectively. The axial Co-Cl bond distances in [CoLCl<sub>2</sub>] complex are 2.27 Å and 2.30 Å. The axial Co-O bond distances in [CoOAc<sub>2</sub>] and [CoL(NO<sub>3</sub>)<sub>2</sub>] complexes are 1.97 Å, 1.97 Å and 1.86, 1.86, respectively. The bond angles N<sub>17</sub>-Co-N<sub>18</sub>, N<sub>18</sub>-Co-O<sub>33</sub>, O<sub>25</sub>-Co-O<sub>33</sub> and N<sub>17</sub>-Co-O<sub>25</sub> are found 95.66°, 83.94°, 98.07° and 82.99°, respectively in [CoLCl<sub>2</sub>] complex. Similar results are obtained in case of [CuL(NO<sub>3</sub>)<sub>2</sub>] and [CuLOAc<sub>2</sub>] complexes. The bond angles Cl-Co-Cl, O<sub>(OAc)</sub>-Co-O<sub>(OAc)</sub> and O<sub>(NO<sub>3</sub>)</sub>-Co-O<sub>(NO<sub>3</sub>)</sub> were found 173.61°, 175.62° and 172.49°, respectively, which are very close to the linear value. The geometry of cobalt complexes was found to be octahedral.

The two equatorial Ni-N distances are 2.00 Å and 1.87 Å while two equatorial Ni-O distances are 1.96 Å and 2.19 Å in [NiLCl<sub>2</sub>]. The two axial Ni-Cl bond lengths are 2.17 Å and 2.14 Å. The bond angles N<sub>17</sub>-Ni-N<sub>18</sub>, N<sub>18</sub>-Ni-O<sub>33</sub>, O<sub>25</sub>-Ni-O<sub>33</sub> and N<sub>17</sub>-Ni-O<sub>25</sub> bond are found 96.79°, 84.19°, 90.00° and 88.83° respectively in [NiLCl<sub>2</sub>].

complex which are very close to the perpendicular value. The bond angle Cl-Ni-Cl was found to be 172.07°, which is close to the linear value. The geometry of nickel complex was found to be octahedral.

We tried to optimize the geometry of [ZnLCl<sub>2</sub>] by considering the ligand as tetradentate but it could not be done because it gave very much longer Zn-O bonds as well as Cl-Zn-Cl bond angle was not near to the linear value i.e. 180°, but it was very less. Then we optimized it by taking the ligand as bidentate using azomethine nitrogens which are better electron donor in comparison to furan ring oxygen. In the successfully optimized structure, the two Zn-N bond lengths are 2.01 Å and 2.03 Å while two Zn-Cl bond lengths are 2.25 Å and 2.24 Å in [ZnLCl<sub>2</sub>]. The bond angles N<sub>17</sub>-Zn-N<sub>18</sub> and Cl-Zn-Cl are found 95.13° and 140.66° respectively in [ZnLCl<sub>2</sub>] complex. The geometry of Zinc complex was found to be tetrahedral.

The calculated bond lengths and bond angles for the ligand and its metal complexes are listed in Table 4 and Table 5 respectively. The optimized structures of Schiff's base and its metal complexes are given in Fig. 12. The numbering scheme of the optimized structures is given in Fig. 13.

TABLE 4. Optimized geometry of the ligand and its metal complexes (bond length in angstrom).

Parameters	Ligand	[CuLCl <sub>2</sub> ]	[CuL(NO <sub>3</sub> ) <sub>2</sub> ]	[CuLOAc <sub>2</sub> ]	[CoLCl <sub>2</sub> ]	[CoL(NO <sub>3</sub> ) <sub>2</sub> ]	[CoLOAc <sub>2</sub> ]	[NiLCl <sub>2</sub> ]	[ZnLCl <sub>2</sub> ]
C <sub>21</sub> -O <sub>25</sub>	1.39	1.40	1.40	1.40	1.41	1.40	1.41	1.42	1.40
C <sub>24</sub> -O <sub>25</sub>	1.40	1.42	1.41	1.42	1.44	1.43	1.43	1.44	1.41
C <sub>19</sub> -C <sub>24</sub>	1.44	1.46	1.45	1.44	1.45	1.43	1.42	1.45	1.44
N <sub>17</sub> -C <sub>19</sub>	1.29	1.31	1.31	1.32	1.33	1.35	1.37	1.33	1.32
C <sub>19</sub> -H <sub>37</sub>	1.10	1.10	1.11	1.10	1.10	1.10	1.09	1.10	1.11
C <sub>8</sub> -N <sub>17</sub>	1.41	1.43	1.42	1.42	1.44	1.42	1.38	1.43	1.45
C <sub>3</sub> -C <sub>8</sub>	1.44	1.45	1.44	1.44	1.45	1.45	1.45	1.45	1.45
C <sub>2</sub> -C <sub>3</sub>	1.44	1.44	1.45	1.45	1.45	1.44	1.43	1.44	1.45
C <sub>2</sub> -N <sub>18</sub>	1.41	1.45	1.42	1.40	1.45	1.43	1.43	1.44	1.45
N <sub>18</sub> -C <sub>20</sub>	1.29	1.32	1.43	1.46	1.33	1.35	1.35	1.31	1.32
C <sub>20</sub> -H <sub>38</sub>	1.10	1.10	1.11	1.12	1.10	1.10	1.10	1.11	1.11
C <sub>20</sub> -C <sub>32</sub>	1.44	1.44	1.46	1.49	1.44	1.43	1.43	1.45	1.44
C <sub>32</sub> -O <sub>33</sub>	1.40	1.42	1.41	1.41	1.42	1.42	1.42	1.41	1.41
C <sub>29</sub> -O <sub>33</sub>	1.39	1.40	1.40	1.40	1.40	1.41	1.40	1.40	1.40
N <sub>17</sub> -M	-	2.14	2.12	2.12	1.92	1.98	1.86	2.00	2.01
N <sub>18</sub> -M	-	1.86	1.84	1.85	1.79	1.85	1.81	1.87	2.03
O <sub>25</sub> -M	-	2.02	2.04	2.11	2.01	2.09	2.05	1.96	-
O <sub>33</sub> -M	-	2.09	2.07	2.08	2.23	2.24	2.12	2.19	-
M-Cl	-	2.15	-	-	2.27	-	-	2.17	2.25
M-Cl	-	2.24	-	-	2.30	-	-	2.14	2.24
M-O <sub>(NO<sub>3</sub>)</sub>	-	-	1.84	-	-	1.86	-	-	-
M-O <sub>(NO<sub>3</sub>)</sub>	-	-	1.84	-	-	1.86	-	-	-
M-O <sub>(OAc)</sub>	-	-	-	2.02	-	-	1.97	-	-
M-O <sub>(OAc)</sub>	-	-	-	2.05	-	-	1.97	-	-

**TABLE 5. Optimized geometry of the ligand and its metal complexes (bond angle in degree).**

Parameters	Ligand	[CuLCl <sub>2</sub> ]	[CuL(NO <sub>3</sub> ) <sub>2</sub> ]	[CuLOAc <sub>2</sub> ]	[CoLCl <sub>2</sub> ]	[CoL(NO <sub>3</sub> ) <sub>2</sub> ]	[CoLOAc <sub>2</sub> ]	[NiLCl <sub>2</sub> ]	[ZnLCl <sub>2</sub> ]
∠O <sub>25</sub> C <sub>21</sub> H <sub>26</sub>	115.73	112.47	112.54	112.21	111.26	111.53	111.04	113.37	112.90
∠C <sub>21</sub> O <sub>25</sub> C <sub>24</sub>	107.06	105.89	105.31	105.81	105.93	106.50	106.26	105.67	105.97
∠C <sub>19</sub> C <sub>24</sub> O <sub>25</sub>	120.00	114.22	113.87	113.42	111.39	113.42	111.81	107.75	117.17
∠N <sub>17</sub> C <sub>19</sub> C <sub>24</sub>	123.62	117.60	117.03	116.83	116.76	118.46	119.27	113.43	123.82
∠C <sub>24</sub> C <sub>19</sub> H <sub>37</sub>	114.51	115.14	115.78	116.41	116.99	116.80	117.88	118.41	113.31
∠N <sub>17</sub> C <sub>19</sub> H <sub>37</sub>	121.86	127.26	126.93	126.75	126.23	124.73	122.83	127.95	122.86
∠C <sub>8</sub> N <sub>17</sub> C <sub>19</sub>	121.59	121.74	121.21	121.23	121.54	119.87	119.72	120.75	116.91
∠C <sub>3</sub> C <sub>8</sub> N <sub>17</sub>	120.06	117.94	118.12	118.68	118.68	119.24	120.38	119.66	120.23
∠C <sub>2</sub> C <sub>3</sub> C <sub>8</sub>	123.54	126.51	125.26	124.62	125.93	125.94	124.30	126.06	126.80
∠C <sub>3</sub> C <sub>2</sub> N <sub>18</sub>	120.13	122.10	120.12	118.53	121.22	121.30	119.90	120.32	119.98
∠C <sub>2</sub> N <sub>18</sub> C <sub>20</sub>	121.72	119.11	118.80	118.54	118.68	117.67	117.27	120.96	117.73
∠N <sub>18</sub> C <sub>20</sub> H <sub>38</sub>	122.70	125.02	120.83	117.02	123.85	123.46	124.15	124.63	123.23
∠C <sub>32</sub> C <sub>20</sub> H <sub>38</sub>	115.69	116.35	114.81	113.09	116.24	116.01	116.94	115.08	113.50
∠C <sub>20</sub> C <sub>32</sub> O <sub>33</sub>	116.17	114.15	113.56	112.34	115.00	115.18	112.20	115.66	116.99
∠C <sub>29</sub> O <sub>33</sub> C <sub>32</sub>	106.95	105.31	105.90	105.63	105.18	105.51	106.05	105.35	105.98
∠O <sub>33</sub> C <sub>29</sub> C <sub>34</sub>	115.94	113.49	112.89	112.12	113.41	112.98	111.32	113.55	113.02
∠C <sub>8</sub> N <sub>17</sub> M		127.41	124.64	122.42	126.98	125.99	127.62	119.49	118.23
∠MN <sub>17</sub> C <sub>19</sub>		108.34	111.72	116.29	110.95	114.15	112.53	96.85	124.86
∠C <sub>2</sub> N <sub>18</sub> M		126.36	123.49	119.04	124.95	126.56	127.69	124.09	121.42
∠MN <sub>18</sub> C <sub>20</sub>		114.50	112.51	110.80	116.36	115.77	115.01	114.94	120.77
∠C <sub>21</sub> O <sub>25</sub> M		137.64	135.98		130.84	138.90	137.97	127.74	-
∠C <sub>24</sub> O <sub>25</sub> M		109.57	111.27	114.64	103.35	109.77	106.12	102.93	-
∠C <sub>29</sub> O <sub>33</sub> M		146.88	142.08		150.75	149.49	142.31	147.85	-
∠C <sub>32</sub> O <sub>33</sub> M		105.44	107.11	108.68	101.59	103.05	104.76	103.07	-
∠N <sub>17</sub> MN <sub>18</sub>		89.51	85.76	83.60	95.66	94.46	95.58	96.79	95.13
∠N <sub>18</sub> MO <sub>33</sub>		84.57	83.20	86.12	83.94	83.09	83.87	84.19	-
∠O <sub>25</sub> MO <sub>33</sub>		107.01	109.17	110.78	98.07	101.24	95.73	90.00	-
∠N <sub>17</sub> MO <sub>25</sub>		79.20	78.70	76.15	82.99	81.15	85.07	88.83	-
∠CIMCl		165.53	-	-	173.61	-	-	172.07	140.66
∠O <sub>(NO3)</sub> MO <sub>(NO3)</sub>		-	174.37	-	-	172.49	-	-	-
∠O <sub>(OAc)</sub> MO <sub>(OAc)</sub>		-	-	178.40	-	-	175.62	-	-

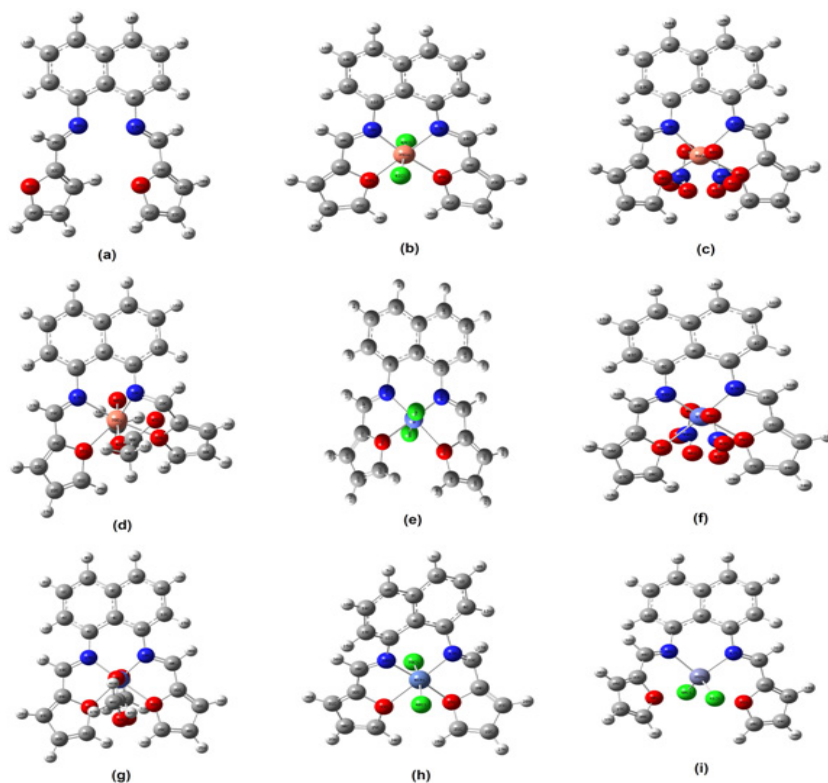


Fig. 12. Geometry optimized structures of (a) Schiff's base, (b)  $[\text{CuLOAc}_2]$ , (c)  $[\text{CoLCl}_2]$ , (d)  $[\text{NiLCl}_2]$ , (e)  $[\text{ZnLCl}_2]$  (colour: H-White, C-Grey, N-Blue, O-Red, Cl-Green Cu-Light orange, Co-light Blue, Ni-Greyish Blue and Zn-Bluish grey).

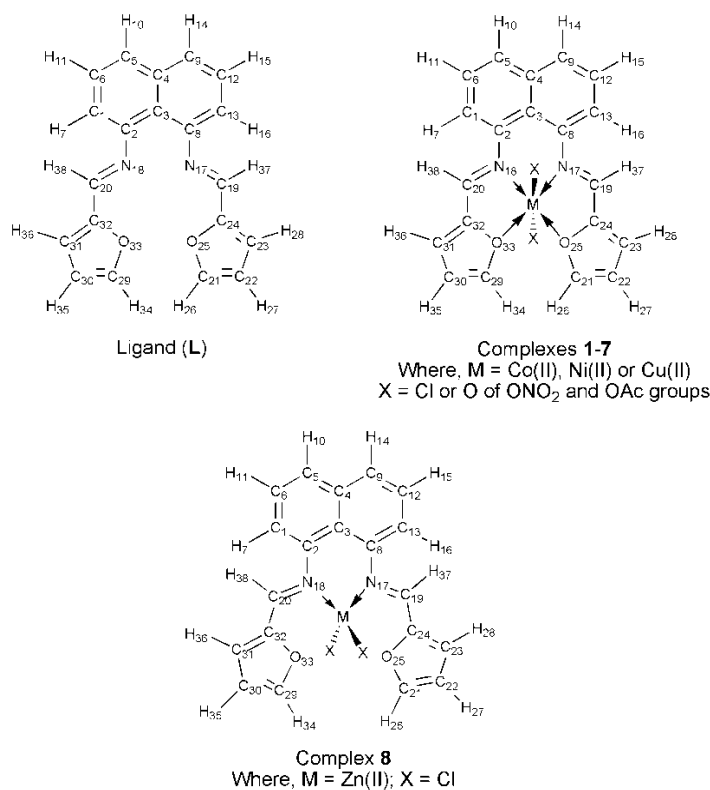


Fig. 13. Numbering Scheme of the optimized structures of the Ligand (L) and metal complexes (1-7 and 8).

### Antimicrobial studies

The antimicrobial screening data shows that all the compounds exhibit different antibacterial capabilities against the tested human pathogenic bacteria. It is important to note that the metal complexes exhibited improved inhibitory effects in comparison to the parent ligand, which indicates that the coordinated metal has more impact on the antibacterial activity. The increased antibacterial activity of metal complexes in comparison to ligand might be due to complexation and chelation, which lead all the potent moieties to come close in the vicinity to interact strongly with bacteria and hinder its growth. Complexation also decreases the positive charge on metal ion and makes it slightly lipophilic in nature, which in turn increases its infusion more effectively into the phospholipid membrane of bacteria and hence killing them more violently [47]. Comparative antibacterial activities are depicted in Fig. 14 and the data is shown in Table 6.

On comparing the antibacterial activity of ligand and its metal complexes with the standard drug Ciprofloxacin, it was concluded that:

- (1) Ligand did not show any significant activity against any human pathogenic bacteria.
- (2) No compound could be highly active except  $[\text{CoLCl}_2]$  against *S. typhi*.
- (3)  $[\text{NiLCl}_2]$  was found highly active against *L. monocytogenes*, *E. coli* and *K. pneumoniae*.
- (4)  $[\text{ZnLCl}_2]$  complex was found active against *E. coli* and *E. faecalis*.
- (5) Against *Y. enterocolitica*, cobalt and copper complexes exhibited the high activity.
- (6)  $[\text{CuL}(\text{OAc})_2]$  and  $[\text{CuLCl}_2]$  complexes were found consistently active against almost all bacteria.

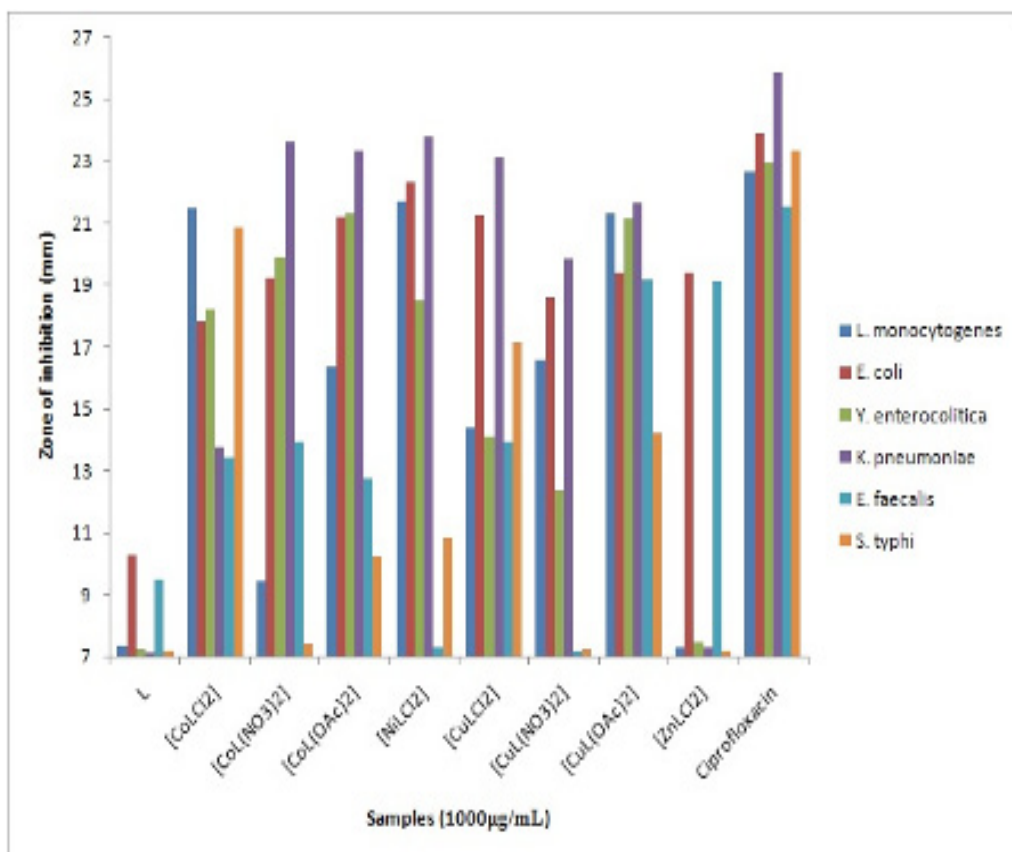


Fig. 14. Graph showing the inhibition zone (mm) of samples against different bacterial species.



TABLE 6. Antibacterial activity data of Schiff's base ligand and its Co(II), Ni(II), Cu(II) and Zn(II) complexes

Samples	Zone of inhibition (mm) (Conc. of microorganisms is 1000 µg mL <sup>-1</sup> )					
	<i>L. monocytogenes</i>	<i>E. coli</i>	<i>Y. enterocolitica</i>	<i>K. pneumoniae</i>	<i>E. faecalis</i>	<i>S. typhi</i>
Ligand	NSI	10.28	NSI	NSI	9.46	NSI
[CoLCl <sub>2</sub> ]	21.50	17.83	18.21	13.76	13.41	20.85
[CoL(NO <sub>3</sub> ) <sub>2</sub> ]	9.42	19.23	19.90	23.60	13.92	NSI
[CoL(OAc) <sub>2</sub> ]	16.36	21.17	21.30	23.31	12.73	10.19
[NiLCl <sub>2</sub> ]	21.50	22.34	18.49	23.76	NSI	10.85
[CuLCl <sub>2</sub> ]	14.39	21.23	14.10	23.11	13.93	17.14
[CuL(NO <sub>3</sub> ) <sub>2</sub> ]	16.57	18.59	12.33	19.85	NSI	NSI
[CuL(OAc) <sub>2</sub> ]	21.32	19.37	21.11	21.62	19.09	14.23
[ZnLCl <sub>2</sub> ]	NSI	19.37	NSI	NSI	19.09	NSI
Ciprofloxacin (Standard)	22.65	23.89	22.93	25.88	21.53	23.34

### Conclusion

A Schiff's base ligand (L) has been synthesized, characterized and its complexation was done with Co(II), Ni(II), Cu(II) and Zn(II) metal ions. On the basis of spectral studies, Co(II) and Ni(II) complexes were assigned octahedral geometry, Cu(II) complexes were assigned elongated tetragonal geometry, whereas the Zn(II) complex was assigned tetrahedral geometry. The thermal studies suggested that the complexes are more stable as compared to ligand and there is no water molecule coordinated with metal ion. Geometries of ligand and metal complexes were optimized and DFT results were found comparable with the experimental ones, which confirmed the suggested structures. The antibacterial screening of the compounds led to the conclusion that Nickel and Copper complexes show comparable activity against *L. monocytogenes*, *E. coli* and *K. pneumoniae*, while cobalt complexes exhibited high activity against *Y. enterocolitica* and *S. typhi*, whereas Zinc complex was found active against *E.*

*faecalis* only. The overall order of activity of metal complexes was found Ni(II) > Cu(II) > Co(II) > Zn(II) > Ligand. This activity against human pathogenic bacteria might be due to the presence of azomethine group (-HC=N-), different hetero atoms (i.e. N and O) and anions.

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