



Synthesis, Characterization, DFT and Antimicrobial Study of Co(II), Ni(II), Cu(II) and Zn(II) Complexes of Novel Schiff Base Ligands Derived from 3-Amino-1,2,4-triazole-5-thiol

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Two novel Schiff base ligands are prepared by condensing 2-hydroxy-4-methoxybenzaldehyde with 3-amino-1,2,4-triazole-5-thiol (**HL**₁) and 2-hydroxy-3-methoxybenzaldehyde with 3-amino-1,2,4-triazole-5-thiol (**HL**₂). The ligands were synthesized and characterized by ¹H NMR, IR, HRMS and analytical data. The synthesized ligands were complexed with metal salts in 1:2 metal:ligand ratio yielded the complexes of type [M(L)₂(H₂O)_x] [where M = Co(II), Ni(II), Cu(II) and Zn(II); x = 2 for Co(II), Ni(II), Cu(II) while x = 0 for Zn(II)]. The metal complexes were characterized by elemental analysis, IR, ESI-mass, UV-visible, ESR, molar conductance, magnetic moment measurement and thermogravimetric analysis. The results from IR spectra revealed that ligands exist in thione and thiol forms. The synthesized complexes show non-electrolytic behaviour as indicated by their molar conductance values. The structure of ligand **HL**₁ and complexes **1-4** were fully optimized using Gaussian 09, taking 6-31g basis set and B3LYP functional. The experimental results based on various spectroscopic and analytical data predicted an octahedral geometry for Co(II), Ni(II) and Cu(II) complexes while for Zn(II) complexes the predicted geometry is tetrahedral. *in vitro* Antibacterial activity against *Bacillus macerans* (Gram-positive) and *Pseudomonas striata* (Gram-negative) and antifungal activity against *Rhizoctonia bataticola*, *Alternaria alternata* and *Fusarium odum* has been evaluated for all synthesized ligands and their metal complexes.

Keywords: Transition metal(II) complexes, 1,2,4-Triazoles, DFT study, Biological activity.

INTRODUCTION

Ligands having azomethine group called 'Schiff base' serves as an important class of therapeutic compounds. They can be easily prepared by the reaction of active carbonyl group with primary amines. Schiff bases synthesized from an aromatic aldehyde are more stable as compare to aliphatic aldehydes because of the conjugation system [1-3]. They serve as a group of ligands that are not only biological active but also stabilize metals in various oxidation states [4-7]. Triazoles having amines and thiol group have been widely studied for their anti-inflammatory and antimicrobial activity and other industrial applications [8-11]. 1,2,4-Triazole show a coordination behaviour with a range of metal ions due to presence of both nitrogen and sulphur atom [12-14]. Ligands derived from 1,2,4-triazole based moiety show a range of industrial applications and biological activities including antimicrobial, anticancer, biomarkers and antitumor [15-19].

Keeping view in mind, the biological importance of 1,2,4-triazole derived Schiff base ligands, we design and synthesize ligands viz., 2-[(5-mercapto-1H-[1,2,4]triazol-3-ylimino)methyl]-5-methoxy phenol (**HL**₁) and 2-[(5-mercapto-1H-[1,2,4]triazol-3-ylimino)methyl]-6-methoxy phenol (**HL**₂) by reaction of 3-amino-1,2,4-triazole-5-thiol with 2-hydroxy-4-methoxybenzaldehyde and 2-hydroxy-3-methoxybenzaldehyde and their complexes with Co(II), Ni(II), Cu(II) and Zn(II) ions.

EXPERIMENTAL

Solvents and chemicals used in the present study were of AnalaR grade. Chemicals were purchased from Sigma-Aldrich, Fluka and E. Merck and were used as received. The C, H, N analysis was carried out on Carlo-Erba 1106 elemental analyzer. Conductivity measurements were carried out by using the ELICO (CM82T) conductivity bridge. ESI-mass spectra were recorded on a VG Biotech Quattro mass spectrometer. Electronic spectra

of the metal complexes in DMSO were studied using Shimadzu UV mini-1240 spectrophotometer. IR spectra in solid state were recorded on FTIR BX-II spectrophotometer. NMR spectra in DMSO- d_6 were recorded on a Bruker Advance DPX-300 spectrometer operating at a frequency of 400 MHz. TMS is used as an internal standard. Thermal analyses were carried out on a Shimadzu TGA-50H thermal analyzer. The solid state X-band EPR spectra of Cu(II) complexes were recorded at room temperature on a E4-EPR spectrometer.

Synthesis of ligands: Schiff base **HL₁** was synthesized by the reaction of 3-amino-1,2,4-triazole-5-thiol with 2-hydroxy-4-methoxybenzaldehyde (1:1) in methanol. On mixing the two contents the reaction mixture was first stirred for 1 h and then refluxed for 12 h. The reaction progress was checked by TLC. The reaction mixture was cooled once the reaction completes. The solid obtained was filtered and washed with methanol, and then finally dried under vacuum over anhydrous CaCl_2 . The ligand **HL₂** was obtained by adopting the similar above mentioned procedure.

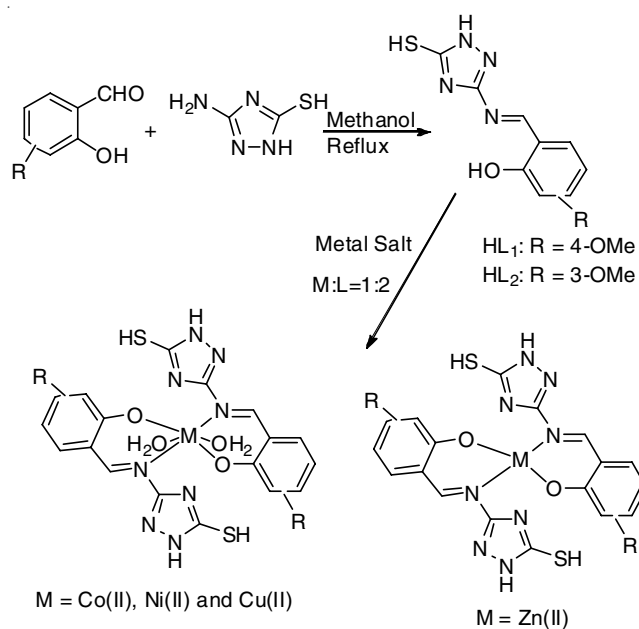
Synthesis of metal complexes: Corresponding metal salt (1 mmol) $\text{MCl}_2 \cdot x\text{H}_2\text{O}$ ($\text{M} = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+} and Zn^{2+} ; $x = 6$ for Co^{2+} and Ni^{2+} , $x = 2$ for Cu^{2+} and $x = 0$ for Zn^{2+}) was dissolved in 20 mL of methanol. This solution was added to 20 mL of hot methanolic solution of the ligand (2 mmol). The reaction mixture was stirred for 4–8 h, then refluxed for another 4–18 h. The resulting reaction mixture was cooled overnight at 0 °C which yielded a crystalline solid. The precipitate was filtered off, washed with cold ethanol and finally with dry ether, then dried under vacuum over P_2O_{10} (**Scheme-I**).

DFT calculations: The gas phase geometry optimization of ligand **HL₁** and complexes (**1–4**) was done using Gaussian 09W suite [20–23].

Antimicrobial activity: All the synthesized compounds were tested for their antibacterial activity against *B. macerans* and *P. striata* by using disc diffusion method [24] and antifungal activity was done using food poison technique [24] against the test fungi, *R. bataticola*, *A. alternata* and *F. odum*. The test compounds were dissolved in DMF in varying concentration. Streptomycin was used as a standard drug for antibacterial and chlorothalonil for antifungal study.

RESULTS AND DISCUSSION

Schiff bases were prepared (**Scheme-I**) by taking equimolar amount of 3-amino-1,2,4-triazole-5-thiol and 2-hydroxy-4-



Scheme-I: Synthesis of Schiff base ligands and their metal complexes

methoxybenzaldehyde (**HL₁**), 3-amino-1,2,4-triazole-5-thiol and 2-hydroxy-3-methoxy benzaldehyde (**HL₂**). The structure of these Schiff bases was confirmed by their IR, ^1H NMR and mass spectrophotometry data. Further, these Schiff bases were used for the synthesis of metal complexes by taking the corresponding metal chloride salts in metal:ligand ratio of 1:2. The monomeric complexes thus obtained are stable in air and decomposed above 280 °C. These complexes show poor solubility in methanol and are soluble in DMF or DMSO. The low value of molar conductance of these complexes suggested their non-electrolytic nature. Physical measurements and the analytical data of all the synthesized compounds are given in Table-1.

Mass spectra: The HRMS mass spectrum of the ligands **HL₁**, **HL₂** and ESI mass spectrum for the metal complexes **1–8** was performed and their m/z are listed in Table-1. In the HRMS spectrum of ligand **HL₁**, a peak corresponding to $[\text{M}+18]$ appeared at m/z value of 268.0196, followed by a series of peaks due to different fragments. The stability of any fragment relates directly with the intensity of the corresponding peak. Similarly, in the mass spectrum of ligand **HL₂** (Fig. 1) a peak corresponds to $[\text{M}+18]$ appear at m/z value of 268.0198 followed by a series of peaks. In the mass spectrum of complex **1**, a peak corresponds to $[\text{M}+1]$ appears at m/z value of 594.19 (Fig. 2).

TABLE-1
PHYSICAL MEASUREMENTS AND ANALYTICAL DATA OF THE LIGANDS (**HL₁**, **HL₂**) AND METAL COMPLEXES (**1–8**)

No.	m.f.	Molar mass	m/z	Yield (%)	Elemental analysis (%): Found (calcd.)			
					C	H	N	M
HL₁	$\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2\text{S}$	250.05	268.0196	82	47.75 (47.99)	3.86 (4.03)	22.14 (22.39)	–
HL₂	$\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2\text{S}$	250.05	268.0198	79	48.22 (47.99)	3.74 (4.03)	22.18 (22.39)	–
1	$\text{C}_{20}\text{H}_{22}\text{N}_8\text{O}_6\text{S}_2\text{Co}$	593.04	594.1900	61	40.22 (40.48)	3.83 (3.74)	18.63 (18.88)	9.72 (9.93)
2	$\text{C}_{20}\text{H}_{22}\text{N}_8\text{O}_6\text{S}_2\text{Ni}$	592.05	593.6700	63	40.22 (40.49)	3.62 (3.74)	18.65 (18.89)	9.63 (9.89)
3	$\text{C}_{20}\text{H}_{22}\text{N}_8\text{O}_6\text{S}_2\text{Cu}$	597.04	596.7800	65	39.91 (40.16)	3.54 (3.71)	18.51 (18.73)	10.39 (10.62)
4	$\text{C}_{20}\text{H}_{18}\text{N}_8\text{O}_4\text{S}_2\text{Zn}$	562.02	562.7300	69	42.30 (42.60)	3.13 (3.22)	19.60 (19.87)	11.34 (11.60)
5	$\text{C}_{20}\text{H}_{22}\text{N}_8\text{O}_6\text{S}_2\text{Co}$	593.04	594.8800	61	40.26 (40.48)	3.56 (3.74)	18.61 (18.88)	9.68 (9.93)
6	$\text{C}_{20}\text{H}_{22}\text{N}_8\text{O}_6\text{S}_2\text{Ni}$	592.05	593.4500	63	40.25 (40.49)	3.51 (3.74)	18.55 (18.89)	9.55 (9.89)
7	$\text{C}_{20}\text{H}_{22}\text{N}_8\text{O}_6\text{S}_2\text{Cu}$	597.04	599.1200	65	39.75 (40.16)	3.48 (3.71)	18.37 (18.73)	10.31 (10.62)
8	$\text{C}_{20}\text{H}_{18}\text{N}_8\text{O}_4\text{S}_2\text{Zn}$	562.02	563.9300	66	42.34 (42.60)	3.10 (3.22)	19.63 (19.87)	11.37 (11.60)

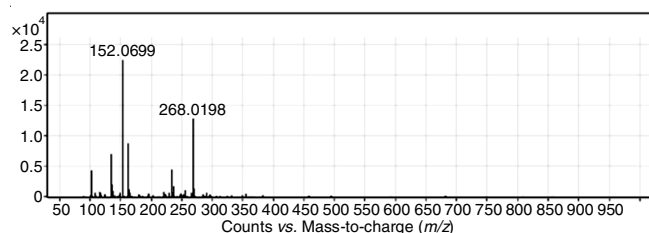
Fig. 1. Mass spectrum of ligand **HL₂**

TABLE-2
IMPORTANT INFRARED SPECTRAL
BANDS (cm⁻¹) AND THEIR ASSIGNMENTS

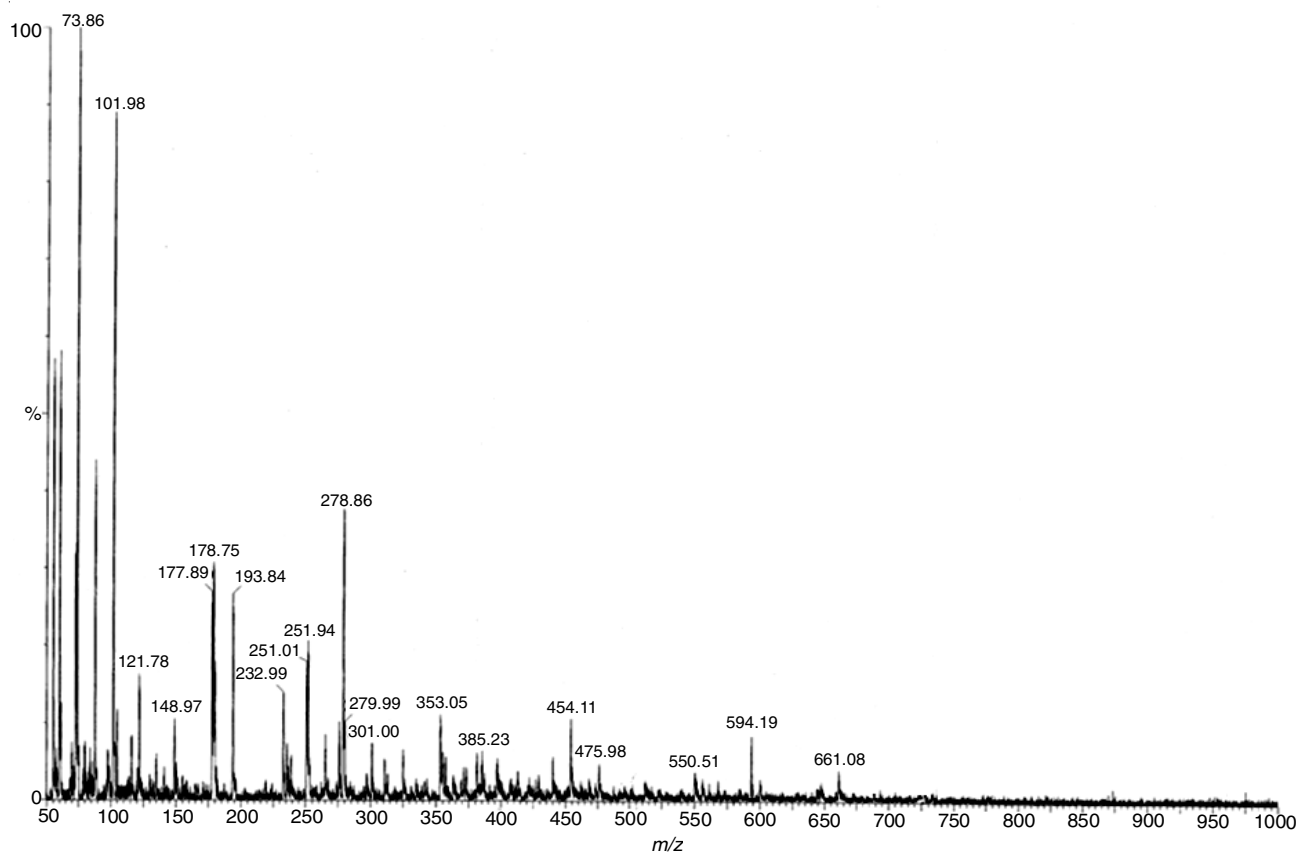
Compound	$\nu(\text{HC}=\text{N})$	$\nu(\text{-OH})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
HL₁	1595	3213	—	—
HL₂	1592	3258	—	—
1	1581	—	542	488
2	1576	—	539	491
3	1578	—	598	492
4	1577	—	598	490
5	1583	—	522	478
6	1589	—	545	483
7	1573	—	538	478
8	1575	—	576	483

¹H NMR spectra: The ¹H NMR spectra of the ligands **HL₁** and **HL₂** were recorded in CDCl₃ with drop of DMSO-*d*₆. In case of ligand **HL₁**, a singlet corresponding to imine (CH=N) proton appears at 8.42 ppm. The signals due to the proton of -OH and -NH group appear as a singlet at 11.90 and 12.78 ppm, respectively. Similarly, peak corresponding to -SH proton appeared at 13.93 ppm. Signals in the range of 6.4 to 7.28 ppm were

due to the aromatic protons. The peak for three protons of OCH₃ appears at 3.78 ppm. All the protons appeared in their expected range.

IR spectra: The key infrared bands of the ligands and their metal complexes are given in Table-2. The coordination of ligand to the corresponding metal ions was confirmed on the basis of shifts in absorption bands of various groups and absence of certain absorptions. The strong band at 1595-1592 cm⁻¹ was assigned to $\nu(\text{HC}=\text{N})$ linkage. This particular band in case of metal complexes shifts to a lower side in the IR spectra by 15-19 cm⁻¹ thereby indicating the involvement of azomethine nitrogen in complexation [25]. This involvement is further supported by the presence of a new band in the range of 492-478 cm⁻¹ corresponding to M-N bond for metal complexes. Broad band which appears in the range of 3258-3213 cm⁻¹ in ligands corresponds to $\nu(\text{OH})$ of aldehyde moiety disappears after metal complexation, which indicates the deprotonation of hydroxyl group in metal complexation. Broad band appears in metal complexes (**1-3** & **5-7**) in the range of 3410-3398 cm⁻¹ was due to $\nu(\text{OH})$ of water [26] however, in case of Zn(II) complexes (**4** & **8**) no such band was observed. No shift is observed in case of $\nu(\text{SH})$ and (C=S), indicating the thiol-thione tautomerism (Fig. 3) of ligand and these groups are not involved in coordination. Similarly, new band in the range of 598-522 cm⁻¹ was due to M-O bond. The results of IR spectra revealed that ligands **HL₁** and **HL₂** show a uninegative bidentate nature and coordination occurs *via* azomethine nitrogen and deprotonated hydroxyl group.

Conductance and magnetic susceptibility measurements: Conductivity measurements for the metal complexes were perfo-

Fig. 2. Mass spectrum of Co(II) complex of ligand **HL₁**

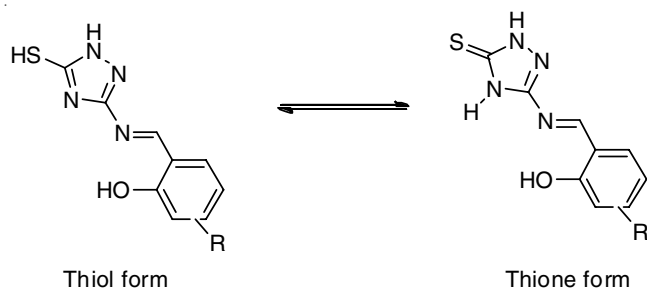


Fig. 3. Tautomeric form of Schiff base

formed at room temperature in DMF solvent and values are given in Table-3. All the complexes showed molar conductance values in the range ($4.2\text{--}10.2\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$), which suggests their non-electrolytic nature. In case of Co(II) complexes the obtained value of magnetic moment (4.96–5.04) B.M. indicates high spin octahedral geometry with three unpaired electrons. For Ni(II) complexes, the obtained magnetic moment value of (2.93–2.98) B.M. indicates two unpaired electrons which suggested an octahedral geometry. In case of Cu(II) complexes, the magnetic moment values of 1.80–1.83 B.M., indicates one unpaired electron.

TABLE-3
CONDUCTIVITY, MAGNETIC AND ELECTRONIC
SPECTRA OF METAL COMPLEXES

Complex No.	Ω_M ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$)	μ_{eff} (B.M.)	$1/\lambda$ (cm^{-1})
1	4.2	4.96	10412, 19123
2	5.4	2.98	11123, 15132, 23098
3	8.1	1.83	13123, 18921, 23741
5	10.2	5.04	10998, 19716
6	7.4	2.93	10715, 16034, 24001
7	9.1	1.80	12082, 18715, 22456

Electronic spectra: The electronic absorption spectral data of Co(II), Ni(II) and Cu(II) complexes of the ligands **HL**₁ and **HL**₂ are listed in Table-3. The electronic spectra of Co(II) complexes showed two transitions corresponding $10412\text{--}10988$ and $19123\text{--}19716\text{ cm}^{-1}$ to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_1); $\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3). The transition ν_2 calculated [27] by using the relation $\nu_2 = \nu_1 + 10Dq$, very close to ν_3 transition is not observed. The

electronic spectra of Ni(II) complexes display three bands in the region $10715\text{--}11123$, $15132\text{--}16034$ and $23098\text{--}24001\text{ cm}^{-1}$, respectively, assigned to the transitions ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$. These bands suggest an octahedral geometry [28] for Ni(II) complexes. In case of Cu(II) complexes, three bands in the range $12082\text{--}13123$, $18715\text{--}18921$ and $22456\text{--}23741\text{ cm}^{-1}$ were observed. These bands may be assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ ($d_{x^2-y^2} \rightarrow d_{z^2}$), ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow 2\text{E}_g$ ($d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$) transitions, respectively, which suggests a distorted octahedral geometry for Cu(II) complexes [28].

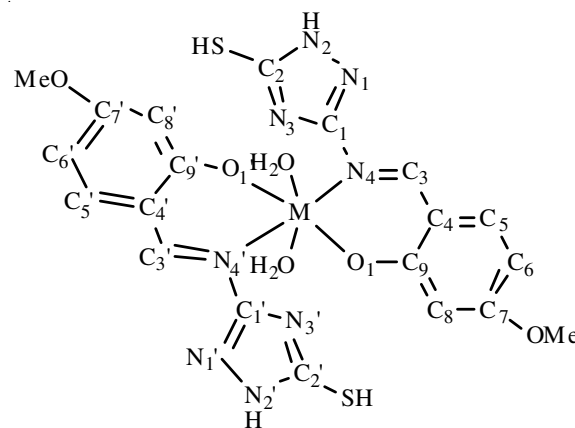
Thermogravimetric study: Thermal behaviour of the complexes (**1–4**) has been studied using thermogravimetric analysis from room temperature to $800\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in nitrogen atmosphere. Complex **1** [$\text{Co}(\text{L}_1)_2(\text{H}_2\text{O})_2$] shows three step decomposition within temperature range of $140\text{--}720\text{ }^\circ\text{C}$. In the first decomposition step, two water molecules are lost (found 6.10% , calcd. 6.07%). A mass loss of 39.12% (calcd. 39.28%) was observed at second stage of decomposition, which corresponds to loss of $\text{C}_{10}\text{H}_9\text{N}_4\text{OS}$. Finally mass loss of 42.18% (calcd. 42.02%) was observed due to the loss of triazole moiety in the third stage of decomposition. As a final product, it leaves CoO as residue (found 12.60% , calcd. 12.63%). Similar pattern was observed in the TGA curve of metal complexes **2–3**. However, complex **4** which is Zn(II) complex show a two step decomposition. The TGA data for the metal complexes **1–4** are given in Table-4.

EPR spectra: The solid state X-band EPR spectra of polycrystalline solid of Cu(II) complexes were recorded in powder form at room temperature. The ESR spectra of Cu(II) complex **3** at room temperature displayed two g values *i.e.* $g_{\parallel} = 2.190$ and $g_{\perp} = 2.053$, while for complex **6** the g values are $g_{\parallel} = 2.193$ and $g_{\perp} = 2.057$. From the observed values, it is clear that $g_{\parallel} > g_{\perp} > 2.0023$ and these parameters suggest that unpaired electron lying predominantly in the $d_{x^2-y^2}$ orbital giving ${}^2\text{B}_{1g}$ as the ground state and are a characteristic of axial symmetry. The above pattern suggests a tetragonal geometry for the Cu(II) complexes [29]. The value of exchange interaction term $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$ gives idea about exchange interactions between Cu(II) centers. The value of $G < 4.0$ (calculated 3.58 for complex **3** and 3.38 for complex **6**) indicates considerable exchange interactions of Cu–Cu in the solid complexes [30].

TABLE-4
THERMAL ANALYSIS DATA OF METAL COMPLEXES (**1–4**)

Compd. No.	Compounds	Stages	Temp. ($^\circ\text{C}$)	Possible evolved species	Residual species	Mass loss (%)	
						Found	Calcd.
1	[$\text{Co}(\text{L}_1)_2(\text{H}_2\text{O})_2$]	1 st	140–190	$2\text{H}_2\text{O}$	CoO	6.10	6.07
		2 nd	190–460	$\text{C}_{10}\text{H}_9\text{N}_4\text{OS}$		39.12	39.28
		3 rd	460–720	Remaining moiety		42.18	42.02
						12.60	12.63
2	[$\text{Ni}(\text{L}_1)_2(\text{H}_2\text{O})_2$]	1 st	140–180	$2\text{H}_2\text{O}$	NiO	6.0	6.08
		2 nd	180–475	$\text{C}_{10}\text{H}_9\text{N}_4\text{O}_2\text{S}$		42.12	42.05
		3 rd	475–790	Triazole moiety		39.35	39.39
						12.53	12.48
3	[$\text{Cu}(\text{L}_1)_2(\text{H}_2\text{O})_2$]	1 st	130–195	$2\text{H}_2\text{O}$	CuO	5.98	6.02
		2 nd	195–470	$\text{C}_{10}\text{H}_9\text{N}_3\text{O}_2\text{S}_2$		44.75	44.72
		3 rd	470–780	Triazole moiety		36.08	36.05
						13.19	13.21
4	[$\text{Zn}(\text{L}_2)_2$]	1 st	110–495	$\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_3\text{S}_2$	ZnO	54.65	54.98
		2 nd	495–720	Remaining moiety		31.15	30.80
						14.20	14.22

DFT calculations: The gas phase geometry optimization of the ligand **HL₁** and the metal complexes (**1-4**) was performed. Numbering (Fig. 4) and the optimized structures for the metal complexes along with the ligand are displayed in Fig. 5. Initially, the optimized geometry of ligand **HL₁** shows planarity of the molecule. After metal complexation, the triazole moiety lost planarity and turns out of plane of the paper. The structures are stable with respect to energy. In complex **1**, which is Co(II) complex of ligand **HL₁**, the metal is coordinated in an octahedral environment and binds on one position through nitrogen of azomethine group and on other through oxygen of deprotonated hydroxyl group, the remaining two positions are occupied by water molecules. The computed bond angle and bond lengths values are in agreement with the reported M–O and M–N bond values. The angles around the coordination sphere are in well agreement with the experimental results.



M = Co(II), Ni(II), Cu(II) and Zn(II)

Fig. 4. Numbering Scheme of ligand and metal complexes

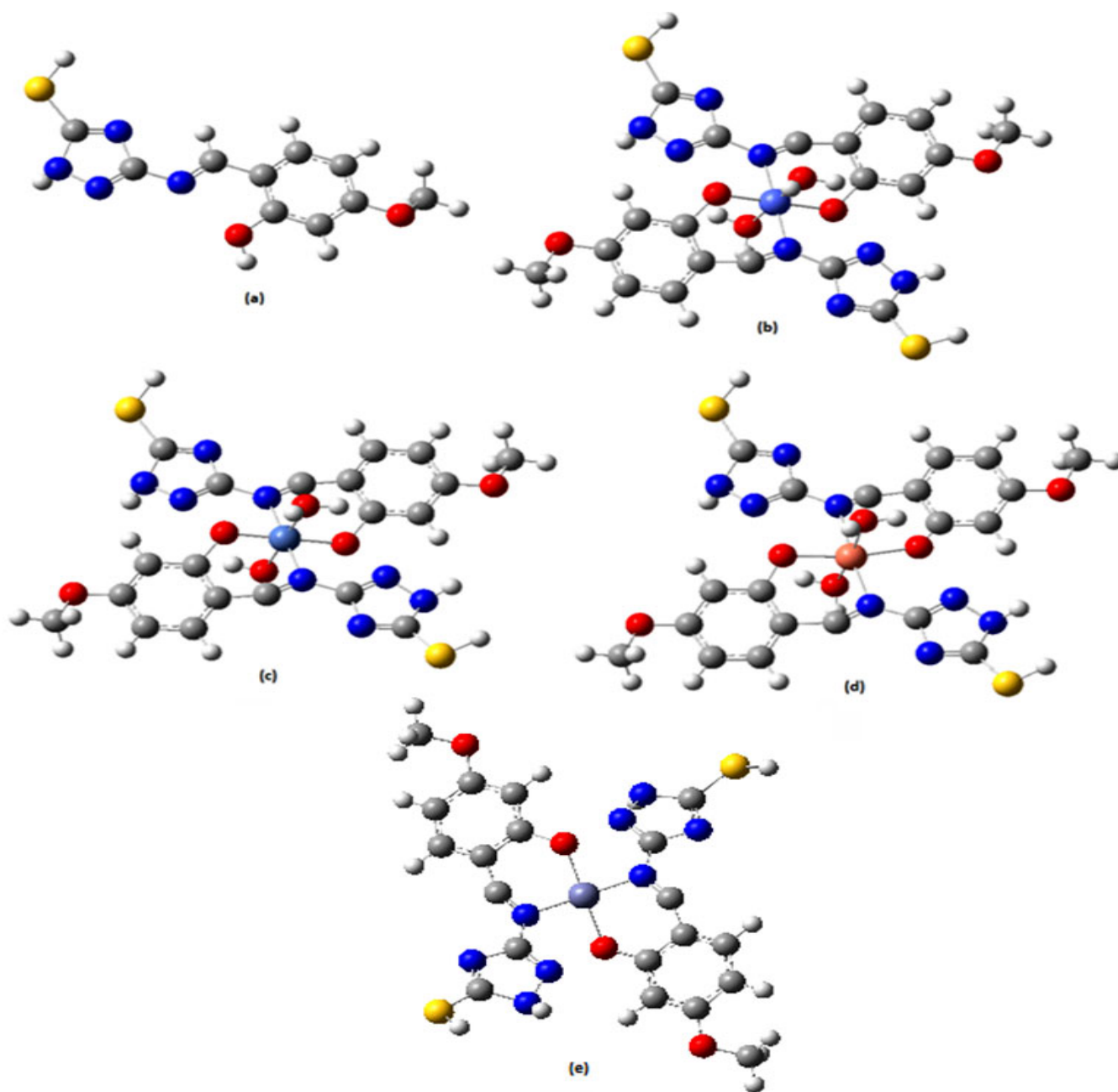


Fig. 5. Optimized structure of ligand **HL₁** (a), Complex **1** (b), Complex **2** (c), Complex **3** (d) and Complex **4** (e)

Similar bonding pattern and parameters values was found in case of Ni(II) complex. Copper(II) complex shows tetragonal geometry which shows a little variation in their bond length and bond angle values due to Jahn-Teller distortions. The bond lengths are slightly elongated and bond angles vary slightly from the experimental values. Zinc(II) complex stabilized in tetrahedral geometry. On the basis of analytical, spectroscopic and theoretical calculation results, following structure has been proposed for metal complexes (Fig. 6).

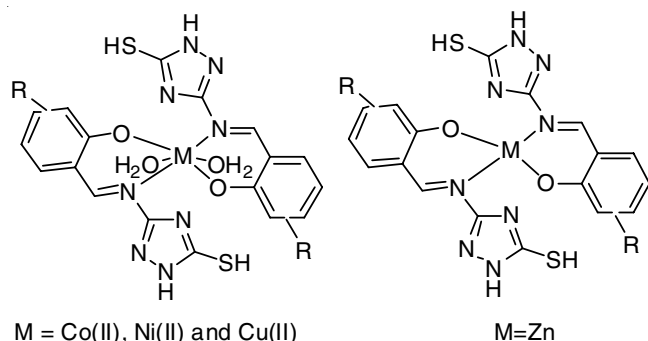


Fig. 6. Proposed structure of metal complexes

Antibacterial activity: *in vitro* Antibacterial activity against *Bacillus macerans* (Gram-positive) and *Pseudomonas striata* (Gram-negative) were evaluated for all synthesized compounds. Streptomycin is the standard drug used for comparison of antibacterial activity of the complexes. The antibacterial screening data (Table-5) showed that the zone of inhibition is larger for ligand HL₂ in between the ligands. Metal complex 5 was most active against Gram-positive bacteria while the metal complex 8 was most active against Gram-negative bacteria. In general, an enhancement in the antibacterial activity of the ligand was observed on complexation. This increase in the activity on complexation as compare to free ligand is explained on the basis of chelation theory [31]. Interestingly, the presence of 2D and 3D rings in the ligand also altered the activity of the compound [32]. The variation can be explained as different compounds have different impermeability in the cells of microbes and the other factor which contributes in the degree of inhibition is the

concentration of tested compound, as activity is directly proportional to concentration of tested compounds.

Antifungal activity: All the synthesized compounds were screened against fungi, *Rhizoctonia batatiola*, *Alternaria alternata* and *Fusarium odum*. Chlorothalonil is used as standard drug. The antifungal screening data is shown in Table-5. In between the ligands, ligand HL₁ was more active while among the metal complexes, complex 2 was most active for *Rhizoctonia batatiola*, complex 1 was most active for *Alternaria alternata* and complex 6 was most active for *Fusarium odum*. From the antifungal data, it may be conclude that all the compounds were moderate to significant active against the tested fungi and the metal complexes were found to be more active as compare to free ligand.

Conclusion

Two novel Schiff bases HL₁ and HL₂ and their Co(II), Ni(II), Cu(II) and Zn(II) metal complexes were synthesized. All the compounds were fully characterized by using various characterization and analytical techniques. The results obtained from these techniques concludes that ligands are uninegative in nature and coordinates in bidentate manner through nitrogen of azomethine group and oxygen of deprotonated hydroxyl group. An octahedral geometry was assigned for Co(II), Ni(II) and Cu(II) complexes while a tetrahedral one was assigned for Zn(II) complexes. The metal complexes exhibited significant antimicrobial activity and the metal complexes are found to be more active as compare to free ligands against the tested antibacterial and antifungal strains.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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TABLE-5
BIOLOGICAL DATA OF LIGANDS AND THEIR METAL COMPLEXES

Compounds	Diameter of inhibition zone (mm) (conc. in µg/mL)														
	Antibacterial						Antifungal								
	<i>Bacillus macerans</i>			<i>Pseudomonas striata</i>			<i>Rhizoctonia bataticola</i>			<i>Alternaria alternate</i>			<i>Fusarium odum</i>		
	250	125	63.5	250	125	63.5	250	125	63.5	250	125	63.5	250	125	63.5
HL ₁	16	10	—	11	—	—	53.7	30.0	16.2	50.1	28.8	13.3	51.1	26.0	11.5
[Co(L ₁) ₂ (H ₂ O) ₂]	29	21	10	17	12	6	72.8	38.4	23.1	79.1	32.0	16.2	56.1	28.4	—
[Ni(L ₁) ₂ (H ₂ O) ₂]	26	17	8	16	10	—	76.0	42.0	19.3	65.8	41.8	20.3	54.0	36.4	19.1
[Cu(L ₁) ₂ (H ₂ O) ₂]	28	18	9	12	11	7	68.1	46.8	32.1	72.6	43.4	15.9	52.3	48.9	22.4
Zn(L ₁) ₂	24	13	8	15	9	—	71.3	47.3	26.7	66.1	37.1	17.1	51.8	46.3	20.1
HL ₂	19	11	7	13	7	—	50.0	28.6	15.5	48.4	23.6	11.3	47.5	28.4	12.3
[Co(L ₂) ₂ (H ₂ O) ₂]	31	20	12	23	13	8	74.0	41.0	29.3	73.8	38.2	15.2	62.3	32.3	25.1
[Ni(L ₂) ₂ (H ₂ O) ₂]	27	16	9	20	12	6	72.7	44.3	22.7	66.5	32.4	11.6	64.0	42.1	27.5
[Cu(L ₂) ₂ (H ₂ O) ₂]	24	13	8	21	12	—	69.2	39.9	26.6	71.0	40.0	19.0	57.0	38.5	24.8
Zn(L ₂) ₂	28	12	10	24	10	7	71.1	40.0	25.4	68.2	33.1	23.2	58.1	39.6	22.3
Streptomycin (standard)	34	26	13	28	18	11	—	—	—	—	—	—	—	—	—
Chlorothalonil (standard)	—	—	—	—	—	—	90.0	78.0	48.0	98.0	80.2	46.3	89.0	74.1	46.5

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