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Some transition metal complexes of Nitrogen, Sulphur donor ligand derived from substituted 1,2,4-triazole and 2-Chloro-5-nitrobenzaldehyde: Synthesis, spectral characterization, thermal and antimicrobial studies

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Abstract:

A triazole-based ligand (HL) and its Nickel(II) and Zinc(II) complexes were prepared and characterized through various spectroscopic methods (UV-vis, IR, ^{1}H-NMR, fluorescence), elemental analysis, thermal analysis, and magnetic measurements. The ligand, 4-(2-Chloro-5-nitrobenzylideneamino)-5-mercapto-3-n-propyl-1,2,4-triazole, was synthesized by refluxing 4-Amino-5-mercapto-3-n-propyl-1,2,4-triazole with 2-Chloro-5-nitrobenzaldehyde. Both the Nickel(II) and Zinc(II) complexes showed octahedral geometries around the metal centres. IR and thermogravimetric analysis confirmed the presence of coordinated water molecules in the 1:1 metal complexes. The ligand and complexes were tested against four bacteria (*Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*) to evaluate antibacterial activity, and against two yeasts (*Candida albicans*, *Saccharomyces cerevisiae*) for antifungal testing. The in vitro antimicrobial tests showed that the metal complexes were found more effective than the free ligand.

Keywords: 4-(2-Chloro-5-nitrobenzylideneamino)-5-mercapto-3-n-propyl-1,2,4-triazole, 4-Amino-5-mercapto-3-n-propyl-1,2,4-triazoles, 2-Chloro-5-nitrobenzaldehyde, metal complexes, spectral studies, antimicrobial activities

1. Introduction

Schiff bases and their metal complexes have attracted considerable attention in coordination chemistry owing to their structural diversity and wide spectrum of biological activities (Anacona & Estacio, 2006; Prakash & Adhikari, 2011; Raman et al., 2007). Triazole-based derivatives occupy a prominent position in medicinal chemistry, as the triazole nucleus is frequently encountered as a core structural motif in biologically active compounds including antifungal, antibacterial, and anti-inflammatory molecules (Hameed et al., 2017; Rollas & Küçükgüzel, 2007; Supuran et al., 1997). The condensation of primary amines with carbonyl compounds yields Schiff bases characterized by the azomethine (–C=N–) linkage, which plays a pivotal role in binding transition metal ions through nitrogen, sulfur, and oxygen donor atoms (Dhar & Taploo, 1982; Özdemir et al., 2011). The presence of thiol (–SH) groups in mercaptotriazole derivatives significantly enhances the chelating ability of the ligand, and the sulfur donor atom exhibits strong affinity for transition metals, making such complexes pharmacologically relevant (Güneş & Gündüz, 2005; Uçan et al., 2006).

Transition metal complexes derived from amino-mercaptotriazoles have been extensively investigated, and the incorporation of electron-withdrawing groups such as nitro and chloro substituents on the aromatic aldehyde component profoundly influences both the coordination behavior and biological activity of the resulting complexes (Sharma et al., 2011; Hossain et al., 1996; Kalanithi et al., 2012). Nickel(II) commonly adopts square planar, tetrahedral, or octahedral geometries and demonstrates notable antimicrobial and antitumor properties (More et al., 2019; Ramesh et al., 2020), while Zinc(II), a biologically essential d^{10} metal ion involved in enzymatic catalysis and gene regulation, forms diamagnetic and often photoluminescent complexes due to its closed-shell electronic configuration (Saha et al., 2022; Yam & Lo, 1999).

The global surge in antimicrobial resistance has created an urgent need for novel therapeutic agents against resistant bacterial and fungal strains (Chohan et al., 2006; Pahontu et al., 2015). Metal complexes have proven to be potent antimicrobial agents, often exhibiting enhanced activity relative to their free ligands due to the chelation effect, whereby coordination to a metal center increases lipophilicity and facilitates greater penetration through microbial cell membranes (Chohan et al., 2006; Pahontu et al., 2015; Gaber et al., 2015). Spectroscopic methods, including UV-Vis, IR, and ^{1}H-NMR spectroscopy, combined with elemental analysis, thermal analysis, and fluorescence measurements, provide a comprehensive toolkit for structural characterization of such complexes (Özdemir et al., 2011; Kalanithi et al., 2012; Saha et al., 2022).

In continuation of ongoing research into triazole-based Schiff base metal complexes (Sharma et al., 2011; Hossain et al., 1996), the present work reports the synthesis and characterization of a novel Schiff base ligand, 4-(2-Chloro-5-nitrobenzylideneamino)-5-mercapto-3-n-propyl-1,2,4-triazole (HL), prepared by condensation of 4-amino-5-mercapto-3-n-propyl-1,2,4-triazole with 2-chloro-5-nitrobenzaldehyde, along with its Nickel(II) and Zinc(II) complexes. The antimicrobial efficacy of the synthesized compounds was evaluated against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Candida albicans*, and *Saccharomyces cerevisiae*

2. Experimental

2.1 Instrumentation and Analysis

Far IR (700-200 cm^{-1}) spectra of metal complexes were recorded on Perkin Elmer-Spectrometer. IR spectra of pure ligand and its metal complexes were carried in the range of 4000-700 cm^{-1} on MB-3000 ABB spectrometer. The elemental analysis (C, H and N) was carried out from Central Instrumentation Laboratory (CIL), Panjab University, Chandigarh. The electronic absorption spectra of solid Ni(II) complexes dissolved in DMF were recorded on a T90 UV/VIS Spectrophotometer in the range 1100-200 nm. Perkin-Elmer instrument (Pyris Diamod) was used for thermogravimetric analysis of metal complexes in the temperature range of 50-500˚C in the atmospheric air at a heating rate of 10˚C min-1 using an alumina powder as a reference. ^{1}H-NMR spectra of the ligand and its Zn (II) metal complexes were recorded in $CDCl_3$/DMSO-d_6 on a Bruker spectrometer (300 MHz).

Magnetic moment measurements were performed on a Vibrating Sample Magnetometer (Model-155) at Institute Instrumentation Centre, IIT Roorkee.

1.2 Synthesis

The chemicals for the synthesis of the ligand and its metal complexes were of analytical grade and used as such without any further purification. 4-Amino-5-mercapto-3-n-propyl-1,2,4-triazole was synthesized by the reported literature methods (Bala et al., 1978).

2.2.1 4-(2-Chloro-5-nitrobenzylideneamino)-5-mercapto-3-n-propyl-1,2,4-triazole (HL)

An ethanolic solution (20 mL) of 4-amino-5-mercapto-propyl-1,2,4-triazole (1.50 g, 9.49 mmol) was mixed with the hot ethanolic solution (20mL) of 2-Chloro-5-nitrobenzaldehyde (1.76 g, 9.49 mmol). The reaction mixture was refluxed for 4 h and then left to cool overnight at room temperature. The coloured product was filtered, washed with cold ethanol, dried, and recrystallized in ethanol.

Colour: Yellow; Yield: 82.2%; m.p.233°C
Anal. Calc. for $C_{12}H_{12}ClN_5O_2S$: C 44.24, H 3.71, N 21.50%
Found: C 44.28, H 3.72, N 21.56%

2.2.2 Synthesis of 1:1 metal complexes of HL

Nickel(II) (0.27 g, 1.07 mmol) and Zinc(II) (0.23 g, 1.07 mmol) acetates were dissolved in ethanol, and their (20 mL) solutions were mixed with hot ethanolic solutions (20 mL) of the ligand (0.35 g, 1.07 mmol) in a 1:1 molar ratio, which resulted in the formation of coloured precipitation of metal complexes. The solid products were kept overnight to cool down at room temperature, filtered, washed with warm water, ethanol, and finally with acetone, and dried on water bath.

Ni(L)OAc.3H_2O: Anal. Calc. for $C_{14}H_{20}ClN_5NiO_7S$: C 33.86, H 4.06, N 14.10, Ni 11.82% Found: C 33.90, H 4.11, N 14.13, Ni 11.90%
Zn(L)OAc.3H_2O: Anal. Calc. for $C_{14}H_{20}ClN_5O_7SZn$: C 33.41, H 4.01, N 13.92, Zn 12.99% Found: C 33.47, H 4.08, N 13.97, Zn 12.95%

2.2.3 Synthesis of 1:2 metal complexes of HL

Hot ethanolic solutions Nickel(II) (0.27 g, 1.07 mmol) and Zinc(II) (0.23 g, 1.07 mmol) acetates were treated with hot ethanolic solutions (25 mL) of the ligand (0.70 g, 2.14 mmol). Coloured metal complexes were formed immediately and were kept overnight at room temperature. The solid products were filtered off with warm water, ethanol, acetone and dried on water bath.

Ni(L)$_2$.2H_2O: Anal. Calc. for $C_{24}H_{26}Cl_2N_{10}NiO_6S_2$: C 38.73, H 3.52, N 18.82, Ni 7.89% Found: C 38.77, H 3.50, N 18.88, Ni 7.92%
Zn(L)$_2$.2H_2O: Anal. Calc. for $C_{24}H_{26}Cl_2N_{10}O_6S_2Zn$: C 38.39, H 3.49, N 18.65, Zn 8.71% Found: C 38.42, H 3.44, N 18.70, Zn 8.80%

2.3 *In Vitro* Antimicrobial Assay

All the microbial cultures were procured from Microbial Type Culture Collection (MTCC), IMTECH, Chandigarh. Bacteria were sub-cultured on nutrient agar medium and yeasts were on malt yeast agar medium. The ligand and its metal complexes were evaluated for their antimicrobial activity against screened *in vitro* against Gram-positive bacteria, *Staphylococcus aureus* (MTCC-96), *Bacillus subtilis* (MTCC-121), Gram-negative bacteria *Pseudomonas aeruginosa* (MTCC-741), *Escherichia coli* (MTCC-1652) and yeasts, *Candida albicans (*MTCC-227), *Saccharomyces cerevisiae* (MTCC-170).

2.3.1 Antibacterial activity (in Vitro)

Antimicrobial activity of the synthesized compounds were evaluated by the agar well diffusion method. All the microbial cultures were adjusted to 0.5 McFarland standards. A microbial suspension of approximately 1.5 $\times 10^8$ cfu/mL was made. 20 mL of agar medium was poured into each Petri plate and plates were swabbed with 100 µL inocula of the test microorganisms and kept for 15 minutes for adsorption. Wells of diameter 8 mm were bored in the seeded agar plates by using sterile cork borer. A 100 µL volume of each compound with a concentration of 4.0 mg/mL of each compound reconstituted in dimethylsulphoxide was loaded in these wells. All these plates were incubated at 37 °C for 24 hours. Zone of growth inhibition against the test organism was measured with a zone reader (Hi Antibiotic zone scale), and antimicrobial activity of the compounds was recorded. Dimethyl sulfoxide (DMSO) as a negative control and Amphotericin B as a positive control were used for fungal cultures. Ciprofloxacin was used as a positive control, and DMSO as a negative control for bacteria. The procedure was performed in three replicate plates for each microorganism (Aneja et al., 2011). Growth of inhibition zones of all the synthesized ligand and its metal complexes was recorded.

2.3.2 Determination of Minimum Inhibitory Concentration (MIC) of Chemical Compounds

Minimum Inhibitory Concentration (MIC) of the synthesized compounds against bacterial and yeast strains was evaluated by using the modified agar well diffusion method (Aneja et al., 2011). A twofold serial dilution of each compound was prepared by reconstituting each compound in DMSO, followed by dilution in sterile distilled water to obtain a concentration range of 400 to 0.5 µg/mL. A 100 µL volume of each dilution was introduced in the wells (in triplicate) of agar plates that were already seeded with 100 µL of standardized inoculum (10^6 cfu/mL) of the test microbial strains. The zone of inhibition was observed on all test plates incubated aerobically at 37 °C for 24 hours. MIC of each chemical compound was recorded. Amphotericin-B and Ciprofloxacin drugs were used as positive control for all strains.

3. Result and Discussion

Schiff base (HL) was soluble in most of the organic solvents, but its metal complexes were found insoluble. These complexes were found soluble in Dimethylglyoxime and Dimethylforamide. All metal complexes were found stable in air at room temperature and decomposed at higher temperature.

3.1 IR spectra

IR spectral data of the Schiff base (HL) and its metal complexes are given in Table 1. The coordination around central metal ion has been investigated by the careful comparison of IR spectra of the ligand and its metal complexes. A strong band appeared at 1605 cm^{-1} assigned to υ(-N=CH-) in the Schiff base was shifted towards higher frequency in the spectra of metal complexes (Sanhatforoush et al., 2009). This indicated the coordination through nitrogen atom of azomethine group. The band observed at 2730 cm^{-1} due to υ(S-H) in the free ligand disappeared in metal complexes, suggesting deprotonation of the thiol group and bonding through the sulphur atom (Singh et al., 2010). The bonding through nitrogen and sulphur atom was further supported by the appearance of new bands in metal complexes in the region 741-784, 488-512, 354-368 cm^{-1} ascribed to υ(C-S), υ(M-N) and υ(M-S) respectively (Singh et al., 2016). A broad band in the region 3256-3410 cm^{-1} due to υ(O-H) indicated the presence of coordinated water molecules. In 1:1 metal complexes, a strong band in the region 1733-1750 cm^{-1} suggested the presence of an acetate group (Singh et al., 2015).

3.2 ^{1}H-NMR Spectra of Schiff Base and its Zinc(II) complexes (in $CDCl_3$/DMSO-d_6)

^{1}H-NMR spectra of the ligand and its Metal complexes were recorded in $CDCl_3$/DMSO-d_6 (ppm) at room temperature. The HL exhibited signals at δ 13.50 (s, 1H, -S**H**), 10.30 (s, 1H, -N=C**H-**), 8.76 (s, 1H, Ar-**H**), 8.13 (d, 1H, Ar-**H**), 7.54 (d, 1H, Ar-**H**), 2.68 (t, 2H, Triazole-C$\mathbf{H_2}$$CH_2CH_3$), 1.60-1.73 (m, 2H, Triazole-CH_2C$\mathbf{H_2}$$CH_3$), 0.86 (t, 3H, Triazole-CH_2CH_2C$\mathbf{H_3}$) (Fig. 1).

Zn(L)OAc.3H$_2$O exhibited signals at δ 10.65 (s, 1H, -N=C**H-**), 8.80 (s, 1H, Ar-**H**), 8.17 (d, 1H, Ar-**H**), 7.58 (d, 1H, Ar-**H**), 2.66 (t, 2H, Triazole-C$\mathbf{H_2}$$CH_2CH_3$), 1.65-1.74 (m, 2H, Triazole-CH_2C$\mathbf{H_2}$$CH_3$), 0.89 (t, 3H, Triazole-CH_2CH_2C$\mathbf{H_3}$), 2.81 (s, 3H, -OCOC**H**$_3$).

Zn(L)$_2$.2H$_2$O exhibited signals at δ 10.68 (s, 1H, -N=C**H**), 8.84 (s, 1H, Ar-**H**), 8.18 (d, 1H, Ar-**H**), 7.55 (d, 1H, Ar-**H**), 2.62 (t, 2H, Triazole-C$\mathbf{H_2}$$CH_2CH_3$), 1.58-1.72 (m, 2H, Triazole-CH_2C$\mathbf{H_2}$$CH_3$), 0.89 (t, 3H, Triazole-CH_2CH_2C$\mathbf{H_3}$).

The Schiff base showed a signal at δ 13.50 assigned to –SH, which disappeared in the metal complexes, indicating deprotonation of the thiol group and bonding through the sulphur atom (Singh et al., 2014). A singlet at δ 10.30, due to the (-N=CH-) proton in the free ligand, shifted downfield, revealing coordination of the azomethine group to the metal ion (Bala et al., 2022). The signals due to aromatic and triazole protons remained almost unchanged in the spectra of the metal complexes, indicating that these moieties were not involved in bonding (Singh et al., 2012).

3.3 Magnetic Moment Measurement and Electronic Spectra

The arrangement of ligands around the metal ion has been elucidated by electronic spectra. Electronic spectral studies were carried out in DMF solution at room temperature. The electronic absorption bands and ligand field parameters are listed in Table 2. The magnetic moments of Ni(II) complexes were measured at room temperature, and the magnetic moment data are given in Table 2.

Nickel(II) complexes

In the electronic spectra of metal complexes three absorption bands in the region 11173-11236, 17361-17483 and 23641-23866 cm^{-1} were observed assignable to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (υ_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (υ_2) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (υ_3). These three transitions reflected octahedral geometry around the Ni(II) ion (Skorokhod et al., 2007). The various ligand field parameters (Dq, B, β and β%) were calculated for Ni(II) complexes by using Band-fitting equation (Oelkrug et al., 1971). The values of these parameters were: Dq = 1117.3-1123.6 cm^{-1}, B = 501-507 cm^{-1}, Dq/B = 2.204-2.243, β = 0.481-0.487 and β% = 51.3-51.9. The crystal field splitting energy (Dq) values indicated octahedral geometry for Ni(II) complexes (Lever, 1998). The ratio υ_2/υ_1 = 1.445-1.565 was well fitted for the octahedral environment around Ni(II) ion (Mishra et al., 2009). The interelectronic repulsion parameter (B) was found lesser than free ion value i.e. 1041 cm^{-1} indicating the partial overlapping of orbitals (Mishra et al., 2009). The Dq/B ratio confirmed transitions from the ground state A_{2g} (Dharmaraja et al., 2014). The nephelauxetic ratio (β) and β% suggested the partial covalent character of metal-ligand bond (Anita et al., 2013). The effective magnetic moments of 1:1 and 1:2 Ni(II) complexes were 3.59 and 3.55 B.M., respectively, suggesting two unpaired electrons (Sumrra et al., 2014). The magnetic moment values indicated high spin octahedral geometry for Ni(II) complexes (Raman et al., 2008).

3.4 Thermal Analysis

The thermal decomposition temperatures, percentage mass losses, and decomposition products of $Zn(L)OAc.3H_2O$ and $Zn(L)_2.2H_2O$ are shown in Table 3. TG analyses of $Zn(L)OAc.3H_2O$ indicated three steps of decomposition. The first step corresponds to the loss of three water molecules, with a mass loss of 10.1% (calc. 10.7%) in the temperature range of 140-260°C. The second step involves the loss of acetate and the organic moiety, with a mass loss of 44.3% (calc. 45.4%) in the temperature range 260-480°C. In the third step, the loss of the triazole moiety with a mass loss of 26.9% (calc. 28.0) occurred in the temperature range 480-700°C (Fig. 2). The residual weight was found to be 17.1% (calc. 16.2%), corresponding to zinc oxide (Singh et al., 2012).

$Zn(L)_2.2H_2O$ decomposed mainly in three steps; loss of two water molecules was observed in the first step, with a mass loss of 4.7% (calc. 4.8%) between 150 and 230°C; the second step corresponded to the loss of the organic moiety, with a mass loss of 45.3% (calc. 45.1%) in the temperature range of 230-320°C; the third step was attributed to the loss of the triazole moiety, with a mass loss of 37.2% (calc. 37.6%) within the temperature range of 320-500°C (Fig. 2). Zinc oxide was formed at 500°C with a mass of 10.6% (calc. 10.8%).

3.5 Fluorescence Spectra

Fluorescence spectral studies of HL and its metal complexes were conducted in DMF (10-3M) at room temperature. The ligand showed a weak emission band at 530 nm under excitation at 265 nm. The 1:1 Ni(II) and Zn(II) complexes exhibited strong emission maxima at 499 and 497 nm, respectively (Fig. 3) (Singh et al., 2017). For the 1:2 Ni(II) and Zn(II) complexes, the fluorescence emission bands were observed at 519 and 501 nm, respectively (Fig. 3) (Gulcan et al., 2014). The metal complexes exhibited higher fluorescence intensity than the Schiff base due to chelate ring formation and the suppression of PET processes. This effect was more pronounced in Zn(II) complexes because of their fully filled d-orbitals (Azam et al., 2012).

3.7 Antimicrobial Discussion

The ligand, HL and its metal complexes were screened against *Bacillus subtilis*, *Staphylococcus aureus* (Gram-positive bacteria), *Escherichia coli*, *Pseudomonas aeruginosa* (Gram-negative bacteria) and *Saccharomyces cerevisiae*, *Candida albicans* (Yeasts). The growth of inhibition and MIC values against *B. subtilis*, *S. aureus*, *E. coli* and *P. aeruginosa* are given in Table 4 and Table 5. The antifungal results of the compounds are summarized in Table 6 and Table 7.

The Schiff base (HL) showed inhibition zone of 6.0 and 19.0 mm against *B. subtilis*, *S. aureus* and 12.0 and 20.0 mm against *E. coli* and *P. aeruginosa* respectively. The Ni(L)OAc.3H_2O and Zn(L)OAc.3H_2O possessed the highest zone of inhibition i.e. 35.0 mm against *B. subtilis* (Table 6). The $Ni(L)_2$.2H_2O exhibited inhibition zone of 32.0 mm against *B. subtilis*. The Ni(L)OAc.3H_2O, $Ni(L)_2$.2H_2O and Zn(L)OAc.3H_2O showed higher zone of inhibition (27.0-29.0 mm) than the standard drug, Ciprofloxacin against *S. aureus*. The Zn(L)OAc.3H_2O and $Zn(L)_2$.2H_2O showed inhibition zone of 26.0 and 23.0 mm respectively against *E. coli*. The $Ni(L)_2$.2H_2O was also found to exhibit good activity against *E. coli*. All newly synthesized compounds were found highly active against *P. aeruginosa* and possessed inhibition zone in the range 22.0-28.0 mm against *P. aeruginosa* (Fig. 4). The Zn(L)OAc.3H_2O exhibited the highest zone of inhibition of 28.0 mm against *P. aeruginosa*. The Ni(L)OAc.3H_2O and $Zn(L)_2$.2H_2O showed inhibition zone of 25.0 mm against *P. aeruginosa*. The zone of inhibition of 24.0 mm has been observed for $Ni(L)_2$.2H_2O against *P. aeruginosa*.

The lowest MIC 6.25 µg/mL has been recorded for Ni(L)OAc.3H_2O, $Ni(L)_2$.2H_2O, and Zn(L)OAc.3H_2O against *B. subtilis*. The $Ni(L)_2$.2H_2O showed the lowest MIC (6.25 µg/mL) against *S. aureus* (Table 5). The Ni(L)OAc.3H_2O, Zn(L)OAc.3H_2O and $Zn(L)_2$.2H_2O possessed MIC 12.50 µg/mL against *S. aureus*. The lowest MIC 12.50 µg/mL was observed for Zn(L)OAc.3H_2O against *E. coli*. The Ni(L)OAc.3H_2O, Zn(L)OAc.3H_2O and $Zn(L)_2$.2H_2O exhibited MIC 12.50 µg/mL against *P. aeruginosa*.

All the newly synthesized compounds of this series exhibited zone of inhibition higher than the standard drug, Amphotericin-B against tested yeasts. The highest inhibition zone of 32.0 and 33.0 mm was recorded for $Ni(L)_2$.2H_2O and Zn(L).OAc.3H_2O respectively against *S. cerevisiae* (Table 6). The highest inhibition zone (16.0 mm) was observed for Zn(L).OAc.3H_2O against *C. albicans*. The $Ni(L)_2$.2H_2O and $Zn(L)_2$.2H_2O possessed inhibition zone of 15.0 mm against *C. albicans*.

The lowest MIC of 6.25 µg/mL was shown by $Ni(L)_2$.2H_2O against *S. cerevisiae* (Table 7).

It has been found that metal complexes were more biological active compared to the free ligand. The higher antibacterial and antifungal activities of the newly synthesized compounds can be explained on the basis of Overtone's concepts and Tweedy's chelation theory (Subharaj et al., 2014). According to Tweedy chelation theory, on chelation, the polarity of metal ion is reduced due to the overlapping of ligand orbitals resulting the sharing of positive charge of metal ion. The lipophilicity of metal complex increases which leads to the easily penetration of complex into the lipid membrane. The complex binds to metal binding sites in enzymes of microorganism and blocks them. This disturbs the respiratory system and prevents the protein synthesis and thus retards the growth of microorganism.

Conclusion

The synthesized Schiff base coordinates to the metal ion through the azomethine nitrogen and sulfur atom. The coordination of the ligand to the metal ion was confirmed by IR, NMR, electronic, and magnetic moment data. The presence of acetate and water molecules in the metal complexes was indicated by thermal and IR data. The various ligand field parameters (Dq, B, β, β%) and the υ2/υ1 ratio provided significant information about the geometry and the nature of the bond character in the complexes. Various physicochemical techniques and Racah parameters suggested octahedral geometry for Ni(II) and Zn(II) complexes (Fig. 8). Thermogravimetric results of the metal complexes showed good agreement with the formulae suggested by analytical data. The fluorescence intensity of the metal complexes was found to be higher than that of the free ligand, due to the chelation-enhanced effect. Antibacterial and antifungal activities of the metal complexes were found to be higher than those of the ligands themselves.

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Table 1: IR frequencies (cm^{-1}) of Schiff base (HL) and its Metal complexes

Compounds	υ(-N=CH-)	υ(S-H)	υ(C-S)	υ(H_2O/OH)	υ(-$OCOCH_3$)	υ(M-N)	υ(M-S)
HL	1605	2730	-	-	-	-	-
Ni(L)OAc.3H_2O	1608	-	784	3358	1733	512	367
$Ni(L)_2.2H_2O$	1610	-	741	3256	-	508	368
Zn(L)OAc.3H_2O	1610	-	741	3268	1750	488	354
Zn(L).2H_2O	1620	-	772	3410	-	495	358

Table 2: Electronic spectral, ligand field parameters and magnetic data of Metal complexes

Compounds	Transitions (cm^{-1})			Dq (cm^{-1})	Ɓ (cm^{-1})	Dq/B	β	β%	υ_2/υ_1	$\mu_{eff.}$ (B.M.)
	υ_1	υ_2	υ_3							
Ni(L)OAc.3H_2O	11173	17483	23641	1117.3	507.0	2.204	0.487	51.3	1.565	3.59
$Ni(L)_2.2H_2O$	11236	17361	23866	1123.6	501.0	2.243	0.481	51.9	1.445	3.55

*Calculated values

Table 3: Thermogravimetric data of Metal complexes of the Ligand (HL)

Compounds	Mass Loss (%)		Temp. (°C)	Decomposition Products
	Calc.	Found		
Zn(L)OAc.3H_2O	10.7	10.1	140-260	Water molecules
[$C_{14}H_{20}ClN_5O_7SZn$]	45.4	44.3	260-480	Acetate, Organic moiety
	28.0	26.9	480-700	Triazole moiety
$Zn(L)_2.2H_2O$	4.8	4.7	150-230	Water molecules
[$C_{24}H_{26}Cl_2N_{10}O_6S_2Zn$]	45.1	45.3	230-320	Organic moiety
	37.6	37.2	320-500	Triazole moiety

Table 4: Zone of Microbial Growth Inhibition for Schiff base (HL) and its Metal complexes

Sr. No.	Compounds	Diameter of Inhibition Zone (mm)$^{\#}$			
		B. subtilis	*S. aureus*	*E. coli*	*P. aeruginosa*
1.	HL	06	19	12	20
2.	$Ni(L)OAc.3H_2O$	35	28	14	25
3.	$Ni(L)_2.2H_2O$	32	29	21	24
4.	$Zn(L)OAc.3H_2O$	35	27	26	28
5.	$Zn(L)_2.2H_2O$	25	17	23	25
6.	Ciprofloxacin	24	26.6	25	22

"-" indicates no activity
"#" values, including diameter of the well (8 mm) are means of triplicates

Table 5: Minimum Inhibitory Concentration (MIC) of Schiff base (HL) and its Metal Complexes

Sr. No.	Compounds	Minimum Inhibitory Concentration (µg/100mL)			
		B. subtilis	*S. aureus*	*E. Coli*	*P. aeruginosa*
1.	HL	50.00	25.00	-	12.50
2.	$Ni(L)OAc.3H_2O$	6.25	12.50	-	12.50
3.	$Ni(L)_2.2H_2O$	6.25	6.25	25.00	25.00
4.	$Zn(L)OAc.3H_2O$	6.25	12.50	12.50	12.50
5.	$Zn(L)_2.2H_2O$	12.50	12.50	25.00	12.50
6.	Ciprofloxacin	6.25	6.25	6.25	12.50

Table 6: Zone of growth Inhibition for Schiff base (HL) and its Metal complexes against *S. cerevisiae* and *C. albicans*

Sr. No.	Compounds	Diameter of Growth Inhibition Zone (mm)$^{\#}$	
		S. cerevisiae	*C. albicans*
1.	HL	15.0	5.0
2.	$Ni(L)OAc.3H_2O$	16.0	-
3.	$Ni(L)_2.2H_2O$	32.0	15.0
4.	$Zn(L)OAc.3H_2O$	33.0	16.0
5.	$Zn(L)_2.2H_2O$	27.0	15.0
6.	Amphotericin-B	19.3	16.6

Table 7: Minimum Inhibitory Concentration (MIC) of Schiff base (HL) and its Metal Complexes against *S. cerevisiae* and *C. albicans*

Sr. No.	Compounds	Minimum Inhibitory Concentration (µg/mL)	
		S. cerevisiae	*C. albicans*
1.	HL	-	-
2.	Ni(L)OAc.3H_2O	50.00	-
3.	$Ni(L)_2.2H_2O$	6.25	-
4.	Zn(L)OAc.3H_2O	6.25	50.00
5.	$Zn(L)_2.2H_2O$	12.50	-
6.	Amphotericin-B	12.50	12.50

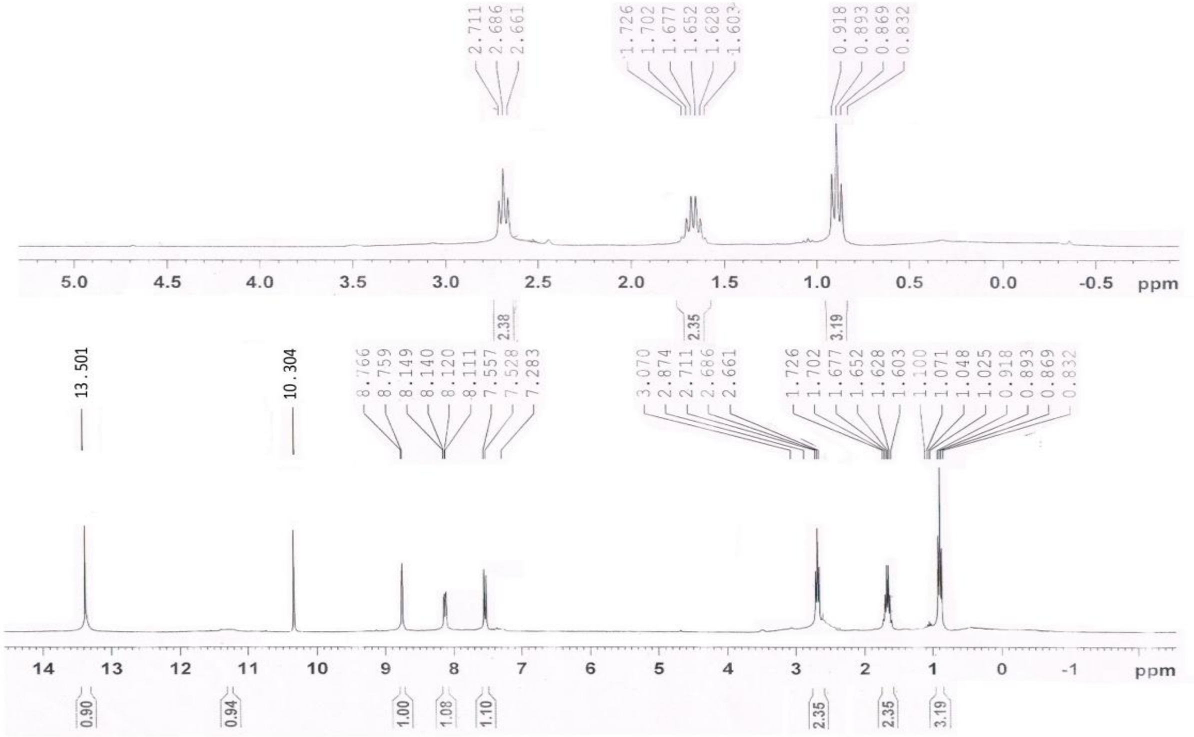


Figure 1: ^{1}H-NMR spectrum of Schiff base (HL)

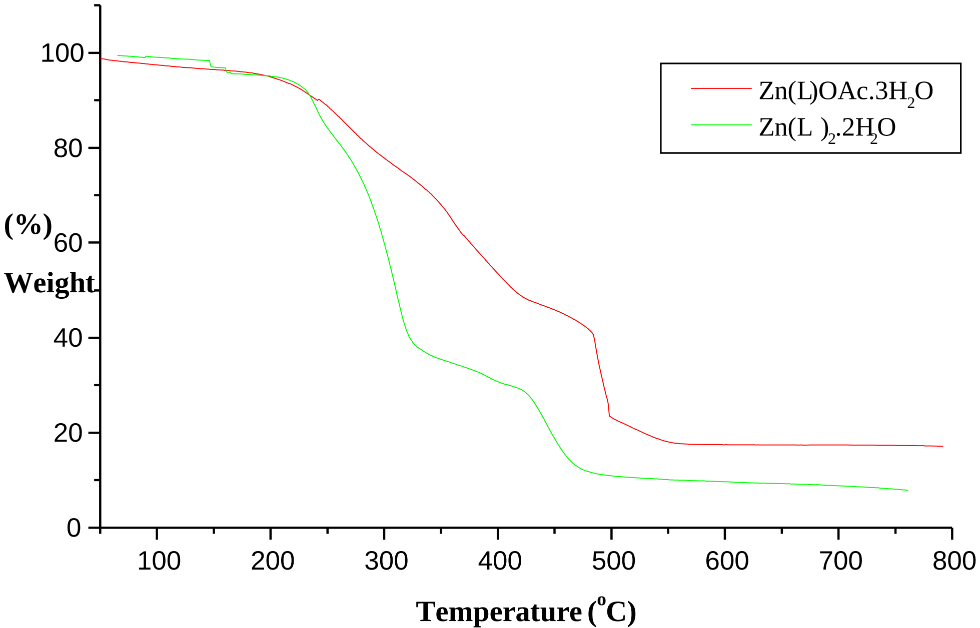


Figure 2: Thermogravimetric curves of $Zn(L)_2.OAc.3H_2O$ and $Zn(L)_2.2H_2O$

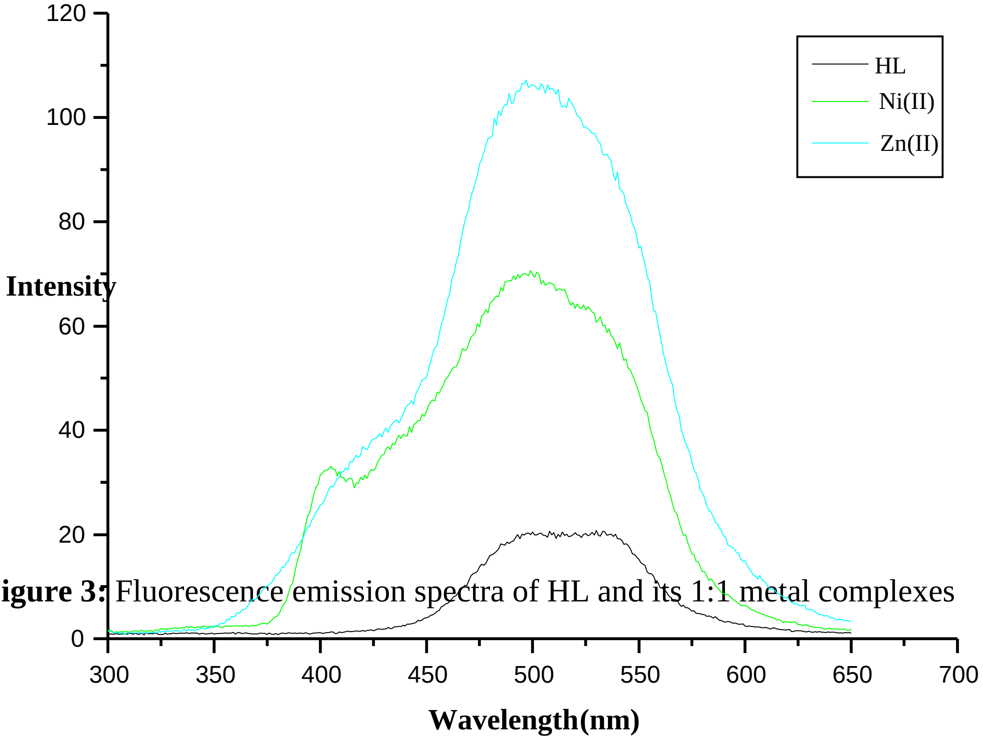


Figure 3: Fluorescence emission spectra of HL and its 1:1 metal complexes

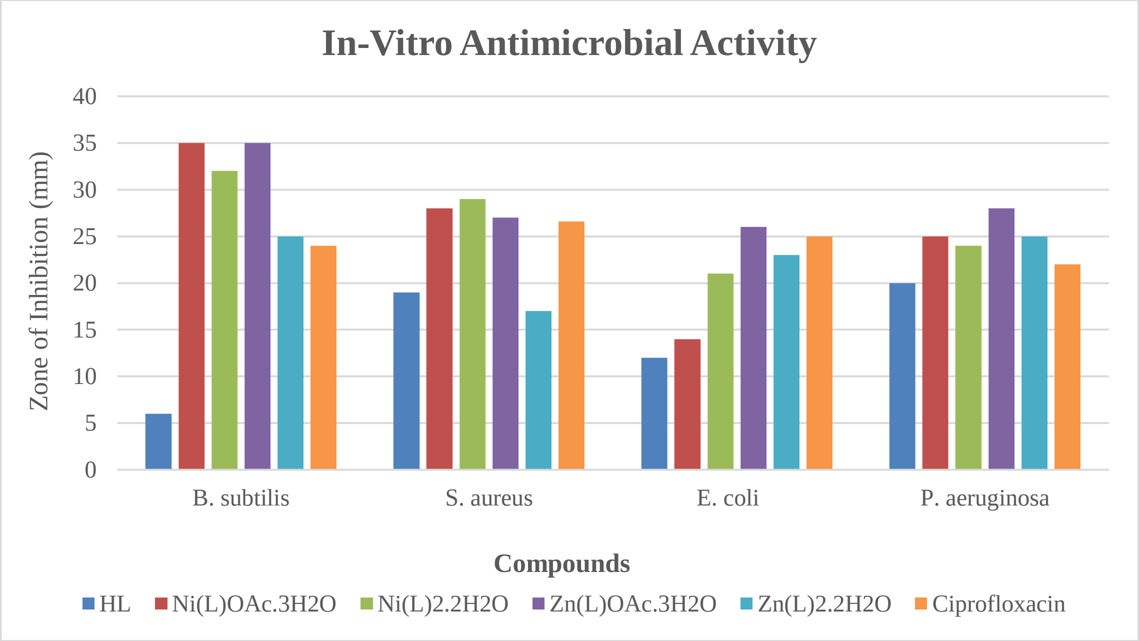


Figure 4: Zone of Inhibition for Schiff base (HL) and its Metal complexes

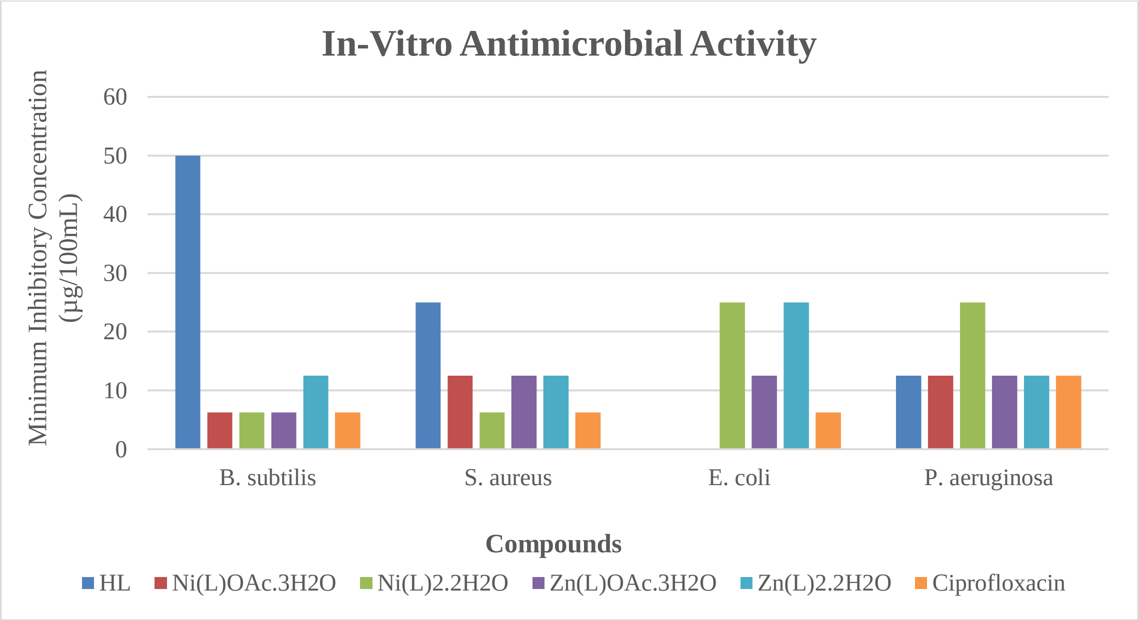


Figure 5: MIC of Schiff base (HL) and its Metal complexes

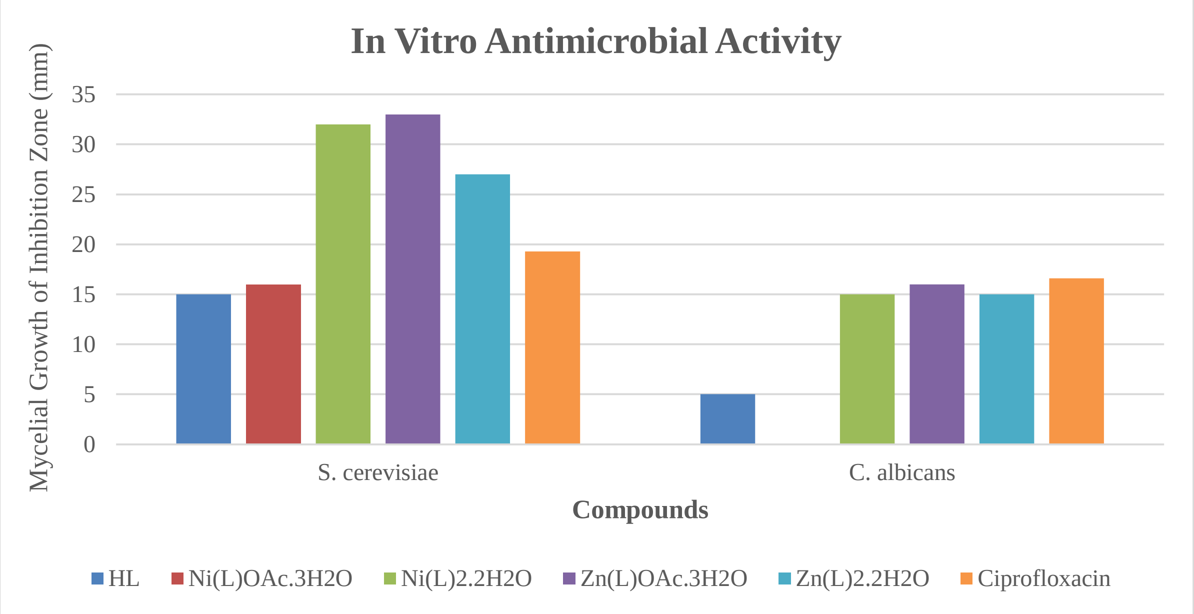


Figure 6: Antifungal activity of Schiff base (HL) and its Metal complexes

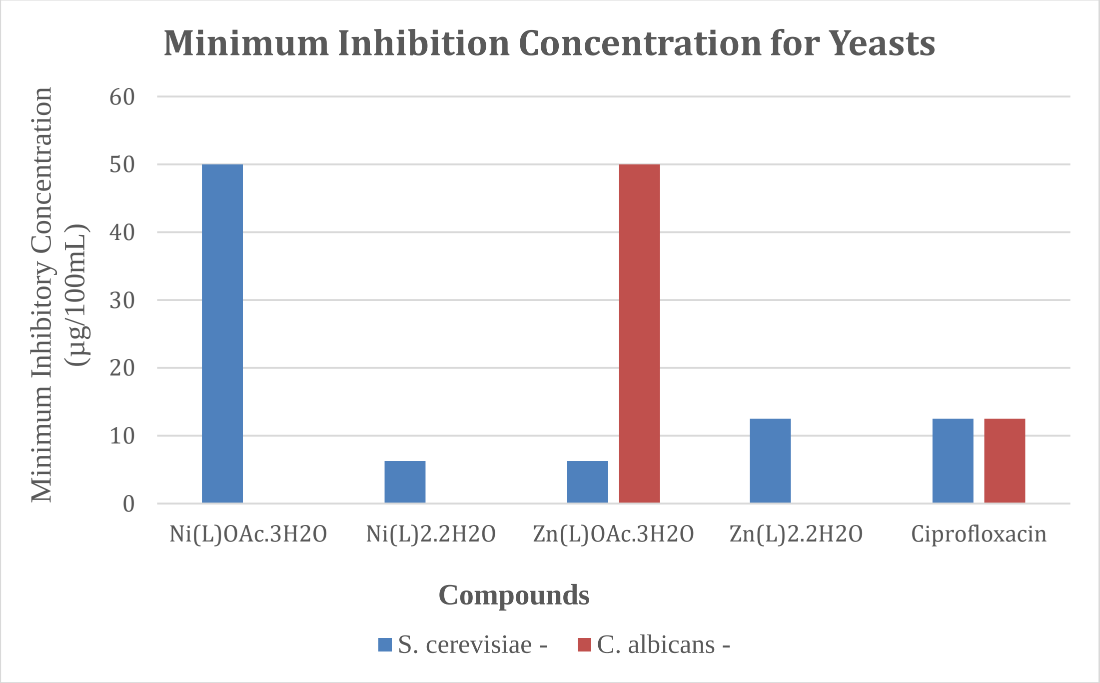
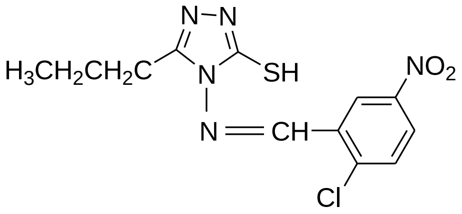
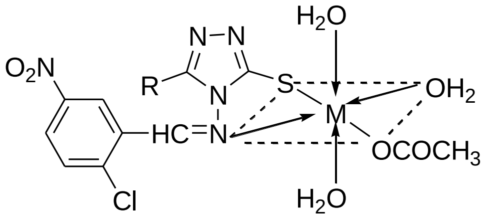


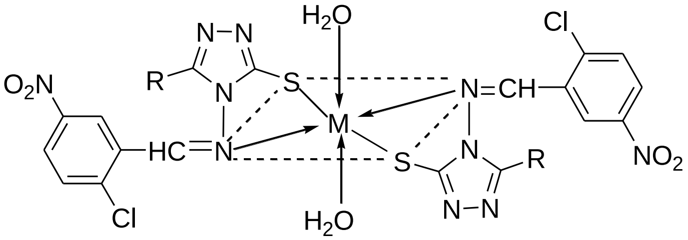
Figure 7: Minimum Inhibitory Concentration (MIC) of Schiff base (HL) and its Metal complexes



Schiff Base (HL)



1:1



1:2

R= $-CH_2CH_2CH_3$, M=Ni(II), Zn(II)

Figure 8: Proposed structures of Schiff base and its Metal complexes