STUDIES ON NOVEL CONJUGATED LIGANDS AND ITS COMPLEXES FOR SENSING APPLICATIONS

Synopsis submitted to

MADURAI KAMARAJ UNIVERSITY

for the award of the degree of

DOCTOR OF PHILOSOPHY IN CHEMISTRY

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NOVEMBER – 2019

STUDIES ON NOVEL CONJUGATED LIGANDS AND ITS COMPLEXES FOR SENSING APPLICATIONS

Cations are extremely important in fields such as biology, chemistry, medicine and environment. Metal cation roles in biological processes range from maintaining potentials across cell membranes to triggering muscle contraction, among other functions. They also have catalytic functions at the active sites of many enzymes. On the other hand, pollutant metals like lead, mercury or cadmium show the undesirable side of the coin, in environmental terms. Due to their importance in so many areas, in the field of molecular recognition the chemistry of cation complexation has played an important role. A great range of selective receptors for cationic species has been prepared and, by coupling those receptors (ionophores) to the adequate fluorophores, powerful chemosensors have been developed. The characteristics of the ionophore in terms of the ligand topology and the number and nature of the complexing atoms must be adequate to the type of cation being studied. According to the scope of the present thesis, emphasis will be given to two distinct types of receptors for metal cation sensors: azo bases and Schiff bases.

A Schiff base (also called imine, or azomethine) is a functional group with general formula RR'C=N-R'', where the nitrogen atom is never connected to a hydrogen. The synthesis of this type of compounds is relatively simple, by reaction between an amine and a carbonyl group. Since the reaction involves a dehydration, the presence of dehydrating agents usually favours the formation of the desired product. During the purification step, however, some precautions must be taken in order to avoid degradation. Silica gel chromatography columns can cause hydrolysis of the imine; the alternative purification method is crystallization.

Schiff bases have been very important in the development of coordination chemistry, in part due to their capability to form stable complexes with the majority of the transition metals. The ability to stabilize most metals in different oxidation states also enhances their performance in catalytic processes.In the field of bioinorganic chemistry, Schiff base complexes have received careful attention, due to their role in providing synthetic models for the metal-containing sites in metalloproteins and enzymes. Regarding their applications in chemical sensing, more specifically in cation detection, Schiff bases offer the advantage of possessing a good electron-donating group, the nitrogen atom, that with its lone electron pair can easily coordinate metal ions. Upon coordination, the properties of the system can be modulated, accordingly to the type of cation and its oxidation state.

Azo compounds are highly important, well known and widely used substances in the textile, paper, coloring agents for foods and cosmetics industries. Other applications include emerging technologies like liquid crystals, organic photoconductors and non-linear optics . Azo compounds serve as significant analytical tools by giving a strongly chromophoric label, the attention of which is easily determined by colorimetric, spectrophotometric or spectrofluorimetric methods. Besides, azo compounds are significant analytical assistance compounds serving as pH indicators, complexometric indicators and to a minor extent, pre-concentration reagents. The pharmacological application of azo compounds invents from the detection of the antibacterial action of Prontosil on streptococcal infections by Dogmagk. Furthermore, azo compounds were reported to show a variety of biological activities including antibacterial, antifungal, pesticidal, antiviral and anti-inflammatory activities.

CHAPTER I

General Introduction

This chapter provides an introduction to Schiff based and azo based compounds, its chemistry, biological importance, sensor applications in various fields. The objectives and scope of the present study have also been discussed in order to justify the choice and significance of the work reported in the thesis. This chapter includes the recent studies on Schiff based and azo based compounds.

CHAPTER II

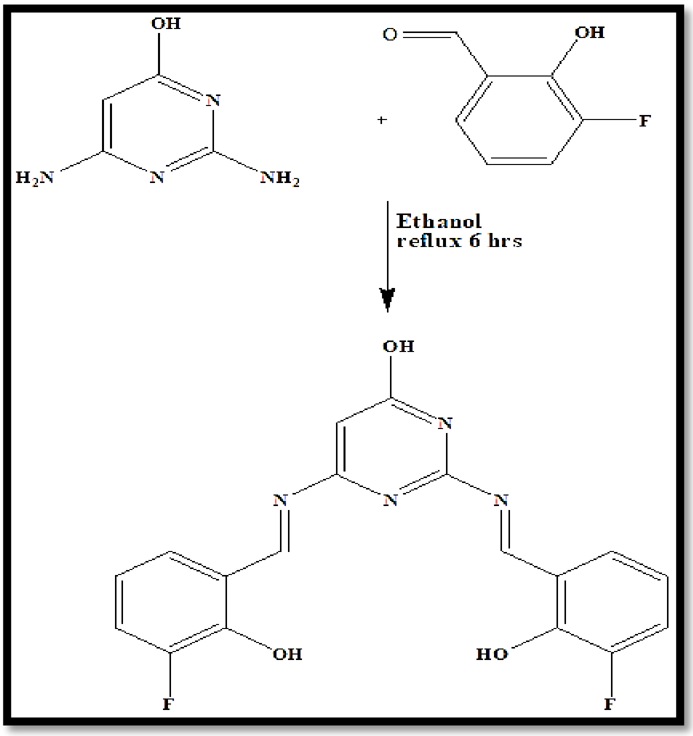
General experimental methods and techniques

This chapter presents the details of the preparation of precursors and experimental techniques used for the characterization of ligand and its metal complexes. This also includes details about the general experimental methods, analytical procedures, antimicrobial studies, magnetic measurements and spectroscopic techniques like UV-Vis., IR, ^{1}H NMR, Mass, XRD, TGA, EPR and cyclic voltammetry used for this work.

CHAPTER III

STUDIES ON METAL(II) COMPLEXES OF 6,6'-(((6-HYDROXY PYRIMIDINE-2,4-DIYL) BIS(AZANYLYLIDENE)) BIS(METHANEYLYLIDENE)BIS (2-FLUORO PHENOL)-(HAMF)

The ligand (HAMF) was obtained by heating the mixture of 3-Fluoro-2-hydroxy benzaldehyde (1 mmol) in ethanol with 2,4-diamino-6-hydroxy pyrimidine (2 mmol) in dry ethanol with constant stirring. The progress of the reaction was monitored by TLC. The resultant light pale brown solid was filtered and dried. Yield is 83 %. The synthesis of HAMF was given in **Scheme 1.** The chelation of the metal complexes has been proposed from elemental, analytical, spectral and magnetic susceptibility measurements. The molar conductance of the complexes in 10^{-3}M ethanol is in the range 5-9 Ω^{-1} cm^2 mol^{-1} indicating that all the complexes are nonelectrolytes.



Scheme 1. Synthesis of ligand (HAMF) L$_1$

The mass spectrum of the ligand (HAMF) shows a molecular ion peak at m/z 499 and the molecular ion peak of cobalt(II) complex was observed at m/z 529 peak confirmed the stoichiometric composition of the metal(II) complexes of [ML] type.

The absorption spectra of the ligand HAMF shows strong peaks at 26040 cm^{-1} (ε, 1396 M^{-1} cm^{-1}) which is due to π - π* transitions due to chromophores C-O and C=N. The current electronic absorption spectrum of cobalt(II) complex of HAMF shows absorption at 35587 and 28409 cm^{-1} due to ILCT and $^2E_g \rightarrow {}^2T_{2g}$ transitions(ε, 1560 M^{-1} cm^{-1}) and (ε, 1492 M^{-1} cm^{-1}) [48].The effective magnetic moment of the cobalt(II) complex is 1.85 B.M. confirming to the square pyramidal geometry around d^7 cobalt(II) ion. The electronic spectrum of the current copper(II) complex of HAMF exhibits absorption bands at 23866 and 12820 cm^{-1}, (ε, 1041 M^{-1} cm^{-1}) and (ε, 162 M^{-1} cm^{-1}) tentatively assigned to $^2B_2 \rightarrow {}^2A_1$ and $^2B_2 \rightarrow {}^2E$ transitions respectively, which is the characteristic of square pyramidal geometry. The magnetic moment of the copper(II) complex is 1.87 B.M. and is also supportive of square pyramidal geometry. , the electronic spectrum of the present nickel(II) complex of HAMF exhibited absorption bands at 35714 cm^{-1} (ε, 1493 M^{-1} cm^{-1}) and 25062 cm^{-1} (ε, 720 M^{-1} cm^{-1})may be tentatively assigned as ILCT and $^2B_2 \rightarrow {}^2A_1$ transitions indicating the Square pyramidal geometry of the complex. The magnetic moment value 2.17 B.M. for Ni(II) complex supports the suggested geometry around the Ni(II) ion .

In the sensing studies UV-Vis spectrum of Ligand is also studied in presence of other metals i.e., Na^{2+} ,Ca^{2+}, Mg^{2+}, Mn^{2+}, Cr^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} and a substantial change was observed in case of $Cu^{2+}$with HAMF at different dilutions. The presence of absorption band at 480 nm is due to formation of Ligand-Cu^{2+}complex whereas the absorption band at 810 nm indicates the presence of C=O group. A well-defined isosbestic point at 650 nm clearly confirms the complex formation of Cu^{2+} with the HAMF resulting in a bathochromic shift. Naked eye photo for sensing of ligand with different cations also confirmed with photo.

The synthesized HAMF has a characteristic imine peak at 1612 cm^{-1}. A sharp peak at 3199 cm^{-1} is due to the presence of v-OH stretching vibrations present in the pyrimidine ring. A sharp peak at 1413 cm^{-1} corresponds to the v(C=N) of the pyrimidine moiety. The peaks of HAMF due to the formation of complex with corresponding metal salts undergo a shift. In HAMF-Nickel complex, a peak at 1612cm^{-1} gets shifted to 1634cm^{-1} and a new peak at 450cm^{-1} (Ni-N) confirms the complex formation. The OH stretching vibrations is at 3444cm^{-1}.v(C=N) stretching peak at 1413cm^{-1} gets shifted to 1432 cm^{-1}due to complexation of pyrimidine ring with Nickel. In HAMF-Copper complex, a band at 1612cm^{-1} shifted to 1623cm^{-1}a new peak at 584cm^{-1} (Cu-N) confirms the complex formation. The OH Stretching vibration is at 3465cm^{-1}. v(C=N) stretching peak at 1413cm^{-1} gets shifted to 1451cm^{-1} due to complexation of pyrimidine ring with Copper. In HAMF-Cobalt complex, the peak at 1612 cm^{-1} shifts to 1632 cm^{-1} due to the bonding of imine nitrogen with Cobalt and a new peak arises at 415 cm^{-1}due to formation of v(Co-N) bond. OH, stretching peak at 3197 cm^{-1}undergoes a great downshift due to the binding of Cobalt with HAMF. v(C=N) stretching peak at 1413 cm^{-1} gets shifted to 1447 cm^{-1} due to complexation of pyrimidine ring with Cobalt.

The ^{1}H-NMR spectrum of the ligand (HAMF) was recorded in DMSO. The Ligand exhibits two singlets at 8.9 ppm and 9.1 ppm for phenolic OH protons. The aromatic protons have resonated in the range of (6.8-7.9) ppm. N=CH has a characteristic peak at 9ppm.

The redox behaviour of copper(II), and nickel(II) complexes has been investigated by cyclic voltammetry using ethanol as solvent and Potassium Chloride (KCl) as supporting electrolyte. The cyclic voltammogram of all the complexes has both reduction and oxidation peaks which distinguishes itself from that of the ligand. Cu(II)complex has two reduction peaks at +0.18V, in cathodic side and oxidation peak at +0.3V in anodic side. The Cu(II) complex exhibits a quasi-reversible behavior as indicated by the non-equivalent current intensity of cathodic and anodic peaks. Ni(II) complex has reduction peak at -0.05V and oxidation peak at -0.01V. The peak separation, ΔE_p = 0.04V which is greater than required for reversible process (59 mV) indicates that the redox couple is irreversible. Cyclic voltammogram of ligand HAMF doesn’t show any oxidation and reduction peaks.

The simultaneous TG/DT analysis of the Ni(II) metal complex was studied from temperature from 30°C to 1000 °C under a nitrogen atmosphere .The TG curve of the Ni(II) complex exhibited no mass loss up to 260 °C. TGA can record directly the weight change as a function of temperature or time for transitions that involve dehydration or decomposition. In the TG curve of Ni(II) complex, the first step of decomposition occurs from 260°C to 340°C. The second step, from 390° C to 610° C which corresponds to the decomposition of the coordinated part of the Ni(II) metal complex. In third step the complex is completely decomposed and removed as (NiO) at above 960 °C. DTG spectrum clearly shows the exothermic nature of the reaction process. The TG curve of the Ni(II) complex shows a two -step decomposition. The TG curve may be attributed to the decomposition of the non-coordinated part of the ligand.

The intensity of the EPR signal significantly decreased which indicates the formation of the [Cu(HAMF)] as shown in the concentration distribution curves and which are denoted by black lines. This phenomenon indicated that the [Cu(HAMF)] species is most probably a monomeric species of the EPR signal. It clearly confirms the square pyramidal geometry of the complex

The Fluorescence spectra of the ligand and its metal complexes were recorded in ethanol at room temperature with excitation wavelength at 320 nm. The Fluorescence spectrum of the ligand exhibited weak Fluorescence emission at 465 nm. On complexation with metals like Co, Cu and Ni the emission peaks are observed at 500nm and 560nm for Cobalt(II) complex, 390 nm and 490 nm for Cu(II) complex and 350 nm and 390 nm for Ni(II) complex. It also confirms the complexation of metals.

Powder XRD patterns of HAMF, Cu(II) Co(II) and Ni (II) complexes of HAMF recorded in the range (2h = 0–80). XRD patterns of the metal complexes show the sharp crystalline peaks indicating their crystalline phase. XRD analysis of nickel(II) complex revealed moderate reflections at 8,14,16,19,28,31,33,38,51 and 70 which were not shown by ligand , verifies the conjugation of the metal(II) (nickel(II)) with the Schiff base. XRD analysis of copper(II) complex revealed moderate reflections at 7,16,23,38,52,55 and 62 which were not shown by ligand , verifies the conjugation of the metal(II) (copper(II)) with the Schiff base. XRD analysis of cobalt(II) complex revealed three moderate reflections at 36, 45 and 77 which were not shown by ligand, verifies the conjugation of the metal(II) (cobalt(II)) with the Schiff base .

On the basis of elemental analyses, molar conductance, magnetic susceptibility measurements, IR, electronic and ESR spectral studies the following structure is proposed for the complexes. **(Fig.1)**

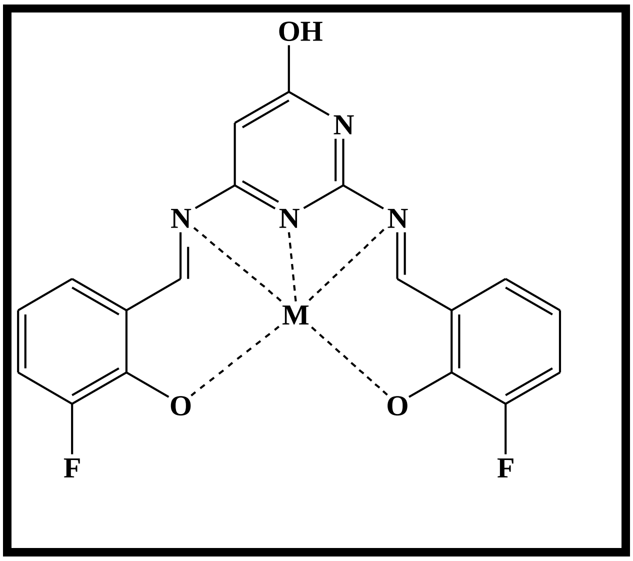


Fig.1. Proposed structure of metal(II) complexes

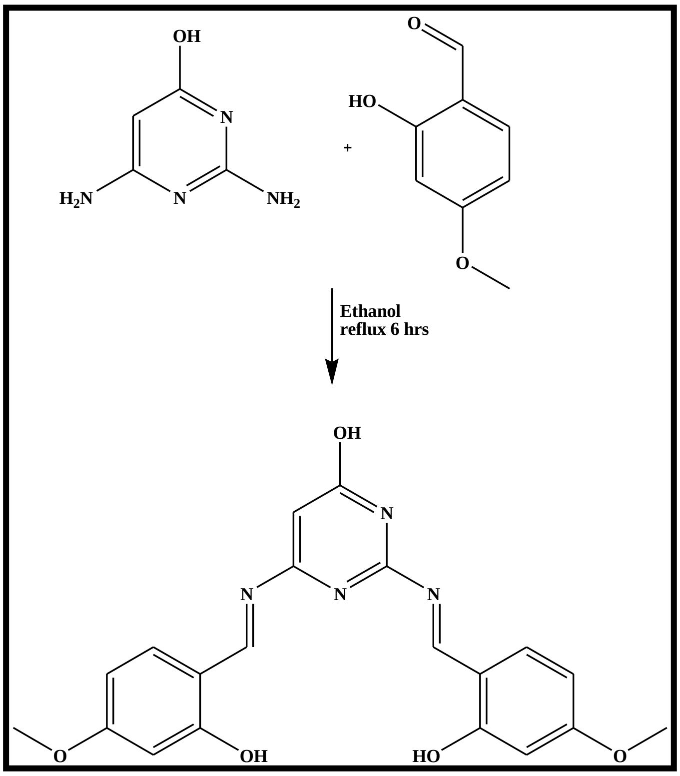
All the tested compounds showed a remarkable biological activity against different types of bacterias. On comparing the biological activity of the ligand and its metal(II) complexes with the standard, it is inferred that, the metal(II) complexes shown potential antibacterial activity against all the bacterial strains. In case of antifungal activity, all the metal(II) complexes were found to be equally active than the free ligand.

The ligand and its metal complexes are fluorescent in nature and potentially active towards all microbial strains. The sensing studies of all the metal complexes show promising results. Such increased activity of the metal complex is of great importance in the sensor and pharmaceutical field.

CHAPTER IV

STUDIES ON METAL(II)COMPLEXES OF 6,6’-(((6-HYDROXY PYRIMIDINE-2,4DIYL) BIS(AZANYLYLIDENE)) BIS(METHANEYLYLIDENE)BIS (3-METHOXYPHENOL))-(HAMP)

Transition metal complexes of copper(II),cobalt(II) and nickel(II) have been synthesized from 2,4-diamino-6-hydroxypyrimidine (0.12g, 10 mmol) was mixed with *O*-Vanillin (0.10g, 20 mmol) dissolved in ethanol (50 ml) and it was refluxed for 6 hrs using acetic acid as the catalyst. The obtained Dark brown precipitate (HAMP) was filtered, dried and washed several times with ethanol. Synthesized ligand (HAMP) was characterized by UV, FT-IR, NMR, EPR and Mass spectral analysis. To elucidate the structures of metal complexes. Spectroscopic and analytical data of the complexes suggested distorted octahedral geometry for copper(II), cobalt(II) and nickel(II) complexes. The molar conductance of the metal(II) complexes was measured to determine the charge of the metal(II) complexes and implies that all the complexes are non-electrolytes.This was given in **Scheme 2.**



Scheme 2. Synthesis of ligand (HAMP) L_2

The mass spectra of the Cu(II) complex shows a peak at m/z 529 which is due to (M-H) confirmed the 1:1 stoichiometric composition of the metal(II) complexes of [M(HAMP)Cl]**.** The peak at m/z 239 is due to the fragmentation of ligand HAMP.

The absorption spectrum of the ligand shows peaks at 25062 cm^{-1} and 13623 cm^{-1} which may be assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions respectively. The spectral data of the ligand and its complexes with molar extinction coefficient or molar absorption coefficient ε ($L\ mol^{-1}\ cm^{-1}$) are calculated. The electronic absorption spectrum of the present Co(II) complex of HAMP exhibits d-d bands at 16393 cm^{-1} (ε, 121 $L\ mol^{-1}\ cm^{-1}$) and 14492 cm^{-1} (ε, 234 $L\ mol^{-1}\ cm^{-1}$) assignable to $^2B_2 \rightarrow {}^2E$ and $^2B_2 \rightarrow {}^2B_1$ transitions [30] respectively, and the magnetic moment value of the cobalt(II) complex 1.75 B.M. confirms the distorted octahedral geometry. The molar intensities are in the range of hundreds indicating the strong metal-ligand interactions. The nickel(II) complex of HAMP under investigation exhibits d-d bands at 29411cm^{-1} (ε, 156 $L\ M^{-1}\ cm^{-1}$) and 24383 cm^{-1} (ε, 119$L\ M^{-1}\ cm^{-1}$), due to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions which arises from an distorted octahedral structure [32]. The Ni(II) complex reported has magnetic moment of 3.01 B.M. which indicates that the Ni(II) complex is six-coordinate and probably distorted octahedral. The absorption at 34482 cm^{-1} with high molar intensity (199$L\ mol^{-1}cm^{-1}$) of copper(II) complex is tentatively assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition and 25062 cm^{-1} (175$L\ mol^{-1}cm^{-1}$) tentatively assigned to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition suggesting distorted octahedral geometry . Charge transfer transitions are higher than the d-d transition. The magnetic moment value 4.82 B.M. falls within the range normally observed for distorted octahedral geometry of Cu(II) complex.

In the sensing studies UV-Vis spectrum of Ligand is also studied in presence of other metal ions [i.e., Na^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cr^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+} and Cd^{2+}] and a significant change was observed in case of Co^{2+} with HAMP in different dilutions. The presence of absorption band at 480 nm is due to formation of Ligand-Ni^{2+}complex whereas the absorption band at 810 nm indicates the presence of chromophore like carbonyl group. The naked eye photo for sensing of Co^{2+} confirms the sensing nature of HAMP.

The synthesized HAMP has a characteristic imine peak at 1639 cm^{-1}. A sharp peak at 3426 cm^{-1} is due to the presence of OH stretching vibrations present in the pyrimidine ring. A sharp peak at 1413 cm^{-1} corresponds to the v(C=N) of the pyrimidine moiety. The peaks of HAMP due to the formation of complex with corresponding metal salts undergo a shift. In HAMP-Cobalt complex, the peak at 1639 cm^{-1} shifts to 1615 cm^{-1} due to the bonding of imine nitrogen with cobalt(II) and a new peak arises at 484 cm^{-1}due to formation of v(Co-N) bond. The -OH stretching peak at 3197 cm^{-1}undergoes a great downshift due to the binding of Cobalt with HAMP. v(N=C) stretching peak at 1413 cm^{-1} gets shifted to 1447 cm^{-1}due to complexation of pyrimidine ring with cobalt(II). In HAMP-Nickel complex, a peak at 1639 cm^{-1} gets shifted to 1610 cm^{-1} and a new peak at 460 cm^{-1} (Ni-N) confirms the complex formation. The OH stretching vibrations is at 3444cm^{-1}. v(N=C) stretching peak at 1413 cm^{-1} gets shifted to 1432 cm^{-1} due to complexation of pyrimidine ring with nickel(II). In HAMP-Copper complex, a band at 1639 cm^{-1} shifted to 1620 cm^{-1}. A new peak at 594 cm^{-1} (Cu-N) confirms the complex formation. The -OH Stretching vibration is at 3465cm^{-1}. v(N=C) stretching peak at 1413cm^{-1} gets shifted to 1451cm^{-1} due to complexation of pyrimidine ring with Copper.

^{1}H NMR spectra of Schiff base ligand (HAMP) was recorded in DMSO. Imine peak resonates at 7.4 ppm. The methoxy proton was observed at 3.5 ppm. Hydroxy pyrimidine (OH) proton resonance was observed in ^{1}H NMR spectrum at 9.6 ppm. The aromatic protons have resonated in the range of 6.2-7.0 ppm. Vanillin OH peaks resonate at 3.8 ppm.

The redox behavior of copper(II), and nickel(II) complexes has been investigated by cyclic voltammetry using ethanol as solvent and Potassium Chloride (KCl) as supporting electrolyte. The cyclic voltammogram of all the complexes has both reduction and oxidation peaks which distinguishes itself from that of the ligand. Copper(II) complex has two reduction peaks at -0.61V, in cathodic side and oxidation peak at 0.58V in anodic side. The Cu(II) complex exhibits a quasi-reversible behaviour as indicated by the non-equivalent current intensity of cathodic and anodic peaks. Nickel(II) complex has reduction peak at 0.18V and oxidation peak at 0.24V. The peak separation, ΔE_p = 0.06V which is greater than required for reversible process (59 mV) indicates that the redox couple is irreversible.

The intensity of the EPR signal significantly decreased which indicates the formation of the [Cu (HAMP)Cl] as shown in the concentration distribution curves and which are denoted by black lines. This phenomenon indicated that the [Cu (HAMP)Cl] species is most probably a monomeric species of the EPR signal. It clearly confirms the distorted octahedral geometry of the complex.

On the basis of the above physico-chemical evidences, the following structure has been assigned for the metal complexes of type [M(HAMP)Cl]. **(Fig.2)**

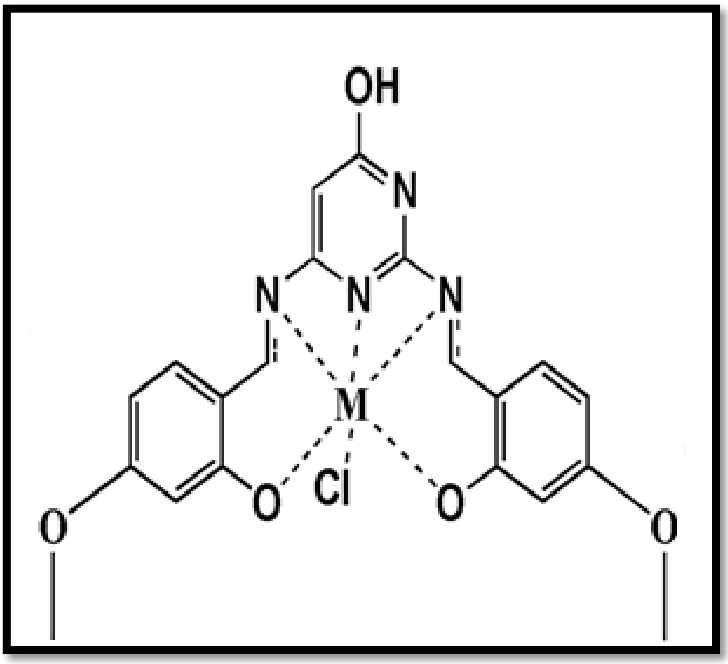


Fig.2. Proposed structure of metal(II) complexes

In order to investigate the effect of M(II) ions on the fluorescence of the ligand, the fluorescence spectra of the ligand and its metal complexes were recorded in DMF at room temperature with excitation wavelength 300 nm. The fluorescence spectrum of the ligand exhibited weak fluorescence emission at 390 and 475 nm. It also confirms the complexation of metal ions. Among all the complexes cobalt(II) complex has highest fluorescence nature with HAMP.

Powder XRD patterns of HAMP, Ni(II), Cu(II) and Co(II) complexes of HAMP recorded in the range (2h = 0–80).XRD patterns of the metal complexes show the sharp crystalline peaks indicating their crystalline phase. XRD analysis of nickel(II) complex revealed moderate reflections at 11,13,17,20,28,32,38,44,48, 56,65,68,70 and 78 which were not shown by ligand, verifying the conjugation of the nickel(II) with the Schiff base. XRD analysis of copper(II) complex revealed moderate reflections at 9,13,21,22,28,32,38,44 and 65 which were not shown by ligand, verifying the conjugation of the metal ion (copper(II)) with the Schiff base. XRD analysis of cobalt(II) complex revealed moderate reflections at 17,31,38,44,54,60 and 74 which were not shown by ligand, verifying the conjugation of the metal ion(cobalt(II)) with the Schiff base.

The thermal behaviour of the ligand HAMP was analysed, and the decomposition starts at 90°C to 240°C.Its corresponding metal complex displays a mass loss on the TGA and DTG curve at 450 °C and complete decomposition takes place at 680 °C .

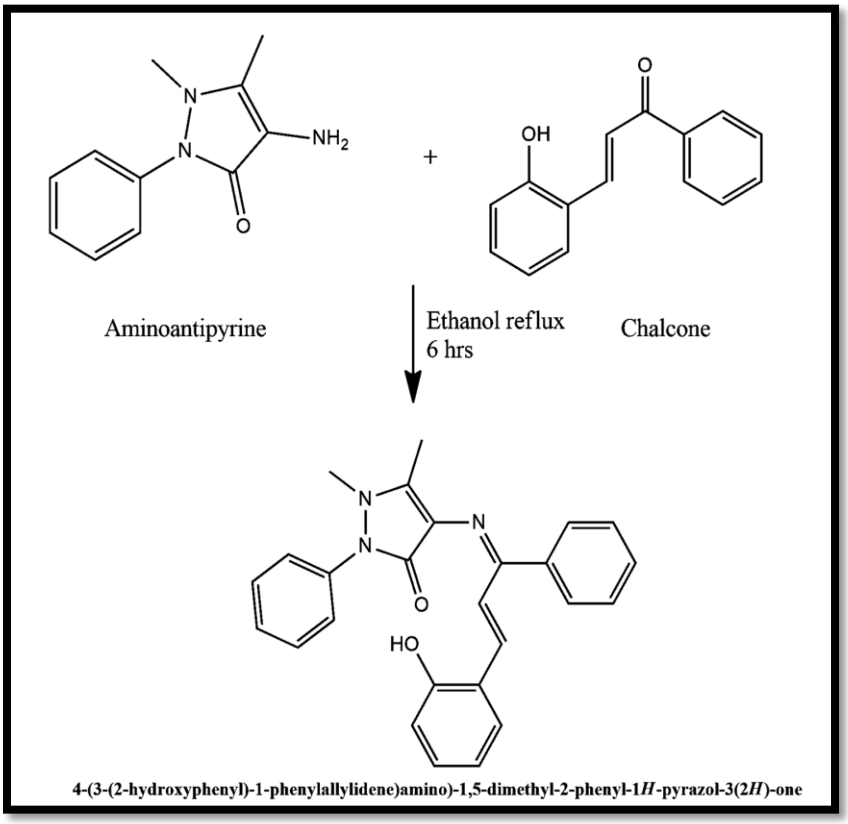
Biological study reveals that the complexes exhibit higher antimicrobial activity than the ligand. Such an enhanced activity can be explained on the basis of chelation theory.The copper complex is found to be more effective against *Streptococus* and *Pseudomonas* with the zone of inhibition 20 mm.

From the results, it is clear that, the cobalt complxe exhibits appreciable sensing in comparison with other cations, hence the compound can be studied for sensing material for further applications. Ligand and its metal(II) complexes are fluorescent in nature. Most of the metal chelates show better antimicrobial activity than ligand, particularly Co(II) complex has higher antimicrobial activity compared to other complexes.

CHAPTER V

STUDIES ON METAL(II) COMPLEXES OF 4-(3-(2-HYDROXYPHENYL)-1-PHENYLALLYLIDENE) AMINO)-1,5-DIMETHYL-2-PHENYL-1H-PYRAZOL-3(2H)-ONE (HPDP)

Schiff based ligand 4-(3-(2-hydroxyphenyl)-1-phenylallylidene) amino)-1,5-dimethyl-2-phenyl-1h-pyrazol-3(2h)-one (HPDP) L_3 **(Scheme 3)** and its copper(II), cobalt(II) and zinc(II) complexes have been synthesized from Amino antipyrine(10mmol) was mixed with chalcone(20mmol) in ethanol and refluxed for 6hr. The growth of the reaction was supervised by TLC. A dark yellow colour precipitate starts separating out, it was filtered and dried.It is concluded that the ligand act as monodentate forming tetrahedral geometry with metal ions in case of [ML]Cl type metal(II) complexes. The molar conductivity measurement of metal(II) complexes of [ML]Cl type indicates the ionic nature of these complexes, hence they considered as electrolyte.



Scheme 3. Synthesis of ligand (HPDP) L_3

The fluorescence intensity was plotted against the molar fraction of the chemosensor under a constant total concentration. A maximum intensity was observed when the molar fraction was 0.5 M, which indicates a 1:1 ratio for the Zn^{2+} complex. Limit of detection was found out to be 0.1 µm. In order to confirm the formation of metal complex in 1:1 stoichiometry HR-LCMS mass spectrum for the complex was analysed and the value was observed at m/z 543 which is accounted by the presence $(M+Cl^-+H)$ from that of expected mass of m/z 507.

The absorption spectrum of the ligand (HPDP**)** shows strong peaks at 27247cm^{-1} (ε, 4400 mol^{-1} cm^{-1}), and 15552 cm^{-1} (ε, 4900 mol^{-1} cm^{-1}), which are attributed to n- π* and π-π* transitions respectively.Three absorption bands for the cobalt(II) complex (HPDP) appeared at 23809(ε, 252 mol^{-1} cm^{-1}), and 12820 cm^{-1} (ε, 990mol^{-1} cm^{-1})due to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transitions indicates the Tetrahedral geometry, which is also supported by its magnetic moment value 4.91 B.M. The electronic absorption spectrum of the present copper(II) complex (HPDP) shows bands at 23809 and 29411 cm^{-1}, which are assigned as an intra ligand charge-transfer band and one d-d band at 13513 cm^{-1} is due to $^2E_g \rightarrow {}^2T_{2g}$ transition. This d-d band strongly favours an octahedral geometry around the metal ion. It is further supported by its magnetic susceptibility value 1.84 B.M. The absence of absorption below 10000 cm^{-1} excludes the possibility of tetrahedral geometry for the complex. The molar absorption coefficient for Copper (II) complexes are 146,382 and 451 in (L mol^{-1} cm^{-1}**)** The Zn(II) complex is diamagnetic and according to the empirical formula, an tetrahedral geometry is proposed for this complex.

In the sensing studies absorption spectra of both HPDP have been recorded in presence of different concentrations of Zn^{2+} in ethanol solution. Free HPDP shows peak at 349 nm. When Zn^{2+} ions are added to HPDP, spectral behaviour changes markedly. A new peak emerges at 415nm with gradual increase intensity (bathochromic shift) with the addition of Zn^{2+} ion while the intensity of probe 349 nm decreases. Changes in the intensities almost saturate when one equivalent of Zn^{2+} is added. Isosbestic point is noticed at 399 nm. Upon gradual addition of the metal ion, intensity at 349 nm decreases sequentially and at the same time, a new peak at 417nm emerges with increasing intensity. The N, O donor atoms of both the Schiff-bases coordinate to the metal centre to form the chelate ring. As a consequence, conjugation in the structure is extended, showing the new absorption band at a longer wavelength. All of these facts suggest that Zn^{2+} is able to interact with both the probes to form the corresponding Zn-bound Schiff-base compound.

The IR spectral studies of the ligand and metal (II) complex were carried out in the range 4000-400 cm^{-1}. A broad band centred at 3108 cm^{-1} is due to (OH). The IR spectrum of the ligand shows a broad band at 3138cm^{-1} which is a characteristic of ν (N-H) stretching vibration shifted itself to 3109 in Zn(II) HPDP complex. The band at 1628 cm^{-1} is assigned to ν(C =N) which is downshifted to 1598 cm^{-1}. ν(M-O) peak is at 712 ν(M-N) peak is at 568 cm^{-1}. IR spectrum of the Metal (II) complex show considerable variations compared with the ligand (HPDP).

The ligand (HPDP) was characterized using ^{1}H-NMR data. 1H-NMR was recorded using DMSO as the solvent. (N-CH) has a characteristic peak at 7.27 (δ). The aromatic protons has resonated in the range of (7.0-7.8).

Fluorescence spectra of HPDP have been recorded in the presence of different concentrations of Zn^{2+} in ethanol. HPDP displays emission peaks at 425 nm with moderate intensity when it is excited at 350 nm.The addition of Zn^{2+} ions to the HPDP results in a gradual increase in emission intensity at 425 nm. The increase in emission intensity of HPDP. The addition of Zn^{2+} ion causes significant changes in the fluorescence spectrum of HPDP. The enhancement in emission intensity of HPDP could be explained based on the photo induced electron transfer (PET). Due to the formation of metal complex with Zn^{2+} PET is turned on.

The TG curve of the Zn(II) complexes exhibited no mass loss up to 210 °C. TGA can record directly the weight change as a function of temperature or time for transitions that involve dehydration or decomposition. In the TG curve of Zn(II) complex, the first step of decomposition from 210°C to 250°C. The second step, from 260°C to 360 °C which corresponds to the decomposition of the coordinated part of the Zn(II) metal Complex. The TG curve of the Zn(II) complex shows a two -step decomposition. The DTA curve, may be attributed to the decomposition of the non-coordinated part of the ligand. The anhydrous complex exhibited a single-step decomposition from 210 °C - 360°C, with a considerable mass loss and a broad exothermic peak in the DTA.

Powder XRD patterns of HPDP, Zn(II), Cu(II) and Co(II) complexes of HPDP recorded in the range (2h = 0–80). XRD patterns of the metal complexes show the sharp crystalline peaks indicating their crystalline phase. XRD analysis of zinc complex revealed four moderate reflections at 14, 16, 33 and 60 which were not shown by ligand, verifying the conjugation of the metal (Zinc) with the Schiff base.

XRD analysis of copper complex revealed three moderate reflections at 28, 34 and 53 which were not shown by ligand, verifying the conjugation of the metal (copper) with the Schiff base.XRD analysis of cobalt complex revealed three moderate reflections at 12, 22 and 27 which were not shown by ligand , verifying the conjugation of the metal (cobalt) with the Schiff base.

On the basis of elemental analyses, molar conductance, magnetic susceptibility measurements, IR, electronic,mass and NMR spectral studies the following structures may be proposed for the complexes. **(Fig.3)**

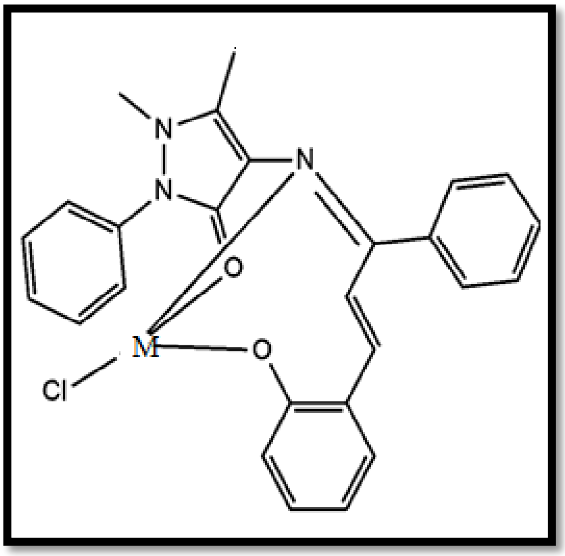


Fig.3. Proposed structure of metal(II) complexes

In vitro antibacterial activity data reveals that all the newly synthesized compounds display moderate to significant activity in comparison to standard. It is found that zinc(II) complex shows significant activity against *E.Coli, P. Aeruginosa, A.niger and Staphy. Aureus* when compared to other complexes.All other compounds achieved substantial activity against the all species. Such increased activity of the metal(II) complexes over the ligand can be explained on the basis of Overton's concept and chelation theory.

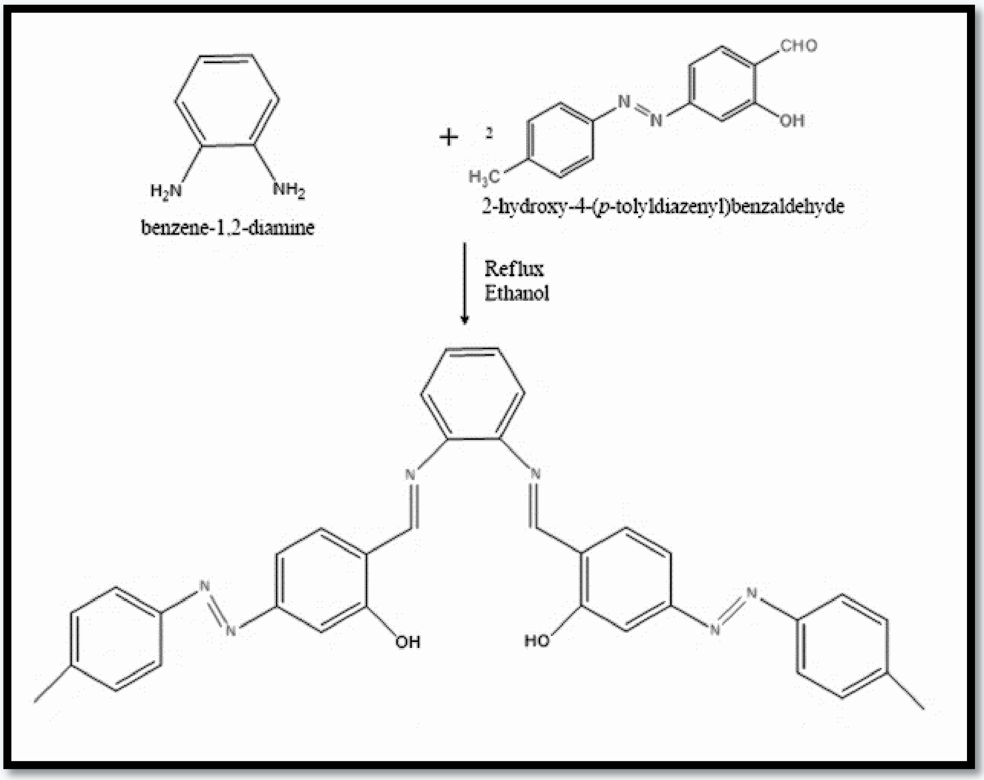
In this chapter, the ligand and its metal(II) complexes are highly fluorescent in nature and also found to exhibit considerable sensing properties in comparison with ligand. Most of the metal(II) complexes show better antimicrobial activity than the free ligand. It is suggested that chelation of ligand with different metal ions make them stronger bacteriostatic agents, thus inhibiting the growth of bacteria more than the parent ligand. Therefore, they seem to be really promising compounds for their antimicrobial activities and sensing applications.

CHAPTER VI

STUDIES ON METAL(II)COMPLEXES OF

1, 5-BIS (2-HYDROXY-4-(P-TOLYLDIAZENYL) PHENYL) PENTA-1, 4-DIEN-3-ONE (HTDPPD)

Novel azo based 1, 5-bis (2-hydroxy-4-(p-tolyldiazenyl) phenyl) penta-1, 4-dien-3-one (HTDPPD) L_4 **(Scheme 4)** ligand synthesized from 2-hydroxy-4-(p-tolyldiazenyl) benzaldehyde and acetone in alkaline solution was stirred at room temperature for half an hour. Gradually red precipitate separates out, and then it was filtered and washed thoroughly with ethanol. The resulting product was recrystallized from ethanol.Analytical data of the complexes suggest square planar geometry for metal(II) complexes. The ligand acts as a tetradentate ligand coordinates through Schiff base nitrogen and (OH) oxygen to the metal. The molar conductance value of the metal complexes was measured to establish the charge of the metal(II) complexes and it varies forms implies that all the complexes are non-electrolytes.



Scheme 4. Synthesis of ligand (HTDPPD) L_4

The mass spectra of the Cu(II)(HTDPPD) shows a peak at m/z 525 which is due to ($M+Cl^-+H$) confirmed the 1:1 stoichiometric composition of the metal(II) complexes of [M(HTDPPD)Cl]. The peak at m/z 191 is due to the fragmentation of ligand HTDPPD.

The electronic absorption spectra of Ligand, recorded in Ethanol at room temperature displays one of strong intensity located in the UV and the other, of weaker intensity, in the visible spectral region. The occurrence of such bands can be assigned to π-$\pi^*$and n-π^* electronic transitions of the azobenzene moiety. The sharp band located at 351 nm is due to the presence of $\pi\rightarrow\pi^*$ transition of the of the transform of azobenzene . A very weak n-π^* transition peak and also intramolecular charge transfer interaction is observed at 382nm. The intramolecular CT band can be assigned to the existence of tautomeric equilibrium originating from hydroxyl group in o-position of aromatic ring In most cases, trans→cis isomerization is promoted by irradiation with wavelengths between 320–350 nm, while exposures to 380–410 nm favour the cis→trans photo reversion. The absorption peaks at 220 nm and 312 nm shows the presence of C=O and Ar-OH respectively.

The UV-vis absorption spectra were recorded using a variety of solvents such as DMF, DMSO, Ethyl Acetate, Ethanol, THF and Water. The concentration range is kept constant at 10^{-5}M. It was found that the absorption band at 375–416 nm generally shows hypso chromic shift (negative solvatochromism) as the polarity of solvent was increased, indicating the removal of double bond by saturation. The other bands at 425–500 nm shows bathochromic shift (positive solvatochromism) upon increasing solvent polarity. This positive solvatochromism exhibited by the dyes may be due to the effect of dipole moment changes of the excited state and/or due to increase in the conjugation. The general increasing order of polarity of solvents is: THF<Ethyl acetate<DMF <DMSO<Ethanol< Water.To gain further insights about the equilibrium between the tautomeric hydrazone-azo forms acid–alkali studies has been performed at different pH. Under acidic conditions (pH 1 to 6) the low energy bands with respect to the hydrazine-azo form diminished almost completely and a new high energy band appeared at 383 nm. Upon changing the pH from 7 to 14 the absorptivity of the low energy bands decreased with the hypsochromic shift and high energy bands corresponding to the hydrazone-azo form dominate .The new bands observed at 299nm – 304nm and 462 nm are assigned to $n \rightarrow \pi^*$and $\pi \rightarrow \pi^*$ electronic transition of azo–aromatic chromophore of the aromatic ring and intra molecular charge transfer interaction. The disappearance of absorption band at 383 nm indicates the cis-trans isomerism.

UV-Vis spectrum of Ligand is also studied in presence of other metals i.e., Na^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cr^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+} and a significant change was observed in case of Cu^{2+}. The presence of absorption band at 279 nm is due to formation of Ligand-Cu^{2+}complex whereas the absorption band at 237 nm indicates the presence of C=O group. Due to the complexation with Cu^{2+}, distinct colour change occurs from red to light blue. During coordination with Cu^{2+}, de-protonation of phenolic-OH of ligand affects the electronic properties of ligand which results in colour from red to light blue.

IR spectral technique is the most suitable one to arrive information related to nature of bonding of the ligand to the metal ion. The IR spectra of both the free ligand and metal complexes were carried out in the range 4000-400 cm^{-1}. The spectrum of the ligand shows a peak at 3396 cm^{-1} which may be due to ν(NH) stretching vibration. The aromatic ring shows ν(C-H) at 2924cm^{-1} ,ν(C=C) at 1679 cm^{-1} and 1444 cm^{-1}.The bands at 1190 and 1147 cm^{-1} are assigned to ν(C-N) stretching and a band at 1120 cm^{-1} corresponds to alcoholic ν(C-O) respectively. The ligand shows peak at 840-810cm^{-1} due to C-H bending in it. A band at 3390cm^{-1} and a weak band at 1580cm^{-1} shows the presence of phenolic ν(-OH)and ν(N=N), respectively.

The redox behaviour of the ligand was performed in DMSO solution at room temperature with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte; glassy carbon as working electrode; Pt wire as auxiliary electrode; Ag/AgCl as reference electrode in order to monitor spectral and structural changes accompanying electron transfer. The ligand exhibited one-step reversible reduction peak at -0.75 V (cathodic side) and one oxidation peak at -0.60 V (anodic side). Also, an irreversible oxidation wave is observed at 0.90 V. The azo-dyes display oxidation at more positive potential as a consequence of the destabilizing effect of the electron-withdrawing group on the arylazo moiety. This process may also be associated with the reduction of the azo bonds.

The photoluminescence property of ligand was studied at room temperature. From the observed fluorescence peak at 417nm which is related to the absorption band observed at 351 nm giving the Stoke shift of the order of 66 nm. The emission peak at 500nm obviously corresponding to absorption peak at 375nm leading to Stokes shift of the order of 125nm.The fluorescence intensity with high-quantum yield, and the excitation at 426–799 nm gives an emission at 442–804 nm,assigned to π-π^*intraligand fluorescence.The fluorescence quantum yield of the ligand was obtained using the following relation. $\Phi_S = A_S / A_R \times (AbS)_R / (AbS)_S \times \Phi_R$, Where Φ_S– fluorescence quantum yield of the sample,Φ_R– fluorescence quantum yield of the reference,A_S– area under the fluorescence spectra of the sample,A_R– area under the fluorescence spectra of the reference,AbS – optical density of the sample.AbR–optical density of the reference solution at the wavelength of excitation.

On the basis of above discussion, which is based upon elemental analysis, molar IR, electronic and mass spectral studies, the following structure was proposed for the complexes. **(Fig.4)**

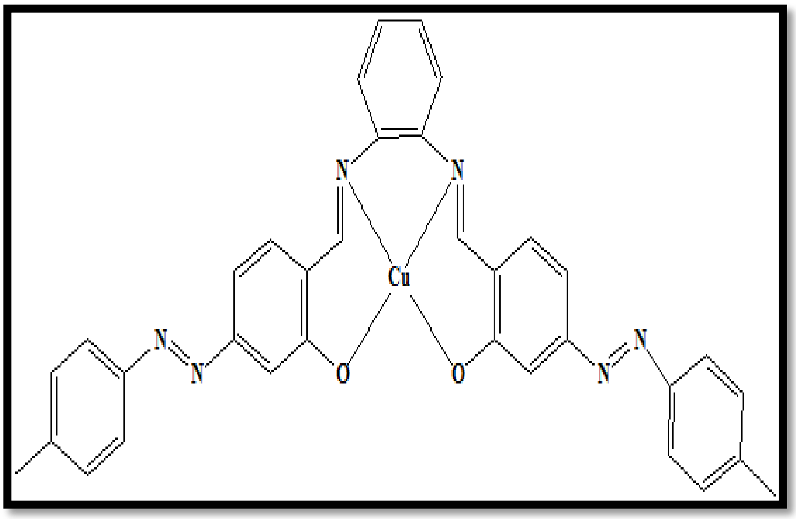


Fig.4. Proposed structure of metal(II) complexes

In vitro antibacterial activity data reveals that all the newly synthesized compounds display moderate to significant activity in comparison to standard. It is found that cobalt(II) complex shows significant activity against *S.Aureus, E.coli, P.Aeruginosa and B.Subtills***.** when compared to other complexes. All other compounds achieved substantial activity against the all species. Such increased activity of the metal(II) complexes over the ligand can be explained on the basis of Overton’s concept and chelation theory. The newly synthesized azo based ligand and its complex exhibited more intense fluorescence and UV absorption than the previously studied Schiff based derivatives.

Concluding Remarks

- The ligand 4-(3-(2-hydroxyphenyl)-1-phenylallyllidene) amino)-1,5-dimethyl1-2phenyl-1H-pyrazol-3(2H)-one.(L_3) exhibit highest fluorescence activity than the other ligands.
- All the synthesized triazine based ligands have remarkable biological activities. Zn(II) complex (L_3) is highly potent against almost all the test bacteria's. Cu(II) and Co(II) complexes (L_1) also exhibit higher antibacterial activity against *Bacteroides and Pseudomonas Aeruginosa* .
- Among the four metal complexes two ligands selectively sensing Cu(II) metal,other two ligands sensing Co(II) and Zn(II)metal ions. So, all the metal(II) complexes are selectively sensing one metal(II) ion and exhibit isosbestic point that could be useful in sensor devices.
- The TGA studies shows that Schiff based metal complexes are thermally stable which can be used for sensor and antimicrobial applications.