

DEVELOPMENT OF NOVEL POLYDENTATE LIGANDS AND ITS METAL DERIVATIVES FOR SENSING AND ANTIMICROBIAL EVALUATION

The major threat to the global health care is infectious diseases caused by the microorganisms. Recently, most of hospital deaths are caused by infectious pathogens. When viruses, bacteria, or other microbes enter into your body, they begin to multiply and infection occurs. This damage the cells in the body and an illness appear. The incidence of disease varies greatly depending on the particular pathogen and individual susceptibility. Antibiotics cure disease by killing or injuring bacteria. Special strains of the bacteria such as Gram strains, can be used to identify bacteria under the microscope and may help which species of bacteria is causing infection. They are commonly used to treat bacterial infections, which are known to target the growth process of the bacteria.

Schiff bases derived from an amino and carbonyl compound that coordinates to metal ions via azomethine nitrogen atom. Azomethine (C=N) has been reported to have significant antibacterial, biological activities. The complexes of Schiff bases with metal ions are very foremost in the development of coordination chemistry field. These complexes are also known to have biological activities such as antimicrobial, antifungal and anticonvulsant.

In addition to their interesting ligational properties, Schiff bases and their complexes have important biological and industrial applications and they are also of importance due to their complexing, catalytical and biological properties. They found to be important as biochemical, analytical and antimicrobial agent exhibiting bacteriostatic and other biochemical activities.

Biological activities are seen in compounds containing azo, azomethine linkages and chlorine groups, it was thought of interest to inspect the effect of having all of above functionalities present in one structure. Based on this perception and their

outstanding features, we thus decided to synthesize and characterize Schiff base derivatives and its transition metal(II) complexes. Hence, it is no wonder why these kinds of compounds have been the matter of discussion in recent research. We are interested in design, synthesis, characterize and study the sensing and fluorescence properties of novel compounds with potential bioactivity.

This thesis comprises of six chapters and the contents of each chapter in concise are demarcated here and there.

CHAPTER I

General Introduction

This chapter provides an introduction to Schiff based compounds, its chemistry, biological importance, sensing property and 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 compounds.

CHAPTER II

General experimental methods and techniques

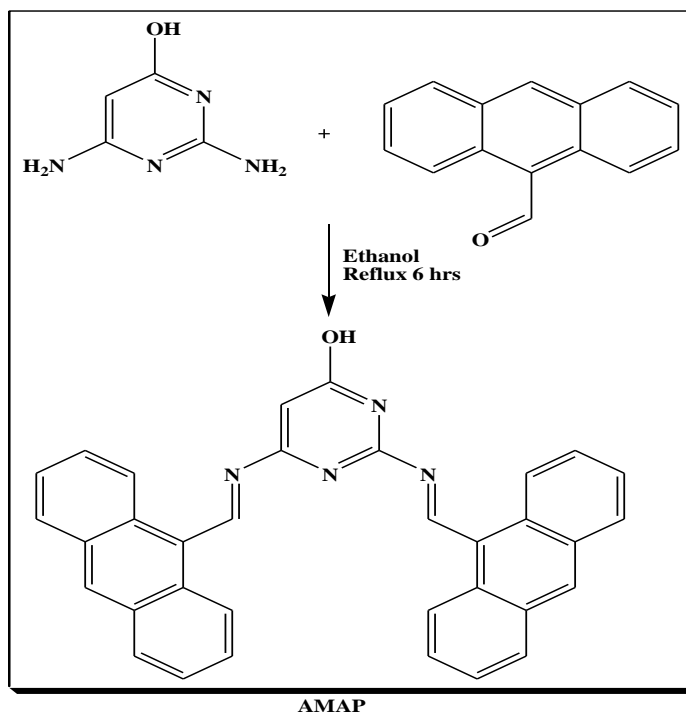
This chapter describes the general experimental methods, analytical procedures, antimicrobial procedures, magnetic measurements and spectroscopic techniques like UV-Vis., IR, ¹H-NMR, HPLC-mass, EPR, Cyclic voltammetry, Thermogravimetric analysis and X-ray diffraction studies used in the work.

CHAPTER III

Studies on metal(II) complexes of 2,6-bis((anthracen-9-ylmethylene)amino)pyrimidin-4-ol-[AMAP]

A new series of transition metal(II) complexes of the type [ML.Cl₂] (where M= Co(II), Ni(II) and Cu(II)) have been synthesized from 2,6-bis((anthracene-9-ylmethylene)amino)pyrimidin-4-ol (**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 $5-9 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating that all the complexes are non electrolytes.



Scheme 1. Synthesis of ligand (AMAP)

¹H-NMR spectrum of the ligand (AMAP) was recorded in DMSO. The CH=N group resonates as two sharp singlets at 8.2 ppm. The signal at 9.0 ppm was assigned to the C-H proton of pyrimidine ring. The -OH proton of hydroxy pyrimidine resonates at 11.5 ppm. The aromatic protons have resonated in the range of 6.0-8.0 ppm.

The Ligand (AMAP) was studied with various metals like Cu²⁺, Co²⁺, Zn²⁺, Mg²⁺, Mn²⁺, Fe²⁺, Fe³⁺, Cr³⁺, Al³⁺, Ba²⁺, Sr²⁺ and Ni²⁺. Among the cations, Ni²⁺ has a significant effect with the ligand. The presence of absorption band with increasing intensity at 405 nm which corresponds to ³B₁(F) → ³E(P) shows a bathochromic shift is due to the formation of [Ni(AMAP)Cl₂]. Other metal ions like Cu²⁺, Co²⁺, Zn²⁺, Mg²⁺, Mn²⁺, Fe²⁺, Fe³⁺, Cr³⁺, Al³⁺, Ba²⁺ and Sr²⁺ cations has no effects with the ligand.

The absorption spectrum of the AMAP shows absorption peaks at 26,315 cm^{-1} (ϵ , 1406 $\text{M}^{-1} \text{cm}^{-1}$), 25,316 cm^{-1} (ϵ , 1315 $\text{M}^{-1} \text{cm}^{-1}$) and 24,813 cm^{-1} (ϵ , 1120 $\text{M}^{-1} \text{cm}^{-1}$) which is attributed to $n-\pi^*$ intra ligand charge transition and $\pi-\pi^*$ transitions respectively arising from azomethine (CH=N) chromophores that were present in the compounds.

The electronic absorption spectrum of Co(II) complex of AMAP displayed two bands at 27,247 cm^{-1} (ϵ , 1615 $\text{M}^{-1} \text{cm}^{-1}$) and 15,552 cm^{-1} (ϵ , 381 $\text{M}^{-1} \text{cm}^{-1}$) which can be assigned to the transitions ${}^4\text{A}_2 + {}^4\text{E} \rightarrow {}^4\text{A}_2(\text{P})$ and ${}^4\text{A}_2 + {}^4\text{E} \rightarrow {}^4\text{E}(\text{P})$ and respectively which are characteristic of square pyramidal geometry. The nickel(II) complex of AMAP exhibits three d-d bands at 24,691 cm^{-1} (ϵ , 1021 $\text{M}^{-1} \text{cm}^{-1}$), 14,450 cm^{-1} (ϵ , 652 $\text{M}^{-1} \text{cm}^{-1}$) and 12,820 cm^{-1} (ϵ , 151 $\text{M}^{-1} \text{cm}^{-1}$) and these bands may be tentatively assigned as ${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{E}(\text{P})$, ${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{A}_2(\text{P})$ and ${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{E}(\text{F})$ transitions respectively suggesting square pyramidal geometry. The copper(II) complex of AMAP showed two bands at 24,937 cm^{-1} (ϵ , 1214 $\text{M}^{-1} \text{cm}^{-1}$) and 13,245 cm^{-1} (ϵ , 602 $\text{M}^{-1} \text{cm}^{-1}$), which are assigned to the transitions ${}^2\text{B}_1 \rightarrow {}^2\text{E}$, and ${}^2\text{B}_1 \rightarrow {}^2\text{B}_2$ respectively are characteristic of square pyramidal geometry. The copper(II) complex of AMAP at 1.64 B.M. is interpreted as suggestive of a five coordinate square pyramidal geometry due to distortion in the complexes. These magnetic moment value and spectral data confirm the square pyramidal geometries around metal(II) ions. Co(II) and Ni(II) complexes of AMAP have magnetic moment values 3.45 and 2.86 B.M respectively, also further confirms the square pyramidal geometry.

The synthesized AMAP has a characteristic imine peak at 1633 cm^{-1} . The IR spectrum of the Schiff base exhibits bands at 3138 cm^{-1} assignable to $\nu(\text{-OH})$ stretching vibrations present in the pyrimidine ring. The band at 3138 cm^{-1} is attributed for $\nu(\text{-OH})$ in pyrimidine ring which is almost unchanged in the complexes, indicating that this group is not participating in coordination. The peak at 1273 cm^{-1} corresponds to the $\nu(\text{C=N})$ present in the pyrimidine ring. The peak at 1633 cm^{-1} shifts to 1610 cm^{-1} due to the bonding of imine nitrogen with Co(II) and a new peak arises at 505 cm^{-1} due to formation of (Co-N) bond. Since chlorine is present in the complex, a new peak at 541 cm^{-1} rises. The Peak at 1633 cm^{-1} gets shifted to 1612 cm^{-1}

in Ni(II)-AMAP complex and a new peak at 512 cm^{-1} due to $\nu(\text{Ni-N})$ stretching, confirm the complex formation and the presence of chlorine is confirmed by a peak at 663 cm^{-1} . The band at 1633 cm^{-1} shifted to 1620 cm^{-1} in Cu(II)-AMAP complex and a new peak at 510 cm^{-1} due to $\nu(\text{Co-N})$ stretching, confirm the complex formation and presence of chlorine is confirmed by a peak at 651 cm^{-1} .

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. Cu(II) complex has two reduction peaks at -0.18V , -0.55V in cathodic side and oxidation peak at 0.23V in anodic side exhibits a quasi-reversible behaviour. Ni(II) complex has reduction peak at 0.9V and oxidation peak at 0.25V . The peak separation, $\Delta E_p = 0.65\text{V}$ which is greater than required for reversible process (59 mV) indicates that the redox couple is irreversible.

The mass spectra of the Ni(II) complex shows a peak at $m/z\ 627$ which is due to (M-H) confirmed the 1:1 stoichiometric composition of the metal(II) complexes of $[\text{M}(\text{AMAP})\text{Cl}_2]$. The peak at $m/z\ 325$ is due to the fragmentation of ligand AMAP.

The thermal behaviour of the ligand was analysed and the decomposition starts at 110°C . Its corresponding metal(II) complex displays a mass loss on the TGA and DTG curve at 230°C and complete decomposition takes place at 410°C .

The fluorescence spectra of the ligand and its metal(II) 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 nm and 475 nm . Significant differences in positions of emission maximum of ligand and its complexes establish the complexation process. Quenching of fluorescence of ligand by transition metal ions through complexation is a quite ordinary phenomenon which is explained by processes such as redox-activity, electronic energy transfer. It also confirms the complexation of metals.

Powder XRD patterns of AMAP, Ni(II), Cu(II) and Co(II) complexes of AMAP recorded in the range ($2\theta = 0-80$) and these spectra show the sharp crystalline peaks indicating their crystalline phase. It revealed moderate reflections at 14 , 16 , 21 and 32 which were not shown by the ligand, verifying the conjugation of nickel(II)

with the Schiff base. XRD analysis of copper(II) complex revealed three moderate reflections at 15, 31 and 39 which were not shown by the ligand, which confirms the conjugation of copper(II) with the Schiff base. In cobalt(II) complex, it revealed three moderate reflections at 19, 31 and 38 which were not shown by the ligand, confirming the conjugation of 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)

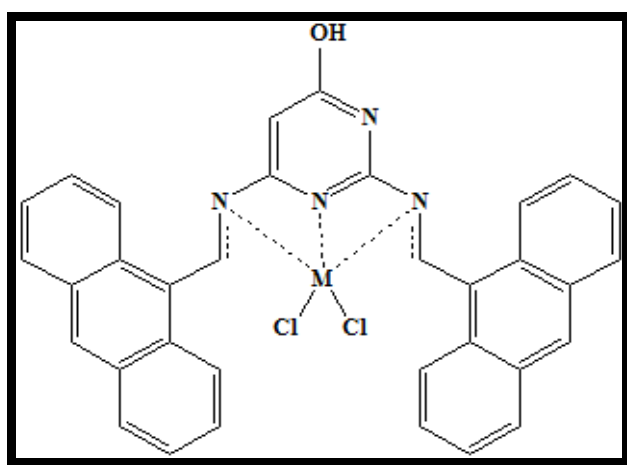


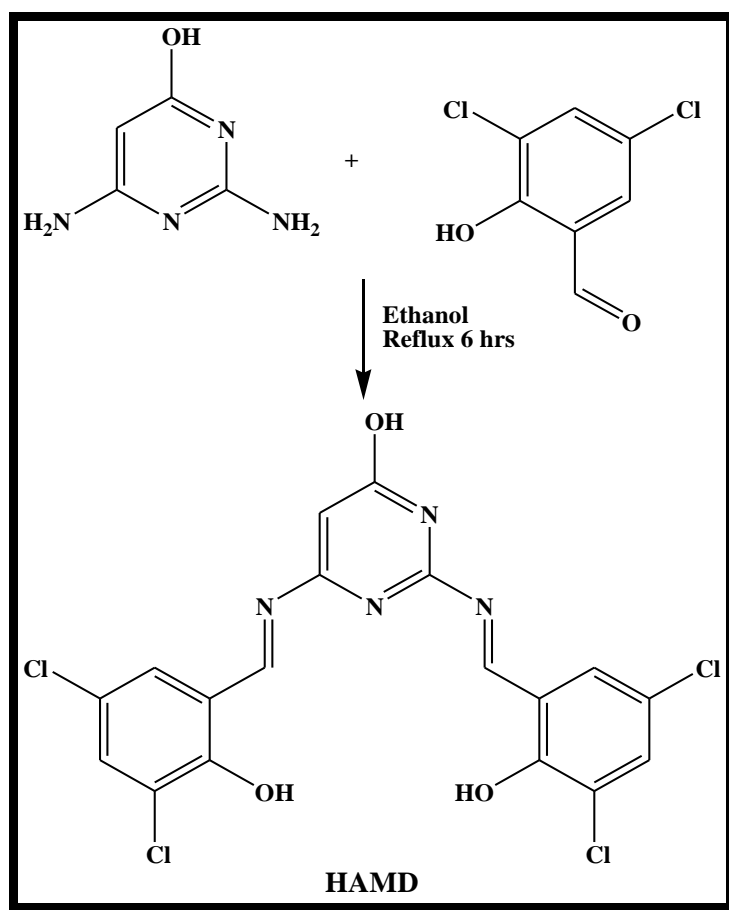
Fig. 1. Proposed structure of the metal(II) complexes of AMAP

All of the tested compounds showed a remarkable biological activity against different types of Gram-positive and Gram-negative bacteria and against fungi species. On comparing the biological activity of the Schiff base and its metal complexes with the standard (Amikacin and Ketoconazole), it is inferred that, the Co(II), Cu(II) and Ni(II) complexes show potential antibacterial activity against all the bacterial strains. In general all the metal(II) complexes possess higher antimicrobial activity than the ligand (AMAP). This may be due to the change in structure due to coordination and chelating tends to make metal complexes act as more powerful and potent bacteriostatic agents, thus inhibiting the growth of the microorganisms. The main reason for the increasing antimicrobial activity of the compounds is due to the presence of two azomethine groups in the same molecule. It is concluded that the Ni(II) complex showed higher activity towards the bacteria. Other metal(II) complexes like Cu(II) and Co(II) complexes exhibit moderate antibacterial activity.

CHAPTER IV

Studies on metal(II) complexes of 6,6'-(6-hydroxypyrimidine-2,4-diyl)bis (azanylylidene) (bis (methanylylidene)) bis(2,4-dichlorophenol)-[hamd]

Transition metal complexes of cobalt(II), nickel(II) and copper(II) have been synthesized from the ligand 6,6'-(6-hydroxypyrimidine-2,4-diyl)bis (azanylylidene) (bis (methanylylidene)) bis(2,4-dichlorophenol) (**Scheme 2**). UV-Visible, magnetic susceptibility, Infrared, ¹H-NMR, Mass and Electron spin resonance (ESR), powder XRD and TGA techniques have been used to elucidate the structures of metal(II) complexes.

**Scheme 2. Synthesis of ligand (HAMD)**

The $^1\text{H-NMR}$ spectrum of the ligand (HAMD) was recorded in DMSO. The ligand exhibits two singlets at 4.4 ppm and 4.8 ppm for phenolic-OH protons. The aromatic protons have resonated in the range of 6.0 ppm-6.5 ppm. The N=CH has a characteristic peaks at 7.0 ppm and 7.5 ppm. The -OH proton of hydroxy pyrimidine resonate at 9.5 ppm.

The ligand (HAMD) was studied with various metals like Cu^{2+} , Co^{2+} , Zn^{2+} , Mg^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Cr^{3+} , Al^{3+} , Ba^{2+} , Sr^{2+} and Ni^{2+} . Among the cations, Co^{2+} has a significant effect with the ligand. The presence of absorption band with increasing intensity at 610 nm showed a bathochromic shift is due to the formation of $[\text{Co}(\text{HAMD})]$. Other metal ions like Cu^{2+} , Zn^{2+} , Mg^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Cr^{3+} , Al^{3+} , Ba^{2+} , Sr^{2+} and Ni^{2+} has no effects with the ligand.

The absorption spectrum of the HAMD shows absorption peaks at $39,840\text{ cm}^{-1}$ (ϵ , $2108\text{ M}^{-1}\text{ cm}^{-1}$), $35,971\text{ cm}^{-1}$ (ϵ , $1987\text{ M}^{-1}\text{ cm}^{-1}$) which is attributed to $n\text{-}\pi^*$ intra ligand charge transition and $\pi\text{-}\pi^*$ transitions respectively arising from azomethine (CH=N) chromophores that were present in the compounds. The electronic absorption spectrum of Co(II) complex of HAMD displayed three bands at $33,898\text{ cm}^{-1}$ (ϵ , $1865\text{ M}^{-1}\text{ cm}^{-1}$), $16,393\text{ cm}^{-1}$ (ϵ , $410\text{ M}^{-1}\text{ cm}^{-1}$) and $14,492\text{ cm}^{-1}$ (ϵ , $682\text{ M}^{-1}\text{ cm}^{-1}$) which can be assigned to the transitions $^4\text{A}_2 + ^4\text{E} \rightarrow ^4\text{A}_2(\text{P})$, $^4\text{A}_2 + ^4\text{E} \rightarrow ^4\text{E}(\text{P})$ and $^4\text{A}_2 + ^4\text{E} \rightarrow ^4\text{B}_1$ respectively which are characteristic of square pyramidal geometry. The nickel(II) complex of HAMD exhibits two d-d bands at $31,250\text{ cm}^{-1}$ (ϵ , $1795\text{ M}^{-1}\text{ cm}^{-1}$) and $27,397\text{ cm}^{-1}$ (ϵ , $1752\text{ M}^{-1}\text{ cm}^{-1}$) and these bands may be tentatively assigned as $^3\text{B}_1(\text{F}) \rightarrow ^3\text{E}(\text{P})$ and $^3\text{B}_1(\text{F}) \rightarrow ^3\text{A}_2(\text{P})$ transitions respectively suggesting square pyramidal geometry. The UV-Vis spectrum of the copper(II) complex of HAMD showed two bands at $36,496\text{ cm}^{-1}$ (ϵ , $2015\text{ M}^{-1}\text{ cm}^{-1}$) and $27,247\text{ cm}^{-1}$ (ϵ , $1704\text{ M}^{-1}\text{ cm}^{-1}$) suggesting the transitions $^2\text{B}_1 \rightarrow ^2\text{E}$, and $^2\text{B}_1 \rightarrow ^2\text{B}_2$ respectively are characteristic of square pyramidal geometry. The copper(II) complex of HAMD at 1.98 B.M. is interpreted as suggestive of a five coordinate square pyramidal geometry. Co(II) and Ni(II) complexes of HAMD have magnetic moment values 4.61 and 2.65 B.M respectively, also further suggesting the square pyramidal geometry.

The synthesized HAMD has a characteristic imine peak at 1639 cm^{-1} . A sharp peak at 3426 cm^{-1} is due to the presence of ν (-OH) stretching vibrations present in the pyrimidine ring. A sharp peak at 1413 cm^{-1} corresponds to the ν (-C=N) of the pyrimidine moiety. A sharp peak at 2980 cm^{-1} corresponds to the phenolic ν (-OH) stretching vibration. The peaks of HAMD due to the formation of complex with corresponding metal salts undergo a shift.

In [Co(HAMD)] complex, the peak at 1639 cm^{-1} shifts to 1615 cm^{-1} due to the bonding of imine nitrogen with Co(II) and a new peak arises at 484 cm^{-1} due to formation of ν (Co-N) bond. ν (OH) stretching peak at 3430 cm^{-1} undergoes a great downshift due to the binding of Co(II) with HAMD. ν (-C=N) stretching peak at 1413 cm^{-1} gets shifted to 1447 cm^{-1} due to complexation with cobalt(II) ion. A sharp peak at 2980 cm^{-1} corresponds to the phenolic ν (-OH) stretching vibration is diminished due to complexation. In [Ni(HAMD)] 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 ν (-OH) stretching vibrations is at 3444 cm^{-1} . ν (-C=N) stretching peak at 1413 cm^{-1} gets shifted to 1432 cm^{-1} due to complexation with nickel(II) ion. A sharp peak at 2980 cm^{-1} corresponds to the phenolic ν (-OH) stretching vibration is diminished due to complexation. In [Cu(HAMD)] complex, a band at 1639 cm^{-1} shifted to 1620 cm^{-1} and a new peak at 474 cm^{-1} ν (Cu-N) confirms the complex formation. The ν (-OH) stretching vibration is at 3455 cm^{-1} . ν (-C=N) stretching peak at 1413 cm^{-1} gets shifted to 1451 cm^{-1} due to complexation with copper(II) ion. A sharp peak at 2980 cm^{-1} corresponds to the phenolic ν (-OH) stretching vibration is diminished due to complexation.

The redox behaviour of nickel(II) and copper(II) complexes has been investigated by cyclic voltammetry using ethanol as solvent and potassium chloride (KCl) as supporting electrolyte. Ni(II) complex has reduction peak at 0.9 V and oxidation peak at 0.25 V. The peak separation, $\Delta E_p = 0.65\text{ V}$ which is greater than required for reversible process (59 mV) indicates that the redox couple is irreversible.

Cu(II) complex has two reduction peaks at -0.18 V, -0.55 V in cathodic side and oxidation peak at 0.23 V 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.

Mass spectrometry displays the spectra of the masses of the molecules comprising a sample of material. It is used for elucidating the chemical structures of molecules. The mass spectra of the **Cu(II)(HAMD)** shows a peak at m/z 529 which is due to (M-1) confirmed the 1:1 stoichiometric composition of the metal(II) complexes of **[M(HAMD)]** type. The peak at m/z 239 is due to the fragmentation of ligand HAMD.

The simultaneous TG/DT analysis of the Ni(II) 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 210 °C. TGA can record directly the weight change as a function of temperature or time for transitions that involve dehydration or decomposition. The TG curve of the Ni(II) complex shows a two -step decomposition. In the TG curve of Ni(II) complex, the first step of decomposition is 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 Ni(II) metal complex. 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.

The profile X-band ESR spectrum of the powdered Cu^{2+} complex is consistent with square pyramidal geometry around Cu^{2+} center which agree with the electronic spectral data. The positive contribution of g value of Cu^{2+} complex from the value of free electron (**2.0023**) is due to the measurable covalent character in the M→L bonding.

The fluorescence spectra of the ligand and its metal(II) complexes were recorded in ethanol at room temperature with excitation wavelength at 320 nm. Significant differences in positions of emission maximum of ligand and its complexes establish the complexation process. Enhancement of fluorescence through complexation is much interested as it opens up the opportunity for photochemical applications of these complexes. The fluorescence spectrum of the ligand exhibited weak fluorescence emission at 465 nm. On complexation with metals like Co(II), Ni(II) and Cu(II) the emission peaks are observed. The peaks observed at 500 nm and 560 nm for cobalt(II) complex of HAMD, the peak observed at 495 nm for nickel(II)

complex of HAMD, the peaks observed at 400 nm and 490 nm for copper(II) complex of HAMD confirm the complexation of metal(II) ions with the ligand.

Powder XRD patterns of HAMD, Co(II), Ni(II) and Cu(II) complexes of HAMD recorded in the range show the sharp crystalline peaks indicating their crystalline phase.

XRD analysis of cobalt(II) complex of HAMD revealed three moderate reflections at 12, 22 and 27 which were not shown by ligand, verifying the complexation of the metal ion (Co(II)) with HAMD. X-ray diffraction analysis of nickel(II) complex of HAMD revealed four moderate reflections at 14, 16, 33 and 60 which were not shown by ligand. It confirms the complexation of the metal ion (Ni(II)) with HAMD. XRD analysis of copper(II) complex of HAMD revealed three moderate reflections at 28, 34 and 53 which were not shown by ligand confirming the complexation of the metal ion (Cu(II)) with HAMD.

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.2)

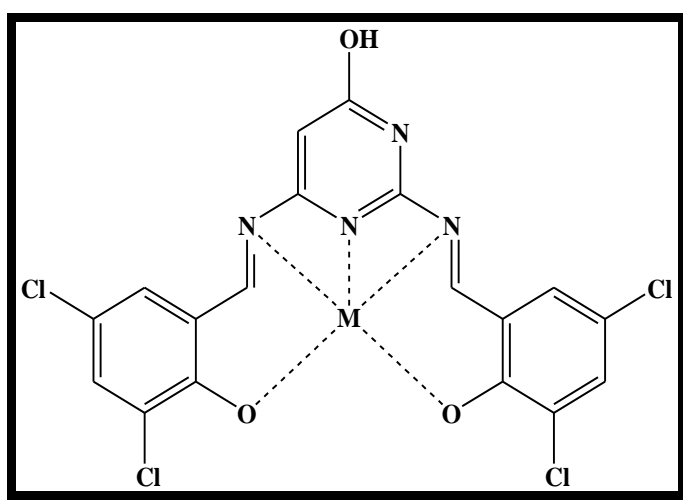


Fig.2. Proposed structure of metal(II) complexes

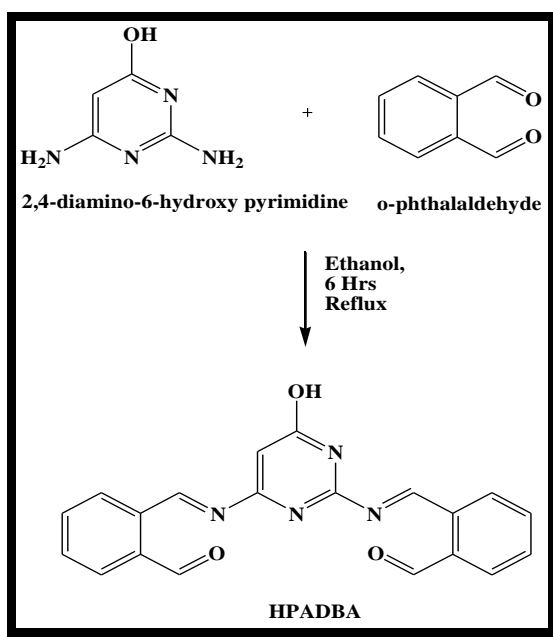
All the newly synthesized ligand HAMD and the metal(II) complexes were screened for their *in vitro* antimicrobial activity. The microorganisms employed for antibacterial studies were gram negative bacteria such as *Escherichia coli*, *Pseudomonas aeruginosa*, and gram positive bacteria such as *Staphylococcus aureus*,

and *Bacillus subtilis*. The antimicrobial activity data clearly illustrates that the metal(II) complexes have significant antibacterial activity against tested organism. All complexes display a high order of antibacterial activity than the ligand. It is concluded that the Co(II) complex showed higher activity towards gram negative bacteria (*E.coli*, *P.aeruginosa*) and gram positive bacteria (*Bacillus subtilis* and *Staphy.aureus*). Ni(II) and Cu(II) complexes have significant activity towards all the bacteria.

CHAPTER V

Spectral and biological studies on metal(II) complexes of 2,2'-((6-hydroxypyrimidine-2,4-iy1)bis(azanylylidene))bis(methanylylidene)) dibenzaldehyde [HPADBA]

Schiff base metal(II) complexes derived from *o*-phthalaldehyde with 2,4-diamino-6-hydroxy pyrimidine (**Scheme 3**) and their Co(II), Cu(II) and Zn(II) complexes have been synthesized. UV-Visible, magnetic susceptibility, Infrared, ¹H NMR, Mass and Electron spin resonance (ESR), powder XRD and TGA techniques have been used to elucidate the structures of metal complexes. Spectroscopic and analytical data of the complexes suggested distorted octahedral geometry for cobalt(II), copper(II) and zinc(II) complexes.



Scheme 3. Synthesis of ligand (HPADBA)

The ligand (HPADBA) was characterized using $^1\text{H-NMR}$, which was recorded using DMSO as the solvent. (N=CH) has a characteristic peak at 7.27 ppm. The aromatic protons has resonated in the range of (7.0-7.8) ppm.

The Ligand (HPADBA) was studied with various metals like Cu^{2+} , Co^{2+} , Zn^{2+} , Mg^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Cr^{3+} , Al^{3+} , Ba^{2+} , Sr^{2+} and Ni^{2+} . Among the cations, zinc(II) has a significant effect with the ligand. The presence of absorption band with increasing intensity at 430 nm shows a bathochromic shift. Other metal ions like Cu^{2+} , Co^{2+} , Mg^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Cr^{3+} , Al^{3+} , Ba^{2+} , Sr^{2+} and Ni^{2+} has no effects with the ligand.

Co(II) complex of HPADBA exhibit three d-d bands in electronic absorption spectrum at $19,685\text{ cm}^{-1}$, $33,557\text{ cm}^{-1}$ and $45,871\text{ cm}^{-1}$ assignable to $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})$, $^4\text{T}_{1g} \rightarrow ^4\text{A}_{2g}$ and $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$ transitions respectively, and the magnetic moments for the cobalt(II) complex in the 4.64 BM supporting octahedral geometry. The Cu(II) complex of HPADBA under the present investigation display two to three absorption bands at $33,557\text{ cm}^{-1}$, $25,062\text{ cm}^{-1}$ and $13,297\text{ cm}^{-1}$ which are assigned as intraligand charge transfer (INCT) bands and $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$ transitions respectively. Their μ_{eff} values of 1.84-1.95 BM supportive of octahedral geometry around Cu(II). Their molar extinction coefficient (ϵ) varies to several hundred $\text{M}^{-1}\text{ cm}^{-1}$ supporting again the non centro symmetric nature of the complex.

A broad band centred at 3320 cm^{-1} is the characteristic of $\nu(\text{-OH})$. The IR spectrum of the metal(II) complexes show bands at 720 cm^{-1} , 713 cm^{-1} and 718 cm^{-1} . These vibrations are due to the bonding of salicylaldehydic oxygen with the metals, $\nu(\text{M-O})$ stretching vibrations in the complexes. The $\nu(\text{C-H})$ bending peak is arrived at 810 cm^{-1} . The bands at 1620 cm^{-1} , 3220 cm^{-1} are due to $\nu(\text{C}=\text{N})$ stretching, pyrimidine -OH stretching respectively. IR spectrum of the metal(II) complexes show significant variations and lower shifts compared with the free ligand confirms the complex formation.

The redox behaviour of copper(II), zinc(II) and cobalt(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.

The Cu(II) complex has one reduction peak at -0.12V in cathodic side and oxidation peak at 0.11V in anodic side. The Co(II) complex has reduction peak at -1.8V and oxidation peak at 0.05V. The Zn(II) complex has reduction peak at -0.8V and oxidation peak at 0.1V. The peak separation, $\Delta E_p = 0.75V$ which is greater than required for reversible process (59 mV) indicates that the redox couple is irreversible.

The mass spectra of the Zn(II) complex of HPADBA shows a peak at m/z 529 which is due to $(M+H+38)$ confirmed the 1:1 stoichiometric composition of the metal(II) complexes of $[M(HPADBA)Cl]Cl$ type. The adduct formation is due to K^+ ions in it. The peak at m/z 239 is due to the fragmentation of ligand HPADBA.

The simultaneous TG/DT analysis of the Zn(II) metal complex was studied from temperature from 30°C to 1000 °C under a nitrogen atmosphere .The TG curve of the Zn(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 Zn(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 Zn(II) metal complex. In third step the complex is completely decomposed and removed as (ZnO) at above 960 °C. DTG spectrum clearly shows the exothermic nature of the reaction process. The Differential Thermal Analysis curve may be attributed to the decomposition of the non-coordinated part of the ligand.

The slow rotation of the complex is resulted in room temperature. As a result a sharp spectrum which is well simulated is obtained. The intensity of the EPR signal significantly decreased which indicates the formation of the copper(II) complex of HPADBA as shown in the concentration distribution curves and which are denoted by black lines. This phenomenon indicated that the complex is most probably a monomeric species of the EPR signal.

The fluorescence spectra of the ligand and its metal(II) 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(II), Cu(II) and Zn(II), the emission peaks are

observed at 500 nm and 560 nm for cobalt(II) complex, 390 nm and 490 nm for copper(II) complex and 350 nm and 390 nm for zinc(II) complex. It also confirms the complexation of metal(II) ions. Significant differences in positions of emission maximum of ligand and its complexes establish the complexation process.

Powder X-ray diffraction patterns of the metal complexes show the sharp crystalline peaks indicating their crystalline phase. XRD analysis of copper(II) complex revealed three moderate reflections at 23, 38, 52 and 62 which were not shown by the ligand (HPADBA), confirms the conjugation of the metal ion (copper(II)) with the ligand. XRD analysis of cobalt(II) complex revealed three moderate reflections at 36, 44 and 77 which were not shown by ligand, suggests the conjugation of the metal ion (cobalt(II)) with HPADBA. XRD analysis of zinc(II) complex revealed four moderate reflections at 16, 28, 51 and 70 which were not shown by ligand, verifies the conjugation of the zinc(II) with the ligand.

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. 3**)

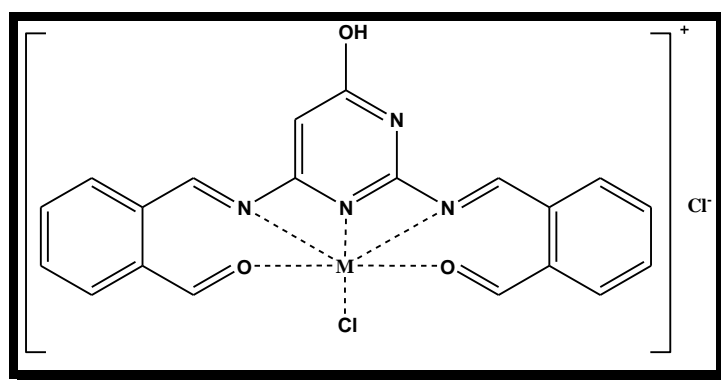


Fig.3. Proposed structure of metal(II) complexes of HPADBA

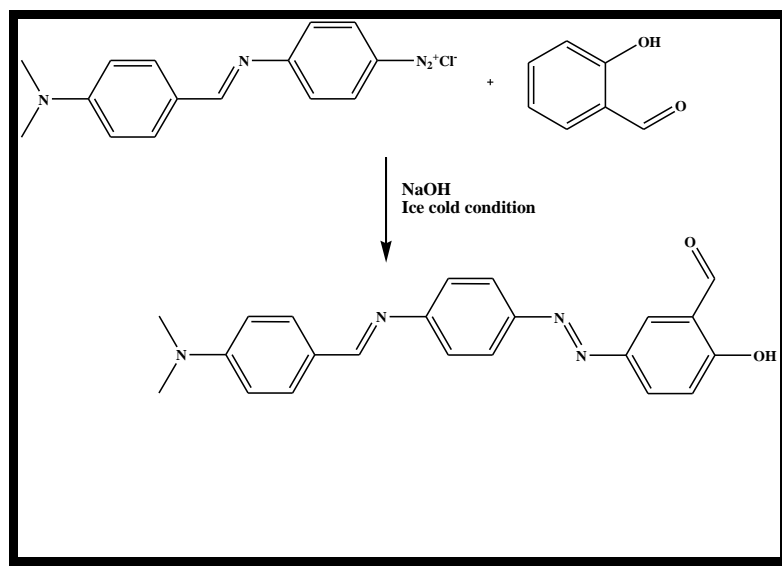
All the compounds showed a significant biological activity against four bacteria species. On comparing the biological activity of the ligand and its metal(II) complexes with the standard, the zinc(II) complex shows potential antibacterial activity against all the bacterial strains.

CHAPTER VI

Studies on metal(II) complexes of

5-((4-((4-(dimethylamino)benzylidene) amino)phenyl)diazynyl)-2-hydroxybenzaldehyde [DBAPDH]

The synthesized ligand 5-((4-((4-(dimethylamino)benzylidene) amino)phenyl)diazynyl)-2-hydroxybenzaldehyde (**Scheme 4**) and its Co(II), Cu(II) and Zn(II) complexes have been synthesized. UV-Visible, magnetic susceptibility, Infrared, ^1H NMR, Mass and Electron spin resonance (ESR), powder XRD and TGA techniques have been used to elucidate the structures of metal(II) complexes.



Scheme 4. Synthesis of ligand (DBAPDH)

The ^1H NMR spectrum of ligand (DBAPDH) is recorded in DMSO. The ^1H NMR spectrum of the ligand has a peak at 3.50 ppm which corresponds to N- $(\text{CH}_3)_2$ Protons. N=CH protons resonate at 5.0 ppm. The aromatic protons are resonating at 7.8- 8.0 ppm. The aldehydic protons resonate at 12.8 ppm and 13.0 ppm.

The ligand (DBAPDH) was studied with various metals like Na^{2+} , Ca^{2+} , Mg^{2+} , Co^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} and Cd^{2+} . Among the cations copper has a significant effect with the ligand. The presence of absorption band at 858 nm shows a bathochromic

shift. Other metal ions like Na^{2+} , Ca^{2+} , Mg^{2+} , Co^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} and Cd^{2+} has no effects with the azo ligand. A distinct colour change from red to brown occurs due to the complexation of the ligand with Cu^{2+} .

The Co(II) complex of DBAPDH exhibit three d-d bands at $14,492\text{ cm}^{-1}$, $19,607\text{ cm}^{-1}$ and $21,276\text{ cm}^{-1}$ assignable to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions respectively, and the magnetic moment for the cobalt(II) complex in the 4.76 BM supporting octahedral geometry. Ni(II) complex of DBAPDH show bands at $12,738\text{ cm}^{-1}$, $15,748\text{ cm}^{-1}$ and $21,978\text{ cm}^{-1}$ due to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions respectively with comparatively low intensities (ϵ). The magnetic moments value of above Ni(II) complexes fall the range of 3.21-3.31 BM range normally observed for octahedral coordination geometry. The Cu(II) complex of DBADPH under the present investigation display two to three absorption bands at $11,655\text{ cm}^{-1}$ and $16,949\text{ cm}^{-1}$ which are assigned as an intraligand charge transfer (ILCT) band and ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transitions respectively. Their μ_{eff} values of 1.84-1.95 BM supportive of distorted octahedral geometry around Cu(II). Their molar extinction coefficient (ϵ) varies to several hundred $\text{M}^{-1}\text{ cm}^{-1}$ supporting again the non centro symmetric nature of the complex.

A broad band centered at 3420 cm^{-1} in the ligand is the characteristic of $\nu(\text{-OH})$. The IR spectrum of the ligand shows a broad band at 3133 cm^{-1} which is due to $\nu(\text{N-H})$ stretching vibration. A peak at 828 cm^{-1} is due to (C-H) bending. The band at 1182 cm^{-1} is assigned to $\nu(\text{C}=\text{N})$ stretching and a band at 3420 cm^{-1} and two weak bands at 1550 cm^{-1} and 1601 cm^{-1} show the presence of phenolic $\nu(\text{-OH})$ and $\nu(\text{N}=\text{N})$ respectively. The peaks of the ligand undergo a considerable shift due to complexation with metal ions and there by confirming the formation of complex.

In $[\text{Co}(\text{DBAPDH})_2\text{Cl}_2]$ complex the peak at 1399 cm^{-1} shifts to 1325 cm^{-1} due to the bonding of oxygen with Co(II) and a new peak arises at 510 cm^{-1} due to formation of (Co-N) bond. A peak at 3420 cm^{-1} corresponding to $\nu(\text{-OH})$ shifts to 3104 cm^{-1} due to bonding with metal(II) ion. In $[\text{Ni}(\text{DBAPDH})_2\text{Cl}_2]$ complex the peak at 1399 cm^{-1} shifts to 1330 cm^{-1} due to the bonding of oxygen with Ni(II) and a new peak arises at 480 cm^{-1} due to formation of (Ni-N) bond. A peak at 3420 cm^{-1}

corresponding to ν (-OH) shifts to 3010 cm^{-1} due to bonding with metal(II) ion. In $[\text{Cu}(\text{DBAPDH})_2\text{Cl}_2]$ complex the peak at 1399 cm^{-1} shifts to 1339 cm^{-1} due to the bonding of oxygen with Cu(II) and a new peak arises at 492 cm^{-1} due to formation of (Cu-N) bond. A peak at 3420 cm^{-1} corresponding to ν (-OH) shifts to 3130 cm^{-1} due to bonding with metal(II) ion.

The Cyclic voltammogram of copper(II) complex shows oxidation peaks at 0.16V and -0.4V. The peak separation, $\Delta E_p = 0.5\text{ V}$ [41] which is greater than required for reversible process (59mV) indicates that the redox couple is irreversible and the ratio of cathodic to anodic peak current corresponding to a simple one electron process.

The mass spectra of the Cu(II) complex of DBAPDH shows a peak at m/z 877 which is due to (M+H) confirmed the 1:2 stoichiometric composition of the metal(II) complexes of $[\text{M}(\text{DBAPDH})_2\text{Cl}_2]$. The peak at m/z 325 is due to the fragmentation of ligand DBAPDH.

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

The ligand (DBAPDH) shows fluorescence excitation maximum at 390 nm, 561 nm and emission maximum at 545 nm in DMSO solvent. The Cu(II) complex exhibit emission bands at 560-610 nm. Significant differences in the positions of emission maximum of ligand and its complex establish the coordination of the metal ion to the ligand.

Powder XRD patterns of DBAPDH and its Co(II), Ni(II) and Cu(II) complexes recorded in the range ($2\theta = 0-80$) show the sharp crystalline peaks indicating their crystalline phase. XRD analysis of cobalt(II) complex revealed three moderate reflections at 17, 38 and 74 which were not shown by the ligand (DBAPDH), verifying the conjugation of the cobalt(II) with DBAPDH. XRD analysis of nickel(II) complex revealed four moderate reflections at 13, 20, 32 and 65 which

were not shown by the ligand, verifying the conjugation of the nickel(II) with DBAPDH. XRD analysis of copper(II) complex revealed three moderate reflections at 21, 28 and 44 which were not shown by the ligand, verifying the complexation of the Cu(II) with DBAPDH. From the fluorescence study it is evident that these azo Schiff based compounds might possess potential molecular sensing or photoconductive applications.

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. 4)

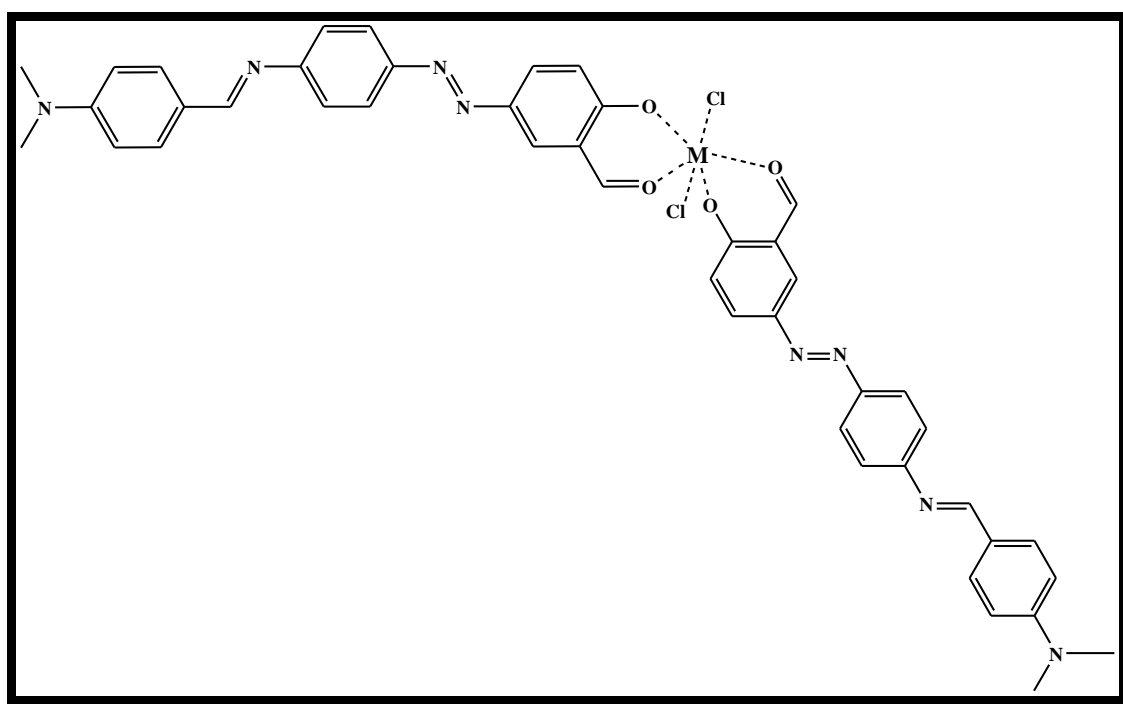


Fig.4. Proposed structure of metal(II) complexes

All the tested compounds showed a remarkable biological activity against different types of bacteria species. On comparing the biological activity of the ligand and its metal(II) complexes with the standard, it is inferred that, the copper(II) complex shows potential antibacterial activity against all the bacterial strains. It is concluded that the Cu(II) complex showed higher activity towards the bacteria. Other metal(II) complexes exhibit moderate antibacterial activity. Ni(II) and Co(II) complexes have significant activity. From the data it is found that all the compounds have displayed good activity.

Concluding Remarks

- In general all the synthesized Schiff base compounds might have potential application for high thermal stability and have selectively sensing character because of their structural modifications.
- All the complexes are considered as a new class of fluorescence material and exhibit appreciable photoactive properties that could be useful in photonic devices.
- The Cu(II) complexes of all the ligands are reported to undergo an irreversible electron transfer process.
- On comparison with all the complexes and ligands, the copper(II) complexes reveal remarkable antimicrobial activity.
- Comparing the solvatochromic behaviour of (**AMAP**) and (**HAMD**) the bathochromic shift of (**AMAP**) was not strong due to the absence of electron withdrawing Cl group whereas in (**HAMD**) the presence of two chlorine atoms and pyrimidine moiety enhances the strong shift with increasing solvent polarity.
- The architectural beauty with tremendous applications of these compounds are due to the presence of azomethine moiety with hydroxy pyrimidine in a same compound.