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RESEARCH ARTICLE .....!!!

**SYNTHESIS AND CHARACTERIZATION OF SCHIFFBASE METAL(II)  
COMPLEXES DERIVED FROM BENZOYLACETONE****M. Kalaimathi, K. Southamani, R. Anitha, Y. Yesuthangam**

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**KEYWORDS:**

UV, IR, antimicrobial activity, ligand, steric effect.

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India.**ABSTRACT**

Naturally occurring coordination compounds are important to the living organisms. These compounds play a variety of essential roles in biological systems. Electrical conductivity and thus dissociation properties of the complexes were measured by applying a current through aqueous solutions. Werner's theory provided the basis for all modern theories of chemical bonding. Crystal field theory for co-ordination complexes was proposed by Bethe, which permitted to predict the properties. It has been proposed to synthesize the complexes of bivalent metal ions and to characterize them with the aid of modern physico-chemical to biochemically relevant studies. Due to the difficulty in synthesis faced, it has been suggested to synthesize and characterize the metal (II) complexes of Schiff base derived from aldehyde or ketone and amine. It has been proposed to characterize them with the aid of conductance measurement, melting point, solubility and to determine structure and bonding with the aid of physical techniques like IR, UV and  $^1\text{H}$ NMR spectral studies and also the antimicrobial activity. Since the ligand chosen is a bulkier one, it is thought that it may induce a particular configuration on metal complexes. Steric effect may lead to the preferential stability of stereochemistry.

## INTRODUCTION

Chemistry has played a leading role in changing people's lives, due to its impact in areas such as agrochemicals, the clothing industry, food technology, energy and transport, the pharmaceutical industry and most recently in the manufacture of electronic devices. However, discoveries about eco toxic effects such as endocrine disruption [1] indicated that synthetic chemicals released into the environment have a negative impact on the world ecosystem. Industrial incidents involving explosions at a major South African petrochemical company [2-3] the discovery of persistent organic pollutants and the global warming are examples of chemical disasters. It is because of this reason that chemists are compelled to shoulder the responsibility for the consequences and thus develop new synthetic protocols that are environmentally benign. These new synthetic protocols should comply with green chemistry principles [4]. As an alternative to organic solvents, chemists should employ other strategies to perform chemical reactions, namely ionic liquids, supercritical fluids, water as a solvent and solvent-free conditions. Conventionally, chemical transformations have been carried out in the presence of a solvent to provide a homogeneous medium for the reagents to interact effectively as well as for the isolation and purification of the desired product [5-6].

The key break through occurred when co-ordination chemistry emerged from the works of Alfred Werner, a Swiss chemist who was awarded the Nobel prize in 1913, examined different compounds composed of cobalt(III) chloride and ammonia. The resulting observations made by Werner suggested the existence of complex or co-ordination compounds where the central metal ion is closely bound to a ligand forming a complex compound or ion. Complex can then be bound to other ions which neutralize the charge of the complex ion.

Ligands directly bound to the central metal. The multilevel binding of a co-ordination complexes play an important role in determining the dissociation of these complexes in aqueous solution. Electrical conductivity and thus dissociation properties of the complexes were measured by applying a current through aqueous solutions. Werner's theory provided the basis for all modern theories of chemical bonding. Crystal field theory for co-ordination complexes was proposed by Bethe, which permitted to predict the properties (i.e.) the interpretation of spectra of complexes, magnetic behaviors, stability and stereochemistry of complexes. By forming co-ordination compounds, the properties of both the metal and the ligand are altered.

The nature of bond between the metal and ligand is stronger than intermolecular force because they form directional bonds between the metal ion and the ligands. Metal complexes often have

spectacular colors caused by electronic transitions by the absorption of light. Most transitions that are related to colored metal complexes are either d-d transitions (or) charge transfer bands.

Metal complexes that have unpaired electrons are magnetic. Hence the magnetic behavior depends upon the number of unpaired electron spins present in a complex. Spectral studies provide the direct route for investigating the bonding in complexes [7].

Many metal complexes have powerful antimicrobial activities and are already in common day-to-day use in medicinal field such as silver bandages for treatment of burns, zinc antiseptic creams, bismuth drugs for the treatment of ulcers and metal clusters as anti-HIV drugs. The potential for further development of metal-based drugs and treatments as an antimicrobial agent is enormous and also of great importance with the evolution of drug-resistant bacteria and threats from a range of viral diseases. The discovery and development of antibiotics are among the most powerful and successful achievements of modern science and technology for the control of infectious diseases. The most spectacular advances in medicinal chemistry have been made when heterocyclic compounds played an important role in regulating biological activities. The transition metal complexes of 4-aminoantipyrine and its derivatives have been extensively examined due to their wide applications in various fields like biological, analytical and therapeutical [8-9]. Further, they have been investigated due to their diverse biological properties as antifungal, antibacterial, analgesic, sedative, antipyretic and anti-inflammatory agents [10-12]. Redox active complexes can provide an alternative tool for redox regulation as a therapeutic basis, interfering in oxidative trigger mechanisms in cells. Specific ligands can be useful in the modulation of metal ion reactivity, by modifying their redox potential, hydrophilic/lipophilic characteristics or saturating its coordination sphere and therefore avoiding undesirable interactions with cell components. Particularly, copper based compounds have been investigated that endogenous metals may be less toxic [13].  $\text{Cu}^{2+}$  is a host of low molecular-weight copper complexes have been proven beneficial against several diseases such as tuberculosis, rheumatoid, gastric ulcers and cancers [14-15]. With the increasing incidence of deep mycosis in recent years, there has been an increasing emphasis on screening new and more effective antimicrobial drugs with low toxicity.

Drug resistance has become a growing problem in the treatment of infectious diseases caused by bacteria, fungi, parasite and virus. Infectious diseases like diarrhea, dysentery, tuberculosis, acute respiratory tract infections, AIDS and recently SARS are global threat and their incidences are increasing significantly day by day. Although a number of chemotherapeutic agents are available in market places, the pathogenic organisms are developing resistance to these agents. So, it is important to find out safer, more effective and inexpensive chemotherapeutic agents.

Metals have an esteemed place within medical biochemistry, although until recently this has been restricted predominantly to organic drugs. Recently however, more research has been done in the area of inorganic chemistry, which has led to developments in cancer care, infection control, diabetes, ulcers and neurological, cardiovascular and anti-inflammatory drugs. Metal coordination complexes have been widely studied for their antimicrobial [16-17] and anticancer properties [18]. Many drugs possess modified pharmacological and toxicological properties when administered in the form of metallic complexes. Platinum anticancer drugs are now the widely used anticancer drugs in the world e.g. Cisplatin, carboplatin, oxaliplatin, tetraplatin *etc.*

The coordination environment around copper plays the key role in stabilizing its different oxidation states and hence dictates the redox properties of the central atoms. The treatment with copper complexes produces remarkable pharmacological effects, which are not observed when the parent ligands or inorganic forms of copper are used [19]. Various copper complexes have been reported to inhibit bacterial, fungal, yeast, algal, mycoplasma, and viral growth, as well as to cause the death of these organisms [20].

#### **MATERIALS AND METHODS**

A detailed account of the materials used, the analytical methods employed and physico-chemical methods employed are discussed. The general procedures for the preparation of the ligand and the complexes are also described.

##### **Materials required:**

Absolute alcohol

Benzoylacetone

p-amino phenol

Potassium Carbonate

##### **Metal Salts**

Copper Chloride

Cobalt Chloride

Zinc Chloride

Nickel Chloride

##### **Determination of melting point:**

A small amount of the substance was taken in a cleaned dry mortar with pestle. It was powdered and taken in a small capillary tube and kept in the melting point apparatus. Melting point was noted for the ligand and complexes.

**Electrical conductivity measurement:**

Molar conductance of the complexes were measured in DMSO at room temperature using conductivity bridge with a conductivity cell (cell constant=1.0907). All the measurements were taken at room temperature on freshly prepared solution.

**Synthesis of Schiff base1 (L1):**

This Schiff base was prepared by Benzoyl acetone (5mmol) and p-aminophenol (10mmol) with potassium carbonate in Ethanol (50ml). The reaction mixture was refluxed for 6 hours. The black colored solution was set aside to evaporate and the black crystals that separated were filtered off. The precipitate was washed with pet-ether and recrystallized from ethanol.

**Synthesis of Metal (II) complex:**

(4mmol) of Schiff base Ligand was dissolved in 10 ml of ethanol and (2mmol) of copper chloride was added and stirred for 3 hours at room temperature. The precipitate obtained was filtered and dried. It was washed with pet-ether and recrystallized from ethanol.

The obtained complexes were colored powders and stable for a long time in the open atmosphere. The analytical data for the ligand and its complexes together with some physical properties are summarized in Table.1

**Solubility and conductivity:**

The Schiff base ligands and its metal (II) complexes are soluble in ethanol and DMSO and other common organic solvents. The molar conductance of the complexes is in the range 30-60  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ , which are consistent with non electrolytic nature of the complexes. The table is given below.

**Table: 1 Physical properties of L1 and its complexes**

S.No	Compounds	M.F.	Colour	Melting point	Conductance(mho $\text{cm}^2 \text{mol}^{-1}$ )
1.	Ligand1	$\text{C}_{22}\text{H}_{20}\text{O}_2\text{N}_2$	Black	$89^\circ\text{C}$	-
2.	Cu(II) complex	$\text{Cu}[(\text{L}1)_2 \text{Cl}_2].2\text{H}_2\text{O}$	Black	$232^\circ\text{C}$	8
3.	Co(II) complex	$\text{Co}[(\text{L}1)_2 \text{Cl}_2].2\text{H}_2\text{O}$	Brown	$214^\circ\text{C}$	5
4.	Ni(II) complex	$\text{Ni}[(\text{L}1)_2 \text{Cl}_2].2\text{H}_2\text{O}$	Black	$267^\circ\text{C}$	6
5.	Zn(II) Complex	$\text{Zn}[(\text{L}1)_2 \text{Cl}_2].2\text{H}_2\text{O}$	Black	$228^\circ\text{C}$	8

### Electronic spectra

The energy required for the promotion of an electron from one orbital to another, or more precisely, the excitation of a molecule from its electronic ground state to an electronic excited state, corresponds to absorption of the light in the near infrared, visible or ultraviolet regions of the electromagnetic spectrum. For the complexes of most transition metals, these absorption bands have relatively low intensity and are associated with transition localized on the metal atom. In addition to these bands, most transition metal complexes have considerably stronger bands in the ultraviolet region which are called C.T bands.

There are selection rules for the electronic transitions in complexes. Thus transitions between states of different spin multiplicity are forbidden. These are referred to as 'Spin forbidden' transitions. Further, transitions within a given set of p or d orbitals are forbidden, if the molecule or ion has 'Laporte forbidden' transitions. Spin and Laporte forbidden transitions are very weak, and crystal field theory provides an explanation for this.

The electronic spectrum of the ligand and the representative Metal (II) Schiff base complex is given in Fig. 1-4 respectively and the spectral data has been given in Table 2. The absorption of the ligand L2 is characterized by two main absorption bands in the regions 200-500 nm. The band at  $\lambda_{\max}=235\text{nm}$  is attributed to  $n \rightarrow \pi^*$  transition. The band at  $\lambda_{\max} = 343 \text{ nm}$  corresponds to the  $\pi \rightarrow \pi^*$  transition of the azomethine group. The electronic spectrum of the Cu(II) Complex shows the transition at 468nm and due to  ${}^2E_g \rightarrow {}^2T_{2g}$ . The electronic spectrum of the Co(II) Complex shows the transition at 458nm which may be assigned to ligand metal charge transfer and  ${}^4T_{1g(F)} \rightarrow {}^4T_{2g(P)}$  transition. The electronic spectrum of the Ni(II) Complex shows the transition at 418nm due to  ${}^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$ . These transitions suggest the distorted octahedral geometry for the metal complexes. Details are given in Table 2.

**Table : 2 Electronic Spectral data for L1 and its metal complexes**

S.No	Compound	Wavelength(nm)	Transition	$\mu_{\text{eff}}$	Geometry of the complex
1.	Ligand	343 235	$\pi-\pi^*$ $n-\pi^*$	--	--
2.	Cu(II) complex	468	${}^2E_g \rightarrow {}^2T_{2g}$	1.78	Octahedral
3.	Co(II) complex	432	${}^4T_{1g(F)} \rightarrow {}^4T_{2g(P)}$	4.71	Octahedral
4.	Ni(II) complex	418	${}^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$	3.28	Octahedral

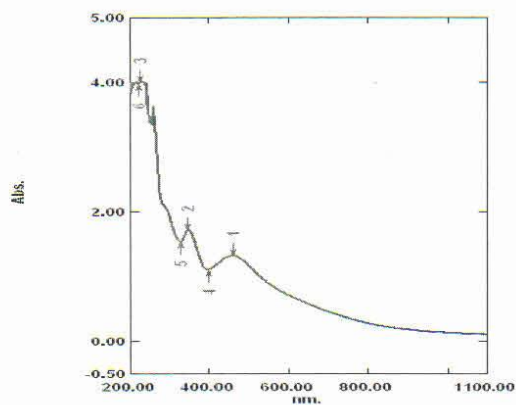


Figure 3 UV-Visible spectra of  $[\text{Co}(\text{L}1)_2 \text{Cl}_2] \cdot 2\text{H}_2\text{O}$

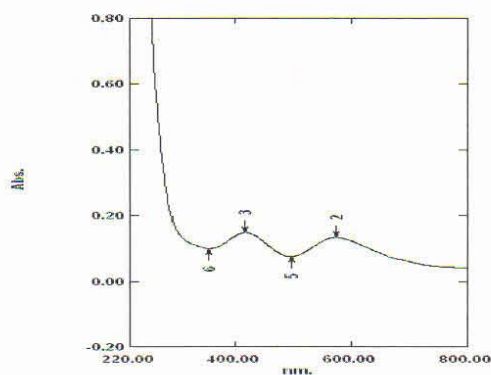


Figure 4 UV-Visible spectra of  $[\text{Ni} (\text{L}1)_2 \text{Cl}_2] \cdot 2\text{H}_2\text{O}$

#### Infrared Spectra:

The Infrared spectra of metal complexes are useful in determining the coordinating groups and atom of the ligands. The shift in the bands give information regarding the mode of linkage in these complexes.

The band at  $1442\text{cm}^{-1}$  corresponds to  $\nu\text{C}=\text{N}$  of the ligand in complexes this strong band shifts to lower frequency indicating the involvement of N present in  $\text{C}=\text{N}$  to the central metal ion. In complexes strong band at  $3263\text{cm}^{-1}$  indicating the presence of water molecules out of the coordination sphere. The synthesised ligands are bidentate in nature. Two among the octahedral sites are occupied by Cl atoms from metal chlorides. The band at  $354\text{ cm}^{-1}$  and  $524\text{ cm}^{-1}$  corresponding to  $\nu\text{M}-\text{N}$  and  $\nu\text{M}-\text{Cl}$ . The values are given in Table 3.

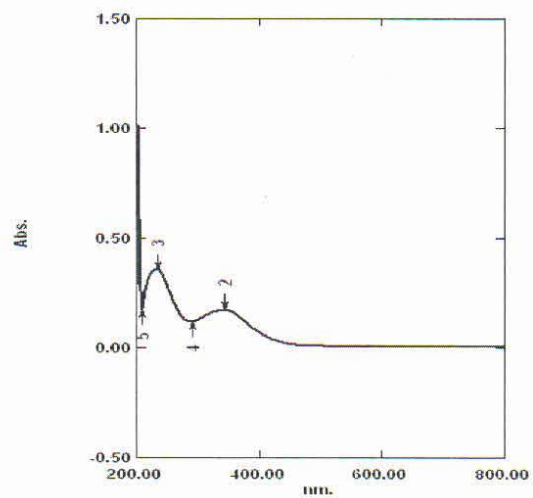


Figure 1 UV-Visible spectra of L1

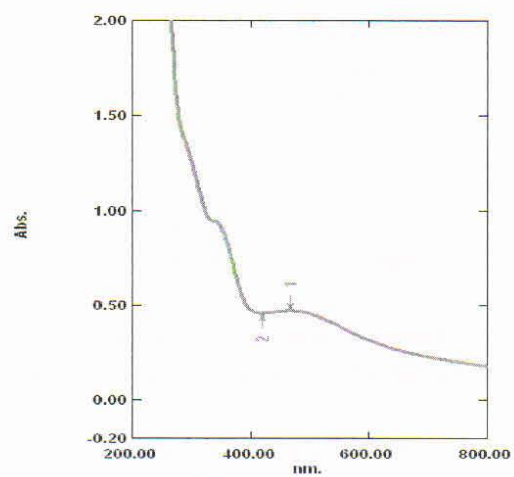
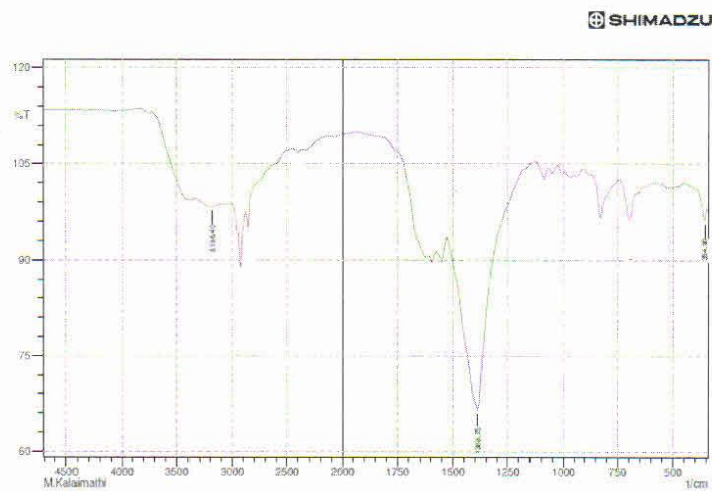


Figure 2 UV-Visible spectra of [Cu(L1)<sub>2</sub> Cl<sub>2</sub>].2H<sub>2</sub>O



**Table : 3 IR Spectral data for L1 and its metal complexes**

Compound	$\nu\text{C}=\text{N}(\text{azomethine})$ $\text{cm}^{-1}$	$\nu\text{OH}(\text{H}_2\text{O})$ $\text{cm}^{-1}$	$\nu\text{M}-\text{N}$ $\text{cm}^{-1}$	$\nu\text{M}-\text{Cl}$ $\text{cm}^{-1}$
Ligand 1	1442	-	-	-
$\text{CuL}_2\text{Cl}_2$	1404	3263	524	408
$\text{CoL}_2\text{Cl}_2$	1388	3186	694	354
$\text{NiL}_2\text{Cl}_2$	1404	3232	502	354
$\text{ZnL}_2\text{Cl}_2$	1381	3210	532	355

**Figure 5 FT-IR Spectra of Ligand 1**

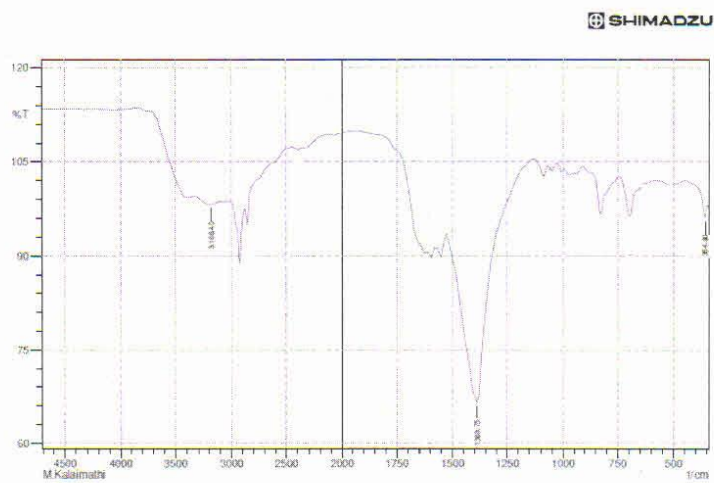


Figure 6 FT- IR Spectrum of [Co(L1)<sub>2</sub> Cl<sub>2</sub>].2H<sub>2</sub>O Complex

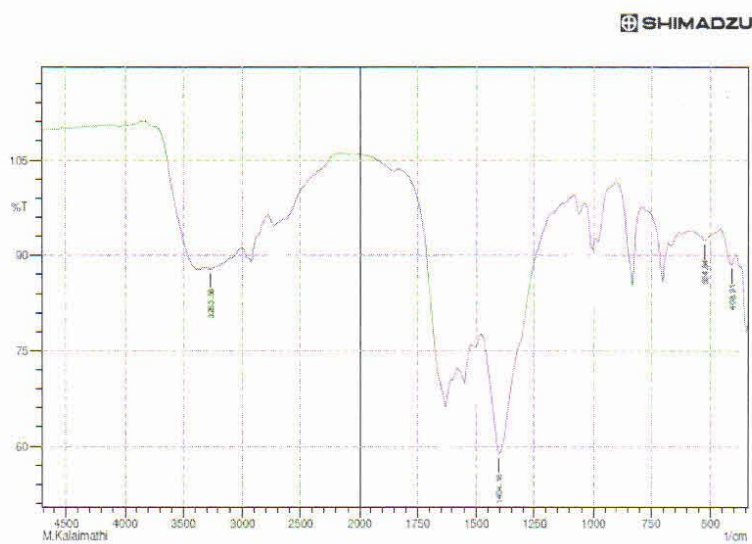
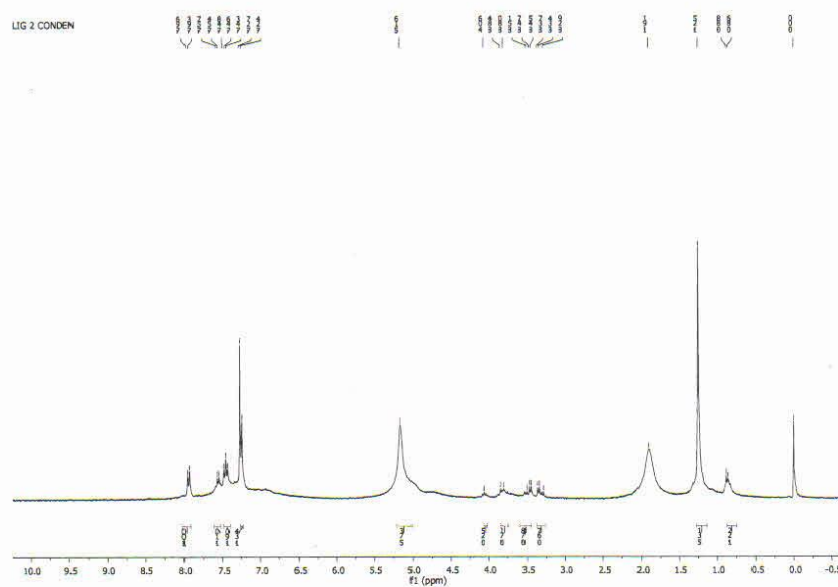


Figure 7 FT- IR Spectrum of [Cu(L1)<sub>2</sub> Cl<sub>2</sub>].2H<sub>2</sub>O Complex

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

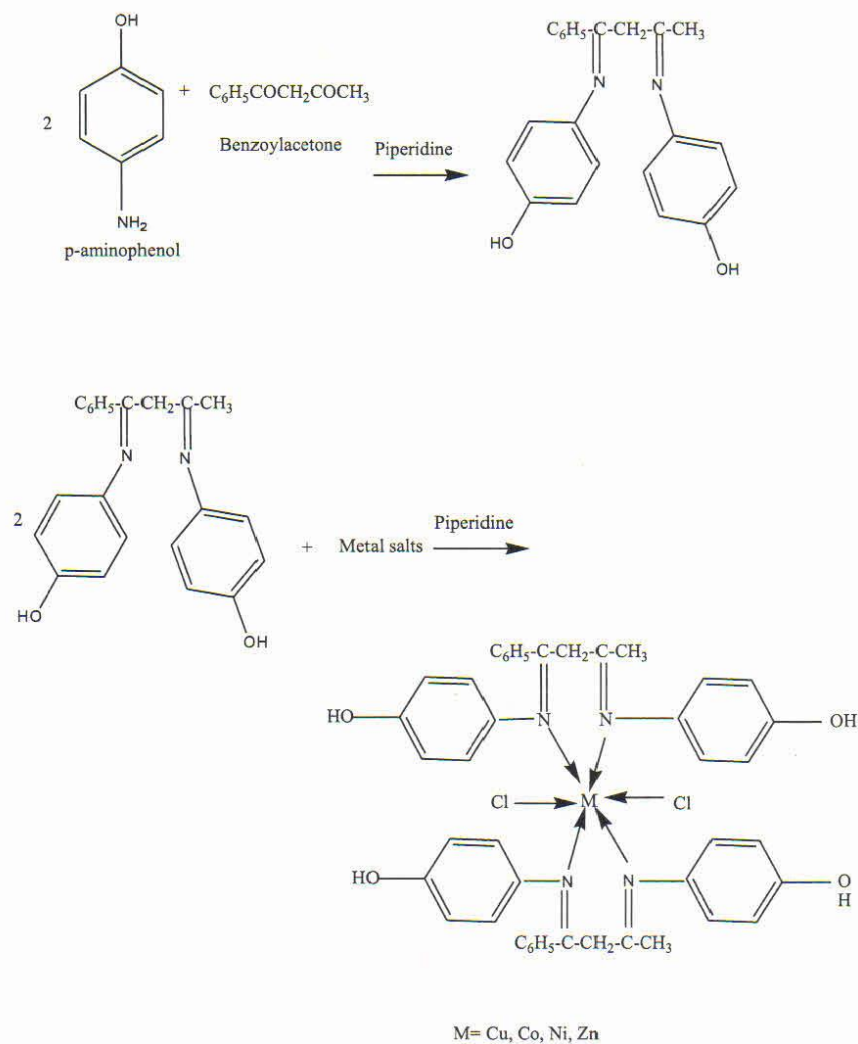
$^1\text{H}$ NMR Spectra of the schiffbase ligand was taken to confirm the binding nature of schiffbase.  $^1\text{H}$ NMR spectra provides the information regarding types of protons present in the ligands.  $^1\text{H}$ NMR spectra of L1 and L2 is given below.

In Ligand1 the signals at 4.50 corresponding to methyl protons and signals at 2.7 corresponding to methylene protons. For aromatic protons, multiplet appeared at 7.2-7.9. The signal at 5.3 corresponds to OH protons.



**Figure 8  $^1\text{H}$ NMR Spectra of L1**

From this spectral data and conductivity measurement the following structures are proposed for L1 and their metal complexes Figure



### Biological Studies:

The ligand and its metal complexes were evaluated for antibacterial activity against gram positive bacteria. *Staphylococcus aureus*, gram negative bacteria *Escherichia coli* and fungi *Candida albicans* by well diffusion agar technique [21]. The antibacterial and antifungal tests were carried out at single concentration 5 mg/ml in ethanol (for ligand) and acetonitrile (for complexes) as solvents. Amikacin and Ketoconazole were used as reference compounds for antibacterial and

antifungal activities respectively. The nutrient agar was used as culture medium. The zone of inhibition was measured in mm. From the observed result, metal complexes showed enhanced antimicrobial activity in some cases over the free ligand [22]. Such increased activity of the metal complexes can be explained on the basis of and chelation theory [23]. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. The delocalization of the  $\pi$ -electrons over the whole chelate ring increases there by it enhances the penetration of the complexes into the lipid membrane and blocks the metal binding sites in the enzymes of microorganisms [24]. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism [25-27].

**Table: 4 Biological activity of L1 and its complexes**

S.No.	Compound	E.Coli	S.aureus	C.albicans
1.	Ligand	6	4	-
2.	Cu(II) complex	8	10	4
3.	Co(II) complex	6	12	4
4.	Ni(II) complex	7	6	5
5.	Zn(II) complex	7	10	4

#### CONCLUSION

The Schiff Base ligand and its metal complex have been synthesized and characterized on the basis of IR, UV-visible, and  $^1\text{H}$ NMR spectral data, the ligands coordinated to metal ions in bidentate manner. The octahedral geometry has been proposed for the metal complexes. The ligands show mild activity against fungi. The antibacterial activities are more pronounced for the S.Aureus than E.Coli the antibacterial activities of complexes are greater than ligands.

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