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RESEARCH ARTICLE!!!

**SYNTHESIS AND CHARACTERIZATION OF SCHIFFBASE METAL (II)
COMPLEXES DERIVED FROM BENZOYLACETONE AND P-
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Mother Teresa Women's University, Kodaikanal, India.¹PG & Research Center of Chemistry, The American College, Madurai.**KEYWORDS:**Schiff base; S.Aureus;
E.coli; IR; UV-visible
and H¹NMR.**For Correspondence:****M. Kalaimathi *****Address:**PG & Research Center of
Chemistry, Jayaraj
Annapackiam College for
Women Affiliated to
Mother Teresa Women's
University, Kodaikanal,
India.**ABSTRACT**

The Schiff bases and their complexes were recently reported to be significant antifungal agents. so we have evaluated in vitro antifungal activity of our complexes against various fungi. 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-visible and HI NMR spectral studies and also the antimicrobial activity. In the present work, we synthesized and characterized the Schiff base metal complexes. In addition the results of their antifungal and antimicrobial activities are also reported. The nature of bond between 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 transition by the absorption of light, most transitions that are related to colored metal complexes are either d-d transition (or) charge transfer bands. The Schiff base ligand and its metal complex have been synthesized and characterized on the basis of IR, UV-visible, and HI NMR spectral data, the ligands coordinated to metal ions in bidentate manner. The octahedral geometry has been proposed for the metal complexes. The antimicrobial activities are more pronounced for S.Aureus than E.Coli. Anti bacterial activities of complexes are greater than ligand.

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].

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. 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 [5].

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 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 [6-7]. Further, they

have been investigated due to their diverse biological properties as antifungal, antibacterial, analgesic, sedative, antipyretic and anti-inflammatory agents [9-11]. 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 [12-13] and anticancer properties [14]. 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 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 [15]. 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 [16].

Generally the stability of complex decreases with increasing atomic number for more electropositive metals. The chelate effect is larger for transition metal ions than for non-transition metal ions. Nitrogen and Oxygen as co-coordinating chromophores for the stablest and structurally well characterized complexes.

The Schiff bases and their complexes were recently reported to be significant antifungal agents [17]. So we have evaluated the in vitro antifungal activity of our complexes against various fungi. In the present work, we report here the synthesis and structural characterization of copper (II) complexes with Schiff bases. In addition, the results of their antifungal and antibacterial activities are also reported.

The growing importance of the Schiff bases and their metal complexes in modern coordination chemistry is attributable to recent observations about their antibacterial, anti-fungal and oxygen

carrier properties. A general study of the structural and bonding features of the various Schiff base complexes can better help the understanding of these complexes. Schiff bases derived from the condensation of 4-aminopyridine with diketones represent an important class class of chelating ligands and their metal complexes are of great interest because of their applications in analytical chemistry, industry, modeling in some biosystems, transport processes, stabilization of higher oxidation states, catalytic and extraction properties [18-22]. Schiff base complexes showed greater activity than other metal complexes.

Antibacterial activity is dependent on

- i. Molecular structure of the compounds,
- ii. Solvent used,
- iii. Bacterial strain considerations.

The biological activity of the complexes follow the order
 $\text{Co(II)}=\text{Fe(II)}>\text{Ni(II)}=\text{Zn(II)}=\text{Cu(II)}>\text{Cd(II)}$.

Magnetic susceptibility measurements of the complexes in the solid state were determined using a Gouy balance at room temperature by using copper sulphate as calibrant. Magnetic susceptibility values of the complexes at room temperature are consistent with square planar geometry around the central metal ion. Except for the Mn (II) and Vo (II) complexes which show octahedral and square pyramidal geometry respectively have been studied and the neutral nature of the ligand through the conductance measurements [23].

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
Benzoyl acetone
P- Anisidine
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-anisidine (10mmol) with potassium carbonate in Ethanol (50ml). The reaction mixture was refluxed for 6 hours. The white colored solution was set aside to evaporate and the white color crystals that separated was filtered off. The precipitate was washed with pet-ether and recrystallized from ethanol.

Synthesis of Metal (II) complex:

(4mmole) of Schiff base Ligand was dissolved in 10 ml of ethanol and (2mmol) of cobalt 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 Schiffbase ligand 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.

Table:1 Physical properties

S.No	Compounds	M.F.	Colour	Melting point	Conductance(mho $\text{cm}^2 \text{mol}^{-1}$)
1.	Ligand	$\text{C}_{22}\text{H}_{20}\text{O}_2\text{N}_2$	Dark green	89°C	-
2.	Cu(II) complex	$\text{Cu}[\text{C}_{30}\text{H}_{28}\text{O}_6\text{N}_2\text{Cl}_2].2\text{H}_2\text{O}$	Black	23s2°C	10
3.	Co(II) complex	$\text{Co}[\text{C}_{30}\text{H}_{28}\text{O}_6\text{N}_2]$	Brown	214°C	16
4.	Ni(II) complex	$\text{Fe}[\text{C}_{30}\text{H}_{28}\text{O}_6\text{N}_2]$	Black	267°C	14

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. 1-5, respectively and the spectral data has been given in Table 2. The absorption of the ligand L 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 ${}^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$. The electronic spectrum of the Zn(II) Complex shows the transition at 468nm and due to ${}^2E_g \rightarrow {}^2T_{2g}$. These transitions suggest the distorted octahedral geometry for the metal complexes

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

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

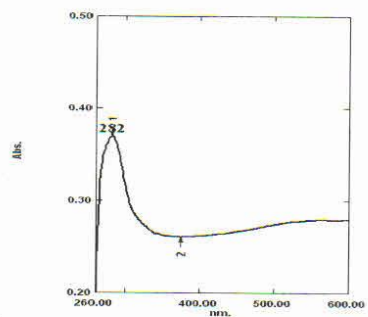


Figure 1 UV-Visible spectra of L1

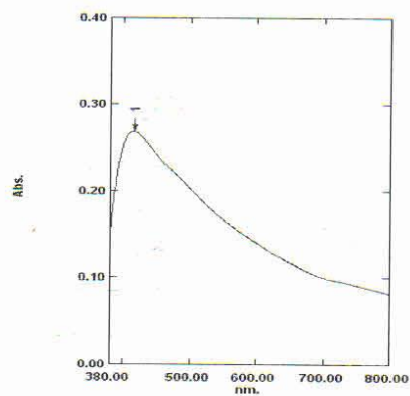


Figure 2 UV-Visible spectra of [Cu(L2)₂ Cl₂].2H₂O

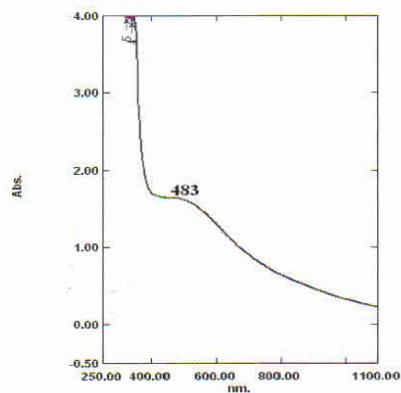


Figure 3 UV-Visible spectra of $[Co(L1)_2 Cl_2].2H_2O$

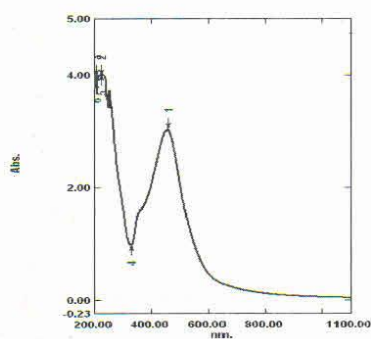
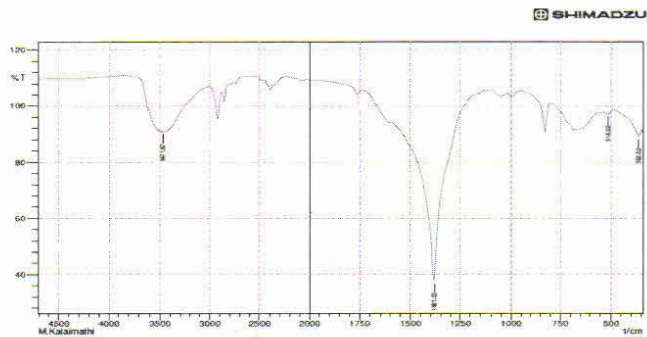


Figure 4 Visible spectra of $[Ni (L1)_2 Cl_2].2H_2O$

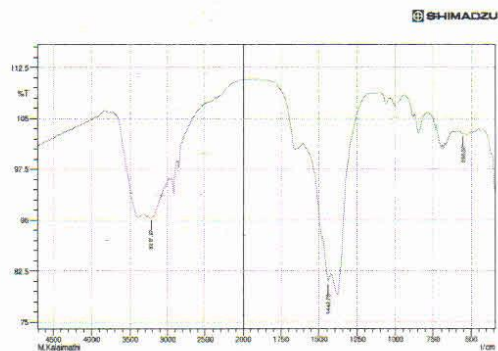
Infrared Spectra:

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 1442cm^{-1} corresponds to $\nu C=N$ of the ligand in complexes this strong band shifts to lower frequency indicating the involvement of N present in $C=N$ to the central metal ion. In complexes strong band at 3263cm^{-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 cm^{-1} and 524 cm^{-1} corresponding to $\nu M-N$ and $\nu M-Cl$. The values are given in Table 3



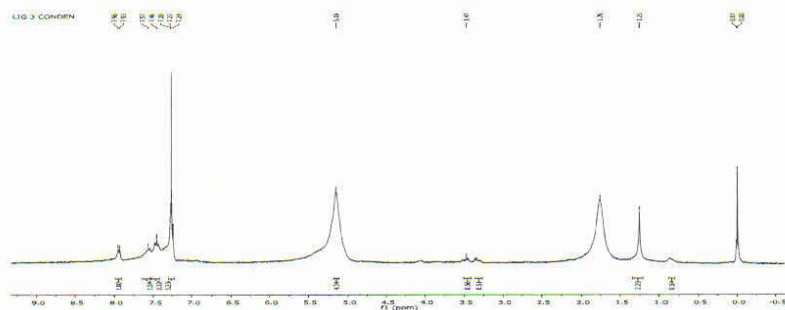
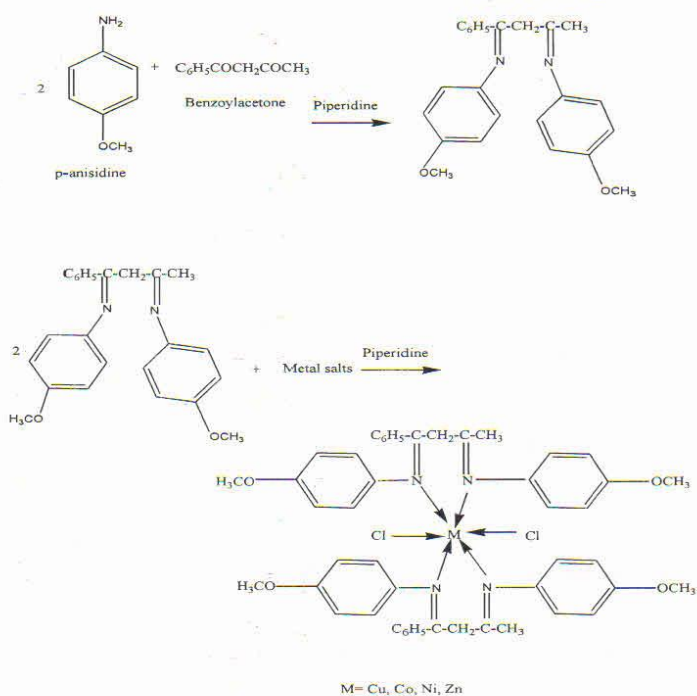
FT- IR Spectrum of [Co(L2)₂ Cl₂].2H₂O Complex



FT- IR Spectrum of [Cu(L2)₂ Cl₂].2H₂O Complex

¹H NMR

¹H NMR Spectra of the schiffbase ligand was taken to confirm the binding nature of schiffbase. In ligand the signals at

 **^1H NMR Spectra of L1****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 [24]. 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 [25]. Such increased activity of the metal complexes can be explained on the basis of and chelation theory [26]. 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 π -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 [27]. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism [27-31].

Table:3 Biological activity

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

CONCLUSION

The Schiff Base ligand and its metal complex have been synthesized and characterized on the basis of IR, UV-visible, and ^1H 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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