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RESEARCH ARTICLE!!!

SYNTHESIS AND CHARACTERISATION OF DIKETIMINE COMPLEX

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ABSTRACT**KEYWORDS:**

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

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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. The literature survey shows that several studies were employed for the synthesis and characterization of Schiff base complexes. Though literature is abundant on physico-chemical properties of various symmetrical Schiff base and chelates, little is known on asymmetric Schiff base complexes. It has been proposed to synthesis 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 synthesis and characterizes Cu (II) complexes of Schiff base derived from aldehyde or ketone and amine. It has been proposed to characterize them with the aid of elemental, thermal analysis and to determine structure and bonding with the aid of physical techniques like IR and UV spectral studies and also the microbial 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 ecotoxic 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]. 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.

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]. 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.

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
Piperidine
Benzoyl acetone
P-Chlorobenzaldehyde
P-toluidine

Metal Salts

Copper 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 complex.

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 Knoevenagel Condensate:

Ethanol solution of Benzoyl acetone (10mmol) was mixed with ethanolic solution of P-Chlorobenzaldehyde (10mmol) and piperidine (0.05cm^3), and the reaction mixture was stirred thoroughly for 6 hours with occasional cooling. Yellow colored precipitate was separated. The reaction mixture was washed with petroleum- ether to remove the unreacted reagents. The precipitate was recrystallised from an ethanol and petroleum-ether to give a pure yellow colored Knoevenagel Condensate. This was used as the starting material for the preparation of Schiff base.

Synthesis of Schiff base:

This Schiff base was prepared by Knoevenagel condensate (5mmol) and p-toluidine (10mmol) with piperidine (0.05cm^3) in Ethanol (50ml). The reaction mixture was kept stirring for 6 hours at room temperature. The dark yellow solution was set aside to evaporate and the dark yellow crystals that separated was filtered off and recrystallised from ethanol.
Yield:

Synthesis of Copper (II) complex:

(2mmole) of Schiff base Ligand (MF) was dissolved in 10 ml of ethanol and 0.34g/ (2mmol) of copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) was added and stirred for 3 hours at room temperature. The precipitate obtained was filtered and dried. Melting point=144°C (colour=dark green)

RESULTS AND DISCUSSION

Experimental details of the preparation of the complexes and their analysis were already described in the previous chapter. The interpretations of the results are discussed in this chapter.

a. Solubility and conductivity:

The Schiffbase ligand and its copper (II) complex are found to be air stable. The ligand is soluble in ethanol but the complex is soluble only in DMSO. The molar conductance of the complex is in the range $30\text{-}60 \text{ Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$, which are consistent with electrolytic nature of the complexes. (Table.1)

Table:1 Physical properties

S.No	Compounds	Colour	Melting point	Conductance(mho $\text{cm}^2 \text{mol}^{-1}$)
1.	Ligand	Dark yellow	81	-
2.	Cu metal complex	Dark Green	169	59

b. 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 copper complex gives absorption band at 973nm and is assignable to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ apart from INCT transitions which are assigned to octahedral is shown in figure.2 .

The complexes formed by L1 are octahedral in nature. Here the two water molecules must be directly attached to the central metal atom.

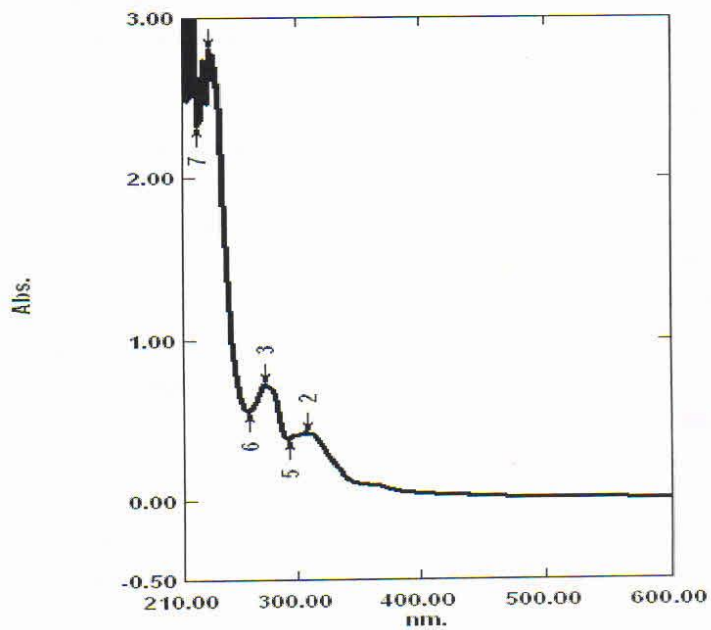


Figure.1 UV-Visible spectra of L1

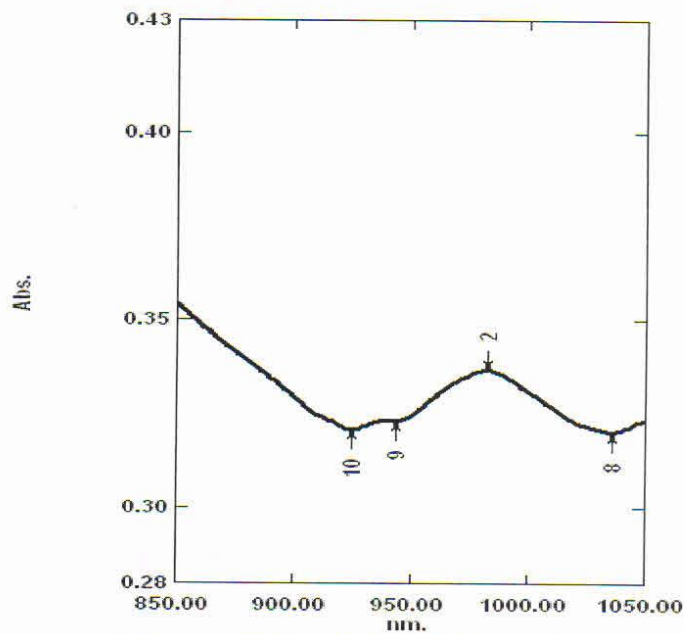
Figure.2 UV-Visible spectra of $[\text{Cu}(\text{L}1)_2 \cdot 2\text{H}_2\text{O}]\text{Cl}_2$

Table:2 Electronic spectral data

S.No	Compound	Frequency(nm)	Transition
1.	Ligand	352	$\pi-\pi^*$
		275	$n-\pi^*$
2.	Cu (II) complex	1092	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$
		973	

c. Infrared spectra

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

The band at 1614cm^{-1} corresponds to $\nu(\text{CH}=\text{N})$ of the ligand. In complexes this strong band shifts to 1608cm^{-1} indicating the coordination to metal ion. The ligand shows a strong band at

3482 characteristics of ν (O-H) group in ligand. In complexes this strong band shifts to 3532 indicating the presence of coordinated water molecule

The IR spectra of complexes indicate the octahedral coordination for Cu(II) complexes.

Table:3 IR Spectral data

Compound	ν (C=N)	ν (O-H)	ν (M-N)
Ligand	1614	3482	-
Cu(II) complex	1608	3532	456

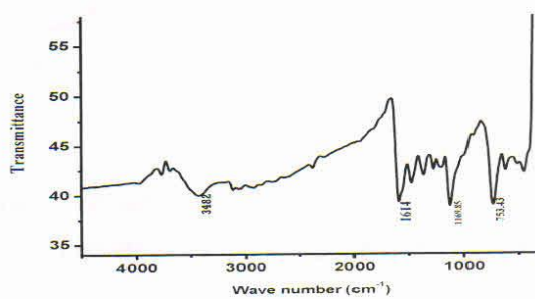


Figure.3 IR SPECTRUM OF L1

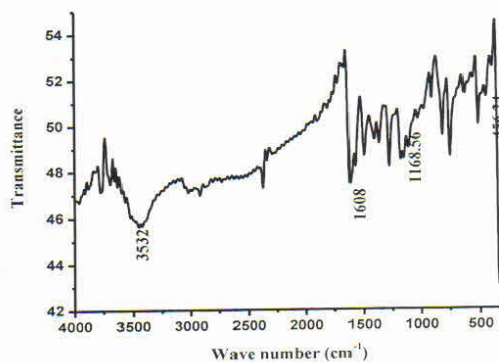
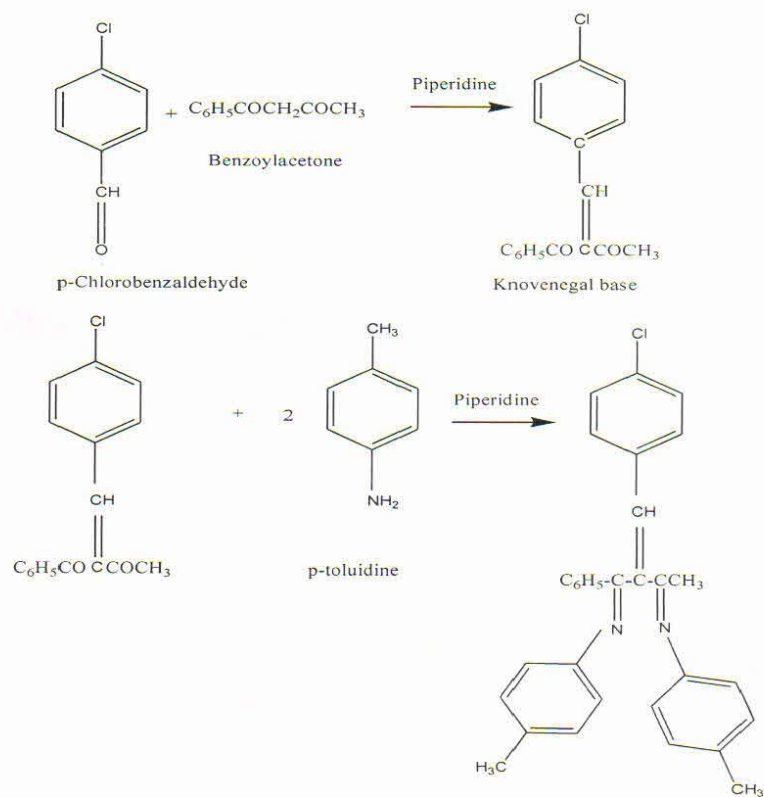
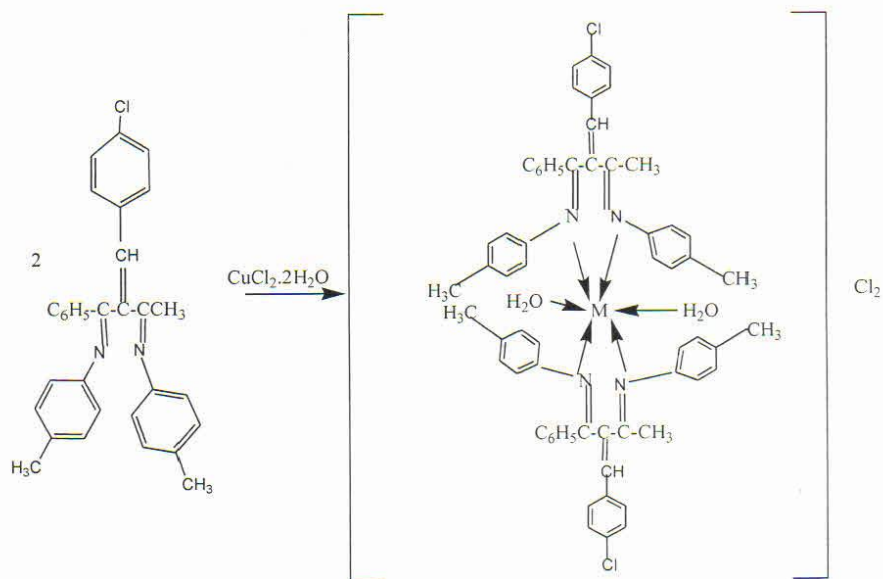


Figure.4 IR SPECTRUM OF [Cu (L1)₂ · 2H₂O]Cl₂

Scheme:1



Scheme:2

**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 [16]. 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 [17]. Such increased activity of the metal complexes can be explained on the basis of chelation theory [18]. 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 [19]. These complexes also disturb the

respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism [20-22].

Table:4 Biological activity

Compound	E.Coli	S.aureus	C.albicans
Ligand	6	4	-
Cu(II) complex	8	16	-

CONCLUSION

The Schiff base ligand and its metal complex have been synthesized and characterized on the basis of IR,UV. From the spectral studies, the ligands coordinate to metal ions in bidentate manner. The octahedral geometry has been proposed for the Cu(II) complex. The ligand and its complex does not show any antifungal activity. The antibacterial activities are more pronounced for the S.aureus than E.coli. The antibacterial activity higher for the complex than the ligand.

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