

INTRODUCTION OF SCHIFF BASES

Abstract

This chapter provides an engaging overview of Schiff bases, highlighting their versatility in various chemical applications. Covering the synthesis, structural diversity, and multifaceted reactivity of Schiff bases, the introduction delves into their significance in coordination chemistry, bioinorganic systems, and medicinal chemistry. With a focus on the intriguing properties that make Schiff bases indispensable in scientific research, this abstract invites readers to embark on a journey through the fascinating realm of these nitrogen-containing compounds.

Keywords: Schiff bases, synthesis, structural diversity, reactivity, applications.

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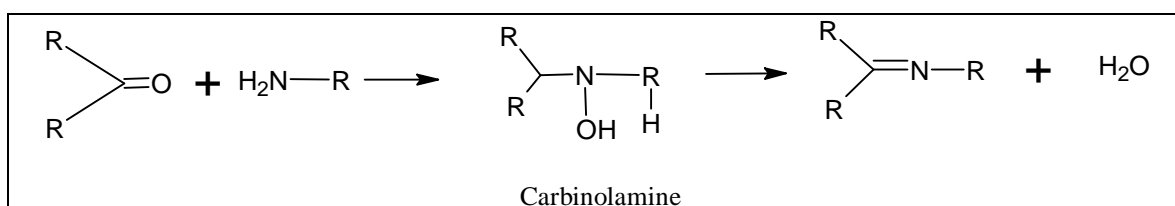
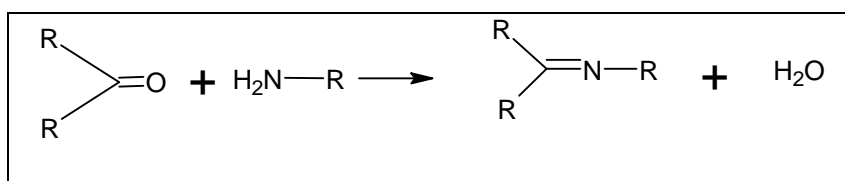
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I. INTRODUCTION OF SCHIFF BASES

Schiff base are macrocyclic or macro-acyclic chelating agents that contains both nitrogen and oxygen donors atoms and are often multidentate and have chelating ability. Schiff bases and their metal coordination compounds have immense role as a ligand in the co-ordination chemistry even after their discovery over a century^[1-2]. Schiff bases are the condensation products of primary amine and carbonyl compounds developed by a German chemist, Hugo Schiff (Nobel Prize in Chemistry in 1864)^[3]. He had condensed carbonyl compounds and primary amines to obtain azomethine group ($>C=N$) as follows:



The reaction taken place through the formation of carbinolamine as an intermediate:

A Schiff base is type of chemical compound where bonding to the alkyl or aryl group is through the Nitrogen atom and not through the Hydrogen atom. The another name for Schiff base is imine or azomethine because the carbonyl group is replaced by these group^[4-5]

Schiff bases acts as an excellent ligands to form complexes with various transition metal ions due to its ability to donate electrons and also major role played by the bonding sites, which help in possibilities various stereochemical structures and provides immense information about the kinetic and thermodynamic stability of various complexes. Denticity of the ligand was also a key factor which responsible for the chelation of the ligand and metal ions. Various monodentate ligands of Schiff bases were prepared and they were used for the formation of number of complexes which has bi-dentate, tri-dentate, tetra-dentate ligands, which are generally called as multidentate ligands. This chelation ability of Schiff bases leads to the formation of complexes with extra-stability and also responsible for the various geometries of the complexes^[6].

There are many polydentate Schiff base ligands which found to have characterized functional group azomethine, and possess potential donor sites which has various electronegative atoms such as Oxygen, Nitrogen, and Sulphur. It is observed that complexes of Schiff bases are extensively used in various industries such as dye-stuff industry, Pigment industry and also have good application in the textile industry^[7]. Due to their immense chelating ability they have also been applied in the most growing polymer industry^[8]. Apart from the Schiff base complexes with transition metal ions, Schiff base complexes with inner-transition metal ions also played a magnificent role in the various reactions e.g., lanthanide complexes of the tridentate Schiff base ligand salicylaldehyde-2-picolinoylhydrazone were

found to be more effective in the catalytic oxidation of aniline as compared to other catalytic reagents^[9]. Most of the efforts have been carried out for synthesizing cluster type structures of the inner-transition metal ions with the salen-type Schiff based ligands. Twenty three such type of complexes have been developed and characterized. It has been found that most of these clusters exhibits interesting “encapsulated” and drum-like structures which serves as antennas that absorbs excitation light and transfer the energy to the lanthanide centres, hence they shown impressive luminescent properties^[10].

The inner –transition metal ions complexes of Schiff base were extensively studied for their medicinal properties like, antimalarial, antibacterial, antifungal, insecticide, fungicide, anticancer, bacteriostatics. Novel lanthanide complexes with general formula $[\text{Ln}(\text{L})(\text{ONO}_2)(\text{H}_2\text{O})_2]$ have been synthesized and characterized where Ln =La(III), Ce(III), Pr(III), Eu(III), Sm(III), Nd(III) and Y(III). The magnetic, spectral, molar conductance and thermal studies have shown that the ligand coordinated through sulphur, azomethine nitrogen and phenolic oxygen. La, Eu, and Yb shown antibacterial activities against gram negative bacteria such as *E.Coli*, *Pseudomonas aeruginosa* etc.^[11]. Semi-carbazones and thio-carbazone derivatives of Schiff bases showing similar medicinal properties have been reported^[12]. Due to their excellent ligation ability they have also been used as a prominent analytical reagent in analytical chemistry^[13].

Now-a- days chemistry of coordination chemistry have attracted the attention of inorganic chemists as their potential application in organic, inorganic, analytical and medicinal fields. The versatile feature of the coordination compounds is that they form coordinate bond between central metal ion and ligands. It is very difficult to give an idea about the origin of the coordination chemistry. It is believed that the coordination chemistry came into existence when a complex of Prussian blue was prepared by a colour maker Diesbach in 1704. The short push to this discovery was given by the Tassaert in 1798 where he obtained isolated orange crystals of $\text{CoCl}_3 \cdot 6\text{NH}_3$ by allowing a mixture of cobalt(III) chloride and aqueous ammonia to stand in air^[14]. Satisfactory research in the era of coordination chemistry had been done by Prof. Jørgenson, was the first, who could collect information about the complexes and extended this area of research to a larger extent. The complexes of Schiff bases are found to occupy a main position in the branch of coordination chemistry after the coordination theory put forward by Alfred Werner^[15]. He was the first inorganic chemist who awarded a Nobel Prize in the subject of chemistry for his work in the co-ordination compounds in 1913.

Stailings obtained the product which are dark green crystalline solid from the reaction of cupric acetate, salicylaldehyde and aqueous ammonia^[16]. In addition to these Schiff base complexes have also been synthesized from the condensation of urea and salicylaldehyde^[17]. Schiff bases are the important mediators for the preparation of bioactive molecules. Most of the Schiff bases are found to possess chiral properties and hence can be used as chiral auxiliaries in symmetric preparations. From the above mentioned facts we came to conclusion that Schiff bases are significant not only in inorganic chemistry but also have a vast applications in the organic, bio-organic, biochemical and medicinal chemistry.

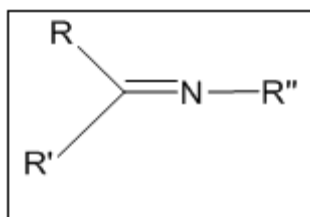
II. FORMATION OF THE SCHIFF BASE

Condensation between aldehyde and amines are proceed out under different conditions and in different solvents such as methanol or ethanol. Formation of Schiff bases

occur at room temperatures or in refluxing conditions. The condensation byproduct water is removed by magnesium sulphate which is a good dehydrating agent. The confirmation of the Schiff base can be done by using chromatography technique but it is not so useful because it causes some degree of decomposition through hydrolysis. If it do so then the purification can be carried out by crystallization. The formation of Schiff base from aldehyde or ketone is a reversible reaction and generally takes place under acidic or basic conditions, or on heating. The removal of water generally driven the reaction to completion. Most of the Schiff bases can be hydrolysed back to the aldehyde or ketones.

III. MECHANISM OF FORMATION OF SCHIFF BASE

The Schiff base formation takes place through a sequence of reaction; addition followed by elimination. There is a nucleophilic addition to the carbonyl group. Amine plays a role of nucleophile. In the first step the amine condensed with the aldehyde or ketone to give unstable addition product called carbinolamine. In the next step the carbinolamine loses water by the acid or base catalysis. Carbinolamine is an alcohol which undergoes dehydration catalysed by an acid. The rate determining state in this reaction is dehydration of the carbinolamine and hence catalysis occurred by acids. Since amines are involved hence the concentration of acid should not be high. If the amine is protonated then it becomes non-nucleophilic, equilibrium is shifted to the left and formation of carbinolamine cannot occur. Because of this reason many synthesis of Schiff base are required middle acidic p^H and hence carried out at this p^H . Dehydration by base catalysis can also occur but this is somewhat similar to E_2 elimination reaction. It proceeds in two steps through anionic intermediates. In general Schiff bases are stable solids and could be effectively prepared because there is sufficient scope of varying amines and aldehydes. The mono-, di-, tri-, multidentate Schiff base ligands can be prepared according to the binding environment provided by the metal ion. The structural characteristic of this compound is the azomethine group which can be represented structurally as



Where R, R', R'' are the alkyl or the aryl substituents or hydrogen at the point of contact to the imino carbon or nitrogen.

Imines are classified in two classes based on the R group attached to azomethine group: aldimines and ketimines. Aldimines are compounds in which R is aryl or alkyl and R' is hydrogen while ketimines are the compounds where both R and R' are alkyl or aryl. Schiff bases can be formed more easily with aldehydes rather than the ketones. Schiff bases of aliphatic aldehydes are relatively less stable and easily polymerisable. The imine which is initially formed undergoes subsequent aldol condensations which can be eliminated by using amines attached with tertiary alkyl groups. Due to steric hindrance it is very difficult to undergo aldol condensations. Tertiary aliphatic and aromatic aldehydes react readily and nearly quantitatively with amines to give corresponding imines even at room

temperature. In case of aromatic aldehydes imines are generally formed without the loss of water formed during the reaction.

However Schiff bases and their metal chelates can be synthesized in different ways which are described as follows:

- 1. Direct Ligand Synthesis Followed by Complex Formation:** In this method the isolation and purification of Schiff bases are carried out before the complexation. The complexation is then carried out by treating the metal ion and Schiff base. This method is advantageous because spectral characterisation of the complex can be possible by using spectral data of ligands.
- 2. Template Synthesis:** In this method the synthesis of complexes are carried out without the isolation of Schiff bases by interacting amines and metal compound in one step reaction^[18-19]. In this the metal ion catalyzes the reaction by acting as a reaction template. According to Busch templates are the chemical species which assemble the atoms with respect to one or more geometry, so that particular linking of atoms can be formed. Template synthesis has been more effective in the cases of rotaxanes, helicates, catenanes^[20]. Due to this the templating agent must have the required information to organize a collection of building blocks so that they can be linked together in specific manner. Two types of templating processes can be possible i.e. Thermodynamic and Kinetic. Thermodynamic templation can be carried by the binding the templates with one of the reactant and shifts equilibrium towards the formation of product. Kinetic templation can be carried out under the irreversible conditions stabilising all the transition states and hence leads to the formation of desired products. But in actual case the prediction of the process of template formation under thermodynamic control or kinetic control is very difficult.
- 3. Rearrangement of Heterocycles (Thiazole, Oxazole etc.):** The straight approach of synthesis of Schiff base from the condensation of o-hydroxy, o-amino with the carbonyl compounds lead to the formation of the unwanted side reaction which involves the ring closure and results in the heterocyclic compounds. To avoid this problem Schiff by preparing the Schiff complex in the form of metal chelates by reacting the metal complex of one of the starting material with the other one^[21-22]. Benzothiazoline and benzoxazole rings are reported to open in the specific environment in presence of metal ions, and rearrangement of the ring leads to formation of corresponding metal chelates of the Schiff base.
- 4. Green Route Method:** In spite of conventional method of formation of Schiff bases a green route method was also adopted. In this method the condensation of various aromatic aldehydes and amines in water was carried out at room temperature. The reaction was completed in shorter time than expected and with also high efficient yields. This method required simple work up procedures i.e. simple filtration techniques to obtain the product as they are water insoluble and the desired products were obtained with sufficient yield without any further purification. On the basis of the reaction time and the percentage of yield obtained (94-98%) this method was considered as green, environmental benign, clean and safe to employ the synthesis at room temperatures of various Schiff bases^[23].

IV. METAL CHELATES AND CHELATING AGENTS

A coordination compound is formed when the central metal ion combine with the group containing donor atoms. They are later referred as ligands and denoted by the symbol 'L'. These ligands may be a negative ions or the neutral molecules that posses donor atoms like Oxygen ,Sulphur and Nitrogen. The bond that is formed is called as metal-ligand bond and symbolizes as M-L.If there are two or more donor atoms present in the ligand then they form a metal chelates with the heterocyclic rings. The process of formation of metal-ligand bond is also referred as chelation and the donor groups are called as chelating agents. The properties of the formed chelates will be decided by most of the factors, out of which some are summerized as follows:

- Central metal ion
 - The nature of the ligand
 - The nature of the bonding between the central metal ion and the chelating agents.
- 1. Central Metal Ion:** The properties of the complexes formed are influenced to the greater extent by the nature, oxidation number and coordination number of central metal ion. It also depends upon the availability of the vacant d-orbitals or f-orbitals available for the bonding that will be provided by the central metal ion. The structure and the properties of the complex formed are also influenced by the oxidation number of the central metal ion. Every metal ion has their own coordination number which is variable from metal to metal. This also affects the chelating ability of the ligands.
 - 2. The Nature of the Ligand:** Ligands are the negative ions or the neutral molecules that possess donor atoms. These ligands can form covalent bond or co-ordinate bonds. For chelating with the Schiff bases the Schiff base must satisfy the following two conditions:
 - The molecule must possess two or more functional groups ,so that it will be very easy for the donor groups to donate the electrons and forms coordinate bonds with central metal ion.
 - The molecule must have the functional group in such a way that it can easily involved in the chelation process.

These two conditions are the minimum conditions but in some cases some sterical factors may also influences the chelating ability.

- 3. The Nature of the Bonding Between the Central Metal Ion and the Chelating Agents:** As co-ordinate bond is formed between central metal ion and the ligands ,the ligand must possess good donor groups. Also the metal ion must provide good ligation environment by making vacant orbitals available. The stability of the resultant complex is depends on the strength of the co-ordinate bond formed. Strong bond character will result in the stable complex.

V. STABILITY OF SCHIFF BASES

The family of Schiff bases derived from the diammines and phenolic aldehydes proved to be very effective ligand for the coordination with various transition metal ions. The

composition of the products formed is depends upon the several factors out of which the nature of the starting diamine is very important .There are three groups of diammines which enhances the reaction to the completion; aliphatic diammines which are more flexible and strongly nucleophilic, cycloaliphatic which are nucleophilic and rigid and aromatic diammines which are slightly nucleophilic and highly rigid. The stability of the Schiff base depends upon the various factors such as strength of the C=N bond formed ,steric hinderence due to the substituents present etc.The spectral characterisation and the X-ray techniques helps to determine the structure of Schiff base. Substituents at the imine group plays vital role to attain the appropriate spectral data^[24].

Donor atoms present in the Schiff bases plays significant role in the formation of the chelate .Since in the Schiff bases the donor atoms are the N atoms ,the close proximity of the another donor atoms from other functional groups enhances the chelation effect and complex formed with high stability e.g the presence of –OH and –SH groups near to the N atom of the azomethine group increases the chelating effect and results in formation of the ring^[25].The Schiff bases formed from Salicyldehyde and 2-Hydroxy naphthaldehyde fulfilled the requirement. The condensation between the salicyaldehyde derivative and those of diamine derivative gives the interesting product which is N₂O₂schiff base compounds. These type of ligands are called salen ligand ,which was originally used to describe the tetradentate Schiff bases derived from salicyaldehyde and ethylenediamine. Nowadys the salen ligand is used in the literature to describe double Schiff bases. Porphyrin rings posseses common features with salen ligands which are being reported^[26]. Self-assembly of organic and inorganic polymeric coordination framework promoted by use of organic spacers and metal ions has become a active tool in the recent years, these coordination polymers are also called as superamolecularcomplexes. Dong and others^[27] have been suggested that there are so many factors which affects the formation of such type of coordinating polymers or superamolecularcomplexes. The factors which affects are as follows :

- Properties of organic spacers such as orientation of donor atoms ,length ,geometry ,the coordination ability etc.
- Choice of the organic ligand which is utmost important.

VI. CLASSIFICATION OF SCHIFF BASES

The Schiff bases possess more than two position through which they can form a covalent bond or co-ordinate bond with the central metal ion. The Schiff bases may be classified on the basis of the type and the functional groups which is present in the molecule. General example is that the bidentate ligands are classified into three categories:

- Those containing two acidic groups
- Those containing two basic groups
- Those containing one acidic group and one basic group.

Schiff bases and their complexes are grouped on the basis of donor atoms they possess. Hence there are large number of organic and inorganic ligands containing O,N&S donor atoms.

- 1. Metal Complexes of Oxygen Ligand:** The Schiff bases which coordinates through the oxygen donor atoms such as dicarboxylates, oxyanions, o-hydroxy carbonyl compounds etc .are included in this category. It was assumed to form four membered chelate containing M-C=O bond in the complexes. The complex may also have five membering which were suggested from the spectral and electronic studies. Genarallysix, seven and eight membered ring structures have been reported for the higher homologues of dicarboxylic acid^[28].
- 2. Metal Complexes of Nitrogen Ligand:** Schiff bases of nitrogen containing ligands include substituted 1,10-phenanthroline , alkyl and aryl diamines , 2,2'-bipyridyl derivatives etc. The chelates of this type mainly divided into two groups one has alkyl and aryl amine metal complexes and second is aromatic heterocyclic base complexes.
- 3. Metal Complexes of Sulphur Ligand:** The Schiff base ligand which coordinate through sulphur atom with the central metal ion are included in this category. Such Schiff bas ligands contains oxazole, thiazole derivatives.

VII. TYPES OF SCHIFF BASES

The types of the Schiff bases obtained depend upon the type of amines being used. Generallydiamine bases appears as tetradentate ligands .The main interaction in the diamine Schiff base is that there is the chromophore –chromophore mutual interactions possible which affects the physical and chemical properties of the molecule. It has been reported that the monoamine Schiff bases shows strong fluorescence through the proton transfer between the hydroxyl group and azomethine group which enhances the probabilities of optical properties derived from the interaction between two chromophores in the diamine Schiff base. The length of bridge between the two chromophores strongly influences the fluorescence intensities. The Schiff base which shows the said behaviour was synthesized by Kawasaki and others. They synthesized thirteen N,N'-bis(α -substituted salicylidene)diammines and their excitation, absorption and fluoroscense properties have also been investigated for the purpose of getting information about the effect of the length of bridge on their optical properties. It has been shown that many factors such as solvent polarity, substituents also affects the optical properties. It has also been concluded that polar solvents facilitates the proton transfer between the hydroxyl group and azomethine group and hence fluorescence intensities have been increased rather than in non polar solvents.

The new class of the Schiff base came into existences called Schiff base macrocycle which formed between the diammines and the dicarbonyl compounds^[29].This macrocycle have been prepared via condensation reaction through template synthesis^[30].This macrocycle Schiff base behave as model ligand for the natural enzymes as metal ion selective ligands and as metal chelating agents. This macrocycle provides unusual ligand environment for the variouds transition metal ions and thus increases the probabilities of novel chemical properties such as stabilization of low and high oxidation states, lessening the ligand lability through the chelating effects which facilitates the trapping of various metal ions in the close proximity within the same molecule. Macrocyclic ligands having the various donor atoms in the ring have been more preferly studied because of their capacity to bind various metal ions with different valencies and hence set an example as a model for metalloproteins.

Quinoxalline Based Schiff Bases and Complexes: The study of the heterocyclic chemistry is one of the versatile tool in the chemistry branch. Quinoxallines being a most important nitrogen containing heterocyclic compounds has gain more attention in last several years in various areas due to its vast application in the various fields. The other name for the quinoxalline is the benzopyrazines because they contains the benzene ring fused with the pyrazine ring. The properties of the quinoxalline Schiff based ligands are expected to be quite interesting. The presence of the electron withdrawing group lowers the number of the lone pair of electrons. Therefore the schiff base conataining electron withdrawing ring derived from quinoxalline -2-carboxaldehyde would be weaker than the Schiff base derived from the salicylaldehyde ,but increase in the coordination site increases the chelate effects, which lead to the involvement of different environment from those schiff bases derived from the salicylaldehyde .

VIII. DENTICITY AND BASICITY OF SCHIFF BASE

Ligands are the species which have one or more donor atoms like O,N,S. The number of donor atoms through which they binds to the central metal ion is called as denticity of the ligand. Thus they can be classified as mono, bi, tri, quadraetc. dentate ligand. The summary of such ligands is as follows :

- 1. Monodentate Ligand:** This ligand posses only one donor atom through which it attach to the central metal ion. For example, $[\text{Co}(\text{NH}_3)_6]^{3+}$. In this it can be seen that only one donor atom i.e N is binds to the central metal ion and hence it is a monodentate ligand
- 2. Bidentate Ligand:** This ligand posseses two donor atoms through which it attach to the central metal ion .For example, Ethylenediammine (en) posseses two donor atom i.e two N atoms which binds to the central metal ion
- 3. Tridentate Ligand:** This ligand posseses three donor atoms through which it attaches to the central metal ion. For example, Dien (Diethylenetriamine) has three donor atoms i.e N atoms through which it binds to the central metal ion
- 4. Hexadentate Ligands:** This ligand posseses six donor atoms through which it binds to the central metal ion. For example EDTA(Ethylene Diammine Tetra Acetic acid) which has six points of attachments i.e four O and two N.
- 5. Ambidentate Ligand:** Some ligands have two or more donor atoms, and they coordinate through either of the one donor atom to central metal ion. That means the coordination site depends upon the donor atoms and hence such ligands are called as ambidentateligand. The best examples for the ambidentate ligands are NO_2 , SCN^- , NCS^- etc. NO_2 has two donor sites i.e O and N hence they are capable of coordination with central metal ion through any one of them. Similar behaviour observed in the case of thiocyanato (SCN) and isothiocyanato(NCS) since they have two donor sites for the coordination.

When donor sites of ligands occupy two or more coordination positions on the same central metal ion then it forms a closed ring structure .The phenomenon of this closed ring structure is called as Chelate and this word was first coined by Morgan and Dew in 1920.

Since the Schiff bases are the condensation products of primary amine and carbonyl compounds hence donor capability of the ligand is most probably depends upon the type of the aldehyde or ketone used and the nature of the primary amine is being used. The donor atom in most of the Schiff bases is N. A large number of tetradentate Schiff base ligand have been reported in the literature. Most of them are derived from the salicylaldehyde and 1,2-diamines. A variety of tridentate ligands have also been reported^[31-32]. The basicity of the Schiff base plays an important role in the formation and stabilisation of complexes. The tautomerism is induced by the –OH and –SH ligand leads to the formation of complexes with various different structures. The deprotonation of the thiolic, alcoholic and phenolic Schiff bases are favoured due to stabilization of various oxidation states.

IX. CONVIENIENCY OF THE SCHIFF BASE LIGAND

For several reasons Schiff bases have been found to be most convenient and fascinating ligand for forming complexes. The steric hindrance and electronic effects around the central metal ion core is largely affected by an appropriate selection of bulky and electron donating or withdrawing substituents incorporated in the Schiff bases. The second reason is that the two donor atoms N and O, of the chelated Schiff base exert two opposite electronic effects, the phenolate oxygen is hard donor and stabilizes the higher oxidation state and the imine nitrogen is border line donor atom and hence stabilizes the lower oxidation state^[33]. The another and most convenient reason is that the Schiff bases are currently prepared in high yield and also by green route methods. The Schiff bases containing the sulphur donor atoms being most attractive because they behave as soft base prefer to combine with late transition metal atoms and also metal ions with low oxidation state. The O,N,S donor Schiff base shows symbiosis, the presence of sulphur atom which is a soft base softens the hardness of the oxygen atom and enables such ligands to incorporate with the many metal ions with various structural diversity.

X. APPLICATION OF THE SCHIFF BASE COMPLEXES

Schiff base and their complexes with the various transition and inner- transition metal ions have a diverse application. Some of them are as follows:

- Catalytic application
- Analytical applicaton
- Industrial application
- Pharmaceutical applications

XI. OBJECTIVE OF THE THESIS

From the above mentioned aspects, it can be concluded that the Schiff base represents an important group of ligands which are commonly used for the synthesis of various transition metal ions coordination compounds. They also shows various biological activities like antibacterial, antimalarial, anticancer, antidiabetic^[34-35]. Schiff base complexes of various inner transition metal ions have also been reported and shows very interesting properties like luminescence properties, magnetic properties and also biological properties^[36-38]. But Schiff base complexes of inner transition metal ions are not so common. Inner transition metal complexes of the Schiff bases have inspired many researchers due to spectral

electronic configuration. It has also been shown that the ligand containing both N and O as a donor atoms acts as good building blocks for the formation of the various inner transition metal ion complexes.

Owing to these, it is very important to study and investigate the coordination ability of donor atoms of the Schiff base with various inner transition metal ions, their structural elucidation, their potential application as a biological catalyst. The present work deals with the synthesis, characterisation of the Schiff base complex with the various inner transition metal ions and study of their biological activity to provide proper justification for the selection of the Schiff base ligand with the additional oxime group and also the replacement of the carbonyl oxygen by imino group with various inner transition metal ions in the present work.

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