The page features a decorative design with three blue circles of varying sizes, each composed of concentric rings in different shades of blue. Two thin, light blue lines intersect at the top left, forming a large 'V' shape that frames the central text. The circles are positioned in the top right, middle right, and bottom right areas of the page.

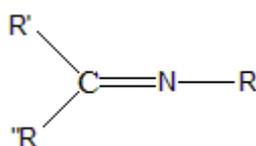
**CHAPTER-1:**  
**AN INTRODUCTION TO THE THESIS**

## 1. Introduction

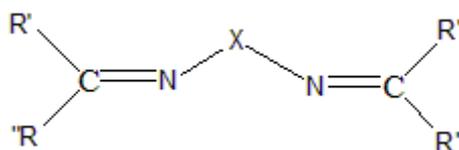
Schiff bases and their metal complexes are an extensively investigated area of chemistry. They are useful in the preparation of medicines, industrial catalysts, analytical reagents, agro chemicals and other industrial products.

### 1.1 Schiff bases

Schiff bases are a class of compounds containing the 'Azomethine' as the functional group [1] which is a carbon-nitrogen double bond ( $>C=N-$ ), nitrogen being attached to an alkyl or aryl group, but not hydrogen. These compounds are named after Hugo Schiff and are represented by the general structure.



R stands for a phenyl or an alkyl group which makes the Schiff bases a stable imine. These compounds are capable of coordinating with metal ions through the imine nitrogen and other groups linked to the Schiff base. Because of the versatility of the active groups these compounds can contain as per the requirement, they are called 'privileged ligands'. Chemists prepare now a days well designed bridged Schiff bases which are represented as shown below.



Where  $R' = H$  or alkyl group,  $R'' =$  phenyl or substituted phenyl group and  $X =$  an alkyl or phenyl group.

Schiff bases are derived from an amine and a carbonyl compound [2]. They are well known, versatile chelating agents with multiple donor atoms like O, N, S etc. A large number of metal complexes of multi-dentate Schiff base ligands with O, N, S donors have been reported with numerous applications.

### 1.1.2 Types of Schiff bases based on chelating property

- Bidentate Schiff base ligand with O, N donors[3]

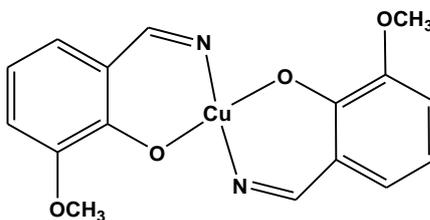


Figure 1.1

- Tridentate Schiff base ligand with O, N, N donors[4]

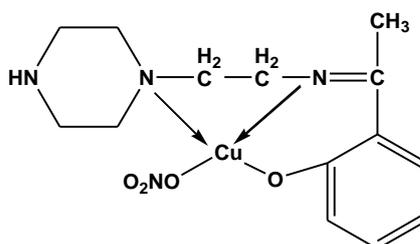


Figure 1.2

- Tridentate Schiff base ligand with O, N, N donors [5]

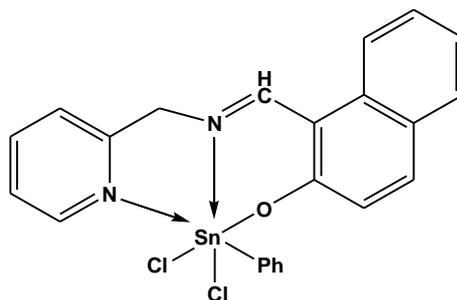


Figure 1.3

- Tridentate Schiff base ligand with O, N, S donors [6]

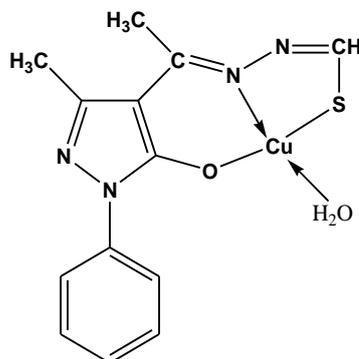


Figure 1.4

- Tetra dentate Schiff base ligands with O, N, N, O donors[7]

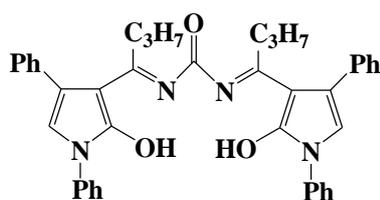
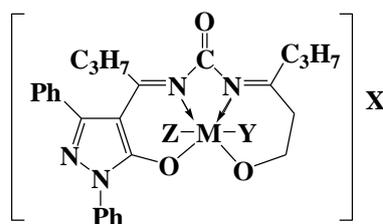


Figure 1.5: Suggested structure of the Schiff base ligand



M	X	Y	Z
OV(IV)	-	H <sub>2</sub> O	-
Cr(III) / Fe(III)	H <sub>2</sub> O	H <sub>2</sub> O	NO <sub>3</sub>
Fe(II), Ni(II), Cu(II) or Zn(II)	H <sub>2</sub> O	H <sub>2</sub> O	-
UO <sub>2</sub> (VI)	-	-	H <sub>2</sub> O

Figure 1.6: Suggested structure of the metal complexes with ONNO donor Schiff base

- Hexa-dentate with N,N,N,N,N,N donors[8,9]

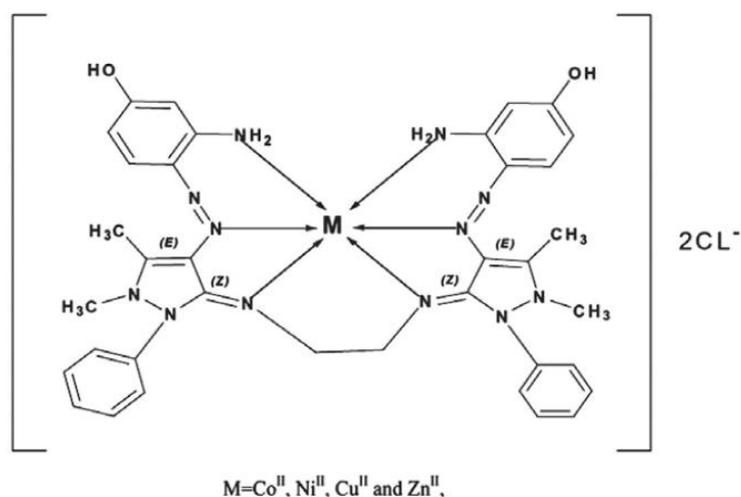


Figure1.7: Structure of Hexadentate Metal complex

## 1.2 Applications of Schiff bases and their metal complexes

Schiff bases and their metal complexes are very important in various biological systems and find applications in polymers, dyes, medicine, agriculture and industry. They are also used as analytical or separation reagents. This section outlines the major uses and applications of different Schiff bases and their metal complexes [10,11].

## 1.2.1 Applications in the biological systems

Due to their preparative accessibility and structural variety, Schiff bases and their metal complexes are considered to be models of biological systems. Their biological activity has one of the fundamental bases for inorganic biochemistry. Schiff bases derived from different sources and their metal complexes show antibacterial, antifungal, antitumor, antiviral activities and work also as therapeutic agents against biological disorders like cancer, inflammation and allergy [12-15].

### 1.2.1.1 Antibacterial activity

Indoline-2,3-dione and 2-amino benzoic acid Schiff base and its tin complexes showed antibacterial activity against *S. aureus*. The results compared with standard drug (imipinem) have shown that compounds were active but the activity was lesser than that of the standard drug. This activity must be due to the presence of a hydroxyl and phenyl group. The increased activity of organotin complexes may be due to the co-ordination and polarity of a tin (IV) atom with oxygen of the ligand [16].

Complexes of Co(II), Cu(II), Ni(II), Mn(II) and Cr(III) with Schiff bases derived from 2,6-diacetylpyridine and 2-pyridine carboxaldehyde with 4-amino, 2,3-dimethyl,1-phenyl,3-pyrazoline-5-one show antibacterial and antifungal activities against *E. coli*, *S. aureus*, *Klebsiella pneumonia*, *Mycobacterium smegmatics*, *Pseudomonas aeruginosa*, *Enterococcus cloacae*, *Bacillus megaterium* and *Micrococcus letens*. Metal complexes have a greater effect than the Schiff base ligands against almost all bacteria [17].

The Schiff base 4-chloro-2-(2-morpholinoethylimino)methylphenolato-methanol and its Zn(II) complexes were screened for antibacterial activity against two gram positive bacterial strains (*B. subtilis*, *S. aerus*) and two gram negative bacterial strain (*E. coli* and *P. fluorescense*) by the MTT method. The Schiff base showed significant activity against two gram positive bacterial strains with MIC of  $12.5 \mu\text{gm L}^{-1}$ , but was inactive against two gram negative strains. The Zn complex showed wide range of bactericidal activity against gram positive and gram negative bacteria. It was more potent than or similar to commercial antibiotics (Kanamycin and Penicillin) [18].

Bidentate complexes of Co(II), Ni(II), Cu(II), Cd(II) and Hg(II) with benzofuran-carbohydrazone and benzaldehyde (BPMC) or 3,4-dimethoxybenzaldehyde [BDMePMC] showed biological activities. Co(II) and Cd(II) complexes of BPMC are moderately active toward *E. coli* whereas Cu(II), Zn(II) and Ni(II) complexes of BDMeOPMC are more active against *S.aerous* as compared to free ligands. None of the complexes are active against *Aspergillus niger* but in the case of *A. fumigatus*, Cu(II), Co(II), Ni(II) and Cd(II) complexes of [BDMeOPMC] are more active than the parent ligands [19].

Amino acid Schiff base derived from 2-hydroxy-5-methylacetophenone and glycine and its transition metal complexes showed antibacterial activities. The ligand was bacteriostatic against bacterial strains of *Proteus vulgaris*, *Shigella flexneri* and *Bacillus coagulans*. All complexes are either resistant or less sensitive against *P. vulgaris*. However, compared to the antibacterial activity of standard antibiotic streptomycin, the activity exhibited by the ligand and metal complexes was lower. The metal complexes showed higher activity than free ligand against the same organism under identical experimental conditions and such increased activity can be explained on the basis of chelation theory [20].

Chelation theory: The in vitro antimicrobial activity of the investigated compounds was tested against the bacteria such as *S. aureus*, *E. coli*, *K. pneumoniae* and also fungi *C. albicans* and *R. stolonifer* by the serial dilution method. The minimum inhibitory concentration (MIC) values of the compounds against the growth of microorganisms are summarized. A comparative study of the ligand and its complexes (MIC values) indicates that the complexes exhibit slightly higher antimicrobial activity than the free ligand. Such increased activity of the complexes can be explained on the basis of Overtone's concept and Tweedy's Chelation theory. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favours the passage of only the lipid-soluble materials due to which liposolubility is an important factor, which controls the antimicrobial activity. 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. Further, it increases the delocalization of  $\pi$ -electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membranes and

blocking of the metal binding sites in the enzymes of microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of the proteins that restricts further growth of the organism. Furthermore, the mode of action of the compound may involve formation of a hydrogen bond through the azomethine group with the active centre of cell constituents, resulting in interference with the normal cell process.

Mixed ligand complexes with 2,6-pyridine-carboxaldehyde bis (p-hydroxy phenyl amine)  $L^1$ , 2,6-pyridine-carboxaldehyde bis (o-hydroxy phenyl amine)  $L^2$  showed antibacterial activities. The data obtained reflect that the Schiff base ligand  $L^1$  and  $L^2$  have moderate activity in comparison with *S.aureus*, *E. coli* and are less active in comparison with *Pseudomonas aeruginosa*.  $L^1$  shows a moderate activity towards *B. subtilis* while  $L^2$  ligand is less active. The remarkable activity of two Schiff base ligands may arise from the pyridyl-N and the hydroxyl group which may play an important role in the antibacterial activity [21] as well as from the presence of two imine groups which explains the mechanism of transformation reaction in biological system [22].

Tetra and hexa-coordinate metal chelate complexes of phosphate Schiff base ligands were found to possess remarkable antibacterial properties but biological activities get enhanced in complexation with metal ions [23]. Neutral tetradentate complexes of transition metal with Schiff base derived from 2-amino phenol or 2-amino thiophenol and 1-phenyl-2,3-dimethyl-4-(4-iminopentan-2-one)-pyrazol-5-one showed antibacterial activity against *S. aerous*, *B. subtilis*, *K. imeumoniac*, *Salmonella typhi*, *P. aeruginosa*, *Shigella flexneri*, *A. niger* and *Trichoderma viridi*. Most of the complexes have higher activity than that of the free ligands [24].

Complexes of transition metal with Schiff base derived from 2,3-dihydrazinoquinoxaline (DHQ) showed antibacterial activity. Preliminary testing of the ligand and metal complexes for antimicrobial activity on the gram positive *Staphylococcus aureus* and gram negative *E. coli* shows that the ligand is active only against *S. aureus* and the activity is enhanced by complexation. The metal complexes exhibit more bacteriostatic activity against *E. coli*. The appearance of activity may be due to synergistic mechanisms [25].

A tridentate Schiff base derived from condensation of S-benzylthiocarbazate with salicylaldehyde and transition metal complexes showed significant bioactivity against *P. aeruginosa* (gram negative) and *B. circus* (gram positive), while the uranium analogue was effective against *B. circus* and showed very weak activity against *Candida albicans*fungi [26].

### 1.2.1.2 Antifungal activity

The antifungal activity of many Schiff bases and their metal complexes was observed and here also, the activity is more pronounced in the case of complexes than in the case of ligands. For example, antifungal activity of N-(2-hydroxy-1-naphthalidine phenyl glycine and its transition metal complexes was investigated and it was found that, compared to free ligand, its metal complexes showed better antifungal activity [27] which also can be explained by the chelation theory.

Semicarbazone and thiosemicarbazone complexes of Ni(II) showed antifungal activity against pathogenic fungi. The complexes were moderately active against all pathogenic fungi, but were lower in activity compared to standard fungicide Nystatin [28]. Co(II), Ni(II) and Cu(II) complexes with Schiff base 3-3'-thiodipropionic acid bis(4-amino-5-ethylimino-2,3-dimethyl-1-phenyl-3-pyrazoline) showed antifungal activity against *Alternaria brassica*, *Aspergillus niger* and *Fusariumoxysporum* and the results indicate that the complexes show enhanced activity in comparison to free ligands[29].

Ligand hydrazine and carbothioamide and their metal complexes show antifungal activity against *Alternariaalternata* and *Helminthosporiumgraminicum*. Mo and Mn complexes control diseases caused by *A. alternata* in brinjal crop[30].

### 1.2.1.3 Antiviral activity

Schiff bases of gossypol show high antiviral activity [31]. Silver complexes in oxidation state +1 shows inhibition against cucumber mosaic virus [32]. Ag(I) gave effective results up to 74.7% towards cucumber mosaic virus [33].

## 1.2.2 Therapeutic applications

Several Schiff bases are found to possess anti-inflammatory, radical scavenging property, analgesic [34] and anti-oxidative actions [35]. Schiff bases

derived from thiazole show analgesic and anti-inflammatory activity [36]. Schiff bases of chitosan and carboxymethyl-chitosan show anti-oxidant activity such as superoxide and hydroxyl scavenging [37]. Furan semicarbazone metal complexes exhibit significant anthelmintic and analgesic activities [38]. Antitumor and cytotoxic properties are exhibited by some Schiff bases and their metal complexes. Salicylidienanthranilic acid possesses antiulcer activity and complexation with Cu shows an increase in antiulcer activities [39]. Some Schiff bases synthesized from salicylaldehyde, 2,4-dihydroxy-benzaldehyde-glycine and L-alanine and their metal complexes containing Cu, Ni, Zn and Co were found to have antitumor activity. The activity is highest with Ni followed by Cu, Zn and Co varying with metal though Schiff base is not changed [40]. Amino Schiff bases derived from aromatic and heterocyclic amine possess high activity against human tumor cell lines [41].

### 1.2.3 Industrial applications

Schiff bases are reported to contribute to dyes and polymer industries. Chromium azomethane complexes [42], cobalt complexes of Schiff base [43] are reported to give colors to leather, food packages and wools. Azo group containing metal complexes are used for dyeing cellulose polyester textiles [44]. Cobalt complexes of salicylaldehyde with diamine have excellent resistance to light and storage ability does not degrade in acidic gases like CO<sub>2</sub> [45]. Novel tetradentate Schiff bases act as a chromogenic reagent for determination of nickel in some natural food samples [46]. ATNR (amine terminated liquid natural rubber) is generated by photochemical degradation of natural rubber in presence of ethylene diamine [47]. ATNR on being treated with glyoxal gives poly Schiff bases which improve resistance to ageing [47]. Organo cobalt complexes with tridentate Schiff bases act as an initiator of emulsion polymerization and co-polymerization of diene and vinyl monomers [48].

### 1.2.4 Agricultural applications

In agriculture, Schiff bases find application as insecticides and also as plant growth regulators. Certain Schiff bases show toxicity against insects. Such Schiff bases derived from sulfanethiodiazole and salicyl aldehyde or thiophene-2-aldehyde and their metal complexes are examples for this [49]. These Schiff bases when complexed with Mo(IV) show insecticidal activity against ball worm and promote

survival rate of mung bean sprouts [50]. Fluorination of the aldehyde part of the insecticide enhances the insecticidal activity [51].

Schiff bases also show significant activity on plant hormones such as auxins and cytokinins on root growth [52]. N-acylated compounds show growth inhibitory activity on seedlings of wheat, rye and barley [53]. Schiff bases of thiodiazole have good plant growth regulator activity like auxins and cytokins [54].

### **1.2.5 Application as catalysts**

Co(II), Fe(III) and Ru(III) complexes of Schiff bases obtained from hydroxy benzaldehyde are used as catalysts in the oxidation of cyclohexane to cyclohexanol and cyclohexenone in presence of  $H_2O_2$  [55]. Co(III) complexes of indoxylthiosemicarbazone (ITSC) shows one pair of well defined reduction peaks at different potentials in the forward scan which represent the reduction of  $Co^{+3}$  to  $Co^{+2}$  by one electron process and subsequent oxidation of  $Co^{+2}$ . The quasi reversible nature of the  $Co^{+3}/Co^{+2}$  is due to the inherent reducing tendency of thiosemicarbazone ligand [56].

Ni(II) complexes with Bidentate (N-N) ligands become an efficient catalyst precursor for olefin oligomerization in presence of an activator [57].

A wide variety of Co(II) complexes are known to bind oxygen reversibly and are, therefore, frequently studied as model compounds for natural oxygen carrier. They are used in  $O_2$  storage, as well as in organic synthesis due to their catalytic properties under mild conditions [58].

### **1.2.6 Applications in analytical chemistry**

Application of Schiff bases in qualitative and quantitative analyses has been reported. A number of Schiff base chelating agents used for the detection of metal ions can be applied for their quantitative determinations. In most cases, the procedures remain largely similar. The main step in the above application is the complex formation which depends mainly on pH, temperature, cation size and the structure of ligand. Optimization of these factors to enhance the stability of the complexes leads to high selectivity of the developed analytical method [59].

#### **1.2.6.1 Photometric method of analysis**

Photometric methods have been extensively used for the detection and quality determination of trace elements. They are based on colour formation resulting from the reaction of the Schiff bases and the ions. For example, o-[N-(o-hydroxyphenyl)formimidoyl]-phenol known as manganon forms with Mn(II) at pH 9.1 to 11.6 a brown complex, the absorbance of which is measured at 428nm. 2,2'-(2,6-pyridiniyl BIS methylidynenitrito) phenol has been used for the spectrophotometric determination of uranium(VI) [60]. The red colour developed is measured at 500nm and absorbativity is  $1.9 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

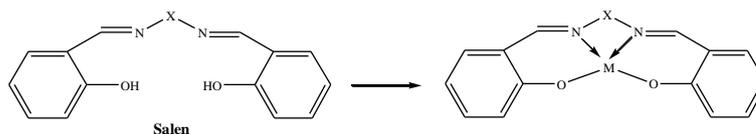
Trace level of palladium(II) has been determined by extraction of Pd(II)-biacetyl monoxime-2-pyridyl hydrazone (BMPH) from aqueous acidic solution into chloroform to form a purple reddish complex. The molar absorbativity of the Pd(II)BMPH complex is about  $7500 \text{ L mol}^{-1} \text{ cm}^{-1}$  at 560nm in the chloroform extract [61].

#### 1.2.6.2 Fluorometry in analysis

Holezbecher reported that Schiff bases obtained from salicyl aldehyde and aniline fluoresce in alkaline medium and therefore can be used as indicators for acid base titrations. He proposed o-[-(o-hydroxyphenyl)formidoyl] phenol for quantitative determination of Aluminum. The analytical importance of such indicators lies in the fact that they make possible acid-base titration in coloured solutions when the use of conventional indicators is precluded. In this analysis there is always the dependence of fluorescence on the pH similar to that of acid-base fluorescence indicators. It is a good method for the detection and determination of inorganic ions [62].

#### 1.2.6.3 Potentiometric sensors

Ganjali *et al.* have prepared sensors for Dy(III) based on bis-pyrrolidene Schiff base. The electrode has also been used in the potentiometric determination of fluoride ions in mouthwash by titration against Dy(III). They also prepared a bromide sensor based on Fe(III)-salen. This sensor has high bromide selectivity over a wide range of organic and inorganic anions especially iodide, chloride and hydroxide ions [63]. Salen is tetradentate –O-N-N-O- donor Schiff base synthesized from a diamine and two equivalence of salicylic aldehyde. It forms square planer metal complexes.



A large number of different Schiff base ligands have been used as cation carriers in potentiometric sensors as they have shown excellent selectivity, sensitivity and stability for specific metal ions.

The potentiometric sensors are based on the development of a potential between molecular species under zero or very low current flow. The advantage of this kind of analysis is that it is cheap, highly sensitive and specifically selective in detection of ionic activities [64].

#### 1.2.6.4 Schiff base as solvent extractant

Kimet *al* studied the solvent extraction of Ni(II), Cu(II) and Co(II) using salophen and trace determination of these ions was done in water samples [65]. Macrocyclic Schiff bases containing thiophene or phenol subunits were synthesized and the effect of ligand atoms on the liquid-liquid extraction of bi-valent transition metals was studied. The phenol groups in the macrocycle lead to an increase in the extraction of transition metal ions. Also, the extractability of acyclic Schiff bases was found to be greater than that of macrocyclic Schiff bases [66].

#### 1.2.6.5 Application in HPLC

Schiff base metal chelates are extractable metal chelates. The separation of neutral Ni and Cu chelates of two representative of Schiff base ligands, N-N'-ethylene bis (acetyl acetone imine) and N-N'-ethylene bis (salicylaldimine) is reported on a column of 10  $\mu\text{m}$  diameter silica. Both pairs of chelates are well resolved with good peak shape efficiency when the mobile phase is 4:1: methylene chloride: acetonitrile [67]. An HPLC method for determination of Sc(III) was developed with diacetyl-N,N-bis (4-hydroxy benzoylhydrazone) (DBHB) as a pre column chelating agent. Tetra dentate DBHB formed a 1:1 chelate with Sc(III). Sc(III)-DBHB chelate was separated on a C<sub>18</sub>-silica gel column with a mobile phase of acetonitrile-water containing tetramethyl ammonium bromide and hexamethylenetetraimine buffer [68]. Kanbayshiet *al.* have developed a method for highly selective determination of trace amount of Co<sup>+2</sup>, Cu<sup>+2</sup>, Ni<sup>+2</sup>, V<sup>+5</sup> ions by reversed phase liquid chromatography and

spectrophotometric detection was accomplished without the addition of any chromogenic reagent to the eluent [69].

### 1.3 Objectives and Methodology of the present work

As evident from the fore-going discussion, Schiff bases have evoked keen interest among the researchers of chemistry in terms of their easy preparation, easy complex formation and versatility of structure and applications. Special mention should be made about their potential uses as good sensors which is a field of brilliant research now a days. Since we found these Schiff bases and their metal complexes as an evergrowing branch of coordination compounds full of promises, we thought of undertaking a research on some of the special Schiff bases and their metal complexes derived from some wellknown parent compounds such as pyrazolones, o-vanillin, antipyrine and pyridine.

This thesis proposes the synthesis of a series of Schiff bases with donors ON, ONN and ONO atoms and some of their metal complexes in terms of their synthesis, characterization and also a limited study of their biological activity *in vitro* as well as *in silico*.

*In silico*, achem-bioinformatic study of these Schiff base compounds and their metal complexes to predict their potential as medicine is also proposed. In the formation of complexes some atoms and molecules/ ligands act as donors of electron pairs to the central metal atom. The most common Schiff base donor atoms are N, O and S as in aminonitrogen or azo-methane nitrogen, phenolic oxygen or the oxygen of water molecules and sulphur as in thiosemicarbazides respectively.

In the study, a series of Schiff base ligands and the metal complexes are synthesized and characterized using usual methods like: thermal analysis, conductivity measurements, elemental analysis, magnetic measurements and x-ray crystallography. In an attempt to find some applications of these compounds and complexes, their biological activity has been estimated in a limited way as also their potentials to be medicines. The parent compounds selected for the aldehyde component are pyrazolone and o-vanillin on which considerable research has been done. The derivatives of pyrazolone, 4-formyl-1-(1-N-p-toluy)-3methoy-pyrazol-5-

one and 4-acyl-1-(1-N-p-toluy)-3methyl-pyrazol-5-one, are used for the carbonyl group. Another series of Schiff bases are synthesized from o-vanillin, that is, 2-hydroxy-3-methoxy benzaldehyde.

The amines used for the synthesis of Schiff bases are as varied as aromatic primary amines and heterocyclic amines such as 4-amino antipyrine, a derivative of pyrazolone, 2-amino-5-methyl-pyridine and 2-amino-5-bromo-pyridine.

In the second chapter, the Schiff bases with O,N donor atoms and their metal complexes are studied. They include the Schiff bases derived from 4-formyl-pyrazolone and aromatic primary amines which are treated in part one of chapter two. In part two, chapter two, the Schiff bases derived from o-vanillin and 4-aminoantipyrine, again with O,N donors, and their metal complexes are investigated.

In part three of the same chapter, Schiff bases of o-vanillin with aromatic primary amines, all with O,N donors and their metal complexes are treated.

In chapter three, Schiff bases of 4-acyl pyrazolone derivatives with ethanol amine, all O,N,O donors, their Cu(II) complexes and their binding with ct-DNA are investigated.

In chapter four, Schiff bases of o-vanillin with heterocyclic amines, 2-amino-5-methyl pyridine and 2-amino-5-bromo pyridine, all O,N,N donors, and their metal complexes are treated with respect to their synthesis, characterization and biological activity.

In the last and fifth chapter, a Chem-bioinformatic study of the above Schiff bases is undertaken to see if they are of some utility as potential medicines.

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