Chapter 1
Introduction
1.1. INTRODUCTION

Schiff Base

A Schiff Base, named after Hugo Schiff, is a compound with a functional group [1] that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group, not hydrogen (Figure 1.1). Schiff bases in a broad sense have the general formula $R^1R^2C=NR^3$, where $R$ is an organic side chain. In this definition, Schiff base is synonymous with azomethine (Figure 1.2). Some restrict the term to the secondary aldimes (azomethines where the carbon is connected to a hydrogen atom), thus with general formula $RCH=NR'$ [2].

The chain of the nitrogen makes the Schiff base a stable imine. A Schiff base derived from aniline, where $R^3$ is a phenyl or a substituted phenyl, can be called an anil [3].

![Figure 1.1. General Structure of a Schiff Base](image1)

![Figure 1.2. General Structure of an azomethine](image2)

![Figure 1.3. General Structure of an anil](image3)
1.2. HISTORICAL BACKGROUND

Schiff bases [4] have been known since middle of nineteenth century. First of all Ettling [5] in 1840 has isolated Schiff base complexes of copper. But the systematic synthetic study of Schiff base complexes started with the work of Pfeiffer and coworkers in 1931 [6]. Jencks [7] has shown the formation of carbinolamine as an intermediate product which loses a water molecule to yield a Schiff base (Figure 1.4).

![Figure 1.4. Systematic route for the synthesis of Schiff base](image)

Aldehydes in general give polymeric materials with amines which may be due to the ease with which the imine formed initially undergoes subsequent aldol condensation (Figure 1.5).

![Figure 1.5](image)

Aliphatic and aromatic aldehydes react readily with amines at room temperature to yield stable monomeric bases. The reactions of the aliphatic ketones with amines are slower than those with aldehydes. The aromatic ketones react even more slowly than the
Introduction

aliphatic ketones. Proton, Lewis acid catalysts and high reaction temperature are therefore required for such reactions. Mourea and Mignonac [8] have also synthesized the Schiff bases by the reaction of the Grignard’s reagent with aryl cyanide followed by careful hydrolysis of the intermediate product (Figure 1.6).

\[
\text{ArCN + R'MgBr} \rightarrow \text{Ar} \equiv \text{C} \equiv \text{NMagBr} + \text{H}_2\text{O} \rightarrow \text{Ar} \equiv \text{C} \equiv \text{NH} + \text{MgBr}_2
\]

1.3. METAL COMPLEXES OF SCHIFF’S BASE

Metal complexes of Schiff bases have occupied a central role in the development of coordination chemistry. This situation is manifested by the huge number of publications [9-15]. In general, metal complexes of Schiff bases were prepared by one of the following general method:

\[
\text{Metal salt} + \text{Schiff bases} \rightarrow \text{Complex}
\]

\[
\text{MX} + \text{SB} \rightarrow [\text{MSB}]X
\]

Where, \(X = \text{NO}_3^-, \text{Cl}^-, \text{CH}_3\text{COO}^-\) and \(\frac{1}{2} \text{SO}_4^{2-}\) etc.

\(M = \text{Lanthanides} / \text{Transition metal ions.}\)

Schiff base-metal complexes [16] were formed by nearly all the metals of the periodic table. Although the number of known complexing agents is very large, the donor atoms, which undergo combination with the metal, were restricted to the strongly non-metallic elements of group 15 and 16.

1.4. SEMICARBAZONES AND THIOSEMICARBAZONES – IMPORTANT SCHIFF’S BASES

In organic chemistry, a semicarbazone/ thiosemicarbazone is a derivative of an aldehyde or ketone formed by a condensation reaction between a ketone or aldehyde and semicarbazide/thiosemicarbazide.
H₂NNHC(=X)NH₂ + RC(=O)R → R₂C=NNHC(=O)NH₂

Adehyde or Ketone

For semicarbazide X = O then product is aldehyde/ ketone semicarbazone

For thiosemicarbazide X = S then product is aldehydes/ ketone thiosemicarbazone

1.5. MODE OF COORDINATION IN SEMICARBAZONES AND THIOSEMICARBAZONES COMPLEXES

On the basis of coordination behavior of the semicarbazones and thiosemicarbazones can be classified in to the following groups.

i. Bidentate semicarbazones and thiosemicarbazones

ii. Tridentate semicarbazones and thiosemicarbazones

iii. Tetradentate semicarbazones and thiosemicarbazones

iv. Polydentate semicarbazones and thiosemicarbazones

i. Bidentate semicarbazones and thiosemicarbazones

T. L. Zhang et al. [17] reported the study on two coordination compounds using Semicarbazide (SCZ as bidentate ligands) (Figure 1.7 a,b)
M. Wang et al. [18] reported the antitumor activity of transition metal complexes with thiosemicarbazones derived from 3-acetyl umbelliferon. The ligand coordinates through azomethine nitrogen and thione sulphur atoms (Figure 1.7 c).

Figure 1.7. Bidentate semicarbazones and thiosemicarbazones

**ii. Tridentate semicarbazones and thiosemicarbazones**

M. Alaudeen et al. [19] reported the synthesis, characterization, thermal studies and molecular modeling of embelin semicarbazone and its metal complexes. (Figure 1.8.a)
**Introduction**

J. S. Oxford et al. [20] reported the inhibition of the particle-associated RNA-dependent RNA polymerase activity of influenza viruses by chelating agent (isatin 3-thiosemicarbazone) coordination in tridentate manner. (Figure 1.8.b)

![Figure 1.8.b](image)

*Figure 1.8.b*  
**Figure 1.8.** Tridentate semicarbazone and thiosemicarbazone

**iii. Tetradentate semicarbazones and thiosemicarbazones**

M. Nagar et al. [21] reported the antifungal activities of mixed ligand complexes of Co(II), Ni(II), and Cu(II) with cis-3,7-di-2,6-octadiene semicarbazone and amino acid. (Figure 1.9.a)

![Figure 1.9.a](image)

*Figure 1.9.a*
A. R. jalian et al. [22] reported the development \[^{163}\text{Pd} \]-labeled–bis(N4-methyl thiosemicarbazone complexes as possible therapeutic agent. (Figure 1.9.b)

\[
\begin{align*}
\text{R}_1 & \quad \text{NNHCSNHCH}_3 \\
\text{R}_2 & \quad \text{NNHCSNHCH}_3
\end{align*}
\]

\[
\begin{align*}
\text{Pd} & \quad \text{N} \\
\text{S} & \quad \text{S} \\
\text{NHCH}_3 & \quad \text{R}_1 \\
\text{R}_2 & \quad \text{NNHCSNHCH}_3
\end{align*}
\]

Figure 1.9.b

**Figure 1.9.** Tetr dentate semicarbazone and thiosemicarbazone

iv. Polydentate semicarbazones and thiosemicarbazones

J. S. Casas et al. [23] reported the main group metal complexes of semicarbazone and thiosemicarbazone. A structural view of Zn-polydentate semicarbazone and thiosemicarbazone has been given in Figure 1.10 (a) and (b)

\[
\begin{align*}
\text{Zn} & \quad \text{Cl}_2 \\
\text{OH}_2 & \quad \text{C}_\text{H}_3 \\
\text{Cl} & \quad \text{C}_\text{H}_3 \\
\text{O} & \quad \text{C}_\text{H}_3 \\
\text{N} & \quad \text{H}_2\text{N} \\
\text{C}_\text{O} & \quad \text{C}_\text{H}_2 \\
\text{H}_2\text{N} & \quad \text{N} \\
\text{H} & \quad \text{H}_2\text{N}
\end{align*}
\]

Figure 1.10 (a)

\[
\begin{align*}
\text{Zn} & \quad \text{OH}_2 \\
\text{S} & \quad \text{H}_2\text{N} \\
\text{C}_\text{H}_3 & \quad \text{C}_\text{H}_3 \\
\text{N} & \quad \text{H}_2\text{N} \\
\text{H} & \quad \text{H}_2\text{N}
\end{align*}
\]

Figure 1.10 (b)

**Figure 1.10.** Polydentate semicarbazone and thiosemicarbazone

1.6. DESIGNING OF SEMICARBAZONES COMPLEXES

The semicarbazide may act as a monodentate or bidentate chelating agent. Crystal structure studies by Nardelli et al. [24] of some semicarbazide complexes viz; \([\text{Cu(SC)}_2\text{Cl}_2 \quad [\text{Zn(SC)}_2\text{Cl}_2\) show that semicarbazide is bidentate. According to these
Introduction

authors, in both the compounds each metal atom is surrounded by a transplanar arrangement of two ‘O’ and two ‘N’ atoms lying at the corners of square. Six co-ordination is completed by two chloride atoms which occupy the axial positions so that the whole polyhedron can be described as a distorted octahedron. The semicarbazide molecule is planar and there are no significant differences in the bond distances between metal coordinated semicarbazide and semicarbazide hydrochloride (Figure 1.11)

![Figure 1.11](image)

Semicarbazone and substituted semicarbazide are also expected to use one oxygen atom of the carbonyl group and/or the hydrazinic nitrogen atom to coordinate as a bidentate or monodentate ligand.

In the present study semicarbazones of the entire studied carbonyl compounds act as a bidentate ligand coordinate through oxygen of carbonyl group and hydrazinic nitrogen.

1.7. DESIGNING OF THIOSEMICARBAZONE COMPLEXES

It has been shown [25] that the thiosemicarbazide molecule itself exists in the trans configuration (Figure 1.12) and while during complexing in this configuration, it behaves as a monodentate ligand, bonding may also occur through the sulphur atom. Gerbeleu et al. [26] have shown that bonding may also occur through the hydrazinic nitrogen and the amide nitrogen (Figure 1.13) if the sulphur centre is substituted. On reinvestigating the crystal structure of thiosemicarbazide hydrochloride, Coghi et al. [27] explained these conformational changes on the basis of protonated ⇔deprotonated isomeric forms and steric effects. In most of the complexes studied the thiosemicarbazone function coordinated to the metal ion in the cis-configuration,
(Figure 1.14) as a bidentate ligand bonding both through the thione/thiol sulphur atom and the hydrazine nitrogen atom in a bidentate manner.

\[ \text{Figure 1.12} \quad \text{Figure 1.13} \quad \text{Figure 1.14} \]

When an additional coordinating functionality is present in the proximity of the SN donating centres, the ligands are found to act as tridentate species, (Figure 1.15) yielding a polymeric compound in some cases.

\[ \text{Figure 1.15} \]

Recently Gerbeleu and co-workers [28] showed that alkylation of the thiocarbonylsulphur of thiosemicarbazone derivatives induces not only complexation through the terminal amino group but also enough acidic character for it to function as a monoacidic ligand. In the presence of various metal salts e.g. Cu(II), Ni(II) and CO(II), these ligands are capable of condensing at terminal amino nitrogen atom through another aldehyde or ketone to yield quadridentate ligands of type (Figure 1.16) using such template reactions as shown in Scheme (1), Gerbeleu and Zhovmir [29] claimed to have isolated thiosemicarbazone complexes without sulphur coordination. Relevant to the bonding in thiosemicarbazone complexes is the ability to locate the various group frequencies corresponding to typical linkages. Although there have been many attempts to assign empirically a few infrared bands of metal complexes of thiosemicarbazone ligands, no complete assignment of their IR spectra had been available. A fairly reliable
assignment of infrared frequencies is now possible for Semicarbazide and its hydrochloride [30]. Solenosemicarbazide and thiosemicarbazide [31] (along with its ionic and neutral complexes of the type MS$_2$N$_2$) through normal coordinate analysis using Wilson’s GF Matrix method and the Urey Bradley force field function [32]. A computational method based on a normal coordinate analysis and quantum chemical dipole moment calculations has been suggested for predicting transition moment directions and dichloric rations in molecular crystals of law symmetry such as thiosemicarbazide [33].

Figure 1.16

Scheme 1
(M = VO$^{2+}$, Ni$^{2+}$ or Cu$^{2+}$; R=H$^+$, NH$_4^+$, Na$^+$ or K$^+$)
In the present study thiosemicarbazones of all the studied carbonyl compounds also act as bidentate ligands, coordinating through sulphur and hydrazinic nitrogen.

1.8. OBJECT AND SCOPE OF THE PRESENT WORK

a. Metal complexes of semicarbazones and thiosemicarbazones have structural similarity to biological systems which help in further understanding of the binding, thermodynamics and kinetics of biomolecules.

b. Metal complexes of semicarbazones and thiosemicarbazones afford two main differences relative to Macrocyclic ligands
   
   i. Easier access to mixed donor environments.
   ii. An open equatorial ring the hole size of which can in principle accommodate more easily the expected changes in metal size upon oxidation reduction.

c. Metal complexes of semicarbazones and thiosemicarbazones have excellent luminescence properties with high quantum yields because of strong absorption in near UV-visible region by the Schiff base ligands. So they can be used for luminescence and laser materials.

d. Metal complexes of semicarbazones and thiosemicarbazones have excellent solubility in low dielectric constants solvents such as THF, CH₂Cl₂ etc. The advantage of solubility in such solvents is that the more facile characterization of polymer of these Schiff bases and convenient means for the preparation of polymer films which should greatly expand the potential applications of semicarbazones and thiosemicarbazones based polymers.

The preparation of a new ligand was a perhaps the most important step in the development of metal complexes which exhibit unique properties and novel reactivity. The electron donor and electron acceptor properties of the ligand, structural functional groups and the position of the ligand in the coordination sphere together with the reactivity of coordination compounds may be the factor for different studies [34-35]. Schiff bases were important class of ligands. These ligands and their metal complexes
had a variety of applications including biological, clinical, analytical and industrial in addition to their important roles in catalysis and organic synthesis [36–41]. Important applications of Schiff’s base and their metal complexes are listed here:

**i. Fluorimetric Analytical Reagents**

Many Schiff bases were prepared by condensation reaction of certain aromatic amines with aromatic aldehydes derivatives, and then the fluorescence properties of these Schiff bases were examined in acidic and basic media. It shows that, these compounds can be used for spectrofluorimetric monitoring of small pH changes [42, 43].

**ii. As acid base indicators**

Semicarbazones and thiosemicarbazones have not been studied previously as neutralization indicators. However, both groups show a resonance structure with an acidic hydrogen atom, and if conjugated with aromatic systems that can exist in benzenoid form and quinonoid form, can have a visible-region absorption spectrum that is pH-dependent [44].

The paper firstly announces the possibility of using a Schiff base as an acid-base indicator. This surprising phenomenon can be considered as an interest due to the fact that Schiff bases are usually unstable in solutions and definitely undergo hydrolysis. It was found that such a specific observation depends merely upon the chemical structure and type of the substitute of amine that reacts with aldehyde to give the Schiff base. The latter reagent 4[4-(4-dimethylamino-benzylidene)-amino]-benzene sulphonamide was synthesized from the condensation of sulphanilamide with p-dimethylaminobenzaldehyde. The reagent solution shows a reproducible change in its color due to the addition of an acid and base. A UV-Vis spectroscopic characterization and acid-base equilibrium study of the reagent for its possible use as an indicator were investigated. The results show that the reagent is an amphoteric which possesses four ionization constants $K_a_1$, $K_a_2$, $K_b_1$ and $K_b_2$ of weak dibasic and diacidic properties. The value of $pK_a_2$ (9.80) is parallel to the observed transition interval of pH 9.5 (yellow) and pH 10.5 (colorless), which is considered to be the indicator exponents $pK_i$. It was concluded that the benzyl sulphonamide group plays a key role in the stability of the reagent towards hydrolysis and also for indicator characteristics through breaking the conjugation. [45].
Introduction

iii. In Spectrophotometry
Several vicinal α-dithiosemicarbazones have been used as analytical reagents in spectrophotometry. Most of the transition metals form some kind of stable colored complex with these compounds. Usually they act as chelating ligands by bonding through the sulphur and hydrazinic nitrogen atoms. These complexes were stable due to the formation of five chelate rings [46]. Semicarbazones and thiosemicarbazones form colored metal complexes in conditions ranging from moderately acidic to moderately alkaline. Only a few are used to determine metal ions in highly acidic medium. 3-Hydroxypicolinaldehyde thiosemicarbazone was used to determine Co(II) in highly acidic medium [47]. Similarly glyoxal dithiosemicarbazone reacts with Ag(1) and Hg(II) at pH 1.1 [48]. Salicylaldehyde thiosemicarbazone has been used to determine Mo(VI) in the presence of iron in highly acidic medium [49].

iv. Corrosion inhibitors
Rapid developments in recent years, is an attempt to prevent or retard acid dissolution of metals in general and mild steel in particular. Therefore such substances were known as corrosion inhibitors in the metal-corrodent systems. Finley and Hackerman [50] stated that polar organic compounds containing sulphur and nitrogen were good corrosion inhibitors for the acid dissolution of metals. Thiosemicarbazones (TSC) are a special class of compounds containing nitrogen and sulphur [51] and are possible corrosion inhibitors. The work of Babaqi et al. [52] on the effect of 4-phenyl-1-acetophenone-3-thiosemicarbazone in the acid corrosion of aluminium is highly appreciable. The inhibition of corrosion of mild steel (98% Fe) in hydrochloric acid (HCl) by derivatives of thiosemicarbazones has been studied using weight loss and hydrogen evolution techniques. The examples of thiosemicarbazone derivatives used as corrosion inhibitors were 2-acetylpymidine-(4-phenylthiosemicarbazone) (2AP4PTSC) and 2-acetylpymidine-(4-methylthiosemicarbazone)(2AP4MTSC). 2AP4PTSC exhibited higher maximum inhibition efficiency (80.67%) than 2AP4MTSC (74.59%). Generally, inhibition was found to increase with increasing inhibitor concentration and decreasing temperature. A first-order type of mechanism has been deduced from the kinetic treatment of the results, and the process of inhibition was attributed to physisorption. The difference in the inhibition behavior of the two compounds is explained in terms of
the difference in their molecular structures [53]. There are numbers of other papers which also explain anticorrosion activities of metal complexes of semicarbazones and thiosemicarbazones [54-60].

v. Pulse Polarography

Three thiosemicarbazones corresponding to pycolinaldehyde, 2,2’-dipyridylketone, and benzophenone have been studied by differential pulse polarography with the aim of elucidating the influence of the ring bonded to the thiosemicarbazone group on its electroreduction. The mechanisms proposed, supported by the reduction products detected, account for this influence [61].

vi. As gravimetric reagents

Only a very few semicarbazones and thiosemicarbazones were used in the gravimetric determination of metal ions. Komatsu and Hiroaki [62] used a 0.1% ethanolic solution of p-ethylsulphonylbenezaldehyde thiosemicarbazone for gravimetric determination of the Hg$^{2+}$ in acidic medium (< 2.5N). It gives a yellow precipitate which is washed with 1M hydrochloric acid and dried at 110-120°C. It is also used for estimation of Pd(II) [63] giving an orange-yellow precipitate in 5M hydrochloric acid, which is washed with 1% hydrochloric acid and water, and dried at 110-120°C.

vii. Potentiometric studies

The complexes of Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$ and VO$^{2+}$ were studied with 2-hydroxy-1-naphthaldehyde-4-phenyl-3-by Bhatt et al. [64] by pH-titration. The proton-ligand stability constant was 1.43x10$^{10}$. The stability constants were determined by several methods in 70% dioxan medium. All four metals formed 1:2 complexes. The order of the stability constants was VO$^{2+}$$>$Cu$^{2+}$$>Co^{2+}$$>Ni^{2+}$. Complexation by salicylaldehyde-4-phenyl-3-thiosemicarbazone has also been studied potentiometrically by Bhatt et al. [65] at 25 °C and ionic strength 0.1 in 50% aqueous dioxane. The proton-ligand stability constant is 7.94 x 10$^9$ and the log β values for the complexes are 9.44, 10.28, 9.84 and 8.94 for VO$^{2+}$, Cu$^{2+}$, Co$^{2+}$, and Ni$^{2+}$ respectively. Similar studies were done on the 2-hydroxy-5-methylacetophenone thiosemicarbazone complexes [66] of Cu(II), Mn(II), Co(II), Zn(II) and Ni(II), at 40 °C in water-dioxan (1:3). The order of the stability constants was Zn$<$Cu $>Co>Ni>Mn$.

viii. As visual indicators
The most common application is the direct titration of the metal against EDTA solution with thiosemicarbazones and semicarbazones as indicators. With o-thymol aldosemicarbazone, [67] addition of acid or alkali has no effect on the complex formed. Phenanthraquinone monothiosemicarbazone [68] was used to determine Cu in brass and gun metal and Ni in monel K and Brightway G. Phosphate, molybdate, tungstate and sulphate were titrated with lead nitrate, with 1, 2-naphthoquinone-2-semicarbazone as indicator [69]. Aluminium was determined by EDTA back-titration, with 1,2-naphthoquinone-2-thiosemicarbazone-4-sulphonic acid as indicator and zinc solution as titrant [70]. Aluminium and copper were determined together by breaking the Al-EDTA complex by addition of sodium fluoride and titrating the released EDTA with zinc [71]. Iodide has been determined by mercurimetric titration in isopropyl alcohol, with the same indicator [72].

**ix. Antimicrobial activities**

Semicarbazones, thiosemicarbazones and their metal complexes present a wide range of applications that stretch from their use in analytical chemistry, through pharmacology to nuclear medicine [73–75]. The presence of amide, imine and thione groups makes them potential polydentate ligands [76,77] and it is not surprising that numerous thiosemicarbazones complexes have been prepared and characterized [78]. In addition, in the last few years there has been a growing attention towards thiosemicarbazones related to their range of biological properties, specifically as antifungal, antiviral, antibacterial and anticancer agents, Anti – Mycobacterium tuberculosis activity and cytotoxicity [79-87]. Thiosemicarbazone metal complexes have also been investigated as radical scavengers [88]. Schiffs base metal complexes were also found to be active against yeast [89] and also act as herbicides, insecticides, rotenticides, plant growth regulator and their usage in the treatment of diseases such as antitumor, leprosy, mental disorders, etc. [90-92] have sustained the interest of researchers in these compounds.

**x. As catalyst**

Recent studies [94] showed that transition metal complexes of Schiff’s bases have emerged as highly efficient catalysts in various fields of synthesis and other useful reactions. Synthetic chemists sometimes seek to imitate the efficiency and elegance of the biosynthetic machinery by designing biomimetic reactions that approximate natural
Introduction

reaction pathways. Probably the most astonishing biomimetic reactions were processes, which combine several transformations in sequence and produce complicated structures from comparably simple starting materials, in a simple laboratory operation. In such a simple but elegant method, Matsumoto et.al. [93] used Co(II), Mn(II) and Fe(II) with the Schiff base ligand, bis(salicylaldehyde)ethylenediimine (salen) as catalyst for the synthesis of carpanone in good yield by the oxidation of trans-2-(1-propenyl)-4,5-methylenedioxyphenol with molecular oxygen. A special catalytic application of Schiff base complexes was reported by Kim et.al. [94] Electrochemical reduction of thionyl chloride had been carried out at glassy carbon and molybdenum electrodes with surface modified by binuclear tetradeutate Schiff base, (3,3,’4,4’-teterasalycildineimino-1,1-biphenyl) complexes of Co(II), Fe(II), Ni(II) or Cu(II). The catalyst molecules were adsorbed on the electrode surface and reduced thionyl chloride resulting in the formation of oxidised catalyst molecule. The reduction current of thionyl chloride were increased and the reduction potentials were shifted to the negative region.

xii. Applications of Schiff base metal chelates to site-specific cleavage of a trypsin.
Iron(III) and copper(II) chelates of amidine-containing Schiff base were prepared from alpha-amino acid, metal ion, and salicylaldehyde. These chelates behaved as specific inhibitors of trypsin, with $K_i$ values in the range $10^{-5} - 10^{-6}$ M. Selective cleavage of the trypsin backbone resulting from specific binding of the chelate to the trypsin active site was investigated. Cleavage was observed when trypsin was incubated with amidine-containing Cu(II) or Fe(III) chelate, $H_2O_2$, and ascorbate. Examination of the three-dimensional structure of trypsin suggests that cleavage occurred at a peptide bond within the Gly195-Ala204 sequence [95].

xiii. Schiff’s base metal complexes as sensors
The electrode based on copper(II) chelates of unsymmetrical tetradeutate Schiff base, o-hydroxybenzophenone-1,2-diaminobenzene-pyrrole-2-carbaldehyde, as carriers, exhibited fairly good response characteristics for thiocyanate. High selectivity and sensitivity, a wide linear range and a low detection limit, very short response time, and stable reading, as well as a near-Nernstian slope were observed. These properties make the electrode suitable for the content detection of thiocyanate in real samples [96].
A new solvent polymeric membrane electrode based on Schiff base complexes of Co(II) was described which demonstrates excellent selectivity toward the iodide ion. The resulting electrode exhibits fairly low detection limits and good selectivity properties. The selectivity sequence observed was iodide > thiocyanate - nitrite > perchlorate - bromide > nitrate > chloride > sulfate. The excellent selectivity for iodide was related to the unique interaction between the central Co(II) ion and iodide. The response mechanism of the electrode was also studied with the ac impedance and spectroscopic techniques [97].

xiv. Schiff’s base metal complexes in Dyes
Chromium azomethine complexes [98], cobalt complex Schiff’s base [99] unsymmetrical complex 1:2 chromium [100,101] dyes give fast colors to leathers, food packages, wools etc. Azo group containing metal complexes [102,103] are used for dying cellulose polyester textiles. Some metal complexes [104] are used to mass dye polyfibers. Cobalt complex of Schiff’s base [99] has excellent light resistance and storage ability. Novel tetradentate Schiff base act as a chromogenic reagent for the determination of Ni in some natural food samples [105,106].

1.9. PRESENT WORK
The present thesis contains the results of physicochemical characterization on transition metal complexes of semicarbazide and thiosemicarbazide based ligands. The transition metal that have been taken for study are Mn(II), Co(II), Ni(II), Cu(II). All the complexes synthesized were characterized by elemental analysis, magnetic moments, IR, electronic and EPR spectral studies. Newly synthesized ligands and their some of the complexes have also been screened against different bacterial and fungal species. In- vitro screening of antibacterial activity of the two ligand and its some of the metal complexes were tested by using paper disc diffusion method against Xanthomonas campestris pv. Campestris and Ralstonia solanacearum. The preliminary fungitoxicity screening of some of the compounds at different concentrations was performed in vitro against the test fungi, Botrytis cinerea, Macrophomina phaseolina and Phoma glomerata by the food poison technique. The efficacy of the effective compounds was
studied for their application in seed treatment. The activity of most effective antifungal complex was also compared and correlated with natural oil (Geranium oil). The mortality of *helicoverpa armigera* has been checked with some of the synthesized compounds.

The semicarbazide and thiosemicarbazide based ligands (Figure 1.20) which have been synthesized and characterized by elemental analyses, IR, UV, $^1$H NMR, and mass spectral studies, are as follows:

3-Bromoacetophenone semicarbazone ($L_1$)
3-Bromoacetophenone thiosemicarbazone ($L_2$)
1-Tetralone semicarbazone ($L_3$)
1-Tetralone thiosemicarbazone ($L_4$)
Flavanone semicarbazone ($L_5$)
Flavanone thiosemicarbazone ($L_6$)

The transition metal complexes with these ligands are characterized on the basis of element analysis, molar conductance measurement, magnetic susceptibility measurement, IR, UV and EPR spectral studies.
1.10. **FURTHER SCOPE OF THE WORK**

In continuation to the work, there is scope of further studies along the following lines:-

1) Low temperature magnetic susceptibility measurements of the complexes which show existence of high-spin and low equilibria or temperature involved reversible stereochemical conversion.

2) To synthesize the complex of 4d and 5d transition metal ions.

3) Studies on crystals, particularly evaluation of principal magnetic moment and principal $g$ - values of complexes.

4) Studies on electrochemical behavior of complexes.
5) The chelating ligands with amide or thioamide terminals could further be used to produce highly cross linked polymers with ethylene glycol-dimethylacrylate (EGDMA) and self-assembled coordination polymers.

6) Stabilization of unusual oxidation states of transition metals ions.

7) They can be used to build diamondoid networks with big cavities because they have the perspective to be used as porous materials or for the catalytic purpose.

8) Metal complexes can be used as optical and electrochemical sensors, as well as various chromatographic methods, to enable detection of enhanced selectivity and sensitivity.

9) Physical and analytical chemistry required to carry meaningful thermodynamic and kinetic template effect studies.

10) Fluorescence and chemiluminescence’s characters of carry compounds can be studied.

11) To study their biophysical as well as catalytic properties.

12) Whether such complex can mimic certain enzyme system. If so, what will be the consequence of such mimicry?

13) To study antimicrobial activities other than antifungal, antibacterial and insecticidal which have been studied in present work.
REFERENCES

Introduction