CHAPTER – I

INTRODUCTION

(A) ACID HYDRAZIDE SCHIFF BASES:

The condensation products of compounds containing aldehydic or ketonic group and primary amines are known as schiff’s bases after the name of the discoverer. The Schiff bases derived from aldehydes are usually termed as anils while those obtained from ketones are known as keto anils.

\[ R - \text{CHO} + \text{NH}_2\text{Ar} \rightarrow \text{RCH} = \text{NAr} \quad \text{Anil} \]

These bases are characterized by the presence of C=N group, which is usually known as azomethine group.

MECHANISM OF FORMATION OF SCHIFF BASES:

The mechanism of the formation of Schiff bases may be explained as follows:

\[ R - \text{C} = \text{O} + \text{H}_2\text{NAr} \leftrightarrow \text{R} - \text{C} = \text{NAr} + \text{H}_2\text{O} \]

(where \( R = \text{Alkyl / aryl group}, \quad R' = \text{H/alkyl/aryl group} \))

The formation of Schiff base is catalysed by an azeotropic agent, e.g. anhydrous ZnCl\(_2\).
“Acid hydrazide Schiff bases are the compounds obtained by the condensation of an acid hydrazide and a carbonyl compound”.

Acid hydrazides and their derivatives have gained prominence because of their antibacterial activity and potentiality as versatile coordinating agents\(^{(1,2)}\). Isonicotinic acid hydrazide is found superior to some other pyridine and nonpyridine hydrazides towards tuberculostatic activity\(^{(3)}\).

Schiff bases are well known to possess pronounced biological activities\(^{(4–12)}\). Anils obtained by the condensation of salicylaldehyde and aromatic amines, o–aminophenol and polymethylene diamines are found as useful bactericidal and fungicidal agents\(^{(13)}\). Anticancer Schiff bases\(^{(14)}\) have been prepared by condensing aniline with some substituted benzaldehydes. Hydrazide Schiff bases, mainly those derived from aromatic hydroxy aldehydes have been shown quite important for their pharmaceutical\(^{(15–18)}\) and analytical\(^{(19,20)}\) applications. They exhibit the tendency of forming more or less stable metal chelates\(^{(21–23)}\).

Heterocyclic Schiff base ligands containing an additional azo function find various applications. They have been of great importance due to their synthetic flexibility, selectivity and sensitivity towards the metal ions. Heterocyclic ring containing sulphur, nitrogen and or oxygen impart special biological activity to these Schiff bases and their metal complexes.\(^{(24)}\) Metal complexes with ligands containing N, O, and S–donor atoms are useful as potential drugs, fungicidal and antibacterial agents. Semicarbazones and thiosemicarbazones presents a wide range of bioactivities and their chemistry and pharmacological applications have been extensively investigated. The biological properties of semicarbazones and thiosemicarbazones are often related to the metal ion coordination. Thiosemi–
carbazone derivatives of various aldehydes and their transition metal complexes present vide biological activities.

**COORDINATION BEHAVIOUR OF ACID HYDRAZIDE SCHIFF BASES:**

As ligands, they provide two potential donor sites, viz. O & N. Owing to the presence of lone pair of electrons on the nitrogen atom of the azomethine group, Schiff bases form several complexes with metal ions. The field of Schiff bases is fast developing on account of wide variety of structures possible for the ligands depending upon the aldehyde and amine\(^{(25-27)}\). Much interest has been shown recently by scientists into the study of compounds of transition metals with Schiff bases\(^{(28)}\), as many of these compounds are pharmaceutically applicable\(^{(29,30)}\). Some specific structural requirements are essential for complexation to occur\(^{(31)}\) and these requirements are fully satisfied in these compounds. The coordination chemistry of hydrazine and substituted hydrazines as well as of acid hydrazide Schiff bases is of special interest because of variety of ways in which these species can be bonded to the metal ions\(^{(32,33)}\). Further as the acid hydrazide Schiff bases show keto–enol tautomerism, the carbonyl oxygen atom or enolic oxygen atom after deprotonation may form a bond with the metal ion.

![Keto form](image)

![Enol form](image)

**(B) **MANNICH BASES:

Mannich base is the condensation product of a compound containing at least one active hydrogen atom, HCHO and ammonia or a primary or secondary amine. The main feature of the reaction is the replacement of the active hydrogen atom by an aminomethyl or substituted aminomethyl group.
MECHANISM OF FORMATION OF MANNICH BASES:

Liebermann and Wagner\(^{(34)}\) proposed that the Mannich reaction is due to the addition of a methylene ammonia cation or a protonated dialkyl amino ethanol to a carbanion.

\[
\begin{align*}
\text{CH}_2&\equiv\text{N}^+\text{R}_2 + \text{CH} \quad \text{C} \quad \rightarrow \quad \text{CH} \quad \text{C} \\
\text{CH}_2 &\quad \text{NR}_2
\end{align*}
\]

The addition of amine to formaldehyde has been considered as the first step of the reaction\(^{(35,36)}\). The introduction of an aminomethyl group in a number of acid hydrazides has been found to increase the therapeutic value. Singh, Gupta and Yadav\(^{(37)}\) have prepared a number of salicylic acid hydrazide Mannich bases by using different amines.

2–Amino benzothiazole mannich bases prepared by Jacques and Co–workers\(^{(38)}\) showed interesting analgesic activity in mice. The Mannich bases of 7–hydroxy and 7–hydroxy–4–methyl coumarins synthesized with aliphatic amines have been found to have powerful stimulating effect on central nervous system.\(^{(39)}\) Mannich bases derived from 5–(p)–chlorophenyl–1,3,4 oxadiazol–2–thione have been found to exhibit remarkable fungicidal activity. In addition to the biological significance, Mannich bases have been quoted as potential polydentate ligands.\(^{(40)}\)

COORDINATION BEHAVIOUR OF MANNICH BASES:

These compounds exhibit the electron donor property. They contain nitrogen as an essential electron donor atom. Mannich bases, particularly of acid hydrazides and hydroxy ketones, contain oxygen also act as donor atom. In this
manner they act as versatile co-ordinating agents. Some new Cu(II), Ni(II) and Co(II) complexes of 3–(p-Dimethylaminoanilino)–methyl salicylic acid hydrazide have been synthesized and characterized on the basis of elemental analysis, magnetic and I.R. spectral data by Agarwal and Co–Workers\textsuperscript{(41)}. 3–(α–Naphtylaminomethyl) salicylic acid hydrazide has been used as an analytical reagents for the gravimetric determination of Ni(II) and Pd(II) by Agarwal and Chandra.\textsuperscript{(42)}

(C) **METALS AND THEIR OXOCATIONS:**

The actinides are an important group of elements. The two earlier members of the actinides, e.g. thorium and uranium, available in large quantities, are relatively inexpensive and their naturally occurring isotopes are fairly easy to handle\textsuperscript{(43)}. They find significant use as nuclear fuel. The low neutron absorbing character of Zirconium coupled with its desirable metallurgical properties make Zr an attractive metal for cladding in nuclear reactor construction. The radioactive 95\textsuperscript{Zr} is a useful isotope for Zr tracer studies. The complex chemistry of molybdenum has of late gathered much importance due to the participation of variable valency molybdenum cofactors in several redox enzyme systems. Enzymes such as nitrogenase, nitrate reductase, xanthine dehydrogenase, xanthine oxidase, sulphite oxidase and aldehyde oxidase contain molebdenum atoms bonded through O, N and/or S atoms. These Mo sites are supposed to be the active centres for the catalytic activity of the enzymes\textsuperscript{(44)}. Except nitrogenase, other molybdenum– enzymes are found\textsuperscript{(45)} to be EPR–active during electron transfer, which is attributed to the presence of Mo(V) centres; EXAFS studies have indicated\textsuperscript{(46)} the presence of an oxo group attached to molybdenum. The vanadium ion has been thought to be an essential element in both animals and plants.\textsuperscript{(47)}
Although there are nearly sixty oxometal entities known with the transition and non–transition metals of the type MO$_x^{n+}$ (where x may be 1,2 or 3 and n may be 1,2,3,4 or 5), stereochemistry of many of their complexes have not been studied in detail. Among them a number of compounds have been studied whose spectra contain the M=O stretching frequency to ascertain how it varies under different circumstances. All the oxocations are conveniently classified in three groups$^{(48)}$. Class (a) contains those compounds in which there is only one metal oxygen bond per metal atom; this bond has a high double bond character; class (b) is similar except that there are two such M=O bonds per metal atoms and class (c) contains all compounds with more than two M=O bonds, including complex oxides, in which there may be no appreciable decrease in double bond character. Oxozirconium and oxovanadium, in which only one oxygen atom per metal atom is present, comes under class (a), while the dioxouranium (vi) containing two oxygen atoms comes in class (b).

Uranyl compounds have been the subject of investigation since several years because of their interesting photochemical properties. Among the various uses of uranyl compounds, one of the important application is their utility as luminescent materials, because of their high fluorescence yield when irradiated with suitable radiations. The most extensively studied, best characterized and most suitable oxometal entities are the dioxouranium(vi)$^{(49,50)}$ and oxovanadium(iv)$^{(51)}$ ions. The strongly bound oxygen atoms of these oxometal entities remain intact during chemical reactions and thus provide additional means for studying the complexes of the oxo–cations beyond those normally available with transition metal complexes. Stability, structure and bonding in the oxometal ion species are
greatly influenced by anionic environment and the nature of the donor atoms of the ligands.\(^{(52-56)}\)

(D) **COMPLEXES:**

Schiff base complexes have been studies extensively\(^{(57-59)}\) due to various reasons like manifestation of novel structural features, abnormal magnetic properties and relevance of biological process. The study of various transition metal complexes as models for understanding the many biochemical processes requiring metal atoms is very much interesting\(^{(60,61)}\). The importance and need for the study of transition metal complexes for their biological significance have been stressed\(^{(62,63)}\). Cancer formation and the inhibition both involved chelation. Carcinogenic metals are generally transition metals which have pronounced tendency for chelation and are associated with vitamins, proteins and nucleic acids. Drugs show increased activity when used in the form of their metal complexes and a number of metal chelates inhibit tumour growth. It has been observed that the bacteriostatic activity of the compound increase when it forms chelate with metal.

The vanadium and molybdenum complexes have received considerable attention recently\(^{(64-71)}\) due to their biochemical importance. Cause of great importance is the ability of molybdenum to bind sulphur donors like thiol groups of proteins. It is interesting that the only other early transition metal which has a number of readily interconvertible oxidation states and some affinity for sulphur, is vanadium. Vanadium will replace molybdenum in nitrogenase with maintenance of enzymatic activity. The binary complexes of the vanadyl ion with anthranilic acid, dicarboxylic acids\(^{(72)}\) and hydroxy acids\(^{(73)}\) have been extensively studied. The ternary complexes of oxovanadium(iv) with dicarboxylic or hydroxy acids
have also been reported\(^{(74)}\). Oxovanadium(iv) complexes exhibit various interesting coordination feature like bridged and chained structures, uncommon subnormal magnetic moments\(^{(75,76)}\) etc. Tetrameric zirconium(iv) complexes with bidentate ligands have been isolated and characterized\(^{(77)}\). Synthetic and physio-chemical studies on some oxozirconium(iv) and dioxouranium(vi) Schiff base complexes have been carried out\(^{(78)}\).

Large number of stable and well defined dioxomolybdenum(vi) complexes of the type, \(\text{MoO}_2\text{L}_2\) (LH=bidentate ligand) have been isolated and characterized\(^{(79–82)}\). There has been appreciable interest in \(\text{UO}_2^{2+}\) complexes with various organic ligands\(^{(83)}\). The ability of the \(\text{UO}_2^{2+}\) ion to react with poly functional ligands containing carboxylic groups to give complex species of various kinds has been established by several authors\(^{(84–88)}\). The uranyl ion has strong affinity for oxygen donor ligands because of its hard acceptor properties\(^{(89–95)}\). In the case of uranyl complexes, it can be expected that the basicities of the ligands influences the stabilities of the complexes to a very little extent, while the steric factors and the chelate ring sizes play an important role.

(E) **WORK DONE:**

A perusal survey of the literature revealed that no considerable work seems to have been done so far on the coordination compounds of acid hydrazide Schiff bases and Mannich bases with oxocations such as \(\text{VO(IV)}, \text{ZrO(IV)}, \text{UO}_2^{(VI)}\) \(\text{MO(VI)}\) etc. It was, therefore, decided to prepare some new acid hydrazide Schiff bases and acid hydrazide/hydroxy acetophenone Mannich bases and to study their reaction with some oxocations such as \(\text{VO(IV)}, \text{ZrO(IV)}, \text{UO}_2^{(VI)}, \text{MoO(V)} \& \text{MoO}_2^{(VI)}\).
STRUCTURES OF LIGANDS

(A) ACID HYDRAZIDE SCHIFF BASES

1. 

![Structure 1]

Fig. 1: 2-Thiophene Carboxalidene 8-quinolinoyl Hydrazide (TCqH) (C_{15}H_{11}N_{3}OS)

2. 

![Structure 2]

Fig. 2: Terephthalalidene Bis (8-quinolinoyl Hydrazide) (TqH) (C_{28}H_{20}N_{6}O_{2})

3. 

![Structure 3]

Fig. 3: Phenyl Glyoxalidene–2–Furoic acid Hydrazide (PGFH) (C_{13}H_{10}N_{2}O_{3})

4. 

![Structure 4]

Fig. 4: 2–Furion Phenoxyacetyl Hydrazide (FPAH) (C_{18}H_{16}N_{2}O_{5})
Fig. 5: 2:4–Dimethyl benzalidene Benzoyl Hydrazide (DBBH) (C$_{16}$H$_{16}$N$_{2}$O)

(B) MANNICH BASES

1.

Fig. 6: 3–(2,2$^1$–Dimethyl p,p$^1$–Diaminodiphenyl) Methylsalicyloyl Hydrazide (DDMSH) (C$_{22}$H$_{24}$N$_{4}$O$_{2}$)

2.

Fig. 7: 3–(p–Diethylamino Anilino) Methyl Salicyloyl Hydrazide (DEAMSH) (C$_{18}$H$_{24}$N$_{4}$O$_{2}$)
In the present work efforts have been made in the direction of establishing a correlation between analytical, magnetic, spectral and thermal properties of coordination compounds.

In brief the work done in the present thesis is summarized in the following lines:

(1) Five acid hydrazide Schiff bases have been synthesized by the condensation of 2-thiophene carboxaldehyde and quinolinoyl hydrazide, terephthal-aldehyde and quinolinoyl hydrazide, phenyl glyxaoal and 2-furoic hydrazide, 2-furoin and phenoxy acetyl hydrazide, 2:4-Dimethyl salicyldehyde and benzoyl hydrazide.

(2) Four Mannich bases of salicyloyl hydrazide and hydroxy acetophenones have been prepared by the condensation of the hydrazide/hydroxy acetophenone, formalin and a primary or a secondary amine.
(3) The synthesized ligands have been characterized by analytical and spectral studies.

(4) Preparation of the chelates of VO(IV), ZrO(IV), UO$_2$(VI), MoO(V) and MoO$_2$(VI) has been carried out with the synthesized organic ligands. The chelate have been isolated in the purified solid form.

(5) The nature of the bonding involved between ligand and metal is thoroughly discussed on the basis of advanced physical techniques viz. IR, Electronic/Reflectance spectral (wherever applicable) studies.

(6) The stereochemistry of the coordination compounds is established on the basis of spectral and magnetic moment studies.

(7) The ligand field parameter Ds, Dt, Dq, DS, DT and DQ have been calculated for oxovanadium(IV) complexes.

(8) Ionization potential and log k values have been calculated for oxozirconium(IV) complexes.

(9) The thermogravimetric and differential thermal analysis (TGA and DTA) of some of the isolated chelates have been carried out.
CHAPTER–I

REFERENCES


