Chapter I
INTRODUCTION
A. DEVELOPMENT IN THE CHEMISTRY OF SCHIFF BASES

Of the variety of Schiff bases ranging from monodentates to heptadentates, bidentate Schiff bases having diverse coordinating sites have been thoroughly investigated. The vast amount of information added to the understanding of the structures of bidentate Schiff base complexes rather makes it difficult to render a critical estimate of them. However, most of the review articles published to date have made considerable tribute to the bidentate Schiff bases and their complexes (1,2).

It is not the aim of the author to give an exhaustive account of all the Schiff bases hitherto reported, but only to give a brief resume of the work done in the field, which is relevant to the subject embodied in the thesis. Stress is given on the bidentates and their varied behaviour and tridentates with donor sequences such as NNN, NNO, ONO, ONS etc. A mention is made of tetradentates containing ONNO and SNNS sequences and other higher multidentate Schiff bases.

Amidst the innumerable Schiff bases, the monodentate Schiff bases containing only one coordinating site viz. CH=N are the simplest ones and have been tried for the
group IV metal chlorides (3). The adducts prepared hitherto have 1:2 stoichiometry and are non-electrolytes. The evidence for the donor-acceptor bond is sought in the infrared spectral studies.

The instability of ammonia and ethylenediamine iron (II) complexes and the unusual stability of dipyridyl and 1,10-phenanthroline complexes suggest that the presence of an unsaturated group is critical in the formation of complexes. In an endeavour to construct a ligand containing

\[ -\text{N} = \text{C} = \text{N} - \]

in the structure Bahr et al. (4), Krumholz (5), Bailar and Busch (6), Stourfer and Busch (7) and Karause and Busch (8), have synthesised a series of bases containing

\[ -\text{N} = \text{C} = \text{C} = \text{N} - \]
The preparation and various physicochemical aspects of the complexes have been discussed and structures have been proposed. A few years later Kogan and coworkers (5) have reported Ti (IV) and Sn (IV) complexes having 1:2 stoichiometry with 2-methoxybenzylidene-aniline wherein coordination bond is found to exist between C=N and metal moiety.

Stapfer et al. (10,11), Schlosser and Hoyer (12) have prepared iron, nickel and titanium (IV) complexes with the
bases which contain the skeleton or Krumhoiz's base viz

\[
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{C} \\
\text{N} \\
\text{N} \\
\text{M}
\end{array}
\]

Stapfer et al. (10,11), have shown that the complexes have tetrahedral configuration.

\[
\begin{array}{c}
\text{X} \\
\text{X} \\
\text{Co} \\
\text{N} \\
\text{N} \\
\text{X} \\
\text{N}
\end{array}
\]

The work on the monovalent bidentate Schiff bases and their complexes traces as back as 1840. Pfeiffer and coworkers (13) who stumbled on the synthesis of Ni(II) complex in aqueous medium claimed the priority of preparing the complex for the first time, found on surveying the literature that Etting (14), Schiff (15) and Delephne (16) had reported a series of similar type of complexes at an earlier date.
Pfeiffer et al. (17) have reported a range of Cu(II), Ni(II), and Zn(II) complexes with o-hydroxy acetophenone Schiff bases.

Further the X-ray analysis by Cox et al. (18), and Stakleberg (18) have shown that the donor atoms arrange in the trans positions because of the mutual repulsion of the like polar groups having equal ionic charges.

In a review article, Holm et al. (1), have discussed thoroughly the bidentate salicylaldimines and β-ketoamines
and stereochemistries of the complexes formed by them.

Recently it has been demonstrated by the Russian workers (19) that the monovalent bidentate Schiff bases can form 1:2 adducts with Group IV metal tetrachlorides showing monodentate behaviour. Holm and coworkers (20) have shown that Schiff bases are capable of displaying keto-enol tautomerism.

Hence it is possible that in the complexes they can exist even in the keto form. Bamfield (21) has isolated Co(II) complexes having 1:3 stoichiometry and has shown with the aid of infrared spectra that the Schiff base exist in the keto form thus showing bidentate behaviour.
Yamada et al. (22), in the dioxo uranium(IV) complexes, have proved that the coordination takes place through the o-hydroxy group of the Schiff base.

Kogan and coworkers (23) in an attempt to synthesise Ti(IV) complexes have prepared a complex wherein the C=N has not bound coordinately to the Ti moiety but only oxygen has formed bonds with Ti(IV). Recently a series of Ti(IV), Sn(IV), Zr(IV) and Th(IV) complexes with bidentate Schiff bases have been reported (24, 25). For the first time, Biradar and Kulkarni (26) have reported oxovanadium(V) and lead(IV) complexes with salicylideneanilines and have shown that lead(IV) and oxovanadium(V) exhibit coordination number six in these complexes. A range of oxovanadium complexes
having coordination number five can be cited in the literature (27).

Schiff bases of thiosalicylaldehyde with amines are recorded in the literature. A number of Cu(II), Ni(II), and Zn(II) complexes are also reported (28).

Bose and Patel (29) have prepared the Ni(II) complexes with a new base containing NN sequence i.e., Desylaniline-hydrazone and have characterised them spectrochemically and magnetochemically.
The stability of terpyridine complexes is believed to be related to the arrangement in terpyridine which gives rise to many resonating structures involving π-bond formation (30).

\[ \text{N} - \text{C} - \text{C} = \text{N} - \text{C} - \text{C} = \text{N} - \]

This arrangement can conveniently be had by condensing 2-aldehydopyridine with 2-amino pyridine.

Morgan and Brustall (31) consider three arrangements of two chelate molecules. Only one of these possible arrangements satisfies the condition of coplanarity of the pyridine rings in which the two molecules of the base are arranged into two equatorial planes.
The attempts to resolve Ru(II) and Ni(II) complexes were not fruitful. However, the octahedral complexes resulted from 1-(α-pyridyl methyl amino)quinoline have been obtained in the enantiomeric forms because of the inherent unsymmetrical nature of the base.

Recently Litzow et al., have prepared metal complexes of the base 2-methyl-8-(6-methyl-2-pyridyl) methyl aminoquinoline (32).
Condensation of quinoline 8-aldehyde with 2-amino methyl pyridine results in a base which can behave as a tridentate forming one five membered and another six membered ring (33).

If α-pyridyl hydrazine is condensed with 2-pyridine aldehyde, a base which can coordinate tridentately with the transition metals is formed.
This base can easily be protonated to yield highly coloured complexes. Lions et al. (34), have shown that these bases are capable of forming square planar or trigonal bipyramidal complexes depending on the coordination at the fourth site.

2-Pyridinaldazine (PAA) has been proved to be an interesting tridentate and yields intense coloured complexes with Fe(II) and Ni(II).

\[
\text{\includegraphics[width=0.5\textwidth]{image.png}}
\]

It can behave as a double bidentate forming complexes of the type \( \text{Mg}^\text{(PAA)}^4 \). The quadridentate function is sterically impossible (35).

The bases derived from 2,6-dialdehydropyridine yield ideal tridentates. The planarity of the complex molecules had made them to be non-resolvable (36).
Recently Midollini and Bacci (37) have prepared vanadium(IV) and oxomolybdenum complexes with similar type of ligand and have shown with the help of infrared, electronic spectra and magnetic data that they are hexacoordinated. They have compared oxomolybdenum (IV) with oxovanadium(IV) and have located the Mo = 0 stretch.

Yet another type of tridentate contains either NNO or NNNS sequence. The simple example of the base containing NNO sequence is the result of the condensation of 2-aldehydropyridine with o-aminophenol.
A similar type of structure can also occur in acetyl acetone-8-quinolineamine (34).

In the recent review articles on complexes of 3d metals, Sacconi (38) has thoroughly discussed the Schiff bases formed from salicylaldehyde and N-substituted ethylenediamine and their Ni(II), Cu(II), and Co(II) complexes.

\[ \text{Y} = \text{NH or O} \]
\[ \text{R} = \text{C}_2\text{H}_5 \text{ or CH}_3 \]
Sacconi et al. (39), have opened a new chapter in the field of Schiff base complexes, called complexes of hybrid ligands.

\[
\begin{align*}
&\text{Z} = \text{P, As} \\
&\text{Y} = \text{NH, O, S.}
\end{align*}
\]

Following the work of Sacconi et al., a series of five coordinate bivalent Fe, Co, Ni, Cu and Zn complexes have been published in the recent years (40,41).
Livingston and his coworkers (42) have shown that 2-amino benzenethiol undergoes a rearrangement when treated with metal acetates and forms tridentate Schiff bases having NNS sequence.

\[
M(OAc)_2 + 2
\]

Mention may be made of a novel double tridentate synthesised by Fernelius et al. (43), who have shown that the base instead of behaving as a hexadentate behaves as a double tridentate.
Zelentsov and Suvorova (44) have isolated a new series of tridentate Schiff base complexes of Ni(II), Co(II) and Cu(II) with Schiff bases resulted by the condensation of acetylacetone and propionylacetone either with 2-mercaptopethylamine or with 2-mercaptopropyramine.

A wide range of transition metal complexes have been documented in the literature with bivalent tridentate Schiff bases having ONO or SNO sequences. These are the reaction products of various substituted salicylaldehydes or thiosalicylaldehyde and substituted o-amino phenol or thiophenol. In all the cases the structures have been corroborated with the help of infrared, electronic spectra and magnetic data and they are invariably shown to be dimeric in nature (45). Typical bases are shown below.
Thiosemicarbazones form an interesting series of tridentates (46). These can behave as monovalent tridentates or as bivalent tridentates. Complexes of both types are known in the literature. Most of the credit to synthesise such type of complexes goes to Gingras et al. (47) and Ablov et al. (48).

Recently Ablov et al. (49) have also reported few transition metal complexes with seleno-semicarbazones.
The tetradentate Schiff bases are the products of condensation of diamines with o-hydroxy aldehydes, o-mercaptoaldehyde or pyridine-2-aldehydes. Lions et al. (50), Bailar and Busch (6) have reported the bases containing four donor sites. These are the neutral tetradentates which contain four co-ordinating sites. Campbell and Urbach (51) have recently reported complexes of Cu(II) with such neutral tetradentate ligands. The bases containing ONNO sequences which can behave as bivalent tetradentates have thoroughly been investigated (30). The spectroscopic evidences prove that these ligands prefer to have cis configuration in the complexes. A number of Schiff bases which contain two active and two co-ordinating centres but fail to behave as tetradentates are also known in the literature. These are mainly the bases derived from m-phenylene diamine, p-phenylene diamine or benzidine (52). A number of tetradentate Schiff bases having ONNO sequences have been tried very recently for a good number of transition metals (53) and in all the cases the conclusions have been founded on the basis of spectrochemical and
magnetochemical investigation. Sacconi et al. (54), have synthesised a new Schiff base containing SNNNS sequence and prepared the complexes of Ni(II), Co(II) and Zn(II).

\[
\begin{array}{c}
\text{\includegraphics[width=0.3\textwidth]{schematic.png}}
\end{array}
\]

Mention may be made of the work by Warren et al. (55), who have isolated a dimeric Cu(II) complex with \(\alpha\)-diketone-bis-(thiosemicarbazone) and have suggested the following structure.

\[
\begin{array}{c}
\text{\includegraphics[width=0.3\textwidth]{structure.png}}
\end{array}
\]

Of the higher multidentates, the linear sexadentates have been extensively studied but relatively few quinque-dentates have been synthesised (30). Most of these have
been the result of condensation of \( \alpha-\omega \)-diamines with aromatic aldehydes to give bases (56) of the general formula shown below where \( X \) and \( Y \) may be \( 0, N \) and \( S \).

\[
\begin{array}{c}
\text{Y} \\
\text{N} \\
\text{X} \\
\text{N} \\
\text{Y}
\end{array}
\]

The ligand of the type indicated below prepared by Sacconi and Bertini (57) form five-co-ordinated complexes, presumably because the sixth co-ordination site on the metal is blocked by the bulky groups on the ligands. These complexes have been shown to be intermediate between square pyramidal and trigonal bipyramidal geometry. Taylor and Coleman (58) have extended the pentadentate ligands to include further examples to the chemical literature. Seyhan and Fernelius (43) have reported a new Schiff base having ONNNO sequence which is capable of attaching itself
pentadentately to the metal ion. The base is the condensation product of 4-methyl, 2,6-dialdehydo pyridine and o-aminophenol.

Recently Taylor and Coleman (59), Sacconi et al. (57), Black and McClean (60), have reported few more new pentadentate Schiff bases.

There is much information available on the sexadentate Schiff bases and their complexes (30). A few heptadentate Schiff bases and their complexes are also known (61, 62). In all the cases the structural information has been adduced with the help of physicochemical methods.

B. BENZIMIDAZOLES

Benzimidazoles are widely used as good analytical reagents (63-65). Till the work of Ghosh et al. (66) who reported Cu(II) complexes, there has been little attention
attached to these ligands. They have isolated two types of complexes in which benzimidazole shows two types of behaviour, i.e. monodentate and bidentate.

Livio et al. (67) have reported Co(II) and Co(III) complexes of benzimidazoles and characterised them magneto-chemically. Later Freiser et al. (68), have studied a few transition metal complexes with benzimidazoles and have shown that unsaturated nitrogen has more co-ordinating tendency than secondary nitrogen and it depends mainly on the pH in the case of nitrogen.

Recently Dutta and Lahiry (69) have isolated two types of oxovanadium(V) complexes with 2-guanidino-benzimidazole, depending on the reaction conditions. In one, 2-guanidino-benzimidazole behaves as a neutral bidentate whereas in the other it shows monovalent bidentate behaviour. Both the structures are shown below.
Studies of Nazaki et al. (70) have doubtlessly proved that Cu(II) cannot form planar complexes with imidazoles because of the marked overlapping of the Van der Waals radii or hydrogen atoms on the adjacent imidazole molecule. Lane and Quinlan (71) also support the views of Nazaki et al. (70), in the case of Cu(II) benzimidazole complexes.
Lane and coworkers (72) have isolated a few transition metal chelates of the following type with 2-(o-hydroxyphenyl)benzimidazole and 2-(β-pyridyl)benzimidazole.

These structures have been established in the light of infrared spectral evidences. In all these complexes unsaturated nitrogen takes part in the co-ordinate bond formation.

Within the span of few years, quite a large number of complexes of benzimidazoles have been added to the list and these have been well characterised with the aid of various physico-chemical methods (73). Recently Biradar et al. (74), have reported two types of lead(IV) complexes with 2-substituted benzimidazoles and characterised them using spectral evidences. In the complexes of lead(IV) isolated from 20% HCl medium, benzimidazoles exist as
protonated species. Thorium(IV) benzimidazole complexes have also been reported recently by the Russian group of workers (75). They have also observed that the unsaturated nitrogen of the benzimidazole forms coordinate bond with thorium(IV).

C. Survey of the Previous Work:

Amongst the Group IV elements of the periodic table, the chemistry of tin, titanium and zirconium has been extensively studied. Few papers have been published on the Schiff base complexes of zirconium(IV) (24,76-81). In all these cases zirconium(IV) chloride has been used for preparing the complexes. Only few authors have synthesized the Schiff base complexes using zirconyl chloride (84-85). Macarovici et al. (84) have reported dimeric zirconium complexes containing no Zr=O bonds with bis-(salicylidene) benzidine.

Though the theoretical promises account for a wide range of coordination numbers viz. 4 to 8, the majority of the Schiff base complexes of zirconium documented in the literature exhibit coordination number six (84). Podder and Biswas (80) have reported 1:2 complex of zirconium(IV)
with tetradentate Schiff base, bis-(salicylidene) ethylenediamine having coordination number eight. Biradar et al. (85), have prepared pentacoordinate complexes of zirconium with bidentate aromatic Schiff bases. Recently Biradar and Locker (86) have synthesised the complexes of coordination number eight with tetradentate Schiff bases derived from ethylene-diamine using zirconyl chloride. These have been characterised with the help of infrared spectra.

Not much information is available on zirconium(IV) benzimidazole complexes except the one due to Pyanushkin et al. (75). They have suggested that the unsaturated nitrogen of the benzimidazole involves in the coordination bond formation.

D. AIM OF THE PRESENT WORK:

Schiff bases, especially bidentates have been extensively investigated and proved to be promising chelating agents for a number of transition metals (1,2). A reviewed interest attached to these bases has resulted in increasing the literature about the Group IV elements.
The varied behaviour of zirconium, exhibition of wide range of coordination numbers (4-8) and the scanty information available on zirconyl complexes with Schiff bases and benzimidazoles have instigated the author to extend the study on zirconyl complexes to some bi-, tri- and tetradeutate Schiff bases and 2-substituted benzimidazoles.

A few successful studies report that the zirconium salts in pepton bath reduce the indole formation of Escherichia Coli, increase the pyrocyanine formation of Pseudomonas, lower the virulence of chicken cholera and Bacillus anthracis. The compounds are effective as insecticides against Tribolium ferrugineum. These are proved to be effective in inhibiting egg cultivated tumors without affecting embryos (87).

Schiff bases are known to possess tuberculostic, fungicidal, bacteriostatic activities (88). They are also known to be effective antitumor agents (89). The phenolic compounds in which the azomethine group is situated on the ortho position to the hydroxy group are known to give chelates which possess antibacterial and fungicidal activities (90). The benzimidazoles are also known for their manifold biological activities (91).
It is therefore hoped that these Schiff bases and benzimidazoles when completed with zirconium salts may yield some interesting complexes, which might prove to possess antibacterial and fungicidal activities.
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