CHAPTER-II
2.1 HISTORICAL KNOWLEDGE:

The condensation of aldehydes or ketones with primary amines yields imines (aldimines or ketimines) which contain a \( \text{C}=\text{N} \) bond. These compounds either decompose or poly-merize rapidly unless there is at least an aryl group bonded to the nitrogen or carbon atom. The latter imines are called Schiff bases. The most common method of obtaining a Schiff base is a simple condensation between the aldehyde / ketone and primary amine involving the formation of an intermediate.

\[
\begin{align*}
\text{R} & \quad \text{C}=\text{O} + \text{R'}\text{NH}_2 \rightarrow [\text{R'-C-(NHR')}(\text{OH})\text{R'}] \\
\text{R'} & \quad \text{H}_2\text{O} + \text{R''N} = \text{C} \cdot \\
\text{R} & \quad \end{align*}
\]

Where \( \text{R} \), \( \text{R'} \) and \( \text{R''} \) are alkyl, cycloalkyl, aryl or heterocyclic groups which may also be substituted. The presence of nitrogen and oxygen donors at suitable positions make Schiff bases an excellent ligand. This is because the complexation with a metal ion may lead to the formation of a five or six membered cyclic structure. Salicylideneaniline and its methyl derivatives were the first Schiff bases synthesized by Schiff\(^1\) in 1864, after whom these were named subsequently. Afterwards several compounds of this kind were synthesized and studied. A comprehensive and systematic study of Schiff bases was initiated in 1940 by Pfeiffer and coworkers.\(^{2,3}\)
They studied problems of synthesis, esterification, transamination, ligand replacement, metal exchange and stereo chemistry of the complexes in particular reference to salicylaldimine derivatives of copper (II). For the first time, Domagk et. al. ⁴ (1946) reported the antitumor activity in some thiosemicarbazide derived Schiff bases. The emerging areas of medicinal and biological applications are fungicides, insecticides, algacides, plant growth regulators, enzymatic decarboxylation, catalysts, enzymatic aldolization catalysis, antiviral, antibiotic, anaesthetic, antituberculosis, antitumor, anticancer and oxygen carrier in biological systems ⁵, 8, 13, 14, 24, 30, 35, 40.

The applications of the Schiff bases and their derivatives are enormous. Some traditional and industrial uses are as : pigments and dyes for cotton, wool, synthetic fibres and plastics, photographic emulsions, heat resistant polymers, high temperature stabilizers for lubricating oils, inhibitors against acid corrosion of metals and alloys, antiknocking agents and burning rate modifiers, polyolefine stabilizers etc. ⁶, 7, 11, 15, 16, 19, 20, 28.

In 1963, Layer ⁹ reviewed the preparation and properties of Schiff bases. Their chelating characteristics were described in a monograph by Dwyer ¹⁰ and Mellor. Holm and coworkers ¹² published an excellent review on the metal complexes of Schiff bases. Applications of Schiff bases in inorganic analysis have been described by Jungeis et. al. ¹⁷. Researches are on progress over bi or tricentered (polymetallic) Schiff base complexes, ¹⁸, ³³, ⁴³, ⁴⁶, macrocyclic Schiff base complex, ²³, ³⁰, ⁴⁷, polymeric
Schiff base chelates\textsuperscript{32, 34, 47} and Schiff base derivatives of metals in low valence\textsuperscript{48} state.

Dayagi and Degani\textsuperscript{21} reviewed the methods of Schiff base synthesis. Lipkin\textsuperscript{22} synthesized seventeen different Schiff bases having antimicrobial activity. In 1974, it was shown that palladium and copper chelates of dithiocarbazide possess antitumor activity. In recent past some antineoplastic activity in the chelates of platinum group metals and some of the 3d-transition metal with the Schiff bases derived from 5-methyl dithiocarbazate, purine, 6-mercaptopurine and thioguanine.\textsuperscript{25-26} Schiff base complexes of transition and some inner transition metals have widely been studied.\textsuperscript{27,29,39, 41} Mehrotra et. al.\textsuperscript{31} studied Schiff base complexes of some IV group elements. The Schiff base complexes of main group elements\textsuperscript{36,37,42} have been studied with emphasis on their applications in biology and industry. A good review on some coordination polymers have been published by Dey.\textsuperscript{44} Calligris and Randaceio\textsuperscript{49} have published comprehensive review on acyclic polydentate Schiff base ligands.
2.2 RELEVANT LITERATURE SURVEY:

Ansari and Ahmad\textsuperscript{50} have studied the rare earth complexes with Schiff bases derived from vanillin and benzidene. Goel and coworkers\textsuperscript{51} have studied potentiometrically the equilibrium constant values of bivalent metal ion complexes with o-vanillin. Some metal complexes of Schiff bases obtained from substituted salicylaldehyde and 2-amino pyridine derivatives were studied by Yamada and Yamanowchi.\textsuperscript{52} Biradar and coworkers\textsuperscript{53} have studied the complexes of Pd with monodentate Schiff bases from benzaldehyde/anisaldehyde and amines viz. Phenyl amine, p-toludine, p-chloroaniline and p-anisidine. Cobalt (II) complexes with Schiff bases derived from vanillin and o-phenylenediamine and benzidine have been prepared and characterized by Biradar et. al.\textsuperscript{54} Titanium (IV) complexes of monodentate Schiff bases derived from benzaldehyde and anisaldehyde with p-chloroaniline, p-anisidine and p-toludine were studied by Biradar and Kulkarni.\textsuperscript{55} Reactivity of chelated o-vanillin have been reported.\textsuperscript{56} Sen et. al.\textsuperscript{57} have prepared and characterized the transition metal complexes of β-furfuraldoxime. The electrometric studies of Schiff bases involving p-bromoaniline, was done by Chandel\textsuperscript{58} Biradar\textsuperscript{59} and Gaudar studied the Nb(IV) salicylidene-p-chloroaniline complexes.

Ni(II) and Cu(II) complexes with quadridentate Schiff bases obtained by condensing aliphatic diamines and dihydroxy acetophenone, dihydroxy-propiophenone and dihydroxy benzophenone have been studied by Dave and Mohankumar.\textsuperscript{60} Dave & coworkers\textsuperscript{61} have also synthesized the Ni(II) complexes of
Schiff bases derived from o-hydroxyacetophenone, o-hydroxypropiophenone and o-hydroxybenzophenone. Biradar\textsuperscript{62} and coworkers have prepared the 4 and 6-coordinated isonicotinyl hydrazone complexes of Mn(II). Fe (II) complexes with p-chloroaniline Schiff bases have been characterized by Maeda et al.\textsuperscript{63} Complexes of silicon(IV) with Schiff bases of salicylaldehyde and p-anisidine, p-chloroaniline and aniline were synthesized and analysed by Biradar et al.\textsuperscript{64}

Rastogi & Pachauri\textsuperscript{65} studied the complexes of Cu(II) and Pd(II) with 2-(2'-amino ethyl) pyridine Schiff bases. Metal complexes with Schiff bases derived from bis-vanillin and o-phenylenediamine have been prepared by Ansari et al.\textsuperscript{66} Ranganathan and Ramaswamy\textsuperscript{67,68} have studied the 3d-bivalent transition metal complexes of Schiff bases derived from salicylaldehyde and 2-amino pyridine and their derivatives. Sharma et. al.\textsuperscript{69} synthesized and characterized the complexes of lanthanide ions with Schiff base derived from vanillin and triethylenetetramine. Kaushik and Sharma\textsuperscript{70} have done the solid state studies of complexes of titanium (IV) with bidentate Schiff bases derived from salicylaldehyde and 4-anisidine, 4-phenetidine, 4-chloroaniline. Shukla et. al.\textsuperscript{71} have reported the synthesis of some furan-2-aldoxime-Cu(II) complexes. Jenson\textsuperscript{72} prepared Cu(II) complexes with Schiff bases derived from reactions of diamines and dihydroxybenzophenone/dihydroxyacetophenone. Idam and Luciano\textsuperscript{73} have prepared the Cu(II)-2-aminobenzophenone complexes and characterized them by magnetic, spectral and x-ray techniques.
Ali and coworkers\textsuperscript{74} have synthesized and characterized the transition metal complexes of Schiff bases derived from p-dimethyl aminobenzaldehyde and 3-propanediamine. Co(II) chelates of some bi and tridentate Schiff bases from toluidine and chloroaniline have been studied by Perkin and Shah.\textsuperscript{75} Syamal and Niazi\textsuperscript{76} have reported some new copper(II) coordination compounds of the Schiff bases derived from hydroxyacetophenone and hydroxybenzophenone. The metal complexes of furan-2-carboxamide have been investigated by Sanyal and Mudi.\textsuperscript{77} Sarkar et al.\textsuperscript{78} have characterized the 4-aminoantipyrine Schiff base complexes of lanthanides and uranyl ions. Schiff base behaved as a bidentate ligand. Some rare earth iodide complexes of 4-N(-2'hydroxy-1'-napthylidene) aminoantipyrine were synthesized and studied by Radhakrishnan.\textsuperscript{79} N-isonicotinamido-salicylimine complexes of UO$_2$(II), Al(III) and Zn(II) were studied by Srivastava et al.\textsuperscript{80} Jha and Joshi\textsuperscript{81} characterized the triorganoantimony (V) complexes of Schiff base involving salicylaldehyde and 2-aminopyridine. Platinum (II) complexes of 2-furfurylidene-thiosemicarbazone have been synthesized by Mukkan\textsuperscript{82} and. A report on the complexes of cobalt (II), nickel(II) and copper (II) with substituted 2-furoylthiosemicarbazide was published by Hiremath and coworkers.\textsuperscript{83} Bouet\textsuperscript{84} studied a series of complexes of $\beta$-furfural-doxime.

Ni(II), Pd(II) and Pt(II) complexes with Schiff bases derived from 2-furfuraldehyde and thiosemicarbazone have been synthesized and characterized by Umapathy et al.\textsuperscript{85} Some trivalent lanthanide complexes of bis (p-dimethylaminobenzylidene)
benzidine have been characterized by Ifti khar and coworkers.\textsuperscript{6} Mehta and others\textsuperscript{87} have studied the spectral and magnetic properties of bipo sitive metal complexes of tridentate ligand, involving N-furfurylidine group. Copper(II) complexes of 6-furfuralaminopurine have been studied by Crbras\textsuperscript{88} in 1988. Synthesis and spectral properties of a few U(VI) and Th(IV) complexes with Schiff bases derived from 2,6-diaminopyridine and vanillin.\textsuperscript{89} Khan and coworkers\textsuperscript{90} studied the complexes of transition metal with 5-salicylaldimino-5-chlorobenzophenone in solid state. Some of these complexes have been found biologically and pharmacologically active. Complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with some bi and tridentate p- dimethylamino benzylidene amino-5-mercapto-3-trifluoro-methyl-5-triazole (DBMTT) have been studied by Dubey and Kaushik.\textsuperscript{91}

Synthesis, characterization and antimicrobial studies of Cu(II), Ni(II) and Zn(II) complexes with Schiff bases have been reported by Xiarong et al.\textsuperscript{92} Panda et al.\textsuperscript{93} have synthesized and characterized the thorium (IV) complexes with furfurylidene arylamine Schiff base. Ten complexes of lanthanide with o-vanillinoxime have been synthesized and characterized by elemental analysis, electronic spectra, magnetic moment, i.r. spectra and thermal analysis by Dhar and coworkers.\textsuperscript{94} Synthesis and characterization of some lanthanide nitrate and perchlorate complexes of 4-(pyridine-2'-carboxalidene) aminoantipynine have been reported by Radhakrishnan.\textsuperscript{95} Magnetic and ligand field spectral studies of iron (II),
ruthenium (III), rhodium (III), palladium (II), cobalt(II), nickel(II) and N-(α-pyridyl) furfural-2-aldehyde-thiosemicarbazone complexes have been studied by Jain et al. 96

Some rare earth complexes of Schiff bases derived from vanillin have been synthesized. 97,99 Muneem et al. 98 studied the complexes of some bipoitive, metal ions with vanillin-anthranilate.

Verma and Prabhakaran 100 studied the complexes with Schiff base derived from N-isonicotinylhydrazone and p-dimethylaminebenzaldehyde. El-gaber et al. 101 have prepared Co(II), Ni(II) and Cu(II) complexes of Schiff bases derived from chromone with o-substituted anilines. These were characterized by elemental analysis, infrared, electronic spectra, magnetic measurements and thermal analysis. Some transition metal chelates of furfurylidene and 5-nitrofurfurylidene-benzylhydrazone were synthesized by Rao and Ganorkar. 102 Kumar and Sharma 103 have reported some complexes of bivalent transition metal ions with vanillin and quinazoline-4-ones derived Schiff bases. Some o-amino pyridine derived Schiff base complexes of Cr(III), Co(II), Ni(II) and Cu(II) have been studied by Thomas and Parmeswaran. 104

Garg et al. 105 have reported the copper(II) complexes of Schiff base derived from furan-2-aldehyde and dapsone. Duggal and Agrawala 106 have characterized some Schiff base complexes of 2-furfuraldehyde-salicylhydrazone with bipoitive 3d-cations. Coordination capabilities of acido anions in metal complexes of isatin and vanillin derivatives have been reported. 107 Tsyoshi and Koichi 108 have reported
the reaction between photoexcited benzophenone and several aromatic amines by a
time resolved E.S.R. technique in micellar solutions at room temperature. Madhava
et. al.\textsuperscript{109} studied the potentiometric and electrochemical investigation of some Zn(II)-
Schiff base complexes derived from salicylidene-2-hydroxyaniline etc. Complexes of
manganese (II), cobalt(II), nickel (II) and copper (II) complexes of a macrocyclic
Schiff base ligand derived from N-N’-bis(2-aminophenyl)-o-phenylenediamine and
acetal acetone were studied by Ahmad and coworkers.\textsuperscript{110} Synthesis and application
of macrocyclic Schiff bases were studied by Guerriero et. al.\textsuperscript{111} Nickel (II) complexes
of O-N-donor Schiff bases derived from 4-antipyrine-carboxaldehyde and aromatic
amines have been studied by Maurya and coworkers(1992).\textsuperscript{112}

Goyal and Lal\textsuperscript{113} have studied the complexes of oxovanadium (IV), iron (III),
cobalt (II), nickel (II) and copper (II) with Schiff bases derived from sulphaphenazole
and 5-nitro-salicylaldehyde and 5-chloro-salicylaldehyde. Synthesis, characterization
and biological activities of Ni(II), Cu(II), Zn(II) and Cd(II) of quadridentate
Schiff bases derived from 5-methyl and 5-benzyldithiocarbazate with glyoxal have
been studied by Ali and coworkers.\textsuperscript{114}

Ramalingam et. al.\textsuperscript{115} have synthesized and characterized the Cu(II) and Ni(II)
complexes of 4-amino antipyrine Schiff base derivatives. Synthesis and
characterization studies of some Co(II) chelates of Schiff bases derived from
2,3-dimethyl-4-formyl-1-phenyl-3-pyrazoline-5-one with aromatic amines were
studied by Maurya et.al.\textsuperscript{116} Syamal and Singh \textsuperscript{117} have studied the complexes of Cu(II),
Ni(II), Co(II), Fe(III), Zn(II), Cd(II) and Zr(IV) with Schiff bases derived from salicylaldehyde and 1-amino-2-naphthol-4-sulfonic acid. Lanthanide complexes with macrocyclic Schiff base derived from 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane have been studied by Zheng et al. Elsonbati and coworkers have studied some transition metal complexes of Schiff base derived from fluorenone and phenylthiosemicarbazide. Synthesis and characterization studies of lanthanide Schiff base complexes derived from 1,2,4,8,10,11-hexaza-3,9-bis-4-pyrido-tetradeca 3,9,12,14 tetraene have been done by Siddiqi et al. Ruthenium (II)-Schiff base complexes derived from salicylaldehyde and L-amino acids have been studied by Kureshy and coworkers. Characterization and antifungal properties of transition metal complexes of Schiff bases derived from 5-methyl-β-N-(2-amino phenyl)-methylene-thio-o-carbazate and pyridine-2-aldehyde have been reported by Rahman and Ali. Syamal et al. studied the complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Mo(II) and U(VI) of Schiff base derived from salicylaldehyde and anthranilic acid.

Complexes of Ni(II) and Cu(II) of Schiff base derived from N, N-Bis(2-hydroxy-3-carboxybenzylidene)-1, 2-diaminoethane were studied by Lam et al. Novel enantioselective reaction of diketone with aldehydes promoted by chiral Schiff base titanium alkoxide complex have been studied by Hayashi and coworkers in 1994. Synthesis and characterization of novel Ru (II) chelates with some Schiff bases derived from 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one sulpha
drugs have been studied by Maurya et al.\textsuperscript{126} Kumar and coworkers\textsuperscript{127} have characterized the dinuclear Cu(II) complexes of 2-pyrazolate bridging groups formed from 26-membered oxamine and polyamine macrocycles (3, 5-disubstituted 1H-pyrazole). Complexes of Co(II), Ni(II), Cu(II) and Pd(II) and Schiff base derived from alpha-benzylmonoxime have been synthesized and characterized by Emam and coworkers.\textsuperscript{128} Guskos and coworkers \textsuperscript{129} (1995) have studied the Cu(II) complexes of Schiff bases derived from o-hydroxyaldehydes and 1, 5-diaminonaphthalene. Non-isothermal decomposition and kinetic parameters of Schiff base metal chelates derived from salicylidene-anthranilic acid were studied by Mishra \textsuperscript{130} \& and Ayed\textsuperscript{131} isolated and characterized the Co(II), Zn(II) and Cu(II) complexes with Schiff base derived from salicylidene-2-aminobenzothiazole. Butcher and coworkers\textsuperscript{132} have studied binuclear Cu(II) complexes containing phenols and catechols. Ligands were formed by the condensation of substituted salicylaldehydes and 1, 3-diamino-2-propanol and 1, 5-diamino-3-pentanol. Hirotsu\textsuperscript{133} and others have studied the stereochemistry and electrochemistry of Co(II) and Co(III) complexes containing optically active tetradentate Schiff base ligands. Thermal studies of mononuclear and binuclear copper (II) complexes with Schiff bases derived from 1-phenyl-2,3- dimethyl -4- amino -5- pyrazolone were done by Tumer Mehmet et al.\textsuperscript{134} Binuclear Cu(II), Ni(II) and Co(II) chelates with tetradentate Schiff base derived from 1,5- diaminonaphthalene have been studied by Koksal and coworkers.\textsuperscript{135} Naik, Purohit and Patel\textsuperscript{136} have studied the complexes of
Cu(II), Ni(II) and Co(II) with Schiff base derived from salicylaldehyde and o-aminophenol. Mishra\textsuperscript{137} and coworkers have studied the complexes of cobalt, nickel and copper (II) with 2-furfurylidene-p-nitroaniline and 2-furfurylidene-m-nitroaniline Schiff base. Metal complexes of a chiral quadridentate Schiff base [-N, N'-bis (3, 5-di-tert-butylsalicylidene) cyclohexane-1, 2-diamine] have been reported by Leung et al.\textsuperscript{138} Diaminomaleonitrile with salicylaldehyde and diformylphenols derived Schiff base complexes have been studied by Maclachlan, Murray and coworkers.\textsuperscript{139} Palladium and nickel complexes of Schiff base derived from benzaldehyde/salicylaldehyde with 2- or 3-aminopyridines/3-aminoquinolins have been reported by Allar\textsuperscript{140} and others. Li et al.\textsuperscript{141} have studied the non-isothermal kinetics of thermal decomposition reactions of Schiff base transition metal complexes derived from salicylidene / o-vanillin with o-aminobenzoic acid. Preparation and characterization of Cu(II)-N-salicylidene anthranilic acid have been done by Tascioglu et al.\textsuperscript{142} Naik\textsuperscript{143} and coworkers have studied the complexes of Cu(II), Ni(II) and Co(II) with Schiff base derived from salicylaldehyde and anthranilic acid with some neutral ligands.

EPR and electronic spectra of copper (II) complexes with Schiff base N-salicylidene - (R,S) - alaminato involving derivatives of imidazole and pyrazole have been studied by Plesch\textsuperscript{144} and coworkers in (1997). Kruger et al.\textsuperscript{145} have studied the synthesis, magnetism and electrochemistry of tetranuclear Ni(II) and Cu(II) complexes of an unsymmetrical bis-pentadentate Schiff base ligand derived from 1
(1 - methyl -3- oxobut -1- enylamino)- 3- (amino) propane -2-ol and the dialdehyde, 5,5' - methylene-bis-salicylaldehyde. Optical activity of Cu(II) complexes with Schiff bases N, N' - (1R,2R) - (-) - 1, 2 - cyclohexylene bis (salicylidene iminato) and N,N' - (1R,2R) - (-) - 1, 2 -cyclohexylene bis (2- hydroxyaceto - phenoniminato) have been recorded by Larsen\textsuperscript{146} and coworkers. Choudhary et al.\textsuperscript{147} have studied the complexes of Co(II), Ni(II) and Hg(II) with bidentate Schiff base ligand derived from (4-hydroxy-3-methoxybenzylidene)-2- or -3- amino pyridine. Tumer\textsuperscript{148} and coworkers have studied the complexes of Co (II), Ni(II) and Zn(II) with Schiff bases derived from 4- hydroxysalicylaldehyde and o- vanillin with 3,5 - di (tert - butyl) -4- hydroxyaniline. Optically active nickel (II) Schiff base coordination compound N, N' - (1R,2R) - (-) - 1, 2 -cyclohexylene bis ( salicylidene iminato) have been studied by Wojtczak et al.\textsuperscript{149} Ismail\textsuperscript{150} and coworkers have studied the spectroscopic and magnetic behaviour of some Cu(II) - antipyrine Schiff base derivatives. Divalent cobalt, copper and zinc complexes of N-salicylideneamino acids have been studied by Sharma et al.\textsuperscript{151} Preparation and characterization of novel cyclic tetranuclear manganese(II) complexes of Schiff base derived from N, N' - disubstituted - salicylidene - 1,3-diaminobenzene have been studied by Torayama\textsuperscript{152} and others.
REFERENCES:


