The chemistry of Schiff base complexes has developed rapidly in the last thirty years. Schiff base ligands are able to coordinate metals through imine nitrogen. Several studies showed that the presence of a lone pair of electrons in an sp² hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. In fact, Schiff bases are able to stabilize many different metals in various oxidation states and control the performance of metals in a large variety of useful catalytic transformations.
Versatility of Schiff base ligands and biological, analytical and industrial applications of their complexes make further investigations in this area highly desirable. Furthermore, the transition metal complexes of Schiff bases have emerged as highly efficient catalysts in various fields of synthesis and other useful reactions.

1.1 Preparation of Schiff bases

Condensation of carbonyl compound and primary amines leads to the formation of Schiff bases. Both aldehydes and ketones form Schiff base ligands. Synthesis of Schiff base ligands from salicylaldehyde and different amines are shown in Figure 1.1. However, Schiff base ligands with ketones are formed less readily than those with aldehydes. Condensation reactions are carried out in different reaction conditions, and in different solvents. The common solvents used for the preparation of the Schiff base are methanol or ethanol. The presence of dehydrating agents normally favors the formation of Schiff bases. Magnesium sulphate is commonly employed as a dehydrating agent. The water produced in the reaction can also be removed from the equilibrium using the Dean Stark apparatus, when conducting the synthesis in toluene or benzene.

Salicylaldehyde and ethylenediamine can be condensed in 2:1 ratio to form interesting tetradeutate N$_2$O$_2$ Schiff base ligands. They are usually called as salen ligands. The term salen is also used in the literature for the N$_2$O$_2$ tetradeutate Schiff base ligands formed from the salicylaldehyde derivatives and diamine derivatives. Degradation of the Schiff bases can occur during the purification step. Chromatography of Schiff bases on silica gel can cause some degree of decomposition of the Schiff bases through hydrolysis. In such cases, it is better to purify the Schiff base by crystallization. If the Schiff bases are insoluble in hexane or cyclohexane, they can be purified by stirring the crude reaction mixture in these solvents; sometimes a small portion of a more polar solvent (diethyl ether, dichloromethane) are added to eliminate impurities.
A variety of Schiff bases can be obtained by changing aldehydes or amines. Thus synthesis of large number of Schiff bases with diverse structural features could be possible with ease. They can have additional donor groups like oxygen, sulphur, phosphorus etc. which makes them good candidates for metal ion complexation and for mimicking biological systems. They can be functionalized by the insertion of appropriate groups in the aliphatic or aromatic chains.

In the present study, 1,8-diaminonaphthalene was used as the diamine for the preparation of Schiff base ligands. Instead of forming the Schiff bases, the condensation results in the formation of perimidines. However, these heterocyclic compounds open up easily in the presence of metal ions to form Schiff base complexes. A discussion on the perimidines is therefore included in this chapter.


### Chapter 1

#### 1.2 Perimidines

Heteroaromatic systems can be divided\(^4-6\) into compounds with an excess of \(\pi\) electrons (e.g. pyrrole) and those with a deficiency of \(\pi\) electrons (e.g. pyridine). Electrophilic substitution and oxidation reactions are characteristic of the former, while the latter compounds react mainly with nucleophiles and are comparatively readily reduced. A heteroaromatic system exhibiting simultaneously the distinct properties of compounds with an excess and deficiency of \(\pi\) electrons\(^7\) could be quite interesting. Such a system is perimidine (Figure 1.2).

![Figure 1.2: Perimidine](image)

Perimidine was first obtained and described in detail by Sachs in 1909\(^8\), while 2-methylperimidine had been described by Mayberry and Shishkin or Vysochin\(^9, 10\). A review on perimidines was published in 1958\(^11\) when few data were available on their physical properties and reactivity. Perimidines were synthesized as early as the past century\(^12-14\) by the interaction of 1,8-diaminonaphthalene with a series of carboxylic acids and their derivatives. However, the compounds could not be obtained in a pure state and their structure could not be established. The name "perimidine" has been confirmed by IUPAC rules\(^15\), however other names can also be encountered in the literature such as \(lH\)-naphtho-[1,8-d,e]pyrimidine, \(lH\)-benzo[d,e]quinazoline, perinaphthimidazole, and \(lH\)-l,3-diazaphenalene.
1.2.1 Preparation of perimidines

The methods of synthesis of perimidines are based on the reaction of 1,8-diaminonaphthalene and its derivatives with various compounds containing a carbonyl group. Variety of perimidines were synthesized by the reaction of 1,8-diaminonaphthalene with formic acid\textsuperscript{16}, acyl chlorides\textsuperscript{17}, aryl anhydrides\textsuperscript{18}, aldehydes\textsuperscript{19} and ketones\textsuperscript{20}.

When the diamines are refluxed with an excess of formic acid, 1-methylperimidine, 1-phenylperimidine\textsuperscript{21}, and 1-(2,4-dinitrophenyl)perimidine\textsuperscript{22} are formed in high yields (Scheme 1.1).

\begin{equation*}
\begin{array}{c}
\text{(a)} \\
\begin{array}{c}
\text{NHRNH}_2 \\
\text{NHR}
\end{array}
\end{array}
\xrightarrow{\text{HCOOH}}
\begin{array}{c}
\text{(b)} \\
\begin{array}{c}
\text{NHR}
\end{array}
\end{array}
\end{equation*}

(i) \( \text{R} = \text{H} \), (ii) \( \text{R} = \text{CH}_3 \), (iii) \( \text{R} = \text{C}_6\text{H}_5 \), (iv) \( \text{R} = 2,4-(\text{NO}_2)_2\text{C}_6\text{H}_3 \).

Scheme 1.1: Preparation of perimidines from various cyclising agents

The reaction of diamines with acyl halides leads to the formation of 1,2-disubstituted perimidines\textsuperscript{23, 24} and also compounds such as 1,4-bis(2-perimidinyl) benzene and 1,5-bis(2-perimidinyl)naphthalene\textsuperscript{25} (Scheme 1.2).

\begin{equation*}
\begin{array}{c}
\begin{array}{c}
\text{NHRNH}_2 \\
\text{NHR}
\end{array}
\end{array}
\xrightarrow{\text{RCOX}}
\begin{array}{c}
\begin{array}{c}
\text{NHRNH}_2 \\
\text{NHR}
\end{array}
\end{array}
\xrightarrow{-\text{H}_2\text{O}}
\begin{array}{c}
\begin{array}{c}
\text{NHR}
\end{array}
\end{array}
\end{equation*}

\( \text{R} = \text{H} \)

Scheme 1.2: Preparation of perimidines from acyl halides
Chapter 1

Heating of 1,8-diaminonaphthalene with acetic\textsuperscript{26, 27} and trifluoroacetic\textsuperscript{28} anhydrides constitutes the best method of synthesizing 2-methyl- and 2-trifluoromethyl-perimidines. It is of interest that, when 1-amino-8-dimethylaminonaphthalene is refluxed with acetic anhydride, 1,2-dimethylperimidine (final product in Scheme I.3) is formed. The process is accompanied by the elimination of the N-methyl group. At room temperature the reaction stops at the stage involving the formation of compound (C)

\begin{equation}
\text{NHNHRH}
\end{equation}

\textbf{Figure 1.3: 2,3-dihydroperimidines}

1,8-Diaminonaphthalene interacts with aldehydes in alcohol or benzene leading to the formation of 2,3-dihydroperimidines (Figure 1.3), where R = H, CH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5}, C\textsubscript{6}H\textsubscript{5}, C\textsubscript{6}H\textsubscript{5}, different halogeno-groups\textsuperscript{31}, hydroxy-group\textsuperscript{32}, methoxy group\textsuperscript{33}, 3,4-methylenedioxy-group, dialkylamino-groups, nitrophenyl\textsuperscript{34}, 4-biphenyl, α-naphthyl, ferrocenyl\textsuperscript{35}, 2-thienyl,2-furyl\textsuperscript{36}, 5-methyl, 5-halogeno-groups or 5-nitro-2-furyl. The reaction proceeds as a rule with a high yield and terminates after 2 to 3 h even at room temperature.
Ketones also interact with 1,8-diaminonaphthalene to form 2,2-disubstituted 2,3-dihydroperimidines. Thus the reactions with acetone and acetophenone yield compounds a and b (Figure 1.4) respectively

![Figure 1.4: 2,2-disubstituted 2,3-dihydroperimidines](image)

(a) $R' = R'' = \text{CH}_3$;  
(b) $R' = \text{CH}_3, R'' = \text{C}_6\text{H}_5$

After a prolonged storage, dihydroperimidines gradually darken and decompose. Perimidine molecule is a 14π-electron system, but one of its electrons is not delocalized, which leads to a decrease of aromaticity. The ease of autoxidation is a characteristic property of all perimidines. Perimidines are best alkylated in alkaline media. In view of the possibility of the autoxidation of the N-anion of perimidines, the process must be carried out in an inert atmosphere.

In the solid state, perimidine derivatives are stable. Upon dissolution in nonpolar solvents (e.g., hydrocarbons or tetrachloromethane), an equilibrium is gradually established between the ring closed and imine form. However, the ring opening exists only for micro seconds and cannot be distinguished via UV-visible spectroscopy. The ring closed form transforms to a ring opened species having an extended conjugation that result in the formation of a deep coloration. Tamaoki and Davis have shown that equilibrium is established between ring closed and ring opened states upon dissolution in nonpolar solvents. In 1981, Stalhandske reported in his crystal structure that only weak intermolecular hydrogen bonds are present and also two non-equivalent intramolecular NH...N hydrogen bonds are formed. In 1994, Platteborze and
Lambrecht\textsuperscript{44} showed this non-equivalence brings about splitting of the vibration. Recently, we have reported the loss of planarity\textsuperscript{45} of the perimidine ring.

### 1.3 Schiff base metal complexes

Schiff base complexes have attracted wide attention due to their important role in analytical chemistry, organic synthesis, metallurgy, refining of metals, electroplating and photography. Pfeiffer \textit{et al.}\textsuperscript{46} have made a systematic study on Schiff base complexes. Properties of these complexes depend on the nature of metal ion as well as on the nature of the ligands. There is a continuing interest in the synthesis of Schiff base complexes of metal ions due to their preparative convenience\textsuperscript{47-49} and wide applications\textsuperscript{50, 51}.

A review on metal complexes of Schiff bases by Holm \textit{et al.} shows that more than half of these reported complexes were derived from salicylaldehyde\textsuperscript{52}. Complexes of Schiff base ligands derived from salicylaldehyde were first used by Pfeiffer \textit{et al.}\textsuperscript{53}. A wide variety of ligands with salicylaldehyde may be obtained through condensation of primary amine, which varies in denticity, flexibility, nature of donor atoms and in electronic properties. Schiff base complexes are well known to have pronounced biological activities\textsuperscript{54-56}. Schiff bases derived from salicylaldehyde and 2-aminophenylisulphide or 2-aminoethylisulphide were complexed with Ni(II) ions and the electrochemistry of the complexes was reported\textsuperscript{57}. Spectroscopic properties and magnetic behavior of the N-substituted salicylaldimine ligands and their Co(III) and Cu(II) complexes were studied and the molecular structures were determined by single crystal X-ray analysis\textsuperscript{58}.

Recently\textsuperscript{59}, a series of macrobicyclic unsymmetrical binuclear copper(II) complexes of compartmental ligands were synthesized from the Schiff base condensation of 1,8\[N,N'-bis\{(3-formyl-2-hydroxy-5-methyl)benzyl}\]-1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethylyclotetradecane with diamines like 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,2-
diaminobenzene and 1,8-diaminonaphthalene (Scheme 1.4). The chemistry of macrocyclic tetraaza ligands bearing pendant coordinating side arms is a most fascinating area of research\textsuperscript{60}. ESR spectra of the binuclear copper(II) complexes show a broad signal at $g = 2.10$ and $\mu_{\text{eff}}$ values in the range $1.46-1.59$ BM, which convey the presence of antiferromagnetic coupling. The copper(II) complexes have been found to promote cleavage of plasmid pBR 322 DNA from the supercoiled form I to the open circular form II.

\textbf{Scheme 1.4: Synthesis of the macrobicyclic binuclear copper(II) complexes}

*(Adopted from Ref. 59)*
Schiff bases from thiazole derived salicylaldehyde derivatives are reported to have significant anticancer activity\(^61-63\). Many of the anticancer drugs are viable ligands\(^64\). Some of these drugs exhibit increased anticancer activity when administered as metal complexes\(^65, 66\). Investigation on the preparation and characterization of Co(II) and Cu(II) complexes\(^67\) with monodentate 2-amino-6-methylbenzothiazole (L) and 2-amino-6-chlorobenzothiazole (L’) of the composition [M(L or L’)_2X_2] and [ML’_4]Y_2 where X = Cl\(^-\), Br\(^-\), SCN\(^-\), NO\(_3^-\) or OAc\(^-\) and Y = ClO\(_4^-\) showed that the Co(II) complexes are tetrahedral and that the Cu(II) complexes are square planar in nature.

A few complexes of Schiff bases derived from 1,8-diaminonaphthalene have been reported. A novel series of complexes of the type [M(L)X]X_2, where M = Cr(III), Fe(III) or Mn(III), X = Cl\(^-\), NO\(_3^-\), CH\(_3\)COO\(^-\) and (L) corresponds to the tetradehtate macrocyclic ligand, were synthesized in methanolic media by the template condensation of 1,8-diaminonaphthalene and 2,3-butanedioine (diacetyl) in the presence of trivalent metal salts. Based on the spectroscopic studies, a five-coordinate square pyramidal geometry for all the prepared complexes was proposed\(^68\). The oxovanadium(IV) complexes have been prepared with the Schiff base bis(benzylidene)-1,8-diaminonaphthalene\(^69\). These oxovanadium(IV) complexes show higher fungitoxic activity as compared with that of the free ligands.

A new series of complexes\(^70\) of the type [M(L)X]X_2, where M = Cr(III), Fe(III) or Mn(III), X = Cl\(^-\), NO\(_3^-\) or CH\(_3\)COO\(^-\), has been synthesized by template formation of Schiff base (L) from 1,8-diaminonaphthalene and glyoxal in the presence of trivalent metal salts in methanolic medium. On the basis of the spectroscopic studies, a five-coordinate square pyramidal geometry for all of these complexes has been proposed. A series of preparations were reported for the complexes of the following ligands, potassium salt of salicylidene-\(\beta\)-alanine, 2,2’-bipyridylamine, bis(benzylidene)ethylenediamine, thiophene-o-carboxaldene-aniline, thiophene-o-carboxaldene-p-toluidine, bis (benzylidene) -
1,8-diaminonaphthalene, bis(acetophenone)ethylenediamine] and oxovanadium(IV) ion. Relevant spectroscopic studies indicate octahedral structure for all the complexes. The complexes are paramagnetic in nature. The antifungal activity of the complexes against *A. niger*, *F. oxysporum*, and *A. flavus* species was reported. All the tested complexes show higher antifungal activity as compared to that of the free ligands. A new vic-dioxime ligand, \( N,N^\prime\)-bis-(8-salicylideneimino-1-naphthyl)-diaminoglyoxime, was synthesized from anti-dichloroglyoxime and 1-amino-8-salicylideneiminonaphthalene, which has been prepared via the condensation product of 1,8-diaminonaphthalene and salicylaldehyde. The vic-dioxime ligand forms trinuclear complexes with Cu(II), Ni(II), Co(II), and Pd(II). The uranyl complex of this ligand has a 2:1 metal-ligand ratio and a binuclear structure with \( \mu\)-hydroxo bridges.

The reactions of Schiff bases (formed by the condensation of acetylferrocene with ethylenediamine, o-phenylenediamine, 4-methyl-o-phenylenediamine, 1,8-diaminonaphthalene or 2,6-diaminopyrididine) with bis(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride and mono (cyclopentadienyl)titanium(IV) trichloride have been studied and complexes of the types \([\text{Cp}_2\text{M}(\text{L})\text{Cl}]\text{Cl}\) (\(\text{M} = \text{Ti(IV)}\) or \(\text{Zr(IV)}\)), \([\text{CpTiCl}_3(\text{L})]\) have been isolated and characterized by spectroscopic studies. The partial Schiff base condensation reactions between 2,6-diacetylpyrididine and 1,8-diaminonaphthalene in the presence of lanthanum(III), praseodymium(III) and neodymium(III) nitrates produced the new hexadentate \(N_4O_2\)-open chain complexes. 2,2′-Biperimidine and perimidine-2-formaldoxime have been prepared by an one-pot reaction of E,E-dichloroglyoxime or anti-monochloroglyoxime with 1,8-diaminonaphthalene. Metal complexes of 2,2′-biperimidine are also described.

The diaminonaphthalene copper complex showed excellent activity for electrocatalytic reduction of oxygen. The excellent adhesivity and dense structure of the film obtained by electrochemical synthesis of poly (1,8-
diaminonaphtalene\textsuperscript{77-79} are of great advantage to the modification of electrodes. Park et al. described the formation of Schiff base complexes from 1,8-diaminonaphthalene and Co(II) nitrate hexahydrate\textsuperscript{80}.

Shakir et al\textsuperscript{81}. reported the synthesis and spectroscopic studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes of Schiff base formed from the condensation of 2-pyridinecarboxaldehyde and 1,8-diaminonaphthalene. In the same year, this group have reported the template condensation reaction between 1,8-diaminonaphthalene and glyoxal resulting in the formation of 14-membered Schiff base tetraazamacrocyclic complexes\textsuperscript{82}.

The synthesis of the Schiff base of O,O-diethylthionophosphorylhydrazine with \textit{o}-vanillin and it's Ni(II) complex were reported along with the crystal structure\textsuperscript{83}. The mono- and bis-Schiff bases of \textit{o}-vanillin and 2,3-diaminopyridine have been used as ionophores in a Cu(II) selective electrochemical sensor. The synthesis and the ligating properties of the Schiff base ligand derived from \textit{o}-vanillin and 2-dimethylaminoethylamine with Ni(II) and Cu(II) metal ions with different kinds of bridging ligands have been reported. The Schiff bases behave either as a tetradeutate (N\textsubscript{2}O\textsubscript{2}) or tridentate (N\textsubscript{2}O) ligand, depending upon the nature of the anions present and the reaction conditions\textsuperscript{84, 85}.

Maurya et al. have reported\textsuperscript{86} a series of complexes of two Schiff bases, N-(\textit{o}-vanilliniendene)-p-anisidine (o-VPAH) and N\textsubscript{2}N’-bis(\textit{o}-vanillinidene) ethylenediamine (o-VEDH\textsubscript{2}). In all of the complexes, o-VPAH acts as a monobasic-bidentate ligand and o-VEDH\textsubscript{2} acts as a dibasic-tetradeutate ligand. In 1997, Tumer et al\textsuperscript{87}. reported the complexes of cobalt(II), nickel(II) and zinc(II) with two new Schiff bases derived from 3,5-di(tert-butyl)-4-hydroxyaniline and 4-hydroxysalicylaldehyde or \textit{o}-vanillin. Hingorani and Agarwala\textsuperscript{88} reported six new mixed ligand complexes of copper(II) with tridentate o-vanillinthiosemicarbazone or \textit{o}-vanillin-4-phenylthiosemicarbazone.
IR spectral studies have shown that coordination occurs through thioenolic sulphur and azomethine nitrogen.

Recently, poly-2,3-bis[(2-hydroxy-3-methoxyphenyl)methylene]diamino pyridine has been synthesized and characterized. This azomethine polymer was found to form complexes readily with Cu(II), Zn(II), Co(II), Pb(II), and Fe(II). From IR and UV-Vis studies, the phenolic oxygen and imine nitrogen of the ligand were found to be the coordination sites. Metal complexes of Schiff base derived from o-vanilin (3-methoxysalicylaldehyde) and sulfametrole [N\(^1\)-(4-methoxy-1,2,5-thiadiazole-3-yl)sulfanilamide] were synthesized and characterized. The synthesized ligand, and their metal complexes were screened for antibacterial activity against bacterial species, *Escherichia coli*, *Salmonella typhi*, *Bacillus subtilus*, *Staphylococcus aureus* and Fungi (*Aspergillus terreus* and *Aspergillus flavus*). The activity data show that the metal complexes are more potent antimicrobial than the parent Schiff base ligand. Our group has reported complexes of Schiff base formed by condensing quinoxaline-2-carboxaldehyde with 2-amino-5-methylpheno and the formation of Schiff base complexes from ring closure compound. A new benzothiazoline derivative, 3-(2,3-dihydro-1,3-benzothiazol-2-yl)quinoxalin-2(1\(H\))-one, has been synthesized by the reaction of 3-hydroxyquinoxaline-2-carboxaldehyde with 2-mercaptoaniline. Its complexation with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions proceeds with the rearrangement of benzothiazoline ring to form the corresponding Schiff base chelates. Spectroscopic studies reveals that the copper(II) complex is square planar, zinc(II) complex is tetrahedral and the manganese(II), cobalt(II), and nickel(II) complexes are octahedral in geometry.

There are numerous literature reviews on the Schiff base complexes. The synthesis of the well known Schiff base complex, N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride, is presented in Scheme 1.5. This manganese complex is known as Jacobsen’s catalyst. The Schiff base can be successfully prepared by the condensation between *trans*-1,2-
diaminocyclohexane and 3,5-di-tert-butyl-2-hydroxybenzaldehyde and finally Jacobsen’s catalyst can be prepared from the ligand by treatment with manganese(II) acetate followed by oxidation with air.

Scheme 1.5: Synthesis of Jacobsen’s catalyst (Adopted from Ref. 96)

1.4 Application of Schiff base complexes as catalysts

Schiff base complexes of transition metal ions have received much attention as oxygen transfer agents to organic compounds. Direct participation of dioxygen in the oxidation of organic compounds is effected by such complexes. Reactions of organic compounds with dioxygen are restricted by spin conservation. This may be overcome by the usage of metal complexes. Salen complexes are known to transfer oxygen atom to alkenes to form epoxides. Schiff base complexes catalyses a large number of organic reactions such as
Introduction

oxidation of sulphides\textsuperscript{99}, redox reactions\textsuperscript{100}, hydrolysis\textsuperscript{101}, decarboxylation\textsuperscript{102}, elimination\textsuperscript{103} and aldol condensation\textsuperscript{104}.

The metal complexes (Figure 1.5) of phenoxy imine were efficient catalysts in the polymerization of ethylene at atmospheric pressure. Amongst these catalysts, the zirconium catalyst was exceptionally active\textsuperscript{105}.

![Image of metal complexes](image)

Figure 1.5.

Numerous Co(II) Schiff base complexes are known to form superoxo or \(\mu\)-peroxo complexes by reaction with dioxygen. The best known of these is Co(II)salen Schiff base complexes studied extensively by Calvin and Martell\textsuperscript{106}. The reactions of organic substrates with molecular oxygen in the presence of Co(II) Schiff base complexes were studied by Nishinaga \textit{et al.}\textsuperscript{107}. They observed that the complexes reversibly bind with the molecular oxygen and form \(\mu\)-peroxo complexes and a superoxo in the presence of pyridine or imidazole derivatives.

The epoxidation of olefins using tri and tetra dentate Schiff base complexes of Fe(III) as catalysts and iodosylbenzene as oxidant have been studied\textsuperscript{108}. Cyclohexene gave cyclohexene oxide, cyclohexanol and cyclohexanone. At higher concentration of catalyst, low yield but high selectivity of epoxide was observed. Similarly the yield of epoxide increases with increase in concentration of cyclohexene. The addition of pyridine, NaH\textsubscript{2}PO\textsubscript{4}, NaHCO\textsubscript{3} were found to increase the yield of epoxide while addition of cetyltrimethylammonium bromide completely inhibits the epoxidation. Another reaction, which is considered as interesting, is the catalytic oxidation of the ascorbic acid to dehydroascorbic acid.
Chapter 1

by metal complexes. The use of first raw transition metal complexes of the Schiff bases derived from quinoxaline-2-carboxaldehyde in the oxidation reaction have been reported\(^{109}\). A number of other reports on the oxidation of ascorbic acid by metal complexes\(^{110-114}\) are also available in literature. A detailed kinetic study of the oxidation of ascorbic acid in methanol-water mixture was carried out and the mechanism of oxidation was proposed\(^{114}\).

Co(II)salen catalyzed oxidation of phenols to the corresponding quinines was first studied by Van Dort and Geursen\(^{115}\) and later by others\(^{116, 117}\). The best results are reported to be obtained in DMF as solvent. The oxidative cleavage of 3-substituted indoles proceeds at ambient temperatures in presence of Co(II)salen\(^{118}\) in CH\(_2\)Cl\(_2\). This reaction is markedly retarded by strong coordinating solvents such as DMF and pyridine. The complex [(Fe\(^{10}\)salen)\(_2\)O] favors the stereoselective oxidation of adamantane\(^{119}\) at the secondary position. New Schiff base\(^{120}\) square planar complexes of nickel(II) with \(N, N'\)-bis(2-hydroxyphenyl)ethylenediimine and \(N\)-(2-hydroxyphenyl)acetylaldimine–\(N\)-(2-hydroxyphenyl)acetamide have been prepared in good yield by direct interaction of 2-aminophenol, glyoxal, methylacetatotate and NiCl\(_2\) and characterized by physico-chemical analysis. Catalytic ability of nickel(II) complexes were examined and found that both the complexes can effectively catalyze the epoxidation of olefins viz. cyclohexene, 1-hexene, \(cis\)- and \(trans\)-stilbenes, indene in the presence of NaOCl as oxidant.

Schiff base complexes are used as catalyst in Heck reaction\(^{121}\). Usually complexes of phosphene ligands are used to catalyze this reaction. But compared to phosphene, Schiff bases can easily be prepared. Palladium(II) complexes of salen Schiff base ligands showed high catalytic activity in Heck reaction than the commercially used phosphene complexes\(^{122}\). In 2003, Legros and Bolm\(^{123}\) reported the preparation of a tridentate Schiff base iron catalyst, prepared in situ from Fe(acac)\(_3\), which is able to promote the enantioselective oxidation of sulfides to sulfoxides.
Matsumoto and Kuroda\textsuperscript{124} used Co(II), Mn(II) and Fe(II) complexes of the Schiff base ligand, bis(salicylaldehyde)ethylenediimine (salen), as catalysts 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\textsuperscript{125}. 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 reduction current of thionyl chloride were increased and the reduction potentials were shifted to the negative region in the case of Cu(Salen) complexes prepared by the reaction of salen with copper acetate in ethanol. Cu(Salen) is able to coordinate \textit{via} the interaction with the oxygen of the Schiff base\textsuperscript{126}. The Cu(Salen) is stable when exposed to air and moisture, and it is possible to perform enantioselective alkylation in phase transfer conditions.

1.5 Homogeneous catalysis involving Schiff base complexes

Homogeneous transition metal catalyzed reactions are of important in organic synthesis. The very positive aspects of homogeneous catalysts are that, they have well defined reactive centers, which lead to high and reproducible selectivity and operation at low temperatures and pressures. Information regarding their structure, environment of the metal atom, the number of ligands attached and how the coordination changes during a reaction etc. can be obtained proficiently. Thus, design of catalysts, which lead to better selectivity, is possible. An important land mark in the development of homogeneous catalysis by transition metal chemistry was the discovery (in 1959) of the Wacker process reported by Smidt and co-workers\textsuperscript{127-129}. This palladium(II) catalyzed oxidation of ethylene to acetaldehyde is with molecular oxygen as terminal oxidant. The commercial success of the Wacker process provided an enormous stimulus for further studies of palladium and other noble metal complexes as homogeneous
Chapter 1

catalysts. This development led to the discovery of a variety of important homogeneous, liquid phase processes involving noble metal catalysts such as hydroformylation, carbonylation, hydrogenation, isomerization and oligomerization.

Many positive aspects are associated with homogeneous catalysts. They can operate at low temperature and pressure and yield products with higher selectivity and purity. Moreover, reaction mechanisms of homogeneous catalysis are better understood than the surface reactions of heterogeneous systems. The reversible binding of molecular oxygen to transition metal complexes can modify their properties to a great extent. The mixed ligand complexes of transition metal complexes containing ligands with N, S and N, S, O donors show interesting stereochemical, electrochemical and electronic properties.

There are numerous examples of a wide variety of reactions catalyzed by homogeneous transition metal complexes. The first effective homogeneous catalyst designed for hydrogenation is the square planar rhodium complex, chlorotris(triphenylphosphine)rhodium(I), which is well known as Wilkinson’s catalyst. The water-gas shift reaction involving the conversion of CO to CO₂ is catalyzed by a variety of homogeneous metal carbonyl complexes like [HFe(CO)₄]⁻, [Rh(CO)₂I₂]⁻ and [Ru(bpy)₂(CO)C]⁺. The hydroformylation reaction producing about 5 million tons of aldehydes and aldehyde derivatives annually makes use of cobalt and rhodium complexes to accelerate the reaction. One of the great successes of homogeneous catalysis is in the conversion of methanol to acetic acid. The Monsanto acetic acid process can be initiated using the rhodium complex, [Rh(CO)I₂]⁻. The one reaction that requires special mention is the enantioselective electrocatalytic epoxidation of olefins in the presence of chiral Schiff base complexes of manganese.

The chiral complex, diphenylmethylenene imino palladium(II) have increased enantioselectivity in alkylation of enolates. The cobalt complexes of
3-oxobutylideneaminato ligands are efficient catalysts for the enantioselective borohydride reduction of ketones, imines and \( \alpha,\beta \)-unsaturated carbonyl compounds to afford the corresponding secondary alcohols\textsuperscript{139}.

Homogeneous catalysts have limited applications due to their high susceptibility to reaction conditions and the difficulty of their separation from the product mixture. The low thermal and chemical stabilities of such systems result in their slow decomposition. All the problems encountered by homogeneous catalysts can be overcome by immobilizing them on a suitable matrix. The immobilization of homogeneous catalysts leads to higher thermal and chemical stabilities. The product selectivity and substrate specificity is increased to a greater extent by steric crowding around the metal atom. In addition to all these qualities, the ease of separation of the supported catalysts makes them more beneficial when compared to their homogeneous counterparts.

### 1.6 Heterogenisation of homogeneous systems

Recent years have witnessed a great deal of interest in the study of heterogeneous catalytic systems due to their importance as catalysts for many reactions. Heterogenised homogeneous catalysts possess the advantage of both homogeneous and heterogeneous systems. They offer several advantages such as the simplification of the reaction procedures, easy separation of products, recyclability of expensive catalysts, possibility to design continuous flow processes, good control of morphology of polymers and high polymer bulk density\textsuperscript{140-144}.

The term heterogenisation refers to the process of immobilization of homogeneous transition metal complexes by anchoring them to an inert polymer or inorganic support. This type of bonding to a solid surface stabilizes the complex and generates catalytically active centers\textsuperscript{145}. The supported complexes possess higher selectivity and greater catalytic activity than their homogeneous analogues. Infact, the greatest challenge in catalysis is the development of
systems with good selectivity and in this context, there is an urgent need to develop highly efficient ecofriendly heterogeneous catalytic systems.

Several methods can be employed for supporting homogeneous catalysts that can be broadly classified into two categories. The organic supports widely used are polymers like polystyrene and poly(4-vinyl pyridine) and the inorganic support include silica, alumina, zeolites, clay etc. Interest in inorganic supports has arisen because of their unique characteristics of rigidity and stability. Inorganic supported catalysts by means of their rigid structure can act as bio-functional catalysts\(^{146}\). Of all the supports used, the use of zeolite molecular sieves has gained considerable importance due to their ability to tailor the structure of the catalyst to maximize their activity\(^{147}\). The process of encapsulation provides a simple way of coupling the reactivity of transition metal complexes with the robustness and stereochemistry of a zeolite.

### 1.7 Zeolite encapsulated complexes: Synthesis and structural aspects

Significant progresses are made in the design and synthesis of zeolite encapsulated complexes for catalytic applications\(^{148}\). Interestingly, subsequent studies on these encapsulated complexes have shown their unique reactivity for many industrially important reactions. For example, encapsulated complexes have been successfully employed for epoxidation\(^{149}\), oxidation of phenols\(^{150}\), direct oxidation of methane to methanol\(^{151}\) and oxidation of p-xylene to terephthalic acid\(^{152}\). In zeolites, twenty four tetrahedron constitute a sodalite unit, which is a three dimensional array of \(\text{SiO}_4\) and \(\text{AlO}_4\) tetrahedra in the form of a truncated octahedron with 24 vertices and six four-membered rings and eight six-membered rings. The basic building units of sodalite have an internal diameter of 6.6 Å and the enclosed void space is called the sodalite cage.

These units that are connected by hexagonal prisms constituting a larger void space called the supercage. The cavity of the sodalite unit is known as the \(\beta\)-cage while the cavity of the supercage is the \(\alpha\)-cage. Zeolite Y belongs to the
faujasite type of zeolites. Zeolite Y is formed by the joining of the hexagonal six-membered faces of the sodalite units (D6R). The Si/Al ratio of the zeolite Y is about 2.5. The diameters of α-cage and β-cage are approximately 13 Å and 6.6 Å respectively.

All these structural aspects of zeolites have resulted in an interesting behavior of zeolites, which include high catalytic activity, ion exchange capacity, shape selectivity, specific adsorption behavior and good flexibility for adjustment by isomorphous substitution of the constituents in the framework.

1.7.1 Synthesis of zeolite Y encapsulated complexes

The polyhedral cavities in zeolite Y inscribe a cavity of substantial dimensions that they could be able to hold clusters of small molecules in addition to the appropriate numbers of exchangeable cations. Proper choice of complex molecule of correct size that fit securely with in the ~ 13 Å supercages of zeolite Y ensures that the molecule cannot escape through the ~ 7 Å ring opening of the supercage. A wide variety of metal clusters, organometallic compounds and coordination compounds have been encapsulated in a range of different hosts. Such immobilization of known homogeneous complexes on solid supports would combine the advantages of homogeneous and heterogeneous catalysts while minimizing the disadvantages of both. Enhanced selectivity and ease of separation and purification of reactants and products would accompany its activity in solution phase.

Many coordination complexes can be formed within the zeolite pores by simple reaction of the exchangeable cations with various organic molecules. Reviews\textsuperscript{153-156} on the early work on mono, bi- and polydentate based complexes are available. The following methods are used for the encapsulation of transition metal complexes in the supercages of zeolite Y.
1.7.1.1 Flexible ligand method.

This method was first exploited by Herron\textsuperscript{157} to prepare Co(salen) complexes in the supercages of faujasite. It is applied to the free ligands that are flexible enough to pass through the smaller windows to the larger cages of the zeolite host material. The free unfolded ligand is able to enter the pores of the zeolite due to the free rotation around the carbon-carbon $\sigma$ – bond as depicted below (Figure 1.6) for the Schiff base salen.

![Figure 1.6: Synthesis of zeolite Y encapsulated metal salen complexes via the flexible ligand method.](image)

The ligand, that enters the zeolite cages, complexes with the previously exchanged transition metal ions. The complex so formed adopts a square planar configuration, which is unable to escape from the cavity of zeolite matrix. Thus the metal complex is physically entrapped in the supercages of faujasite. In this method, the ion exchanged and dried zeolite is mixed with the pre dried ligand, filled in a glass tube, evacuated, sealed and finally heated for several hours at a temperature slightly above the melting point of the ligand until a bright color is observed. After the reaction, soxhlet extraction with acetone, acetonitrile or dichloromethane is applied to purify the zeolite from the uncomplexed ligand.

This method is generally used for the encapsulation of complexes. The transition metal ions as well as the structure of the ligands were varied to prepare
large numbers of encapsulated complexes. They possess interesting electrochemical properties. The resulting zeolite encapsulated complexes have been used to act as oxygen carriers mimicking haemoglobin, as selective oxidation catalysts or as catalysts for selective hydrogenation.

1.7.1.2 Ship-in-a-Bottle method

This method was first proposed by Romanovsky and Gabrielov and later reported by many workers in this field. The term ‘ship– in– a– bottle’ was first coined by Herron et al. This method is generally used for the encapsulation of transition metal phthalocyanines and porphyrazines in zeolites. Based on molecular graphics analysis, it has been argued that in the case of zeolite Y encapsulated phthalocyanines, the planarity of the complex must be disturbed, since the dimensions of the ligand (14–15 Å) exceed the effective diameter of the zeolite super cages (13 Å). Herron proposed that intrazeolite phthalocyanines have a saddle shaped structure with the benzene groups protruding out of the 7 Å windows of the supercages. Clearly, phthalocyanines and porphyrazines cannot be incorporated directly into the 13 Å zeolites by flexible ligand method. Thus the most promising was the template synthesis for them.

This method involves assembling of the ligands from smaller species inside the zeolite cavities. Reaction of metal exchanged zeolites or pre-adsorbed labile metal complex such as a carbonyl or a metallocene with 1,2-dicyanobenzene at 250 °C to 350 °C results in phthalocyanine formation and complexation for cobalt, nickel and copper zeolites. Water is the electron source in this process and hence complexation does not occur if the ion-exchanged zeolite was strongly dehydrated before the complexation step.

Zeolite encapsulated complex was purified by the successive soxhlet extraction for a period of 3-5 days using acetone, pyridine or dimethylformamide and again by acetone to remove unreacted dicyano benzene and the side products such as phthalimide, phthalocyanine and metal-phthalocyanine, formed on the
outer surface of zeolite framework. A “ship-in-a-bottle” approach to entrap the chiral (salen) Mn complexes within the cages of zeolite Y was reported.

1.7.1.3 Template Synthesis

During the method of synthesis by template method, a pre-formed metal complex acting as a template is added to the synthesis gel. The metal complex acting as the templating agent must be stable during all stages of the synthesis. The above condition restricts the formation of large number of complexes by this method. But there are various advantages associated with this method of synthesis. The important one is that well defined encapsulated metal complexes with a pre-determined coordination can be obtained. Template method has been used in the synthesis of zeolite encapsulated phthalocyanine complexes of iron, cobalt, nickel, copper and manganese.

1.8 Catalysis by zeolite-encapsulated transition metal complexes

The use of zeolite encapsulated transition metal complexes to catalyze organic reactions has gained considerable attention in recent years on account of their fascinating properties. Homogeneous catalysts immobilized in the cage system of zeolite Y are expected to be stabilized against aggregation or bimolecular deactivation. Furthermore, the zeolite cage system may favor unique selectivity of a catalytic reaction due to changed complex geometries, transition-state modifications and diffusional selectivity for the substrate molecules. The evidence for the location of metal complexes inside the zeolite cages are obtained from a large number of data like the changes in spectra with respect to solution analogues, scanning electron microscopy before and after soxhlet extractions, failure to extract the complexes with strong donor solvents and recovery of the complexes after dissolution of the zeolite with acid. The combined effects of the shape selectivity of the zeolites and high dispersive power of metal ions of transition metal exchanged zeolites are of great interest in catalytic studies. But it is crucial to understand the distribution of metal ions in
such systems and to find out if large complex molecules formed inside the intracrystalline spaces are under distortion or affected in any way by the zeolite lattice leading to unusual physical and chemical behaviour\(^\text{166}\).

Reports about metal phthalocyanine complexes trapped within the zeolite cages are already available\(^\text{167}\). These large macrocyclic metal complexes have a tendency to aggregate or dimerize in solution and act as inhibitors to certain redox processes\(^\text{168}\). The zeolite encapsulated iron-phthalocyanine complexes are found to act as effective catalysts in the selective oxidation of cyclohexane to cyclohexanone in the presence of tert-butyl peroxide\(^\text{169}\). The corresponding simple phthalocyanine complexes of iron were found to undergo oxidative destruction under the same reaction conditions\(^\text{170}\) which brings into focus the unique catalytic properties of zeolite. The synthesis and structural properties zeolite encapsulated phthalocyanine complexes of cobalt, copper, nickel and manganese are already reported\(^\text{171-175}\). All these encapsulated complexes enhance the rate of hydroxylation of phenol in the presence of hydrogen peroxide, which is an industrially important reaction\(^\text{176}\). The cobalt analogue is an active catalyst in the oxidation of ethylbenzene with molecular oxygen and the copper complexes catalyze the epoxidation reaction of styrene\(^\text{177}\).

Various reactions like hydration of olefins, dehydration of alcohols, ester formation, transesterification etc. are catalyzed by zeolite systems\(^\text{178, 179}\). The emergence of supported salen complex of manganese as an important catalyst for the oxidation of olefins has find major applications in pharmaceutical industry\(^\text{180, 181}\). Zeolite entrapped carbonyl clusters of osmium act as selective stable catalysts for CO hydrogenation\(^\text{182}\). The experiments conducted on tris(2,2’-bipyridine)iron(II) complexes of zeolite Y provides evidence for the dynamic feature of complex equilibrium in presence of a ligand-eliminating process with the cage openings acting as sinks for such a draining system. Detailed studies are conducted on the formation of paramagnetic oxygen adducts in cobalt exchanged-Y type zeolites containing adsorbed ethylenediamine\(^\text{183}\). An anionic
Co(II) cyanide complex which reversibly binds oxygen inside zeolite Y has been prepared\textsuperscript{184}.

Zeolite encapsulated complexes exhibit some fine properties of the enzymes and so they are called ‘zeoenzymes’\textsuperscript{185}. The entrapped complexes exhibit the high specificity and activity of the enzymes since the channels and cages within the three dimensional pore structures of zeolites are similar to those present in natural enzymes\textsuperscript{186, 187}. A number of such complexes are reported to mimic certain enzymes\textsuperscript{188-192}. Zeolite encapsulated porphyrin type complexes mimicking the enzyme cytochrome P-450 is a topic of intense research in recent years\textsuperscript{193-195}. The encapsulation of copper acetate dimers in zeolite Y finds application as catalysts in the hydroxylation of phenol\textsuperscript{196}.

The zeolite supported Schiff base complexes display an enhanced activity and selectivity in a multitude of organic reactions. In view of the highly desirable attributes of such complexes, a vast number of supported Schiff base complexes have been designed and synthesized. Zeolite Y encapsulated Cu(salen) complex prepared by Ratnasamy \textit{et al.}\textsuperscript{197} are efficient catalysts in the presence of hydrogen peroxide\textsuperscript{198}. A similar analogue of Co(salen) complex and V(salen) complex with tetragonal distortion show catalytic activity towards phenol hydroxylation\textsuperscript{199}. These distortions in molecular geometries as a result of encapsulation lead to depletion of electron density at the metal sites and subsequent increase in catalytic activity.

Much attention has recently given to bipyridyl complexes entrapped in zeolite cages due to their specific properties. The epoxidation of alkenes is hindered by several complications arising from their auto-oxidation. Several metal carbonyl clusters grafted on zeolite supports are studied in detail to understand their action as catalysts. There are reports of zeolite encapsulated clusters of iron, rhodium, iridium, palladium and molybdenum\textsuperscript{200-204}. They can be prepared by the usual procedure of ion exchange followed by
Clusters of osmium carbonyl supported on zeolite can catalyze the hydrogenation of carbon monoxide to form hydrocarbons.

A lot of work has been done to explain the reason behind the enhanced catalytic activity of encapsulated transition metal complexes in the selective oxidation of methane using tert-butyl hydroperoxide under mild conditions. It is very interesting to note that simple complexes show only mild activity in comparison with the supported analogues. Zeolite Y encapsulated copper complexes of Schiff base derived from salicylaldehyde and 2-aminomethylbenzimidazole are effective catalysts for the oxidation of phenol and styrene in the presence of hydrogen peroxide. Schiff base complexes of chromium(III), manganese(II), iron(II), cobalt(II), nickel(II) and copper(II) were encapsulated in zeolites and tested for their activity in the oxidation of cyclohexane to cyclohexanol and cyclohexanone. Co(II) Schiff base complexes encapsulated in zeolite-Y having the general formula Co(II)L-Y (where L= salicylaldehyde-o-phenylenediamine (saloph), chloro-salicylaldehyde-o-phenylenediamine (Cl-saloph), bromo-salicylaldehyde-o-phenylenediamine, (Br-saloph) and nitro-salicylaldehyde-o-phenylenediamine, (nitro-saloph) and Y= zeolite Na-Y) have been synthesized and characterized for their physicochemical and spectroscopic properties. The neat and encapsulated catalysts were tested for their catalytic activities in the oxidation of b-isophorone (BIP) to keto-isophorone (KIP) using air as an oxidant at ambient conditions of pressure and temperature. It was found that the catalytic activities of encapsulated catalysts were higher than their homogeneous analogues in the oxidation reaction. Copper(II) complexes of two biologically important ligands, viz., embelin (2,5-dihydroxy-3-undecyl-2,5-cyclohexadien1,4-dione) and 2-aminobenzimidazole were entrapped in the cages of zeolite Y by the flexible ligand method were reported in 2002. The capability of these compounds in catalyzing the reduction of oxygen (industrially known as deoxo reaction) was
Efficient catalysts for the oxidation of α-pinene under commercially viable and environmentally acceptable reaction conditions have been developed with encapsulation of [Co(II)saloph] and [Ru(III)saloph], [saloph = N,N’-bis(salicylidene)-o-phenylenediamine] complexes in zeolite\textsuperscript{211}. The thermal stability of carbonyl complexes of nickel supported inside zeolites has become a subject of wide investigation\textsuperscript{212}. The application of intrazeolite compounds in the separation and purification of gases can be achieved on knowing the steric distortion of materials in zeolites. The first experimental evidence for the distortion of intrazeolite compounds is obtained from the studies of [FeL\textsubscript{3}]\textsuperscript{2+} ions (where L = ethylenediamine, bipyridine and phenanthrene) in zeolite supercages\textsuperscript{213}. The mononuclear dioxygen complexes of cobalt were synthesized as model compounds for oxygen carriers and they have been stabilized by immobilization of the complexes inside zeolite\textsuperscript{214, 215}. The formations of encapsulated six coordinate cobalt(II) methyl isocyanide complexes with D\textsubscript{4h} symmetry illustrates the formation of fully coordinated complexes in the supercages of zeolite. The hydroxylation of phenol can be accelerated by engaging various supported complexes like Cu(II) thiazolylhydrazone, Co(II) phenanthroline and VO(salen) in zeolite Y. Bis(dimethyl glyoxime) complexes of different transition metals entrapped in zeolite lattice find immense applications as catalysts in a large number of synthetic reactions. Notable among them is the selective oxidation of propene\textsuperscript{216}. Inomata\textit{et al.}\textsuperscript{217} reported zeolite Y encapsulating two distinct metal complexes. This zeolite contains Ru(bpy)\textsubscript{3} (bpy = 2,2’-bipyridine) and Mn(saloph) [saloph = N,N’-bis(salicylidene)-o-phenylenediamine] as photoinducing and oxidative catalytic sites, respectively. The zeolite showed the quenching of the emission, resulting in the effective electron/energy transfer from the Ru\textsuperscript{II} center to the Mn\textsuperscript{II} center in it (Figure 1.7). The mechanism of the acceleration of the oxidation reaction by photoirradiation.
is not clear yet. The main active intermediate in this reaction is predicted to be a metal oxide species from the reaction products. The photoirradiation probably promotes the production of M=O species in the zeolite.

Figure 1.7: Schematic view of Y-type zeolite encapsulating two distinct metal complexes (Adopted from Ref. 217)

1.9 Scope of the present work

Schiff base complexes were found to have immense application in various fields. Study of transition metal complexes has gained much attention because of their potential diverse applications such as catalysts, chemotherapeutic agents, insecticides, fungicides and organic light emitting diodes. In the recent years, there is an upsurge in synthesizing compounds suitable for such applications.

The present work was undertaken with a view to synthesize some new simple and zeolite encapsulated transition metal complexes of Schiff bases. A search through the literature has revealed that only very few complexes of Schiff bases derived from 1,8-diaminonaphthalene have been reported. Furthermore, it has been reported that the isolation of free Schiff bases in these cases could not be done as they immediately form ring closure compounds, perimidines.
However, these perimidines are known to exist in equilibrium along with the Schiff base derived from this compound. This prompted us to synthesize new Schiff base complexes derived from the perimidines.

The work embodied in this thesis was carried out with the following objectives:

- To study the interaction of 1,8-diaminonaphthalene with the aldehydes like quinoxaline-2-carboxaldehyde, 2-hydroxy-3-methoxybenzaldehyde and 4-hydroxy-3-methoxybenzaldehyde and to characterize the product formed.
- To use the products isolated from the above reaction as ligands for the synthesis of Mn(II), Co(II) and Cu(II) complexes.
- To know whether the product isolated acts as Schiff base ligand or perimidines in metal complexes.
- To study the mode of coordination of the ligands with Mn(II) Co(II) and Cu(II) metal ions using techniques like elemental analysis, molar conductance measurements, FT-IR, UV-Visible, EPR etc.
- To anchor the complexes in zeolite Y matrix and characterize the zeolite encapsulated complexes.
- To use the resulting complexes as catalysts for oxidation reaction.

References

12. De Aguiar, A. Ber. 7 (1874) 309.
13. Ladenburg, A. Ber. 11 (1878) 1650.
14. Meyer, R.; Muller, W. Ber. 30 (1897) 775.


52. Holm, R. H; Everett Jr, G. W.; Chakravorty, A. Prog. Inorg. Chem. 7 (1966) 83.
64. Williams, D. R. Chem. Rev. 72 (1972) 203.


Introduction


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