Ph.D Thesis

STUDIES ON SIMPLE AND ENCAPSULATED TRANSITION METAL COMPLEXES OF SCHIFF BASES DERIVED FROM DIAMINONAPHTHALENE

By
Varsha. G

Department of Applied Chemistry
Cochin University of Science and Technology
Kochi – 682 022

May 2011

Ph.D Thesis
May 2011

STUDIES ON SIMPLE AND ENCAPSULATED TRANSITION METAL COMPLEXES OF SCHIFF BASES DERIVED FROM DIAMINONAPHTHALENE

Varsha.G

Department of Applied Chemistry
Cochin University of Science and Technology
Kochi – 682 022

STUDIES ON SIMPLE AND ENCAPSULATED TRANSITION METAL COMPLEXES OF SCHIFF BASES DERIVED FROM DIAMINONAPHTHALENE

Thesis submitted to
Cochin University of Science and Technology
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Chemistry
under the Faculty of Science

By
Varsha. G

Department of Applied Chemistry
Cochin University of Science and Technology
Kochi – 682 022

May 2011

Dedicated to my loving parents, brother
&
my dear husband

Department of Applied Chemistry
Cochin University of Science and Technology
Kochi – 682 022

Certificate

*This is to certify that the thesis entitled "**Studies on Simple and Encapsulated Transition Metal Complexes of Schiff Bases Derived from Diaminonaphthalene**" is an authentic record of research work carried out by Mrs. Varsha. G under my supervision in partial fulfillment of the requirements for the degree of Doctor of Philosophy of Cochin University of Science and Technology, and further that no part thereof has been presented before for any other degree.*

Kochi
25-05-2011

Dr. K. K. Mohammed Yusuff
(Supervisor)

Declaration

I hereby declare that the work presented in the thesis entitled **"Studies on Simple and Encapsulated Transition Metal Complexes of Schiff Bases Derived from Diaminonaphthalene"** is entirely original and was carried out by me independently under the supervision of Dr. K. K. Mohammed Yusuff, (Emeritus Professor, Department of Applied Chemistry, Cochin University of Science and Technology) and has not been included in any other thesis submitted previously for the award of any other degree.

Kochi-22 **Varsha. G.**
25-05-2011

Acknowledgement.............

"A hundred times a day I remind myself that my inner and outer life are based on the labours of others"

Albert Einstein

My fascination with inorganic chemistry and catalysis started during the last four years of stay in the laboratory of ***Prof. Dr. K. K. Mohammed Yusuff****. I am extremely thankful to* ***Yusuff sir****, who offered me the chance to do research in the field of coordination chemistry under his supervision. His constant guidance, invaluable discussions and perpetual inspiration always acted as motivating factors to my research works. Prof. Yusuff, in the truest sense, played the ideal role of a philosopher, father and guide to me.*

I am grateful to ***Prof. Dr. K. Sreekumar****, Head of the department for providing the necessary facilities. I express my gratitude to former heads of the department* ***Prof. Dr. M. R. Prathapachandra Kurup*** *and* ***Prof. Dr. K. Girish Kumar*** *for their immense help during the various stages of my research. I relish the blessings and encouragement of* ***Prof. S. Sugunan*** *and* ***Dr. P. M. Sabura Begum****. I am very much thankful to all non teaching staff specially* ***Usha chechi*** *for all the help and support.*

I recall with gratitude the selfless help and involvement of my friends ***Dr. P. P. Robinson, Dr. V. Arun, Dr. Manju Sebastian, Dr. Jose Mathew, P. Leeju*** *and* ***Digna Varghese, Laina, A. L*** *at different stages of my work. I am also thankful to* ***Dr. Rani Abraham, Dr. Annu Anna Varghese, Dr. Pearly Sebastian Chittilappilly, Dr. Reshmi*** *and* ***Dr. N. Sridevi*** *who gave me support and reassurance in different ways. I am happy to acknowledge the services of SAIF at STIC, CUSAT; IIT, Mumbai and IIT, Madras for their help in sample analyses. I thank CSMCRI, Gujarat and Central University, Hyderabad for single crystal XRD analysis.*

Best friends are rare to find, but I was fortunate enough to get someone like Geetha. I cherish the moments with Linu and Merli. My friends were the chief contributors to what *all I had been able do as part of research and I am heavily indebted to all of my friends in the Department of Applied Chemistry, various other departments of CUSAT and other research institutions. They made my time here an enjoyable and positive one.*

Most importantly, I'd like to thank my achan, Amma, Kuttappi, Baby amma, Jayan Chettan, Chippy kuppy, Ammal's, Kavya, Raghavan Uncle, Pupa aunty and my dearest husband Chintu. My mother is the one who sincerely raised me with her care and love. None of this would be possible without my family. Their undying love, support and motivation has allowed me to reach here. I am also thankful to Pamman Kochachan, whenever I need a help, you were there.

Above all, I would like to thank God, The Almighty, for having made everything possible by giving me strength and courage to do this work.

Varsha

Preface

***

Schiff base complexes of transition metal ions have played a significant role in coordination chemistry. The convenient route of synthesis and thermal stability of Schiff base complexes have contributed significantly for their possible applications in catalysis, biology, medicine and photonics. Significant variations in catalytic activity with structure and type are observed for these complexes. Hence there is a persisting interest in the synthesis of new Schiff base complexes. In the present study we have synthesized some new Mn(II), Co(II) and Cu(II) complexes of Schiff bases derived from 1,8-diaminonaphthalene. Even though we could not isolate these Schiff bases (as they readily cyclise to form the perimidine compounds), we were able to characterize unequivocally the complexes synthesized from these compounds as complexes of Schiff bases.

We synthesized three perimidine derivatives, 2-(quinoxalin-2-yl)-2,3-dihydro-1*H*-perimidine, 2-(2,3-dihydro-1*H*-perimidin-2-yl)-6-methoxyphenol and 4-(2,3-dihydro-1*H*-perimidin-2-yl)-2-methoxyphenol by the condensation of 1,8-diaminonaphthalene with quinoxaline-2-carboxaldehyde, 2-hydroxy-3-methoxybenzaldehyde or 4-hydroxy-3-methoxybenzaldehyde respectively. These compounds were used as precursor ligands for the preparation of Schiff base complexes. The complexes were characterized using elemental analysis, conductance and magnetic susceptibility measurements, infrared and UV-Visible spectroscopy, thermogravimetric analysis and EPR spectroscopy. We also encapsulated the complexes in zeolite Y matrix and these encapsulated complexes were also characterized. We have also tried these complexes as catalysts in the oxidation of cyclohexanol and decomposition of hydrogen peroxide. The details of these studies are presented in this thesis.

Contents

***

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Chapter 6

Chapter 7

Chapter 8

Chapter

Introduction 1

Contents

> *"Fortunately, science, like nature to which it belongs, is neither limited by time nor by space. It belongs to the world, and is of no country and no age. The more we know, the more we feel our ignorance, the more we feel how much remains unknown, and in philosophy, the sentiment of the Macedonian hero can never apply – there are always new fields to conquer."*
>
> ***Sir Humphry Davy***

The chemistry of Schiff base[1] complexes has developed rapidly in the last thirty years. Schiff base ligands are able to coordinate metals through imine nitrogen. Several studies[2,3] showed that the presence of a lone pair of electrons in an sp^2 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 tetradentate N_2O_2 Schiff base ligands. They are usually called as salen ligands. The term salen is also used in the literature for the N_2O_2 tetradentate 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.

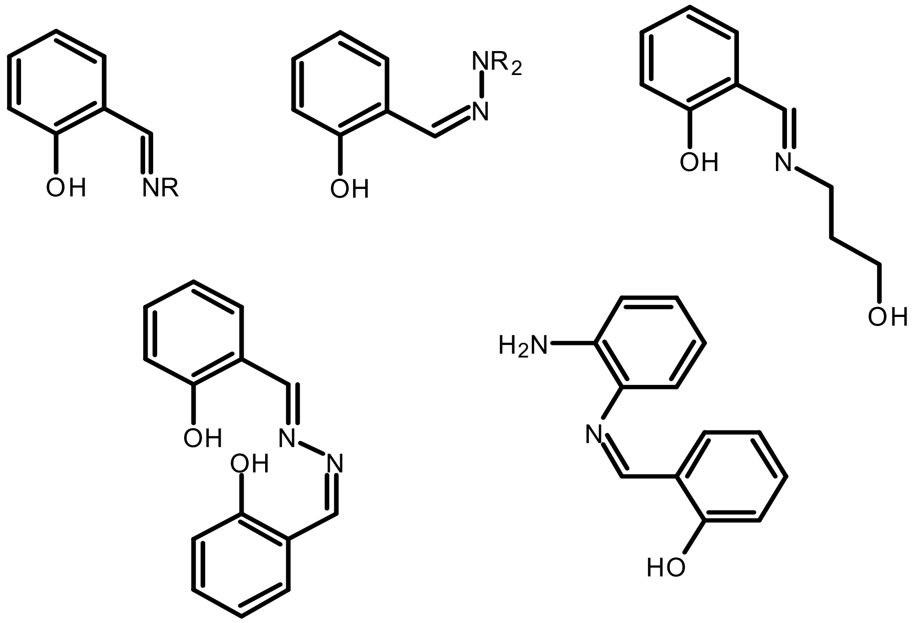


Figure 1.1: Schiff base ligands derived from salicylaldehyde and different amines

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.

1.2 Perimidines

Heteroaromatic systems can be divided[4-6] into compounds with an excess of π electrons (e.g. pyrrole) and those with a deficiency of π 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 π electrons[7] could be quite interesting. Such a system is perimidine (Figure 1.2).

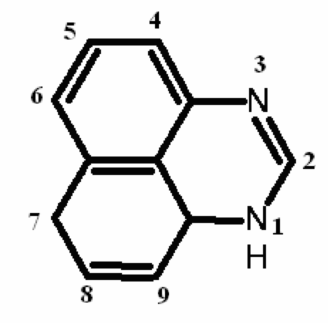


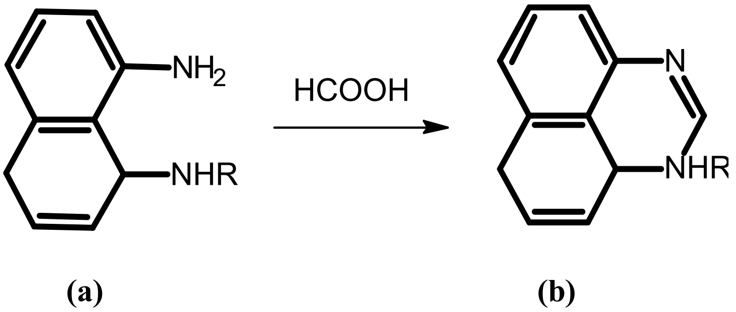
Figure 1.2: Perimidine

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 1*H*-naphtho-[1,8-d,e]pyrimidine, 1*H*-benzo[d,e]quinazoline, perinaphthimidazole, and 1*H*-1,3-diazaphenalene.

1.2.1 Preparation of perimidines

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

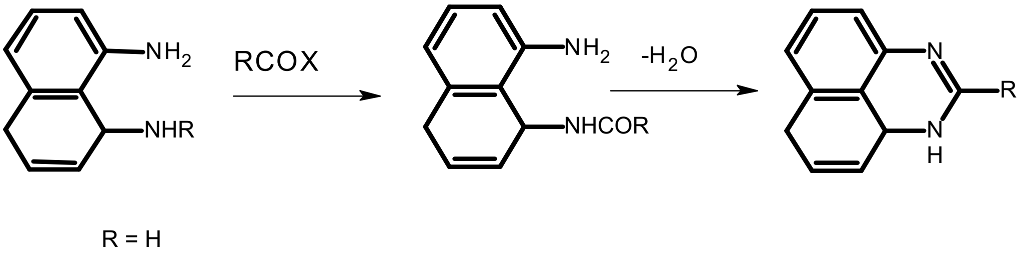
When the diamines are refluxed with an excess of formic acid, 1-methylperimidine, 1-phenylperimidine[21], and l-(2,4-dinitrophenyl)perimidine[22] are formed in high yields (Scheme 1.1).



(i) R = H, (ii) R = CH_3, (iii) R = C_6H_6, (iv) R = 2,4-$(NO_2)_2C_6H_3$.

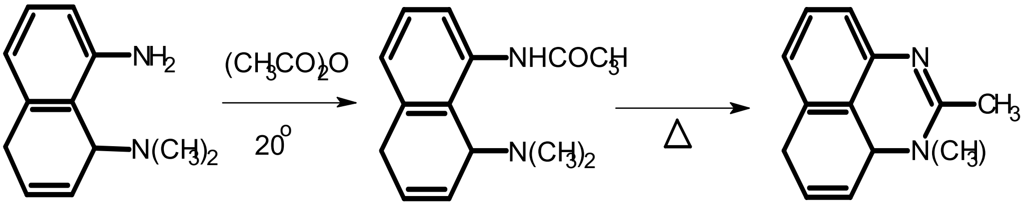
Scheme 1.1: Preparation of perimidines from various cyclising agents

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



Scheme 1.2: Preparation of perimidines from acyl halides

Heating of 1,8-diaminonaphthalene with acetic[26, 27] and trifluoroacetic[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)



(C)

Scheme I.3: Preparation of perimidines from acid anhydrides

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_3, CCl_3[29], C_2H_5, n-C_3H_7, iso-C_6H_{13}, C_6H_5[30], different halogeno-groups[31], hydroxy-group[32], methoxy group[33], 3,4-methylenedioxy-group, dialkylamino-groups, nitrophenyl[34], 4-biphenylyl, α-naphthyl, ferrocenyl[35], 2-thienyl,2-furyl[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.

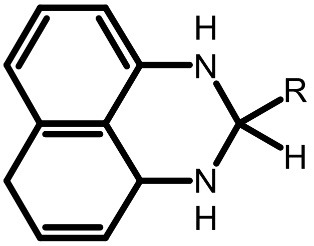
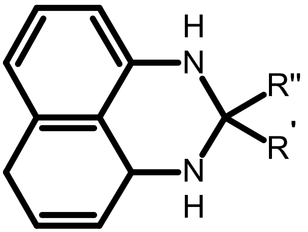


Figure 1.3: 2,3-dihydroperimidines

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[37].



(a) R' = R'' = CH_3;

(b) R' = CH_3, R'' = C_6H_5

Figure 1.4: 2,2-disubstituted 2,3-dihydroperimidines

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[38].

In the solid state, perimidine derivatives are stable. Upon dissolution in nonpolar solvents[39] (e.g., hydrocarbons or tetrachloromethane), an equilibrium is gradually established[40, 41] between the ring closed and imine form. However, the ring opening exists only for micro seconds[42] 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[42] have shown that equilibrium is established between ring closed and ring opened states upon dissolution in nonpolar solvents. In 1981, Stalhandske[43] 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[44] showed this non-equivalence brings about splitting of the vibration. Recently, we have reported the loss of planarity[45] of the perimidine ring.

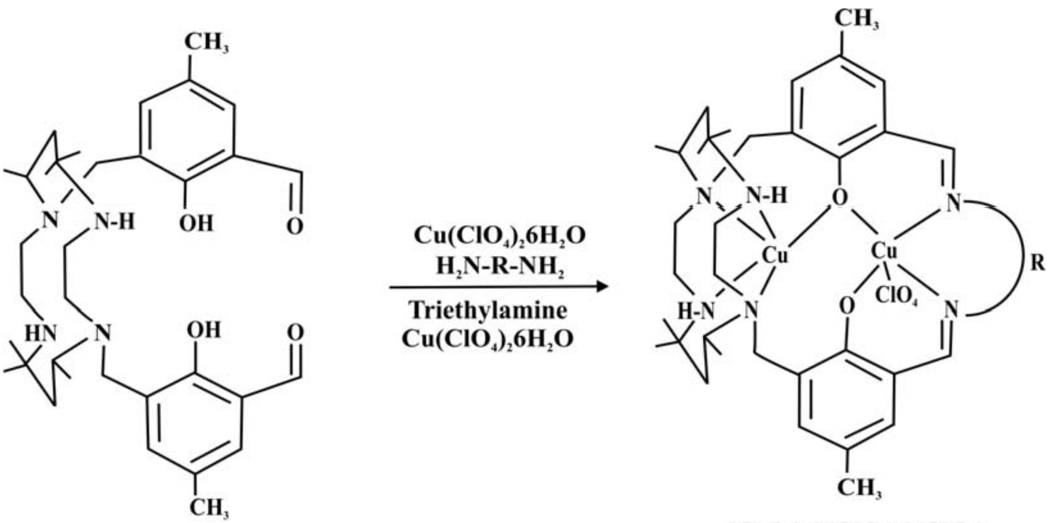
1.3 Schiff base metal complexes

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 *et al.*[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[47-49] and wide applications[50, 51].

A review on metal complexes of Schiff bases by Holm *et al.* shows that more than half of these reported complexes were derived from salicylaldehyde[52]. Complexes of Schiff base ligands derived from salicylaldehyde were first used by Pfeiffer *et al.*[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[54-56]. Schiff bases derived from salicylaldehyde and 2-aminophenyldisulphide or 2-aminoethyldisulphide were complexed with Ni(II) ions and the electrochemistry of the complexes was reported[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[58].

Recently[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-hexamethylcyclotetradecane 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[60]. ESR spectra of the binuclear copper(II) complexes show a broad signal at g = 2.10 and μ_{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 1 to the open circular form II.



PC

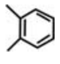
[CuL1-5(ClO_4)$_2$](ClO_4)

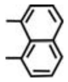
R

L^1 = -$(CH_2)2^-$

L^2 = -$(CH_2)3^-$

L^3 = -$(CH_2)4^-$

L^4 = 

L^5 = 

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 $[M(L \text{ or } L')_2X_2]$ 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_3COO^- and (L) corresponds to the tetradentate macrocyclic ligand, were synthesized in methanolic media by the template condensation of 1,8-diaminonaphthalene and 2,3-butanedione (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_3COO^-, 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-β-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[71] 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[72], N,N′-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 μ-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-diaminopyridine) with bis(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride and mono (cyclopentadienyl)titanium(IV) trichloride have been studied and complexes of the types [$Cp_2M(L)Cl$]Cl (M=Ti(IV) or Zr(IV)), [$CpTiCl_3(L)$] have been isolated and characterized by spectroscopic studies[73]. The partial Schiff base[74] condensation reactions between 2,6-diacetylpyridine 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[75].

The diaminonaphthalene copper complex showed excellent activity for electrocatalytic reduction of oxygen[76]. The excellent adhesivity and dense structure of the film obtained by electrochemical synthesis of poly (1,8-

diaminonaphtalene)[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[80].

Shakir *et al*[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[82].

The synthesis of the Schiff base of O,O-diethylthonophosphorylhydrazine with *o*-vanillin and it's Ni(II) complex were reported along with the crystal structure[83]. The mono- and bis-Schiff bases of *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 *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 tetradentate (N_2O_2) or tridentate (N_2O) ligand, depending upon the nature of the anions present and the reaction conditions[84, 85.]

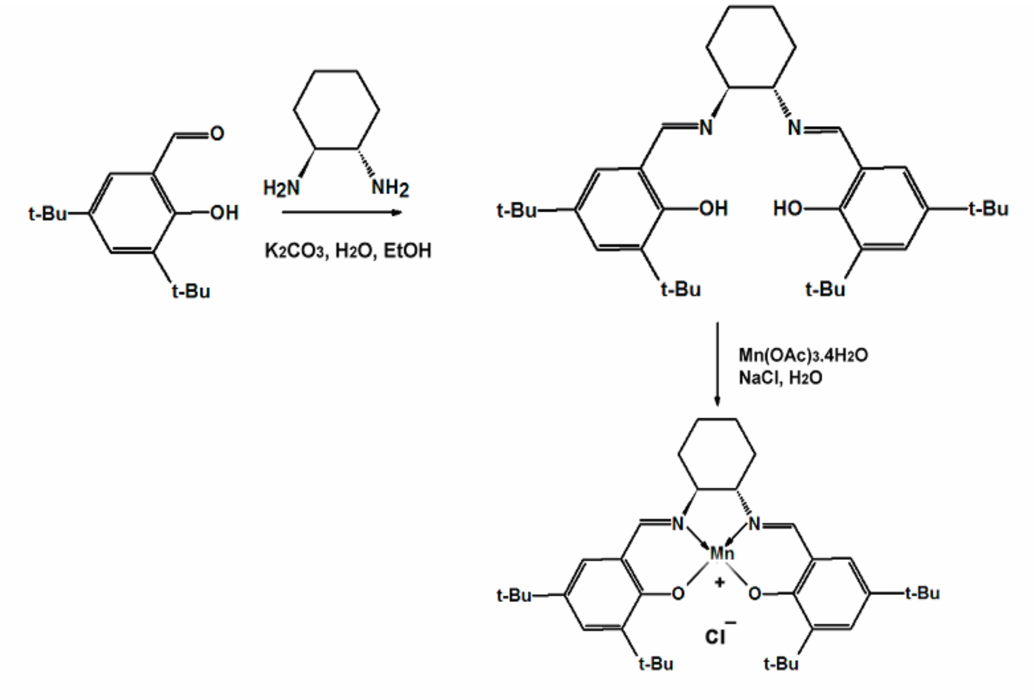
Maurya *et al.* have reported[86] a series of complexes of two Schiff bases, N-(o-vanillinidene)-p-anisidine (o-VPAH) and N,N'–bis(o-vanillinidene) ethylenediamine (o-VEDH$_2$). In all of the complexes, o-VPAH acts as a monobasic-bidentate ligand and o-VEDH$_2$ acts as a dibasic-tetradentate ligand. In 1997, Tumer *et al.*[87] reported the complexes of cobalt(II), nickel(I1) and zinc(I1) with two new Schiff bases derived from 3,5-di(tert-butyI)-4-hydroxyaniline and 4-hydroxysalicylaldehyde or o-vanillin. Hingorani and Agarwala[88] reported six new mixed ligand complexes of copper(II) with tridentate o-vanillinthiosemicarbazone or o-vanillin-4-phenylthiosemicarbazone.

IR spectral studies have shown that coordination occurs through thioenolic suplhur and azomethine nitrogen.

Recently[89] 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[90]. The synthesized ligand, and their metal complexes were screened for antibacterial activity against bacterial species, *Escherichia coli*, *Salmonella typhi*, *Bacillus subtillus, 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-methylphenol[91] and the formation of Schiff base complexes[92] 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[93-96]. 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[97-99]. 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 oxidation of sulphides[99], redox reactions[100], hydrolysis[101], decarboxylation[102], elimination[103] and aldol condensation[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[105].

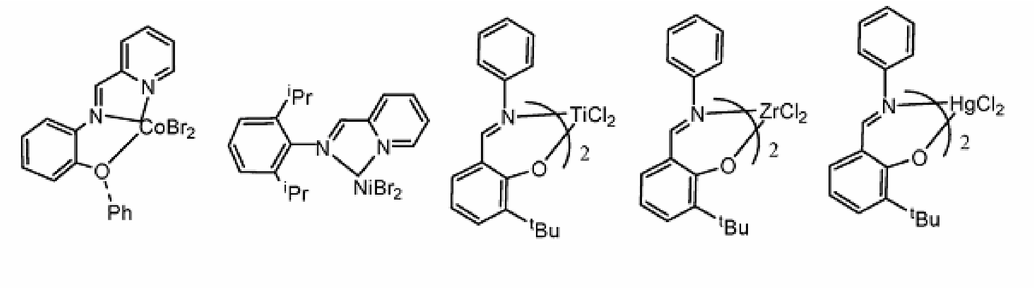


Figure 1.5.

Numerous Co(II) Schiff base complexes are known to form superoxo or μ-peroxo complexes by reaction with dioxygen. The best known of these is Co(II)salen Schiff base complexes studied extensively by Calvin and Martell[106]. The reactions of organic substrates with molecular oxygen in the presence of Co(II) Schiff base complexes were studied by Nishinaga *et al.*[107]. They observed that the complexes reversibly bind with the molecular oxygen and form μ-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[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_2PO_4, $NaHCO_3$ 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 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_2Cl_2. This reaction is markedly retarded by strong coordinating solvents such as DMF and pyridine. The complex $[(Fe^{III}salen)_2O]$ favors the stereoselective oxidation of adamantine[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[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-methylnedioxyphenol with molecular oxygen. A special catalytic application of Schiff base complexes was reported by Kim *et al*[125]. Electrochemical reduction of thionyl chloride had been carried out at glassy carbon and molybdenum electrodes with surface modified by binuclear tetradentate 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 *via* the interaction with the oxygen of the Schiff base[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[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 catalysts[130-133]. 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 selectiviy 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[134]. 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[135].

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 CO_2 is catalyzed by a variety of homogeneous metal carbonyl complexes like $[HFe(CO)_4]^-$, $[Rh(CO)_2I_2]^-$ and $[Ru(bpy)_2(CO)C]^+$. The hydroformylation[136] 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, $[Rh(CO)I_2]^-$. The one reaction that requires special mention is the enantioselective electrocatalytic epoxidation of olefins in the presence of chiral Schiff base complexes of manganese[137].

The chiral complex, diphenylmethylene imino palladium(II) have increased enantioselectivity in alkylation of enolates[138]. The cobalt complexes of

3-oxobutylideneaminato ligands are efficient catalysts for the enantioselective borohydride reduction of ketones, imines and α,β-unsaturated carbonyl compounds to afford the corresponding secondary alcohols[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 sterric 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[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[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 SiO_4 and 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 β-cage while the cavity of the supercage is the α-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[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[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 σ – bond as depicted below (Figure 1.6) for the Schiff base salen.

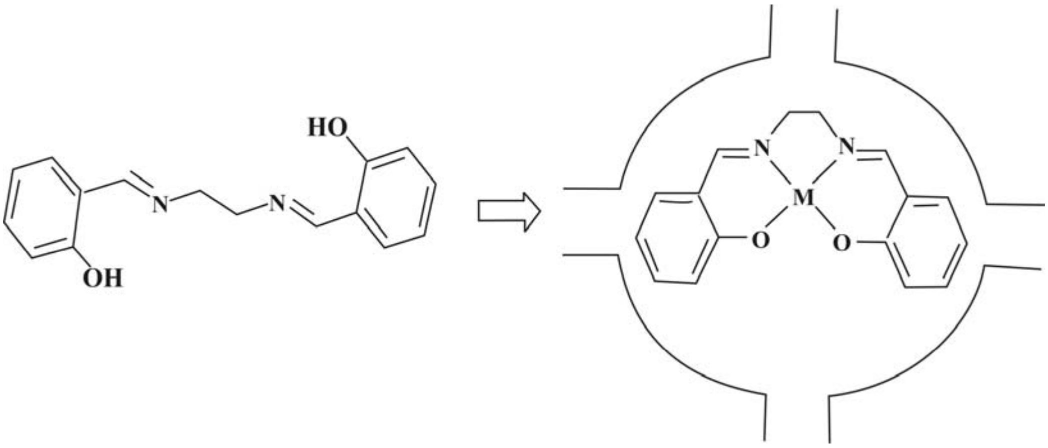


Figure 1.6: Synthesis of zeolite Y encapsulated metal salen complexes via. the flexible ligand method.

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 dicholromethane 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[158]. The resulting zeolite encapsulated complexes have been used to act as oxygen carriers mimicking haemoglobin[159], as selective oxidation catalysts or as catalysts for selective hydrogenation[160].

1.7.1.2 Ship-in-a-Bottle method

This method was first proposed by Romanovsky and Gabrielov[161] and later reported by many workers in this field[162]. The term 'ship– in– a– bottle' was first coined by Herron *et al.*[163]. 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)[159]. 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[164].

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 frame work. A “ship-in-a-bottle” approach to entrap the chiral (salen) Mn complexes within the cages of zeolite Y was reported[165].

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[166].

Reports about metal phthalocyanine complexes trapped within the zeolite cages are already available[167]. These large macrocyclic metal complexes have a tendency to aggregate or dimerize in solution and act as inhibitors to certain redox processes[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[169]. The corresponding simple phthalocyanine complexes of iron were found to undergo oxidative destruction under the same reaction conditions[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[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[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[177].

Various reactions like hydration of olefins, dehydration of alcohols, ester formation, transesterification etc. are catalyzed by zeolite systems[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[180, 181]. Zeolite entrapped carbonyl clusters of osmium act as selective stable catalysts for CO hydrogenation[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[183]. An anionic

Co(II) cyanide complex which reversibly binds oxygen inside zeolite Y has been prepared[184].

Zeolite encapsulated complexes exhibit some fine properties of the enzymes and so they are called 'zeoenzymes'[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[186, 187]. A number of such complexes are reported to mimic certain enzymes[188-192]. Zeolite encapsulated porphyrin type complexes mimicking the enzyme cytochrome P-450 is a topic of intense research in recent years[193-195]. The encapsulation of copper acetate dimers in zeolite Y finds application as catalysts in the hydroxylation of phenol[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 *et al.*[197] are efficient catalysts in the presence of hydrogen peroxide[198]. A similar analogue of Co(salen) complex and V(salen) complex with tetragonal distortion show catalytic activity towards phenol hydroxylation[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[200-204]. They can be prepared by the usual procedure of ion exchange followed by carbonylation[205]. Clusters of osmium carbonyl supported on zeolite[206] 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[207]. 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[208]. Co(II) Schiff base complexes encapsulated[209] in zeolite-Y having the general formula Co(II)L-Y (where L= salicylaldehyde-*o*-phenylenediimine (saloph), chloro-salicylaldehyde-*o*-phenylenediimine (Cl-saloph), bromo-salicylaldehyde-*o*-phenylenediimine, (Br-saloph) and nitro-salicylaldehyde-*o*-phenylenediimine, (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[210] 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 explored and the results indicate an enhancement of the catalytic properties from that of the simple copper ion exchanged zeolite.

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[211]. The thermal stability of carbonyl complexes of nickel supported inside zeolites has become a subject of wide investigation[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 $[FeL_3]^{2+}$ ions (where L= ethylenediamine, bipyridine and phenanthrene) in zeolite supercages[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[214, 215]. The formations of encapsulated six coordinate cobalt(II) methyl isocyanide complexes with D_{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) thiazoylhydrazone, 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[216]. Inomata*et al.*[217] reported zeolite Y encapsulating two distinct metal complexes. This zeolite contains $Ru(bpy)_3$ (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^{II} center to the Mn^{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.

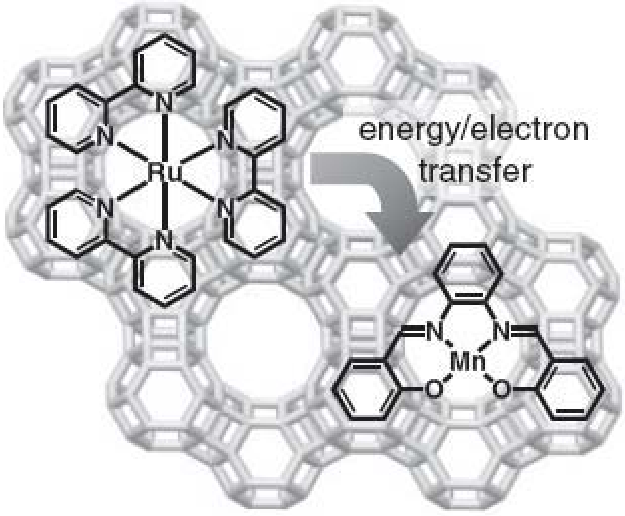


Figure 1.7: Schematic view of Y-type zeolite encapsulating two distinct metal complexes *(Adopted from Ref. 217)*

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

1. Schiff, H. Ann. Suppl. 3 (1864) 343.
2. Clercq, B. D.; Verpoort, F. J. Mol. Catal. A: Chem. 180 (2002) 67.
3. Yamada, S. Coord. Chem. Rev. 1 (1966) 415; Yamada, S. Coord. Chem. Rev. 2 (1967) 82.
4. Albert, A. Heterocyclic Chemistry. An Introduction, The Athlone Press: London. (1968).

5. Klyuev, N. A.; Pozharskii, A. F.; Belikov, A. B.; Adanin, V. M. Chem. Heterocycl. Compd. 16 (1980) 535.
6. Yakhontov, L. N. Chem. Heterocycl. Compd. 18 (1980) 873.
7. Woodgate, P. D.; Herbert, J. M.; Denny, W. A. Heterocycles. 26 (1987) 1029.
8. Sachs, F. Annalen. 365 (1909) 53.
9. Mayberry, W. E. Biochemistry. 6 (1967) 1320.
10. Shishkin, G. V.; Vysochin, V. I. Chem. Heterocycl. Compd. 16 (1980) 1069.
11. Richmond, J. H. Six-Membered Heterocyclic Nitrogen Compounds with Three Condensed Rings, Acad. Press: New York. (1958) 518.
12. De Aguiar, A. Ber. 7 (1874) 309.
13. Ladenburg, A. Ber. 11 (1878) 1650.
14. Meyer, R.; Muller, W. Ber. 30 (1897) 775.
15. Sagadeev, E. V.; Kafiatullin, R. A.; Sagadeev, V. V.; Sagadeev, V. I. Theor. Found. Chem. Eng. 37 (2003) 524.
16. Ivashchenko, A. V.; Dziomko, V. M. Russ. Chem. Rev. 46 (1977) 115.
17. Yavari, I.; Adib, M.; Jahani-Moghaddam, F.; Bijanzadeh, H. R. Tetrahedron. 58 (2002) 6901.
18. Yasaei, Z.; Mirzaei, P.; Bazgir, A. Comptes Rendus Chimie. 13 (2010) 1308.
19. Jung, I. G.; Son, S. U.; Park, K. H.; Chung, K.-C.h.; Lee, J. W.; Chung, Y. K. Organometallics. 22 (2003) 4715.
20. Sachs, F. Ber. 39 (1906) 3006.
21. Pozharskii, A. F.; Dal'nikovskaya, V. V. Russ. Chem. Rev. 50 (1981) 816.

22. Sachs, F.; Forster, R. B. Ber. 44 (1911) 1738.
23. Filatova, E. A.; Borovlev, I. V.; Pozharskii, A. F.; Starikova, Z. A.; Vistorobskii, N. V. Mendeleev Commun. 10 (2000) 178.
24. Pozharskii, A. F.; Yurchuk, G. G. Khim.Geterotsikl. Soed. (1981) 838.
25. Yoshida, Z.; Shimada, Y.; Oda, R. J. Chem. Soc. Japan, 55 (1952) 523.
26. Pesin, V. G.; Sergeev, V. A.; Barkalaya, E. V. Chem. Heterocycl. Compd. 4 (1968) 587.
27. Paragamian, V.; Baker, M. B.; Puma, M. B.; Reale, J. J. Hetereocycl. Chem. 5 (1968) 591.
28. Pozharskii, A. F.; Yurchuk, G. G. Chem. Heterocycl. Compd. 15 (1979) 346.
29. Pozharskii, A. F.; Yurchuk, G. G.; Gervits, L. L. Chem. Heterocycl. Compd. 15 (1979) 342.
30. Smellie, I. A. S.; Fromm, A.; Moggach, S. A.; Paton, M. Carbohydr. Res. 346 (2011) 43.
31. Popp, F. D.; Catala, A. J. Heterocycl. Chem. 1 (1964) 108.
32. Kim, S.; Seus, P.; Meier, H. Eur. J. Org. Chem. 8 (2004) 1761.
33. Wasulko, W.; Noble, A. C.; Popp, F. D. J. Med. Chem. 9 (1966) 599.
34. Starshikov, N. M.; Pozharskii, A. F. Khim. Geterotsikl. Soed. 96 (1980).
35. Popp, F. D.; Moynahan, E. B. J. Heterocycl. Chem. 7 (1970) 739.
36. Pozharskii, A. F.; Ryabtsova, O. V.; Ozeryanskii, V. A.; Degtyarev, A. V.; Kazheva, O. N.; Alexandrov, G. G.; Dyachenko, O. A. J. Org. Chem. 68 (2003) 10109.
37. Bradbury, S.; Rees, C. W.; Storr, R. C. J. Chem. Soc. 141. Perkin Trans. I. (1972)

38. Quast, H.; Ndling, W.; Klemm, G.; Kirschfeld, A.; Neuhaus, P.; Sander, W.; Hrovat, D. A.; Borden, W. T. J. Org. Chem. 73 (2008) 4956.
39. Minkin, V. I. Chem. Rev. 104 (2004) 2751.
40. Minkin, V. I.; Komissarov, V. N.; Kharlanov, V. A. Perimidinespirocyclohexadienones. In Organic Photochromic and Thermochromic compounds; Crano, J. C.; Guglielmetti, R. J. Eds., Plenum Press: New York. 1 (1999) 315.
41. Komissarov, V. N.; Gruzdeva, E. N; Kharlanov, V. A.; Olekhnovich, L. P.; Borodkin, G. S.; Khrustalev, V. N.; Lindeman, S. V.; Struch Kov, Y. T.; Kogan, V. A. Minkin, V. I. Izv. Akad. Nauk. SSSR. 46 (1997) 2028.
42. Davis, R.; Tamaoki, N. Org. Lett. 7 (2005) 1461.
43. Stalhandske, C. Crystal Struct. Comm. 10 (1981) 1081.
44. Platteborze, K.; Lambrecht, I. J. Mol. Struct. 327 (1994) 337.
45. Varsha, G.; Robinson, P. P.; Sebastian, M.; Varghese, D.; Leeju, P.; Jayachandran, V. P.; Yusuff, K. K. M. Tetrahedron Lett. 51 (2010) 2174.
46. Pfeiffer, P. E.; Buchholz, E.; Bauer, O. J. Prakt. Chem. 129 (1931) 163.
47. Usman, A.; Fun, H.-K.; Karmakar, T. K.; Ghosh, B. K.; Chandra, S. K. Acta Crystallogr., Sect. E: Struct. Rep. Online. E59 (2003) m387.
48. Calligaris, M.; Nardin, G. Coord. Chem. Rev. 7 (1972) 385.
49. Hobday, M. D.; Smith, T. D. Coord. Chem. Rev. 9 (1973) 311.
50. Sheldon, R. A.; Kochi, J. K. Metal Catalysed Oxidations of Organic compounds. Academic Press: New York. (1981).
51. Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. J. Am. Chem. Soc. 113 (1991) 7063.
52. Holm, R. H; Everett Jr, G. W.; Chakravorty, A. Prog. Inorg. Chem. 7 (1966) 83.

53. Pfeiffer, P. E.; Tsumaki, T. T. Leibigs. Ann. Chem. 84 (1933) 503.
54. Nie, Y. Acta Crystallogr., Sect. E: Struct. Rep. Online. E64 (2008) o471.
55. Dash, B.; Patra, M.; Praharaj, S. Ind. J. Chem. 19B (1980) 894.
56. Tiwari, S. S.; Husain, M. I.; Srivastava, G. C. J. Indian Chem. Soc. 58 (1981) 214.
57. Labisbal, E.; Romero, J.; de Blas, A.; García-Vázquez, J. A.; Duran, M. L.; Castineiras, A. Polyhedron. 11 (1992) 53.
58. Lal De, R.; Samanta, K.; Samanta, C.; Mukherjee, A. K. Ind. J. Chem. 38A (1998) 1010.
59. Sengottuvelan, N.; Saravanakumar, D.; Kandaswamy, M. Polyhedron. 26 (2007) 3825.
60. Adam, K. R.; Atkinson, I. M.; Lindoy, L. F. Inorg. Chem. 36 (1997) 480.
61. Cacic, M.; Trkovnik, M.; Cacic, F.; Has-Schon, E. Molecules. 11 (2006) 134.
62. Patra, M.; Mahapatra, S. K.; Dash, B. J. Indian Chem. Soc. 51 (1974) 1031.
63. Modi, D.; Sabnis, S. S.; Deliwala, C. V. J. Med. Chem. 13 (1970) 935.
64. Williams, D. R. Chem. Rev. 72 (1972) 203.
65. Dumas, P.; Girault, J.-P.; Guerin, P. Polym. Bull. 2 (1980) 257.
66. Zhang, S.; Wu, Y.; Li, H.; Analyst.125 (2000) 753.
67. Misra, R. P.; Mahapatra, B. B.; Guru, S. J. Indian Chem. Soc. 58 (1981) 808.
68. Singh, D. P; Kumar, K. J. Serb. Chem. Soc. 75 (2010) 475.
69. Parekh, H. M.; Panchal, P. K.; Patel, M. N. Toxicol. Environ. Chem. 88 (2006) 579.

70. Singh, D. P.; Kumar, K.; Dhiman, S. S.; Sharma, J. J. Enzyme Inhib. Med. Chem. 25 (2010) 21.

71. Parekh, H. M.; Panchal, P. K.; Patel, M. N. Pharm. Chem. J. 40 (2006) 494.

72. Hamuryudan, E.; Bayir, Z. A.; Bekaroglu, O. Monatsh. Chem. 131 (2000) 175.

73. Srivastava, S. K.; Srivastava, B. K.; Sengupta, S. K.; Pandey, O. P. Indian J. Chem., Sect A. 37 (1998) 544.

74. Radecka-Paryzek, W.; Patroniak, V. Polyhedron. 10 (1991) 683.

75. Bayir, Z. A.; Bekaroglu, O. Synth. React. Inorg. Met.-Org. Chem. 27 (1997) 1483.

76. Boophathi, M.; Won, M.-S.; Kim, Y. H.; Shin, S. C.; Shim, Y.-B. J. Electrochem. Soc. 149 (2002) E265.

77. Pałys, B. J.; Skompska, M.; Jackowska, K. J. Electroanal. Chem. 433 (1997) 41.

78. Kudelski, A.; Bukowska, J.; Jackowska, K. J. Mol. Struct. 291 (1999) 482.

79. Nasalska, A.; kompska, M. J. Appl. Electrochem. 33 (2003) 113.

80. Park, H.; Kwon, T. G.; Park, D. S.; Shim, Y. B. Bull. Korean Chem. Soc. 27 (2006) 1763.

81. Shakir, M.; Azam, M.; Parveen, S.; Khan, A. U.; Firdaus, F. Spectrochim. Acta, Part A. 71 (2009) 1851.

82. Firdaus, F.; Fatma, K.; Azam, M.; Khan, S. N.; Khan, A. U.; Shakir, M. Spectrochim. Acta, Part A. 72 (2009) 591.

83. Xu, L.; Ye, Q.; Li, H.; Jiao, K.; Zhang, S. J. Chem. Crystallogr. 30 (2000) 7.

84. Dey, S. K.; Mondal, N.; Fallah, M. S. E.; Vicente, R.; Escuer, A.; Solans, X.; Bardfa, M. F.; Matsushita, T.; Gramlich, V.; Mitra, S. Inorg. Chem. 43 (2004) 2427.

85. Choudhury, C. R.; Dey, S. K.; Karmakar, R.; Wu, C. D.; Lu, C. Z.; Fallah, M. S. E.; Mitra, S. New J. Chem. 27 (2003) 1360.

86. Maurya, R. C.; Patel, P.; Rajput, S. Synth. React. Inorg. Met.-Org. Chem. 33 (2003) 817.

87. Tumer, M.; Koksal, H.; Serin, S.; Patat, S. Synth. React. Inorg. Met.-Org. Chem. 27 (1997) 59.

88. Hingorani, S.; Agarwala, B. V. Synth. React. Inorg. Met.-Org. Chem. 20 (1990) 123.

89. Kaya, I.; Bilici, A.; Gul, M. Polym. Adv. Technol. 19 (2008) 1154.

90. Mohamed, G. G.; Sharaby, C. M. Spectrochim. Acta, Part A. 66 (2007) 949.

91. Sebastian, M.; Arun, V.; Robinson, P. P.; Leeju, P.; Varghese, D.; Varsha, G. Yusuff, K. K. M. J. Coord. Chem. 63 (2010) 307.

92. Sebastian, M.; Arun, V.; Robinson, P. P.; Yusuff, K. K. M. Synth. React. Inorg. Met.-Org. Chem. 40 (2010) 541.

93. Vigato, P. A.; Tamburini. S. Coord. Chem. Rev. 248 (2004) 1717.

94. Kojima, M.; Taguchi, H.; Tsuchimoto, M.; Nakajima. K. Coord. Chem. Rev. 237 (2003) 183.

95. Costamagna, J.; Vargas, J.; Latorre, R.; Alvarado, A.; Mena. G. Coord. Chem. Rev. 119 (1992) 67.

96. Cozzi, P. G. Chem. Soc. Rev. 33 (2004) 410.

97. Siddal, T. C.; Miyara, N. J. Chem. Soc. Chem. Commun. (1983) 1185.

98. Samsel, E. G.; Srinivasan, K. J. Am. Chem. Soc. (1985) 107.

99. Bansal, V.; Sharma, P. K.; Banerji, K. K. Ind. J. Chem. 39A (2000) 654.

100. Zhang, W.; Loebach, J. L. J. Am. Chem. Soc. 112 (1990) 2801.

101. Kitajima, N.; Fukui, H.; Moro-oka, Y. J. Chem. Soc. Chem. Commun. (1988) 485.

102. Khan, M. M. T.; Martell, A. E. Homogeneous Catalysis by Metal Complexes, Academic Press: New York. (1981).

103. Ballantine, J. A.; Purnell, J. H.; Rayanakorn, M.; Williams, K. J.; Thomas, J. M. J. Mol. Catal. 30 (1985) 373.

104. Nath, M.; Kamaluddin, J. Ind. J. Chem. 32A (1993) 108.

105. Matsui, S.; Fujita, T. Catal. Today. 66 (2001) 63.

106. Calvin, M.; Martell, A. E. Chemistry of Metal Chelate Compounds. Prentice-Hall, Inc., Englewood Cliffs. New Jersey. (1959) 254.

107. Nishinaga, A.; Tomita, H.; Shimizu, T.; Matsuura, T. Tetrahedron Lett. 21 (1980) 4849.

108. Agarwal, D. D.; Bhatnagar, R. P.; Jain, R.; Srivastava, S. J. Mol. Catal. 59 (1990) 385.

109. Santiago, M. A. N.; Sánchez-Castillo, M. A.; Cortright, R. D.; Dumesic, J. A. J. Catal. 193 (2000) 16.

110. Hughes, D. E. H. Anal. Chem. 57 (1985) 555.

111. Garcia, B.; Ruiz, R.; Leal, J. M. J. Phys. Chem. 112 (2008) 4921.

112. Martinez, P.; Zuluaga, J.; Uribe, D.; Van Eldik, R. Inorg. Chim. Acta. 136 (1987) 11.

113. Banch, B.; Martinez, P.; Zuluaga, J.; Uribe, D.; Van Eldik, R. J. Phys. Chem. 170 (1991) 59.

114. Mayadevi, S.; Sridevi, N.; Yusuff, K. K. M. Ind. J. Chem. 37A (1998) 413.

115. Van Dort, H. M.; Geursen, H. J. Metal-Catalyzed Oxidations of Organic Compounds. Academic Press: New York. (1981)

116. Bianchini, C.; Zoellner, R. W. Adv. Inorg. Chem. 44 (1996) 263.

117. Fullerton, T. J.; Ahern, S. P. Tetrahedron Lett. 17 (1976) 139.

118. (a) Nishinaga, A. Chem. Lett. (1975) 273; (b) Nishinaga, A.; Tomita, H. J. Mol. Catal. 7 (1980) 179.

119. Tabushi, I.; Nakajima, T.; Seto, K. Tetrahedron Lett. 21 (1980) 2565.

120. Ahmed, A. H. J. Appl. Sci. Res. 6 (2010) 1142.

121. Kumar, A.; Agarwal, M.; Singh, A. K. Polyhedron. 27 (2008) 485.

122. Iyer, S.; Kulkarni, G. M.; Ramesh, C. Tetrahedron. 60 (2004) 2163.

123. Legros, J.; Bolm, C. Angew. Chem., Int. Ed. 42 (2003) 5487.

124. Matsumoto, M.; Kuroda, K. Tetrahedron Lett. 22(1981) 4437.

125. Kim, W.-S.; Choi, Y.-K.; Kim, C.-Y.; Chjo, K.-H.; Kim, J.-S. J. Korean Chem. Soc. 8 (1993) 37.

126. Belokon, Y. N.; North, M.; Churkina, T. D.; Ikonnikov, N. S.; Maleev, V. I. Tetrahedron. 57 (2001) 2491.

127. Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Ruttinger, R.; Kojer, H. Angew. Chem. Int. Ed. 71 (1959) 176.

128. Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Sabel, A. Angew. Chem. Int. Ed. 1(1962) 80.

129. Smidt, J. Chem. Ind. London. (1962) 54.

130. Maitlis, P. M. The organic chemistry of Palladium. Vols. 1 and 2. Academic Press: New York. (1971).

131. Stern, E. W. Transition Metals in Homogeneous Catalysis, G. N. Schrauzer, ed. Dekker, New York (1971) 93.

132. Heck, R. F. Organotransition Metal Chemistry. Academic Press: New York. (1974).

133. Gates, B. C.; Katzer, J. R.; Schuit, G. A. Chemistry of Catalytic Processes. McGraw–Hill, New York (1979) 129.

134. Gatehouse, B. M.; Mclachlan, G.; Martin, L. L.; Martin, R. L.; Spiccia, L. Aust. J. Chem. 44 (1991) 351.

135. Don, M.-J.; Yang, K.; Bott, S. G.; Richmond, M. G. J. Organomet. Chem. 544 (1997) 15.

136. Davidson, E. R.; Kunze, K. L.; Machado, F. B. C.; Chakravorty, S. J. Acc. Chem. Res. 26 (1993) 628.

137. Jacobsen, E. N.; Schaus, S. E.; Dossetter, A. G.; Jamison, T. F. US Patent. (1999) 255480.

138. Nakogi, M.; Kanayama, T.; Okino, T.; Takemoto, Y. J. Org. Chem. 67 (2002) 7418.

139. Yamada, T.; Ikeno, T.; Ohtsuka, Y.; Kezuka, S.; Sato, M.; Iwakura, I. Sci. Technol. Adv. Mater. 7 (2006) 184.

140. Garber, S. B.; Kingbury, J. S.; Gray, B. L.; Hovedya, A. H. J. Am. Chem. Soc. 122 (2000) 8168.

141. Kingbury, J. S.; Garber, S. B.; Giftos, J. M.; Gray, B. L.; Okamoto, M. M.; Farrer, R. A.; Fourkas, J. T.; Hovedya, A. H. Angew. Chem. Int. Ed. 40 (2001) 4251.

142. Hultzisch, K. C.; Hovedya, A. H.; Jernelius, J. A.; Schrock, R. R. Angew. Chem. Int. Ed. 41 (2002) 589.

143. Clark, J. H.; Macquarrie, D. J. Chem. Soc. Rev. 25 (1996) 303.

144. Clark, J. H.; Macquarrie, D. J. Org. Process. Res. Dev. 1 (1997) 149.

145. Corma, A.; Garcia, H. Chem. Rev. 102 (2000) 3837.

146. Murrell, L. L. Advanced materials in catalysis, Academic Press: New York. (1977).

147. Romanovsky, B. V.; Zakharov. V. Y.; Borisova, T. G. Modern Problems of Physical Chemistry (Ed. K. V. Topchieva), Moscow. Univ. Publ. (1982) 170.

148. Ozin, G. A.; Gil, C. Chem. Rev. 89 (1989) 1749.

149. Choudary, B. M.; Kantam, M. L.; Bharathi, B.; Sreekanth, P.; Figueras, F. J. Mol. Catal. A 159 (2000) 417.

150. Jacob, C. R.; Varkey, S. P.; Ratnaswamy, P. Appl. Catal. A 168 (1998) 353.

151. Varkey, S. P.; Jacob, C. R. Indian J. Chem. A 38 (1999) 320.

152. Chavan, S.; Srinivas, D.; Ratnasamy, P. J. Catal. 192 (2000) 286.

153. Lunsford, J. H. Catal. Rev-Sci. Eng. 12 (1975) 137.

154. Lunsford, J. H. Molecular Sieves-II American Chemical Society Symposium series, DC, USA. (1977) 473.

155. Mortier, W. J.; Schoonheydt, R. A. Prog. Solid State Chem. 16 (1985) 1.

156. Ozin, G. A.; Gil, C. Chem. Rev. 89 (1989) 1749.

157. Herron, N. Inorg. Chem. 25 (1986) 4714.

158. Bedioui, F.; Roue, L.; Briot, E.; Devynck, J.; Balkus, K. J. J. Electroanal. Chem. 373 (1994) 19.

159. Bowers, C.; Dutta, P. K. J. Catal. 122 (1990) 271.

160. Bedioui, F. Coord. Chem. Rev. 144 (1995) 39.

161. Romanovsky, B. V.; Gabrielov, A. G. Surf. Sci. Rep. 72 (1992) 443.

162. (a) Chen, S.-M.; J. Mol. Catal. A: Chem. 112 (1996) 277.; (b) Deeney, F. A.; Harding, C. J.; Morgan, G. C.; Mckee, V.; Nelson, J.; Teat, S. J.;

Clegg, W. J. Chem. Soc., Dalton Trans. (1998) 1837.; (c) Yersin, H.; Top. Curr. Chem. 241 (2004) 1.

163. Herron, N.; Stucky, G. D.; Tolman, C. A.; Inorg. Chim. Acta. 100 (1985) 135.
164. Sabater, M. J.; Corma, A.; Domenech, A.; Fornes, V.; Carcia, H. Chem. Commun. (1997) 1285.
165. Vanko, G.; Homonnay, Z.; Nagy, S.; Vertes, A.; Spiering, H.; Gutlich, P. J. Chem. Phys. 108 (1998) 8472.
166. Neves, I. C.; Cunha, C.; Pereira, M. R.; Pereira, M. F. R.; Fonseca, A. M. J. Phys. Chem. 114 (2010) 10719.
167. Balkus Jr, K. J.; Felipe Diaz, J. New. J. Chem. 20 (1996) 12.
168. Parton, R. F.; Pere, G. J.; Neys, P. E.; Jacobs, P. A. Stud. Surf. Sci. Catal. 59 (1991) 395.
169. Mansuy, D. Coord. Chem. Rev. 125 (1993) 129.
170. Mozo, E. P.; Gabriunas, N.; Lucacioni, F.; Acosta, D.; Patrono, P.; Ginestra, A. L.; Reiz, P.; Delmon, B. J. Phys. Chem. 97 (1993) 12819.
171. Mozo, E. P.; Gabriunas, N.; Maggi, R.; Acosta, D.; Reiz, P.; Delmon, B. J. Mol. Catal. 91 (1994) 251.
172. Raja, R.; Ratnaswamy, P. J. Catal. 170 (1997) 244.
173. Seelan, S.; Sinha, A. K.; Sreenivas, D.; Sivasankar, S. J. Mol. Catal. A: Chem. 157 (2000) 103.
174. Romanovsky, B. V.; Gabrielov, A. G. J. Mol. Catal. 74 (1992) 293.
175. Seelan, S.; Sinha, A. K. Appl. Catal. A: General. 238 (2003) 201.
176. Van Der Voort, P.; Babitch, I. B.; Grobet, P. J.; Verberckmoes, A. A.; Vansant, E. F. J. Chem. Soc., Faraday Trans. 92 (1996) 3635.

177. Hoelderich, W. F.; Hesse, M.; Naeumann, F. Angew. Chem. Int. Ed. 27 (1988) 226.

178. Chu, W.; Echizen, T.; Kamiya, Y.; Okuhara, T. Appl. Catal., A. 259 (2004) 199.

179. Katasuki, T. Coord. Chem. Rev. 140 (1995) 189 and references therein.

180. Hentemann, M. F.; Fuchs, P. L. Tetrahedron Lett. 38 (1997) 5615.

181. Biswas, A. N.; Das, P.; Kandar, S. K.; Agarwala, A.; Bandyopadhyay, D.; Bandyopadhyay, P. Transition Met. Chem. 35 (2010) 527.

182. Kohler, S. D.; Ekerdt, J. G. J. Phys. Chem. 98 (1994) 4336.

183. Taylor, R. J.; Drago, R. S.; Hage, J. P. Inorg. Chem. 31 (1992) 253.

184. Parton, R. F.; Vankelecom, F. J.; Casselman, M. J. A.; Bezoukhanova, C. P.; Uytterhoevan, J. B.; Jacobs, P. A. Nature. 370 (1994) 541.

185. Lin, M.; Sen, A. J. Am. Chem. Soc. 114 (1992) 7307.

186. De Vos, D. E.; Thibault-Starzyk, F.; Knops-Gerrits, P. P. ; Parton, R. F. ; Jacobs, P. A. Macromol. Symp. 80 (1994) 157.

187. Gallion, L.; Sajot, N.; Bedioui, F.; Devynck, J.; Balkus Jr, K. L. J. Electroanal. Chem. 345 (1993) 157.

188. Bedioui, F.; De Boysson, E.; Devynck, J.; Balkus Jr, K. L. J. Chem. Soc., Faraday Trans. 87 (1991) 3831.

189. Balkus Jr, K. J.; Welch, A. A.; Gnade, B. E. Zeolites. 10 (1990) 722.

190. Wiester, M. J.; Ulmann, P. A.; Mirkin, C. A. Angew. Chem. Int. Ed. 50 (2011) 114.

191. De Vos, D. E.; Thibault-Starzyk, F.; Jacob, P. A. Angew. Chem. Int. Ed. 33 (1994) 431.

192. Nakamura, M.; Tatsumi, T.; Tominaga, H. Bull. Chem. Soc. Jpn. 63 (1990) 3334.

193. Herrmann, W. A.; Herdtweck, E.; Pajdla, L. Inorg. Chem. 30 (1991) 2579.

194. Prosser-McCartha, C. M.; Hill, C. L. J. Am. Chem. Soc. 112 (1990) 3671.

195. de Goor, G. V.; Lindlar, B.; Felsche, J.; Behrens, P. J. Chem. Soc., Chem. Commun. 24 (1995) 2559.

196. Topsøe, H.; Clausen B. S.; Massoth, F. E. Catalysis Science and Technology; Anderson, J. R., Boudart, M., Eds.; Springer: Berlin, 11 (1996) 1.

197. Ratnasamy, C.; Murugkar, A.; Padhye, S. Ind. J. Chem. 36A (1996) 1.

198. Ulagappan, N.; Krishnasamy, V. Ind. J. Chem. 35A (1996) 787.

199. Herron, N. Chemtech. (1989) 542.

200. Rao, L. F.; Fukuoka, A.; Kosugi, N.; Kuroda, H.; Ichikawa, M.; Rode, B. J.; Davis, M. E.; Hanson, B. E. J. Catal. 96 (1985) 574.

201. Iwamaoto, M.; Kagawa, S. J. Phys. Chem. 90 (1986) 5244.

202. Voskobojnikov, T. V.; Shpiro, E. S.; Landmesser, H.; Jaeger, N. I.; Schulz-Ekloff, G. J. Mol. Catal. A: Chem. 104 (1996) 299.

203. Dossi, C.; Fusi, A.; Psaro, R.; Roberto, D.; Ugo, R. Mater. Chem. Phys. 29 (1991) 191.

204. Shido, T.; Yamaguchi, A.; Suzuki, A.; Inada, Y.; Asakura, K.; Nomura, M.; Iwasawa, Y. J. Synchrotron Rad. 8 (2001) 628.

205. Jacobs, P.; Gates, B. C.; Guezi, L.; Knozinger, H. Metal Clusters in Catalysis, Eds. Elsevier, Amsterdam. (1986).

206. Zhou, P.-L.; Maloney, S. D.; Gates, B. C. J. Catal. 129 (1991) 315.

207. Maurya, M. R.; Anil, K. C.; Chand, S. J. Mol. Catal. A. Chem. 263 (2006) 227.

208. Hueso-Urena, F.; Illan-Cabeza, N. A.; Moreno-Carretero, M. N.; Martinez-Martos, J. M.; Ramirez-Exposito, M. J. J. Inorg. Biochem. 94 (2003) 326.

209. Joseph, T.; Halligudi, S. B.; Satyanarayan, C.; Sawant, D. P.; Gopinathan, S. J. Mol. Catal. A: Chem. 168 (2001) 87.

210. Abraham, R.; Yusuff, K. K. M. J. Mol. Catal. A: Chem. 198 (2003) 175.

211. Joseph, T.; Sawant, D. P.; Gopinath, C. S.; Halligudi, S. B. J. Mol. Catal. A: Chem. 184 (2002) 289.

212. Azuma, N.; Lee, C. W.; Kevan, L. J. Phys. Chem. 98 (1994) 1217.

213. Umemura, Y.; Minai, Y.; Tominaga, T. J. Phys. Chem. B. 103 (1999) 647.

214. Mizuno, K.; Imamura, S.; Lunsford, J. H. Inorg. Chem. 23 (1984) 3510.

215. Hoshino, M.; Yamamoto, K.; Lillis, J. P.; Chijimatsu, T.; Uzawa, J. Coord. Chem. Rev. 132 (1994) 235.

216. Pınzaru, S. C.; Pavel, I.; Leopold, N.; Kiefer, W. J. Raman Spectrosc. 35 (2004) 338.

217. Inomata, T.; Nagai, Y.; Ohata, N.; Funahashi, Y.; Ozawa, T.; Masuda, H. Jpn. J. Appl. Phys. 50 (2011) 01AJ03.

****✺****

Chapter 2

Materials and Experimental techniques

Contents

"Imagination is more important than knowledge"

Albert Einstein

2.1. Introduction

This chapter deals with the details regarding the reagents used for synthesis and describes the methods employed for the synthesis of ligands, metal exchanged zeolite and zeolite-encapsulated complexes. The details of the various analytical and physico-chemical methods used for the characterization of the synthesized complexes and the methods used to study the catalytic activity of the different complexes are also presented in this chapter.

2.2. Reagents

O-Phenylenediamine (Loba Chemie), glacial acetic acid (SRL), methanol (Merck), 1,8-diaminonaphthalene (Sigma Aldrich), 4-hydroxy-3-methoxy benzaldehyde (SRL) and 2-hydroxy-3-methoxy benzaldehyde (SRL) were used as starting materials for the preparation of organic compounds. The metal salts used were $MnCl_2.4H_2O$, $CoCl_2.2H_2O$, and $CuCl_2.2H_2O$ (Merck). All the other chemicals used were of analytical grade unless otherwise specified.

1,8-Diaminonaphthalene was purified [1,2] before use. The solvents used were either 99% pure or purified by standard procedures[3]. The support used for anchoring the metal complexes was zeolite Y with a Si/Al ratio of 2.6 and surface area of 650 m^2/g obtained from Zeolyst International, Netherlands.

2.3 Synthesis of aldehyde

2.3.1 Synthesis of quinoxaline-2-carboxaldehyde

The following procedure was adopted to synthesize quinoxaline–2–carboxaldehyde[4,5]. Refluxing D–glucose (36 g, 0.2 mol) with o–phenylenediamine (21.6 g, 0.2 mol) in the presence of hydrazine hydrate (5 mL, 0.1 mol) and glacial acetic acid (6 mL) on a boiling water bath under carbon dioxide atmosphere (provided by the addition of a pinch of sodium bicarbonate) for 5 hours gave the compound, 2(D–arabinotetrahydroxybutyl)quinoxaline. This product was purified by recrystallisation from hot water. The recrystallised 2(D–arabinotetrahydroxybutyl)quinoxaline (5g, 0.02 mol) was dissolved in water (300 mL) containing glacial acetic acid (10 mL) and sodium metaperiodate (13g, 0.06 mol) and was kept at room temperature (28 ± 2 °C) with controlled stirring for 16 hours. It was then filtered and the filtrate was then neutralized with sodium bicarbonate. The neutral solution was then extracted with ether. The ether extract was dried with anhydrous sodium sulphate. It was then filtered and evaporated to dryness. The resulting residue was recrystallised from petroleum ether to give pure quinoxaline–2–carboxaldehyde (Figure 2.1) (Yield: 60%, M. P.: 107 °C).

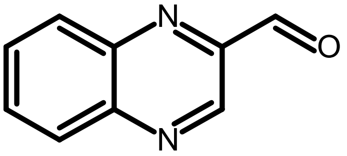


Figure 2.1: Structure of quinoxaline–2–carboxaldehyde

2.4. Preparation of precursor ligands

We have synthesized[6] three new precursor ligands by taking quinoxaline–2–carboxaldehyde, 4-hydroxy-3-methoxy benzaldehyde and 2-hydroxy-3-methoxy benzaldehyde. The amine chosen was 1,8-diaminonaphthalene. The precursor ligands synthesized are:

1. 2-(quinoxalin-2-yl)-2,3-dihydro-1*H*-perimidine (qdp)
2. 2-(2,3-dihydro-1*H*-perimidin-2-yl)-6-methoxyphenol (2dpm)
3. 4-(2,3-dihydro-1*H*-perimidin-2-yl)-2-methoxyphenol (4dpm)

The formations of Schiff base complexes through the rearrangement[7, 8] of perimidines are also studied. The details regarding analysis and characterization of the above mentioned precursor ligands are described in the respective chapters.

2.5. Synthesis of zeolite Y supported metal complexes.

The zeolite Y used for encapsulation was modified by the following techniques.

2.5.1 Preparation of sodium exchanged zeolite (NaY)

The zeolite Y obtained was modified using the standard ion exchange procedure, which is based on the method suggested by Yonemoto *et al.*[9] Zeolite Y (5 g) was mixed with a solution of NaCl (0.1 M, 500 mL) and stirred for 24 hours at room temperature. Any other cations present in the sample could be thus substituted with Na^+ ion. The slurry was then filtered to get the sodium-exchanged form of the zeolite, which was made chloride free by washing with distilled water till the filtrate become free of chloride ions. The NaY thus formed was dried at 120 °C for four hours.

2.5.2 Preparation of metal exchanged zeolite (MY)

The sodium ions in NaY were replaced by transition metal ions by stirring sodium exchanged zeolite (5 g) with metal chloride solution (0.001 M) at 70 °C for 24 hours. Low concentration of metal salt solution was used, since there are chances for dealumination at higher concentrations[10]. The slurry obtained after the stipulated time was filtered and washed with distilled water several times to make it free from chloride ions. The metal exchanged zeolite was dried at 120 °C for four hours, and was then dehydrated in muffle furnace at 400 °C for two hours[11]. Zeolite MY so obtained was kept over calcium chloride.

2.5.3 Preparation of zeolite encapsulated metal complexes

Transition metal cations exchanged into zeolite Y are capable of forming well defined complexes with certain ligands within the large cavities of the zeolite framework[12]. The pore structure of zeolite offers the possibility for the preparation of complexes inside the zeolite. In the present study, the encapsulated metal complexes were prepared using the flexible ligand method, where flexible ligand molecules enter the supercages of the zeolite and react with the metal ions already present in the cage.

2.6. Characterization methods

Variety of physico-chemical methods were employed to characterize the structure of organic Schiff base ligands and their metal chelates and to study the catalytic activity of the complexes. Experimental details of these methods are given below:

2.6.1 Elemental analyses

2.6.1.1. CHN analysis

Microanalysis for carbon, hydrogen and nitrogen in the synthesized ligands, neat complexes and encapsulated complexes were done on an Elementar model Vario EL III at SAIF, Sophisticated Test and Instrumentation Centre, Kochi.

2.6.1.2. Analysis of Si, Al, Na and transition metal ion in the zeolite sample

A small amount of the zeolite sample was accurately weighed (w) and taken in a beaker. About 40 mL of conc. H_2SO_4 was added and heated strongly. It was then cooled, diluted with water (200 mL) and filtered using an ash less filter paper. The filtrate was collected in a standard flask. The residue was heated in a platinum crucible, cooled and weighed (w_1). Hydrofluoric acid was then added in drops and heated strongly to dryness to remove silica as H_2SiF_6. This process was repeated three to four times. The remaining solid was then ignited to 800 ^{o}C for about one hour, cooled and weighed (w_2). The amount of silica present in the sample was calculated using the equation.

$$\% \ SiO_2 = (w_1 - w_2) \times 100 / w$$

The residue in the crucible was treated with potassium persulphate and fused till a clear melt was obtained. It was dissolved in water and combined with the earlier filtrate collected in the standard flask. The metals present in this solution were determined by ICP – AES method. The Si to Al ratio provides the unit cell formula and the ion exchange capacity of the zeolite. The comparison of the ratio of the encapsulated complexes with that of the pure zeolite shows the retention of the zeolite frame work after encapsulation.

2.6.1.3. Estimation of metal ions in the complexes.

In all the cases, the organic part of the complexes was completely eliminated before the estimation of metal ions. The following procedure was adopted for this purpose in the case of all the complexes. A known weight (0.2 – 0.3 g) of the metal complex was treated with concentrated sulphuric acid (5 mL) followed by concentrated nitric acid (20 mL). After the reaction was subsided, perchloric acid (5mL, 60%) was added. This mixture was kept aside until the color of the solution changes to that of the metal salt. The clear solution thus obtained was evaporated to dryness on water bath. After cooling, concentrated nitric acid (15 mL) was added and again evaporated to dryness on a water bath. The residue was dissolved in water and this neutral solution was used for the estimation of metals. The estimation of metals was carried out on a Thermo Electron Corporation, M series Atomic Absorption Spectrophotometer.

2.6.1.4. Estimation of chloride

Chlorine present in the complexes was converted into soluble sodium chloride by the peroxide fusion. An intimate mixture of the complex (0.2 g), sodium carbonate (3 g) and sodium peroxide (2 g) was fused on a nickel crucible for nearly two hours. It was then treated with concentrated nitric acid. Chloride was then volumetrically estimated by Volhard's method[13]. Chloride was precipitated as silver chloride by the addition of a known volume of standard silver nitrate solution. The excess silver nitrate was titrated against standard ammonium thiocyanate solution using ferric alum as indicator.

2.6.2. Conductance measurements.

Molar conductance of the complexes was determined in DMF at 28 ± 2 °C using a systronic conductivity bridge with a dip type cell and platinum electrode. The concentration of the solution was 10^{-3} M.

2.6.3 Magnetic susceptibility measurements.

Simple Gouy type magnetic balance was used for magnetic susceptibility measurements at room temperature, 28 ± 2 °C. The Gouy tube was standardized using $Hg[Co(SCN)_4]$ as approved by Figgis and Nyholm[14]. The effective magnetic moments were calculated using the equation:

$$\mu_{eff} = 2.84\ (X_m^{Corr}\ T)^{1/2}.\ BM$$

where T is the absolute temperature and X_m^{Corr} is the molar susceptibility corrected for diamagnetism of all other atoms and groups present in the complex using Pascal's constants [15-17].

2.6.4. Surface area and pore volume analysis.

The surface areas of the anchored complexes were measured to ensure the encapsulation of metal complexes in the zeolite cavity. The surface areas of the samples were determined by the multipoint BET method[18] of nitrogen absorption at liquid nitrogen temperature using 'Micromeritics Gemini 2360 surface area analyzer'. This method involves the measurement of the amount of gas adsorbed by the respective samples. Initially a very small amount of the sample was accurately weighed and taken in a clean dry sample tube. This was heated to about 473 K and kept at this temperature for about three hours in an atmosphere of nitrogen gas. The volatile impurities on the surface of the catalyst were completely removed by the heat treatment. Then the sample was allowed to cool to room temperature and again the sample tube containing the complex was weighed. The sample was kept fixed in the instrument and cooled to very low temperature of about 77 K using liquid nitrogen. The adsorption of nitrogen on the surface of the sample lowers the pressure inside the chamber and equilibrium is established between the adsorbed gas and the free gas phase. The BET equation used for calculating the surface area is

$P / V (P_0-P) = 1 / V_mC + (C-1) P / V_mCP_0$ where

V = volume of the gas adsorbed at relative pressure P / P_0

V_m = volume of the gas in the monolayer

P_0 = saturation vapor pressure of the adsorbate

C = BET constant which is related to the heat of adsorption

The plots of the left side of the BET equation against P / P_0 gives a straight line with slope $(C-1) P / VmC$ and intercept $1 / V_mC$. The volume of the gas in the monolayer, V_m can be obtained from these values and hence the number of moles of nitrogen adsorbed (X_m) can be calculated. BET surface area is calculated using the equation, $S_{BET} = Xm\ N\ A_m\ 10^{-20}$ where N = Avogadro number and A_m = cross sectional area of the adsorbate molecule.

2.6.5. Powder X-ray diffraction analysis (XRD).

The X-ray diffraction patterns of the parent zeolite, ion exchanged zeolite and encapsulated complexes were recorded to know their crystalline nature. The comparisons of these diffraction patterns enable us to tell whether any changes occurred in the internal crystalline structure of the zeolite upon encapsulation[19]. The X-ray diffractometer used to study the sample was Bruker AXSD8 advance diffractometer. The apparatus consist of a stationary X-ray source, Ni filtered radiation with wavelength 1.5404 Å and a movable detector to scan the intensity of the diffracted radiation as a function of the angle 2θ between the incident and the diffracted beam.

2.6.6. Thermogravimetric analysis (TG).

In this technique the sample under consideration is heated at controlled rate in an atmosphere of nitrogen and the weight loss of the substance is recorded as function of temperature. The thermograms obtained are characteristic for a given sample due to unique sequence of physico-chemical reactions occurring over definite temperature ranges which in turn depends upon the structure of the molecule[20]. The changes in weight occur as a result of rupture or formation of various physical and chemical bonds at elevated temperatures. TG analyses were carried out on a Perkin Elmer, Diamond thermogravimetric analyzer at a heating rate of 10 °C per minute in an atmosphere of nitrogen.

2.6.7. Scanning electron microscopy (SEM) analysis.

Scanning electron microscopy analysis of the zeolite encapsulated complexes before and after soxhlet extraction was done using LEOL-JSM-840A SEM. It reveals the presence of materials adsorbed on the surface of the support and the morphological changes associated with encapsulation. A narrow beam of electrons from a tungsten filament is passed through the sample. In order to protect the zeolite sample from surface charging and thermal damage due to collision with electron beam, a thin film of gold is coated over them. The amount of back-scattered or secondary radiation is noted as function of the primary beam. These analyses were carried out to understand the effectiveness of soxhlet extraction in removing the substances adsorbed on the surface.

2.6.8. Infrared spectra

The IR spectra provide valuable information regarding the structure of the complex and the nature of the functional groups present. Hence it can be used as an effective tool to confirm the formation of the complexes within the zeolite pores and to detect the coordination of ligands to the transition metals Infrared spectra of the ligands, simple complexes and the metal encapsulated complexes in the region 4000-400 cm^{-1} were recorded using Jasco-8000 Fourier Transform Infrared Spectrophotometer. Each zeolite encapsulated complex exhibits a characteristic IR pattern[21] and these vibrations are observed in the region 1250-400 cm^{-1}. The shift of the characteristic bands on chelation is sometimes masked by the well-defined strong bands of zeolite.

2.6.9. Diffuse Reflectance spectra (DRS).

The diffuse reflectance spectra were recorded at room temperature in the range 250-850 nm using Jasco V 570 UV-Vis spectrophotometer. Sodium exchanged zeolite (NaY) is used as the blank for zeolite samples. The spectra were computer processed and plotted as percentage reflectance verses wavelength. To get the spectra in the absorbance mode, one has to apply Kubelka - Munk equation, which is as follows,

$$\text{Log}\left((1 - r_\alpha) / 2\, r_\alpha \right) = \log K - \log S$$

Here $r_\alpha = R_\alpha$ (sample) / R_α (standard)

R_α (sample) is the diffuse reflectance of the sample and R_α (standard) is taken as 1. K is the absorption coefficient and S is the scattering coefficient. The Kubelka – Munk factor, $F(R) = (1 - r_\alpha)^{2} / 2\, r_\alpha = K / S$. The plot of $(1 - r_\alpha)^{2} / 2\, r_\alpha$ as function of wavelength gives the absorption curve. This is a very effective technique for getting information about d-d transitions and charge transfer transitions in metal complexes encapsulated in solid supports from which, coordination geometries of the encapsulated complexes can be realized. Diffuse reflectance spectra of the Zeolite samples were recorded at room temperature within the wavelength range 200 to 850 nm. The spectra were computer processed and recorded directly in absorbance mode.

2.6.10. UV-Visible spectra

Electronic spectra of the ligands and its complexes were recorded in various solvents on a Thermoelectron Nicolet evolution 300 UV-vis spectrophotometer. UV-visible electronic spectroscopy is a valuable tool for coordination chemists to draw important information about the structural aspects of the complexes. The ligands, which are organic compounds, have absorption in the ultraviolet region and in some cases these bands extend to higher wavelength region due to conjugation. Upon complexation with transition metal ions, changes will take place in the electronic properties of the system. New features or bands in the visible region due to d-d absorption and charge transfer spectra from metal to ligand (M→L) or ligand to metal (L→M) can be observed and this data can be processed to obtain information regarding the structure and geometry of the complexes.

2.6.11. EPR spectra

EPR spectroscopy is a reliable method to determine the geometry and electronic structure of the complexes. The EPR spectra of the complexes in DMF were recorded on Varian E-112 X/Q band spectrophotometer at liquid nitrogen temperature and the standard used was tetracyanoethylene (TCNE) with g value of 2.0027. The EPR spectra of transition metal complexes contain a wealth of information about their electronic structures. The interpretation of the EPR spectra of these complexes can be done on the basis of the ligand field theory. The degeneracy of the d orbitals and the presence of the unpaired electrons give rise to orbital contributions as a result of which anisotropic g values are obtained.

2.6.12. Single crystal XRD

X–ray crystal structure determination of 2-(quinoxalin-2-yl)-2,3-dihydro-1*H*-perimidine and 4-(2,3-dihydro-1*H*-perimidin-2-yl)-2-methoxyphenol were performed with a Bruker SMART APEX CCD X–ray diffractometer at University of Hyderabad and at CSMCRI Gujarat using graphite monochromated MoKα radiation (λ=0.71073 Å, φ and ω scans). The data was reduced using SAINTPLUS and a multiscan absorption correction using SADABS[22] was performed. The structure was solved using SHELXS–97, and full matrix least squares refinement against F^2 was carried out using SHELXL–97 in anisotropic approximation for non-hydrogen atoms[23]. All hydrogen atoms were assigned on the basis of geometrical considerations and were allowed to ride upon the respective carbon atoms.

2.6.13. NMR Spectra

^{1}H NMR spectra of all the synthesized ligands were recorded in $CDCl_3$ on a Bruker AVANCE III 400 MHz NMR spectrometer using TMS as the internal standard at the SAIF, Sophisticated Test and Instrumentation Centre, Kochi. NMR spectral data provide valuable information regarding the structure of ligands.

2.7 Catalytic studies

2.7.1. Gas Chromatography

The analysis of the reactants and products of the different catalytic reactions was conducted using a Chemito 8510 Gas Chromatograph. In gas chromatography, the separation is carried out in a tubular column made of metal and an adsorbent which serves as the stationary phase is filled in this column. The carrier gas serving as the mobile phase is made to flow continuously through the column. The instrumentation consists of a tank of carrier gas, an injection port for introducing the sample, the column and a detector. The various components in the reaction mixture were separated using an OV-17 or carbowax column. The peaks appearing on the recorder were characteristic of the different components and the peak area is proportional to the amount of the component present in the mixture.

References

1. Al-Betar, A-R.; El-Rayyes, A.; Klein, U. K. A. J. Fluoresc. 15 (2005) 689.
2. Alder, R. W.; Bryce, M. R.; Goode, N. C.; Miller, N. J. Chem. Soc., Perkin Trans. 1. (1981) 2840.

3. Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. Vogels' Text Book of Practical Organic Chemistry-5th edn., ELBS-Longman Singapore Publishers. (1996).
4. Ohle, M. H. Ber. 74B (1941) 13.
5. Leese, C. L.; Rydon, H. N. J. Chem. Soc. (1955) 303.
6. Varsha, G.; Arun. V.; Robinson, P. P.; Manju, Sebastian.; Digna, Varghese.; Leeju, P.; Jayachandran, V. P.; Yusuff, K. K. M. Tetrahedron Lett. 51 (2010) 2174.
7. Hernanddez-Molina, R.; Mederos, A. In Acyclic and Macrocyclic Schiff base Ligands in Comprehensive Coordination Chemistry II; McCleverty, J. A. Meyer, T. J. Eds., Pergamon Press: New York. 2 (2004) 411.
8. Minkin, V. I. Chem. Rev. 104 (2004) 2751.
9. Yonemoto, E. H.; Kim, Y.; Schmehl, R. H.; Wallin, J. O.; Shoulders, B. A.; Richardson, B. R.; Haw, J. F.; Mallouk, T. E. J. Am. Chem. Soc. 116 (1994) 10537.
10. Beyer, H. K.; Belenykaja, I. M.; Hange, F.; Tielen, M.; Grobet, P. J.; Jacobs, P. A. J. Chem. Soc., Faraday Trans. 1. 81 (1985) 2889.
11. Taylor, R. J.; Drago, R. S.; George, J. E. J. Am. Chem. Soc. 111 (1989) 6610.
12. Howe, R. F.; Lunsford, J. H. J. Phys. Chem. 79 (1975) 17.
13. Stuart, A. T. J. Am. Chem. Soc. 33 (1911) 1344.
14. Figgis, B. N.; Nyholm, R. S. J. Chem. Soc. (1958) 4190.
15. Figgis, B. N.; Lewis, J. Modern Coordination Chemistry; Lewis, J., Wilkins, R. G., Eds.; Interscience: New York. (1960) 403.
16. Selwood, P. W. Magnetochemistry. Interscience Publishers, Inc., 2nd Eds.; New York. (1956) 75.

17. Figgis, B. N.; Lewis, J. Prog. Inorg. Chem. 6 (1964) 197.

18. Brunauer, S.; Emmett, P. H.; Teller, E. J. Am. Chem. Soc. 60 (1938) 309.

19. Paez-Mozo, E.; abriunas, N.; Lucaccioni, F.; Acosta, D. D.; Patrono, P.; Loginestra, A.; Ruiz, P.; Delmon, B. J. Phys. Chem. 97 (1993) 12819.

20. Jeffery G. H. Vogel's Text Book of Quantitative Chemical Analysis, 5th ed. (Reprint), ELBS, 1996.

21. Breck, D. W. Zeolite Molecular Sieves Structure Chemistry and Use, Wiley Interscience Publications. 1 (1973).

22. Sheldrick, G. M. SADABS, Program for Empirical Absorption Correction, University of Gottingen, Germany. (1996).

23. Sheldrick, G. M. SHELX–97, programs for Crystal Structure Analysis, University of Gottingen, Germany. (1997).

**** ⁂ ****

Chapter

3

Synthesis and characterization of copper(II) complexes of the Schiff base quinoxaline-2-carboxalidine-1,8-diaminonaphthalene

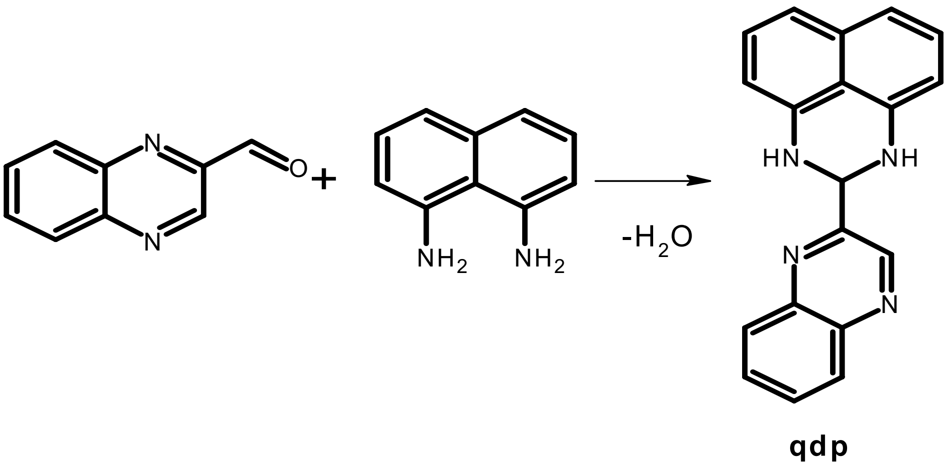
Contents

> *"An experiment is a question which science poses to Nature, and the measurement is the recording of Nature's answer"*
>
> ***Max Plank***

3.1. Introduction

The chemistry of quinoxaline and its derivatives attracts continuous attention because of their wide applicability in various areas. The literature survey reveals that substituted quinoxaline[1-3] derivatives exhibit a wide variety of biological activities. They are an important class of nitrogen-containing heterocycles in medicinal chemistry[4]. Quinoxaline structure is recognized in a great number of naturally occurring compounds, such as riboflavin (vitamin B2), flavoenzymes, molybdopterines and antibiotics of streptomyces type, that are implicated in considerable intra and interelectron transfer biochemical processes. A number of quinoxaline based Schiff bases have been prepared in view of their wide applications. Schiff bases derived from quinoxaline-2-carboxaldehyde would be interesting as their ligand field strengths are expected to be weaker than the more common Schiff bases derived from salicylaldehyde. An additional interest in studying new Schiff bases arises from their significant antibacterial, antiviral, anticancer, antifungal and insecticidal activities[5-20].

Pozharskii and Dalnikovskaya or Cameron *et al.* have shown that the condensation of an aldehyde or ketone with 1,8-diaminonaphthalene does not lead to isolation of the corresponding Schiff base, but to the isolation of 2,3-dihydroperimidines[21, 22]. In the solid state, perimidines and their derivatives are stable. When dissolved in non-polar solvents, (e.g., hydrocarbons or tetrachloromethane) the ring compound opens up and an equilibrium[23, 24] is gradually established between the ring closed perimidines and Schiff bases[25] derived from the perimidines. However, these Schiff bases cannot be isolated as such. There are a few reports on the transition metal complexes of Schiff bases formed by condensation of 1,8-diaminonaphthalene with 3-hydroxyquinoxaline-2-carboxaldehyde[26], salicylaldehyde, 2-pyridine carboxaldehyde[27] and glyoxal[28]. But Schiff bases derived from quinoxaline-2-carboxaldehyde and 1,8-diaminonaphthalene are hitherto unknown. We have made an attempt to synthesize this Schiff base. As in the case of the other Schiff bases derived from 1,8-diaminonaphthalene, we could not isolate the Schiff base. Instead, we have been able to synthesize a perimidine compound[29] 2-(quinoxalin-2-yl)-2,3-dihydro-1*H*-perimidine (qdp). The formation of qdp is given in Scheme 3.1. We have characterized the complexes obtained by the interaction of qdp with copper(II) ions. The compounds isolated were found to be complexes of Schiff bases derived from qdp. Recently, we have reported the formation of Schiff base complexes when metal ions[30] are treated with ring closure compound[31] formed by condensing 2-aminothiophenol with 3-hydroxyquinoxaline-2-carboxaldehyde. The results of the characterization of Schiff base complexes derived from qdp are presented in this chapter.



Scheme 3.1: The formation of qdp by ring closure

3.2 Experimental

3.2.1 Materials and methods

The materials and techniques employed for the synthesis and characterization of qdp and metal complexes of the Schiff base derived from qdp are given in chapter II.

3.2.2 Preparation of the product derived from quinoxaline-2-carboxaldehyde and 1,8-diaminonaphthalene

An orange compound was separated on mixing 1,8-diaminonaphthalene (0.16 g; 1 mmol) and quinoxaline-2-carboxaldehyde (0.16 g; 1mmol) in methanol (50 mL) and keeping the reaction mixture at room temperature (27 ±2 °C) for 8 hours. The crystals separated out were of good quality. (Yield: 85% m.p.: =164 °C)

3.2.3 Preparation of complexes

The copper(II) complexes were prepared by the following general procedure:

The orange compound, qdp (1 mmol, 0.75 g) was dissolved in 1:1 hexane–chloroform solution (~25 mL) and was magnetically stirred in a round bottom flask followed by drop wise addition of 1:1 methanol–chloroform solution (~25 mL) of $CuCl_2.2H_2O$ (1 mmol, 0.43 g), $Cu(OAc)_2.H_2O$ (1 mmol, 0.50 g), $Cu(NO_3)_2.3H_2O$ (1 mmol, 0.60 g) or $Cu(ClO_4)_2.6H_2O$ (1 mmol, 0.93 g) at room temperature (27±2 °C). The precipitate formed was filtered off, washed several times with small quantities of hexane and dried in vacuum over anhydrous calcium chloride.

3.3 Results and discussion

3.3.1 Characterization of the orange compound, qdp

The compound was characterized by elemental analysis, infrared spectra, ^1H NMR spectra and single crystal X-ray diffraction analysis. The details are as follows:

3.3.1.1 Elemental analysis

The analytical data (Found: C, 76.35; H, 4.54; N, 18.65) of the orange colored compound, qdp is in good agreement with the expected molecular formula of the perimidine compound, qdp (Scheme 3.1) $C_{19}H_{14}N_4$ (Calculated: C, 76.49; H, 4.73; N, 18.78).

3.3.1.2 Infrared Spectra

IR spectrum of the compound is given in Figure 3.1. The spectrum exhibits sharp band at 3284 cm^{-1} which indicates the presence of =NH group. Bands in the range of 3045–2990 cm^{-1} indicate aromatic –CH group. Another sharp band at 1599 cm^{-1} can be attributed to the presence of C=N group of quinoxaline ring.

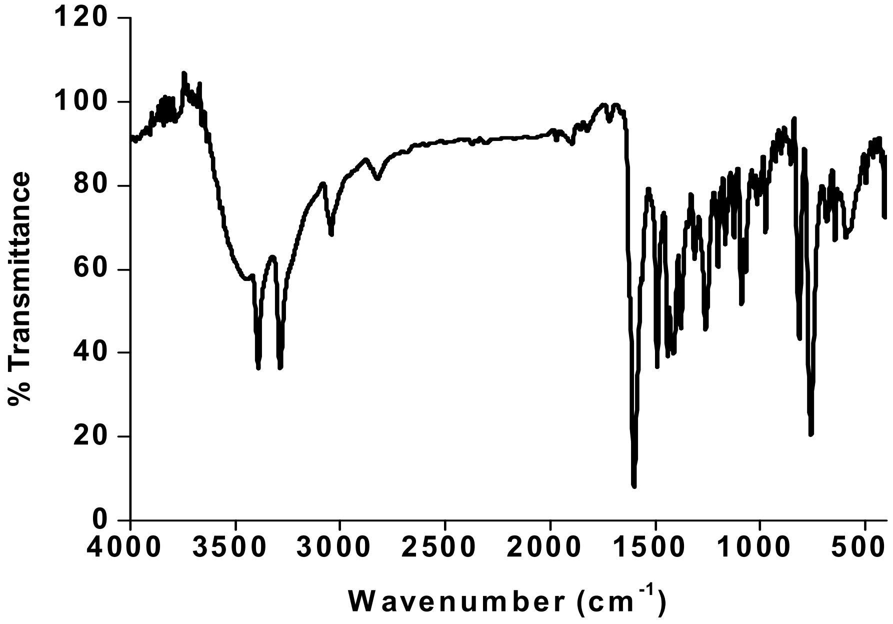


Figure 3.1: IR spectrum of qdp

3.3.1.3 ^{1}H NMR spectra

The ^{1}H NMR spectra of the compound was recorded in d_6-dimethylsulphoxide solution using TMS as the internal standard (Figure 3.2). The chemical shifts of different protons are as follows:

^{1}H NMR (400 MHz, DMSO-d_6): δ 5.01 (s, 2H, NH), 5.83 (s, 1H, CH), 6.67-6.68 (m, 3H, aromatic), 7.79-7.84 (m, 4H, aromatic), 8.09-8.15 (m, 4H, aromatic) ppm.

The singlet observed at 5.01 ppm is assignable to the –NH proton in the heterocyclic ring and a peak at 5.83 ppm confirms the presence of =CH– proton in the fused ring[29]. Multiplet signals observed in the 6.67 – 8.15 ppm range are due to aromatic protons. The NMR spectra indicate a ring structure (perimidine) for the compound.

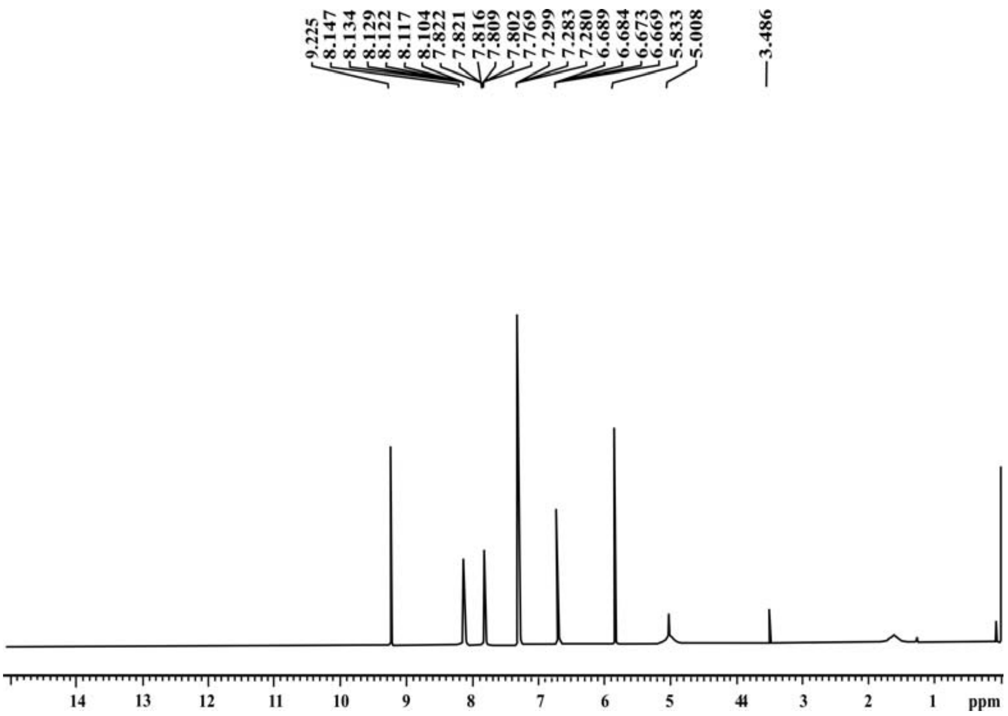


Figure 3.2: ^{1}H NMR spectrum of qdp

3.3.1.4 Single crystal X-ray diffraction analysis

The single crystal[29] suitable for XRD was obtained by the slow evaporation of methanolic solution of the compound. The compound crystallizes in a monoclinic crystal system with the space group $P2_1/c$. A summary of crystallographic data and refinement parameters are given in Table 3.1.

The molecular structure of the compound was solved at 298 K. Figure 3.3 gives the ORTEP diagram of the compound with atomic labeling scheme. The naphthalene moiety of the perimidine ring and quinoxaline ring of qdp is nearly parallel. The loss of planarity of the compound is affected by the position of C9 which is 0.559 Å above the plane of quinoxaline ring. There is no classical hydrogen bonding observed in this compound. The CH.... π interaction of C9–H9 with symmetry-related naphthalene ring at a distance of 2.46 Å contributes to the stability of crystal packing. In this, the carbon atoms C8 and C9 lie 0.578–0.559 Å above the perimidine ring plane.

Table 3.1: Crystal data summary of qdp

Crystal Data	
Parameters	**qdp**
empirical formula	$C_{19}H_{14}N_4$
formula weight	298.34
temperature (K)	298(2)
crystal system	Monoclinic
space group	$P2_1/c$
a (Å)	13.729 (4)
b (Å)	5.3352 (15)
c (Å)	20.104 (5)
α *(deg)*	90
β *(deg)*	97.530
γ *(deg)*	90
V (Å^3)	1459.9(7)
Z	4
D_{cal} (Mg/m^3) (calcd)	1.357
M(mm^{-1})	0.08
F (000)	624
T_{min}	0.977
T_{max}	0.991
No. of reflns with I $> 2\sigma$(I)	1662
R[$F^2 > 2\sigma(F^2)$]	0.129
wR(F^2)	0.257

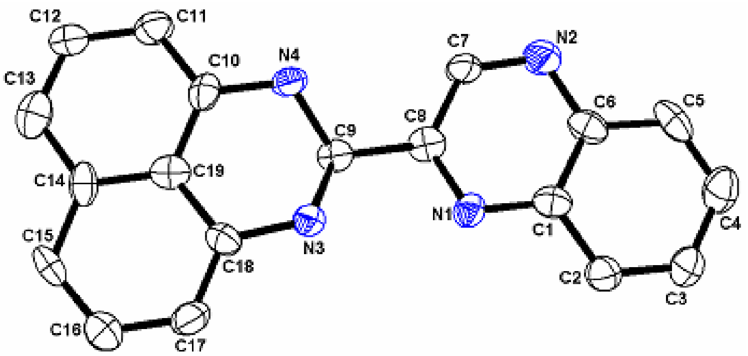


Figure 3.3: ORTEP diagram of compound qdp showing the atom labeling scheme with 50% probability ellipsoids.

Spectral data and crystal studies of the qdp indicate that the compound is not a Schiff base, but is a ring closed compound, 2-(quinoxalin-2-yl)-2,3-dihydro-1*H*-perimidine (qdp) as depicted in Scheme 3.1.

3.3.2 Characterization of the complexes derived from qdp

The Cu(II) complexes were prepared by the stoichiometric reaction of the metal ions with the compound, qdp. The colour, yield and elemental analysis data of the complexes derived from qdp are given in Table 3.2. The molar conductivity values (Table 3.3) in 10^{-3} M DMF solutions suggest non-electrolytic[32] nature of the complexes.

Table 3.2: Analytical data of the complexes derived from qdp

Compound	Colour	Yield (%)	Analytical data. Found (calculated)%				
			M (%)	C (%)	H (%)	N (%)	Cl (%)
The chloro complex	black	56	13.05 (13.07)	46.87 (46.89)	4.14 (4.17)	11.51 (11.53)	14.56 (14.58)
The acetato complex	brown	63	11.51 (11.53)	50.04 (50.05)	5.11 (5.12)	10.15 (10.17)	–
The nitrato complex	black	70	13.08 (13.10)	46.97 (46.99)	2.90 (2.91)	17.30 (17.33)	–
The perchlorato complex	brown	59	10.04 (10.05)	36.06 (36.08)	3.50 (3.52)	8.85 (8.87)	11.20 (11.22)

Table 3.3: Conductivity and magnetic moment data of complexes

Compound	μ_{eff} (BM)[a]	Molar conductance ($ohm^{-1}cm^{2}mol^{-1}$)[b]
The chloro complex	1.70	30
The acetato complex	1.72	25
The nitrato complex	1.92	13
The perchlorato complex	1.70	39

[a] Magnetic moment value per metal atom in the complex

[b] 10^{-3} M solution in DMF

3.3.2.1 Thermal analysis

Thermal stability of the complexes was investigated using TG–DTG under nitrogen atmosphere at a heating rate of 10 °C min^{-1} over a temperature range of 40–1000 °C. The TG–DTG plots of the complexes are given in Figures 3.4–3.7. The weight loss observed for the Cu(II) complexes in the range 90-120 °C indicates the presence of lattice water molecules. The weight loss observed in the region 150-200 °C for the chloro, acetato and perchlorato complexes can be attributed to the loss of coordinated water molecules[33–35]. Table 3.4 presents the thermogravimetric analysis results below 220 °C. For all complexes the TG data exhibit multi stage decomposition pattern. In nitrogen atmosphere, the decomposition was not completed even after 1000 °C. The data also show good agreement with the molecular formula of the complexes arrived from the analytical data.

Table 3.4: Thermogravimetric analysis data (below 220 °C)

Compound	Temperature range, °C	% loss	Fragment lost	Nature of water lost
The chloro complex	90-130	4.5	1 H_2O	Lattice water
	140-200	7.5	2 H_2O	Coordinated water
The acetato complex	90-110	4.8	1 H_2O	Lattice water
	140-210	7.9	2 H_2O	Coordinated water
The nitrato complex	90-130	8.3	2 H_2O	Lattice water
The perchlorato complex	90-130	7.8	2 H_2O	Lattice water
	180-220	8.1	2 H_2O	Coordinated water

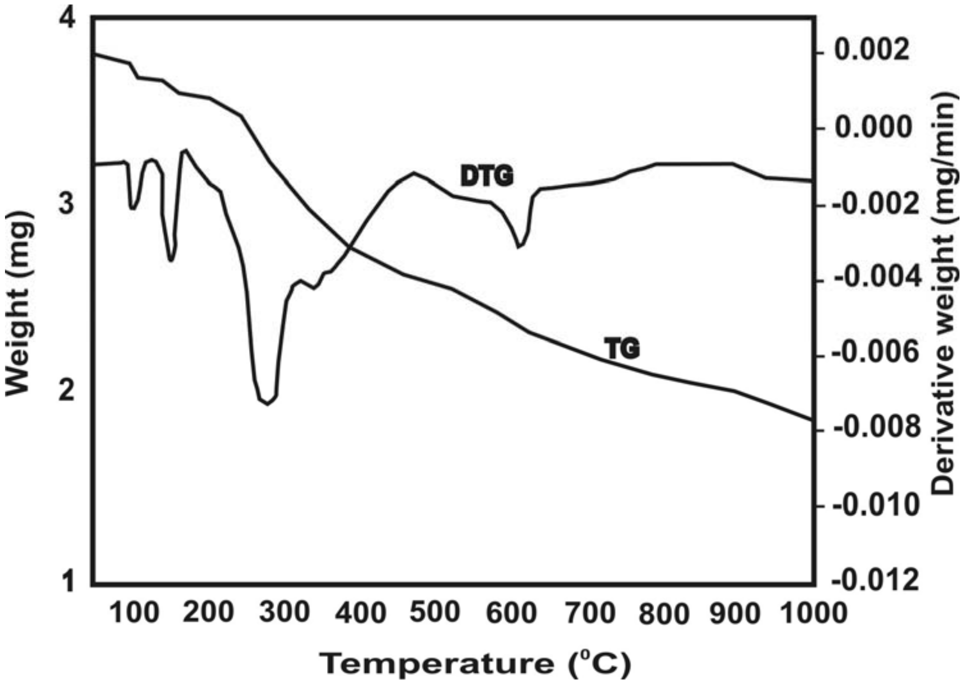


Figure 3.4: TG–DTG of the chloro complex

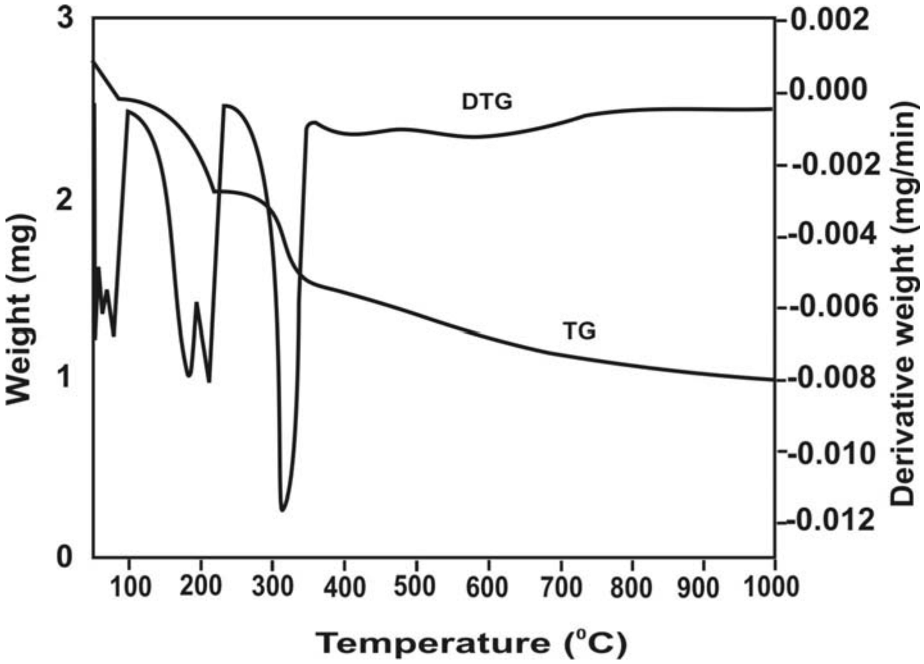


Figure 3.5: TG–DTG of the acetato complex

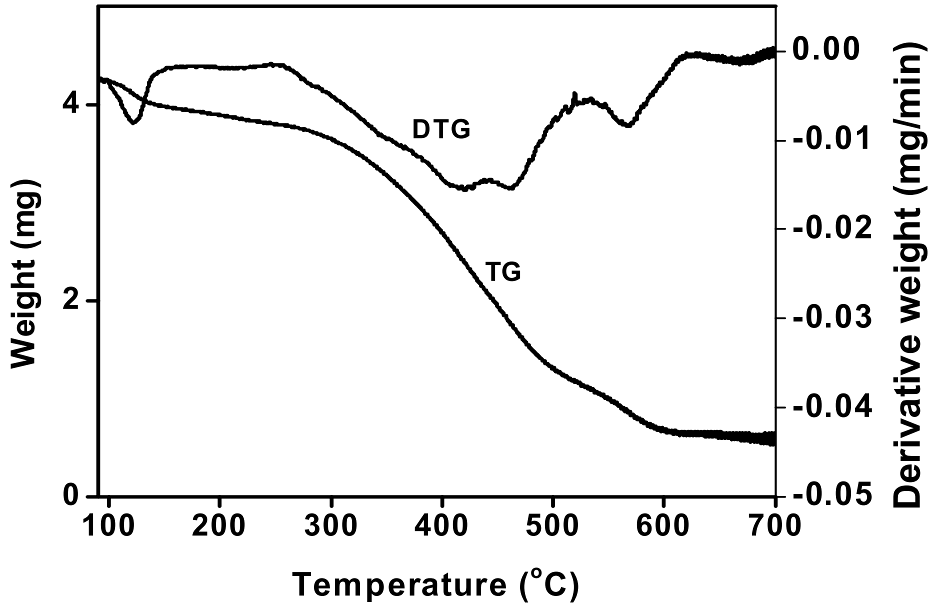


Figure 3.6: TG–DTG of the nitrato complex

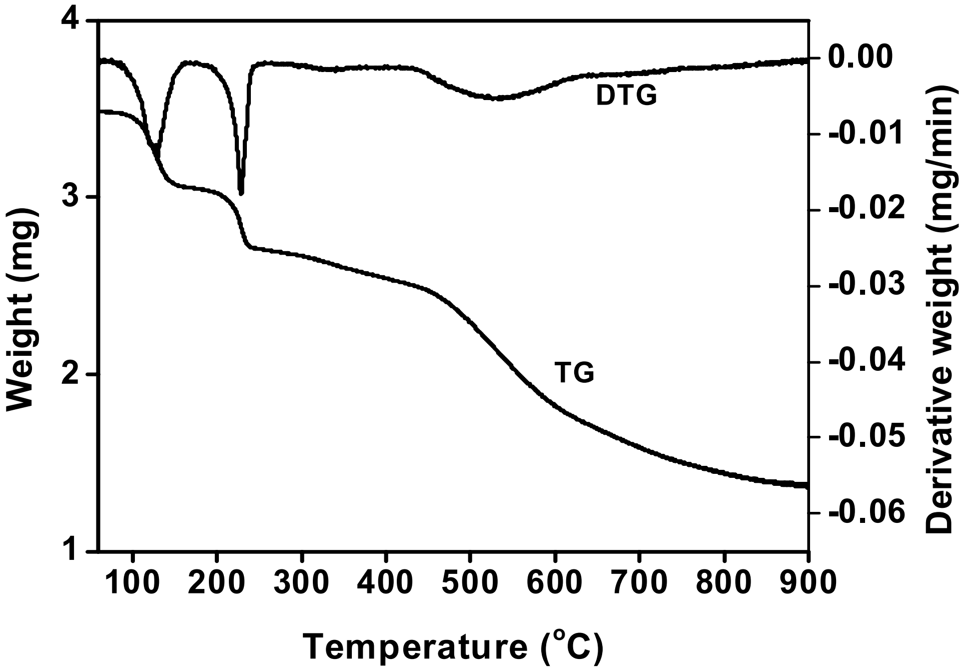


Figure 3.7: TG–DTG of the perchlorato complex

3.3.2.2 Infrared spectra

Most important IR spectral bands of qdp and the metal complexes derived from qdp are listed in Table 3.5. The IR spectra of the complexes when compared with that of qdp (Figure 3.1) show remarkable differences. The compound qdp exhibit band at 1599 cm^{-1} indicative of the presence of C=N– group of quinoxaldehyde ring. Presence of quinoxaline C=N stretching in the region 1550–1600 cm^{-1} has been reported[36-38] in the case of quinoxaline-2-one compounds. This band is seen to be shifted to lower region indicating the involvement of this nitrogen in the coordination to the metal. The complexes exhibit a broad band in the range 3100–3500 cm^{-1} due to the –OH stretching of water molecules[39] (Figures 3.8–3.11).

The Cu(II) complexes show the presence of strong bands in the range 1613–1648 cm^{-1}. This band is not seen in the spectrum of qdp. The position and nature of this band suggest the band be due to azomethine C=N stretching. This has resulted from the opening of the ring compound qdp, which gives a strong evidence for the conversion of qdp into Schiff base in the presence of the metal ion[37]. Conclusive evidence of the bonding is also shown by the presence of new bands in the region 400–420 cm^{-1} in the spectra of the complexes due to (M–N) stretching vibrations[40-43]. The bands observed for the nitrato complex in the finger print region at 1469 and 1384 cm^{-1} correspond to unidentate nitrato[44-47] group. A new band at 461 cm^{-1} in the spectrum of the chloro complex might be due to $\upsilon_{\text{M-Cl}}$[48]. The strong non-splitting absorption band of uncoordinated perchlorate anion is usually observed at 1110 cm^{-1}. This band is distinctly split to two components, one at 1090 and the other at 1120 cm^{-1} for the perchlorato complex (Figure 3.7.1). Also the strong absorption band expected for the uncoordinated perchlorate ion (centered at 620 cm^{-1}) seen to be split into 610 and 628 cm^{-1} in the spectrum of the compound. These features indicate unidentate coordination of the perchlorate group[49-51]. For the acetato complex, the acetate stretching is found to be at 1560 and 1401 cm^{-1}. The energy separation between

$\upsilon_{asym}(COO^-)$ and $\upsilon_{sym}(COO^-)$ is found to be greater than 144 cm^{-1}, which indicates the unidentate nature of the acetate ion[52, 53].

Table 3.5: IR spectral data of qdp and its complexes

Assignments (in cm^{-1})	$\upsilon(C=N)^a$	$\delta(O-H)^b$	$\upsilon(C=N)^c$	$\upsilon(M-N)$	$\upsilon_{NO3(mono\ dentate)}$	$\upsilon_{(COO^-)}$	$\upsilon_{unidentate\ perchlorate}$
qdp	1566	–	–	–	–	–	–
The chloro complex	1548	1126	1648	415	–	–	–
The acetato complex	1548	1119	1613	409	–	1560 1401	–
The nitrato complex	1562	1129	1614	498	1469, 1384	–	–
The perchlorato complex	1567	1153	1616	409	–	–	1090, 1120

$^a\upsilon(C = N)$ of quinoxaldehyde ring; $^b\upsilon(O—H)$ of coordinated water molecule; ^{c}–CH=N of azomethine group;

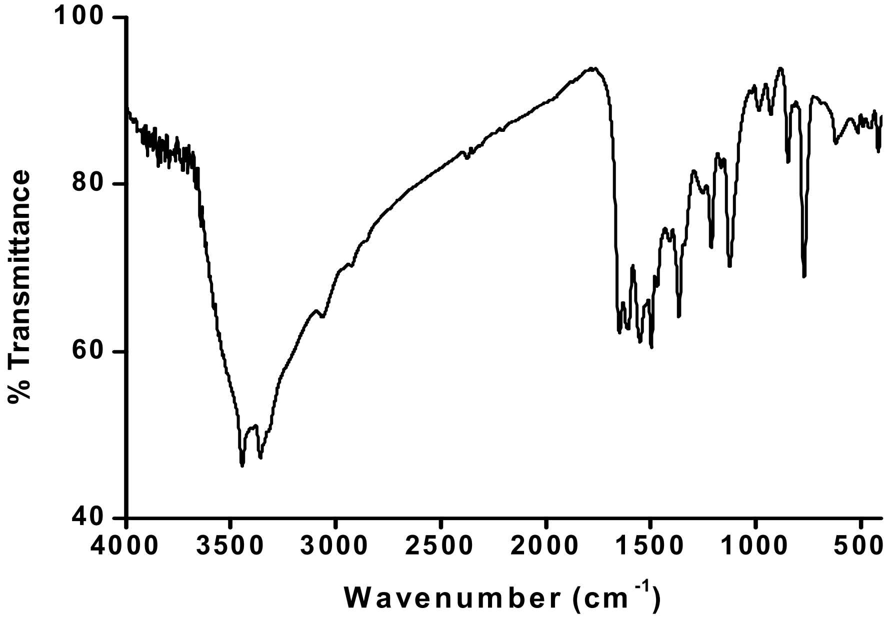


Figure 3.8: FT-IR spectrum of chloro complex

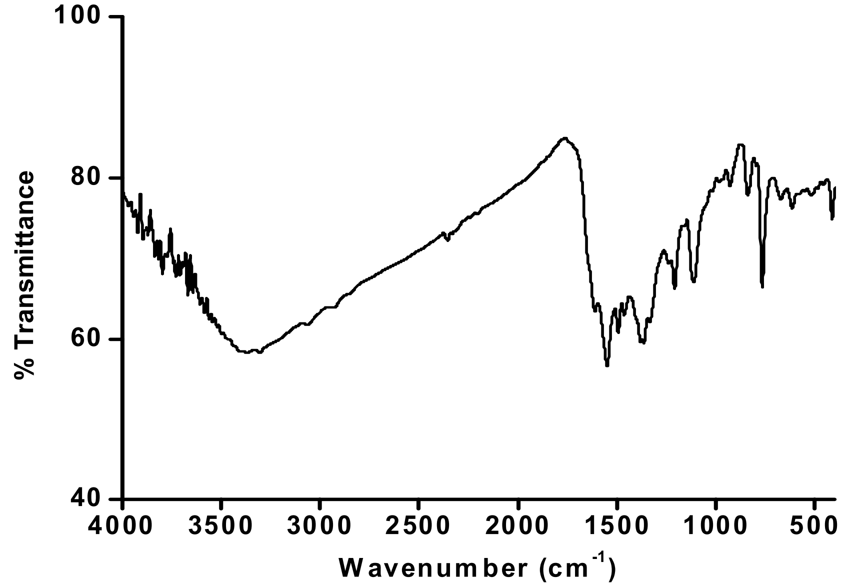


Figure 3.9: FT-IR spectrum of acetato complex

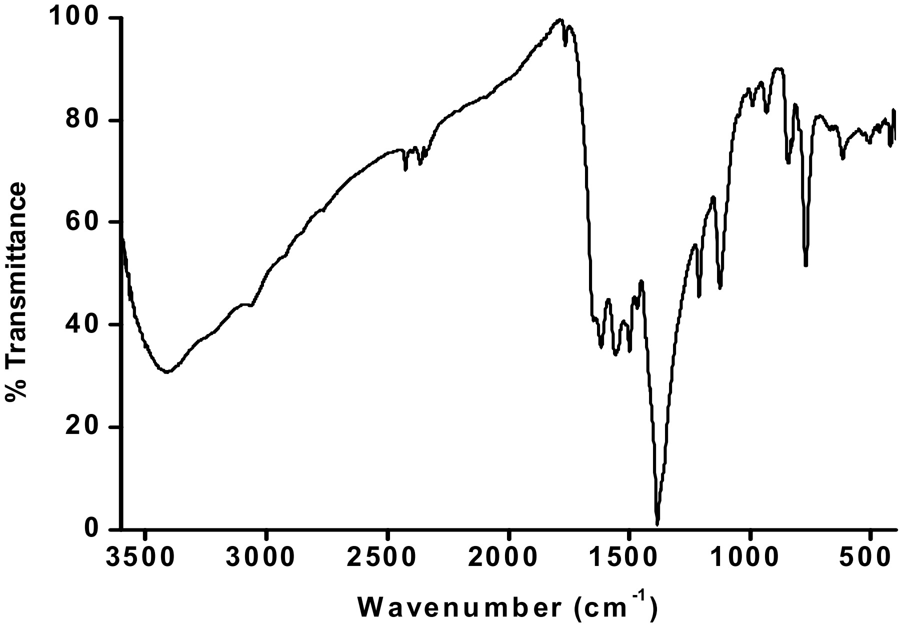


Figure 3.10: FT-IR spectrum of nitrato complex

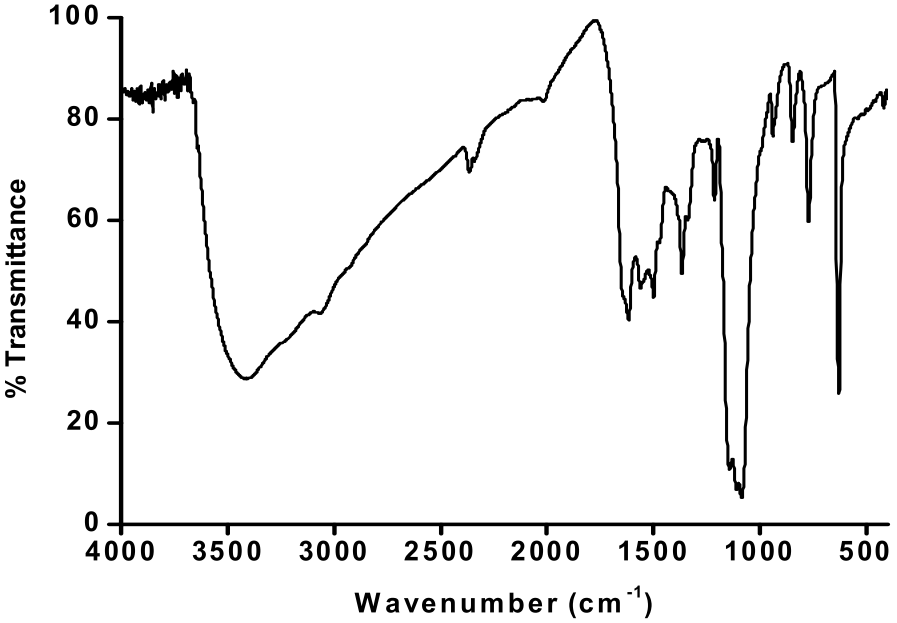


Figure 3.11: FT-IR spectrum of perchlorato complex

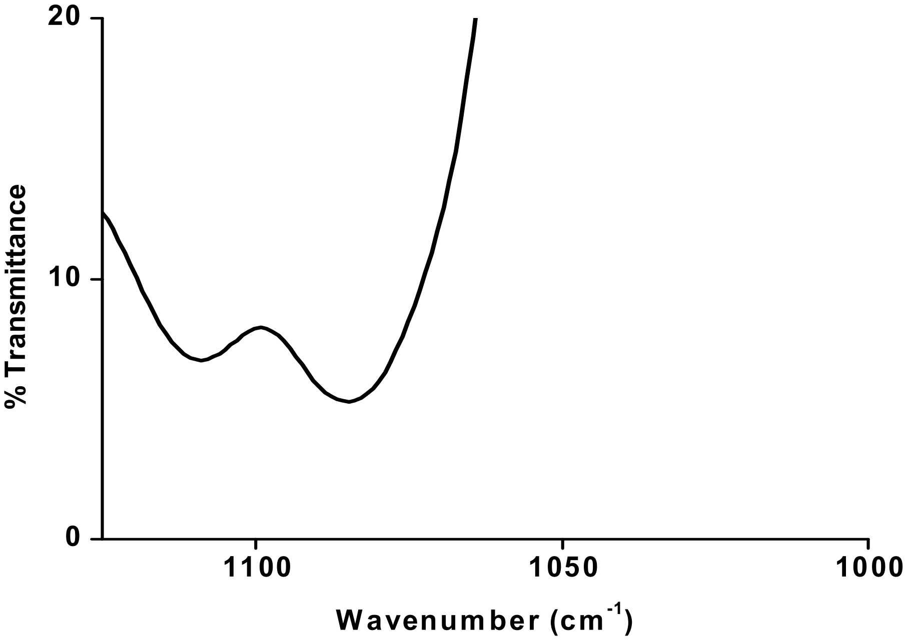
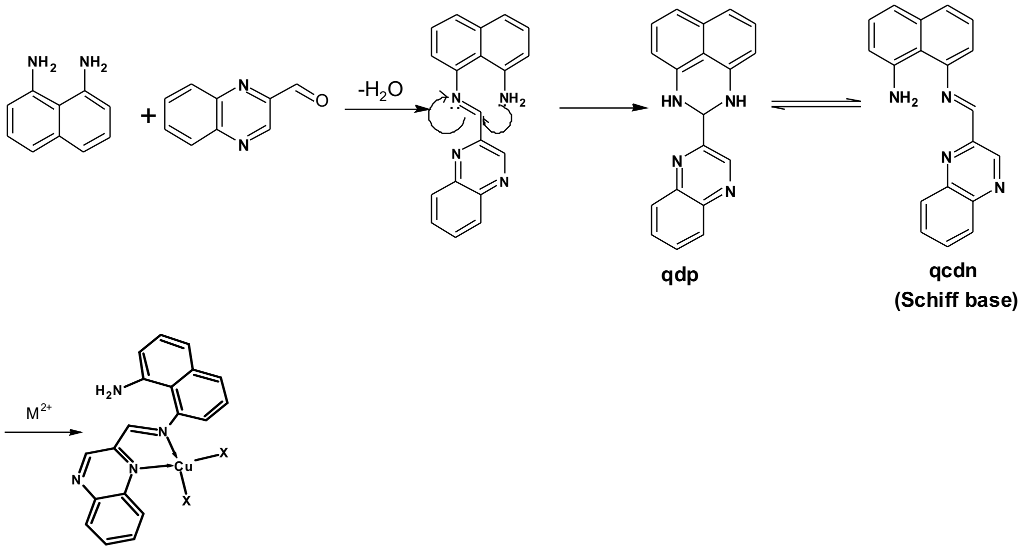


Figure 3.11.1: The portion of FT-IR spectrum of perchlorato complex showing splitting pattern

Thus in the complexes, the ligand is not the perimidine (qdp), but is a Schiff base quinoxaline–2–carboxalidine–1,8–diaminonaphthalene (qcdn), derived from qdp. Further more studies indicate qcdn act as a bidentate ligand coordinating through azomethine C=N stretching and nitrogen atom of quinoxaline C=N group. Based on the elemental analysis, molar conductance, TG and IR studies, the following molecular formula were assigned for the complexes $[Cu(qcdn)Cl_2(H_2O)_2]H_2O$ (for the chloro complex), $[Cu(qcdn)(OAc)_2(H_2O)_2]2H_2O$ (for the acetato complex), $[Cu(qcdn)(NO_3)_2]$ $2H_2O$ (for the nitrato complex) and $[Cu(qcdn)(ClO_4)_2(H_2O)_2]2H_2O$ (for the perchlorato complex). The analytical data of the complexes agree with the above mentioned molecular formula. The calculated values are shown in brackets in Table 3.2.

3.3.2.3 Mechanism of formation of the Schiff base complex

The mechanism of the reaction involves the following steps[29]. The first step is the condensation to form Schiff base. The imino (or azomethine, C=N) carbon is partially positively charged, and therefore is susceptible to intermolecular or intramolecular nucleophilic attack[54]. The second step is the intramolecular nucleophilic attack of the amino group at the imino carbon to bring about the C–N coupling leading to the formation of five- or six-membered heterocycles. In the solid state, most of the perimidines and their derivatives are stable in the ring closed form, but upon dissolution in non polar solvents equilibrium is gradually established[23–25] between the ring closed and an extended π-conjugated system of the ring opened imine form (Schiff base), which could form Schiff base complexes with metal ions[31].



X = Cl for chloro, OAc for acetato, NO_3 for nitrato and ClO_4 for perchlorato complex

Scheme 3.2: Formation of metal complexes of qcdn

3.3.2.4 Magnetic susceptibility measurements

The room temperature magnetic moment (μ_{eff}) values of the complexes are presented in Table 3.3. The values suggest that copper in these complexes are in +2 oxidation state. Further more, the values indicate a distorted octahedral geometry[55, 56] for the chloro, acetato and perchlorato complex. However, for the nitrato complex, which is a four coordinated complex, the value does not favor tetrahedral structure and probability might be square planar.

3.3.2.5 Electronic spectra

The UV-Vis spectra of the compound qdp and the complexes of qcdn are recorded in dichloromethane in the frequency range from 50000–10000 cm^{-1}. Electronic spectra of qdp and the complexes of qcdn are given in Figures 3.12–3.15. The spectral data are presented in Table 3.6. The electronic spectra of qdp in dichloromethane (10^{-5} mol l^{-1}) exhibit four major peaks. The bands at 42550 and 36900 cm^{-1} are attributed to the $\pi \rightarrow \pi^*$transition of the benzene ring. The band at 30120 cm^{-1} is assigned to the n → π^*transition of azomethine group and ring (C=N) groups[57]. The shift in the positions of some of these regions of absorption in the spectra of complexes can be taken as a positive evidence of complex formation. Such shift in absorption bands on complex formation was reported by the earlier workers[58]. The spectra of Cu(II) complexes show medium intensity multiple bands, assigned to various transitions involving $^2B_1$ ground term and $^2B_2$, $^2A_1$ and ^2E high energy terms due to distorted octahedral geometry[59].

The spectra of $[Cu(qcdn)Cl_2(H_2O)_2]H_2O$ in solution showed broad maxima in the range ~17700 – 19250 cm^{-1} which is an indication of distorted octahedral[60] nature of the complex. The electronic spectra of the chloro complex show mainly three bands. The band at 34010 cm^{-1} corresponds to $\pi \rightarrow \pi^*$ transition, whereas a transition at 17850 and 16950 cm^{-1} corresponds to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions respectively. In the spectra of $[Cu(qcdn)(NO_3)_2]2H_2O$, a broad band in the range19370 – 22840 cm^{-1} is seen due to the $^2B_{1g} \rightarrow {}^2E_g$ $(d_{x^2-y^2} \rightarrow d_{xz}, d_{yz})$ transition and the band at 18180 cm^{-1} is seen due to $^2B_{1g} \rightarrow {}^2A_{1g}$ $(d_{x^2-y^2} \rightarrow d_{z^2})$ transition of Cu(II) ion in square planar geometry. The intensity of the bands and the magnetic moment value also supports the square planar geometry[61, 62] of the nitrato complex. The acetato and perchlorato complex exhibit a band around ~16280 cm^{-1} corresponding to the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition and the nature of the bands indicate an distorted octahedral geometry around the Cu(II) ion[63, 64]. Cu(II) ion (d^9) split under the influence of the tetragonal distortion, three transitions are expected. $^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2B_{2g}$and $^2B_{1g} \rightarrow {}^2A_{1g}$[65]. But their very close energies of these bands make them appear in the form of a broad band in the range of ~17000 cm^{-1}.

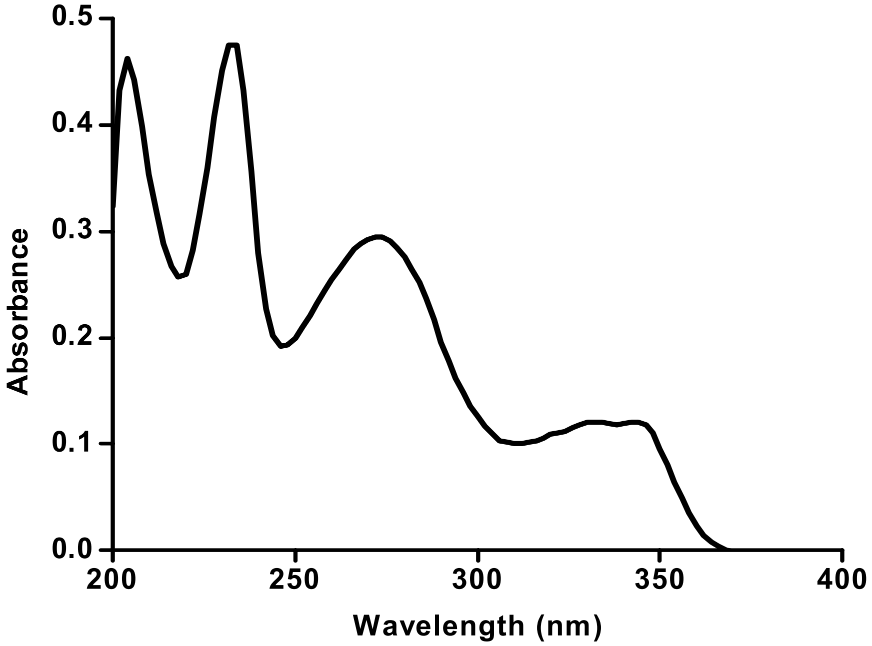


Figure 3.12: The UV-Vis spectrum of qdp

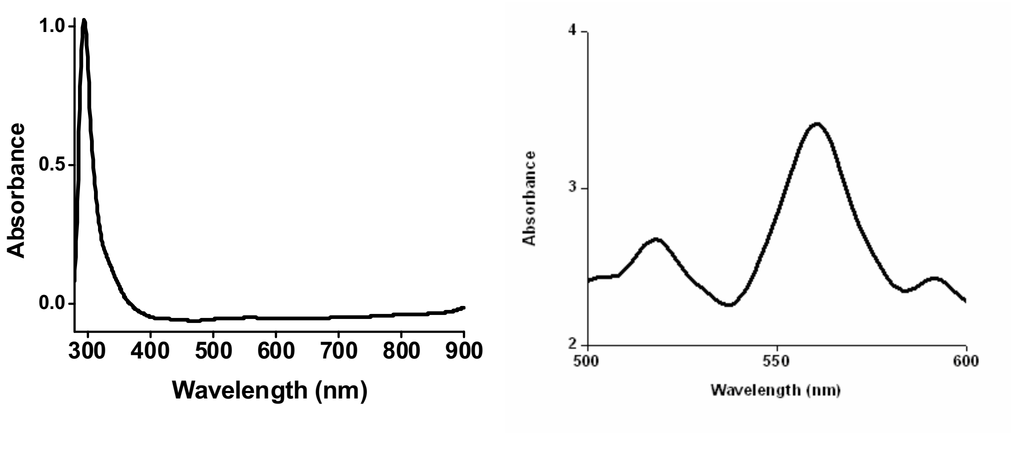


Figure 3.13: The UV-Vis spectrum of $[Cu(qcdn) Cl_2(H_2O)_2].H_2O$

$[Cu(qcdn)Cl_2(H_2O)_2].H_2O$ (conc.)

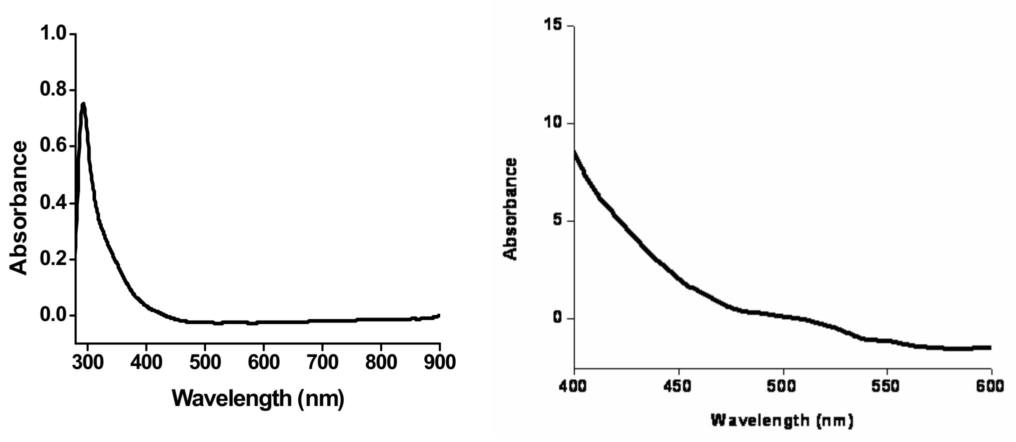


Figure 3.14: The UV-Vis spectrum of
$[Cu(qcdn)(NO_3)_2].2H_2O$

$[Cu(qcdn)(NO_3)_2].2H_2O$ (conc.)

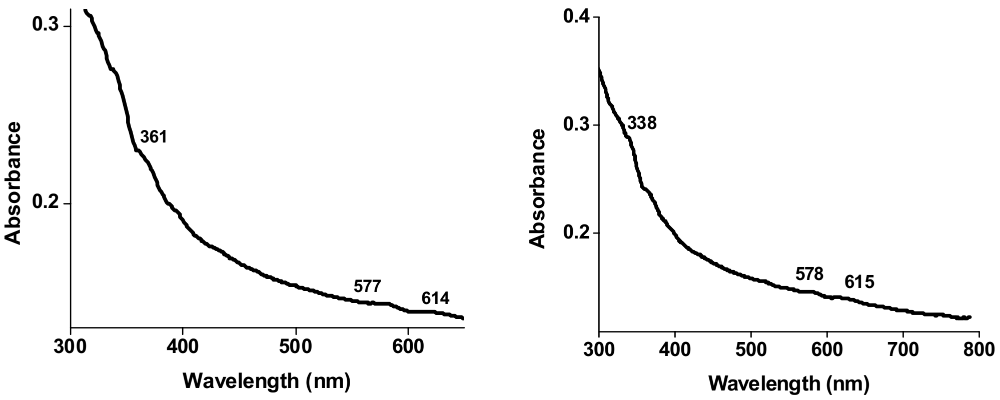


Figure 3.15: The UV-Vis spectrum of
$[Cu(qcdn)(OAc)_2(H_2O)_2].2H_2O$

$[Cu(qcdn)(ClO_4)_2(H_2O)_2].2H_2O$

Table 3.6: UV-Vis spectral assignments of qdp and complexes

Compound	Absorption Maxima		Tentative assignments
	(cm^{-1})	log ε (ε in L mol^{-1} cm^{-1})	
qdp	42550	4.74	$\pi \rightarrow \pi^*$
	36900	2.92	$\pi \rightarrow \pi^*$
	30120	1.21	$n \rightarrow \pi^*$
$[Cu(qcdn)Cl_2(H_2O)_2].H_2O$	34010	3.96	$\pi \rightarrow \pi^*$
	17850	0.81	$^2B_{1g} \rightarrow {}^2A_{1g}$
	16950	0.93	$^2B_{1g} \rightarrow {}^2B_{2g}$
$[Cu(qcdn)(OAc)_2(H_2O)_2].2H_2O$	27700	3.89	$\pi \rightarrow \pi^*$
	17330	0.72	$^2B_{1g} \rightarrow {}^2A_{1g}$
	16290	1.30	$^2B_{1g} \rightarrow {}^2B_{2g}$
$[Cu(qcdn)(NO_3)_2].2H_2O$	33890	3.45	$\pi \rightarrow \pi^*$
	19490	0.89	$^2B_{1g} \rightarrow {}^2A_{1g} (d_{x^2-y^2} \rightarrow d_{z^2})$
	18180	0.77	$^2B_{1g} \rightarrow {}^2E_g (d_{x^2-y^2} \rightarrow d_{xz}, d_{yz})$
$[Cu(qcdn)(ClO_4)_2(H_2O)_2].2H_2O$	29580	3.91	$\pi \rightarrow \pi^*$
	17300	0.93	$^2B_{1g} \rightarrow {}^2A_{1g}$
	16260	0.78	$^2B_{1g} \rightarrow {}^2B_{2g}$

3.3.2.6 EPR spectra

The EPR spectra (Figures 3.16–3.19) of the Cu(II) complexes in the polycrystalline state at 298 K and in solution (DMF) at 77 K were recorded in the X–band, using 100 kHz field modulation and the g tensors were calculated relative to the standard marker TCNE (g=2.003). The EPR parameters calculated from the spectra are given in Table 3.7.

The $[Cu(qcdn)Cl_2(H_2O)_2]H_2O$ complex exhibits the $g_{||}$ value of 2.3 and $g_{\perp}$ value of 2.1. $[Cu(qcdn)(NO_3)_2]2H_2O$ complex in DMF at LNT shows four well-resolved peaks. However, the spectrum does not exhibit features characteristic of a binuclear complex. In tetragonal and square planar complexes, the unpaired electrons lies in the $d_{x^2-y^2}$ orbital giving $^2B_{1g}$ as the ground state with the $g_{||} > g_{\perp}$.

From the observed values, it is clear that $g_{||} > g_{\perp}$ (2.4 > 2.1) which suggests that the nitrato complex is square planar. Also it is supported by the fact that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital[66-72] and the spectral features are characteristic of an axial symmetry. The spectra of $[Cu(qcdn)(OAc)_2(H_2O)_2].2H_2O$ and $[Cu(qcdn)(ClO_4)_2(H_2O)_2].2H_2O$ are axial in nature with $g_{||} = 2.4$ and $g_{\perp} = 2.1$ respectively.

Table 3.7: EPR spectral data of the complexes

Complexes	EPR parameter
$[Cu(qcdn)Cl_2(H_2O)_2].H_2O$	$g_{||} = 2.3$; $g_{\perp} = 2.1$; $A_{||} = 0.017\ cm^{-1}$
$[Cu(qcdn)(OAc)_2(H_2O)_2].2H_2O$	$g_{||} = 2.4$; $g_{\perp} = 2.1$
$[Cu(qcdn)(NO_3)_2].2H_2O$	$g_{||} = 2.4$; $g_{\perp} = 2.1$; $A_{||} = 0.0014\ cm^{-1}$
$[Cu(qcdn)(ClO_4)_2(H_2O)_2].2H_2O$	$g_{||} = 2.4$; $g_{\perp} = 2.1$

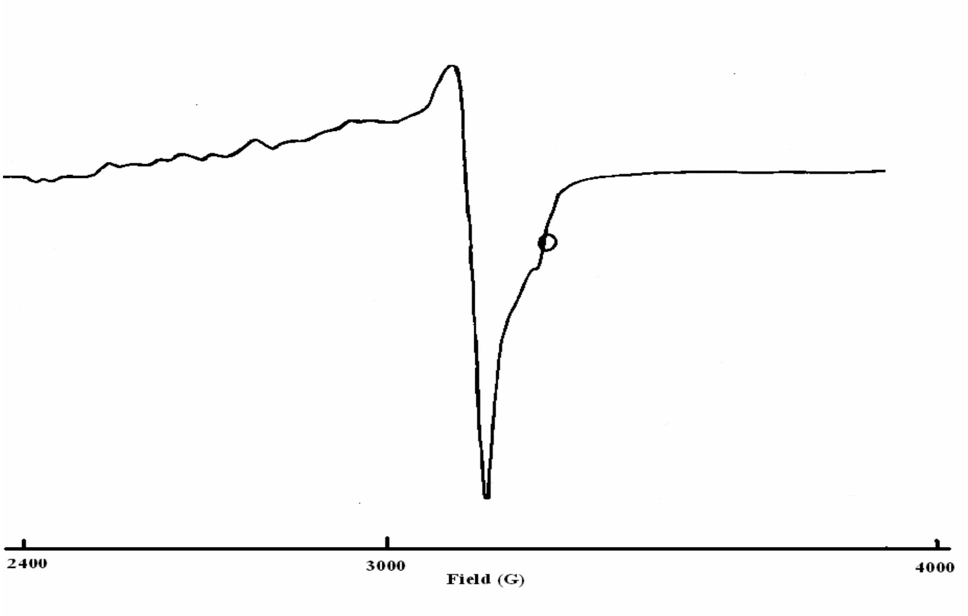


Figure 3.16: EPR spectrum of $[Cu(qcdn)Cl_2(H_2O)_2].H_2O$ in DMF at LNT

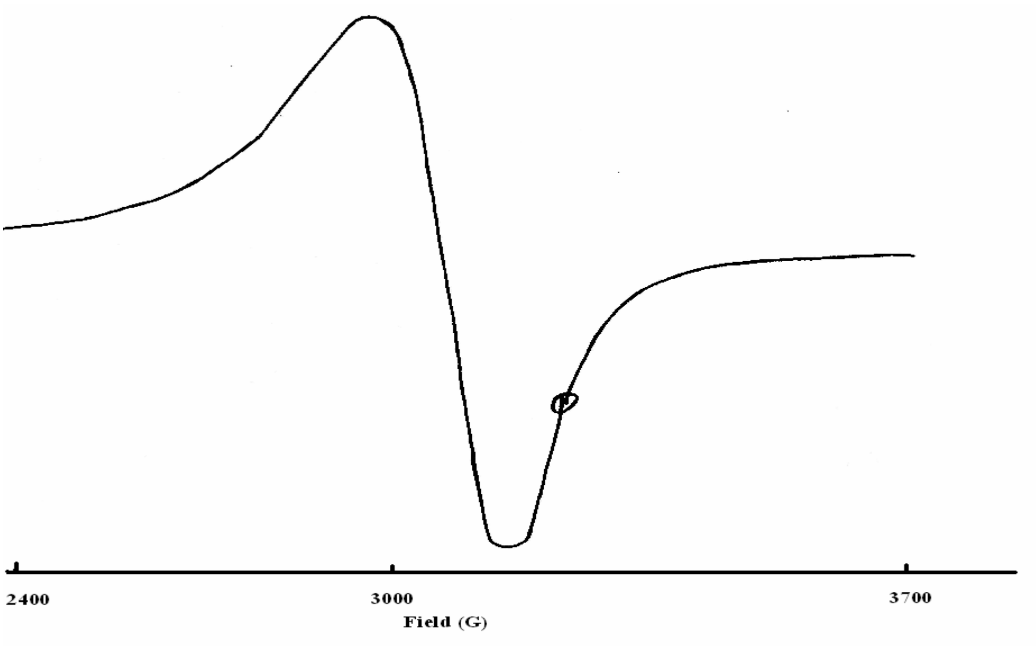


Figure 3.17: EPR spectrum of [Cu(qcdn)(OAc)$_2$(H$_2$O)$_2$].2H$_2$O in polycrystalline state at 298K

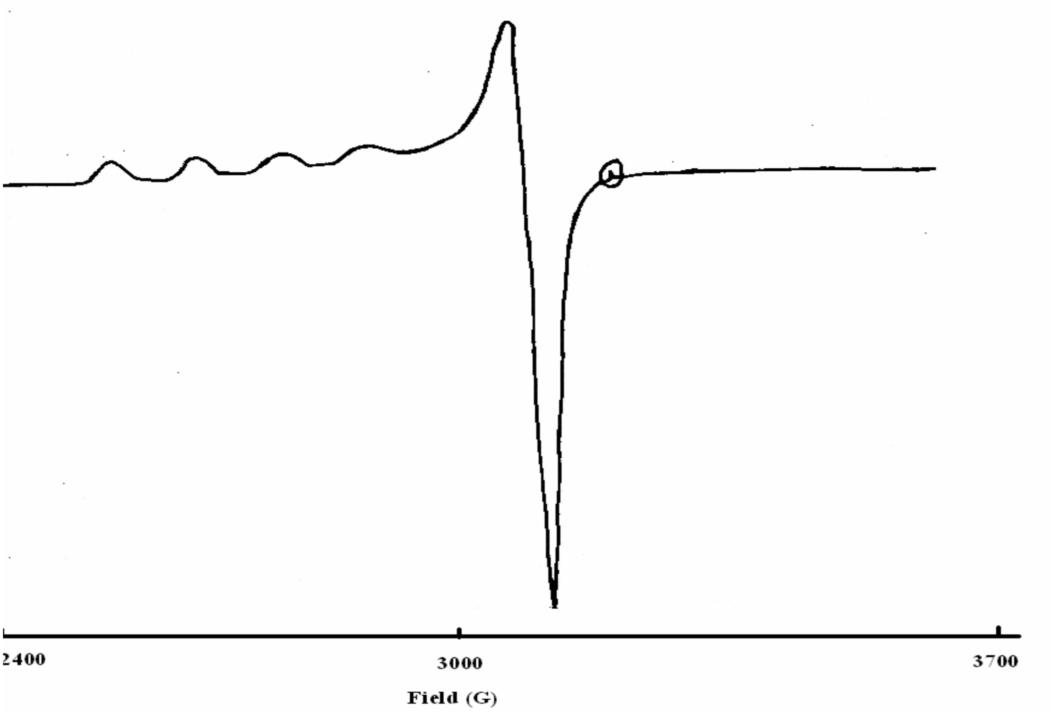


Figure 3.18: EPR spectrum of [Cu(qcdn)(NO$_3$)$_2$].2H$_2$O in DMF at LNT

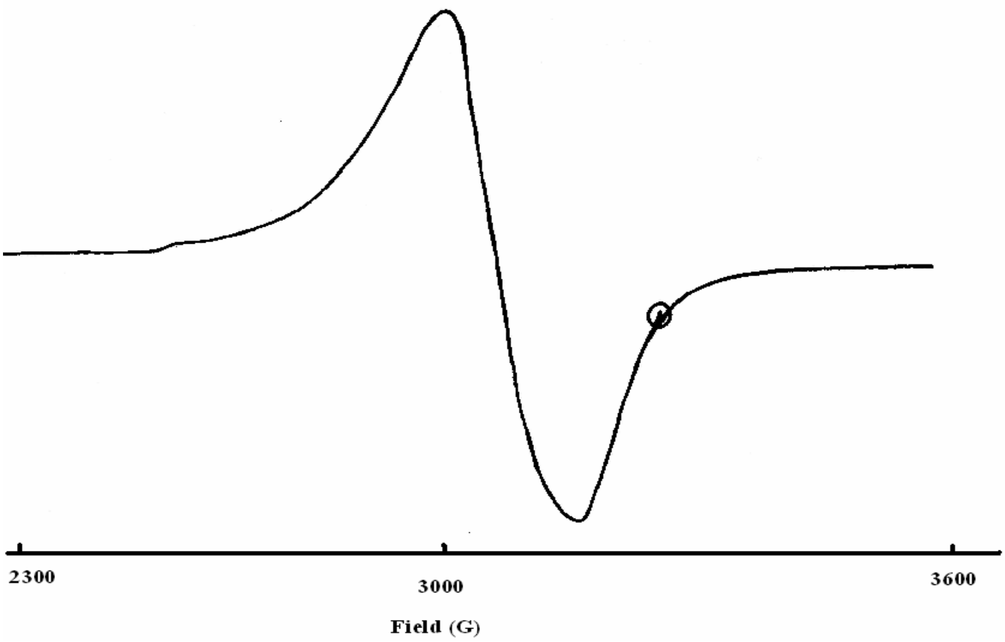


Figure 3.19: EPR spectrum of [Cu(qcdn)(ClO$_4$)$_2$(H$_2$O)$_2$].2H$_2$O in polycrystalline state at 298K

3.4 Conclusions

A novel perimidine derivative 2-(quinoxalin-2-yl)-2,3-dihydro-1*H*-perimidine has been synthesized and characterized by elemental analysis, IR and NMR spectroscopy and Single crystal X-ray diffraction analysis. In non-polar solvents, this compound (qdp) gets rearranged to form bidentate Schiff base, qcdn, and forms Schiff base complexes with Cu(II). All the complexes were characterized by physicochemical and spectroscopic techniques. These studies suggest that the [Cu(qcdn)(NO$_3$)$_2$]2H$_2$O is square planar and [Cu(qcdn)Cl$_2$(H$_2$O)$_2$]H$_2$O, [Cu(qcdn)(OAc)$_2$(H$_2$O)$_2$]2H$_2$O and [Cu(qcdn)(ClO$_4$)$_2$(H$_2$O)$_2$]2H$_2$O complexes are distorted octahedral in geometry (Figure 3.20).

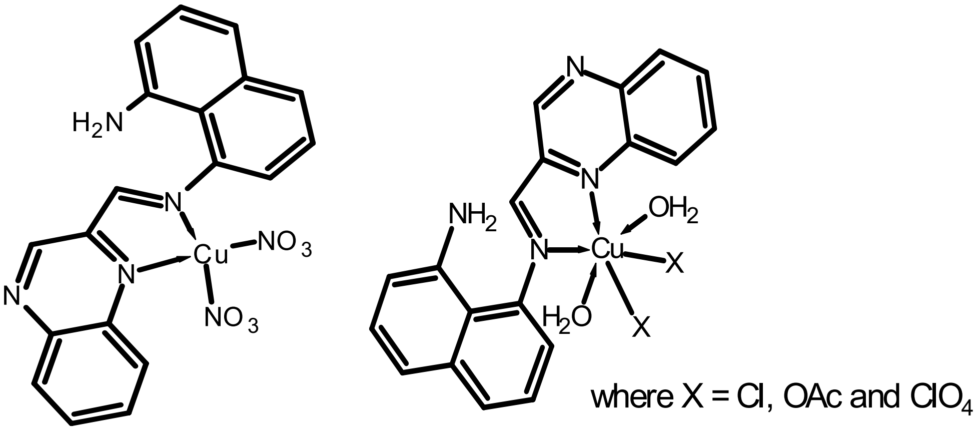


Figure 3.20: The proposed structure of the complexes (solvated water molecules are omitted)

References

1. Brown, D. J. Quinoxalines: Supplement II. In The Chemistry of Heterocyclic Compounds: A Series of Monographs; Taylor, E. C.; Wipf, P., Eds.; John Wiley & Sons: New Jersey. 61 (2004).

2. Porter, A. E. A. In Comprehensive Heterocyclic Chemistry; Katritsky, A.R.; Rees, C.W. Eds., Pergamon: Oxford (1984) 157.

3. Woo, G. H. C.; Snyder, J. K.; Wan, Z-K. Prog. Heterocycl. Chem. 14 (2002) 279.

4. (a) Jaso, A.; Zarranz, B.; Aldana, I.; Monge, A. J. Med. Chem. 48 (2005) 2019; (b) Carta, A.; Paglietti, G.; Nikookar, M. E. R.; Sanna, P.; Sechi, L.; Zanetti, S. Eur. J. Med Chem. 37 (2002) 355; (c) Dell, A.; William, D. H.; Morris, H. R.; Smith, G. A.; Feeney, J.; Roberts, G. C. K. J. Am. Chem. Soc. 97 (1975) 2497; (d) Bailly, C.; Echepare, S.; Gago, F.; Waring, M. J. Anti-Cancer Drug Des. 14 (1999) 291.

5. Catarzi, D.; Colotta, V.; Varano, F.; Lenzi, O.; Filacchioni, G.; Trincavelli, L.; Martini, C.; Montopoli, C.; Moro, S. J. Med. Chem. 48 (2005) 7932.
6. Lakshmi, V. M.; Hsu, F. F.; Zenser, T. V. Chem. Res. Toxicol. 18 (2005) 1038.
7. Turesky, R. J.; Goodenough, A. K.; Ni, W.; McNaughton, L.; LeMaster, D. M.; Holland, R. D.; Wu, R. W.; Felton, J. S. Chem. Res. Toxicol. 20 (2007) 520.
8. Sundaram, G. S. M.; Singh, B.; Venkatesh, C.; Ila, H.; Junjappa, H. J. Org. Chem. 72 (2007) 5020.
9. Naylor, M. A.; Stephen, M. A.; Nolan, J.; Sutton, B.; Tocher, J. H.; Fielden, E. M.; Adams, J. E.; Strafford, I. Anti-Cancer Drug Des. 8 (1993) 439.
10. Harmenberg, J.; Akesson-Johansson, A.; Graslund, A.; Malmfors, T.; Bergman, J.; Wahren, B.; Akerfeldt, S.; Lundblad, L.; Cox, S. Antiviral Res. 15 (1991) 193.
11. Fournet, A.; Mahieux, R.; Fakhfakh, M. A.; Franck, X.; Hocquemiller, R.; Figadere, B. B. Bioorg. Med. Chem. Lett. 13 (2003) 891.
12. Munos, M.-H.; Mayrargue, J.; Fournet, A.; Gantier, J.-C.; Hocquemiller, R.; Moskowitz, H. Chem. Pharm. Bull. 42 (1994) 1914.
13. Sarges, R.; Howard, H. R.; Browne, R. C.; Label, L. A.; Seymour, P. A. J. Med. Chem. 33 (1990) 2240.
14. Sakata, G.; Makino, K.; Kurasawa, Y. Heterocycles. 27 (1998) 2481.
15. Arthur, G.; Elor, K. B.; Robert, G. S.; Guo, Z. Z.; Richard, J. P.; Stanley, D.; John, R. K.; Sean, T. J. J. Med. Chem. 48 (2005) 744.
16. Zarranz, B.; Jaso, A.; Aldana, I.; Monge, A. Bioorg. Med. Chem. 12 (2004) 3711.

17. Tandon, V. K.; Yadav, D. B.; Maurya, H. K.; Chaturvedi, A. K.; Shukla, P. K. Bioorg. Med. Chem. 14 (2006) 6120.

18. Kushida, M.; Wanibuchi, H.; Morimura, K.; Kinoshita, A.; Kang, J. S.; Puatanachokckai, R.; Wei, M.; Funae, Y.; Fukushima, S. Cancer Sci. 96 (2005) 747.

19. Kotb, E. R.; Anwar, M. A.; Soliman, M. S.; Salama, M. A. Phosphorus, Sulfur Silicon Relat. Elem. 182 (2007) 1119.

20. Ali, I. A. I.; Al-Masoudi, I. A.; Aziz, N. M.; Al-Masoudi, N. A. Nucleosides, Nucleotides & Nucleic Acids. 27 (2008) 146.

21. Pozharskii, A. F.; Dalhikovskaya, V. V. Russ. Chem. Rev. 50 (1981) 816.

22. Cameron, D. W.; Samuel, E. L. Austral. J. Chem. 29 (1976) 2499.

23. Minkin, V. I.; Komissarov, V. N.; Kharlanov, V. A. Perimidinespirocyclohexadienones. In Organic Photochromic and Thermochromic compounds; Crano, J. C.; Guglielmetti, R. J. Eds., Plenum Press: New York. 1 (1999) 315.

24. (a) Komissarov, V. N.; Gruzdeva, E. N; Kharlanov, V. A.; Olekhnovich, L. P.; Borodkin, G. S.; Khrustalev, V. N.; Lindeman, S. V.; Struch Kov, Y. T.; Kogan, V. A. Minkin, V. I. Izv. Akad. Nauk. SSSR. 46 (1997) 2028; (b) Davis, R.; Tamaoki, N. Org. Lett. 7 (2005) 1461.

25. Minkin, V. I. Chem. Rev. 104 (2004) 2751.

26. Arun, V. Ph.D Thesis. Cochin University of Science and Technology, Kerala. June (2009).

27. Shakir, M.; Azam, M.; Parveen, S.; Khan, A. U.; Firdaus, F.; Spectrochim. Acta, Part A. 71 (2009) 1851.

28. Firdaus, F.; Fatma, K.; Azam, M.; Khan, S. N.; Khan, A. U.; Shakir, M. Spectrochim. Acta, Part A. 72 (2009) 591.

29. Varsha, G.; Arun. V.; Robinson, P. P.; Manju, Sebastian.; Digna, Varghese.; Leeju, P.; Jayachandran, V. P.; Yusuff, K. K. M. Tetrahedron Lett. 51 (2010) 2174.

30. Damus, H.; Fernaxdo, QReiser, H. Inorg. Chem. 3 (1964) 928.

31. Sebastian, M.; Arun, V.; Robinson, P. P.; Yusuff, K. K. M. Synth. React. Inorg. Met.-Org. Chem. 40 (2010) 541.

32. Geary, W. J. Coord. Chem. Rev. 7 (1971) 81.

33. Aranha, P. E.; Souza, J. M.; Romera, S.; Ramos, L. A.; dos Santos, M. P.; Dockal, E. R.; Cavalheiro, E. T. G. Thermochim. Acta. 453 (2007) 9.

34. Wasi, N.; Singh, H. B. Synth. React. Inorg. Met.-Org. Chem. 18 (1988) 473.

35. Parekh, H. M.; Patel, M. N. Russ. J. Coord. Chem. 32 (2006) 431.

36. Mamedov, V. A.; Kalinin, A. A.; Azancheev, N. M.; Levin, Y. A. Russ. J. Org. Chem. 39 (2003) 125.

37. Mamedov, V. A.; Kalinin, A. A.; Gubaidullin, A. T.; Isaikina, O. G.; Litvinov, I. A. Russ. J. Org. Chem. 41 (2005) 599.

38. Mamedov, V. A.; Kalinin, A. A.; Gubaidullin, A. T.; Nurkhametova, I. Z.; Litvinov, I. A.; Levin, Y. A. Chem. Heterocycl. Comp. 35 (1999) 1459.

39. Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed., John Wiley and Sons, Inc, New York (1986).

40. Abdallah, S. M.; Mohamed, G. G.; Zayed, M. A.; Abou El-Ela, M. S. Spectrochim. Acta, Part A. 73 (2009) 833.

41. El-Tabl, H. M.; El-Saied, F. A.; Ayad, M. I. Synth. React. Inorg. Met.-Org. Chem. 32 (2002) 1245.

42. Farona, M. F.; Perry, D. C.; Kuska, H. A. Inorg. Chem. 7 (1968) 2415.

43. Shebl, M. Spectrochim. Acta, Part A. 73 (2009) 313.
44. Nakamoto, K. Infrared and Raman Spectra of Inorganic coordination compounds. Part-B, 5th Ed., Wiley Interscience, New York. (1990).
45. Gatehouse, B. M.; Livinstone, S. E.; Nyholm, R. S. J. Chem. Soc. (1957) 4222.
46. Curtis, N. F.; Curtis, Y. M. Inorg. Chem. 4 (1958) 804.
47. Duff, E. J.; Aughes, M. N.; Rutt, K. J. J. Chem. Soc. (1969) 2126.
48. Clark, R. J. H.; Williams, C. S. Inorg. Chem. 4 (1965) 350.
49. Nakamoto, K. Infrared and Raman spectra of Inorganic and Coordination Compounds, Wiley, New York. (1978).
50. Hathaway, B. J.; Underhill, A. E. J. Chem. Soc. (1961) 3091.
51. Lewis, D. L.; Estes, E. D.; Hodgson, D. J. Cryst. Mol. Struct. 67 (1975) 5.
52. Bailey, R. A.; Kozak, S. L.; Michelson, T. W.; Mills, W. N. Coord. Chem. Rev. 6 (1971) 407.
53. Hester, R. E.; Grossman, W. E. L. Inorg. Chem. 5 (1966) 1308.
54. Hernanddez-Molina, R.; Mederos, A. In Acyclic and Macrocyclic Schiff base Ligands in Comprehensive Coordination Chemistry II; McCleverty, J. A.; Meyer, T. J. Eds., Pergamon Press: New York. 2 (2004) 411.
55. Cotton, F.A.; Wilkinson, G.; Murillo, C. A.; Bochmann. M. Advanced Inorganic Chemistry, 6th edn., Wiley, New York. (1999).
56. Kohout, J.; Hvastijova, M.; Kozisek, J.; Diaz, J. G.; Valko, M.; Jager, L.; Svoboda, I. Inorg. Chim. Acta. 287 (1999) 186.
57. Seok, Y. J.; Yang, K. S.; Kim, S. T.; Huh, W. K.; Kang, S. O. J. Carbohydr. Chem. 15 (1996) 1085.

58. Mazumdar, A. K. D.; Saha, N. K.; Banerji, K. D. J. Ind. Chem. Soc. LVI, (1979) 999.

59. Lever, A. B. P. Inorganic Spectroscopy. 2nd Edn, Elsevier, Amsterdam. (1984).

60. Campbell, M. J. M.; Grizeskoviak, R. Inorg. Nucl. Chem. Lett. 5 (1969) 27.

61. Faniran, J. A.; Patel, K. S.; Nelson, L. O. J. Inorg. Nucl. Chem. 38 (1976) 77.

62. Nicolini, M.; Pecile, C.; Turco, A. Coord. Chem. Rev. 1 (1966) 133.

63. Lever, A. B. P.; Lewis, J.; Nyholm, R. S. J. Chem. Soc. (1963) 5042.

64. Ballhausen, C. J. An Introduction to Ligand Field; 3rd Edn., McGraw Hill: New York. (1962).

65. Harrish, A. D.; Josasses, B.; Archer. R. D. Inorg. Chem. 4 (1965) 147.

66. Babu, S.; Ramesh, V.; Raghuram, A.; Naidu, P. R. R. Polyhedron. 16 (1997) 607.

67. Djebbar-Sid, S.; Benali-Baitich, O.; Deloume, J. P. Polyhedron. 16 (1997) 2175.

68. Drago, R. S.; Desmond, M. J.; Corden, B. R.; Miller, K. A. J. Am. Chem. Soc. 105 (1983) 2287.

69. Hathaway, B. J.; Billing, D. E. Coord. Chem. Rev. 5 (1970) 143.

70. Ray, R. K.; Kauffman, G. R. Inorg. Chem. Acta. 173 (1990) 207.

71. Jayasubramanian, K.; Samath, S. A.; Thambidurai, S.; Murugesan, R.; Ramalingam, S. K. Trans. Met. Chem. 20 (1995) 76.

72. Anthonisamy, V. S. X.; Murugesan, R. Chem. Phys. Lett. 287 (1998) 353.

* * *

Chapter

4

Synthesis and characterization of 2-hydroxy-3-methoxybenzalidine-1, 8-diaminonaphthalene and it's Mn(II), Co(II) and Cu(II)complexes

Contents

"What men call knowledge is the reasoned acceptance of false appearance. Wisdom looks behind veil and sees"

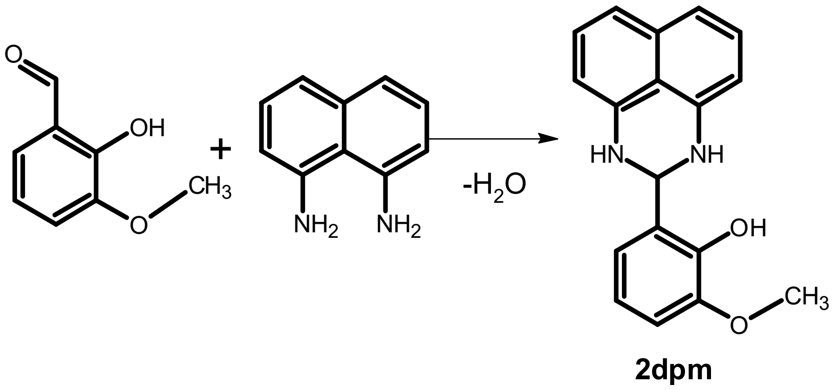
Sri Aurobindo

4.1 Introduction

2-Hydroxy-3-methoxybenzaldehyde (o-vanillin) is important to the pharmaceutical industry due to its antibacterial and anticancerous action. The Schiff base complexes derived from this compound have attracted considerable importance in the past decades due to continuing biological activities of *o*-vanillin. A number Schiff bases have been synthesized by condensing *o*-vanillin with different amines[1,2]. The presence of a phenolic hydroxyl group imparts an additional donor site in the molecule making it bidentate. Metal complexes with the Schiff base ligands are becoming increasingly important as biochemical, analytical and antimicrobial reagents, in the design of molecular ferromagnets, in materials chemistry and so on[3-8].

Our attempt to prepare Schiff base derived from *o*-vanillin and 1,8-diaminonaphthalene has resulted in the formation of a ring closure compound 2-

(2,3-dihydro-1*H*-perimidin-2-yl)-6-methoxyphenol (2dpm). The formation of 2dpm is given in Scheme 4.1. The interaction of this compound with Mn(II), Co(II) and Cu(II) has resulted in the isolation of complexes. The studies on the characterization of 2dpm and the complexes derived from 2dpm are presented in this chapter.



Scheme 4.1: The formation of 2dpm by ring closure

4.2 Experimental

4.2.1 Materials and methods

The materials and techniques employed for the synthesis and characterization of 2dpm and metal complexes of the Schiff base derived from 2dpm are given in chapter II.

4.2.2 Preparation of the product derived from 2-hydroxy-3-methoxy benzaldehyde and 1,8-diaminonaphthalene

The colorless compound was separated by refluxing purified[9, 10] 1,8-diaminonaphthalene (0.16 g; 1 mmol) and 2-hydroxy-3-methoxy benzaldehyde (0.15 g; 1 mmol) in absolute ethanol (50 mL) for three hours and keeping the reaction mixture at room temperature (27 ±2 °C). The product obtained was used without further purification. (Yield: 80% m.p.: = 162 °C)

4.2.3 Preparation of complexes

The complexes of Mn(II), Co(II) and Cu(II) were prepared by the following procedure:

The colorless compound (2 mmol, 1.5 g) was dissolved in 1:1 hexane–chloroform solution (~25 mL) and was magnetically stirred in a round bottom flask followed by drop wise addition of 1:1 methanol–chloroform solution (~25 mL) of corresponding metal salt manganese(II) chloride tetrahydrate (1 mmol, 0.50 g), cobalt(II) chloride hexahydrate (1 mmol, 0.32 g) or copper(II) chloride dihydrate (1 mmol, 0.43g) at room temperature (27±2 °C). The precipitate formed was filtered off, washed several times with small quantities of hexane and dried in vacuum over anhydrous calcium chloride.

4.3 Results and discussion

4.3.1 Characterization of the perimidine compound, 2dpm

On reacting 1,8-diaminonaphthalene with 2-hydroxy-3-methoxy benzaldehyde, a colorless compound was separated. This compound 2dpm was characterized by elemental analysis and infrared and ^{1}H NMR spectroscopy.

4.3.1.1 Elemental analysis

The analytical data (Found: C, 73.95; H, 5.52; N, 9.58) of the colourless compound, 2dpm is in good agreement with the expected molecular formula of the perimidine compound; $C_{18}H_{16}N_2O_2$ (Calculated: C, 73.97; H, 5.54; N, 9.60).

4.3.1.2 Infrared Spectra

IR spectrum of the compound is given in Figure 4.1. The spectrum shows bands at 3363 and 3302 cm^{-1} indicating the presence of –OH and =NH groups respectively. The band at 2920 cm^{-1} is due to alkyl C–H bond stretching of methoxy group.

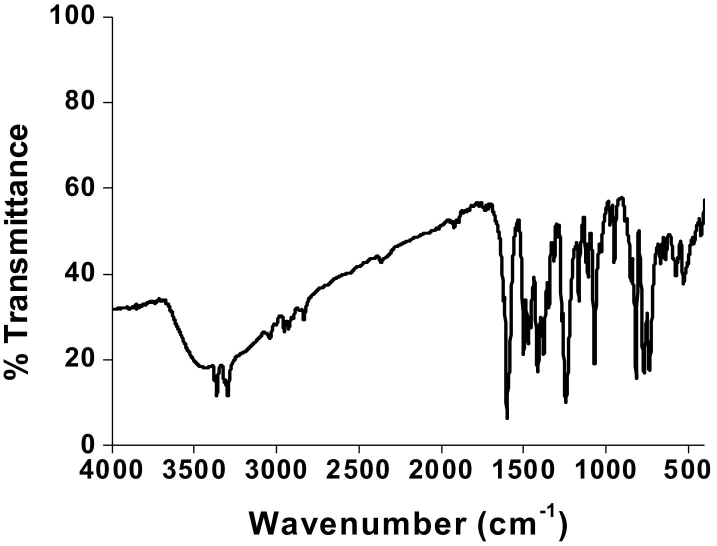


Figure 4.1: IR spectrum of 2dpm

4.3.1.3 ^{1}H NMR spectra

The ^{1}H NMR spectrum of the compound (2dpm) was recorded in d_6-dimethylsulphoxide solution using TMS as the internal standard. The spectrum is shown in Figure 4.2. The chemical shifts of different protons are as follows:

^{1}H NMR (400 MHz, DMSO-d_6): δ 3.90 (s, 3H, CH_3), 4.69 (s, 2H, NH), 5.66 (s, 1H, CH), 9.83 (s, 1H, OH), 6.56-6.59 (m, 2H, aromatic), 6.84-7.27 (m, 3H, aromatic)

The peak observed at 4.69 ppm is assignable to the –NH proton in the fused heterocyclic ring and a peak at 3.90 ppm confirms the presence of methyl proton. The –OH protons appear at 9.83 ppm and multiplet signals observed in the 6.56 – 7.27 ppm range are due to aromatic protons. The spectrum suggests the formation of perimidine instead of the Schiff base as in the case of reaction of quinoxaline-2-carboxaldehyde and 1,8-diaminonaphthalene.

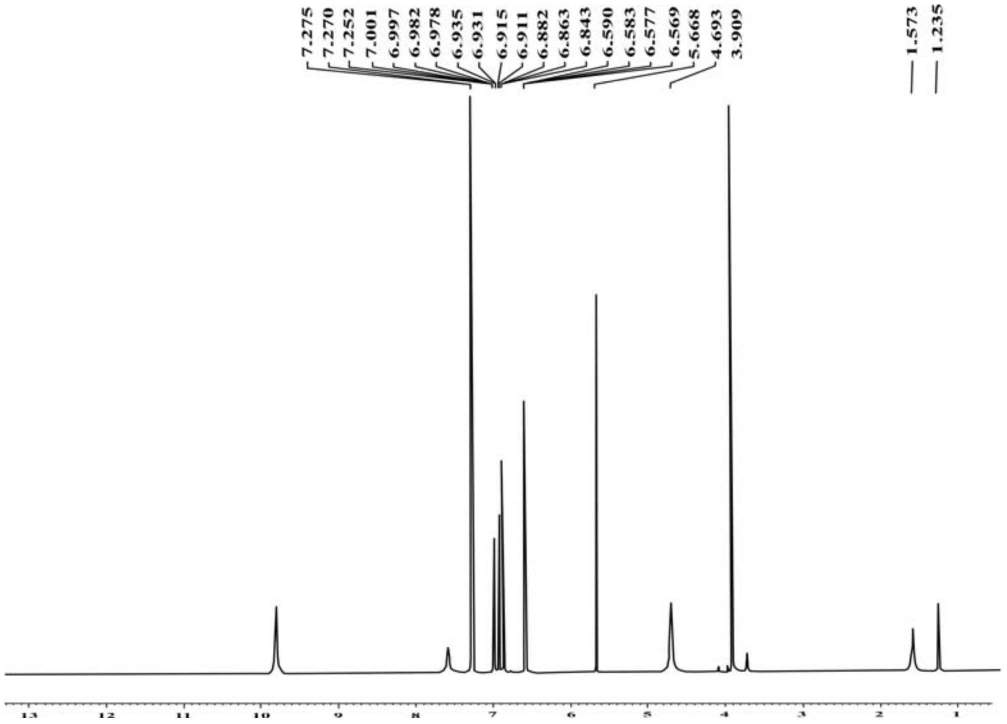


Figure 4.2: ^{1}H NMR spectrum of 2dpm

4.3.2 Characterization of the complexes derived from 2dpm

The Mn(II), Co(II) and Cu(II) complexes were prepared by the stoichiometric reaction of the metal ions with the compound, 2dpm. The colour, yield and elemental analysis data of the complexes derived from 2dpm are given in Table 4.1. The molar conductivity values (Table 4.2) in 10^{-3} M DMF solutions suggest non-electrolytic[11] nature of the complexes.

Table 4.1: Analytical data of the complexes derived from 2dpm

Compound	Color	Yield (%)	Analytical data. Found (calculated)%			
			M (%)	C (%)	H (%)	N (%)
The manganese complex	brown	56	7.94 (7.96)	62.52 (62.55)	5.25 (5.28)	8.10 (8.12)
The cobalt complex	brown	63	9.19 (9.20)	67.39 (67.40)	4.71 (4.73)	8.73 (8.75)
The copper complex	black	70	9.07 (9.10)	61.75 (61.80)	5.18 (5.20)	8.00 (8.05)

Table 4.2: Conductivity and magnetic moment data of complexes

Compound	μ_{eff} (BM)[a]	Molar conductance ($ohm^{-1}cm^2mol^{-1}$)[b]
The manganese complex	5.80	14
The cobalt complex	4.66	33
The copper complex	2.01	24

[a]Magnetic moment value per metal atom in the complex

[b]10^{-3} M solution in DMF

4.3.2.1 Thermal analysis

The thermogravimetric studies have been made in the temperature range 50–1000 °C. In the present study, the heating rates were suitably controlled at 10 °C/min under nitrogen atmosphere. The TG–DTG curves are represented in Figures 4.3–4.5. With TG/DTG analysis it is often possible to check whether there is coordinated or lattice water in the complexes[12]. Table 4.3 presents the thermogravimetric analysis results below 220 °C.

In the case of cobalt complex there is significant weight loss below 120 ℃ suggesting the presence of lattice water molecules. Mass loss in the temperature range 130−220 ℃ for manganese and copper complexes corresponds to the presence of two coordinated water molecules[13-15]. The decomposition of the organic part of the complexes takes place in two or three steps. In nitrogen atmosphere the decomposition was not seen to be completed even after 1000 ℃.

Table 4.3: Thermogravimetric analysis data (below 220 °C)

Complex	Temperature range, °C	% loss	Fragment lost	Nature of water lost
The manganese complex	90-130	4.5	1 H_2O	Lattice water
	140-200	7.5	2 H_2O	Coordinated water
The cobalt complex	170-210	7.9	2 H_2O	Coordinated water
The copper complex	90-130	4.3	1 H_2O	Lattice water
	150-210	8.4	2 H_2O	Coordinated water

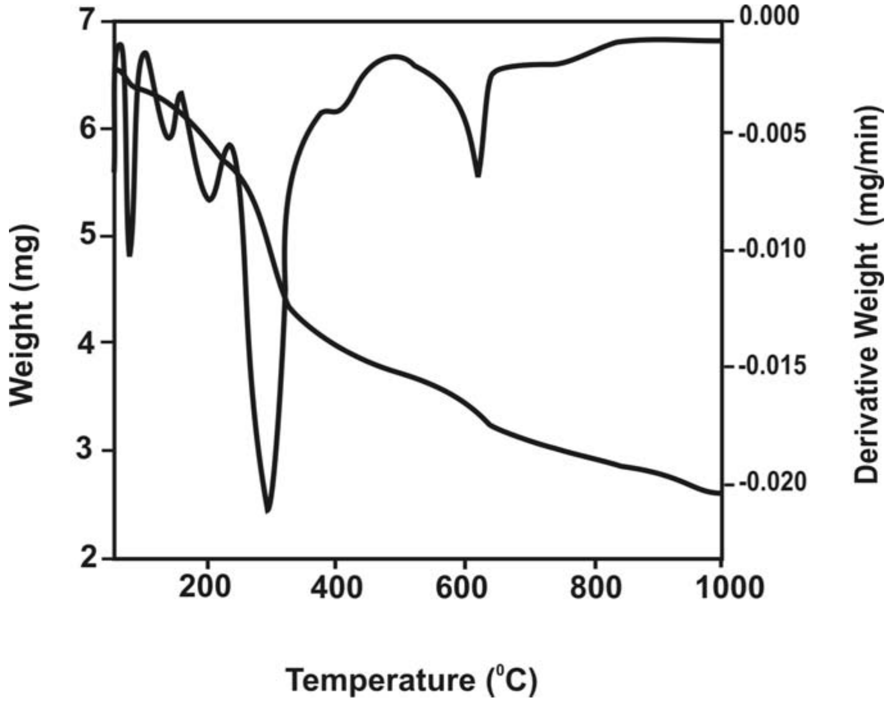


Figure 4.3: TG–DTG of the manganese complex

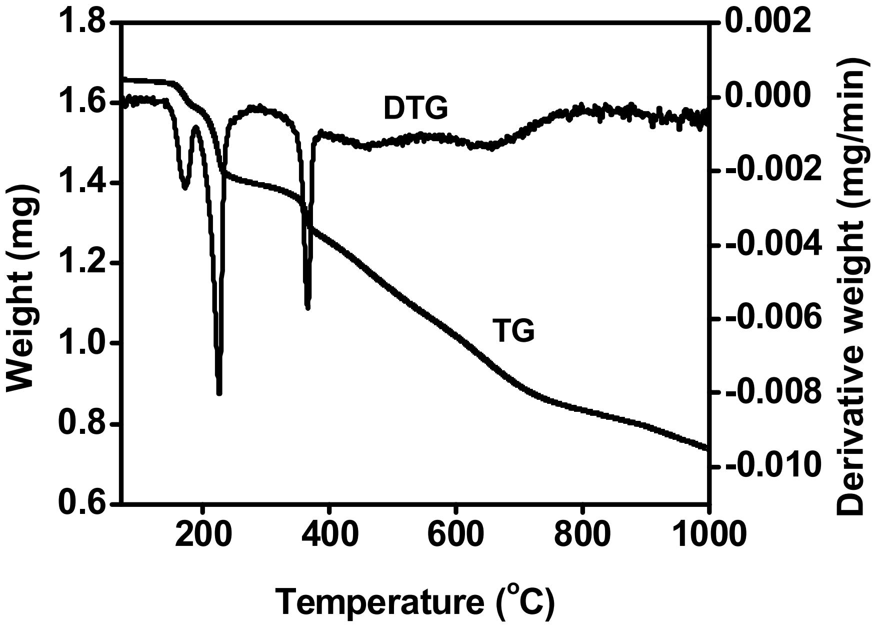


Figure 4.4: TG–DTG of the cobalt complex

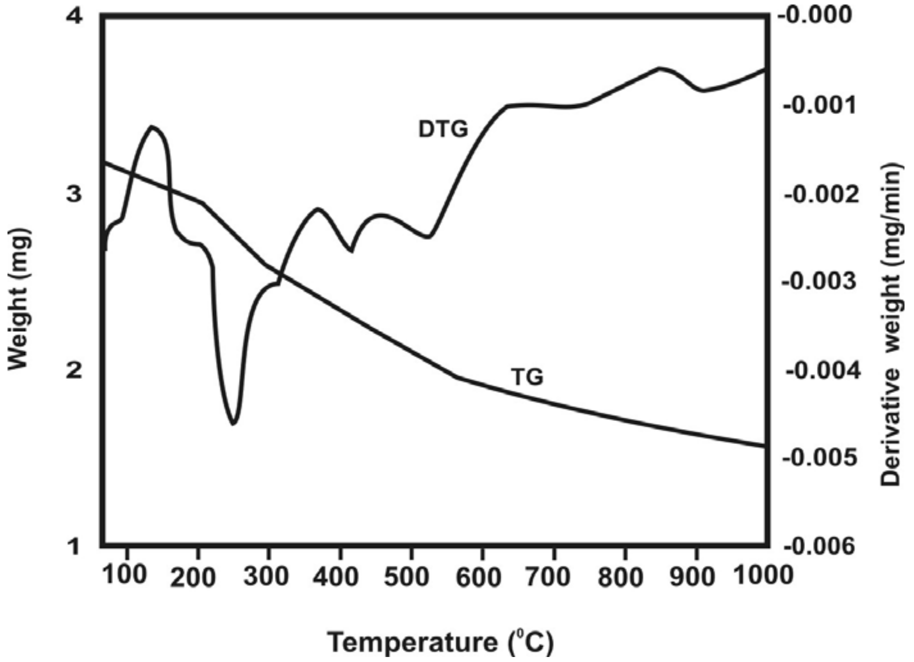


Figure 4.5: TG–DTG of the copper complex

4.3.2.2 Infrared spectra

Relevant IR spectral bands of 2dpm and metal complexes (Figures 4.6–4.8) derived from 2dpm is listed in Table 4.4. The IR spectra of the complexes when compared with that of 2dpm (Figure 4.1) show remarkable differences.

The broad absorption band[16] at ~3420 cm $^{-1}$ might be due to the hydroxyl group of water, phenolic hydroxyl or due to the NH_2 group formed by opening up of the ring. The coordination of phenolic OH group to the metal could not be ascertained from this region as the complex exhibits bands due to water molecule and NH_2 group.

The shift of the phenolic C–O stretching vibration from 1246 cm^{-1} to ~ 1373 cm^{-1} supports the coordination of phenolic oxygen atom[17]. All the complexes show the presence of strong bands in the range 1607–1628 cm^{-1}. This band is not seen in the spectrum of 2dpm. The position and nature of this band suggest C=N stretching of the azomethine group, which has resulted from the opening of the ring compound 2dpm. This gives a strong evidence for the conversion of 2dpm into Schiff base during the complex formation[18]. Furthermore, in these complexes, the bands in the regions 509−540 cm^{-1} and 421−435 cm^{-1} can be assigned to υ(M–O) and υ(M–N), respectively[19].

Table 4.4: IR spectral data of 2dpm and its complexes

Compound	υ(O–H)[a/b]	υ(C=N)[c]	υ(C–O)[d]	υ(M–O)	υ(M–N)	δ(O–H)[e]
2dpm	3302,3363	–	1246	–	–	–
The manganese complex	3376[f]	1607	1373	535	422	1159, 1193
The cobalt complex	3382[f]	1628	1361	510	415	–
The copper complex	3269	1626	1361	569	409	1152

[a]υ(N–H)/ υ(O–H) of the precursor ligand or; [b]υ(O—H) of coordinated water molecule; [c]–CH=N of azomethine group; [d]phenolic υ(C–O); [e] δ(O–H) of coordinated water molecule; [f]broad absorption band

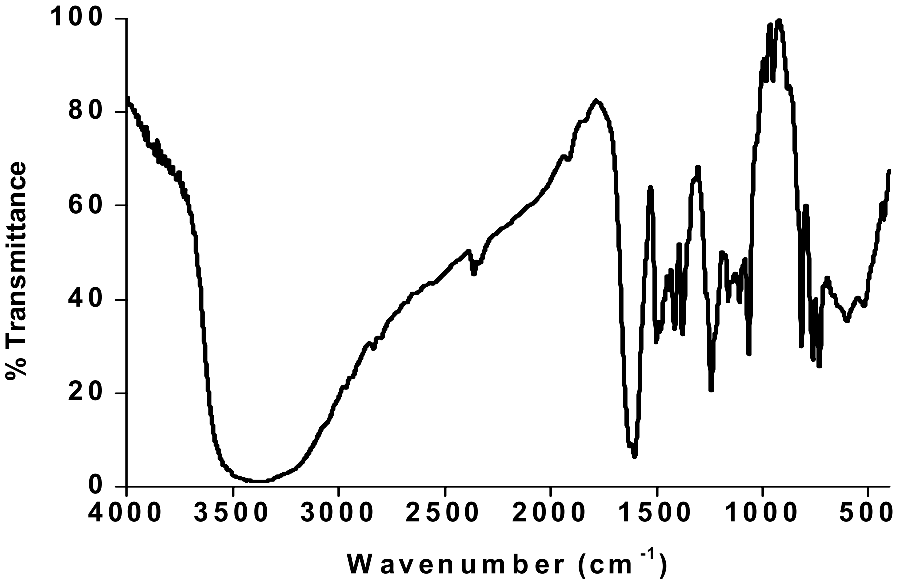


Figure 4.6: FT-IR spectrum of manganese complex

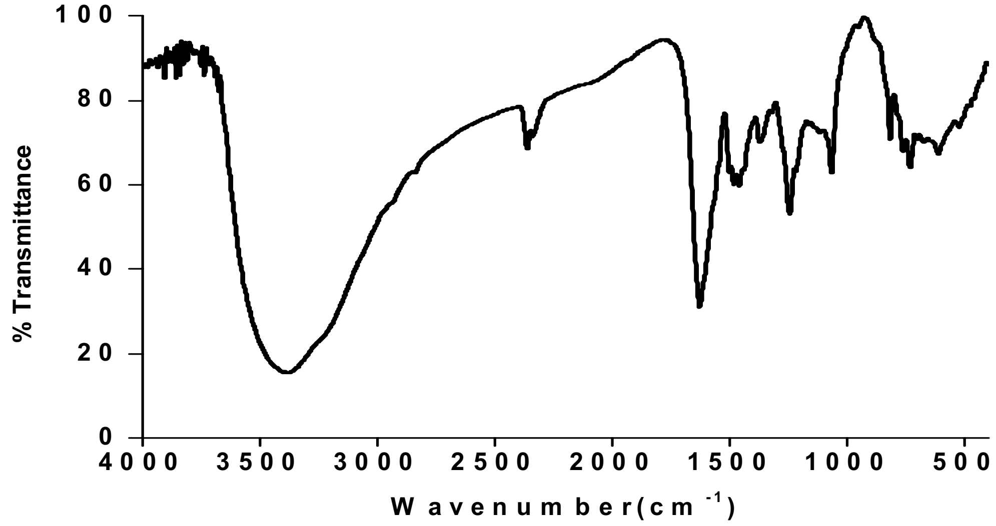


Figure 4.7: FT-IR spectrum of cobalt complex

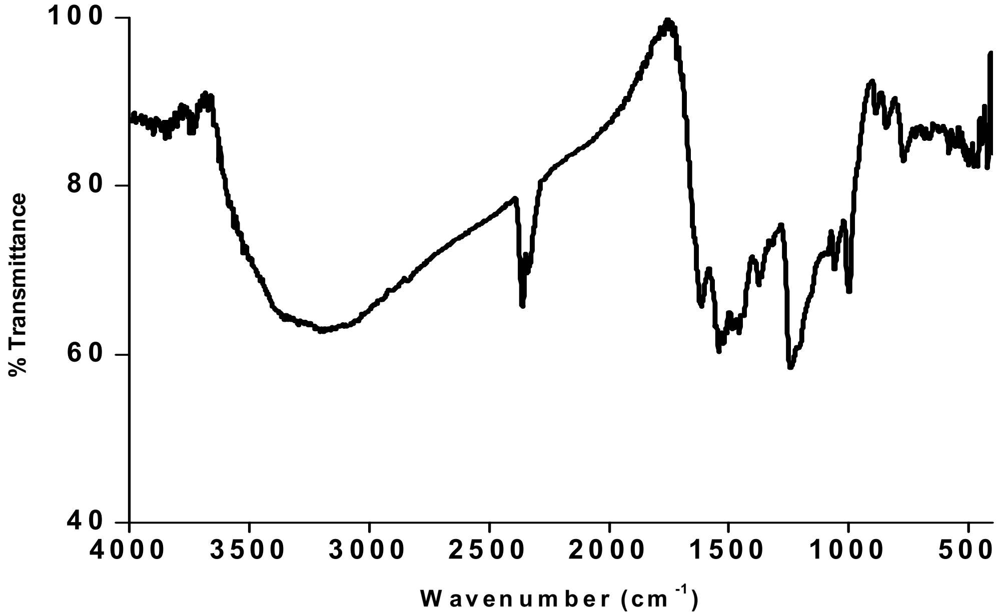


Figure 4.8: FT-IR spectrum of copper complex

Thus based on the elemental analysis, molar conductance, TG and IR studies, the following molecular formula were assigned for the complexes $[Mn(ohmbd)_2(H_2O)_2]H_2O$ (for the manganese complex), $[Co(ohmbd)_2]2H_2O$ (for the cobalt complex) and $[Cu(ohmbd)_2(H_2O)_2]H_2O$ (for the copper complex). The analytical data of the complexes agree with the above mentioned molecular formula (Table 4.1). Thus in the complexes, the perimidine (2dpm) has been rearranged to form the Schiff base 2–hydroxy–3–methoxybenzalidine–1,8–diaminonaphthalene (Hohmbd).

4.3.2.3 Magnetic susceptibility measurements

The room temperature magnetic moment (μ_{eff}) values (Table 4.2) suggest that all these complexes are in +2 oxidation state. The magnetic moment of 2.01 B.M. falls within the range normally observed for octahedral Cu(II) complexes[20]. The magnetic moment value of Co(II) is 4.66 B.M indicating tetrahedral geometry[21, 22] for the complex. The magnetic moment value of Mn(II) complex was found to be 5.8 B.M, which agrees with the value expected for high spin octahedral d^5complexes[23].

4.3.2.4 Electronic spectra

The UV-Vis spectra of the compound 2dpm and the complexes of Hohmbd are recorded in dichloromethane in the frequency range from 50000–10000 cm^{-1}. Electronic spectra of 2dpm and the complexes of Hohmbd are given in Figures 4.9–4.12. The spectral data are presented in Table 4.5. The electronic spectra of 2dpm in dichloromethane (10^{-5} mol l^{-1}) exhibit three major peaks. The aromatic band at 34360 cm^{-1} is due to benzene $\pi \rightarrow \pi^*$transition [24, 25]. The band at 30210 cm^{-1} can be assigned to the imino $\pi \rightarrow \pi^*$transition. By dissolving in non-polar solvents like dichloromethane equilibrium is gradually established[26–29] between the ring closed and an extended π-conjugated system of the ring opened imine form[30].

Shift in the positions of some of these regions of absorption in the spectra of the complexes can be taken as a positive evidence of complex formation. Cobalt complex shows two bands around 34480 cm^{-1} and 29410 cm^{-1} which can be assigned to the charge transfer transitions. The ground state of tetrahedral d^7 system is $^4A_2$. The bands at 23310 cm^{-1} and 11190 cm^{-1} can be assigned to $^4A_2 \rightarrow {}^4T_1(P)$ and $^4A_2 \rightarrow {}^4T_1(F)$ transitions respectively. Tetrahedral complexes for Co(II) are in fact more in number than those for other metal ions, since octahedral site preference energy is smaller for Co(II) ion compared to other metal ions. The deep greenish – blue color of the complex is also indicative of tetrahedral geometry.

In the case of copper(II) complex, the spectrum consists of bands centered in the range 15870 – 16,420 m^{-1} and 17,540 – 22,020 cm^{-1}. The ^2E_g and $^2T_{2g}$ states of the octahedral Cu(II) ion (d^9) split under the influence of the tetragonal distortion, and the distortion can be such as to cause the 3 transitions, $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{2g}$ to remain unresolved in the spectra[31]. This assignment is in agreement with the general observation that Cu(II) d-d transitions are normally close in energy[32]. A moderately intense peak observed in the range of 21,450 – 26,450 cm^{-1} is due to ligand-metal charge transfer transition[33]. For the high spin Mn(II) complexes, the ground state is $^6A_1$ in a weak field so that all excited states of d^5 ion have different spin multiplicity and hence transitions to them are spin forbidden. Therefore absorption bands due to d-d transitions are extremely weak and were not observed.

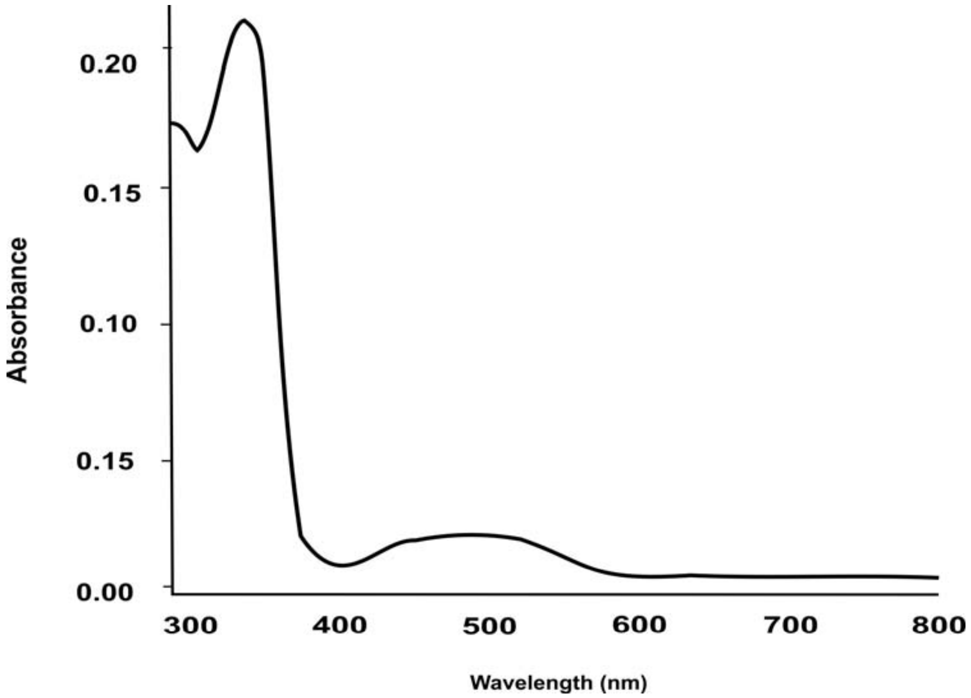


Figure 4.9: The UV-Vis spectrum of 2dpm

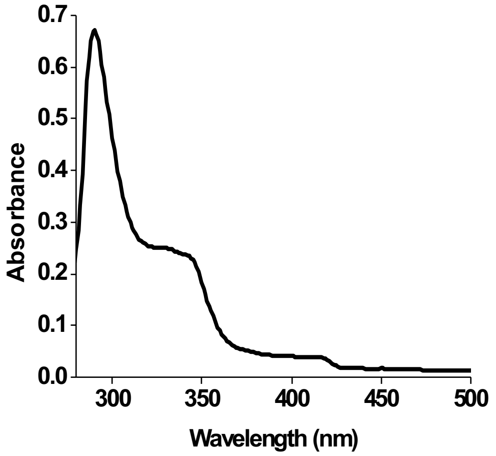
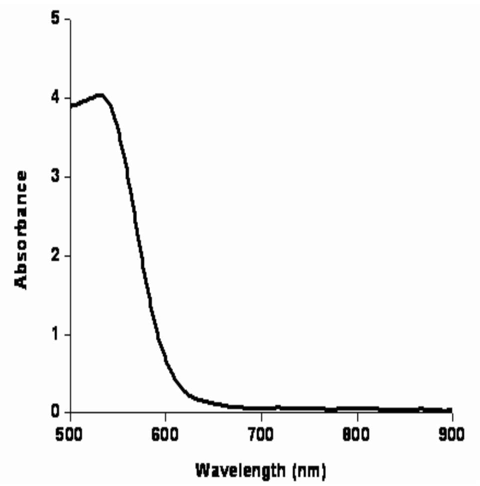
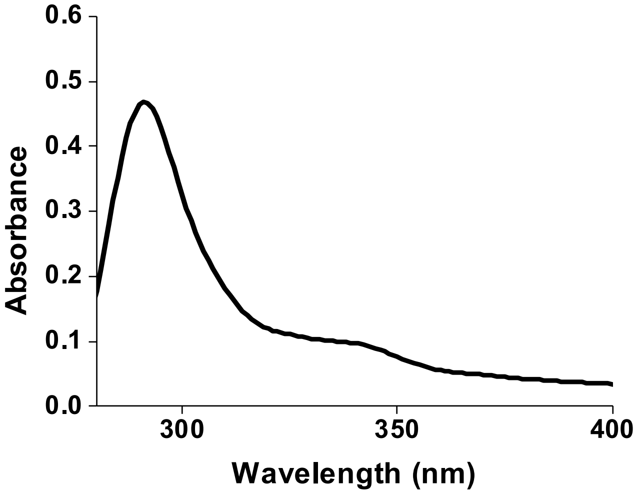


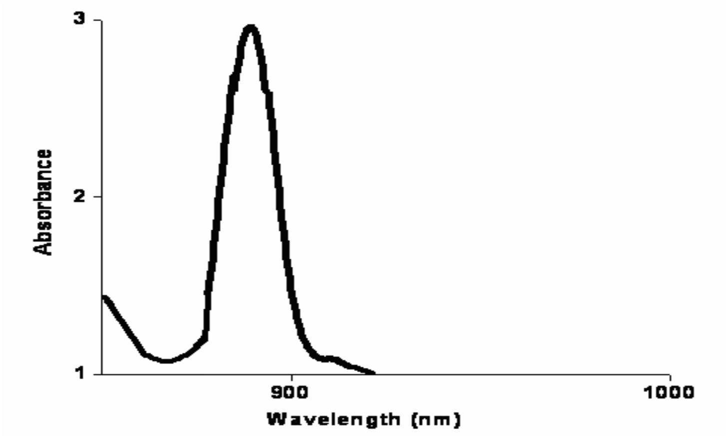
Figure 4.10: The UV-Vis spectrum of $[Mn(ohmbd)_2(H_2O)_2].H_2O$



$[Mn(ohmbd)_2(H_2O)_2].H_2O$ (conc.)



[Co(ohmbd)$_2$].2H$_2$O



Co(ohmbd)$_2$].2H$_2$O (conc.)

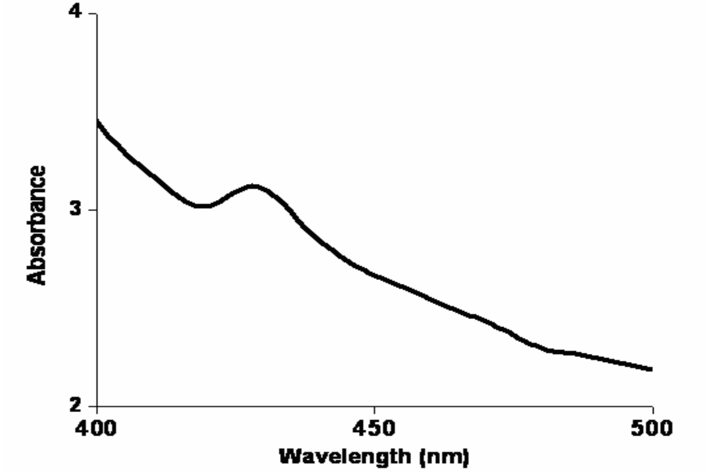


Figure 4.11: The UV-Vis spectrum of [Co(ohmbd)$_2$].2H$_2$O (conc.)

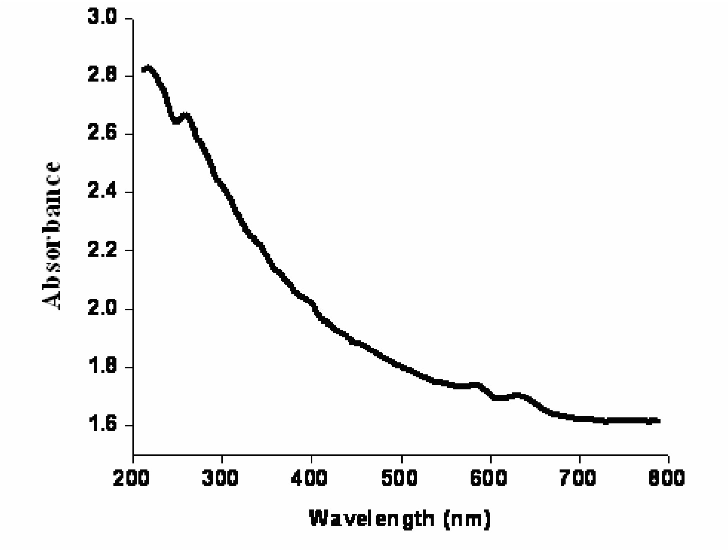


Figure 4.12: The UV-Vis spectrum of $[Cu(ohmbd)_2(H_2O)_2].H_2O$

Table 4.5: UV-Vis spectral assignments of 2dpm and complexes

Compound	Absorption Maxima		Tentative assignments
	(cm^{-1})	log ε (ε in L mol^{-1} cm^{-1})	
2dpm	34360	3.74	$\pi\rightarrow\pi^*$
	30210	2.92	$\pi\rightarrow\pi^*$
$[Mn(ohmbd)_2(H_2O)_2].H_2O$	34240	3.55	$\pi\rightarrow\pi^*$
	29760	3.26	$\pi\rightarrow\pi^*$
	24090	0.89	$^2B_{1g} \rightarrow {}^2E_g$
	18650	0.93	$^2B_{1g} \rightarrow {}^2A_{1g}$
$[Co(ohmbd)_2].2H_2O$	34480	3.89	$\pi\rightarrow\pi^*$
	29410	3.43	CT
	23310	0.73	$^4A_2 \rightarrow {}^4T_1(P)$
	11190	1.40	$^4A_2 \rightarrow {}^4T_1(F)$
$[Cu(ohmbd)_2(H_2O)_2].H_2O$	38910	3.47	$\pi\rightarrow\pi^*$
	25250	3.43	$\pi\rightarrow\pi^*$
	15870	0.66	$^2B_{1g} \rightarrow {}^2B_{2g}$

4.3.2.5 EPR spectra

The EPR spectra of the complexes (Figures 4.16 and 4.17) in the polycrystalline state at 298 K in solution (DMF) at 77 K were recorded in the X–band, using 100 kHz field modulation and the g tensors were calculated relative to the standard marker TCNE (g=2.003). The EPR parameters calculated from the spectrum are given in Table 4.6.

For the copper(II) complex, absence of hyperfine splitting may be due to strong dipolar and exchange interaction between the copper(II) ions in the unit cell. . The spectrum of copper complex is axial with $g_{||} = 2.4$ and $g_{\perp} = 2.1$ (Figure 4.13). This type of spectra unfortunately gives no information on the electronic ground state of the copper(II) ion present in the complexes. We could not get the EPR spectrum of the copper(II) complex in solution at LNT due to low solubility in solvents.

The EPR spectrum of the Mn(II) complex shows the usual Mn(II) [S = 5/2] six-line hyperfine pattern (assigned to the $\Delta M_I = 0$ spin allowed transitions) at g = 2.0 (Figure 4.14). Such a strong signal corresponds to dilute mononuclear high-spin Mn(II). The overall structural study of the $[Mn(ohmbd)_2(H_2O)_2]H_2O$ suggest an octahedral geometry.

Table 4.6: EPR spectral data of the complexes

Complexes	EPR parameter
$[Cu(ohmbd)_2(H_2O)_2]H_2O$	$g_{||} = 2.4$ and $g_{\perp} = 2.1$
$[Mn(ohmbd)_2(H_2O)_2]H_2O$	g = 2.0 and A = 0.011 cm^{-1}

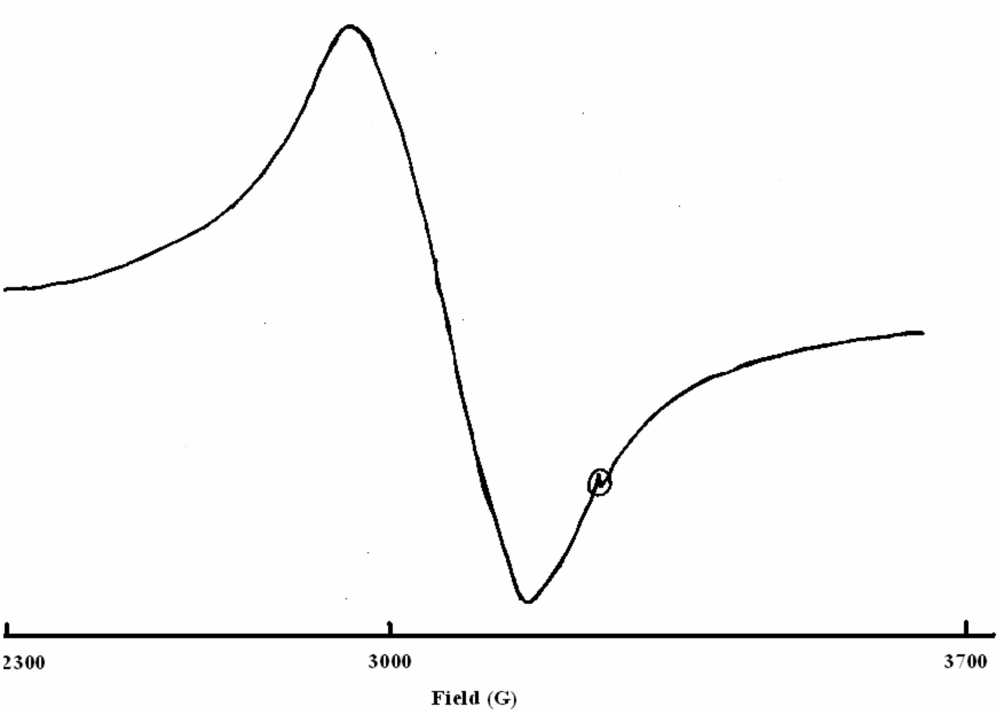


Figure 4.13: EPR spectrum of Cu(II) complex in polycrystalline state at 298K

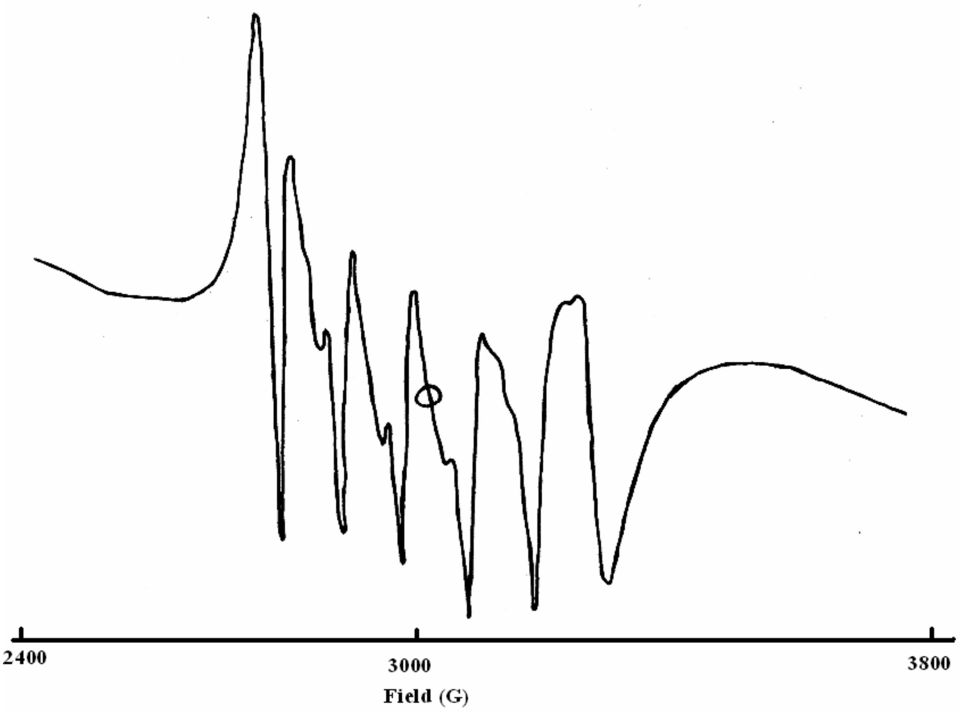
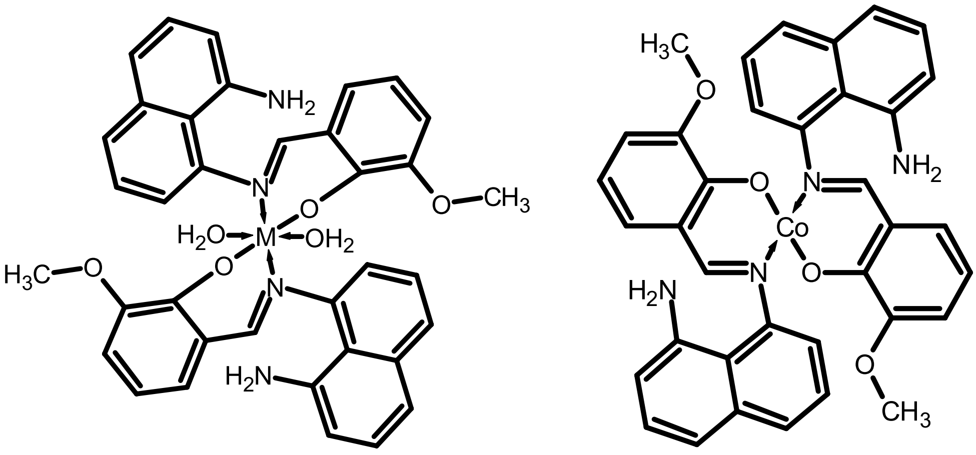


Figure 4.14: EPR spectrum of Mn(II) complex in DMF at LNT

4.4 Conclusions

A new Schiff base is derived from 1,8-diaminonaphthalene and 2-hydroxy-3-methoxy benzaldehyde, by the rearrangement of the perimidine compound, 2dpm. The compound is characterized by elemental analysis, IR and NMR spectra. In non-polar solvents, the perimidine compound (2dpm) gets rearranged to form Schiff base (Hohmbd) in the presence of metal ions. Mn(II), Co(II) and Cu(II) complexes of this Schiff base have been synthesized and characterized. Based on the physicochemical and spectroscopic studies, we propose the following structures for the complexes (Figure 4.15).



M = Mn and Cu

Figure 4.15: The proposed structure of the complexes (solvated water molecules are omitted)

References

1. Dey, S. K.; Mondal, N.; Fallah, M. S. E.; Vicente, R.; Escuer, A.; Solans, X.; Bardfa, M. F.; Matsushita, T.; Gramlich, V.; Mitra, S. Inorg. Chem. 43 (2004) 2427.

2. Choudhury, C. R.; Dey, S. K.; Karmakar, R.; Wu, C. D.; Lu, C. Z.; Fallah, M. S. E.; Mitra, S. New J. Chem. 27 (2003) 1360.

3. Holm, R. H.; OConnor, M. Prog.Inorg. Chem. 14 (1971) 401.
4. Holm, R. H.; Evert, G. W.; Chakravorty, A. Prog. Inorg. Chem. 7 (1966) 83.
5. Coles, S. J.; Hursthouse, M. B.; Kelly, D.G.; Toner, A. J.; Walker, N. M. J. Chem. Soc., DaltonTrans. (1998) 3489 and references therein.
6. Miyasaka, H.; Ieda, H.; Matsumoto, N.; Crescenzi, R.; Floriani, C. Inorg. Chem.37 (1998) 255.
7. Trosch, A.; Vahrenkamp, H. Inorg. Chem. 40 (2001) 2305.
8. Kato, M.; Muto, Y. Coord. Chem. Rev. 92 (1988) 45.
9. Al-Betar, A-R.; El-Rayyes, A.; Klein, U. K. A. J. Fluoresc. 15 (2005) 689.
10. Alder, R. W.; Bryce, M. R.; Goode, N. C.; Miller, N. J. Chem. Soc., Perkin Trans. 1. (1981) 2840.
11. Geary, W. J. Coord. Chem. Rev. 7 (1971) 81.
12. Sallam, S. A. Transition Met. Chem. 30 (2005) 341.
13. Annigeri, S. M.; Sathisha, M. P.; Revankar, V. K.; Transition Met. Chem. 32 (2007) 81.
14. Issa, Y. M.; Abdel Fattah, H. M.; Soliman, A. A. J. Therm. Anal. Calorim. 42 (1994) 1175.
15. Abdel-Ghani, N. T.; Sherif, O. E. Thermochim. Acta. 156 (1989) 69.
16. Yeap, G. Y.; Ha, S. T.; Ishizawa, N.; Suda, K.; Boey, P. L.; Mahmood, W. A. K. J. Mol. Struct. 658 (2003) 87.
17. Rodriguez deBarbarin, C. O.; Bailey, N. A.; Fenton, D. E.; He, QY. J. Chem. Soc. Dalton Trans. (1997) 161.
18. Damus, H.; Fernaxdo, QReiser, H. Inorg. Chem. 3 (1964) 928.

19. Nakamoto, K. Coordination Compounds. In Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th Ed.; John Wiley and Sons, Inc.: New York. (1986).

20. Krzyminiewska, V. P.; Litkowska, H.; Paryzek, W. R. Monatsh. Chem. 130 (1999) 243.

21. Prasad, R.; Thankachan, P. P.; Thomas, M. T.; Pathak, R. J. Ind. Chem. Soc. 78 (2001) 28.

22. Gaur, N. K.; Sharma, R.; Sindhu, R. S. J. Ind. Chem. Soc. 78 (2001) 26.

23. Lever, A. B. P. Inorganic Electronic Spectroscopy. Elsevier, New York. (1968).

24. Mazumdar, A. K. D.; Saha, N. K.; Banerji, K. D. J. Ind. Chem. Soc. LVI (1979) 999.

25. Mathes, R. A.; Gregory, J. T. J. Amer. Chem. Soc, 74 (1952) 3867.

26. Minkin, V. I. Chem. Rev. 104 (2004) 2751.

27. Minkin, V. I.; Komissarov, V. N.; Kharlanov, V. A. Perimidinespirocyclohexadienones. In Organic Photochromic and Thermochromic compounds; Crano, J. C.; Guglielmetti, R. J. Eds., Plenum Press: New York. 1 (1999) 315.

28. (a) Komissarov, V. N.; Gruzdeva, E. N; Kharlanov, V. A.; Olekhnovich, L. P.; Borodkin, G. S.; Khrustalev, V. N.; Lindeman, S. V.; Struch Kov, Y. T.; Kogan, V. A. Minkin, V. I. Izv. Akad. Nauk. SSSR. 46 (1997) 2028.

29. Maloshitskaya, O.; Sinkkonen, J.; Ovcharenko, V. V.; Zelenin, K. N.; Pihlaja, K. Tetahedron. 60 (2004) 6913.

30. Davis, R.; Tamaoki, N. Org. Lett. 7 (2005) 1461.

31. Manonmani, J.; Thirumurugan, R.; Kandaswamy, M.; Kuppayee, M.; Raj, S. S. S.; Ponnuswamy, M. N.; Shanmugam, G.; Fun, H. K. Polyhedron. 19 (2000) 2011.

32. Sanmartin, J.; Bermejo, M. R.; Deibe, A. M. G.; Maneiro, M.; Lage, C.; Filho, A. J. C. Polyhedron. 19 (2000) 185.

33. Bertoncello, K.; Fallon, G. D.; Murray, K. S.; Tiekink, E. R. T. Inorg. Chem. 30 (1991) 3562.

****◆****

Chapter

4-Hydroxy-3-methoxybenzalidine-1, 8-diaminonaphthalene and it's Mn(II), Co(II) and Cu(II) complexes: Synthesis and characterization

5

Contents

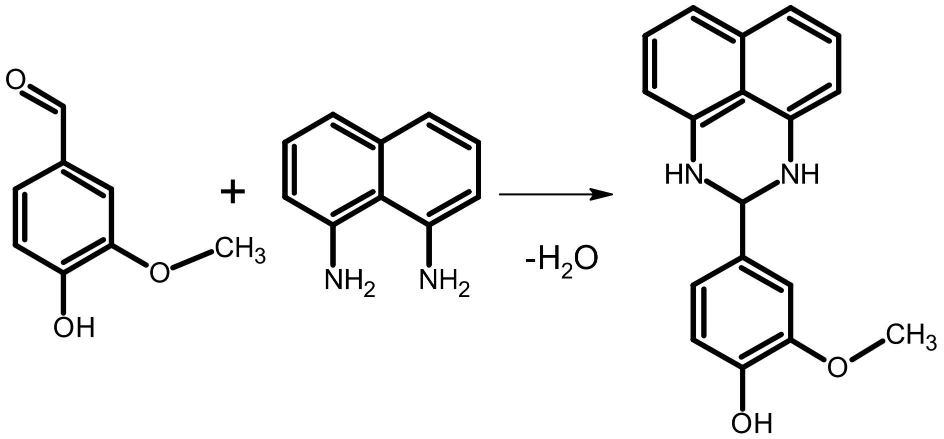
> *"In nature's infinite book of secrecy a little can be read"*
>
> ***William Shakespeare***

5.1 Introduction

4-Hydroxy-3-methoxybenzaldehyde has both aldehydic and phenolic groups and is capable of undergoing many types of reactions. About 40 % of this compound is consumed in manufacturing drugs such as Aldomet, L-dopa and Trimethaprim[1]. Synthetic vanillin is used in both food and non-food applications, in fragrances and as a flavoring in pharmaceutical preparations. There are number of reports on the Schiff bases derived from 4-hydroxy-3-methoxy benzaldehyde and different amines[2-4].

We have tried the reaction of 4-hydroxy-3-methoxy benzaldehyde with 1,8-diaminonaphthalene; which yielded a ring closure compound, 4-(2,3-dihydro-1*H*-perimidin-2-yl)-2-methoxyphenol[5] (4dpm). The formation of 4dpm is given in Scheme 5.1. The interaction of this compound with Mn(II), Co(II) and

Cu(II) lead to the formation of the Schiff base, 4–hydroxy–3–methoxybenzalidine–1,8–diaminonaphthalene (hmbd) which has resulted from the opening up[6, 7] of the perimidines. The complexes have been characterized by various physico chemical and spectroscopic techniques. In this chapter, the results of our studies on these complexes are presented.



Scheme 5.1: The formation of 4dpm by ring closure

5.2 Experimental

5.2.1 Materials and methods

The materials and techniques employed for the synthesis and characterization of 4dpm and metal complexes of the Schiff base derived from 4dpm are given in chapter II.

5.2.2 Preparation of the product formed from 4-hydroxy-3-methoxy benzaldehyde and 1,8-diaminonaphthalene

The compound was prepared[5] by refluxing purified[8, 9] 1,8-diaminonaphthalene (0.16 g; 1 mmol) and 4-hydroxy-3-methoxy benzaldehyde (0.15 g; 1 mmol) in methanol (50 mL) for three hours under nitrogen atmosphere(in view of possibility of autoxidation, the process is carried out under inert atmosphere). The product was collected by removing the solvent with rotavapor. The crude product was purified by chromatography on silica gel with hexane/ethyl acetate (80/20 mixture) in 80% yield. The crystal suitable for X-ray crystallography was obtained by keeping the solution of the purified compound in methanol for 4-5 days (yield: 80% m.p.: = 160 °C)

5.2.3 Preparation of complexes

The complexes of Mn(II), Co(II) and Cu(II) were prepared by the following procedure:

The 4dpm (2 mmol, 1.5 g) was dissolved in 1:1 hexane–chloroform solution (~25 mL) and was magnetically stirred in a round bottom flask followed by drop wise addition of 1:1 methanol–chloroform solution (~25 mL) of corresponding salt $MnCl_2.4H_2O$ (1 mmol, 0.50 g), $CoCl_2.6H_2O$ (1 mmol, 0.32 g) or $CuCl_2.2H_2O$ at room temperature (27±2 °C). The precipitate formed was filtered off, washed several times with small quantities of hexane and dried in vacuum over anhydrous calcium chloride.

5.3 Results and discussion

5.3.1 Characterization of the perimidine compound, 4dpm

The 4dpm was characterized by elemental analysis, Infrared spectra, ^{1}H NMR spectra and single crystal X-ray diffraction analysis.

5.3.1.1 Elemental analysis

The analytical data (Found: C, 73.67; H, 5.39; N, 9.42.) of the colourless compound, 4dpm is in good agreement with the expected molecular formula of the perimidine compound; $C_{18}H_{16}N_2O_2$ (Calculated: C, 73.95; H, 5.52; N, 9.58).

5.3.1.2 Infrared Spectra

The important features of the ring closed compound, 4dpm and corresponding spectra are given in Figure 5.1. The IR spectrum of the compound shows bands at 3421 and 3364 cm^{-1}, which might be due to the presence of –OH and =NH groups respectively. The band at 2930 cm^{-1} is due to alkyl C–H bond stretching of methoxy group.

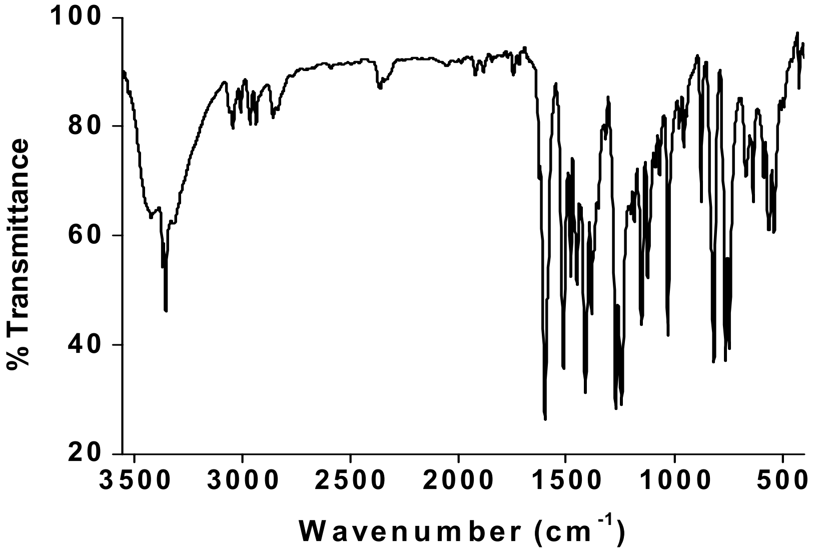


Figure 5.1: IR spectrum of 4dpm

5.3.1.3 ^{1}H NMR spectra

The ^{1}H NMR spectra of the compound (4dpm) was recorded in d$_6$-dimethylsulphoxide solution using TMS as the internal standard as given in Figure 5.2. The chemical shifts of different protons are as follows:

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 3.91 (s, 3H, CH$_3$), 4.50 (s, 2H, NH), 5.37 (s, 1H, OH), 5.79 (s, 1H, CH), 6.49-6.52 (m, 2H, aromatic), 6.91-7.04 (m, 2H, aromatic), 7.19-7.27 (m, 5H, aromatic) ppm.

The peak observed at 4.50 ppm is assignable to the –NH proton in the fused heterocyclic ring and a peak at 3.91ppm confirms the presence of methyl proton. The –OH protons appear at 5.37 ppm and multiplet signals observed in the 6.49 – 7.27 ppm range are due to aromatic protons.

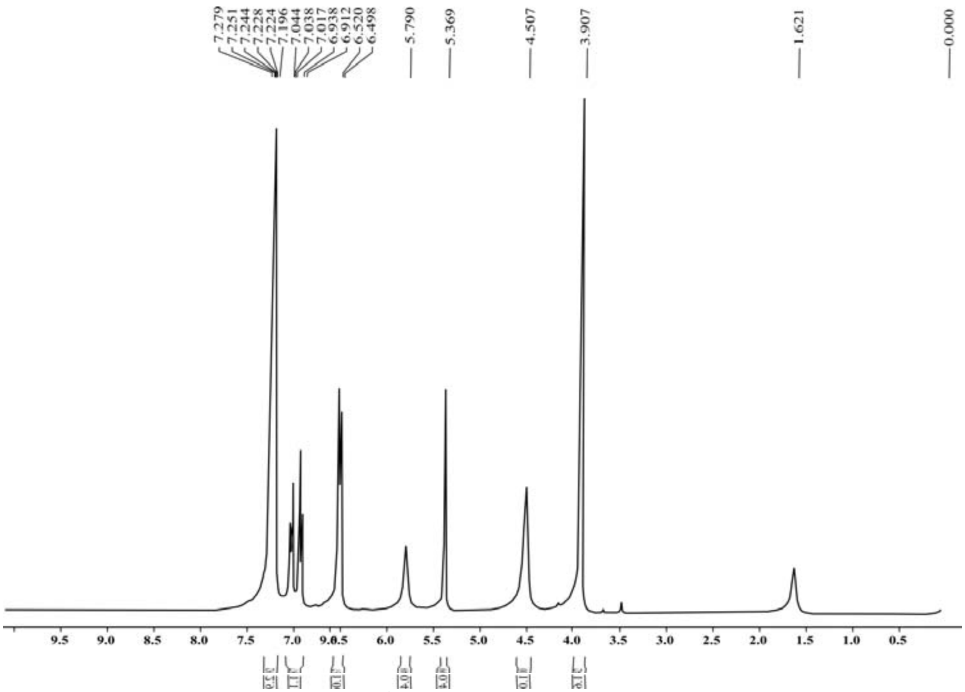


Figure 5.2: ^{1}H NMR spectrum of 4dpm

5.3.1.4 Single crystal X-ray diffraction analysis

The single crystal^5 suitable for XRD was obtained by the slow evaporation of methanolic solution of the compound. The compound crystallizes in an orthorhombic crystal system with the space group $Pna2_1$. A summary of crystallographic data and refinement parameters are given in Table 5.1.

The molecular structure of the compound was solved at 298 K. Figure 5.3 gives the ORTEP diagram of the compound with atomic labeling scheme. The asymmetric unit of compound contains two crystallographically independent molecules. The naphthalene moiety of perimidine ring and benzene ring of 3-methoxy-4-hydroxybenzaldehyde is nearly perpendicular with an angle of 86.53°. The loss of planarity of the perimidine ring is worth mentioning. The C8 atom lies 0.578 Å above the plane of perimidine ring and hence there is a large deviation. The compound, 4dpm is stabilized by intermolecular O–HO. hydrogen bonding.

Table 5.1: Crystal data summary of 4dpm

Crystal data	
Parameters	**4dpm**
Empirical formula	$C_{18}H_{16}N_2O_2$
Formula weight	292.33
Temperature (K)	298(2)
Crystal system	Orthorhombic
Space group	$Pna2_1$
a (Å)	8.7813 (15)
b (Å)	7.4057 (12)
c (Å)	45.282 (8)
α (deg)	90
β (deg)	90
γ (deg)	90
V ($Å^3$)	2944.8(9)
Z	8
D_{cal} (Mg/m^3)	1.319
M(mm^{-1})	0.09
F (000)	1232
T_{min}	0.971
T_{max}	0.990
No. of reflns with I $>$ 2σ(I)	2713
$R[F^2 > 2\sigma(F^2)]$	0.061
$wR(F^2)$	0.157

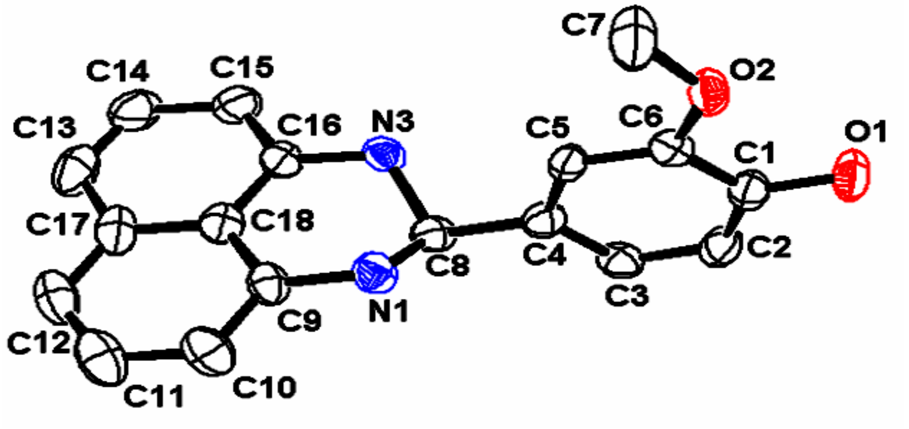


Figure 5.3: ORTEP diagram of compound 4dpm showing the atom labeling scheme with 50% probability ellipsoids

Spectral data and crystal studies of the 4dpm indicate that the compound is not a Schiff base, but is a ring closed compound (perimidine) as depicted in Scheme 3.1.

5.3.2 Characterization of the complexes derived from 4dpm

The Mn(II), Co(II) and Cu(II) complexes were prepared by the stoichiometric reaction of the metal ions with the compound, 4dpm. The color, yield and elemental analysis data of the complexes derived from 4dpm are given in Table 5.2. The molar conductivity values (Table 5.3) in 10^{-3} M DMF solutions suggest non-electrolytic nature of the complexes[10].

Table 5.2: Analytical data of the complexes derived from 4dpm

Compound	Color	Yield (%)	Analytical data. Found (calculated)%				
			M (%)	C (%)	H (%)	N (%)	Cl (%)
The manganese complex	orange	55	7.19 (7.20)	56.55 (56.56)	5.01 (5.03	7.33 (7.35)	9.27 (9.28)
The cobalt complex	brown	65	7.67 (7.68)	56.26 (56.28)	4.98 (4.99)	7.29 (7.30)	9.23 (9.24)
The copper complex	black	70	8.22 (8.23)	55.92 (55.94)	4.95 (4.97)	7.25 (7.27)	9.17 (9.18)

Table 5.3: Conductivity and magnetic moment data of complexes

Compound	μ_{eff} (BM)[a]	Molar conductance ($ohm^{-1}cm^2mol^{-1}$)
The manganese complex	5.80	20
The cobalt complex	5.10	39
The copper complex	1.90	14

[a]Magnetic moment value per metal atom in the complex

5.3.2.1 Thermal analysis

Thermal stability of the complexes of qcdn was investigated using TG–DTG under nitrogen atmosphere at heating rate of 10 °C min^{-1} over a temperature range of 40–1000 °C. The TG–DTG plots of the complexes are given in Figures 5.4–5.6. There is weight loss below 120 °C for all the complexes suggesting the presence of lattice water molecules[11]. The thermogravimetric analysis data of the complexes upto 200 °C give an indication about number and nature of water molecules in the complex (Table 5.4). Loss of one lattice water and two coordinated water molecules[12-14] was observed for all the complexes in the temperature range 50–210 °C. Above 350 °C, the complexes begin to decompose and finally give the corresponding metal oxide. All the complexes are found to be thermally stable and exhibit multi stage decomposition pattern.

Table 5.4: Thermogravimetric analysis data (below 220 °C)

Complex	Temperature range, °C	% loss	Fragment lost	Nature of water lost
The manganese complex	90-130	4.5	1 H_2O	Lattice water
	150-200	7.5	2 H_2O	Coordinated water
The cobalt complex	80-120	4.8	1 H_2O	Lattice water
	200-220	7.9	2 H_2O	Coordinated water
The copper complex	90-120	4.3	1 H_2O	Lattice water
	170-210	8.4	2 H_2O	Coordinated water

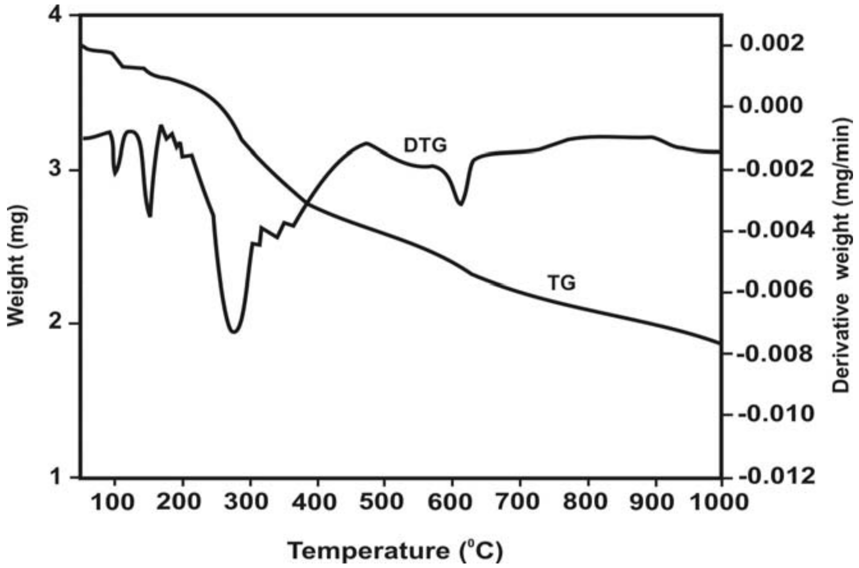


Figure 5.4: TG–DTG of the manganese complex

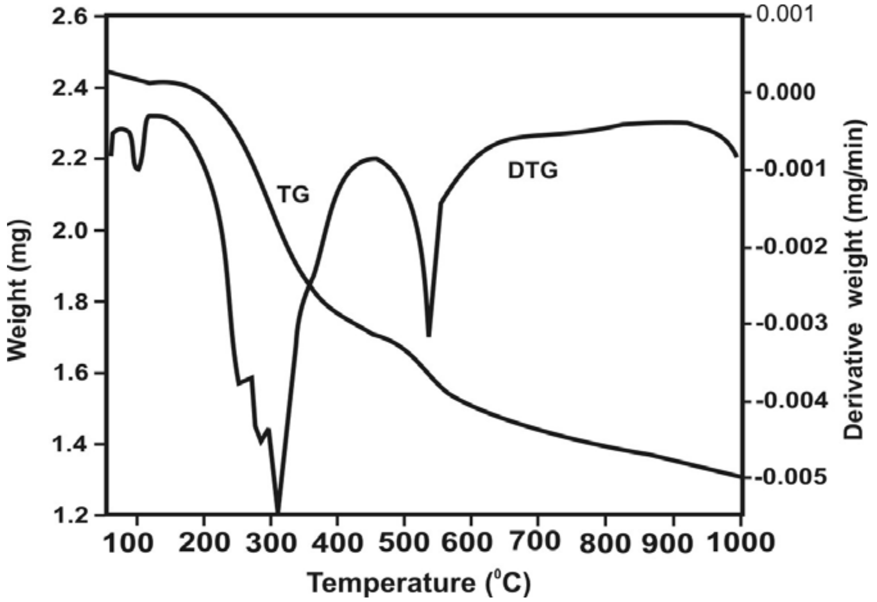


Figure 5.5: TG–DTG of the cobalt complex

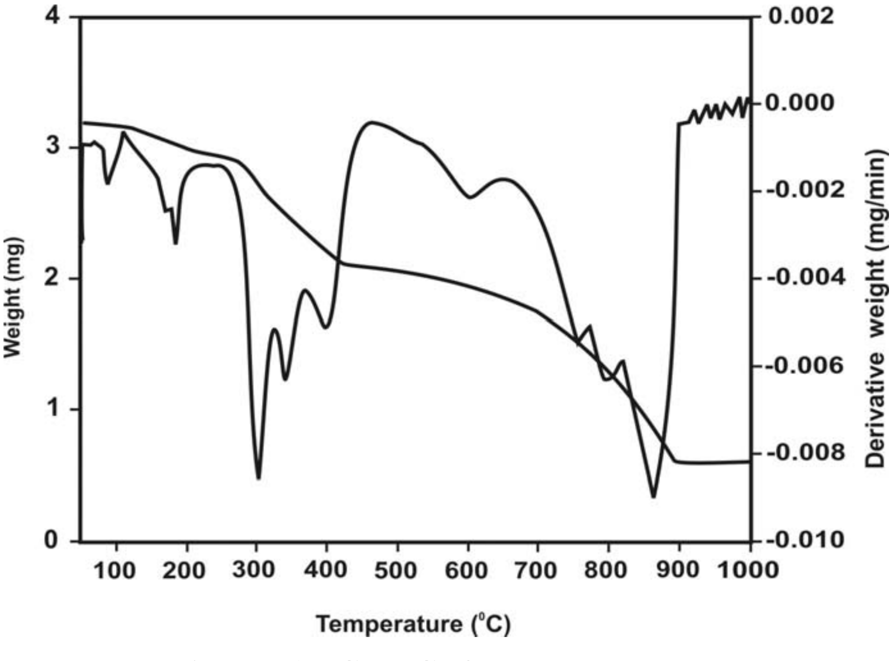


Figure 5.6: TG–DTG of the copper complex

5.3.2.2 Infrared spectra

Most important IR spectral bands of 4dpm and metal complexes derived from 4dpm are listed in Table 5.5. The IR spectra of the complexes when compared with that of 4dpm (Figure 5.1) show remarkable differences. In the IR spectrum of 4dpm, –NH stretching frequency occur at 3364 cm^{-1}. The complexes exhibit a broad band in the range 3100–3500 cm^{-1} due to the –OH stretching of water molecules[15] (Figures 5.7–5.9). All the complexes show the presence of strong bands in the range 1607–1621 cm^{-1} indicative of the existence of azomethine stretching suggesting the conversion of 4dpm into Schiff base during complexation[16].

The retention of two bands in the range 3361–3444 cm^{-1} in all the spectra of the complexes indicates the non-involvement in coordination to the metal. The broad band is characteristic of υ(OH) of water[17]. This indicates that oxygen atoms are involved in coordination with the metal. Furthermore, bands in the region 825 cm $^{-1}$ due to rocking vibrations of water[18] are characteristic of coordinated water molecules. Bands observed at 426–465 and 488–548 cm^{-1} are due to υ(M–N) and υ(M–O) respectively[19, 20].

Table 5.5: IR spectral data of 4dpm and its complexes

Assignments (in cm^{-1})	υ(O–H)$^{a/b}$	υ(C=N)^{c}	υ(C–O)^{d}	υ(M–N)	δ(O–H)^{e}
4dpm	3296,3416	–	1028	-	-
The manganese complex	3296, 3416	1621	1027	455	1159
The cobalt complex	3296, 3461	1615	1028	449	1153
The copper complex	3289, 3416	1607	1023	449	-

^{a}υ(N–H)/ υ(O–H) of the precursor ligand or; ^{b}υ(O—H) of coordinated water molecule; ^{c}–CH=N of azomethine group; ^{d}methoxyl υ(C–O); ^{e}δ(O–H) of coordinated water molecule.

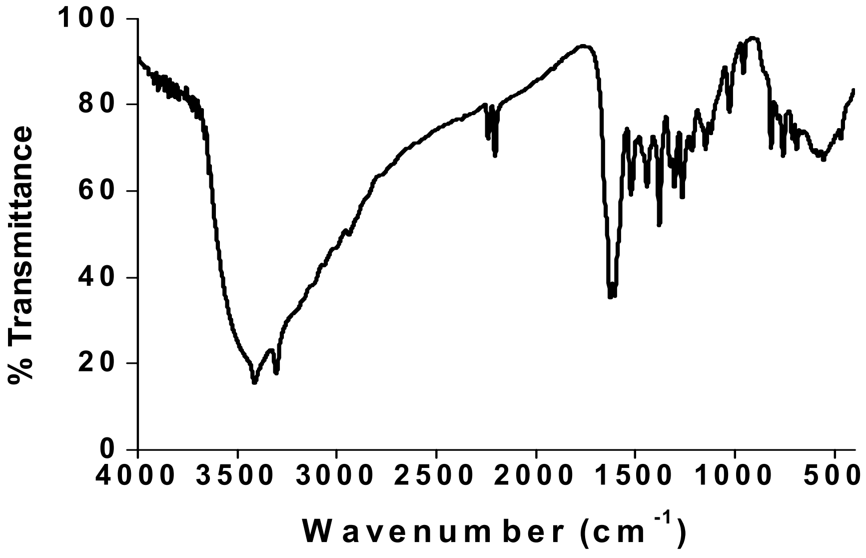


Figure 5.7: FT-IR spectrum of manganese complex

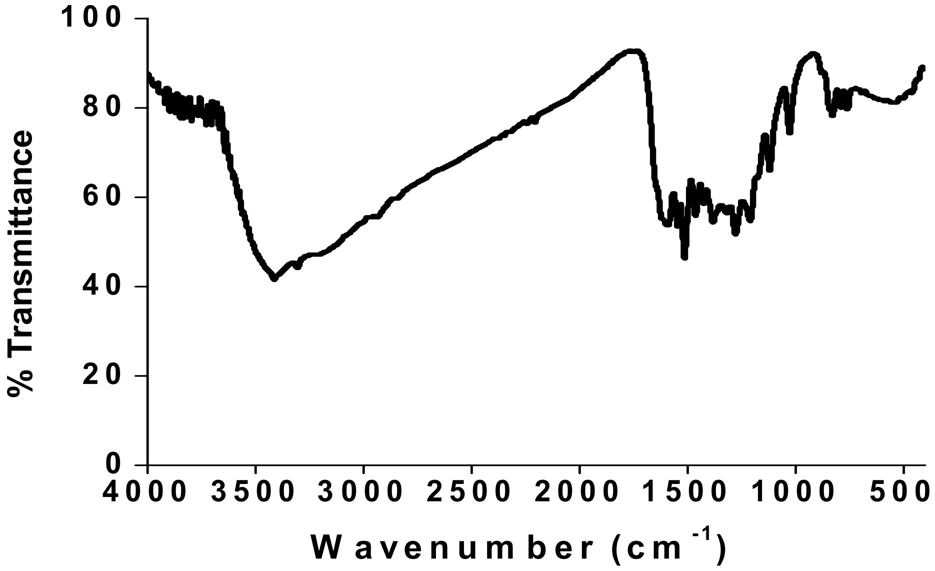


Figure 5.8: FT-IR spectrum of cobalt complex

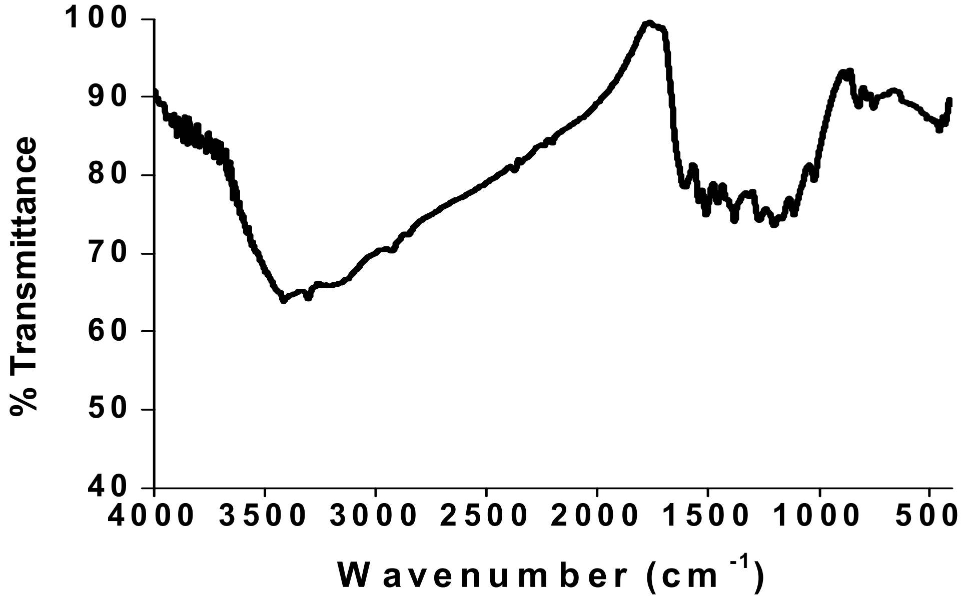


Figure 5.9: FT-IR spectrum of copper complex

Thus based on the elemental analysis, molar conductance, TG and IR studies, the following molecular formula were assigned for the complexes $[Mn(hmbd)_2Cl_2(H_2O)_2]H_2O$ (for the manganese complex), $[Co(hmbd)_2Cl_2(H_2O)_2]H_2O$ (for the cobalt complex) and $[Cu(hmbd)_2Cl_2(H_2O)_2]H_2O$ (for the copper complex). The analytical data of the complexes agree with the above mentioned molecular formula. The calculated values are shown in brackets in Table 5.2. Thus in the complexes, the perimidine (4dpm) does not exist as such but get converted to the Schiff base 4–hydroxy–3–methoxybenzalidine–1,8–diaminonaphthalene (hmbd).

5.3.2.3 Magnetic susceptibility measurements

The room temperature magnetic moment (μ_{eff}) values of the complexes are presented in Table 5.3. The values suggest that all these complexes are in +2 oxidation state. The magnetic moment value of the Manganese(II) complex was found to be 5.8 B.M, which lies very near to the value expected for high spin octahedral complex[9]. The ground state is $^4T_{1g}$ for the cobalt(II) octahedral complexes. Therefore a large orbital contribution to magnetic moment is expected in these cases. The ground state for the tetrahedral cobalt(II) complex is $^4A_2$ and a value close to the spin only value of 3.8 might be expected. The magnetic moment of 5.1 B.M suggest an octahedral structure for this complex. The magnetic moment of 1.93–2.07 B.M. falls within the range normally observed for octahedral copper(II) complexes [21].

5.3.2.4 Electronic spectra

The UV-Vis spectra of the compound 4dpm and the complexes of hmbd are recorded in dichloromethane in the frequency range from 50000–10000 cm^{-1}. Electronic spectra of 4dpm and the complexes of hmbd are given in Figures 5.10–5.13. The spectral data are presented in Table 5.6.

The electronic spectra of the compound, 4dpm in dichloromethane (10^{-5} mol l^{-1}) exhibit four major peaks. In this spectrum the bands at 45660 and 37030 cm^{-1} are attributed to benzene $\pi \rightarrow \pi^*$transition. The band at 29670 cm^{-1} is assigned to the imino $\pi \rightarrow \pi^*$transition. Compared to the precursor ligand 4dpm, imine $\pi \rightarrow \pi^*$transitions of the complexes were shifted to some extent, probably because of the coordination of the nitrogen atom of the imine group to the metal ion [22-24].

The electronic spectrum of manganese(II) complex exhibits strong bands in the region of 40000 cm^{-1} to 25000 cm^{-1}, which might be due to the high intensity of $\pi \rightarrow \pi^*$ transitions. For the high spin Mn(II) complexes, the ground state is $^6A_1$ in a weak field so that all excited states of d^5 ion have different spin multiplicity and hence transitions to them are spin forbidden. Therefore absorption bands due to d-d transitions are extremely weak and were not seen in the spectrum.

The Co(II) complex exhibits two d-d transitions at 11,580 and 19,120 cm^{-1} and these bands can be assigned to $^4T_{1g} \rightarrow {}^4T_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ respectively. The other transition expected for an octahedral structure $^4T_{1g} \rightarrow {}^4A_{2g}$ is normally weak and this band was not observed for the complex. The electronic spectral data thus suggest a distorted octahedral structure[25] for the complex. A band at 16, 120 cm^{-1} is due to $^2B_{1g} \rightarrow {}^2B_{2g}$ transition for the Cu(II) complex and an effective magnetic moment of 1.9 B. M. are suggestive of an octahedral geometry around Cu(II) ion[26-28].

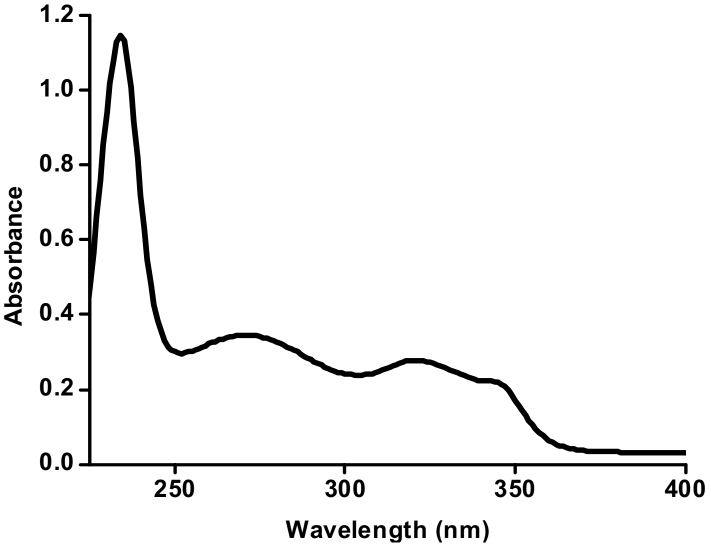


Figure 5.10: The UV-Vis spectrum of 4dpm

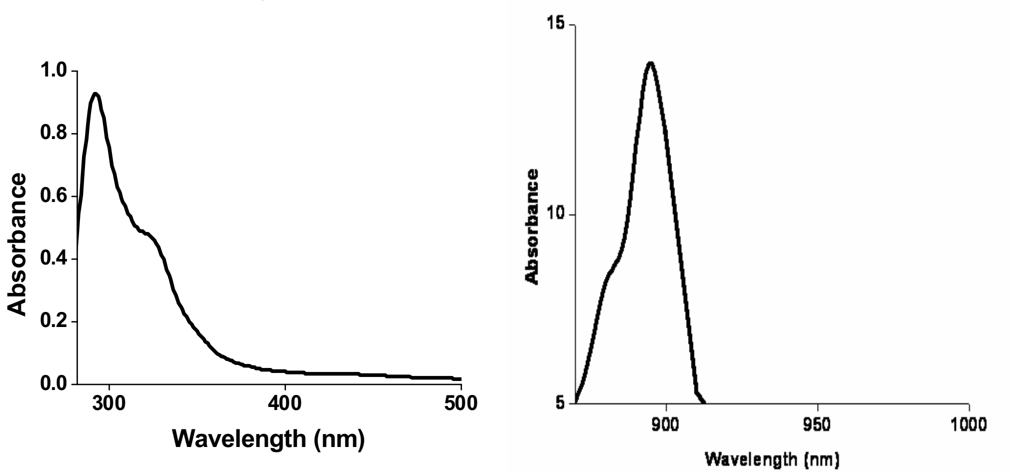


Figure 5.11: The UV-Vis spectrum of $[Mn(hmbd)_2Cl_2(H_2O)_2]H_2O$

$[Mn(hmbd)_2Cl_2(H_2O)_2]H_2O$ (conc.)

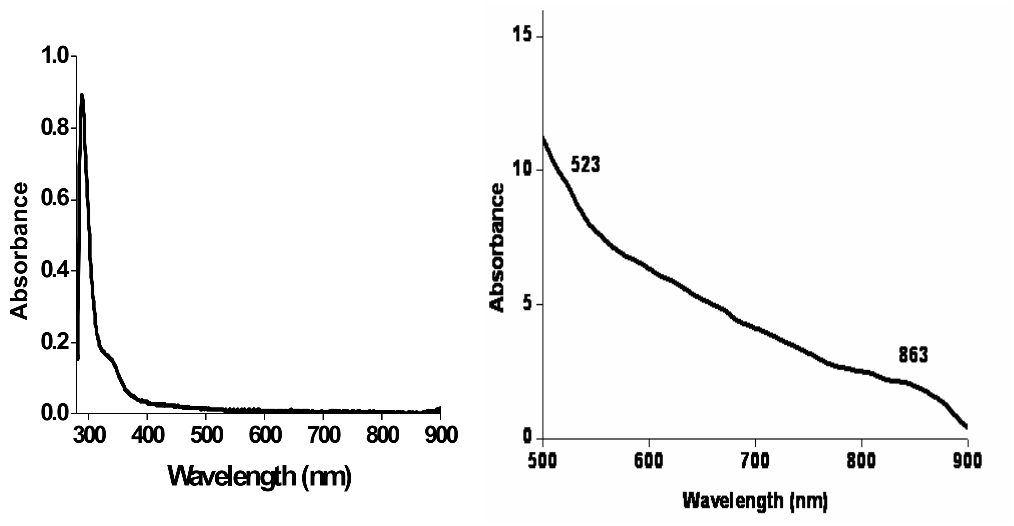


Figure 5.12: The UV-Vis spectrum of **$[Co(hmbd)_2 Cl_2(H_2O)_2]H_2O$(conc.)**

$Co(hmbd)_2Cl_2(H_2O)_2]H_2O$

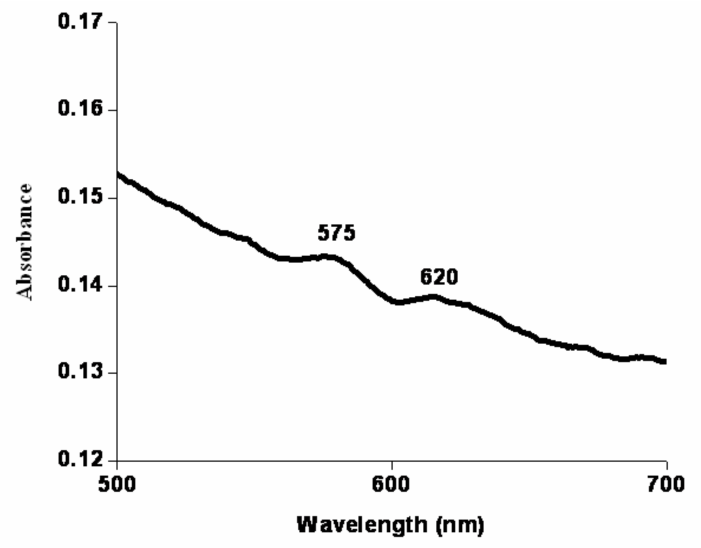


Figure 5.13: The UV-Vis spectrum of Cu(II)

Table 5.6: UV-Vis spectral assignments of 4dpm and complexes

Compound	Absorption Maxima (cm^{-1})	log ε (ε in L mol^{-1} cm^{-1})	Tentative assignments
4dpm	45660	3.74	$\pi \rightarrow \pi^*$
	37030	2.92	$\pi \rightarrow \pi^*$
	29670	1.90	$\pi \rightarrow \pi^*$
$[Mn(hmbd)_2Cl_2(H_2O)_2]H_2O$	34240	3.53	$\pi \rightarrow \pi^*$
	30860	3.25	$\pi \rightarrow \pi^*$
	23250	0.62	CT
	11170	0.93	$^2B_{1g} \rightarrow {}^2A_{1g}$
$[Co(hmbd)_2Cl_2(H_2O)_2]H_2O$	34482	3.70	$\pi \rightarrow \pi^*$
	29410	3.33	$\pi \rightarrow \pi^*$
	19120	1.10	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$
	11580	1.30	$^4T_{1g} \rightarrow {}^4T_{2g}$
$[Cu(hmbd)_2Cl_2(H_2O)_2]H_2O$	17390	0.94	$^2B_{1g} \rightarrow {}^2A_{1g}$
	16120	0.79	$^2B_{1g} \rightarrow {}^2B_{2g}$

5.3.2.5 EPR spectra

The EPR spectra of the complexes in the polycrystalline state at 298 K in solution (DMF) at 77 K were recorded in the X–band, using 100 kHz field modulation and the g tensors were calculated relative to the standard marker TCNE (g=2.003). The EPR parameters calculated from the spectrum are given in Table 5.7.

In polycrystalline state at 298 K (Figure 5.14), copper complex shows three g'values g_1, g_2 and g_3 at 2.2, 2.1 and 2.0 respectively[29]. The anisotropic rhombic g-tensors with $G < 4.0$ ($G = (g_3 - 2.0023)/ g_\perp - 2.0023)$; $g_\perp = (g_1+g_2)/2$; $G = 0$) suggest exchange coupling interactions in the complex[30]. The absence of hyperfine splitting may be due to strong dipolar and exchange interaction between the copper(II) ions in the unit cell.

In the case of Mn^{2+} ions with five unpaired electrons, $S={}^5/_2$ has $M_s = \pm{}^5/_2$, $\pm{}^3/_2$, $\pm{}^1/_2$ indicate the presence of doubly degenerate spin states known as Kramers degeneracy and no $M_s = 0$ state, leads to special case of zero field splitting. These doublet sets will be slightly different in energy from each other due to the zero field already present. On the application of a magnetic field, each of the doubly degenerate sets will further split, and hence a series of lines will appear in the spectrum (Figure 5.15). Since the manganese nucleus has a nuclear spin $I = {}^5/_2$, each spectral lines due to a particular M_s level undergoes hyperfine splitting into six fine lines. Hence we get a spectrum with five sets of lines corresponding to five transitions with different energy[31] appear at different positions, each with five hyperfine splitting (Figure 5.16). Such a spectrum is obtained in the case of compound $Mn(hmbd)_2Cl_2(H_2O)_2H_2O$ in DMF with five g values of 5.04, 4.99, 3.20, 2.80 and 2.02 (Figure 5.17).

Table 5.7: EPR spectral data of the complexes

Complexes	EPR parameters
$[Cu(hmbd)_2Cl_2(H_2O)_2]H_2O$	g_1 = 2.2; g_2 = 2.1; g_3 = 2.0
$[Mn(hmbd)_2Cl_2(H_2O)_2]H_2O$	g_1 = 5.04; g_2 = 4.99; g_3 = 3.20; g_4 = 2.80; g_5 = 2.02

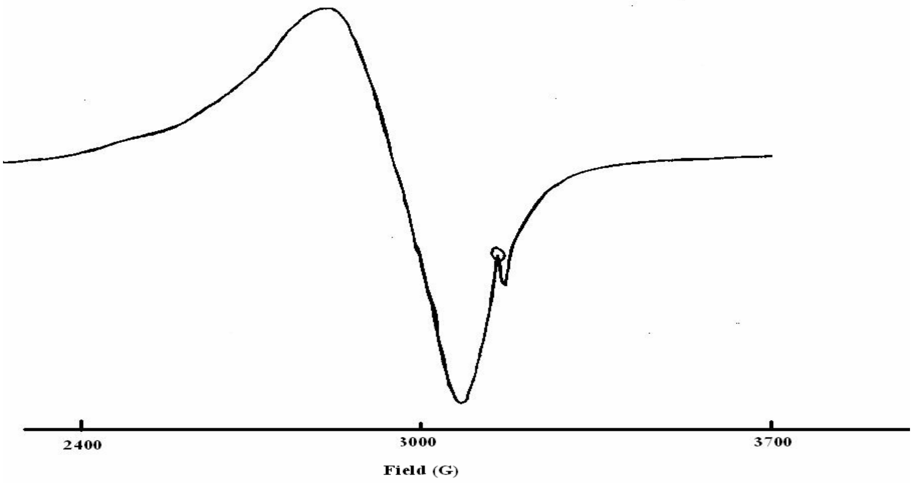


Figure 5.14: EPR spectrum of Cu(II) complex in polycrystalline state at 298K

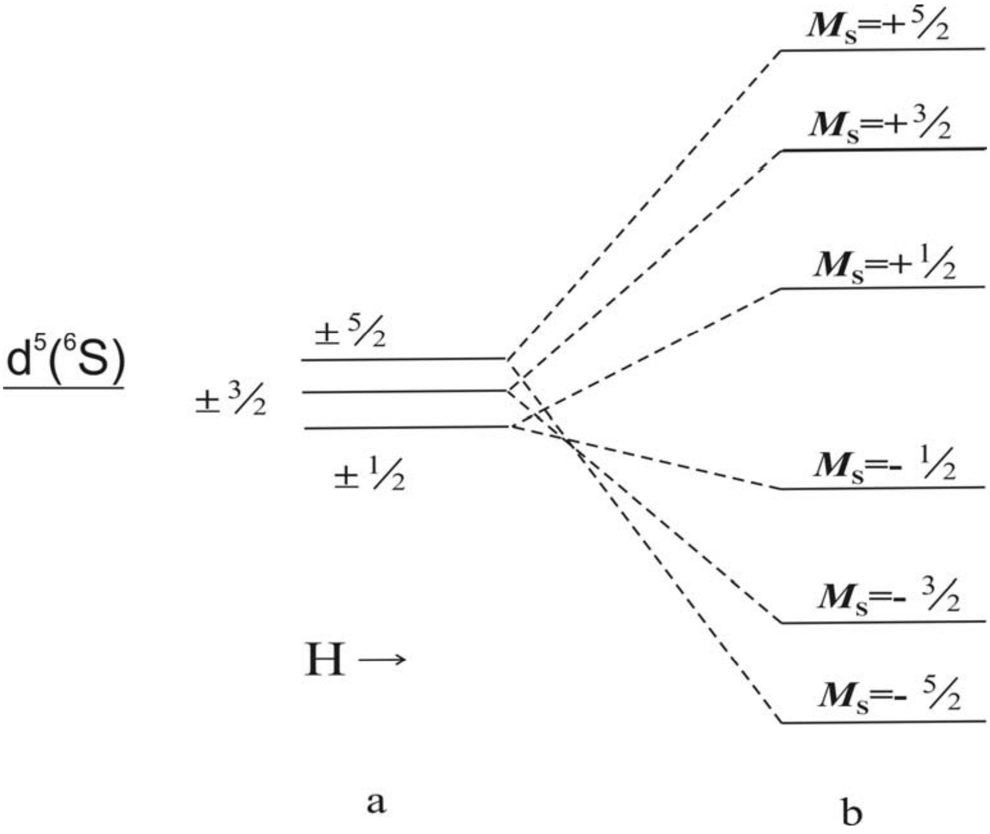


Figure 5.15: Kramer's degeneracy (a) zero field splitting of high-spin d^5 Mn(II) (b) splitting of M_s levels on application of magnetic field.

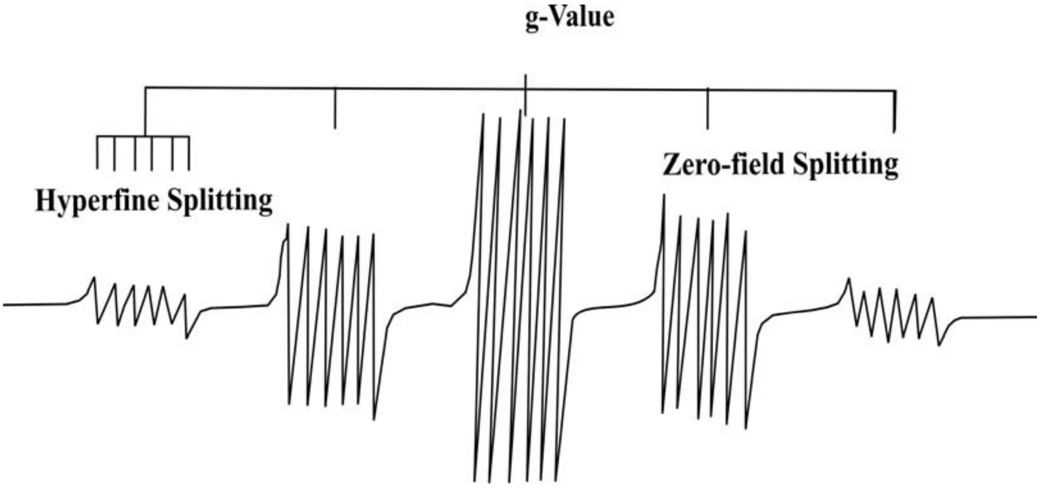


Figure 5.16: Spectrum of Mn(II) showing hyperfine splitting and zero-field splitting on the application of a magnetic field

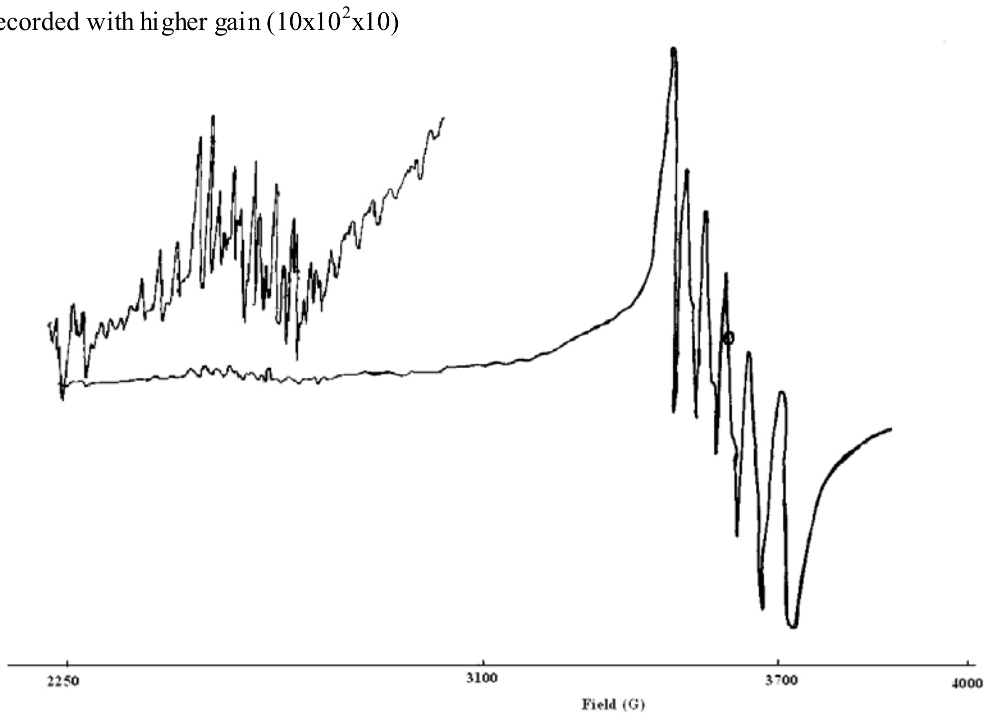


Figure 5.17: EPR spectrum of $[Mn(hmbd)_2Cl_2(H_2O)_2]H_2O$ in DMF at LNT

5.4 Conclusions

A new Schiff base is derived from 1,8-diaminonaphthalene and 4-hydroxy-3-methoxy benzaldehyde, by the rearrangement of the ring closure compound. The compound is characterized by elemental analysis, IR, NMR spectra and Single Crystal X-ray diffraction analysis. In non-polar solvents, the ring closure compound (4dpm) gets rearranged to form Schiff base (hmbd) in the presence of metal ions. The complexes synthesized in this study have mono nuclear structure as suggested by elemental analysis, conductivity studies, magnetic susceptibility measurements, IR, UV-visible, EPR and thermal analysis. The molecular formulae of the complexes were found to be $[M(hmbd)_2Cl_2(H_2O)_2]H_2O$, where M = Mn(II), Co(II) and Cu(II). The physicochemical and spectral data reveal an octahedral structure for manganese and copper complexes and a distorted octahedral geometry for the cobalt complex. Based on the physicochemical and spectroscopic studies, we propose the following structures for the complexes (Figure 5.18).

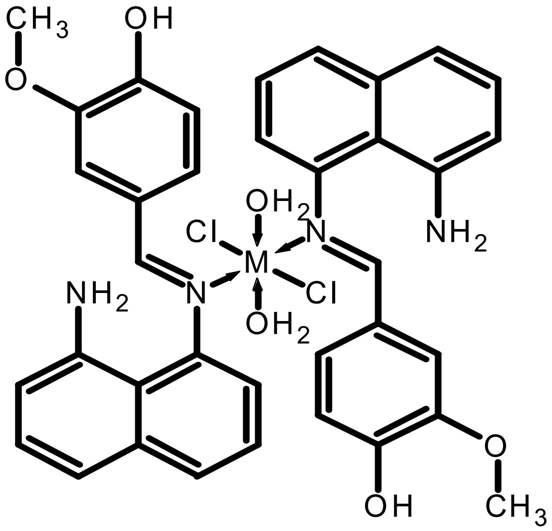


Figure 5.18: The proposed structure of the complexes (solvated water molecules are omitted)

References

1. Hocking, M. B. J. Chem. Educ. 74 (1997) 1055.
2. Kumar, K. G.; John, K. S.; Poduval, R. J. Appl. Polym. Sci. 98 (2005) 1536.
3. Dubey, P. K.; Dubey, V. K.; Mishra, C. M. Indian J. Chem., Sect A. 47 (2008) 1208.
4. Maurya, R. C.; Patel, P.; Rajput, S. Synth. React. Inorg. Met.-Org. Chem. 33 (2003) 817.
5. Varsha, G.; Arun. V.; Robinson, P. P.; Manju, Sebastian.; Digna, Varghese.; Leeju, P.; Jayachandran, V. P.; Yusuff, K. K. M. Tetrahedron Lett. 51 (2010) 2174.

6. Minkin, V. I.; Komissarov, V. N.; Kharlanov, V. A. Perimidinespirocyclohexadienones. In Organic Photochromic and Thermochromic compounds; Crano, J. C.; Guglielmetti, R. J. Eds., Plenum Press: New York. 1 (1999) 315.

7. (a) Komissarov, V. N.; Gruzdeva, E. N.; Kharlanov, V. A.; Olekhnovich, L. P.; Borodkin, G. S.; Khrustalev, V. N.; Lindeman, S. V.; Struch Kov, Y. T.; Kogan, V. A.; Minkin, V. I. Izv. Akad. Nauk. SSSR. 46 (1997) 2028; (b) Davis, R.; Tamaoki, N. Org. Lett. 7 (2005) 1461.

8. Al-Betar, A-R.; El-Rayyes, A.; Klein, U. K. A. J. Fluoresc. 15 (2005) 689–696.

9. Alder, R. W.; Bryce, M. R.; Goode, N. C.; Miller, N. J. Chem. Soc., Perkin Trans. 1, (1981) 2840.

10. Geary, W. J. Coord. Chem. Rev. 7 (1971) 81.

11. Omar, M. M.; Mohamed, G. G. Spectrochim. Acta A. 61 (2005) 929.

12. Annigeri, S. M.; Sathisha, M. P.; Revankar, V. K. Transition Met. Chem. 32 (2007) 81.

13. Issa, Y. M.; Abdel Fattah, H. M.; Soliman, A. A. J. Therm. Anal. Calorim. 42 (1994) 1175.

14. Abdel-Ghani, N. T.; Sherif, O. E. Thermochim. Acta. 156 (1989) 69.

15. Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed., John Wiley and Sons, Inc, New York. (1986).

16. Damus, H.; Fernaxdo, QReiser, H. Inorg. Chem. 3 (1964) 928.

17. Kandil, S. S.; El-Hefnawy, G. B.; Bakr, E. A.; Abou, A. Z. Trans. Met. Chem. 28 (2003) 168.

18. Bellamy, L. J. The Infrared Spectra of Complex Molecules, Vol. 1, 3. Auflage, Chapman and Hall Ltd., London. (1975).

19. Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, J. Wiley, New York. (1978).

20. Sonmez, M.; Sekerci, M. Synth. React. Inorg. Met.-Org. Chem. 34 (2004) 485.

21. Mohamed, G. G.; El-Wahab, Z. H. A. Spectrochim. Acta, Part A. 61 (2005) 1059.

22. Koksal, M.; Tumer, M.; Serin, S. Synth. React. Inorg. Met.-Org. Chem. 26 (1996) 1577.

23. Tumer, M.; Koksal, M.; Serin, S. Synth. React. Inorg. Met.-Org. Chem. 27 (1997) 775.

24. Garg, B. S.; Singh, P. K.; Sharma, J. L. S. Synth. React. Inorg. Met.-Org. Chem. 30 (2000) 803.

25. (a) Rana, V. B.; Singh, D. P.; Singh, P.; Teotia, P. Transition Met. Chem. 6 (1981) 36; (b) Rana, V. B.; Singh, D. P.; Singh, P.; Teotia, P. Transition Met. Chem. 7 (1982) 174.

26. Lever, A. B. P. Inorganic Electronic Spectroscopy. 2nd Ed. Elsevier, Amsterdam. (1984).

27. Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry. 5th Ed. Wiley, New York. (1988).

28. Shakir, M.; Azam, M.; Parveen, S.; Khan, A. U.; Firdaus, F. Spectrochim. Acta, Part A. 71 (2009) 1851.

29. Rapheal, P. F.; Manoj, E.; Kurup, M. R. P. Polyhedron. 26 (2007) 818.

30. Zhan, S-Z.; Miao, Y.; Li, P.; Yuan, C-W. Transition Met. Chem. 24 (1999) 311.

31. Krishnan, S.; Laly, K.; Kurup, M. R. P. Spectrochim. Acta, Part A. 75 (2010) 585.

****◆****

Chapter

Zeolite encapsulated copper(II) complexes

6

Contents

> *"Truth is ever to be found in the simplicity, and not in the multiplicity and confusion of things"*
>
> ***Sir Issac Newton***

6.1. Introduction

Incorporation of transition metal complexes in the supercages of zeolites offers number of advantages over their counterparts in homogeneous solution. Encapsulation in microporous solids such as zeolite is an attractive technique for heterogenization, since no leaching is observed when the complex is confined exclusively in the zeolite pores[1]. In addition, zeolite encapsulated complexes promise better control of selectivity for the reaction and higher stability due to reduced dimerization of complexes in the cavity[2]. Furthermore, zeolite encapsulated complexes have also been suggested as model compounds for enzyme mimicking[3-5] in which zeolite framework behave as the protein mantle of the enzyme and the entrapped metal complex mimics the active sites of the enzyme[3]. The prepared materials can have many interesting applications including chromotropism, size/shape–selective catalysis, gas separation/purification, electro and photocatalysis etc[6,7]. Zeolite complexes posses a number of structural similarities to metalloenzymes and therefore they are expected to mimic enzyme active sites for the catalytic reaction such as oxidation[8] hydrogenation[9] dehalogenation[10] etc.

The encapsulated complexes are believed to be stable and reusable due to the following reasons: (1) complexes are immobilized in the cavities (2) reduced formation of inactive oxo and peroxo dimeric and other polymeric species in the cavities due to the steric effects of the zeolite frame work and (3) the interaction of encapsulated complexes with the zeolite lattice[11-18]. Basically, there have been two main approaches to prepare zeolite encapsulated complexes, namely the zeolite synthesis[19] and flexible ligand[20, 8]methods. In the flexible ligand method, a flexible ligand diffuse freely through the zeolite pores and coordinates with a previously exchanged metal ion. Upon complexation, the resulting complex becomes too large and rigid to escape from the cage.

In the this chapter, studies on zeolite Y encapsulated copper(II) complexes of the Schiff bases, 2–hydroxy–3–methoxybenzalidine–1,8–diaminonaphthalene (Hohmbd), 4–hydroxy–3–methoxybenzalidine–1,8–diaminonaphthalene (hmbd) and quinoxaline–2–carboxalidine–1,8–diaminonaphthalene (qcdn) are presented.

6.2. Experimental

The details concerned with the synthesis of the perimidines (which act as precursor for the Schiff base ligands) and the metal exchanged zeolite are presented in Chapter II.

6.2.1. Synthesis of zeolite encapsulated copper(II) complexes

The encapsulation of copper complexes of quinoxaline–2–carboxalidine–1,8–diaminonaphthalene, 2–hydroxy–3–methoxybenzalidine–1,8–diaminonaphthalene and 4–hydroxy–3–methoxy benzalidine–1,8–diaminonaphthalene was achieved by flexible ligand method[21-25]. The metal exchanged zeolite CuY (5g) was added to the perimidines (precursor ligand for corresponding Schiff bases) dissolved in hexane (50 mL). The concentration of the ligand was adjusted in such a way to obtain 1:1 and 2:1 (ligand to metal ratio) for CuYqcdn and CuYohmbd or CuYhmbd respectively. The mixture was refluxed on a water bath for about 12 hours. The penetration of the organic compound molecules through the zeolite pores result in the formation of large metal complexes inside the framework. The encapsulated zeolite was filtered and soxhlet extracted with methanol and dichloromethane for 3–4 days till the extract become colorless. This ensures the complete removal of the surface species. The complex was then back exchanged with NaCl solution (0.01 M, 250 mL) for 24 hours to replace all uncomplexed metal ions with sodium ions, then repeatedly washed with distilled water to make the complex chloride free and dried in vacuum. The resulting encapsulated complexes denoted as CuYqcdn, CuYohmbd and CuYhmbd were stored in vacuum over anhydrous calcium chloride.

6.3 Characterizations

The details regarding the techniques used for characterization are presented in chapter II.

6.4. Results and discussion

Interaction of copper(II) chloride dihydrate with the perimidines (see respective chapters) has resulted in the formation of Schiff base complexes. Therefore, we have used these perimidines for preparing the encapsulated Schiff base complexes.

6.4.1. Chemical analysis

The analytical data of the sodium exchanged zeolite-Y and copper exchanged zeolite–Y is given below. The amount of silica, alumina and Si/Al ratio are very decisive in determining the stability and crystallinity of the resulting complexes.

The data calculated for NaY: Si, 20.86; Al, 8.05; Na, 9.37. Found: Si, 20.84; Al, 8.02; Na, 9.32.

The data calculated for CuY: Si, 20.75; Al, 7.88; Na, 7.25; M, 1.20. Found: Si, 20.72; Al, 7.85; Na, 7.20; M, 1.98.

The Si to Al ratio of NaY was found to be 2.6, which correspond to the unit cell formula, $Na_{54}(AlO_2)_{54}(SiO_2)_{138}.nH_2O$. This ratio was retained even after the metal exchange, which confirms that dealumination has not occurred during the exchange reaction. This proves beyond doubt that the zeolite framework is unaltered by encapsulation. The retention of Si to Al ratio was observed in earlier studies also[26].

In the preparation of metal exchanged zeolite, very dilute solutions of metal ions are used, as high concentration of metal chloride may result in dealumination and destruction of the framework[27]. If x represents the fraction of Cu^{+2} ions exchanged with Na^+ ions in the zeolite, then the equation representing the ion exchange is

$$Na_{54}Y + xM^{+2} \longrightarrow M_xNa_{54-2x}Y + 2x\,Na^+$$

The degree of ion exchange and the unit cell formula of the metal exchanged zeolite can be calculated from the obtained data. The percentage of metal in CuY gives the unit cell formula of copper-exchanged zeolite as $Na_{43.14}Cu_{3.62}(SiO_2)_{138}(AlO_2)_{54}.nH_2O$. The unit cell formula is a representation of the composition of a unit cell in the metal exchanged zeolites. The degree of ion exchange for CuY is 20.11%. The analytical data of the encapsulated complexes are given in Table 6.1.

Table 6.1: Analytical data of the encapsulated complexes CuYhmbd, CuYqcdn and CuYohmbd

Compound	Color	Analytical data. Found (calculated)%						
		%Si	% Al	% Na	% M	% C	% H	% N
CuYhmbd	Ash	20.36 (20.40)	7.83 (7.85)	6.32 (6.34)	0.60 (0.62)	1.36 (1.38)	2.81 (2.82)	0.77 (0.78)
CuYqcdn	Black	20.66 (20.67)	7.93 (7.96)	6.99 (7.01)	0.82 (0.84)	1.58 (1.60)	2.93 (2.95)	0.98 (0.99)
CuYohmbd	Dark Grey	20.62 (20.64)	7.88 (7.90)	6.56 (6.57)	0.78 (0.80)	1.03 (1.05)	2.96 (2.98)	1.01 (1.04)

In all the complexes, the Si/Al ratio is 2.6, which is an indication of the retention of the zeolite framework without any damage after complex formation. The analytical data of the encapsulated complexes show that the percentage of metal is slightly in excess of what is required for the formation of 1:1 complexes. This may be due to the presence of uncomplexed metal ions in the zeolite cages even after back exchange. The uncomplexed metal ions present are usually removed during back exchange with NaCl solution. But in some cases excess concentration of metal ions may result due to the occupation of more than one metal ion in the same cage of the zeolite. There are chances for the complex formed or trapped ions to hinder the approach of further ligands and prevent further complex formation with other metal ions.

The percentages of carbon, hydrogen and nitrogen indicate the encapsulation of complexes in the zeolite cages. The metal ions in the zeolite are in a dynamic system that involves the migration of metal for coordination. The presence of large ligands makes it difficult for them to enter the small cages and the most probable site for complex formation is the supercage. Hence there is the migration of metal ions to the supercages for complexation. The metal – oxygen bonds in the lattice are broken during this process in which the complexes are formed and there are chances for the formation of new bonds with the ligands[28-32].

6.4.2 Surface area and pore volume

The surface area and pore volume of zeolite-Y, sodium exchanged zeolite (NaY), copper exchanged zeolite (CuY) and the encapsulated complexes, CuYhmbd, CuYqcdn and CuYohmbd, are determined by BET method and the results are presented in Table 6.2.

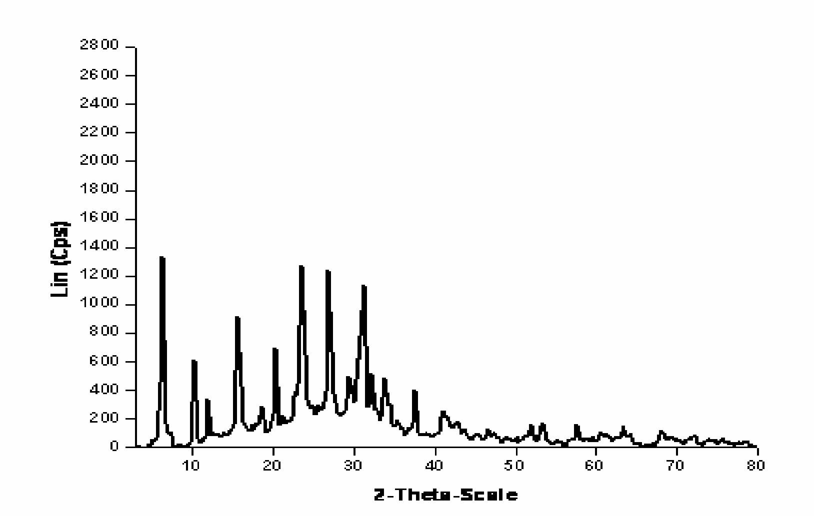
Table 6.2: Surface area and Pore volume values

Sample	BET surface area (m^2/g)	Pore volume (cc/g)
Zeolite Y	799	0.40
NaY	692	0.34
CuY	683	0.35
CuYhmbd	518	0.28
CuYqcdn	499	0.27
CuYohmbd	498	0.26

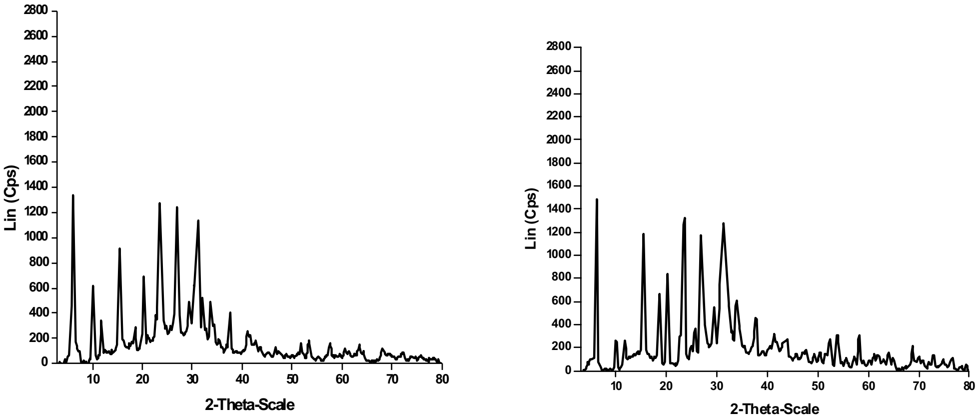
There is not much difference in the surface area of NaY and CuY whereas there is a significant decrease in surface area upon encapsulation of complexes[8]. The significant reduction in surface area and pore volume is due to the encapsulation of complexes within the zeolite pores. The surface area of zeolite is mainly internal surface area and the blocking of pores due to complex formation results in a decrease in surface area[33]. The decrease in surface area is a clear indication of the formation of complexes within the zeolite cages[8]. The lowering of surface area and pore volume with encapsulation has been reported earlier[34].

6.4.3. X-ray diffraction patterns

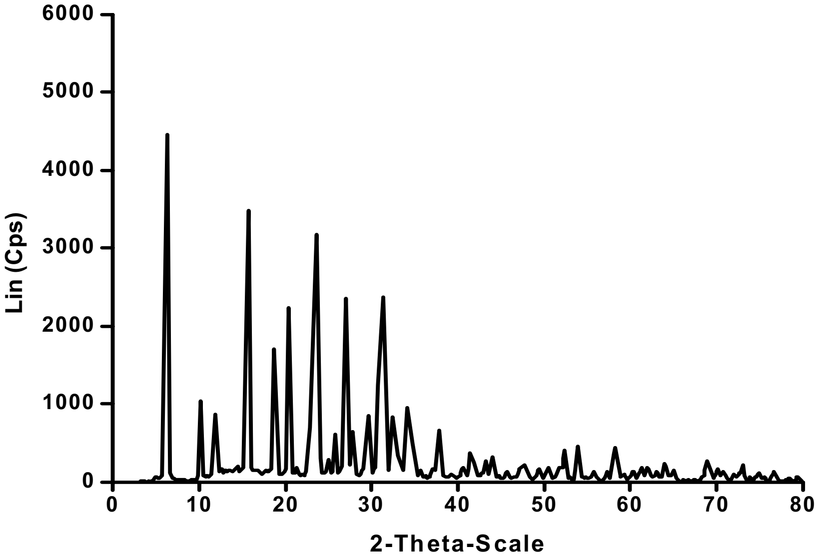
XRD patterns obtained for NaY, CuY and the encapsulated complexes CuYhmbd, CuYqcdn and CuYohmbd are given in the Figure 6.1.The comparison of these patterns show that the XRD patterns of the encapsulated complexes exactly match with that of the metal exchanged zeolite and NaY. This is a strong evidence for the fact that the zeolite framework remains intact on encapsulation[35]. The characterization by diffraction technique is very important as it provides valuable information on crystallinity and changes in unit cell parameters occurring during encapsulation[36-38]. Similarity in diffraction patterns of CuY and encapsulated complexes suggests that the reduction in surface area is not due to the breakage of crystalline structure of the zeolite but due to encapsulation of complexes within the super cages of the zeolite.



XRD spectra of CuY



CuYqcdn **CuYohmbd**

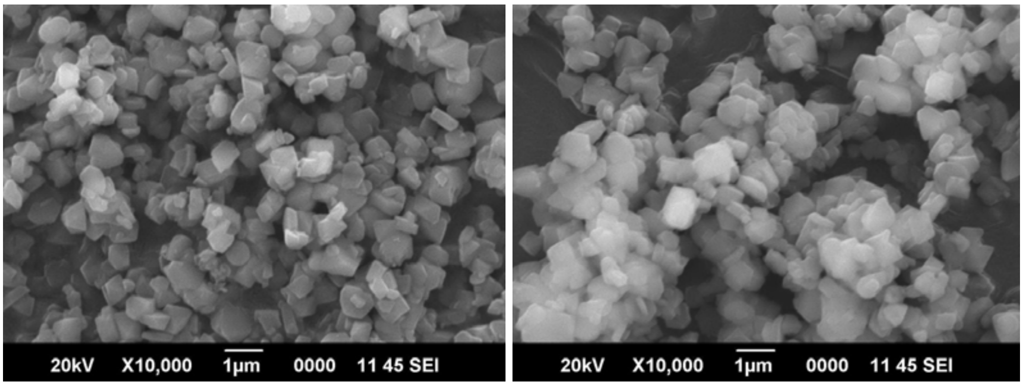


CuYhmbd

Figure 6.1: XRD spectra of encapsulated complexes

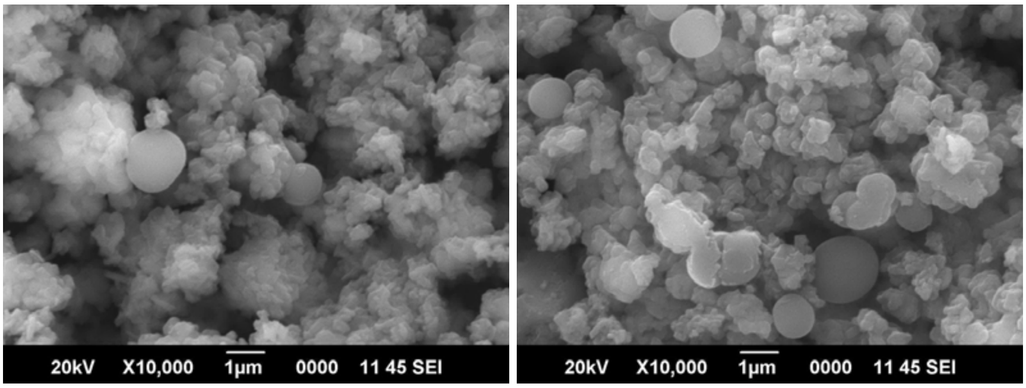
6.4.4 SEM analysis

Scanning electron micrographs of the zeolite encapsulated complexes before and after soxhlet extraction are depicted in figures 6.2–6.4. In the micrographs taken before soxhlet extraction, aggregates of species are visible on the surface but in the micrographs taken after soxhlet extraction the surface appears to be clean. This shows that soxhlet extraction with a suitable solvent can be successfully employed for removing the surface species present. During the soxhlet extraction procedures, the extraction is done for a longer period of time so that well-defined crystals of complexes formed should be free from ions present on the external surface. Clear zeolite surfaces are reported in the case of phthalocyanine and salen complexes[39, 40].



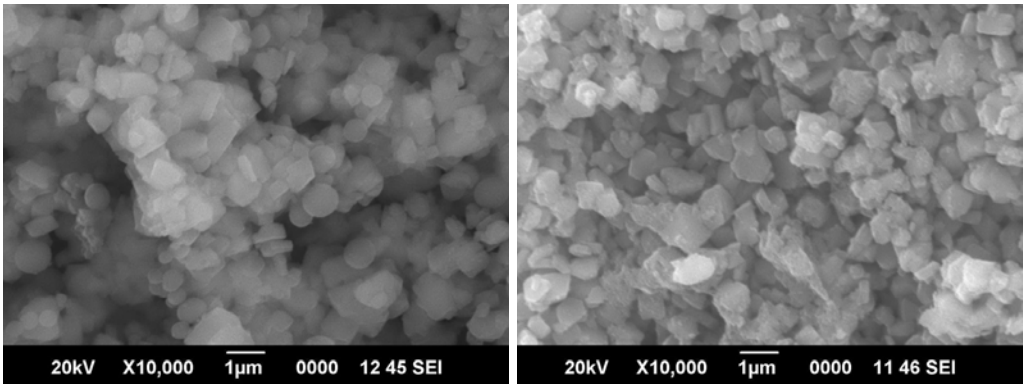
(i) (ii)

Figure 6.2: Scanning electron micrographs of CuYhmbd (i) before and (ii) after soxhlet extraction.



(i) (ii)

Figure 6.3: Scanning electron micrographs of CuYqcdn (i) before and (ii) after soxhlet extraction.



(i) (ii)

Figure 6.4: Scanning electron micrographs of CuYohmbd (i) before and (ii) after soxhlet extraction.

6.4.5 Thermal analysis

The thermal behavior of the zeolite samples was studied and their TG/DTG curves were recorded at a heating rate of 10 °C per minute up to 1000 °C in an atmosphere of nitrogen (Figures 6.5–6.7) and the TG data are tabulated in Table 6.3. The corresponding changes in weight occur due to the rupture or formation of chemical bonds on raising the temperature or due to the removal of volatile products[41]. The thermal stability of heterogeneous complexes is found to be greater than that of the analogous homogeneous ones. The well-defined TG patterns obtained in the case of simple complexes may not be obtained for the zeolite samples. One reason for this discrepancy might be due to the very low concentration of metal complexes within the supercages of the zeolite. However TG data provide clear information about decomposition temperature of the complexes under study.

The decomposition patterns were found to be of similar type for CuYhmbd and CuYohmbd. In both the cases, two stages of decomposition were observed. The first stage in the temperature range of 50-200 °C corresponds to the loss of coordinated water along with the physisorbed water. The percentage mass loss of 2.1 in the temperature range 200-700 °C is consistent with the decomposition of the synthesized complex. In the case of CuYqcdn, the initial stage of decomposition starts from 50 °C and continue till 200 °C. A weight loss of 22.9% occurs during this stage. This stage indicates the removal of water entrapped in the cages of the zeolite structure with the peak temperature occurring at 110 °C. The decomposition occurs slowly thereafter. A weight loss of 17.8% is observed up to 400 °C. The decomposition of the complex might be occurring in this region. Then a constant weight loss is maintained till 700 °C and above this temperature destruction of the framework occurs.

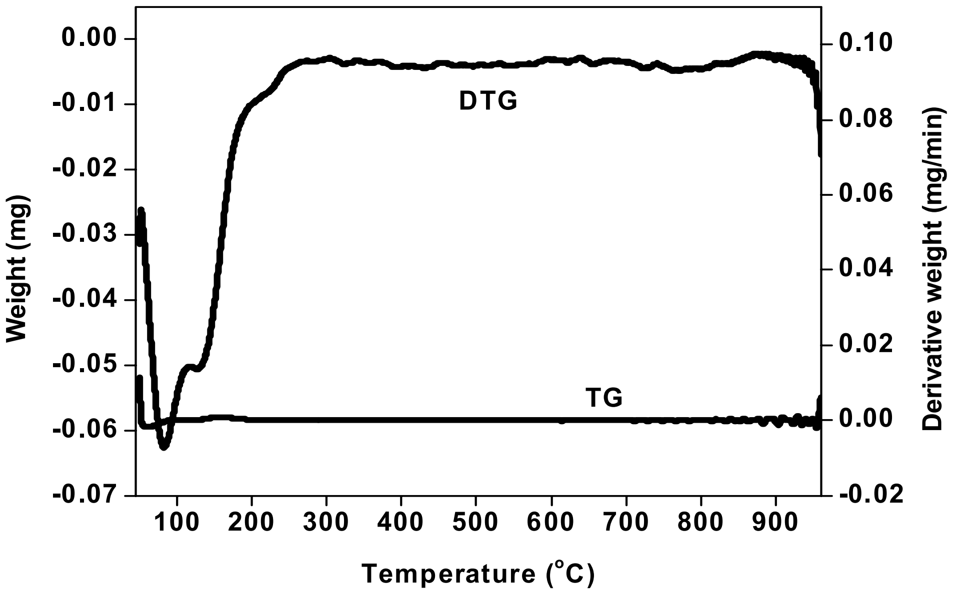


Figure 6.5: TG–DTG curve of CuYhmbd

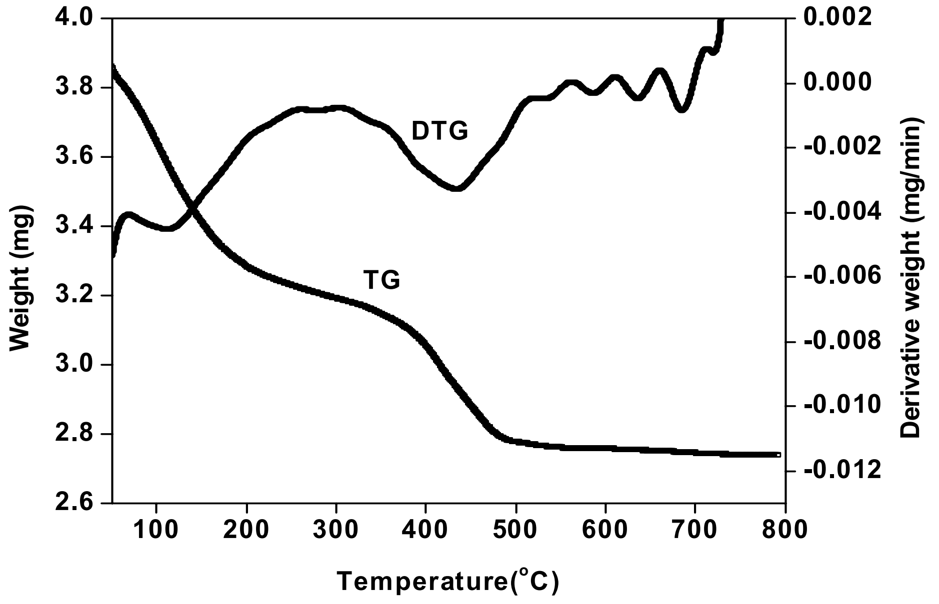


Figure 6.6: TG–DTG curve of CuYqcdn

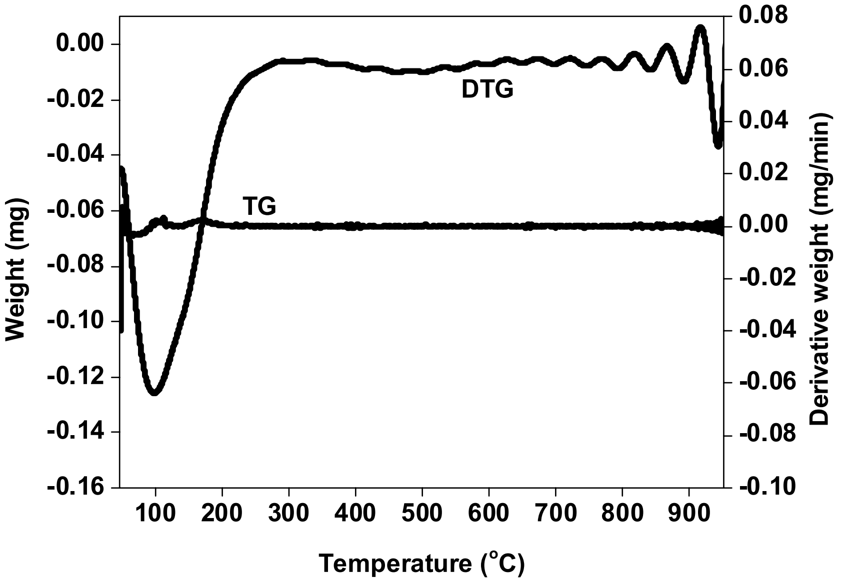


Figure 6.7: TG–DTG curve of CuYohmbd

Table 6.3: Thermogravimetric analysis data of encapsulated complexes

Encapsulated complexes	Stability	Temperature range (°C)	Mass loss (%)
CuYhmbd	Ambient	50-200	21.8
		200-700	2.1
CuYqcdn	Ambient	50-200	22.9
		200-400	17.8
		400-700	2.2
CuYohmbd	Ambient	50-200	22.8
		200-700	2.0

6.4.6 Infrared spectra

The characteristic spectral bands of the zeolite can be classified in to two groups. The first group consists of the internal vibrations of the primary units of the structure and the other group comprises of the bands arising due to the linkage between the primary units. The second set of bands depends mainly on the structure of the zeolite samples. The IR spectrum of CuY is almost the same as that of zeolite Y, which shows that the basic zeolite structure remains intact on metal exchange[42, 43]. The IR spectrum of CuY is given in Figure 6.8.

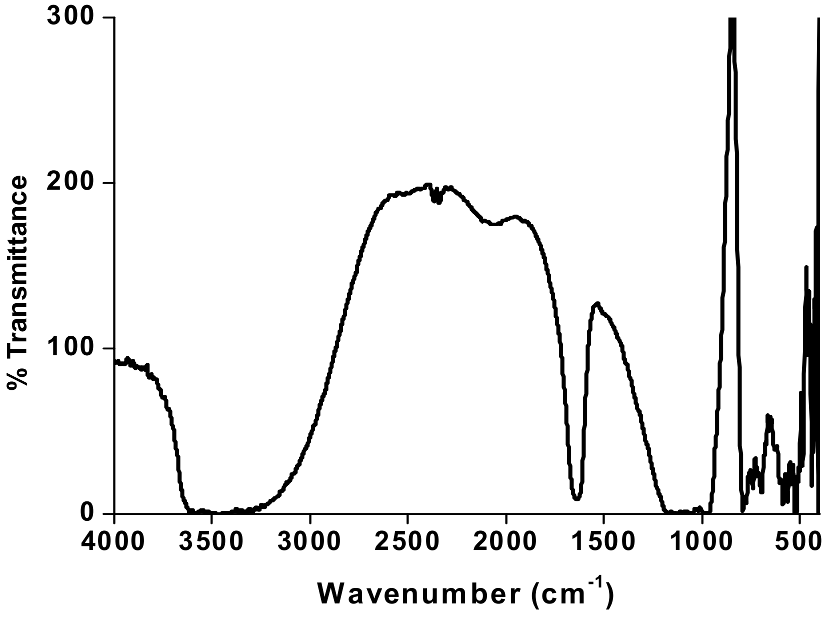
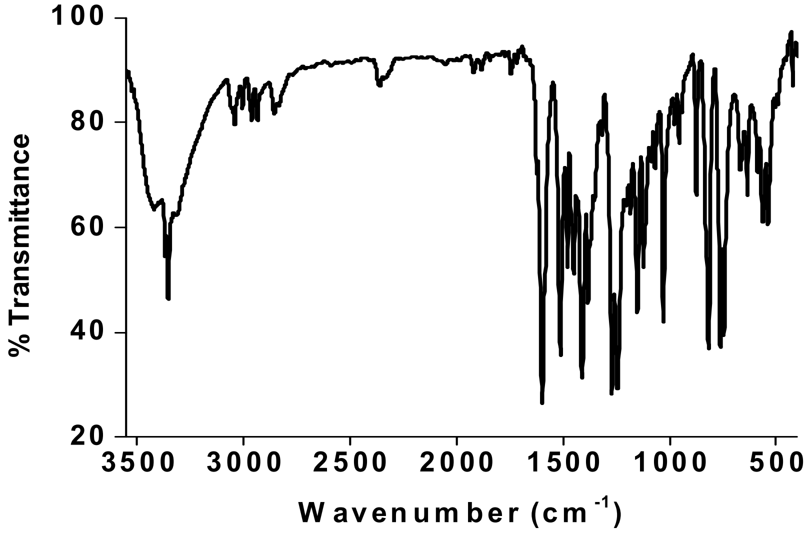
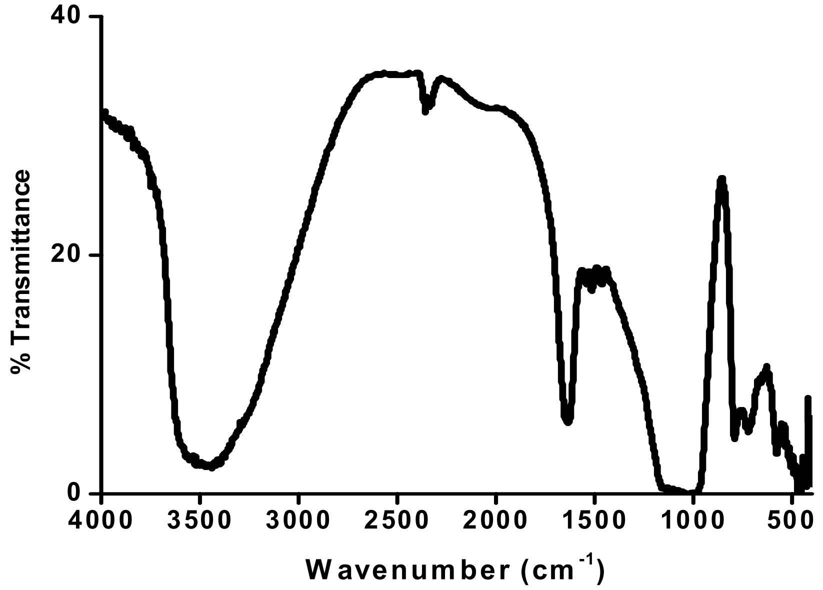


Figure 6.8: Infrared spectrum of CuY

The bands in the region 700-900 cm^{-1} may be due to symmetric stretching and that around 900-1250 cm^{-1} is due to asymmetric stretching. The IR spectra of the ligands and the encapsulated complexes are given in Figures 6.9–6.11 and the spectral data are given in Table 6.4.



FT-IR spectrum of hmbd



FT-IR spectrum of CuYhmbd

Figure 6.9: FT-IR spectrum of hmbd and CuYhmbd

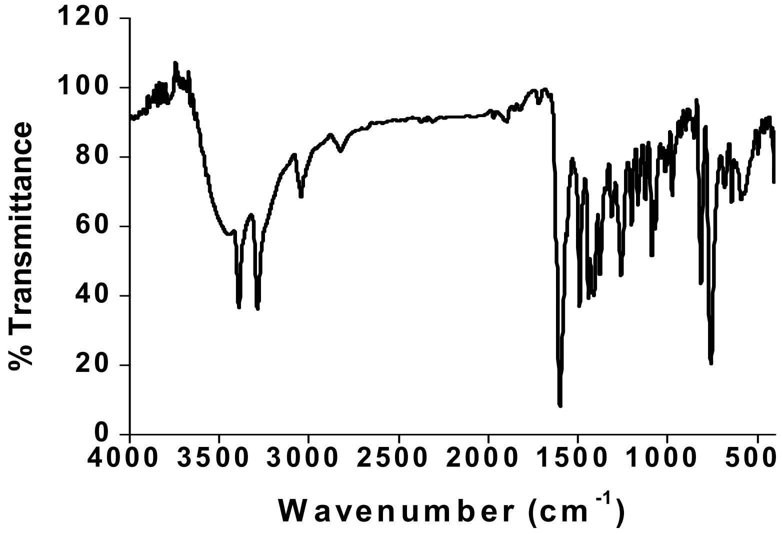
Table 6.4: IR Spectral data (cm^{-1}) of the encapsulated complexes

Assignments (in cm^{-1})	$\upsilon(O-H)^{a/b}$	$\upsilon(C=N)^{c}$	$\upsilon(C-O)^{d}$	$\upsilon(M-N)$	$\upsilon_{zeolite}$
hmbd	3296, 3416	–	1028	–	–
CuYhmbd	3461	1635	1028	445	576
qcdn	–	–	–	–	–
CuYqcdn	3450	1649	–	450	562
Hohmbd	3302, 3363	–	1246	–	–
CuYohmbd	3450	1641	1245	453	574

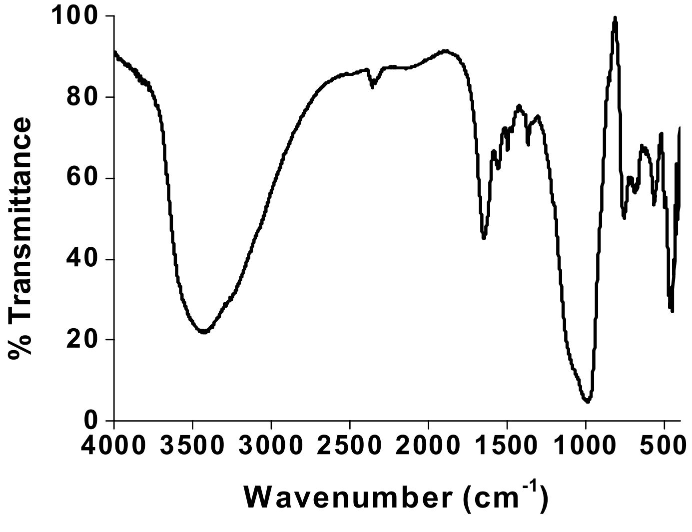
$^{a}\upsilon(N-H)/\ \upsilon(O-H)$ of the free Schiff base; $^{c}-CH=N$ of azomethine group; ^{d}methoxyl $\upsilon(C-O)$.

The spectral data of the encapsulated complexes confirm the formation of complexes inside the zeolite cages[44]. The ligand hmbd could coordinate through the nitrogen atom of the azomethine group, the oxygen of the phenolic hydroxyl group and oxygen of the carbonyl group. IR spectrum of CuYhmbd shows the presence of strong band at 1635 cm^{-1} indicative of the existence of azomethine stretching in the presence of metal ion. The bands around 1008 and 721 cm^{-1}

may be due to the rocking and wagging modes of water. The band seen around 3461 cm^{-1} is due to the merging of υ_{O-H} and υ_{N-H} frequencies. Some bands observed in the spectrum of the ligand are not seen in the spectrum of the encapsulated complex as they are masked by the strong absorption bands of the zeolite. Certain new bands seen in the spectrum of the complex are those of the zeolite support.

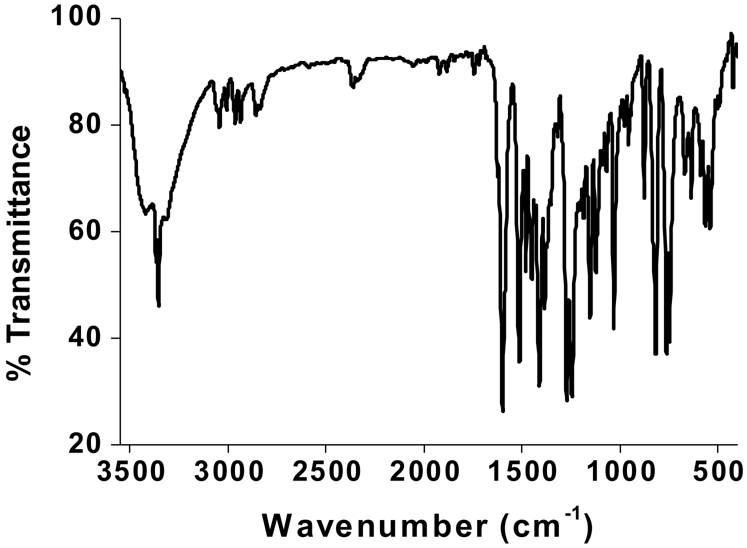


FT-IR spectrum of qcdn

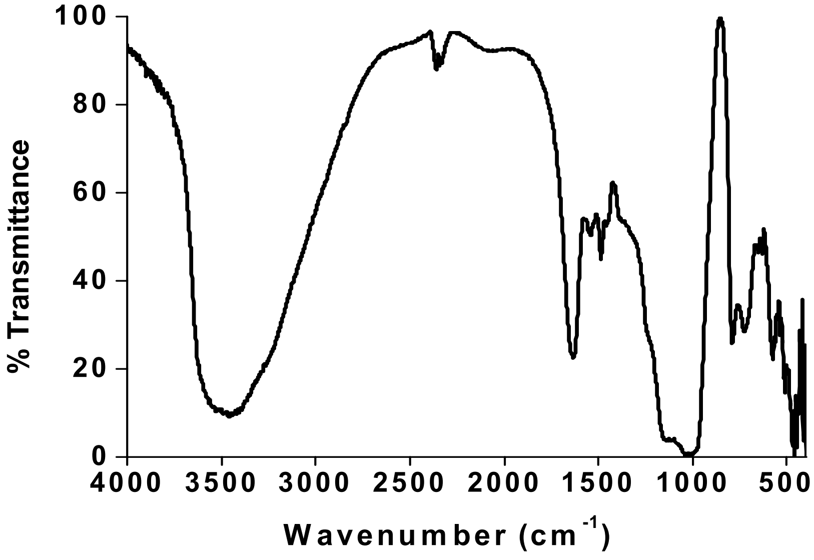


FT-IR spectrum of CuYqcdn

Figure 6.10: FT-IR spectrum of qcdn and CuYqcdn



FT-IR spectrum of Hohmbd



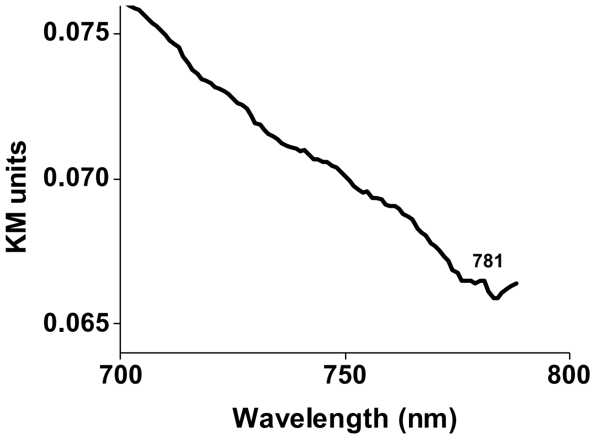
FT-IR spectrum of CuYohmbd

Figure 6.11: FT-IR spectrum of Hohmbd and CuYohmbd

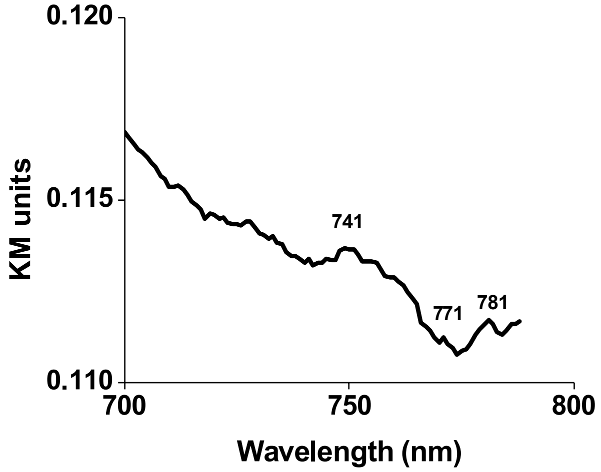
In the course of complex formation, a new band is observed at 1644 cm^{-1} for CuYqcdn is due to –C=N stretching vibration, which suggests that azomethine nitrogen is involved in coordination. The band at 3363 cm^{-1} due to υ_{OH} stretching of the phenolic group present in the precursor ligand Hohmbd disappears with encapsulation indicating deprotonation of the phenolic group on complexation. The O-H stretching and bending vibration of water is seen around 3462 cm^{-1} in the spectra of all the supported complexes revealing the presence of water molecules in the zeolite lattice. A clear spectral band expected for the stretching mode of C=N vibration is observed at 1631 cm^{-1} in the spectrum of CuYohmbd. This can be taken as a strong proof for the coordination of nitrogen of azomethine group to the metal. This coordination involves the donation of lone pair of electrons on nitrogen to the empty d orbitals present in the metal[45].

6.4.7 UV-Visible Reflectance Spectra

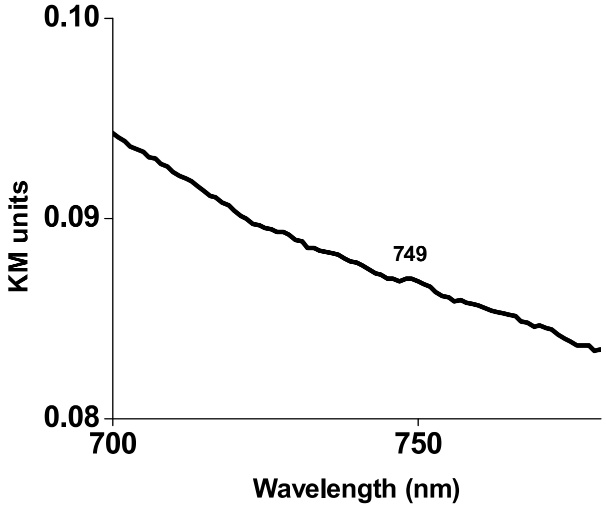
The location and coordination taken up by the metal cations in the complexes within the zeolite cavities is well understood by the diffuse reflectance spectral data of the complexes. The electronic spectra of all the encapsulated complexes show d–d band in the range 781 nm and suggest an octahedral structure. The axial positions in the octahedral symmetry might have occupied by either water molecules or oxide ions of zeolite lattice. Due to the low intensity of the observed bands some uncertainties arise in the detailed assignments of the bands. The absorption maxima of these complexes and their assignments are given in Table 6.5 and the electronic spectrum of the complexes is given in Figure 6.12 respectively.



UV-Visible reflectance Spectrum of CuYhmbd



UV-Visible reflectance Spectrum of CuYqcdn



UV-Visible reflectance Spectrum of CuYohmbd

Figure 6.12: Diffuse reflectance Spectrum of the encapsulated complexes

Table 6.5: Electronic spectral data of the encapsulated complexes

Encapsulated complexes	Absorbance Max:		Tentative Assignments
	nm	cm^{-1}	
CuYhmbd	781	12804	d–d transition
CuYqcdn	741	13495	d–d transition
	749	13351	"
	771	12970	"
	781	12804	"
CuYohmbd	749	13351	d–d transition

6.4.8 EPR spectra

The electronic paramagnetic resonance spectra of the complexes help us to determine the electronic state and geometry of the encapsulated complexes[46]. The EPR spectra of the complexes were recorded at liquid nitrogen temperature to gather information regarding the symmetry of the ligand field. The spectra are represented in Figures 6.13–6.15 and the EPR parameters are tabulated in Table 6.6.

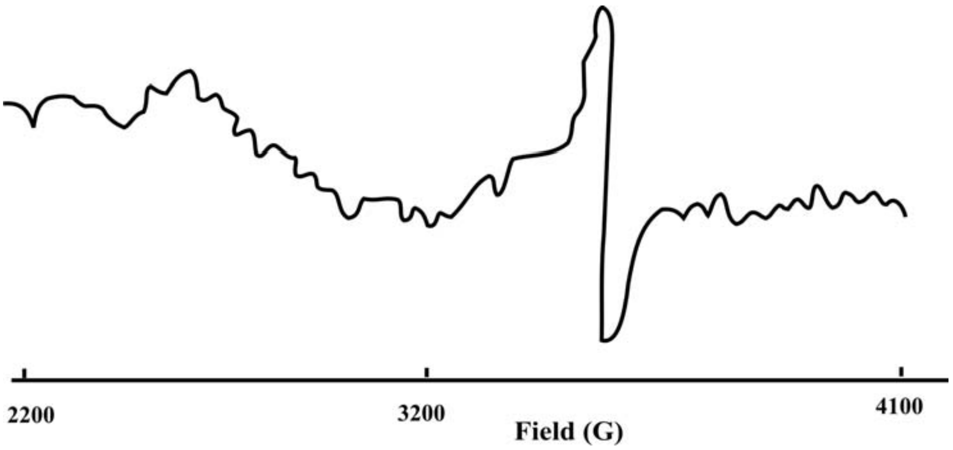


Figure 6.13: EPR spectrum of CuYhmbd

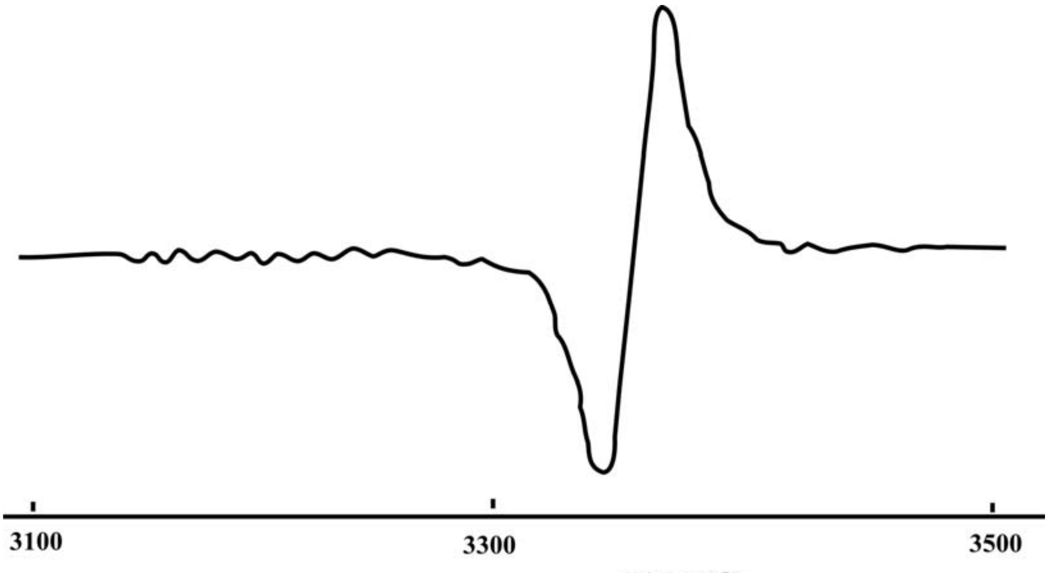


Figure 6.14: EPR spectrum of CuYqcdn

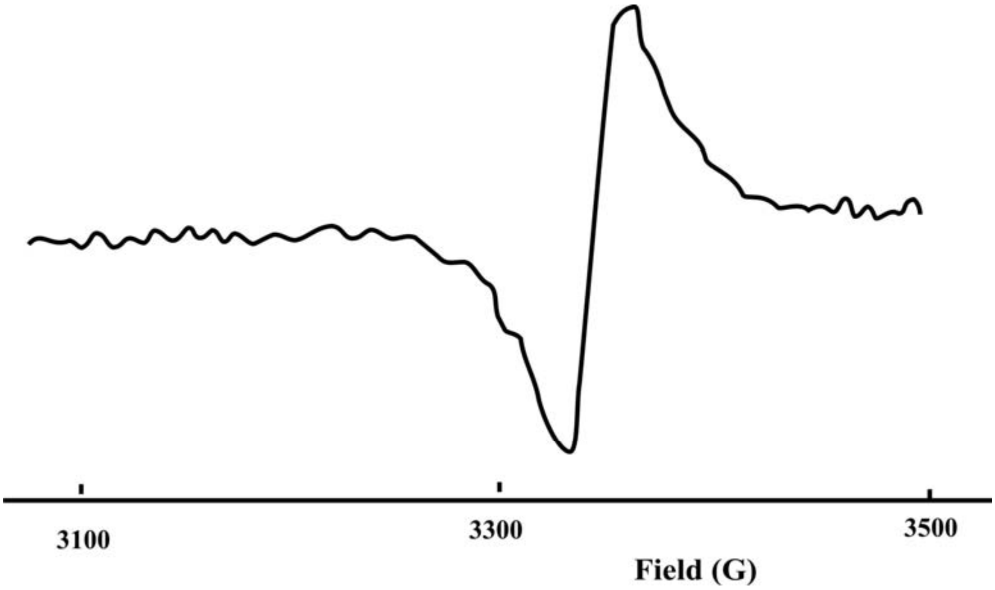


Figure 6.15: EPR spectrum of CuYohmbd

Table 6.6: EPR Spectral data of the encapsulated complexes

Encapsulated Complexes	EPR parameter
CuYhmbd	$g_1 = 2.1; g_2 = 2.2; g_3 = 2.0$
CuYqcdn	$g_{\parallel} = 1.9; g_{\perp} = 2.1$
CuYohmbd	$g_{\parallel} = 2.0; g_{\perp} = 2.1$

A well resolved hyperfine splitting pattern is obtained for encapsulated complexes that are similar to that in dilute solutions indicating the formation of the monomeric complexes within the zeolite supercages. The spectrums of CuYhmbd give three g values indicating rhombohedral distortion of octahedral geometry. The presence of two g values in the case of CuYqcdn and CuYohmbd indicative of the six coordinate environments around the copper atom in the complexes. The interactions of the zeolite framework with the encapsulated complex could induce some distortions in the expected structure.

6.5 Conclusions

This chapter presents studies involving the preparation and characterization of zeolite Y encapsulated complexes of CuYhmbd, CuYqcdn and CuYohmbd. The analytical data shows that the Si/Al ratio is 2.6, which is an indication of the retention of the zeolite framework without any damage after complex formation. Surface area, pore volume analysis, XRD patterns and FTIR also indicate the retention of zeolite framework and the encapsulation of complexes within the cavities. SEM of the zeolite encapsulated complexes before and after soxhlet extraction indicates that complexes adsorbed on the surface of zeolite framework has been removed by soxhlet extraction. Analytical data and diffuse reflectance spectra show that all the zeolite encapsulated Cu(II) complexes have octahedral geometry. TG–DTG data indicate that the decomposition temperature for the encapsulated complexes is higher than that of the simple complexes suggesting the higher thermal stability of the encapsulated complexes.

References

1. Medina, J. C.; Gabriunas, N.; Paez-Mozo, A. J. Mol. Catal. 115 (1997) 233.
2. Kowalak, S.; Weiss, R. C.; Balkus Jr. K. J. J. Chem. Soc., Chem. Commun. (1991) 57.
3. Gabrielov, A. G.; Balkus Jr, K. J.; Bell, S. L.; Bedioui, F.; Devynck, J. Microporous Mater. 2 (1994) 119.
4. Choudary, B. M.; Rani, S. S.; Rao, Y. V. S.; Kantam, M. L. J. Chem. Soc., Perkin Trans. 1. 9 (1991) 2274.
5. Parton, R.; Vos, D. D.; Jacob, P. A. Kluwer Academic Publishers. The Netherlands. (1994) 555.
6. Ramamurthy,V. P.; Lakshminarasimhan, C. P.; Johnston, L. J. Chem. Commun. (1998) 2411.

7. Sykora, M. K.; Maruszewski, S. M.; Kincaid, J. R. J. Am. Chem. Soc. 120 (1998) 3490.

8. Balkus Jr, K. I.; Gabrielov, A. G. J. Inclus. Phenom. Molec. Recog. Chem., 21 (1995) 159.

9. Chatterjee, D.; Bajaj, H. C.; Das, A.; Bhatt, K. J. Mol. Catal. 92 (1994) 235.

10. Seelan, S.; Agashe, M. S.; Srinivas, D.; Sivasanker, S. J. Mol. Catal. A: Chem. 168 (2001) 61.

11. Choudary, B. M.; Kantam, M. L.; Bharathi, B.; Sreekanth, P.; Figueras. F. J. Mol. Catal. A: Chem. 159(2000) 417.

12. Chavan, S.; Srinivas, D.; Ratnasamy, P. J. Catal. 192 (2000) 286.

13. Varkey, S. P.; Jacob, C. R. Indian J. Chem. 38A (1999) 320.

14. Jacob, C. R.; Varkey, S. P.; Ratnaswamy, P. Appl. Catal. A. 182 (1999) 91.

15. Vankelecom, I. F. J.; Parton, R. F.; Casselman, M. J. A.; Uytterhoeven, J. B.; Jacobs, P. A. J. Catal. 163 (1996) 457.

16. Fan, B.; Li, R.; Liu, Z.; Cao, J.; Zhong, B. Stud. Surf. Sci. Catal. 129 (2000) 311.

17. Raja, R.; Ratnaswamy, P. J. Catal. 170 (1997) 244.

18. Xavier, X. O.; Chacko, J. ; Yusuff, K. K. M. J. Mol. Catal. A: Chem. 178 (2002) 275.

19. Balkus Ir, K. J.; Gabrielov, A. G.; Bell, S. Inorg. Chem. 33 (1994) 67.

20. Bowers, C. P. K. J. Catal. 122 (1990) 271.

21. Maurya, M. R.; Titinchi, S. J. J.; Chand, S. Appl. Catal., A. 228 (2002) 177.

22. Schulz – Ekloof, S.; Ernst, S. Handbook of Heterogeneous Catalysis; Ertil, G.; Knozinger, J.; Weitramp, J. (Eds) Wiley-VCH. (1997) 734.
23. Bowers, C.; Dutta, P. K. J. Catal. 122 (1990) 271.
24. Kubinyi, H. Curr. Opin. Drug Discovery Dev. 1 (1998) 16.
25. Devos, D. E.; Feijen, E. J. P.; Schoonheydt, R. A.; Jacobs, P. A. J. Am. Chem. Soc. 116 (1994) 4746.
26. Smeets, P. J.; Woertink, J. S.; Sels, B. F.; Solomon, E. I.; Schoonheydt, R. A. Inorg. Chem. 49 (2010) 3573.
27. Beyer, H. K.; Belenykaja, I. M.; Hange, F.; Tielen, M.; Grobet, P. J.; Jacobs, P. A. J. Chem. Soc., Faraday Trans. 1. 81 (1985) 2889.
28. Egerton, T. A.; Hagan, A.; Stone, F. S.; Vickerman, J. C. J. Chem. Soc., Faraday Trans. 168 (1972) 723.
29. Howard, J.; Nicol, J. M. Zeolites. 8 (1988) 142.
30. Lunsford, J. H.; Vansant, E. F. J. Chem. Soc., Faraday Trans. 69 (1973) 1028.
31. Dutta, P. K.; Lunsford, J. H. J. Chem. Phys. 6 (1977) 4716.
32. Lange, J.-P.; Klier, K. Zeolites. 14 (1994) 462.
33. Mozo, E. P.; Gabriunas, N.; Lucaccioni, F.; Acosta, D. D.; Patrono, P.; Givestra, A. L.; Reiz, P.; Delmon, B. J. Phys. Chem. 97 (1993) 12819.
34. Varkey, S. P.; Jacob, C. R. Ind. J. Chem. 37A (1998) 407.
35. Herron, N.; Stucky, G. D.; Tolman, C. A. J. Chem. Commun. (1986) 1521.
36. Simpson, H. D.; Steinfink, H. J. Am. Chem. Soc. 91 (1969) 6225.
37. Simpson, H. D.; Steinfink, H. J. Am. Chem. Soc. 91 (1969) 6229.
38. Gallezot, P.; Taarit, Y. B.; Imelik, B. J. Catal. 26 (1972) 205.

39. Thomas, J. M.; Catlow, C. R. A. Progr. Inorg. Chem. 35 (1988) 1.

40. Phan, N. T. S.; Sluys, M. V. D.; Jones, C. W. Adv. Synth. Catal. 348 (2006) 609.

41. Diegruber, H.; Plath, P. J.; Schulz-Ekloff, G.; Mohal, M. J. Mol. Catal. 24 (1984) 115.

42. Tapp, N. J.; Cardile, C. M. Zeolites. 10 (1990) 680.

43. Alexander, S. M.; Coddington, J. M.; Howe, R. F. Zeolites. 11 (1991) 368.

44. Edgardo, P. M.; Nyole, G.; Fabio, L.; Acosya, D. D.; Pasquale, P.; Aldo, L. G.; Patricio, R.; Bernard, D. J. Phy. Chem. 97 (1993) 12819.

45. Yusuff, K. K. M.; Sreekala, R. J. Polym. Sci., Part A: Polym. Chem. 30 (1992) 2595.

46. Lever, A. B. P. Inorganic Spectroscopy, Second Ed, Elsevier, New York. (1984).

****◆****

Chapter 7

Studies on catalytic activity of simple and zeolite Y encapsulated transition metal complexes

Contents

> *"A scientist in his laboratory is not a mere technician: he is also a child confronting natural phenomena that impress him as though they were fairy tales."*
>
> ***Marie Curie***

7.1 Introduction

Worldwide demand for environmentally friendly chemical processes and products requires the development of novel approaches to pollution prevention. Most of these approaches make use of catalysts. Thus the area of catalysis is often referred to as a 'foundational pillar' to the green chemistry[1]. The search for recoverable catalysts is a challenging problem in homogeneous catalysis involving transition metal complexes. The molecular structure and homogeneously dissolved nature of these catalysts are the most severe limitations for their application in practical catalysis. Many attempts have been made to combine the high activity and selectivity of soluble catalysts with the easy separation of them from reaction medium. Immobilization on solid support was one such approach. Catalysis is predominantly known for its importance in product selectivity and process efficiency starting from large scale industrial to small-scale reactions. Today a large number of catalysts are used in all areas of chemical industries and many national laboratories and academic institutions are pursuing research for the development of catalysts. With the objective to develop new oxidation catalysts, encapsulated transition metal complexes have been synthesized and characterized.

Zeolite encapsulated metal complexes have been extensively studied[2] and their catalytic activities have been reported for the oxidation of olefins[3], oxidation of cyclohexane[4], oxidation of carbon monoxide, acid-base reactions[2], hydrogen peroxide decompositions[5, 6], oxidation of organic compounds[7, 8], alkylation reactions[9], epoxidations[10], hydrocarbon processing and chemical synthesis[11-13], selective hydrogenation reactions[14] and for hydroxylation reactions[15].

The catalytic activity of the zeolite encapsulated complexes was studied for the following reactions.

1. decomposition of hydrogen peroxide.
2. oxidation of cyclohexanol by TBHP.

For convenience, this chapter is divided into the following two sections. The first section (7.2) deal with the studies on the catalytic activity of the Zeolite Y encapsulated complexes in the decomposition of hydrogen peroxide and the section 7.3 deals with the studies on the catalytic activity of the complexes in the partial oxidation of cyclohexanol to cyclohexanone by TBHP.

7.2 Catalytic activity in the decomposition of hydrogen peroxide

7.2.1 Introduction.

Hydrogen peroxide is widely accepted as a green oxidant as it is relatively nontoxic and breaks down readily to benign byproducts. Use of nature's major oxidants, oxygen and hydrogen peroxide, could reduce the environmental burden of pollutants based on oxidation processes. The availability of effective catalysts increases the potential of these oxidants in clean up applications for eliminating the toxic pollutants. In recent years ligand design strategy[16] has succeeded in attaining efficient and selective catalysts for activating hydrogen peroxide in an ideal manner for greening chemical technologies as well as for cleanup processes. Craig Jones[17] has written an excellent monograph on hydrogen peroxide chemistry. Hydrogen peroxide is also an important reagent in numerous enzymatic oxidations.

Decomposition of hydrogen peroxide has been investigated extensively as a homogeneous reaction catalyzed by transition metal ions and their complexes[18] as well as by enzyme such as catalase[19]. It was used in electrolysis of water for the production of oxygen[20] and also in the oxidation of organic substrates[21]. Various copper compounds have been investigated as models for enzymes by testing their ability to decompose hydrogen peroxide in basic aqueous solution[22]. For this reaction, diamine copper (II) complexes encapsulated in zeolite Y matrix was reported[5, 6, 23].

7.2.2. Experimental

7.2.2.1 Hydrogen peroxide solution.

Hydrogen peroxide solution was prepared in the reaction flask itself from commercially available hydrogen peroxide solution (Merck, 30%) which was kept in a dark polyethylene bottle preserved in refrigerator to retard decomposition. The hydrogen peroxide content was determined by titration using potassium permanganate as prescribed in literature[24].

7.2.2.2 Catalysts.

Simple and zeolite Y encapsulated Cu(II) complexes of hmbd, qcdn and Hohmbd were screened for the catalytic activity towards the decomposition of hydrogen peroxide. Details regarding the preparation and characterization of these complexes are presented chapters 3, 4, 5 and 6. The complexes were dried in an air oven before use.

7.2.2.3 Apparatus and Procedure.

A gas burette (Figure 7.1) was used for measuring the volume of oxygen liberated during the decomposition of hydrogen peroxide in the presence of catalysts. It consists of a graduated U tube having a stopper at the bottom. Both the arms of the gas burette were filled with ~ 20% NaCl solution, which was acidified with dilute HCl and was colored to orange red with methyl orange indicator.

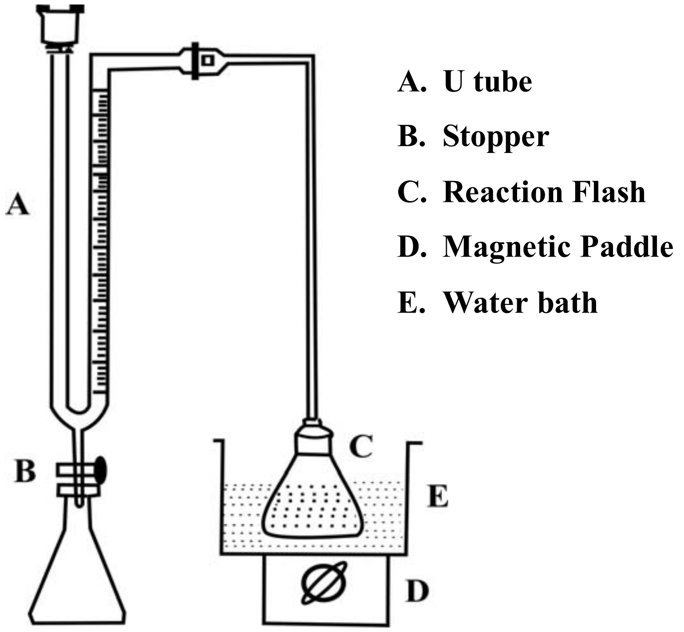


Figure 7.1: Experimental set up for monitoring the decomposition of H_2O_2

To the reaction flask of 100 mL capacity containing a magnetic paddle, distilled water (18 mL) and 30% hydrogen peroxide solution (2 mL) were added using a graduated pipette. The reaction flask was placed in a water bath for 15 minutes to attain the equilibrium room temperature. The catalyst (40 mg) was accurately weighed into a plastic float and placed above the hydrogen peroxide solution in the reaction flask. One arm of the gas burette was connected to the reaction flask through a rubber pressure tube. The solution level in both the arms of the gas burette was equalized such that the arm attached to the reaction flask read zero by adding or withdrawing solution from the gas burette. On starting the magnetic stirring, the catalyst in the plastic float gets dispersed in to H_2O_2 solution. A stopwatch was started simultaneously when the catalyst was just dispersed in H_2O_2 solution. As time passes, oxygen evolved was collected by the downward displacement of NaCl solution in the gas burette. The evolution of oxygen during the course of decomposition of hydrogen peroxide was monitored as a function of time at intervals of ten minutes after equalizing the solution level at both arms of the gas burette. The reaction was carried out for one hour. The reaction was carried out for one hour. The data on the evolution of the oxygen during the decomposition of hydrogen peroxide per hour is shown in Table 7.1.

To know the self-decomposition of hydrogen peroxide under identical conditions, a blank study was conducted. This was carried out by studying the hydrogen peroxide decomposition in exactly the same way as has been done for the catalytic activity study but with out adding any catalyst. Negligible volume of oxygen was collected in this case. Therefore evolution of oxygen (see Table 7.1) was obviously due to the activation of decomposition by the added catalysts. The volume of oxygen gas liberated while using NaY or metal exchanged zeolites were also negligible.

It is noted that addition of a drop of very dilute sodium hydroxide to the hydrogen peroxide solution containing catalyst increases the decomposition rate appreciably. However, addition of a drop of pyridine to the solution containing catalyst decreases the rate of decomposition. Probably, the active sites must have been blocked by pyridine and were made unavailable for interaction with hydrogen peroxide. Recycling test was also conducted with the catalysts. For this purpose, the catalyst was filtered from the reaction media using a G4 sintered crucible and washed with acetone, dried and again used for the decomposition reaction. The catalyst maintained almost the same activity after recycling. The color of the catalyst was also seen to be preserved. This indicates that the complexes are not leached out of the zeolite cavity and the sites are active for the catalyst reaction.

7.2.3 Results and Discussion.

The volume of oxygen liberated during 1 hr period of the decomposition reaction in the presence of complexes is presented in the Table 7.1. Comparison of catalytic activities of the encapsulated complexes with that of the neat complexes is shown as a bar diagram in Figure 7.2.

On comparison of the simple and zeolite Y encapsulated complexes, it can be seen that the catalytic activity of simple complexes are almost same as that of the zeolite Y complexes. However, a close examination would reveal that the zeolite encapsulated complexes are more active than the simple complexes, as the metal ion concentrations per unit mass of zeolite Y complexes in the reaction mixture are very low when compared with that of the simple complexes. On comparing the activities, CuYohmbd complex was found to be more active than the other copper encapsulated complexes. However, encapsulated as well as neat complexes show very low TOF values on comparison with the literature reports[25]. So, we have excluded further studies on this.

Table 7.1: Catalytic activity of the complexes in the decomposition of hydrogen peroxide at room temperature

Reaction conditions:

Catalyst weight = 60mg H_2O_2 10% = 20 mL

Temperature = 30 ± 0.1 °C Duration = 3 hours.

Simple complex/encapsulated complexes	TOF (h^{-1})
CuYhmbd	14
CuYqcdn	5
CuYohmb	15
Cuhmbd	13
Cuqcdn	4
Cuohmbd	13

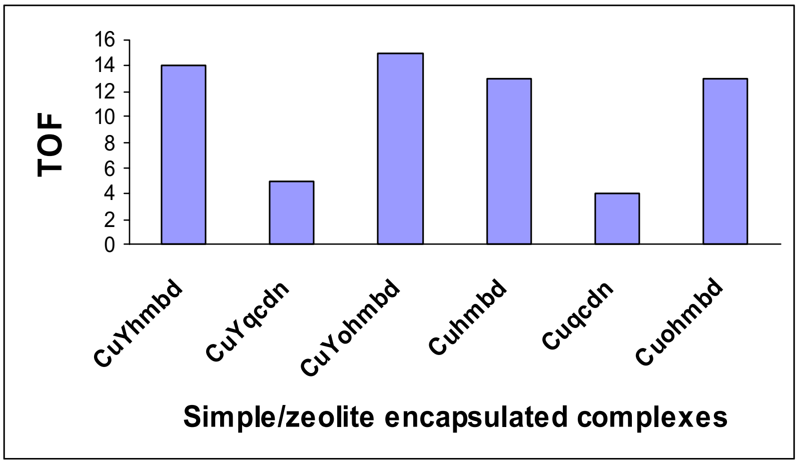


Figure 7.2: Screening studies using the synthesized complexes for decomposition of hydrogen peroxide

7.3 Catalytic activity in the partial oxidation of cyclohexanol to cyclohexanone using TBHP

7.3.1 Introduction.

Partial oxidation of cyclohexanol to cyclohexanone is an industrially important reaction extensively used for the production of polyamides, urethane foams, adipic acid, lubricating additives etc. The present commercial process for the conversion of cyclohexanol to cyclohexanone involves passing the substrate over a Cu-SiO_2 catalyst at around 300 ^oC. Since the selectivity is not sufficient with the usual processes, a lot of study was made to enhance the selectivity. Recently zeolite Y encapsulated metal complexes have been extensively used for carbonylation reactions as well as for hydroformylation[26-28] reactions.

7.3.2 Experimental

7.3.2.1 Cyclohexanol.

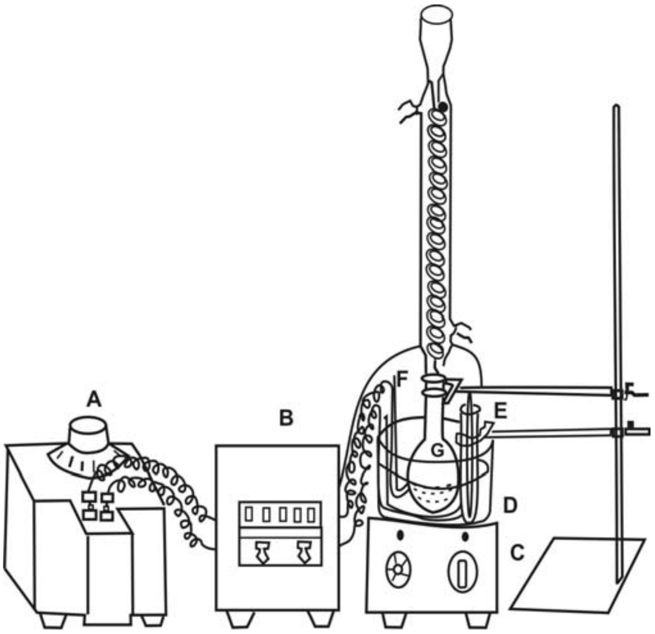
Cyclohexanol (BDH) was obtained commercially.

7.3.2.2 Catalysts.

CuYhmbd, CuYqcdn, CuYohmbd, Cuohmbd, Cuqcdn and Cuhmbd were the catalysts selected for the catalytic activity study on the oxidation of cyclohexanol by TBHP. The catalysts were dried in an air oven before use.

7.3.2.3 Experimental Set up.

The reaction (Figure 7.3) was carried out in a round-bottom flask fitted with a reflux condenser. The specified amount of catalyst was added and the oxidation initiated by the addition of the oxidant. The whole set up was kept in an oil bath and stirred magnetically using a stirrer for three hours at a particular temperature. The flask was cooled after the experiment and the catalyst was removed by filtration. The product and the unreacted substrate were analyzed using a gas chromatograph to estimate the conversion. The peaks were identified and quantified using authentic pure samples prior to the analysis.



A. Dimmerstat
B. Temperature controller
C. Magnetic stirrer
D. Oil bath
E. Thermo couple
F. Heating element
G. Reaction flask

Figure 7.3: Experimental set up for oxidation reaction

7.3.2.4 Procedure for cyclohexanol oxidation.

The oxidation of cyclohexanol with 70% TBHP as the oxidant and chlorobenzene as solvent at 70 ^{o}C was carried out in the presence of zeolite encapsulated complexes. The product cyclohexanone was analyzed by GC using a carbowax column. The reaction was carried out at different conditions to study the influence of different factors like reaction time, amount of catalyst, temperature and solvent. All the GC results obtained are reproducible within ±0.3%. The appropriate choice of the amount of the catalyst and the reaction conditions are crucial for catalytic effect. The catalysts were recycled and used to study the oxidation reactions. Characterization of the catalyst at the end of the oxidation reaction revealed that no leaching of the metal occurred during the reaction. This suggests that the metal complexes selected for study are intact inside the zeolite cages.

7.3.3 Results and Discussion

7.3.3.1 Screening studies

The zeolite encapsulated copper complexes of hmbd, Hohmbd and qcdn in the liquid phase were evaluated for their activity for the partial oxidation of cyclohexanol to cyclohexanone using t-butyl hydroperoxide at 70 ^{o}C keeping the oxidant to substrate ratio as 2. The percentage conversion of cyclohexanol was noted after 3 hours and the activities corresponding to different complexes are presented in Table 7.2 and the results are represented graphically in Figure 7.4. From the studies, it can be pointed out that among all the complexes present CuYhmbd and CuYohmbd are more active, whereas CuYqcdn is the least active showing only 52.3% conversion.

Table 7.2: Results of screening studies using Zeolite encapsulated complexes for cyclohexanol oxidation using TBHP

Catalyst Used	Conversion (%)	TOF(h^{-1})
CuYhmbd	63.9	160
CuYqcdn	52.3	82
CuYohmbd	72.8	165
Cuhmbd	58.4	147
Cuqcdn	48.6	75
Cuohmbd	69.7	158

Reaction conditions:

Amount of catalyst	:	20 mg
Oxidant to substrate mole ratio	:	2
Temperature	:	70 ^{o}C
Time	:	3 hours

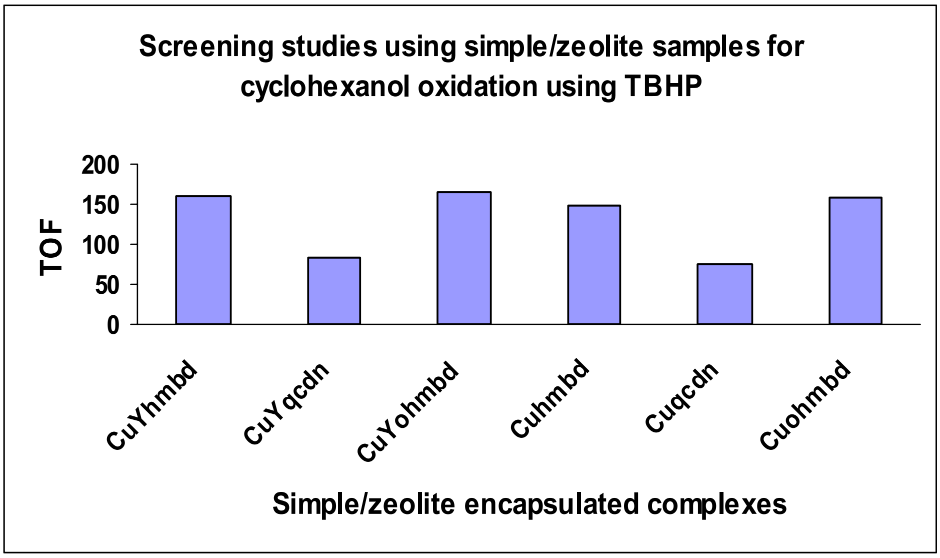


Figure 7.4: Screening studies using the synthesized complexes for cyclohexanol oxidation using TBHP

7.3.3.2 Blank run

The blank run was conducted at 70 °C keeping the conditions same as that of screening experiments but without any catalyst. No conversion occurred even after three hours duration, which indicates that TBHP by itself will not aid the oxidation of cyclohexanol in the absence of catalyst.

7.3.3.3 Factors influencing the oxidation of cyclohexanol

The effects of various parameters on catalysis were studied by varying the following factors.

1. Amount of catalyst
2. Reaction time
3. Temperature

7.3.3.3.1 Influence of the amount of catalyst

The extent to which oxidation proceeds depends on the amount of catalyst present in the reaction mixture. Therefore the influence of catalyst was studied by varying the amount of catalyst from 20 mg to 60 mg. The percentage conversion of cyclohexanol showed no substantial increase with increase in the amount of catalyst; hence 20 mg of catalyst was used for detailed studies. The data showing the conversion of cyclohexanol on varying the amount of catalyst are presented in Table 7.3. Further the percentage conversions are represented graphically in Figure 7.5.

Table 7.3: Effect of the amount of catalyst on the oxidation of cyclohexanol

Simple/zeolite encapsulated complexes	TOF(h^{-1})		
	Amount of catalyst (mg)		
	20	40	60
CuYhmbd	147	152	160
CuYqcdn	70	74	81
CuYohmbd	155	160	165
Cuhmbd	123	139	151
Cuqcdn	55	68	73
Cuohmbd	145	147	153

Reaction conditions:

Oxidant to substrate ratio	:	2
Temperature	:	70 ^{o}C
Time	:	3 hour

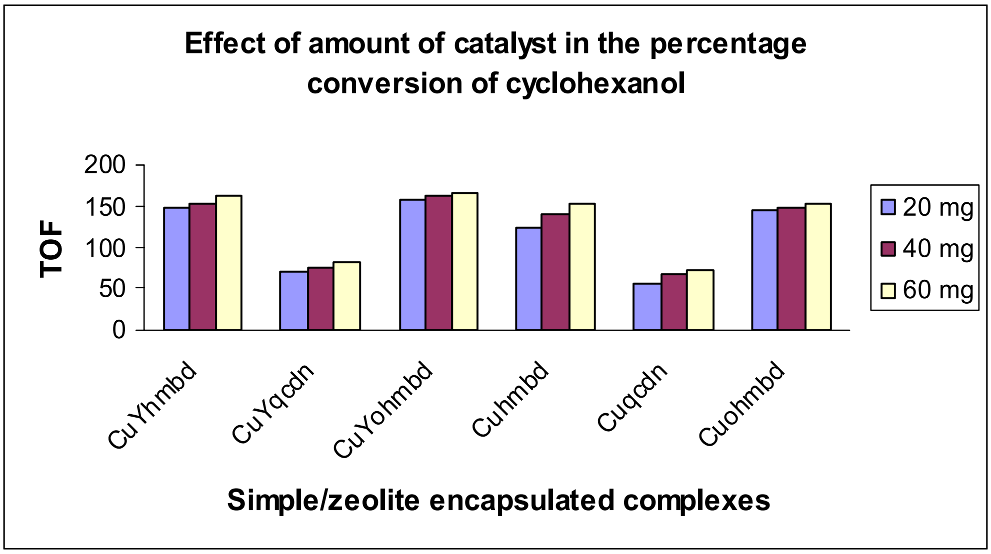


Figure 7.5: Influence of the amount of catalyst for cyclohexanol oxidation using TBHP

7.3.3.3.2 Influence of reaction time

In order to find out the influence of time on the percentage conversion of cyclohexanol, the oxidation reaction was conducted for different durations from one to four hours. Aliquots of the reaction mixture was withdrawn and subjected to gas chromatic analysis for products and results of the above studies are presented in table 7.4. Figure 7.6 is the corresponding graphical representation. The conversion was found to increase considerably with time for all the complexes studied. For two hours very little conversion was found to occur for all complexes. But when the reaction was allowed to proceed after three hours, darkening of the solution was observed indicating tar formation or tarry products. So the optimum time for the reaction was set as three hours.

Table 7.4: Effect of reaction time on the oxidation of cyclohexanol

Simple/ zeolite encapsulated complexes	TOF(h^{-1})		
	Reaction time (h)		
	1	2	3
CuYhmbd	30	58	107
CuYqcdn	10	38	57
CuYohmbd	60	73	122
Cuhmbd	24	48	100
Cuqcdn	9	32	45
Cuohmbd	51	68	112

Reaction conditions:

Amount of catalyst : 20 mg

Oxidant to substrate ratio : 2

Temperature : 70 °C

Time : 3 hours

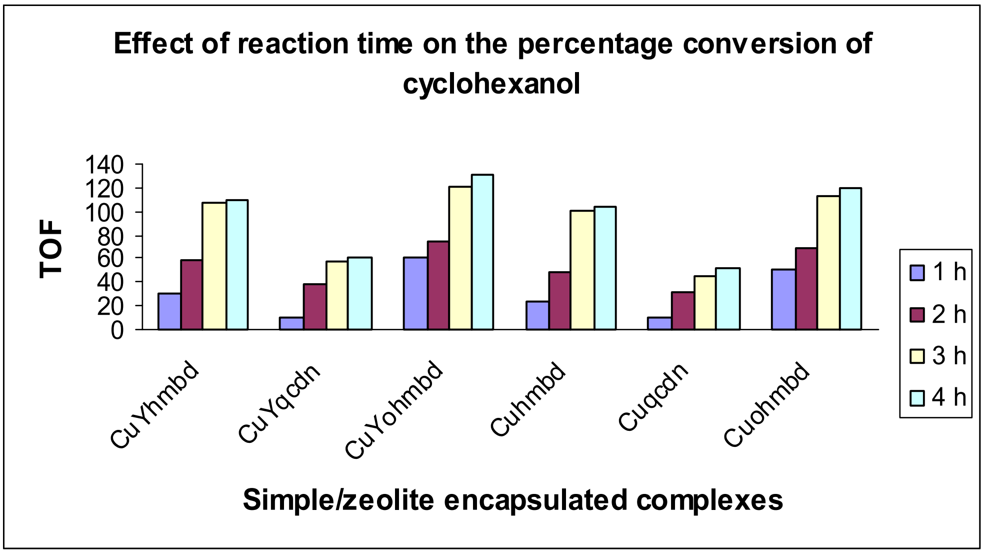


Figure 7.6: Influence of reaction time in cyclohexanol oxidation using TBHP

7.3.3.3.3 Influence of temperature

The oxidation reaction for the complexes under study CuYhmbd, CuYqcdn and CuYohmbd were conducted under identical conditions at three different temperatures 30 °C, 50 °C, and 70 °C to find out the optimum temperature for the reaction. The results obtained for the various encapsulated complexes are presented in Table 7.5. The percentage conversion increases with increase of temperature in the case of all the above mentioned catalysts as evident from the Figure 7.7. The maximum conversion occurred at 70 °C and it was selected as the optimum temperature for detailed studies.

Table 7.5: Influence of temperature on the oxidation of cyclohexanol

Simple/ zeolite encapsulated complexes	TOF(h^{-1})		
	Temperature (°C)		
	30	30	30
CuYhmbd	81	139	160
CuYqcdn	34	55	81
CuYohmbd	82	153	165
Cuhmbd	72	124	150
Cuqcdn	31	51	78
Cuohmbd	74	144	159

Reaction conditions:

Amount of catalyst : 20 mg

Oxidant to substrate ratio : 2

Time : 3 hours

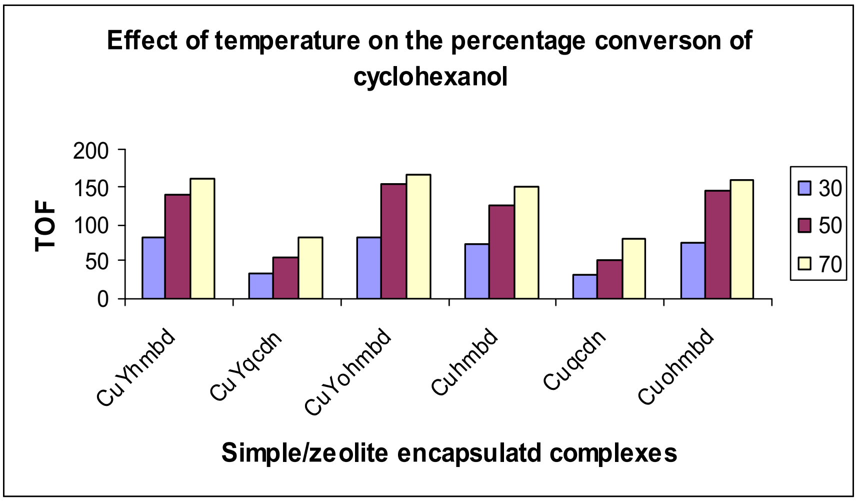


Figure 7.7: Influence of temperature in cyclohexanol oxidation using TBHP

7.3.3.3.4 Recycling studies

The encapsulated complexes CuYhmbd, CuYqcdn, CuYohmbd employed for oxidation studies were separated from the reaction mixture, washed with acetone several times and dried in oven to remove the impurities attached to the catalyst. Then reactions were carried out using recycled catalyst under the same conditions. The percentage conversions of the recycled catalysts are given in Table 7.6. A graphical comparison of the activities of the fresh and recycled samples is presented in Figure 7.8. The similar activity and the spectroscopic properties of the recycled catalyst indicated the preservation of the structural integrity of the synthesized complexes.

Table 7.6: Results of recycling studies

Sample used	Fresh sample	Recycled sample	Third Run
CuYhmbd	160	151	147
CuYqcdn	81	78	75
CuYohmbd	165	163	156
Cuhmbd	147	139	131
Cuqcdn	75	68	59
Cuohmbd	158	149	137

Reaction conditions:

Amount of catalyst	:	20 mg
Oxidant to substrate ratio	:	2
Temperature	:	70 °C
Time	:	3 hours

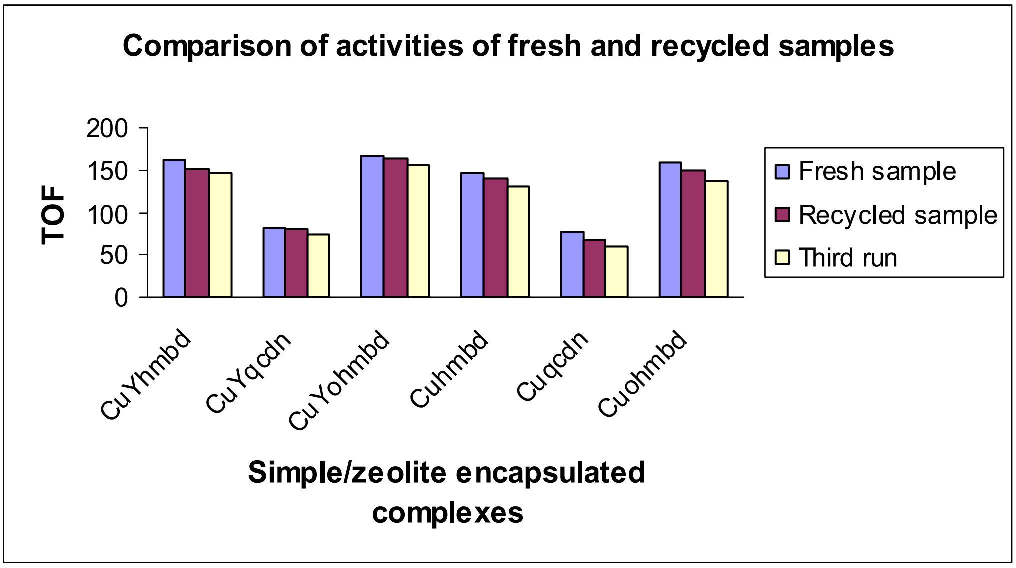


Figure 7.8: Comparative studies of the activity of fresh and recycled samples in the oxidation of cyclohexanol using TBHP.

7.3.4. Conclusions

The zeolite encapsulated copper complexes of 4–hydroxy–3–methoxy benzalidine–1,8–diaminonaphthalene (hmbd), quinoxaline–2–carboxalidine–1,8–diaminonaphthalene (qcdn) and 2–hydroxy–3–methoxy benzalidine–1,8–diaminonaphthalene (Hohmbd) were used to catalyze the oxidation of cyclohexanol. The comparisons of their catalytic activity indicate that CuYohmbd act as most effective catalyst in this oxidation reaction followed by CuYhmbd. The enhanced activity exhibited by encapsulated complexes can be attributed to several factors. The distortion of the molecular geometry from planarity to a puckered structure, greater depletion of electron density at the site of metal ion facilitating nucleophilic attack by anionic reagents are identified as the reasons for the increased catalytic activity[27]. The oxidation reaction did not take place in the absence of catalyst.

Zeolite encapsulated complexes act as heterogeneous catalysts and offer several advantages when compared to homogeneous catalysts. They can be separated from the reaction mixture by simple methods like filtration. Another advantage lies in the fact that they can be recycled which enables continuous processing. Also it reduces the problem of environmental pollution by different chemical reagents. The use of encapsulated complexes as catalysts allows the cyclohexanol oxidation process to follow the heterogeneous – homogeneous reaction mechanism. The oxidation reactions were also conducted with NaY and CuY, no significant conversion occurs with NaY supporting the fact that zeolite support by itself does not ensure oxidation. The encapsulated copper complexes are held firmly inside the zeolite pores by electrostatic forces of attraction, which enhances their catalytic activity.

The reaction was conducted with varying amounts of catalyst to study the influence of the amount of catalyst. The percentage conversion of cyclohexanol increases only by a small extent with increase in the amount of catalyst. The excess amount of catalyst increases the number of active sites thereby enhancing the reaction. Experimental results have showed that the reaction takes three hours for completion and running the reaction for a period more than the optimum time results in the formation of undesired products. The oxidant to substrate ratio too plays an important role in the reaction. The optimum oxidant to substrate ratio was found to be 2. In order to study the effect of temperature, the reaction was conducted at three different temperatures 30 °C, 50 °C and 70 °C. The percentage conversion increased on raising the temperature and maximum yield was obtained at 70 °C. So 70 °C was selected as the optimum temperature for further studies. In all reactions, only one product (cyclohexanone) was produced, therefore, the selectivity (%) is 100 with respect to it.

An important advantage of zeolite-encapsulated complexes is their ability to be recycled. The recycling studies were done after washing the used samples several times with acetone and heating them in an oven. They were able to retain their activity that can be taken as a solid evidence for the stability of the complexes inside the zeolite pores. The retention of catalytic activity recycled samples is a proof of their ability to withstand the regeneration process.

References

1. Anastas, P. T.; Kirchhoff, M. M.; Williamson, T. C. Appl. Catal., A. 221 (2001) 3. (b) Anastas, P. T.; Kirchhoff, M. M. Acc. Chem. Res. 35 (2002) 686.
2. Coughlan, B.; Narayanan, S.; McCann, W. A.; Carroll, W. M. J. Catal. 49 (1977) 97.
3. Berthomieu, D.; Delahay, G. Cat. Rev. - Sci. Eng. 48 (2006) 269.
4. Mochida, J.; Jitsumatsu, T.; Kato, A.; Seiyama, T. Bull. Chem. Soc. Jap. 44 (1971) 2595.
5. Xavier, K. O.; Chacko, J.; Yusuff, K. K. M. Appl. Catal., A. 258 (2004) 251.
6. Pape, B. E.; Rodgers, D. H.; Flynn, T. C. J. Chromatogr. A. 134 (1977) 1.
7. Ratnasamy, C.; Murugkar, A.; Padhye, S. Ind. J. Chem. 35 A (1996) 1.
8. Joseph, T.; Sajanikumari, C. S.; Pande, S. S. D.; Gopinathan, S. Ind. J. Chem. 38 A (1999) 792.
9. Bhattacharya, D.; Pandey, A. K.; Singh, A. D. Recent advances in Basic and Applied aspects of Industrial Catalysis Studies in Surface Science and Catalysis, Elsevier Science.113 (1998) 737.

10. Bowers, C.; Dutta, P. K. J. Catal. 122 (1990) 271.
11. Gellin, P.; Naccache, C.; Tarrit, Y. B. Pure Appl. Chem. 8 (1988) 1315.
12. Auroux, A.; Bolis, V.; Wierachoski, P.; Grzvelle, P.; Vedrine, J. J. Chem. Soc. Faraday. Trans. (1979) 2544.
13. Long, J.; Wang, X. L.; Zhang, G.; Dong, J.; Yan, T.; Li, Z.; Fu, X. Chem. Eur. J. 13 (2007) 7890.
14. Knops-Gerrits, P.-P.; De Vos, D. E.; Feijen, E. J. P.; Jacobs, P. A. Microporous Mater. 8 (1997) 3.
15. Ulgappan, N.; Krishnasamy, V. Ind. J. Chem. 35 A (1996) 787.
16. Collins, T. J. Acc. Chem. Res. 27 (1994) 279.
17. Jones, C. W. Applications of Hydrogen Peroxide and Derivatives, Royal Society of Chemistry, Cambridge. (1999).
18. Sharma, V. S.; Schubert, J. J. Am. Chem. Soc. 91 (1969) 6291.
19. Karakhanov, E. A.; Narin, S. Y.; Dedov, A. G. Appl. Organomet. Chem. 5 (1991) 445.
20. Sengupta, S. K.; Preethi, L. Ind. J. Tech. 30 (1992) 172.
21. Sheldon, R. A.; Kochi, J. K. Metal Catalysed Oxidations of Organic Compounds, Academic Press: New York (1981).
22. Peisach, J.; Aisen, P.; Blumberg, W. E. The Biochemistry of Copper, Eds.; Academic Press: New York. (1966) 371.
23. Patri, U. B.; Aksu, S.; Babu, S. V. J. Electrochem. Soc. 153 (2006) G650.
24. Vogel, A. I. A Text Book of Qualitative Inorganic Analysis, Longmans-Green; London. (1978).
25. Sreekumara, K.; Rajab, T.; Kiranb, B. P.; Sugunana, S.; Rao, B. S. Appl. Catal., A. 182 (1999) 327.

26. Pesquera, C.; González, F.; Blanco, C.; Benito, I.; Mendioroz, S. Thermochim. Acta. 219 (1993) 179.

27. Ramesh, R. Inorg. Chem. Commun. 7 (2004) 274.

28. Srinivas, D.; Sivasankar, S. Catal. Surv. Asia. 7 (2003) 2.

****◆****

Chapter

8

Summary and Conclusion

Schiff bases play key role in the development of coordination chemistry. Modern chemists still prepare Schiff bases, and nowadays active and well-designed Schiff base ligands are considered as “privileged ligands”. 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. There is continuing interest in the synthesis of new Schiff base complexes with a view to use them as effective homogeneous catalysts. To have more practical application, many of these complexes are being encapsulated in zeolite cavities or anchored to polymeric supports. The chemistry of zeolite encapsulated complexes has been an area of particular interest because of their high activity, unique size and shape-selective catalytic properties. The supported Schiff base complexes, as a result of their particular structure, display an enhanced activity and selectivity in a multitude of organic reactions.

Taking into consideration the highly desirable attributes of such complexes, new Schiff base complexes were designed and synthesized. The present thesis deals with the synthesis, characterization and catalytic activity studies of complexes of manganese(II), cobalt(II) and copper(II) with the Schiff bases derived from diaminonaphthalene. The copper(II) complexes were encapsulated in zeolite Y and their application as catalysts in the decomposition hydrogen peroxide and oxidation of cyclohexanol was studied.

The thesis is divided into seven chapters. Contents of the various chapters are briefly described as follows:

Chapter 1

This chapter presents a general introduction to Schiff bases and a brief discussion of their applications in various catalytic processes. The synthetic methodologies and various applications of perimidines are also discussed in this chapter for the reason that the Schiff base ligands for the preparation of transition metal complexes are generated through the ring opening of perimidines. A brief literature survey on the zeolite encapsulated metal complexes and the advantages of heterogenization of metal complexes are also presented. It also gives an account of the catalytic activity of the encapsulated complexes in various reactions. The scope of the present work and the possible application of these complexes in various fields are also discussed in this chapter.

Chapter 2

The chapter 2 contains details regarding the materials used, methods employed for the preparation of ligands, metal exchanged zeolite and the characterization techniques used to study the nature and geometry of the synthesized complexes. The methods used for carrying out catalytic activity studies and estimation of percentage conversion are also included in this chapter. Information about the synthesis and spectral characterization of the three new perimidine derivatives such as 4-(2,3-dihydro-1*H*-perimidin-2-yl)-2-methoxyphenol, 2-(quinoxalin-2-yl)-2,3-dihydro-1*H*-perimidine and 2-(2,3-dihydro-1H-perimidin-2-yl)-6-methoxy phenol are also included in this chapter. These perimidines formed via the condensation of 1,8-diaminonaphthalene with 4-hydroxy-3-methoxy benzaldehyde, quinoxaline-2-carboxaldehyde or 2-hydroxy-3-methoxy benzaldehyde. In the solid state, most of the perimidines and their derivatives are stable in the ring closed form but upon dissolution in non polar solvents, equilibrium is gradually established between the ring closed and an extended π-conjugated system of the ring opened imine form. The opened form, acts as Schiff base ligand. The generated Schiff base ligands used in the present study are quinoxaline–2–carboxalidine–1,8–diaminonaphthalene (qcdn), 2–hydroxy–3–methoxybenzalidine–1,8–diaminonaphthalene (Hohmbd) and 4–hydroxy–3–methoxybenzalidine–1,8–diaminonaphthalene (hmbd). The details regarding the methods used to characterize the complexes such as CHN analysis, XRD studies, scanning electron micrographs, TG analysis, surface area, pore volume determination and diffuse reflectance, FT-IR, UV-visible and EPR spectroscopy are also presented in this chapter.

Chapter 3

In this chapter, a discussion on the synthesis and characterization of copper(II) complexes of quinoxaline–2–carboxalidine–1,8–diaminonaphthalene (qcdn) is presented.

The complexes were prepared by the reaction of 2-(quinoxalin-2-yl)-2,3-dihydro-1*H*-perimidine with copper(II) salts. The synthesized complexes have the general molecular formula $[Cu(qcdn)X_2(H_2O)_2]$ ($X = Cl^-$, CH_3COO^-, ClO_4^-) except for the nitrato complex. In the case of nitrate complex, the formula is $[Cu(qcdn)(NO_3)_2]$. The analytical data reveal that all the complexes are formed in the metal:ligand ratio 1:1. All the complexes are stable and are non electrolytes in DMF. FT-IR spectra of these complexes reveal that all the complexes contain the band due to the azomethine stretching in the range 1610–1650 cm^{-1}. Further the IR data suggest the ligand qcdn act as bidentate ligand coordinating through the nitrogen atom of the azomethine group and quinoxaldehyde C=N group. The EPR spectra of all the complexes were recorded and are axial in nature. The electronic spectral and magnetic moment studies of the complexes reveal an distorted octahedral geometry for the chloro, acetato and perchlorato complexes and square planar geometry for the nitrato complex.

Chapter 4

Details regarding the synthesis and characterization of Mn(II), Co(II) and Cu(II) complexes of the Schiff base, 2–hydroxy–3–methoxybenzalidine–1,8–diaminonaphthalene (Hohmbd) are presented in chapter 4. The complexes were prepared by the reaction of 2-(2,3-dihydro-1*H*-perimidin-2-yl)-6-methoxyphenol with manganese(II), cobalt(II) and copper(II) salts. The analytical data show that the complexes have the general empirical formula $[M(ohmbd)_2(H_2O)_2]$ for the manganese(II) and copper(II) complexes and $[M(ohmbd)_2]$ for the cobalt(II) complex. All the complexes are found to be stable and could be stored for months without any appreciable change. The conductivity studies show that the complexes are non electrolytes in DMF. The band in the IR spectra of the complexes occurring in the range 1600–1630 cm^{-1} is attributed to C=N stretching. The ligand ohmbd acts as a bidentate ligand coordinating through the nitrogen atom of the azomethine group and oxygen atom of the phenol hydroxyl group. The EPR spectra of the manganese(II) and copper(II) complexes were recorded. The physicochemical and spectral data suggest an octahedral geometry for both the manganese(II) and copper(II) complexes; whereas tetrahedral structure is assigned for the cobalt(II) complex.

Chapter 5

This chapter presents the studies on the complexes of 4–hydroxy–3–methoxy benzalidine–1,8–diaminonaphthalene (hmbd). The complexes were prepared by the reaction of 4-(2,3-dihydro-1*H*-perimidin-2-yl)-2-methoxyphenol with manganese(II), cobalt(II) and copper(II) salts. The analytical data reveal that all the complexes are formed in the metal:ligand ratio 1:2. The complexes have the general empirical formula $[M(hmbd)_2Cl_2(H_2O)_2]$ for manganese(II), cobalt(II) and copper(II) complexes. All the complexes are stable and non electrolytes in DMF. In the IR spectra, the band in the range 1600 – 1620 cm^{-1} suggest the involvement of –C=N in bonding to the metal ion. The physicochemical and spectral data suggests that all these complexes have a mononuclear structure with octahedral geometry around the metal centre.

Chapter 6

This chapter describes the synthesis and characterization of zeolite Y encapsulated Cu(II) complexes of the ligands quinoxaline–2–carboxalidine–1,8–diaminonaphthalene (qcdn), 2–hydroxy–3–methoxy benzalidine–1,8–diaminonaphthalene (Hohmbd) and 4–hydroxy–3–methoxybenzalidine–1,8–diaminonaphthalene (hmbd). The complexes synthesized by flexible ligand method were purified by soxhlet extraction. The retention of the Si/Al ratio of the zeolite Y indicates that there is no loss in crystallinity of the zeolite structure by encapsulation. This is further confirmed by the similar XRD patterns. Reduction in surface area and pore volume value of the complexes compared to the copper-exchanged zeolite suggests encapsulation within the supercages of the zeolite. The first stage of decomposition till 200 ^{o}C in the TG might be due to the loss of coordinated water along with the physisorbed water. The mass loss in the second stage is consistent with the decomposition of the encapsulated complex. Then a constant weight is maintained till 850 ^{o}C and above this temperature, the destruction of the framework occurs. IR spectra of zeolite encapsulated complexes indicate the involvement of azomethine nitrogen in coordination. The electronic spectra of all the encapsulated complexes show d–d band in the range 12800–13500 cm^{-1} and indicate octahedral structure. The solid state EPR spectra of the copper complexes were recorded at room temperature and indicate axial spectra.

Chapter 7

This chapter contains study of the decomposition of hydrogen peroxide in the presence of simple and encapsulated complexes of hmbd, qcdn and Hohmbd. Among all the complexes synthesized, CuYHohmbd was found to be the most active catalyst. A comparative study of the activities of the simple complexes and the zeolite samples revealed that encapsulated complexes act as more effective catalysts in the decomposition reaction. However, rate of decomposition is very low when compared to that for the complexes reported in the literature.

This chapter also deals with the results obtained for cyclohexanol oxidation using hydrogen peroxide in the presence of simple and zeolite encapsulated complexes of hmbd, qcdn and Hohmbd. The product formed and the unreacted substrate was analyzed using a gas chromatograph to estimate the percentage conversion. The conversion was found to be very low with hydrogen peroxide. Therefore we have changed the oxidant as TBHP. The reaction was carried out with TBHP under different conditions to study the influence of different factors like reaction time, amount of catalyst, temperature etc. An estimation of the catalyst at the end of the oxidation reaction revealed that no leaching of metal occurred during the reaction, which suggests that the complexes are intact with the zeolite cages.

The comparison of their catalytic activities indicates that CuYHohmbd act as the most effective catalyst followed by CuYhmbd. The percentage conversion with CuY is found to be very low in comparison with supported encapsulated complexes. Experimental results have shown that there is an optimum time for the completion of the reaction and when the reaction was allowed to proceed after this time, unwanted products are formed. The reaction was studied at three different temperatures 30 °C, 50 °C and 70 °C in order to determine the influence of temperature on the oxidation. The percentage conversion increased on raising the temperature. The maximum conversion was observed at 70 °C and so it was selected as the optimum temperature for further studies. The recycling studies were done after washing the used samples several times with acetone and heating them in an oven. They were able to retain most of their activity, which can be taken as a solid evidence for the stability of the complexes inside the zeolite pores and their ability to withstand the regeneration process.

****◆****

List of Publications

1. **G. Varsha., V. Arun., P. P. Robinson., Manju Sebastian., Digna Varghese., P. Leeju., V. P. Jayachandran and K. K. M. Yusuff (2010).** Two new fluorescent heterocyclic perimidines: first syntheses, crystal structure and spectral characterization. Tetrahedron Letters. 51: 2174-2177.

2*. **G. Varsha., V. Arun., Manju Sebastian., P. Leeju., Digna Varghese and K. K. M. Yusuff. (2009).** (2*Z*)2-amino-3-{[(*E*)-phenylmethylidene]amino}but-2-enedinitrile. Acta Crystallographica Section E. E65: o919.

3*. **V. Arun., P. P. Robinson., S. Manju., P. Leeju., G. Varsha., V. Digna and K. K. M. Yusuff. (2009).** A novel fluorescent bisazomethine dye derived from 3-hydroxyquinoxaline-2-carboxaldehyde and 2,3-diaminomaleonitrile. Dyes and Pigments. 82: 268-275.

4*. **Manju Sebastian., Vasudevan Arun. Ponminiessary P. Robinson., Pally Leeju., Digna Varghese., Gopalakrishnan Varsha and Karukapadath K. Mohammed Yusuff (2010).** Synthesis, characterization and structure of a new Cobalt (II) Schiff-base complex with quinoxaline-2-carboxalidine-2-amino-5-methylphenol. Journal of Coordination Chemistry. 63: 307-314.

5*. **P. Leeju., V. Arun., Manju Sebastian., G. Varsha., Digna Varghese and K. K. M. Yusuff. (2009).** N-[(E)-quinoxalin-2-ylmethylidene]-1*H*-indazol-5-amine. Acta Crystallographica Section E. E65: o1981.

6*. **Digna Varghese., V. Arun., P. P. Robinson., Manju Sebastian., P. Leeju., G. Varsha., and K. K. M. Yusuff. (2009).** Two novel bis-azomethines derived from quinoxaline-2-carbaldehyde. Acta Crystallographica Section C. C65: o612–o614.

* Not related to the work presented in this thesis