Synthesis, Characterization and Application Studies of Some Polymer Supported Metal Complexes

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Dr.K.Girish Kumar 15-11-2006

Reader in Analytical Chemistry

Certificate

Certified that the present work entitled "**Synthesis, characterization and application studies of some polymer supported metal complexes**", submitted by Mr.Jose P.Kalloopparambil in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry to Cochin University of Science and Technology is an authentic and bonafide record of the original research work carried out by him under my supervision at the Department of Applied Chemistry. Further, the results embodied in this thesis, in full or in part, have not been submitted previously for the award of any other degree.

Dr. K. Girish Kumar
(Supervising Guide)

Declaration

I hereby declare that the work presented in this thesis entitled **"Synthesis, characterization and application studies of some polymer supported metal complexes"**, is based on the original work carried out by me under the guidance of Dr. K. Girish Kumar, Reader in Analytical Chemistry, 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 **Jose P. Kalloopparambil**

15-11-2006

Acknowledgement

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PREFACE

Polymer supported chemistry has been in the limelight for the last three decades because of its versatility and efficiency as reagents, substrates and catalysts. An advancement in this field is the tailor-made polymer supports with the desired combination of properties. Recently there has been observed a growing interest in the synthesis of polymer supported metal complexes as polymer supported schiff bases show great affinity for metal ions. Complexes of many transition metal ions are found to be good catalysts.

Hence it is worthwhile to synthesize and characterize polymer supported schiff base ligands and metal complexes out of them. Thus three schiff bases of amino methylated polystyrene with aldehydes such as p-hydroxy benzaldehyde, p-dimethyl amino benzaldehyde and 3-nitro benzaldehyde were synthesized. Subsequently three series of complexes of Cu[II], Ni[II], Co[II], Fe[III], Mn[II] and Zn[II] were prepared and all of them were characterized.

Polymer supported ligands are found to be efficient complexing agents and their high selectivity enables the removal and analysis of traces of heavy metal ions even in the presence of large amounts of sodium and potassium ions. Heavy metal ions are toxic to all the living organisms of land and sea. Therefore the metal ion removal studies were carried out to develop optimum conditions using the schiff bases of amino methylated polystyrene with p-hydroxy benzaldehyde and p-dimethyl amino benzaldehyde for the removal of Cu[II] and Fe[III] respectively.

Polymer supported membranes function as ion selective potentiometric sensors which allow the exchange of specific ions among other ions of the same charge. The complex of Cu(II) with the schiff base obtained by the condensation of amino methylated polystyrene with p-dimethyl amino benzaldehyde is used as the ionophore for the fabrication of the copper sensor electrode.

Chapter 1 gives an introduction to polymer supports, polymer supported complexes and a brief review on application of polymer supported complexes.

Chapter 2 explains the materials and instruments used and the procedure adopted for the synthesis and characterization of schiff bases and complexes.

Chapter 3 illustrates the results of characterization that led to the ascertainment of the structure of the synthesized schiff bases and complexes.

Chapter 4 focuses on metal ion removal studies using the schiff base of amino methylated polystyrene with 4-hydroxy benzaldehyde and schiff base of amino methylated polystyrene with p-dimethyl amino benzaldehyde. The efficiency of the method and optimum conditions developed is described.

Chapter 5 describes the fabrication of the $\mathbf{Cu}^{2+}$ ion selective sensor electrode, its selectivity, response behaviour and applicability.

Chapter 6 Summary and conclusions.

Contents

Page No

1. INTRODUCTION ....

2. MATERIALS AND METHODS ....

3. SYNTHESIS AND CHARACTERIZATION ....

4. METAL ION REMOVAL WITH POLYMER SUPPORTS ....

CHAPTER

1

INTRODUCTION

Contents

1.1. Polymer Supports

Polymer supports have been widely used as reagents, substrates and catalysts for many reaction systems. Both organic and inorganic polymer supports are extensively used for carrying out reactions more conveniently at controlled rates. Certain inorganic polymer supports are found to have electrical, optical and thermal properties[1]. Functionalized polymers are highly versatile to open an excellent area of research.

A functionalized polymer contains a functional group that is able to perform a chemical transformation. The chemical activity of the polymer support depends greatly on structural factors and on the chemical nature of the functional group. The polymer support should be porous to allow the access of the reagent and the solvent and it should be with sufficient mechanical, chemical and thermal stability. Polystyrene, PMMA, PVC, PAN, poly acrylic acids, polysulfones, PEG, poly vinyl acetate, cellulose and silica are some among them. Polystyrene cross linked with 1-2% divinyl benzene satisfies the requirement for a good polymer support as reagent and substrate. It is microporous and microreticular. It is highly swollen in solvents like DMF, THF, dichloromethane etc. It allows the access of the reagent and solvent. They are less fragile and require less care in handling, react faster in functionalization and application reactions and they possess higher loading capacities.

Highly cross linked polystyrene provide rigid structures. So they are useful as ion-exchange resins which can be easily removed from a reaction system. A poly ion in the form of a membrane exposed to an electrolyte will allow the counter ion to pass through it and it will retain a barrier to the complementary ion.

The pioneering work on polymer substrate technology in solid phase polypeptide synthesis developed by R. B. Merrifield was one of the greatest achievements[2]. It is very useful in confirming the structure of naturally occurring bio-macromolecules and it is a source for bio-macromolecules which showed more desirable biological activity. Since then investigations on polymer supports is progressing.

Polymer catalysts are of many advantages. They are less toxic, easy to handle and more resistant to atmospheric contaminants. Further the removal of the catalyst is also very simple. Sulphonated polystyrene, super acids like nafion[3] are also good catalysts. Polymer phase transfer catalysts act as the meeting place for two immiscible reactants.

Polymer supported drugs are of potential advantages when compared with the low molecular weight drug. They can be employed where a sustained and delayed action of drug is required. Immobilized enzymes are prepared of polymeric supports which are found to have increased stability to pH and temperature.

Polymeric photosensitizers are prepared from benzophenone and polystyrene[4]. Polymer supported bio-membranes are a promising approach for the development of biosensor devices[5]. Ion-exchange membranes are perm selective. Thus polymer supported membranes can be used as ion selective electrodes. The hydrophilicity of moderately ionic polymers leads to another type of membrane application called reverse osmosis.

Now polymer supported reactive chemistry is being developed and exploited at an amazing rate and it seems to join the routine world of synthesis and to become a methodology [7].

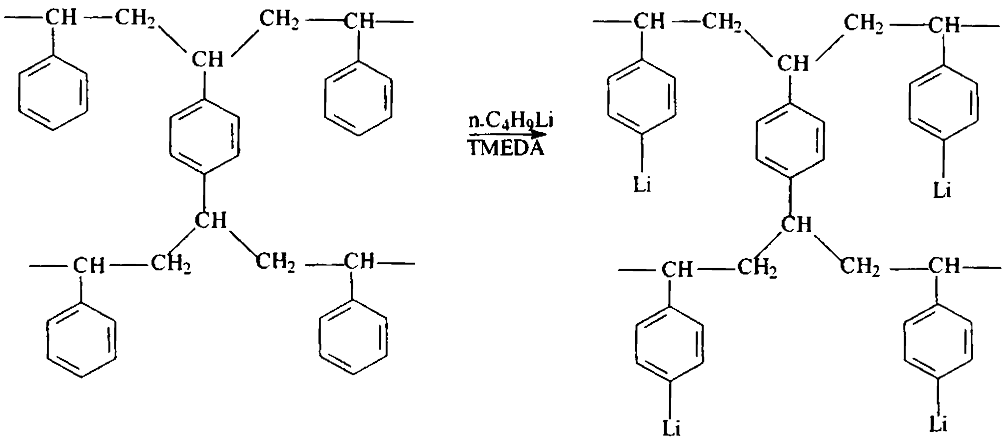
1.2. Polymer Supports as Ligands

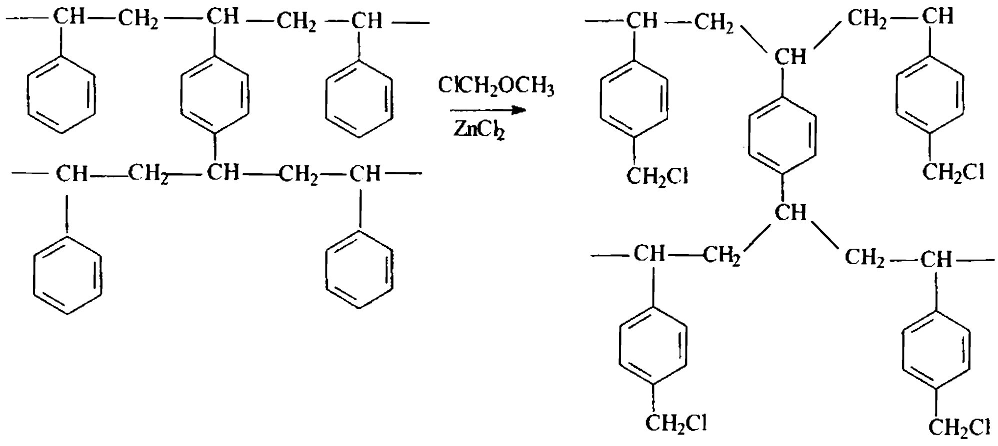
Polymers are used as efficient complexing agents. The wide variety of ligands include amines, schiff bases, dithiocarbammates, iminodiacetic acid, amidoximes, thiosemicarbazones etc. for the complexation of metal ions. Recently there observed a growing interest in the use of functionalized polymers for the preparation of metal complexes for various applications. More polar and flexible cross linking agents are found to enhance the metal ion intake of the polymer supported ligand. Thus the extend of complexation depends on the hydrophilicity of the polymer support [8]. DVB cross linked polystyrene supports are insoluble and they can be easily separated from the reaction system and products of high purity are obtained. Highly cross linked resins are more brittle, hard and more impervious. Functional groups in the immediate vicinity of cross links are prone to steric hindrances from chelating with the metal ions. Among the various chelating groups, iminodiacetic acid supported on styrene divinyl benzene matrix forms a large group with N and O as donor atoms.

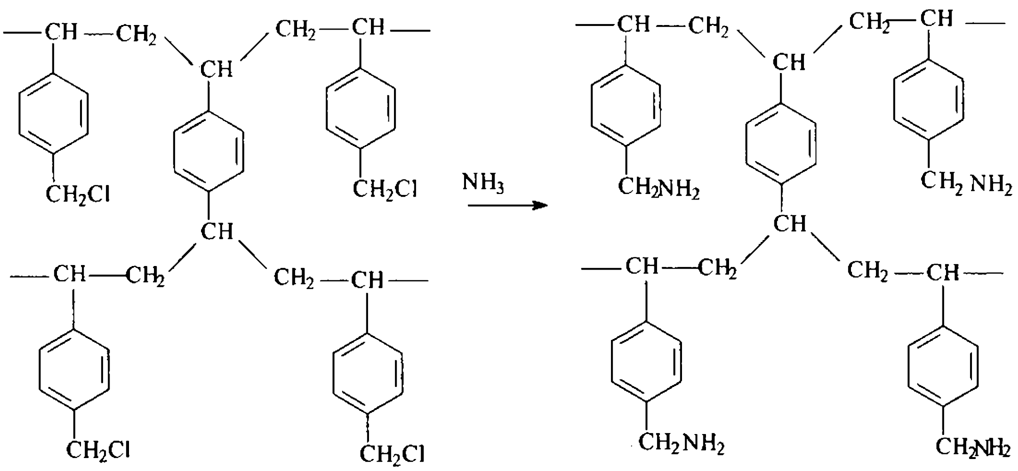
Polymer support containing 8-hydroxy quinoline units are useful for the complexation of metal ions like Ni^{2+},Co^{2+} and Cu^{2+}. Here the complexation is through N and O atoms. The metal can be separated from the polymer by changing the pH. There are polymers containing chiral groups for resolving racemic mixtures into enantiomers [9] where one of the enantiomers is complexed more strongly than the other and thus separation is achieved. Macrocyclic crown ethers like 18-crown-6 and cryptands are useful for binding metal ions because of their high degree of selectivity for specific metal ions.

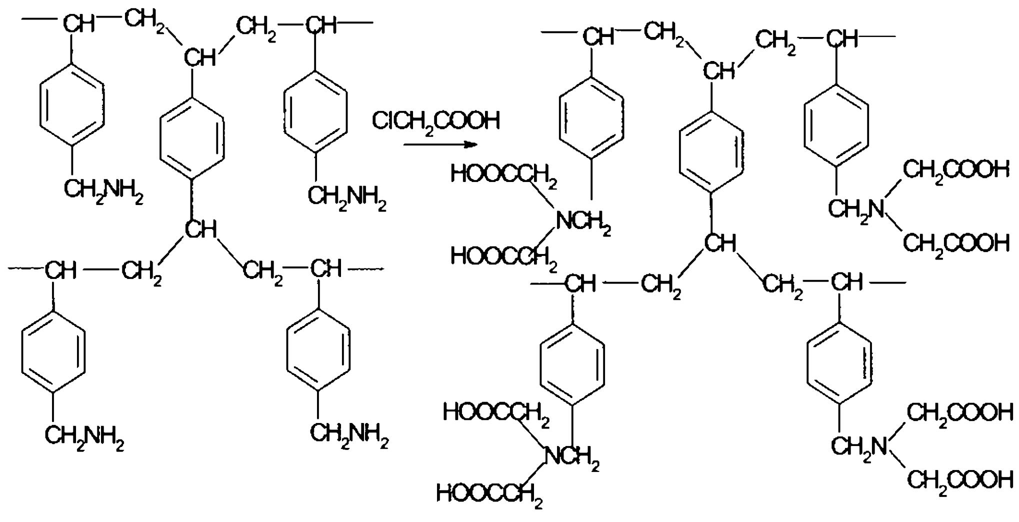
1.2.1. Functionalization of Polymers

A functionalized polymer can be prepared by different methods. The monomer containing the desired functional group can be polymerized or copolymerized to get a functionalized polymer. Polymerization of p-vinyl benzyl chloride gives chloromethylated polystyrene. Poly[4(5)vinyl imidazole], synthesized by the polymerization of the monomer, is used as a catalyst. A wide range of functionalized polystyrenes are prepared by electrophilic and nucleophilic substitutions with suitable reagents. Chloromethyl and lithio derivatives are the most useful among them. Lithio derivative of polystyrene can be easily converted to polystyrene containing OH, COOH, $B(OH)_2$, $RSnCl_2$ and $P\Phi_2$ groups. Chloromethylated polystyrene on treatment with an amine or ammonia gives amino methylated polystyrene. Amino methylated polystyrene on treatment with chloroacetic acid gives the iminodiacetic acid derivative. Another type of functional polymer is telechelic polymer which contains functional groups such as OH or COOH at each end . They are useful for synthesizing block copolymers by step polymerization.









Polystyrene iminodiacetic acid

1.3. Polymeric Metal Complexes

If a polymer supported ligand possess an ordered structure, the complex formed will also be of definite geometry .Parameters like surface area, apparent density and pore structure of the polymer matrix are found to have profound influence on complexation. The efficiency of complexation also depends on the arrangement of functional groups in the polymer support. The swelling characteristics of the polymer matrix also depends on the flexibility of the cross linking agent. The kinetics of metal ion complexation, adsorption of metal ions and the interaction between complexed and adsorbed species are also affected by the rigidity of the cross linking agent [10].

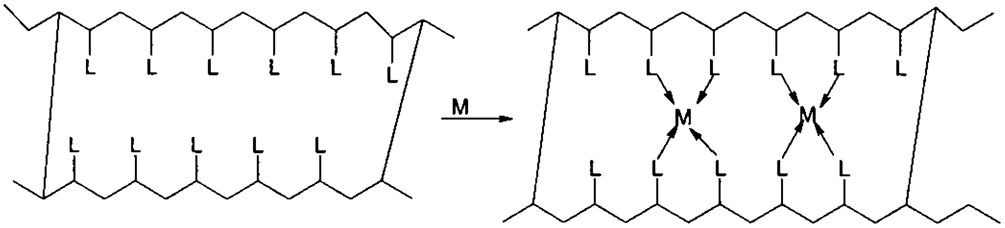
A cross linked polymeric ligand forms a stable metal complex than a linear polymer and it shows definite selectivity for metal ions due to its characteristic structure . But highly cross linked resins are macroporous and macro reticular and the complexes formed from them are unstable. These macroporous structures are found to be efficient ion-exchange resins. Cross linked polystyrene functionalized with quaternary ammonium groups are anion exchange resins and that functionalized with sulphonic, carboxylic, phenolic etc. groups are cation exchange resins.

The iminodiacetic acid supported on polystyrene forms compact 1:1 complexes with copper, iron and other heavy metals and it is highly selective [Chelex 100].An important application of chelating resins is ligand exchange chromatography. An ion-exchanger containing a complexing metal ion like Cu^{2+} or Ni^{2+} can be used as a solid sorbent .The successful application of ligand exchange depends on keeping the complexing metal ion in the resin. The potential ligands like amines, amino acids, polyhydric alcohols etc are sorbed from solutions on the basis of the stabilities of ligand-metal complexes.

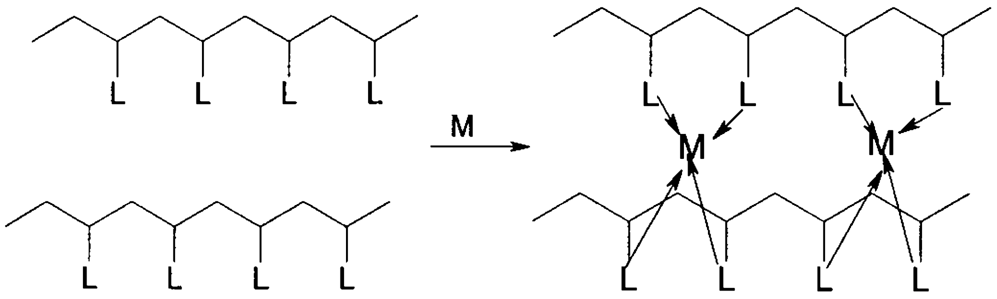
Various transition metals including Rh, Pt, Pd, Co and Ti bound to polymer supports have been used as catalysts in hydrogenation, hydroformylation and hydrosilation reactions. The incorporation of metal atoms in to a polymer is found to improve its electrical conductivity. Poly[ferrocenylene] polymer on oxidation with I_3^- shows a tremendous increase in conductivity.

When a polymer supported ligand is treated with a metal ion, a polymeric metal complex is formed. Here the co-ordinating site may be the functional group containing atoms like O,N,S etc. or the co-ordinating group is incorporated by a reaction with a small molecular weight substance. Thus the metal ion will form co-ordinate bonds with the ligand moeity of the same polymer chain or it will form complex with the chelating sites of two adjacent polymer chains [Scheme 1].

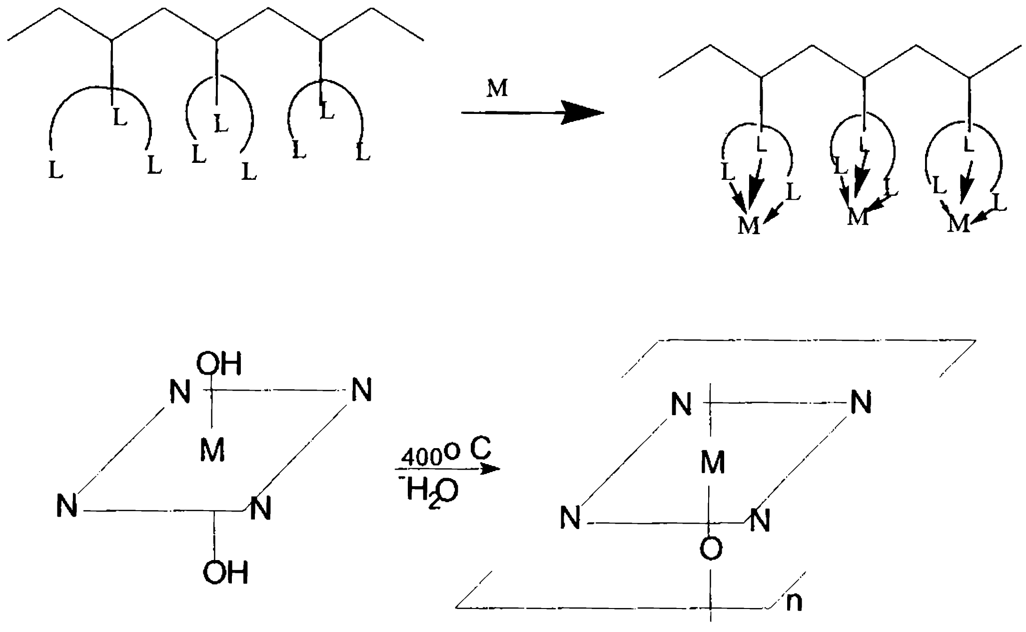
When the polymer support contains multi-dentate ligands, chelate complexes will be formed [Scheme 2].Recently there has been considerable activity in bringing phthalocyanine moiety into polymer structures. Dehydration of the phthalocyanine diols at high temperature gives phthalocyanine polymers. [Scheme 3]



Scheme 1

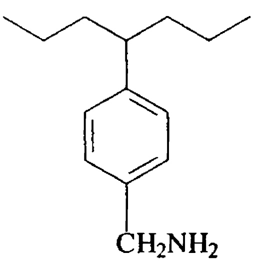


Scheme 2

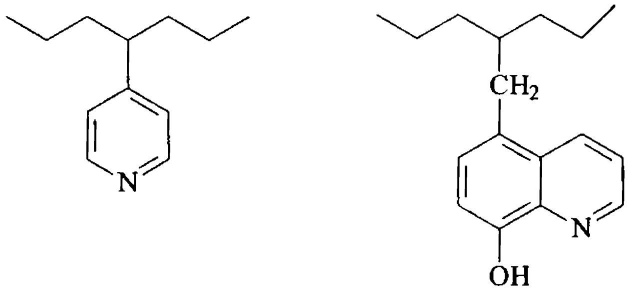


Scheme 3

Here the coordinating group may be amino group of amino methylated poly styrene (a), nitrogen of a polymer supported heterocyclic base (b), polymer anchored schiff bases (c), poly methyl acrylic acids (d), phosphonic acid groups in a polymer matrix (e), polymer supported dithiocarbammates(f), polymer anchored sulphonamides (g), iminodiacetic acids (h), etc.



(a)



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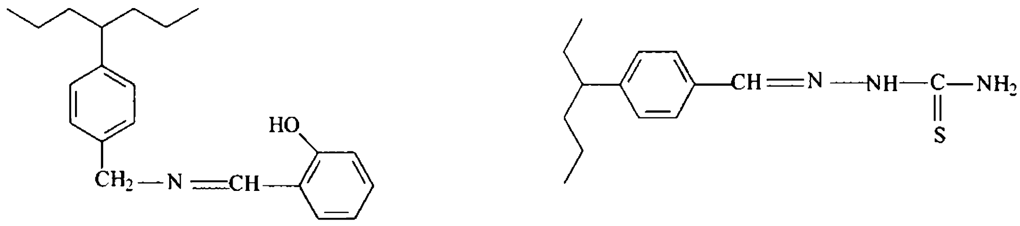
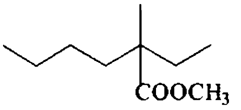


(c)



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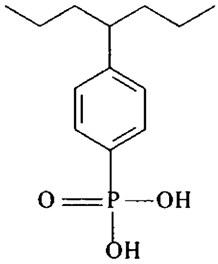
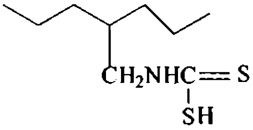
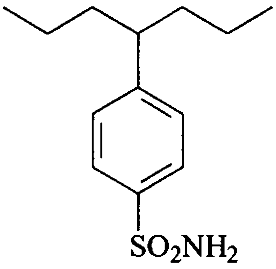


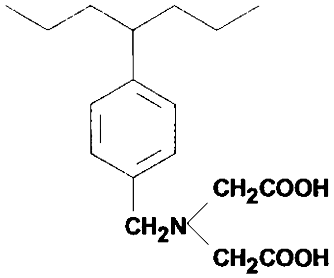
(e)



(f)



(g)



(h)

1.4. Polymer Supported Ligands for the Removal of Metal Ions

An important application of functionalized polymers is metal ion removal for analytical, preparative and for industrial purposes. The wide variety of these ligands include polymer supported 8-Hydroxy quinoline, iminodiacetic acid, thiosemicarbazones, functionalized polystyrenes, schiff bases on polymer supports etc. The high selectivity of these resins for heavy metals enables the removal and analysis of traces of these metal ions in solution even in the presence of large amounts of sodium and potassium due to the high stability of these complexes. These complexes are separated and upon changing the pH the ligand will be regenerated and it can be recycled. So this method can be employed for the treatment of industrial waste. Macrocyclic ethers are also used to separate metal ions and they are also highly selective. It is observed that the copper desorbed amino resins showed specificity to copper ions in the presence of other metal ions like cobalt, nickel and zinc. This reveals the fixing of stereo structure of copper complex[11]. Recently chelating resins are used as ion-exchangers instead of the conventional type. The affinity of a particular metal ion for a certain chelating resin depend mainly on the nature of the chelating group. The selective behaviour of the resin is mainly due to the stabilities of metal complexes arising from the high binding energy of these resins. Recent investigations led to the remediation of ground water contamination by heavy metal ions by selective ion exchange methods. Many super fast polymeric sorbents with multifunctionalities for the removal of various types of ions have been developed.

1.5. Polymer Supports as Ion Selective Electrodes

Ion selective membranes emerged as a potential tool for monitoring our environment with world wide applications of pollution control, water quality management, food quality control, medical diagnosis and hygiene control, soil and fertilizer analysis, industrial production control, waste water management etc. Polymer membrane electrodes are of various ion-exchange materials in an inert matrix such as PVC, polyethylene, silicone rubber, teflon etc. Synthetic membranes can be tailored for the transport of specific ions among other ions of the same charge. This method enables the qualitative and quantitative analysis of electrolytes from very low concentrations. The potential developed at the surface of a membrane is proportional to the concentration of the specific ion.

Ion selective electrodes can also be employed to ions which are not measurable potentiometrically .

The liquid membrane ion-selective electrode produced in 1967 provided a means for determining the activity of Ca $^{2+}$ ions in solution [6]. A significant advancement in this field was the discovery of a calcium sensor membrane in which the organic liquid of the liquid membrane was immobilized on to PVC to produce a polymer film [12]. This contained about 70% of the plasticizer, 30% of PVC and 1% of the ionophore. Later on sensors for ions like Mg $^{2+}$, Na^+, K^+ , Ba^{2+}, NO_3^-, NH_4^+,Cu $^{2+}$, Cd $^{2+}$, Eu $^{2+}$ etc have' been developed. Other polymers like polystyrene, PMMA, polyamides, polyimides, etc are also used as the support. Although the development of ISE occurred rapidly in the past three decades, promising investigations are still going on.

1.6. A Brief Review on Applications of Polymer Supports, Polymer Supported Ligands and Complexes

The literature of polymer supported chemistry is enriched with the innovative investigations of the past three decades. Metal ions dissolved in polyhydric alcohols impregnated in the pores on the surface of polymer supports are found to be useful for the separation of saturated hydrocarbon from unsaturated ones[13].

Polymer supported quaternary ammonium salts, polymeric phosphonium etc. salts are found to be good phase transfer catalysts[14]. It was found that the solubility properties of substrates, ligands and catalysts can be controlled by the usage of polymer supports[15].

Synthesis and structural characterization of Ni^{2+} and Co^{2+} complexes with polymer supported linear bis(catechol) amide ligand was carried out by Marilyn et al [16]. Thus it was found that polymer supported sulfonated catechol amide ligands could be employed for the selective metal ion removal from aqueous solutions [17]. Investigations on the competitive complexations of Ag^+, Hg^{2+} and Cu^{2+} using N-sulfonyl ethylene bis(dithiocarbammate) ligand on macroporous polystyrene support showed that the overall selectivity is[18] $Hg^{2+}>Ag^{2+}>Cu^{2+}>Pb^{2+}>Cd^{2+}>Fe^{3+}>Al^{3+}$. A novel biodegradable carboxy functional lactose copolymer showed high complexing activity[19] for metal ions like Cr^{3+} and Fe^{3+}.

Ion-exchange membranes are modern applications of poly-ions. Insoluble poly-electrolytes in the form of water swellable beads with macroporous structure give access to ion-exchange sites. Amberlite IR-120, Dowex SBR etc are widely used as ion-exchange resins. Studies on[20] ion-exchange equilibria using cation exchanger Amberlite-120 showed that it is more selective for Cu^{2+}, Cd^{2+} and Zn^{2+} than for Mg^{2+}.

Applications of poly (4-styrene sulfonate) liquid binding layer for measurement of Cu^{2+} and Cd^{2+} with the diffusive gradients in thin film technique showed that poly styrene sulfonate behaved like a cation exchanger [21]. CO_2 fixation has been achieved by Cu(II) complexes of a tetrapyridinophane aza receptor [22]. Polymer supported Ru(II) complexes are used as metal ion sensors [23]. A new type of organotin chloride supported on highly porous cross linked polystyrene showed good activity and stability towards dehalogenation and radical cyclization [24]. The effect of synthetic conditions on the formation of copper complexes with polyethylene grafted polyacrylic acid was investigated by Pomogailo et al [25].

Microgels prepared of cross linked polystyrene are used as supports for organic synthesis [26]. Recently a polymer support based on poly ethylene glycol with high loading capacities has been developed [27]. A novel polymer support based on glycerol with cross linked polystyrene has been developed for polypeptide synthesis. The support has unique characteristics as the functionality hydroxyl group in the cross linker is introduced into the support in the polymerization stage itself. The utility of the resin was tested by the synthesis of a 19 residue peptide and it was compared with the Merrifield resin [28].

Chiral bisoxazolines [box] supported on modified polyethylene glycol is used as ligands in some asymmetric transformations under homogeneous conditions[29]. They are also used for the enantio-selective synthesis when supported [box] is used in combination with Cu(II) salts. Polysulfones containing pendant aldehyde groups have potential uses as reactive polymer supports to bind enzymes and ligands[30]. Poly tetrahydrofuran cross linked polystyrene is employed for solid phase organic synthesis. When poly tetrahydrofuran was incorporated in polystyrene the overall polarity increased and the resin swelled to a greater extent than polystyrene –divinyl benzene matrix. It also enables the easier isolation of products [31]. Polymeric aldehyde may also be used to bond inorganic species to the matrix . A novel method for the recovery of precious metal ions from strongly acidic solutions was developed with the polymer supported o-phenylene diammine hydrochloride ligand [32]. The transport characteristics of polyglycol liquid membranes are made use for removing organics from aqueous solutions [33]. A highly effective water soluble polymer supported catalyst , polyethylene glycol bound ligand is used for two phase asymmetric hydrogenation[34]. When the complexation was carried out on polymer supported dibenzo-18-Crown-6, peculiarities were observed for complexes K_2PdCl_4 and K_2PtCl_4 [35]. Enantio pure poly [glycidyl methacrylate co-ethylene glycol dimethacrylate] is found to be a new material for catalytic asymmetric hydrogen transfer reduction [36].

Microgels supported on polystyrene have good solubility in organic solvents and they can be precipitated by methanol. They can be used as scavengers to remove the unreacted isocyanate. Microgel supported sodium borohydride is used as a reducing agent[37]. Functionalized polymer support was prepared by the co-polymerization of styrene and acryloyl chloride and it is used as an electrophilic scavenger which reacted readily with N,O,S and C nucleophiles. Scavenging ability was demonstrated by the removal of benzyl amine from aqueous solution at room temperature[38]. Polymer supported calix [4] arenes are used for sensing and for the conversion of NO_2/NO_4 [39]. Photo oxygenation was carried out successfully with polystyrene supported tetraphenyl or tetratolyl porphyrin sensitizers. It is highly swollen in organic solvents and so it is irradiated under air using allylic alcohol [40]. Hydrogel characteristics of electron beam immobilized poly[vinyl -pyrollidone] film on PET support were characterized by ellipsometry, XPES and Atomic force microscopy. These studies showed that cross linked layers swell in aqueous solution by a factor 7.Electron beam cross linking of pre adsorbed hydrophilic polymers permits a durable fixation of a swellable polymer network on polymer support [41].

Palladium(II) complexes supported on silica-poly vinyl pyridine are also reported as hydrogenation catalysts [42]. Polymer supported Rhodium(I) $2,2'$ bipyridine complex is also found to catalyze hydrogenation reactions [43]. Zupan and Segatin found that bromination of organic compounds can be done conveniently by polymer supported bromine complexes[44]. Polystyrene supported phosphonotungstic complexes are used for epoxidation reactions [45]. Synthesis and characterization of transition metal complexes of $2,2'$ bis imidazole supported on polycarbonates was reported by Collier and Cho[46] . Schiff base complexes of Cu(II),Ni(II),Co(II), Mn(II) and Zn(II) were prepared on Urea-Formaldehyde polymer support [47]. Oxidation of 2,6 xylenol is catalyzed by polymer supported Cu(II) complexes [48].

The synthesis of polystyrene supported resin containing schiff bases derived from salicylaldehyde and triethylene tetramine and its complexes of Cu(II), Ni(II), Co(II), Fe(III), Zn(II), Cd(II), Mo(VI), and U(VI) were reported by Symal and Singh [49]. Polymer supported chromium peroxide complex is found to be very effective for the selective oxidation of alcohols [50]. Enantio-selective parallel synthesis was carried out using polymer supported chiral Co[salen] complexes[51]. Polystyrene supported thiosemicarbazone complexes of Cu(II), Ni(II), Fe(III), and Co(II) are found to be very effective catalysts for the decomposition of H_2O_2 and in the epoxidation of cyclohexene and styrene . The study also revealed the dependence of reaction rate on the degree of cross linking[52].

Silica supported chitosan-palladium complex is reported as an efficient catalyst for the asymmetric hydrogenation of ketones[53]. Polymer supported Fe(III) complex is a good catalyst for the coupling reaction between acylchloride and Grignard reagent[54]. Polymer supported bis oxazoline copper complexes are used as catalysts in cyclopropanation reactions[55]. Metal nano particles on functionalized polymer supports are also found to be efficient catalysts [56]. A novel hydrazine linker resin is employed for the solid phase synthesis of α-branched primary amines[57]. Spectacular achievements in catalytic asymmetric epoxidation of olefins have been reported using chiral and recyclable Mn(III) [Salen] complexes[58]. The catalytic activity of schiff base complex of Fe(III) on polystyrene was reported by Antony et al[59]. A novel silica-poly glycol supported bimetallic palladium based catalyst is found to be effective for the dechlorination of aromatic chlorides [60].

An interesting feature of a polystyrene supported oxo rhenium complex is that it is a catalyst for alcohol oxidation with DMSO and for the de-oxygenation of epoxides to alkenes with triphenyl phosphine[61]. Polybenzimidazole supported $[Rh(cod)Cl]_2$ complex is an effective catalyst for the preparation of substituted polyacetylenes which are widely used in non linear optics[62]. A new homogeneous catalyst of poly[N-vinyl-pyrollidone] $CuCl_2$ complex is employed for the oxidative carbonylation of methanol to dimethyl carbonate [63]. Saladino et al have found that polymer supported methyl rhenium tri-oxide and hydrogen peroxide are very effective for the selective oxidation of phenol and anisole derivatives to quinones[64]. Polyethylene glycol supported Cu(II) triaza cyclononane is found to be an efficient, recoverable and recyclable catalyst for the cleavage of phospho diester [65]. Silica supported poly α–amino propyl silane complexes of Cu(II), Ni(II), and Co(II) are efficient catalysts for Heck vinylation reactions[66]. Investigations carried out on metal complexation with functionalized polymer supports revealed that it is an adsorption/ complexation phenomena[67]. Studies on the catalase like activity of polystyrene supported schiff base metal complexes showed the dependence of activity on the nature and degree of cross linking and the metal uptake is found to be in the order [68] Cu(II) > Co(II) > Ni(II) >Fe(III) . Catalytic activity is found to be high for polymer supports having a lower degree of cross linking. Polymer supported Cu(II) complexes are very effective for C—N and C—O cross coupling reactions with aryl boronic acids [78]. Surface functionalized polyethylene and polypropylene are found to be good humidity sensors[79].

1.7. Scope of the Present Investigation

Polymer supports have become inevitable as they have been employed successfully and efficiently as reagents, catalysts and substrates. An important application of polymer supports is the separation of trace metals and toxic metal ions from impure water by complexation. Super fast sorbents of ions of multiple functionalities are recent developments.

Polymer supported metal complexes are also found to be highly versatile. Many of them are used as catalysts for the synthesis of organic compounds of industrial and scientific importance. Preparation of potable water, desalination of water and recovery of metal ions including precious metals are new achievements. Development of perm selective membranes and their applicability as ion-selective electrodes are promising achievements. So the present investigations have been carried out on this expanding area of polymer supported metal complexes. The objectives of the work are the following

1. Synthesis and characterization of polymer supported complexes of Cu(II), Ni(II), Fe(III),Co(II), Mn(II) and Zn(II) with schiff bases obtained by
    - Condensing amino methylated polystyrene with 4-hydroxy benzaldehyde
    - Condensing amino methylated polystyrene with p-dimethyl amino benzaldehyde
    - Condensing amino methylated polystyrene with 3-nitro benzaldehyde
2. Metal ion removal studies using
    - Schiff base of amino methylated polystyrene with 4-hydroxy benzaldehyde
    - Schiff base of amino methylated polystyrene with p-dimethyl amino benzaldehyde
3. Preparation of Cupric ion selective potentiometric sensor using the complex of Cu(II) with the schiff base obtained by the condensation of amino methylated polystyrene with p-dimethyl amino benzaldehyde

The above mentioned studies have been incorporated in the thesis

CHAPTER

2

MATERIALS AND METHODS

Contents

2.1. Introduction

This chapter deals with the reagents and procedure employed for the synthesis and characterization of schiff bases and metal complexes. The various methods used for characterization and the procedure for application studies are also included.

2.2. Reagents and Instruments

Amino methylated polystyrene is a product of Thermax Corporation Ltd., Pune, obtained as a gift sample. The aldehydes, 4-hydroxy benzaldehyde, p-dimethyl amino benzaldehyde and 3-nitro benzaldehyde are products of Merck. The metal salts, $Cu(CH_3COO)_2.H_2O$, $CuCl_2.2H_2O$, $Ni(CH_3COO)_2.4H_2O$, $NiCl_2.2H_2O$, Fe $(CH_3COO)_3.H_2O$, Co $(CH_3COO)_2.6H_2O$, $Mn(CH_3COO)_2.H_2O$, $Zn(CH_3COO)_2.2H_2O$, and solvents such as dimethyl formamide (DMF), methanol and diethyl ether are also from Merck.

The CHN analysis was performed on PE 2400 model from Perkin Elmer. Magnetic susceptibility measurements were carried out on a PAR 155 Vibrating sample magnetometer at IIT Roorkee. The electronic spectra was recorded on a Ocean Optics, Inc.S D 2000 Fiber Optic spectrometer attached with a charge device detector. IR spectra of the schiff base and the complexes were recorded in KBr on a Perkin Elmer FTIR spectrometer. Thermogravimetric analysis was performed on a Perkin Elmer Diamond TG DTA. Potential measurements were carried out on a digital voltmeter. The pH measurements were carried out on a Systronics Digital pH meter. AAS was carried out using a PE 3110 spectrophotometer.

2.3. Experimental

2.3.1. Synthesis of schiff base of 4-hydroxy benzaldehyde and amino methylated polystyrene [PS-HB]

Amino methylated polystyrene ($1x10^{-3}$ mol dm^{-3}) was suspended in DMF (10mL) for 1 h so that the polymer swells considerably. A solution of 4-hydroxy benzaldehyde ($2x10^{-3}$ mol dm^{-3}) in DMF (10mL) was added to the above suspension .The mixture was heated under reflux for 18 h with stirring. It is cooled to room temperature. The golden brown coloured polymer supported ligand was filtered, washed with DMF, methanol, distilled water and finally with diethyl ether and dried in vacuo.

2.3.2. Synthesis of schiff base of p-dimethyl amino benzaldehyde with amino methylated polystyrene [PS-DMAB]

Amino methylated polystyrene ($1x10^{-3}$ mol dm^{-3}) was soaked in DMF (10mL) for 1 h and p-dimethyl amino benzaldehyde ($2x10^{-3}$ $moldm^{-3}$) dissolved in DMF (10 mL) was added to the polymer suspension. This mixture was then refluxed for 18 h with stirring to form the chocolate coloured polymer anchored ligand. It was then filtered, washed with DMF, methanol, distilled water and finally with diethyl ether and dried in vacuo.

2.3.3. Synthesis of schiff base of 3-nitro benzaldehyde with amino methylated polystyrene [PS-NB]

A solution of 3-nitro benzaldehyde ($2x10^{-3}$ mol dm^{-3}) in DMF (10mL) was added to a suspension of amino methylated polystyrene ($1x10^{-3}$ mol dm^{-3}) in DMF (10mL) and refluxed for 18 h with stirring. The yellow coloured product thus obtained was filtered washed with DMF, methanol, distilled water and finally with diethyl ether and dried in vacuo.

2.4. Synthesis of Complexes

Three series of metal complexes of the three schiff bases were prepared. Each of these series consisted of complexes of metals such as Cu (II), Ni (II), Co (II), Mn(II),Fe(III) and Zn (II).The metal and ligand are taken in the ratio 1:2 for the preparation of these complexes.

2.4.1. Metal complexes of the schiff base of p-hydroxy benzaldehyde and amino methylated polystyrene [PS-HB]

The required metal salt (1x10^{-3}mol dm^{-3}) [Cu $(CH_3COO)_2.H_2O$, $CuCl_2.2H_2O$, $Ni(CH_3COO)_2$. $4H_2O$, $NiCl_2$. $2H_2O$, Co $(CH_3COO)_2$. $6H_2O$, Mn $(CH_3COO)_2$. H_2O, Fe $(CH_3COO)_3$. H_2O, $Zn(CH_3COO)_2.2H_2O$] was suspended in DMF (10mL) and it was added to the polymeric schiff base (2x10^{-3} mol dm^{-3}) suspended in DMF(10mL). The mixture was heated under reflux for 6-10 h and cooled to room temperature. The complex formed was washed with DMF, methanol, distilled water and with diethyl ether. It was then dried in vacuo.

2.4.2. Metal complexes of the schiff base of p-dimethyl amino benzaldehyde and amino methylated polystyrene[[PS-DMAB]

The polymeric schiff base (2x10^{-3} mol dm^{-3}) was suspended in DMF(10mL) and kept for 1h.The metal salt (1x10^{-3}mol dm^{-3}) [$Cu(CH_3COO)_2.H_2O$, $CuCl_2$. $2H_2O$, Ni $(CH_3COO)_2$. $4H_2O$, $NiCl_2$. $2H_2O$, $Co(CH_3COO)_2.6H_2O$, Mn $(CH_3COO)_2$. H_2O, $Fe(CH_3COO)_3.H_2O$, $Zn(CH_3COO)_2.2H_2O$] was also suspended in DMF (10mL) and it was added to the polymer suspension. The mixture was heated under reflux for 6-10 h. The complex formed was cooled, filtered, washed with DMF, methanol, distilled water and finally with diethyl ether and dried in vacuo.

2.4.3. Metal complexes of the schiff base of 3-nitro benzaldehyde and amino methylated polystyrene [PS-NB]

A solution of the required metal salt (1x10^{-3}mol dm^{-3}) [Cu $(CH_3COO)_2$. H_2O, $CuCl_2.2H_2O$, $Ni(CH_3COO)_2.4H_2O$,$NiCl_2.2H_2O$, $Co(CH_3COO)_2$.6H2O, Mn $(CH_3COO)_2.H_2O$, $Fe(CH_3COO)_3.H_2O$, Zn $(CH_3COO)_2.2H_2O$] in DMF (10mL) is added to a suspension of the polymeric schiff base (2x10^{-3} mol dm^{-3}) in DMF (10mL) and heated under reflux for 6-10 h. It was then cooled, filtered and washed with DMF, methanol, distilled water and finally with diethyl ether and dried in vacuo.

2.5. Characterization of the Complexes

The complexes were characterized by elemental analysis, IR, UV diffused reflectance, TG and magnetic susceptibility measurements. The details of these techniques are given below.

2.5.1. Elemental Analysis

Elemental analysis was carried out to resolve the molecular formulae of these complexes and it also enabled to compare the theoretical and calculated values. CHN analysis was carried out on a Perkin Elmer, PE 2400 model instrument. The metal content were determined by titrimetric, gravimetric, complexometric and by AAS methods. Chloride was estimated as AgCl by the classical titrimetric method.

2.5.2 Infra Red spectral analysis

The characteristic group frequencies in IR spectra are highly useful in predicting structure and geometry of ligands and complexes. On comparing the spectra of ligands and complexes ,the co-ordination sites in the ligand and the geometry of the complexes are ascertained. IR spectra was taken using KBr pellets on a Perkin Elmer 1600 series FT-IR spectrometer in 4000-200 cm^{-1} region.

2.5.3 Magnetic Susceptibility measurements

Magnetic moments were determined in a PAR 155 model vibrating sample magnetometer by the application of a magnetic field. From the molar susceptiblities χ_m, the magnetic moment μ_{eff} of the substance is calculated.

$$\mu_{eff} = 2.84[\chi_m T]^{1/2} \quad \text{B.M}$$

So the number of unpaired electron in the molecule is determined. Thus the geometry of the molecule can be predicted.

2.5.4 Thermal studies

It gives information about the thermal stability of the polymer complex. In thermo gravimetric analysis the mass of the sample is recorded as a function of temperature when temperature is raised at a constant rate to about 800°C.The pattern of decomposition is highly characteristic of the polymeric substance. The analysis was carried out in a Perkin Elmer Diamond TG DTA.

2.5.5 Diffuse Reflectance UV-Visible Spectroscopy

Information regarding the electronic structure of the metal ion, stereochemistry and co-ordination structure of polymer supported complexes of transition metals are obtained from electronic spectra.

The electronic spectra of transition metal complexes are mainly due to d-d transitions within the transition metals and due to charge transfer from metal to ligand or from ligand to metal. Information regarding oxidation state and coordination environment of the transition metal ion is obtained from d-d transitions. Charge transfer transitions lead to intense lines and it gives information regarding donor and acceptor atoms in the complex. The diffused reflectance was measured using Ocean Optics, Inc. SD 2000 Fiber Optic spectrophotometer.

2.6 Application Studies

2.6.1 Metal ion removal

Metal ion removal studies were carried out with the schiff base of p-hydroxy benzaldehyde and amino methylated polystyrene and with the schiff base of p- dimethyl amino benzaldehyde and amino methylated polystyrene by complexing with Cu(II) and Fe(III) ions respectively. These studies were carried out quantitatively to develop efficient metal ion removing agents working under optimum conditions. The above said polymer supported ligands were developed as excellent metal ion removing agents.

In this method, a definite amount of the polymer supported schiff base was suspended in DMF for 1 h and weighed amount of metal salt solution was added to the schiff base and refluxed for a definite interval of time. The unreacted metal ion was filtered and quantitatively transferred to a standard flask (50mL) and the metal ion content of Cu(II) and Fe(III) were determined spectrophotometrically. Thus the effect of time, ligand concentration ,metal concentration, effect of pH and the interference due to other ions such as NH_4^+,Na^+,K^+, Co^{2+},Mn^{2+},Ca^{2+},Ni^{2+},Cl^-,Br^-, SO_4^{2-},NO_3^- and CH_3COO^- have been studied. Interference studies were carried out by mixing with definite amounts of the above mentioned metal ion to the mixture of the ligand and Cu(II) or Fe(III) solution and the experiment was repeated.

2.6.2 Preparation of Cupric Ion Selective Electrode

The ion selective electrode was developed from Cu(II) complex with the schiff base of p-dimethyl amino benzaldehyde and amino methylated polystyrene as the ionophore. The ionophore was prepared by refluxing a suspension of polymer supported schiff base of p-dimethylamino benzaldehyde (1×10^{-3}mol dm^{-3}) with a DMF solution (10 mL) of $Cu(CH_3COO)_2.H_20$ for 6 h. The complex formed was cooled filtered, washed with DMF, methanol, distilled water, and finally with diethyl ether and then dried in vacuo.

The ionophore (100 mg) [Cu(II) complex with the schiff base of p-dimethyl amino benzaldehyde and amino methylated polystyrene] was mixed with pure graphite(900mg) and made in to a slurry with tributyl phosphate as the binder. This is taken in a glass tube having an inner diameter 5mm and

140mm length and it is fitted with a plastic top. A steel rod with threaded screw head is introduced into the glass tube for electrical contact and it is suitably fixed at the top of the glass tube. This electrode is kept in a solution of copper sulphate (0.1mol dm $^{-3}$) for 24 h to attain equilibrium. The electrode is coupled with a calomel electrode and potential is measured using a digital voltmeter. Thus the cell is

Ion selective electrode / Test solution //Saturated calomel electrode.

The potential of the electrode was measured at different concentrations of Cu^{2+} for studying the response of the electrode. The effect of pH on electrode potential was studied using Cu^{2+} ion solutions in different buffer solutions and optimum pH was determined. Cu^{2+} ion solution of the same concentration was mixed with solutions of varying concentrations of ions such as NH_4^+, K^+, Co^{2+}, Zn^{2+}, Ca^{2+},Ni^{2+},Cl^-, $(COO)_2^{2-}$,SO_4^{2-} and NO_3^- for studying the interference of these ions.

CHAPTER

3

SYNTHESIS AND CHARACTERIZATION

Contents

3.1 Introduction

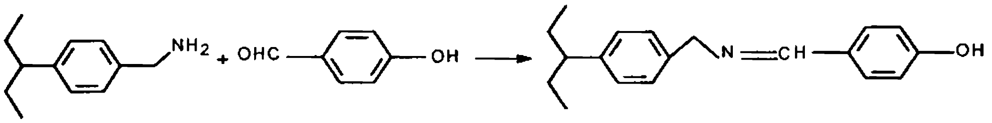
Functionalized polymers formed the basis for the important trends in polymer science for the last three decades. They have the combination of properties that are derived from the macromolecular structure as well as due to the functional group. Higher sophistication in the use of advanced polymeric materials led to an increased demand on the design of macromolecular structures with the desired combination of properties. Now greater emphasis is given for the spacing of functional group with respect to the macromolecular backbone for optimal functionality. An interesting feature of functional polymers is their affinity towards metal ions. Polymer supported ligands are prepared from functional polymers. These polymeric ligands are able to co-ordinate with transition metal ions to form polymeric complexes which are of wide applicability.

This chapter explains the synthesis and characterization of three series of polymeric schiff base complexes of Cu(II), Ni(II), Co(II), Mn(II),Fe(III) and Zn(II).

3.2. Results and Discussion

3.2.1 Metal complexes of p- hydroxy benzaldehyde schiff base of amino methylated polystyrene

The synthesis of the ligand and metal complexes are presented in chapter II. The flesh coloured ligand became brown, red, pale green and yellow upon complexation with the metal ions. Both the ligand and the complexes are insoluble in most of the organic solvents.



Scheme 4

3.2.1.1. Elemental analysis

The results of elemental analysis are presented in Table 1.The results obtained are found to be in agreement with the theoretical values.

3.2.1.2. Infra red spectra

IR spectral data of ligand and complexes are presented in Table 2 and in Fig.1.The co-ordination sites of the polymer supported ligand was identified from the IR spectra of the ligand and the complex. A strong IR band at 1677 cm^{-1} in the ligand showed a negative shift by about 10-20 cm^{-1} in the complex confirming the co-ordination of the azomethine group (C = N) through nitrogen[80]. The co-ordination of the solvent DMF through oxygen was ascertained by the lowering absorption frequency of ν(C = O) band by 15-40 cm^{-1}in the spectrum of the complex .The symmetric (COO) stretching frequency and the anti symmetric stretching frequency of acetate ion are shifted to 1391-1393 cm^{-1} and 1604-1612 cm^{-1} .The frequency difference of 210-225 cm^{-1} between the two types of vibrations indicate the monodentate nature of the acetate ion [81]. The new bands obtained at 480-416 cm^{-1} in the spectra of complexes indicate the co-ordination of metal ions (M—N) through nitrogen of the azomethine group [81].

3.2.1.3. Electronic spectra

The electronic spectral data of complexes are presented in Table 3 and in Fig.2. UV-Visible spectra can provide valuable information regarding the bonding and structure of complexes. The electronic spectra of Cu(II) complex $[Cu(PSHB)_2.OAc.DMF]$ exhibits bands at 16100 cm^{-1} due to $^2B_{1g} \rightarrow {}^2A_{2g}$ transition and a strong absorption at 33330 cm^{-1} which is probably due to charge transfer transition indicating square planar geometry for the complex[82].The Cu(II) complex $[Cu(PSHB)_2.Cl.DMF]$ also shows a band at 17300 cm^{-1} and another intense band at 38400 cm^{-1}.These absorptions may be due to $^2B_{1g} \rightarrow {}^2A_{2g}$

transition and due to charge transfer transition respectively and these transitions are also indicative of its square planar structure. The reflectance spectrum of Ni(II)complex shows bands at 9590cm^{-1},15384 cm^{-1}, and at 22202 cm^{-1} which may be assigned to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions respectively suggesting an octahedral structure for the complex [Ni(PSHB)$_2$.OAc.3DMF][83] .Bands obtained for the Ni(II) complex, [Ni(PSHB)$_2$.Cl.3DMF], at 9256 cm^{-1} ,15530 cm^{-1} ,23529 cm^{-1} are also consistent with the octahedral structure of the complex. The Co (II) complex [Co (PSHB)$_2$.OAc.3DMF] exhibited bands at 9090 cm^{-1}, 20830 cm^{-1} and at 11111 cm^{-1}.The lowest energy band may be assigned to $^4T_{1g} \rightarrow {}^4T_{2g}$ transition and the band at 20830 cm^{-1}is assigned to $^4T_{1g} \rightarrow {}^4A_{2g}$ .Another characteristic band obtained at 11111 cm^{-1} may be due to $^4T_{1g} \rightarrow {}^2E_g$ .These spectral bands suggests an octahedral structure for Co(II) complex[84]. The reflectance spectrum of Fe(III) complex [Fe(PSHB)$_2$.OAc.3DMF] gave bands at 10526 cm^{-1},15873 cm^{-1} and at 23809 cm^{-1}which may be assigned to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$,$^6A_{1g} \rightarrow {}^4T_{2g}(G)$, and $^6A_{1g} \rightarrow {}^4A_{1g}(G)$ transitions respectively .These transitions indicate an octahedral structure for the complex[83].

The Mn(II) complex [Mn(PSHB)$_2$ OAc.3DMF] exhibits bands at 10989 cm^{-1} and 15151 cm^{-1} ,which may be due to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ and $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ transitions respectively and a strong band obtained at 24570 cm^{-1} ,which is probably due to $^6A_{1g} \rightarrow {}^4A_{1g}(G)$ and $^6A_{1g} \rightarrow {}^4E_g$ transitions which are degenerate These transitions are in favour of an octahedral structure for Mn(II) complex[84].

3.2.1.4. Magnetic moments

The magnetic moments of complexes are presented in Table 4. The Cu (II) complex shows a magnetic moment of 1.97 BM suggesting square planar geometry for the complex. The Ni(II) complex records a magnetic moment of 3.22 BM which falls in the range for octahedral geometry[85]. The Fe(III) complex has a magnetic moment of 5.96 BM which is very close to the spin only value of octahedral complexes of Fe (III)[85] .The Co(II) complex exhibits a slightly high magnetic moment of 4.72 BM indicative of high spin octahedral geometry. The high magnetic moment may be due to the orbital contribution[86]. The Mn(II) complex has a magnetic moment of 5.94 BM which correspond to the octahedral geometry of the molecule. The Zn(II) complex is diamagnetic which is consistent with its d^{10} configuration.

3.2.1.5. Thermogravimetric analysis

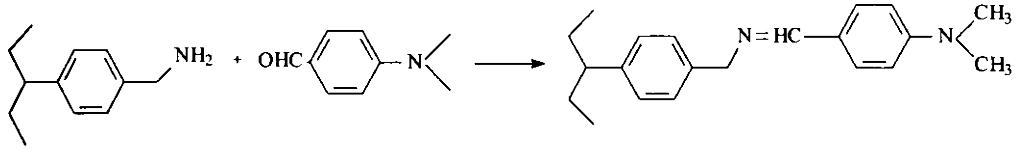
The results of thermal studies of some selected complexes are presented in Table 5 and in Fig. 3. Thermogravimetric analysis showed that the weight loss of about 6.8 to 8.5 % correspond to the elimination of acetate in the temperature range of 110 to 200 ^{0}C and the weight loss of 13 to 23 % upto about 300 ^{0}C correspond to the loss of one molecule of DMF from Cu(II) complex and three molecules of DMF from Ni(II) and Mn(II) complexes . These results are consistent with the suggested molecular formula of the complexes.

3.2.1.6. Conclusion

Eight metal complexes have been prepared from p- hydroxy benzaldehyde schiff base of amino methylated polystyrene and all of them have been characterized by analytical, IR & UV spectral, thermal and magnetic moment studies. Thus it was confirmed that Cu (II) complexes, $[Cu(PSHB)_2. OAc.DMF]$ and $[Cu(PSHB)_2.Cl.DMF]$ have square planar structures(Fig.4.&Fig.5) where as the Ni(II) complexes $[Ni(PSHB)_2.OAc.3DMF]$ and $[Ni(PSHB)_2.Cl.3DMF]$ (Fig. 6&7), Co(II) complex $[Co(PSHB)_2.OAc.3DMF]$ (Fig.8), Fe(III) complex, $[Fe(PSHB)_2.OAc.3DMF]$ (Fig.9), and the Mn(II) complex, $[Mn(PSHB)_2. OAc.3DMF]$ (Fig.10) are of octahedral geometry (Fig.).The Zn(II) complex, $[Zn(PSHB)_2.OAc.DMF]$ is found to have tetrahedral structure (Fig.11)

3.2.2. Metal complexes of p-dimethyl amino benzaldehyde schiff base of amino methylated polystyrene

Details regarding the synthesis of p-dimethyl amino benzaldehyde schiff base of amino methylated polystyrene(Scheme 5) and its complexes were discussed in Chapter II. The flesh coloured ligand became dark brown, orange, grey, red brown and yellow colour upon complexation with various metal ions. The complexes are stable and are insoluble in water and in other common inorganic solvents but sparingly soluble in DMF.



Scheme 5

3.2.2.1. Elemental analysis.

The elemental analytical data of ligand and complexes are presented in Table 6. The observed values are found to be consistent with theoretical values.

3.2.2.2. Infra red spectra

IR spectral data of ligand and complexes are presented in Table 7 and in Fig.12. The polymer supported ligand [PSDMAB] exhibits a band at 1678 cm^{-1} which shows the characteristic stretching vibrations of azo methine group (C=N) whereas in complexes it was lowered by 10-15 cm^{-1} indicating the co-ordination of azo methine group through nitrogen[80]. Moreover additional bands at 480-415 cm^{-1} confirm the nitrogen co-ordination to the metal (M-N)[81] . The frequency of absorption due to v(COO)sym. and v(COO) anti.sym. occur at 1388-1393 cm^{-1} and 1604-1613 cm^{-1} respectively. The monodentate nature of acetate ion was confirmed by this energy difference[81]. The shift in absorption frequency of 1681 cm^{-1} by 25-50 cm^{-1} suggest the co-ordination of DMF to the metal ion through oxygen[81].

3.2.2.3. Electronic spectra

The electronic spectral data of complexes of PSDMAB are presented in Table 8 and in Fig.13. The electronic spectrum of Cu(II) complex, [Cu(PSDMAB)$_2$.OAc.DMF] exhibits a band at 15384 cm^{-1} which may be assigned to $^2B_{1g} \rightarrow {}^2A_{2g}$ transition and an intense band. The intense band observed at 31250 cm^{-1} may be due to charge transfer transition[82]. These transitions are in favour of square planar geometry for the complex. The Cu(II) complex, [Cu(PSDMAB)$_2$.Cl.DMF] gives bands at 17241 cm^{-1} and at 27770 cm^{-1} which may be due to $^2B_{1g} \rightarrow {}^2A_{2g}$ transition and due to charge transfer transition respectively. These transitions are in agreement with its square planar geometry. The Ni(II) complex [Ni(PSDMAB)$_2$.OAc.3DMF] has bands at 10309 cm^{-1} ,16393 cm^{-1} , 25641 cm^{-1} which may be due to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$,$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions respectively. These transitions indicate that Ni(II) complex have an octahedral structure[83]. The bands obtained for [Ni(PSDMAB)$_2$.Cl.3DMF] at 10989 cm^{-1} ,14285 cm^{-1} ,24390 cm^{-1} are also in favour of its octahedral structure. The reflectance spectrum of Co(II) complex is highly informative. The Co(II) complex [Co(PSDMAB)$_2$.OAc.3DMF] shows peaks at 8928 cm^{-1} ,16393 cm^{-1} , 10526 cm^{-1} . These peaks may be assigned to $^4T_{1g} \rightarrow {}^4T_{2g}$,, $^4T_{1g} \rightarrow {}^4A_{2g}$, and to $^4T_{1g} \rightarrow {}^2E_g$ transitions respectively suggesting an octahedral structure for the complex[84] .The Fe(III) complex, [Fe(PSDMAB)$_2$.OAc.3DMF] exhibits peaks at 10416 cm^{-1} ,15873 cm^{-1} ,21978 cm^{-1} which are probably due to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$, $^6A_{1g} \rightarrow {}^4A_{1g}(G)$ transitions respectively in an octahedral environment[83]. The Mn (II) complex, [Mn(PSDMAB)$_2$.OAc.3DMF] has bands at 10638 cm^{-1} ,15384 cm^{-1} which may be due to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$,$^6A_{1g} \rightarrow {}^4T_{2g}(G)$ transitions and an intense peak at

4390 cm^{-1} is due to the degenerate $^6A_{1g} \rightarrow {}^4A_{1g}(G)$ and $^6A_{1g} \rightarrow {}^4E_g$ transitions which are highly characteristic of an octahedral geometry[84].

3.2.2.4. Magnetic moments

The magnetic moment data of complexes are presented in Table 9. The Cu (II) complex [Cu(PSDMAB)$_2$.OAc.DMF] has a magnetic moment of 1.86 BM which is in the normal range observed for square planar complexes. The Ni (II) complex [Ni (PSDMAB)$_2$.OAc.3DMF] exhibits a magnetic moment of 3.31 BM indicative of octahedral geometry for the complex[85]. The Fe (III) complex [Fe(PSDMAB)$_2$.OAc.3DMF] records a magnetic moment of 5.97 BM which is consistent with the spin only value observed for octahedral complexes[85].The magnetic moment observed for Co(II) complex [Co(PSDMAB)$_2$.OAc.3DMF] is 4.50 BM which is slightly high. But this can be attributed to spin orbit coupling observed for octahedral complexes[86]. The Mn(II) complex [Mn(PSDMAB)$_2$. OAc.3DMF] exhibits a magnetic moment of 5.96 BM which is close to the spin only value observed for Mn(II) octahedral complexes. The Zn (II) complex is found to be diamagnetic.

3.2.2.5. Thermo gravimetric analysis

Thermogravimetric analysis of some selected complexes are carried out and the results are presented in Table 10 and in Fig.14. Thermal studies shows that the weight loss of about 6.5 to 8% indicates the loss of acetate in the temperature range 120-200 °C and a subsequent weight loss of 10- 25.5% correspond to the loss of one and three molecules of DMF from Cu(II) and Co(II) complexes respectively. These results agrees with the suggested molecular formula of the complex.

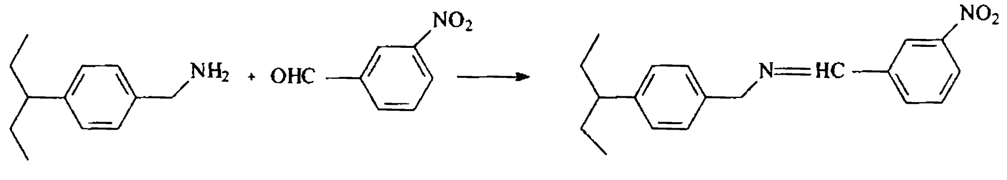
3.2.2.6. Conclusion

The second series consists of eight metal complexes prepared from p-dimethyl amino benzaldehyde schiff base of amino methylated polystyrene.

They are characterized by analytical, IR& UV spectral, thermo gravimetric analysis and magnetic susceptibility measurements. From these results it is confirmed that the Cu(II) complexes, [Cu(PSDMAB)$_2$.OAc.DMF] and [Cu(PSDMAB)$_2$. Cl.DMF] have square planar structure (Fig.15&16). The Ni(II) complexes, [Ni(PSDMAB)$_2$.OAc.3DMF] and [Ni(PSDMAB)$_2$.Cl.3DMF] (Fig.17&18), the Co(II)complex, [Co(PSDMAB)$_2$. OAc.3DMF] (Fig.19), the Fe (III) complex, [Fe (PSDMAB)$_2$. OAc.3DMF] (Fig.20), and the Mn(II) complex, [Mn(PSDMAB)$_2$. OAc.3DMF] (Fig.21) are of octahedral geometries. The Zn (II) complex [Zn(PSDMAB)$_2$.OAc.DMF] (Fig.22) is confirmed to have a tetrahedral structure.

3.2.3. Metal complexes of 3-nitro benzaldehyde schiff base of amino methylated polystyrene

The preparation of the ligand, 3-nitro benzaldehyde schiff base of amino methylated polystyrene (PSNB) [scheme 6], and its metal complexes are presented in chapter II. The ligand (PSNB) is greenish yellow and it changes to coffee brown, brown, red brown, gray , golden yellow and flesh colour upon complexation with the metal ion. They are stable at room temperature ,insoluble in water and in other common organic solvents but sparingly soluble in DMF.



Scheme 6

3.2.3.1. Elemental analysis

The results of elemental analysis are presented in Table 11.The percentage composition obtained is found to be consistent with the theoretical values.

3.2.3.2. Infra red spectra

The IR spectral data are presented in Table 12 and in Fig.23. The IR spectrum of the polymer anchored ligand (PSNB) shows a band at 1646 cm^{-1} which is probably due to the azo methine group. A positive shift of this band by 10-25 cm^{-1} is observed in metal complexes indicating nitrogen co-ordination of the azo methine group .The increase in frequency of absorption may be due to the enhanced bond strength [87]. The co-ordination of nitrogen to metal is further confirmed by the appearance of additional bands[81] in the range 479-417 cm^{-1}. The co-ordination of DMF though O is indicated by a negative shift[81] of the band at 1680 cm^{-1} through 20-45 cm^{-1}. The vibrational frequencies of symmetric and antisymmetric stretching of acetate is obtained in the range 1391-1394 cm^{-1} and 1604-1610 cm^{-1} respectively. The difference of energy between these two bands suggest the monodentate nature of acetate ion[81].

3.2.3.3. Electronic spectra

The UV-Vis spectral data are presented in Table 13 and in Fig.24. The reflectance spectrum of Cu(II) complex [Cu(PSNB)$_2$.OAc.DMF] exhibits a band at 16393 cm^{-1} which may be due to $^2B_{1g} \rightarrow {}^2A_{2g}$ transition and a strong band at 26315 cm^{-1} which may be attributed to charge transfer transition[82].These bands suggest a square planar structure for the complex. In the case of [Cu(PSNB)$_2$.Cl.DMF] complex absorption bands are obtained at 16129 cm^{-1} , and at 35714 cm^{-1}. These bands also may be due to $^2B_{1g} \rightarrow {}^2A_{2g}$ transition and due to charge transfer transitions respectively indicating square planar geometry for the molecule. Three peaks are obtained for the Ni(II) complex [Ni(PSNB)$_2$.OAc.3DMF] at 10526 cm^{-1} ,16000 cm^{-1},24390 cm^{-1} which are probably due to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$,$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions respectively, suggesting an octahedral structure for the complex[83]. The [Ni(PSNB)$_2$.Cl.3DMF] complex also registers bands at 10309 cm^{-1} ,17241 cm^{-1} , and at 27027 cm^{-1} which are also in favour of its octahedral geometry. The electronic spectrum of Co(II) complex, $[Co(PSNB)_2.OAc.3DMF]$ has peaks at 9100 cm^{-1},15875 cm^{-1} and at 10869 cm^{-1} .These spectral bands are highly characteristic of Co(II) octahedral complexes and they may be assigned to $^4T_{1g} \rightarrow {}^4T_{2g}$, $^4T_{1g} \rightarrow {}^4A_{2g}$, and to $^4T_{1g} \rightarrow {}^2E_g$ transitions respectively[84]. The Fe(III) complex $[Fe(PSNB)_2.OAc.3DMF]$ shows peaks at 10256 cm^{-1}, 14814 cm^{-1} and at 25641 cm^{-1} .These peaks are probably due to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$, $^6A_{1g} \rightarrow {}^4A_{1g}(G)$ transitions respectively indicating an octahedral structure for the complex[83].The Mn(II) complex, $[Mn(PSNB)_2.OAc.3DMF]$ registers bands at 10204 cm^{-1} ,15184 cm^{-1} and an intense band at 24971 cm^{-1}.The first two bands may be due to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ transitions .The strong band obtained is characteristic of Mn(II) complexes which is probably due to the degenerate $^6A_{1g} \rightarrow {}^4A_{1g}(G)$ and $^6A_{1g} \rightarrow {}^4E_g$ transitions[84].

3.2.3.4. Magnetic moments

The results of magnetic susceptibility measurements are presented in Table 14. The Cu(II) complex records a magnetic moment of 1.81 BM which is very close to the spin only value of square planar Cu(II) complexes. The Ni(II) complex has a magnetic moment of 3.19 BM which corresponds an octahedral structure[85]. A slightly high magnetic moment of 4.63 BM was recorded for Co(II) complex which is usually observed for octahedral structures and it is due to the orbital coupling[86]. The magnetic moment of Fe(III) complex is found to be 5.90 BM which is consistent with the spin only value for octahedral complexes[85]. The Mn(II) complex exhibits a magnetic moment of 5.74 BM which is in the normal range observed for Mn(II) octahedral complexes . The Zn(II) complex is found to be diamagnetic.

3.2.3.5. Thermogravimetric analysis

The results of thermal studies of these complexes are presented in Table 15 and in Fig.25.From thermo gravimetric analysis it is found that the weight loss of 6.5 to 8% in the temperature range of 120-180 °C correspond to the loss of acetate from Cu(II), Ni(II) and Co(II) complexes. Another weight loss of 10-25% was observed in the temperature range 150 to 320 °C which indicate the loss of one molecule of DMF from Cu(II) complex and three molecules of DMF from Ni(II) and Co(II) complexes.

3.2.3.6. Conclusion.

The third series also contains eight metal complexes prepared from 3-nitro benzaldehyde schiff base of amino methylated polystyrene. The characterization of the ligand and complexes were carried out by analytical, IR&UV spectral, magnetic susceptibility measurements and by thermo gravimetric analysis. Thus it is confirmed that the Cu(II) complexes [Cu(PSNB)$_2$.OAc.DMF] and [Cu(PSNB)$_2$.Cl.DMF] have square planar structures (Fig.26&27).The Ni(II) complexes [Ni(PSNB)$_2$.OAc.3DMF] and [Ni(PSNB)$_2$.Cl.3DMF] (Fig.28&29), the Co(II) complex [Co(PSNB)$_2$.OAc.3DMF](Fig.30),the Fe(III) complex [Fe(PSNB)$_2$. OAc.3DMF] (Fig.31) and the Mn(II) complex [Mn(PSNB)$_2$. OAc.3DMF] (Fig.32) are found to have octahedral structure. The Zn (II) complex [Zn(PSNB)$_2$.OAc.DMF] is of tetrahedral structure (Fig.33).

Tables And Figures

Characterization of Complexes

Table 1 : Analytical data of p-Hydroxy Benzaldehyde schiff base of amino methylated polystyrene and its complexes

Compound	**Found (Calculated) %**				
	C	**H**	**N**	**Cl**	**M**
PSHB	81.09 (81.01)	6.28 (6.32)	5.95 (5.91)		
Cu(PSHB)$_2$. OAc.DMF	65.83 (66.31)	5.79 (5.98)	5.98 (6.27)		10.51 (9.48)
Cu(PSHB)$_2$.Cl.DMF	65.07 (65.03)	5.68 (5.73)	6.46 (6.5)	5.41 (5.49)	9.97 (9.82)
Ni(PSHB)$_2$.OAc.3DMF	63.08 (63.14)	6.12 (6.16)	8.71 (8.63)		7.07 (7.26)
Ni(PSHB)$_2$.Cl.3DMF	62.65 (62.53)	6.44 (6.48)	8.97 (8.89)	4.39 (4.48)	7.34 (7.46)
Co(PSHB)$_2$.OAc.3DMF	63.74 (63.63)	6.62 (6.65)	8.61 (8.64)		7.24 (7.27)
Fe(PSHB)$_2$.OAc.3DMF	63.92 (63.87)	6.64 (6.68)	8.59 (8.66)		7.12 (6.92)
Mn(PSHB)$_2$.OAc.3DMF	63.91 (63.95)	6.65 (6.69)	8.70 (8.67)		6.76 (6.81)
Zn(PSHB)$_2$.OAc.DMF	66.09 (66.13)	5.90 (5.95)	6.28 (6.26)		9.81 (9.74)

Table 2: IR spectral data of p-Hydroxy Benzaldehyde schiff base of amino methylated polystyrene and its complexes

Compound	υ (C=N) cm^{-1}	υ (C=O) cm^{-1}	υ (COO) sym.str. cm^{-1}	υ (COO) anti.sym cm^{-1}	υ (M-N) cm^{-1}
PSHB	1677	---	----	---	----
Cu(PSHB)$_2$. OAc.DMF	1660	1642	1392	1604	418
Cu(PSHB)$_2$.Cl.DMF	1666	1640	----	-----	416
Ni(PSHB)$_2$.OAc.3DMF	1667	1641	1391	1604	480
Ni(PSHB)$_2$.Cl.3DMF	1664	1640	-----	-----	462
Co(PSHB)$_2$.OAc.3DMF	1666	1646	1391	1606	449
Fe(PSHB)$_2$.OAc.3DMF	1667	1651	1393	1612	447
Mn(PSHB)$_2$.OAc.3DMF	1667	1641	1391	1606	418
Zn(PSHB)$_2$.OAc.DMF	1665	1645	1391	1612	417

Table 3: Electronic spectral data of complexes of p-Hydroxy Benzaldehyde schiff base of amino methylated polystyrene

Complex	Absorption(cm^{-1})	Tentative assignments
Cu(PSHB)$_2$. OAc.DMF	16100 33330	$^2B_{1g} \rightarrow {}^2A_{2g}$ Charge transfer
Cu(PSHB)$_2$.Cl.DMF	17300 38400	$^2B_{1g} \rightarrow {}^2A_{2g}$ Charge transfer
Ni(PSHB)$_2$.OAc.3DMF	9590 15384 22202	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$
Ni(PSHB)$_2$.Cl.3DMF	9256 15530 23529	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$
Co(PSHB)$_2$.OAc.3DMF	9090 20830 11111	$^4T_{1g} \rightarrow {}^4T_{2g}$ $^4T_{1g} \rightarrow {}^4A_{2g}$ $^4T_{1g} \rightarrow {}^2E_g$
Fe(PSHB)$_2$.OAc.3DMF	10526 15873 23809	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4A_{1g}(G)$
Mn(PSHB)$_2$.OAc.3DMF	10989 15151 24570	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4A_{1g}(G), {}^4E_g$

Table 4: Magnetic moments of metal complexes of p-Hydroxy Benzaldehyde schiff base of amino methylated polystyrene and its complexes

Complex	Colour	Magnetic moment (B M)	Geometry
$Cu(PSHB)_2.Cl.DMF$	Dark brown	1.97	Square planar
$Ni(PSHB)_2.Cl.3DMF$	Yellow	3.22	Octahedral
$Fe(PSHB)_2.OAc.3DMF$	Red brown	5.96	Octahedral
$Co(PSHB)_2.OAc.3DMF$	Ash	4.72	Octahedral
$Mn(PSHB)_2.OAc.3DMF$	Pale brown	5.94	Octahedral
$Zn(PSHB)_2.OAc.DMF$	Golden yellow	Diamagnetic	Tetrahedral

Table 5: TG data of metal complexes of p-Hydroxy benzaldehyde schiff base of amino methylated polystyrene and its complexes

Complex	Weight loss %	Temperature range ^0C	Conclusion
$Cu(PSHB)_2$. OAc.DMF	8.5	120-200	Loss of acetate
	13	200-300	Loss of 1DMF
$Ni(PSHB)_2.OAc.3DMF$	7	120-180	Loss of acetate
	23	150-300	Loss of 3DMF
$Mn(PSHB)_2.OAc.3DMF$	6.8	120-200	Loss of acetate
	22	150-320	Loss of 3DMF

Table 6 : Analytical data of p-Dimethyl amino benzaldehyde schiff base of amino methylated polystyrene and its complexes

Compound	Found (Calculated) %				
	C	H	N	Cl	M
PSDMAB	81.94 (81.81)	7.51 (7.58)	10.55 (10.61)		
Cu(PSDMAB)$_2$. OAc.DMF	67.74 (68.01)	6.70 (6.91)	9.48 (9.67)		9.63 (8.78)
Cu(PSDMAB)$_2$.Cl.DMF	66.67 (66.86)	6.59 (6.71)	9.77 (10.02)	5.19 (5.07)	9.56 (9.07)
Ni(PSDMAB)$_2$.OAc.3DMF	65.48 (65.22)	7.36 (7.41)	11.21 (11.33)		6.52 (6.79)
Ni(PSDMAB)$_2$.Cl.3DMF	64.59 (64.20)	7.10 (7.25)	11.41 (11.65)	4.29 (4.22)	6.84 (6.98)
Co(PSDMAB)$_2$.OAc.3DMF	65.37 (65.21)	7.32 (7.40)	11.15 (11.33)		6.67 (6.48)
Fe(PSDMAB)$_2$.OAc.3DMF	65.26 (65.44)	7.29 (7.42)	11.17 (11.38)		7.03 (6.92)
Mn(PSDMAB)$_2$.OAc.3DMF	65.78 (65.57)	7.38 (7.44)	11.28 (11.37)		6.26 (6.38)
Zn(PSDMAB)$_2$.OAc.DMF	64.83 (64.72)	7.26 (7.34)	11.01 (11.25)		7.82 (7.51)

Table 7: IR spectral data of p-Dimethyl amino benzaldehyde schiff base of amino methylated polystyrene and its complexes

Compound	υ (C=N) cm^{-1}	υ (C=O) cm^{-1}	υ (COO) sym.str. cm^{-1}	υ (COO) anti.sym cm^{-1}	υ (M-N) cm^{-1}
PSDMAB	1678	……	……	…….	……
Cu(PSDMAB)$_2$. OAc.DMF	1664	1645	1391	1605	415
Cu(PSDMAB)$_2$.Cl.DMF	1667	1651	-----	-----	418
Ni(PSDMAB)$_2$.OAc.3DMF	1668	1652	1392	1604	479
Ni(PSDMAB)$_2$.Cl.3DMF	1667	1655	------	------	480
Co(PSDMAB)$_2$.OAc.3DMF	1667	1651	1391	1604	451
Fe(PSDMAB)$_2$.OAc.3DMF	1667	1647	1388	1613	465
Mn(PSDMAB)$_2$.OAc3DMF	1667	1646	1393	1611	419
Zn(PSDMAB)$_2$.OAc.DMF	1666	1647	1391	1613	418

Table 8: Electronic spectral data of complexes p-Dimethyl amino benzaldehyde schiff base of amino methylated polystyrene

Complex	Absorption(cm^{-1})	Tentative assignments
Cu(PSDMAB)$_2$. OAc.DMF	15384 31250	$^2B_{1g} \rightarrow {}^2A_{2g}$ Charge transfer
Cu(PSDMAB)$_2$.Cl.DMF	17241 27770	$^2B_{1g} \rightarrow {}^2A_{2g}$ Charge transfer
Ni(PSDMAB)$_2$.OAc.3DMF	10309 16393 25641	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$
Ni(PSDMAB)$_2$.Cl.3DMF	10989 14285 24390	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$
Co(PSDMAB)$_2$.OAc.3DMF	8928 16393 10526	$^4T_{1g} \rightarrow {}^4T_{2g}$ $^4T_{1g} \rightarrow {}^4A_{2g}$ $^4T_{1g} \rightarrow {}^2E_g$
Fe(PSDMAB)$_2$.OAc.3DMF	10416 15873 21978	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4A_{1g}(G)$
Mn(PSDMAB)$_2$.OAc.3DMF	10638 15384 24390	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4A_{1g}(G), {}^4E_g$

Table 9: Magnetic moments of complexes of p-Dimethyl amino benzaldehyde schiff base of amino methylated polystyrene

Complex	Colour	Magnetic moment (B M)	Geometry
$Cu(PSDMAB)_2.OAc.DMF$	Coffee brown	1.86	Square planar
$Ni(PSDMAB)_2.OAc.3DMF$	Brown	3.31	Octahedral
$Fe(PSDMAB)_2.OAc.3DMF$	Red brown	5.97	Octahedral
$Co(PSDMAB)_2.OAc.3DMF$	Grey	4.50	Octahedral
$Mn(PSDMAB)_2.OAc.3DMF$	Brown	5.96	Octahedral
$Zn(PSDMAB)_2.OAc.DMF$	Golden brown	Diamagnetic	Tetrahedral

Table 10: TG data of complexes of p-Dimethyl amino benzaldehyde schiff base of amino methylated polystyrene

Complex	Weight loss %	Temperature range ^0C	Conclusion
$Cu(PSDMAB)_2. OAc.DMF$	8 10	120-200 180-300	Loss of acetate Loss of 1DMF
$Co(PSDMAB)_2.OAc.3DMF$	6.5 25.5	120-180 150-320	Loss of acetate Loss of 3DMF

Table11: Analytical data of 3- Nitro benzaldehyde schiff base of amino methylated polystyrene and its complexes

Compound	Found (Calculated) %				
	C	H	N	Cl	M
PSNB	72 .54 (72.18)	4.97 (5.26)	10.41 (10.53)		
$Cu(PSNB)_2$. OAc.DMF	60.87 (61.03)	5.04 (5.22)	9.39 (9.63)		9.45 (8.72)
$Cu(PSNB)_2$.Cl.DMF	59.80 (59.65)	4.73 (4.97)	9.81 (9.95)	4.97 (5.05)	8.86 (9.02)
$Ni(PSNB)_2$.OAc.3DMF	60.03 (59.40)	5.76 (5.98)	11.12 (11.29)		6.49 (6.76)
$Ni(PSNB)_2$.Cl.3DMF	58.56 (58.25)	5.62 (5.80)	11.74 (11.61)	4.14 (4.22)	6.69 (6.95)
$Co(PSNB)_2$.OAc.3DMF	59.61 (59.40)	5.78 (5.98)	11.35 (11.28)		6.49 (6.77)
$Fe(PSNB)_2$.OAc.3DMF	59.71 (59.60)	5.90 (6.01)	11.10 (11.31)		6.94 (6.45)
$Mn(PSNB)_2$.OAc.3DMF	60.01 (59.66)	6 .11 (6.02)	11.41 (11.33)		6.02 (6.34)
$Zn(PSNB)_2$.OAc.DMF	58.68 (58.95)	5.82 (5.94)	11.34 (11.20)		7.75 (7.47)

Table 12: IR spectral data of 3-Nitro benzaldehyde Schiff base of amino methylated polystyrene and its complexes

Compound	**υ (C=N) cm^{-1}**	**υ (C=O) cm^{-1}**	**υ (COO) sym.str. cm^{-1}**	**υ (COO) anti.sym cm^{-1}**	**υ (M-N) cm^{-1}**
PSNB	1646	---	----	---	----
Cu(PSNB)$_2$. OAc.DMF	1664	1641	1391	1604	419
Cu(PSNB)$_2$.Cl.DMF	1662	1640	-----	-----	417
Ni(PSNB)$_2$.OAc.3DMF	1669	1642	1391	1606	479
Ni(PSNB)$_2$.Cl.3DMF	1666	1646	------	------	464
Co(PSNB)$_2$.OAc.3DMF	1681	1644	1391	1606	448
Fe(PSNB)$_2$.OAc.3DMF	1667	1642	1391	1606	457
Mn(PSNB)$_2$.OAc.3DMF	1663	1640	1394	1604	417
Zn(PSNB)$_2$.OAc.DMF	1667	1637	1392	1610	419

Table 13: Electronic spectral data of complexes of 3-Nitro Benzaldehyde schiff base of amino methylated polystyrene

Complex	Absorption(cm^{-1})	Tentative assignments
Cu(PSNB)$_2$. OAc.DMF	16393 26315	$^2B_{1g} \rightarrow {}^2A_{2g}$ Charge transfer
Cu(PSNB)$_2$.Cl.DMF	16129 35714	$^2B_{1g} \rightarrow {}^2A_{2g}$ Charge transfer
Ni(PSNB)$_2$.OAc.3DMF	10526 16000 24390	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$
Ni(PSNB)$_2$.Cl.3DMF	10309 17241 27027	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$
Co(PSNB)$_2$.OAc.3DMF	9100 15875 10869	$^4T_{1g} \rightarrow {}^4T_{2g}$ $^4T_{1g} \rightarrow {}^4A_{2g}$ $^4T_{1g} \rightarrow {}^2E_g$
Fe(PSNB)$_2$.OAc.3DMF	10256 14814 25641	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4A_{1g}(G)$
Mn(PSNB)$_2$.OAc.3DMF	10204 15184 24971	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4A_{1g}(G), {}^4E_g$

Table 14: Magnetic moments of complexes of 3- Nitro benzaldehyde schiff base of amino methylated polystyrene

Complex	Colour	Magnetic moment (B M)	Geometry
$Cu(PSNB)_2.OAc.DMF$	Coffee brown	1.81	Square planar
$Ni(PSNB)_2.OAc.3DMF$	Brown	3.19	Octahedral
$Fe(PSNB)_2.OAc.3DMF$	Red brown	5.90	Octahedral
$Co(PSNB)_2.OAc.3DMF$	Grey	4.63	Octahedral
$Mn(PSNB)_2.OAc.3DMF$	Brown	5.74	Octahedral
$Zn(PSNB)_2.OAc.DMF$	Flesh	Diamagnetic	Tetrahedral

Table 15: TG data of complexes of 3-Nitro benzaldehyde schiff base of amino methylated polystyrene

Complex	Weight loss %	Temperature range ^0C	Conclusion
$Cu(PSNB)_2. OAc.DMF$	8 10	120-200 180-300	Loss of acetate Loss of 1DMF
$Ni(PSNB)_2.OAc.3DMF$	6.8 25	120-220 150-300	Loss of acetate Loss of 3DMF
$Co(PSNB)_2.OAc.3DMF$	6.5 25	120-180 150-320	Loss of acetate Loss of 3DMF

Fig.1 : IR spectra of PSHB and its complexes

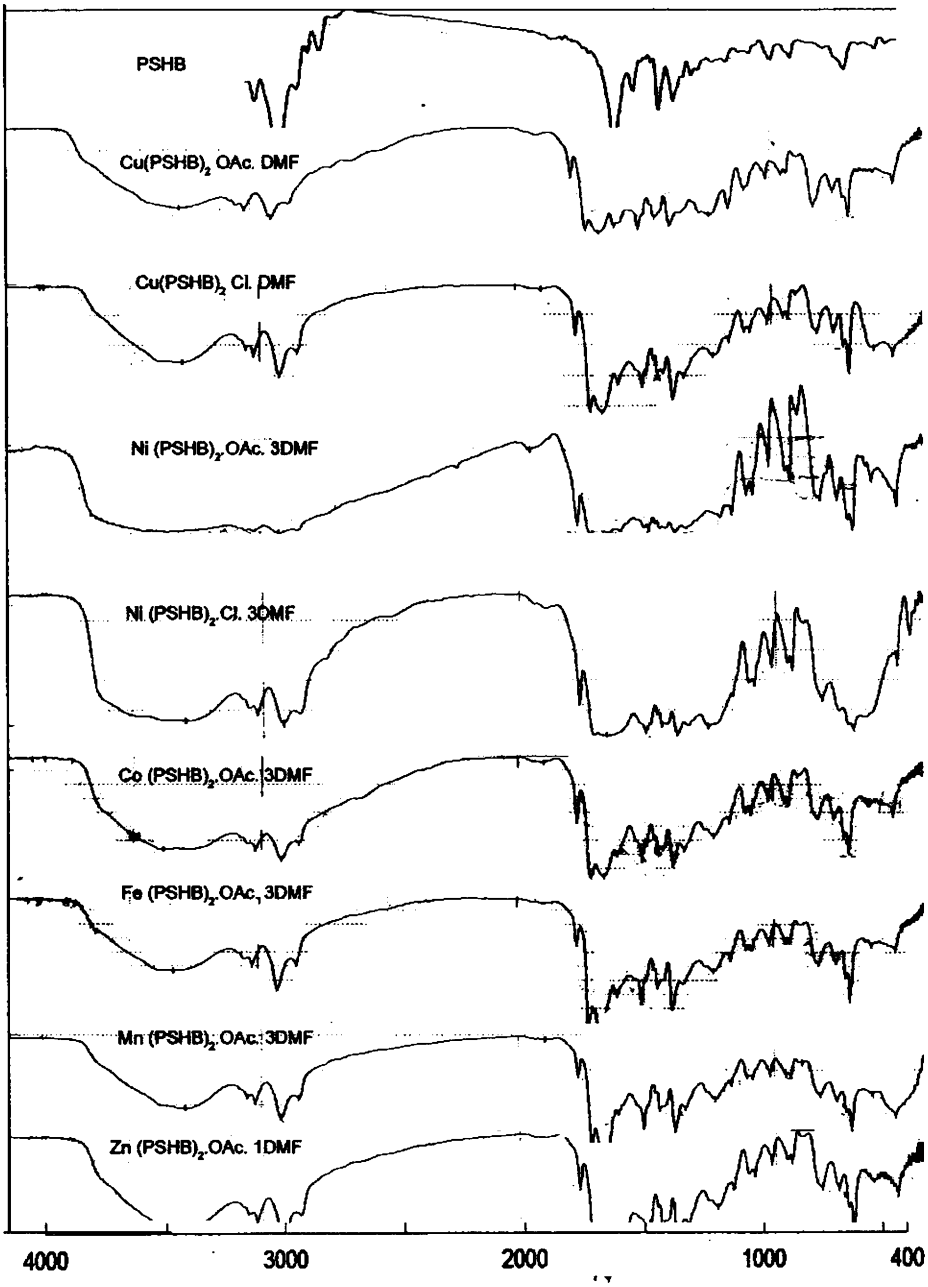


Fig.2: Electronic spectra of PSHB complexes

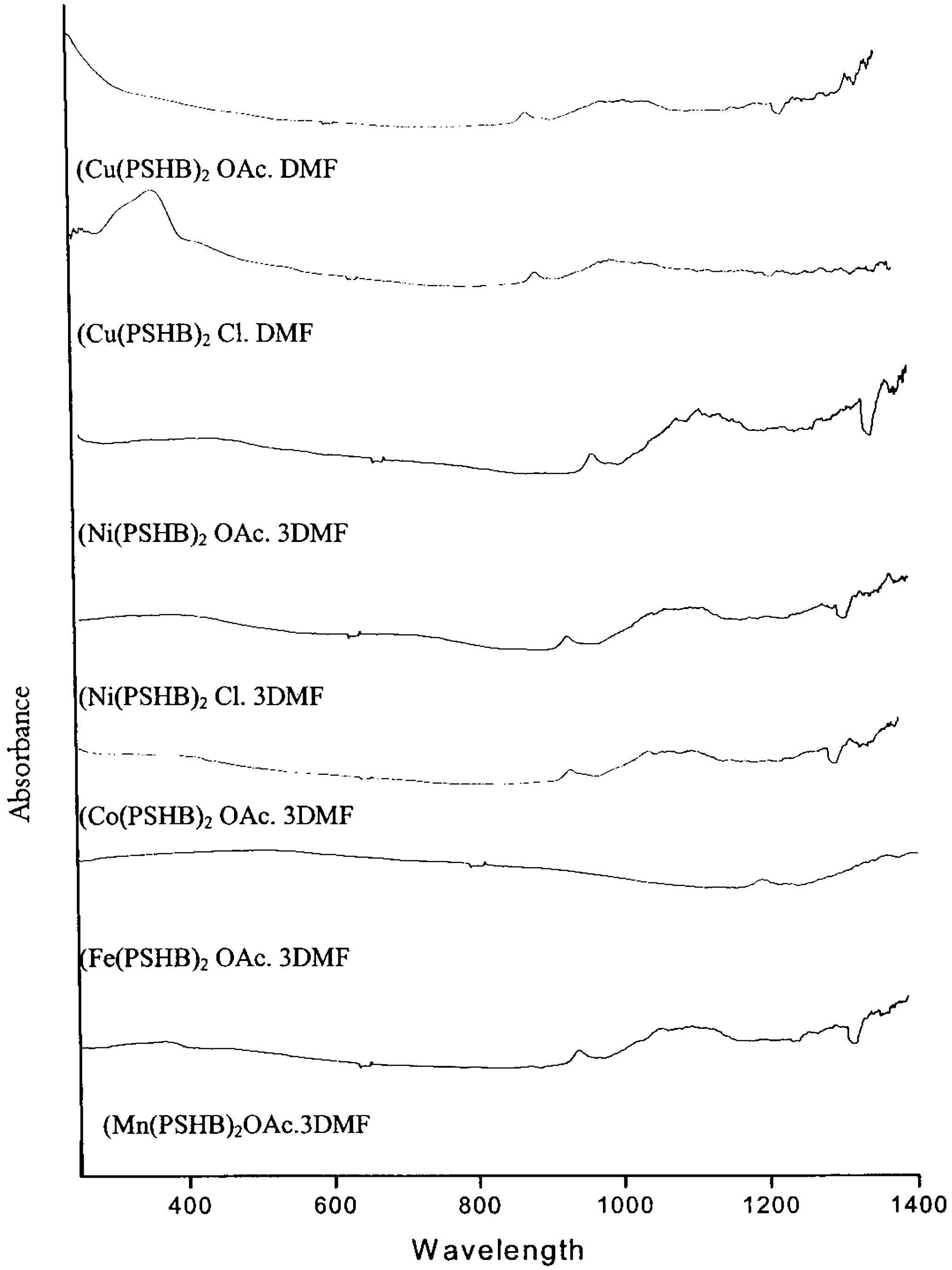


Fig.3: TG – DTG curves of PSHB complexes

Fig.3.3(a) [Cu$(PSHB)_2$OAc.DMF]

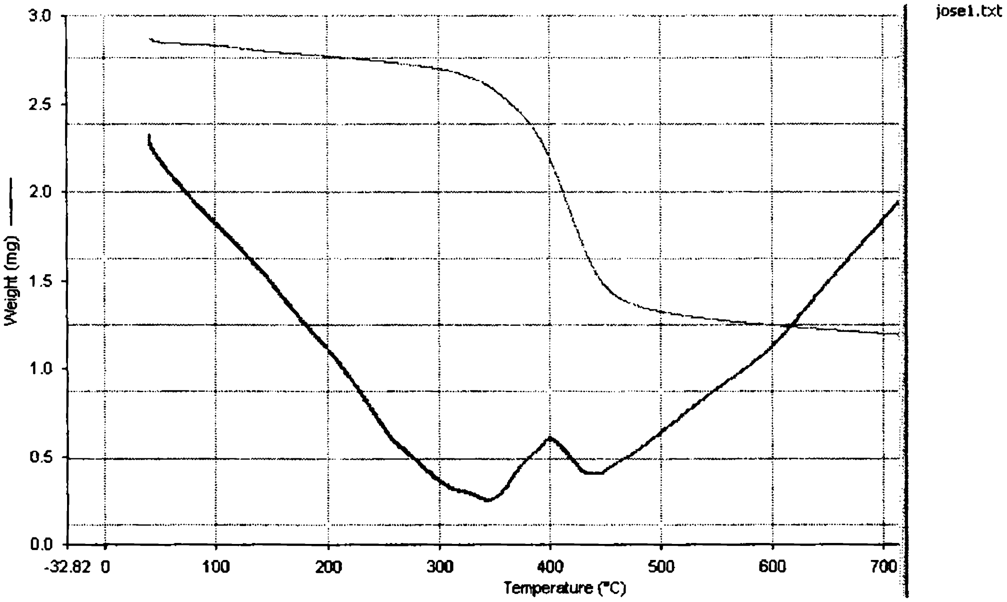


Fig 3(b) : [Ni$(PSHB)_2$OAc.3DMF]

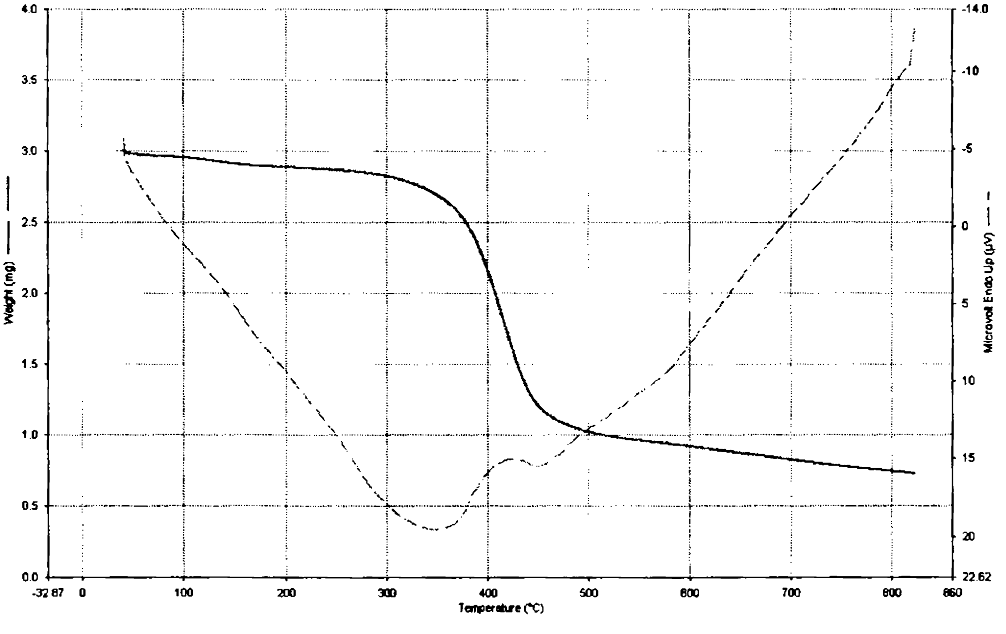


Fig 3 (c) [Mn(PSHB)$_2$.OAc.3DMF]

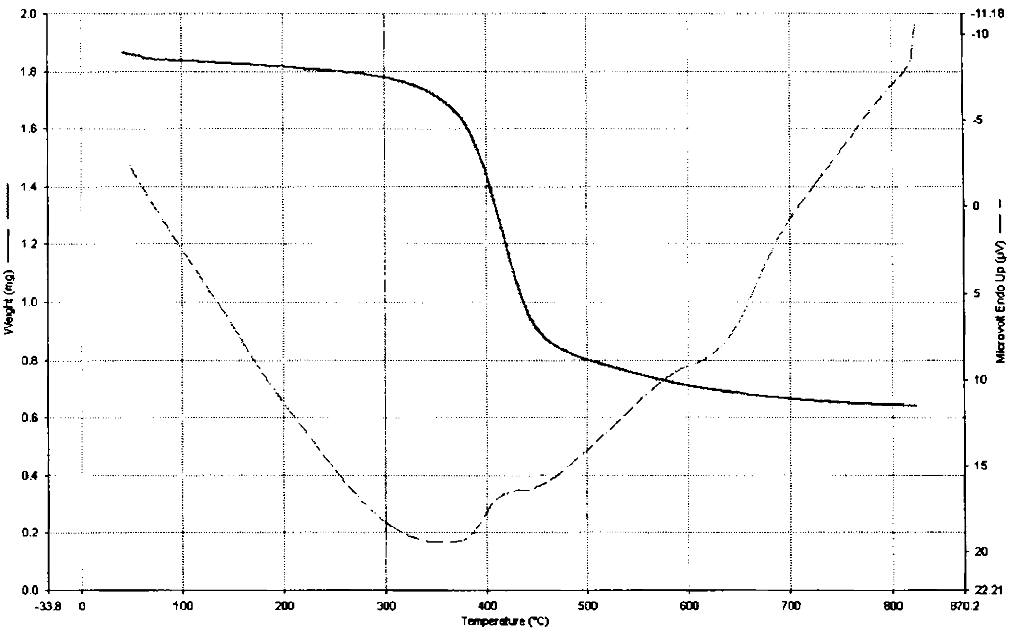


Fig. 4 : [Cu(PSHB)$_2$OAc.DMF]

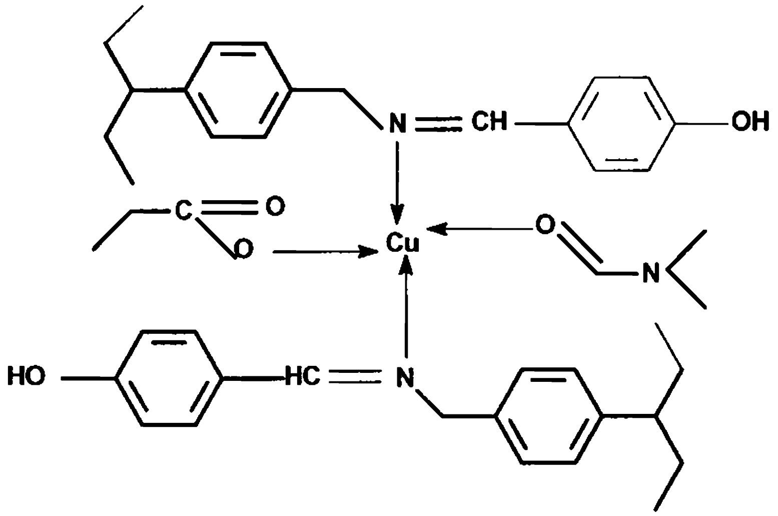


Fig.5: [Cu(PSHB)$_2$Cl.DMF]

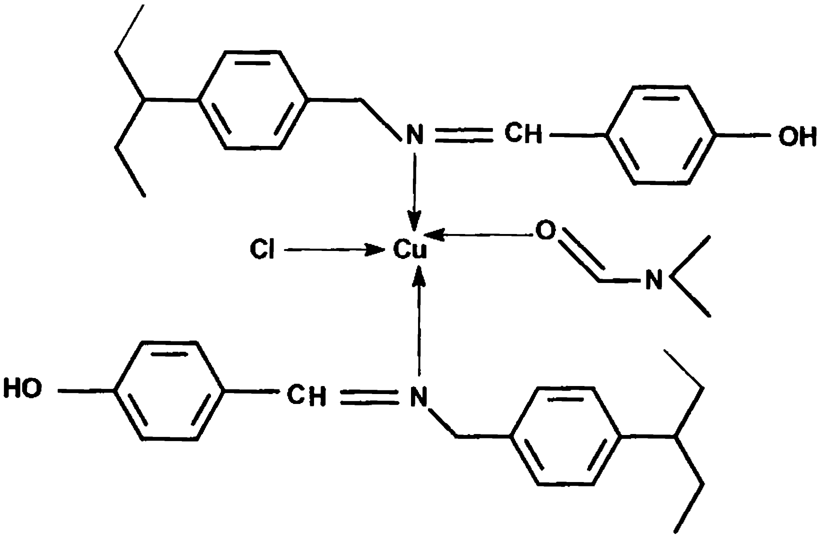


Fig.6: [Ni(PSHB)$_2$OAc.3DMF]

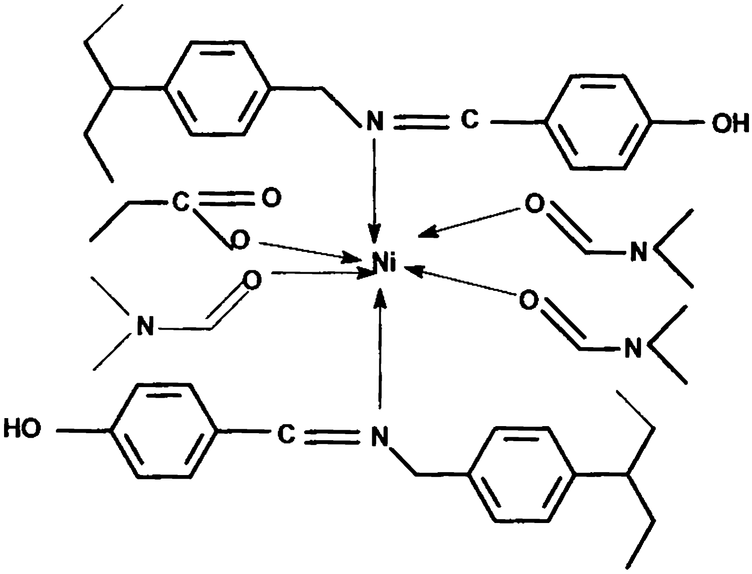


Fig.7: [Ni(PSHB)$_2$Cl.3DMF]

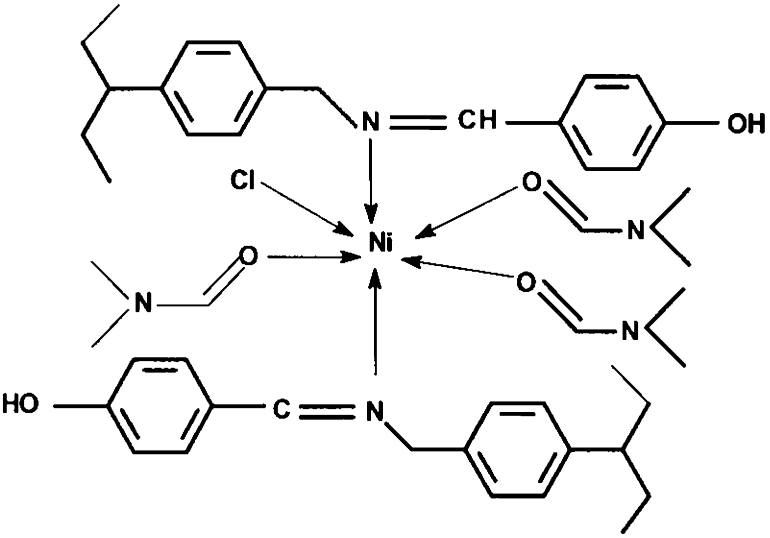


Fig. 8: [Co(PSHB)$_2$.OAc.3DMF]

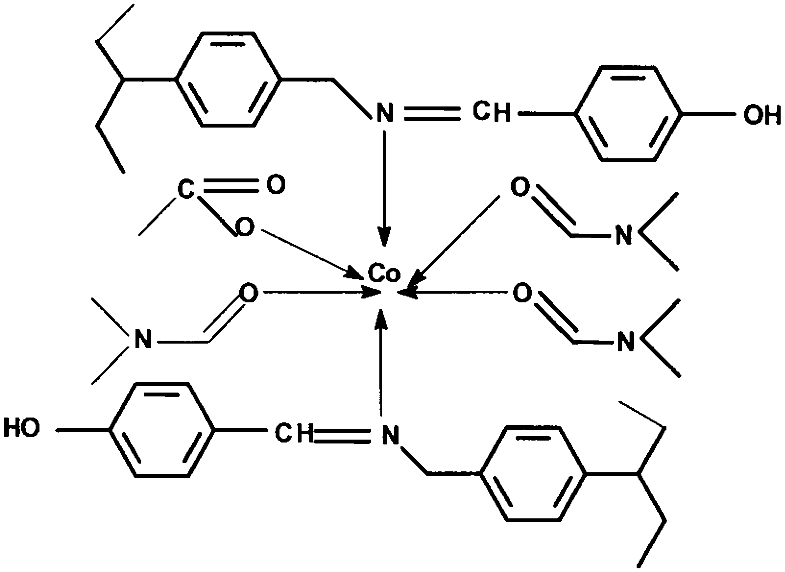


Fig. 9: [Fe $(PSHB)_2OAc.3DMF$]

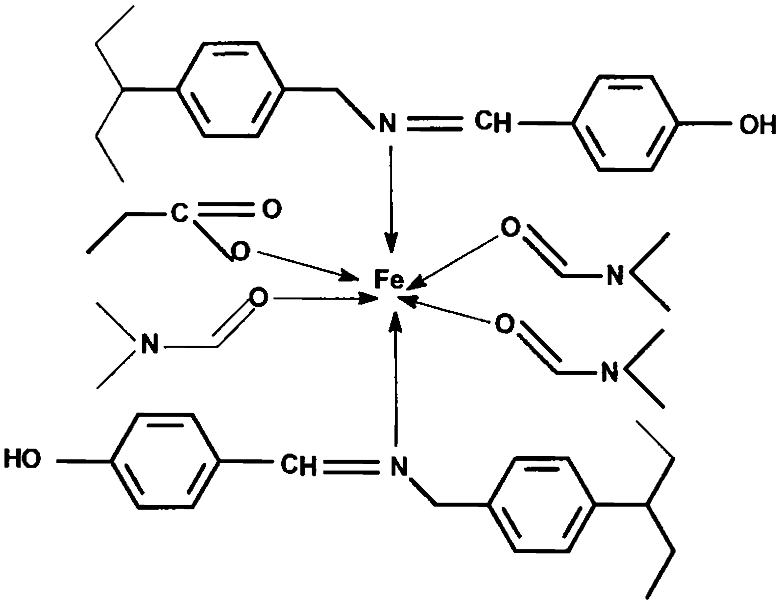


Fig. 10 : [Mn$(PSHB)_2$.OAc.3DMF

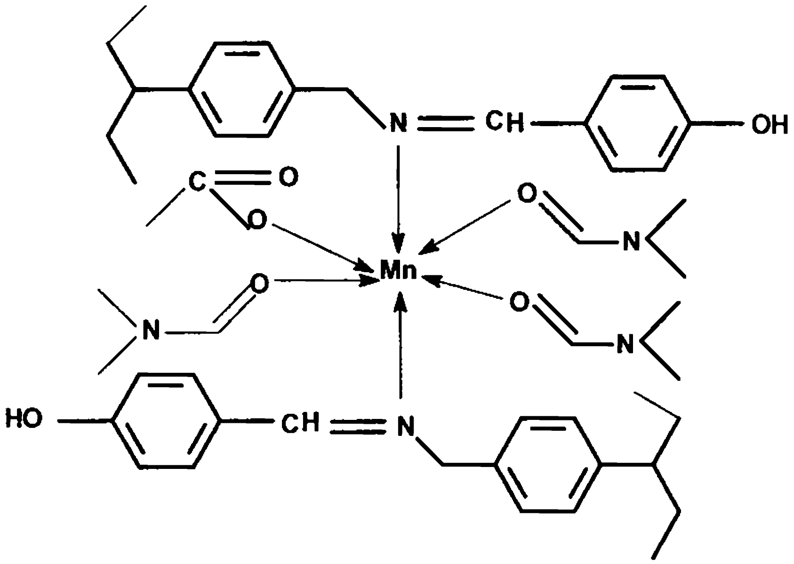


Fig. 11: [Zn(PSHB)$_2$.OAc.DMF]

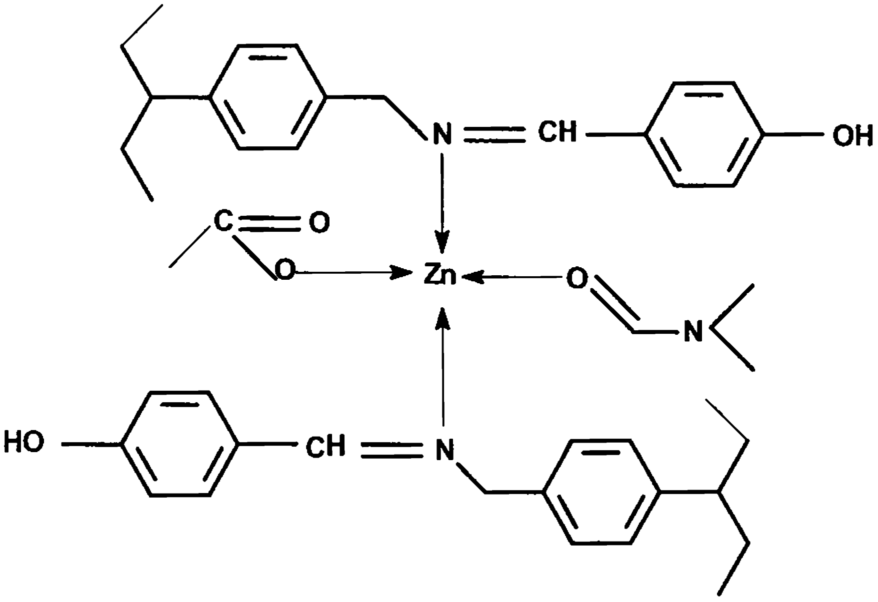


Fig.12: IR spectra of PSDMAB and its complexes

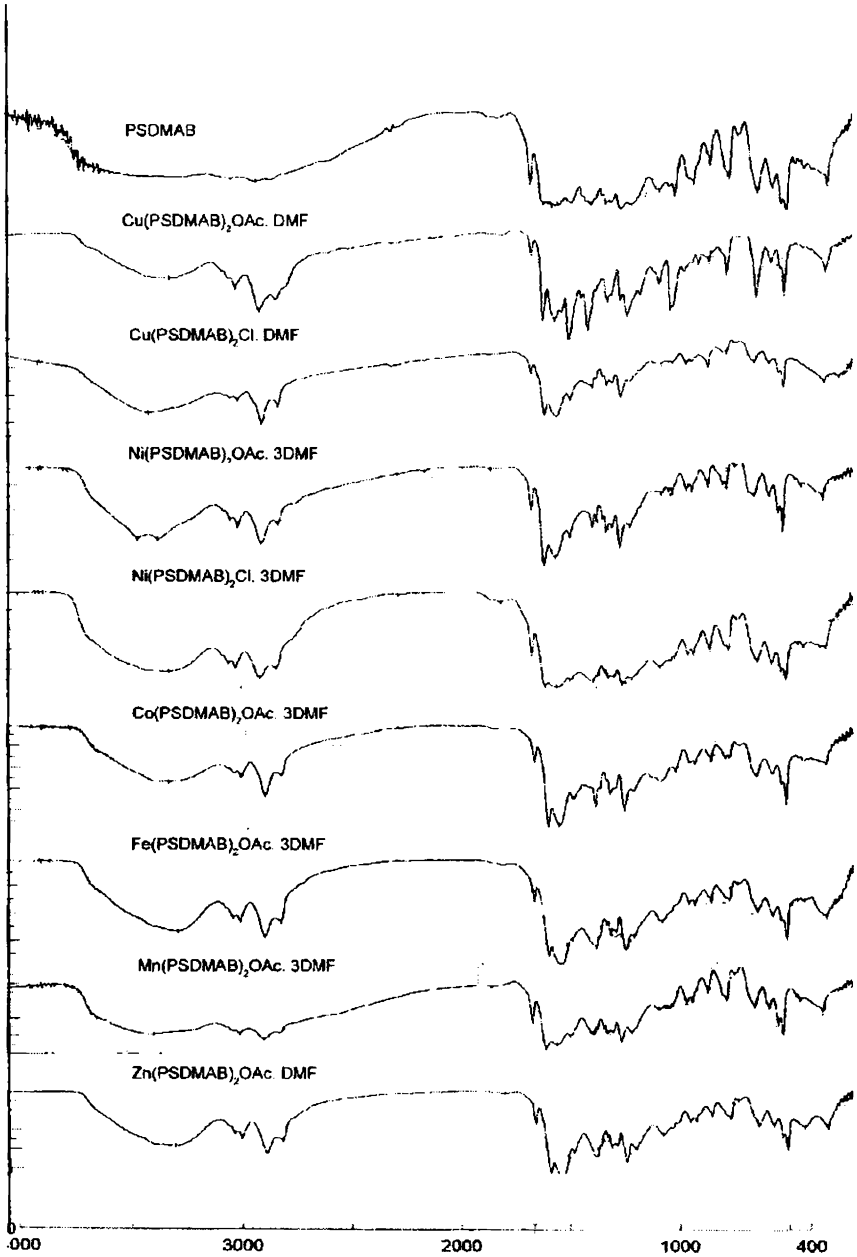


Fig. 13: Electronic spectra of PSDMAB complexes

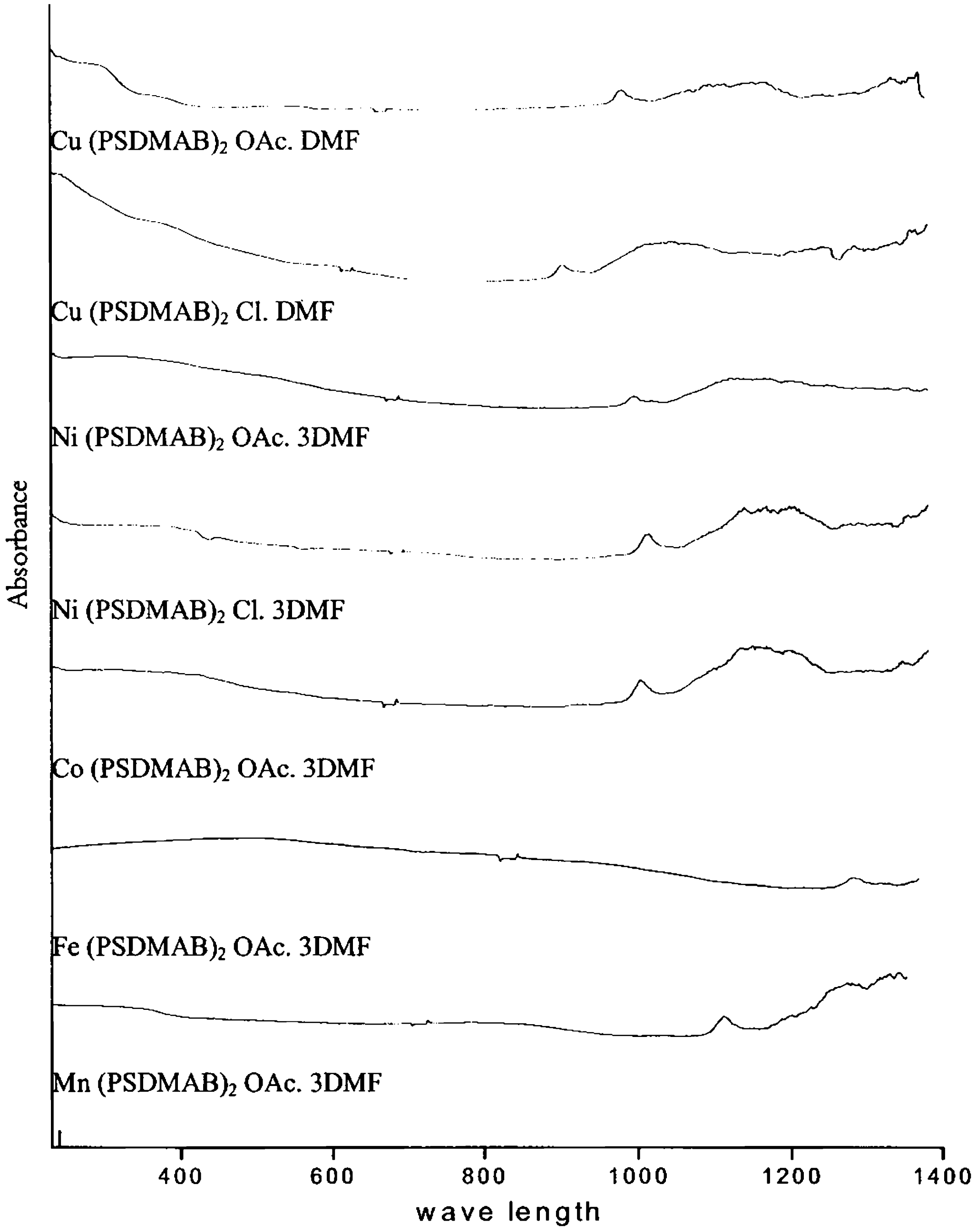


Fig.14: TG – DTG curves of PSDMAB complexes

Fig. 14 (a) [Cu(PSDMAB)$_2$OAc.DMF]

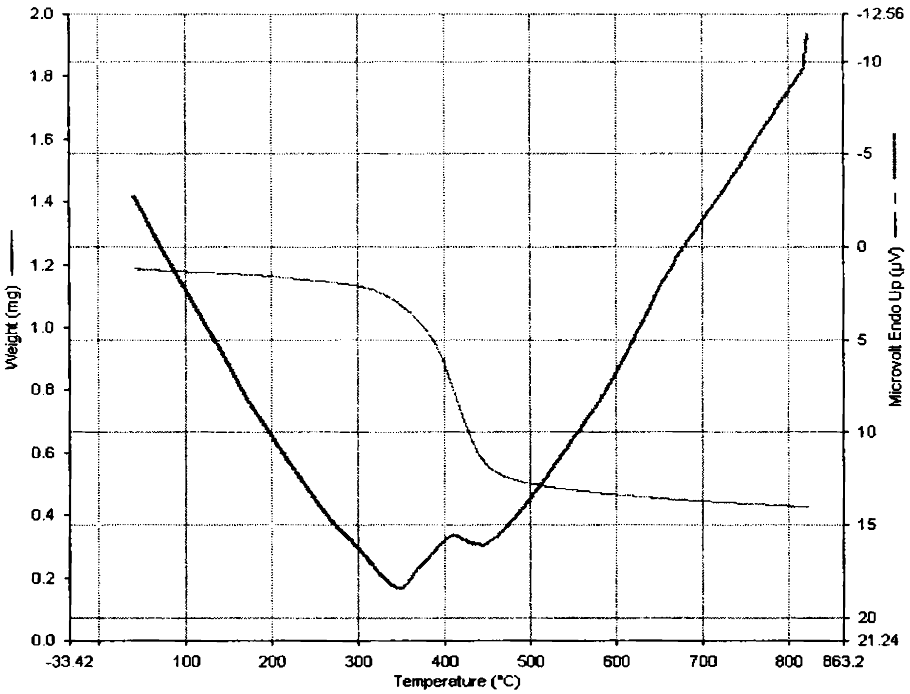


Fig. 14 (b) [Co(PSDMAB)$_2$OAc.3DMF]

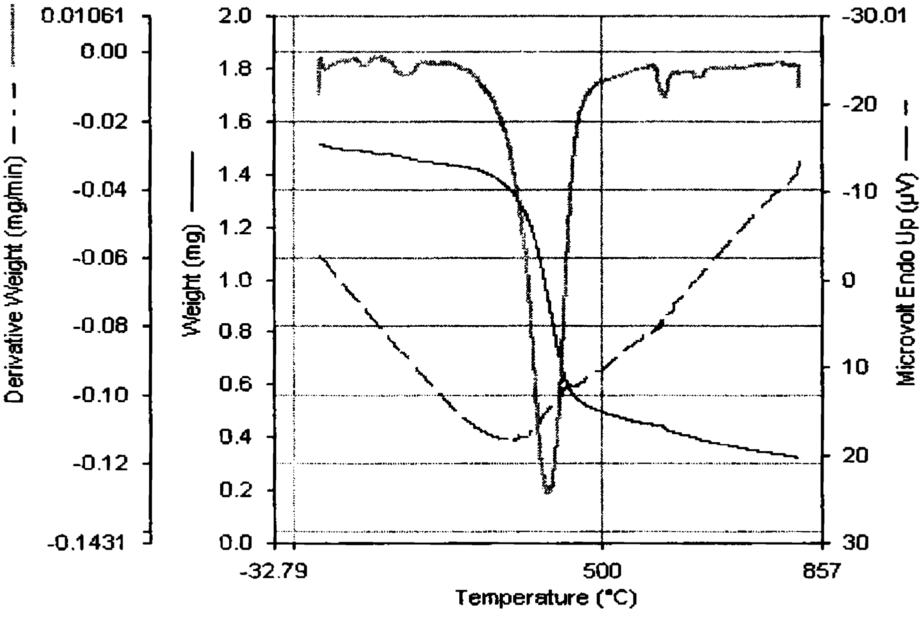


Fig.15: [Cu(PSDMAB)$_2$OAc.DMF]

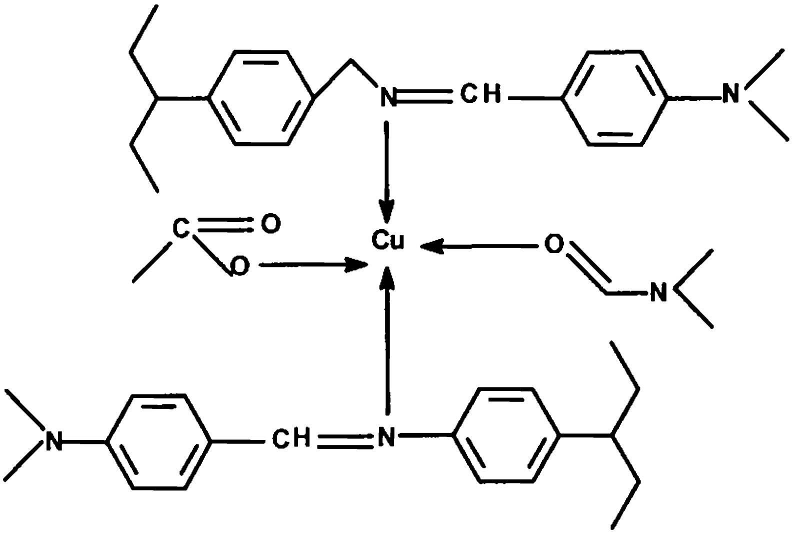


Fig.16: [Cu(PSDMAB)$_2$Cl.DMF]

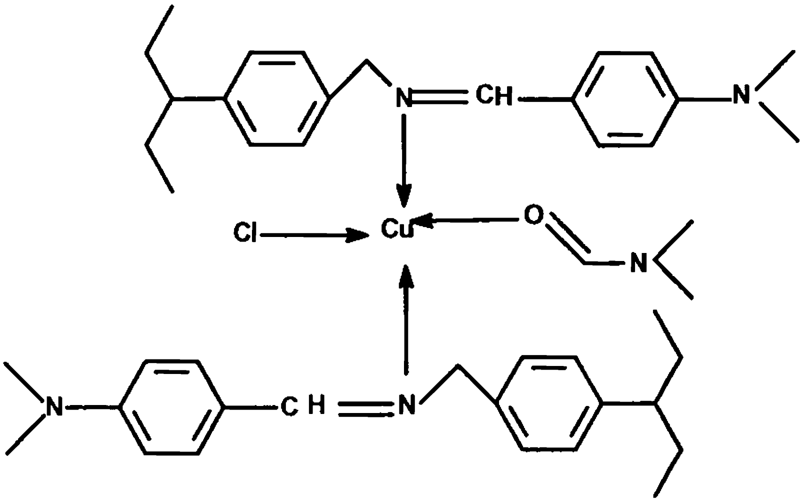


Fig.17: [Ni(PSDMAB)$_2$OAc.3DMF]

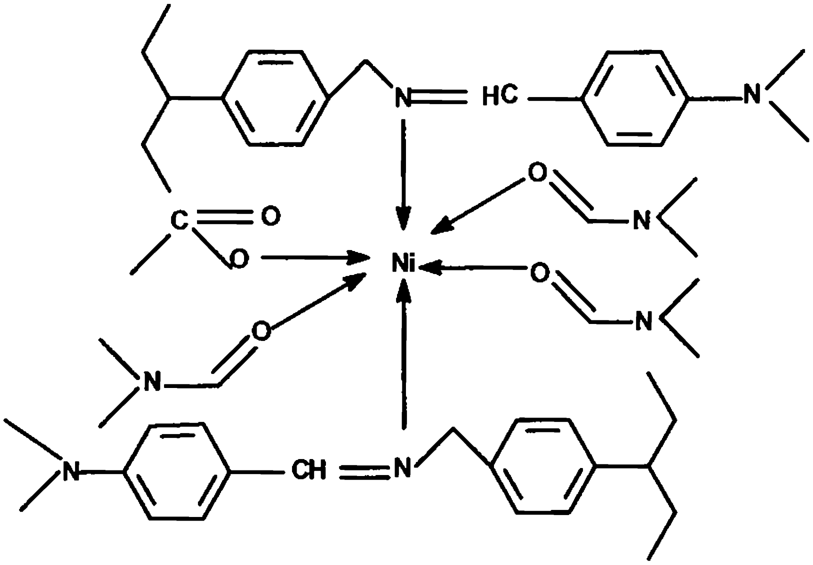


Fig.18: [Ni(PSDMAB)$_2$Cl.3DMF]

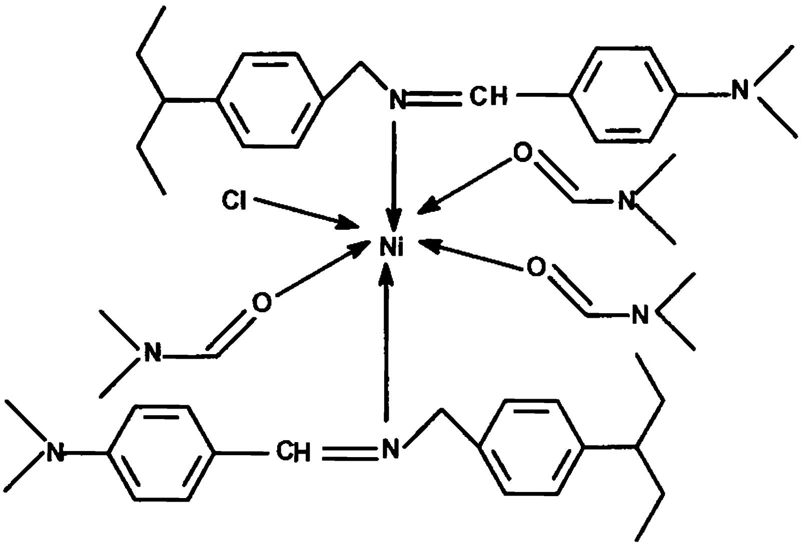


Fig.19: [Co(PSDMAB)$_2$OAc.3DMF]

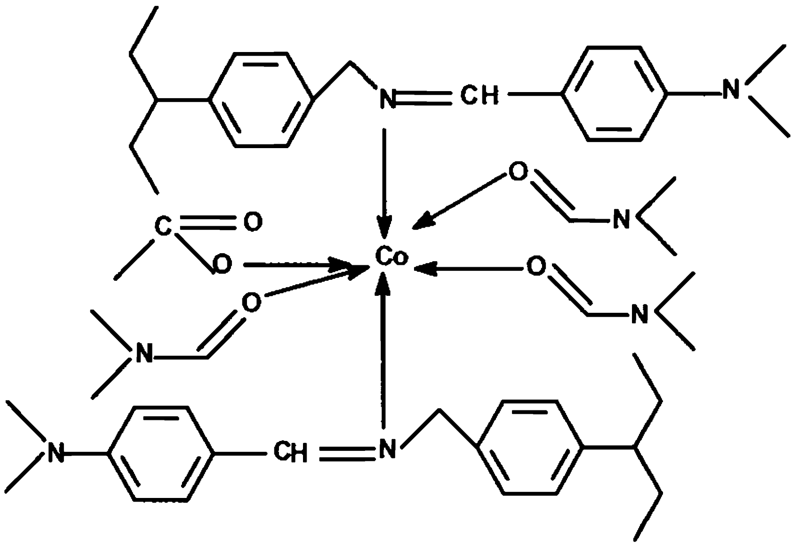


Fig.20: [Fe(PSDMAB)$_2$OAc.3DMF]

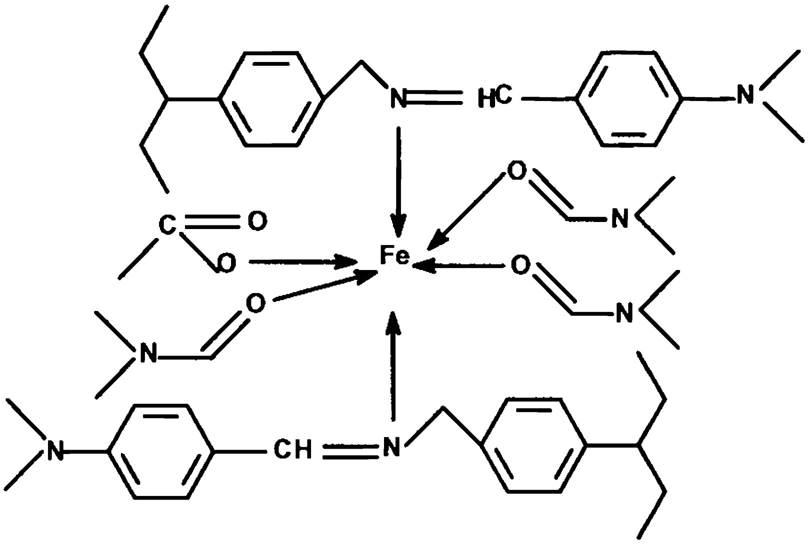


Fig.21: [Mn(PSDMAB)$_2$OAc.3DMF]

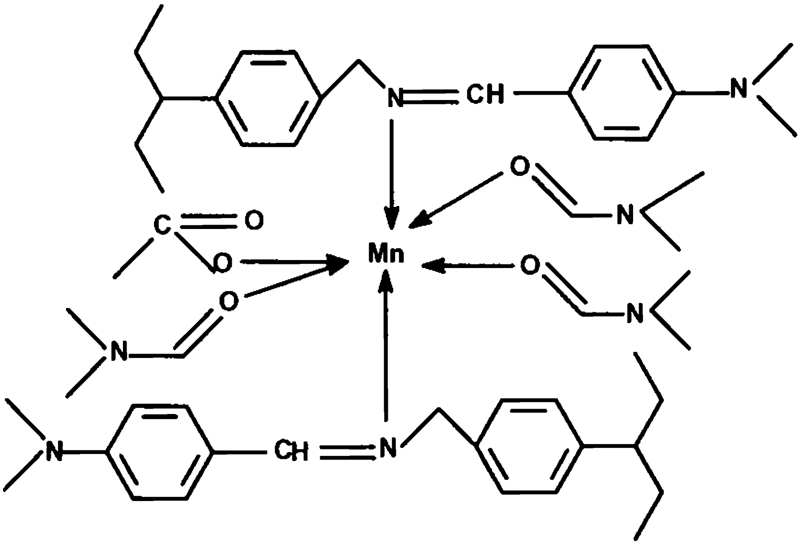


Fig.22: [Zn(PSDMAB)$_2$OAc.DMF]

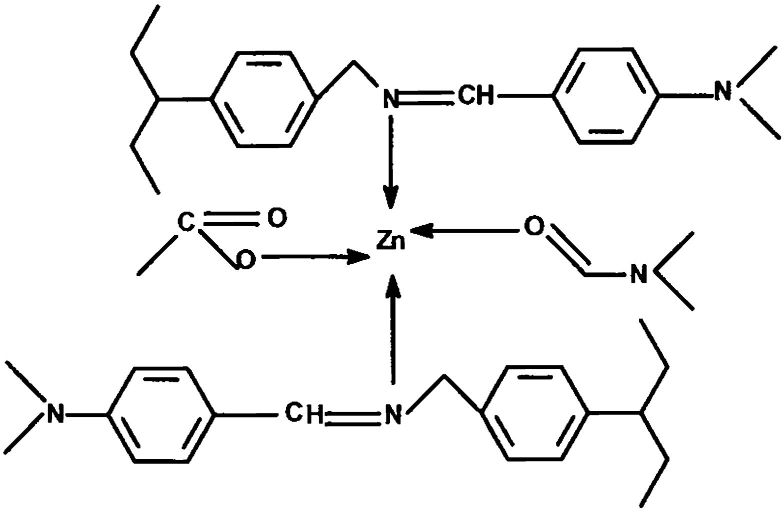


Fig.23: IR spectra of PSNB and its complexes

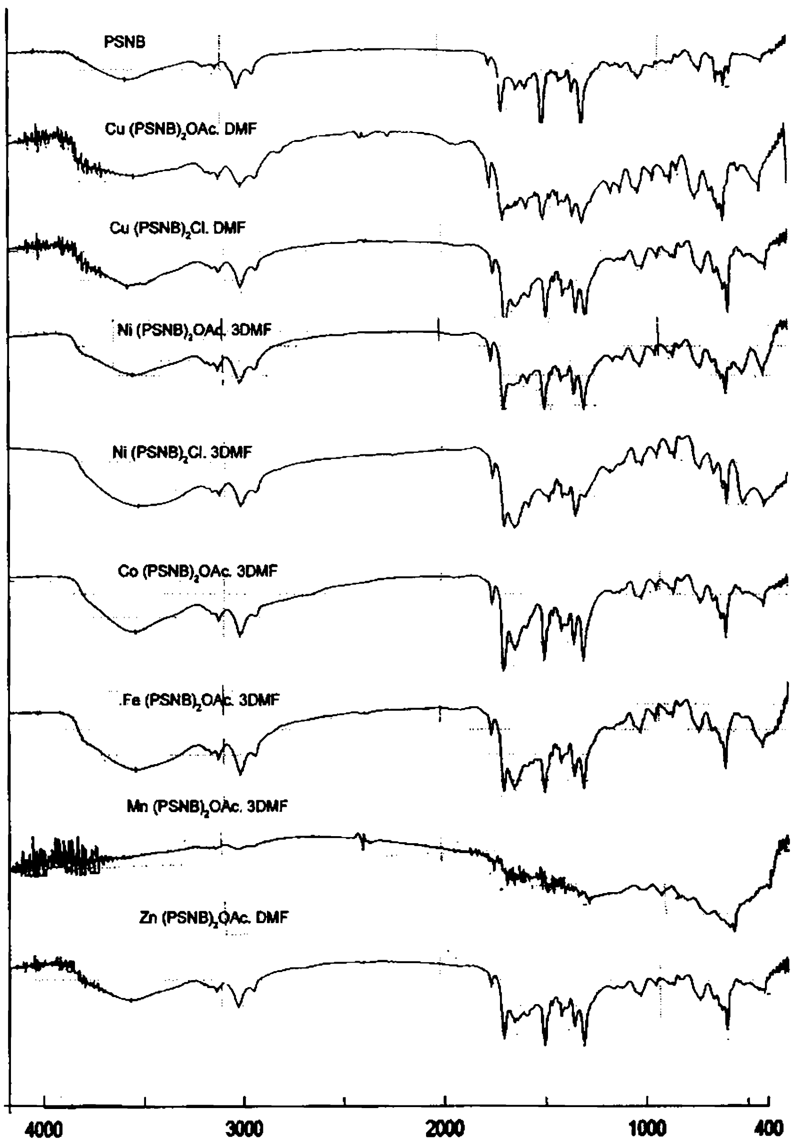


Fig.24: Electronic spectra of PSNB complexes

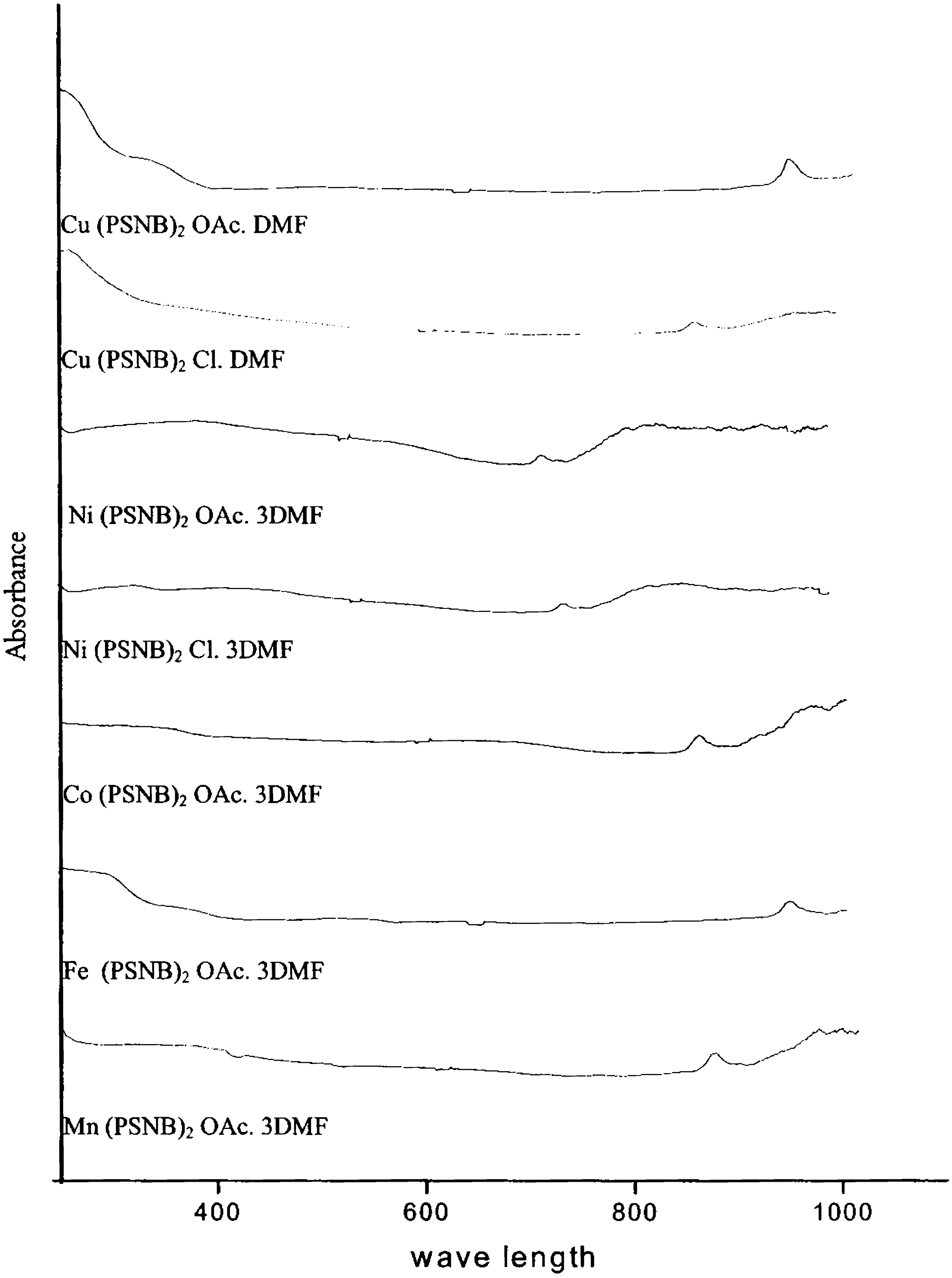
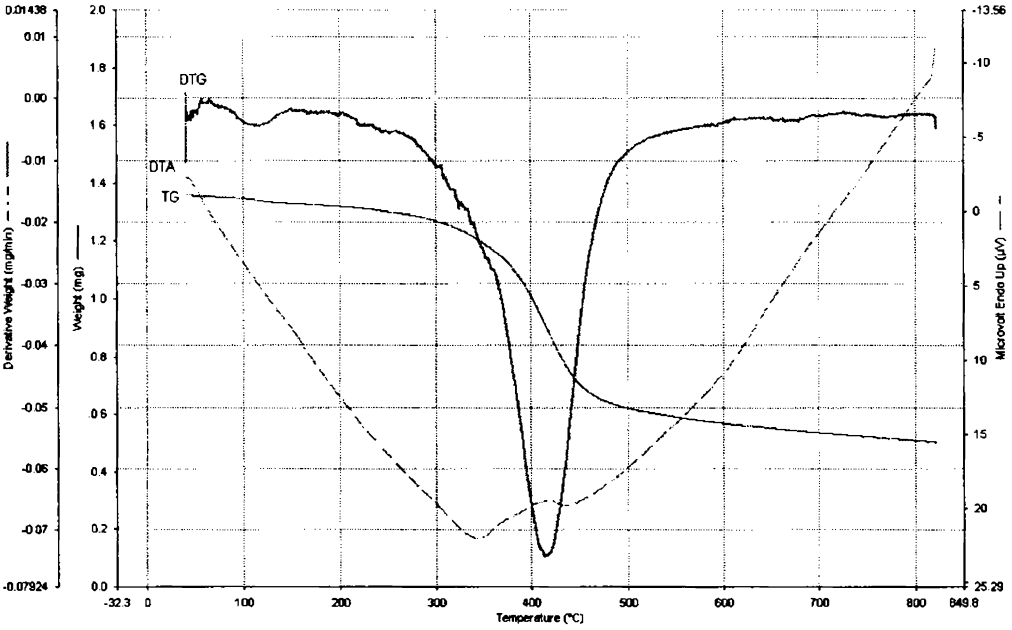
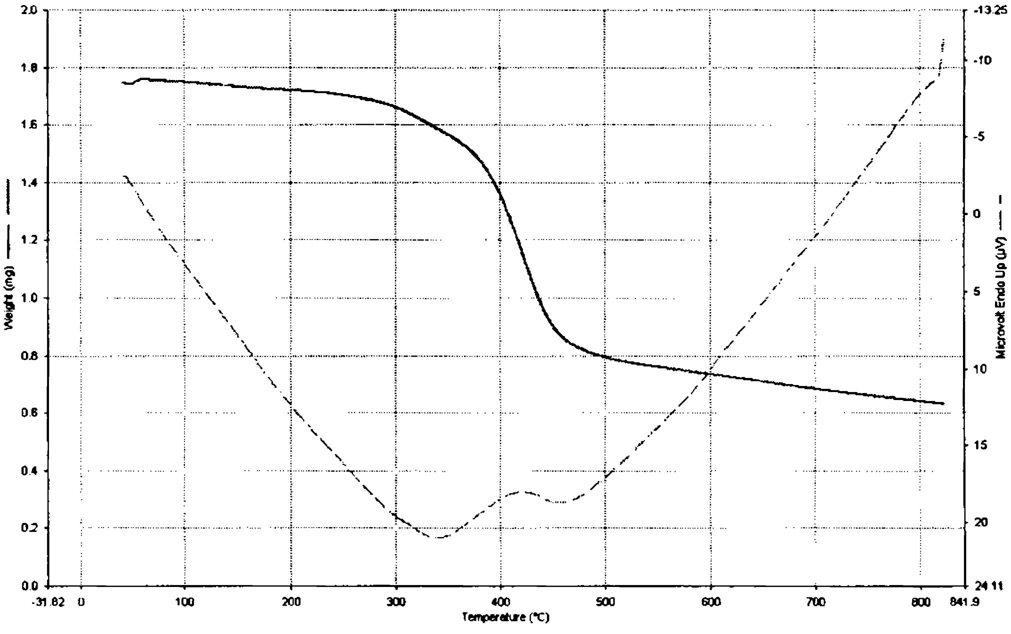


Fig.25: TG-DTG curves of PSNB complexes

(a) [$Cu(PSNB)_2OAc.DMF$]



(b) [$Ni(PSNB)_2OAc.3DMF$]



(c)[Co(PSNB)$_2$OAc.3DMF]

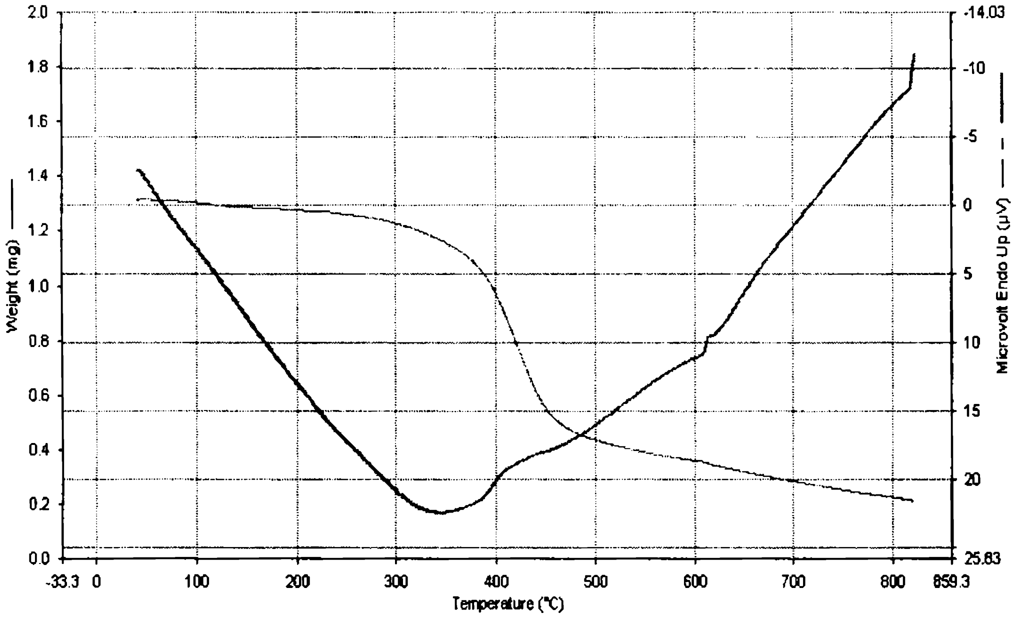


Fig.26: [Cu(PSNB)$_2$OAc.DMF]

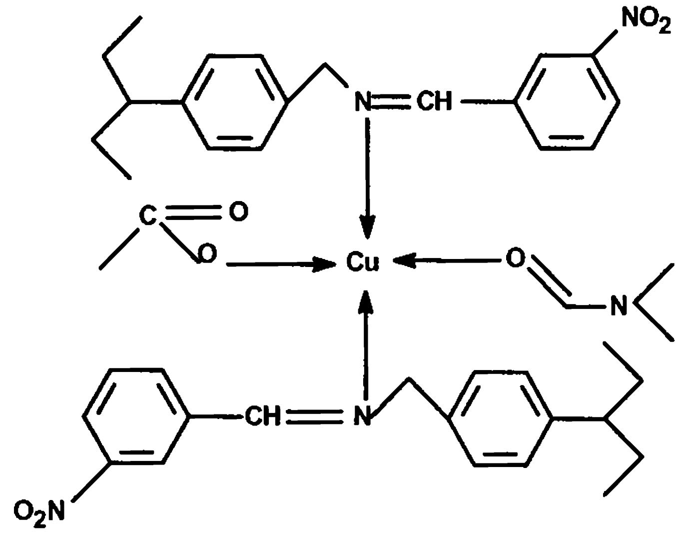


Fig.27: [Cu(PSNB)$_2$Cl.DMF]

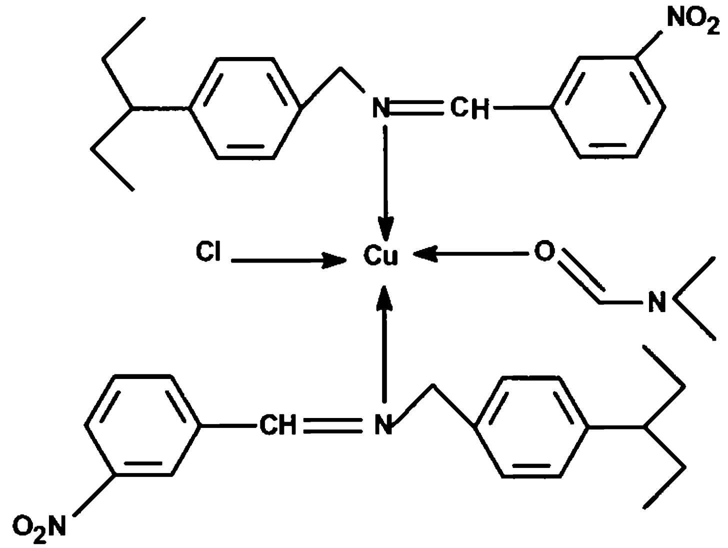


Fig.28: [Ni(PSNB)$_2$OAc.3DMF]

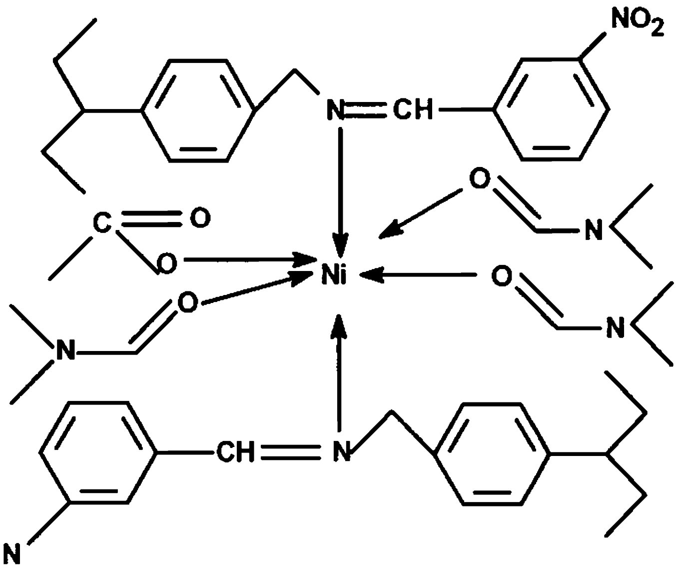


Fig.29: [Ni(PSNB)$_2$Cl.3DMF]

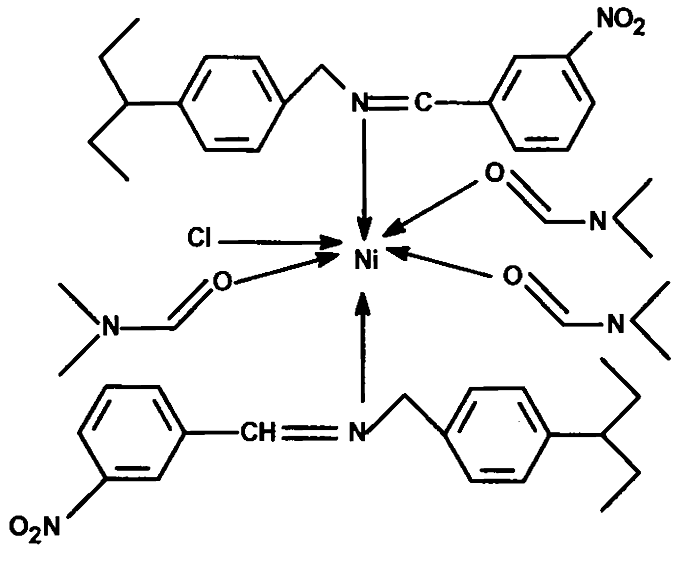


Fig.30: [Co(PSNB)$_2$OAc.3DMF]

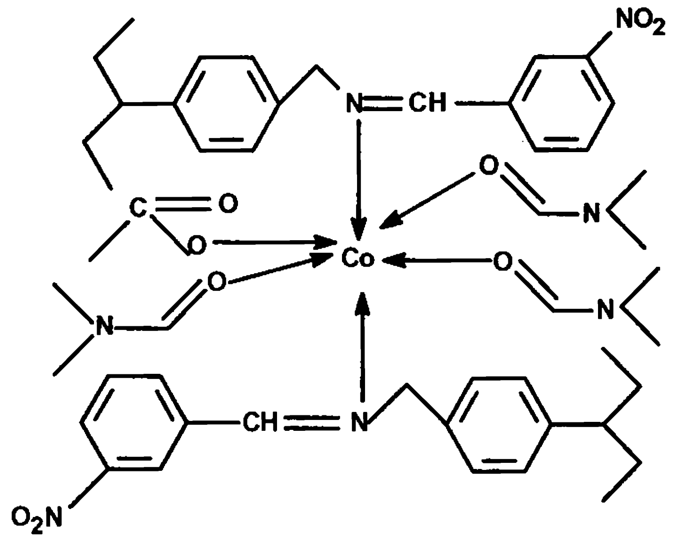


Fig.31: [Fe(PSNB)$_2$OAc.3DMF]

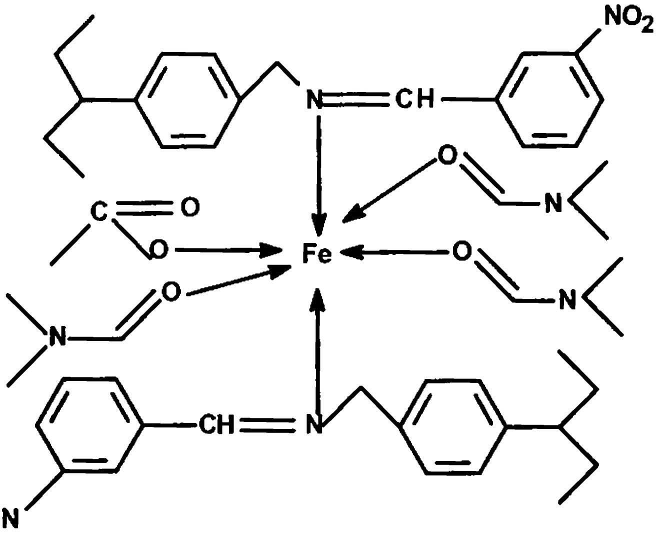


Fig.32: [Mn(PSNB)$_2$OAc.3DMF]

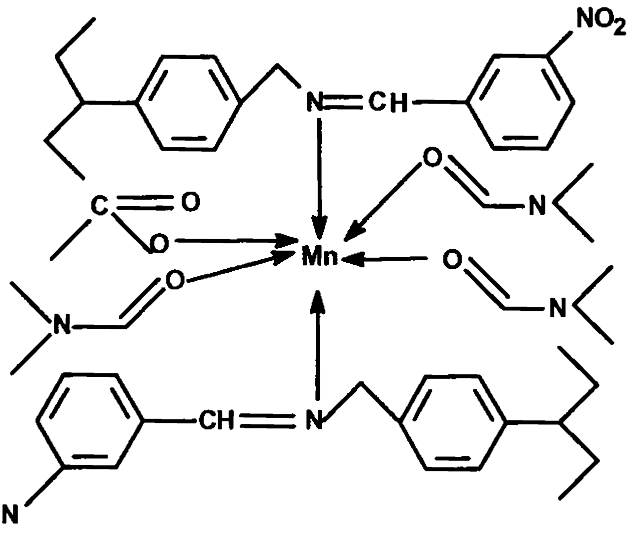
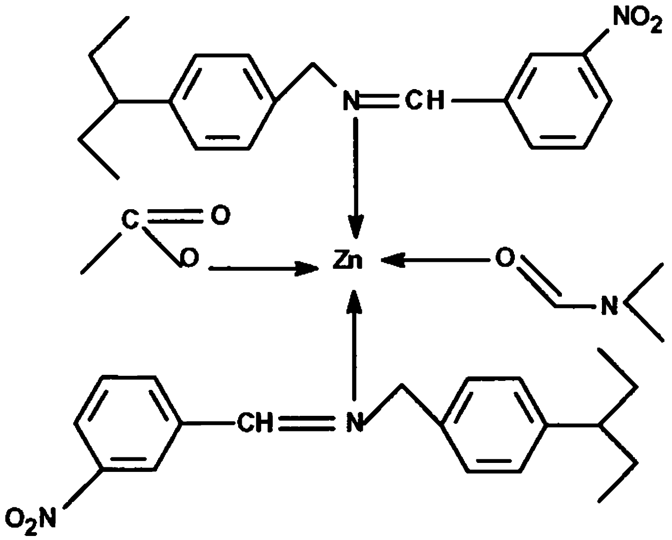


Fig.33: [Zn(PSNB)$_2$OAc. DMF]



CHAPTER

4

METAL ION REMOVAL WITH POLYMER SUPPORTS

Contents

4.1 Introduction

Water purification and waste water treatment have become the current topics of research as many industrial processes produce effluents loaded with heavy metal ions and other toxic materials . Removal of metal ions from industrial wastes and from impure water are important for the recovery of metal ions and to prevent the contamination of the environment as many of the heavy metal ions are toxic. This is achieved mainly by solvent extraction, ion exchange methods, solid extraction, floatation methods, bio-sorbents and by biological methods. Solvent extraction is an efficient method for the quantitative removal of ions by employing neutral chelates, with ion association complexes and by synergistic extraction methods. But this is not often advisable as pure water cannot be prepared by this method and the method is more expensive.

Various ion exchange resins containing active functional groups are extensively used for the separation of metal ions from effluents and from impure water. These resins are highly selective and even traces of metal ions can be removed in the presence of sodium and potassium. Polystyrene cross linked with divinyl benzene is widely used for the preparation of ion exchange resins. Macro porous and macro reticular resins have extended its applicability.

It was found that N-[hydroxy methyl] thio amide resins are found to be very effective as stationary phases in ion-exchange chromatography for metal ion separation[69]. A cation exchange resin of Cu(II) was found to be a useful activator in the reduction of ketones [70]. Fujiwara et al have studied the adsorption behaviour of noble metals on the ion exchange resin with quaternary phosphonium chloride[71]. Van Berkel et al found that the rapid uptake of Cu(II) is possible with bis[benzimidazole] modified oxirane and thiirane resins [72]. They also found that the selectivity of Cu(II) is enhanced by resins based on bis[benzimidazole] modified glycidyl methacrylate polymers [73]. Ion exchange resins containing amino phosphonate functional groups are found to be very effective for the selective sorption of heavy metals [74]. A novel ion exchange resin based on poly [glycidyl methacrylate co-ethylene dimethacrylate] beads modified with aspartic acid derivatives are found to be highly selective for Cu(II) [75]. A new ion exchange resin derived from 8-hydroxy quinoline is developed for the selective elution of metal ions [76].

Solid phase extraction is also found to be effective for the separation of metal ions from water. The study of Cu(II) ion complexing resin columns by solid phase extraction was carried out by Pesvento etal [77]. Ion floatation is a new technique employed for the separation heavy metal ions. Competitive floatation of Cd(II) and Zn(II) occur from very dilute aqueous by proton ionizable lariat ethers in the presence of foaming agents[88]. Recent investigations revealed that many biological systems can also be used for the separation of heavy metal ions. Quinaldic acid supported on polystyrene is found to be very effective for the selective removal of Al^{3+} from aqueous solution [89]. DNA encapsulated poly ether sulfone hollow micro spheres are very effective for the removal of heavy metal ions[90]such as Ag^+, Cu^{2+},and Zn^{2+} . A new chitosan biosorbent, prepared by coating chitosan on to ceramic alumina, is found to have greater absorption capacities for hexavalent chromium [91].A super fast sorbent based on textile grade poly acrylonitrile fiber is employed for the rapid removal of uranium from mildly acidic aqueous solution of low concentration [92].

Recently, polymer anchored ligands have been increasingly used for the selective removal of metal ions, as polymer supported ligands shows great affinity towards metal ions and they are able to form polymeric complexes. Polymer supported sulphonated catechol and linear catechol amide ligands are found to be very efficient ligands for the selective[93] metal ion removal and recovery from aqueous solutions as a function of pH. Cross linked polyacryl amide hydrogels having different functional groups were prepared from ethylene diammine and diethylene triammine. They were used[94] for the removal of Cu(II), Cd(II) and Pb(II). A new polymer supported vanillin schiff base prepared from amino methylated polystyrene has been developed as an efficient complexing agent for the removal of Ni(II) from aqueous solution[95].

As heavy metal ions, even in trace quantities, is hazardous to all living organisms it is essential to remove these ions from water in our environment. Among the various current technologies the application of polymer supports for metal ion removal has emerged as a promising method.

In this investigation, the ligands p-hydroxy benzaldehyde schiff base and p-dimethyl amino benzaldehyde schiff base have been found to be very effective for the separation of Cu(II) and Fe(III) ions respectively from effluents and industrial wastes. These ligands are also found be very selective in chelation.

The experimental studies carried out for developing optimum conditions for the separation of heavy metal ions and the interferences due to other ions are discussed in this chapter

4.2. Experimental

The procedure adopted for metal ion removal studies are presented in Chapter II.

4.3. Results and Discussion

4.3.1. Removal of Cu^{2+} using p-hydroxy benzaldehyde schiff base of amino methylated polystyrene

4.3.1.1.Effect of metal ion concentration

The results obtained from the study of the effect of metal ion concentration are presented in Table 16. The optimum metal ion concentration that can be removed by a definite amount of ligand (0.01g) was studied using metal ion solutions of varying concentrations (10ppm-60ppm) .The results show that the optimum metal ion removal of 96 % is achieved up to a concentration of 30ppm and thereafter it decreases.

4.3.1.2.Effect of ligand concentration

These results of the study of ligand concentration are presented in Table 17. The spectrophotometric analysis of metal ion solution (30ppm) was carried out after comlexation with varying amounts of the ligand (0.003g-0.03g). It was observed that the minimum amount of ligand required for the removal of a maximum of 96% of metal ion is 0.01g.

4.3.1.3.Effect of time

The effect of time on metal ion removal was studied and the results are presented in Table 18. A standard solution of the metal ion (30ppm) was refluxed with a definite mass of the ligand (0.01g) at varying time intervals. The optimum time required was found to be 10 minutes.

4.3.1.4. Effect of pH

The effect of pH was studied and the results are presented in Table 19 and in Fig.34. Metal ion removal study was carried out with standard solutions of the metal ion (30ppm) at varying pH using buffer solutions. The most favourable pH was found to be in the range 4.58-6.04

4.3.1.5.Interference studies

The results of interference studies are presented in Table 20. The interference of other cations and anions in the removal of Cu^{2+} was studied by adding varying amounts of these ions to a solution of Cu^{2+} ion of definite strength (30ppm) and it was refluxed with a fixed mass of the ligand (0.01g). It was found that the interference by the ions such as Fe^{3+}, Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Na^{+}, K^{+}, NH_4^{+}, Ca^{2+}, SO_4^{2-}, Cl^{-}, $NO_3^{-}$and CH_3COO^{-} is negligible.

4.3.2 Removal of Fe(III) using p-dimethyl amino benzaldehyde schiff base of amino methylated polystyrene

4.3.2.1 Effect of metal ion concentration

The effect of metal ion concentration was studied and the results are presented in Table 21. Inorder to develop optimum conditions for metal ion removal, a definite mass of the ligand (0.01g) was refluxed with varying concentrations of ferric ion solutions (10-60ppm). It was found that the percentage of metal ion removal reaches the maximum of 92% when the metal ion concentration is 30ppm and then it decreases.

4.3.2.2. Effect of ligand concentration

The results of the effect of ligand concentration study are presented in Table 22.Varying amounts of ligand (0.001g-0.03g) were refluxed with metal ion solution of a definite concentration (30ppm) for 20 minutes and the percentage of metal ion removal was determined spectrophotometrically. It was found that only 0.01g of the ligand is needed for the removal of a 30ppm metal ion from solution.

4.3.2.3. Effect of time

The effect of time on metal ion removal was studied and the results are presented in Table 23. A definite mass of the ligand (0.01g) was refluxed with a standard solution of the metal ion (30ppm) at varying time intervals to study the effect of time. It was found that the optimum time required was 15 minutes.

4.3.2.4. Effect of pH

The effect of pH was observed and the results are presented in Table 24 and in Fig.35. A standard solution of the metal ion (30ppm) was refluxed with definite mass of the ligand (0.01g) at varying pH using buffer solutions. It was found that maximum amount of metal ion was removed in the pH range of 3.72-4.70.

4.3.2.5. Interference studies

The analytical data obtained from interference studies is presented in Table 25.The interference due to other ions have been studied by adding varying amounts of ions such as Cu^{2+}, Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Na^{+}, K^{+}, NH_4^{+}, Ca^{2+}, SO_4^{2-}, Cl^{-}, NO_3^{-} and CH_3COO^{-} to a standard solution(30ppm) of Fe(III) and it was refluxed with a definite mass of ligand (0.01g).The results show that these ions had not interfered in the complexation of Fe(III) with p-dimethyl amino benzaldehyde schiff base of amino methylated polystyrene.

4.3.2.6. Conclusion

Metal ion removal studies of two polystyrene supported schiff bases have been conducted .It was found that the removal of Cu(II) was very fast with p-hydroxy benzaldehyde schiff base of amino methylated polystyrene and 96% of Cu(II) was removed. A 30ppm of metal ion solution required only 0.01 g of the ligand. These studies show the selectivity of the ligand to Cu(II).

Fe (III) was removed by p-dimethyl amino benzaldehyde schiff base of amino methylated poly styrene. 92% of the metal ion was removed by 0.01g of the ligand from a 30ppm solution of the metal. The advantage of the method is that the complexation of both these metal ions are uninhibited by other ions.

Tables and Figures

Results Of Metal Ion Removal Studies

(I) Removal of Cu(II) ion using p-hydroxy benzaldehyde schiff base of amino methylated poly styrene

Table 16: Effect of metal ion concentration

Mass of ligand =0.01g Time = 15min.

Cu(II) taken ppm	10	20	30	40	50	60
Cu(II) concn. after complexation (ppm)	0.9	1.5	1.2	11.1	22	32.4
Percentage removal	91	92.5	96	72.25	56	46

Table 17: Effect of ligand concentration

Cu(II) ion concentration = 30 ppm Time = 15 min.

Mass of ligand(g)	0.003	0.005	0.0075	0.01	0.02	0.03
Cu(II) concn. (after complexation ppm)	6	3.3	2.4	1.2	1.2	1.2
Percentage removal	80	89	92	96	96	96

Table 18: Effect of time

Cu (II) taken =30 ppm Mass of ligand =0.01g

Time(min)	5	10	15	20	25
Cu(II) concn. after complexation (ppm)	7.5	1.2	1.2	1.2	1.2
Percentage removal	75	96	96	96	96

Table 19 : Effect of pH

Cu(II) taken =30 ppm Mass of ligand =0.01g Time =15 min.

pH	1.5	2	3.48	4.58	5.7	6.04	7
Cu(II) concn. After complexation ppm	1.7	10.5	8.1	1.2	1.2	1.2	5.7
Percentage removal	61	65	73	96	96	96	81

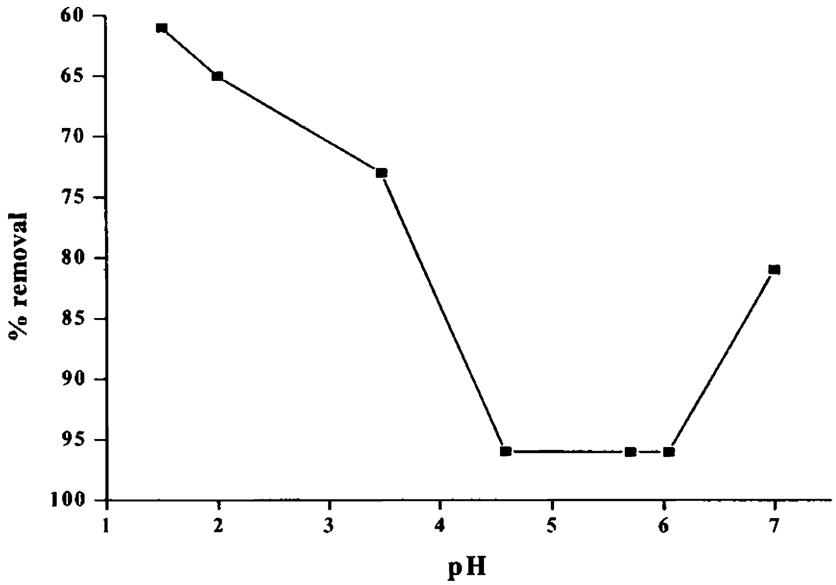
Table 20: Interference by other ions

Cu(II) taken =30 ppm   Mass of ligand =0.01 g   Time = 15 min.

Concentration of other ions = 10 ppm -50 ppm

Foreign ion taken	Cu(II) concentration after complexation (ppm)	Percentage removal
Fe(III)	1.2	96
Fe(II)	1.2	96
Mn(II)	1.2	96
Co(II)	1.2	96
Ni(II)	1.2	96
NH_4^+	1.2	96
Na^+	1.2	96
K^+	1.2	96
Ca^{2+}	1.2	96
SO_4^{--}	1.2	96
NO_3^-	1.2	96
Cl^-	1.2	96
CH_3COO^-	1.2	96

Fig. 34.



(2) Removal of Fe(III) ion using p-dimethyl amino benzaldehyde schiff base of amino methylated polystyrene

Table 21: Effect of metal ion concentration

Mass of ligand =0.01g Time = 15min.

Fe(III) taken ppm	10	20	30	40	50	60
Fe(III) Concentration after complexation ppm	1.5	2.6	2.4	12.5	23.5	34
Percentage removal	85	87	92	68.75	53	43.4

Table 22: Effect of ligand concentration

Fe(III) ion concentration = 30 ppm Time = 15 min.

Mass of ligand(g)	0.003	0.005	0.0075	0.01	0.02	0.03
Fe(III) concentration after complexation ppm	6	3.3	3	2.4	2.4	2.4
Percentage removal	80	89	90	92	92	92

Table 23 : Effect of time

Fe(III) ion concentration = 30 ppm Mass of ligand = 0.01g

Time(min)	5	10	15	20	25
Fe(III) concentration after complexation ppm	7.5	4.8	2.4	2.4	2.4
Percentage removal	75	84	92	92	92

Table 24 : Effect of pH

Fe(III) taken =30 ppm Mass of ligand =0.01g Time =15 min.

pH	1.48	2.1	3.72	4.7	5.71	6.40
Fe(III) concn. after complexation ppm	10.8	5.7	2.4	2.4	4.8	6.9
Percentage removal	64	81	92	92	84	77

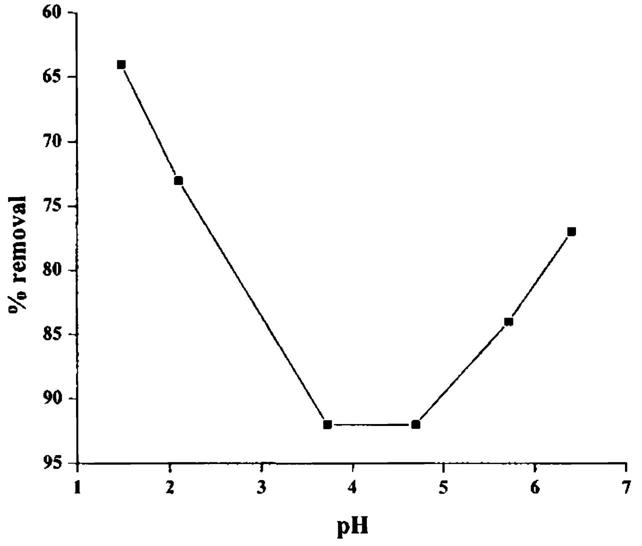
Table 25: Interference studies

Fe(III) taken = 30 ppm Mass of ligand = 0.01g

Concentration of other ions = 10ppm-50 ppm Time =15 min.

Foreign ion taken	Fe(III) concentration after complexation (ppm)	Percentage removal
Cu(II)	2.4	92
Fe(II)	2.4	92
Mn(II)	2.4	92
Co(II)	2.4	92
Ni(II)	2.4	92
NH_4^+	2.4	92
Na^+	2.4	92
K^+	2.4	92
Ca^{2+}	2.4	92
SO_4^{--}	2.4	92
NO_3^-	2.4	92
Cl^-	2.4	92
CH_3COO^-	2.4	92

Fig. 35.



CHAPTER

5

A NEW ION SELECTIVE POTENTIOMETRIC SENSOR BASED ON A POLYMERIC COMPLEX

Contents

5.1 Introduction

Ion selective electrodes [ISE] are highly versatile eletro-analytical tools developed for monitoring every aspects of our environment and our life. It provides a convenient and quick analytical procedure for the estimation of ions in solution which may be turbid , coloured or containing additives. ISEs have the unique advantages of short response time and lower detection limits. Studies of single ion transfer energetics and the kinetics at interfaces of insoluble, ionic crystalline, mobile and fixed site plasticized polymer and immiscible liquid-liquid electrolytes are some among the frontiers of electro-analytical research [96].

The discovery of response of thin glass membrane in 1906 was a land mark in the history of electrochemistry. ISE technology uses ion conductors as membranes. There is a built in site density of fixed or mobile hydrophobic ion sites which determines whether the membrane is perm selective. An electric field can facilitate the counter ion transport through the membrane by diffusion. High ionic mobility is not essential for potentiometric response.

James Ross and Martin Frant of Orion Research are the founding fathers of ISE. The calcium and fluoride ISEs they developed in 1960 were the big bang that revolutionized the world of electro analytical research. Tailor-made polymer membranes which allowed the transport of specific ions from among the ions of the same charge were prepared. These amazing discoveries led to the development of neutral and charged ionophores and ion selective electrodes. A robust membrane matrix based ionophore was found to produce good results. Polymers such as polystyrene, PVC, poly ethylene, poly amides, schiff bases, silicone rubber, cellulose acetate etc. are used for making perm selective membranes. The unique features of PVC makes it an excellent polymer matrix for ionophores.

The rapid development in potentiometry is due to the introduction of new ISEs .There has been a continuing interest in the preparation of molecular carriers possessing electrical neutrality, lipophilic character and capability to bind metal ions selectively and reversibly to induce a selective permeation of one metal ion through the membrane electrodes. In 1964 Moore and Berton observed that neutral macro cyclic antibiotics induce ion permeation in mitochondria, leading to the development of neutral carrier electrodes. A significant advancement in the field of ISE technology is the discovery of immobilizing a liquid membrane ion selective electrode into PVC to produce homogeneous and flexible films with good mechanical stability[12]. The cyclic antibiotic valinomycin supported on PVC is found to be an excellent ionophore for sensing K^+ in biological fluids. By this discovery ISEs have became one of the most important subjects in clinical and environmental chemistry[97].

Various other PVC supported carrier membranes which are selective to NO_3^-, Na^+,Li^+,NH_4^+,Ba^{2+},Mg^{2+}, Zn^{2+} and ClO_4^- ions with neutral and charged ionophores have been reported. Conducting polymer membranes are also employed for low activity potentiometric ion sensing[98].

A polystyrene based heterogeneous ion-exchange membrane of Ce(IV) phosphomolybdate has been developed as a Cu(II) ion selective electrode with Nernstian response and it shows selectivity over 15 other interfering ions[99].The selective potentiometric determination of cupric ion was carried out by the use of a molecular deposition film electrode based on water soluble copper phthalocyanine [100]. A macrocyclic diamide was used as a membrane active component in a Cu(II) selective electrode which was used as an indicator electrode in potentiometric titration with EDTA .The built in configurational rigidity induced by N-substituted amides present in the periphery of macro cycles invokes reorganization leading to ionophoric selectivity [101].

A Cu(II) selective membrane electrode based on naphthol derivative schiff base is found to have a very short response time of 5s having a wide range of concentration and it was directly applied to the potentiometric titration[102] of Cu^{2+}.A highly selective and sensitive Cu(II) membrane coated graphite electrode based on a Schiff base shows a low [103] detection limit of $3x10^{-8}$ M. Sensors have been prepared from inexpensive and disposable graphite electrodes produced by screen printing are then doped with Cu_2S to form useful, reproducible, fast and selective Cu^{2+} membranes[104].

Cu(II) selective membrane developed using 2,2'dithiodianiline is found to have Nernstian slope, of short response time of 10s and with no interference caused by [105] Pb^{2+},Cd^{2+} and Fe^{2+}.

Three different aza thioether containing 1,10 phenanthrolline sub unit as Cu(II) ion carrier is found to have good selectivity with respect to alkali metals, alkaline earth metals and other transition metal ions [106]. Another Cu(II) selective membrane based on 1, 3 dithiane ,2- (4-methoxy phenyl) shows selectivity over 15 other cations [107]. A novel Cu(II) membrane based on diphenyl isocyanate bis (acetyl acetone) ethylene diimine shows good selectivity and it used for the determination of Cu(II) in black tea ,in electro -platings and in waste water [108].

A Cu(II) complex of ethambutol, a synthetic diammine derivative having four co-ordinating sites, was used in the preparation of a Cu(II) selective membrane with a long life period of six months is used as an indicator electrode in the EDTA titrations as well as for the analysis of Cu^{2+} solutions[109]. A sol-gel electrode based on thiosemicarbazone is used for the detection of Cu(II) ion in solution[110]. A Cu(II) selective membrane using schiff base complexes derived from 2,3 diaminopyridine and o-vanilin have been prepared and it is found to have a detection limit of 0.3 ppm and good selectivity[111]. Another Cu(II) selective electrode based on salens as carriers exhibited good selectivity with respect to alkali metals, alkaline earth metals and some transition metal ions [112]. It was successfully applied for the determination of copper in sample of brass and in a sample of Wilson patient's urine. Highly selective and sensitive potentiometric sensors for Ni(II) and have been developed in our own laboratory [113,114]

Copper is one of the most widely distributed element in the environment in industrialized countries. It is also present in all organisms of land and sea. Although it is an essential element, it is toxic at higher concentration. So there is an urgent need for monitoring Cu^{2+} in various industrial, medicinal and environmental samples by preparing more selective, economical and simple ISEs .

As a part of the present investigation a potentiometric sensor has been developed for the determination of Cu(II). It is found to be selective with respect to alkali metal ions alkaline earth metal ions, to most other transition metal ions and to a number of anions. This membrane electrode has a short response time of 30s and a life of 2 months. Cu(II) complex of the p-dimethyl amino benzaldehyde schiff base of amino methylated polystyrene has been used as the ionophore in the fabrication of this sensor.

5.2 Experimental

The method of preparation of the sensor electrode is discussed in chapter II. The response behaviour of the sensor was studied using hydrated copper sulphate solutions of varying concentrations [1×10^{-1} to 5×10^{-6}] and the potential was measured. The effect of pH was studied by measuring the potential at varying pH (1.5 to 7).The interference due to other ions were studied by measuring the electrode potential of the solution containing (10^{-2}M) hydrated copper sulphate with varying concentrations of other ions such as Zn^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+}, Co^{2+}, Na^{+}, K^{+}, NH_4^{+}, Ca^{2+}, SO_4^{2-}, Cl^{-}, NO_3^{-} and CH_3COO^{-} . The developed electrode has been used for the determination of cupric ions

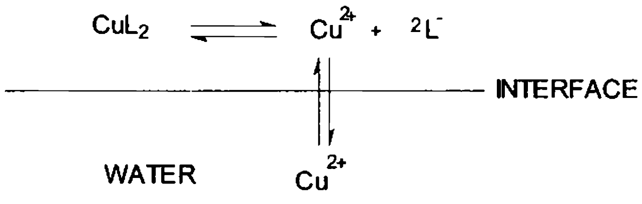
5.3. Results and Discussion

5.3.1. Response behaviour of the electrode

The Cu(II) ion selective electrode is coupled with a calomel electrode to form the cell,

Ion selective electrode / Test solution // Saturated calomel electrode

When the electrode is placed in the test solution and coupled with the calomel electrode, the potentials developed within a short response time of 30s show a linear change for Cu^{2+} solutions having concentrations in the range $5x10^{-6}$ mol dm^{-3} to $1x10^{-1}$mol dm^{-3}. The slope of E vs – log $[Cu^{2+}]$ is 26.2 mV/ decade of Cu^{2+} which shows sub Nernstian nature of the electrode [Fig.36]. The sensor retained the linear slope for a month of continuous usage. It also showed reproducible potentials for a period of two months. The probable mechanism for the development of potential at the interface may be due to an exchange of Cu^{2+} ion between the sensor and the solution.



The developed sensor is used to measure potentials of Cu^{2+} solutions of different concentrations and the results obtained for concentrations (Table 27) shows that the electrode can be employed for the quantitative analysis of copper.

5.3.2 Effect of pH

The effect of pH was studied by measuring the potentials of Cu^{2+} solution (0.01 mol dm^{-3}) at varying pH, from 1.5 to 7. It was found that steady potentials were obtained in the pH range 2.72 to 5.36 .(Fig.37)

5.3.3 Interference studies

The effect of various other cations and anions on the response behaviour of the electrode was studied by calculating the selectivity coefficients using the Nikolski-Eisenman equation[114]. The selectivity of the electrode determines its applicability as an electrode for testing real samples. The selectivity coefficients can be calculated from the equation

$$K_{i,j}^{pot} = \frac{a_i}{(a_j)^{z_i/z_j}}[10^{\frac{(E_2-E_1)Fz_i}{2.303RT}-1}]$$

where a_i and a_j are activities of Cu^{2+} ion and the interfering ion, z_i and z_j are the charges carried by the Cu^{2+} ion and interfering ion respectively. The difference between potentials of solution containing the Cu^{2+} ion and interfering ion and of Cu^{2+} ion solution alone is ΔEMF. Electrode potentials were measured by mixing with varying concentrations of the interfering ion(0.1M & 0.2M) with a definite concentration of Cu^{2+} ion (0.01M).Interference studies were carried out with ions such as Zn^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+}, Co^{2+}, Na^+, K^+, NH_4^+, Ca^{2+}, SO_4^{2-}, Cl^-, NO_3^- and CH_3COO^- . The values obtained are presented in Table 26.The results obtained for selectivity coefficients indicate that the sensor is selective for Cu^{2+} ions. The electrode was also used to study the concentrations of various Cu^{2+} ion solution.

5.3.4. Conclusion

A Cu(II) sensor electrode is developed from polymer supported complex with the schiff base from p-dimethyl amino bezaldehyde and amino methylated polystyrene. This electrode is found to be highly selective to copper with a short response time of 30s and having a sub Nernstian slope of 26.2 mV/decade of Cu^{2+} ion. It shows a linear potential response in the concentration range $5x10^{-6}$ mol dm^{-3} to $1x10^{-1}$mol dm^{-3} and it shows reproducible electrode potentials in the pH range 2.72 to 5.36 . So it is advisable to use the electrode for the quantitative analysis of cupric ions even at very low concentrations.

Tables & Figures

Table 26 : Selectivity coefficients of interfering ions

Concentration of Cu^{2+} = 0.01 mol dm^{-3}

Interfering ion	Molar conc. of interfering ion (mol dm^{-3})	K_{ij}^{Pot}	Interfering ion	Molar conc. of interfering ion (mol dm^{-3})	K_{ij}^{Pot}
Zn^{2+}	0.1 0.2	3.32×10^{-2} 7.10×10^{-3}	NH_4^+	0.1 0.2	7.03×10^{-3} 1.91×10^{-3}
Ni^{2+}	0.1 0.2	2.72×10^{-2} 4.3×10^{-3}	Ca^{2+}	0.1 0.2	6.18×10^{-2} 1.62×10^{-3}
Fe^{2+}	0.1 0.2	2.23×10^{-2} 6.50×10^{-3}	SO_4^{2-}	0.1 0.2	3.75×10^{-3} 1.01×10^{-3}
Mn^{2+}	0.1 0.2	2.21×10^{-2} 5.30×10^{-3}	Cl^-	0.1 0.2	8.32×10^{-3} 2.08×10^{-3}
Co^{2+}	0.1 0.2	3.04×10^{-2} 8.12×10^{-3}	NO_3^-	0.1 0.2	7.10×10^{-3} 1.80×10^{-3}
Na^+	0.1 0.2	6.72×10^{-3} 1.70×10^{-3}	CH_3COO^-	0.1 0.2	6.80×10^{-3} 1.72×10^{-3}
K^+	0.1 0.2	8.50×10^{-3} 2.13×10^{-3}			

Table 27: Determination of concentration of Cupric ion

Cupric ion taken		E (mV)	Cupric ion found		Error (%)
$[Cu^{2+}]$	$-\log[Cu^{2+}]$		$-\log[Cu^{2+}]$	$[Cu^{2+}]$	
2×10^{-1}	0.6990	224	0.7000	1.995×10^{-1}	0.25
2×10^{-2}	1.6990	197	1.6960	2.014×10^{-2}	0.70
2×10^{-3}	2.6990	169	2.6934	2.026×10^{-3}	1.30
2×10^{-4}	3.6990	141	3.6950	2.018×10^{-4}	0.90
2×10^{-5}	4.6990	112	4.7075	1.975×10^{-5}	1.25

Calibration graph

Fig.36

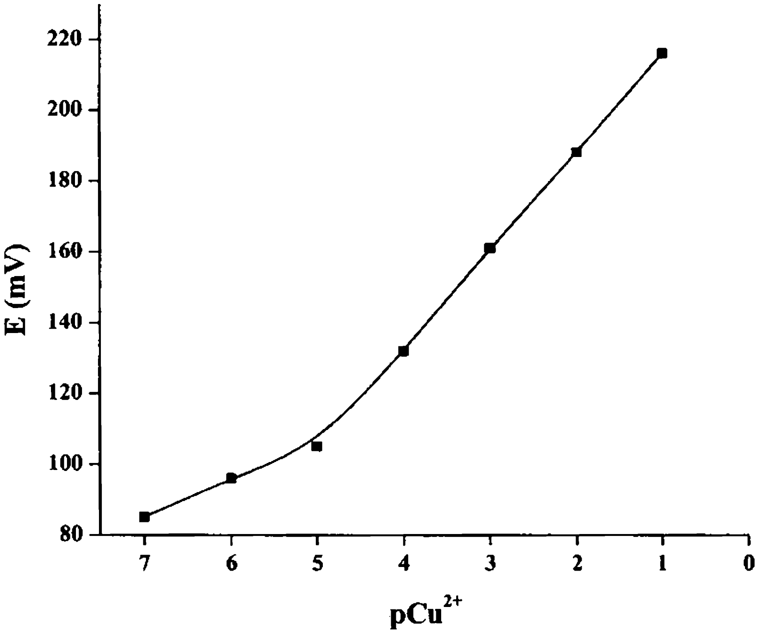
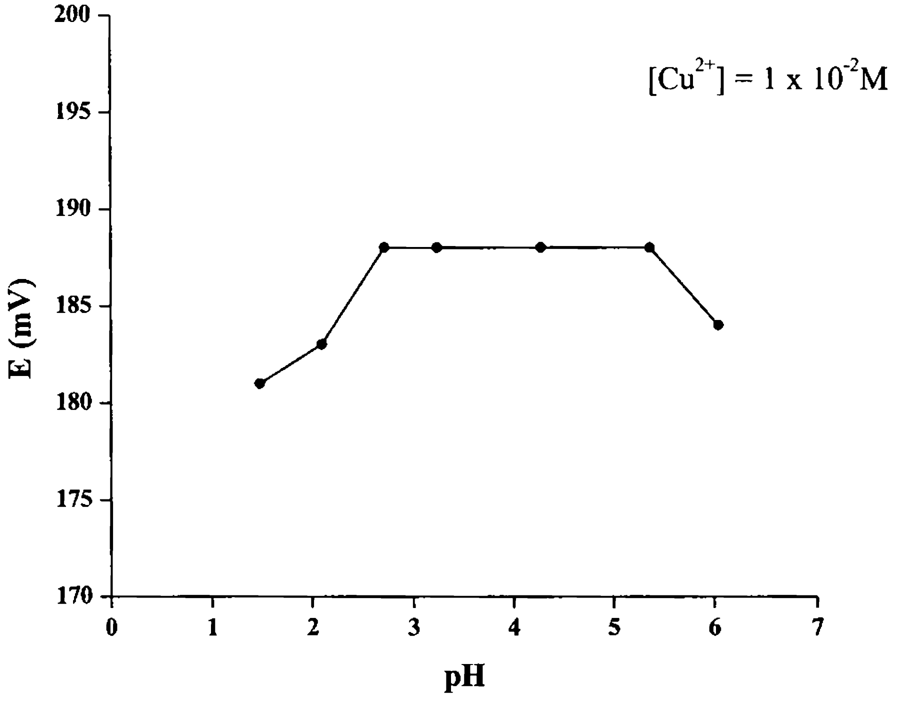


Fig.37



CHAPTER

6

SUMMARY

Summary

Polymer supports and polymeric complexes are highly versatile and they are successfully employed as efficient reagents, substrates and catalysts. Recently there observed a growing interest in the synthesis of tailor-made polymer supports and functionalized polymers for the preparation of metal complexes for various applications. They have the combination of properties due to the macromolecular structure as well as due to the reactivity of the functional group. An interesting feature of functional polymers is their affinity towards metal ions. Therefore the synthesis, characterization and application of such polymeric complexes have great scientific and analytical importance.

In this investigation three series of polymeric complexes of transition metal ions are prepared from three schiff bases. All the complexes and polymeric schiff bases were characterized by analytical, spectral and thermal methods.

The polymeric schiff bases, p-hydroxy benzaldehyde schiff base of amino methylated polystyrene and p-dimethyl amino benzaldehyde schiff base of amino methylated polystyrene, are found to be excellent chelating agents for the removal of Cu^{2+} and Fe^{3+} ions respectively. Moreover the Cu(II) complex of p-dimethyl amino benzaldehyde schiff base of amino methylated polystyrene has been developed as an efficient sensor electrode which shows high selectivity for Cu^{2+} ions.

The thesis consist of six chapters. The first chapter contains an introduction and a brief review on application of polymer supports, polymer supported ligands and complexes. The second chapter gives the details of reagents and instruments used and the procedure adopted for the preparation of ligands and complexes. The third chapter explains the methods employed for characterization and the results are also discussed. The fourth chapter gives a detailed study of metal ion removal using ligands whereas the fifth chapter describes the development of the Cu^{2+} ion sensor electrode. The sixth chapter is the summary of the thesis and references are presented at the end.

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