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Review Article

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Co-ordination Polymers of Schiff Bases and Their Applications: A Review

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Abstract

The condensation of primary amines with carbonyl compounds was first reported by Schiff and condensation products often referred as Schiff bases. These bases have general structure RC=NR' where R and R' are alkyl, cyclohexyl, aryl or heterocyclic radicals which may be differently substituted. Schiff bases are also known as anils, imines or azomethines. Various studies have shown that >C=N- group has considerable biological importance. The presence of lone pair of electrons in a sp^2 hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance.

Keywords: Schiff bases, Poly-Schiff bases, Co-ordination Polymers, Applications

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1. Introduction

The condensation product of primary amines with carbonyl compounds was first reported by Schiff and these condensation products often referred as Schiff bases. Because of easiness of preparation, synthetic flexibility and special property of >C=N- group, Schiff bases are excellent chelating agents especially when functional group like –OH, -SH is present close to azomethine group so as to form a five or six membered ring with metal ion[1,2]. Metal complexes of Schiff bases have considerable interest and as such they have occupied a central role in the development of coordination chemistry of metal chelate systems. This situation is manifested by large number of publications ranging from purely synthetic to modern physico-chemical relevant studies of these complexes [3, 4]. As stated, these complexes have been known since 1864, Schiff in 1869 isolated the corresponding phenyl and aryl derivatives and established the 1:2 metal:ligand stoichiometry[5], where he discovered the exceedingly important synthetic technique of preparing salicylaldiamine complexes by performing reaction of metal with salicylaldehyde and primary amines. Subsequently, Schiff and then Delepine prepared several such complexes [6, 7].

Poly-Schiff bases in Coordination Chemistry:

The polymer containing –C=N- group as replacing unit of polymeric chain are known as polyazines, azomethine polymers or poly-Schiff bases. Research interest in polyazomethines continues owing to their different characteristic such as chelating properties, thermal stability, liquid crystal properties as well as intrinsic conductivity. The rapidly expanding field of coordination polymers and polychelates of polymeric ligands are attracting the attention of chemists and underwent spectacular growth during last few years. Recently so called poly-Schiff bases and their complexes with metal cations have been extensively investigated [8-10]. One of the interesting outcomes of this investigation may be synthesis of several polymeric Schiff bases [11-13].

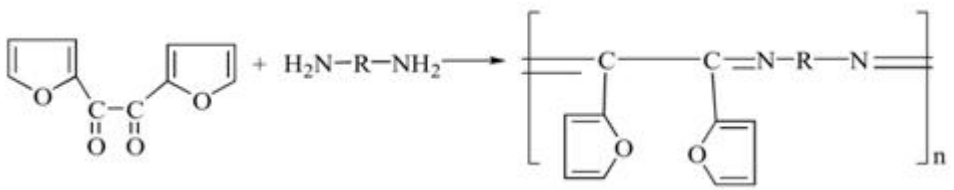
Transition metal chelates derived from poly-Schiff bases have also played an important role in the development of coordination chemistry of polychelates [14,15]. Among the metal chelates derived from the poly-Schiff bases occupied a central role in the development of coordination chemistry. Polychelates derived from bis-bidentate ligands have been also received much attention in recent years due to their semiconducting, catalytic and biological properties [16].

Polymeric metal complexes have attracted most researcher's interest, because they not only exhibit the properties of polymers, but also possesses properties of inorganic and organic small molecule metal complexes, such as thermal stability, process ability and early film forming capability [17]. The metal atoms attached to polymer backbone are bound to exhibit characteristic catalytic behavior, which are distinctly different from their low molecular weight analogue.

2. Co-ordination Polymers

When coordination polymer is used as a general term, it covers a wide group of compounds including polynuclear complexes and polymerical metal salts. The term coordination polymer includes a variety of substances and in general can be defined as a macromolecular entity involving a metallic element which form an integral part of the back bone. The synthesis of coordination polymers usually achieved by one of the following ways : i) a metal complex may yield a polymeric material during its formation due to favorable donor groups in the ligand ii) ligand itself be a preformed organic polymer to which a metal ion suitably be coordinated and iii) a metal ion may be coordinated with ligand and monomeric metal complex reacted with another organic compound to form polymeric complex. Casually, these polymers can be divided into two categories, (a) a pair of donor groups and (b) two pairs of donor groups. Coordination polymers of type (b) are of great interest both from applied as well as academic point of view and are often termed as chelate polymers. The possibilities for wide choice, both of the metal ion and the ligand, makes this area particularly fascinating for the preparation of polymeric materials. Systematic investigations on the preparation of pure polymeric chelating reagents and important physicochemical properties such as polyelectrolytic behavior, structure and stability of transition metal ion in polychelates are reported by many workers. [17, 18-21].

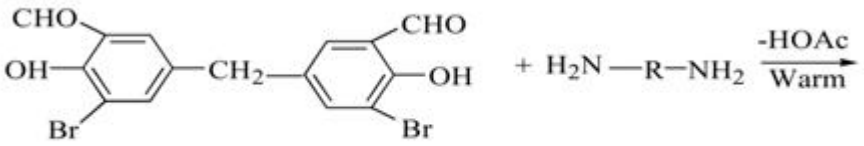
Polymeric complexes obtained by condensation of pyridinedialdehyde and ethylenediamine were reported by Lions *et. al.*[22].Bailar and co-workers [23,24], used triethylene tetraamine-*5,5'*-methylene bis-salicylaldehyde and *bis*-(2-pyridinal)biphenylene-4,4'diamine as ligand to obtain coordination polymers with Cu(II), Ni(II), Co(II), Fe(II), Cr(II).Savich *et. al.*[25] reported Schiff base polymers derived from 3,3'-methylene *bis*-(5-bromosalcylaldehyde) or 5-chlorosalcylaldehyde with *o/p*phenylenediamines. Some linear polymers prepared from Schiff bases derived from methylene or sulphonyl-bis-salicylaldehyde and ortho-diamines have been reported in the literature [26,27]. Polymers obtained from poly Schiff bases with semiconducting properties also been reported by Davydov and co-workers [28].Karampurwala [29] synthesized polymeric complexes from the poly Schiff base derived from5,5'-methylenebis salicylaldehyde and aniline. Poly Schiff base derived from polymeric complexes of furil and diamine were studied by Patel *et. al.*[30]. Diamines used were 4,4'-diaminodiphenylmethane, *o*-toludene, *o*-dianisidene, *m*-phenylenediamine, 1,6-hexamethyldiamine (I).



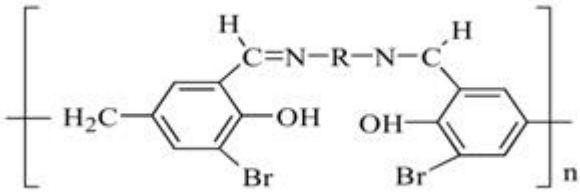
I

R= 4,4'diaminodiphenylmethane,*o*-toludene,*o*-dianisidene,*m*-phenylenediamine, 1,6 hexamethyldiamine

Patel and Jani synthesized poly Schiff bases derived from 4,4'-dihydroxy diacetyl biphenyl and 4,4'-diaminodiphenyl methane and their polymeric complexes with bivalent metal ions having general formula $(ML)_n$[31]. Patel *et. al.*[32] prepared poly Schiff bases by condensing 5,5'-methylene*bis*-(*3*-bromosalicylaldehyde) and hexane 1,6-diamine polymeric complexes with bivalent metal ions were studied.

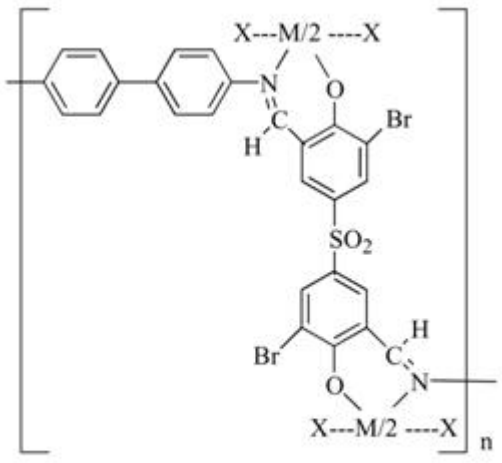


5,5| - methylene bis- (3-bromosalicylaldehyde) & hexane 1,6 diamine



II

Polymeric Schiff bases of 5,5'-methylene bis-(3-nitrosalicylaldehyde) with diamines 1,3-diaminopropane, 1,4-diaminobutane, benzidine and *o*-toludene (II) are also reported by Patel *et. al*[33]. Polychelates of transitions metal ions with Schiff base derived from bis (bromosalicylaldehyde) sulphone and benzidine (III) have been synthesized and their electrical, thermal, magnetic and spectral properties were reported by Patel and co-workers [34]. Patel have [35] prepared polychelates of oxovanadium(IV) and dioxouranium(VI) with 2,4–dihydroxybenzaldehyde oxime-formaldehyde polymer. Elemental analysis indicates 1:2 metal: ligand stoichiometry. Patel et al [36] synthesized a series of new cation exchanges based on the monomer, *d*-(3-hydroxy-4-acetyl phenyl) maleimide by addition polymerization. Their chelating properties towards metal ions have been studied.

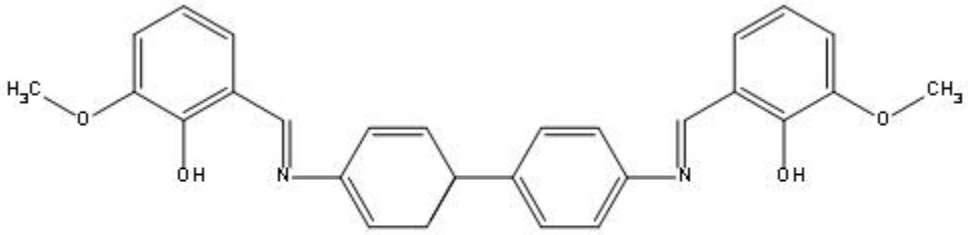


bis- (bromosalicylaldehyde) sulphone & benzidine

III

Coordination polymers synthesized from the poly Schiff base derived from methylene bis-salicylaldehyde and diaminodiphenyl ether (DPE) were studied by Patel *et. al.* [37]. Metal chelates of some bioactive Schiff bases were reported by Mishra and co-workers [38]. Karampurwala and co-workers[39] reported polychelates of bis–semicarbazone of 5,5'-methylene *bis*-salicylaldehyde with VO(II), Mn(II), Cr(III), Fe(III) and Zn(II). Raj [40] prepared coordination polymers based on the mixed *bis*-ligand 5(3-acetyl-4-hydroxy-1-phenylazo)-8-quinolinol with Zn(II), Cu(II), Ni(II), Co(II) and Mn(II). The ligand derived from 4,4'-diaminodiphenylmethane and its substituted derivatives and salicylaldehyde in which one of the coordinating groups i.e. phenolic oxygen and one azomethine

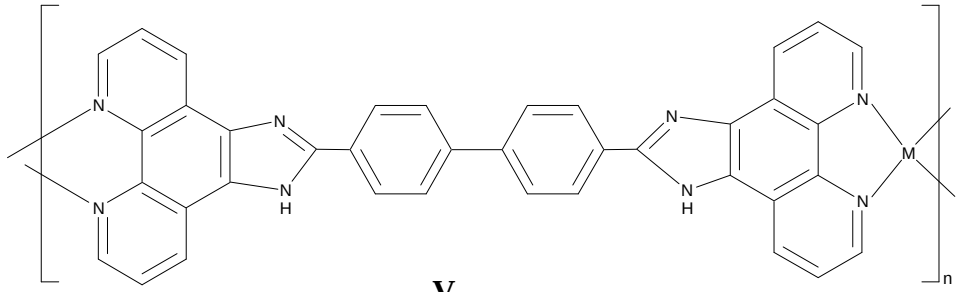
nitrogen are coordinated to uranium atom while other coordinating groups are coordinated to other one. Maurya and co-workers prepared Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Sm(II) and UO_2(VI)polymeric complexes of dibasic tetradentate bis(*o*-vaniline) benzidine (IV)[41].



IV

Bis(*o*-vanillin)benzidine

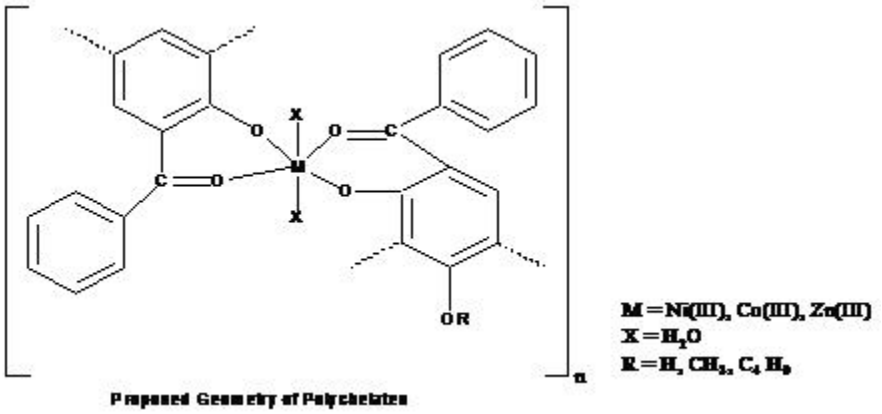
Yan He and co-workers [42] synthesized Cu(II), Zn(II) polymeric complexes from 4,4*'-bis*(1,10-phenonthroline-[5,6-d]imidazole-2-yl)-biphenyl (BPIBP)(V) and systematically investigated photo luminescent properties.



V **20**

4,4'-bis(1,10-phenonthroline-[5,6-d]imidazole-2-yl)biphenyl (BPIBP)

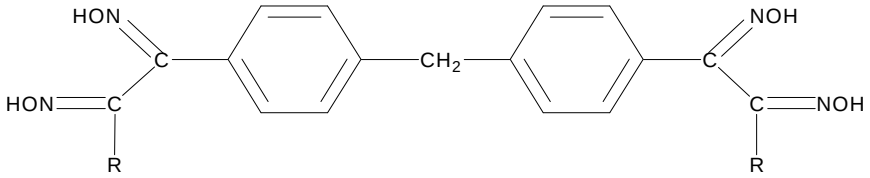
Joshi, *et. al.*[43] synthesized polychelates of benzophenone formaldehyde and benzophenone- diol resins (VI) with Cu(II), Ni(II), Co(II) and Zn(II) metal ions. It is found that the phenolic–OHand >C=O groups of different polymeric chains forms coordinated covalent bonds with metal ions to give polychelates. All are having octahedral geometry exceptCu(II) polychelate, which had square planar geometry.



VI

Kalliyappan *et. al.*[44] have synthesized polychelates of poly(2-hydroxy-4- methacryloyloxy benzophenone) with transition metal ions and studied their thermal, catalytic and magnetic properties. X-ray diffraction study shows that ligands are amorphous in nature whereas polychelates are crystalline in nature. Substituted bis-(amionophenylgly oxime) methanes and their polymeric complexes with Cu(II), Ni(II) and Co(II) salts (VII) are reported by Karipcin

and Karatas. Structures of these complexes were identified with the help of IR, ^{1}H-NMR spectral data, elemental analyses and magnetic measurements [45].

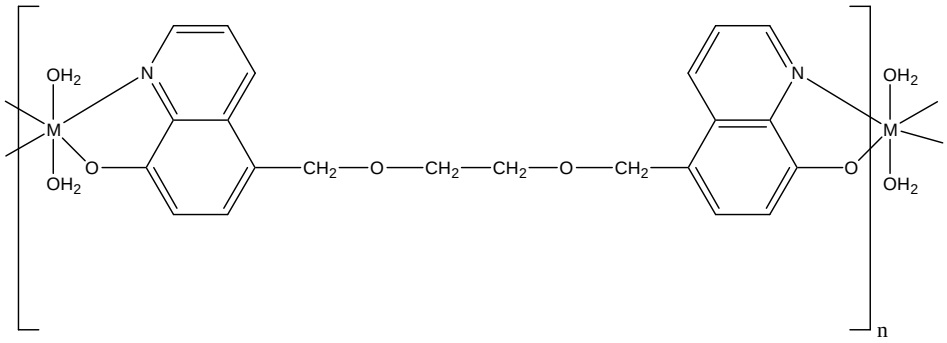


R=Benzylamino,Phenylamino,4-Acetylphenylamino,4-Methylphenylamino

VII **e - 22**

Bis(aminophenyl glyoxime)methane

Coordination polymers of 1,6-*bis*(8-hydroxyquinoline-5-yl)-2,5- dioxohexane (VIII) were prepared with metal ions Zn(II), Cu(II), Ni(II), Co(II) and Mn(II) by Shah *et. al.* The thermal stability and number- average molecular weights (M_n) of these coordination polymers were determine by TGA and non-aqueous conductometric techniques [46].

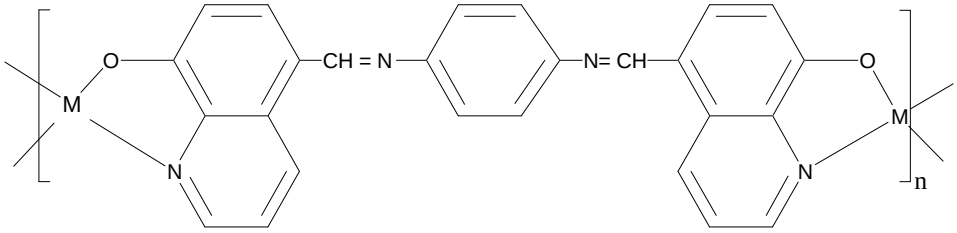


M=Cu,Ni,Co,Mn and Zn

VIII **e - 23**

1,6-bis(8-hydroxyquinoline-5-yl)-2,5-dioxohexane

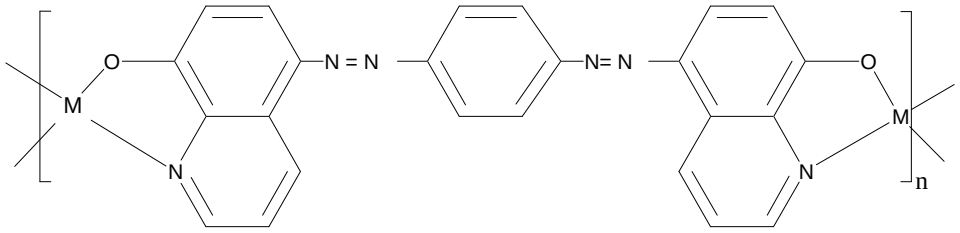
Bis (biuret) polymeric complexes (VIII) of some transition metal were studied by Munshi *et. al.* [47] A detailed thermal study of polymeric chelates were carried out to ascertain their thermal stability. Poddar and Saha [48] prepared polymeric complexes of transition metals with Schiff bases derived from 5-formyloxime and *p*-phenyl enediamine (IX).



IX 07

5-FORMYL OXINE-PHENYLENEDIAMINE

Banerjie and Day [49] reported polymers derived from *8*-quinolinol and tetra ammonium chlorides of *p*-phenylene diamine, benzidine and *o*-dianisidine. Mn(II), Fe(II), Zn(II), Cd(II), Ni(II), Co(II), and Cu(II) forms coordination polymers with quadrifunctional dyes (X-XII).



X - 08

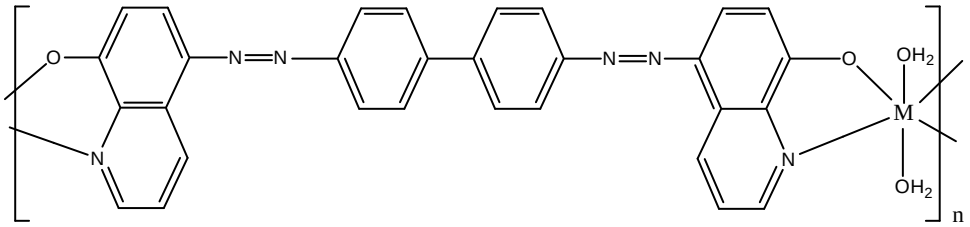
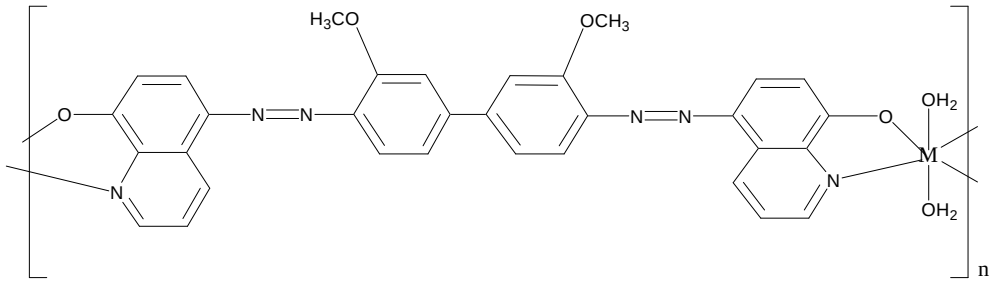


Figure - 09

XI

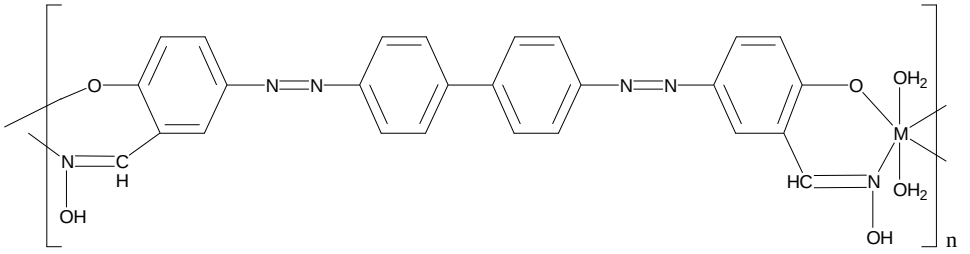


XII

e -10

QUINOLINOL SCHIFF BASES

These polymeric complexes were prepared by refluxing equimolar solution of ligand with metal acetate in DMSO. All these dark brown complexes were amorphous in nature and insoluble in all common organic solvents. 5,5'-(benzidinebiazo) salicyladoxime (XIII) have been also employed for the synthesis of coordination polymers of transition metals.

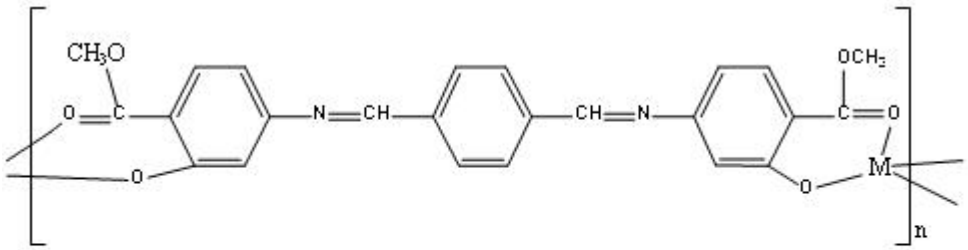


XIII

- 11

5,5'-(BENZIDINEBIAZO)SALICYLADOXIME

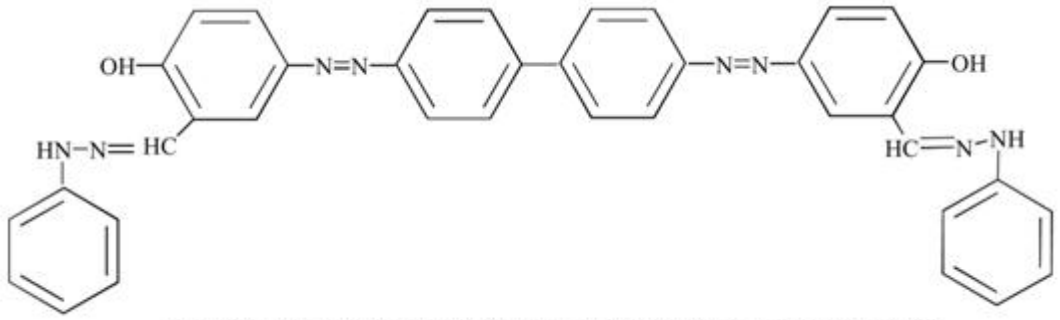
Pfeiffer and Pfitzner [50] were the first to study *bis*-(Schiff bases) as catenating ligands. They derived copper derivative of bis-(Schiff bases) from the diamines and salicylaldehyde having polymeric structure. Marcu and Dima [51] investigated the polyco-ordination of dimethyl-4,4'-[*p*-phenylenebis (methyl- idenenitrito)]disalicylate (XIV) with Co(II), Ni(II) and Cu(II) in DMF.



XIV

IMETHYL- 4,4'-[P-PHENYLENE- IS(ME HYLE ENENITRITO)]DISALICYLATE

Coordination polymers of Schiff bases derived from aromatic diamines, like *p*-phenylenediamine, benzidine, *o*-dianisidine and phenolic aldehyde like 2-hydroxy-1- naphthaldehyde are reported in literature. Ligand bridged polychelates of 4,4'-(4,4'-biphenylenebisazo)disalicyl- aldehyde phenylhydrazine (PH-B-PH) were studied by Jadeja *et. Al.*[52].



4,4'- (4,4'-bisphenylenebisazo)-disalycyladehyde phenylhydrazine (PH-B-PH)

XV

Aswar and Co-worker reported coordination polymers derived from polyschiff bases with transition and inner transition metal ion and studied their semiconducting behiour [53-58].

3. Applications of Coordination Polymers

Polychelates or metal chelates or coordination polymers synthesized from the Schiff bases has wide range of applications in various fields which are important from technology point of view. Recently many workers have reviewed the different applications of polymers [59-62]. Indeed, many synthetic polymer metal complexes have been found to possess high catalytic efficiency in addition to semiconducting, heat resistance and biomedical potentials.

Catalysts:

Coordination complexes are used as catalysts for diverse range of organic reactions. They are often used for polymerization reactions. In this respect platinum group metal complexes are dominating. Metal complexes are also used as hydrogenation catalysts particularly in enantioselective reactions. Enantioselective epoxidation using chiral Mn(III) has become a useful preparative method in organic synthesis [63]. The development of thermoplastics requires copolymerization of alkenes and carbon monoxide and the use of palladium complexes, with chelating bidentate phospene ligand is reported. Salen type ligands with *N* and *O* atoms are important since their metal complexes find wide spread application as homogeneous catalysts in variety of reaction such as olefin polymerization. [64,65]. Schiff base complexes with salen ligands are well known to activate molecular oxygen and catalyse the oxidation of electron rich substrates such as phenols[66-68], activated olefins[69], amines[70] and hydrazones[71]. Oxidations of various olefins have been carried out using Mn(III) complexes of Schiff bases derived from the condensation of salicylaldehyde and its derivatives with 1,3-diaminopropanol by Bhattacharya[72]. Ganeshpure *et.al.* [73] Reported the epoxidation of alkene with iodosylbenzene catalyzed by polymeric Schiff base chelates, in which metal ions, Mn(II), Cr(III) and Fe(III), were anchored on polymeric Schiff base backbone. The

catalytic activities of polymeric Schiff base chelates for the epoxidation of alkenes were compared using styrene and norboranes as substrates.

Molybdenum complexes have been used as catalysts for hydrodesulphonization and olefin epoxidation [74]. Catalytic activity of styrene-allylchloride copolymer supported Co(II) Schiff base complex compound was studied by Gupta *et.al.* [75]. Catalytic activity of coordination polymer for various oxidation and reduction reactions have been reported in number of reviews [76-78]. The porous nature of some coordination polymers and presence of catalytically active transition metal centre is seen selective catalytic application of such materials. Joshi *et. al.* have carried out synthesis of Biginelli three component one pot synthesis of 3,4-dihydropyrimidine-2(1H) ones and their derivatives with different aldehydes and β-keto esters using different metal polychelates [79].

Biological and Medicinal Field:

Coordination compound has large number of application in the field of medicine. Rosenberg [80, 81] successfully employed *cis*-platin as a anticancer drug. This leads to active research in platinum chemistry and for continuing research for the most effective anticancer drugs[82-85]. Coordination complexes are going to have increasing importance in recent year particularly in the design of repository, slow release or long acting drugs in nature and in the study of metabolism [86]. Schiff bases and their complexes have shown biological activities as carcinogenic and antitumor because of their specific structures [87]. They also possess various biological activities such as fungicidal and insecticidal [88]. The coordination chemistry of oxovanadium (IV) with multidentate ligand is important due to its growing applications [89,90] and therapeutics [91]. Vanadium in traces has multiple biological role, therapeutic value in small doses and toxic in excess. Vanadium containing compounds have their utility as insulin mimetic [92,93] and antimoebic agent [94]. The coordination chemistry of molybdenum follows discovery of Mo in number of enzymes such as aldehyde oxidase, sulphide oxidase, xanthine oxidase, nitrogenase etc.[95]. Antitumor activity of Cu(I)/(II) complexes have been reported[96, 97]. Lippard *et. al.*highlighted the importance of coordination chemistry in neuroscience[98]. Some chelates polymers are also reported to have in controlling the antitumor activity in symphocytic leukemia test system in mice.

Environmental Pollution

Coordination compounds plays important role in environmental chemistry for determination of pollutants by complexometric and spectrophotometric methods. Chelating polymeric ligands have more interest, due to their applications in bioinorganic industry, water purification and selective removal of waste material from nuclear plants[99-101], pollution control [102], selective removal of metal ion from the dilute solution [103-104], as protective coating on metal surface or coating on paper, fiber, fabrics and selective binding enzymes [105,106]. Juneja *et. al.* reported that coordination polymers as converters of solar energy and removal of SO_2 and NO_2 from the environment[107,108]. Polymeric Schiff bases from diaminobenzenethiol and glyoxal was synthesied and used to concentrate gold specifically and without interference from other metals, from water taken from the Gulf of Neples containing 1.4 μ_g gold/100 liters[109]. Thus the coordination compounds have a great role in the control of environmental pollution.

Dyes and Pigments:

As almost all transition metal complexes are coloured, this property of their metal chelates has been successfully used in dye and pigment industry. Polymers can be used as dyes. Many dyes react with wood silk and modified cellulose fibers[110]. This interesting subject, has been reviewed by Taber *et. al.*Reactive dyes comprises a chromophore and reactive group and owe their excellent wet fastness to formation of covalent bond with fiber. Reactive azodyes have commercial importance and have wide applicability[111]. Patel *et. al.* have reported fiber reactive dyes for viscouse rayon, wool and silk[112,113].Synthesis of *4,4'*-methylene *bis*-*o*-chloroaniline bases bisazo reactive dyes and their application are reported by Patel *et.al.* [114]. Dammert *et al*[115] also reported that 4,4'-*bis*[{(2-hydroxy-1-naphthyl) methylene}amino] biphenyl-3,3'-dicarboxylic acid and its calcium derivative can be used as red pigments for lacquers, plastic, latexes or spin dopes and fast to light colours and as solvents.

Semiconducting Materials:

The coordination polymers have gained much attention due to their semiconducting and catalytic properties [26]. The metal containing polymers were used as conductor and semiconductors. Polymerization reactions involving the formation of metal chelates of Schiff bases have been extensively studied. Polymeric Schiff bases are known for their good semiconducting properties [116]. Poly Schiff bases with semiconducting properties have been reported by Davydov and co-workers[117]. The presence of conjugation and heteroatom in the backbone chain of polymer are considered to be responsible for the semiconducting property. Polymeric complexes with system of conjugated >C=C< and >C=N- bonds possess semiconducting property. Coordination polymers are used as organometallic semiconductors. Coordination polymers find interesting application as semiconducting material. Review of their application is taken by many workers[118-126]. π conjugated polymers are of much important because of their interesting electrical, electrochemical and optical properties. Such a polymeric complex derived from poly (6,6'-diallkyl-2,2'-bipyridine-5,5'-diyl) was prepared by Yamamoto *et. al.*[127] and its optical and electrochemical properties were studied. Marcu and Dima [128] studied the polycondensation reaction of dimethyl 4,4'-[*p*-

phenylene-*bis*(methylidiene nitrito)]discilicylate with cobalt, nickel and copper ions and the coordination polymers obtained there from are heat stable, coloured and semiconducting materials.

Coating Materials:

Coordination polymers find many applications in coating industry in the form of paints, varnishes, lacquers, water base paints etc [129].

Agriculture:

Recently few Schiff base have been used as fungicides and herbicide and for other similar purposes [130]. Schiff base complexes of tin, lead, mercury etc. finds use as active reagents against the plant enemies. The mono(imido) Schiff base ligands and their complexes derived from the reaction of salycylaldehyde, *5*-bromosalicylaldehyde and *2*-hydroxy acetophenone with thiosemicarbazide shows antifungal properties[131]. Viel *et. al.* studied some Schiff base complexes which favour germination[132]. Fischer and co-workers [133] synthesized *p*-hydroxy acetophenone cyclohexylimine *N*-methyl carbamate and used it in post emergent tests. It destroyed beet, corn, charlock to some extent.

Miscellaneous:

The potential application of coordination polymers are as detergents, lubricants, heat shields for artificial satellite and space ships, nose cones of missiles, construction material in aerospace industry and space vehicle, electrical insulators, semiconductors etc[134]. Fundamental research on the photo reaction in the microheterogeneous environment provided by the polymer has been reported [135]. Polymeric Schiff bases are very useful as detergents in lubricating oils [136]. Some polymeric Schiff bases found to have photo-conducting properties [137, 138]. Polymer having metal linkages in the backbone are of interest in the scientific and industrial area. They have various applications in material science including bio-chemical fields[139-150]. These polymers have a wide variety of products that lead different applications such as aqueous thickness, impregnants, textile sizers, adhesives, additives, resins, catalysts [151-155]. Structural studies of polymers supported compounds appears to be have useful application such as in organic synthesis[156], immobilization of enzymes[157], biological systems[158], dyes[159], analytical chemistry[160], catalysts[161], substrate carriers[162], protecting groups[163], and heavy metal uptake[164]. Chaofan Zhong *et. al.* [27] reported polymeric complexes of Cu(II) and Zn(II) and systematically investigated photo luminescent properties of these complexes for the first time. The polymeric complexes are considered to be promising materials for organic electroluminescent diodes (OLEPs). Here attempt is made to account some coordination polymers and their applications. This is an expanding field of study which provide much more information from application point of view in future.

4. Conclusion

Because of easiness of preparation, synthetic flexibility and special property of >C=N- group, Schiff bases are excellent chelating agents. The use of Poly-Schiff bases have also played an important role in the development of coordination chemistry of polychelates. Schiff bases attracting researchers due to their novel use in medicinal chemistry and agricultural chemistry. With the account some coordination polymers and their applications, this is an expanding field of study which provide much more information from application point of view in future.

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