
Introduction and Review

1.1 Introduction

Metal complexes with unusual structures are compounds of great current interest for, the property changes that are brought about by geometry modification are very interesting and of great practical importance.¹⁻⁴ The highly specific reactivities of metallo enzymes and other related bioinorganic molecules and the key reactions of several important metal based catalytic processes have been attributed to the existence of such uncommon entities.⁵ While the nature of metal ion and the coordination ability (Dq) of ligands determine the overall structure of metal complexes there are methods by which such conventional geometries can be modified.⁶⁻⁹ An often adopted strategy is by designing tailor-made multidentate ligands which by the very nature of their structural disposition could force the metal ion to adopt unusual geometries while forming their metal complexes.^{10,11} The presence of steric group also play a dominant role in this.¹²

The role of substituent groups in deciding the nature and course of chemical reactions of organic compounds is paramount. Examples abound to illustrate the cases where some groups activate on otherwise unreactive species while certain other groups make it more inert.^{1,13} What in essence the substituent groups do on the molecule is to bring about redistribution of electron density on the molecular frame work. The orbital energy levels get rearranged, and consequently, the redox characteristics get altered. The magnitude of the

effect, therefore, depends upon both the nature of substituent and the core molecule. In the realm of inorganic chemistry also one can find such parallels in the coordination compounds and organometallic species. Organic ligand moieties on coordinatively binding to metal ions get modified significantly in their electronic properties. It is on this electronic rearrangement of metal complexes, the geometric alteration and substituent modification mentioned above bring about additional tuning.

Schiff-base complexes

Metal complexes of Schiff-bases have been known for over one fifty years. In 1869 Schiff¹⁴ established 1:2 metal ligand stoichiometry in several copper Schiff-base complexes. But at present a large number of Schiff-base complexes of many metals with different ligand framework are known. This class of compounds have a significant role in the development of coordination chemistry.

Definition

Schiff-bases are those compounds containing azomethine group ($-RC=N$) and are often formed by the condensation of a primary amine and a reactive carbonyl compound. Most of this preparation is found to be very simple and can be prepared by mixing stoichiometric amount of primary amine and aldehyde in minimum volume of solvent. On gentle heating or refluxing the mixture there get the product Schiff-base. Schiff-base ligands are very effective in coordination with metal ions if they bears a functional group, usually OH, sufficiently near the site of condensation. Though Schiff-base complexes are numerous these complexes on a polymer support is not studied extensively. But there are some

reports which dealt with the study of polymer supported Schiff-bases and its complexes.¹⁵⁻¹⁸

1.2 A brief survey of polymer-supported strategy

The application of functionalised polymers for affecting a host of organic chemical transformations has achieved wide spread acceptance ever since the introduction of the solid-phase peptide synthesis by Merrifield.^{19,20} For the last three decades a number of such systems which find application in the field of organic chemistry,²¹ analytical chemistry,²² biochemistry,²³ biology,²⁴ and medicines²⁵ have been developed. Idea of polymer-supported ligands made considerable changes in the field of inorganic chemistry especially in coordination chemistry.

A large number of different types of polymers has been used as the support for transition metal complexes. When polymers are used as supports for organic reagents, or catalysts, the reactivity of these attached functions are seriously affected by the so called, polymer effect. By same means, properties of complexes also change by the support of polymer matrix. This may be due to the physical properties such as diffusion effects, site isolation effects and local concentration effects. It may also be due to microenvironmental interaction and coordination unsaturation. So polymers are not only supports but also can govern reactivity and availability of the reaction site. In metalloenzymes, the macromolecular protein part decides the chemical structure and catalytic activity of the enzyme. It has been proved that metalloenzymes such as oxidase and hemoglobin, where metal complex is the active site, macromolecular protein part plays a significant role, or even controls the reactivity of the metal complex. Many of the polymer metal complexes are very good catalysts. Catalytic

properties of transition metals or their complexes are not often inhibited when they are appended on a polymer-support but in addition by the selective modification of polymer framework it is possible to tune the efficiency of the catalytic property.

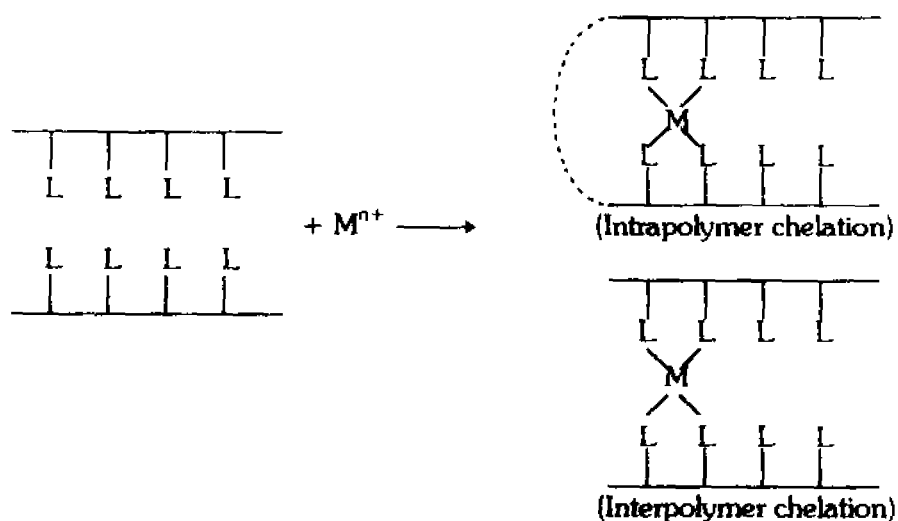
One major practical limitation of homogeneous catalysts in the liquid phase is the difficulty of separating products from catalysts. This difficulty is fully solved by affixing soluble molecular catalysts on a variety of insoluble supports including crosslinked polymers. Thus the catalyst acquires the property of insolubility while maintaining the activity exhibited in solution.

In most cases synthetic polymers are used with organic functions. But when organic polymeric ligands are metallated there generates inorganic functions over organic functions. This mixture of behaviour can be suitably assembled for the better activity of the species.

1.2.1 Polymer metal complexes

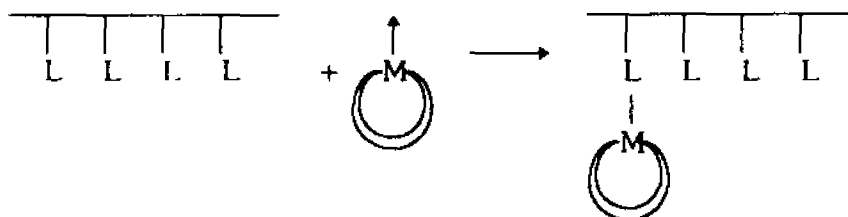
Here central metal ions are surrounded by macromolecular chain. It can be prepared by different ways. The polymer chain can cause steric, electrostatic, hydrophobic, configurational and cooperative effects upon complex formation, and catalytic activity on the polymer metal complex.²⁶ Based on the polymeric ligand the polymer-metal complex shows interesting and important characteristics different from ordinary metal complex of low molecular weight. So as regard to polymer metal complex much attention has received in the field of chemists due to the revolutionary invention of efficient catalysts, immobilised reagents and selective adsorbers. Heterogeneous nature of immobilised reagents makes it easy for separation and work up.

Depending on the ligand functions on polymers and mode of anchoring metal complexes on the matrix it can be classified into several types. Of the various types crosslinked or non crosslinked polymers having ligand binding sites are the simplest. It can be prepared by functionalisation of available crosslinked or non crosslinked polymers and subsequent incorporation of transition metal complexes/metal ions. Another way is by the homopolymerisation or copolymerisation of functionalised monomers and subsequent incorporation of transition metal ions/complexes. So large number of polymer resins can be prepared which contains coordinating groups or atoms mainly nitrogen, oxygen and sulphur in the polymer skeleton. When transition metal ions are put into polymer ligand, complexation can take place in different ways. The coordinating ligands required for the metal ion may get from the same polymer chain if the resin is flexible or may get from neighbouring polymer chains if it is rigid. Sometimes one or two coordination sites of the complex remaining to be coordinated may filled by solvent or water molecules. If ligands from same polymer chain is employed for coordination the chelation may be termed as intrapolymer chelation and if the chelation is by neighbouring polymer chain it is referred as interpolymer chelation.



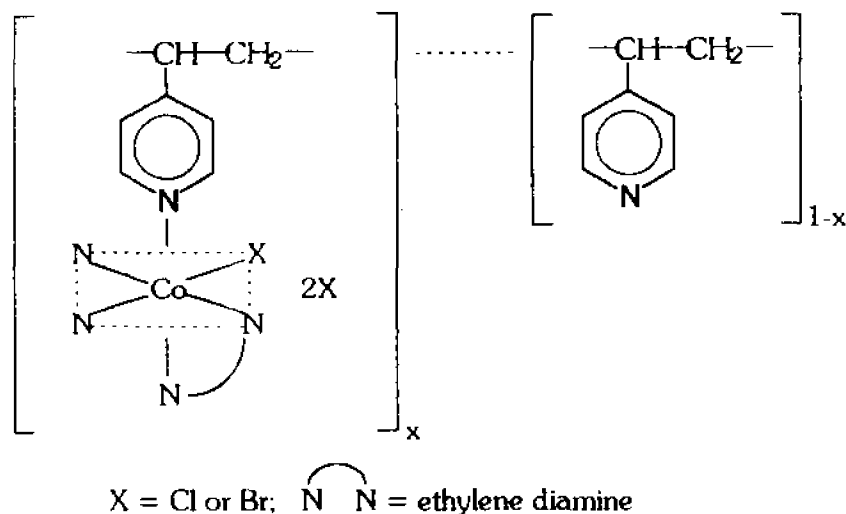
Besides polymer possessing repeating units of monodentate ligands there are polymers bearing multidentate ligand sites as repeating units. This type of polymer ligands are numerous. Homopolymerisation or copolymerisation of metal complexes containing polymerisable groups is another way of preparing polymeric metal complexes.

In some cases coordinatively unsaturated but stable metal complexes can be used for affixing on the polymer through ligands on polymer chain. This results in the enlargement of coordination sphere of the central metal ion which is already coordinated with low molecular weight ligands. Metalloporphyrins and cobaltic chelates are good examples which undergoes this kind of polymer metal complex formation.

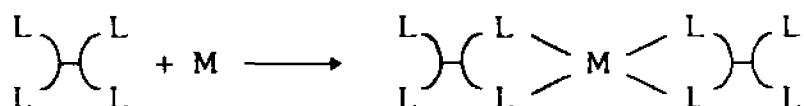


Thus a polymer ligand is made to coordinate to a vacant site of a previously prepared, stable, low molecular weight metal complex. Tsuchida and Nishide^{27,28} prepared pendant type polymer-metal complexes having a uniform structure by the substitution reaction between a polymer ligand and a Co(III) or Cr(III) chelate, where the chelate is inert in ligand substitution reactions. Cis[Co(en)₂PVPCI]Cl₂ complex is prepared by mixing an aqueous solution of the complex [Co(en)₂Cl₂]Cl to ethanolic solution of PVP and then heating. After some hours it is filtered and washed with cold water and evaporated to dryness we get dark-reddish filmy substance. These authors prepared a series of Co(III)

and Cr(III) complexes and studied degree of coordination against time in the polymer appending reaction.



In the case of some monomer ligand molecules coordinating ligand sites are at the two ends of the molecules. Addition of metal ions cause formation of polymer metal complexes. Neighbouring ligand molecules are combined by metal ions through coordination bond.



Whatever may be the method by which a polymer-metal complex is formed it is interested to consider the polymer effect which is operated on the complex unit in comparison with the monomeric complex. Sometimes the structure within the coordination sphere will be identical in a polymer complex and in a monomeric complex and their reactivity may also be same even though the complex is bound to a polymer chain. But in many cases it is seen that the coordination sphere is much influenced by the attached polymer chain. So the

polymer ligand existing outside the coordination sphere and surrounds the metal complex has a governing role over reactivity of the metal. This aspect may be on the basis of several other factors like concentration of metal complex on the polymer ligand, rigidity of the polymer ligand, different conformation of the ligand in solution and hydrophobic and hydrophilic nature of the polymer environment, etc.

1.2.2 Formation and stability of polymer chelates

When a metal ion solution is treated with a polymer ligand such as polyacrylic acid, poly(vinyl alcohol), poly(ethylene imine) or poly(vinyl pyridine) a polymer chelate is formed. But the formation constant of a complex involving a polymer ligand is not easily estimated. Bjerrums method for formation constants was modified by Gregor²⁹ by taking into account of the electrostatic effect of both polymer ligand and polymer metal complex. Another scientist, Marinsky³⁰ has evaluated distribution of mobile metal ions neighbouring a polymer and the difference in potential for a metal ion between the surface of a polymer and a bulk solution.

Studies on the formation of polymer chelates have been most exclusively concerned with Cu(II) ion. This is because copper(II) ions can be easily determined by atomic absorption spectrophotometry, and it forms polymer chelates with polymer ligands. More over copper(II) chelates are stable in aqueous solution and are active towards both visible and EPR spectra. Rate constants for the complexation of polyacrylic acid with Cu(II) have been determined by temperature—jump method,³¹ the magnitude of formation—rate constant (K_f) and the dissociation rate constant (K_d) were 10^8 l/mol sec and 10^4 l/sec, respectively or nearly equal to those of the corresponding monomeric

dicarboxylic acid, glutamic acid. The complex formation of polyethylene imine with Cu(II) has been monitored by stopped—flow spectroscopic method.³²

Copper forms complex with pyridine as well as with poly(4-vinyl pyridine). The d-d absorption maximum of the copper complex shifts gradually to shorter wavelength as the concentration of copper ions in aqueous solution decreases and this shows the stepwise formation of the complex $\text{Cu}(\text{pyridine}) \rightarrow \text{Cu}(\text{pyridine})_4$. But the absorption spectrum of the copper complex of PVP does not show any shift and that helps to make the conclusion that complex formation between copper and PVP is not a step-by-step mechanism, as in monomers but that the composition of the copper complex in PVP remains almost constant throughout the course of the reaction. Similarly the EPR spectrum of the pyridine-copper complex changes with ligand ratio, in accordance to the stepwise formation of $\text{Cu}(\text{pyridine})_4$ complex. But in the case of PVP-copper system the completely coordinated copper ions in the polymer ligand coexist with free uncomplexed copper ions even at low ligand ratio. This also suggests that PVP-copper chelate is formed in a one step reaction. Viscosity measurements can be used for finding the shape of a polymer chelate and metal appended polymer.³³ The decrease in viscosity of PVP solution with increasing concentration of metal ion is due to the marked contraction of polymer-ligand chain by intrapolymer chelation. An intrapolymer chelate will be very compact and metal ions are crowded within the contracted polymer chain. It is also observed that contracted structure of an intrapolymer chelate is also depends on the metal ion species.

In many of the cases the overall formation constant of the four coordinate copper complexes with polymer ligands is one to five times greater than in the monomeric copper-complex system. This is due to the fact that copper chelate in the polymer ligand forms spontaneously.

1.2.3 Polymer effect in catalytic rate

Catalysts functioning as a polymer support generally show, very high degree of activity corresponding to homogeneous state. There are several reactions which illustrates this phenomenon.³⁴ The carbonylation of allyl chloride by palladium supported catalyst and of homogeneous catalyst were studied and it is observed that the reaction rate is considerably favoured by polymer supported catalyst. The dimerisation cum methoxylation of butadiene to 1-methoxy octa-2,7-diene by Pd(0) species on a polymer support is found to be in high yield.

2,6-Xylenol was oxidatively polymerised by Cu-poly(vinyl pyridine) complex or copper partially-quarternised PVP (QPVP) complex in a homogeneous dimethyl sulphoxide solution and the mechanism of catalysis of the polymeric copper complexes were discussed. The polymerisation rate increased in the order Cu pyridine < CuPVP < CuQPVP. The polymerisation rates are listed in Table 1.1.

Table 1.1. Rate of the polymerisation of 2,6-xylenol catalysed by copper complex.³⁵

Catalyst	Rate of polymerisation 10 ⁴ (mol/L min)	
	[CuCl] 0.01 mol/L	[CuCl] 0.001 mol/L
Cu-QPVP	25	1.1
Cu PVP	a	0.75
Cu Py	12	0.20
Cu-DMSO	2.9	0.08

a - Cu-PVP complex insoluble in DMSO.

1.2.4 Polymer-supported chromium(VI) compounds

It has been found that Cr(VI) derivatives supported on an insoluble organic or inorganic matrix are particularly convenient for organic synthesis.^{36,39} The insoluble support provides a specific environment, capable of enhancing and modifying the reactivity of bound reagent. Therefore it is possible to carry out oxidation under mild conditions using solvents which may be rather unusual for Cr(VI) oxidations. The reaction seems to be quite general. Allylic, benzylic and saturated primary and secondary alcohols can be converted to the corresponding carbonyl compounds in high yield.

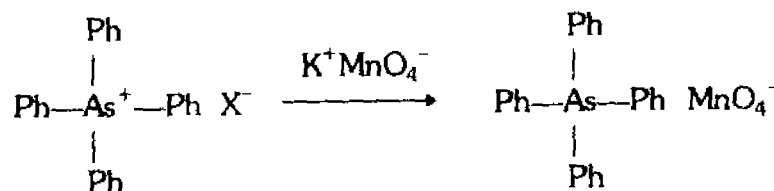
Cainelli et al.⁴⁰ reported the use of chromic acid as anion exchange resin in the oxidation of alcohols to aldehydes and ketones. It was found to be very good oxidising agent and the method of oxidation involves stirring excess of resin with alcohol in a suitable refluxing solvent. Modified polymeric reagents were developed by Frechet et al.⁴¹ to improve the recycling of the polymer as well as its efficiency.

Alcohols can be oxidised to carbonyl compounds by silica gel supported chromic acid reagent and it was reported by Singh et al.⁴² Very recently a number of complex chromates have been reported as soluble models and supported species for organic oxidations.

1.2.5 Polymer-supported permanganate reagents

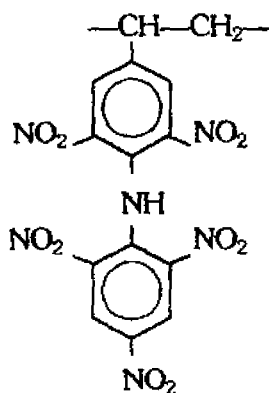
The permanganate ion has been widely used by organic chemists for its strong oxidising properties towards organic substrates.⁴³⁻⁴⁵ The low solubility of permanganate ion in organic solvents require the use of oxidation-resistant solvent such as acetic acid, acetone or t-butyl alcohol. Gibson et al.^{46,49} reported permanganate oxidations in non aqueous solvents. They used tetraphenyl

arsonium permanganate as a recyclable oxidising agent in organic solvents. The corresponding arsonium dichromate has no oxidising property.



1.3 Ion-exchange resins

The lack of selectivity of conventional ion-exchange resins has led to the discovery and development of new class of polymers which are now known as specific and selective ion-exchange resins. The first attempt was that of Skogseid⁴⁸ who devised a polystyrene derivative containing dipicrylamine groups and it is found to be very specific for potassium ion.



After this formulation there comes different types of polymeric matrices with a variety of chelating groups on the resin.⁴⁹⁻⁵¹ But the task for the elucidation of an ion selective resin continued with incorporating various contemporary refinements of coordination chemistry.

A variety of solid supports and matrices both inorganic and organic have been used for anchoring various chelating groups onto them. Silica is used as an inorganic support and cellulose is employed as an organic support.

1.3.1 Historical developments

As regards to complexing and chelating resins the historical developments has been lucidly summarised by Millar⁵² and Hering.⁵³ Erlenmeyer and Dahn⁵⁴ brought the idea of chromatographic separation of cations from mixture of cations by passing it on 8-hydroxy quinoline supported on a solid base. Also ions can be selectively adsorbed on the solid support by suitably adjusting the pH.⁵⁵ Mellor and Gregor^{56,57} suggested the preparation of several resins containing a variety of chelating groups known to form complexes with wide range of metal ions whose selectivity and stability is pH dependent. The work of Hale and Skogseid⁴⁸ supports that if a chelating group in a resin is very selective towards a particular ion and not specific is always expected of resins containing groups similar to those in chelating groups. Kennedy and Davies⁵⁸ observed that thorium (IV), iron(III) and vanadyl(VI) formed relatively strong complexes with phosphates and phosphonates whereas alkaline earth and bivalent transition metal ions and lanthanides formed either weak complexes or common salts. A number of biologically active compounds⁵⁹⁻⁶¹ such as desferrioxamine B and porphyrins have also grafted as different types of polymeric supports and their chelating properties have been studied.

1.3.2 Criteria for a compound to act as a selective ion-exchangers

A chelating ion-exchange resin contains essentially two part in a chelating group and a polymer matrix. A large number of chelating ion exchangers have

been found to be selective for one metal ion or another. So the criteria for selectivity depends on both components. Gregor et al.⁶² postulated that a suitable chelating group for incorporation into a polymeric matrix must have following properties.

- (1) It should be capable of resin formation, or be capable of substitution into a polymeric matrix.
- (2) It should be sufficiently stable to withstand the polymerisation or resinification process.
- (3) It should be compact enough so that its chelating ability is not hindered by the dense polymeric matrix.
- (4) Both arms of a chelate structure should be present on the same monomer unit in proper spatial configuration.

Also a good chelating ion exchanger should possess usual property of mechanical stability and resistance towards acids and bases used for regeneration of resin.

1.3.3 Theoretical aspects

Most of the theories developed in the case of conventional ion-exchange resins are also applicable to chelating ion-exchange resins.^{63,64} One important theory is regarding to ion-exchange equilibria and its application to chelating ion-exchange resins. The various aspects of the effect of complex formation on ion exchange equilibria and on the distribution of metal ions between liquid and resin phase have been extensively studied.^{65,66} Stability constant of the complex is an important aspect and it can be evaluated by the application of law of mass action to the equilibria involving the complexes.⁶⁷ But the concentration of

chelating functional group on the macromolecular frame work is also an important factor in evaluating the stability constants of the resin phase.⁶⁸ One approximation made in this regard is that the coordination or complexation behaviour of a chelating exchange resin is similar to that of the corresponding monomeric repeating chelating unit in aqueous solution. Second approximation is that the stability constants determined²⁸ for such a repeating units are valid for the respective equilibria inside a swollen gel.⁶⁹ These assumptions are applicable only if complexes (metal to ligand) are formed in the resin phase and the compact molecular structure of the chelating functional group limits the influence of the matrix on the process of complex formation.

1.3.4 Nature of polymeric matrices

Basically two types of polymeric matrices can be considered, that is, inorganic and organic. Inorganic supports have high mechanical strength, high thermal stability and good ability to withstand high pressure and stability both towards organic solvents and mineral acids.⁷⁰ But the impossibility of creating high degree of functionalisation in inorganic support is its disadvantage, consequently low ion exchange capacity and low ion exchange rates. Silica is the most extensively used inorganic support. Organic matrices used for ion exchange resins may be naturally occurring polymers or synthetic polymers. Among naturally occurring polymers cellulose has been most extensively used support for chelating ion exchange resins. Unsubstituted cellulose has very low ion-exchange capacity. But the ion-exchange cellulose means modified cellulose accomplished by oxidation, esterification or etherification. The ion-exchange properties of cellulose are similar to other ion-exchange resins. But cellulose ion-exchangers are more finely divided than ordinary ion exchange resins, present a larger surface and because of their porous structure of larger molecules which are

not readily adsorbed by other resins. The rate of exchange is also very rapid in the case of cellulose ion-exchangers. Another important naturally occurring polymer used as a chelating resin chitin, poly(N-acetyl-D-glucosamine) and its deacetylated derivative chitosan, which have been useful for removing heavy metal ions from discharge water.

1.3.5 Characterisation of chelating ion-exchange resins and their metal complexes

The characterisation of newly synthesised chelating ion-exchange resins and their metal complexes is of prime importance. In the case of chelating ion-exchange resins, characterisation involves the use of analytical and physical techniques. The use of physical method in the characterisation of this type of ion exchanges is assuming greater importance as the selectivity is considered to depend on chelating functional group. So a knowledge about the coordination behaviour of the functional group towards, metal ions and the geometry around the metal ion is essential for the further development of metal-ion selective ion-exchange resins. The capacity of an ion-exchanger is defined as the number of counter ion equivalents in a specified amount of the material. Another closely related parameter is the distribution coefficient D .

$$D = \frac{\text{Amount of metal ion per gram of dry resin}}{\text{Amount of metal ion per C. C. of solution}}$$

Another important parameter is the selectivity coefficient for the exchange of two ions A and B of charge a and b , respectively, given by the expression.⁷¹

$$K_{B/A} = \frac{[\bar{A}]^a [\bar{B}]^b}{[\bar{A}]^b [\bar{B}]^a}$$

Here the bars indicate the concentration of ion in resin phase and the other indicate concentration of ion in aqueous phase. Both the distribution and selectivity coefficients depend on the degree of crosslinking, specific capacity (the number of equivalents of the fixed exchange groups per gram of the resin) and on the nature of the chelating groups.^{72,73} A number of physicochemical methods mainly based on the spectral and magnetic properties of chelating ion exchange resins and their metal complexes are now used for characterising polymeric compounds. IR spectroscopy provides an excellent tool for characterising chelating ion exchange resins to locate coordination or bonding site in the metal complexes of chelating resin. Metal ligand vibrations can be traced by far IR. EPR spectroscopy is being increasingly used to study coordination structure. The interaction between the spin of central metal ion and coordinated ligand decides the absorption pattern and its g values which in turn can be used to study the metal-ligand bond.^{74,75} The reflectance spectra are used for determining the geometry around the transition metal ions. Magnetic susceptibility measurements have been used to determine spin state of metal ion in such complex.^{76,77} Thermal studies (TGA and DTA) provide various physical and chemical transformations happening on the ion-exchange resins as well as complexes of chelating ion-exchange resin. The great improvement in C^{13} NMR study in recent years provide more sharpened tool for analysing the polymer. Mossbaür spectroscopy provides⁷⁷ easier study of iron and some lanthanide complexes of chelating ion exchange resins. A list of some common chelating ion-exchange resins are given in Table 1.2.

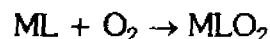
Table 1.2 Some chelating ion exchange resins.

Common name	Polymer	Bonding site	Remark	Reference
Sumi chelate CR-2	DVB-crosslinked PVP	Nitrogen	Very effective in capturing chromium	78
Dia ion CR-40	Polystyrene graft ethylene diamine on chloromethyl polystyrene	Nitrogen	Metal ion like Cu(II) Hg(II) and Co(II)	79
Dowex A-1	Iminodiacetic acid on crosslinked polystyrene	Nitrogen	Very selective for transition metal ions	80, 81
IDA cellulose	Iminodiacetic acid ethyl cellulose	N and O	Coordinates many transition metals	82
Unicellex UR-50	Copolymer of N-(o-hydroxy benzyl) iminodiacetic acid with phenol and formaldehyde	N and O	Cu(II) > Ni(II) > Zn(II) > Co(II) strong affinity to Fe(III)	83
ES 346	Crosslinked polyacrylic matrix having amidoxime functional group	N and O	Captures Fe(III), U(VI), Cu(II), Ni(II), Cr(III)	83
Sphero oxime -1000	Crosslinked polystyrene in which chelating is linked through an azo group	N and O	Cu(II), Ni(II), Co(II)	84
Spheron salicyl-1000	Salicylic acid chemically bound to hydrophilic glycol methacrylate via side chain azo group	Oxygen	Fe(III) and Al(III)	85

Besides nitrogen and oxygen there are sulphur containing complexing ligand reported by several investigators.^{86,87}

1.4 Dioxygen complexes

It is seen that in some complexes molecular oxygen make, intimate connection with metal ion centres contained in diverse states of chemical environments.



This adduct formation occurs without the metal (M) or the ligand (L) being irreversibly oxidised. A metal superoxide or metal peroxide complex is one which the coordinated dioxygen resembles a superoxide O_2^- or peroxide O_2^{2-} anion. Molecular oxygen reacts with a large number of iron-proteins involved in the physiological transport of molecular oxygen in the oxidative metabolism of a wide variety of compounds and in the hydroxylation of a number of metabolites. The reversible reactions of dioxygen (O_2) with protein complexes containing Fe(II) or Cu(II) are of critical importance to advanced and primitive forms of animal life. Some kind of role is exhibited by hemovanadin, found in ascidians⁸⁸ in which vanadium(II) complex combines with dioxygen. These proteins help in binding, transporting, storing and releasing dioxygen.

1.4.1 Synthetic dioxygen carriers

Synthetic dioxygen carriers are used as very good models of natural dioxygen carriers. They are used in dioxygen separation and storage, industrial process and catalysis. Until recently industrial importance in dioxygen complexes was centred around modelling of industrially important reactions of dioxygen including manufacture of sulphuric acid by contact process and that nitric acid⁸⁹ by ostwald process. Recently manganese dioxygen complexes have been suggested for use in separating dioxygen from air by a pressure swing

absorption process and for scavenging minute traces of dioxygen from inert atmosphere.⁹⁰

Many dioxygen complexes especially those of cobalt are employed as good catalyst in a variety of reactions leads intensifying the interest in this branch in recent years. A series of iron porphyrin complexes has been synthesised which will catalytically reduce dioxygen to water but this occurs with intermediate formation of peroxide. A variety of copper(I) complexes has been reported to catalyse⁹¹ the reduction of primary and secondary alcohols to aldehydes and ketones.

Dioxygen complexes has of considerable theoretical importance since they exhibit a wide range of stabilities and reactivities which vary appreciably and predictably with changes in the ligands employed. Moreover they display interesting structural and electronic properties.⁹² There are variety of synthetic porphyrins with chemically inactive side chains and provide a symmetric square planar environment for a metal coordinated in a porphyrin core. The electronic property of octaethyl porphyrin is very much close to that of natural porphyrin. One advantage of TPPH₂ over OEPH₂ and natural porphyrin is that it is possible to study the electronic property of metalloporphyrin systems especially electron density on the metal by varying the substitution of phenyl rings of tetraphenyl porphyrin.

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