



Chapter 1

Introduction

One of the fascinating areas of coordination chemistry is the developing branch of coordination polymers. These systems with metal complexes bound or stacked together in wide variety of structural dispositions have been of intense interest to chemists, physicists, material scientists and theoreticians alike. Their concerted efforts backed by the skill of synthetic chemists have yielded multitudes of interesting and novel polymeric materials which find extensive applications. Unlike pure organic or inorganic polymers the coordination polymers have the mix of properties of both of them. Often this imparts unique and novel properties to the molecular systems formed which go on to make them very useful materials in the form of molecular ferromagnets, synthetic metallic conductors, non-linear optical materials, ferroelectrics, and one-dimensional conductors. While the attempt on this thesis is to develop such extended molecular systems it is worthwhile to discuss briefly on some aspects of coordination polymers in general.

1.1 Coordination Polymers

A coordination polymer is defined as a polymeric substance containing a coordination compound⁽¹⁾ or metal complex in its repeating unit. The metal complex is not necessarily part of the polymer backbone. Fifteen to twenty years ago, the main interest in coordination polymers depended on the



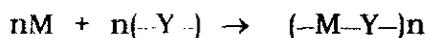
expectation of increased thermal stability for the materials. Thermal, moisture and oxidative stabilities of many coordination polymers fell below expectation at that time, and despite the vast number of coordination polymers already prepared many problems and limitations still exist. However as shown by more recent studies, many earlier problems have been overcome, and new, unanticipated applications have been realised.

A general problem in the characterisation of coordination polymers arises because of the extreme intractability of many of the materials and the consequent lack of available structural information. Often, where solubility exists, it leads to complete depolymerisation. However, molecular weight data is available for selected soluble polymers. Thus the structures depicted in the literature and here are in some cases quite speculative. Owing to the difficulty of obtaining single crystals of the materials, relatively few X-ray structure determinations have been carried out on coordination polymers, and spectroscopic techniques have provided only limited insight into structure.

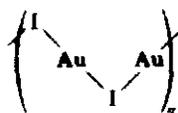
1.1.1 General Methods of Preparation

Three general methods have been employed in the preparation of transition-metal coordination polymers.

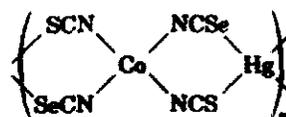
1. Ligands capable of simultaneously coordinating to two metal atoms generate the desired polymer, i.e.,



where M is a metal and Y is a ligand. Common examples of such ligands^(2,3) used in polymer formation include halide or pseudohalide ligands to form polymers **1** and **2**.

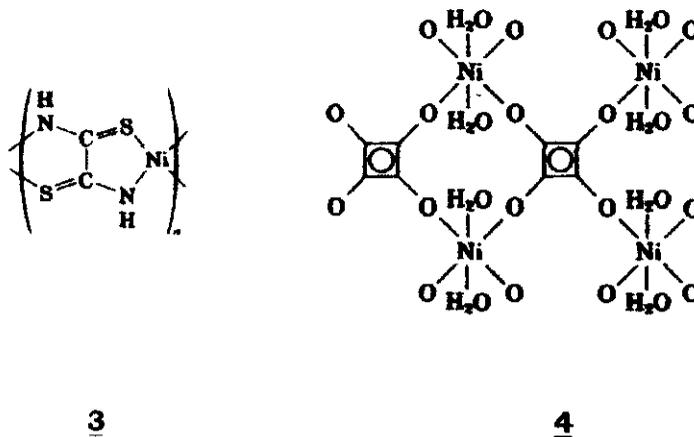


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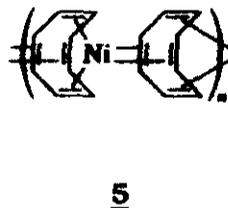


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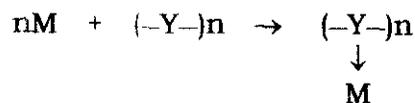
The ligands may also be multidentate. Bischelating agents such as rubeanate or squarate^(4,5) may be used to form structures such as **3** and **4** respectively.



Another example involves π -coordination to multi-unsaturated complexes, as depicted in **5**.⁽⁶⁾

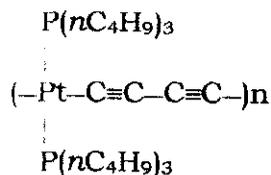


2. Preformed polymers to which metal atoms are attached may be used to produce polymers with advantageous properties, i.e.



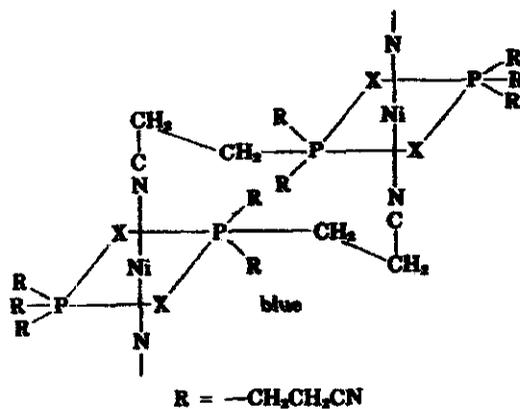
Polystyrene^(7,8) and silica are often used as polymer supports (**6** and **7**); common functional groups on polystyrene supports are phosphines, amines or cyclopentadienyl ligands.⁽¹⁰⁾

Coordination complexes other than metallocenes also undergo polymerization. For example, $\text{Pt}[\text{P}(n\text{-C}_4\text{H}_9)_3]_2\text{Cl}$ condenses with $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$ to form the rigid rod-like polymer depicted in **10**.⁽¹³⁾



10

Square planar $\text{NiX}_2[\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3]_2$ ($\text{X}=\text{Cl},\text{Br}$) complexes polymerize either in solution or in the solid state to form octahedrally coordinated linear chains as the nitrogen atom of one cyanoethyl chain bonds to the nickel atom of an adjacent complex (**11**).⁽¹⁴⁾



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1.1.2 Classification of Coordination Polymers

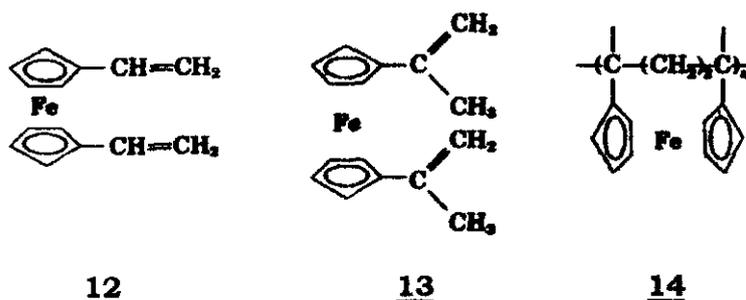
The transition metal coordination polymers that have been prepared may be classified into different groups according to the position of the metal in the macromolecule; (a) the metal is a pendent group; (b) the metal acts as a cross-linking agent; (c) metal is enmeshed in a polymer (parquet polymers); (d) the metal is an integral part of the polymer back bone; (e) stacked metal chain complexes; (f) magnus green salt; (g) polymetallocenes; (h) poly(yn)s; (i) shiskabob polymers.



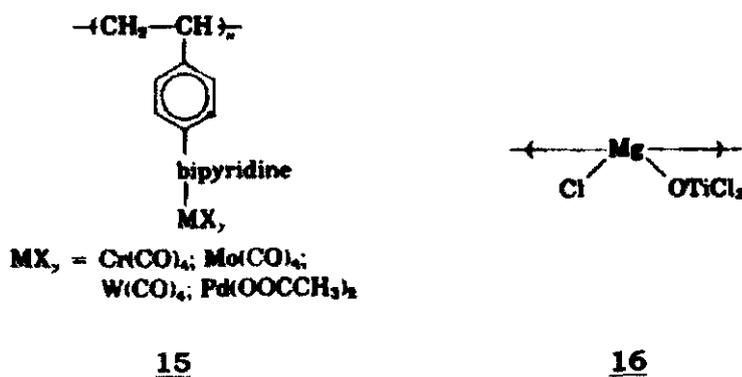
1.1.2.1 Pendent metal groups

Polymers that contain the metal as a part of the pendent or substituent group may be formed when a coordination complex containing functionalised ligands undergoes polymerisation, usually by addition, or a preformed polymer acts as ligand and is complexed by a metal atom or ion.

The most widely studied complexes are the addition polymers of monosubstituted vinyl metallocenes. Vinyl ferrocene **8**, for example, behaves much like its organic analogue, styrene. It undergoes homopolymerisation using radical, cationic or anionic initiators under bulk, solution, or emulsion conditions.^(15,16) With radical or cationic initiation, the 1,1'-disubstituted ferrocenes **12** and **13** undergo cyclopolymerization to form products such as **14**.

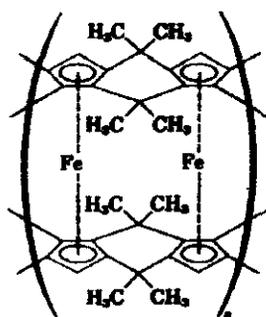


Polymer bound catalysts also have metal-containing pendent groups. These polymers are formed from prepolymers and metals. In addition to the two examples (**6** and **7**) given previously **15** and **16**^(9,17) are also worth mentioning.

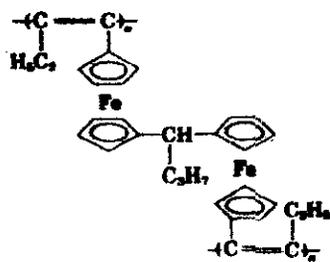


1.1.2.2 Polymers cross-linked by metals

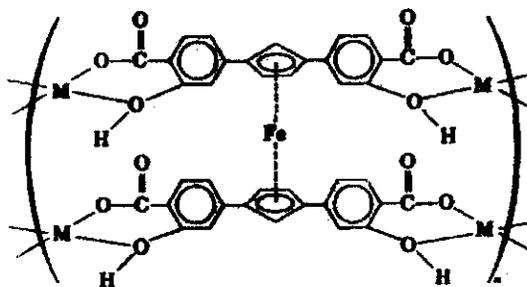
The condensation of several substituted ferrocenes can result in the formation of linear polymer chains cross-linked by ferrocene moieties. Several polymers containing ferrocene cross-links have been reported. Many are of interest because of their semiconducting properties. For example, the condensation of ferrocene with acetone in the presence of $ZnCl_2$ and HCl at $56^\circ C$ yields a soluble polymer⁽¹⁸⁾ proposed to have structure **17**. This semiconducting polymer has a molecular weight of 3000-3200 and a melting point of $320-360^\circ C$. Other ferrocene-linked polymers include the proposed structures **18** and **19**. Structure **18** is formed by the condensation of butanal with carbamyl ferrocene. The polymer **19** is obtained by the treatment of ferrocene with diazonium salt of p-aminosalicylic acid, followed by reaction with di- and trivalent metals ($M=Fe(II), Cu(II)$).⁽¹⁹⁾



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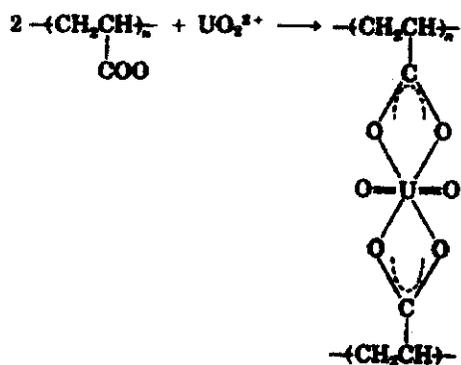


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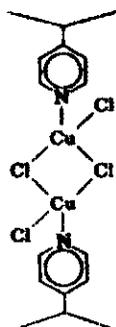
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Preformed polymers containing chelating groups on interaction with metal ions such as UO_2^{2-} also resulted in cross-linking (**20**).

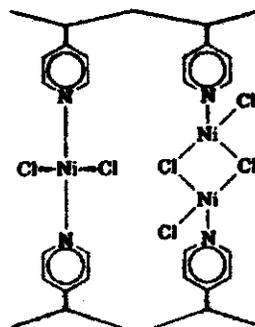


20

Poly(4-vinylpyridine) complexes of various transition metal halides have been prepared both by the reaction of monomeric $\text{MX}_2(4\text{-VP})_2$ complexes in the solid state and by the reaction of the transition-metal halide with the preformed 4-vinylpyridine polymer.⁽²⁰⁾ Structures proposed for the copper(II) chloride and nickel(II) chloride complexes prepared from the preformed polymer are depicted in **21** and **22** respectively. Whereas the copper complex is thought to involve a square planar copper cross-link, it has been proposed that the nickel complex consists of a mixture of two stoichiometries of tetrahedrally coordinated nickel atoms.

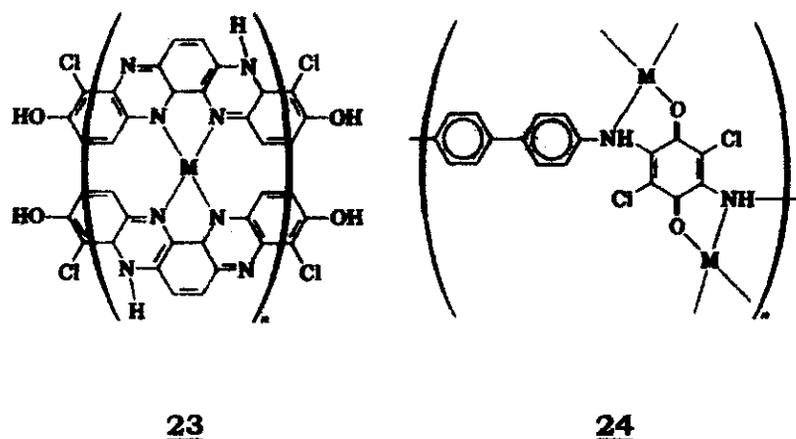


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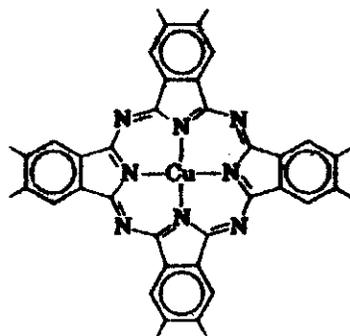
Other polymers that function as ligands and produce metal cross-linked polymers appear in **23** and **24**. Compound **23** is a black semiconducting polymer prepared by dissolving the preformed polymer in dimethyl formamide and adding the desired metal salt⁽²¹⁾ is a low molecular weight polyaminoquinone containing 6-12% metal [M(II) = Cu (II) or Cd (II)].



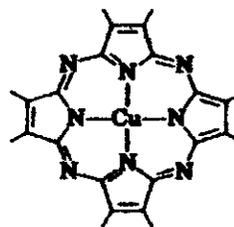
1.1.2.3 Parquet polymers

Parquet polymers are flat, net like organic macromolecules in which a metal is completely enmeshed. Polyphthalocyanato and polyporphyrinato complexes are the most common examples. These polymers are of interest because of their thermal stability, potential electrical properties, and similarities to homoproteins. Construction of these polymers is done by polymerisation of the organic net without altering the environment of the metal, or through coordination of one organic net to a neighbouring metal atom, thereby increasing the coordination number of the metal while retaining the monomeric organic unit.

The common examples of parquet polymers formed by polymerization of the organic net⁽²²⁾ are depicted in **25** and **26**.



25



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1.1.2.4 Polymers with back bone metals

Polymers containing transition metals as part of their backbones are formed by using ligands that can simultaneously coordinate to two different metal atoms or that have the potential to undergo addition or condensation thereby linking monomeric units. These polymers may be linear, planar or three dimensional, depending on the identity of the ligand and the coordination of the metal. The complexes have been synthesized from their monomeric units, but many are formed as polymers by direct reaction.

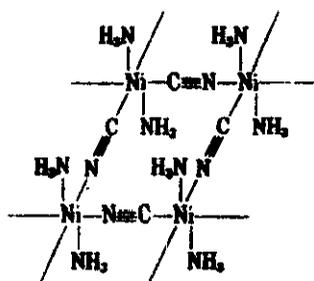
The most common examples of polymers formed by the simultaneous coordination of a ligand to two different transition metals are those containing halides or pseudohalide bridges; one-, two-, and three-dimensional polymer have been formed. For example, consider the cyanides. Gold cyanide $(\text{AuCN})^{(23)}$ obtained by heating $\text{H}[\text{Au}(\text{CN})_2]$ at 110°C is a yellow powder that is slightly soluble in water, ethanol, and ether and very soluble in aqueous cyanide solutions. Like the analogous colourless AgCN , it forms infinite linear polymer chains, as depicted in **27**.



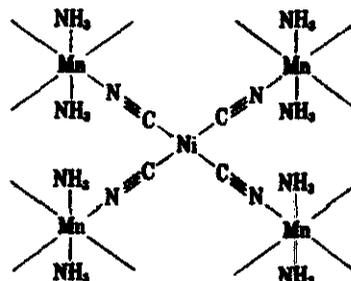
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On the other hand, crystal structure analysis of $\text{Ni}(\text{CN})_2\text{NH}_3 \cdot 1/4\text{H}_2\text{O}$ **28** and $\text{Mn}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ **29** reveal planar polymeric structures of these

complexes,⁽²⁴⁾ in which each metal centre is coordinated to four cyano groups, thereby forming a two-dimensional polymeric network **28**.

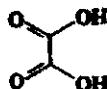


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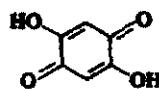


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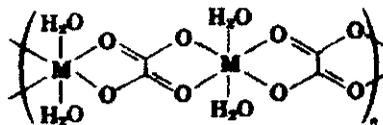
The M(II) complexes (M=Cu, Fe, Ni, Co) of **30** are believed to consist of linear chains, as depicted in **32** whereas Fe(II) and Cu(II) complexes of **31** form planar complexes, as depicted in **33**.



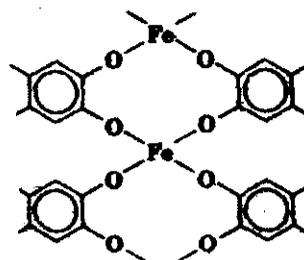
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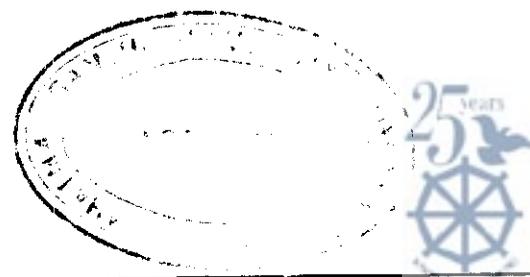


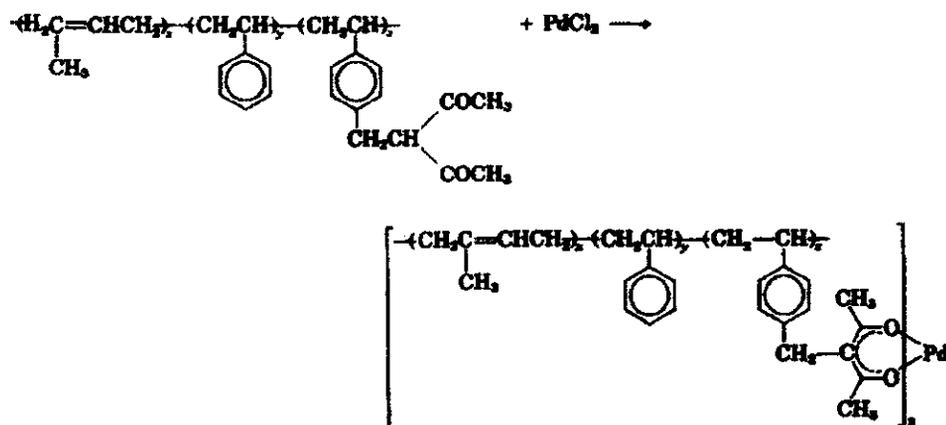
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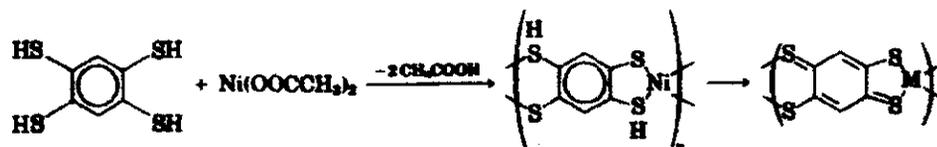
Another type of complexes in this category result when preformed polymers react with metals to give cross-linking sites which, in turn, result in products with elastomeric properties **34**.





34

Reaction of benzene-1,2,4,5-tetrathiol with $\text{Ni}(\text{OOCCH}_3)_2$ (or other divalent metal salts) gives the potentially conducting substance poly(benzodithiolene) **35**.



35

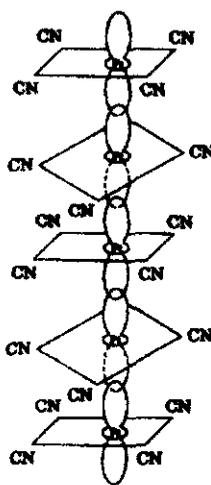
This is an example of the use of a conjugated ligand as a direct bridge between metal centres. Interesting properties such as electrical conductivity, paramagnetism, ferromagnetic and/or antiferromagnetic interactions, electro activity (allowing applications in electrode materials), and imposed mixed valency can result from these structures.

Just within the subclass of coordination polymers, the structural variety is great. For example, three-dimensional networks around and are represented by the catana μ -(N,N'-disubstituted dithioxamido) copper complex polymer **36**, resulting from the reaction of Cu(II) with dithioxamides. Such materials are amorphous and insoluble.^(27,28)

1.1.2.5 Stacked metal chain complexes

Stacked metal-chain complexes **39** without macrocyclic ligands are also known. Tetracyanoplatinate-stacked complexes resemble the metal phthalocyanine polymeric structure **49** except that coordinating macrocycles do not chelate each metal atom. Instead stacks of square planar $\text{Pt}(\text{CN})_4$ units are formed with anions between the stacks.

The cyano groups surrounding Pt are staggered with respect to those coordinating the adjacent Pt atoms. These well studied materials⁽³⁰⁻³²⁾ are one-dimensional conductors with conductivities greater than $1 \Omega^{-1} \text{cm}^{-1}$.



39

1.1.2.6 Magnus green salt

Magnus green salt, $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]^{(33)}$ belonging to the class of compounds, consists of linear chains of Pt atoms which result from the columnar stacking of the constituent planar complex units. The Pt-Pt separations within these chains (3.25\AA) are substantially shorter than the separation between the chains (6.39\AA), which suggest the possibility of highly directional solid state interactions. The extended interactions of the filled d_{z^2} and empty p_z -orbitals on the Pt atoms in the linear chains is viewed as giving rise to energy bands of appreciable width in the solid state like the energy

bands in covalent inorganic superconductors, only highly directional in character.^(34,35)

Bromine doped complexes of $K_2[Pt(CN)_4]$, $K_2[Pt(CN)_4]Br_{0.3} \cdot 3H_2O$, also is known to act as one dimensional conductor. These anisotropic properties arise from stronger intermolecular interactions in one dimension in the crystal than in the remaining directions.

1.1.2.7 Polymetalloenes

Since the early 1950's, the rapid development of organometallic chemistry of the transition elements has resulted in a tremendous variety of new and often remarkable molecular structures and a range of novel catalytic species.⁽³⁶⁾ As it is well known that the properties of polymers can be modified dramatically by subtle changes in chemical structure, the possibility of using organometallic structural moieties to prepare macromolecular materials with interesting and possible useful characteristics has turned out to be a very attractive and prospective one.

At present two major classes of organometallic polymers exist with transition metals in the main chain. The first type poly(metalloenes) which were targeted in the early 1960's were of low molecular weight but with very poorly defined structures. However high molecular weight examples are now well known and have been found to possess a range of interesting properties. The second major class comprising of rigid rod polymers such as metal acetylides or poly(yn) materials are also now well known which are seen to be quite stable, presumably because of the $M(d\pi)$ and acetylide($p\pi$) interaction which can effectively strengthen the M-C bonds.

Multidecker sandwich structure⁽³⁷⁾ apart from those in which the stacking take place upon crystallisation, can be classified in various forms shown below.(Fig. 1.1).



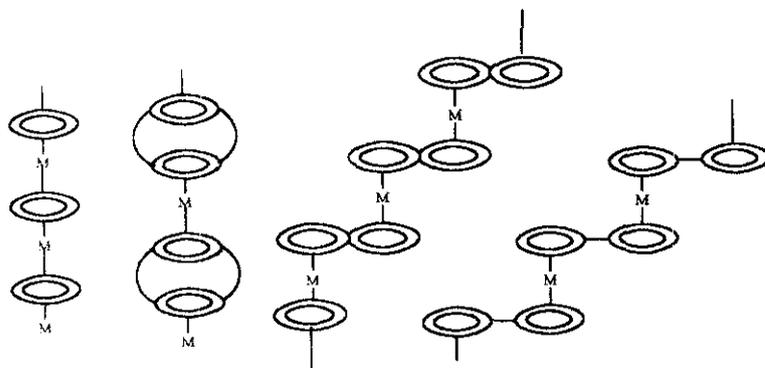
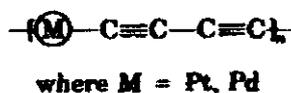
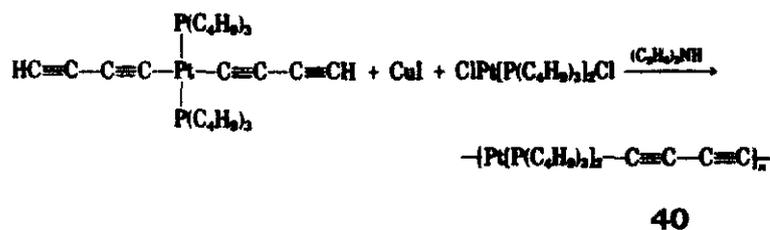


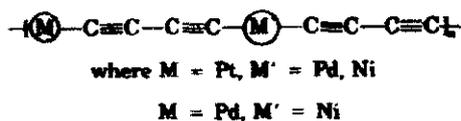
Fig.1.1 Various forms of sandwich structures

1.1.2.8 Poly(ynes)

An unusual class of organometallic polymers is the transition-metal poly(yn) polymers,⁽³⁸⁻⁴²⁾ which contain transition metals bound to carbon within the main chain and which might vaguely be considered coordination polymers. The Pt and Pd copolymers of this class have rod like structures as indicated by **40** and **41-48** (Fig.1.2.). The linear structure results from the all-trans configurations at the Pt and Pd atoms.



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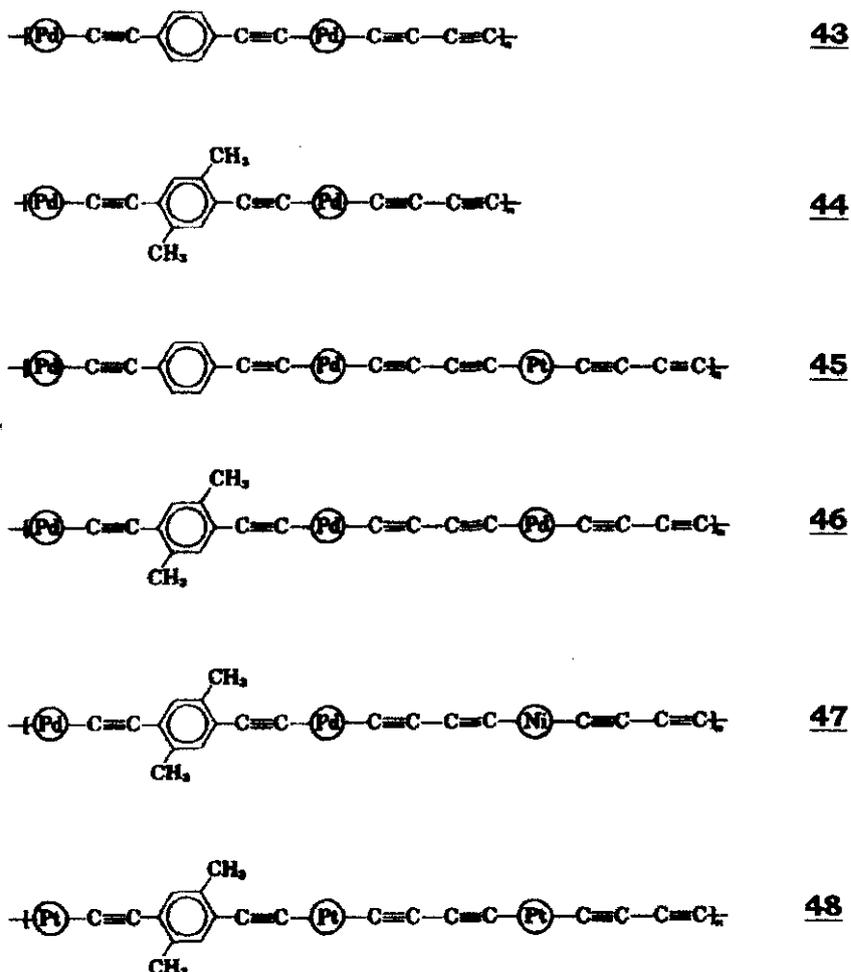


Fig.1.2 Rod like polymers. Encircled metals M= trans-M[P(C₄H₉)₃]₂

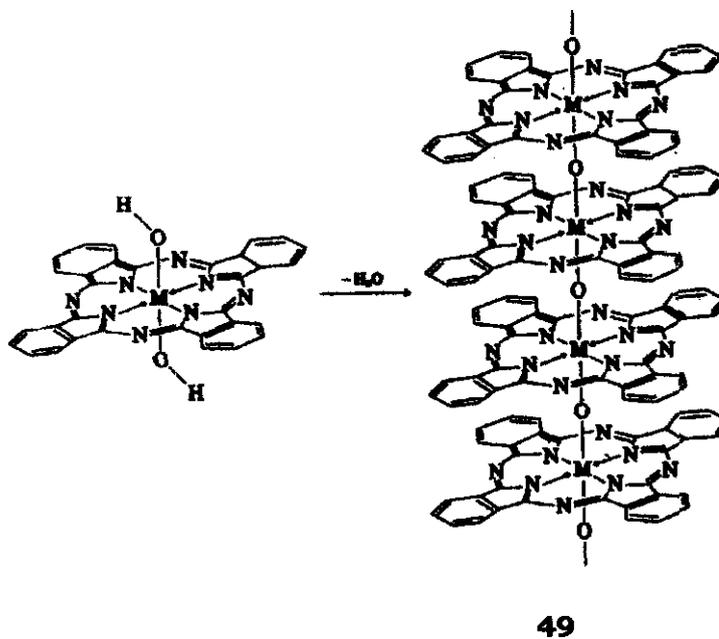
1.1.2.9 Shiskabob polymers

The Shiskabob approach yields another class of coordination polymer of stacked macrocyclic metal complexes. Here macrocyclic complexes are linked together by axial coordination of bridging ligands.

a) O-bridged polymeric compounds

Shiskabob macromolecules with the stacked metal phthalocyanine structure **49** (M=Si, Ge) have been made^(44,45) $\overline{DP} > 100$ was obtained with M=Si and $\overline{DP} > 70$ with M=Ge starting from Si(Pc)Cl₂ and Ge(Pc)Cl₂, where Pc=phthalocyanine. The dichlorides give M(Pc)(OH)₂, which undergoes polycondensation to give the (MO)_n

repeating group, and cofacial arrays of the metallophthalocyanines are achieved (Fig.1.3).



where M = Si, Ge, Sn

Fig.1.3 Formation of polymeric metallophthalocyanines

In general, metal complexes of macrocyclic ligands, such as phthalocyanine, crystallise in stacks to afford linear chains that have the ability to conduct electricity along the stack axis. Phthalocyanine polymers containing bridging ligands between the metal atoms **49** conduct electricity through their metal-ligand-metal linkages. Dehydration of phthalocyanine complexes of Si, Ge and Sn produces face to face stacks of oxygen bridged metal phthalocyanine units as shown in Fig.1.3. Upon oxidation with iodine, a mixed-valence polymeric cation is formed with intercalated I_3^- ions between the chains. Conductivities range from $2 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$ for $[\text{SiPcOI}_{1.40}]_n$ and $1 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$ for $[\text{GePcOI}_2]_n$ to $2 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ for $[\text{SnPcOI}_{5.5}]_n$. The low conductivity of tin polymer is attributed to a larger distance between the phthalocyanine units.

b) S-bridged polymeric compounds

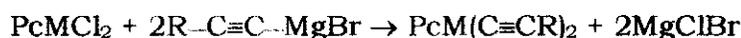
A change in the bridging ligand was made in an attempt to get some information on the mechanism of electrical conductivity of chalcogen bridged IVB metals with phthalocyanine as macrocycle.⁽⁴⁶⁾ Sulphur instead of oxygen was used to see if the better d-orbital overlap has any influence on the conductivity before and after doping. In comparison with [PcGeO]_n, polycrystalline samples of [PcGeS]_n do not show a pronounced increase in electrical conductivity.

c) F-bridged polymeric compounds

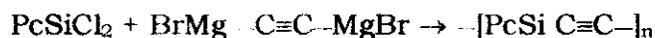
Polymeric stacks of bridged metallofluorophthalocyanines, (PcMF)_n with M=Al, Ga, Cr were prepared first by Kenney et al.⁽⁴⁷⁾ PcAlCl and PcGaCl were converted with NH₄OH or pyridine into PcAlOH and PcGaOH respectively which react with concentrated aqueous (48%) HF to form [PcMF]_n.

d) Alkynyl-bridged polymers

Alkynyl-bridged ligands other than O²⁻ and S²⁻ have also been used to prepare polymeric stacked metallomacrocycles. But a very little was known about metal-carbon bonds in metallophthalocyanine compounds⁽⁴⁸⁾ and synthesized polytrans-ethynylphthalocyaninato silicon. These are obtained by reacting phthalocyaninato metal dichlorides with appropriate grignard reagents⁽⁴⁹⁾



where, M = Si, Ge, Sn and R = H, -CH₃, -C₆H₅, -C(CH₃)₃.



The basic problem with the reaction of phthalocyaninato IVB metal chlorides with mono and bis grignard reagents of acetylene and its derivatives is the poor solubility of which results in a heterogeneous reaction mixture. The products are only very slightly soluble in organic solvents also. These disadvantages led to the synthesis of peripherally substituted phthalocyaninato derivatives which are known to be soluble in organic solvents.



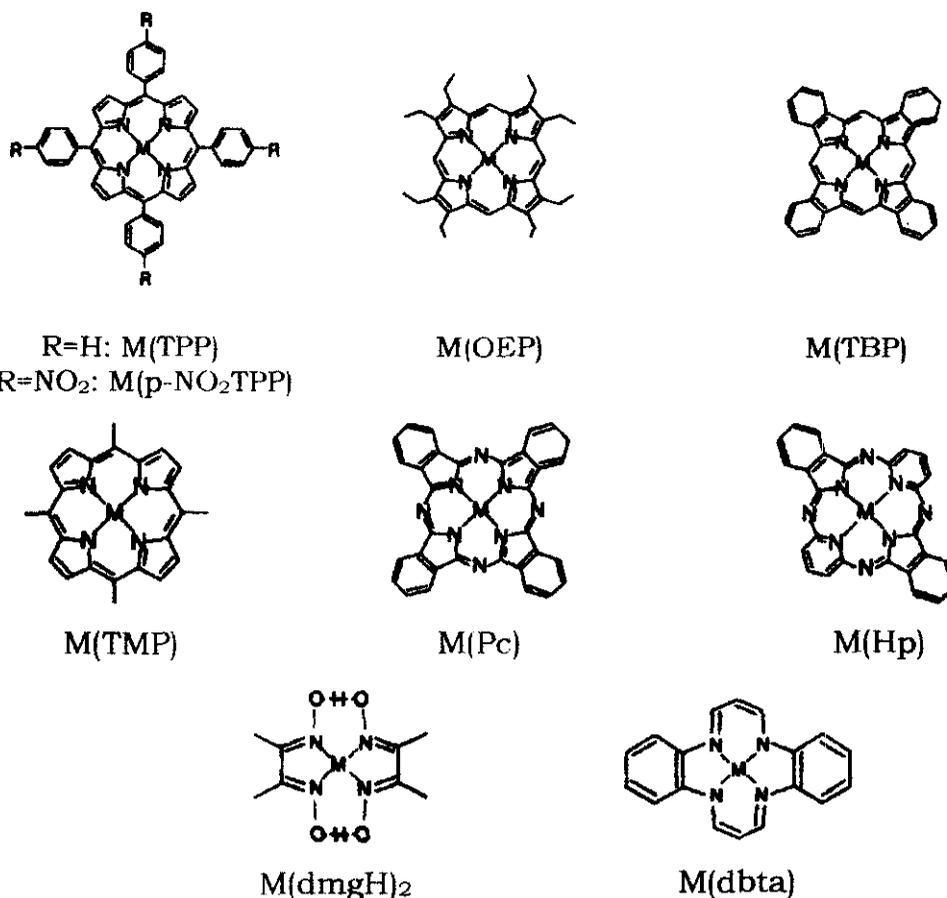


Fig.1.4 Various metalocyclic complexes suitable for one-dimensional stacking structures

TBP-Tetrabenzoporphyrin, TPP-Tetraphenylporphyrin, OEP-Octaethylporphyrin, TMP-Tetramethylporphyrin, Pc-Phthalocyanin, Hp- Hemiporphyrazine
 dbta-dihydrodibenzotetraaza [14]annulene, dmgh - dimethyl glyoxime

In addition to phthalocyanine, a large number of planar metal complexes also form one dimensional stacked structures.⁽⁵⁰⁻⁵⁶⁾ These are usually complexes of transition metals with flat π -conjugated ligands (Fig.1.4). Although there is a variety of possible spatial arrangements for the one-dimensional stacking structures, they all suffer instability and none are super conductors even at low temperatures.

1.2 Properties of Coordination Polymers

The electrical, optical and magnetic properties of coordination polymers are a complex function of their chemical, electronic and architectural structures. Bridging the gap between molecular characteristics and bulk properties

remains a continuing challenge to both the chemical and material sciences. In the structures of one-dimensional coordination polymers, a well-defined cooperative interactions between discrete molecules provide a continuum between the fields.

Molecular based ferromagnets, synthetic-metal conductors, non-linear optical (NLO) materials and ferroelectric materials are among the most important applications of such coordination polymers.

1.2.1 Molecular Ferromagnets

In the 1980's, several prototypes of the light-weight molecular magnets, emerged, based on one-dimensional coordination polymers.⁽⁵⁷⁾ These molecular based magnets are in contrast to the traditional atom-based inorganic magnetic materials. Antiferromagnetism, ferrimagnetism and ferromagnetism all originate from the cooperative behaviour of magnetic spins within a solid. For molecular-based magnets, an appropriate molecular structure must be designed to avoid the antiferromagnetic coupling of spin centres.⁽⁵⁸⁾ To design molecular materials displaying a zero-field magnetisation below some critical temperature T_c , one must assemble paramagnetic molecular units so that the interaction between the local spin carriers results in a non-zero spin on the bulk material scale.

At first glance, one might expect antiferromagnetic and ferromagnetic coupling to be equally likely. However, less than 5% of well characterised dinuclear complexes have been reported to be ferromagnetically coupled.⁽⁵⁹⁾ Ferromagnetic coupling results only if the state of high spin multiplicity is more stable than that of low spin multiplicity. A general strategy to achieve the ferromagnetic coupling between two spin centres is to make the magnetic orbitals of adjacent centres orthogonal. This proves to be a synthetically difficult task.^(60,61)

The first approach is represented by the work of Gatteschi and co-workers on metal complexes of nitronyl oxides, the 2-substituted-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NIT-R).^(62,63) With one stable unpaired electron delocalised over two equivalent N-O groups, NIT-R can form linear chains by bridging two individual metal complexes. For example $[M(\text{hfac})_2(\text{NIT-R})]_n$.



derived from $M(\text{hfac})_2$, where M is Mn(II) , Ni(II) or Cu(II) and hfac is hexafluoroacetylacetonate (Fig.1.5). The magnetic properties of these polymer chains can be either ferromagnetic (as with Cu(II)) or alternating spin ferrimagnetic (as with Mn(II) or Ni(II)). The nitronyl oxides not only acts as the bridging ligand for the chain structure but also provide the unmatched spin. This leads to non-compensated net moments after antiparallel alignment with those of metal ions.

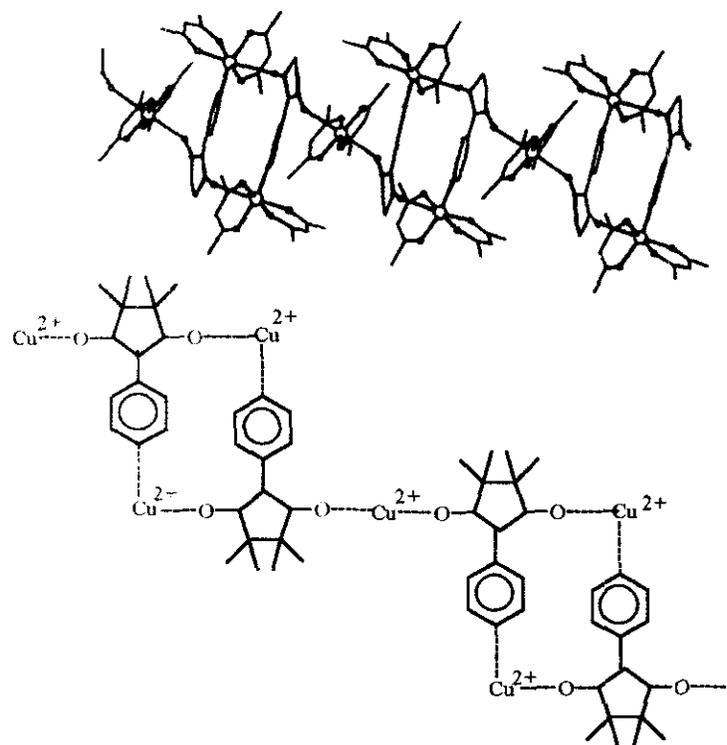


Fig. 1.5 The chain structure formed by dimeric $[\text{Cu}(\text{hfac})_2(\text{NIT-pPy})]_2$ unit bridged by $\text{Cu}(\text{hfac})_2$

The ordered biheterometal approach is illustrated by the work of Kahn and co-workers.⁽⁶⁴⁻⁶⁶⁾ They used Cu(II) complexes of the diamagnetic ligand 1,3-propylenebis(oxamate) and its 2-hydroxy derivative (pba and pbaOH, respectively) as the building blocks for the polymeric chains. The two sets of α -dicarbonyl groups on $[\text{Cu}(\text{pba})]^{2-}$ and $[\text{Cu}(\text{pbaOH})]^{2-}$ can coordinate to different metal ions, thus forming equally spaced biheterometallic chains. If Mn(II) or Ni(II) ions are coordinated to the Cu complex, then the two local spins ($S=1/2$ of Cu(II) vs $S=5/2$ of Mn(II) or $S=1$ of Ni(II)) will be non-compensable even

with antiferromagnetic coupling. It has been shown that a spontaneous ferromagnetic magnetization occurs in $[\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3]_\infty$ at 5K. $[\text{MnCu}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}]_\infty$, however, orders antiferromagnetically at 2.2K. Although these compounds have very similar chain structures, the relative positions of the chains within the lattice are slightly different.

1.2.2 Metallic and Superconducting Polymers

Electrical conductivity of polymers continues to be one of the most important research areas for material science. The conductivity of metals (typically $10^2 \sim 10^3 \text{ } \Omega^{-1}\text{cm}^{-1}$ at room temperature) are generally higher than semiconductors, but it is the temperature dependence that truly defines the difference; electrical conductivity of metallic substances increases with decreasing temperature, while that of a semiconductor decreases.

The interest in superconducting materials parallels the interest in synthetic metals. In a sense, the copper oxide high temperature superconductors (eg, $\text{Yb}_2\text{Cu}_3\text{O}_{7-x}$ with $T_c \sim 95\text{K}$) are two-dimensional coordination polymers.^[67,68]

Another class of synthetic metals is based on π -conjugative organic molecules which form one-dimensional stacks or two-dimensional sheet structures.^[69,70] TTF-TCNQ (TTF=tetrathiofulvalene, TCNQ= tetracyanoquinodimethane) was the first organic with metallic conductive behaviour. This class of molecular-based conductors possesses an important structural feature: segregated, double one-dimensional stacks with partial charge-transfer between stacks. This has become a common model for most other synthetic organic conductors. In a few cases, coordination polymers of anions promote the superconductivity of these materials. For example in $\beta\text{-(ET)}_2\text{X}$ (where ET = bis(ethylenedithio)tetrathiafulvalene; X = IBr_2^- , AuI_2^- and I_3^-), the longer the anions, the higher the superconducting transition temperature; $T_c = 2.8, 5$ and 8K for X = IBr_2^- , AuI_2^- and I_3^- respectively. This suggests that, if the anions form a polymeric sheet-like 2D structure, the anticipated donor radical network is expected to be layer-like similar to the proven organic superconductors.



Another type of one dimensional coordination polymer conductors has direct overlap of dz^2 orbitals of metal atoms. Best known are the cyanoplatinum salts $[\text{Pt}(\text{CN})_4]^{n-}$ (discussed in section 1.1.2.5 and 1.1.2.6) and halocarbonyl iridium salts $[\text{Ir}(\text{CO})_2\text{Cl}_2]^{n-}$. They both are cation-deficient salts (with $n < 1$) and have metal-metal distances shorter than 2.9\AA .

A large number of planar metal complexes also form (discussed in section 1.1.2.9, Shiskabob polymers) one-dimensional stacked structures. Although there is a variety of possible spatial arrangements for the one dimensional stacking structures (Fig.1.6) they all suffer instability and none are superconductors even at low temperatures.

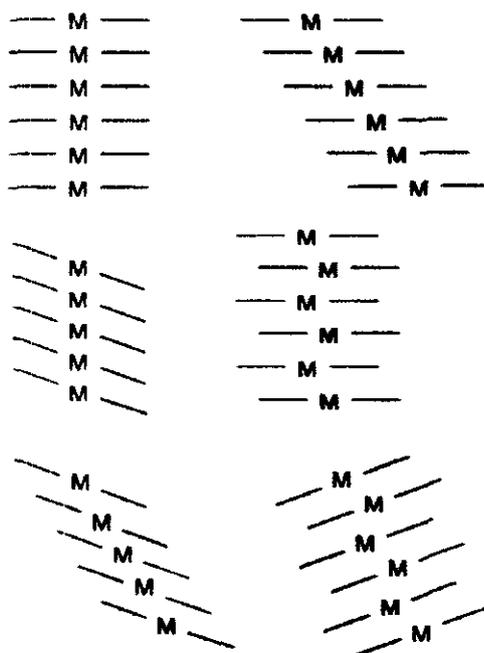


Fig. 1.6 One-dimensional stacked metal complexes with a variety of spatial arrangements

Phthalocyanine complexes have been intensely studied as coordination polymers. Its polysiloxane polymers $[\text{M}(\text{Pc})\text{X}]_n$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}; \text{X} = \text{O}$) were first synthesized in the early 1960s by Joyner and Kenney from dehydration of dihydro derivatives (discussed in Section 1.1.2.9.a) $\text{M}(\text{Pc})(\text{OH})_2$ *in vacuo*. Similar polymeric structures with $\text{M} = \text{Al}, \text{Ga}, \text{Cr}; \text{X} = \text{F}$ have been reported. The structure of these single atom bridged polymers was not verified until the X-ray single crystal structure of

the fluoro-bridged gallium phthalocyanine $[\text{Ga}(\text{Pc})\text{F}]_n$ was obtained in 1982. The conductivity of these polymers was heavily studied by Kenney and co-workers and Marks and co-workers. These single-atom bridged polymers, doped by halogens or other inorganic or organic acceptors result in dramatic enhancements in electrical conductivity as well as in the appearance of the characteristic magnetic and optical signatures of a molecular metal.

Recently Collmann et al reported similar Shiskabob polymers of the type $[\text{M}(\text{OEP})(\text{L-L})]_n$ ($m = \text{Fe, Ru, Os}$ and $\text{L-L} = \text{pyz, dabco}$) and examined their conductivities. Many of these coordination polymers can be doped with iodine which drastically increases their conductivity (Fig.1.7).

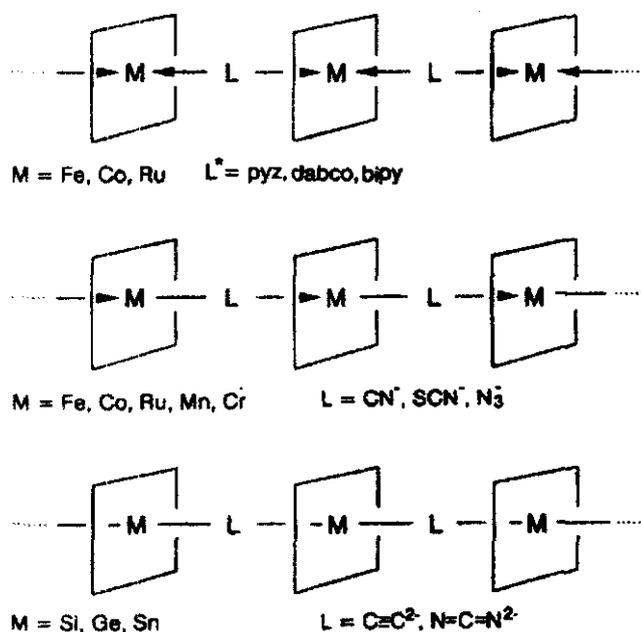


Fig.1.7 Various “shiskabob” one-dimensional coordination polymers

1.2.3 Non Linear Optical Materials

Enormous efforts are being made in the development of NLO materials for their use in frequency conversion and intensity modulation.⁽⁷¹⁾ There are two common classes of NLO materials; inorganic metal oxides or phosphates with distorted metal oxygen octahedral structures (eg, LiNbO_3 , KTiOPO_4 , KH_2PO_4) and organic



molecular solids composed of donor-acceptor substituted aromatic molecules (eg, 2-methyl-4-nitro aniline and 3-methyl-4-nitropyridine-N-oxide).⁽⁷²⁾ More recently, poled organic polymer films containing NLO organic molecule are finding potential applications in the fabrication of integrated electro-optical circuits. There are, however, only a few cases of one-dimensional coordination polymers studied for their NLO properties.

Metal-nitrido complexes have also been known to form polymeric chain structures. The polymeric chains consist of alternating short (<1.7 Å) and long (>2.6Å) M-N bonds, corresponding formally to triple and weak dative single bonds, respectively. The alternating bond system $-N-M\equiv N-$ can be regarded as an inorganic analog of hydrocarbon polyenes and polyynes whose NLO properties have been extensively studied.

Thompson and co-workers synthesized one-dimensional coordination polymers of $M(\text{SALEN})(X)$ where $M = \text{Cr, Mn, Fe}$ and Co and $X = \text{NCCH}_2^-$, $\text{NC}_5\text{H}_4\text{NHCH}_2\text{CO}_2^-$ and $\text{NC}_5\text{H}_4\text{NHCH}_2\text{SO}_3^-$ (Fig.1.8a).⁽⁷³⁾ $M(\text{SALEN})(X)$ complexes form dipolar coordination polymer in the solid-state because of the bridging ligands. The bridging ligand have donor and acceptor substituents and align in a head to tail direction forming a polar polymer chain in the solid state, as shown in the crystal structure of $[\text{Mn}(\text{SALEN})(\text{O}_3\text{SCH}_2\text{NHC}_5\text{H}_4\text{N})]_\infty$.

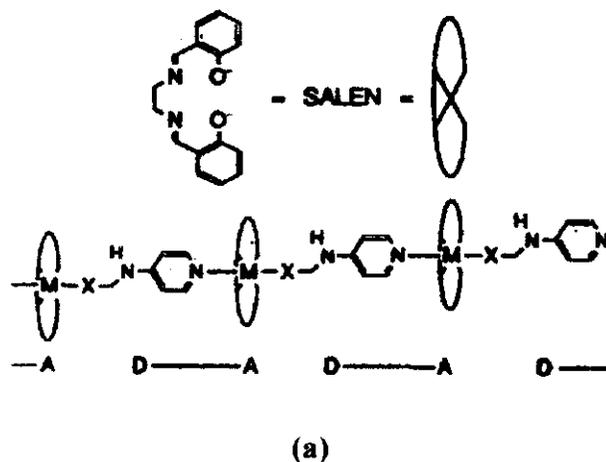


Fig.1.8a Structure of SALEN and dipolar coordination polymers

Due to the non-linear geometry of RCO_2^- and RSO_3^- , the chains propagate in a zigzag fashion resulting in an almost perpendicular orientation of the adjacent SALEN rings. The intramolecular charge-transfers (ICT) of these polymers originate from both the M(SALEN) centre (MLCT or LMCT) and the donor-acceptor substituted bridging ligands. The configuration of zig-zag polymer chain results in a partial cancellation of the overall polarisation, thus reducing the SHG efficiencies of these polymers. Furthermore, these polymers tend to pack with an antiparallel arrangement, which makes them ineffective for second-order NLO properties.

1.2.4 Ferroelectric Materials

Very little work has been done on the development of coordination polymers as molecular based ferroelectric materials. Ferroelectrics carry a permanent, macroscopic electric dipole moment (polarisation) in the absence of electric field. Furthermore, the polarisation of ferroelectric materials can be switched with the application of an electric field. Ferroelectrics have unusual electro-optical, photorefractive and pyroelectric properties. They can be fabricated into electronic oscillators, high frequency filters, electroacoustic converters, pyroelectric radiant-energy receivers, and non-linear capacitive elements.

In a further development of Shiskabob class of polymer, metallo porphyrin coordination polymers have been suggested as possible ferroelectric materials.⁽⁷⁴⁻⁷⁶⁾ Coordination polymers of non-planar metalloporphyrins with non-symmetrical bridging ligands carry a net and aligned dipole moment along the stacking axes (Fig. 1.10). The dipole moment originates from the charge separation between the bowl shaped porphyrinato core and the metal atom. Metal atoms tend to be pulled out of the porphyrin plane by a stronger axial ligand. If the metallo porphyrin has two different axial ligands, the metal atom will be pulled towards one side or the other, depending on relative ligation strength and steric demands (Fig.1.9).



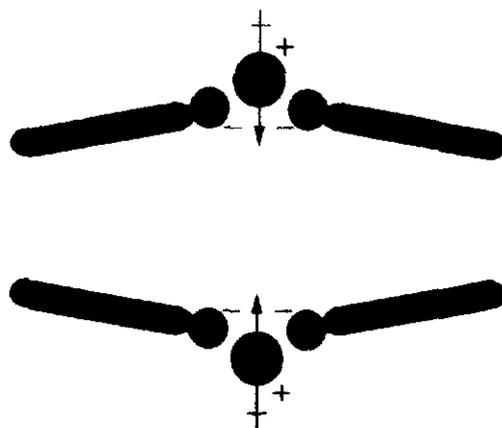


Fig.1.9 The dipole moment of metalloporphyrins

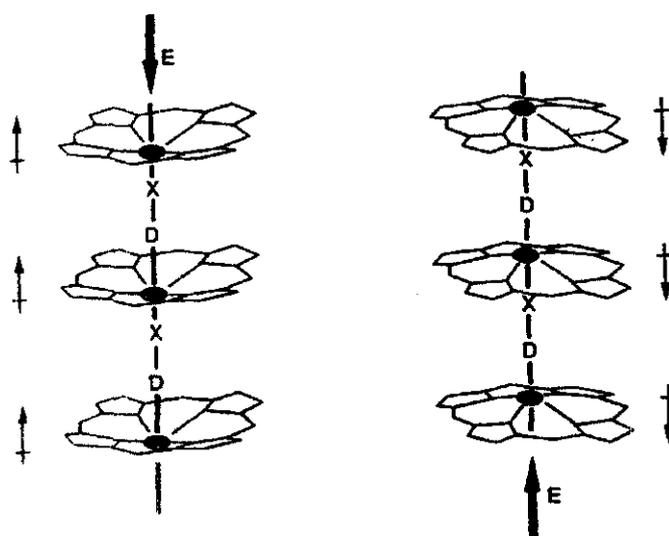


Fig.1.10 Schematic representation of ferroelectric coordination polymer and dipole moment switching in response to an external field

Owing to the fundamental importance and versatile material utilities as briefly mentioned above, work in the area of developing new variety of coordination polymers is of great significance. Our effort in this thesis is to develop some linearly linked polymeric metal complexes which are expected to have interesting one-dimensional features. Mentioned in Chapter 2 are some of our specific objectives in brief.

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