

## *CHAPTER I*

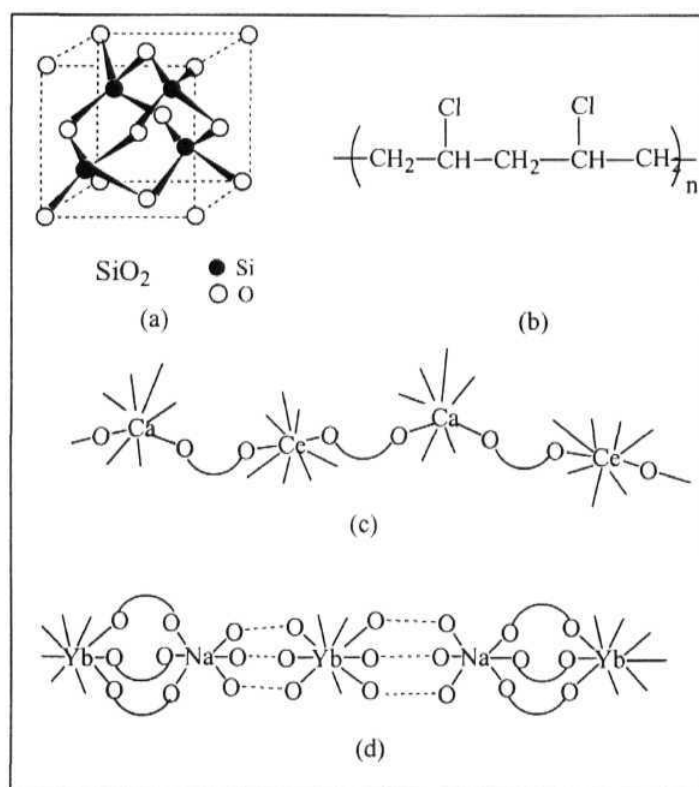
### **Coordination Polymers - A Brief Review**

#### **1.1. Introduction**

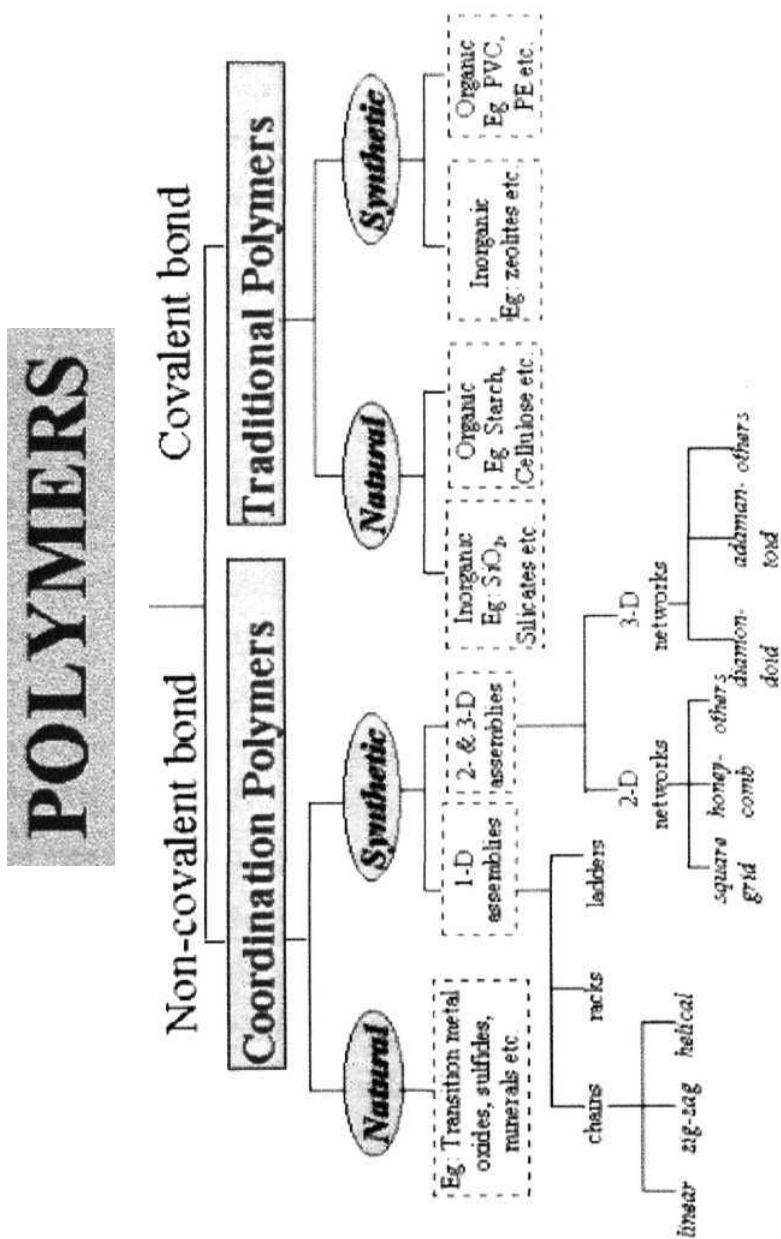
Classically, polymers were recognized as compounds with several repeat units connected to each other extending over a long range. Several polymers, both organic and inorganic in nature, were known since more than a century. The prominent examples include starch, cellulose, rubber, silica and minerals. The structures of naturally occurring silica, silicates and other minerals may all be considered as polymeric in nature in a broad sense, as they extend in all the three dimensions by the connectivity of the repeat units. Mimicking natural systems, the first polymers synthesized were primarily organic in nature, where the carbon atom formed the backbone of the chain. These organic polymers were built by a handful of elements like C, H, N, O, S and halogens. The classical covalent bond functioned as the connecting link between the repeat units in all these polymeric systems. These organic polymers, typically polyethylene (PE) and polyvinylchloride (PVC) brought such a revolutionary change in the human life that they were recognized as new generation materials of the 20<sup>th</sup> century. The first organic polymers synthesized were polyvinyls first made in 1838, followed by polystyrene. Closely parallel to the research in organic polymer chemistry, the field of coordination chemistry developed with the pioneering work of the Swiss chemist Alfred Werner during 1866 - 1919. It was later realized that the coordination complexes can also be

connected to each other through bridging ligands. The metal - ligand bond was initially termed semi-polar bond by Lowry and later as coordinate covalent bond by Sidgwick.<sup>1</sup> Structures formed by the coordinative linking of the bridging ligands to the metal centers were termed as "coordination polymers" by Bailar.<sup>2</sup> In such cases, the coordinate bond acting as the connecting thread between the monomeric complex repeat units, was treated similar to the covalent bond. Hence, any structural entities with metal elements forming the polymeric backbone were traditionally treated as coordination polymers.<sup>3-4</sup> With research progressing rapidly, besides the coordinate bond, other forces like hydrogen bond, stacking interactions, atom - atom interactions and atom -  $\pi$  interactions, which are weak compared to the covalent bond, were also found to be capable of assembling the repeat units, thus giving rise to polymeric structures.<sup>5</sup> Being very weak in nature (usually  $< 40$  kcal/mol), these forces were called non-covalent forces. As the energy of coordinate bond is nearly same as these weak forces and also it differs from the covalent bond in terms of electron pair contribution to the bond, the coordinate bond was later recognized as a non-covalent force along with others. Therefore, in modern terms the coordination polymers may be defined as *structural entities formed by a large number of repeat units made of coordination complexes connected intermolecularly through the operation of non-covalent forces*. The traditional polymers connected by covalent bond and the modern coordination polymers connected by non-covalent bonds are shown in Figure 1.1. The repeat units of these coordination polymers may be made of a single metal atom or often two (or more) metal atoms. The two metal atoms may be same or different giving rise to either homobimetallic or heterobimetallic coordination polymers. When the polymeric chain made of homo- or heterometallic repeat units extends in space in one dimension, one-dimensional (1-D) coordination polymers result, while extension of

while extension of repeat units in two or three dimensions gives rise to two or three dimensional (2- or 3-D) networks. Scheme 1.1 differentiates between covalent and coordination polymers.



**Figure 1.1** Schematic representation of covalently connected (a) silica and (b) polyvinyl chloride; (c) coordinatively connected coordination polymer in  $\text{Ce}(\text{dipic})_3\text{Ca}(\text{dipicH}_2)(\text{OH}_2)_3 \cdot 5\text{H}_2\text{O}^6$  and (d) alternating coordinate and hydrogen bonded polymer in  $\text{Na}_3[\text{Yb}(\text{dipic})_3] \cdot \text{NaClO}_4 \cdot 10\text{H}_2\text{O}^7$ .

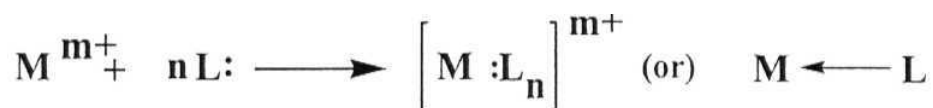


**Scheme 1.1** Various kinds of polymers based on the type of bond present.

## 1.2. Definition of the non covalent forces

In decreasing order of energy, the weak forces are described as follows.<sup>8,10</sup>

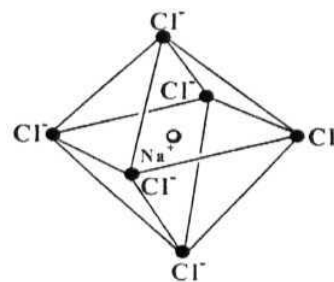
**(a) Coordinate Bond:** This is the basic linkage involved in the formation of all coordination complexes and acts as a primary link in connecting the repeat units of coordination polymers. Though first treated as a *semi-polar bond* by Lowry due to the inequality of charge distribution that arises during the bond formation, the term "coordinate covalent bond" was given by Sidgwick for bonds of this type<sup>1</sup> as represented in Scheme 1.2. Energy of this bond lies approximately in the range 40 - 100 kcal/mo l.



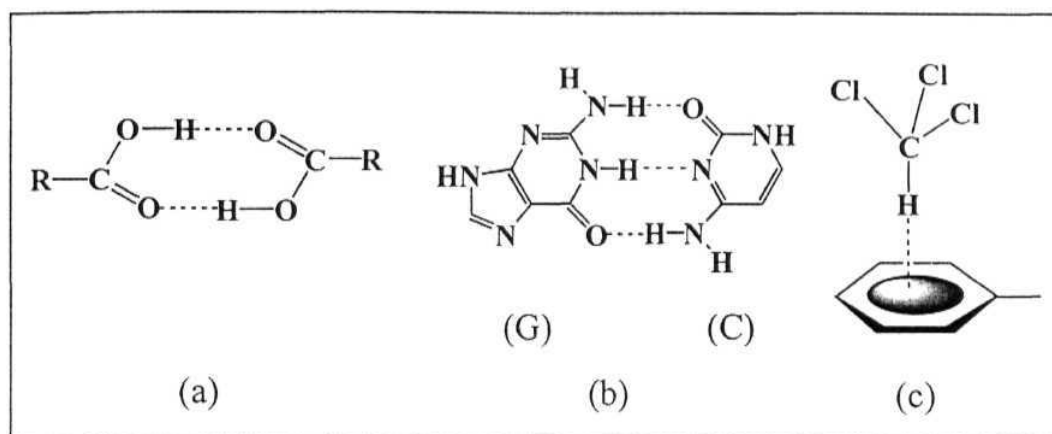
where M is the metal ion; L is the ligand; m+ is the primary valency and n is the secondary valency of the metal ion.

Scheme 1.2 Pictorial representation of the coordinate bond.

**(b) Ion - Ion Interactions:** Weak attractive interactions existing between ions as in the crystal lattice of NaCl are known as ion - ion interactions. These are non - directional and purely electrostatic in nature. Energy of this interaction lies usually in the range 25 - 80 kcal/mol. A representation of the cation surrounded by the six nearest neighbour anions in NaCl crystal is shown in Figure 1.2.

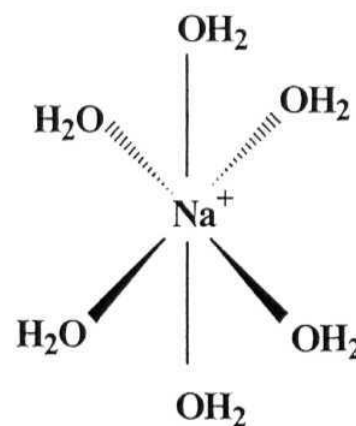


**(c) Hydrogen Bond:** This force comes next in the energy scale for non-covalent interactions and is often exploited for the deliberate design and synthesis of novel coordination polymers. Conventionally, hydrogen bond is a weak interaction operating between hydrogen atom covalently bonded to an electronegative atom (referred to as hydrogen bond donor, D) and another electronegative atom (referred to as hydrogen bond acceptor, A) and included all bonds like O-H...O in water and carboxylic acid dimers (Figure 1.3a) and N-H...O in DNA base pairs (Figure 1.3b). Later on, the interactions between less electronegative donors like C, and acceptors like O, Cl and the  $\pi$  cloud of phenyl ring were also recognized as weak non-conventional hydrogen bonds which include C-H...O, C-H...X and C-H... $\pi$  interactions (Figure 1.3c). The hydrogen bond energy ranges from 4 - 40 kcal/mol. for the “strong” type and less than about 4 kcal/mol. for the “weak” bonds.<sup>11</sup> Extensive literature discussing the nature, strength and importance of hydrogen bond as a design element,<sup>11-17</sup> its directional and metrical properties,<sup>18-19</sup> role in the directed structure formation<sup>20-25</sup> and its influence on the structure stabilization,<sup>21,26-31</sup> and the resulting properties<sup>32,36</sup> is available. The relevance of hydrogen bond in structural biology is well described by Jeffrey and Saenger.<sup>37</sup>



**Figure 1.3** Schematic representation of commonly seen strong hydrogen bonds in (a) acid dimer (b) DNA base pairs Guanine(G) and Cytosine(C) and (c) the weak hydrogen bond seen in chloroform - phenyl interactions.<sup>38</sup>

**(d) Ion - Dipole Interactions:** The attractive interactions operating between an ion and a dipole may be regarded as ion - dipole interactions. These are directional interactions and fall off with distance as a function of  $1/r^2$ . This interaction is responsible for the solvation of ions (Figure 1.4), dissolution of ionic solids like NaCl in polar solvents like H<sub>2</sub>O and attraction between M<sup>n+</sup> and crown ethers. The interaction has energy in the range 12 - 50 kcal/mol.



**Figure 1.4**

**(e) Dipole - Dipole Interactions:** These are the attractive forces arising from the alignment of dipoles relative to each other with energies in the range 1-12 kcal/mol. These interactions may be operational in a head to tail arrangement of dipoles as shown in Figure 1.5a or in an antiparallel arrangement as shown in Figure 1.5b for the carbonyl dipole. These are weaker than the ion-dipole interactions and fall off rapidly with distance ( $1/r^3$ ). These interactions are also directional and are responsible for the association and structure of polar liquids.

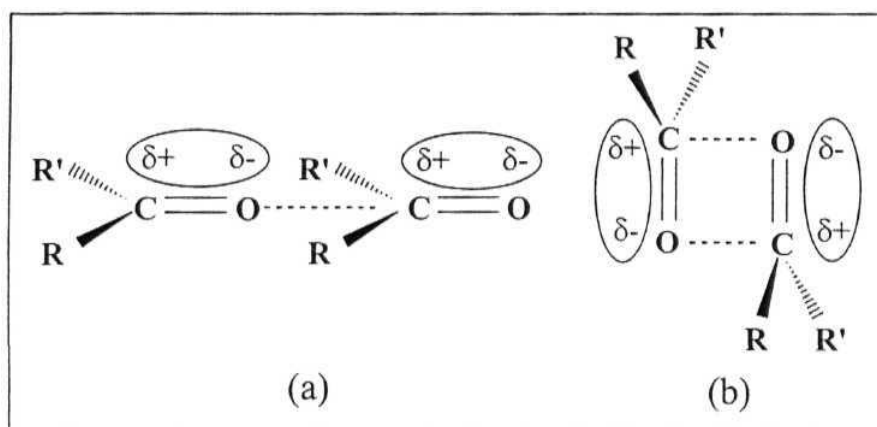
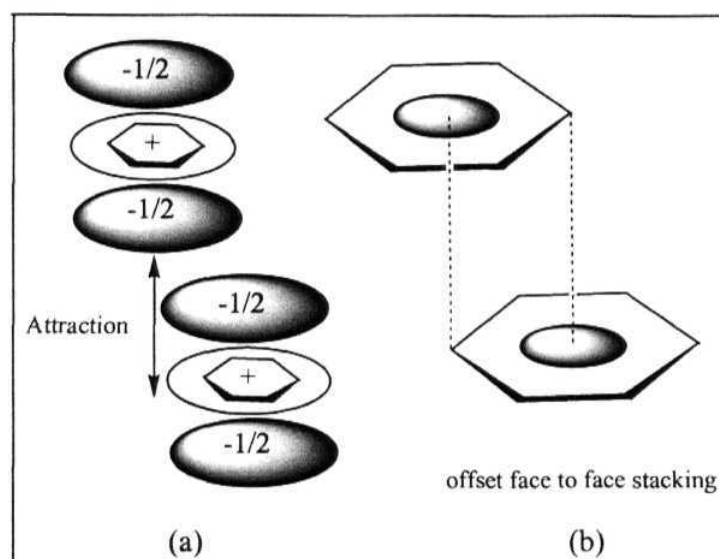


Figure 1.5 (a) Head-to-tail and (b) anti-parallel arrangement of dipoles in carbonyls.

**(f) Stacking ( $\pi \cdots \pi$ ) Interactions:** This interaction is due to a weak attractive force operating between the  $n$  electron clouds of two aromatic rings. According to Sanders and Hunter,<sup>39</sup> this arises because of the attraction between the negatively charged  $n$  cloud of one molecule and the positively charged  $\sigma$  framework of its adjacent molecule (Figure 1.6a). There are perhaps no examples of perfect face to face stacking but offset face to face stacking (Figure 1.6b) is seen where one ring is slipped



relative to the second ring. This offset face to face stacking may be thought of as responsible for the slippery feel of graphite and its lubricant properties. Several intermediate geometries may also be present depending upon the steric requirements. The nature and role of this interaction in molecular recognition has been reviewed by Hunter.<sup>40</sup> There are several examples for the role and influence of this interaction in stabilizing structures and giving rise to specific properties.<sup>41,54</sup>

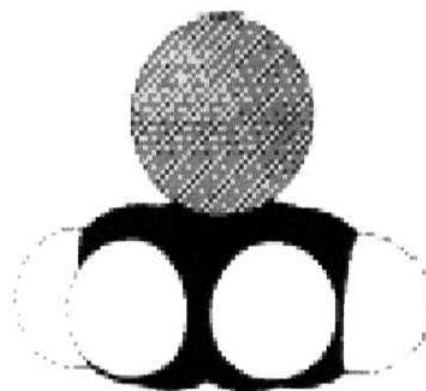


**Figure 1.6** Aromatic  $n$  stacking: the attractive interactions operating between  $\pi$  cloud and  $\sigma$  framework of the aromatic ring (a) leading to an offset face to face  $\pi - \pi$  stacking (b).<sup>39</sup>

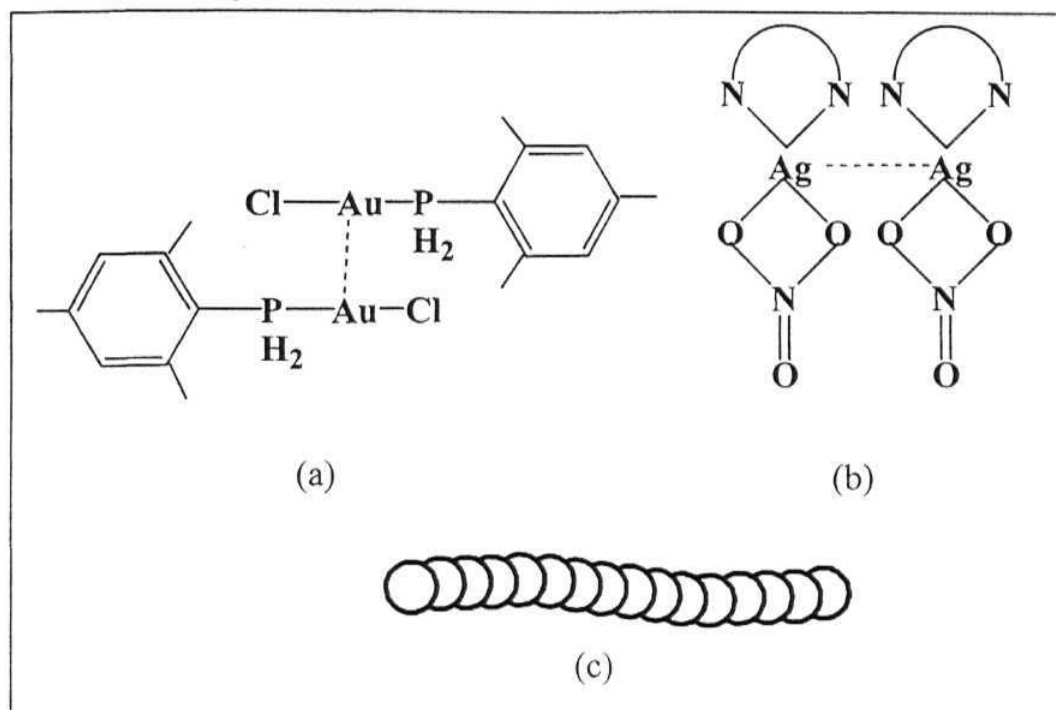
**(g) Atom -  $n$  Interaction:** This is a similar type of interaction as stacking, but instead of operating between two  $n$  clouds, it operates between an atom or a cation and a

$n$  cloud of an aromatic ring or double bond. Typical interactions of this kind are the ones operating between  $K^+$  and benzene (Figure 1.7). It has been shown that this interaction has energy in the range 10-40 kcal/mol. in the case of simple ions like  $K^+$ ,  $Na^+$  etc. with benzene ring and in the range 10-20 kcal/mol in the case of alkylated ammonium ions and substituted benzenes. The nature of this interaction, a physical model for it and its presence in biological structures and synthetic systems has been reviewed recently by Ma and Dougherty.<sup>55</sup> The distance dependence is proposed to be  $1/r^n$  ( $n < 2$ ). In a recent report, Lindemann et al. examines the structural features of  $Ag \cdots$ arene interaction.<sup>56</sup> Besides, this type of interaction observed between  $Ag^+$  and toluene,<sup>57</sup>  $Cs^+$  and imidazole,<sup>58</sup> there are examples of atom- $\pi$  interaction like  $S \cdots \pi$ <sup>59,60</sup> where S atom points normally to the center of the ring.

**(h) Atom - Atom Interactions:** Weak intermolecular attractive interactions operating between two identical or similar atoms may be termed as atom - atom interactions. This force may be thought of as mainly operating due to charge polarization, when the electron density around one nucleus is attracted by the second nucleus and vice-versa. There are several examples of solid state structures stabilized by



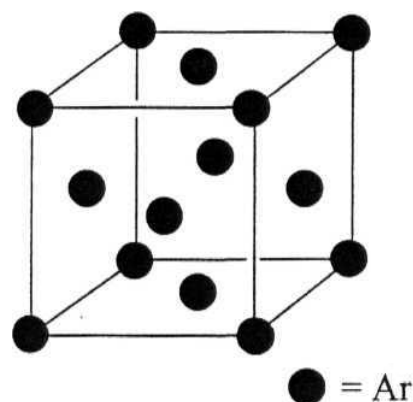
**Figure 1.7**  $K^+$  - benzene complex (gas phase) at its optimized geometry.<sup>55</sup>



**Figure 1.8** (a) Au...Au interactions in  $[2,4,6-(t\text{-Bu})_3\text{C}_6\text{H}_2\text{PH}_2\text{AuCl}]_2$ <sup>75</sup>  
 (b) Ag...Ag interactions in  $\text{Ag}(\text{dmbp})\text{NO}_3$ <sup>76</sup> (c)  $\text{I}_8^{2-}$  chains formed by  
 "normal" as well as weak I...I interactions in  $\text{Mn}(\text{bpy})_3\text{I}_8$ .<sup>77</sup>

**(i) Van der Waals Interactions:** Forces arising out of the polarization of an electron cloud by an adjacent nucleus due to momentary imbalance in electron distribution resulting in weak electrostatic attraction may be termed as van der Waals interactions. Also known as London dispersion forces, these are the weakest of all known forces available to a chemist. These interactions operate only at very short distances and

fall off very rapidly ( $1/r^6$ ). These are non-directional and have energy  $< 1$  kcal/mol. These weak interactions are responsible for the liquefaction of noble gases and the formation of inclusion compounds. Figure 1.9 shows the close packed structure of Ar in the crystal lattice.<sup>78</sup>



**Figure 1.9**

### 1.3. Synthetic Strategy

**(a) Self - Assembly Approach:** The main strategy for synthesizing coordination polymers or networks involves metal ion directed self assembly. In the present context, self-assembly may be defined<sup>79</sup> as the spontaneous association of either a few or many molecular components under equilibrium conditions resulting in stable, structurally well defined aggregates joined by non-covalent bonds. The components that undergo self - assembly are called tectons, tecton meaning builder in greek. These builder units may in all probability be the metal ions and ligands of the polymer chain repeat units. The spontaneous association takes place through the recognition of the complementary tectonic units under the control of the non-covalent interactions operating intermolecularly. For these tectons to associate, their reacting sites should have favorable spatial disposition such that their complementary sites can approach closely by recognition, which may lead to interaction without any steric inhibition. Self- assembly of an architecture is a multi - step process which involves reversibility of the connecting

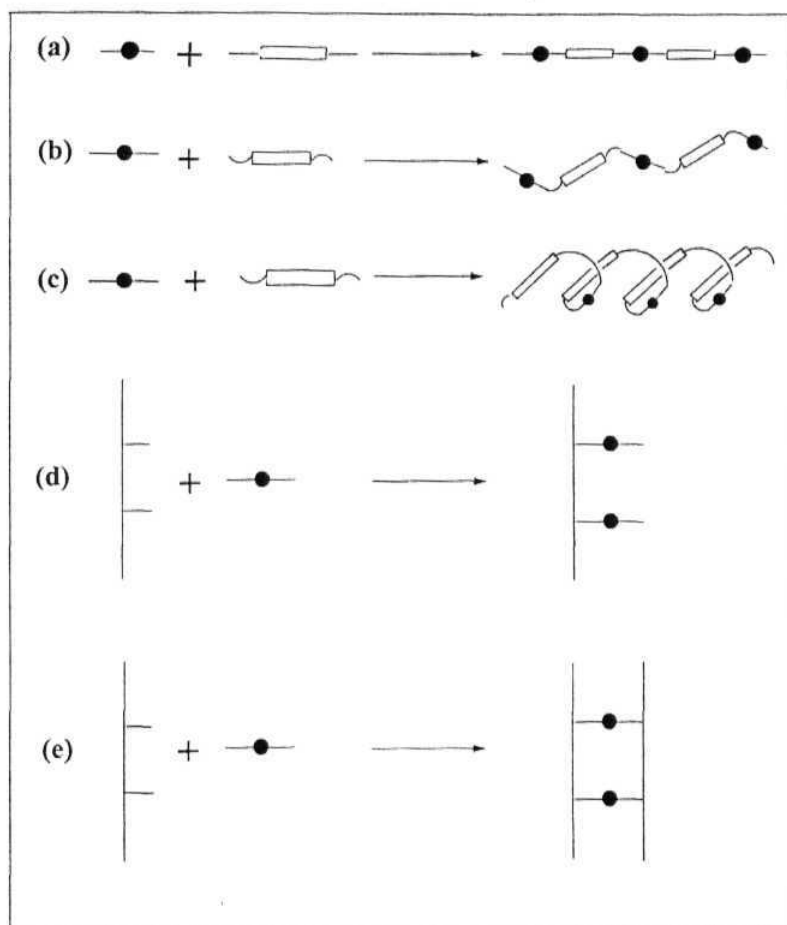
events in order to achieve global energy minimum. The kinetic lability offers such recognition induced self - assembly systems, the ability to undergo annealing and self - healing of defects. This is possible only because the forces involved in bond making and breaking in these systems are weak non - covalent interactions. Such a process is not seen in covalently linked systems involving relatively non - labile species and stronger bonds. The role of recognition and self - assembly in achieving various types of solid state structural entities like linear chains,<sup>80,90</sup> zig-zag chains,<sup>57,86,91,98</sup> helicates,<sup>99,100</sup> helical chains,<sup>100-121</sup> 1-D racks,<sup>122,124</sup> 1-D ladders,<sup>31,47,64,125,127</sup> supramolecular boxes,<sup>128-129</sup> capsules,<sup>130</sup> 2-D square networks,<sup>131,135</sup> 2-D honeycomb networks,<sup>136,141</sup> diamondoid networks,<sup>142</sup> adamantoid networks,<sup>43,44,142,146</sup> nanostructures,<sup>147</sup> and other possible structural motifs<sup>148</sup> have been reviewed. Some of the structural motifs are represented in Scheme 1.3.

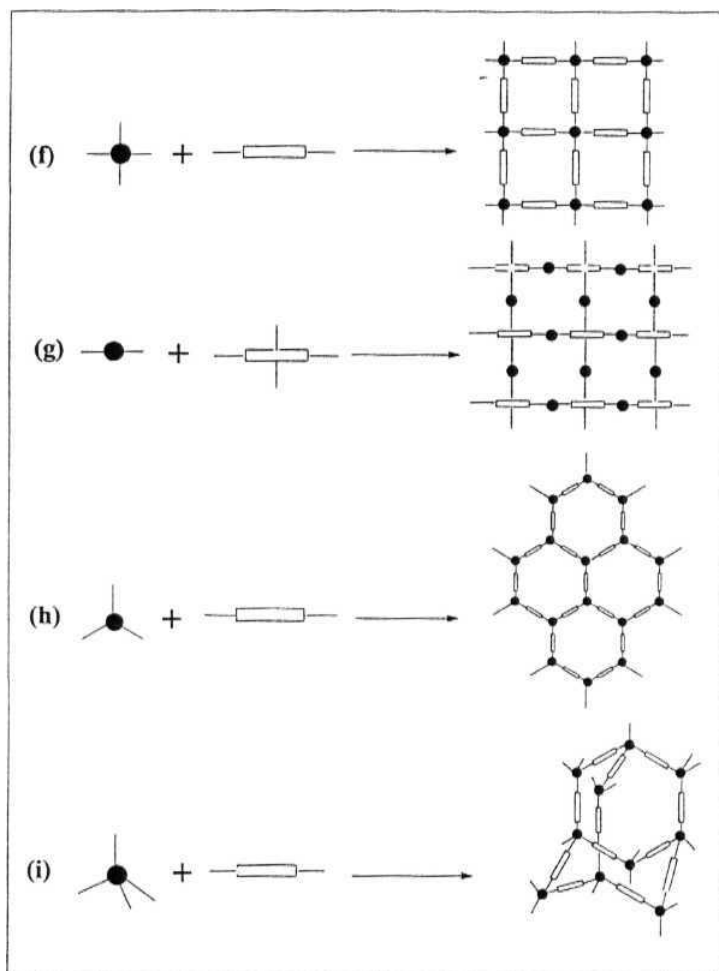
(b) Hydrothermal **Synthesis:** While self-assembly from solutions under ambient conditions has been very fruitful for the synthesis of non-covalent structures, hydro(solvo)thermal procedures are sometimes employed. This method involves a one pot reaction at high pressures and temperatures. The best example for this type of reaction is the mineral formation in earth's crust, where temperatures above 100 °C and pressure above 1 bar are provided naturally. Mimicking these conditions this method was originally used by geologists and mineralogists to understand the geological processes that led to mineral formation. In industry, this method has been used extensively to prepare pure quartz crystals with sufficiently large size to study its properties for varied applications.

This method has the following advantages over the conventional chemical methods:

- (a) To obtain compounds with elements in oxidation states that are otherwise difficult to obtain,
- (b) to obtain low temperature phases,
- (c) to obtain metastable compounds and
- (d) for getting single crystals of new compounds which are otherwise difficult to obtain.

Application of this method for growing single crystals for various purposes and the role of hydro thermal synthesis in preparative chemistry have been reviewed .<sup>149-152</sup> In recent times, several polymeric coordination compounds were synthesized using this method as a preparative tool, which exhibit properties like magnetism,<sup>153,155</sup> luminescence,<sup>84,125-156-157</sup> nonlinear optical activity,<sup>158,159</sup> and microporosity.<sup>160</sup> A recent review by Feng and Xu<sup>161</sup> gives an overview of different materials being synthesized using this technique, while the review by Hagrman et al.,<sup>151</sup> illustrates use of this method in the preparation of organodiamine templated molybdenum oxides.





Scheme 1.3 (a) 1-D linear chain (b) 1-D zig-zag chain (c) 1-D helical chain (d) 1-D rack (e) 1-D ladder (f & (g) 2-D square network (h) 2-D honeycomb network (i) 3-D adamantoid network. From (a) - (e) only two coordinate metal ions are shown. In principle, metal ions with other coordination numbers and geometry may also form these structures.



#### 1.4. Factors Influencing Self-Assembly Process

Design of coordination networks takes into account the coordination characteristics (*viz.*, geometrical and ligand atom preferences) of the metal ion as well as the structural features (*viz.*, charge, multifunctionality, chelate and/or bridge forming ability) of the ligand.

The geometrical preference refers to the preferred coordination geometry (linear, trigonal planar, square planar etc.) of the metal ion in a complex under given set of conditions. Ligand atom preferences refer to the specific coordination of the metal ion to a specific atom of the ligand when there is a possibility of several atoms for binding. This tendency of coordination to a specific ligand atom is usually a consequence of the hard and soft acid-base nature of the ions.<sup>162</sup>

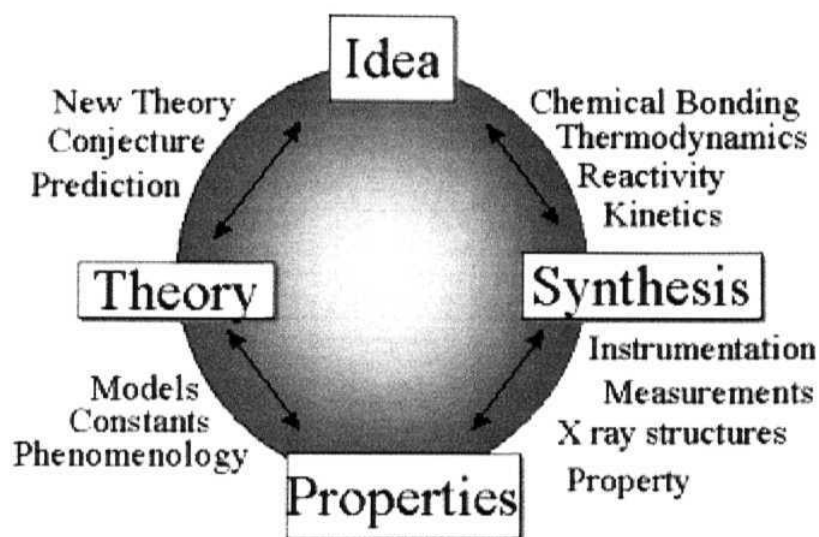
For a ligand, multifunctionality refers to the number of functional groups it possesses and thus the number of available sites for coordination. When a monofunctional ligand like pyridine with one coordinating site N, coordinates to a metal atom, complexation terminates there. But, for a ligand like aminomethylpyridine (amp) , along with the pyridine N atom, there is an amino N atom available for coordination. So, a single amp can bridge two metal centers by simultaneous coordination using both the N atoms. Hence, it can be understood that multifunctional ligands aid polymer or network formation. Besides these multifunctional ligands, there are examples of single atom bridges, mainly the halide and oxide bridges.<sup>71,163-167</sup>

Chelate or bridge forming ability refers to the ability of the ligand to function as a chelate or as a bridge between metal centers. Ligands like 1,10-phenanthroline and 2,2'-bipyridine can only function as chelates by coordinating to the adjacent (*cis*) sites of the

metal atom. Ligands like 2-amp can act as chelating as well as bridging ligand while its isomers 3-amp and 4-amp can act only as bridging ligands. The chelate formation is also influenced by the bite of the ligand and the ring dimensions. Though the ligand has adjacent coordinating sites which can give rise to chelate formation, the ring so formed will be stable only if it is not under strain. It has been observed that five membered rings are most stable as their geometry is optimum. Higher membered chelate rings are less stable and hence occur less frequently.

### **1.5. Applications of Coordination Polymers**

Rapid growth in the field of coordination polymers and networks in recent times can be attributed to their expected role as new materials like molecular magnets, metallic and superconducting polymers, optical (luminescence/SHG) materials, ion-exchangers and microporous solids. Further, the novel solid state structures they generate are often quite appealing and aesthetically pleasing. Figure 1.10 schematically illustrates how an idea can be turned to a new material with desired properties. A brief discussion of the applications of the coordination polymers is presented in the following paragraphs.



**Figure 1.10** Pictorial representation of the inter-relationship between an idea and other factors to achieve the desired property (adapted from ref. 170).

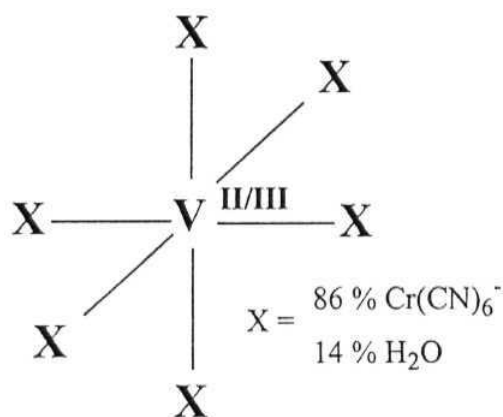
**(a) Molecular Magnets:** Molecular magnetism deals with the synthesis and characterization of new materials with predictable magnetic properties followed by correlation of the results to the proposed theory. It plays an important role in the emerging field of *molecular electronics*, where molecular magnetic systems are used in digital display systems and in devising novel magnetic systems useful for information storage and processing.<sup>168-170</sup> Kahn, in his famous book, "Molecular Magnetism"<sup>171</sup> gives an excellent account of the theory and examples of molecular systems exhibiting magnetic interactions. The goal of all studies in this field is to have FM materials which exhibit magnetic ordering at RT. With an aim to develop materials exhibiting magnetism

at RT, several systems have been designed and their magnetic behavior studied which often showed good FM or AFM interactions. High  $T_c$  (315 K) molecular magnet has been first realized in the prussian blue analog,  $V[Cr(CN)_6]_{0.86} \cdot 2.8H_2O$ .<sup>172</sup> This system is structurally similar to the prussian blue, except for the small variation in the geometry of  $V^{II}$ . As the stoichiometry of  $Cr^{III}$  to  $V^{II}$  (0.86/1) is less than 1, only 86% of the coordinating sites around V are occupied by the  $[Cr(CN)_6]^{3-}$  ions. The remaining 14% sites is filled by the water molecules, which are coordinated to V through the oxygen atoms. The overall structure is similar to the rock salt structure of prussian blue with short range order (Figure 1.11). From the IR data, a -  $Cr^{III}$  - C = N - ( $V^{II} / V^{III}$ ) sequence has been ascertained. The antiparallel spins of  $Cr^{III}$  (3/2) and  $V^{II}$  (3/2) cancel each other. But the uncompensated antiparallel spins of  $Cr^{III}$  (3/2) and  $V^{III}$  (1) give rise to short range anti ferromagnetic interactions. The AFM interaction explains the low saturation magnetization at 10 K. The long range order of the uncompensated antiferromagnetically coupled spins makes this system a high  $T_c$  ferrimagnet.

While the above system is a high  $T_c$  molecular magnet, it is a non stoichiometric as well as a mixed oxidation state material. Following this observation, the groups of Girolami and Miller reported similar non - stoichiometric and mixed oxidation state V and Cr systems, characterized by powder X-ray and having a formula  $KV^{II}[Cr^{III}(CN)_6] \cdot 2.8H_2O \cdot 0.1KOTf$  which has a  $T_c$  of 376 K<sup>173</sup> and  $K_{0.058}V^{II/III}[Cr^{III}(CN)_6]_{0.79} \cdot (SO_4) \cdot 0.93H_2O$  with  $T_c$  of 372 K<sup>174</sup> respectively. The 3D ferrimagnetic order in these systems have been suggested as a promising route to other high  $T_c$  molecular magnets.

Other recent systems with promising magnetic properties (transition towards FM or AFM) include heterobimetallic polymers involving dicyanamide anion;<sup>49138</sup>

bimetallic systems consisting of transition metals and  $U^{IV}$  with schiff base ligands;<sup>175</sup> infinite networks and chains with polynitrile ligands;<sup>143,176-180</sup> azide bridged networks;<sup>181-184</sup> 3-D stacked honeycomb systems;<sup>140,185</sup> linear chains;<sup>184,186-188</sup> free-radical systems<sup>34-189</sup> and clusters.<sup>190-195</sup> Besides these, there are examples of systems synthesized under hydrothermal conditions<sup>46-153</sup> exhibiting interesting magnetic properties. Also, there is a recent report of optically active molecular magnet.<sup>196</sup>



**Figure 1.11** First high  $T_c$  ferrimagnet,  $V[\text{Cr(CN)}_6]_{0.86} \cdot 2.8\text{H}_2\text{O}$ .

**(b) Metallic and Superconducting Polymers:** The review by Chen and Suslick,<sup>2</sup> gives an overall view of various coordination polymeric systems showing conductivity similar to that of metals. These include stacked structures having  $[\text{Pt(CN)}_4]^{2-}$  stacks, planar metal complexes like  $\text{Ni(Pc)(I}_3)_{0.33}$ , iodine doped polysiloxane polymers of phthalocyanine,  $[\text{M(Pc)X}]$ , ( $\text{M} = \text{Si, Ge, Sn, Al, Ga, Cr}$ ;  $\text{X} = \text{O, F}$ ) ( $\text{Pc}$  = the dianion of phthalocyanine), macrocyclic complexes linked by bridging ligands like  $[\text{M(Pc)(L-L)}]_\infty$  ( $\text{L-L} = \text{pyrazine, bipyridine, tz, CN}^-, \text{N}_3^-$  etc.). Also there are reports of metal coordinated

TTF systems<sup>197200</sup> showing good conducting properties when doped with iodine (5-7 orders of magnitude higher) than their undoped analogues. Extremely high metallic conductivity of the order  $500\,000\text{ Scm}^{-1}$  at 3.5 K and decreasing steadily with temperature, was found in the radical anion salt 2,5-Dimethyl-N,N'-dicyanoquinonediimine and Cu(I).<sup>52</sup> (Figure 1.12a). Iodine doped Ag(I) coordination polymer of TTM-TTP exhibiting good conductivity (RT conductivity  $0.85\text{ Scm}^{-1}$ )<sup>69</sup> was reported recently.

The well known high  $T_c$  ceramic based superconductors,<sup>201</sup> eg.,  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (Figure. 1.12b) can be considered as examples of 3D networked coordination polymers.

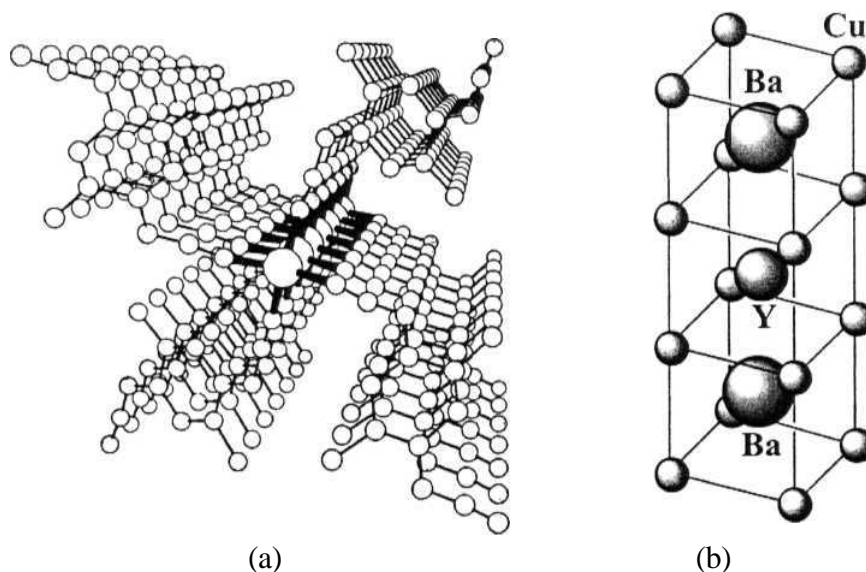
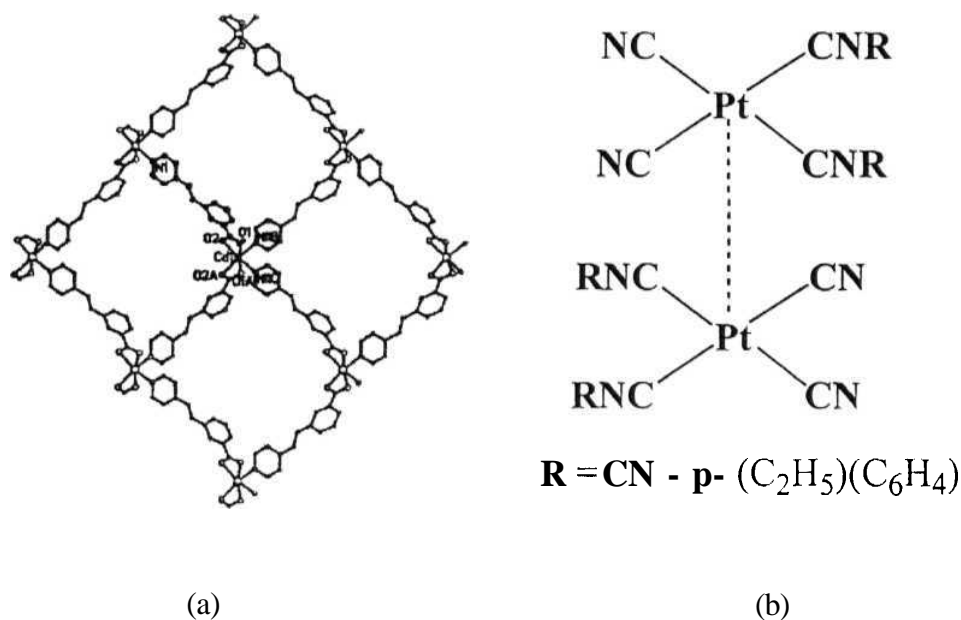


Figure 1.12 (a)  $n$  stacks responsible for metallic conductivity in the coordination polymer  $[\text{2,5-DM-DCNQI}]_2\text{Cu}$ <sup>52</sup> and (b) high  $T_c$  ceramic based superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .<sup>201</sup>

**(c) Optical (SHG/Luminescent) Materials:** The two optical properties of coordination polymers studied extensively are second harmonic generation (SHG) and luminescence, for their possible use in information acquisition, processing, storage and transmission. The non-linear nature of light and its associated property like SHG have a large impact on fields like telecommunications, signalling etc. This property is best exhibited by inorganic salts like potassium titanyl phosphate (KTP), potassium dihydrogen phosphate (KDP) and lithium niobate ( $\text{LiNbO}_3$ ). Other systems exhibiting good SHG response among coordination polymers include, a Ag coordination polymer,<sup>202</sup> 1-D helical chain made of heterobimetallic(La & Ag) clusters,<sup>110</sup> 1-D coordination polymer of  $\text{Mn}(\text{hfac})_2(\text{NIT-R})$ ,<sup>2</sup> square networks of Zn(II) and Cd(II) with *m*-pyridine carboxylates,<sup>158</sup> (Figure 1.13a) diamondoid networks of Zn(II) and Cd(II) with *p*-pyridine carboxylates,<sup>159</sup> and several  $\pi$ -conjugated organic systems.<sup>2</sup>

Besides exhibiting NLO activity, several self-assembled coordination polymers showing luminescence were reported. These luminescent compounds may find use in blue light emitting diode (LED) devices. Such systems include tetranuclear Cu(I) clusters,<sup>203-204</sup> 2-D layered polymers of Cu(I),<sup>157</sup> zinc coordination polymers assembled under hydrothermal conditions,<sup>156</sup> a tetranuclear Zn compound,<sup>205</sup> square grid compound of Zn(II) with norfloxacin,<sup>206</sup> unidimensional Ag polymer,<sup>207</sup> heterometallic dirhodium-silver chains,<sup>208</sup> neutral molecular rectangles of Re,<sup>209</sup> lanthanide coordination polymers,<sup>84</sup> and triple helical chain polymer of Hg.<sup>106</sup> A Pt(II) luminescent compound which detects aromatic hydrocarbon vapors has been reported recently.<sup>210</sup> (Figure 1.13b) This example throws light on their use as an "electronic nose" or as a detecting or emitting layer in a LED.

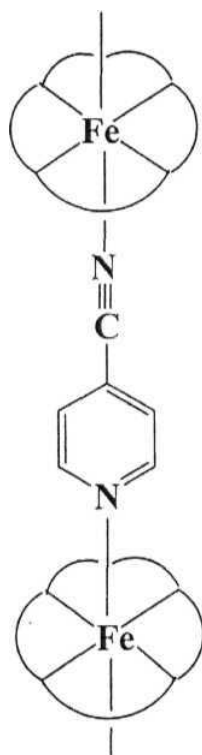


**Figure 1.13** (a) Square network of  $\text{Cd}\{3\text{-}[2\text{-(4-pyridyl)ethenyl]benzoate}\}_2$ , with SHG efficiency of  $\sim 1.2$  times that of  $\text{LiNbO}_3$ <sup>159</sup> and (b) Pt - Pt interactions leading to the stacked structure in  $\text{Pt}[\text{CN-p}-(\text{C}_2\text{H}_5)\text{C}_6\text{H}_4]_2$  (luminescence sensor for hydrocarbon vapours. (adapted from ref. 210).

**(d) Ferroelectric Materials:**<sup>2</sup> Ferroelectricity is analogous to ferromagnetism. This type of materials exhibit unusual electro-optical, photorefractive and pyroelectric properties and find use in electronic oscillators, high-frequency filters, electroacoustic converters, pyroelectric radiant energy receivers and non-linear capacitive elements. Though most ferroelectrics are metal oxides like  $\text{BaTiO}_3$  and  $\text{LiNbO}_3$  and some are



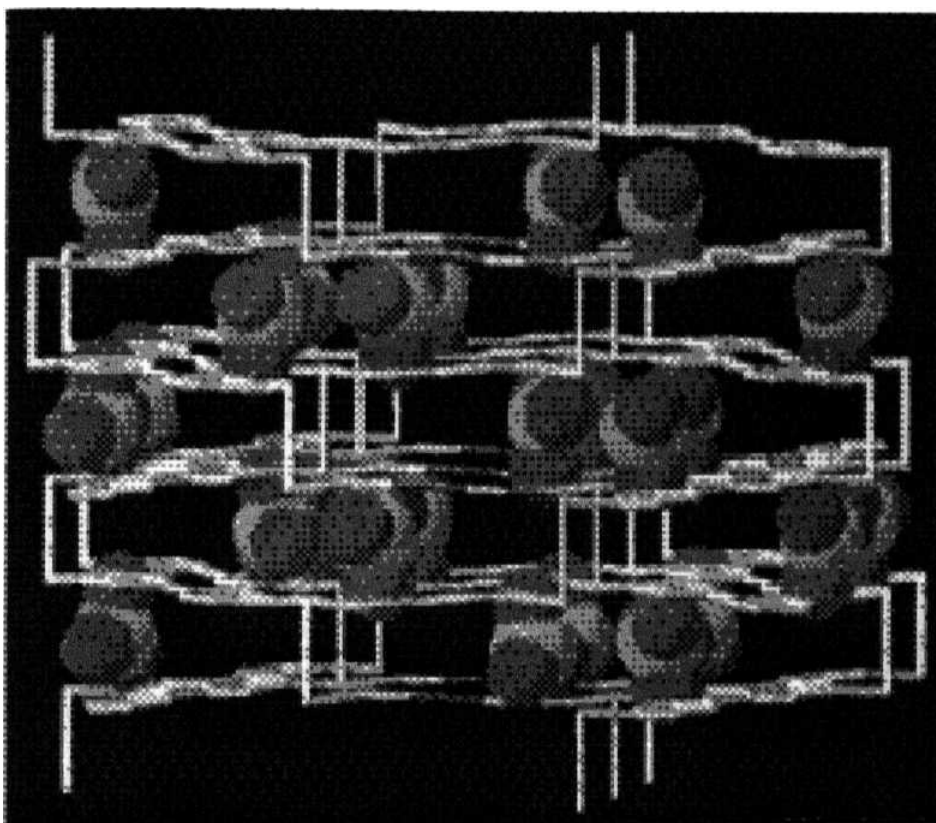
liquid-crystals, polymers of metalloporphyrins, for example,  $[\text{Fe}^{\text{II}}(\text{TPP})(\text{pyCN})]$  and  $[\text{Fe}^{\text{III}}(\text{TPP})(\text{pyCO}_2)]$  have been suggested as ferroelectric materials (Figure 1.14). Similar to porphyrins, stacked systems without bridging ligands formed by bowl- or cone-shaped molecules with ferroelectric properties have been reported for lead phthalocyanines, metallocyclophanes and cyclotncatechylenes.



**Figure 1.14** Infinite chain of  $[\text{Fe}^{\text{II}}(\text{TPP})(\text{pyCN})]$  connected by the bridging cyanopyridine, exhibiting ferro - electric properties (adapted fom ref. 2).

(e) **Microporous Materials:** Coordination polymers with open network structures can be fine tuned to generate cavities with desirable sizes which can act as ion-exchangers and also show microporosity for guest exchange. This property can be exploited to synthesize compounds that can function as substitutes to zeolites, besides their application in heterogeneous catalysis and adsorption. In this respect it is necessary to **maintain** the crystal integrity while being porous to the exchange of ions. Hence, strategies for having compounds which are thermally stable and porous to guest exchange are required. With a view to synthesize such open framework compounds with thermal stability, work by several groups resulted in basically three types of compounds. These are channels of (a) diamondoid type,<sup>26,146,211</sup> (b) open frameworks with rectangular,<sup>21,22,14</sup> square,<sup>133,135,215,217</sup> and hexagonal type<sup>137,218,220</sup> and (c) other network/layered solids.<sup>53,85,132,141,160,221-229</sup> Microporous materials crystallized from solvents are invariably obtained as solvates. The desolvated material obtained by heating or by applying vacuum may sometimes retain its crystallinity and porosity as judged from single crystal diffraction<sup>230</sup> or powder diffractograms.<sup>228,231</sup> It has also been possible to conduct experiments on reversible desolvation / solvation cycles<sup>231</sup> and guest exchange reactions.<sup>53,132,139,141,218</sup> Insoluble porous solids containing anions inside cavities are known to exchange with other anions present in the solution.<sup>146,213</sup>

Engineering the networks by controlling the self-assembling features for functioning as zeolite substitutes in different types of solids have been reviewed by several groups.<sup>142,232,233</sup> Helical polymers with large chiral cavities<sup>62,119,234</sup> have been reported which represent a prototype of new chiral porous materials which may find applications in the field of stereospecific synthesis and enantioselective separations.



**Figure 1.15** Structure of  $\text{Ag}(4,4'\text{-bpy})\text{NO}_3$  showing large channels containing (disordered)  $\text{NO}_3^-$  ions. The anions exchange readily with  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{MoO}_4^{2-}$  and  $\text{SO}_4^{2-}$ , when the solid is suspended in an aqueous solution containing the anions.<sup>213</sup>

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