Introduction

1. Crystal Engineering

R. Pepinsky in 1955 introduced "Crystal Engineering" as new concept for engineering crystals with advantageous properties.[1a] In 1971, G. M. J. Schmidt used it extensively for addressing the packing principles of organic molecules in their crystal structures in connection with the photodimerisation reactions of crystalline cinnamic acid derivatives.[1b] Since its initial use, the meaning of the term gradually broadened to include many aspects of solid-state supramolecular chemistry. Major boost came to the field in 1987 when the importance of the work by D. J. Cram,[2] J. M. Lehn[3] and C. J. Pedersen[4] on crown ethers and cryptands in the area of host-guest chemistry has been recognized by the noble committee. In the subsequent decade supramolecular chemistry has established itself as one of the most active fields of science. Currently, an ocean of literature has been generated in the field and turned into an interdisciplinary area of research.

In 1989, G. R. Desiraju provided the modern definition of crystal engineering as *"the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties".*[5]

Supramolecular chemistry is the chemistry of non-covalent interactions. These interactions include electrostatic interactions (ion-ion, ion-dipole and dipole-dipole interactions), hydrogen bonding, coordinative bonding, π-π stacking, other π-interactions and van der Waals forces. To build supramolecular assemblies in more predictable manner, the basic knowledge about various aspects of interactions such as their strength, geometrical features and directionalities of acceptors are prerequisite. Single interaction is generally much weaker however the cooperative effect of two or more above mentioned interactions leads to a supramolecular species that are more stable under different conditions.[6] Currently hydrogen bonding and coordinate bonding are major interactions which are in regular use in crystal engineering.

The aim of crystal engineering is to design molecules that form predefined architectures with specified properties from the knowledge of intermolecular interactions.

An understanding of these interactions is therefore very important in this context. The most fundamental problem in crystal engineering is the prediction of crystal structure for a given molecular structure. The use of functional groups that form predictable and robust supramolecular synthons simplifies this problem in tailor made compounds. However the existence of multiple functional groups in a molecule causes interference in the formation of a robust supramolecular synthon and increases the complicacies with the prediction of supramolecular architectures.

Some of the important aspects of hydrogen bonding, coordinative bonding, coordination polymers, crystal engineering of functional materials with hydrogen bonding and coordinate bonding and the utilization of amide functionality in crystal engineering are described in the following sections.

1.1 Hydrogen Bond

George A. Jeffrey and Wolfram Saenger have quoted in their book that "*The discovery of the Hydrogen Bond could have won someone the Nobel Prize, but it didn't*".[7] This statement signifies the importance of hydrogen bonding and without it there would have been no water on earth and hence no life.

Hydrogen bond is a type of attractive interaction between an electronegative atom and a hydrogen atom bonded to another electronegative atom. Bernal and Huggins in 1935-36 proposed the actual term "Hydrogen bond".[8] Pimentel and McClellan have provided a more general definition that "a hydrogen bond exists if (1) there is evidence of a bond formation and (2) there is evidence that this bond sterically involves a hydrogen atom already bonded to another atom".[9] This definition didn't specify the chemical nature of the atoms and hence it can include various weak hydrogen bonds such as C-H⋯O, C-H⋯N, C-H⋯X and so on.

In a hydrogen bond X-H⋯A, the group X-H is called the donor and A is called the acceptor. The parameters involved in hydrogen bond are d, D, θ and ϕ (Scheme 1.1). D and d are the X⋯A and H⋯A distances respectively whereas the angles θ and ϕ are the X-H⋯A and B-A⋯H respectively. The angle θ represents the linearity of the hydrogen bond and ϕ represents the directionality of the acceptor atom A. For the formation of a hydrogen bond, the D and d should be less than the sum of the van der Waals radii of the atoms and the θ value should be close to linearity.
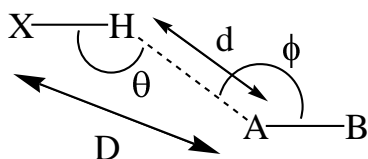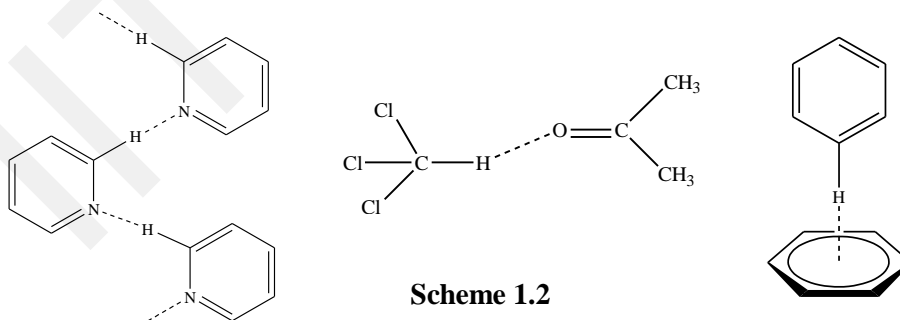
X = donor
A = acceptor

Scheme 1.1

In the solid state the hydrogen bonds can be identified as very strong, strong and weak depending on the geometrical parameters as stated below.

	Very Strong	Strong	Weak
Bond Energy (kJ/mol)	60-170	16-60	<16
Bond Lengths	X-H ≈ H···A	X-H < H···A	X-H << H···A
X···A range (Å)	2.2-2.5	2.5-3.0	3.0-4.5
H···A range (Å)	1.2-1.5	1.5-2.2	2.2-3.5
X-H···A angle range (°)	175-180	130-180	90-150
Effect on crystal packing	Strong	Distinctive	Variable
Examples	$[N···H···N]^+$, $[F···H···F]^-$ P-OH···O=P	O–H···O, O–H···N, N–H···O, N-H···N	C-H···O, C-H···N, C-H···X (halide)

Weaker hydrogen bonds or interactions also play a very important role in assembling the molecules, in particular in the solid state (Scheme 1.2). In several instances the weaker interactions found to alter the robust synthons of strong hydrogen bonding functional groups. For example, it was shown that the -COOH dimer synthon in phenylpropiolic acid derivatives is being altered to catmeric synthon due to the preference for weak C-H···O hydrogen bond.[10]

Scheme 1.2

1.1.1 Experimental Analysis of Hydrogen Bond

The formation of hydrogen bond causes a small shift of electron density from the proton acceptor to the donor which can be taken as a characteristic for the formation of a hydrogen bond. Experimental techniques such as IR, NMR, X-ray diffraction and neutron diffraction can be utilized to investigate and analyze the hydrogen bonds.

In IR spectroscopy, the formation of hydrogen bond shifts the band to lower wave number due to the lengthening of the X-H bond. The strength of intermolecular hydrogen bond is directly related to the intensity of the X-H band. Stronger the hydrogen bond greater is the shift to lower wave number than the normal value and vice-versa. Also there is an increase in the intensity and broadening of the band is observed.

In NMR spectroscopy, it has been observed that a hydrogen atom involved in hydrogen bonding resonates at the downfield in comparison to the one which does not. This is due to the fact that the electron density around the proton that is involved in hydrogen bonded interaction is less than the non hydrogen bonded proton. The downfield shift depends upon the strength of hydrogen bonding.

The atomic positions derived for a hydrogen atom using X-ray are approximate one, due to the fact that X-rays are scattered by electrons. The electron density around hydrogen atom is less and in most of the cases it is displaced towards the electronegative atom to which it is bonded. Therefore in X-ray, the distance D and θ are considered as better characteristic features than the distance d. The accurate position of hydrogen atom is located by the neutron diffraction analysis since the scattering, in this case, occurs from atomic nuclei and hence accurate hydrogen bond parameters can be determined.
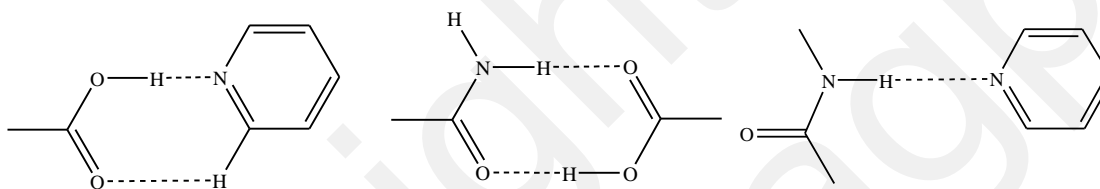
1.1.2 Supramolecular Synthon

The term "Supramolecular Synthon" was introduced by G. R. Desiraju in 1995 in the context of supramolecular synthesis. He defined supramolecular synthon as *"structural units within supermolecules which can be formed andlor assembled by known or conceivable synthetic operations involving intermolecular interactions"*.[11] Supramolecular synthons *via* conventional hydrogen bonds are of most popular and commonly used but supramolecular synthons involving weak interactions such as halogen bonding, halogen-halogen interaction and π-π interactions are also important in the context of assembling the molecules. Supramolecular synthons are classified as

homomeric synthons and heteromeric synthons. In homomeric synthon the interaction is between the same functionality e.g. carboxylic acid dimer, self-complementary hydrogen bonds of amide, hydroxyl and so on (Scheme 1.3). However in heteromeric synthon the interaction is between two different functionalities e.g. interactions between acid-pyridine, acid-amide, amide-pyridine and pyridine-hydroxyl. The judicial use of these structure directing synthons can lead to the desired supramolecular assembly.

Homomeric Synthons
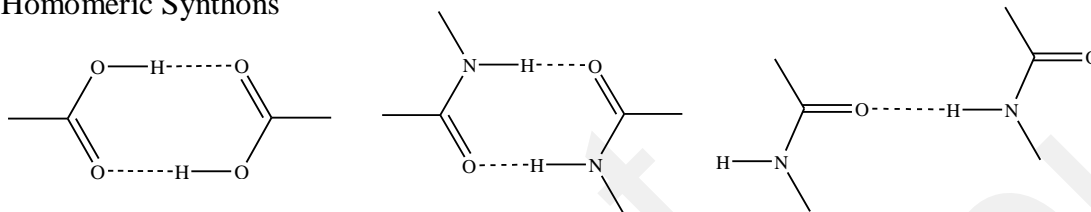
Heteromeric Synthons

Scheme 1.3

As E. J. Corey's synthon approach is useful for the synthesis of an organic molecule;[12] the supramolecular synthon approach is useful for the synthesis of supramolecular assemblies. The criteria for a particular synthon to be used as a tool for designing the network depend on its robustness and the frequency of occurrence. The robustness of a particular synthon can be understood by studying the molecules containing multiple functional groups capable of forming hydrogen bonds. Therefore, the rationalization of the variety of structural features from the library of crystal structures is essential for the understanding of frequency of occurrence and robustness of a synthon. Such study provides more control over the network geometry and minimizes the discrepancies between the designed and experimentally obtained supramolecular assembly.

Popular supramolecular synthons can be easily investigated using Cambridge Structural Database (CSD) which is a very important research tool for crystal engineers.[13] CSD provides compound name, journal reference and molecular formula and coordinates. Further, in CSD it is easy to search any particular interaction pattern, with required

geometrical restraints, between various functional groups. Once such patterns are discovered and rationalized from the group of crystal structures they can be utilized as supramolecular synthons for the design of new materials.

1.1.3 Synthon Interference (or Interaction Interference)

The molecules with carboxylic acid and amide functional groups are usually known to form robust synthons in the absence of other strong hydrogen bonding functional groups. But the presence of more number of functional groups in a molecule results in the interference between the various possible supramolecular synthons. For example, the carboxylic acid forms a dimeric synthon in the absence of any other strong hydrogen bonding functionalities; however the presence of a pyridyl moiety may result in the formation of acid-pyridine synthon. The formation of the final supramolecular array in a crystal is a result of the balance between all the intermolecular interactions and the geometry of the molecules.

The change in the common pattern of a particular functional group due to the presence of some other functional group in a molecule was referred by Desiraju as an interaction interference.[11] The understanding of the interference effects is very important for general applicability of crystal engineering. The factors that influence the interference are:

1) The matching of the strengths of donor and acceptor

2) The cooperative effects of a synthon

3) The balance of number of donors and acceptors

4) Solvation effects

M. C. Etter in 1990 proposed the hydrogen bonding hierarchy rule based on matching of strengths of donors and acceptors.[14] According to this rule, the best donor pairs with the best acceptor and the next best donor pairs with next best acceptor, and so on. This may be true in an ideal situation where the other four effects listed above are seemingly negligible. The balance of the number of acceptors and donors is also very important to have a control over the interference phenomena. Solvation effect drives the crystallization process and has the major say on final structural outcome. Finally the process of crystallization is the compromise of all above effects. Therefore thorough

understanding of all these effects is necessary to predetermine the structural or functional properties of a material.

1.2 Coordinative Bonding and Coordination Polymers

In coordinate bond (also known as dative bond) formation both the electrons come from the same atom. The atom, which provides the electron pair, is termed as the donor atom, while the other atom, which accepts it, is termed as the acceptor atom. This occurs when a Lewis base donates electrons to a Lewis acid. An arrow pointing from donor towards the acceptor atom represents a coordinate bond.
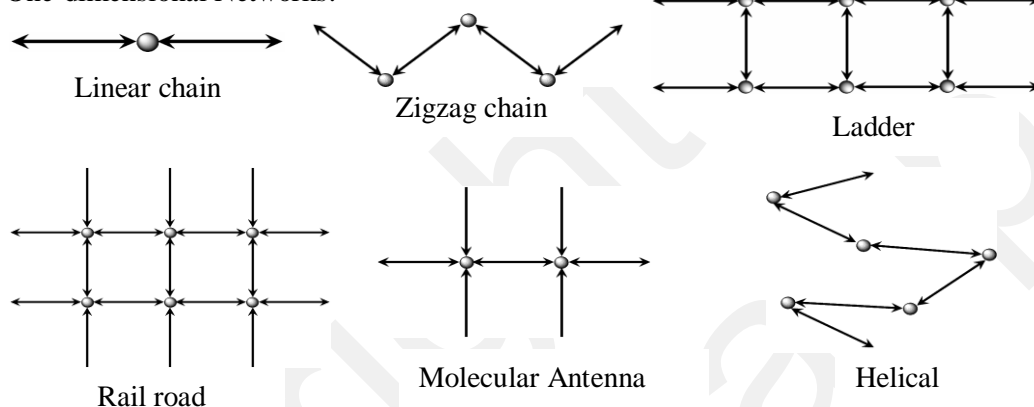
One of the common features associated with coordinate bond is that, most of the reactions are one pot reactions. Therefore, coordination complexes/polymers can be synthesized without disturbing the covalent bonds present in the ligand molecules. Since coordinate bond is weaker compared to covalent bond the reversible reaction i.e. breaking of coordinate bond can be achieved without any effect on covalent bonds in the assembly.

J. C. Bailar in 1964 defined the term "coordination polymer" while comparing the organic polymers with inorganic compounds which can be considered as polymeric species.[15] In wikipedia coordination polymer was defined as "*the term given in inorganic chemistry to a metal coordination compound where a ligand bridges between metal centers, where each metal center binds to more than one ligand to create an infinite array of metal centers*".[16] As the literature on coordination polymers (CPs) is growing enormously, several other terminologies were put forward by the researchers depending on the properties of the materials. Among these, the popular ones are metal-organic framework (MOF), porous coordination polymer (PCP) and organic-inorganic hybrid materials. While the term coordination polymer is more general and signifies the metal to ligand connection, but doesn't provide the information of property of material or morphology.[17] Recently, the differences between various terminologies of CPs were clearly outlined by Biradha *et al*.[18] In a nutshell, it was proposed that CPs with 3D-networks can be termed as MOFs while those with 1D and 2D-networks should termed as coordination polymers.
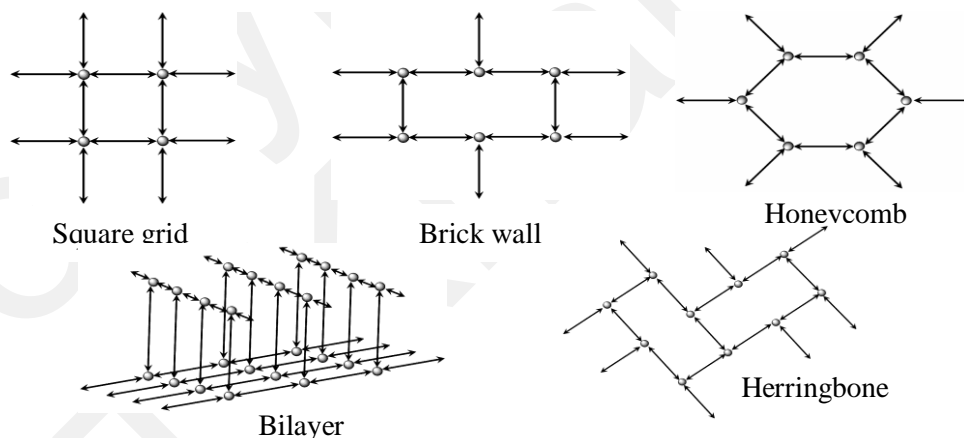
In 1977 A. F. Wells put forward the concept of nodes and spacers for the simplification of network topologies of inorganic compounds.[19] Later Robson *et al.* simplified the concept for CPs by considering metal centers as nodes and ligands as

spacers for linking the metal centers (Scheme 1.4).[20] The conformational flexibility of the ligand diversifies the network topologies and complicates the prediction of network geometries compared to rigid ligands. In addition to the nature of the ligand, the network topology also depends on several other factors such as metal coordination geometry, metal to ligand ratios, counter anions, pH values, guest molecules and finally the process of crystallization. A systematic investigation is necessary to understand the importance of each factor. The key strategy for this exercise is to vary one of the factors while keeping the others constant.
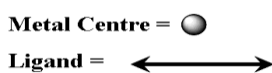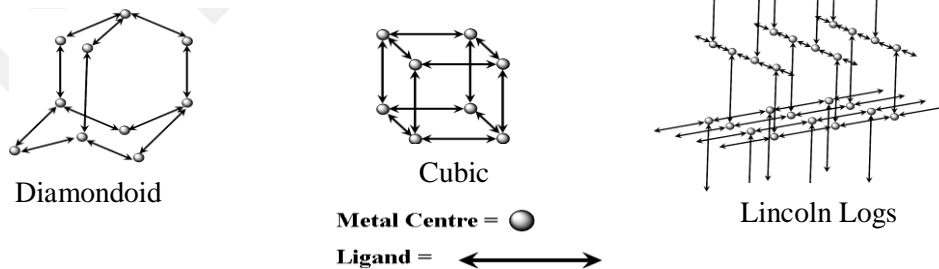
One-dimensional Networks:

Linear chain

Zigzag chain

Ladder

Rail road

Molecular Antenna

Helical

Two-dimensional Networks:

Square grid

Brick wall

Honeycomb

Bilayer

Herringbone

Three-dimensional Networks:

Diamondoid

Cubic

Lincoln Logs

Metal Centre = ⬤

Ligand = ⬌

Scheme 1.4

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As the most important constituents of coordination polymers are metal and ligand, the general knowledge about the coordination geometries of various metals is of immense help for obtaining the networks with desired topologies. Further, the concept of secondary building unit (SBU) is also of in regular use for obtaining coordination networks with predictable geometries. The term SBU is used for a polynuclear cluster that acts as a node in coordination network (Scheme 1.5).[21] SBUs are crucial since they provide the directionality and robustness to the frameworks. [22]
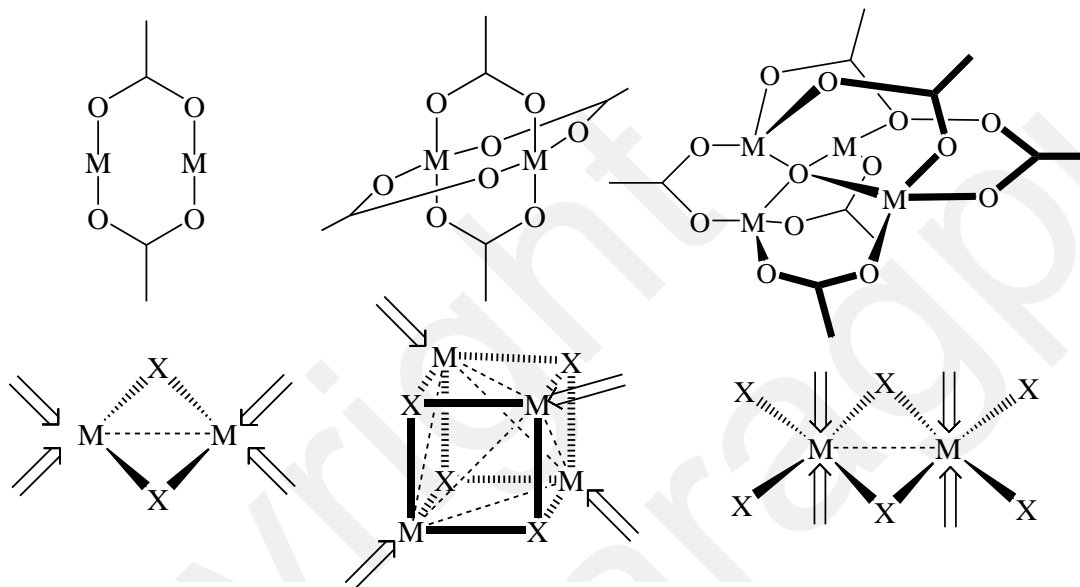
Scheme 1.5: Some of the Secondary Building Units (SBUs) usually observed in Metal-carboxylate clusters and M(I)X halides.

1.2.1 Synthesis of Coordination Polymers

Different techniques are being adopted for the synthesis of coordination polymers. The goal of all these techniques is to obtain the crystalline product suitable for single crystal X-ray diffraction. The reaction conditions can be optimized in several ways by varying the conditions such as metal to ligand ratio, guest molecules, counter anions, pH of the solution, concentration or solvent used in the reaction. Following are the present popular techniques in use for the synthesis of crystalline CPs.

1.2.1.1 Direct Mixing

In this process metal solution is directly mixed in to the ligand solution and the clear solution is kept for solvent evaporation which may produce crystals of desired CPs. However, in most of the cases this technique gives precipitates. In some cases these

precipitates can be dissolved by heating or adding some other polar solvent and hope for obtaining single crystals by slow evaporation.

1.2.1.2 Layering Technique

In this technique slow diffusion of solution of one component (either metal or ligand) in to the solution of other components is carried out. Solvents of different densities can be utilized for this purpose where the component in lower density solvent is slowly layered on top of the other component present in the higher density solvent.

1.2.1.3 Hydrothermal or Solvothermal Synthesis

Here all the ingredients and H_2O or solvent is taken in a sealed tube and heated to very high temperatures for certain time. Slow cooling of this mixture at a controlled rate results in single crystals of desired CPs.

1.2.2 Coordination Polymers involving Carboxylic Acid or Pyridine Moiety

As shown in scheme 1.6 to date several novel networks have been constructed with different ligands and metal salts. Ligands containing carboxylic acid or pyridine moiety share a major portion of coordination polymers explored so far. Several potential ligands with different geometries have been designed by incorporating exclusively either carboxylic acid functionality or pyridine moiety or both together. Recently the ligands containing imidazole moieties have received attention due to their versatile coordination abilities.

Ciani *et al.*[23], Fujita *et al.*[24], Kitagawa *et al.*[25], Robson *et al.*[26], Yaghi *et al.*[27] and Zaworotko *et al.*[28] have reported several coordination polymers using linear bidentate ligand 4,4'-bipyridine and its analogues. These CPs have exhibited versatile topologies (Scheme 1.6) depending on the metal atom, anion, guest, metal-ligand ratios, flexibility of ligand and the coordination of the metal atom. For example the complex exhibiting 1:1 metal to ligand ratio exhibits either linear, zig-zag or helical chain, 1:1.5 forms ladder, bilayer, herringbone, brickwall or honeycomb networks, while 1:2 produces square grid, cubic or diamondoid networks. Yaghi *et al.* have established carboxylate based coordination polymers with diverse rigid spacers utilizing the concept of SBUs (Scheme 1.5) and have extensively explored the gas absorption capabilities of such materials. Some of these materials contain 1,4-benzenedicarboxylic acid (MOF-5), 1,3,5-

benzenetricarboxylic acid (MOF-4) and 1,3,5,7-admantanetetracarboxylic acid (MOF-32) as ligands.[29]

1.3 Combination of Hydrogen Bond & Coordinate Bond in Crystal Engineering

Studies dealing exclusively with coordinate bond or exclusively with hydrogen bond have generated enormous literature in supramolecular chemistry, however very few examples are reported with the combination of both. Combination of these two aspects is expected to provide more control over the network geometries. For such studies the presence of at least two functional groups are necessary in a ligand. One of those functional groups coordinates with the metal while the other may form self recognition patterns or helps in guest enclathration or may be utilized for the post functionalization of the channels/cavities of coordination networks.

Generally the functional groups capable of forming strong hydrogen bonds are incorporated in the ligand since the synthons involving weak hydrogen bonds loose their self recognition in the complexation reaction due to other hydrogen bonding moieties such as coordinated water or counter anions. Accordingly the functional groups such as carboxylic acid, amide or hydroxyl groups are used in the ligands for hydrogen bonding purposes. In this section some of the examples of coordination complexes/polymers involving carboxylic acid groups will be discussed. The coordination polymers with the ligands bearing amide functional groups will be discussed in the next section.

The metal complexes of iso-nicotinic acid or nicotinic acid were shown as good and simple examples for such studies by Puddephatt *et al*.[30] In these complexes, pyridyl nitrogen coordinates to the metal and the carboxylic group forms self-dimers with itself. For example the $PdCl_2$ complexes of iso-nicotinic acid and nicotinic acid were shown to form predictable linear and zig-zag chains respectively *via* carboxylic acid dimers (Figure 1.1a-b).

Further, Sekiya *et al* have shown that the one-dimensional chains of $Ni(SCN)_2$ can be joined into two-dimensional layers *via* pyridine coordination and -COOH dimers in the crystal structure of $Ni(SCN)_2$ and iso-nicotinic acid (Figure 1.1c). [31]. These layers were shown to be capable of including several solid and liquid guest molecules by changing the packing modes. Subsequently, the strategy of building 2D-layers *via*

coordination and acid dimers was expanded further by using the longer spacers such as 3-(4-pyridyl)propenoic acid and 4-(4-pyridyl)benzoic acid in place of iso-nicotinic acid.[32]
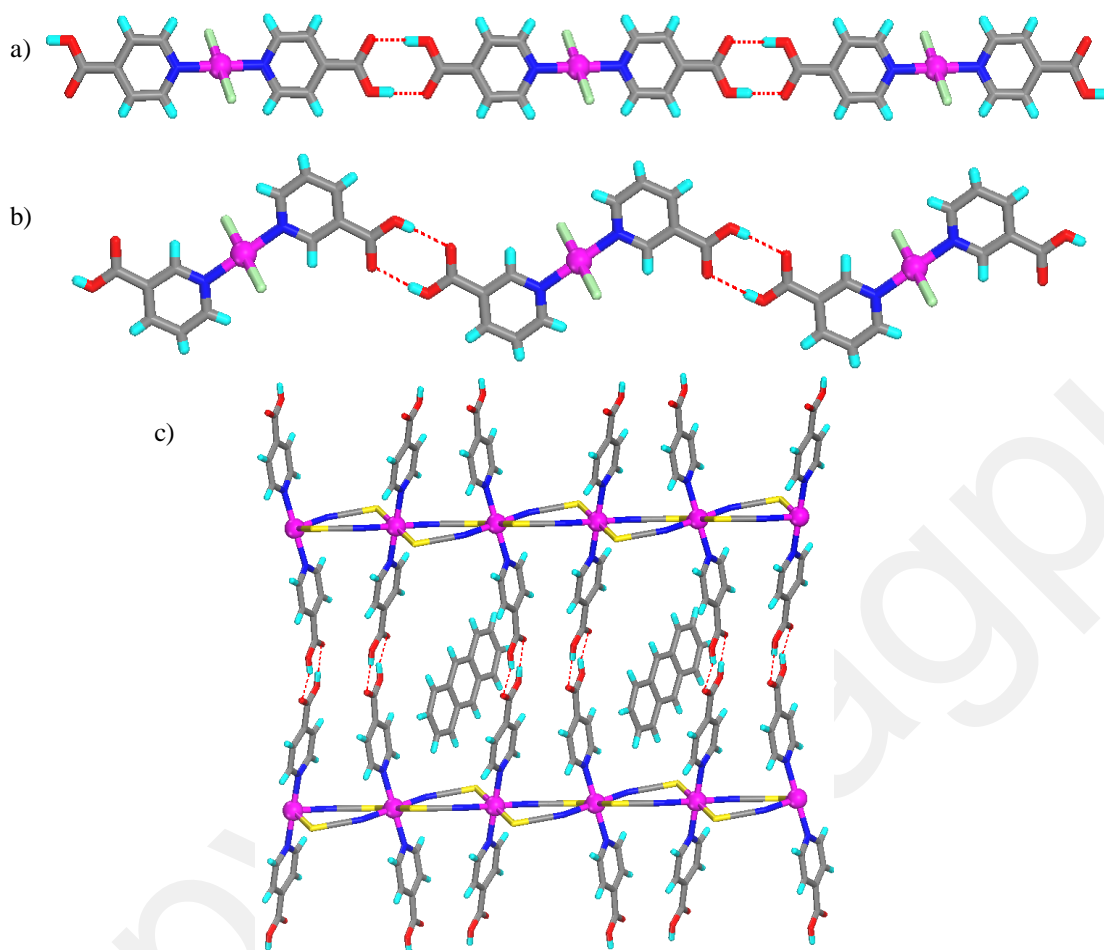

Figure 1.1: Formation of 1D chain involving carboxylic acid dimer in the coordination complex of a) iso-nicotinic acid and b) nicotinic acid. c) Assembling 1D chains in to 2D layer in iso-nicotinic acid coordination polymer (anthracene guest inclusion is shown here).

1.4 Crystal Engineering involving Amide Functionality

Amides are major constituents of proteins and play a crucial role in almost all biological processes of animals. They are present in several natural or synthetic molecules. Comprehensive Medicinal Chemistry database has revealed that the carboxamide group appears in more than 25% of the known drugs.[33] Primary or secondary amides are well known for their self recognition since they exhibit self recognition synthons which sustains in the presence of several other functionalities. Scheme 1.6 shows the recognition patterns of different types of amides.

Primary Amide

Secondary Amide

Cyclic Amide

Urea Based Amide

Scheme 1.6

α-sheet

Antiparallel β-sheet
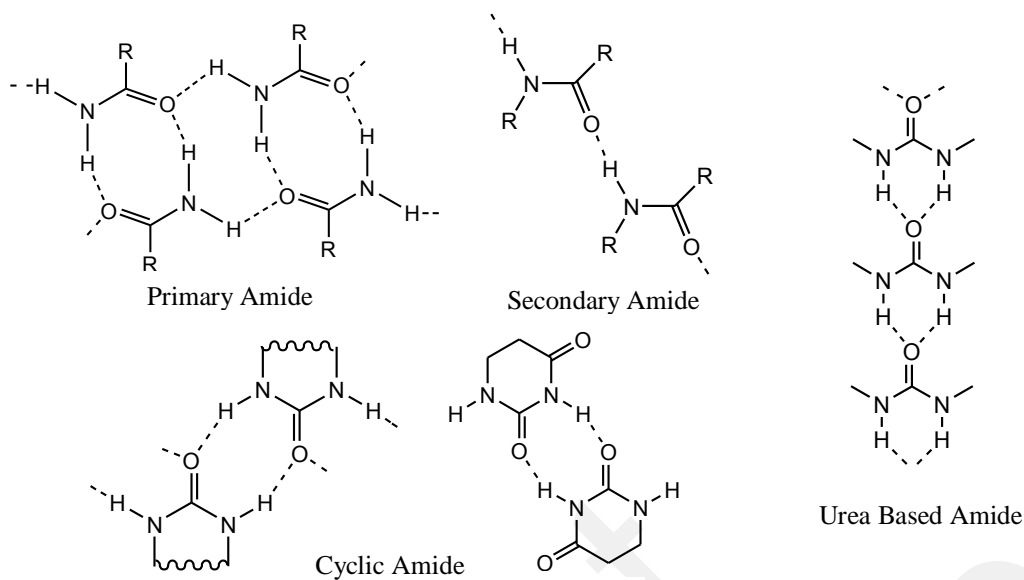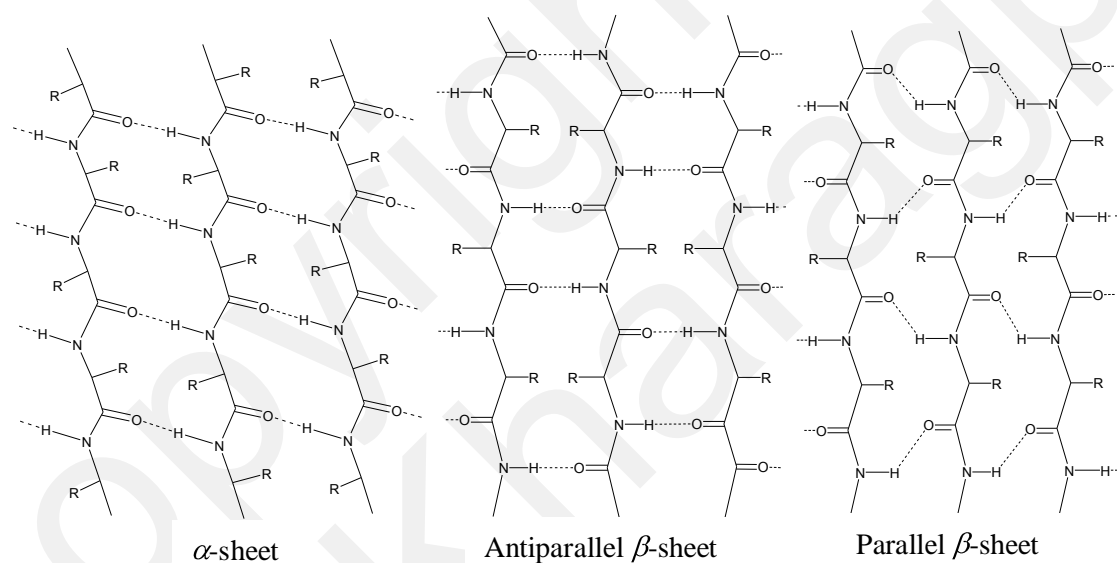
Parallel β-sheet

Scheme 1.7

The linear poly-peptide chains are known to form two types of patterns *via* amide-to-amide hydrogen bonds (Scheme 1.7) which were termed as α-sheet and β-sheet (parallel or anti-parallel). The secondary structure of proteins also exhibits these types of patterns. The crystal structure of urea and urea based molecules known to exhibit α-sheet network.[34] β-sheet networks are generally observed in several synthetic polymers such as nylon 6, nylon 6,6, kevlar and so on.

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Plethora of literature reports exist in the supramolecular chemistry based on amides due to their robust self recognition motifs. The molecules containing amides were often used to design several supramolecular networks such as sheets, helices, tubes and ribbons.[35] Amides were shown to exhibit the tendency for self recognition even in the presence of other potential hydrogen bonding functional groups in a molecule. For example, Lauher *et al.* designed the molecules (ureylenedicarboxylic acids) containing both urea and carboxylic acid functionalities to study the preferences between homo (acid-to-acid & amide-to-amide) and hetero (acid-to-amide) recognitions.[36] In the crystal structures of these class of compounds it was observed that homo recognition was favored over the hetero recognition to form α-sheet or β-sheet networks (Figure 1.2a). These results imply that the presence -COOH had not interfered in the formation amide-to-amide synthon or vice-versa. In our laboratory, homologous series of bis(pyridylcarboxamido)alkanes were shown to aggregate through β-sheet recognition of amides without any interference from pyridine functionality (Figure 1.2b) in their crystal structures.[37]
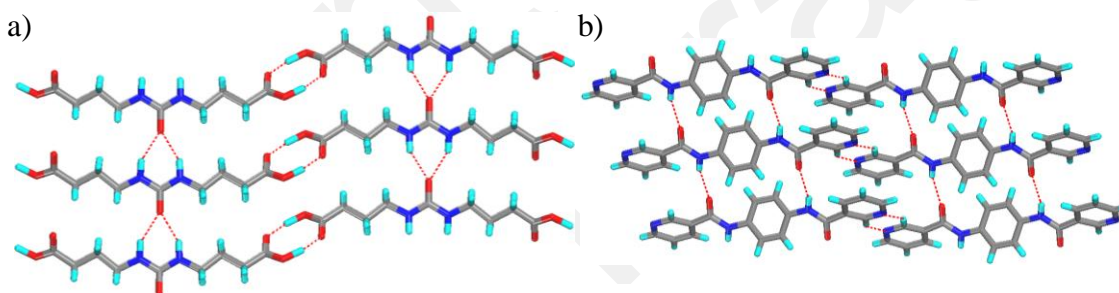
a) b)

Figure 1.2: Amide to amide recognition in the form of a) α-sheet in ureylenedicarboxylic acid derivative and b) β-sheet in bis(pyridylcarboxamido)alkane derivative.

Amides, due to their robust self recognition patterns can play an important role in assembling the coordination complexes or polymers. For such studies, the ligand should contain amide and pyridine functional groups. Several ligands were designed based on this concept, some of those ligands which are explored for the assembling of CPs *via* amide-to-amide hydrogen bonds were shown in scheme-1.8.

Scheme 1.8

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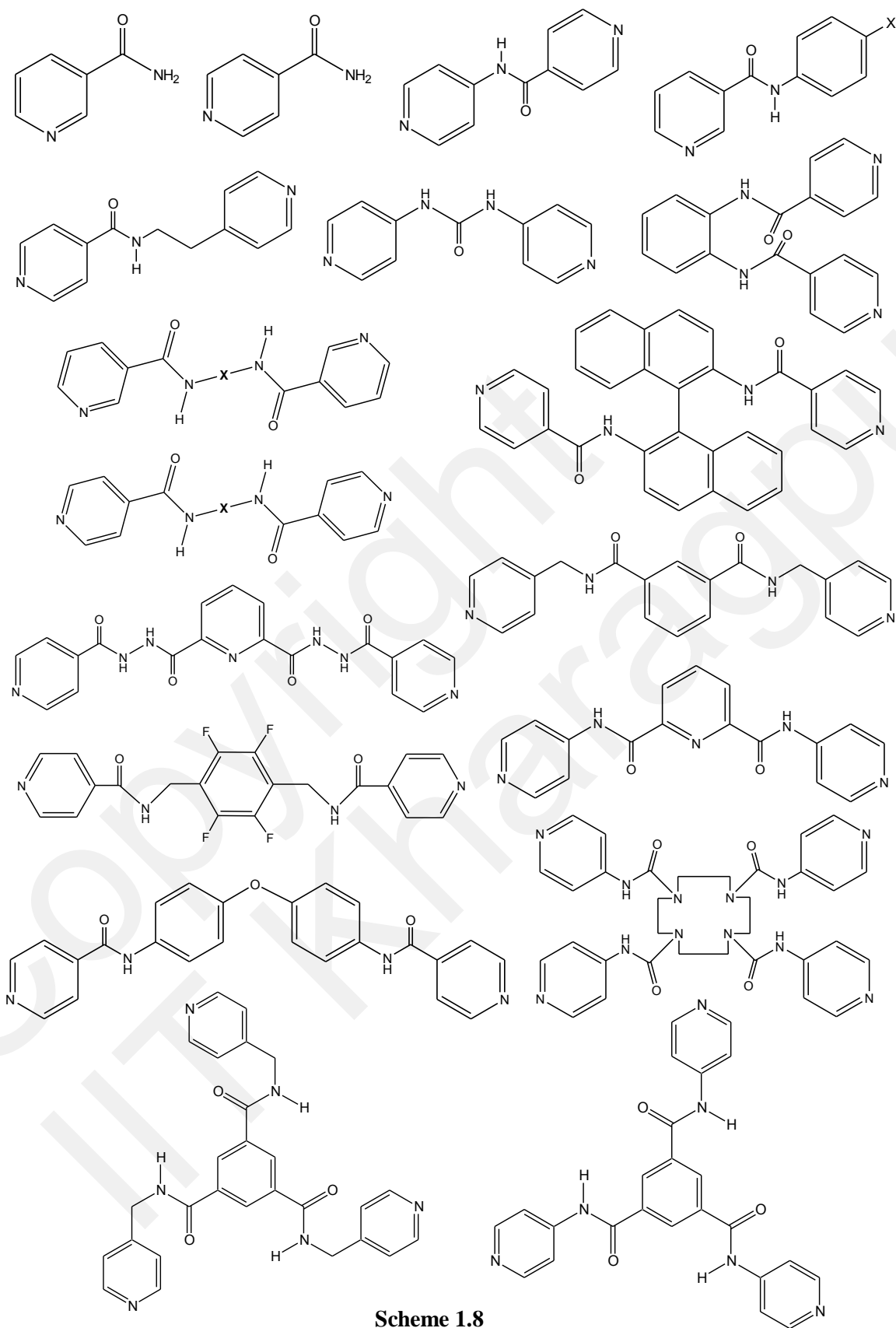
Nicotinamide and isonicotinamide are of prototypic examples of such ligands for assembling metal complexes *via* amide-to-amide hydrogen bonds.[38] In the metal complexes of these ligands, the amide groups found to exhibit self recognition either in the form of amide dimer or in the form of ribbon like N-H⋯O hydrogen bonds to assemble the discrete units in to higher dimensionalities. Some of the examples are shown in figure 1.3.
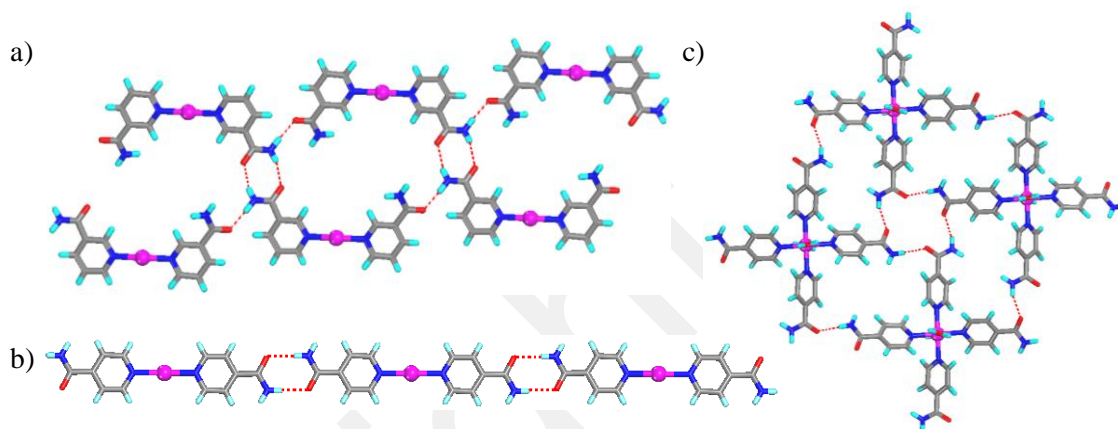

Figure 1.3: Amide-to-amide hydrogen bonded a) ladder & b) linear chain in Ag(I)-nicotinamide complex and c) sheet in Ni(II)-iso-nicotinamide complex.

Kitagawa *et al.* have assembled the coordination polymers of N-(pyridyl)nicotinamide or isonicotinamide in to higher dimensionalities through amide-to-amide hydrogen bonds.[39] Amide moieties in these complexes help for guest inclusion in which the guest is easily removed or exchanged with new guest and transformation of one network in to other was achieved.

From our laboratory several coordination polymers using ligands containing amide and pyridine functional groups were reported. Many novel architectures have been successfully achieved with the series of bis(pyridylcarboxamido)alkane derivatives either by varying the alkyl spacer or the position of the pyridine nitrogen in the ligand.[40] The networks include 1D linear or wavy chains with or without cavities, open and interpenetrated (4,4)-nets with or without guest inclusion, pseudo-diamondoid network and so on. For example, the 2D-coordination networks were shown to recognize each others *via* α-sheet or β-sheet in several of those materials (Figure 1.4).
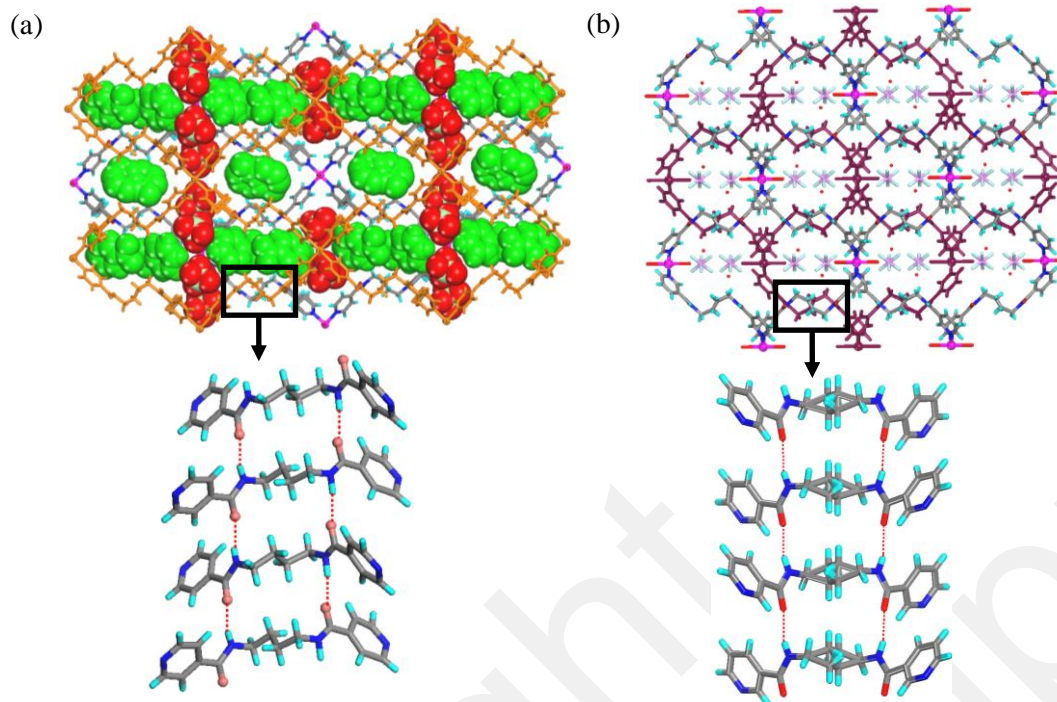
Figure 1.4: Offset-offset packing of the layers with a) nitrobenzene and ClO_4^- ions in the channels and β-sheet hydrogen bonding between the layers, b) PF_6^- anions and H_2O in the cavities and α-sheet hydrogen bonding between the layers.

2. Aim of the Present Study

The aim of this thesis is to establish the relationship between molecular structure and crystal structure which is the fundamental aspect in crystal engineering. This exercise is somewhat simpler with tailor made compounds in which a single functional group exists in preferred positions and forms a robust and predictable synthon. It becomes quite complicated if the molecules contain flexibility as well as multiple functional groups because of the possibility of several stable conformations and therefore several supramolecular architectures for a given molecule. Such complex systems were dealt in this thesis by studying the groups of crystal structures of the various analogous compounds. In particular the thesis has the following objectives: 1) discovering new robust synthons; 2) robustness of well known synthons; 3) interference of pyridine in amide-to-amide hydrogen bonds; 4) iso-structurality on closely related classes of compounds; 5) the transfer of molecular recognition synthons observed in organic materials into coordination polymers; 6) guest inclusion properties.

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The three classes of compounds were considered for this purpose are 1) bis-pyridyl based amides containing alkyl or aryl spacers; 2) 1,3,5-benzenetricarboxamides containing pyridyl or *p*-halophenyl substitution on N-atom of amides; 3) Ethylenediamine-N,N,N',N'-tetraamides containing aryl or pyridyl substitution on N-atom of amides. The scope of these studies covers the exploration of properties such as polymorphism, co-crystallization, porosity, topology, guest exchange, anion exchange and templating effects.

The above mentioned classes of ligands are expected to achieve the following objectives: a) Inserts the functional groups into the polymeric networks; b) These functional groups helps in fine tuning of the cavities and for the inclusion of wide range of guest molecules; c) Functional group self recognition patterns act as communicators for assembling the polymeric networks into various novel architectures.

The fulfilling of above mentioned objectives primarily depend upon finding the suitable crystallization conditions for obtaining the crystalline materials with desired properties. The second objective is to explore these materials for their functional properties such as polymorphism, co-crystallization, porosity, topology, guest exchange, anion exchange and template effects.

3. References

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