Supramolecular synthesis of some organic and metal-organic complexes by co-crystallization

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in

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by

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Dedicated to my beloved parents

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CERTIFICATE

This is to certify that the work presented in the thesis entitled **“Supramolecular synthesis of some organic and metal-organic complexes by co-crystallization”** submitted by **S. Marivel**, was carried out by the candidate at National Chemical Laboratory, Pune, under my supervision. Such materials as obtained from other sources have been duly acknowledged in the thesis.

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DECLARATION

I hereby declare that the thesis entitled **"Supramolecular synthesis of some organic and metal-organic complexes by co-crystallization"** is the result of investigations carried out by me in the Division of Organic Chemistry, National Chemical Laboratory, Pune under the supervision of **Dr. V. R. Pedireddi**. Also, this work has not been submitted to any other university or institution.

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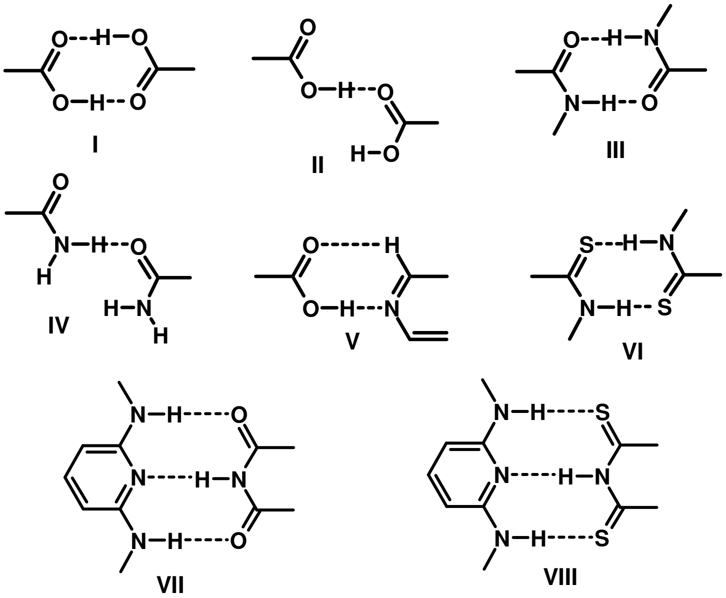
ABSTRACT

The objective of thesis entitled "**Supramolecular synthesis of some organic and metal-organic complexes by co-crystallization**" is to explore the utility of different organic functional groups in the design and synthesis of novel molecular complexes as well as metal-organic assemblies with exotic supramolecular architectures. Thus, the observations made during the course of investigations have been compiled into four chapters. Chapter 1 gives an account of introduction to supramolecular chemistry with detailed discussion on the nature of noncovalent interactions and self-assembly through illustrative examples from the literature. Chapter 2 describes a study of supramolecular assemblies of symmetrically substituted donor and acceptor functional moiety, such as cyanuric acid (**CA**) with various aza-donor compounds towards the construction of novel network structures and their structural rationalization. In Chapter 3, the results obtained on the studies of synthesis and structural analysis of supramolecular assemblies of various isomers of dihydroxybenzoic acid with different aza-donor compounds have been compiled. Finally, supramolecular assemblies of coordination polymers of some organo-phosphorous acids with transition metals and aza-donor compounds are discussed in Chapter 4.

Chapter 1

In supramolecular chemistry, synthetically designed organic molecules interact with each other, through a variety of noncovalent interactions in the form of distinct patterns (see Scheme 1), in a directed and specific way to form numerous supramolecular assemblies, for example, host-guest complexes, lamellar sheets etc. The ability to tailor the interplay of interactions with respect of desired chemical design, specificity, and molecular switching opened up the development of new molecular materials through molecular recognition and self-assembly. In this direction, the synthesis and characterization of organic as well as metal-organic assemblies with channel structures that provide varied shapes, sizes and chemical environments are of great interest in the contemporary research areas. This is not only because of the intriguing structural diversity of the assemblies, thus, synthesized but also because of the potential applications in many areas including molecular adsorption, ion exchange, and heterogeneous catalysis.



Scheme 1

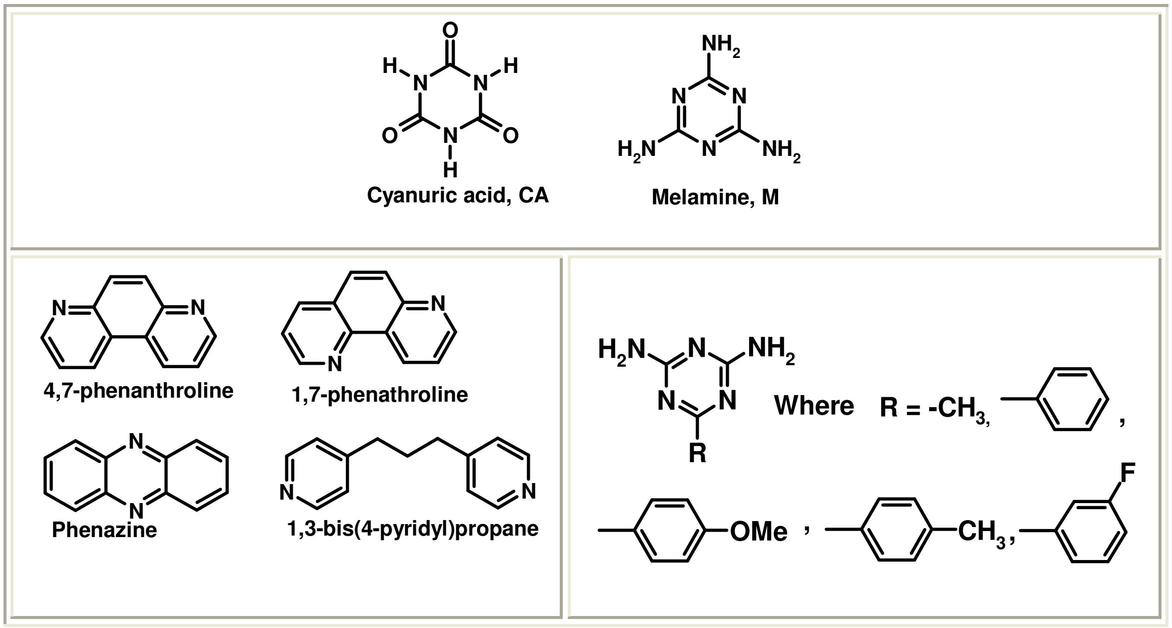
A detailed discussion about the fascinating feature of this novel frontier research area, along with illustrative examples from the literature, has been compiled in Chapter 1.

Chapter 2

Considering the analogy given by Lehn that molecules and intermolecular interactions are for supramolecular synthesis as atoms and bonds are for the molecular synthesis, each molecular entity can provide different types of supramolecular assemblies utilizing its molecular recognition capabilities. In this connection, numerous exotic supramolecular assemblies reported in the literature, for example, rosette structure formed between cyanuric acid (**CA**) and melamine (with 18 hydrogen bonds) is a superb example not only for the structural elegance but also for aiding and strengthening to establish fundamental concepts of supramoelcular synthesis.

Thus, to understand the ability of **CA** to form different kinds of hydrogen bonding patterns, synthesis of a numerous co-crystallization experiment of **CA** with complimentary compounds, in particular, aza-donor compounds, (see Scheme 2) has been carried out.

Scheme 2



All the complexes were characterized by single crystal X-ray diffraction methods and schematic diagram in Figure 1 shows differences in hydrogen bonding patterns as well as two-dimensional packing arrangement upon changing the topology of the aza-donor compounds. A detailed analysis of the exotic structural features of these complexes would be discussed in Chapter 2.

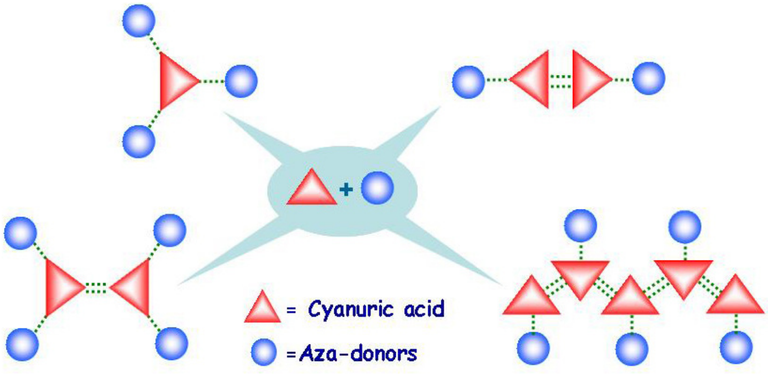


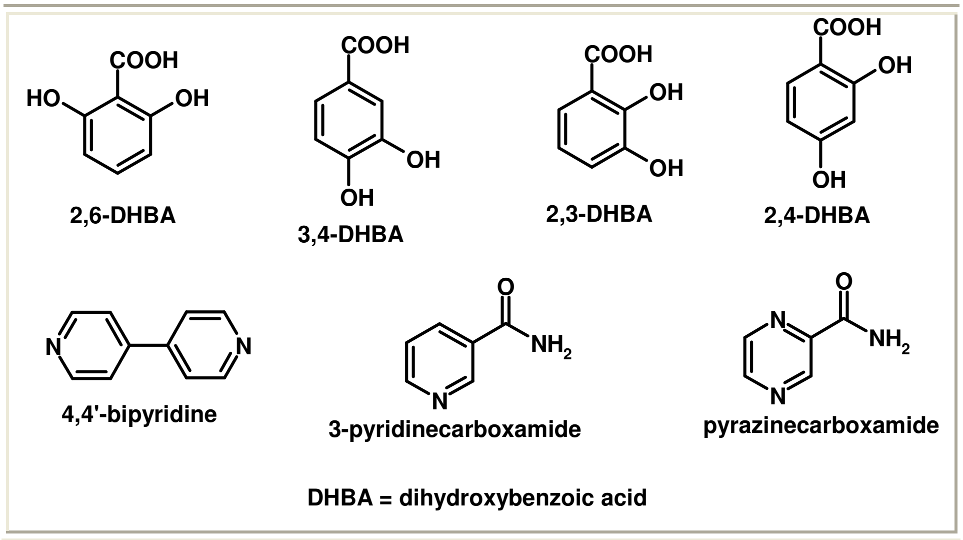
Figure 1. Schematic diagram depicting the different hydrogen bonding patterns observed in the complexes of **CA**

Chapter 3

Hydroxy (–OH) moieties are effective functional groups in supramolecular synthesis as they form a variety of hydrogen bonded networks in solid state, depending upon the availability of the co-ligands used in the reaction. For example, phluroglucinol (symmetrically substituted trihydroxybenzene and also a topological analogue of enol form of cyanuric acid) has been well utilized for the construction of novel supramolecular assemblies.

Recently, it has been demonstrated that –OH groups in conjunction with –COOH form ladder structure through the supramolecular assemblies formed by 3,5-dihydroxybenzoic acid with different types of aza-donor compounds and the nature of the ultimate assembly of the resultant complex is attributed to the position of the –OH functional group on the aromatic moieties. Thus, a study of other isomers of dihydroxybenzoic acid is expected to yield several exotic structures. In Chapter 3, illustration of the results obtained on the studies of synthesis and structural analysis of supramolecular assemblies formed by various dihydroxybenzoic acids with different aza-donor compounds (see Scheme 3) is given.

Scheme 3



As expected, structural analysis reveals that the position of the substitution of hydroxyl groups lead to the formation of different types of supramolecular networks and some of the representative examples are shown in Figure 2.

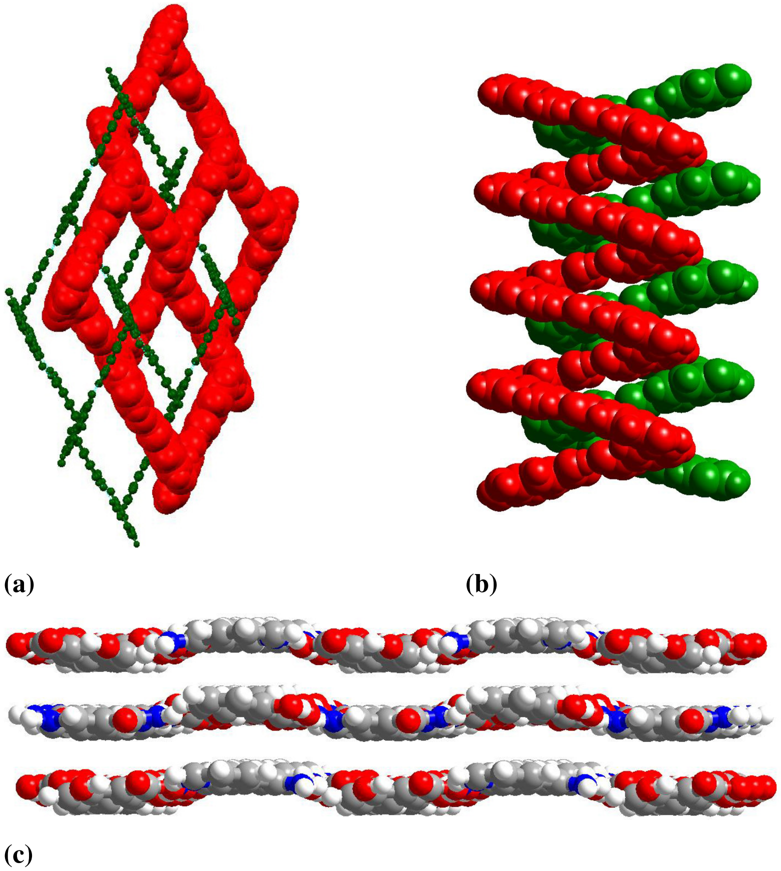


Figure 2. (a) Interpenetration formed by molecules of 2,4-dihydroxybenzoic acid and pyrazinamide. (b) Helices observed in the complex of 3,4-dihydroxybenzoic acid and pyrazinamide (c) Planar sheets formed by the molecules of 2,6-dihydroxybenzoic acid and picolinamide.

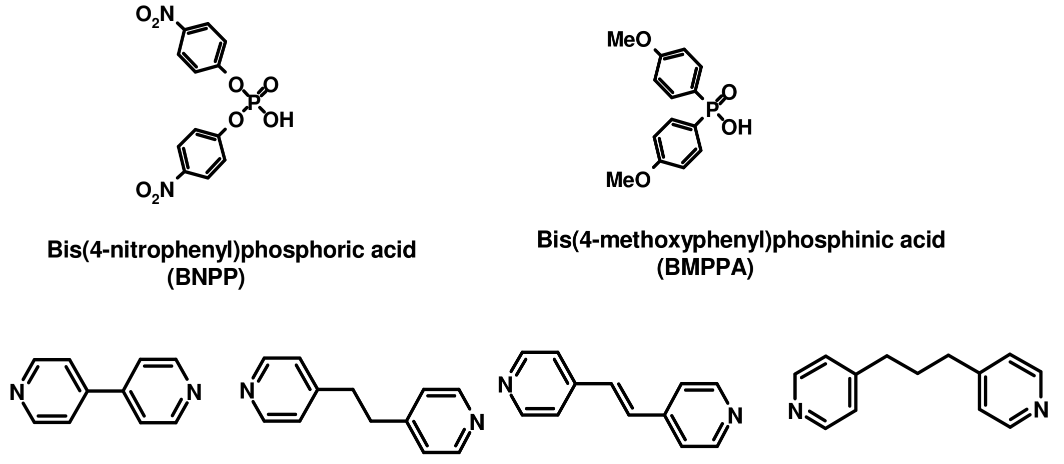
Chapter 4

Organic-inorganic hybrid supramolecular assemblies, which are often, being referred to as coordination polymers, with fascinating as well as exotic architectures are important materials with many potential applications in the areas of separation technology, catalysis, nanotechnology, etc. Design and synthesis of these assemblies are challenging, and continuous efforts to tune the nature of the interactions between the reactants, to obtain the desired topological arrangement are always at the forefront in the areas of supramolecular chemistry research. Several carboxylates have widely been utilized to synthesize this sort of materials with varied architectures for the application of various fields including catalysis and gas sorption.

However, phosphates of organo-phosphorous acids, which mimic carboxylates, have not been well explored in the synthesis of organic-inorganic hybrid mateials. Thus, a combination of these moieties with metal ions would be of very much interesting, as the ultimate geometry could be tuned through the interactions involving organic substituents as well, especially to develop channel structures mimicking natural zeolites that are made up of phosphate mediated networks.

For this purpose, synthesis of metal complexes of *bis*(4-nitrophenyl)phosphoric acid, **1** and *bis*(4-methoxyphenyl)phosphinic acid, **2**, with some transition metals has been carried out in the presence of aza-donor compounds, 4,4'-bipyridine (*bpy*), 1,2-*bis*(4-pyridyl)ethane (*bpyea*), 1,2-*bis*(4-pyridyl)ethene (*bpyee*), and 1,3-bis(4-pyridyl)propane (*bpypa*) (see Scheme 4). The schematic diagram in Figure 3 shows the typical network structure of coordination polymers formed by Zn(II) with **1**, in the presence of aza-donor compounds *bpy*, *bpyea*, *bpyee* and *bpypa*.

Scheme 4



Bis(4-nitrophenyl)phosphoric acid (BNPP)

Bis(4-methoxyphenyl)phosphinic acid (BMPPA)

4,4'-bipyridine (bpy)

1,2-bis(4-pyridyl)ethane (bpyea)

1,2-bis(4-pyridyl)ethene (bpyee)

1,3-bis(4-pyridyl)propane (bpypa)

Also, the metal complexes formed by *bis*(4-methoxyphenyl)phosphinc acid (**BMPPA**) show the similar features that of complexes of **BNPP** in terms of structural arrangement as well as the coordination mode. A detailed discussion about the structural assemblies of these coordination complexes would be presented in this chapter.

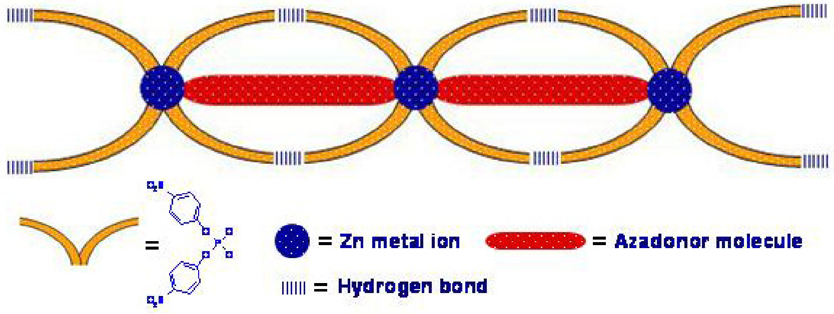


Figure 3. Schematic diagram showing the coordination mode of Zn(II) ion in the coordination polymers of **1**.

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CHAPTER ONE

AN OVERVIEW OF SUPRAMOLECULAR CHEMISTRY IN ORGANIC AND COORDINATION ASSEMBLIES

1.1 Introduction

Molecular chemistry, the chemistry of the covalent bond, is concerned with uncovering and mastering the rules that govern the structures, properties and transformations of molecular species.[1] Supramolecular chemistry[2] is concerned with the study of the interactions (*i.e.* noncovalent interactions) between the molecules. Lehn defined supramolecular chemistry as "*supermolecules are to molecules and the intermolecular bond what molecules are to atoms and the covalent bond*".[3] Thus, understanding of intermolecular interactions is quite essential to supramolecular chemistry as the understanding of the covalent bond to molecular chemistry. Development of supramolecular chemistry requires the use of all of the resources of molecular chemistry, that is, the chemistry of the covalent bond, combined with the designed manipulation of noncovalent interactions in order to form supramolecular entities possessing features such as molecular recognition and self-assembly.[4]

1.2 Noncovalent interactions

A noncovalent interaction[5] is a type of chemical bond, typically between molecules, that does not involve the sharing of electrons, but rather electromagnetic in nature. There are four major types of noncovalent interactions such as hydrogen bonding, π-π interactions, van der Waals and electrostatic interactions. Noncovalent interactions that are selective, directional, and strongly attractive can induce the self-assembly of predictable supramolecular aggregates. Thus, these interactions play a significant role in determining the structures and properties of molecular assemblies in chemistry, biology and materials science. Some of the salient examples to demonstrate the efficacy of noncovalent interactions are DNA double helix, protein folding, enzyme-substrate bindings, etc.[6] Among all known noncovalent interactions, the hydrogen bonds, because of strength and directionality, have been widely utilized in the area of supramolecular chemistry for the construction of novel networks.[7]

1.2.1 Hydrogen bond

Hydrogen bond[8] is a type of attractive force that exists between two partial electric charges of opposite polarity. Although stronger than most other intermolecular forces, the typical hydrogen bond is much weaker than both ionic and covalent bonds. The fundamental importance of hydrogen bond lies in its role of assembling the molecules. As the name "hydrogen bond" implies, an hydrogen atom involves in the bond, which is attached to the electronegative atom like, oxygen, nitrogen or carbon, and it was defined by Pualing as given below.

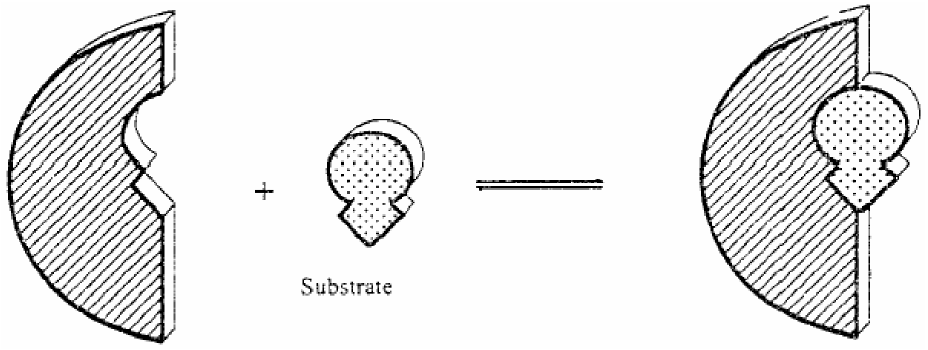
> Pauling's definition of hydrogen bond:[9]
>
> *An atom of hydrogen, under certain conditions, is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them.*

The distinctive geometrical parameters of the hydrogen bond in D-H$\cdots$A-X are (i) the distances of D-A and H$\cdots$A, (ii) the hydrogen bond angle D-H$\cdots$A, which is referred to as θ, (iii) the H$\cdots$A-X angle, which is usually termed as ϕ and (iv) the planarity of the DHAX system. The typical values for D-H$\cdots$A distance are 1.6-2.0 Å for O-H$\cdots$O bonds and 1.8-2.0 Å for N-H$\cdots$O bonds.[10]

Strength of the hydrogen bonds is continuum in a narrow range (2-20 KJmol^{-1}) depending upon the environment and such flexibility allows hydrogen bonds for quick association and dissociation at ambient temperature. The most ubiquitous, and perhaps simplest, example of a hydrogen bond is found between water molecules.[8c] The high boiling point of water is attributed to the high number of hydrogen bonds present in the system. Thus, hydrogen bonds determine the physical and chemical properties of the molecules.[11]

1.3 Molecular recognition

"Molecular recognition"[12] in the contemporary supramolecular chemistry is considered as an approach of the molecules towards each other in a particular way, by minimizing the potential energy significantly more than it would for a different manner of approach because of some specific interaction between the molecules.[13] Lehn defined molecular recognition as "*a process involving both binding and selection of substrate(s) by a given receptor molecule, as well as possibly a specific function.*"[14] This directly implies the existence of a structurally well-defined pattern for establishment of intermolecular (noncovalent) interactions. The concept of molecular recognition is the foundation for antibody activity, enzyme catalysis, and the exercise of the fundamental dogma of molecular biology, etc. Fischer[15] enunciated the first rudimentary molecular recognition principle in 1894 with his "lock-and-key model" for the explanation of geometric features prerequisite for enzyme catalysis. According to this model, a specific substrate fits only one receptor (enzyme), like a key fits one lock (see Figure 1).



Receptor Receptor-substrate complex

Figure 1. Fischer's rigid lock and key model

Kitaigorodskii proposed that organic molecules in crystals are close packed and tend to fill space as tightly as possible and this is achieved when the "bumps" of one molecule fit into the "hollows" of adjacent molecules.[16] Kitaigorodskii considered that for a given molecule, the actual crystal structure corresponds to one of the most densely packed of all conceivable structures. This was well demonstrated for many hydrocarbon structures successfully.

Structures held together by hydrogen bonds, however, may be exceptional, because the strongly directional nature of such bonds can lead to more open arrangements. Thus, the crystallization process appears to involve the phenomenon of molecular recognition, or rather molecular self-recognition, at an amazing high degree of reliability. Thus, molecules recognize each other through a combination of geometrical and chemical factors leading to the formation of numerous multi component architectures.[17] Some imperative hydrogen bonding patterns of complementary functional groups that are involved in the molecular recognition processes are depicted in Chart 1.

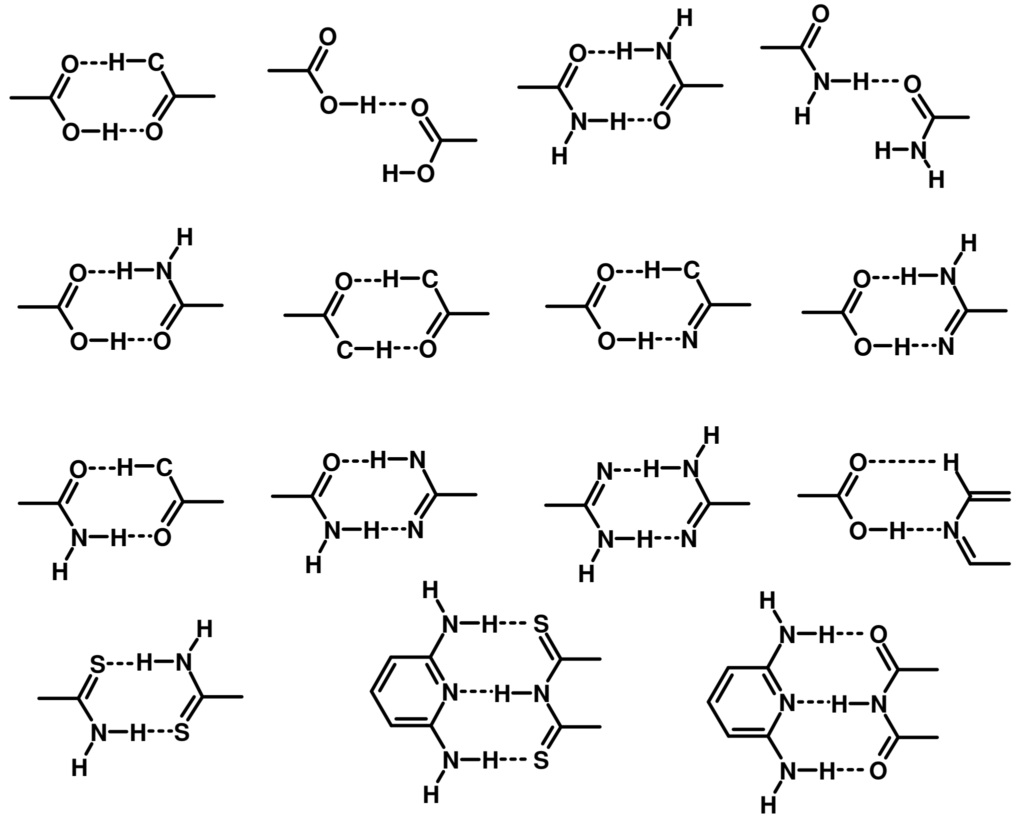
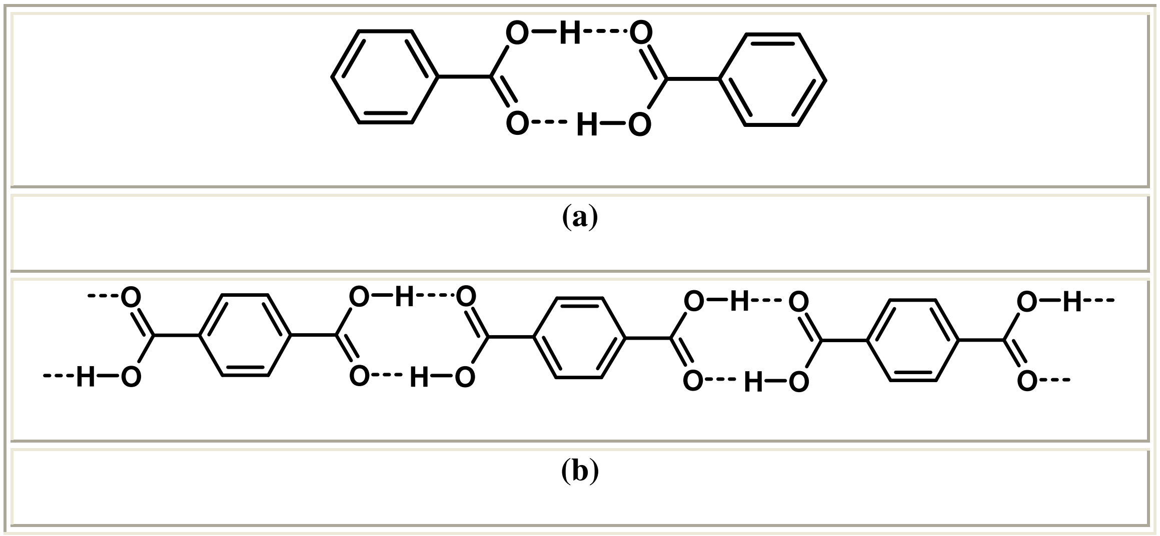


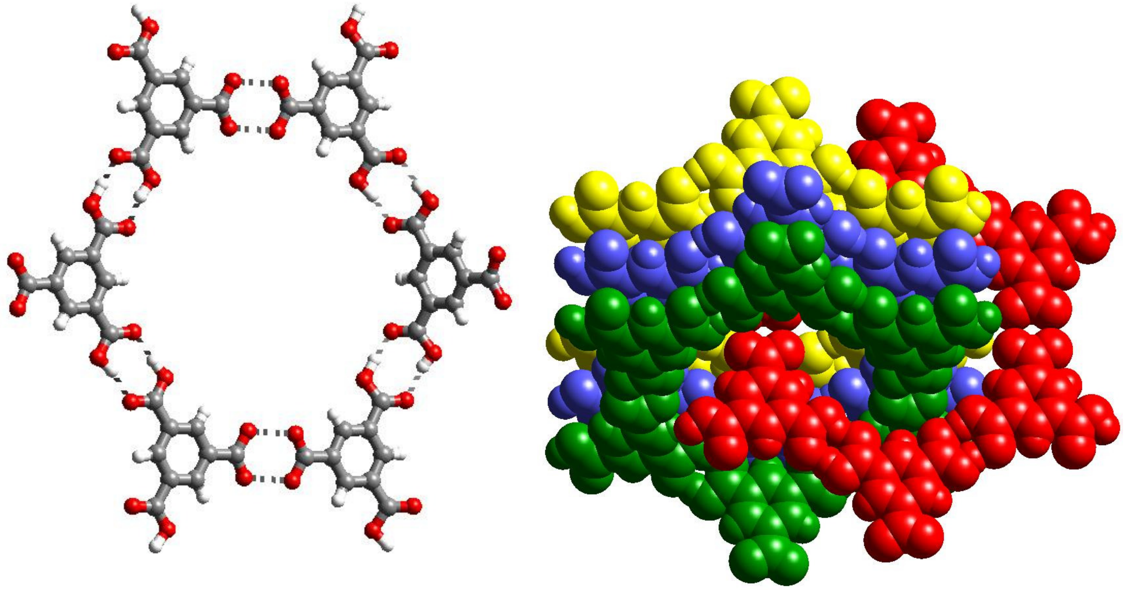
Chart 1. Some of the representative hydrogen bonding patterns observed in the molecular recognition processes.

There are several reports from various researchers describing the importance of molecular recognition process for the construction of numerous supramolecular networks.[18] For example, carboxylic acid functional group (-COOH) has been thoroughly studied because of the robust hydrogen bonds that it can form on its own or with co-ligands used in the co-crystallization experiments.[19] In the molecular recognition process, -COOH forms cyclic hydrogen bonded dimers through O-H···O hydrogen bonds, and also less common catemeric interaction, in which each carboxylic group is linked to two adjacent carboxyl groups through single O-H···O hydrogen bond. Thus, the ultimate geometry of a supramolecular assembly, in general, depends on the number of functional groups and their conformations. For example, if only one carboxylic acid functionality is present per molecule (i.e. benzoic acid), discrete dimers are formed in solid state,[20] but, if two carboxylic acid groups are present (i.e. terephthalic acid) infinite one-dimensional chains are formed.[21] (see Scheme 1).



Scheme 1. (a) A zero-dimensional cyclic dimer formed between benzoic acid molecules. (b) One-dimensional chain formed between terephthalic acid molecules.

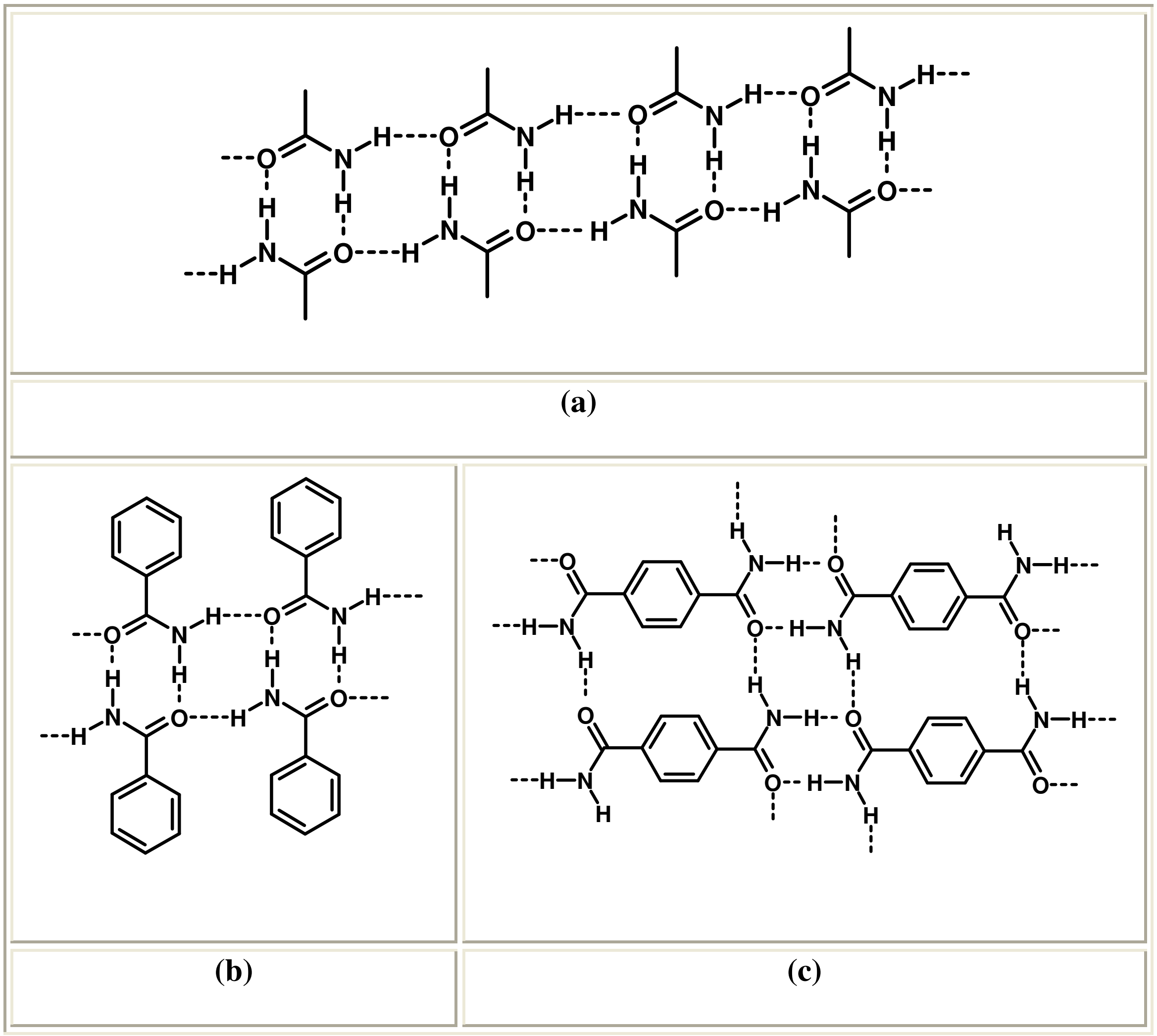
Trimesic acid (1,3,5-benzenetricarboxylic acid), with its three-fold symmetry, self assembles yielding a hexameric network through cyclic dimers –COOH functional groups. Further, such hexameric networks, as associated with void space, undergo catenation process, as shown in Figure 2b, for the purpose of effective close packing, enhancing the density of the solids aggregate in three-dimension forming a chicken wire network.[22]



(a) (b)

Figure 2. (a) Trimesic acid forms hexameric network in two-dimension showing the cavity. (b) Chicken wire network formed by the catenation of the hexameric networks.

Another prominent functional group, well studied in the molecular recognition process, is the amide (-$CONH_2$). Much like the carboxylic acid cyclic dimer, the primary amides also form such dimers through N-H···O hydrogen bond. However, unlike the carboxylic acid functional group, amide functionalities facilitate the formation of secondary interactions to yield two-dimensional network *via* the second hydrogen atom present on –NH_2 group by forming additional N-H···O hydrogen bond.[23] Some of the salient amide functional group mediated hydrogen bonded networks are shown in Scheme 2.



Scheme 2. (a) A common hydrogen bonded ribbon in primary amide. Solid-state architecture assembled via amide head-to-head interactions (b) when only one amide functionality is present. (c) when there are two amide functionalities present.

By comparing the similarity of the solid-state structure of carboxamide with that of carboxylic acid, one could easily appreciate the fact that the amide functionality may be used to assemble supramolecular architecture in much the same way as carboxylic acid functionality. Thus, when one functionality is present per molecule (i.e. benzamide), cyclic dimers are formed. In addition, these dimers are propagated into one-dimensional tape through two complementary N-H···O hydrogen bonds between neighboring dimers. If there are two amide functionality present per molecule (i.e. terephthalamide), infinite one-dimensional chains are produced. These chains then are propagated into the corresponding two-dimensional sheets via a second hydrogen bond involving the extra amide proton and the carbonyl oxygen of neighboring amide.

1.4 Supramolecular Chemistry

Supramolecular chemistry may be defined as "chemistry beyond the molecule", bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular interactions.[2,24] In fact, considering intermolecular interactions as supramolecular glue, one may easily appreciate that a crystal is one of the finest examples to represent a supermolecule *par excellence*.[25]

Supramolecular chemistry is rapidly expanding as interdisciplinary frontier area bridging different branches of science with exciting and innovative concepts, which are fundamentals in nature, to exotic applications in various industrial sectors such as, pharmaceuticals, polymers, etc.[26] In principle, supramolecular chemistry can be classified into two major parts depending upon the nature of the ligands and their interactions towards forming a certain type of bonds.

(i) Supramolecular assemblies involved organic building blocks

(ii) Supramolecular assemblies of metal-organic complexes

1.4.1 Supramolecular assemblies of organic building blocks

The design of molecular building blocks that self-assemble into well-defined, discrete structures in solid state or in solution is a contemporary challenging in supramolecular chemistry.[27] In particular, synthesis and structural characterization of the supramolecular complexes employing organic building blocks are fascinating not only because of their intriguing structural features with different architectures, such as porous network, host-guest assemblies, lamellar sheets etc.[28] but also because of the readily available synthetic procedure to prepare such building blocks. The porous supramolecular networks derived from such organic assemblies, indeed, may be correspond to well known porous structures, entirely composed by inorganic constituents, such as zeolites, but inherently less robust because the molecules are held together by hydrogen bonds and other noncovalent interactions.[29] Several reports from various research groups showed the utility of variety of organic compounds in the extensive preparation of the numerous supramolecular complexes. The structural features of some of the selective and fascinating examples of such supramolecular complexes are discussed herein.

Zimmerman and coworkers reported the supramolecular assembly formed by trimesic acid and pyrene molecules, which is a representative example for host-guest complex mediated by purely hydrogen bonds. Creation of host-guest complexes of trimesic acid is, in general, difficult due to the tendency of open framework to interwoven yielding catenated and/or interpenetrated structure.[22] In the case of trimesic acid, the “chicken-wire” networks are pleated and the 14Å holes are filled by a mutual triple catenation (see Figure 2b). But, in the complex of trimesic acid and pyrene, the interpenetration inherited by trimesic acid has been successfully precluded by filling the cavities by pyrene molecules (Figure 3). The co-crystal was prepared by slow evaporation of the reaction mixture from ether/ethanol solution. The structure consists of stacked layers of non-interpenetrated hydrogen bonded networks that superficially resemble the chicken-wire motif found in trimesic acid.[30]

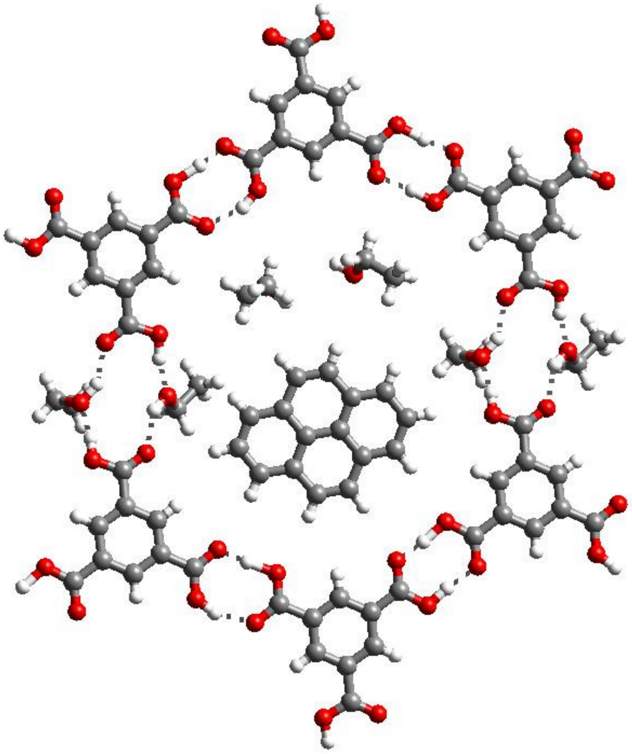
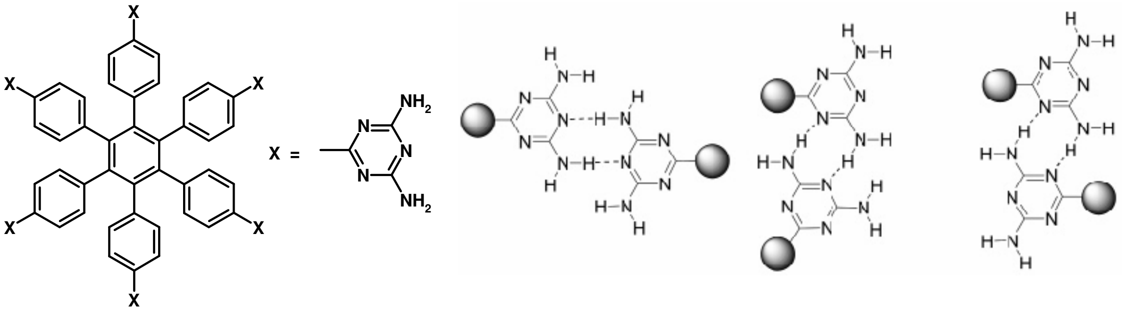


Figure 3. The cavity structure formed by trimesic acid and pyrene molecules.

Wuest and coworkers termed molecular building blocks that are independent of the conformational flexibility and stable to the reaction conditions, yielding highly predictable molecular assemblies, as “molecular tectons”.[31] Several organic molecular tectons with various functional groups have been identified/designed for the preparation of numerous supramolecular complexes with particular focus towards the creation of porous networks. One of the fascinating examples is the supramolecular complexes of hexakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]benzene (Figure 4a), which can adopt three different types of hydrogen bonding patters as described in Figure 4b.[32]

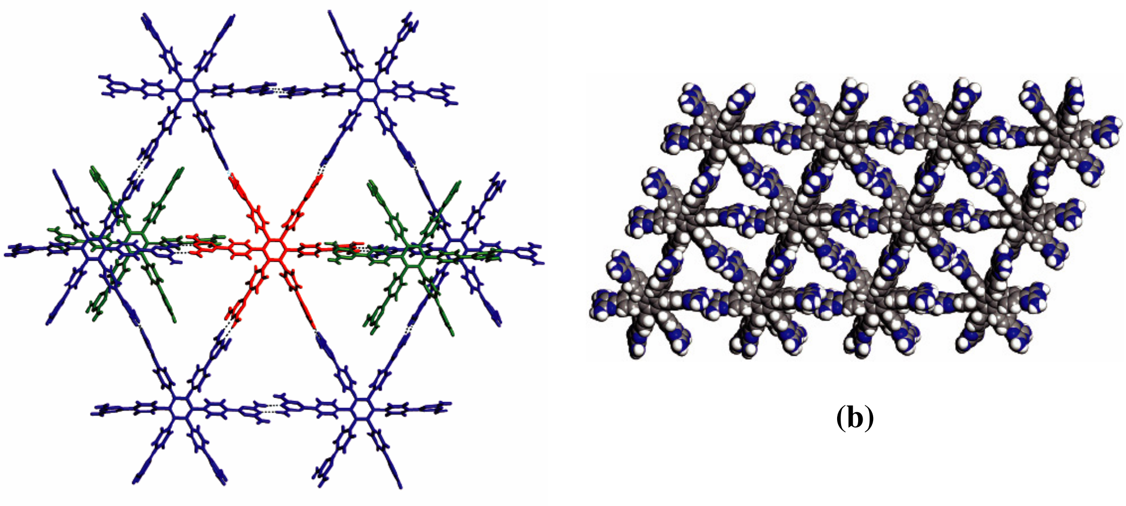


Type I **Type II** **Type III**

(a) **(b)**

Figure 4. (a) Structure of molecular tecton. (b) Three different possible types of hydrogen bonding patterns of tecton.

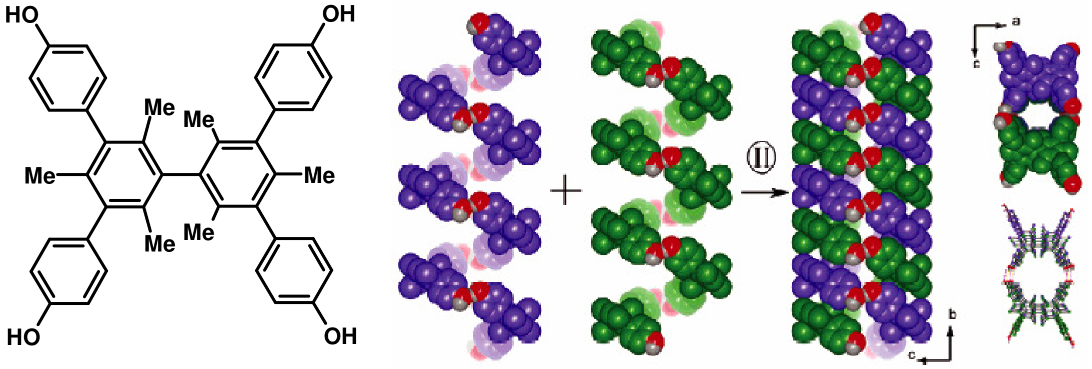
The three-dimensional arrangement of crystal structure of tecton, as shown in Figure 5a reveals, that a central molecule (red) is hydrogen-bonded to its eight neighbors (blue and green). Six of the neighbors (blue) lie approximately in the plane of the central molecule and interact according to motif **I**, and the other two (green) lie above and below the plane and form hydrogen bonds of type **III** with the central molecule (red). A space filling model along the *b*-axis that shows the large triangular channels (see Figure 5b). In this structure, 70% of the volume of the crystal is accessed by the guest molecules.



(a) (b)

Figure 5. (a) Three-dimensional arrangement of crystal structure of tecton. (b) A space filling model along the *b*-axis.

Also, Moorthy and coworkers have shown the significance of the position of functional groups on a given substrate, such as hydroxyl and carboxyl groups, through a study of complex formed by 3,3',5,5'-tetraphenylbimesityl that gave host-guest complex *via* hydrogen-bonded networks.



(a) (b)

Figure 6. (a) The molecular structure of tetrakis(4-hydroxyphenyl)bimesityl. (b) Formation of a porous channel from two parallel helices generated each by the self-assembly of the given molecule *via* O-H···O hydrogen bonds.

The crystallization of tetrakis(4-hydroxyphenyl)bimesityl (Figure 6a) from a solution of ethanol yielded a complex, in which the molecules are self-assembled through O-H···O hydrogen bonds to produce a hydrogen bonded "*pseudo helical spine*". Further such parallel helices are interconnected through C-H···O hydrogen bond to form porous channels as described in Figure 6b. The space-filling diagram in Figure 7 reveals that the voids resulted from the self-assembly of adjacent porous channels *via* O-H···O hydrogen bonds, which are being occupied by ethanol molecules as guest that are shown in ball-and-stick model.[33]

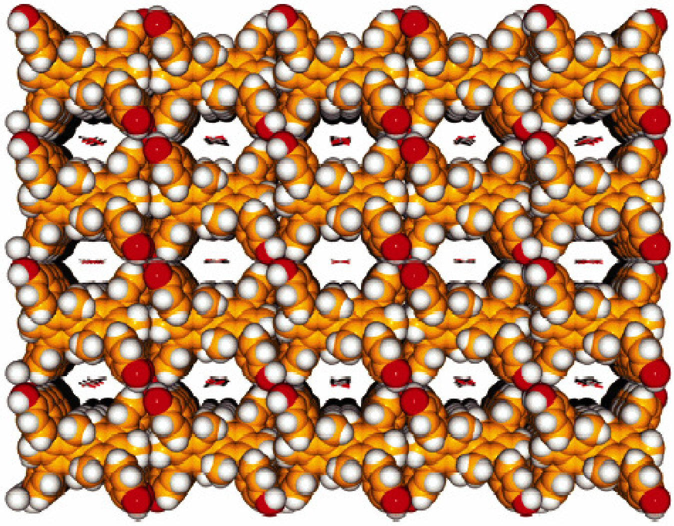


Figure 7. Space-filling diagram reveals the voids that are filled by guest ethanol molecules.

Pedireddi and Arora have reported the host-guest assemblies formed by 1,2,4,5-benzenetetracarboxylic acid with various aza-donor compounds like, 1,10-phenanthroline, 1,7-phenanthroline, phenazine, 4-(N,N'-dimethylamino)pyridine, 1,2-bis(4-pyridyl)ethene, and 1,2-bis(4-pyridyl)ethane. Structure determination of all these complexes reveals several common and distinct unique features. The typical example shown in Figure 8 is the supramolecular host-guest network formed between the tetracarboxylic acid and 1,10-phenanthroline. The complex exists in hydrated form with constituent molecules being in 1:1:1 ratio, yielding a host-guest assembly.

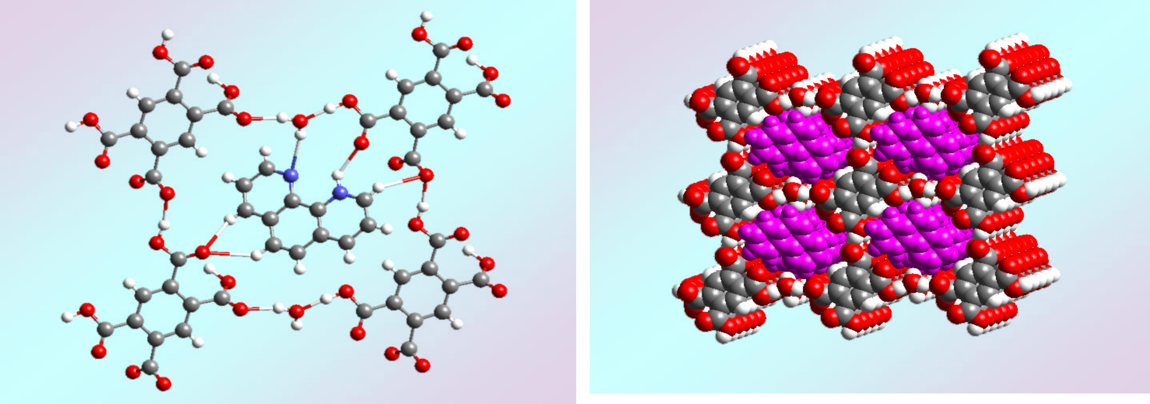


Figure 8. Cavity (9 x 12 Å^2) formed by tetracarboxylic acid and 1,10-phenanthroline molecules in two-dimensional arrangement (left) and host-guest network formed in three-dimension and are being occupied by phenanthroline molecules (right).

The structure analysis reveals that the molecules are connected through O-H···O hydrogen bonds formed by the –COOH with adjacent moieties as well as with H_2O molecules leading to the formation of closed network with cavities of 9 x 12 Å^2, which are being occupied by 1,10-phenanthroline molecules as shown in Figure 8.[34]

In addition, Pedireddi *et al.*[35] have thoroughly studied the ability of cyclic imide and amide functional groups in the formation supramolecular complexes taking into account the importance of amide functional group in biology as well. It has been shown that 3,5-dinitrobenzamide and 4,4'-bipyridine form two solvated complexes by co-crystallizing from either CH_3OH or H_2O. Although, both the complexes form similar host-guest network structures in three-dimensional arrangement, the analysis of host network around each cavity revealed that in CH_3OH solvated structure (see

Figure 9a-c), the molecules in host arrangement formed helical structure and similar molecules formed regular hexagonal networks in the hydrated structure (see Figure 9d).[36]

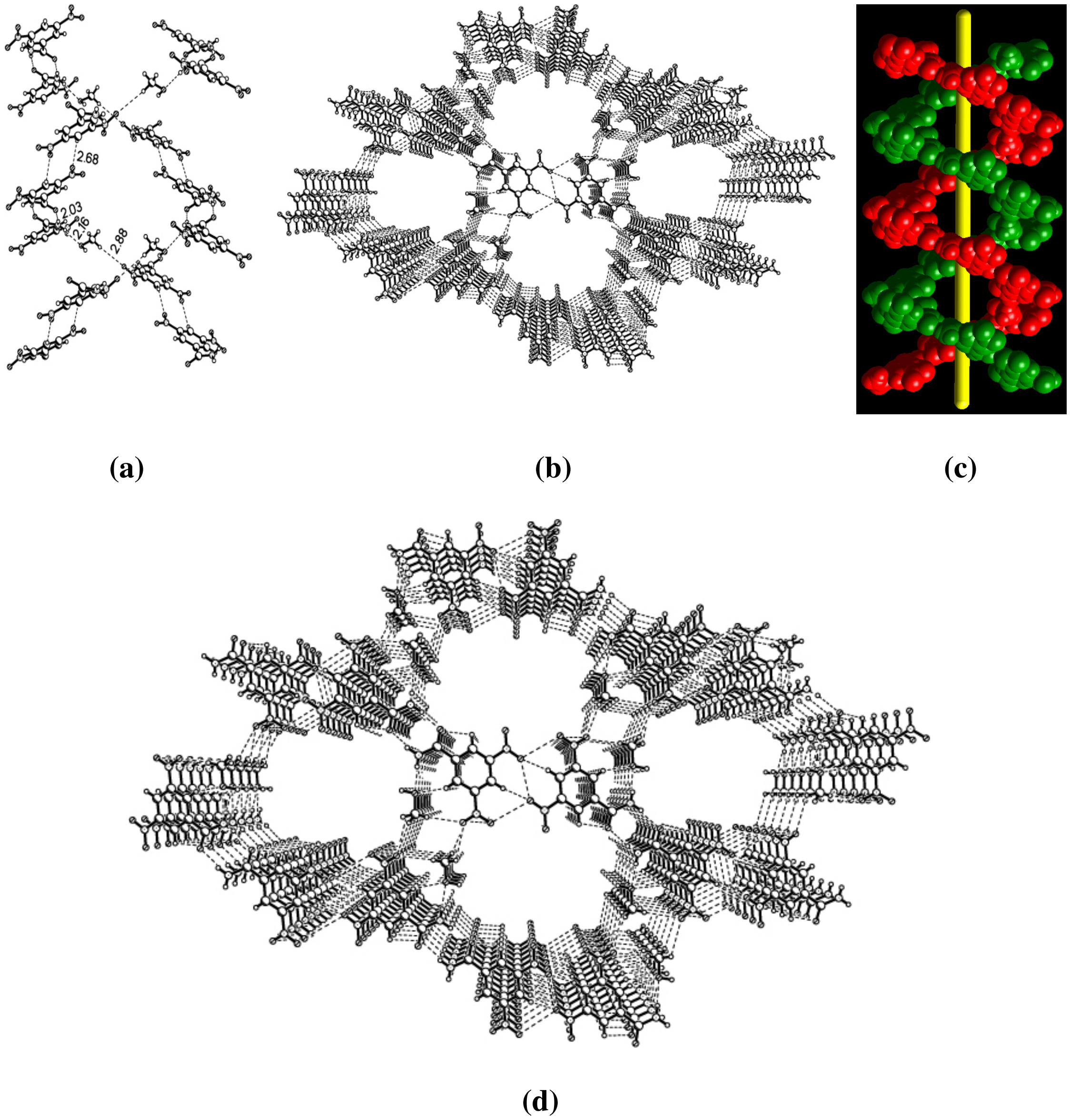
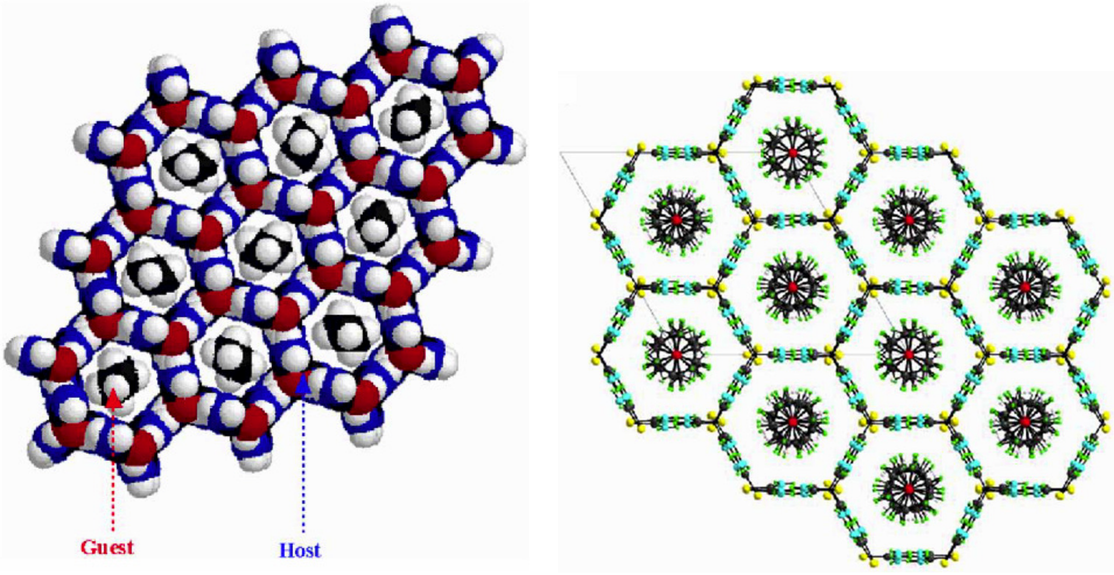


Figure 9. (a) Double helix found in CH_3OH solvated structure. (b) Three-dimensional host network of CH_3OH solvated structure, the guest molecules are omitted for clear vision of the host. (c) Space filling model of double helix of CH_3OH solvated structure. (d) Stacking of the planar sheets of hydrated structure to yield host network.

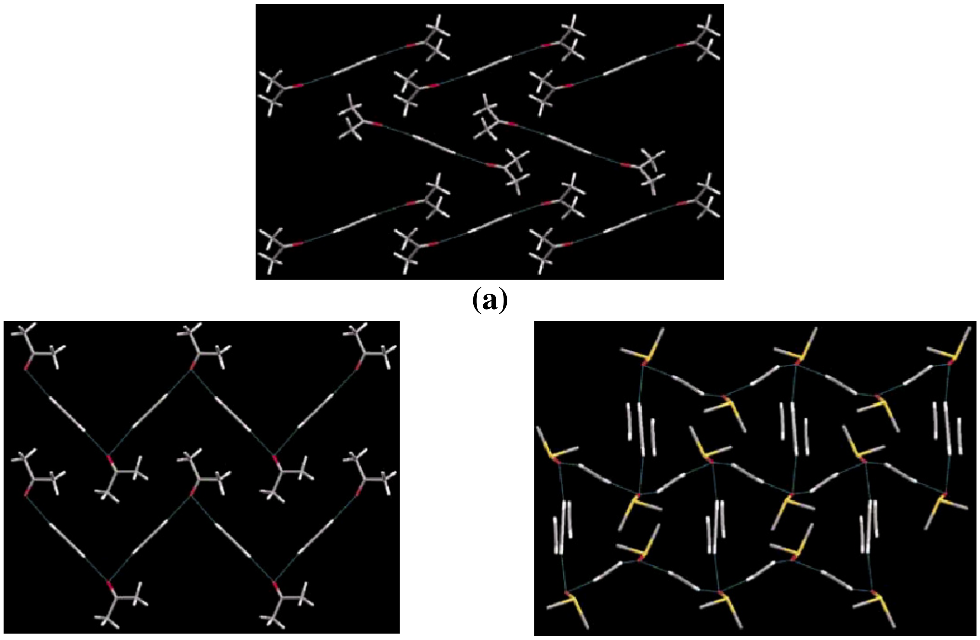
Similarly, Harris and coworkers have shown the efficacy of supramolecular host networks for the guest inclusion. Host networks formed by urea as well as its sulphur analogue –thiourea- were used for the guest inclusion (Figure 10). The tunnels in the thiourea host structure are larger in cross-sectional area than those in the urea host structure, and as a consequence, the urea and thiourea host structures tend to incorporate different types of guest molecule. It was noted that the urea tunnels are stable only when the tunnels are filled with the dense packing of guest molecules.[37]



(a) **(b)**

Figure 10. (a) Structure of the hexadecane/urea inclusion compound at ambient temperature, showing nine complete tunnels viewed along the tunnel axis. (b) Crystal structure of the 1-bromoadamantane/thiourea inclusion compound viewed along the tunnel axis of the thiourea host structure.

Roland and coworkers have reported supramolecular complexes that are prepared by the co-crystallization of gases and liquids.[38] Acetylene was co-crystallized with acetone as well as dimethylsulphoxide (DMSO) to yield different supramolecular complexes. To prepare the single crystal of the complexes, the components were condensed at -196 ºC into a quartz capillary (0.3mm diameter) on a vacuum line to trap the corresponding solutions. The structural details of the complexes are shown in Figure 11.



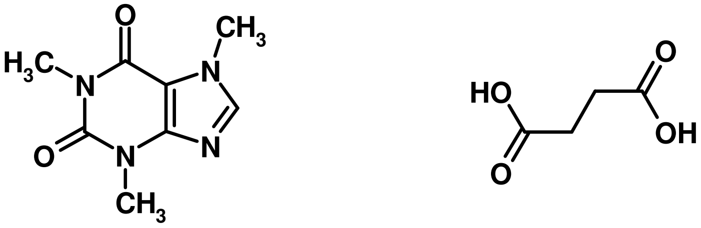
(a)

(b) (c)

Figure 11. (a) Structure of co-crystal of acetylene:acetone 1:2; view of the (100) plane. (b) Structure of co-crystal of acetylene:acetone 1:1 view of the (100) plane. (c) Structure of co-crystal of acetylene:dimethyl sulfoxide 2:1 view of the (101) plane.

Jones and coworkers have demonstrated the method of solid state grinding, *i.e.* the use of mechanical forces to create new molecular and supramolecular assemblies.[39] This method can also be called as mechanochemistry and can be regarded as an attractive and eco-friendly alternative route, avoiding the use of large amount of solvents, to prepare the crystals of the supramolecular complexes of two or more components. The following example shows the supramolecular host network constructed from caffeine and succinic acid (Scheme 3) in 1:1 stoichiometric ratio incorporating solvent of crystallization, 1,4-dioxane, which could also be prepared by the neat grinding of the constituents with a few drops of 1,4-dioxane, as confirmed by powder X-ray diffraction methods (see Figure 12b).

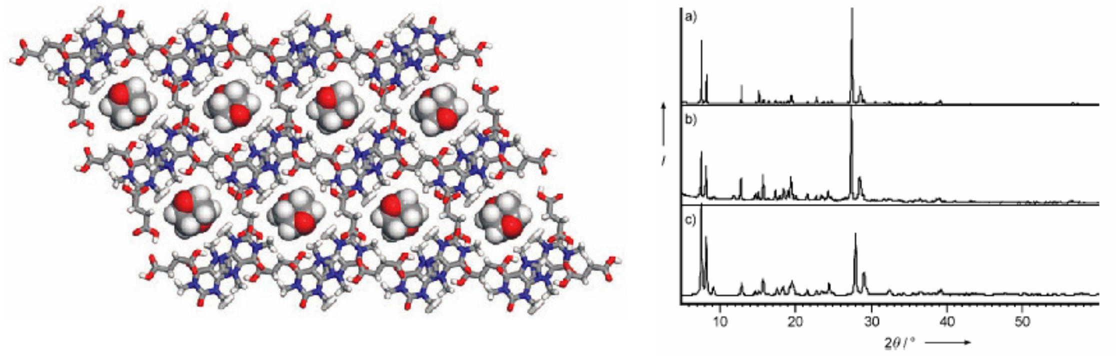
Scheme 3



Caffeine

Succinic acid

Structure determination by single-crystal X-ray diffraction, reveals that the constituent molecules are held together by O-H$\cdots$O, O-H$\cdots$N, and pairs of C-H$\cdots$O hydrogen bonds and yield layer structures. Stacking of such layers produced the host network with channels, which are being occupied by columns of disordered 1,4-dioxane molecules as shown in the Figure 12a.[40]



(a)

(b)

Figure 12. The host-guest network formed by caffein, succinic acid and 1,4-dioxane. The host network is shown in wire-frame and the guest molecules in space-filling representations.

Braga[41] and coworkers also have used the mechanochemistry method for the preparation of numerous supramolecular complexes of organometallics and organic entities. The supramolecular complexes formed between pyridine derivative of ferrocene complex and aliphatic carboxylic acids are shown herein. In all the cases, the organic and organometallic moieties are held together by hydrogen bonds formed between the –COOH and the pyridine nitrogen atoms through O-H···N hydrogen bonds.

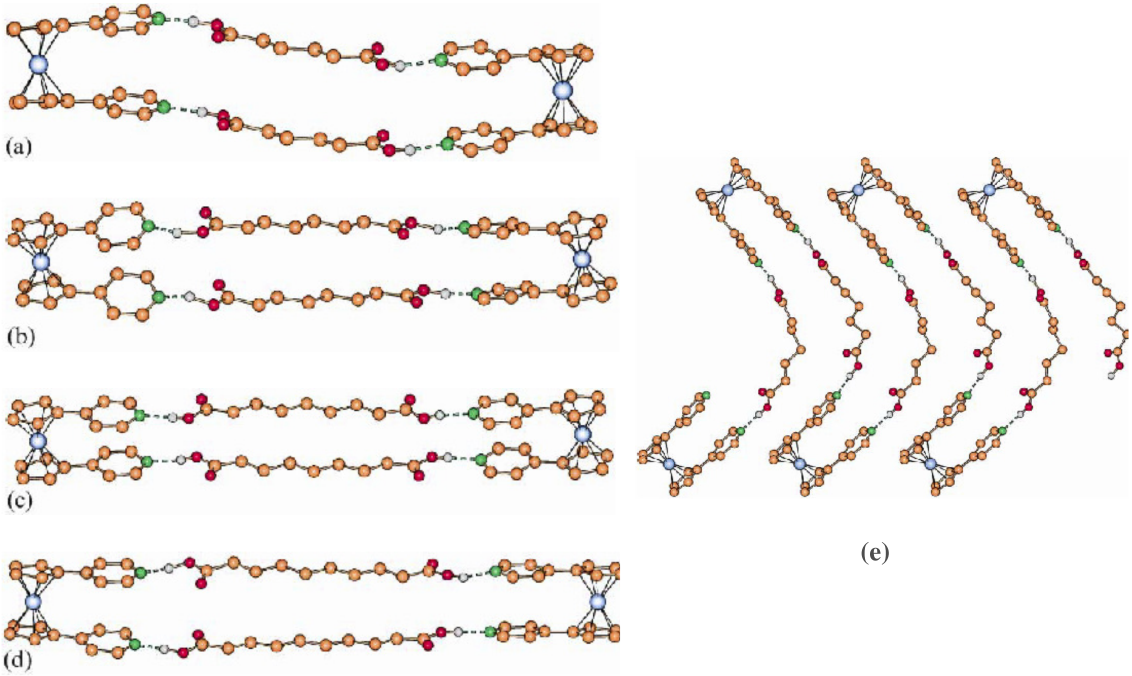


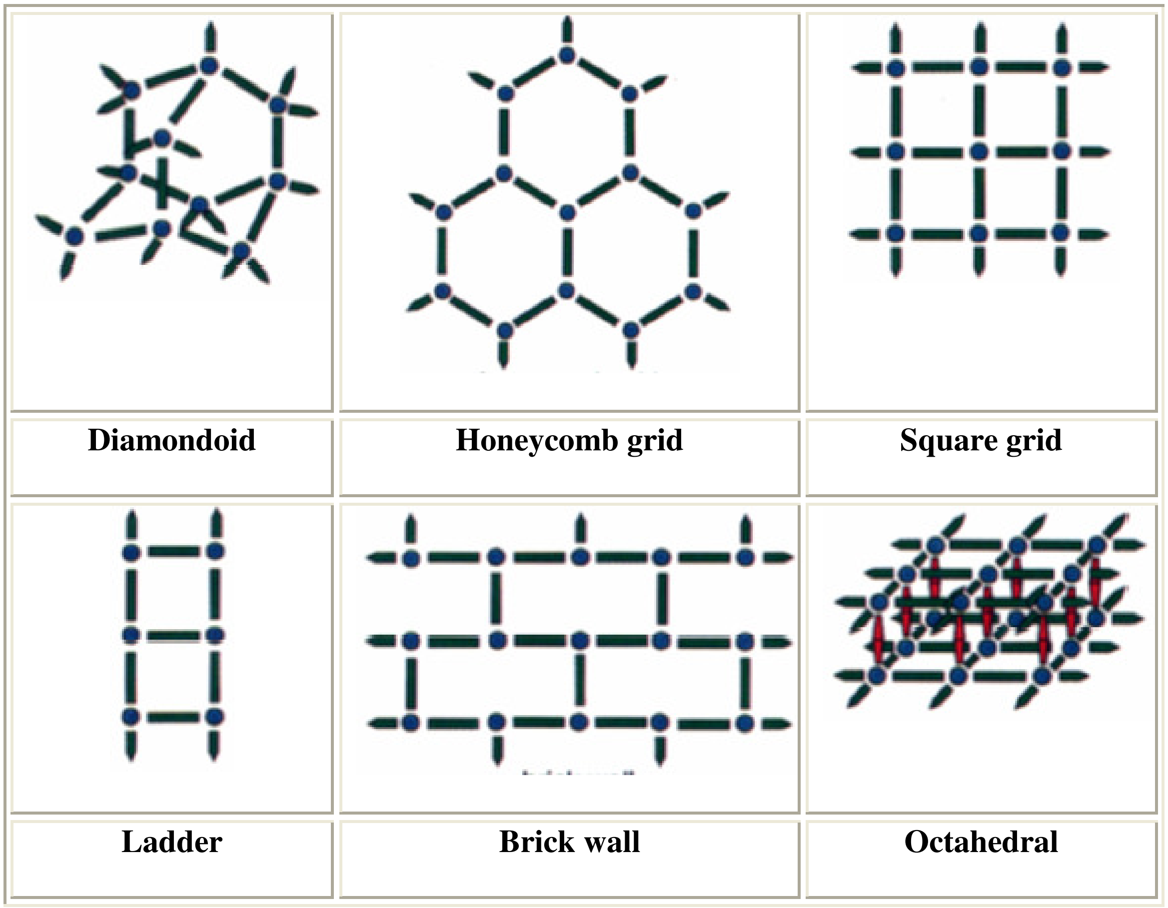
Figure 13. The supramolecular structures of the macrocycles obtained from ferrocene complex with (a) adipic (4), (b) suberic (6), (c) azelaic (7) and (d) sebacic (8) acids showing the hydrogen bond links between the two outer organometallic molecules and the inner organic spacers. (e) The *zig-zag* chain found in complex of pimelic acid (5).

More specifically, manual grinding of the solid organometallic complex [Fe(η^5-$C_5H_4C_5H_4N)_2$] with the solid dicarboxylic acids of formula HOOC$(CH_2)_n$COOH [where n =4 (adipic), 5 (pimelic), 6 (suberic), 7 (azelaic) and 8 (sebacic)] in the presence of traces of MeOH (by kneading) gave five novel compounds, with general formula {[Fe(η^5-$C_5H_4C_5H_4N)_2$].[HOOC(CH_2)nCOOH]}. Structures of these complexes are shown in Figure 13.[42]

1.4.2 Supramolecular assemblies of metal-organic complexes

Besides the design and synthesis of supramolecular assemblies mediated, completely, by organic compounds for various purposes, parallel development on the creation of networks of metal–organic frameworks, also referred as coordination polymers, derived from inorganic and organic building blocks lead to the preparation of myriad of assemblies.[43] Coordination polymers[44] are compounds with backbones constructed from metal ions as connectors and the organic ligands as linkers with the dative bonds formed between the metal ion and organic ligands.[45] The phrase, "coordination polymers" appeared in the early 1960s, and the area was first reviewed in 1964.[46] The key to success in the preparation of coordination polymers in the form of infinite one, two, and three-dimensional networks is the design of the molecular building blocks, which direct the formation of the desired architectural, chemical, and physical properties of the resulting solid-state materials.[47] Construction of metal-organic frameworks (MOFs) using dative bonds are not only well known for their fascinating, aesthetic architectures but also shows potential applications in catalysis, ion-exchange, molecular sensing, gas storage, gas separation, etc.[48]

Recently, remarkable progress has been made in synthesizing a wide variety of supramolecular coordination polymers and discrete networks exhibiting different types of topologies, such as diamondoid, honeycomb, grid, ladder, brickwall and octahedral etc, from tetrahedral, trigonal and octahedral metal templates (eg. Co^{II}, Zn^{II}, Cd^{II}, Fe^{II}, Ag^{I}, Cu^{I}).[49] Especially the constructions and characterizations of organic-inorganic hybrid materials, in addition to the ones based on transition metal carboxylates, are of continuous interest because of their unusual topologies and relevance in a wide range of applications in materials science including superconductors, magnetic materials, catalysts, and luminescent materials.[50] For example, assemblies of the neutral linkers like, pyrazine, 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethane and 1,2-bis(4-pyridyl)ethene, and the oxides of the aza-donor ligands as well as various anionic linkers such as di-, tri-, tetra- and hexa-carboxylates and organophosphates were extensively studied for the creation of MOFs; as schematically shown in Figure 14.[51-53]



Diamondoid

Honeycomb grid

Square grid

Ladder

Brick wall

Octahedral

Figure 14. Some of coordination polymer frameworks formed from metal ions and linear ditopic ligands.

Yaghi *et al*.[54] have extensively studied the systematic design and construction of a series of metal organic frameworks (MOFs) with varied pore functionalities and sizes. The basic building blocks were symmetric organic molecules, which bound the metal ions to form metal–organic layers with void space, whose composition was determined by the functionalization of the organic molecules. Several materials of this type have the pore sizes in mesoporous range (>20Å) as well as the lowest crystal density. For example, reaction of trimesic acid with cobalt nitrate forms metal-organic framework with porous network, as shown in Figure 15, and the pores were used to bind aromatic guest molecules selectively. The crystal lattice, thus, formed is thermally stable up to 350 °C, even after removal of included guest molecules, also could be selectively readsorbed.[55]

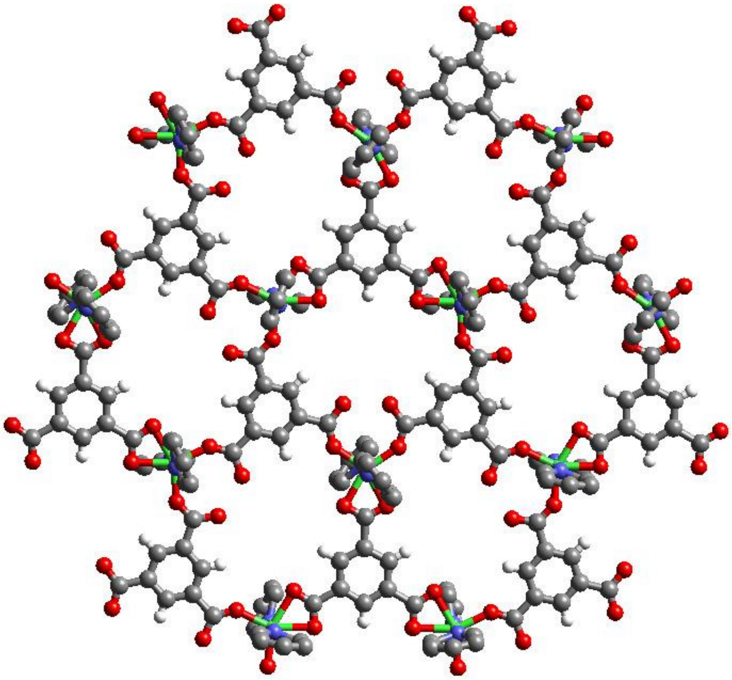


Figure 15. Porous network formed between trimesic acid and cobalt metal ion.

Braga and coworkers reported solid-state and solution reactions between silver acetate and *trans*-1,4-diaminocyclohexane [$H_2NC_6H_{10}NH_2$] which yielded coordination polymers with two isomers depending upon the solvent evaporation conditions. Crystals of Ag[$H_2NC_6H_{10}NH_2$][CH_3COO]0.5H_2O were obtained by co-crystallization of constituents from a CH_3OH solution under argon flow, while crystals of Ag[$H_2NC_6H_{10}NH_2$][CH_3COO].3H_2O were obtained by slow evaporation in the air. The structures of two different isomers are shown in Figure 16.[56]

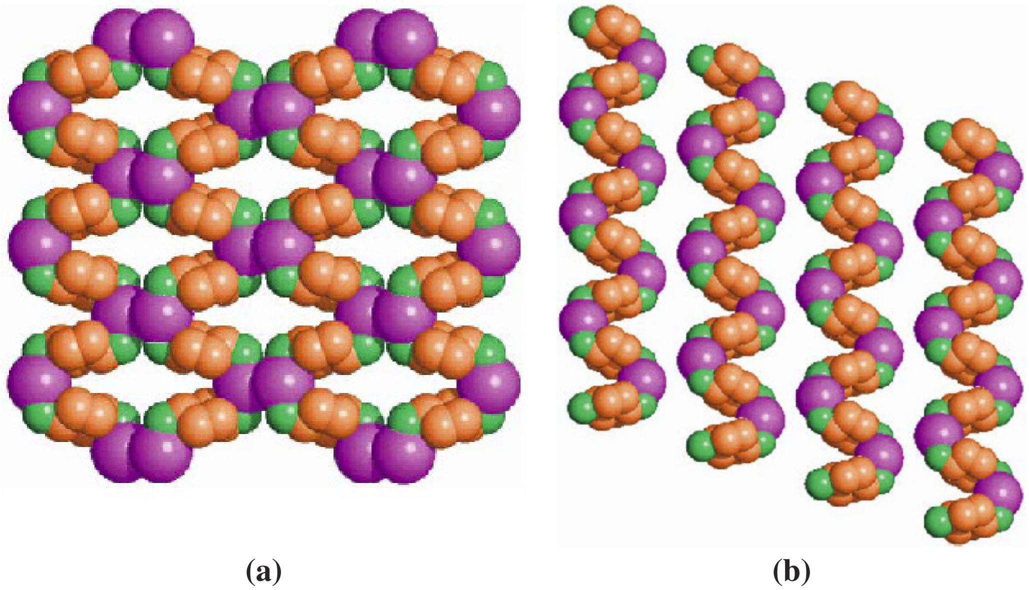


Figure 16. Structural arrangement of coordination complex, (a) Ag[$H_2NC_6H_{10}NH_2$]-[CH_3COO]0.5H_2O, and (b) Ag[$H_2NC_6H_{10}NH_2$][CH_3COO].3H_2O.

Zaworotko and coworkers reported a complex formed by neutral linkers like 4,4'-bipyridine (*bpy*) and Co^{2+} metal ion, which forms an open framework as the first example of noninterpenetrated molecular ladder. The complex gave an infinite ladder that clathrates small organic guests, despite possessing a cavity that is large enough to self assemble. In a typical coordination assembly, formed between *bpy* and

Co^{2+}, obtained from CH_3CN or $CHCl_3$, square hydrophobic cavities with dimensions of 11.4 x 11.4 $Å^2$ were identified, which are being filled by the solvent of the crystallization like CH_3CN, $CHCl_3$, etc. The solvent molecules, in the void space, remain intact by forming hydrogen bonds with the grid networks (see Figure 17).[57]

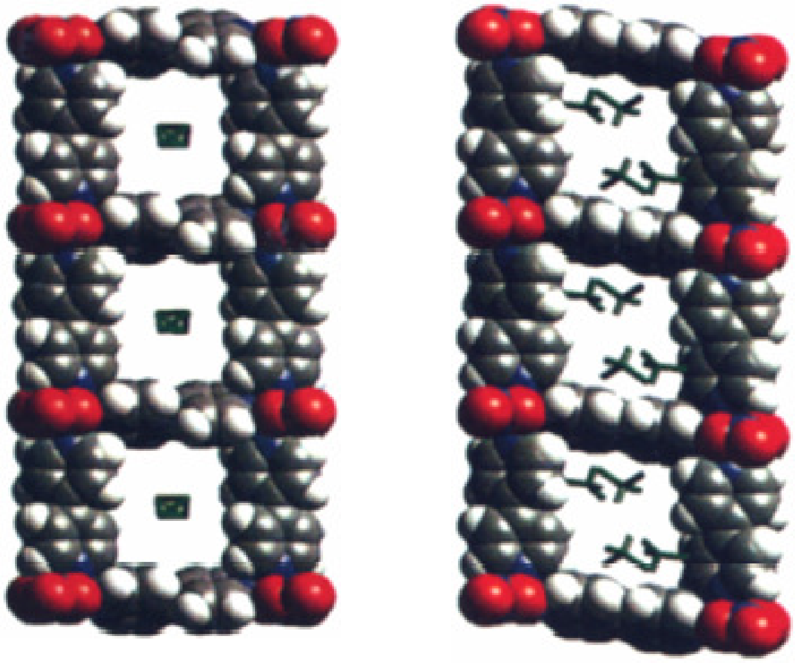
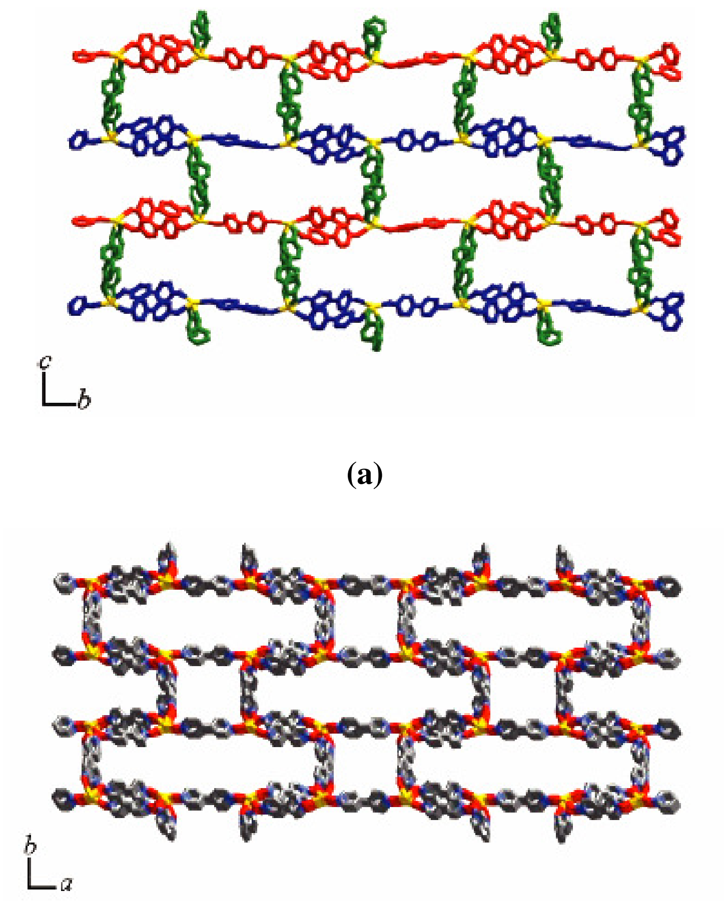


Figure 17. Space-filling views of molecular ladders of CH_3CN solvate (left) and CH_3Cl solvate (right). Enclathrated solvent molecules are shown in green in stick form.

In addition to bipyridine, 4,4'-bipyridine-N,N'-dioxide has also been used in the synthesis of coordination polymers. Schröder and coworkers reported two remarkable lanthanide coordination polymers $\{[La_4L_{10}(CH_3OH)_{10}Cl_3]Cl(BPh_4)_8.\text{-}22CH_3OH\}_\infty$ and $\{[LaL_{2.5}(CH_3OH)(Ph_2B(OMe)_2)]\text{-} (BPh_4)2.4.5CH_3OH\}_\infty$, (L = 4,4'-bipyridine-N,N'-dioxide), formed by the reaction between a lanthanide salt and 4,4'-bipyridine-N,N'-dioxide. These two complexes consist of unusual five-connected lanthanum nodes sustained by bridging ligands L. These structures verify that the flexible modes and high coordination of lanthanide ions suit the formation of frameworks with unusual and highly connected nodes.

In complex **11**, 4,4'-bipyridine-N,N'-dioxide ligands bridge the metal centers to yield a 3D framework structure of $4^4 6^6$ (see Figure 18a) and $4^6 6^2 8^2$ (see Figure 18b) topologies. These linking chains are alternately distributed on either side of the plane nets, thus forming large "six-metal-membered" channels of effective cross-section of ~ 8 x 18 Å parallel to the *a*-axis. Most of the space within the channels is occupied by the bulky BPh_4^- counter ions, of which there are 16 per unit cell.[58]

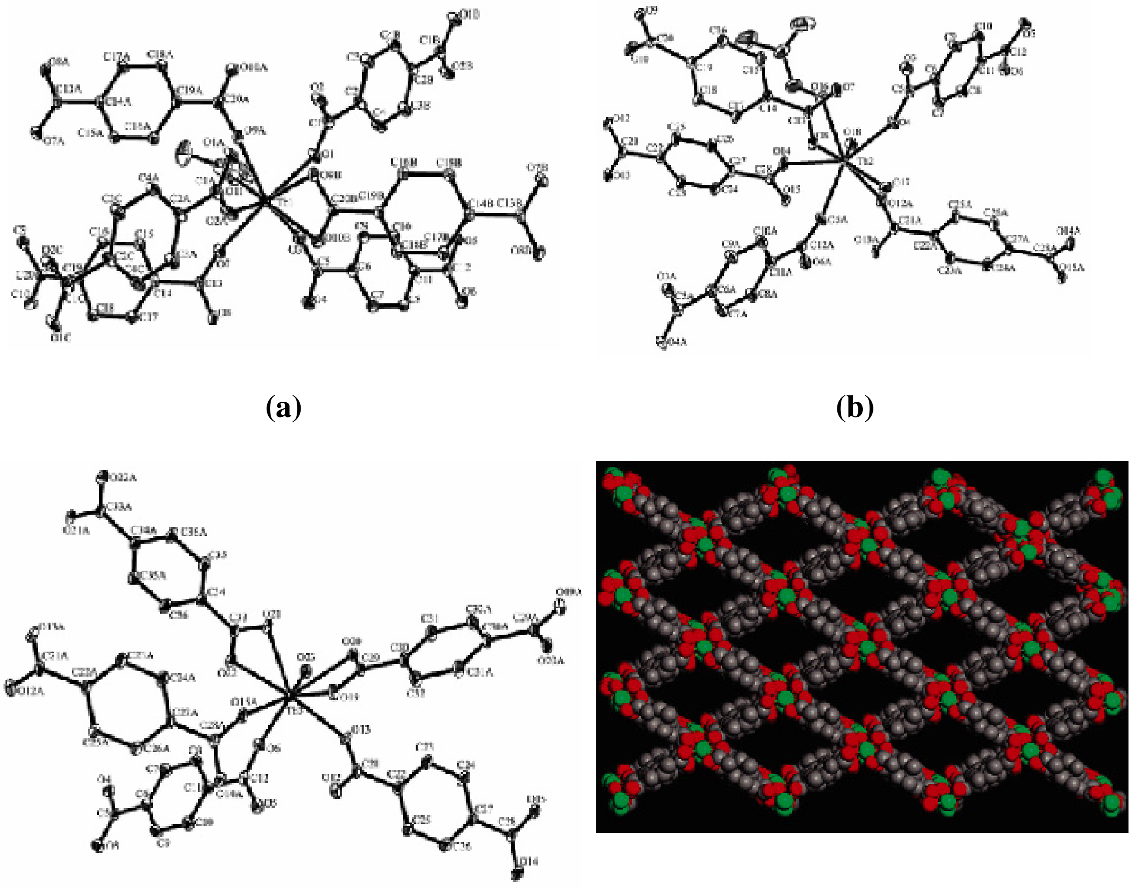


(a)

(b)

Figure 18. (a) View along a crystallographic *a*-axis of the "six-metal-membered" channels in compound of $4^4 6^6$ topology network. (b) View along the *c*-axis in the compound of $4^6 6^2 8^2$ topology network shows the "eight-metal-membered" and "four-metal-membered" channels.

Qui et. al reported several interesting example of coordination polymers constructed from discrete rod shaped $Ln_6(CO_2)_{18}$, inorganic secondary building units (SBUs), with 1,4-benzendicaroboxylic acid (BDC) linkers. The following example shows the structure of coordination polymer, $Tb_3(BDC)_{4.5}(DMF)_2(H_2O)_3.(DMF)$-$(H_2O)$, formed by terbium ion and BDC in the presence of mixture of N,N-dimethylformamide (DMF), H_2O and EtOH.



(a) **(b)**

(c) **(d)**

Figure 19. Coordination environment of (a) Tb_1, (b) Tb_2, (c) Tb_3 in complex with non-hydrogen atoms represented by thermal ellipsoids drawn. (d) One-dimensional channels viewed along the [011] direction (Tb, green; O, red; C, gray). Guest molecules are omitted for clarity.

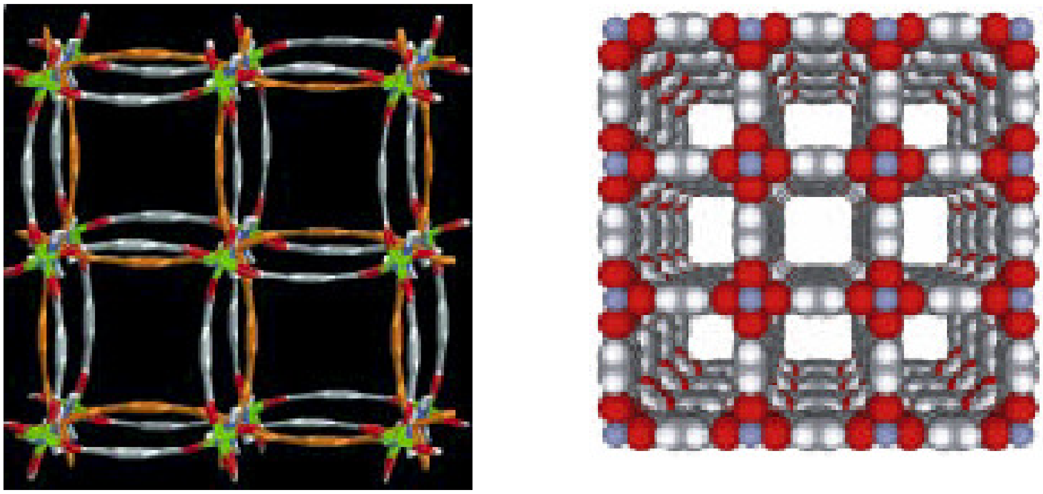
The analysis reveals that the metal ion exists in three different types of coordination modes within a complex as shown in Figure 19a-c. In three-dimension, the complex forms an one-dimensional channels of 4 x 6 Å in dimension, along the [0,-1,1] direction (see Figure 19d) and the channels are being occupied by the solvent molecules (DMF and H_2O).[59]

Thus, all the examples discussed in the above sections show the different types of organic building blocks and metal ions for the preparation of variety of supramolecular coordination polymers that are prepared by various synthetic procedures. These coordination polymers are used for various applications, in areas of *heterogeneous catalysis*, *gas storage*, *separation technologies*, *ion exchange*, *electronics, magnetism,* etc. Some of the selective applications of the coordination polymers are discussed herein.[48]

1.4.3 Heterogeneous catalysis

The unique porous properties of porous coordination polymers (PCPs), along with their designable structures and flexibility, could be key factors that make them useful for the highly selective recognition, accommodation, and reaction of target molecules. Thus, these materials could be used as catalysts for specific controlled reactions.[60-61]

Recently, Kitagawa and coworkers have studied the controlled polymerization within functional nanospaces based on PCP materials as a strategy to overcome the difficulties in conventional polymerization. They have reported the selective linear radical polymerization of *para* and *meta* divinylbenzenes (DVBs) in the channels of $[Zn_2(1,4\text{-bdc})_2(\text{ted})]_n$ (bdc = benzenedicarboxylate; ted = triethylenediamine) which have regular and continuous one-dimensional nanochannels with a pore size of 7.8 x 7.8 Å^2 along its *c*-axis (see Figure 20). The key to this selective polymerization is an appropriate channel size for monomer inclusion and/or specific framework flexibility.[62]



(a) **(b)**

Figure 20. (a) The view along fourfold axis of the metal –organic framework structure of the complex. One Layer of the complex is colored orange to emphasize the alternation of stacking layer. Hydrogen atoms and guest molecules are omitted (b) Space-filling representation of evacuated framework, which emphasizes the open square channels; view along fourfold axis.

Polymerization of *p*-DVB (molecular dimensions: 8.5 x 4.4 Å^2) in the above nanochannels was performed as follows (see Figure 21). After the adsorption of *p*-DVB into the nanochannels, the hybrid DVB was heated at 100º C for five days in a closed system in the presence of 2,2'-azobis(isobutyronitrile) (AIBN) as the radical initiator. The polymerization of *p*-DVB requires a higher temperature and longer reaction time, probably because the large DVB monomers are tightly encapsulated in the channel. The poly(*p*-DVB), thus, formed was then quantitatively released by decomposing the host in ethylenediaminetetraacetic acid (EDTA) solution. It is noteworthy that the recovered poly (*p*-DVB) is soluble in various organic solvents (e.g.THF, $CHCl_3$, DMF, DMSO), which contrasts with the insoluble product usually obtained from the radical polymerization of DVBs in solution and bulk.

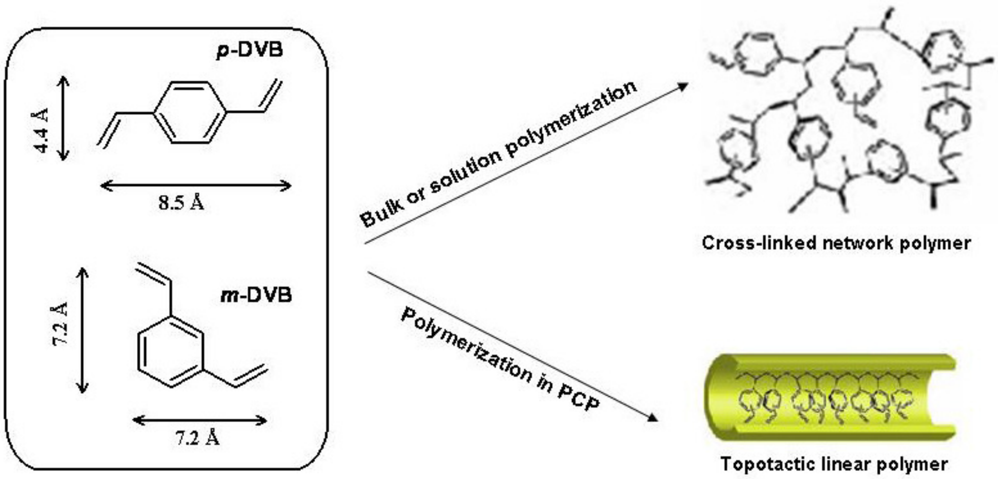


Figure 21. The usual cross-linked network polymerization of DVBs and the topotactic linear polymerization in the one-dimensional channels of PCPs.

1.4.4 Gas adsorption

Gas storage in the porous materials is currently receiving great interest in many areas of science. Among all the gas storages, hydrogen storage is of great interest as a method of providing the gas as a fuel for zero-emission energy production.[63] The approaches currently being adopted for the design of hydrogen storage materials are based on many different types of material, ranging from metal hydrides and carbon nanotubes and nanohorns to gas clathrates although all have inherent problems attached to them. Metal–organic porous materials, with the inherent large internal pore volumes and surface areas are the obvious choice to explore for the preparation of high-capacity storage materials.[64]

Kubota et. al. have reported the gas storage of metal-organic framework (MOF) materials. The material used was CPL-1, that is $[Cu_2(pzdc)_2(pyz)]_n$ (pzdc = pyrazine-2,3-dicarboxylate, pyz = pyrazine), which has a pillared layer structure with uniform nanochannels of 4 x 6 Å^2 (see Figure 22). Significant lattice expansion occurred between 90 and 110 K upon hydrogen adsorption in the nanochannels of the CPL-1 materials. Powder pattern at 90 K shows the peak shift and a slight profile broadening due to the hydrogen adsorption (see Figure 23a). The amount of H_2 molecules adsorbed in CPL-1 at 90 K at 102 kPa was determined to be 0.3 molecules per Cu atom from the measurement of the hydrogen-adsorption isotherm (see Figure 23b).[65]

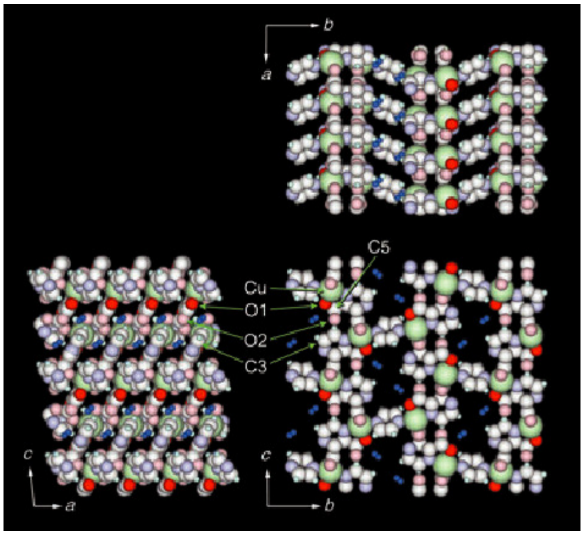
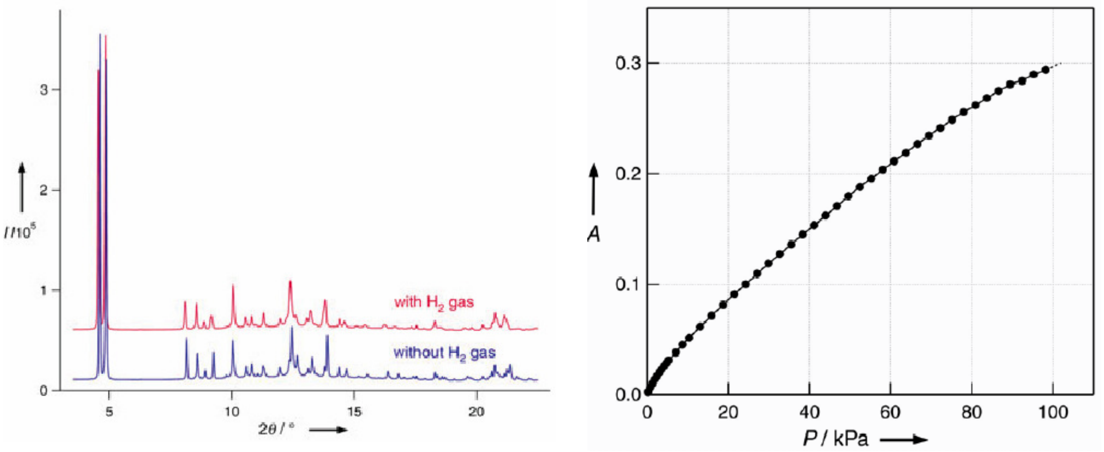


Figure 22. Crystal structure of CPL-1 with adsorbed H_2 molecules. The adsorbed H_2 molecules and the oxygen atoms (O1) of the carboxylate group in the framework are presented as blue dumbbells and red balls, respectively. The adsorbed H_2 molecules randomly occupy the site with a probability of 0.3.



(a) **(b)**

Figure 23. (a) Synchrotron X-ray powder diffraction patterns of CPL-1 (90 K) with hydrogen gas (102 kPa) and without hydrogen gas. (b) Hydrogen gas adsorption isotherm at 89(2)K. *A* = amount of adsorption [H_2/Cu].

1.4.6 Separation of natural gases

Microporous metal-oragnic frameworks are potential materials for the alkane separations because of their selective adsorption and high thermal stability.[44] In the petroleum industry, the separation of alkane isomers is a very important process, and some narrow-pore zeolites have been used for this purpose. Yaghi and coworkers have shown the first example of microporous metal-organic framework for high selective separation of alkanes. They synthesized microporous compound Zn(BDC)(*bpy*)$_{0.5}$ (MOF-508; BDC =1,4-benzenedicarboxylic acid, *bpy* =4,4'-bipyridine), which has a primitive cubic framework with pores that can be tuned by double interpenetration to have 1D channels of approximately 4 x 4 Å^2 in cross section (Figure 24).

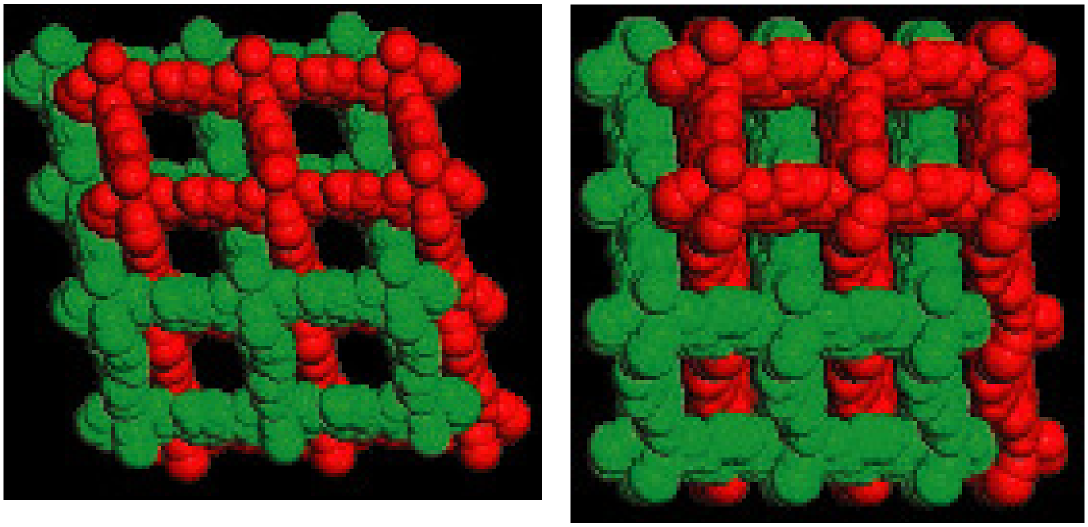


Figure 24. Space-filling representations of the structures of (a) the open phase Zn(BDC)(*bpy*)·(DMF)$(H_2O)_{0.5}$ which contains one-dimensional channels of 4 x 4 $Å^2$. (b) The dense phase Zn(BDC)$(bpy)_{0.5.}$

The solvothermal synthesis of H_2BDC, *bpy*, and $Zn(NO_3)_2.6H_2O$ in DMF/ethanol yielded a guest filled complex with formula of Zn(BDC)(*bpy*)·(DMF)$(H_2O)_{0.5}$. TGA data indicate that complex releases its guest molecules over the temperature range 25–145 ºC to form the guest-free phase Zn(BDC)$(bpy)_{0.5}$ (MOF-508b), which is thermally stable up to 360 ºC.

The chromatography column of 120 cm was packed with the single crystal of above mensioned coordination polymer and used for the gas separation. The GC separation was examined in detail for linear and branched isomers of pentane and hexane. The column could clearly separate *n*-pentane from *n*-hexane with retention times of 6.39 min and 12.06 min, respectively. Branched 2-methylbutane (retention time of 5.31 min) elutes from the column before its linear isomer *n*-pentane. Similarly, 2-methylpentane (retention time of 9.16 min) runs through the column faster than its linear isomer *n*-hexane, while 2,2-dimethylbutane, the isomer of hexane with the shortest linear chain, elutes even faster at a time of 7.40 min. The chromatograms in Figure 25 show the rate of separation of the natural gas mixture.[66]

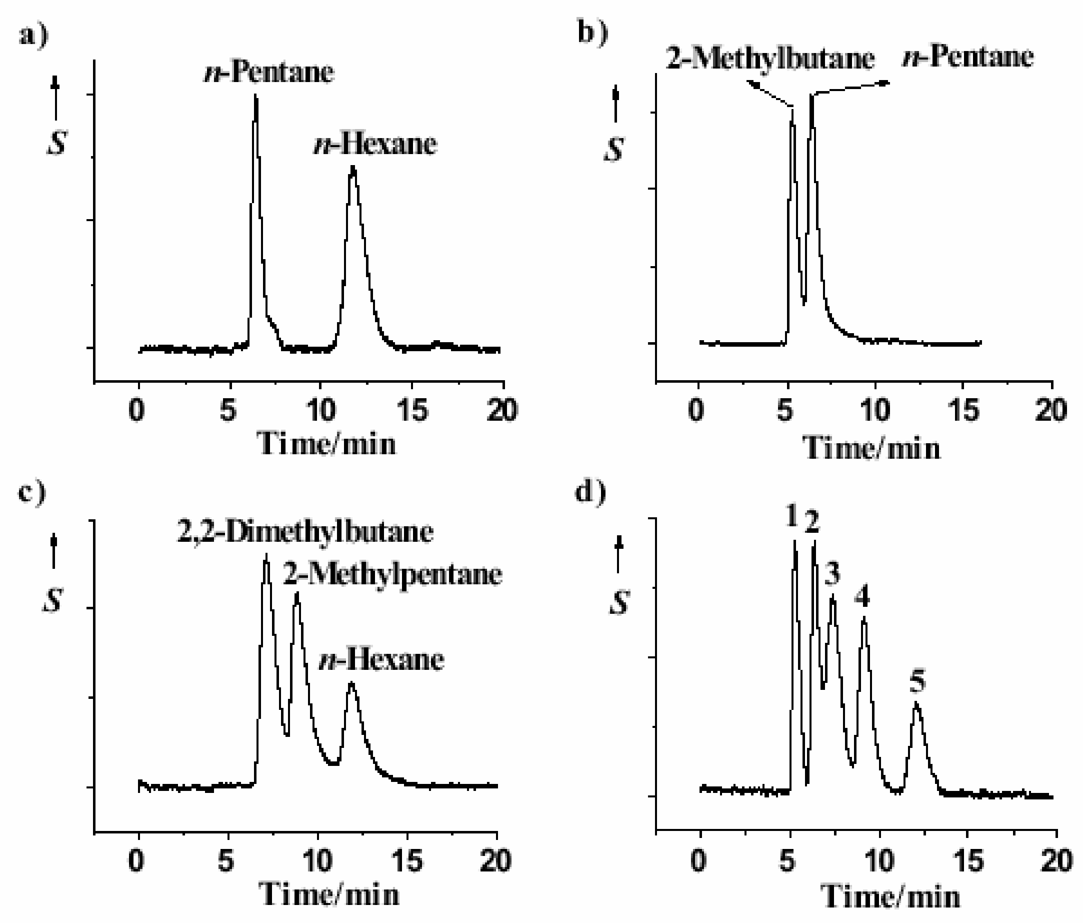


Figure 25. Chromatograms of alkane mixtures separated on the column of the above coordination polymer.

1.5 Conclusions

The supramolecular architectures formed by organic building blocks as well as metal-organic complexes are important materials not only because of their fascinating structural features but also because of their potentials in the applications of in many aspects as discussed above. Synthesis and structural characterization of several supramolecular complexes with their exotic structural features were discussed with illustrative examples from the literature. There are several reports depict the supramolecular complexes formed by carboxylic acid moieties and pyridyl ligands. However, the utility of functional groups, like amide, cyclic imide, cyclic thioimide, hydroxyls and organophosphorous acids, in the synthesis of supramolecular architectures are still not well explored not only in terms of creating topological networks of exotic in nature but also with respect to the various possible networks that can be formed. Since nature of functional group abilities alone is not the sole factor in the assemblies ultimately formed, study of co-crystallization experiments with various ligands of each is of great significance. For this purpose, the study focused on assembly of cyanuric acid, some organophosphorous acids and hydroxyl compounds have been compiled in the following chapters, describing exciting feature of these complexes.

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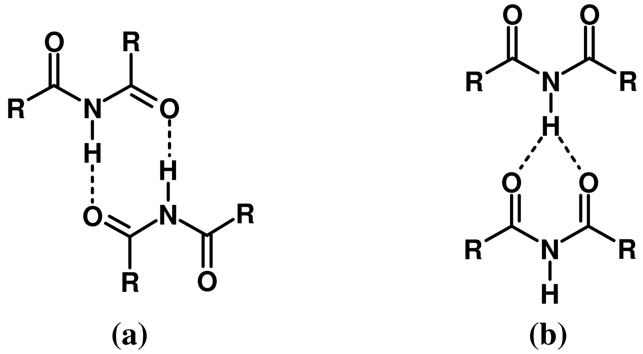
CHAPTER TWO

SYNTHESIS AND RATIONAL ANALYSIS OF ORGANIC SUPRAMOLECULAR ASSEMBLIES: CO-CRYSTALS OF CYANURIC ACID WITH VARIOUS AZA-DONOR COMPOUNDS

2.1 Introduction

Supramolecular synthesis using small molecular building blocks, through noncovalent interactions, is a promising methodology for the development of organic solids and functional materials.[1] Such supramolecular synthesis also provides insights into the molecular recognition phenomena,[2] well known in macromolecular aggregates such as DNA, which play significant role in many biological processes.[3] The modern supramolecular chemistry guided by directional and selective noncovalent interactions focuses on understanding the interplay of numerous intermolecular interactions for the preparation of myriad of supramolecular assemblies of exotic architectures.[4] In this connection, many carboxylic acids, for example, mono-, di-, tri- and tetracarbolylic acids, various amides, pyridine derivatives, amino compounds, etc., which have affinity to yield a variety of intermolecular interactions, have been well explored for the preparation of targeted synthesis of desired supramolecular complexes with unprecedented topological networks.[5]

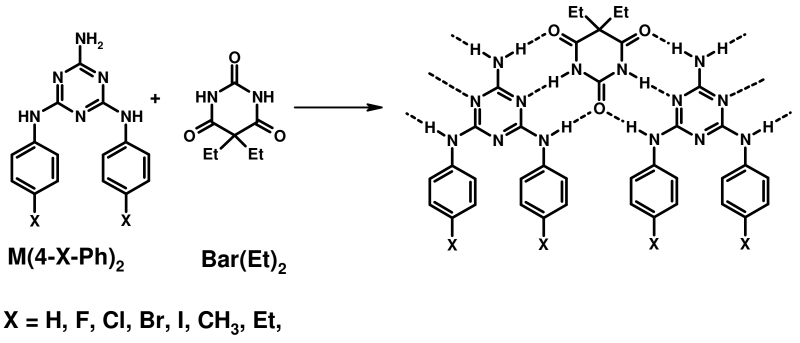
The most attractive functional groups for general use in controlling intermolecular orientations are those that can participate in hydrogen bonding. Etter has suggested that strong hydrogen bond donors and acceptors will always engage in hydrogen bonding in organic solids.[6] In specific, symmetrically substituted organic molecules are known to form exotic supramolecular assemblies in a variety of geometrical arrangements on their own or in combination with complementary molecules.[7] For example, timesic acid (1,3,5-benzenetricarboxylic acid) and pyromellitic acid (1,2,4,5-benzenetetracarbolylic acid) are very intriguing ligands as they can form attractive host-guest assemblies, lamellar sheets, etc.,[8] and, indeed, these host-guest complexes could also be used for the guest inclusion and chemical separations, as discussed in Chapter I.[9] Apart from –COOH functionality, extensive studies on amide groups were due to the following unique features, (i) amides are minimal planar self-aggregating structures; (ii) two amide groups (i.e. diamides) allow for extended hydrogen bonded aggregates to form; (iii) use of secondary amides equalizes the number of hydrogen bonding donors (NH) and acceptors (C=O); and (iv) use of *cyclic* amides restrict the amide groups to use the *cis* conformation, thus promoting two-point dimeric interactions rather than single point interactions, as defined by Whitesides.[10]



Scheme 1. Two patterns of hydrogen bonds based on different conformations of acyclic imides: (a) dimer of *cis*, *trans*-acyclic imides; (b) chain of *trans*, *trans*-acyclic imides.

Similarly, secondary imides form two different hydrogen bonding motifs; a chain and a dimer (Scheme 1). Synthesis of solid-state structures of several barbituric acid derivatives have been thoroughly studied, in particular, by Whitesides and coworkers and reported several robust hydrogen bonded networks formed between barbituric acid derivatives and other organic ligands. For example, some of the solid-state structure of molecules of $M(4\text{-}X\text{-}Ph)_2$ and $Bar(Et)_2$ (derivatives of melamine and barbituric acid respectively) and elucidated the generality of the tape formations for the range of substitutions on melamine and barbiturates.[11]

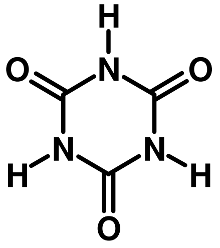
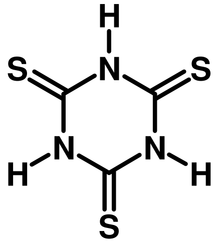
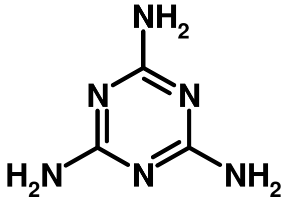
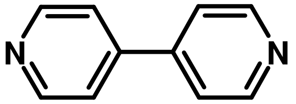
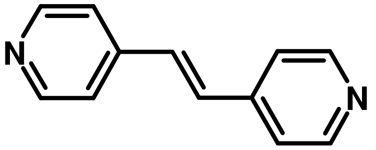
The main advantage of choosing compounds of the type $M(4\text{-}X\text{-}Ph)_2$ and $Bar(Et)_2$ is due to the rigid heterocyclic core. Thus, the bidirectional hydrogen bonding necessary for construction of extended solid-state structures is not dependent on conformations of flexible linkers. Moreover, the simple trigonal shapes also require consideration of only a few orientations of hydrogen-bonding moieties, simplify the packing predictions. The following example shows the typical tape structure of co-crystals formed between 5,5-diethylbarbituric acid, $Bar(Et)_2$, and derivatives of diphenylmelamine substituted at *para* position with different substituents, as shown in Scheme 2, and it is important to note that the variations in the substituents on phenyl group of N-substituted melamine change the two-dimensional architectures. For example, Cl, Br, I and CH_3 substituted melamine gave tape structures and in the case of methyl or ethyl ester substituted melamine, the components are self-assembled, yielding ribbons.[12]



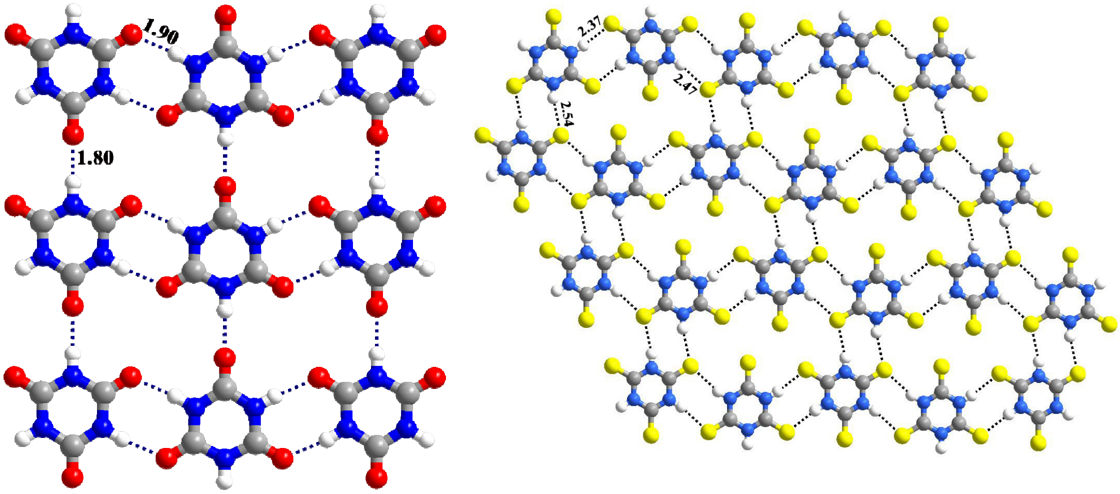
Scheme 2. Typical tape structure formed between derivatives of diphenylmelamine and 5,5-diethylbarbituric acid.

Two other interesting cyclic imides which have gained considerable attention in supramolecular chemistry are cyanuric acid, **CA**, and its sulfur analogue trithiocyanuric acid, **TCA** (Chart I). Both the molecules are symmetrically substituted, possessing three-fold symmetry, and each contains three hydrogen bond donors and three hydrogen bond acceptors with the capability of participating in multiple hydrogen bonding patterns with other organic ligands.[13, 14]

Chart I

		
Cyanuric acid, **CA**	Trithiocyanuric acid, **TCA**	Melamine, **M**
		
4,4-bipyridine, ***bpy***	1,2-bis(4-pyridyl)ethene, ***bpyee***	

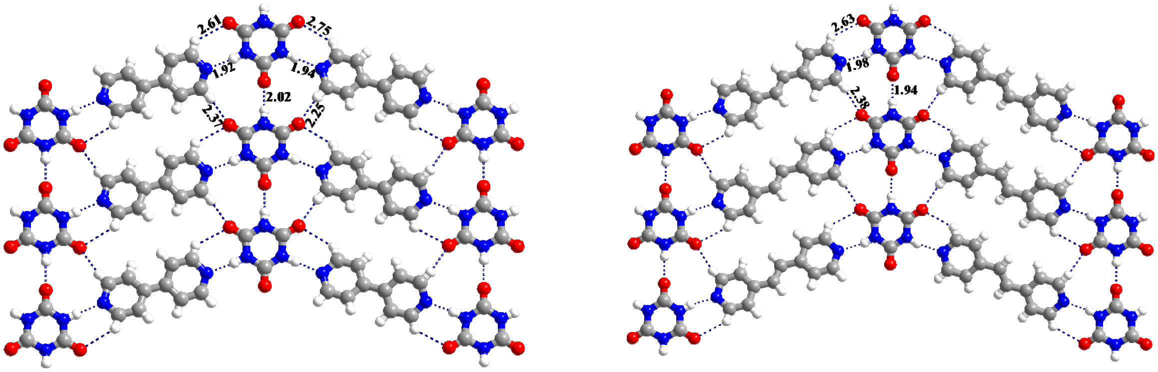
Cyanuric acid, **CA**, is prone to form infinite tapes on its own by pair-wise and cyclic N-H···O hydrogen bonds between the adjacent **CA** molecules and further such tapes are being connected by single N-H···O hydrogen bonds to yield a two-dimensional planar sheet (Figure 1a).[15] However, crystal structure of **TCA**, determined by single crystal X-ray diffraction method, is not yet been reported, although several co-crystal structure of **TCA** with different substrates are known. This was mainly due to the fact that **TCA** has a strong propensity to form solvates upon re-crystallization.[13c] Nevertheless, recently, taking advantage of the current developments in the three-dimensional structure determinations by powder X-ray diffraction data, Harris and Pedireddi determined the three-dimensional structure of **TCA** using PXRD data. It has been observed that **TCA** also forms hydrogen bonded molecular tapes as observed in **CA**, but, there are significant differences in the topological arrangement of the hydrogen bonding networks within the tapes as well as sheets. **TCA** molecules form zigzag molecular tapes (see Figure 1b) which are further held together by cyclic N-H···S dimers to yield planar sheets.[14h]



(a) (b)

Figure 1. (a) Two-dimensional sheet formed by **CA** molecules which are connected through N-H···O hydrogen bonds. (b) The adjacent tapes formed by **TCA** are connected by cyclic N-H···S dimers to yield two-dimensional sheet.

CA, with its three hydrogen bonds donors and three hydrogen bond acceptors, can form variety of supramolecular architectures with other organic compounds.[13, 14] Indeed, co-crystallization of **CA** with 4,4'-bipyridine (***bpy***) and 1,2-bis(4-pyridyl)ethene (***bpyee***) (Chart I) gave two exotic supramolecular complexes. The structural analysis of these complexes revealed that, both the aza-donor molecules act as spacers got inserted into within the molecular tapes of **CA**, by forming N-H···N hydrogen bonds, formed between **CA** and aza-donor compounds (see Figure 2). Also, the molecules in both complexes are strongly held together by additional C-H···O hydrogen bonds.[16,17]

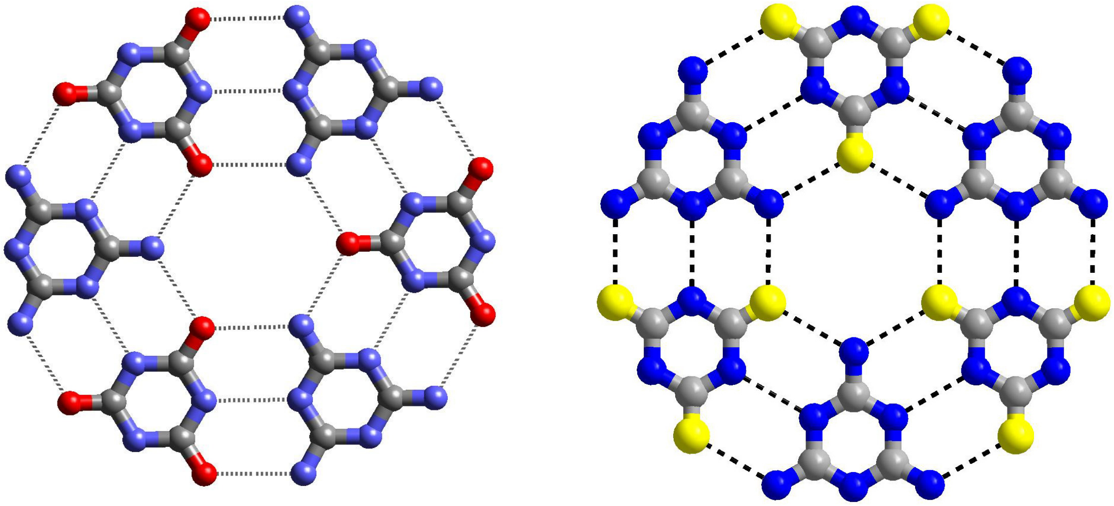


(a) (b)

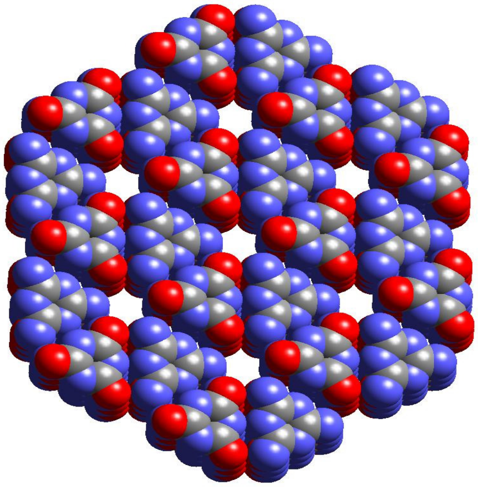
Figure 2. (a) Two-dimensional arrangement of **CA** and ***bpy*** in the 1:1 hydrogen-bonded adduct. (b) Two-dimensional planar sheet formed by **CA** and ***bpyee*** molecules. Notice the insertion of spacer molecules **CA** molecules within the tapes.

Further, Pedireddi *et al*. reported a rosette structure (see Figure 3), comprising of 18 hydrogen bonds, formed by each **CA** and **TCA** with melamine (**M**). The molecular packing analysis of complexes of **CA.M** and **TCA.M** reveals the formation of an hexameric unit (rosette network) as shown in Figure 3a and 3b, respectively.

Such hexameric units are arranged in two dimensions to form planar sheets, and further these planar sheets are stacked in three dimensions to give channels with a diameter of 4 Å, which are comparable to the cavities in cryptands. Typical three-dimensional rosette structure observed in both **CA**.**M** and **TCA**.**M** is shown in Figure 3c.[18]



(a) **(b)**



(c)

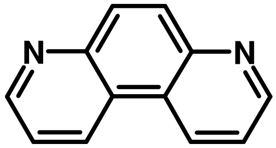
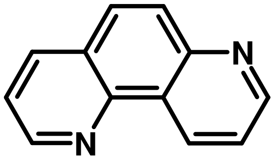
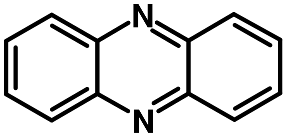
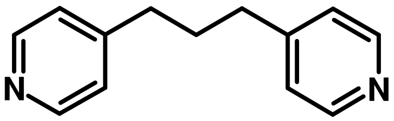
Figure 3. (a) A rosette structure formed between cyanuric acid (**CA**) and melamine (**M**) in the adduct of **CA**.**M**. (b) **TCA** and melamine in the adduct of **TCA**.**M**. Notice the cavity of diameter of approximately 4 Å in both the cases. (c) A typical three-dimensional rosette structure observed in adducts of **CA**.**M** and **TCA**.**M**.

2.2 Supramolecular synthesis of cyanuric acid, CA, with various azadonor compounds

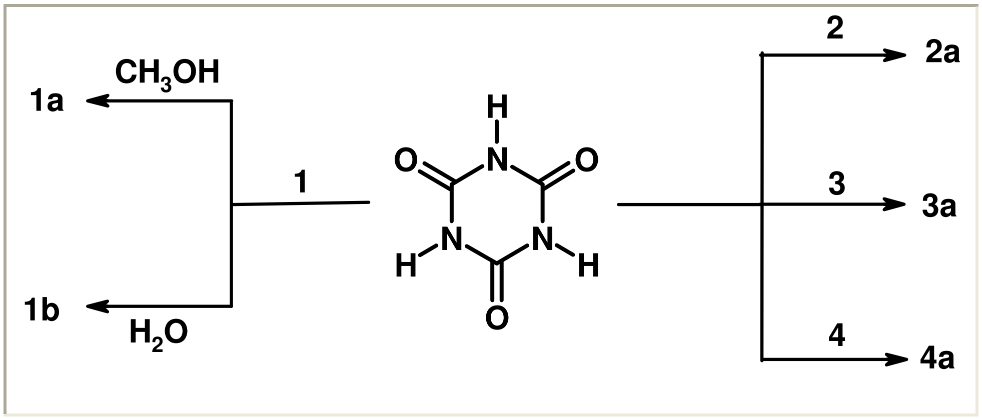
In most of the reported structures of co-crystals of **CA**, it was observed that **CA** forms infinite homomeric molecular tapes, in which the adjacent molecules are connected through cyclic N-H···O hydrogen bonds.[14] Despite the fact that **CA** has the propensity to form multiple hydrogen bonds with other compatible ligands, it is evident from the recent literature that, the number of molecular complexes of **CA** is inadequate, as a search on Cambridge Structural Database (CSD), version 5.29, reveals only 27 structures.[19] Thus, in order to expose the exotic hydrogen bonding networks of **CA** to form myriad of supramolecular assemblies, a thorough study of co-crystallization experiments employing **CA** are of great significant. For this purpose, several molecular complexes of **CA** with different aza-donor compounds have been prepared taking into account the availability of the symmetrically substituted donor groups (-NH) on **CA**, which can interact with pyridyl–N atoms.

Thus, co-crystallization of **CA** with 4,7-phenanthroline, 1,7-phenanthroline, phenazine, and 1,3-*bis*(4-pyridyl)propane, from an appropriate solvent (Chart II), yielded five different complexes which are denoted as **1a**, **1b**, and **2a - 4a** (see Scheme 3), respectively. The detailed structural features of these supramolecular complexes of **CA**, with different type of hydrogen bonding networks, would be discussed in the following sections.

Chart II

		**Reactants**	**Solvent used**
		CA+1	**CH_3OH**
4,7-phenanthroline, 1	**1,7-phenanthroline, 2**	**CA+1**	**H_2O**
		**CA+2**	**DMF**
		CA+3	**CH_3OH**
Phenazine, 3	**1,3-bis(4-pyridyl)propane, 4**	**CA+4**	**CH_3OH**

Scheme 3



2.2.1 Molecular complex of methanol solvate of CA and 4,7-phenanthroline, 1a

Co-crystallization of **CA** and 4,7-phenanthroline, **1**, from a CH_3OH solution gave single crystals of molecular complex, **1a**, that were suitable for structure determination by X-ray diffraction methods. The structural analysis reveals that, solvent of crystallization, i.e. CH_3OH, is also incorporated in the crystal lattice along with 1:1 ratio of **CA** and **1**, as shown in Figure 4. The crystallographic details of the complex are given in Table 2.1.

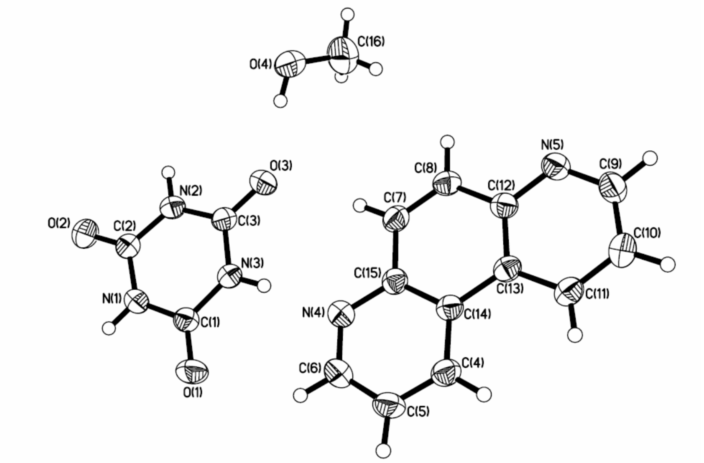


Figure 4. ORTEP diagram of asymmetric unit in the molecular complex **1a**.

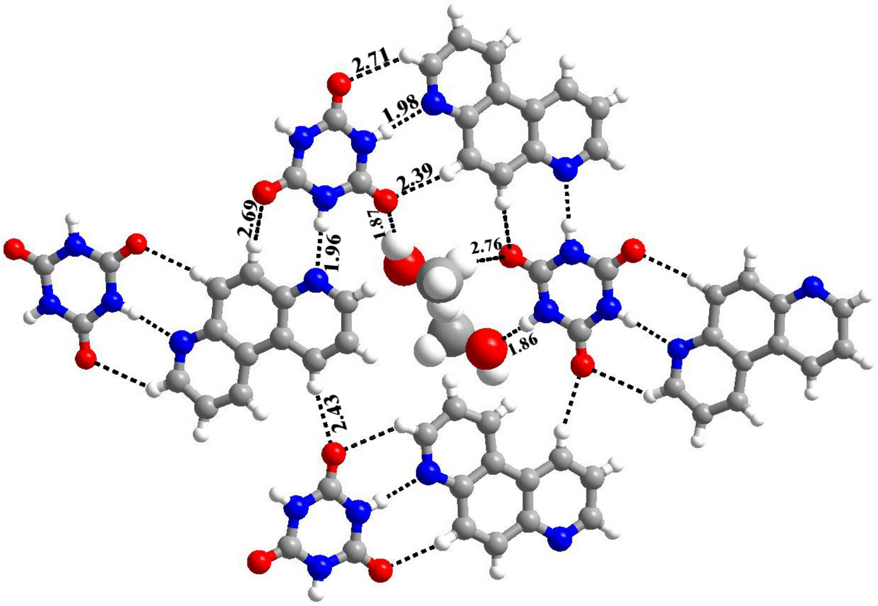


Figure 5. Molecular arrangement in two-dimensions with cavities being occupied by CH_3OH molecules.

The molecular packing analysis shows that **CA** and molecules of **1** interact each other through a triple hydrogen bonding pattern, comprising of an N-H···N (H···N, 1.98 Å) and two C-H···O hydrogen bonds (H···O, 2.39 and 2.71 Å). The details of hydrogen bond distances are given in Table 2.3. Each of three such adjacent supermolecules interact through a cyclic hydrogen bonding pattern of N-H···N and C-H···O hydrogen bonds, with H···N and H···O distances being 1.96 and 2.69 Å, respectively. These trimers are further held together by a single C-H···O hydrogen bond of H···O distance, 2.43 Å, creating a cavity as shown in Figure 5, which is being occupied by two CH_3OH molecules and established interaction with the **CA** molecules in the host network, by forming different types of O-H···O, C-H···O and N-H···O hydrogen bonds. These cavities align to yield channels in three-dimensional packing as shown in Figure 6. The solvent molecules in the channels have been omitted for clear vision of the channels.

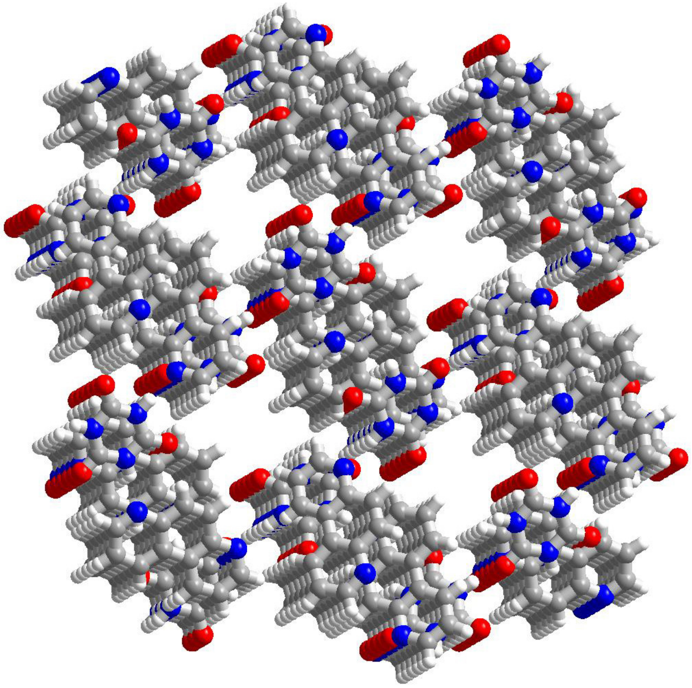


Figure 6. Three-dimensional arrangement of molecules of **CA** and **1** along a crystallographic axis, forming channels, which are being occupied by CH_3OH molecules (solvent molecules in the channels have been omitted).

Thus, in the co-crystals of **1a**, molecules of **CA** exist only in heteromeric form, unlike in the majority of its complexes reported in the literature, wherein **CA** forms only homomeric interactions. Further, it seems that, the CH_3OH molecules are strongly bound to the network as loss of solvent molecules could not be observed in thermogravemeric experiments up to 200 ^oC. This may also be interpreted as solvent directed supramolecular assembly with the observation of totally a different network in the complex, **1b** that was prepared by dissolving **CA** and **1** in water. Hence, it may be possible that **CA** and **1** give different type of assemblies by changing solvent of crystallization and such studies would be of great utility to evaluate other possible topological arrangement between **CA** and **1**. However, the attempts of co-crystallization of **CA** and **1**, from a large number of solvents, did not yield crystals of good quality for diffraction studies, except from water.

2.2.2 Molecular complex of water solvate of CA and 4,7-phenanthroline, 1b

Molecular complex **1b** was obtained, when **CA** was co-crystallized with **1** from water, wherein water molecules also present in the crystal lattice. In **1b**, the composition of constituents is in the ratio of 2:2:3 (**CA**:**1**:$\mathbf{H_2O}$), as shown in ORTEP diagram in Figure 7. In three-dimensional arrangement, a channel structure, as observed in **1a**, is formed (see Figure 9), with channels being occupied by water molecules. However, the arrangement of molecules around channels and also in two-dimensions is quite different in **1a** and **1b**, although basic recognition unit remains the same-a triple hydrogen bond pattern (see inset in Figure 8) with N-H$\cdots$N (H$\cdots$N, 2.02 Å) and C-H$\cdots$O (H$\cdots$O, 2.52 and 2.69 Å) hydrogen bonds. Two such adjacent supermolecules are held together by cyclic N-H$\cdots$O hydrogen bonds (H$\cdots$O, 1.97 and

1.99 Å) formed between the **CA** molecules, leading to the formation of dimers of **CA**, as shown in Figure 8.

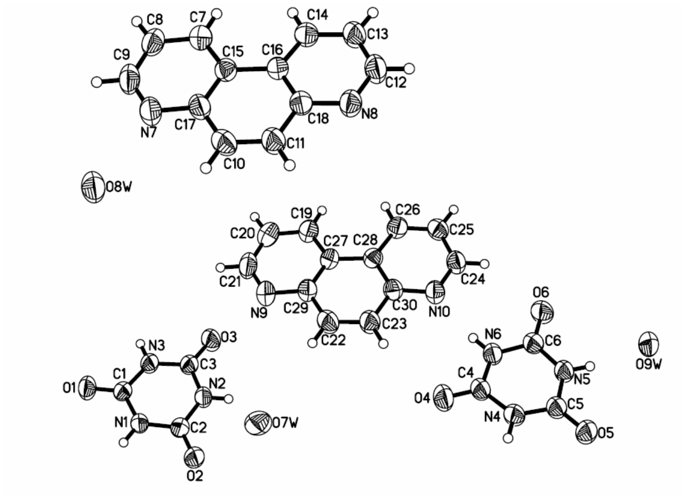


Figure 7. ORTEP diagram of contents present in asymmetric unit of complex, **1b**.

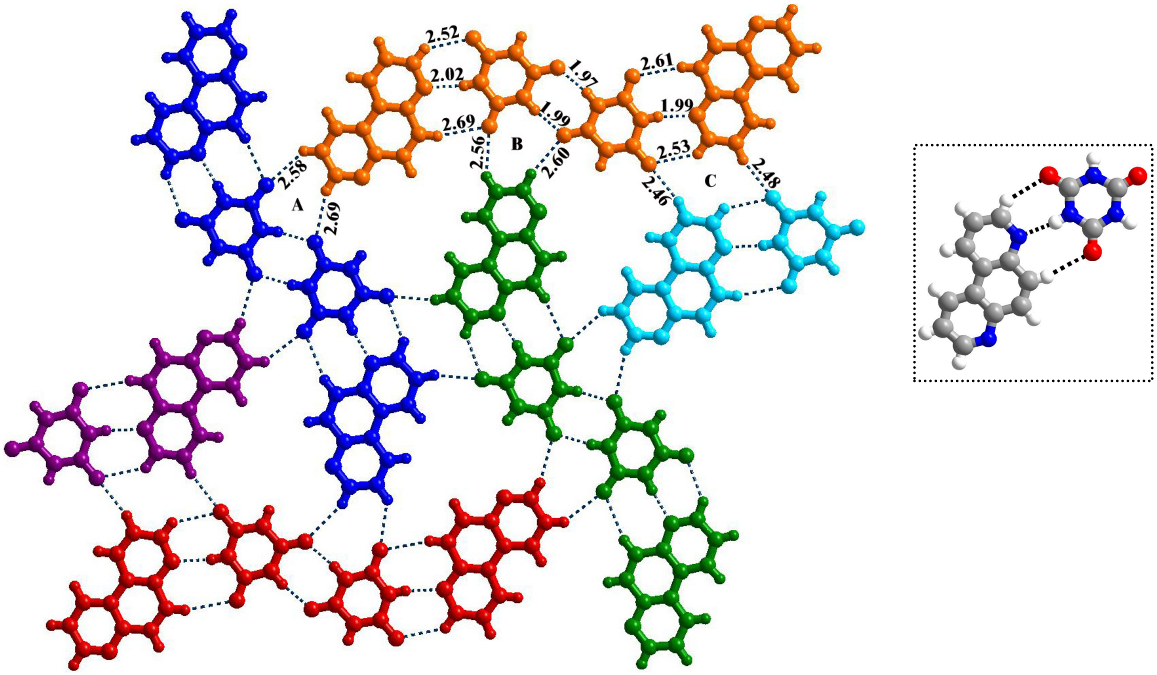
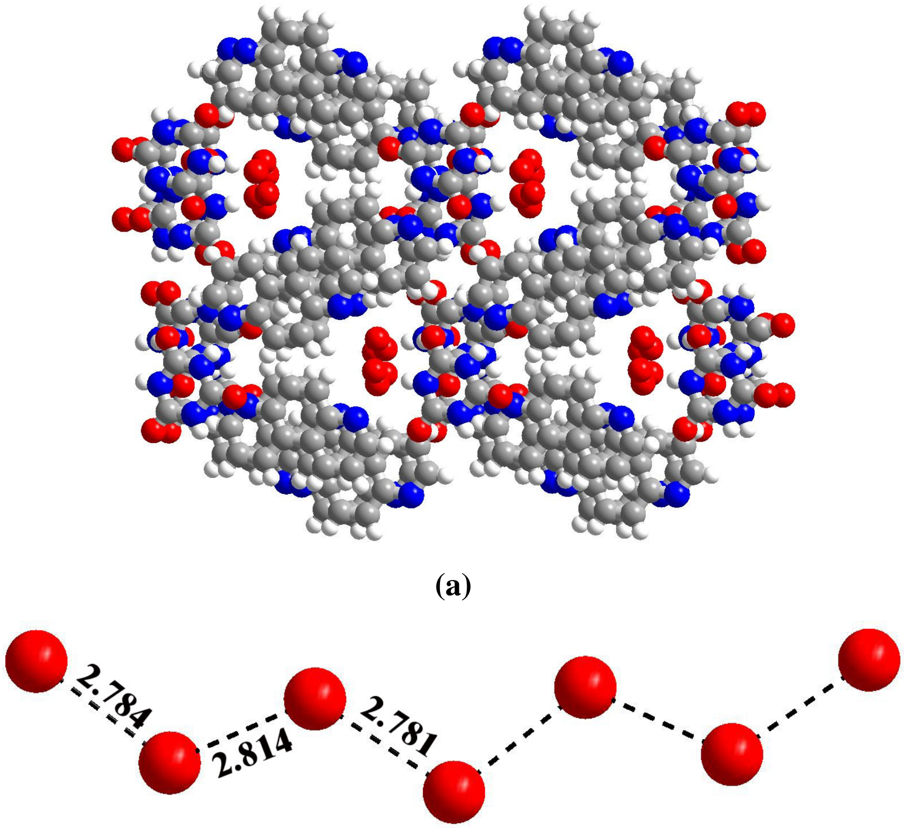


Figure 8. A two-dimensional planar sheet observed in the complex, **1b**, that shows the intermolecular interactions of molecules **CA** and **1**. Notice the molecular tape formed between **CA** and **1**, which are shown in different colors. The inset shows the triple hydrogen bonding pattern observed between **CA** and **1**.

Thus, a quartet assembly of two molecules of each **CA** and **1** is formed. Such adjacent quartets (shown in different colours in Figure 8) are further held together by different types of C-H¨O hydrogen bonds, constituting a void space. As a result, a channel structure is obtained in three-dimensional packing with water molecules occupying the channels (see Figure 9a).



(a)

(b)

Figure 9. (a) Three-dimensional arrangement of molecules in the crystal structure of **1b**, with channels being occupied by water molecules. (b) The one-dimensional water chain formed by O-H¨O hydrogen bonds, in crystal structure of **1b**.

The water molecules exist within the channels as one-dimensional chains (see Figure 9b), held together by O-H¨O hydrogen bonds. An interesting observation is that, in the two-dimensional arrangement, **CA** molecules exist as dimers, unlike in **1**, wherein it remains as monomer. In fact, such dimers are not known in the other crystal structures of complexes/adducts of **CA**, known to date.

Encouraged by such variations in the self-assembly process of **CA**, further attempts have been made to study co-crystallization experiments with other aza-donor compounds that are mentioned in Chart II. The interesting structural features of complexes, thus obtained, are discussed in the following sections

2.2.3 Molecular complex of cyanuric acid and 1,7-phenanthroline, 2a

Co-crystallization of **CA** with 1,7-phenathroline, **2**, from a solution of dimethylformamide (DMF), yielded a molecular complex, **2a**, with 1:1 ratio of the constituent molecules of **CA** and **2**, as shown in ORTEP diagram in Figure 10. In this complex also, **CA** forms a triple hydrogen bonding pattern comprising of N-H⋯N (H⋯N, 1.85 Å) and C-H⋯O (H⋯O, 2.29 and 2.81 Å) hydrogen bonds with **2**, as it was observed in **1a** and **1b**, as described in the previous sections. Further, structural analysis reveals that, crystal structure is an ensemble of stacking of two-dimensional sheets, unlike host-guest assembly observed in **1a** and **1b**. Three-dimensional packing is shown in Figure 11. The arrangement of the molecules within a sheet is shown in Figure12.

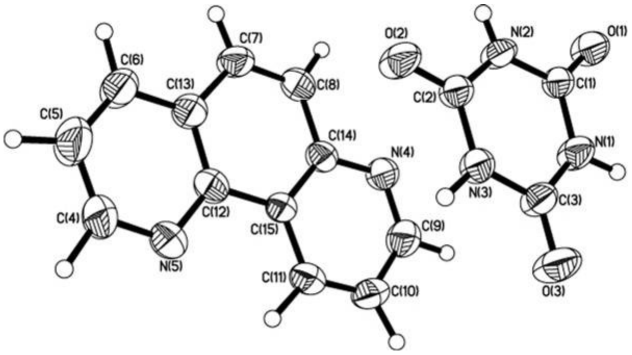


Figure 10. ORTEP diagram of the asymmetric unit in the molecular complex of **2a**.

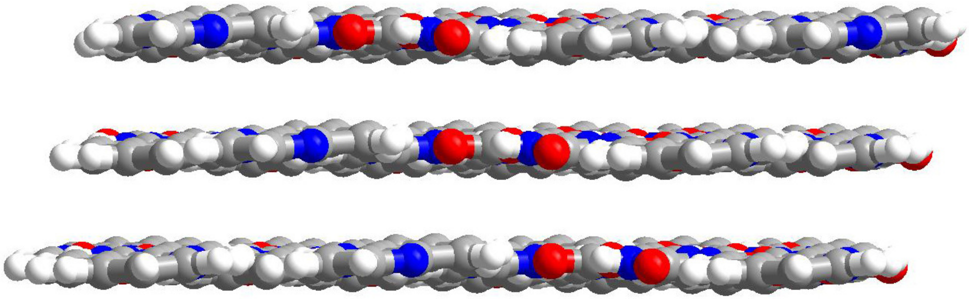


Figure 11. Stacking of planar sheets in the crystal structure of molecular adduct, **2a**.

In each sheet, **CA** molecules exist as infinite tapes, with the adjacent molecules being held together by cyclic N-H···O hydrogen bonds (H···O, 1.79 and 1.98 Å), as observed in many supramolecular complexes of **CA**. Since, each **CA** molecule forms heteromeric interactions with **2**, in two-dimensional arrangement, each **CA** layer is separated by molecules of **2**, as shown in Figure 12.

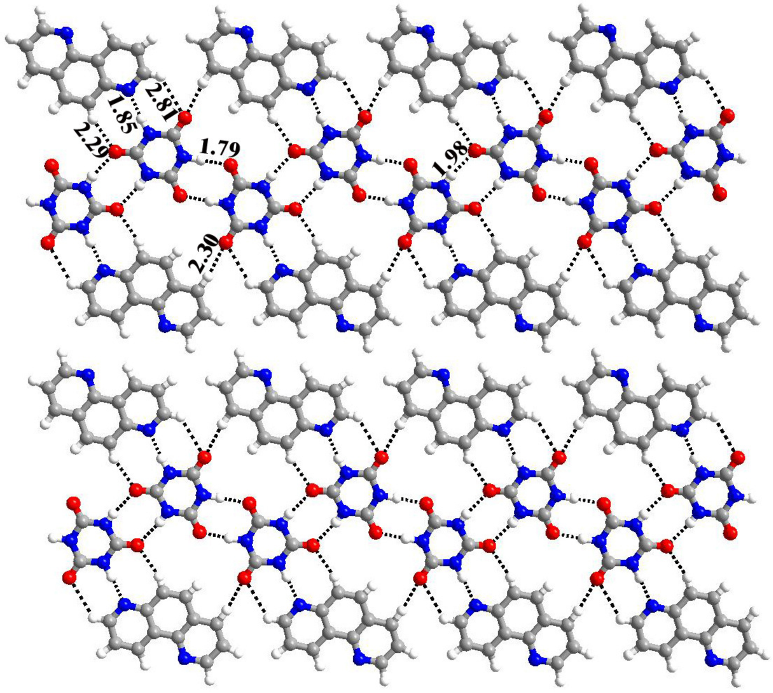


Figure 12. Arrangement of molecules of **CA** and **2** in a typical two-dimensional sheet of complex, **2a**.

2.2.4 Molecular complex of cyanuric acid and phenazine, 3a

The co-crystallization of **CA** with phenazine, **3**, yielded a 2:1 molecular complex, **3a**, as shown in ORTEP diagram, in Figure 13. Structural analysis reveals that the molecular complex, **3a**, also forms two-dimensional planar sheets as it was observed in the case of **2a**. But, arrangement of the molecules within the sheets is different; as the molecular tapes of **CA** are arranged alternatively between the layers of phenazine molecules (see Figure 14a).

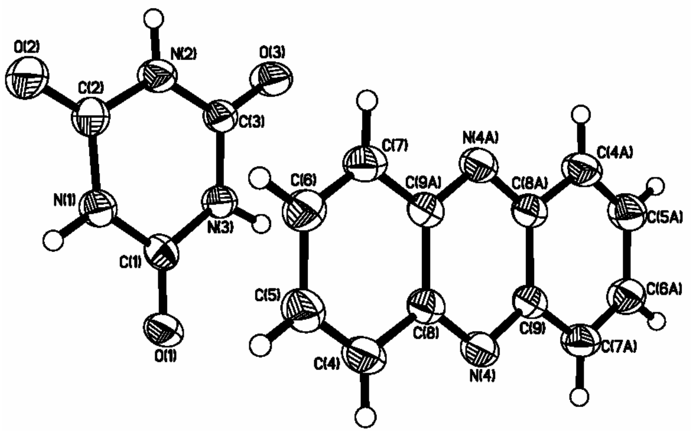


Figure 13. ORTEP diagram shows 2:1 ratio of constituent molecules in complex, **3a**.

In a typical sheet structure observed in **3a**, **CA** molecules form tapes with adjacent molecules being held together by cyclic N-H···O hydrogen bonds, (H···O, 1.19 and 1.95 Å). Each **CA** molecule, within the tapes, is connected to molecule of **3**, by three hydrogen bonds (two C-H···O (H···O, 2.29 and 2.49 Å) and one N-H···N (H···N, 2.35 Å)), as it was observed in the cases of **1a**, **1b** and **2a**. The overall two-dimensional arrangement has a close relation with that of **2a**, except that the layers of **CA** and **3** are alternatively arranged in the planar sheet of **3a**. Such planar sheets are stacked in three-dimensions, as shown in Figure 14b.

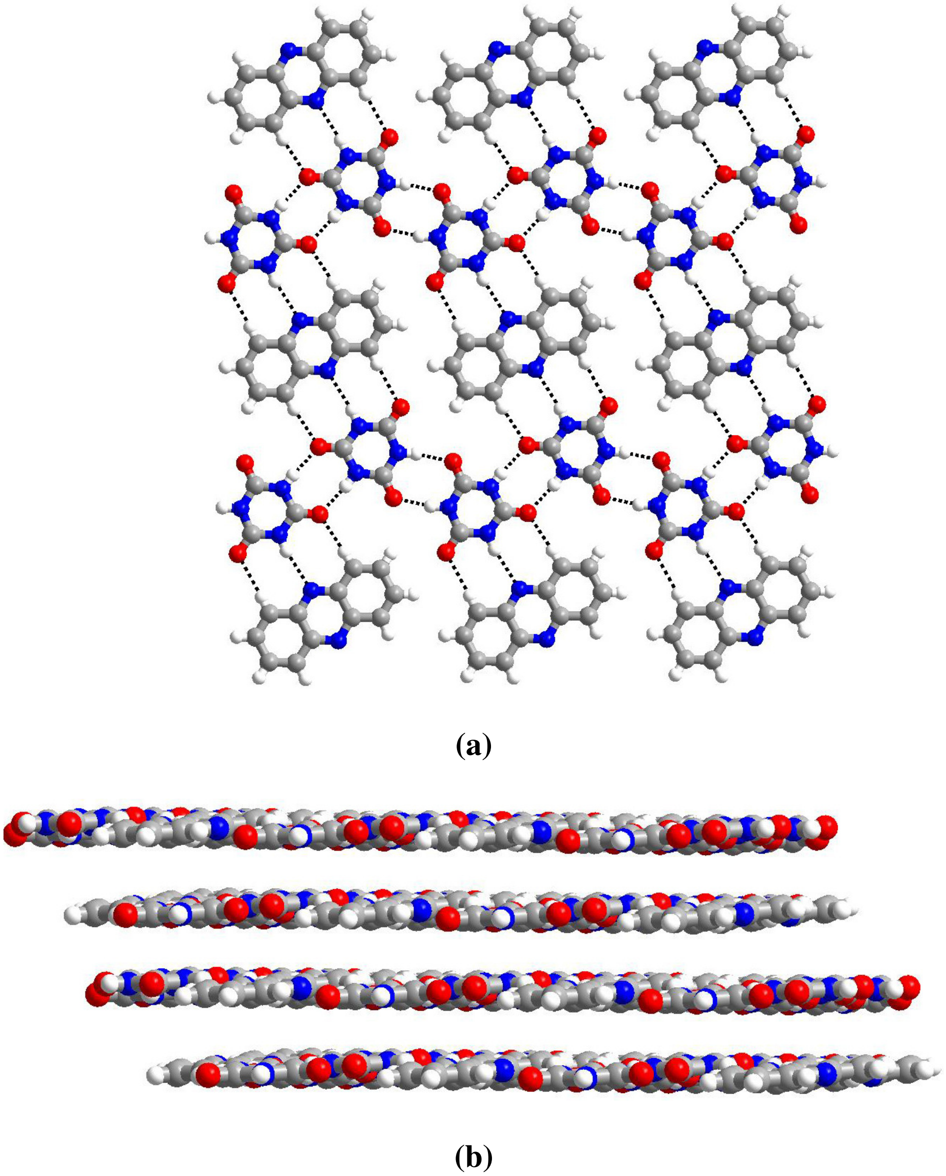
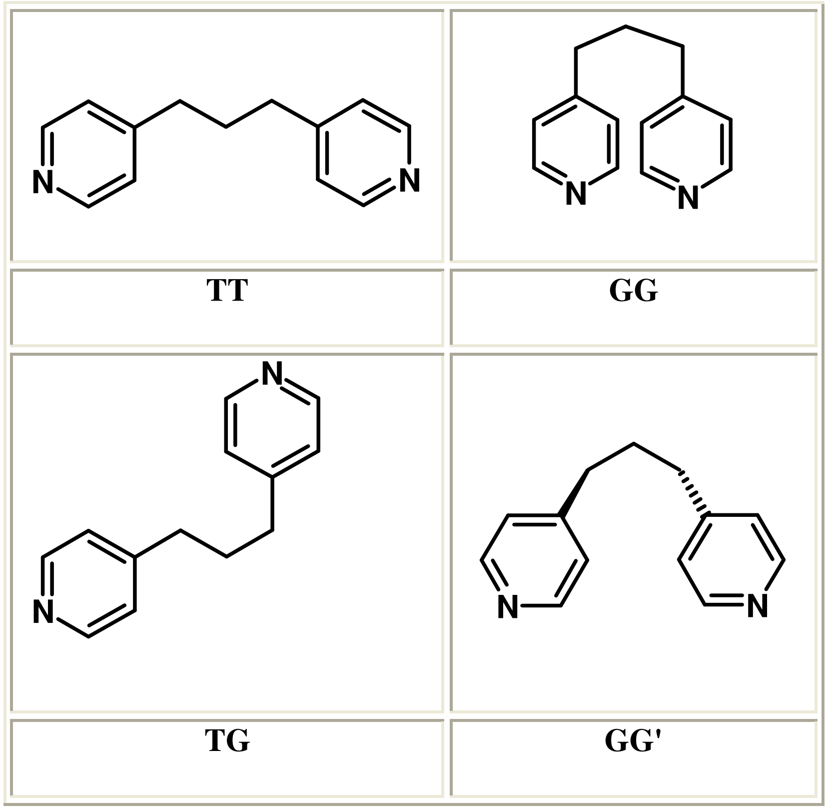


Figure 14. (a) Alternate arrangement of molecules of **CA** and **3** in a typical two-dimensional sheet. (b) A view of planar sheets stacked in three-dimension.

In continuation of preparation of other co-crystals of **CA**, the flexible ligands like 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethene and ethene have already been elucidated, in which the spacer molecules were inserted between the molecules within the tapes of **CA** (see Figure 2), co-crystallization of 1,3-bis(4-pyridyl)propane (which can potentially adopt four different type of conformations (see Scheme 4), TT, TG, GG, GG' (T = *trans*, G = *guache*) depending upon the relative orientations of $–CH_2$-CH_2-$CH_2^–$ moiety),[20] has been carried out. Although numerous experiments were carried out, varying the conditions, only one type of crystal structure is obtained all the time, which is indeed quit intriguing, as described in the following section.

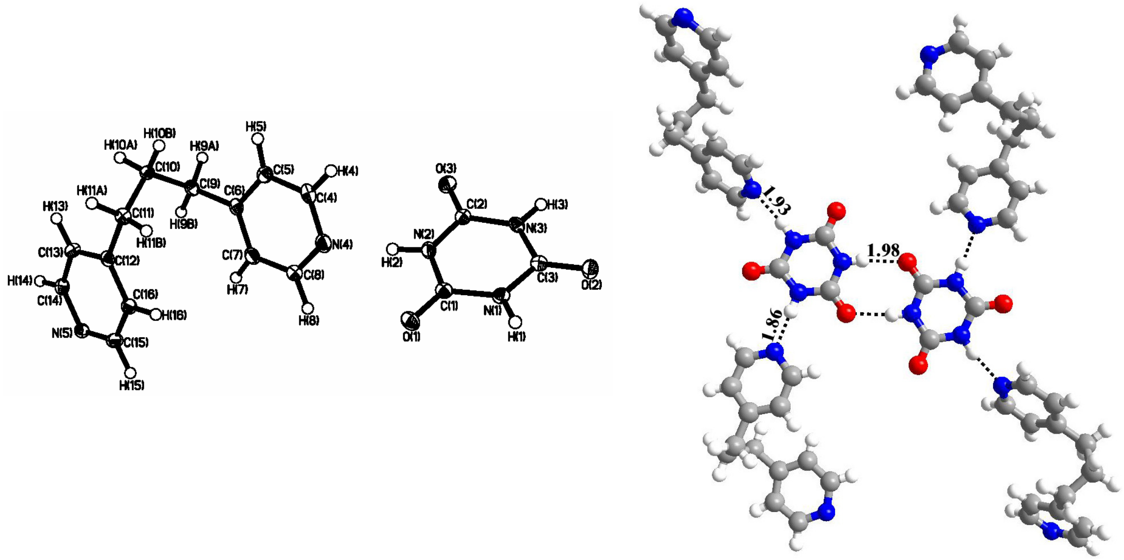
Scheme 4



2.2.5 Molecular complex of cyanuric acid and 1,3-bis(4-pyridyl)propane, 4a

The molecular complex, **4a**, was obtained by the co-crystallization of **CA** with 1,3-bis(4-pyridyl)propane, **4**, from a CH_3OH solution. ORTEP diagram of the asymmetric unit in the molecular complex, **4a**, shows that **4** has adopted the GG' conformation (see Figure 15a). Complex **4a** exhibits similar features to the structure of

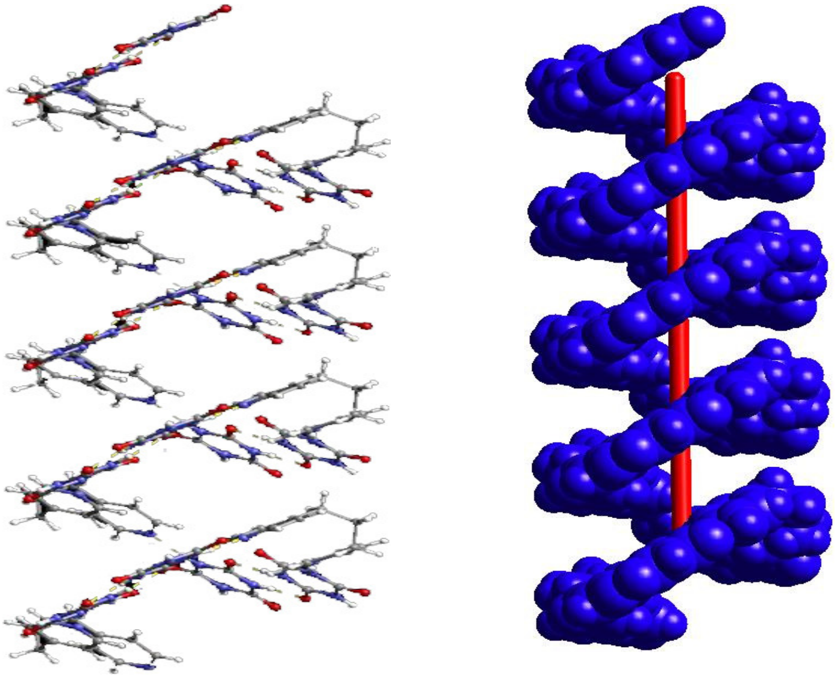
1b by forming dimers of **CA**, as shown in Figure 15b, while analogues of **4**, such as 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethene, etc., form structures somewhat similar to **2a** and **3a**.[17]



(a) **(b)**

Figure 15. (a) ORTEP diagram of the asymmetric unit in the molecular complex, **4a**. (b) Recognition feature between **CA** and **4** in the molecular complex, **4a**. Notice the **CA** dimers are being connected by four molecules of **4**.

Furthermore, in the structure of **4a**, the primary recognition between **CA** and **4** is established through single N-H···N hydrogen bond (H···N, 1.86 and 1.93 Å), formed between **CA** and **4**, as shown in Figure 15b, instead of triple hydrogen bonding pattern, as observed in **1a**, **1b**, **2a** and **3a**. In addition, such adjacent units are held together by cyclic N-H···O hydrogen bonds (H···O, 1.98 Å) formed between **CA** molecules, leading to the constitution of dimers of **CA**. Such an ensemble packed in the crystal lattice in the form of helices in three-dimensional arrangement (see Figure 16), perhaps, that is being facilitated by the flexible geometry of **4**.



(a) (b)

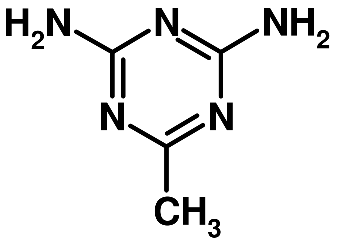
Figure 16. Helical arrangement of molecules, through hydrogen bonds (a) in ball and stick mode and (b) close packing mode.

Thus, through the study of molecular complexes, **1a**, **1b** and **2a** - **4a**, it is evident that, **CA** forms a variety of solid-state structures, through different types of self-assembling process yielding homomeric and heteromeric entities, which may significantly influence the ultimate geometrical arrangements like, channels, planar sheets and helix, etc. Also, one could easily observe that, the effect of the solvent used for the crystallization and the topology of the aza-donor ligands play a significant role in changing the solid-state structure of **CA** and, thus, by changing the three-dimensional networks of the complexes.

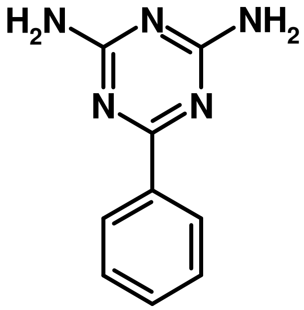
2.3 Supramolecular synthesis of cyanuric acid, CA, with triazine ligands

The aza-donor compounds utilized in the co-crystals synthesis, described in the previous section, interact with **CA** using the hetero –N atoms only as no other potential acceptor-donor functional groups are available. To understand further the ability of **CA** to form exotic hydrogen bonding networks, in addition to the features described in the previous sections, study through several derivatives of azadonor moieties are of great significant. In this direction, it is well known from the literature about the hydrogen bonding capabilities of various triazine derivatives, pyridine, pyrimidine and other azadonor compounds, the interest was extended to triazine ligands, knowing the potentials of these ligands in the formation of stable robust hydrogen bonding patterns with **CA**. For example, as it was described in the section 2.1, melamine, a triazine ligand, is the complimentary molecule for **CA** and it forms a well known triple hydrogen bonding pattern (two N-H···O and one N-H···N hydrogen bonds) with **CA**, which indeed resulted a robust rosette structure in three-dimensions. Also, as it was discussed in the case of co-crystals of barbituric acid and derivatives of melamine that the substitution on the melamine derivatives would change the hydrogen bonding patterns between the constituent molecules, which, indeed, directed the change in two-dimensional networks.

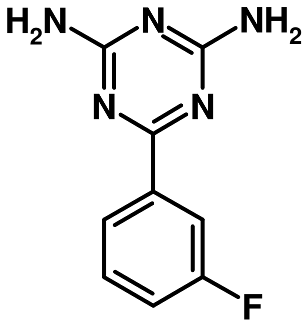
Thus, co-crystallization experiments of **CA** with various derivatives of triazine core (Chart III) have been carried out, which yielded molecular complexes, **5a** – **9a** (Chart IV). The remarkable changes in the hydrogen bonding patterns, as well as three-dimensional arrangement that are observed in these complexes are described in the following sections. All the complexes were characterized by single crystal X-ray diffraction methods and the detailed crystallographic data of complexes are compiled in Table 2.2.



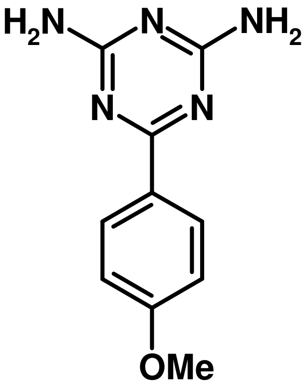
2,4-Diamino-6-methyl-1,3,5-triazine, 5



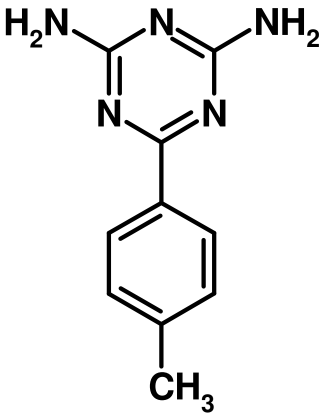
2,4-Diamino-6-phenyl-1,3,5-triazine, 6



2,4-Diamino-6-(3-flouro phenyl)-1,3,5-triazine, 7



2,4-Diamino-6-(4-methoxy phenyl)-1,3,5-triazine, 8



2,4-Diamino-6-(4-methylphenyl)-1,3,5-triazine, 9

Chart III. Structures of triazine ligands used in the study

Chart IV

S. No.	Reactants	Solvents	Products
1	**CA + 5**	**DMF**	**5a**
2	**CA + 6**	**DMF/H_2O**	**6a**
3	**CA + 7**	**DMF/CH_3OH**	**7a**
4	**CA + 8**	**DMF/H_2O**	**8a**
5	**CA + 9**	**CH_3OH**	**9a**

2.3.1 Complex of cyanuric acid and 2,4-diamino-6-methyl-1,3,5-triazine, 5a

Co-crystallization of **CA** and 2,4-diamino-6-methyl-1,3,5-triazine, **5**, from a dimethylformamide (DMF) solution, yielded good quality single crystals of complex, **5a** that were used for structure determination by X-ray diffraction methods. An ORTEP diagram, in Figure 17, shows 1:1 ratio of molecules of **CA** and **5** present in the asymmetric unit of complex, **5a**.

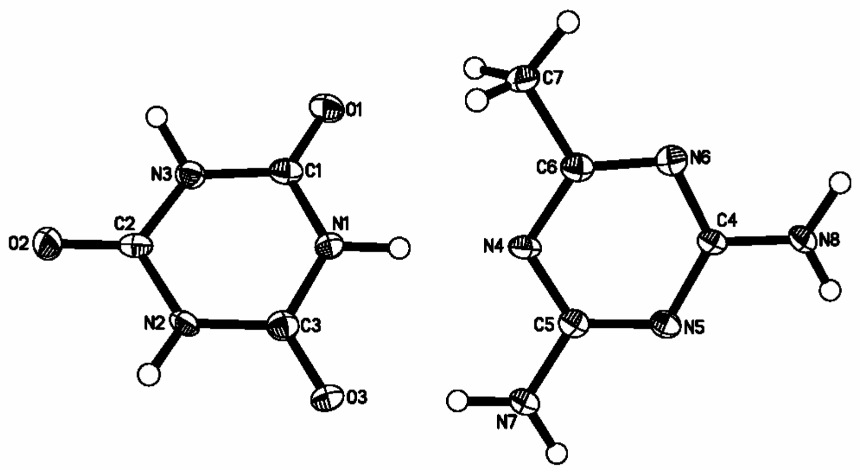


Figure 17. ORTEP diagram of complex, **5a**.

The structural analysis shows that, **CA** and **5** form a heteromeric aggregation, in the complex **5a**, through the formation of different types of triple hydrogen bonding patterns comprising of N-H···O (H···O, 1.87, 1.97 and 1.99 Å), N-H···N (H···N, 1.82, 1.88 and 2.07 Å) and C-H···O (H···O, 2.61 and 2.20 Å) hydrogen bonds. The detailed hydrogen bonded distances are given in Table 2.4. Such adjacent molecular ensembles are connected to each other, yielding a twelve membered cyclic network, as shown in Figure 18. In further packing, ensembles with voids are effectively packed through catenation, as shown in Figure 19. Such catenation networks are well known in the literature both in covalent and non-covalent supramolecular assemblies, which demonstrate the elegancy of natural process of effective close packing of all the available void space, in the absence of appropriate additional resources available.

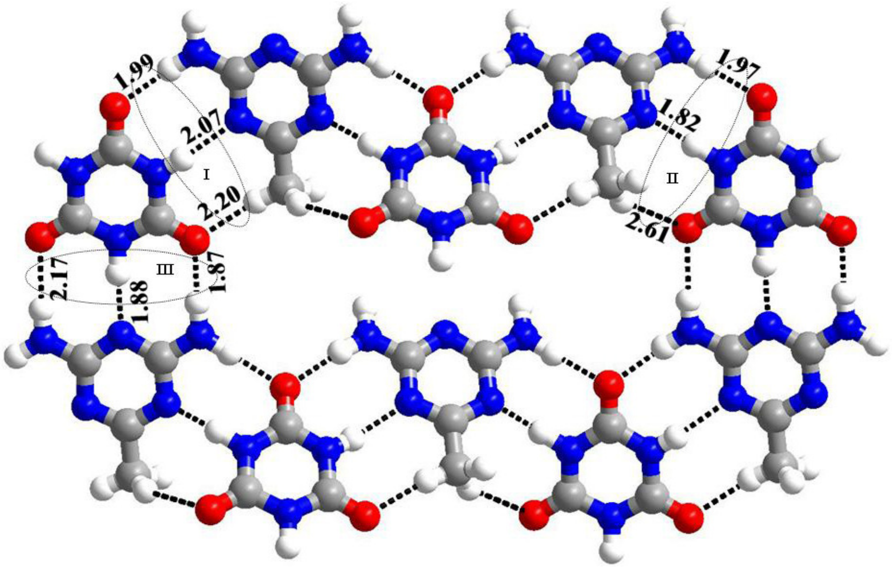


Figure 18. The adjacent molecular tapes formed by **CA** and **5** are connected to yield a 12-membered cyclic network.

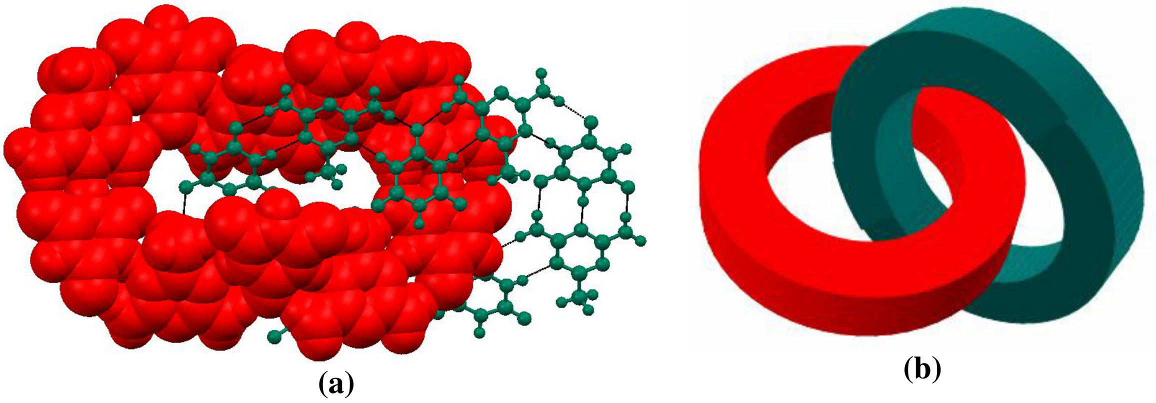
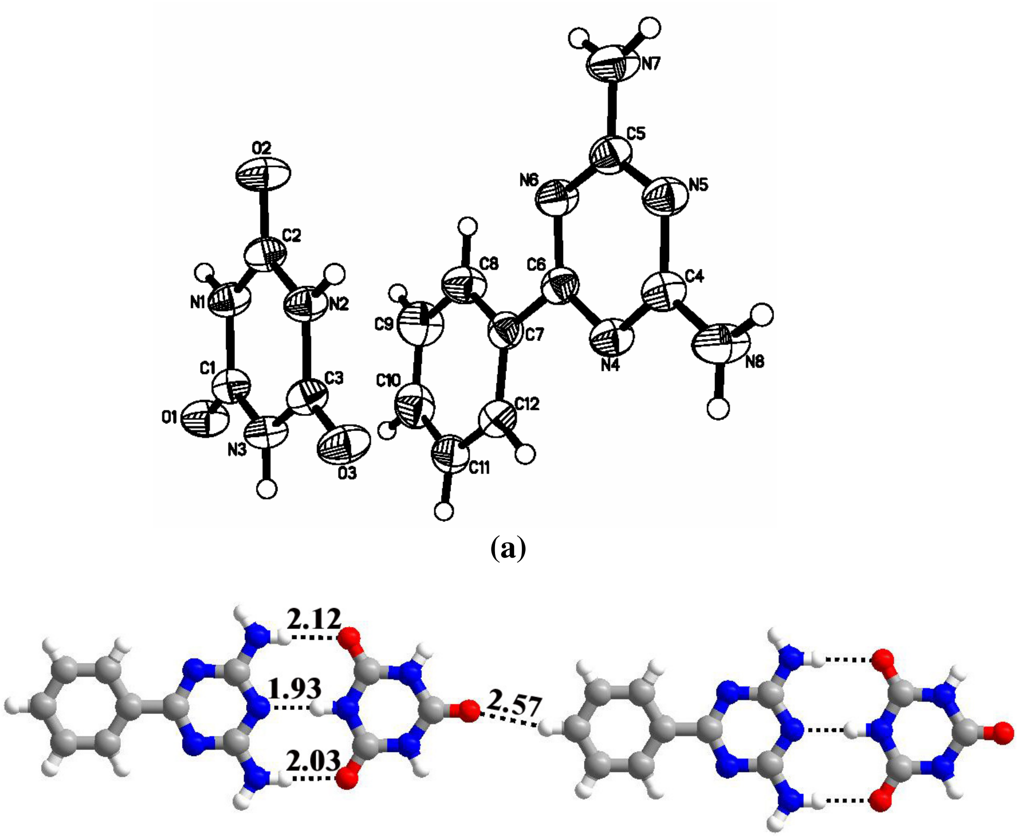

(a) (b)

Figure 19. (a) Catenation formed by two 12-membered cyclic units in the complex, **5a**. (b) Schematic diagram showing the catenation formed by 12-membered cyclic units.

It appears that the catenation observed in **5a** was due to the lack of effective functional moieties on **5** to fill the available void space. Close observation of the 12-membered network, shown in Figure 18, it may be possible to obtained a structure devoid of empty space if the $–CH_3$ is replaced by bulky substituents. Hence, co-crystallization of **CA** with 2,4-diamino-6-phenyl-1,3,5-triazine, **6**, has been carried out and the structural details are as given below.

2.3.2 Complex of CA and 2,4-diamino-6-phenyl-1,3,5-triazine, 6a

Co-crystallization of **CA** with 2,4-diamino-6-phenyl-1,3,5-triazine, **6,** from a mixture of DMF and water yielded a molecular complex, **6a**. An ORTEP drawing of asymmetric unit is shown in Figure 20a. The structural analysis of complex **6a**, revealed that **CA** and **6** are held together to yield a heteromeric unit through the triple hydrogen bonding pattern, comprising of N-H$\cdots$N (H$\cdots$N, 1.93 Å) hydrogen bond, stuffed between N-H$\cdots$O (H$\cdots$O, 2.12 and 2.03 Å) hydrogen bonds. Such recognition pattern is shown in Figure 20b. Further, such supermolecules are connected each other through C-H$\cdots$O hydrogen bond (H$\cdots$O, 2.57 Å), formed between C-H of phenyl ring of **6** and C=O of **CA**, leading to the formation of linear chain (see Figure 20b).



(a)

(b)

Figure 20. (a) ORTEP diagram shows 1:1 ratio of molecules of **CA** and **2** in complex **2a**. (b) One-dimensional chain formed by the molecules of **CA** and **2**.

In three-dimensions, the infinite chains are arranged in a crossed manner to yield a herringbone pattern as shown in Figure 21. Notice the change in hydrogen bonding patterns as well as in three-dimensional arrangement of the molecules in complexes, **5a** and **6a**, upon changing the substitution on the triazine ligands.

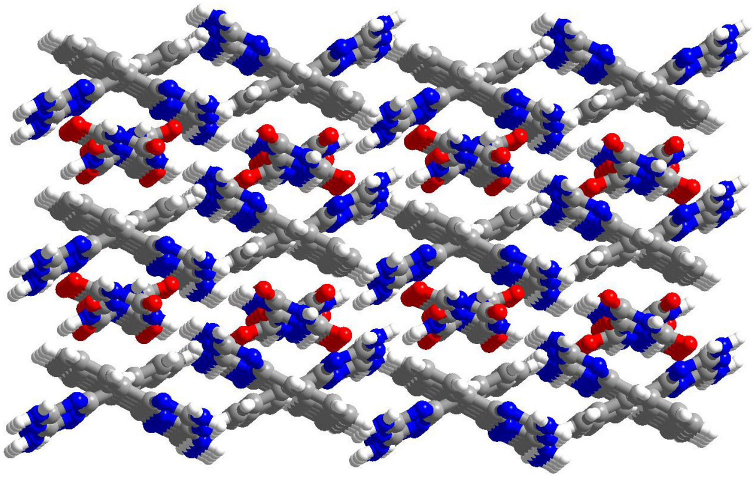
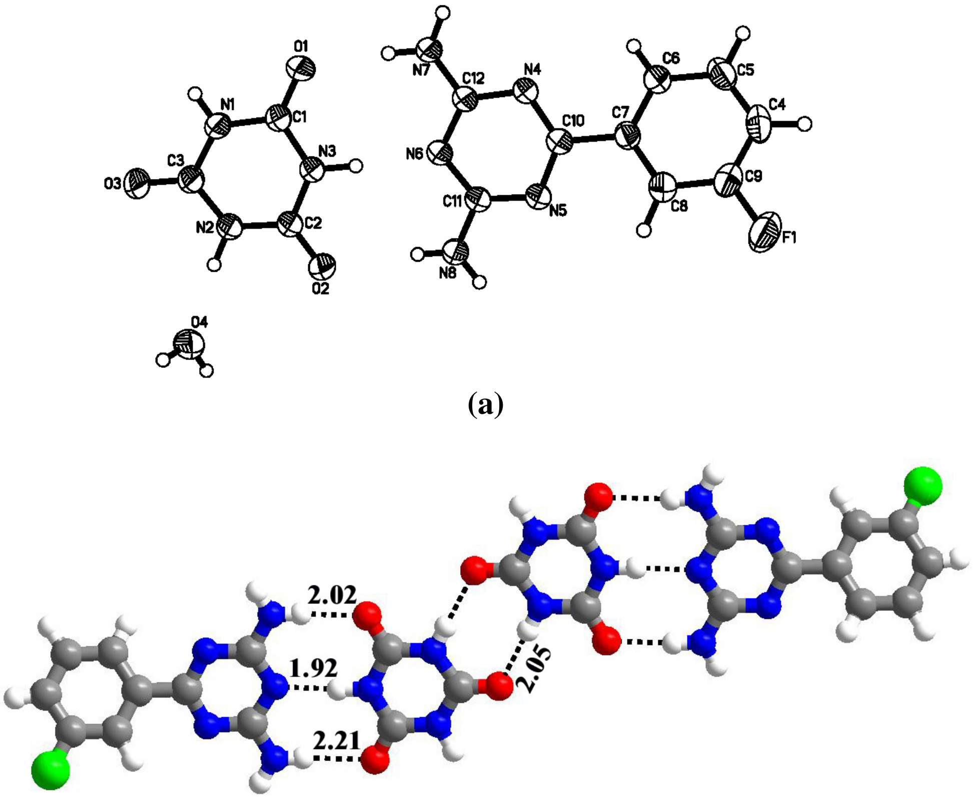


Figure 21. The three-dimensional herring-bone pattern formed by **CA** and **6** in molecular complex, **6a.**

Although, as the expected catenation was not observed in **6a**, in comparison with **5a**, even cyclic network was also not been noticed. In order to obtain a cyclic structure without catenation, further investigations with some derivatives of **6** have been carried out by co-crystallization with **CA**. It was noticed that no catenated structures were observed when the substituents were -F and –OCH_3, but, surprisingly, methyl substituted derivative gave catenated structures, as described in the complexes **7a – 9a**.

2.3.3 Complex of CA and 2,4-diamino-6-(3-flourophenyl)-1,3,5-triazine, 7a

The fluorine substitution on the phenyl group of the triazine ligand, 2,4-diamino-6-(3-flourophenyl)-1,3,5-triazine, **7**, has played a crucial role in yielding a 1:1 supramolecular complex with **CA** that possesses a remarkable difference in hydrogen bonding patterns as well as molecular arrangement in two-dimensional arrangement. Complex **7a**, which was obtained by the co-crystallization of **CA** and **7** from a mixture of DMF and CH_3OH reveals that, one water molecule is also present in the crystal lattice along with 1:1 ratio of **CA** and **7** (see Figure 22a). The structure adopts a stacked sheet arrangement in three-dimensions.



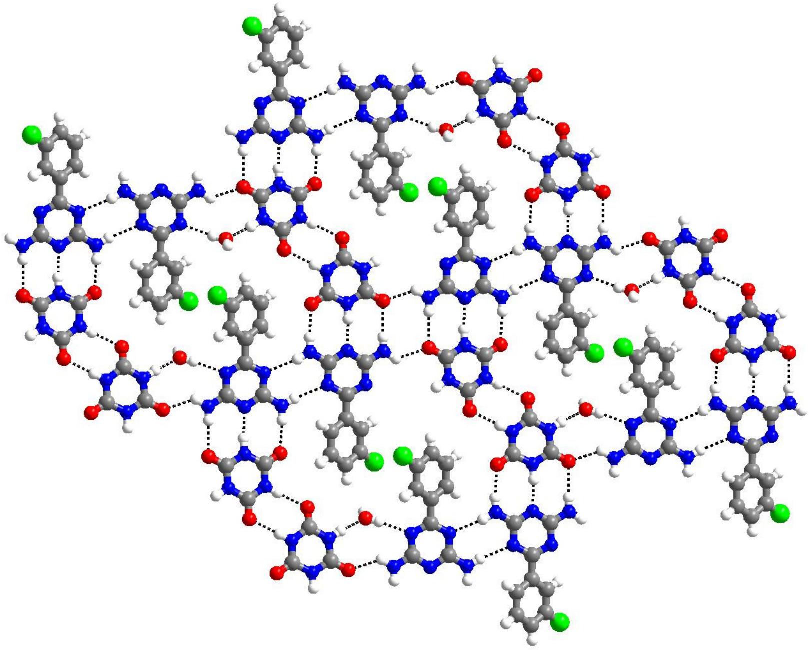
(a)

(b)

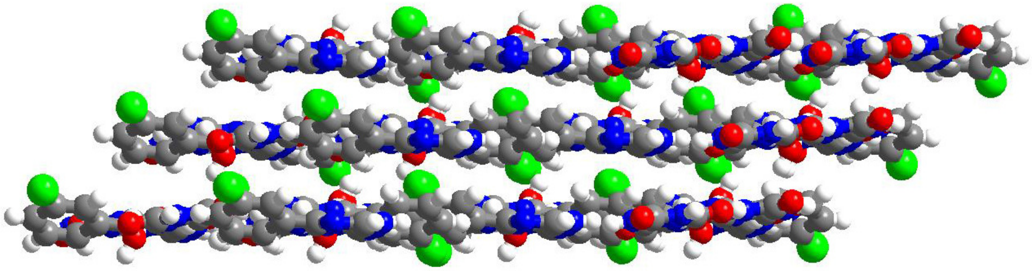
Figure 22. (a) ORTEP diagram shows 1:1 ratio of molecules of **CA** and **7** in complex **7a**. (b) A quartet assembly formed between **CA** and **7**.

Within each sheet, the constituent molecules form heterodimers as observed in **6a**, through N-H¨N and N-H¨O hydrogen bonds, with the H¨N and H¨O distances being 1.92, 2.02 and 2.21 Å, respectively. Such units are, further, held together by cyclic N-H¨O hydrogen bonds, with H¨O distances of 2.05 Å, due to the homomeric recognition between **CA** molecules, yielding a quartet assembly, as shown in Figure 22b.

These ensembles are, further, connected to each other through cyclic N-H···N dimer formed between molecules of **7** (H···N, 2.22 Å), and N-H···O hydrogen bonds formed between **CA** and **7** (H···O, 2.24 Å), yielding planar sheet with cavities, which are being occupied by the phenyl moieties of the ligand **7**, as shown in Figure 23a. Such sheets are stacked in three-dimensions, as shown in Figure 23b.



(a)



(b)

Figure 23. (a) Cavity structure formed in two-dimension. (b) Stacking of the planar sheets in three-dimensions.

This kind of association has lead to an environment that the void space is effectively filled by fluoro substituted phenyl moieties, which interact with each other through F···F contacts. Similar environment should have been observed even in **6a**, but apparently the C-H···O hydrogen bonding between the heterodimers, perhaps, precluded it.

2.3.4 Complex of CA and 2,4-diamino-6-(4-methoxyphenyl)-1,3,5-triazine, 8a

The crystal structure determination of complex **8a**, which was obtained by co-crystallization of **CA** and 2,4-diamino-6-(4-methoxyphenyl)-1,3,5-triazine, **8**, from a mixture of DMF and water reveals that, as observed in **6a** and **7a**, the constituent molecules did interact each other through a triple hydrogen bonding pattern. The ORTEP diagram, in Figure 24, shows the molecules present in the asymmetric unit.

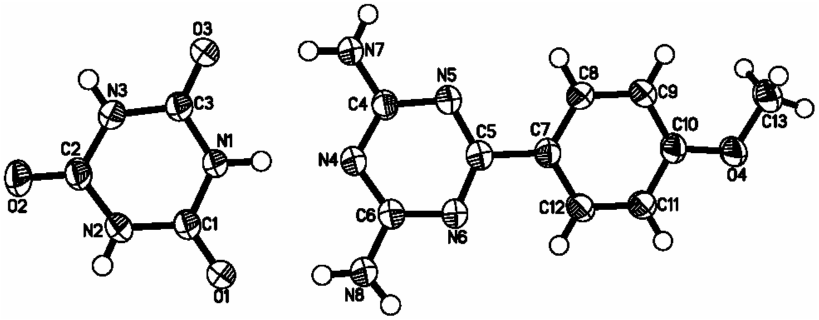
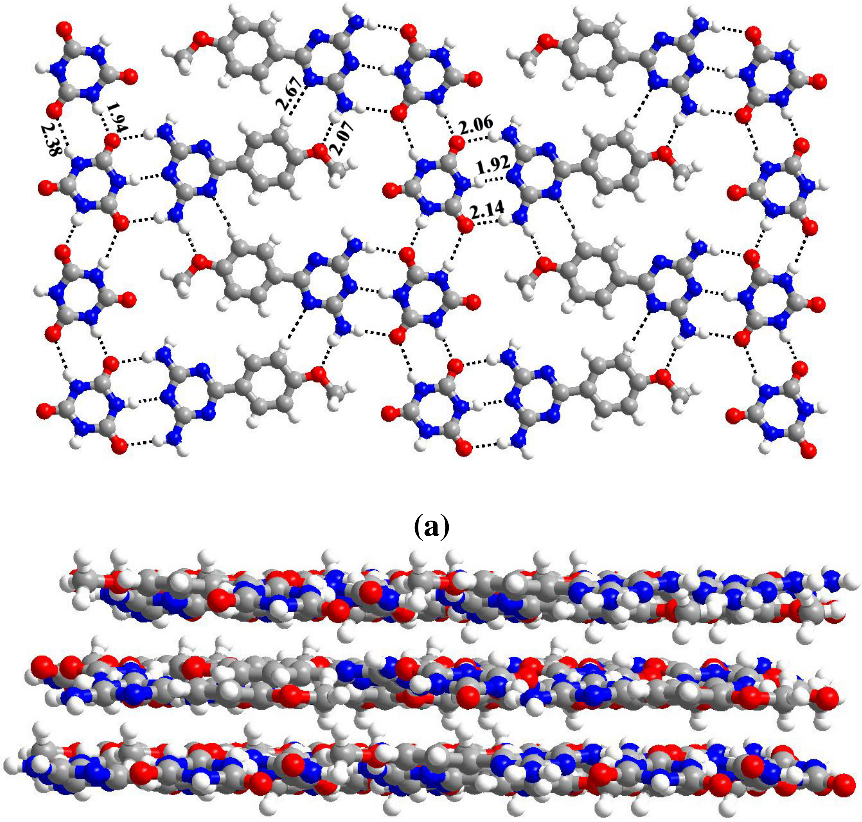


Figure 24. ORTEP diagram shows 1:1 ratio of molecules of **CA** and **8** in complex **8a**.

Such moieties, in two-dimensional arrangement, constituted molecular tapes of **CA**, formed through homomeric aggregations, by cyclic N-H···O hydrogen bonds, with molecules of **8** being inserted between the tapes, as shown in Figure 25a, like in the structure of co-crystals of **3a** (Figure 14a). However, molecules of **8** also undergo homomeric aggregation through N-H···O (H···O, 2.07 Å) and C-H···N (H···N, 2.67 Å) hydrogen bonds, yielding a planar sheet (see Figure 25a). These sheets are stacked in three-dimensional arrangement, as shown in Figure 25b.



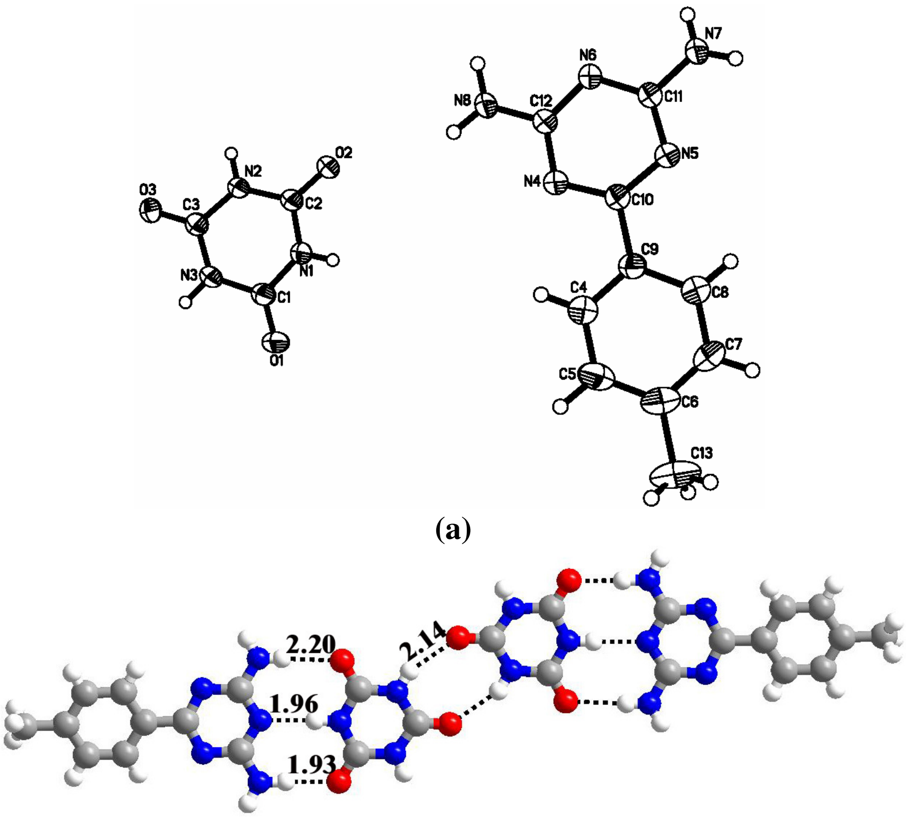
(a)

(b)

Figure 25. (a) A two-dimensional sheet arrangement observed in **8a**, notice the tapes formed by the molecules of **CA**. (b) The stacking of planar sheets in three-dimensions.

2.3.5 Complex of CA and 2,4-diamino-6-(4-methylphenyl)-1,3,5-triazine, 9a

Co-crystallization of **CA** with 2,4-diamino-6-(4-methylphenyl)-1,3,5-triazine, **9**, in a CH_3OH solution yielded a colorless crystal of molecular complex, **9a**. The ORTEP diagram of the complex, **9a**, is given in Figure 26a. The structural determination of **9a**, by X-ray diffraction method, reveals that molecules **CA** and **9** are connected, through a triple hydrogen bonding pattern, with two N-H···O (H···O, 2.20 and 1.93 Å) and one N-H···N (H···N, 1.96 Å) hydrogen bonds. Two such adjacent dimeric units are connected by cyclic N-H···O hydrogen bonds (H···O, 2.14 Å), formed between **CA** molecules, leading to the formation of quartet assemblies (see Figure 26b), as it was observed in the case of **7a**.



(a)

(b)

Figure 26. (a) ORTEP diagram shows 1:1 ratio of molecules of **CA** and **9** in complex **9a** (b) Quartet assembly formed between the molecules of **CA** and **9**.

Such adjacent quartet units are self-assembled through cyclic N-H···N (H···N, 2.12 and 2.25 Å) hydrogen bonds, formed between the molecules of **9**, leading to the formation of a square network with cavities, as described in the structure of **5a**.

Incidentally, in the complex, **5a**, also, the triazine ligand is a methyl derivative. Further, such square networks undergo catenation, yielding an interpenetrated network in three-dimensions, as shown in Figure 27.

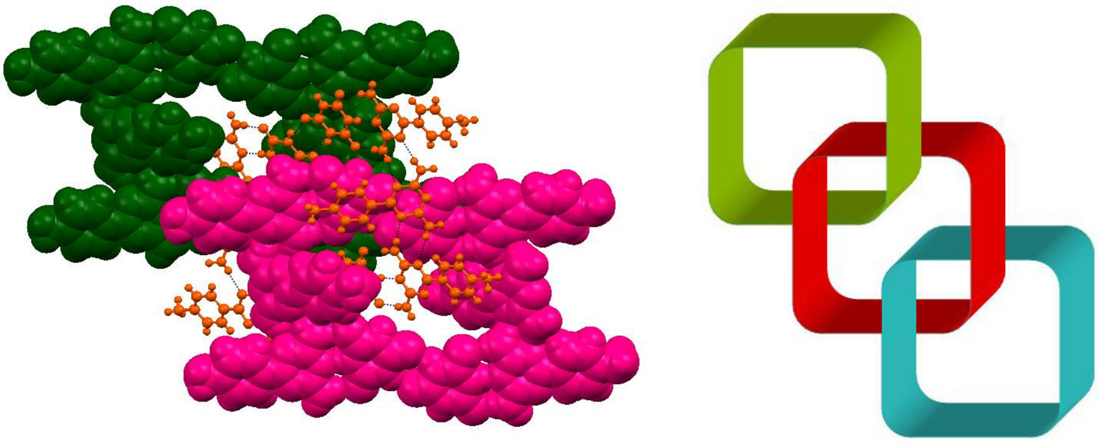


Figure 27. Catenation arrangement formed by the self-assembly of quartet units in three-dimensions as observed in the crystal structure of **9a** (left) and schematic diagram (right).

2.4 Conclusions

In conclusion, several supramolecular complexes of **CA** with different type of azadonor compounds have been prepared and exotic structural features of all the complexes were discussed. It is noteworthy to mention that, while complexes of **CA** with aza-donor compounds signify the adoption of different types of homomeric and heteromeric forms of **CA** molecules (see Figure 28), in the complexes formed by **CA** with triazine ligands, the substitution of different type of alkyl groups on triazine moiety have exhibited remarkable differences in hydrogen bonding patterns as well as three-dimensional arrangement of ultimate supramolecular architectures. It is observed that, in all the complexes, **CA** formed expected triple hydrogen bonding pattern, comprising of two N-H···O and one N-H···N hydrogen bonds, with triazine ligand. This study also signifies the importance of combinatorial type synthesis of supramolecular assemblies of each molecular entity to unravel many possible structural features and molecular recognition features.

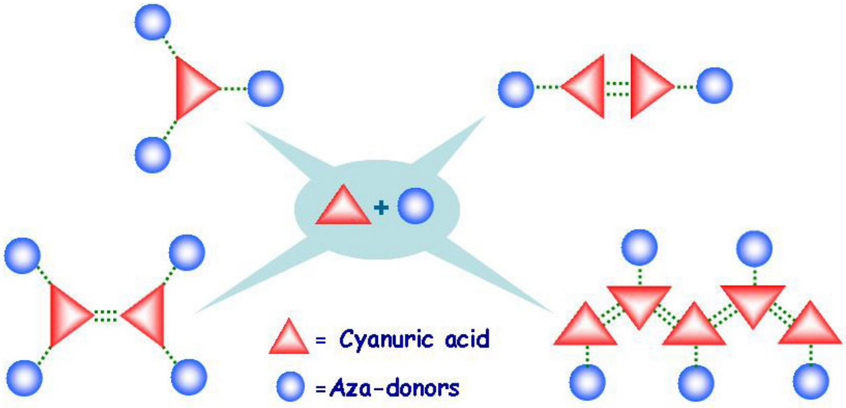


Figure 28. Different type of hydrogen bonding patterns observed in the complexes, **1a**, **1b**, and **2a-4a**.

2.5 Experimental section

2.5.1 Synthesis

All the chemical reagents and solvents, used in this study, were obtained from commercial suppliers and used as such without any further purification. The synthetic procedures of all the complexes are described herein. Good quality crystals of all the complexes were obtained by the slow evaporation of the reaction mixtures.

Complex of methanol solvate of CA and 4,7-phenanthroline, 1a.CH_3OH.

CA (20 mg , 0.1561 mmol) was dissolved in 5 ml of MeOH, by prolonged heating, to this clear solution was added 4,7-phenanthroline, **1**, (28.13 mg, 0.1561 mmol) and heated. After all the reactants were dissolved, the clear solution of the reaction mixture was kept for slow evaporation. The good quality colorless crystals that are suitable for studies by single crystal X-ray diffraction methods were obtained over the period of three days.

Complex of water adduct of CA and 4,7-phenanthroline, 1b.H_2O

CA (20 mg, 0.1561 mmol) was dissolved in 3 ml of distilled water by heating, to this clear solution was added 4,7-Phenanthroline, **1**, (28.13 mg, 0.1561 mmol) and the reaction mixture was heated further. The clear solution obtained was kept for slow evaporation. The good quality colorless crystals were obtained over the period of seven days.

Complex of cyanuric acid and 1,7-phenanthroline, 2a

To a warm solution of **CA** (20 mg, 0.1561 mmol) in 5ml of DMF was added 1,7-Phenanthroline, **2**, (28.13 mg, 0.1561 mmol) and heated for 5 minutes. The clear solution of the reaction mixture was kept for slow evaporation. The good quality colorless needle crystals were obtained over the period of ten days.

Complex of cyanuric acid and phenazine, 3a

CA (20 mg , 0.1561 mmol) was dissolved in 5 ml of MeOH by prolonged heating, to this clear solution was added phenazine, **3**, (28.13 mg, 0.1561 mmol) and heated for 5 minutes. The reaction mixture was kept for slow evaporation. The good quality yellow crystals were obtained over the period of two days.

Complex of cyanuric acid and 1,3-bis(4-pyridyl)propane, 4a

CA (20 mg, 0.1561 mmol) was dissolved in 5 ml of MeOH by prolonged heating, to this clear solution was added 4,4'-Trimethylenedipyridine (30.9 mg, 0.1561 mmol) and heated. The reaction mixture was kept for slow evaporation. The good quality pale red needle crystals were obtained, over the period of five days.

Complex of CA and 2,4-diamino-6-methyl-1,3,5-triazine, 5a

CA (26 mg, 0.2 mmol) in 5 ml of solution of dimethylformamide (DMF) was heated for 5 minutes, to this warm solution was added 25 mg (0.2 mmol) of **5** gradually. The solution mixture was heated for 10 minutes to make the reactant completely soluble. Thus, the clear solution obtained was kept for slow evaporation. The good quality colorless crystals were obtained after 7 days, which became unstable upon exposure to the air. Hence, the crystals were protected in mother liquor and used for data collection at low temperature (133 K).

Complex of CA and 2,4-diamino-6-phenyl-1,3,5-triazine, 6a

A solution of **CA** (26 mg, 0.2 mmol) in 5 ml of DMF was heated for 5 minutes and to this clear solution was added 37 mg (0.2 mmol) of **6** which yielded a precipitate. The precipitate was dissolved by adding the mixture of 5 ml of DMF-water. Thus, the clear solution obtained was kept for slow evaporation. Good quality colorless crystals were obtained over the period of 7 days.

Complex of CA and 2,4-diamino-6-(3-flourophenyl)-1,3,5-triazine, 7a

The solution of **7** (41 mg, 0.2 mmol) in DMF was heated for 5 minutes to make the substance completely dissolved. To this clear solution was added **CA** (26 mg, 0.2 mmol) in 5 ml of CH_3OH drop by drop and this mixture was heated for a while. The resulted clear solution was kept for slow evaporation which yielded a colorless good quality crystal over the period of 5 days and the crystals, thus, obtained was used for the structural characterization by X-ray diffraction method.

Complex of CA and 2,4-diamino-6-(4-methylphenyl)-1,3,5-triazine, 8a

CA (26 mg, 0.2 mmol) was dissolved in excess of CH_3OH by prolonged heating and to this hot solution was added 40 mg of **8** (0.02 mmol). The reaction mixture was further heated for a while and the clear solution thus obtained was kept for slow evaporation. Good quality single crystals were obtained after 3 days which were used for the structural characterization by X-ray diffraction techniques.

Complex of CA and 2,4-diamino-6-(4-methoxyphenyl)-1,3,5-triazine, 9a

CA (26 mg, 0.2 mmol) was dissolved in 3 ml of water by warming on the hot plate, to this clear solution was added a solution of **9** (43 mg, 0.2 mmol) in DMF by drop wise. The solution mixture was heated for another 5 minutes and the resulted clear solution was kept for slow evaporation. The good quality crystals were obtained after 7 days which were used for the data collection.

2.5.2 Crystal structures determination

Good quality single crystals of **1a**, **1b**, **2a**, **3a**, **4a** and **5a - 9a** obtained by the procedures described above, have been chosen by viewing under microscope and glued to a glass fiber using an adhesive to mount on a goniometer of Bruker single crystal X-ray diffractometer equipped with APEX CCD area detector. The data collections were smooth in all the cases without any complications and the all the crystals were found to be stable, except in **5a**, through out data collection period. The data collection of **5a** was done at 133 K as the crystal was unstable. The intensity data were processed using Bruker suite of programmes,[21] SAINT, followed by absorption correction by SADABS. The structures were solved by using XS and refined by least-squares methods using XL.[22] All the structures converged to good *R* factors. All the non-hydrogen atoms were refined by anisotropical methods. All the structural refinements converged to good *R*-factors and the intermolecular interactions were computed using PLATON.[23]

Table 2.1 Crystallographic data of the molecular complexes, **1a**, **1b**, and **2a** - **4a**.

	1a	**1b**	**2a**	**3a**	**4a**
Formula	$(C_3H_3N_3O_3):(C_{12}H_8N_2):(CH_3OH)$	$2(C_3H_3N_3O_3): 2(C_{12}H_8N_2): 3(H_2O)$	$(C_3H_3N_3\ O_3): (C_{12}H_8N_2)$	$2(C_3H_3N_3O_3):(C_{12}H_8N_2)$	$(C_3H_3N_3O_3):(C_{13}H_{14}N_2)$
M	341.33	672.62	309.29	438.37	327.35
crystal habit	Needles	blocks	needles	needles	blocks
crystal system	Monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\ 2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	7.199(3)	13.251(2)	4.816(2)	5.989(1)	6.666(8)
b/Å	17.072(2)	17.228(2)	10.434(4)	7.366(1)	8.110(1)
c/Å	12.839(1)	14.042(2)	14.040(6)	10.408(2)	28.824(3)
α/°	90	90.00	81.07(2)	87.14(1)	90
β/°	94.00(2)	102.49(3)	89.49(1)	86.00(1)	90.19(2)
γ/°	90	90.00	77.72(4)	84.73(3)	90
V/Å ^{3}	1574.1(7)	3129.8(7)	680.8(5)	455.7(1)	1558.3(3)
Z	4	4	2	1	4
D_c/g cm^{-3}	1.440	1.427	1.509	1.598	1.395
μ/mm^{-1}	0.107	0.109	0.110	0.125	0.100
2θ range[°]	51.00	50.08	51.34	51.00	50
T/K	298(2)	298(2)	298(2)	298(2)	298(2)
F(000)	712	1400	320	226	688
λ/Å	0.7107	0.7107	0.7107	0.7107	0.7107
$\Delta\rho_{min.max}$/e Å^{-3}	0.174/-0.256	0.553/-0.245	0.699/-0.377	0.268/-0.239	0.279/-0.288
total reflections	8012	22198	6652	2327	7373
unique reflections	2914	5541	2427	1636	2737
reflectios used	2467	2818	1495	1191	2151
R1, I > 2σ(I)	0.0449	0.0535	0.0827	0.0638	0.0495
wR,I > 2σ(I)	0.1125	0.1313	0.1950	0.1867	0.1085

Table 2.2 Crystallographic data of the molecular complexes, **5a – 9a**.

	5a	**6a**	**7a**	**8a**	**9a**
Formula	$(C_3H_3N_3O_3):(C_4H_7N_5)$	$(C_3H_3N_3O_3): (C_9H_9N_5)$	$(C_3H_3N_3O_3):(C_9H_8N_5F):(H_2O)$	$(C_3H_3N_3\ O_3): (C_{10}H_{11}N_5)$	$(C_3H_3N_3O_3):(C_{10}H_{11}N_5O)$
M	254.23	316.30	352.30	330.32	346.32
crystal habit	blocks	needles	needles	blocks	needles
crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$C\ 2/\ c$	$P\ 2_1/c$	$P\bar{1}$	$P\ 2_1/c$	$P\ 2_1/c$
a/Å	18.458(6)	7.471(1)	5.316(2)	11.127(2)	7.230(2)
b/Å	6.820(2)	15.582(2)	11.180(4)	10.771(2)	12.159(3)
c/Å	18.723(6)	12.447(2)	13.568(5)	12.420(2)	16.967(5)
α/º	90.00	90.00	68.75(2)	90.00	90.00
β/º	119.53(1)	109.07(1)	83.87(1)	96.95(1)	93.46(1)
γ/º	90.00	90.00	81.43(2)	90.00	90.00
V/Å^3	2050.7(1)	1369.5(3)	741.9(5)	1477.6(5)	1488.8(7)
Z	8	4	2	4	4
D_c/g cm^{-3}	1.647	1.534	1.577	1.485	1.545
μ/mm^{-1}	0.133	0.117	0.131	0.112	0.120
2θ range[°]	50.02	50.04	50.62	46.56	50.04
T/K	133(2)	298(2)	298(2)	298(2)	298(2)
F(000)	1056	656	364	688	720
λ/Å	0.7107	0.7107	0.7107	0.7107	0.7107
$\Delta\rho_{min.max}$/e Å^{-3}	0.379/-0.322	0.278/-0.436	0.180/-0.245	0.377/-0.240	0.193/-0.174
total reflections	7006	9622	7092	8840	13586
unique refl.	1808	2418	2684	2118	2628
reflectios used	1323	2157	2119	1749	2232
R1, I > 2σ(I)	0.0825	0.0428	0.0416	0.0358	0.0455
wR,I > 2σ(I)	0.1441	0.1215	0.1144	0.1013	0.1235

Table 2.3 Characteristic hydrogen bond distances (Å) and angles (°) of the molecular complexes, **1a**, **1b**, and **2a** - **4a**.[#]

	1a			**1b**			**2a**			**3a**			**4a**		
N-H···O	1.86	2.76	176	1.97	2.81	164	1.98	2.79	171	1.91	2.78	171	1.98	2.86	172
				1.97	2.83	171	1.79	2.83	170	1.95	2.84	165			
				1.98	2.83	171									
				1.99	2.85	164									
N-H···N	1.96	2.87	175	1.99	2.84	171	1.85	2.85	173	2.35	3.22	168	1.86	2.77	176
	1.98	2.87	175	2.02	2.87	169							1.93	2.86	171
C-H···O	2.39	3.33	168	2.46	3.35	160	2.30	3.37	172	2.28	3.19	170	2.46	3.40	162
	2.43	3.33	165	2.48	3.38	162	2.29	3.24	159	2.49	3.38	172	2.53	3.24	129
	2.69	3.51	143	2.52	3.28	140							2.57	3.42	145
	2.71	3.47	137	2.53	3.27	137									
	2.76	3.53	137	2.56	3.35	144									
				2.58	3.32	137									
				2.60	3.51	165									
				2.61	3.52	163									
				2.69	3.57	158									
				2.69	3.59	163									
O-H···O	1.87	2.74	176												
O···N					2.75	147									
					2.75	174									

[#] Three columns for each structure represent H···A, D···A distances and D-H···A angle, respectively for a typical hydrogen bond, being represented as D-H···A.

Table 2.4 Characteristic hydrogen bond distances (Å) and angles (°) of the molecular complexes, **5a – 9a**.$^{\$}$

	5a			**6a**			**7a**			**8a**			**9a**		
N-H···O	1.87	2.82	1.90	1.90	1.90	173	1.90	2.84	170	1.93	2.87	173	1.94	2.79	174
	1.99	2.97	2.02	2.02	2.02	178	2.02	2.92	173	2.12	2.87	155	2.06	2.92	175
	2.00	2.95	2.05	2.05	2.05	172	2.05	2.92	177	2.13	2.97	157	2.08	2.93	167
	2.17	3.07	2.20	2.20	2.20	177	2.20	3.07	176	2.20	3.03	173	2.14	3.02	179
			2.24	2.24	2.24		2.24	2.91	132				2.38	3.19	168
N-H···N	1.82	2.79	1.92	1.92	1.92	171	1.92	2.89	171	1.96	2.87	177	1.92	2.85	176
	1.88	2.86	2.21	2.21	2.21	179	2.21	3.09	166	2.12	3.01	169			
	2.06	2.97								2.25	3.07	171			
C-H···O	2.20	3.19				169									
C-H···N										2.56	3.49	167			
O-H···N			2.21	2.21	2.21		2.21	2.93	168						
O-H···O			2.24	2.24	2.24		2.24	2.98	147						

$^{\$}$Three columns for each structure represent H···A, D···A distances and D-H···A angle, respectively for a typical hydrogen bond, being represented as D-H···A

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CHAPTER THREE

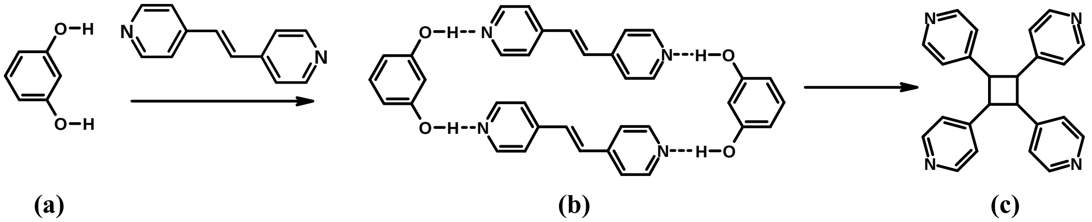
SUPRAMOLECULAR ASSEMBLIES OF ISOMERS OF DIHYDROXYBENZOIC ACID WITH DIFFERENT AZA-DONOR COMPOUNDS

3.1 Introduction

Supramolecular chemistry is facilitated by molecular building blocks that possess different functional groups, which have the capability of forming a variety of hydrogen bonds.[1] In this regard, while symmetrically substituted aromatic compounds, by a single functional group like, trimesic acid, benzenetriamide etc., are of great significance, compounds possessing multiple functional groups, situated at positions to yield the desired assemblies, have driven contemporary supramolecular synthesis to search for numerous novel ligands.[2,3] In fact, there are many examples known in the literature exemplifying such type of polyfunctional molecules.[4,5] For example, in recent times, compounds, like pyromellitic acid (1,2,4,5-benzenetetracarbolylic acid), 3,5-dinitrobenzoic acid, 3,5-dinitrobenzamide, etc., which possess multiple functional groups like, -COOH, -CONH$_2$, -OH, -NO$_2$, have been extensively studied in our research group as well as in many other laboratories, for the preparation of numerous supramolecular assemblies with exotic architectures like, host-guest assemblies, lamellar sheets, etc.,[6] as discussed in Chapter I.

Among many functional groups, known to form potential hydrogen bonds through self-assembly process, hydroxyl group (-OH) is one of the effective moieties, as it can form hydrogen bonds of strength even comparable to –COOH group.[7] In recent times, MacGillivray and co-workers, extensively, studied the role of –OH functional groups in the synthesis of variety of supramolecular complexes, in which, polyenes, used as co-ligands, organize with a reparative distances of ~ 4.2 Å, within the crystal environment, facilitating a photochemical reaction, to yield novel cyclobutane products. For example, the co-crystallization of resorcinol (1,3-benzenediol) with *trans-bis*(4-pyridyl)ethene (*bpyee*) produced a four-component molecular assembly, 2(resorcinol)·2(*bpyee*), in which each resorcinol molecule pre-organizes two polyenes, through two O-H···N hydrogen bonds, for [2+2] photoaddition (see Scheme1).[8]

Scheme 1



Further, additional functional groups on the benzene ring of the dihydroxy system did not affect the hydrogen bonding pattern of –OH groups with aza-donor compounds, as it was exemplified through a study on homologous series of phluroglucinols.[9] In this connection, Pedireddi and Varughese, recently, have shown the influence of -COOH substitution on dihydroxybenzene system, which also has the capability of forming O-H···N hydrogen bond with aza-donor compound, in the formation of different hydrogen bonded networks. For this purpose, 3,5-dihydroxybenzoic and 4-bromo-3,5-dihydroxybenzoic acids were co-crystallized with various aza-donor compounds, in order to explore the competitive nature of –COOH and –OH functional groups towards aza-donor compounds, taking into account the affinity of these functional groups to form O-H···N and O-H···N/C-H···O pair-wise hydrogen bonds in supramolecular synthesis, which, ultimately, lead to the creation of a myriad of supramolecular assemblies with exotic architectures.

The typical example, shown in Figure 1, is the structure of supramolecular complex of 3,5-dihydroxybenzoic acid and 2-*bis*(4-pyridyl)ethene (*bpyee*), which yielded a five-membered supramolecular entity, formed between the acid and aza-donor molecules, through O-H···N hydrogen bonds, which was otherwise expected be a four-membered unit (see Scheme 1b). Within the five-membered ring, the recognition between the constituents is established in such a manner that, one *bpyee* molecule forms O-H···N hydrogen bonds, exclusively, with -OH groups, while the other *bpyee* interacts with both -OH as well as -COOH functional groups.[10]

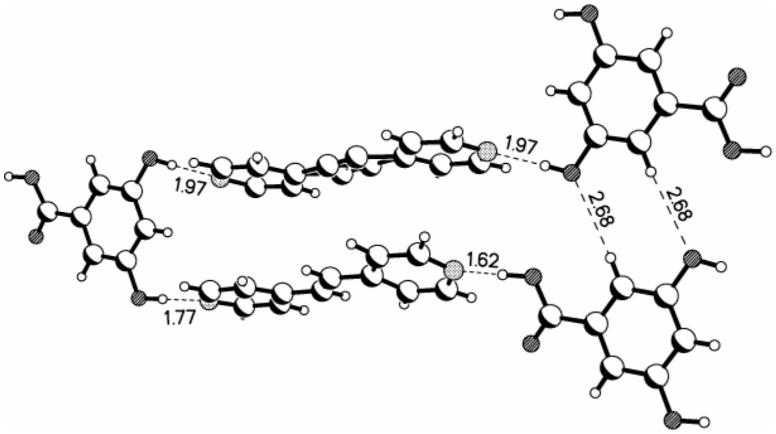
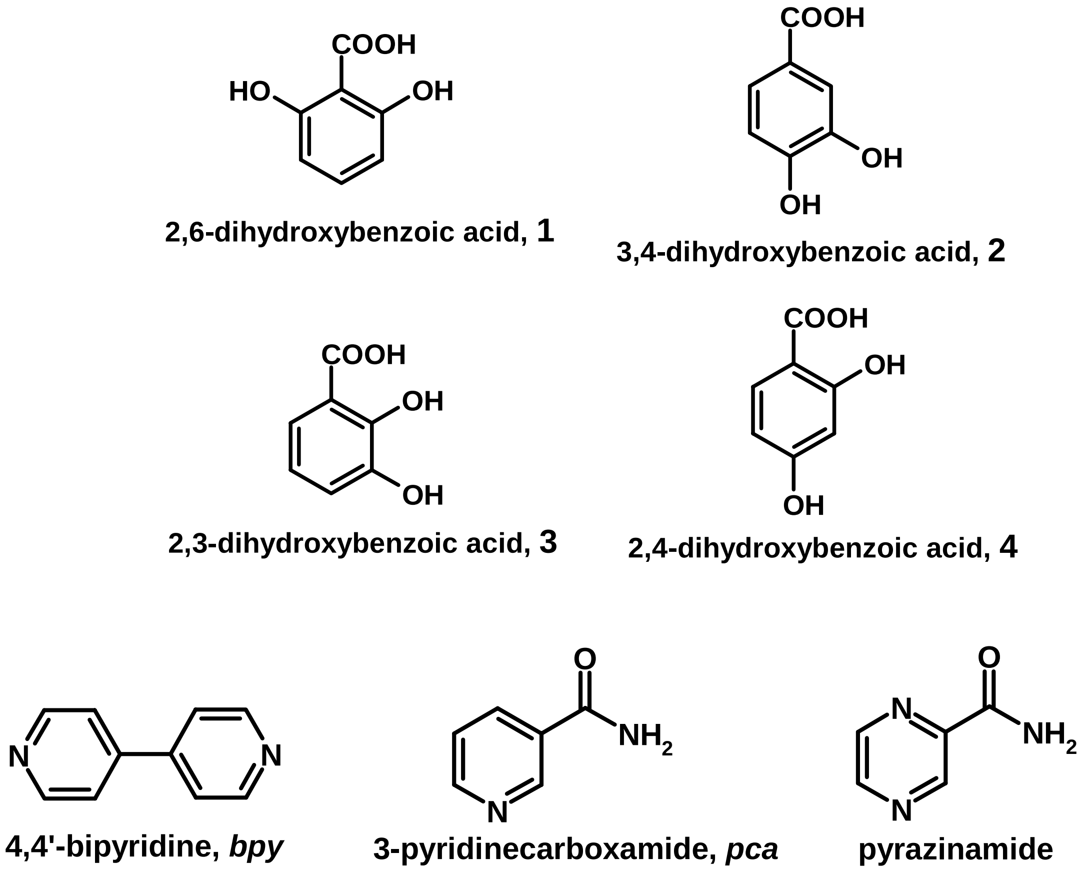


Figure 1. The recognition pattern in the complex of 3,5-dihydroxybenzoic acid and *bpyee*. Notice change in expected four-membered ring, due to the presence of –COOH group at the *para*-position of the dihydroxybenzene system.

From all the above examples, discussed, thus, so far, it is apparent that the effect of multiple functional groups, either symmetrically substituted or at the positions that offer effective recognition pattern, are well explored and rational analysis was documented.[11] However, role of different isomers, which arise due to the variations in the placement of functional groups are not well known in the literature, towards the creation of supramolecular assemblies. In this regard, taking into account the ability of 3,5-dihydroxybenzoic acid to form different isomers by changing the position of –OH groups, numerous co-crystallization studies of each isomer with different co-ligands (Scheme 2) have been carried out, as illustrated in Chart I. The obtained supramolecular assemblies in terms of there exotic architectures, molecular recognition features etc., have been discussed in the following sections.

3.2 Supramolecular assemblies of different isomers of dihydroxybenzoic acid



2,6-dihydroxybenzoic acid, 1

3,4-dihydroxybenzoic acid, 2

2,3-dihydroxybenzoic acid, 3

2,4-dihydroxybenzoic acid, 4

4,4'-bipyridine, *bpy*

3-pyridinecarboxamide, *pca*

pyrazinamide

Scheme 2. Various dihydroxybenzoic acid and aza-donor ligands.

Chart I

Reactants	Products
1+*bpy*	**1a**
2+*bpy*	**2a**
1+*pca*	**1b**
3+*pca*	**3b**
1+pyrazinamide	**1c**
2+pyrazinamide	**2c**
3+pyrazinamide	**3c**
4+pyrazinamide	**4c**

3.2.1 Molecular complex of 2,6-dihydroxybenzoic acid and 4,4'-bipyridine, 1a

Co-crystallization of 2,6-dihydroxybenzoic acid, **1**, and 4,4'-bipyridine, ***bpy***, from a CH_3OH solution, yielded good quality single crystals of molecular complex **1a**, by slow evaporation of the solvent, at ambient conditions, over a period of 3 days. Structural characterization, by X-ray diffraction techniques, revealed that the composition of the constituents is in the ratio of 2:1 of **1** and ***bpy*** with molecular formula of $2(C_7H_5O_4).(C_{10}H_{10}N_2)$. The crystallographic details of the complex **1a** are given in Table 3.1. From the ORTEP diagram, as shown in Figure 2a, it is apparent that the acid molecule is deprotonated, which is taken up by the ***bpy*** molecule. The –OH groups present on **1**, undergo intramolecular O-H$\cdots$O (H$\cdots$O, 1.59 and 1.70 Å) hydrogen bonding with carboxylate group, as shown in Figure 2b. Further, structural analysis reveals that, the constituent molecules form a herringbone pattern with *zig-zag* layers, in three-dimensions, as shown in Figure 3a.

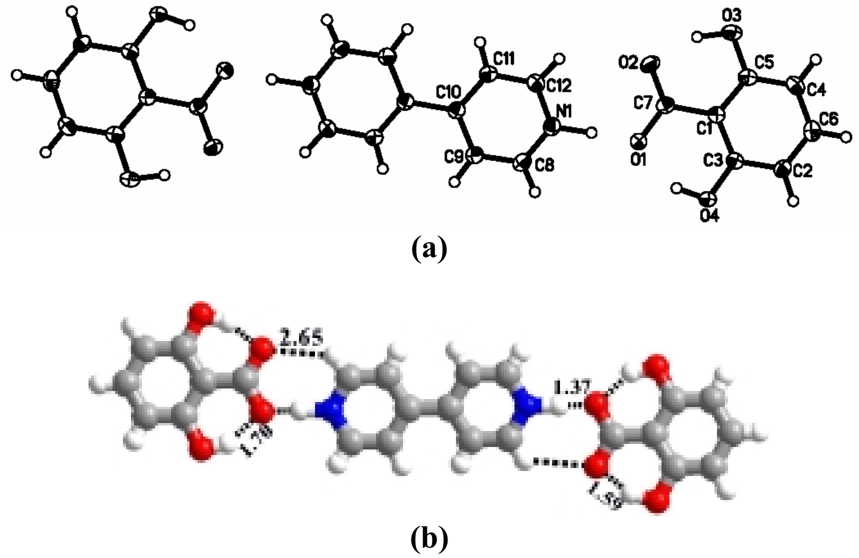
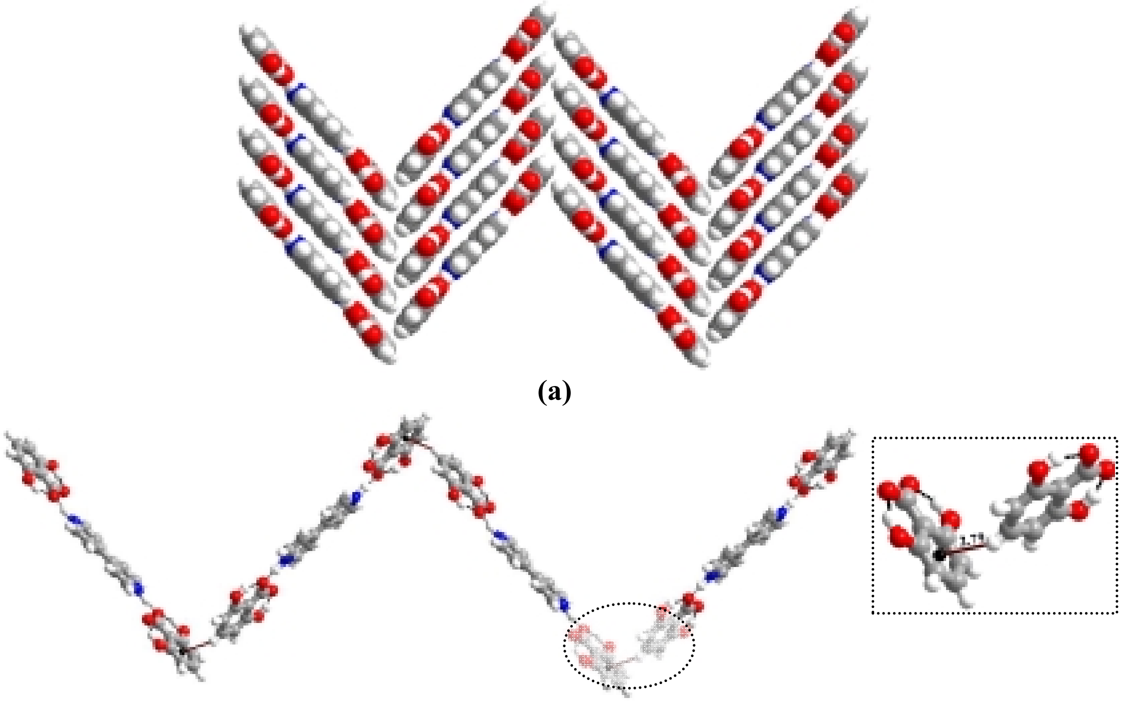


Figure 2. (a) ORTEP diagram of the complex **1a**. (b) Three-dimensional herringbone pattern, formed by the molecules of **1** and ***bpy*** in complex **1a**.

In a typical *zig-zag* layer, the basic recognition between **1** and ***bpy*** molecules is being established through strong N^{+}-H$\cdots$$O^{-}$ hydrogen bonds, with the H$\cdots$$O^{-}$ distance of 1.37Å, formed between the protonated ***bpy*** and the carboxylate moiety of molecules of **1** (see Figure 2b). The characteristic hydrogen bond distances are given in Table 3.3. Hence, a trimeric unit is formed, with two molecules of **1** are connected to ***bpy*** in such a way that, the molecules of **1** are being separated by the ***bpy*** ligand. Further, the adjacent supramolecular ensembles, i.e. the trimeric units, are connected to each other through C-H$\cdots$$\pi$ interactions, formed between the molecules of **1** (see inset in Figure 3b), leading to the formation of a *zig-zag* chain.



(a)

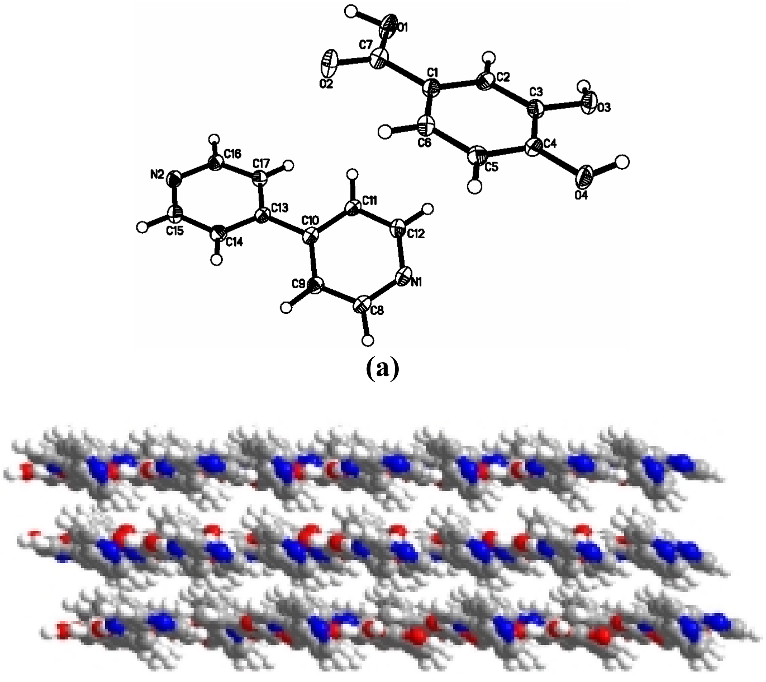
(b)

Figure 3. (a) A trimeric unit formed due to the molecular recognition between **1** and ***bpy***. (b) Adjacent trimeric unit interconnected trough C-H···π interaction to yield *zig-zag* chain. The inset shows the interaction between the trimeric units.

It is apparent from the structural analysis of **1a** that, –OH groups do not participate in intermolecular interactions with co-ligands, due to their involvement in the intramolecular hydrogen bonding, which is perhaps, because of the position of –OH groups. However, taking into account the position of –OH groups on the isomers, **2**, **3** and **4** (Scheme 2), at least one of the –OH groups may be available for intermolecular interaction, thus, the supramolecular assemblies constructed would possess hydrogen bonds of both –COOH and –OH groups. Hence, co-crystallization of **2** with ***bpy*** has been carried out and the features of the complexes are discussed in the following section.

3.2.2 Molecular complex of 3,4-dihydroxybenzoic acid and 4,4'-bipyridine, 2a

The supramolecular complex **2a**, was prepared by co-crystallizing 3,4-dihydroxybenzoic acid, **2**, with ***bpy***, from a CH_3OH solution, by slow evaporation of the solvent, at room temperature. The colorless good quality single crystals, thus, obtained were used for the characterization, through the single crystal X-ray diffraction technique. The structural elucidation reveals that, the molecular composition present in the asymmetric unit of the complex **2a** is in the ratio of 1:1 of **2** and ***bpy***, as shown in the ORTEP diagram in Figure 4a.

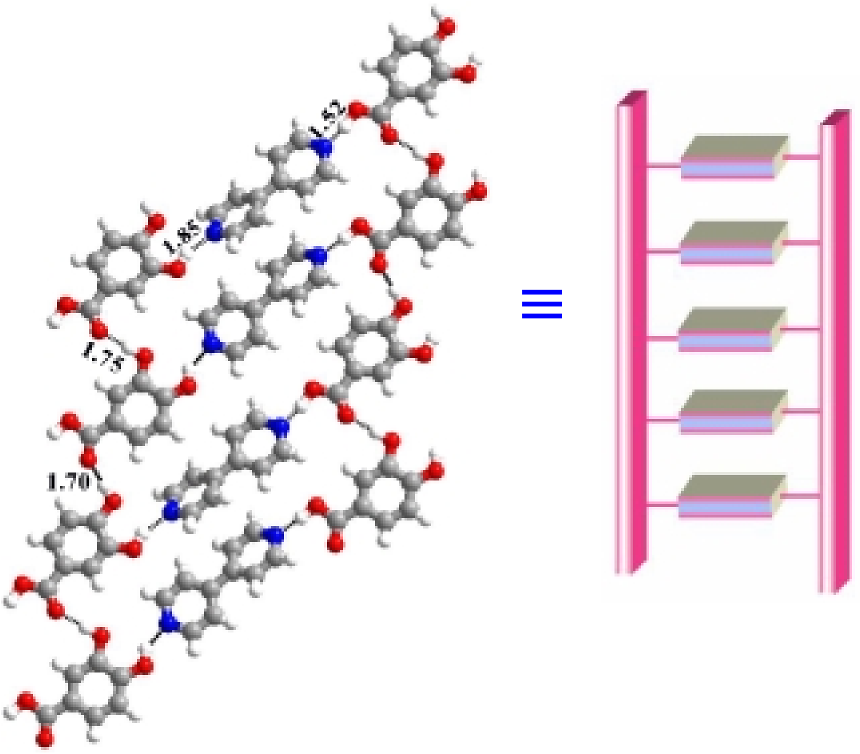


(a)

(b)

Figure 4. (a) ORTEP diagram shows the constituent molecules present in the asymmetric unit of the complex **1a**. (b) Stacking of the planar sheets in three-dimensions.

As expected, there is no intramolecular hydrogen bonding within the acid molecules, in the complex **2a**. In three-dimensions, the constituent molecules are arranged to yield stacked planar sheets, as shown in Figure 4b. The molecules of **2** and ***bpy*** interact with each other, within a typical sheet, through the interaction established by both –COOH and –OH as well as with pyridyl N-atom of ***bpy***, through O-H··N hydrogen bonds, (H··N, 1.52 and 1.85 Å), such that the ***bpy*** molecules are being inserted between acid molecules. The adjacent ensembles are, further, held together by O-H··O hydrogen bonds (H··O, 1.75 and 1.70 Å), formed between –COOH and –OH groups, as shown in Figure 5. Thus, in two-dimensional arrangement, the molecules in the structure of supramolecular assembly, **2a**, gave a ladder structure, in which the acid chains are arranged as rods, while the ***bpy*** molecules form rungs (see Figure 5a), which is schematically depicted in Figure 5b.



(a) **(b)**

Figure 5. (a) The molecular ladder formed by the molecules of **2** and ***bpy*** in complex **2a**. (b) Schematic diagram that mimics the ladder structure observed in complex **2a**.

However, co-crystallization experiments of **3** and **4** with ***bpy*** did not yield suitable single crystals for analysis, by single crystal X-ray diffraction methods. Nevertheless, powder diffraction patterns of the residues obtained from the co-crystallization experiments show that, indeed, new phases have formed, with the appearance of new peaks and the absence of the peaks corresponding to either of the reactants. For example, the diffractogram, shown in Figure 6, has new peaks at 10.64 and 16.02°, while the prominent peaks corresponding to reactants at 13.57, 27.88° (for **3**) and 12.44, 19.58° (for ***bpy***) are absent, suggesting the formation of complex between **3** and ***bpy*** (**3a**).

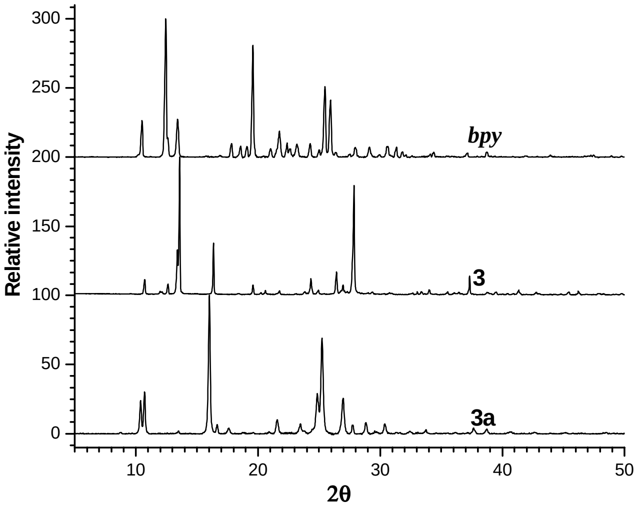


Figure 6. X-ray powder diffraction pattern, corresponding to complex **3a**.

Similarly, in the Figure 7, while new peaks appeared at 13.64, 16.31 and 26.85°, the reactant peaks at 8.49 and 24.70° (for **4**) and 12.44, 19.58° (for ***bpy***) are completely absent. In fact, the observation of different powder patterns, in Figure 6 and 7, corresponding to possibly **3a** and **4a**, suggest that these two are not isomorphs and form different type of assemblies

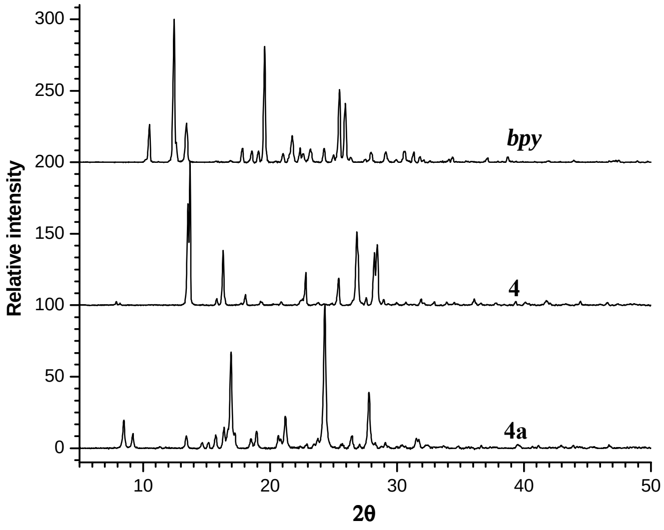


Figure 7. X-ray powder diffraction pattern, corresponding to complex **4a**.

Thus, it is clearly seen that the three-isomers of dihydroxybenzoic acid form different type of supramolecular assemblies, with same co-ligand, i.e. ***bpy***. While 3,5-dihydroxybenzoic acid and ***bpy*** form a bracelet type structure, reported in the literature, herringbone pattern was observed in **1a** (a complex of 2,6-dihydroxybenzoic acid and ***bpy***) and 3,4-dihydroxybenzoic acid with ***bpy*** formed ladder type structure. Further, considering the competitive nature of –OH and –COOH groups towards ***bpy*** ligand to form O-H···N hydrogen bonds, the study was extended with aza-donor compounds that possess other functional groups, which may also compete for the complimentary groups available on the isomers of dihydroxybenzoic acid.

Thus, in particular, knowing the potential of $–CONH_2$ groups to form hydrogen bonds with the carboxyl (-COOH) groups, the amide substituted aza-donor ligands were chosen for the study of co-crystallization with various isomers of dihydroxybenzoic acid. Thus, it was anticipated that, while carboxylic acid forms hydrogen bond with amide group, the hydroxyl groups can interact with the pyridyl N-atoms, which can subsequently yield exotic supramolecular architectures.

In this direction, several co-crystallization experiments of various dihydroxybenzoic acids with 3-pyridinecarboxamide, ***pca***, as well as pyrazinamide, (Scheme 2), were carried out. The salient features of, thus, synthesized complexes would be discussed in the following sections.

3.2.3 Molecular complex of 2,6-dihydroxybenzoic acid and 3-pyridine-carboxamide, 1b

Co-crystallization of **1** and ***pca***, from a CH_3OH solution, by slow evaporation of the solvent, at ambient conditions, yielded good quality colorless crystals of complex **1b** of formula unit of $(C_7H_5O_4)(C_6H_6N_2O)$. The structure elucidation, carried out by X-ray diffraction methods, reveals that the constituents present in the asymmetric unit is in the ratio of 1:1 of **1** and ***pca*** (see Figure 8). Within the asymmetric unit, the acid molecules are deprotonated, as found in **1a**.

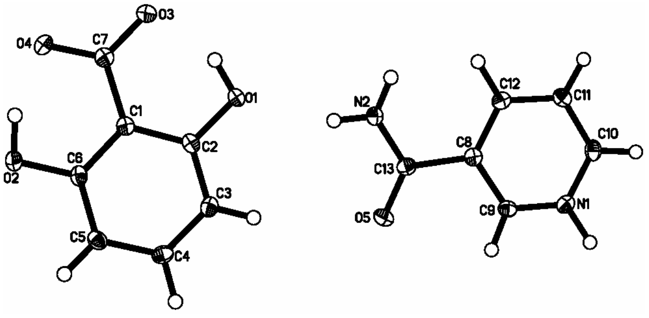
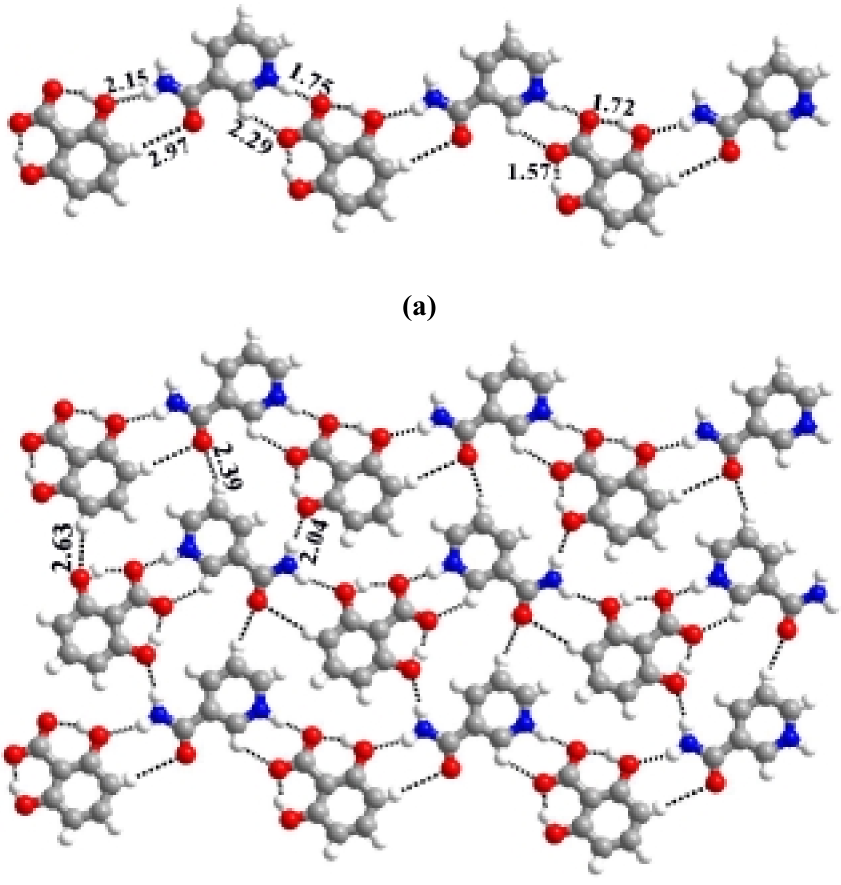


Figure 8. ORTEP diagram of the complex **1b**. Notice that the acid proton is taken up by ***pca***.

Further, in **1b**, also, both the –OH groups are involved in intramoelcular O-H···O hydrogen bonding with $-COO^-$ moiety (H···O, 1.57 and 1.72 Å). Under such circumstances, while the carboxylate group establishes interaction with protonated pyridyl N-atom of the ***pca***, and the amide moiety of the ***pca*** interacts with –OH groups, forming N-H$^{\cdots}$O hydrogen bond (H$^{\cdots}$O, 2.04 Å). Such an arrangement constituted molecular tapes (see Figure 9a), which are, in turn, held to each other through C-H$^{\cdots}$O (H$^{\cdots}$O, 2.63 and 23.9 Å) hydrogen bonds, formed between CH moiety and O-atom of caboxamide group of adjacent ***pca*** molecules, as well as N-H$^{\cdots}$O hydrogen bonds (H$^{\cdots}$O, 2.04 Å), formed between -NH moiety and O-atom of –OH group of ***pca***, constituting a two-dimensional sheet, as shown in Figure 9b.



(a)

(b)

Figure 9. (a) Molecular tapes, formed by the molecules of **1** and ***pca***. (b) Two-dimensional planar sheet formed by adjacent molecular tapes.

In three-dimensions, the two-dimensional sheets are stacked along *c*-axis, as shown in Figure 10, with a separation distance of 3.5 Å.

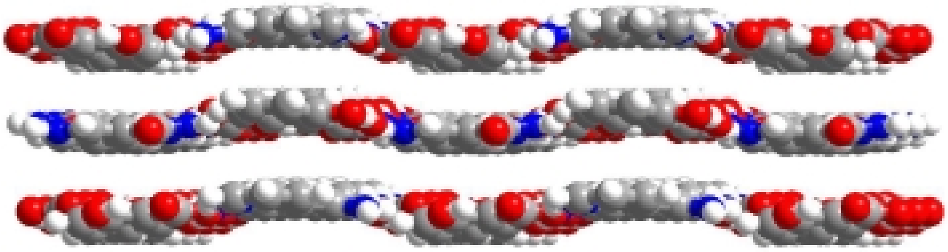


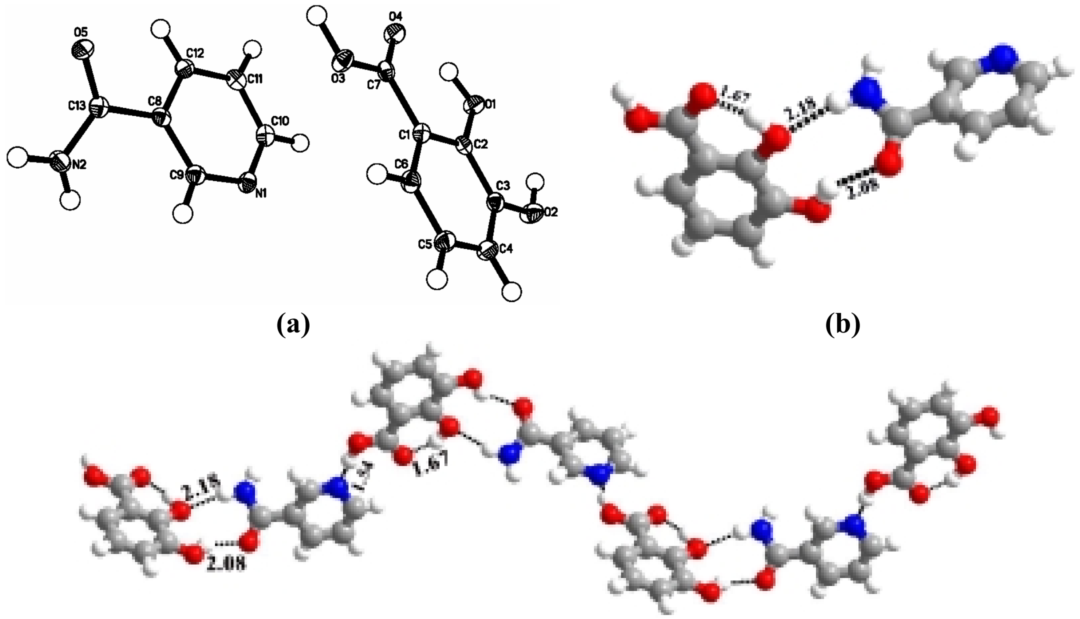
Figure 10. Stacking of the two-dimensional planar sheets in three-dimensions.

Following the same concept underlined for **1a** and **2a**, in terms of controlling the intramolecular hydrogen bonding, co-crystallization of ***pca*** with **2**, **3** and **4** has been carried out. However, while **3** and ***pca*** yield a complex **3b**, with good quality single crystals, suitable for the analysis by X-ray diffraction methods, the other two isomers, **2** and **4**, are not only failed to yield single crystals but also the samples are not crystalline enough for qualitative analysis even by powder X-ray diffraction methods. Hence the structural features of **3b** only are discussed in detail herein.

3.2.4 Molecular complex of 2,3-dihydroxybenzoic acid and pyridineoxamide, 3b

Complex **3b**, was also prepared, by following the same procedure employed for the synthesis of **1b**, by co-crystallizing **3** with ***pca***, from a CH_3OH solution, by slow evaporation of the solvent, at ambient conditions. The crystal structure analysis reveals that the constituents present in the asymmetric unit is in 1:1 ratio of **3** and ***pca*** (see Figure 11a).

Analysis of the molecular packing indicates that, unlike in the case of **1b**, the –COOH moiety in **3b** is not deprotonated. The recognition between the constituent molecules is almost similar to that of the pattern observed in **1b**, with –COOH establishing interaction with pyridyl N-atom of ***pca***, through O-H···N (H···N, 1.54 Å), while amide moiety through –OH groups, forming N-H···O (H···O, 2.18 Å) and O-H···O (H···O, 2.08 Å) hydrogen bonds (see Figure 11b). Such an aggregation ultimately constitutes infinite crinkled chains (see Figure 11c), unlike linear tapes observed in **1b**.



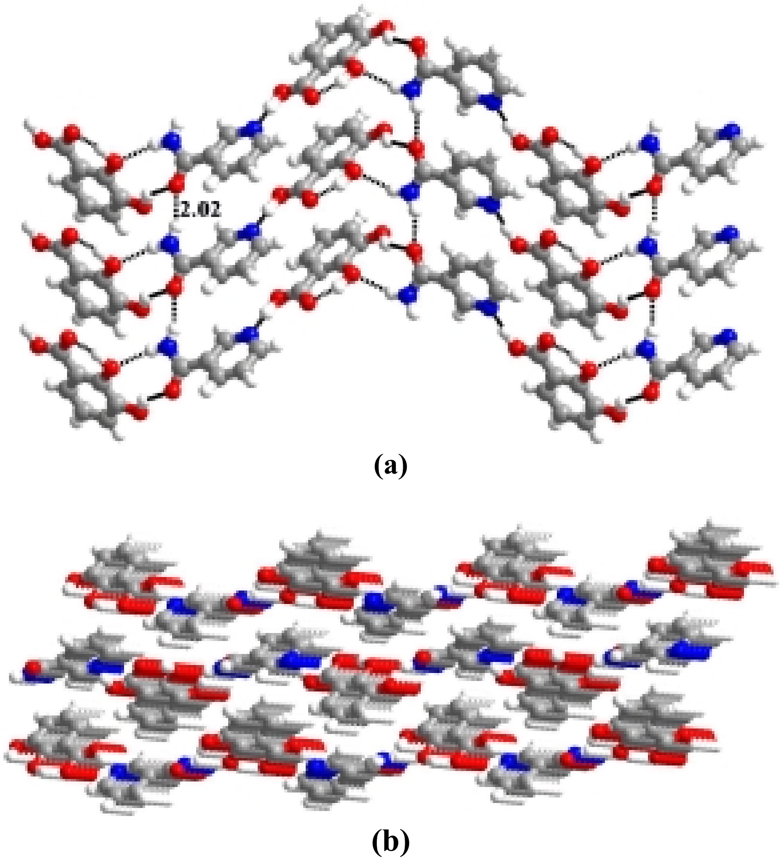
(a) **(b)**

(c)

Figure 11. (a) ORTEP diagram of the complex **3b**. (b) Primary recognition between the constituent molecules in complex **3b**. (c) The supramolecular crinkled chain constituted by the molecules of **3** and ***pca*** in complex **3b**.

Further, these adjacent molecular chains are held together through N-H···O (H···O, 2.02 Å) hydrogen bonds, formed between the amide groups in the adjacent chains, constituting a layer like structure along *a*-axis, as shown in Figure 12a, which in turn, are stacked along *b*-axis, in the three-dimensional arrangement, as shown in Figure 12b.

Although, the structure of **2b** and **4b** could not be established, it is evident from the structure of **1b** and **3b** that, strong acid and base recognition pattern appears to be well reflected as in both the cases –COOH (irrespective of deprotonation or not) established interaction, always, with highly basic N-atom, despite the possibility of forming interaction with –$CONH_2$.



(a)

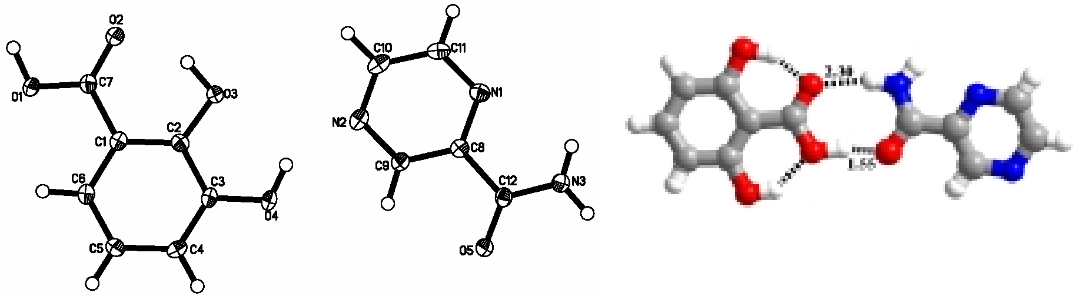
(b)

Figure 12. (a) The layered structure formed by adjacent supramolecular chains that are interconnected through N-H$\cdots$O hydrogen bonds. (b) Stacking of the layers along *b*-axis in three-dimensions, in the crystal lattice of complex **3b**.

To investigate, further, for possible perturbation of acid-base recognition pattern, by incorporating an additional hydrogen bonding site, pyridinecarboxamide has been replaced by pyrazinamide, which has two pyridyl N-atoms. Interestingly, all the isomers of dihydroxybenzoic acid formed co-crystals with pyrazinamide, as illustrated below.

3.2.5 Molecular complex of 2,6-dihydroxybenzoic acid and pyrazinamide, 1c

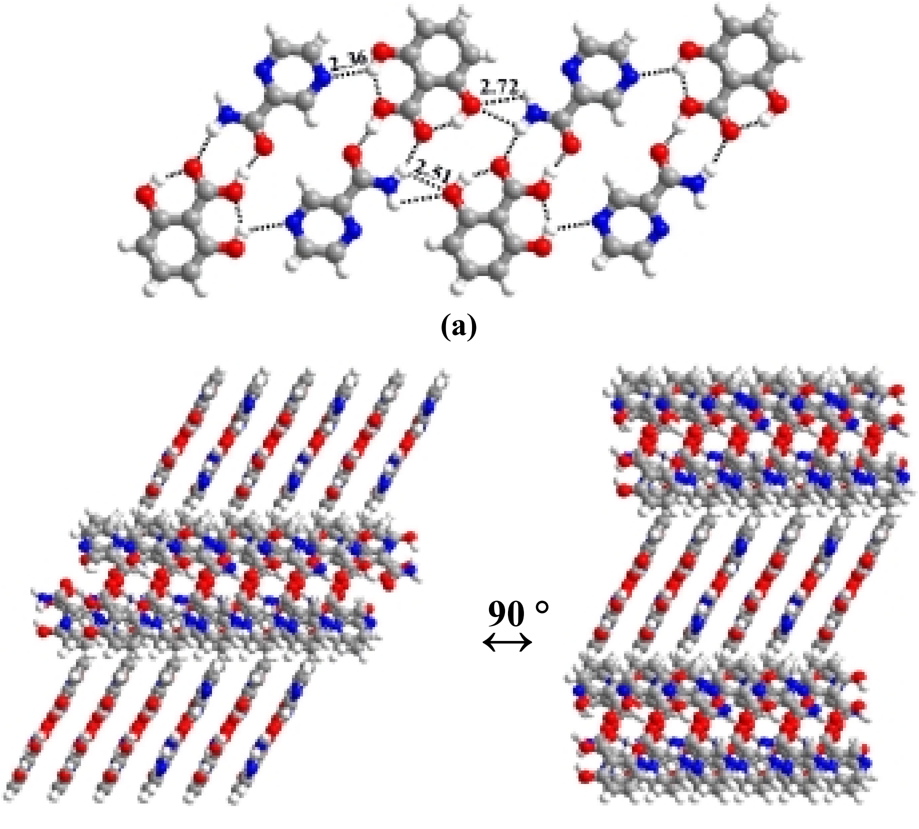
Good quality single crystals of complex **1c** were obtained, from a CH_3OH solution, by co-crystallizing acid **1** with pyrazinamide in 1:1 ratio. The crystal structure analysis reveals that, the constituent molecules present in the asymmetric unit are in the ratio of 1:1. The ORTEP diagram of the complex **1c** is given in Figure 13a, and the relevant crystallographic information is given in Table 3.2.



(a) **(b)**

Figure 13. (a) ORTEP diagram of the complex **1c**. (b) The $R_2^2(8)$ hydrogen bonding pattern formed between acid and amide functionalities in complex **1c**.

Analysis of molecular structure in the complex **1c** reveals that, as observed in **1a** and **1b**, both the –OH groups on **1** are involved in the intramolecular hydrogen bonding but deprotonation of –COOH has not been observed. However, unlike in the previously discussed complexes **1b** and **3b**, wherein –$CONH_2$ is also present on the co-ligand, the basic recognition between the constituent molecules in complex **1c** is established by $R_2^2(8)$ hydrogen bonding pattern, formed between acid and amide functionalities, through cyclic N-H$\cdots$O (H$\cdots$O, 2.30 Å) and O-H$\cdots$O (H$\cdots$O, 1.55 Å) hydrogen bonds, which was observed in many of the acid-amide molecular complexes (see Figure 13b). Such dimers are interconnected through O-H···N (H···N, 2.36 Å) hydrogen bonds, formed between –OH of **1** and N-atom of pyrazinamide, constituting a four membered cyclic unit, which in turn, are aggregated, as shown in Figure 14a, through bifurcated N-H···O (H···O, 2.51 and 2.72 Å) hydrogen bonds. Such ensembles are packed in three-dimensions by stacking as piles, arranged perpendicular to each other, as shown in Figure 14b-c.



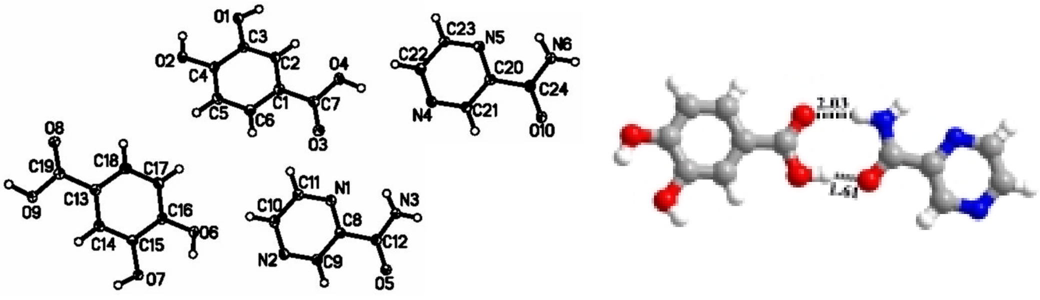
(a)

(b) (c)

Figure 14. (a) The four membered cyclic units are aggregated through bifurcated hydrogen bond. (b) The three-dimensional stacking of aggregated layers. (c) Another view of three-dimensional arrangement, obtained by rotating the original structure through 90°.

3.2.6 Molecular complex of 3,4-dihydroxybenzoic acid and pyrazinamide, 2c

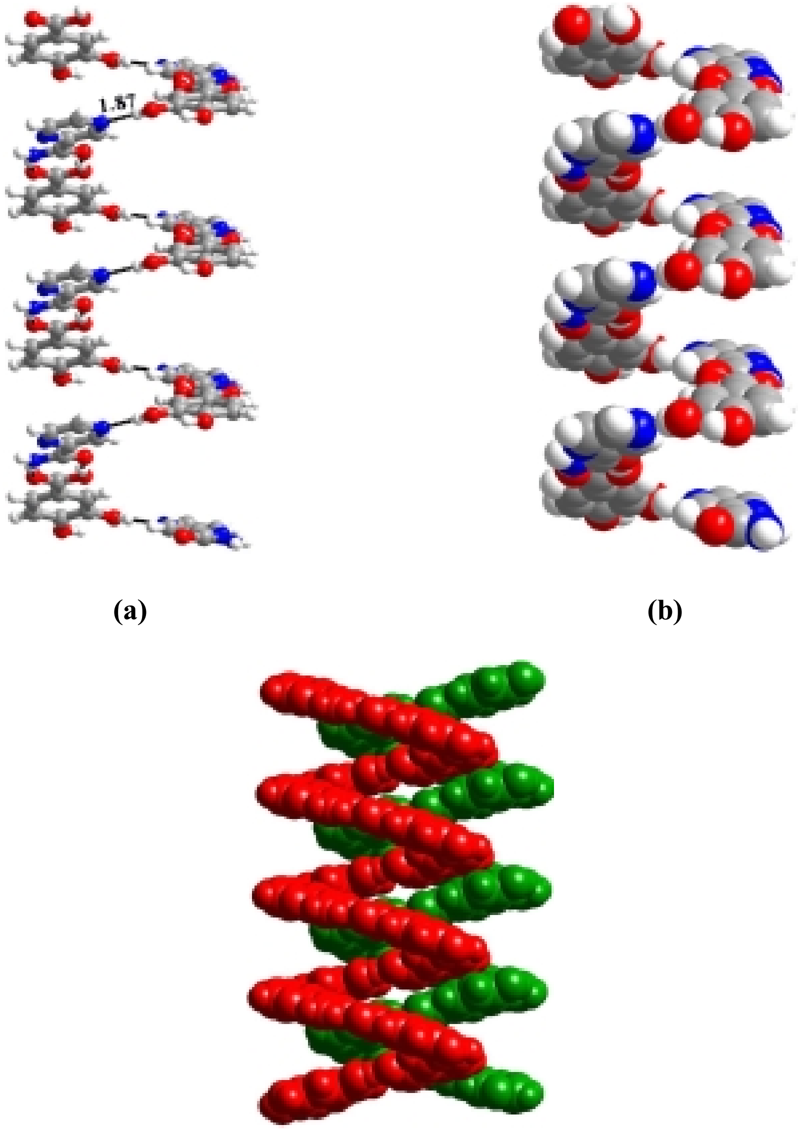
Co-crystallization of **2** and pyrazinamide, from a CH_3OH solution, gave the 1:1 complex **2c**. The ORTEP diagram of the complex **2c** is shown in Figure 15a. The crystal structure analysis reveals that, the three-dimensional packing of the complex **2c**, is quite interesting as an exotic helical structure is realized in the structure of **2c**. Also, as observed in **2a**, no intramolecular hydrogen bond is observed in complex **2c**.



(a) **(b)**

Figure 15. (a) ORTEP diagram of the complex **2c**. (b) The primary interaction between the constituent molecules in the complex **2c**.

Further, the primary recognition between the constituent molecules in the complex **2c** is similar to that of complex **1c**, forming a cyclic hydrogen bonding pattern, between acid and amide functionalities of **2** and pyrazinamide, respectively, as shown in Figure 15b. The H···O distances corresponding to N-H···O and O-H···O hydrogen bonds are 2.06 and 1.61 Å, respectively. Such adjacent supramolecular ensembles are interconnected through a single O-H···N (H···N, 1.87 Å) hydrogen bond, formed between the –OH of **2** and N-atom of the amide, constituting a helix, as shown in Figure 16a. Further, in three-dimensions, such adjacent helices are stacked along the *a*-axis, as shown, in the space-filling mode, in Figure 16c and the two different handed helices are shown in two different colours.



(a) (b)

(c)

Figure 16. (a) The helical structure observed in the complex **2c**, (b) and in space filling mode. (c) Two adjacent helices are stacked in three-dimensions along *a*-axis.

3.2.7 Molecular complex of 2,3-dihydroxybenzoic acid and pyrazinamide, 3c

Complex **3c** was also prepared, by following the same procedures employed for **1c** and **2c**. Good quality, colorless, single crystals, thus, obtained have been used for the crystal structural analysis by X-ray diffraction techniques. The ORTEP diagram of constituents present in the asymmetric unit of complex **3c**, is given in the Figure 17.

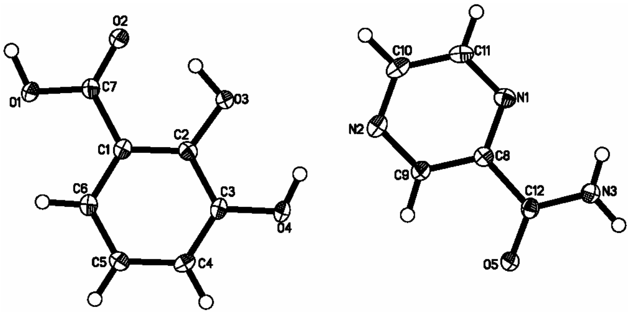


Figure 17. ORTEP diagram of the complex **3c**.

The packing analysis reveals that, in complex **3c**, also, the recognition between the constituent molecules is established through the cyclic N-H···O and O-H···O hydrogen bonds, as observed in the complexes **1c** and **2c**, with the H···O distances being 2.07 and 1.59 Å, respectively, yielding binary units. Such adjacent units are connected through O-H···N hydrogen bonds (H···N, 1.96 Å), formed between the –OH of **2** and N-atom of the amide, leading to the formation of an one-dimensional chain, as shown in Figure 18.

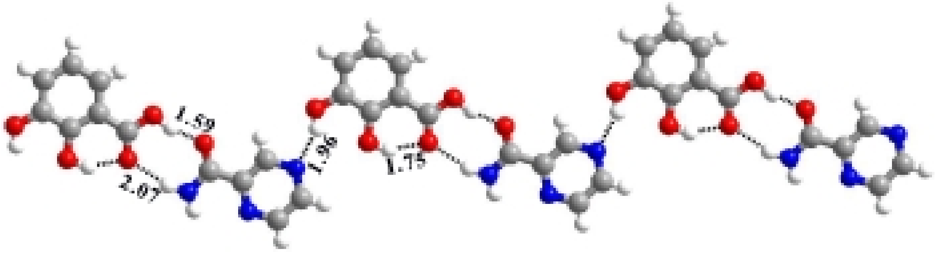
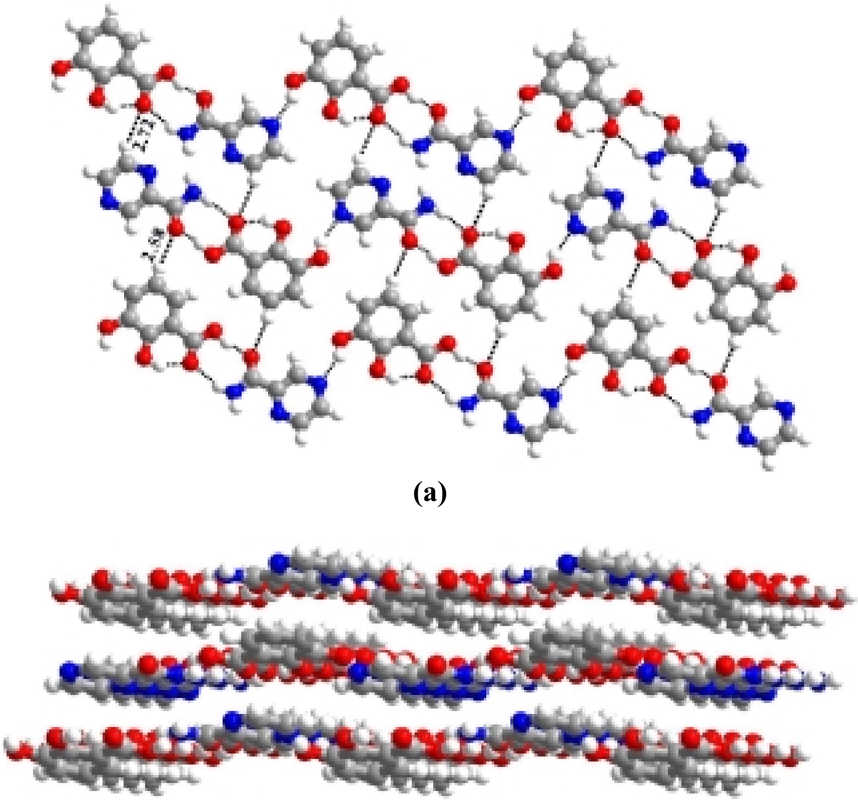


Figure 18. The one-dimensional chain formed by **3** and pyrazinamide in complex **3c**.

Further, these one-dimensional chains, thus, formed, are held together by C-H···O hydrogen bonds (H···O, 2.72 Å), yielding a two-dimensional planar sheet, as shown in Figure 19a, which are, further, stacked in three-dimensions, as shown in Figure 19b, in the crystal structure.



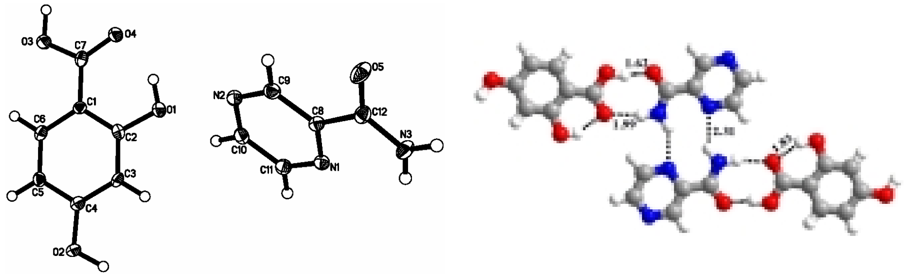
(a)

(b)

Figure 19. (a) A two-dimensional sheets formed by the constituent molecules in complex **3c**. (b) Stacking of two-dimensional sheets in three-dimensions.

3.2.8 Molecular complex of 2,4-dihydroxybenzoic acid and pyrazinamide, 4c

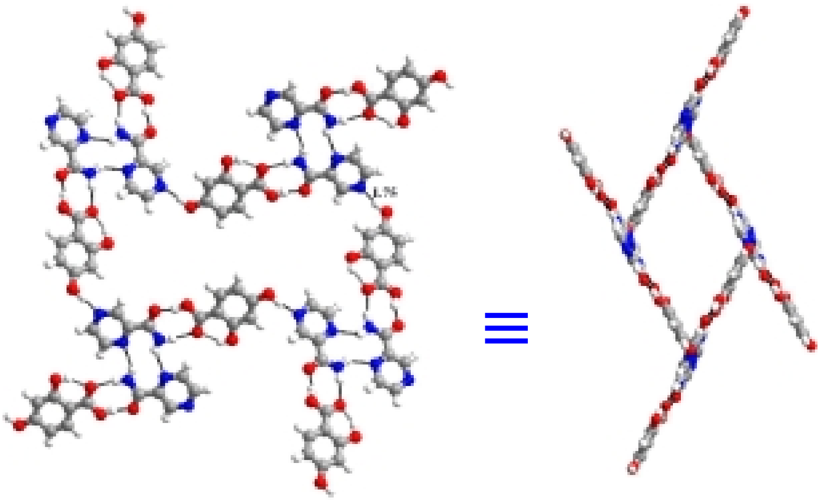
Good quality colorless crystals of complex **4c** of formula unit of $(C_7H_6N_3O_4)(C_6H_5N_2O)$, were prepared, by following the same procedures, employed for the complexes **1c**-**3c**, by co-crystallizing **4** and pyrazinamide, from a CH_3OH solution, by evaporating the solvent, at ambient conditions. The structure elucidation, carried out by X-ray diffraction methods, gave the asymmetric unit, as shown in Figure 20a.



(a) (b)

Figure 20. (a) The ORTEP diagram of the asymmetric unit, in the complex **4c**. (b) The quartet unit formed by the aggregation of dimeric unit of **4** and pyrazinamide.

Like in complex **3c**, one of the –OH group is involved in the intramolecular hydrogen bonding in complex **4c** and the primary recognition pattern, between the constituent molecules, is established by a cyclic N-H···O (H···O, 1.99 Å) and O-H···O (H···O, 1.62 Å) hydrogen bonds, through $R_2^2(8)$ hydrogen bonding pattern, yielding a dimeric unit, as observed in the previous complexes **1c**-**3c**.



(a) (b)

Figure 21. (a) A void space constructed due to the aggregation of the constituents in the crystal lattice of complex **4c**. (b) The void space in a different orientation.

But, the three-dimensional arrangement in the crystal lattice is entirely different than that of complexes **1c**-**3c**. Two adjacent dimeric units, thus, formed are held by a cyclic N-H···N (H···N, 2.31 Å) hydrogen bonds, formed between adjacent pyrazinamide molecules, forming a quartet unit, as shown in Figure 20b. These quartet ensembles are, further, held together by O-H···N hydrogen bonds (H···N, 1.75 Å), formed between –OH of **4** and N-atom of pyrazinamide. Such an association, indeed, created a huge void space (17 x 10 Å^2) in two-dimensions, as shown in Figure 21.

In general, such void structures are quite unstable, unless there is an appropriate guest molecule present, wherein, the void space would be occupied by such guest species. Otherwise, the void space would be effectively being filled by catenation or interpenetration, as well known in the representative example, like trimesic acid. In complex **4c** also, as no appropriate guest species are available, the void spaces, thus, formed do undergo catenation, yielding an exotic two-fold interpenetrated network, as shown in Figure 22. The interpenetrated networks are represented in two different colors, for the better visualizing of the two-fold interpenetrations.

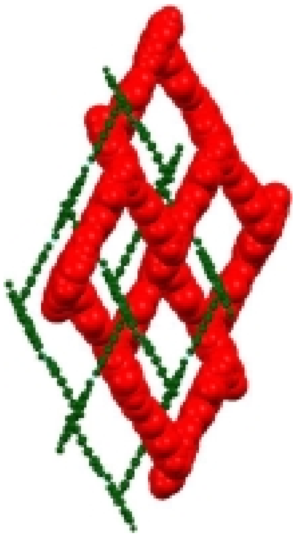


Figure 22. The two-fold interpenetrated structure observed in the crystal lattice of complex **4c**.

Thus, mere changing position of functional group, i.e. different isomers of a compound, has a propensic effect in supramolecular syntheses resulting in structures of varied geometry, as observed from the discussion on the structures of different isomers of dihydroxybenzoic acid with various co-ligands, as illustrated above, in detail, in this chapter.

3.3 Conclusions

In conclusion, it is apparent that, changing the position of –OH functional groups in dihydroxybenzoic acid, which, ultimately, gave several isomers of the acid, resulted in yielding different types of supramolecular assemblies upon co-crystallizing with the complimentary co-ligands. Also, it is evident that the affinity of -COOH and -OH groups towards aza-donor compounds is fairly competitive and this is in a way reflected in the formation of different recognition patterns, which, ultimately, lead to the formation of different type of exotic supramolecular networks, like two-fold interpenetrated network, helices, lamellar sheets, etc. It is interesting to note that, in the complexes **1a** and **1b**, the acid molecules are deprotonated, wherein, the proton is taken by N-atom of the corresponding aza-donor molecule and also in both complexes, the acid molecules undergo intramolecular O-H···O hydrogen bonds, in which, both the –OH groups are hydrogen bonded to $–COO^-$ group.

3.4 Experimental section

3.4.1 Synthesis

All the chemicals, reagents and solvents were obtained from commercial suppliers and used without further purification. Spectroscopic-grade solvents were used in all co-crystallization studies. All co-crystals, **1a**, **2a**, **1b**, **3b** and **1c–4c**, were prepared by dissolving the respective reactants in a ratio of 1:1 in methanol and allowing the solvent to evaporate under ambient conditions. In all the cases, single crystals, suitable for X-ray diffraction analysis, were obtained over the period of 3-5 days.

General procedure for the synthesis of complexes 1a, 2a, 1b, 3b and 1c–4c.

In a typical co-crystallization experiment, 2,6-dihydroxybenzoic acid (0.100 mmol) and the aza-donor ligand (***bpy***, ***pca*** or pyrazinamide) (0.100 mmol), as the case may be, were dissolved in methanol (10 mL) in a 25 mL conical flask, by warming on a water bath for 10 minutes. The resultant clear solution was allowed to evaporate, at ambient conditions and good quality single crystals were obtained over the period of 3-5 days.

3.4.2 Crystal structures determination

Good quality single crystals of **1a**, **2a**, **1b**, **3b** and **1c–4c**, were carefully selected with the aid of a polarized Leica microscope equipped with CCD camera, and glued to a glass fiber using an adhesive (cyanoacrylate). In all the cases, the crystals were smeared in the adhesive solution to prevent decay of crystals upon exposure to X-rays. The intensity data were collected on a Bruker single crystal X-ray diffractometer, equipped with an APEX detector, at room temperature (298 K). Subsequently, the data were processed using Bruker suite of programmes (SAINT)[12] and the convergence was found to be satisfactory with good R_{ini} parameters. The details of the data collection and crystallographic information are given in Table 3.1 and Table 3.2. The structure determination by direct methods and refinements by least-squares methods on F^2 were performed using SHELXTL-PLUS[13] package. The processes were smooth without any complications. All non-hydrogen atoms were refined anisotropically. All the intermolecular interactions were computed using PLATON.[14]

Table 3.1 Crystallographic data of the molecular complexes **1a**, **2b**, **1b** and **3b**.

	1a	**2a**	**1b**	**3b**
Formula	$2(C_7H_5O_4)(C_{12}H_{10}N_2)$	$(C_7H_6O_4)(C_{12}H_8N_2)$	$(C_7H_5O_4)(C_6H_7N_2O)$	$(C_7H_6O_4)(C_6H_6N_2O)$
M	464.42	310.30	276.25	276.25
crystal habit	blocks	blocks	prismatic	planar
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	8.767(3)	8.648(4)	6.976(7)	10.902(1)
b/Å	5.359(2)	13.191(5)	12.561(1)	5.078(5)
c/Å	21.817(7)	13.372(6)	13.426(1)	22.660(2)
α/°	90	72.75(4)	90	90
β/°	92.05(3)	80.97(4)	92.42(8)	96.51(8)
γ/°	90	80.33(3)	90	90
V/Å^3	1024.36(6)	1426.85(1)	1175.4(2)	1246.5(2)
Z	2	4	4	4
D_c/g cm^{-3}	1.506	1.444	1.561	1.472
μ/mm^{-1}	0.115	0.105	0.122	0.115
F(000)	484	648	576	576
λ/Å	0.7107	0.7107	0.7107	0.7107
$\Delta\rho_{min.max}$/e Å^{-3}	0.170/-0.173	0.194/-0.145	0.175/-0.310	0.166/-0.263
total reflections	14608	15115	8820	8881
unique reflections	1808	5014	2064	2185
reflectios used	1588	3983	1669	1718
R1, I > 2σ(I)	0.0281	0.0272	0.0372	0.0414
wR,I > 2σ(I)	0.0828	0.0757	0.0821	0.0937

Table 3.2 Crystallographic data of the molecular complexes **1c-4c**.

	1c	**2c**	**3c**	**4c**
Formula	$(C_7H_6O_4)(C_6H_5N_3O)$	$(C_7H_6O_4)(C_6H_5N_3O)$	$2(C_7H_6O_4).2(C_6H_5N_3O)$	$(C_7H_6O_4)(C_6H_5N_3O)$
M	277.24	277.24	277.24	277.24
crystal habit	planar	planar	blocks	prismatic
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å	10.020(1)	32.322(4)	6.573(1)	7.603(1)
b/Å	5.071(1)	6.847(1)	7.190(1)	6.798(1)
c/Å	23.104(3)	10.973(2)	13.047(2)	23.710(4)
α/°	90	90	105.31 (2)	90
β/°	100.689(10)	98.74(4)	96.34(2)	93.218(2)
γ/°	90	90	93.03(2)	90
V/Å^3	1153.5(2)	2400.3(2)	588.95(2)	1223.6(4)
Z	4	8	2	4
D_c/g cm^{-3}	1.596	1.534	1.563	1.505
μ/mm^{-1}	0.127	0.122	0.124	0.120
2θ range[°]	55.00	50.00	50.00	50.00
F(000)	576	1152	288	576
λ/Å	0.7107	0.7107	0.7107	0.7107
$\Delta\rho_{min.max}$/e Å^{-3}	0.207/-0.310	0.190/-0.356	0.191/-0.174	0.145/-0.210
total reflections	10026	22220	9252	9069
unique reflections	2650	4223	2086	2142
reflectios used	1999	3717	1548	1246
R1, $I > 2\sigma(I)$	0.0355	0.0346	0.0266	0.0306
wR,$I > 2\sigma(I)$	0.0813	0.0908	0.0653	0.0502

Table 3.3 Characteristic hydrogen bond distances (Å) and angles (°) of the molecular complexes, **1a**, **2b**, **1b** and **3b**.[#]

D-H⋯A	1a			2a			1b			3b		
N-H⋯O	*1.37	2.52	177				*1.75	2.78	176	2.02	2.91	161
							2.04	2.94	172	2.18	3.05	157
							2.16	3.01	160			
O-H⋯O	1.59	2.54	156	1.70	2.64	174	1.57	2.47	160	1.67	2.57	156
	1.70	2.54	147	1.75	2.69	179	1.72	2.57	153	2.08	2.80	144
O-H⋯N				1.52	2.56	169				1.55	2.61	177
				1.63	2.64	175						
				1.84	2.66	144						
				1.85	2.73	155						
C-H⋯O	2.40	3.13	132				2.29	2.97	126	2.44	3.29	143
	2.42	3.22	144				2.39	3.28	150			
							2.49	3.38	148			

[#] The three columns for each structure represent H⋯A, D⋯A distances and D-H⋯A angle, respectively for a typical hydrogen bond, being represented as D-H⋯A. The * in the table indicates the N^{+}-H⋯O^{-} interaction.

Table 3.4 Characteristic hydrogen bond distances (Å) and angles (°) of the molecular complexes **1c**–**4c**.$^{\$}$

	1c			**2c**			**3c**			**4c**		
N-H···O	2.03	2.92	161	2.05	2.93	163	2.07	2.98	164	1.99	2.96	170
	2.51	2.95	109	2.06	2.95	165						
	2.72	2.95	95	2.45	3.24	149						
				2.45	3.25	149						
N-H···N										2.31	3.05	142
O-H···O	1.56	2.54	169	1.61	2.59	168	1.59	2.55	168	1.62	2.58	166
	1.68	2.56	148	1.62	2.59	170	1.75	2.63	150	1.83	2.64	149
	1.84	2.61	142	2.00	2.77	144						
				2.10	2.82	139						
O-H···N	2.36	2.96	124	1.87	2.76	165	1.96	2.75	147	1.75	2.75	172
				1.87	2.74	168						
C-H···O	2.46	3.34	150	2.29	3.17	147	2.58	3.45	151	2.34	3.29	163
	2.55	3.34	141	2.30	3.22	154				2.45	3.38	150
				2.56	3.43	149				2.56	3.37	137
C-H···N				2.57	3.47	156						
				2.59	3.43	146						

$^{\$}$The three columns for each structure represent H···A, D···A distances and D-H···A angle, respectively for a typical hydrogen bond, being represented as D-H···A.

3.5 References

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CHAPTER FOUR

NOVEL SUPRAMOLECULAR ASSEMBLIES OF COORDINATION POLYMERS FORMED BY ORGANOPHOSPHOROUS ACIDS WITH TRANSITION METALS AND SOME AZA-DONOR COMPOUNDS

4.1 Introduction

Synthesis and characterization of organic-inorganic hybrid materials,[1,2] often referred as coordination polymers, metal-organic frameworks, etc., are challenging as well as at the forefront in the areas of supramolecular chemistry research.[3] Hybrid materials with organic and inorganic moieties are attractive materials due to their composite properties, which can be tuned to use in many application processes,[4] for example, as sorbents, ion exchangers, catalysts, gas storage materials, etc.[5] In this direction, metal carboxylate-directed hybrid structures with varied architectures and unusual properties are of great value in both academic and industrial aspects, providing avenues for a thorough understanding of the nature of the fundamental aspects such as metal and ligand interaction, parameters that influence the ultimate geometry of the resultant assembly.[6,7] Numerous contributions by several researchers employing various carboxylic acids, in the form of carboxylates, with different metal species are unique not only because of their exotic structural features, but also because of their potential applications for gas sorption, catalysis, chemical separations, etc.[8,9]

In a parallel direction, apart from the metal carboxylates, metal-phosphates have also been well studied, especially to develop channel structures mimicking natural zeolites that are made up of phosphate mediated networks.[10,11] In this regard, fascinating architectures were designed and synthesized using different types of synthetic strategies ranging from simple crystallization to hydrothermal methods.[12] The major interest in these assemblies is also due to the ease of structural transformations under mild conditions.[13] For example, the well known aluminophosphate synthesized and reported by Ozin and co-workers, as early as, in 1998 have been used in recent times for the creation of myriad of supramolecular assemblies by transforming linear chains of corner-sharing metal phosphate units progressively into ladder, layer, and three-dimensional structures through simple varied conditions in the synthetic procedures.[14] Similarly in many tin phosphates, four-rings of the metal phosphate clusters transformed into larger rings and give rise to yield layered and other exotic structures.[15]

Among a wide range of metal-phosphates, the assemblies formed by organophosphates, organophosphonates are of special interest as the evolved structures possess different types of functional moieties that can influence the overall physical and chemical properties of the assemblies.[16]

Rao and co-workers reported the open-framework metal-phosphate structures which were synthesized hydrothermally in the presence of structure directing amines. It was demonstrated that the role of amines and phosphates to yield various metal phosphate structures, is paramount, with the aid of X-ray crystallography technique. Based on the observation of isolation of several amine phosphates as bye products along with metal phosphates, it was also concluded that reactions proceed through the formation of aminophosphates, which subsequently react with metal species. For example, the reaction of 1,3-diaminopropane phosphate with Zn(II) ion, under hydrothermal conditions, gave a zinc phosphate with a ladder structure involving edge-shared four-ring metal phosphate units (see Figure 1), in the presence, or absence, of a structure-directing agent (1,3-diaminopropane).[17]

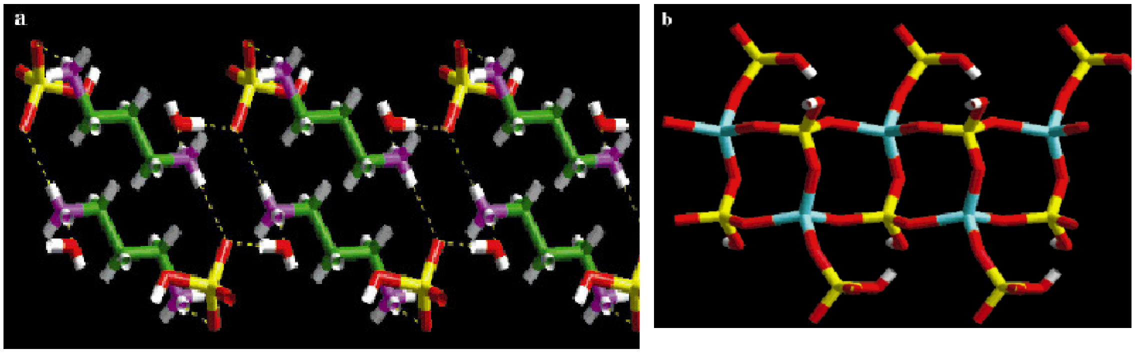
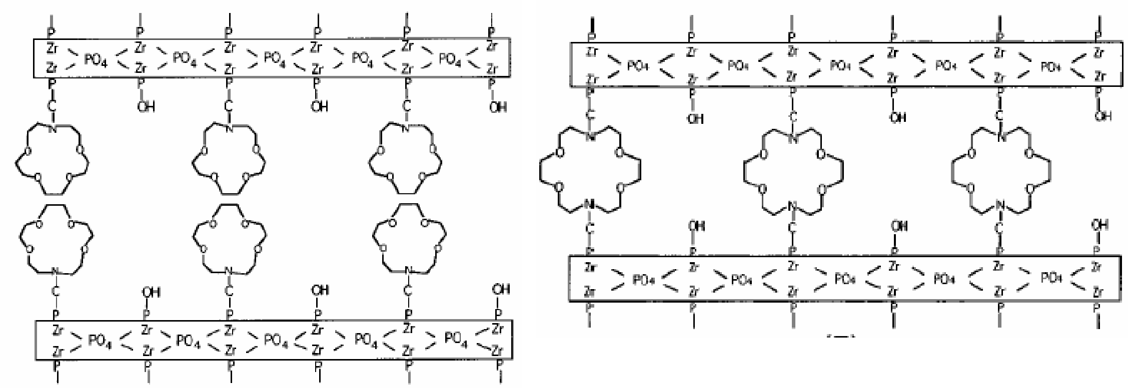


Figure 1. (a) Hydrogen bonded assemblies observed in the structure of diaminopropane phosphate (DAPP) (blue: Zn, yellow: P, red: O, green: C, pink: N, white: H). (b) The one-dimensional zinc phosphate ladder structure.

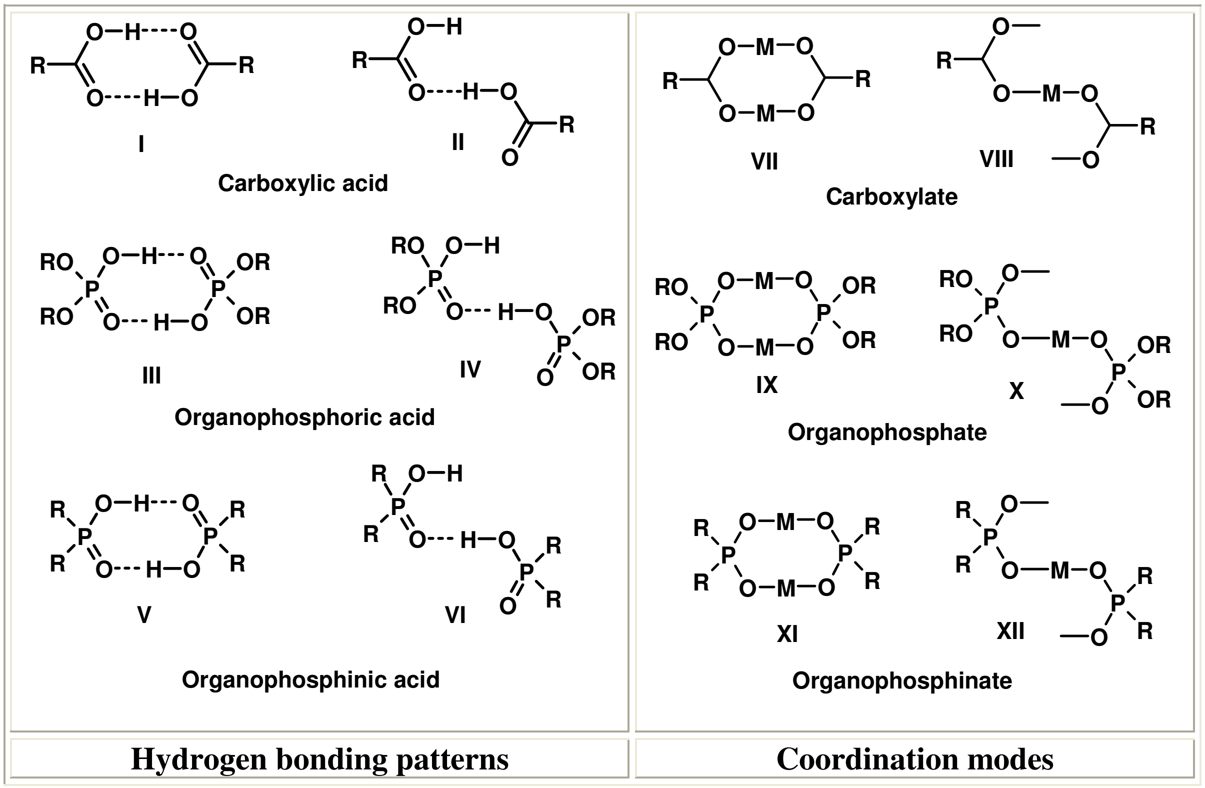
Clearfield and co-workers have extensively studied the structural and chemical properties of the several metal-organophosphonates.[10,18] The following examples, coordination assemblies of two phosphonic acids, N-(phosphonomethy)-aza-15-crown-5 and N-(diphosphonomethy)-aza-15-crown-5 with $ZrOCl_2.8H_2O$, are the representative examples of crown ether pillared R-zirconium phosphonate, in which crown ethers were incorporated onto zirconium phosphonate layers (see Figure 2). The crown ether precursors used here are 1-aza-15-crown-5 and 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane. These two precursors were converted into phosphonic acids by a Mannich type reaction, from which a series of bridged and unbridged zirconium phosphonates were synthesized.[19]



(**a**) (**b**)

Figure 2. Schematic structure of the interlayer arrangement of two zirconium phosphonate complexes synthesized from phosphonomethyl ligand (Figure 2a) and diphosphonomethyl ligand (Figure 2b).

Whatsoever the systems (metal-carboxylates or phosphates), the emphasis is mostly on the properties of metal ions, in particular, the coordination number, by which the geometry of the resultant assembly is often able to be deduced.[1,2,20] However, attention towards the molecular geometry of the organic components, which play a significant role in metal-organic hybrids, are not well explored, probably, because, the geometries of the ligands generally being used in the study like carboxylates, phosphates etc., are more or less rigid. However, if flexible organic ligands, such as, organophosphonic, organophosphinic acids, etc., are used, it is possible to obtain a variety of supramolecular assemblies with varied geometrical features. In fact, even in the structural arrangement, the organophosphorous acids would be as reliable as carboxylic acid with the formation of similar hydrogen bonding networks as described in Scheme 1.



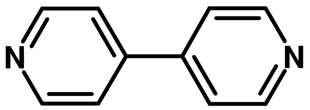
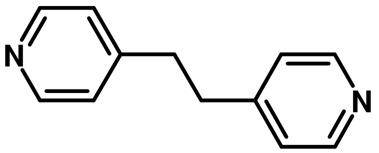
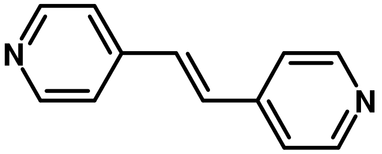
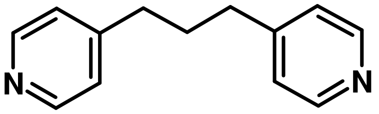
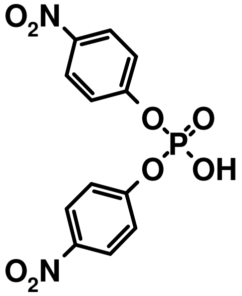
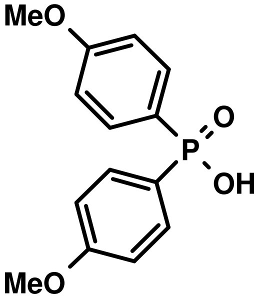
Scheme 1. Some of the observed recognition patterns in carboxylic acid, phosphoric and phosphinic acids.

In addition, it is apparent that, due to the large amount of possible special arrangements of the substituted ligands in phosphorous acids, the resulted assemblies may have exotic structural features.[21] Thus, a combination of these moieties with metal ions would be very interesting, as the ultimate geometry could be tuned through the interactions involving organic functional groups, along with metal coordination geometry. Hence, attempts have been made to explore the creation of supramolecular assemblies of bis(4-nitrophenyl)phosphoric acid, **1**, and bis(4-methoxyphenyl)-phosphinic acid, **2**, (Chart II) with various transition metals and aza-donor compounds, as discussed in the following sections.

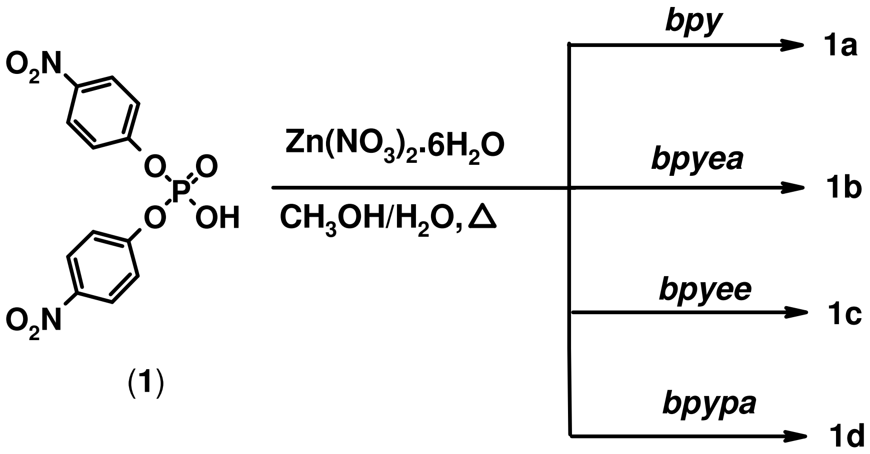
4. 2 Coordination polymers of Zn(II) and bis(4-nitrophenyl)-phosphoric acid with some aza-donor compounds

Co-crystallization of bis(4-nitrophenyl)phosphoric acid, **1**, with Zn(II) in the presence of aza-donor compounds, ***bpy***, ***bpyea***, ***bpyee*** and ***bpypa***, (Chart I), gave well grown single crystals of complexes, **1a**, **1b**, **1c** and **1d**, as illustrated in Scheme 2. The complexes were characterized by elemental analysis, FT-IR and single crystal X-ray diffraction methods. Elucidation of three-dimensional structures revealed several exotic structural features of these complexes.

Chart 1

	
4,4'-bipyridine (***bpy***)	1,2-bis(4-pyridy)ethane (***bpyea***)
	
1,2-bis(4-pyridyl)ethene (***bpyee***)	1,3-bis(4-pyridyl)propane(***bpypa***)
	
Bis(4-nitrophenyl)phosphoric acid, **1**.	Bis(4-methoxyphenyl)phosphinic acid, **2**.

Scheme 2



4.2.1 Infrared Spectroscopy Study

IR spectra of all the complexes are given in Figure 12. The IR spectrum of pure **1** has very broad bands centred around at 2860 and 2360 cm^{-1}. Based on the reported data for the diphosphoric acids, the bands can be attributed for the PO-H and P-O streching vibrations.[22] Absence of such peaks in the complexes and appearance of a sharp peak at 1020 cm^{-1} represents the P-O stretching corresponding to metal phosphates. Both the sharp peaks at 1102 and 1232 cm^{-1} can be accounted for the P=O stretching of phosphate groups of the metal complexes. Two strong absorptions at 1348, 1379 and one at 1510 cm^{-1} are due to the symmetrical and asymmetrical NO_2 stretching frequencies respectively.

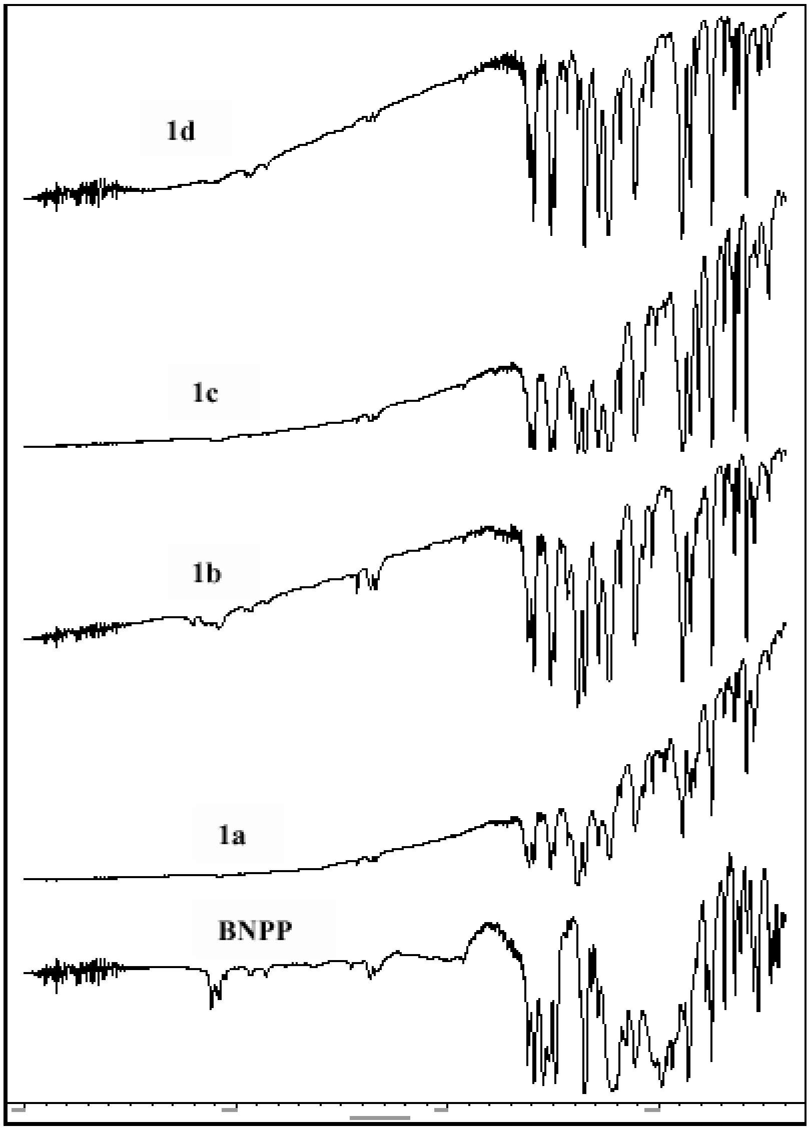


Figure 12. IR spectra of the complexes **1a–1d**.

4.2.2 Coordination complex Zn[($C_{12}H_8N_2O_8P_1$)$_2$.($C_{10}H_{10}N_2$)], 1a

Co-crystallization of phosphoric acid, **1**, with Zn(NO_3)$_2$.6H_2O, in the presence of ***bpy***, from a mixture of CH_3OH and H_2O, yielded good quality colorless crystals of coordination complex **1a**, by slow evaporation of the solvent, over a period of four days, at ambient conditions. The molecular composition in **1a** is confirmed by X-ray diffraction technique as Zn[$(C_{12}H_8N_2O_8P_1)_2.C_{10}H_{10}N_2$]. Full crystallographic details are given in Table 4.1. The asymmetric unit of the complex **1a** is shown in Figure 3, as ORTEP diagram.

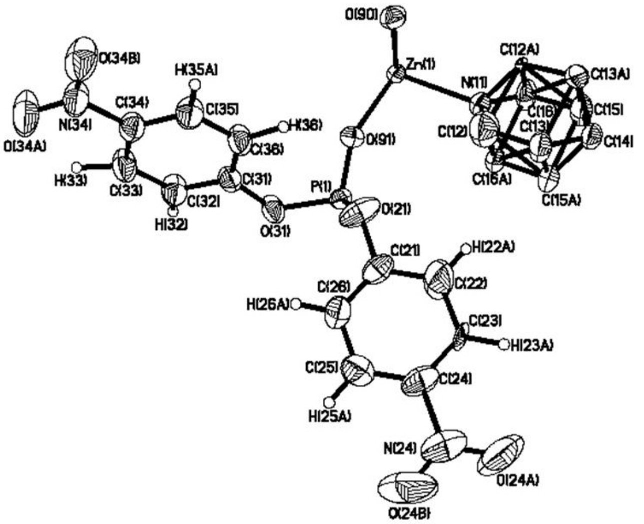


Figure 3. ORTEP diagram of the complex **1a**, which also shows the coordination environment of Zn(II) in the complex.

The structural analysis of complex **1a**, reveals that the ***bpy*** molecules are disordered in two different orientations, in a 50:50 ratio, and both orientations are shown in Figure 3. Further, bonding analysis reveals that, each Zn(II) forms coordination bonds with four molecules of **1** through one of the O-atoms of the phosphate moiety by forming, monodentate Zn-O bonds. The Zn-O bonds observed are in the range of 2.04 and 2.12 Å. Such ensemble of Zn-phosphate units are connected through the disordered ***bpy*** molecules, by Zn-N dative bonds, formed between Zn(II) and ***bpy***, with distance being 2.21 Å. Thus, each Zn(II) form hexa coordinated assembly, yielding one-dimensional polymer. In each one-dimensional polymer, the nitrophenoxy moieties on the adjacent Zn(II) species interact with each other, encompassing ***bpy*** molecules, because of the spatial arrangement of the nitrophenoxy groups around the P-atom in **1**.

In two dimensions, the coordination polymer chains are arranged such that, the adjacent nitrophenoxy moieties from the adjacent chains interact through C-H$^{\cdot\cdot}$O hydrogen bonds,[22] formed between aromatic H-atoms and O-atoms on NO_2 groups (see Figure 4). The H$^{\cdot\cdot}$O distances lie in the range of 2.4-2.8 Å (see Table 4.4). In three-dimensional arrangement, the layers are stacked and held together through Zn-O coordination bonds, formed by the remaining O-atoms on each phosphate group.

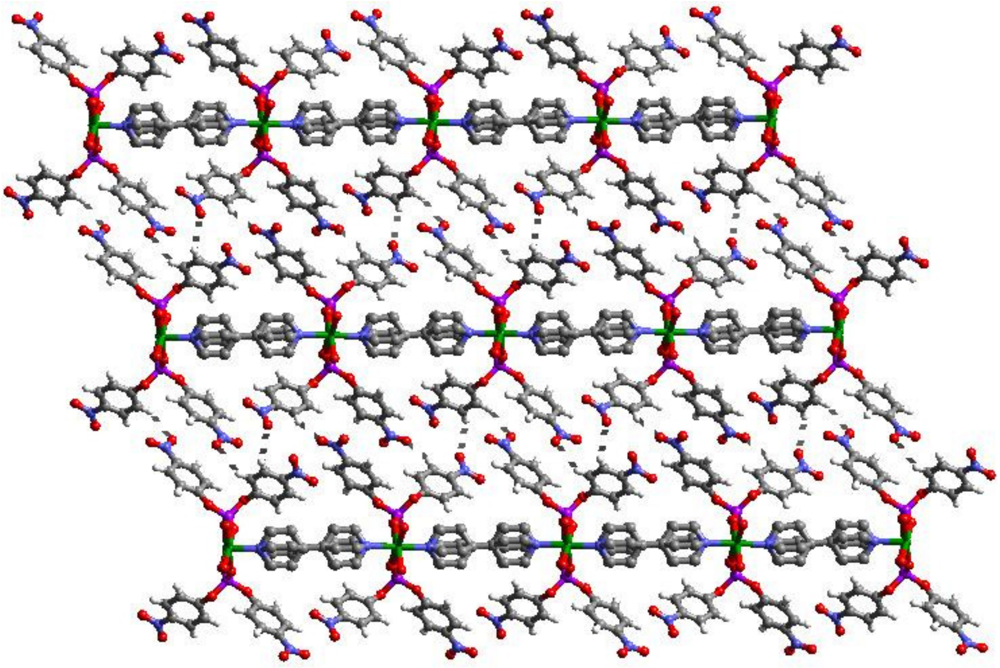


Figure 4. The one-dimensional coordination polymer chains of complex **1a** are interconnected through C-H$^{\cdot\cdot}$O hydrogen bonds. Notice the encompassing of ***bpy*** molecules by nitorphenoxy moieties of molecules of **1**.

4.2.3 Coordination complex Zn[($C_{12}H_8N_2O_8P_1$)$_2$.($C_{12}H_{12}N_2$)], 1b

Complex **1b** of formula unit of Zn[($C_{12}H_8N_2O_8P_1$)$_2$.$C_{12}H_{12}N_2$] was prepared by dissolving **1** and $Zn(NO_3)_2.6H_2O$ with ***bpyea***, in a mixture of CH_3OH and H_2O, and allowing for slow evaporation of the solvent. The ORTEP diagram, in Figure 5, shows the chemical constituents present and the coordination environment of Zn(II) in the complex **1b**. The structural analysis reveals that in the structure of **1b**, unlike in **1a**, the pyridine moieties of ***bpyea*** ligands are static but the methylene bridge is disordered in a 50:50 ratio. However, the coordination environment around each metal center is similar between **1a** and **1b**, with four molecules of **1** and two molecules of ***bpyea*** forming Zn-O and Zn-N dative bonds, respectively, with Zn(II). But, the structural arrangement of nitrophenoxy moieties within polymer chains is somewhat different (see Figure 6), between **1a** and **1b**, mainly due to the difference in the dihedral angle between the nitrophenoxy groups on **1**, in **1a** and **1b**.

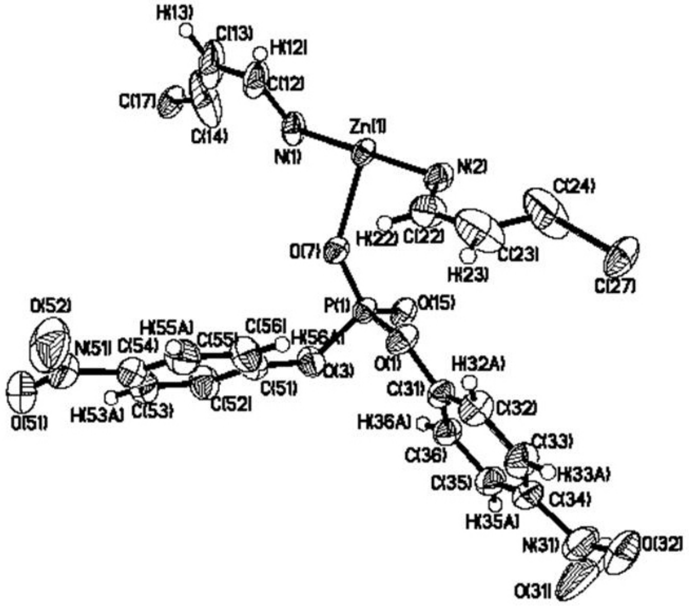
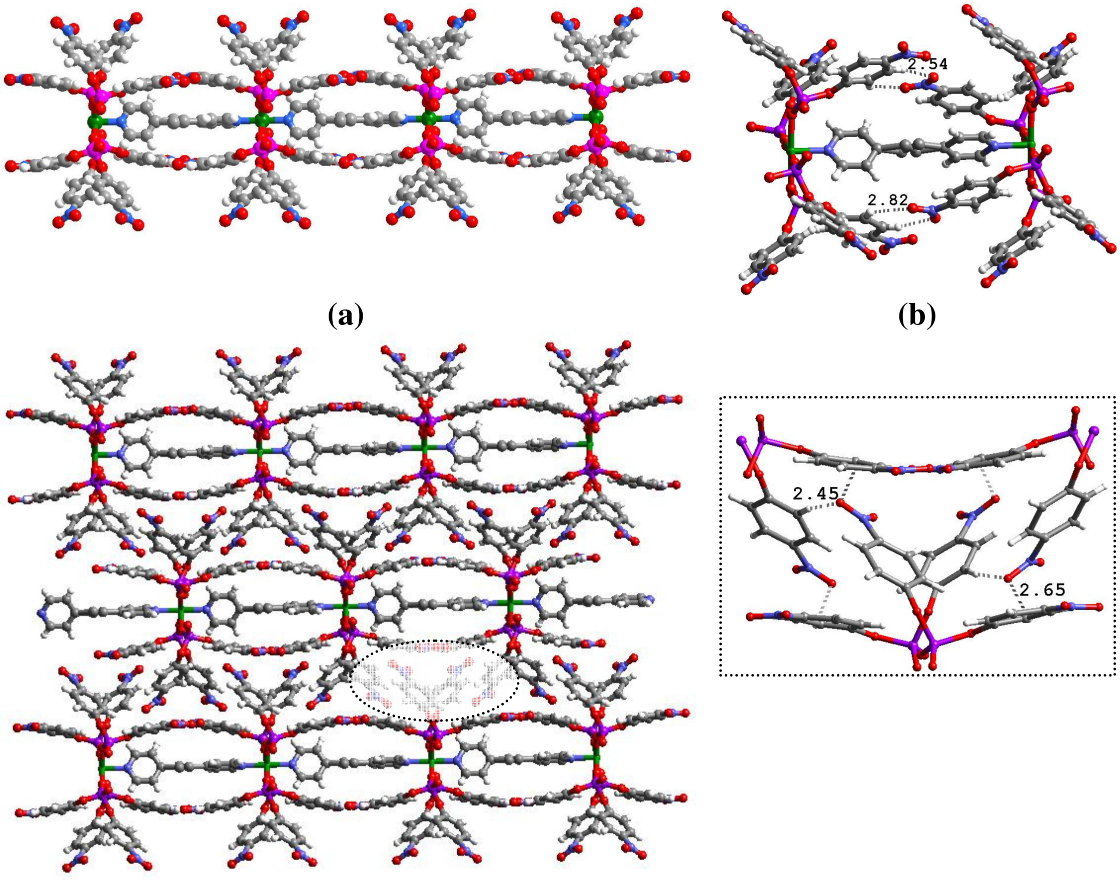


Figure 5. ORTEP diagram shows the chemical constituents present in the complex **1b** and the coordination environment of Zn(II).

Thus, in **1b**, nitrophenoxy moieties within one-dimensional coordination polymer chains are interconnected by C-H···O hydrogen bonds (H···O, 2.54 and 2.82 Å), as depicted in Figure 6b, thus, by captivating the ***bpyea*** ligands that are coordinated to the Zn(II) ions, as shown in Figure 6a.



(a) (b)

(c)

Figure 6. (a) One-dimensional coordination polymer chain, formed due the coordination of **1** with Zn(II) ions and ***bpyea*** ligands, and (b) the interactions between nitrophenoxy moieties of **1** in the one-dimensional polymer. (c) Two dimensional view of the self-assembled coordination polymers of complex **1b**. It is worth to notice that ***bpyea*** ligands are covered by the nitrophenoxy moieties of **1** in the crystal lattice, and the inset shows the interactions between adjacent coordination polymers chains.

Further, such adjacent polymer chains are held together by C-H···O hydrogen bonds (H···O, 2.45 and 2.65 Å), leading to the formation of two-dimensional layered structure (see Figure 6c). In three-dimensional arrangement, the stacking of layers is also quite similar to that was observed in **1a** with the adjacent layers being connected through Zn-O coordination bonds.

4.2.4 Coordination complex $Zn[(C_{12}H_8N_2O_8P_1)_2.(C_{12}H_{10}N_2)]$, 1c

The good quality colorless crystals of complex **1c** of formula unit of $Zn[(C_{12}H_8N_2O_8P_1)_2.(C_{12}H_{10}N_2)]$ were also prepared by following the same procedures employed for **1a** and **1b**, by co-crystallizing **1** and $Zn(NO_3)_2.6H_2O$ with ***bpyee***, from a mixture of CH_3OH and H_2O, by slow evaporation of the solvent, at ambient conditions. The structure elucidation, carried out by X-ray diffraction methods, gave the asymmetric unit shown in Figure 7. The structural analysis of **1c** reveals that the situation is exactly identical to that of **1b**, including a disordered pattern of the aza-donor compound, ***bpyee***, except that for the distances of C-H···O hydrogen bonds.

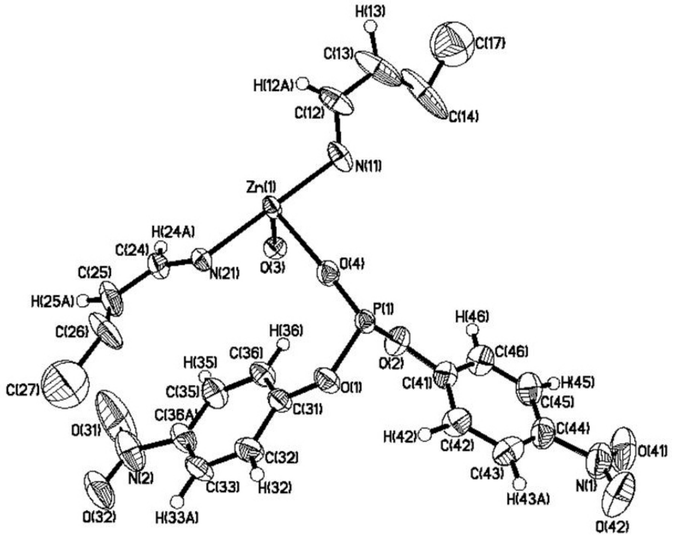


Figure 7. ORTEP diagram of the complex **1c** that shows the coordination environment of Zn(II) ion.

Thus, complex **1c** also form one-dimensional coordination polymer chain, in which the nitophenoxy moieties are interconnected by C-H···O hydrogen bonds (H···O, 2.50 and 2.71 Å), with adjacent polymer chains being held together by C-H···O (H···O, 2.51 and 2.92 Å) hydrogen bonds, similarly as observed in **1b**, yielding two-dimensional layered structure, as shown in Figure 8.

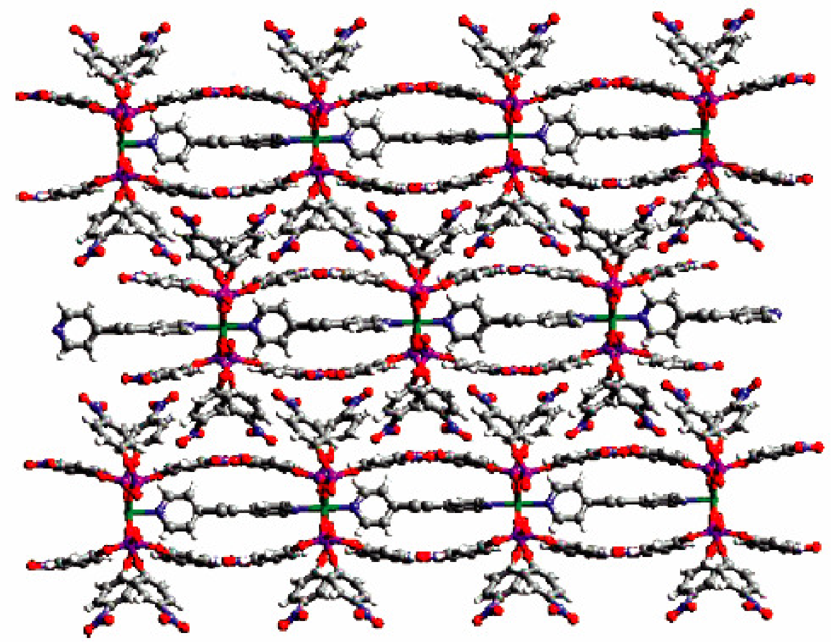


Figure 8. Two-dimensional layered structure of complex **1c** that shows the interaction of **1**, ***bpyee***, and Zn(II) in the crystal structure. Compare this with Figure 6c to appreciate the similarity between **1b** and **1c**.

4.2.5 Complex $Zn_2[(C_{12}H_8N_2O_8P_1)_4.(C_{13}H_{14}N_2)_2]$, 1d

Reaction of **1** with $Zn(NO_3)_2.6H_2O$, in the presence of ***bpypa***, in a solvent mixture of CH_3OH and H_2O, yielded good quality colorless crystals of coordination complex **1d** with the formula unit of $Zn_2[(C_{12}H_8N_2O_8P_1)_4.(C_{13}H_{14}N_2)]$ as confirmed by X-ray diffraction technique. ORTEP drawing of contents of asymmetric unit is shown in Figure 9. The structural analysis reveals that the coordination geometry around the metal ion, Zn(II), is the same as that found in **1a-1c** forming one-dimensional coordination polymers with ***bpypa*** molecules surrounded by nitrophenoxy moieties.

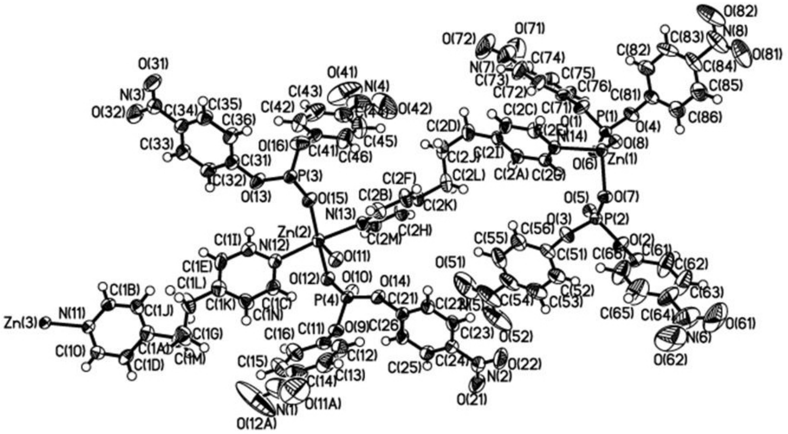


Figure 9. ORTEP diagram of the complex **1d** shows the coordination environment of Zn(II) ion.

However, in contrast to **1a-1c**, nitrophenoxy moieties within the coordination polymer chains that are surrounding the ***bpypa*** did not form intermolecular interactions, which could be attributed to the length of the alkyl chain (propane group) of ***bpypa*** ligand. However, the adjacent coordination polymers are held together by C-H···O hydrogen bonds, the typical H···O distance is 2.47 Å (refer Table 4.4), leading to the formation of a two-dimensional layered structure, as shown in Figure 10.

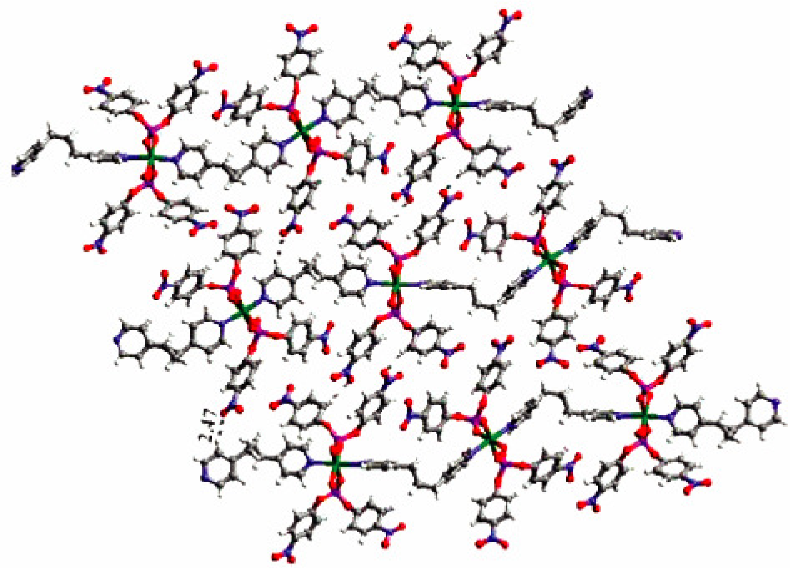


Figure10. Two-dimensional projection of molecules of **1**, ***bpypa***, and Zn(II) in the crystal structure of **1d**. Notice the adjacent coordination polymer chains are being connected by C-H···O hydrogen bonds.

4.2.6 Correlations of structures, 1a-1d

In all the complexes **1a**-**1d**, the composition of the constituents are in a 2:1:1 ratio of **1**, Zn(II) and the respective aza-donor compound (***bpy***, ***bpyea***, ***bpyee*** and ***bpypa***, as the case may be), as confirmed by the single crystal X-ray diffraction technique.

In the crystal structures, each Zn(II) ion is coordinated to four molecules of **1** and two molecules of the corresponding aza-donor compound. Typical coordination geometry is shown in Figure 11, for complex **1a**. Each molecule of **1** forms bismonodentate Zn-O coordinate bonds bridging two adjacent Zn(II). The complete details of the dative bonds are given in Table 4.3.

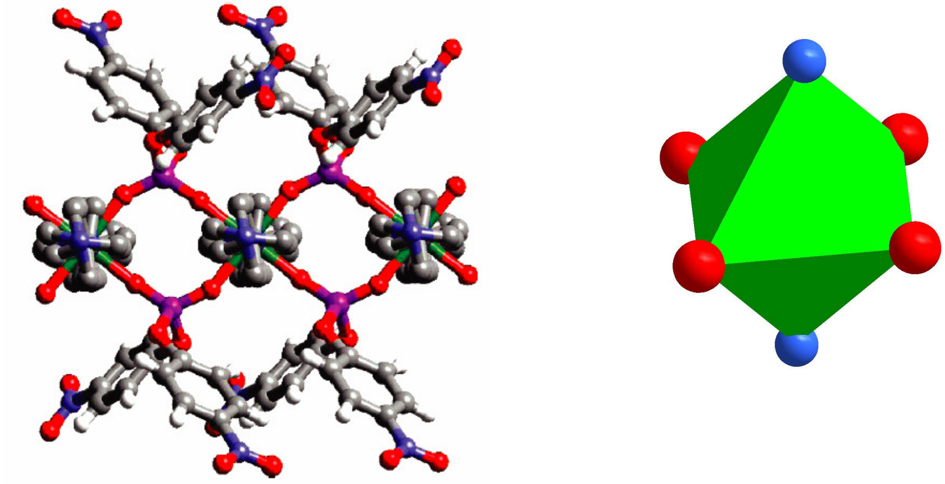


Figure 11. (a) Coordination geometry around each Zn(II). The moieties in perpendicular to the molecules of **1** are ***bpy*** molecules, connected to Zn(II). (b) A typical coordination environment of Zn(II) in the complexes **1a**-**1d**, where Zn(II) is shown in polyhedron, which is coordinated to four oxygen (in red) of **1** and two nitrogen (in blue) of aza-donor compounds

.

Thus, the molecules of **1** occupy the equatorial coordination sites of Zn(II). The aza-donor compounds, ***bpy***, ***bpyea***, ***bpyee*** and ***bpypa***, form Zn-N coordination bonds in an axial direction, completing the hexa coordination geometry around each Zn(II). In one-dimensional arrangement, these coordination units are held together yielding polymer chains due to the formation of Zn-N dative bonds through the second hetero N atom on the aza-donor compounds.

All the complexes are quite similar in their three-dimensional arrangement irrespective of the varied dimensions of the aza-donor compounds. Thus, the exotic features obtained in **1a**-**1d** directed towards further exploration of many such assemblies with various other organophosphorous acids to obtain novel networks due to the flexible geometry of the organic ligands. Thus, the supramolecular synthesis of coordination polymers of organophosphinic acid with transition metals was carried out to develop novel networks. The exotic structural features of the complexes that are obtained during the investigation would be discussed in the section 4.3.

4.3 Supramolecular assemblies of coordination polymers of Co(II), Mn(II) and bis(4-methoxyphenyl)phosphinic acid with some aza-donor compounds

Organophosphinic acids are also the class of compounds that can mimic carboxylic acids, in terms of hydrogen bonding patterns, as well as, in the mode of coordination to the metal ion, in the similar way, as discussed earlier, for organophosphoric acid (see Scheme 1). Hence, these compounds are also potential candidates for the construction of variety of novel metal-organic complexes with exotic networks. In this connection, bis(4-methoxyphenyl)phosphinic acid, **2**, (Chart

II) was chosen for the synthesis of numerous coordination complexes by co-crystallizing with different metal species along with other appropriate ligands. The salient features of these complexes would be discussed in following sections.

In general, native structure of the ligand under consideration provides enough information to design the strategies for the creation of novel supramolecular assemblies. Since the structure of phosphinic acid, **2**, is not known in the literature, based on the CSD[23] analysis, endeavors of preparation of supramolecular assemblies of **2** has been initiated with the structure determination of **2**. For this purpose, the compound **2** was crystallized from CH_3OH and the good quality colorless crystals, which were obtained over the period of three-days, have been chosen for the structural characterization by single crystal X-ray diffraction method. The ORTEP diagram, in Figure 14, shows the molecule present in the asymmetric unit.

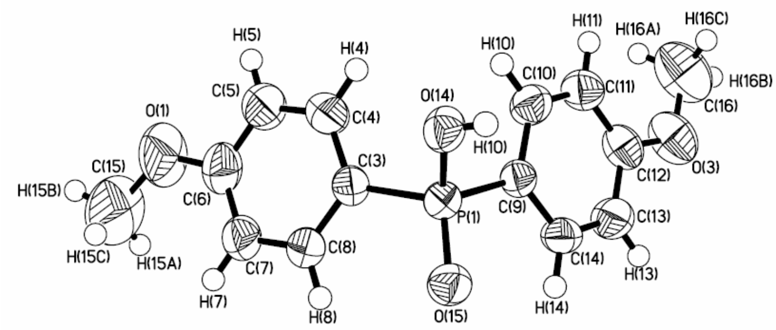


Figure 14. ORTEP diagram of crystal structure of **2**.

The structural analysis reveals that, the arrangement of molecules of **2** in crystal lattice is quite intriguing. Six molecules of **2** are connected to each through C-H···O (H···O, 2.71 Å) hydrogen bonds, formed between one of phenyl moieties and phosphate oxygen, to yield a hexameric network, as shown in Figure 15. Such an arrangement indeed provided an environment such that, the conformation of second phenyl moieties on these molecules are arranged, constituting another hexagonal network realized through C-H$\cdots\pi$ (3.12 Å) interactions. Thus, the combination of C-H$\cdots$O and C-H$\cdots\pi$ bonds formed by phenyl moieties attributed a novel and exotic double-walled hexameric network. It is, further, interesting to note that the network is completely stabilized by weak hydrogen bonds[24] rather than by strong hydrogen bonding patterns, despite the presence of strong phosphinic acid moieties, which is capable of forming strong hydrogen bonds.

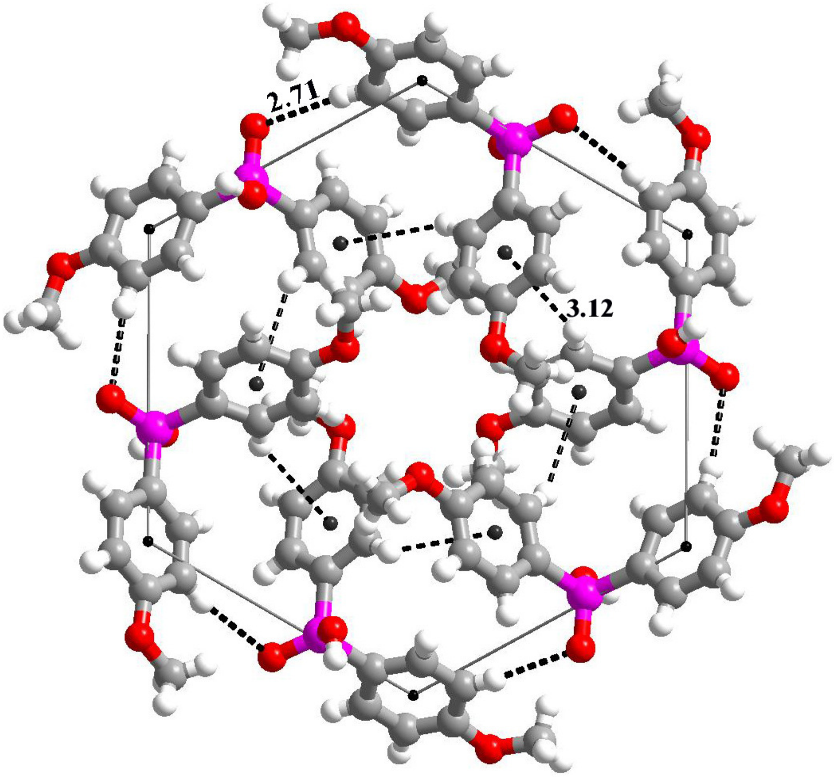
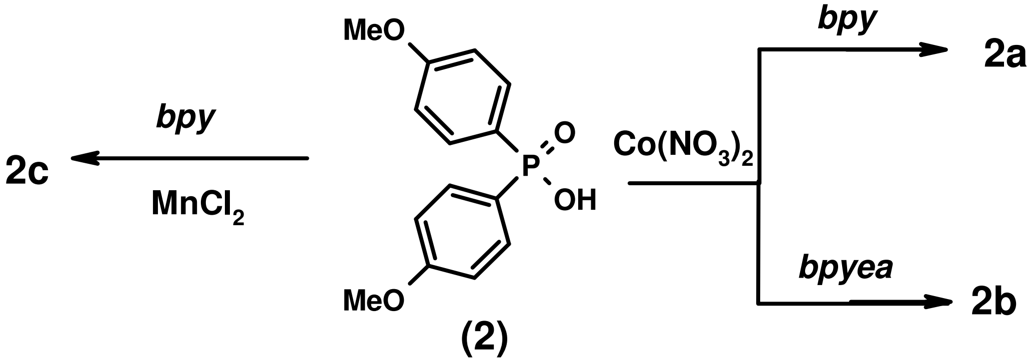


Figure 15. Hexameric aggregation of molecules of **2**. Notice the hexameric network is being completely stabilized by weak interactions such as, C-H$\cdots$O and C-H$\cdots\pi$ interactions.

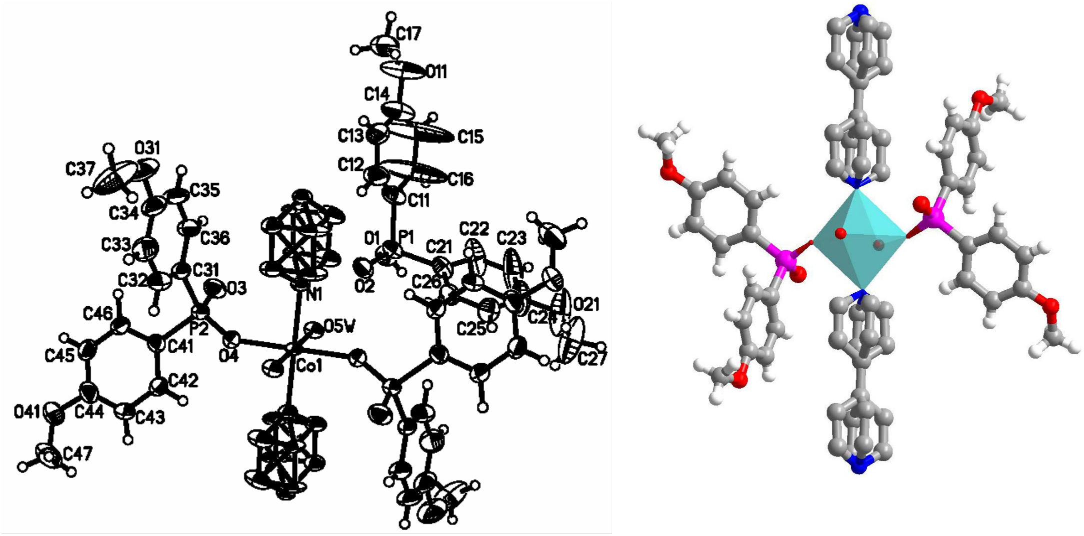
In fact, such a network created void space of 6Å, and also it is quite interesting to note that, the voids are enriched with oxygen atoms of methoxy groups. The structures of this type are of great interest to use as gas-sorption materials, if the void space is tuned further. To evaluate such features, phosphinic acid, **2**, has been co-crystallized with many transition metals and aza-donor compounds. The complexes, thus, obtained have been illustrated in Scheme 3.

Scheme 3



4.3.1 Coordination complex $Co[(C_{14}H_{14}O_4P)_2.(C_{10}H_8N_2)_2.2H_2O](C_{14}H_{15}O_4P)$, 2a

Co-crystallization of **2** with cobalt nitrate hexahydrate, $Co(NO_3)_2.6H_2O$, in the presence of ***bpy***, from a mixture of CH_3OH and H_2O by slow evaporation, over a period of four days, yielded pink crystals of coordination complex **2a**, with the formula unit of $Co[(C_{14}H_{14}O_4P)_2.(C_{10}H_8N_2).2H_2O](C_{14}H_{15}O_4P)$, as confirmed by X-ray diffraction technique. The details of crystallographic data are given in Table 4.2. Thus, one uncoordinated molecules of **2** also present in the asymmetric unit of **2a** (see the ORTEP diagram in Figure 16a). Further, ***bpy*** molecules are disordered and the two orientations are found to be in 50:50. Each Co(II) ion is coordinated to two molecules of each of **2**, ***bpy*** and water molecules, fulfilling the required hexa coordination around the metal ions (see Figure 16b). All the ligands (***bpy***, **2** and water) are coordinated to Co(II) through monodentate dative bonds. The characteristic coordination bonds, Co-N and Co-O, are given in Table 4.5.



(**a**) (**b**)

Figure 16. (a) ORTEP diagram asymmetric unit that shows molecules present in the complex **2a**. (b) A small unit of the coordination polymer showing the coordination environment of the Co(II) metal ion.

Such coordination spheres constituted two-dimensional layer structure in the crystal lattice, as shown in Figure 17. It is interesting to note that in each layer, the phosphinic moieties coordinated to Co(II) are arranged as sandwiched between the coordination chains of Co(II) and ***bpy***. Further, the phosphinic acid moieties interact each other through cyclic C-H···O hydrogen bonds (H···O, 2.70 Å), as well as, single C-H···O hydrogen bonds (H···O, 2.48 Å) and C-H···π interactions (H···π, 2.96 Å). The typical hydrogen bonding patterns are shown in the inset in Figure 17. Characteristic hydrogen bond distances are given in Table 4.6

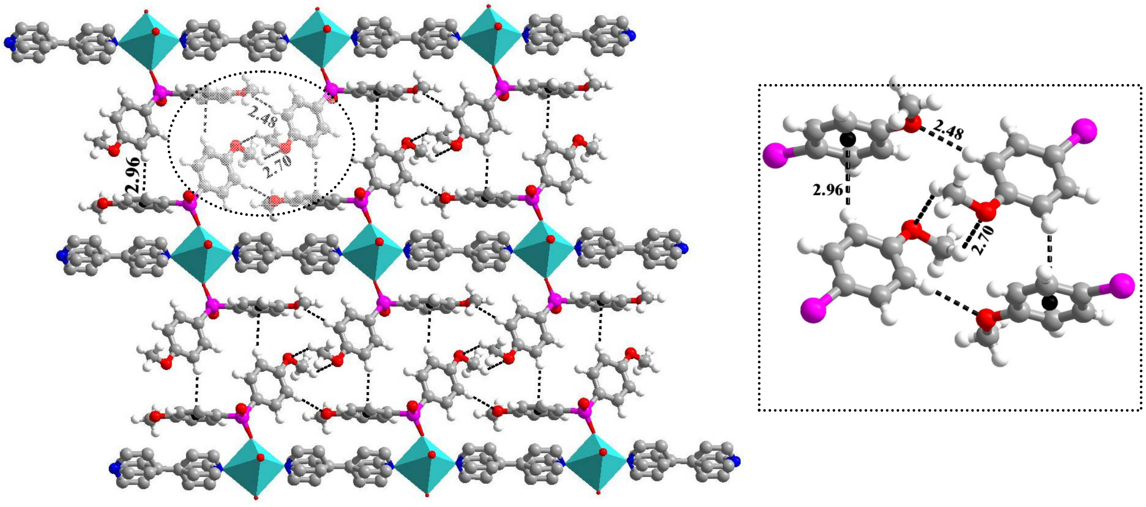
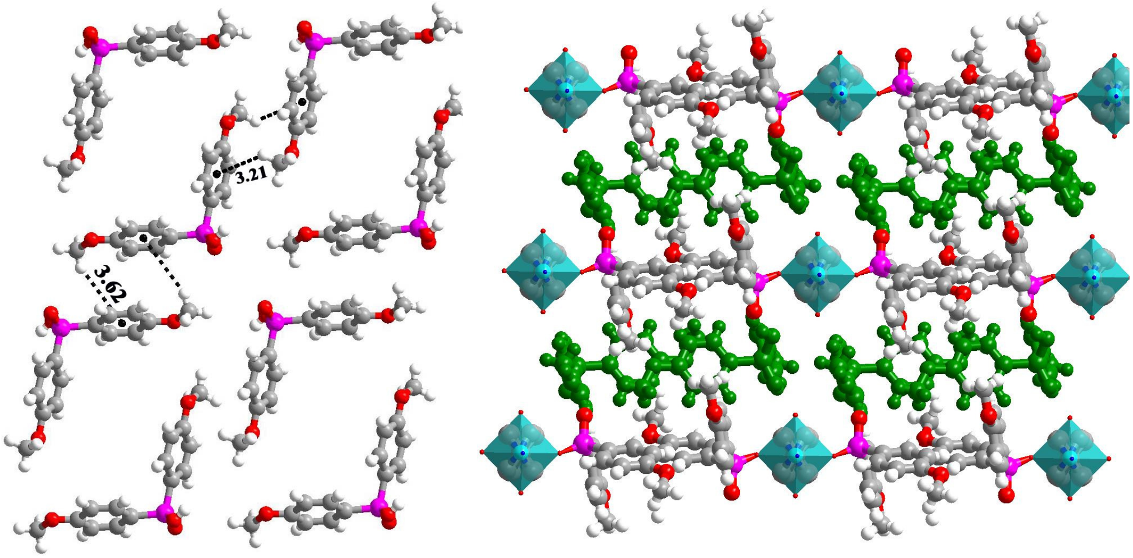


Figure 17. Coordination polymer sheet formed due to the weak interaction formed between one-dimensional coordination polymer chains. The inset shows the interactions between adjacent coordination polymer chains.

These two-dimensional layers are arranged in three-dimensions being separated by a layer of uncoordinated phosphinic acid, **2** (see Figure 18b). Within the layers of organic layer, the molecules of **2** constitute a sheet structure completely stabilized by C-H$^{\cdots}\pi$ interactions (H$^{\cdots}\pi$, 3.21 and 3.62 Å), as shown in Figure 18a. Further, the organic layers established the interactions with the metal-organic layers by forming O-H$^{\cdots}$O hydrogen bond (H$^{\cdots}$O, 1.67 Å) with uncoordinated oxygen atom available on phosphinate of the coordination polymer layers, as well as, with the water molecules that are coordinated to Co(II). Thus, the weak noncovalent interactions, being formed by the phosphinic acid, **2**, are still largely directing the overall structural features even in the metal-organic assemblies.



(**a**) (**b**)

Figure 18. (a) A planar sheet arrangement formed by uncoordinated molecules of **2** that are inserted between the coordination polymer sheets. (b) A three-dimensional sandwich structure, viewed along *b*-axis, formed due to stacking between coordination polymer sheets and layers of uncoordinated molecules of **2** (shown in green).

4.3.2 Coordination complex Co[($C_{14}H_{14}O_4P$).($C_{12}H_{12}N_2$).NO_3], 2b

Complex **2b** was prepared by mixing the CH_3OH solution of **2** and ***bpyea*** with the aqueous solution of $Co(NO_3)_2.6H_2O$, by evaporating the resultant solution, at ambient conditions. The structure of complex **2b** was established by single crystal X-ray diffraction techniques and the complete crystallographic details are given in Table 4.2. The molecular formula of the complex was found to be Co[($C_{14}H_{14}O_4P$)-.($C_{12}H_{12}N_2$).NO_3], which shows the presence of a nitrate anion in the asymmetric unit, along with 1:1 ratio of **2** and ***bpyea*** molecules, as shown in the ORTEP diagram, in Figure 19. In complex **2b**, the hexacoordination of each Co(II) ion is completed by two molecules of **2** and ***bpyea*** each, and one nitrate anion (see Figure 20).

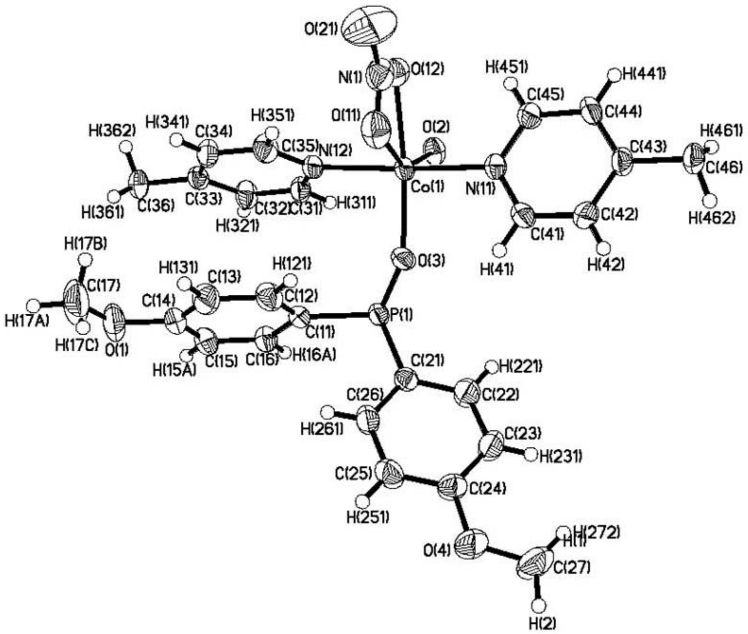


Figure 19. ORTEP diagram of the complex **2b** shows the coordination environment of Co(II) ion.

In each coordination unit, the ***bpy*** and phosphinic moieties formed monodentae dative bonds with Co(II), while nitrate anion is coordinated through bidentated mode. The resultant Co-N, Co-O dative bonds are listed in Table 4.5. In contrast to the features observed in **2a**, the second oxygen atom on **2** is, further, coordinated to Co(II), yielding bridging bimetallic coordination environment. Further, such coordination ensembles gave one-dimensional coordination polymer chains (see Figure 20), with adjacent chains being held together by C-H···O (H···O, 2.67Å) hydrogen bonds formed by C-H of aromatic group of **2** and oxygen atom of nitrate anion, as described in Figure 20.

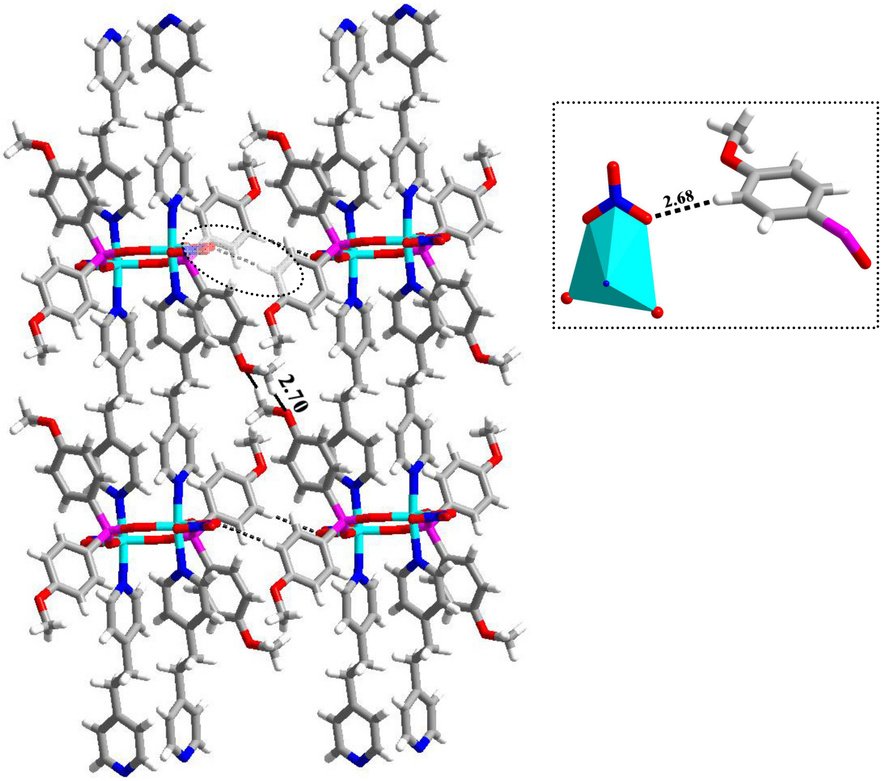
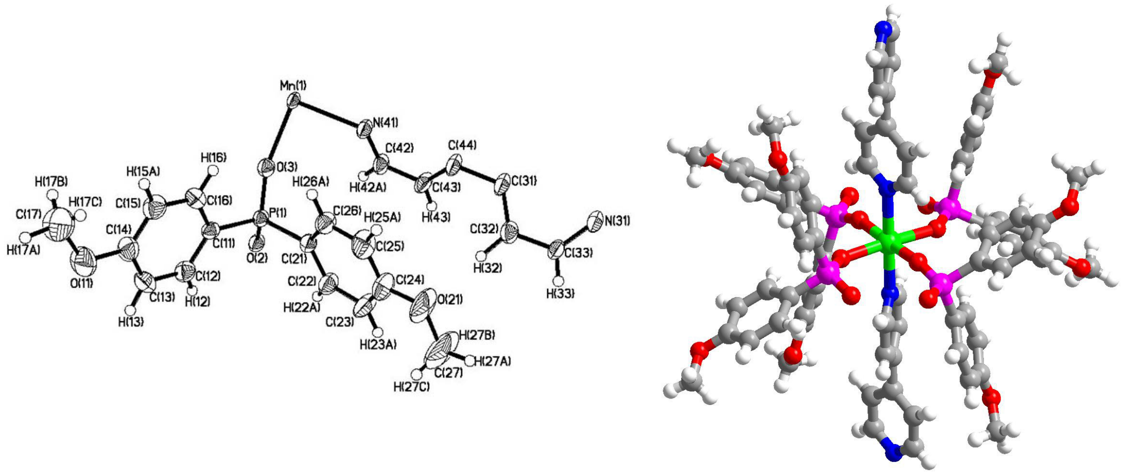


Figure 20. The adjacent coordination polymer chains are interconnected by C-H···O hydrogen bonds. The interactions between methoxyphenyl group of **1** and bidentate –NO_2 group (inset).

4.3.3 Coordination complex $Mn_2[(C_{14}H_{14}O_4P).(C_{10}H_8N_2)]$, 2c

Complex **2c**, with the formula unit of $Mn_2[(C_{14}H_{14}O_4P_1)_2.(C_{10}H_8N_2)]$, was prepared by co-crystallizing **2** with $MnCl_2.4H_2O$ in the presence of ***bpy***. The structural analysis by X-ray diffraction technique reveals that, the coordination around Mn(II) and the chemical constituents, present in the asymmetric unit, are different from that of both **2a** and **2b** (see Figure 21a). In a typical metal centre, Mn(II) is coordinated to four molecules of **2** and two ***bpy*** ligands completing the hexacoordination environment, as shown in Figure 21b. Such coordination units are arranged in crystal lattice, through the formation of polymer rods, comprising of Mn(II) and ***bpy***, with the molecules of **2** are being glued to those coordination rods in a perpendicular directions (see Figure 22). Further, such adjacent ensembles interact with each other through C-H···O (H···O, 2.52 Å) hydrogen bonds formed between phosphinic O-atoms and phenyl hydrogen atoms (see the inset in Figure 22). As a result, ***bpy*** molecules appeared to be captivated by molecules of **2**. Thus, structural arrangement in **2c** is almost identical to the features observed in the complexes **1a**-**1c**.



(**a**) (**b**)

Figure 21. (a) ORTEP diagram of the complex **2c** shows chemical constituents present in the asymmetric unit. (b) The coordination environment of Mn(II) in the complex **2c**.

It is interesting to note that, changing metal ion, Co(II) to Mn(II), there is a great significant change in the ultimate geometry formed between **2a** and **2c**. But, at the same time, similarity between the structures of **1a**-**1c** and **2c**, wherein, metal and coordinating aspects are different, suggest that target directed metal-coordination assemblies of phosphorous acids need to be studied at large, to deduce accurate reaction paths and conditions, for the creation of assemblies of tailor made properties.

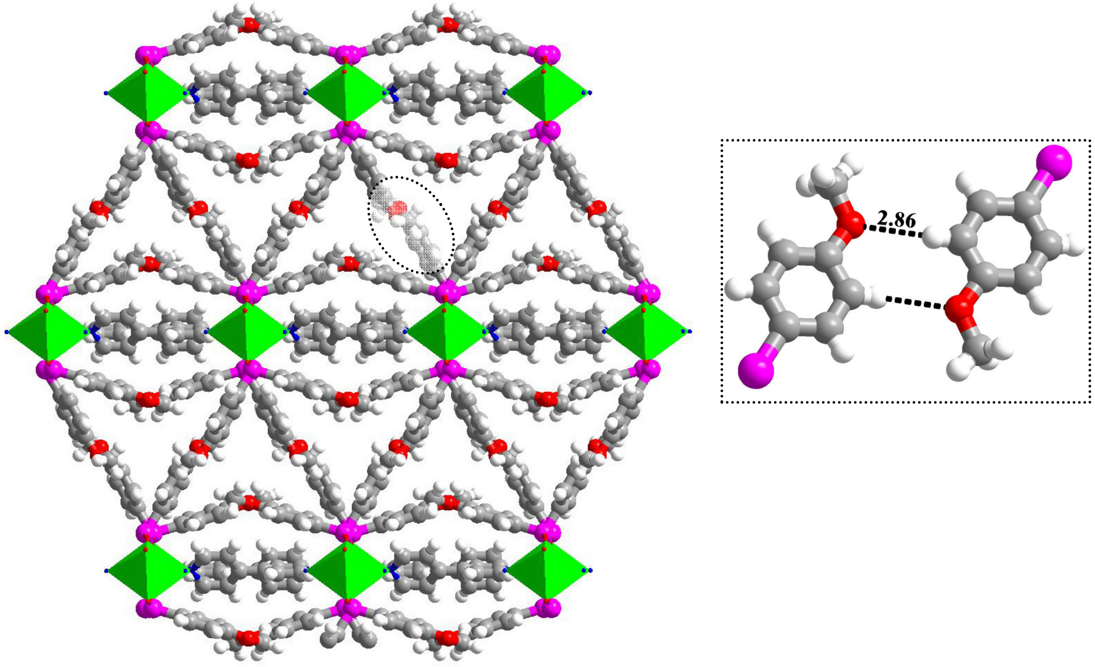


Figure 22. A three-dimensional view, along *c*-axis, in crystal structure of complex **2c**. Notice that ***bpy*** ligands are being captivated by the molecules of **2.** The C-H$\cdots$O hydrogen bonds established between methoxyphenyl groups of **2** of adjacent coordination polymer chains.

4.4 Conclusions

In conclusions, several metal-organic complexes were prepared by using different types of organophosphorous acids. It was noticed that the resultant supramolecular networks of all the complexes were stabilized by the weak interactions such as C-H$\cdots$O and C-H$\cdots\pi$ interactions. This may be facilitated due to the presence of additional functional groups like $-NO_2$ and $-OCH_3$, on the aromatic moieties of phosphorous acids. This study also reveals the tandem effect of coordination bonds and weak interactions in the formation of variety of supramolecular assemblies, by introducing subtle variations in the functional groups on organophosphorous acids, as well as, different aza-donor compounds, as schematically shown in Figure 23. Furthermore, this study also emphasizes the thrust for the exploration of many other organic functional groups in the design and synthesis of novel supramolecular architectures, rather than relying on the robust and well-explored carboxylates, phosphates, etc.

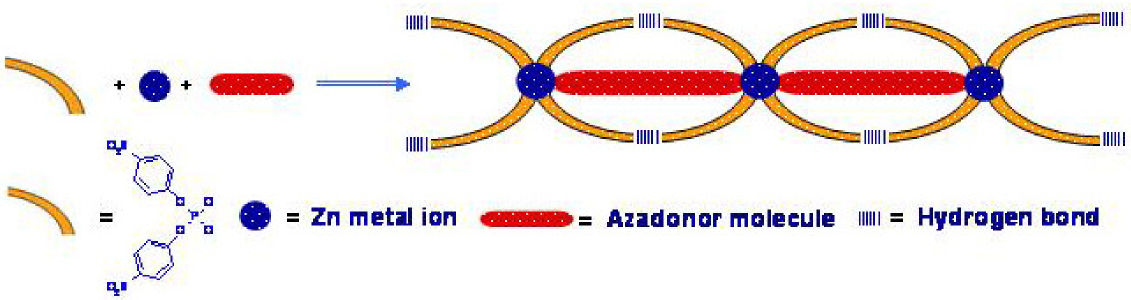


Figure 23. A typical supramolecular network observed in complexes **1a**-**d**, formed by **1** and Zn(II) with corresponding aza-donor compound.

4.5 Experimental Section

4.5.1 Synthesis

All the chemicals were obtained commercially, and the crystallization experiments were carried out by dissolving the constituent reactants in spectroscopic-grade solvents, as the case may be at warm condition and subsequent slow evaporation at room temperature. The synthesis of each complex is described below.

Synthesis of complex Zn[($C_{12}H_8N_2O_8P_1$)$_2$.($C_{10}H_{10}N_2$)], 1a

0.020 g (0.059 mmol) of **1** was dissolved in 10 mL of CH_3OH, by gentle warming. To this solution was added the aqueous solution of $Zn(NO_3)_2.6H_2O$ (0.017 g, 0.059 mmol in 5 mL H_2O). To the resulting solution, a solution of ***bpy*** (0.009 g, 0.059 mmol) in CH_3OH was added drop by drop over the period of 5 minutes under warm conditions. The solution was cooled down to room temperature and allowed for slow-evaporation to obtain single crystals over a period of two days. The experiment was repeated in a bit of high scale to improve the quantity of the crystals for the purpose of characterization. The crystals thus obtained were used for characterization by elemental analysis, FT-IR spectroscopy and single crystal X-ray diffraction.

Synthesis of complex $Zn[(C_{12}H_8N_2O_8P_1)_2.(C_{12}H_{12}N_2)]$, 1b

0.050g (0.147 mmol) of **1** was dissolved in 25 mL of CH_3OH, by warming. To this clear solution was added a solution of $Zn(NO_3)_2.6H_2O$ (0.044 g, 0.147 mmol) in 10mL of H_2O and heated for a while. To the resulting solution, a solution of ***bpyea*** (0.027 g, 0.147 mmol) in 20 mL of CH_3OH was added drop by drop over the period of 10 minutes under warm conditions. The clear solution thus obtained was kept for slow evaporation and good quality colorless single crystals were obtained over the period of 3 days. The crystals thus obtained were used for the characterization.

Synthesis of complex $Zn[(C_{12}H_8N_2O_8P_1)_2.(C_{12}H_{10}N_2)]$, 1c

Sample of **1** (0.050 g, 0.147 mmol) was dissolved in 25 mL of CH_3OH, by warming. To this clear solution was added a solution of $Zn(NO_3)_2.6H_2O$ (0.044 g, 0.147 mmol) in 10mL of H_2O and heated for a while. To the resulting solution, a solution of ***bpyee*** (0.027 g, 0.147 mmol) in 20 mL of CH_3OH was added drop by drop over the period of 10 minutes under warm conditions. The clear solution thus obtained was kept for slow evaporation and good quality colorless single crystals were obtained over the period of 3 days. The crystals thus obtained were used for the characterization.

Synthesis of complex of $Zn_2[(C_{12}H_8N_2O_8P_1)_4.(C_{13}H_{14}N_2)_2]$, 1d

0.050 g (0.147 mmol) of **1** was dissolved in 25 mL of CH_3OH, by warming. To this clear solution was added a solution of $Zn(NO_3)_2.6H_2O$ (0.044 g, 0.147 mmol) in 10mL of H_2O and heated for a while. To the resulting solution, a solution of ***bpypa*** (0.029 g, 0.147 mmol) in 20 mL of CH_3OH was added drop by drop over the period of 10 minutes under warm conditions. The clear solution thus obtained was kept for slow evaporation and good quality colorless single crystals were obtained over the period of 3 days. The crystals thus obtained were used for the characterization.

Synthesis of $Co[(C_{14}H_{14}O_4P)_2.(C_{10}H_8N_2)_2.2H_2O](C_{14}H_{15}O_4P)$, 2a

0.050 g (0.179 mmol) of **2** was dissolved in 25 mL of CH_3OH, by gentle warming. To this solution was added the aqueous solution of $Co(NO_3)_2.6H_2O$ (0.052 g, 0.179 mmol in 5 mL H_2O), mixed well by stirring the flask and heated for 5 minutes. To the resultant solution, a solution of ***bpy*** (0.028 g, 0.179 mmol) in CH_3OH was added drop by drop over the period of 5 minutes under warm conditions and the mixture was cooled down to room temperature and allowed for slow-evaporation to obtain single crystals over a period of four days. The crystals thus obtained were used for characterization by single crystal X-ray diffraction technique.

Synthesis of $Co[(C_{14}H_{14}O_4P).(C_{12}H_{12}N_2).NO_3]$, 2b

Sample of **2** (0.050g, 0.179 mmol) was dissolved in 25 mL of CH_3OH, by warming and to this clear solution was added aqueous solution of $Co(NO_3)_2.6H_2O$ (0.052 g, 0.179 mmol) in 5 mL H_2O, in a drop wise manner and mixed well. To the resultant solution was added, drop by drop, a solution of ***bpyea*** (0.033 g, 0.179 mmol) in 10 mL of CH_3OH and the reaction mixture was heated well. The clear, thus, obtained was cooled down to room temperature and kept for the slow evaporation, which yielded good quality pink crystals over the period of four days.

Synthesis of $Mn_2[(C_{14}H_{14}O_4P).(C_{10}H_8N_2)]$, 2c

$MnCl_2.6H_2O$ (0.035 g, 0.179 mmol) was dissolved in 5mL of H_2O and heated for 5 minutes, to this hot solution was added a solution of ***bpy*** (0.028 g, 0.179 mmol) in 5 mL of CH_3OH and heated for a while. The resultant hot solution was mixed with the solution of **2** (0.050 g, 0.179 mmol) in 20 mL of CH_3OH and reaction mixture was heated for 5 minutes and then cooled down to room temperature. The slow evaporation this solution yielded good quality single crystals of colorless needles over the period of six days, which were used for the characterization.

4.5.2 FT-IR Spectra

The FT-IR spectra were recorded on a SHIMADZU FT-IR-8400 in the 4000–400 cm^{-1} region using KBr pellets. **1a**: 582m, 640m, 748s, 885s, 1026s, 1102s, 1232s, 1348vs, 1379vs, 1510vs, 1614vs, cm^{-1}. **1b**: 582s, 640m, 748s, 887vs, 1112s, 1234vs, 1350vs, 1384vs, 1510vs, 1589s, 1618s, 3082s, cm^{-1}. **1c**: 582vs, 642s, 746vs, 885vs, 1110vs, 1230vs, 1284vs, 1348vs, 1384vs, 1510vs, 1589vs, 1610vs, cm^{-1}. **1d**: 582s, 640m, 848s, 889vs, 1112s, 1180m, 1238vs, 1284s, 1350vs, 1510vs, 1591s.cm^{-1}.

4.5.3 Elemental Analysis

Complex **1a**: C, 45.17%; H, 2.57%; N, 9.12%; P, 6.75%. Calcd: C, 45.37%; H, 2.69%; N, 9.34%; P, 6.88%. Complex **1b**: C, 46.32%; H, 3.01%; N, 8.99%; P, 6.56%. Calcd: C, 46.59%; H, 3.05%; N, 9.05%; P, 6.67%. Complex **1c**: C, 46.47%; H, 2.75%; N, 8.96%; P,6.56% . Calcd: C, 46.69%; H, 2.83%; N, 9.08%; P, 6.69%.

Complex **1d**: C, 47.02%; H, 3.10%; N, 8.77%; P, 6.43%. Calcd: C, 47.17%; H, 3.22%; N, 8.92%; P, 6.57% .

4.5.4 X-ray structures determination

Good quality single crystals of the complexes **1a-1d** and **2a-2c** were carefully selected with the aid of a polarized Leica microscope equipped with CCD camera, and glued to a glass fiber using an adhesive (cyano acrylate). In all the cases, the crystals were smeared in the adhesive solution to prevent decay of crystals upon exposure to X-rays. The intensity data were collected on a Bruker single crystal X-ray diffractometer, equipped with an APEX detector, at room temperature (298 K). Subsequently, the data were processed using Bruker suite of programmes (SAINT), [24] and the convergence was found to be satisfactory with good R_{ini} parameters. The details of the data collection and crystallographic information are given in Table 4.1. (for complexes **1a**-**1d**) and Table 4.2. (for complexes **2a**-**2c**). The structure determination by direct methods and refinements by least-squares methods on F^2 were performed using SHELXTL-PLUS[24] package. The processes were smooth without any complications. All non-hydrogen atoms were refined anisotropically. All the intermolecular interactions were computed using PLATON.[25]

Table 4.1 Crystallographic data for coordination complexes **1a-1d**.

	1a	**1b**	**1c**	**1d**
Formula	$C_{34}H_{24}O_{16}N_6P_2Zn_1$	$C_{36}H_{28}O_{16}N_6P_2$ Zn_1	$C_{36}H_{26}O_{16}N_6P_2$ Zn_1	$C_{74}H_{60}N_{12}O_{32}P_4$ Zn_2
M	899.90	927.95	925.94	1883.96
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Triclinic
Space group	*C*2/*c*	*Pbcn*	*Pbcn*	$P\bar{1}$
a/Å	30.154(5)	25.780(4)	25.742(6)	10.727(3)
b/Å	5.396(1)	13.529(2)	13.556(3)	16.014(4)
c/Å	22.978(4)	10.874(2)	10.828(2)	23.426(6)
α/°	90	90	90	98.86(1)
β/°	106.76(1)	90	90	92.60(1)
γ/°	90	90	90	94.44(1)
V/Å^3	3580(1)	3792.6(1)	3778.5(1)	3957.5(2)
Z	4	4	4	2
D_{calc}(g cm^{-3})	1.655	1.618	1.624	1.581
μ/mm^{-1}	0.862	0.817	0.820	0.785
T/K	298	298	298	298
Mo kα	0.7107	0.7107	0.7107	0.7107
2θ range (deg)	50	50	50	50
F(000)	1832	1896	1888	1928
Indep. reflns	3155	3348	3328	13891
Measured reflns	8532	25691	17775	38588
Observed refns. (I > 2σ(I))	2175	2736	2684	8138
Parameters	336	299	305	1193
GOF on F^2	0.957	1.080	0.820	0.916
R1, (observed)	0.037	0.042	0.038	0.047
wR2 (observed)	0.094	0.125	0.117	0.097
R1 (all)	0.051	0.054	0.049	0.095
wR2 (all)	0.108	0.135	0.128	0.134

Table 4.2 Crystallographic data of crystal structure of **2** and the complexes **2a–2c**.

	2	**2a**	**2b**	**2c**
Formula	$(C_{14}H_{14}O_4P_1)$	$[(C_{14}H_{14}O_5P_1)Co]_2$ $(C_{14}H_{15}O_4P1)_2:(C_{10}H_8N_2)$	$[(C_{14}H_{14}O_4P_1)Co]$: $(N_10_3):(C_{12}H_{12}N_2)$	$[(C_{14}H_{14}O_4P_1)Mn]_2$: $(C_{10}H_8N_2)$
M	278.23	1358.01	582.40	765.57
crystal habit	needles	block	blocks	blocks
crystal system	trigonal	triclinic	monoclinic	monoclinic
space group	*R-3*	$P\bar{1}$	$P\,2_1/c$	*C 2/c*
a/Å	27.294(1)	9.718(3)	11.497(3)	28.653(5)
b/Å	27.294(1)	11.285(4)	13.603(3)	11.695(2)
c/Å	9.582(9)	14.784(5)	16.230(4)	10.995(2)
α/°	90	80.93(1)	90	90.00
β/°	90	83.13(2)	93.78(1)	101.77(1)
γ/°	120	86.59(2)	90	90.00
V/Å^3	6181.9(7)	1588.2(8)	2532.7(1)	3606.9(1)
Z	18	1	4	4
D_c/g cm^{-3}	1.345	1.420	1.527	1.410
μ/mm^{-1}	0.207	0.445	0.793	0.510
2θ range[°]	50.00	50.64	56.86	50.00
T/K	298(2)	298(2)	298(2)	298(2)
F(000)	2628	707	1204	1588
λ/Å	0.7107	0.7107	0.7107	0.7107
$\Delta\rho_{min.max}$/e Å^{-3}	0.565/-0.307	0.805/-0.941	0.601/-0.319	0. 0.954/-0.589
total reflections	10508	11517	29040	8840
unique reflections	2429	5743	6080	3172
reflectios used	1846	3864	4126	1663
R1, I > 2σ(I)	0.0659	0.0607	0.0360	0.0540
wR,I > 2σ(I)	0.1839	0.1585	0.0808	0.1232

Table 4.3 Bond distances of coordination bonds and phosphate groups in the molecular complexes **1a-1d**.

Bond	1a	1b	1c	1d
Zn-O	2.042(2) 2.117(2)	2.129(3) 2.140(3)	2.131(2) 2.133(2)	2.102(3), 2.105(3), 2.108(3), 2.108(3), 2.110(3), 2.135(3), 2.137(3), 2.170(3)
Zn-N	2.213(2)	2.084(4) 2.090(5)	2.096(3) 2.102(3)	2.142(3), 2.156(3), 2.159(3), 2.175(4)
P-O	1.448(2) 1.463(2) 1.590(2) 1.598(2)	1.467(3) 1.475(3) 1.610(3) 1.614(3)	1.463(2) 1.475(2) 1.607(2) 1.618(2)	1.468(3), 1.468(3), 1.472(3), 1.472(3), 1.473(3), 1.473(3), 1.474(3), 1.477(3), 1.597(3), 1.602(3), 1.604(3), 1.604(3), 1.607(3), 1.610(3), 1.611(3), 1.617(3)

Table 4.4 Characteristic hydrogen bond distances (Å) and angles (°) of the molecular complexes **1a-1d**.[#]

D-H···O	1a			1b			1c			1d		
C-H···O	2.39	3.307	170	2.45	3.375	172	2.50	3.365	171	2.41	3.317	164
	2.55	3.367	160	2.54	3.411	157	2.51	3.377	156	2.42	3.239	146
	2.60	3.132	125	2.64	3.422	142	2.55	3.408	150	2.43	3.248	147
	2.60	3.402	157	2.65	3.311	128	2.71	3.250	127	2.46	3.208	140
	2.89	3.747	162	2.72	3.355	126	2.81	3.342	128	2.47	3.373	164
				2.76	3.521	135	2.81	3.373	124	2.47	3.339	153
				2.81	3.552	137	2.92	3.532	138	2.54	3.184	127
C-H···N				2.80	3.623	148	2.87	3.627	146			

[#] Three columns for each structure represent H···A, D···A distances and D-H···A angle, respectively for a typical hydrogen bond, being represented as D-H···A.

Table 4.5 Characteristic coordination bonds in complexes **2a–2c**.

	2a	**2b**	**2c**
M-O	2.065(3)	2.007(2)	2.196(3)
	2.146(3)	2.023(2)	2.129(3)
M-N	2.119(3)	2.155(2)	2.350(6)
		2.156(2)	2.278(5)
P-O	1.537(3)	1.495(2)	1.503(3)
	1.481(3)	1.506(2)	1.499(3)
O-M-O		108.24(7)	90.68(2)
N-M-N	180	171.64(7)	180
O-P-O	116.15(2)	115.45(1)	118.61(2)

M = Co(II), Mn(II)

Table 4.6 Characteristic hydrogen bond distances (Å) and angles (°) of the crystal structure of **2**, and the complexes **2a**-**2c**.[$]

	2			**2a**			**2b**			**2c**		
O-H···O	1.75	2.57	172	1.67	2.43	150						
C-H···O	2.71	3.62	169	2.48	3.26	150	2.68	3.56	170	2.68	3.62	141
							2.69	3.31	121			
C-H···π	3.12	3.91	144	2.96	3.81	157						
				3.21	3.78	119						
				3.62	4.51	156						

[$] Three columns for each structure represent H···A, D···A distances and D-H···A angle, respectively for a typical hydrogen bond, being represented as D-H···A.

4.6 References

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Publications

1) Novel Supramolecular Assemblies of Coordination Polymers of Zn(II) and Bis(4-nitrophenyl)phosphoric Acid with Some Aza-Donor Compounds. Marivel, S.; Shimpi, M. R.; Pedireddi, V. R. *Crystal Growth & Design,* **2007**, *7,* 1791-1796.

2) Molecules to supermolecules and self assembly: a study of some co-crystals of cyanuric acid. Marivel. S.; Suresh, E.; Pedireddi, V. R. *Tetrahedron Lett*. **2008**, *49*, 3666-3671.

3) Novel supramolecular assemblies of bis(4-Methoxyphenyl)phosphinic acid and its coordination assemblies. S. Marivel and V.R.Pedireddi. (Under preparation)

4) Supramolecular synthesis of cyanuric acid with triazine ligands: preparation of some novel architectures using symmetrically substituted molecules. S. Marivel and V. R. Pedireddi. (Under preparation)

5) Supramolecular assemblies of isomers of dihydroxybenzoic acid with different aza-donor compounds S. Marivel, S. Varughese and V. R. Pedireddi (Under preparation)

Coursework and Seminars Attended

International

***Innovation in Crystal Poloymorphism – An International Workshop in Bologna,* 31st January – 2nd February 2008, ITALY.**

National

1) **A Rational Study of Some Supramolecular Complexes of Cyanuric Acid. S. Marivel and V. R. Pedireddi. in *RSC – West India Section Ph.D. Student Symposium 2007.* 19th – 20th, Goa University, Goa.**

2) ***35th National Seminar on Crystallography, 22-24 February 2006,* National Physical Laboratory, New Delhi-110012, INDIA.**

3) **Novel Supramolecular Assemblies of *bis*(4-Methoxyphenyl)phosphinic acid Samipillai Marivel and V. R. Pedireddi*. in 8th National Symposium in chemistry (Chemical Research Society of India) 3-5 February, 2006,* Indian Institute of Technology, Powai, Bombay, INDIA.**

4) **Course work attended as a part of Ph. D program during September 2004 – April 2005. National Chemical Laboratory, Pune. 411 008.**