SUPRAMOLECULAR SYNTHESIS OF ORGANIC AND COORDINATION ASSEMBLIES UTILIZING SOME AROMATIC BORONIC ACIDS

Thesis submitted to

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Doctor of Philosophy

in

Chemistry

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 Organic and Coordination Assemblies Utilizing Some Aromatic Boronic Acids" submitted by **Seetha Lekshmi N.**, 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.

September 2008 **Dr. V. R. Pedireddi, FRSC**
Pune **(Research Guide)**

DECLARATION

I hereby declare that the matter embodied in this thesis entitled "**Supramolecular Synthesis of Organic and Coordination Assemblies Utilizing Some Aromatic Boronic Acids**" 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**.

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

September 2008 **Seetha Lekshmi N.**
Pune

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ABSTRACT

The research work reported in this thesis entitled “SUPRAMOLECULAR SYNTHESIS OF ORGANIC AND COORDINATION ASSEMBLIES UTILIZING SOME AROMATIC BORONIC ACIDS” was carried out to evaluate the utility of boronic acids in the supramolecular synthesis. In this endeavor, the results and observations found during the course of the synthesis and solid-state structural analysis of novel and exotic organic and coordination supramolecular assemblies, making use of various aromatic boronic acids have been documented into four chapters. While, Chapter 1 gives an account of the contemporary research in the area of supramolecular chemistry, with an emphasis on the design and synthesis of supramolecular assemblies of boronic acids, Chapters 2 and 3 illustrate the structural analysis of various aromatic boronic acids and synthesis of their molecular complexes with *N*-donor compounds. In Chapter 4, analysis of 4-carboxyphenylboronic acid and its hydrates as well as the preparation and structural features of its coordination assemblies are discussed.

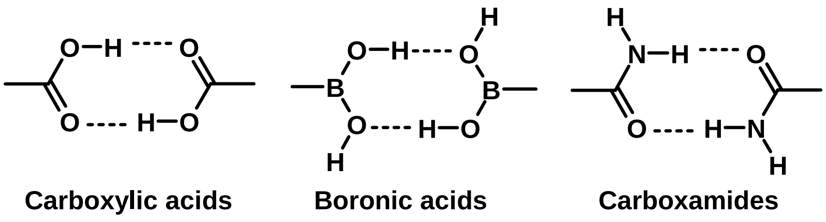
Chapter 1:- An introduction to supramolecular chemistry

Preparation of supramolecular assemblies by the utilization of the knowledge of intermolecular interactions like hydrogen bonds, halogen bonds, electrostatic interaction etc., and evaluating their properties in the context of crystal packing, is a frontier area of research due to its potential utility in the synthesis of complex and

topologically directed materials with tailor-made properties.[1,2] In the design and synthesis of supramolecular assemblies, the selection of suitable building blocks and reaction conditions are critical due to their structure directing properties in the formation of desired three-dimensional architectures. In this regard, molecules with suitable functional groups like –COOH, –$CONH_2$, –OH, etc., have been well utilized in the supramolecular synthesis for the preparation of exotic assemblies.[3,4]

Boronic acids, which possess –$B(OH)_2$ as the functional moiety, with hydrogen bond patterns similar to –COOH and –$CONH_2$, have not been well employed in the supramolecular synthesis (Scheme 1).[5,6] In fact, boronic acids are highly valuable as pharmaceutical agents and also as reagents for the synthesis of a variety organic compounds.[7,8] Thus, exploration of supramolecular assemblies of various boronic acids have been carried out to substantiate their utility in different applications. For this purpose, an account of well-known examples, emphasizing the utility of several functional groups, with an attention on the contemporary research work progressing in the preparation and analysis of novel assemblies of boronic acids are discussed in this Chapter.

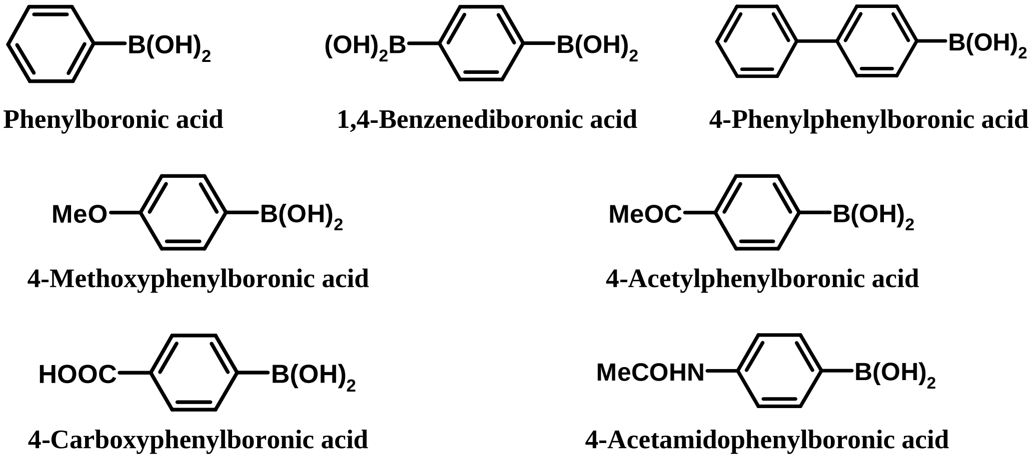
Scheme 1



Chapter 2:- Solid state structural analysis of aromatic boronic acids and their molecular complexes

Cambridge Structural Database (CSD) [9] analysis revealed the structural reports of only a few boronic acids, but their utility in the synthesis of supramolecular assemblies were in scanty. Thus, three-dimensional structures of various aromatic boronic acids (Scheme 2) have been determined and studied the influence of other functional groups in the recognition pattern of $-B(OH)_2$ functionality followed by the synthesis and structural elucidation of their co-crystals with *N*-donor compounds.

Scheme 2



Phenylboronic acid

1,4-Benzenediboronic acid

4-Phenylphenylboronic acid

4-Methoxyphenylboronic acid

4-Acetylphenylboronic acid

4-Carboxyphenylboronic acid

4-Acetamidophenylboronic acid

It was observed that, the position of functional groups play a significant role in the formation of different types of recognition patterns, as exemplified below for two thiopheneboronic acids.

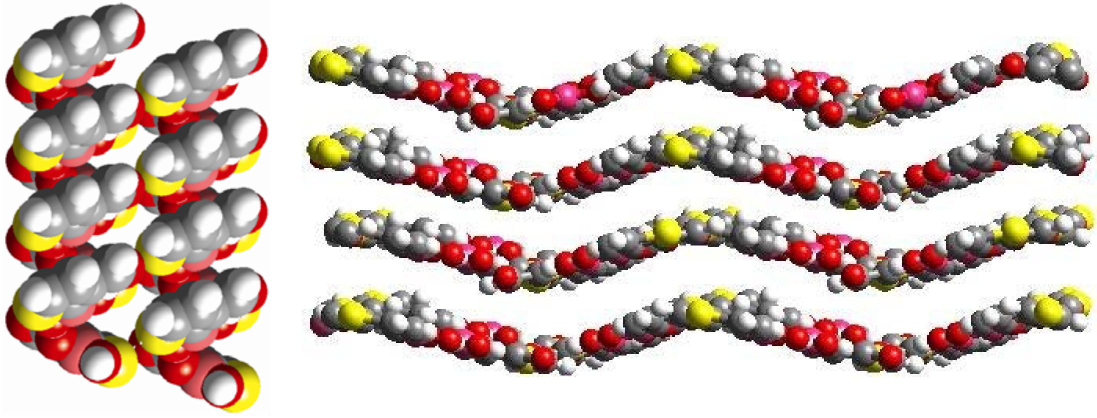


Figure 1: (a) The helical assembly observed in the three-dimensional crystal structure of 3-formyl-2-thiopheneboronic acid. (b) Stacking of the corrugated sheet structure observed in 2-formyl-3-thiopheneboronic acid.

Three-dimensional structure analysis of two isomeric thiopheneboronic acids, (3-formyl-2-thiopheneboronic acid and 2-formyl-3-thiopheneboronic acid) revealed that, the self-assembly of 3-formyl-2-thiopheneboronic acid yielded a helical assembly with opposite handedness arranged in an edge-sharing fashion, while, a corrugated sheet structure was formed in the case of 2-formyl-3-thiopheneboronic acid (Figure 1).

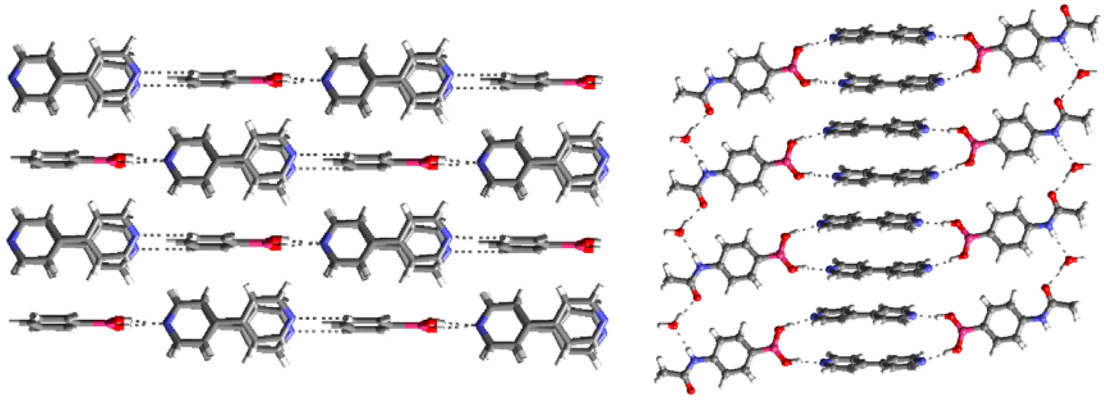


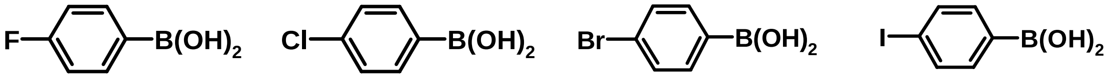
Figure 2: (a) Phenylboronic acid yielded one-dimensional tapes and (b) 4-acetamido phenylboronic acids gave a ladder like assembly with 4,4'-bipyridine.

Further, in molecular complexes, as shown in typical examples of phenylboronic and 4-acetamidophenylboronic acids with 4,4'-bipyridine (***bpy***), the interaction between –$B(OH)_2$ group and pyridyl -*N* atoms are established through O-H···N hydrogen bonds (Figure 2). Details of the nature of intermolecular interactions and three-dimensional architectures of various co-crystals of boronic acids are compiled in the chapter.

Chapter 3:- Supramolecular assemblies of 4-halophenylboronic acids

Apart from hydrogen bonds, among other structure directing interactions, in recent times, halogen bonding has been thoroughly employed in the supramolecular synthesis. Halogen bonds are generally represented as D···X-Y, in which D is electron donor (Lewis base), X is a halogen atom (Lewis acid) and Y is generally C, N or halogen.[10] In order to explore the utility of halogen bonding in the molecular recognition and solid-state structures of boronic acids, three-dimensional structures of several halogen substituted phenylboronic acids (Scheme 3) and their molecular complexes have been studied.

Scheme 3



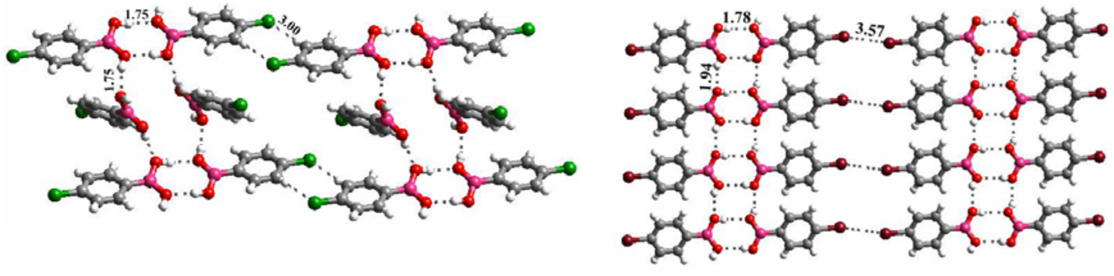
4-Fluorophenylboronic acid **4-Chlorophenylboronic acid** **4-Bromophenylboronic acid** **4-Iodophenylboronic acid**

The obtained results are discussed in this Chapter in two sections. While, 'Part A' deals with the structural analysis of various solid-state forms of 4-

halophenylboronic acids, the preparation and analysis of their molecular complexes with various *N*-donor compounds are discussed in ‘Part B’.

Part A: Structural analysis of 4-halophenylboronic acids

Crystallization of various 4-halophenylboronic acids (-F, -Cl, -Br and -I) was carried out from various solvent systems. However, we were unsuccessful in obtaining the pure crystal structure for the 4-fluro and 4-iodophenylboronic acids. The nature of intermolecular interactions and three-dimensional packing of 4-chloro and 4-bromophenylboronic acids have been discussed in this section.



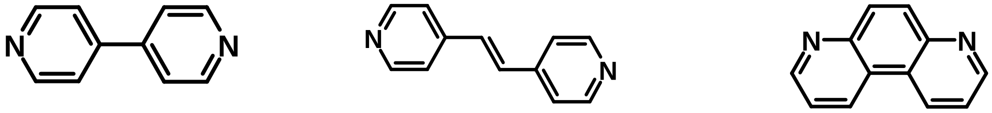
(a) **(b)**

Figure 3: The basic recognition pattern present in the crystal structure of (a) 4-chloro and (b) 4-bromophenylboronic acids.

Part B: Molecular complexes of 4-halophenylboronic acids

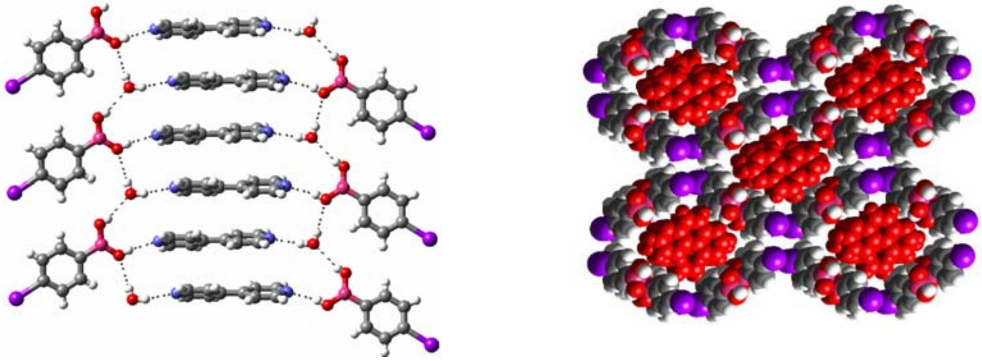
Molecular complexes of halogen mediated boronic acids have been prepared by co-crystallizing with various *N*-donor compounds like 4,4'-bipyridine, *trans*-1,2-bis(4-pyridyl)ethene and 4,7-phenanthroline (Scheme 4).

Scheme 4



4,4'-bipyridine *trans*-1,2-bis(4-pyridyl)ethene 4,7- phenanthroline

The recognition between the boronic acids and the *N*-donor ligands yielded supramolecular assemblies with various topologies like ladders, molecular chains, host-guest assemblies etc., as shown in Figure 4, for 4-iodophenylboronic acid. Detailed discussion of these assemblies along with the three-dimensional arrangements observed for other complexes are illustrated in this section.



(a) **(b)**

Figure 4: 4-Iodophenylboronic acid yielded various architectures like (a) molecular ladders with 4,4'-bipyridine, (b) the host-guest assembly with 4,7-phenanthroline.

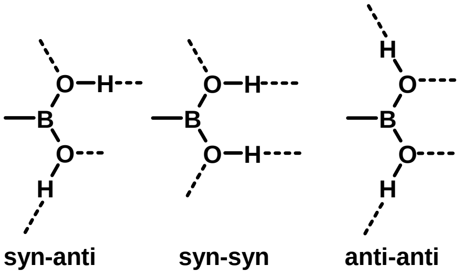
Chapter 4: Coordination assemblies of 4-carboxyphenylboronic acid

In this Chapter, analysis of various solid state forms of 4-carboxyphenylboronic acid and coordination assemblies have been described in two-sections as given below.

Part A: **4-Carboxyphenylboronic acid and its hydrates**

4-Carboxyphenylboronic acid upon crystallization from acetone gave an anhydrous form. However, crystallization from methanol and 2-propanol yielded a monohydrate and quarter hydrated forms, respectively. All the structures have been well characterized by single crystal x-ray diffraction methods.

Scheme 5



Among the three conformations, known to date, for boronic acid functionality (Scheme 5), *syn*-*anti* and *anti*-*anti* were found in the crystal structure of 4-carboxyphenylboronic acid. It was observed that, in three-dimensional arrangement, the amount of water molecules present in the crystal lattice, play a key role in the ultimate supramolecular architectures in the hydrated structures (Figure 5). Detailed description of the three-dimensional assemblies is compiled in this section.

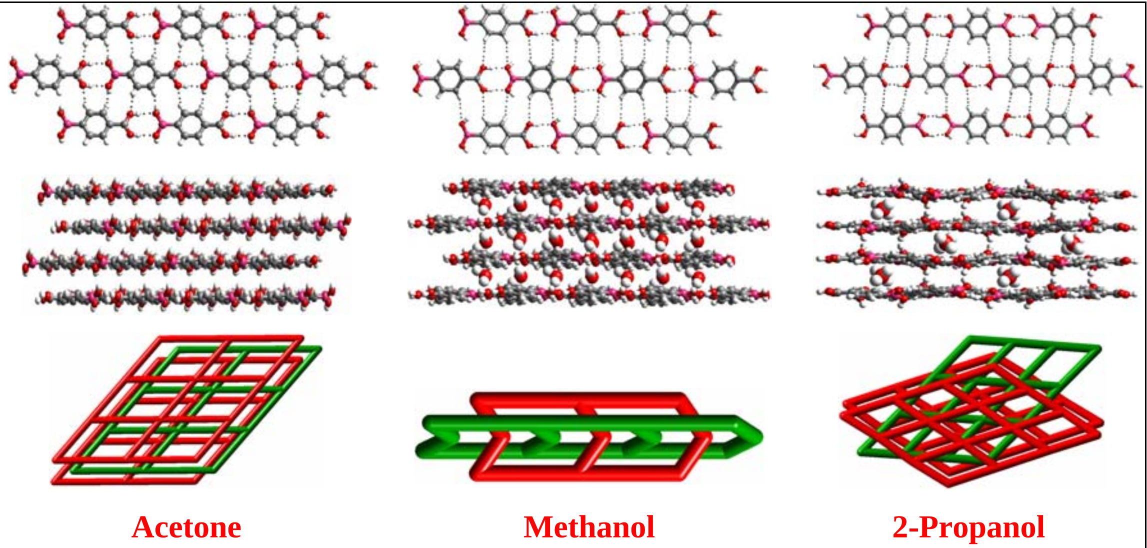


Figure 5: Nature of intermolecular interaction and the three-dimensional architectures of various solid-state forms of 4-carboxyphenylboronic acid.

Part B: Coordination complexes of 4-carboxyphenylboronic acid

Design and synthesis of coordination assemblies with novel architectures and potential application are of great interest in the recent times due to their utility in various fields like gas storage, catalysis, anion recognition etc.[11,12] Preparation of metal-organic frameworks (MOFs) with tailor made properties is often governed by the functionalities present on the organic ligands together with the coordination features of the metal ions.[13,14] Thus, identification of suitable building blocks is always a challenging exercise, especially new functionalities with high flexibility and multiple coordination sites. In this respect, since coordination complexes of boronic acids were hitherto unknown, exploration of the possibility of boronic acids as new potential ligands, that could play a vital role in the further development of coordination assemblies, have been carried out.

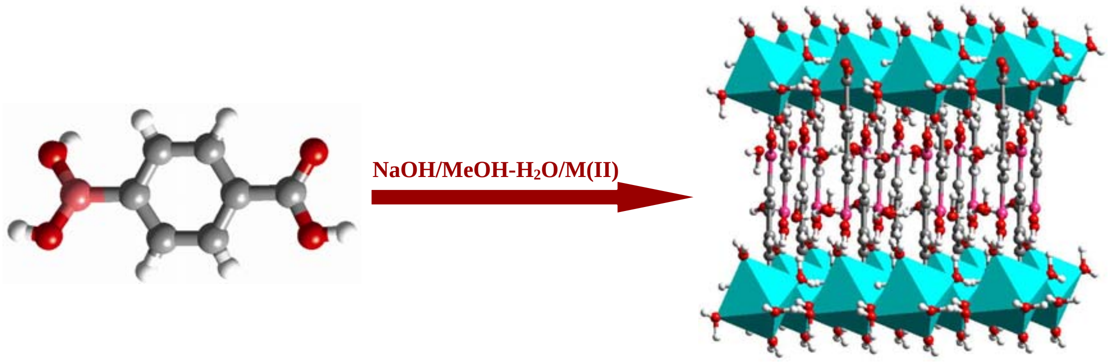


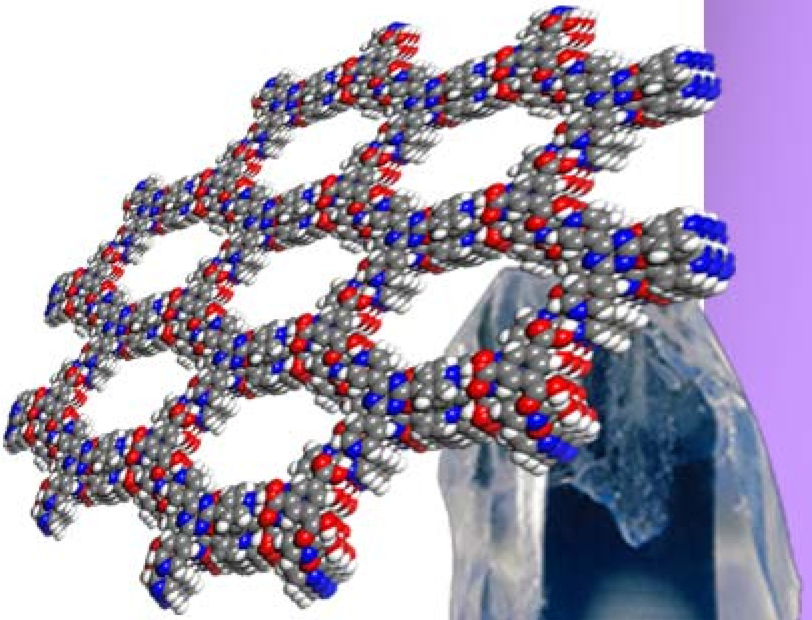
Figure 6: Three-dimensional structure of coordination assemblies of 4-carboxy phenylboronic acid and various metal ions, (M(II)= Mn(II), Co(II), and Ni(II)).

Metal-organic assemblies of 4-carboxyphenylboronic acid, with Mn(II), Co(II), and Ni(II) metal ions yielded isostructural complexes, interestingly without

forming coordination bonds between the metal ion and boronic acid moieties, but yielded clay-like architectures through the second sphere coordination (Figure 6). The nature of intermolecular interactions and structural features of the complexes have been illustrated in detail in this section.

Chapter 1

An Introduction to Supramolecular Chemistry



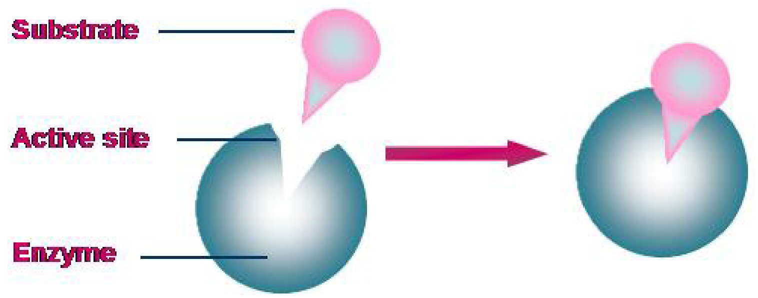
1.1 Introduction

Molecular synthesis has always been a major focus since the synthesis of urea by Friedrich Wöhler in 1826.[1] Since then, considerable progress has been made in the targeted synthesis of organic compounds, involving the transformations of covalent bonds, in a controlled and precise fashion. But, in the recent times, research is much focussed on the understanding of self-assembly of molecules and intermolecular interactions for the design and synthesis of new materials with novel properties. Such studies, in fact, have given rise to a new field of research - *supramolecular chemistry* - which focuses on the synthesis of assemblies with tailor made properties, generally, through molecular recognition and self-assembly process.[2] Although the initial studies were based on the molecular recognition between alkali metal ions and natural antibiotics, synthetic macro(poly)cyclic polyethers etc., current research in supramolecular chemistry has advanced, through the knowledge of intermolecular interaction, to mimic the structure and function of natural supramolecular assemblies such as DNA, protein, peptides etc.[3]

1.2 Molecular recognition and self-assembly

Molecular recognition refers to the specific interactions established between two or more molecules, by making use of the various non-covalent forces.[4] The importance of molecular recognition was realized around the middle of the nineteenth century, when Pasteur noticed the existence of tartaric acid in two different kinds of crystals.[5] These chiral isomers spontaneously self-recognize, resulting in the separate crystallization of each type. Later, in 1894, the process of molecular recognition was conceptualized by Emil Fischer by proposing that, enzymes recognize substrates through a "*lock and key*" mechanism (Scheme 1.1).[6]

Scheme 1.1



Often molecules involved in the recognition process exhibit molecular complementarities and the precise recognition between these complimentary units produces well-defined complex. Pauling and Delbrück stated that, "… *in any kind of molecular recognition, and this includes the recognition between identical molecules, it is the dissimilar rather than the similar functionalities that come into closest contact*".[7] Further, the interaction of the components with their environment can strongly influence the course of recognition process.[8] When several types of molecular interactions work together, a co-operative enhancement in molecular association is often observed.

Complementarity: Both the donor and the acceptor must have mutual spatially and electronically complimentary binding sites to form a supramolecular aggregate.

Co-operativity: Two or more binding sites acting in a concerted fashion to produce a combined interaction that is stronger than when the binding sites act independently of each other.

Self-Assembly: The spontaneous and reversible association of molecular species to form larger, more complex supramolecular entities according to the intrinsic information contained in the components.

Thus, the molecular recognition, brought about by the non-covalent interactions, that are selective, directional and strongly attractive, can induce the formation of supramolecular aggregates through the self-assembly process. The self-assembly occurs when complimentary molecules interact with one another through a balance of attractive and repulsive forces (Figure 1.1), which are generally weak and non-covalent in nature.[9]

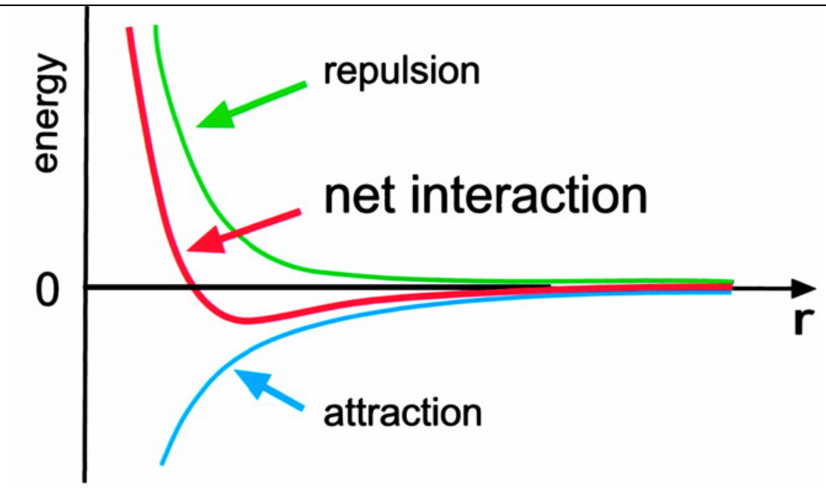
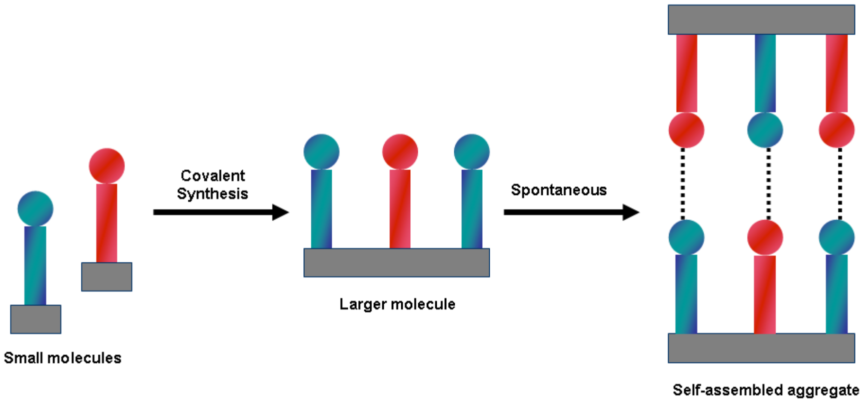


Figure 1.1: Molecular aggregation occurs when there is a net attraction and an equilibrium separation between the components.

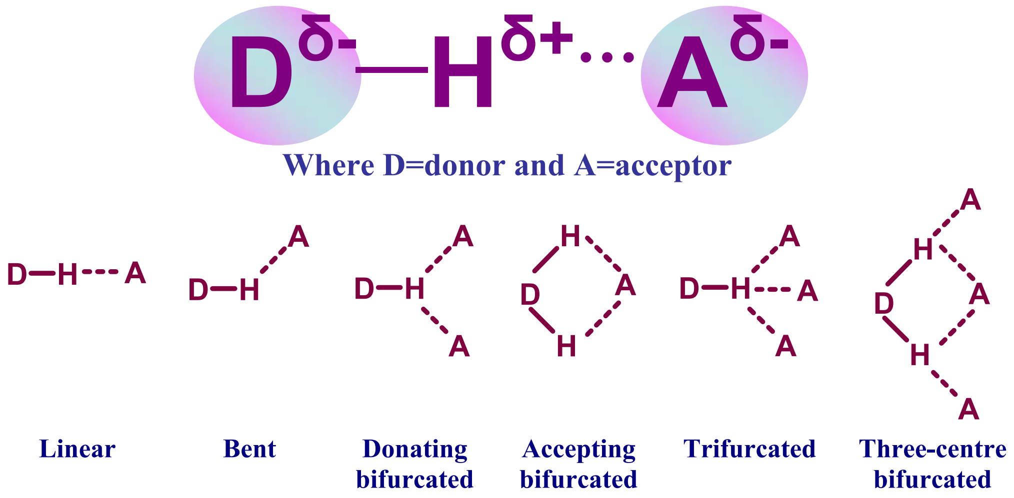
Self-assembly or self-organization is a reversible process, by which the controlled molecular association results in the formation of assemblies with specific shape and characteristics, determined by the strength of the binding forces and the nature of the components (Scheme 1.2).[10] Nature offers a wide array of self-assemblies with exquisite architectural controls and the examples vary from simple water clusters to complex biological molecules such as nucleic acids, proteins, viruses etc. The best-known self-assembling structure in biological systems is deoxyribonucleic acid (DNA), which exists in a double helical form, in which the two complimentary strands are entwined by means of hydrogen bonds and π-π stacking.[11]

Scheme 1.2



During the molecular recognition and self-assembly process, the selectivity and efficiency is often achieved through the combination of various intermolecular interactions like hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π-π interactions, electrostatic forces etc.[12] Finding an appropriate combination of functionalities to bring about effective molecular interactions is, thus, the key in designing novel supramolecular assemblies.

Scheme 1.3

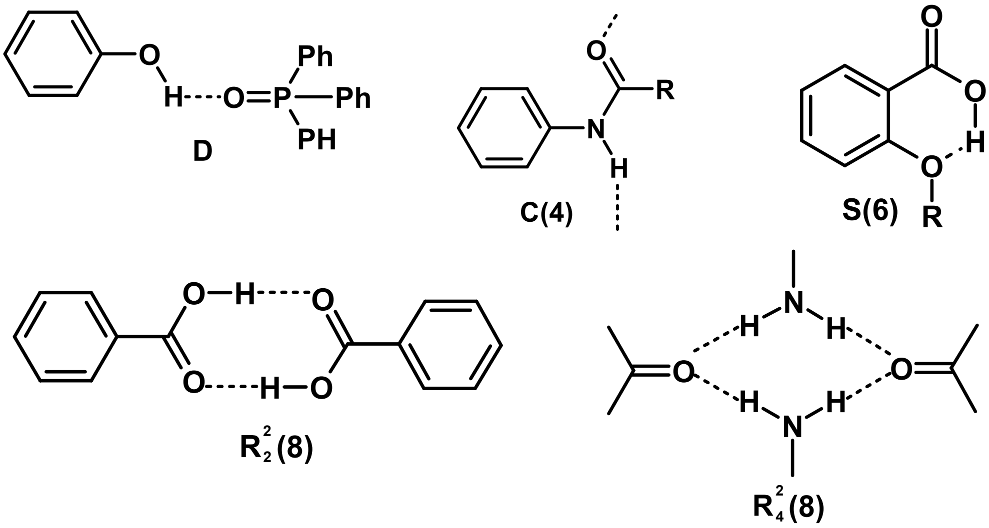


Among the various non-covalent interactions, hydrogen bond is the most important and intensively studied one in the structural chemistry as well as in biology (Scheme 1.3).[13] Due to its strength and high degree of directionality, the hydrogen bond is able to control and direct the formation of molecular assemblies efficiently.[14]

Although hydrogen bonds were first observed by Latimer and Rodebush, [15] its utility in determining the properties of materials were noted by Pauling. In 1935, in his book, '*The Nature of the Chemical Bond'*, the term "hydrogen bonding" was introduced to account the residual entropy of ice[16] and stated that ''*under certain conditions an atom of hydrogen 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.*'' Since then, there were several attempts to define and classify the hydrogen bonds systematically, and amongst Pimental and McClellan's contributions are quite significant and it was proposed that, *"...a hydrogen bond exists when there is evidence of a bond, and it specifically involves a hydrogen atom already bonded to another atom.*"[17] Further, there have been many efforts to understand its role in the structural arrangement and this led to the introduction of a nomenclature for the hydrogen bond patterns in the solid state chemistry, as proposed by Etter and coworkers - *graph set analysis* - based on the network topology and number of atoms involved in the bond formation.[18-22]

The purpose of graph-set assignments is to define different types of hydrogen bonds, based on the nature of the donors and acceptors in a hydrogen bond, present in the structure. As shown in Scheme 1.4, different types of hydrogen bonds are characterized by one of the four designators, which are, **C** (chain), **R** (ring), **D** (dimer or other finite set) and **S** (intramolecular hydrogen bond). The number of donors and acceptors are assigned as subscripts and superscripts respectively, and the number of atoms in the repeat unit is indicated in parentheses.

Scheme 1.4



Thus, based on the analysis of the intermolecular interactions, such as their nature and propensity of formation, attempts were made to design and synthesize supramolecular assemblies in an efficient and reliable manner. This gave rise to the development of new synthetic strategies under "*supramolecular synthesis*" process.[23]

1.3 Supramolecular synthesis

Supramolecular synthesis involves the control of both intermolecular interactions and three-dimensional arrangements of the molecules, there by producing well-designed and long-range structures, optimally designed for special functions. Due to the weak nature of intermolecular interactions compared to the covalent bonds, the supramolecular species are thermodynamically less stable, kinetically more labile and dynamically more flexible.[24] Also, the formation of supramolecular assemblies are believed to be both enthalpy and entropy-driven.[25]

Rapid developments in analytical techniques have contributed extensively in characterizing molecular interactions and structures of the resulting supramolecular architecture. While the diffraction techniques like single crystal x-ray diffraction, neutron diffraction etc., with CCD technology coupled with high power generators like rotating anode, has enhanced the pace and accuracy of the structure determination and analysis of intermolecular interactions, the spectroscopic techniques like NMR, UV, IR etc., and the imaging techniques such as SEM, TEM, AFM etc., have contributed to a great extent in characterizing materials at atomic level precision.

In fact, supramolecular synthesis is not only limited to the assemblies being formed by simple organic molecules, but also much focus has been given to the studies of metal-organic assemblies. Depending upon the nature of molecular entities employed for the preparation, the resulting supramolecular assemblies can be broadly classified into: (i) organic assemblies and (ii) coordination assemblies. Some of the illustrative examples of exotic supramolecular assemblies of both the types, prepared following supramolecular synthetic protocols, are discussed in the following sections.

1.3.1 Organic supramolecular assemblies

Hydrogen bonding is the major cohesive force used in most of the organic assemblies. Multiple hydrogen bonds, formed between complimentary functional groups, drive the formation of dimeric and oligomeric aggregates. The most economical and efficient approach in designing a self-assembling aggregate is through the employment of the self-complimentary molecule. This has been the approach used in the preparation of a vast ensemble of supramolecular assemblies; and the examples vary from the simple dimeric assemblies to stable porous three-dimensional networks obtained from various molecular building units.[26]

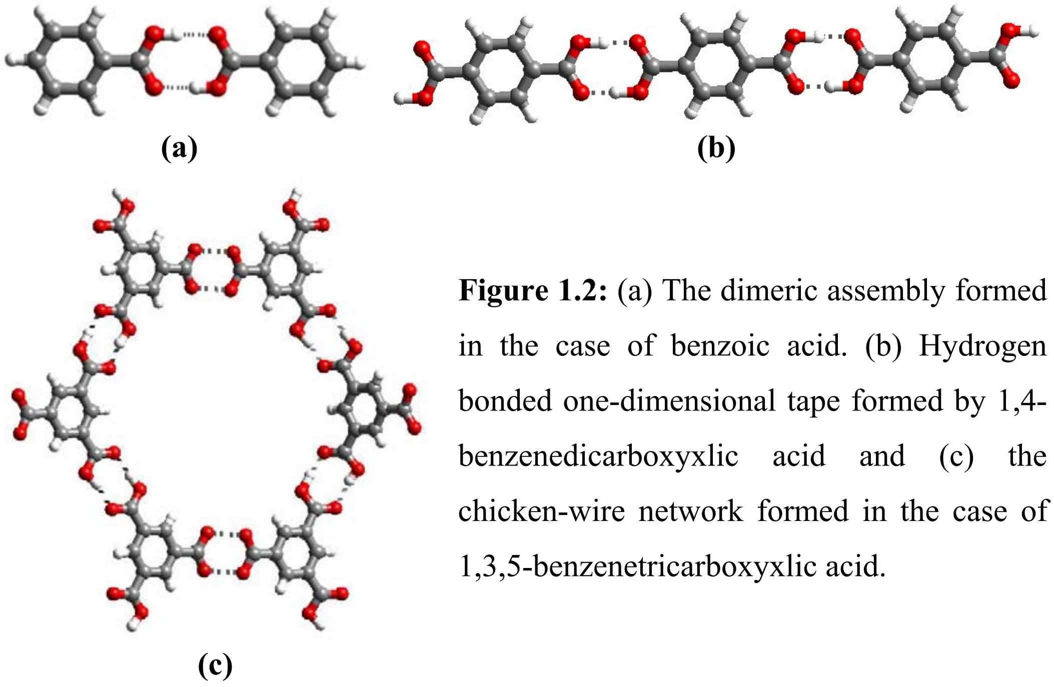
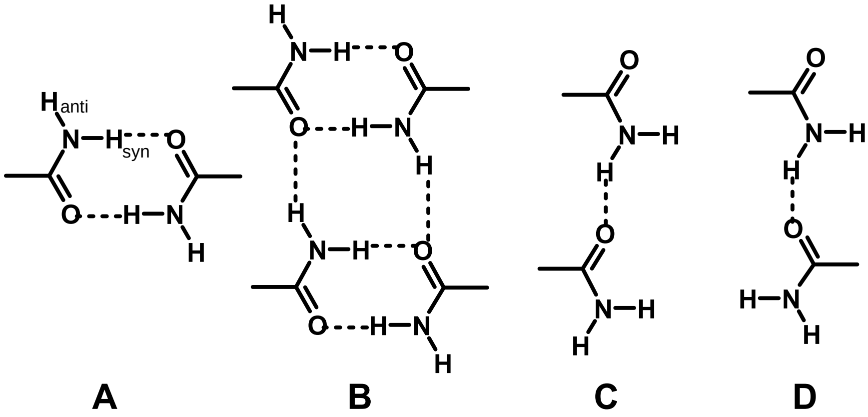


Figure 1.2: (a) The dimeric assembly formed in the case of benzoic acid. (b) Hydrogen bonded one-dimensional tape formed by 1,4-benzenedicarboxyxlic acid and (c) the chicken-wire network formed in the case of 1,3,5-benzenetricarboxyxlic acid.

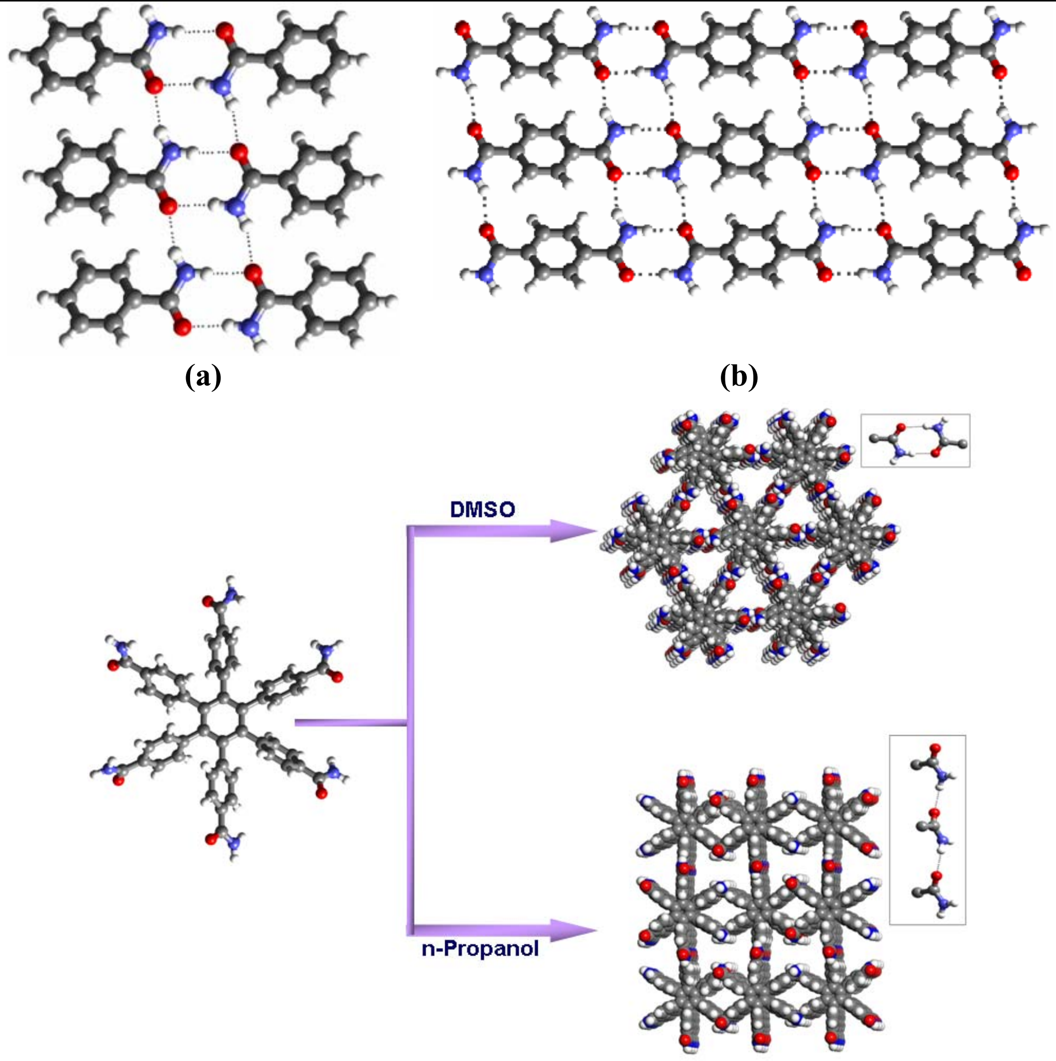
Molecules with multiple hydrogen-bonding sites are known to form well-defined supramolecular networks. In this respect, assemblies based on carboxylic acids (-COOH) are well studied due to the robust hydrogen bonds it can form on its own as well as with appropriate receptors. Articulation of the discrete zero-dimensional dimer to yield exotic structures by the incorporation of multiple carboxylic acid group at appropriate sites on a molecule, for example mono, di and tri substituted benzoic acids (Figure 1.2), is one of the highly utilized strategy in the supramolecular synthesis.[27]

Another prominent class of compounds which find utility in the supramolecular synthesis is the primary amides. The most distinctive feature of primary amide group is the presence of hydrogen atoms at different orientations, *syn* and *anti*, with which they can yield a variety of hydrogen bond patterns. The commonly found hydrogen bonded motifs in primary amides are shown in the Scheme 1.5.

Scheme 1.5



Hydrogen bond patterns present in the solid state structures of some of the amides are shown in Figure 1.3. For example, simple molecules like benzamide and terephthalamide give dimeric pattern (see pattern A in Scheme 1.5), which further extend in two-dimension, as shown in Scheme 1.5B.[28] However, both dimers as well as catamers (pattern A and C shown in scheme 1.5) were observed in the solid state structure of hexakis(4-carbamoylphenyl)benzene, obtained upon crystallization from different solvents. Both the forms yielded porous network with varying topology in three-dimensional arrangement (Figure 1.3(c)).[29]



(a) **(b)**

(c)

Figure 1.3: Hydrogen bonding pattern present in the crystal structure of (a) benzamide and (b) terephthalamide. (c) Space-filling representation for three-dimensional hydrogen-bonded networks present in the solid state structures of the hexakis(4-carbamoylphenyl)benzene obtained from DMSO and n-propanol *(Guest solvents molecules are omitted for clarity).*

Crystalline molecular complexes, often referred as co-crystals, in which the interactions between the complimentary functional groups present on two or more different entities, are of particular interest due to their utility in designing assemblies with novel properties.[30] In this regard, several attempts were made to synthesize various binary and ternary complexes, by the careful selection of compounds with suitable functional groups, based on their propensity to form hydrogen bonds (Figure 1.4).[31]

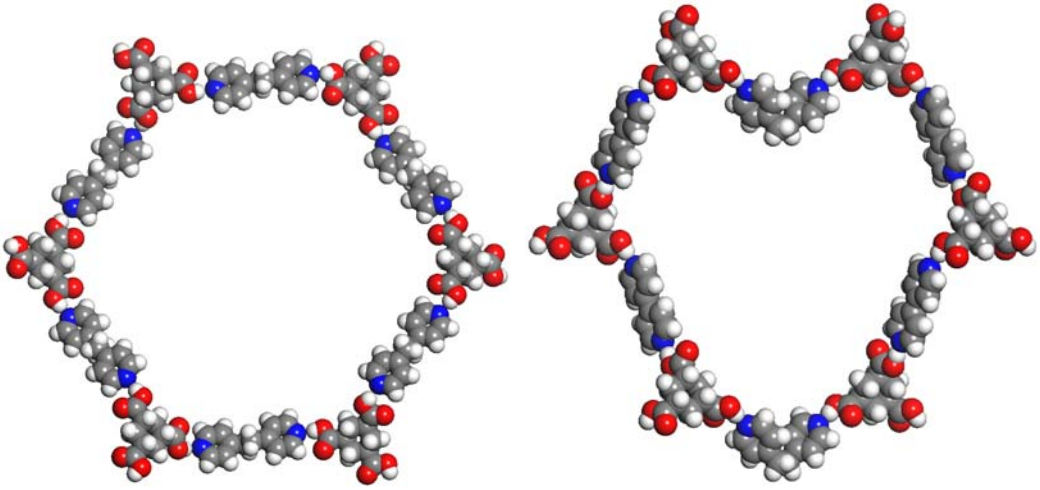
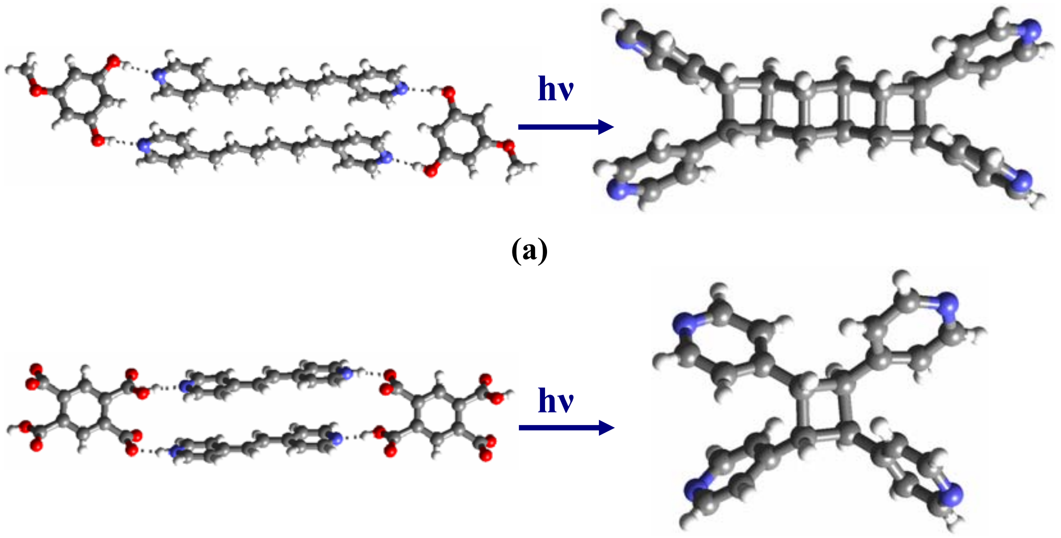


Figure 1.4: (a) Hexagonal assembly formed by 1,3,5-cyclohexanetricarboxylic acid and 1,2-bis(4-pyridyl)ethane. (b) The ternary complex, with necklace topology, obtained from 1,3,5-cyclohexanetricarboxylic acid, 4,4'-bipyridine and 1,2-bis(4-pyridyl)ethane.

Usually, co-crystals are synthesized by slow evaporation of the solution that contains stoichiometric amounts of the components (co-crystal formers). However, sublimation, growth from the melt, slurries, and grinding two solid co-crystal formers in a ball-mill etc., have been widely used in modern synthetic strategies.[32]

Co-crystals are not only exotic in terms of structural aspects, but also find great significance in carrying out unusual chemical transformations that otherwise appear to be either difficult or complex in nature.[33] In this regard, elegant studies by MacGillivray and co-workers demonstrated the facile synthesis of ladderanes by co-crystallization and subsequent photochemical irradiation of resorcinol and pyridyl substituted polyenes (Figure 1.5(a)).[34] Similarly, Jones and co-workers utilized the adducts of 1,2,4,5-benzenetetracarboxylic acid and the unsaturated *N*-donor molecule, *trans*-1,2-bis(4-pyridyl)ethene (Figure 1.5(b)), for the efficient [2+2] photo-addition reaction.[35]

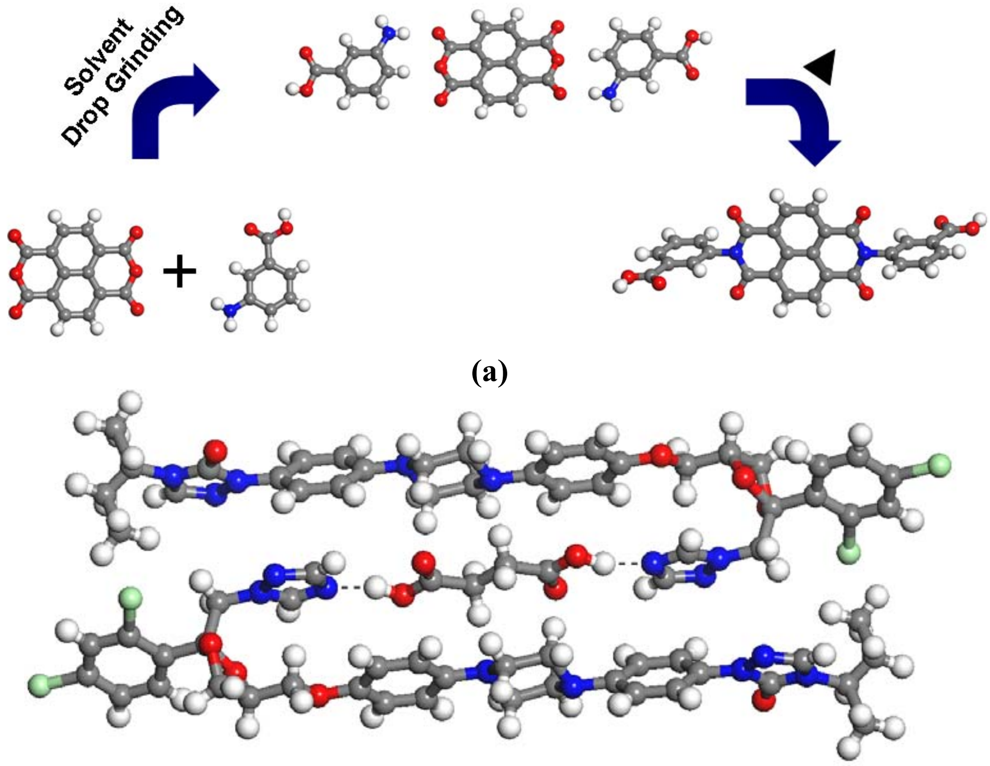


(a)

(b)

Figure 1.5: (a) Photochemical irradiation of the molecular complex 5-methoxyresorcinol and *trans*-1,6-bis(4-pyridyl)hexatriene yielded the [2+2] photodimerized product (ladderane) in 100% yield. (b) In the molecular complex of 1,2,4,5-benzentetracarboxylic acid and *trans*-1,2-bis(4-pyridyl)ethane, the acid molecules act as templates for bringing two olefinic bridges to reactive distance to carry out photodimerization reaction.

Controlled solid state synthesis using co-crystallization techniques offers broad potential in the context of green chemistry as well. Recently, Zaworotko et al. reported the solid state synthesis of imides via heating of the complex formed between an acid anhydride and aromatic amine co-crystal formers (Figure 1.6(a)).[36] Further, the preparation of co-crystals involving active pharmaceutical ingredients (APIs) attracted much attention in recent times and the strategy affords new paradigm in the formulation process of drugs, that might address several property issues in the context of drug development and delivery.[37] For example, co-crystallization of *itraconazole* (a water-insoluble antifungal drug) with succinic acid gave a complex which shows enhanced solubility than the pure drug molecule in either amorphous or crystalline form (Figure 1.6(b)).[38]



(a)

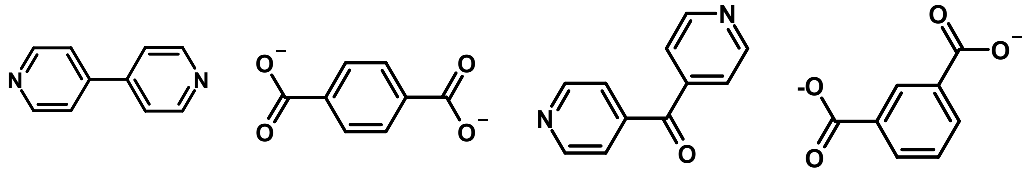
(b)

Figure 1.6: (a) A pictorial representation of the condensation reaction of 3-aminobenzoic acid and 1,4,5,8-naphthalenetetracarboxylic dianhydride *via* the co-crystal solvate, which dehydrates to generate the diimide after heating for 24hrs at 200^{o}C. (b) The crystal structure of itraconazole-succinic acid complex.

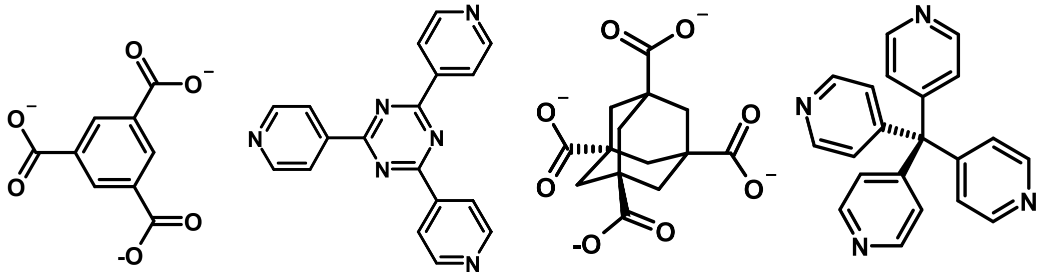
1.3.2 Coordination assemblies

Networks with exotic architectures can also be prepared by a strategy based on the coordinate bonds formed between metal centres and organic molecules containing multiple sites of coordination. In this process, often the metal ions in association with organic ligands, usually, provide control over the resulting topologies. Thus, based on the coordination geometry of the metal species and the ligand functionality under consideration, coordination polymers or metal–organic frameworks (MOFs) with varying architectures can be prepared.[39] Some of the organic ligands, that have been explored thoroughly for the preparation of the coordination assemblies, are given in Scheme 1.6.

Scheme 1.6



Linear connectors **Angular connectors**



2D (trigonal) connectors **3D (tetrahedral) connectors**

Metal-directed assemblies are not only elegant for the generation of well-defined discrete structures, but also show potential applications in catalysis, anion recognition, selective separation etc.[40] The phrase, "coordination polymers" appeared in early 1960s, and since then versatile synthetic approaches have been developed for the preparation of targeted assemblies with potential applications.[41] However, only recently, an exponential growth of research activity is witnessed for the preparation of porous coordination polymers (PCPs).[42] Porous coordination polymers have a wide range of advantages, such as regular channel structures, controllable pore size, dynamic pores that respond to guest molecules, and unique surface potentials and functionality (Figure 1.7).[43]

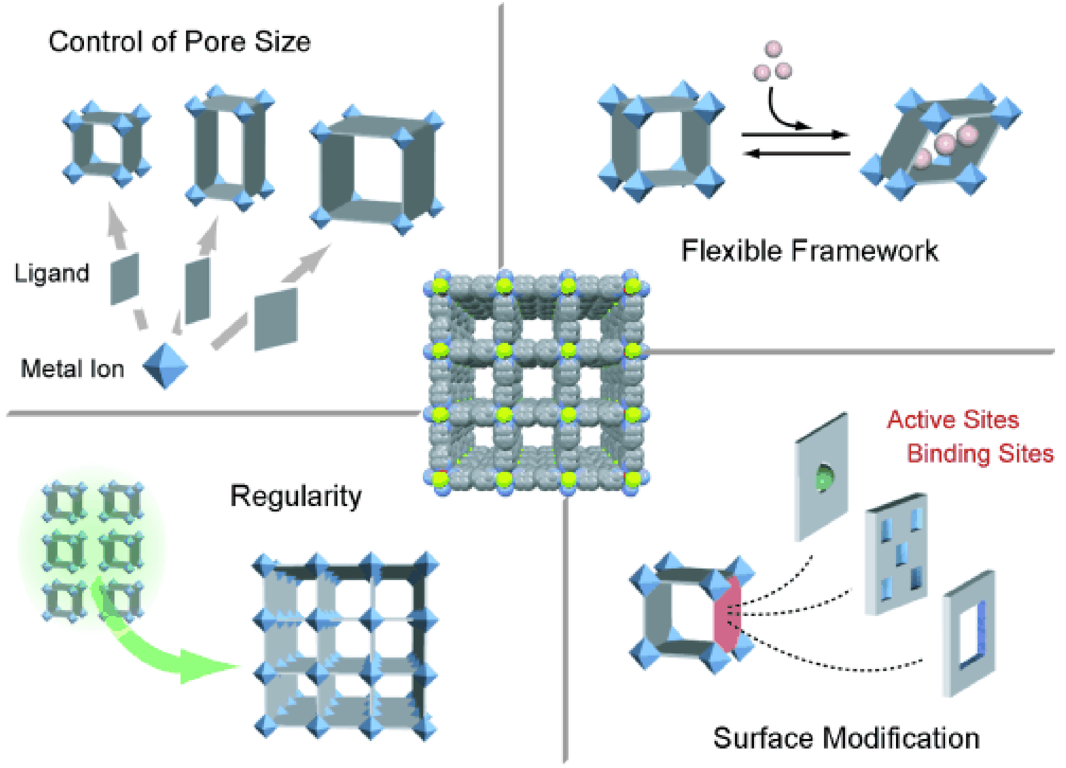


Figure 1.7: Characteristic functions of porous coordination polymers.

Considering the attractive features of porous coordination polymers, Kitagawa and co-workers demonstrated the utility of one-dimensional channels of the crystalline porous compound, [{M_2(1,4-benzenedicarboxylate)$_2$ triethylenediamine}$_n$], where, M=Cu^{2+} or Zn^{2+}, in the controlled polymerization reactions of styrene (Figure 1.8).[44]

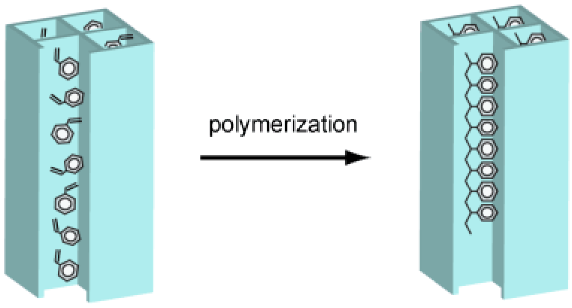
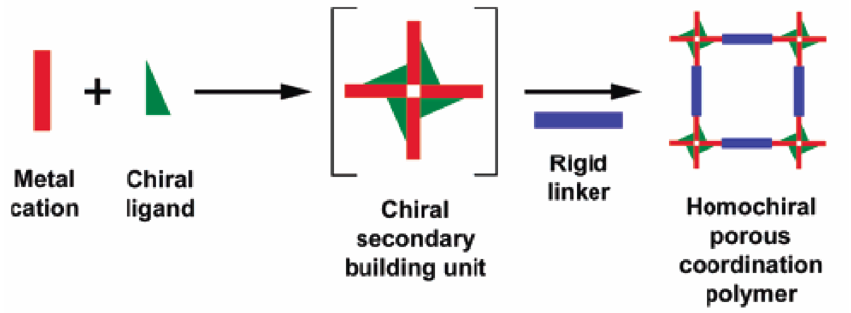


Figure 1.8: Schematic representation of the controlled polymerization in the one-dimensional nanochannels of porous coordination polymers

Homochiral porous coordination polymers, with regular asymmetric centers incorporated into the metal-organic framework, are another important class of assemblies, best suited for stereoselective catalytic activation in mild conditions and are also capable of stereoselective sorption and chiral resolution of racemic mixtures onto different enantiomers.[45,46] One of the significant constraints in the synthesis of porous homochiral structures is that organic bridging ligands, which are chiral, rigid, and lengthy enough to provide sufficient mechanical stability and porosity for the hybrid structure, are not available at ease. Recently, a novel approach for the rational synthesis of homochiral porous coordination polymers has been introduced (Scheme 1.7), in which the key feature is the utilization of two organic ligands simultaneously, with one of them bearing asymmetric centers, while the other one acting as a rigid spacer for the porosity of the metal-organic framework. Based on this strategy, Kim and co-workers reported the preparation of a framework, [Zn_2(1,4-benzenedicarboxylate)(L-lactate)(dmf)]·(dmf), which shows permanent porosity, size- and enantioselective guest-sorption properties as well as remarkable catalytic activity in the oxidation of thioethers to sulfoxides.[47]

Scheme 1.7



Preparation of materials with flexible and dynamic frameworks, in particular, that reversibly change their structures and properties in response to external stimuli have gained momentum in recent years.[48] In this direction, the metal–organic assembly, [Zn_2(1,4-benzenedicarboxylate)$_2$(1,4-diazabicyclo[2.2.2] octane)]·4DMF·$^1/_2H_2O$, serve as a representative example for unusual guest-dependent dynamic behavior (Figure 1.9). During the process of absorption and desorption, the complex with square channels changes to the rhombic channels, brought about by variations in the orientation of dicarboxylic acid linker molecules.[49]

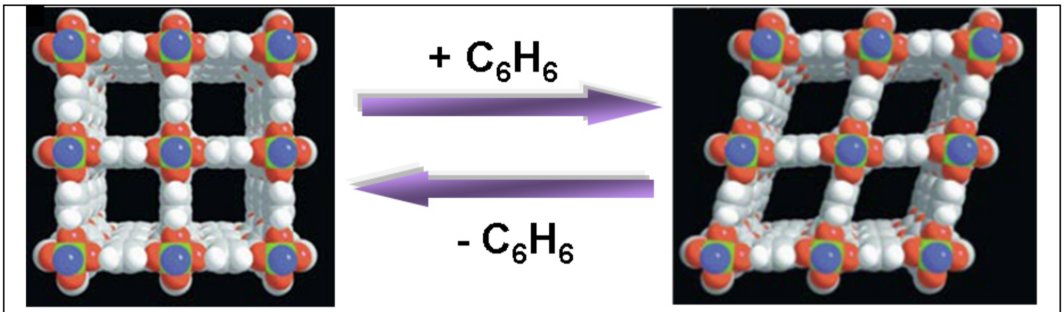


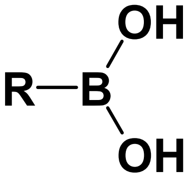
Figure 1.9: The schematic representation of the dynamic nature of channel upon adsorption and desorption of benzene guest molecules.

Thus, in the case of supramolecular assemblies, the topology and the properties are mainly governed by the reaction conditions and the building units involved in the recognition process. Of the various molecules studied in the preparation and analysis of supramolecular assemblies, a large number belongs to the recognition processes involving carboxylic acids, amides, alcohols, *N*-donor heterocycles etc. However, identification and utilization of new class of molecules, with appropriate donor-acceptor sites, for the preparation of supramolecular assemblies is always a challenging process. Towards this, in the recent times, there have been increased interest to utilize compounds like boronic acids, phosphonic acids, sulphonic acids etc.[50]

Boronic acids are class of compounds that are well studied in various organic transformations, but, its utility in supramolecular synthesis is unexplored, until we reported the organic assemblies of some aromatic boronic acids and their complexes with *N*-donor ligands, in the year 2003.[51] Since then several attempts were made to utilize the hydrogen bonding networks of boronic acids in the supramolecular synthesis and the recent developments in this direction are described in the following section.

1.4 An introduction to boronic acids

Boronic acids are trivalent boron containing organic compounds, which possess an alkyl/aryl substituent and two hydroxyl groups as shown below.



Where R=alkyl or aryl

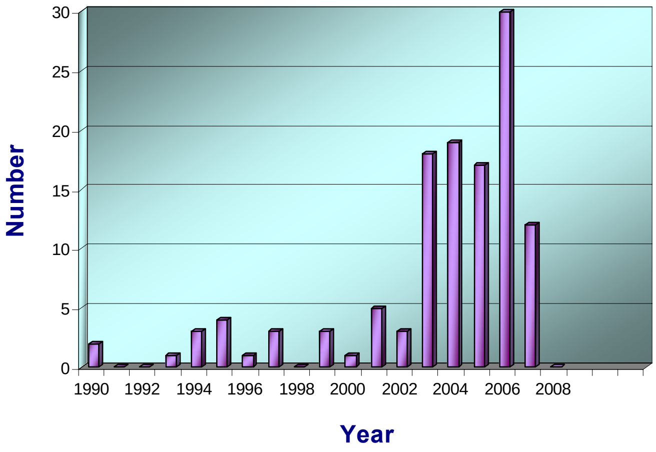
Since the first preparation and isolation of a boronic acid by Frankland in 1860, until the report of Pd-catalyzed cross coupling reaction with carbon halides by Suzuki and Miyaura in 1979, there have been limited advances in the study of boronic acids.[52,53] In recent times, boronic acids have been well explored as reactive intermediates in different synthetic strategies of C-C bond forming reactions, due to their unique properties like mild Lewis acidity, stability and ease of handling.[54] Because of the low toxicity and their ultimate degradation into the eco-friendly boric acid, boronic acids can be regarded as "green" compounds.[55]

Boronic acid in Suzuki-coupling reaction

$$\text{Ar'—B(OH)}_2 + \text{Ar''—X} \xrightarrow[\text{Base}]{\text{Pd catalyst}} \text{Ar'—Ar''}$$

The interest in boronic acids increased tremendously during the last few years due to their utility in the synthesis of biologically active compounds and also as pharmaceutical agents, in the form of enzyme inhibitors, for the treatment of cancer as boron neutron capture therapy (BNCT) agents, feedback controlled drug delivery polymers, saccharide sensors etc.[56,57]

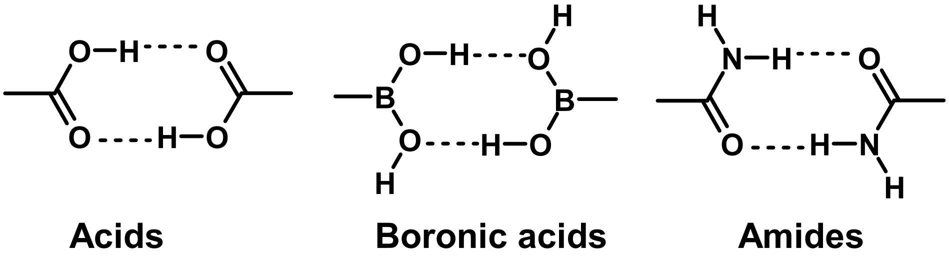
Graph 1.1



Although, the first crystal structure of boronic acid was reported in 1958, a systematic structural study of this class of compounds was unexplored, as evident from the database (CSD) analysis that was carried out in the early 2003.[58,59] The analysis revealed that, only a handful of structural reports were available for boronic acids and no supramolecular assemblies were reported. Nevertheless, a recent analysis (CSD version 5.2, 2008-January update) revealed tremendous growth of structural reports during the years 2003-2007, as shown in Graph 1.1.

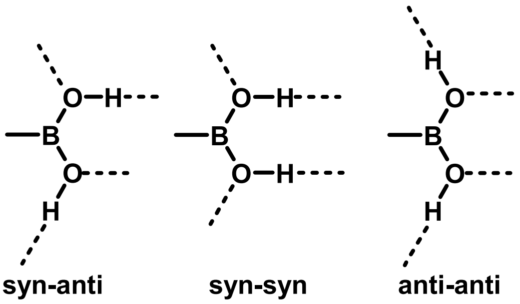
The boronic acid functional group, $–B(OH)_2$, find particular interest in the non-covalent synthesis due to the topological similarity of its hydrogen bond patterns with that of the carboxylic acid (–COOH) and carboxamides ($–CONH_2$), as shown in Scheme 1.8.

Scheme 1.8



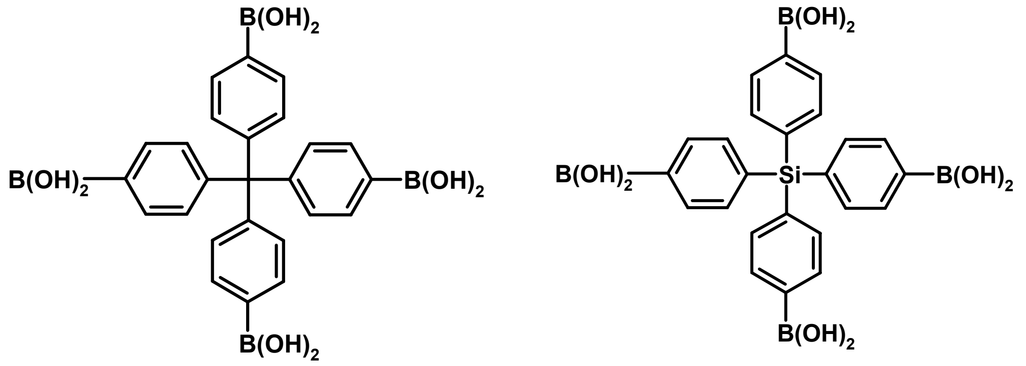
In addition, the $–B(OH)_2$ group, is known to exist in three different conformations (*syn-anti*, *syn-syn* and *anti-anti*) based on the position of the –OH functionality with respect to the C–B bond (Scheme 1.9).

Scheme 1.9



Thus, the formation of robust hydrogen-bonded networks together with the flexibility of the functional groups makes boronic acids as potential substrates to yield exotic supramolecular assemblies with novel topologies. In this direction, Wuest and co-workers reported stable frameworks with elegant diamondoid networks, obtained by the self-assembly of two tetraboronic acids. The molecules possess four –$B(OH)_2$ groups, oriented tetrahedrally around the cores derived from tetraphenylmethane and tetraphenylsilane (Scheme 1.10).[60]

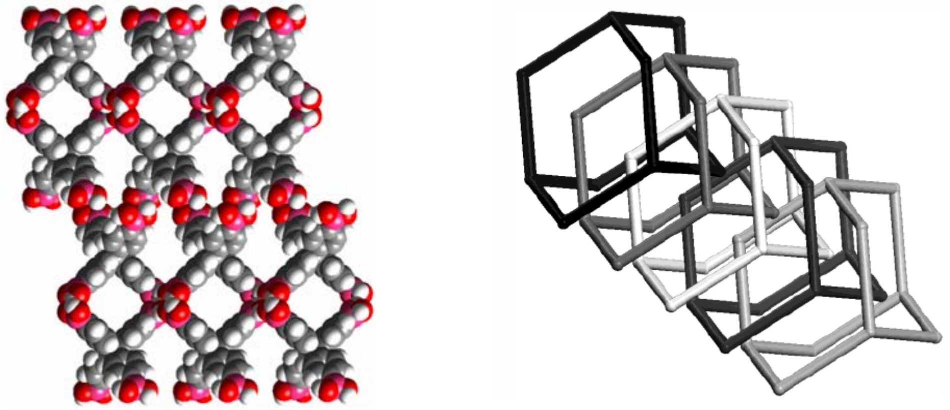
Scheme 1.10



(Methanetetrayltetra-4,1-phenylene) tetrakis boronic acid

(Silanetetrayltetra-4,1-phenylene) tetrakis boronic acid

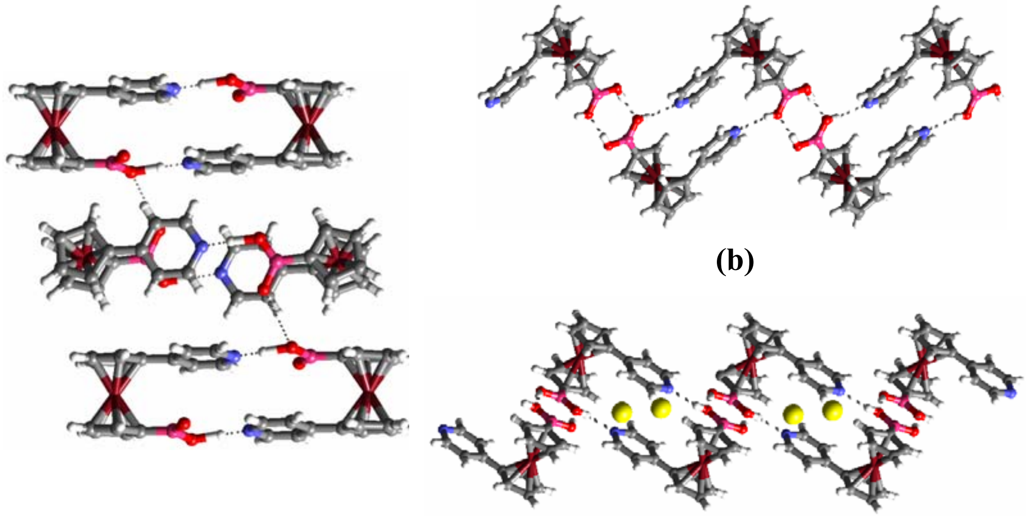
Further, solid state structural analysis of these tetraboronic acids reveals that more than 60% of volumes in the crystal lattices remain empty for the inclusion of guest molecules (Figure 1.10).



(a) (b)

Figure 1.10: (a) The network constructed by the arrangement of molecules in the boronic acid $C_{24}SiH_{24}B_4O_8$ and the (b) schematic representation of the 5-fold interpenetrated diamondoid networks.

In the year 2003, Braga and co-workers reported two anhydrous forms and a monohydrate form of 1'-(4-pyridyl)ferrocene-1-boronic acid, $[Fe(\eta^5\text{-}C_5H_4\text{-}4\text{-}C_5H_4N)(\eta^5\text{-}C_5H_4\text{-}B(OH)_2)]$.[61]



(b)

(a) **(c)**

Figure 1.11: (a) The dimers formed by O-H$\cdots$N interactions present in form-1. The basic recognition pattern observed in form-II & form-III are shown in (b) and (c). Water molecules present in the hydrate form are shown in yellow colour.

In the crystal structure of the first anhydrous form (form-I), obtained from CH_2Cl_2/CH_3OH mixture by slow evaporation at 4 °C, the ferrocenyl unit, in a *cisoid* conformation, forms centrosymmetric dimers through O-H$\cdots$N hydrogen bonds (Figure 1.11(a)). Two such dimeric units are linked through the lateral O-H$\cdots$O hydrogen bonds, formed by the –OH functionality at *anti*- position. In form-II (obtained from acetone by slow evaporation at 4 °C) the molecules are in staggered conformation and form O-H$\cdots$O hydrogen bonded dimers. These units, further, interact with the pyridyl acceptors through O-H$\cdots$N hydrogen bonds (Figure 1.11(b)). The hydrated form (form-III) shows similar hydrogen bonding pattern as that of from-II and the water molecules are trapped in the framework.

Similarly, Höpfl et al., reported the solid state structure of an anhydrous and a tetrahydrate form of the 1,4-benzenediboronic acid.[62] Interestingly, both the forms were obtained upon recrystallization of the boronic acid from water and the $–B(OH)_2$ moiety adopted *syn-anti* conformation. In the anhydrous form, the interaction between the boronic acid molecules is established through O-H$\cdots$O hydrogen bonds and formed an infinite sheet structure in two-dimension. The recognition pattern and three-dimensional packing of the molecules are shown in Figure 1.12(a) and (b), respectively.

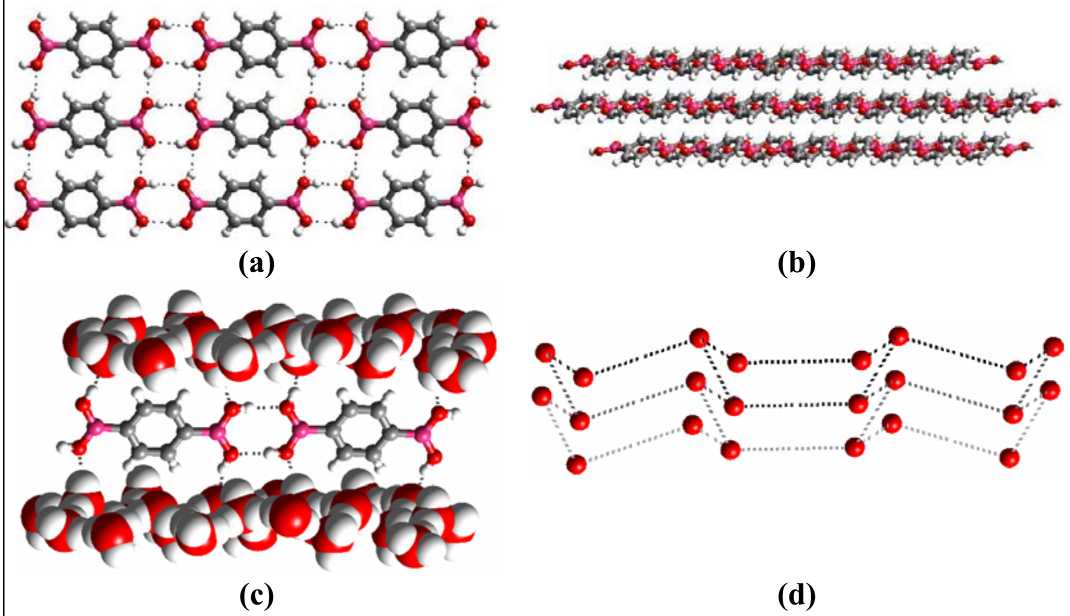


Figure 1.12: (a) The O-H$\cdots$O hydrogen bonds observed in the anhydrous form of 1,4-benzenediboronic acid leading to the formation of an infinite sheet structure in two-dimension. (b) Stacking of sheets in three-dimension. (c) The one-dimensional chains of 1,4-benzenediboronic acid molecules are inserted between the water layers. (d) 2D hydrogen-bonding pattern found in the water layer with hexameric rings that have both chair and boat conformations.

In the hydrated form, the boronic acid molecules form centrosymmetric dimers through O-H$\cdots$O hydrogen bonds, thus, leading to the formation of infinite one-dimensional chains. However, unlike in the anhydrous form, these chains are intercalated between the two-dimensional sheets of water molecules (Figure 1.12(c)). The water molecules present in the lattice interact with each other forming hexameric-rings of all-chair and all-boat conformations arranged alternately (Figure 1.12(d)).

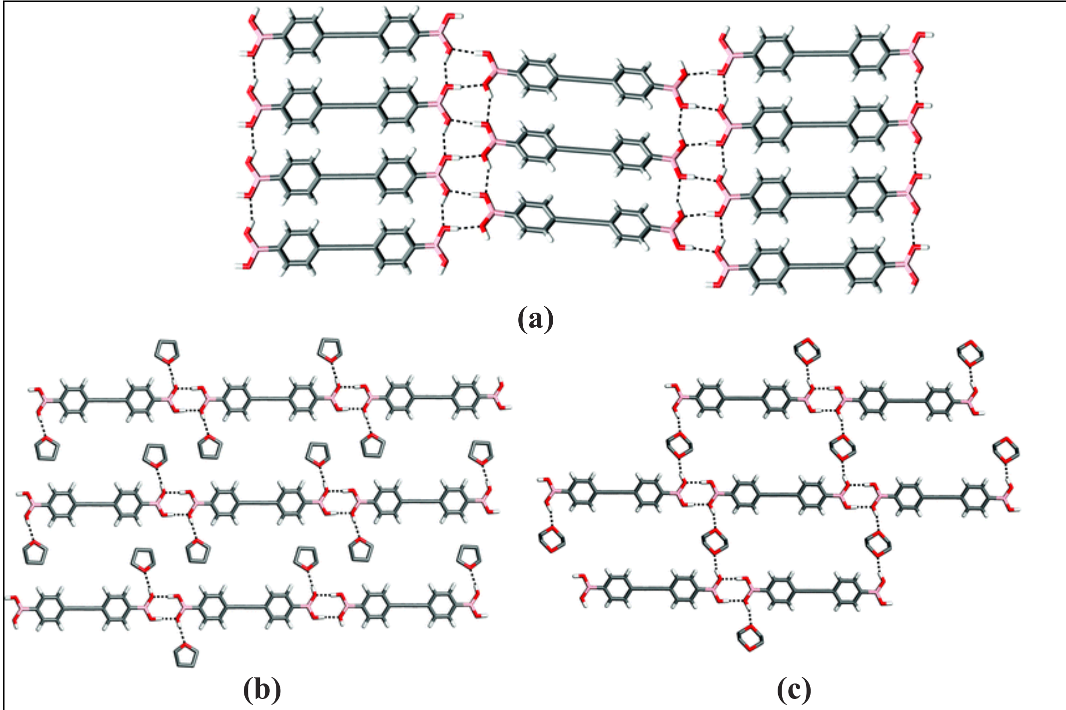
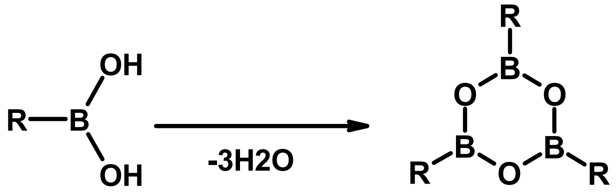


Figure 1.13: (a) Hydrogen-bonded sheet present in the crystal structure of diboronic acid grown from ethyl acetate. View of the hydrogen-bonded chains in the crystals grown from tetrahydrofuran and dioxane are given in (b) and (c) respectively.

Further, Wuest and coworkers reported various solid state forms of 1,2-ethynediylbis(1,4-benzene)diboronic acid.[63] While, the pure crystalline form was obtained from ethyl acetate, the solvated forms were obtained upon crystallization from tetrahydrofuran and dioxane, as the case may be. In the two-dimensional arrangement, the extended analogue also incorporates hydrogen-bonded sheets as observed in the case of 1,4-benzenediboronic acid. But, unlike the chains held together by the dimeric motif shown by –B(OH)$_2$ moiety in 1,4-benzenediboronic acid, in this case, the molecules interacts with each other through catameric hydrogen bonding, thus, forming infinite molecular chains. These molecular chains are further held together by O-H···O hydrogen bonds involving the –OH group at *syn*- position (Figure 1. 13(a)). In the solvated forms, molecules of the diboronic acid interact with two neighbouring units to form one-dimensional tapes through the formation of centrosymmetric O-H···O dimers. In both the structures, intervening solvent molecules (THF or dioxane) act as pendent units and are connected through O-H···O hydrogen bonds to the boronic acid backbone (Figure 1.13(b) and (c)).

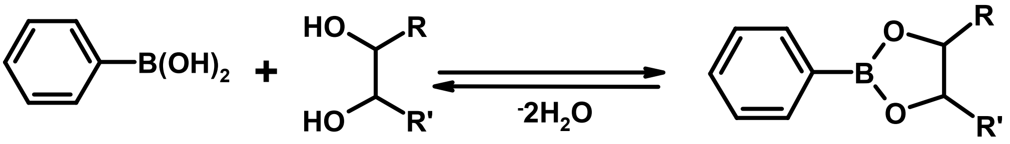
Boronic acids readily undergo dehydration to form cyclic trimeric anhydrides known as *boroxines* (Scheme 1.11).[64] This tends to occur spontaneously at room temperature, in which three boronic acid molecules converge to form a planar six-membered B_3O_3 ring, with the elimination of three water molecules.

Scheme 1.11



Further, the ease with which boronic acids react with diols (Scheme 1.12), has of great significance in the carbohydrate chemistry, especially, for the development of receptors and sensors for saccharides.[65]

Scheme 1.12



The conversion into the anhydride boroxine and the reversible boronate ester formation of boronic acids with vicinal diols took a new turn when Yaghi and co-workers utilized this property in the preparation of covalent organic frameworks (COFs).[66] For example, condensation of 1,4-benzenediboronic acid gave expanded porous graphitic layers which are staggered (COF-1, $P6_3/mmc$), while in the presence of hexahydroxytriphenylene, it forms an eclipsed structure (COF-5, $P6/mmm$), as shown in Figure 1.14(a) and (b), respectively.

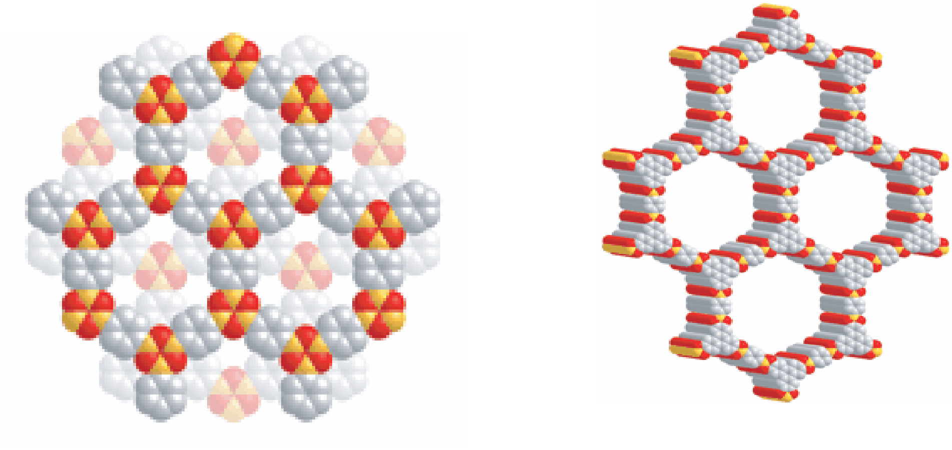
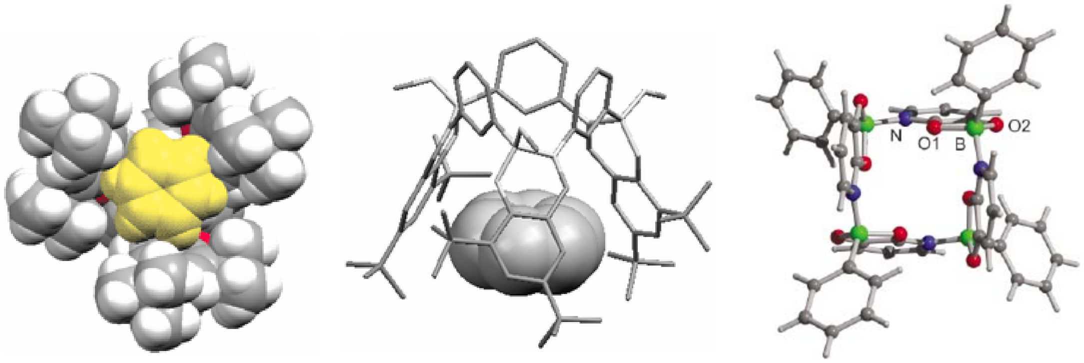

(a) **(b)**

Figure 1.14: Structural representations of (a) COF-1, possessing layers that are staggered and (b) COF-5, possessing eclipsed layers based on powder diffraction studies.

From the DFT calculations it was observed that the pores have dimensions ranging from 7 to 27Å and also show high thermal stability (up to 500 to 600 °C), permanent porosity and high surface areas.

The preparation and analysis of macrocyclic cage-like organic assemblies for their utilization in gas storage, separation and as host-guest materials are of great interest in the contemporary research fronts in materials chemistry.[67] While, traditionally calixarenes are extensively studied, boronic acid complexes with molecules containing –OH or –NH_2 functionalities are of current interest for the preparation of macrocyclic systems.[68] It is mainly due to the ability of boron compounds to react with nucleophilic reagents, because of the vacant *p*-orbital on boron, to yield tetravalent boron complexes. These novel features have been well utilized in the preparation of stable macrocyclic or cage-like assemblies for the supramolecular evaluation, as described below.

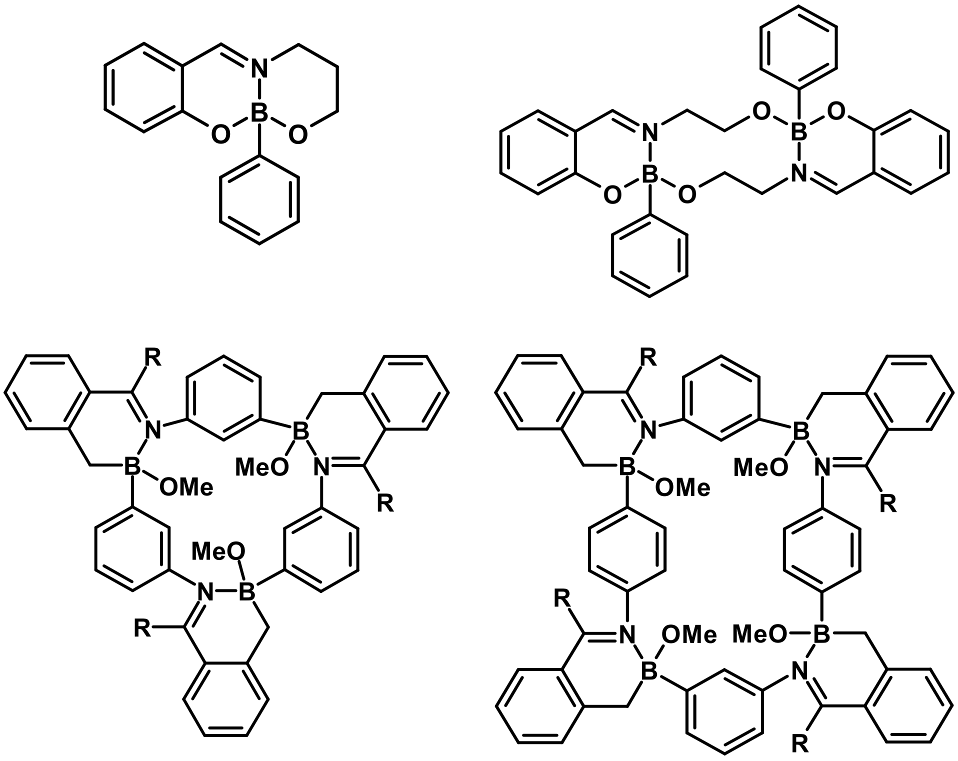


(a) **(b)** **(c)**

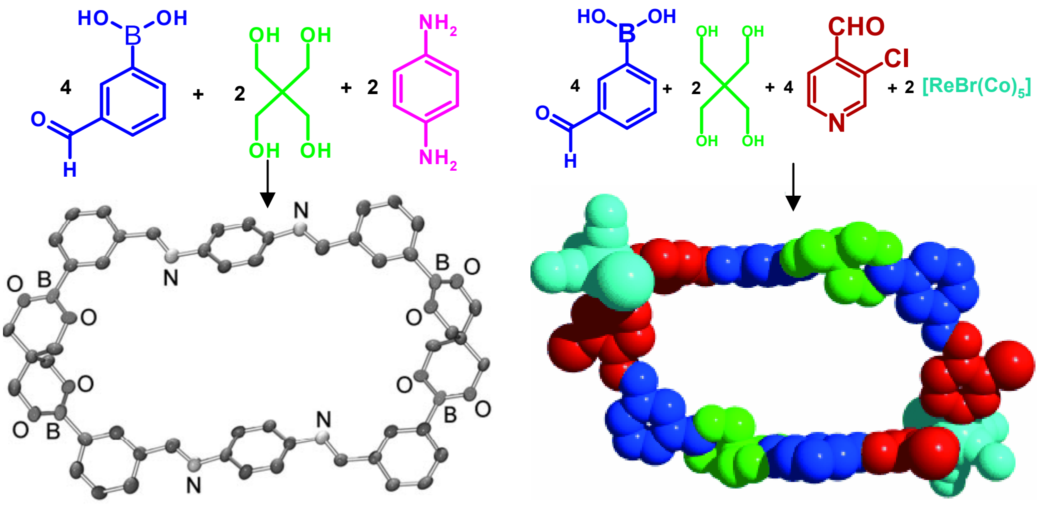
Figure 1.15: (a) Perspective view of the host-guest complex formed between the macrocycle and benzene (shown in yellow colour). (b) Side view of the macrocycle using a stick model for the host and a space-filling model for the guest. (c) The tetrameric macrocycle formed by the condensation of phenylboronic acid with 2,3-dihydroxypyridine

Preparation of a trimeric macrocyclic compound by simple condensation reaction of 3,5-di-*tert*-butyl salicylaldehyde and 3-aminophenylboronic acid was reported by Höpfl and co-workers (Figure 1.15(a) and (b)).[69] A detailed analysis of the structure confirmed that, the boron–nitrogen macrocycle adopts a cone-like conformation and the presence of a strong B–N bonds (having an average distance of 1.620 Å) was observed. The macrocycle, thus, formed exhibit good ability to form host-guest complexes, by the intake of solvents like THF, benzene, ethylacetate etc., as confirmed by ^{1}H NMR spectroscopy and x-ray crystallography. Another recurring example, reported in the recent literature, explains the formation of a tetrameric macrocycle formed by the condensation of phenylboronic acids with 2,3-dihydroxypyridine (Figure 1.15(c)).[70]

Scheme 1.13



Due to the effective and economic synthesis, there were several studies in the preparation of boron-containing macrocycles with varying dimensions such as monomeric, dimeric, trimeric, tetrameric etc. (Scheme 1.13). Such macrocycles have been effectively utilized in the molecular recognition studies and the recent developments have been compiled in a review.[71]



(a) **(b)**

Figure 1.16: (a) The macrocyclic structure obtained by the condensation of 3-formylphenylboronic acid, pentaerythritol, and 1,4-diaminobenzene from THF/toluene solution. (b) The metallamacrocycle obtained by the condensation of 3-aminophenylboronic acid with pentaerythritol, 4-formylpyridine, and [ReBr(CO)$_5$].

As shown by Severin and his co-workers, the one pot reaction of boronate ester formation with diols and imine condensation reactions of aldehydes have also been used to construct macrocyclic systems.[72] The macrocycle, shown in Figure 1.16(a), was formed by the condensation of 3-formylphenylboronic acid, pentaerythritol, and 1,4-diaminobenzene, in a 4:2:2 ratio, followed by the elimination of 12 water molecules. Also, the nanometer-sized macrocycles are prepared by employing the same method together with metal-ligand interactions (Figure 1.16(b)).

The above mentioned examples provide a vivid picture of the versatility of $–B(OH)_2$ functional group in the synthesis of various supramolecular assemblies. However, for the exhaustive exploration of $–B(OH)_2$ functionality for the creation of myriad of supramolecular assemblies with novel architectures, co-crystallization experiments with various strategies are essential.

1.5 Conclusions

Supramolecular chemistry, based on the intermolecular interaction, has developed into a coherent and extremely lively body of concepts and objectives, which incorporate ways and means for progressively unraveling the complexity of the matter through self-organization processes. This is evident from the vast ensemble of supramolecular assemblies available in the literature. For the preparation of assemblies with well-defined architecture and optimum properties, identification of the molecular building units possessing suitable functional groups is essential. In this regard, variety of functionalities like –COOH, $–CONH_2$, –OH etc. have been effectively utilized in the preparation and evaluation of the supramolecular assemblies. But, the utility of boronic acid functional group, $–B(OH)_2$, is not well unexplored, although there has been a growing interest of this novel class of compounds in non-covalent synthesis and much attention has to be given in this direction. The following chapters open a small window to the utility of this novel functionality in the non-covalent synthesis and give a systematic structural evaluation of various aromatic boronic acids and their utility in the preparation and evaluation of supramolecular assemblies.

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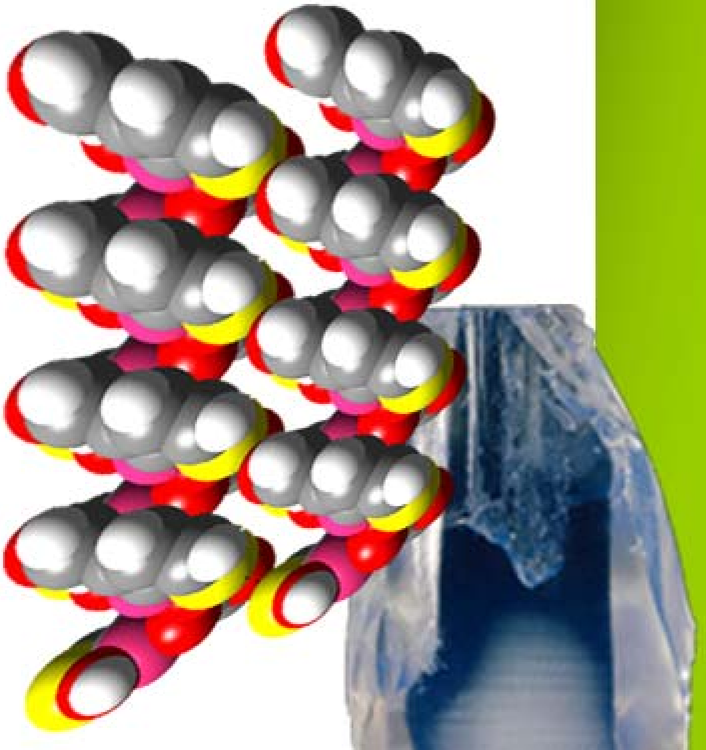
Chapter 2

Solid State Structure Analysis of Aromatic Boronic Acids and their Molecular Complexes

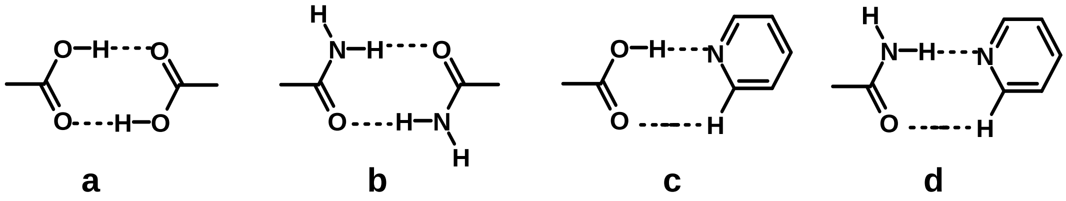


2.1 Introduction

Rapid technology developments in several analytical techniques such as x-ray diffraction, neutron diffraction, synchrotron radiation etc., and microscopic techniques like optical microscopy, SEM, TEM, AFM, STM etc., which are essential tool for the structural characterization of self-assembly of molecules in the sold state, has opened new horizons in the context of designing new materials with tailor-made properties and applications.[1] In particular, single crystal x-ray diffraction has been a powerful tool in the structure analysis of organic molecules and enabled the researchers to understand the principles of self-assembly and also to evaluate various intermolecular interactions involved in the process.[2] Such systematic studies, indeed, attributed qualification to the crystal as supermolecule "*a supermolecule par excellence*" and its assembly, governed by chemical and geometrical factors of individual molecules, is the perfect example of solid state molecular recognition.[3] Thus, creation of supramolecular assemblies through molecular recognition has evolved as a contemporary frontier area of research, in which different molecular entities are being aggregated through non-covalent interactions by co-crystallization process.[4]

Co-crystallization is a process of bringing different molecular species together into one periodic crystalline lattice.[5] As this technique has been proved to be quite efficient in the synthesis of novel supramolecular assemblies with unprecedented properties, such studies are prolific in the recent times.[6,7] In the preparation of co-crystals, one of the major challenges involved in the synthetic strategy is the selection of molecules with desired topology and complimentary functional groups. Literature analysis reveals that, among the different classes of compounds, *homomeric* assemblies of carboxylic acids or amides (Scheme 2.1(a) an d (b)) and their assemblies with *N*-donor ligands (Scheme 2.1(c) and (d)) have been well studied in the supramolecular synthesis.[8]

Scheme 2.1



For example, 1,3,5-benzenetricarboxylic acid (**BTC**) gives chicken wire networks (Figure 2.1(a)) through the formation of cyclic hydrogen bonding patterns, as shown in Scheme 2.1(a), while amides like 3,5-dinitrobenzamide (**DNBA**) forms extended one-dimensional chains (Figure 2.1(b)), by establishing centrosymmetric recognition patterns, as shown in Scheme 2.1(b).[9]

But, in the presence of various other substrates like *N*-donor ligands, the –COOH functional group tend to form *heteromeric* assembly, as observed in **BTC** and 4,4'-bipyridine complex (Figure 2.1(c)).[10] Further, functional groups like –OH, –SH, –NH_2, halogens (F, Cl, Br, I) etc., are also well studied in the non-covalent synthesis.[11]

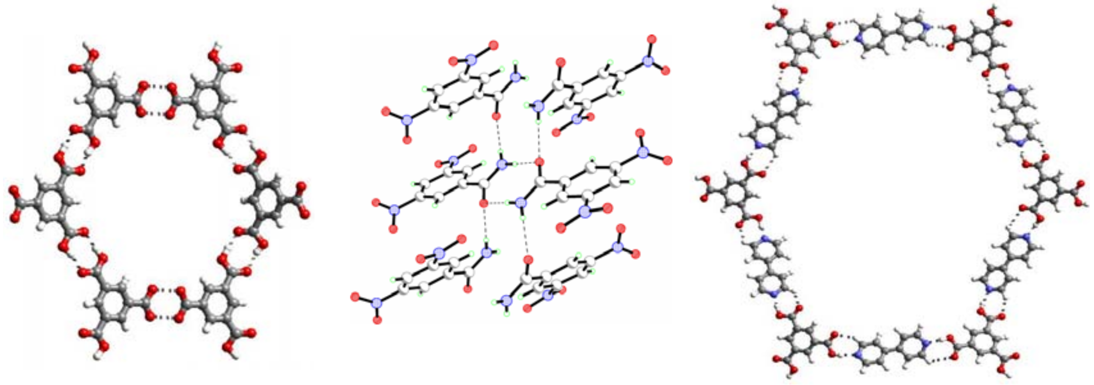


Figure 2.1: (a) Chicken wire networks formed by **BTC** in two-dimensional arrangement. (b) Aggregation of amide moieties in the structure of **DNBA**. (c) The *heteromeric* ensemble obtained by the co-crystallization of **BTC** and 4,4'-bipyridine.

Boronic acids, with a general representation R–B(OH)$_2$ (where R= alkyl or aryl), have been widely used in several biological processes as inhibitors of proteases, sensors for carbohydrates, etc.[12-13] This proves the inherent property of –B(OH)$_2$ functional moiety to form non-covalent bonds, since many of these processes proceed through molecular recognition. Hence, solid state structural analysis of some boronic acids and their molecular complexes with *N*-donor compounds have been carried out to demonstrate the efficiency of boronic acids in supramolecular synthesis. The observations are described in the following sections.

2.2 Influence of substituents and isomerism on the recognition pattern of boronic acid

In the solid state structure of phenylboronic acid, the molecules interact with each other to form dimers through centrosymmetric O-H$\cdots$O hydrogen bonds, involving the –B(OH)$_2$ functionality. This dimeric unit is further linked to four similar units through O-H···O hydrogen bonds, making use of the *anti* –OH functionality, to give an infinite array of tapes, arranged in a crossed-manner (Figure 2.2a). In the three-dimensional arrangement, the molecules yielded a close-packed structure, as shown in Figure 2.2(b).

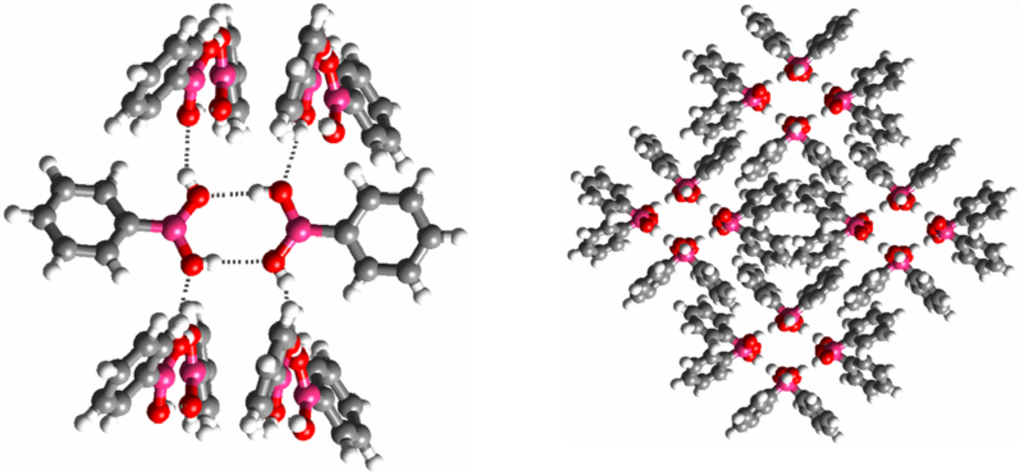
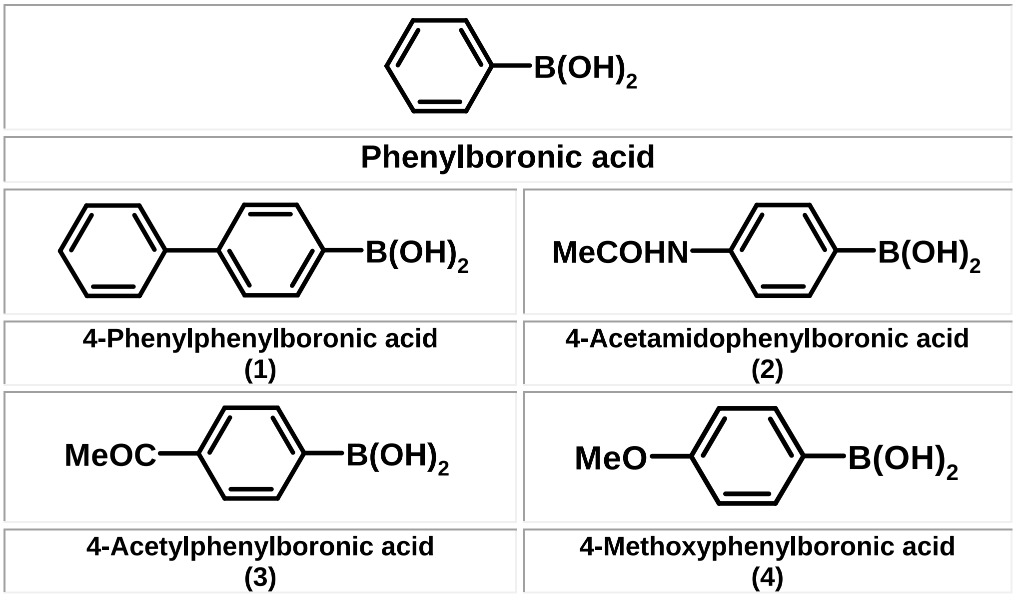


Figure 2.2: (a) The O-H···O hydrogen bonds observed in the crystal structure of phenylboronic acid. (b) Packing of molecules in the three-dimensional arrangement.

It is well-known from the literature that, the hydrogen bond forming ability of a functional group can greatly be influenced by the presence of other neighboring functional groups and this, in turn, can influence the topology of the resulting supramolecular assemblies.[15] Thus, by the judicious selection of functional groups, the intermolecular interactions involved in the recognition and stabilization of the assemblies can be tuned. Several studies regarding the substitution effect in the formation of supramolecular assemblies are known in the literature, but, such studies are rare in the case of boronic acids.

In this regard, to analyze the possible variations in the recognition pattern and three-dimensional architecture brought about by the influence of other functional groups, solid state structure analysis of some *para*-substituted derivatives of phenylboronic acids were carried out. Towards this, different boronic acid derivatives such as 4-phenylphenylboronic acid, **1**, 4-acetamidophenylboronic acid, **2,** 4-acetylphenylboronic acid, **3** and 4-methoxyphenylboronic acid, **4**, have been chosen to study the structural features in detail (Scheme 2.2).

Scheme 2.2

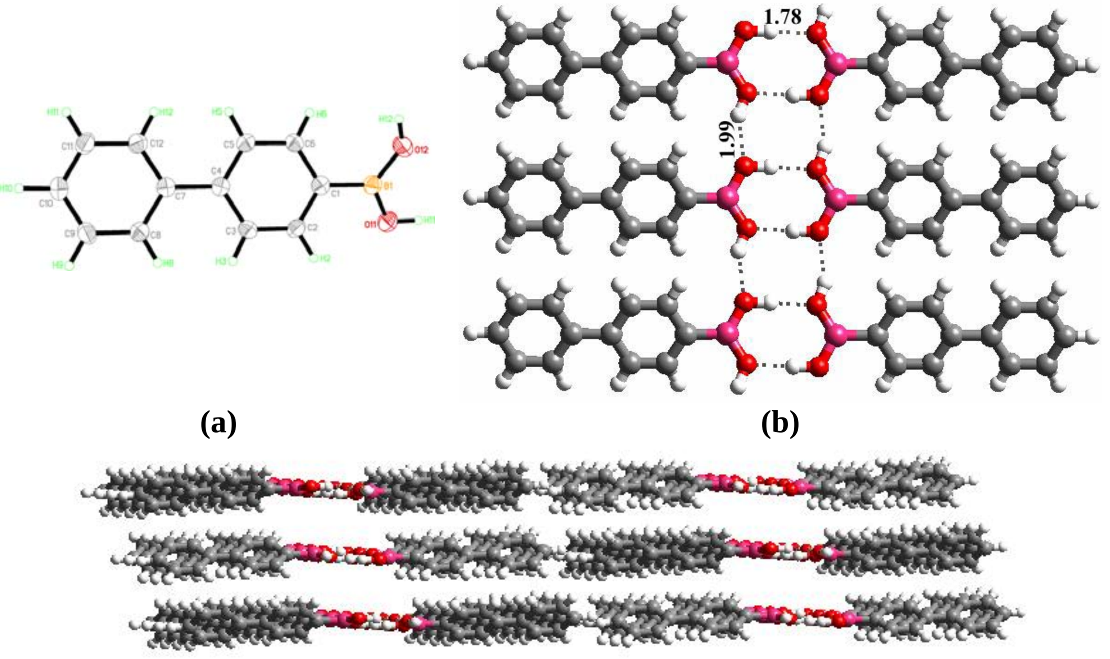


2.2.1 4-Phenylphenylboronic acid ($C_{12}H_{11}BO_2$), 1:

Analysis of the colorless block-type crystals of 4-phenylphenylboronic acid, **1**, obtained from methanol revealed that, the boronic acid functionality, $-B(OH)_2$, adopts *syn-anti* conformation (Figure 2.3(a)) and forms centrosymmetric O-H···O hydrogen bonded dimers (H···O, 1.78 Å), as observed in the crystal structure of phenylboronic acid. The crystallographic information and the details of intermolecular interactions are given in Table 2.1 and Table 2.2, respectively. Further, the adjacent dimers interact with each other to form a sheet-like structure in two-dimensional arrangement, through O-H···O hydrogen bonds (H···O, 1.99 Å). Thus, unlike in the case of phenylboronic acid, the solid state structure of **1** has a hydrogen bonding pattern similar to the one that commonly observed in many amides (Figure 2.3(b)).[16]

It was observed that, the biphenyl moiety and –$B(OH)_2$ functionality are inclined at an angle of 25^o and as a result, in addition to the O-H···O hydrogen bonds formed by the –$B(OH)_2$ functionality, the biphenyl moiety also contribute to the stabilization of the assembly by an edge type π···π (3.49Å) interaction. The layers, thus formed, stack in three-dimensional arrangement, stabilized by C-H···π (2.90Å) interactions formed between the molecules present in the adjacent layers (Figure 2.3(c)).

Although, the basic recognition pattern was not influenced to a great extent, the sterically demanding phenyl substitution at the *para*- position imparted significant variation in the three-dimensional arrangement, in comparison with phenylboronic acid. It may be due to the low tendency of phenyl moiety to compete in the hydrogen bond formation; but, its ability to involve in the formation of π···π and C-H···π interactions may have played a major role for the observed changes in the three-dimensional architecture.



(a) (b)

(c)

Figure 2.3: (a) The asymmetric unit of 4-phenylphenylboronic acid, **1**. (b) Molecular recognition pattern observed in the crystal structure of **1**. (c) Packing of molecules in three-dimension.

To further understand the effect of other functional groups on the recognition pattern of the –B(OH)$_2$ group, structural analysis of 4-acetamidophenylboronic acid, which has higher propensity to form hydrogen bonds, was carried out. Moreover, the compound 4-acetamidophenylboronic is a structural analogue of paracetamol, the well-known drug, in which the –OH group is replaced by the –B(OH)$_2$ group.[17]

2.2.2 4-Acetamidophenylboronic acid ($C_8H_{10}BNO_3$), 2:

In the solid state structure of 4-acetamidophenylboronic acid, **2**, the –B(OH)$_2$ functionality adopted *syn-anti* conformation (Figure 2.4), and the adjacent molecules form centrosymmetric dimers through O-H···O hydrogen bonds (H···O, 1.83 Å), as observed in the structure of phenylboronic acid.

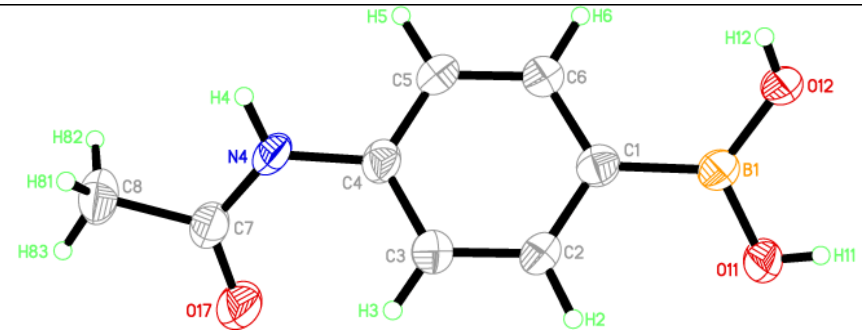


Figure 2.4: The asymmetric unit of 4-acetamidophenylboronic acid, **2**.

The resulting dimers, further, interact with two adjacent units through O-H···O hydrogen bonds (H···O, 1.90 Å), yielding a topology similar to the one observed in **1** **(**Figure 2.5(a)). The –NHCOCH$_3$ functionality establish N-H···O hydrogen bonds (H···O, 1.98 Å) through the self-complimentary –NHCO– units, juxtapositioned on the adjacent molecules. The interactions between the molecules, involving the –B(OH)$_2$ and –NHCOCH$_3$ groups, yielded a layered assembly and are stacked in the three-dimensional arrangement, as shown in Figure 2.5(b).

Thus, in the crystal lattice of **2**, each functional group (–B(OH)$_2$ and –NHCOCH$_3$) forms its own recognition patterns independently. It also appears from Figure 2.5(a) that, the complementarity of –NH– and –CO– groups within the acetamido functionality seemingly has preference for the *homomeric* recognition rather than the *heteromeric* interactions. It appears that, if the –NH– group was not available, then the carbonyl (>C=O) group, known for its ability to form stable hydrogen bonded networks, would have played a significant role in the formation of inter-functional group interactions. To augment the proposition, the structural elucidation and packing analysis of 4-acetylphenylboronic acid was carried out.

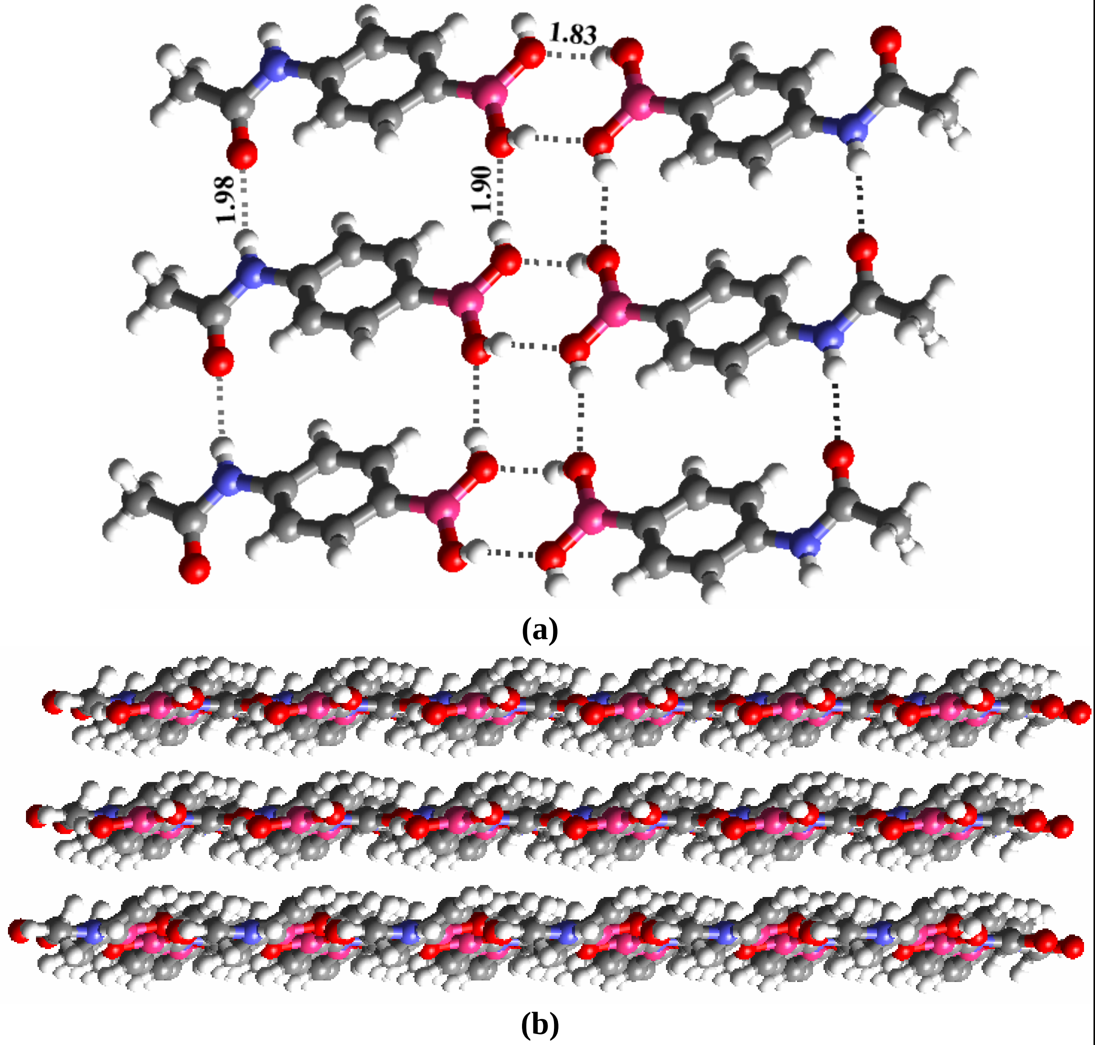


Figure 2.5: (a) The basic recognition pattern observed due to the self-assembly of molecules in the crystal structure of **2**. (b) Stacking of layers in three-dimensional arrangement.

2.2.3 4-Acetylphenylboronic acid ($C_8H_9BO_3$), 3:

4-Acetylphenylboronic acid, **3**, was dissolved in methanol and slow evaporation of the solution, at room temperature, yielded colorless block-type crystals.

X-ray diffraction studies revealed that, **3** crystallizes in orthorhombic (*Pbca*) space group and the –B(OH)$_2$ functionality is in *syn-anti* conformation (Figure 2.6).

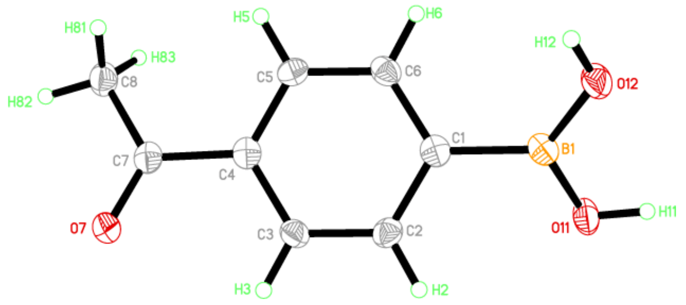
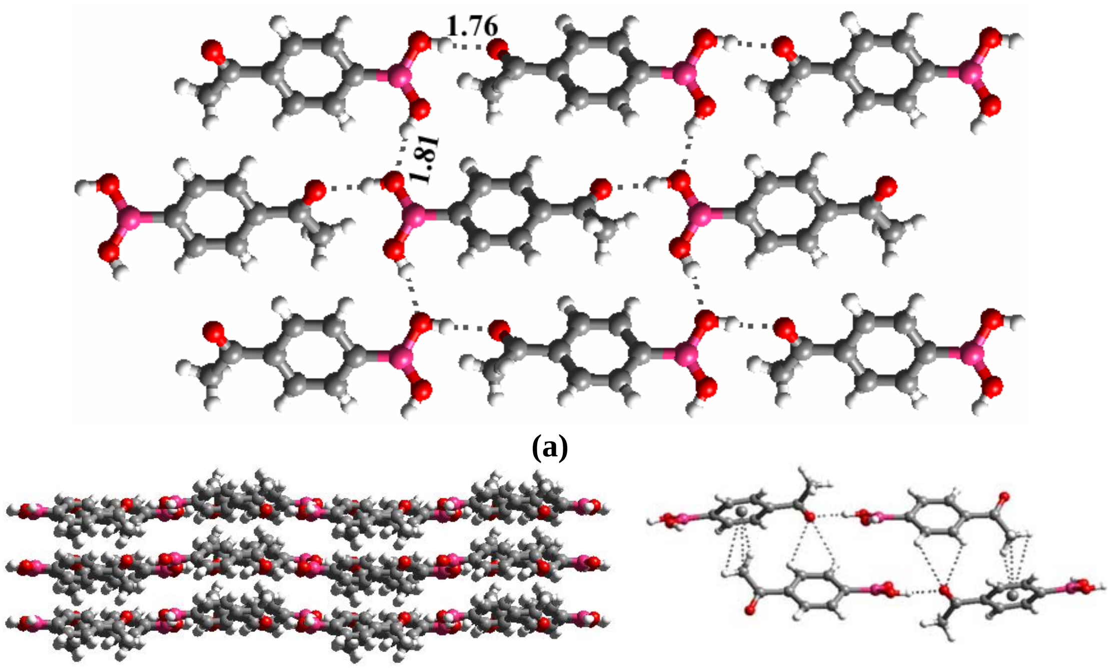


Figure 2.6: Asymmetric unit of 4-acetylphenylboronic acid, **3**.

In the structure of **3**, adjacent molecules interact with each other through O-H···O hydrogen bonds (H···O, 1.76Å), formed between the *syn* –OH moiety of –B(OH)$_2$ group and the carbonyl group of the acetyl functionality, yielding one-dimensional molecular tapes. The adjacent tapes are held together by catameric O-H···O hydrogen bonds (H···O, 1.81Å), involving the *anti* –OH group of the boronic acid. Such an aggregation gave a stacked-layered assembly (Figure 2.7(a)), in the three-dimensional arrangement. In addition, the structure is stabilized by C-H···O hydrogen bonds (H···O, 2.89 and 2.92Å) and C-H···π interactions (3.36Å), formed between the molecules present in the adjacent layers (Figure 2.7(c)).

Thus, by the introduction of acetyl functional group, having a strong hydrogen bond acceptor >C=O group at the *para-* position, the *homomeric* cyclic recognition pattern of the boronic acids has been intercepted. However, the –B(OH)$_2$ group plays a major role in the structural arrangement, through the formation of catameric hydrogen bonds involving the *anti* –OH group.



(a)

(b) (c)

Figure 2.7: (a) The *syn–anti* conformation the –B(OH)$_2$ group yielded catameric interaction with the adjacent molecules in two-dimensional arrangement. (b) Stacking of layers in the three-dimensional crystal structure of **3**. (c) Representation of C-H···O hydrogen bonds and C-H···π interactions observed in the structure.

Furthermore, to evaluate the mutual influence of –B(OH)$_2$ group and other hydrogen bond forming moieties, crystal structure of 4-methoxyphenylboronic acid was determined, as –OCH$_3$ is also known to form different types of hydrogen bonds with complimentary groups.

2.2.4 4-Methoxyphenylboronic acid ($C_7H_9O_3B$), 4:

4-Methoxyphenylboronic acid, **4**, crystallizes in the monoclinic space group ($P2_1/n$) and the –B(OH)$_2$ group is in *syn-anti* conformation (Figure 2.8(a)). It adopts a stacked sheet-like structure in the three-dimensional arrangement, similar to the boronic acids, **1-3** (Figure 2.8(b)).

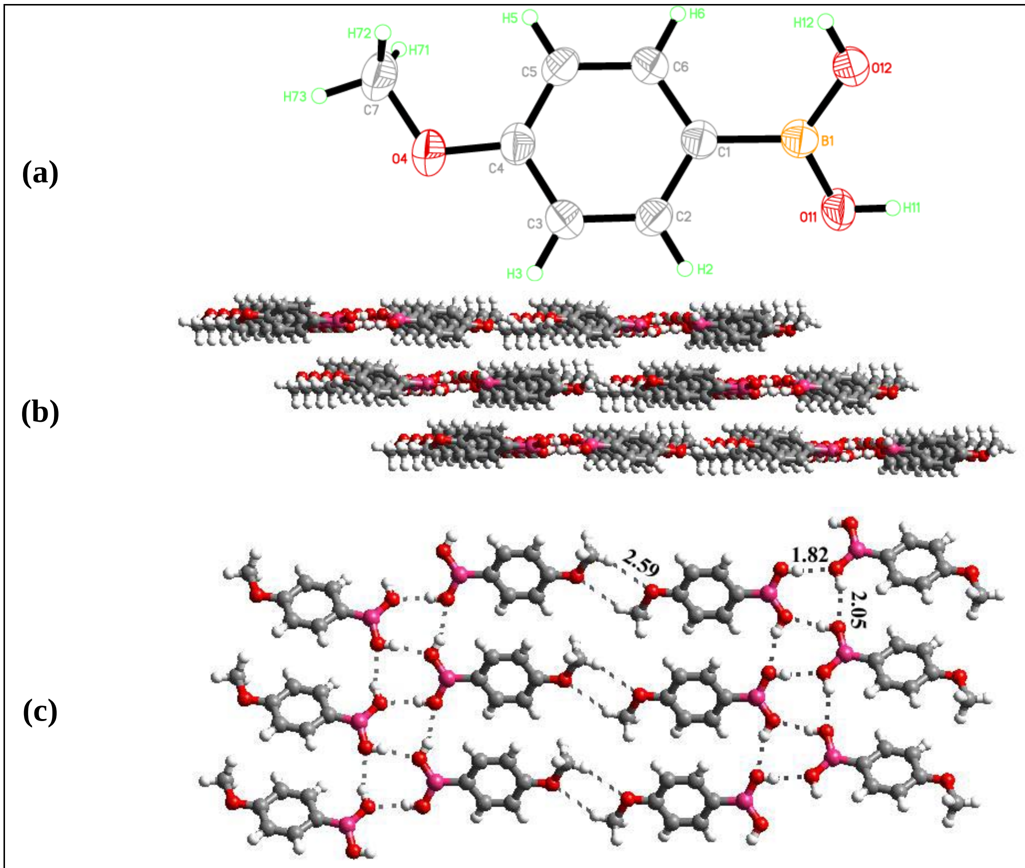


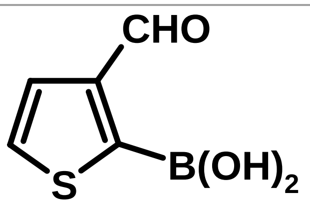
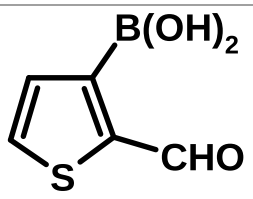
Figure 2.8: (a) Asymmetric unit of 4-methoxyphenylboronic acid, **4**. (b)Three-dimensional packing showing stacked layers of **4**. (c) The basic recognition pattern present in the 2-dimensional arrangement. Note the formation of cyclic C-H···O hydrogen bonds between –OCH_3 moieties.

But, in contrast to the centrosymmetric cyclic hydrogen bonding pattern observed in the earlier examples, in the crystal structure of **4**, boronic acid moieties form catameric O–H···O hydrogen bonds (H···O, 2.05Å), constituting linear chains of molecules. In the two-dimensional arrangement, such adjacent chains are held together by O–H···O and centrosymmetric C–H···O hydrogen bonds (H···O, 1.82, 2.59 Å), involving the –B(OH)$_2$ and –OCH$_3$ groups, respectively (Figure 2.8(c)).

The recognition patterns of the –B(OH)$_2$ group, indeed, show resemblance to the structure of 1,2-ethynediylbis(1,4-benzene)diboronic acid, recently reported by Wuest and co-workers.[18] Thus, the –OCH$_3$ group also show significant influence on the hydrogen bonding pattern of the –B(OH)$_2$ group as observed for –COCH$_3$ in the structure of **3**.

Thus, the study reveals the influence of functional groups, with varying ability to form hydrogen bonds, on the recognition pattern of the –B(OH)$_2$ functionality. In the supramolecular synthesis, not only the specificity of the substituents, but their position (isomers) can also bring about subtle variation in the recognition pattern and there by the three-dimensional arrangement.[19,20] However, there are only a few reports of the systematic studies regarding the influence of isomerism in the supramolecular synthesis.

In this regard, solid state structural analysis of the positional isomers involving –B(OH)$_2$ and other functionalities have been carried out by identifying two formyl-substituted thiopheneboronic acids (3-formyl-2-thiopheneboronic, **5** and 2-formyl-3-thiopheneboronic acids, **6**) for structure elucidation by x-ray diffraction studies (Scheme 2.3). The analysis of packing of molecules and hydrogen bonding patterns are discussed below.

Scheme 2.3	
	
3-Formyl-2-thiopheneboronic acid (5)	**2-Formyl-3-thiopheneboronic acid (6)**

2.2.5 3-Formyl-2-thiopheneboronic acid ($C_5H_5BO_3S$), 5:

The crystals of 3-formyl-2-thiopheneboronic acid, **5**, suitable for x-ray diffraction studies were obtained as colorless blocks, from an acetone solution by slow evaporation process at room temperature, over a period of two days. Structure analysis revealed that, **5** crystallizes in an orthorhombic system (*Pna*2_1) and the asymmetric unit is shown in Figure 2.9.

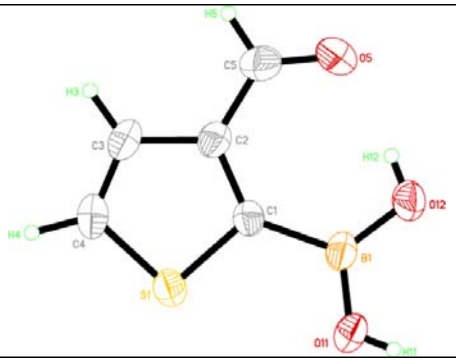
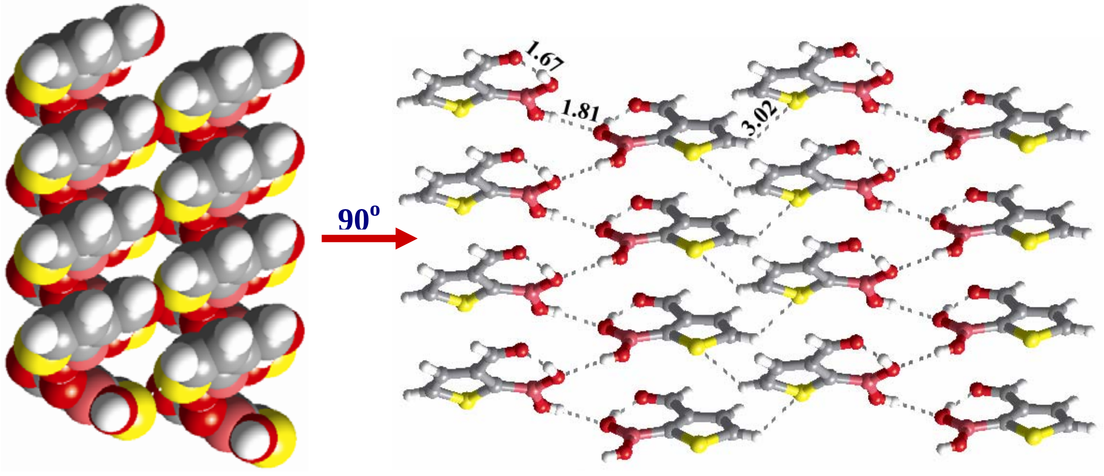


Figure 2.9: Asymmetric unit of 3-formyl-2-thiopheneboronic acid, **5**.

In the crystal structure of **5**, the –B(OH)$_2$ functionality adopts *syn-anti* conformation and the *anti* –OH group involves in an intramolecular O-H···O hydrogen bond (H···O, 1.67 Å) with the –CHO group.



(a) **(b)**

Figure 2.10: (a) Helical assembly observed in the crystal structure of **5** (view along *y*-axis). (b) The helices formed by O-H···O hydrogen bonds are further connected each other through C-H···S hydrogen bonds (view along *x*-axis).

In the crystal lattice, the molecules form an helical assembly, stabilized by catemeric O-H···O hydrogen bonds (H···O, 1.81Å) involving –B(OH)$_2$ group. Such helices, further, interact with each other by the C-H···S hydrogen bonds (H···S, 3.02 Å), involving the S-heteroatom and the aromatic C-H group (Figure 2.10).

2.2.6 2-Formyl-3-thiopheneboronic acid ($C_5H_5BO_3S$), 6:

The structure analysis revealed that, similar to the case of **5**, in the case of boronic acid **6**, the –B(OH)$_2$ functional group retains the *syn-anti* conformation and it is involved in the formation of intramolecular O-H···O hydrogen bonding (H···O, 1.68 Å) with the adjacent –CHO group (Figure 2.11(a)).

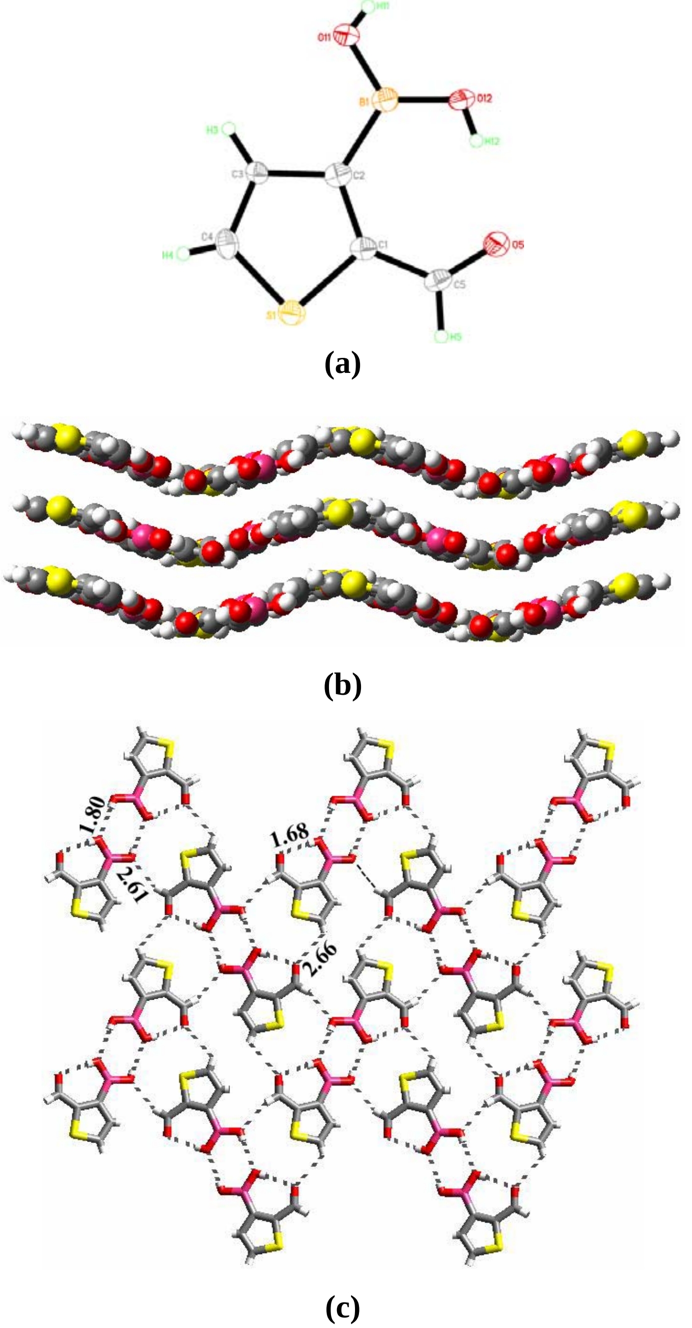


Figure 2.11: (a) An asymmetric unit of **6**. (b) The layered architecture obtained in the three-dimensional structure of **6**. (c) Hydrogen bonding pattern formed within a layer.

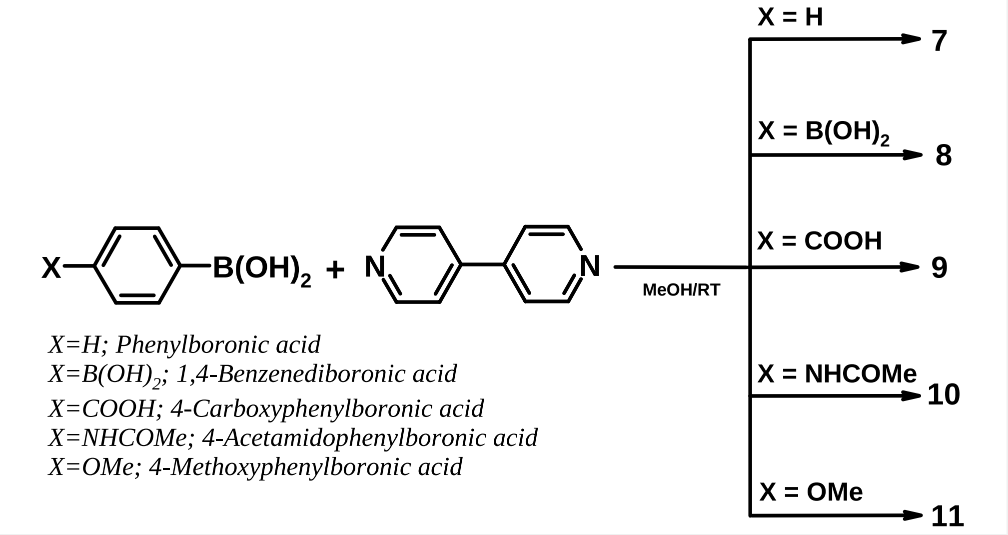
However, unlike the helical structure observed in **5**, in the crystal lattice of **6**, the molecules form corrugated sheet-like assembly that stack in the three-dimensional arrangement, as shown in Figure 2.11(b). Within a typical sheet, the adjacent molecules form dimers through centrosymmetric O-H···O hydrogen bonds (H···O, 1.80 Å), involving the $–B(OH)_2$ functional groups (Figure 2.11(c)). These dimers are further connected by C-H···O interactions (H···O, 2.61, 2.66 Å).

It is apparent from the structural analysis of the two isomeric thiopheneboronic acids that, the positional isomerism can induce a notable variation in the recognition and self-assembly process, which in turn can affect the resulting three-dimensional architecture. Also, the structural features of different boronic acids, **1**-**6**, reveals the flexibility of $–B(OH)_2$ group to form different types of hydrogen bonding networks, possibly being influenced by other functional groups, by nature and position. In fact, such tuning of non-covalent interactions would be of great advantage in the supramolecular synthesis to prepare assemblies with exotic networks. Hence, the preparation of molecular complexes mediated by $–B(OH)_2$ functionality have been carried out by co-crystallization technique, employing the *N*-donor ligand, 4,4'-bipyridine.

2.3 Molecular complexes of various boronic acids

In a typical co-crystallization experiment (Scheme 2.4), a boronic acid, as the case may be, and ***bpy*** were dissolved in a 1:1 molar ratio, in methanol. Slow evaporation of the respective solutions, at ambient conditions, yielded crystals of the complexes **7**-**11**, which were analyzed by single crystal x-ray diffraction technique. The basic recognition patterns and the influence of the substitution on the recognition as well as the three-dimensional arrangements are discussed in the following section.

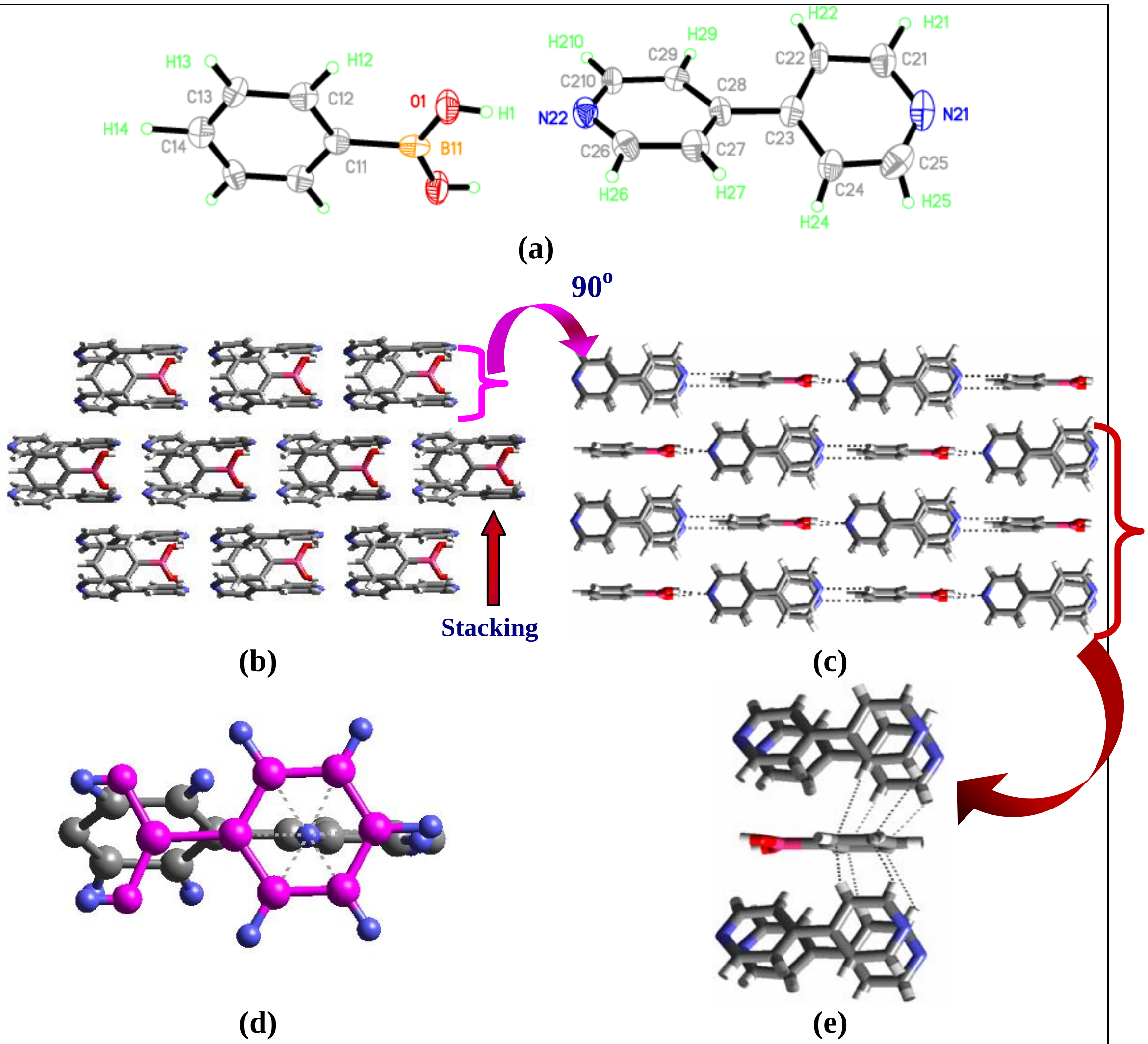
Scheme 2.4



X=H; Phenylboronic acid
X=B(OH)$_2$; 1,4-Benzenediboronic acid
X=COOH; 4-Carboxyphenylboronic acid
X=NHCOMe; 4-Acetamidophenylboronic acid
X=OMe; 4-Methoxyphenylboronic acid

2.3.1 Phenylboronic acid - 4,4'-bipyridine, $(C_6H_7O_2B):2(C_{10}H_8N_2)$, 7:

Co-crystallization of phenylboronic acid with 4,4'-bipyridine, ***bpy***, from methanol yielded a 1:2 molecular complex, **7**. The asymmetric unit of the complex is shown in Figure 2.12(a), in which the –B(OH)$_2$ moiety of the phenylboronic acid adopts a *syn*-*syn* conformation. The self-assembly of the molecules yielded a close packed structure in three-dimensional arrangement in which, the boronic acid molecules appear as sandwiched between the ***bpy*** units (Figure 2.12(b)). Further, each boronic acid molecule interacts with two ***bpy*** units through the formation of O-H$\cdots$N hydrogen bonds (H$\cdots$N, 1.86Å), involving the –B(OH)$_2$ group, thus, acting as a clip binding two ***bpy*** units. Interestingly, the second *N*-atom on ***bpy*** unit interacts with the phenyl C-H functionality, through C-H$\cdots$N hydrogen bonds (H$\cdots$N, 2.93 Å), forming a four-membered cyclic ensemble.



(a) (b) (c) (d) (e)

Figure 2.12: (a) Asymmetric unit of complex **7**. (b) Packing of molecules in the three-dimensional arrangement (*view along y-axis*). (c) The basic recognition pattern observed in the two-dimensional arrangement (*view along x-axis*). (d) and (e) C–H···π interaction observed between phenylboronic acid and ***bpy***.

The two-dimensional arrangement of the tapes is shown in Figure 2.12(c). In the crystal lattice, while the adjacent ***bpy*** molecules along the stacking direction are held together by an edge type π···π interactions (3.65 Å), the C–H···π interactions (2.89 Å) formed between C–H groups of ***bpy*** and the phenyl moiety of the boronic acid stabilize the adjacent tapes along the perpendicular direction to the stacking (Figure 2.12 (d) and (e), respectively).

Formation of the tetrameric cyclic unit through O-H···N and comparatively weaker C-H···N hydrogen bonds in the complex **7** is quite interesting, as such an ensemble could have been formed exclusively through the interaction of $–B(OH)_2$ group with both the *–N* atoms of ***bpy***. However, observed deviation appears to facilitate the formation of infinite one-dimensional tapes, which would not have been possible otherwise. It suggests that, if the *para-* position on phenylboronic acid is substituted by any functional moiety, with the ability to form hydrogen bond, would yield a similar structure. For this purpose, various *para-* substituted phenylboronic acids (see Scheme 2.4) have been co-crystallized with ***bpy***.

2.3.2 1,4-Benzenediboronic acid - 4,4'-bipyridine, $(C_6H_8B_2O_4)$:$2(C_{10}H_8N_2)$, 8:

1,4-Benzenediboronic acid (0.0165g, 0.1mmol) and ***bpy*** (0.0156g, 0.1mmol), yielded a 1:2 molecular complex, **8** (Figure 2.13). The crystallographic information is given in Table 2.5. As observed in complex **7**, structural analysis revealed that, both the $–B(OH)_2$ groups in complex **8** are in *syn-syn* conformation.

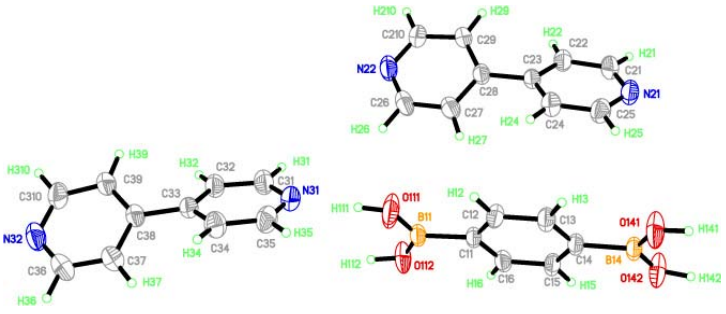
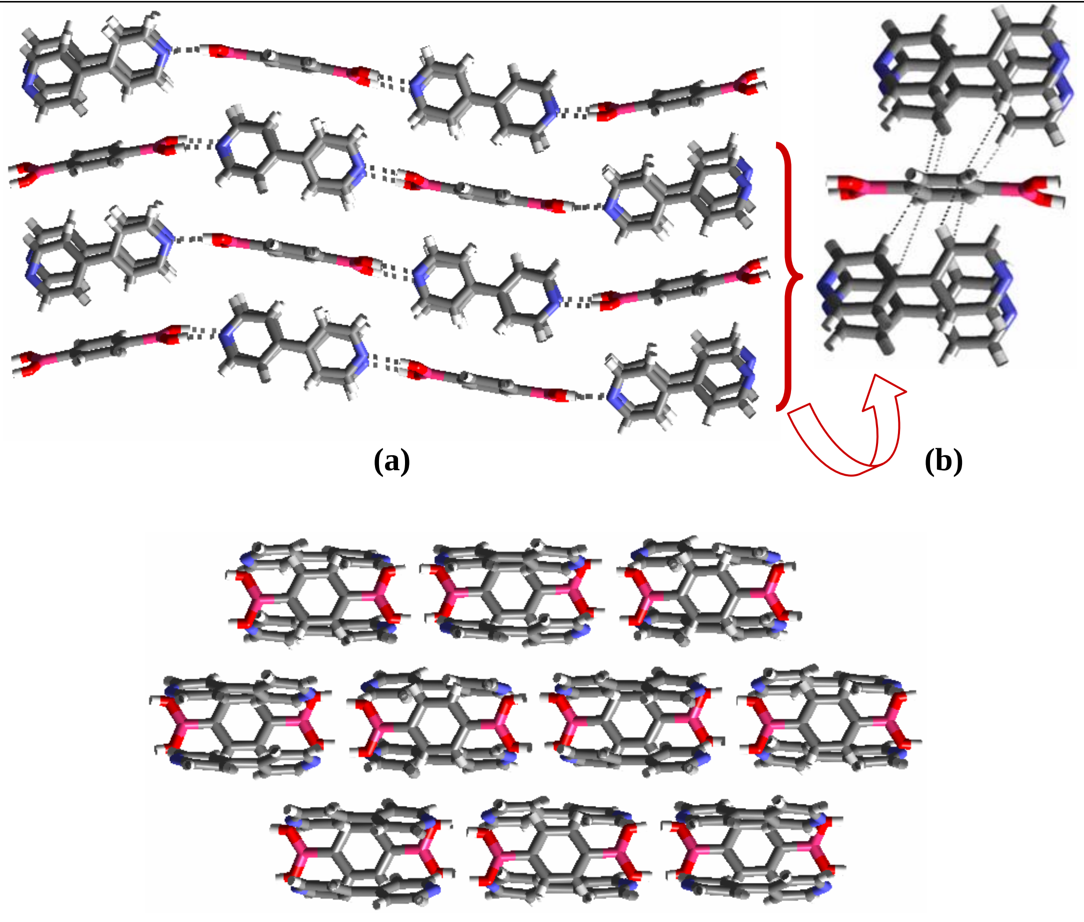


Figure 2.13: The asymmetric unit of the complex **8**.


(a)

(b)

(c)

Figure 2.14: (a) Two-dimensional arrangement of molecules in the complex **8** (*view along x-axis*). (b) C-H⋯π interaction formed between ***bpy*** and boronic acid molecules. (c) The three-dimensional arrangement of molecules (*view along y-axis*).

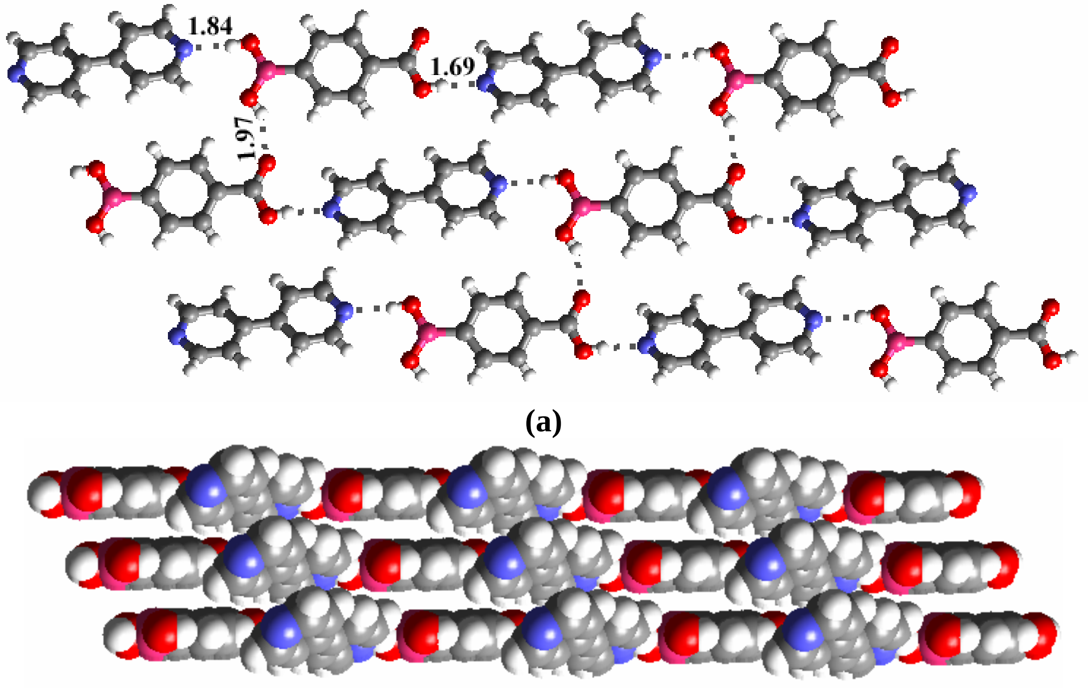
In addition, it was found that the complex **8** shows topologically similar recognition pattern, as observed in the complex **7**, with the formation of a four-membered supramolecular ensemble comprising two molecules each of boronic acid and ***bpy***. But unlike in **7**, both the hetero-atoms of ***bpy*** now interact with $–B(OH)_2$ functionality through O-H⋯N hydrogen bonds and these units further extend to form molecular tapes, as shown in Figure 2.14(a). In the two-dimensional arrangement, adjacent molecular tapes are stabilized by the C-H$\cdots\pi$ interactions (3.00 Å), formed between the boronic acid and ***bpy*** molecules (Figure 2.14(b)). These tapes are stacked in such a manner that, in the three-dimensional arrangement, the boronic acid molecules appear as sandwiched between the ***bpy*** units (Figure 2.14(c).

Thus, the structural analysis of **8** revealed its close relationship, in the recognition pattern as well as the three-dimensional assembly, with complexes formed between phenylboronic acid and ***bpy***.

2.3.3 4-Carboxyphenylboronic acid - 4,4'-bipyridine, $(C_7H_7BO_4)$:$(C_{10}H_8N_2)$, 9:[21]

Co-crystallization of 4-carboxyphenylboronic acid with ***bpy***, in methanol, gave complex, **9**, in which, the –$B(OH)_2$ unit is in *syn-anti* conformation and both the –$B(OH)_2$ and –COOH groups of the boronic acid molecule are involved in the recognition process.

In a typical assembly, each ***bpy*** molecule is connected to two boronic acid molecules, through O-H$\cdots$N hydrogen bonds (H$\cdots$N, 1.69, 1.84 Å) involving both the –$B(OH)_2$ and –COOH groups, forming one-dimensional tapes. In the two-dimensional arrangement, the adjacent tapes are held together by O-H$\cdots$O hydrogen bonds (H$\cdots$O, 1.97 Å), formed between –COOH and –$B(OH)_2$ group, constituting sheets, which are stacked in three-dimensional arrangement, as shown in Figure 2.15(b).



(a)

(b)

Figure 2.15: (a) The hydrogen-bonding pattern observed in the complex **9**. (b) Three-dimensional arrangement of molecules in the complex **9**.

The study reveals that, interactions between the –B(OH)$_2$ functionality and the *N*-donor ligands is similar to the assemblies formed between carboxylic acids and *aza*-donor compounds and it was further supported by the complexes formed by 4-acetamido and 4-methoxyphenyl boronic acids, as described below.

2.3.4 4-Acetamidophenylboronic acid - 4,4'-bipyridine, ($C_8H_{10}BNO_3$): ($C_{10}H_8N_2$): 2(H_2O), 10:

Molecular complex, **10**, was prepared by the co-crystallization of 4-acetamidophenylboronic acid (0.0178g, 0.1mmol) with ***bpy*** (0.0156g, 0.1mmol), from a methanolic solution (10 mL), by slow evaporation at room temperature. In the crystal lattice, the components are present in a 1:1 ratio along with two water molecules and the $–B(OH)_2$ group of the boronic acid adopts *syn-syn* conformation, as observed in the complexes **7** and **8** (Figure 2.16(a)). The crystallographic information is compiled in Table 2.5. Further, the interaction between the molecules of boronic acid and ***bpy*** is established through O-H···N hydrogen bonds (H···N, 1.79Å) and form a four-membered cyclic unit, as observed in the complex **8**.

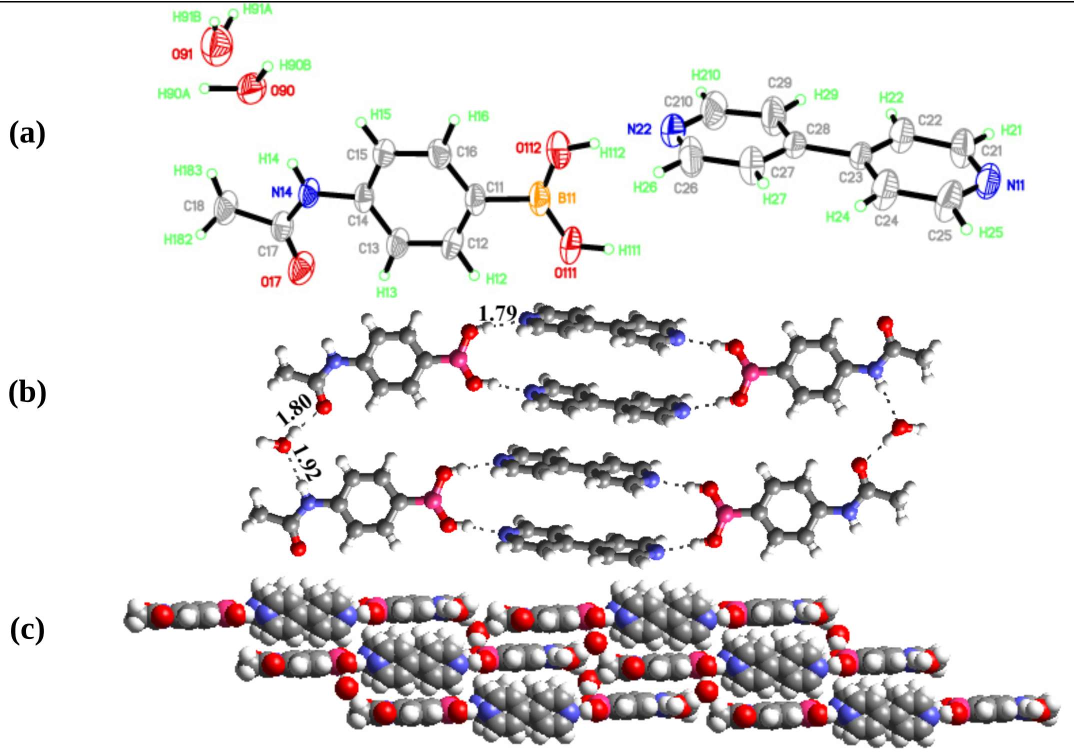


Figure 2.16: (a) The asymmetric unit of the complex **10**. (b) With the help of the water molecules present in the crystal lattice the cyclic tetrameric ensembles are further connected with each other in two-dimensional arrangement. (c) Packing of molecules in three-dimensional arrangement.

In the two-dimensional arrangement, similar units are further connected with each other through O-H···O as well as N-H···O hydrogen bonds (H···O, 1.80, 1.92 Å), involving the water molecules and the $–NHCOCH_3$ functionality (Figure 2.16(b)). In the three-dimensional arrangement, it forms a sheet-like structure (Figure 2.16(c)) and the molecules from the adjacent sheets are connected through various O-H···O and N-H···O hydrogen bonds (Table 2.6), formed between the lattice water and the boronic acid molecules.

2.3.5 4-Methoxyphenylboronic acid - 4,4'-bipyridine, $2(C_7H_9O_3B):(C_{10}H_8N_2)$,11:

Molecular complex **11**, with the composition, $2(C_7H_9O_3B):(C_{10}H_8N_2)$, was prepared by the co-crystallization of 4-methoxyphenylboronic acid (0.0151g, 0.1mmol) and ***bpy*** (0.0156g, 0.1mmol) from methanol, by slow evaporation of the solution at ambient conditions. Structure analysis of complex **11** has revealed several interesting features in both molecular and supramolecular aspects. It was found that, the $-OCH_3$ group as well as the –Ph moieties of the boronic acid and the pyridine rings of ***bpy*** are disordered, as shown in Figure 2.17.

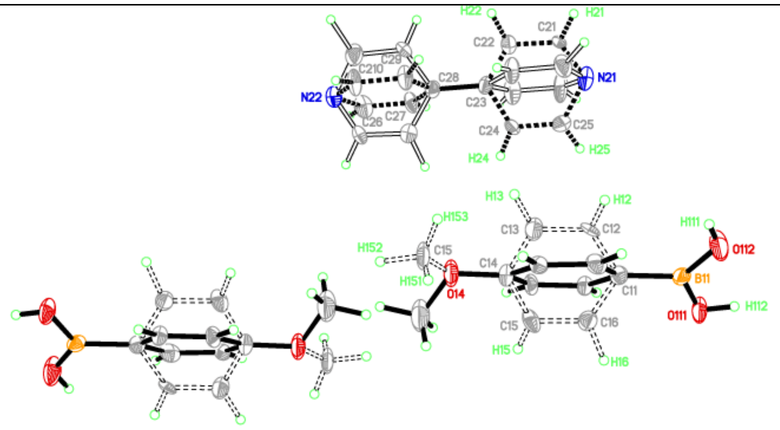


Figure 2.17: The asymmetric unit of the molecular complex **11**.

In complex **11**, the $-B(OH)_2$ group adopts *syn-anti* conformation and interact with ***bpy*** units through O-H···N hydrogen bonds (H···N, 1.79Å), involving the *syn* –OH group, as shown in Figure 2.18(a). Also a C-H···O (H···O, 2.74Å) hydrogen bond is observed between the aromatic C-H group and –B(OH)$_2$ moiety. Thus, O-H···N/C-H···O pair wise hydrogen bond patterns observed are similar to the one commonly found in the complexes of carboxylic acids and *N*-donor ligands.

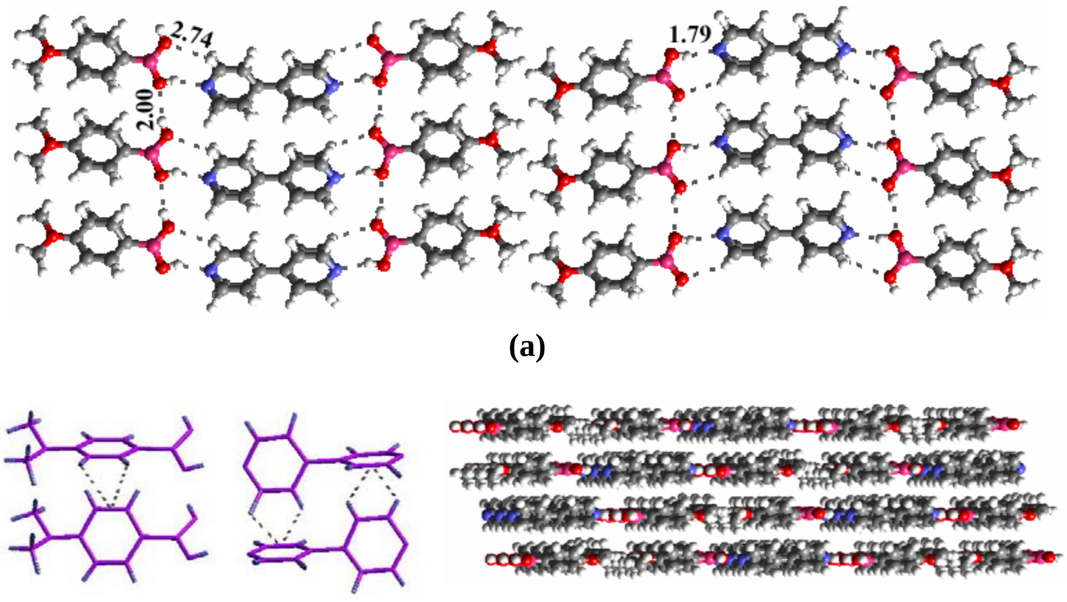


Figure 2.18: (a) The ladder-like assembly obtained by the O-H···N/C-H···O pair wise hydrogen bonds in the complex **11**. (b) The *homomeric* edge type C-H···π interaction observed in the complex **11**. (c) The three-dimensional packing of the complex **11**.

In a typical assembly, each ***bpy*** unit interacts with two boronic acid molecules, thus, forming a three-membered supramolecular entity. Adjacent three-membered units are held together by O-H···O hydrogen bonds (H···O, 2.00 Å) involving the *anti* –OH functionality, leading to the formation of a ladder-like assembly. In the two-dimensional arrangement, adjacent ladders are juxtaposed through hydrophobic interactions present between the $–CH_3$ group of the disordered $–OCH_3$ functionality. Within a sheet, due to the disorder, the molecules in different planes establish an edge type C–H···π interactions (2.40 and 3.12 Å), as illustrated in Figure 2.18(b). The stacking of sheets in the three-dimensional arrangement is shown in Figure 2.18(c).

Thus, in the molecular complex **11**, the $–OCH_3$ at the *para*- position did not play any significant role towards the formation of hydrogen bonds, unlike in its native structure wherein it formed centrosymmetric C-H···O hydrogen-bonded dimers.

From the structural analysis of the complexes **7-11**, it could be established that, even though the recognition of the $–B(OH)_2$ group towards the *N*-donor compound, ***bpy***, remains the same, different topological arrangements were obtained depending upon the ability of other functional groups in the formation of non-covalent bonds.

2.4 Conclusions

The study involves the analysis of structural features of various aromatic boronic acids and also their utility in the synthesis of supramolecular assemblies. It was observed that, the presence of functional groups such as –Ph, $–NHCOCH_3$, $–COCH_3$ and $–OCH_3$ with varying propensity to form hydrogen bonds, influence the basic recognition pattern of the $–(BOH)_2$ group, as well as the three-dimensional architecture. In addition to the substitution, the position of the functional group also has significant role in determining the molecular recognition, as observed in the isomers of formylthiopheneboronic acid.

Further, the ability of boronic acids in the preparation of binary complexes was highlighted by the structural analysis of molecular complexes of various boronic acids with 4,4'-bipyridine. It was observed that, hydrogen bonds formed by other functional groups also showed significant influence in the resulting topology and packing of molecules in the crystal lattice.

2.5 Experimental section

All the boronic acids used for the studies were obtained commercially and the crystallization experiments were carried out by dissolving them in spectroscopic grade methanol. Co-crystals **7-11** were prepared by dissolving the respective reactants in 1:1 ratio, in methanol, and allowing the solvent to evaporate under ambient conditions. In all the cases, single crystals were obtained over a period of one week.

A general procedure for the synthesis of complexes 7-11

In a typical co-crystallization experiment the *N*-donor ligand, ***bpy***, (0.156g, 0.100 mmol) and the boronic acid (0.100 mmol), as the case may be, were dissolved in methanol (10 mL) in a 25 mL conical flask. The resultant solution was allowed to evaporate under ambient conditions and colorless single crystals were obtained over a period of one week time. The crystals were separated from the mother liquor by filtration, washed with ice-cold methanol, and dried under vacuum.

X-ray crystallography

Good quality single crystals of the compounds **1-11** have been carefully chosen by viewing under a Leica microscope supported by a rotatable polarizing stage and a CCD camera. The crystals, thus, selected were glued to a thin glass fiber using an adhesive (cyanoacrylate) and mounted on a diffractometer equipped with an APEX

CCD area detector. The data were collected at 133K and the data collection was smooth in all the cases. The intensity data were processed using Bruker's suite of data processing programs (SAINT), and absorption corrections were applied using SADABS. The structure solution of all the complexes was carried out by direct methods, and the refinements were performed by full-matrix least-squares on F^2 using the SHELXTL suite of programs.[22] All the structures converged to good R factors. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms obtained from Fourier maps were refined isotropically. For all the structures, the intermolecular interactions were computed using the HBOND-NORM option of the PLATON program.[23]

Tables

Table 2.1: Crystallographic information of the structures **1-4**.

	1	2	3	4
Formula	$C_{12}H_{11}BO_2$	$C_8H_{10}BNO$	$C_8H_9BO_3$	$C_7H_9BO_3$
Formula Wt.	198.02	178.98	163.96	151.95
Crystal habit	Block	Block	Block	Needle
Crystal color	Colorless	Colorless	Colorless	Colorless
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	*Pbca*	$P2_1/n$
***a* (Å)**	23.450(7)	5.061(2)	9.774(1)	11.259(3)
***b* (Å)**	5.210(2)	7.203(2)	8.258(1)	5.064(1)
***c* (Å)**	8.090(2)	12.281(5)	19.777(4)	13.878(3)
α (°)	90.00	91.260(8)	90.00	90.00
β (°)	99.54(5)	100.060(5)	90.00	111.04(1)
γ (°)	90.00	98.430(5)	90.00	90.00
V (Å^3)	974.7(6)	435.5(3)	1596.3(4)	738.5(3)
Z	4	2	8	4
D_{calc} (g cm^{-3})	1.349	1.365	1.365	1.367
T(K)	133(2)	298	133(2)	133(2)
(λ)Mo K$_\alpha$	0.71073	0.71073	0.71073	0.71073
μ(mm^{-1})	0.089	0.102	0.101	0.103
2θ range (°)	46.56	46.54	46.50	46.58
Total Reflns.	5696	2632	6316	3009
Unique Reflns.	1402	1241	1144	1065
Reflns. Used	1191	1043	1020	876
No. Parameters	180	146	145	136
GOF on F^2	1.039	1.304	1.095	0.998
Final R_1, wR_2	0.0341, 0.0960	0.0736, 0.1936	0.0352, 0.0970	0.046, 0.082

Table 2.2: Characteristics of hydrogen bonds (distances/ Å and angles/°) [#]

Hydrogen bond (D-H···A)	1	2	3	4
O–H···O	1.78 2.76 173 1.99 2.90 153	1.83 2.79 164 1.90 2.84 158	1.76 2.74 172 1.81 2.77 165	1.82 2.80 171 2.05 2.90 143
N-H···O		1.98 2.97 164		
C-H···O			2.52 3.41 138 2.87 3.68 131 2.89 3.57 121 2.92 3.60 121	2.60 3.60 155

[#] The three numbers in each column indicate H···A(O), D(O/N/C)···A distances and D-H···A angles, respectively

Table 2.3: Crystallographic information for the structures **5** and **6**.

	5	6
Formula	$C_5H_5BO_3S$	$C_5H_5BO_3S$
Formula Wt.	155.96	155.96
Crystal habit	Block	Needle
Crystal color	Colorless	Colorless
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$P2_1/c$
a (Å)	12.632(9)	3.750(5)
b (Å)	13.454(9)	13.721(2)
c (Å)	3.866(3)	12.457(2)
α (°)	90.00	90.00
β (°)	90.00	96.10(2)
γ (°)	90.00	90.00
V (Å^3)	657.0(8)	637.3(9)
Z	4	4
D_{calc} (g cm^{-3})	1.577	1.625
T(K)	133(2)	133(2)
(λ)Mo K_α	0.71073	0.71073
μ(mm^{-1})	0.424	0.437
2θ range (°)	54.76	46.60
Total Reflns.	4864	4300
Unique Reflns.	1351	877
Reflns. Used	1312	804
No. Parameters	111	107
GOF on F^2	1.100	1.033
Final R_1, wR_2	0.0250, 0.0641	0.0492, 0.1326

Table 2.4: Characteristics of hydrogen bonds (distances/ Å and angles/°) #

Hydrogen bond (D-H···A)	5	6
O–H···O	1.67 2.64 168 1.81 2.78 173	1.68 2.65 170 1.80 2.78 172
C-H···O	2.40 3.17 127 2.69 3.75 166	2.61 3.44 133
C-H···S	3.02 3.80 129	

#The three numbers in each column indicate H···A(O/S), D(O/C)···A distances and D-H···A angles, respectively

Table 2.5: Crystallographic information for the complexes **7-11**.

	7	8	9	10	11
Formula	$(C_6H_7O_2B)$: $2(C_{10}H_8N_2)$	$C_6H_8B_2O_4$: $2(C_{10}H_8N_2)$	$(C_7H_7BO_4)$: $(C_{10}H_8N_2)$	$(C_8H_{10}BNO_3)$: $(C_{10}H_8N_2)$:$(2H_2O)$	$2(C_7H_9O_3B)$: $(C_{10}H_8N_2)$
Formula Wt.	434.29	478.11		370.19	460.09
Crystal habit	Needle	Needle	Needle	Needle	Needle
Crystal color	Colorless	Colorless	Colorless	Colorless	Colorless
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	*Fdd*2	$P2_1/c$	*P*1	$P\bar{1}$	*C*2/*c*
a **(Å)**	26.52(2)	14.981(3)	3.9552(8)	6.944	23.736(6)
b **(Å)**	9.245(8)	9.483(2)	8.362(1)	11.432	5.216(1)
c **(Å)**	17.612(2)	17.603(4)	11.670(2)	13.195	18.544(5)
α **(°)**	90.00	90.00	101.61(3)	74.29(2)	90.00
β **(°)**	90.00	107.13(1)	98.91(4)	77.76(2)	96.11(6)
γ **(°)**	90.00	90.00	98.04(4)	72.77(1)	90.00
V (Å^3)	4318.0(6)	2389.8(9)	367.59	953.1	2282.7(1)
Z	8	4	1	2	4
D_{calc} **(g cm^{-3})**	1.336	1.329	1.455	1.290	1.339
T**(K)**	133(2)	133(2)	133(2)	133(2)	133(2)
(λ)Mo K_α	0.71073	0.71073	0.71073	0.71073	0.71073
μ(mm^{-1})	0.086	0.090	0.094	0.094	0.095
2θ range (°)	46.66	50.00	50.00	50.00	46.52
Total Reflns.	4496	41782	7012	7012	4594
Unique Reflns.	1428	7252	3333	3333	1645
Reflns. Used	1300	4710	2785	2785	901
No. Parameters	197	421	328	328	340
GOF on F^2	1.030	0.995	1.044	1.044	0.802
Final R_1, wR_2	0.0522, 0.1271	0.0493, 0.1328	0.0446, 0.0446	0.0435, 0.1328	0.0463, 0.0819

Table 2.6: Characteristics of hydrogen bonds (distances/ Å and angles/º) #

Hydrogen bond (D-H···A)	Complex				
	7	8	9	10	11
O–H···O			1.97 2.84 146	1.80 2.78 170 1.81 2.79 171 1.90 2.87 169	2.00 2.95 162
O–H···N	1.86 2.83 167	1.79 2.76 167 1.81 2.79 173 1.83 2.80 166 1.84 2.81 170	1.69 2.67 173 1.84 2.81 172	1.79 2.77 177	1.79 2.74 159
N-H···O				1.92 2.93 169	
C-H···O			2.45 3.50 163 2.63 3.66 159		
C-H···N	2.93 3.58 128				

#The three numbers in each column indicate H···A(O/N), D(O/N/C)···A distances and D-H···A angles, respectively.

2.6 References

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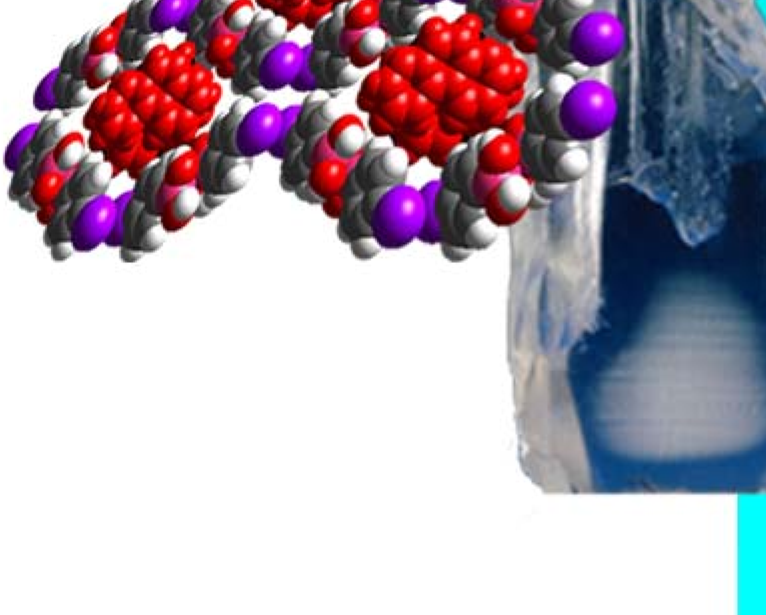
Chapter 3

Supramolecular Assemblies of 4-Halophenylboronic Acids



3.1 Introduction

In general, variations in the packing of molecules in the crystals are accomplished by the conformational flexibility of the molecule and various intermolecular interactions formed between the complimentary functional moieties.[1] In this direction, hydrogen bonding is, by far, the most frequently occurring non-covalent interaction in molecular recognition processes, as illustrated in Chapter 1. Another prominent interaction, which is of current interest in the supramolecular chemistry, is the halogen bonding. Halogen bonding, with general representation C-D···X-Y, is the attractive interaction formed between hetero-atoms (D=N, O, S or a metal centre) and halogen atoms (X=I, Br, Cl, F), where, the D···X distance is less than sum of the van der Waals radii of D and X.[2] Theoretical and experimental data prove that all four halogens are halogen bond donors, and the tendency to form strong interactions is I > Br > Cl > F.[3] Practically all the energetic and geometric features known for hydrogen bonded complexes are encountered in halogen bonding complexes as well.[4] However, halogen being larger than hydrogen, halogen bond is more sensitive to steric hindrance than hydrogen bond.[5]

Recently, Resnati and co-workers have demonstrated the utility of halogen bonding as a structure directing force in the realization of three-dimensional solid state assemblies through molecular complexes formed by pentafluoroiodobenzene or 2,3,5,6-tetrafluoro-1,4-diiodobenzene with basic amines or imines.[6] Some of the other illustrative examples of halogen bonding interactions are shown in Figure 3.1.[7] These non-covalent interactions show significant influence in design and manipulation of aggregation, which find application in the areas as diverse as superconductors, liquid crystals and also in biological process such as substrate-receptor bindings.[8]

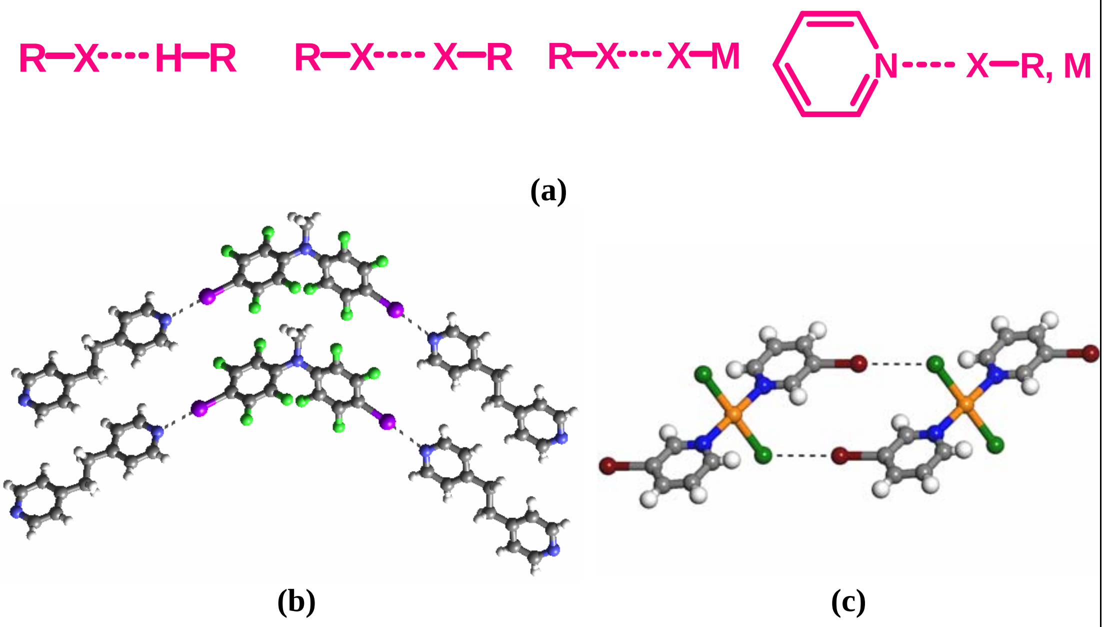


Figure 3.1: (a) Some examples of possible halogen bonding interactions, where X=Cl, Br and I, R=alkyl or aryl, M=metal centre. Halogen bonding present in the crystal structures of (b) N, N-bis(2,3,5,6-tetrafluoro-4-iodophenyl)methylamine-1,2-bis(4-pyridyl)ethane complex and (c) $[PtCl_2(C_5H_4NBr)_2]$.

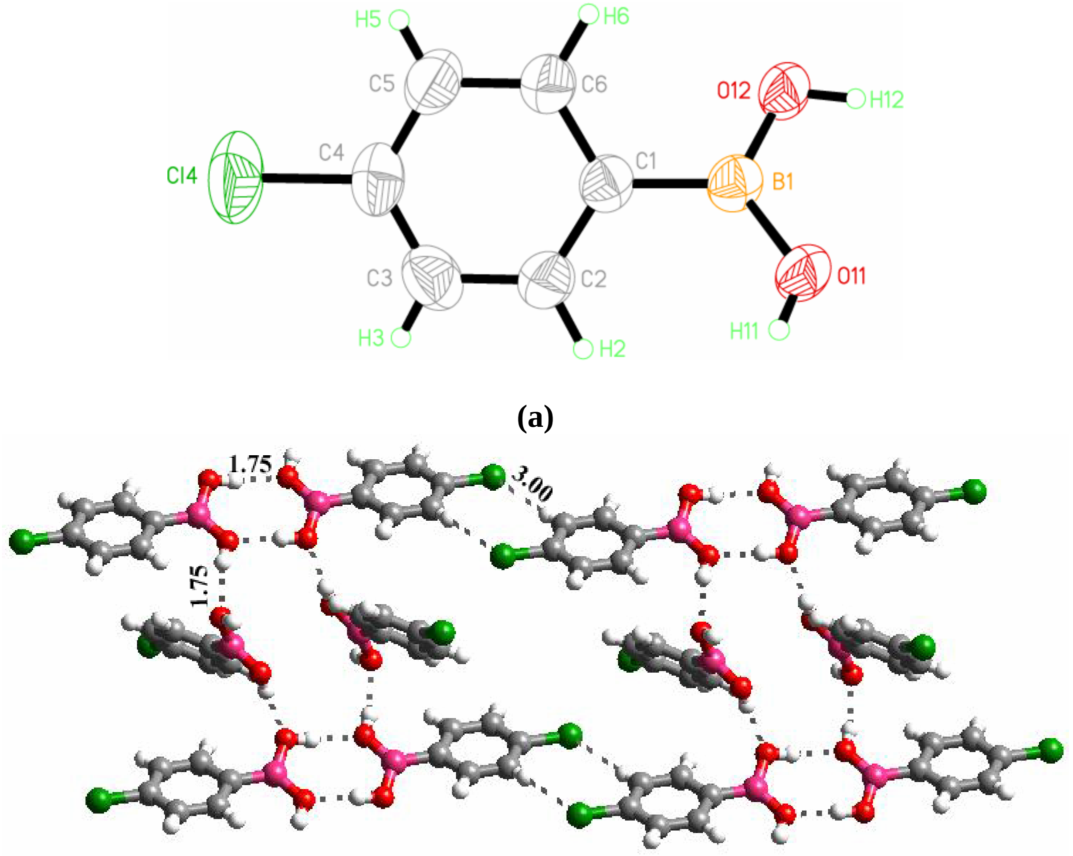
Since boronic acids are well known for their utility in the field of synthetic chemistry as well as in biology, especially, halophenylboronic acids for their pharmaceutical utility as antibacterial agents and as Boron Neutron Capture Therapy (BNCT) agent, studies pertain to halogen bonding in conjunction with other intermolecular interactions of halophenylboronic acids may expand their potential applications.[9] In this regard, endeavors have been initiated with the structure determination of 4-halophenylboronic acids followed by their co-crystallization with *N*-donor ligands, as illustrated below.

3.2 Structural analysis of 4-halophenylboronic acids

Crystallization of 4-halophenylboronic acids (4-flurophenylboronic acid, **1**, 4-chlorophenylboronic acid, **2**, 4-bromophenylboronic acid, **3**, 4-iodophenylboronic acid, **4**) from water gave good quality single crystals only for **2** and **3**, which were suitable for structure elucidation by single crystal x-ray diffraction methods, while 1 and 4 always gave either precipitates or hydrated forms. The structural features of **2** and **3** are quite interesting, with significant contributions from the interactions formed by the halogen atoms (–Cl and –Br) towards packing of molecules in the crystal lattices, as described below.

3.2.1 4-Chlorophenylboronic acid ($C_6H_6BClO_2$), 2:

Colorless block-like crystals, obtained upon crystallization from water, were analyzed by single crystal x-ray diffractions methods and found that the $–B(OH)_2$ functionality of 4-chlorophenylboronic acid, **2** (monoclinic, $P2_1/c$), adopts *syn-anti* conformation (Figure 3.2(a)). In the solid state structure of **2**, the $–B(OH)_2$ group forms recognition pattern, similar to the one observed in the structure of phenylboronic acid.



(a)

(b)

Figure 3.2: (a) The asymmetric unit of **2** in which, the –B(OH)$_2$ moiety adopts the commonly observed *syn-anti* conformation. (b) The hydrogen bonding pattern present in the crystal structure of **2**. A cyclic network is formed through O-H$^{\cdots}$O and C-H$^{\cdots}$Cl interactions.

The arrangement of molecules in the crystal lattice is shown in Figure 3.2(b). Molecules of **2** related by center of inversion are held together by O-H$^{\cdots}$O hydrogen bonds (H$^{\cdots}$O, 1.75 Å). The details of other characteristics of hydrogen bonds are given in Table 3.2. The dimers, thus, formed are extended through O-H$^{\cdots}$O hydrogen bonds, with each one being connected to four similar units, (H$^{\cdots}$O, 1.75 Å), involving the *anti*

–OH group of the –$B(OH)_2$ functionality. Such adjacent ensembles are held together by centrosymmetric C-H···Cl interactions (H···Cl, 3.00 Å).

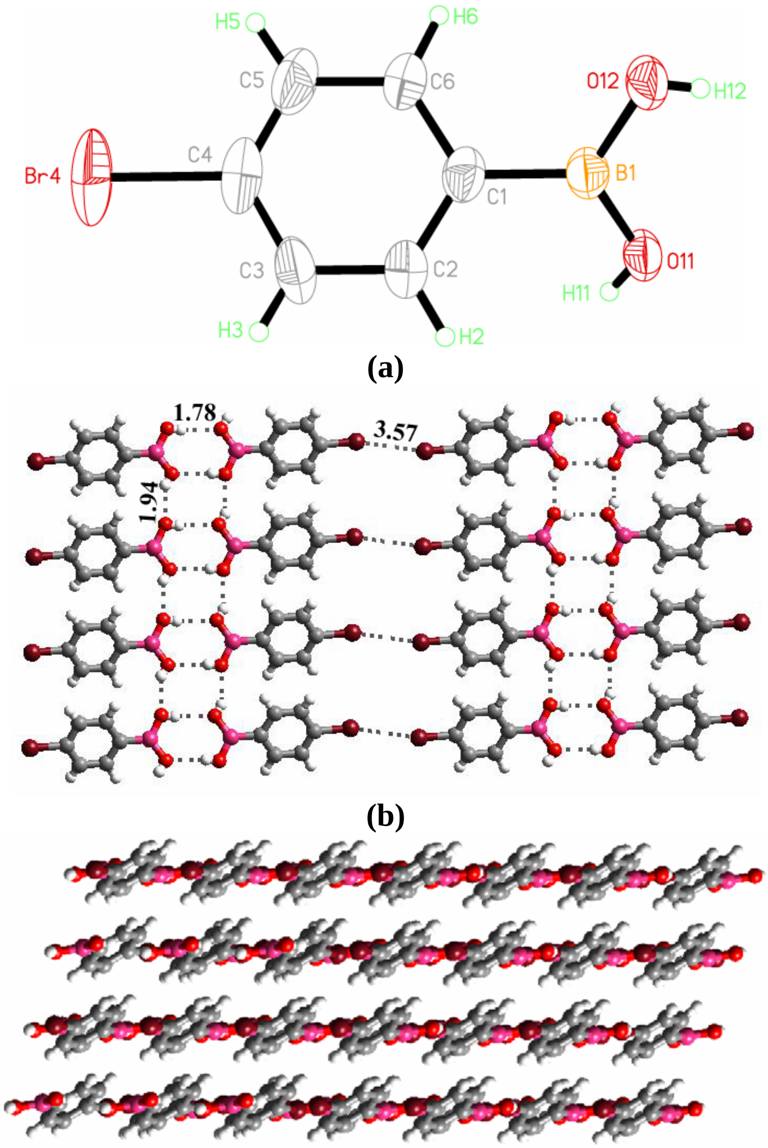
Thus, in the structure of **2**, it was observed that, the –Cl atom is involved in an interaction, which stabilizes the ensembles formed through the –$B(OH)_2$ moieties.

3.2.2 4-Bromophenylboronic acid, 3:

Single crystals of 4-bromophenylboronic acid **3**, obtained from H_2O, adopt triclinic space group $P\bar{1}$, and the asymmetric unit is shown in Figure 3.3(a). In the crystal lattice, the –$B(OH)_2$ group adopts *syn-anti* conformation and form centrosymmetric dimers through O-H···O hydrogen bonds (H···O, 1.78Å). These dimers are connected to two neighboring units through O-H···O hydrogen bonds (H···O, 1.94Å), thus, yielding columnar blocks, which are further held together by Br···Br interactions (Figure 3.3(b)).

Unlike in the case of **2**, the halogen atom (-Br) in **3** form Br···Br interactions, rather than C-H···Br, and sheet-like structure in two-dimensional arrangement. The Br···Br interactions observed belong to the type-I halogen···halogen interactions with the C-Br···Br angle of 165^{o}. Stacking of these sheets in the three-dimensional arrangement is depicted in Figure 3.3(c).

Analysis of the packing of molecules in the structure of **2** and **3** reveals that, the halogen atoms play a significant role in the arrangement of molecules in the crystal lattice. To further explore the effect of it in directing the formation of exotic supramolecular assemblies, co-crystallization experiments of **1-4** with various *N*-donor compounds have been carried out.



(a)

(b)

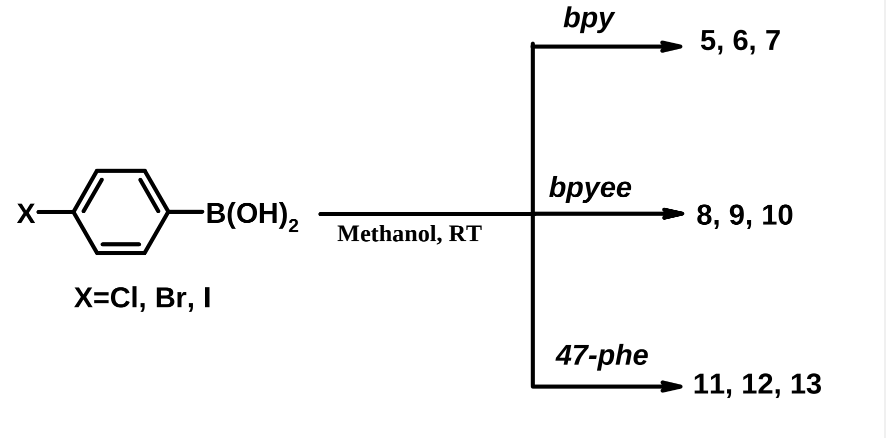
(c)

Figure 3.3: (a) The asymmetric unit of **3**. (b) The hydrogen bonding pattern present in the crystal structure of **3**. (c) Three-dimensional packing of sheets in the crystal lattice of **3**.

3.3 Molecular complexes of 4-halophenylboronic acids

Molecular complexes were prepared by the co-crystallization of 4-halophenylboronic acids with various *N*-donor compounds such as 4,4'-bipyridine, ***bpy***, *trans*-1,2-bis(4-pyridyl)ethene, ***bpyee*** and 4,7-phenanthroline, ***47phe***.

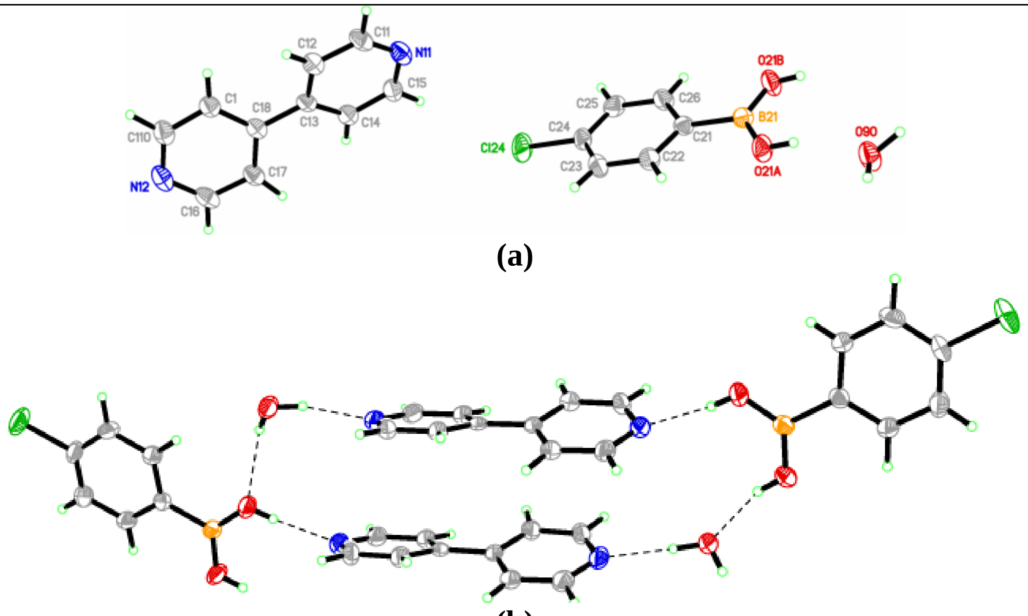
Scheme 3.1



However, crystallization of **1** with *N*-donor compounds did not yield single crystals; while all other boronic acids, **2**-**4**, gave crystals suitable for x-ray diffraction studies (Scheme 3.1). The structures have been analyzed to evaluate recognition patterns and the supramolecular architectures, as discussed in the following sections.

3.3.1 Molecular complexes with 4,4'-bipyridine, 5-7:

Co-crystallization of 4-chlorophenylboronic acid, **2** (0.0156g, 0.1mmol) and ***bpy*** (0.0156g, 0.1mmol) from methanol yielded molecular adduct, **5**, with the composition, ($C_{10}H_8N_2$):($C_6H_6BO_2Cl$):(H_2O). In the asymmetric unit, along with the molecules of ***bpy*** and boronic acid, one molecule of water is also present, as shown in Figure 3.4(a).



(a)

(b)

Figure 3.4: (a) The asymmetric unit of the complex **5**. (b) The cyclic unit formed by the recognition between the boronic acid, ***bpy*** and the lattice water molecules.

In the molecular complex **5**, the –B(OH)$_2$ moiety adopts *syn*-*syn* conformation and interacts with the ***bpy*** unit through O-H···N hydrogen bonds (H···N, 1.74Å) while, the second pyridyl *N*-atom of ***bpy*** is involved in an O-H···N hydrogen bond (H···N, 1.92Å) with the water molecule. Two such units, in turn, couple to yield a cyclic structure through O-H···O hydrogen bonds, formed between the water and boronic acid molecules (Figure 3.4(b)). Details of the hydrogen bonds are given in Table 3.4. In the two-dimensional arrangement, the adjacent cyclic units self-assemble to form a ladder-like assembly. The adjacent ladders are connected through C-H···Cl hydrogen bonds (H···Cl, 2.95 Å), as shown in Figure 3.5.

Thus, from the structure analysis, it was found that the –B(OH)$_2$ group adopted an entirely different conformation, than the one observed in the structure of **2**, which may be accounted to the molecular recognition with ***bpy***. However, the –Cl atom retains its tendency to form C-H···Cl interaction, as observed in the structure of **2**.

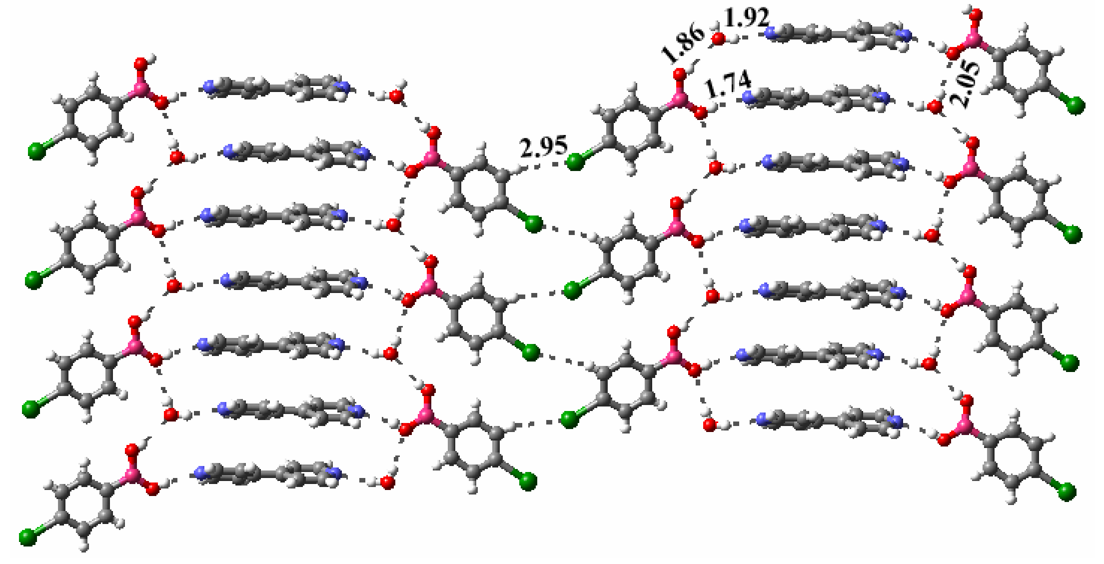
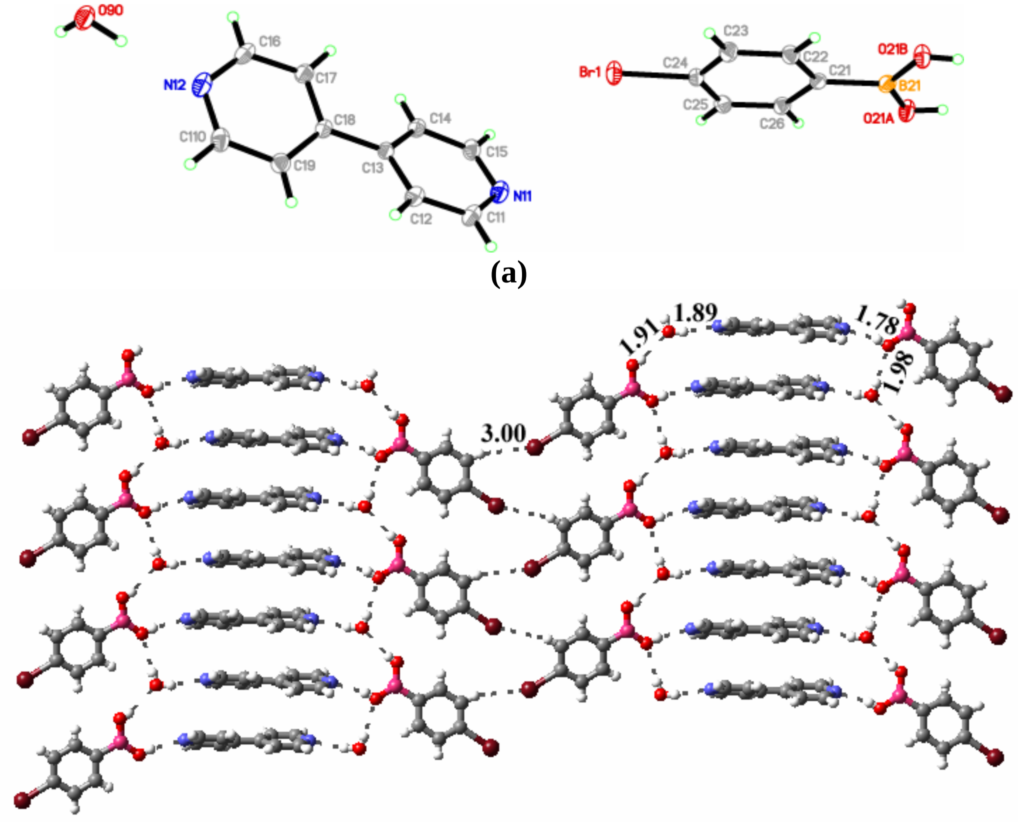


Figure 3.5: Ladder assembly formed in the crystal structure of **5**. The adjacent ladders are connected through C-H···Cl interactions.

Co-crystallization of 4-bromophenylboronic acid, **3**, with ***bpy*** yielded the molecular complex **6** with the composition, $(C_{10}H_8N_2)$:$(C_6H_6BO_2Br)$:(H_2O) and is isostructural to **5**. The asymmetric unit and the two-dimensional arrangement of molecules are shown in Figure 3.6. The –B(OH)$_2$ functionality, in *syn*-*syn* conformation, together with the lattice water molecules interact with the ***bpy*** molecules, yielding a ladder-like assembly. However, these ladders are further stabilized by C-H···Br (H···Br, 3.00Å) interactions rather than Br···Br interactions.

Thus, complex **6** halogen bonding is not observed unlike in the native structure of **3**, discussed earlier.

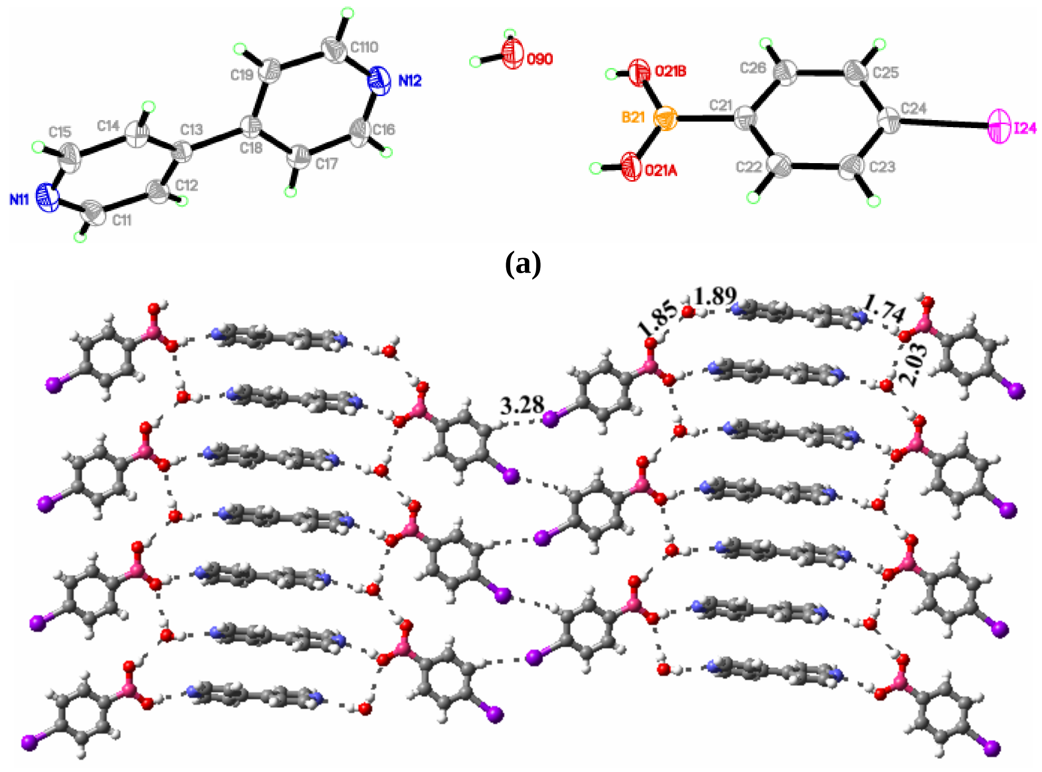


(a)

(b)

Figure 3.6: (a) The asymmetric unit of the complex **6**. (b) The ladder assembly formed by the two-dimensional arrangement of molecules. C-H···Br interactions connect the adjacent ladders.

Similarly, in the complex **7**, obtained by the co-crystallization of 4-iodophenylboronic acid, **4**, and ***bpy*** from methanol, the structural arrangement is reminiscent to **5** and **6** except for C-H···I hydrogen bonds (H···I, 3.28 Å). The asymmetric unit of the complex and two-dimensional arrangement of the molecules are shown in Figure 3.7.



(a)

(b)

Figure 3.7: (a) The asymmetric unit of complex **7**. (b) The recognition pattern present in the crystal structure of the complex **7**. C-H···I interaction connects the adjacent ladders.

Thus, analysis of the complexes **5-7** illustrates that, irrespective of the halogen atom present, all the boronic acid molecules have similar recognition pattern towards the *N*-donor compound, ***bpy***. In all the complexes, water plays a significant role in the molecular recognition by connecting boronic acid and ***bpy*** through O-H···O and O-H···N hydrogen bonds.

Further, the ladder structure observed in complexes **5-7** is quite interesting, as such networks were found to be attractive in the chemical synthesis of ladderanes when appropriate ligands are present for a favorable reaction.[10] Thus, to verify the robustness of ladder structure, ***bpy*** was replaced by *trans*-1,2-bis(4-pyridyl)ethene, ***bpyee***, and the obtained complexes were analyzed, as described below.

3.3.2 Molecular complexes of *trans*-1,2-bis(4-pyridyl)ethene, 8-10:

Reaction between **2** (0.0156g, 0.1mmol) and ***bpyee*** (0.0182g, 0.1mmol), from methanol, at ambient conditions gave a complex, **8**, with the composition $(C_{12}H_{10}N_2)$:$(C_6H_6BClO_2)$:(H_2O), as confirmed by x-ray diffraction studies. Two molecules each of the boronic acid, the pyridyl ligand and water molecules are present in the asymmetric unit (Figure 3.8(a)). Among the two molecules of ***bpyee***, one is disordered about the olefinic (–CH=CH–) bridge. The $–B(OH)_2$ functionality of both the molecules of boronic acids adopt *syn-anti* conformation.

In the complex **8**, the boronic acid and ***bpyee*** interact in the same way as that of the ***bpy*** complex **5**-**7**. Thus, a cyclic network is formed comprising of two molecules each of boronic acid, water and ***bpyee***, as shown in Figure 3.8(b) and (c). But, unlike the ***bpy*** complexes, there exists two unique cyclic units brought about by the recognition between two symmetry independent ***bpyee*** units (ordered and disordered) and boronic acids. These independent cyclic units are arranged alternately and are stabilized through O-H···O hydrogen bonds, involving the *anti* –OH moiety of the $–B(OH)_2$ functionality and water molecules, thus, forming one-dimensional molecular tapes (Figure 3.9(a) and (b)). The hydrogen bond distances are given in Table 3.4.

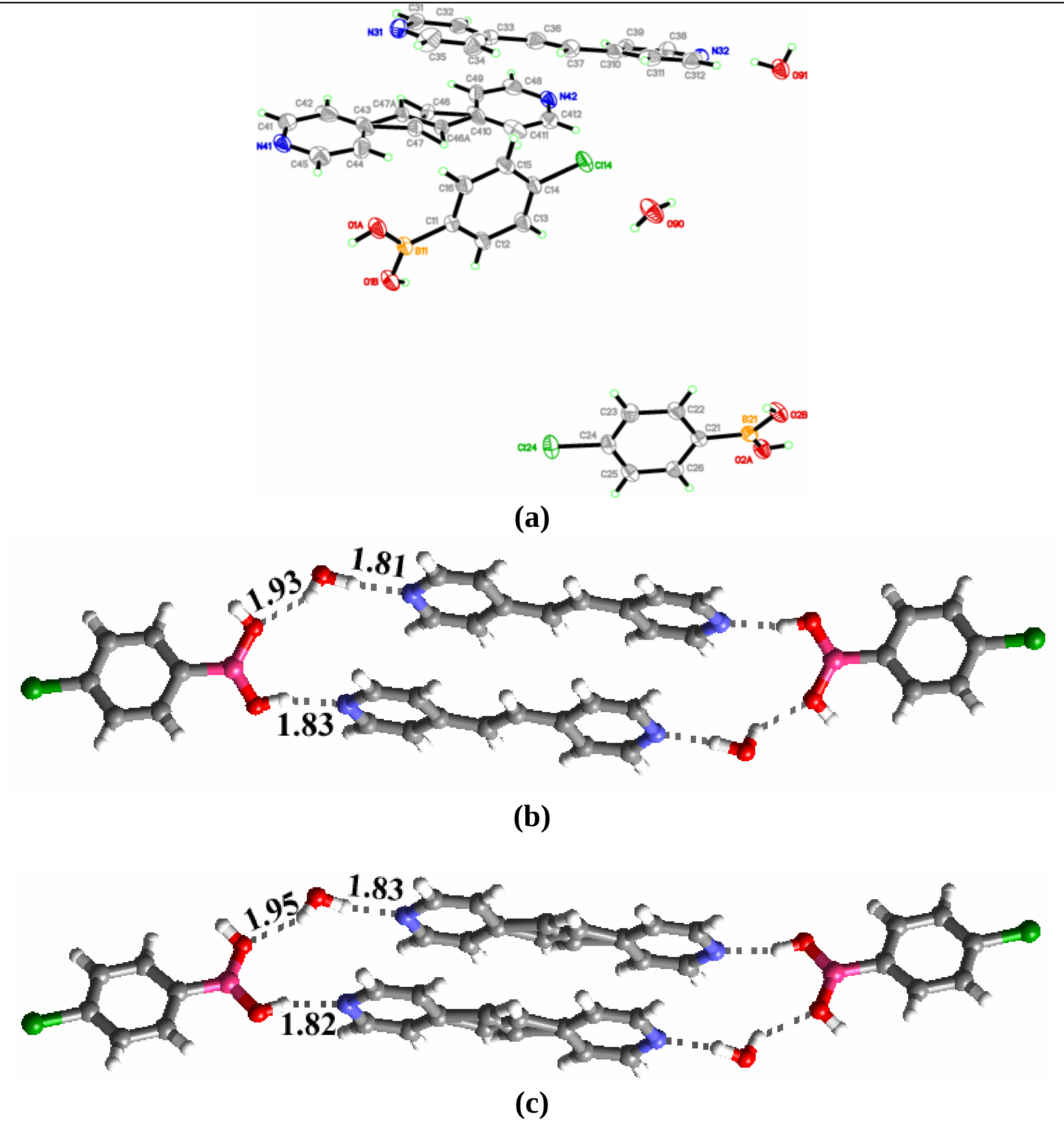


Figure 3.8: (a) The asymmetric unit of the complex **8**. The basic six-membered cyclic recognition pattern present in the crystal structure of **8** is represented in (b) and (c).

The resulting molecular tapes are further connected by Cl···Cl interactions (3.35 Å), yielding void space of dimension 13 X 48 $Å^2$ (Figure 3.9(c)). In the three-dimensional arrangement, the void space is effectively filled by the interweaving of adjacent layers, as shown in Figure 3.9(d).

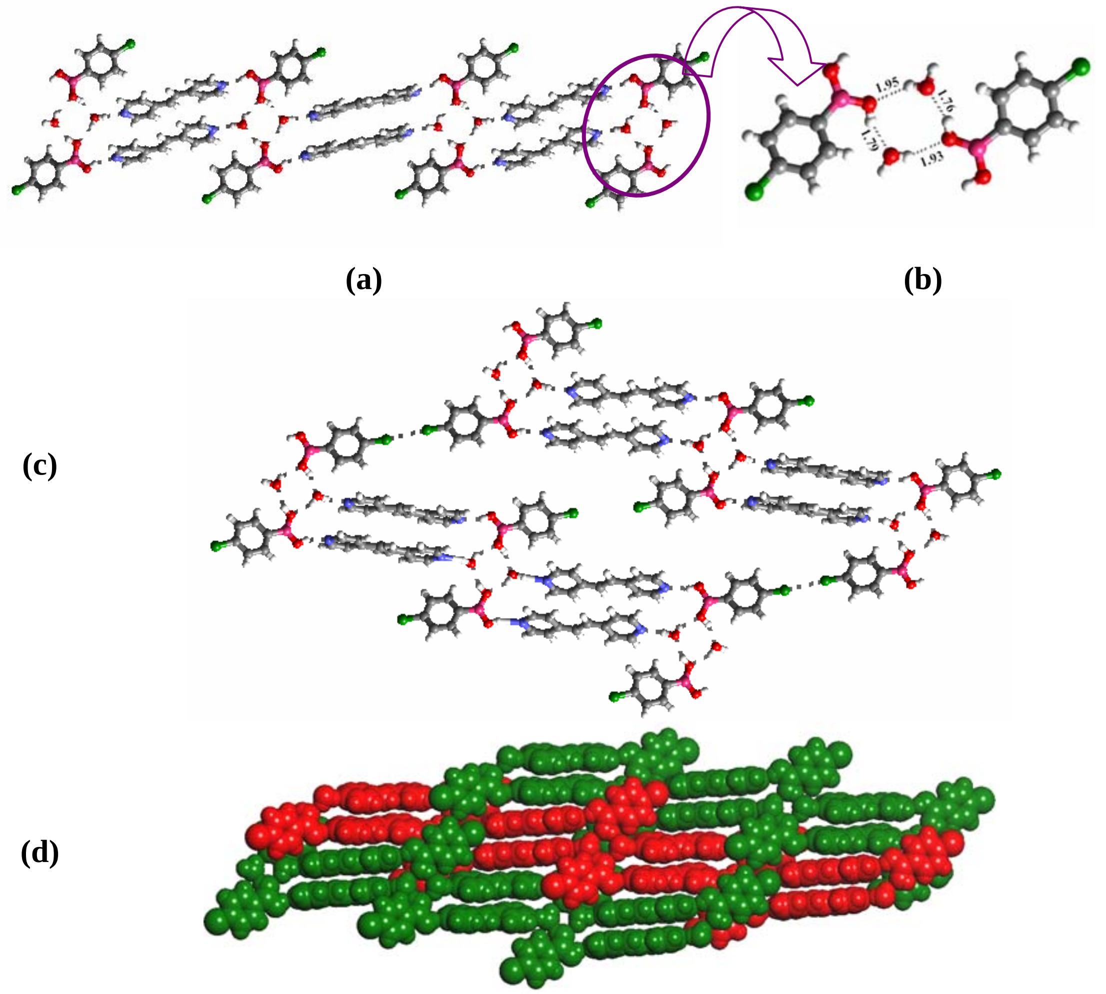


Figure 3.9: (a) Recognition between the molecules leads to the formation of one-dimensional molecular tapes. (b) Molecules of **2** and water interacting with each other through O-H···O hydrogen bonds. (c) Adjacent tapes are connected through Cl···Cl interactions, thus, forming a cyclic network. (d) The resultant interweaving network.

It is interesting to note that, by replacing ***bpy*** with ***bpyee***, the ladder structure is perturbed and formed an interweaving architecture, although a similar recognition pattern was observed. However, in a typical cyclic unit, the adjacent ***bpyee*** molecules are positioned at a photo-reactive distances (3.73 and 4.01 Å respectively for the disordered and ordered molecules). Another noteworthy observation is the formation of halogen bonding (Cl···Cl) by the –Cl atoms. In fact, similar features have been noted in the complex **9**, obtained by the reaction of 4-bromophenylboronic acid, **3**, and ***bpyee***, as shown in Figure 3.10.

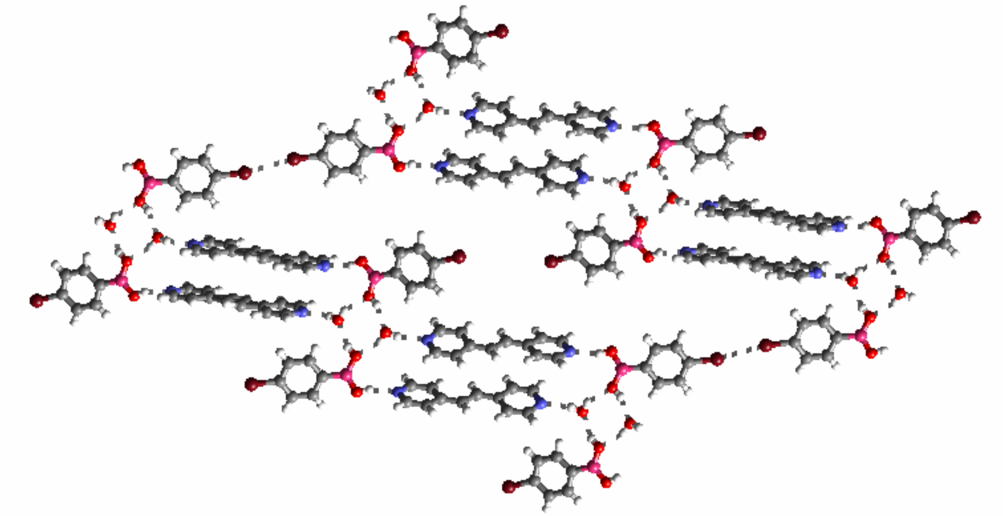


Figure 3.10: Recognition between the molecules leads to the formation of one-dimensional molecular tapes, which are further connected through Br···Br interactions (3.42Å).

However, the complex **10**, formed between 4-iodophenylboronic acid, **4**, and ***bpyee***, adopted an entirely different network with a composition, 3($C_{12}H_{10}N_2$): 2($C_6H_6BIO_2$), as revealed by the x-ray diffraction studies (Figure 3.11).

In the complex **10**, the –B(OH)$_2$ moiety adopts *syn-syn* conformation, as observed in the complexes **5-7**, and interacts with the ***bpyee*** molecules through O-H···N hydrogen bonds (H···N, 1.81, 1.95 Å), yielding a four-membered cyclic network

(Figure 3.12(a)). The second ***bpyee*** molecule present in the lattice act as a linker to connect adjacent cyclic units and are stabilized by I$\cdots$N interactions (3.09 Å), thereby forming one-dimensional molecular tapes (see Figure 3.12(b) and (c)). Thus, in the complex **10**, both the hydrogen and halogen bonds play significant role in the molecular recognition.

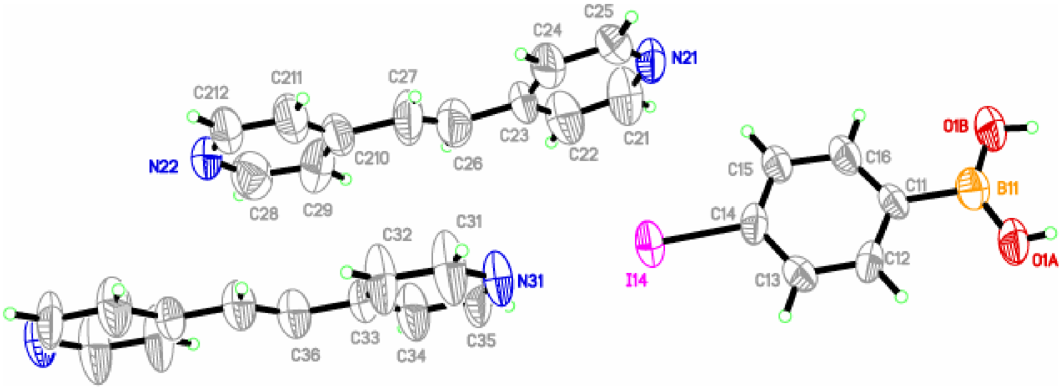
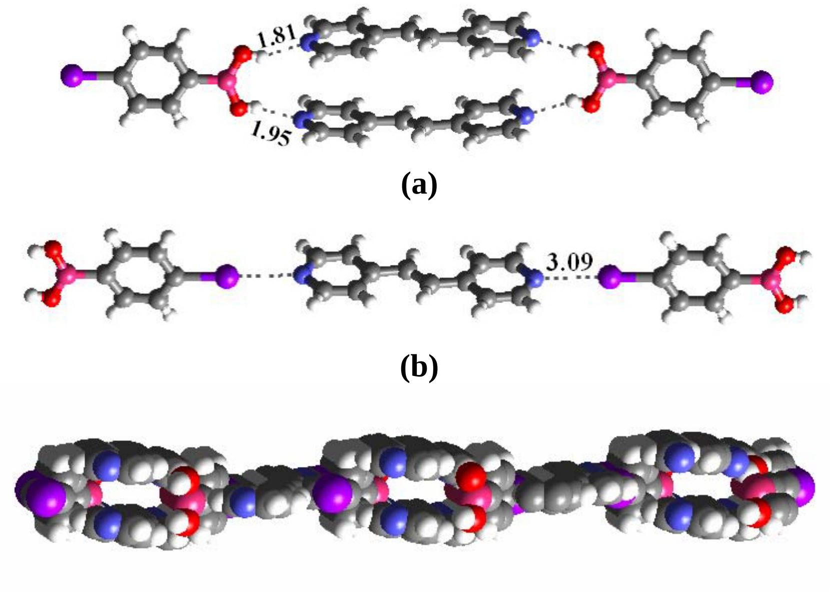


Figure 3.11: The asymmetric unit of complex **10**.

In fact, the formation of I$\cdots$N halogen bond is not surprising as it is known that, the affinity of halogen atom towards pyridyl nitrogen also increases with increase in size. Also, the recent literature provides enough examples that point towards the effect of the polarizability of electron clouds of I-atom and its influence in the formation of stable halogen bonds such as C-I$\cdots$N.[11]

To analyze the possible variation in the recognition process towards an *N*-donor ligand, with a non-linear coordination behavior, 4,7-phenanthroline was employed for the preparation and evaluation of molecular complexes with 4-halophenylboronic acids.



(a)

(b)

(c)

Figure 3.12: (a) Basic recognition pattern present in the crystal structure of the complex **10**. (b) The three-dimensional supramolecular entity formed by I···N interaction. (c) Open-bracelet architecture formed by the self-assembly of the molecules.

3.3.3 Molecular complexes of 4,7-phenanthroline, 11-13:

The molecular complex **11**, was prepared by the co-crystallization of **2** (0.0156g, 0.1mmol) and ***47-phe*** (0.0180g, 0.1mmol) from methanol, by slow evaporation, at ambient conditions. As shown in Figure 3.13(a), in the asymmetric unit the reactants are present in a 1:1 ratio.

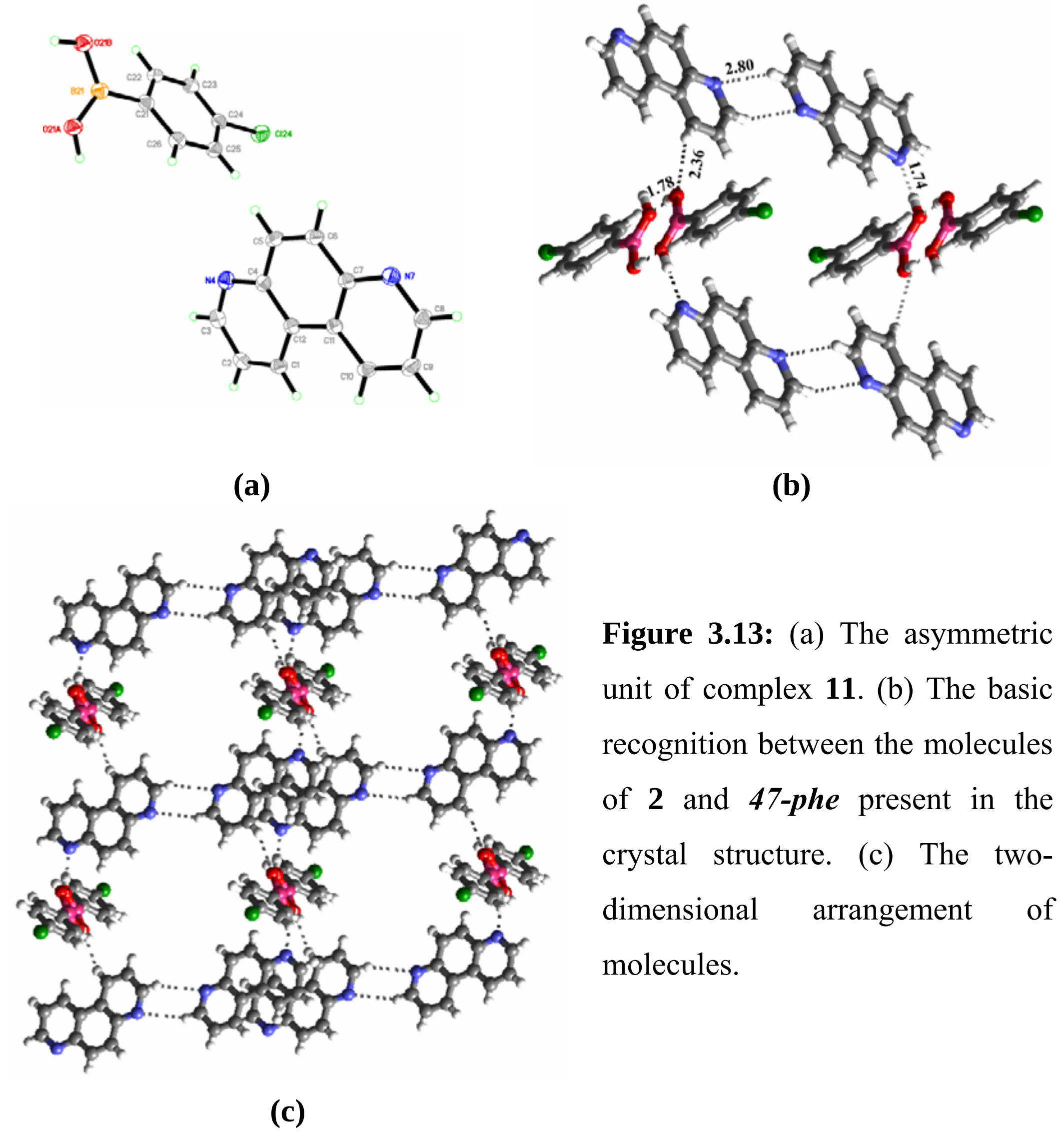


Figure 3.13: (a) The asymmetric unit of complex **11**. (b) The basic recognition between the molecules of **2** and ***47-phe*** present in the crystal structure. (c) The two-dimensional arrangement of molecules.

In the complex **11**, the –B(OH)$_2$ moiety adopts *syn-anti* conformation and the molecules of **2** and ***47-phe*** form dimers independently through O-H$\cdots$O (H$\cdots$O, 1.78 Å) and C-H$\cdots$N (H$\cdots$N, 2.80 Å) hydrogen bonds respectively. The resulting dimeric units are further held together by O-H$\cdots$N as well as C-H$\cdots$O hydrogen bonds (1.74 and 2.36 Å respectively), creating a void space of 11 X 11 Å^2 dimension (Figure 3.13(b)). In the three-dimensional arrangement, the cyclic networks are arranged in such a manner that, the void space is being filled by the molecules of boronic acids from the adjacent layers yielding a poly-threading architecture, as shown in Figure 3.14.

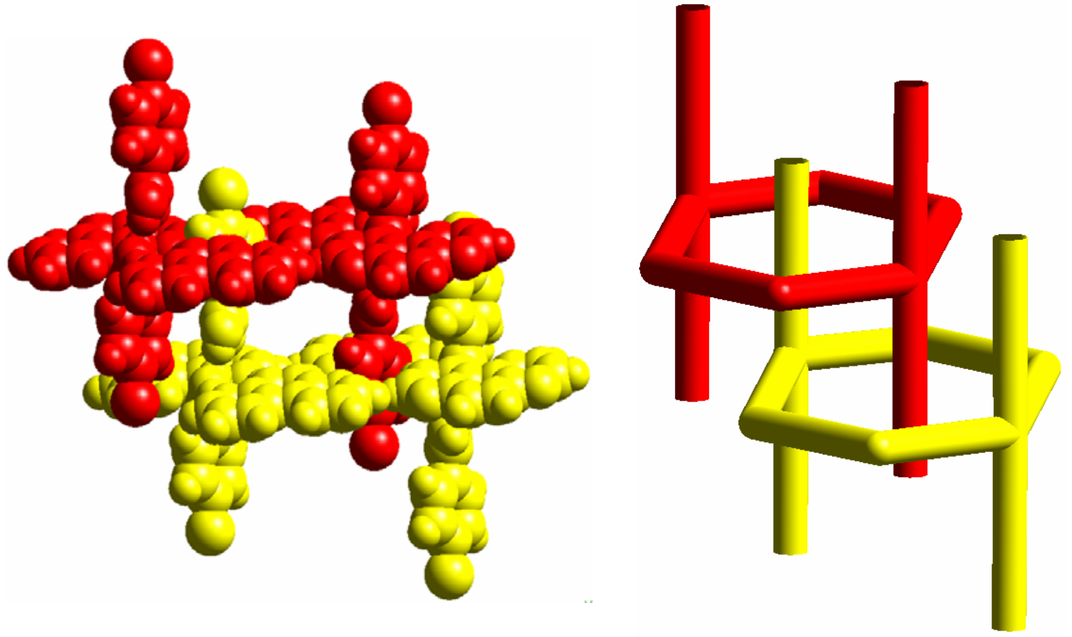
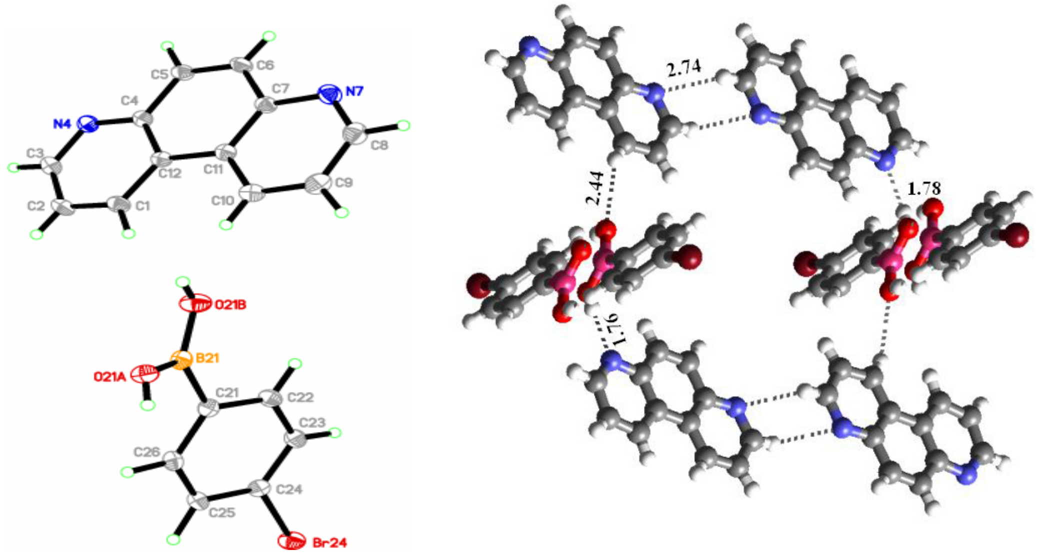


Figure 3.14: (a) Molecules of **2** is protruding through the void space created by the interaction between ***47-phe*** and **2** there by producing a poly-threading architecture. (b) Schematic illustration of the mutual polythreading of two layers.

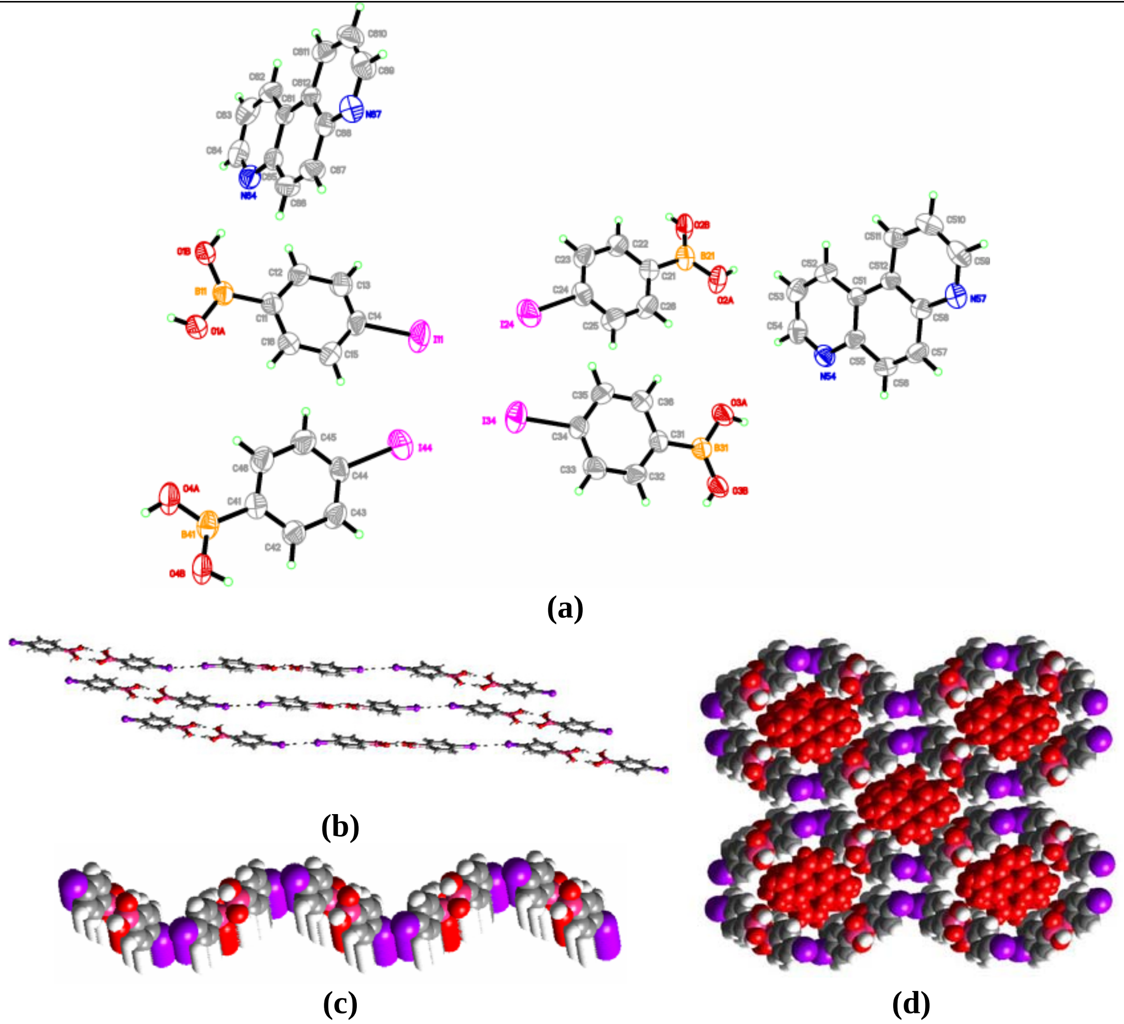
An isostructural assembly, **12**, was formed between 4-bromophenylboronic acid, **3**, with ***47-phe***. The asymmetric unit of the complex and the basic interactions existing between the components in the complex are shown in Figure 3.15. As in the case of **11**, the present complex also yielded three-dimensional polythreading architecture.



(a) **(b)**

Figure 3.15: (a) The asymmetric unit of complex **12**. (b) The basic recognition pattern present in the crystal lattice of **12**.

However, reaction of **4** with ***47-phe*** gave a complex, **13**, with four molecules of boronic acid and two ***47-phe*** units in the asymmetric unit (Figure 3.16(a)). In the complex **13**, the –B(OH)$_2$ group adopts *syn-anti* conformation and form centrosymmetric dimers through O-H$\cdots$O hydrogen bonds. These dimers are further held together by I$\cdots$I interactions (I$\cdots$I, 3.78 Å), yielding corrugated tapes (Figure 3.16(b) and (c)). The boronic acid tapes are stacked in the three-dimensional arrangement, forming a void space with dimension, 4 X 26 Å^2, which are being filled by ***47-phe*** molecules, as shown in Figure 3.16(d). The guest molecules establish interaction with the host framework through O-H$\cdots$N and C-H$\cdots$O hydrogen bonds (H$\cdots$N and H$\cdots$O respectively 1.81, 2.28Å).



(a)

(b)

(c)

(d)

Figure 3.16: (a) The asymmetric unit of complex **13**, in which four boronic acid and two ***47-phe*** molecules are present. (b) The intermolecular interactions formed by the molecules of **4** in the complex **13**. (c) The corrugate sheets represented in the space-fill mode. (d) In three-dimensional arrangement, the molecules of **4** form cavity structures that are being occupied by ***47-phe*** molecules (shown in red color).

Thus, formation of the complexes, **5-13**, has proved the efficacy of 4-halophenylboronic acids in the preparation of binary molecular complexes. It is evident that –Cl and –Br derivatives of phenylboronic acid yield almost similar assemblies. But, the –I derivative tends to form assemblies with entirely different recognition pattern and crystal packing. This can be attributed to the bigger size and the effective polarizability of the electron density of I-atom, which in turn, leads to an entirely different architecture in the three-dimensional arrangement.

3.4 Conclusions

The studies substantiate the utilization of 4-halophenylboronic acids in the preparation and analyses of supramolecular assemblies by synchronously employing the functional groups that can yield halogen bonds and hydrogen bonds. Further, the study of the native crystal structure of **2** and **3** signifies the role of halogen atoms, with the formation of C-H···Cl and Br···Br interactions, in the structure stabilization. In both the cases, the $–B(OH)_2$ functionality adopts the *syn-anti* conformation, as observed in many other crystal structures discussed in the earlier chapters.

Further, with *N*-donor compounds, 4-halophenylboronic acids yielded molecular complexes with topologies varying from simple ladders to interweaving and polythreading structures, as discussed in the complexes **5-13**. In the complexes, while –Cl and –Br substituted compounds gave isostructural assembly, –I derivative formed different network structure, perhaps due to the electronic effect of iodine atom and its propensity to form halogen bonds (I···I and I···N).

Although, many more examples are required for a full understanding of these non-covalent interactions and to make clear prediction of three-dimensional architectures, the above mentioned examples represents a lead off for the boronic acid based assemblies.

3.5 Experimental section

All the boronic acids and *N*-donor compounds were obtained commercially and the crystallization experiments were carried out by dissolving them in spectroscopic grade solvents, as the case may be. Single crystals suitable for x-ray diffraction were obtained, over a period of one week time, by slow-evaporation of the respective solution at room temperature. All co-crystals, **5-13**, were prepared by dissolving the respective reactants in a ratio of 1:1 in methanol and allowing the solvent to evaporate under ambient conditions.

A general procedure for the synthesis of complexes, 5-13

In a typical co-crystallization experiment, 4-halophenylboronic acid (–Cl, –Br or –I) (0.100 mmol) and the *N*-donor ligand (***bpy***, ***bpyee*** or ***47-phe***) (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. The resultant solution was allowed to evaporate under ambient conditions and colorless single crystals were obtained over a period of one week time. The crystals were separated from the mother liquor by filtration, washed with ice-cold methanol and dried under vacuum.

X-ray crystallography

Single crystals suitable for x-ray diffraction studies were carefully chosen after they were viewed through a Leica microscope supported by a rotating polarizing stage and a CCD camera. The crystals were glued to a thin glass fiber using an adhesive (cyanoacrylate) and mounted on a diffractometer equipped with an APEX CCD area detector. The data were collected at low temperature and the data collection was smooth in all the cases. The intensity data were processed using Bruker's suite of data processing programs (SAINT), and absorption corrections were applied using SADABS. The structure solution was carried out by direct methods, and the refinements were performed by full-matrix least-squares on F^2 using the SHELXTL suite of programs.[12] All the structures converged to good R-factors. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms obtained from Fourier maps were refined isotropically. All calculations of intermolecular interactions were done with the HBOND NORM option of PLATON.[13]

Tables

Table 3.1: Crystallographic information of the structures **1a-4b**

	2	3
Formula	$C_6H_6BClO_2$	$C_6H_6BBrO_2$
Formula Wt.	156.37	200.83
Crystal habit	Blocks	Blocks
Crystal color	Colorless	Colorless
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	14.678(4)	5.010(3)
b (Å)	5.951	7.241(4)
c (Å)	9.030(2)	10.989(6)
α (°)	90	103.30(8)
β (°)	105.72(4)	97.06(9)
γ (°)	90	100.52(9)
V (Å^3)	759.3(3)	375.7(4)
Z	4	2
D_{calc} (g cm^{-3})	1.368	1.775
T(K)	133(2)	133(2)
(λ)Mo K$_\alpha$	0.71073	0.71073
μ(mm^{-1})	0.433	5.400
2θ range (°)	46.58	46.60
Total Reflns.	4363	1607
Unique Reflns.	1085	1069
Reflns. Used	881	867
No. Parameters	115	115
GOF on F^2	1.104	0.970
Final R$_1$, wR$_2$	0.0385, 0.1115	0.0622, 0.1607

Table 3.2: Characteristics of various intermolecular interactions (distances/Å and angles/°)[#]

Compound	Hydrogen bond (D-H···A)				
	O–H···O	C-H···O	C-H···Cl	C-H···Br	X···X
2	1.75 2.72 168 1.75 2.73 175	2.77 3.57 131	3.00 4.07 170		
3	1.78 2.75 172 1.94 2.80 144	2.67 3.58 143 2.74 3.75 155		3.15 4.09 147	**(Br···Br)** 3.57

[#] The three numbers in each column indicate H···A(O//Cl/Br), D(O/C)···A distances and D-H···A angles, respectively.

Table 3.3: Crystallographic information of the structures **5-13.**

	5	6	7
Formula	$(C_6H_6BO_2Cl)$: $(C_{10}H_8N_2)$:(H_2O)	$(C_6H_6BO_2Br)$: $(C_{10}H_8N_2)$:(H_2O)	$(C_6H_6BO_2I)$: $(C_{10}H_8N_2)$:(H_2O)
Formula Wt.	330.57	375.03	422.02
Crystal habit	Block	Block	Block
Crystal color	Colorless	Colorless	Colorless
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a **(Å)**	12.606(5)	12.805(3)	13.251(5)
b **(Å)**	6.878(3)	6.834(1)	6.858(3)
c **(Å)**	18.873(8)	18.647(4)	18.594(8)
α **(°)**	90	90	90
β **(°)**	102.79(7)	102.74(3)	103.50(7)
γ **(°)**	90	90	90
V **(Å^3)**	1595.8(1)	1591.6(6)	1643.1(1)
Z	4	4	4
D_{calc} **(g cm^{-3})**	1.376	1.565	1.706
T**(K)**	133(2)	120(2)	133(2)
(λ)Mo K$_\alpha$	0.71073	0.71073	0.71073
μ**(mm^{-1})**	0.254	2.598	1.964
2θ range (°)	50.14	66.34	56.64
Total Reflns.	7645	25462	13672
Unique Reflns.	2806	6089	3837
Reflns. Used	2389	4546	3301
No. Parameters	272	216	272
GOF on F^2	1.161	1.005	1.085
Final R_1, wR_2	0.0566, 0.1430	0.0332, 0.0748	0.0395, 0.0886

Table 3.3 *(Contd…):*

	8	9	10
Formula	$(C_6H_6BO_2Cl)$: $(C_{12}H_{10}N_2)$:(H_2O)	$(C_6H_6BO_2Br)$: $(C_{12}H_{10}N_2)$:(H_2O)	$2(C_6H_6BO_2I)$: $3(C_{12}H_{10}N_2)$
Formula Wt.	356.60	401.06	1042.30
Crystal habit	Block	Block	Plate
Crystal color	Colorless	Colorless	Colorless
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a **(Å)**	12.259(5)	12.301(3)	10.129(4)
b **(Å)**	12.938(2)	12.969(2)	10.900(4)
c **(Å)**	13.211(3)	13.309(1)	12.521(4)
α **(°)**	96.91(1)	96.25(1)	69.96(8)
β **(°)**	116.79(2)	116.94(1)	66.85(8)
γ **(°)**	99.83(2)	100.13(1)	70.21(7)
V **(Å^3)**	1796.1(1)	1819.8(2)	1160.4(7)
Z	4	4	1
D_{calc} **(g cm^{-3})**	1.319	1.464	1.492
T**(K)**	120(2)	120(2)	298(2)
(λ)Mo K$_\alpha$	0.71073	0.71073	0.71073
μ**(mm^{-1})**	0.232	2.278	1.405
2θ range (°)	56.54	66.32	50.14
Total Reflns.	21875	35702	8478
Unique Reflns.	8872	13851	3961
Reflns. Used	6490	9042	1841
No. Parameters	507	495	284
GOF on F^2	1.029	0.896	0.830
Final R_1, wR_2	0.0465, 0.1246	0.0385, 0.0876	0.0549, 0.1271

Table 3.3 *(Contd…):*

	11	12	13
Formula	$(C_{12}H_8N_2)$: $(C_6H_6BO_2Cl)$	$(C_{12}H_8N_2)$: $(C_6H_6BO_2Br)$	$(C_{12}\ H_8\ N_2)$: $2(C_6H_6BO_2I)$
Formula Wt.	336.57	381.03	675.84
Crystal habit	Block	Block	Block
Crystal color	Yellow	Yellow	Yellow
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	7.506(2)	7.621(4)	7.202(2)
b (Å)	9.118(2)	9.054(5)	34.347(8)
c (Å)	11.635(4)	11.668(6)	21.339(5)
α (°)	79.24(3)	80.58(2)	90
β (°)	88.39(2)	88.21(2)	105.660(8)
γ (°)	84.33(2)	84.07(2)	90
V (Å^3)	778.4(4)	789.9(7)	5083(2)
Z	2	2	8
D_{calc} (g cm^{-3})	1.436	1.602	1.766
T(K)	120(2)	120(2)	298(2)
(λ)Mo K_α	0.71073	0.71073	0.71073
μ(mm^{-1})	0.258	2.615	2.508
2θ range (°)	46.50	66.28	50.08
Total Reflns.	6062	11774	25538
Unique Reflns.	2234	5648	8980
Reflns. Used	1960	4517	5605
No. Parameters	225	273	625
GOF on F^2	1.135	0.936	1.000
Final R_1, wR_2	0.0275, 0.0744	0.0289, 0.0650	0.0420, 0.1002

Table 3.4: Characteristics of various intermolecular interactions (distances/Å and angles/º) #

Compound	Hydrogen bond (D-H···A)							
	O–H···O	O–H···N	C-H···O	C-H···N	C-H···Cl	C-H···Br	C-H···I	X···X
5	1.86 2.79 158 2.05 2.96 154	1.74 2.71 172 1.92 2.86 159	2.66 3.71 163 2.84 3.65 131		2.95 3.74 130			
6	1.91 2.78 147 1.98 2.95 171	1.78 2.70 154 1.89 2.86 169	2.60 3.64 161 2.75 3.83 175			3.00 3.84 134		
7	1.85 2.79 160 2.03 3.02 177	1.74 2.71 166 1.89 2.86 167	2.55 3.60 158 2.62 3.52 140				3.28 4.12 136	
8	1.76 2.66 155 1.79 2.67 151 1.93 2.80 146	1.81 2.78 169 1.82 2.77 162 1.83 2.77 161	2.47 3.47 152 2.56 3.62 166 2.58 3.59 154	2.69 3.79 179 2.97 3.81 135	2.66 3.71 161 2.77 3.73 148			
9	1.75 2.70 157 1.79 2.69 152 1.92 2.81 147	1.81 2.76 161 1.82 2.79 167 1.83 2.77 159	2.48 3.45 149 2.51 3.51 154 2.55 3.63 169	2.66 3.76 177 2.76 3.65 139		2.79 3.84 161 2.85 3.78 145		**(Br···Br)** 3.42
10		1.81 2.74 157 1.95 2.84 151						**(I···N)** 3.09
11	1.78 2.76 177	1.74 2.70 164	2.36 3.30 142 2.57 3.36 129	2.80 3.80 152	2.93 3.67 126			
12	1.78 2.76 171	1.76 2.70 159	2.44 3.35 141 2.54 3.37 132	2.74 3.77 159				
13	1.73 2.71 171 1.78 2.76 173 1.80 2.78 173 1.86 2.84 175	1.78 2.75 168 1.81 2.77 165 1.82 2.76 159	2.28 3.22 144					**(I···I)** 3.78

#The three numbers in each column indicate H···A(O/F/Cl/Br/I), D(O/C)···A distances and D-H···A angles, respectively

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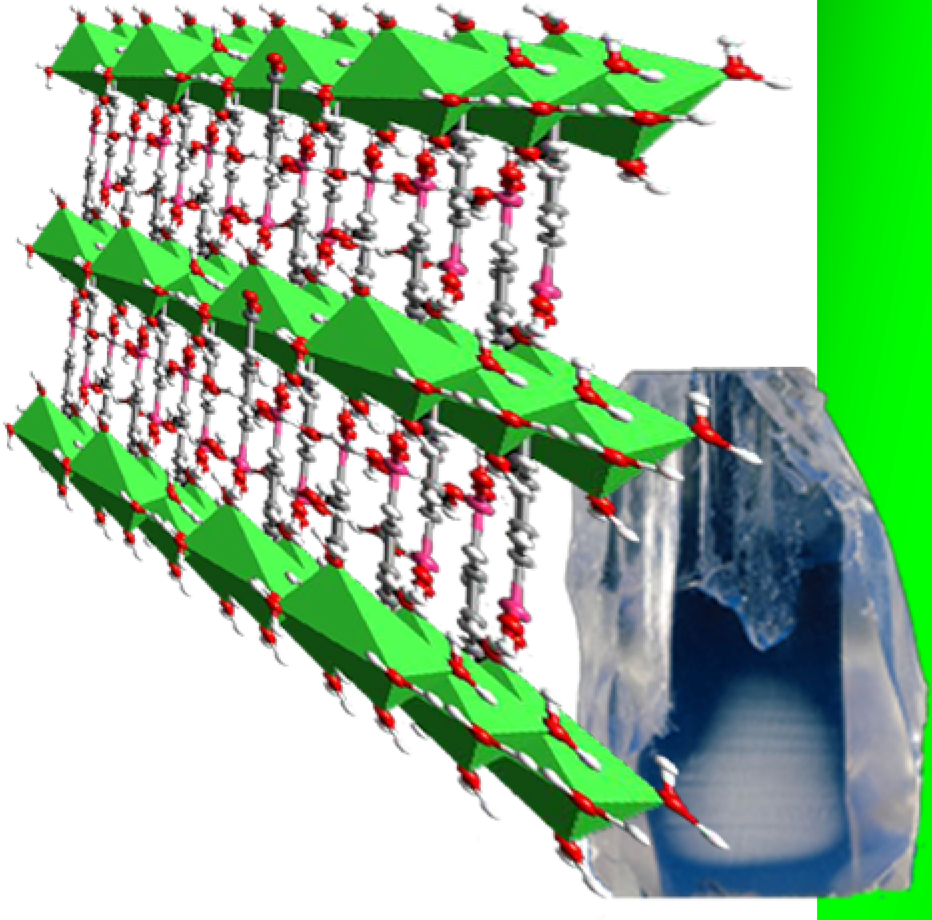
Chapter 4

Coordination Assemblies of 4-Carboxyphenylboronic Acid



4.1 Introduction

The study of coordination assemblies, with novel and exotic architectures and unusual chemical and physical properties, designed by careful selection of molecular building units is a prolific area of research in the contemporary supramolecular chemistry. The properties of the resulting assemblies are very much dependent on the characteristics of metal ions (coordination number, hybridization, oxidation etc.) and organic moieties (functional groups, chirality, topology etc) employed in the synthesis.[1] In addition, reaction conditions like solvent of crystallization, temperature, pressure, pH etc. and auxiliary components like counter ions, nonbonding guests, template molecules etc., would play a crucial role in the self-assembly process.[2,3] Schematic representation of some of the diverse topologies of coordination assemblies known in the literature is shown in Figure 4.1.

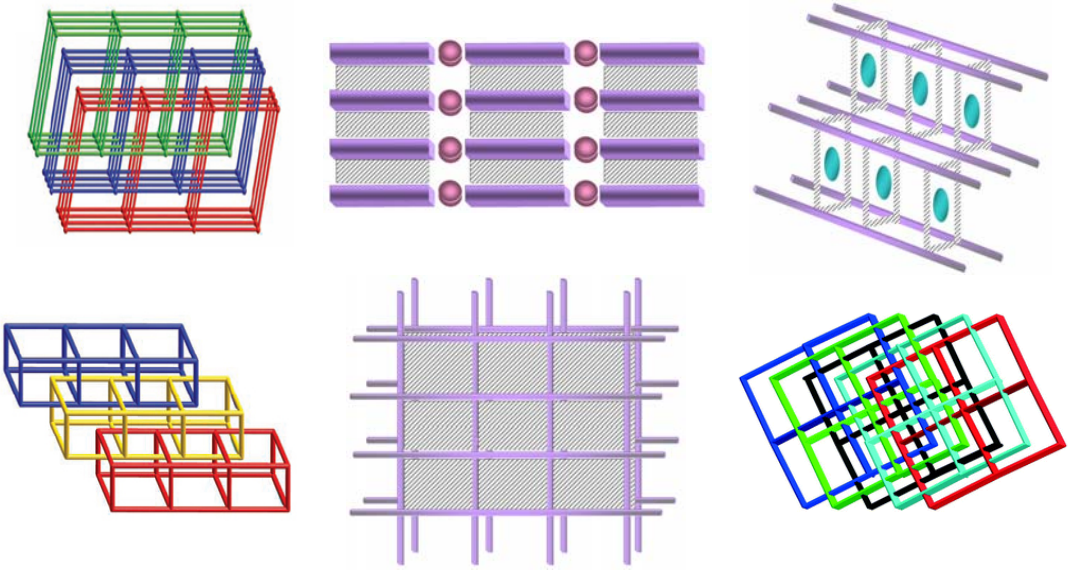


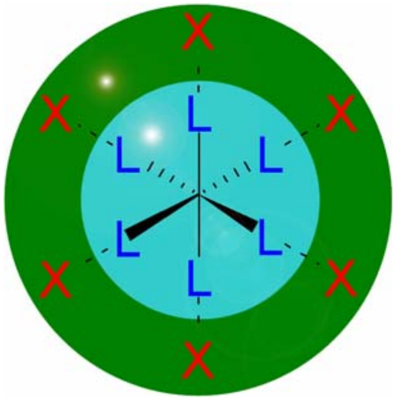
Figure 4.1: Schematic representation of the structural frameworks that can be constructed by using different metal ions and organic linkers.

Among the vast number of ligands employed in the preparation of coordination assemblies, *N*-donor spacer ligands and molecules with multiple bridging moieties such as carboxylate groups are the best studied. Towards this, seminal contributions made by Yaghi, Kitagawa, Zaworotko, Braga, Hosseini, Stang, Schröder etc., are noteworthy.[4] The coordination assemblies are well studied for their utility in gas storage, selective separation and catalysis due to the unique properties exhibited by these materials in the nanoporous environment of their frameworks. In addition, the electronic, optical and magnetic properties of the metal centres together with the contribution from the organic ligands can produce assemblies with unprecedented properties. [5]

In general, coordination assemblies are formed and stabilized through coordinate bond formed between the metal ions and organic ligand i.e.; through the primary or first coordination sphere. However, in some instances, coordination spheres are being separated by secondary interactions like non-covalent interactions cooperatively with the metal ligation, well known in the literature as second-sphere coordination (Scheme 4.1).[6]

The idea that a transition metal complex can interact with neutral or charged species in the second-sphere of coordination dates back to Werner's original description of coordination chemistry. Werner found that, the concept of second-sphere coordination is essential to explain the phenomena like solvents of crystallization, the dependence of optical rotations on the nature of solvent and anion, as well as adduct formation between amines and saturated complexes etc.[7]

Scheme 4.1

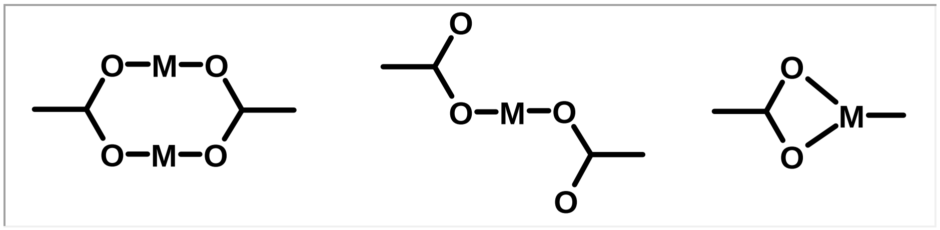


A schematic depiction of the first (blue) and second-spheres (green) of coordination for an octahedral ML_6 species.

The systematic investigations and analysis of the second coordination sphere, based upon non-covalent interactions of the first-sphere ligands with neutral or charged species, represent an active area of research in the supramolecular chemistry.[8] Among the various ligands, NH_3 and H_2O show greater tendency to yield structures directed by second-sphere coordination.[9] Since, coordination of H_2O or NH_3 species to an electropositive metal increases the acidity of the aqua or ammine species, it facilitates second-sphere hydrogen bonding to a neutral ligand or a charged anion.

Second-sphere coordination can play a pivotal role in biological systems, as these interactions can induce micro-environmental changes around the metal complex in biological systems and brings about perturbation of the electronic state of the metal complexes.[10] Molecular recognition through second coordination shell is also useful for the selective bulk liquid membrane transport and anion recognition.[11] Thus, the understanding of such network interactions coupled with the judicious choice of cations and anions could provide means of constructing intricate and novel molecular entities based on second-sphere coordination.

Scheme 4.2



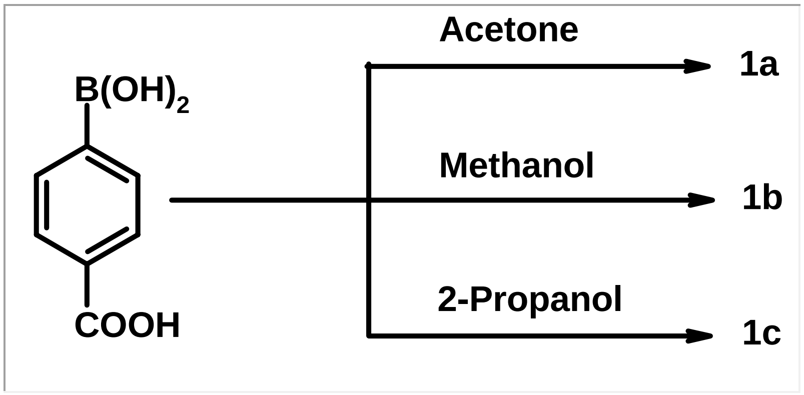
As described in the previous chapters, boronic acids have not been well explored in the supramolecular synthesis and that includes the studies of coordination assemblies as well. In this context, to demonstrate the ability of boronic acids in the design of metal-organic hybrid assemblies, compounds possessing exclusively –$B(OH)_2$ functionality, such as phenylboronic acid, 1,4-benzenediboronic acid, naphthaleneboronic acid etc., were employed. However, it was noted that none of these boronic acids yielded coordination complexes with the metal ions. Thus, boronic acids with additional functional moiety like –COOH, which is known to form dative bonds, have been chosen for the further exploration (Scheme 4.2).[12] In this regard, 4-carboxyphenylboronic acid, **1**, was identified and it has been observed that, its structural information is not known in the literature.

Thus, attempts were made to analyze the solid state structure of **1** and subsequently use it for the preparation of coordination assemblies. Interestingly, **1** gave three different solid state forms, with different recognition patterns, depending upon the solvent of crystallization.

4.2 4-Carboxyphenylboronic acid and its hydrates

4-Carboxyphenylboronic acid, **1**, was crystallized from various solvents by slow evaporation technique. While, anhydrous form (**1a**) was obtained from acetone, the monohydrate (**1b**) and the quarter-hydrate (**1c**) forms were obtained from methanol and 2-propanol respectively (Scheme 4.3). The resulting assemblies were characterized by single crystal x-ray diffraction method and the structural details of the resulting assemblies are discussed in the following sections.

Scheme 4.3



4.2.1 4-Carboxyphenylboronic acid (anhydrous form), 1a:

Colorless block-type crystals of the anhydrous form of 4-carboxyphenylboronic acid, **1a**, obtained from acetone, crystallize in a monoclinic space group (*C*2/*c*). Crystallographic details of **1a** are given in Table 4.1.

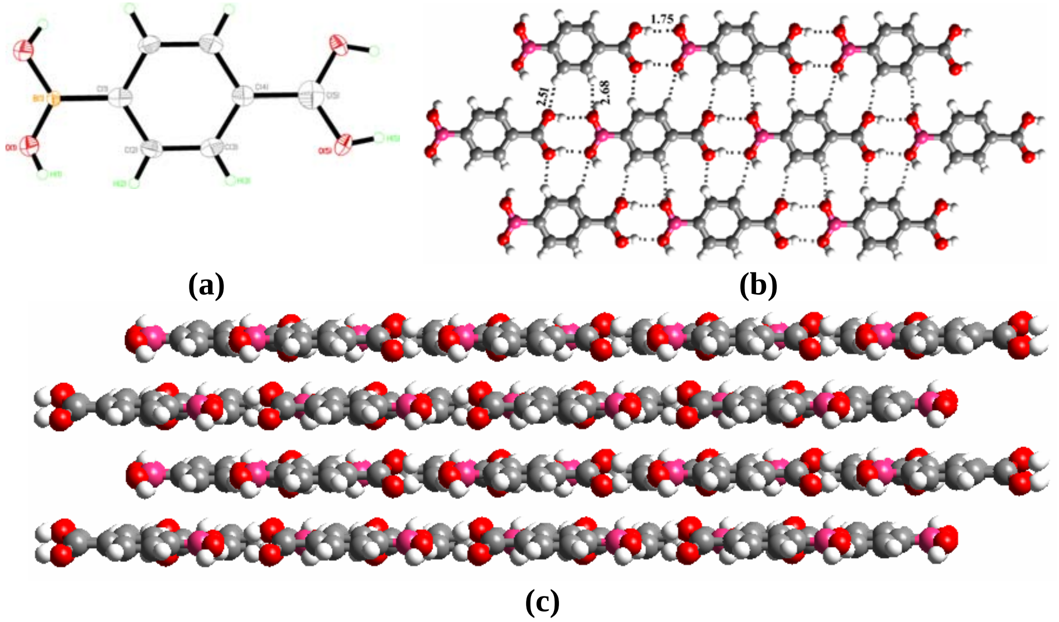
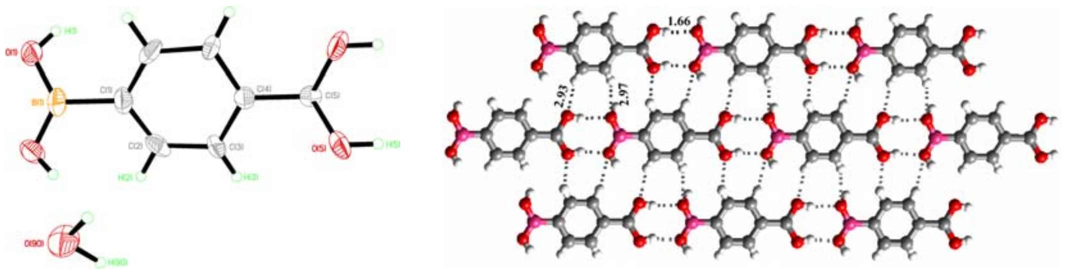


Figure 4.2: (a) The asymmetric unit of **1a**. (b) The molecules of **1** recognize each other through O-H···O as well as C-H···O hydrogen bonds forming a sheet like architecture in two-dimension. (c) Stacking of sheets in the three-dimensional crystal lattice.

Structure analysis revealed that, $–B(OH)_2$ group adopts *anti-anti* conformation and the –COOH group is disordered (Figure 4.2(a)). In the crystal lattice, the adjacent molecules interact with each other through O-H···O hydrogen bonds (H···O, 1.75 Å), formed between the $–B(OH)_2$ and –COOH groups, yielding one-dimensional tapes. Adjacent tapes are connected through C-H···O hydrogen bonds (H···O, 2.51, 2.68 Å), to form a sheet-like architecture (Figure 4.2(b)) and are stacked in three-dimensional arrangement, as shown in Figure 4.2(c).

4.2.2 Hydrates of 4-carboxyphenylboronic acid, 1b and 1c:

Slow evaporation of a methanol solution of **1** at ambient conditions, yielded colorless crystals of **1b** that crystallizes as monohydrate in a non-centrosymmetric space group, *Ccc*2. It was observed that, conformation of –B(OH)$_2$ and –COOH group in **1b** is similar to that of **1a** (Figure 4.3(a)).



(a) **(b)**

Figure 4.3: (a) The asymmetric unit of **1b**. (b) Two-dimensional arrangement of molecules in the crystal lattice of **1b**.

Structure analysis revealed that, the recognition pattern of the functional groups in **1b** are similar to that observed in **1a** with the formation of molecular tapes in one-dimension and a sheet-like architecture in two-dimensional arrangement. However, the three-dimensional arrangement is quite different between **1a** and **1b**, due to the presence of lattice water molecules. The water molecules, present in the crystal lattice, are inserted between the stacked layers of boronic acids (Figure 4.4(a)). It is quite interesting to note that, by using its donor-acceptor property, each water molecule interacts with four molecules of **1** (Figure 4.4(b)), present in the adjacent layers, through O-H$\cdots$O hydrogen bonds (O$\cdots$O distance 2.82Å). These interactions formed between the boronic acid and the water molecules, in turn, lead to the formation of a catenated structure, as shown in Figure 4.4(c).

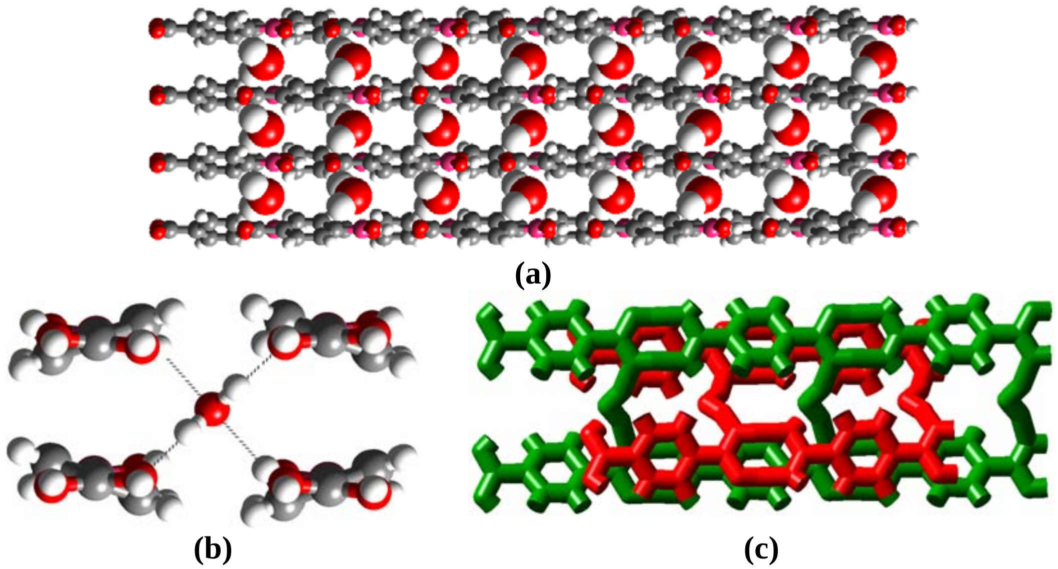


Figure 4.4: (a) The three-dimensional arrangement of molecules in the crystal structure of **1b**. (b) Water molecule is interacting with four molecules of **1** from the adjacent layers through O-H···O hydrogen bonds. (c) The catenated structure formed through the interaction of water molecules and **1**.

The second hydrated form, **1c** (quarter-hydrate), was obtained by crystallization of **1** from 2-propanol. In **1c**, the boronic acid and the water molecule are present in a 4:1 ratio in the crystal lattice. The molecules of **1** show distinct variation from the anhydride form **1a** and the monohydrate form **1b**, as the $–B(OH)_2$ group adopts *syn-anti* conformation and the –COOH group is fully ordered. However, the water molecule present in **1c** shows disorder, as illustrated in Figure 4.5.

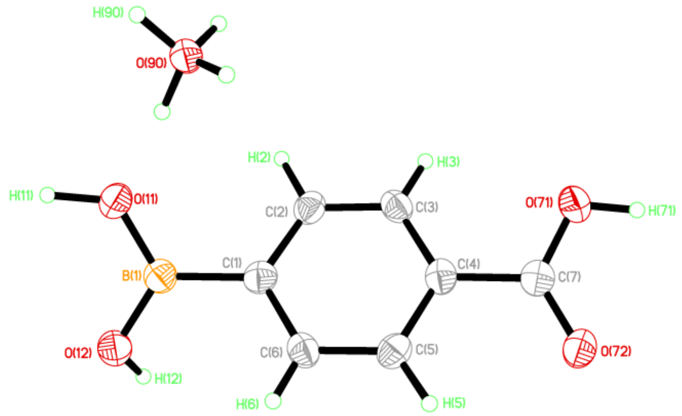
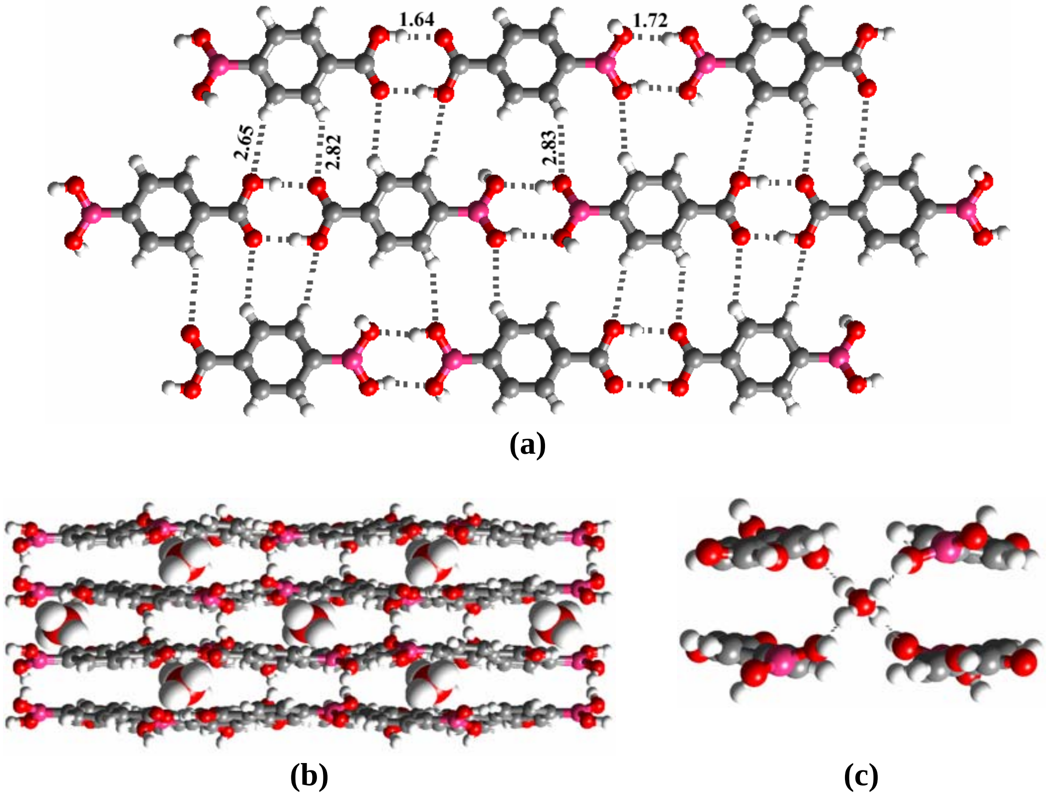


Figure 4.5: The asymmetric unit of **1c**.

In **1c**, the –COOH and –B(OH)$_2$ moieties form centrosymmetric *homomeric* dimers (–COOH$\cdots$HOOC– and –B(OH)$_2$$\cdots$(OH)$_2$B–), rather than the *heteromeric* interactions observed in **1a** and **1b**. This leads to the formation of molecular tapes, that are further connected through C-H$\cdots$O hydrogen bonds (H$\cdots$O, 2.63, 2.82, 2.83 Å), forming planar sheets in two-dimensional arrangement (Figure 4.6(a)).

The disordered water molecules are inserted between the sheets of boronic acid molecules (Figure 4.6(b)) and interact with the molecules of **1** lying in the adjacent layers (Figure 4.6(c)). In **1c**, the adjacent layers exhibit a staggered arrangement and are not stacked in either parallel or anti-parallel manner, as generally observed in the centrosymmetric structures.



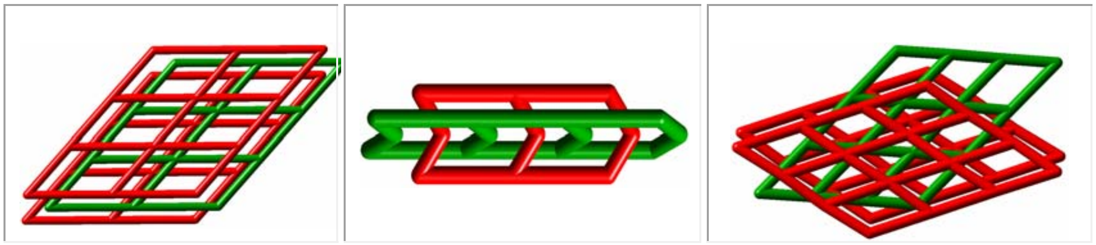
(a)

(b) (c)

Figure 4.6: (a) Two-dimensional arrangement of the molecular chains yielding a planar sheet like structure in **1c**. (b) Stacking of the boronic acid sheets in three-dimensional arrangement with water molecules are inserted between the layers. (c) The disordered water molecule present in the lattice is interacting with four acid molecules through O-H···O hydrogen bonds.

A collective analysis of the solid state forms **1a**-**1c** revealed that, in all the cases the molecules form a tape-like topology even though they have variation in the basic recognition patterns. In the case of **1a** and **1b**, non-centrosymmetric *heterodimers* are formed, by making use of the disordered –COOH functionality and *anti-anti* conformation of the –$B(OH)_2$ group. But in the case of **1c**, the tape-like topology is formed by the centrosymmetric *homodimers* involving the –$B(OH)_2$ and –COOH groups. All the structures form stacked layered architectures with water molecules being inserted between the layers in the hydrate forms. In the three-dimensional arrangement, **1a** yielded a stacked layered assembly while, **1b** forms a catenated structure with water molecules acting as nodes connecting two adjacent layers. Although **1c** forms a layered assembly, the alternate layers are not related by translational symmetry as observed in **1a**. The structural variations observed in all the three forms are represented in Scheme 4.4.

Scheme 4.4



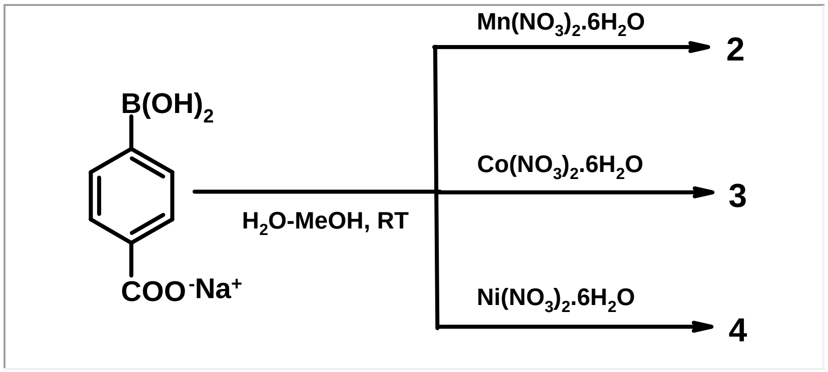
1a **1b** **1c**

Considering the ability of **1** to form a variety of hydrogen bonding patterns, in particular, the *homomeric* pattern observed in **1c**, preparation of its coordination complexes with various metal ions have been carried out, and the resulting assemblies were analyzed and the details are discussed in the following section.

4.3 Coordination complexes of 4-carboxyphenyl boronic acid

Coordination complexes were prepared by the reaction of monosodium salt of 4-carboxyphenylboronic acid with various metals(II) salts and the reaction yielded isostructural complexes with the formation of clay-like architecture, as revealed by the x-ray analysis (Scheme 4.5).

Scheme 4.5



4.3.1 Coordination complexes 2-4:

Complex **2**, was prepared by the reaction of monosodium salt of **1** and $Mn(NO_3)_2.6H_2O$ in a 1:1 methanol-water mixture and allowing the solution for slow evaporation at ambient conditions. Pale yellow block-type crystals obtained were used for the analysis by single crystal x-ray diffraction technique.

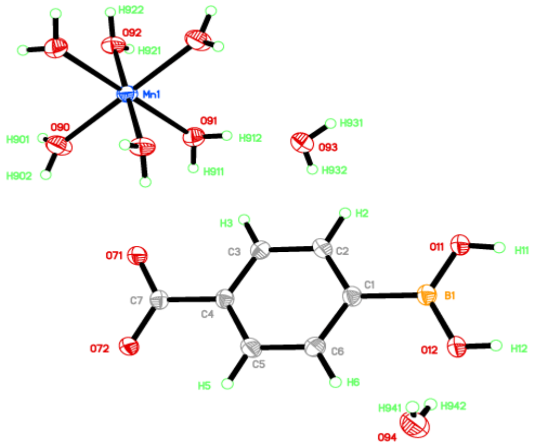


Figure 4.7: The asymmetric unit of the coordination complex **2**.

The complex **2**, with composition $[Mn(H_2O)_6].4(H_2O).2(C_7H_6BO_4)$, crystallizes in a triclinic system ($P\bar{1}$) and the asymmetric unit contains Mn(II) ion in the octahedral geometry with all its coordination sites occupied by water molecules. Along with this, one boronic acid molecule and two free water molecules are also present in the crystal lattice (Figure 4.7). Thus, 4-carboxyphenylboronic acid did not form any coordinate bond with the metal ions even in the presence of the –COO$^-$ group, which is well-known for its interaction with the metal ions. In the complex, the –B(OH)$_2$ group adopts *syn-syn* conformation and interact with the –COO$^-$ moiety of the adjacent molecules through the formation of cyclic O-H$\cdots$O$^-$ interactions (H$\cdots$O$^-$, 1.68Å), thus yielding one-dimensional tapes.

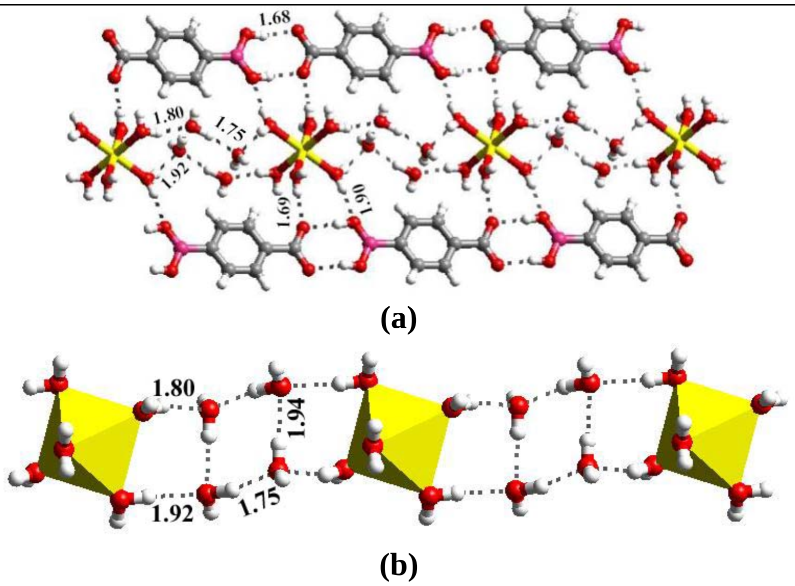


Figure 4.8: (a) The interaction between Mn(II) center and the molecules of **1** are established through second-sphere coordination. (b) The adjacent Mn^{II}(H$_2$O)$_6$ units are connected through the tetrameric water clusters.

Further, the octahedral Mn(H$_2$O)$_6$ units are connected together by the lattice water molecules through O-H$\cdots$O hydrogen bonds, which extends in one-dimension to form an inorganic tape. In the two-dimensional arrangement, the organic tapes of boronic acids are embedded between the inorganic $Mn(H_2O)_6$ layers, as shown in Figure 4.8(a). The organic and inorganic tapes are connected through O-H$^{\cdots}$O (H$^{\cdots}$O, 1.90 Å) and O-H$^{\cdots}$O$^-$ (H$^{\cdots}$O$^-$, 1.69 Å) hydrogen bonds, thus, establishing second-sphere coordination.

In the complex, water molecules play a major role in the formation and stabilization of the coordination assembly. The free water molecules present in the crystal lattice are self-assembled to form a tetrameric unit through O-H$^{\cdots}$O hydrogen bonds (H$^{\cdots}$O, 1.75, 1.94 Å). The tetramers, thus formed, interacts with four coordinated water molecules on the neighboring $Mn(H_2O)_6$ centers through O-H$^{\cdots}$O hydrogen bonds (H$^{\cdots}$O, 1.80, 1.92Å), forming a finite octameric water cluster, as shown in Figure 4.8(b). In the three-dimensional arrangement, the complex yielded an inorganic clay-like architecture, in which the inorganic layers are being separated by boronic acid layers, as shown in Figure 4.9.

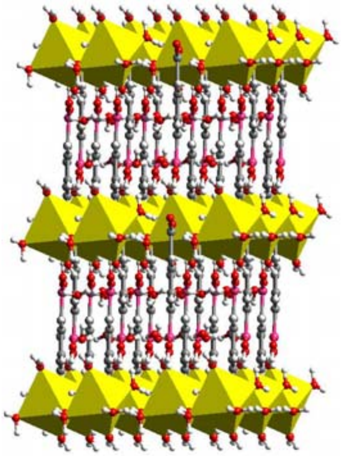


Figure 4.9: Three-dimensional packing of the complex **2**. The metal centers are shown in yellow color.

Similarly, a reaction between the $Co(NO_3)_2.6H_2O$ and monosodium salt of **1** yielded complex **3**, having composition $[Co(H_2O)_6].4(H_2O).2(C_7H_6BO_4)$. Further, the structural analysis revealed that, the complex **3** **(**triclinic, $P\bar{1}$) is isostructural to complex **2** except for the distances and angles (see Table 4.4) of the intermolecular interactions. The asymmetric unit of the complex is shown in Figure 4.10.

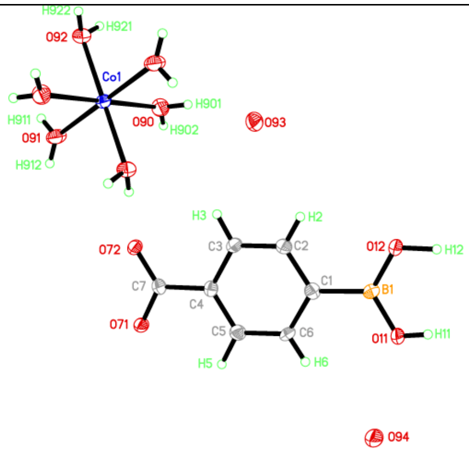
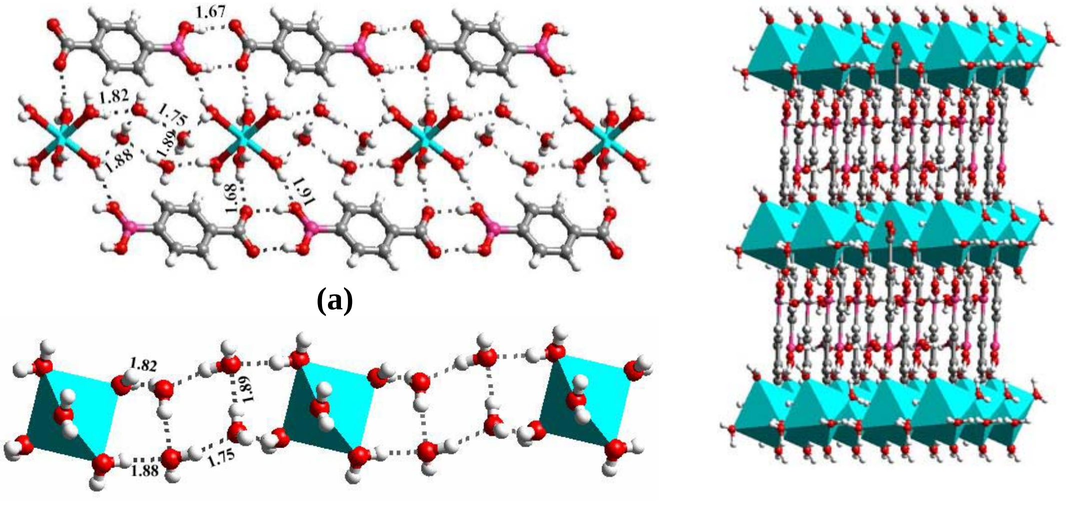


Figure 4.10: The asymmetric unit of the complex **3**.

As observed in complex **2**, in complex **3** also, the interaction between **1** and Co(II) centers are established through the second-sphere coordination. The free water molecules form tetramers and connect the adjacent octahedral Co(II) metal centerss through $O\text{-}H\cdots O$ hydrogen bonds ($H\cdots O$, 1.82, 1.88 Å), yielding one-dimensional inorganic tapes. The boronic acid tapes, formed by the recognition between the –$B(OH)_2$ and –COO^- functionalities ($H\cdots O^-$, 1.67Å), are inserted between the inorganic layer, thus yielding a clay-like architecture in three-dimensional arrangement (Figure 4.11).



(a)

(b) (c)

Figure 4.11: (a) The interaction between the octahedral Co(II) metal center and the molecules of **1** are established through second-sphere coordination. (b) The adjacent $Co^{II}(H_2O)_6$ units are connected through the tetrameric water clusters. (c) The clay-like architecture present in the three-dimensional arrangement of the complex **3**.

Complex **4**, was indeed prepared by employing the same method described in the cases of complexes **2** and **3**, except for the metal salt employed, and obtained as green-colored blocks. Analysis of the crystals by single crystal x-ray diffraction technique revealed that, the complex **4** has the composition $[Ni(H_2O)_6].4(H_2O).2(C_7H_6BO_4)$ and retains all the structural features as that of complexes **2** and **3**, with the formation of clay-like architecture in three-dimensional arrangement (see Figure 4.12).

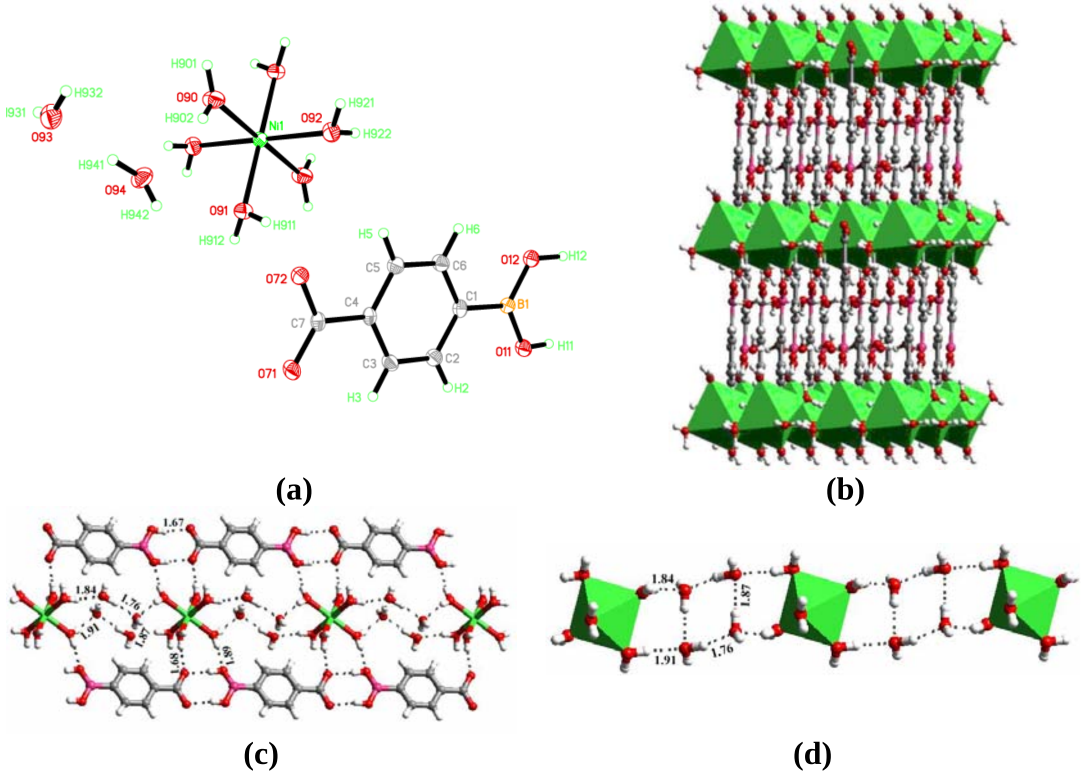


Figure 4.12: (a) The asymmetric unit of the complex **4.** (b) The clay-like architecture present in the three-dimensional arrangement of the complex **4**. (c) The interaction between the Ni(II) ions and the molecules of **1** are established through second-sphere coordination. (d) The adjacent $Ni^{II}(H_2O)_6$ units are connected through the tetrameric water clusters.

Thus, all the complexes, **2-4**, were found to be isostructural and no coordinate bonds were observed between the metal centre and the boronic acid molecules. Instead, the assemblies are stabilized through second-sphere coordination and in the three-dimensional arrangement all the complexes form an inorganic clay-like architecture. Further, both the coordinated and the free water molecules played a major role in the formation and stabilization of the complexes.

A close analysis of structural features of the complexes **2-4**, in particular, formation of clay-like architecture, with inorganic layers being separated by organic layers, suggests the possibility of developing materials with anisotropic properties, such as electronic, optical and magnetic, if the metal centers are held together by species that can be conducive for charge propagation. For this purpose, different types of ligands, to replace both coordinated and lattice water, have been employed in the preparation of novel coordination assemblies. However, only 1,2-bis(4-pyridyl)ethane gave single crystals with sodium salt of 4-carboxyphenylboronic acid and Co(II).

4.3.2 Coordination complex $[Co(H_2O)_2(C_{12}H_{12}N_2)_2].2C_7H_6BO_4$, 5:

Slow evaporation of the 1:1:1 solution of $Co(NO_3)_2.6H_2O$, sodium salt of **1** and 1,2-bis(4-pyridyl)ethane at room temperature yielded the complex **5**. The complex **5** crystallizes in the monoclinic system, *C*2/*c*, and has the composition, $[Co(H_2O)_2(C_{12}H_{12}N_2)_2].2C_7H_6BO_4$, as determined by x-ray diffraction studies.

In the complex **5**, the Co(II) metal center is in the octahedral geometry, with its coordination sites being satisfied by four bridging ***bpyea*** units (in the equatorial plane) and two water molecules in the axial positions. One of the ***bpyea*** molecules is disordered and in a typical arrangement, the ***bpyea*** units exhibit the bent conformation and act as bridging ligands, connecting the adjacent Co(II) metal centers thus, yielding one-dimensional coordination polymer (Figure 4.13(a)). As observed in complexes **2-4**, the molecules of **1** are not coordinated to the Co(II) metal center, but, forms a separate layer through several hydrogen bonds, as shown in Figure 4.13(b).

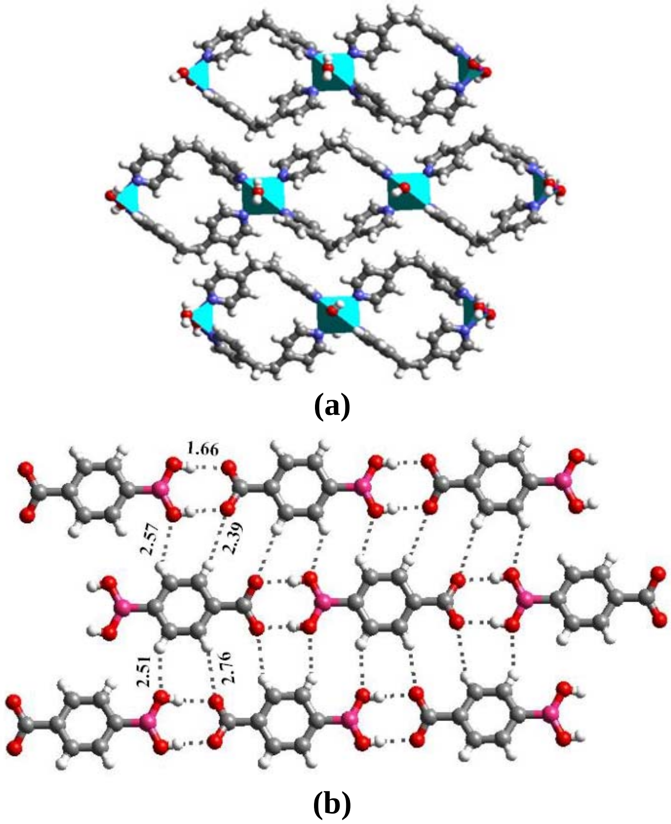


Figure 4.13: (a) Coordination polymers formed in the crystal structure of **5** through two water molecules and four molecules of 1,2-bis(4-pyridyl)ethane. (*The disorder of the* ***bpyea*** *ring is omitted for the purpose of clarity*.) (b) Molecular sheet formed by the arrangement of boronic acid molecules in two-dimension.

In the three-dimensional arrangement, the sheets formed by boronic acid molecules and Co(II)-pyridyl hybrid layers are arranged alternately, forming an inorganic clay-like architecture (Figure 4.14).

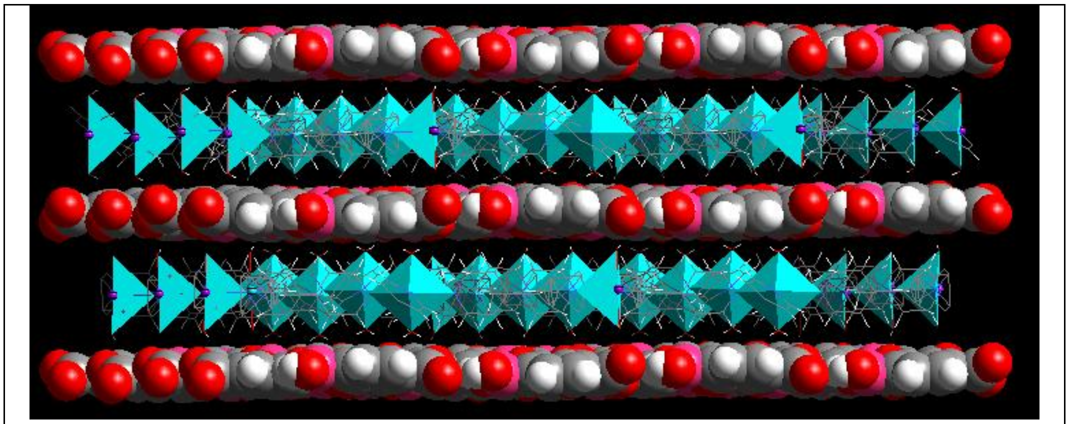


Figure 4.14: Three-dimensional representation of the complex **5**. The sheets formed by boronic acid molecules and Co(II) coordination spheres are stacked alternatively, forming a clay-like architecture.

Thus, in all the complexes, **2-5**, the boronic acid molecule showed the tendency to form only hydrogen bonded interactions with the primary coordination sphere. In the presence of the spacer ligand like, 1,2-bis(4-pyridyl)ethane, a coordination polymer was formed by the replacement of the hydrated primary coordination environment. But, the boronic acids form second sphere coordination, without any direct interaction with the metal centre.

4.4 Conclusions

The study reports the utilization of 4-carboxyphenylboronic acid in the preparation and analysis of coordination assemblies. In all the cases, the obtained assemblies have a clay-like structure in the three-dimensional arrangement with organic and inorganic layers arranged alternately. It is noteworthy to mention that, the assemblies are essentially stabilized by second-sphere coordination. Also, water molecules, both the lattice and the coordinated ones, played a significant role in the structure stabilization.

In addition, various solid-forms of 4-carboxyphenylboronic acid, **1a**-**1c**, obtained, by varying the solvent of crystallization and reaction conditions, demonstrated the flexibility and versatility of the $–B(OH)_2$ functional group to exist in various conformations such as *syn-anti* and *anti-anti*.

4.5 Experimental section

4-Carboxyphenylboronic acid was obtained commercially and the crystallization experiments were carried out at room temperature by dissolving it in spectroscopic-grade solvents, as the case may be. A non-ambient technique like hydrothermal method was also employed for the crystallization and it was noted that the compound **1** is stable up to 180^{o}C. In a typical experiment, 4-carboxyphenylboronic acid (0.165g, 0.1mmol) was added to 15 mL distilled water in a Teflon-lined stainless-steel autoclave with autogenous pressure, and heated to 180 ^{o}C for 24 hours. For the preparation of the coordination complexes, the monosodium salt of 4-carboxyphenylboronic acid was prepared by constant stirring with NaOH, in a 1:1 molar ratio, in methanol. The resulting solution was warmed on a water bath for 30 minutes and then the solvent was removed.

A general procedure for the synthesis of complexes 2-4

To a hot aqueous solution of $M^{II}(NO_3)_2.6H_2O$ (1 mmol), (where M^{II} = Mn, Co or Ni) was added a methanolic solution (5 mL) of sodium salt of 4-

carboxyphenylboronic acid (0.187g, 1 mmol), with constant stirring over a period of five minutes. The reaction mixture was warmed on a water bath for a while and the resulting solution was filtered and kept for slow evaporation at room temperature. Single crystals of **2-4** suitable for x-ray diffraction studies were obtained over a period of 4-5 days. The crystals thus, obtained were washed thoroughly using cold distilled water and dried.

Synthesis of complex 5

To a hot aqueous solution of $Co(NO_3)_2.6H_2O$ (0.291g, 1 mmol), methanolic solution (5 mL) of sodium salt of 4-carboxyphenylboronic acid (0.187gm, 1mmol) was added drop wise with constant stirring. To this mixture 1,2-bis(4-pyridyl)ethane (0.184g, 1 mmol) in methanol (5 mL) was added drop wise. This reaction mixture was warmed for about 20 minutes and the resulting pink solution was filtered and kept for slow evaporation at room temperature. Pink colored block type crystals suitable for x-ray diffraction studies were obtained over a period of one week.

X-ray crystallography

Single crystals of **1a**-**1c** and the complexes **2**-**5**, were carefully chosen after they were viewed through a Leica microscope supported by a rotatable polarizing stage and a CCD camera. The crystals were glued to a thin glass fiber using an adhesive (cyanoacrylate) and mounted on a diffractometer equipped with an APEX CCD area detector. The intensity data were processed using Bruker's suite of data processing programs (SAINT), and absorption corrections were applied using

SADABS. The structure solution of all the complexes was carried out by direct methods, and refinements were performed by full-matrix least-squares on F^2 using the SHELXTL-PLUS suite of programs.[13] All the structures converged to good *R* factors. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms obtained from Fourier maps were refined isotropically. And for all the structures, the calculations of intermolecular interactions were carried by using the HBOND NORM option of the PLATON program.[14]

Tables

Table 4.1: Crystallographic information of the structures **1a**, **1b** and **1c**.

	1a	**1b**	**1c**
Formula	$C_7H_7BO_4$	$(C_7H_7BO_4):(H_2O)$	$(C_7H_7BO_4):0.25(H_2O)$
Formula Wt.	165.94	183.95	170.44
Crystal habit	Block	Block	Needle
Crystal color	Colorless	Colorless	Colorless
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	*C*2/*c*	*Ccc*2	*Fddd*
a **(Å)**	11.378(5)	7.566(5)	13.140(3)
b **(Å)**	9.825(5)	11.929(7)	18.138(5)
c **(Å)**	7.245(3)	9.769(6)	25.328(7)
α **(°)**	90	90	90
β **(°)**	120.08(7)	90	90
γ **(°)**	90	90	90
V **(Å^3)**	700.8(6)	881.7(9)	6037(3)
Z	4	4	32
D_{calc} **(g cm^{-3})**	1.573	1.386	1.500
T**(K)**	133(2)	298(2)	133(2)
(λ)Mo K$_\alpha$	0.71073	0.71073	0.71073
μ**(mm^{-1})**	0.126	0.116	0.122
2θ range (°)	46.60	54.34	56.56
Total Reflns.	1444	2925	12537
Unique Reflns.	505	495	1797
Reflns. Used	388	435	1181
No. Parameters	61	69	137
GOF on F^2	1.084	1.433	1.058
Final R_1, wR_2	0.0758, 0.2161	0.0713, 0.1587	0.0523, 0.1335

Table 4.2: Characteristics of hydrogen bonds (distances/Å and angles/º) #

Hydrogen bond (D-H···A)	1a	1b	1c
O–H···O	1.75 2.70 161 2.08 2.91 141	1.66 2.61 163 1.88 2.82 160	1.64 2.62 178 1.67 2.65 173 1.72 2.69 173 1.84 2.72 148
C-H···O	2.51 3.48 149 2.68 3.61 143 2.85 3.57 124	2.93 3.75 132 2.97 3.84 137	2.65 3.68 158 2.82 3.69 137 2.83 3.71 139 2.90 3.80 140

#Three numbers in each column correspond to distances H···A(O), D(O,C)···A and angle D-H···A.

Table 4.3: Crystallographic information for the complexes **2-5**.

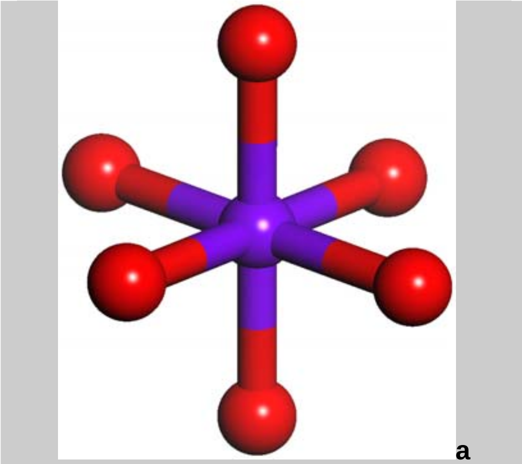
	2	3	4	5
Formula	$[Mn(H_2O)_6]$ $4(H_2O)$ $2(C_7H_6BO_4)$	$[Co(H_2O)_6]$ $4(H_2O)$ $2(C_7H_6BO_4)$	$[Ni(H_2O)_6]$ $4(H_2O)$ $2(C_7H_6BO_4)$	$[Co(H_2O)_2(C_{12}H_{12}N_2)_2]$ $2(C_7H_6BO_4)$
Formula Wt.	564.96	568.95	568.73	786.23
Crystal habit	Block	Block	Block	Block
Crystal color	Yellow	Pink	Blue	Pink
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	6.862(2)	6.776(3)	6.781(2)	19.478(5)
b (Å)	9.705(3)	9.592(4)	9.572(3)	16.672(4)
c (Å)	9.806(3)	9.786(5)	9.824(3)	22.781(6)
α (º)	98.33(5)	98.19(7)	97.89(4)	90
β (º)	92.21(5)	91.66(8)	92.05(5)	93.23(5)
γ (º)	108.22(5)	108.35(7)	108.55(4)	90
V (Å^3)	611.3(3)	595.7(5)	596.7(3)	7386(3)
Z	1	1	1	8
D_{calc} (g cm^{-3})	1.535	1.586	1.583	1.414
T(K)	133(2)	133(2)	133(2)	133(2)
(λ)Mo K$_\alpha$	0.71073	0.71073	0.71073	0.71073
μ(mm^{-1})	0.621	0.804	0.897	0.529
2θ range (º)	56.70	56.56	56.38	56.50
Total Reflns.	7016	6817	3532	21571
Unique Reflns.	2776	2699	2557	8363
Reflns. Used	2448	2141	2261	4455
No. Parameters	224	224	224	539
GOF on F^2	1.022	0.963	1.016	0.954
Final R_1, wR_2	0.034, 0.088	0.041, 0.099	0.041, 0.098	0.091, 0.238

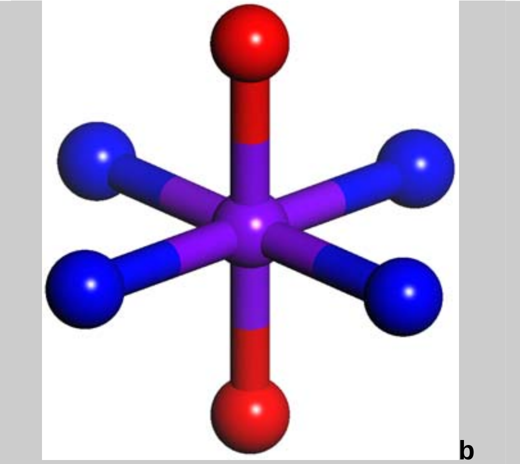
Table 4.4: Characteristics of hydrogen bonds (distances/Å and angles/º)[#] for the complexes **2-5**.

Hydrogen bond (D-H···A)	2	3	4	5
O–H···O	1.75 2.72 166 1.80 2.78 171 1.87 2.85 177 1.89 2.83 157 1.92 2.83 153 1.94 2.85 153 1.94 2.86 154	1.75 2.71 165 1.82 2.79 166 1.88 2.82 161 1.89 2.87 171 1.90 2.86 164 1.91 2.88 168 1.91 2.84 157	1.76 2.74 171 1.84 2.80 165 1.87 2.82 160 1.88 2.83 159 1.89 2.87 174 1.91 2.82 153 1.91 2.87 165	1.66 2.64 174 1.78 2.66 146 1.80 2.67 146 1.81 2.69 148
O-H···O$^-$	1.67 2.66 178 1.68 2.66 174	1.67 2.65 178 1.68 2.66 170	1.67 2.65 178 1.68 2.66 170	1.78 2.66 146 1.80 2.67 146 1.81 2.69 148
C-H···O	2.62 3.58 146 2.65 3.56 140 2.94 3.78 135	2.64 3.40 126 2.66 3.62 148 2.69 3.56 137	2.63 3.56 144 2.64 3.58 145 2.99 3.77 129	2.51 3.32 130 2.57 3.56 152
C-H···O$^-$				2.37 3.45 178 2.39 3.35 146 2.76 3.79 160

[#] The three numbers in each column correspond to distances H···A(O, O$^-$), D(O,C)···A and angle D-H···A.

Table 4.5: Coordination environment of the M(II) center (M=Mn, Co and Ni) in the complexes, **2-5** (Bond lengths in Å).





Complex	**M(II)**	**M(II)-O**	**M(II)-N**
2	Mn	2.130(1) 2.182(1) 2.192(1)	
3	Co	2.038(2) 2.088(2) 2.109(2)	
4	Ni	2.022(2) 2.058(2) 2.060(2)	
5	Co	2.030(4) 2.050(3) 2.054(4)	2.186(3) 2.186(3) 2.236(3) 2.240(4)
a – metal center of complexes 2,3 and 4		***b – metal center of complexes 5***	

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National

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