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STUDIES OF SUPRAMOLECULARLY ORGANIZED CHEMICAL SYSTEMS

AND

OF OPEN-FRAMEWORK METAL SQUARATES AND ORGANIC AMINE SQUARATES

A thesis submitted in partial fulfillment of the
Requirements of the degree of Master of Science as a part of the
Integrated Ph.D. programme

By

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CERTIFICATE

This is to certify that the thesis entitled "Studies of supramolecularly organized chemical systems and of open-framework metal squarates and organic amine squarates" by K. SIVASHANKAR is a record of original bonafide work carried out under my guidance and has not been submitted in any University or Institute for a degree.

Prof. C. N. R. Rao

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PART I

STUDIES OF A FEW SUPRAMOLECULARLY ORGANIZED CHEMICAL SYSTEMS[*]

Summary

In this part, results of the investigations of supramolecular organic and organic-inorganic systems formed by cyanuric acid, melamine and 4,4'-bipyridyl are discussed.

Complexes of melamine (**M**) with 4,4'-bipyridyl and $AgNO_3$ having compositions, $C_{10}H_8N_2{:}0.5(C_3H_6N_6){:}H_2O$ and $[Ag(C_3H_6N_6)]NO_3$ respectively, have been prepared for the first time. A crystallographic investigation has shown unique hydrogen bonding patterns in the two systems. The melamine-4,4'-bipyridyl complex shows a supramolecular organization wherein hydrogen bonding between melamine and water molecules results in molecular tapes. The tapes are connected by hydrogen bonding to 4,4'-bipyridyl giving rise to rectangular molecular boxes. In the melamine-$AgNO_3$ complex, the melamine molecules are bound to Ag^+ ions forming a coordination polymer consisting of helical **M**-Ag-**M** chains. These helices interact with each other through N – H...N hydrogen bonds.

A complex between cyanuric acid (**CA**), 4,4'-bipyridyl (**BP**) and Ag(I), with the composition, $[Ag_2(C_3H_2N_3O_3\text{-}\kappa N)_2(C_{10}H_8N_2\text{-}\kappa N)]$ has been prepared.

Crystal structure analysis shows that the **CA** molecules are linked to the **BP** units through silver atoms by the formation of N-Ag-N bonds, wherein one of the hydrogens of **CA** is replaced by Ag(I). The structure resembles the chain structure of the **CA.BP** adduct where **CA-BP-CA** chains are formed by N – H...N hydrogen bonds, linked to one another by N – H...O hydrogen bonds between the **CA** molecules. A C – H...O induced coplanarity of the pyridyl rings in 4,4'-bipyridyl moiety is observed. The structure also displays an N – H...O and C – H...O assisted hydrogen bonded staircase.

Hydrogen bonded complexes of cyanuric acid (**CA**) with pyridine, $[C_3N_3H_3O_3: C_5H_5N]$, **1**, and guanidinium carbonate $[C_3H_2N_3][C(NH_2)_3]$, **2**, have been prepared at room temperature and characterized by single-crystal X-ray diffraction. Structure of **1** shows pyridine molecules substituting the inter-tape hydrogen bond in **CA** by N – H...N and C – H...O hydrogen bonds. The structure reveals **CA** - pyridine hydrogen bonded single helices held together by dimeric N – H...O hydrogen bonding between **CA** molecules. In **2**, the **CA** tapes, resembling a sine wave, interact with the guanidinium cations through N – H...O and N – H...N hydrogen bonds forming guanidinium cyanurate sheets.

A potassium thallium cyanurate with the composition $[KTl(C_3HN_3O_3\text{-}\kappa N)(C_3H_3N_3O_3)(H_2O)_2]$ has been prepared and its structure studied. The structure is formed of infinite two dimensional potassium thallium cyanurate framework. A detailed analysis of the structure has shown the presence of

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cyanuric acid guest molecules in the channels of the potassium thallium cyanurate host. The guest molecules form an extended tape through N – H...N hydrogen bonding.

1. INTRODUCTION

Intermolecular bond is to supramolecular chemistry what interatomic bond is to molecular chemistry. The goal of supramolecular chemistry has been to harness the power of intermolecular bonds. Supramolecular chemistry studies the chemistry beyond a molecule.[1]

Molecules spontaneously assemble when they identify a favorable source of interaction between them. The chemical information concerning the intermolecular bond such as the type of interaction, energy involved, the directionality of bonding are already stored in the molecule in its architecture, number of binding sites, their size, shape, electronic properties (Charge, polarity, polarizability, Van der Waals attraction and repulsion) and their disposition in the molecular framework. This chemical info is read out as the rate of formation and dissociation of the supermolecule.

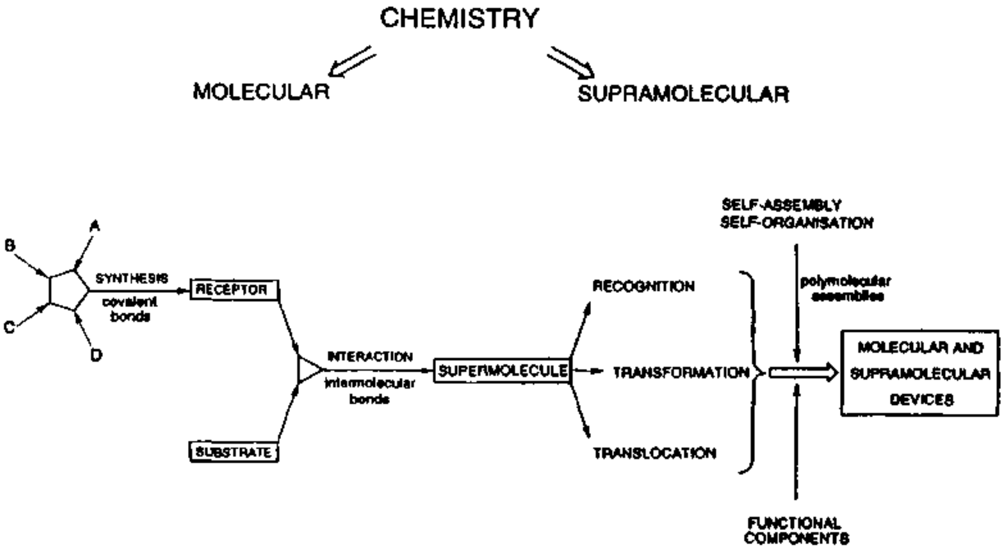


Fig.1.1 Evolution and the components of supramolecular chemistry

The high degree of specificity towards the formation of a receptor-substrate complex witnessed in biological systems (enzyme-substrate, harmone-glands etc.) involves the process of molecular recognition. Unlike self-assembly, molecular recognition is binding with a purpose. All processes of molecular recognition are events of spontaneous self-assembly although the reverse is not true. High recognition by a receptor molecule consists in the large difference between binding free energies of a given substrate from that of other substrates in the medium.[2]

The molecules in a supermolecule are analogous to atoms in molecules. A molecular crystal can be regarded as an infinitely large supermolecule. The supermolecules that are the objects of supramolecular chemistry possess well-defined properties. They are characterized both by the spatial arrangement of their components and the nature of inter-component binding. They possess well-defined structural, conformational, thermodynamic, kinetic and dynamical properties.

The molecular self-assembly can occur in solid, liquid or gaseous states. The study of their association in liquid and gaseous states is mostly effected by spectroscopic methods. Provided a good quality single crystal of the supramolecular complex is available, X-ray diffraction studies can be done to obtain most reliable details of the various structural features of the network.

The formation of a crystal from the chaotic jumble of molecules in solution involves a careful balancing between the directional requirements of intermolecular interactions and the geometrical restraints of close packing. These forces can sometimes be in agreement and sometimes in conflict. The molecular packing coefficient (k), which is the ratio of the molecular volume to the available volume per molecule in the crystal, is generally between 0.65-0.77. It has been observed that the k's of all the organic molecular solids fall in this range. The value of 'k' essentially signifies close packing. Molecules crystallize in high symmetry space groups provided the packing coefficient is not low. Otherwise they tend to choose low symmetry space groups such as the $P2_1/c$ to achieve a higher density. The maximum number of crystal structures of organic solids has been found to fall in one of the monoclinic space groups.[3]

Intermolecular interactions are fundamental causes for the formation and crystallization of supermolecules and are found between atoms that are not directly bonded. These interactions can be classified from the crystal engineering standpoint, by their distance dependence and directionality. These forces can be non-directional such as the dispersion and repulsion forces (Van der Waals forces), donor-acceptor interactions and π-π stacking or directional as metal ion coordination and hydrogen bonding. Intermolecular forces are however weaker than covalent bonds, so that supramolecular species are thermodynamically less stable, kinetically more labile and dynamically more flexible than molecules. Non-directional forces (2-10kJ/mole) include C...C, C...H and H...H interactions.[4] The relative importance of these interactions in any particular crystal depends on the C: H stoichiometry. Aromatic compounds (high C: H ratios) have a much stronger tendency to stack, since this would increase the number of C...C interactions. For planar aromatic compounds these interactions result in the characteristic T-shaped herringbone pattern.[5] Crystal structures are also known where an unusually acidic C-H group (alkyne) makes close contacts with conjugated π-systems. The non-directional forces contribute largely to crystal energy, for all parts of the molecule are involved in them.[6]

The major player among the non-covalent interactions is the hydrogen bond, which lies central to the supramolecular construction of molecular networks. Hydrogen bond such as A – H....B – X is characterized by well defined geometric attributes such as A – B and H....B distances, the A – H...B angle, the H...B – X angle, and the dihedral angle of the AHBX system.[7] Multi-centered hydrogen bonding (commonly upto 4 centers) is not uncommon. The features of a given hydrogen bond are variables that are dependent upon the charge densities of the atoms involved and the geometrical disposition of the participating groups.

Well studied hydrogen bonding patterns observed in motifs such as amide, substituted amide and carboxylic acid, have been reliably put to use in supramolecular construction of designed patterns. The element of predictability in these hydrogen-bonded patterns is very high. It should however be borne in mind that the crystal structure of the resultant complex is not easy to predict. An expected hydrogen-bonding pattern may even fail to show up in the crystal structure in answer to the demands of close packing.

Highly directional and very strong hydrogen bonding is achieved when hydrogen atom lies between highly electronegative atoms. This kind of bonding is observed in O – H...O, N – H...O, N – H...N, N – H...S, O – H...S etc. involve interaction energies about 20-40 kJ/mole.[8]

Long range forces such as, O – H...C, N – H...C, C – H...N, [9] C – H...O,[10] N – H...C (π) hydrogen bonds, halogen interactions such as (Cl, Br, *I)...(Cl, Br, I), (Cl, Br, I)...(N, O, S) and C – H...Cl, C – H...F,*[9c] *C – H...Se* [9d] and chalcogen atom interactions (S, Se)...(S, Se) can be classified as weakly directional forces. The energy of these bonds is of the order of 2-20 kJ/mole. There are a few cases, when several such interactions present, control crystal packing decisively, and sometimes even distort the symmetrical scaffolding of the strongly directional forces.

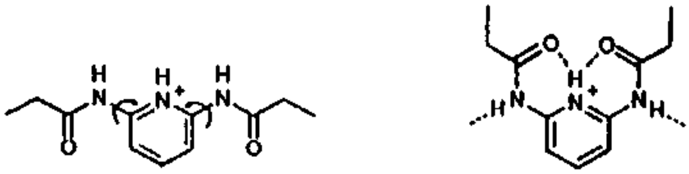
While the C – H...O hydrogen bonds are well known the complementary O – H...C (π) are rare, since carbon atom is not as electronegative as oxygen and also since the unsaturated C atoms are not often situated in sterically unhindered positions, unlike carbonyl or ethereal O atoms which permit easy access for C – H groups to form C – H...O bonds.[11] In spite of these limitations, a sufficiently electron rich carbon atom (alkyne, alkene, aromatic) has a propensity to form a hydrogen bond like interaction with O-H groups thus contributing to crystal stability.

The CO ligand is a base unique to organometallic compounds. It has been understood that the ligand is more important for C – H...O bonding than for an O – H...O bonding.[12] This has been explained by invoking HSAB principle extended to supramolecular chemistry and labeling CO as a soft acceptor, which thus prefers a soft donor such as the C – H.

Atomic polarization effects are essentially the cause of halogen interactions as their efficacy decrease as I > Br > C1.[13] These effects are also important for S, which is known to form short directional contacts of type S...N, S...S, S...Cl. These contacts have been thoroughly studied in the crystal chemistry of the TTF – TCNQ family of compounds.[14]

Hydrogen bonding like interaction has also been observed between (O, N) – H groups with a sufficiently electron rich carbon atom (alkyne, alkene, aromatic). These are referred to as "π-hydrogen bonds"

Proton induced conformational switching from inwardly to outwardly directed amide N - H groups observed in acylated mono- and di-aminopyridine derivatives illustrate an impressive example of environment dependent molecular recognition event.[15]



(A) (B)

Fig. 1.2 Change of conformation about C – N bond upon protonation activating a molecular recognition event.

Upon protonation there is a repulsive interaction introduced and the parallel orientation destabilized. This leads to the rotation about the pyridine-amide bonds and the formation of two intramolecular hydrogen bonds to the carbonyl oxygen. The resulting conformation now contains two outwardly directed amide NH groups capable of intermolecular hydrogen bonding.

Hexagonal network of tricyanobenzene-hexamethyl benzene complex illustrates the significance of weak interactions such as the C – H...N in steering the crystal structure.[16]

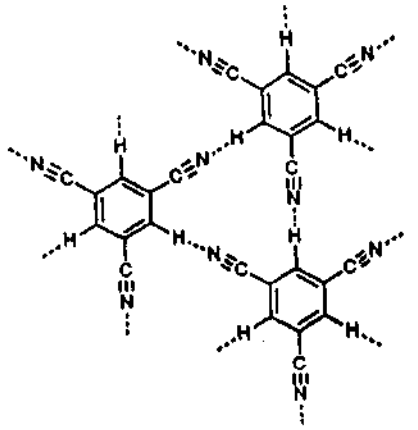


Fig. 1.3 C – H...N mediated hexagonal networks in 1,3,5-tricyanobenzene

A formation of such hexagonal network has been witnessed earlier to the above, mediated with much weaker N...Cl bonds.[17]

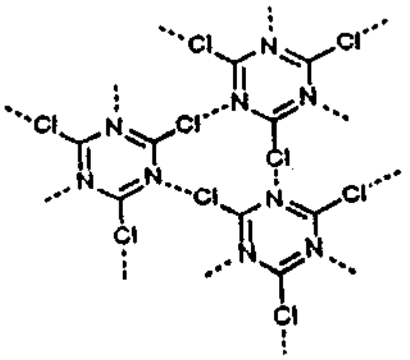


Fig. 1.4 N...Cl mediated hexagonal networks in trichloro triazine

Another example of weak interactions guiding crystal structure is witnessed in 1,3,5-trinitrobenzene-dibenzylidene ketone complex wherein the molecular components are held by C – H...O hydrogen bonds.[18] The components have been deliberately so chosen in order to strengthen the C – H...O bond. The nitro group is known to be a good hydrogen bond acceptor and the (sp^2) C – H group a good donor (owing to the acidity of the C atom).

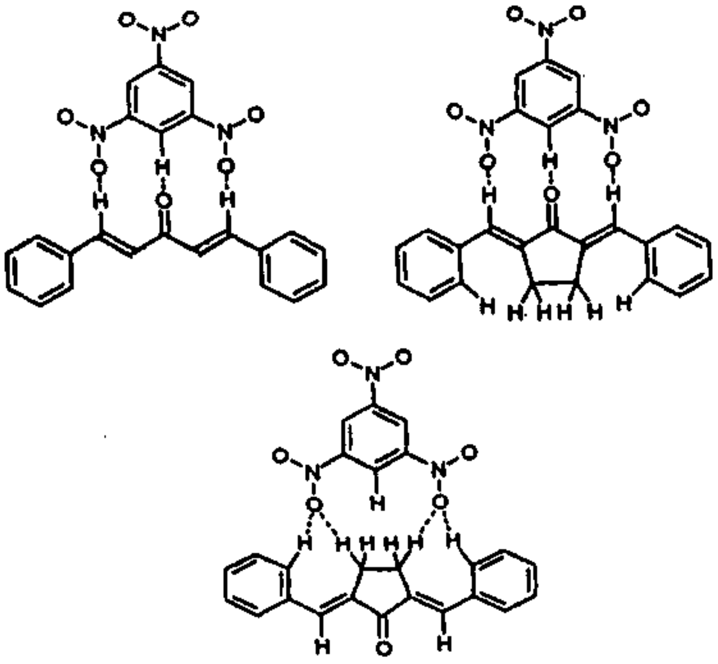


Fig. 1.5 (π) C – H...O (nitro) interaction observed in 1,3,5-trinitrobenzene-dibenzylidene complex

The C – H...O interaction has been observed in a number of biological systems too. The bond energy (1-2kcal/mole) is just in range where it can compete with conformational forces in small molecules. The C – H...O interactions seem to determine the ordering of CO and alkylidyne molecules in a mixed adsorbate on a clean pt (111) surface and to specify the stereochemistry of CH_3OH inclusion within ZSM-5 zeolite channels.

Tetrakis (4- iodophenyl) methane[19] provides one of the several instances of weak I...I interaction directing the crystal packing arrangements. The structure reveals the formation of tetrahedral I_4 synthons. Isomorphous structure of bromo derivative is also known. The I...I distances are 3.949 Å and 4.161 Å compared to the Br_4 synthon in which the Br...Br distance is

3.910 Å. The crystal structure of (4-iodophenyl) triphenylmethane exhibits I...ph intermolecular interaction with I...centroid distance of 3.745 Å.

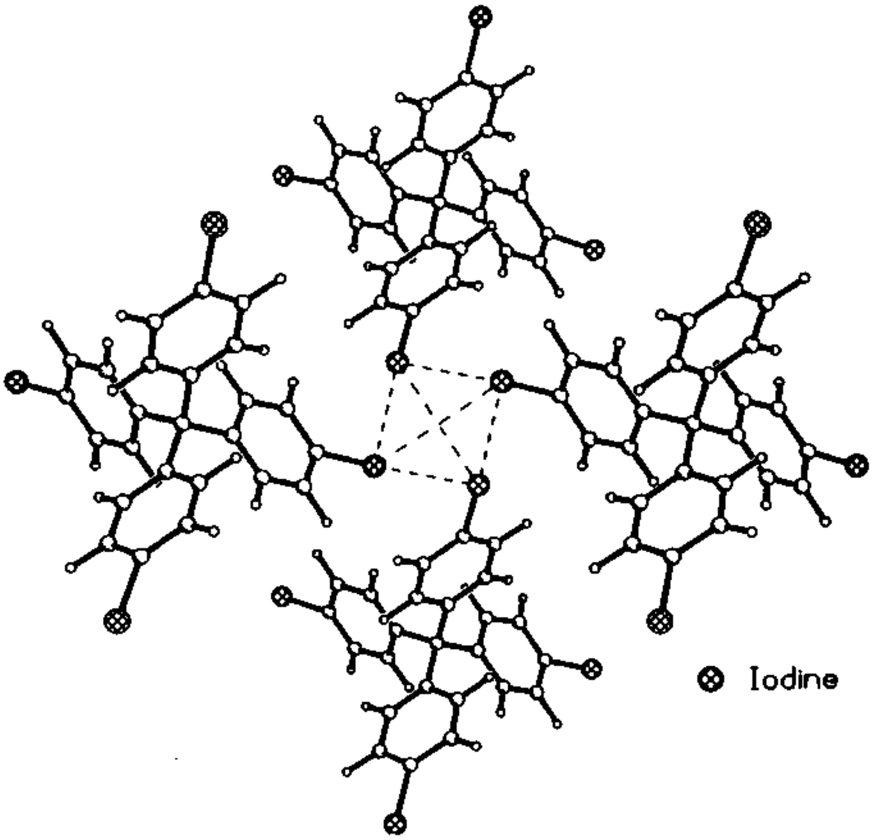


Fig. 1.6 I_4 synthons in the structure of tetrakis (4-iodophenyl)methane

Supramolecular symmetry Vs Molecular Symmetry

The carry over of molecular symmetry into the crystal is a matter of immense significance. Kitaigorodskii's laws of close packing[20] emphasize that the molecular symmetry is a poor guide to the molecular site symmetry in the crystal. The inversion center is the only molecular symmetry element that is routinely carried over into the crystal because it is the only crystal symmetry element that does not entail loss of packing efficiency by its presence. This means that a high symmetry molecule almost always do not adopt higher crystal symmetries.

The molecular shape is an important factor that needs to be taken into account. Beyond a certain degree of shape awkwardness, which is still not really quantifiable, close packing is problematic leading to formation of open networks in which the full molecular symmetry is retained and a second molecular species is included as a guest to improve the packing efficiency. For example, 1,3,5-triphenylbenzene forms 1:3 host-guest complexes with benzene whereas mesitylene, 1,3,5-trichlorobenzene, 1,3,5-trinitrobenzene form single component crystals. Yet another instance where the molecular symmetries have been fully retained in the crystal is the 1,3,5-trinitrobenzene-Trimethylisocyanate 1:1 complex. The complex crystallizes in hexagonal space group P –6.

The molecular symmetry can however be carried on to the supramolecular network by introducing hydrogen-bonding groups symmetrically with respect to the molecular fragment. The symmetry results due to the inability to compromise on the directionality of hydrogen bonds. Gross violations of close packing principle may be sometimes met with resulting in guest molecule inclusion (hydroquinone-C_{60}), catenation of networks, or simultaneous inclusion and catenation (hydroquinone with small guests, trimesic acid).

Supramolecular networks are sometimes formed with symmetries higher than the molecular symmetry as in urea, thiourea, Dianins compound and alicyclic diols.

The following example provides an interesting illustration of the evolution of the final crystal structure symmetry of substituted urea dicarboxylic acids from the initial molecular symmetries.[21]

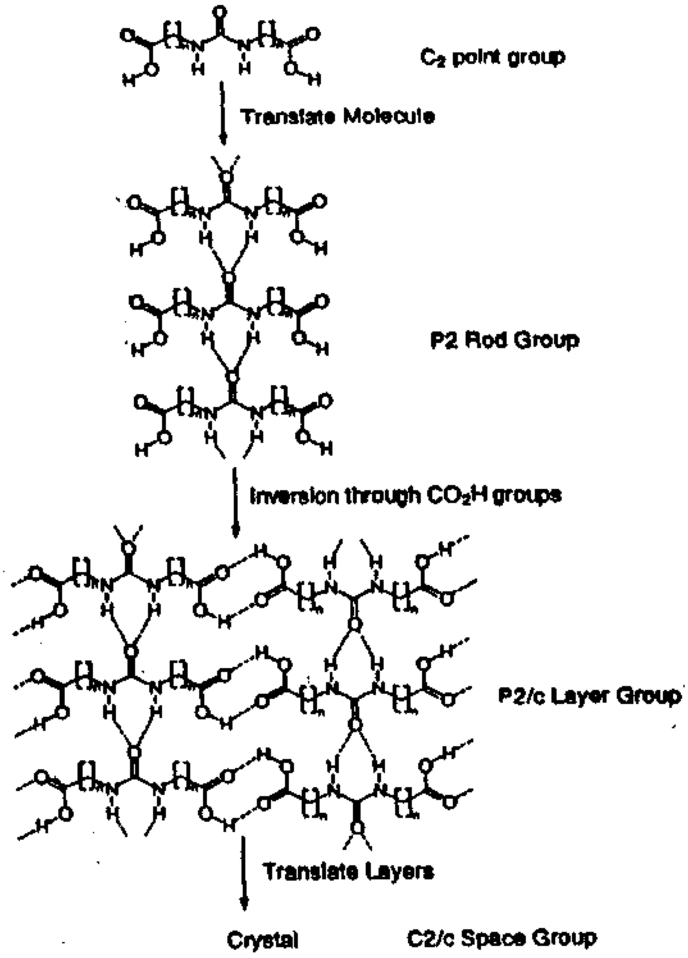


Fig. 1.7 Evolution of the crystal structure symmetry of symmetric substituted ureas

Symmetric ureas have a 2-fold axis through the carbonyl and importantly can retain this 2-fold when they form a one-dimensional hydrogen bonded α-network via a simple crystallographic translation. From the principles of group theory, the *P2* rod group is generated. The carboxylic acid residues on the ends of the side chains characteristically dimerize about crystallographic inversion centers giving a 2-d β-network. Adding an external inversion center to the *P2* rod group generates the *P2/c* layer group. The β-network layers stack on the top of each other to form the crystal, with no further hydrogen bonds available presumably the layers are held together mainly van der Waals interactions. One could conceive two simple ways for this stacking to occur. If the layers were directly on top of each other using a simple translation operator then the space group of the final molecular assembly and the crystal would be *P2/c*. However, it seems more likely that the layers would be offset such that the molecules of one layer fall over the groves between the molecules of the next layer. This would generate a centering operation and the final space group would be *C2/c*. Experimentally, this has been found to be the case.

2. SCOPE OF THE PRESENT INVESTIGATIONS

2.1 Melamine complexes with 4,4'-bipyridyl and silver nitrate

Melamine, **M**, crystallizes as a hydrogen-bonded solid comprising molecular tapes formed by N - H...N hydrogen bonds between the adjacent molecules; the tapes give rise to a sheet structure.[22] Melamine is known to form interesting adducts with heterocyclic compounds and imides. Thus, **M** forms complexes with barbituric acid.[23] Whitesides and coworkers[24] have characterized adducts of substituted melamines with barbituric acid derivatives which possess structures involving molecular tapes, crinkled tapes and rosettes. Lehn and co-workers[25] have described a variation of the linear tape formed by the adducts of **M**. The formation of supramolecular 1:1, 1:2 and 1:3 complexes of melamine with imides such as succinimide and glutarimide have been studied.[26] In the melamine-succinimide complex, every donor and acceptor site available for hydrogen bonding in the two molecules is used. In this case too, a molecular tape results through the formation of N - H...O and N - H...N bonds. The formation of a robust hydrogen-bonded supramolecular aggregate of **M** with cyanuric acid, **CA**, where the aggregate is stabilized by 18 hydrogen bonds in a cyclic $\mathbf{CA_3.M_3}$ rosette was proposed sometime ago by Mathias et al.[27] This **M-CA** adduct was synthesized recently by the hydrothermal method and the structure of the rosette as well as the three-dimensional channel structure derived from the stacking of the rosette have been described.[28]

We were interested to study structural features of the hydrogen bonded complex of **M** with 4,4'-bipyridyl and silver ion directed self-assembly of the melamine molecules. A crystallographic investigation has revealed unique hydrogen bonding patterns in the two systems. The melamine-4, 4'-bipyridyl complex shows a supramolecular organization wherein hydrogen bonding between melamine and water molecule results in tapes. The tapes are connected by hydrogen bonding to 4,4'-bipyridyl giving rise to a rectangular box. In the melamine-$AgNO_3$ complex, the melamine molecules are directed by Ag^+ ions to form N-Ag-N chains, giving rise to a single helix. These helices are held together by inter-chain hydrogen bonds between the melamine molecules.

2.2 Replacing the hydrogen in the intermolecular hydrogen bond of the cyanuric acid-bipyridyl adduct by Ag(I)

Cyanuric acid (**CA**) forms interesting hydrogen-bonded structures with the aid of the three secondary *cis*-amide bonds.[29] It is known to form a variety of adducts when co-crystallized with heterocyclics and also with metal ions.[30] When co-crystallized with 4,4'-bipyridyl (**BP**), it forms different hydrogen-bonded assemblies depending on the solvent of crystallization, the structures bearing some resemblance to the hydrogen-bonded supramolecular assemblies of **CA** crystallized from the respective solvents.[31] **CA** also forms an adduct of the composition, Ag_2**CA** with Ag(I) which has a layer structure comprising two-dimensional sheets of silver atoms which are pillared by chains of **CA** molecules.[32] In this complex, two of the hydrogens of **CA** are replaced by Ag. Recently, a mercury complex of **CA** of the composition, Hg_3[**CA**-κN]$_2$3.5H_2O wherein Hg replaces all the hydrogens of **CA** has been prepared.

Co-crystallization of **CA** and **BP** from water gives a 1:1 adduct. This adduct has a chain structure which is comparable to that of the **CA**.H_2O complex, wherein water is replaced by **BP** molecules to form N-H...N hydrogen bonds. The hydrogen-bonded chains of **CA** and **BP** are held together by N-H...O hydrogen bonds between the **CA** molecules.[33] We were interested in substituting the intermolecular N-H...N hydrogen bonds in **CA.BP** with N – Ag – N bond. The structure of the complex were observed to have features similar to that of chain structure of the **CA.BP** adduct where **CA** – **BP** - **CA** chains formed by N - H...N hydrogen bonds are linked to one another by N - H...O hydrogen bonds between the **CA** molecules.

2.3 Complexes of cyanuric acid with pyridine and guanidinium carbonate

The complex of cyanuric acid with pyridine is essentially an acid base complex and contains unique hydrogen bonding features. Similar to that found in **CA** – **BP** adduct, we observe the formation of **CA** – **Py** chains. These chains are held together by the dimeric hydrogen bonding between the **CA** fragments. It has been possible to rationalize the unit cell parameters of the resultant complex with respect to that of **CA**.

In the complex of cyanuric acid and guanidinium carbonate, mono-deprotonation of **CA** occurs, with the formation of hydrogen bonded **CA** tapes with the guanidinium cations between the tapes. The structure is largely stabilized by hydrogen bonds. Here too, the unit cell parameters of the complex could be rationalized with respect to that in **CA**.

2.4 Potassium thallium cyanurate, [K Tl ($C_3HN_3O_3$-κN) ($C_3H_3N_3O_3$)(H_2O)$_2$]

Thallium (I) resembles group one elements in many ways. Substitution of the protons in the cyanuric acid-bipyridyl adduct by Ag^+ ions forming two dimensional layers containing silver atoms was mentioned. We were interested in examining the nature of Tl (I) in a cyanurate. Cyanuric acid upon reaction with thallous ions forms a white precipitate, which could not be crystallized under a variety of conditions. Hydrothermal synthesis of the precipitate under different conditions gave bad quality crystals which were not suitable for a single crystal X-ray analysis. However, good quality single crystals formed in the presence of K^+ ions at room temperature. The compound had the formula [KTl($C_3HN_3O_3$-κN)($C_3H_3N_3O_3$)(H_2O)$_2$] and the structural features of this compound were investigated. Interestingly, crystallographic analysis of the structure revealed free cyanuric acid molecules as guests within channels formed by potassium thallium cyanurate host framework. The guest **CA** molecules interact within the channels forming hydrogen bonded molecular tapes.

3 EXPERIMENTAL

3.1 Melamine with 4,4'-bipyridyl and $AgNO_3$

Single crystals of the 1:2 complex of melamine with 4,4'-bipyridyl containing the water of crystallization, were obtained by slow evaporation of an aqueous solution containing the two compounds. The composition of this complex, **1**, is [$C_{10}H_8N_2$: 0.5($C_3H_6N_6$): H_2O]. Addition of a solution of melamine to a silver nitrate solution gave a white precipitate. Using hydrothermal methods in an attempt to crystallize this complex yielded tiny crystals which upon analysis with X-rays gave super cells. In order to obtain larger crystals, the precipitate was taken in water and digested on a hotplate. The water was allowed to evaporate slowly upon heating and distilled water was added freshly and the process repeated. This procedure proved to be effective in obtaining bigger sized and good quality single crystals. Further analysis of the complex was carried out by the X-ray diffraction of the crystal.

3.2 Interaction of Ag (I) with the cyanuric acid-bipyridyl adduct

The complex containing **CA**, **BP** and Ag (I), **1**, with the composition, [$Ag_2(C_3H_2N_3O_3\text{-}\kappa N)_2(C_{10}H_8N_2\text{-}\kappa N)$] was prepared by hydrothermal method by the following procedure. In a typical preparation, 10mL of a solution of **CA**, **BP** and $AgNO_3$ (1:1:1 molar ratio) taken in a teflon flask was placed in a steel bomb and kept in a oven maintained at 160°C for 36h and then cooled to room temperature over a period of 6h to obtain good quality single crystals of the complex. The crystals were colorless and had needle-shaped geometry.

3.3 Complexes of cyanuric acid with pyridine and guanidinium carbonate

Good quality rod-shaped single crystals of the complex of **CA** with pyridine were obtained from solution of cyanuric acid in pyridine at room temperature in a sealed vessel left for a few days. The complex could however be obtained sooner by preparing a concentrated solution of **CA** in pyridine by warming the mixture (within a fume cupboard) for some time over a hot plate though the quality of single crystals obtained thus, not so good. The crystals were found to be unstable, turning powdery due to loss of solvent when left at room temperature and outside the solution. The single crystal chosen were smeared with glue (araldite) as soon as they were removed from the solvent, removing the adhering solvent with a tissue paper. This way they were stable for a long time.

The complex of Guanidinium Cyanurate was obtained by reacting 1 mmol of **CA** and guanidinium carbonate in water. The clear solution thus obtained was left undisturbed over a week's time to obtain transparent crystals of the complex. The crystal was subjected to X-ray analysis.

3.4 Potassium thallium cyanurate, K Tl ($C_3H\,N_3O_3$-κN) ($C_3H_3N_3O_3$)(H_2O)$_2$

The addition of aqueous solution of thallous carbonate to that of **CA** gave a white precipitate, but good quality single crystals could not be obtained. However, in the presence of K^+ cations in the medium gave good quality single crystals suitable for X-ray diffraction.

0.1mmol Tl_2CO_3 was dissolved in distilled water and acetic acid added in drops to neutralize the solution. During the first attempt, by a careless addition of a slight excess of the acid had lead to a weakly acidic medium. A dilute solution of KOH was added in drops till the solution was neutral to litmus. The resultant neutral solution was mixed with aqueous solution of 0.1mmol of **CA**. The resultant solution was colorless and a clear one. The solution was filtered and allowed to crystallize over a week time. Colorless crystals that were obtained were checked with Energy Dispersive Analysis of X radiation (EDAX) to check presence of Thallium. However, the analysis also showed presence of potassium in an equal proportion to that of Tl(I). Powder diffraction pattern showed new phase in comparison with the starting materials. The crystals had needle shaped geometry. Routine analyses by X-ray diffractometry were carried out to obtain the final structure.

3.5 Single crystal X-ray diffraction

The molecular and the crystal structures of all the co-crystals mentioned in the earlier sections have been determined using single crystal X-ray diffractometry. Good quality single crystals of these complexes were carefully chosen viewing under a polarizing microscope to check for any possible twinning in the sample. The crystals thus chosen were mounted on the tip of a glass fibre using glue (super glue or araldite) for fixing. The glass fibre is held by the clay packed within a open brass cylindrical tube of diameter ~2-3mm. This is then mounted on to the goniometer and centered in the path of X-radiation. Intensity data were collected on the X-ray diffractometer equipped with Siemens CCD area detector[34] and a three circle goniometer. The structures were refined and solved by a full matrix least square on F^2 using the SHELXTL-PLUS package.[35] All the non-hydrogen atoms were anisotropically refined. The hydrogen atoms located from the difference Fourier maps were refined isotropically. The Non-covalent interactions were computed assisted by PLATON.[36]

Table 4.1 Crystal structure details of the supramolecular complexes

Complex	Formula	Space Group	Cell parameters						
			a	b	c	α	β	γ	Cell volume
CA[1] – Ag – BP[2]	$[Ag_2(C_3H_2N_3O_3\text{-}\kappa N)_2(C_{10}H_8N_2\text{-}\kappa N)]$	$P2_1/n$	13.089	4.586	15.996	90	104.75	90	928.5
CATLK	$[K\ Tl\ (C_3HN_3O_3\text{-}\kappa N)$ $(C_3H_3N_3O_3)(H_2O)_2]$	$P2_1/c$	6.558	11.803	16.585	90	94.518	90	1279.77
M-BP	$[C_{10}H_8N_2{:}0.5(C_3H_6N_6){:}H_2O]$	$C2/c$	18.114	7.289	19.342	90	113.05	90	2349.96
M-AgNO$_3$	$[Ag(C_3H_6N_6)(NO_3)]$	$P2_1/n$	6.692	11.763	10.293	90	101.24	90	794.72
CA-pyridine	$[C_3N_3H_3O_3 : C_5H_5N]$	$P2_1/c$	10.815	11.989	7.425	90	94.282	90	963.66
Guanidinium cyanurate	$[C_3H_2N_3O_3][C(NH_2)_3]$	$P-1$	3.774	9.848	10.499	87.92	83.21	79.23	380.69

1) CA – Cyanuric acid
2) BP – 4,4'- bipyridyl; M- Melamine

4. RESULTS AND DISCUSSION

4.1 Supramolecular organization in Melamine complexes with 4,4'- bipyridyl and $AgNO_3$

Melamine - 4,4'-bipyridyl, 1: The 1:2 complex of Melamine (**M**) with 4,4'-bipyridyl (**BP**), $[C_{10}H_8N_2{:}0.5(C_3H_6N_6){:}H_2O]$, **1**, crystallizes in a *monoclinic* (*C2/c*) (Table 2.1) space group.

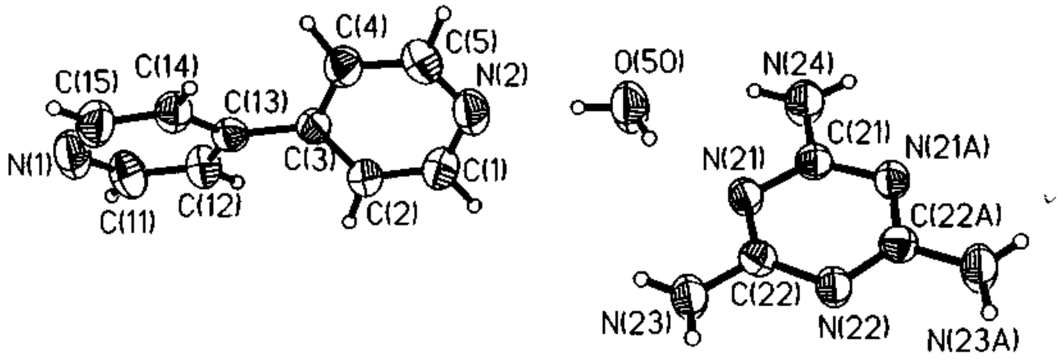


Fig. 4.1 Asymmetric unit of M.BP adduct with water molecule of crystallization. The thermal ellipsoids are shown with 50% probability.

The asymmetric unit of **1** is shown in Figure 4.1. The details of the unit cell of are presented in table 4.1. The atomic coordinates and the isotropic thermal displacement parameters are given in table 4.2. The bond lengths and bond angles are provided in table 4.3. The hydrogen bond distances and angles are presented in table 4.4. The structure of **1** shown in Figure 4.2 reveals that the melamine molecules are connected to one another through water molecules by forming N - H...O (H...O, 2.16Å) and O - H...N (H...N, 2.08Å) hydrogen bonds giving rise to a molecular tape. The **BP** molecules connect the tapes. The **BP** molecules interact with the tapes by forming N - H...N

(H...N, 2.13Å) bonds with **M** and O - H...N (H...N, 2.06Å) bonds with the water molecules as can be seen from Figure 4.2. Such a hydrogen-bonding network results in a rectangular box type structure comprising two molecules each of **M**, **BP** and water. In this structure, the two rings of the bipyridyl molecule are not coplanar and form an angle of 32°.

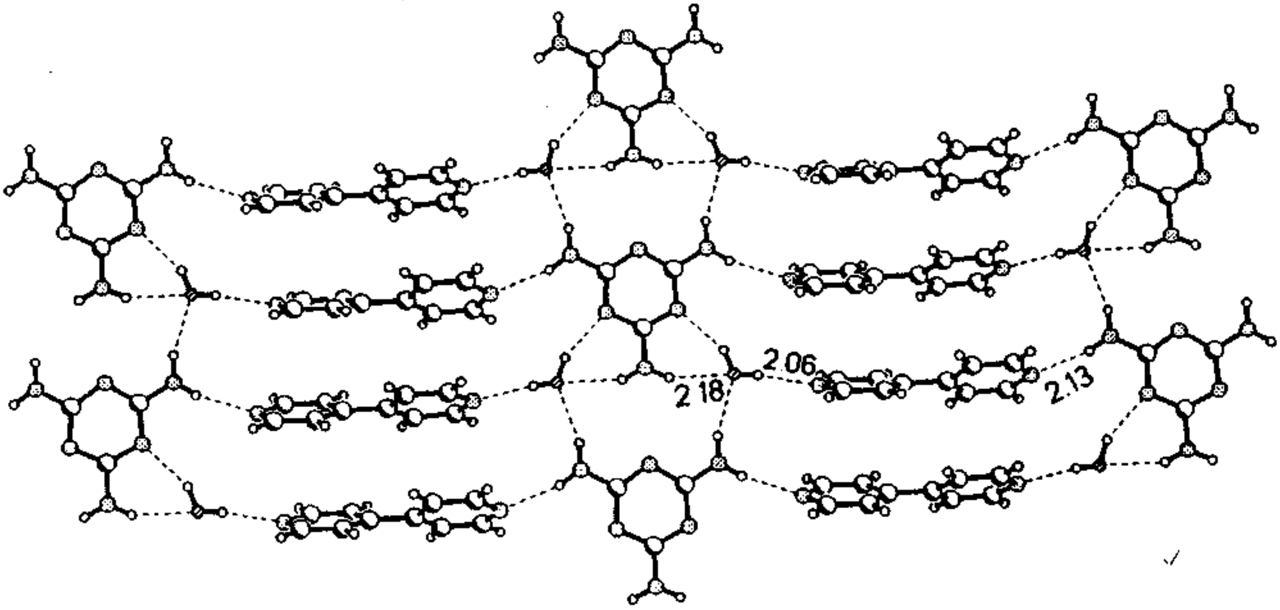


Fig. 4.2 Rectangular box like features in structure of M.BP

The structure of **1** bears close similarity to that of the **BP**-water adduct [52]. Unlike melamine which has hydrogen-bonded tapes of the molecule, the crystal structure of the **BP**-water adduct possesses a rectangular box comprising two molecules of **BP** and water.

Melamine – $AgNO_3$ complex, 2: The 1:1 complex of **M** with $AgNO_3$, [Ag $(C_3H_6N_6)$] NO_3, **2**, crystallizes in a monoclinic (*P2₁/n*) space group (Table 4.1). The asymmetric unit of **2** is shown in Figure 4.3. In this complex, the melamine molecule gets bonded to the Ag atom through the ring nitrogen, forming an Ag - N bond (2.29 Å). The coordination number of the Ag atom is two. The structure of **2** is shown in 2D in Figure 4.4. The adjacent melamine molecules are connected through Ag - N bonds forming **M** – Ag – **M** - Ag chains. The N – Ag – N bonds in such complexes are generally linear, but this is not the case here.

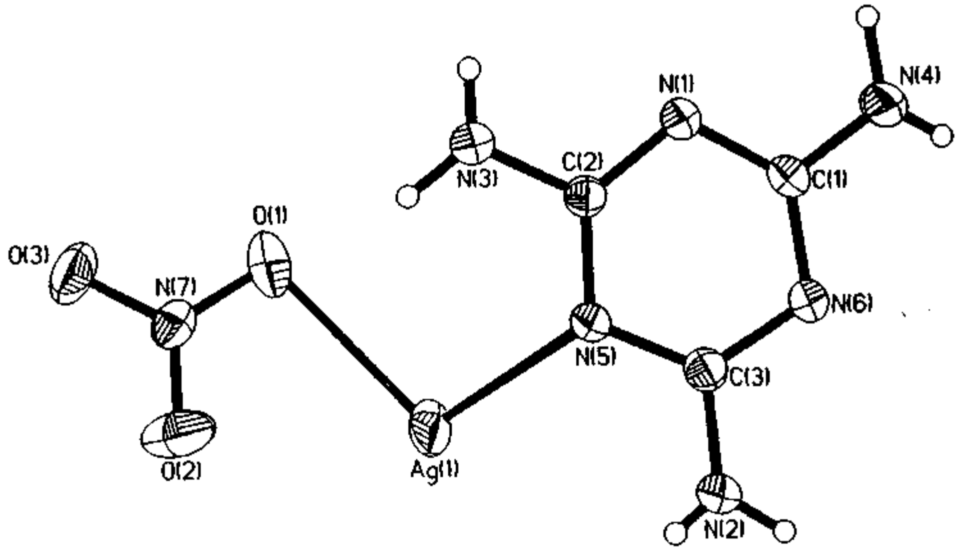


Fig. 4.3 Asymmetric unit of melamine-$AgNO_3$ adduct. The thermal ellipsoids are shown with 50% probability

The N – Ag – N bond in **2** is bent, the angle being 127° leading to the formation of a helical conformation rather than a linear chain. The Ag – N bonds seem to have compromised on their linearity in order to accommodate the N – H...N bonding between the **M** molecules, which is otherwise not possible. We show the helical nature in Figure 4.4, the twist resulting from hydrogen bonding between the adjacent chains.

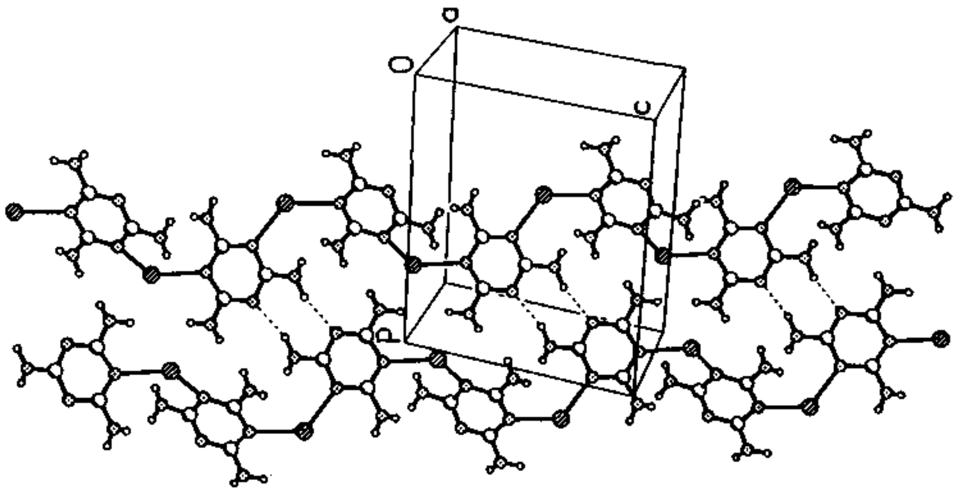


Fig. 4.4 M – Ag – M single helices bonded by N – H...N interactions

The M –Ag - M helices are held together in a two-dimensional arrangement by N – H...N hydrogen bond (H...N 2.16 Å) between the melamine molecules of adjacent chains. In **2**, two of the ring nitrogens of each melamine molecule are coordinated to a Ag atom, with the third nitrogen atom binding to melamine molecule of the adjacent chain by dimeric N – H...N bonds. Out of the three amino groups of melamine, two of them interact with two different NO_3^- ions through N - H...O hydrogen bonds. The third amino group is involved in intermolecular N – H...O (by interaction with one NO_3^- ion) and N – H...N hydrogen bonding with a neighboring melamine molecule. A similar helical structure has been found in a polymeric Ag (I) complex, $[Ag_4(bpsb)_2(NO_3)_4]_n$ where bpsb stands for 1,2-bis[(2-pyrimidinyl)-sulfanylmethyl]benzene. In this complex, the array of ligands linked by Ag atom forms a single stranded helix and each silver atom is tetracoordinated.[53]

The structure of **M**.$AgNO_3$ is somewhat comparable to the parent structure of melamine.[42] In the structure of melamine, adjacent molecules are held together by N – H...N hydrogen bonds to yield molecular tapes, producing a hexagonal network. In **2**, N-Ag-N coordinate bonds replace the hydrogen bonds. There are two N-Ag bonds in the place of two hydrogen bonds. However, the interaction between the adjacent tapes in melamine or the chains in **2** is similar, being governed by N – H...N hydrogen bonds.

4.2 Replacing the hydrogen in the intermolecular hydrogen bond of the cyanuric acid-bipyridyl adduct by Ag(I)

The asymmetric unit of the Ag (I) complex of cyanuric acid – 4,4'-bipyridyl is shown in Figure 4.5. It contains two **CA** molecules, one **BP** molecule and two Ag atoms as expected. We show the detailed structure of the complex in figures 4.6 and 4.7.

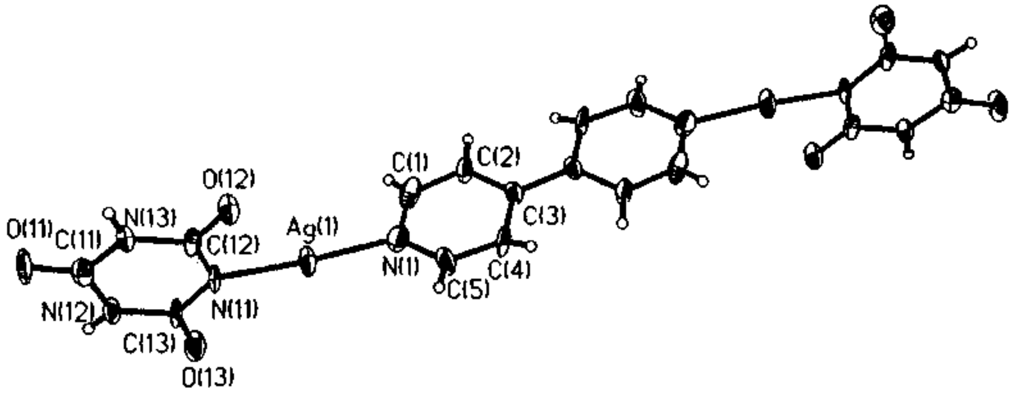


Fig. 4.5 Asymmetric unit of $[Ag_2(C_3H_2N_3O_3\text{-}\kappa N)_2(C_{10}H_8N_2\text{-}\kappa N)]$ adduct. The thermal ellipsoids are shown with 50% probability.

The unit cell information is presented in table 4.1. The atomic coordinates are given in table 4.8. The details regarding the bond lengths, bond angles and the hydrogen bond details are presented in tables 4.9 and 4.10. The complex has a chain structure resembling the structure of the **CA.BP** adduct. What is interesting is that Ag (I) replaces one of the hydrogens of **CA** to bond to the ring nitrogen of **BP** forming N-Ag-N bonds (N-Ag, 2.12Å). Thus, the Ag(I) ion takes the role of a proton in forming the intermolecular chain. The **CA**-Ag-**BP**-Ag-**CA** chains are connected to one another by intermolecular N – H...O bonds (H...O, 1.95Å), between the **CA** molecules of adjacent chains. In addition there are also C – H...O interactions between the 3,3' -CH groups of the bipyridyl and the oxygen of **CA**.

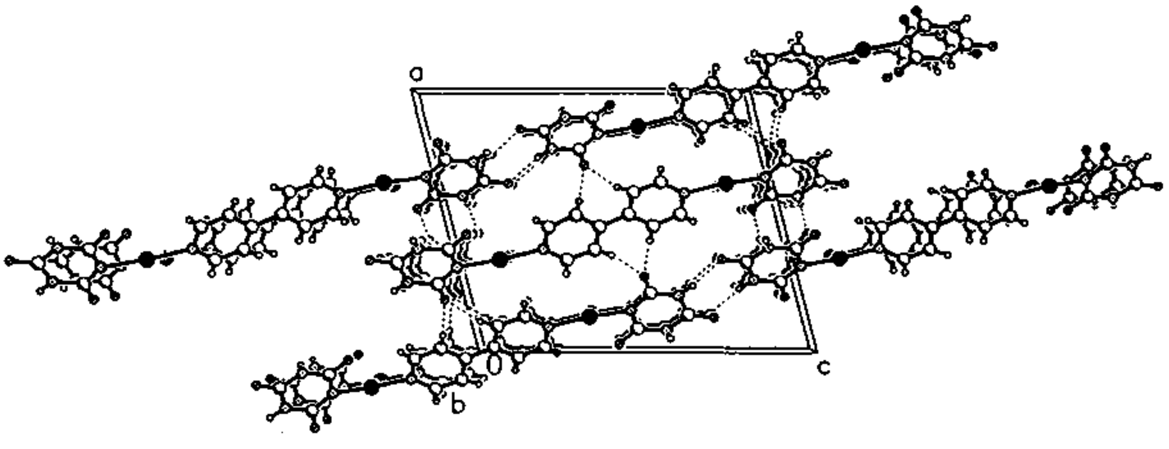


Fig. 4.6 projection along *ac* plane showing different hydrogen bonding features

The N-Ag-N angle in the complex is 173.5°, unlike in the melamine-$AgNO_3$ complex where it is 127°. The Ag-N distance is 2.12Å. Unlike in melamine-4, 4'-bipyridyl complex, the two pyridine rings in this complex, $[Ag_2(C_3H_2N_3O_3\text{-}\kappa N)_2(C_{10}H_8N_2\text{-}\kappa N)]$ are coplanar, the torsion angle being only 0.7° . The pyridyl rings have been forced into coplanarity by the two weak C – H...O bonds that involve the meta –CH group of both the rings. The **CA** fragments in each covalently bonded unit oriented perpendicular to the plane of bipyridyl fragment. This results in the formation of a staircase like pattern (figure 4.8). The intramolecular contribution to the formation of each such staircase comes from the Ag...O (2.82 Å) and N – H...O bonds. These staircases are held together exclusively by the C – H...O interactions (figure 4.7).

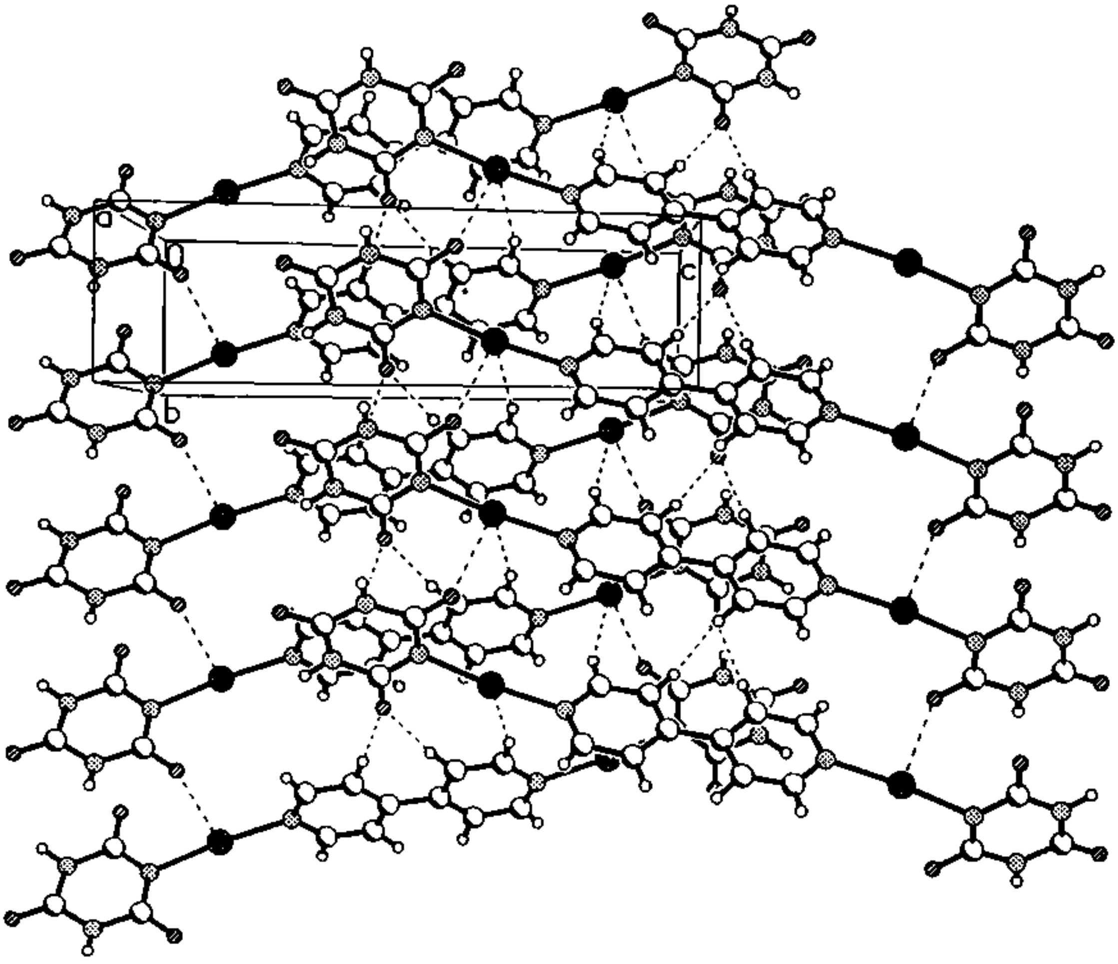


Fig. 4.7 Projection along *bc* plane showing hydrogen bonding connectivity

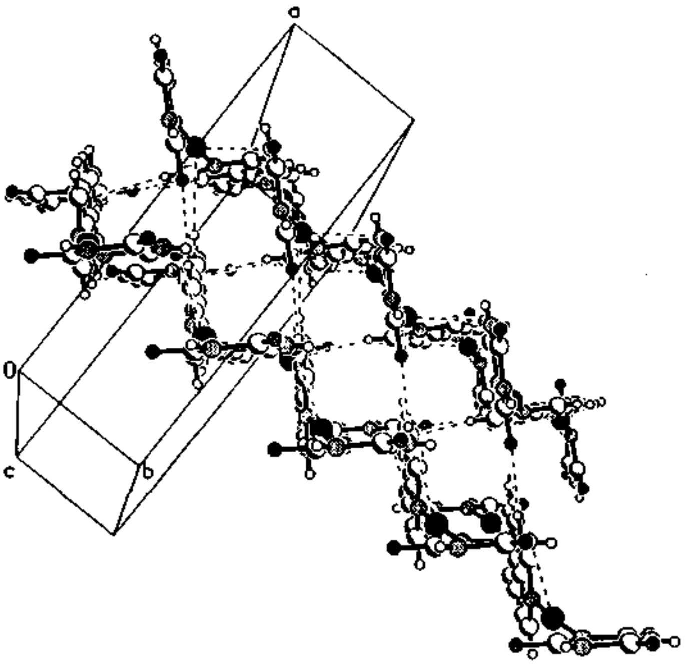


Fig.4.8 N – H...O and C – H...O assisted hydrogen bonded staircase

4.3 Hydrogen bonding in Complexes of Cyanuric acid with Pyridine and Guanidinium Carbonate

Cyanuric Acid – Pyridine adduct, 1: The 1:1 complex of **CA** with pyridine, $C_3N_3O_3H_3$: C_5H_5N, **1**, crystallizes in a monoclinic ($P2_1/c$) space group. The asymmetric unit of **1** (figure 4.9) consists of one molecule each of **CA** and pyridine as expected. The relevant crystallographic details are presented in tables 4.11, 4.12 and 4.13. The structure of **1** shown in figure 4.10 reveals that the molecular tapes formed by dimeric N – H...O hydrogen bonds in **CA** are retained. The pyridine molecules replace the inter-tape N – H...O hydrogen bond in **CA** by a strong N – H...N (H...N, 1.75Å) bond in addition to C – H...O (H...O, 2.55Å) interaction. The H...O distance of 2.55Å suggests that the C – H...O bond is moderately strong.

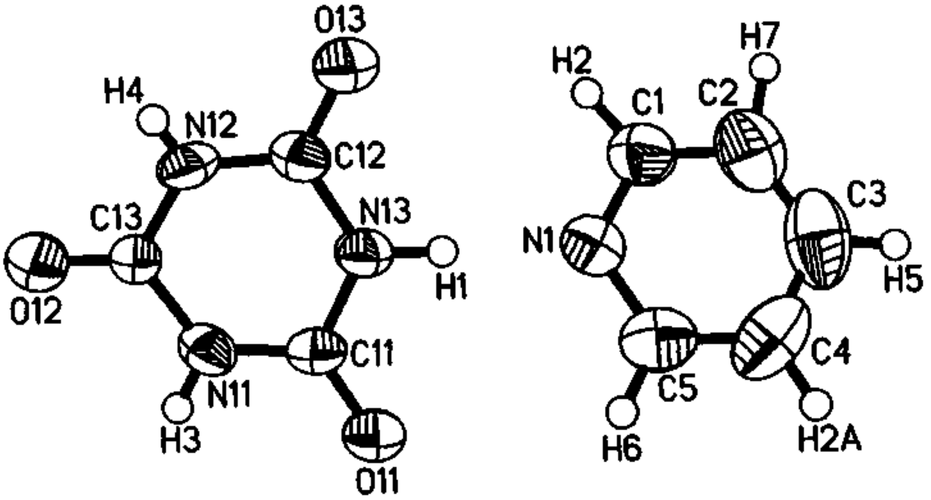


Fig. 4.9 Asymmetric unit of **CA** – pyridine adduct

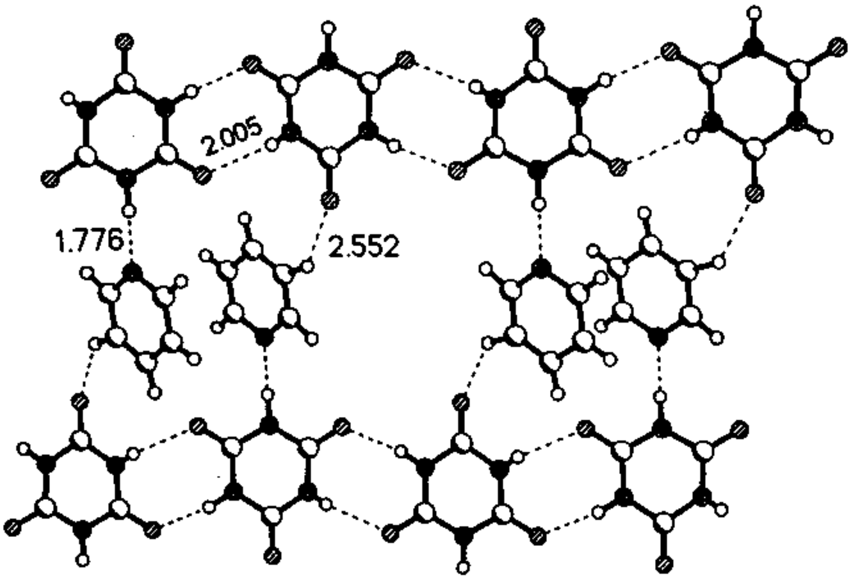


Fig. 4.10 Pyridine molecules between **CA** tapes interacting by N – H...O and C – H...O bonds

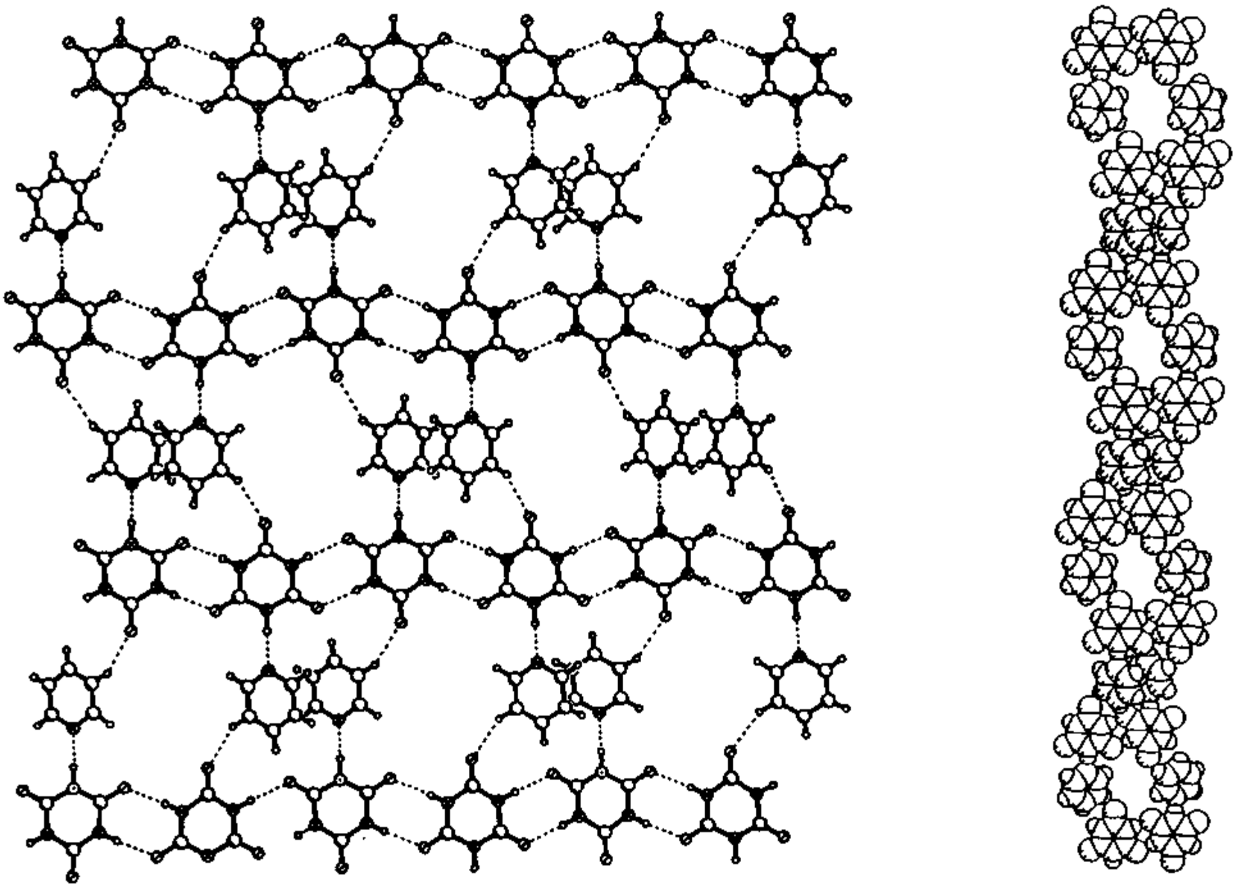


Fig. 4.11 Single helices of **CA**-pyridine chains bonded with inter – **CA** hydrogen bonds

In **1**, cyanuric acid is able to accommodate a foreign molecule such as pyridine without making any significant compromise in its original H-bonding features. The cell parameter along the direction of the **CA** tapes in both **CA** and **1** show only a 0.05 Å difference. The increase along the *c* axis in **1** roughly corresponds to the size of the pyridine molecule with the hydrogen bonding distances. The structure also shows single helices of hydrogen bonded **CA** and pyridine held by the dimeric N – H...O hydrogen bonds between the **CA** molecules (figure 4.11). The distance between the adjacent helices is about 5.99Å. The helicity of chains here is induced by the pyridine molecules, which tilt from the plane of the **CA** tapes. This tilting provides additional interaction to the molecule through the C – H...O bonds involving its meta –CH group. The preference for the C – H...O donor from meta rather than the para position could be due to the higher acidity of meta –CH and hence its better donor ability. All the **CA** molecules of a particular chain are in the same plane.

Guanidinium cyanurate, 2: Guanidinium cyanurate, **2**, crystallizes in a triclinic (*P -1*) space group. The asymmetric unit of **2** is shown in figure 4.12. The asymmetric unit consists of cyanurate mono anion and the guanidinium cation. The cell parameters of the unit cell are given in table 4.1. The other relevant crystallographic information is presented in tables 4.14, 4.15 and 4.16.

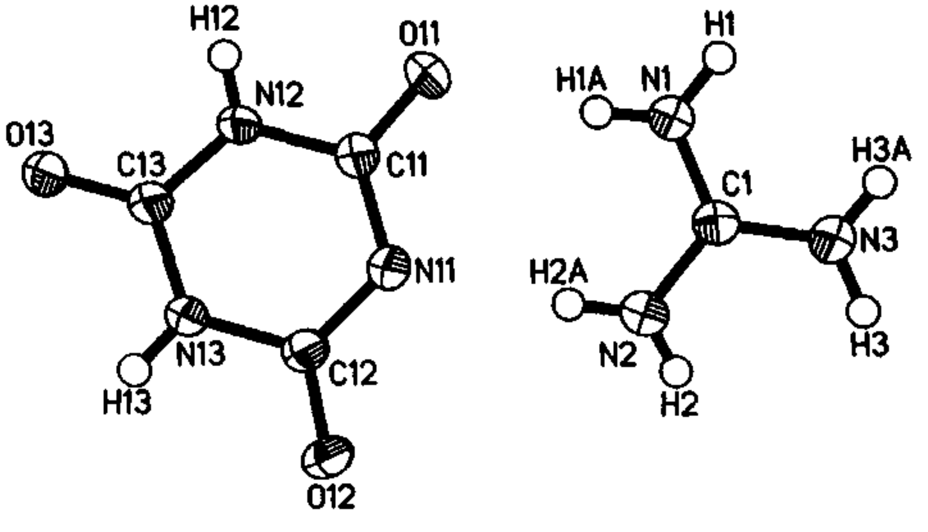


Fig. 4.12 Asymmetric unit of guanidinium cyanurate. The thermal ellipsoids are shown with 50% probability

The structure of **2** contains **CA** tapes and the guanidinium cations held between the adjacent tapes by N – H...N and N – H...O hydrogen bonds (figure 4.13). The **CA** tapes resemble a sine wave unlike the linear tapes present in both **CA** and **1**. The axis parameter along the direction of the tapes is shorter (10.4987 Å) in comparison to that in **CA** (11.912 Å) due to the sine wave like structure of the tapes adopted by **CA** molecules. The effect of the negative charge on N(11) manifests itself in the distances of the neighboring bonds. Thus, the C – N bond distances of C(11) – N(11) and C(12) – N(11) are shorter than the other C – N distances observed in the fragment. The carbonyl groups adjacent to N(11) show an increase in the bond length. The N(12) – C(12) and N(13) – C(13) bonds also show an increase in their lengths. The above variations in the bond distances result from the delocalization of the negative charge on N(11) to the adjacent carbonyls. The increase in the bond lengths of the above mentioned C – N distances can be attributed to the suppression of resonance effect involving N(12) and N(13) lone pairs due to the dominating influence from the negatively charged participant.

The greater availability of the lone pairs on N(12) and N(13) towards resonance involving the third carbonyl reflect in the decrease in bond lengths of the N(12) – C(13) and N(13) – C(13) bonds and increase in the C(13) – O(13) bond length. It is to be noted that this change in bond lengths is of lesser magnitude when compared to that involving the N(11) anion.

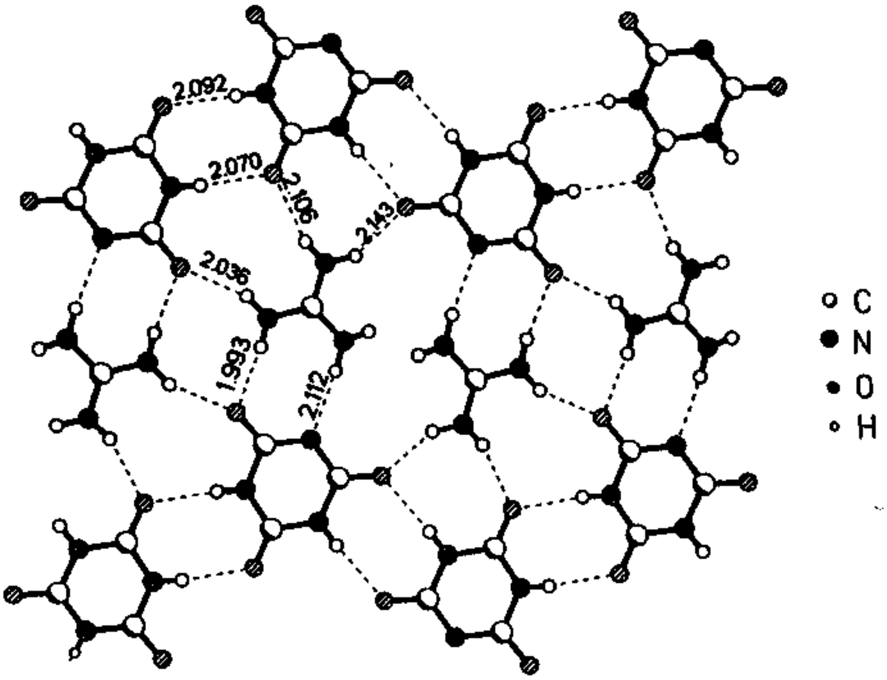


Fig. 4.13 Sine-wave like **CA** tapes holding guanidinium cations by N – H...O and N – H...N bonds

There is about 16.4% increase in the double bond character of the C(11) – N(11) and C(12) – N(11) bonds and about 7.5% for the C(13) – N(12) and C(12) – N(13) bonds. Four of the six hydrogens in the guanidinium fragment participate in N – H...O hydrogen bonding with carbonyl oxygens of **CA** with distances of 2.036Å, 2.106Å, 2.143Å, and 1.993Å. The last is a particularly strong hydrogen bond, considering that the N – H...N bond angle is 172°. Of the two remaining hydrogens, H(2) hydrogen bonds to anionic N(11) and the other remains free. The bonding distance of N(2) – H(2)...N(11) (H...N, 2.11Å) is comparable with the other N – H...O distances in the structure. The hydrogen, H(2A) of the guanidinium ion, which does not participate in hydrogen bonding, has the shortest N – H distance of all N – H bonds in the moiety.

4.4 Potassium thallium cyanurate K Tl ($C_3H\ N_3O_3$-κN)($C_3H_3N_3O_3$)(H_2O)$_2$: In the potassium thallium cyanurate, one of the amidic protons of **CA** has been substituted with Tl (I) to form N – Tl bond. The asymmetric unit (figure 4.14) consists of two **CA** molecules, one Tl $^+$ and K $^+$ ion, along with two water molecules.

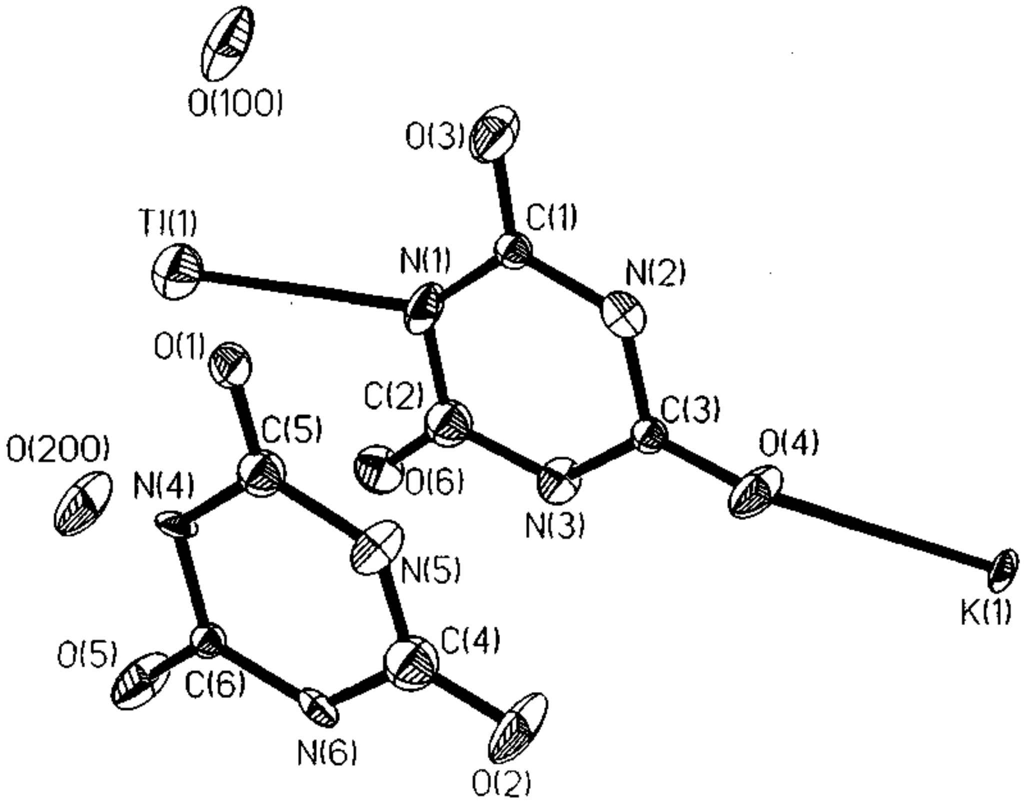


Fig. 4.14 Asymmetric unit of cyanuric acid –Tl(I) structure.

The details of the unit cell are provided in table 4.1. The atomic coordinates, bond lengths and bond angles are presented in tables 4.17 and 4.18.

The **CA** has reacted with Tl (I) through the nitrogen N(1), to form a Tl – N bond (2.75 Å). The oxygens, O(1) and O(2) are bound to K^+ ion with a distance of 2.722 Å. The Tl (I) ions exhibit Tl...Tl interaction, with a distance of 3.73 Å. Tl – K distance was found to be 4.29 Å. The **CA** – Tl units exist as dimers of **CA** – Tl ...Tl – **CA** and the K^+ cations bound to the oxygens of **CA** and the two water molecules.

There were problems related to thermal parameter encountered during structure solution. The carbon atoms were excluded in the anisotropic refinement to obtain the final structure. Similar crystal of Tl(I) with Na^+ cation included, with an isomorphous structure, also encountered similar problems during structure solution.

The structure reveal layers of Tl(I) and K^+ cations pillared by cyanuric acid molecules, forming an infinite two dimensional network. Interesting feature of the complex is the inclusion of free **CA** molecules as guest species residing within channels (figure 4.15). These free **CA** exist as a tape formed by intermolecular dimeric N – H...O bonds.

The structure above is similar to that of one of the compositions of potassium cyanurate structure we obtained, with a composition $K_{1.5}(H_2\mathbf{CA})(H_3\mathbf{CA})(OH)_{0.5}(H_2O)_3$. This also was found to have a free cyanuric acid guest molecule similarly placed within the channels.

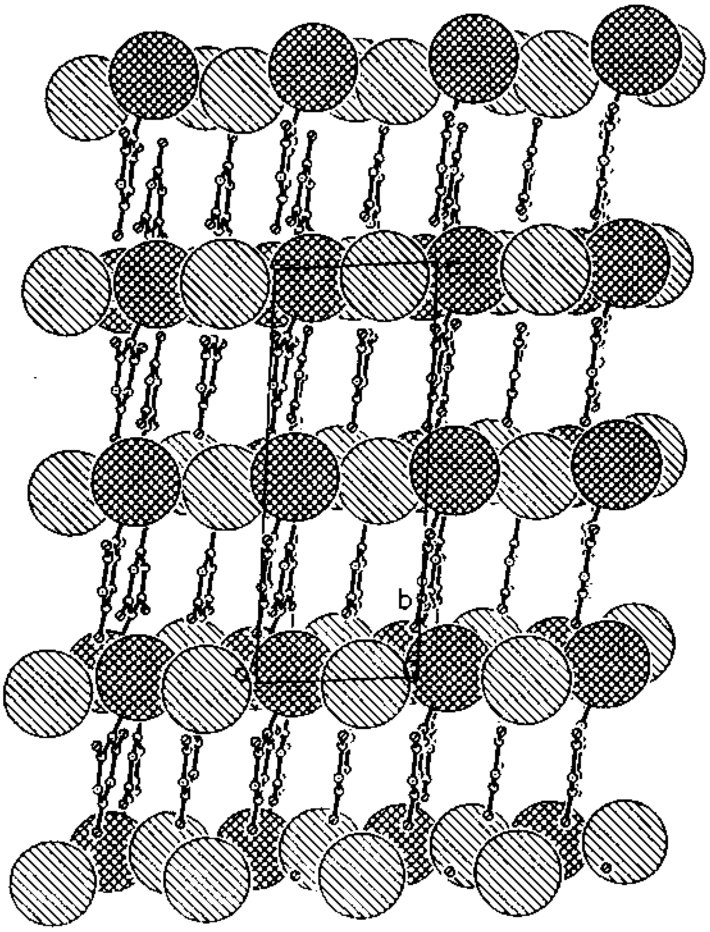


Fig. 4.15 Layers of Tl and K cations pillared by bound **CA** molecules. Free **CA** molecules forming a tape along [010] direction within the channels.

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Table 4.2 Atomic coordinates and equivalent isotropic displacement parameters [Å^2] of Melamine-4,4'-bipyridyl, **1**

Atom	x	y	z	U(eq)
N(13)	0.0337(2)	0.2034(4)	0.3171(1)	0.039(1)
N(14)	0	0.4899(5)	0.2500	0.041(1)
N(11)	0	-0.0635(6)	0.2500	0.059(1)
C(12)	0.0302(2)	0.3885(5)	0.3132(2)	0.037(1)
C(11)	0	0.1220(6)	0.2500	0.038(1)
N(12)	0.0613(2)	0.4788(5)	0.3784(2)	0.052(1)
C(3)	0.2151(2)	0.3058(4)	0.6885(2)	0.041(1)
N(2)	0.3320(2)	0.3171(4)	0.9287(2)	0.059(1)
C(6)	0.2548(2)	0.3050(4)	0.7715(2)	0.041(1)
C(2)	0.1352(2)	0.2580(5)	0.6507(2)	0.051(1)
N(1)	0.1399(2)	0.3142(4)	0.5311(2)	0.065(1)
C(4)	0.2564(2)	0.3587(5)	0.6443(2)	0.050(1)
C(10)	0.3357(2)	0.2670(5)	0.8079(2)	0.052(1)
C(7)	0.2134(2)	0.3470(5)	0.8162(2)	0.050(1)
C(9)	0.3711(3)	0.2755(5)	0.8850(2)	0.061(1)
C(5)	0.2163(3)	0.3609(5)	0.5675(2)	0.062(1)
C(1)	0.1011(3)	0.2627(5)	0.5740(2)	0.062(1)
C(8)	0.2534(3)	0.3501(5)	0.8931(2)	0.058(1)
O(1)	0.4186(2)	0.3846(4)	1.0843(2)	0.079(1)
H(1)	0.044(3)	0.225(4)	0.547(2)	0.08(1)
H(5)	0.247(2)	0.400(4)	0.539(2)	0.07(1)
H(8)	0.225(2)	0.386(5)	0.924(2)	0.07(1)
H(9)	0.429(3)	0.240(4)	0.910(2)	0.08(1)
H(12B)	0.059(2)	0.602(5)	0.380(2)	0.07(1)
H(2)	0.103(2)	0.221(4)	0.678(2)	0.05(1)
H(7)	0.157(2)	0.377(4)	0.796(2)	0.05(2)
H(12A)	0.080(2)	0.414(5)	0.420(2)	0.06(1)
H(10)	0.369(2)	0.238(4)	0.779(2)	0.06(1)
H(101)	0.396(3)	0.375(6)	1.040(2)	0.09(2)
H(4)	0.314(2)	0.398(5)	0.669(2)	0.07(2)
H(100)	0.427(3)	0.498(7)	1.101(2)	0.12(2)
H(11B)	0.020(2)	-0.116(5)	0.294(2)	0.08(1)

Table 4.3 Bond lengths [Å] and angles [°] for complexes **1**

Moiety	bond length	Moiety	bond length
N(13)-C(11)	1.338(3)	N(13)-C(12)	1.351(4)
N(11)-C(11)	1.352(6)	N(14)-C(12)	1.348(3)
C(3)-C(4)	1.394(4)	C(12)-N(12)	1.336(4)
N(2)-C(9)	1.331(5)	C(3)-C(2)	1.387(5)
C(6)-C(10)	1.383(4)	C(3)-C(6)	1.478(4)
C(2)-C(1)	1.366(5)	N(2)-C(8)	1.338(5)
N(1)-C(1)	1.334(5)	C(6)-C(7)	1.383(4)
C(10)-C(9)	1.375(5)	N(1)-C(5)	1.328(5)
C(7)-C(8)	1.376(5)	C(4)-C(5)	1.374(5)
Moiety	bond angle	Moiety	bond angle
C(11)-N(13)-C(12)	113.3(3)	N(12)-C(12)-N(13)	116.5(3)
N(12)-C(12)-N(14)	117.2(3)	N(13)-C(11)-N(11)	116.3(2)
N(14)-C(12)-N(13)	126.3(3)	C(2)-C(3)-C(6)	122.4(3)
C(2)-C(3)-C(4)	116.5(3)	C(9)-N(2)-C(8)	115.8(3)
C(4)-C(3)-C(6)	121.1(3)	C(10)-C(6)-C(3)	121.5(3)
C(10)-C(6)-C(7)	116.8(3)	C(1)-C(2)-C(3)	120.0(4)
C(7)-C(6)-C(3)	121.7(3)	C(5)-C(4)-C(3)	118.9(4)
C(5)-N(1)-C(1)	115.8(3)	C(8)-C(7)-C(6)	119.6(4)
C(9)-C(10)-C(6)	119.7(4)	N(1)-C(5)-C(4)	124.8(4)
N(2)-C(9)-C(10)	124.1(4)	N(2)-C(8)-C(7)	123.8(4)
N(1)-C(1)-C(2)	124.0(4)		

Table 4.4. Hydrogen bond distances (Å) and angles (°) **1**(a)

D – H…A	D – H	D … A	H … A	Angle D – H…A
N24 – H35A…O50	0.9409	2.1322	2.9863	150.34
O50 – H35…N21	0.8301	2.1582	2.9230	153.16
N23 – H37…N1	0.8525	2.1380	2.9812	170.00
N23 – H38…O50	0.8586	2.2057	3.0319	161.39
N50 – H50B…N2	0.8594	1.9768	2.8348	176.22

(a) D , donor ; H , acceptor

Table 4.5 Atomic coordinates and equivalent isotropic displacement parameters [$Å^2$] of Melamine – $AgNO_3$, 2

Atom	x	y	z	U(eq)
Ag(1)	0.2058(1)	0.1191(1)	0.8991(1)	0.043(1)
N(1)	0.4020(3)	0.1244(2)	1.1077(2)	0.022(1)
N(7)	0.0699(4)	-0.1094(2)	0.7648(3)	0.027(1)
C(3)	0.4607(4)	0.2249(2)	1.1660(3)	0.023(1)
C(1)	0.3973(4)	0.0374(2)	1.1928(3)	0.022(1)
N(5)	0.4754(4)	0.1660(3)	1.5009(3)	0.036(1)
N(4)	0.3694(5)	-0.0677(2)	1.1407(3)	0.035(1)
O(3)	0.0085(3)	-0.2037(2)	0.7205(2)	0.045(1)
O(2)	0.1267(4)	-0.0378(2)	0.6933(3)	0.051(1)
O(1)	0.0772(3)	-0.0871(2)	0.8851(2)	0.044(1)
N(6)	0.4860(5)	0.3121(3)	1.0886(3)	0.036(1)
C(2)	0.4627(4)	0.1514(2)	1.3720(3)	0.024(1)
N(2)	0.4219(4)	0.0463(2)	1.3239(2)	0.026(1)
N(3)	0.4961(3)	0.2432(2)	1.2978(2)	0.024(1)
H(5B)	0.482(5)	0.232(3)	1.529(4)	0.03(1)
H(6B)	0.484(5)	0.306(3)	1.017(4)	0.04(1)
H(6A)	0.506(6)	0.375(3)	1.118(5)	0.05(1)
H(5A)	0.468(7)	0.104(4)	1.549(5)	0.07(1)
H(4A)	0.346(5)	-0.117(3)	1.192(4)	0.03(1)
H(4B)	0.336(6)	-0.072(4)	1.059(5)	0.05(1)

Table 4.6 Bond lengths [Å] and angles [°] for complexes **2**

Moiety	bond length	Moiety	bond angle
Ag(1)-O(1)	2.569(2)	Ag(1)-N(1)	2.289(2)
N(1)-C(1)	1.351(3)	N(1)-C(3)	1.350(3)
N(7)-O(3)	1.238(3)	N(7)-O(2)	1.226(3)
C(3)-N(6)	1.330(4)	N(7)-O(1)	1.258(4)
C(1)-N(2)	1.331(4)	C(3)-N(3)	1.347(4)
N(5)-C(2)	1.325(4)	C(1)-N(4)	1.346(4)
C(2)-N(3)	1.366(4)	C(2)-N(2)	1.340(4)
Moiety	bond length	Moiety	Bond angle
N(1)-Ag(1)-O(1)	101.69(7)	C(3)-N(1)-C(1)	114.6(2)
C(3)-N(1)-Ag(1)	120.3(2)	C(1)-N(1)-Ag(1)	120.4(2)
O(2)-N(7)-O(3)	120.9(3)	O(2)-N(7)-O(1)	119.4(2)
O(3)-N(7)-O(1)	119.7(3)	N(6)-C(3)-N(1)	118.0(3)
N(6)-C(3)-N(3)	117.5(3)	N(1)-C(3)-N(3)	124.5(2)
N(2)-C(1)-N(4)	117.1(3)	N(2)-C(1)-N(1)	125.7(2)
N(2)-C(1)-N(1)	117.2(3)	N(7)-O(1)-Ag(1)	101.6(2)
N(5)-C(2)-N(3)	118.2(3)	N(5)-C(2)-N(2)	117.3(3)
C(1)-N(2)-C(2)	115.0(2)	C(3)-N(3)-C(2)	114.9(2)
N(2)-C(2)-N(3)	124.5(2)	N(5)-Ag(1)-N(6)	127.2(2)

Table 4.7 Hydrogen bond distances (Å) and angles (°) in **2** (a)

D – H...A	D – H	D ... A	H ... A	Angle D – H...A
N11 - H11A...O3	0.6444	2.5544	3.1981	177.08
N11 – H11B...O2	0.8728	2.0978	2.9446	163.31
N12 – H12A...O3	0.7706	2.3859	2.9133	126.77
N12 – H12B...O1	0.8851	2.1980	2.9606	144.07
N13 – H13A...O1	0.7732	2.4175	3.1774	167.76
N13 – H13B...N1	0.9252	2.1946	3.0773	159.25

(a) D , donor ; H , acceptor

Table 4.8 Atomic coordinates and equivalent isotropic displacement parameters [Å^2] of the complex, $[Ag_2(C_3H_2N_3O_3\text{-}\kappa N)_2(C_{10}H_8N_2\text{-}\kappa N)]$, 3

Atom	x	y	z	$U_{(eq)}$
Ag(1)	0.6404(1)	0.2286(2)	0.8551(1)	0.036(1)
N(3)	0.6671(6)	0.0460(2)	0.9803(4)	0.025(2)
O(3)	0.5473(5)	-0.3005(1)	0.9221(4)	0.032(2)
O(1)	0.7895(5)	0.3815(1)	1.0463(4)	0.036(2)
N(4)	0.6019(6)	0.3713(2)	0.7248(4)	0.032(2)
O(2)	0.6431(5)	-0.2005(1)	1.2135(4)	0.044(2)
C(1)	0.7300(7)	0.1831(2)	1.0505(5)	0.026(2)
C(3)	0.6019(6)	-0.1732(2)	0.9863(5)	0.021(2)
C(2)	0.6527(7)	-0.1278(2)	1.1428(5)	0.026(2)
N(2)	0.5967(7)	-0.2577(2)	1.0682(4)	0.025(2)
N(1)	0.7217(6)	0.0825(2)	1.1308(4)	0.026(2)
C(6)	0.5229(7)	0.4745(2)	0.5470(5)	0.026(2)
C(7)	0.4803(8)	0.6161(2)	0.6082(5)	0.031(2)
C(5)	0.6061(8)	0.2888(2)	0.5777(5)	0.034(2)
C(4)	0.5228(9)	0.5521(3)	0.6956(6)	0.037(3)
H(7)	0.430(8)	0.768(2)	0.588(6)	0.030(3)
H(8)	0.497(6)	0.654(2)	0.727(5)	0.020(2)
H(1)	0.757(7)	0.184(2)	1.180(6)	0.040(3)
H(5)	0.630(7)	0.175(2)	0.533(6)	0.050(3)
H(4)	0.693(6)	0.107(2)	0.676(5)	0.023(3)
H(2)	0.569(7)	-0.380(2)	1.073(6)	0.030(3)

Table 4.9 Bond lengths [Å] and angles [°] in 3

Moiety	Bond length	Moiety	Bond length
Ag(1)-N(3)	2.116(6)	Ag(1)-N(4)	2.120(7)
N(3)-C(3)	1.338(10)	N(3)-C(1)	1.365(11)
O(3)-C(3)	1.238(10)	O(1)-C(1)	1.210(10)
N(4)-C(8)	1.316(12)	N(4)-C(4)	1.349(12)
O(2)-C(2)	1.215(10)	C(1)-N(1)	1.395(10)
C(3)-N(2)	1.384(11)	C(2)-N(2)	1.368(11)
C(2)-N(1)	1.368(11)	C(6)-C(5)	1.372(12)
C(6)-C(7)	1.404(12)	C(5)-C(4)	1.370(12)
C(7)-C(8)	1.398(13)		
Moiety	Bond angle	Moiety	Bond angle
N(3)-Ag(1)-N(4)	173.5(3)	C(3)-N(3)-C(1)	123.3(7)
C(3)-N(3)-Ag(1)	114.3(5)	C(1)-N(3)-Ag(1)	121.0(5)
C(8)-N(4)-C(4)	116.3(8)	C(8)-N(4)-Ag(1)	120.8(6)
C(4)-N(4)-Ag(1)	121.8(7)	O(1)-C(1)-N(3)	124.3(7)
O(1)-C(1)-N(1)	120.1(8)	N(3)-C(2)-N(1)	115.6(8)
O(3)-C(3)-N(3)	122.6(7)	O(3)-C(3)-N(2)	119.7(8)
N(3)-C(3)-N(2)	117.7(8)	O(2)-C(3)-N(2)	122.2(9)
O(2)-C(2)-N(1)	123.5(8)	N(2)-C(2)-N(1)	114.2(8)
C(2)-N(2)-C(3)	124.0(9)	C(2)-N(1)-C(1)	124.9(8)
C(5)-C(6)-C(7)	117.2(8)	C(8)-C(7)-C(6)	118.3(9)
C(4)-C(5)-C(6)	120.1(8)	N(4)-C(4)-C(5)	123.7(10)
N(4)-C(8)-C(7)	124.3(9)		

Table 4.10 Hydrogen bond distances (Å) and angles (°) in 3^a

D – H...A	D – H	D...A	H...A	Angle D – H...A
N1 - H1...O2	0.9194	1.9496	2.8432	163.50
N2 - H2...O3	0.6736	2.137	2.7986	167.56
C5 - H5...O1	0.9684	2.318	3.2662	166.05
C7 - H7...O1	0.9731	2.3869	3.3566	174.25

(a) D , donor ; H , acceptor

Table 4.11. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of cyanuric acid-pyridine adduct, $[(C_3N_3H_3O_3)(C_5H_5N)]$, 4

Atom	x	y	z	U (eq)
N(13)	0.4693(2)	0.4616(1)	0.2161(2)	0.041(1)
N(12)	0.4632(2)	0.2698(1)	0.2315(2)	0.042(1)
N(11)	0.6238(2)	0.3660(1)	0.3839(2)	0.041(1)
O(13)	0.3132(1)	0.3653(1)	0.0665(2)	0.061(1)
O(12)	0.6191(1)	0.1771(1)	0.3889(2)	0.051(1)
O(11)	0.6220(1)	0.5547(1)	0.3798(2)	0.049(1)
C(13)	0.4079(2)	0.3655(2)	0.1641(3)	0.041(1)
C(12)	0.5719(2)	0.2656(2)	0.3370(3)	0.039(1)
C(11)	0.5747(2)	0.4664(2)	0.3289(3)	0.039(1)
N(1)	0.8477(2)	0.3703(2)	0.5823(2)	0.052(1)
C(1)	0.9299(2)	0.2911(2)	0.5545(3)	0.062(1)
C(3)	1.0885(3)	0.3842(3)	0.7239(4)	0.085(1)
C(4)	1.0054(3)	0.4667(3)	0.7550(4)	0.080(1)
C(5)	0.8861(2)	0.4567(2)	0.6811(4)	0.064(1)
C(2)	1.0496(2)	0.2951(3)	0.6220(4)	0.080(1)
H(13)	0.4388(19)	0.5244(19)	0.1837(29)	0.052(7)
H(12)	0.4319(19)	0.2066(19)	0.1998(28)	0.051(6)
H(5)	0.8262(23)	0.5128(21)	0.6967(33)	0.078(8)
H(3)	1.1665(32)	0.3918(25)	0.7740(43)	0.115(11)
H(1)	0.9006(22)	0.2275(20)	0.4796(34)	0.074(8)
H(11)	0.6998(23)	0.3664(18)	0.4563(32)	0.071(7)
H(4)	1.0249(27)	0.5255(26)	0.8289(43)	0.105(11)
H(2)	1.1068(29)	0.2323(25)	0.5972(43)	0.111(10)

Table 4.12 Bond lengths and angles in 4

Moiety	Bond length	Moiety	Bond length
N(13)-C(11)	1.367(2)	N(13)-C(13)	1.370(2)
N(13)-H(13)	0.85(2)	N(12)-C(12)	1.365(2)
N(12)-C(13)	1.371(2)	N(12)-H(12)	0.86(2)
N(11)-C(12)	1.363(2)	N(11)-C(11)	1.365(2)
N(11)-H(11)	0.95(2)	O(12)-C(12)	1.228(2)
O(13)-C(13)	1.211(2)	O(11)-C(11)	1.223(2)
N(1)-C(5)	1.320(3)	N(1)-C(1)	1.327(3)
C(1)-C(2)	1.355(4)	C(3)-C(2)	1.359(4)
C(3)-C(2)	1.359(4)	C(3)-C(4)	1.368(5)
C(3)-H(3)	0.90(3)	C(4)-C(5)	1.369(4)
C(4)-H(4)	0.91(3)	C(5)-H(5)	0.95(3)
C(2)-H(2)	1.00(3)		
Moiety	**Bond angle**	**Moiety**	**Bond angle**
C(11)-N(13)-C(13)	125.0(2)	C(11)-N(13)-H(13)	115(2)
C(13)-N(13)-H(13)	120(2)	C(12)-N(12)-H(12)	115.6(14)
C(12)-N(12)-C(13)	125.1(2)	C(13)-N(12)-H(12)	119.1(14)
C(12)-N(11)-C(11)	123.9(2)	C(12)-N(11)-H(11)	118.2(14)
C(11)-N(11)-H(11)	117.8(14)	O(13)-C(13)-N(13)	122.7(14)
O(13)-C(13)-N(12)	123.0(2)	N(13)-C(13)-N(12)	114.3(2)
O(12)-C(12)-N(11)	121.9(2)	O(12)-C(12)-N(12)	122.2(2)
N(11)-C(12)-N(12)	115.8(2)	O(11)-C(11)-N(13)	122.5(2)
N(11)-C(11)-N(13)	115.8(2)	C(5)-N(1)-C(1)	117.5(2)
N(1)-C(1)-C(2)	123.3(3)	N(1)-C(1)-H(1)	116.9(14)
C(2)-C(1)-H(1)	119.8(14)	C(2)-C(3)-C(4)	118.9(3)
C(2)-C(3)-H(3)	124(2)	C(4)-C(3)-H(3)	118(2)
C(3)-C(4)-C(5)	118.7(3)	C(3)-C(4)-H(4)	122(2)
C(5)-C(4)-H(4)	119(2)	N(1)-C(5)-H(5)	116(2)
C(4)-C(5)-H(5)	116(2)	C(1)-C(2)-C(3)	118.9(3)
C(1)-C(2)-H(2)	119(2)	C(3)-C(2)-H(2)	122(2)

Table 4.13. Hydrogen bond distances (Å) and angles (°) in 4[a]

D	H	A	D --- H	H...A	D...A	D --- H...A
N(11)	H(11)	N(1)	0.966	1.776	2.738	174
N(12)	H(12)	O(11)	0.878	1.967	2.839	171
N(13)	H(13)	O(12)	0.843	2.004	2.846	175
C(2)	H(2)	O(13)	0.995	2.551	3.486	156

(a) D , donor ; H , acceptor

Table 4.14 Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of guanidinium cyanurate, $[(C_3N_3O_3)(CN_3H_6)]$, 5

Atom	x	Y	z	U (eq)
N(13)	0.0635(4)	0.4576(2)	0.3216(2)	0.033(1)
N(12)	0.2084(4)	0.3744(2)	0.1191(2)	0.035(1)
O(13)	-0.1664(4)	0.5816(1)	0.1524(1)	0.044(1)
N(11)	0.4450(4)	0.2394(2)	0.2904(1)	0.037(1)
O(12)	0.2826(4)	0.3326(2)	0.4883(1)	0.049(1)
N(3)	1.2808(5)	-0.2266(2)	0.3070(2)	0.040(1)
O(11)	0.5778(4)	0.1695(2)	0.0836(1)	0.050(1)
N(2)	0.8662(5)	-0.0340(2)	0.3704(2)	0.042(1)
C(13)	0.0225(5)	0.4780(2)	0.1951(2)	0.031(1)
N(1)	1.0551(6)	-0.0696(2)	0.1582(2)	0.053(1)
C(12)	0.4181(5)	0.2556(2)	0.1642(2)	0.033(1)
C(1)	1.0687(5)	-0.1105(2)	0.2773(2)	0.032(1)
H(13)	-0.0394(68)	0.5200(27)	0.3744(26)	0.049(6)
H(12)	0.1969(53)	0.3794(20)	0.0414(25)	0.032(6)
H(3A)	1.4238(66)	-0.2704(25)	0.2487(25)	0.044(6)
H(3)	1.3155(67)	-0.2469(26)	0.3886(28)	0.055(7)
H(2A)	0.7439(68)	0.0499(30)	0.3511(24)	0.051(7)
H(1)	1.1976(73)	-0.1179(28)	0.091(28)	0.066(8)
H(2)	0.8639(89)	-0.0693(34)	0.4399(34)	0.084(11)

Table 4.15 Bond lengths and bond angles in **5**

Moiety	Bond length	Moiety	Bond length
N(13)-C(13)	1.358(2)	N(3)-C(1)	1.318(3)
N(13)-C(12)	1.389(2)	N(3)-H(3A)	0.840(3)
N(13)-H(13)	0.850(3)	N(3)-H(3)	0.890(3)
N(12)-C(13)	1.353(2)	O(11)-C(11)	1.240(2)
N(12)-C(11)	1.387(2)	N(2)-C(1)	1.336(3)
N(12)-H(12)	0.820(3)	N(2)-H(2A)	0.890(3)
O(13)-C(13)	1.233(2)	N(2)-H(2)	0.800(4)
N(11)-C(11)	1.342(2)	N(1)-C(1)	1.303(3)
N(11)-C(12)	1.345(2)	N(1)-H(1A)	0.840(3)
O(12)-C(12)	1.242(2)	N(1)-H(1)	0.870(3)
Moiety	**Bond angle**	**Moiety**	**Bond angle**
C(13)-N(13)-C(12)	123.6(2)	O(13)-C(13)-N(13)	123.4(2)
C(13)-N(13)-H(13)	119(2)	N(12)-C(13)-N(13)	114.1(2)
C(12)-N(13)-H(13)	117(2)	C(1)-N(1)-H(1A)	118(2)
C(13)-N(12)-C(11)	123.9(2)	C(1)-N(1)-H(1)	119(2)
C(13)-N(12)-H(12)	119.7(14)	H(1A)-N(1)-H(1)	123(3)
C(11)-N(12)-H(12)	116.3(14)	O(12)-C(12)-N(11)	122.8(2)
C(11)-N(11)-C(12)	119.1(2)	O(12)-C(12)-N(13)	117.6(2)
C(1)-N(3)-H(3A)	119(2)	N(11)-C(12)-N(13)	119.7(2)
C(1)-N(3)-H(3)	120(2)	O(11)-C(11)-N(11)	123.1(2)
H(3A)-N(3)-H(3)	119(2)	O(11)-C(11)-N(12)	117.3(2)
C(1)-N(2)-H(2A)	119(2)	N(11)-C(11)-N(12)	119.6(2)
C(1)-N(2)-H(2)	114(2)	N(1)-C(1)-N(3)	121.0(2)
H(2A)-N(2)-H(2)	126(3)	N(1)-C(1)-N(2)	119.4(2)
O(13)-C(13)-N(12)	122.5(2)	N(3)-C(1)-N(2)	119.6(2)

Table 4.16. Hydrogen bond distances (Å) and angles (°) in **5**[a]

D	H	A	D --- H	H...A	D...A	Angle D — H...A
N1	H1	O11	0.871	2.035	2.859	157
N1	H1A	O11	0.844	1.993	2.831	172
N2	H2A	N11	0.891	2.111	2.999	174
N3	H3	O12	0.891	2.142	2.908	143
N3	H3A	O13	0.840	2.106	2.916	161
N12	H12	O13	0.820	2.070	2.886	172
N13	H13	O12	0.848	2.091	2.939	177

(a) D , donor ; H , acceptor

Table 4.17 Atomic coordinates and equivalent isotropic displacement parameters /10^4 [Å^2] of the complex, [Tl K($C_3HN_3O_3$)($C_3H_3N_3O_3$)], **6**.

Atom	x	y	z	$U_{(eq)}$
C(6)	5145(27)	5271(14)	1829(10)	14(4)
C(5)	5014(31)	3269(17)	1853(11)	22(4)
C(4)	4759(33)	4283(18)	3083(12)	30(5)
C(3)	-202(27)	3094(15)	3143(9)	15(4)
C(2)	137(32)	4103(18)	1883(11)	27(5)
C(1)	-103(28)	2118(14)	1893(10)	15(4)
Tl(1)	1543(2)	3673(1)	16(1)	38(1)
K(1)	-3411(7)	3667(3)	5207(2)	22(1)
O(1)	5189(21)	2357(10)	1528(7)	22(3)
O(2)	4498(28)	4344(13)	3807(7)	42(4)
O(100)	2196(26)	898(16)	197(8)	43(4)
O(200)	2736(36)	6242(14)	25(8)	53(5)
O(3)	-92(28)	1169(11)	1537(8)	35(4)
O(4)	-513(26)	3128(11)	3879(7)	35(4)
O(5)	5235(28)	6180(11)	1464(7)	35(4)
O(6)	314(23)	4985(11)	1538(8)	29(3)
N(1)	184(27)	3088(15)	1484(8)	28(4)
N(2)	-237(22)	2135(12)	2697(8)	16(3)
N(3)	-122(25)	4074(13)	2701(9)	21(3)
N(4)	5189(28)	4261(13)	1428(8)	26(4)
N(5)	4866(28)	3320(12)	2665(8)	22(4)
N(6)	4960(23)	5285(12)	2638(9)	17(3)

Table 4.18 Bond lengths [Å] and angles [°] in 6

Moiety	Bond length	Moiety	Bond angle	Moiety	Bond angle
C(6)-O(5)	1.24(2)	O(5)-C(6)-N(6)	119(2)	C(1)-N(1)-C(2)	119(2)
C(6)-N(6)	1.36(2)	O(5)-C(6)-N(4)	121(2)	C(1)-N(1)-Tl(1)	136.5(12)
C(6)-N(4)	1.37(2)	N(6)-C(6)-N(4)	120(2)	C(2)-N(1)-Tl(1)	103.3(12)
C(5)-O(1)	1.21(2)	O(1)-C(5)-N(5)	120(2)	C(1)-N(2)-C(3)	123.8(14)
C(5)-N(5)	1.36(2)	O(1)-C(5)-N(4)	121(2)	C(3)-N(3)-C(2)	124(2)
C(5)-N(4)	1.38(3)	N(5)-C(5)-N(4)	119(2)	C(6)-N(4)-C(5)	119.1(14)
C(4)-O(2)	1.23(2)	O(2)-C(4)-N(5)	125(2)	C(4)-N(5)-C(5)	124(2)
C(4)-N(5)	1.34(3)	O(2)-C(4)-N(6)	119(2)	C(6)-N(6)-C(4)	122(2)
C(4)-N(6)	1.41(3)	N(5)-C(4)-N(6)	116(2)		
C(3)-O(4)	1.25(2)	O(4)-C(3)-N(2)	124(2)		
C(3)-N(2)	1.35(2)	O(4)-C(3)-N(3)	121(2)		
C(3)-N(3)	1.37(2)	N(2)-C(3)-N(3)	114.3(14)		
C(2)-O(6)	1.20(2)	O(6)-C(2)-N(1)	122(2)		
C(2)-N(1)	1.37(3)	O(6)-C(2)-N(3)	121(2)		
C(2)-N(3)	1.38(2)	N(1)-C(2)-N(3)	118(2)		
C(1)-O(3)	1.27(2)	O(3)-C(1)-N(2)	119(2)		
C(1)-N(2)	1.34(2)	O(3)-C(1)-N(1)	121(2)		
C(1)-N(1)	1.35(2)	N(2)-C(1)-N(1)	120(2)		
Tl(1)-N(1)	2.75(2)	C(3)-O(4)-K(1)	149.1(13)		

PART II

STUDIES OF OPEN-FRAMEWORK METAL SQUARATES AND ORGANIC AMINE SQUARATES

Summary

In this part of the thesis, the results of investigations on open-framework metal squarates and organic amine squarates are described.

Open-framework cobalt squarates with amine molecules as structure directing agents have been synthesised for the first time by solvothermal means. Cobalt squarate with 1,4-Diazabicylco[2.2.2]octane (DABCO), $[(C_6H_{13}N_2)_2][Co_2(C_4O_4)_3(H_2O)_4]$, has been synthesized and its structure studied. The structure has linear cobalt squarate chains with a unique cobalt squarate cluster as the building block. The inter-chain interactions form a hydrogen-bonded layer holding the monoprotonated DABCO in the interlayer space.

The reaction of Co(II) in aqueous solution in presence of imidazole at a near neutral pH yielded a coordination polymer of the formula, $[Co(C_4O_4)(C_3H_4N_2)_2(H_2O)_2]$, with coordinating imidazole and bridging squarate ligands. The structure reveals chains of cobalt imidazole squarate with coordinating water molecules. The structure exhibits interesting self-complementarity in hydrogen bonding between the adjacent polymeric

chains. Isomorphous Zn(II) imidazole squarate, $[Zn(C_4O_4)(C_3H_4N_2)_2(H_2O)_2]$ was also obtained.

A layered Cobalt (II) squarate with diprotonated 1,4- dimethyl piperazine of the formula, $[((CH_3)_2N_2C_4H_{10})][Co(C_4O_4)_2(H_2O)_2]$, has been prepared and the structure studied. The crystal structure consists of unique four membered rhombus shaped grids as the building unit. The diprotonated amine occupies the interlayer space.

A cobalt squarate containing monoprotonated imidazole and with the formula, $[(C_3H_5N_2)_2][Co_2(C_4O_4)_3(H_2O)_4]$, has been synthesized and the structural features analyzed. The structure possesses an identical building block as in structure of cobalt squarate with DABCO. The study reveals an amine-induced change in arrangement adopted by the cobalt squarate chains. The structure exhibits three-dimensional hydrogen bonding connectivity. The hydrogen-bonded network of cobalt squarate chains host the monoprotonated imidazole moieties within their uni-dimensional channels.

The squarate derivatives of the following amines have been prepared and the structures solved: 1,3-propane diammonium squarate hydrate, 1,5-pentane diammonium squarate hydrate, tetramethyl guanidinium squarate, 1,4- dimethyl piperazinium squarate, 1,4-Diaza[2.2.2]bicylooctane diammonium squarate and 1,4-butane diammonium squarate.

1,3- propane diammonium squarate hydrate, $[(C_3N_2H_{12})(C_4O_4).(H_2O)]$, has hydrogen bonded squarate water-layers forming rectangular molecular boxes. The layers are arranged in AA fashion forming channels that host the alkyl ammonium moieties.

1,5-pentane diammonium squarate hydrate, $[(C_5N_2H_{16})(C_4O_4)(H_2O)]$, exhibits few features similar to that found in 1,3-propane diammonium squarate hydrate. Interestingly, the layers adopt a wave like conformation, which stack in an AB fashion enclosing quasi-cylindrical cavities, which encapsulates the alkyl ammonium cations.

Tetramethyl guanidinium squarate, $[(C_5N_3H_{14})(C_4O_4H)(H_2C_4O_4)]$, consists of self-complementary O – H...O bonding between the squarate moieties similar to that found in carboxylic acids. These squarate dimers interact by O – H...O bond forming chains of such squarate dimers. These chains are stacked one upon another with the squarates of the adjacent chains facing each other. Each tetramethyl guanidinium moiety interacts with two chains simultaneously, orienting themselves perpendicular to the axis of these chains. This results in the formation of hydrogen bonded channels.

1,4-dimethyl piperazinium squarate, $[(CH_3)_2C_4H_{10}N_2\ (HC_4O_4)_2]$, consists of hydrogen bonded tapes between the amine molecules, assisted by the oxygen of the squarate moiety. N –H...O and C – H...O bonding stabilizes the structure. It is also observed that the C – H...O bonding between the adjacent –CH groups of the piperazine ring, are directed trans (i.e., assumes axial-equatorial orientation) to each other.

In DABCO squarate hydrate, $[(C_6N_2H_{14})(HC_4O_4)_2(H_2O)]$, three hydrogen squarate moieties along with a water molecule form five membered molecular rings, which extends one dimensionally. The diprotonated DABCO interact with these molecular rings forming irregular hydrogen bonded tetrahedra. The proton of the amine moiety exhibits a trifurcated hydrogen-bonding pattern.

1,4-butane diammonium squarate, $[(C_4N_2H_{14})(C_4O_4)]$, does not have the water molecule of crystallization found in the other amine squarates. All the oxygens of the squarate moiety involve in a bifurcated hydrogen-bonding pattern with the surrounding diprotonated amine moieties. The two diagonally opposite oxygens of the squarate moiety involve in hydrogen bonding differently. Hydrogen bonding features between the diprotonated amine and the squarate dianions is described.

1. INTRODUCTION

The design of inorganic and organic framework solids with novel structures and properties has been of great fascination to materials chemist. Apart from their chemical and structural diversity and aesthetic appeal, these materials are attractive owing to the possible control in their construction. An important class of open-framework materials are porous solids of which, zeolites constitute a significant position. There has also been a lot of metal phosphates, carboxylates, oxalates etc.which have been synthesized recently.

The zeolites are hydrated crystalline aluminosilicates[1] that organize into stable discrete framework. These framework involve tetrahedral units of AlO_4 and SiO_4 as their primary building units, where each oxygen atom is shared between two tetrahedra to produce open-frameworks with the chemical formula $[Al_xSi_{1-x}O_2]^{x-}$. The covalent lattices thus obtained can either be neutral or negatively charged. The negative charge is balanced by extra-framework positive ions, such as the alkali or alkaline metal cations, organic cations or combination of both, which reside inside the channels and cages of the zeolite. As a consequence of this ordered structure, zeolite both benefit from and are limited by their highly geometrical nature. The process of forming complex microporous crystalline aluminosilicate is called zeolitization. Zeolites are generally synthesized hydrothermally from a mixture of silicon and aluminium compounds, alkali metal cations, organic molecules and water in an alkaline supersaturated solution.

There has been several fundamental building blocks,[2] called the secondary building blocks or SBUs (the primary building block being the tetrahedral unit) (figure 1.1). These are constructed out of four to sixteen tetrahedral units which, when assembled, form the known zeolite structure types (figure 1.1). These are schematically shown. The zeolite ZSM-5, as well as ferrierite can be described by their 5-1 building units.[1b] Framework density is an important parameter and is a measure of the available pore volume in a zeolite structure. It is defined as the number of tetrahedral atoms per 1000Å^3. Most condensed silicate structures such as α-quartz, cristoballite and tridymite, have values around 20, whereas most zeolites range from 12-19. Cloverite, a gallophosphate, which has one of the largest 20-member ring systems, has a value of 11.1 [3] (figure 1.2).

For almost one and half decades now, materials with different chemical compositions but with similar structural characteristics have been prepared. Most of the aluminophosphates ($AlPO_4$) discovered by Flanigen and co-workers in 1982.[4] The microporous phosphates are synthesized by hydrothermal methods in the temperature range of 100-250°C and using amines or quartenary ammonium salts as templates under mild acidic conditions in contrast to the alkaline conditions employed for zeolites. In contrast to the zeolites, majority of the aluminophosphates exhibit frameworks with Al and P occupying the alternating tetrahedral sites. During the past decade, microporous aluminophosphate based materials have witnessed many novel topologies. Davis and co-workers initiated the quest for large-pore molecular sieves with the synthesis of VPI-5. This molecular sieve contains one-dimensional circular channels with an 18-membered ring aperture and possesses a free diameter of 12-13Å.

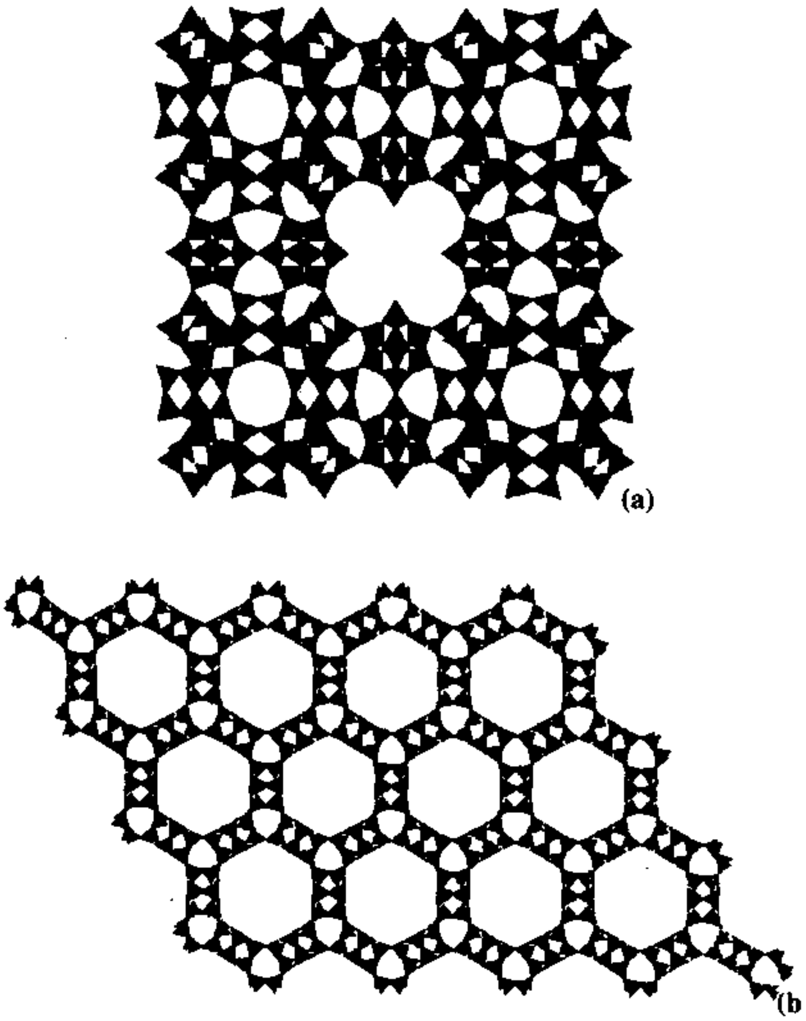

Fig. 1.2 (a) 20-membered channel structure of gallophosphate 'cloverite' (b) 18-membered channels present in aluminophosphate 'VPI-5'.

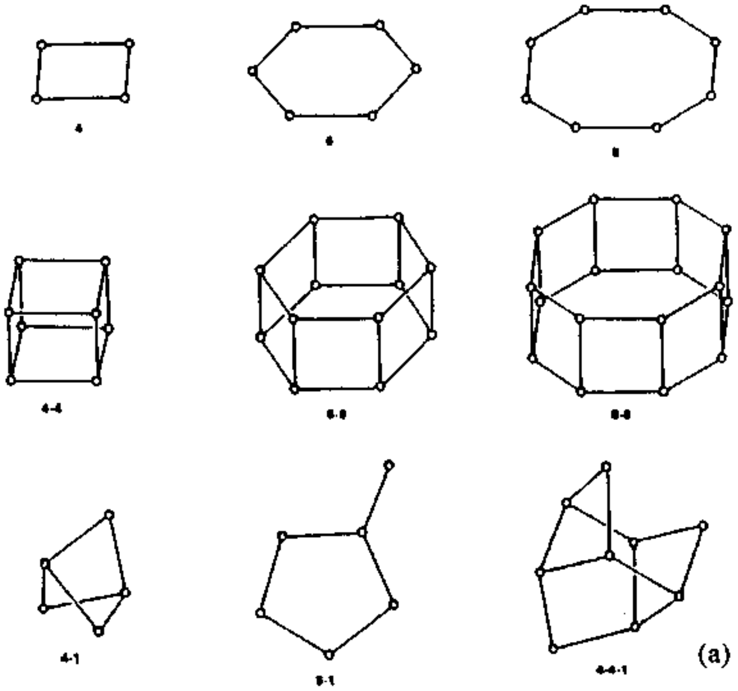

Fig. 1.1Secondary building blocks (SBUs) found in Zeolite structures

The incorporation of Si into a number of AlPOs has resulted in SAPOs. Substitution of metal in SAPO leads to metal silicoaluminophosphates. Interest in the incorporation of metal ions came up primarily due to the implications these solids may have as catalysts. AlPOs can tolerate a higher degree of elemental substitution into the tetrahedral cation sites, giving rise to MAPOs (M=Li, Be, Mg, Zn, B, Ga, V, Cr, Mn, Fe, Co, Ni, Ge, and As).

The other elements in Group 13, B, Ga and In also form phosphate based framework solids. Gallium occurs in 4-, 5-, and 6-fold coordination in these phosphate frameworks but prefers higher coordination when compared to aluminium. The increase in progress in the synthesis of gallophosphates came with the introduction of flouride ions as a mineralizer in the synthesis medium[5]. The flouride ions have sometimes got incorporated in the $AlPO_4$ and $GaPO_4$

frameworks. The first fluorophosphate was cloverite, a gallophosphate with extra-large pore openings comprising of 20 tetrahedral atoms and a three dimensional channel system.

Indium, in comparison to smaller sized Al and Ga, which favour 4-, 5- and 6-fold coordination, prefers to be octahedral. The first report of indium phosphate came from Haushalter, which was templated with ethylenediamine molecules. Several other indium phosphates have followed this work with various amine molecules.

Surprisingly few studies have been reported in the synthesis of microporous boron phosphates. From a crystal chemistry point of view, BPO_4 possesses the same dense structures as those of silica and $AlPO_4$,[6] and one might assume that it would be relatively easy to produce open-framework BPO_4 architectures. Boron is commonly found in trigonal or tetrahedral surroundings and it should be a good candidate for the preparation of solids based on (4:2) connected networks, as in zeolites. Boron has been incorporated in the $AlPO_4$-5 framework,[7] where it substitutes for aluminium, but there are no reports to date of open-framework BPO_4 structures.

Transition metal ions with d-electrons display a wide variety of electronic and magnetic properties. A considerable effort has gone into synthesis of transition metal phosphate frameworks. Some of the prominent transition metal phosphates are discussed below.

Haushalter et al. successfully prepared MoPOs with open frameworks by allowing a molybdenum source (MoO_3 + Mo or $MoCl_5$) to react with phosphoric acid and an organic cationic template in an autoclave in the temperature range 200-400 °C[9].

The catalytic applications of vanadyl pyrophosphates had driven interest in favour of vanadium phosphate family of materials. The association of various vanadium oxidation states (5, 4, 3) with their various polyhedra (tetrahedra, square pyramids, distorted and regular octahedra) leads to a very large diversity for the resulting structures. Very unusual pentameric unit of square pyramidal coordinated vanadium atoms $[V_5O_9(PO_4)_{4/2}]$ have been found in the structures of $Cs_3[V_5O_9(PO_4)_2].xH_2O$ and its analogue with DABCO and potassium.[10]

In addition to the above there has been many Iron phosphates of both open and dense tetrahedral and octahedral frameworks, have been reported.[11] Open-framework Cobalt (II) phosphates have been drawing attention owing to the interesting magnetic properties that they can exhibit, similar to what has been known with iron. Open-framework compounds of Mn have however been very scarce[12] as in the case of Nickel phosphates. A large number of Zinc phosphates have been synthesized with vertex-sharing networks of ZnO_4 and XO_4 (X=P.As) tetrahedra, corresponding to anionic frameworks $[MXO_4^-]$. There have also been reported several three-dimensional topologies with interrupted networks.

Use of tetravalent cations such as Zr, Ti has often lead to the formation of two-dimensional frameworks.[13]

The present day solids involve an interdisciplinary dependence on organic, metal-organic systems, with increasing diversity and complexity. True success in the field would be when a deliberate control of the structure and hence the properties and function of the material is achieved. The area of framework solids is definitely a field of promise for much of the needs that await fulfillment.

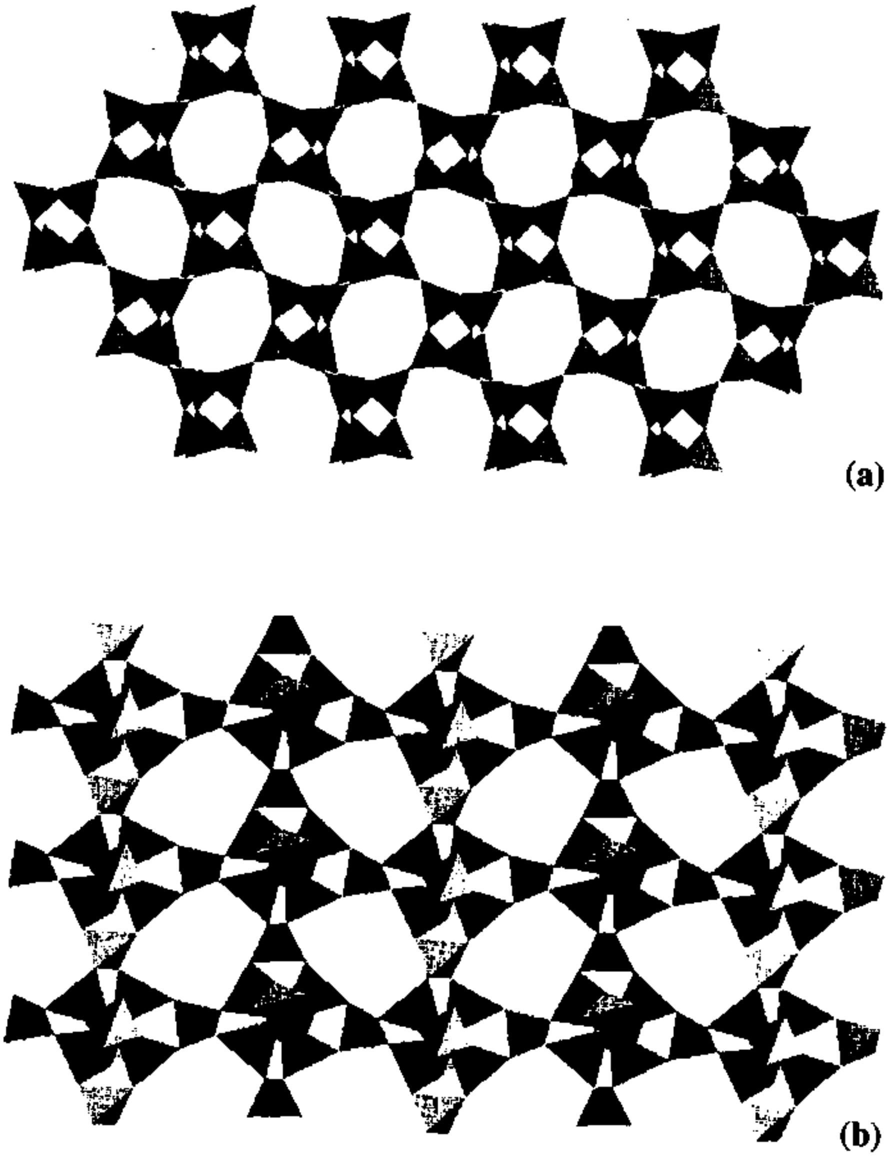

Fig 1.3 (a) Zinc phosphate with ABW structure (b) $A_3Zn_4(XO_4)_3.nH_2O$ (A=alkaline, X = P, As) showing the Zn_4O clusters.

2. SCOPE OF THE PRESENT INVESTIGATIONS

2.1 Solvothermal synthesis of metal amine squarates

In recent years, open framework structures of metal carboxylates have been discovered. Metal carboxylates have recently been used to bridge the metal oxygen networks made from edge- and/or corner shared polyhedra[13], giving rise to three-dimensional connectivity possessing channels. Some of the open framework metal oxalates have been synthesised in the presence of organic amines.[14] Interesting feature of this work is that monomeric and dimeric species and chain structures have been obtained. We were interested to examine if open framework structures could be prepared using squarates. Several metal squarates, especially that of transition metal squarates[15] have been reported in literature. Recently, Ayyappan et al. have described open framework tin (II) and lanthanum (II) squarates[16]. We were interested in preparing open framework squarates in presence of organic amines under hydrothermal conditions. We have carried out some studies in this direction. We'll describe results of cobalt (II) squarate preparation in presence of organic amines.

2.2 Synthesis and structure of organic amine squarates

It has been recently shown that organic amine phosphates react with metal ions giving open framework compounds. Similarly, organic amine oxalates have given rise to open framework oxalates on reaction with metal ions. It would be interesting to carry out the reaction of organic amine squarates with metal ions to obtain open framework metal squarates. We have got structures of amine squarates in that direction.

3. EXPERIMENTAL

3.1 Metal amine squarates

All the metal amine squarates (MASQ) were synthesized by solvothermal methods. The reaction mixture was taken in a teflon flask and placed within a cylindrical steel vessel which is left for heating at a high temperatures (100-150 °C) for a few days. The parameters used to control the reaction were temperature, solvent, solution pH, heating time and composition. These parameters were varied systematically to obtain the single crystals of the MASQ's. The solvents mainly used were H_2O and THF. There were other solvents such as dioxan, CH_3CN, EtOH, MeOH tried which had not resulted in the formation of the compounds. The formation of MASQ was critically dependent upon the solution pH when H_2O was used. The MASQs form at a pH about 6-8. A number of attempts done by changing composition of the reaction mixture in aqueous solution showed that condensed metal squarates result at a pH less than 5. These are mostly the metal squarate chains, which have isomorphous structures for Zn and Co compounds. A number of attempts when 1,3-diaminopropane had been used in the reaction, in both water and THF as solvent, a chelating diimine was obtained by reaction of the $-NH_2$ groups of amine with 1,2- carbonyls of the squarate fragment. Changing from H_2O to THF as solvent had resulted in forming unligated protonated imidazole unlike ligating imidazole when H_2O was used. The building block found in the chain structures, a cobalt squarate cluster has been observed for the first time in two of the compounds obtained. Attempts to obtain similar structures with Zn were not successful. The reactions were carried out by systematically varying the composition of one reactant with respect to the others in the reaction mixture. The formation of good quality single crystals was found to be very critical towards initial composition of the reaction mixture. A very minor change of composition could yield powder stuff of the same material (as confirmed by powder X-ray diffraction). The figures for composition that have been quoted in Table 3.1 indicate those that have produced a better yield of good quality single crystal.

3.2 Amine squarates

All the amine squarates were prepared in aqueous solution at room temperature by slow evaporation. The solution of the amine in water was mixed with aqueous solution of squaric acid. The solution was warmed over a water bath for sometime and the clear solution allowed to crystallize at room temperature.

3.3 Characterization by single crystal X-ray diffraction

In all the cases above, high quality single crystals were carefully chosen under a polarizing microscope and mounted on to the tip of a thin glass fibre supported in clay filled brass tube (diameter ~2-3mm), using a suitable glue (superglue, araldite). X-ray diffraction intensities were measured at room temperature by ω scans using Siemens three-circle diffractometer attached with a CCD area detector and a graphite monochromator for the MoKα radiation (40kV, 40mA). A hemisphere of reciprocal space was collected using SMART [5] software with 2θ setting of the detector at 28°. The crystal-to-detector distance was 5 cms. The data reduction was performed using the SAINT program and the orientation matrix along with the detector and cell parameters were refined for every 40 frames on all measured reflections. The crystal structures were solved by direct methods SHELXTL program [6] and refined by full matrix least squares on F^2. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by the difference Fourier method and were refined isotropically. In few cases PLATON were used to calculate the hydrogen bond lengths and angles in the structure. PLATON [36] was also used to check for any missing symmetry and hence the correctness of the space groups using the CALC MISSYM option. The correctness of the space groups were however was checked by the agreement between the simulated and the experimentally observed powder X-ray diffraction patterns. LATCON was used for the refinement in the cell parameters.

3.4 Thermogravimetric analysis

Thermogravimetric analysis has been carried out to study the temperature of decomposition of the metal amine squarates of Co and Zn using Mettler-Toledo TG850 instrument. The compounds were heated in the furnace attached to the instrument over the temperature range 30-800 °C. The weight loss of most the amines were observed in the temperature range of 300-400 °C with subsequent loss due to decomposition of the metal squarate framework. The weight loss thus observed is compared with the composition of amine molecule and the coordinated water molecule determined by single crystal diffraction for their agreement.

3.5 Powder X-ray diffraction

The powder diffraction patterns of all the samples were obtained using Seifart X-ray powder diffractometer equipped with a Cu-Kα radiation source employing 0.01° step size in 2θ. The powder pattern was matched with the simulated pattern of the structure obtained from single crystal determination.

Table 3.1Compositions of reaction mixtures used

Metal amine squarate	**Composition of the reaction mixture (figures in mmol)**	**Composition of the resulting material**
Cobalt DABCO [1] squarate	0.11 Co(II)[2] + 0.98 DABCO + 0.24 SA [3] + 12 THF [4]	$[(C_6H_{13}N_2)_2][Co_2(C_4O_4)_3(H_2O)_4]$
Cobalt imidazole squarate	0.1 Co(II)+ 0.61 Imz + 0.24 SA + 55 H_2O	$[Co(C_4O_4)(C_3H_4N_2)_2(H_2O)_2]$
Zinc imidazole squarate	0.1 ZnO + 0.61 Imz + 0.24 SA + 55 H_2O	$[Zn(C_4O_4)(C_3H_4N_2)_2(H_2O)_2]$
Cobalt dimethyl piperazine squarate	0.1 Co(II) + 0.44 dmp [6] + 0.24 SA + Et_3N + 12 THF	$[((CH_3)_2N_2C_4H_{10})][Co(C_4O_4)_2(H_2O)_2]$
Cobalt imidazole squarate	0.1 Co(II) + 0.63 Imz [5] + 0.24 SA + 12 THF	$[(C_3H_5N_2)_2][Co_2(C_4O_4)_3(H_2O)_4]$
Zinc piperazine squarate	0.1 Zn(II) + 0.84 piperazine + 0.34 SA + 55 H_2O	$[Zn(C_4O_3)_2(C_4N_2H_8)(H_2O)_2]$

1) DABCO- 1,4-Diaza[2.2.2]bicyclooctane
2) Cobalt chloride hexahydrate used as the cobalt source in all cases
3) SA – Squaric acid
4) THF – Tetrahydrofuran (solvent)
5) Imz – Imidazole
6) Dmp – dimethyl piperazine

Table 4.1 Crystal structure details of the metal amine squarates

Metal amine squarate	Formula	Space Group	Cell parameters						
			a	*b*	*c*	α	β	γ	Cell volume
Cobalt (DABCO)[1] squarate	$[(C_6H_{13}N_2)_2][Co_2(C_4O_4)_3(H_2O)_4]$	$P2_1/n$	8.0317	9.3589	19.3360	90	96.70	90	1443.46
Cobalt imidazole squarate (from H_2O)	$[Co(C_4O_4)(C_3H_4N_2)_2(H_2O)_2]$	*Pbca*	8.0028	11.5042	14.2248	90	90	90	1309.63
Zinc imidazole squarate	$[Zn(C_4O_4)(C_3H_4N_2)_2(H_2O)_2]$	*Pbca*	7.9793	11.4236	14.3350	90	90	90	1306.67
Cobalt (dimethyl piperazine squarate)	$[((CH_3)_2N_2C_4H_8)][Co(C_4O_4)_2(H_2O)_2]$	*Cc*[3]	16.584	13.854	7.385	90	94.64	90	1691.33
Cobalt imidazole squarate (from THF)[2]	$[(C_3H_5N_2)_2][Co_2(C_4O_4)_3(H_2O)_4]$	$P\bar{1}$	7.7857	8.2811	9.4415	91.21	104.44	97.98	582.81
Zinc piperazine squarate	$[Zn(C_4O_3)_2(C_4N_2H_8)(H_2O)_2]$	$P2_1/n$	5.4525	11.5905	10.1386	90	98.85	90	633.09

1) DABCO- 1,4-Diaza[2.2.2]bicyclooctane
2) THF – Tetrahydrofuran (solvent)
3) Problems encountered in determining space group. Details given in page 71.

4. RESULTS AND DISCUSSION

4.1 Synthesis and structure of cobalt and zinc amine squarates

Cobalt squarate with DABCO, $[(C_6H_{13}N_2)_2][Co_2(C_4O_4)_3(H_2O)_4]$, 1: The asymmetric unit of cobalt squarate with 1,4-Diaza[2.2.2]bicylooctane (DABCO) consists of 23 heavy atoms (figure 4.1) of which 15 are involved in the formation of the anionic framework with the formula, $[Co(C_4O_4)_{1.5}(H_2O)_2]^-$. The remaining 8 atoms belong to the protonated amine molecule, $[C_6H_{13}N_2]^+$, which balance the uni-negative charge of the framework. The formula of the asymmetric unit was arrived at by assuming a +2 oxidation state for cobalt, which was obtained from bond valence calculations.[20] The details pertaining to the unit cell are provided in table 4.1. The atomic coordinates bond lengths and bond angles are presented in table 4.3 and 4.4 at the end of this chapter.

The cobalt atom is octahedrally coordinated to 6 oxygen atoms, two of which are from water molecules and four from squarate ligands. The structure is constructed by translating the building block (figure 4.2) uni-dimensionally along the [010] direction. The structure essentially contains these infinite 1D chains (figure 4.3) between which mono protonated DABCO moieties lie, stabilized by hydrogen bonding. The compound crystallizes in $P2_1/c$ space group. The axis of the chains thus coincides with the two-fold screw of the unit cell.

The building block represents a cobalt squarate cluster with two differently ligating squarate ligands. One of squarates bridge the two cobalt atoms of the cobalt squarate cluster through the 1,2- carbonyl groups and other bridges the adjacent clusters through 1,3- carbonyl groups. Of the two coordinated water molecules, one of them bridges the two cobalt atoms in the cluster and other one is terminal. The building block is essentially two cobalt octahedra face shared.

A detailed analysis of the structure show presence of hydrogen bonded layers formed of cobalt squarate chains as shown in figure 4.4. There is formation of small cavities due to the space complementarity achieved in inter-chain hydrogen bonding. These layers are packed along [001] direction with the adjacent layers displaced from each other by half a unit cell displacement along both [100] and [010] directions. In other words, an ABAB kind of sphere packing is obtained if we assume the clusters as being equivalent to spheres. The monoprotonated DABCO molecules stay in cavities between the layers. These cavities are analogous to the voids of ABAB sphere packing. In absence of such a staggered arrangement of these layers, there would have been channels present along [100] direction.

The layers do not interact directly, but do so through the protonated DABCO molecule (figure 4.5). The amine molecule interact via N – H...O bonds involving the terminal water molecule at one end and via C – H...O bonds involving the unligated squarate oxygens at the other end. The details of the hydrogen bond interactions are presented in table 4.4.

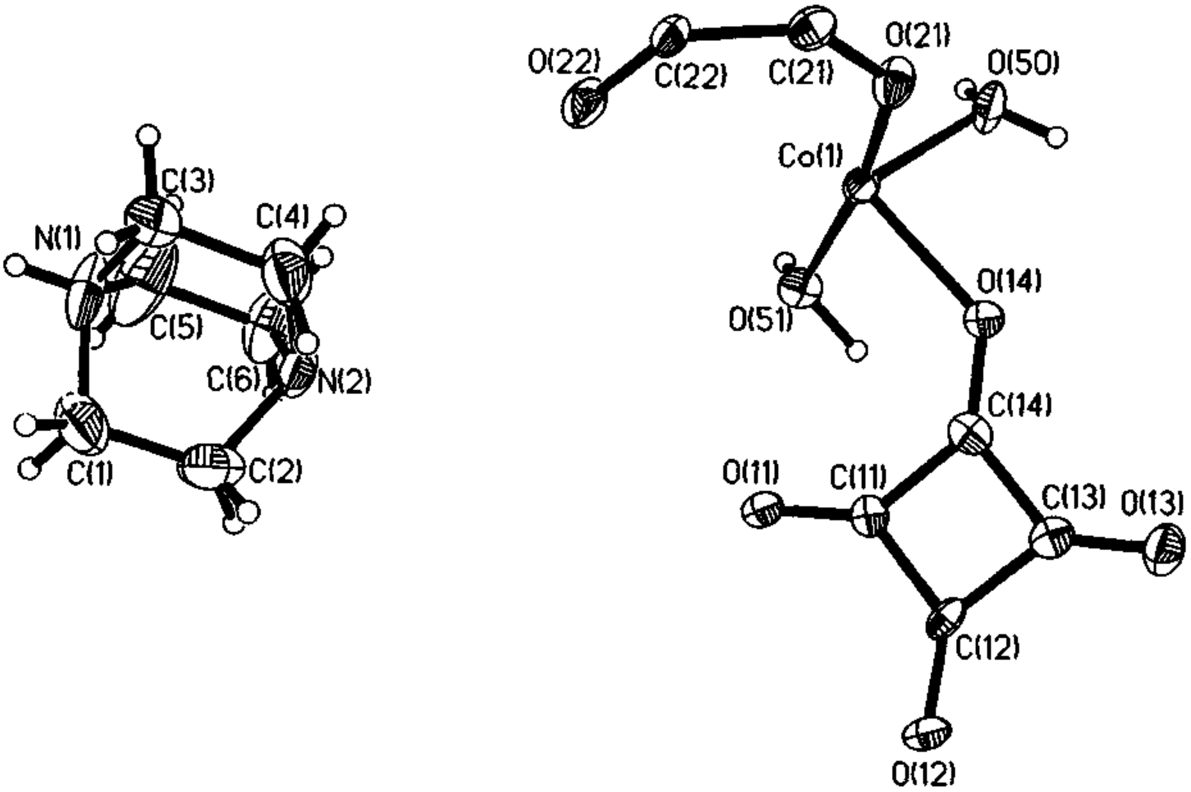

Fig. 4.1 Asymmetric unit of cobalt DABCO squarate. The thermal ellipsoids are shown with 50% probability

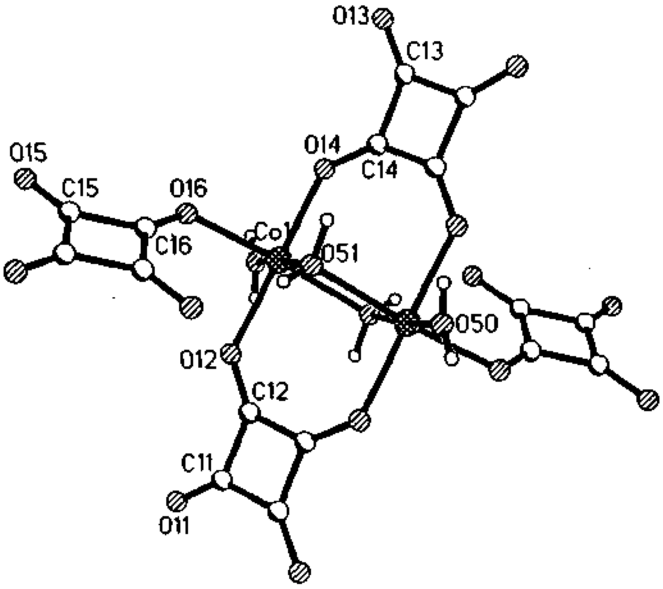

Fig. 4.2 Building block of cobalt squarate chains

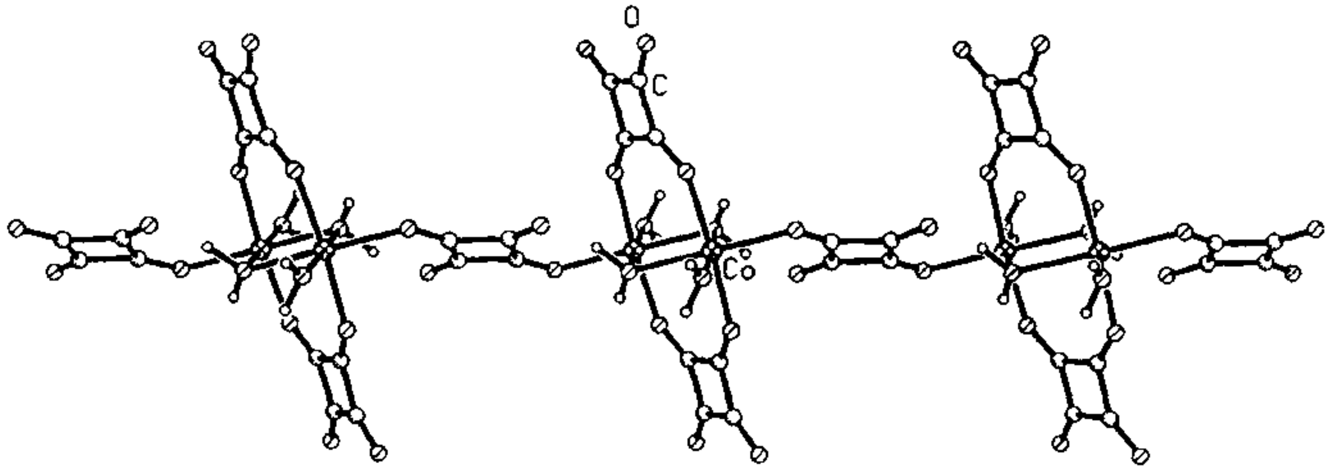

Fig. 4.3 Cobalt squarate chains with two differently ligating squarate ligands

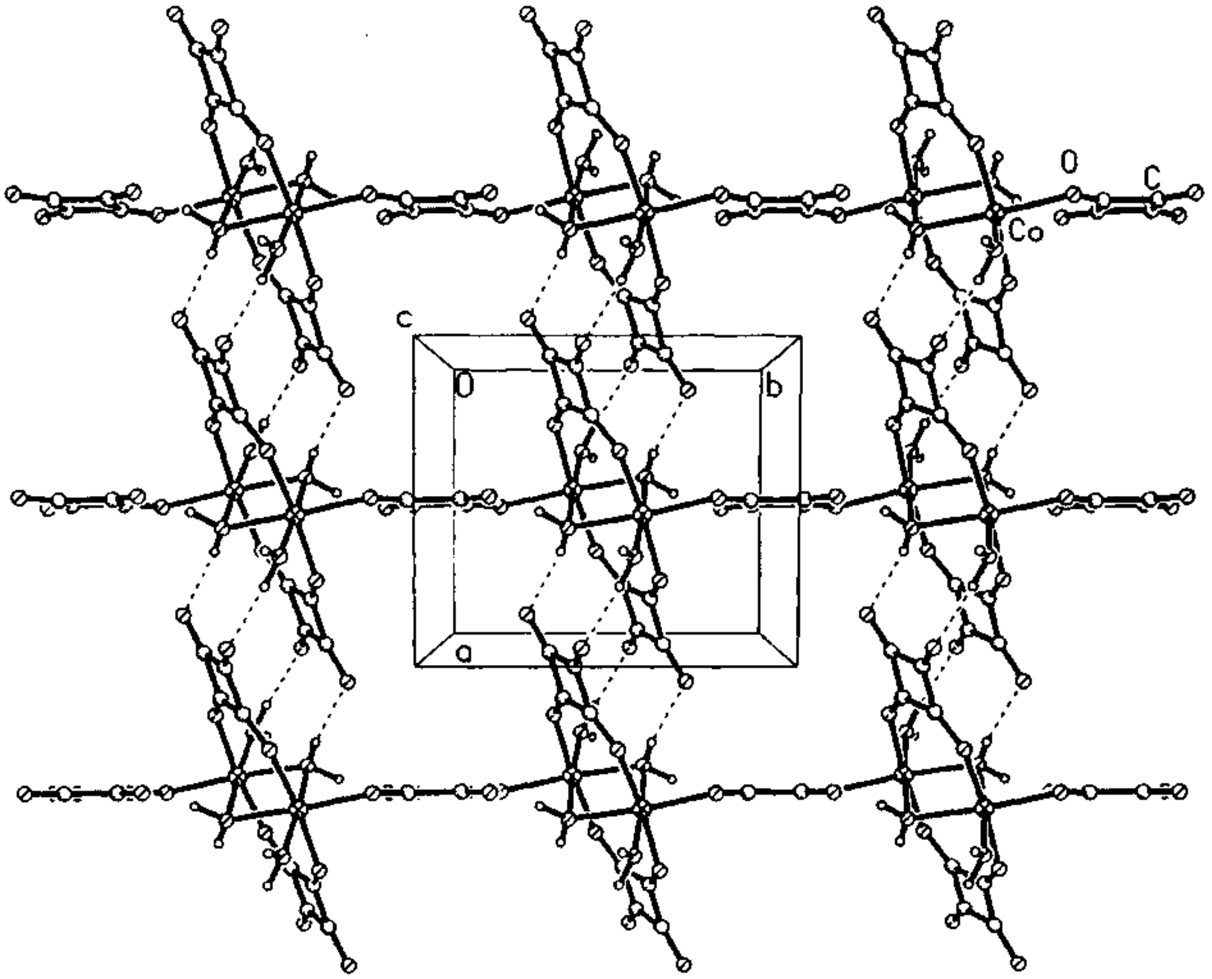

Fig. 4.4 Hydrogen bonded layers of cobalt squarate chains

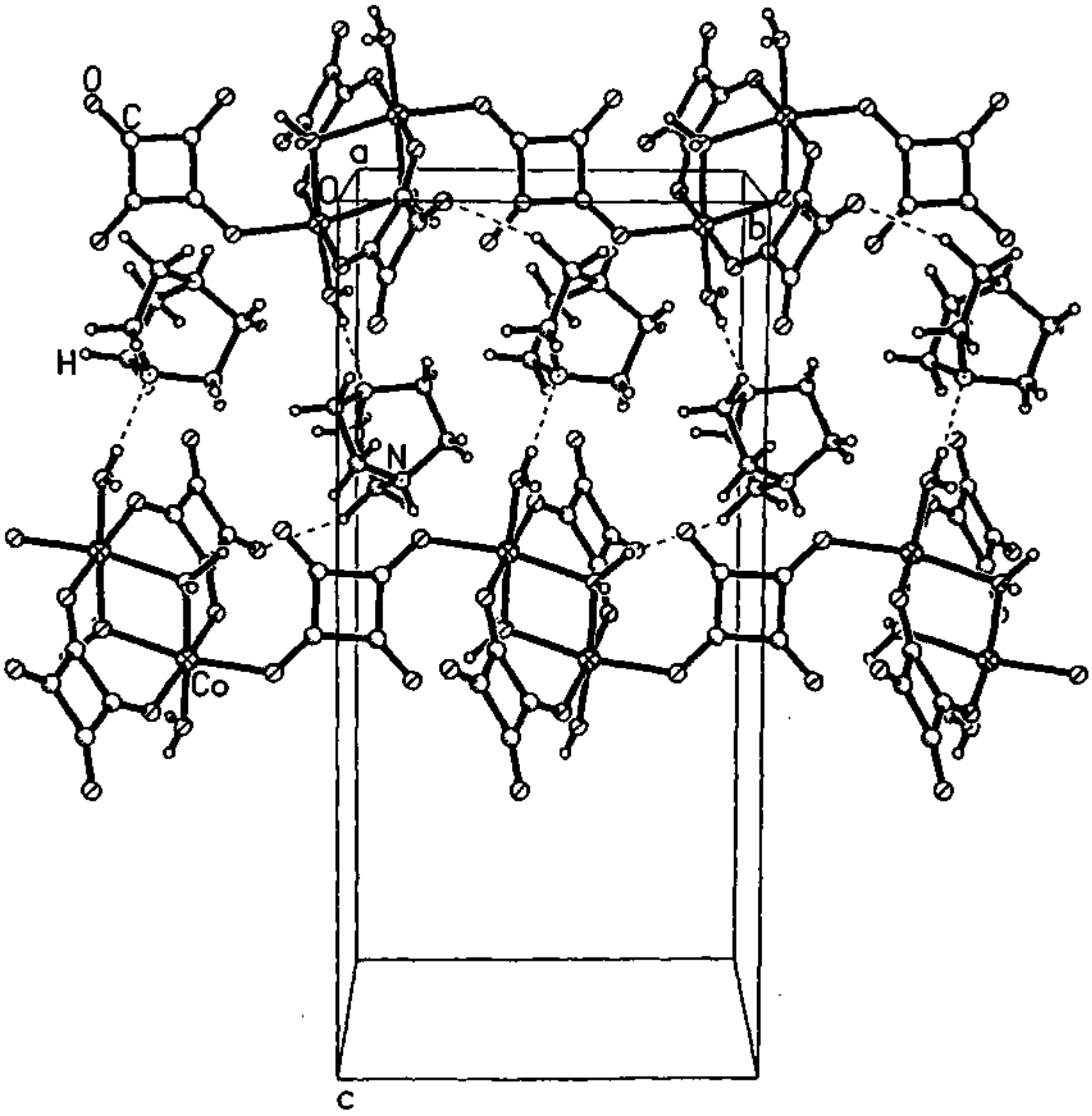

Fig. 4.5 Mono protonated DABCO interacting with adjacent cobalt squarate chains via N – H...O and C – H...O bonds.

The TGA of the sample was carried out in the temperature range 30 °C-800°C in nitrogen atmosphere with a heating rate of 10°C/min. The analysis showed loss of terminal and bridging water molecules around 150°C. The amine loss occurs around 360°C. There is a continuos weight loss observed till ~700 °C, presumably due to decomposition of the squarate framework with the loss of CO after 400 °C.

There are two types of magnetic exchanges possible between the cobalt centers. One of them is through the oxygen of the bridging H_2O and other is through the bridging squarate ligands. With respect to the magentic exchange that is possible, the above system could be considered as an alternating 1-dimensional chain. It is possible that the system exhibits high magnetization due to 3-dimensional coupling at low temperatures.

Cobalt squarate with imidazole, $[Co(C_4O_4)(C_3N_2H_4)_2(H_2O)_2]$, 2: The asymmetric unit of cobalt imidazole squarate consists of 11 heavy atoms (figure 4.6). There appears one cobalt atom in special position with a site occupancy factor of 0.5, one full imidazole molecule that is coordinating to the cobalt center, and oxygen from a coordinating water molecule. The crystal structure was solved in *Pbca*, a centrosymmetric orthorhombic space group. The crystallographic information related to unit cell (table 4.1), atomic coordinates (table 4.6), bond length and bond angles (table 4.7) are presented at the end of the chapter. The oxidation state of cobalt was found to be +2 from Co – L (L = donor atom) bond lengths using bond valence calculations as before. The positive charge contribution from the cobalt atom will be +1 since it occupies a special position with occupancy of 0.5. The charge on each completely deprotonated squarate unit is –2. Only half of the squarate appears in the asymmetric unit, thus contributing –1 charge. The imidazole and the water molecules are neutral ligands offering no contribution of charge in any form. This explains the formula presented.

The structure of **2** is essentially of a coordination polymer consisting of imidazole ligating to cobalt (II) and squarate ligands bridging the octahedral cobalt centers through their 1,3- carbonyl groups. There are additionally two water molecules coordinating to each Co(II).

The bridging of the cobalt octahedra by the squarate results in one-dimensional chains along [010] direction (figure 4.7). These chains interact with each other by O – H...O bonds forming wave-like hydrogen bonded layers. The –NH group of imidazole involve in N – H...O bonding with the squarate oxygens of neighboring chains thereby establishing an inter-layer contact. This binding as shown in figure 4.8 and 4.9 is mutually complementary.

Isomorphous structure of zinc imidazole squarate $[Zn(C_4O_4)(C_3N_2H_4)_2(H_2O)_2]$, **3**, with an identical composition to **2**, has also been obtained with no difference in any of the structural features observed in the above case. The cell parameters of **3** are given in table 4.1. The information pertaining to atomic coordinates and isotropic thermal parameters, bond lengths and bond angles, and the hydrogen bond lengths and angles are provided in tables 4.9, 4.10 and 4.11 respectively.

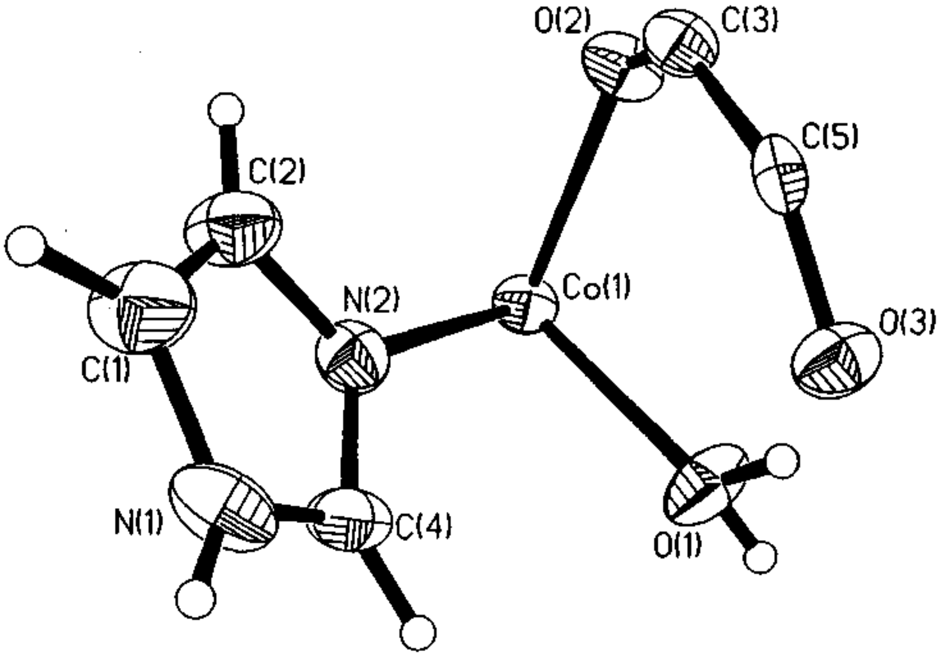

Fig. 4.6 Asymmetric unit of cobalt imidazole squarate. The thermal elllipsoids are shown with 50% probability.

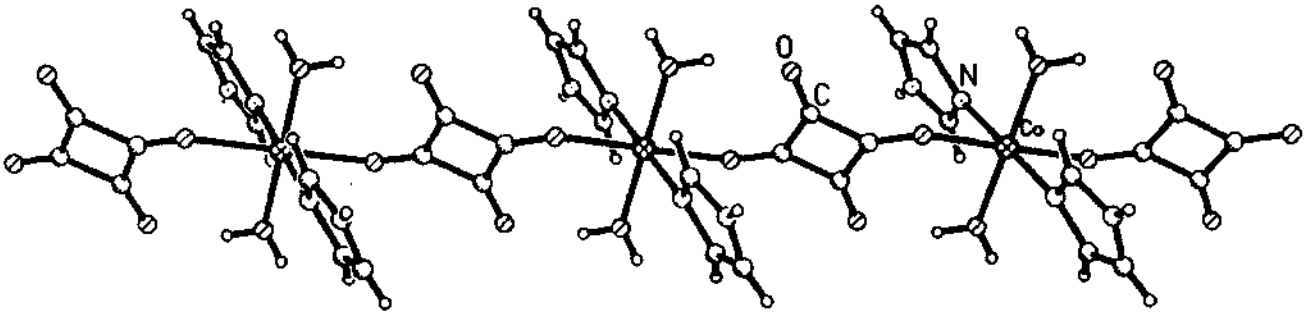

Fig. 4.7 Cobalt imidazole squarate chains with coordinating imidazole and bridging squarate.

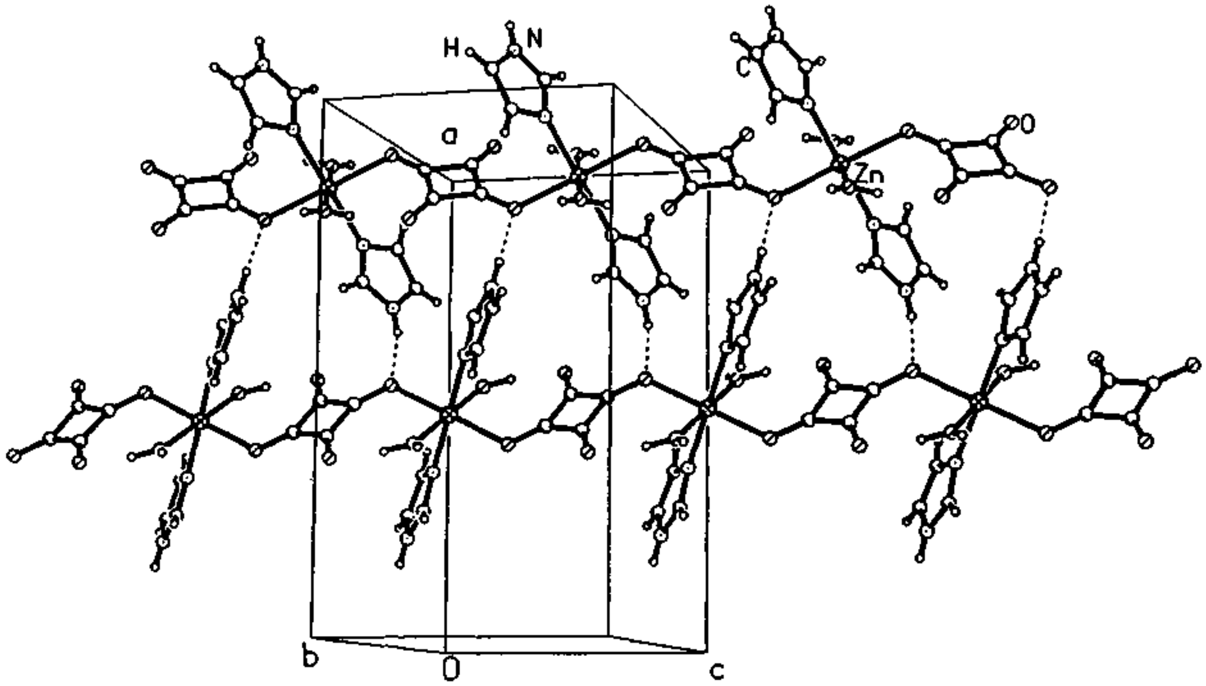

Fig. 4.8 Cobalt imidazole squarate chains with inter-chain N – H...O bonding.

TGA of the sample (30-800°C; 10°C/min; N_2 atmosphere) shows weight loss corresponding to loss of coordinated water around 270°C. Loss of imidazole is observed to occur around 385°C with subsequent loss, due to the framework decomposition.

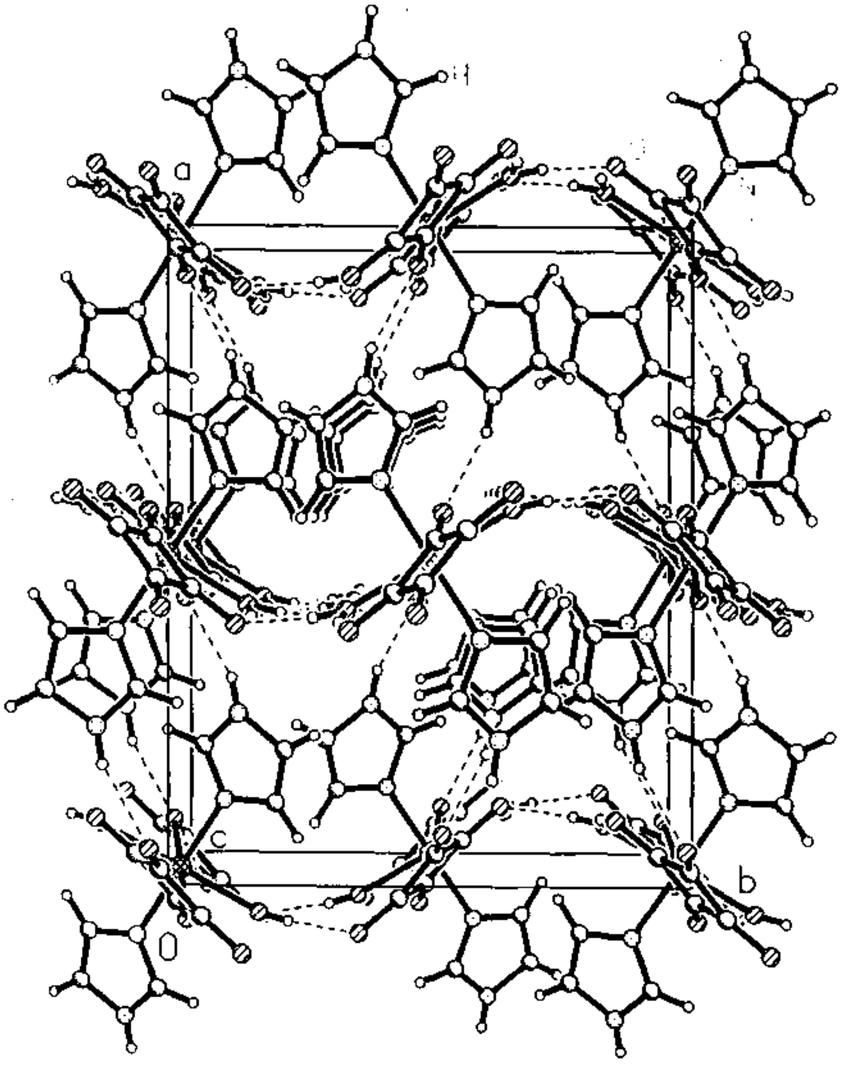

Fig. 4.9 Inter-chain hydrogen bonding between cobalt squarate chains. Notice mutually complementary N – H...O binding by imidazole of adjacent chains.

Cobalt squarate with 1,4-dimethyl piperazine, $[((CH_3)_2N_2C_4H_8)]$ $[Co(C_4O_4)_2(H_2O)_2]$, 4 : The asymmetric unit (figure 4.10) of 4 consists of totally 27 atoms of which 19 of them form the framework with a negative charge and 8 of them belong to the dimethyl piperazine which occupies the extra-framework space. The structure was solved in *Cc* space group. The actual space group however was identified to be centrosymmetric *C2/c* by the PLATON's CALC MISSYM option. A matrix transformation needs to be done to convert the present atomic coordinates to the unit cell corresponding to that of *C2/c* space group. The structure and the composition of the compound presented here however remain the same. The cobalt atom is in its +2 oxidation state. There are two squarate that appear, offering four negative charges totally. The framework possesses a net –2 charge, which is balanced by the +2 charge from the diprotonated amine molecule. The crystallographic information related to the structure is provided in tables 4.1, 4.12 and 4.13.

The cobalt atom is coordinated to four squarate ligands and two water molecules. All the squarates are found bridging the cobalt atoms through their 1,3 carbonyl groups, a feature that has been observed in both the structures studied before. The structure reveals formation of rhombus shaped grids with a dimension 7.873 Å with four cobalt octahedra as its participants (figure 4.11). These extend two dimensionally, thus resulting in a layered material with an inter-layer distance of 7.967Å. Dimethyl piperazine molecules, which are diprotonated, are found to occupy the inter-layer space (figure 4.12). An additional interesting feature is that the layers are packed along [001] direction in an AA.. fashion with the amine moiety occupying the space directly between two cobalt octahedra of the adjacent cobalt squarate layers.

The TGA of the sample (30-800°C; 10°C/min; N_2 atmosphere) shows weight loss corresponding to H_2O loss around 270°C. The amine loss is found to occur around 384 °C with the subsequent loss due to framework decomposition.

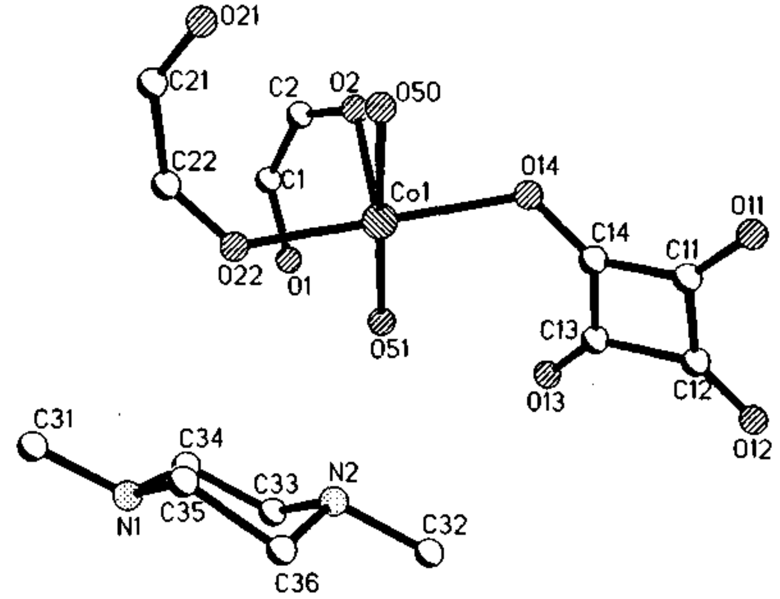

Fig. 4.10 Asymmetric unit of cobalt dimethyl piperazine squarate.

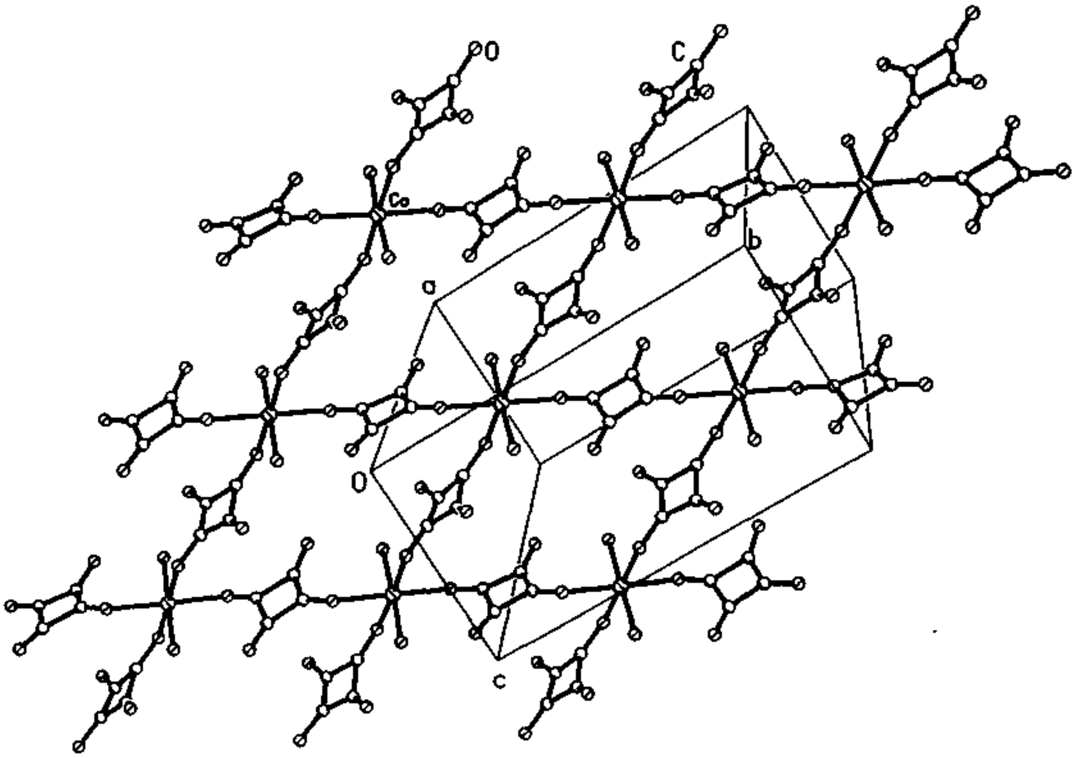

Fig. 4.11 Cobalt squarate layer constructed out of rhombus shaped grids as building units.

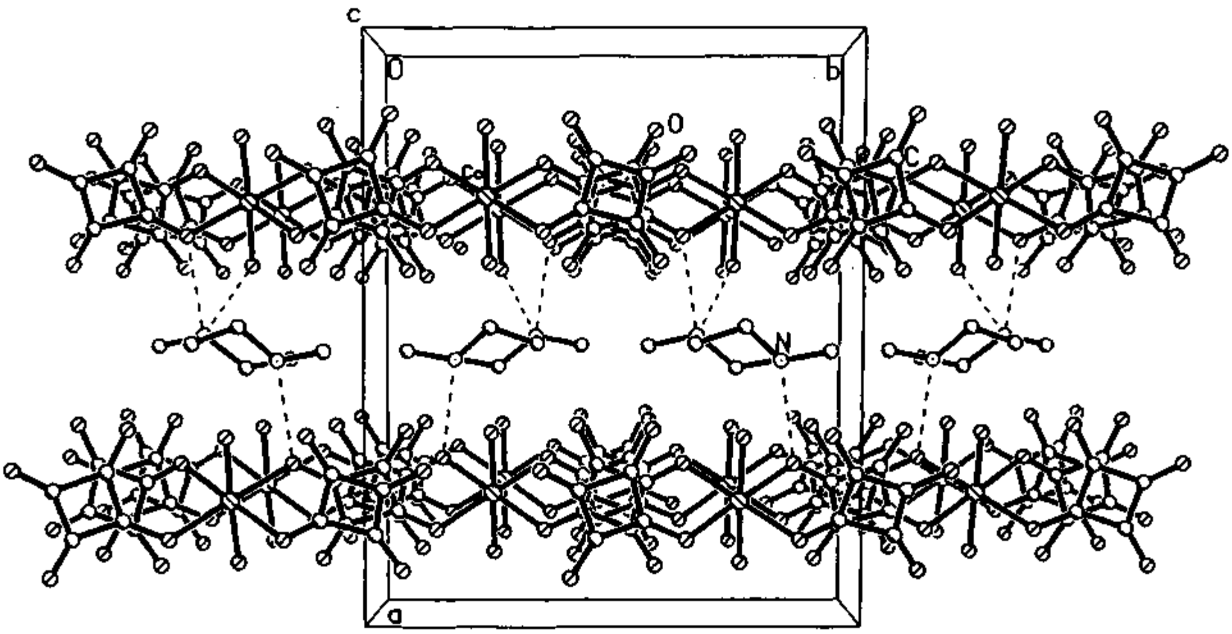

Fig. 4.12 *ab* projection of cobalt squarate dimethyl piperazine between the layers.

The system is two dimensionally uniform layer consisting entirely Co(II) octahedra. The system could possibly exhibit a long range ordering of spins.

Cobalt squarate with imidazole, $[(C_3H_5N_2)_2]$ $[Co_2(C_4O_4)_3(H_2O)_4]$, 5 : There are in total 20 non-hydrogen atoms located in the asymmetric unit of 5 (figure 4.13). There are 15 of them that are involved in formation of the framework and **5** belong the mono protonated imidazole moiety. The crystallographic information pertaining to the structure is presented in tables 4.1, 4.14 and 4.15.

Unlike in the cobalt imidazole squarate, **2**, the imidazole molecules in this structure are protonated and hence do not ligate with the metal center. The structure exhibit three-dimensional hydrogen bonding connectivity and bears resemblance to the cobalt DABCO squarate, **1**, with respect to the building units. Both the structures contain cobalt squarate chains (figure 4.3) that are constructed out of identical cobalt squarate cluster as the building block (figure 4.2).

The study of hydrogen bonding features found between the framework atoms and the protonated amine molecule could be an interesting exercise. The information regarding the hydrogen bond lengths and angles are provided in table 4.16. Among the 1,2 related carbonyl oxygens of the squarate, one of them accepts hydrogen bond from the –OH group of the terminal water and the other from bridging water molecule of the chain below. The same kind of acceptance of bonds is found between the squarate below with the water molecules above. Thus, there is a mutual 'give and take' of hydrogen bonds between the cobalt squarate chains.

Additionally, the cobalt squarate chains do interact with each other through O – H...O (H...O 2.07 Å) hydrogen bonding thus resulting in a three-dimensional hydrogen bonded structure. The imidazole is monoprotonated and is hydrogen bonded to the adjacent chains by N – H...O (H...O 1.92 Å, 1.98 Å) and C – H...O (H...O 2.45 Å) bonding (figure 4.14). The details of hydrogen bond lengths and angles are given in table 4.16.

The imidazole molecules are held slanted roughly by 45 degrees to the cobalt squarate chains (figure 4.15). This maximizes the interactions between the chains and between the chains and the protonated amine.

TGA of the sample (range 30-800°C; 10°C/min; in N_2) showed water loss in two ill-defined steps within 200°C. The amine loss is found to occur around 300°C with the subsequent loss due to framework decomposition.

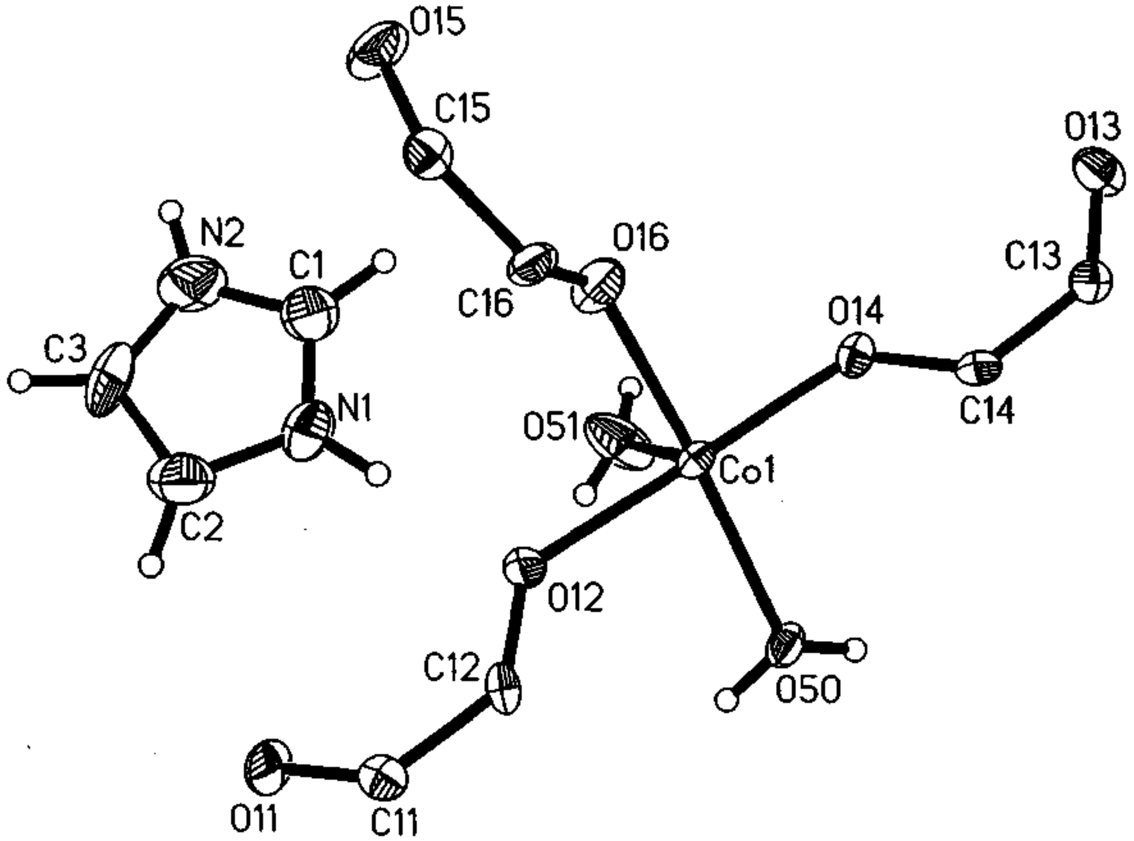

Fig. 4.13 Asymmetric unit of cobalt imidazole squarate. The thermal ellipsoids are shown with 50% probability.

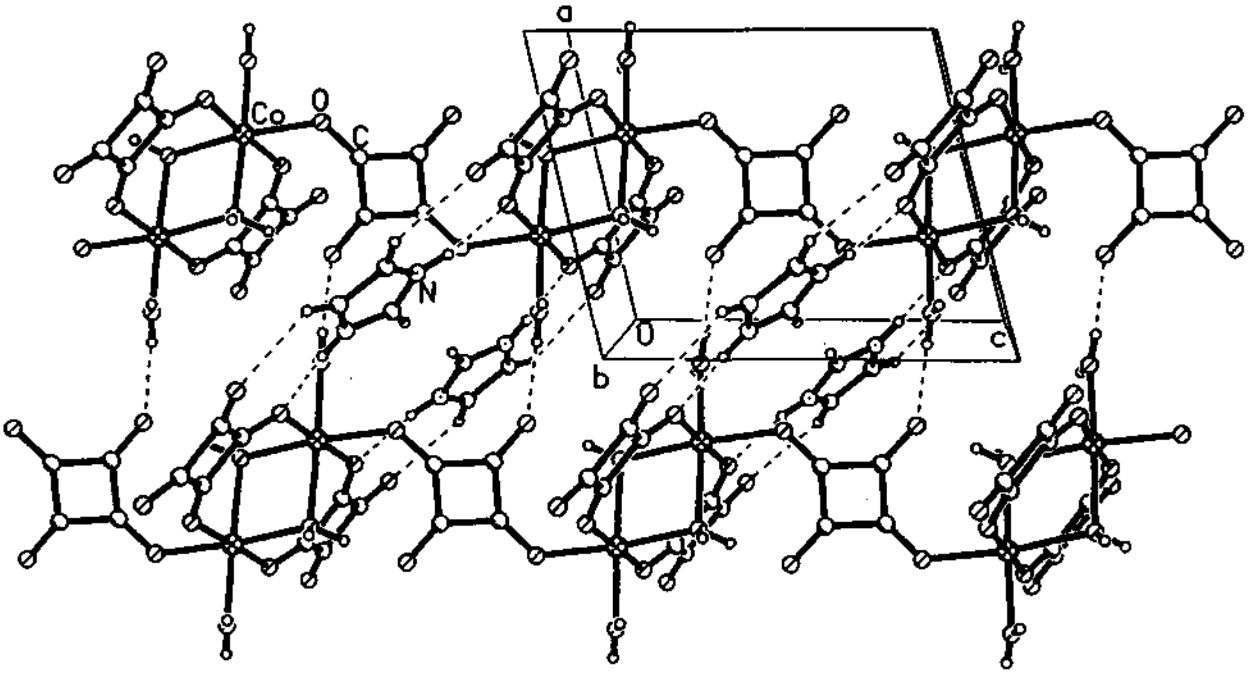

Fig. 4.14 Protonated imidazole held between the adjacent chains by N – H...O and C – H...O bonds.

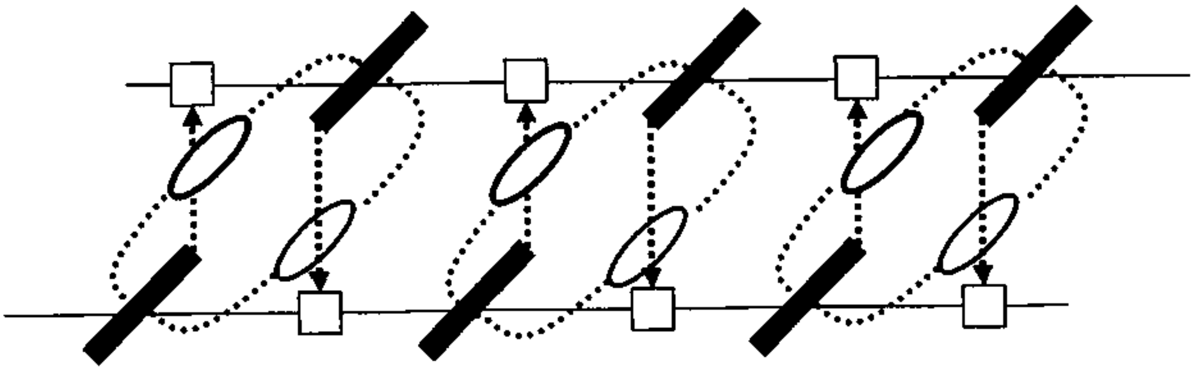

Fig. 4.15 Schematic illustration of inter-chain hydrogen bonding (dotted) in 5, showing the protonated imidazole (oval) sharing bonding with both the chains. The squares represent cobalt squarate cluster and the lines, the connecting squarate ligands.

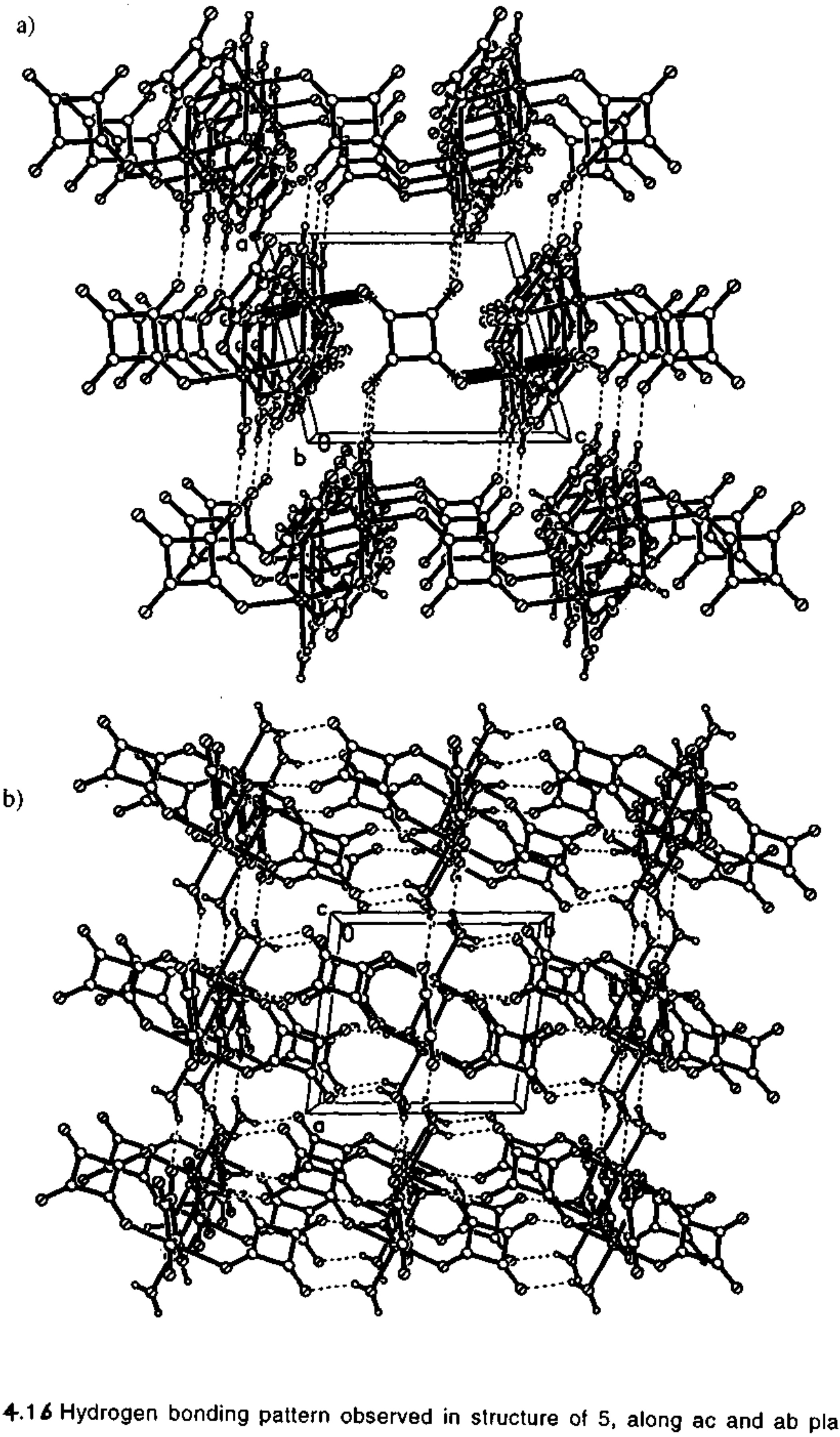

Fig. 4.16 Hydrogen bonding pattern observed in structure of 5, along ac and ab planes. Note the channels in 4.16a. The protonated imidazole moieties are not shown.

Zinc piperazine squarate, [Zn($C_4N_2H_{14}$)(C_4O_3)$_2$ (H_2O)$_2$], 6: The asymmetric unit of zinc piperazine squarate consists of 12 non-hydrogen atoms (figure 4.17). The Zn atom lies in a special position with a site occupancy factor of 0.5. The charge contribution from the Zn is thus +1. There appears one squarate moiety with only three carbonyl groups. The fourth carbonyl group had reacted with the piperazine molecule to form a C – N bond. The nitrogen of the piperazine can be assumed to have substituted the –OH group of the squarate moiety. This way the charge contribution from the squarate fragment as shown would be –1. This satisfies the single positive charge from Zn atom. The atomic coordinates and the isotropic thermal displacement parameters are provided in table 4.17. The bond lengths and bond angles are given in table 4.18.

The Zn atoms are octahedrally coordinated to four squarate ligands and two water molecules similar to that in structure of **4**. The structure reveals layers of zinc squarate, which are connected to each other by piperazine moieties. The piperazine molecules connect the adjacent such layers through a C – N covalent bond involving both its nitrogen atoms (figure 4.18). The connection between the layers is simple and as depicted in scheme below (figure 4.19). In the absence of such a reaction between the amine and the squarate fragments, the structure would have essentially been a layered one similar to structure of **4**.

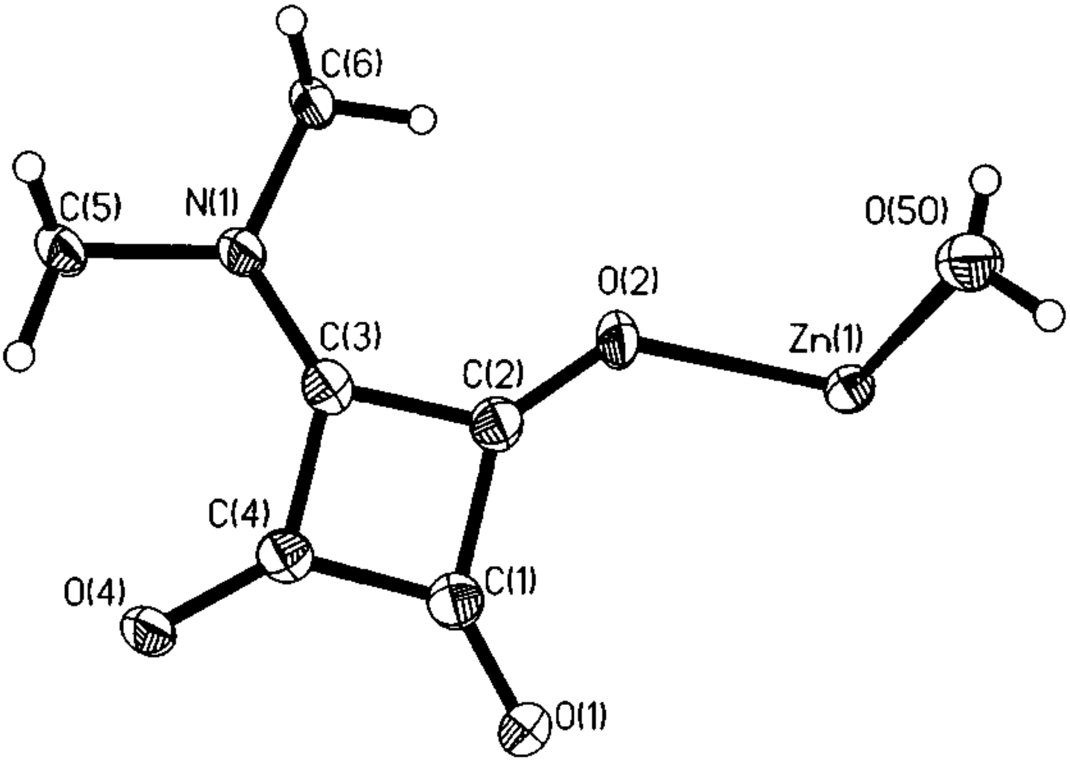

Fig. 4.17 Asymmetric unit of Zinc piperazine squarate. The thermal ellipsoids are shown with 50% probability.

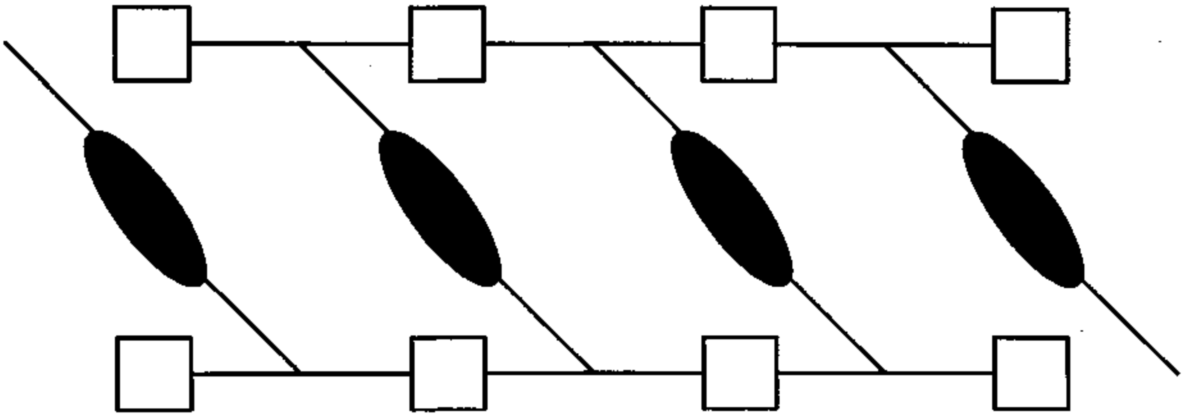

Fig. 4.18 Schematic representation of the piperazine moieties (filled ovals) establishing a covalent connection between the zinc squarate layers (squares connected with lines).

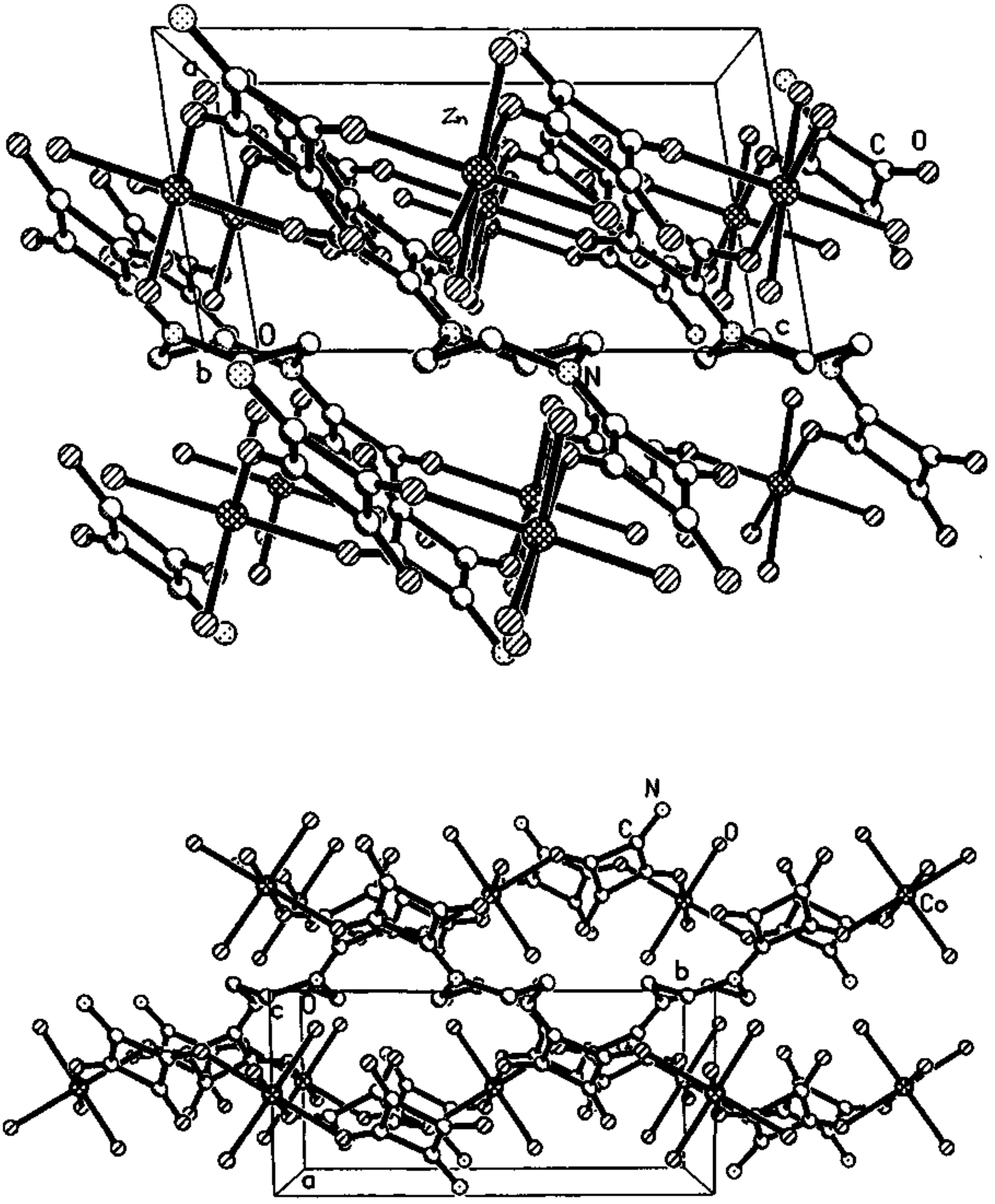

Fig. 4.19 Projection along *ac* and *ab* planes showing zinc squarate layers covalently connected by piperazine molecules.

Table 4.2 Crystal structure details of Amine squarates

Amine squarate	**Formula**	**Space Group**	**Cell parameters**						
			a	*b*	*c*	α	β	γ	Cell volume
1,3-propane diammonium squarate	$[(C_3N_2H_{12})(C_4O_4)(H_2O)]$	*Pba2*	11.264	11.264	4.061	90	90	90	559
1,5-pentane diammonium squarate	$[(C_5N_2H_{16})(C_4O_4)(H_2O)]$	*Pccn*	12.579	9.988	11.214	90	90	90	1409
Tetramethyl guanidinium squarate	$[(C_4O_4H)(C_4O_4H_2)(C_5N_3H_{14})]$	*P -1*	7.989	10.110	11.544	70.32	75.86	68.12	807.2
1,4-dimethyl piperazine squarate	$[(C_6N_2H_{16})(HC_4O_4)_2]$	$P2_1/c$	9.074	12.317	7.138	90	100.78	90	783.80
DABCO squarate	$[(C_6N_2H_{14})(HC_4O_4)_2.H_2O]$	*Pnma*	14.435	7.228	14.524	90	90	90	1515.5
1,4-butane diammonium squarate	$[(C_4N_2H_{14})(C_4O_4)]$	$P2_1/c$	4.403	12.031	9.074	90	94.84	90	479.06

DABCO- 1,4-Diaza[2.2.2]bicylcooctane

4.2 Synthesis and structure of amine squarates

1,3-propane diammonium squarate, $[(C_3N_2H_{12})(C_4O_4)(H2O)]$, 1:

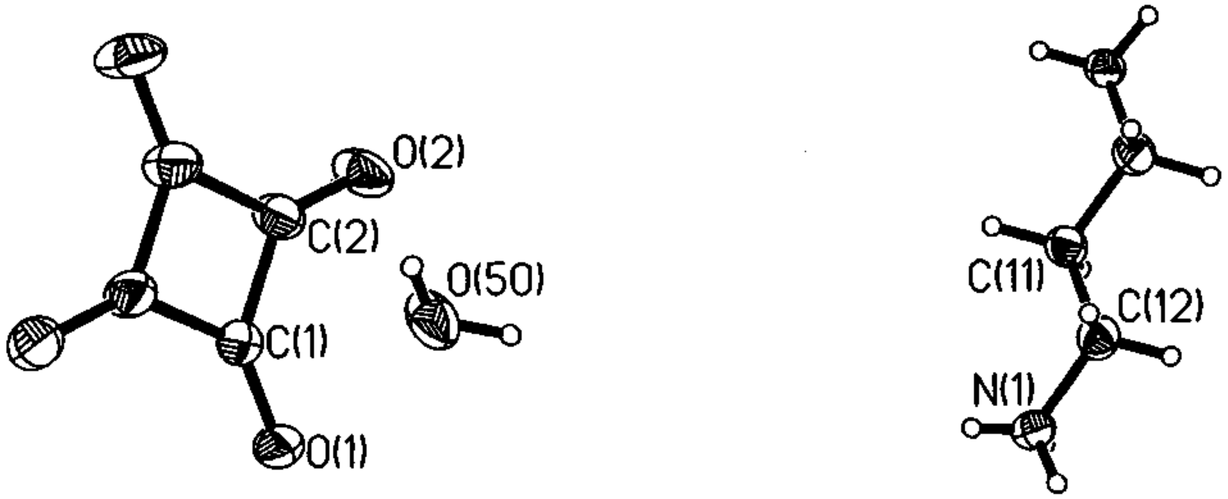

Fig. 4.20 Asymmetric unit of 1,3-propane diammonium squarate. The thermal ellipsoids are shown with 50% probability

The asymmetric unit of 1,3-propane diammonium squarate (figure 4.20) consists of half a molecule of squarate a water molecule and half of the diprotonated amine moiety. The alkyl diammonium moiety is found to adopt the common all trans conformation. The relevant crystallographic information is provided in tables 4.2, 4.19 and 4.20.

Both the protons of squaric acid are deprotonated as expected. The structure of the amine squarate consists of rectangular hydrogen bonded molecular boxes constructed out of squarate and the water molecules utilizing the O – H...O (H...O 1.89Å, 1.83Å) bonding. Each molecular box is built out of four water molecules and four squarate anions, which extend two dimensionally forming squarate-water layers. These molecular boxes host propane diammonium cations (figure 4.21) and stabilize them by N – H...O and C – H...O bonding. The N – H...O bonding involves the oxygen of water (H...O 1.86Å) and the squarate moiety (H...O 1.87, 2.05). The C – H...O bond (H...O 2.52Å, 2.59Å) is formed between C(12) of the alkyl fragment and the squarate oxygens. The molecular boxes upon packing are unblocked by the subsequent layers, thus resulting in channels along [001] direction. The hydrogen bond lengths and angles are given in table 4.21.

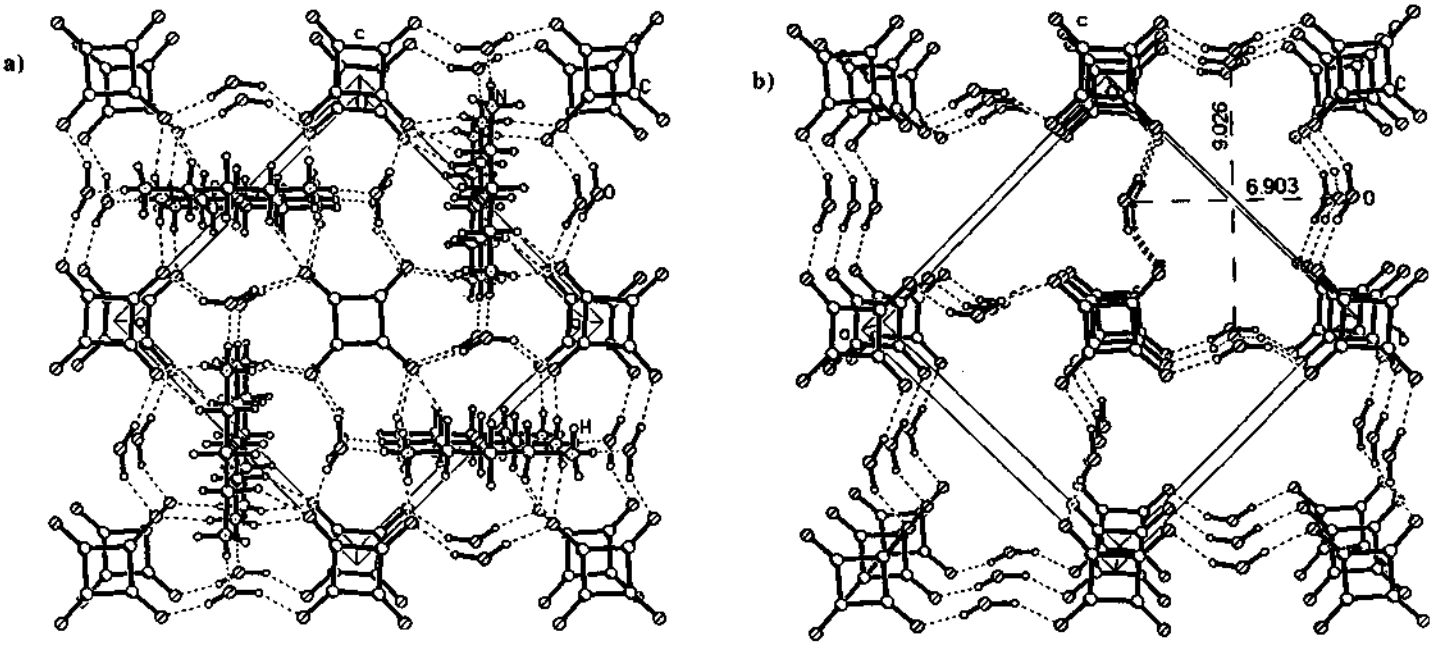

Fig. 4.21 Hydrogen bonded molecular boxes accommodating propane diammonium ions. Note the channels down *c* axis. In 4.21b amine atoms deleted for clarity.

1,5-pentane diammonium squarate, $[(C_5N_2H_{16})(C_4O_4)(H_2O)]$, 2:1,5-diammonium squarate crystallizes with half a molecule of squarate, a molecule of water and half of protonated alkyl diammonium cation appearing in the asymmetric unit (figure 4.22). The atomic coordinates the bond lengths and angles are given in table 4.2, 4.22 and 4.23.

The crystal structure of 2 is similar to that of 1 in that, the formation of rectangular molecular boxes is witnessed here too (figure 4.23). However,

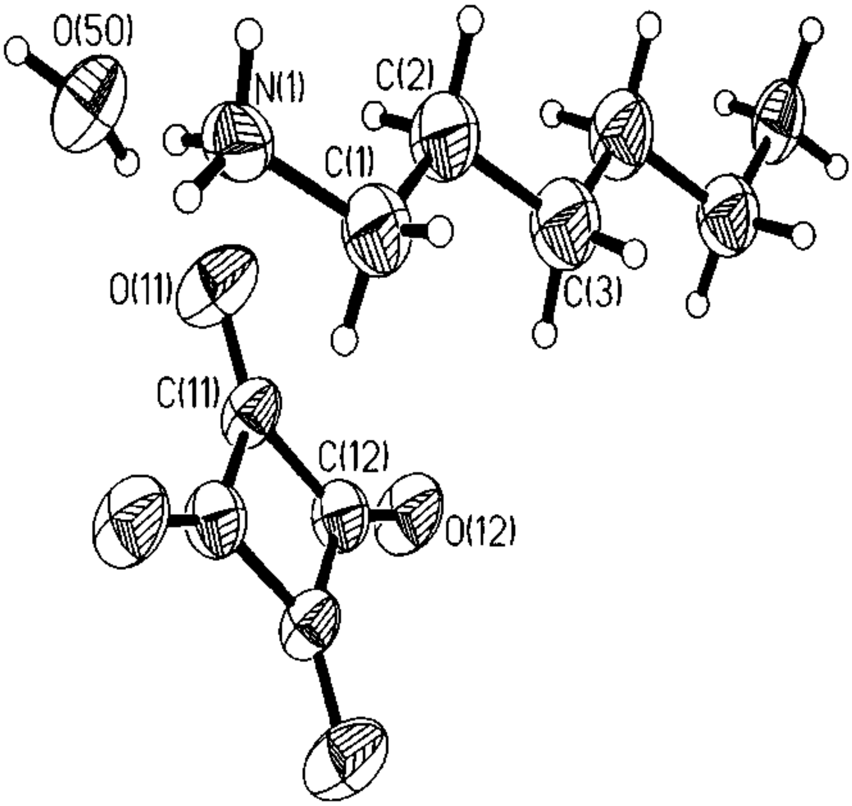

Fig. 4.22 Asymmetric unit of 1,5-pentane diammonium squarate. The thermal ellipsoids are given with 50% probability.

owing to the large size of the pentane diammonium molecules, there is no formation of channels that hold the amine molecules. The layer containing the molecular boxes is not planar, but adopt a wave like pattern along [001] direction. These layers upon packing enclose cavities between them (figure 4.24), in which the amine molecules are accommodated stabilized by N – H...O bonds with oxygen of water molecules (H...O 1.83Å) and squarate anions (H...O 1.85, 1.90). Unlike in **1**, there was no C – H...O interactions observed. The hydrogen bond lengths and angles are given in table 4.24.

The rectangular molecular arrangement has been achieved through the O – H...O (H...O 1.89Å) bonding between the squarate dianions and the water molecules crystallization. The squarate-water layers are found in *bc* place in the present case and the *ab* plane in dapsq one. The dimensions of the box in **2**, which is 10.630Å x 6.657Å differs from that of 9.026 x 6.903 boxes found in **1**.

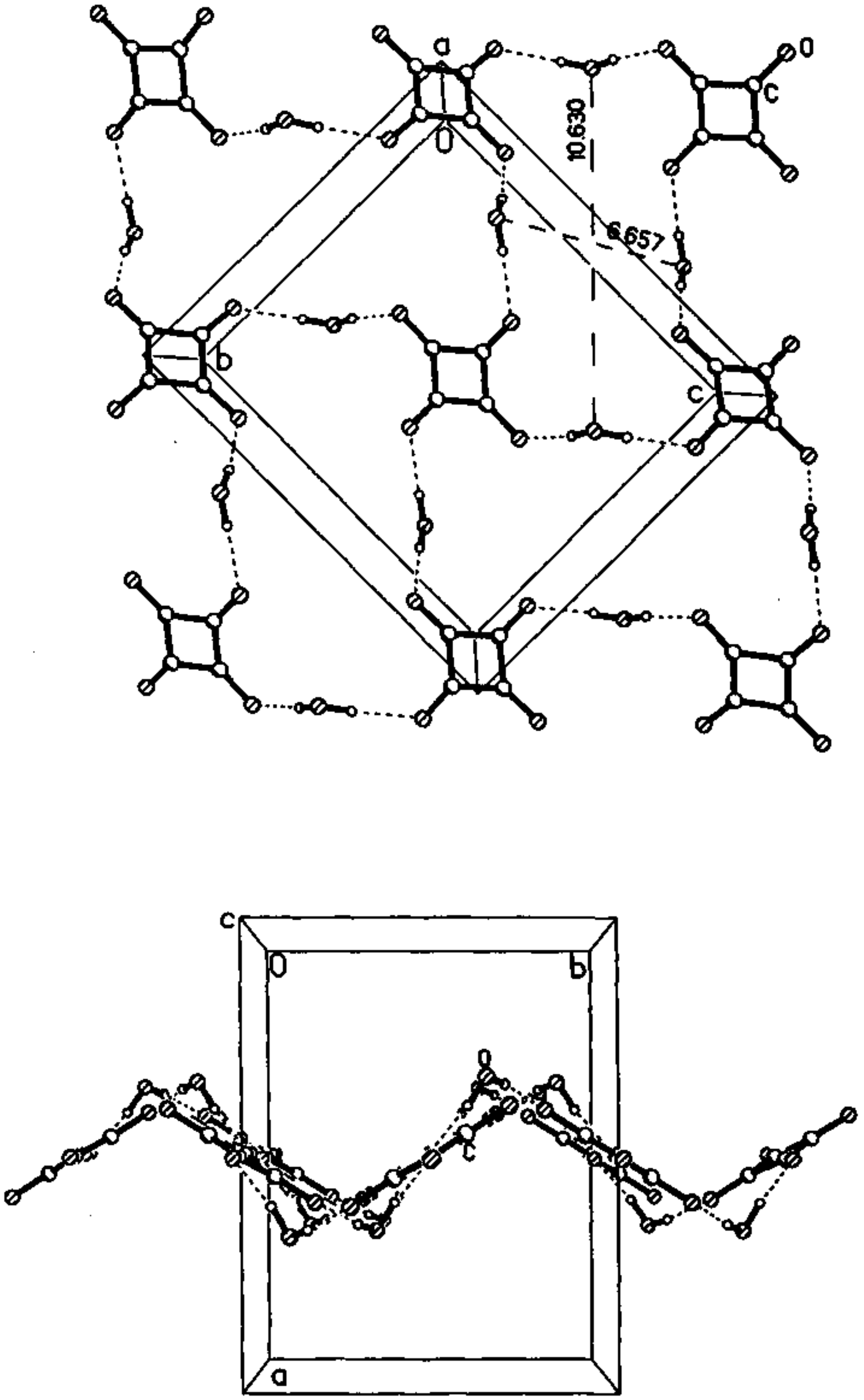

Fig. 4.23 Hydrogen bonded layers involving squarate units and H_2O. Note rectangular molecular boxes adopting a wave like pattern along ab plane

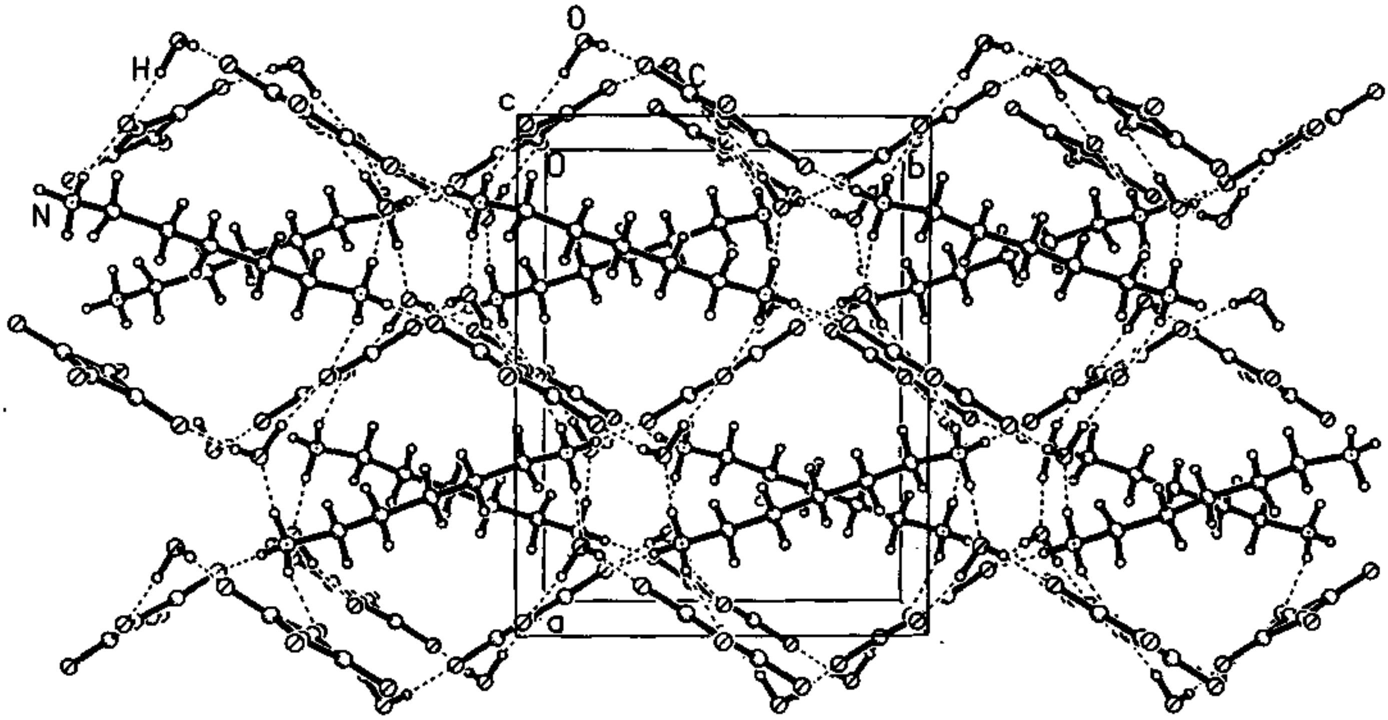

Fig. 4.24 Pentane diammonium cations accommodated in cavities formed by squarate water layers

Tetramethyl guanidinium squarate, $[(C_5N_3H_{14})(C_4O_4H)(C_4O_4H_2)]$, 3:

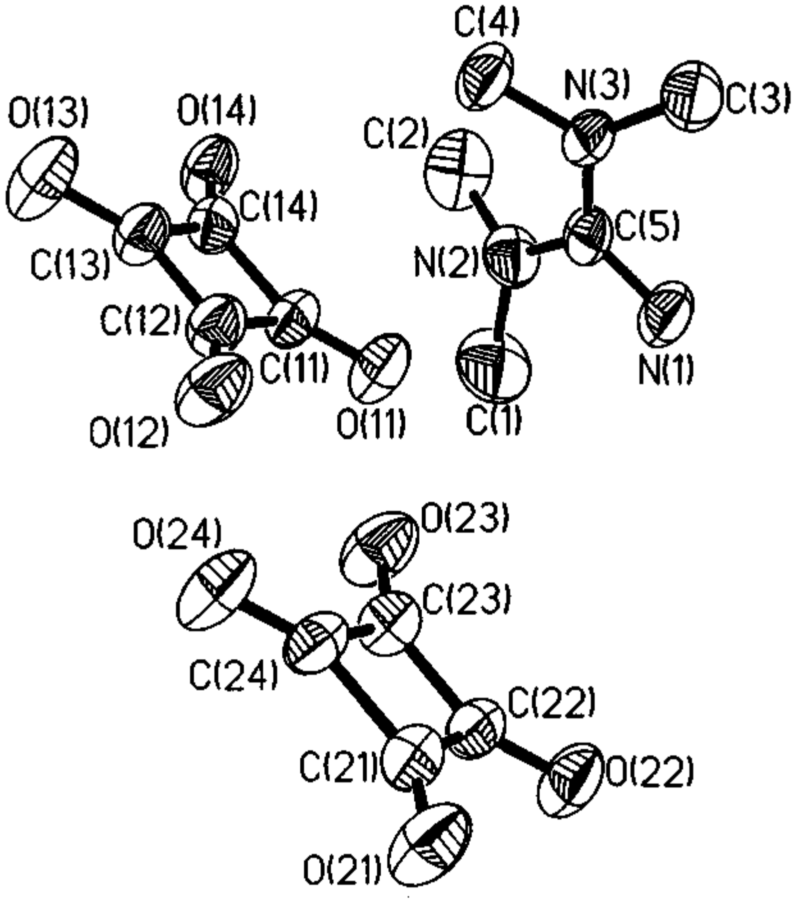

Fig. 4.25 Asymmetric unit of tetramethyl guanidinium squarate. The thermal ellipsoids are shown with 50% probability.

The asymmetric unit of **3** consists of a hydrogen squarate moiety, a free squaric acid molecule and one unit of tetramethyl guanidine (figure 4.25). The compound crystallizes in *P-1* space group. The cell parameters are provided in table 4.2. The atomic coordinates and isotropic displacement parameters are mentioned in table 4.25. The bond length and bond angles are given in table 4.26.

The amine is mono protonated as expected. The mono protonation of the amine shall result in positive charge in the central carbon atom, stabilized by the lone pairs of the nitrogen atoms surrounding it. The C – N bond length involving the central carbon atom are 1.32Å, 1.33Å and 1.34Å, varying only in the second decimal. One of the squarates is mono deprotonated and the other is a free squaric acid molecule. There is a strong O – H...O interaction (1.33Å, 1.57Å, and 1.62Å) between the squarate fragments. In addition to this, there is moderately strong C – H...O interaction (H...O 2.37Å, 2.44Å, 2.56Å) found between the methyl –CH donors of the guanidinium moiety and squarate oxygen acceptors. The relevant hydrogen bond distances and angles are given in table 4.27. Formation of self-complementary dimeric hydrogen bonded units similar to that in carboxylic acids is witnessed between the squarate fragments. These dimers extend as a chain along [001] direction through O – H...O bonding (figure 4.26). The adjacent such chain is arranged in such a way that the plane of the squarate of each chain is parallel to each other. These chains are arranged one on top of other with a centroid...centroid (with respect to the squarate ring) distance of 3.774 Å. There could be a weak pi-pi stacking interaction between the squarate moieties. These chains form hydrogen bonded channels when viewed down the [001] direction (figure 4.27).

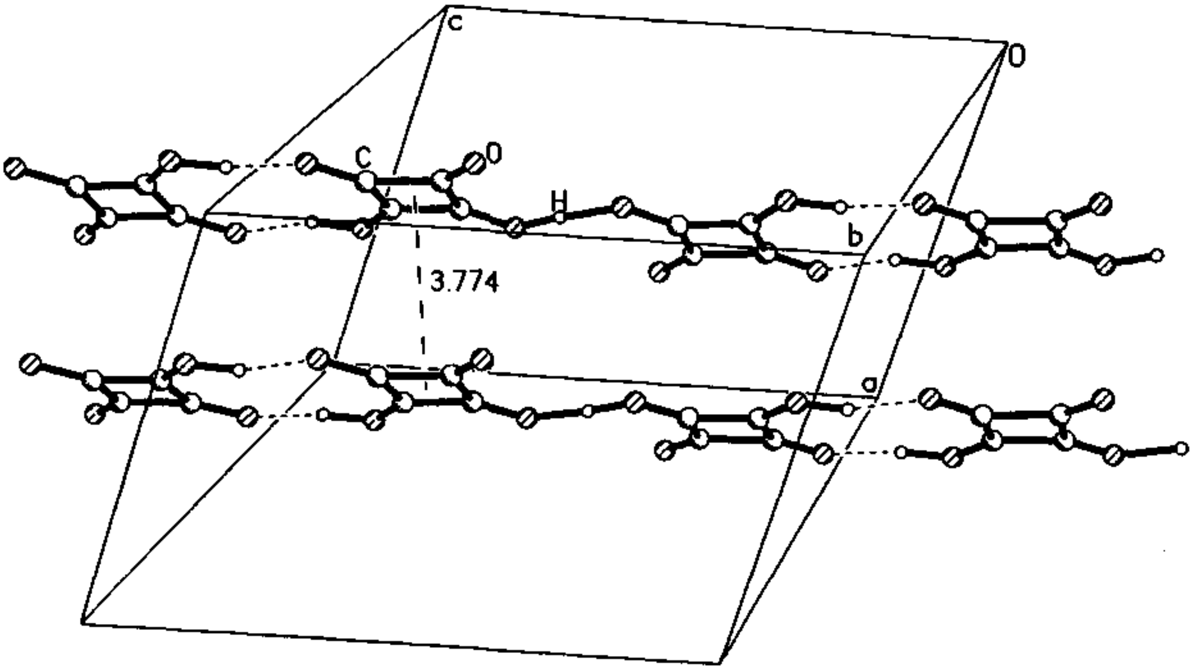

Fig 4.26 Parallelly arranged chain of squarate dimers with the centroid...centroid distance quoted

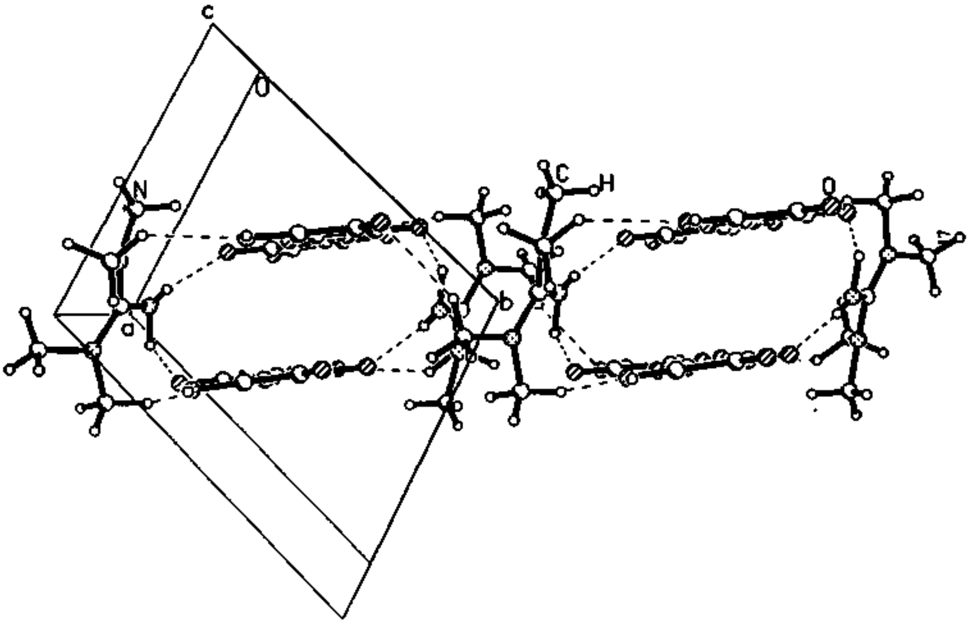

Fig. 4.27 Rectangular hydrogen bonded channels along [001] direction in tetramethyl guanidinium squarate

Dimethyl piperazine squarate, $[(C_6N_2H_{16})(HC_4O_4)_2]$, 4: The dimethyl piperazine squarate crystallizes in a monoclinic, *P2(1)/c* space group with one unit of hydrogen squarate and half an unit of diprotonated dimethyl piperazine squarate showing up in the asymmetric unit (figure 4.28). The relevant crystallographic details are given in tables 4.1, 4.28, and 4.29.

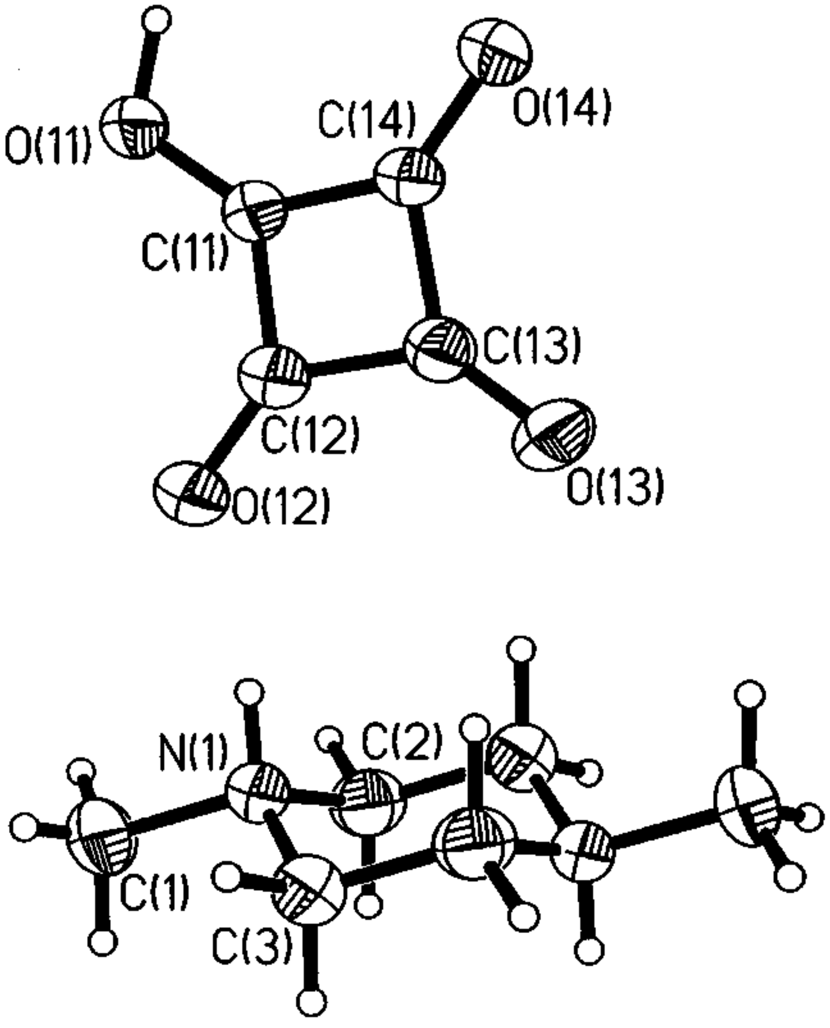

Fig 4.28 Asymmetric unit of dimethyl piperazine squarate. The thermal ellipsoids are shown with 50% probability

The squaric acid molecule is mono deprotonated and is involved in dimeric O – H...O bonding thereby forming isolated dimers, which are hydrogen bonded to the amine molecules. The hydrogen-bonding pattern is shown in figure 4.29.

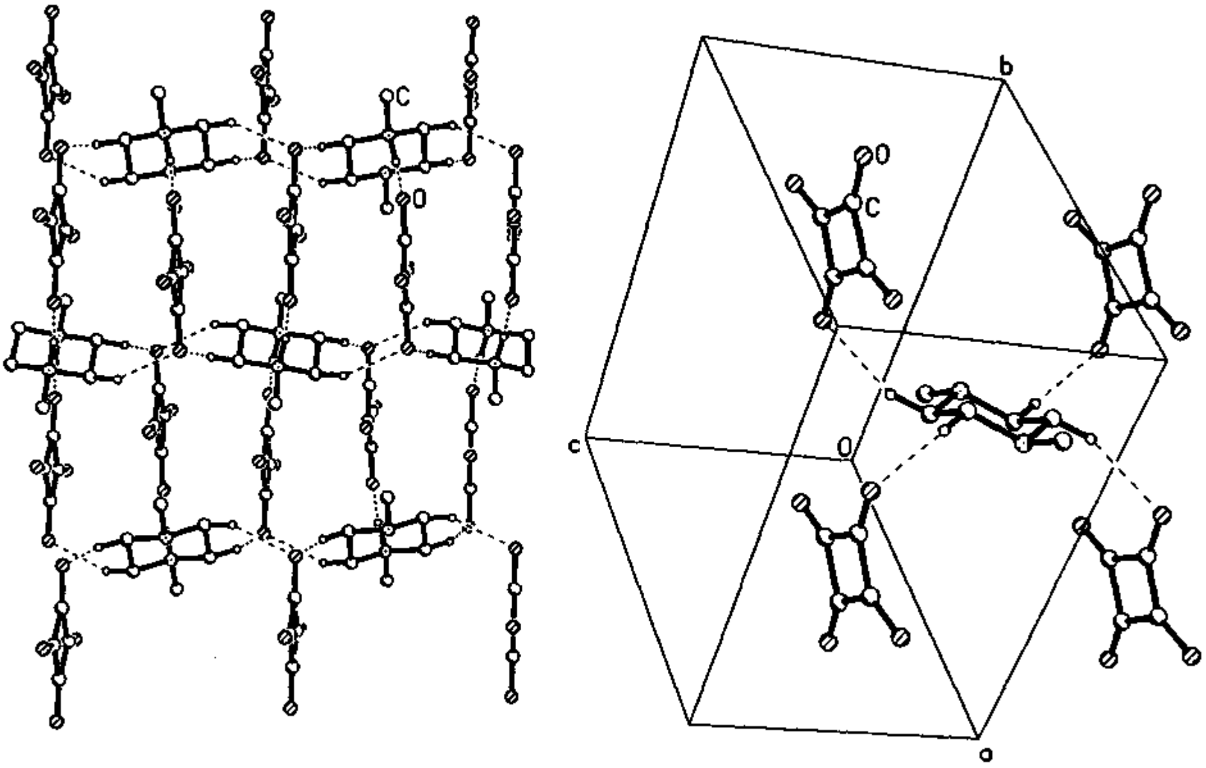

Fig. 4.29 Hydrogen bonding pattern in 1,4-dmpsq. Non participating hydrogens deleted for clarity

There is a formation of tapes containing the amine molecules and oxygen of the hydrogen squarate anions. These tapes are bridged by the same anions that are involved in tape formation also (figure 4.29). The dimethyl piperazine moiety has adopted a chair conformation as is commonly known. It is interesting to note the C – H...O (2.2-2.5Å) bonding involving the ring –

CH groups of the amine molecule. The information related to the hydrogen bonds found is given in table 4.30. Further, the adjacent C – H...O bonds are trans related to each other.

1,4-Diaza[2.2.2]bicylooctane diammonium squarate, $[(C_6N_2H_{14})(HC_4O_4)_2(H_2O)]$: The asymmetric unit of DABCO squarate (figure 4.30) consists of two hydrogen squarate anions, a diprotonated DABCO molecule with a water molecule of crystallization. The atomic coordinates of the atoms appearing in the asymmetric unit are provided in table 4.31. The relevant bond length and the angles are given in table 4.32. The unit cell details are presented in table 4.2.

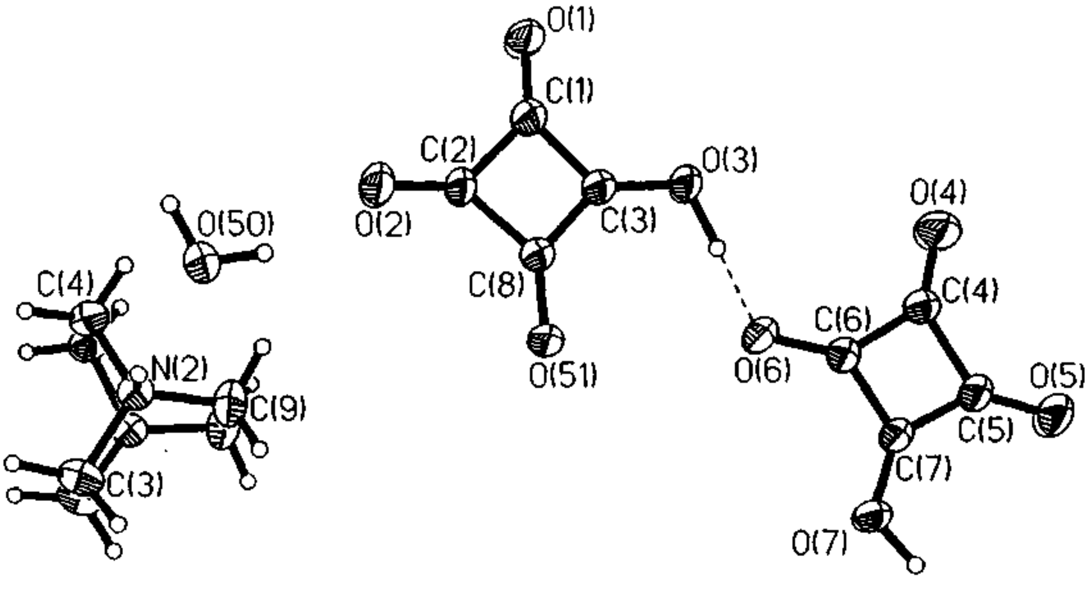

Fig. 4.30 Asymmetric unit of DABCO squarate. The thermal ellipsoids are shown with 50% probability.

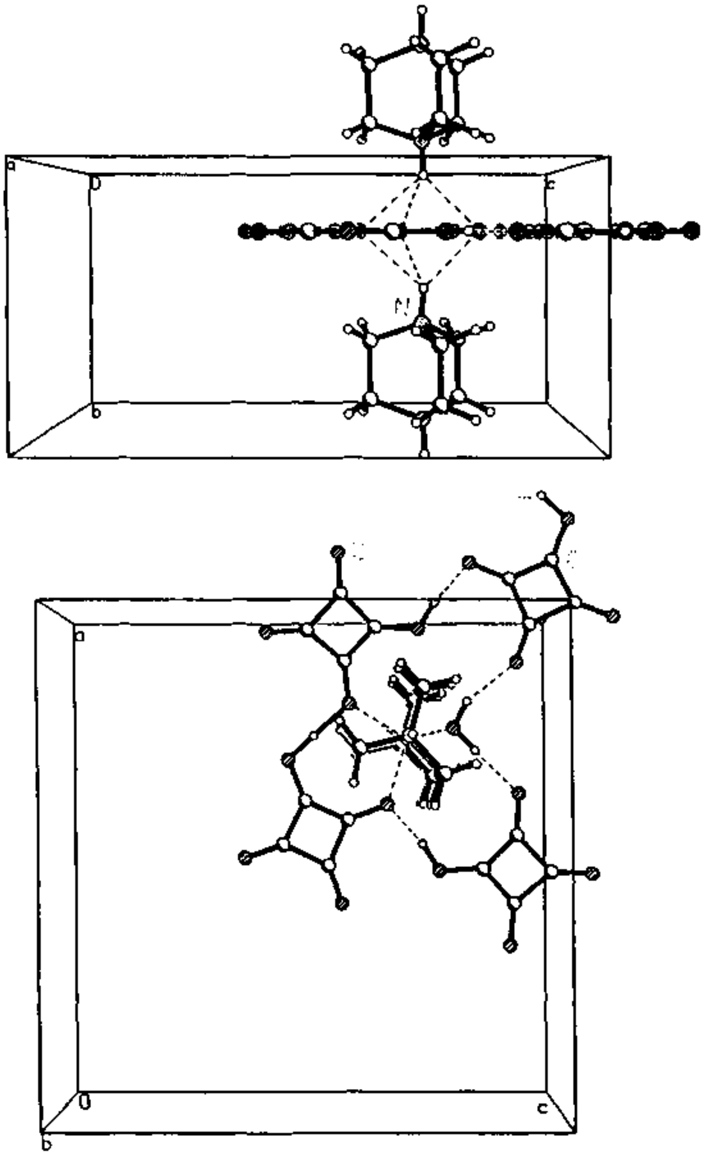

Fig. 4.31 Hydrogen bonding patterns observed in dabco squarate

The hydrogen squarate molecules form a very strong O – H...O bond (H...O 1.42Å) with themselves and with water molecule (H...O 1.57Å) as shown in figure 4.31. Three hydrogen squarate moieties along with a water molecule form five membered molecular rings, which extends one dimensionally. The structure reveal formation of irregular hydrogen bonded tetrahedrons with one of its vertex at the hydrogen of the protonated DABCO. This proton exhibits a trifurcated hydrogen-bonding pattern involving three weak N –

H...O bonds (H...O 2.8 - 3.07Å). The protonated dabco molecules thus bridge the layers through N – H...O interactions.

1,4 -butane diammonium squarate, [($C_4N_2H_{14}$)(C_4O_4)]: The asymmetric unit of butane 1,4-diammonium squarate (figure 4.33) consists of half a fragment of squarate and half of the protonated amine. There are however, no water molecules of crystallization as was found with both propane and the pentane analogues. The unit cell details, and other crystallographic data are included in tables 4.2, 4.34 and 4.35.

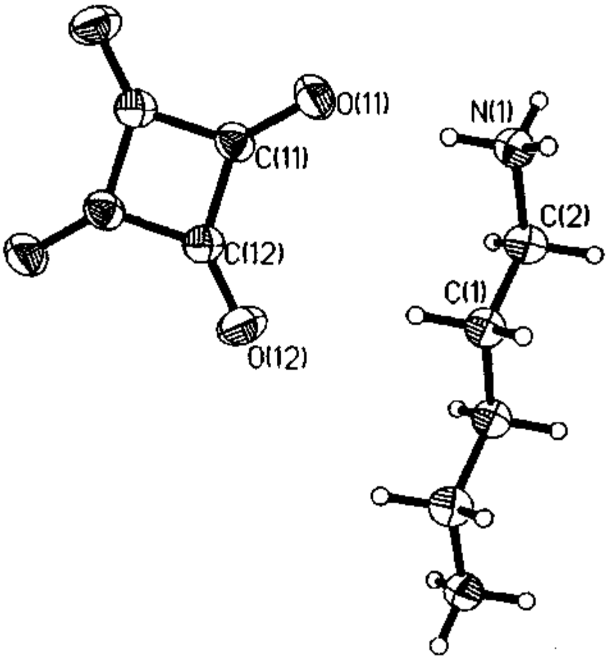

Fig. 4.33 Asymmetric unit of 1,4-butane diammonium squarate. The thermal ellipsoids are shown with 50% probability.

There are no channels or cavities observed. The structure is obtained of O – H...O, N – H...O and C – H...O hydrogen bonded squarate dianion and the diprotonated amines. Each squarate dianion participates in hydrogen bonding with four of the surrounding protonated amine molecules. The C (1) - H group of the amine participates in moderately strong C – H...O (2.44 Å) bonding with the oxygen of squarate. All the oxygens of the squarate exhibit a bifurcated hydrogen bonding pattern and form two hydrogen bonds each. The two diagonally opposite carbonyls of the squarate take part in hydrogen bond differently. One of them form only N – H...O (H...O 1.91-1.94 Å) bonds, while the other forms one N – H...O and one C – H...O bond, which results in formation of 9 membered, rings (figure 4.34). The details of hydrogen bond distances and angles are presented in table 4.36.

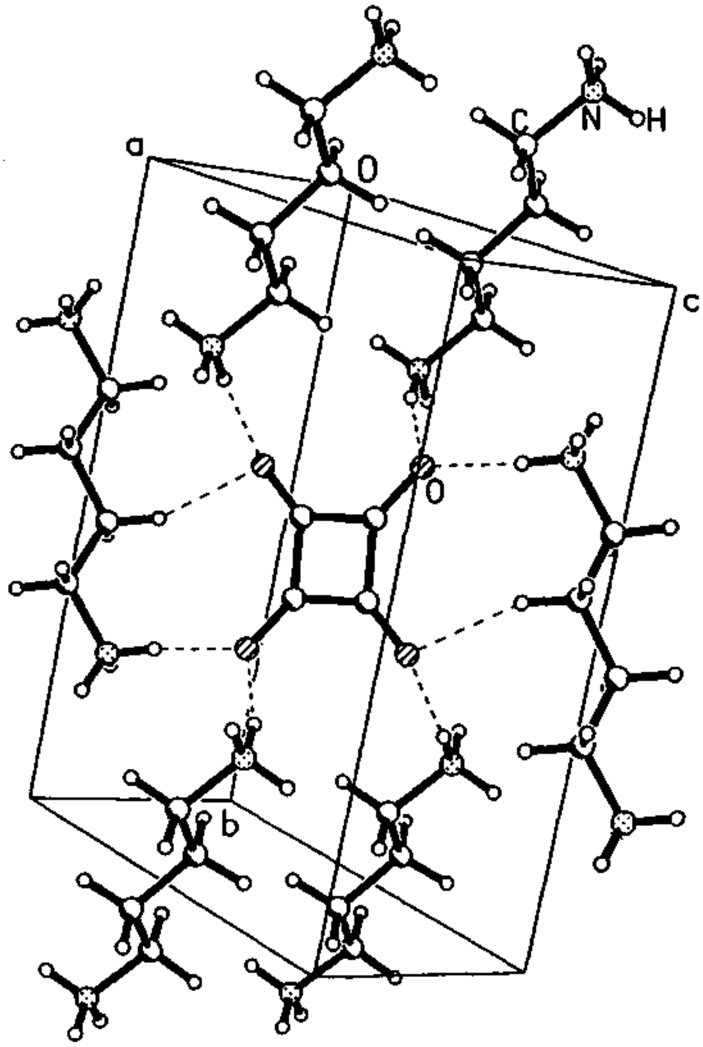

Fig. 4.34 N – H...O and C – H...O bonded butane diammonium squarate molecules.

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Table 4.3 Atomic coordinates and equivalent isotropic displacement parameters [Å^2] of Cobalt DABCO squarate, $[(C_6N_2H_{13})_2][Co_2(C_4O_4)_3(H_2O)_4]$, 1.

Atom	x	y	z	U(eq)
Co1	0.0423	0.89724	0.06829	0.0187
O11	0.26511	0.84427	0.03332	0.0261
O12	0.61742	0.76582	-0.01467	0.0265
O13	0.51735	0.92905	-0.16341	0.0302
O14	0.16995	1.03277	-0.11032	0.025
O21	-0.0161	0.68097	0.07929	0.0256
O22	-0.02126	0.33939	0.08813	0.0299
O50	0.1779	0.92227	0.16539	0.0295
O51	-0.08708	0.88724	-0.0363	0.0213
C11	0.33092	0.87159	-0.02127	0.0185
C12	0.49048	0.83312	-0.04366	0.0183
C13	0.44881	0.90838	-0.10991	0.0209
C14	0.28925	0.95303	-0.08573	0.0203
C21	-0.0074	0.58355	0.03522	0.0218
C22	-0.00986	0.4271	0.03948	0.0194
N1	0.57847	0.61832	0.11765	0.0477
N2	0.46989	0.51686	0.22329	0.0317
C1	0.41111	0.54817	0.09653	0.0656
C2	0.35079	0.49028	0.16049	0.0631
C3	0.55522	0.73732	0.16632	0.0417
C4	0.49341	0.67095	0.23103	0.0495
C5	0.7007	0.51311	0.15009	0.0823
C6	0.62927	0.4502	0.21349	0.0491

U (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 4.4 Bond lengths [Å] and angles [°] in, 1.

Moiety	Bond length	Moiety	Bond length
Co1 -O11	2.0465	N1 -C1	1.5089
Co1 -O21	2.0941	N1 -C3	1.4839
Co1 -O50	2.071	N1 -C5	1.4775
Co1 -O51	2.1652	N2 -C2	1.4766
C1 -C2	1.4824	N2 -C4	1.4599
C3 -C4	1.5306	N2 -C6	1.4562
O11 -C11	1.2606	C5 -C6	1.5306
O12 -C12	1.2717	C1 -H1B	1.0473
O13 -C13	1.2424	C2 -H2A	1.0499
O21 -C21	1.2555	C3 -H3A	1.0164
O22 -C22	1.2599	C3 -H3B	0.9409
C11 -C14	1.466	C4 -H4B	0.9636
C12 -C13	1.466	C5 -H5A	0.97
C13 -C14	1.475	C5 -H5B	0.97
C21 -C22	1.4668	C6 -H6A	0.9517
O50 -H5	0.9105	C6 -H6B	0.9762
O50 -H50A	0.7429	O51 -H51A	0.9963
O51 -H51B	0.7963		
Moiety	**Bond angle**	**Moiety**	**Bond angle**
O11 -Co1 -O21	90.82	O14 -C14 -C11	135.67
O11 -Co1 -O50	86.52	O14 -C14 -C13	134.21
O11 -Co1 -O51	91.37	C11 -C14 -C13	90.09
O21 -Co1 -O50	96.75	C1 -N1 -C5	110.6
O21 -Co1 -O51	87.95	O22 -C22 -C21	134.03
O50 -Co1 -O51	174.86	Co1 -O50 -H5	120.33
Co1 -O11 -C11	134.09	Co1 -O50 -H50 A	112.58
Co1 -O51 -H51 B	113.68	H5 -O50 -H50 A	107.34
H51A -O51 -H51 B	102.03	Co1 -O51 -H51 A	103.71
Co1 -O21 -C21	127.02	C1 -N1 -C3	108.91
O11 -C11 -C12	132.33	C3 -N1 -C5	110.95
O11 -C11 -C14	137.81	C2 -N2 -C4	108.32
C12 -C11 -C14	89.85	C2 -N2 -C6	108.41
O12 -C12 -C11	133.21	C4 -N2 -C6	109.35
O12 -C12 -C13	135.46	N1 -C1 -C2	107.5
C11 -C12 -C13	91.26	N2 -C2 -C1	112.4
O13 -C13 -C12	136.41	N1 -C3 -C4	106.9
O13 -C13 -C14	134.88	N2 -C4 -C3	111.56
C12 -C13 -C14	88.7	N1 -C5 -C6	107.68
O21 -C21 -C22	133.21		

Table4.5 Hydrogen bond distances (Å) and angles (°) in 1. (a)

D – H...A	D – H	D ...A	H...A	Angle D – H...A
N1 -- H1# ... O12	0.7544	2.2189	2.9557	165.65
O50 -- H5 ... N2	0.9105	1.8149	2.7244	176.66
O50 -- H50A ... O13	0.7429	2.0777	2.8198	176.91
O51 -- H51A ... O22	0.9963	1.5605	2.5424	167.54
O51 -- H51B ... O12	0.7963	1.9391	2.7076	161.98
C1 -- H1# ... O12	1.0949	2.3578	3.333	147.42
C1 -- H1B ... O11	1.0473	2.2088	3.196	156.37
C3 -- H3A ... O14	1.0164	2.5599	3.3516	134.49
C3 -- H3B ... O11	0.9409	2.5698	3.4127	149.28
C3 -- H3B ... O13	0.9409	2.5952	3.1757	120.31
C5 -- H5A ... O21	0.97	2.5608	3.2004	123.53
C5 -- H5B ... O22	0.97	2.4111	3.1129	128.88

(a) D- donor, A- acceptor

Table 4.6 Atomic coordinates and equivalent isotropic displacement parameters [Å^2] of cobalt imidazole squarate, $[Co(C_4O_4)(C_3N_2H_4)_2(H_2O)_2]$, 2.

Atom	x	y	z	U(eq)
Co1	0	½	½	0.0239
O11	-0.06483	0.47313	0.25966	0.0296
O12	0.09712	0.64292	0.10142	0.0304
O50	0.07064	0.65257	0.43108	0.0369
N1	0.25525	0.37721	0.2854	0.038
N2	0.11592	0.4077	0.39527	0.0299
C1	0.11568	0.30548	0.30569	0.0394
C2	0.19953	0.28498	0.23878	0.0452
C3	0.2014	0.44857	0.38084	0.0338
C11	-0.02858	0.4881	0.11836	0.0249
C12	0.04429	0.56391	0.04712	0.0241
H1	0.0554	0.26071	0.29164	0.032
H2	0.22538	0.21759	0.17126	0.0577
H3	0.2241	0.52537	0.42845	0.0406
H11	0.32401	0.39061	0.26501	0.0779
H50A	0.08403	0.66916	0.30907	0.1035
H50B	0.08349	0.72686	0.4957	0.0895

U (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 4.7 Bond lengths [Å] and angles [°] in 2.

Moiety	Bond length	Moiety	Bond length
Co1 -O11	2.1524	C1 -C2	1.3351
Co1 -O50	2.0891	C11 -C12	1.4706
Co1 -N2	2.1371	O50 -H50A	1.0100
O11 -C11	1.2528	O50 -H50B	1.0099
O12 -C12	1.2551	N1 -H11	1.0100
N1 -C2	1.3732	C1 -H1	1.0099
N1 -C3	1.3562	C2 -H2	1.0100
N2 -C1	1.3691	C3 -H3	1.0099
N2 -C3	1.3155		
Moiety	**Bond angle**	**Moiety**	**Bond angle**
O11 -Co1 -O50	95.37	N2 -C1 -C2	110.86
O11 -Co1 -N2	85.22	N1 -C2 -C1	106.26
O50 -Co1 -N2	86.13	N1 -C3 -N2	111.42
H50A -O50 -H50 B	107.43	O11 -C11 -C12	136.25
C2 -N1 -H11	129.76	O12 -C12 -C11	135.91
C3 -N1 -H11	123.64	Co1 -O50 -H50 A	120.14
N2 -C1 -H1	119.48	Co1 -O50 -H50 B	130.93
Co1 -O11 -C11	127.1	C2 -C1 -H1	129.5
C2 -N1 -C3	106.42	N1 -C2 -H2	121.08
Co1 -N2 -C1	128.53	C1 -C2 -H2	132.59
Co1 -N2 -C3	125.61	N1 -C3 -H3	123.39
C1 -N2 -C3	105.04	N2 -C3 -H3	125.11

Table 4.8 Hydrogen bond distances (Å) and angles (°) in 2 [(a)]

D – H...A	D – H	D ....A	H...A	Angle D – H...A
N1 -- H11 ... O11	1.01	1.8609	2.8236	158.17
O50 -- H50A ... O12	1.01	1.6938	2.6594	158.48
O50 -- H50B ... O12	1.0099	1.7213	2.7294	175.66

(a) D – Donor, A- Acceptor

Table 4.9 Atomic coordinates and equivalent isotropic displacement parameters [Å^2] of [$Zn(C_4O_4)(C_3H_4N_2)_2(H_2O)_2$], 3.

Atom	x	y	z	U (eq)
Zn1	0	0	½	0.0251
O11	-0.0675	0.02333	0.25762	0.0308
O12	0.09724	-0.14218	0.10154	0.0325
O50	0.07392	-0.15302	0.43272	0.0403
N1	0.25274	0.12264	0.28635	0.039
N2	0.11464	0.09165	0.39866	0.0284
C1	0.19771	0.21401	0.24086	0.0435
C2	0.1137	0.1942	0.31021	0.0386
C3	0.20045	0.05212	0.38045	0.0352
C11	-0.02994	0.00986	0.11679	0.0238
C12	0.04434	-0.06342	0.04678	0.0255
H1	0.22233	0.27303	0.17983	0.0636
H2	0.05811	0.23878	0.30458	0.0415
H3	0.22207	-0.02104	0.41755	0.0469
H11	0.30777	0.11011	0.26252	0.0423
H50A	0.08572	-0.21344	0.47946	0.0373
H50B	0.0891	-0.16378	0.32709	0.0703

U (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 4.10 Bond lengths [Å] and angles [°] in 3.

Moiety	Bond length	Moiety	Bond length
Zn1 -O11	2.1813	C1 -C2	1.3389
Zn1 -O50	2.1236	C11 -C12	1.4653
Zn1 -N2	2.1074	O50 -H50A	0.8081
O11 -C11	1.257	O50 -H50B	0.8812
O12 -C12	1.2586	N1 -H11	0.8197
N1 -C1	1.3624	C1 -H1	0.9079
N1 -C3	1.3351	C2 -H2	0.9452
N2 -C2	1.3777	C3 -H3	0.9455
N2 -C3	1.3128		
Moiety	Bond angle	Moiety	Bond angle
O11 -Zn1 -O50	95.49	N1 -C1 -C2	105.78
O11 -Zn1 -N2	86.44	N2 -C2 -C1	110.52
O50 -Zn1 -N2	86.24	N1 -C3 -N2	111.77
Zn1 -O11 -C11	126.44	O11 -C11 -C12	136.16
C1 -N1 -C3	107.46	N2 -C3 -H3	125.31
Zn1 -N2 -C2	128.33	O12 -C12 -C11	135.66
Zn1 -N2 -C3	126.19	Zn1 -O50 -H50 A	134.55
C2 -N2 -C3	104.47	Zn1 -O50 -H50 B	118.80
N1 -C1 -H1	120.03	H50A -O50 -H50 B	105.75
C2 -C1 -H1	134.11	C1 -N1 -H11	128.64
N2 -C2 -H2	119.94	C3 -N1 -H11	123.89
C1 -C2 -H2	129.54	N1 -C3 -H3	122.56

Table4.11 Hydrogen bond distances (Å) and angles (°) in 3.(a)

D – H...A	D – H	D ....A	H...A	Angle D – H...A
N1 -- H11 ... O11	0.8197	2.0456	2.8272	159.29
O50 -- H50A ... O12	0.8081	1.9365	2.7398	172.54
O50 -- H50B ... O12	0.8812	1.8254	2.6734	160.84

(a) D- donor, A- acceptor

Table 4.12 Atomic coordinates and equivalent isotropic displacement parameters [Å^2] of Cobalt dimethyl piperazine squarate, $[((CH_3)_2N_2C_4H_8)][Co(C_4O_4)_2(H_2O)_2]$, 4.

Atom	x	y	z	U (eq)
Co1	0.2815	0.24897	1.20733	0.0157
O1	0.39688	0.08875	0.89659	0.0832
O2	0.22209	0.13998	1.0412	0.0155
O11	0.16722	0.58209	1.01489	0.0315
O12	0.33986	0.63788	0.85335	0.0261
O13	0.38773	0.40966	0.86119	0.0224
O14	0.2218	0.3608	1.0443	0.0175
O21	0.16013	-0.07597	0.96914	0.0142
O22	0.33966	-0.13999	0.85959	0.0278
O50	0.1739	0.25042	1.34385	0.0259
O51	0.38872	0.25267	1.06992	0.0136
C1	0.33181	0.03542	0.95144	0.0263
C2	0.25454	0.06463	0.99121	0.0136
C11	0.23058	0.53678	0.98755	0.0198
C12	0.3056	0.56419	0.90612	0.0211
C13	0.3305	0.45869	0.91453	0.0249
C14	0.25318	0.44007	0.99299	0.0117
C21	0.22513	-0.03392	0.96775	0.0115
C22	0.30646	-0.06088	0.90716	0.0191
N1	0.05108	0.33271	1.07352	0.0202
N2	0.00979	0.16994	0.84185	0.0347
C31	0.03625	0.42818	1.14268	0.0401
C32	0.02791	0.07041	0.74069	0.0426
C33	0.06568	0.24577	0.78718	0.0147
C34	-0.00176	0.25738	1.13596	0.0395

U (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 4.13 Bond lengths [Å] and angles [°] in 4.

Moiety	Bond length	Moiety	Bond length
Co1 -O2	2.1355	C1 -C22	1.4288
Co1 -O14	2.1535	C2 -C21	1.4554
Co1 -O50	2.1195	C11 -C12	1.4747
Co1 -O51	2.1181	C11 -C14	1.391
O1 -C1	1.3947	C12 -C13	1.5187
O2 -C2	1.2441	C13 -C14	1.472
O11 -C11	1.2543	C21 -C22	1.5022
O12 -C12	1.2461	N1 -C31	1.4461
O13 -C13	1.2561	N1 -C34	1.4612
O14 -C14	1.2855	N1 -C35	1.5234
O21 -C21	1.2261	N2 -C32	1.6082
O22 -C22	1.2881	N2 -C33	1.4786
C1 -C2	1.3975	N2 -C36	1.5399
C34 -C36	1.556	C33 -C35	1.5195
Moeity	**Bond angle**	**Moeity**	**Bond angle**
O2 -Co1 -O14	91.01	C12 -C11 -C14	91.47
O2 -Co1 -O50	85.01	O12 -C12 -C11	139.43
O2 -Co1 -O51	96.2	O12 -C12 -C13	132.21
O14 -Co1 -O50	83.83	C11 -C12 -C13	88.34
O14 -Co1 -O51	94.62	O13 -C13 -C12	135.84
O50 -Co1 -O51	178.06	O13 -C13 -C14	137.14
Co1 -O2 -C2	124.98	C12 -C13 -C14	86.68
Co1 -O14 -C14	126.92	O14 -C14 -C11	135.8
O1 -C1 -C2	130.68	O14 -C14 -C13	130.7
O1 -C1 -C22	130.42	C11 -C14 -C13	93.5
C2 -C1 -C22	93.48	O21 -C21 -C2	136.98
O2 -C2 -C1	137	O21 -C21 -C22	134.07
O2 -C2 -C21	132.35	C2 -C21 -C22	88.19
C1 -C2 -C21	90.43	O22 -C22 -C1	137.11
O11 -C11 -C12	133.01	O22 -C22 -C21	134.97
O11 -C11 -C14	134.8	C1 -C22 -C21	87.38
C33 -N2 -C36	107.84	C31 -N1 -C34	114.73
N2 -C33 -C35	113.29	C31 -N1 -C35	105.53
N1 -C34 -C36	108.48	C34 -N1 -C35	115.23
C32 -N2 -C36	111.83	C32 -N2 -C33	109.72
N2 -C36 -C34	108.21	N1 -C35 -C33	108.06

Table 4.14 Atomic coordinates and equivalent isotropic displacement parameters [$Å^2$] of Cobalt imidazole squarate, $[(C_3H_5N_2)][Co_2(C_4O_4)_3(H_2O)_4]$, 5.

Atom	x	Y	z	U(eq)
Co1	0.66725	0.49415	0.14321	0.0182
O11	0.42141	-0.12229	0.17967	0.0297
O12	0.5485	0.26075	0.17659	0.0243
O13	0.08609	-0.1002	-0.10534	0.0322
O14	0.21062	0.27755	-0.11574	0.0247
O15	0.73017	0.54435	0.70724	0.0328
O16	0.70955	0.55133	0.36634	0.0277
O50	0.59331	0.42482	-0.08725	0.0215
O51	0.90495	0.40561	0.18063	0.0442
C11	0.35928	-0.01214	0.10373	0.0204
C12	0.41639	0.16314	0.0988	0.0164
C13	0.2089	-0.00303	-0.02548	0.0211
C14	0.26878	0.17187	-0.02745	0.0179
C15	0.60324	0.52033	0.59452	0.0235
C16	0.59367	0.52324	0.43596	0.0228
N1	0.75212	0.14483	0.4300	0.0408
N2	0.92838	0.13981	0.63905	0.043
C1	0.87926	0.23286	0.53079	0.0433
C2	0.71875	-0.00916	0.47383	0.0397
C3	0.8332	-0.01095	0.61012	0.0449
H50A	0.64242	0.46678	-0.14918	0.0355
H50B	0.58777	0.30318	-0.10766	0.0625
H51A	0.88091	0.32659	0.16164	0.0348
H51B	0.99536	0.44853	0.21284	0.0237
H1A	0.6965	0.18004	0.34631	0.0489
H1B	0.84315	-0.10018	0.67136	0.0539
H2A	0.63393	-0.09708	0.42109	0.0476
H2B	0.92697	0.34382	0.5261	0.052
H3A	1.01229	0.17149	0.71985	0.0516

U (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 4.15 Bond lengths [Å] and angles [°] in, 5.

Moiety	Bond length	Moiety	Bond length
Co1 -O12	2.0931	C15 -C16	1.4828
Co1 -O16	2.0843	O50 -H50A	0.833
Co1 -O50	2.1523	O50 -H50B	1.0149
Co1 -O51	2.0352	O51 -H51A	0.6635
O11 -C11	1.2504	O51 -H51B	0.7307
O12 -C12	1.2728	N1 -C1	1.3113
O13 -C13	1.2383	N1 -C2	1.3627
O14 -C14	1.275	N2 -C1	1.309
O15 -C15	1.2506	N2 -C3	1.347
O16 -C16	1.2423	C2 -C3	1.3742
C11 -C12	1.4654	N1 -H1A	0.88
C11 -C13	1.4786	N2 -H3A	0.88
C12 -C14	1.4476	C1 -H2B	0.95
C13 -C14	1.4629	C2 -H2A	0.95
C3 -H1B	0.95		

Moiety	Bond angle	Moiety	Bond angle
O12 -Co1 -O16	88.1	O14 -C14 -C12	138.23
O12 -Co1 -O50	87.73	O14 -C14 -C13	131.38
O12 -Co1 -O51	87.59	C12 -C14 -C13	90.26
O16 -Co1 -O50	173.63	O15 -C15 -C16	133.37
O16 -Co1 -O51	90.55	O16 -C16 -C15	132.95
O50 -Co1 -O51	94.07	Co1 -O50 -H50 A	125.68
H50A -O50 -H50 B	103.71	Co1 -O50 -H50 B	112.45
C1 -N2 -C3	110.87	Co1 -O51 -H51 A	103.68
Co1 -O12 -C12	132.26	H51A -O51 -H51 B	127.51
Co1 -O16 -C16	124.62	Co1 -O51 -H51 B	128.65
O11 -C11 -C12	134.57	C1 -N1 -C2	110.05
O11 -C11 -C13	136.29	N1 -C1 -N2	107.45
C12 -C11 -C13	88.96	N1 -C2 -C3	105.75
O12 -C12 -C11	132.08	N2 -C3 -C2	105.87
O12 -C12 -C14	136.95	C1 -N1 -H1A	124.97
C11 -C12 -C14	90.95	C2 -N1 -H1A	124.97
O13 -C13 -C11	136.53	C1 -N2 -H3A	124.56
O13 -C13 -C14	133.57	C3 -N2 -H3A	124.57
C11 -C13 -C14	89.83	N1 -C1 -H2B	126.27
N1 -C2 -H2A	127.13	N2 -C1 -H2B	126.27
C3 -C2 -H2A	127.12	N2 -C3 -H1B	127.06
C2 -C3 -H1B	127.07		

Table 4.16 Hydrogen bond distances (Å) and angles (°) in 5 (a)

D – H...A	D – H	D ...A	H...A	Angle D – H...A
N1 -- H1A ... O12	0.88	1.9221	2.7961	171.94
N2 -- H3A ... O14	0.88	1.9853	2.8562	170.06
O50 -- H50A ... O15	0.833	1.7613	2.5918	174.62
O50 -- H50B ... O11	1.0149	1.6164	2.6132	166.14
O51 -- H51A ... O13	0.6635	2.0052	2.6276	156.65
O51 -- H51B ... O15	0.7307	2.0727	2.7416	152.47
C3 -- H1B ... O13	0.95	2.4595	3.0861	123.39
C2 -- H2A ... O11	0.95	2.4486	3.1703	132.65

(a) D- donor, A- acceptor

Table 4.17 Atomic coordinates and equivalent isotropic displacement parameters [Å^2] of Zinc piperazine squarate, $[Zn(C_4O_3)_2(C_4N_2H_{14})(H_2O)_2]$, 6.

Atom	x	y	z	U(eq)
Zn1	½	0	0	0.0214
O1	0.33524	0.23093	0.28166	0.0456
O2	0.70702	0.1605	0.0633	0.0257
O4	0.62056	0.47659	0.32315	0.0253
O50	0.81613	-0.09717	0.06178	0.0316
N1	0.94098	0.41963	0.09287	0.0228
C1	0.5071	0.27585	0.23523	0.0254
C2	0.67135	0.24517	0.13489	0.0211
C3	0.77805	0.36017	0.15097	0.0187
C4	0.63382	0.38829	0.25286	0.0195
C5	1.02604	0.53561	0.13917	0.023
C6	1.03617	0.37804	-0.02618	0.0227
H5	0.78847	-0.15101	0.10848	0.0528
H5A	1.20045	0.53028	0.16229	0.018
H5B	0.95448	0.55684	0.21521	0.0086
H6A	1.21504	0.37027	0.00488	0.02
H6B	0.95985	0.30534	-0.05284	0.0137
H50B	0.89261	-0.10948	0.01865	0.011

Table 4.18 Bond lengths [Å] and angles [°] in, 6.

Moiety	Bond length	Moiety	Bond length
Zn1 -O2	2.2137	C2 -C3	1.4501
Zn1 -O50	2.0683	C3 -C4	1.4264
O1 -C1	1.225	C1 -C4	1.4696
O2 -C2	1.2509	O50 -H5	0.8097
O4 -C4	1.2529	O50 -H50B	0.6633
N1 -C3	1.3287	C5 -H5A	0.9434
N1 -C5	1.4716	C5 -H5B	0.9468
N1 -C6	1.4641	C6 -H6A	0.9792
C1 -C2	1.4953	C6 -H6B	0.9578
Moiety	**Bond angle**	**Moiety**	**Bond angle**
O2 -Zn1 -O50	90.36	O2 -C2 -C3	133.44
Zn1 -O50 -H5	111.91	C1 -C2 -C3	88.69
Zn1 -O50 -H50B	119.65	N1 -C3 -C2	135.06
H5 -O50 -H50B	114.27	N1 -C3 -C4	132.93
N1 -C5 -H5A	105.9	C2 -C3 -C4	91.99
N1 -C5 -H5B	110.27	O4 -C4 -C1	136.3
Zn1 -O2 -C2	134.94	O4 -C4 -C3	133.04
H5A -C5 -H5B	109.86	C1 -C4 -C3	90.62
C3 -N1 -C5	121.96	N1 -C6 -H6A	103.1
C3 -N1 -C6	122.62	N1 -C6 -H6B	109.08
C5 -N1 -C6	115.31	H6A -C6 -H6B	112.07
O1 -C1 -C2	137.01	C2 -C1 -C4	88.51
O1 -C1 -C4	134.44	O2 -C2 -C1	137.86

Table 4.19 Atomic coordinates and equivalent isotropic displacement parameters [Å^2] of 1,3- propane diammonium squarate, [($C_3N_2H_{12}$)(C_4O_4)(H2O)], **1**.

Atom	x	y	z	(Ueq)]
N1	0.34361	0.156	0.95158	0.0297
C11	1/2	0	0.96472	0.0312
C12	0.42199	0.07806	0.76769	0.0324
O1	0.20264	-0.01208	0.24953	0.0459
C1	0.09178	-0.00549	0.24819	0.0343
O2	0.01247	0.20252	0.24918	0.0466
C2	0.0054	0.09168	0.24906	0.0342
O50	0.21694	0.28358	0.52086	0.0549
H1	0.37312	0.20571	1.06071	0.0703
H2	0.30007	0.20003	0.81677	0.0244
H3	0.29465	0.10526	1.0618	0.0465
H11	0.55755	0.05825	1.07977	0.0414
H12A	0.37159	0.02924	0.6345	0.059
H12B	0.48059	0.13338	0.63264	0.0569
H50A	0.14729	0.26633	0.44944	0.1032
H50B	0.26784	0.34481	0.43295	0.0976

U (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 4.20 Bond lengths [Å] and angles [°] in, **1**

Moiety	Bond length	Moiety	Bond length
N1 -C12	1.4855	C12 -H12B	1.0854
C11 -C12	1.5162	O1 -C1	1.2509
N1 -H1	0.8095	O2 -C2	1.251
N1 -H2	0.9161	C1 -C2	1.4645
N1 -H3	0.9309	O50 -H50A	0.8673
C11 -H11	1.0525	O50 -H50B	0.9769
C12 -H12A	0.9844		
Moiety	**Bond angle**	**Moiety**	**Bond angle**
N1 -C12 -C11	112.02	N1 -C12 –H12B	108.73
C12 -N1 -H1	119.26	N1 -C12 – H12A	108.21
C12 -N1 -H2	106.53	C11 -C12 –H12A	110.59
C12 -N1 -H3	105.89	C11 -C12 –H12B	107.12
H1 -N1 -H2	103.33	H12A -C12 –H12B	110.16
H1 --N1 -H3	110.98	O1 -C1 –C2	135.04
H2 -N1 -H3	110.7	O2 -C2 –C1	134.71
C12 - C11 -H11	105.74		

Table4.21 Hydrogen bond distances (Å) and angles (°) in **1**.[(a)]

D – H...A	D – H	D ...A	H...A	Angle D – H...A
N1 -- H1 ... O2	0.8095	2.0547	2.8066	154.39
N1 -- H2 ... O50	0.9161	1.8608	2.7753	175.93
N1 -- H3 ... O1	0.9309	1.8722	2.7981	172.67
O50 -- H50A ... O2	0.8673	1.8977	2.7516	167.79
O50 -- H50B ... O1	0.9769	1.8336	2.7473	154.40
C12 -- H12A ... O1	0.9844	2.5914	3.5140	156.07
C12 -- H12B ... O2	1.0854	2.5299	3.5166	150.68

(a) D , donor ; H , acceptor

Table 4.22 Atomic coordinates and equivalent isotropic displacement parameters [Å^2] of, 1,5- pentane diammonium squarate, [($C_5N_2H_{16}$)(C_4O_4)(H_2O)], **2**.

Atom	x	y	z	U(eq)
N1	0.15707	-0.10329	0.15816	0.0419
C1	0.21596	0.13146	0.15352	0.0529
C2	0.18141	0.01324	0.08041	0.0491
C3	1/4	1/4	0.07819	0.0543
O11	0.00518	0.49528	0.20326	0.0587
O12	0.09699	0.69377	-0.00209	0.0539
C11	0.0024	0.49854	0.09141	0.0399
C12	0.0433	0.58777	-0.00064	0.0385
O50	0.16169	0.64567	0.30406	0.0565
H1A	0.16113	0.15819	0.21211	0.0789
H1B	0.27058	0.10404	0.21149	0.0842
H2A	0.11542	0.03395	0.03706	0.0564
H2B	0.23328	-0.0142	0.02161	0.0613
H3A	0.1987	0.27474	0.02202	0.0694
H11	0.22147	-0.12784	0.20711	0.0748
H12	0.10204	-0.08341	0.20734	0.0671
H13	0.13933	-0.17545	0.11178	0.0463
H50A	0.10749	0.60514	0.27983	0.0736
H50B	0.14433	0.68909	0.36412	0.0936

U (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 4.23 Bond lengths [Å] and angles [°] in **2**.

Moiety	Bond length	Moiety	Bond length
N1 -C2	1.4862	C2 -H2B	0.9673
C1 -C2	1.5018	C3 -H3A	0.935
C1 -C3	1.5162	O11 -C11	1.2552
N1 -H11	1.0088	O12 -C12	1.2559
N1 -H12	0.9071	C11 -C12	1.4576
N1 -H13	0.9164	O50 -H50A	0.8382
C1 -H1A	0.9893	C2 -H2A	0.9840
C1 -H1B	0.9847	O50 -H50B	0.8303
Moiety	Bond angle	Moiety	Bond angle
C2 -C1 -C3	113.05	C1 -C2 -H2A	110.4
N1 -C2 -C1	110.8	C1 -C2 -H2B	113.56
C2 -N1 -H11	110.13	C1 -C3 -H3A	112.76
C2 -N1 -H13	109.46	H2A -C2 -H2B	106.97
H11 -N1 -H12	109.58	C2 -N1 -H12	110.03
H11 -N1 -H13	108.25	O11 -C11 -C12	135.54
H12 -N1 -H13	109.36	O12 -C12 -C11	135.6
C2 -C1 -H1A	111.9	H1A -C1 -H1B	97.07
C2 -C1 -H1B	110.1	H50A -O50 -H50B	107.54
C3 -C1 -H1A	110.87	N1 -C2 -H2A	106.3
C3 -C1 -H1B	112.83	N1 -C2 -H2B	108.48

Table4.24 Hydrogen bond distances (Å) and angles (°) in **2.** (a)

D – H…A	D – H	D …A	H…A	Angle D – H…A
N1 -- H11 ... O50	1.0088	1.8368	2.838	171.18
N1 -- H12 ... O11	0.9071	1.8553	2.7478	167.45
N1 -- H13 ... O12	0.9164	1.9028	2.8124	171.49
O50 -- H50A ...O11	0.8382	1.8968	2.7222	167.98
O50 -- H50B ... O12	0.8303	1.9937	2.8214	174.6

D - donor; B – acceptor

Table 4.25 Atomic coordinates and equivalent isotropic displacement parameters [Å^2] of, Tetramethyl guanidinium squarate, [$(C_4O_4H)(C_4O_4H_2)(C_5N_3H_{14})$], 3.

Atom	x	y	z	U(eq)
N1	0.16014	0.86447	0.43890	0.0693
N2	0.22467	0.96088	0.22716	0.0548
N3	-0.05451	0.92416	0.31323	0.0467
C1	0.38132	0.98985	0.24278	0.0869
C2	0.22332	0.95475	0.10175	0.0705
C3	-0.16002	0.83954	0.41219	0.0686
C4	-0.16074	1.04132	0.21953	0.0564
C5	0.11068	0.91477	0.32641	0.0457
O11	0.99227	0.27949	0.30687	0.0625
O12	0.66083	0.58566	0.33572	0.0628
O13	0.58727	0.65783	0.06609	0.0672
O14	0.91889	0.35996	0.0222	0.0531
C11	0.88609	0.37984	0.24072	0.0449
C12	0.7387	0.51748	0.25101	0.0457
C13	0.70752	0.54862	0.13032	0.0456
C14	0.85047	0.41707	0.11025	0.0413
O21	0.45306	0.33086	0.14652	0.0597
O22	0.10972	0.61755	0.20023	0.0572
O23	0.19954	0.53448	0.47291	0.0638
O24	0.53591	0.24389	0.42689	0.0600
C21	0.38279	0.38398	0.23634	0.0426
C22	0.23483	0.50881	0.26244	0.0424
C23	0.27222	0.47578	0.3837	0.0423
C24	0.42523	0.34317	0.36439	0.0456

U (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 4.26 Bond lengths [Å] and angles [°] in **3**.

Moiety	Bond length	Moiety	Bond length
N1 -C5	1.3256	O11 -C11	1.2187
N2 -C1	1.4503	O12 -C12	1.2867
N2 -C2	1.4726	O13 -C13	1.303
N2 -C5	1.344	O14 -C14	1.2465
N3 -C3	1.4684	C11 -C12	1.4693
N3 -C4	1.4594	C11 -C14	1.4963
N3 -C5	1.33	C12 -C13	1.3849
N1 -H1	0.7134	C13 -C14	1.4398
Moiety	**Bond angle**	**Moiety**	**Bond angle**
C1 -N2 -C2	115.29	N3 -C4 -H4A	110.23
C1 -N2 -C5	120.58	O11 -C11 -C12	137.14
C2 -N2 -C5	122.89	O11 -C11 -C14	135.5
C3 -N3 -C4	114.31	C12 -C11 -C14	87.35
C3 -N3 -C5	120.52	O12 -C12 -C11	136.41
C4 -N3 -C5	123.44	O12 -C12 -C13	132.11
N1 -C5 -N2	120	C11 -C12 -C13	91.46
N1 -C5 -N3	119.53	O13 -C13 -C12	130.85
N2 -C5 -N3	120.43	O13 -C13 -C14	136.21
C5 -N1 -H1	122.41	C12 -C13 -C14	92.93
N2 -C2 -H2B	109	O14 -C14 -C11	135.46
N2 -C2 -H2C	104.59	O14 -C14 -C13	136.26
N2 -C2 -H3A	109.54	C11 -C14 -C13	88.25
H2B -C2 -H2C	112.75	C12 -O12 -H23	113.56
H2B -C2 -H3A	107.82	C13 -O13 -H21	112.81
H2C -C2 -H3A	113.04	O21 -C21 -C22	137.28
C22 -C23 -C24	89.84	O21 -C21 -C24	134.04
O24 -C24 -C21	136.1	C22 -C21 -C24	88.66
O24 -C24 -C23	135.66	O22 -C22 -C21	135.39
O23 -C23 -C22	134.4	O22 -C22 -C23	131.37
O23 -C23 -C24	135.72	C21 -C22 -C23	93.23
C21 -C24 -C23	88.24	C22 -O22 -H14	114.96

Table4.27 Hydrogen bond distances (Å) and angles (°) in **3**.(a)

D – H...A	D – H	D ...A	H...A	Angle D – H...A
N1 -- H1 ... O24	0.7134	2.2214	2.8652	150.78
O22 -- H14 ... O14	0.994	1.5797	2.5597	167.68
O13 -- H21 ... O21	0.9145	1.6221	2.5121	163.40
O12 -- H23 ... O23	1.1182	1.3351	2.4469	171.65
C3 -- H1# ... O23	1.0418	2.3747	3.3436	154.21
C2 -- H2C ... O13	1.0506	2.4469	3.3729	146.47
C4 -- H3# ... O14	0.948	2.5681	3.4423	153.44
C4 -- H3#.... N2	0.948	2.5718	2.8927	100.09

(a) D – Donor, A- Acceptor

Table 4.28 Atomic coordinates and equivalent isotropic displacement parameters [Å^2] of, Dimethyl piperazine squarate, $[(C_6N_2H_{16})(HC_4O_4)_2]$, **4**.

Atom	X	y	z	U $_{eq}$
N1	0.85225	0.04077	0.51267	0.0401
C1	0.74297	0.12904	0.5372	0.0675
C2	0.97168	0.02818	0.68581	0.0453
C3	0.92031	0.06186	0.34272	0.0439
O11	0.56255	0.17189	-0.01685	0.0571
O12	0.3467	0.37423	0.02358	0.0539
O13	0.08277	0.20973	0.08708	0.0579
O14	0.30084	0.00513	0.04956	0.0488
C11	0.42454	0.18071	0.01398	0.038
C12	0.33302	0.27341	0.03196	0.0397
C13	0.21164	0.19855	0.06189	0.0376
C14	0.31412	0.10705	0.04321	0.037
H1	0.82684	0.06425	0.21961	0.0722
H1A	0.68855	0.11122	0.65538	0.1097
H1B	0.78468	0.18927	0.54742	0.0732
H1C	0.64252	0.13429	0.4206	0.1548
H2A	0.92317	0.01582	0.81198	0.0669
H2B	1.02992	0.0979	0.70214	0.0502
H3B	0.97851	0.13072	0.35671	0.056
H11	0.78259	-0.02337	0.49494	0.1127

U (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 4.29 Bond lengths [Å] and angles [°] in **4**.

Moiety	Bond length	Moiety	Bond length
N1 -C	1.5037	C3 -H1	1.1017
N1 -C2	1.4916	C3 -H3B	0.9943
N1 -C3	1.4836	O11 -C11	1.3159
N1 -H11	1.0049	O12 -C12	1.2506
C -H1A	1.0769	O13 -C13	1.2237
C -H1B	0.8298	O14 -C14	1.2628
C -H1C	1.1153	C11 -C12	1.4317
C2 -H2A	1.0847	C11 -C14	1.3961
C2 -H2B	1.0037	C12 -C13	1.4823
C13 -C14	1.483		

Moiety	Bond angle	Moiety	Bond angle
C -N1 -C2	111.8	N1 -C3 -H1	106.31
C -N1 -C3	110.68	N1 -C3 -H3B	111.21
C2 -N1 -C3	110.29	H1 -C3 -H3B	111.87
C -N1 -H11	99.8	C11 -C14 -C13	89.95
C2 -N1 -H11	111.41	O11 -C11 -C12	131.83
C3 -N1 -H11	112.52	O11 -C11 -C14	134.7
N1 -C -H1A	110.66	C12 -C11 -C14	93.46
N1 -C -H1B	110.9	O12 -C12 -C11	136.32
N1 -C -H1C	114.82	O12 -C12 -C13	135.05
H1A -C -H1B	112.45	C11 -C12 -C13	88.62
H1A -C -H1C	99.55	O13 -C13 -C12	135.03
H1B -C -H1C	108.02	O13 -C13 -C14	136.99
N1 -C2 -H2A	110.97	C12 -C13 -C14	87.96
N1 -C2 -H2B	107	O14 -C14 -C11	136.67
H2A -C2 -H2B	108.08	O14 -C14 -C13	133.37

Table 4.30 Hydrogen bond distances (Å) and angles (°) in **4**.(a)

D – H…A	D – H	D …A	H…A	Angle D – H…A
N1 -- H11 ... O12	1.0049	1.7108	2.7128	174.56
C3 -- H1 ... O14	1.1017	2.2207	3.2321	151.53
C -- H1A ... O14	1.0769	2.5345	3.4685	144.55
C2 -- H2A O14	1.0847	2.4346	3.4059	148.36
C2 -- H2B ... O13	1.0037	2.582	3.493	150.86
C3 -- H3B ... O13	0.9943	2.4957	3.1349	121.74

(a) D- donor, A- acceptor

Table 4.31 Atomic coordinates and equivalent isotropic displacement parameters [Å^2] of, 1,4-Diaza[2.2.2]bicylooctane diammonium squarate, [$(C_6N_2H_{14})(HC_4O_4)_2.H_2O$], **5**.

Atom	x	y	z	U (eq)
N2	0.25423	0.07746	0.30114	0.0279
C9	0.16039	0.14508	0.27369	0.0396
O1	0.49555	3/4	0.63292	0.0567
O2	0.59141	3/4	0.43272	0.0627
O3	0.29408	3/4	0.54198	0.0403
O51	0.38541	3/4	0.3371	0.0318
C1	0.46732	3/4	0.5537	0.0362
C2	0.51172	3/4	0.45982	0.0355
C8	0.41807	3/4	0.41889	0.0267
O4	0.02793	3/4	0.58492	0.0577
O5	-0.13716	3/4	0.43458	0.0601
O6	0.17866	3/4	0.41463	0.036
O7	0.02166	3/4	0.27006	0.0463
C5	-0.05173	3/4	0.43046	0.035
C6	0.09077	3/4	0.42361	0.0269
C7	0.01795	3/4	0.3598	0.0291
O50	0.22851	3/4	0.1999	0.0326
H4	0.2268	0.09831	0.43487	0.0541
H5	0.25462	-0.04781	0.29858	0.0499
H6	0.14728	0.09222	0.21194	0.0597
H7	0.3445	0.0882	0.40839	0.0655
H8	0.30895	0.09365	0.17549	0.0487
H9	0.1162	0.0916	0.31657	0.069
H10	0.38585	0.08671	0.25483	0.0411
H1	0.24449	3/4	0.48799	0.1217
H3	-0.03344	3/4	0.23569	0.0911
H2	0.27581	3/4	0.1546	0.0841
H11	0.1746	3/4	0.17057	0.0822

U (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 4.32 Bond lengths [Å] and angles [°] in **5**.

Moiety	Bond length	Moiety	Bond length
O3 -H1	1.0618	C1 -C2	1.5067
N2 -C9	1.4943	C2 -C8	1.4768
N2 -H5	0.9063	O5 -C5	1.2346
O7 -C7	1.3045	O6 -C6	1.2754
C9 -H6	0.9931	C5 -C7	1.437
C9 -H9	0.9717	C6 -C7	1.4014
O1 -C1	1.2207	O7 -H3	0.9391
O2 -C2	1.2158	O50 -H2	0.9482
O51 -C8	1.2781	O50 -H11	0.8872
Moiety	**Bond angle**	**Moiety**	**Bond angle**
O2 -C2 -C8	137.37	O2 -C2 -C1	134.06
C1 -C2 -C8	88.56	O51 -C8 -C2	135.38
C9 -N2 -H5	108.75	O5 -C5 -C7	137.2
O6 -C6 -C7	132.73	C5 -C7 -C6	93.02
N2 -C9 -H6	106.73	C7 -O7 -H3	119.76
O1 -C1 -C2	135.32	H2 -O50 -H11	107.36
N2 -C9 -H9	107.1	O7 -C7 -C5	137.93
H6 -C9 -H9	107.5	O7 -C7 -C6	129.05

Table 4.33 Hydrogen bond distances (Å) and angles (°) in **5**.[a]

D – H...A	D – H	D ...A	H...A	Angle D – H...A
O3 -- H1 ... O6	1.0618	1.4277	2.4894	179.34
O3 -- H1 ... O6	1.0618	1.4277	2.4894	179.34
O50 -- H2 ... O5	0.9482	1.8045	2.7523	178.06
O50 -- H2 ... O5	0.9482	1.8045	2.7523	178.06
O7 -- H3 ... O51	0.9391	1.578	2.5081	170.05
O7 -- H3 ... O51	0.9391	1.578	2.5081	170.05
N2 -- H5 ... O6	0.9063	2.4858	3.0838	123.84
N2 -- H5 ... O50	0.9063	2.0814	2.8111	136.78
N2 -- H5 ... O51	0.9063	2.4522	3.0759	126.22
N2 -- H5 ... O6	0.9063	2.4858	3.0838	123.84
N2 -- H5 ... O50	0.9063	2.0814	2.8111	136.78
N2 -- H5 ... O51	0.9063	2.4522	3.0759	126.22
O50 -- H11 ... O2	0.8872	1.9217	2.7617	157.37
O50 -- H11 ... O2	0.8872	1.9217	2.7617	157.37
C2# -- H4 ... O5	0.9938	2.544	3.289	131.61
C2# -- H4 ... O5	0.9938	2.544	3.289	131.61

Table 4.34 Atomic coordinates and equivalent isotropic displacement parameters [Å^2] of 1,4- butane diammonium squarate, $[(C_4N_2H_{14})(C_4O_4)]$, **6.**

Atom	X	Y	Z	U (eq)
N1	0.02063	0.22996	0.34031	0.0354
C1	0.08238	0.05029	0.47176	0.0309
C2	-0.1401	0.13536	0.40483	0.0347
O11	0.31131	0.16092	0.09009	0.0478
O12	0.39356	-0.0967	0.20661	0.0451
C11	0.41372	0.07116	0.04196	0.0311
C12	0.45084	-0.04298	0.09371	0.0299
H1	-0.11859	0.27987	0.30076	0.0531
H2	0.1445	0.26353	0.41237	0.0531
H3	0.13438	0.20438	0.26828	0.0531
H4	-0.26639	0.16348	0.48201	0.0417
H5	-0.27748	0.09975	0.32667	0.0417
H6	0.2183	0.02606	0.3964	0.0371
H7	0.21019	0.08453	0.55461	0.0371

U (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 4.35 Bond lengths [Å] and angles [°] in, **6**.

	Moiety		Bond length		Moiety		Bond length
	N1	-C2	1.4863		C1	-H7	0.9901
	C1	-C2	1.5085		C2	-H4	0.99
	N1	-H1	0.91		C2	-H5	0.99
	N1	-H2	0.9099		O11	-C11	1.2624
	N1	-H3	0.9101		O12	-C12	1.2549
	C1	-H6	0.99		C11	-C12	1.456
	Moiety		Bond angle		Moiety		Bond angle
N1	-C2	-C1	111.31	N1	-C2	-H4	109.37
C2	-N1	-H1	109.47	N1	-C2	-H5	109.37
C2	-N1	-H2	109.47	C1	-C2	-H4	109.36
C2	-N1	-H3	109.47	C1	-C2	-H5	109.37
H1	-N1	-H2	109.48	H4	-C2	-H5	108
H1	-N1	-H3	109.47	O11	-C11	-C12	136.79
H2	-N1	-H3	109.47	C2	-C1	-H6	109.37
C2	-C1	-H7	109.37	O12	-C12	-C11	136.41
H6	-C1	-H7	108				

Table4.36 Hydrogen bond distances (Å) and angles (°) in **6**.[a]

D – H...A			D – H	D ...A	H...A	Angle D – H...A
N1	-- H1	... O12	0.91	1.9137	2.7796	158.29
N1	-- H2	... O11	0.9099	1.9408	2.8301	165.21
N1	-- H3	... O11	0.9101	1.9256	2.8241	168.89
C1	-- H6	... O12	0.99	2.4429	3.3693	155.57

(a) D- donor, A- acceptor