Crystal Engineering and Molecular Architecture

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Abstract

The aim of this paper is to provide a link between research projects and education to optimize teaching and learning of related subjects. In a research project, three compounds including an intermolecular proton transfer compound, a hydrated carboxylic acid, and a metallic complex were synthesized, all of them have non-covalent interactions such as O−H···O, O−H···N and C−H···O hydrogen bonds as well as van der Waals forces and π-π stacking resulting to different supramolecular structures. The structures of compounds are characterized by single crystal X-ray diffraction method. The classic concepts and definitions related to the subject are given in the last section.

Keywords

Chelidamic acid, Pyridine-2,6-dicarboxylic acid, Zinc, Hydrogen bond, Stacking, Proton transfer, Supramolecular chemistry, Crystal structure.

1. Introduction

In recent years, the crystal engineering of supramolecular architectures based on metal and organic building blocks has rapidly emerged as an exciting area of supramolecular chemistry because of their novel and diverse topologies and potential applications in host–guest chemistry, catalysis, electrical conductivity, and magnetism. The creation of metal-organic coordination networks based on complexes of transition metals and multifunctional bridging ligands has proven to be a fertile field due to the intriguing network topologies and potential functions as new classes of materials. These metal-containing supramolecular frameworks can be constructed through two different types of interaction: (i) coordinate covalent bonds linking metal centers and organic ligands, and (ii) noncovalent intermolecular forces such as hydrogen bonding, π-π stacking, and coulombic interactions. These weaker noncovalent interactions, especially hydrogen bonds, play a crucial role in fundamental biological processes, such as the expression and transfer of genetic information, and are essential for molecular recognition between receptors and substrates as well as construction of complicated supramolecular arrays through self-organization of molecules in the field of supramolecular chemistry. Currently, the rational design and synthesis of new extended supramolecular networks by means of both coordinative covalent and hydrogen-bonding interactions are of great interest and have brought forth a great variety of such frameworks with fascinating structural motifs. In general, extended networks possessing higher dimensionalities can be obtained by the assembly of coordination polymers, polymers with lower dimensionalities via hydrogen bonding interactions and π-π stacking. However, it is still a challenge when we hope to control the final products. The studies in this respect are limited because the assembly of molecules through weak interactions requires incorporation of many factors which cannot be completely controlled until now. For this, proper selection of metal ions and ligands are the key issues in designing self-assembly [1].

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1.1 Proton transfer compounds and their complexes

Proton transfer compounds are good samples having supramolecular structures. In these compounds there are two essential fragments, one is a donor species or generally a Lewis acid that has a site –for example a phenolic oxygen atom– capable to give proton(s), and another is an acceptor species or a Lewis base with a site –for example an amine nitrogen atom– able to accept proton(s). So many organic acids and bases have a potential to form proton transfer compounds. There are several papers on the phenomena of proton transfer from a carboxylic acid to a heterocyclic amine [2-9]. Continuing our researches on proton transfer ion pair systems, now we have found a certain route to a one-pot reaction between various carboxylic acids with various amines and produce some almost water-soluble self-associating ion pair systems, which can react with metal ions and result in different complexes. In these systems, we have often applied pyridine-2,6-diamine (pyda) [10a, b, 11], creatinine (creat) [10c], guanidine (G) [10d, e], N, N- diethyll-2 –amino-6 -methyl-4 -pyrimidinol (pyrim) [10f], and ethylenediguanidine [10g] as proton acceptors and pyridine-2,6-dicarboxylic acid (H_2pydc) [10a, b, d, h], 1,10-phenanthroline-2,9-dicarboxylic acid (phendcH_2) [10c, i], 4-hydoxypyridine-2,6-dicarboxylic acid [10e] and pyridine-2,6-bis(monothiocarboxylic) acid [10j] as proton donor units to synthesize a novel pre-designed ion pair.

The synthesized proton transfer ion pairs have some remaining donor sites to react with metallic ions and give complexes of main group or transition metals like Mg^{II}[11a], Ga^{III}[11b], In^{III}[11b, c], Tl^{III}[11b, d], Sn^{IV}[11e], Pb^{II}[11f, g], Sb^{III}[11h, i], Bi^{III}[11j, k, l], Ti^{IV}[12a], Zr^{IV}[12b], V^{IV}[11m], V^{V}[11n], Cr^{III}[12c, d], Mn^{II}[11o], Fe^{III}[11p], Co^{II}[10i,12e, f], Ni^{II}[12g, h], Pd^{II}[11d, 12i], Cu^{II}[12j, k], Zn^{II}[12l, m, n, o, p, q], Cd^{II}[12r, s, t, u], Hg^{II}[12v, w], or few rare earths like La^{III}[12f] and Ce^{III}[11c, j, q].

As mentioned above, in all reported ion pairs or complexes, the most important interaction is hydrogen bonding which links the species in the crystals, since as a “rule of thumb” all good proton donors and acceptors are used in hydrogen bonding [13]. The second interaction is π-π stacking which acts in longer distances and is responsible for almost layered structures. Pyridine-2,6-dicarboxylic acid (H_2pydc) is a versatile N-O chelating agent that can act as a bidentate, tridentate, meridian or bridging ligand with different metal ions [14].

In this paper, we intend to report three supramolecular compounds involving an intermolecular proton transfer compound, a hydrated carboxylic acid, and a metallic complex. The structures of compounds were determined by single crystal X-ray diffraction method.

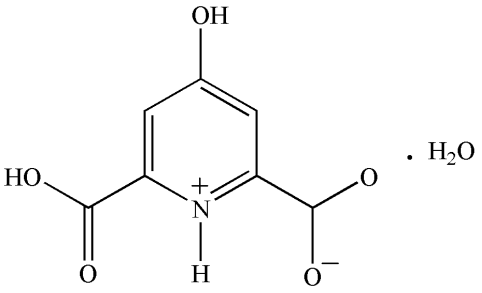
2. Experimental

2.1 Chelidamic acid monohydrate, 1

The title compound, $H_3Chel\cdot H_2O$, **1** (H_3Chel: chelidamic acid or H_2hypydc: 4-hydroxypyridine-2,6-dicarboxylic acid) formulated as $C_7H_7NO_6$, **1**, despite of its neutral charge, is a zwitterionic compound obtained from an intermolecular proton transfer phenomena between carboxylic acid group and pyridine nitrogen atom. Water molecules are responsible for expanding the supramolecular structure in 2D infinite layers of essentially planar rings and linking the parallel arrays to each other. Intermolecular O−H···O, O−H···N and C−H···O hydrogen bonds as well as van der Waals forces are the main interactions of the crystal structure.

2.1.1 Comment

Chelidamic acid (H_3Chel) is used widely in biochemistry, organic chemistry, medical chemistry and even in HIV investigation. In addition, as an emblematical polydentate ligand, it was also of great interest in the study of coordination chemistry. Though the initial report of H_3Chel was published in 1926, its crystal structure was not determined until 2000 [15]. It is a good way to expand the chemistry of chelidamic acid and master its function or reaction conditions to research a variety of metal complexes with chelidamic acid [16].



Scheme 1. structure of compound 1.

Continuing our procedure to synthesize proton transfer compounds with propane-1,3-diamine [17, 18], the aim of this work was synthesis of an ion pair including chelidamic acid and propane-1,3-diamine. It was supposed to observe a proton transfer phenomena between the acid and the base, but unexpectedly an intermolecular proton transfer was occurred within the acid and the base was remained in the solution. The compound **1** is crystallized in monoclinic system with space group $P2_1/n$. The ORTEP and packing diagram of **1** are shown in Figs. 1 and 2, respectively. The planar zwitterions as structure units form an angle of 19.90° in **1** with each other (Fig. 3). Crystallographic data, selected bond lengths and angles and hydrogen bonds geometry of compound **1** are tabulated in Tables 1, 2 and 3, respectively.

As seen in Table 3, the planar units of zwitterions form O−H···O hydrogen bonds with each other and with water molecules, and N−H···O hydrogen bonds with water molecules. Also, there is a weak C−H···O hydrogen bond with the length of 3.032(2) Å and angle of 130°.

By expanding, it is found that the compound consists of two-dimensional layers of structure units due to hydrogen bonding and the layers are situated parallel to each other. The distance between layers is about 3 Å that is measured as the distance between defined parallel planes passing through structure units (see Fig. 4). The layers are parallel to A-face*.

2.1.2 Synthesis and crystallography of 1

The compound was synthesized by adding 10 mmol chelidamic acid to 10 mmol propane-1,3-diamine in tetrahydrofuran, and refluxing it for 20 minutes. After a while, a precipitate was obtained which was recrystallized to colorless crystals suitable for single crystal diffractometry.

For compound **1**, the hydrogen atoms of OH groups and H_2O molecules were found in difference Fourier synthesis and were refined isotropically. The H(C) atom positions were calculated and were refined in isotropic approximation in riding model with the *U*iso(H) parameters equal to 1.2 *U*eq(Ci) where *U*eq(Ci) are the equivalent thermal parameters of the carbon atoms to which corresponding H atoms are bonded.

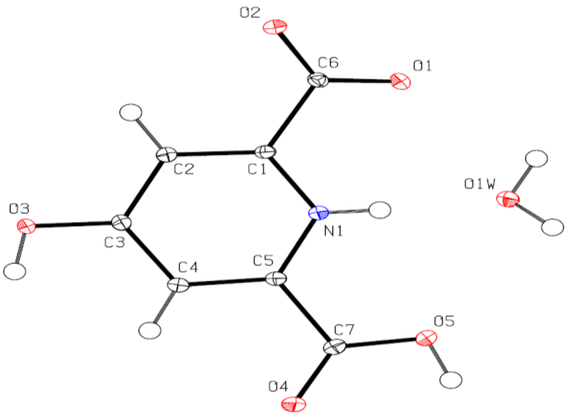


Figure 1 The ORTEP diagram of 1, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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* Crystallographically speaking A-face is a face consisting of *b* and *c* as cell parameters.

Table 1 Crystallographic data of compound 1

Crystal data	
$C_7H_5NO_5 \cdot H_2O$	$Z = 8$
$M_r = 201.14$	$D_x = 1.747$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 13.436(1)$ Å	$\mu = 0.16$ mm^{-1}
$b = 9.0391(9)$ Å	$T = 100(2)$ K
$c = 13.714(1)$ Å	Prism, colourless
$\beta = 113.347(2)°$	0.45 × 0.32 × 0.27 mm
$V = 1529.2(3)$ Å^3	
Data collection	
Bruker APEX2 CCD area detector diffractometer	4773 independent reflections
phi and ω scans	2337 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.026$
20272 measured reflections	$\theta_{\text{max}} = 31.0°$
Refinement	
Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.0103P)^2 + 3.3865P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.108$	$(\Delta/\sigma)_{\text{max}} = 0.004$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.51$ e Å^{-3}
4773 reflections	$\Delta\rho_{\text{min}} = -0.27$ e Å^{-3}
277 parameters	Extinction correction: none

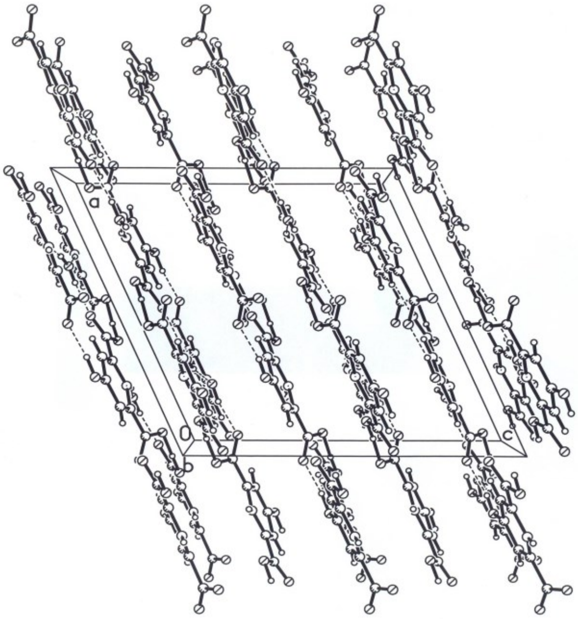


Figure 2 The packing diagram with unit cell of 1. Hydrogen bonds are shown as dashed lines.

Table 2 Selected bond lengths, bond angles and torsion angles (Å, °) of compound 1

O1−C6	1.259(2)	O4−C7	1.222(2)
O2−C6	1.248(2)	O5−C7	1.298(2)
O3−C3	1.331(2)		
N1−C1−C6	117.4(1)	N1−C5−C4	121.2(1)
N1−C1−C2	121.3(1)	O2−C6−O1	128.1(1)
C2−C1−C6	121.2(1)	O2−C6−C1	116.2(1)
O3−C3−C4	121.6(1)	O1−C6−C1	115.7(1)
O3−C3−C2	119.7(13)	O4−C7−O5	126.4(2)
C2−C3−C4	118.6(1)	O5−C7−C5	115.2(1)
N1−C5−C7	120.8(1)	O4−C7−C5	118.4(1)
C4−C5−C7	118.0(1)		
C5−N1−C1−C6	178.2(1)	N1−C1−C6−O1	23.2(2)
C1−C2−C3−O3	−179.8(1)	C2−C1−C6−O1	−157.4(2)
O3−C3−C4−C5	−179.0(1)	N1−C5−C7−O4	172.8(2)
C1−N1−C5−C7	−175.6(1)	C4−C5−C7−O4	−5.2(2)
N1−C1−C6−O2	−156.8(1)	N1−C5−C7−O5	−7.0(2)
C2−C1−C6−O2	22.6(2)	C4−C5−C7−O5	175.0(1)

Data collection: *APEX2* [19]; cell refinement: *APEX2* [19]; data reduction: *APEX2* [19]; program(s) used to solve structure: *SHELXTL* ver. 5.1 [20]; program(s) used to refine structure: *SHELXTL* ver. 5.1 [20]; molecular graphics: *SHELXTL* [20]; software used to prepare material for publication: *SHELXTL* ver. 5.1 [20]

Table 3 Hydrogen bond geometry (Å, °) of compound 1

D−H···*A*	*D*−H	H···*A*	*D*···*A*	∠*D*−H···*A*
O3−H3···O2^{i}	0.85	1.74	2.585 (2)	178
O5−H5···O1^{ii}	0.85	1.64	2.486 (2)	174
N1−H1A···O1W	0.86	1.88	2.694 (2)	158
O1W−H1W···O3^{iii}	0.85	2.06	2.908 (2)	175
O1W−H2W···O4^{iv}	0.85	1.92	2.764 (2)	173
C4−H4A···O2^{v}	0.93	2.35	3.032(2)	130

.Symmetry codes: (i) *x*, -*y*+1/2, *z*-1/2; (ii) *x*, -*y*+3/2, *z*-1/2; (iii) *x*, *y*+1, *z*; (iv) *x*, -*y*+3/2, *z*+1/2, (v) *x*, -*y*-1/2, *z*-3/2.

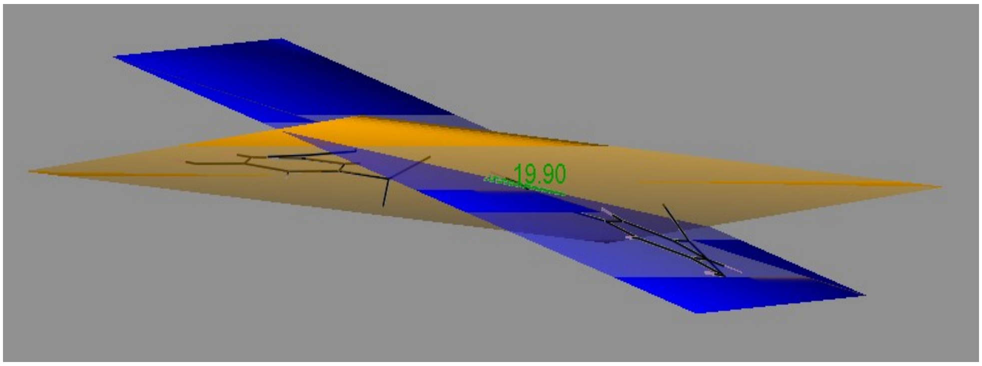


Figure 3 The angle 19.90° between planes of two zwitterionic units of 1.

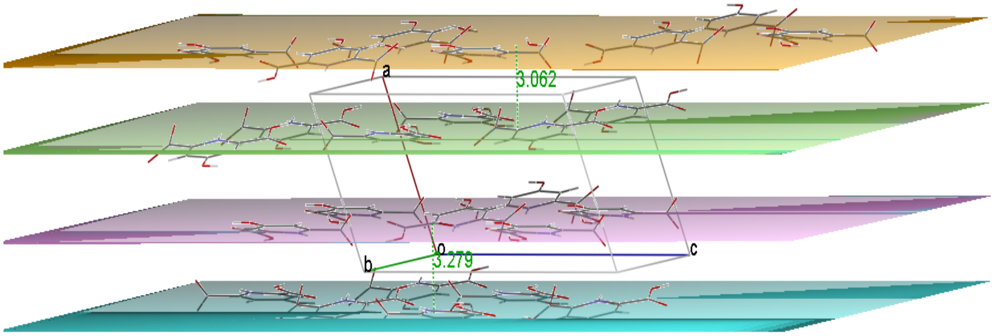


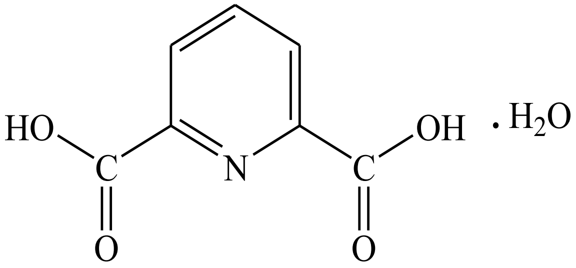
Figure 4 The interplanar distances between parallel layers of 1.

2.2 Pyridine-2,6- dicarboxylic acid dihydrate, 2

The title compound, $H_2pydc \cdot H_2O$, **2** (H_2pydc: pyridine-2,6-dicarboxylic acid) formulated as $C_7H_7NO_5$, **2**, is crystallized in monoclinic system and space group $P2_1$. The extensive hydrogen bonding between pyridine-2,6-dicarboxylic acid and water molecules throughout the lattice of this compound play an important role in stabilizing the crystal and construction of the three-dimensional supramolecular structure framework. The crystal packing diagram of this compound shows a variety of O−H···O and O−H···N hydrogen bonding interactions connecting the fragments of this compound.

2.2.1 Comment

Pyridine-2,6-dicarboxylic acid as a very important carboxylate derivative has attracted much interest in coordination chemistry [21]. It is a good ligand with respect to its three donor atoms and limited steric hindrance also is a good hydrogen bond acceptor to form strong hydrogen bonds, and even hydrogen-bonded networks, with hydrogen donors [1]. The acid has a rigid 120° angle between the central pyridine ring and two carboxylate groups and therefore could potentially provide various coordination motifs to form both discrete and consecutive metal complexes under appropriate synthesis condition [21]. Metal pyridinedicarboxylates have interesting properties in biological systems, and their presence seems to be related with metal-transport and cell membrane protection in some microorganisms. These compounds are derived from pyridinedicarboxylic acids (H_2pydc) that form a series that includes the 2,3-, 2,4-, 2,5- and 2,6-pyridinedicarboxylic isomers [22]. Also, 3,5- pyridinedicarboxylic isomer is applied by our research group [23].



Scheme 2 structure of compound 2.

2.2.2 Synthesis and crystallography of 2

In this compound, protons from the carboxylic acid unit are not transferred to proton acceptor, therefore, pyridine-2,6-dicarboxylic acid is not a proton transfer compound. It is simply crystallized with two water molecules forming a supramolecular network. The ORTEP, hydrogen bonds and packing diagram are illustrated in Figures 5, 6 and 7, respectively. Crystallographic data, selected bond lengths and angles and hydrogen bonds geometry of compound **2** are tabulated in Tables 4, 5 and 6, respectively. The compound is crystallized in monoclinic system and space group *P*2_1. As shown in Figure 6, all three atoms of water molecule are involved in hydrogen bondings: one hydrogen atom to nitrogen atom of pyridine ring, other hydrogen atom to deprotonated oxygen atom of carboxylate group, and oxygen atom to acidic hydrogen atom. The acid, in turn, is concerned with its five atoms in hydrogen bonds. In Fig. 7, it can be seen that the structure is layered and the layers are linked to each other by hydrogen bonds. Since there is not any charged species or stacking, the only interaction to expand the crystal structure is hydrogen bonding. As seen in Table 6, the best hydrogen bond is formed between O1−H1O···O2W, O3−H3O···O2, O5−H5O···O1W and O8−H8O···O6 with shortest H···O length and relatively least deviated angle from linearity. These bonds are classified as *strong* hydrogen bond that will be discussed in the last section.

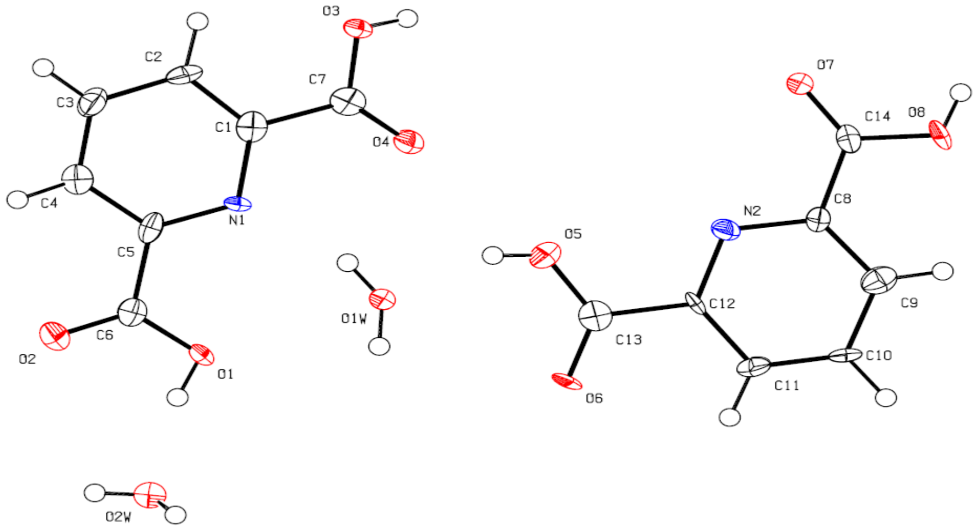


Figure 5 The ORTEP view of (H_2pydc)·$2H_2O$, 2, the ellipsoids are shown at 50% probability.

Table 4 Crystallographic data of compound 2

Crystal data	
$C_7H_5N_1O_4 \cdot H_2O$	$Z = 4$
$M_r = 185.14$	$D_x = 1.632$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$
$a = 6.642$ (5) Å	$\mu = 0.14$ mm^{-1}
$b = 12.119$ (9) Å	$T = 120$ (2) K
$c = 9.375$ (7) Å	Plate, colorless
$\beta = 93.084$ (15)°	0.20 × 0.15 × 0.05 mm
$V = 753.6$ (10) Å^3	
Data collection	
Bruker SMART 1000 CCD area detector diffractometer	2814 independent reflections
phi and ω scans	1399 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan SADABS (Sheldrick, 1998a)	$R_{\text{int}} = 0.064$
5357 measured reflections	$\theta_{\max} = 26.0°$
Refinement	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.086$	$(\Delta/\sigma)_{\max} = 0.002$
$wR(F^2) = 0.201$	$\Delta\rho_{\max} = 0.73$ e Å^{-3}
$S = 0.98$	$\Delta\rho_{\min} = -0.38$ e Å^{-3}
2814 reflections	Extinction correction: none
235 parameters	Absolute structure: Flack H D (1983), *Acta Cryst.* A39, 876-881
H-atom parameters constrained	Flack parameter: 0 (4)

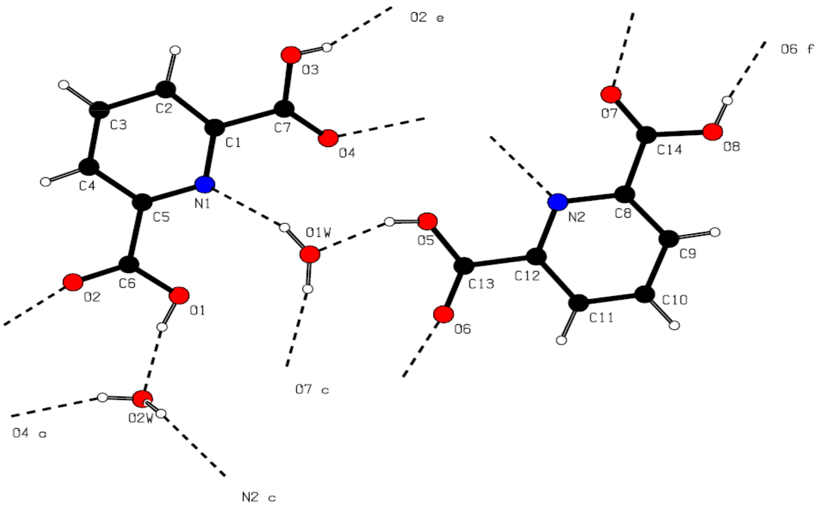


Figure 6 Hydrogen bonds as dashed lines linking the water and (H_2pydc) molecules to each other in

Table 5 Selected bond lengths, bond angles and torsion angles (Å, °) of compound 2

O1−C6	1.296(11)	O5−C13	1.295(11)
O2−C6	1.224(11)	O6−C13	1.215(10)
O3−C7	1.319(11)	O7−C14	1.197(10)
O4−C7	1.213(10)	O8−C14	1.343(10)
C2−C1−C7	120.7(8)	N2−C8−C14	115.4(7)
N1−C1−C7	115.4(7)	C9−C8−C14	122.2(8)
N1−C1−C2	123.9(8)	N2−C8−C9	122.5(8)
N1−C5−C6	118.2(7)	N2−C12−C13	117.7(8)
C4−C5−C6	117.6(9)	C11−C12−C13	119.3(8)
N1−C5−C4	124.29)	N2−C12−C11	123.0(8)
O2−C6−C5	119.5(8)	O6−C13−C12	118.1(8)
O1−C6−C5	115.6(9)	O5−C13−C12	116.8 (8)
O1−C6−O2	124.9(8)	O5−C13−O6	125.0(9)
O4−C7−C1	124.8(8)	O7−C14−C8	125.9(8)
O3−C7−C1	110.9(7)	O8−C14−C8	110.4(7)
O3−C7−O4	124.2(8)	O7−C14−O8	123.7(8)
N1−C5−C6−O2	174.7 (7)	N2−C12−C13−O6	173.9 (7)
C4−C5−C6−O2	−5.5 (11)	C11−C12−C13−O6	−6.1 (11)
N1−C5−C6−O1	−5.4 (11)	N2−C12−C13−O5	−5.7 (10)
C4−C5−C6−O1	174.4 (7)	C11−C12−C13−O5	174.3 (7)
C2−C1−C7−O4	−166.6 (7)	N2−C8−C14−O7	−5.2 (12)
N1−C1−C7−O4	11.7 (11)	C9−C8−C14−O7	174.9 (8)
C2−C1−C7−O3	12.3 (10)	N2−C8−C14−O8	173.6 (7)
N1−C1−C7−O3	−169.4 (6)	C9−C8−C14−O8	−6.3 (10)

Table 6 Hydrogen bond geometry (Å, °) of compound 2

D−H⋯*A*	*D*−H	H⋯*A*	*D*⋯*A*	∠*D*−H⋯*A*
O1W−H1W1⋯N1	0.82	2.08	2.852(8)	156
O1−H1O⋯O2W	0.82	1.75	2.558(8)	168
O1W−H1W2⋯O7^{i}	0.82	2.11	2.907(8)	165
O2W−H2W1⋯O4^{i}	0.82	2.12	2.918(8)	164
O3−H3O⋯O2^{ii}	0.82	1.84	2.590(9)	152
O2W−H2W2⋯N2^{i}	0.82	2.24	2.943(8)	144
O5−H5O⋯O1W	0.82	1.79	2.521(9)	148
O8−H8O⋯O6^{ii}	0.82	1.79	2.594(9)	165

Symmetry codes: (i) *x*, *y*, 1+*z*; (ii) *x*, *y*,-1+*z*.

For compound **2**, the hydrogen atoms of water molecules were found in the difference Fourier synthesis. The H(C) atom positions were calculated. All the hydrogen atoms were refined in isotropic approximatiom within riding model with the U_{iso}(H) parameters equal to 1.2 U_{eq}(Ci), 1.5 U_{eq}(Oj) where U(Ci) and U(Oj) are the equivalent thermal parameters of the carbon or oxygen atoms to which corresponding H atoms are bonded.

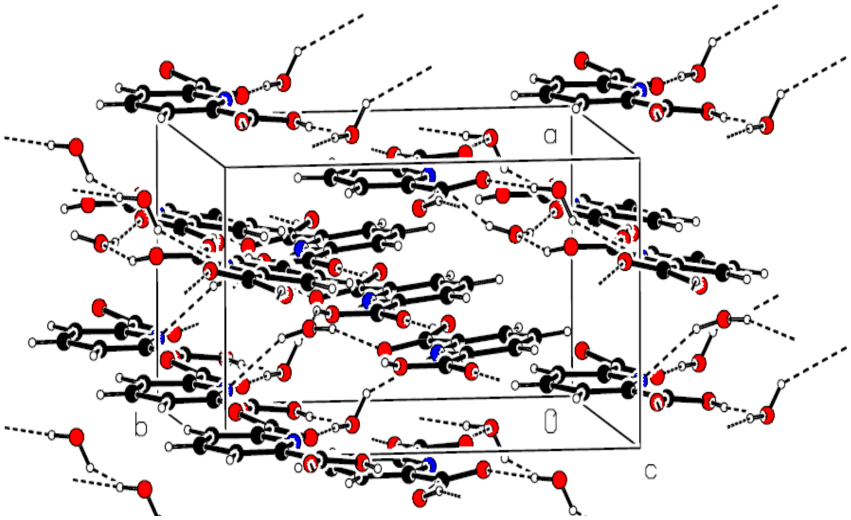


Figure 7 Crystal packing diagram of $(H_2pydc)\cdot2H_2O$, 2, hydrogen bonds are shown as dashed lines.

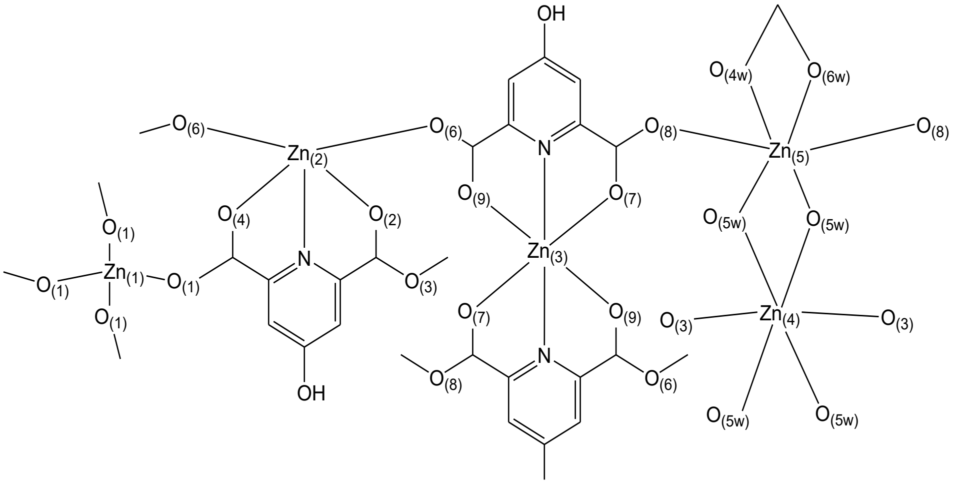
Data collection: *SMART* [24]; cell refinement: SAINTPlus [25]; data reduction: SAINTPlus [25]; program(s) used to solve structure: *SHELXTL* [26]; program(s) used to refine structure: *SHELXTL* ver. 5.1 [26]; molecular graphics: *SHELXTL* ver. 5.1 [26]; software used to prepare material for publication: *SHELXTL* ver. 5.1 [26].

2.3 A novel polymeric Zn^{II} complex, 3

A new polymeric complex of zinc(II) with a proton transfer compound, obtained from 4-hydroxypyridine-2,6-dicarboxylic acid, $H_2hypydc$ (or H_3Chel: chelidamic acid), and piperazine, pipz, $(pipzH_2)(hypydc)$ as ligand, was synthesized and characterized using single crystal X-ray diffractometer. The complex with chemical formula $[Zn_{12}(hypydc)_{12}(H_2O)_{10}\cdot12H_2O]_n$, **3** crystallizes in tetragonal system and $I4_1/amd$ space group. The important feature of the complex is three different coordination numbers (4, 5, 6) around Zn^{II}. Non-covalent interactions such as hydrogen bonding and π-π stacking are involved.

2.3.1 Comment

In recent years, we have been interested in synthesis of proton transfer compounds and study of their behavior with metal ions. We have focused on the proton delivery from dicarboxylic acids, which are considered as very good donors.



Scheme 3 Polymeric structure of compound 3.

Several proton acceptors were selected and employed. The results were production of several proton transfer compounds possessing anionic forms of diacid as donors. Applications of these compounds in preparation of metal-organic structures were also investigated as several metal complexes (see section 1.1). Some of the complexes showed the contribution of both cationic and anionic fragments of the starting proton transfer compound, while some others contained only one of these species as ligands. In the present work, we study the complexation of (pipzH_2)(hypydc), (hypydcH_2: 4-hydroxypyridine-2,6-dicarboxylic acid or its old name H_3Chel: chelidamic acid , pipz: piperazine) with Zn^{II} as central metal.

2.3.2 Synthesis and crystallography of 3

The reaction of piperazinium 4-hydroxypyridine-2,6-dicarboxylate with zinc(II) sulphate seven-hydrate in a 2:1 molar ratio in water was carried out. The colorless crystals of the complex were obtained after three weeks. The complex decomposed above 400 °C. The ORTEP view, hydrogen bonds with atom numbering, a fragment of structure and π-π stacking of **3** are illustrated in Figures 8, 9, 10 and 11, respectively. Crystallographic data, selected bond lengths and angles and hydrogen bonds geometry of compound **3** are tabulated in Tables 7, 8 and 9, respectively.

The polymeric complex was crystallized in the tetragonal system, space group $I4_1/amd$ with four formula units in the unit cell. X-ray data were collected by graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). The structure was solved by automatic direct methods using SHELXTL ver. 5.1 program [26]. The structure was refined by a full-matrix least-square analysis on F^2 with SHELXTL ver. 5.1. The absorption was performed semiempirically from equivalent by means of the SADABs program. The hydrogen atoms of water molecules O(1W), O(2W) and O(3W) and hydroxyl groups were found in difference Fourier synthesis.

The H(C) atom positions were calculated. All the hydrogen atoms were refined in isotropic approximatiom within riding model with the U_{iso}(H) parameters equal to 1.2 U_{eq}(Ci), 1.5 U_{eq}(Oj) where U(Ci) and U(Oj) are the equivalent thermal parameters of the carbon or oxygen atoms to which corresponding H atoms are bonded. The water molecules that coordinate Zn(4) and Zn(5) metal atoms are probably disordered, however due to low quality of the single crystal and weak reflection ability it was impossible to resolve the disorder. For the refinement, the restrains for the Zn–O(water) distances were applied. Due to above facts, hydrogen atoms were not localized at O(4W), O(5W) and O(6W) water molecules. High positive residual density of 1.41 e.Å^{-3} is probably also due to the unresolved disorder and restrains.

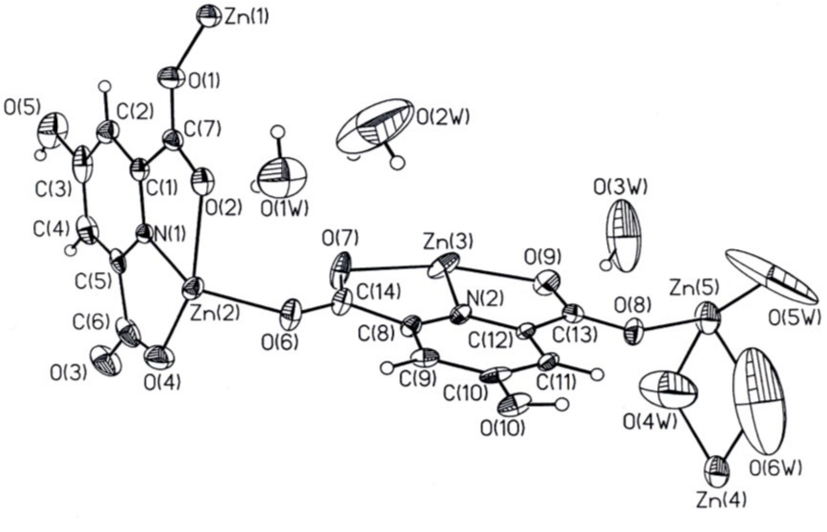


Figure 8 ORTEP view of Zn^{II} complex, 3, showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level.

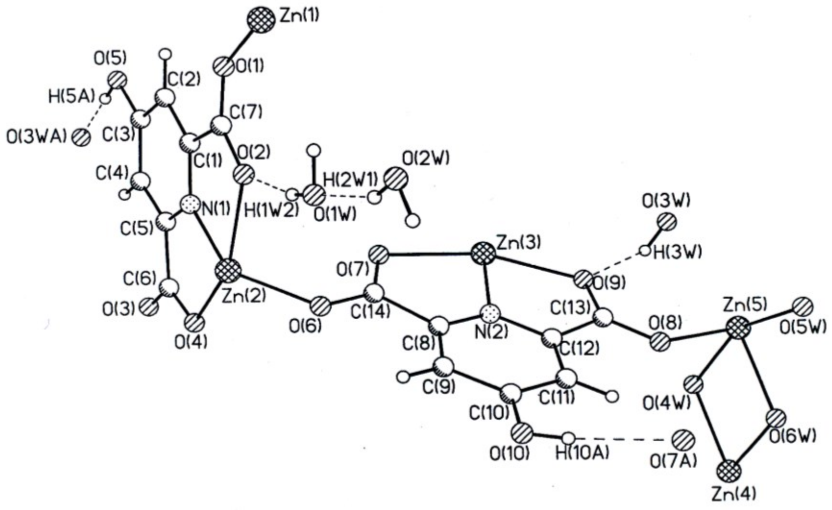


Figure 9 Atom numbering of Zn^{II} complex, 3, hydrogen bonds shown as dashed lines.

Table 7 Crystallographic data of Zn^{II} complex, 3

Crystal data	
$C_{84}H_{56}N_{12}O_{70}Zn_{12}\cdot 12(H_2O)$	$V = 11773.6$ (6) Å^3
$M_r = 3354.08$	$Z = 4$
Tetragonal, $I4_1/amd$	$D_x = 1.892$ Mg m^{-3}
$a = 19.8328$ (4) Å	Mo $K\alpha$
$b = 19.8328$ (4) Å	$\mu = 2.52$ mm^{-1}
$c = 29.9325$ (12) Å	$T = 120$ (2) K
$\alpha = 90°$	Prism, colorless
$\beta = 90°$	0.2 × 0.2 × 0.1 mm
$\gamma = 90°$	
Data collection	
Bruker SMART 1000 CCD area detector diffractometer	3972 independent reflections
phi and ω scans	2625 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan SADABS (Sheldric, 1998a)	$R_{int} = 0.062$
$T_{min} = 0.621$, $T_{max} = 0.777$	$\theta_{max} = 29.0°$
60364 measured reflections	
Refinement	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.011P)^2 + 284.5P]$
$R[F^2 > 2\sigma(F^2)] = 0.081$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.157$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.01$	$\Delta\rho_{max} = 1.32$ e Å^{-3}
3972 reflections	$\Delta\rho_{min} = -1.19$ e Å^{-3}
255 parameters	Extinction correction: none
H-atom parameters constrained	

Table 8 Selected bond lengths, bond angles and torsion angles (Å, °) of Zn^{II} complex, 3

Zn(1)–O(1)	1.927(7)	Zn(4)–O(4W)	2.122(9)
Zn(2)–N(1)	1.986(6)	Zn(4)–O(6W)	2.152(10)
Zn(2)–O(2)	2.260(7)	Zn(5)–O(8)	2.075(5)
Zn(2)–O(4)	2.163(9)	Zn(5)–O(4W)	2.131(9)
Zn(2)–O(6)	1.943(5)	Zn(5)–O(5W)	2.144(10)
Zn(3)–N(2)	1.996(4)	Zn(5)–O(6W)	2.160(10)
Zn(3)–O(7)	2.334(5)	O(6)–C(14)	1.266(8)
Zn(3)–O(9)	2.129(5)	O(8)–C(13)	1.244(8)
Zn(1)–O(1)–C(7)	133.3(7)	N(2)–Zn(3)–O(9)	108.88(19)
N(1)–Zn(2)–O(2)	75.5(2)	Zn(4)–O(4W)–Zn(5)	104.1(5)
N(1)–Zn(2)–O(4)	76.7(3)	Zn(4)–O(6W)–Zn(5)	102.1(5)
N(1)–Zn(2)–O(6)	134.31(15)	Zn(5)–O(8)–C(13)	128.8(5)
O(2)–Zn(2)–O(6)	97.3(2)	O(4W)–Zn(4)–O(6W)	77.1(4)
O(4)–Zn(2)–O(6)	102.0(2)	O(5W)–Zn(5)–O(6W)	149.9(5)
Zn(2)–O(6)–C(14)	129.8(5)	O(8)–Zn(5)–O(4W)	91.31(18)
N(2)–Zn(3)–N(2)	169.1(3)	O(8)–Zn(5)–O(5W)	87.87(18)
N(2)–Zn(3)–O(7)^{i}	73.95(18)		
O(2)–Zn(2)–O(6)–C(14)	-79.6(7)	Zn(5)–O(8)–C(13)–O(9)	-1.0(11)
O(4)–Zn(2)–O(6)–C(14)	80.3(7)	Zn(5)–O(8)–C(13)–C(12)	179.5(4)
O(6)–C(14)–O(7)–Zn(3)	-178.8(6)	C(13)–O(9)–Zn(3)–O(7)^{i}	97.3(5)
O(8)–C(13)–O(9)–Zn(3)	177.2(6)	C(14)–O(7)–Zn(3)–O(9)^{i}	106.4(6)

Symmetry code: (i) $y+1/4$, $x-1/4$, $-z+1/4$

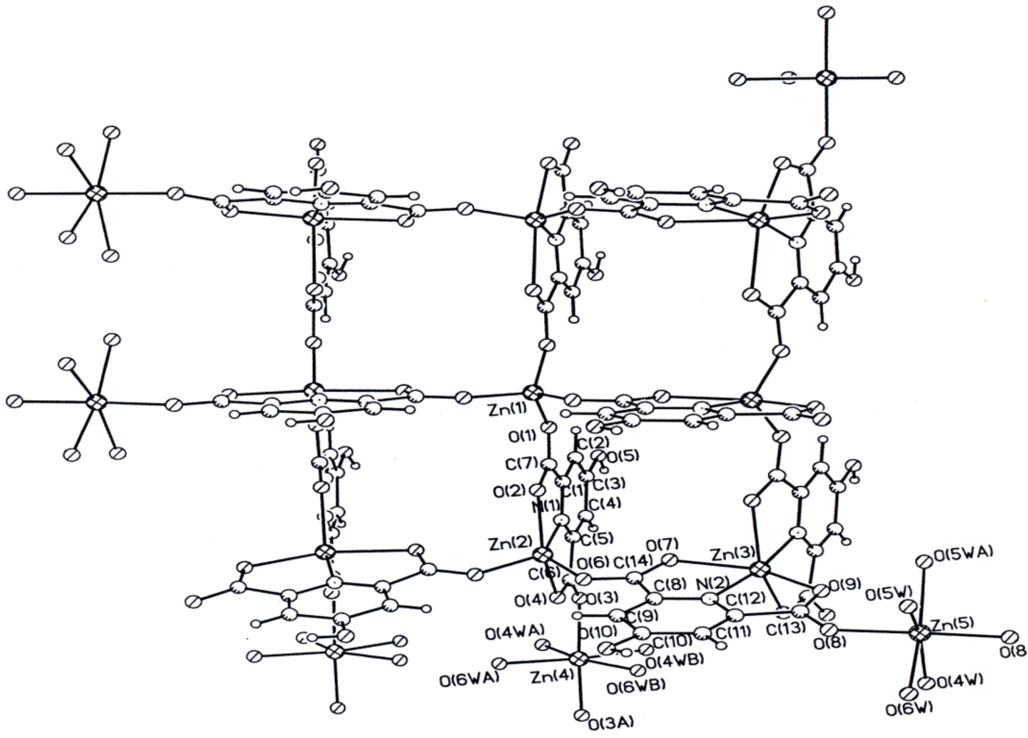


Figure 10 A fragment of polymeric structure of 3. Numbering is given for symmetrically independent part. Only water molecule that are coordinated to Zn(4) and Zn(5) atoms are shown.

Table 9 Hydrogen bond geometry (Å, °) of Zn^{II} complex, 3

D−H···*A*	*D*−H	H···*A*	*D*···*A*	∠*D*−H···*A*
O(5)−H(5A)···O(3W)^{i}	0.85	1.99	2.84(2)	179
O(10)−H(10A)···O(7)^{ii}	0.85	2.09	2.927(8)	170
O(1W)−H(1W2)···O(2)^{iii}	0.85	1.92	2.758(11)	167
O(2W)−H(2W1)···O(1W)^{iii}	0.85	2.35	3.15(3)	157
O(3W)−H(3W)···O(9)^{iii}	0.85	2.07	2.774(8)	140

Symmetry codes: (i) *x*, *y*-1/2, -*z*; (ii) -*y*+1/4, *x*-1/4, *z*+1/4; (iii) *x*, *y*, *z*

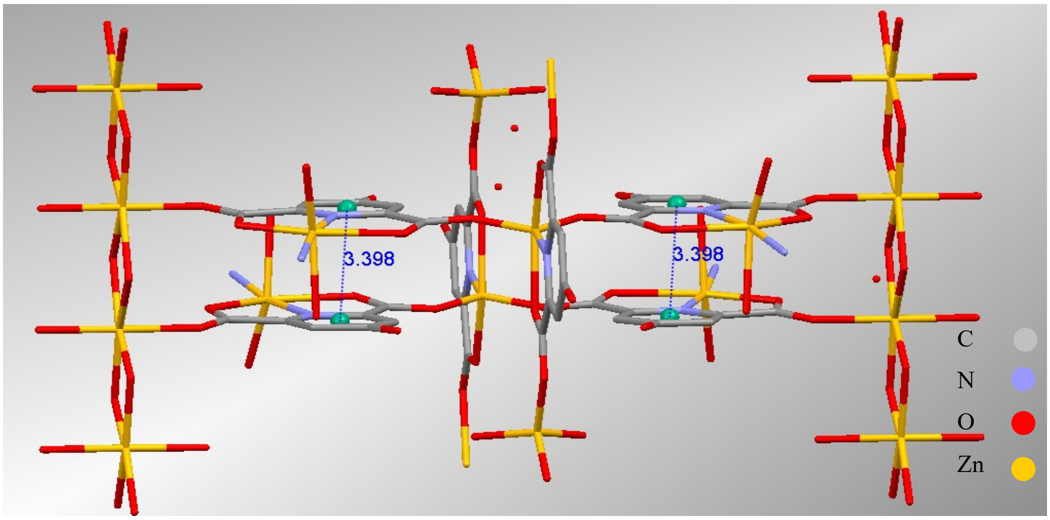


Figure 11 π-π Stacking and the distance between rings of Zn^{II} complex 3, hydrogen atoms are omitted for clarity.

The complex is crystallized in the space group *I*4$_1$/*amd* of tetragonal system with four molecules per unit cell. This polymer has shown three coordination numbers (4, 5, 6) around Zn^{II}. The Zn(1) showing a distorted tetrahedral environment, is attached to four hydroxyl oxygen atoms of four (hypydc)$^{2-}$ groups. Zn(2) is originally attached to one (hypydc)$^{2-}$ anion as an O,N,O tridentate ligand. Its two other coordination sites are occupied by the hydroxyl oxygen atoms of other (hypydc)$^{2-}$ groups. The geometry around Zn(2) is a distorted trigonal bipyramid. Zn(3) is coordinated by two (hypydc)$^{2-}$ anions as O,N,O tridentate ligands. The Zn(3) complex with the coordination number of six, represents a distorted octahedral geometry. The N(2)−Zn(3)−N(2)^{i} (i: *y*+1/4, *x*-1/4, -*z*+1/4) angle, shows a deviation of 11.9° from linearity. The C(13)−O(9)−Zn(3)−O(7)^{I}and(14)−O(7)−Zn(3)−O(9)^{i} torsion angles are 97.3(5) and 106.4(6)°, respectively. These data confirm that the (hypydc)$^{2-}$ anions are almost perpendicular to each other. The polymeric chain is continued by coordination of O(8) and O(6) of (hypydc)$^{2-}$ groups, which are attached to Zn(2), Zn(3), and Zn(5). The O(4W), O(6W) and two O(5W) water molecules fill the remaining sites to form a distorted octahedron. The O(4W) and O(6W) water molecules play a bridging role between Zn(4) and Zn(5). The intermolecular forces existing in Zn^{II} complex, in addition to covalent bonds, are hydrogen bonding and π-π stacking (Fig. 11) with the distance of 3.398 Å. The extensive intermolecular hydrogen bonding are present between coordinated and uncoordinated water molecules, carboxylate groups of (hypydc)$^{2-}$ and hydroxyl group species.

3. Educational results and discussion

After undergoing the research project, now we want to conclude some classic and educational aspects as follows:

3.1 Crystal engineering

"*What would the properties of materials be if we could really arrange the atoms the way we want them?* "[27] When *Feynman* applied the above sentence, or when *Von hippel* defined and used the term “molecular engineering” in 1962 for the first time, nobody knows that they will be precursors of a phenomenon called "Crystal Engineering".

Crystal engineering is predicting and designing shape and arrangement of molecules with the aim of giving desired properties to them [28]. Simply thinking, it is just like a molecular *LEGO*! (Fig. 12) It is based on a knowledge, or at least consideration of the steric, topological and intermolecular bonding capabilities of constituent building blocks, kinetics and thermodynamics of crystal nucleation, the requirements of crystal close packing and the relative importance of the multiplicity of interactions that go together to assemble the crystal entity. Crystal engineering design strategies include knowledge of optimum intermolecular interactions, molecular shape, topology, and electronic properties [28].

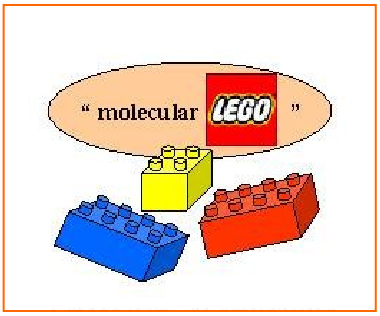


Figure 12 Supramolecular chemistry is like a molecular *LEGO*!

3.2 Supramolecular chemistry

Supramolecular chemistry is a branch of chemistry that mainly studies the interactions between molecular constituents and considers them as a huge unit. In the unit there are weaker noncovalent interactions than in a single molecule, such as hydrogen bonding, ion pairing, ligand to metal coordination, hydrophobic forces, van der Waals forces, π-π interactions, and electrostatic effects to assemble molecules into multimolecular complexes. Hydrogen bonding is the most important interaction in forming supramolecular networks.

3.3 Non-covalent bonds in supramolecular chemistry

Just as there is a field of *molecular chemistry* based on the covalent bond, there is a field of *supramolecular chemistry*, the chemistry of molecular assemblies and of the intermolecular bond. Supramolecular species are characterized both by the spatial arrangement of their components, their architecture or superstructure, and by the nature of intermolecular bonds that hold these components together. Various types of interactions may be distinguished, that present different degrees of strength, directionality, dependence on distances and angles [29].

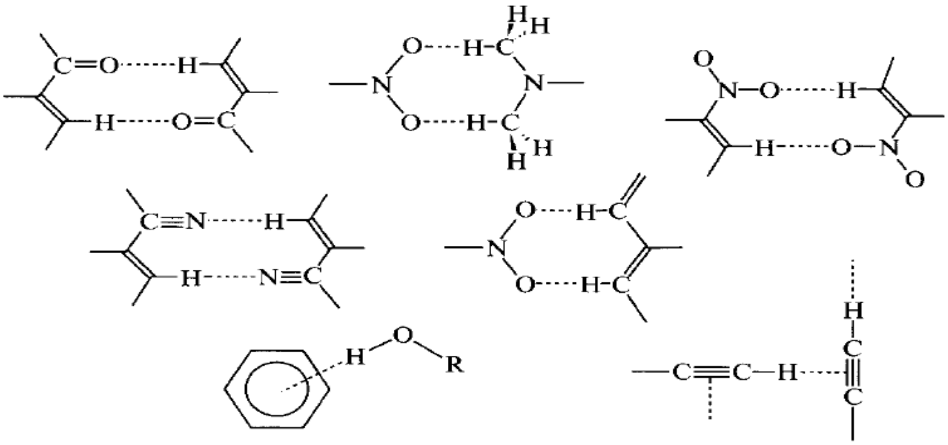


Figure 13 Supramolecular species involving C−H···O hydrogen bonds. [31]

3.3.1 Hydrogen bonding

Hydrogen bonding is one of the several types of non-covalent interactions in many organic and inorganic species, which results in aggregation and controls self-assembly, in some cases. There are some atoms like nitrogen that can give various hydrogen bonds shown as D−H···A symbol in which D is the donor atom, H is the shared hydrogen atom, and A is the acceptor atom. In the symbol, the straight line (−) shows a covalent bond, and the dashed line (···) illustrates a hydrogen bond. For example, N–H···O is a hydrogen bond between oxygen and hydrogen atom that has covalent bond to nitrogen atom. A conventional definition involves only nitrogen, oxygen and fluorine as the most electronegative atoms to give hydrogen bonding. Recently, in many papers and textbooks the definition has been expanded to include other atoms especially carbon atom with an electronegativity approximately same as hydrogen. So, the term C−H···O is observed in many papers. In fact, it is a true hydrogen bond and is supported by *ab initio* quantum calculation. It's weaker with about 1/3 strength of conventional H-bonds and longer than them with optimum distance about 3.3Å [30]. Some examples of C−H···O hydrogen bond are illustrated in Fig. 13. With these considerations, the hydrogen bonds are classified into three groups, strong, moderate and weak. The classification is illustrated in Table 10 [32]. Also there is another classification with some similarities to Table 10, which is given in Table 11, the classes are very strong, strong and weak [33]. Some examples of strong bonds are given in Fig. 14.

Table 10 Three types of hydrogen bonding

	Strong	Moderate	Weak
D−H···A interaction	Mainly covalent	Mainly Electrostatic	Electrostatic
Bond Energy	60-120 (kJ/mol)	16-60 (kJ/mol)	<12 (kJ/mol)
H···A length	1.2-1.5 (Å)	1.5-2.2 (Å)	2.2-3.2 (Å)
D···A length	2.2-2.5 (Å)	2.5-3.2 (Å)	3.2-4.0 (Å)
Bond angle	175-180°	130-180°	90-150°

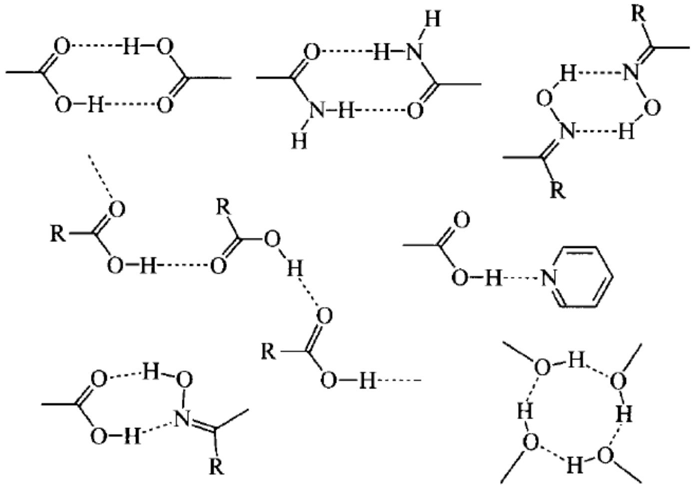


Figure 14 Some examples of strong hydrogen bonds.

As seen in Fig. 14, one type of strong hydrogen bonds is O−H···O bond. Another example of O−H···O bond in our works can be observed in $Zn(phen)_3]_4[H(Hpydc)_2](NO_3)_7·26H_2O$, as given in Fig. 15. In the complex, O···O distances are in the range of 2.493-3.024Å.

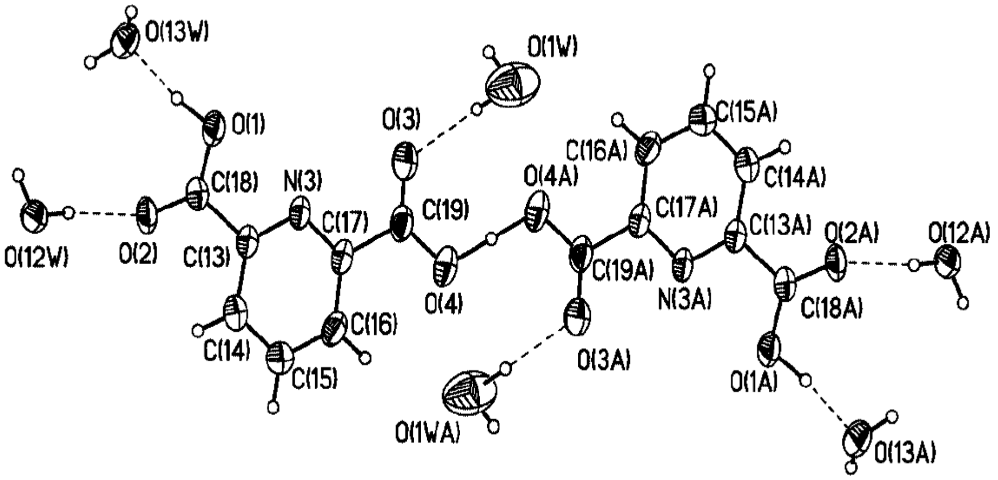


Figure 15 An example of O−H···O hydrogen bond in $[Zn(phen)_3]_4[H(Hpydc)_2](NO_3)_7·26H_2O$, nitrate and some water molecules are omitted for clarity. [12*l*]

Weak hydrogen bonds play an important role in crystal engineering. Although C−H···O hydrogen bond was first identified by J. D. Sutor in 1962 [34], but very recent reports shows its significance in nucleic acid base pairs, protein and polypeptide structures, organometallic structures, cocrystalline structures, drug design and drug macromolecular interactions and finally interaction of water with small biological molecules. This type of non-covalent interactions requires having two parallel π-rings in the crystal structure in the distance of about 3.5Å provided that the rings as Fig. 16 do not overlap directly. Since this is an electrostatic interaction, so exact overlapping of rings will cause repulsion of π-clouds.

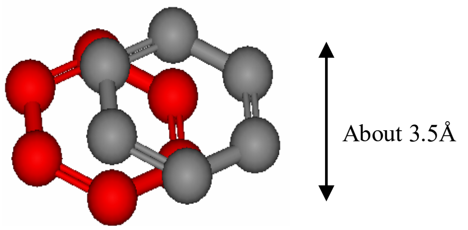
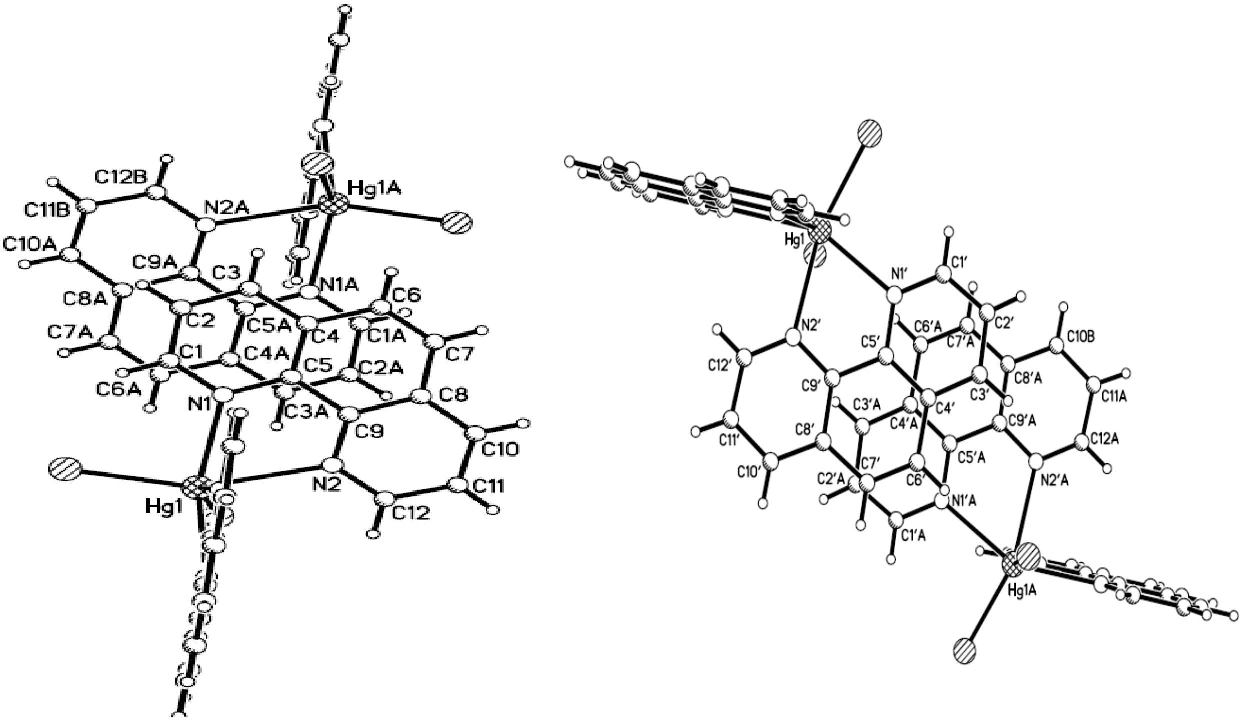


Figure 16 π- π Stacking or face-to-face stacking.

Table 11. Another classification of hydrogen bonding

	Very strong	Strong	Weak
Bond Energy (kcal/mol)	15-40	4-15	<4
Examples	$[F\cdots H\cdots F]^-$	O−H···O=C	C−H···O
	$[N\cdots H\cdots N]^+$	N−H···O=C	N−H···F−C
	P−OH···O=P	O−H···O−H	O−H···π
Bond lengths	D−H ≈ H···A	D−H < H···A	D−H << H···A
D···A range (Å)	2.2-2.5	2.5-3.0	3.0-4.5
H···A range (Å)	1.2-1.5	1.5-2.2	2.2-3.5
D−H···A angles range (˚)	175-180	130-180	90-180



(a) **(b)**

Figure 17 Two views of parallel planes of the aromatic ligands in $[HgCl_2(phen)_2]$ a) With a distance of 3.303Å. [Symmetry code: (A) 2-*x*, -*y*, 1-*z*.] b) With a distance of 3.371Å. [Symmetry code: (A) 1-*x*, 1-*y*, 1-*z*].

This type of non-covalent interactions requires having two parallel *π*-rings in the crystal structure in the distance of about 3.5Å provided that the rings as Fig. 16 do not overlap directly. Since this is an electrostatic interaction, so exact overlapping of rings will cause repulsion of *π*-clouds.

There are some examples in our team works, for example as in Fig. 17, in a complex of mercury(II), [$HgCl_2(phen)_2$] (phen: 1,10-phenanthroline, at a distance of 3.303 and 3.371Å, we have a π-π stacking interaction. As mentioned above, it can be seen another example of the interaction in Fig. 11 of Zn^{II} complex.

3.3.3 C–H···π Stacking

There is a weak interaction between C−H bond and π ring, if they are in an optimum distance and angle to each other (Fig. 18). It is also referred to as *edge-to-face stacking*. As an example in Fig. 19, in a proton transfer compound, propane-1,3-diaminium pyridine-2,3-dicarboxylate monohydrate [17], it can be observed a C−H···π stacking at H···π distance of 2.806Å and C−H···π angle of 137.23˚.

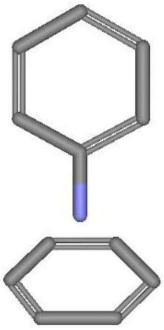


Figure 18 C−H···π Stacking or edge-to-face stacking.

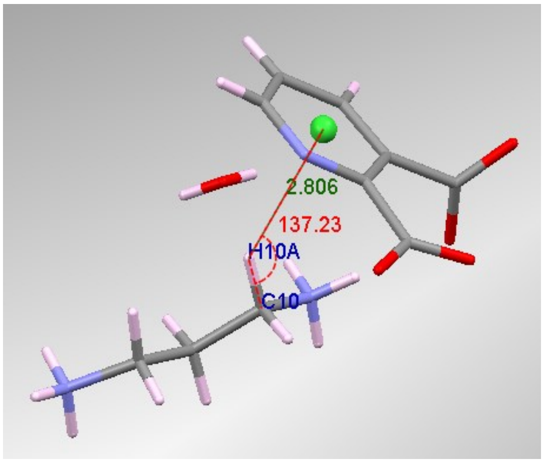
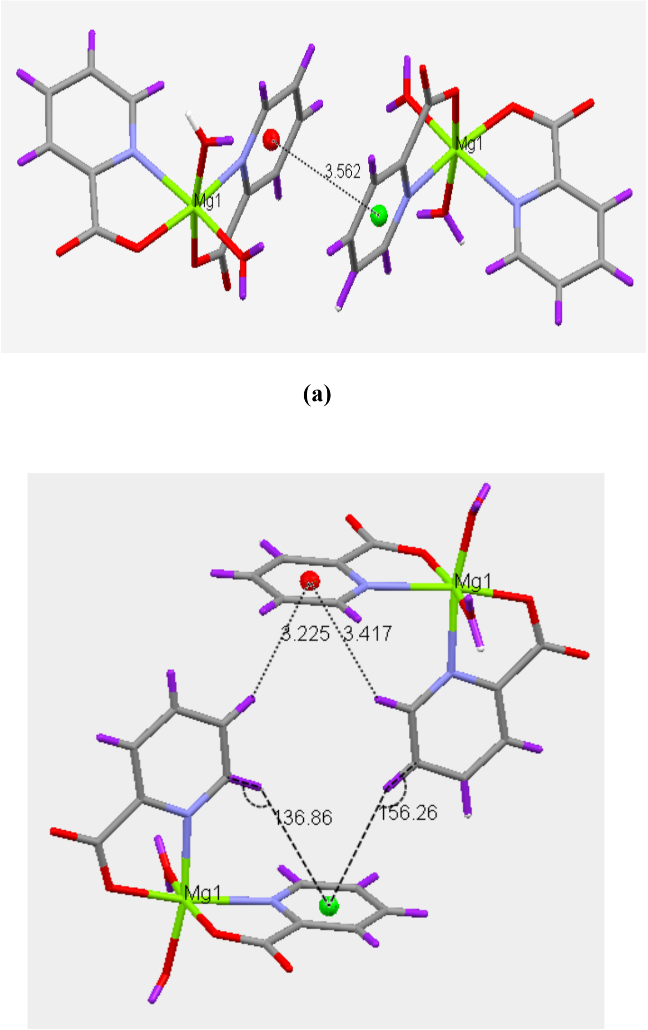


Figure 19 C−H···π Stacking with its distance and angle inpropane-1,3-diaminium pyridine-2,3-dicarboxylate monohydrate.

In addition, there are some other interesting examples in our recent work, *i.e.* $Mg(pyc)_2(H_2O)_2]\cdot 0.15\ H_2O$ (pyc: pyridine-2-carboxylate) which as shown in Fig. 20, has π-π and C−H···π stackings, simultaneously [35].



(a)

(b)

Figure 20 a) C−H···π and b) π-π stacking with the distances and angles in Mg^{II} complex with pyridine-2-carboxylate and water ligands.

3.3.4 Other types of interactions

In some supramolecular networks such as an antimony(III) complex that is illustrated in Fig. 21, there are weak interactions like C−H···Cl and C−H···S as well as C−H···π contacts. In this example, C−H···Cl distances are 3.298(6), 3.287(5), 3.6519(6) and 3. 869(5)Å, C−H···S distances are 3.414(5) and 3.380(5)Å, and C−H···π distance is 3.852(1)Å [36].

Like the above structure, there are many other examples with such weak interactions like C−H···O, N−H···F–C and O−H···π (see Table 10). As a conclusion, the interactions discussed here and any other interactions such as van der Waals or ion pairing generally have an electrostatic force foundation.

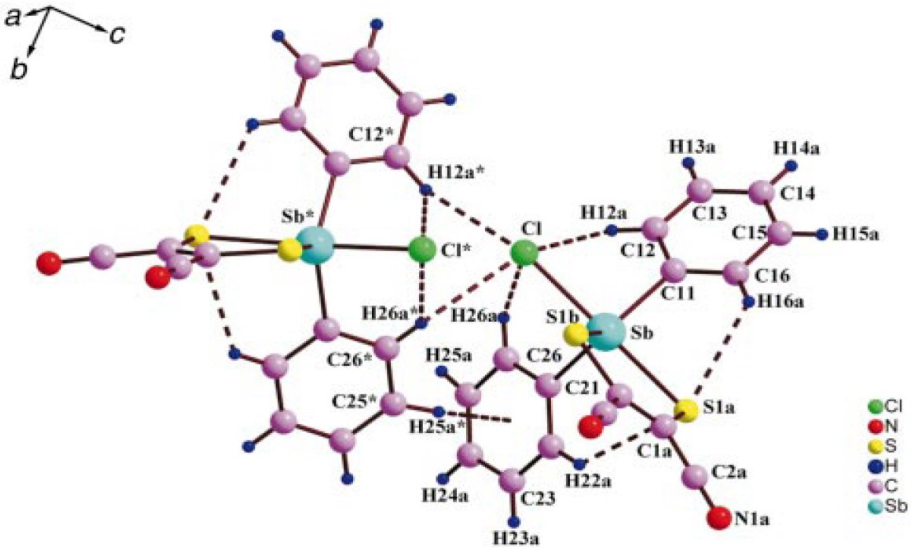


Figure 21 Inter- and intramolecular C−H···Cl and C−H···S as well as C−H···π contacts in a Sb^{III}

References

[1] Wang L., Duan L., Wang E., Xiao D., Li Y., Lan Y., Xu L. and Hu C., Transition Metal Chemistry, Vol. 29 , pp. 212–215, **2004**.

[2] Smith G., Wermuth U. D. and White J. M., Aust. J. Chem., Vol. 54, p. 171, **2001**.

[3] Smith G., Wermuth U. D., Bott R. C., White J. M. and Willis A. C., Aust. J. Chem., Vol. 54, p. 165.., **2001**.

[4] Smith G., Bott R. C., Rae A. D. and Willis A. C., Aust. J. Chem., Vol. 53, p. 531, **2000**.

[5] Smith G., Pascoe C. E., Kennard C. H. L. and Byriel K. A., Aust. J. Chem., Vol. 52, p. 71, **1999**.

[6] Lynch D. E., Smith G., Byriel K. A. and Kennard C. H. L., Aust. J. Chem., Vol. 47, p. 1789, **1994**.

[7] Smith G., Hartono A. W., Wermuth U. D., Healy P. C., White J. M. and Rae A. D., Aust. J. Chem., Vol. 58, p. 47, **2005**.

[8] Lynch D. E., Smith G., Byriel K. A., Kennard C. H. L. and Whittaker A. K., Aust. J. Chem. Vol. 47, p. 309, **1994**.

[9] Arora K. K. and Pedireddi V. R., J. Org. Chem., Vol. 68, pp. 9177-9185, **2003.**

[10] a) Moghimi A., Ranjbar M., Aghabozorg H., Jalai F., Shamsipur M., Yap G. A. P. and Rahbarnoohi H., J. Mol. Struct., Vol. 605, 2002, pp. 133-149. b) Aghabozorg H., Saie A. A. and Ramezanipour F., Acta Crystallogr., 2005, Vol. E61, pp. o3242-o3244. c) Soleimannejad J., Sharif M., Sheshmani S., Alizadeh R., Moghimi A. and Aghabozorg H., Anal. Sci., Vol. 21, 2005, pp. x49-x50. d) Moghimi A., Aghabozorg H., Soleimannejad J. and Ramezanipour F., Acta Crystallogr., Vol. E61, 2005, p. o442-o444. e) Moghimi A., Aghabozorg H., Sheshmani S. and Soleimannejad J., Anal. Sci., Vol. 21, 2005, pp. x71-x72. f) Aghabozorg H., Soleimannejad J., Sharif M. A., Sheshmani S. and Moghimi A., Anal. Sci., Vol. 21, 2005, x73-x74. g) Moghimi A., Aaghabozorg H., Sheshmani S., Kickelbick G. and Soleimannejad J., Anal. Sci., Vol. 21, 2005, x141-x142. h) Aghabozorg H., Ghadermazi M. and Ramezanipour F., Acta Crystallogr., Vol. E62, 2006, pp. o1143-o1146. i) Moghimi A., Alizadeh R., Shokrollahi A., Aghabozorg H. and Shockravi M. A., Inorg. Chem., Vol. 42, 2003, pp. 1616-1624. j) Moghimi A., Moosavi S. M., Kordestani D., Maddah B., Shamsipur M., Aghabozorg H., Ramezanipour F. and Kickelbick G., J. Mol. Struct. Vol. 828, pp. 38–45, **2007**.

[11] a) Aghabozorg H., Ghasemikhah P., Ghadermazi M. Soleimannejad J. And Adams, H., Acta Cryst., Vol. E63, 2007, pp. m1487-m1489. b) Aghabozorg H., Ramezanipour F., Dalir Kheirollahi P., Saie A. A., Shokrollahi A., Shamsipur M., Manteghi F., Soleimannejad J. and Sharif M., Z. Anorg. Allg. Chem., Vol. 632, 2006, pp. 147-154. c) Ramezanipour F., Aghabozorg H., Shokrollahi A., Shamsipur M., Stoeckli-Evans H., Soleimannejad J. And Sheshmani S., J. Mol. Struct., Vol. 779, 2005, pp. 77-86. d) Aghabozorg H., Ghadermazi M., Manteghi F. and Nakhjavan B., Z. Anorg. Allg. Chem., Vol. 632, 2006, pp. 2058-2064. e) Ranjbar M., Aghabozorg H. and Moghimi A., Anal. Sci., Vol. 19, 2003, pp. x71-x72. f) Ranjbar M., Moghimi A. and Aghabozorg H., Anal. Sci., Vol. 19, 2003, pp. 803-804. g) Aghabozorg H., Ghasemikhah P., Ghadermazi M. and Sheshmani S., Acta Cryst., Vol. E62, 2006, pp. m2835-m2837. h) Aghabozorg H., Dalir Kheirollahi P., Moghimi A. and Sadr-Khanlou, E., Anal. Sci., Vol. 21, 2005, pp. x79-x80. i) Aghabozorg H., Saei A. A., Sadr-Khanlou E. and Moghimi A., Anal. Sci., Vol. 21, 2005, pp. x207-208. j) Sheshmani S., Dalir Kheirollahi P., Aghabozorg H., Shokrollahi A., Kickelbick G., Shamsipur M., Ramezanipour F. and Moghimi A., Z. Anorg. Allg. Chem., Vol. 631, 2005, pp. 3058-3065. k) Ranjbar M., Aghabozorg, H.; Moghimi, A. Z. Kristallogr. NCS 2003, 218, pp. 432-434. l) Sharif M. A., Aghabozorg H. and Moghimi A., Acta Cryst., Vol. E63, 2007, m1599-m1601. m) Aghabozorg H., Motyeian E., Aghajani Z, Ghadermazi M. and Attar Gharamaleki J., Acta Cryst. Vol. E63, 2007, pp. m1754-m1755. n) Aghabozorg H. and Sadr Khanlou E., Acta Cryst., Vol. E63, 2007, p. m1753. o) Aghabozorg H., Ghasemikhah P., Soleimannejad J., Ghadermazi M. and Attar Gharamaleki, J., Acta Cryst., Vol. E62, 2006, pp. m2266-m2268. p) Aghabozorg H., Sadr Khanlou E., Soleimannejad J. and Adams H., Acta Cryst., Vol. E63, 2007, p. m1760. q) Aghabozorg H., Mohammadpanah F. and Sadr Khanlou E., Acta Cryst., Vol. E62, pp. m2509-m2511, **2006**.

[12] a) Dalir Kheirollahi P., Aghabozorg H. and Moghimi A., Anal. Sci., Vol. 21, 2005, pp. x153-x154. b) Aghabozorg H., Moghimi A., Manteghi F. and Ranjbar M., Z. Anorg. Allg. Chem., Vol. 21, 2005, pp. 909-913. c) Moghimi A., Alizadeh R., Aragoni M. C., Lipolis V., Aghabozorg H., Norouzi P., Isaia F. and Sheshmani S., Z. Anorg. Allg. Chem., Vol. 631, 2005, pp. 1941-1946. d) Moghimi A., Shokrollahi A., Shamsipur M., Aghabozorg H. and Ranjbar M., J. Mol. Struct., Vol. 701, 2004, pp. 49-56. e) Sheshmani S., Aghabozorg H., Mohammad Panah F., Alizadeh R., Kickelbick G., Nakhjavan B., Moghimi A., Ramezanipour F. and Aghabozorg H. R., Z. Anorg. Allg. Chem., Vol. 632, 2006, pp. 469-474. f) Moghimi A., Ranjbar M., Aghabozorg H., Jalali F., Shamsipur M. and Chadha K. K., Can. J. Chem., Vol. 80, 2002, pp. 1687-1696. g) Moghimi A., Ranjbar M., Aghabozorg H., Jalali F., Shamsipur M. and Chadah R. K., J. Chem. Research(S), 2002, pp. 2-4. h) Aghabozorg H., Attar Gharamaleki J., Ghasemikhah P., Ghadermazi M. and Soleimannejad J., Acta Cryst., Vol. E63, 2007, pp. m1710-m1711. i) Ranjbar M., Aghabozorg H. and Moghimi A., Z. Kristallogr. NCS. Vol. 218, 2003, pp. 75-76. j) Moghimi A., Alizadeh R., Aghabozorg H., Shockravi A., Aragoni M.C., Demartin F., Isaia F., Lippolis V., Harrison A., Shokrollahi A. and Shamsipur M., J. Mol. Struct., Vol. 750, 2005, pp. 166-173. k)

Aghabozorg H., Zabihi F., Ghadermazi M., Attar Gharamaleki J. and Sheshmani S., Acta Cryst., Vol. E62, 2006, pp. m2091-m2093. l) Moghimi A., Sheshmani S., Shokrollahi A., Shamsipur M., Kickelbick G. and Aghabozorg H., Z. Anorg. Allg. Chem., Vol. 631, 2005, pp. 160-169. m) Moghimi A., Sharif M. A., Shokrollahi A., Shamsipur M., and Aghabozorg H., Z. Anorg. Allg. Chem., Vol. 631, 2005, pp. 902-908. n) Aghabozorg H., Nakhjavan B., Zabihi F., Ramezanipour F. and Aghabozorg H. R., Acta Cryst., Vol. E61, 2005, pp. m2664-m2666. o) Aghajani Z., Sharif M. A., Aghabozorg H. and Naderpour A., Acta Cryst., Vol. E62, 2006, pp, m830-m832. p) Moghimi A., Sharif M. A. and Aghabozorg H., Acta Cryst., Vol. E60, 2004, pp. o1790-o1792. q) Ranjbar M., Moghimi A., Aghabozorg H. and Yap G. P. A., Anal. Sci., Vol. 18, 2002, pp. 219-220. r) Moghimi A., Sheshmani S., Shokrollahi A., Aghabozorg H., Shamsipur M., Kickelbick G., Aragoni M. C. and Lippolis V., Z. Anorg. Allg. Chem., Vol. 630, 2004, pp. 617-624. s) Ramezanipour F., Aghabozorg H., Sheshmani S., Moghimi A. and Stoeckli-Evans H., Acta Cryst., Vol. E60, 2004, pp. m1803-m1805. t) Ranjbar M., Aghabozorg H. and Moghimi A., Acta Cryst., Vol. E58, 2002, pp. m304-m306. u) Aghabozorg H., Aghajani Z. and Sharif M. A., Acta Cryst., Vol. E62, 2006, pp. m1930-m1932. v) Ramezanipour F., Aghabozorg H. and Soleimannejad J., Acta Cryst., Vol. E61, 2005, pp. m1194-m196. w) Aghabozorg H., Ghasemikhah P., Ghadermazi M., Attar Gharamaleki J. and Sheshmani S., Acta Cryst., Vol. E62, pp. m2269-m2271, **2006**.

[13] Etter M. C., Acc. Chem. Res., Vol. 23, p. 120, **1990**.

[14] Gonzalez-Baro´ A. C., Castellano E. E., Piro O. E. and Parajo´n-Costa, B. S., Polyhedron, Vol. 24, p. 49, **2005**.

[15] Hall A. K., Harrowfield J. M., Skelton B. W. and White A. H., Acta Cryst., Vol. C56, pp. 448-450, **2000**.

[16] Zhou G., Guo G., Liu B., Wang M., Cai L. and Huang J., Bull. Korean Chem. Soc., Vol. 25(5), pp. 676-680, **2004**.

[17] Manteghi F., Ghadermazi M., Aghabozorg A., Acta Cryst. Vol. E63, p. o2809, **2007**.

[18] Aghabozorg H., Ghadermazi M., Sheshmani S. and Attar Gharamaleki J., Acta Cryst., Vol. E63, pp. o2985-o2986, **2007**.

[19] Bruker, APEX2 softwarwe package, Bruker AXS Inc., 5465, East Cheryl Parkway, Madison, WI 5317, **2005**.

[20] Sheldrick, G. M. SHELXTL v. 5.10, Structure determination software suite, Bruker AXS, Madison, Wisconsin, USA, **1998**.

[21] Gao H., Yi L., Zhao B., Zhao X., Cheng P., Liao D. and Yan, S., Inorg. Chem., Vol. 45, pp. 5980-5988, **2006**.

[22] Mendoza-Dı´az G., Rigotti G., Piro O. E. and Sileo, E. E., Polyhedron, Vol. 24, pp. 777-783, **2005**.

[23] Aghabozorg H., Ghadermazi M. and Nemati A., Anal. Sci., Vol. 22, pp. x233-x234, **2006**.

[24] Bruker, SMART, v. 5.059, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, Wisconsin, USA, **1998b**.

[25] Bruker, SAINTPlus, v. 6.01, Data Reduction and Correction Program, Bruker AXS, Madison, Wisconsin, USA, **1998a**.

[26] Sheldrick, G. M. SHELXTL, v. 5.10, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, **1998b**.

[27] Feynman R., Eng. Sci., pp. 22-36, **1960**.

[28] Steed J. W., Atwood J. L., "Supramolecular chemistry," J. Wiley and sons, **2000**.

[29] Lehn J. M., "Supramolecular chemistry," VCH, **1995**.

[30] Jiang L. and Lai L., J. Biol. Chem., Vol. 277(40), pp. 37732-37740, **2002**.

[31] Desiraju G. R., "Crystal design: structure and function," John Wiley and sons, **2003**.

[32] Jeffrey J. A., "an introduction to hydrogen bonding," Oxford University Press, **1997**.

[33] Desiraju G. R., Steiner T., "the Weak hydrogen bonds in structural chemistry and biology," Oxford University Press, **1999**.

[34] Sutor J. D., The C-H…O Hydrogen bond in Crystals, Nature, Vol. 195, pp. 68-69, **1962**.

[35] Sharif M. A., Aghabozorg H., Motyeian E., Ghadermazi M. and Attar Gharamaleki J., Acta Cryst., Vol. E63, pp. m2235-m2236, **2007**.

[36] Chandrasekhar V., Baskar V., Kingsley S., Nagendrana S. and Butcherb R. J., Cryst. Eng. Comm., Vol. 17, pp. 1–3, **2001**.