

A Brief Review on Structural Concepts of Novel Supramolecular Proton Transfer Compounds and Their Metal Complexes

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Our research group has been interested in synthesis of proton transfer compounds as new supramolecular synthons for the one-pot preparation of self-assembled transition metal complex-organo-networks since 2000. We have focused on the proton delivery from acids, which are considered as suitable proton donors, to amines as proton acceptors. The results were production of several proton transfer ion pairs possessing some remaining donor sites applied for coordination to metallic centers in preparation of metal-organic structures. Some of the complexes showed contributions of both cationic and anionic fragments of the starting ion pair, while some others contained only one of these species as ligand. Much of the investigations on reviewed compounds focused on the concept of supramolecular systems, co-crystallization, stereochemically active lone pairs, coordination polyhedron and mainly on various interactions involve including van der Waals, ion pairing, hydrogen bondings, face to face π - π stackings and edge to face C-H $\cdots\pi$, C-O $\cdots\pi$, N-H $\cdots\pi$, S-O $\cdots\pi$, Ti $\cdots\pi$ and Hg-Cl $\cdots\pi$ interactions. The mentioned interactions are the most commonly used strategies in the extension of supramolecular structures.

Keywords: Proton transfer compounds, Supramolecular systems, Hydrogen bonds and π - π stacking, Stereochemically active lone pair, Coordination polyhedron, Crystal structure

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 [1].

The existing design strategies for the synthesis of extended inorganic networks follow two principal methods based on the different nature of the interactions responsible for their

networking. In one approach, which is the more frequently used, coordinative covalent bonds engaged between main group, transition or lanthanide elements and various organic linkers, propagate the coordination geometry into infinite architectures of various dimensionality and topology [2-16]. The other method, still far less common, exploits weaker intermolecular forces (particularly π - π stacking, hydrogen bonding, and ion pairing) as a guide to the assembly of molecular coordination complexes into extended organized networks [9-12].

The approach we have applied in the preparation of such systems is the use of proton transfer ion pairs obtained from processes between appropriate carboxylic acids and amines.

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This is because functionalized carboxylic acids and amines can enhance the intermolecular forces between the obtained cationic and anionic fragments, and interactions described above can provide a large part of the stabilization energy of resulting self-assembly systems. In complexes thus obtained, the ion pairs act as ligand or counter ion, partially or totally, as

extensively given in Table 1. The anionic fragment of the ion pair is usually, not always, coordinated to metallic ion and lies in the *ligand domain*, and the counter ion remains in the *periphery domain* [17]. In all of the reviewed compounds, we noticed a significant contribution of hydrogen bonding to the stabilization of resulting 3D networks in the crystal structures.

Table 1. The Proton Transfer Compounds, Metal Complexes, Cocrystal and Adducts Reported

Proton transfer compounds, metal complexes, cocrystal and adducts	Studies	Crystal system and space group	Coordination polyhedron	Ref. no.
(pydaH ₂)(pydc) ^a	¹³ C NMR, Mass, solution studies, crystal structure	Monoclinic, $P2_1/c$	-	[31]
(pydaH)(pydcH) ^a	IR, crystal structure	Monoclinic, $P2_1/c$	-	[32]
(pydaH) ₂ [Co(pydc) ₂].H ₂ O ^b	¹ H, ¹³ C NMR, solution studies, crystal structure	Monoclinic, $P2_1/n$	Distorted octahedral	[33]
(pydaH) ₂ [Ni(pydc) ₂].H ₂ O ^b	¹³ C NMR, Es-MS, elemental analysis, solution studies, crystal structure	Monoclinic, $P2_1/n$	Distorted octahedral	[34]
(pydaH) ₂ [Cu(pydc) ₂].H ₂ O ^b	IR, solution studies, crystal structure	Monoclinic, $P2_1/n$	Distorted octahedral	[35]
(pydaH) ₂ [Bi ₂ (pydc) ₄ (H ₂ O) ₂].4H ₂ O ^b	Crystal structure	Triclinic, $P\bar{1}$	Distorted dodecahedron	[36]
(pydaH) ₂ [La ₂ (pydc) ₄ (H ₂ O) ₄].2H ₂ O ^b	¹ H, ¹³ C NMR, solution studies, crystal structure	Triclinic, $P\bar{1}$	Distorted tricapped trigonal prism	[33]
(pydaH) ₂ [Ce(pydc) ₂ (H ₂ O) ₂].2H ₂ O ^b	IR, ¹ H, ¹³ C NMR, elemental analysis, solution studies, crystal structure	Triclinic, $P\bar{1}$	Distorted tricapped trigonal prism	[37]
(pydaH) ₂ [Zr(pydc) ₃].5H ₂ O ^b	IR, NMR, Es-MS, elemental analysis, crystal structure	Triclinic, $P\bar{1}$	Distorted tricapped anti-prism	[38]
(pydaH) ₂ [PdCl ₄] ^b	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted square planer	[39]

Table 1. Continued

(pydaH)[Sb(pydc) ₂].3H ₂ O.0.5CHCl ₃ ^b	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted tetragonal	[40]
(pydaH)[Ga(pydc) ₂].3.25H ₂ O.CH ₃ OH ^b	IR, ¹ H, ¹³ CNMR, elemental analysis, solution studies, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[41]
(pydaH)[Cr(pydc) ₂].pydcH ₂ .0.5H ₂ O ^b	IR, crystal structure	Monoclinic, $P2_1/c$	Distorted octahedral	[42]
(pydaH)[Zn(pydc)(pydcH)].3H ₂ O ^b	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[43]
(pydaH)[V(pydc)O ₂] ^b	IR, crystal structure	Monoclinic, $P2_1/m$	Distorted trigonal bipyramid	[44]
{(pydaH)[HgCl(pydc)].H ₂ O} _n ^b	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[45]
[{BiCl(H ₂ O)(pydc)} ₂] _n ^b	IR, crystal structure	Monoclinic, $P2_1/c$	Distorted pentagonal bipyramidal	[46]
{[Pb(pydc)(pydcH ₂)(H ₂ O) ₂] ₂ } _n ^b	IR, crystal structure	Triclinic, $P\bar{1}$	Highly distorted octahedral plus three weak interactions	[47]
{(pydaH) ₂ [Hg(pydc)Cl] ₂ .2H ₂ O} _n ^b	IR, ¹ H, ¹³ CNMR, elemental analysis, solution studies, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[48]
[Cd(pydc)(H ₂ O) ₃] ₂ .2pydcH ₂ ^b	IR, crystal structure	Monoclinic, $P2_1/c$	Distorted pentagonal bipyramidal	[49]
[Sn(pydc)(OH)(H ₂ O)(μ-OH)] ₂ .4H ₂ O ^b	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted pentagonal bipyramidal	[50]
[Sb(pydc)(H ₂ O)] ₂ O ^b	IR, crystal structure	Monoclinic, $P2_1/n$	Distorted tetragonal pyramidal	[51]
[In(pydc)(pydcH)(H ₂ O) ₂].5H ₂ O ^b	IR, ¹ H NMR, elemental analysis, solution studies, crystal structure	Orthorhombic, $Pna2_1$	Distorted bicapped trigonal prism	[41]

Table 1. Continued

[Ni(pydcH) ₂].3H ₂ O ^b	¹³ C NMR, Es-Ms, elemental analysis, solution studies, crystal structure	Monoclinic, <i>P2₁/c</i>	Distorted octahedral	[34]
Ti(pydc)(Cp) ₂ ^b	IR, crystal structure	Tetragonal, <i>P4₃2₁2</i>	Highly distorted trigonal bipyramidal	[52]
[Pd(pydc)(oxa)].H ₂ O ^b	IR, crystal structure	Triclinic, <i>P$\bar{1}$</i>	Distorted square planar	[53]
(pydaH ₂)(phencd) ^a	IR, NMR, UV-Vis, Es-Ms, elemental analysis	-	-	[54]
(pydaH) ₂ [Co(phencd) ₂].10H ₂ O ^b	IR, ¹³ C CP-MAS NMR, elemental analysis, crystal structure	Monoclinic, <i>P2₁/n</i>	Distorted octahedral	[54]
(pydaH) ₂ [Cu(phencd) ₂].10H ₂ O ^b	IR, ¹³ C CP-MAS NMR, elemental analysis, solution studies, crystal structure	Monoclinic, <i>P2₁/n</i>	Distorted octahedral	[55]
(pydaH) ₂ [Cu(phencd)(phencdH)] ₂ .5H ₂ O ^b	IR, ¹³ C CP-MAS NMR, elemental analysis, solution studies, crystal structure	Monoclinic, <i>P2₁/c</i>	Distorted octahedral	[55]
(pydaH)[Cr(phencd) ₂].5H ₂ O ^b	IR, elemental analysis, cyclic voltammetry, crystal structure	Monoclinic, <i>P2₁/n</i>	Distorted octahedral	[56]
(phenH) ₂ (pydc) ^a	IR, ¹ H, ¹³ C NMR, ¹³ C CP-MAS NMR, solution studies	-	-	[57]
[Zn(pydc) ₂][Zn(phen) ₂ (H ₂ O) ₂].7H ₂ O ^b	¹ H, ¹³ C NMR, solution studies, crystal structure	Triclinic, <i>P$\bar{1}$</i>	Distorted octahedral	[57]
[Zn(phen) ₃] ₄ (H(pydcH) ₂)(NO ₃) ₇ .26H ₂ O ^b	¹ H, ¹³ C NMR, solution studies, crystal structure	Triclinic, <i>P$\bar{1}$</i>	Distorted octahedral	[57]
[Cd(pydc)(phen) ₂].pydcH ₂ .4H ₂ O ^b	IR, ¹ H, ¹³ C NMR, crystal structure	Triclinic, <i>P$\bar{1}$</i>	Distorted pentagonal bipyramidal	[58]

Table 1. Continued

$[\text{In}_2\text{SO}_4(\text{pydc})_2(\text{phen})_2(\text{H}_2\text{O})_2].5.5\text{H}_2\text{O}^{\text{b}}$	IR, solution studies, crystal structure	Triclinic, $P\bar{1}$	Distorted pentagonal bipyramidal	[59]
$\{\text{Ce}(\text{pydc})(\text{pydcH})(\text{H}_2\text{O})_2\}.4\text{H}_2\text{O}\}_n^{\text{b}}$	IR, solution studies, crystal structure	Monoclinic, $P2_1/c$	Distorted tricapped trigonal prism	[59]
$[\text{HgCl}_2(\text{phen})_2]^{\text{b}}$	IR, crystal structure	Monoclinic, $P2_1/c$	Distorted octahedral	[60]
$(\text{phenH})_2[\text{Bi}(\text{pydc})_2(\text{H}_2\text{O})_2].5\text{H}_2\text{O}^{\text{b}}$	IR, ^1H , ^{13}C NMR, solution studies, crystal structure	Triclinic, $P\bar{1}$	Distorted bicapped trigonal prism	[37]
$[\text{Sn}(\text{pydc})(\text{phen})(\text{OH})_2].3\text{H}_2\text{O}^{\text{b}}$	IR, crystal structure	Triclinic, $P\bar{1}$	Pentagonal bipyramidal with slight distortion	[61]
$\{\text{Sb}(\text{pydc})(\text{phen})_2\}.2\text{DMSO}.4\text{H}_2\text{O}^{\text{b}}$	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted pentagonal pyramidal	[61]
$[(\text{Ti}(\text{pydcH}))_n]^{\text{b}}$	IR, crystal structure	Monoclinic, $P2_1/c$	Distorted square pyramidal	[61]
$(\text{phenH})_3[\text{Y}(\text{pydc})_3].\text{DMSO}.5\text{H}_2\text{O}^{\text{b}}$	Crystal structure	Triclinic, $P1$	Distorted tricapped trigonal prism	[62]
$(\text{GH})_2(\text{pydc}).\text{H}_2\text{O}^{\text{a}}$	IR, ^1H , ^{13}C NMR, solution studies, crystal structure	Monoclinic, $C2/c$	-	[63]
$(\text{GH})_2[\text{Cd}(\text{pydc})_2].2\text{H}_2\text{O}^{\text{b}}$	IR, ^1H , ^{13}C NMR, solution studies, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[63]
$(\text{GH})_3[\text{Ce}(\text{pydc})_3].3\text{H}_2\text{O}^{\text{b}}$	IR, crystal structure	Orthorhombic, $Pbca$	Tricapped trigonal prism	[64]
$(\text{GH})_2[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{pydc})_2]_2^{\text{b}}$	IR, ^1H , ^{13}C NMR, crystal structure	Monoclinic, $P2_1/n$	Distorted & regular octahedrals	[65]
$(\text{GH})[\text{Zn}(\text{pydc})(\text{pydcH})].(\text{pydcH}_2).4\text{H}_2\text{O}^{\text{b}}$	IR, ^1H , ^{13}C NMR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[66]
$(\text{GH})_2(\text{phendc})^{\text{a}}$	IR, ^1H , ^{13}C NMR	-	-	[65]
$(\text{GH})_2[\text{Co}(\text{phendc})_2].4\text{H}_2\text{O}^{\text{b}}$	IR, ^1H , ^{13}C NMR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral environment	[65]
$(\text{tataH}_2)(\text{pydc})^{\text{a}}$ $(\text{tataH})_2(\text{pydc})^{\text{a}}$	IR, ^1H , ^{13}C NMR, CPMAS ^{13}C NMR	-	-	[67]

Table 1. Continued

$(\text{tataH}_2)_2[\text{Pb}(\text{pydc})_2]_2 \cdot 2\text{tata} \cdot 4\text{H}_2\text{O}^b$	IR, ^1H , ^{13}C NMR, CPMAS ^{13}C NMR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[67]
$(\text{tataH})_2[\text{Zn}(\text{pydc})_2] \cdot 10\text{H}_2\text{O}^b$	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[68]
$(\text{tataH})_2[\text{Cd}(\text{pydc})_2]^b$	IR, crystal structure	Monoclinic, Cc	Distorted octahedral	[69]
$\{(\text{tataH})[\text{Bi}(\text{pydc})_2(\text{H}_2\text{O})]\}_n^b$	IR, crystal structure	Monoclinic, $P2_1/c$	Distorted square antiprism	[70]
$(\text{tataH})_2[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{pydc})_2]_2 \cdot 4\text{H}_2\text{O}^b$	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[71]
$(\text{tataH})_2[\text{Ni}(\text{pydc})_2] \cdot 5.25\text{H}_2\text{O}^b$	IR, crystal structure	Monoclinic, $P2_1/c$	Distorted octahedral	[72]
$(\text{pipzH}_2)(\text{pydc})^a$	IR, ^1H , ^{13}C NMR, crystal structure	Triclinic, $P\bar{1}$	-	[73]
$(\text{pipzH}_2)[\text{Pd}(\text{pydc})_2] \cdot 2\text{H}_2\text{O}^b$	IR, ^1H , ^{13}C NMR, crystal structure	Triclinic, $P\bar{1}$	Square planar	[73]
$(\text{pipzH}_2)(\text{Tl}_2(\text{pydc})_2\text{Cl}_4(\text{H}_2\text{O})_2) \cdot 4\text{H}_2\text{O}^b$	IR, ^1H , ^{13}C NMR, crystal structure	Triclinic, $P\bar{1}$	Distorted pentagonal bipyramidal	[73]
$[\text{Mg}(\text{pydc})(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}^b$	IR, crystal structure	Monoclinic, $P2_1/n$	Distorted octahedral	[74]
$(\text{pipzH}_2)_3[\text{In}(\text{pydc})_3]_2 \cdot 12\text{H}_2\text{O}^b$	IR, crystal structure	Monoclinic, $P2_1/c$	Distorted dodecahedron	[75]
$(\text{pipzH}_2)[\text{Ni}(\text{pydc})_2] \cdot 4\text{H}_2\text{O}^b$	IR, crystal structure	Monoclinic, $P2_1/n$	Distorted octahedral	[76]
$(\text{pipzH}_2)[\text{Cu}(\text{pydc})_2] \cdot 4\text{H}_2\text{O}^b$	IR, crystal structure	Monoclinic, $P2_1/n$	Distorted octahedral	[77]
$(\text{pipzH}_2)[\text{Mn}(\text{pydc})_2] \cdot 6\text{H}_2\text{O}^b$	IR, crystal structure	Orthorhombic, $Pbcn$	Distorted octahedral	[78]
$(\text{pipzH}_2)[\text{Pb}(\text{pydc})_2] \cdot 2\text{H}_2\text{O}^b$	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[79]
$(\text{pipzH}_2)[\text{Zn}(\text{pydc})_2] \cdot 4\text{H}_2\text{O}^b$	IR, ^1H , ^{13}C NMR, crystal structure	Monoclinic, $P2_1/n$	Distorted octahedral	[80]
$(\text{pipzH}_2)[\text{Hg}(\text{pydc})_2] \cdot 6\text{H}_2\text{O}^b$	IR, crystal structure	Orthorhombic, $Pbcn$	Distorted octahedral	[81]
$(\text{pipzH}_2)[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{pydc})_2]_2 \cdot 8\text{H}_2\text{O}^b$	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[82]
$(\text{pipzH}_2)_{1/2}[\text{Al}(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}^b$	IR, crystal structure	Monoclinic, $P2_1/n$	Octahedral	[83]

Table 1. Continued

(pipzH ₂)(ox).H ₂ O ^a	IR, crystal structure	Monoclinic, $P2_1/c$	-	[84]
[Mn(ox)(H ₂ O) ₂] _n ^b	IR, crystal structure	Monoclinic, $C2/c$	Distorted octahedral	[85]
(pipzH ₂)[V(ox) ₂ O(H ₂ O)].2H ₂ O ^b	IR, crystal structure	Monoclinic, $P2_1/n$	Distorted octahedral	[86]
(pipzH ₂) _{1/2} (py-2,3-dcH) ^a	IR, crystal structure	Monoclinic, $P2_1/c$	-	[87]
{(pipzH ₂)[Zn(py-2,3-dc) ₂].4H ₂ O} _n ^b	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[88]
[Cd(py-2,3-dc)(H ₂ O) ₃] _n ^b	IR, crystal structure	Orthorhombic, $Pca2_1$	Distorted octahedral	[89]
(pipzH ₂)(py-2,5-dc).2H ₂ O ^a	IR, crystal structure	Triclinic, $P\bar{1}$	-	[90]
(pipzH ₂)[Cd(py-2,5-dc) ₂ (py-2,5-dcH)].3H ₂ O ^b	IR, crystal structure	Monoclinic, $P2_1/n$	Distorted octahedral	[91]
{(pipzH ₂)[Zn(py-2,5-dc) ₂ (H ₂ O)].2H ₂ O} _n ^b	IR, crystal structure	Monoclinic, $P2_1/c$	Distorted octahedral	[92]
[Ni(py-2,5-dc)(H ₂ O) ₄].H ₂ O ^b	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[93]
(pipzH ₂)(pydcH) ₂ .3H ₂ O ^a	IR, crystal structure	Monoclinic, $C2/c$	-	[94]
(pipzH ₂)[Fe(pydc) ₂].H ₂ O ^b	IR, crystal structure	Monoclinic, $P2_1/n$	Distorted octahedral	[95]
{(pipzH ₂)[Bi ₂ (pydc) ₄ (H ₂ O)].2H ₂ O} _n ^b	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[96]
(pipzH ₂) ₃ [Nd(pydc) ₃] ₂ .15.33H ₂ O ^b	IR, crystal structure	Trigonal, $P\bar{3}$	Distorted tricapped trigonal prism	[97]
(pipzH ₂) _{1/2} (pydcH).(pydcH ₂).H ₂ O ^a	IR, crystal structure	Triclinic, $P\bar{1}$	-	[98]
pyc·pydcH ₂ .H ₂ O ^c	IR, crystal structure	Monoclinic, $P2_1/c$	-	[99]
(EDGH ₂)(pydc).3H ₂ O ^c	¹ H, ¹³ C NMR, crystal structure	Triclinic, $P\bar{1}$	-	[100]
(EDGH ₂)[Zn(pydc) ₂].3H ₂ O ^b	IR, ¹ H, ¹³ C NMR, crystal structure	Monoclinic, $P2_1/c$	Distorted octahedral	[79]
(creatH)(pydcH).H ₂ O ^a	IR, ¹ H, ¹³ C NMR, solution studies, crystal structure	Orthorhombic, $Pnam$	-	[101]
(creatH)[Zn(pydc)(pydcH)].4H ₂ O ^b	IR, ¹ H, ¹³ C NMR, solution studies, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[102]
[Ti ₂ (pydcH) ₃ (pydc)(H ₂ O) ₂] _n ^b	IR, ¹ H, ¹³ C NMR, elemental analysis, solution studies, crystal structure	Triclinic, $P\bar{1}$	Distorted pentagonal bipyramidal	[41]

Table 1. Continued

[Cu(pydc)(pydcH ₂)] ₂ .2H ₂ O ^b	IR, solution studies, crystal structure	Orthorhombic, <i>Pnna</i>	Distorted octahedral	[103]
[(Fe(pydc)(H ₂ O) ₂) ₂ ox].6H ₂ O ^b	IR, solution studies, crystal structure	Triclinic, $P\bar{1}$	Distorted pentagonal bipyramidal	[103]
[Tl(pydcH)] _n ^b	IR, solution studies, crystal structure	Monoclinic, <i>C2/c</i>	Distorted square pyramidal	[103]
(creatH) ₂ [Bi(pydc) ₂] ₂ .4H ₂ O ^b	IR, solution studies, crystal structure	Triclinic, $P\bar{1}$	Distorted pentagonal bipyramidal	[103]
(creatH)(phendcH).H ₂ O ^a	IR, crystal structure	Triclinic, $P\bar{1}$	-	[104]
(GH)(hypycH) ^a	IR, crystal structure	Orthorhombic, <i>Pbca</i>	-	[105]
(GH)(hypycH).H ₂ O ^a	IR, crystal structure	Triclinic, $P\bar{1}$	-	[106]
(GH) ₂ [Ni(hypyc) ₂].2H ₂ O ^b	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[107]
(pnH ₂)(pydcH) ₂ .2(pydcH ₂).8H ₂ O ^a	IR, crystal structure	Triclinic, $P\bar{1}$	-	[108]
(pnH ₂)(pydc)(pydcH ₂).2.5H ₂ O ^a	IR, crystal structure	Triclinic, $P\bar{1}$	-	[109]
(pnH ₂)[Co(pydc) ₂].4H ₂ O ^b	IR, ¹ H, ¹³ C NMR, elemental analysis, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[110]
(pnH ₂)[Cu(pydc) ₂].4H ₂ O ^b	IR, ¹ H, ¹³ C NMR, elemental analysis, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[110]
(pnH ₂)[Cd(pydc) ₂].3.5H ₂ O ^b	IR, ¹ H, ¹³ C NMR, elemental analysis, crystal structure	Monoclinic, <i>P2₁/c</i>	Distorted octahedral	[110]
(pnH ₂)[Zn(pydc) ₂].4H ₂ O ^b	IR, ¹ H, ¹³ C NMR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[79]
(pnH ₂) ₂ [Ce(pydc) ₃](NO ₃).3.5H ₂ O ^b	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted tricapped prism	[111]
[Pb(pydc)] _n ^b	IR, crystal structure	Monoclinic, <i>P2₁/n</i>	Highly distorted pentagonal bipyramidal	[112]
(pnH ₂)(py-2,3-dc).H ₂ O ^a	IR, crystal structure	Triclinic, $P\bar{1}$	-	[113]
{(pnH ₂)[Cu(py-2,3-dc)] ₂ }.3H ₂ O _n ^b	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedral	[114]
(pnH ₂)(py-3,5-dc).H ₂ O ^a	IR, crystal structure	Monoclinic, <i>P2₁/c</i>	-	[115]
[Ba(py-3,5-dc)(H ₂ O) ₃] _n ^b	IR, crystal structure	Monoclinic, <i>P2₁/c</i>	Almost tricapped trigonal prism	[116]

Table 1. Continued

$[\text{Sr}(\text{py-3,5-dc})(\text{H}_2\text{O})_4]_n^b$	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted dodecahedral	[117]
$(\text{pnH}_2)_2(\text{btc}).2\text{H}_2\text{O}^a$	IR, crystal structure	Monoclinic, $P2_1$	-	[118]
$\{(\text{pnH}_2)[\text{Ni}(\text{btc})(\text{H}_2\text{O})_2].0.5\text{H}_2\text{O}\}_n^b$	IR, crystal structure	Orthorhombic, $Ima2$	Distorted octahedral	[119]
$\{(\text{pnH}_2)[\text{Co}(\text{btc})(\text{H}_2\text{O})_2].0.5\text{H}_2\text{O}\}_n^b$	IR, crystal structure	Orthorhombic, $Ima2$	Distorted octahedral	[120]
$(\text{dmpH})[\text{V}(\text{pydc})\text{O}_2].\text{H}_2\text{O}^d$	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted trigonal bipyramidal	[121]
$(\text{dmpH})[\text{Fe}(\text{pydc})_2].2\text{H}_2\text{O}^d$	IR, crystal structure	Monoclinic, $P2_1/n$	Distorted octahedral	[122]
$(\text{dmpH})(\text{H}_5\text{O}_2)[\text{Ni}(\text{pydc})_2].0.5\text{H}_2\text{O}^d$	IR, elemental analysis, crystal structure	Orthorhombic, $Fddd$	Distorted octahedral	[123]
$(\text{dmpH})(\text{H}_5\text{O}_2)[\text{Cu}(\text{pydc})_2].0.5\text{H}_2\text{O}^d$	IR, elemental analysis, crystal structure	Orthorhombic, $Fddd$	Distorted octahedral	[123]
$(\text{dmpH})(\text{H}_5\text{O}_2)[\text{Zn}(\text{pydc})_2].0.5\text{H}_2\text{O}^d$	IR, ^1H , ^{13}C NMR, elemental analysis, crystal structure	Orthorhombic, $Fddd$	Distorted octahedral	[123]
$[\text{Zn}(\text{py-2,3-dcH})_2(\text{H}_2\text{O})_2]^d$	IR, crystal structure	Monoclinic, $P2_1/n$	Distorted octahedral	[124]
$[\text{Zn}(\text{phen})_3](\text{NO}_3)_2.2\text{GluH}_2.2\text{H}_2\text{O}^d$	IR, crystal structure	Monoclinic, $C2/c$	Distorted octahedral	[125]
$[\text{Fe}(\text{bipy})_3][\text{Fe}(\text{pydc})_2]_2(\text{pydcH}_2)_{1/2}.6.5\text{H}_2\text{O}^d$	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted octahedrals	[126]
$(4,4'\text{-bipyH}_2)[\text{Sr}(\text{pydc})_2(\text{H}_2\text{O})_3].3\text{H}_2\text{O}^d$	IR, crystal structure	Triclinic, $P\bar{1}$	Distorted tricapped trigonal prism	[127]
$[\text{Cu}(\text{H}_2\text{O})(\text{phen})(\text{hypydc})].4.5\text{H}_2\text{O}^d$	IR, crystal structure	Orthorhombic $Fdd2$	Distorted octahedral	[128]
$[\text{Ni}(\text{hypydc})(\text{H}_2\text{O})_3].1.5\text{H}_2\text{O}^d$	IR, crystal structure	Monoclinic, $C2/c$	Distorted octahedral	[129]
$[\text{Zn}_{12}(\text{hypydc})_{12}(\text{H}_2\text{O})_{10}.12\text{H}_2\text{O}]_n^d$	crystal structure	Tetragonal, $I4_1/amd$	Distorted tetrahedral, trigonal bipyramid, octahedral	[130]
$[\text{Mg}(\text{py-2-c})_2(\text{H}_2\text{O})_2].0.15\text{H}_2\text{O}^d$	IR, crystal structure	Monoclinic, $P2_1/n$	Distorted octahedral	[131]
$(\text{phenH})_4(\text{btcH}_3)_2(\text{btcH}_2)^a$	IR, crystal structure	Triclinic, $P\bar{1}$	-	[132]
$(\text{daptzH})\text{Cl}. \text{H}_2\text{O}^a$	IR, crystal structure	Monoclinic, $P2_1/c$	-	[133]

Table 1. Continued

(daptzH) ₂ (ox) ^a	IR, crystal structure	Monoclinic, <i>P2₁/c</i>	-	[134]
(DA18C6H ₂)(pydcH) ₂ .0.25H ₂ O ^a	IR, ¹ H, ¹³ C NMR, crystal structure	Monoclinic, <i>P2₁/c</i>	-	[135]
(pycH) ₂ (btcH ₂).2H ₂ O ^a	IR, crystal structure	Monoclinic, <i>C2/m</i>	-	[136]
(pyrimH){H(pydcH) ₂ } ^a	IR, crystal structure	Triclinic, <i>P$\bar{1}$</i>	-	[137]
(pydcH) ₂ .2H ₂ O ^a	IR, crystal structure	Triclinic, <i>P$\bar{1}$</i>	-	[138]
(NH ₄)(pydcH) ^a	IR, crystal structure	Monoclinic, <i>C2/c</i>	-	[139]
(2-apyH)(pdtcH) ^a	IR, ¹ H, ¹³ C NMR, solution studies, crystal structure	Monoclinic, <i>P2₁/c</i>	-	[140]

^aProton transfer compounds. ^bComplexes. ^cCocrystals. ^dMetallic adducts.

CRYSTAL ENGINEERING AND MOLECULAR ARCHITECTURE

The title refers to plan and design of crystal structures that will depend very largely on thinking supramolecularly and on viewing a crystal structure as a blend of a very large number of interactions of various types and strengths. Within this complexity, one must try to identify interactions or supramolecular synthons that will carry through across an entire family of structures with the aim of identifying a set of related molecules that yield a set of related crystal structures [18]. The key to successful construction of supramolecular architecture is the control and manipulation of coordination bonds and non-covalent interactions by carefully selecting the coordination geometry of the metal centers and the organic ligands containing appropriate functional groups such as polycarboxylic acid and multipyridine [19]. The greatest achievement(s) of crystal engineering in the past three decades can be summarized in a phrase, *i.e.*, “viewing crystal structures as networks” [20]. The use of di- or polytopic ligands in conjunction with metal centers to construct predictable one-, two- or three-dimensional coordination networks has received considerable attention recently [21].

SUPRAMOLECULAR CHEMISTRY IN COORDINATION COMPLEXES

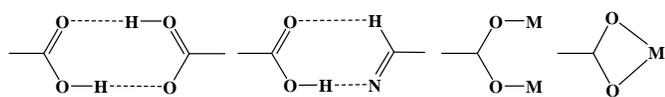
Although supramolecular compounds are general and were recognized more than 100 years ago, beginning with “lock-

and-key principle” of enzyme substrate recognition, the real rise of this field started in the late 1960s or early 1970s [21]. It seems that supramolecular chemistry was first developed in the field of organic chemistry, but several papers concerning coordination supramolecular complexes with various dimensions and topologies have been published up to now. As a simple definition, the latter are coordination compounds having some functional groups as sites capable to give supramolecular interactions including van der Waals forces, variety of weak to strong hydrogen bonds, different π - π stackings, ion pairings and so forth, resulting to an extended network.

In this direction, solid-state structures with well-defined molecular networks of different types such as molecular tapes, molecular sheets, three-dimensional architectures possessing cavities and channels, and so forth have been synthesized by employing both hydrogen bonds and dative bonds. However, in all these cases, invariably, evolution of an assembly depends on the properties of the functional group under consideration. In this respect, assemblies based on the carboxylic group (-COOH) are very well-known because of its ability to form robust hydrogen bonds on its own and also with several aza compounds forming either O-H \cdots N or O-H \cdots N/C-H \cdots O pairwise hydrogen bonds, as well as dative bonds through the carboxylate group. A schematic representation of some of these networks is shown in Scheme 1 [22].

Polycarboxylic acids, which are ubiquitous in organic chemistry and play key roles in cell metabolism, are also good organic supramolecular synthons, due to the ability of the

A Brief Review on Structural Concepts of Novel Supramolecular



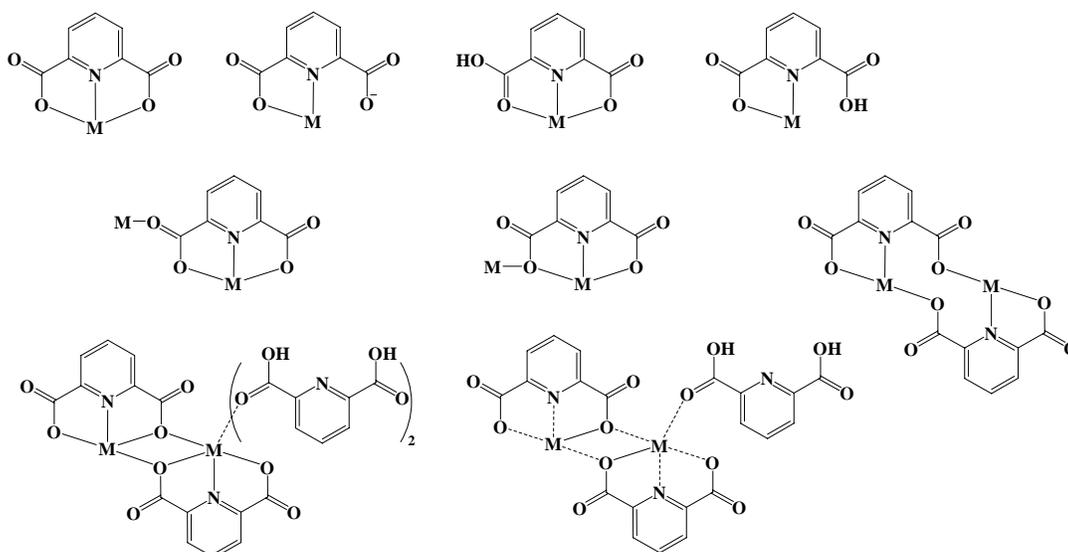
Scheme 1. Representation of some networks based on carboxylic group.

carboxylic acid groups to form moderate to strong hydrogen bonds, with the same group acting as both donor and acceptor. Within this class of compounds, benzene, pyridine and polyazine derivatives are of special interest, because they represent a unique example where a high level of predictability of potential supramolecular arrangements is achieved [23].

It is well known that carboxylate ligands play an important role to construct novel metal organic frameworks in coordination chemistry. They usually adopt binding modes diverse as terminal monodentate, chelating to one metal center, bridging bidentate in a syn-syn, syn-anti, and anti-anti configuration to two metal centers and bridging tridentate to two metal centers.

Amongst the acids used in the present reviewed compounds, pyridine-2,6-dicarboxylic acid (pydcH₂), as a very important carboxylate derivative, has attracted much interest in coordination chemistry. It 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 [24]. An investigation of our synthesized metallic complexes based on pydcH₂ gives rich coordination motifs for (pydc)²⁻, (pydcH)⁻ and pydcH₂ species (Scheme 2). Other ligands applied in this review are not as general as pydcH₂.

Considering only the water molecules of the lattice bonded to each other by pure O-H...O hydrogen bonding leads to interesting “water clusters“. Although a hexadecameric water cluster present in the cavity of a supramolecularly built metal-organic framework (MOF) is reported recently [25], both experiment and theory strongly suggest that the water trimer, tetramer and pentamer possess cyclic, quasi-planar minimum energy structures [26]. Some structures for six-molecule water clusters, namely hexamers, have been reported [27-29]. The water clusters in the structure of some complexes of this review will be mentioned in following sections.



Scheme 2. Coordination motifs of (pydc)²⁻, (pydcH)⁻ and pydcH₂ in the reviewed compounds.

EXPERIMENTAL METHODS

Synthesis

A part of project is defined to prepare proton transfer compounds as novel supramolecular systems, some of which can function as suitable starting materials in the synthesis of metal complexes. The compounds were prepared by the reaction between appropriate acids, as proton donors, and amines, as proton acceptors, at room temperature or, in few cases, under hydrothermal conditions in suitable solvents with 1:1 and 1:2 molar ratios. Unfortunately, due to the competitive solvation of donor and acceptor sites by polar solvent, only few systems having this ability are known. Cocrystals are synthesized using the same method. Addition a solution of metal ion to a solution of proton transfer compounds (in 1:1, 1:2 or 1:3 molar ratio) in a suitable solvent at room temperature or under mild temperature or, in few cases, the hydrothermal conditions resulted in the formation of metal complexes. Also, in some cases the reaction was run using all three materials *i.e.* acid, amine and metallic salt in a *one pot* approach (see following sections). To obtain suitable single crystals of the products, it was often necessary to select a suitable second solvent for recrystallization, although some products give single crystals in the primary solution.

Characterization

The proton transfer compounds and their metal complexes were characterized by IR, ^1H and ^{13}C NMR, Es-MS and UV-Vis. spectroscopies, elemental analysis and single crystal X-ray diffraction methods.

Solution Studies

A potentiometric *pH* titration method was used to evaluate the protonation constants of the building blocks of the amine-acid adduct, the equilibrium constants for the acid-base reactions, the stoichiometry and stability of the resulting complexes with proton transfer compounds in aqueous solution. The results are presented in the form of distribution diagrams revealing the concentrations of individual complex species as a function of *pH*. Also, the results presented the complexation strength of metallic ions with the present species, as a whole or individually. In effect, the formation of metallic complexes in solution with stoichiometries close to

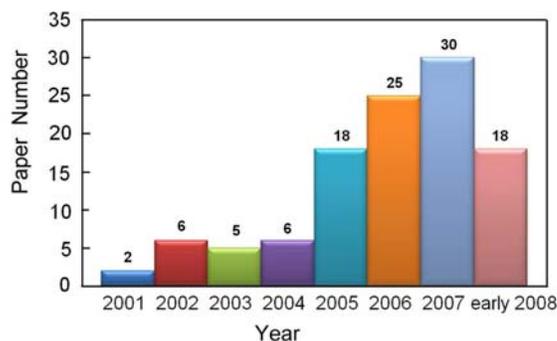


Fig. 1. Number of papers on the compounds given in Table 1 per year.

those of the solid state is strongly supported by the results of the potentiometric *pH* titration studies in aqueous solutions.

SYNTHESIZED PROTON TRANSFER COMPOUNDS AND CORRESPONDING METAL COMPLEXES

In recent years, our research group has been involved in the study of several proton transfer compounds and mono-, di-, tri-, tetra-, or pentavalent metal ion complexes, including main group, transition and lanthanide elements. The histogram of the published papers on the given compounds in Table 1 is shown in Fig. 1.

The proton transfer ion pairs have been prepared using the following acids and bases. The acids used as proton donors included pyridine-2-carboxylic acid (py-2-cH), pyridine-2,3-dicarboxylic acid (py-2,3-dcH₂), pyridine-2,5-dicarboxylic acid (py-2,5-dcH₂), pyridine-2,6-dicarboxylic acid (pydcH₂), pyridine-3,5-dicarboxylic acid (py-3,5-dcH₂), benzene-1,2,4,5-tetracarboxylic acid (btcH₄), oxalic acid (oxH₂), 4-hydroxypyridine-2,6-dicarboxylic acid (hypydcH₂), glutaric acid (gluH₂), pyridine-2,6-bis(monothiocarboxylic) acid (pdtcH₂), and 1,10-phenanthroline-2,9-dicarboxylic acid (phendcH₂), and the proton acceptor bases were pyridine-2,6-diamine (pyda), 1,10-phenanthroline (phen), guanidine (G), 2,4,6-triamino-1,3,5-triazine (melamine) (tata), creatinine (creat), N,N'-diethyl-2-amino-6-methyl-4-pyrimidinol (pyrim), ethylenediguanidine (EDG), 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (DA18C6), piperazine (pipz), propane-

1,3-diamine (pn), 2,2'-bipyridine (bipy), 4,4'-bipyridine (4,4'-bipy), benzene-1,3-diamine (bda), 2,6-diamine-4-phenyl-1,3,5-triazine (daptz), 2,9-dimethyl-1,10-phenanthroline (dmp), 2-aminopyridine (2-apy), and pyridine-4-carboxamide (pyc). Table 1 shows the synthesized proton transfer compounds and their metallic complexes, using all three constituents (*i.e.*, proton donors, proton acceptors and metallic salts) in a one pot approach. The complexes are given immediately after the corresponding proton transfer ion pair in Table 1. Also, Scheme 3 illustrates the synthesized proton transfer compounds whose crystal structures have been determined.

As mentioned above, several interactions are responsible for extending supramolecular networks amongst them hydrogen bonding is the most important one. Although the bonds between hydrogen and O, N and F atoms are considered as classic and formal hydrogen bonds, it is not long ago that weaker C-H...O hydrogen bonds are regarded as true hydrogen bonds, as supported by *ab initio* quantum calculations [30]. In the reviewed compounds, there exist C-H...O bonds with various distances and angles. Figure 2 illustrates the angle-distance scatter plot of some compounds listed in Table 1.

Pyridinium-2,6-diamine-Pyridinium-2,6-dicarboxylate, (pydaH)(pydcH), and Its Metal Complexes

According to the crystal structure, the protons were assigned to the amino groups of the cation. Thus, the supramolecular system consists of a dication and dianion unit, which form extended one-dimensional ribbons [31]. A crystal structure redetermination (pydaH)(pydcH) [32], which corrected a previous report based on (pydaH₂)(pydc) [31], assigned the protons to the ring N atoms of both cation and anion. The structure of (pydaH)(pydcH) shows both intra- and intermolecular proton transfers from carboxy groups to the ring N atoms of (pydc)²⁻ and pyda. Ion pairing and hydrogen bonding interactions link the components of the system. A number of N-H...O hydrogen bonds are observed in the crystal structure, producing a three-dimensional network.

There is also evidences for π - π stacking between parallel planes of (pydaH)⁺ fragments, with an interplanar distance of about 3.3 Å [32].

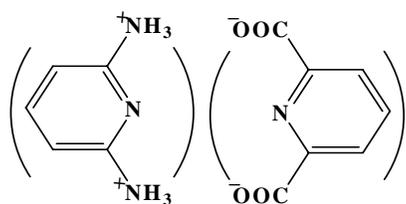
The central atom in the complexes (pydaH)₂[Co(pydc)₂].H₂O [33], (pydaH)₂[Ni(pydc)₂].H₂O [34] and (pydaH)₂[Cu

(pydc)₂].H₂O [35], is hexacoordinated by pyridine-2,6-dicarboxylate as tridentate ligand, one of which is illustrated in Fig. 3 [33-35]. The intermolecular forces that result in the formation of supramolecular coordination compounds consist of both ion pairing and hydrogen bonding (O-H...O and N-H...O are present between the two (pydaH)⁺ cations, one [M(pydc)₂]²⁻ anion, and one uncoordinated water molecule) [33-35].

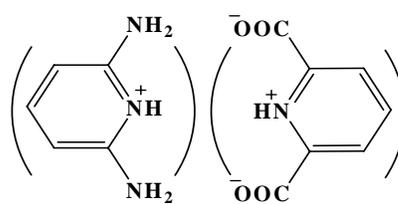
The molecular structures of (pydaH)₂[Bi₂(pydc)₄(H₂O)₂].4H₂O [36], (pydaH)₂[La₂(pydc)₄(H₂O)₄].2H₂O [33] and (pydaH)₂[Ce(pydc)₂(H₂O)₂].2H₂O [37] complexes consist of two metal fragments linked *via* a central four-membered M₂O₂ ring. The protonated site of the cationic counter ion in all complexes is the pyridine nitrogen [33,36,37]. As illustrated in Fig. 4, the existence of a stereochemically active lone pair on the Bi^{III} atoms is noteworthy [36]. The intermolecular forces existing between anionic and cationic units in these complexes consist of both hydrogen bonding and ion pairing [33,36,37]. In the Ce^{III} complex, some π - π stacking interactions among (pydaH)⁺ cations and also between (pydaH)⁺ and (pydc)²⁻ moieties are observed due to the short distances of ~3.3 Å among these planes [37].

In (pydaH)₂[Zr(pydc)₃].5H₂O [38], the Zr^{IV} is nine-coordinated by three (pydc)²⁻ units, thus forming a distorted tricapped antiprism surrounded the metal center. Whereas in the (pydaH)₂[PdCl₄] complex, the two (pydc)²⁻ species are not contributed in complexation and [PdCl₄]²⁻ forms a distorted square planar geometry [39]. In (pydaH)[Sb(pydc)₂].3H₂O.0.5CHCl₃ [40], pyridine-2,6-dicarboxylate acts as a bidentate ligand *via* one oxygen and one nitrogen atoms [40], whereas in the complexes (pydaH)[Ga(pydc)₂].3.25H₂O.CH₃OH [41], (pydaH) [Cr(pydc)₂].pydcH₂.0.5H₂O [42] and (pydaH)[Zn(pydc)(pydcH)].3H₂O [43], the pyridine-2,6-dicarboxylate acts as tridentate [41-43]. The structure of Cr^{III} complex has a rather complicated crystal structure consisting of two crystallographic independent pairs of ions in the unit cell along with solvating water and pydcH₂ molecules, which are bonded to the complex *via* hydrogen bonding [42].

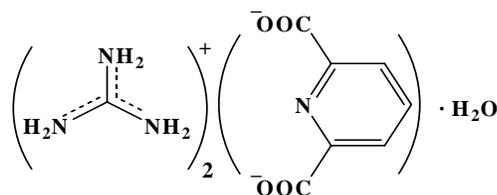
In (pydaH)[V(pydc)O₂] [44], the crystal structure contains [V(pydc)O₂]⁻ and (pydaH)⁺ fragments, that are held together by both electrostatic forces and hydrogen bonding [44]. The {(pydaH)[HgCl(pydc)].H₂O}_n [45] complex has a polymeric structure consisting of binuclear units (pydaH)₂[HgCl(pydc)]₂.



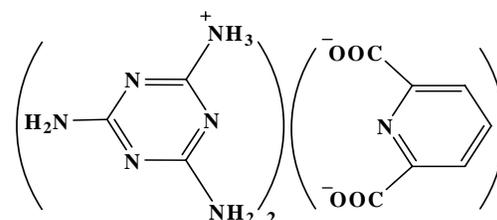
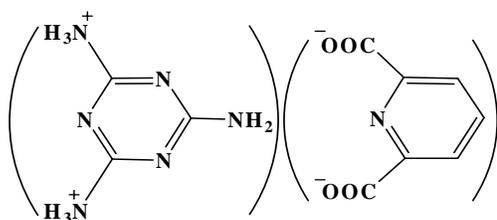
(pydaH₂)(pydc), [31]



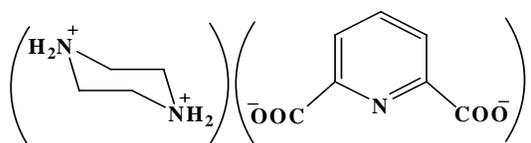
(pydaH)(pydCH), [32]



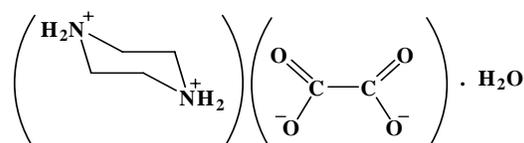
(GH)₂(pydc).H₂O, [63]



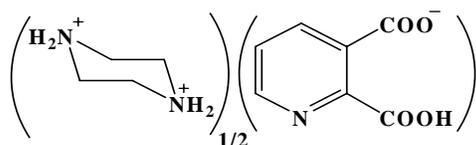
(tataH₂)(pydc), (tataH)₂(pydc), [67]



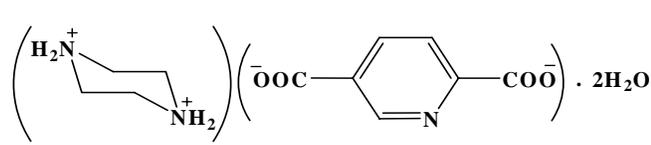
(pipzH₂)(pydc), [73]



(pipzH₂)(ox).H₂O, [84]



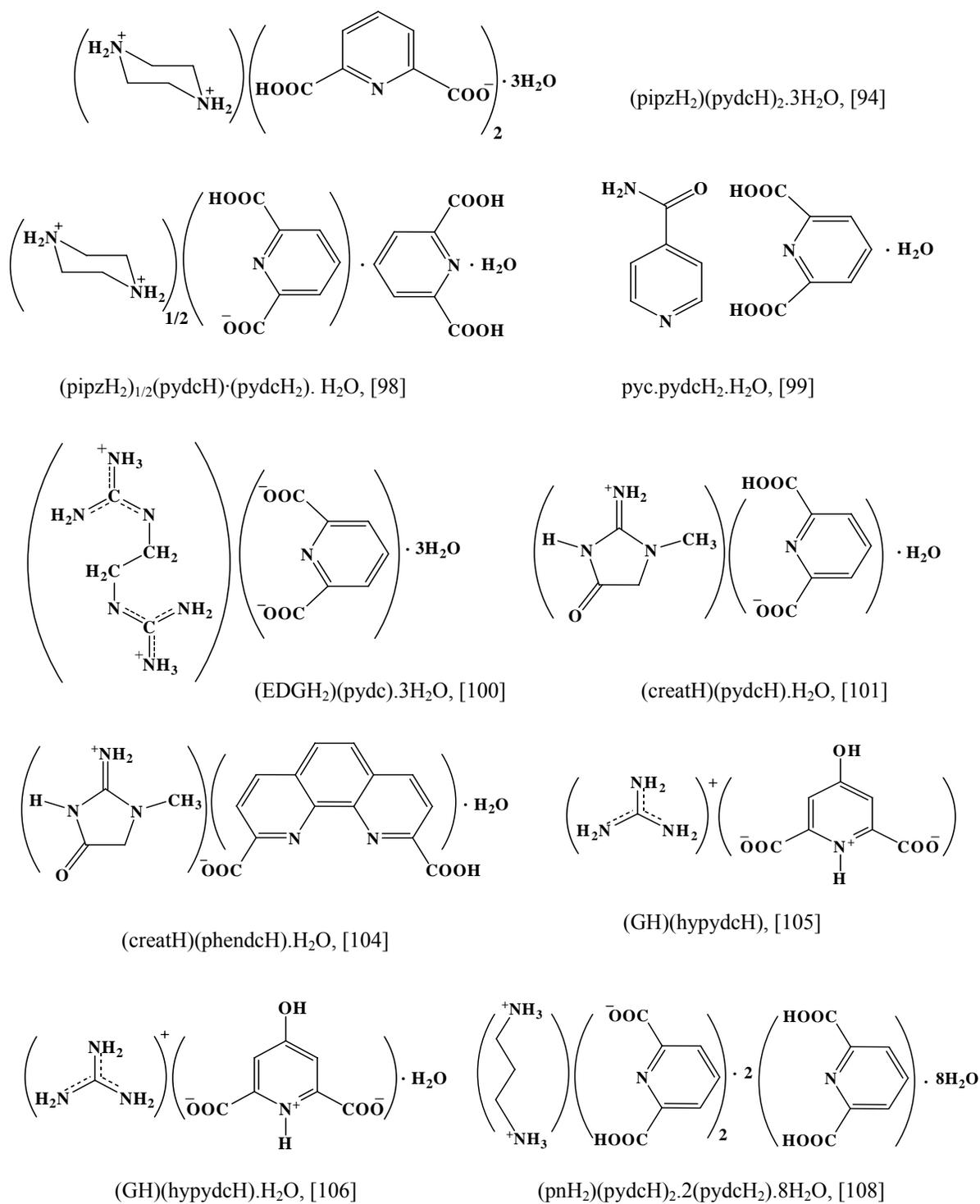
(pipzH₂)_{1/2}(py-2,3-dcH), [87]



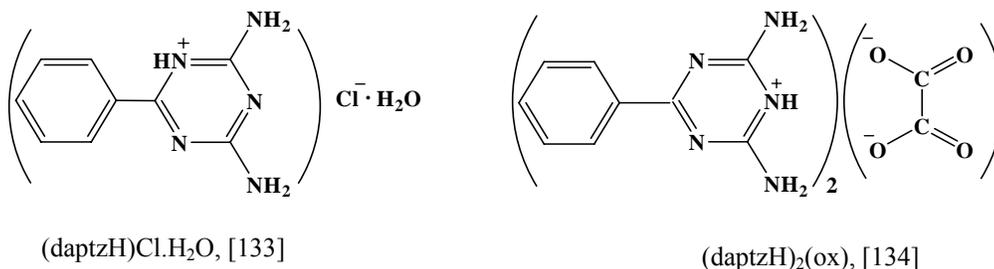
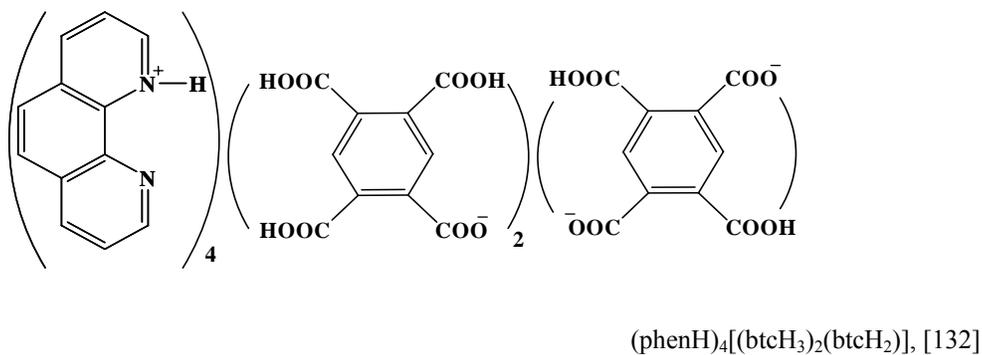
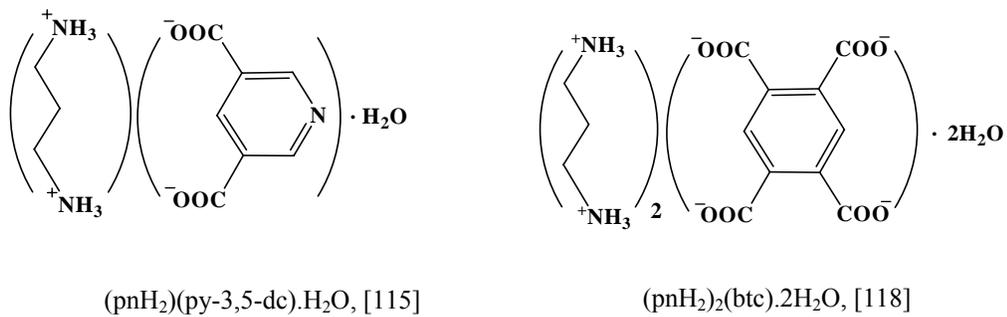
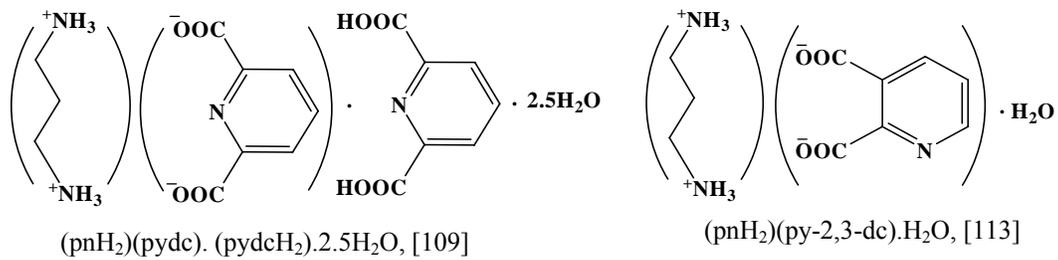
(pipzH₂)(py-2,5-dc).2H₂O, [90]

Scheme 3. Schematic drawing of synthesized proton transfer compounds and cocrystals possessing crystal structures with their reference numbers.

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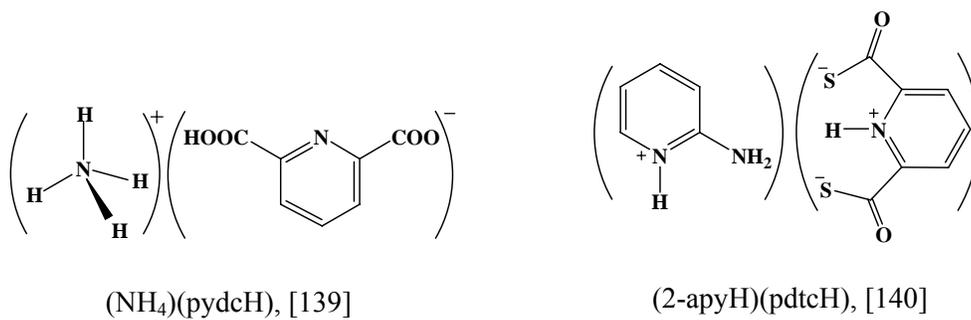
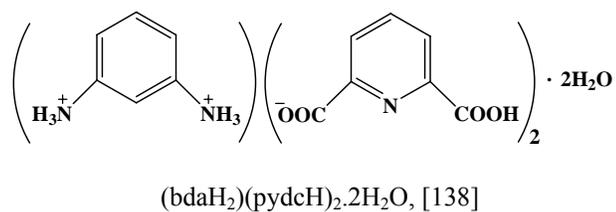
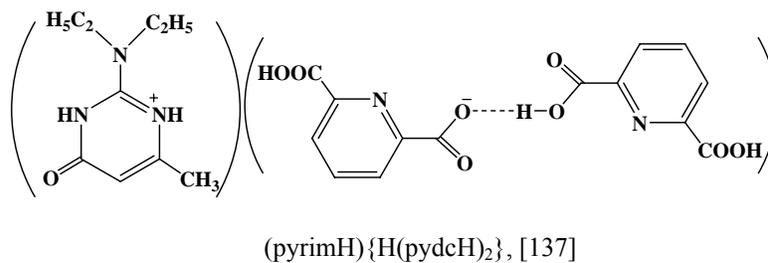
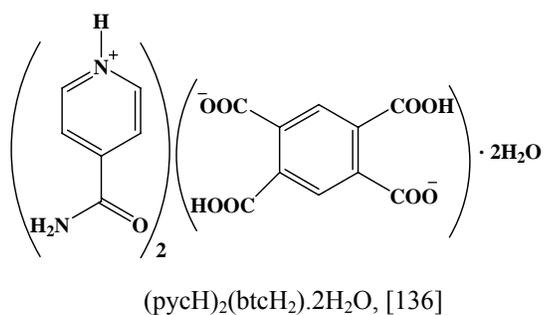
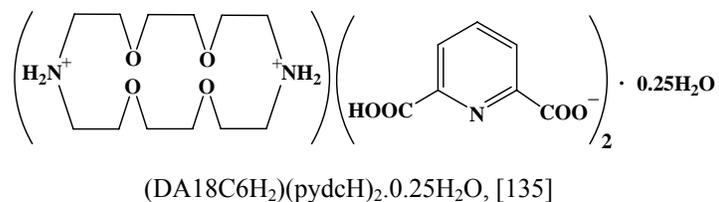


Scheme 3. Continued.



Scheme 3. Continued.

A Brief Review on Structural Concepts of Novel Supramolecular



Scheme 3. Continued.

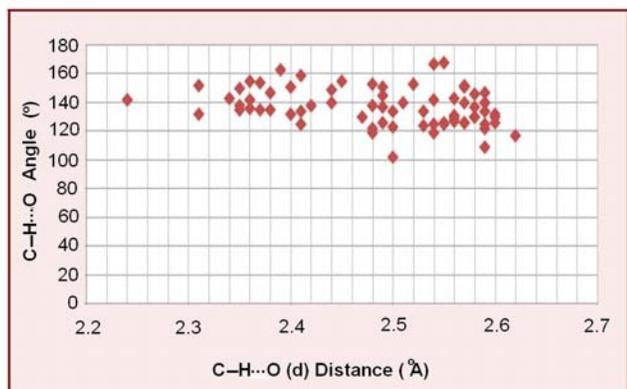


Fig. 2. The angle-distance scatter plot for C-H...O hydrogen bonds in some reviewed compounds.

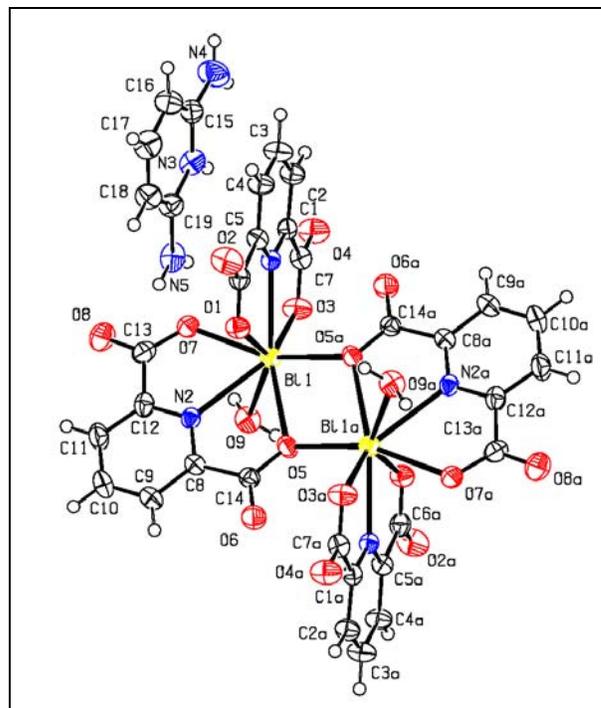


Fig. 4. Stereochemically active lone pair on Bi^{III} in (pydaH)₂[Bi₂(pydc)₄(H₂O)₂].4H₂O results in distortion of coordination polyhedron, uncoordinated water molecules are omitted for clarity.

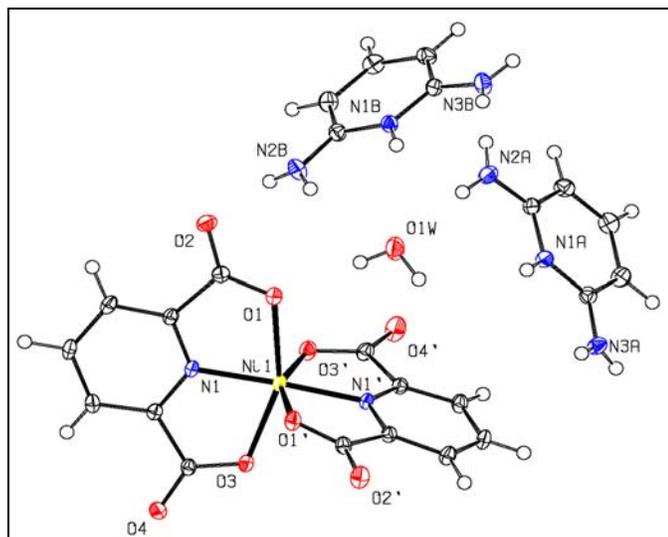


Fig. 3. Molecular structure of (pydaH)₂[Ni(pydc)₂].H₂O.

2H₂O, in which the (pydc)²⁻ moieties act as a tridentate ligand. The two (pydc)²⁻ units that participate in the binuclear complex formation are kept together through an eight-membered Hg₂C₂O₄ ring. These dimeric units are then linked into an infinite system *via* additional Hg-O bonds [45].

The molecular structure of {[BiCl(H₂O)(pydc)]₂]_n [46] complex consists of dimeric [BiCl(H₂O)(pydc)]₂ units, in which the (pydc)²⁻ moiety acts as a tridentate ligand. The

crystal is built of dimeric units in which two halves of these units are kept together through a four-membered Bi₂O₂ ring. Therefore, each Bi^{III} atom is coordinated with one tridentate bridging (pydc)²⁻, one water molecule, one chlorine atom, one carbonyl oxygen of the other (pydc)²⁻ unit and one oxygen of bridging (pydc)²⁻. These dimeric units are linked into an infinite system *via* additional Bi-O bonds [46].

In the {[Pb(pydc)(pydcH₂)(H₂O)₂]₂]_n [47] complex, the arrangement of (pydc)²⁻ as a tridentate ligand, (pydcH₂) as a monodentate ligand and water molecules shows a free space in coordination geometry around the Pb^{II}, occupied possibly by a stereochemically active lone pair of electrons on the Pb^{II} atom. The structure of {(pydaH)₂[Hg(pydc)Cl]₂.2H₂O}_n [48] complex consists of (pydc)²⁻ as tridentate ligand, one chlorine atom and two carbonyl oxygens from two adjacent carboxylato groups positioned at the two neighboring layers.

The two latter oxygen atoms, in fact, bridge between Hg^{II} atoms. The resulting ionic complex has a polymeric structure consisting of binuclear units $(\text{pydaH})_2[\text{Hg}(\text{pydc})\text{Cl}]_2 \cdot 2\text{H}_2\text{O}$. In addition to ion pairing and hydrogen bonding among the three components, $(\text{pydaH})^+$, $(\text{pydc})^{2-}$ and the uncoordinated water molecules, the π - π interactions are also involved in the construction of a three dimensional layered network [48].

The molecular structures of $[\text{Cd}(\text{pydc})(\text{H}_2\text{O})_3]_2 \cdot 2\text{pydcH}_2$ [49], $[\text{Sn}(\text{pydc})(\text{OH})(\text{H}_2\text{O})(\mu\text{-OH})]_2 \cdot 4\text{H}_2\text{O}$ [50], $[\text{Sb}(\text{pydc})(\text{H}_2\text{O})]_2\text{O}$ [51] complexes consist of two metal fragments linked *via* a central four-membered M_2O_2 (where $\text{M} = \text{Cd}^{\text{II}}$, Sn^{II} and Sb^{III}) ring [49,50]. In these complexes, in addition to $[\text{In}(\text{pydc})(\text{pydcH})(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}$ [41], it is obvious that (pyda) is not involved [41,49-51].

In $[\text{Ni}(\text{pydcH})_2] \cdot 3\text{H}_2\text{O}$ [34], the two $(\text{pydcH})^-$ units act as tridentate ligands and hydrogen bonding takes place between the three water molecules and the neutral complex. The molecular structure of $\text{Ti}(\text{pydc})(\text{Cp})_2$ [52] consists of one $(\text{pydc})^{2-}$ as a tridentate ligand and two cyclopentadienyl (Cp) rings [52]. An interesting $\text{Ti} \cdots \pi$ interaction, classified as cation $\cdots \pi$ interaction and defined as the attraction between a cation and the face of a simple π system with an electrostatic origin [21], with a distance of 2.089 Å together with a weak π - π stacking with the distance of 3.84 Å are observed. The crystal structure of $[\text{Pd}(\text{pydc})(\text{oxa})] \cdot \text{H}_2\text{O}$ [53] consists of monomeric units in which the $(\text{pydc})^{2-}$ anions and oxazole, act as coordinating ligands [53]. The crystal structure is stabilized by strong intermolecular $\text{O} \cdots \text{H} \cdots \text{O}$ and weak $\text{C} \cdots \text{H} \cdots \text{O}$ hydrogen bonds, linking the ions to form a three dimensional network [53].

Pyridine-2,6-diaminium-1,10-Phenanthroline-2,9-dicarboxylate, $(\text{pydaH}_2)(\text{phencd})$, and Its Metal Complexes

Although attempts to synthesize a good crystal of $(\text{pydaH}_2)(\text{phencd})$ were not successful, its structure was proposed using other methods [54]. While, the complexes $(\text{pydaH})_2[\text{Co}(\text{phencd})_2] \cdot 10\text{H}_2\text{O}$ [54] and $(\text{pydaH})_2[\text{Cu}(\text{phencd})_2] \cdot 10\text{H}_2\text{O}$ [55] were synthesized and their structures were determined. In both complexes, the metal center is hexacoordinated by 1,10-phenanthroline-2,9-dicarboxylate as tridentate ligand.

The structure of $(\text{pydaH})_2[\text{Cu}(\text{phencd})(\text{phencdH})]_2 \cdot 5\text{H}_2\text{O}$

[55] consists of two independent $[\text{Cu}(\text{phencd})(\text{phencdH})]^-$ anions, two $(\text{pydaH})^+$ cations and five water molecules per asymmetric unit. In $(\text{pydaH})[\text{Cr}(\text{phencd})_2] \cdot 5\text{H}_2\text{O}$ complex [56], 1,10-phenanthroline-2,9-dicarboxylate acts as a tridentate ligand. In this complex, ribbons are formed by interacting $[\text{Cr}(\text{phencd})_2]^-$ and $(\text{pydaH})^+$ *via* hydrogen bondings through $\text{N} \cdots \text{H} \cdots \text{O}$ bonds [56]. Extensive $\text{O} \cdots \text{H} \cdots \text{O}$ [55,56], $\text{N} \cdots \text{H} \cdots \text{O}$ [55, 56] and $\text{C} \cdots \text{H} \cdots \text{O}$ [56] hydrogen bonding as well as ion pairing were also observed.

Bis(1,10-phenanthroline)-Pyridine-2,6-dicarboxylate, $(\text{phenH})_2(\text{pydc})$ and Its Metal Complexes

The proton transfer ion pair, $(\text{phenH})_2(\text{pydc})$ [57] with no crystal structure was applied to synthesize the two complexes $[\text{Zn}(\text{pydc})_2][\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2] \cdot 7\text{H}_2\text{O}$ [57] and $[\text{Zn}(\text{phen})_3]_4(\text{H}(\text{pydcH})_2)(\text{NO}_3)_7 \cdot 26\text{H}_2\text{O}$ [57]. A novel feature of the latter complex is the participation of the phen molecule in complexation as a bidentate ligand, leaving supramolecular hydrogen bis(6-carboxypyridine-2-carboxylate) anion, $[\text{H}(\text{pydcH})_2]^-$, as an uncoordinated unit (Fig. 5). Therefore, the two monoanionic pydcH^- units are joined together by a proton to generate a supramolecular anion. Most of the hydrogen bridges that exist in the crystal lattice of this complex represent a strong H-bonding. Both D-H and H-A bond distances in $(\text{H}(\text{pydcH})_2)^-$ are 1.25 Å with a DHA value of 180°, which strongly support the existence of fully-symmetric charge-assisted quasi-covalent H-bonding [57].

In both $[\text{Cd}(\text{pydc})(\text{phen})_2] \cdot \text{pydcH}_2 \cdot 4\text{H}_2\text{O}$ [58] and $[\text{In}_2\text{SO}_4(\text{pydc})_2(\text{phen})_2(\text{H}_2\text{O})_2] \cdot 5.5\text{H}_2\text{O}$ [59] complexes, (phen) acts as a bidentate and $(\text{pydc})^{2-}$ as tridentate ligand in the complexation reaction. The latter is a binuclear system containing two metal fragments, which are linked through a bridging SO_4^{2-} group. As shown in Fig. 6, there are two $\text{S} \cdots \text{O} \cdots \pi$ interactions in the structure of In^{III} complex with $\text{O} \cdots \pi$ distances of 3.307 and 3.501 Å.

In $\{[\text{Ce}(\text{pydc})(\text{pydcH})(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}\}_n$ [59] complex, 1,10-phenanthroline is removed completely upon complexation. The $(\text{pydc})^{2-}$ anion has a bridging role linking the fragments of the polymeric system through one of its carboxylate groups. The tridentate ligand $(\text{pydcH})^-$ is also observed in the structure [59]. The crystal packing in these complexes involve many $\text{O} \cdots \text{H} \cdots \text{O}$ [58,59] and $\text{O} \cdots \text{H} \cdots \text{N}$ [58] hydrogen bonds. Hydrogen bonding is an interesting feature of the structure of Ce^{III}

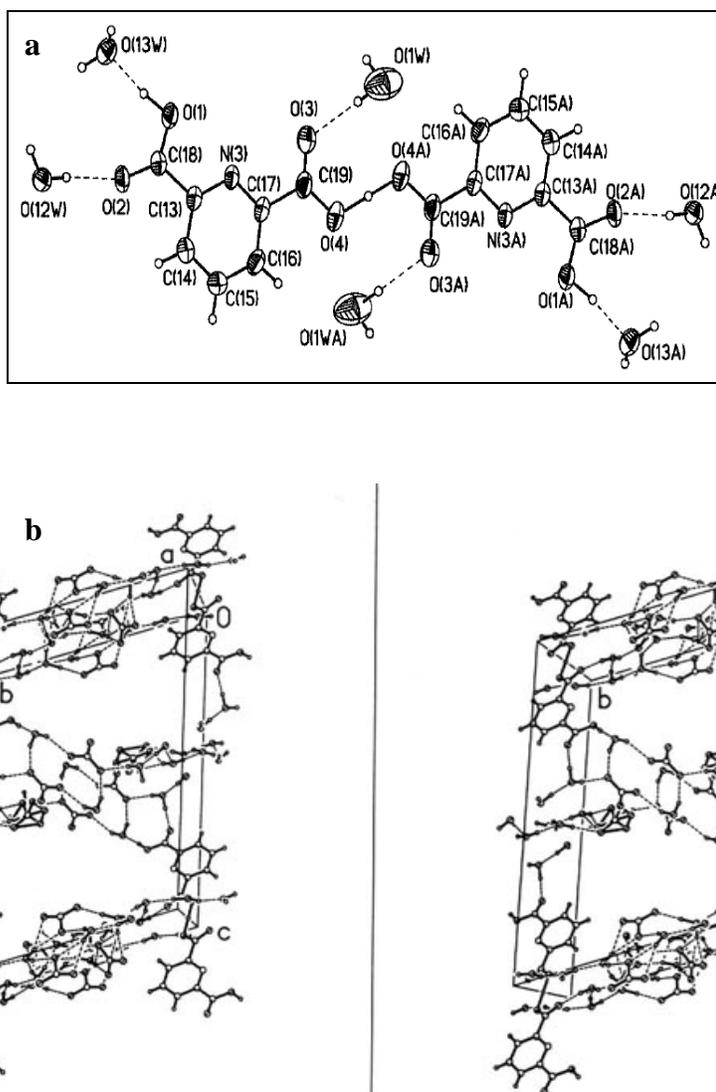


Fig. 5. a) Anionic [H(pydcH)₂]⁻ and some water molecules forming supramolecular anion. b) Stereopacking diagram of [Zn(phen)₃]₄(H(pydcH)₂)(NO₃)₇.26H₂O, cations are omitted for clarity.

complex. The O-H \cdots O hydrogen bonds, with short D \cdots A distances as 2.481(3) Å and 2.631(3) Å, form an infinite network through the crystal (Figs. 7 and 8) [59]. Another non-covalent interaction is π - π stacking among (pydc)²⁻ and phen planes and also between two phen species due to the short distances of about 3.3 Å [59].

In [HgCl₂(phen)₂] complex [60] (Fig. 9), there exist short distances of 3.303 and 3.371 Å between parallel aromatic

groups (Figs. 10 and 11), and it also has C-H \cdots Cl hydrogen bonds in the range of 2.65-2.82 Å (H \cdots Cl length).

The molecular structure of (phenH)₂[Bi(pydc)₂(H₂O)]₂.5H₂O [37] is built of binuclear units of [Bi(pydc)₂(H₂O)]₂²⁻, in which each (pydc)²⁻ moiety acts as a tridentate ligand. Two halves of these units are kept together through an eight-membered ring. It is interesting to note that, like the other Bi^{III} complex [36] mentioned above (Fig. 4), the stereochemically

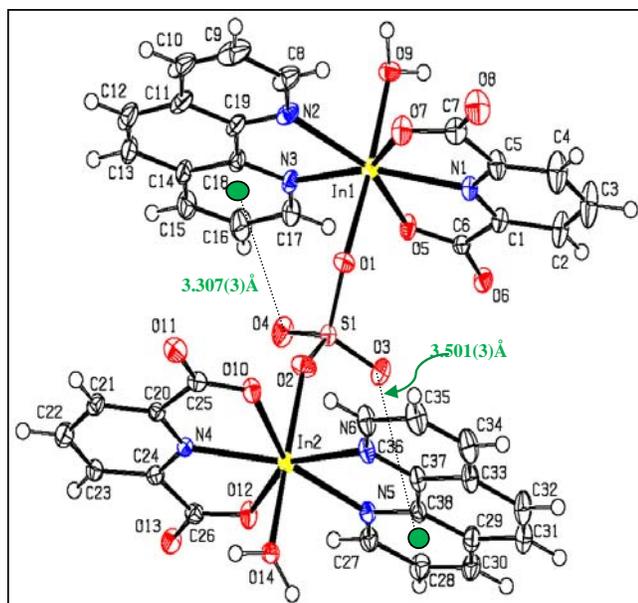


Fig. 6. Two S-O $\cdots\pi$ interactions in the structure of In^{III} complex [59] with the O $\cdots\pi$ distances of 3.307 and 3.501 Å.

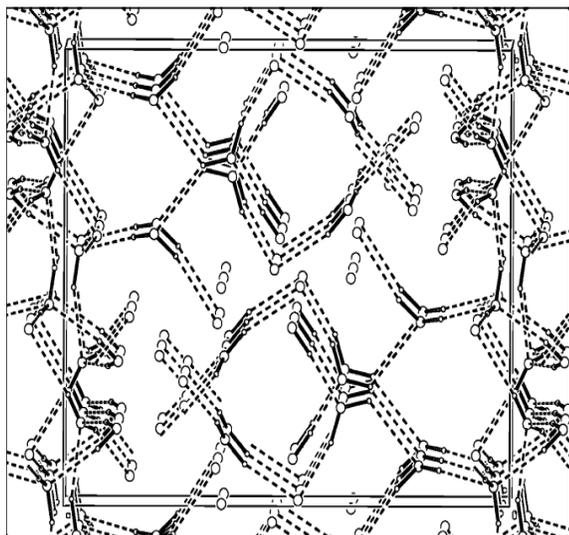


Fig. 7. Hydrogen bonding cluster of $\{[\text{Ce}(\text{pydc})(\text{pydch})(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}\}_n$, all atoms except those of water molecules and carboxyl oxygen atoms are omitted for clarity.

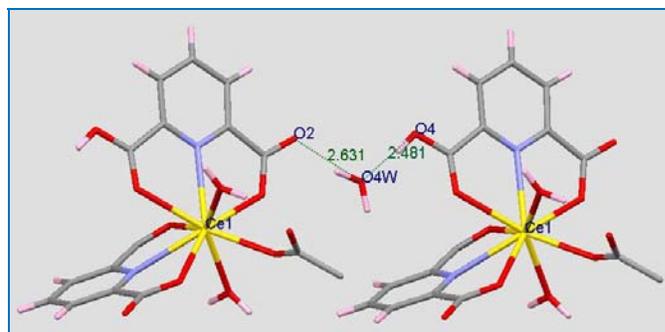


Fig. 8. The O-H \cdots O hydrogen bonds with the D \cdots A distances as short as 2.481(3) Å and 2.631(3) Å in a fragment of $\{[\text{Ce}(\text{pydc})(\text{pydch})(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}\}_n$.

active lone pair are existed on the Bi^{III} atoms. There are π - π stacking interactions between cation-cation and anion-anion π -rings with distances of 3.494 and 3.169 Å, respectively [37].

The structures of $[\text{Sn}(\text{pydc})(\text{phen})(\text{OH})_2]\cdot 3\text{H}_2\text{O}$ [61] and $\{[\text{Sb}(\text{pydc})(\text{phen})_2\text{O}]\cdot 2\text{DMSO}\cdot 4\text{H}_2\text{O}\}$ [61] complexes show that both cationic and anionic fragments of the starting proton transfer compound are involved in the complexation. The phen and $(\text{pydc})^{2-}$ ligands are linked to the central atom as bidentate and tridentate ligands, respectively. Whereas the structure of $[\text{Tl}(\text{pydch})]_n$ [61] demonstrates that only the anionic fragment of $(\text{phenH})_2(\text{pydc})$ is contributed to the complexation and $(\text{phenH})^+$ cation is lost. These complexes show a variety of structural features including mononuclear, binuclear and polymeric structures. In the Sb^{III} complex, the uncoordinated water molecules form small tetrameric water clusters located in the cavities of the structure. In these complexes, both intra- and intermolecular hydrogen bonds (O-H \cdots O and C-H \cdots O) are observed. Consequently, a supramolecular network is formed in which the fragments of the crystal lattice are linked together throughout the structure *via* hydrogen bonds [61].

Due to the large metallic center, the structure of $(\text{phenH})_3[\text{Y}(\text{pydc})_3]\cdot \text{DMSO}\cdot 5\text{H}_2\text{O}$ [62] has a coordination number of nine and a distorted tricapped trigonal prismatic arrangement forms around the Y^{III} center. Considerable π - π and C-H $\cdots\pi$ stacking interactions exist between the aromatic rings of $(\text{pydc})^{2-}$ (with distances of 3.659 (4) and 3.662 (4) Å), and between the CH groups of DMSO with the benzene rings

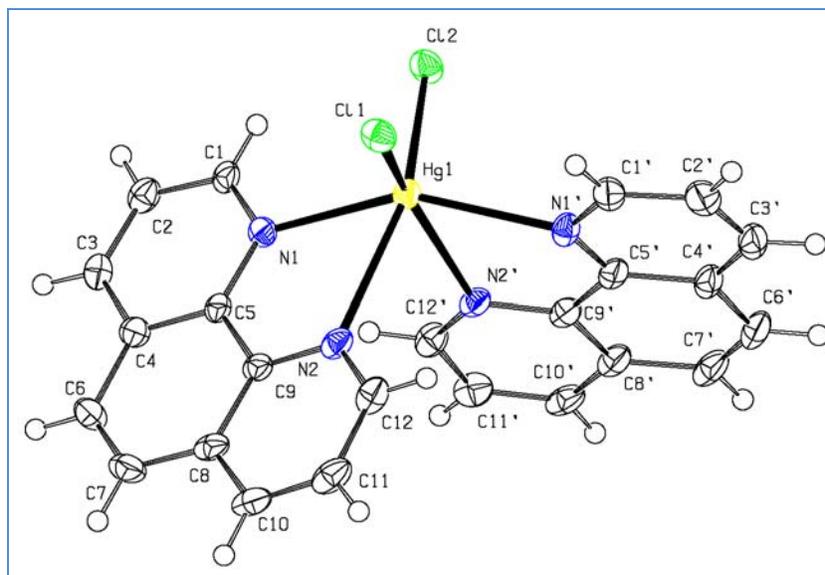


Fig. 9. Molecular structure of asymmetric unit of $[\text{HgCl}_2(\text{phen})_2]$.

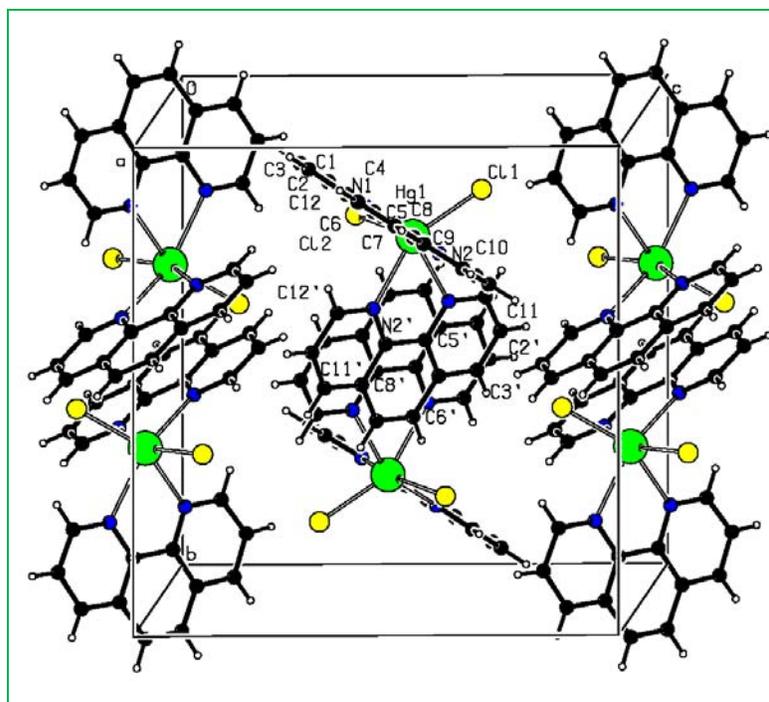


Fig. 10. The rings in neighboring molecules of $[\text{HgCl}_2(\text{phen})_2]$ indicate π - π stacking interactions.

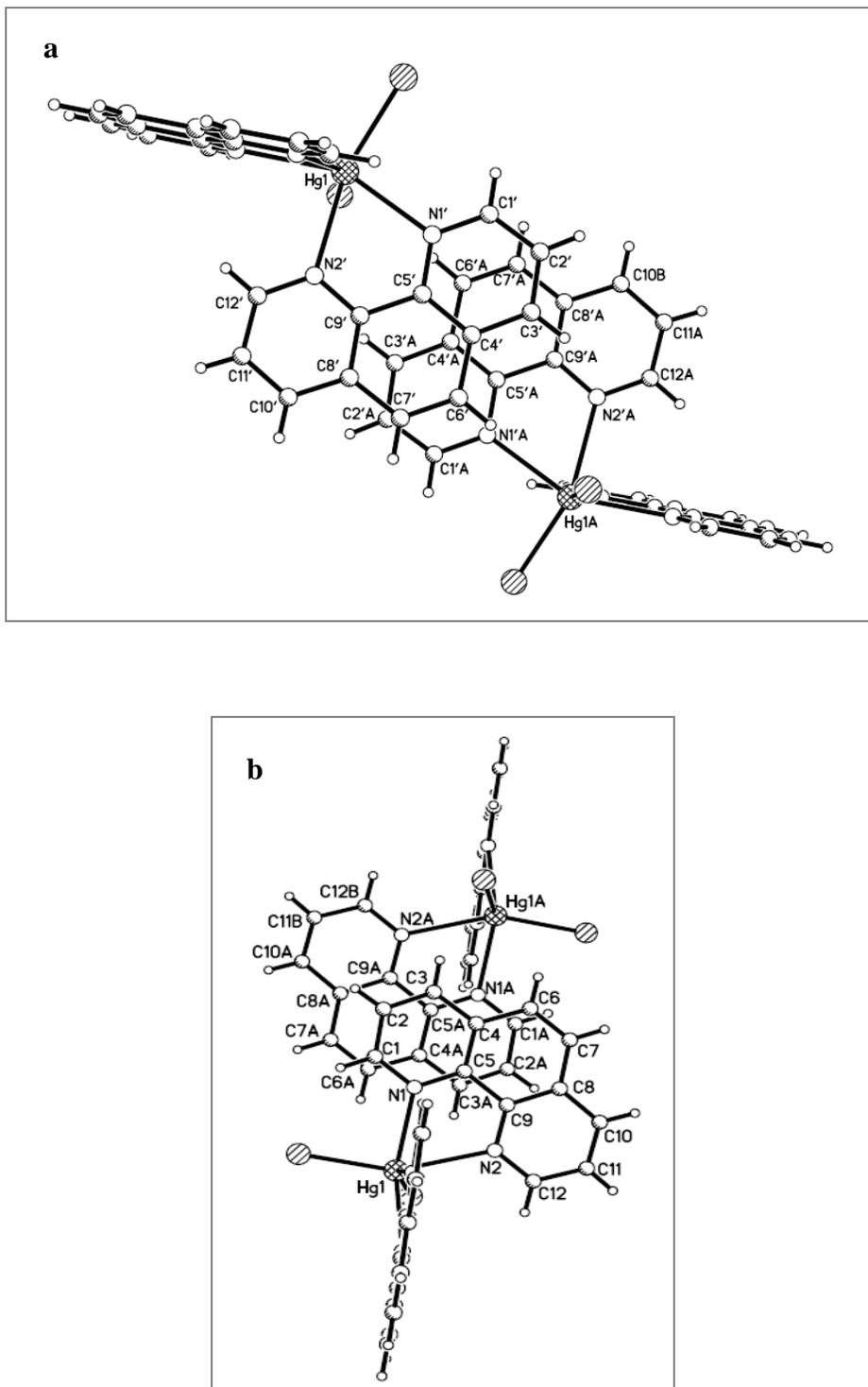


Fig. 11. Two views of parallel planes of the aromatic ligands in [HgCl₂(phen)₂], a) With a distance of 3.371 Å. [Symmetry code: (A) 1-x, 1-y, 1-z]. b) With a distance of 3.303 Å. [Symmetry code: (A) 2-x, -y, 1-z].

of the (pydc)²⁻ fragments. In the crystal structure, a wide range of non-covalent interactions consisting of hydrogen bonding (of the types O-H...O, O-H...S, N-H...O and C-H...O), ion pairing, π - π and C-H... π stacking connect the various components into a supramolecular structure. A variety of interactions, the coordination polyhedron and the layers of the compound are shown in Fig. 12.

Bis(guanidinium)-Pyridine-2,6-dicarboxylate Monohydrate, (GH)₂(pydc).H₂O, and Its Metal Complexes

The proton transfer compound (GH)₂(pydc).H₂O [63] was prepared in two steps. Guanidine hydrochloride was first neutralized by sodium hydroxide followed by a proton transfer process with pyridine-2,6-dicarboxylic acid in 2:1 molar ratio. The asymmetric unit of (GH)₂(pydc).H₂O consists of one (pydc)²⁻, two (GH)⁺ ions and a water molecule. The most important feature of the crystal structure of this compound is the existence of a self-associated cation-dianion system [63]. The metal ion of (GH)₂[Cd(pydc)₂].2H₂O [63] is hexacoordinated by pyridine-2,6-dicarboxylate as has a tridentate ligand. The structure of complex (GH)₃[Ce(pydc)₃].3H₂O [64] shows a coordination number of nine by three (pydc)²⁻ ligands. The most important feature of (GH)₂[Co(H₂O)₆][Co(pydc)₂]₂ [65], is the simultaneous formation of both anionic [Co(pydc)₂]²⁻ and cationic [Co(H₂O)₆]²⁺ complexes and (GH)⁺ ion, (Fig. 13). In the Ce^{III} complex, the water molecules interact to form trimeric water clusters; they also interact with the planar cations and anion. Bifurcated N-H...O bonds are present; these three center hydrogen bonds have a tendency towards planarity, which follows directly from hydrogen-bond linearity [64]. The intermolecular forces in these complexes consist of hydrogen bonding as type O-H...O [63-65], N-H...O [63-65] and C-H...O [64] and ion pairing. In addition, the π - π stacking in Co^{II} complex, occurs between anion-anion fragments with interplanar distance of ~3.5 Å [65]. The main hydrogen bonds produce an infinite three-dimensional framework [63,64].

The (GH)[Zn(pydc)(pydcH)].(pydcH₂).4H₂O [66] complex has (pydc)²⁻ and (pydcH)⁻ units as tridentate ligands. The intermolecular forces, which exist between anionic and cationic units in the Zn^{II} complex, consist of hydrogen bonding (O-H...O, N-H...O and C-H...O) and ion pairing. The least distance between (pydc)²⁻ rings is 3.323 Å and deviation

of parallelism is 3.75°, thus maximizing π - π interactions between neighboring (pydc)²⁻ rings. These interactions play important roles in the construction of its two dimensional supramolecular network [66].

Bis(guanidinium)-1,10-Phenanthroline-2,9-dicarboxylate, (GH)₂(Phendc), and Its Metal Complex

Only one complex has been derived from (GH)₂(phendc) [65] formulated as (GH)₂[Co(phendc)₂].4H₂O [65] in which the central atom is coordinated by two (phendc)²⁻ units as tridentate ligands. The most important features of the complex are ion pairing and extensive N-H...O hydrogen bondings, in addition to π - π stacking between anion-anion fragments with inter planar distance of ~3.5 Å.

2,4,6-Triamino-1,3,5-triazine-1,3-diium-Pyridine-2,6-dicarboxylate, (tataH₂)(pydc), and Bis(2,4,6-triamino-1,3,5-triazine-1-ium)-Pyridine-2,6-dicarboxylate, (tataH)₂(pydc), and Their Metal Complexes

The reaction between pyridine-2,6-dicarboxylic acid and 2,4,6-triamino-1,3,5-triazine (tata), also named as melamine, at 1:1 and 1:2 molar ratios leads to the formation of (tataH₂)(pydc) and (tataH)₂(pydc) adducts, respectively [67]. Both compounds have been characterized by spectroscopic methods as mentioned in Table 1. Derived from (tataH)₂(pydc), (tataH)₂[Pb(pydc)₂].2tata.4H₂O [67] is a binuclear complex with two metal fragments linked *via* a central ten-membered ring. Also, the arrangement of two (pydc)²⁻ as ligands show a free space in the coordination geometry around the Pb^{II}, occupied possibly by a stereochemically active lone pair of electrons on the Pb^{II} atom.

In isostructural (tataH)₂[Zn(pydc)₂].10H₂O [68] and (tataH)₂[Cd(pydc)₂] [69] complexes, the metallic centers are six-coordinated by pyridine-2,6-dicarboxylate as a tridentate ligand. In the Zn^{II} complex, cations and anions are connected *via* hydrogen bonds and form a one-dimensional chain. In addition, the uncoordinated water molecules form a three-dimensional network through further hydrogen bondings [68]. In the crystal structure of Cd^{II} complex, there are some π - π stacking interactions with short distances between parallel aromatic rings. The shortest distances between the π -systems of the cations and the anions are in the ranges 3.538-3.849 and 3.076-3.550 Å, respectively. The shortest distances between

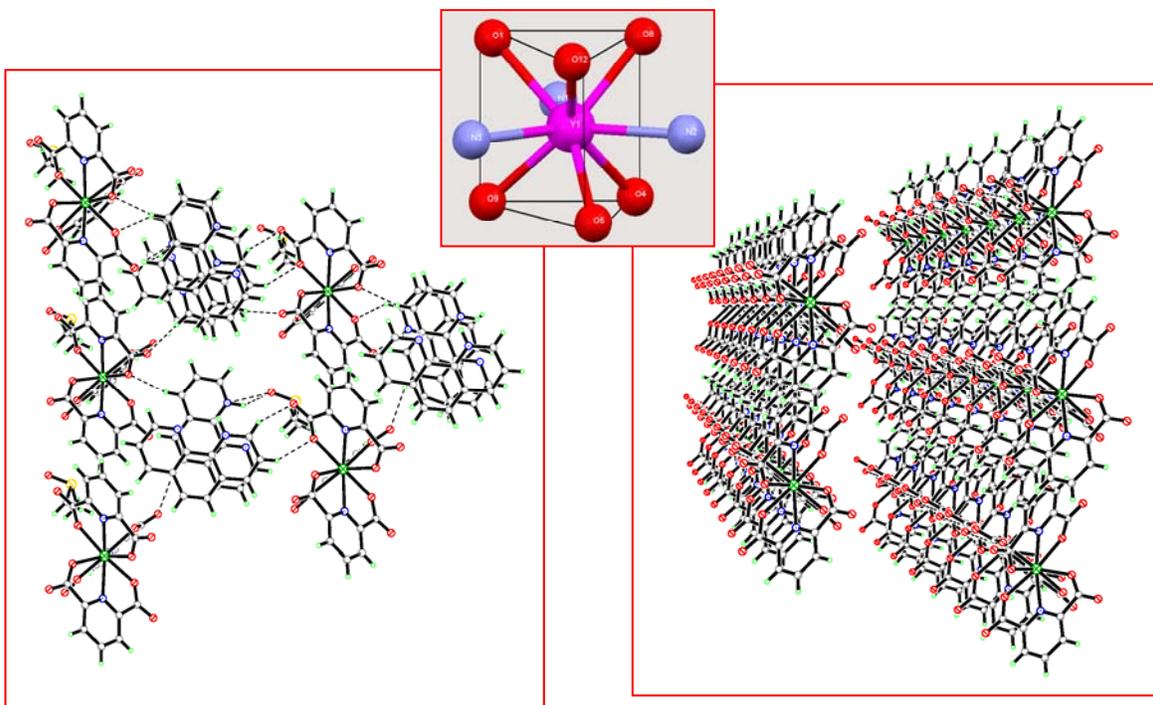


Fig. 12. a) Supramolecular interactions, b) Coordination polyhedron and c) Layers of $(\text{phenH})_3[\text{Y}(\text{pydc})_3] \cdot \text{DMSO} \cdot 5\text{H}_2\text{O}$.

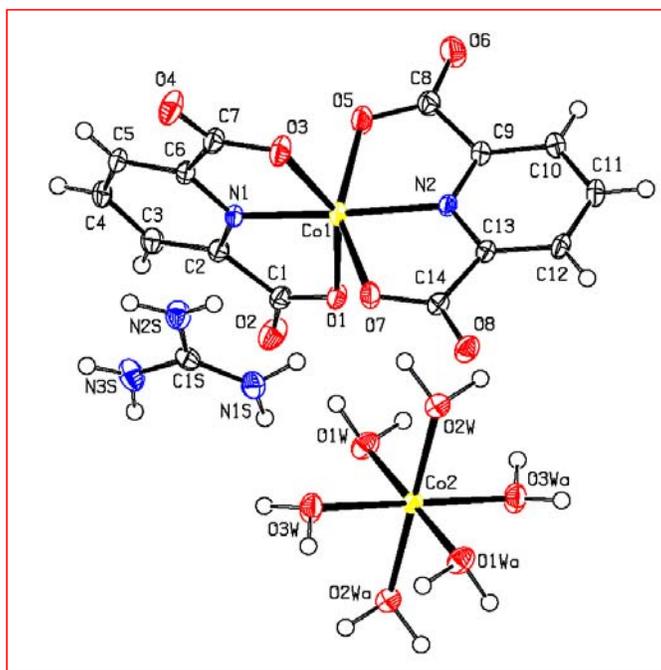


Fig. 13. Molecular structure of $(\text{GH})_2[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{pydc})_2]_2$, ellipsoids are illustrated at 50% probability level.

the π -systems of other cations and anions are in the ranges of 3.414-3.870 and 3.068-3.455 Å, respectively [69]. Therefore, in the formation of Pb^{II} , Zn^{II} and Cd^{II} complexes, ion pairing, metal-ligand coordination, O-H \cdots O [68], N-H \cdots O [67-69] and N-H \cdots N [67,69] hydrogen bondings involving anionic complex and cationic fragment and π - π stacking play important roles in the construction of three-dimensional network.

The crystal structure of $\{(\text{tataH})[\text{Bi}(\text{pydc})_2(\text{H}_2\text{O})]\}_n$ [70] contains $[\text{Bi}(\text{pydc})_2(\text{H}_2\text{O})]_n^{n-}$ polymeric fragments. The $(\text{tataH})^+$ cations form pairs, with their planes parallel and separated by 3.27(1) Å, indicating a π - π stacking interaction between them. Extensive O-H \cdots O and N-H \cdots O hydrogen bondings exist between the anionic polymers and the $(\text{tataH})^+$ cations. In $(\text{tataH})_2[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{pydc})_2]_2 \cdot 4\text{H}_2\text{O}$, as the newest compound of this group [71], similar to two other compounds of Co^{II} [65,81], there are two cationic and anionic complexes of Co^{II} in the structure (Fig. 14). There are extensive O-H \cdots O, N-H \cdots N, O-H \cdots N and C-H \cdots O hydrogen bonds in the structure, as well as π - π stacking between $(\text{pydc})^{2-}$ ligands with an interplanar distance of 3.484 (15) Å. Finally, the compound $(\text{tataH})_2[\text{Ni}(\text{pydc})_2] \cdot 5.25\text{H}_2\text{O}$ [72] has a six-coordinated Ni^{II} in a supramolecular network, the most important features of which include ion-pairing, metal-ligand coordination and a large number of O-H \cdots O, O-H \cdots N, N-H \cdots O, N-H \cdots N and C-H \cdots O hydrogen bonds.

Piperazinediium-Pyridine-2,6-dicarboxylate, (pipzH_2) (pydc), and Its Metal Complexes

In the proton transfer compound $(\text{pipzH}_2)(\text{pydc})$ [73], the protons are transferred from pyridine-2,6-dicarboxylic acid to nitrogen atoms of piperazine.

There is an ion pairing electrostatic interaction between $(\text{pydc})^{2-}$ and $(\text{pipzH}_2)^{2+}$ fragments and hydrogen bonds between four hydrogen atoms of NH_2^+ groups of piperazinediium and oxygen atoms of $(\text{COO})^-$ groups of three individual $(\text{pydc})^{2-}$ fragments so that, as shown in Fig. 15, each piperazinediium ion is trapped in a cage made of three anions by hydrogen bonds.

The molecular structure of $(\text{pipzH}_2)[\text{Pd}(\text{pydc})_2] \cdot 2\text{H}_2\text{O}$ [73] reveals that the Pd^{II} is four-coordinated by two $(\text{pydc})^{2-}$ as bidentate ligands. There are also O-H \cdots O and C-H \cdots O hydrogen bonds in the asymmetric unit linking the cationic

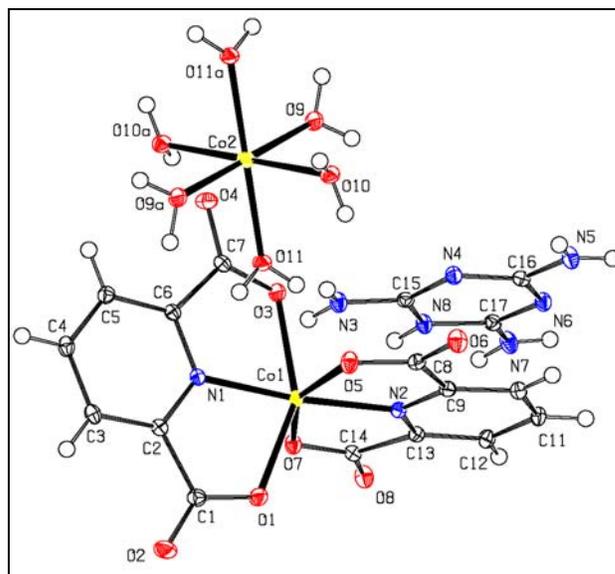


Fig. 14. Molecular structure of $(\text{tataH})_2[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{pydc})_2]_2 \cdot 4\text{H}_2\text{O}$, with two complexes of Co^{II} , ellipsoids are illustrated at 50% probability level. Uncoordinated water molecules are omitted for clarity.

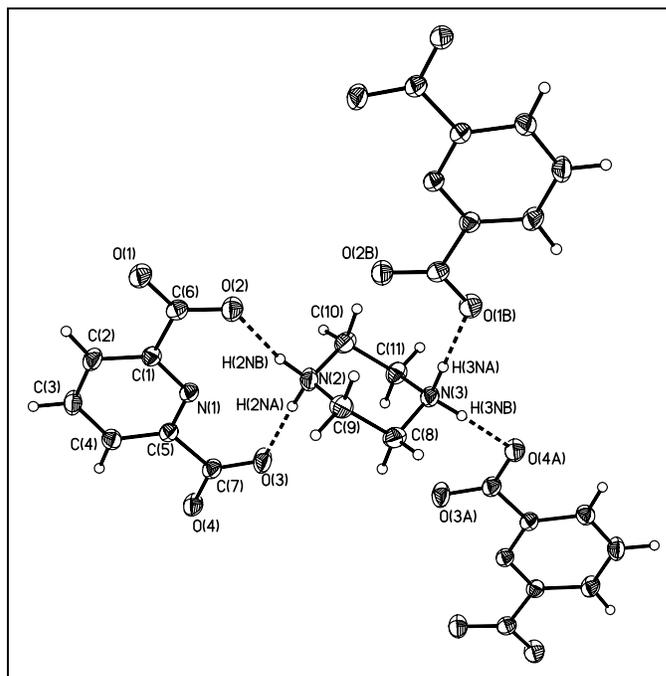


Fig. 15. A piperazinediium ion trapped between three pyridine-2,6-dicarboxylate ions by hydrogen bonds in $(\text{pipzH}_2)(\text{pydc})$.

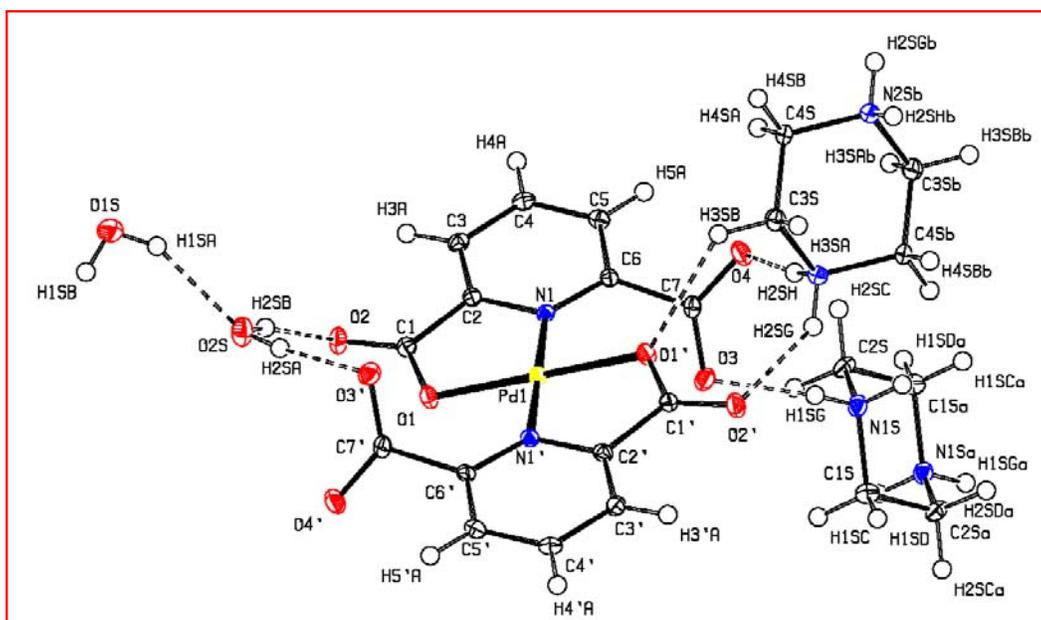


Fig. 16. Asymmetric unit of $(\text{pipzH}_2)[\text{Pd}(\text{pydc})_2] \cdot 2\text{H}_2\text{O}$ with O-H \cdots O and C-H \cdots O hydrogen bonds therein.

and anionic fragments and water molecules (Fig. 16).

In the $(\text{pipzH}_2)(\text{Ti}_2(\text{pydc})_2\text{Cl}_4(\text{H}_2\text{O})_2) \cdot 4\text{H}_2\text{O}$ [73] complex, the anionic moiety has a binuclear-bridged structure. Each Ti^{III} is seven-coordinated by two carboxylate oxygens and one nitrogen of $(\text{pydc})^{2-}$ group, two chloride, one water molecule and one carboxylate oxygen of another $(\text{pydc})^{2-}$ group. In this complex, we can find small six-membered cyclic water clusters built up from four-membered rings with two substitutions hydrogen bonded, as shown in Fig. 17.

According to five usual hexamer structures, *i.e.*, ring, book, bag, cage, prism [26], it seems that the structure of the water cluster is not a common case.

In $[\text{Mg}(\text{pydc})(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ [74], the $(\text{pydc})^{2-}$ species acts as a tridentate ligand through the two oxygens and one nitrogen atom. There are many intermolecular O-H \cdots O hydrogen bonds involving the $(\text{pydc})^{2-}$ species and water molecules in the crystal structure. In complex $(\text{pipzH}_2)_3[\text{In}(\text{pydc})_3] \cdot 12\text{H}_2\text{O}$ [75], the central In^{III} atom is eight-coordinated by two tridentate and one bidentate pyridine-2,6-dicarboxylate ligands. In this complex, extensive O-H \cdots O and N-H \cdots O hydrogen bondings are observed [75].

All $(\text{pipzH}_2)[\text{Ni}(\text{pydc})_2] \cdot 4\text{H}_2\text{O}$ [76], $(\text{pipzH}_2)[\text{Cu}(\text{pydc})_2] \cdot 4\text{H}_2\text{O}$ [77], $(\text{pipzH}_2)[\text{Mn}(\text{pydc})_2] \cdot 6\text{H}_2\text{O}$ [78], $(\text{pipzH}_2)[\text{Pb}$

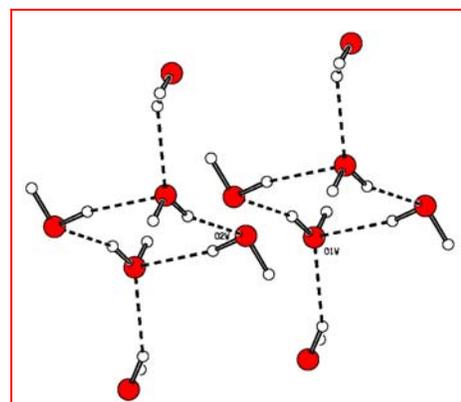


Fig. 17. Two six-membered water clusters formed by H-bonds between coordinated and uncoordinated water molecules in complex $(\text{pipzH}_2)[\text{Ti}_2(\text{pydc})_2\text{Cl}_4(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, the other fragments are omitted for clarity.

$(\text{pydc})_2] \cdot 2\text{H}_2\text{O}$ [79], $(\text{pipzH}_2)[\text{Zn}(\text{pydc})_2] \cdot 4\text{H}_2\text{O}$ [80] and $(\text{pipzH}_2)[\text{Hg}(\text{pydc})_2] \cdot 6\text{H}_2\text{O}$ [81] complexes have the formula of $(\text{pipzH}_2)[\text{M}(\text{pydc})_2] \cdot x\text{H}_2\text{O}$, where $\text{M} = \text{Ni}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Pb}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}$ and Hg^{II} . Although their cations are isostructural and

anions are the same, the differences between the seven complexes are first the number of water molecules participating in the structure and second the type of supramolecular interactions and their strengths. For example, when $M = \text{Ni}^{\text{II}}$ and Cu^{II} , considerable π - π stacking with distances of 3.4695-3.503 Å are observed (Fig. 18).

Also, when $M = \text{Pb}^{\text{II}}$, the π - π stacking distances between the centroids are 3.35-3.95 Å, and when $M = \text{Zn}^{\text{II}}$, considerable π - π stacking interactions exist with an average distances of 3.49 Å (Fig. 19). Extensive intra- and intermolecular $\text{O-H}\cdots\text{O}$, $\text{N-H}\cdots\text{O}$ [76-81] and $\text{C-H}\cdots\text{O}$ [76,77,79-81] hydrogen bonds involving the $(\text{pydc})^{2-}$ ligand, $(\text{pipzH}_2)^{2+}$ counter-ion and water molecules connect the various components into a supramolecular structure. The most important feature of $(\text{pipzH}_2)[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{pydc})_2]\cdot 2.8\text{H}_2\text{O}$ [82] is the simultaneous formation of both anionic $[\text{Co}(\text{pydc})_2]^{2-}$ and cationic $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complexes and $(\text{pipzH}_2)^{2+}$ ion. In the anionic complex, Co^{II} is hexacoordinated by $(\text{pydc})^{2-}$ as a tridentate ligand. In the $(\text{pipzH}_2)_{1/2}[\text{Al}(\text{H}_2\text{O})_6](\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$ [83] complex, the structure consists of Al^{III} coordinated to six water molecules together with the tetrahedral sulfate, piperazinedium cation and uncoordinated water molecules linked by hydrogen bonds. Extensive $\text{O-H}\cdots\text{O}$ [82,83], $\text{N-H}\cdots\text{O}$ [82, 83] and $\text{C-H}\cdots\text{O}$ [82] hydrogen bonds as well as ion pairing and π - π interactions existing between anionic fragments (3.5277(15) Å) [82] play an important role in stabilizing the structures and formation of a three-dimensional supramolecular network [82,83].

Piperazinedium Oxalate Monohydrate, $(\text{pipzH}_2)(\text{ox})\cdot\text{H}_2\text{O}$, and Its Metal Complexes

The proton transfer compound $(\text{pipzH}_2)(\text{ox})\cdot\text{H}_2\text{O}$ [84] possesses intra- and intermolecular $\text{O-H}\cdots\text{O}$, and $\text{N-H}\cdots\text{O}$ hydrogen bonds which link the components into a three-dimensional framework, resulting in the formation of a supramolecular structure based on a hydrogen bonded network. In $[\text{Mn}(\text{ox})(\text{H}_2\text{O})_2]_n$ [85] complex, one-dimensional linear chains are formed through bidentate oxalate ligands bridging the Mn^{II} atoms (Fig. 20). These structural units are held together by $\text{O-H}\cdots\text{O}$ hydrogen bonds and form a channel structure (Fig. 21). The asymmetric unit of the $(\text{pipzH}_2)[\text{V}(\text{ox})_2\text{O}(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ [86] complex contains the $[\text{V}(\text{ox})_2\text{O}(\text{H}_2\text{O})]^{2-}$ complex anion, two water molecules and

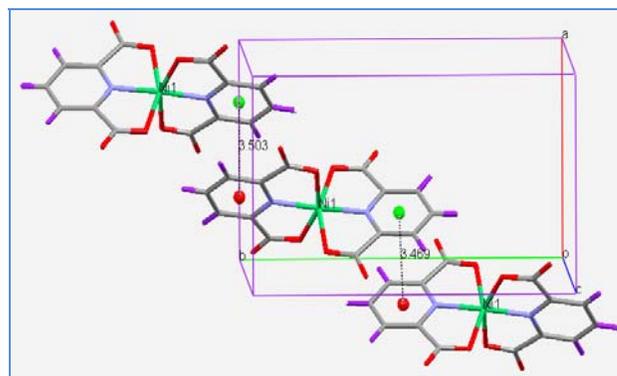


Fig. 18. The π - π stacking with distances of 3.469 and 3.503 Å in $(\text{pipzH}_2)[\text{Ni}(\text{pydc})_2]\cdot 4\text{H}_2\text{O}$.

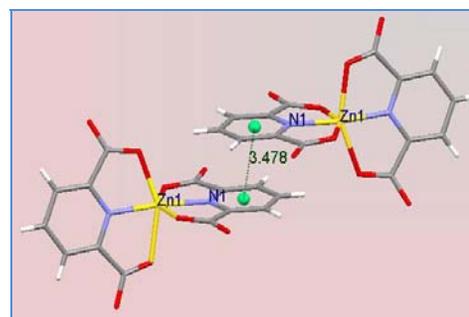


Fig. 19. The π - π stacking with distances of 3.478 Å in $(\text{pipzH}_2)[\text{Zn}(\text{pydc})_2]\cdot 4\text{H}_2\text{O}$.

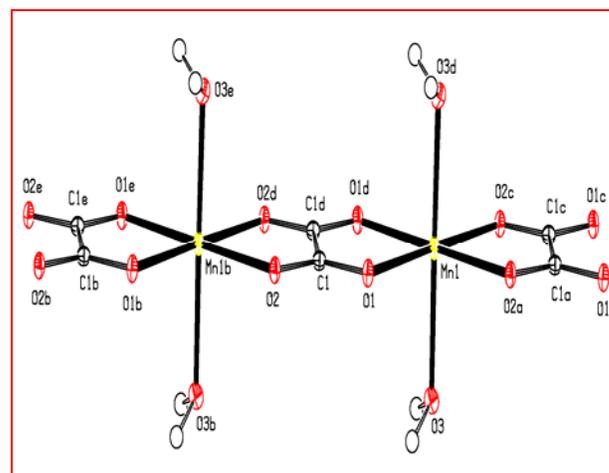


Fig. 20. Molecular structure of polymeric $[\text{Mn}(\text{ox})(\text{H}_2\text{O})_2]_n$.

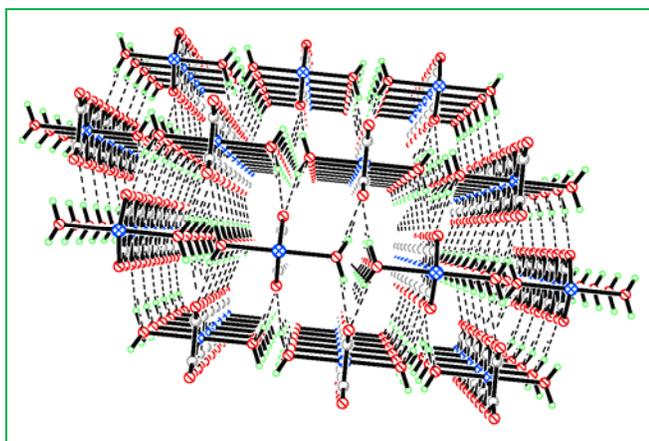


Fig. 21. The $[\text{Mn}(\text{ox})(\text{H}_2\text{O})_2]_n$ complex shows channels due to cavities present in each layer.

$(\text{pipzH}_2)^{2+}$ cation. This structure exhibits intermolecular N-H \cdots O and C-H \cdots O hydrogen bonds. The uncoordinated water molecules contribute to the formation of a supramolecular structure *via* O-H \cdots O hydrogen bonds [86].

Piperazinediium-Bis(pyridine-2,3-dicarboxylate), $(\text{pipzH}_2)_{1/2}(\text{py-2,3-dcH})$, and Its Metal Complexes

In the title proton transfer ion pair [87], although the orientation of two carboxylate groups is not in such a manner that the anionic fragment can act as good as pyridine-2,6-dicarboxylate ion in its many complexes, it can well coordinate to some metallic ions such as Zn^{II} and Cd^{II} [88,89].

In the polymeric complex $\{(\text{pipzH}_2)[\text{Zn}(\text{py-2,3-dc})_2 \cdot 4\text{H}_2\text{O}]_n$, [88] each Zn^{II} is coordinated by two bidentate pyridine-2,3-dicarboxylate ligands, which also act as bridging ligands between Zn^{II} atoms. The four donor atoms of the two coplanar $(\text{py-2,3-dc})^{2-}$ anions form a square-planar arrangement around the Zn^{II} center. In the crystal structure, extensive O-H \cdots O, N-H \cdots O and C-H \cdots O hydrogen bonds as well as ion pairing and π - π stacking (with a distance of 3.8693(8) Å between two aromatic rings) between different fragments, play an important role in the stabilization of the supramolecular structure [88]. The $[\text{Cd}(\text{py-2,3-dc})(\text{H}_2\text{O})_3]_n$ [89] polymeric complex is synthesized from the title proton transfer compound from which $(\text{pipzH}_2)^{2+}$ ion is not incorporated (Fig. 23).

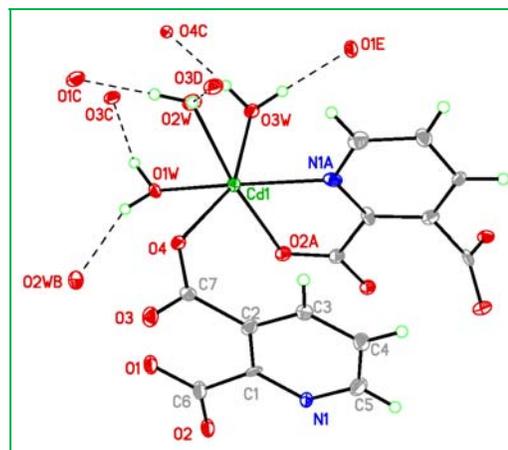


Fig. 22. Molecular structure of $[\text{Cd}(\text{py-2,3-dc})(\text{H}_2\text{O})_3]_n$.

Piperazinediium-Pyridine-2,5-dicarboxylate Dihydrate, $(\text{pipzH}_2)(\text{py-2,5-dc}) \cdot 2\text{H}_2\text{O}$, and Its Metal Complexes

In packing diagram of proton transfer compound $(\text{pipzH}_2)(\text{py-2,5-dc}) \cdot 2\text{H}_2\text{O}$ [90], it can be seen that the intermolecular O-H \cdots O and N-H \cdots O hydrogen bonds and C-H \cdots π interactions between piperazinediium and the aromatic ring of pyridine-2,5-dicarboxylate are responsible for extending the structure into a three-dimensional supramolecular network.

The $(\text{pipzH}_2)[\text{Cd}(\text{py-2,5-dc})_2(\text{py-2,5-dcH})] \cdot 3\text{H}_2\text{O}$ [91], $\{(\text{pipzH}_2)[\text{Zn}(\text{py-2,5-dc})_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}\}_n$ [92] and $[\text{Ni}(\text{py-2,5-dc})(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ [93] complexes have extensive O-H \cdots O, N-H \cdots O and C-H \cdots O hydrogen bonds connecting the various components into a supramolecular structure. Also, considerable π - π stacking with a 3.76 Å distance are observed between two aromatic rings of py-2,5-dc [92,93].

Piperazinediium-Bis(6-carboxypyridine-2-carboxylate) Trihydrate, $(\text{pipzH}_2)(\text{pydcH})_2 \cdot 3\text{H}_2\text{O}$, and Its Metal Complexes

The proton transfer compound $(\text{pipzH}_2)(\text{pydcH})_2 \cdot 3\text{H}_2\text{O}$ [94] whose crystal structure has two monoanionic units joined together *via* hydrogen bonding, forms a supramolecular structure. The O-H \cdots O, N-H \cdots O, and N-H \cdots N hydrogen bonds are responsible to construct the three-dimensional

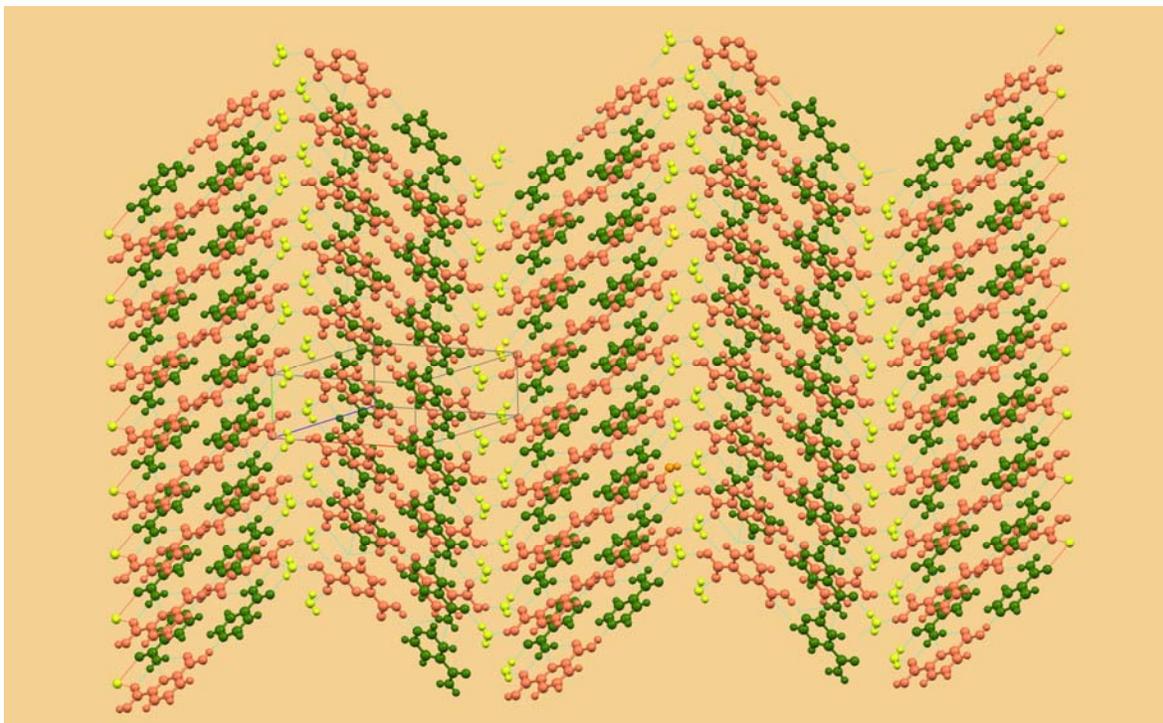


Fig. 23. The packing of hydrogen-bonded chains in the crystal structure of pyc.pydcH₂.H₂O. Hydrogen bonds are shown as dashed lines.

framework.

The (pipzH₂)[Fe(pydc)₂]₂.H₂O [95], {(pipzH₂)[Bi₂(pydc)₄(H₂O)].2H₂O}_n [96] and (pipzH₂)₃[Nd(pydc)₃]₂.15.33H₂O [97] complexes are derived from (pipzH₂)(pydcH)₂.3H₂O. Although Fe²⁺ ions are used as starting material, it seems that Fe²⁺ ions oxidize into Fe³⁺ ions during the synthesis process [95]. In the Bi^{III} complex, (pydc)²⁻ acts as a tridentate ligand and also has a bridging role. These binuclear units consist of two Bi^{III} atoms, four (pydc)²⁻ ligands, one uncoordinated and one coordinated water molecules and one (pipzH₂)²⁺ which acts as counter ion. There are some inter- and intramolecular interactions in supramolecular compounds of Fe^{III} and Bi^{III} including O-H...O, N-H...O, and C-H...O interactions and π - π stackings [95] with shortest distance of 3.50 Å and C-H... π interactions of 3.64 and 3.65 Å [96]. In Nd^{III} complex, the nine donor atoms of the three (pydc)²⁻ fragments form a distorted tricapped trigonal prism arrangement around the Nd^{III} center. Considerable C-O... π stacking interactions between CO groups of carboxylate fragments and aromatic rings of (pydc)²⁻ with

distances of 3.135 (5)-3.255 (5) Å are observed. Also there exist a wide range of non-covalent interactions consisting of O-H...O, N-H...O and C-H...O hydrogen bonds with D...A ranging from 2.608 (10) to 3.278 (7) Å, ion pairing and C-O... π stacking which connect the various components into a supramolecular structure [97].

Piperazinediium-6-Carboxypyridine-2-carboxylate-Pyridine-2,6-dicarboxylic Acid Monohydrate, (pipzH₂)_{1/2}(pydcH).(pydcH₂).H₂O

The given results about (pipzH₂)_{1/2}(pydcH).(pydcH₂).H₂O adduct [98] indicate that the reaction between piperazine and pyridine-2,6-dicarboxylic acid reached to the transfer of carboxylic acid protons to hetero-nitrogen atoms of piperazine as Lewis base, composing a (pipzH₂)²⁺ and (pydcH)⁻ complex. Thus proton transferred (pydcH)⁻ and non proton transferred (pydcH₂) are standing with (pipzH₂)²⁺. This phenomenon enables us to have not only the ordinary hydrogen bonds, but also weak ones (C-H...O). According to the presence of these

hydrogen bonds, the (pydcH)⁻(pydcH₂) and (pydcH)⁻(pydcH)⁻ chains are made and cause a layered motif. The chains give a two-dimensional self-assembled supramolecular sheet. The inter-sheet distances between the same molecules (pydc)²⁻ and different molecules (pydcH)pydcH₂) are 3.6 and 3.4 Å, respectively. These distances and the spatial positions of (pydc)²⁻ derivatives will result in a face-to-face π-π stacking between their aromatic parts [98].

Pyridine-4-carboxamide-Pyridine-2,6-dicarboxylic Acid-Water (1/1/1), (pyc)(pydcH₂).H₂O

In the crystal structure of pyc.pydcH₂.H₂O [99] as a cocrystal, the water molecules bridge between the organic components through hydrogen bonds, forming infinite zigzag chains, which are further linked together to form a hydrogen-bonded three-dimensional network. A remarkable feature in the crystal structure of this compound is the presence of a large number of O-H...O, O-H...N, N-H...O and C-H...O hydrogen bonds (Fig. 23).

Ethylenediguanidinediium-Pyridine-2,6-dicarboxylate Trihydrate, (EDGH₂)(pydc).3H₂O, and Its Metal Complex

The most important features of the crystal structure of proton transfer compound (EDGH₂)(pydc).3H₂O [100] are the interactions between (EDGH₂)²⁺ and (pydc)²⁻ fragments consisting of ion pairing, and hydrogen bonding. In addition, the π-π stacking occurs between the anion-anion fragments with the interplanar distance of 3.34 Å.

The intermolecular forces in (EDGH₂)[Zn(pydc)₂].3H₂O [79] between the anionic and cationic units consist of hydrogen bonding and ion pairing. There is also an infinite one-dimensional chain of cation and one of the water molecules using a bifurcated acceptor hydrogen bond. These chains by aid of two other bifurcated acceptor hydrogen bonds make a two dimensional layer. Therefore, three types of hydrogen bonding (*i.e.*, O-H...O, N-H...O, and C-H...O) are present.

Creatinium-6-Carboxypyridine-2-carboxylate Monohydrate, (creatH)(pydcH).H₂O, and Its Metal Complexes

The structure of proton transfer compound (creatH)

(pydcH).H₂O [101] consists of (creatH)⁺ and (pydcH)⁻ ions and a disordered water molecule. The intermolecular interactions among the three fragments consist of ion pairing, hydrogen bonding and π-π stacking.

In the complex (creatH)[Zn(pydc)(pydcH)].4H₂O [102], the protonated position of counter ion is the imine nitrogen of endocyclic creatinine. The intermolecular forces which exist between anionic and cationic units in the Zn^{II} complex consist of hydrogen bonding, ion pairing and π-π stacking. The existing four uncoordinated water molecules increase the number of hydrogen bonds in the crystal lattice. The intercentroid and interplaner distances between (pydc)²⁻ rings are 4.318 and 2.841 Å, respectively, thus maximizing π-π interactions between neighboring (pydc)²⁻ rings [102]. The chemical formula and the molecular structure of [Tl₂(pydcH)₃(pydc)(H₂O)₂], [41] indicates that the cationic fragment, (creatH)⁺, has been missed during complexation and only the anionic species of the starting proton transfer compound has contributed to the complex. A remarkable feature is that, in the obtained complex, both mono- and dianionic forms of ligand are observed. Short distances between parallel aromatic rings of (pydcH)⁻ and (pydc)²⁻ in neighboring molecules indicate π-π stacking interactions [41].

Among the [Cu(pydc)(pydcH₂)].2H₂O [103], [(Fe(pydc)(H₂O)₂)₂ox].6H₂O [103], [Tl(pydcH)]_n [103] and (creatH)₂[Bi(pydc)₂]₂.4H₂O [103] complexes, the molecular structure of Cu^{II} complex illustrated that the cationic fragment of the starting ion pair has been removed and only the anionic species has contributed to the complexation.

The Fe^{III} complex has a binuclear structure, with an oxalate ligand, linking two central atoms. It is noticeable that the oxalate ion wasn't present in the starting materials and is produced during the synthesis process. The Fe^{III} structure with its π-π stacking distance is illustrated in Fig. 24.

The Tl^I complex is a polymeric system, showing only the contribution of the anionic species of (creatH)(pydcH).H₂O to the complexation. From Fig. 25 it can be seen that the Bi^{III} complex is a dimeric system, showing contributions from both the cationic and anionic fragments. Also, there are a number of plays a linking role between the fragments of the crystal. A remarkable feature of this complex is the presence of N-H...π stacking with distance of 3.464 Å between N-H group of creatinine and aromatic ring of (pydc)²⁻ fragments, as

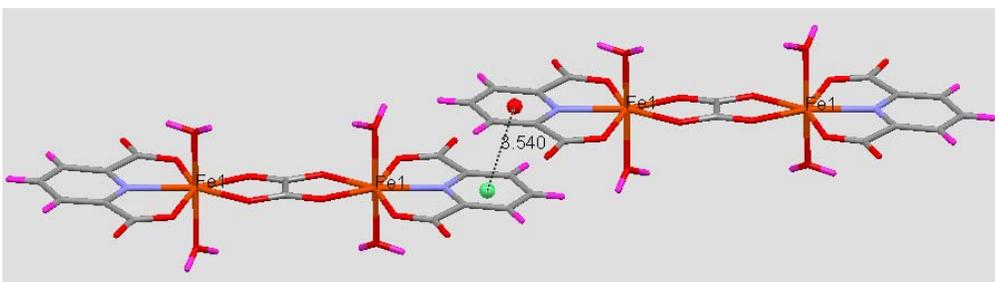
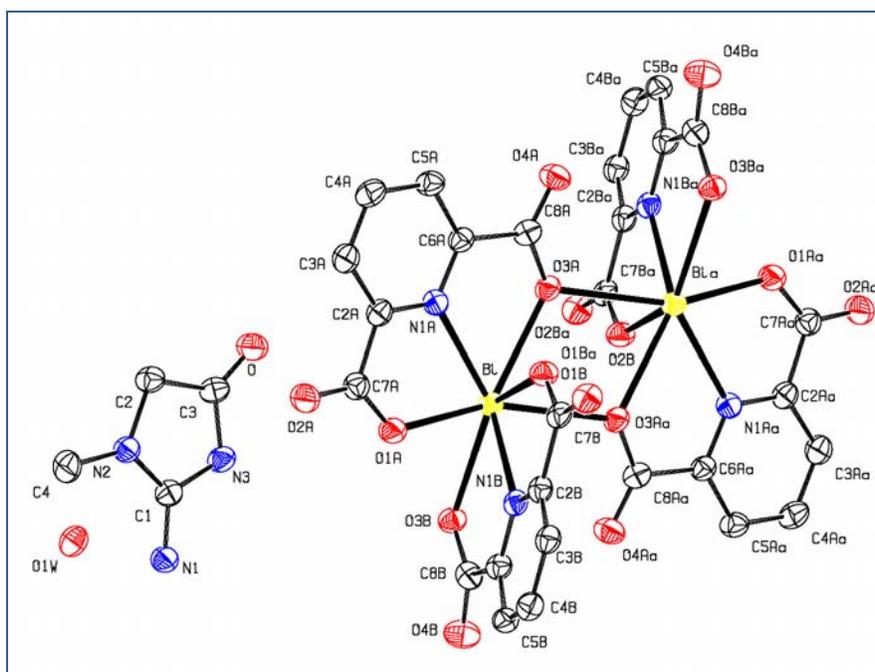


Fig. 24. The π - π stacking in compound $[(\text{Fe}(\text{pydc})(\text{H}_2\text{O})_2)_2\text{ox}]\cdot 6\text{H}_2\text{O}$.



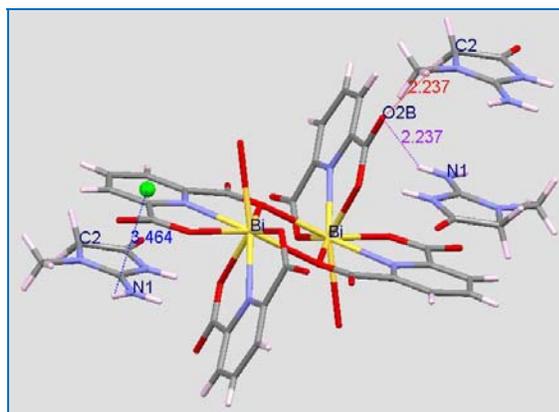


Fig. 26. N-H $\cdots\pi$ stacking, N-H \cdots O and C-H \cdots O hydrogen bonds in (creatH)₂[Bi(pydc)₂]₂.4H₂O.

distance is reported to be 3.3 Å for this compound.

Guanidinium-4-Hydroxypyridinium-2,6-dicarboxylate Anhydrate and Monohydrate, (GH)(hypycdH), (GH)(hypycdH).H₂O, and Its Metal Complex

The proton transfer ion pairs (GH)(hypycdH) [105] and (GH)(hypycdH).H₂O [106], which are obtained in two similar synthetic paths, have similar structures differing only in the number of water molecules. The crystal structures of both compounds show that both intra- and intermolecular proton transfers have occurred. In effect, a single proton from one of the carboxyl groups was transferred to the double-bonded N atom of the guanidine molecule. On the other hand, an interesting feature exhibited by the crystal structure is that an intramolecular proton transfer has occurred from the other carboxyl group to the N atom of the aromatic ring which was not observed when pyridine-2,6-dicarboxylic acid was used as the proton donor to guanidine [63]. The O-H \cdots O and N-H \cdots O hydrogen bonding interactions, in addition to ion pairing forces, are observed between the cation and anion.

In the (GH)₂[Ni(hypycd)₂].2H₂O [107] complex, considerable N-H $\cdots\pi$ and C-O $\cdots\pi$ stacking interactions between N-H groups of guanidine and C-O groups of carboxylate fragments with phenyl ring of (hypycd)²⁻ with distances of 3.2642(9) and 3.3212(8) Å are observed, respectively. A wide range of non-covalent interactions consisting of O-H \cdots O and N-H \cdots O hydrogen bonding, ion

pairing, N-H $\cdots\pi$ and C-O $\cdots\pi$ stacking connect the various components into a supramolecular structure.

Propane-1,3-diaminium-6-Carboxypyridine-2-carboxylate-Pyridine-2,6-dicarboxylic Acid-Water (1/2/2/8), (pnH₂)(pydcH)₂.2(pydcH₂).8H₂O, and Propane-1,3-diaminium-Pyridine-2,6-dicarboxylate-Pyridine-2,6-dicarboxylic Acid-Water (1/1/1/2.5), (pnH₂)(pydc)(pydcH₂).2.5H₂O, and Their Metal Complexes

In both proton transfer compounds, (pnH₂)(pydcH)₂.2(pydcH₂).8H₂O [108] and (pnH₂)(pydc)(pydcH₂).2.5H₂O [109], a variety of hydrogen bonds connect the various fragments into a supramolecular structure. In (pnH₂)(pydcH)₂.2(pydcH₂).8H₂O, several π - π stackings ranging 3.5108(11)-3.5949(11) Å are also observed. Many complexes were prepared using the second proton transfer compound and related metallic salts. In the (pnH₂)[Co(pydc)₂].4H₂O [110], (pnH₂)[Cu(pydc)₂].4H₂O [110] and (pnH₂)[Cd(pydc)₂].3.5H₂O [110] complexes, each [M(pydc)₂]²⁻ anionic complex (where M = Co^{II}, Cu^{II}, and Cd^{II}) are accompanied by one (pnH₂)²⁺ as counter ion and water molecules. In the complexes, ribbons of anionic complexes connect to ribbons of the cationic parts and water molecules by several strong O-H \cdots O, N-H \cdots O and C-H \cdots O hydrogen bonds to construct a supramolecular species. In the Co^{II} and Cu^{II} complexes, π - π stacking is observed between two pyridine rings with distance of 3.41 and 3.51 Å, respectively [110].

In (pnH₂)[Zn(pydc)₂].4H₂O [79] the distances between (pydc)²⁻ rings in two neighboring anionic fragments are measured as 3.400(4) and 3.604(4) Å. In the Zn^{II} complex and (pnH₂)₂[Ce(pydc)₃](NO₃).3.5H₂O [111], in addition to van der Waals and dipole-dipole interactions, which are important in the packing of the crystal system, there are also O-H \cdots O [79,110], N-H \cdots O [79,110] and C-H \cdots O hydrogen bonding interactions. The crystal packing diagram indicates the infinite two dimensional network [79]. Another compound of this group is [Pb(pydc)]_n [112] which does not have any counter ion in the structure. It is a binuclear compound of Pb^{II} with a four-membered Pb₂O₂ ring formed between metal centers and oxygen atoms of carboxylate groups. Considering the Pb-O bond lengths and their meaningful differences, it is apparent that the atoms around Pb^{II} atoms have a hemi-directed configuration, which is caused by the activity of lead's

electron lone pair. Crystallographically speaking, the main structure of this self-assembling compound is formed along the 2_1 screw axis.

Propane-1,3-diaminium-Pyridine-2,3-dicarboxylate Monohydrate, $(\text{pnH}_2)(\text{py-2,3-dc})\cdot\text{H}_2\text{O}$, and Its Metal Complexes

The proton transfer ion pair $(\text{pnH}_2)(\text{py-2,3-dc})\cdot\text{H}_2\text{O}$ [113] has intramolecular $\text{N-H}\cdots\text{O}$ and intermolecular $\text{O-H}\cdots\text{O}$, $\text{N-H}\cdots\text{O}$, $\text{N-H}\cdots\text{N}$ and $\text{C-H}\cdots\text{O}$ hydrogen bonds and edge to face π - π stacking together with ion pairing resulting in expansion of the structure in three dimensions. The distances and angles of $\text{C-H}\cdots\pi$ stacking are 2.81 Å ($\text{H}\cdots\pi$) and 136° ($\text{C-H}\cdots\pi$).

The $\{(\text{pnH}_2)[\text{Cu}(\text{py-2,3-dc})_2]\cdot 3\text{H}_2\text{O}\}_n$ [114] complex includes $(\text{py-2,3-dc})^{2-}$ as a bidentate ligand. One dimensional linear chains are propagated by bridging pyridine-2,3-dicarboxylates. The π - π stacking between two aromatic rings of $(\text{py-2,3-dc})^{2-}$ fragments with distance of 3.539(3) Å are observed. The $\text{C-O}\cdots\pi$ distances are 3.240(5) Å. Intermolecular $\text{O-H}\cdots\text{O}$, $\text{O-H}\cdots\text{N}$, $\text{N-H}\cdots\text{O}$, $\text{C-H}\cdots\text{O}$ and $\text{C-H}\cdots\text{N}$ hydrogen bonds cause formation of an interesting supramolecular structure.

Propane-1,3-diaminium-Pyridine-3,5-dicarboxylate Monohydrate, $(\text{pnH}_2)(\text{py-3,5-dc})\cdot\text{H}_2\text{O}$, and Its Metal Complexes

A remarkable feature in the crystal structure of $(\text{pnH}_2)(\text{py-3,5-dc})\cdot\text{H}_2\text{O}$ [115] is the presence of a large number of $\text{O-H}\cdots\text{O}$, $\text{N-H}\cdots\text{O}$, and $\text{N-H}\cdots\text{N}$ hydrogen bonds. The hydrogen bonds connect different components, thus forming infinite layers that are finally linked together to form hydrogen bonded three-dimensional network. The $[\text{Ba}(\text{py-3,5-dc})(\text{H}_2\text{O})_3]_n$ [116] and $[\text{Sr}(\text{py-3,5-dc})(\text{H}_2\text{O})_4]_n$ [117] complexes are derived from the mentioned ion pair. The propane-1,3-diaminium cation is not incorporated in both crystal structures. The Ba^{II} atom is nine-coordinated with six carboxylate oxygen atoms from the $(\text{py-3,5-dc})^{2-}$ ligands and three oxygen atoms from the coordinated water molecules in a polymeric form (Fig. 27 in which one coordinated oxygen atom is not shown for clarity). The coordination polyhedron is an almost tricapped trigonal prism around Ba^{II} atom.

In the latter, the Sr^{II} atom is eight-coordinated by four oxygen atoms of three pyridine-3,5-dicarboxylate ligands and

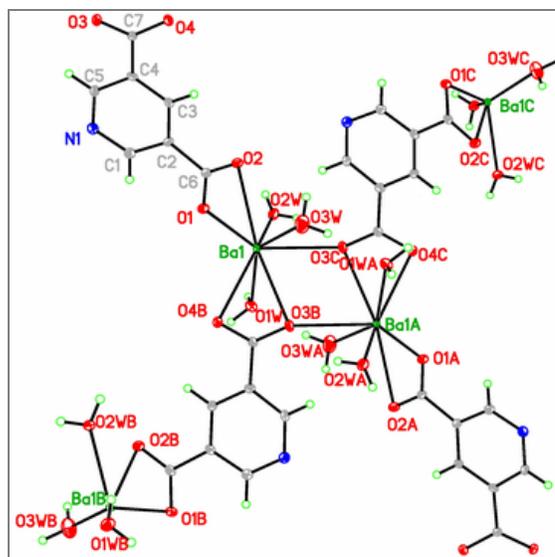


Fig. 27. Molecular structure of $[\text{Ba}(\text{py-3,5-dc})(\text{H}_2\text{O})_3]_n$.

four oxygen atoms of four coordinated water molecules (Fig. 28a). The coordination polyhedron is distorted dodecahedron around the Sr^{II} atom. The binuclear units are connected together *via* carboxylate oxygen atoms to build a one-dimensional polymeric chain. Hydrogen bonds ($\text{X-H}\cdots\text{O}$, $\text{X} = \text{O}$, N and C) are observed in the chain. In both crystal structures, noncovalent interactions consisting of hydrogen bonds and π - π stacking interactions connect the various components into the supramolecular structure; the π - π stackings of Sr^{II} compound is shown in Fig. 28b.

Bis(propane-1,3-diaminium)-Benzene-1,2,4,5-tetracarboxylate Dihydrate, $(\text{pnH}_2)_2(\text{btc})\cdot 2\text{H}_2\text{O}$, and Its Metal Complexes

In the crystal structure of $(\text{pnH}_2)_2(\text{btc})\cdot 2\text{H}_2\text{O}$ [118], a number of $\text{O-H}\cdots\text{O}$, $\text{N-H}\cdots\text{O}$, and $\text{C-H}\cdots\text{O}$ hydrogen bonds are observed, producing a three-dimensional network which results in the formation of a supramolecular structure. Ion pairing and van der Waals interactions are also effective in the packing of the crystal structure.

The outstanding feature of both $\{(\text{pnH}_2)[\text{Ni}(\text{btc})(\text{H}_2\text{O})_2]\cdot 0.5\text{H}_2\text{O}\}_n$ [119] and $\{(\text{pnH}_2)[\text{Co}(\text{btc})(\text{H}_2\text{O})_2]\cdot 0.5\text{H}_2\text{O}\}_n$ [120] complexes (Fig. 29) is the presence of $\text{C-H}\cdots\pi$ stacking

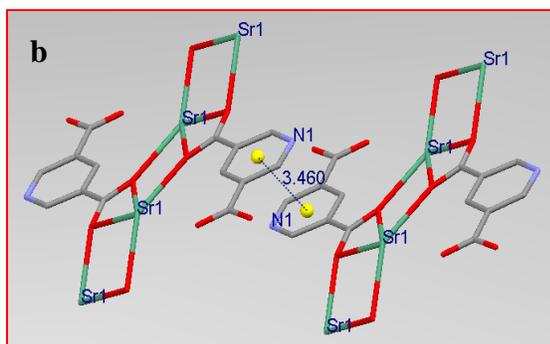
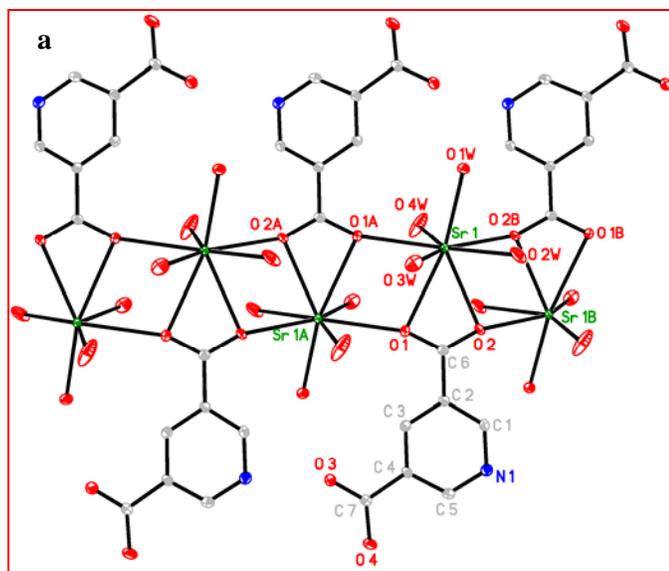


Fig. 28. a) Molecular structure and b) $\pi\cdots\pi$ Stacking in eight-coordinated $[\text{Sr}(\text{py-3,5-dc})(\text{H}_2\text{O})_4]_n$, water molecules are omitted for clarity.

interactions between C-H groups of $(\text{pnH}_2)^{2+}$ cations and aromatic ring of $(\text{btc})^+$ fragments.

The C-H $\cdots\pi$ distances in Ni^{II} complex are 2.60 and 2.97 Å (Fig. 30a). The most important feature of both complexes is a number of O-H \cdots O, N-H \cdots O, and C-H \cdots O hydrogen bonds between $(\text{pnH}_2)^{2+}$, anionic fragments and uncoordinated water molecules. Ion pairing, C-H $\cdots\pi$ stacking and van der Waals forces are also effective in the stabilization of the crystal structure, resulting in the formation of an interesting

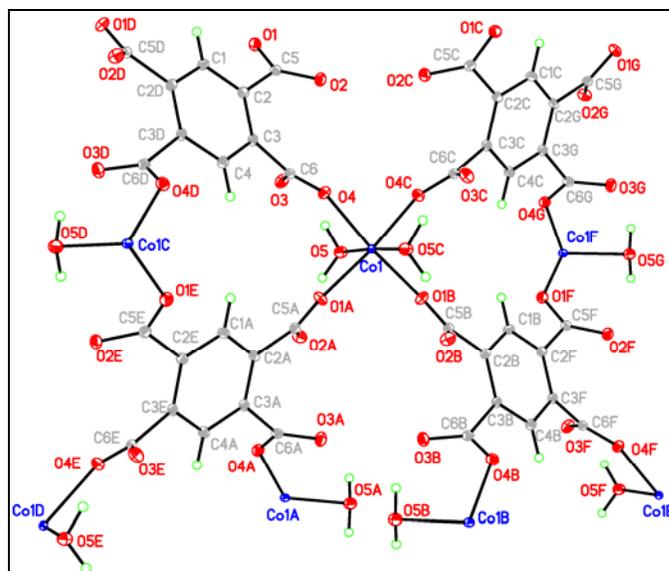


Fig. 29. Full environment of Co1 center for polymeric $\{(\text{pnH}_2)[\text{Co}(\text{btc})(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}\}_n$ complex, Co1C and Co1F atoms belong to a twofold axis. Co atoms labeled with A-G are obtained by the following symmetry codes: A: $x, -y+3/2, z-1/2$; B: $-x+1, y+1/2, z-1/2$; C: $-x+1, -y+1, z$; D: $-x+3/2, y, z$; E: $-x+3/2, -y+3/2, z-1/2$; F: $x-1/2, y-1/2, z-1/2$; G: $x-1/2, -y+1, z$.

supramolecular structure in both complexes, the 3D network of Ni^{II} compound is illustrated in Fig. 30b.

Metal Complexes Including 2,9-Dimethyl-1,10-phenanthroline and Pyridine-2,6-dicarboxylate Fragments, dmpH-pydc

The $(\text{dmpH})[\text{V}(\text{pydc})\text{O}_2] \cdot \text{H}_2\text{O}$ [121] and $(\text{dmpH})[\text{Fe}(\text{pydc})_2] \cdot 2\text{H}_2\text{O}$ [122] complexes were prepared from the reaction between three constituents dmp, pydcH₂ and corresponding metallic salts. In the $(\text{dmpH})[\text{V}(\text{pydc})\text{O}_2] \cdot \text{H}_2\text{O}$ complex, each V^{V} is attached to the neighboring complex and four $(\text{dmpH})^+$ units *via* C-H \cdots O interactions. These interactions, coming in concert, make infinite layers. The water molecule resides between two ionic units making a bridge-like hydrogen bond. The important characteristic of the crystal structure of $(\text{dmpH})[\text{Fe}(\text{pydc})_2] \cdot 2\text{H}_2\text{O}$ is the infinite

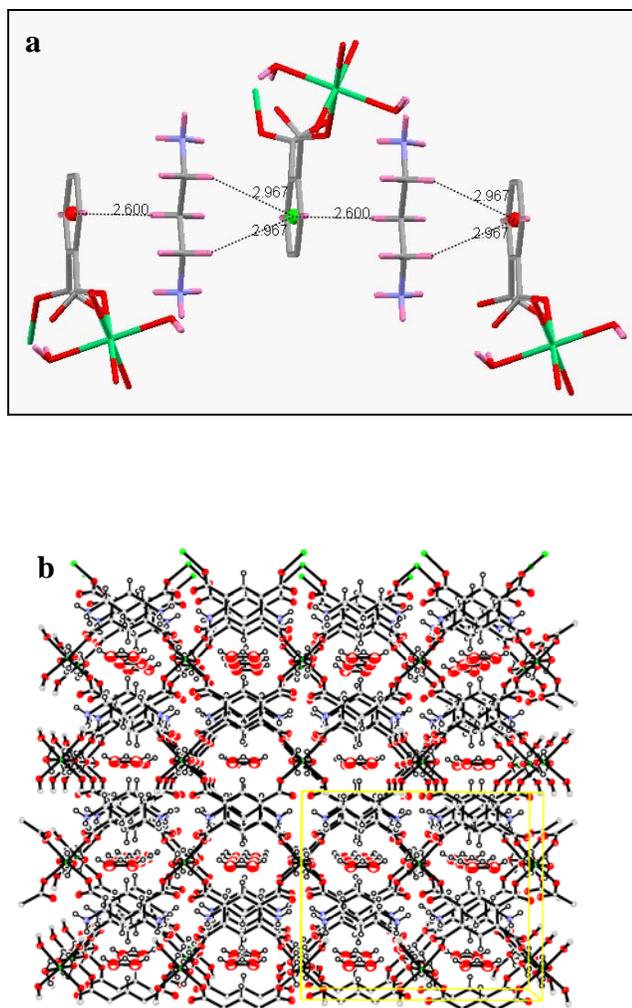


Fig. 30. a) The C-H $\cdots\pi$ stacking interactions and b) 3D crystal packing of $\{(\text{pnH}_2)[\text{Ni}(\text{btc})(\text{H}_2\text{O})_2]\cdot 0.5\text{H}_2\text{O}\}_n$.

one dimensional chains. Therefore, in the formation of these complexes, ion pairing, metal-ligand coordinations, O-H \cdots O, N-H \cdots O, C-H \cdots O, and O-H \cdots N (only in V^V complex) hydrogen bonding as well as van der Waals forces play important role in the construction of the observed three-dimensional supramolecular structure.

In the V^V complex, considering the average values for intercentroid (3.644(12) Å) and interplanar (3.297(16) Å) distances and for Fe^{III} complex centroid to centroid separation 3.531 and 3.457 Å) for (dmpH)⁺ ions, the π - π stacking

interaction (3.531 between cations can be established [121,122]. The Fe^{III} complex has an interesting hydrogen bond pattern with the graph set analysis symbols shown in Fig. 31. The (dmpH)(H₅O₂)[Ni(pydc)₂].0.5H₂O [123], (dmpH)(H₅O₂)[Cu(pydc)₂].0.5H₂O [123], and (dmpH)(H₅O₂)[Zn(pydc)₂].0.5 H₂O [123] complexes were synthesized in the same three-constituents manner.

A Metal Complex Including 3-Carboxypyridine-2-carboxylate Fragment, py-2,3-dcH

The metal center in [Zn(py-2,3-dcH)₂(H₂O)₂] [124] is hexacoordinated by two (py-2,3-dcH)⁻ bidentate ligands and two water molecules. Although we have used 2,9-dimethyl-1,10-phenanthroline as starting materials of this compound, it has not incorporated in the structure. This structure has an infinite three-dimensional framework. The stabilizing interactions existing in the crystal structure are intermolecular O-H \cdots O and very strong intramolecular O-H \cdots O hydrogen bonds [124].

A Metal Complex Including 1,10-Phenanthroline and Glutaric Acid Fragments, phen-GluH₂

The cation of the [Zn(phen)₃](NO₃)₂.2GluH₂.2H₂O [125] complex contains a six-coordinated Zn^{II} atom with three 1,10-phenanthroline molecules as bidentate ligands. The asymmetric unit also contains an uncoordinated nitrate anion, glutaric acid and water molecules. The presence of nitrate ions as well as uncoordinated glutaric acid and water molecules leads to the most important characteristic of the complex *i.e.* the presence of strong hydrogen bonding interactions. The anions and neutral molecules of the crystal structure are connected together by O-H \cdots O hydrogen bonds, forming infinite chains, where the complex anion is located between the chains.

A Metal Complex Including 2,2'-Bipyridine, Pyridine-2,6-dicarboxylate and Pyridine-2,6-dicarboxylic Acid Fragments, bipy-pydc-pydcH₂

In the [Fe(bipy)₃][Fe(pydc)₂]₂(pydcH₂)_{1/2}.6.5H₂O [126] complex, the 2,2'-bipyridine and (pydc)²⁻ act as bi-, and tridentate ligands, respectively. The hydrogen bonds cause the crystal to have two cyclic water trimers. In the formation of this lattice, metal-ligand coordination, O-H \cdots O and C-H \cdots O

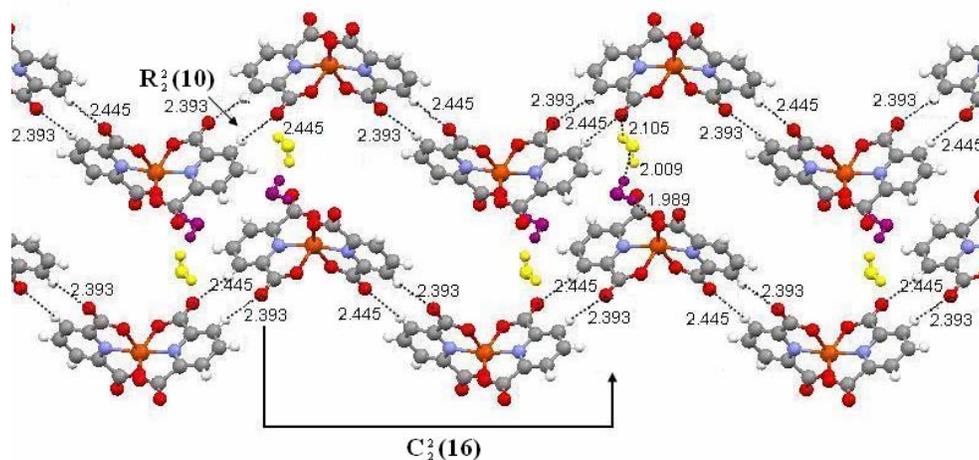


Fig. 31. Hydrogen bond pattern in (dmpH)[Fe(pydc)₂].2H₂O with the graph set analysis symbols.

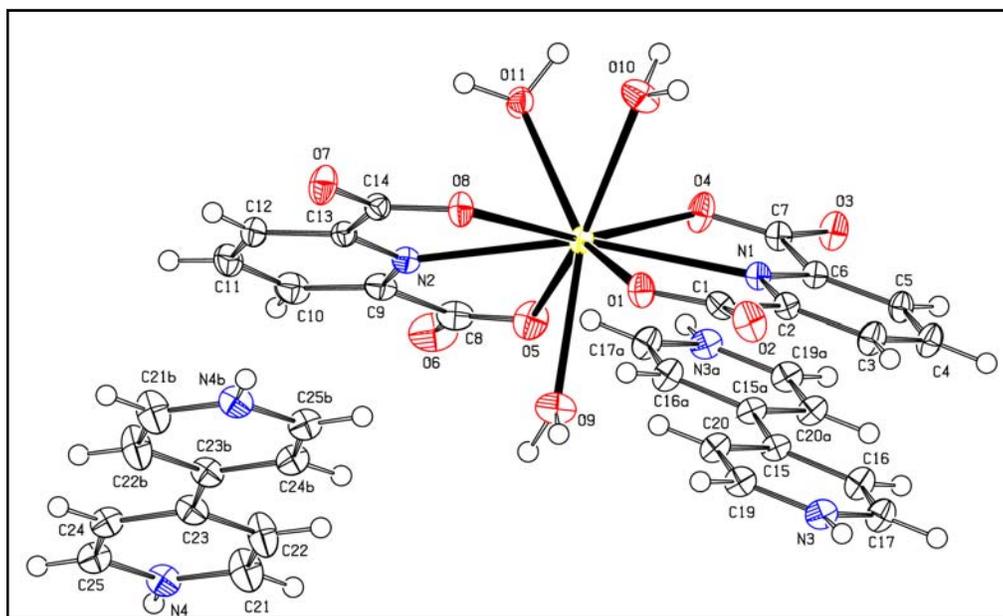


Fig. 32. The molecular structure of (4,4'-bipyH₂)[Sr(pydc)₂(H₂O)₃].3H₂O, uncoordinated water molecules are omitted for clarity.

hydrogen bonding and ion pairing throughout the lattice play important roles in stabilizing the three-dimensional network.

A Metal Complex Including 4,4'-Bipyridine and Pyridine-2,6-dicarboxylate Fragments, 4,4'-bipy-pydc

The adduct compound formulated as (4,4'-bipyH₂)[Sr(pydc)₂(H₂O)₃].3H₂O [127] has a nine-coordinated metallic center. Moreover, the structure has a variety of intermolecular O-H...O, N-H...O and C-H...O hydrogen bonds, π - π stackings and C-O... π stacking which connect the various components into a supramolecular structure (Fig. 32).

A Metal Complex Including 1,10-Phenanthroline and 4-Hydroxypyridine-2,6-dicarboxylate Fragments, phen-hypydc

The title compound, $[\text{Cu}(\text{H}_2\text{O})(\text{phen})(\text{hypydc})].4.5\text{H}_2\text{O}$ [128] is a mixed ligand complex with neutral (phen) and anionic (hypydc)²⁻ species as ligands in which a big water cluster can be found. Moreover, π - π stacking interactions are responsible to extend the supramolecular structure.

Piperazinediium-4-Hydroxypyridine-2,6-dicarboxylate, (pipzH₂)(hypydc), and Its Metal Complexes

The non-crystalline proton transfer compound (pipzH₂)(hypydc) was applied to synthesize the $[\text{Ni}(\text{hypydc})(\text{H}_2\text{O})_3].1.5\text{H}_2\text{O}$ complex [129]. In this complex, the (pipzH₂)²⁺ fragment of the starting ion pair is lost, and Ni^{II} is coordinated by the tridentate dianionic ligand and three water molecules. Also, two halves of the $[\text{Ni}(\text{hypydc})(\text{H}_2\text{O})_3]$ unit are kept together through O-H \cdots O hydrogen bonds between water molecules and carboxylate groups.

Also, a polymeric complex formulated as $[\text{Zn}_{12}(\text{hypydc})_{12}(\text{H}_2\text{O})_{10}.12\text{H}_2\text{O}]_n$ [130] is synthesized using the title ion pair that shows three different coordination numbers 4, 5 and 6 for Zn^{II} ion. In addition to covalent and coordination bonds, there are π - π interactions and hydrogen bonds binding

the fragments to each other (Fig. 33).

Piperazinediium-Pyridine-2-carboxylate, (pipzH₂)(py-2-c), and Its Metal Complex

Although there is no crystal structure for the proton transfer ion pair in determined structure of $[\text{Mg}(\text{py-2-c})_2(\text{H}_2\text{O})_2].0.15\text{H}_2\text{O}$ [131], the Mg^{II} atom is six-coordinated by two bidentate pyridine-2-carboxylate groups and two oxygen atoms of water molecules, which are located in *cis* positions.

In the crystal structure, intermolecular O-H \cdots O and C-H \cdots O hydrogen bonds, and π - π stacking (3.5616(8) Å) and C-H \cdots π stacking (3.225(1) and 3.417(1) Å) connect the various components into a supramolecular structure (Fig. 34).

1,10-Phenanthroline-2,4,5-Tricarboxybenzoate-2, 5-Dicarboxybenzene-1,4-dicarboxylate (4/2/1), (phenH)₄(btcH₃)₂(btcH₂)

As can be seen from the packing diagram of (phenH)₄(btcH₃)₂(btcH₂) [132], intermolecular O-H \cdots O and N-H \cdots N hydrogen bonds link the ions to form a three-dimensional network. The π - π stacking interactions are observed between two symmetry-related aromatic rings of 1,10-phenanthroline, with an average distance of 3.236 Å that is a relatively short distance (Fig. 35).

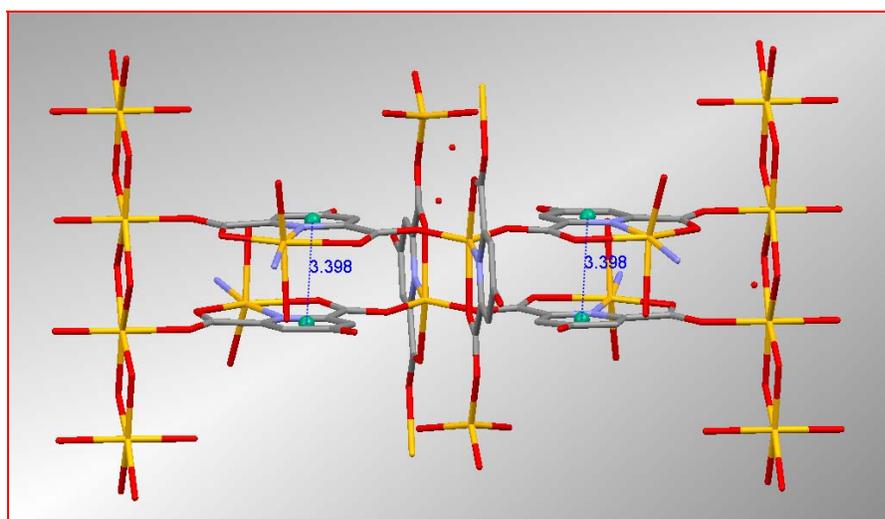


Fig. 33. π - π Interactions of $[\text{Zn}_{12}(\text{hypydc})_{12}(\text{H}_2\text{O})_{10}.12\text{H}_2\text{O}]_n$.

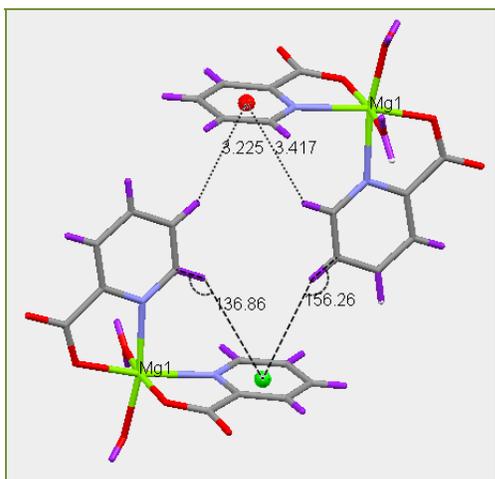


Fig. 34. The C-H... π stacking with distances and angles in [Mg(py-2-c)₂(H₂O)₂].0.15 H₂O complex.

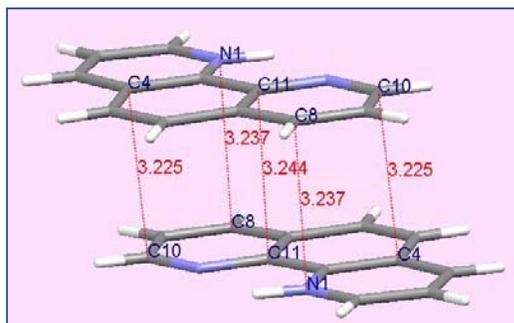


Fig. 35. The π - π stacking between a part of π -rings of two (phenH)⁺ species in (phenH)₄(btcH₃)₂(btcH₂).

2,6-Diamino-4-phenyl-1,3,5-triazinium Chloride Monohydrate, (daptzH)Cl.H₂O

The asymmetric unit of (daptzH)Cl.H₂O [133] contains one cation, one anion and one water molecule. Intermolecular N-H...O, N-H...N, O-H...Cl, and N-H...Cl hydrogen bonds seem to be effective in the stabilization of the crystal structure, resulting in the formation of a three-dimensional framework.

Bis(2,6-diamine-4-phenyl-1,3,5-triazinium) Oxalate, (daptzH)₂(ox)

The most important features of crystal structure of (daptzH)₂(ox) [134] are ion pairing and N-H...O and N-H...N

hydrogen bonds, which brings the two cations together.

1,4,10,13-Tetraoxa-7,16-diazacyclooctadecanediium-Bis(6-carboxypyridine-2-carboxylate) 0.25-Hydrate, (DA18C6H₂)(pydcH)₂.0.25H₂O

The (DA18C6H₂)(pydcH)₂.0.25H₂O [135] is a proton transfer compound where the asymmetric unit consists of one (DA18C6H₂)²⁺ cation interacting with two (pydcH)⁻ anions *via* hydrogen bonds involving the protonated amine groups of the diazacrown ether. In particular, one of two NH₂⁺ groups of the cation is H-bonded to both ionized and unionized carboxylic groups of a (pydcH)⁻ anionic unit, while the remaining NH₂⁺ group is H-bonded to the unionized carboxylic group and the N-donor of the other (pydcH)⁻ anionic unit. 6-Carboxypyridine-2-carboxylate anions interact with each other *via* a -COOH...⁻OOC- head-to-tail binding pattern to give chains running along [10 $\bar{1}$] which are cross-linked by (DA18C6H₂)²⁺ cations, thus generating 2D (010)-oriented undulating layers in the crystal lattice. The most important feature of the crystal structure of the (DA18C6H₂)(pydcH)₂.0.25H₂O aggregate is the formation of a 2D network *via* intermolecular hydrogen bonding and π - π interactions determined by the existence of a self-associated cation-anion system and by the conformation adopted by the macrocyclic cation.

Pyridinium-4-carboxamide-Benzene-1,4-dicarboxylate-2,5-dicarboxylic Acid Dihydrate, (pycH)₂(btcH₂).2H₂O

Different rings and infinite layers are observed within the crystal lattice of the proton transfer compound (pycH)₂(btcH₂).2H₂O [136], which have been made *via* intermolecular hydrogen bonds of the type O-H...O and N-H...O. This compound can be considered as a supramolecular structure formed by non-covalent interactions.

N,N'-Diethyl-2-amino-6-methyl-4-pyrimidinolium-[Hydrogen bis(6-carboxypyridine-2-carboxylate)], (pyrimH){H(pydcH)₂}

The proton transfer compound (pyrimH){H(pydcH)₂} [137] has two monoanionic (pydcH)⁻ units joined together by a proton, where extensive hydrogen bonding occurs to form the two-dimensional sheet-type supramolecular structure. The

proton transfer process results in the formation of a self-associated system consisting of $\{\text{H}(\text{pydcH})_2\}^-$ fragments. The intermolecular forces between the anionic and cationic units in this compound consist of hydrogen bonding and ion pairing. In addition, the π - π stacking exists between the anion-anion fragments, and the interplanar distance is 3.351(3) Å.

Benzene-1,3-diaminium-Bis(6-carboxypyridine-2-carboxylate) Dihydrate, (bdaH₂)(pydcH)₂·2H₂O

In the proton transfer compound (bdaH₂)(pydcH)₂·2H₂O [138], the protons of the two carboxylic acid units are transferred to the nitrogen atoms of benzene-1,3-diamine. Hydrogen bonding plays an important role in the construction of the resulting three-dimensional crystal structure framework. In the crystal structure, the 6-carboxypyridine-2-carboxylate ions are connected together *via* hydrogen bonds. It is notable that the crystal packing diagram indicates a layered structure. The space provided between two layers, consisting of (pydcH)⁻ fragments, is filled with a layer of (bdaH₂)²⁺ cations. The most important feature of the crystal structure of the ion pair aggregate is the existence of a self-associated cation-anion system.

Ammonium-6-Carboxypyridine-2-carboxylate, (NH₄)(pydcH)

In the compound (NH₄)(pydcH) [139], a hydrogen atom between the carboxyl and carboxylate groups is disordered; this is consistent with the short and strong O-H...O hydrogen bond across an inversion center between these groups in neighboring anions. Ion pairing and intermolecular O-H...O and N-H...O hydrogen bonds contribute to the crystal packing stability.

2-Aminopyridinium-Pyridine-2,6-bis(monothio-carboxylate), (2-apyH)(pdtcH)

The crystal structure analysis of proton transfer ion pair (2-apyH)(pdtcH) [140] reveals that intra- and intermolecular proton transfers from the diacid pdtcH₂ to the base 2-apy results in the formation of a supramolecular network, which self-assembled *via* N-H...S and N-H...O hydrogen bonding, ion pairing and π - π interactions, simultaneously.

CONCLUSIONS

In a brief review, we tried to illustrate a great team work during seven years. Although all the efforts were mentioned, the detailed and real aspects of them should be sought in the main papers. Here, it was shown that how starting with good proton donors and acceptors can result in supramolecular proton transfer compounds and how supramolecular metal complexes, namely metal organic frameworks, can be built, using a rich variety of metal ions including *s*-, *p*-, *d*- and sometimes *f*-block metals. The great importance of weak and strong interactions "beyond molecule" including hydrogen bonds, van der Waals forces, ion pairing and π - π interactions caused by different functional groups and their effect on explaining the structures has also been discussed. In this way, the experimental approaches parallel to theoretical concepts are of great importance. This is noteworthy especially in optimization the reaction conditions, and also in the field of crystal growth and finding the best solvents for running the reactions or obtaining the high quality crystals, *etc.* Meanwhile, as expected, some selected materials and conditions did not work indicating that much of the path is remaining to undergo and we must do our best in the future.

FUTURE PROSPECTS

Although searching other starting materials to synthesize novel compounds can be a good target point, it should not be the whole final purpose. As is obvious, if a great fundamental research project cannot find its way to applied purposes, soon it will be forgotten. Thus, as a future prospect, finding the new synthetic approaches, and compounds with new structural characteristics, as well as new applications and practical usages of the compounds will be an outstanding aim. However, from the viewpoint of constructing functional proton transfer compounds, it will also become important to incorporate functional groups in those parts of them that act as ligands, instead of only using carbon and hydrogen containing moieties. In this way, the understanding and application principles of the "crystal engineering", as a main tool, will be helpful and effective.

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