

Synopsis

The thesis is divided into four chapters

Chapter 1 provides a brief introduction to the metal-nucleic acid interactions, the role of synthetic models to understand them with both solution (potentiometric) and solid state (Crystallographic) studies. Further the work done in the area of nucleobase [purines and pyrimidines] metal complexes and nucleotide metal complexes are briefly reviewed.

Chapter 2 contains an account of synthesis and characterizations of metal [Cu/Co] purine [adenine] complexes and is divided into two sections Viz., **Section I** and **Section II**.

Section I Five crystals structures of copper adenine dimeric complexes are synthesized and characterized with 1, 10-phenanthroline as coligand.

The **first** ternary $[\text{Cu}_2(\text{phen})_2(\mu\text{-ade})_2\text{Cl}_2]\cdot 3\text{H}_2\text{O}$ complex (**2a**) crystallizes in the orthorhombic space group $Pna2_1$. In the crystal structure of **2a** it has been observed that the five and six membered rings of adenine are arranged in such a way that the five membered ring nitrogen atoms N9 and N9A are coordinated to Cu1 while the nitrogen atoms N3 and N3A are coordinated with Cu2 center. This is the first time such co-ordination is observed for the copper-adenine dimeric complexes, while the earlier report shows an alternate coordination. In the complex adenine-adenine dimer formation is observed, mediated via N-H \cdots N hydrogen bond interactions which give rise to a corrugated sheet like pattern along the *bc* plane. The 1,10-phenanthroline rings and water molecules are packed in the grooves of these corrugated sheets via non covalent interactions.

The **second** ternary $[\text{Cu}_2(\text{phen})_2(\mu\text{-ade})(\mu\text{-Cl})\text{Cl}_2]\cdot 5\text{H}_2\text{O}$ complex (**2b**) obtained under same reactant conditions, as **2a**, by changing the ratio of the reactants, is the unique example of a dimeric copper complex with one adenine acting as a bridging ligand. The complex **2b** crystallizes in the monoclinic centric space group $P2_1/c$. Interestingly, the crystal packing of complex **2b** does not show any direct adenine-adenine hydrogen bond interactions as was seen for **2a**, but adenine moieties of neighboring molecules interact indirectly, mediated via N-H \cdots O and O-H \cdots N hydrogen bonds through solvent water molecules forming a zig-zag pattern. It is interesting to note that two hydrogen bond networks are running across the body

diagonal like “X” mediated by the nitrogen atoms of the adenine base and the chlorine atom, axially coordinated to copper centre. Similarly the water molecule O4 and N7 are involved in forming a four membered ring at the body center through the non covalent interactions. As seen for the complex **2a**, complex **2b** also depicts the presence of slipped π - π stacking intra and intermolecular interactions for the 1,10-phenanthroline rings.

The **third** complex $[\text{Cu}_2(\text{phen})_2(\mu\text{-ade})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ complex (**2c**), obtained by post synthetic modification of **2a**, crystallizes in the monoclinic space group *Cc*. The adenine moieties forms a dimer mediated via N-H...N hydrogen bonds at the pseudo two fold and are connected to the neighboring dimers through the possible hydrogen bond between the nitrogen atom N1 and the axially coordinated oxygen atom O1 of the water molecule. The perchlorate anions are trapped in the pockets surrounded by the adenine and 1,10-phenanthroline moieties. The Nitrogen atom N6, N6A of the adenine bases forms hydrogen bond with N7, N7A of the five membered rings of adenine bases and the oxygen atom O4, O7 of both perchlorate ions, the other oxygen atoms O3, O5 from Cl1 and O8 of Cl2 are involved in C-H...O hydrogen bonds but the remaining oxygen atoms O6, O9 and O10 of the perchlorate ions are not involved in hydrogen bond network. Thus the dimerization involves axial oxygen atoms and the five and six membered nitrogen atoms N7 and N1. The 1,10-phenanthroline rings show both intra as well as intermolecular slipped π - π stacking interactions.

The **fourth** complex $[\text{Cu}_2(\text{phen})_2(\mu\text{-ade})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2$ complex (**2c**), obtained by post synthetic modification of **2a**, crystallizes in the monoclinic space group *Cc*. The adenine moiety forms intermolecular N-H...N hydrogen bonds with the neighboring adenine moieties at the pseudo two fold and is connected to the neighboring dimers through the N-H...O hydrogen bond via axial water molecule. The dimerization of the neighboring adenine moieties is favored through the hydrogen bond between the oxygen atom O2 of Cu2 and N1 of the six membered ring, in return the oxygen atom O1 of second molecule is hydrogen bonded to the nitrogen N7 of the five membered ring of the first molecule. Interestingly the three fluorine atoms F1, F2 and F3 are involved in hydrogen bond and in the second BF_4 ion only two fluorine atoms F6 and F7 are involved where F1 and F6 acts as a bifurcated hydrogen bond acceptor while the remaining fluorine atoms are not taking part. Here too, as

in the previous case of **2c** 1,10-phenanthroline rings show both intra as well as intermolecular slipped π - π stacking interactions.

The **fifth** complex $[\text{Cu}_2(\text{phen})_2(\mu\text{-ade})_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$ complex (**2c**), obtained by post synthetic modification of **2a**, crystallizes in the monoclinic space group *Cc*. The adenine moiety forms intermolecular N-H...N hydrogen bonds with the neighboring adenine moieties at the pseudo two fold and is connected to the neighboring dimers through the N-H...O hydrogen bond via axial water molecule. As observed in the previous structure of **2c** and **2d** the dimerization of the neighboring molecule is favored through the hydrogen bond between the oxygen atom O2 of Cu2 and N1 of the six membered ring, in return the oxygen atom O1 of second molecule is hydrogen bonded to the nitrogen N7 of the five membered ring of the first molecule. Interestingly the nitrogen atom N6 of the six membered ring is involved in four hydrogen bonds, Where one H is hydrogen bonded to N1 of the neighboring base while the second hydrogen atom is being shared by three fluorine atoms belonging to the second PF_6 ion and in turn all these three fluorine atoms acts as bifurcated acceptor of the hydrogen bond with the carbon atoms of 1,10-phenanthroline. It is noteworthy that the fluorine atoms F3, F4, F5 and F6 are involved in single hydrogen bonds with the 1,10-phenanthroline carbon atoms. At the same time the rest of the fluorine atoms are not involved in any non covalent interactions. Here too, as in the previous cases of **2c** and **2d** 1,10-phenanthroline rings show both intra as well as intermolecular slipped π - π stacking interactions.

The complexes **2c**, **2d** and **2e** are isostructural. All the three complexes crystallized in the noncentric space group *Cc* as the precursor complex **2a** [*Pna2*₁] with the difference being the nature of the complex, **2a** being neutral whereas **2c**, **2d** and **2e** are complex salts. All the three complexes have similar bond lengths between the coordinating atoms and the central copper metal but they differ in the angles subtended by the ligands at the copper centres which are also reflected in the dihedral angle between the planes of the coordinating ligands. Though the molecular structure of the three complexes differs only in the nature of the counter ion, the crystal packing analysis reveals the finer differences. The interaction of adenine with neighboring adenine is same for the three complexes **2c**, **2d** and **2e** but differs from the precursor complex **2a**.

Section II covers the synthesis and characterization of cobalt adenine binary and ternary complexes with 1,10-phenanthroline and 2,2'-bipyridyl as coligands for the ternary complexes.

The **first** binary $[\text{Co}_2(\mu\text{-Hade})_2(\mu\text{-H}_2\text{O})_2(\text{H}_2\text{O})_4](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ complex (**2f**) crystallizes in the centric space group $P2_1/c$. Though there were four water molecules, coordinated to the metal Co centres, available for intra molecular hydrogen bond interactions with the base nitrogen atoms the orientation of the coordinated bases is not favorable to enable the C-H...O hydrogen bond formation, but intermolecular hydrogen bonds were observed. The structure is stabilized mainly through the O-H...O and N-H...O hydrogen bond interactions between the neighboring molecules via nitrate ions. Interestingly there is an absence of any direct adenine-adenine interactions. The terminally coordinated water molecule O2 forms hydrogen bond with nitrate anion on both sides, which in turn the nitrates hold the bases of two different molecules as the network is running -N6-O10-O9-O2-O5-N6-. Both the nitrate anion oxygen atoms are involved in hydrogen bond where all the oxygen atoms are bifurcated acceptor. The nitrate ions with nitrogen atoms N10 and N11 are making a nine and eight membered ring through hydrogen bond with adenine nitrogen atoms [N6 and N7] and coordinated water molecules [O2 and O3] respectively.

The **second** binary $[\text{Co}(\text{Hade})_2(\text{H}_2\text{O})_4]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ complex (**2g**) crystallizes in the centric space group $P2_1/n$. Interestingly, only one adenine [N3A] is involved in forming the O-H...N intramolecular hydrogen bond with the water molecule while the adenine on other side is not in favorable orientation. All the water molecules coordinated to the metal center are involved in forming hydrogen bonds where O1, O2 and O4 form two hydrogen bonds while, O3 forms three hydrogen bonds. The water molecule and sulphate ions are trapped in between the adenine bases and forming an interesting network of hydrogen bond running in opposite directions. In general the sulphate and the water molecule are holding the symmetry related molecules connecting the nitrogen atoms N6 and N7 of the adenine. The crystal structure of **2g** shows the presence of intermolecular π - π stacking interaction between the six membered rings of the neighboring adenine molecules along a axis. These stacked adenine moieties looks like a zig- zag pattern when viewed down a axis. Here too as in previous case of **2f** there are no adenine-adenine interactions present.

It is noteworthy that both of these complexes [differing only in the nature of salts i.e. CoNO_3 and CoSO_4] differ in the adenine coordination to the cobalt centre [N9 and N3 co-ordination in **2f**; N9 coordination in **2g**].

The **third** ternary $[\text{Co}_2(\mu\text{-ade})_2(\mu\text{-OH})_2(\text{phen})_2](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ complex (**2h**) was synthesized by a one pot reaction and crystallizes in the triclinic space group *P*-1. Though there are two hydroxyl ions coordinated to the metal centre there is no favorable intramolecular hydrogen bond formation. The adenine moieties of **2h** interact with each other forming a dimer at the inversion centre, which looks like a zig-zag sheet pattern, via N-H \cdots N hydrogen bond. In addition to this the hydroxyl O1 forms hydrogen bond with water oxygen and the oxygen atom of the disordered nitrate anion. These chains are further linked to neighboring chains by N-H \cdots O hydrogen bond and a slipped π - π interaction between the 1,10-phenanthroline rings forming a sheet like pattern.

The **fourth** ternary $[\text{Co}_2(\mu\text{-ade})_2(\mu\text{-OH})_2(\text{phen})_2](\text{OTs})_2 \cdot 6\text{H}_2\text{O}$ complex (**2i**), was also synthesized by a one pot reaction and crystallizes in the triclinic space group *P*-1. Similar to previous case though there are two hydroxyl groups bridging the metal centres as dimers, no intramolecular hydrogen bonds were observed. The adenine moieties interact with each other forming a zig-zag pattern via N-H \cdots N hydrogen bond like in the previous structure **2h**. Interestingly, contrary to the previous case where two such zig-zag sheets interacted with each other through slipped π - π stacking between the 1,10-phenanthroline rings, no such interaction was found among the neighboring sheets. Instead, the 1,10-phenanthroline rings interact with tosylate counter ion through C-H \cdots O hydrogen bonds. Down the *c* axis projection, at the inversion centre tosylate ion and the water molecules form an eight membered ring where the water oxygen O1W acts as a donor in the two hydrogen bonds and the oxygen atom O2 of the tosylate acts as bifurcated acceptor. On the other side, the tosylate oxygens form a twelve membered ring with the water oxygen atom O2W. Thus, eight membered and twelve membered rings are formed alternately and both are subtending an angle of 113°. It is noteworthy that the tosylate ion is parallel to the adenine base while perpendicular to the 1,10-phenanthroline rings favoring the π - π and C-H \cdots π stacking interactions between the neighboring zig zag chains.

The **fifth** ternary $[\text{Co}_2(\mu\text{-ade})_2(\mu\text{-OH})_2(\text{bpy})_2](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ complex (**2j**) synthesized via one pot reaction and crystallizes in the triclinic space group $P2_1/n$. Similar to previous two cases there are two hydroxyl groups bridging the metal centres as dimers, no intramolecular hydrogen bonds were observed in the present case. The adenine moieties interact with each other forming a zig-zag pattern via N-H...N hydrogen bond as observed in the previous two structures **2h** and **2i**. The adenine also interacts with nitrate ion through N-H...O hydrogen bond. The nitrate groups are oriented parallel to the adenine base. The adenine base nitrogen atom N6 is involved in holding the neighboring adenine nitrogen atom N7 in addition to the nitrate oxygen atoms O3 and from the same nitrate the other oxygen atoms O4 is involved in hydrogen bond with the carbon atom C8 thus forming a nine membered ring. These chains interact with the parallel chains by slipped π - π stacking interaction similar to that observed in complex **2h**.

Chapter 3 describes the syntheses and characterizations of copper pyrimidine [uracil, cytosine and thymine] ternary complexes with 1,10-phenanthroline as coligand.

The **first** polymeric $[\text{Cu}(\text{phen})(\mu\text{-ura})(\text{H}_2\text{O})]_n \cdot \text{H}_2\text{O}$ complex (**3a**) crystallizes in the monoclinic space group $P2_1/c$. The protons of the water oxygen O1W is oriented towards the uracil rings enabling O-H...O intramolecular hydrogen bonds with O2 as a bifurcated bond acceptor of the uracil on either sides and the chain extends to infinity along the *c* axis. The structure is stabilized by slipped π - π stacking interactions between the 1,10-phenanthroline rings of neighboring polymeric chains. Each polymeric chain also interacts through C-H...O hydrogen bond between the neighboring chains.

The **second** polymeric $[\text{Cu}(\text{phen})(\mu\text{-ura})(\text{H}_2\text{O})]_n \cdot \text{MeOH}$ complex (**3b**) is isostructural to (**3a**) and crystallizes in the monoclinic space group $P2_1/c$. Similar to **3a** the coordinated water oxygen O1w is oriented towards the uracil rings enabling O-H...O intramolecular hydrogen bonds with O2, as a bifurcated hydrogen bond acceptor, of the uracil on either sides and the chain extends to infinity along the *c* axis. The structure is stabilized by slipped π - π stacking interactions between the 1,10-phenanthroline rings of neighboring polymeric chains. Each polymeric chain also interacts through C-H...O hydrogen bond between the neighboring chains.

Both these complexes differ only in the lattice solvent molecule i.e. water for **3a** and methanol for **3b**. These complexes are the first example of direct uracil to metal coordination structurally characterized. Also, both the ring nitrogen atoms N1 and N3 are involved in coordination to the metal.

The **third** polymeric $[\text{Cu}_4(\text{cytosine})_3\text{Cl}_3(\text{OH})_2]_n \cdot 14\text{H}_2\text{O}$ complex **3c** is the first polymeric complex known with cytosine and 1,10-phenanthroline as coligands. It crystallizes in the orthorhombic centric space group *Pbca*. Out of the four, three copper centres adopts square pyramidal [4+1] geometry $\{\tau = 0.17 [\text{Cu}1], 0.028 [\text{Cu}3]$ and $0.053 [\text{Cu}4]\}$, whereas the fourth copper centre exhibits distorted trigonal bipyramidal [3+2] geometry. $\{\tau = 0.66 [\text{Cu}2]\}$. Two copper centres Cu1 and Cu3 have same co-ordination environment viz., the basal plane of the square pyramid is formed by cytosine [N1 and N1A], 1,10-phenanthroline [N7, N8 and N11, N12] and chlorine ligands [Cl1, Cl3] while the axial site is occupied by other chlorine atom [Cl2] which act as a bridge between Cu1 and Cu3 in the polymeric chain. The cytosine ring attached to Cu1 and Cu3 act as tridentate ligand co-ordinating to two other copper centres [Cu2, Cu4] via O2, O2A and N3, N3A respectively. Thus remaining three sites of Cu2 are occupied by 1,10-phenanthroline [N9, N10] and a bridged hydroxyl [O1D] moiety. The hydroxyl moiety [O1D] acts as a bridging ligand between Cu2 and Cu4. Thus the basal plane of the trigonal bipyramid for Cu2 is formed by N9, O2 and O2A while axial sites are occupied by N10 and O1D. The basal plane for Cu4 is formed by N3, N3A, O1D and N3C [from third cytosine ligand] while the axial site is occupied by a hydroxyl ion [O1]. The structure is stabilized by slipped π - π intra molecular stacking interactions between the 1,10-phenanthroline rings. The cytosine moieties interact with each other through bifurcated N-H...O hydrogen bond where the proton of N6c is involved with O2 and O2A of the other two cytosine moieties coordinated to the same copper centre. The neighboring chains of the polymer are linked by inter molecular slipped π - π stacking interactions between the cytosine ring attached to Cu4 and the 1,10-phenanthroline rings. The chains are also connected through C-H...Cl hydrogen bonds where the chlorine atom Cl4 is involved in the bifurcated hydrogen bond one as intramolecular and the second as intermolecular. Both the Nitrogen atoms [N6, N6A] of different cytosine are involved in the noncovalent interactions, with the water [O41, O10W] as intermolecular hydrogen bond as well as intramolecular hydrogen

bond with chlorine atoms [Cl4, Cl4* (* symmetry generated)] respectively. The water molecules pack between the polymeric chains via noncovalent interactions. Thus this complex is the first example of its kind where all the possible binding modes of cytosine are utilized.

The **fourth** [Cu₂(Phen)₂(thy)(μ -OH)₂(H₂O)].HCO₃·4.5H₂O complex (**3d**) obtained as the minor product along with **3e** crystallizes in the triclinic space group *P1* with two molecules in the asymmetric unit. The structure displays the presence of a pseudo centre of inversion between the two molecules. But careful analysis of the structure reveals that the two different tautomeric forms of thymine are coordinated to the two copper centres in each molecule, thus making it a cocrystal. The molecule shows the presence of O-H...O intramolecular hydrogen bond between the thymine oxygen and the bridged hydroxyl ion. The structure is stabilized by slipped π - π stacking and C-H... π interactions between the 1,10-phenanthroline rings of neighboring molecules. The molecules also interact with solvent molecules and counter ions through non covalent C-H...O interactions.

The **fifth** [Cu₂(Phen)₂(thy)(μ -OH)₂(H₂O)]Cl·3H₂O complex (**3e**) which was the major product along with **3d** also crystallizes in the triclinic space group *P1* with two molecules in the asymmetric unit. The difference between **3d** and **3e** is the change in the nature of counter ion i.e. HCO₃⁻ for **3d** and Cl⁻ for **3e**. Similar to **3d** the two different tautomeric forms of thymine are coordinated to the two copper centres in each molecule, thus making it a cocrystal. The molecule shows the presence of O-H...O intramolecular hydrogen bond between the thymine oxygen and bridged hydroxyl ion. The structure is stabilized by slipped π - π stacking and C-H... π interactions between the 1,10-phenanthroline rings of neighboring molecules. The molecules also interact with solvent molecules and counter ions through non covalent C-H...O and C-H...Cl interactions.

The **sixth** Cu(phen)(thy)₂ complex (**3e**) was obtained just by changing the pH in the reaction condition for **3d** and **3e** and crystallizes in the monoclinic centric space group *C2/c*. Here a different tautomer of thymine other than that observed for **3d** and **3e** was coordinated to the central copper metal. The structure is mainly stabilized by slipped π - π stacking

between the 1,10-phenanthroline rings of neighboring molecules as well as between the thymine rings. The thymine molecules also interact with neighboring thymine molecules through non covalent N-H...O interactions. These thymine thymine interactions were absent in **3d** and **3e**.

Chapter 4 presents the synthesis and characterization of ternary copper 5'-Adenosine monophosphoric acid (5'-AMP)/ 5'-cytidine monophosphoric acid (5'-CMP) complexes with 2,2'-bipyridine/1,10-1,10-phenanthroline as coligands.

The **first** Cu(bpy)(5'-AMP)₂·2H₂O complex (**4a**), obtained at pH = 3.0, crystallizes in the triclinic space group *P1* with two molecules in the asymmetric unit Viz., complex A and Complex B. The phosphate group of 5'-AMP which has two protons in the uncoordinated state gets monodeprotonated at one hydroxyl group during the complex formation and is coordinated to the copper centre. Thus in each complex the charge on the central copper atom is balanced by 5'-AMP monodeprotonated ligand. The environment around both copper centres is same, Cu1 and Cu2 exhibits square planar geometry. The least square plane analysis reveals that the ribose sugar moieties adopt envelope conformation. The Φ_{CN} angle, which is the torsion angle of the base with respect to sugar, are 84(2)°, 41(2)° for complex A and -43(2)°, 47(2)° for complex B suggesting a *anti* conformation about the glycosyl bond for all the four 5'-AMP ligands. All the four ribose ring are puckered with one carbon atom of the ring, [C4' and C3'A for complex A, C4'B and C3'C for complex B], displaced from the best four atom plane of furanose ring on the same side as C5'. [C4' = -0.539(2) Å, C3'A = -0.539(2) Å for complex A; C4'B = 0.509(17) Å, C3'C = 0.535(20) Å for complex B], suggesting in each complex, the confirmation of the ribose sugar of two 5'-AMP ligands are different. [C4' *endo* and C3'A *endo* for complex A; C4'B *endo* and C3'C *endo* for complex B] Both the complexes A and B are stabilized by C-H...O intramolecular interaction between the adenine base and the phosphate oxygen atom. The structure is stabilized through a complicated network of C-H...O and N-H...O hydrogen bond interactions between the neighboring molecules where the oxygen atoms of the water molecules are involved in forming the network of bifurcated hydrogen bond. The adenine rings interact with each other through the N-H...N hydrogen bonds forming a dimer between the N6-N7 and N7-N6 similar to the base pairing observed in the DNA molecule, in addition to this the atom N6 is

involved in forming a bifurcated hydrogen bond with the O7 atom of the phosphate group. Additionally, there is a presence of slipped $\pi\cdots\pi$ stacking interaction, between the bipyridine rings and adenine rings in a -B-A:A-B- fashion [B= 2,2'-bipyridine and A:A= adenine adenine adduct].

The **second** $\{\text{Cu}_2(\text{bpy})_2(\mu\text{-5'-AMP})_2(\text{H}_2\text{O})_2\cdot 2[\text{Cu}(\text{bpy})(\text{5'-AMP})(\text{H}_2\text{O})_2]\cdot 10\text{H}_2\text{O}\}$ complex (**4b**) is a cocrystal obtained at pH = 6.0, crystallizes in the monoclinic space group C2. The crystal structure of **4b** can be described as a cocrystal made up of one dimeric [complex D] and two monomeric [complex M] copper (II) complexes. Both the complexes are ternary with 5'-AMP and 2,2'- bipyridine as co ligands. These complexes are neutral in nature with the charge on the copper centres balanced by the 5'-AMP ligands. The asymmetric unit consists of half of this two component cocrystal system. The basal plane for the monomeric complex M is formed by two nitrogen atoms [N10A, N11A] from the 2, 2'- bipyridine, one water molecule [O1A] and a phosphate oxygen atom [O9A] from one of the 5'-AMP ligand, while the axial site is occupied by the other water molecule, O1W. The basal plane for the dimeric complex D is formed by two nitrogen atoms [N10, N11] from the 2, 2'- bipyridine, and two phosphate oxygen atom [O9 and O7] from two bridging 5'-AMP ligand, while the axial site is occupied by the other water molecule O2A. The 5'-AMP ligand bridges the two copper centres to form the dimeric complex. It is noteworthy that both the axial water molecules of complex D are on the same side.

The least square plane reveals that the ribose sugar moieties adopt envelope conformation. The Φ_{CN} angle, which is the torsion angle of the base with respect to sugar, $72(1)^\circ$ for complex D and $77(1)^\circ$ for complex M, suggest an *anti* conformation for both the complexes about the glycosyl bonds. The ribose rings are puckered in both complex D and M, with C3' and C3'A displaced from the best four atom plane of furanose ring. C3' deviates from the sugar plane by $0.604(13) \text{ \AA}$ which is opposite to C5', imply C3' *exo* conformation for the ribose ring. While for the ribose moiety in complex M, C3'A deviates from the sugar plane by $0.585(11) \text{ \AA}$ which is on the same side of C5', confirm C3'A *endo* conformation for the ribose ring. The conformation around the C4'-C5' bond described by the angles Φ_{OO} [O1'-C4'-C5'-O5' = $-60(1)^\circ$] and Φ_{OC} [C3'-C4'-C5'-O5' = $-179.8(9)^\circ$] is *gauche trans*, a rare conformation, for the complex D while around the C4'A-C5'A bond the angles Φ_{OO} [O1'A-

C4'A-C5'A-O5'A = $-59(1)^\circ$] and Φ_{OC} [C3'A-C4'A-C5'A-O5'A = $57(1)^\circ$] suggest the commonly observed *gauche gauche* conformation.

The structure is stabilized through the extensive network of C-H...O and N-H...O hydrogen bond interactions between the neighboring molecules. The adenine rings interact with each other through the N-H...N hydrogen bonds forming a dimer between N6-N7 and N7-N6, mimicking the base pair observed in the DNA molecule, in addition to this N6 is involved in the formation of a bifurcated hydrogen bond with the O8 atom of the phosphate group. Additionally, there is a presence of slipped $\pi\cdots\pi$ stacking interaction, between the bipyridine rings and adenine rings in a -B-B-A:A-B-B- fashion [B= bipyridine and A:A= adenine adenine adduct].

The **third** [Cu₂(bpy)₂(μ -5'-AMP)₂].14H₂O complex **4c** crystallizes in the triclinic space group *P1* with one molecule in the asymmetric unit. The complex is neutral in nature with the charge on the copper centres being balanced by the 5'-AMP ligands. It is noteworthy that both the axial water molecules of complex are on the opposite side to each other which is in contradiction to the orientation of the water molecule in dimeric complex D of the molecule **4b**. The least square plane analysis of the ribose sugar moiety reveals that the sugar moiety adopts envelope conformation. The Φ_{CN} angle, which is the torsion angle of the base with respect to sugar, is $2(4)^\circ$ for one 5'-AMP ligand and $69(4)^\circ$ for other 5'-AMP ligand, suggesting an *anti* conformation for both the complexes about the glycosyl bonds.

The ribose rings are puckered in both the ligands, with C3' and C2'A displaced from the best four atom plane of furanose ring. C3' deviates from the sugar plane by $-0.624(3)\text{\AA}$ which is on the same side of C5', reveals C3' *endo* conformation for the ribose ring. While for the other ribose moiety, C2'A deviates from the sugar plane by $0.509(3)\text{\AA}$ which is on the same side of C5', confirms C2'A *endo* conformation for the ribose ring. The conformation around the C4'-C5' bond described by the angles Φ_{OO} [O1'-C4'-C5'-O5' = $-76(3)^\circ$] and Φ_{OC} [C3'-C4'-C5'-O5' = $41(3)^\circ$] is *gauche gauche* for one of the 5'-AMP ligand. Also around the C4'A-C5'A bond the torsion angles Φ_{OO} [O1'A-C4'A-C5'A-O5'A = $-59(2)^\circ$] and Φ_{OC} [C3'A-C4'A-C5'A-O5'A = $59(3)^\circ$] suggest the commonly observed *gauche gauche* conformation for the other 5'-AMP ligand.

The complex is stabilized by C-H...O and N-H...O intramolecular interactions between the adenine base and the phosphate oxygen atom. The phosphate oxygen atoms O8 and O8A become bifurcated by hydrogen bonding to O1W and O4W. In turn by symmetry relation it forms a sheet like structure extending to infinity. The adenine also interacts with the bipyridine ring with slipped $\pi\cdots\pi$ stacking interaction. The structure is stabilized by extensive net work of C-H...O and N-H...O hydrogen bond interactions between the neighboring molecules. The adenine rings interact with each other through the N-H...N hydrogen bonds forming a dimer between N6-N7 and N7- N6, mimicking the base pair observed in the DNA molecules, in addition to this N6 is involved in the formation of a hydrogen bond with the O8 atom of the phosphate group. Very interestingly, the axially coordinated water molecules O1A, O2A along with the phosphate oxygen atoms O8, O8A and water molecules O1W, O4W form a six membered ring in the chair conformation of a cyclohexane ring through hydrogen bonds mediated by the water molecules. Additionally, there is a presence of slipped $\pi\cdots\pi$ stacking interaction, between the bipyridine rings and adenine rings in a -B-B-A:A-B-B- fashion [B= bipyridine and A:A= adenine adenine adduct]. This is similar to previous two structures.

All the three structures show the presence of different coordinating nature of phosphate groups obtained just by varying the pH conditions. The presence of cocrystal suggests that more than one type of coordination can exist at the same time.

The **fourth** $[\text{Cu}_2(\text{bpy})_2(\mu\text{-}5'\text{CMP})(\mu_3\text{-}5'\text{CMP})(\text{Cl})]_n \cdot 3\text{H}_2\text{O}$ polymeric complex (**4d**) crystallizes in the Orthorhombic space group $P2_12_12_1$. The polymer can be described as follows. There are two 5'-CMP ligand in the asymmetric unit viz., I and II. I acts as bidentate bridging ligand co-ordinating through base [N3] and phosphate oxygen [O9] to Cu1 and Cu2 respectively. II acts as a tridentate ligand co-ordinating to Cu1 through phosphate oxygen [O7A] while to Cu2 through the base [N3A] and phosphate oxygen [O9A]. Thus ligand I connects Cu1 and Cu2 forming a chain along the *a* axis while this chain is extended in *b* axis direction via ligand II.

The least square plane analysis of the ribose sugar moiety reveals that both sugar moieties adopt envelope conformation. The Φ_{CN} angle, which is the torsion angle of the base

with respect to sugar, are $40.0(8)^\circ$ [for ligand I] and $19.2(8)^\circ$ [For ligand II] suggesting an *anti* conformation for both sugar moieties about the glycosyl bond. Both the ribose ring adopt a puckered confirmation with C2' and C3'A displaced from the best four atom plane of furanose ring by $0.511(7) \text{ \AA}$ and $0.461(7) \text{ \AA}$ for ligand I and II respectively. Both the atoms C2' and C3'A are on the same side as C5', hence the conformation is C2' *endo* [for ligand I] and C3'A *endo* [for ligand II] respectively. The conformation around the C4'-C5' bond described by the angles Φ_{OO} [O1'-C4'-C5'-O5' = $-86.0(6)^\circ$ {for I} and O1'A-C4'A-C5'A-O5'A = $-72.8(2)^\circ$ {for II}] and Φ_{OC} [C3'-C4'-C5'-O5' = $33.9(8)^\circ$ {for I} and C3'A-C4'A-C5'A-O5'A = $45.6(6)^\circ$ {for II}] is *gauche gauche* for both the ribose rings in the polymeric complex.

The polymeric strand is stabilized by N-H...O intramolecular interaction between the cytosine base and the phosphate oxygen atom. The cytosine base also interacts with the axial Chlorine atom to form N-H...Cl hydrogen bond. The structure is stabilized through the extensive network of N-H...O, C-H...O and O-H...O hydrogen bond interactions between the water molecules and polymerizing, making the sheets to run in third direction. The chlorine atom Cl1 at the same time along with the water molecule O1W and O8W of the phosphate group forms an envelope shape five membered ring [Cl1-O2W-O8-O1W-O3W-Cl1] via hydrogen bond. Thus the water molecules, the phosphate oxygen atoms, the chlorine atoms and the nitrogen atoms of the base make the network of hydrogen bonds in three dimension. In the three dimensional network the copper atoms, the base and the sugar with the phosphate are running anti parallel direction pushing the bipyridyl ring on the outer side, thus remaining as the back bone of the sheet. Additionally, there is a presence of slipped $\pi \cdots \pi$ stacking interaction, both intra and inter strand, between the 2, 2'-bipyridine rings. Thus the bipyridine rings, stacked between the water molecules present in the interior of the sheets near phosphate group and sugar group linked via hydrogen bond form the hydrophilic centre.

The **fifth** $[\text{Cu}_2(\text{phen})_2(\mu\text{-}5'\text{CMP})(\mu\text{-OH})(\mu\text{-Cl})]\cdot 3\text{H}_2\text{O}$ ternary complex (**4e**) crystallizes in the monoclinic space group $P2_1$. The complex is dimeric in nature. The environment around both copper centres is same, Cu1 exhibits [4+1] square pyramidal geometry [$\tau = 0.15$] while geometry for Cu2 is a distorted [4+1] square pyramidal geometry [$\tau = 0.51$]. 5'-CMP acts as a bidentate ligand bridging the two copper centres via phosphate

oxygen atoms. [O9 to Cu1, O7 to Cu2]. Thus the basal plane for each copper is made up of 1,10-phenanthroline, a bridged hydroxyl group and phosphate oxygen of 5'-CMP molecule, while the axial site is occupied by a bridged chlorine atom.

The least square plane analysis of the ribose sugar moiety reveals that the sugar moiety adopts envelope conformation. The Φ_{CN} angle, which is the torsion angle of the base with respect to sugar, is $68.3(6)^\circ$ suggesting an *anti* conformation about the glycosyl bond. The ribose ring is puckered with C2' displaced from the best four atom plane of furanose ring by $0.573(5)\text{\AA}$ on the same side as C5', hence it is C2' *endo* conformation for the ribose ring. The conformation around the C4'-C5' bond is described by the angles Φ_{OO} [O1'-C4'-C5'-O5' = $-64.4(5)^\circ$] and Φ_{OC} [C3'-C4'-C5'-O5' = $56.3(6)^\circ$] confirms *gauche gauche* for the complex.

The structure is stabilized by extensive network of C-H...O, O-H...O and N-H...O hydrogen bond interactions between the neighboring molecules. In 3-dimension packing the copper atoms, hydroxyl ions, chlorine atom and the phosphate groups are running anti parallel along the a axis is flanked on either side by the 1,10-phenanthroline and the cytosine rings. There is also the presence of C-H... π interaction between the 1,10-phenanthroline ring and cytosine ring which further stabilizes the molecules. It is noteworthy that the cytosine rings interact with each other through N-H...O hydrogen bond interactions. The other major interactions are the slipped π - π stacking interaction between the 1,10-phenanthroline rings.

This complex represent the first example of a dimeric monobridged 5'-CMP copper ternary complex.

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