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Synthesis, crystal structures and supramolecular architectures of square pyramidal Cu(II) complexes containing aromatic chelating N,N'-donor ligands

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Abstract

Background: Design of new metal complexes is an interesting field for development of new functional molecular-based materials. In this process by the usage of mixed functional ligands one can precisely tune the physical and chemical properties of those metal complexes. However, it is difficult to obtain the desired complex in many cases for factors like different coordination abilities of the ligands and the types of anions have a great influence on the structure.

Results: A series of five copper(II) complexes [Cu(Bipy) (5-TPC)₂(H₂O)] (1), [Cu(Phen) (5-TPC)₂(H₂O)] (2), [Cu(NO₃) (4,7-Phen) (5-TPC) (H₂O)].H₂O (3), [Cu(Bipy)₂(5-TPC)]₂.(ClO₄)₂ (4), and [Cu₂(Bipy)₄(H₂PO₄)] (5) (where Bipy = 2,2'-bipyridine, Phen = 1,10-phenanthroline, 4,7-Phen = 4,7-hydroxy-1,10-phenanthroline, 5-TPC = 5-chloro-2- thiophene carboxylate) has been synthesized and characterised using single crystal X-ray diffraction studies. In all the compounds, the N,N' ligand coordinates in a bidentate chelating manner and the copper has a square pyramidal geometry.

Conclusions: Complexes (1,2) are expected to be isostructural due to similarity of the N,N'-chelating ligands used, but due to the difference in supramolecular architectures no similar unit cells were observed. This is important in crystal engineering point of view. Complexes (1–4) possess the neutral mononuclear and complex (5) possesses a dinuclear entity. These entities are connected by intermolecular interactions like X...π, H...X, (X = Cl) generating supramolecular architectures.

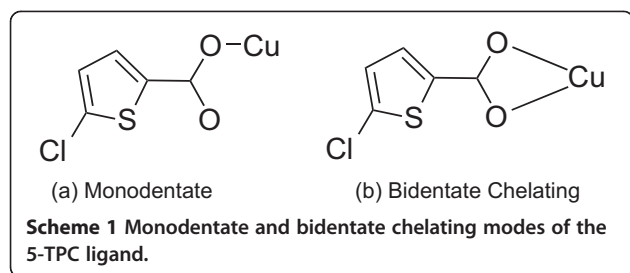
Keywords: Copper(II) complexes, 2,2'-bipyridine, 1,10-phenanthroline, 4,7-hydroxy-1,10-phenanthroline, Single crystal X-ray diffraction

Background

Bipyridines and its analogues such as phenanthroline as well as substituted phenanthrolines are widely used in the formation of metal complexes [1-3] for their potential applications in electrochemistry, catalysis, analytical chemistry, biochemistry and also in the mimic chemistry as a substitute for amino acid side group [4-19]. These ligands due to their chelating nature in metal complexes effectively control the aggregation behavior by effectively chelating around the metal centre. In this regard some of the substituted bipyridine and phenanthroline like ligands have been studied [20-23]. The substitution of a methyl or

hydroxy group in the bipyridine has a steric influence which alters the structural behavior of these compounds. Due to the presence of an extended π-system, various non covalent π-interactions which mimic various biological processes, the study of these complexes have gained importance [24]. The coordination geometry of the copper(II) complexes depends on on the ligands, co-ligands, and counter ions [25-38]. Numerous Cu in different coordination environments have been developed to study the supramolecular Cu networks [39-42]. The five coordinated copper(II) complexes which containing N,N' chelating ligands and monodentate co-ligands have diverse stereo and physicochemical properties [25-37]. Recently in addition to investigations of the

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copper(II) complexes of these ligands with simple anions such as Cl^- , Br^- there are also reports of their mixed ligand complexes and tris chelate mixed ligand complexes. 5-TPC (5-TPC = 5-chloro-2- thiophene carboxylate) not only shows versatile coordination modes but also exhibit non covalent interactions like $\text{Cl}\dots\pi$ and $\text{C-H}\dots\text{Cl}$ [43-48].

Experimental

Materials and methods

Commercial starting materials were used without further purification. 5-chloro thiophene 2- carboxylic acid (Hoechst

Aktiengesellschaft), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cu}(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$ Aldrich, Methanol (Qualigens) and other organic ligands (Aldrich) were used. Single crystal diffraction studies were done on a BRUKER SMART APEXII CCD area-detector diffractometer (Scheme 1).

Synthesis of $[\text{Cu}(\text{Bipy}) (\text{5-TPC})_2 (\text{H}_2\text{O})]$ (1), $[\text{Cu}(\text{Phen}) (\text{5-TPC})_2 (\text{H}_2\text{O})]$ (2), and $[\text{Cu}(\text{NO}_3) (\text{4,7-Phen}) (\text{5-TPC}) (\text{H}_2\text{O})]$. H_2O (3)

A solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (g) in 10 ml of (1:1) $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ mixture was stirred over a hot plate magnetic stirrer for half an hour and 5-chloro thiophene 2-Carboxylic acid (0.0833g) dissolved in 10 ml of CH_3OH was added to it. The mixture was stirred for an additional of 2 hours. A green colored solution was formed. About (0.0442g) of (2-2'-bipyridine) was dissolved in 10ml of hot water and added to the reaction mixture. The mixture was stirred for 3 hours. The precipitate was filtered off and the resulting solution was kept for slow evaporation. Green block-shape single crystals of (1) suitable for X-ray analysis were obtained after few days. The synthesis

Table 1 Crystal data and structure refinement information for complexes (1–5)

	Complex (1)	Complex (2)	Complex (3)	Complex (4)	Complex (5)
Empirical formula	$\text{C}_{20} \text{H}_{14} \text{Cl}_2$ $\text{Cu} \text{N}_2 \text{O}_5 \text{S}_2$	$\text{C}_{22} \text{H}_{14} \text{Cl}_2$ $\text{Cu} \text{N}_2 \text{O}_5 \text{S}_2$	$\text{C}_{17} \text{H}_{12} \text{Cl} \text{Cu} \text{N}_3$ $\text{O}_8 \text{S}, \text{H}_2\text{O}$	$\text{C}_{25} \text{H}_{18} \text{Cl} \text{Cu}$ $\text{N}_4 \text{O}_2 \text{S}, \text{Cl} \text{O}_4$	$\text{C}_{20} \text{H}_{22} \text{Cu}_2$ $\text{N}_4 \text{O}_{16} \text{P}_4$
Formula weight	560.92	584.94	535.38	636.95	827.41
Temp, K	296	296	296	296	296
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	C2/c	P2 ₁ /c	P-1	P-1	C2/c
a (Å)	23.8658(4)	13.4364(3)	8.6712(3)	14.9443(2)	19.1486(9)
b (Å)	16.6525(4)	10.4855(3)	10.3617(4)	15.1728(2)	8.1694(3)
c (Å)	11.3381(2)	20.0390(4)	12.2860(4)	15.3055(2)	19.1208(8)
α (°)	90	90	95.336(2)	111.948(1)	90
β (°)	99.994(1)	123.741(1)	96.851(2)	116.673(1)	102.385(4)
γ (°)	90	90	107.630(2)	97.606(1)	90
V (Å ³)	4437.67(15)	2347.69(10)	1034.75(7)	2681.17(8)	2921.5(2)
Z	8	4	2	4	4
ρ calcd (g/cm ³)	1.679	1.655	1.718	1.578	1.877
μ (mm ⁻¹)	1.449	1.374	1.342	1.140	1.758
F (000)	2264	1180	542	1292	1664
Crystal size (mm)	0.03×0.10×0.10	0.08×0.09×0.09	0.06×0.08×0.09	0.04×0.05×0.08	0.05×0.06×0.07
Number restraints	0	0	0	0	0
No of reflections collected	7358	5848	3540	7676	3286
Goodness-of-fit on F ²	1.00	1.02	1.04	1.04	1.14
Final R ₁ index [$I > 2\sigma(I)$]	0.0335	0.0375	0.0331	0.0644	0.0366
wR ₂ (all data)	0.0919	0.1060	0.0885	0.2156	0.1471
Largest difference in peak and hole (e Å ⁻³)	-0.32, 0.38	-0.55, 0.48	-0.23, 0.36	-0.48, 2.17	-1.07, 0.69

Table 2 Hydrogen bond metrics for complexes (1–5)

D—H...A	H...A (Å)	D...A (Å)	L·D -H...A	Symmetry operation
Complex 1				
O1W-H1W...O4	1.83(2)	2.594(2)	163(2)	
O1W-H2W...O2	1.69(3)	2.584(2)	172(2)	
C3 -H3 ...O2	2.5400	3.255(2)	134.00	$x, -y, -1/2 + z$
C11-H11...O1W	2.4600	2.996(2)	116.00	
C17-H17...O1	2.4800	3.341(2)	154.00	$1/2 - x, 1/2 - y, 1 - z$
C20-H20...O3	2.4500	2.951(2)	114.00	
Complex 2				
O1W-H1W...O4	1.90(4)	2.633(4)	158(4)	
O1W-H2W...O2	1.62(4)	2.578(4)	172(3)	
C8 -H8 ...O1	2.4900	3.293(3)	145.00	$1 - x, -y, 1 - z$
C9 -H9 ...Cl1	2.8000	3.704(4)	164.00	$-1 + x, y, z$
C11-H11...O1W	2.6000	3.087(4)	113.00	
C12-H12...O4	2.5200	3.234(4)	134.00	$1 - x, 1/2 + y, 1/2 - z$
C18-H18...O2	2.3900	3.298(4)	165.00	$x, 3/2 - y, 1/2 + z$
C20-H20...O3	2.5200	2.987(3)	112.00	
Complex 3				
O1W-H1W...O2	1.86(5)	2.556(4)	155(5)	
O1W-H2W...O6	1.98(5)	2.798(4)	172(5)	$-x, -y, 1 - z$
O3 -H3A...O2W	1.67(5)	2.624(4)	175(3)	$x, y, 1 + z$
O2W-H3W...O2	2.01(5)	2.747(3)	174(6)	
O4 -H4A...O5	1.94(5)	2.634(3)	163(6)	$-1 + x, y, z$
O2W-H4W...O7	2.09(5)	2.883(4)	159(5)	$1 - x, -y, 1 - z$
C6 -H6 ...O1	2.5400	3.016(3)	112.00	
C17-H17...O4	2.5200	3.421(4)	162.00	$-1 - x, -y, 2 - z$
Complex 4				
C1 -H1 ...O11	2.5100	3.200(14)	131.00	$1 - x, 1 - y, 1 - z$
C3 -H3 ...Cl1	2.8200	3.424(10)	124.00	$-1 + x, y, z$
C4 -H4 ...O2	2.3900	3.222(10)	148.00	$1 - x, 1 - y, 1 - z$
C7 -H7 ...O2	2.4900	3.376(11)	159.00	$1 - x, 1 - y, 1 - z$
C8 -H8 ...O12	2.4600	3.361(17)	164.00	
C10-H10...O1	2.5300	3.009(12)	112.00	
C19-H19...O10	2.6000	3.309(15)	134.00	$x, 1 + y, z$
C24-H24...O7	2.5800	3.447(16)	155.00	$1 + x, y, z$
C29-H29...O4	2.4100	3.084(13)	129.00	$-x, -y, 2 - z$
C34-H34...O11	2.5500	3.224(17)	129.00	$-1 + x, y, z$
C35-H35...O3	2.5200	3.030(13)	115.00	
C37-H37...O8	2.5900	3.457(16)	156.00	$1 - x, 1 - y, 2 - z$
C39-H39...O9	2.4300	3.233(15)	145.00	$1 - x, -y, 1 - z$
Complex 5				
O2 -H12...O8	1.86(4)	2.580(4)	175(7)	$1 - x, 1 - y, -z$
O3 -H13...O8	1.88(4)	2.586(4)	159(4)	$x, -1 + y, z$
O7 -H17...O5	1.86(4)	2.590(3)	174(4)	$1 - x, y, 1/2 - z$

Table 2 Hydrogen bond metrics for complexes (1–5)
(Continued)

D—H...O	H...O (Å)	D...O (Å)	L·D -H...O	Symmetry operation
O6 -H18...O1	1.97(4)	2.683(4)	165(4)	
C1 -H1 ...O4	2.5100	2.976(4)	111.00	$1 - x, 1 - y, -z$
C7 -H7 ...O8	2.5400	3.189(5)	127.00	$-1/2 + x, -1/2 + y, z$
C10-H10...O3	2.5200	3.376(5)	153.00	

procedures of (2, 3) were the same as that of (1) except PHEN and 4,7-PHEN were used in the place of BIPY. The crystals were filtered and washed with small portions of methanol and were dried in air (yield 75% based on Cu).

Synthesis of [Cu(Bipy)₂(5-TPC)]₂(ClO₄)₂ (4)

Complex (4) was obtained by same reaction procedures as that of (1) except Cu(ClO₄)₂·6H₂O was used in the place of Cu(NO₃)₂·3H₂O. The crystals were filtered and washed with small portions of methanol and were dried in air (yield 69% based on Cu).

Synthesis of [Cu₂(Bipy)₄(H₂PO₄)] (5)

The complex (5) was synthesized by the same procedure as that of (1). To the resulting green solution 2ml of H₃PO₄ was added. The mixture was stirred for 3 hours. The resulting solution was kept for slow evaporation. Blue block-shape single crystals of (5) suitable for X-ray analysis were obtained after a few days.

X-ray crystallography

Intensity data sets were collected at room temperature, on a BRUKER SMART APEXII CCD [49] area-detector diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The data were reduced by using the program SAINT [49] and empirical absorption corrections were done by using the SADABS

Table 3 Comparison of coordination modes of various carboxylates and some structural parameters around the copper(II) ion

Complex	Coordination mode of	Coordination mode of the anion	τ value	Deviation of Cu atom above the plane (Å)	Axial bond length (Å)	
1	5-TPC	Monodentate	0.0380	0.150	2.317	
2	5-TPC	Monodentate	0.0630	0.153	2.243	
3	5-TPC	Monodentate	0.0015	0.121	2.401	
4	Cu1	5-TPC	Monodentate	0.0421	0.227	2.166
	Cu2	5-TPC	Monodentate	0.1196	0.252	2.182
5	H ₂ PO ₄	Bidentate Bridging	0.0488	0.134	2.200	
	H ₂ PO ₄	Monodentate	0.0488	0.134	2.200	

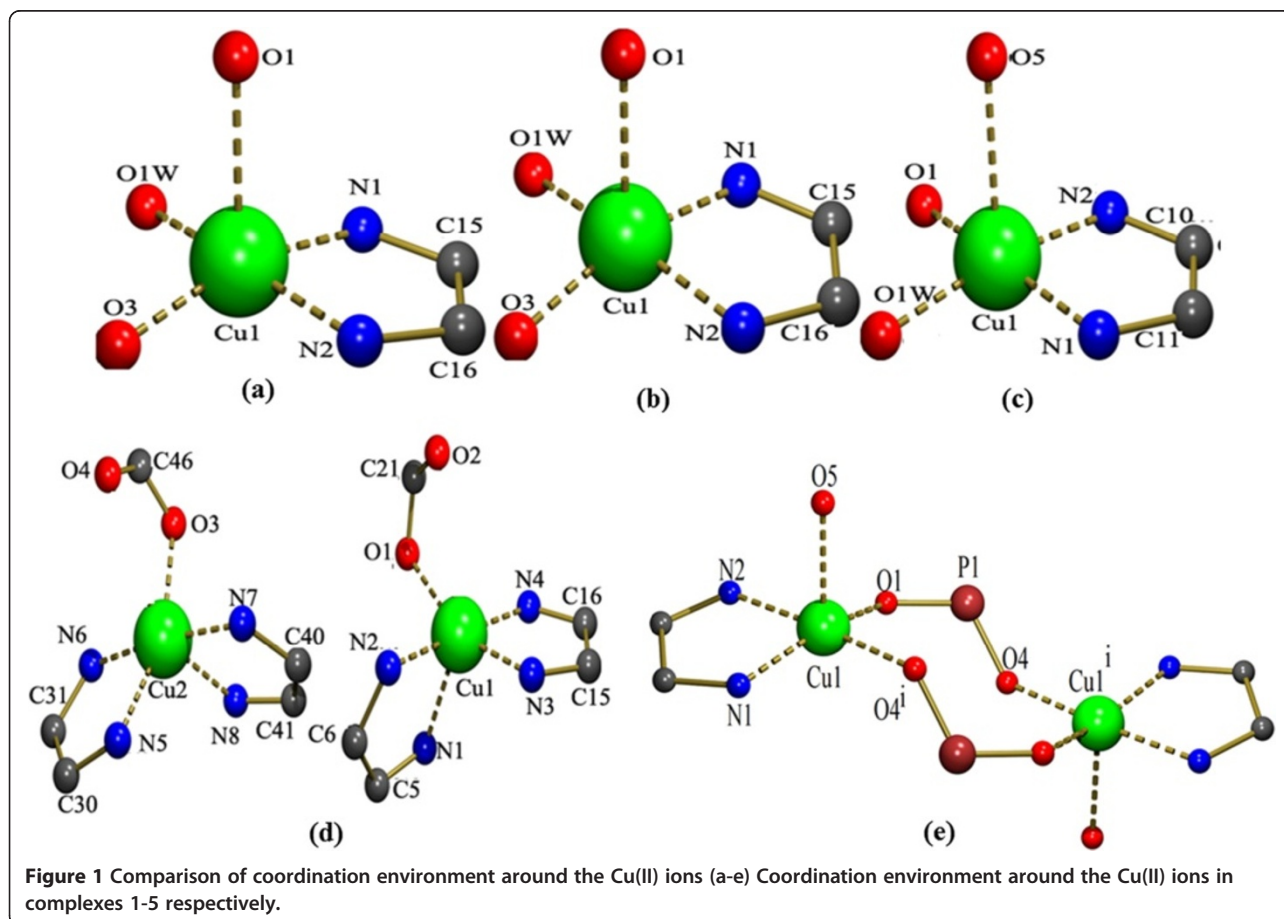
[49]. The structures were solved by direct methods using SHELXS-97[50] and subsequent Fourier analyses, refined anisotropically by full-matrix least-squares method using SHELXL-97 [50] within the WINGX suite of software, based on F^2 with all reflections. All carbon hydrogens were positioned geometrically and refined by a riding model with U_{iso} 1.2 times that of attached atoms. All non H atoms were refined anisotropically. The molecular structures were drawn using the ORTEP-III [51], POV-ray [52] and MERCURY [53]. Crystal data and the selected parameters for complexes (1–5) were summarized in (Tables 1 and 2) respectively. The crystals remained stable throughout the data collection. The H atoms of the water molecules in the structure of (1) were located from the difference map and refined with no positional constraints. The water H atoms of (2 and 3) were located in a difference Fourier map and refined as riding on the O atom in these positions with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. Comparisons of various coordination modes of carboxylates are given (Table 3), Additional file 1.

Results and discussion

Geometry around Cu(II) atoms

The coordination environment of metal center in both complexes (1) and (2) is square pyramidal in which two

equatorial sites are occupied by the nitrogen atoms of the BIPY and the PHEN rings (respectively in 1 and 2) and the remaining two sites are occupied by two oxygen atoms of which one is from a coordinated water molecule and the other is from monodentate 5-TPC anion and the apical site is occupied by another monodentate 5-TPC anion (Figure 1). Complex (3) has a similar geometry around the central Cu(II) atom, but unlike those two complexes the NO_3 group in (3) mimics the role of one of the carboxylate. The square pyramidal geometry of each Cu(II) ion is furnished by the two nitrogen atoms from the 4,7-PHEN and two oxygen atoms (O1W, O1) from coordinated water molecule and monodentate 5-TPC anion respectively in the basal plane and one oxygen (O5) of the NO_3 anion in the apical position. Apart from the coordinated water molecule, there is one more water molecule (O2W) at the lattice. (4) has two monodentate Cu(II) atoms with the an identical square pyramidal environment. The same square pyramidal geometry like that of (1–3) is observed in (4). The equatorial positions are occupied by three nitrogen atoms of BIPY molecules and oxygen of the monodentate carboxylate molecules. The axial position is occupied by one of the nitrogens of a BIPY molecule. There are two perchlorate anions in the lattice.

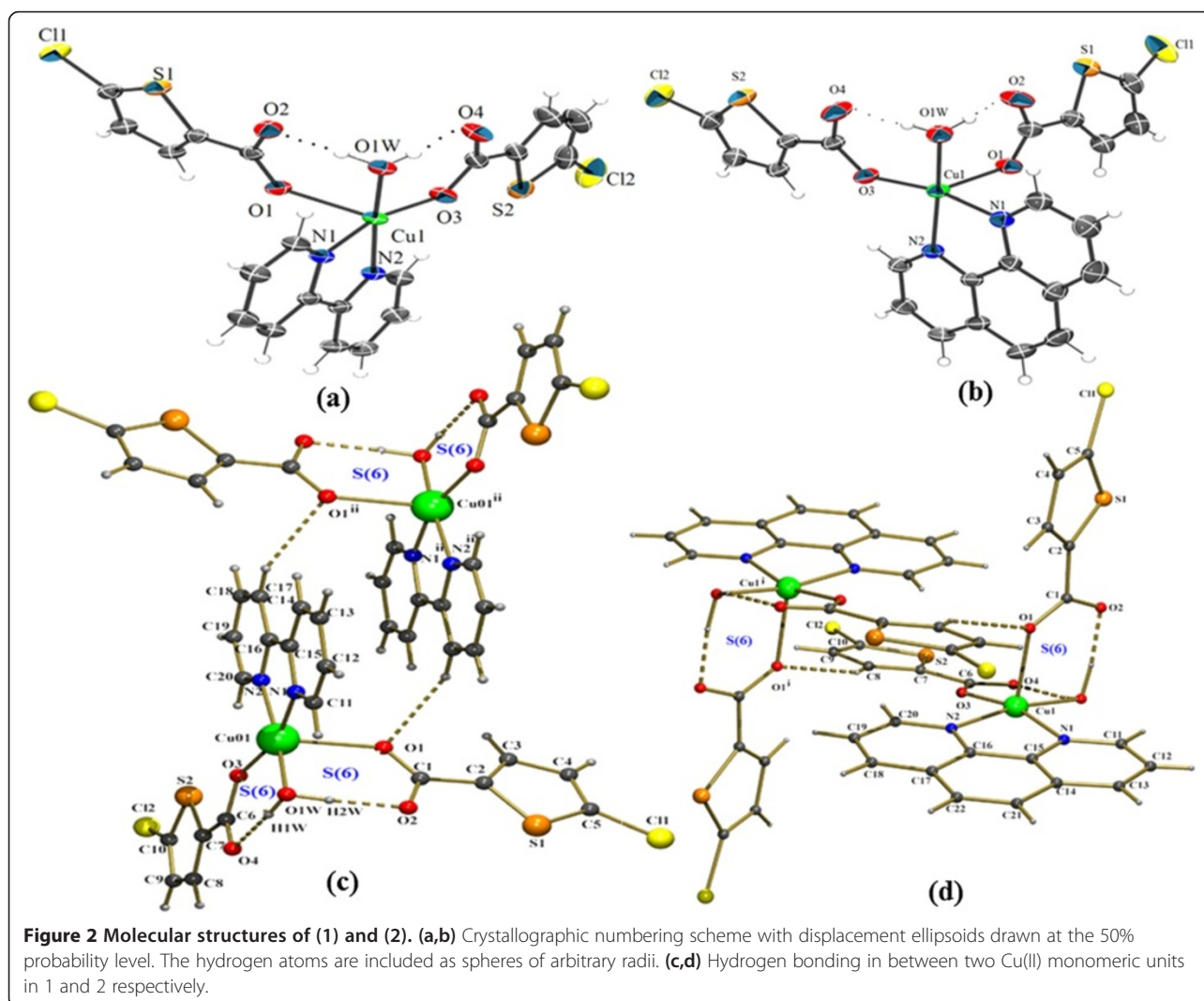


Complex (5) is a discrete Cu(II) dimer. The molecular structure consists of two square pyramidal copper(II) ions bridged by two oxygens (O1,O4) from two dihydrogen phosphate ions (H_2PO_4^-) in the basal plane to form a dimer; the rest of the coordination sites of each copper ion in the basal plane are occupied by two nitrogen atoms from the BIPY molecule. The apical position of each copper is accommodated by one oxygen from the dihydrogen phosphate. The distance between two copper metal centers in the dimer is 5.100Å. The assignment of P = O, P - O⁻, and P - OH bonds are consistent with the literature [54]. The largest angle around the Cu(II) center (β) is considerably different from the second largest one(α). The distortion of the coordination polyhedron from the square-pyramidal geometry in (1–5) is rather small as reflected in the structural index τ (where $\tau = (\beta - \alpha)/60$) (Table 3) [55]. The deviation of the Cu atoms above the basal plane of the square pyramid as well as the axial bond lengths are given in (Table 3).

Crystal structure description of [Cu(Bipy) (5-TPC)₂(H₂O)] (1), [Cu(Phen) (5-TPC)₂(H₂O)] (2)

The ORTEP drawings of the asymmetric units of (1) and (2) with the atom-numbering schemes are illustrated in (Figure 2a, b) and, respectively. Complexes (1) and (2) crystallize in two different space groups ($C2/c$ and $P2_1/c$ respectively) but contain both the same neutral mononuclear unit with general formula [Cu(L) (5-TPC)₂(H₂O)] where L = BIPY in (1) and PHEN in (2). The copper(II) ion in the complex [Cu(L) (5-TPC)₂(H₂O)] unit displays a square-pyramidal coordination with the same CuN₂O₂O' chromophore.

The most characteristic feature of both the complexes is the involvement of both the water hydrogens (apical water) in O-H...O hydrogen bonding with the monodentate carboxylate leading to two a graph set motifs with graph set notation of S(6) (Figure 2c,d) [56-58]. Although the first order coordination of both complexes is same they



differ in their supramolecular architectures. In (1) each monomer is linked to another monomer in the crystallographic *c* axis through the π - π stacking interactions inbetween the BIPY rings. The stacked molecules further extend into a chain by a C-H...O interaction. Further this chain is still stabilized by a Cl- π interaction inbetween Cl2 \rightarrow Cg5ⁱⁱⁱ and π - π stacking interactions [59]. Each of this chain is linked to the adjacent chain by a Cl- π interaction inbetween Cl1 \rightarrow Cg2ⁱⁱⁱ (Figure 3).

In (2) two of the monomeric units linked by C-H...O interactions are linked into a chain by a pair of C-H...Cl interactions inbetween the hydrogen of a 5-TPC ring and Cl of the adjacent 5-TPC (C9^{iv}-H9^{iv}...Cl1). Also this chain is stabilized by π - π stacking interactions in between the thiophene rings Cg1 \rightarrow Cg1ⁱⁱⁱ (where Cg1 = S1, C2-C5). As in the case of (1), here each of this chain is linked to the adjacent chain by Cl- π interaction inbetween Cl1 \rightarrow Cg2ⁱⁱⁱ (Figure 4).

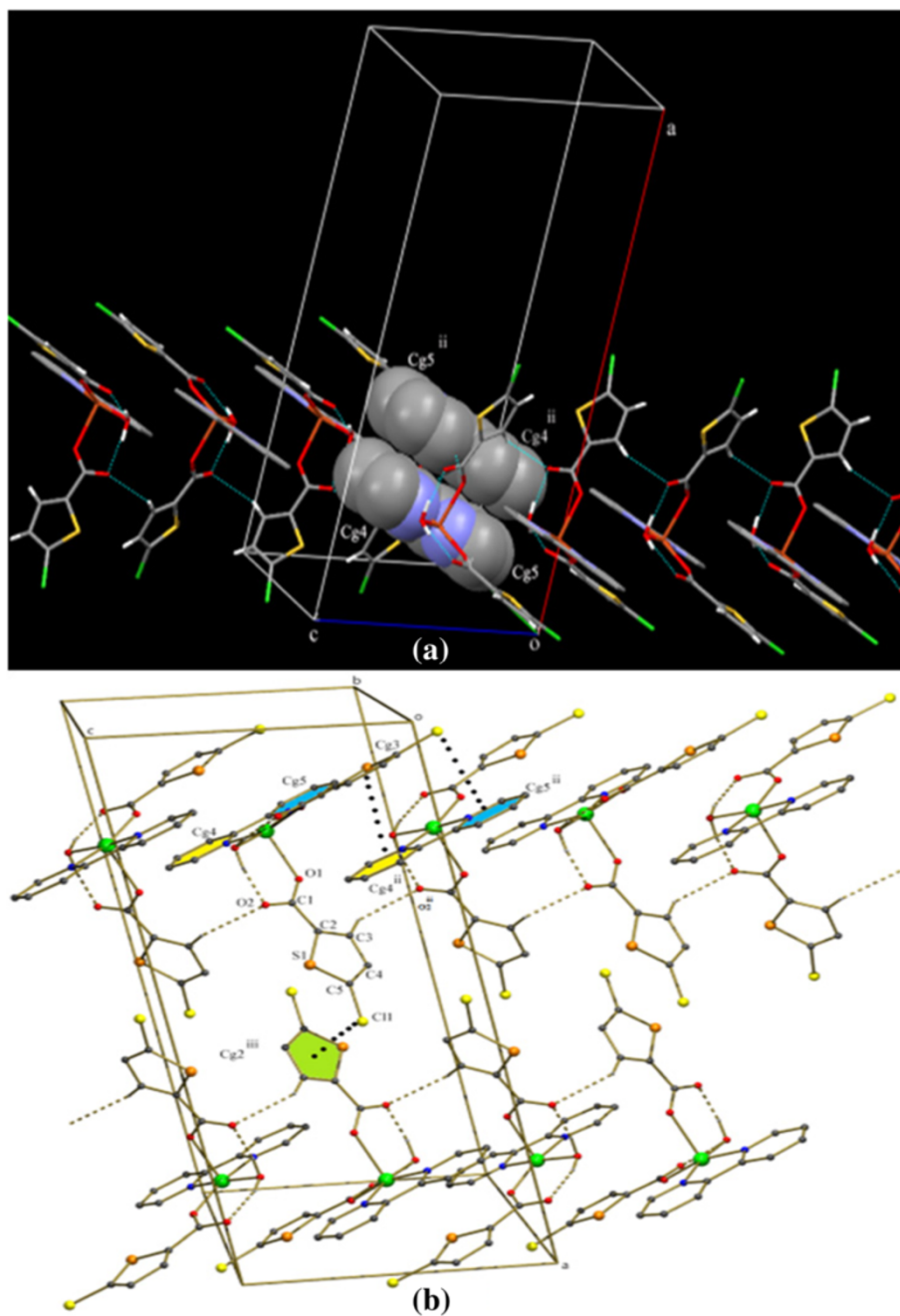


Figure 3 π - π stacking and C-H...O interactions. (a) Formation of chain by π - π stacking and C-H...O interactions. (b) Two of these chains linked by Cl- π interactions.

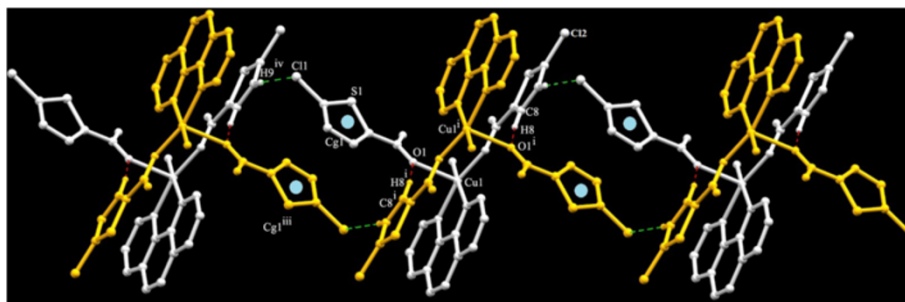


Figure 4 Formation of a chain in 2 by C-H...O and C-H...Cl interactions.

Crystal structure description of [Cu(NO₃) (4,7-Phen) (5-TPC) (H₂O)].H₂O (3)

In complex (3) one of the water hydrogens (apical water) is involved in O-H...O hydrogen bonding with the monodentate carboxylate leading to a S(6) graph set motif as in (1) and (2) (Figure 5a). The presence of coordinated water molecule, carboxylate and nitrate groups, together with the molecule of solvation (H₂O) causes extensive hydrogen bonding interactions in complex (3). The H-bonds to a charged carboxylate group or nitrate anion can be termed “charge-assisted H-bonds”, here the carboxylate or nitrate groups as hydrogen bond acceptors carry negative ionic charges. Such charge-assisted H-bonds are much stronger than hydrogen bonds between neutral atoms [60-67]. Each of the monomer is connected to each other by (O1W-H2W...O6^X (symmetry code $x = -x, -y, 1-z$ hydrogen bonds) inbetween the coordinated apical nitrate anions and coordinated water molecules (Figure 5b). Also the presence of hydroxyl groups in the ligand (4,7-PHEN) introduces a steric influence in the structural behavior of the (3). This hydroxyl group (O4) of a 4,7-PHEN is involved in

C17-H17...O4 hydrogen bonding with another 4,7-PHEN in the same plane giving rise to a hydrogen-bonding motif with the graph-set descriptor R₂²(10). One of the hydrogen atoms of the uncoordinated water molecule (H3W) and hydrogen of another 4,7-PHEN lying in the same plane are connected by two O-H...O hydrogen bonds (O2W-H3W...O2, O3-H3A...O2W). Consequently, the layer like pattern is formed by C-H...O and O-H...O hydrogen bonds (Figure 6).

As depicted in (Figure 6), two of these layers are linked to each other by four sets of O-H...O hydrogen bonds inbetween the coordinated nitrate, carboxylate and uncoordinated water molecules. Also there is a Cl... π interaction observed inbetween the Cl1 and Cg5 [where Cg5 = C9, C10, C11, C12, C17, C16].

In general, the coordination bond lengths in complexes (1–3) are in good agreement with those found for the corresponding bonds in similar five-coordinate copper(II) complexes which possess axial water molecules [Cu(BIPY) (OXL) (H₂O)].2H₂O, [Cu(OXL) (H₂O) (NPHEN)].2H₂O, [Cu(OXL) (H₂O) (PHEN)].H₂O, [Cu

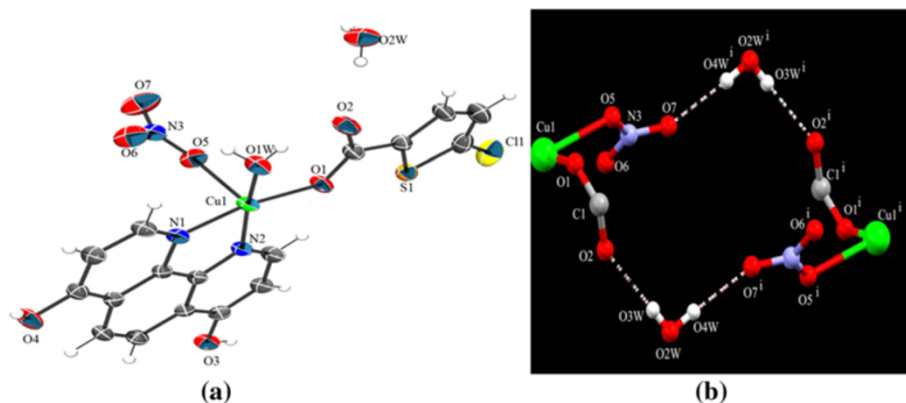


Figure 5 Molecular structure of 3 displaying the crystallographic numbering scheme. **a)** Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms are included as spheres of arbitrary radii. **b)** Two of the Cu(II) monomers linked by O-H...O interactions.

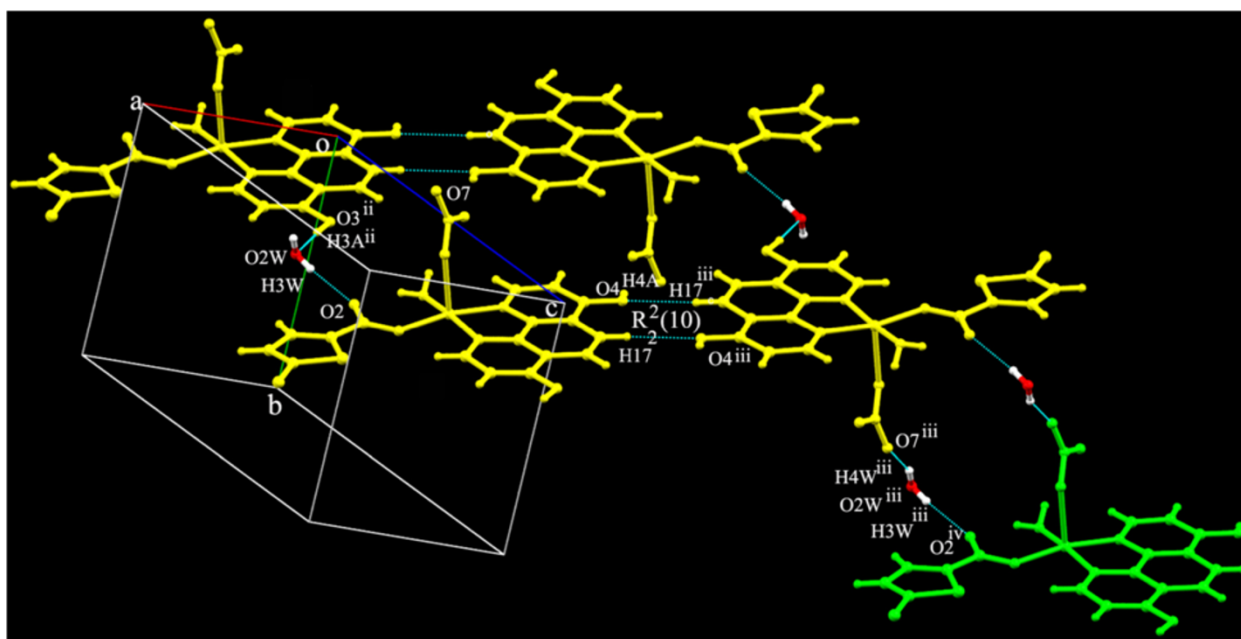


Figure 6 Formation of layers (yellow and green) by C-H...O and O-H...O hydrogen bonds and layers connected by uncoordinated water molecules.

(BIPY) (OXL) (H₂O)].H₂O, [Cu(BIPY) (OXL) (H₂O)].HOXL (NPHEN = 5-nitro-1,10-phenanthroline, HOXL = oxalic acid and OXL = oxalate) [68-71].

Crystal structure description of [Cu(Bipy)₂(5-TPC)]₂(ClO₄)₂ (4)

In (4), two crystallographically independent Cu(II) monomeric units are found. In each unit a monodentate carboxylate as well as two BIPY ligands chelate the Cu (II) ion to form a square pyramidal environment; there are two perchlorate anions to make the charge balance (Figure 7). Each of the monomeric unit is connected to adjacent monomeric unit by the C-H...O hydrogen bonds inbetween the BIPY and the monodentate

carboxylate oxygen (C4-H4...O2ⁱ, C7-H7...O2ⁱ symmetry code i = 1-x,1-y,1-z). Also these monomeric units are held together by a pair of C-H...O hydrogen bonds inbetween the BIPY and the ClO₄⁻ anion (C1ⁱ-H1ⁱ...O11, C8-H8...O12 symmetry code i = 1-x,1-y,1-z). These monomeric units are linked to the next pair of monomeric units by a pair of C-H...Cl interactions inbetween 5TPC and BIPY molecules. Thus these monomeric units are bridged by this C-H...Cl interactions which extend into a chain (Figure 8). The bridging thiophene rings are linked to another ClO₄⁻ anion by C-H...O interactions inbetween the hydrogen of the thiophene ring and the perchlorate oxygen (C24-H24...O7). These

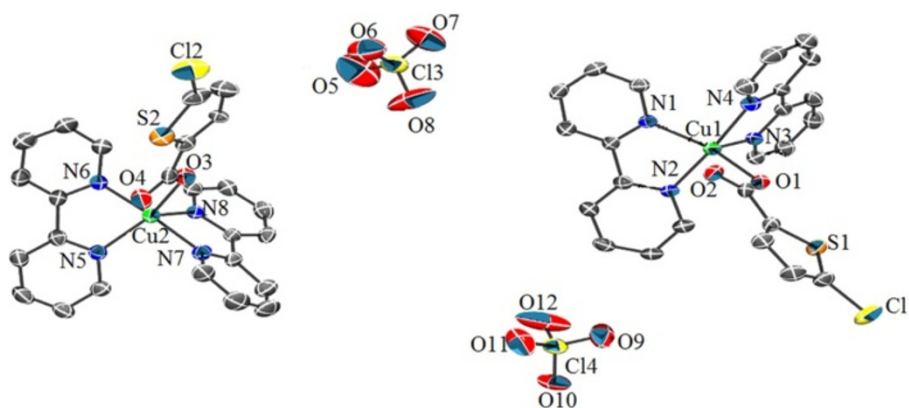


Figure 7 Molecular structure of 4 displaying the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms are included as spheres of arbitrary radii.

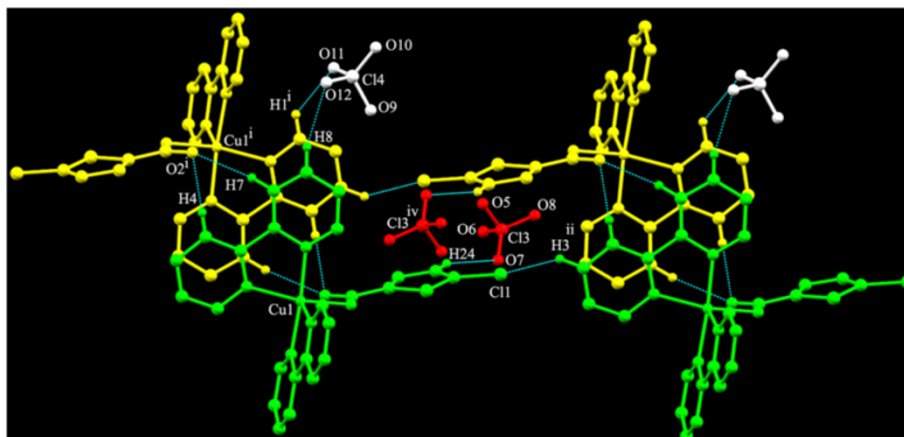


Figure 8 Formation of chain by C-H...Cl interaction and a chain connected to uncoordinated perchlorate molecules (white and red).

perchlorate anions play a major role in extending these supramolecular architectures.

Crystal structure description of $[\text{Cu}_2(\text{Bipy})_4(\text{H}_2\text{PO}_4)]$ (5)

The complex (5) is a discrete copper dimer that crystallizes in monoclinic space group $C2/c$. The complex was obtained by serendipity and is totally different from the rest of the complexes. The dihydrogen phosphate anions show two type of coordination such as bidentate bridging and monodentate (Figure 9). In the crystal structure each of the dimer is linked to the next dimer by a pair of O-H...O hydrogen bonds. These interactions are found inbetween the axially coordinated H_2PO_4 anions. This results in the formation of $R_2^2(8)$ motif (Figure 10a).

This $R_2^2(8)$ motif is frequently observed in carboxylic acid dimers. This leads to a chain of O-H...O hydrogen bonds extending along the crystallographic c axis. This

chain is linked to the next chain by two O-H...O hydrogen bonds in between the bridging H_2PO_4 anions of one chain and axial H_2PO_4 anions of the next chain (Figure 10b). These chains extend along the crystallographic a axis perpendicular to the direction of previous chain.

Conformations of 2,2'-bipy in complexes 1,4,5

Conformations of 2-2'-bipy in the complexes (1, 4-5) are different depending on the anion. The dihedral angles between two pyridyl rings of 2-2'-bipy are listed in (Table 4). The above complexes show different structures with different coordination modes of carboxylate, different numbers of 2-2'-bipy coordinated to the Cu^{2+} ion.

Conclusions

We have presented a systematic investigation of one dinuclear and four mononuclear Cu(II) complexes. Their

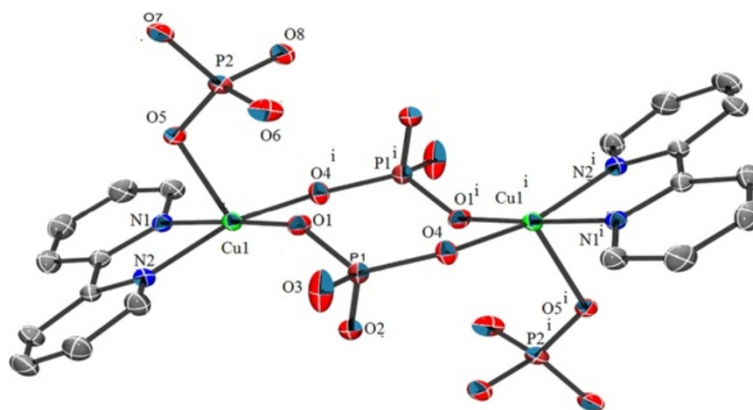


Figure 9 Molecular structure of 5 displaying the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms are included as spheres of arbitrary radii.

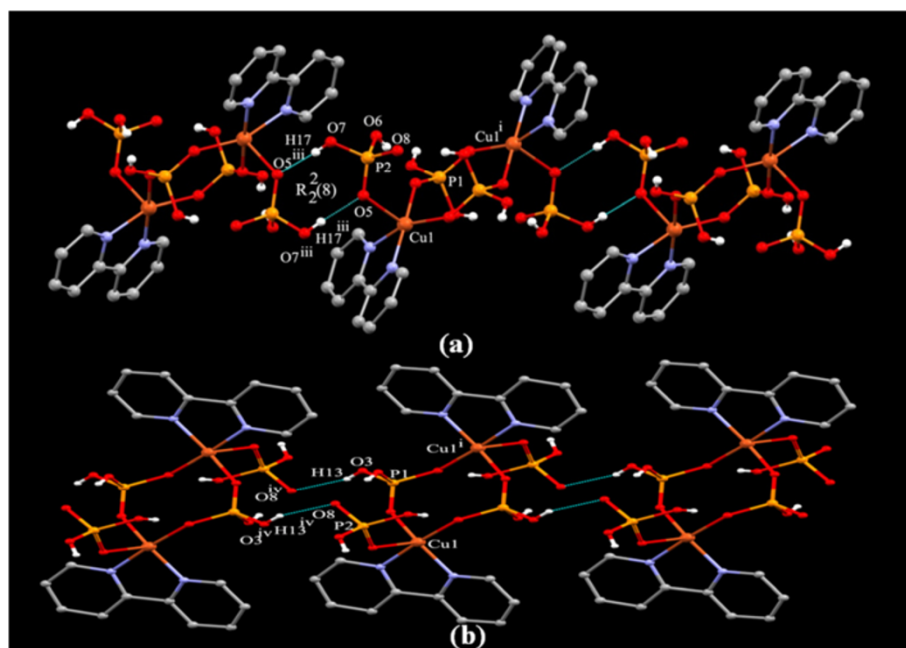


Figure 10 O-H...O interactions in 5. (a) A view of the complex showing the $R_2^2(8)$ motif in between two dinuclear units and the chain by O-H...O interactions extending along the crystallographic *c* axis. (b) O-H...O hydrogen bonds in between the bridging H_2PO_4 anions of one chain and axial H_2PO_4 anions

structures show various coordination modes depending on the anions. Since different anions provide different coordination environment around the Cu^{2+} , it is clear that selection of appropriate anion can control the coordination geometry of the Cu^{2+} ion. Also comparing structures (1–5) we can find the role of anion in controlling the supramolecular architectures. In structures (1) and (2) the primary coordination of the Cu(II) ion is unchanged, even in presence of different chelating N,N-ligands. In (3) the NO_3 anion mimics the role of a carboxylate when compared to (1) and (2). The observation of structures (1–5) reveals the structural changes made just by the replacement of the anion alone. In addition to noncovalent interaction like C-

H...O, which is the reason for assembly of primary motifs, various other interactions like $X\cdots\pi$, $H\cdots X$, ($X = Cl$) add additional support in organizing these supermolecules in to extended architectures.

Additional file

Additional file 1: Supplementary crystallographic data for the complexes 1–5 respectively and can be obtained free of charge via <http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/DataRequest.aspx?>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

This work was prepared in the research group of PTM. He proposed the work and drafted the manuscript. SJJ participated in the design and presided over the experiments, collected the X-ray data and drafted the manuscript. Both authors read and approved the final manuscript.

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Table 4 The dihedral angles ($^\circ$) between two pyridyl rings of 2-2'-bipy in complexes 1,4 and 5

Complex	Dihedral angle ($^\circ$) inbetween the two pyridyl rings of BIPY			
1	0.98(9)			
4	Cu1	Cu2		
	Bipy 1	Bipy 2	Bipy 1	Bipy 2
	7.2(3)	1.5(5)	1.7(4)	12.2(5)
5	Cu1			
	9.25(19)			

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