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Syntheses and characterization of three diphenyl phosphate based Cu(II) complexes and the effect of non-covalent interactions on their supramolecular framework

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Abstract. Assembly of diphenylphosphate (dpp) with Cu(II) salts in combination with the different N-donor linkers, e.g., pentamethyldiethylenetriamine (*pmdeta*), bis-(3-aminopropyl)amine (*bapa*) and 4-Picolene (*4-pic*), yielded three new metal-organic coordination complexes, namely $\{[Cu(dpp)(pmdeta)]\cdot ClO_4.H_2O\}_2$ (**1**), $\{[\{[Cu(dpp)(bapa)H_2O]\cdot ClO_4\}$ (**2**) and $[Cu(dpp)_2(4\text{-}pic)_2]_2$ (**3**) by stirring the constituent reactants at room temperature. Complexes **1**–**3** were characterized by single crystal X-ray diffraction analysis and were further characterized by elemental analysis, infrared spectroscopy (IR) and powder X-ray diffraction (PXRD) studies. Compound **1** exhibits a dimeric Cu(II) complex which forms a 1D supramolecular chain along the crystallographic *c*-axis by means of intermolecular $\pi \ldots \pi$ interactions. Compounds **2** and **3** form a monomeric and dimeric complex of Cu(II) respectively, which are further extended into a supramolecular 2D structure via C-H..π interactions for **2** and a 3D structure for **3** with the help of both intermolecular C-H..π and $\pi \ldots \pi$ interactions for **3**. In addition, the solid state UV-Vis spectra of compounds **1-3** and free dpp ligand have been investigated at room temperature.

Keywords. Metal-organic coordination complexes; X-ray structure analysis; supramolecular interaction; copper (II); UV-Vis spectra.

1. Introduction

Metal-organic coordination compounds, in which the metal centres are interconnected by organic ligands exhibiting a variety of infinite supramolecular networks have become a fascinating area of chemical research.[1,2] The chemistry of such compounds are of interest to the synthetic chemist because of their intriguing supramolecular architecture and also due to their potential use in catalysis,[3,4] gas adsorption,[5-8] magnetism,[9,10] ion exchange,[11,12] conductance,[13,14] and photo luminescence.[15-17] The metal nodes and the N-donor ligands are combined to such complexes, due to their inherent capability to create self-assembled structures.[18,19] The desired structural motifs of the complexes have been achieved mostly by the judicious choice of the organic linkers.[20-23] Besides the active role of organic linkers, there are many other essential factors such as the metal ions,[24] counter anions,[25] reaction temperature,[26,27] pH of the medium,[28,29] and solvents[30,31] that also play a vital role to create the struc-

tural diversities observed in such complexes. Recently, the charged linkers have also been extensively used as co-ligands along with the N,N′-donor ligands for the extension of the polymeric structure of metal-organic coordination complexes with fascinating topology. In this context, O-donors or mixed N/O donors ligands such as succinate, gluterate, pydinedicarboxylate, nicotinate, isonicotinate, etc.,[32-34] have been widely used. The use of these different carboxylates with different sizes and shapes and its diverse coordination modes have been well-established to create the diversity in the structures of the complexes as well as in their supramolecular structures.[1,2] On the contrary, the use of phosphate in the fabrication of such supramolecular architecture are not so common but it has the similar prospect when it can be utilized in combination with suitable organic groups. In this context, we have used diphenylphosphate (dpp) with different N-donor ligands to propagate the acquired knowledge from carboxylate to phosphate. Moreover, the two phenyl groups can be utilized for creating $\pi \ldots \pi$ interactions in the solid state structure for the stabilization of the extended structure of the complexes. Here,

we have obtained three new Cu(II) complexes namely
{[Cu(*dpp*)(*pmdeta*)].ClO$_4$.H$_2$O}$_2$ (**1**), {[Cu(*dpp*)(*bapa*)
H$_2$O]·ClO$_4$} (**2**) and [Cu(*dpp*)$_2$(*4-pic*)$_2$]$_2$ (**3**) [where
pmdeta = pentamethyldiethylenetriamine, *bapa* = bis-
(3-aminopropyl)amine and *4-pic* = 4-Picolene]. All the
complexes exhibit supuramolecular[1,2] self-assembly
through $\pi \ldots \pi$ and C-H$\ldots \pi$ interactions with the
phenyl ring of dpp ligand which acts as a bridging as
well as a monodentate ligand in the resulting archi-
tecture. It is worth to mention that the preparation of
phosphate based materials are very important to the
synthetic chemist because of their potential use in pro-
ton conduction,[35,36] ion exchange,[11,12] and catalysis.[3,4]
Moreover, the metal phosphates are also essential in
designing optical materials such as phosphors,[37] non-
linear optical materials[38,39] and laser optics materials[40]
because the phosphate anions do not absorb in the
UV-visible light. On the other hand, the phosphodi-
ester has been also used to make several important
materials e.g., the preparation of organo-phosphorus
polymers,[41,42] insecticides,[43] reagents in solvent extrac-
tion of heavy metal ions,[44] etc., but their use in the
design of metal-organic coordination compounds was
very limited. Though there are several reports on sub-
stituted metal-phosphate[45–47] complexes in literature,
the effect of substituents on phosphate in the result-
ing solid state structure of the complexes have not been
explored scrupulously. Hence, with the aim of explor-
ing the role of *dpp* in the design of framework, here we
report the syntheses, characterization and single crys-
tal X-ray structures of three diphenyl phosphate based
Cu(II) complexes with the variation of N-donor ligands
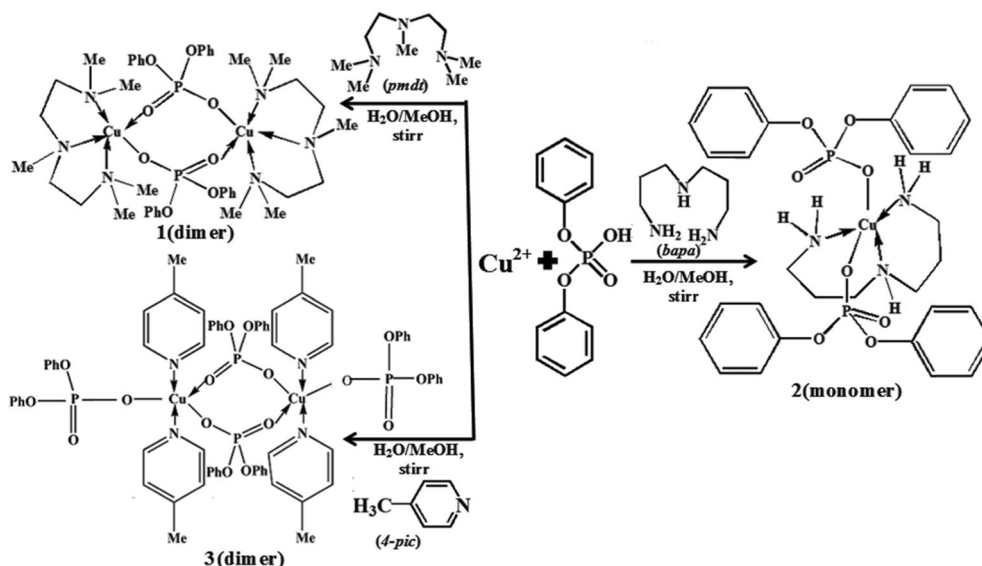(Scheme 1).

2. Experimental

2.1 *Materials*

High purity copper(II) perchlorate, copper(II) nitrate
trihydrate, diphenyl phosphate (*dpp*), pentamethyl-
diethylenetriamine (*pmdeta*), bis-(3-aminopropyl)amine
(*bapa*) and 4-Picolene (*4-pic*), were also obtained from
Sigma-Aldrich Chemical Co. Inc. All other chemi-
cals, including solvents were of AR grade and used
as received.

2.2 *Physical measurements*

The elemental analyses (carbon, hydrogen, and nitro-
gen) of compounds **1**–**3** were carried out on a Perkin–
Elmer 240C elemental analyzer. The Infrared spectra
were obtained using KBr pellets on a Perkin–Elmer
Spectrum BX-II IR spectrometer in the 4400–400 cm^{-1}
region. The X-ray powder diffraction (PXRD) pat-
terns of the bulk samples were recorded in a Bruker
D8 Discover instrument using Cu-Kα radiation (λ =
1.5418 Å) at room temperature; whereas the single
crystal X-ray diffraction analysis was performed at
room temperature using Bruker APEX II diffractome-
ter, equipped with a normal focus, sealed tube X-ray
source with graphite monochromated Mo-Kα radiation
(λ = 0.71073 Å). UV-Vis spectra were recorded on a
Perkin–Elmer Lambda 35 UV-vis spectrophotometer.

2.3 *Syntheses*

2.3a *Synthesis of {[Cu(dpp)(pmdeta)].ClO$_4$.H$_2$O}$_2$(1)*:
1 mmol of Cu(ClO$_4$)$_2$.6H$_2$O (i.e., 0.3704 gm) was

Scheme 1. Synthetic outline of complexes **1**–**3**.

dissolved in 10 mL water in a 50 mL flat bottom flask. Then 1 mmol (i.e., 0.21 mL) of pentamethyldiethylene-triamine (*pmdeta*) was dissolved in 10 mL MeOH in a beaker. This solution was added to the flat-bottom flask. After that the above mixture was stirred for 30 min when a deep blue color appeared. Then 1 mmol (i.e., 0.250 gm) aqueous solution of diphenyl phosphate (*dpp*) was added to the deep blue solution and the resultant mixture was stirred for 4 h. The resulting blue solution was filtered and filtrate was kept in desk. After seven days block shaped blue crystals suitable for X-ray diffraction analysis were obtained in the reaction beaker. The crystals were separated and washed with methanol–water (1:1) mixture and dried under air (Yield: 60%). Anal. Calc.(%) for $C_{21}H_{35}N_3O_9PClCu$: C, 41.80; H, 5.85; N, 6.96. Found(%): C, 41.84; H, 5.81; N, 6.92. IR spectra (cm^{-1}): ν(CH-Ar), 3061–2940; ν (C=C), 1608–1457; ν(P=O), 1320–1140; ν(P-O), 996–905 and ν(Ar-O), 1242–1110.

2.3b *Synthesis of {[Cu(dpp)(bapa)H$_2$O].ClO$_4$} (2)*: This compound was synthesized by following the same procedure as that of **1**, but using bis-(3-aminopropyl) amine (*bapa*) (1 mmol, 0.14 mL) instead of pentamethyldiethylenetriamine (*pmdeta*) (1 mmol, 0.21 mL). After ten days, block shaped blue crystals suitable for X-ray diffraction analysis were obtained in the reaction beaker. The crystals were separated and washed with methanol–water (1:1) mixture and dried under air (Yield: 72%). Anal. Calc.(%) for $C_{18}H_{24}N_3O_9PClCu$: C, 38.86; H, 4.35; N, 7.55. Found(%): C, 38.83; H, 4.39; N, 7.51. IR spectra (cm^{-1}): ν(CH-Ar), 3420–2945; ν(N-H, amine), 3331; ν(C=C), 1599–1419; ν(C-H), 2895; ν(P=O), 1320-1140; ν(P-O), 996–905 and ν(Ar-O), 1242–1110.

2.3c *Synthesis of [Cu(dpp)$_2$(4-pic)$_2$]$_2$ (3)*: This compound was synthesized by following the same procedure as that of **1**, but using 4-Picolene (*4-pic*) (2 mmol, 0.2 mL) instead of pentamethyldiethylenetriamine (*pmdeta*) (1 mmol, 0.21 mL). After two weeks block shaped blue crystals suitable for X-ray diffraction analysis were obtained in the reaction beaker. The crystals were separated and washed with methanol-water (1:1) mixture and dried under air (Yield: 72%). Anal. Calc.(%) for $C_{36}H_{34}N_2O_8P_2Cu$: C, 57.80; H, 4.58; N, 3.74. Found(%): C, 57.83; H, 4.55; N, 3.71. IR spectra (cm^{-1}): ν(CH-Ar), 3410–2930; ν(C=N), 1599; ν(C=C), 1599–1419; ν(C-H), 2945, ν(P=O), 1320–1140; ν(P-O), 996–905 and ν(Ar-O), 1242–1110.

The bulk products of complexes **1**–**3** have been synthesized by direct mixing of the corresponding aqueous-methanolic ligands mixture with the aqueous solution of Cu(II) salt in equal-molar ratio. After 12 hours, the bulk products are separated from the solution and washed with H$_2$O-MeOH solution repeatedly. Then the purity of the bulk products was verified by PXRD, which gave identical peak positions with their simulated PXRD patterns. The purity of the bulk compounds were also confirmed by the results of elemental analysis and IR spectra as well, which were found to be in accordance with the data obtained for the single crystals.

2.4 *Crystallographic data collection and refinement*

The single crystals of compounds **1**, **2** and **3** were mounted on the tips of glass fibers with commercially available glue. X-ray data collection of all three single crystals were performed at room temperature using Bruker APEX II diffractometer, equipped with a normal focus, sealed tube X-ray source with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were integrated using SAINT[48] program and the absorption corrections were made with SADABS.[49] All the structures were solved by SHELXS-97[50] using Patterson method and followed by successive Fourier and difference Fourier synthesis. Full matrix least-squares refinements were performed on F^2 using SHELXL-97[51] with anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were fixed geometrically by HFIX command and placed in ideal positions in case of both structures. Calculations were carried out using SHELXS-97,[50] SHELXL-97[51] PLATON v1.15,[52] ORTEP-3v2,[53] WinGX system Ver-1.80.[54] Data collection and structure refinement parameters and crystallographic data for all the complexes are given in Table 1.

3. Results and discussion

3.1 *Synthesis*

Complexes **1**–**3** have been synthesized using the aqueous solutions of Cu(ClO$_4$)$_2$·6H$_2$O and diphenyl phosphate (*dpp*) along with the methanolic solutions of different N-donor neutral ligands (i.e., *pmdeta*, *bapa* and *4-pic*) with stirring the reaction mixture at room temperature (Scheme 1), wherein *dpp* acts as a mono anionic co-ligand for the formation of neutral complexes.

3.2 *Infrared spectra*

The IR spectra of complexes **1**–**3** discussed in the synthesis part of experimental Section exhibit sharp

**Table 1.** Crystallographic and structural refinement parameters for complexes **1**, **2** and **3**.

	1	2	3
Formula	$C_{21}H_{35}N_3O_9PClCu$	$C_{18}H_{24}N_3O_9PClCu$	$C_{36}H_{34}N_2O_8P_2Cu$
Formula weight	603.4908	556.37	748.14
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	P-1	$P2_12_12_1$	P-1
a/Å	10.2164(3)	8.9628(3)	9.8920(3)
b/Å	11.2536(3)	14.5821(5)	12.1474(4)
c/Å	12.1162(3)	18.3142(7)	15.2681(5)
α/°	90.732(1)	90	86.730(2)
β/°	99.518(1)	90	84.780(2)
γ/°	98.528(1)	90	72.423(1)
V/Å^3	1357.66(6)	2393.60(15)	1740.89(10)
Z	1	4	1
D_c/g cm^{-3}	1.471	1.544	1.427
μ/mm^{-1}	1.014	1.143	0.774
$F(000)$	626	1144	774
θ range/°	1.7–25.9	1.8–27.5	1.8–27.5
Reflections collected	20546	39730	26991
Unique reflections	5254	5487	7923
Reflections $I > 2\sigma(I)$	4627	4355	6767
R_{int}	0.028	0.085	0.022
goodness-of-fit (F^2)	1.03	1.02	1.04
$R1$ ($I > 2\sigma(I)$) [a]	0.0396	0.0521	0.0331
$wR2(I > 2\sigma(I))$[a]	0.1173	0.1417	0.0974
$\Delta\rho$ min / max /e Å^3	−0.44, 0.57	−0.40, 1.21	−0.54, 0.34

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

and strong peaks ranging from 1320–1140 cm^{-1} due to the stretching of the P=O moiety of diphenyl phosphate, which is strong in IR but medium in Raman. The P-O-Ar exhibits two different characteristic bands, O-Ar and P-O which shows the absorption bands at 1242–1110 cm^{-1} and 996–905 cm^{-1} respectively. The absence of any absorption bands at around 2725 cm^{-1} for O-H bond of diphenyl phosphate confirms that it adopts a completely deprotonated monoanionic form which coordinates with the metal centres.

3.3 *Crystal structure description of the complexes*

3.3a *Structural description of {[Cu(dpp)(pmdeta)]·ClO_4 H_2O}_2 (1)*: Compound **1** crystallizes in the triclinic *P*-1 space group with Z = 1. The structure analysis reveals the formation of a dimeric complex of Cu(II) with the combination of diphenyl phosphate and *pmdeta*. The asymmetric unit of **1** contains one crystallographically independent Cu(II) atom, one chelating *pmdeta* ligand, one diphenyl phosphate (*dpp*), one perchlorate counter ion and one lattice water forming a distorted trigonal bipyramid geometry with CuN$_3$O$_2$ coordination environment (Figure 1). The equatorial positions around the Cu(II) atoms are occupied by two oxygen atoms (O1 and O2^a where: $a = 1 - x, 2 - y, 1 - z$) of two diphenyl phosphate forming a bridge in between two
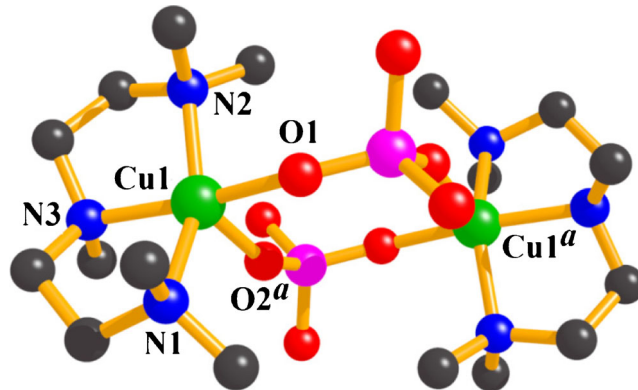
Figure 1. View of coordination environment of complex **1** with atom labeling scheme: Cu (green), N (blue), O (red) and C (gray) (phenyl rings of *dpp* are omitted for clarity).

Cu(II) centers and N3 atom of chelating N-donor ligand. The Cu-O bond distances range from 1.9714(17) to 2.1568(18) Å and Cu-N bond distance is 2.051(2) in basal plane (Table 2). Two nitrogen atoms (N1 and N2) of the chelating ligand are in the axial position with Cu-N distance varying from 2.052(2) to 2.052(2) Å (Table 2). In the solid state structure, each Cu(II) dimeric units are organized in such a way so that one of the phenyl rings of *dpp* ligands from each dimeric units are held together by intermolecular $\pi \ldots \pi$ interactions.

This intermolecular $\pi \ldots \pi$ interactions are responsible for the formation of supramolecular 1D chain along crystallographic *c*-axis (Figure 2 and Table 3). Moreover, there are intramolecular C-H...π interactions (Figure 2 and Table 3) which is also responsible for the stability of the solid state structure.

3.3b *Structural descriptions of {[Cu(dpp)(bapa)H$_2$O]. ClO$_4$} (2)*: Compound **2** crystallizes in the Orthorhombic $P2_12_12_1$ space group with Z = 4. The structure analysis reveals the formation of a monomeric complex of Cu(II) with the combination of diphenyl phosphate and chelating N-donor bis-(3-aminopropyl)amine (*bapa*) ligand. The asymmetric unit of **2** contains one crystallographically independent Cu(II) atom, one chelating *bapa*, one *dpp*, one perchlorate counter ion and one coordinated water forming a distorted octahedral geometry with CuN$_3$O$_3$ coordination environment (Figure 3).

Table 2. Selected bond lengths (Å) and bond angles (°) for complex **1**.

Cu1-O1	1.9714(17)	Cu1-N1	2.055(2)
Cu1-N2	2.052(2)	Cu1-N3	2.051(2)
Cu1-O2^a	2.1568(18)	O1-Cu1-N1	90.25(8)
O1-Cu1-N2	93.17(8)	O1-Cu1-N3	168.47(9)
O1-Cu1-O2^a	93.32(7)	N1-Cu1-N2	152.19(8)
N1-Cu1-N3	85.73(9)	O2^a-Cu1-N1	102.29(8)
N2-Cu1-N3	85.49(10)	O2^a-Cu1-N2	105.05(8)
O2^a-Cu1-N3	98.09(9)		

Symmetry code: $a = 1 - x, 2 - y, 1 - z$.
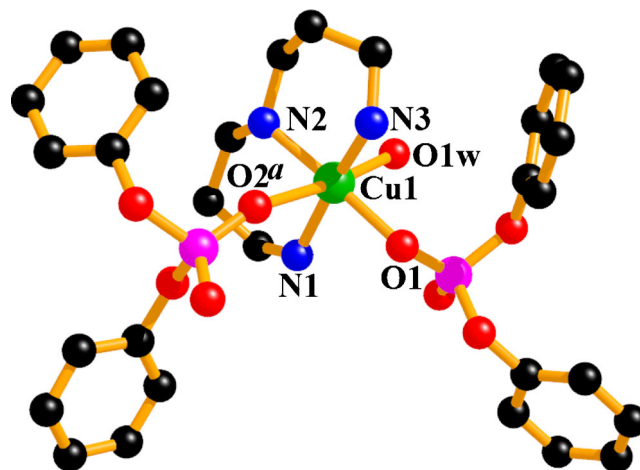
Figure 3. View of coordination environment of complex **2** with atom labeling scheme: Cu (green), N (blue), O (red) and C (gray).
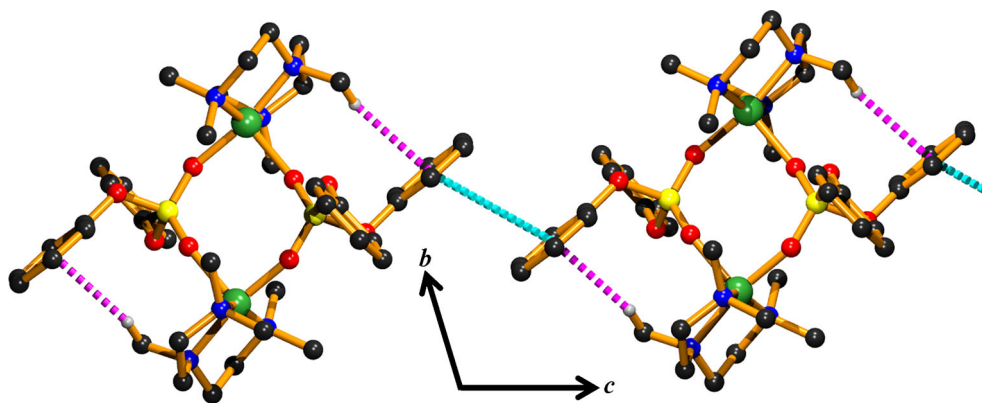
Figure 2. Formation of supramolecular 1D chain via intermolecular π-π interactions and intra-molecular C-H...π interaction in **1** (π-π interaction and C-H...π interaction: cyan and magenta dotted lines respectively).

Table 3. π-π interactions and C-H...π interaction in **1**.

Ring(i) → ring(j)	distance of centroid(i) from ring(j),(Å)	dihedral angle (i,j) (deg)	distance between the (i,j) ring centroids,(Å)
R(1) → R(1)^i	5.018(2)	0	3.4153(16)
C-H → ring(j)	H...R distance (Å)	C-H...R angle (deg)	C...R distance (Å)
C(9)-H(9A)→ R(1)^{ii}	2.86	146	3.690(4)

Symmetry code: i = 2−X, 3−Y, 1−Z; ii = 1−X, 2−Y, 1−Z.
R(i)/R(j) denotes the ith/jth rings in the corresponding structures: R(1)=C(10)/C(11)/C(12)/C(13)/C(14)/C(15).

The equatorial positions around the Cu(II) atoms are occupied by three oxygen atoms (O1, O2^a and O1w; where: $a = -1/2+x, 1/2-y, 2-z$.) of two diphenyl phosphate and one coordinated water molecule respectively and N2 atom of chelating bis-(3-aminopropyl)-amine (*bapa*) ligand. The Cu-O bond distances range from 2.052(3) to 2.639(3) Å and Cu-N bond distance is 2.042(4) in basal plane (Table 4). Two nitrogen atoms (N1 and N3) of the chelating ligand are in the

axial position with Cu-N distance values lying between 1.989(4) to 2.001(4) (Table 4). In the crystal packing, the monomeric Cu(II) units are organized in a manner such that the phenyl rings of dpp is held by the intermolecular C-H...π interaction. These non-covalent interactions link the monomeric fragments to give rise to a supramolecular 2D arrangement in solid state (Figure 4 and Table 5).
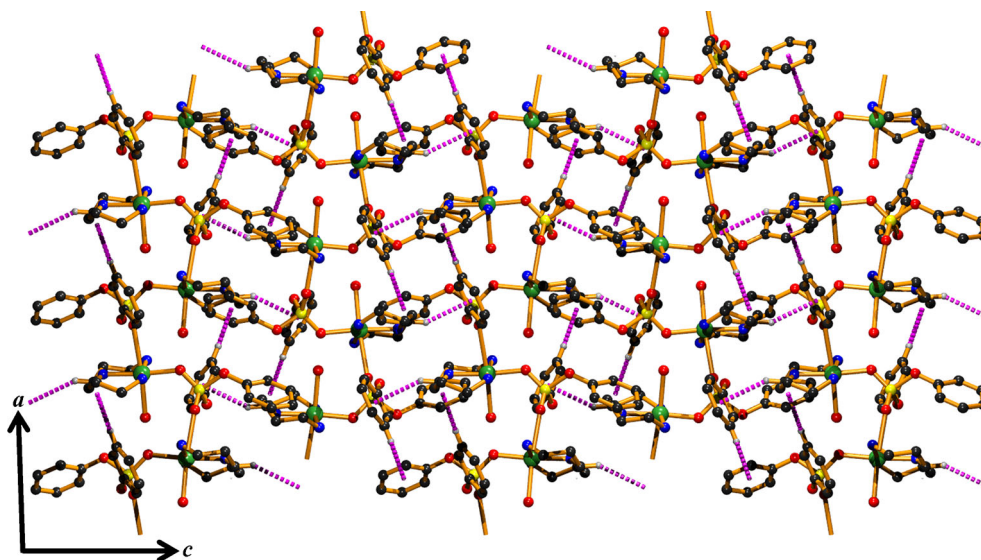
3.3c *Structural descriptions of [Cu(4-pic)$_2$(dpp)$_2$]$_n$ (3)*: Compound **3** crystallizes in the triclinic *P*-1 space group with Z = 1. The structure analysis reveals the formation of a dimeric complex of Cu(II) with the combination of diphenyl phosphate and 4-picoline. The asymmetric unit of **3** contains one crystallographically independent Cu(II) atom, two N donor picoline ligand (*4-pic*), two diphenyl phosphate (*dpp*) forming a distorted trigonal bipyramidal geometry with CuN$_2$O$_3$ coordination environment (Figure 5). The equatorial positions around the Cu(II) atoms are occupied by three oxygen atoms (O1, O4^a and O5; where: $a = -x, -y, 1-z$) of three diphenyl phosphate. The Cu-O bond distances range from 1.9986(13) to 2.1639(13) Å in basal plane (Table 6). Two nitrogen atoms (N1 and N2) of two
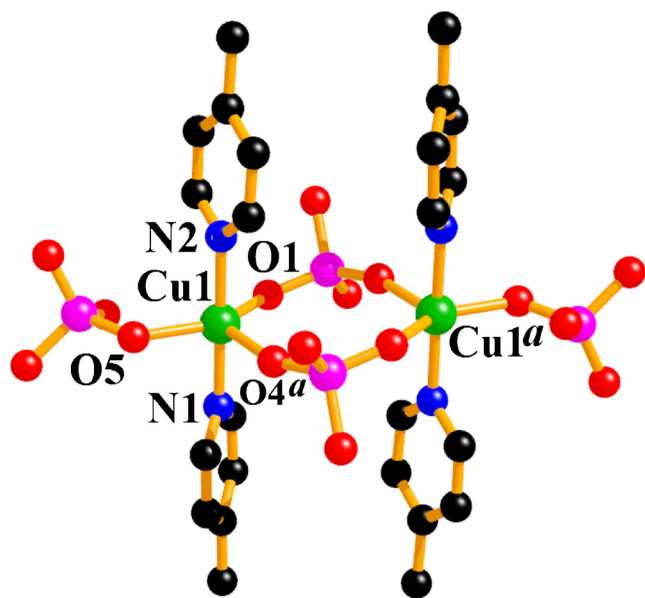
Table 4. Selected bond lengths (Å) and bond angles (°) for complex **2**.

Cu1-O1	2.052(3)	Cu1-O1W	2.362(4)
Cu1-N1	2.001(4)	Cu1-N2	2.042(4)
Cu1-N3	1.989(4)	Cu1-O2^a	2.639(3)
O1-Cu1-O1W	91.27(11)	O1-Cu1-N1	85.40(13)
O1-Cu1-N2	175.33(13)	O1-Cu1-N3	85.22(13)
O1-Cu1-O2^a	93.52(10)	O1W-Cu1-N1	93.81(13)
O1W-Cu1-N2	93.38(13)	O1W-Cu1-N3	98.41(13)
O1W-Cu1-O2^a	174.82(11)	N1-Cu1-N2	94.72(16)
N1-Cu1-N3	164.74(15)	O2^a-Cu1-N1	88.56(12)
N2-Cu1-N3	93.66(16)	O2^a-Cu1-N2	81.82(12)
O2^a-Cu1-N3	80.04(12)		

Symmetry code: $a = -1/2+x, 1/2-y, 2-z$.

Figure 4. Supramolecular 2D structure by means of intermolecular C-H...π interaction in complex **2** (C-H...π interaction: magenta dotted lines).

Table 5. Intermolecular C-H...π interaction in **2**.

C-H → ring(j)	H...R distance (Å)	C-H...R angle (deg)	C...R distance (Å)
C(4)-H(4A)→R(1)^i	2.75	149	3.617(6)
C(11)-H(11)→R(2)^{ii}	2.70	155	3.568(6)

Symmetry code: i = 3/2−X, 1−Y, −1/2+Z; ii = 1−X, 1/2+Y, 5/2−Z
R(i)/R(j) denotes the ith/jth rings in the corresponding structures: R(1)=C(7)/C(8)/C(9)/C(10)/C(11)/C(12); R(2)=C(13)/C(14)/C(15)/C(16)/C(17)/C(18)

coordinating 4-picoline are in the axial positions with Cu-N distance values lying between 1.9981(15) to 2.0018(16) (Table 6). Similar to **1** and **2** the crystal packing of **3** also has the dimeric fragments of Cu(II) organized in solid state in such a way so that non-covalent interactions can be useful to enhance the

dimensionality of the compounds. Here both intermolecular $\pi \dots \pi$ and C-H$\dots \pi$ interactions involving phenyl rings of diphenyl phosphate creates the supramolecular 3D structure (Figures 6 and S4 and Table 7). In addition, there are also intramolecular $\pi \dots \pi$ interactions (Figures 6 and S4) involved in this structure which gives extra stabilization energy towards the solid state packing.

3.4 *Powder X-ray diffraction (PXRD)*

To confirm the phase purity of the bulk materials with the simulated patterns powder X-ray diffraction (PXRD) analysis was carried out for **1–3** at room temperature. The experimental PXRD patterns of **1–3** are well-matched with the simulated ones obtained from their corresponding single crystal structures (Figures S5–S7), confirming the phase purity of the compounds **1–3**.

3.5 *Solid-state absorption spectra*

The UV-Vis absorption spectra of complexes **1–3** and *dpp* co-ligand were measured in the solid state at room temperature. As shown in Figure 7, *dpp* shows absorption maximum at 256 nm in the UV range, which corresponds to the $\pi - \pi^*$ or n–π^* transition of the aromatic ring.[55,56] However, complexes **1**, **2** and **3** exhibit

Figure 5. View of coordination environment of complex **3** with atom labeling scheme: Cu (green), N (blue), O (red) and C (gray) (phenyl rings of *dpp* are omitted for clarity).

Table 6. Selected bond lengths (Å) and bond angles (°) for complex **3**.

Cu1-O1	1.9986(13)	Cu1-O5	2.0063(14)
Cu1-N1	1.9981(15)	Cu1-N2	2.0018(16)
Cu1-O4^a	2.1639(13)	O1-Cu1-O5	144.61(5)
O1-Cu1-N1	89.72(6)	O1-Cu1-N2	87.81(6)
O1-Cu1-O4^a	115.88(5)	O5-Cu1-N1	89.40(6)
O5 -Cu1-N2	91.50(6)	O4^a-Cu1-O5	99.47(5)
N1-Cu1-N2	176.86(6)	O4^a-Cu1-N1	88.69(6)
O4^a-Cu1-N2	94.13(6)		

Symmetry code: $a = -x, -y, 1 - z$.
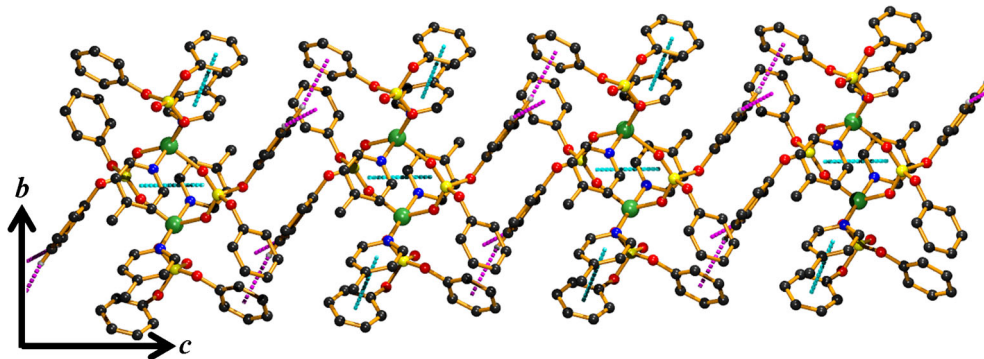
**Figure 6.** Supramolecular 3D structure by intermolecular π-π and C-H$\dots \pi$ interaction in **3** (π-π interaction and C-H$\dots \pi$ interaction: cyan and magenta dotted lines respectively).

Table 7. π-π interactions and C-H...π interaction in **3**.

ring(i) → ring(j)	distance of centroid(i) from ring(j) (Å)	dihedral angle (i,j) (deg)	distance between the (i,j) ring centroids (Å)
R(1) → R(3)^i	3.9257(17)	25.30(14)	3.9133(8)
R(2) → R(2)^{ii}	4.2488(13)	0	3.5718(9)
R(3) → R(1)^i	3.9257(17)	25.30(14)	3.4268(14)
C-H → ring(j)	H...R distance (Å)	C-H...R angle (deg)	C...R distance (Å)
C(16)-(16) → R(4)^{iii}	2.99	150	3.827(2)
C(17)-(17) → R(5)^{iv}	2.68	156	3.549(2)

Symmetry code: i = X, Y, Z; ii = 1−X, −Y, 1−Z; iii = −X, 1−Y, 1−Z; iv = −1−X, 1−Y, 1−Z
R(i)/R(j) denotes the ith/jth rings in the corresponding structures: R(1)=N(1)/C(1)/C(2)/C(3)/C(4)/C(5); R(2)=N(7)/C(7)/C(8)/C(9)/C(10)/C(11); R(3)=C(25)/C(26)/C(27)/C(28)/C(29)/C(30); R(4)=C(31)/C(32)/C(33)/C(34)/C(35)/C(36); R(5)=C(19)/C(20)/C(21)/C(22)/C(23)/C(24).
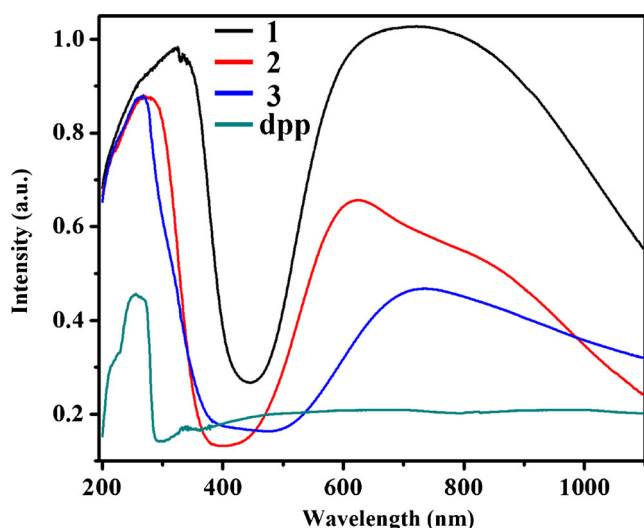
Figure 7. Solid state UV-vis spectra of complexes **1–3** and free *dpp* ligand.

absorption maxima at 322 and 700 nm, 274 and 620 nm and 256 and 729 nm respectively which are different from that of the *dpp* ligand, suggesting that it might have originated from an intraligand transition (ILCT) or metal to ligand charge transfer (MLCT) in the UV range and the absorption in the range 430–800 nm may be due to the visible d-d transitions.

4. Conclusions

Three diphenylphosphate (*dpp*) based Cu(II) complexes varying with the different N-donor linkers, e.g., pentamethyldiethylenetriamine (*pmdeta*), bis-(3-aminopropyl)amine (*bapa*) and 4-Picolene (*4-pic*) have been successfully synthesized and characterized. Complexes **1–3** show fascinating supramolecular 1D, 2D and 3D structures respectively by means of intermolecular $\pi \ldots \pi$ and C-H...π interactions additively or individually. The variation of structures have been originated due to different coordination modes of *dpp* co-ligand used which exhibits the bis-bridging mode for complexes **1** and **3** and mono-bridging mode for **2** respectively. In addition, the active role of the N-donor ligands used also directs the structural changes and affords new network structures. In summary, this work may give a new light to the design of diphenyl phosphate based mixed ligand metal-organic coordination complexes in solid state containing lattice perchlorate ions. These complexes maybe useful in different potential applications like proton conduction, ion exchange, sensors, etc., in future.

Supplementary Information (SI)

IR and PXRD patterns of complexes **1–3** related to the crystal structures are presented in supplementary section (see www.ias.ac.in/chemsci). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data Centre, CCDC 1501058-1501060. Copies of the data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: (internet) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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