Hydrothermal Synthesis and Crystal Structures of Monomeric and Polymeric Copper Phosphates with 4,4'-Bipyridine

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The self-assembly of highly organized metal-organic frameworks comprised of metal ions as nodes and bridged ligands as spacers has achieved considerable progress in supramolecular chemistry and material chemistry.[1-4] The increasing interest in this field is not only because of their intriguing variety of architectures and topologies, but also because of their potential applications as functional materials.[5-9] By selecting appropriate metal ions and bridged ligands, coordination polymers with fantastic structures and desirable properties can be obtained. The 4,4'-bipy ligand and d-block metal ions have been extensively used in much of this work.[10] The coordination polymers bearing 4,4'-bipy ligands have been shown to form a wide range of interesting network topologies, for example, chains, ladders, grids, and adamantoid networks.[11] Although the thousands of structure already reported with 4,4'-bipy, we focus to extend the yet undiscovered structural variety of M-4,4'-bipy systems. In this work, we report on two new monomeric and polymeric copper coordination compounds assembled using 4,4'-bipyridine as a spacer ligand and phosphate anion

Experimental

Synthesis. All chemicals and reagents are commercially available and were used as received without further purification. Elemental analyses (C, H, N) were performed on a Carlo Erba EA-1106 Elemental Analyzer. Infrared spectra were recorded in the range from 4000 to 400 cm^{-1} on a Mattson Polaris FT-IR Spectrophotometer using KBr pellets. TG analysis was performed on a Shimadzu DTG-60 instrument in flowing N_2 with a heating rate of 10 $^oC\cdot min^{-1}$. The initial and final pH of the reaction was measured using Sentron 1001 pH meter. The reactions for both compounds were carried out in polytetrafluoroethylene-lined stainless-steel containers under autogenous pressure. The vessel was volume 23 mL and was filled approximately to 40% capacity.

Synthesis of $[Cu^{II}(4,4'\text{-bipy})_2(H_2PO_4)_2]\cdot 2H_2O$ (1). A mixture of $Cu(OAc)_2\cdot H_2O$ (0.120 g, 0.60 mmol), 4,4'-bipy (0.094 g, 0.60 mmol), H_3PO_4 (0.073 g, 0.74 mmol), and H_2O (3 mL, 167 mmol) in the mole ratio 1.00 : 1.00 : 1.23 : 278 was placed in a 23 mL Teflon-lined Parr acid digestion bomb and heated for 4 d. at 170 ^oC under autogenous pressure. The mixture was removed from the oven and allowed to cool under ambient conditions for 3 d. Blue needle crystals of **1** suitable for X-ray diffraction were isolated in *ca*. 61% (0.219 g) yield based on copper. Initial pH, 3.0; final pH, 4.0. *Anal. Calc.* for $C_{20}H_{24}N_4O_{10}P_2Cu$: C, 39.65; H, 3.99; N, 9.25. Found: C, 39.62; H, 3.97; N, 9.29. IR (KBr pellet, cm^{-1}): 3450 (m), 3385 (m), 3045 (w), 2923 (w), 2339 (m), 1603 (s), 1536 (w), 1491 (w), 1414 (s), 1325 (w), 1219 (m), 1089 (s), 961 (s), 808 (s), 724 (w), 633 (m), 502 (m).

Synthesis of $[Cu^{I}(4,4'\text{-bipy})(H_2PO_4)]_n\cdot nH_2O$ (2). The coordination polymer **2** was synthesized by the similar method to the above compound **1**, except the reaction was carried at reaction temperature 200 °C instead of 170 °C. Yellow needle crystals. Yield. 32% (0.063 g) *Anal.* Calc. for $C_{10}H_{12}N_2O_5PCu$: C, 35.88; H, 3.61; N, 8.37. Found: C, 35.82; H, 3.65; N, 8.19. IR (KBr pellet, cm^{-1}): 3465 (s), 3043 (m), 2924 (w), 2361 (w), 2339 (w), 1649 (w), 1599 (w), 1526 (w), 1481 (w), 1409 (w), 1059 (s), 955 (m), 800 (m), 633 (m), 608 (m), 553 (m).

X-ray crystallography. Structural measurements for **1** and **2** were performed on a STOE STADI4[12] four-circle diffractometer using graphite monochromatized Mo-Ka

Table 1. Crystal data and structure refinement for $[Cu(4,4'\text{-bipy})_2(H_2PO_4)_2]\cdot 2H_2O$ (**1**) and $[Cu(4,4'\text{-bipy})(H_2PO_4)]_n\cdot nH_2O$ (**2**)

	1	**2**
Empirical formula	$C_{20}H_{24}CuN_4O_{10}P_2$	$C_{10}H_{12}CuN_2O_5P$
Formula weight	605.91	334.73
T (K)	298(2)	298(2)
λ (Å)	0.71069	0.71069
Crystal system	Triclinic	Monoclinic
Space group	P −1	P2/n
a (Å)	7.9871(7)	8.484(2)
b (Å)	10.259(1)	8.919(2)
c (Å)	14.515(2)	17.887(4)
α (°)	85.448(8)	90
β (°)	82.124(7)	102.66(3)
γ (°)	88.849(7)	90
V ($Å^3$)	1174.4(2)	1320.6(5)
Z	2	4
μ (mm^{-1})	1.132	1.791
Reflections collected	5414	3022
Independent reflections	5414	3022
R_1 [$I \geq 2\sigma(I)$]	0.0921	0.0685
wR_2 [$I \geq 2\sigma(I)$]	0.2472	0.1808
R_1 (all data)	0.1267	0.0936
wR_2 (all data)	0.2943	0.2071
Largest peak and hole ($eÅ^{-3}$)	1.488 and −1.453	0.850 and –0.975

radiation (λ = 0.71069 Å) at 298(2) K. The unit cell parameters were calculated by least-squares fit of 30 (**1**) and 28 (**2**) reflections in the ranges of $9.6 < \theta < 10.5\times$ (**1**) and $9.7 < \theta < 10.4^{o}$ (**2**), respectively. Intensities of three reflections monitored periodically exhibited no significant variation. The structures were solved by direct method[13] and refined on F^2 by full-matrix least-squares procedures.[14] All non-hydrogen atoms were refined using anisotropic thermal parameters. The carbon and oxygen-bound H atoms were positioned geometrically [$U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ and $1.5U_{\mathrm{eq}}(\mathrm{O})$], and were included in the refinement in the riding-model approximation. The ware H atoms were located in a difference Fourier map and were refined with a distance restraint of O-H = 0.85 Å; their displacement parameters were freely refined. In the compound **2**, two solvated water molecules are located as positional disorder.

A summary of crystal data and structure refinement for the compounds **1** and **2** are listed in Table 1.

Results and Discussion

Synthesis. Both compounds **1** and **2** were synthesized from the reaction mixtures of $Cu(OAc)_2 \cdot H_2O$, 4,4'-bipy, H_3PO_4, and H_2O in the mole ratio 1.00 : 1.00 : 1.23 : 278 at 170 (**1**) and 200 °C (**2**), respectively, by the hydrothermal technique. Though the starting material in the synthesis of compound **2** was divalent $Cu(OAc)_2 \cdot H_2O$, the hydrothermal reaction afforded monovalent complex. The oxidation state of Cu(I) as expected from overall charge considerations for the complex **2** indicates that Cu(II) has undergone reduction process during the synthesis. Some similar complexes are presented, which implies that Cu(II) can be reduced to Cu(I) by 4,4'-bipy or pyridine derivatives under hydrothermal conditions.[15,16]

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

$[Cu(4,4'\text{-bipy})_2(H_2PO_4)_2] \cdot 2H_2O$ (**1**)			
Cu-N(1)	2.021(14)	Cu-N(2)	2.024(14)
Cu-O(1)	1.941(13)	Cu-O(5)	1.943(13)
Cu-O(9)	2.643(15)	Cu-O(10)	2.743(16)
P(1)-O(1)	1.512(13)	P(1)-O(2)	1.513(15)
P(1)-O(3)	1.567(13)	P(1)-O(4)	1.563(15)
P(2)-O(5)	1.512(13)	P(2)-O(6)	1.508(14)
P(2)-O(7)	1.559(13)	P(2)-O(8)	1.571(14)
O(1)-Cu-N(1)	91.1(6)	O(1)-Cu-N(2)	89.5(6)
O(5)-Cu-N(1)	88.7(6)	O(5)-Cu-N(2)	90.7(6)
O(1)-Cu-O(5)	1 78.9(5)	N(1)-Cu-N(2)	179.4(6)
P(1)-O(1)-Cu	135.2(9)	P(2)-O(5)-Cu	136.3(9)
$[Cu(4,4'\text{-bipy})(H_2PO_4)]_n \cdot nH_2O$ (**2**)			
Cu-N(1)	1.914(4)	Cu-N(2)	1.924(4)
Cu-O(1)	2.347(5)	P-O(1)	1.502(4)
P-O(2)	1.540(5)	P-O(3)	1.509(5)
P-O(4)	1.532(5)		
N(1)-Cu-N(2)	155.8(2)	N(1)-Cu-O(1)	102.3(2)
N(2)-Cu-O(1)	101.5(2)	O(1)-P-O(2)	108.9(2)
O(1)-P-O(3)	112.5(3)	O(1)-P-O(4)	109.7(3)
P-O(1)-Cu	115.3(3)		

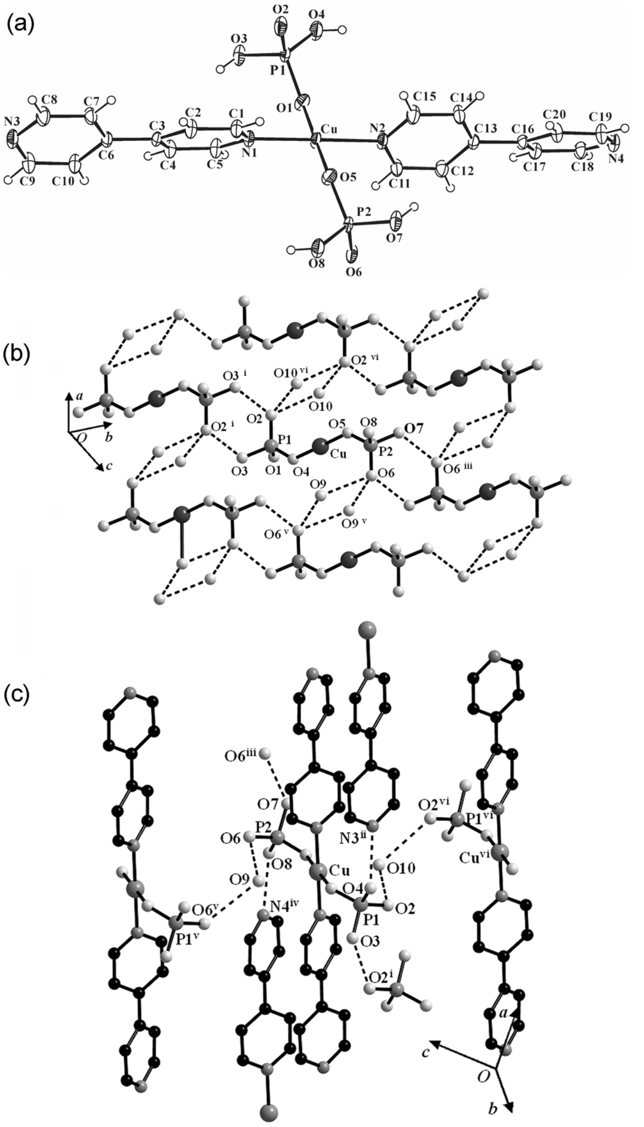

Figure 1. (a) An ORTEP view of the coordination geometry of copper sites in **1**, showing the atom-labelling scheme and the 30% thermal ellipsoids. H atoms are drawn as spheres of arbitrary radii. (b) 2D network assembled through hydrogen bonding between phosphate oxygens, and between phosphates and solvated water molecules. (c) All hydrogen bonging diagram in **1**. Symmetry code as in Table 3.

Crystal structure of compound 1. The ortep drawing of the compound **1**, as shown in Figure 1a, contains one copper, two 4,4'-bipy, two $H_2PO_4^-$ ions, and non-coordinated two water molecules. The coordination geometry around Cu(II) ion comprising N_2O_2 as donor atoms (Cu-N (av) = 2.02(1) and Cu-O (av) = 1.94(1) Å) can be described as a distorted quadrilateral with two set of bond angles (88.7-91.1(6) and $178.9(5)\text{-}179.4(6)^{o}$) close to the expected ideal angles for square planar geometry. The distances of Cu-N and Cu-O bonds agree well with those of similar compounds.[17] Two bipy and two phosphate ligands are located at *trans* position to each other, respectively. The 4,4'-bipy ligand possesses typical geometrical parameters, and their non-hydrogen atoms for each pyridyl group are essentially planar (rms deviations; 0.002 Å for N1C1-C5 and 0.015 Å for C6-C10N3 plane) with the dihedral angle 21.7(3)° between them. The rms deviation of the N_2O_2 plane is 0.008 Å and dihedral angles to the adjacent pyridine ring of 4,4'-bipy are 21.7(3) and 28.6(3)° for the plane N1C1-C5 and N2C11-C15, respectively. The two phosphate ligands are coordinated tetrahedrally to the metal. The average P-O distance in two crystallographically distinct P atoms is 1.54(1) Å (Table 2). The long distances of P(1)-O(3)=1.57(1), P(1)-O(4)=1.56(2), P(2)-O(7)=1.56(1), and P(2)-(O8)=1.57(1) Å suggest that oxygen atoms are protonated.[18] The P-O distances agree well with those reported for similar compounds.[18,19] The bond distances between Cu^{2+} ion and non-coordinated water oxygen atoms are 2.64(2) and 2.74(2) Å, which are far from the distances 2.000(2)-2.329(3) Å for the copper(II)-coordinated water compounds.[20]

Although the compound **1** does not form a polymeric structure with the help of bridging 4,4'-bipy ligands as in the case of **2**, the presence of intermolecular hydrogen bonding between the protonated oxygen and terminal oxygen atoms of phosphate ions (P-OH···O-P), and between the phosphate oxygens and solvated water molecules (P-O···H-O_w) results in the formation of hydrogen-bonded two-dimensional polymeric network (Fig. 1b). Meanwhile, this 2D sheet is also connected through single hydrogen bonding between another protonated oxygen atoms of phosphates and the pyridyl nitrogen atoms of 4,4'-bpy (Fig. 1c). The D···A bond distance and D-H···A angles are listed in Table 3. The values are well in the range suggested for similar O-H···O(N) hydrogen bonds.[10,21]

Table 3. Hydrogen bonds in $[Cu(4,4'\text{-bipy})_2(H_2PO_4)_2]\cdot 2H_2O$ (**1**) and $[Cu(4,4'\text{-bipy})(H_2PO_4)]_n\cdot nH_2O$ (**2**) (Å, °)

D–H···A	d (D–H)	d (H···A)	d (D···A)	∠ (DHA)
$[Cu(4,4'\text{-bipy})_2(H_2PO_4)_2]\cdot 2H_2O$ (**1**)				
O(3)-H(3O)···$O(2)^{i)}$	0.82	2.07	2.57(2)	118.8
O(4)-H(4O)···$N(3)^{ii)}$	0.82	1.87	2.64(2)	156.6
O(7)-H(7O)···$O(6)^{iii)}$	0.82	2.08	2.57(2)	118.4
O(8)-H(8O)···$N(4)^{iv)}$	0.82	1.91	2.66(2)	152.2
O(9)-H(9A)···O(6)	0.90	1.95	2.82(2)	161.9
O(9)-H(9B)···$O(6)^{v)}$	0.85	2.09	2.94(2)	174.4
O(10)-H(10A)···O(2)	0.96	1.84	2.80(2)	173.6
O(10)-H(10B)···$O(2)^{vi)}$	0.89	2.05	2.94(2)	176.2
$[Cu(4,4'\text{-bipy})(H_2PO_4)]_n\cdot nH_2O$ (**2**)				
O(2)-H(2O)···$O(1)^{i)}$	0.82	1.73	2.524(6)	163.5
O(5)-H(5B)···$O(4)^{ii)}$	0.85	2.48	3.02(1)	122.8
O(5)-H(5B)···O(6)	0.85	2.07	2.40(1)	102.6

Symmetry transformations used to generate equivalent atoms for compound **1**: i) 1−x, 1−y, 1−z, ii) 1+x, y−1, z, iii) 2−x, 1−y, 2−z, iv) x−1, 1+y, z, v) 1−x, 1−y, 2−z, vi) 2−x, 1−y, 1−z ; for compound **2**: i) 1−x, −y, 1−z, ii) x−1/2, 1−y, z−1/2, iii) x−1/2, −y, 1/2+z, iv) 1−x, 1−y, 1−z.

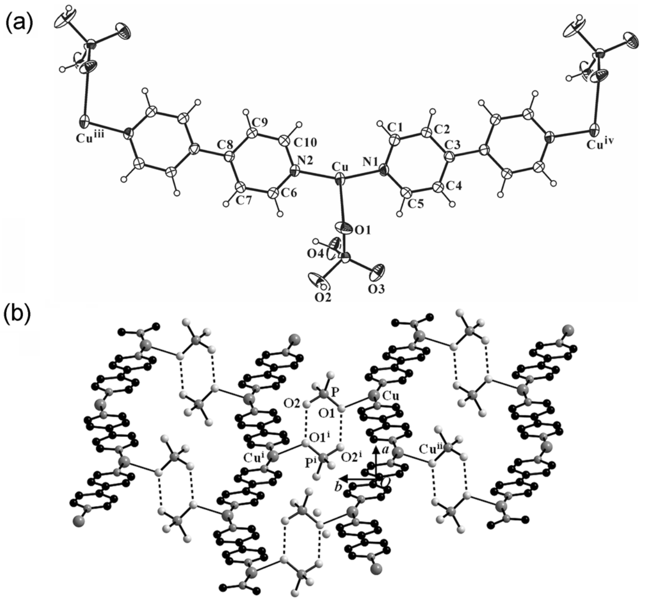

Figure 2. (a) The chain structure of **2**, showing the atom-labelling scheme. H atoms are drawn as spheres of arbitrary radii. (b) Hydrogen bonding network by protonated O atoms of phosphate ions in **2**. The hydrogen bonding by disordered water molecules were omitted. Symmetry code as in Table 3.

Crystal structure of compound 2. The polymeric structure of **2**, as shown in Figure 2(a), is composed of monovalent copper sites linked into $\{Cu(bipy)\}_n^{1+}$ one-dimensional chain through the 4,4'-bipy ligands and phosphate ions. Cu(I) sites in the molecule are coordinated in an approximately ‘T-shaped’ fashion by two nitrogen donors from two 4,4'-bipy ligands and a phosphate oxygen atom. The so called ‘T-shaped’ geometry is a characteristic feature of many Cu(I) complexes.[20a] Table 2 lists selected bond distances and angles for **2**. The Cu-O and Cu-N(av) bond distances are 2.343(5) and 1.920(4) Å, respectively, which agree well with those reported for similar compounds.[20a] The distances between the two copper atoms connected by 4,4'-bipy is 10.941(3) Å, which is similar to those reported in reference.[22] The bipy-Cu-bipy chain is not linear, the N-Cu-N angle is 155.8(2)°. Two pyridine rings of 4,4'-bipy ligand are nearly co-planar with the dihedral angles of 3.4(3)° between them. The dihedral angles between adjacent pyridyl planes of 4,4'-bipy in two chains are 3.5(1)° and interchain distances are in the range 3.49 and 3.53 Å. These values are enough to make π-π interaction between 4,4'-bipy planes. However, there is no π-π interaction because of the adjacent pyridyl planes of 4,4'-bipy are cross to each other.

The phosphate groups protrude from the chain alternately on different sides with the remaining one non-coordinated oxygen atoms and two protonated OH being exposed to solvated water molecules for possible hydrogen bonds. As in the case of **1**, the PO_4 bond distances are in the range of 1.502(5)-1.542(2) Å, which is close to those found in related compounds.[19a,b,20a] The distances of P(1)-O(2)=1.540(5) and P(1)-O(4)=1.535(5) are significantly longer than the other P-O distances due to protonation, respectively. The bond valence sum calculations[23] based upon observed bond distances are consistent with the assigned formal oxidation states of the cations; the calculated valences for Cu^+ and P^{5+}

cations are +0.818 and +5.15, respectively.

The adjacent linear chains, as shown in the extended structure (Fig. 2b), are assembled through hydrogen-bondings between phosphate oxygens (P-OH···O-P) to accomplish two-dimensional network. In addition, the hydrogen bonds through non-coordinate water molecules to phosphates or adjacent another water molecules (P-O···H-O_w, and O_w-H···O_w) are also expected. However, it is inappropriate for hydrogen-bonding because of the solvated water molecules are disordered over two positions. The distances and angles involved are listed in Table 3. These data are well within the range as in the case of **1**. In both complexes **1** and **2**, it is noteworthy that phosphate acts as terminal compared to many phosphate-bridged copper(II) organic-inorganic hybrid compounds isolated up to now.[19a,b,20a]

The IR spectra of both complexes include strong bands at 3451 and 3385 cm^{-1} for **1** and 3467 cm^{-1} for **2** correspond to the stretching vibrations of O-H groups, and the very strong bands due to the P-O stretching vibration are observed at 1089 and 1058 cm^{-1} for **1** and **2** compound, respectively.[19a,c]

TG analysis of both compounds **1** and **2** were carried out under a flow of nitrogen atmosphere in the range from 0 to 800 °C using heating rate of 10 °C min^{-1}. The TGA curves of each compounds exhibited multi-step decomposition process. The complex **1** is stable up to 156 °C, above which three abrupt weight losses of 16.55, 15.34, and 5.50% were observed in the temperature range 156-191, 191-259, and 259-331 °C, respectively, followed by a gradual weight loss of 24.92% above 331 °C. These results implies that two moles of water molecules per formula unit (calculated value 5.94%) and 4,4'-bipy groups may be lost synchronously. The total weight loss of 62.31% is more than the calculated value (57.49%) corresponding to the losses of two moles of water molecules and 4,4'-bipy ligands, implying that some unknown decomposition procedures may happen at the higher temperature. However, complex **2** reveals the weight loss of 7.91% from 50 to 106 °C corresponding to a water molecule per formula unit (calculated value 5.38%). The thermal decomposition behaviors above 106 °C are similar to the complex **1**. There is a further 49.02% weight loss in continuous steps up to 800 °C, which compares with the calculated loss (46.66%) for the 4,4'-bpy ligand.

In conclusion, two new inorganic-organic hybrid solids, $[Cu^{II}(4,4'\text{-bipy})_2(H_2PO_4)_2]\cdot 2H_2O$ (**1**) and $[Cu^{I}(4,4'\text{-bipy})(H_2PO_4)]_n\cdot nH_2O$ (**2**) have been synthesized by hydrothermal reaction, respectively. The synthesis of both compounds were performed under the same reaction mixtures, stoichiometries, and reaction time, except the different reaction temperatures at 170 (**1**) and 200 °C (**2**). This result suggests the example that the reaction temperature plays an important role to give reaction product under hydrothermal reactions. Compound **1** is monomer and the coordination geometry around Cu(II) ion, comprising N_2O_2 from two 4,4'-bipy and $H_2PO_4^-$ ligands, is a square planar. However, the structure of **2** contains linear Cu-bipy-Cu chain linked alternately on different sides by phosphate ion. The Cu(I) sites are three-coordinate, so called 'T-shaped' geometry.

Supplementary materials. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-618521(**1**) and 618522(**2**)). These 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: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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