

# Syntheses and Structures of Layered Copper(II) Diphosphonates with Mixed Ligands

Ping Yin,<sup>[a]</sup> Yang Peng,<sup>[a]</sup> Li-Min Zheng,<sup>\*,[a,b]</sup> Song Gao,<sup>[b]</sup> and Xin-Quan Xin<sup>[a]</sup>

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This paper describes the syntheses and crystal structures of two new copper(II) diphosphonates with mixed ligands:  $[\text{Cu}_3(\text{hedpH})_2(4,4'\text{-bipy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (**1**) and  $[\text{Cu}_3(\text{hedpH})_2(4,4'\text{-azpy})(\text{H}_2\text{O})_2] \cdot 1.6\text{H}_2\text{O}$  (**2**) (hedp = 1-hydroxyethylidene-diphosphonate, 4,4'-bipy = 4,4'-bipyridine, 4,4'-azpy = 4,4'-azobispyridine). Both adopt a two-dimensional layer structure containing neutral ladder-like chains of  $[\text{Cu}_3(\text{hedpH})_2(\text{H}_2\text{O})_2]_n$  linked by 4,4'-bipy or 4,4'-azpy ligands. The adja-

cent layers are held together by strong hydrogen bonds, thus generating a three-dimensional network with rectangular shaped channels. The lattice water is found in these channels. The magnetic properties of compounds **1** and **2** have also been investigated.

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## Introduction

Research on metal phosphonates is undergoing rapid expansion because of their potential applications in the areas of sorption, ion exchange, catalysis, sensors, and nonlinear optics.<sup>[1–5]</sup> Many efforts have been devoted to the exploration of metal phosphonate materials with new structure types, especially open-framework structures.<sup>[6–10]</sup> Among the metal phosphonates reported so far, the number of copper phosphonates is still limited. Most of them were prepared by direct reactions of copper salts and phosphonic acids.<sup>[11–16]</sup> By introducing a second organic ligand, a few copper phosphonates with mixed ligands have been synthesised, including a dodecanuclear cage compound containing 3,5-dimethylpyrazole.<sup>[17–19]</sup> We are interested in both the structures and magnetic properties of copper diphosphonates based on 1-hydroxyethylidenediphosphonate [hedp,  $\text{CH}_3\text{C}(\text{OH})(\text{PO}_3)_2^{4-}$ ], and a series of compounds have been obtained using a template approach.<sup>[20]</sup> In order to construct open-framework structures of Cu-hedp compounds, we tried to introduce a second bridging ligand into the system, and compound  $[\text{Cu}_4(\text{hedp})_2(\text{pz})(\text{H}_2\text{O})_4]$ , with a three-dimensional structure, was prepared successfully.<sup>[21]</sup> This compound also shows interesting metamagnetic properties. In this paper we report the syntheses and structures of two new layered copper phosphonates containing 4,4'-

bipyridine (4,4'-bipy) or 4,4'-azobispyridine (4,4'-azpy) ligands.

## Results and Discussion

### Crystal Structures of 1–2

The structures of  $[\text{Cu}_3(\text{hedpH})_2(4,4'\text{-bipy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (**1**) and  $[\text{Cu}_3(\text{hedpH})_2(4,4'\text{-azpy})(\text{H}_2\text{O})_2] \cdot 1.6\text{H}_2\text{O}$  (**2**) were determined by X-ray crystallography. Crystallographic and refinement details are listed in Table 3, with selected bond lengths and angles in Table 1 for **1** and Table 2 for **2**. The fundamental building unit of **1** is shown in Figure 1, with the atomic labeling scheme. Apparently, there are two types

Table 1. Selected bond lengths [Å] and angles [deg] for **1**

Cu(1)–O(1) <sup>[a]</sup>	1.922(4)	Cu(1)–O(4)	1.970(4)
Cu(2)–O(3B)	1.915(3)	Cu(2)–O(2)	1.949(3)
Cu(2)–O(5)	2.004(3)	Cu(2)–N(1)	2.025(6)
Cu(2)–O(1w)	2.191(4)	Cu(2)–N(1')	2.037(6)
P(1)–O(1)	1.507(4)	P(1)–O(2)	1.527(3)
P(1)–O(3)	1.514(4)	P(2)–O(4)	1.501(4)
P(2)–O(5)	1.519(3)	P(2)–O(6)	1.562(4)
O(1)–Cu(1)–O(4)	92.66(16)	O(3B)–Cu(2)–O(2)	158.76(16)
O(3B)–Cu(2)–O(5)	88.35(14)	O(2)–Cu(2)–O(5)	92.61(14)
O(3B)–Cu(2)–N(1)	89.0(3)	O(2)–Cu(2)–N(1)	87.3(3)
O(5)–Cu(2)–N(1)	172.3(3)	O(3B)–Cu(2)–O(1w)	103.19(16)
O(2)–Cu(2)–O(1w)	97.82(15)	O(5)–Cu(2)–O(1w)	95.97(16)
N(1)–Cu(2)–O(1w)	91.6(3)	P(1)–O(1)–Cu(1)	128.2(2)
P(1)–O(2)–Cu(2)	129.1(2)	P(1)–O(3)–Cu(2C)	140.0(2)
P(2)–O(4)–Cu(1)	125.1(2)	P(2)–O(5)–Cu(2)	130.9(2)
C(3)–N(1)–Cu(2)	122.9(4)	C(7)–N(1)–Cu(2)	120.0(4)

<sup>[a]</sup> Symmetry code: A,  $-x + 1, -y, -z$ ; B,  $x - 1, y, z$ ; C,  $x + 1, y, z$ .

<sup>[a]</sup> State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093, P. R. China  
Fax: (internat.) + 86-25/3314502  
E-mail: lmzheng@netra.nju.edu.cn

<sup>[b]</sup> State Key Laboratory of Rare Earth Materials and Applications, Peking University, Beijing 100871, P. R. China

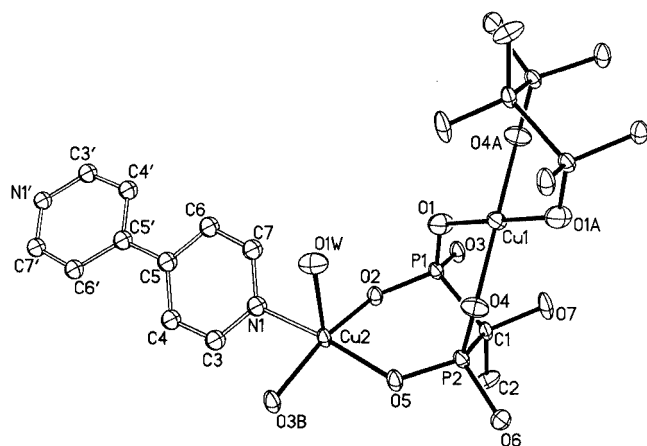


Figure 1. Building unit of **1** with the atomic labeling scheme (50% probability)

of copper atoms. The Cu(1) atom, sitting at an inversion center, has a square-planar environment. The four coordination sites are provided by two pairs of oxygens [O(1), O(4)] from two equivalent hedpH<sup>3-</sup> ligands. The Cu(2) atom resides in a general position, and bears a distorted square-pyramidal coordination geometry. The basal positions are filled with three phosphonate oxygens from two hedpH<sup>3-</sup> groups and one nitrogen atom from a 4,4'-bipyridine ligand. The largest deviation of the basal plane, defined by O(2), O(5), O(3B), and N(1), is 0.112(7) Å at O(3B). The Cu(2) atom lies out of this plane by 0.243(3) Å. The apical position is occupied by O(1w) from the water molecule. The Cu–O bond lengths are similar to those in other copper phosphonates, although the Cu(2)–O(1w) distance is slightly longer [2.192(4) Å]. The Cu(2)–N(1) bond length [av. 2.031(6) Å] is in agreement with that in [Cu(dmp)(MeCN)<sub>2</sub>(μ-4,4'-bipy)]<sup>2+</sup> [2.070(4) Å].<sup>[22]</sup>

Each hedpH<sup>3-</sup> group in **1** serves as a bis-chelating ligand, and bridges the Cu(1) and Cu(2) atoms using four of its six phosphonate oxygens. One of the remaining two oxygen atoms, O(3), is further linked to the equivalent Cu(2) atom, forming an infinite chain along the [100] direction (Figure 2). The O(6) atom is protonated [P(2)–O(6) 1.562(4) Å]. The ladder-like chains are connected by 4,4'-bipy ligands, forming a zigzag layer in the (101) plane (Figures 2

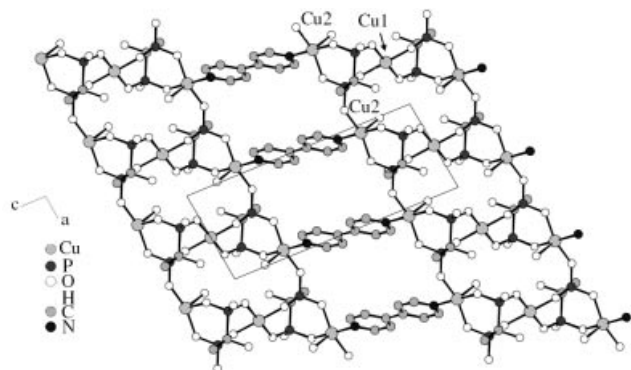


Figure 2. One layer of structure **1** viewed along the *b* axis; all the H atoms and half of the disordered 4,4'-bipy are omitted for clarity

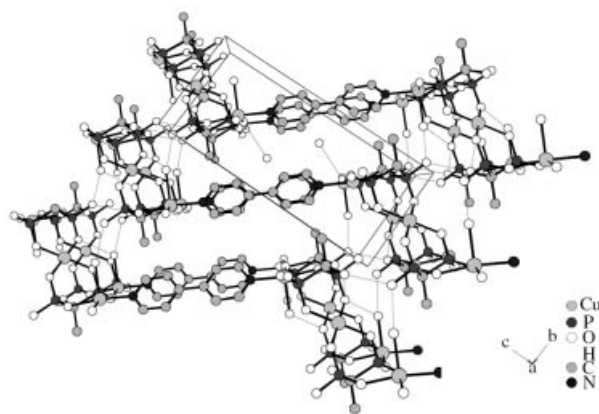


Figure 3. Structure of **1** packed along the *a* axis; all the H atoms and half of the disordered 4,4'-bipy are omitted for clarity

and 3). These layers are held together by strong interlayer hydrogen bonds between the phosphonate ligands. The shortest inter-layer O...O distances are 2.594(5) and 2.757(5) Å for O(6)···O(7)<sup>i</sup> and O(7)···O(5)<sup>ii</sup>, respectively (symmetry code: i,  $-x + 1, -y + 2, -z$ ; ii,  $x + 1, y, z$ ). Hence, a three-dimensional open network structure is constructed with rectangular channels generated along the *a* axis. The lattice water resides in these channels (Figure 3).

The structure of compound **2** is analogous to that of **1**, except that 4,4'-bipy is replaced by a longer bi-functional ligand 4,4'-azpy (Figure 4, Table 2). It also has a layer structure in which the ladder-like chains of {Cu<sub>3</sub>(hedpH)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub>} are connected by 4,4'-azpy (Figure 5). As the ligand is arranged approximately along the [001] direction, the *c* axis in **2** (16.071 Å) is longer than that in **1** (15.469 Å). Strong interlayer hydrogen bonds are also observed.

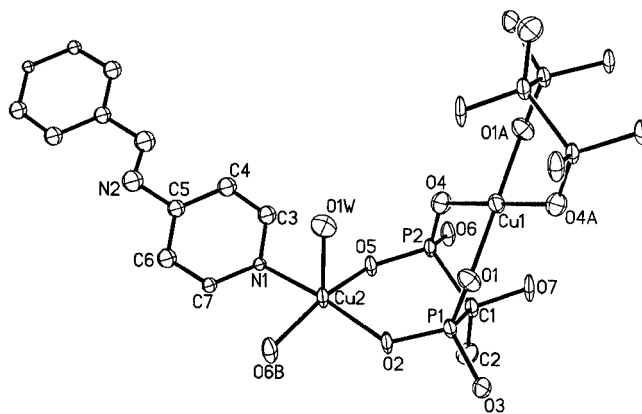


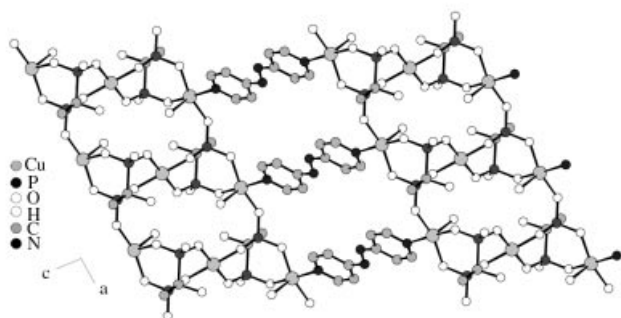
Figure 4. Building unit of **2** with the atomic labeling scheme (50% probability); all the H atoms and half of the disordered 4,4'-azpy are omitted for clarity

The layer structures of compounds **1** and **2** are different from that of [Cu<sub>4</sub>(hedp)<sub>2</sub>(pz)(H<sub>2</sub>O)<sub>4</sub>],<sup>[21]</sup> where a three-dimensional open-framework structure is observed. Although all three contain similar layers built up from {Cu<sub>3</sub>(hedp)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>} double chains and bifunctional organic linkages, the contacts between the layers are completely different. In compounds **1** and **2**, it is mainly the hydrogen bonds between the phosphonate or hydroxy oxy-

Table 2. Selected bond lengths [Å] and angles [deg] for **2**

Cu(1)–O(4) <sup>[a]</sup>	1.930(3)	Cu(1)–O(1)	1.964(3)
Cu(2)–O(6B)	1.916(3)	Cu(2)–O(5)	1.936(3)
Cu(2)–O(2)	2.022(3)	Cu(2)–N(1)	2.059(5)
Cu(2)–O(1w)	2.195(4)	Cu(2)–N(1X)	2.065(6)
P(1)–O(1)	1.502(4)	P(1)–O(2)	1.505(3)
P(1)–O(3)	1.569(3)	P(2)–O(4)	1.508(4)
P(2)–O(5)	1.525(3)	P(2)–O(6)	1.507(3)
O(4)–Cu(1)–O(1A)	87.05(15)	O(6B)–Cu(2)–O(5)	159.16(15)
O(6B)–Cu(2)–O(2)	88.46(13)	O(5)–Cu(2)–O(2)	92.09(13)
O(6B)–Cu(2)–N(1)	89.0(2)	O(5)–Cu(2)–N(1)	87.1(2)
O(2)–Cu(2)–N(1)	170.7(2)	O(6B)–Cu(2)–O(1w)	102.12(15)
O(5)–Cu(2)–O(1w)	98.56(14)	O(2)–Cu(2)–O(1w)	95.62(14)
N(1)–Cu(2)–O(1w)	93.7(2)	P(1)–O(1)–Cu(1)	125.0(2)
P(1)–O(2)–Cu(2)	130.5(2)	P(2)–O(6)–Cu(2C)	140.0(2)
P(2)–O(4)–Cu(1)	127.9(2)	P(2)–O(5)–Cu(2)	129.6(2)
C(7)–N(1)–Cu(2)	123.3(4)	C(3)–N(1)–Cu(2)	118.3(4)

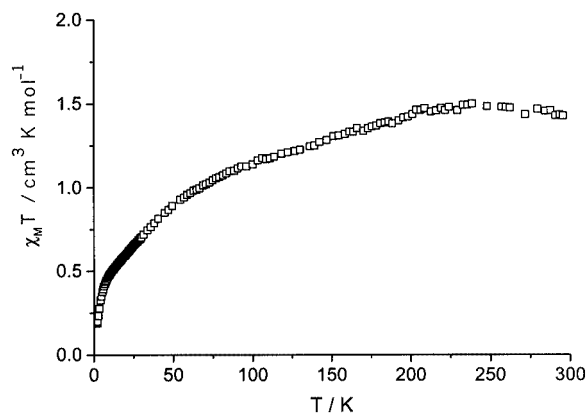
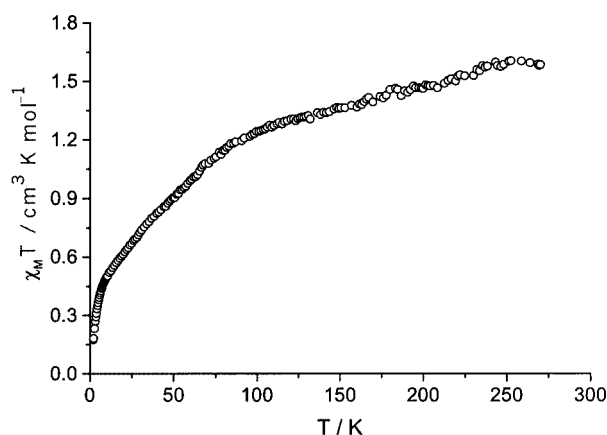
[a] Symmetry code: A,  $-x + 1, -y + 1, -z + 1$ ; B,  $x - 1, y, z$ ; C,  $x + 1, y, z$ .

Figure 5. One layer of structure **2** viewed along the *b* axis; all the H atoms and half of the disordered 4,4'-azpy are omitted for clarity

gens of the  $\{\text{Cu}_3(\text{hedp})_2(\text{H}_2\text{O})_2\}$  chains that connect the layers into a supramolecular network. In compound  $[\text{Cu}_4(\text{hedp})_2(\text{pz})(\text{H}_2\text{O})_4]$ , however, the  $\{\text{Cu}_3(\text{hedp})_2(\text{H}_2\text{O})_2\}$  chains from the neighboring layers are linked by  $\text{CuO}_4$  units through corner-sharing of  $\text{CPO}_3$  tetrahedra and  $\text{CuO}_4$  planes, forming a unique open-framework structure. This structure can also be viewed as being composed of  $\{\text{Cu}_4(\text{hedp})_2(\text{H}_2\text{O})_2\}$  layers and pz linkages. Furthermore, the phosphonate oxygens in compound  $[\text{Cu}_4(\text{hedp})_2(\text{pz})(\text{H}_2\text{O})_4]$  are all deprotonated, while in compounds **1** and **2** one oxygen is protonated in order to balance the overall charges and to stabilize the lattice through interlayer hydrogen bonds.

### Magnetic Properties

Figure 6 shows the temperature-dependent magnetic susceptibility for **1** in the form of a  $\chi_{\text{M}}T$  vs.  $T$  plot. The effective magnetic moment at 295 K, calculated from  $\mu_{\text{eff}} = 2.828(\chi_{\text{M}}T)^{1/2}$ , is  $3.38 \mu_{\text{B}}$  per  $\text{Cu}_3$ , in agreement with the calculated value ( $3.00 \mu_{\text{B}}$ ) for three isolated spin 1/2 nuclei. Upon cooling,  $\chi_{\text{M}}T$  decreases continuously, and more steeply below 10 K towards zero, indicating a dominant antiferromagnetic interaction. The magnetic behavior of **2** is very similar to that of **1** (Figure 7).

Figure 6. The  $\chi_{\text{M}}T$  vs.  $T$  plot for **1**Figure 7. The  $\chi_{\text{M}}T$  vs.  $T$  plot for **2**

Both compounds **1** and **2** have a layer structure made up of  $\{\text{Cu}_3(\text{hedp})_2(\text{H}_2\text{O})_2\}$  chains and organic linkages. Between the layers, the magnetic interactions are very weak because the shortest  $\text{Cu}\cdots\text{Cu}$  distance is  $7.009 \text{ Å}$ . The exchange coupling within the layer can be propagated either through the organic bridging ligand or through the O–P–O units. Considering that the  $\text{Cu}\cdots\text{Cu}$  distances through the 4,4'-bipyridine and 4,4'-azobispyridine ligands are  $11.165$  (for **1**) and  $13.087 \text{ Å}$  (for **2**), the bulk magnetic behavior should be mainly attributed to the  $\{\text{Cu}_3(\text{hedp})_2(\text{H}_2\text{O})_2\}$  chain. Within the double chain, the  $\text{Cu}(1)\cdots\text{Cu}(2)$  distance through the O–P–O bridge is ca.  $4.8 \text{ Å}$ , and the  $\text{Cu}(2)\cdots\text{Cu}(2)$  distance is ca.  $6.2 \text{ Å}$  (Figure 2). The exchange between Cu(1) and Cu(2) should be more efficient. The susceptibility data were thus analyzed by an expression based on a topological 1D ferrimagnet model.<sup>[23]</sup> This theoretical fitting was, however, unsuccessful. It is worth noting that, for a homometallic chain like  $\{\text{Cu}_3(\text{hedp})_2(\text{H}_2\text{O})_2\}$ , the odd number of magnetic centers should result in a ferrimagnetic behavior within the chain. The overall antiferromagnetic interactions observed in compounds **1** and **2** could be due to the dominant antiferromagnetic exchange couplings between the chains through the organic linkages and/or space at low temperature.

## Conclusion

Two new copper(II) diphosphonates  $[\text{Cu}_3(\text{hedpH})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (**1**) and  $[\text{Cu}_3(\text{hedpH})_2(4,4'\text{-azpy})-(\text{H}_2\text{O})_2] \cdot 1.6\text{H}_2\text{O}$  (**2**) have been reported in this paper. Their structures are two-dimensional with strong inter-layer hydrogen-bond interactions. Within the layer, the ladder-like chains of  $\{\text{Cu}_3(\text{hedpH})_2(\text{H}_2\text{O})_2\}_n$  are linked by 4,4'-bipy or 4,4'-azpy ligands. The magnetic studies show that both compounds exhibit dominant antiferromagnetic interactions. The results demonstrate that novel metal phosphonates may be anticipated by combining with second organic ligands.

## Experimental Section

**Materials and Methods:** The 50% aqueous solution of 1-hydroxyethylidenediphosphonic acid ( $\text{hedpH}_4$ ) was purchased from Nanjing Shuguang Chemical Factory. All other starting materials were reagent grade and used as purchased. The elemental analyses were performed with a PE 240C elemental analyzer. The infrared spectra were recorded on a Nicolet 170SX FT-IR spectrometer with pressed KBr pellets. Thermal analyses were performed in nitrogen in the temperature range 20–600 °C with a heating rate of 5 °C/min on a TGA-DTA V1.1B TA Inst 2100. Variable-temperature magnetic susceptibility data were obtained on polycrystalline samples (27.9 mg for **1**, 27.5 mg for **2**) from 2 to ca. 300 K in a magnetic field of 10 kOe after zero-field cooling using a MagLab System 2000 magnetometer. Diamagnetic corrections were estimated from Pascal's constants.<sup>[24]</sup>

**Synthesis of  $[\text{Cu}_3(\text{hedpH})_2(4,4'\text{-bipy})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (**1**):** A mixture of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (1 mmol, 0.2450 g), 4,4'-bipy (1 mmol, 0.1543 g), 50%  $\text{hedpH}_4$  (2.5 mmol, 1 cm<sup>3</sup>), 1 M NaOH (6 cm<sup>3</sup>), and water (2 cm<sup>3</sup>) with a pH of approximately 3 was transferred to a Teflon-lined autoclave (25 cm<sup>3</sup>) and kept at 165 °C for 48 h. After slow cooling, blue plate-like crystals were obtained together with some yellow flocculent material. The blue crystals were isolated and their purity judged by a powder X-ray diffraction measurement. These crystals were further used for the structural determination and the physical property measurements. Yield: 22% based on Cu.  $\text{C}_{14}\text{H}_{26}\text{Cu}_3\text{N}_2\text{O}_{18}\text{P}_4$ : calcd. (found) C 20.73 (20.38), H 3.28 (3.18), N 2.85 (3.40). IR (KBr):  $\tilde{\nu}$  = 3654 m, 3573 m, 3414 m, 3078 m, 2760 m, 1634 m, 1611 m, 1492 m, 1414 m, 1227 m, 1166 s, 1131 s, 1039 s, 940 s, 821 m, 674 m, 572 m, 444 m cm<sup>-1</sup>.

When a molar ratio of Cu/4,4'-bipy/hedp/Na was 1:1:1.25:2 (pH  $\approx$  3), a similar hydrothermal reaction at 140 °C led to the same compound with a higher yield (58%). Thermal analysis of **1** showed two decomposition steps between 20 and 180 °C. The total observed weight loss (8.45%) is in agreement with the theoretical value (8.74%) for the removal of two lattices plus two coordinated water molecules.

**Synthesis of  $[\text{Cu}_3(\text{hedpH})_2(4,4'\text{-azpy})(\text{H}_2\text{O})_2] \cdot 1.6\text{H}_2\text{O}$  (**2**):** A mixture of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (1 mmol, 0.2440 g), 4,4'-azpy (1.1 mmol, 0.2081 g), 50%  $\text{hedpH}_4$  (1.25 mmol, 0.5 cm<sup>3</sup>), 1 M NaOH (2 cm<sup>3</sup>), and water (6 cm<sup>3</sup>) with a pH of approximately 3 was transferred to a Teflon-lined autoclave (25 cm<sup>3</sup>) and kept at 140 °C for 48 h. After slow cooling, green crystals appeared as a single phase. Yield: 78% based on Cu.  $\text{C}_{14}\text{H}_{27.2}\text{Cu}_3\text{N}_4\text{O}_{17.6}\text{P}_4$ : calcd. (found) C 20.64 (19.81), H 3.19 (3.21), N 6.60 (6.61). IR (KBr):  $\tilde{\nu}$  = 3575 m, 3413

m, 3093 m, 2771 m, 1605 m, 1484 w, 1421 m, 1166 s, 1130 s, 1039 s, 940 s, 827 m, 675 m, 574 s, 419 m cm<sup>-1</sup>. Compound **2** can be obtained at pH = 1.6–3.6 with a Cu:hedp molar ratio of 1:2.5. Thermal analysis of **2** revealed that the total weight loss (7.14%) in the temperature range 30–160 °C corresponds to the release of 3.6 H<sub>2</sub>O molecules (7.64%).

**Crystallographic Studies:** Single crystals of dimensions 0.30  $\times$  0.30  $\times$  0.20 mm for **1** and 0.40  $\times$  0.05  $\times$  0.05 mm for **2** were used for structure determinations (Table 3). Data corrections for compound **1** were made at room temperature on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromatized Mo- $K_\alpha$  radiation ( $\lambda$  = 0.71073 Å), operating in  $\omega$ -2 $\theta$  scanning mode. The unit cell parameters were obtained by least-squares refinement of 25 well-centred reflections. Intensity data were collected in the  $\theta$  range 1.33–24.97°. Corrections for Lorentz and polarization factors were applied to the intensity values.

Table 3. Crystallographic data for **1–2**

Compound	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{14}\text{H}_{26}\text{Cu}_3\text{N}_2\text{O}_{18}\text{P}_4$	$\text{C}_{14}\text{H}_{27.2}\text{Cu}_3\text{N}_4\text{O}_{17.6}\text{P}_4$
<i>F</i> <sub>w</sub>	824.87	847.7
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> [Å]	6.2250(12)	6.2097(9)
<i>b</i> [Å]	7.0090(14)	7.0149(10)
<i>c</i> [Å]	15.469(3)	16.081(3)
$\alpha$ [deg]	90.73(3)	99.085(3)
$\beta$ [deg]	97.41(3)	94.852(3)
$\gamma$ [deg]	98.39(3)	97.937(3)
<i>V</i> [Å <sup>3</sup> ]	661.8(2)	681.02
<i>Z</i>	1	1
<i>D</i> [g·cm <sup>-3</sup> ]	2.070	2.062
$\mu(\text{Mo-}K_\alpha)$ [cm <sup>-1</sup> ]	27.17	26.44
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>[a]</sup>	0.0331, 0.1046	0.0484, 0.1366
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data) <sup>[a]</sup>	0.0399, 0.1327	0.0547, 0.1467

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

Data corrections for compound **2** were made at room temperature on a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromatized Mo- $K_\alpha$  radiation ( $\lambda$  = 0.71073 Å). A hemisphere of data was collected in the  $\theta$  range 3.03–25.02° using a narrow-frame method with scan widths of 0.30° in  $\omega$  and an exposure time of 20 s/frame. The data were integrated using the Siemens SAINT program,<sup>[25]</sup> with the intensities corrected for Lorentz factors, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. An empirical absorption correction was applied for both compounds.

The structures were solved by direct methods and refined on  $F^2$  by a full-matrix least-squares procedure using SHELXL 97.<sup>[26]</sup> All the non-hydrogen atoms were refined anisotropically except the O atom of lattice water and the C and N atoms of 4,4'-bipy (for **1**) and 4,4'-azpy (for **2**). The latter are disordered and were refined isotropically. Hydrogen atoms were either put in calculated positions or found by Fourier syntheses, and were refined isotropically. The H atoms of lattice water were not located in either compound. In the final Fourier-difference map of **2** the deepest hole was  $-0.737 \text{ e} \cdot \text{\AA}^{-3}$  and the highest peak  $1.994 \text{ e} \cdot \text{\AA}^{-3}$  [located near C(6); 1.729 Å]. The X-ray fluorescence spectrum measurement excludes the possible presence of Cl.

CCDC-184721 (**1**) and CCDC-184722 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or

from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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