

基于 6-羟基-2-吡啶基膦酸配体的铜配合物的合成、结构及磁性

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摘要: 在水热条件下,以 6-羟基-2-吡啶基膦酸为主配体,4,4'-联吡啶(bpy)及 1,2-二(4-吡啶基)乙烯(bpe)为桥联配体,合成了 2 个铜膦酸配位聚合物 $[\text{Cu}_3(\text{L})_2(\text{bpy})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**1**), $[\text{Cu}_3(\text{L})_2(\text{bpe})_2(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ (**2**)。配合物 **1** 中, Cu^{2+} 离子由膦酸配体连接成一条链,该链由 bpy 桥联成二维层,层与层之间通过氢键作用构成三维结构。配合物 **2** 与配合物 **1** 是同构的,桥联配体是 bpe。磁性研究表明,配合物 **1** 与 **2** 中铜离子之间存在反铁磁性耦合。

关键词: 铜配合物; 有机膦酸; 晶体结构; 磁性

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Syntheses, Structures and Magnetic Properties of Two Copper Phosphonates Based on 6-Hydroxy-2-pyridinephosphonic Acid

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Abstract: Two copper phosphonates $[\text{Cu}_3(\text{L})_2(\text{bpy})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Cu}_3(\text{L})_2(\text{bpe})_2(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ (**2**) (H_3L =6-hydroxy-2-pyridinephosphonic acid, bpy=4,4'-bipyridine, bpe=*trans*-1,2-bis(4-pyridyl)ethylene) were synthesized under hydrothermal conditions. In compound **1** the Cu^{2+} ions are bridged by the phosphonate ligand into one chain, which are further bridged by bpy into a 2D layer. The layers are interlinked by hydrogen bonds into 3D supramolecular network. Compound **2** is isostructural to compound **1**, however, the bridge ligand is bpe. Magnetic measurements indicate antiferromagnetic interactions are propagated among the Cu^{2+} centers in compound **1** and **2**. CCDC: 1044790, **1**; 1044791, **2**.

Key words: copper compound; phosphonic acid; crystal structure; magnetic properties

During the past several decades, copper phosphonates have received considerable attention, not only due to their structural diversity but also for their potential applications in many fields such as ion

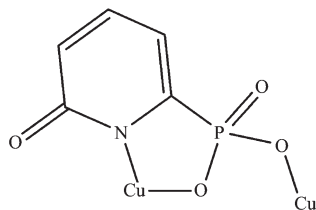
exchange, sorption, catalysis, sensors, nonlinear optics, as well as magnetism etc.^[1-7]. The study of copper phosphonates started in the 1990s when simple alkyl-^[8] and phenyl-phosphonates^[9] were prepared with the

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purpose to obtain layered host materials for intercalation reactions. To extend intriguing topologies and explore their properties, scientists continually researched the topic of copper phosphonates. Through summarizing the work of predecessors, we find that there are at least three approaches to construct these compounds. The first one is using of different steric hindered phosphonic acids, such as the $R-(PO_3H_2)_n$ ($n=1$ or 2) ligands (where $R=CH_3^{[10]}$, $C_2H_5^{[11]}$, $(CH_2)_4^{[12]}$, $(CH_2)_5^{[12]}$, tert-butyl^[13], $C_6H_9^{[14]}$, trityl^[15], etc.). The second is introducing a second auxiliary ligand. For instances, pyrazine (pyz), 2,2'-bipyridine (2,2'-bipy), 4,4'-bipyridine (bpy), as well as 1,10-phenanthroline (phen) are common ancillary ligands. $[Cu((CH_3)_2C_6H_2(PO_3H_2)_2)(pyz)(H_2O)_2]_n^{[16]}$ shows a 3D framework structure. When introducing 2,2'-bipy and bpy, $[Cu(2,2'-bipy)(HO_3PCH(OH)CO_2(H_2O))] \cdot H_2O^{[17]}$ and $[Cu^I_2Cu^{II}(CH_3C(OH)(PO_3H_2)_2(bpy)_2) \cdot 2H_2O]^{[18]}$ were isolated. Both of them display 2D layered structures. Incorporating the phen into the reaction, $[Cu(phen)(H_2O)(O_2CC_6H_4PO_3H)]^{[19]}$ was produced, which shows a one-dimensional and composed of helical chains. The third approach is decorating the phosphonate ligands with other coordinating functional groups, such as hydroxy, carboxylate, sulfonate, amino, pyridyl, and pyrimidyl etc. to the phosphonate ligands. Examples for this scheme include $Cu_4\{CH_3C(OH)(PO_3)_2\}_2(C_4H_4N_2)(H_2O)_4^{[20]}$, $Cu_3[NH_2(CH_2PO_3)_2]_2^{[21]}$, $[Cu(C_6H_5CONHPO_3H)_2]_n^{[22]}$, $[Cu(para-HO_2CC_6H_4PO_3)]_n^{[23]}$, $[Cu_2(O_3PC_2H_4SO_3)(OH)(H_2O)] \cdot 3H_2O^{[24]}$, $Cu(2-C_5H_4NPO_3H)_2$, $Cu_3(OH)_2(2-C_5H_4NPO_3)_2 \cdot 2H_2O$ and $Cu(2-C_5H_4NPO_3)^{[25]}$, $\{[(5-C_4H_4N_2PO_3H)_2Cu_2(OH)_5](CF_3SO_3)_2(H_2O)\}_n^{[26]}$. In this paper, we select 6-hydroxy-2-pyridinephosphonic acid to react with copper salt. Two copper phosphonates **1** and **2** were obtained by employing the ancillary bipyridinyl ligands bpy and bpe. The magnetic properties were studied.



Scheme 1 Coordination mode of the ligand

1 Experimental

1.1 Materials and methods

6-hydroxy-2-pyridinephosphonic acid was prepared according to the literature^[27]. All other chemicals and solvents were commercially purchased and used as received. Elemental analyses were performed on a PE 240C elemental analyzer. The IR spectra were recorded on a NICOLET 380 spectrometer with pressed KBr pellets. All the magnetic studies were performed on microcrystalline state. The magnetic susceptibilities were measured on a Quantum Design MPMS SQUID-XL7 magnetometer. Diamagnetic corrections were made for both the sample holder and the compound estimated from Pascal's constants^[28].

1.2 Syntheses

$[Cu_3(L)_2(bpy)_2(H_2O)_2] \cdot 2H_2O$ (**1**): A mixture of $Cu_2(OH)_2CO_3$ (0.012 g, 0.05 mmol), H_3L (0.017 5 g, 0.10 mmol), and bpy (0.015 6 g, 0.10 mmol) was dissolved in 2 mL H_2O . The resulting solution was placed in a glass tube, which was sealed and heated at 140 °C for 2 days. On cooling the dark green block crystals were obtained (Yield: 47% based on Cu). Anal. Calcd. for $C_{30}H_{30}Cu_3N_6O_{12}P_2(\%)$: C 39.20, H 3.29, N 9.14; Found(%): C 39.15, H 3.32, N 9.11. IR (KBr, cm^{-1}): 3 421.67 (vs), 1 609.84 (s), 1 403.87 (s), 1 059.11 (s), 999.04 (s), 812.28 (m), 709.75 (m), 601.40 (w), 513.62 (w).

$[Cu_3(L)_2(bpe)_2(H_2O)_3] \cdot 2H_2O$ (**2**): The synthesis of **2** is similar to **1** except bpe was chosen as the bridge ligand (Yield: 40% based on Cu). Anal. Calcd. for $C_{34}H_{36}Cu_3N_6O_{13}P_2(\%)$: C 41.28, H 3.67, N 8.49; Found (%): C 42.03, H 3.55, N 8.63. IR (KBr, cm^{-1}): 3 409.42 (vs), 3 166.01 (vs), 1 612.26 (s), 1 507.64 (s), 1 061.68 (s), 969.37 (s), 969.37 (m), 828.83 (m), 553.99 (w), 515.14 (w).

1.3 X-ray crystallography

Single crystals with dimensions 0.22 mm×0.25 mm×0.30 mm for **1** and 0.22 mm×0.25 mm×0.30 mm for **2** were selected for indexing and intensity data collection with a Rigaku SCX mini CCD diffractometer by using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.710 73$ nm) at room temperature. A hemisphere of data was collected in the θ range of 3.2°~27.5° for

1 and $3.1^\circ \sim 25.0^\circ$ for **2** by using a narrow-frame method with scan widths of 0.03° in ω and an exposure time of 10 s per frame. The numbers of observed and unique reflections are 8 533 and 3 690 ($R_{\text{int}}=0.038$) for **1** and 16 187 and 6 637 ($R_{\text{int}}=0.077$) for **2**. Cell parameters were refined by using the program CrystalClear^[29] on all observed reflections. The collected data were reduced by using the program CrystalClear, and an absorption correction (multiscan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The structures

were solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL^[30]. All the non-hydrogen atoms were located from the Fourier maps and were refined anisotropically. All H atoms were refined isotropically with the isotropic vibration parameters related to the non-H atom to which they are bonded. Crystallographic and refinement details of **1~2** are listed in Table 1. Selected bond lengths and angles are given in Table 2 for **1~2**, respectively.

CCDC: 1044790, **1**; 1044791, **2**.

Table 1 Crystal data and structure refinements for **1** to **2**

	1	2
Empirical formula ^a	C ₃₀ H ₃₀ Cu ₃ N ₆ O ₁₂ P ₂	C ₃₄ H ₃₆ Cu ₃ N ₆ O ₁₃ P ₂
Molecular weight	919.19	989.25
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	0.802 32(16)	1.110 8(2)
b / nm	0.979 2(2)	1.146 0(2)
c / nm	1.145 9(2)	1.595 4(3)
α / ($^\circ$)	103.88(3)	110.44(3)
β / ($^\circ$)	110.33(3)	92.24(3)
γ / ($^\circ$)	93.54(3)	95.10(3)
V / nm ³	0.809 1(4)	1.890 2(7)
Z	1	2
D_c / (g·cm ⁻³)	1.887	1.738
μ / mm ⁻¹	2.130	1.832
$F(000)$	465	1 006
R_{int}	0.038	0.077
GOF on F^2	1.001	1.023
R_1, wR_2 [$I > 2\sigma(I)$] ^b	0.040 4, 0.085 5	0.067 2, 0.131 9
R_1, wR_2 (all data) ^b	0.057 0, 0.093 0	0.117 7, 0.154 5
$(\Delta\rho)_{\text{max}} (\Delta\rho)_{\text{min}}$ / (e·nm ⁻³)	380, -540	1 160, -720

^a Including solvent molecules; ^b $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$, $wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for **1** and **2**

1					
Cu1-O3	0.193 4(2)	Cu1-O3A	0.193 4(2)	Cu1-N3	0.200 2(3)
Cu1-N3A	0.200 2(3)	Cu2-O4	0.193 3(2)	Cu2-O5	0.194 5(3)
Cu2-N1	0.203 1(3)	Cu2-N2	0.204 2(3)	Cu2-O4B	0.239 9(2)
N1-C1	0.136 8(4)	N1-C5	0.137 1(4)	C1-C2	0.137 2(5)
C2-C3	0.140 1(5)	C3-C4	0.135 1(5)	C4-C5	0.142 6(5)
O3-Cu1-N3	90.26(12)	O3-Cu1-O3A	180.00	O3-Cu1-N3A	89.74(12)
O3C-Cu1-N3	89.74(12)	O3C-Cu1-N3A	90.26(12)	N3-Cu1-N3A	180.00

Continued Table 2

O4-Cu2-O5	170.81(11)	O4-Cu2-N2	90.49(11)	O4-Cu2-N1	85.98(11)
O5-Cu2-N1	94.45(12)	O4-Cu2-O4B	84.47(9)	O4B-Cu2-O5	86.38(9)
O5-Cu2-N2	91.86(12)	O4B-Cu2-N1	97.91(10)	N1-Cu2-N2	161.86(12)
O4B-Cu2-N2	99.45(10)				
2					
Cu1-O3	0.194 1(5)	Cu1-O6	0.193 4(5)	Cu1-N2A	0.200 2(6)
Cu1-N3	0.200 2(6)	Cu1-O11	0.254 9(5)	Cu2-O1	0.194 0(4)
Cu2-O10	0.194 2(5)	Cu2-N1	0.203 6(6)	Cu2-N4	0.205 2(6)
Cu2-O1B	0.243 2(4)	Cu3-O9	0.195 2(5)	Cu3-N8	0.205 2(6)
Cu3-O5C	0.193 5(5)	Cu3-N7C	0.203 6(6)	Cu3-O5D	0.240 1(5)
O3-Cu1-O6	172.2(2)	O3-Cu1-N3	89.0(2)	O3-Cu1-N2A	89.8(2)
O6-Cu1-N3	90.9(2)	O6-Cu1-N2A	89.5(2)	N2A-Cu1-N3	174.2(2)
O3-Cu1-O11	94.06(18)	O6-Cu1-O11	93.76(18)	N3-Cu1-O11	89.6(2)
N2A-Cu1-O11	96.2(2)	O1-Cu2-O10	169.97(19)	O1-Cu2-N1	85.9(2)
O1-Cu2-N4	90.3(2)	O1-Cu2-O1B	85.21(17)	O10-Cu2-N1	94.0(2)
O10-Cu2-N4	92.8(2)	O1B-Cu2-O10	84.88(17)	N1-Cu2-N4	162.2(2)
O1B-Cu2-N1	98.1(2)	O1B-Cu2-N4	98.93(17)	O9-Cu3-N8	92.6(2)
O5C-Cu3-O9	170.75(19)	O9-Cu3-N7C	93.8(2)	O5D-Cu3-O9	85.85(18)
O5C-Cu3-N8	90.1(2)	N7C-Cu3-N8	161.1(2)	O5D-Cu3-N8	101.3(2)
O5C-Cu3-N7C	86.3(2)	O5C-Cu3-O5D	84.95(18)	O5D-Cu3-N7C	96.85(17)

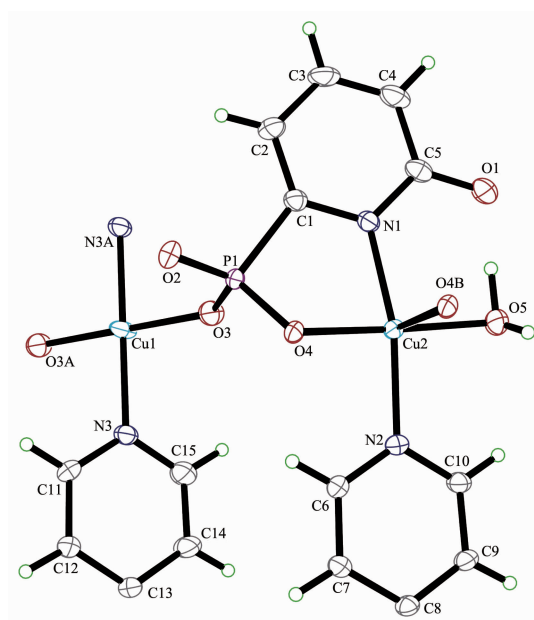
Symmetry codes: for **1**: A: 1-x, 2-y, 1-z; B: 1-x, 2-y, -z; for **2**: A: 1+x, 1+y, z; B: 2-x, -y, -z; C: -1+x, -1+y, z; D: 1-x, 1-y, 1-z

2 Results and discussion

2.1 Structure description

X-ray single crystal diffraction reveals that compound **1** crystallizes in the triclinic space group $P\bar{1}$ (Table 1). As shown in Fig.1, the asymmetric unit contains one and a half copper atoms, one L^{3-} , one bpy, one coordinated water, and one lattice water. A curious feature of the structure is the presence of two distinct Cu^{2+} geometries. Cu1 locates on an inversion center with 0.5 occupations and has square-planar coordination geometry. The atoms around Cu1 atom are (O3 and O3A) from two different L^{3-} ligands and (N3 and N3A) from two separate bpy. The Cu1-O and Cu1-N bond lengths are 0.193 4(2) nm and 0.200 2(3) nm (Table 2), respectively. Cu2 is square-pyramidally coordinated, surrounded by (O4, O4B, O5, N1 and N2) from two phosphonate ligands, bpy and water. The O4B fills on the axial position with the Cu2-O4B distance of 0.239 9(2) nm. The Cu2-O/N lengths on the planar position range from 0.193 3(2) to 0.204 2(3) nm, which are in consistent with that observed in

other copper phosphonates such as $Cu(2-C_5H_4NPO_3H)_2$ ^[25]. The Cu2 and Cu2B atoms are bridged together



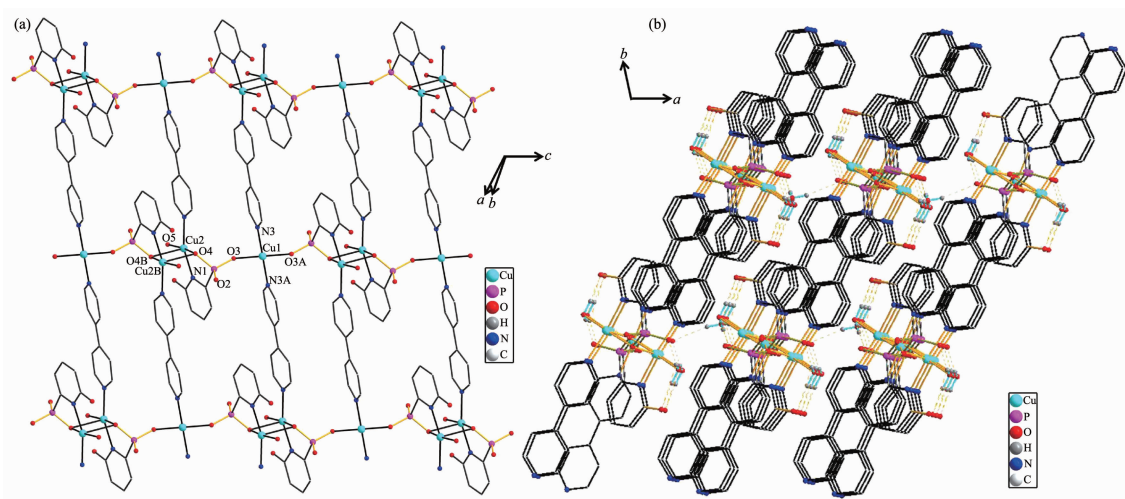
Symmetry codes: A: 1-x, 2-y, 1-z; B: 1-x, 2-y, -z; Displacement ellipsoids are drawn at the 30% probability level

Fig.1 View of the coordination environments of Cu^{2+} ions in compound **1**

through phosphonate oxygen atoms to form a dimer $[\text{Cu}_2\text{O}_2]$ with $\text{Cu2}\cdots\text{Cu2B}$ distance of 0.322 3 nm. The Cu2-O4-Cu2B bond angle is 95.53° . Furthermore, the dimers and Cu1 atoms are linked together through the O-P-O groups to form one infinite chain along the c -axis (Fig.2a). The chains are joined together by bpy to form a layer, which are stabilized by hydrogen bonding interactions (Table 3) into a 3D network (Fig. 2b). Charge balance calculation shows that the ligand is minus trivalent (Scheme 1). The anionic ligand is coordinated to the copper in the lactam form, as evidenced by the C5-O1 bond length, 0.127 6(4) nm, which is shorter than that in the free ligand (0.130 6 nm)^[27]. Thus we assume that the C5-O1 is character-

istic of a double bond. The C-C distances in the ligand are different and correspond to single and double bonds^[31].

Compound **2** crystallizes in the triclinic space group $P\bar{1}$. There are three Cu atoms, two phosphonates, two bpe ligands, three coordinated water, and two lattice water (Fig.3). Cu1 is square-pyramidal coordinated by (O3, O6, O11, N3, N2A) from two phosphonates, two bpe ligands and one coordinated water. The O11 locates on the axial position. The Cu1-O3, Cu1-O6 and Cu1-O11 are 0.194 1(5), 0.193 4(5) and 0.254 9(5) nm, respectively. The Cu-N bond lengths are 0.200 2(6) nm. The Cu2 and Cu3 atoms also have square-pyramidal environment. The five coordination



All H atoms and lattice water molecules are omitted for clarity; Dashed lines show the hydrogen bonding interaction

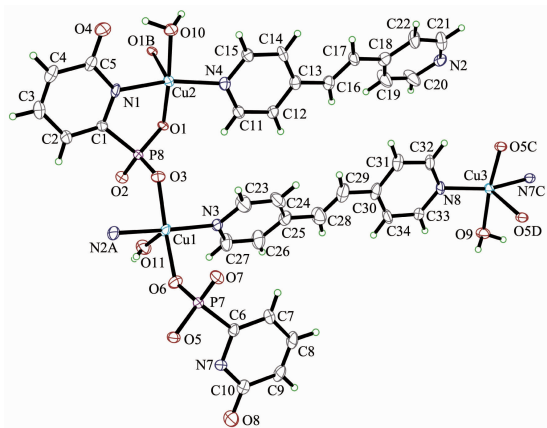
Fig.2 (a) View of the 2D layered structure of compound **1**; (b) View of the 3D framework for compound **1**

Table 3 Hydrogen bonds in **1** and **2**

D-H \cdots A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
1				
O(5)-H(5A) \cdots O(2)A	0.085(3)	0.207(3)	0.286 7(3)	156(4)
O(6)-H(6A) \cdots O(2)	0.084(4)	0.196(4)	0.279 1(4)	171(4)
O(6)-H(6B) \cdots O(2)B	0.084(3)	0.212(3)	0.295 0(4)	167(5)
2				
O(9)-H(9C) \cdots O(7)B	0.085(7)	0.209(7)	0.290 2(7)	160(7)
O(10)-H(10B) \cdots O(2)C	0.085(5)	0.205(6)	0.286 4(7)	160(6)
O(11)-H(11A) \cdots O(2)	0.085(4)	0.193(5)	0.276 8(8)	172(4)
O(11)-H(11B) \cdots O(2)D	0.085(6)	0.203(6)	0.286 7(8)	166(6)
O(12)-H(12A) \cdots O(7)A	0.084(9)	0.201(9)	0.277 6(9)	150(8)
O(12)-H(12B) \cdots O(7)B	0.084(7)	0.214(10)	0.289 1(9)	148(9)
O(13)-H(13A) \cdots O(12)	0.085	0.208	0.292 6(13)	179

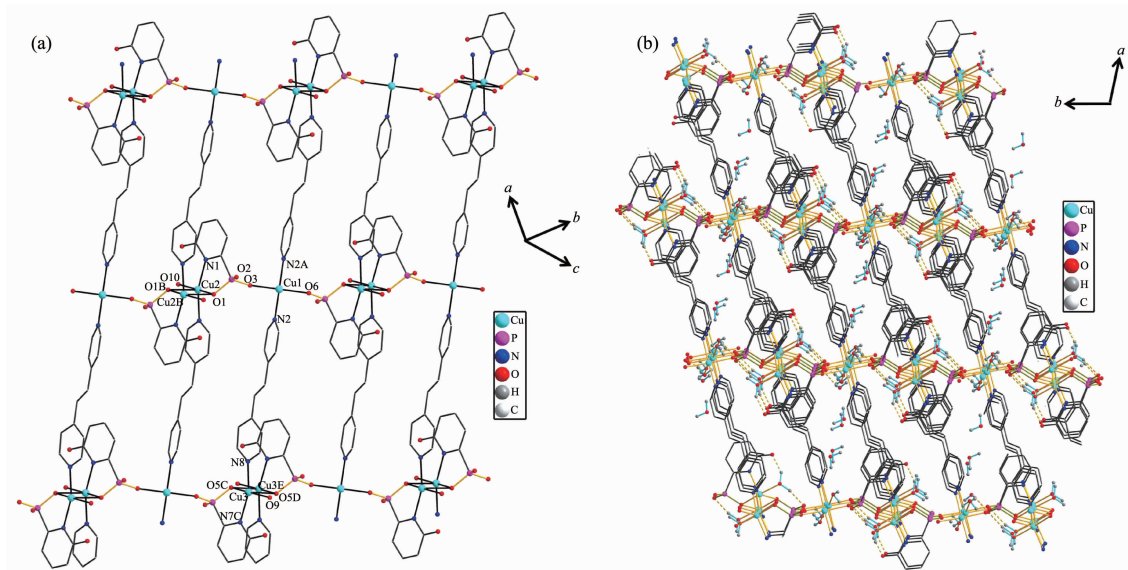
Symmetry codes: for **1**: A: $1-x, 2-y, -z$; B: $2-x, 2-y, 1-z$; for **2**: A: $-1+x, -1+y, z$; B: $1-x, 1-y, 1-z$; C: $2-x, -y, -z$; D: $2-x, 1-y, -z$

sites around the Cu2 atom are occupied by pyridyl nitrogen (N1), bpe nitrogen (N4), phosphonate oxygen (O1, O1B) atoms from two equivalent phosphonates and (O10) from water. Those around Cu3 atoms are provided by pyridyl and bpe nitrogen (N7C, N8) and phosphonate oxygen (O5C, O5D) atoms from two different phosphonate groups and oxygen atom (O9) from water. The Cu2-O1B (0.243 2(4) nm) and Cu3-



Symmetry codes: A: $1+x, 1+y, z$; B: $2-x, -y, -z$; C: $-1+x, -1+y, z$; D: $1-x, 1-y, 1-z$; Displacement ellipsoids are drawn at the 30% probability level

Fig.3 View of the coordination environments of Cu^{2+} ions in compound **2**



All H atoms and lattice water molecules are omitted for clarity; Dashed lines show the hydrogen bonding interaction

Fig.4 (a) View of the 2D layered structure of compound **2**; (b) View of the 3D framework for compound **2**

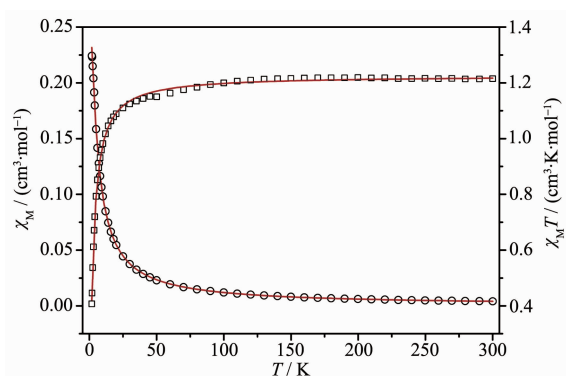
2.2 Magnetic properties

The variable-temperature dc magnetic susceptibilities measurement for **1** and **2** are shown in Fig.5 and

O5D (0.240 1(5) nm) bond lengths on the axial position are longer than that in the planar positions (0.193 5(5) to 0.205 2(6) nm) (Table 2). The overall structure of **2** is isostructural to compound **1** (Fig.4a). In the one-dimensional chain, the Cu2...Cu2B and Cu3...Cu3E distances are 0.323 6 and 0.321 4 nm, similar to that in compound **1**. The Cu2-O1-Cu2E and Cu3-O5C-Cu3E bond angles are 94.79° and 95.05° . The adjacent layers are connected by the classic hydrogen bonds (Table 3) to form a 3D supramolecular framework (Fig.4b).

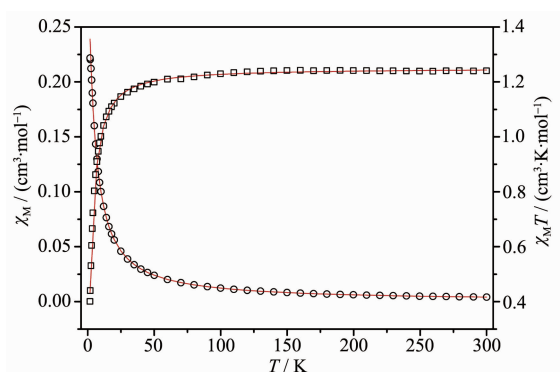
The 2D layered structures of **1** and **2** are remarkably different from $[\text{Cu}_3(\text{O}_2\text{CC}_5\text{H}_3\text{NPO}_3)_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}(\text{HO}_2\text{CC}_5\text{H}_3\text{NPO}_3\text{H})_2]$ with 2-phosphonic isonicotinic acid as ligand. Compound $[\text{Cu}_3(\text{O}_2\text{CC}_5\text{H}_3\text{NPO}_3)_2(\text{H}_2\text{O})_2]$ has a pillar-layered structure, while, $[\text{Cu}(\text{HO}_2\text{CC}_5\text{H}_3\text{NPO}_3\text{H})_2]$ has a chain-like structure^[32]. The structure of **1** can be compared with $\text{Cu}[(\text{HO}_3\text{PCH}_2)_2\text{C}_6\text{H}_4(4,4'\text{-bipy})] \cdot 2\text{H}_2\text{O}$, in which the phosphonate-copper chains are bridged by bpy into a 2D layer^[33]. This research demonstrates that the 6-hydroxy-2-pyridine-phosphonic acid ligand can be used to construct structurally diverse coordination polymers.

Fig.6. The room temperature $\chi_{\text{M}}T$ values are 1.24 and $1.21 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for **1** and **2**, respectively. These values are consistent with that of the expected for



Solid line is the best fit obtained

Fig.5 χ_M and $\chi_M T$ vs T for **1**



Solid line is the best fit obtained

Fig.6 χ_M and $\chi_M T$ vs T for **2**

three isolated copper ions $1.125 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ ($g=2$)^[28]. On lowering the temperature, $\chi_M T$ slowly decreases until 50 K and then falls drastically reaching a value of 0.40 and $0.40 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for **1** and **2**, respectively, at 1.8 K. The decrease of $\chi_M T$ as the temperature is lowered indicating antiferromagnetic coupling between the Cu^{2+} centers. According to the structure of both compounds, the magnetic exchange between the Cu ions may be propagated through the $\mu\text{-O(P)}$ bridges within the $\{\text{Cu}_2\text{O}_2\}$ dimer and the O-P-O and bpy/bpe bridges. It is known that comparing the $\mu\text{-O}$ bridge, O-P-O and bpy/bpe bridges play a negligible role in propagating the magnetic exchange. Therefore the susceptibility data were analyzed by Bleaney-Bowers expression based on a Heisenberg Hamiltonian $H = -2JS_1S_2$ and an isolated Cu^{2+} ion^[28]:

$$\chi_M = \frac{2Ng^2\beta^2}{kT} \times \frac{1}{3+e^{-2J/(kT)}} + \frac{0.09375g^2}{T}$$

Where $2J$ is the singlet-triplet energy gap and N , g , β , k have their usual meaning. Considering the

intermolecular interaction (zJ'), good fit results were obtained in the solid line in Fig.5 and Fig.6, with the parameters $g=2.1$, $J=-2.0 \text{ cm}^{-1}$, $zJ'=-0.6 \text{ cm}^{-1}$ for **1**, and $g=2.1$, $J=-1.7 \text{ cm}^{-1}$, $zJ'=-0.7 \text{ cm}^{-1}$ for **2**. The minus J values observed here indicate that antiferromagnetic interactions are propagated among the Cu centers.

3 Conclusions

Through hydrothermal reactions, two copper phosphonates $[\text{Cu}_3(\text{L})_2(\text{bpy})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_3(\text{L})_2(\text{bpe})_2(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ were constructed by using 6-hydroxy-2-pyridinephosphonic acid as ligand. Both compounds show 2D layered structures with bpy/bpe as bridges. Although the hydroxyl group does not coordinate with metal centers, it experiences a deprotonation reaction under the hydrothermal reaction condition. Both compounds show antiferromagnetic interactions among the Cu^{2+} centers. Further work is in progress by employing the longer bipyridinyl bridge ligand in the reaction system.

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