

Influence of Preparation Conditions on the Formation of Copper (II) Architectures with Pyrazine-2,3,5-tricarboxylic Acid

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Three new metal-organic copper(II) complexes, $[\text{Cu}(\text{H}_2\text{PZTC})_2]_n \cdot 2n\text{H}_2\text{O}$ (**1**), $[\text{Cu}(\text{HPZTC}) \cdot 2\text{H}_2\text{O}]_n \cdot 2n\text{H}_2\text{O}$ (**2**), and $\text{Cu}_2[(\text{PZHD})(\text{OH})(\text{H}_2\text{O})_2]_n$ (**3**) (H_3PZTC = pyrazine-2,3,5-tricarboxylic acid, PZHD^{3-} = 2-hydroxypyrazine-3,5-dicarboxylate), have been synthesized from $\text{Cu}(\text{II})/\text{H}_3\text{PZTC}$ system under different synthetic conditions, and characterized by single-crystal X-ray diffraction, elemental analysis, IR spectroscopy and thermogravimetric analysis. In complexes **1** and **2**, H_3PZTC ligands lose one and two protons, which were transformed into H_2PZTC^- anion and HPZTC^{2-} dianion under different preparation condition, respectively. Furthermore, two ligands coordinate with $\text{Cu}(\text{II})$ cations in different modes, leading to the formation of the different chain structures. In complex **3**, H_3PZTC ligand was converted into a new ligand-PZHD by *in situ* decarboxylation and hydroxylation under a higher pH value than that for complexes **1** and **2**. PZHD ligands link the $\text{Cu}(\text{II})$ cations to form a 2D layer structure. These results demonstrate that the preparation conditions, including pH value and reaction temperature etc, play an important role in the construction of complexes based on H_3PZTC ligand.

Key Words : Pyrazine-2,3,5-tricarboxylic acid, Preparation condition, *In situ* reaction

Introduction

The metal-organic frameworks (MOFs) have received intensive interests, mostly motivated by their intriguing variety of architectures and potential applications in various areas such as catalysis, magnetism, gas storage, and luminescence, etc.¹⁻¹² The reported data have demonstrated that not only the selection of proper organic linkers and metal ions but also the synthetic conditions such as reaction temperatures and pH values *et al.*,¹³⁻¹⁸ have a great influence on the structures and properties of the complexes.

Recently, multicarboxylate ligands have been usually selected as multifunctional organic linkers for the abundant coordination modes, and also for the ability to act as hydrogen bond acceptors or donors to assemble supramolecular structures.^{19,20} Pyrazine-2,3,5-tricarboxylic acid (H_3PZTC) is one of the above mentioned multicarboxylate ligands and therefore a multifunctional organic linker. It has several remarkable features as follows: (1) It contains three carboxylate groups and two nitrogen atoms, which can coordinate to metal ions in various coordination modes, and assemble into novel and fantastic structures. (2) The three carboxylate groups are very sensitive to the acidity/basicity of the reaction system, which can be partially or fully deprotonated under different pH values, and then assembly into different architectures. (3) Moreover, the coordination features of this ligand and the dependence of its complex structures on various preparation conditions have been little investigated to date.^{21,22}

Therefore, we selected the H_3PZTC as organic ligand and synthesized three new copper(II) complexes, $[\text{Cu}(\text{H}_2\text{PZTC})_2]_n \cdot 2n\text{H}_2\text{O}$ (**1**), $[\text{Cu}(\text{HPZTC}) \cdot 2\text{H}_2\text{O}]_n \cdot 2n\text{H}_2\text{O}$ (**2**) and $\text{Cu}_2[(\text{PZHD})(\text{OH})(\text{H}_2\text{O})_2]_n$ (**3**) based on $\text{Cu}/\text{H}_3\text{PZTC}$ system under different synthetic conditions. In this paper, we report the syntheses, crystal structure and thermal properties of the title complexes.

Experimental Section

Materials and General Methods. Pyrazine-2,3,5-tricarboxylic acid dihydrate was synthesized according to the literatures.²³⁻²⁵ All the other reagents were used as received without further purification. The C, H, N microanalyses were carried out on a Vario EL elemental analyzer. The IR spectrum was recorded on a Nicolet Avatar 360 FT-IR spectrometer by using the KBr pellet technique. The TG experiment for the complex was performed using a NETZSCH STA 409 PG/PC thermogravimetric analyzer under N_2 atmosphere. The heating rate was $10^\circ\text{C min}^{-1}$ from ambient temperature to 1000°C with a flow rate of $20\text{ mL}\cdot\text{min}^{-1}$.

Crystal Structure Determinations. The single-crystal X-ray data collections for complexes **1-3** were performed on a Bruker SMART 1000 CCD area detector diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The raw data integrated into SHELX-format reflection files and semi-empirical absorption corrections were applied by using the SADABS program.²⁶ The structures were solved

Table 1. Crystal data and structure refinement parameters for complexes **1-3**

Complex	1	2	3
Chemical formula	C ₁₄ H ₁₀ CuN ₄ O ₁₄	C ₇ H ₁₀ CuN ₂ O ₁₀	C ₆ H ₆ Cu ₂ N ₂ O ₈
Formula weight	521.80	345.71	361.21
Temperature [K]	133(2)	133(2)	133(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P ₁	P2 ₁ /c	P2 ₁
<i>a</i> (Å)	6.728(13)	6.594(13)	9.222 (18)
<i>b</i> (Å)	7.854(16)	12.493(3)	6.191(12)
<i>c</i> (Å)	9.638(19)	14.112(4)	9.470(19)
α (°)	83.12(3)	90	90
β (°)	83.79(3)	107.30(3)	116.99(3)
γ (°)	77.95(3)	90	90
<i>V</i> (Å ³)	492.68(17)	1109.9(5)	481.8(2)
<i>Z</i>	1	4	2
<i>F</i> (000)	263	700	356
ρ [mg m ⁻³]	1.759	2.069	2.490
μ [mm ⁻¹]	1.194	2.029	4.455
θ range (deg)	2.67-27.04	3.02-27.00	2.41-27.49
Reflections collected	3359	7376	3349
Total independent,	2134, 0.0301	2411, 0.0361	1690, 0.0528
<i>R</i> _{int}			
Goodness-of-fit on <i>F</i> ²	0.996	1.053	1.052
Flack parameter			0.02(2)
<i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0311 w <i>R</i> ₂ = 0.0730	<i>R</i> ₁ = 0.0313, w <i>R</i> ₂ = 0.0736	<i>R</i> ₁ = 0.0344, w <i>R</i> ₂ = 0.0727

by direct methods²⁷ and refined by full-matrix least squares on *F*² by using SHELXS 97 and SHELXL 97 programs, respectively.^{27,28} All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. The crystallographic data for complexes **1-3** are listed in Table 1. Selected bond lengths (Å) and angles (°) are listed in Table 2 and 3. The details of the hydrogen bonds for the complexes are listed in Table 4.

Synthesis of [Cu(H₂PZTC)₂]_n·2nH₂O (1**).** Cu(NO₃)₂·2H₂O (0.15 g, 6.2 mmol) was added into 15 mL aqueous solution of H₃PZTC (0.20 g, 8 mmol) under vigorous stirring over a period of 20 min. The solution was filtered and maintained at room temperature for crystallization by slow evaporation. After two weeks, the blue block-like crystals of **1** were obtained. Crystals were isolated by filtration and air-dried. Yield: 64.3%. Anal. Calc. for C₁₄H₁₀CuN₄O₁₄: C, 37.56; H, 1.92; N, 10.73. Found: C, 36.93; H, 2.27; N, 11.20%. IR (KBr pellet, cm⁻¹): 3468(b), 1658(s), 1430(m), 1360(m), 1312(s), 1180(s), 1108(m), 850(m), 790(m), 724(w).

Synthesis of [Cu(HPZTC)·2H₂O]_n·2nH₂O (2**).** A mixture of H₃PZTC (0.050 g, 0.2 mmol), Cu(NO₃)₂·2H₂O (0.072 g, 0.3 mmol), NaN₃ (0.013 g, 0.2 mmol), NaOH (0.15 mL, 0.65 mol·L⁻¹), and H₂O (8 mL) was put into a 25 mL stainless steel bomb and heated at 130 °C for 4 days, then cooled slowly to room temperature. Blue-green crystals of **2** were obtained by filtration. Yield: 72.2%. Anal. Calc. for C₇H₁₀CuN₂O₁₀: C, 24.29; H, 2.89; N, 8.10. Found: C, 23.84;

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

Complex 1			
Cu(1)-O(1)	1.9543(15)	Cu(1)-N(1)	1.9931(18)
Cu(1)-O(4)	2.3978(15)	O(1)-Cu(1)-O(1)#1	180.0
O(1)-Cu(1)-N(1)	83.87(7)	O(1)#1-Cu(1)-N(1)	96.13(7)
O(1)-Cu(1)-N(1)#1	96.13(7)	O(1)#1-Cu(1)-N(1)#183.87(7)	
N(1)#1-Cu(1)-N(1)	180.00(1)	O(1)-Cu(1)-O(4)#2	88.76(6)
O(1)#1-Cu(1)-O(4)#2	91.24(6)	N(1)#1-Cu(1)-O(4)#291.79(6)	
N(1)-Cu(1)-O(4)#2	88.21(6)	O(4)#2-Cu(1)-O(4)#3180.0	
O(1)-Cu(1)-O(4)#3	91.24(6)	O(1)#1-Cu(1)-O(4)#388.76(6)	
N(1)-Cu(1)-O(4)#3	91.79(7)	N(1)#1-Cu(1)-O(4)#388.21(6)	
Complex 2			
Cu(1)-O(7)	2.0271(16)	Cu(1)-O(8)	2.0329(16)
Cu(1)-O(3)#1	2.1939(17)	Cu(1)-O(1)	2.2179(17)
Cu(1)-N(1)	2.241(2)	Cu(1)-O(6)	2.3012(17)
Cu(1)-N(2)#1	2.397(2)		
O(7)-Cu(1)-O(8)	173.30(7)	O(7)-Cu(1)-O(3)#1	95.63(7)
O(8)-Cu(1)-O(3)#1	88.98(6)	O(7)-Cu(1)-O(1)	92.14(6)
O(8)-Cu(1)-O(1)	93.73(6)	O(3)#1-Cu(1)-O(1)	75.48(6)
O(7)-Cu(1)-N(1)	89.13(7)	O(8)-Cu(1)-N(1)	89.60(7)
O(3)#1-Cu(1)-N(1)	147.44(7)	O(1)-Cu(1)-N(1)	72.16(6)
O(7)-Cu(1)-O(6)	87.33(6)	O(8)-Cu(1)-O(6)	86.08(6)
O(3)#1-Cu(1)-O(6)	144.03(6)	O(1)-Cu(1)-O(6)	140.36(6)
N(1)-Cu(1)-O(6)	68.21(6)	O(7)-Cu(1)-N(2)#1	86.95(7)
O(8)-Cu(1)-N(2)#1	90.14(7)	O(3)#1-Cu(1)-N(2)#169.35(6)	
O(1)-Cu(1)-N(2)#1	144.53(7)	N(1)-Cu(1)-N(2)#1	143.19(7)
O(6)-Cu(1)-N(2)#1	75.06(6)		

Symmetry transformations used to generate equivalent atoms. For **1**: #1 -x+1, -y+1, -z+1 #2 x+1, y, z #3 -x, -y+1, -z+1, For **2**: #1 x, -y+1/2, z-1/2

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

Complex 3			
Cu(1)-O(7)	1.916(4)	Cu(1)-O(5)	1.921(4)
Cu(1)-O(1)	1.983(3)	Cu(1)-N(1)#1	1.994(4)
Cu(1)-O(8)	2.493(4)	Cu(1)-O(5) #1	2.706(4)
Cu(2)-O(7)	1.937(3)	Cu(2)-O(6)	1.957(4)
Cu(2)-N(2)#2	2.014(4)	Cu(2)-O(1)	2.058(4)
Cu(2)-O(2)#2	2.382(4)	Cu(2)-O(3)#2	2.383(4)
O(7)-Cu(1)-O(5)	170.38(15)	O(7)-Cu(1)-O(1)	79.69(14)
O(5)-Cu(1)-O(1)	92.41(14)	O(7)-Cu(1)-N(1)#1	98.58(17)
O(5)-Cu(1)-N(1)#1	88.58(17)	O(1)-Cu(1)-N(1)#1	172.8(2)
O(7)-Cu(2)-O(6)	92.06(15)	O(7)-Cu(2)-N(2)#2	175.35(18)
O(6)-Cu(2)-N(2)#2	92.41(16)	O(7)-Cu(2)-O(1)	77.38(13)
O(6)-Cu(2)-O(1)	169.18(15)	N(2)#2-Cu(2)-O(1)	98.20(16)
O(7)-Cu(2)-O(2)#2	106.56(13)	O(6)-Cu(2)-O(2)#2	93.09(16)
N(2)#2-Cu(2)-O(2)#2	74.47(15)	O(1)-Cu(2)-O(2)#2	87.74(15)
O(7)-Cu(2)-O(3)#2	102.55(14)	O(6)-Cu(2)-O(3)#2	90.31(16)
N(2)#2-Cu(2)-O(3)#2	76.15(15)	O(1)-Cu(2)-O(3)#2	94.27(16)
O(2)#2-Cu(2)-O(3)#2	150.54(11)	O8-Cu1-O5#1	155.41(13)
O8-Cu1-O5	88.19(13)	O8-Cu1-N1#1	100.95(13)

Symmetry transformations used to generate equivalent atoms. #1 -x, y+1/2, -z+1 #2 -x+1, y+1/2, -z+1.

Table 4. Hydrogen bonds geometries (Å, °) for complexes **1-3**

D-H...A	d(D-H)	d(H...A)	(D...A)	∠ DHA	Symmetry code
Complex 1					
O(3)-H(3)···O(7)	0.82	1.72	2.529(2)	169.1(2)	[-1+x, y+1, z]
O(6)-H(6)···O(2)	0.82	1.74	2.554(2)	171.9(2)	[x, y, z+1]
O(7)-H(7A)···N(2)	0.85	2.28	3.073(2)	155.6(2)	[-x, -y+1, 1-z]
O(7)-H(7A)···O(5)	0.85	2.41	3.044(2)	132.2(2)	[-x, -y+1, 1-z]
O(7)-H(7B)···O(5)	0.85	2.05	2.894(3)	168.3(2)	[x+1, y-1, -1+z]
Complex 2					
O(5)-H(5)···O(4)	0.90	1.52	2.399(2)	168(5)	[x, y, z]
O(7)-H(7A)···O(10)	0.85	1.92	2.686(2)	148.8(2)	[-x+2, y-1/2, -z+3/2]
O(7)-H(7A)···O(6)	0.85	2.53	2.995(2)	115.2(2)	[x, y, z]
O(7)-H(7B)···O(3)	0.85	2.26	2.881(2)	130.1(2)	[-x+2, y+1/2, -z+3/2]
O(7)-H(7B)···O(8)	0.85	2.33	3.015(2)	138.7(2)	[x+1, y, z]
O(8)-H(8A)···O(1)	0.86	1.90	2.729(2)	163.2(2)	[-x+1, -y+1, -z+1]
O(8)-H(8B)···O(9)	0.85	1.91	2.684(2)	149.7(2)	[x, -y+1/2, z-1/2]
O(9)-H(9A)···O(2)	0.86	1.91	2.757(2)	169.0(2)	[-x+1, y-1/2, -z+3/2]
O(9)-H(9B)···O(4)	0.85	2.03	2.824(2)	154.9(2)	[-x+1, y+1/2, -z+3/2]
O(10)-H(10A)···O(2)	0.86	2.01	2.816(2)	155.8(2)	[-x+1, y-1/2, -z+3/2]
O(10)-H(10B)···O(5)	0.85	2.06	2.899(2)	167.5(2)	[x, -y+1/2, z+1/2]
Complex 3					
O(6)-H(6A)···O(4)	0.85	1.73	2.567(5)	170.0(2)	[-x+1, y+3/2, -z+1]
O(6)-H(6B)···O(8)	0.85	2.16	2.700(5)	121.2(2)	[-x+1, y+1/2, -z+1]
O(7)-H(7A)···O(3)	0.85	2.20	3.035(5)	169.3(2)	[x, y+1, z+1]
O(8)-H(8A)···O(3)	0.84	1.96	2.804(5)	177.4(2)	[-x+1, y+1/2, -z+1]
O(8)-H(8B)···O(7)	0.85	2.04	2.886(6)	172.6(2)	[x, y-1, z]

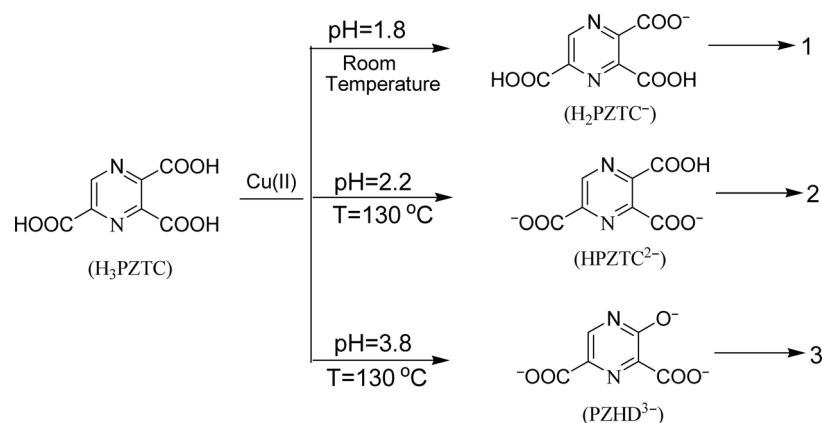
H, 2.47; N, 7.83%. IR (KBr pellet, cm^{-1}): 2960(b), 1668(s), 1509(m), 1446(m), 1387(s), 1348(s), 1189(m), 1140(m), 1060(w), 928(w), 792(w), 711(w).

Synthesis of $[\text{Cu}_2(\text{PZHD})(\text{OH})(\text{H}_2\text{O})_2]_n$ (3**).** A mixture of H_3PZTC (0.025 g, 0.1 mmol), $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (0.048 g, 0.2 mmol), NaN_3 (0.013 g, 0.2 mmol), NaOH (0.15 mL, $0.65 \text{ mol} \cdot \text{L}^{-1}$), and H_2O (10 mL) was put into a 25 mL stainless steel bomb and heated at 130°C for 4 days, then cooled slowly to room temperature. Blue-green crystals of **3** were obtained by filtration. Yield: 54.2%. Anal. Calc. for $\text{C}_6\text{H}_6\text{Cu}_2\text{N}_2\text{O}_8$: C, 19.93; H, 1.66; N, 7.76. Found: C, 19.66;

H, 2.15; N, 8.14%. IR (KBr pellet, cm^{-1}): 3365(b), 1665(s), 1584(m), 1508(s), 1382(s), 1314(m), 1201(s), 1126(w), 973(w), 824(m), 712(w).

Results and Discussion

Syntheses. As shown in Scheme 1, complexes **1**, **2** and **3** were obtained from the $\text{Cu}(\text{II})/\text{H}_3\text{PZTC}$ system under different synthetic conditions. In the routine condition, complex **1** was prepared by refluxing the aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and H_3PZTC with the pH value of 1.8. In

**Scheme 1.** Simplified routes of syntheses for complexes **1-3**.

the complex, only one carboxylate group of H_3PZTC ligand is deprotonated, which is transformed into H_2PZTC^- anion. Furthermore, the H_2PZTC^- anion linked $\text{Cu}(\text{II})$ ions into 1D double chain structure. Different from the procedure of **1**, complex **2** was obtained with two carboxylate groups of H_3PZTC ligand deprotonated under hydrothermal condition with the synthetic temperature of 130°C and pH of 2.2. In the complex, the H_3PZTC is transformed into HPZTC^{2-} dianion, which coordinates with $\text{Cu}(\text{II})$ ions to form 1D zigzag chain structure. Complex **3** was obtained at pH value of 3.8 and with the same temperature as that for complex **2**. In **3**, H_3PZTC ligand was converted to 2-hydroxypyrazine-3,5-dicarboxylic acid (PZHD) by *in situ* decarboxylation and hydroxylation reaction. The PZHD ligand further connects the $\text{Cu}(\text{II})$ ions to form 2D layer structure. The results indicate that the formation of complexes **1-3** shows significant dependence on synthesis conditions, such as temperature and pH value etc. Higher temperature and higher pH favors *in situ* $\text{Cu}(\text{II})/\text{H}_3\text{PZTC}$ reaction. In the *in situ* metal/ligand reaction, the PZHD ligand has not been prepared in organic synthesis field yet. This shows that the *in situ* metal/ligand reaction can act as a bridge between coordination chemistry and organic synthesis.

In addition, it is noteworthy that both complexes **2** and **3** have been successfully prepared in the presence of NaN_3 , but the NaN_3 was not coordinated to $\text{Cu}(\text{II})$ ions. When we try to synthesize complexes **2** and **3** at the same condition except without NaN_3 , no single-crystal appropriated were obtained. Meanwhile, when we try to synthesize the complexes at the same pH value, which was adjusted by NaOH solution, no such product were obtained. Even though the mechanism is not very clear, but this may suggest that NaN_3 play a role in adjusting the microenvironment of the system and promote the formation of single-crystals. The mechanism of action deserves further discussion.

Structural Description of $[\text{Cu}(\text{H}_2\text{PZTC})_2]_n \cdot 2n\text{H}_2\text{O}$ (**1**).

The asymmetric unit of **1** consists of one half $\text{Cu}(\text{II})$ atom, one partially deprotonated H_2PZTC^- anion and one lattice water molecule. The $\text{Cu}(\text{II})$ atom lies on the inversion center

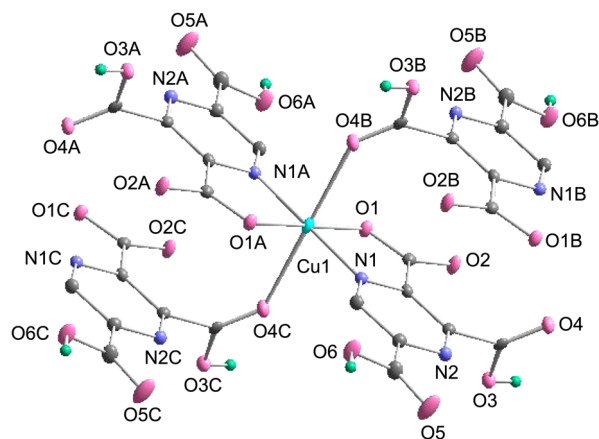
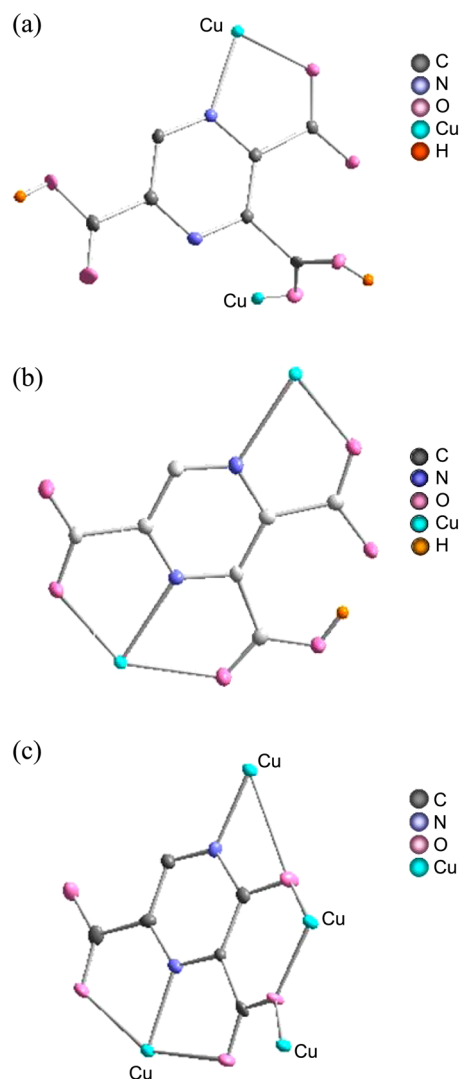


Figure 1. The coordination environment of $\text{Cu}(\text{II})$ ion in **1** drawn at 50% probability level. All non-protonated hydrogen atoms and lattice-water molecules are omitted for clarity.

and is coordinated with four O atoms and two N atoms (see Fig. 1). The equatorial plane contains four perfectly coplanar atoms, O1 and O1A [$\text{Cu}-\text{O1}$ (O1A) = $1.9543(15) \text{ \AA}$] from two carboxylate groups of two H_2PZTC^- anions, N1 and N1A [$\text{Cu}-\text{N1}$ (N1A) = $1.9931(18) \text{ \AA}$] from two H_2PZTC^- anions. O4B and O4C [$\text{Cu}-\text{O4B}$ (O4C) = $2.3978(15) \text{ \AA}$] from two protonated carboxylate groups of two H_2PZTC^- anions occupy the axial sites with the $\text{O4B}-\text{Cu1}-\text{O4C}$ angle of 180.0° . Thus, $\text{Cu}(\text{II})$ atom displays distorted octahedral coordination environment.

In complex **1**, the H_3PZTC ligand only loses one proton, which is transformed into H_2PZTC^- anion. Each H_2PZTC^- anion adopts tridentate modes to coordinate with two Cu atoms (see Scheme 2a). Atom O1 of the deprotonated carboxylate group and atom N1 of pyrazine ring adopt bidentate chelating mode to connect one Cu atom. Atom O4 of one protonated carboxylate group links the other Cu atom. The remaining protonated carboxylate group is free. To the best of our knowledge, this type of coordination mode for H_2PZTC^- ligand has not been reported in the literatures.

In this way, each Cu atom is connected by the H_2PZTC^-



Scheme 2. Coordination modes of the ligands in complexes **1-3**.

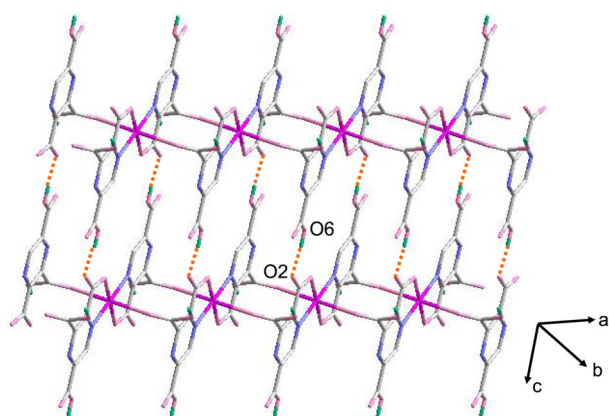


Figure 2. Supramolecular structure of **1** containing the hydrogen bonds.

anions to form infinite 1-D double chain along the *a*-axis direction. These chains are further linked by hydrogen bonds ($\text{O6-H6}\cdots\text{O2}$, 2.554(2) Å, 171.9(2)°) with protonated carboxylate groups as donors and deprotonated carboxylate groups as acceptors into 2D supramolecular network along the *a*-axis (see Fig. 2). Free water molecules reside between the layers and involve in the formation of hydrogen bonds between the protonated carboxylate groups and the uncoordinated nitrogen atom, which further build up the three-dimensional supramolecular network.

Structural Description of $[\text{Cu}(\text{HPZTC})\cdot 2\text{H}_2\text{O}]_n\cdot 2n\text{H}_2\text{O}$ (2**).** The asymmetric unit of **2** consists of one Cu(II) atom, one HPZTC^{2-} dianion and two coordinated water molecules together with two lattice water molecules. Cu(II) atom is seven-coordinated with a N_2O_5 donor set and displays distorted pentagonal bipyramidal geometry (see Fig. 3). Five basal positions are filled with N1, O1, O6, N2A and O3A atoms from two HPZTC^{2-} dianions. The Cu-O bond lengths are in the range of 2.1939 (17) to 2.3012(17) Å. The Cu-N bond distances are 2.241(2) Å and 2.397(2) Å. The axial sites are filled with two aqua oxygen atoms (O7 and O8), the Cu-O distances are 2.0271(16) Å and 2.0329(16) Å, the angle of O7–Cu1–O8 is 173.30(7)°.

Different from **1**, HPZTC^{2-} dianion in **2** is formed from H_3PZTC by losing two protons. Each HPZTC^{2-} dianion links two Cu atoms (see Scheme 2b) in pentadentate modes:

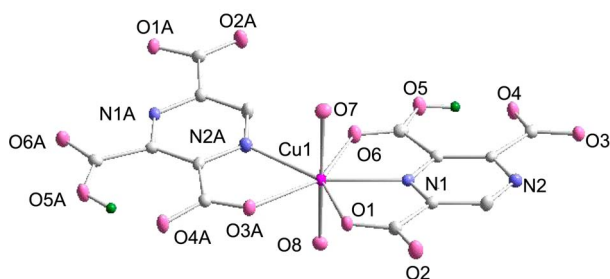


Figure 3. The coordination environment of Cu(II) ion in **2** drawn at 50% probability level. All hydrogen atoms except the not deprotonated (green ball) and lattice-water molecules are omitted for clarity.

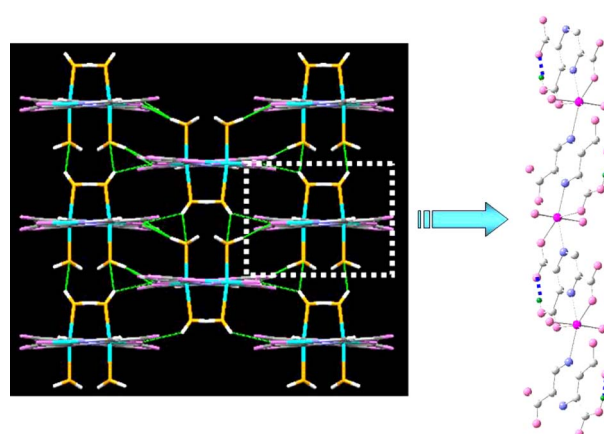


Figure 4. 3D supramolecular network of **2** viewed along the *c*-axis direction.

pyrazine nitrogen atom (N1) and two neighboring oxygen atoms (O1 and O6) of carboxylate groups connect one Cu atom, the other nitrogen atom (N2) of pyrazine ring and oxygen atom (O3) of the third carboxylate group link the second Cu atom. Thus, a one-dimensional (1D) polymeric zigzag chain is formed along *c*-axis direction. In the 1D chain, intra-molecular hydrogen bonds ($\text{O5-H5}\cdots\text{O4}$, 2.399(2) Å, 168.0(5)°) exist between protonated and deprotonated neighboring carboxylate groups. Each 1D zigzag chain is further linked with six neighbors *via* hydrogen bonds ($\text{O7-H7B}\cdots\text{O8}$, 3.015(2) Å, 138.7(2); $\text{O7-H7B}\cdots\text{O3}$, 2.881(2) Å, 130.1(2)°; $\text{O8-H8A}\cdots\text{O1}$, 2.729(2) Å, 163.2(2)°) between coordinated water molecules and oxygen atoms of carboxylate groups into 3D supramolecular network containing small 1D channels viewed along *c*-axis (see Figure 4). The free water molecules reside in channel spaces and form hydrogen bonds with the carboxylate groups and coordinated water molecules, which further stabilize the structure.

Structural Description of $[\text{Cu}_2[(\text{PZHD})(\text{OH})(\text{H}_2\text{O})_2]]_n$ (3**).** Asymmetric unit of complex **3** consists of two crystallographically independent Cu atoms, one PZHD ligand, two coordinated water molecules and one hydroxyl group. The coordination environments of Cu atoms are shown in Figure

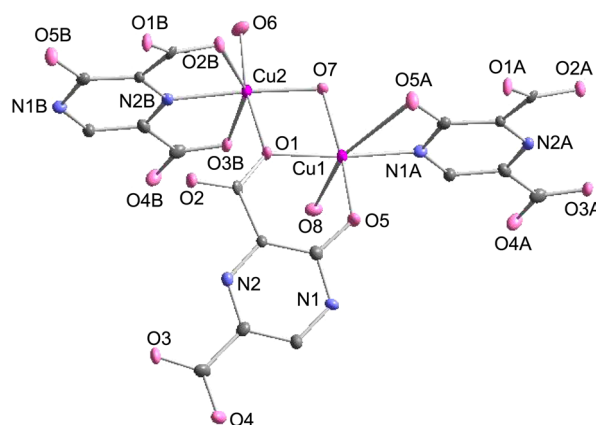


Figure 5. The coordination environments of Cu(II) ions in **3** drawn at 50% probability level. All hydrogen atoms and lattice-water molecules are omitted for clarity.

5. Cu1 atom is six-coordinated with a NO5 donor set; the equatorial plane contains atoms O1, O5, N1A [Cu1–O1 = 1.983(3) Å, Cu1–O5 = 1.921(4) Å, Cu1–N1A = 1.994(4) Å] from two PZHD ligands, and O7 [Cu1–O7 = 1.916(4) Å] from hydroxyl group. Atoms O8 and O5A [Cu1–O8 = 2.493(4) and Cu1–O5A = 2.706(4) Å] occupy the axial sites, which from water molecule and carboxylate group of PZHD ligand with the O8–Cu1–O5A angle of 155.41(13)°. Thus, the coordination environment of Cu1 can be described as distorted octahedron. Cu2 atom is also six-coordinated with a NO5 donor set, and displays distorted octahedral geometry, but the coordination environment is different. The basal plane contains atoms O2B, O3B and N2B [Cu2–O2B = 2.382(4) Å, Cu2–O3B = 2.383(4) Å, Cu2–N2B = 2.014(4) Å] from the same one PZHD ligand, and atom O7 [Cu2–O7 = 1.937(3) Å] from hydroxyl group. The axial sites are occupied by atoms O1 and O6 [Cu2–O1 = 2.058(4) and Cu2–O6 = 1.957(4) Å] from carboxylate group of the other PZHD ligand and one water molecule. The angle of O6–Cu2–O1 is 169.18(15)°.

In complex **3**, each PZHD ligand adopts octadentate mode to bind four Cu atoms, as shown in Scheme 2c: one pyrazine nitrogen atom together with two adjacent carboxylate oxygen atoms coordinate one Cu(II) atom, the other one pyrazine nitrogen atom and the adjacent hydroxyl group oxygen atom coordinate the second Cu(II) atom. Simultaneously, the hydroxyl group oxygen atom and the adjacent carboxylate group oxygen atom link the third Cu(II) atom, the same carboxylate oxygen atom link the fourth Cu(II) atom. This kind of coordination mode for PZHD ligand is different from our previously reported.²¹ As a result, PZHD ligands connect the Cu(II) atoms into 2D layer structure (see Fig. 6).

In the 2D layer structure, there are two different rings, one is 4-membered ring containing the {Cu₂O₂} unit. In the {Cu₂O₂} unit, Cu(II) atoms are linked by carboxylate μ_2 -O bridge and μ_2 -OH bridge, the Cu–Cu separation is 3.015(12) Å. The other is the 14-membered ring containing five Cu atoms. Furthermore, these layers are assembled *via* hydrogen bonds into 3D supramolecular network.

Thermal Stability Analyses. In order to test the thermal stability of the title complexes **1–3**, the thermogravimetric analysis of them were carried out. For complex **1**, the thermal decomposition process shows two steps: the first weight loss of 7.22%, which occurred between 49 and 108

°C, corresponds to the release of two water molecules (calculated: 6.70%). As temperature rose, no obvious plateau appeared indicating that complex **1** continued to decompose and finally CuO power was obtained with 16.03% (calculated: 15.90%).

For complex **2**, the thermal decomposition process displays three steps: the first weight loss of 13.33% occurring between 146 and 212 °C may correspond to the release of two uncoordinated water molecules and 0.5 coordinated water molecules (calculated: 13.02%). And then the second weight loss of 34.82% (calcd 33.27%) between 262 and 315 °C may correspond to release of the remaining 1.5 coordinated water molecules and two carboxylate groups. The framework collapsed rapidly above the temperature 315 °C.

For complex **3**, a complicated decomposition reaction takes place. The first weight loss started at 108 °C, as temperature rose, decomposition continued and no obvious plateau appeared, which indicates that not strong boundaries between the losing water molecules and PZHD ligands. This shows that hydrogen bonds play an important role in the assembly of the 3D supramolecular network from 2D metal-organic framework.

Conclusions

Three new copper complexes were synthesized from Cu(II)/H₃PZTC system under different synthetic conditions, and characterized by single-crystal X-ray diffraction. Structure analyses of the title complexes have show that three carboxylate groups of H₃PZTC ligand are very sensitive to pH values, and can partially or fully deprotonate under different pH values. In complexes **1** and **2**, H₃PZTC ligands loose one and two protons at pH = 1.8 and 2.2, respectively. Such behavior of deprotonation at different acidity can help us to investigate the pH effect on the formation of coordination networks. In complex **3**, H₃PZTC ligand converted into PZHD by *in situ* decarboxylation and hydroxylization reaction under hydrothermal condition with the synthetic temperature at 130 and pH = 3.3. The study on Cu/H₃PZTC system has shown that the final reaction product is significantly affected by the preparation conditions.

Supplementary Materials. Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary publication: CCDC Nos. 759021–759023 for **1–3**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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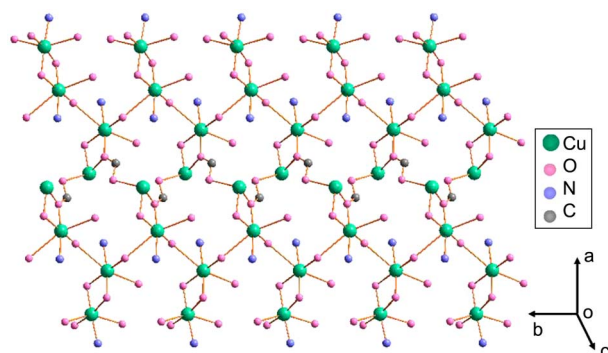


Figure 6. The 2D metal-organic framework of **3**.

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