两种新型 Cu(II)混配聚合物的合成和晶体结构

陈金喜* 刘保花 孟伟伟 (东南大学化学化工学院,南京 211189)

摘要:用水热法合成了 2 种新型的配位聚合物[Cu(4-Pya)(2,4-PydcH)]_n (1)和[Cu₂(2,6-Ndc)₂(Bpobp)]_n (2)(4-Hpya=4-吡啶羧酸,2,4-pydcH₂=吡啶-2,4-二羧酸,2,6-H₂ndc=2,6-萘二酸,Bpobp=4,4'-二(3-吡啶羟基)-联苯胺),并测定了其晶体结构。1 属于正交晶系, $Pna2_1$ 空间群,晶胞参数 a=2.138 20(2) nm,b=0.990 60(1) nm,c=0.608 40(1) nm,V=1.288 65(3) nm³,Z=4, R_1 =0.023, R_2 =0.067。2 属于三斜晶系,P1 空间群,晶胞参数 a=0.810 2(3) nm,b=0.997 9(4) nm,c=1.270 5(5) nm, α =86.282(6)°, β =73.517(5)°, γ =89.107(6)°,V=0.982 9(7) nm³,Z=2, R_1 =0.082,R=0.160 2。配合物 1 为三维结构,其中五配位的铜为扭曲的四方锥构型。配合物 2 展示了由车轮状二铜结构单元连接而成的非互穿的三维网络结构。

关键词:配位聚合物;水热合成法;晶体结构

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Synthesis and Crystal Structures of Two Novel Copper(II) Coordination Polymers Constructed from Different Ligands

CHEN Jin-Xi* LIU Bao-Hua MENG Wei-Wei

(School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189)

Abstract: Two novel coordination polymers of $[Cu(4-Pya)(2,4-PydcH)]_n$ (1) and $[Cu_2(2,6-Ndc)_2(Bpobp)]_n$ (2) (4-Hpya=4-pyridinecarboxylic acid, 2,4-pydcH₂ =pyridine-2,4-dicarboxylic acid, 2,6-Ndc =2,6-naphthalenedicarboxylate, Bpobp=4,4'-bis(3-pyridoxy)-biphenyl)) have been hydrothermally prepared by the reaction of $Cu(NO_3)_2 \cdot 3H_2O$ and mixed ligands, and characterized by single crystal X-ray diffraction. 1 crystallizes in the orthorhombic system, and the space group is $Pna2_1$, with the crystal cell parameters a=2.138 20(2) nm, b=0.990 60(1) nm, c=0.608 40(1) nm, V=1.288 65(3) nm³, Z=4, R_1 =0.023, wR_2 =0.067. 2 crystallizes in the triclinic system with space group $P\overline{1}$, a=0.810 2(3) nm, b=0.997 9(4) nm, c=1.270 5(5) nm, α =86.282(6)°, β =73.517(5)°, γ =89.107(6)°, and V=0.982 9(7) nm³, Z=2, R_1 =0.082, wR_2 =0.160 2. Complex 1 displays a three-dimensional framework, in which the five-coordinated Cu^{2+} shows distorted square pyramidal geometry. Complex 2 reveals a noninterpenetrating three-dimensional framework structure based on the dicopper paddle-wheel building units. CCDC: 770496, 1; 770497, 2.

Key words: coordination polymer; hydrothermally prepare; crystal structure

0 Introduction

The field of coordination polymers has attracted considerable interest at present^[1-3]. Coordination poly-

mers exhibit various types of properties such as zeolitic behavior, electrical conductivity, luminescence, non-linear optics, catalysis, magnetism etc^[1-2]. Generally, transition metal ions act as excellent connectors due to

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^{*}通讯联系人。E-mail:chenjinxi@seu.edu.cn;会员登记号:S060019162M。

第一作者:陈金喜,男,39岁,教授;研究方向:配位化学。

their versatility in coordination geometry as well as number. Much attention has been given to the synthesis of one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) extended materials involving copper^[4-11].

The development of synthetic routes to systems containing two or more different bridging ligands is very challenging subject^[12-14]. A guiding principle of our work is the attempt to construct the products containing heteroleptic bridging ligands. As a ligand, pyridine-2,4dicarboxylic acid has unique feature that its adjacent carboxylate groups are with an angle of 120° and exhibits different coordination modes. The aforesaid organic anions can coexist with neutral organic ligands, containing two or more pyridyl groups separated by rigid or flexible spacers, such as 4,4'-bipyridine, 1,2bis(4'-pyridyl) propane etc, have been used to generate an affluent variety of metal-organic architectures [15-17]. Noticeably, in complex 1, 2-carboxyl group of part of pyridine-2,4-dicarboxylic acid was decomposed during the hydrothermal reaction process, so the Cu^{2 +} was linked by pyridine-2,4-dicarboxylate and pyridine-4carboxylate, which was rare in the area of coordination polymers.

Rigid ligands produce robust 2D grids with metal ions, 3D open framework can be easily obtained through flexible ligands link these grids. Our exploration of the hydrothermal chemistry of the Cu-2,6-Ndc-Bpobp system has obtained a novel coordination polymer [Cu₂(2,6-Ndc)₂(Bpobp)]_n. Herein, we report two coordination polymers of [Cu(4-Pya)(2,4-Pydc)]_n (1) and [Cu₂(2,6-Ndc)₂(Bpobp)]_n (2) synthesized in hydrothermal conditions in high purity and good yield.

1 Experimental

1.1 Materials and instruments

Commercially available solvents and chemicals were used without further purification. Infrared (IR) spectra were recorded from KBr pellets in the range of 400~4 000 cm⁻¹ on a Nicolet Avatar 360 FTIR spectrometer. Elemental analyses were performed on a Vario El elemental analyzer. The crystal structure was performed with Bruker Smart Apex II CCD single-

crystal diffractometer.

1.2 Synthesis of coordination polymers

1.2.1 Synthesis of $[Cu(4-Pya)(2,4-PydcH)]_n$ (1)

The title compound was synthesized by the hydrothermal reaction of $Cu(NO_3)_2 \cdot 3H_2O$ (0.6 mmol, 0.145 0 g), pyridine-2,4-dicarboxylic acid (0.5 mmol, 0.083 6 g) and H_2O (5 mL) in a Teflon-lined autoclave, at the beginning, the temperature rose to 180 °C through 3 h, then heated at 180 °C for 3 days. After the reaction autoclave was slowly cooled to room temperature for 24 h, blue block single crystals suitable for X-ray diffraction analysis were obtained, isolated by filtration and washed with water. Elemental microanalysis (%) Cacld. for $C_{13}H_8CuN_2O_6$: C, 44.35; H, 2.27; N, 7.96. Found: C, 44.12; H, 2.41; N, 7.78. IR (KBr): ν (cm⁻¹), 3 449.3, 3 069.4, 1 707.0, 1 633.1, 1 558.4, 1 503.5, 1 423.5, 1 365.3, 1 321.1, 1 234.5, 1 211.5, 1 069.7, 1 034.6, 870.1, 840.7, 774.3.

1.2.2 Synthesis of $[Cu_2(2,6-Ndc)_2(Bpobp)]_n$ (2)

In a typical synthesis of $[Cu_2(2,6\text{-Ndc})_2(Bpobp)]_n$, a mixture of 1 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ with 0.5 mmol of 2,6-naphthalenedicarboxylic acid and 0.5 mmol 4,4′-bis(3-pyridoxy)-biphenyl in 8 mL water was sealed in a 23 mL Teflon-lined steel vessel and then was heated at 160 °C for 72 h. Overnight cooling of the resulting solution in the vessel yielded a green microcrystalline solid with some suitable single crystals for X-ray structure determination. Elemental microanalysis (%) Cacld. for $C_{23}H_{14}CuNO_5$: C, 61.62; H, 3.13; N, 3.13. Found: C, 61.91; H, 3.01; N, 3.26. IR (KBr): ν (cm⁻¹), 3 448.8, 3 071.6, 1 578.0, 1 492.5, 1 477.4, 1 406.2, 1 356.8, 1 245.5, 1 191.2, 1 166.8, 1 102.6, 922.9, 878.6, 813.9, 783.9, 699.6, 504.5.

1.3 Determination of crystal structures

A blue single crystal of **1** with dimension 0.2 mm× 0.3 mm×0.3 mm and green single crystal of **2** with dimension 0.1 mm×0.1 mm×0.1 mm were employed for data collection at 293 K on a BRUKER SMART APEX II diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ =0.071 073 nm) in an ω scan mode. For complex **1**, a total of 2 099 reflections and 2 099 unique ones were collected in the range of 2.80° $\leq \theta \leq$ 30.50°, of which 2 083 observed reflections with

 $I>2\sigma(I)$ were used in the succeeding structural calculations. For complex **2**, a total of 4 131 reflections and 3 411 unique ones were collected in the range of 1.67° $\leq \theta \leq 25.01^{\circ}$ with R_{int} =0.049 5, of which 2 400 observed reflections with $I>2\sigma(I)$ were used in the succeeding structural calculations. The structures were solved by direct method and subsequent difference Fourier syntheses. The non-hydrogen atoms were refined by full-matrix least-squares techniques on F^2 with anisotropic thermal parameters. All calculations were carried out with SHELX-97 program^[18].

The complex **1** belongs to orthorhombic system, and the space group is $Pna2_1$, with the crystal cell parameters a=2.138 20(2) nm, b=0.990 60(1) nm, c=0.608 40(1) nm, and V=1.288 65(3) nm³, M_r =351.75, D_c =1.813 Mg·m³, μ =1.729 mm³, F (000) =708, R_1 [I>2 σ (I)]=0.023, wR_2 [I>2 σ (I)]=0.067, S=1.106, $\Delta \rho_{max}$ =275 e·nm³, and $\Delta \rho_{min}$ =-802 e·nm³. **2** crystallizes in the triclinic system with space group $P\bar{1}$, a=0.810 2 (3) nm, b=0.997 9(4) nm, c=1.270 5(5) nm, α =86.282(6)°, β =73.517(5)°, γ =89.107(6)°, and V=0.982 9(7) nm³, Z=2, M_r =447.89, D_c =1.513 Mg·m³³, μ =1.147 mm¹¹, F(000)

=456, R_1 [$I > 2\sigma(I)$]=0.082, wR₂ [$I > 2\sigma(I)$]=0.160 2, S = 1.086, $\Delta \rho_{\text{max}}$ =692 e·nm⁻³, and $\Delta \rho_{\text{min}}$ =-698 e·nm⁻³.

CCDC: 770496, 1; 770497, 2.

2 Results and discussions

2.1 IR spectra

The infrared spectra of [Cu (4-Pya) (2,4-PydcH)]_n show the presence of the vibrational bands characteristic of the -OH groups at 3 449.3 cm⁻¹. The characteristic absorptions near 1 558.4, 1 503.5, and 1 423.5 cm⁻¹ are attributed to the carboxyl groups. The band at 1 707 cm⁻¹ is assigned to the O-H vibrations of COOH groups.

The infrared spectra of $[Cu_2(2,6\text{-Ndc})_2(B\text{pobp})]_n$ clearly show the presence of the vibrational bands characteristic of the -(O-C-O)- groups around 1 578 and 1 477 cm⁻¹, confirming the presence of the dicarboxylate within the compounds.

2.2 Crystal structures

The crystal data and structure refinement parameters for 1 and 2 are given in Table 1. The selected bond distances and angles for 1 are given in Table 2 and for 2 in Table 3.

Table 1 Crystal data and structure refinement parameters for 1 and 2

| | 1 | 2 |
|--|---------------------|----------------------|
| Empirical formula | $C_{13}H_8O_6N_2Cu$ | $C_{23}H_{14}O_5NCu$ |
| Formula weight | 351.75 | 447.89 |
| Crystal size / mm | 0.20×0.30×0.30 | 0.10×0.10×0.10 |
| T / K | 293(2) | 293(2) |
| $\mu(\text{Mo }K\alpha)$ / nm | 0.071 073 | 0.071 073 |
| Crystal system | Orthorhombic | Triclinic |
| Space group | $Pna2_1$ | $P\overline{1}$ |
| a / nm | 2.138 20(2) | 0.810 2(3) |
| <i>b</i> / nm | 0.990 60(1) | 0.997 9(4) |
| c / nm | 0.608 40(1) | 1.270 5(5) |
| α / (°) | | 86.282(6) |
| β / (°) | | 73.517(5) |
| γ / (°) | | 89.107(6) |
| Flack | 0.067(12) | |
| V / nm^3 | 1.288 65(3) | 0.982 9(7) |
| Z | 4 | 2 |
| $D_{\rm c}$ / (Mg·m ⁻³) | 1.813 | 1.513 |
| μ / mm ⁻¹ | 1.729 | 1.147 |
| F(000) | 708 | 456 |
| θ range for data collection / (°) | 2.80~30.50 | 1.67~25.01 |

| Continued | |
|-----------|--|
| | |
| | |

| Limiting indices | $0 \le h \le 30, 0 \le k \le 14, 0 \le l \le 8$ | $-9 \le h \le 8, -11 \le k \le 9, -15 \le l \le 14$ |
|---|---|--|
| Reflections collected / unique $(R_{ m int})$ | 2 099 / 2 099 (0.000 0) | 4 131 / 3 411 (0.049 5) |
| Completeness to $\theta = 30.50^{\circ}$ / % | 98.00 | 98.40 |
| Refinement method | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2 099 / 0 / 223 | 3 411 / 0 / 265 |
| Goodness-of-fit on \mathbb{F}^2 | 1.106 | 1.067 |
| Final R indices $[I>2\sigma(I)]$ | $R_1^{\text{a}}=0.023 \ 3, \ wR_2^{\text{b}}=0.067 \ 1$ | $R_1^a = 0.082 \ 0, \ wR_2^b = 0.160 \ 2$ |
| R indices (all data) | $R_1^{\text{a}}=0.023 5, wR_2^{\text{b}}=0.067 4$ | $R_1^{\text{a}}=0.122 \text{ 8, } wR_2^{\text{b}}=0.179 \text{ 8}$ |
| Largest diff. peak and hole / $(e \cdot nm^{-3})$ | 275 and -802 | 692 and -698 |

 $^{^{}a}R = \sum ||F_{o}| - |F_{c}|| \sum |F_{o}|; wR (F^{2}) = [\sum w(F_{o}^{2} - F_{c}^{2})^{2}/\sum w(F_{o}^{2})^{2}]^{1/2}; w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0506P)^{2} + 0.2363P], \text{ where } P = (\text{Max}(F_{o}^{2}, 0) + 2F_{c}^{2})/3 \text{ for } \mathbf{1}; w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0731P)^{2} + 1.2558P], \text{ where } P = (\text{Max}(F_{o}^{2}, 0) + 2F_{c}^{2})/3 \text{ for } \mathbf{2}.$

Table 2 Selected bond lengths (nm) and bond angles (°) for 1

| Cu(1)-O(1) | 0.194 83(15) | Cu(1)-O(5) | 0.201 09(14) | Cu(1)-N(2)b | 0.197 34(16) |
|-------------------------------------|--------------|-------------------------------|--------------|--|--------------|
| Cu(1)-O(2) ^a | 0.224 33(15) | Cu(1)-N(1) | 0.199 69(15) | | |
| O(1)-Cu(1)-N(1) | 82.85(6) | N(2)b-Cu(1)-O(2) ^a | 89.93(6) | N(2)b-Cu(1)-O(5) | 88.93(7) |
| N(2)b-Cu(1)- $N(1)$ | 175.85(7) | $N(1)$ - $Cu(1)$ - $O(2)^a$ | 94.17(6) | N(1)- $Cu(1)$ - $O(5)$ | 91.25(6) |
| O(1)- $Cu(1)$ - $N(2)$ ^b | 95.49(7) | $O(5)$ - $Cu(1)$ - $O(2)^a$ | 97.08(6) | $\mathrm{O}(1)\text{-}\mathrm{Cu}(1)\text{-}\mathrm{O}(2)^a$ | 103.99(6) |
| O(1)-Cu(1)-O(5) | 158.45(7) | | | | |

Symmetry transformations used to generate equivalent atoms: a -x, -y+2, z+1/2; b -x+1/2, y+1/2, z-1/2.

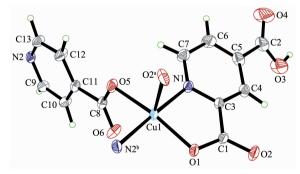
Table 3 Selected bond lengths (nm) and bond angles (°) for 2

| | | 8 \ | , , | , , , | |
|-------------------------|------------|------------------------------|------------|---|------------|
| Cu(1)-O(1) ^a | 0.195 0(5) | Cu(1)-O(3) | 0.197 9(5) | Cu(1)-N(1) | 0.214 1(5) |
| Cu(1)-O(2) | 0.197 6(5) | Cu(1)-O(4) ^a | 0.198 3(5) | | |
| O(1)a-Cu(1)-O(2) | 167.00(19) | O(2)-Cu(1)-O(4) ^a | 89.8(2) | O(3)-Cu(1)-N(1) | 90.2(2) |
| O(1)a-Cu(1)-O(3) | 90.5(2) | $O(3)$ - $Cu(1)$ - $O(4)^a$ | 166.8(2) | O(4)a-Cu(1)-N(1) | 102.9(2) |
| O(2)-Cu(1)-O(3) | 88.8(2) | O(1)a-Cu(1)-N(1) | 100.1(2) | $\mathrm{O}(1)\mathrm{a}\text{-}\mathrm{Cu}(1)\text{-}\mathrm{O}(4)^{\mathrm{a}}$ | 87.9(2) |
| O(2)-Cu(1)-N(1) | 92.8(2) | | | | |

Symmetry transformations used to generate equivalent atoms: $^a -x$, -y, -z+2.

The molecular structure of the complex 1 is shown in Fig.1. Complex 1 displays a three-dimensional framework, in which the asymmetric unit consists of one pyridine-2,4-dicarboxylate anion, one pyridine-4-carboxylate anion, and one copper cation. There is one crystallographically independent copper atom, which is surrounded by five atoms coming from the two different bridging ligands. The five-coordinated Cu²⁺ shows a distorted square pyramidal geometry. Here, two basal coordination sites are occupied by one nitrogen and one of the carboxylate oxygen atom of pyridine-2,4-dicarboxylic acid ligand and other two basal coordination sites are occupied by one nitrogen and one of the carboxylate oxygen atom of pyridine-4-carboxylic

acid ligand which bridges another copper(II) center. The apical coordination site is occupied by the carboxylate oxygen atom coming from another pyridine-2,4-



Symmetry transformations: a -x, -y+2, z+1/2; b -x+1/2, y+1/2, z-1/2

Fig. 1 Coordination environment of the copper atom in the polymer ${\bf 1}$

dicarboxylic acid ligand. The three-dimensional structure of complex 1 is displayed in Fig.2. Noticeably, in complex 1, 2-carboxyl group of part of pyridine-2,4-dicarboxylic acid was decomposed during the hydrothermal reaction process.

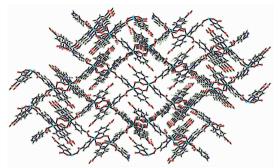


Fig. 2 Three-dimensional framework along the c-axis in the polymer 1

The asymmetric unit of compound **2** is shown in Fig.3. **2** reveals a noninterpenetrating 3D coordination network structure with paddle-wheel $\text{Cu}_2\text{O}_8\text{C}_4$ core, which has a crystallographic inversion centre imposing on the centre of Cu-Cu vector. In the dinuclear core, the copper ions display a distorted square pyramidal geometry with equatorial Cu-O bond lengths that disclose comparable values in a range from 0.195 0(5) to 0.198 1(5) nm. The apical position of each metal is occupied by one N atom from a Bpobp ligand [Cu(1)-N(1)=0.214 3(5)] and the Cu-Cu distance is about 0.266 31(18) nm, which is comparable to those relating discrete bicopper(II) metal-carboxylates^[19]. The metals

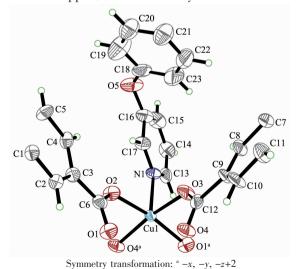


Fig.3 Coordination environment of the copper atom in the polymer 2

are displaced by about 0.026 nm from the mean O₄ basal plane towards the axial N donor. The copper ions adopt a very distorted square pyramidal geometry with the N1-Cu1-Cu(1a) angle is about 167.55(4)°. The paddle-wheel building units are linked by the naphthalene rings to form a 2D (4,4)-layered structure. The sheets are stacked so that 1D channels are formed along [110] with dimensions of 1.298 7×1.298 7 nm (without consideration of Van der Waals radii). The sheets are bridged by flexible ligands, Bpobp, to form the 3D frameworks. Simply, the structure can be imaged by two portions, one is the 2D-sheet formed by naphthalene rings linking the Cu₂O₈C₄ cores, and the other is the ribbon formed by the flexible Boobp ligand bridging the copper center. The ribbons diagonally link the neighboring sheets with distance about 0.364 7 nm, thus formed the 3D coordination network [Cu₂(2.6-Ndc)₂ (Bpobp)_n (Fig.4). The pyridine rings of Bpobp located in the channels.

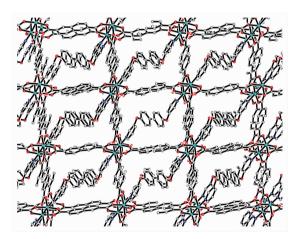


Fig. 4 Three-dimensional framework along the c-axis in the polymer 2

3 Conclusions

In summary, two novel 3D coordination polymers based on copper, [Cu(4-Pya)(2,4-pydcH)]_n (1) and [Cu₂(2,6-Ndc)₂(Bpobp)]_n (2) have been synthesized and characterized. Compound 1 exhibits a three-dimensional framework, in which the five-coordinated Cu²⁺ shows distorted square pyramidal geometry. Compound 2 reveals a noninterpenetrating three-dimensional coordination network structure based on the dicopper paddle-wheel building units.

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