

# Hydrothermal synthesis of two copper helical coordination polymers with acentric three-dimensional framework constructing from mixed pyridine carboxylates

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Received 12 September 2007; received in revised form 30 November 2007; accepted 10 December 2007

Available online 15 December 2007

## Abstract

Two copper helical coordination polymers,  $[\text{Cu}(2\text{-pc})(3\text{-pc})]_n$  **1** and  $[\text{Cu}(2\text{-pc})(4\text{-pc})]_n$  **2** (2-pc = 2-pyridine carboxylate, 3-pc = 3-pyridine carboxylate, 4-pc = 4-pyridine carboxylate) have been hydrothermally synthesized directly from pyridine carboxylic acids and copper nitrate. The crystal structure were determined by single-crystal X-ray diffraction with the following data: compound **1**, orthorhombic,  $P2_12_12_1$ ,  $a = 6.591(3) \text{ \AA}$ ,  $b = 8.692(5) \text{ \AA}$ ,  $c = 20.548(9) \text{ \AA}$ ,  $V = 1177.2(9) \text{ \AA}^3$ ,  $Z = 4$ ; compound **2**, orthorhombic,  $Pna2_1$ ,  $a = 21.160(10) \text{ \AA}$ ,  $b = 9.095(5) \text{ \AA}$ ,  $c = 6.401(3) \text{ \AA}$ ,  $V = 1231.9(11) \text{ \AA}^3$ ,  $Z = 4$ . The acentric three-dimensional (3D) framework of **1** is constructed from right-handed helical Cu(2-pc) chains and left-handed Cu(3-pc) helices. As for **2**, Cu(2-pc) helical chains, in which left- and right-handed helices are coexisting, and Cu(4-pc) zigzag chains combined together to form acentric 3D architecture of **2** as well. Additionally, besides general spectral characterization, we first introduce generalized 2D correlation spectroscopy to explore the coordination polymers and ascertain the stretching vibration location of carboxylate groups of compounds **1** and **2**.

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**Keywords:** Coordination polymers; Helical chains; Copper; Three-dimensional framework

## 1. Introduction

Over the past few decades, there has been intense research effort on metal-organic framework structures (MOFs) in coordination chemistry [1,2]. The rapid development of MOFs not only due to their intriguing structural topologies but fascinating properties such as adsorption, ion-exchange, non-linear optical (NLO) materials and heterogeneous catalysis [3–9].

Meanwhile, the fascination of the structure, potential application in anti-symmetric catalysis, NLO materials and biomimetic chemistry as well as understanding of molecular self-assembly process, have prompted chemists to design and synthesize metal complexes exhibiting helical

architecture recently [10–15]. The self-assembly of helical structure is still a challenging subject due to the difficulty of the selection of optimal components, although considerable strategies have been developed and many coordination polymers with helical structures have been reported [16–24]. Generally, the extended structures based on helical chains can be produced through either connection of neighboring helices to each other via cross-linking or introduction of additional bridging ligands into reaction system [25]. Though deprotonated pyridine carboxylic acids, 2-pc = 2-pyridine carboxylate, 3-pc = 3-pyridine carboxylate and 4-pc = 4-pyridine carboxylate can play above two roles in construction of helical coordination polymers in theory, the reported examples are few [26–30]. Nevertheless it is noteworthy that various bridging types that carboxylate groups (e.g. syn–syn, anti–anti, syn–anti and mono-monodentate and mono-bidentate, etc.) can adapt make them used widely in the field of construction

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MOFs [31–35]. Numerous structures constructed from only one of these three deprotonated or protonated pyridine carboxylic acids or introducing secondary ligands simultaneously have been widely reported [36–45]. However, to the best of our knowledge, the coordination polymers contain any two of above three kinds of pyridine carboxylate at the same time are numberable [46,47]. And what's more, the helical coordination polymers synthesized from two kinds of pyridine carboxylic acids have not been reported before, except one example that crystallized via ligand *in situ* solvothermal hydrolysis [48].

Taking the advantage of above factors, we have successfully synthesized two three-dimensional (3D) helical copper coordination polymers [Cu(2-pc)(3-pc)]<sub>n</sub> **1** and [Cu(2-pc)(4-pc)]<sub>n</sub> **2** by adopting pyridine carboxylic acids and copper nitrate as synthesis source. Both compounds crystallize in non-centrosymmetric space groups, *P2*<sub>1</sub>*2*<sub>1</sub>*2*<sub>1</sub> and *Pna2*<sub>1</sub>, respectively. Additionally, whereas our research group has successfully introduced the generalized 2D correlation spectroscopy proposed by Noda [49–51] to the polyoxometalates (POMs). The results indicate that 2D IR correlation spectroscopy can not only improve to recognize the structure of POMs but provide valuable dynamic information for in-depth study of POMs [52–56]. Now, we try to extend 2D IR correlation spectroscopy to explore the coordination polymers and some interesting results were obtained as well.

## 2. Experimental

### 2.1. General procedures

All analytical reagent grade chemicals were commercially purchased and used without purification. The elemental analyses of C, H, and N were performed with an Elementar Vario EL III elemental analyzer. The IR spectra were recorded with a Perkin-Elmer Spectrum 2000 FT-IR spectrometer in the range of 400–4000 cm<sup>-1</sup> using the KBr pellet technique. In order to get the dynamic IR spectra, the magnetic intensity variation was controlled by a homemade magnetic intensity controller from 2 to 20 mT at intervals of 2 mT. By way of parenthesis introducing, the magnetic intensity was controlled by altering the voltage of Potentiostatic Apparatus which was demarcated by Gauss Meter in advance. 2D IR correlation spectra were obtained by treatment of the series of dynamic spectra with 2D IR correlation analysis software provided by Tsinghua University. The ultraviolet–visible diffuse reflection integral spectrum (UV–vis DRIS) was measured by a Perkin-Elmer Lambda 900 UV–vis spectrometer. Thermo-gravimetric (TG) analyses were conducted on a Perkin-Elmer TGA7 Thermal analyzer in an argon atmosphere with a heating rate of 10 °C min<sup>-1</sup> from room temperature to 800 °C.

### 2.2. Synthesis of compounds

Synthesis of **1**: Cu(NO<sub>3</sub>)<sub>2</sub> · 2H<sub>2</sub>O (0.224 g, 1 mmol) was added to the hot aqueous solution (4 cm<sup>-3</sup>) of 2-pyridine

carboxylic acid (0.061 g, 0.5 mmol) and 3-pyridine carboxylic acid (0.061 g, 0.5 mmol), then the solution was dropped with 15% NaOH to adjust pH with 3.0 value. Finally, the mixture was sealed in a Teflon-lined stainless autoclave and heated at 150 °C for 3 days under autogenous pressure and then cooled to room temperature unaffectedly. Blue block crystals of **1** suitable for X-ray analysis were obtained in about 62% yield (based on Cu). Anal. calc. for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>Cu: C, 46.79 wt%; H, 2.60 wt%; N, 9.10 wt%; Found: C, 46.05 wt%; H, 2.68 wt%; N, 9.34 wt%. IR (KBr, cm<sup>-1</sup>): 3070(w) for ν(C–H); 1653(vs), 1616(vs) and 1603(w) for ν<sub>as</sub>(=COO); 1365(vs) for ν<sub>s</sub>(=COO), 1149(m) and 1048(m) for ν(C–C); 850(m) and 766(s) for γ(C–H); 696(m) for δ(OCO).

Synthesis of **2**: The synthesis method of **2** is similar to **1** except using 4-pyridine carboxylic acid instead of 3-pyridine carboxylic acid. And a mixture of 3 cm<sup>-3</sup> distilled water and 1 cm<sup>-3</sup> anhydrous ethanol was used as solvent. Additionally, the pH value of the solution was adjusted to 2.2 with dropping 15% NaOH as well. Dark blue block crystals of **2** were harvested in 50% yield (based on Cu) suitable for X-ray analysis. Anal. calc. for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>Cu: C, 46.79 wt%; H, 2.60 wt%; N, 9.10 wt%; Found: C, 46.20 wt%; H, 2.77 wt%; N, 9.33 wt%. IR (KBr, cm<sup>-1</sup>): 3064(w) for ν(C–H); 1659(vs), 1614(vs) and 1557(vs) for ν<sub>as</sub>(=COO); 1371(vs) for ν<sub>s</sub>(=COO); 1048(s)

Table 1  
Crystallographic data and structure refinement for **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub> Cu	C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub> Cu
Formula mass	307.74	307.74
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>P2</i> <sub>1</sub> <i>2</i> <sub>1</sub> <i>2</i> <sub>1</sub>	<i>Pna2</i> <sub>1</sub>
<i>a</i> (Å)	6.591(3)	21.160(10)
<i>b</i> (Å)	8.692(5)	9.095(5)
<i>c</i> (Å)	20.548(9)	6.401(3)
<i>V</i> (Å <sup>3</sup> )	1177.2(9)	1231.9(11)
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.736	1.659
<i>Z</i>	4	4
<i>F</i> (000)	620	620
λ(MoKα) (Å)	0.71073	0.71073
θ range (°)	3.07–27.47	3.66–27.48
Limiting indices	–8 ≤ <i>h</i> ≤ 8 –11 ≤ <i>k</i> ≤ 11 –24 ≤ <i>l</i> ≤ 26	–26 ≤ <i>h</i> ≤ 27 –11 ≤ <i>k</i> ≤ 11 –6 ≤ <i>l</i> ≤ 8
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.013	1.096
Collected reflections	9974	10563
Independent reflections ( <i>R</i> <sub>int</sub> )	2693(0.0692)	2591(0.0560)
observed reflections ( <i>I</i> > 2σ( <i>I</i> ))	2232	2043
Final <i>R</i> factors ( <i>I</i> > 2σ( <i>I</i> ))	<i>R</i> <sub>1</sub> <sup>a</sup> = 0.0402 w <i>R</i> <sub>2</sub> <sup>b</sup> = 0.0755	<i>R</i> <sub>1</sub> <sup>a</sup> = 0.0389 w <i>R</i> <sub>2</sub> <sup>b</sup> = 0.0914
Final <i>R</i> factors (all data)	<i>R</i> <sub>1</sub> = 0.0550 w <i>R</i> <sub>2</sub> = 0.0810	<i>R</i> <sub>1</sub> = 0.0563 w <i>R</i> <sub>2</sub> = 0.1093
Largest difference map peak and hole e Å <sup>-3</sup>	0.405 and –0.573	0.375 and –0.373

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2)]^2} \right\}^{1/2}$$

for  $\nu(\text{C}-\text{C})$ ; 841(s), 760(m) and 710(s) for  $\gamma(\text{C}-\text{H})$ ; 696(s), 696(m) for  $\delta(\text{OCO})$ .

### 2.3. X-ray crystallography

The reflection intensities for **1** and **2** were collected on a Rigaku Weissenburg IP diffractometer with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at  $298 \pm 2 \text{ K}$ . Lp correction and a  $\psi$  empirical absorption correction were made for the intensity data. The structures of both crystals were solved by the direct methods and successive Fourier difference syntheses, and refined by the full-matrix least-squares method on  $F^2$  with anisotropic displacement parameters for all non-hydrogen atoms. The remaining hydrogen atoms were generated geometrically and not refined. The isotropic

displacement parameters of all hydrogen atoms were defined as  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . Further details of the crystallographic data and structure refinement for both are tabulated in Table 1. Selected bond lengths and angles are listed in Table 2. All calculations were performed on a computer with SHELXTL-PC program package [57,58].

Table 2  
Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **1** and **2**

Compound 1		Compound 2	
Cu(1)–O(1)	1.961(3)	Cu(1)–O(3)	1.952(3)
Cu(1)–O(4)#1	1.968(3)	Cu(1)–O(1)#3	1.970(3)
Cu(1)–N(2)	1.992(3)	Cu(1)–N(1)	1.988(4)
Cu(1)–N(1)	1.994(3)	Cu(1)–N(2)	1.991(4)
Cu(1)–O(2)#2	2.268(3)	Cu(1)–O(4)#4	2.224(4)
O(1)–Cu(1)–O(4)#1	165.05(12)	O(3)–Cu(1)–O(1)#3	164.18(17)
O(1)–Cu(1)–N(2)	91.77(12)	O(3)–Cu(1)–N(1)	92.54(15)
O(4)#1–Cu(1)–N(2)	91.91(12)	O(1)#3–Cu(1)–N(1)	89.38(14)
O(1)–Cu(1)–N(1)	82.15(12)	O(3)–Cu(1)–N(2)	82.66(14)
O(4)#1–Cu(1)–N(1)	92.26(12)	O(1)#3–Cu(1)–N(2)	93.67(15)
N(2)–Cu(1)–N(1)	170.70(14)	N(1)–Cu(1)–N(2)	172.41(17)
O(1)–Cu(1)–O(2)#2	104.21(12)	O(3)–Cu(1)–O(4)#4	101.21(17)
O(4)#1–Cu(1)–O(2)#2	90.29(11)	O(1)#3–Cu(1)–O(4)#4	94.53(16)
N(2)–Cu(1)–O(2)#2	89.82(12)	N(1)–Cu(1)–O(4)#5	88.70(15)
N(1)–Cu(1)–O(2)#2	98.46(12)	N(2)–Cu(1)–O(4)#4	97.97(16)

Symmetry codes. #1:  $-x, y-1/2, -z+1/2$ ; #2:  $x-1/2, -y+3/2, -z$ ; #3:  $-x+1/2, y-1/2, z+1/2$ ; #4:  $-x+1, -y+1, z+1/2$ ; #5:  $-x+1, -y+1, z-1/2$ .

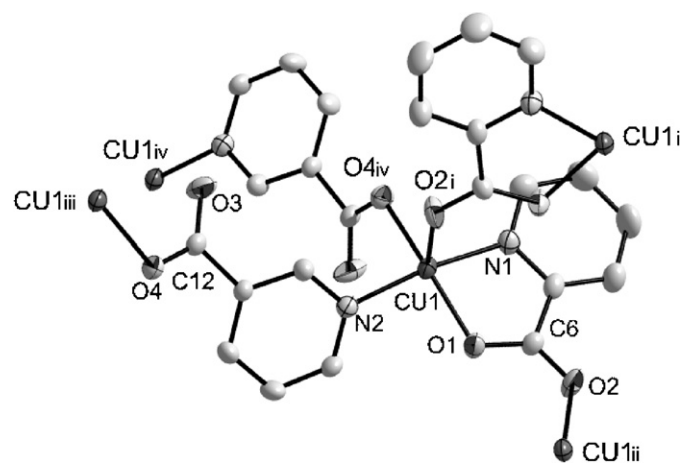


Fig. 1. Perspective view of the coordination environment of compound **1** (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity. Symmetry code for the generated atoms: (i)  $-0.5+x, 1.5-y, -z$ ; (ii)  $0.5+x, 1.5-y, -z$ ; (iii)  $-x, 0.5+y, 0.5-z$ ; (iv)  $-x, -0.5+y, 0.5-z$ .

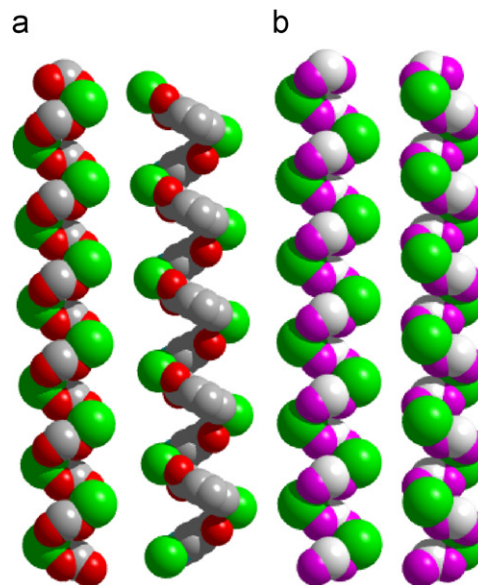


Fig. 2. View of the helices in compound **1**(a) and **2**(b): two kinds of helices one in right-handed (left) and the other in left-handed (right). All hydrogen atoms and some carbon, nitrogen atoms are omitted for clarity. Color code: Cu: black; C and N: white; O: gray.

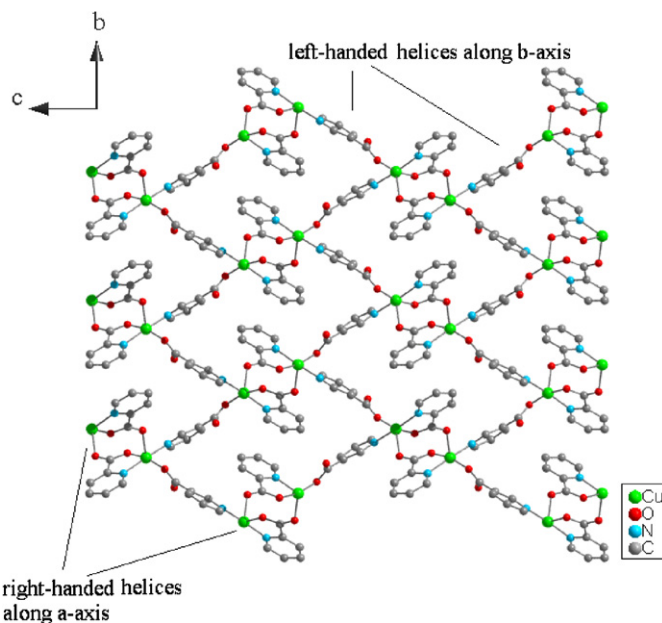


Fig. 3. View of structure of the compound **1** down the  $a$  direction, showing the combination of Cu(2-pc) helices and Cu(3-pc) helices. The hydrogen atoms are omitted for clarity.

### 3. Results and discussion

#### 3.1. Structural description of $[Cu(2-pc)(3-pc)]_n$ **1**

The X-ray crystal structure analysis reveals that compound **1** crystallizes in space group  $P2_12_12_1$ . The atom labeling scheme for **1** is shown in Fig. 1. The copper atom is located at the bottom center of tetragonal pyramid with a little deviation ( $0.188(2)\text{\AA}$ ) from basal plane constructed by  $N_2O_2$  coordination sphere from one 2-pc and two 3-pc units. Additionally, one oxygen of another 2-pc occupied the axial position ( $Cu-O = 1.961(3)-2.268(3)\text{\AA}$ ,  $Cu-N = 1.992(3)-1.994(3)\text{\AA}$ ,

$N(O)-Cu-O(N) = 82.15(12)-170.70(14)^\circ$ ). Moreover, all of the  $Cu-O$  and  $Cu-N$  bond lengths fall within the range found for other similar compounds,  $Cu(3-pc)(4-pc)$ ,  $Cu_2(\mu_3-OH)(4-pc)_2(BDC)_{0.5}$  ( $BDC = 1,3$ -benzenedicarbox-

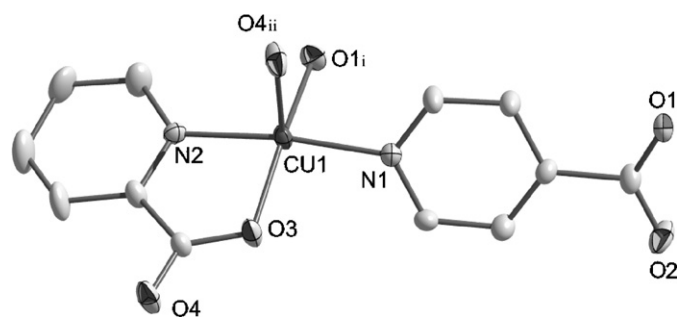


Fig. 4. Thermal ellipsoid plot (30%) showing the coordinate environment of copper in compound **2**. Hydrogen atoms are omitted for clarity. Symmetry code for the generated atoms: (i)  $0.5-x, -0.5+y, 0.5+z$ ; (ii)  $1-x, 1-y, 0.5+z$ .

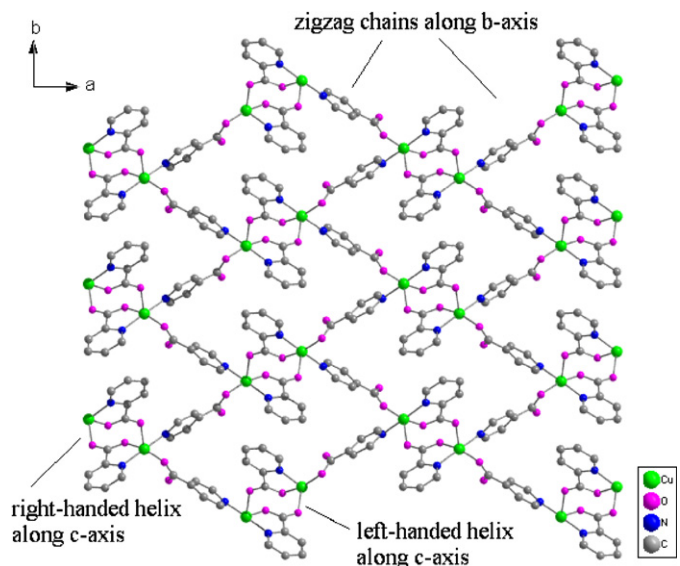


Fig. 5. View of structure of the compound **2** down the  $c$  direction, showing the combination of  $Cu(2-pc)$  helices and  $Cu(4-pc)$  zigzag chains. The hydrogen atoms are omitted for clarity.

ylate),  $[Cu(4-pc)]EtOH$  and  $Cu(3-pc)_2$  [38,46]. As illustrated in Fig. 1, the 2-pc acts as  $N,O,O'$ -tridentate bridging ligand, in which one oxygen atom and nitrogen atom chelated to copper atom and the carboxylate groups adapt the syn-anti bridging pattern. Compared to 2-pc, 3-pc is in  $N,O$ -bidentate bridging mode with one of the carboxylic oxygen not taking part in the coordination. Furthermore, copper atoms and 2-pc combine together to form the right-handed helices along  $a$ -axis and 3-pc bond copper atoms to build left-handed one along  $b$ -axis as well, and the helical pitch lengths are  $6.591(3)$  and  $8.692(5)\text{\AA}$ , respectively (Figs. 2(a) and 3). Additionally, the  $2_1$  screw axes which lie along  $b$ -axis and  $c$ -axis created two symmetrically equivalent left-handed and two right-handed helices in the unit cell and exist by turns, respectively. The  $Cu(2-pc)$  helices alternate crossly with one connecting to nearby four by bidentate bridging 3-pc. Meanwhile, two sides of every  $Cu(3-pc)$  helix are decorated by numerous

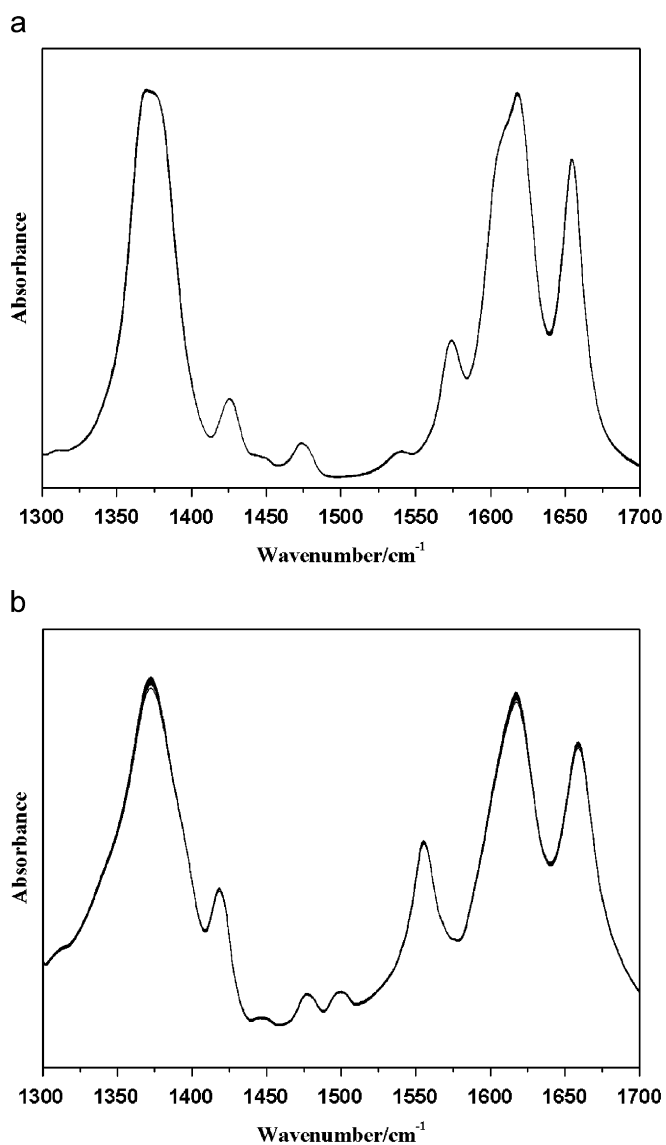


Fig. 6. Magnetism-dependent IR spectra of compounds **1** (a) and **2** (b) over a magnetic intensity from 2 to 20 mT.

Cu(2-pc) helices (Fig. 3). Ultimately, numerous cross-linking helical chains along *a*-axis and *b*-axis further result in an unprecedented 3D framework structures as shown in Fig. 3.

### 3.2. Structural description of $[Cu(2-pc)(4-pc)]_n$ **2**

Compound **2** crystallizes in space group  $Pna2_1$  and is isostructural with the reported compound  $[Zn(2-pc)(4-pc)]_n$  [48]. The synthesis sources of these two compounds were distinct: Zn(2-pc)(4-pc) was achieved with *in situ* solvothermal hydrolysis of ligand PPO(2-(2-pyridyl)-5-(4-pyridyl)-1,3,4-oxadiazole) to 2-pc and 4-pc, while compound **2** we obtained was successfully synthesized directly from a mixture of 2-pc and 4-pc. At the same time, compared to compound **1**, there are several similarities and differences between compound **1** and **2**. First of all, the coordination environment of copper atom in **2** is similar to that of **1**, with the deviation 0.189(1) Å from the plane (Fig. 4). Then, the coordination modes of ligands are identical except that 4-pc was used instead of 3-pc (Fig. 5). Lastly, the view of combination of Cu(2-pc) helices and Cu(4-pc) zigzag chains down the *c* direction are look-alike to the view of combination of Cu(2-pc) helices and Cu(3-pc) helices in **1** down the *a* direction. However, compared to two symmetrically equivalent right-handed Cu(2-pc) helical chains in **1**, the Cu(2-pc) helices in **2** are in different helicity: left-handed and right-handed helices running

along crystallographic  $2_1$  axis in the *c* direction coexist with the pitch length of 6.401(3) Å and helices are connected by bidentate 4-pc (Figs. 2(b) and 5). Meanwhile, copper atoms and 4-pc form zigzag chains along *b*-axis substitute the left-handed Cu(3-pc) helices in **1** (Fig. 5). In a word, the similarities and differences during the ligands (2-pc, 3-pc, 4-pc) lead to the similarities and differences of structure of compounds **1** and **2**.

### 3.3. IR analysis

The IR spectra of **1** and **2** show the absence of free carboxyl groups fairly by virtue of no absorption around  $1700\text{ cm}^{-1}$  [59]. The strong absorptions at the range of  $1659\text{--}1557\text{ cm}^{-1}$  and  $1371\text{--}1365\text{ cm}^{-1}$  of two compounds are attributed to anti-symmetric and symmetrical stretching vibrations of the coordinated carboxylate groups, respectively. The difference between the anti-symmetric and symmetric carboxylate groups stretchings,  $\Delta$  ( $\Delta = \nu_{as} - \nu_s$ ), cover a broad range, which suggests that the carboxylate groups in **1** and **2** are in unidentate and bridging bidentate coordination mode simultaneity [60–62]. These inferences are in accordance with the X-ray diffraction analysis.

In order to clarify the structural changes of COO stretching more efficiently, 2D correlation analysis is applied in the spectral region of  $1300\text{--}1700\text{ cm}^{-1}$ . Figs. 6 and 7 depict the magnetism-dependent IR spectra and the

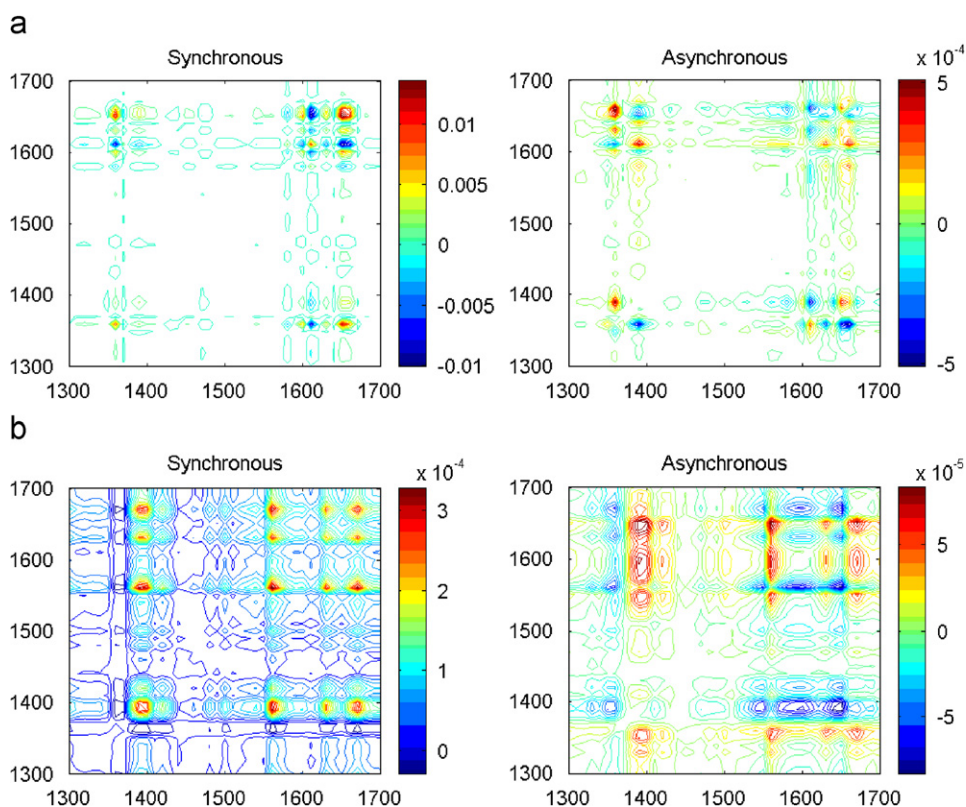


Fig. 7. Synchronous and asynchronous correlation spectra of compounds **1** (a) and **2** (b) in the range of  $1300\text{--}1700\text{ cm}^{-1}$  over a magnetic intensity from 2 to 20 mT.

synchronous and asynchronous 2D correlation spectra of compounds **1** and **2**, respectively. As shown in Fig. 7(a), four strong autopeaks along the diagonal line are unambiguously detected at 1365, 1603, 1616 and 1653  $\text{cm}^{-1}$ , which demonstrate the intensity change of COO band is sensitive to the magnetism variation. According to the rule of Noda [49], the response at the cross-peaks in the synchronous and asynchronous spectra indicate the vibration direction of the symmetrical and anti-symmetric stretching vibrations of COO and the vibration order of two, respectively. The similar results can be obtained for compound **2** from Fig. 7(b), with four strong autopeaks at 1371, 1557, 1614 and 1659  $\text{cm}^{-1}$ . These results illuminate that the generalized 2D IR correlation spectroscopy with magnetism perturbation can ascertain the location of stretching vibrations of carboxyl in copper(II)-pyridine carboxylate coordination polymers. In a word, due to the interaction between magnetic particles and exoteric magnetic field, 2D IR correlation spectroscopy with magnetism perturbation can probe the sensitive response of the coordination groups which coordinate to magnetical particles. Apparently, it is meaningful to explore more function of generalized 2D IR correlation spectroscopy with various perturbations (such as magnetism, light, heat, electricity, chemistry, etc.) in coordination polymers.

#### 4. Conclusion

In summary, two copper helical coordination polymers compounds **1** and **2** were successfully synthesized under hydrothermal conditions. It is worth noting that Cu(2-pc) helical chains are in different helicity for these two compounds: both right-handed for **1** and left- and right-handed coexisting for **2**. Moreover, in compound **1**, Cu(2-pc) helices are connected by left-handed Cu(3-pc) helical chains to extend to acentric 3D framework, while the 3D architecture of **2** are built by linking Cu(4-pc) zigzag chains and Cu(2-pc) helices together. In addition, we first try to introduce 2D IR correlation spectroscopy to coordination polymers and it is worthwhile to explore the in-depth function of 2D IR correlation spectroscopy analysis in MOFs.

#### Acknowledgments

We gratefully acknowledge the financial support from the State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, and the Young Talent Programmed of Fujian Province (Project no. 2006F3072). We thank Prof. Sun Suqin and Zhou Qun (Tsinghua University, Beijing, China) for providing the 2D IR correlation analysis software.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2007.12.006.

#### References

- [1] L. Carlucci, G. Ciani, D.M. Proserpio, *Coord. Chem. Rev.* 246 (2003) 247.
- [2] N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi, *Accounts Chem. Res.* 38 (2005) 176.
- [3] B. Moulton, M.J. Zaworotko, *Chem. Rev.* 101 (2001) 1629.
- [4] B.F. Hoskins, R. Robson, *J. Am. Chem. Soc.* 112 (1990) 1546.
- [5] M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* 116 (1994) 1151.
- [6] M. Eddaoudi, H.L. Li, O.M. Yaghi, *J. Am. Chem. Soc.* 122 (2000) 1391.
- [7] S. Noro, S. Kitagawa, M. Kondo, K. Seki, *Angew. Chem.-Int. Ed.* 39 (2000) 2082.
- [8] L.C. Tabares, J.A.R. Navarro, J.M. Salas, *J. Am. Chem. Soc.* 123 (2001) 383.
- [9] O.R. Evans, W.B. Lin, *Accounts Chem. Res.* 35 (2002) 511.
- [10] K. Maruoka, N. Murase, H. Yamamoto, *J. Org. Chem.* 58 (1993) 2938.
- [11] C.T. Chen, K.S. Suslick, *Coord. Chem. Rev.* 128 (1993) 293.
- [12] E.J. Corey, C.L. Cywin, M.C. Noe, *Tetrahedron Lett.* 35 (1994) 69.
- [13] L. Carlucci, G. Ciani, D.W. von Gudenberg, D.M. Proserpio, *Inorg. Chem.* 36 (1997) 3812.
- [14] A.M. Schuitema, A.F. Stassen, W.L. Driessen, J. Reedijk, *Inorg. Chim. Acta* 337 (2002) 48.
- [15] J.Y. Lu, V. Schauss, *Inorg. Chem. Commun.* 6 (2003) 1332.
- [16] C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* 97 (1997) 2005.
- [17] S. Sailaja, M.V. Rajasekharan, *Inorg. Chem.* 39 (2000) 4586.
- [18] A. Erxleben, *Inorg. Chem.* 40 (2001) 412.
- [19] S. Sailaja, K.R. Reddy, M.V. Rajasekharan, C. Hureau, E. Riviere, J. Cano, J.J. Girerd, *Inorg. Chem.* 42 (2003) 180.
- [20] D. Braga, L. Maini, M. Polito, E. Tagliavini, F. Grepioni, *Coord. Chem. Rev.* 246 (2003) 53.
- [21] E. Yang, J. Zhang, Z.J. Li, S. Gao, Y. Kang, Y.B. Chen, Y.H. Wen, Y.G. Yao, *Inorg. Chem.* 43 (2004) 6525.
- [22] Y.T. Wang, M.L. Tong, H.H. Fan, H.Z. Wang, X.M. Chen, *J. Chem. Soc., Dalton Trans.* (2005) 424.
- [23] L. Han, M. Hong, *Inorg. Chem. Commun.* 8 (2005) 406.
- [24] X.D. Chen, T.C.W. Mak, *J. Chem. Soc., Dalton Trans.* (2005) 3646.
- [25] R.H. Wang, L. Han, Y.Q. Sun, Y.Q. Gong, D.Q. Yuan, M.C. Hong, *J. Mol. Struct.* 694 (2004) 79.
- [26] F. Jaber, F. Charbonnier, R. Faure, M. Petramel, *Z. Kristallogr.* 209 (1994) 536.
- [27] G. Smith, A.N. Reddy, K.A. Byriel, C.H.L. Kennard, *Polyhedron* 13 (1994) 2425.
- [28] X.L. Bai, Y.G. Li, E.B. Wang, L. Xu, *Inorg. Chim. Acta* 358 (2005) 2571.
- [29] M.A.M. Abu-Youssef, *Polyhedron* 24 (2005) 1829.
- [30] W.J. Feng, Y. Xu, G.P. Zhou, C.L. Zhang, X.F. Zheng, *Inorg. Chem. Commun.* 10 (2007) 49.
- [31] G.B. Deacon, R.J. Phillips, *Coord. Chem. Rev.* 33 (1980) 227.
- [32] M. Melnik, *Coord. Chem. Rev.* 36 (1981) 1.
- [33] M. Kato, Y. Muto, *Coord. Chem. Rev.* 92 (1988) 45.
- [34] Y.H. Wang, R.F. Song, F.Y. Zhang, *J. Mol. Struct.* 752 (2005) 104.
- [35] L.P. Sun, S.Y. Niu, J. Jin, G.D. Yang, L. Ye, *Eur. J. Inorg. Chem.* (2006) 5130.
- [36] P. Segl'a, M. Jamnicky, M. Koman, J. Sima, T. Glowiak, *Polyhedron* 17 (1998) 4525.
- [37] O.R. Evans, R.G. Xiong, Z.Y. Wang, G.K. Wong, W.B. Lin, *Angew. Chem.-Int. Ed.* 38 (1999) 536.
- [38] M.E. Chapman, P. Ayyappan, B.M. Foxman, G.T. Yee, W.B. Lin, *Cryst. Growth Des.* 1 (2001) 159.
- [39] J.Y. Lu, A.M. Babb, *Chem. Commun.* (2002) 1340.
- [40] C.D. Wu, C.Z. Lu, H.H. Zhuang, J.S. Huang, *Z. Anorg. Allg. Chem.* 629 (2003) 693.
- [41] F.C. Liu, Y.F. Zeng, J.R. Li, X.H. Bu, H.J. Zhang, J. Ribas, *Inorg. Chem.* 44 (2005) 7298.

- [42] J.P. Deloume, R. Faure, H. Loiseleur, *Acta Crystallogr. Sect. B—Struct. Commun.* 33 (1977) 2709.
- [43] P. Naumov, G. Jovanovski, M.G.B. Drew, S.W. Ng, *Inorg. Chim. Acta* 314 (2001) 154.
- [44] R. Song, K.M. Kim, Y.S. Sohn, *Inorg. Chem.* 42 (2003) 821.
- [45] A.M. Madalan, C. Paraschiv, J.P. Sutter, M. Schmidtman, A. Muller, M. Andruh, *Cryst. Growth Des.* 5 (2005) 707.
- [46] J. Zhang, Y. Kang, J. Zhang, Z.J. Li, Y.Y. Qin, Y.G. Yao, *Eur. J. Inorg. Chem.* (2006) 2253.
- [47] Y. Kang, J. Zhang, Y.Y. Qin, Z.J. Li, Y.G. Yao, *J. Mol. Struct.* 827 (2007) 126.
- [48] Y.T. Wang, H.H. Fan, H.Z. Wang, X.M. Chen, *Inorg. Chem.* 44 (2005) 4148.
- [49] I. Noda, *Appl. Spectrosc.* 47 (1993) 1329.
- [50] I. Noda, *Appl. Spectrosc.* 54 (2000) 994.
- [51] I. Noda, A.E. Dowrey, C. Marcott, G.M. Story, Y. Ozaki, *Appl. Spectrosc.* 54 (2000) 236.
- [52] Y.N. Cao, H.H. Zhang, C.C. Huang, Q.Y. Yang, Y.P. Chen, R.Q. Sun, F.L. Zhang, W.J. Guo, *J. Solid State Chem.* 178 (2005) 3563.
- [53] Y.P. Chen, H.H. Zhang, X.Z. Wang, C.C. Huang, Y.N. Cao, R.Q. Sun, *J. Solid State Chem.* 179 (2005) 1674.
- [54] Y.P. Chen, X.M. Shen, H.H. Zhang, C.C. Huang, Y.N. Cao, R.Q. Sun, *Vib. Spectrosc.* 40 (2006) 142.
- [55] Y.P. Chen, H.H. Zhang, C.C. Huang, Y.N. Cao, R.Q. Sun, W.J. Guo, *Spectrochim. Acta A, Mol. Biomol. Spectrosc.* 63 (2006) 536.
- [56] Y.P. Chen, H.H. Zhang, D.M. Ke, X.M. Shen, C.C. Huang, R.Q. Sun, *Chin. J. Struct. Chem.* 24 (2005) 1033.
- [57] G.M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement, University of Gottingen, Gottingen, Germany, 1997.
- [58] G.M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Solution, University of Gottingen, Gottingen, Germany, 1997.
- [59] L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958.
- [60] K. Nakamoto, *14a Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley Interscience, New York, 1986.
- [61] P. Koczon, J. Piekut, M. Borawska, W. Lewandowski, *J. Mol. Struct.* 651 (2003) 651.
- [62] B. Liu, L. Xu, G. Guo, *J. Solid State Chem.* 179 (2006) 883.