

基于邻苯二甲酰-*L*-丙氨酸配体的两例 Cu(II) 纯手性同质多晶配合物:合成与结构

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摘要: 合成了 2 例 Cu(II) 的纯手性同质多晶 [CuL₂(Phen)] (HL=邻苯二甲酰-*L*-丙氨酸, Phen=1, 10-菲咯啉), 并对其进行了表征。X 射线单晶衍射测定表明, 邻苯二甲酰-*L*-丙氨酸在 2 例配合物中采取了相同的配位方式, Cu(II) 原子具有变形的八面体配位环境, 分别和 2 个邻苯二甲酰-*L*-丙氨酸离子上的 2 个羧基氧原子, 1 个 1, 10-菲咯啉的 2 个氮原子配位。不同的是这 2 例同质多晶显示出不同的颜色, 并且配合物 **1** 属于单斜晶系, *C*₂ 空间群, 配合物 **2** 属于正交晶系, *P*₂₁₂₁₂₁ 空间群。配合物 **1** 通过 $\pi \cdots \pi$ 堆积作用形成一维链状结构, 配合物 **2** 是简单小分子结构。此外, DFT 理论研究表明, 配合物 **1** 具有较低的能量, 稳定性更高。

关键词: 手性铜(II)配合物; 晶体结构; 同质多晶; 异构体

中图分类号: O614.121

文献标识码: A

文章编号: 1001-4861(2018)01-0083-09

DOI: 10.11862/CJIC.2018.001

Two Concomitant Polymorphs of Homochiral Cu(II) Coordination Compounds Based on *N*-phthalyl-*L*-alanine: Syntheses and Crystal Structures

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Abstract: Two isomers of novel homochiral coordination compound [CuL₂(Phen)] (HL=*N*-phthalyl-*L*-alanine, Phen=1,10-phenanthroline) have been synthesized simultaneously and structurally characterized by elemental analyses, IR and single crystal X-ray diffraction. The two polymorphs **1** and **2** exhibit different colors. HL in these two complexes adopts same conformations, the molecular structures vary only slightly between the two forms. Cu(II) ions are all distorted octahedral geometry and coordinated by two pairs of oxygen atoms from two L and two nitrogen atoms from one Phen in complexes **1** and **2**, with a monoclinic space group *C*₂ and an orthorhombic space group *P*₂₁₂₁₂₁, respectively. Complex **1** is self-assembled to form 1D double chains through $\pi \cdots \pi$ stacking interactions of the aromatic rings of L ligands from two adjacent structures, with face-to-face distances of *ca.* 0.366 4 nm. There is no stacking in the structure of complex **2**. Furthermore, the DFT theoretical calculation shows that complex **1** is lower in energy and more stable than **2**. CCDC: 727552, **1**; 727553, **2**.

Keywords: copper(II) complex; crystal structure; polymorphism; conformers; homochiral

收稿日期: 2017-05-29。收修改稿日期: 2017-10-25。

河北省自然科学基金(No.B2012205040)和河北师范大学基金(No.L2016K03)资助项目。

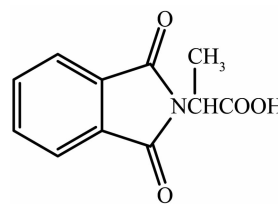
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0 Introduction

Concomitant polymorphism refers to the appearance of two or more polymorphs within the same crystal batch^[1-2]. Polymorphism is a well-established phenomenon with the same substance having different crystal forms^[3-4]. The crystallization process leading to a polymorph is generally sensitive to variation in the conditions of temperature, pressure and/or the manner in which the crystals are obtained^[5-7]. Supramolecular isomerism or polymorphism is of particular importance because the superstructure plays an essential role in determining the properties of crystalline materials^[8]. For example, in drug industry, the drug activity of a material might change abruptly from one polymorph to another^[9]. Therefore, the study of polymorphism has gained considerable impetus not only in fundamental research, but also in industrial interest, especially for pharmaceutical industry^[10-13]. The concomitant polymorphism are common in the synthesis of organics^[14-17]. Though organic matter concomitant polymorphs occur frequently, the observation of metal-organic complex concomitant polymorphs is not very common. Despite some scattered successful examples of polymorph have reported^[18-19], it is also believed that the discovery of concomitant polymorphs is often serendipitous and gaining control over the crystallization process in order to selectively obtain a desired polymorph or suppress an undesired one is hard, and the success of controlling and obtaining a new polymorph remains a major challenge to this day. Subsequently, this may enable us to design and control crystallization of coordination networks by organic ligands and trans-metal ions.

Coordination polymers by amino acid or amino acid derivatives are more importance in the bioorganic chemistry, due to the antimicrobial activities, antipyrotic activities, binding to DNA, and interaction with the cell membrane^[20-21]. *N*-phthalyl-*L*-alanine (HL, Scheme 1) is a derivative of amino acids, which holds diverse function groups and can give various possibilities to form coordination. Some coordination polymers by alanine and alanine derivatives have

been obtained successfully^[22-24]. However, there is few report of coordination compound prepared with ligand HL^[25]. So we have prepared the ligand HL, and have been investigating its complexes with transition metals. The reaction of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, HL and 1,10-phenanthroline (Phen) produced unexpectedly two novel concomitant isomers **1** and **2**, namely, the simultaneous crystallization of different forms of the same species ($[\text{CuL}_2(\text{Phen})]$). The complexes were characterized by elemental analyses, IR and single crystal X-ray diffraction. Furthermore, the energy of them were carried with DFT theoretical calculation.



Scheme 1 Structure of *N*-phthalyl-*L*-alanine (HL)

1 Experimental

1.1 Materials and methods

The ligand HL was prepared by the reported method^[26]. Starting materials (phthalic anhydride and *L*-alanine) for the synthesis of the ligand HL were of reagent grade and were used without further purification. Other reagents and solvents for syntheses were purchased from commercial sources and were used without further purification. Elemental analyses (C, H and N) were performed on an Elemental Vario EL elemental analyzer. The infrared spectrum ($400 \sim 4\,000\text{ cm}^{-1}$) was recorded from KBr pellets on a FTIR-8900 spectrophotometer.

1.2 DFT calculations

Calculations were performed on polymorphs **1** and **2**, taking molecular structures from the X-ray determined coordinates as the starting geometries. Then, equilibrium geometries were fully optimized at the DFT M06-2X/6-31G** level using the GAUSSIAN 09W program package^[27]. Harmonic frequencies were calculated based on the equilibrium geometries.

1.3 Synthesis of the complex $[\text{CuL}_2(\text{Phen})]$

A ethanol solution (5 mL) of HL (21.9 mg, 0.1 mmol) and a methanol solution (5 mL) of 1,10-

phenanthroline (9.9 mg, 0.05 mmol) were mixed by stirring. $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (10 mg, 0.05 mmol) in 5 mL H_2O was added slowly to this reaction mixture with continuous stirring. Single-crystals were grown by slow evaporation at room temperature. Green and blue block shape crystals of **1** and **2** suitable for X-ray diffraction were obtained simultaneously within one week (Fig.1 and Fig.2). Complexes **1** and **2** possess the same chemical composition formulated as $[\text{CuL}_2(\text{Phen})]$. Anal. Calcd.(%): C 60.04, H 3.56, N 8.24; Found(%): C 59.90, H 3.56, N 7.86 for complex **1**; Found(%): C 59.84, H 3.59, N 5.24 for complex **2**; IR for **1** (cm^{-1}): 3 456(b), 3 060(w), 2 993(w), 2 943(w), 1 772~1 761(d), 1 708(vs), 1 603(vs), 1 520(s), 1 471~1 453(d), 1 428(m), 1 396(s), 1 349(m), 1 281(m), 1 198(m), 1 177(m), 1 151(s), 1 084(s), 1 023(s), 922(m), 884(m), 848

(m), 807(w), 779(m), 724(s), 640(m), 601(w), 558(w), 532(m), 461(w). IR for **2** (cm^{-1}): 3 449(b), 2 991(w), 2 942(w), 1 772~1 760(sh), 1 708(vs), 1 626(vs), 1 522(w), 1 452(w), 1 430(m), 1 391(vs), 1 342(m), 1 278(m), 1 175(w), 1 153(m), 1 074(sh), 1 023(m), 918(w), 884(m), 848(w), 784(w), 723(s), 641(m), 531(m), 436(w).

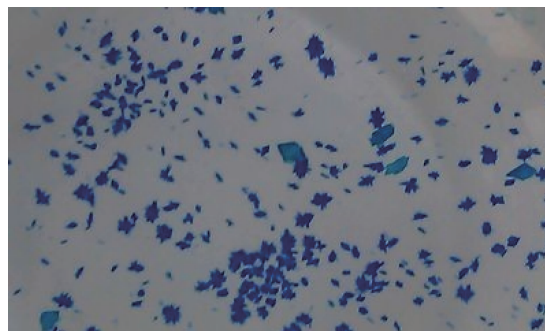


Fig.1 Photograph of the two forms of $[\text{CuL}_2(\text{Phen})]$ growing in MeOH/EtOH (1:1, V/V)

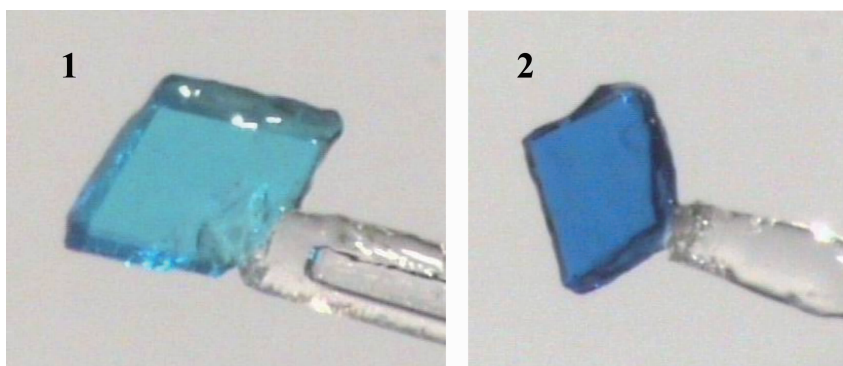


Fig.2 Photograph of the two complex, **1** gives the green diamond-like crystals and **2** is the blue diamond-like crystals

1.4 X-ray crystallography

Single-crystal X-ray diffraction data for all complexes were recorded on a Bruker SMART-CCD area detector diffractometer using graphite-monochromated $\text{Mo } K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 298(2) K by the ω - φ scan technique. The structures were solved by direct methods using the SHELXS-97 program, and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods on F^2 using the

SHELXL-97 program^[28]. Hydrogen atoms were added in geometrical positions and were not refined. A semi-empirical absorption correction was applied to the intensity data using SADABS^[29-30]. A summary of the crystallographic data and refinement parameters is given in Table 1. Selected bond lengths and angles are given in Table 2 and 3.

CCDC: 727552, **1**; 727553, **2**.

Table 1 Crystal data and structure refinement for complexes **1** and **2**

Complex	1	2
Formula	$\text{C}_{34}\text{H}_{24}\text{CuN}_4\text{O}_8$	$\text{C}_{34}\text{H}_{24}\text{CuN}_4\text{O}_8$
Formula weight	680.11	680.11
Crystal size / mm	0.45×0.36×0.18	0.40×0.38×0.14
Crystal system	Monoclinic	Orthorhombic
Space group	$C2$	$P2_12_12$

Continued Table 1

a / nm	1.381 1(3)	1.218 4(2)
b / nm	1.021 80(19)	1.092 5(2)
c / nm	1.121 7(2)	1.138 4(2)
$\beta / (^{\circ})$	111.648(2)	
V / nm^3	1.470 9(5)	1.515 4(5)
Z	2	2
$D_c / (\text{Mg} \cdot \text{m}^{-3})$	1.536	1.491
μ / mm^{-1}	0.806	0.782
θ range / $(^{\circ})$	1.95~25.50	1.79~25.03
$F(000)$	698	698
Index ranges	$-16 \leq h \leq 14, -12 \leq k \leq 12, -13 \leq l \leq 13$	$-13 \leq h \leq 14, -13 \leq k \leq 12, -11 \leq l \leq 13$
GOF on F^2	1.051	1.037
$R_1, wR_2^* [I > 2\sigma(I)]$	0.028 8, 0.070 3	0.029 0, 0.069 0
R_1, wR_2^* (all data)	0.029 6, 0.070 7	0.032 2, 0.070 3

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

Table 2 Selected bond distances (nm) and angles ($^{\circ}$) for complex 1

Cu(1)-O(1)	0.197 50(19)	O(3)-C(8)	0.120 4(3)	N(2)-C(12)	0.132 8(4)
Cu(1)-N(2)	0.200 8(2)	O(4)-C(1)	0.119 8(3)	N(2)-C(17)	0.133 9(4)
Cu(1)-O(2)	0.249 3(2)	C(1)-C(2)	0.148 8(4)	Cu(1)-C(11)#1	0.253 7(3)
N(1)-C(8)	0.135 8(3)	C(7)-C(8)	0.149 1(4)	O(1)-C(11)	0.127 4(3)
N(1)-C(1)	0.138 8(3)	C(9)-C(10)	0.151 3(4)	O(2)-C(11)	0.122 3(3)
N(1)-C(9)	0.146 7(3)	C(9)-C(11)	0.152 8(4)		
O(1)-Cu(1)-O(1)#1	99.53(12)	O(1)-Cu(1)-C(11)#1	116.89(8)	O(1)-C(11)-C(9)	117.0(2)
O(1)-Cu(1)-N(2)#1	157.28(8)	C(11)-O(1)-Cu(1)	100.41(16)	C(8)-N(1)-C(1)	112.5(2)
O(1)#1-Cu(1)-N(2)#1	93.15(9)	C(11)-O(2)-Cu(1)	77.93(16)	C(8)-N(1)-C(9)	124.0(2)
C(6)-C(7)-C(2)	121.1(2)	C(1)-N(1)-C(9)	122.9(2)	O(1)#1-Cu(1)-N(2)	157.28(8)
C(6)-C(7)-C(8)	130.8(2)	C(12)-N(2)-C(17)	118.8(3)	N(2)#1-Cu(1)-N(2)	81.68(15)
C(2)-C(7)-C(8)	108.1(2)	C(12)-N(2)-Cu(1)	128.1(2)	O(1)-Cu(1)-O(2)	57.57(7)
O(3)-C(8)-N(1)	125.2(2)	C(17)-N(2)-Cu(1)	113.1(2)	O(1)#1-Cu(1)-O(2)	92.10(7)
O(3)-C(8)-C(7)	129.1(2)	O(4)-C(1)-N(1)	124.8(2)	N(1)#1-Cu(1)-O(2)	103.47(8)
N(1)-C(8)-C(7)	105.6(2)	O(4)-C(1)-C(2)	129.6(2)	N(2)-Cu(1)-O(2)	110.62(8)
N(1)-C(9)-C(10)	112.6(2)	N(1)-C(1)-C(2)	105.7(2)	O(1)-Cu(1)-C(11)#1	98.73(8)
N(1)-C(9)-C(11)	110.3(2)	N(2)-C(12)-C(13)	121.6(4)	O(1)#1-Cu(1)-C(11)#1	29.61(8)
C(10)-C(9)-C(11)	113.6(2)	N(2)-C(17)-C(15)	124.1(3)	N(2)#1-Cu(1)-C(11)#1	101.55(9)
O(2)-C(11)-O(1)	123.4(2)	N(2)-C(17)-C(17)#1	116.07(16)	N(2)-Cu(1)-C(11)#1	129.82(9)
O(2)-C(11)-C(9)	119.6(2)	C(15)-C(17)-C(17)	119.8(2)		

Symmetry codes: #1: $-x+1, y, -z+2$ Table 3 Selected bond distances (nm) and angles ($^{\circ}$) for complex 2

C(1)-O(3)	0.119 7(3)	C(8)-N(1)	0.138 7(3)	C(16)-C(16)#1	0.135 7(6)
C(1)-N(1)	0.139 3(3)	C(9)-N(1)	0.146 6(3)	C(17)-N(2)	0.135 0(3)
C(1)-C(2)	0.149 2(4)	C(9)-C(10)	0.151 5(4)	C(17)-C(17)#1	0.144 9(5)
C(2)-C(3)	0.137 2(3)	C(9)-C(11)	0.153 1(3)	Cu(1)-O(1)	0.194 86(16)
C(2)-C(7)	0.138 1(4)	C(11)-O(2)	0.122 3(3)	Cu(1)-N(2)	0.199 95(19)

Continued Table 3

C(7)-C(8)	0.149 4(3)	C(11)-O(1)	0.127 3(3)	Cu(1)-O(2)	0.261 18(19)
C(8)-O(4)	0.119 8(3)	C(12)-N(2)	0.133 3(3)		
O(3)-C(1)-N(1)	124.9(2)	O(2)-C(11)-C(9)	120.6(2)	O(1)-Cu(1)-O(2)	55.52(6)
O(3)-C(1)-C(2)	129.2(2)	O(1)-C(11)-C(9)	115.5(2)	O(1)#1-Cu(1)-O(2)	91.41(7)
N(1)-C(1)-C(2)	105.9(2)	N(2)-C(12)-C(13)	122.0(3)	N(2)-Cu(1)-O(2)	113.13(6)
C(7)-C(2)-C(1)	108.0(2)	N(2)-C(17)-C(15)	124.5(2)	N(2)#1-Cu(1)-O(2)	102.28(6)
C(2)-C(7)-C(8)	108.0(2)	N(2)-C(17)-C(17)#1	115.65(12)	C(8)-N(1)-C(1)	111.9(2)
O(4)-C(8)-N(1)	125.1(2)	C(15)-C(17)-C(17)#1	119.82(15)	C(8)-N(1)-C(9)	124.4(2)
O(4)-C(8)-C(7)	128.9(2)	O(1)-Cu(1)-O(1)#1	94.92(11)	C(1)-N(1)-C(9)	122.6(2)
N(1)-C(8)-C(7)	106.0(2)	O(1)-Cu(1)-N(2)	166.30(7)	C(12)-N(2)-C(17)	117.4(2)
N(1)-C(9)-C(10)	112.1(2)	O(1)#1-Cu(1)-N(2)	92.91(7)	C(12)-N(2)-Cu(1)	129.16(19)
N(1)-C(9)-C(11)	109.22(19)	C(17)-N(2)-Cu(1)	113.46(15)	C(10)-C(9)-C(11)	113.4(2)
O(1)#1-Cu(1)-N(2)#1	166.30(7)	C(11)-O(1)-Cu(1)	105.12(15)	O(2)-C(11)-O(1)	123.9(2)
N(2)-Cu(1)-N(2)#1	81.75(11)	C(11)-O(2)-Cu(1)	75.45(16)		

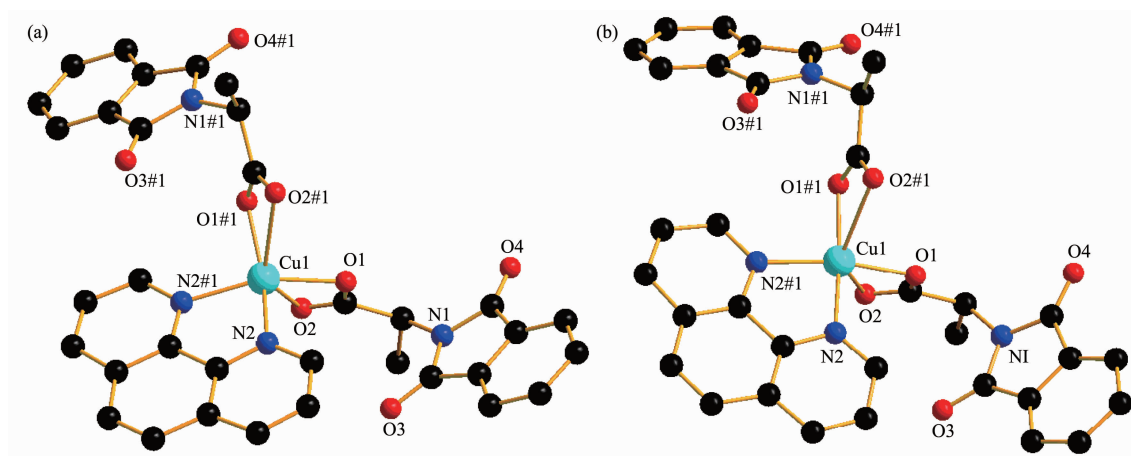
Symmetry codes: #1: $-x+1, y, -z+2$

2 Results and discussion

Co-crystallization of complexes **1** and **2** are obtained by the self-assembly reaction of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, HL and Phen simultaneously. The X-ray crystallographic determination reveal that **1** and **2** have the same composition formulated as $[\text{CuL}_2(\text{Phen})]$. Nevertheless, they form different crystal structures. Complex **1** is a 1D supramolecular double chains formed by $\pi \cdots \pi$ interaction, but complex **2** is a separate mononuclear small molecule.

Complex **1** crystallizes in the monoclinic space group C2, and each asymmetry unit comprises of one

Cu(II) ion, two L ligands and one Phen molecule. Fig. 3a shows the principal structural features with atom-labeling scheme. The central Cu(II) is in a slightly distorted octahedral geometry and coordinated by two pairs of oxygen atoms (O1, O1#1, O2, O2#1) from the carboxyl groups of two different L ligands and two nitrogen atoms (N2, N2#1) from one Phen. The O1 and N2#1 are in the axial positions and the O1#1, O2, O2#1 and N1 atoms are in the equatorial position. The Cu-O bond lengths are $\text{Cu}(1) \cdots \text{O}(1)$ 0.197 50(19) nm, $\text{Cu}(1) \cdots \text{O}(1)\#1$ 0.197 50(19) nm, $\text{Cu}(1) \cdots \text{O}(2)$ 0.249 3(2) nm, $\text{Cu}(1) \cdots \text{O}(2)\#1$ 0.249 3(2) nm, respectively (Table 2). All the Cu-N bond lengths are 0.200 8

Symmetry codes: #1: $-x+1, y, -z+2$ Fig.3 (a) View of the coordination of Cu(II) ions in complex **1**; (b) View of the coordination of Cu(II) ions in complex **2**

nm. The angles around Cu center range from $57.57(7)^\circ$ to $157.28(8)^\circ$. In complex **1**, two L ligands adopt the same coordination modes (asymmetrical bidentate chelating mode) to coordinate the center Cu(II) ion with two carboxylic oxygen atoms. Phen ligand presents symmetrical bidentate chelating mode. Fig.4 clearly shows that the adjacent unit connects with each other through $\pi \cdots \pi$ stacking interactions between the aromatic rings moiety of the L ligands to form a 1D double chains, with the distance of face-to-face about 0.366 4 nm. The adjacent Cu $\cdots$ Cu distance is 1.421 6 nm.

The molecular structure of complex **2** is shown in Fig.3b. The crystal of complex **2** belongs to orthorhombic, space group $P2_12_12_1$. The Cu(II) ion in complex **2** also displays six-coordinated octahedral geometry. The Cu-O bond lengths are Cu(1) $\cdots$ O(1) 0.194 86(16) nm, Cu(1) $\cdots$ O(1)#1 0.194 86(16) nm, Cu(1) $\cdots$ O(2) 0.261 18(19) nm, Cu(1) $\cdots$ O(2)#1 0.261 18(19) nm, respectively. The Cu-N bond length is 0.199 95(19)

nm (Table 3). The angles around Cu center range from $55.52(6)^\circ$ to $166.30(7)^\circ$. The Cu(1) $\cdots$ O(1) bond lengths of complex **1** are longer than complex **2**, but Cu(1) $\cdots$ O(2) bond lengths of complex **1** are shorter than complex **2**, while the Cu-N bond lengths of complex **1** are longer than **2**. In addition, Cu(1) $\cdots$ O(2) bond lengths of complex **1** and **2** are longer than Cu(1) $\cdots$ O(1) due to a Jahn-Teller effect^[31].

As mentioned earlier, complexes **1** and **2** are concomitant polymorphs of each other. Concomitant polymorphs arise when a material crystallizes in two or more forms out of the same reaction mixture^[2]. The concomitant polymorphs sometimes have different colors, but the origin of this phenomenon, called colour polymorphism or chromatormorphism, is not always clear and may be due to different reasons^[32]. There are at least three possible reasons for the different colors of the polymorphs: the first is different molecular conformations; the second is different intermolecular interactions that can theoretically

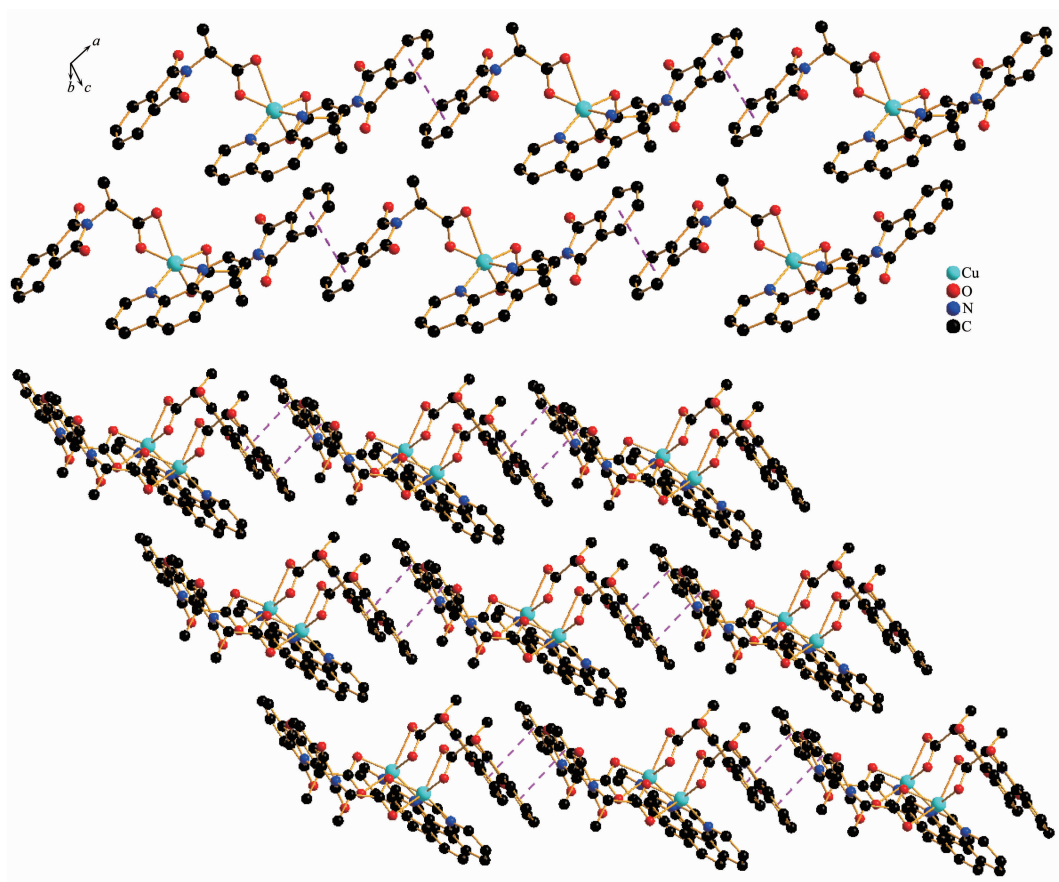


Fig.4 Packing diagram in complex **1**

influence the electronic structure of molecules; the third is different molecular environment and crystal packing motifs. Through the careful analysis of the molecule structure of complexes **1** and **2** as stated above. The two forms have distinct structure, the adjacent unit of complex **1** connected with each other through $\pi \cdots \pi$ stacking interactions to form a 1D supramolecular double chains, but there are no significant weak interaction been observed for complex **2**. We hypothesized that the different intermolecular interactions influence the electronic structure of molecules, so the physical differences of the two polymorphs are revealed in their color^[33].

Concomitant polymorphs can generally be described. Two or more polymorphs appear at the same time from the same mother liquor so-called concomitant polymorphs^[2]. Comparing the stability of complexes **1** and **2**, we suppose that **1** has high relative stability, because complex **1** is a 1D supramolecular double chain, with the distance of face-to-face about 0.3664 nm. While complex **2** is a separate mononuclear small molecule. The adjacent unit of complex **2** do not connect with each other through $\pi \cdots \pi$ stacking interaction between the aromatic rings moiety of the L ligands, with the distance of face-to-face about 0.419 7 nm. The relative stability of the two polymorphs were test. The calculated densities of the two polymorphs are 1.536 and 1.491 g·cm⁻³, respectively, and according to the well known “density rule”^[32], the polymorph **1** with the higher density is most likely to be more stable. Furthermore, all of the calculations in this work were carried out by using the GAUSSIAN 09W program package. Through the calculated energy comparison the two monomer between the complexes **1** and **2**, -3 770.071 136 7 hartree and -3 770.067 595 7 hartree, respectively. It is obviously that complex **1** is lower in energy than **2** for about 0.003 541 hartree, suggesting that **2** is less stable than **1**. In addition, the calculated interaction energy of the dimer of **1** without BBSE is 74.1 kJ·mol⁻¹, and the interaction energy of the dimer of **2** with BBSE is 51.8 kJ·mol⁻¹. On the basis of the above analysis, we find that the complex **1** is more stable

than **2**. The calculation and packing forms are also uniform with the “density rule”. The apparently high density of the complex **1** is consistent with its closest packing with significant $\pi \cdots \pi$ interactions between adjacent unit, which are obviously absent in complex **2**^[33].

Good quality crystals of polymorphs **1** and **2** can be obtained from a solution of $V_{\text{CH}_3\text{OH}}:V_{\text{C}_2\text{H}_5\text{OH}}:V_{\text{H}_2\text{O}}=1:1:1$ by a slow evaporation process. In addition, much effort had been made from hydrothermal synthesis method in different temperatures, solvents, metal salts and reaction time, but a blue precipitate was formed. In order to optimize synthetic methods and reaction conditions, a series of parallel experiments were conducted using the conventional solution method with different reaction conditions, such as $n_{\text{phen}}:n_{\text{M(II)}}:n_{\text{L}}$, solvent ratio and metal salt. When the $n_{\text{phen}}:n_{\text{M(II)}}:n_{\text{L}}$ is 1:1:2 and $V_{\text{CH}_3\text{OH}}:V_{\text{C}_2\text{H}_5\text{OH}}:V_{\text{H}_2\text{O}}$ is 1:1:1. Concomitant polymorphism are obtained. As is known to all, the water, ethanol and methanol are polar with different dipoles. These effects might also be related to the energy of the system. As mentioned above, Crystal structures are readily built-up, because they provide a facile means of reducing the energy of the system, rendering the crystalline state more stable. On the other hand, many parallel experiments were made using the different metal salts (Cu(NO₃)₂, CuSO₄·5H₂O, Cu(CH₃COO)₂·H₂O), when the metal salt is replaced by Cu(CH₃COO)₂·H₂O, the concomitant polymorphs have been obtained. It is worth noting that the presence of metal salt Cu(CH₃COO)₂·H₂O in the system is necessary for successful preparation because no crystals are formed otherwise. The experiments results show that the CH₃COO⁻ plays an important role in the process of crystal formation.

The IR spectra (Fig.S1) of all complexes showed a distinct strong band appeared in the 3 460~3 440 cm⁻¹ range corresponding to the stretching vibration of the uncoordinated NH group of HL^[34]. In addition, the IR spectra of all complexes exhibited a strong band in the 1 630~1 600 cm⁻¹ range and is assigned to the stretching vibration of the coordinated carboxylate

groups. Accordingly, the absence of any band in the $3\ 000\sim 2\ 500\ \text{cm}^{-1}$ region in the IR spectra of the complexes suggests coordination of the COO^- group of the N-protected amino acids to the central metal ions. In the case of two complexes, where the appearance of three bands at $1\ 772$, $1\ 760$ and $1\ 708\ \text{cm}^{-1}$ reveals the incoordination of the benzoyl group of the N-phthalyl alanine acid and benzene ring. However, for all complexes the band appearing at $1\ 430\sim 1\ 391\ \text{cm}^{-1}$ can likely be ascribed to the symmetric vibration of the coordinated carboxylate group^[11]. The $\Delta\nu(\text{COO})$ values ($\nu(\text{COO})_{\text{as}}-\nu(\text{COO})_{\text{s}} < 200\ \text{cm}^{-1}$) are consistent with the bidentate coordination of the carboxylate group of N-acetyl-derivatives of the amino acids^[45].

3 Conclusions

In summary, two unusual concomitant polymorphs, $[\text{CuL}_2(\text{Phen})]$, have observed unexpectedly. They can be discriminated by their visible appearance as they have different colors. We suppose that different colors are caused by different intermolecular interactions. The relative stability of the two polymorphs were tested. Our calculation results suggest that complex **1** is lower in energy and more stable than **2**. Moreover, we optimize synthetic methods and reaction conditions ($n_{\text{Phen}}:n_{\text{M(II)}}:n_{\text{L}}=1:1:2$, $V_{\text{CH}_3\text{OH}}:V_{\text{C}_2\text{H}_5\text{OH}}:V_{\text{H}_2\text{O}}=1:1:1$). Many parallel experiments were made using the different metal salts, and we found that two concomitant polymorphs have been detected only metal salt $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ existing in the system. Although the CH_3COO^- is not coordinated with metal ion, the experiments result clearly reveal the significant effects of CH_3COO^- in the fabrication of crystals. It is also the subtlest and most challenging to control over the crystallization process in order to selectively obtain a desired polymorph. Polymorphs **1** and **2** had been obtained unexpectedly, which urge us to further extend this interesting system in the future. Furthermore, our report should enrich the crystal engineering approach for generating coordination polymers.

References:

- [1] Linas A, Burley J C, Prior T J, et al. *Cryst. Growth Des.*, **2008**,**8**:114-118
- [2] Bernstein J, Davey R J, Henck J O. *Angew. Chem. Int. Ed.*, **1999**,**38**:3440-3461
- [3] Braga D, Cojazzi G, Emiliani D, et al. *CrystEngComm*, **2002**, **4**:277-281
- [4] Braga D, Cojazzi G, Paolucci D, et al. *CrystEngComm*, **2001**, **38**:1-3
- [5] Anirban K, Rupam J S, Jubaraj B B, et al. *Eur. J. Inorg. Chem.*, **2007**,**5**:643-647
- [6] Hu P, Yao Z J, Wang J Q, et al. *Organometallics*, **2011**,**30**: 4935-4940
- [7] Fromm K M, Doimeadios J L, Robin A Y, et al. *Chem. Commun.*, **2005**,**36**:4548-4550
- [8] John S F, Lesibana P L, Orde Q M, et al. *CrystEngComm*, **2008**,**10**:740-747
- [9] Mijanuddin M, Jana A D, Drew M G B, et al. *Polyhedron*, **2009**,**28**:665-672
- [10] O'Donnell L J, Arvind A S, Haong P, et al. *Gut*, **1992**,**33**(7): 947-949
- [11] Bailey M A, Ingram M J, Naughton D P, et al. *Transition Met. Chem.*, **2008**,**33**:195-202
- [12] Kukovec B M, Venter G A, Oliver C L. *Cryst. Growth Des.*, **2012**,**12**:456-465
- [13] Yang C Q, Zhang Z W, Zeng Y L, et al. *CrystEngComm*, **2012**,**14**:2589-2594
- [14] Du M, Zhang Z H, Wang X G, et al. *Cryst. Growth Des.*, **2006**,**6**:1867-1875
- [15] Eccles K S, Deasy R E, Fábíán L, et al. *CrystEngComm*, **2011**,**13**:6923-6925
- [16] Munshi P, Venugopala K N, Jayashree B S, et al. *Cryst. Growth Des.*, **2004**,**4**:1105-1107
- [17] Bond A D, Haynes D A, Pask C M, et al. *Dalton Trans.*, **2002**,**12**:2522-2531
- [18] Field J S, Ledwaba L P, Munro O Q, et al. *CrystEngComm*, **2008**,**10**:740-747
- [19] Procopio E Q, Mauro M, Panigati M, et al. *J. Am. Chem. Soc.*, **2010**,**132**:14397-14399
- [20] Peresypkina E V, Bushuev M B, Virovets A V, et al. *Acta Crystallogr. Sect. B: Struct. Sci.*, **2005**,**B61**:164-173
- [21] Das L K, Biswas A, Gomez-García C J, et al. *Inorg. Chem.*, **2014**,**53**:434-445
- [22] Moreira V F, Ortego M L, Williams C F. *Organometallics*, **2012**,**31**:5950-5957
- [23] Zhuang G L, Chen W X, Zeng G N. *CrystEngComm*, **2012**, **14**:679-683

- [24]Chen Z C, Zhang C B, Liu X L, et al. *Aust. J. Chem.*, **2012**, **65**:1662-1666
- [25]Santiago G R, Beatriz G, Milena R K, et al. *J. Organomet. Chem.*, **2009**,**694**:2191-2197
- [26]Frisch M J T G, Schlegel H B, Scuseria G E, et al. *Gaussian* 09, *Revision A02*, Gaussian Inc., Wallingford, **2009**.
- [27]Ghazzali M, Al-Farhan K, El-Fahama A, et al. *Polyhedron*, **2010**,**29**:2829-2832
- [28]Nuria A A, Marques-G P, Mirte K, et al. *Inorg. Chem.*, **2010**, **49**:9655-9663
- [29]Sahoo S C, Kundu T, Banerjee R. *J. Am. Chem. Soc.*, **2011**, **133**:17950-17958
- [30]Sarma D, Ramanujachary K V, Lofland S E, et al. *Inorg. Chem.*, **2009**,**48**:11660-11676
- [31]Qu Z R, Zhao H, Wang Y P, et al. *Chem. Eur. J.*, **2004**,**10**: 53-60
- [32]Yu L, Stephenson G A, Mitchell C A, et al. *J. Am. Chem. Soc.*, **2000**,**122**:585-591
- [33]Wang J, Ding L Y, Yang C Q. *CrystEngComm*, **2007**,**9**:591-594
- [34]Dong L J, Chu W, Zhu Q L, et al. *Cryst. Growth Des.*, **2011**, **11**:93-99
- [35]Abdel-Rahman L H, Nasser L A E. *Transition Met. Chem.*, **2007**,**32**:367-373