

# 2,6-吡啶雙羧基及 1,2-雙(4-吡啶)乙烷 之銅(II)配位化合物之合成、鑑定、 及其結構分析

## Synthesis, Characterizations, and Crystal Structure of Copper(II) Complex Containing, 2,6-Pyridinedicarboxylate and, 1,2-Bis(4-pyridyl)ethane

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**摘要：**利用水熱合成，得到雙核的銅(II)錯合物， $[\text{Cu}_2(\text{pda})_2(\text{dpe})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (**1**) (其中 pda = 2,6-吡啶雙羧基, dpe = 1,2-雙(4-吡啶)乙烷)。使用 FTIR 光譜儀以及 X-Ray 晶體繞射儀，測定產物晶體結構及其性質，結果顯示錯合物以銅(II)離子為配位中心，五個配位原子為 pda 上的二個羧基各提供一個 O 原子、一個配位水分子、pda 上的 N 原子、及 dpe 上的一個 N 原子，形成扭曲四角錐型的幾何結構。錯合物結構類似啞鈴形狀，包含兩個銅原子，兩個吡啶雙羧酸配位基和一個雙吡啶配基，以及兩個配位水分子和兩個晶格水分子。吡啶雙羧基及配位水分子間的氫鍵作用，以及吡啶環之間的 $\pi$ - $\pi$ 吸引力，此錯合物自組裝成 3-D 超分子化合物。

**關鍵詞：**2,6-吡啶雙羧酸、1,2-雙(4-吡啶)乙烷、氫鍵、水熱合成

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**Abstract:** A novel copper(II) complex,  $[\text{Cu}_2(\text{pda})_2(\text{dpe})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (**1**) (pda = 2,6-pyridinedicarboxylate, dpe = 1,2-bis(4-pyridyl)ethane), has been hydrothermally synthesized and characterized by FTIR spectroscopy and single crystal X-ray diffraction. The metal ion center is in the distorted square-pyramidal coordination environment. Oxygen atom from one water hold the axial sites, and two oxygen atoms from one pda ligand, two nitrogen atoms from one pda ligand and the dpe occupy the square planar sites. The complex **1** is in a dumbbell shape which contains two copper atoms, two pda ligands, one dpe ligand, two coordination water ligands and two lattice water molecules. In addition, the intermolecular O-H...O hydrogen-bonding and  $\pi$ - $\pi$  stacking interactions further extend the title complex to form a 3-D structure.

**Key words:** 2,6-Pyridinedicarboxylic acid, 1,2-Bis(4-pyridyl)ethane, Hydrogen bonding, Hydrothermal synthesis

## I. Introduction

Over the past decades, transition metal coordination polymers constructed by multicarboxylate ligands have been extensively studied due to their potential applications as zeolite-like materials for molecular recognition, catalysis ion exchange, non-linear optics and microelectronics, as well as in a variety of architectures and topologies<sup>1-3</sup>. Recently, the extended structure of supra-molecular compounds by the self-assembly of metal-organic units via hydrogen bonds and  $\pi$ - $\pi$  interaction has attracted much interest<sup>4,5</sup>. The architecture of open metal-organic framework, so far, can be achieved via weaker intermolecular forces and/or coordinate covalent bonds. It should be noted that weak intermolecular forces of hydrogen bond and  $\pi$ - $\pi$  stacking play an important role in the formation of the framework structures<sup>5</sup> which can be designed through proper selection of metal ions and ligands<sup>6</sup>. Multi-carboxylate ligands have been proved to be good candidates because they can be regarded not only as hydrogen-bonding acceptors but also as hydrogen-bonding donors, depending upon the number of deprotonated carboxylic groups<sup>4</sup>. Several studies have used rigid, multifunctional ligands to bridge metal ions into two- or three-dimensional structures. These ligands usually possess high symmetry. For examples, 2,6-pyridinedicarboxylic acid<sup>4,7-10</sup> and 3,5-pyridinedicarboxylic acid<sup>11-14</sup> have been used successfully to synthesize such materials.

In this study, we report the synthesis, crystal structure and characterizations of a new copper(II) complex,  $[\text{Cu}_2(\text{pda})_2(\text{dpe})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (**1**), where pda represents 2,6-pyridinedicarboxylate and dpe represents 1,2-bis(4-pyridyl)ethane. Complex **1** is a novel 3-D supramolecular material based on mixed ligands of 2,6-pyridinedicarboxylate and 1,2-bis(4-pyridyl)ethane.

## II. Experimental Section

### *Materials and methods*

All chemicals purchased were reagent grade and used without further purification. FTIR



spectra were recorded in the range 400-4000  $\text{cm}^{-1}$  on a Bruker Vector 22 FTIR spectrophotometer using a KBr pellet. All measurements were performed at room temperature.

#### Synthesis

An aqueous mixture (10 mL) containing  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.0591 g, 0.20 mmol), 2,6-pyridinedicarboxylic acid (0.0341 g, 0.20 mmol), and 1,2-bis(4-pyridyl)ethane (0.0372 g, 0.20 mmol) and  $\text{Nd}_2\text{O}_3$  (0.0673 g, 0.20 mmol) powder was placed in a 23-mL Teflon-lined stainless steel autoclave, and the autoclave was sealed, heated to 145 $^\circ\text{C}$  under autogenous pressure for 48 h, and then cooled to RT at a rate of 0.5  $^\circ\text{C}/\text{hr}$ . Blue crystals were obtained (yield 34.78 % based on copper). IR (KBr,  $\text{cm}^{-1}$ ): 3377, 3055, 1643 (C=O), 1607 (C=O), 1507 (C=O), 1422, 1353, 1262, 1206, 1178, 1087, 1047, 916, 848, 780.

### III. Results and Discussion

Compound **1** were synthesized by hydrothermal reactions of  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Nd}_2\text{O}_3$  with 2,6-pyridinedicarboxylic acid and 1,2-bis(4-pyridyl)ethane. The product is stable in air and insoluble in water and common organic solvents such as ethanol, acetonitrile, THF, 1,2-dichloroethane, acetone, and DMF.

We tried to synthesize heterometallic complexes but only obtain homometallic complexes. When the preparation of compound **1** was tried in the absence of  $\text{Nd}_2\text{O}_3$ , the experiment only gave very poor crystalline products, and therefore we gave up further characterizations. We cannot give a definite mechanism in this study, because hydrothermal reaction system is rather complicated<sup>15</sup>.

The FTIR spectrum of compound **1** exhibits peaks at 1643, 1607, and 1507  $\text{cm}^{-1}$  that can be assigned to the asymmetric and symmetric C=O stretches, respectively. The FTIR spectrum of ligand also shows strong peaks characteristic of the carboxylate groups at 1706, 1678, and 1575  $\text{cm}^{-1}$  (Fig. 1). The crystal structural data of **1** are listed in Table 1. The valence sum calculations give the average value of 2.008 for Cu atom, suggesting that all Cu centers are in the +2 oxidation state ( $3d^9$ ). The copper atom is coordinated by two oxygen atom (Cu(1)-O(2) = 2.064(2) Å, Cu(1)-O(4) = 2.084(2) Å) from one pda ligand, two nitrogen atoms (Cu(1)-N(1) = 1.901(2) Å, Cu(1)-N(2) = 2.147(2) Å) from one pda ligand and one dpe ligand, respectively, and one coordinated water molecules (Cu(1)-O(1) = 2.393(5) Å) (Table 2), showing a distorted square-pyramid geometry. As for the Cu(1) atom it is bonds as [Cu(1), O(2), O(4), N(1), N(2)] is basically planar position. The O(1) atom in the apical position. The bond angles of [N(2)-Cu(1)-O(2)], [N(1)-Cu(1)-N(2)], [O(1)-Cu(1)-O(4)], [O(1)-Cu(1)-O(2)] and [N(1)-Cu(1)-O(1)] are 101.16(13) $^\circ$ , 173.30(15) $^\circ$ , 161.17(13) $^\circ$ , 86.87(12) $^\circ$  and 90.55(13) $^\circ$ . From Fig. 2, the complex **1** is a binuclear compound having a dumbbell-shaped structure which contains two copper atoms, two pda ligands, one dpe ligand, two composed water ligands and two non-coordination water molecules. The carboxy groups are nearly coplanar with the pyridine ring,



as indicated by the torsion angles [O(4)-C(7)-C(1)-N(1)], [O(5)-C(7)-C(1)-C(2)], [O(2)-C(6)-C(5)-N(1)] and [O(3)-C(6)-C(5)-N(1)] are  $7.05(57)^\circ$ ,  $6.48(77)^\circ$ ,  $4.02(56)^\circ$  and  $4.56(42)^\circ$

The packing diagram of compound **1** is shown in Fig. 3. The diagram shows intermolecular hydrogen bonding interactions between H atoms of the coordinated water molecules and O atoms of the 2,6-pyridinedicarboxylate ligand. The hydrogen-bonding interactions are normal<sup>16</sup>, based on H...A distances of 1.792-2.489 Å, D...A distances of 2.679-3.383 Å, and bond angles of 159.52-167.71° (Table 3). Obviously, these strong hydrogen-bonding interactions play an important role in the formation of the 3-D supramolecular framework. On the other hand, the  $\pi$ - $\pi$  stacking interaction between the pyridine rings from pda ligands also play a definite role in stabilizing the whole crystal structure with the average interplanar separation of pyridine units is ca.3.565 Å. Compound **1** as zero-dimensional(0-D) complex was assembled into 3-D networks via O-H...O hydrogen bond and  $\pi$ - $\pi$  stacking interaction (Fig. 3).

## IV. Conclusions

In this study, a novel copper(II) complex, has been synthesized and structurally characterized. The successful synthesis of the new compound **1** not only proves that the hydrothermal reaction in preparing new metal-organic hybrid materials but also shows that strong intermolecular interactions (hydrogen-bonding and  $\pi$ - $\pi$  stacking interactions) contribute to the formation of higher-dimensional network.

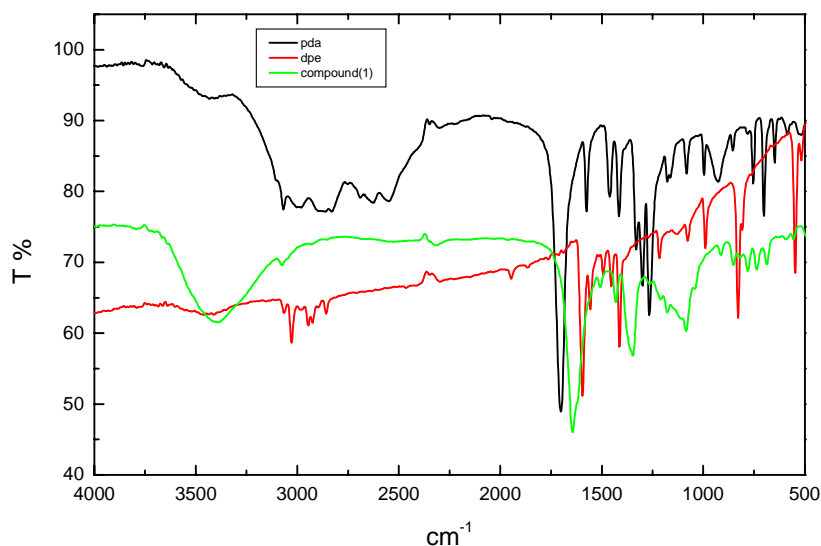


Figure 1 The FTIR spectroscopy of ligand and compound **1**



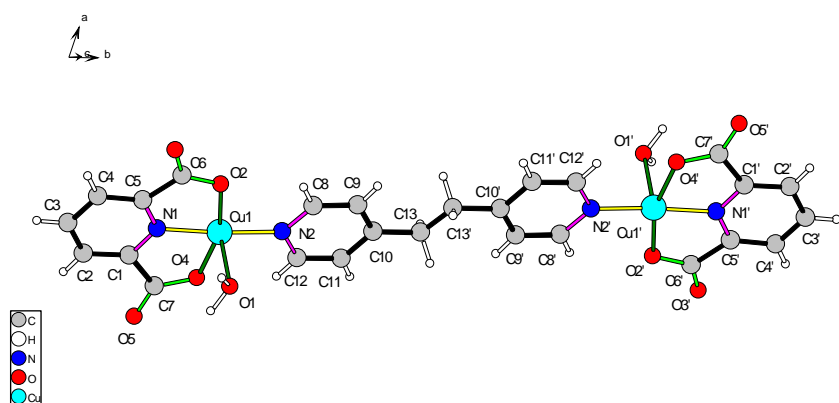


Figure 2 Perspective view of the coordination environment of the copper atom in compound **1**

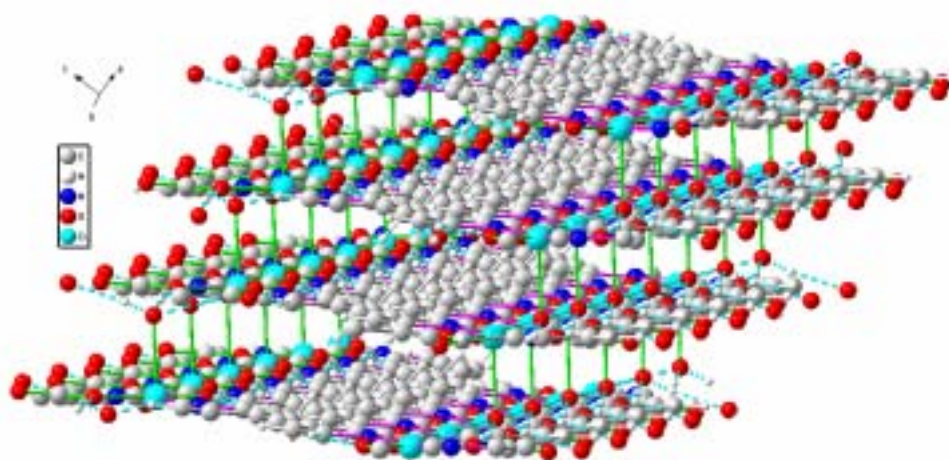


Figure 3 View of the stacking arrangement of **1** along ab-plannar, showing strong hydrogen-bonding and  $\pi$ - $\pi$  stacking interactions



Table 1 Crystal data

$C_{13}H_{13}CuN_2O_6$	$Z = 2$
Mr = 356.79	$D_x = 1.779 \text{ Mg m}^{-3}$
Triclinic P-1	Mo $K\alpha$ radiation
$a = 5.2616(5) \text{ \AA}$	Cell parameters from 3226 reflections
$b = 7.9316(7) \text{ \AA}$	$\theta = 2.5\text{-}25^\circ$
$c = 16.8063(14) \text{ \AA}$	$\mu = 1.673 \text{ mm}^{-1}$
$\alpha = 89.183(2)^\circ$	T = 295(2) K
$\beta = 84.541(2)^\circ$	Blue
$\gamma = 72.557(2)^\circ$	$0.10 \times 0.10 \times 0.25 \text{ mm}^3$
V = 666.01(10) $\text{ \AA}^3$	
Data collection	
Bruker SMART CCD area-detector	2377 independent reflections
Diffractionmeter	2179 reflections with $I > 2\sigma(I)$
$\psi$ and $\omega$ scans	Rint = 0.0360
Absorption correction: multi-scan (SADABS; Sheldrick, 1995)	$\theta_{\text{max}} = 25.12^\circ$
Tmin = 0.88370, Tmax = 0.96803	$h = -6 \rightarrow 6$
5769 measured reflections	$k = -8 \rightarrow 9$
	$l = -19 \rightarrow 19$
Refinement	
Refinement on $F^2$	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)] = 0.0526$	$w = 1/[\sigma^2(F_o^2) + 0.0472P^2 + 0.8688P]$
$wR(F^2) = 0.1156$	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.223	$(\Delta/\sigma)_{\text{max}} = 0.001$
2377 reflections	$\Delta\rho_{\text{max}} = 0.571 \text{ e \AA}^{-3}$
199 parameters	$\Delta\rho_{\text{min}} = -0.462 \text{ e \AA}^{-3}$

Table 2 Selected geometric parameters( $\text{ \AA}, ^\circ$ )

N1-Cu1	1.901(4)	N2-Cu1-O2	101.16(13)
N2-Cu1	2.147(2)	N1-Cu1-N2	173.30(15)
O1-Cu1	2.108(2)	O1-Cu1-O4	161.17(13)
O2-Cu1	2.064(2)	O1-Cu1-O2	86.87(12)
O4-Cu1	2.084(2)	N1-Cu1-O1	90.55(13)



Table 3 Hydrogen-bonding geometry( $\text{\AA}^{\circ}$ )

D-H...A	D-H	H...A	D...A	D-H...A
O1-H1A...O6	0.926(3)	1.792(7)	2.679(8)	159.52(30)
O1-H1B...O2 <sup>(i)</sup>	0.926(4)	1.917(4)	2.808(6)	160.70(26)
C8-H8A...O1 <sup>(ii)</sup>	0.930(5)	2.489(5)	3.381(7)	160.83(33)
C9-H9A...O5 <sup>(iii)</sup>	0.930(5)	2.468(5)	3.383(7)	167.71(31)

Symmetry code: (i)1+x,y,z (ii)-1+x,y,z (iii)-1+x,1+y,z

The H atoms were located in a difference Fourier synthesis but were not refined; their  $U_{\text{iso}}$  values were set to  $0.05 \text{ \AA}^2$ .

Data collection SMART<sup>17</sup>; cell refinement: SMART; data reduction: SAINT<sup>18</sup> program(s) used to solve structure: SHELXS97<sup>19</sup>; program(s) used to refine structure: SHELXL97<sup>20</sup>; molecular graphics: SHELXTL97; software used to prepare material for publication SHELXTL.

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