

## 原位产生的 3-羟基-2,4,6-吡啶三酸配位的 Cu(II) 配合物的合成及配体反应机理分析

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**摘要:** 以 2,4,6-三甲基吡啶(2,4,6-tmpy)和  $\text{Cu}(\text{NO}_3)_2$  为原料,采用水热法原位合成一个新的含 3-羟基-2,4,6-吡啶三酸根(2,4,6-opyta<sup>3-</sup>)的 Cu(II)配合物  $[\text{Cu}_2(2,4,6\text{-opyta})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ , 并对其进行了红外、元素分析和 X-射线单晶衍射测定。单晶结构分析表明,该配合物中 Cu1、Cu2 均采取五配位的四方锥几何构型,  $[\text{Cu}_4(2,4,6\text{-opyta})_2(\text{H}_2\text{O})_4]$  结构基元间通过 Cu1-O5 配位作用连成波浪形的层状结构。结晶水、配位水及羧基氧之间存在丰富的氢键作用进一步将二维层拓展成三维超分子网络。新产生的配体 2,4,6-opyta<sup>3-</sup> 是由 Cu(II)诱导  $\text{HNO}_3$  氧化 2,4,6-tmpy 发生氧化和羟基化反应原位合成的。

**关键词:** 原位反应; 氧化和羟基化; 水热合成; 铜配合物

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## Synthesis of a New Cu(II) Complex with *in situ* Generated 3-Hydroxy-2,4,6-pyridinetricarboxylate Ligand and Analysis of the Reaction Mechanism

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**Abstract:** A new Cu(II) complex  $[\text{Cu}_2(2,4,6\text{-opyta})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  was prepared hydrothermally through 2,4,6-trimethylpyridine (2,4,6-tmpy) and  $\text{Cu}(\text{NO}_3)_2$ , where 2,4,6-opyta<sup>3-</sup> is 3-hydroxy-2,4,6-pyridinetricarboxylate. X-ray analysis indicates that Cu1 and Cu2 centers in this complex both adopt a five-coordinated square-pyramidal geometry. Adjacent  $[\text{Cu}_4(2,4,6\text{-opyta})_2(\text{H}_2\text{O})_4]$  units link each other through Cu1-O5 coordination interaction and form a wave-like 2D layer. These 2D layers further form a 3D supermolecular network through abundant intra-, intermolecular hydrogen-bonding interactions between water molecules and carboxylate oxygen atoms. Furthermore, the new ligand 2,4,6-opyta<sup>3-</sup> is derived from copper-mediated oxidation and hydroxylation of 2,4,6-tmpy by utilizing  $\text{HNO}_3$  as an oxidant. Crystal data of  $[\text{Cu}_2(2,4,6\text{-opyta})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ :  $M_r=422.24$ , Monoclinic,  $P2_1/c$ ,  $a=1.122\ 15(11)$  nm,  $b=0.671\ 53(7)$  nm,  $c=1.715\ 29(18)$  nm,  $\beta=107.109(2)^\circ$ ,  $V=1.235\ 4(2)$  nm<sup>3</sup>,  $Z=4$ ,  $R_1=0.039\ 1$ ,  $wR_2=0.098\ 0$  ( $I>2\sigma(I)$ ). CCDC: 783944.

**Key words:** *in situ* reaction; oxidation and hydroxylation; hydrothermal synthesis; Cu(II) complex

Hydro(solve)thermal *in situ* ligand synthesis is important not only in the crystal engineering of coordination complexes but also in synthetic organic chemistry<sup>[1-2]</sup>. Up to now, more and more important and

interesting *in situ* ligand reactions, such as oxidative hydroxylation of aromatic ring<sup>[3-6]</sup>, dehydrogenative carbon-carbon coupling<sup>[7-9]</sup>, cycloaddition of organic nitriles with azide and ammonia<sup>[10-12]</sup>, and transformation

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of inorganic and organic sulfur<sup>[13-16]</sup>, have been documented. We once reported a one-step oxidation of 2,9-dimethyl-1,10-phenanthroline ligands (dmphen) to 1,10-phenanthroline-2,9-dicarboxylic acid (phendaH<sub>2</sub>) in the presence of Cu(NO<sub>3</sub>)<sub>2</sub><sup>[17]</sup>. Recently, we successfully oxidized 2,3,5-trimethylpyridine and 2,4,6-trimethylpyridine and generated four different pyridinecarboxylates in the presence of copper nitrate under controlled hydrothermal conditions. Moreover, the new generated ligand 3-hydroxy-2,4,6-pyridinetricarboxylic acid (2,4,6-opytaH<sub>3</sub>) have been separated from Cu(II)-complex<sup>[18]</sup>.

As an extension of our previous work, we report here our further investigation on generating new 2,4,6-opyta<sup>3-</sup> contained Cu(II)-complexes. The reaction mechanism of *in situ* generated 2,4,6-opyta<sup>3-</sup> is also discussed here.

## 1 Experimental

### 1.1 Reagents and measurements

The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elemental Vario-EL CHNS elemental analyzer. The FTIR spectra were recorded from KBr pellets in the range 4 000~400 cm<sup>-1</sup> on a Bio-Rad FTS-7 spectrometer.

### 1.2 Synthesis of [Cu<sub>2</sub>(2,4,6-opyta)(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O

A mixture of 2,4,6-tmpy (1 mmol, 0.121 g),

Cu(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (3.5 mmol, 0.720 g) and distilled H<sub>2</sub>O (10 mL) was sealed in a 23 mL Teflon-liner autoclave. The mixture was heated in an oven to 180 °C for 72 h, then cooled to room temperature at a rate of 5 °C·h<sup>-1</sup>, and finally yielded green sheet-like crystals of title complex (yielding 25% based on 2,4,6-tmpy). Elemental analysis calcd. for C<sub>8</sub>H<sub>9</sub>N<sub>1</sub>O<sub>11</sub>Cu<sub>2</sub> (%): C 22.76, H 2.15, N 3.32; Found (%): C 22.46, H 2.31, N 3.10; IR (cm<sup>-1</sup>): 3 400s, 1 603vs, 1 628vs, 1 460m, 1 420s, 1 340s, 1 293m, 1 150m, 970m, 940w, 870m, 830m, 750m, 720s, 610m.

### 1.3 X-ray crystallography

Diffraction intensities of title complex was collected on a Bruker Smart Apex CCD area-detector diffractometer (Mo Kα, λ=0.071 073 nm). Absorption corrections were applied by using multi-scan program SADABS<sup>[19]</sup>. The structure were solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package<sup>[20]</sup>. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C-H 0.096 nm); the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Crystal data as well as details of data collection and refinements for title complex are summarized in Table 1. Selected bond distances and bond angles are listed in Table 2.

CCDC: 783944.

Table 1 Crystallographic data and structure refinement for title complex

Empirical formula	C <sub>8</sub> H <sub>9</sub> NO <sub>11</sub> Cu <sub>2</sub>	Limiting indices	-13 ≤ h ≤ 14, -8 ≤ k ≤ 8, -21 ≤ l ≤ 13
Formula weight	422.24	Crystal size / mm	0.15×0.13×0.10
Temperature / K	293(2)	D <sub>c</sub> / (g·cm <sup>-3</sup> )	2.27
Crystal system	Monoclinic	μ / cm <sup>-1</sup>	0.350 8
Space group	P2 <sub>1</sub> /c	F(000)	840
a / nm	1.122 15(11)	S on F <sup>2</sup>	1.05
b / nm	0.671 53(7)	Reflections collected	7 604
c / nm	1.715 29(18)	Independent reflections (R <sub>int</sub> )	2 613 (0.033 5)
β / (°)	107.109(2)	Data / restraints / parameters	2 613 / 12 / 223
V / nm <sup>3</sup>	1.2354(2)	Final R indices (I>2σ(I))	R <sub>1</sub> <sup>a</sup> =0.039 1, wR <sub>2</sub> <sup>b</sup> =0.098 0
Z	4	Final R indices (all data)	R <sub>1</sub> <sup>a</sup> =0.047 2, wR <sub>2</sub> <sup>b</sup> =0.102 9
θ rang for data collection / (°)	2.48~26.990	Largest diff. peak / hole / (e·nm <sup>-3</sup> )	804 / -591

<sup>a</sup> R<sub>1</sub>=Σ||F<sub>o</sub>|-|F<sub>c</sub>||/Σ|F<sub>o</sub>|, <sup>b</sup> wR<sub>2</sub>=[Σw(F<sub>o</sub><sup>2</sup>-F<sub>c</sub><sup>2</sup>)<sup>2</sup>/Σw(F<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>.

Table 2 Bond length (nm) and bond angle (°) of title complex

Cu(1)-N(1)	0.191 2(3)	Cu(1)-O(7)	0.199 1(3)	Cu(1)-O(1W)	0.219 6(3)
Cu(1)-O(5A)	0.193 5(3)	Cu(1)-O(1)	0.207 7(3)	Cu(2)-O(4B)	0.191 3(3)
Cu(2)-O(2)	0.192 7(2)	Cu(2)-O(3B)	0.194 5(3)		
Cu(2)-O(3)	0.193 4(3)	Cu(2)-O(3W)	0.242 4(4)		
N(1)-Cu(1)-O(5A)	169.31(13)	N(1)-Cu(1)-O(1)	78.96(11)	N(1)-Cu(1)-O(1W)	104.38(13)
N(1)-Cu(1)-O(7)	81.10(12)	O(5A)-Cu(1)-O(1)	105.63(11)	O(5A)-Cu(1)-O(1W)	85.90(13)
O(5A)-Cu(1)-O(7)	93.26(11)	O(7)-Cu(1)-O(1)	159.51(11)	O(7)-Cu(1)-O(1W)	106.48(13)
O(1)-Cu(1)-O(1W)	83.18(12)	O(4B)-Cu(2)-O(3W)	89.09(12)	O(4B)-Cu(2)-O(3)	168.98(11)
O(4B)-Cu(2)-O(2)	96.02(11)	O(2)-Cu(2)-O(3W)	93.65(13)	O(2)-Cu(2)-O(3)	94.76(11)
O(4B)-Cu(2)-O(3B)	91.40(11)	O(3)-Cu(2)-O(3W)	92.52(13)	O(2)-Cu(2)-O(3B)	168.74(12)
O(3B)-Cu(2)-O(3W)	94.93(13)	O(3)-Cu(2)-O(3B)	77.60(12)		

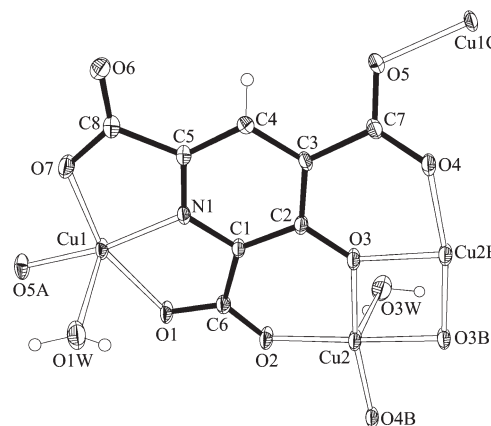
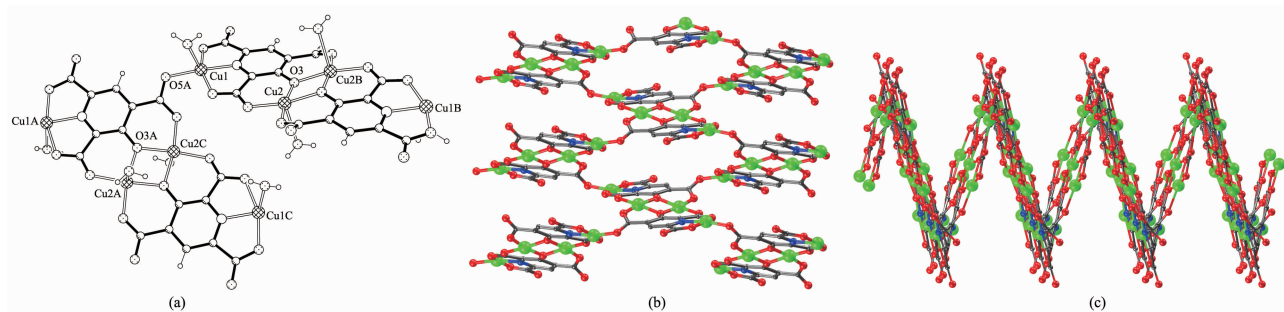
Symmetry codes: A:  $x, -y+1/2, z+1/2$ ; B:  $-x+1, -y+1, -z$ .

## 2 Results and discussion

### 2.1 Crystal structure of $[\text{Cu}_2(2,4,6\text{-opyta})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

X-ray analysis revealed the asymmetrical unit of this complex contains one crystallographically independent  $\mu_4$ -2,4,6-opyta<sup>3-</sup> molecules, two five-coordinated Cu(II), two coordinated water molecules and two solvent water molecules, as shown in Fig.1. Cu1 and Cu2 both adopt distorted square-pyramidal coordination geometry, and Cu1 is surrounded with NO<sub>4</sub> coordination sphere while Cu2 surrounded with four oxygen atoms from 2,4,6-opyta<sup>3-</sup> and one water molecule. (Cu1-O 0.193 5(3)~0.219 6(3) nm, Cu1-N 0.191 2(3) nm, Cu2-O 0.191 3(3)~0.242 4 (4) nm). Two asymmetrical units dimerize into a  $[\text{Cu}_4(2,4,6\text{-opyta})_2(\text{H}_2\text{O})_4]$  unit (C in Scheme 2) through the coordination interaction between Cu2 and  $\mu_2$ -O3. Adjacent Cu<sub>4</sub> units link each other through Cu1-O5

coordination interactions (Fig.2a,b) and form a wave-like two-dimensional (2D) layer (Fig.2c). Adjacent layers further extend into a 3D supermolecular network through

Symmetry codes: A:  $x, -y+1/2, z+1/2$ ; B:  $-x+1, -y+1, -z$ ; C:  $x, -y+1/2, z-1/2$ ; 30% probability displacement ellipsoidsFig.1 Coordination environments of Cu(II) and 2,4,6-opyta<sup>3-</sup>Symmetry codes: A:  $x, -y+1/2, z+1/2$ ; B:  $-x+1, -y+1, -z$ ; C:  $x, -y+1/2, z-1/2$ ; Coordinated and crystallized water molecules and hydrogen atoms are omitted for clarityFig.2 (a) Cu<sub>4</sub> units link together through Cu1-O5 coordination interaction; (b) 2D layer in title complex perspective viewed from *a* axis; (c) 2D layer perspective viewed from *c* axis

inter-/intra hydrogen-bonding interactions between carboxylate oxygen atoms and water molecules. ( $O_w \cdots O_{\text{carboxylate}} = 0.266\ 1(5) \sim 0.329\ 7(6)\ \text{nm}$ ,  $O_w - H_w \cdots O_{\text{carboxylate}} =$

$137(7)^\circ \sim 173(7)^\circ$ ). All hydrogen bond parameters of this complex are listed in Table 3.

Table 3 Bond length and bond angle of hydrogen bond

D-H $\cdots$ A	$d(H\cdots A) / \text{nm}$	$d(D\cdots A) / \text{nm}$	$d(D\cdots H) / \text{nm}$	$\angle(DHA) / (^\circ)$
O(1W)-H(1WA) $\cdots$ O(4W)	0.186(2)	0.266 1(5)	0.084 2(10)	159(5)
O(1W)-H(1WB) $\cdots$ O(7A)	0.199 5(15)	0.281 6(4)	0.084 1(10)	165(5)
O(2W)-H(2WA) $\cdots$ O(1B)	0.206(5)	0.279 0(5)	0.085 0(10)	144(8)
O(2W)-H(2WB) $\cdots$ O(3WC)	0.263(6)	0.329 7(6)	0.084 9(10)	137(7)
O(3W)-H(3WA) $\cdots$ O(6D)	0.210(3)	0.286 3(4)	0.084 5(10)	150(5)
O(3W)-H(3WB) $\cdots$ O(1WE)	0.216 3(15)	0.300 4(5)	0.084 5(10)	173(7)
O(4W)-H(4WB) $\cdots$ O(6F)	0.221	0.296 4(6)	0.085	148.1
O(4W)-H(4WA) $\cdots$ O(2W)	0.209	0.287 8(6)	0.085	154.7

Symmetry codes: A:  $-x, y+1/2, -z+1/2$ ; B:  $-x+1, y+1/2, -z+1/2$ ; C:  $-x+1, -y+1, -z$ ; D:  $x+1, y, z$ ; E:  $-x+1, y-1/2, -z+1/2$ ;

F:  $-x, -y+1, -z$ .

## 2.2 Mechanistic investigation

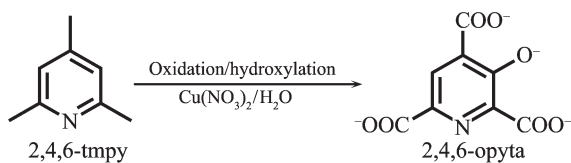
Evans and Lin reported that nitrate might act as oxidant for oxidative coupling of methanol to oxalic acid<sup>[21]</sup>. We found in our previous study that the methyl groups in the pyridine ring could be oxidized to carboxylic acids by nitric acid under hydrothermal condition, where  $\text{HNO}_3$  came from the metal salts and the protons in the solution<sup>[17]</sup>.

To gain insight into the mechanism of generating 2,4,6-opyta<sup>3-</sup> from 2,4,6-tpmy (Scheme 1), we carried out a systematic investigation by controlling the reaction temperature, time, pH value and stoichiometric proportion of reactants. The results showed that this in situ ligand reaction was copper-mediated and depended markedly upon solvents and anions of cupric salts. No similar metal complexes were obtained by using other transition-metal cations such as Zn(II), Ni(II) or Co(II) in place of Cu(II) under similar reaction conditions. If deionized water were replaced by other organic solvents such as acetonitrile, methanol, ethanol or acetone, or the nitrate ion were replaced by other anions, no carboxyl products could be detected. Moreover, auto-

generated pressure upon high temperature ( $T > 160\ ^\circ\text{C}$ ) via hydrothermal condition played a vital role.

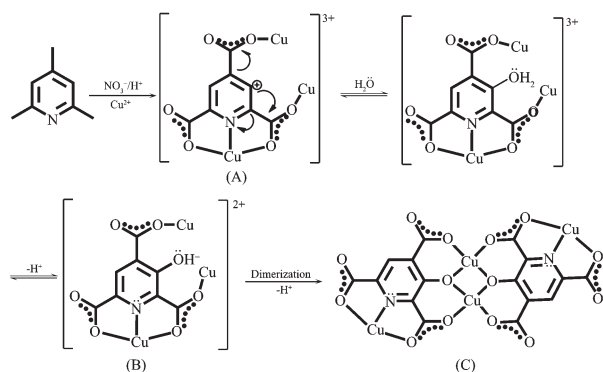
Since 2-, 4-, 6- carboxyl groups always coexist in the final complex, we assume that three methyls of 2,4,6-tpmy are simultaneously oxidized to 2-, 4-, 6- carboxyl groups owing to their similar chemical environment such as electronic disposition and steric hindrance. The hydroxylation of pyridine ring may be affected by the pH value of reaction system, and the acidic environment may prevent further hydroxylation of aromatic ring, which is approved by the successfully got complex  $[\text{Cu}_2(\mu_3\text{-OH})(2,4,6\text{-pyta})]^{[18]}$  (2,4,6-pyta<sup>3-</sup> = 2,4,6-pyridinetricarboxylate) under acidic environment. It is interesting to note that the in situ generated 2,4,6-pyta<sup>3-</sup> is oxidized from 2,4,6-tpmy but hydroxylation of pyridine ring is prevented. Notedly,  $[\text{Cu}_4(2,4,6\text{-opyta})_2(\text{H}_2\text{O})_4]$  unit (C in Scheme 2) exist in all of the 2,4,6-opyta<sup>3-</sup> contained Cu(II)-complexes<sup>[18]</sup> whatever reaction condition changes.

Considering the aforementioned discussion and our former results<sup>[18]</sup>, the reaction mechanism of in situ generating 2,4,6-opyta<sup>3-</sup> ligand could be elucidated as follows (Scheme 2): Firstly, three methyls in the 2-, 4-, and 6-position are oxidized by  $\text{HNO}_3$  to form 2,4,6-pyta<sup>3-</sup>, which followed with the coordination of N,O donors to Cu(II) cations. Surrounded by strong electron withdraw groups such as carboxyl groups and pyridine nitrogen atom,  $\beta$ -carbon atom of pyridine is electron-



Scheme 1 2,4,6-tpmy was in situ oxidized into the new ligand 2,4,6-opyta<sup>3-</sup>

defect (A in Scheme 2). Secondly, hydroxyl or water molecules in solution take nucleophilic substitution reaction to the hydrogen atom of  $\beta$ -carbon. Followed by dehydrogenation of  $\beta$ -hydroxyl,  $[\text{Cu}_4(2,4,6\text{-opyta})_2(\text{H}_2\text{O})_4]$  unit generates by chelating with two units of B. In these procedures, Cu (II) serves not only as a coordinated metal ion, but also mediated the intramolecular electron transfer.



Scheme 2 Possible reaction mechanism of forming  
2,4,6-opyta<sup>3-</sup>

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