

Solid–Solid Synthesis, Crystal Structure and Thermal Decomposition of Copper(II) Complex of 2-Picolinic Acid

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ABSTRACT: The copper(II) complex $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$ was synthesized with 2-picolinic acid (Hpic) and copper acetate as reactants by room temperature solid-solid reaction. The composition and structure of the complex was characterized by elemental analyses, single crystal X-ray diffraction, X-ray powder diffraction, FT-IR spectroscopy and thermogravimetry-differential scanning calorimetry. The crystal structure of the copper(II) complex belongs to triclinic system and space group , with cell parameters of $a = 5.1274(16) \text{ \AA}$, $b = 7.641(2) \text{ \AA}$, $c = 9.209(2) \text{ \AA}$, $\alpha = 74.91(2)^\circ$, $\beta = 84.56(2)^\circ$, $\gamma = 71.58(3)^\circ$, $V = 338.48(15) \text{ \AA}^3$, $Z = 1$, $F(000) = 175$, $R_1 = 0.0530$, and $wR_2 = 0.1141$. The Cu(II) ion is six-coordinated through two nitrogen atoms from two pyridine rings and four carboxyl oxygen atoms from four different 2-picolinic acid anions, forming an elongated octahedral geometry. The interaction of carboxylate O and Cu(II) forms an one-dimensional chain structure, and the complex exhibits a two-dimensional layered structure by hydrogen bonds. The thermal decomposition processes of the complex under air include dehydration and pyrolysis of the ligand, and the final residue at about 400 °C is copper oxide.

KEYWORDS: 2-Picolinic acid; Copper(II) complex; Room temperature solid-solid reaction; Crystal structure; Thermal decomposition.

INTRODUCTION

In recent decades, metal–organic frameworks and supramolecular coordination complexes are undergoing accelerated and sustained growth owing to their fascinating structural motifs and potential applications, such as porous, gas storage, multifunctional materials, magnetic, chemical separation, and catalytic materials [1-10]. It's known that pyridinecarboxylic acid is beneficial compounds for human organism and it is involved in several essential biochemical processes, and can interact with a number of metal ions in the body [11]. In particular, 2-picolinic acid is terminal tryptophan

metabolite, and its carboxyl anion has been used as a valuable chelating ligand [12], and the oxygen atoms of the carboxyl group are coordinated with metal atoms through the diversity of monodentate, chelate and bridge coordination modes, so *N*-heterocyclic polycarboxylate ligands are efficient building blocks for constructing coordination polymers [13-15]. To the best of our knowledge, 2-picolinic acid is not only a potential proton acceptor but also proton donor depending on deprotonated group, a number of high nuclearity transition metals complexes of 2-picolinate have been identified, such as

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the crystal structures of Ni(II), Zn(II), Co(II), and Mn(II) complexes of 2-picolinic acid derivations [12,16,17].

Copper(II) is an essential trace element for human nutrition, and it maintains the normal physiological functions [18]. Metallic complexes can modified pharmacological and toxicological properties for many drugs, and the studies have shown that some low molecular weight copper complexes can beneficial for treatment several diseases, such as rheumatoid, gastric ulcers, tumor, and tuberculosis [19]. Besides, because MOFs are highly porous and low-density materials, it has ability to uptake guest molecules, and has been exploited for use as a drug delivery vehicle [20]. So, 2-picolinate with Cu(II) produces a carboxylate-bridged polymeric copper network which is obtained by self-assembly, and the complex may be generate medicinal utility and biological activity [21]. Copper 2-picolinate is expected as a new feed additive, in order to improve the utilization rate of copper absorption and reduce the pollution of the environment. In this paper, taking into account our recent studies on the coordination chemistry and the biological activity of *N*-heterocyclic polycarboxylate ligands, we report the syntheses and characterization of the bioinorganic complex $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$, using the method of room temperature solid-solid synthesis, which method can be get much higher yield, more inexpensive, faster reaction rate and easier operating, and save energy and environmental friendly [22-24].

EXPERIMENTAL SECTION

Materials and physical measurements

All the chemicals used in the experiments were analytical reagent as received from commercial sources and without further purification. 2-Picolinic acid (Hpic) was purchased from Alfa Aesar, while copper(II) acetate monohydrate was purchased from Merck.

The elemental analyses of carbon, hydrogen, and nitrogen in the complex were measured by a Vario EL CUBE elemental analyzer, and the copper content was determined by EDTA complexometric titration. IR spectra were obtained with a Perkin-Elmer Spectrum One-spectrometer in the range of $400\text{--}4000\text{ cm}^{-1}$ using KBr pellets. The thermogravimetric analysis of the complex was performed by a SDT Q600 thermogravimetric analyzer, and the measurement was recorded from 30 to $500\text{ }^\circ\text{C}$ at the heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under air flow

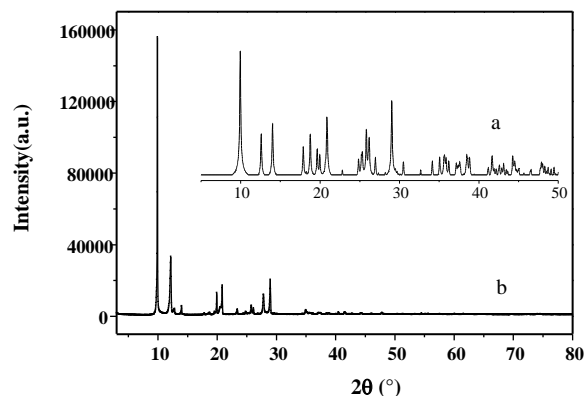
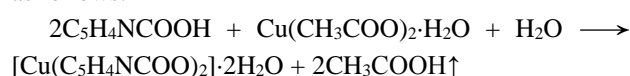


Fig. S1: XRD patterns for title complex generated from the experimental data (a) and simulated from the single crystal X-ray data (b).

of 50 mL/min. X-ray powder diffraction (XRD) was performed using a D/max-II X-ray diffractometer, Cu K_α radiation ($\lambda = 0.154056\text{ nm}$, step width: $2\theta = 0.02^\circ$, scan speed: $8^\circ/\text{min}$).

Synthesis of title complex $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$

The synthetic reaction equation of the title complex is as follows:



2-Picolinic acid (10 mmol, 1.23 g) and copper acetate monohydrate (5 mmol, 1.00 g) of the two reactants were weighed and placed in an agate mortar, and the molar ratio of 2-picolinic acid to copper acetate was 2:1. Then, the mixture was grinded carefully at room temperature, and released a strong irritant gas in the grinding process. The released gas was tested with moist pH paper, and the result indicated that the gas was faintly acid gas. The reason was that the acetic acid was released in the reaction process. When there was no irritant gas escaped, this reaction was complete. The reaction conducted in grinding at room temperature for 4 h, and the mixture became into loose blue powder. After the XRD data of the resultant was collected (see supplementary materials Fig. S1), the product was transferred to a glass beaker and stirred to dissolve with a little distilled water, and the solution was filtered and concentrated. When the concentrated solution was placed at room temperature about 15 days, the blue flake crystals of the copper(II) complex were obtained. The yield of the complex was about 87%. Anal. Calcd. for $\text{CuC}_{12}\text{H}_{12}\text{O}_6\text{N}_2$ (%): C,

Table 1: Crystal data and structure refinement parameters for the title complex.

Empirical formula	CuC ₁₂ H ₁₂ O ₆ N ₂	Absorption coefficient	1.682 mm ⁻¹
Formula weight	343.78 g mol ⁻¹	<i>F</i> (000)	175
Temperature	298(2) K	Crystal size	0.40 mm × 0.31 mm × 0.18 mm
Wavelength	0.71073 Å	Theta range for data collection	3.23–25.01°
Crystal system	Triclinic	Limiting indices	−6 ≤ <i>h</i> ≤ 5, −9 ≤ <i>k</i> ≤ 9, −10 ≤ <i>l</i> ≤ 10
Space group	<i>P</i> $\bar{1}$	Reflections collected / unique	1957/1156 [<i>R</i> (int) = 0.0482]
<i>a</i>	5.1274(16) Å	Completeness to theta = 25.02	99.8%
<i>b</i>	7.641(2) Å	Absorption correction	Semiempirical from equivalents
<i>c</i>	9.209(2) Å	Max. and min. transmission	0.7516 and 0.5526
α	74.91(2)°	Refinement method	Full-matrix least-squares on <i>F</i> ²
β	84.56(2)°	Data / restraints / parameters	1156/0/97
γ	71.58(3)°	Goodness-of-fit on <i>F</i> ²	1.070
<i>V</i>	330.48(15) Å ³	Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0530, <i>wR</i> ₂ = 0.1141
<i>Z</i>	1	<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0682, <i>wR</i> ₂ = 0.1242
Calculated density	1.727 mg cm ⁻³	Largest diff. peak and hole	0.754 and −0.405 e Å ⁻³

41.92; H, 3.52; N, 8.15; Cu, 18.49. Found (%): C, 41.79; H, 3.46; N, 8.04; Cu, 18.62.

X-ray crystal structure determination

X-ray diffraction data for a single crystal of the title complex were collected at 293(2) K on a Bruker SMART APEX II CCD diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda = 0.071073$ Å) using ω and ϕ scan mode. A blue flake crystal with dimensions 0.40 mm × 0.31 mm × 0.18 mm was mounted on a glass fiber. The structures were solved by direct methods and refined by full-matrix least squares on *F*² using the SHELXTL program package [25]. All of the non-hydrogen atoms were refined with anisotropic displacement parameters and all of the hydrogen atoms were found objectively from difference Fourier syntheses. The structure refinement parameters and the crystallographic data for the title complex are given in Table 1, and the crystallographic data are deposited with the Cambridge Crystallographic Data Centre under deposition number CCDC 989358.

RESULTS AND DISCUSSION

X-ray crystal structure analysis

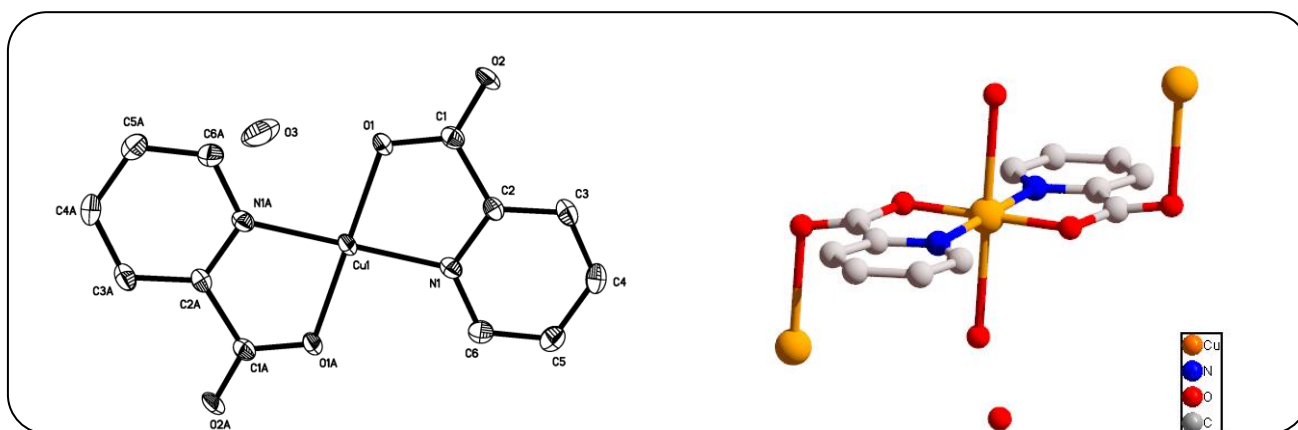
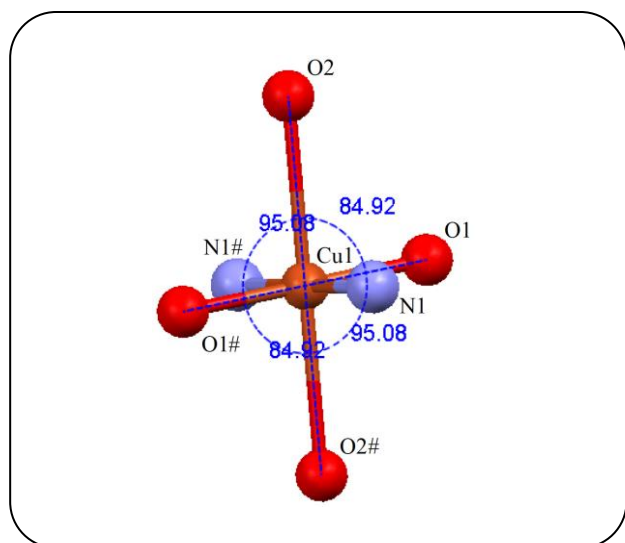
A view of the key fragments of the structure of the complex [Cu(pic)₂] \cdot 2H₂O is shown in Fig. 1, and the selected bond distances and angles are shown in Table 2.

The unit of the complex is composed of one Cu(II) ion, two 2-picolinic acid anions, and two water molecules. The Cu(II) ion is six-coordinated through two nitrogen atoms from two pyridine rings and two carboxyl oxygen atoms from two 2-picolinic acid anions and two oxygen atoms of the carboxylate groups of the adjacent [Cu(pic)₂] units [Cu(1)–N(1), 1.958(3) Å; Cu(1)–N(1)#1, 1.958(3) Å and Cu(1)–O(1), 1.944(3) Å; Cu(1)–O(1)#1, 1.944(3) Å; Cu(1)–O(2), 2.745(4) Å; Cu(1)–O(2)#1, 2.745(4) Å]. The water molecules do not coordinate with the Cu(II) ion in the complex. Its structure bridged through weak interactions between the Cu(II) and the O atoms of the carboxylate groups of the adjacent [Cu(pic)₂] units. Because of the significant Jahn-Teller effect of the Cu(II) ion with d⁹ electron configuration, the copper(II) in the octahedral environment is tetragonally elongated distorted, and the coordination structure usually manifests itself as an axial elongation [17]. So, the bond distances in the equatorial positions [Cu(1)–N(1), Cu(1)–N(1)#1, Cu(1)–O(1), and Cu(1)–O(1)#1] are shorter than the axial positions [Cu(1)–O(2) and Cu(1)–O(2)#1], the axial Cu–O bonds result in no π – π stacking interaction between the layers. Fig. 2 shows that the five atoms of O(1), N(1), Cu(1), O(1)#1, and N(1)#1 are in the equatorial plane, forming two pairs of opposite angles, equals 360°, and show a parallelogram array, and the bond angle of O(1)–Cu(1)–O(1)#1 is 180°. The O(2),

Table 2: Selected bond lengths (Å) and angles (°) for the title complex.

Cu(1)–O(1)#1	1.944(3)	O(1)–Cu(1)–O(1) #1	180.000(1)	O(1)–C(1)–C(2)	115.0(4)
Cu(1)–O(1)	1.944(3)	N(1)#1–Cu(1)–N(1)	180.00(19)	N(1)–C(2)–C(3)	112.0 (4)
Cu(1)–N(1)#1	1.958(3)	O(1)–Cu(1)–N(1)#1	96.51(12)	N(1)–C(2)–C(1)	113.8 (3)
Cu(1)–N(1)	1.958(3)	O(1)#1–Cu(1)–N(1)	96.51(12)	C(1)–O(1)–Cu(1)	114.7(3)
Cu(1)–O(2)	2.745(4)	O(1)–Cu(1)–N(1)	83.49(12)	C(6)–N(1)–C(2)	119.1(4)
Cu(1)–O(2)#1	2.745(4)	C(2)–N(1)–Cu(1)	112.5(3)	O(1)#1–Cu(1)–N(1)#1	83.49(12)
N(1)–C(6)	1.332(5)	C(6)–N(1)–Cu(1)	128.3(3)	O(2)–C(1)–C(2)	119.7(4)
N(1)–C(2)	1.337(5)	H(3C)–O(3)–H(3D)	108.4	O(2)–C(1)–O(1)	125.3(4)
O(1)–C(1)	1.274(5)	H(3C)–O(3)–H(3B)	110.1	N(1)–C(6)–C(5)	122.0(4)
O(2)–C(1)	1.231(5)	H(3D)–O(3)–H(3B)	110.1	N(1)–C(6)–H(6)	119.0

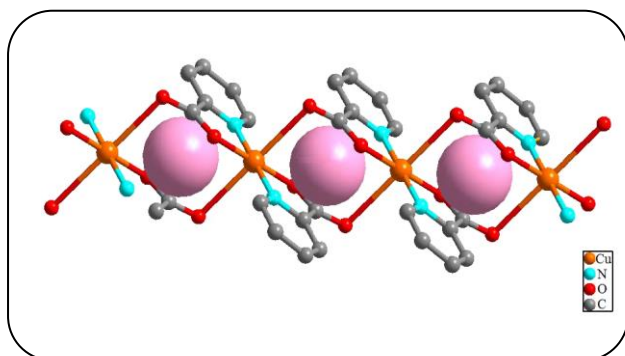
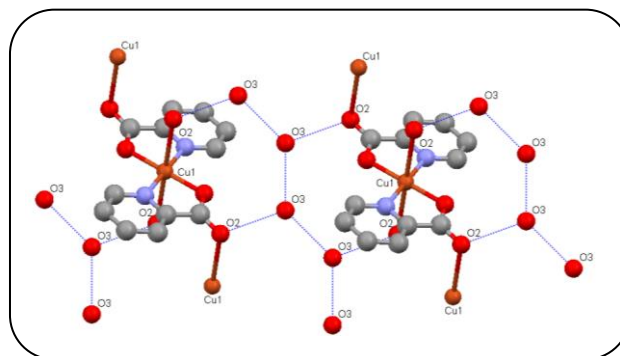
Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$.

**Fig. 1: Molecular structure of the title complex.****Fig. 2: Coordination environment of the Co(II) ion.**

Cu(1), and O(1) atoms are in nearly perpendicular to the equatorial plane, and the angle is 84.92° and the dihedral angle is 95.08° . In Fig. 3, the cavity structure of the distorted parallelogram in the complex is formed by Cu–O(2)–C(1)–O(1)–Cu–O(2)–C(1)–O(1), just like the pink fake atomic sphere fill in the ring, and the cavity sizes for MOF is about $2.74 \times 4.449 \text{ \AA}^2$, which can be used in similar to porous materials. The cavity complex may be exploited for use as a drug delivery vehicle or adsorption material [26]. The interaction of carboxylate O and Cu(II) forms an one-dimensional chain structure. In Fig. 4, the molecule of the complex $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$ is held together by intermolecular hydrogen bonds. Hydrogen bond lengths and bond angles for the title complex are given in Table 3. There are two types of hydrogen bonds in the crystal of the Cu(II) complex,

Table 3: Hydrogen bond lengths (Å) and bond angles (°) for the title complex.

D-H	$d(D-H)$	$d(H\cdots A)$	$\angle DHA$	$d(D\cdots A)$	A symmetry operation
O3-H3C	0.850	2.073	177.40	2.923	O2 [x-1, y, z]
O3-H3D	0.850	1.977	177.94	2.827	O3 [-x, -y+1, -z]
O3-H3B	0.850	2.309	115.11	2.778	O3 [-x+1, -y+1, -z]

**Fig. 3: Cavity structure of the title complex.****Fig. 4: Packing diagram of the title complex showing hydrogen bonding.**

the hydrogen bonds between the crystalline water molecules (O3-H3D \cdots O3, 2.827 Å and O3-H3B \cdots O3, 2.778 Å), and the crystalline water and the oxygen atoms of the carbonyl groups (O3-H3C \cdots O2, 2.923 Å). In fact, the hydrogen bonds between the interstitial water molecules and carboxyl oxygen atoms form a two-dimension layers structure, which is in order to make the structure more stable.

FT-IR spectra

FT-IR spectra of the ligand 2-picolinic acid and the title complex are given in Figs. 5 and 6. Comparison of FT-IR spectrum of the free ligand reveals that the considerable changes in frequencies can determine the coordination sites in chelation. A wide intense absorption band around 3435 cm^{-1} can be assigned to stretching vibration of hydroxyl from the water molecules [27,28]. The bands corresponding to the stretching vibration of the C-H and C=N bonds are situated at 3076 and 1641 cm^{-1} , respectively. The band corresponding to the stretching vibration of the C=O group of the Hpic monomer is situated at 1712 cm^{-1} and disappears in the complex. According to the separation of the bands is indicative of the structure of a given carboxylate, the difference value of 258 cm^{-1} between the asymmetric (1605 cm^{-1}) and symmetric (1347 cm^{-1}) stretching vibration of the carboxylate group is in line with a bidentate bridging coordination mode of coordination [29,30]. In the IR

spectra, the O-H \cdots N type of intermolecular hydrogen bonding of 2-picolinic acid ligand can be seen at 2607 and 2152 cm^{-1} and it disappears in the complex which phenomenon confirms that the nitrogen atom is coordinated to the metal Cu(II) ion. The absorption bands at 1475 and 1445 cm^{-1} are attributed to the $\nu(\text{C}=\text{C})$ vibrations [31]. The absorption peaks of the C-O and C-C bonds for the complex are between 1152 and 1048 cm^{-1} . The ring wagging vibration of the pyridine group is also observed at 695 cm^{-1} region for the complex. The weak band at 546 cm^{-1} is attributed to the Cu-N bond stretching vibration and the absorption peak at 460 cm^{-1} is assigned to the Cu-O bond [32,33].

Thermal analysis

Studying the thermal stability of complexes is helpful to the understanding of the coordination structure of complexes, and it seemed of interest to evaluate the effect of heating on the thermal decomposition process of the prepared complexes in the same way as reported earlier [34-35]. The thermal analysis of the complex was studied by thermogravimetric (TG) and differential scanning calorimetry (DSC) in the temperature range from 30 to 500 °C under air atmosphere with a heating rate of 10 °C min^{-1} . The pertinent thermal decomposition data for the complex are presented in Table 4, and the TG-DSC

Table 4: Thermal decomposition data of the title complex.

Reaction	DSC/ $^{\circ}\text{C}$	Mass loss/%	
		m_{exp}	m_{theor}
$[\text{Cu}(\text{C}_5\text{H}_4\text{NCOO})_2] \cdot 2\text{H}_2\text{O}$			
$\downarrow -2\text{H}_2\text{O}$	84 (endo.)	10.04	10.48
$[\text{Cu}(\text{C}_5\text{H}_4\text{NCOO})_2]$			
$\downarrow -\text{C}_{12}\text{H}_8\text{N}_2\text{O}_3$	364 (exo.)	66.58	66.38
CuO		23.38 ^a	23.14 ^b

^a The experimental mass percent of the residue in the sample, ^b the calculated mass percent of the residue in the sample.

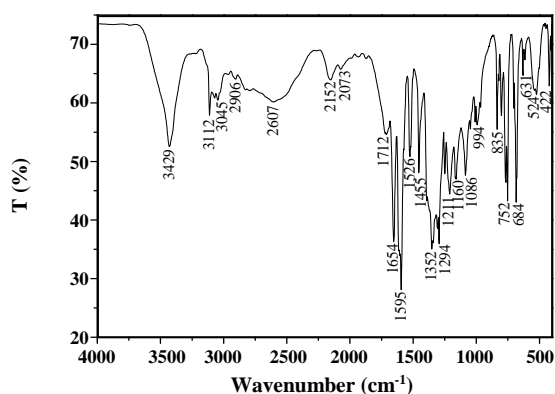


Fig. 5: FT-IR spectrum of the ligand 2-picolinic acid.

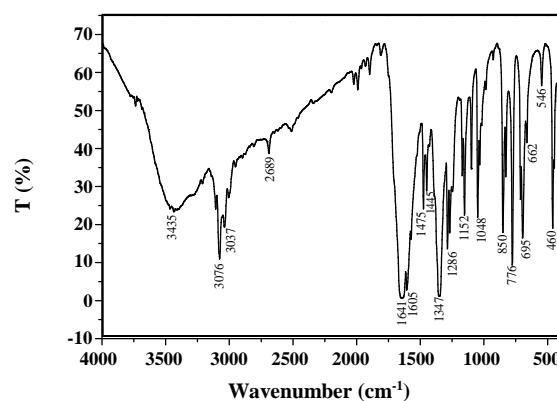


Fig. 6: FT-IR spectrum of the title complex.

curves of the complex are shown in Fig. 7. The thermal decomposition of the complex is divided into two stages, and there is one weak endothermic peak at 84 $^{\circ}\text{C}$ and one strong exothermic peak at 364 $^{\circ}\text{C}$ in the DSC curve. As Fig. 7 shows, the first mass loss of 10.04% occurs between 75 $^{\circ}\text{C}$ and 135 $^{\circ}\text{C}$ in the complex, corresponding to the lost of two crystalline water molecules (calcd. 10.48%). After the two water molecules are lost, and this step decomposition product is $[\text{Cu}(\text{C}_5\text{H}_4\text{NCOO})_2]$. Thereafter, the strong exothermic peak at 364 $^{\circ}\text{C}$ corresponds to oxidative decomposition of the picolinate ligand, and the experimental mass loss (66.58%) is close to the calculated one (66.38%). Afterward, the remaining mass remains almost constant until 500 $^{\circ}\text{C}$ and the final decomposition product consists of copper oxide (CuO), and the experimental result (23.38%) is in agreement with the result of theoretical calculation (23.14%).

CONCLUSIONS

The complex $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$ was synthesized with the room temperature solid-solid reaction of copper

acetate and 2-picolinic acid as the reactants. The composition and structure of the complex was characterized by EA, FTIR, single crystal X-ray diffraction, X-ray powder diffraction, and TG-DSC. The crystal structure of the copper(II) complex belongs to triclinic system and space group $P\bar{1}$, with cell parameters of $a = 5.1274(16)$ \AA , $b = 7.641(2)$ \AA , $c = 9.209(2)$ \AA , $\alpha = 74.91(2)^{\circ}$, $\beta = 84.56(2)^{\circ}$, $\gamma = 71.58(3)^{\circ}$, and $V = 338.48(15)$ \AA^3 . In this complex, the carboxylate of the picolinate acts as a bridge between Cu(II) ions, and the Cu(II) ion is six-coordinated by two N atoms from two pyridine rings and four different carboxyl O atoms from four ligands, and is formed an elongated octahedral geometry. The thermal decomposition processes of the complex under air include dehydration and pyrolysis of the ligand, and the final residue at about 400 $^{\circ}\text{C}$ is copper oxide.

Acknowledgements

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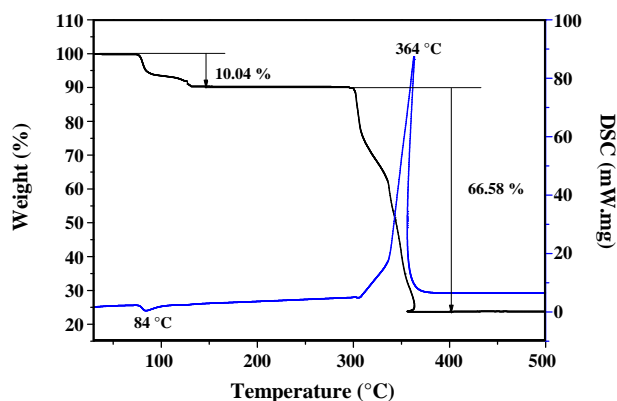


Fig. 7: TG-DSC curves of the title complex.

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SUPPLEMENTARY MATERIALS

Crystallographic data for the title complex $[\text{Cu}(\text{pic})_2] \cdot 2\text{H}_2\text{O}$ has been deposited with the Cambridge Crystallographic Data Centre. The deposition number is CCDC-989358. The data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk, or on the web:

<http://www.ccdc.cam.ac.uk>, or from the authors on request.

X-ray powder diffraction

The X-ray powder diffraction data of the title complex were collected in the diffraction angle range of 3° – 80° . The XRD pattern of the complex is shown in Fig. S1(a). There is the small background, and the high and intense of diffraction peaks in the XRD pattern of the complex, which indicates that the complex has fine crystalline state. The main diffraction peaks appear at $2\theta = 9.90^\circ$, 12.13° , and 28.95° for the title complex. The experimental pattern exhibiting some peaks is slightly broadened in comparison with the simulated pattern in Fig. S1(b), which may be due to the preferred orientation of

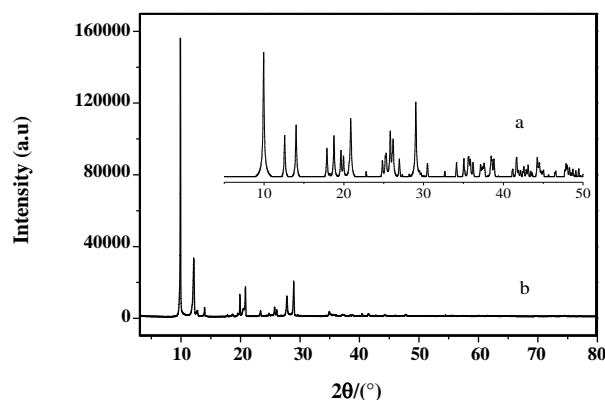


Fig. S1: XRD patterns for title complex generated from the experimental data (a) and simulated from the single crystal X-ray data (b).

the powder samples. The experimental XRD pattern agrees well with the simulated pattern generated on the basis of the single crystal analyses for the title complex.

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