

Solvothermal Synthesis, Crystal Structure and Characterization of a New Binuclear Copper(II) Complex with $K^3:N^1:N^2:N^4$ -3-(Pyridin-2-yl)-1,2,4-triazole (HPT)^①

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ABSTRACT A new binuclear copper(II) complex $[Cu_2(MBBA)_2(HPT)_2(H_2O)_2] \cdot 2H_2O$ (**1**) was synthesized with copper acetate, 2-(4-methylbenzoyl) benzoic acid (MBBA) and 3-(pyridin-2-yl)-1H-1,2,4-triazole (HPT). It crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.722(2)$, $b = 8.8907(12)$, $c = 18.5565(18)$ Å, $\beta = 116.820(7)^\circ$, $V = 2167.6(5)$ Å³, $M_r = 483.96$, $D_c = 1.483$ g/cm³, $Z = 4$, $\mu(MoKa) = 1.049$ mm⁻¹, $F(000) = 981$, the final $GOOF = 0.952$, $R = 0.0586$ and $wR = 0.0823$. The whole molecule consists of two copper ions bridged by two HPT molecules. The central Cu(II) ion is coordinated by six atoms to give a distorted octahedral coordination geometry. The structure of **1** has been determined by X-ray diffraction, IR spectrum and thermal stability analysis. The solid-state fluorescence displays an obvious emission band at 412 nm upon excitation at 330 nm. Magnetic properties indicate that **1** exhibits antiferromagnetic properties.

Keywords: binuclear copper(II) complex, thermal stability, fluorescence, magnetic property;

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1 INTRODUCTION

Carboxylic acids are widely used in the synthesis of complexes because of their various coordination modes, their own ability to slow down the electronegativity of counteracting ion effects, and the easy participation of carboxylic oxygen atoms in forming hydrogen bonds^[1, 2]. At present, studies mainly focus on complexes constructed by benzoic acid and their derivatives, and complexes constructed by derivatives which are substituted by electron-absorbing groups are mostly concentrated in halogens, nitro groups, cyano groups, etc^[3, 4]. *O*-Methylbenzoyl-benzoic acid as a useful organic synthesis intermediate is mainly applied in reducing dyes and fluorescent paints. Considering its both carboxyl and formyl, this acid can coordinate with transition metal ions as end-group or bridge ligands, in which hydrogen bonds are formed with other ligands or free water molecules by means of carboxyl and acyl oxygen atoms at multiple ligand sites^[5, 6]. So far, there have been many reports on the structures of complexes with multiple ligands, but very few on those with *o*-methylbenzoyl-benzoic acid as ligands^[7-9].

1,2,4-Triazole as a triazole heterocyclic compound is an ideal organic bridging ligand, which can be used to construct coordination polymer materials. Most of its complexes have novel structures, high chemical and thermal stability, and broad applications in such fields as selective adsorption, magnetism, catalysis, luminescence, DNA binding, bacteriostatic and anti-cellular activity^[10-14]. To construct new carboxylic acid complexes, we report herein a new binuclear copper(II) complex $[Cu_2(MBBA)_2(HPT)_2(H_2O)_2] \cdot 2H_2O$ (**1**) with 2-(4-methylbenzoyl) benzoic acid (MBBA) and 3-(pyridin-2-yl)-1H-1,2,4-triazole (HPT). **1** exhibits antiferromagnetism in the temperature range of 300~2 K. The thermal stability and fluorescent properties of **1** are also reported.

2 EXPERIMENTAL

2.1 Materials and instruments

All reagents from commercial sources were of analytical grade and used without further purification. HPT was prepared according to the previously reported methods^[15]. Crystal structure was determined on a Bruker SMART CCD

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6000 single-crystal diffractometer. IR spectra were recorded on a Bruker Vector22 FT-IR spectrophotometer using KBr discs. XDR analyses were performed on a D8 advance with voltage 40 KV, current 40 step 0.02 °, test speed 0.1 sec/step, copper target and incoming ray wavelength 0.15418 nm. Thermogravimetric analyses were performed on a simultaneous SPRT-2 pyris 1 thermal analyzer at a heating rate of 10 K/min. Magnetic measurements in the range of 300~2 K were carried out on a MPMS-SQUID magnetometer at a field of 2 kOe on a crystalline sample in the temperature settle mode. The fluorescence for the powdered samples was measured on an RF-5301PC spectrofluorometer with a xenon arc lamp as the light source.

2.2 Synthesis of 1

A mixture of MBBA (48.0 mg, 0.2 mmol), HPT (14.6 mg, 0.1 mmol) and $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ (59.9 mg, 0.3 mmol) was dissolved in 25 mL of mixed solvent. The volume ratio of ethanol and acetonitrile is 2:1. The pH value of the resultant mixture was adjusted to 6.5 by adding ammonium hydroxide. The reaction was kept at 413 K for 60 h, and cooled to room temperature at the speed of 10 K/h. Blue crystals of **1** suitable for X-ray diffraction analysis were obtained in 50.4% yield calculated according to HPT. m.p.: 525~527 K. Anal. Calcd. (%) for $\text{C}_{22}\text{H}_{20}\text{CuN}_4\text{O}_5$: C, 54.60; H, 4.17; N, 11.58. Found (%): C, 54.43; H, 4.18; N, 11.61. Main IR (KBr, cm^{-1}): IR (v/cm^{-1}): 3420(w), 3121(w), 1659(vs), 1613(Vs), 1481 (m),

1362(vs), 1285(m), 1151.5(m), 934(w), 846(m), 720(m), 665(w), 474(w).

2.3 Crystal structure determination

A single crystal with dimensions of 0.26mm \times 0.16mm \times 0.08mm was put on a Bruker SMART CCD 6000 diffractometer equipped with graphite-monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using an ω - Φ scan mode at 296(2) K. A total of 10656 reflections were collected in the range of $2.46 \leq \theta \leq 27.33^\circ$, of which 3807 were independent ($R_{\text{int}} = 0.1040$, $R_{\text{sigma}} = 0.1461$) and 2053 were observed ($I > 2\sigma(I)$). All data were corrected by L_p factors and empirical absorption. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using the SHELX-2014 program package^[16]. The hydrogen and non-hydrogen atoms were corrected by isotropic and anisotropic temperature factors, respectively. The final $R = 0.0553$, $wR = 0.0795$ ($w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$), $(\Delta/\sigma)_{\text{max}} = 0.000$, $S = 0.952$, $(\Delta\rho)_{\text{max}} = 0.802$ and $(\Delta\rho)_{\text{min}} = -0.559 \text{ e \AA}^{-3}$.

3 RESULTS AND DISCUSSION

3.1 Crystal structure of 1

The coordination structure of **1** is revealed in Fig. 1, and the packing diagram in Fig. 2. Selected bond lengths and bond angles are shown in Table 1.

Table 1. Selected Bond Lengths (\AA) and Bond Angles ($^\circ$) of Complex 1

Bond	Dist.	Bond	Dist.	Bond	Dist.
Cu(1)–O(3)	1.954(2)	Cu(1)–O(2)	2.748(3)	Cu(1)–O(7)	2.290(5)
Cu(1)–N(1)	1.981(3)	Cu(1)–N(2)	1.971(3)	Cu(1)–N(4)	2.047(3)
Angle	($^\circ$)	Angle	($^\circ$)	Angle	($^\circ$)
O(2)–Cu(1)–N(1)	86.9(1)	O(3)–Cu(1)–N(1)	91.4(1)	O(7)–Cu(1)–N(1)	88.7(2)
O(2)–Cu(1)–N(2)	108.3(1)	O(3)–Cu(1)–N(2)	159.2(1)	O(7)–Cu(1)–N(2)	104.9(1)
O(2)–Cu(1)–N(4)	93.4(1)	O(3)–Cu(1)–N(4)	91.9(1)	O(7)–Cu(1)–N(4)	93.0(2)
O(2)–Cu(1)–O(3)	52.8(1)	O(2)–Cu(1)–O(7)	146.8(1)	O(3)–Cu(1)–O(7)	94.5(1)
N(1)–Cu(1)–N(4)	176.1(1)	N(2)–Cu(1)–N(4)	79.9(1)	N(1)–Cu(1)–N(2)	96.2(1)

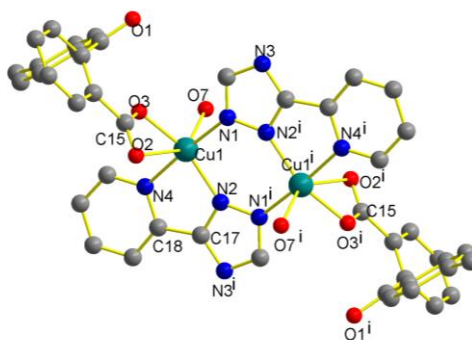


Fig. 1. Coordination structure of the title complex (i: $-x, 1-y, 1-z$)

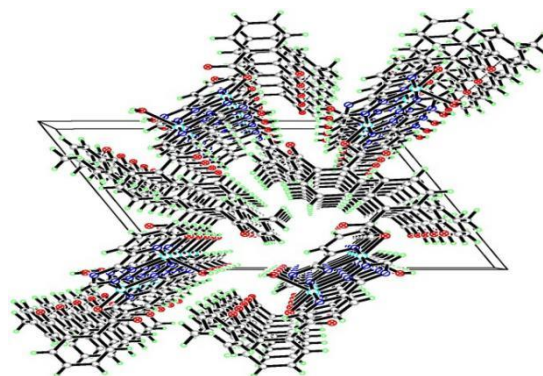


Fig. 2. Packing diagram of the title complex

$[\text{Cu}_2(\text{MBBA})_2(\text{HPT})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**1**) is a binuclear complex in space group $P2_1/c$. As illustrated in Fig. 1, the complex consists of two Cu(II) ions, two HPT molecules and two MBBA^{-1} anions. The whole molecule displays a symmetric dinuclear structure, where two copper atoms are linked with two $K^2\text{:N}^1\text{:N}^2\text{-3-(pyridin-2-yl)-1,2,4-triazole}$ molecules, forming a stable six-membered ring structure. Each Cu(II) coordinates with three oxygen atoms (O(2) and O(3) from MBBA anions and O(7) from water molecule) and three nitrogen atoms (N(4) atom from pyridine ring and N(1) and N(2) from triazole ring in two HPT molecules, respectively), forming a distorted octahedral coordination. The bond lengths and bond angles around the Cu(II) are in the ranges of $1.955(2)\sim 2.290(5)$ Å and $52.83(11)\sim 176.12(14)^\circ$, respectively. The Cu–N bond lengths vary from 1.975 to 2.049 Å, averaged by 2.000 Å, which are very close to those in similar Cu(II) complex $[\text{Cu}_5(\text{Hpt})_5(\text{H}_2\text{O})_2(2,3\text{-PCA})_2]_n$ (Cu–N = 1.989 Å)^[17]. The coordination mode of the carboxylate group is bidentate with the average Cu–O_(carboxyl) distance being 1.955(2) and 2.748 Å. One Cu–O_(carboxyl) bond is slightly longer than that in $[\text{Cu}_5(\text{Hpt})_5(\text{H}_2\text{O})_2(2,3\text{-PCA})_2]_n$ (Cu–O = 2.167(3) Å), and the other Cu–O_(carboxyl) is longer than Cu–O_(water) = 2.264(2) and 2.300 Å, which indicate a weak coordination bond^[18]. More interestingly, a basic binuclear unit $\text{Cu}_2(\text{MBBA})_2(\text{HPT})_2(\text{H}_2\text{O})_2$ consists of two Cu ions, two HPT molecules, two MBBA^{-1} anions, two coordinated water molecules and two free water molecules. In addition, there are one six-membered ring composed of N(1), N(2), Cu(1), N(1A), N(2A) and Cu(1) atoms and one five-membered one consisting of Cu(1), N(1), N(2), C(17) and C(18) atoms. In the six-membered ring, the Cu(1)···Cu(1A) of 3.993 Å falls in the normal range and is close to those in similar Cu(II) complexes: $[\text{Cu}_2(4\text{-C}_5\text{H}_4\text{NCOO})_2(\text{C}_7\text{H}_5\text{N}_4)_2]_n$ (Cu···Cu = 3.965 Å), $\text{Cu}_2(\text{HPT})_2\text{-(TNCA)}_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (Cu···Cu = 4.006 Å)^[19]. Moreover, as

given in Fig. 2, the shortest center distance between aromatic cycles of MBBA^{-1} group is 3.847 Å, longer than 3.700 Å, indicating $\pi\text{-}\pi$ stacking interaction between the aromatic cycles^[20].

3. 2 Powder XRD and thermal stability of **1**

Powder X-ray diffraction (PXRD) experiment at room temperature was carried out to investigate the purity of compound **1** (Fig. 3(a)). The main peaks observed match well with the simulated ones, indicating the phase purity of the as-synthesized product. In addition, the weight loss of the complex in air from room temperature to 873 K occurred mainly in three stages (Fig. 3(b)). The first one between 373 and 433 K with the weight loss of 7.8% corresponds to the release of free and coordinated water molecules (calcd.: 7.44%). During this stage, one thermal absorption peak of DTG appeared at about 423 K, suggesting the decomposition of bound water. The second stage is found at 433 K with the weight loss of 30.0%, resulting from the departure of two HPT molecules (calcd.: 30.00%). Consequently, another DTG thermal absorption peak appeared at about 525 K, the melting point of the complex. The third stage began at 533 K and continued to 723 K. The weight loss during this period was 46.20% (theoretical value: 46.13%), owing to the loss of 30 carbon, 22 hydrogen and 5 oxygen atoms from two MBBA anions. The final product is CuO with the residual rate being 16.40% (calcd.: 16.44%).

3. 3 Magnetic properties

The temperature dependence of the magnetic susceptibility of **1** was investigated from 300 to 2 K with an applied magnetic field of 2 kOe. The $X_M T$ vs. T and $1/X_M$ vs. T curves are depicted in Fig. 4. $X_M T$ of **1** is $3.616 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 300 K. It decreases slowly and then more rapidly below 44 K to reach a value of $2.206 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2 K. Such magnetic behavior indicates antiferromagnetic coupling within the $[\text{Cu}_2(\text{MBBA})_2(\text{HPT})_2(\text{H}_2\text{O})_2]$ dinuclear unit, similar to some

other copper complexes^[21]. The linear regression equation is $1/X_M = 0.2742T + 0.5669$ with the correlation coefficient of 0.9996. According to the Curie-Weiss law: $X_M = C/(T - \theta)$, the Weiss constant θ is calculated to be -2.042 K. These magnetic behaviors show that the title complex exhibits

antiferromagnetism. In this work, the main magnetic interactions may be considered as occurring between adjacent copper(II) ions bridged by triazole rings ($N(1)$, $N(2)$, $N(1)^i$, $N(2)^i$), which is of the same type of bridge in the Cu(II) complexes^[22].

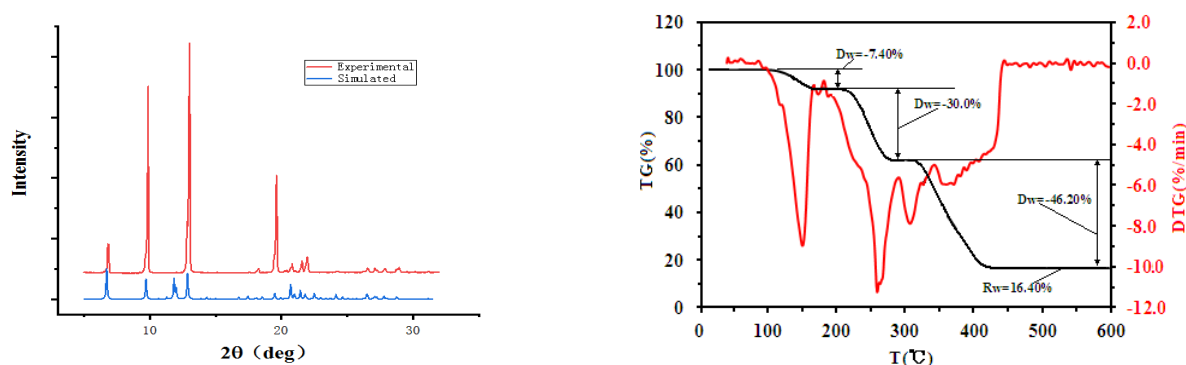


Fig. 3. (a) XRD patterns of **1** simulated from X-ray single-crystal diffraction data and experimental data. (b) TGA curve for **1**

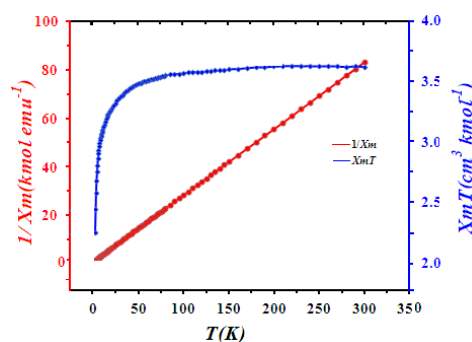


Fig. 4. Temperature dependence of the magnetic susceptibility of the title complex in the form of $X_m T$ vs T and $1/X_m$ vs T

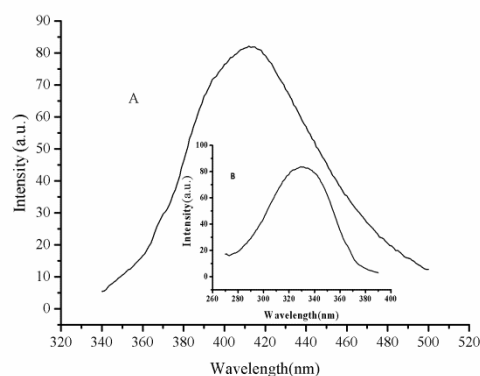


Fig. 5. Fluorescence of **1** in the solid state at room temperature (Curve A: emission spectrum of **1**. Curve B: absorption spectrum of **1**)

3.4 Fluorescence of **1**

The emission spectra of **1** were studied in the solid state at room temperature and depicted in Fig. 5. There are emission bands at 412 nm ($\lambda_{ex} = 330$ nm). Such fluorescence emissions may be assigned to intra-ligand $\pi-\pi^*$ transitions because the

free HPT ligand exhibits a similar broad emission at 450 nm under 340 nm excitation. The emission bands of **1** are blue-shifted by 38 nm as compared to the HPT ligand, which is attributed to the coordinative interactions between the metal atom and the ligand. Such emission bands may be tentatively

assigned to ligand-to-metal charge transfer (LMCT)^[23].

4 CONCLUSION

This paper reports the synthesis and structure of a new

binuclear copper compound $[\text{Cu}_2(\text{MBBA})_2(\text{HPT})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ based on HPT and MBBA. Its XRD, TG analysis and magnetic properties were studied. Our research shows that the magnetic behavior of the complex is antiferromagnetic, and it gives off an intense fluorescence at around 412 nm.

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