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Crystal structure, magnetic, fluorescent, electrochemical properties and thermal stability of a new copper(II) coordination polymer $[\text{Cu}_2(\text{C}_5\text{H}_4\text{NCOO})_2(\text{C}_7\text{H}_5\text{N}_4)_2]_n$

Abstract: A new copper(II) coordination polymer $[\text{Cu}_2(\text{C}_5\text{H}_4\text{NCOO})_2(\text{C}_7\text{H}_5\text{N}_4)_2]_n$ (**1**) has been synthesized with 4-pyridinecarboxylate and 3-(pyridin-2-yl)-1,2,4-triazolyl ligands. The crystal structure shows that two neighboring copper(II) ions are coordinated with two deprotonated (anionic) 3-(pyridin-2-yl)-1,2,4-triazole ligands to form a binuclear structure. Adjacent binuclear units are linked by 4-pyridinecarboxylate anions to form a three-dimensional network structure. The magnetic, fluorescent, and electrochemical properties and thermal stability of **1** were studied. The results show that **1** exhibits antiferromagnetic interaction, and upon excitation at 318 nm, it has an intense fluorescent emission at approximately 430 nm. The electron transfer of **1** is irreversible in electrode reactions. The thermogravimetric analysis shows that **1** is stable below 240 °C.

Keywords: copper(II) coordination polymer; crystal structure; magnetic, fluorescent, and electrochemical properties; thermal stability.

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1 Introduction

Inorganic–organic framework complexes have captured extensive interest of researchers due to their versatile topological structures and potential application in many fields, such as magnetism, catalysis, adsorption, optics, separation, and host–guest recognition [1–10]. Up to now, in this field, much attention has been focused on 1,2,4-*1H*-triazole and its derivatives [11–15], which have versatile coordination modes and a moderate ligand field strength [16, 17]. In addition, the complexes containing 1,2,4-*1H*-triazole may have applications as plant growth regulators, high-temperature catalysts, antibiotics, and molecular electronic devices [18–20]. In this paper, with the aim of preparing novel functional complexes, a new copper(II) framework complex $[\text{Cu}_2(\text{C}_5\text{H}_4\text{NCOO})_2(\text{C}_7\text{H}_5\text{N}_4)_2]_n$ (**1**) has been synthesized using 3-(pyridin-2-yl)-1,2,4-triazole as a ligand and its structure has been determined. Preliminary results of the magnetic, fluorescent, and electrochemical properties and thermal stability of **1** are also reported.

2 Experimental section

1,2,4-*1H*-triazole was synthesized according to the previous procedure, all other reagents were analytical grade and purchased from Reagent No. 1 Factory of Shanghai Chemical Reagent Co., Ltd, China and used without further purification. The C, H, and N analysis was conducted by means of a Perkin Elmer PE-2400(II) apparatus. Magnetic measurements in the range of 2–300 K were performed on an MPMS-SQUID magnetometer at a field of 2 kOe (1 kOe = 7.96×10^4 A m⁻¹) on a crystalline sample in the temperature settle mode. A fluorescence spectrum was obtained at room temperature on an RF-5301PC fluorescence spectrophotometer. The electrochemical properties were measured on an EC550 electrochemical workstation from Wuhan (Ruilian Company, China). Thermal stability

properties were studied on a Perkin Elmer PRT-2 pyris1 instrument.

2.1 Preparation of $[\text{Cu}_2(\text{C}_5\text{H}_4\text{NCOO})_2(\text{C}_7\text{H}_5\text{N}_4)_2]_n$ (**1**)

A mixture of 4-pyridinecarboxylic acid (24.6 mg, 0.2 mmol), 3-(pyridin-2-yl)-1,2,4-triazole (14.6 mg, 0.1 mmol), and copper(II) acetate (39.9 mg, 0.20 mmol) was dissolved in 12 mL water. The solution was poured into a 25 mL hydrothermal reaction autoclave and kept at 433 K for 4 days. After cooling to room temperature within 12 h, blue block crystals of **1** suitable for X-ray diffraction analysis were obtained in 43 % yield. M.p. 561–563 K. Anal. for $[\text{Cu}_2(\text{C}_5\text{H}_4\text{NCOO})_2(\text{C}_7\text{H}_5\text{N}_4)_2]_n$: calculated C 47.20, H 2.74, N 21.17; found: C 47.15, H 2.73, N 21.15. Selected IR data (KBr pellet, cm^{-1}): $\nu = 3398.6(\text{m})$, $1625.9(\text{s})$, $1610.6(\text{s})$, $1355.9(\text{vs})$, $1143.8.9(\text{m})$, $690.5(\text{m})$, $418.6(\text{m})$.

2.2 X-ray structure determination

The X-ray diffraction measurements for **1** were carried out on a Bruker SMART CCD area detector at 296(2) K by using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by Direct Methods and refined by a full-matrix least-squares technique using the programs Shelxs-97 and Shelxl-97 [21, 22]. All hydrogen atoms were generated geometrically and refined isotropically using the riding model.

CCDC 1001517 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

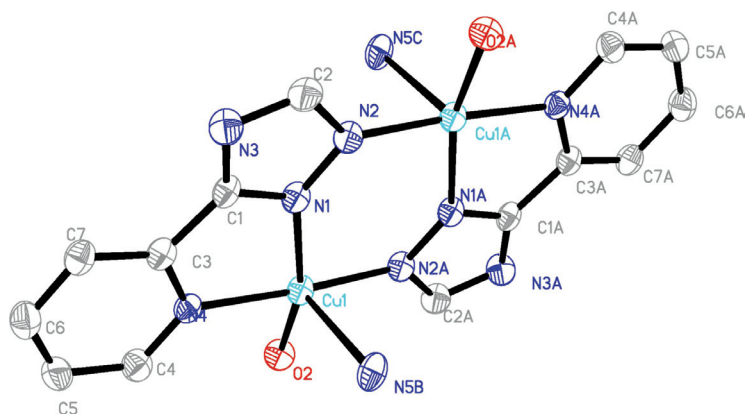


Fig. 1: Part of the crystal structure of **1** with 30 % displacement ellipsoids and with crystallographic atomic numbering scheme adopted. All hydrogen atoms are omitted for clarity.

3 Results and discussion

3.1 Structure description

The crystal structure of **1** is depicted in Fig. 1, a summary of crystal data and refinement conditions is listed in Table 1 and the main bond lengths and bond angles of the complex are listed in Table 2. As shown in Fig. 1, in **1**, two neighboring copper(II) ions are coordinated with two 3-(pyridin-2-yl)-1,2,4-triazolyl anions to form a binuclear centrosymmetrical structure. Adjacent binuclear units are linked by 4-pyridinecarboxylate anions (not shown in Fig. 1) to form a three-dimensional network structure. The copper(II) ions are coordinated with three nitrogen atoms from two 3-(pyridin-2-yl)-1,2,4-triazolyl anions, one oxygen atom, and one nitrogen atom from two 4-pyridinecarboxylate anions to give a distorted square-pyramidal coordination geometry, where N1, N4, O2, and N2A define the base plane and N5B occupies the vertex. The bond angles N1-Cu1-N4, N4-Cu1-O2, O2-Cu1-N2A, and N2A-Cu1-N1 are $80.04(11)^\circ$, $92.15(11)^\circ$, $89.52(11)^\circ$, and $97.36(11)^\circ$, respectively, and their sum is 359.07° . The bond length Cu1-O2 is $1.960(2) \text{ \AA}$. The bond lengths Cu1-N1, Cu1-N4, Cu1-N2A, and Cu1-N5B are $1.992(3)$, $2.042(3)$, $1.973(3)$, and $2.362(3) \text{ \AA}$, respectively, and their average length is 2.092 \AA , which is in the normal range. The bond length Cu1-N5B [$2.362(3) \text{ \AA}$] is longer than that of the other Cu-N probably because N5B is on the top of a distorted square-pyramid.

3.2 Magnetic properties

The temperature dependence of the magnetic susceptibility of **1** was investigated from 2 to 300 K with an applied magnetic field of 2 kOe. The curve $1/\chi_M$ versus T is shown

Table 1: Crystal structure data for **1**.

Empirical formula	C ₁₃ H ₉ CuN ₅ O ₂
M_r	330.79
Crystal size, mm ³	0.18 × 0.17 × 0.16
Crystal system	Monoclinic
Space group	C2/c
a , Å	17.460(4)
b , Å	10.224(2)
c , Å	16.415(5)
β , °	118.368(4)
V , Å ³	2578.5(11)
Z	8
$D_{\text{calcd.}}$, g cm ⁻³	1.70
$\mu(\text{MoK}\alpha)$, cm ⁻¹	1.7
$F(000)$, e	1336
hkl range	± 20, -11 → + 12, -18 → + 19
Reflection measured/unique/ R_{int}	7275/2257/0.0368
Parameters refined	190
$R1(F^2)/wR2(F^2)^b$ (all reflections)	0.0461/0.0947
A/B values for weighting scheme ^b	0.0389/4.2592
GoF (F^2) ^c	1.074
$\Delta\rho_{\text{fin}}$ (max/min), e Å ⁻³	0.29/-0.24

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}, w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}, \text{ where } P = (\max(F_o^2, 0) + 2F_c^2) / 3.$$

$$^c \text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}.$$

Table 2: Selected bond lengths (Å) and angles (°) for **1**, with estimated SDs in parentheses.^a

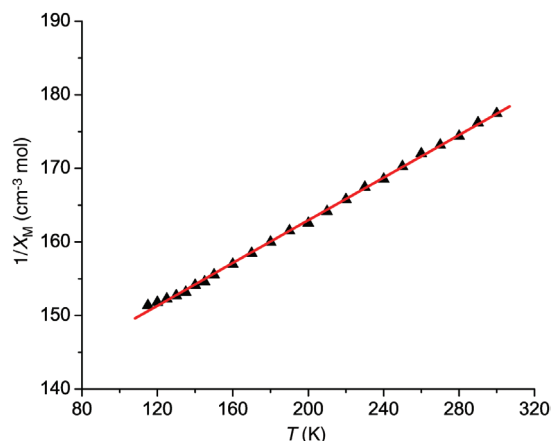
Cu1–O2	1.960(2)	Cu1–N4	2.042(3)
Cu1–N2A	1.973(3)	Cu1–N5B	2.362(3)
Cu1–N1	1.992(3)	Cu1A–N2	1.973(3)
O2–Cu1–N2A	89.52(11)	O2–Cu1–N5B	107.01(11)
O2–Cu1–N1	161.77(11)	N2A–Cu1–N5B	86.45(11)
N2A–Cu1–N1	97.36(11)	N1–Cu1–N5B	90.32(12)
O2–Cu1–N4	92.15(11)	N4–Cu1–N5B	96.37(11)
N2A–Cu1–N4	176.15(11)	N1–N2–Cu1A	123.4(2)
N1–Cu1–N4	80.04(11)	N2–N1–Cu1	138.2(2)

^aSymmetry transformations used to generate equivalent atoms: A: $-x+1/2, -y+1/2, -z$; B: $x, -y+1, z-1/2$.

in Fig. 2. $1/\chi_M$ is proportional to T in the range of 115–300 K. The linear regression equation is $1/\chi_M = 0.145T + 133.94$ with a correlation coefficient of 0.9990. According to the Curie–Weiss law, from $\chi_M = C/(T-\theta)$, the Weiss constant θ can be obtained, being -923.7 K. Its value is negative, which indicates that **1** exhibits antiferromagnetic properties in the paramagnetic regime.

3.3 Fluorescence

As illustrated in Fig. 3, the fluorescence of complex **1** was studied in the solid state at room temperature. There are

**Fig. 2:** Temperature dependence of the magnetic susceptibility of **1** in the form of $1/\chi_M$ vs. T .

emission bands at 430 nm ($\lambda_{\text{ex}} = 318$ nm) for **1**. Such fluorescence emissions may be assigned to intraligand $\pi-\pi^*$ transitions because the free HPT ligand exhibits a similar broad emission at 450 nm upon excitation at 340 nm. The emission bands of **1** are blue shifted by 20 nm 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. This suggests that the complex may be a good candidate of blue-fluorescent materials.

3.4 Electrochemical properties

A conventional three-electrode system was employed for the cyclic voltammetric measurement, where an Ag/AgCl electrode, a glassy carbon electrode, and a platinum electrode were chosen as the reference electrode, the working electrode, and the counter electrode, respectively. Complex **1** was dissolved in a mixture of methanol and water (volume ratio of 1:1), the resulting solution having a concentration of 1×10^{-3} mol L⁻¹. A 0.1 m NaClO₄ solution was used as the supporting electrolyte. The scan range was -0.50 to 0.50 V. The cyclic voltammogram of **1** at a potential scan rate 0.10 V s⁻¹ is shown in Fig. 4a. There exists an oxidation peak with 0.014 V oxidation potential, which corresponds to the Cu(I)/Cu(II) oxidation process [23].

Under the same conditions, the electrochemical properties of **1** were also measured by linear sweep stripping voltammetry. In the potential scan rate range of 0.10 – 0.90 V s⁻¹, the influence of the potential scan rate (ν) on the oxidation peak current (i_{pa}) and the oxidation peak potential (E_{pa}) was studied. i_{pa} is proportional to ν , and the linear regression equation is $i_{\text{pa}} = 24.407\nu - 1.027$ (i_{pa} in μA ; ν in V s⁻¹) with a correlation coefficient of

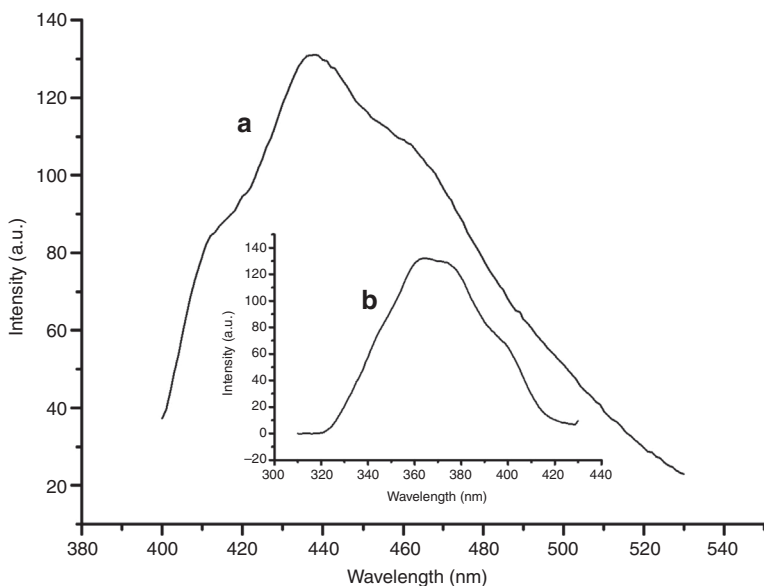


Fig. 3: Fluorescence of **1** in the solid state at room temperature (curve a: emission spectrum of **1** and curve b: absorption spectrum of **1**).

0.9932 (Fig. 4b), which indicates that the electrode reaction process of **1** was controlled by adsorption. In addition, E_{pa} shifts to a more positive value with increasing v , and it is proportional to $\ln v$. The linear regression equation is $E_{pa} = 0.111 \ln v + 0.262$ (E_{pa} in V; v in $V s^{-1}$) with a correlation coefficient of 0.9958 (Fig. 4b).

3.5 Thermal analysis

Thermal stability studies of **1** were performed in air. The thermogravimetric-derivative thermogravimetric

(TG-DTG) curve is shown in Fig. 5. There are two weight-loss stages from room temperature to 700 °C. The first stage takes place from 240 °C to 340 °C with a weight loss of 43.9 %, corresponding to the release of 3-(pyridin-2-yl)-1,2,4-triazole molecules (calculated 43.9 %). There is a strong endothermic peak near 290 °C, which can be attributed to an endothermic melting of the complex. The second stage occurs at 340 °C–450 °C with a weight loss of 32.0 % resulting from the loss of 4-pyridinecarboxylic acid molecules (calculated 32.1 %). In air, the final product is copper oxide with the residual weight being approximately 24.1 % (calculated 24.0 %).

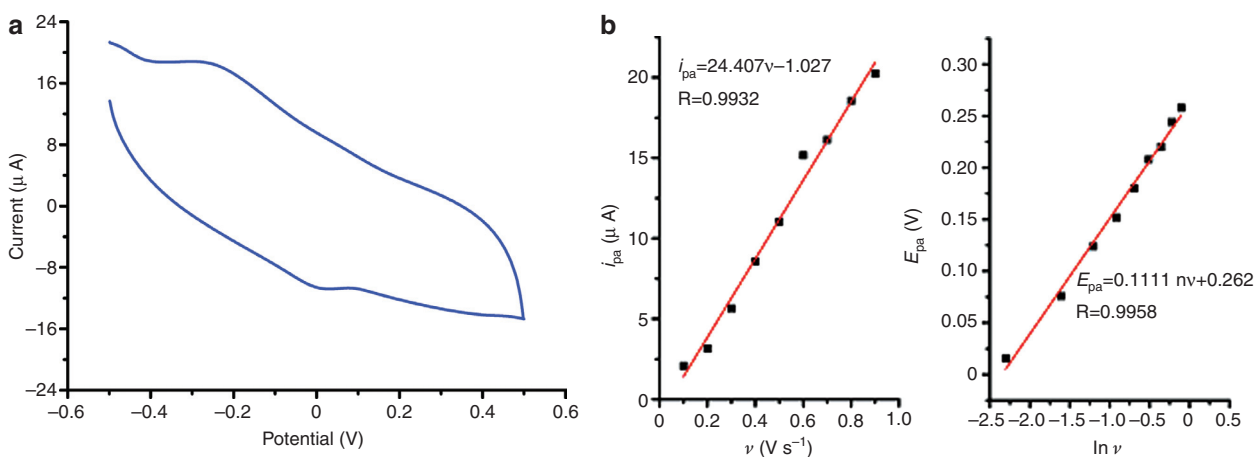


Fig. 4: (a) Cyclic voltammogram of **1** in aqueous methanol (scan rate: $0.10 V s^{-1}$) and (b) effect of the potential scan rate (v) on the oxidation peak current (i_{pa}) and the oxidation peak potential (E_{pa}).

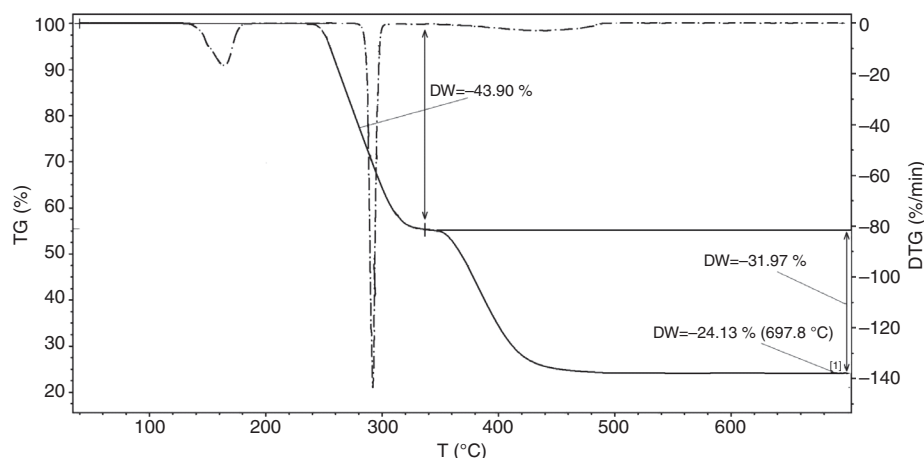


Fig. 5: TG-DTG curve of 1.

4 Conclusion

A new copper(II) coordination polymer $[\text{Cu}_2(\text{C}_5\text{H}_4\text{NCOO})_2(\text{C}_7\text{H}_5\text{N}_4)_2]_n$ was synthesized with 4-pyridinecarboxylate and 3-(pyridin-2-yl)-1,2,4-triazolyl ligands. Its structure was determined and its magnetic, fluorescent, and electrochemical properties as well as thermal stability were examined. Our research shows that the compound exhibits antiferromagnetic properties and gives off an intense fluorescence at approximately 430 nm. The thermogravimetric analysis shows that it is stable below 240 °C.

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