

Crystal Structure and Properties of a New Copper(II) Complex $\text{Cu}_2(\text{phen})_2[\text{C}_7\text{H}_8(\text{COO})_2]_2 \cdot (\text{H}_2\text{O})_{4.5}$

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A new complex $\text{Cu}_2(\text{phen})_2[\text{C}_7\text{H}_8(\text{COO})_2]_2 \cdot (\text{H}_2\text{O})_{4.5}$ (**1**) has been synthesized, with the dianion of bicyclo[2.2.1] hept-2-ene-5,6-dicarboxylic acid $[\text{C}_7\text{H}_8(\text{COOH})_2]$ (LH_2) and 1,10-phenanthroline (phen) as ligands. In **1**, L^{2-} anions link Cu(II) cations to form two binuclear structure units, in which each Cu(II) cation is coordinated by five donor atoms to give a distorted square-pyramidal geometry. The magnetic data of **1** show that it exhibits weak antiferromagnetic properties at low temperature. When the excitation wavelength is at 470 nm, it has an intense photoluminescence. In addition, the cyclovoltammetric electron transfer is quasi reversible in the electrode reaction of **1**, two electrons being involved in the reaction corresponding to Cu(II)/Cu(0).

Key words: Copper(II) Complex, Crystal Structure, Magnetic and Fluorescence Properties

Introduction

Complexes with carboxylate ligands possess versatile topological structures and have extensive applications in magnetic and optical devices, catalysis and biochemistry. Their molecular construction and crystal engineering have long been the interest of coordination chemists [1–7]. The bicyclo[2.2.1] hept-2-ene-5,6-dicarboxylate anions (norbornene-5,6-dicarboxylate anions) are ligands with a particularly high steric hindrance, and several of their complexes have been reported [8–12]. In the past, we have published the two complexes $\{\text{Mn}(\text{phen})_2(\text{H}_2\text{O})[\text{C}_8\text{H}_{11}\text{O}_2(\text{COO})]\}(\text{ClO}_4) \cdot \text{H}_2\text{O}$ [13] and $\{\text{Cd}(\text{I})(\text{phen})(\text{H}_2\text{O})[\text{C}_8\text{H}_{11}\text{O}_2(\text{COO})]\} \cdot \text{H}_2\text{O}$ [14]. Herein, we report the synthesis and crystal structure of a new Cu(II) complex, $\text{Cu}_2(\text{phen})_2[\text{C}_7\text{H}_8(\text{COO})_2]_2 \cdot (\text{H}_2\text{O})_{4.5}$ (**1**). We also report our preliminary results of the magnetic, fluorescence and electrochemical properties of **1**.

Results and Discussion

Structure description

As revealed by the molecular structure determination (Fig. 1), there are two crystallographically inde-

pendent oxygen-bridged $\text{Cu}_2(\text{phen})_2[\text{C}_7\text{H}_8(\text{COO})_2]_2$ dimers in the crystal. Both of the two dimers have crystallographic inversion symmetry. They are connected through intermolecular hydrogen bonds such as $\text{C7} \cdots \text{H7} \cdots \text{O2}$ (3.361(5) Å, 169°) and $\text{C19} \cdots \text{H19} \cdots \text{O6}$ (3.168(5) Å, 142°) and intermolecular weak π – π -stacking interactions of the phen ligands with a centroid separation of 3.655(2) Å. In each dimer, two neighboring Cu^{2+} ions are bridged by a pair of bimonodentate carboxyl groups of different L^{2-} anions. The coordination environment of each Cu(II) cation can be described as a distorted square pyramid. It is noteworthy that the two dimers are very similar to a reported complex with 2,2-bipyridine as coligand [15] as far as their structural features are concerned.

In Fig. 1, the Cu1 cation is coordinated by two nitrogen atoms from 1,10-phenanthroline and three oxygen atoms from two L^{2-} anions. The distances Cu1–Cu1A and Cu2–Cu2B are 3.301 and 3.222 Å, respectively. The bond angles N1–Cu1–N2, N2–Cu1–O1, O1–Cu1–O3, and O3–Cu1–N1 are 81.61(10), 93.86(9), 89.93(8), and 93.27(9)°, respectively. Their sum is 358.67° (close to 360°), suggesting that N1, N2, O1 and O3 are nearly coplanar. The bond lengths Cu1–O3,

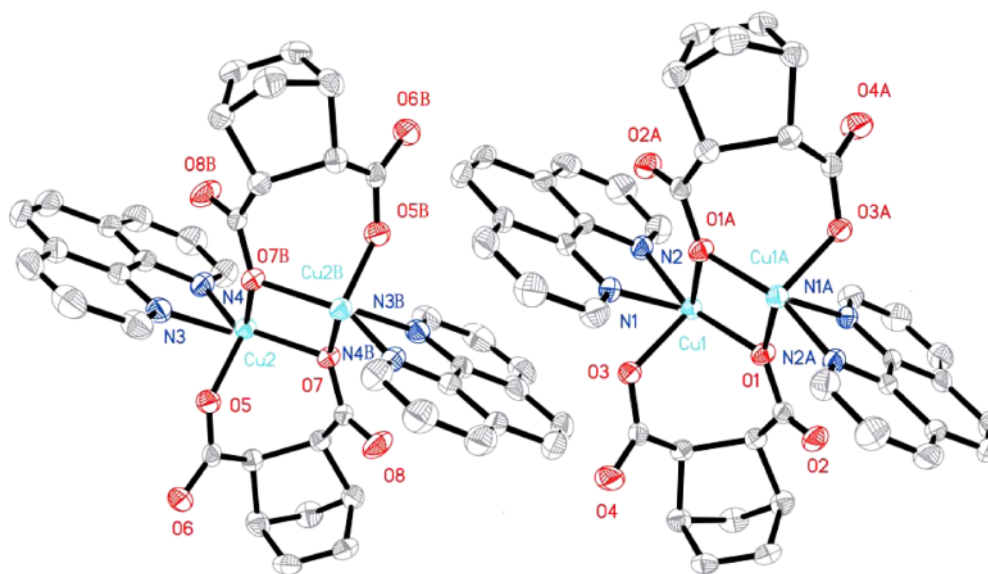


Fig. 1 (color online). Molecular structure of the crystallographically independent dimers of **1** in the crystal (all hydrogen atoms and uncoordinated water molecules are omitted for clarity).

Cu1-O1 and Cu1-O1A are 1.9417(19), 1.9648(18) and 2.2376(19) Å, respectively, with an average of 2.048 Å. Compared with Cu1-O , the lengths of Cu2-O vary from 1.919(2) to 2.231(2) Å, and their average is 2.041 Å. The Cu-N distances are in the normal range of 2.002(3) ~ 2.013(2) Å.

Magnetic properties

With an applied magnetic field of 2 kOe (1 kOe = $7.96 \times 10^4 \text{ A m}^{-1}$), the magnetic susceptibility of **1** was measured in the temperature range of 2.8 ~ 300 K. The temperature dependence of the molar magnetic susceptibility of **1** is presented in Fig. 2 in the form of $\chi_M T$ and $1/\chi_M$ vs. T diagrams. The product of $\chi_M T$ decreases gradually from $1.46 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K to $0.90 \text{ cm}^3 \text{ K mol}^{-1}$ at 15 K. In addition, the data in the range of 150 to 300 K are in a linear relationship between $1/\chi_M$ vs. T , and the linear regression equation is $1/\chi_M = 0.574T + 41.038$ with the correlation coefficient of 0.9956. According to the Curie-Weiss law, $\chi_M = C/(T - \theta)$, the Curie constant ($C = 0.64 \text{ cm}^3 \text{ K mol}^{-1}$) and Weiss constant ($\theta = -71.40 \text{ K}$) are obtained. Such magnetic behavior indicates that **1** exhibits weak antiferromagnetic properties at low temperatures.

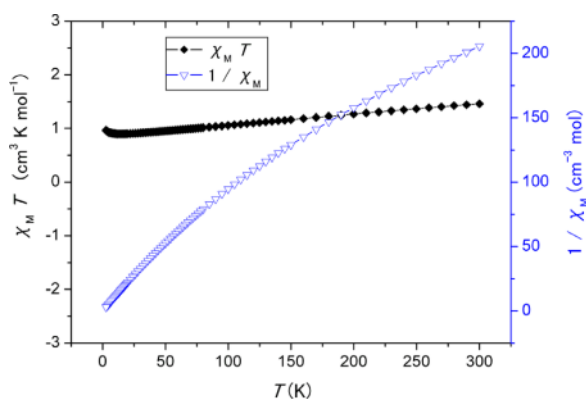


Fig. 2 (color online). Temperature dependence of the magnetic susceptibility of **1** in the form of $\chi_M T$ and $1/\chi_M$ vs. T .

Fluorescence properties

The fluorescence properties of **1** were investigated in the mixture of methanol and water (volume ratio 1 : 5) at room temperature in the range of 220 ~ 750 nm. The emission spectrum is shown in Fig. 3. **1** exhibits one intense fluorescence emission band at around 468 nm with the best excitation wavelength at 470 nm. Under the same conditions, the emission band of the 1,10-phenanthroline ligand was investigated, and it displays fluorescence emission at about 470 nm

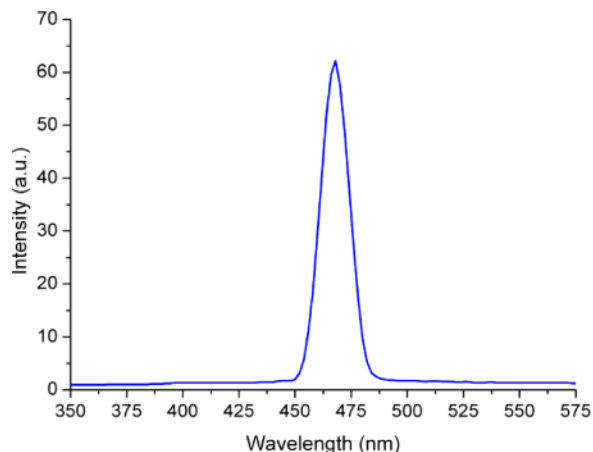


Fig. 3 (color online). Emission spectrum of **1** in a mixed solvent of methanol and water (volume ratio 1 : 5) at room temperature.

with the excitation wavelength at 472 nm. Compared with the 1,10-phenanthroline ligand, **1** has a similar emission band shape and position, which indicates that intraligand excitation is responsible for the emission of **1**. For the respective Cu complex with 2,2-bipyridine as co-ligand the photoluminescence properties have been reported in Ref. [15].

Electrochemical properties

For the cyclic voltammetric measurement (CV), we employed a conventional three-electrode system, where glassy carbon was chosen as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum electrode as the working electrode. The complex was dissolved in methanol, the resulting solution having a concentration of $1 \times 10^{-3} \text{ mol L}^{-1}$. An HAc-NaAc solution ($\text{pH} = 4.0$) was used as buffer. The scan range was $-1.00 \sim 1.00 \text{ V}$. In the range of $0.15 \sim 0.30 \text{ V s}^{-1}$, the influence of the potential scan rate on the reduction peak potential was studied. As revealed in Fig. 4a, there exists a pair of redox peaks in every CV curve, $\Delta E (\Delta E = E_{\text{pc}} - E_{\text{pa}})$ varies from 0.437 to 0.509 V, and i_{pa} is not equal to i_{pc} , which demonstrates that the electron transfer in the electrode reaction is quasi reversible. In addition, the reduction peak potential (E_{pc}) shifts to a more negative value with increasing scan rate (ν), and it is proportional to $\lg \nu$. The linear regression equation is $E_{\text{pc}}(\text{V}) = -0.0528 \lg \nu + 0.0731$ with the correlation

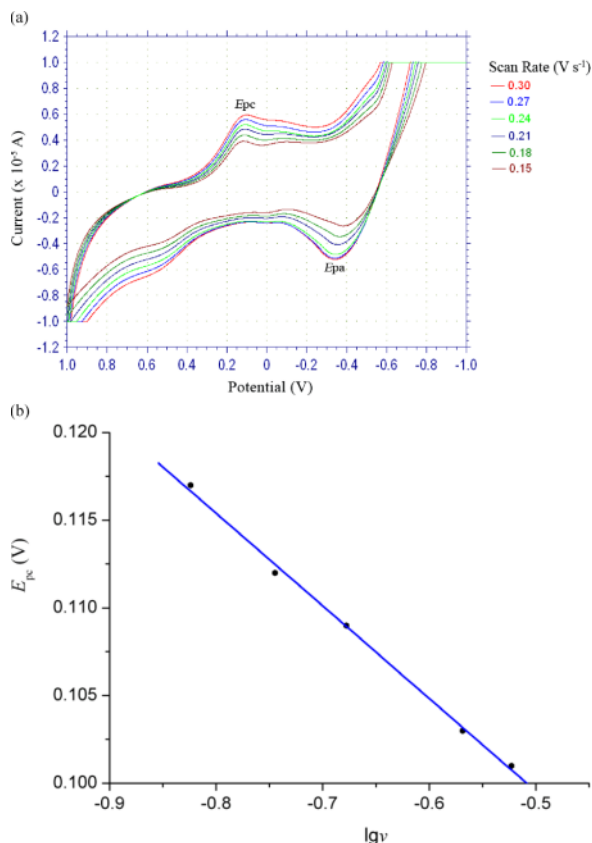


Fig. 4 (color online). (a) Cyclic voltammograms of **1** (scan rate: $0.15 \sim 0.30 \text{ V s}^{-1}$); (b) effect of the potential scan rate on the reduction peak potential.

coefficient of 0.9975 (Fig. 4b). On the basis of the slope of E_{pc} with $\lg \nu$, the number of electrons involved in the reduction of **1** can be evaluated. The αn is calculated to be 1.12. Generally, the electron transfer coefficient α is about 0.5 for a quasi reversible electrode process. So, the value of n is about 2, indicating that two electrons are involved in the electrode reaction, corresponding to $\text{Cu(II)}/\text{Cu(0)}$.

Conclusion

With the dianion of bicyclo[2.2.1] hept-2-ene-5,6-dicarboxylic acid $\text{C}_7\text{H}_8(\text{COOH})_2$, LH_2 , we have synthesized the new Cu(II) complex $\text{Cu}_2(\text{phen})_2[\text{C}_7\text{H}_8(\text{COO})_2]_2 \cdot (\text{H}_2\text{O})_{4.5}$. After determining its structure by X-ray diffraction analysis, we have examined its magnetic, fluorescence and electrochemical properties. Our research shows that

it exhibits a weak antiferromagnetic coupling at low temperature, that it gives off intense fluorescence at around 468 nm, and that the electrode reaction corresponds to $\text{Cu(II)}/\text{Cu(0)}$, the electron transfer being quasi reversible.

Experimental Section

The reagents were obtained from commercial sources and used without further purification. The melting point measurement was determined on a Beijing-made XT4 binocular micromelting point apparatus. IR spectra were recorded on a Shimadzu FTIR-8700 instrument in the range of $400\text{--}4000\text{ cm}^{-1}$ by using KBr discs. C, H, N analysis was conducted by means of a PE-2400(II) apparatus. Magnetic measurements in the range of $2.8\text{--}300\text{ K}$ were performed on a MPMS-SQUID magnetometer at a field of 2 kOe on a crystalline sample in the temperature settle mode. A fluorescence spectrum in a mixed solvent of methanol and water (volume ratio 1 : 5) was obtained at room temperature on a WGY-10 fluorescence spectrophotometer. The cyclic voltammogram was measured on a CHI660D electrochemical workstation from Shanghai Hua Chen.

Preparation of $\text{Cu}_2(\text{phen})_2[\text{C}_7\text{H}_8(\text{COO})_2]_2 \cdot (\text{H}_2\text{O})_{4.5}$ (**1**)

8.744 g LH_2 and 1.768 g basic copper(II) carbonate ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) were dissolved in the mixed solvent of ethanol and water (volume ratio 1:1). After heating for 5 h, the mixture was filtered, and a blue solid was obtained with the dried weight of 2.850 g. This product (0.1816 g) and 1,10-phenanthroline (0.1132 g) were added to a mixed solvent composed of 2 mL water, 2 mL ethanol (95%) and 2 mL *N,N*-dimethylformamide. The mixture ($\text{pH} \approx 7.8$) was heated on a water bath at about 60°C for 18 h. The resulting solution was filtered, and the filtrate was evaporated slowly at room temperature. Blue single crystals of **1** were obtained after six weeks. Yield: 31%. M.p. 180°C . – IR (film): $\nu = 3448.5, 1639.4$ (C=O), $1608.5, 1517.9, 1363.6, 1290.3, 1107.1, 1055.0, 850.0, 723.3, 617.2\text{ cm}^{-1}$. – Anal. for $\text{C}_{42}\text{H}_{41}\text{Cu}_2\text{N}_4\text{O}_{12.5}$: calcd. C 54.31, H 4.45, N 6.03; found C 54.25, H 4.44, N 6.02.

X-Ray structure determination

The X-ray diffraction measurements for **1** were carried out on a Bruker Smart CCD area detector at $296(3)\text{ K}$ by using graphite-monochromatized $\text{MoK}\alpha$ ($\lambda = 0.71073\text{ \AA}$) radiation. The absorption correction was carried out with the program SADABS [16]. The structure was solved by Direct Methods and refined by full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 programs, respectively [16]. All hydrogen atoms were generated geometrically and refined isotropically using the riding model. Details

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

Formula	$\text{C}_{42}\text{H}_{41}\text{Cu}_2\text{N}_4\text{O}_{12.5}$
M_r	928.87
Crystal size, mm^3	$0.18 \times 0.17 \times 0.16$
Crystal system	monoclinic
Space group	$P2_1/c$
a , \AA	18.114(2)
b , \AA	19.881(2)
c , \AA	11.3274(13)
β , deg	98.189(2)
V , \AA^3	4037.9(8)
Z	4
D_{calcd} , g cm^{-3}	1.53
$\mu(\text{MoK}\alpha)$, cm^{-1}	11.3
$F(000)$, e	1916
hkl range	$\pm 21, -17 \rightarrow +23, \pm 13$
$((\sin \theta)/\lambda)_{\text{max}}$, \AA^{-1}	0.727
Refl. measured/unique/ R_{int}	20 444/7110/0.0253
Param. refined	550
$R(F)/wR(F^2)^{a,b}$ (all data)	0.0486/0.1008
A/B values (weighting scheme) ^b	0.0463/3.2448
GoF (F^2) ^c	1.026
$\Delta\rho_{\text{fin}}$ (max/min), e \AA^{-3}	0.73/−0.52

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^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 (\AA) and angles (deg) for **1** with estimated standard deviations in parentheses^a.

Cu1–O3	1.9417(19)	Cu2–O5	1.919(2)
Cu1–O1	1.9648(18)	Cu2–O7	1.974(2)
Cu1–N2	2.010(2)	Cu2–N3	2.002(3)
Cu1–N1	2.013(2)	Cu2–N4	2.011(3)
Cu1–O1A	2.2376(19)	Cu2–O7B	2.231(2)
O(1)–Cu(1)A	2.2376(19)	O(7)–Cu(2)B	2.230(2)
O3–Cu1–O1	89.93(8)	O5–Cu2–O7	90.40(9)
O3–Cu1–N2	162.15(9)	O5–Cu2–N3	91.31(10)
O1–Cu1–N2	93.86(9)	O7–Cu2–N3	171.32(10)
O3–Cu1–N1	93.27(9)	O5–Cu2–N4	166.02(10)
O1–Cu1–N1	174.10(9)	O7–Cu2–N4	94.17(10)
N2–Cu1–N1	81.61(10)	N3–Cu2–N4	82.27(11)
O3–Cu1–O1A	96.33(8)	O5–Cu2–O7B	93.51(9)
O1–Cu1–O1A	76.67(8)	O7–Cu2–O7B	80.13(8)
N2–Cu1–O1A	101.52(9)	N3–Cu2–O7B	108.25(9)
N1–Cu1–O1A	107.86(8)	N4–Cu2–O7B	100.29(9)
Cu1–O1–Cu1A	103.33(8)	Cu2–O7–Cu2B	99.86(8)
C32–O1–Cu1	125.74(18)	C41–O5–Cu2	125.73(19)
C32–O1–Cu1A	127.42(17)	C42–O7–Cu2	119.78(19)
Cu1–O1–Cu1A	103.33(8)	C42–O7–Cu2B	122.10(19)
C33–O3–Cu1	121.87(18)	Cu2–O7–Cu2B	99.86(8)
C2–N1–Cu1	129.3(2)	C14–N3–Cu2	129.3(3)
C1–N1–Cu1	112.65(19)	C13–N3–Cu2	112.1(2)
C11–N2–Cu1	129.0(2)	C23–N4–Cu2	129.5(2)
C12–N2–Cu1	112.81(19)	C24–N4–Cu2	112.4(2)

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

of the crystal parameters, data collection and refinements are summarized in Table 1, and selected bond lengths and angles are listed in Table 2.

CCDC 874921 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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