Structure, Electrochemical and Magnetic Properties of a New Dinuclear Copper(II) Complex: $[Cu_2(C_{12}H_6O_4N_2)_2(2,2'\text{-bipy})_2]\cdot CH_3OH$

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Assembly reaction of copper(I) chloride, 2,2′-bipyridine-3,3′-dicarboxylic acid (H_2L) and 2,2′-bipyridine results in the formation of a new complex $[Cu_2(C_{12}H_6O_4N_2)_2(2,2'\text{-bipy})_2]\cdot CH_3OH$ (**1**). In **1**, two L^{2-} ligands link two Cu(II) ions to form a dinuclear structure. The electrochemical and magnetic properties of **1** were investigated. The results show that the electron transfer is irreversible in the electrode reaction, corresponding to Cu(II)/Cu(0). **1** is paramagnetic and exhibits a weak antiferromagnetic coupling.

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

Introduction

Complexes with carboxylate ligands have captured extensive interest of researchers due to their intriguing structure topology and potential applications in materials and medicinal chemistry, molecular electrochemistry and biochemistry [1 – 5]. Up to now, in this field, much attention has been focused on the pyridine dicarboxylic acid system with multi-connecting ligands. For example, 2,3-, 2,5-, 3,4- and 3,5-pyridine dicarboxylic acids have been found to act as excellent building blocks in the construction of functional complexes [6 – 9]. Compared with the previously investigated pyridine dicarboxylate ligands, 2,2′-bipyridine-3,3′-dicarboxylic acid (H_2L) has the advantage of multiple coordinating atoms and bridging moieties, which leads to a variety of connectivities for transition metal centers and provides various structural motifs [10 – 14].

In order to further investigate the influence of the pyridine carboxylate ligand L^{2-} and of different metal ions on the coordination architectures and properties, in this contribution we report the crystal structure and the electrochemical and magnetic properties of the new Cu(II) complex $[Cu_2(C_{12}H_6O_4N_2)_2(2,2'\text{-bipy})_2]\cdot CH_3OH$ (**1**).

Experimental Section

Reagents and instrumentation

The reagents were obtained from commercial sources and used without further purification. C, H, N analysis was conducted by means of a PE-2400(II) apparatus. Melting point measurements were executed on a XT4 binocular micromelting point apparatus (made in Beijing). Cyclic voltammetry was measured on a LK98 electrochemical analysis system (made by Tianjin Lanlike Chemical and Electronic High-tech Co., Ltd.). Powder X-ray diffraction (PXRD) patterns were measured on a Rigaku D/Max 2500 X-ray diffractometer with CuK_α radiation (λ = 1.54056 Å) at r. t. Magnetic measurements in the range of 2.8 – 300 K were performed on a MPMS-SQUID magnetometer at a field of 2 kOe on a crystalline sample in the temperature settle mode.

Preparation of $[Cu_2(C_{12}H_6O_4N_2)_2(2,2'\text{-bipy})_2]\cdot CH_3OH$ (1)

A mixture of copper(I) chloride (0.70 mmol, 0.069 g), H_2L (0.66 mmol, 0.161 g) and 2,2′-bipyridine (0.20 mmol, 0.031 g) was dissolved in 13 mL of CH_3CH_2OH/DMF (volume ratio 12 : 1). The pH value of the resultant mixture was adjusted to about 6.0 by adding one drop of a triethylamine solution. The mixture was heated in a water bath at 70 °C for 18 h. Afterwards the mixture was filtered, and the filtrate was slowly cooled to r. t. Blue single crystals of **1** were obtained after four weeks. Yield: 24 %. M. p.: 274.0 – 274.5 °C. – Anal. for $C_{22.5}H_{16}CuN_4O_{4.5}$ (477.93): calcd. C 56.55, H 3.37, N 11.72; found C 56.50, H 3.36, N 11.70.

Crystal structure determination

The X-ray data collection for **1** was carried out on a Rigaku Saturn CCD area detector system at 293(2) K by using graphite-monochromatized MoK_α (λ = 0.71073 Å) radiation. The absorption correction was carried out by the

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Table 1. Crystal data and numbers pertinent to data collection and refinement for **1**.

Formula	$C_{22.5}H_{16}CuN_4O_{4.5}$
M_r	477.93
Crystal size, mm^3	$0.20 \times 0.18 \times 0.10$
Crystal system	monoclinic
Space group	$P2_1/n$
a,Å	10.959(2)
b, Å	9.0195(18)
c, Å	20.213(4)
β, deg	91.85(3)
V, Å^3	1996.8(7)
Z	4
D_{calcd}, g cm^{-3}	1.59
$\mu(\text{Mo}K_\alpha)$, cm^{-1}	1.1
$F(000)$, e	976
hkl range	$-12 \le h \le 13$, $-10 \le k \le 10$, $-24 \le l \le 21$
$((\sin\theta)/\lambda)$max, Å^{-1}	0.609
Refl. measured / unique / R_{int}	14868 / 3502 / 0.0592
Param. refined	301
$R_1(F)^a$ / $wR_2(F^2)^b$ (all refls.)	0.0618 / 0.1490
A / B values for weighting scheme^b	0.0381 / 7.4123
GoF $(F^2)^c$	1.156
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	0.61 / −0.37

[a] $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR_2(F^2) = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o{}^2,0) + 2F_c{}^2)/3$; [c] $\text{GoF} = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

Table 2. Selected bond lengths (Å) and bond angles (deg) for **1**.

Cu(1)–O(3)	1.949(3)	Cu(1)–N(4)	1.991(4)
Cu(1)–O(1)	1.973(3)	Cu(1)–N(3)	2.000(4)
O(3)–Cu(1)–O(1)	92.17(15)	O(3)–Cu(1)–N(3)	166.37(16)
O(3)–Cu(1)–N(4)	92.76(16)	O(1)–Cu(1)–N(3)	95.63(16)
O(1)–Cu(1)–N(4)	169.92(16)	N(4)–Cu(1)–N(3)	81.34(17)

program SADABS [15]. The structure was solved by Direct Methods and refined by full-matrix least-squares techniques using the programs SHELXS-97 [16] and SHELXL-97 [17]. All hydrogen atoms were generated geometrically and refined isotropically using the riding model. Details 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 829761 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.

Results and Discussion

Synthesis

It is worth noting that the synthesis of the Cu(II) complex starting from copper(I) chloride was conducted in oxygen atmosphere. During the experimental process, Cu(I)Cl probably reacted first with the ligands resulting in the synthesis of a Cu(I) complex. Then the Cu(I) complex was oxidized by air leading to the Cu(II) complex reported in this paper. Under the conditions reported in this paper, we once tried to synthesize the title complex by using cupric salts such as copper(II) acetate and copper(II) chloride as starting materials, but we did not succeed. On the basis of these facts, we believe that the substitution of Cu(II) for Cu(I) under the reported conditions will possibly not result in the synthesis of this Cu(II) complex.

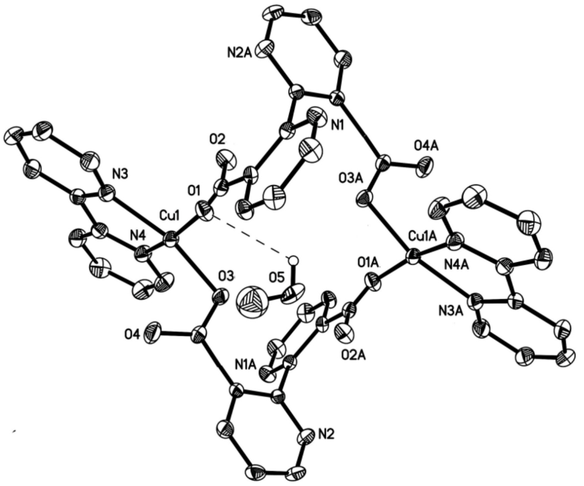

Fig. 1. Molecular structure of **1** (all hydrogen atoms except the one on O5 are omitted for clarity). Symmetry operation: A $-x, -y+2, -z$.

Structure description

Fig. 1 reveals the molecular structure of **1**. The complex contains a $[Cu_2(C_{12}H_6O_4N_2)_2(2,2'\text{-bipy})_2]$ unit and one uncoordinated CH_3OH molecule. In the symmetrical $[Cu_2(C_{12}H_6O_4N_2)_2(2,2'\text{-bipy})_2]$ unit, two copper(II) ions are linked by four carboxylate groups to give a dinuclear structure, where the end positions are coordinated with two 2,2′-bipyridine molecules. The distance between Cu1 and Cu1A is 6.202(12) Å (symmetry operation: A $-x, -y+2, -z$). Each copper(II) ion is coordinated by two nitrogen atoms from 2,2′-bipyridine and two oxygen atoms from two L^{2-} ligands in a distorted square-planar environment. The bond angles N3–Cu1–N4, N4–Cu1–O3, O3–Cu1–O1 and O1–Cu1–N3 are 81.34(17), 92.76(16), 92.17(15), and 95.63(16)°, respectively, and their sum is 361.9°,

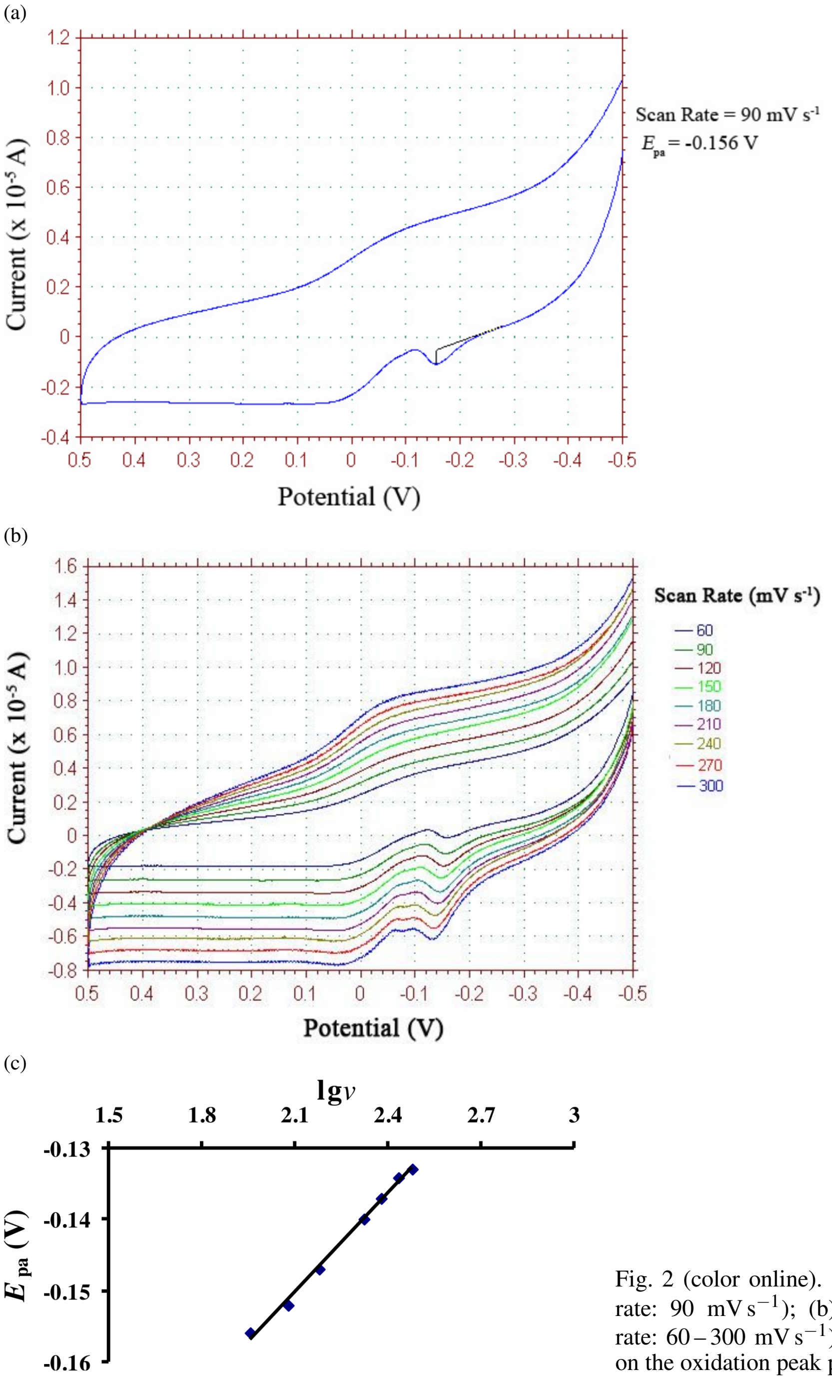

Fig. 2 (color online). (a) Cyclic voltammogram of **1** (scan rate: 90 $mV\,s^{-1}$); (b) cyclic voltammograms of **1** (scan rate: 60 – 300 $mV\,s^{-1}$); (c) effect of the potential scan rate on the oxidation peak potential.

suggesting that N3, N4, O3 and O(1) are nearly coplanar. The bond lengths Cu1–O1 and Cu1–O3 are 1.973(3) and 1.949(3) Å, respectively, and their average length is 1.961(3) Å. The average length of Cu1–N is 1.9955(4) Å, which is in the normal range.

In addition, the CH_3OH solvent molecule and a carboxylate group are linked *via* a O5–H5A···O1 hydrogen bond with a D···A distance of 3.058(8) Å and a D–H–A angle of 120 °. The hydrogen bonds contribute to the overall stability of **1**.

Electrochemical properties

Fig. 2a shows the cyclic voltammogram (CV) of **1**. In the CV measurement, we employed a conventional three-electrode system where glass/C was chosen as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum electrode as the counter electrode. The complex was dissolved in methanol, the resulting solution having a concentration of 1×10^{-5} mol L^{-1}. A HAc-NaAc solution (pH = 4.0) was used as a buffer, and KCl as the supporting electrolyte. The scanning range was −0.5 to 0.5 V, and the scan rate was 90 mV s^{-1}. The results show that there exists only one oxidation peak with a peak potential at −0.156 V, demonstrating that the electron transfer in the electrode reaction is irreversible.

Under the same conditions, the influence of the potential scan rate on the oxidation peak potential was studied in the range 60–300 mV s^{-1} (Fig. 2b). The results show that the oxidation peak potential (E_{pa}) shifts to more positive values with increasing scan rate, and that it is proportional to lg$v$ in the range 90–300 mV s^{-1}. The linear regression equation is $E_{pa}(V) = 0.00463\ \lg v - 0.2474$ with the correlation coefficient 0.9949 (Fig. 2c). Based on the slope of E_{pa} with lg$v$, the number of electrons involved in the oxidation of the title complex can be evaluated. The αn is calculated to be 1.2. Generally, the electron transfer coefficient α is about 0.5 in the totally irreversible electrode process. So, the value of n is about 2, indicating that two electrons are involved in the oxidation of the title complex, and the electrode reaction corresponds to Cu(II)/Cu(0).

PXRD pattern and magnetic properties

The purity of **1** was confirmed by powder X-ray diffraction analyses, in which the experimental pattern of **1** is almost consistent with its simulated pattern (Fig. 3). The temperature dependence of the magnetic susceptibility of **1** was investigated from 300 to 2.8 K with an applied magnetic field of 2 kOe. The curves $\chi_M T$ *vs.* T and $1/\chi_M$ *vs.* T are shown in Fig. 4. The product of $\chi_M T$ decreases gradually from 0.64 cm^3 K mol^{-1} at 300 K to 0.59 cm^3 K mol^{-1} at 2.8 K (Fig. 4a). According to the Curie-Weiss law, $\chi_M = C/(T - \theta)$, the Curie constant (C = 0.64 cm^3 K mol^{-1}) and Weiss constant ($\theta = -1.52$ K) are obtained from a linear fit of the $1/\chi_M$ data between 2.8 and 300 K (Fig. 4b) Such magnetic behavior

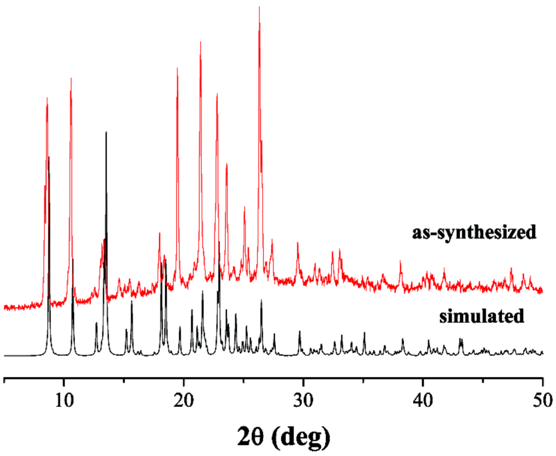

Fig. 3 (color online). The experimental and simulated powder X-ray diffraction patterns of **1**.

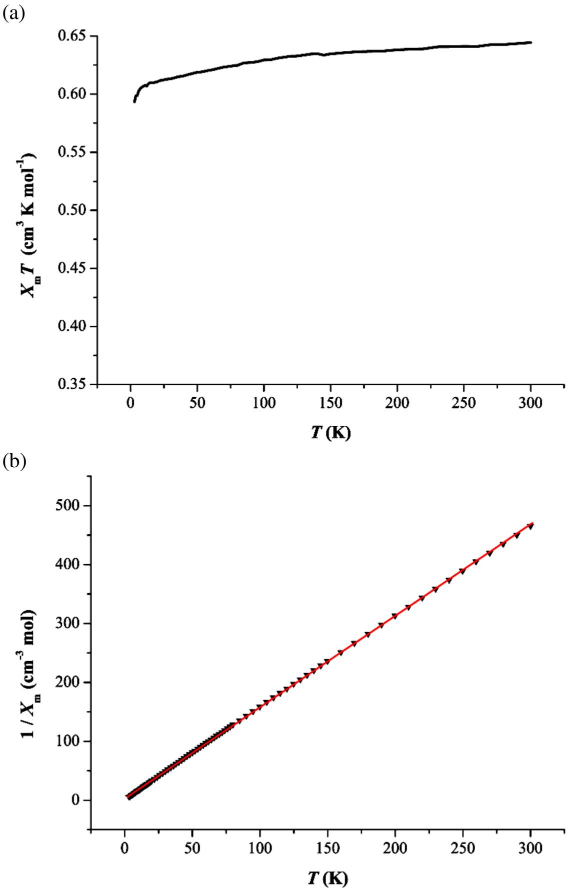

Fig. 4 (color online). (a) Temperature dependence of the magnetic susceptibility of **1** in the form of $\chi_M T$ *vs.* T; (b) temperature dependence of the magnetic susceptibility of **1** in the form of $1/\chi_M$ *vs.* T (the solid line shows the best fit).

indicates that **1** is a paramagnetic system and shows a weak antiferromagnetic coupling.

Conclusion

From 2,2′-bipyridine-3,3′-dicarboxylic acid and copper(I) chloride, we have synthesized a new copper(II) rather than a copper(I) complex. This is because of the oxidation of Cu(I) in the course of the experiment. The complex was characterized by X-ray diffraction analysis, and CV and magnetic measurements. The results indicate that the complex is paramagnetic and shows weak antiferromagnetic coupling.

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