

Synthesis, Structural Characterization and Electrochemical Property of a Dinuclear Cu (II) Complex Material

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Abstract: A novel dinuclear Cu(II) complex material has been synthesized by the reaction of 1, 2-phenylenedioxydiacetic acid, 1,10-phenanthroline (phen) and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. And it has been characterized by elemental analysis, IR, UV and single crystal X-ray diffraction. The crystal belongs to tetragonal, space group $I4_1/a$ with $a = b = 25.381(4) \text{ \AA}$, $c = 32.044(6) \text{ \AA}$, $V = 20643(6) \text{ \AA}^3$, $Z = 16$, $D_c = 1.395 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 0.898 \text{ mm}^{-1}$, $F(000) = 8896$, and final $R = 0.1026$, $\omega R = 0.3142$. The structural analysis shows that two Cu(II) atoms adopt different coordination modes, Cu^1 has five-coordination with a trigonal bipyramidal configuration, and Cu^2 has four-coordination with a distorted square planar configuration. The cyclic voltammetric behaviour of the dinuclear Cu(II) complex has been investigated.

Keywords: Characterization, crystal structure, cyclic voltammetric property, dinuclear Cu(II) complex.

INTRODUCTION

The design and synthesis of Cu (II) complex have always attracted considerable interest, as the Cu (II) complexes have potential applications in so many respects. For example, they can build intriguing molecular architectures [1, 2], and can exhibit excellent properties in molecular magnetism, catalysis, antitumor therapeutic agents, and electrochemistry [3-10]. Both carboxylates and phen are good organic ligand because they not only have rich coordination points and strong coordination ability but can also construct the molecular structure of multiple structures [11-13]. We have synthesized a novel dinuclear Cu(II) complex by the self-assembly of 1, 2-phenylenedioxydiacetic acid, 1,10-phenanthroline (phen) and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in the presence of MgCl_2 [14]. For comparison, we synthesized and reported herein another novel dinuclear Cu(II) complex, based on 1, 2-phenylenedioxydiacetic acid and phen ligands without the presence of MgCl_2 . The cyclic voltammetric behaviour of the Cu(II) complex has also been investigated.

EXPERIMENTAL SECTION

Materials and Methods

1,2-Phenylenedioxydiacetic acid, 1,10-phenanthroline, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and solvents used were of analytical grade.

C, H and N analyses were carried out with a Elementar Vario III EL elemental analyzer. Infrared spectra (4000 cm^{-1} ~ 400 cm^{-1}) were recorded on a Nicolet AVATAR 360 FTIR spectrophotometer with KBr discs. Ultraviolet-Visible

spectra in the 200-700 nm region in H_2O solution were recorded on a thermo UV-340 spectrophotometer. CHI660D electrochemical work station was used. The crystal data of dinuclear Cu (II) complex was collected on a Bruker smart-1000 CCD Area Detector.

Synthesis of Cu (II) Complex

1.0 mmol (0.2262 g) 1,2-phenylenedioxydiacetic acid and 2.0 mmol (0.08 g) of sodium hydroxide were dissolved in 10 mL $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (v:v = 1:1) solution. Then 0.5 mmol (0.0998 g) $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and 1.0 mmol (0.0990 g) phen were added to the above solution. The mixed solution was continuously stirred for 4 h at $80 \text{ }^\circ\text{C}$. The green precipitate was collected by filtration and washed with ethanol, then dried. The filtrate was evaporated in air at room temperature, the single crystal suitable for X-ray determination was obtained after 15 days. Elementary analysis: calcd for $\text{C}_{49}\text{H}_{40}\text{Cu}_2\text{N}_4\text{O}_{17}$: C, 54.25; H, 3.69; N, 5.17%; found: C, 53.92; H, 3.37; N, 4.79%. IR ν_{max} (cm^{-1}): $\nu(\text{H}_2\text{O})$: 3427 cm^{-1} , $\nu_{\text{as}}(\text{COO}^-)$: 1564 cm^{-1} , $\nu_{\text{s}}(\text{COO}^-)$: 1415 cm^{-1} , $\nu(\text{C-O-C})$: 1222 cm^{-1} .

X-Ray Crystallography

All crystal data were collected on a Bruker Smart-1000 CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at $293(2) \text{ K}$. In the range 3.01 - 27.48° , a total of 88570 reflections were collected by using an ω scan mode, of 6465 with $I > 2\sigma(I)$ were independent with $R_{\text{int}} = 0.0621$. The structure was solved by direct method and refined with full-matrix least-squares techniques using SHELXL-97 [15]. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were added according to the theoretical model. Molecular graphics were drawn with the program package SHELXTL-97 crystallographic software package

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[16]. The crystal parameters data collection and refinement results for dinuclear Cu(II) complex are summarized in Table 1. The selected bond distances and angles are listed in Table 2.

Table 1. Crystal data and structure refinement for Cu (II) complex.

Crystal Parameter	Crystallographic Data
Formula	C ₄₉ H ₄₀ Cu ₂ N ₄ O ₁₇
Formula weight	1083.93
Crystal system	tetragonal
Space group	I41/a
<i>a</i> (Å)	25.381(4)
<i>b</i> (Å)	25.381(4)
<i>c</i> (Å)	32.044(6)
Z	16
<i>F</i> (000)	8896
Temperature (K)	293(2)
<i>V</i> (Å ³)	20643(6)
Calculated density (μg·m ⁻³)	1.395
Crystal size (mm ³)	0.24 × 0.22 × 0.20
<i>μ</i> (mm ⁻¹)	0.898
<i>S</i>	1.959
Limiting indices	-22 ≤ <i>h</i> ≤ 23, 0 ≤ <i>k</i> ≤ 32, 0 ≤ <i>l</i> ≤ 41
Reflections collected/unique	11825 / 6420
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.1472, 0.3347
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.1026, 0.3142
Largest diff.peak and hole (e ⁻ ·Å ⁻³)	2.497, -0.878

Table 2. Selected bond distances (Å) and angles (°) for Cu(II) complex.

Bonds	Bond Parameter	Bonds	Bond Parameter
Cu1-O14	1.936(5)	Cu2-O7	1.898(5)
Cu1-O11	1.963(5)	Cu2-O4	1.962(5)
Cu1-N4	2.036(6)	Cu2-N2	1.995(6)
Cu1-O12	2.347(5)	Cu2-N1	1.995(6)
Cu1-N3	2.036(5)		
O14-Cu1-O11	92.3(2)	O4-Cu2-O7	92.1(2)
O14-Cu1-N4	166.2(2)	O7-Cu2-N2	173.5(2)
O11-Cu1-N4	94.1(2)	O4-Cu2-N2	94.3(2)
O14-Cu1-N3	89.7(2)	O7-Cu2-N1	92.8(3)
N3-Cu1-O11	166.4(2)	O4-Cu2-N1	155.6(2)
N4-Cu1-N3	81.3(2)	N2-Cu2-N1	81.0(3)
O12-Cu1-O14	97.58(18)	O12-Cu1-N4	93.41(18)
O11-Cu1-O12	99.94(19)	O12-Cu1-N3	93.12(19)

RESULTS AND DISCUSSION

IR Spectra

The free 1,2-phenylenedioxydiacetic acid and phen ligands show bands at 1670 cm⁻¹ ν(COO⁻) and 1582 cm⁻¹ ν(C=N) of phen, respectively. In the IR spectrum of Cu (II) complex (Fig. 1), they appear at 1564 cm⁻¹ and 1513 cm⁻¹, respectively, which indicates that the oxygen atoms of COO⁻ and the nitrogen atoms of phen are coordinated to Cu (II) ion [17]. The results of IR analysis are consistent with the results of X-ray analysis.

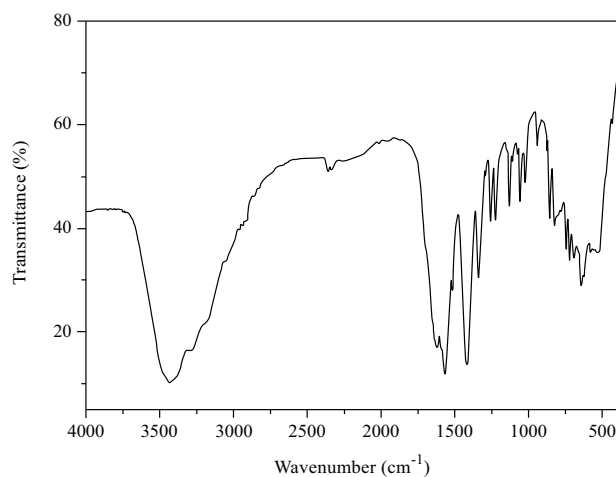


Fig. (1). The IR spectrum of the Cu(II) complex.

UV Spectra

As shown in Fig. (2), the free 1, 2-phenylenedioxydiacetic acid ligand exhibits two absorption bands at 224 nm and 271 nm, which can be assigned to the π-π transitions of the organic ligand. However, the Cu (II) complex show three peaks at 221 nm, 273 nm and 600 nm. The two absorption bands at 221 nm and 273 nm can be assigned to the π-π transitions and the absorption at 600 nm can be assigned to d-d transition. Which indicates that the stable complex is formed by the interaction of ligand and the Cu (II) ion.

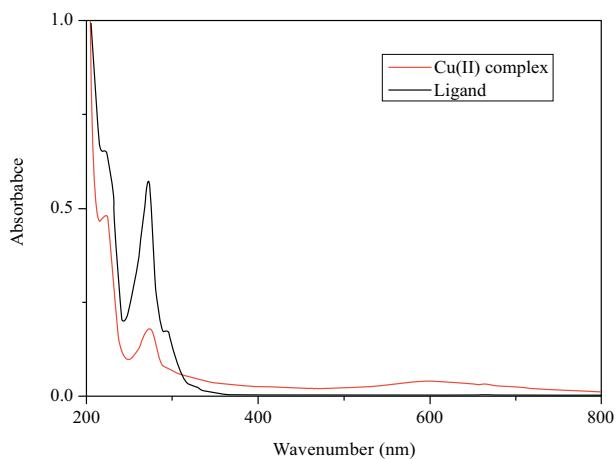


Fig. (2). The UV-vis spectra of 1, 2-phenylenedioxydiacetic acid and its Cu(II) complex.

Structure Description

The molecular structure and molecular packing arrangement are shown in Figs. (3, 4), respectively. Fig. (5) shows the topological structure of the Cu (II) complex. The structure of Cu (II) is different from that of the Cu(II) complex reported previously [14], indicating that the same ligand and metal ion can form different structure when the synthetic condition was changed. As shown in Figs. (3, 4), the Cu^I ion is five-coordinated by two oxygen atoms from 1, 2-phenylenedioxydiacetic acid ligand, one oxygen atom from coordinated water molecule and two nitrogen atoms from phen ligand to form a distorted square pyramid coordination environment. And the Cu² ion is four-coordinated by two oxygen atoms from 1,2-phenylenedioxydiacetic acid ligand and two nitrogen atoms from phen ligand to form a distorted square planar coordination environment. The bond distances of Cu-O are in the range of 1.898(5) Å -2.347(5) Å, and that of Cu-N bonds are in the range of 1.995(6)-2.036(5) Å, respectively. The Cu-O distances and Cu-N distances are close to those of the Cu (II) complex reported previously [18-20].

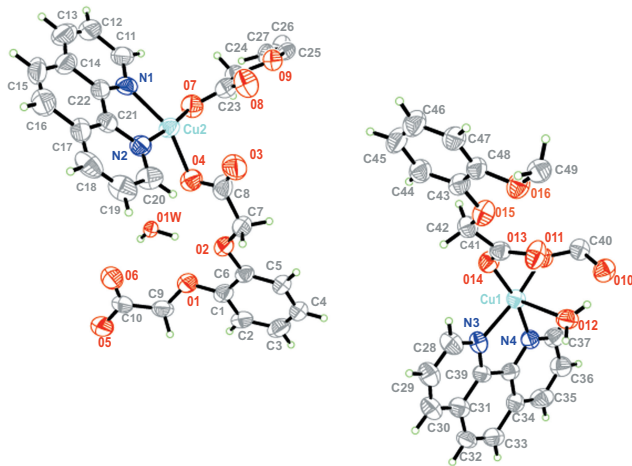


Fig. (3). The molecular structure of the asymmetric unit of Cu(II) complex.

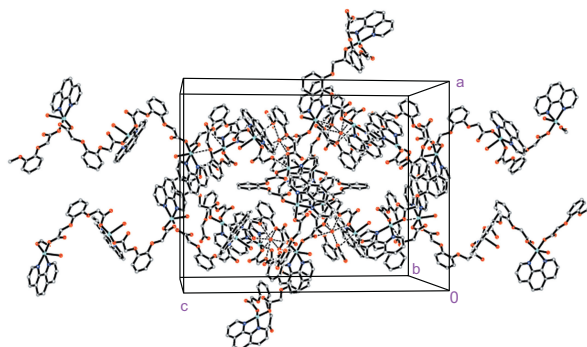


Fig. (4). The molecular packing arrangement of the Cu(II) complex.

Cyclic Voltammetry of Cu (II) Complex

The electrochemical behavior of the Cu (II) complex was determined, and the process of measurement is the same with those reported previously [14]. As shown in Fig. (6), there

appears an obvious oxidation peak at 391 mV, however, no reduction peak is observed, showing that the Cu(II) complex only has reducibility and no oxidizability.

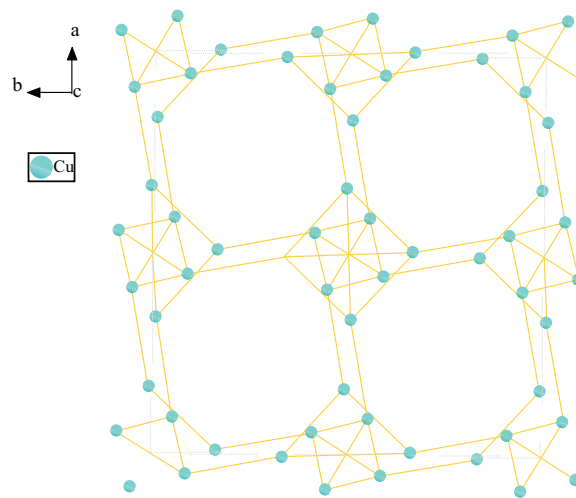


Fig. (5). The topological structure of the Cu(II) complex.

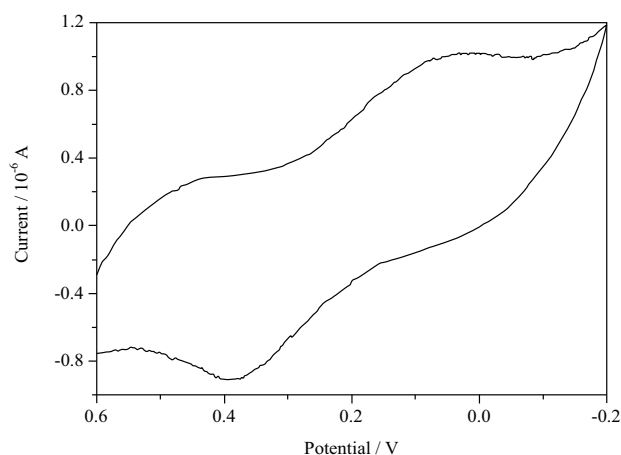


Fig. (6). The cyclic voltammogram using phosphate buffer (pH=6.86).

CONCLUSION

A novel dinuclear Cu (II) complex, based on 1, 2-phenylenedioxydiacetic acid and 1,10-phenanthroline (phen) ligands without the presence of MgCl₂ has been synthesized with structural characterization. In this structure, the Cu (II) atoms adopt two different coordination modes. The cyclic voltammetric behavior of the dinuclear Cu (II) complex has been investigated.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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SUPPLEMENTARY MATERIAL

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1030752. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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