

STUDY ON SYNTHESIS AND CRYSTAL STRUCTURE OF TETRAKIS-(μ_2 -ACETATO)-DIHYDRATE-DICOPPER(II)

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Abstract: A new binuclear Cu(II) complex, tetrakis-(μ_2 -acetato)-dihydrate-dicopper (II), has been prepared by the reaction of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ with 2-formyl-benzenesulfonate-hydrazine in the $\text{CH}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$ ($v : v = 1 : 1$). It was characterized by elemental analysis, IR and X-ray single crystal diffraction analysis. The crystal of the Cu(II) complex belongs to monoclinic, space group C_2/c with $a = 13.162(3) \text{ \AA}$, $b = 8.5572(17) \text{ \AA}$, $c = 13.860(3) \text{ \AA}$, $\beta = 117.06(3)^\circ$, $V = 1390.1(5) \text{ \AA}^3$, $Z = 4$, $D_c = 1.889 \text{ g cm}^{-3}$, $\mu = 3.103 \text{ mm}^{-1}$, $F(000) = 792$, and final $R_1 = 0.0548$, $wR_2 = 0.1410$. Two Cu(II) centers are bridged by oxygen atoms of carboxylato groups. Each Cu(II) center is five-coordinated with four O donor atoms of acetate and a O donor of coordinated water molecule. The molecules form three dimensional network structures by the inaction of π - π stacking and hydrogen bonds.

Keywords: *binuclear, crystal structure, Cu (II) complex, synthesis*

INTRODUCTION

Crystal engineering has attracted considerable interest in recent years, because they display both intriguing architectures and promising potential applications in such fields as catalysis, gas storage, magnetics, luminescence materials, antitumor and so on [1 – 3]. In particular, ligands containing carboxylate groups have been shown to be good building blocks in the design of crystal engineering materials with desired topologies owing to their rich coordination modes [4 – 6], so many studies on carboxylate complexes have been reported [7 – 9]. With considering the points mentioned above, we have synthesized a series of metal-organic hybrid materials containing carboxylate groups [10, 11]. In this paper, a new binuclear Cu(II) complex, tetrakis-(μ_2 -acetato)-dihydrate-dicopper (II), has been successfully prepared by the reaction of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ with 2-formyl-benzenesulfonate-hydrazine in the $\text{CH}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$ solvent.

EXPERIMENTAL

Materials and methods

The 2-formyl-benzenesulfonate-hydrazine ligand was prepared according to the literature method [12]. $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and all other chemicals were commercial materials of analytical grade and used without further purification. Elemental analyses (C, H and N) were carried out on a Elementar Vario EL III elemental analyzer. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the $4000 - 400 \text{ cm}^{-1}$ region. The crystal data was collected on a Bruker smart CCD Area Detector.

Synthesis of the Cu(II) complex

The 1.0 mmol (0.4070 g) of 2-formyl-benzenesulfonate-hydrazine ligand was added to the 10 mL of $\text{CH}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$ ($v:v = 1:1$) solution. After being dissolved, 1.0 mmol (0.1997 g) of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ was added to the solution. The mixture was continuously stirred for 4 h at refluxing temperature and then cooled to room temperature. The production was collected by filtration. Yield: 58 %. Elemental analysis: calculated for $\text{C}_8\text{H}_{12}\text{Cu}_2\text{O}_{10}$: C, 24.29; H, 3.04 %; found: C, 24.04; H, 3.49 %. IR ν_{max} (cm^{-1}): 1588 (s, COO^-). The block crystals were obtained after the filtrate was kept in air for 15 days.

Crystal data and structure refinement

A colorless block single crystal with dimensions of $0.28 \text{ mm} \times 0.24 \text{ mm} \times 0.20 \text{ mm}$ was selected for measurement. Diffraction data of the single crystal were collected by $\varphi \sim \omega$ scan mode using a graphite-monochromatic $\text{Mo } K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 (2) K on a Bruker Smart Apex CCD diffract meter. A total of 6124 reflections were collected in the range $3.30 - 27.49^\circ$, of which 1583 were unique ($R_{\text{int}} = 0.0875$) and 1349 were observed with $I > 2\sigma(I)$. The data were corrected for Lp factors. The structure was solved by direct methods and refined by full-matrix least-squares

techniques on F^2 . The structure was solved by direct methods [13] using SHELXL-97 and expanded using Fourier techniques. All of the non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. The final refinement by full-matrix least squares method was converged at $R = 0.0548$, and $wR = 0.1410$ ($w = 1/[\sigma^2(F_o^2) + (0.0934P)^2 + 0.0000P]$, $P = (F_o^2 + 2F_c^2)/3$, $S = 1.121$, $(\Delta/\sigma)_{\max} = 0.001$). The largest peak in the final difference Fourier map is $0.781 \text{ e}/\text{\AA}^3$ and the minimum peak is $-1.928 \text{ e}/\text{\AA}^3$. Molecular graphics were drawn with the program package SHELXTL-97 crystallographic software package [14]. The most relevant crystal data for complex are quoted in Table 1, and the selected bond distances and angles are listed in Table 2.

Table 1. The most relevant crystal data for the title compound

Formula	$\text{C}_8\text{H}_{12}\text{Cu}_2\text{O}_{10}$
Formula weight	395.26
Crystal system	Monoclinic
Space group	C_2/c
a (Å)	13.162(3)
b (Å)	8.5572(17)
c (Å)	13.860(3)
β (°)	117.06(3)
Z	4
$F(000)$	792
Temperature (K)	293(2)
V (Å ³)	1390.1(5)
Calculated density (g·cm ⁻³)	1.889
Crystal size (mm ³)	0.28×0.24×0.20
μ (mm ⁻¹)	3.103
S	1.121
Limiting indices	$-17 \leq h \leq 16$, $-11 \leq k \leq 11$, $-15 \leq l \leq 17$
Reflections collected	6124
Reflections ($I > 2\sigma(I)$)	1349
Unique reflections	1583
λ (Å)	0.71073
Parameters	91
Restraints	0
$(\Delta/\sigma)_{\max}$	0.001
R_{int}	0.088
R_1, wR_2 [all data]	0.0636, 0.1470
R_1, wR_2 [$I > 2\sigma(I)$]	0.0548, 0.1410
Largest diff. peak and hole (e·Å ⁻³)	0.781, -1.928

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) for the title compound

Bond	Distance
Cu1-O2	1.950(3)
Cu1-O5	1.983(3)
Cu1-O1	2.163(3)
C1-O3	1.253(5)
C2-O4	1.267(4)
Cu1-O3	1.951(3)
Cu1-O4	1.991(3)
C1-O2	1.248(5)
C2-O5	1.250(4)
Angle	($^\circ$)
O2-Cu1-O3	168.60(12)
O5-Cu1-O3	87.19(12)
O2-Cu1-O4	89.22(12)
O5-Cu1-O4	168.67(12)
O5-Cu1-O1	98.18(11)
O3-C1-O2A	126.2(4)
O5-C2-C4	118.8(3)
O2-Cu1-O5	91.09(11)
O4-Cu1-O3	90.28(12)
O2-Cu1-O1	93.39(12)
O1-Cu1-O3	98.01(11)
O4-Cu1-O1	93.11(11)
O5-C1-O4A	124.6(3)

Symmetry code: (A) $-x, -y+2, -z+1$.

RESULTS AND DISCUSSION

Elemental Analysis

The result of elemental analysis indicated that the composition of Cu(II) complex conforms to a 1 : 2 metal-to-ligand stoichiometry, and is accorded with the result of single crystal X-ray diffraction analysis. The Cu(II) complex is soluble in DMF, DMSO, methanol, ethanol and acetone, insoluble in benzene, diethyl and THF. 2-formyl-benzenesulfonate-hydrazine was first designed to form a complex with Cu(II) ions, unfortunately, it was not contained in the complex.

X-Ray structural characterization

X-ray crystallographic analysis reveals that the Cu(II) complex crystallizes in the monoclinic system with C_2/c space group. The crystal structure of the Cu(II) complex is shown in Figure 1. As illustrated in Figure 1, we can see that the complex consists of dinuclear Cu(II) units and has an inversion center with crystallographic symmetry. Each Cu(II) center is five-coordinated with four O donor atoms of acetate and a O donor of coordinated water molecule (Cu1-O2 = 1.950(3) Å, Cu1-O3 = 1.951(3) Å, Cu1-O5 = 1.983(3) Å, Cu1-O4 = 1.991(3) Å, Cu1-O1 = 2.163(3) Å) in a distorted trigonal bipyramidal geometry. Also, the distances of Cu-O are comparable with that observed in other Cu-based complexes [15]. In the Cu(II) complex, all acetate adopt bidentate coordination mode. And the distance of adjacent Cu(II) atoms is 2.6153(9) Å.

The adjacent binuclear Cu(II) units are linked each other by π - π interaction and hydrogen bonds to form a 1D chained structure (Figure 2). The 1D chain extends to three dimensional network structure (Figure 3). Obviously, the π - π interactions increase the stability of the crystal structure.

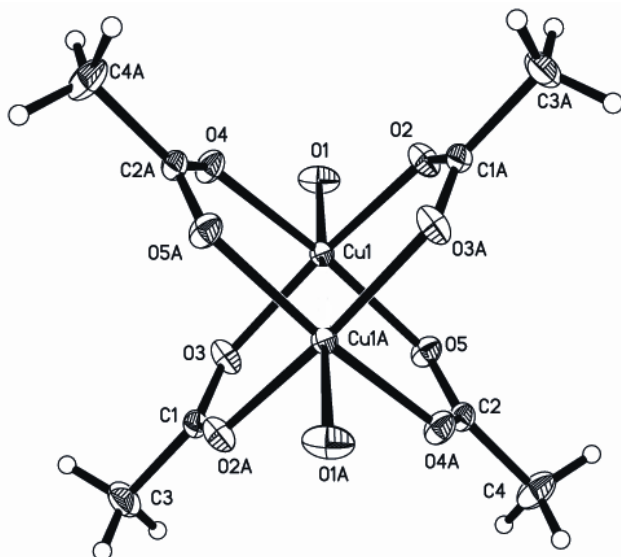


Figure 1. Molecular structure of the Cu(II) complex, where the thermal ellipsoids were drawn at 30 % possibility

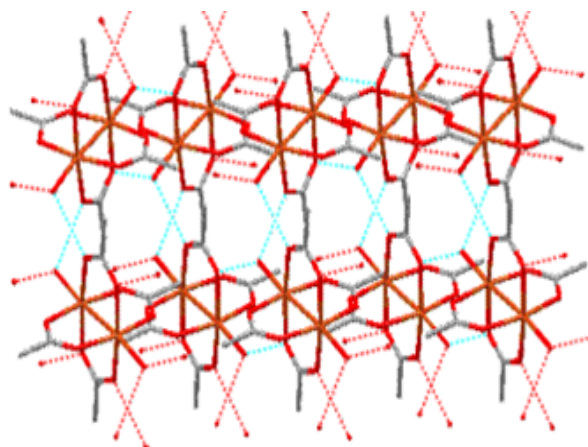


Figure 2. One-dimensional chained structure of the Cu(II) complex

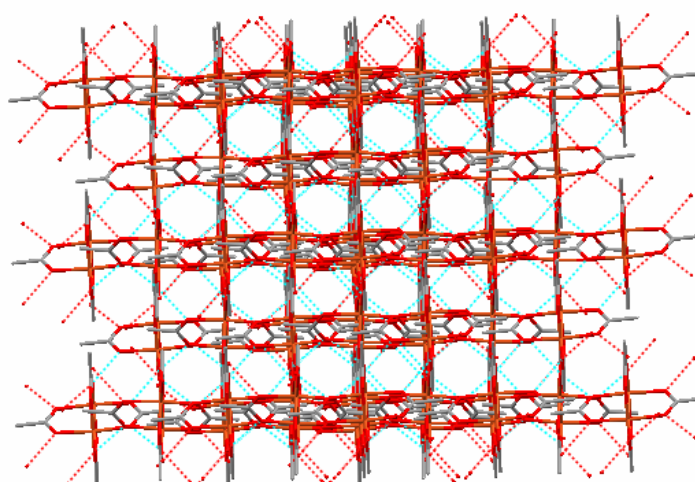


Figure 3. Three dimensional network structure of the Cu(II) complex by π - π stacking

CONCLUSIONS

In summary, a new binuclear Cu(II) complex has been synthesized and structurally characterized. The results show that each Cu(II) center is five-coordinated with four O donor atoms of acetate and an O donor of coordinated water molecule. The molecules form three dimensional network structures by the inaction of π - π stacking and hydrogen bonds.

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