Synthesis and Crystal Structure of Dialkoxo-Bridged Dinuclear Cu(II) Complex with 5-Methoxy-6'-hydroxy-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol

XIN-YING ZHANG*, LI-SHA ZHANG, PENG-FEI LIU, CHENG-JUAN YANG, ZHENG-KUN WANG and JIAO-LONG MENG

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, P.R. China

*Corresponding author: E-mail: zhangxy_88@126.com

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An unexpected dinuclear copper(II) complex, $[\text{Cu}_2(\text{L}^2)_2]$ (H_2L^2 = 4-methoxysalicylaldehyde-O-(2-hydroxyethyl)oxime), has been synthesized through the complexation of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ with an asymmetrical salamo-type compound 5-methoxy-6'-hydroxy-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol (H_3L^1). The catalysis of Cu(II) ions results in the unexpected cleavage of one of the N-O bonds in the ligand H_3L^1 , giving a novel dialkoxo-bridged dinuclear Cu(II) complex possessing a Cu-O-Cu-O four membered ring core instead of the usually desired salamo-type ligand Cu-N₂O₂ mononuclear complex.

Key Words: Asymmetrical salamo-type compound, Cu(II) complex, Synthesis, Crystal structure.

INTRODUCTION

Particular attention has recently been paid to the synthesis and crystal structure of salamo-type compounds and their analogues^{1,2}. These compounds can easily form polynuclear complexes in which the metal centers are bridged through organic ligands, because of their enormous variety of structural topologies as well as their unique properties in host-guest chemistry, magnetism, asymmetric catalysis, electronic conductivity³⁻⁶. This subject is currently being pursued in our research, including the applications and study of salamo-type compounds and their metal complexes.

In this article, we report the synthesis and crystal structure of a dinuclear Cu(II) complex $[\text{Cu}_2(\text{L}^2)_2]$ with the new ligand 4-methoxysalicylaldehyde-O-(2-hydroxyethyl) oxime (H_2L^2) which is formed in the course of complexation of an asymmetrical salamo-type compound 5-methoxy-6'-hydroxy-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol (H_3L^1) and Cu(II) acetate monohydrate. The obtained results show cleavage of one of the N-O bonds in H_3L^1 in the complexation of the ligand H_3L^1 with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and give an unexpected dialkoxo-bridged dinuclear Cu(II) complex possessing a Cu-O-Cu-O four-membered ring core instead of the usually desired salamo-type Cu-N₂O₂ complex.

EXPERIMENTAL

2-Hydroxy-4-methoxybenzaldehyde ($\geq 99\%$) was purchased from Energy Chemical and used without further purification. The others are the same as literature early¹¹.

General procedure

Synthesis of the ligand H_3L^1 : The major reaction steps involved in the synthesis of H_3L^1 are given in **Scheme-I**.

Scheme-I: Synthetic route to the asymmetrical salamo-type compound H_3L^1

1,2-Bis(phthalimidoxy)ethane was prepared according to the literature¹. Yield 87.5 %. m.p. 250 °C. 1,2-Bis(aminoxyl)ethane was synthesized according to an analogous method reported previously¹. Monooxime compound was synthesized with a slightly modified method reported previously in the literature^{1,7}. Yield 75.1 %. m.p. 41-42 °C. Anal. calcd. for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_4$ (%): C, 53.09; H, 6.24; N, 12.38; found (%): C, 53.22; H, 6.27; N, 12.24.

For H_3L^1 , to an ethanol solution (10 mL) of the monooxime compound (226.0 mg, 1.00 mmol) was added dropwise an ethanol solution (8 mL) of 2,3-dihydroxybenzaldehyde (138 mg, 1 mmol). The mixture solution was heated at 55-60 °C for 5 h. When the mixture cooled to room temperature, the precipitate was filtered and washed successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried *in vacuo* and obtained 236.1 mg of white solid. Yield 68.2 %.

m.p. 110–112 °C. Anal. calcd. for $C_{17}H_{18}N_2O_6$ (%): C, 58.96; H, 5.24; N, 8.09. Found (%): C, 59.17; H, 5.13; N, 8.01.

Synthesis of the Cu(II) complex: A solution of $Cu(OAc)_2 \cdot H_2O$ (2.00 mg, 0.01 mmol) in methanol (3 mL) was added dropwise to a solution of H_3L^1 (3.46 mg, 0.01 mmol) in acetone (1 mL) at room temperature. The colour of the mixing solution turned to brown immediately, then stirred for 1 h at room temperature. The mixture was filtered off and the filtrate was allowed to stand at room temperature for about three weeks, the solvent was partially evaporated and obtained brown prismatic single crystals suitable for X-ray crystallographic analysis. Anal. calcd. for $C_{20}H_{22}N_2O_8Cu_2$ (%): C, 44.04; H, 4.07; N, 5.14; Cu, 23.30. Found (%): C, 43.96; H, 4.19; N, 5.03; Cu, 23.46.

X-Ray structure determination: The X-ray structure determination is the same as literature early¹ⁱ. Details of the data collection and refinements of title compound are listed in Table-1. CCDC: 933601.

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR THE COMPLEX

Empirical formula	$C_{20}H_{22}N_2O_8Cu_2$
Formula weight	545.48
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell dimensions, (Å, °)	$a = 5.2234(5)$, $b = 15.317(2)$, $c = 12.976(1)$, $\beta = 100.294(1)$
Volume (Å ³)	1021.5(2)
Z	2
Density (calculated) (mg/m ³)	1.773
Absorption coefficient (mm ⁻¹)	2.135
$F_{(000)}$	556
Index ranges	$-6 \leq h \leq 6$, $-6 \leq k \leq 18$, $-15 \leq l \leq 14$
Reflections collected	3319/1797 [$R_{int} = 0.0252$]
Independent reflections	886
Data/restraints/parameters	1797/0/146
Goodness of fit indicator	1.057
R [$I > 2\sigma(I)$]	$R_1 = 0.0348$, $wR_2 = 0.0822$
Largest diff. peak and hole (e ⁺ Å ⁻³)	0.334 and -0.281

RESULTS AND DISCUSSION

Crystal structure of the Cu(II) complex: For the synthesis of the Cu(II) complex $[Cu_2(L^2)_2]$, the same synthetic route was used for the mononuclear complex according to the previous work¹. However, it is remarkable that an unexpected dinuclear

Cu(II) complex $[Cu_2(L^2)_2]$ was obtained, instead of the desired salamo-type complex $[Cu(L^1)]$, which was formed in the course of the complexation of H_3L^1 and $Cu(OAc)_2 \cdot H_2O$. The results show that because of the catalysis of Cu(II) ions^{8,9}, the complexation resulted in a cleavage of one of the N-O bonds in H_3L^1 , giving a new O-N-O tridentate ligand H_2L^2 , which coordinates with Cu(II) ions forming a dialkoxo-bridged dinuclear Cu(II) complex^{10,11} with a Cu-O-Cu-O four-membered ring core instead of the expected salamo-type Cu-N₂O₂ complex (**Scheme-II**).

(a) Complexation of the ligand H_3L^1 with $Cu(OAc)_2 \cdot H_2O$

(b) 4-Methoxysalicylaldehyde-O-(2-hydroxyethyl)oxime (H_2L^2)

Scheme-II: Complexation of H_3L^1 with $Cu(OAc)_2 \cdot H_2O$ and chemical structure of H_2L^2

The molecular structure and crystallographic atom numbering of the complex $[Cu_2(L^2)_2]$ are given in Fig. 1. Selected bond lengths and bond angles are listed in Table-2.

Fig. 1. ORTEP-style drawing of the Cu(II) complex

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR THE COMPLEX

Bond	Lengths	Bond	Lengths	Bond	Lengths
Cu1-O3	1.879(2)	Cu1-O2	1.904(2)	Cu1-O2 ^{#1}	1.912(2)
Cu1-N1	1.935(3)	Cu1-Cu1 ^{#1}	2.999(1)	O2-Cu1 ^{#1}	1.912(2)
Bond	Angles	Bond	Angles	Bond	Angles
O3-Cu1-O2	170.5(1)	O3-Cu1-O2 ^{#1}	94.4(1)	O2-Cu1-O2 ^{#1}	76.4(1)
O3-Cu1-N1	93.8(1)	O2-Cu1-N1	95.5(1)	O2-Cu1-N1 ^{#1}	171.5(1)
O3-Cu1-Cu1 ^{#1}	132.4(1)	O2-Cu1-Cu1 ^{#1}	38.3(1)	O2-Cu1 ^{#1} -Cu1	38.1(1)
N1-Cu1-Cu1 ^{#1}	133.7(1)	C3-N1-Cu1	125.5(2)	O1-N1-Cu1	122.4(2)
C2-O2-Cu1	125.7(2)	C2-O2-Cu1 ^{#1}	130.0(2)	Cu1-O2-Cu1 ^{#1}	103.6(1)
C5-O3-Cu1	128.3(2)	—	—	—	—

Symmetry transformations used to generate equivalent atoms: ^{#1}-x, -y+1, -z+1.

Single-crystal X-ray structure revealed that the complex is a neutral homobinuclear entity with crystallographic inversion symmetry. The ORTEP shows that two $[\text{Cu}(\text{L}^2)]$ moieties in the same molecule are bridged together through two alkoxo bridges, each of which comes from the new ligand H_2L^2 . The whole complex sits on a center of inversion forming the μ -dialkoxo-bridged binuclear structure with both tetra-coordinated Cu(II) centers. This geometry can be best described as slightly distorted square-planar with CuN_1O_3 coordination (one oxime N1 atom, one phenoxo O3 atom and two bridging alkoxo O2 and $\text{O2}^{\#1}$ atoms). Thus, a planar Cu_2O_2 core is formed by two Cu(II) ions and their bridging two alkoxo oxygen atoms with a $\text{Cu1}\cdots\text{Cu1}^{\#1}$ separation of 2.999(1) Å. The distance of $\text{Cu1}\cdots\text{Cu1}^{\#1}$ is relatively too long to be considered as intramolecular Cu-Cu bonding. The bridging Cu-O bonds are slightly asymmetric, one being short ($\text{Cu1}-\text{O2}$) with 1.904(2) Å and one long ($\text{Cu1}-\text{O2}^{\#1}$) is 1.912(2) Å. The bond lengths $\text{Cu1}-\text{O3}$ and $\text{Cu1}-\text{N1}$ are 1.879(2) and 1.936(3) Å, respectively. The four-membered ring $\text{Cu1}-\text{O2}-\text{Cu1}^{\#1}-\text{O2}^{\#1}$ is exactly planar as required by symmetry. The angles $\text{Cu1}-\text{O2}-\text{Cu1}^{\#1}$ and $\text{O2}-\text{Cu1}-\text{O2}^{\#1}$ are 103.6(1) and 76.4(1)°, respectively. The dihedral angle of the two planes $\text{O2}-\text{Cu1}-\text{O2}^{\#1}$ and $\text{O3}-\text{Cu1}^{\#1}-\text{N1}$ is 3.22° and the Cu1 atom deviates by 0.004(3) Å from the mean plane defined by the atoms O2, $\text{O2}^{\#1}$, O3, N1.

Intermolecular interactions of $[\text{Cu}_2(\text{L}^2)_2]$: The Cu(II) complex in the crystal self-assembles through 12 intermolecular hydrogen bonds. The hydrogen bond data are listed in Table-3. In the crystal structure, four intermolecular hydrogen bonds, $\text{C1}-\text{H1A}\cdots\text{O3}$, are formed between the methylene unit ($\text{C1}-\text{H1A}$) of the O-alkyl chain and the phenolic O3 atom of the $(\text{L}^2)^2$ unit, linking the neighboring molecules into an infinite chain parallel to the *a* axis, as illustrated in Fig. 2. The molecules are further linked by four pairs of hydrogen bonds, $\text{C3}-\text{H3}\cdots\text{O4}$ and $\text{C10}-\text{H10B}\cdots\text{O1}$, forming an infinite 2D layer structure along the crystallographic *ac* plane (Fig. 3). The $\text{C3}-\text{H3}\cdots\text{O4}$ hydrogen bonds are formed between the $-\text{C3H3}$ unit of the oxime groups and the O4 atom of the methoxy group, while the hydrogen bonds $\text{C10}-\text{H10B}\cdots\text{O1}$ are formed between $-\text{C10H10B}$ unit of the methoxy group and the O1 atom of the oxime groups. Thus, each complex is linked to ten other molecules into an infinite 3D supramolecular network through intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds.

Fig. 2. (Colour online). View of the 1D chain motif of the complex units along the *a* axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

D-H $\cdots$ A	d(D-H)	d(H $\cdots$ A)	d(D $\cdots$ A)	$\angle\text{D-H}\cdots\text{A}$
$\text{C10}-\text{H10B}\cdots\text{O1}$	0.96	2.62	3.51(3)	155
$\text{C3}-\text{H3}\cdots\text{O4}$	0.93	2.59	3.49(3)	162
$\text{C1}-\text{H1A}\cdots\text{O3}$	0.97	2.50	3.43(3)	160

Fig. 3. (colour online). View of the 2D layer motif along the *ac* plane (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

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