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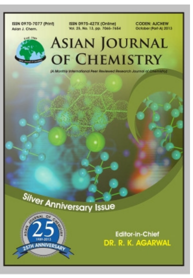

# Synthesis and Crystal Structure of Dialkoxo-Bridged Dinuclear Cu(II) Complex with 5-Methoxy-6'-hydroxy-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol

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An unexpected dinuclear copper(II) complex, $[Cu_2(L^2)_2]$ ($H_2L^2$ = 4-methoxysalicylaldehyde-O-(2-hydroxyethyl)oxime), has been synthesized through the complexation of $Cu(OAc)_2 \cdot H_2O$ with an asymmetrical salamo-type compound 5-methoxy-6'-hydroxy-2,2'-[ethylenedioxy*bis*(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 $Cu\text{-}N_2O_2$ 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 conductivity[3-6]. This subject is currently being pursued in our research, including the applications and study of salamo-type compounds and their metal complexes.

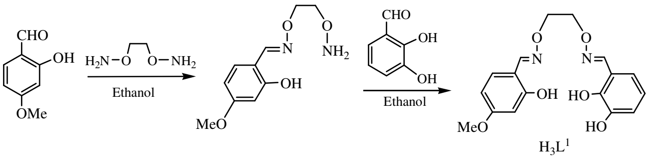
In this article, we report the synthesis and crystal structure of a dinuclear Cu(II) complex $[Cu_2(L^2)_2]$ with the new ligand 4-methoxysalicylaldehyde-O-(2-hydroxyethyl) oxime ($H_2L^2$) which is formed in the course of complexation of an asymmetrical salamo-type compound 5-methoxy-6'-hydroxy-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol ($H_3L^1$) 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 $Cu(OAc)_2 \cdot H_2O$ 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 $Cu\text{-}N_2O_2$ complex.

## EXPERIMENTAL

2-Hydroxy-4-methoxybenzaldehyde (≥ 99 %) was purchased from Energy Chemical and used without further purification. The others are the same as literature early[1i].

### 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 literature[1]. Yield 87.5 %. m.p. 250 ºC. 1,2-*Bis*(aminooxy)-ethane was synthesized according to an analogous method reported previously[1]. Monooxime compound was synthesized with a slightly modified method reported previously in the literature[1,7]. Yield 75.1 %. m.p. 41-42 ºC. Anal. calcd. for $C_{10}H_{14}N_2O_4$ (%): 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 ºC 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 ºC. 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 $Cu(OAc)_2·H_2O$ (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 prismatical 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.

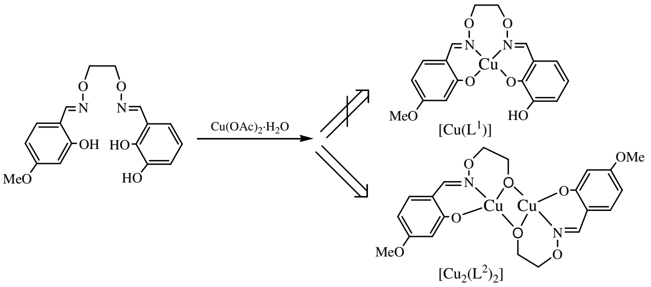
**X-Ray structure determination**: The X-ray structure determination is the same as literature early[1i]. Details of the data collection and refinements of title compound are listed in Table-1. CCDC: 933601.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE COMPLEX

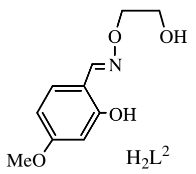
| | |
|---|---|
| Empirical formula | $C_{20}H_{22}N_2O_8Cu_2$ |
| Formula weight | 545.48 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Cell dimensions, (Å, º) | a = 5.2234(5), b = 15.317(2),<br>c = 12.976(1), β = 100.294(1) |
| 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 | $-6 \le h \le 6$, $-6 \le k \le 18$, $-15 \le l \le 14$ |
| 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 >2σ(I)] | $R_1$ = 0.0348, $wR_2$ = 0.0822 |
| Largest diff. peak and hole ($eÅ^{-3}$) | 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 work[1]. 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 $Cu(OAc)_2·H_2O$. 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-$N_2O_2$ complex (**Scheme-II**).



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



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

**Scheme-II:** Complexation of $H_3L^1$ with $Cu(OAc)_2·H_2O$ 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.

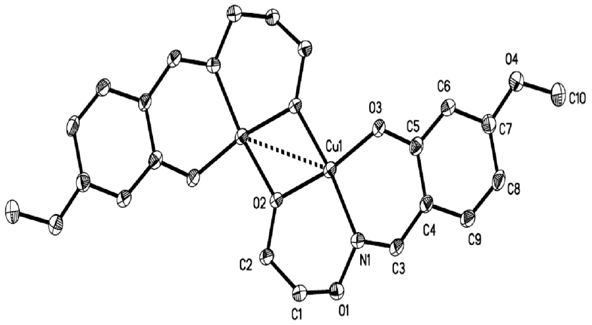


Fig. 1. ORTEP-style drawing of the Cu(II) complex

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (º) 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 [Cu($L^2$)] 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 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 Cu1···Cu1$^{\#1}$ separation of 2.999(1) Å. The distance of Cu1···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 (Cu1-O2) with 1.904(2) Å and one long (Cu1-O2$^{\#1}$) is 1.912(2) Å. The bond lengths Cu1-O3 and Cu1-N1 are 1.879(2) and 1.936(3) Å, respectively. The four-membered ring Cu1-O2-Cu1$^{\#1}$-O2$^{\#1}$ is exactly planar as required by symmetry. The angles Cu1-O2-Cu1$^{\#1}$ and O2-Cu1-O2$^{\#1}$ are 103.6(1) and 76.4(1)º, respectively. The dihedral angle of the two planes O2-Cu1-O2$^{\#1}$ and O3-Cu1$^{\#1}$-N1 is 3.22° and the Cu1 atom deviates by 0.004(3) Å from the mean plane defined by the atoms O2, O2$^{\#1}$, O3, N1.

**Intermolecular interactions of [$Cu_2(L^2)_2$]:** 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, C1-H1A···O3, are formed between the methylene unit (C1-H1A) of the O-alkyl chain and the phenolic O3 atom of the $(L^2)^{2-}$ 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, C3-H3···O4 and C10-H10B···O1, forming an infinite 2D layer structure along the crystallographic ac plane (Fig. 3). The C3-H3···O4 hydrogen bonds are formed between the -C3H3 unit of the oxime groups and the O4 atom of the methoxy group, while the hydrogen bonds C10-H10B···O1 are formed between -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 C-H···O hydrogen bonds.

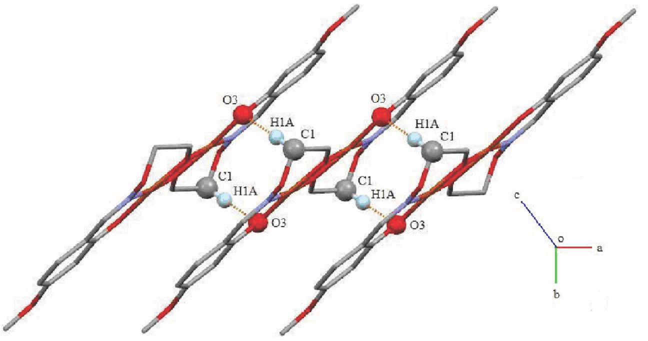


Fig. 2. (Colour online). View of the 1D chain motif of the complex units along the a axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

TABLE-3
DATA FOR HYDROGEN-BONDING INTERACTIONS (Å, º)

| D-H···A | d(D-H) | d(H···A) | d(D···A) | ∠D-H···A |
|---|---|---|---|---|
| C10-H10B···O1 | 0.96 | 2.62 | 3.51(3) | 155 |
| C3-H3···O4 | 0.93 | 2.59 | 3.49(3) | 162 |
| C1-H1A···O3 | 0.97 | 2.50 | 3.43(3) | 160 |

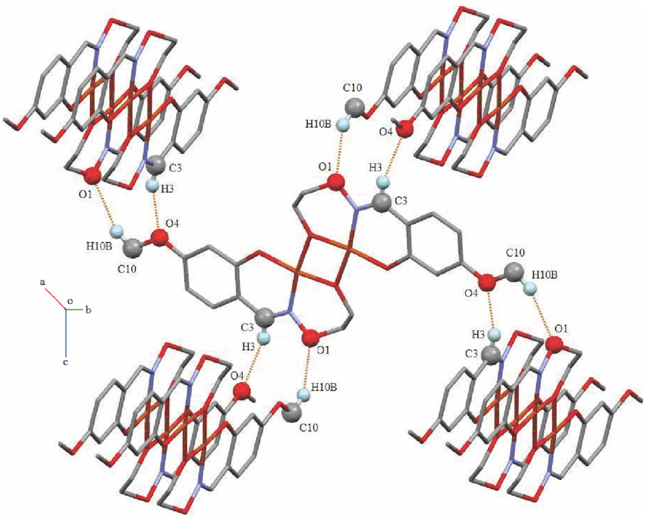


Fig. 3. (colour online). View of the 2D layer motif along the ac plane (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

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