

Synthesis, Crystal and Supramolecular Structure of {2,2'-[Ethylenedioxybis(nitrilomethylidyne)]dinaphthanolato}Cu(II)

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A new Cu(II) complex has been synthesized by the reaction of a new Salamo-type ligand of 2,2'-[ethylenedioxybis(nitrilomethylidyne)]dinaphthanol (H_2L) with Cu(II) acetate monohydrate in acetone/methanol solution and characterized by X-ray diffraction methods. The X-ray crystallography of the Cu(II) complex shows it to be a mononuclear complex, in which the Cu(II) atom is in a distorted square-planar geometry and the center Cu(II) atom is tetra-coordinated lying in the N_2O_2 coordination sphere. The Cu(II) complex crystallizes in the triclinic system, space group P-1. The unit cell contains two crystallographically independent but chemically identical mononuclear Cu(II) complex (molecules A and B). And every complex molecule links four other molecules into an infinite 2D-layer supramolecular structure.

Keywords: Salamo-type ligand, Cu(II) complex, Synthesis, Crystal structure.

INTRODUCTION

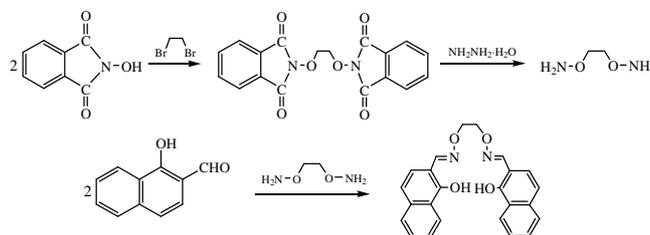
It is well known that transition metal complexes with tetradentate N_2O_2 ligands have been intensively investigated as catalysts for a number of organic redox reactions and electrochemical reduction processes¹. Metallosalen complexes have also been recently used as catalytically active materials to develop surface-modified electrodes for sensing applications², as nonlinear optical materials^{3,4}, exhibit interesting magnetic properties⁵⁻⁹, biological systems¹⁰ and building blocks for cyclic supramolecular structures¹¹. Furthermore, the Cu(II) complexes with a preferable class of Salamo-type ligands based on O-alkyl oxime unit ($-CH=N-O-(CH_2)_n-O-N=CH-$) instead of the imine moiety ($-CH=N-(CH_2)_n-N=CH-$) have been studied. The large electronegativity of oxygen atoms is expected to affect strongly the electronic properties of N_2O_2 coordination sphere, which can lead to different and novel properties and structures of the resulted complexes¹². Herein, a new mononuclear Cu(II) complex was designed and synthesized, which is formed in the course of complexation of a symmetrical Salamo-type ligand 2,2'-[ethylenedioxybis(nitrilomethylidyne)]dinaphthanol (H_2L) and Cu(II) acetate monohydrate.

EXPERIMENTAL

1-Hydroxy-2-naphthaldehyde ($\geq 99\%$) was purchased from Alfa Aesar and used without further purification. The other reagents and solvent were analytical grade from Tianjin

Chemical Reagent Factory. Elemental analysis for Cu was detected by an IRIS ER/S-WP-1 ICP atomic emission spectrometer. C, H and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. X-ray single crystal structure determination was carried out on a Bruker Smart 1000 CCD diffractometer. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and the thermometer was uncorrected.

Synthesis of the ligand H_2L : The major reaction steps involved in the synthesis of H_2L are given in **Scheme-I**.



Scheme-I: Synthetic route to the Salamo-type ligand H_2L

1,2-Bis(aminoxy)ethane was synthesized by a similar method^{12,13}. Yield 75.2%. Anal. calcd. (%) for $C_2H_8N_2O_2$: C 26.08, H 8.76, N 30.42; found. (%) C 25.92, H 8.87, N 30.35.

2,2'-[Ethylenedioxybis(nitrilomethylidyne)]dinaphthanol (H_2L): to an ethanol solution (8 mL) of 1-hydroxy-2-naphthaldehyde (344.3 mg, 2 mmol) was added an ethanol

solution (5 mL) of 1,2-bis(aminooxy)ethane (92.1 mg, 1 mmol). The mixture solution was heated at 55-58 °C for 6 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 314.3 mg of white solid. Yield 78.5 %. m.p. 131-133 °C. Anal. calcd. (%) for C₂₄H₂₀N₂O₄: C, 71.99; H, 5.03; N, 7.00. Found (%): C, 71.81; H, 5.19; N, 7.15.

Synthesis of Cu(II) complex: A solution of Cu(II) acetate monohydrate (12.5 mg, 0.06 mmol) in methanol (30 mL) was added dropwise to a solution of H₂L (25.0 mg, 0.06 mmol) in acetone (30 mL) at room temperature. The colour of the mixing solution turned to dark-brown immediately, then stirred for 0.5 h at room temperature. The mixture was filtered off and the filtrate was allowed to stand at room temperature for about several weeks, the solvent was partially evaporated and obtained dark-brown needle-shaped single crystals suitable for X-ray crystallographic analysis. Anal. calcd. (%) for C₂₄H₁₈N₂O₄Cu: C, 62.40; H, 3.93; N, 6.06; Cu, 13.76. Found (%): C, 62.24; H, 4.09; N, 5.91; Cu, 13.94.

X-ray structure determination: Details of the data collection and structure refinements for the Cu(II) complex are given in Table-1. The single crystal of the Cu(II) complex with the approximate dimensions of 0.38 mm × 0.30 mm × 0.06 mm was placed on a Bruker Smart 1000 CCD area detector. The reflections were collected using a graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 298(2) K. The structure was solved by using the program SHELXL-97 and Fourier difference techniques and refined by the full-matrix least-squares method on F². The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added theoretically. CCDC: 938345.

RESULTS AND DISCUSSION

Crystal structure of Cu(II) complex: X-ray crystallographic analysis reveals that the Cu(II) complex crystallizes in the triclinic system, space group P-1. The unit cell contains two crystallographically independent but chemically identical mononuclear complex (molecules A and B). The molecular structure of the Cu(II) complex is shown in Fig. 1 and selected bond distances and angles are given in Table-2.

The ORTEP shows that the Cu(II) centers (Cu1 and Cu2) are tetra-coordinated, which are linked by two naphtholic oxygen (O3, O4 and O7, O8) atoms and two oxime nitrogen

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR COPPER(II) COMPLEX

Empirical formula	C ₂₄ H ₁₈ N ₂ O ₄ Cu
Formula weight	461.94
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Cell dimensions, (Å, deg)	a = 7.0796(7), b = 14.5948(16), c = 20.474(2), $\alpha = 110.211(3)$, $\beta = 99.110(2)$, $\gamma = 91.422(2)$
Volume (Å ³)	1952.9(4)
Z	4
Density (calculated) (mg/m ³)	1.571
Absorption coefficient (mm ⁻¹)	1.154
F ₍₀₀₀₎	948
Index ranges	-8 ≤ h ≤ 8, -17 ≤ k ≤ 15, -24 ≤ l ≤ 19
Reflections collected	9925/6609 [R _{int}] = 0.0906]
Independent reflections	1199
Data/restraints/parameters	6609/0/560
Goodness of fit indicator	1.010
R [I > 2σ(I)]	R ₁ = 0.0586, wR ₂ = 0.1556
Largest diff. peak and hole (e Å ⁻³)	0.467 and -0.361

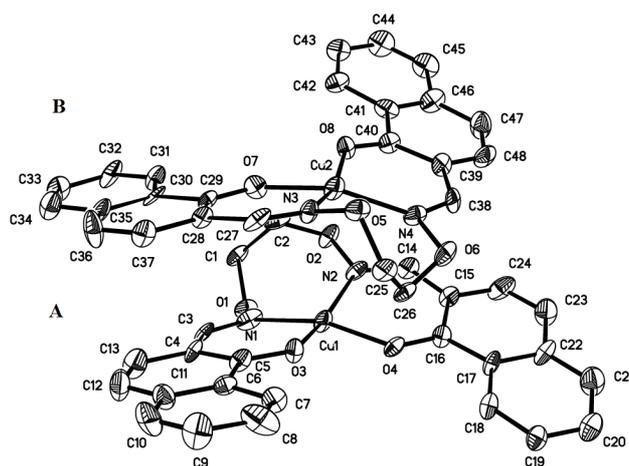


Fig. 1. ORTEP-style drawing of the Cu(II) complex

(N1, N2 and N3, N4) atoms. The dihedral angle between the coordination plane of O4-O3-N1-N2 and that of O8-O7-N3-N4 is 11.05(3)°, with a Cu-Cu separation of 3.792(4) Å which is too long to be considered as intramolecular Cu-Cu bonding, indicating the molecules A and B are crystallographically

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

Bond	Lengths	Bond	Lengths	Bond	Lengths
Cu1-O3	1.903(7)	Cu1-N2	1.977(10)	Cu2-N3	1.939(9)
Cu1-O4	1.902(8)	Cu2-O7	1.900(8)	Cu2-N4	1.963(11)
Cu1-N1	1.946(11)	Cu2-O8	1.896(7)	—	—
Bond	Angles	Bond	Angles	Bond	Angles
O4-Cu1-O3	85.6(3)	O7-Cu2-N3	88.4(4)	C27-N3-Cu2	131.6(9)
O4-Cu1-N1	162.4(4)	O8-Cu2-N4	91.1(4)	O5-N3-Cu2	116.4(6)
O3-Cu1-N1	89.5(4)	O7-Cu2-N4	156.4(4)	C38-N4-Cu2	127.1(9)
O4-Cu1-N2	91.6(4)	N3-Cu2-N4	101.0(4)	O6-N4-Cu2	126.1(8)
O3-Cu1-N2	158.4(4)	C3-N1-Cu1	129.7(8)	C5-O3-Cu1	129.2(8)
N1-Cu1-N2	99.0(4)	O1-N1-Cu1	116.9(7)	C16-O4-Cu1	130.3(7)
O8-Cu2-O7	85.2(3)	C14-N2-Cu1	124.8(8)	C29-O7-Cu2	131.5(7)
O8-Cu2-N3	162.9(4)	O2-N2-Cu1	125.7(8)	C40-O8-Cu2	128.8(8)

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

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠D-H...A	Symmetry code
C18-H18...O5	0.93	2.60	3.35(2)	139	-1 + x, y, z
C26-H26B...O3	0.97	2.54	3.46(1)	157	x, y, z
C32-H32...O2	0.93	2.56	3.48(2)	170	1-x, 1-y, -z

independent to each other. The Cu1 atom deviates by 0.044(3) Å from the coordination plane defined by the atoms O4, O3, N1, N2, while the Cu2 atom deviates by 0.071(3) Å from that of N₂O₂ plane. The dihedral angle between the mean plane of O3-Cu1-N1 and that of O4-Cu1-N2 is 26.00(3)° in the molecule A, while in the molecule B, the dihedral angle is 26.84(4)°, indicating slight distortion towards the tetrahedral geometry from the square-planar structure. In molecule A, the Cu1-N1 (1.946(11) Å) is slightly shorter than the Cu1-N2 (1.977(10) Å), the Cu1-O3 (1.903(7) Å) is slightly longer than the Cu1-O4 (1.902(8) Å) and the bond angles O3-Cu1-N1 and O4-Cu1-N2 are 89.5(4)° and 91.6(4)°, respectively. Similarly, the bond lengths Cu-N and Cu-O and the bond angles O-Cu-N are not also equal in the molecule B, which indicate that the Cu(II) complex is non-crystallographic symmetry.

Intermolecular interactions of the Cu(II) complex: The hydrogen bond data are summarized in Table-3.

In the crystal structure, an intermolecular C26-H26B...O3 hydrogen bond has stabilized a pair of independent molecules A and B by -C26H26B of the methylene groups of the O-alkyl chain in molecule B hydrogen-bonding to the naphtholic oxygen O3 atom of molecule A to form a dimer unit. Furthermore, this dimer link the other dimer unit *via* a pair of C32-H32...O2 hydrogen bond interactions between the -CH groups of the naphtholic rings in molecule B and the oxime oxygen O2 atom in molecule A to form a tetramer unit (Fig. 2). In addition, the -C18H18 groups of the molecule A are hydrogen-bonded to the oxime oxygen O5 atom in the molecule B of the neighboring tetramer units forming two pairs of C18-H18...O5 hydrogen bonds¹⁴⁻¹⁶. Thus, each tetramer unit links the neighboring tetramer unit into an infinite chain parallel to the a axis (Fig. 3).

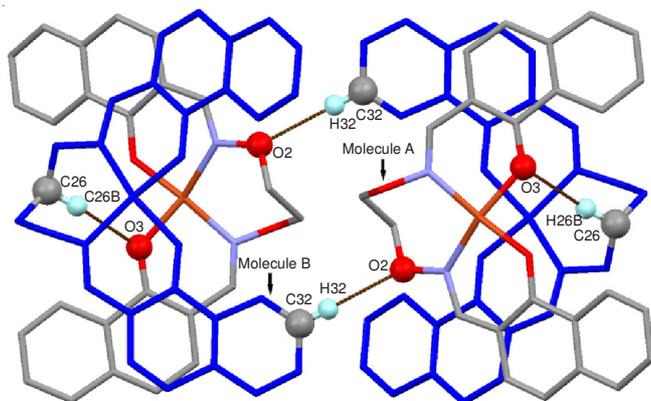


Fig. 2. View of the tetramer unit stabilized by the hydrogen bonds interactions of the Cu(II) complex (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

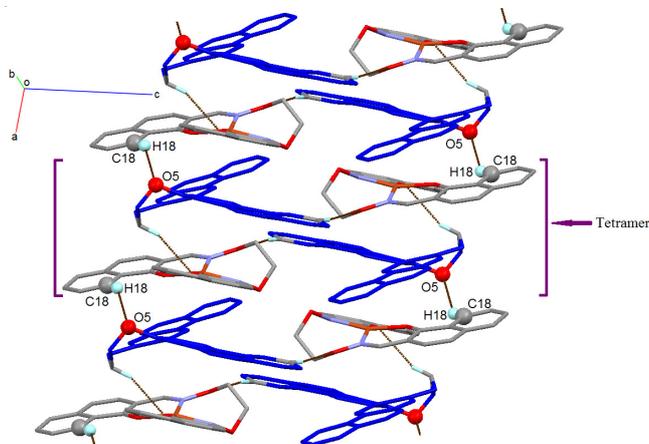


Fig. 3. View of the tetramer unit stabilized by the hydrogen bonds interactions of the Cu(II) complex (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

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