



A Supramolecular Copper(II) Complex with an Asymmetric Salamo-Type Ligand: Synthesis and Crystal Structure

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Received: 12 June 2013;

Accepted: 22 July 2013;

Published online: 15 April 2014;

AJC-15022

A supramolecular mononuclear Cu(II) complex, [CuL], has been synthesized *via* the complexation of copper(II) acetate monohydrate with 4-chloro-4',6'-dibromo-2,2'-[ethylenedioldioxybis(nitrilomethylidyne)]diphenol (H₂L) in methanol/acetone solution and characterized by X-ray diffraction method. X-Ray crystallographic analysis reveals that the Cu(II) atom is tetra-coordinated by N₂O₂ donor atoms from the asymmetric Salamo-type L²⁻ unit, resulting in an almost regular distorted square-planar geometry. With the help of intermolecular C2-H2A...O2 and C2-H2B...Br1 hydrogen-bonding interactions, a self-assembled 2D-layer supramolecular structure is formed.

Keywords: Asymmetric Salamo-type Ligand, Cu(II) Complex, Synthesis, Crystal Structure.

INTRODUCTION

N₂O₂ type ligands such as Salen, which are easily obtained by the reaction of salicylaldehyde with diamines, coordinate to *d*-block transition metals in a tetradentate fashion to afford stable mononuclear complexes¹. Symmetric Salamo-type ligands and their complexes have also attracted much attention for their novel structures and spectral characteristics^{2,3}, especially for their excellent photoluminescence⁴ and interesting magnetic properties⁵. Furthermore, Cu(II) complexes with symmetric Salamo-type ligands have been studied for their fluorescence properties⁶.

Compared with symmetric Salamo-type ligands, a selective synthesis of asymmetrical Salamo-type ligands is important because the electronic and steric effects of the ligands on Salamo metal-assisted catalysis may be controlled by introduction of different substituents into the two benzene rings⁷. The asymmetric configuration would offer opportunities for structural variation and infinite coordination polymers, which would be expected to lead to novel characteristics. Further, this change could create better ways to control polymerization in the context of the infinite coordination polymer structures (different functionality allows to use different metals in the polymerization process)⁸. It has been reported that metal complexes derived from asymmetric Salen ligands sometimes exhibit better enantioselectivities when compared with their symmetric counterparts⁹. In order to study the structural features and spectral characteristics of transition metal

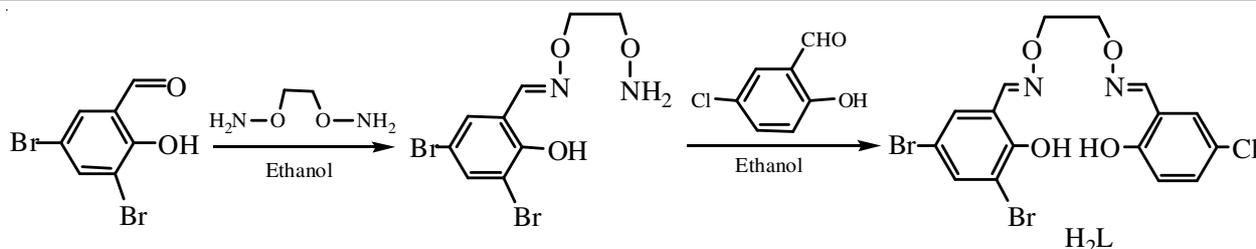
complexes with asymmetric Salamo-type ligands, we herein report a supramolecular complex [CuL] with an asymmetric Salamo-type ligand 4-chloro-4',6'-dibromo-2,2'-[ethylenedioldioxybis(nitrilomethylidyne)]diphenol (H₂L).

EXPERIMENTAL

3,5-Dibromo-2-hydroxybenzaldehyde (≥ 99 %) and 2-hydroxy-5-chlorobenzaldehyde (≥ 99 %) were purchased from Alfa Aesar and used without further purification. 1,2-Bis-(aminoxy)ethane was synthesized according to an analogous method reported earlier^{10,11}. The others are the same as literature early¹².

Synthesis of H₂L: The major reaction steps involved in the synthesis of H₂L are given in **Scheme-I**. H₂L was synthesized according to an analogous method reported earlier¹³. Yield 80.8 %. m.p. 403-404 K. Anal. Calcd. for C₁₆H₁₃N₂O₄Br₂Cl (%): C, 39.02; H, 2.66; N, 5.69. Found: C, 39.28; H, 2.42; N, 5.43.

Synthesis of Cu(II) complex: A solution of Cu(OAc)₂·H₂O (1.99 mg, 0.01 mmol) in methanol (2 mL) was added dropwise to a solution of H₂L (4.93 mg, 0.01 mmol) in acetone (2 mL) at room temperature. The colour of the mixing solution turned to dark-green 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 two days, the solvent was partially evaporated and obtained green block-like single crystals suitable for X-ray crystallographic analysis. Anal. calcd. for C₁₆H₁₁N₂O₄Br₂ClCu (%): C, 34.68; H, 2.00; N, 5.06; Cu, 11.47. Found: C, 34.83; H, 2.08; N, 4.95; Cu, 10.98.



Scheme-I: Synthetic route to 4-chloro-4',6'-dibromo-2,2'-[ethylenedioxybis(nitromethylidene)]diphenol (H_2L)

X-Ray structure determination: The X-Ray structure determination is the same as literature early¹². The crystal data and structure refinement for the Cu(II) complex are given in Table-1.

TABLE-1 CRYSTAL DATA AND STRUCTURE REFINEMENT FOR Cu(II) COMPLEX	
Empirical formula	$C_{16}H_{11}N_2O_4Br_2ClCu$
Formula weight	554.08
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/n$
Cell dimensions, (Å, deg)	$a = 13.7287(12)$, $b = 6.7822(5)$, $c = 19.1223(16)$, $\beta = 109.392(2)$
Volume (Å ³)	1679.5(2)
Z	4
Density (calculated) (mg/m ³)	2.191
Absorption coefficient (mm ⁻¹)	6.244
$F_{(000)}$	1076
Crystal size (mm)	$0.35 \times 0.14 \times 0.09$
Index ranges	$-16 \leq h \leq 16$, $-8 \leq k \leq 7$, $-17 \leq l \leq 22$
Reflections collected	8116/2945 [R(int) = 0.0975]
Independent reflections	1747
Data/restraints/parameters	2945/0/235
Goodness of fit indicator	1.070
R [$I > 2\sigma(I)$]	$R_1 = 0.0643$, $wR_2 = 0.1045$
Largest diff. peak and hole (e Å ⁻³)	2.404 and -1.130

RESULTS AND DISCUSSION

Crystal structure of Cu(II) complex: ORTEP representation of the Cu(II) complex is shown in Fig. 1. Selected bond lengths and angles are listed in Table-2.

X-ray crystallographic analysis reveals that the Cu(II) complex crystallizes in the monoclinic system, space group $P2(1)/n$ with $Z = 4$. The molecular structure of the Cu(II) complex consists of one Cu(II) atom and one L^2 unit. As shown in Fig. 1, the Salamo-type L^2 moiety in the Cu(II) complex is not planar, but has a twisted geometry. The Cu(II) ion is tetra-coordinated in a *cis*- N_2O_2 geometry by two oxime nitrogen (N1 and N2) atoms and two phenoxo oxygen (O3 and O4) atoms from the deprotonated L^2 unit. The dihedral angle between the coordination planes of N1-Cu1-O3 and N2-Cu1-O4 is $27.97(4)^\circ$. Consequently the coordination sphere can be described as a slight distortion toward tetrahedral geometry from the square planar structure. Furthermore, the deviation

TABLE-2 SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE Cu(II) COMPLEX			
Bond	Lengths	Bond	Lengths
Cu1-O3	1.859(6)	Cu1-N2	1.916(9)
Cu1-O4	1.878(7)	Cu1-N1	1.966(8)
Bond	Angles	Bond	Angles
O3-Cu1-O4	87.6(3)	C3-N1-Cu1	124.8(8)
O3-Cu1-N2	161.9(4)	O1-N1-Cu1	90.1(4)
O4-Cu1-N2	90.4(3)	C10-N1-Cu1	128.2(7)
O3-Cu1-N1	90.8(3)	O2-N2-Cu1	118.9(6)
O4-Cu1-N1	157.4(4)	C5-O3-Cu1	130.3(6)
N2-Cu1-N1	97.8(3)	C12-O4-Cu1	130.5(7)

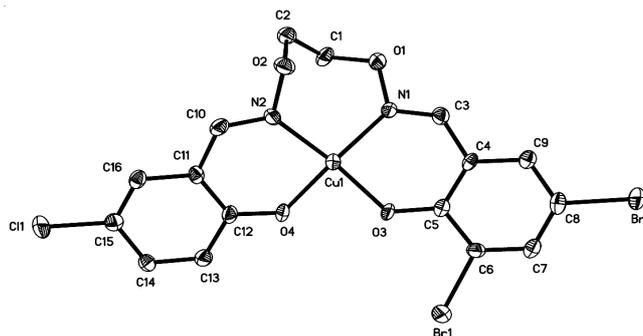


Fig. 1. Molecule structure of the Cu(II) complex with atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at 30 % probability level

of Cu1 atom from the N_2O_2 coordination plane is $0.042(2)$ Å and the four donor (N1, N2, O3 and O4) atoms from their mean plane are $0.299(2)$, $-0.303(4)$, $-0.344(3)$ and $0.348(1)$ Å, respectively. In addition, the ethylenedioxy carbons (C1 and C2) atoms in the Cu(II) complex are buckled asymmetrically from the Cu1N1N2 plane, with the displacement for C1 being $0.1414(4)$ Å toward the plane and for C2 being only $0.483(3)$ Å in the same direction. It is noteworthy that the Cu-N bond lengths, $1.916(9)$ and $1.966(8)$ Å, are considerably longer than the Cu-O bond lengths, $1.859(6)$ and $1.878(7)$, respectively, which is similar to those of previously reported Salamo-type complex¹³.

Intermolecular interactions of the Cu(II) complex: The hydrogen bond data are summarized in Table-3. In the crystal structure, intermolecular $C2-H2B \cdots Br1$ hydrogen bond, is formed between the $-C2H2B$ group from the O-alkyl chain of L^2 unit and bromo (Br1) atom of the benzene ring. The intermolecular $C2-H2B \cdots Br1$ hydrogen bond links two neighboring molecules into an infinite 1D chain supramolecular structure along the b axis, as illustrated in Fig. 2. Furthermore, this linkage is further stabilized *via* intermolecular $C2-H2A \cdots O2$

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
C2-H2A...O2	0.97	2.56	3.453(6)	154	2-x,3-y,-z
C2-H2B...Br1	0.97	2.93	3.774(6)	147	5/2-x,-1/2+y,1/2-z

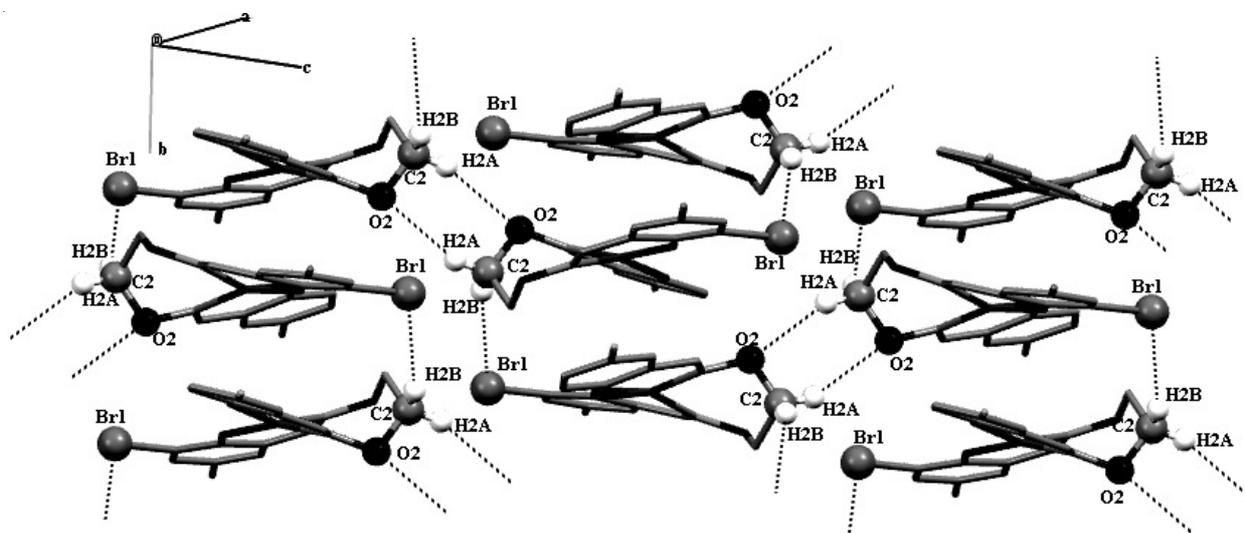


Fig. 3. (Color online). View of the 2D layer motif (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

hydrogen bonds. Thus, every Cu(II) complex molecule links three other molecules into an infinite 2D-layer supramolecular structure on the bc crystallographic plane *via* intermolecular C2-H2B...Br1 and C2-H2A...O2 hydrogen-bonding interactions¹⁴ (Fig. 3).

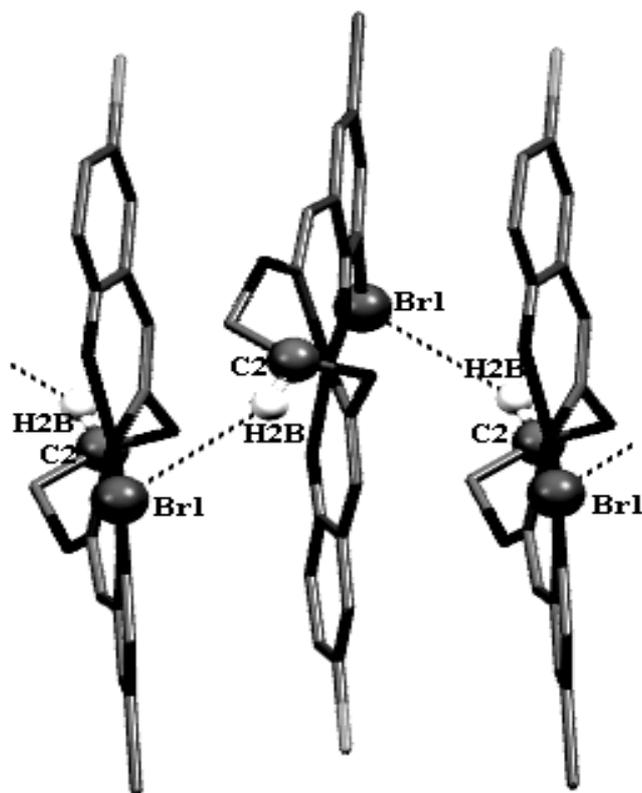


Fig. 2. (Color online). View of the 1D chain motif of the complex units along the b-axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

ACKNOWLEDGEMENTS

This work was supported by the Foundation of Gansu Province Traffic Transportation Dust Control Engineering Technology Research Center (513001-1), the Fundamental Research Funds for the Gansu Province Universities (212086) and the science and technology support funds of Lanzhou Jiaotong University (ZC2012003), which are gratefully acknowledged.

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