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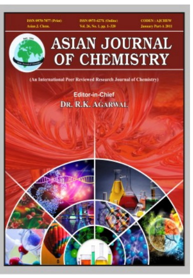

Synthesis and Crystal Structure of Supramolecular Copper(II) Dimer with Asymmetric Salamo-Type Ligand

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A novel Cu(II) dimer, $[CuL]_2$, has been synthesized *via* the complexation of Cu(II) acetate monohydrate with 6-ethoxy-4',6'-dibromo-2,2'-[ethylenedioxy*bis*(nitrilo-methylidyne)] diphenol (H_2L) in methanol/acetone mixed solution and characterized structurally by X-ray diffraction method. X-ray crystallographic analysis reveals that the Cu:L is 2:2 in one dimer molecule and the coordination numbers of copper(II) atoms are four and five, resulting in slightly distorted square-planar and square-pyramidal geometries, respectively. With the help of intermolecular C1-H1A···O9, C19-H19B···O4, C20-H20B···O5 and C25-H25···O6 hydrogen-bonding interactions, a self-assembled 2D-layer supramolecular structure is formed.

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

INTRODUCTION

N,N'-Disalicylideneethylenediamine (H_2Salen) and its analogues are a class of fascinating and versatile chelating ligands, which have been used to form neutral complexes with a number of divalent transition metal ions through the loss of the two hydroxyl protons[1-3]. These complexes are used as catalysts in various organic reactions[4], models of reaction centers of metalloenzymes[5], nonlinear optical materials[6,7] and exhibit interesting magnetic properties[8,9]. In addition, these Salen-type units have also been employed to construct supramolecular structures containing transition metal ions[10]. Three main structural types of complexes with the H_2Salen and its analogues have been reported: (i) mononuclear [M(Salen)]; (ii) binuclear $[M(Salen)]_2$; and (iii) bridged trinuclear $\{[M(Salen)]_2(OAc)_2M\}$. The copper(II)-Salen complexes reported by Bhadbhade *et al.*[11] show structures of $[Cu(Salen)]_2$, $[Cu(5\text{-}MeOSalen)]_2$ and [Cu(5-ClSalen)]. The Cu-salamo complex reported by Akine *et al.*[12] was considered to have a dimeric structure $[Cu(salamo)]_2$ and mononuclear structure [Cu(3-MeOsa-lamo)]. In this paper, we report the synthesis of a Cu(II) dimer with an asymmetric Salamo-type ligand 6-ethoxy-4',6'-dibromo-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol (H_2L). 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 rings[13].

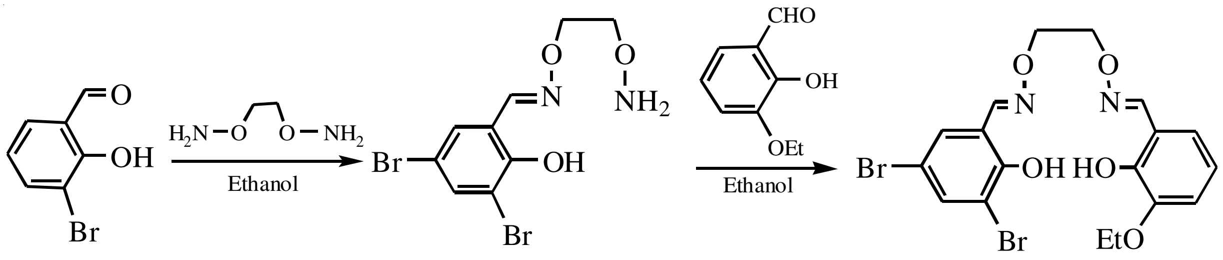
EXPERIMENTAL

3,5-Dibromo-2-hydroxybenzaldehyde (≥ 99 %) and 3-ethoxy-2-hydroxybenzaldehyde (≥ 99 %) were purchased from Alfa Aesar and used without further purification. 1,2-*Bis*(aminooxy) ethane was synthesized according to an analogous method reported earlier[14,15]. The others are the same as literature early[15g].

Synthesis of H_2L: The major reaction steps involved in the synthesis of H_2L are given in **Scheme-I**. H_2L was synthesized according to an analogous method reported earlier[15a]. Yield 86.0 %. m.p. 397-399 K. Anal. Calcd. for $C_{18}H_{18}N_2O_5Br_2$ (%): C, 43.05; H, 3.61; N, 5.58. Found: C, 42.98; H,3.65; N, 5.51.

Synthesis of Cu(II) complex: A solution of $Cu(OAc)_2·H_2O$ (1.99 mg, 0.01 mmol) in methanol (3 mL) was added dropwise to a solution of H_2L (5.03 mg, 0.01 mmol) in acetone (3 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 1 week, the solvent was partially evaporated and obtained dark-green prismatical crystals suitable for X-ray crystallographic analysis. Anal. Calcd. for $C_{36}H_{32}N_4O_{10}Cu_2Br_4$ (%): C, 38.35; H, 2.86; N, 4.97; Cu, 11.27. Found: C, 38.43; H, 2.76; N, 4.95; Cu, 11.19.

X-Ray structure determination: The X-Ray structure determination is the same as literature[15b]. The crystal data and structure refinement for the Cu(II) complex are given in Table-1.



H_2L

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

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENTFOR THE CU(II) COMPLEX

Empirical formula	$C_{36}H_{32}N_4O_{10}Cu_2Br_4$
Formula weight	1127.38
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	P2(1)/n
Cell dimensions, (Å)	a = 16.6945(13), b = 16.5041(12), c =14.1708(11)
Volume (Å^3)	3904.4(5)
Z	4
Density (calculated) (mg/m^3)	1.918
Absorption coefficient (mm^{-1})	5.245
$F_{(000)}$	2216
Crystal size (mm)	0.40 × 0.30 × 0.25
Index ranges	$-19 \leq h \leq 15$, $-19 \leq k \leq 19$, $-16 \leq l \leq 16$
Reflections collected	18601/6442 [R(int) = 0.0967]
Independent reflections	3011
Data/restraints/parameters	6442/1/508
Goodness of fit indicator	1.038
R [I > 2σ(I)]	R_1 = 0.0662, wR_2 = 0.1636
Largest diff. peak and hole (e Å^{-3})	0.965 and -0.986

RESULTS AND DISCUSSION

The crystal structure of the 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) dimer crystallizes in the orthorhombic system, space group $P2_1/n$ with Z = 4. The molecular structure of the Cu(II) dimer consists of two Cu(II) atoms and two deprotonated L^{2-} units. As shown in Fig. 1, both Cu(II) atoms have different coordination numbers. The Cu(II) (Cu1) atom 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 one deprotonated L^{2-} unit, the Salamo-type L^{2-} moiety is not planar, but has a twisted geometry. The dihedral angle between the coordination planes of N1-Cu1-O3 and N2-Cu1-O4 is 14.67(4)°. Consequently the coordination sphere can be described as a square planar geometry distorted tetrahedrally. Furthermore, the deviation of Cu1 atom from the N_2O_2 coordination plane is 0.048(2) Å and the four donor (N1, N2, O3 and O4) atoms from their mean plane are 0.150(2), -0.156(4), -0.178(3) and 0.184(1) Å, respectively. In addition, the ethylenedioxime carbons (C1 and C2) atoms in the Cu(II)

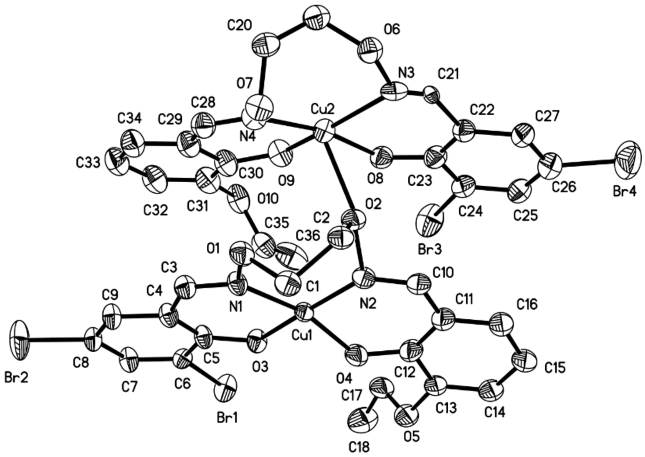


Fig. 1. Molecule structure of the Cu(II) complex with atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30 % probability level

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE Cu(II) COMPLEX

Bond	Lengths	Bond	Lengths	Bond	Lengths
Cu1-O3	1.87(2)	Cu1-N1	2.02(2)	Cu2-N4	1.97(2)
Cu1-N2	1.89(2)	Cu2-O9	1.82(2)	Cu2-N3	2.21(3)
Cu1-O4	1.90(2)	Cu2-O8	1.92(2)	–	–
Bond	**Angles**	**Bond**	**Angles**	**Bond**	**Angles**
O3-Cu1-N2	169.9(1)	O8-Cu2-N4	168.5(1)	C21-N3-Cu2	133(3)
O3-Cu1-O4	83.4(8)	O9-Cu2-N3	165.3(1)	O6-N3-Cu2	109.9(2)
N2-Cu1-O4	89.2(9)	O8-Cu2-N3	85.7(9)	C28-N4-Cu2	127 (2)
O3-Cu1-N1	90.7(7)	N3-Cu2-N4	103.5(1)	O7-N4-Cu2	117.0(2)
O4-Cu1-N1	165.7(1)	C3-N1-Cu1	122.2(2)	C5-O3-Cu1	130.6(1)
N2-Cu1-N1	98.4(9)	O1-N1-Cu1	123.1(1)	C12-O4-Cu1	128.7(2)
O9-Cu2-O8	84.3(9)	C10-N2-Cu1	131.3(2)	C23-O8-Cu2	130.2(2)
O9-Cu2-N4	87.9(9)	O2-N2-Cu1	118.5(2)	C30-O9-Cu2	133.1(2)

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

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠ D-H···A	Symmetry code
C1-H1A···O9	0.97	2.43	3.35(4)	160	1-x,1-y,1/2+z
C19-H19B···O4	0.97	2.43	3.38(3)	169	1-x,1-y,-1/2+z
C20-H20B···O5	0.97	2.35	3.11(4)	136	1-x,1-y,-1/2+z
C25-H25···O6	0.92	2.57	3.48(4)	172	1/2+x,3/2-y,z

complex are buckled asymmetrically from the Cu1N1N2 plane. It is noteworthy that the Cu-N bond lengths, 2.019(19) and 1.89(2) Å, are considerably longer than the Cu-O bond lengths, 1.873(15) and 1.899(18), respectively, which is similar to those of previously reported Salamo-type complex[15].

However, the Cu(II) (Cu2) atom is penta-coordinated by two oxime nitrogen (N3 and N4) atoms and two phenoxo oxygen (O8 and O9) atoms of L^{2-} units defining the N_2O_2 basal plane Cu2-O8, 1.92(2); Cu2-O9, 1.82(2); Cu2-N3, 2.21(3) and Cu2-N4, 1.97(2) Å), plus one oxime oxygen (O2) atom from the other deprotonated L^{2-} unit occupying the axial position (Cu2-O2, 2.511(4) Å). The value of $\tau = 0.053$[16] clearly indicates that the environment of the Cu(II) (Cu2) atom could be best described as a square-pyramidal topology with the metal atom being penta-coordinated. The four coordinated atoms in the basal plane deviate slightly from the mean plane, with O9 and N3 above on average by 0.174(2) and 0.124(2) Å and O8 and N4 below on average by 0.165(2) and 0.133(2) Å, respectively. These deviations indicate a very minor distortion of the basal plane toward a tetrahedron. The Cu2 atom is displaced by 0.021(3) Å from the mean plane. The dihedral angle between the planes O9-Cu2-N4 and O8-Cu2-N3 is 12.95(4)°. Besides, the long distance (Cu1···Cu2 = 4.294(4) Å) between two Cu(II) atoms suggests that there is no interaction between the two Cu(II) centers.

Intermolecular interactions of the Cu(II) complex: The hydrogen bond data are summarized in Table-3. The Cu(II) complex is linked by intermolecular hydrogen bonds. In the crystal structure, the methylene (-C19H19B and -C20H20B) groups of the O-alkyl chain of one of two deprotonated and coordinated L^{2-} units are respectively bound to oxygen (O5 and O4) atoms of the adjacent complex molecule and the phenolic oxygen (O9) atoms of the other adjacent complex molecule to form C1-H1A···O9 hydrogen bonds. Thus, every dimer is further interlinked with two other adjacent dimers into an infinite 1D supramolecular structure along the c axis by intermolecular C1-H1A···O9, C19-H19B···O4 and C20-H20B···O5 hydrogen bonds, as illustrated in Fig. 2. In addition, the adjacent chains along the b axis are held together to form an infinite 2D-layer supramolecular structure by intermolecular C25-H25···O6 hydrogen bonding interactions (Fig. 3).

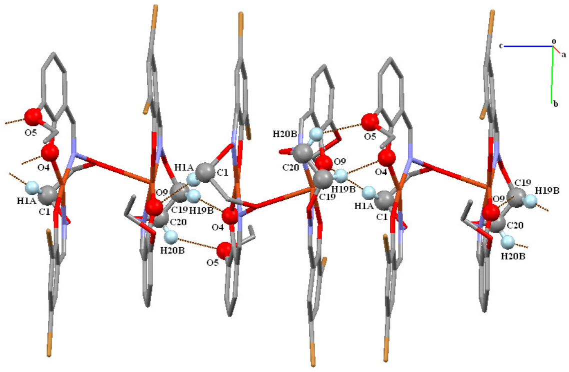


Fig. 2. (colour online). View of the 1D chain motif of the Cu(II) complex units along the *c* axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

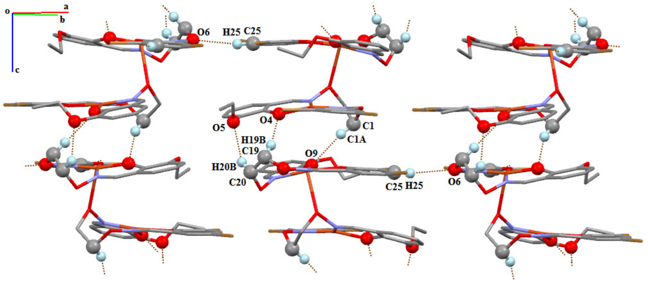


Fig. 3. (colour online). View of the infinite 2D-layer supramolecular of the Cu(II) complex on the *bc* plane (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

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