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# Synthesis, Characterization and Crystal Structure of 2D Copper(II) Complex with 6-Ethoxy-4',6'-dichloro-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol

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A new Cu(II) complex with asymmetric Salamo-type ligand, 6-ethoxy-4',6'-dichloro-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol ($H_2L$) has been synthesized and characterized by elemental analyses, FT-IR, UV-visible spectra and single crystal X-ray crystallography. The X-ray crystal structure of the Cu(II) complex reveals it to be a mononuclear structure, which contains one Cu(II) atom and one deprotonated $L^{2-}$ unit. The center Cu(II) atom is tetra-coordinated, showing that the coordination sphere can be described as a square planar geometry distorted tetrahedrally by 33.07(4)°. In addition, the Cu(II) complex is linked to form an infinite 2D layer supramolecular structure through intermolecular C-H···O and C-H···Cl hydrogen bonds and π···π stacking interactions.

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

## INTRODUCTION

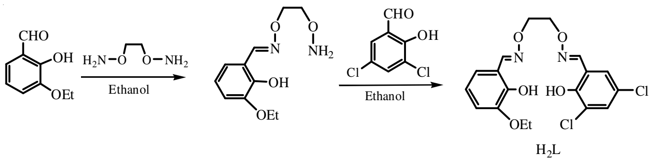
Salen-type ligands and its derivatives are well-known chelating ligands in modern coordination chemistry[1-3]. During the past few decades, transition metal complexes of Salen-type ligands, consisting of two oxygen and two nitrogen donors are of particular interest[4,5]. Factors that have contributed to the widespread and continued interest in Salen-type ligands are the initial recognition that metal complexes containing these types of ligands can reversibly bind oxygen[6], the similarity between Salen-type ligands and heme, hence their use in model complexes[7] and finally, the more recent discovery of Salen-type complexes as efficient chiral catalyst, a field which continues to be at the forefront of research efforts[8,9]. Furthermore, Salen-type Cu(II) complexes have been shown to their relevance as active site structures of metal-proteins and enzymes[10] and partly because of attempts to understand the relationship between the structure and the spectroscopic properties[11]. Moreover, some Salen-type complexes have strong activity with DNA[12] and can be used as elemental building blocks for construction of chain- or cyclic-like coordinated supramolecular structures[13].

Herein, we report the synthesis, characterization and crystal structure of a Cu(II) complex with the new asymmetric Salamo-type ligand 6-ethoxy-4',6'-dichloro-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol ($H_2L$).

## EXPERIMENTAL

2-Hydroxy-3-ethoxybenzaldehyde (≥ 99 %) and 2-hydroxy-3,5-dichlorobenzaldehyde (≥ 99 %) were purchased from Alfa Aesar and used without further purification. The others are the same as literature early[14].

**Synthesis of ligand $H_2L$:** Synthetic route to the asymmetrical Salamo-type ligand $H_2L$ is shown in **Scheme-I**. The ligand $H_2L$ was synthesized with a slightly modified method reported literature[14g]. Yield 75.9 %. m.p. 379-381 K. Anal. Calcd. for $C_{18}H_{18}N_2O_5Cl_2$ (%): C, 52.31; H, 4.39; N, 6.78. Found: C, 52.38; H, 4.47; N, 6.69.



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

**Synthesis of Cu(II) complex:** A solution of $Cu(OAc)_2{\cdot}H_2O$ (2 mg, 0.01 mmol) in methanol (2 mL) was added dropwise to a solution of $H_2L$ (4.20 mg, 0.01 mmol) in acetone (4 mL) at room temperature. The colour of the mixing solution turned to dark green immediately, then stirred for 45 min at room temperature. The mixture was filtered off and the filtrate was allowed to stand at room temperature for about six weeks, the solvent was partially evaporated and obtained brown rhombic single crystals suitable for X-ray crystallographic analysis. Anal. Calcd. for $C_{18}H_{16}N_2O_5Cl_2Cu$ (%): C, 45.54; H, 4.40; N, 5.90; Cu, 13.38. Found: C, 45.47; H, 4.49; N, 5.79; Cu, 13.42.

**X-Ray crystal structure determination:** X-Ray structure determination is the same as literature early[14h]. 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 | $C_{18}H_{16}N_2O_5Cl_2Cu$ |
| Formula weight | 474.77 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Cell dimensions, (Å, deg) | a = 11.3917(14), b = 10.7909(10),<br>c = 15.331(2), β = 94.962(2) |
| Volume (Å$^3$) | 1877.5(4) |
| *Z* | 4 |
| Density (calculated) (mg/m$^3$) | 1.680 |
| Absorption coefficient (mm$^{-1}$) | 1.483 |
| $F_{(000)}$ | 964 |
| Crystal size (mm) | 0.25 × 0.24 × 0.11 |
| Index ranges | $-13 \leq h \leq 8$, $-6 \leq k \leq 12$, $-18 \leq l \leq 16$ |
| Reflections collected | 6434/3310 [R(int) = 0.0594] |
| Independent reflections | 1290 |
| Data/restraints/parameters | 3310/0/254 |
| Goodness of fit indicator | 1.029 |
| R [I > 2σ(I)] | $R_1 = 0.0617$, $wR_2 = 0.1461$ |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.969 and -0.664 |

## RESULTS AND DISCUSSION

**IR spectra of $H_2L$ and its Cu(II) complex:** The FT-IR spectra of $H_2L$ and its corresponding Cu(II) complex exhibit various bands in the 4000-400 cm$^{-1}$ region. The most important FT-IR bands for $H_2L$ and its Cu(II) complex are given in Table-2.

TABLE-2
IR SPECTRAL DATA FOR $H_2L$ AND ITS Cu(II) COMPLEX (cm$^{-1}$)

| Comp. | ν(C=N) | ν(Ar-O) | ν(O-H) | ν (C=C) benzene ring skeleton |
|---|---|---|---|---|
| $H_2L$ | 1611 | 1242 | 3395 | 1570, 1495, 1471 |
| Cu(II) complex | 1604 | 1211 | — | 1541, 1475, 1456 |

The characteristic C=N stretching band of the free ligand $H_2L$ appears at 1611 cm$^{-1}$, while the C=N band of the Cu(II) complex is observed at 1604 cm$^{-1}$. The C=N stretching frequency is shifted by about 7 cm$^{-1}$ upon complexation, indicating a decrease in the C=N bond order due to the coordination of the Cu(II) ion to the oxime nitrogen lone pair[14-16]. The Ar-O stretching band occurs at 1242 cm$^{-1}$ for $H_2L$, whereas that at 1211 cm$^{-1}$ for the Cu(II) complex as reported for similar Salen-type ligands[17]. This shift of Ar-O stretching frequency indicates that the M-O bonds are formed between the Cu(II) ion and the phenolic O atoms of the deprotonated $L^{2-}$ unit[14]. Meanwhile, a O-H stretching band of the free ligand $H_2L$ at 3395 cm$^{-1}$ disappears in the Cu(II) complex, indicating the phenolic hydroxyl of the Cu(II) complex has been completely deprotonated and coordinated to the Cu(II) ion. In the 1570-1456 cm$^{-1}$ region, the observed bands were attributed to aromatic C=C vibrations.

**UV-visible spectra of $H_2L$ and its Cu(II) complex:** The UV-visible spectra of $H_2L$ and its corresponding Cu(II) complex in diluted DMF solution are presented in Table-3. The spectrum of the Cu(II) complex is different from the spectrum of the ligand $H_2L$. The UV-visible spectrum of the free ligand $H_2L$ exhibits two intense absorption peaks at 282 nm and 321 nm. The former absorption peak can be assigned to the $\pi$-$\pi^*$ transition of the benzene rings, while the latter one at 321 nm can be attributed to the intra-ligand $\pi$-$\pi^*$ transition of the C=N bonds[18].

For the Cu(II) complex, the $\pi$-$\pi^*$ transition of the benzene rings of benzaldehyde is slightly shifted in the Cu(II) complex and appears at 277 nm. Meanwhile, the absorption peak disappears at 321 nm due to coordination of the $L^{2-}$ unit in the Cu(II) complex, indicating that the oxime nitrogen atoms are involved in coordination to the Cu(II) atom[19]. In addition, a new moderate absorption peak appears at 376 nm in the Cu(II) complex, which is assigned to the n-$\pi^*$ charge transfer transition from the filled $p_\pi$ orbital of the bridging phenolic oxygen to the vacant *d*-orbital of the Cu(II) ion[20].

TABLE-3
UV-VIS SPECTRA DATA OF $H_2L$ AND ITS Cu(II) COMPLEX

| Comp. | C | First band | Second band |
|---|---|---|---|
| | (×10$^{-5}$ mol L$^{-1}$) | $\lambda_{max}$ (nm) | $\lambda_{max}$ (nm) |
| $H_2L$ | 5.00 | 282 | 321 |
| [Cu(L)] | 5.00 | 277 | 376 |

**Crystal structure of Cu(II) complex:** The structure of the Cu(II) complex was determined by X-ray crystallography, revealing that the formation of a mononuclear structure (Fig. 1). Selected bond lengths and angles are listed in Table-4. X-ray crystallographic analysis reveals that the Cu(II) atom lies in the $N_2O_2$ coordination sphere and crystallizes in the monoclinic system, space group P2(1)/c and the unit cell contains four Cu(II) complex molecules.

Each Cu(II) complex molecule contains one tetra-coordinated center Cu(II) atom and one deprotonated $L^{2-}$ unit. The dihedral angle between the coordination plane of O3-Cu-N1 and that of O4-Cu-$N_2$ is 33.07(4)°, indicating the coordination sphere can be described as a square planar geometry distorted tetrahedrally with N2 and O3 up average by 0.375(4) and 0.405(5) Å and with N1 and O4 below average by 0.368(5) and 0.412(3) Å, respectively. Meanwhile, the Cu(II) atom is displaced by 0.030(3) Å out of the basal plane of the donor (N1, N2, O4 and O3) atoms. The C1 and C2 atoms of the O-alkyl chain are also buckled asymmetrically from the Cu-N1-

TABLE-4
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE Cu(II) COMPLEX

| Bond | Lengths | Bond | Lengths | Bond | Lengths |
|---|---|---|---|---|---|
| Cu1-O3 | 1.900(3) | Cu1-O4 | 1.912(4) | Cu1-N2 | 1.913(4) |
| Cu1-N1 | 2.016(4) | | | | |
| Bond | Angles | Bond | Angles | Bond | Angles |
| O3-Cu1-O4 | 90.9(2) | O4-Cu1-N1 | 155.0(2) | C10-N2-Cu1 | 129.1(4) |
| O3-Cu1-N2 | 158.0(2) | N2-Cu1-N1 | 97.3(2) | O2-N2-Cu1 | 117.5(3) |
| O4-Cu1-N2 | 91.0(2) | C3-N1-Cu1 | 123.8(4) | C5-O3-Cu1 | 127.7(3) |
| O3-Cu1-N1 | 90.1(2) | O1-N1-Cu1 | 126.9(3) | C12-O4-Cu1 | 129.0(3) |

N2 plane, with the displacement for C1 being 1.376(2) Å toward the plane and for C2 being only 0.528(3) Å in the same direction. It is noteworthy that the Cu-N bond lengths, 2.016(4) and 1.913(4) Å, are considerably longer than the Cu-O bond lengths, 1.912(4) and 1.900(3) Å, respectively.

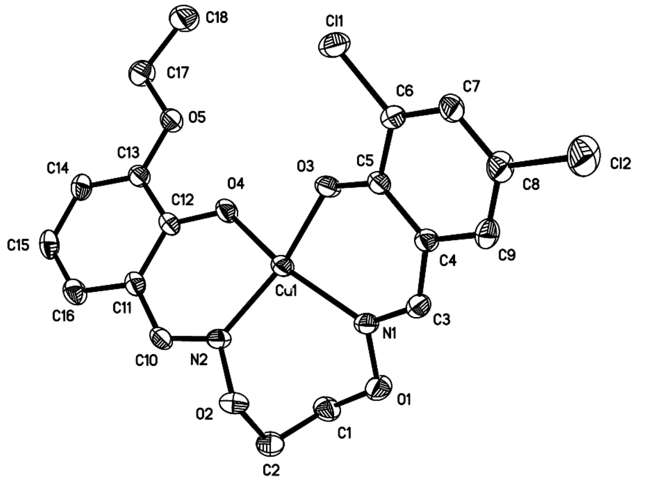


Fig. 1. Molecule structure of the Cu(II) complex with atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30 % probability level

**Intermolecular interactions of Cu(II) complex:** The Cu(II) complex contains four intermolecular hydrogen bonds, π···π stacking interactions of neighboring six-membered rings. Hydrogen bond data are summarized in Table-5.

TABLE-5
DATA FOR INTERMOLECULAR
HYDROGEN-BONDING INTERACTIONS (Å, °)

| D-H···A | d(D-H) | d(H···A) | d(D···A) | ∠D-H···A |
|---|---|---|---|---|
| C1-H1B···O3 | 0.97 | 2.54 | 3.110(7) | 118 |
| C2-H2A···O4 | 0.97 | 2.53 | 3.210(7) | 127 |
| C1-H1A···O5 | 0.97 | 2.70 | 3.388(6) | 129 |
| C1-H1B···Cl1 | 0.97 | 2.91 | 3.543(6) | 124 |

Each Cu(II) complex links two other molecules in the same direction by four pairs of intermolecular C1-H1B···O3, C2-H2A···O4, C1-H1A···O5 and C1-H1B···Cl1 hydrogen-bonding interactions into an infinite 1D two-layer chain along the b axis (Fig. 2). The methylene -C1H1B group of the O-alkyl chain is respectively bound to the phenolic oxygen O3 atom and chloro Cl1 atom, as well as the methylene groups (-C2H2A and -C1H1A) of the O-alkyl chain are respectively bound to the phenolic oxygen O4 atom of the adjacent Cu(II) complex molecule and the ethoxy O5 atom.

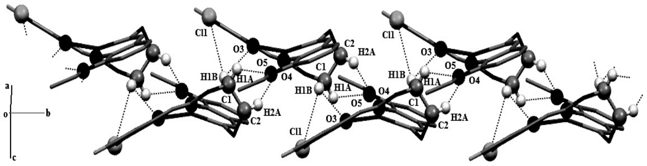


Fig. 2. View of 1D two-layer chain motif of the Cu(II) complex units along the b axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

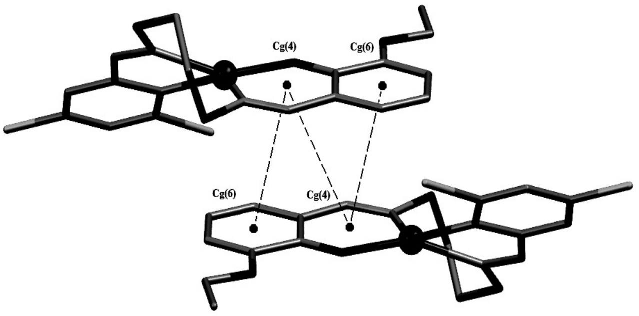


Fig. 3. View of the π···π stacking motif of neighboring six-membered rings of the Cu(II) complex

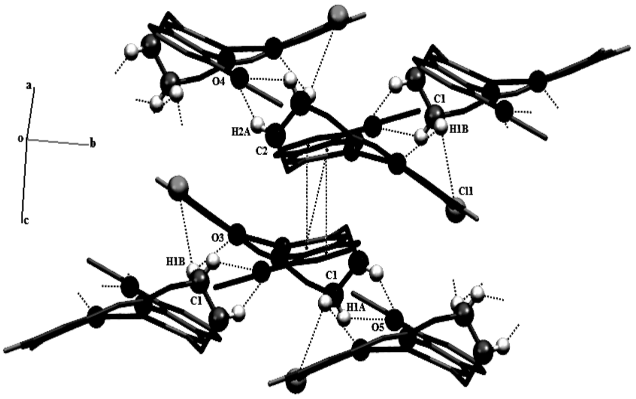


Fig. 4. View of the 2D layer supramolecular motif of the Cu(II) complex units on the bc crystallographic plane (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

Meanwhile, there exists three π···π stacking interactions between the six-membered rings (Cg4) containing Cu(II) atoms and the benzene ring (Cg6) of the L$^{2-}$ unit in the crystal structure, resulting in the Cu(II) complex comes in pairs, as shown in Fig. 3. Thus, every pair of the Cu(II) complexes link four other complex molecules to form an infinite 2D layer supramolecular structure (Fig. 4) through intermolecular C-H···O, C-H···Cl hydrogen bonds and π···π stacking interactions.

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## REFERENCES

1. D. Hall and T.N. Waters, *J. Chem. Soc*., 2644 (1960).
2. J. Reglinski, S. Morris and D.E. Stevenson, *Polyhedron*, **21**, 2167 (2002).
3. A.D. Garnovskii, A.L. Nivorozhkin and V.I. Minkin, *Coord. Chem. Rev*., **126**, 1 (1993).
4. Z.L. You, H.L. Zhu and W.S. Liu, *Z. Anorg. Allg. Chem*., **630**, 1617 (2004).
5. Z.L. You and H.L. Zhu, *Z. Anorg. Allg. Chem*., **630**, 2754 (2004).
6. D. Chen and A.E. Martell, *Inorg. Chem*., **26**, 1026 (1987).
7. K. Oyaizu and E. Tsuchida, *Inorg. Chim. Acta*, **355**, 414 (2003).
8. H.Q. Yang, L. Zhang, L. Zhong, Q. Yang and C. Li, Angew. *Chem. Int. Ed*., **46**, 6861 (2007).
9. S. Jain, X. Zheng, C.W. Jones, M. Weck and R.J. Davis, *Inorg. Chem.*, **46**, 8887 (2007).
10. K.D. Karlin and Z. Tyeklar, Bioinorganic Chemistry of Copper, Chapman & Hall, New York (1993).
11. A. Elmali, C.T. Zeyrek and Y. Elerman, *J. Mol. Struct*., **693**, 225 (2004).
12. E.J. Gao, M.S. Chen, Y. Yu and Y.G. Sun, *Chinese J. Struct. Chem*., **26**, 59 (2007).
13. S.S. Sun, C.L. Stern, S.T. Nguyen and J.T. Hupp, *J. Am. Chem. Soc*., **126**, 6314 (2004).
14. (a) W.K. Dong, Y.X. Sun, C.Y. Zhao, X.Y. Dong and L. Xu, *Polyhedron*, **29**, 2087 (2010); (b) W.K. Dong, Y.X. Sun, G.H. Liu, L. Li, X.Y. Dong and X.H. Gao, *Z. Anorg. Allg. Chem*., **638**, 1370 (2012); (c) W.K. Dong, X.N. He, H.B. Yan, Z.W. Lv, X. Chen, C.Y. Zhao and X.L. Tang, *Polyhedron*, **28**, 1419 (2009); (d) W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta*, **362**, 117 (2009); (e) W.K. Dong, L. Li, C.F. Li, L. Xu and J.G. Duan, *Spectrochim. Acta A,* **71**, 650 (2008); (f) W.K. Dong, J.Y. Shi, L. Xu, J.K. Zhong, J.G. Duan and Y.P. Zhang, *Appl. Organometal. Chem*., **22,** 89 (2008); (g) W.K. Dong, S.J. Xing, Y.X. Sun, L. Zhao, L.Q. Chai and X.H. Gao, *J. Coord. Chem*., **65**, 1212 (2012); (h) W.K. Dong, K.Q. Li, Y. Zhang, L. Xu, L. Wang and X.Y. Dong, *Asian J. Chem*., **25**, 4398 (2013).
15. H.L. Wu, J.K. Yuan, Y. Bai, F. Jia, B. Liu, F. Kou and J. Kong, *Transition Met. Chem.*, **36**, 819 (2011).
16. H.L. Wu, K. Li, T. Sun, F. Kou, F. Jia, J.K. Yuan, B. Liu and B.L. Qi, *Transition Met. Chem*., **36**, 21 (2011).
17. K. Ueno and A.E. Martell, *J. Phys. Chem.*, **60**, 1270 (1956).
18. T. Ghosh, B. Mondal, T. Ghosh, M. Sutradhar, G. Mukherjee and M.G.B. Drew, *Inorg. Chim. Acta,* **360**, 1753 (2007).
19. H.E. Smith, *Chem. Rev*., **83**, 359 (1983).
20. L. Gomes, E. Pereira and B. de Castro, *J. Chem. Soc. Dalton Trans*., 1373 (2000).