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Synthesis, Crystal and Supramolecular Structures of Dinuclear Cu(II) Complex Based on 2,3-Dihydroxybenzaldehyde and 3-Ethoxysalicyladehyde

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A dinuclear copper(II) complex with a asymmetrical Salamo-type chelating ligand 3-ethoxysalicylaldehyde-*O*-(2-hydroxyethyl) oxime (H_2L^2), has been synthesized by the reaction of copper(II) salts with a Salamo-type chelating ligand 6-ethoxy-6'-hydroxy-2,2'-[1,1'-(ethylenedioxy-dinitrilo)dimethylidyne]diphenol (H_3L^1). Obviously in the process of the reaction, there is a cleavage of N-O bond which give the ligand H_2L^2. The formula of Cu(II) complex may be suggested as $[Cu_2(L^2)_2]$.

Keywords: Asymmetrical Salamo-type compound, Cu(II) complex, Synthesis, Structure.

INTRODUCTION

As is well known, transition metal complexes with Salamo-type ligands or their derivatives are excellent compounds in the past few years[1-3]. Due to their unique properties, some of these metal complexes are used in various organic reaction processes as catalysts[4,5], models of reaction centers of metalloenzymes[6,7], nonlinear optical materials[8,9]. and biological models in understanding the structures of biomolecules and biological processes[10]. Some of these complexes possess interesting magnetic properties[11-15]. These Salamo-type ligands have been improved by chemical modifications, which can lead to novel properties and structures. Herein, a new Salamo-type ligand, 6-ethoxy-6'-hydroxy-2,2'-[1,1'-(ethylenedioxy-dinitrilo)-dimethylidyne]diphenol (H_3L^1) and the Cu(II) complex have been synthesized and characterized.

EXPERIMENTAL

2,3-Dihydroxybenzaldehyde (≥ 98.5 %) and 3-ethoxy-salicyladehyde (≥ 99 %) were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. Copper was detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. ^{1}H NMR spectra were recorded on a Mercury-400B spectrometer. X-ray single crystal structure was determined on a Bruker Smart 1000 CCD area detector. 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.

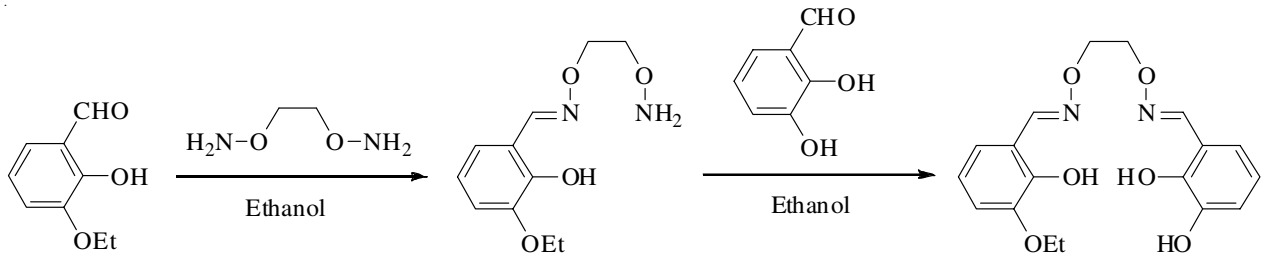
Synthesis of ligand H_3L^1: The reaction steps involved in the synthesis of H_3L^1 are given in **Scheme-I**.

The ligand H_3L^1 was synthesized with a similar method as reported in literature[4]. Yield: 84.7 %. m.p. 131-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.50 (t, *J* = 6.99 Hz, 3H, -CH_3), 4.14 (q, *J* = 6.99 Hz, 2H, -CH_2-), 4.50 (m, 4H, -CH_2-CH_2-), 5.66 (s, 1H, O-H), 6.75 (dd, *J* = 1.42, 7.79 Hz, 1H, Ar-H), 6.85 (m, 3H, Ar-H), 6.94 (dd, *J* = 3.37, 6.18 Hz, 1H, Ar-H), 6.98 (dd, *J* = 1.39, 7.91 Hz, 1H, Ar-H), 8.24 (s, 1H, N=C-H), 8.28 (s, 1H, N=C-H), 9.67 (s, 1H, O-H), 9.94 (s, 1H, O-H).

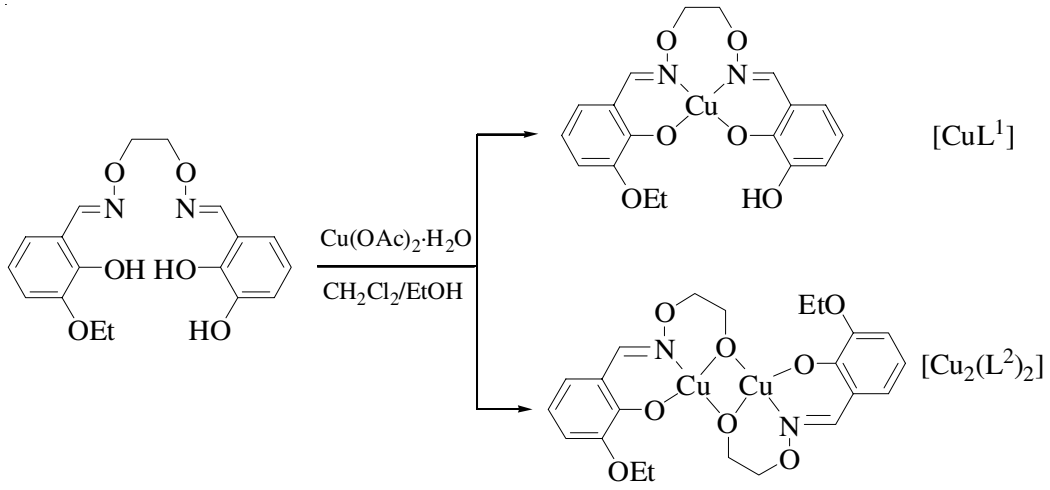
Synthesis of Cu(II) complex: Cleavage of ligand H_3L^1 in the synthesis of Cu(II) complex are given in **Scheme-II**.

A solution of copper(II) aceate monohydrate (2 mg, 0.01 mmol) in ethanol (8 mL) was added dropwise to a solution of H_3L^1 (3.60 mg, 0.01 mmol) in dichloromethane (3 mL) at room temperature. The mixture solution was stirred at 55 °C for 5 h and then filtered off. The filtrate was allowed to stand at room temperature for about two weeks and obtained green prismatical single crystals suitable for X-ray crystallographic analysis. Anal. Calcd. for $C_{22}H_{26}N_2O_8Cu_2$ (%): C, 46.07; H, 4.57; N, 4.88; Cu, 22.16; found: C, 46.01; H, 4.65; N, 4.78; Cu, 22.29.

X-Ray structure determination: The single crystal of the Cu(II) complex, with approximate dimensions of 0.27 mm × 0.25 mm × 0.11 mm was placed on a Bruker Smart 1000 diffractmeter equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK$_\alpha$ radition (λ = 0.71073 Å) at 298(2) K. The structure



Scheme-I: Synthetic route to the asymmetrical Salamo-type ligand H_3L^1



Scheme-II: Complexation of H_3L^1 with $Cu(OAc)_2{\cdot}H_2O$

was solved by using the program SHELXL-97 and fourier difference techniques and refined by the full-matrix least-squares method on F^2. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added theoretically. Details of the data collection and refinements of title compound are listed in Table-1.

RESULTS AND DISCUSSION

A Salamo-type ligand H_3L^1 and its copper(II) complex have been synthesized and their compositions are confirmed by ^1H NMR and elemental analyses.

Crystal structure of Cu(II) complex: The single crystal structure of Cu(II) complex was determined by X-ray crystallography. The molecular structure of Cu(II) complex is shown in Fig. 1. Selected bond distances and angles are listed in Table-2.

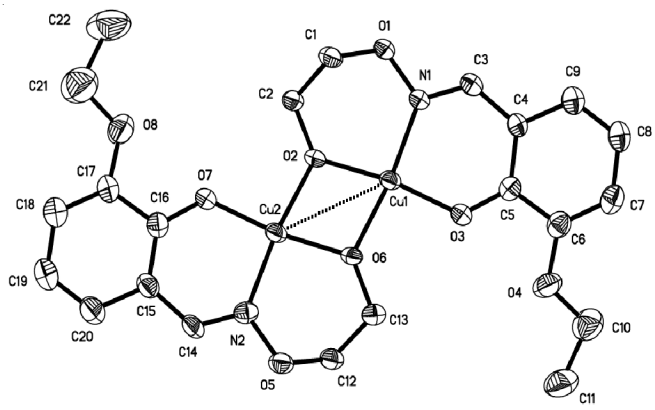


Fig. 1. ORTEP-style drawing of the Cu(II) complex

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

Compound	$[Cu_2(L^2)_2]$
Empirical formula	$C_{22}H_{26}N_2O_8Cu_2$
Formula weight	573.53
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 2(1)/c
a (Å)	a = 16.7483(19)
b (Å)	b = 11.5224(11)
c (Å)	c = 12.7770(13)
β (°)	β = 108.257(2)
Volume (Å^3)	2341.6(4)
Z	4
Calculated density (mg m^{-3})	1.627
Absorption coefficient (mm^{-1})	1.867
θ Range for data collection (°)	2.56 to 25.02
F(000)	1176
Limiting indices	$-19 \le h \le 14$, $-13 \le k \le 13$, $-13 \le l \le 15$
Crystal size (mm)	0.27 × 0.25 × 0.11
Reflections collected	11486/4120 [R_{int} = 0.0849]
Independent reflection	4120
Completeness to 25.01 or 25.02 (%)	99.8
Absorption correction	Semi-empirical from equivalents
Max, min Δρ (e Å^{-3})	0.8210 and 0.6326
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4120/0/309
Goodness-of-fit for F^2	1.041
Final R indices [I > 2σ(I)]	R_1 = 0.0653, wR_2 = 0.1012
R indices (all data)	R_1 = 0.0853, wR_2 = 0.1051
Largest difference peak and hole (e Å^{-3})	1.004 and -0.576

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

Bond	Lengths	Bond	Lengths	Bond	Lengths
Cu1-O3	1.857(6)	Cu1-O6	1.928(5)	Cu2-O6	1.888(6)
Cu1-O2	1.887(6)	Cu1-Cu2	2.9756(15)	Cu2-N2	1.927(7)
Cu1-N1	1.921(6)	Cu2-O7	1.857(6)	Cu2-O2	1.930(5)
Bond	Angles	Bond	Angles	Bond	Angles
O3-Cu1-O2	170.1(2)	O7-Cu2-N2	93.2	C14-N2-Cu2	125.4(7)
O3-Cu1-N1	93.2(3)	O6-Cu2-N2	95.2(3)	O5-N2-Cu2	121.6(6)
O2-Cu1-N1	95.9(3)	O7-Cu2-O2	94.6(2)	C2-O2-Cu1	126.1(5)
O3-Cu1-O6	94.1(2)	O6-Cu2-O2	77.0(2)	C2-O2-Cu2	126.9(5)
O2-Cu1-O6	77.1(2)	N2-Cu2-O2	171.3(3)	Cu1-O2-Cu2	102.4(2)
N1-Cu1-O6	171.8(3)	O7-Cu2-Cu1	132.59(18)	C5-O3-Cu1	129.0(6)
O3-Cu1-Cu2	132.29(18)	O6-Cu2-Cu1	39.26(15)	C13-O6-Cu2	127.6(5)
O2-Cu1-Cu2	39.29(15)	N2-Cu2-Cu1	133.5(2)	C13-O6-Cu1	129.0(5)
N1-Cu1-Cu2	134.1(2)	O2-Cu2-Cu1	38.26(17)	Cu2-O6-Cu1	102.5(2)
O6-Cu1-Cu2	38.28(17)	C3-N1-Cu1	125.8(6)	C16-O7-Cu2	127.5(6)
O7-Cu2-O6	171.5(2)	O1-N1-Cu1	122.2(5)	-	-

The crystal structure of Cu(II) complex is only built up by $C_{22}H_{26}N_2O_8Cu_2$ molecules, in which all bond lengths and angles are in the normal ranges. The molecule crystallizes in monoclinic system, space group *P* 2(1)/c, with four crystallographically independent molecules in the unit cell.

In the crystal structure of Cu(II) complex, there are one intramolecular C2-H2A···O7 hydrogen bond, two intermolecular C3-H3···O6 and C1-H1B···O3 hydrogen bonds. (Fig. 2 and Table-3). There are two intramolecular C-H···π interactions C3-H3···Cg3 and C14-H14···Cg7, two couples of intramolecular π···π interactions Cg3···Cg7 and Cg10···Cg9 (Figs. 3 and 4, Tables 4 and 5).

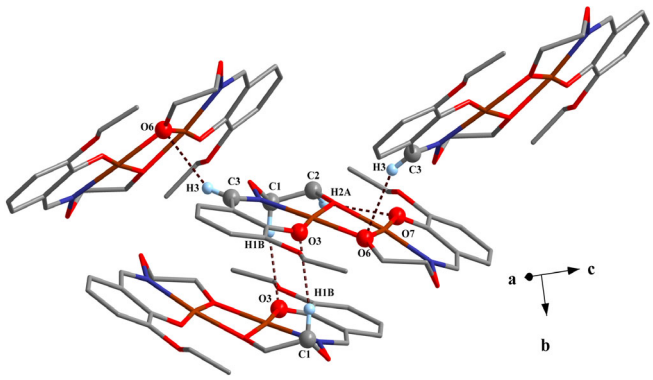


Fig. 2. View of the hydrogen bonding interactions of the copper(II) complex (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

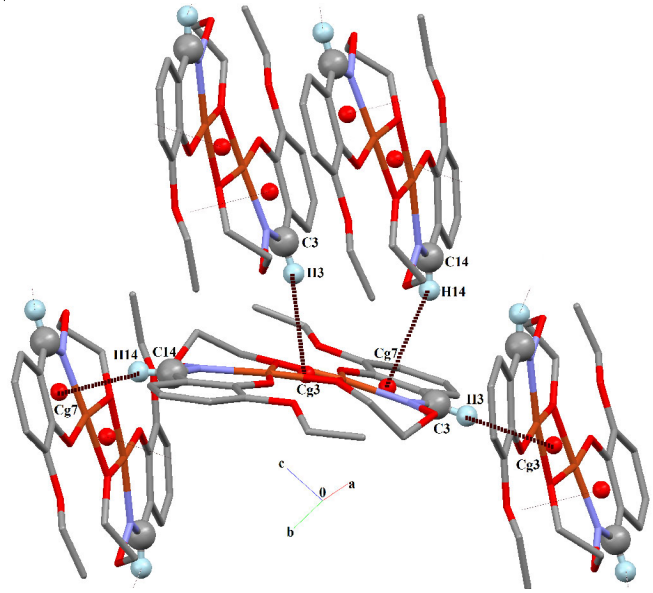


Fig. 3. View of the C-H···π interactions of the copper(II) complex (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

A dimer unit is built through a couple of intermolecular C1-H1B···O3 hydrogen bonds and two couples of intramolecular Cg3···Cg7 and Cg10···Cg9 π···π interactions. And then, one dimer links another adjacent dimer into an infinite one-dimensional supramolecular ribbon structure. (Fig. 5). Furthermore, every dimer further links four other adjacent dimer

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

D-H···A	d(D–H)	d(H···A)	∠DHA	d(D···A)	Symmetry code
C1-H1B···O3	0.97	2.58	167	3.534(10)	1-x, 1-y, 1-z
C2-H2A···O7	0.97	2.52	113	3.040(10)	x, y, z
C3-H3···O6	0.93	2.54	152	3.384(9)	x, 1/2-y, -1/2 + z

TABLE-4
THE DATA FOR C-H··· π INTERACTIONS (Å, º)

D-H···π	d(D-H)	d(H···Cg)	d(D···Cg)	∠D-H···Cg	Symmetry code
C3-H3···Cg3	0.930	2.85	3.738(8)	160	x, 1/2-y, -1/2 + z
C14-H14···Cg7	0.931	2.99	3.798(10)	146	1-x, 1/2 + y, 3/2-z

TABLE-5
THE DATA FOR π ··· π INTERACTIONS (Å, °)

π ··· π	d(Cg···Cg)	α	β	γ	Symmetry code
Cg3···Cg7	3.639(3)	6.9(3)	13.17	10.24	1-x, 1-y, 1-z
Cg7···Cg3	3.641(3)	6.9(3)	10.24	13.17	1-x, 1-y, 1-z
Cg9···Cg10	3.717(5)	13.8(4)	17.75	30.04	1-x, 1-y, 1-z
Cg10···Cg9	3.718(5)	13.8(4)	30.04	17.75	1-x, 1-y, 1-z

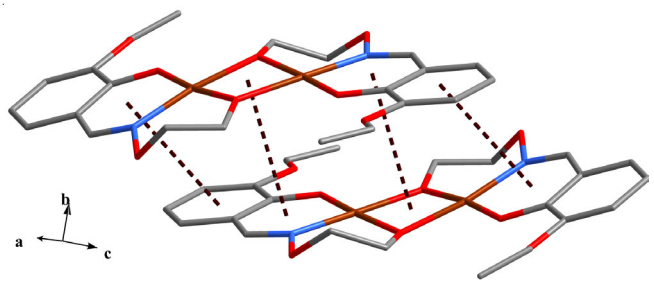


Fig. 4. View of the π···π interactions of the Cu(II) complex (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

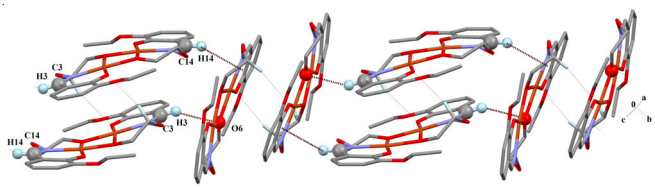


Fig. 5. View of the 1D supramolecular structure within the Cu(II) complex (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

units into an infinite 2D-layer supramolecular structure by four pairs of intermolecular C3-H3···O6 and C14-H14···Cg7 hydrogen bonds (Fig. 6)[16,17].

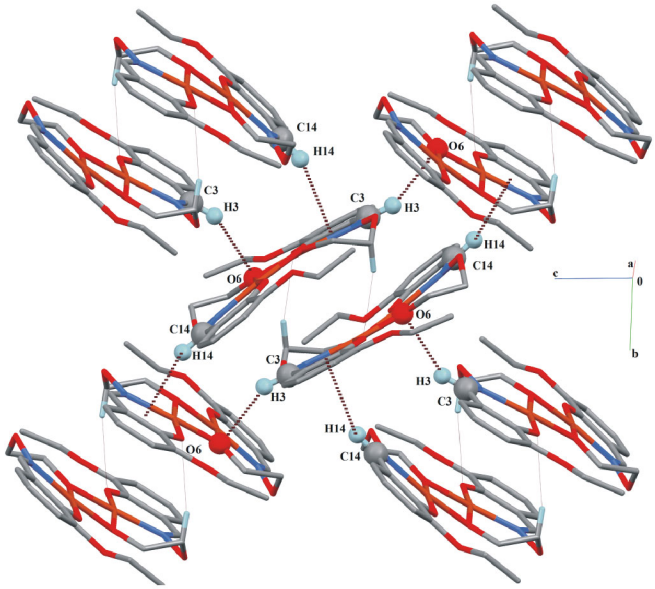


Fig. 6. View of 2D-layer supramolecular structure within the copper(II) complex (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

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REFERENCES

1. T. Katsuki, *Coord. Chem. Rev*., **140**, 189 (1995).
2. A. Bencini, C. Benelli, A. Caneschi, R.L. Carlin, A. Dei and D. Gatteschi, *J. Am. Chem. Soc*., **107**, 8128 (1985).
3. A.D. Garnovskii, A.L. Nivorozhkin and V.I. Minkin, *Coord. Chem. Rev*., **126**, 1 (1993).
4. W.K. Dong, J.G. Duan, Y.H. Guan, J.Y. Shi and C.Y. Zhao, *Inorg. Chim. Acta*, **362**, 1129 (2009).
5. J.-C.G. Bünzli and C. Piguet, *Chem. Rev*., **102**, 1897 (2002).
6. M.F. Summers, L.G. Marzilli, N. Bresciani-Pahor and L. Randaccio, *J. Am. Chem. Soc*., **106**, 4478 (1984).
7. P.G. Lacroix, *Eur. J. Inorg. Chem*., **2001**, 339 (2001).
8. S. Akine, T. Taniguchi and T. Nabeshima, *Chem. Lett*., 682 (2001).
9. S. Akine, T. Taniguchi and T. Nabeshima, *Angew. Chem. Int. Ed*., **41**, 4670 (2002).
10. R.H. Holm, P. Kennepohl and E.I. Solomon, *Chem. Rev*., **96**, 2239 (1996).
11. W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta*, **362**, 117 (2009).
12. X.Q. Song, W.S. Liu, W. Dou, Y.W. Wang, J.R. Zheng and Z.P. Zang, *Eur. J. Inorg. Chem*., **2008**, 1901 (2008).
13. T. Ghosh, B. Mondal, T. Ghosh, M. Sutradhar, G. Mukherjee and M.G.B. Drew, *Inorg. Chim. Acta*, **360**, 1753 (2007).
14. H.E. Smith, *Chem. Rev*., **83**, 359 (1983).
15. K.K. Du and S.X. Liu, *Chinese J. Struct. Chem*., **27**, 49 (2008).
16. W.K. Dong, G. Li, X. Li, C.J. Yang, M.M. Zhao and X.Y. Dong, *Chinese J. Inorg. Chem*., **30**, 1911 (2014).
17. W.K. Dong, W. Du, X.Y. Zhang, G. Li and X.Y. Dong, *Spectrochim. Acta A*, **132**, 588 (2014).