



Synthesis and Supramolecular Structure of {5,5'-Dihydroxy-2,2'-[1,1'-(ethylenedioxydinitrilo)diethylidyne]diphenolato}Cu(II)

LI ZHAO^{*}, QIAN CHENG, YU-JIE ZHANG, XIANG LI and PENG-FEI LIU

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, P.R. China

*Corresponding author: E-mail: zhaoli_72@163.com

(Received: 14 September 2012;

Accepted: 18 February 2013)

AJC-13041

The title complex {5,5'-dihydroxy-2,2'-[1,1'-(ethylenedioxydinitrilo)diethylidyne]diphenolato}Cu(II) with m.f. C₁₈H₂₀N₂O₆:Cu, has been synthesized and characterized structurally. CuI atom is four-coordinated by the four atoms of the donor set (N1, N2, O3 and O5) in the N₂O₂ coordination sphere and CuI approximately lie in a plane. The dihedral angle between the coordination plane of N1-Cu1-O3 and that of N2-Cu1-O5 is 29.1(2)°, indicating that the coordination environment is only slight distortion toward tetrahedral geometry from the square planar structure. Each complex molecule links an adjacent molecule and three crystallizing water molecules into an infinite three-dimensional supramolecular network structure through intermolecular O4-H4...O5, O6-H6...O7, O7-H7C...O3 and O7-H7D...O1 hydrogen-bonding interactions.

Key Words: Bisoxime compound, Cu(II) complex, Synthesis, Supramolecular structure.

INTRODUCTION

N₂O₂ type ligands such as Salen and Salamo, which are easily obtained by the reaction of salicylaldehyde and its derivatives with diamines, coordinate to *d*-block transition metals in a tetradentate fashion to afford stable complexes¹⁻³. Some of the metal complexes are used as a catalyst in various organic reactions⁴, models of reaction centers of metallo-enzymes^{5,6} and nonlinear optical and magnetic materials⁷⁻¹⁰. To tune or improve such functions, a new mononuclear Cu(II) complex [Cu(H₂L)]·H₂O with 5,5'-dihydroxy-2,2'-[1,1'-(ethylenedioxydinitrilo)diethylidyne]diphenol has been synthesized and characterized by the X-ray single crystal diffraction.

EXPERIMENTAL

2,4-Dihydroxyacetophenone was purchased and used without further purification. 1,2-Bis(aminooxy)ethane was synthesized according to an analogous method reported earlier¹¹. 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. 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.

General procedure: 5,5'-Dihydroxy-2,2'-[1,1'-(ethylenedioxydinitrilo)diethylidyne]diphenol (H₄L) was synthesized according to a reported method¹². A solution of 1,2-bis(aminooxy)ethane (99.0 mg, 1.08 mmol) in ethanol (20 mL) was added to a solution of 2,4-dihydroxyacetophenone (308.8 mg, 2.03 mmol) in ethanol (20 mL) and the mixture solution was heated to 328K under stirring for 8 h. After cooling to room temperature, the precipitate was filtered and washed successively with ethanol and ethanol-*n*-hexane (1:4). The product was dried under reduced pressure and purified with recrystallization from ethanol to yield 207 mg of pale-yellow powder-like solid. Yield, 56.7 %, m.p. 490-491 K. Anal. calcd. for C₁₈H₂₀N₂O₆ (%): C, 59.99; H, 5.59; N, 7.77. Found (%): C, 60.72; H, 5.51; N, 7.83.

A solution of Cu(II) acetate monohydrate (2.1 mg, 0.0105 mmol) in *n*-butanol (2 mL) was added dropwise to a solution of H₄L (5.8 mg, 0.0161 mmol) in *n*-butanol (2 mL). The colour of the mixing solution turned brown immediately. The mixture was filtered and the filtrate was allowed to stand at room temperature for about a week, giving several pale-brown prismatic crystals suitable for X-ray diffraction.

X-Ray structure determination: The pale-brown crystal with an approximate dimension of 0.42 × 0.18 × 0.08 mm was placed on a Bruker Smart 1000 diffractometer equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK_α radiation (λ = 0.71073 Å) at 298(2) K. The structure was solved by using

the program SHELXS-97 and Fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97. Details of the data collection and refinements of the present Cu(II) complex are given in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically (CCDC: 900899).

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

Empirical formula	$C_{18}H_{20}N_2O_7Cu$
Formula weight	439.90
Temperature (K)	298(2)
Wavelength (\AA)	0.71073
Crystal system	Triclinic
Space group	P-1
Cell dimensions, (\AA , deg)	$a = 8.1300(7)$, $b = 8.3590(8)$, $c = 13.4530(11)$, $\alpha = 82.878(2)$, $\beta = 80.9460(10)$, $\gamma = 81.979(2)$
Volume (\AA^3)	889.15(14)
Z	2
Density (calculated) (mg/m^3)	1.643
Absorption coefficient (mm^{-1})	1.275
F(000)	454
Index ranges	$-9 \leq h \leq 9$, $-9 \leq k \leq 9$, $-15 \leq l \leq 11$
Reflections collected	4450 / 3027 [R(int) = 0.0655]
Independent reflections	1000
Data/restraints/parameters	3027 / 0 / 255
Goodness of fit indicator	1.041
R [$I > 2\sigma(I)$]	$R_1 = 0.0586$, $wR_2 = 0.0985$
Largest diff. peak and hole ($e \text{\AA}^{-3}$)	0.471 and -0.486

RESULTS AND DISCUSSION

A tetradentate bisoxime chelating ligand, 5,5'-dihydroxy-2,2'-[1,1'-(ethylenedioxydinitrilo)diethylidene]diphenol (H_4L) and its mononuclear Cu(II) complex $[Cu(H_2L)] \cdot H_2O$ have been synthesized. The Cu(II) complex is triclinic crystal and space group P-1 with $a = 8.1300(7) \text{\AA}$, $b = 8.3590(8) \text{\AA}$, $c = 13.4530(11) \text{\AA}$, $\alpha = 82.878(2)^\circ$, $\beta = 80.9460(10)^\circ$, $\gamma = 81.979(2)^\circ$.

X-ray crystallographic analysis revealed the crystal structure of the Cu(II) complex. And the molecule structure is shown in Fig. 1. Selected bond distances and angles are listed in Table-2. The X-crystallography of $[Cu(H_2L)] \cdot H_2O$ indicates that the asymmetric unit consists of a discrete $[Cu(H_2L)]$ section and one crystallizing H_2O . Cu1 atom is four-coordinated by the four atoms of the donor set (N1, N2, O3 and O5) in the N_2O_2 coordination sphere and Cu1 approximately lie in a plane. The dihedral angle between the coordination plane of N1-Cu1-O3 and that of N2-Cu1-O5 is $29.1(2)^\circ$, indicating slight distortion toward tetrahedral geometry from the square planar structure. It is noteworthy that the Cu-N bond lengths, 1.935(9) and 1.982(9) \AA , are considerably longer than the Cu-O bond lengths, 1.852(9) and 1.892(7), respectively. The angles of N1-Cu1-O3 and N2-Cu1-O5 are $89.5(4)$ and $88.2(3)$, respectively. Which is similar to those of previously reported Salamo-type complex^{3,4}.

The introduction of one crystallizing water molecule in the Cu(II) complex successfully leads to the assembly of these monomeric units by intermolecular hydrogen bonds. As illustrated in Fig. 2, the crystallizing water molecule links three

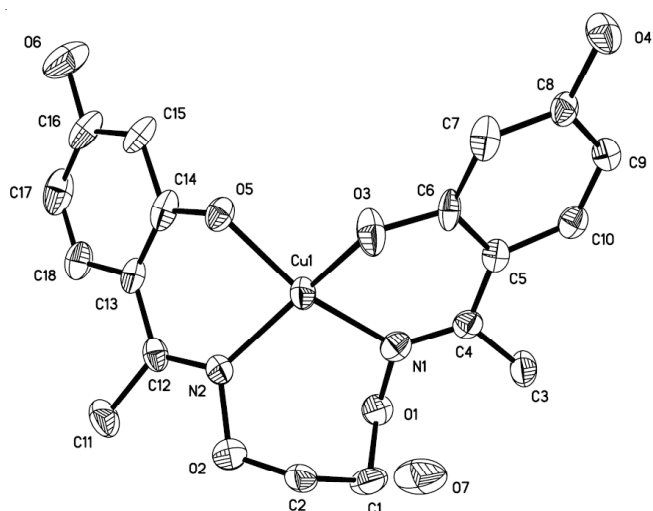


Fig. 1. Molecule structure of the title complex with atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30 % probability level

TABLE-2
SELECTED BOND LENGTHS (\AA) AND
ANGLES ($^\circ$) FOR THE Cu(II) COMPLEX

Bond	Lengths	Bond	Lengths
Cu1-O3	1.852(2)	Cu1-O5	1.892(2)
Cu1-N1	1.935(3)	Cu1-N2	1.982(3)
Bond	Angles	Bond	Angles
O3-Cu1-O5	89.4(2)	O3-Cu1-N1	89.5(2)
O5-Cu1-N1	160.5(2)	O3-Cu1-N2	157.5(2)
O5-Cu1-N2	88.2(2)	N1-Cu1-N2	100.1(2)
C4-N1-Cu1	129.7(2)	O1-N1-Cu1	114.6(2)
C12-N2-Cu1	128.7(2)	O2-N2-Cu1	120.9(2)
C6-O3-Cu1	126.7(2)	C14-O5-Cu1	120.4(2)

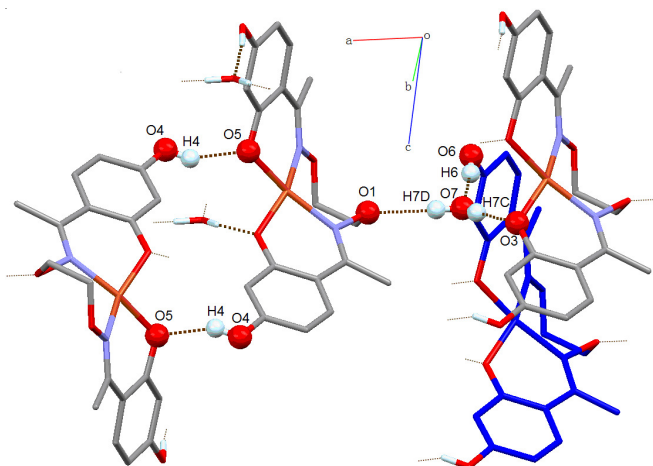


Fig. 2. View of the 3D supramolecular structure within the Cu(II) complex (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

complex molecules through $O6-H6 \cdots O7$, $O7-H7C \cdots O3$ and $O7-H7D \cdots O1$ hydrogen-bonding interactions, respectively (Table-3). The hydroxyl -O7H7C in the crystallizing water molecule bonded to the phenolic oxygen (O3) atom, the -O7H7D hydroxyl bonded to the oxime oxygen (O5) atom and the oxygen (O7) atom is hydrogen-bonded to the phenolic hydroxyl -O6H6 group. Furthermore, a pair of intermolecular

TABLE-3
DATA FOR HYDROGEN-BONDING INTERACTIONS [\AA , $^\circ$]

D-H...A	d(D-H)	d(H...A)	d(D...A)	\angle D-H...A
O4-H4...O5	0.82	1.84	153	2.594(1)
O6-H6...O7	0.82	1.97	169	2.779(2)
O7-H7C...O3	0.85	2.02	172	2.869(2)
O7-H7D...O1	0.85	2.14	173	2.988(2)

hydrogen bonds, O4-H4...O5, between the phenolic hydroxyl (-O4H4) group and the phenolic oxygen (O5) atom of deprotonated H₂L units link the two adjacent molecules together^{13,14}. Thus, each complex molecule links an adjacent molecule and three crystallizing water molecules into an infinite three-dimensional supramolecular network structure through intermolecular O4-H4...O5, O6-H6...O7, O7-H7C...O3 and O7-H7D...O1 hydrogen-bonding interactions¹⁵.

ACKNOWLEDGEMENTS

The authors thank the Young Scholars Science Foundation of Lanzhou Jiaotong University (2011007) for financial support of this work.

REFERENCES

1. T. Katsuki, *Coord. Chem. Rev.*, **140**, 189 (1995).
2. W.K. Dong, Y.X. Sun, S.J. Xing, Y. Wang and X.H. Gao, *Z. Naturforsch.*, **67b**, 197 (2012).
3. W.K. Dong, J.G. Duan, Y.H. Guan, J.Y. Shi and C.Y. Zhao, *Inorg. Chim. Acta*, **362**, 1129 (2009).
4. W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta*, **362**, 117 (2009).
5. T.T. Tsou, M. Loots and J. Halpern, *J. Am. Chem. Soc.*, **104**, 623 (1982).
6. M.F. Summers, L.G. Marzilli, P.N. Bresciani and L. Randaccio, *J. Am. Chem. Soc.*, **106**, 4478 (1984).
7. S. Di Bella and I. Fragala, *Synth. Met.*, **115**, 191 (2000).
8. J.P. Costes, F. Dahan and A. Dupuis, *Inorg. Chem.*, **39**, 165 (2000).
9. W.K. Dong, J.F. Tong, Y.X. Sun, S.S. Gong and L. Li, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **41**, 155 (2011).
10. W.K. Dong and J.G. Duan, *J. Coord. Chem.*, **61**, 781 (2007).
11. W.K. Dong, X.N. He, C.M. Dong, L. Wang, J.K. Zhong, X. Chen and T.Z. Yu, *Z. Kristallogr. New Cryst. Struct.*, **222**, 289 (2007).
12. 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).
13. H.L. Wu, X.C. Huang, J.K. Yuan, F. Kou, F. Jia, B. Liu and Y. Bai, *Z. Naturforsch.*, **66b**, 1049 (2011).
14. W.K. Dong, G. Wang, S.S. Gong, J.F. Tong, Y.X. Sun and X.H. Gao, *Transition Met. Chem.*, **37**, 271 (2012).
15. 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).