Asian Journal of Chemistry; Vol. 27, No. 4 (2015), 1424-1426

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18226

Synthesis and Crystal Structure of Supramolecular Copper(II) Complex Based on N_2O_2 Coordination Sphere

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Received: 31 May 2014; *Accepted*: 1 September 2014; *Published online*: 4 February 2015; AJC-16806

Copper(II) complex has been synthesized *via* the complexation of copper(II) acetate monohydrate with 4,6-dichloro-4',6'-dibromo-2,2'-[ethylenediyldioxy*bis*(nitrilo-methylidyne)]diphenol (H_2L) in acetone/acetonitrile solution and characterized structurally by X-ray diffraction method. X-Ray crystallographic analysis reveals that the Cu(II) atom is four-coodinated by the four atoms of the donor set (N1, N2, O3 and O4) in the asymmetic Salamo-type L^{2-} unit and Cu(II) atom approximately lie in the same plane, resulting in an almost regular distorted square-planar geometry. Each Cu(II) complex molecule links two neighboring molecules into an infinite 1D chain supramolecular structure through intermolecular C1-H1B···O3, C1-H1A···Cl1 and C2-H2A···Br1 hydrogen-bonding interactions.

Keywords: Asymmetric salamo-type ligand, N_2O_2 coordination sphere, Cu(II) complex, Crystal structure.

INTRODUCTION

Salen (2,2'-ethylene*bis*(nitrilomethylidene)diphenol) and salen-type ligands are known to form stable complexes with various *d*-block transition metals[1,2]. Recently, the design and synthesis of symmetric Salen-type complexes have been actively investigated because of not only their unique and attractive structures but also their diverse applications such as optical materials[3], magnetic materials[4], catalysts for organic reactions[5] and multi-metallo receptors[6]. Furthermore, electron-donating and -withdrawing groups are utilized to finely tune the non-linear optical properties of the copper(II) complexes of the Salen-type analogues[7].

Recently, we reported the oxime-type Salen ligand 'Salamo', which is an analogue of Salen; *i.e.*, the imine C=N-C moieties of Salen are replaced by C=N-O oxime bonds[8]. The Salamo ligands exhibited avery high stability that resisted recombination of the C=N-C bonds compared to the parent Salen and are useful for the construction of helical metallo-architectures[3]. In this paper, we report the synthesis and structure of a supramolecular complex [CuL] with an asymmetric Salamo-type ligand 4,6-dichloro-4',6'-dibromo-2,2'-[ethylenediyldioxy*bis*(nitrilo-methylidyne)]diphenol (H_2L).

EXPERIMENTAL

3,5-Dibromo-2-hydroxybenzaldehyde (≥ 99 %) and 3,5-dichloro-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[8].

Synthesis of H_2L: The free ligand H_2L was synthesized according to an analogous method reported earlier[8]. Yield: 82.5 %. m.p. 462-463 K. Anal. Calcd. for $C_{16}H_{12}N_2O_4Br_2Cl_2$ (%): C, 36.47; H, 2.30; N, 5.32. Found: C, 36.20; H, 2.33; N, 5.26.

Synthesis of Cu(II) complex: A solution of $Cu(OAc)_2{\cdot}H_2O$ (1.99 mg, 0.01 mmol) in methanol (2 mL) was added dropwise to a solution of H_2L (5.28 mg, 0.01 mmol) in acetone/acetonitrile (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 three days, the solvent was partially evaporated and obtained green prismatic single crystals suitable for X-ray crystallographic analysis. Anal. calcd. for $C_{16}H_{10}N_2O_4Br_2Cl_2Cu$ (%): C, 32.65; H, 1.71; N, 4.76; Cu, 10.80. Found: C, 32.76; H, 1.89; N, 4.56; Cu, 10.94.

X-Ray structure determination: X-Ray structure determination is same as reported earlier[8]. The crystal data and structure refinement for the Cu(II) complex are given in Table-1.

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. Single-crystal

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

Empirical formula	$C_{16}H_{10}N_2O_4Br_2Cl_2Cu$
Formula weight	588.52
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/n
Cell dimensions, (Å, °)	a = 13. 9453(13), b = 6. 8629(4), c = 19.5316(18), β = 108.362(2)
Volume ($Å^3$)	1774.1(3)
Z	4
Density (calculated) (mg/m^3)	2.203
Absorption coefficient (mm^{-1})	6.064
$F_{(000)}$	1140
Crystal size (mm)	0.26 × 0.08 × 0.04
Index ranges	-14 ≤ h ≤ 16, -8 ≤ k ≤ 5, -20 ≤ l ≤ 22
Reflections collected	6727/3076 [R_{int} = 0.0763]
Independent reflections	904
Data/restraints/parameters	3076/0/282
Goodness of fit indicator	1.026
R [I > 2σ(I)]	R_1 = 0.0373, wR_2 = 0.0916
Largest diff. peak and hole (e $Å^{-3}$)	1.314 and -1.357

X-ray structure reveals that 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 deprotonated L^{2-} unit.

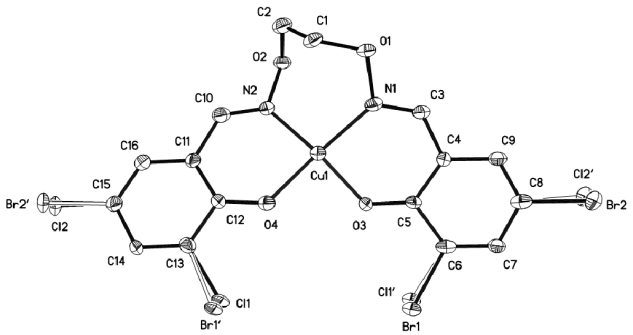

Fig. 1. Molecule structure of Cu(II) complex with atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at 30 % probability level

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 31.50(4)°, which is similar to those of previously reported Salamo-type complex[8]. Consequently the coordination sphere can be described as a slight distortion toward tetrahedral geometry from the square planar structure. Coordination configuration of the Cu(II) complex can been shown in Fig. 2. Moreover, the deviation of Cu1 atom from the N_2O_2 coordination plane is 0.027(2) Å and the four donor (N1, N2, O3 and O4) atoms from their mean plane are 0.340(2), -0.343(4), -0.389(3) and 0.391(1) Å, respectively. The bromo and chloro atoms of the deprotonated L^{2-} unit (Cl1, Cl2, Br1, Br2 and Cl1', Cl2', Br1', Br2') in the Cu(II) complex are disordered unequally over two different positions, which were allowed for during refinement and The bromo and chloro atoms occupancies refined to 0.669(8) (Cl1, Cl2, Br1 and Br2) and 0.331(8) (Cl1', Cl2', Br1' and Br2'). This disordered orientations are similar to those for previously reported Salen-type chelates of [Cu(±-busalcx)][9].

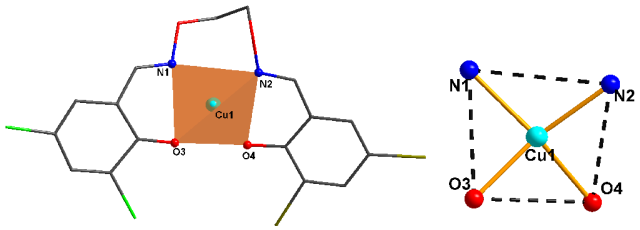

Fig. 2. Coordination configuration of Cu(II) complex

Supramolecular interactions of Cu(II) complex: The hydrogen bond data are summarized in Table-3. In the crystal structure, there are three intermolecular C1-H1B···O3, C1-H1A···Cl1 and C2-H2A···Br1 hydrogen bonds, which are formed between methylene groups from the O-alkyl chain of L^{2-} unit and phenolic oxygen (O3) atom, chloro (Cl1) atom, bromo (Br1) atom of benzene rings. Thus, every Cu(II) complex

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

Bond	Lengths	Bond	Lengths
Cu1-O3	1. 863(12)	Cu1-N2	1. 909(16)
Cu1-O4	1. 915(13)	Cu1-N1	1. 976(15)
Bond	**Angles**	**Bond**	**Angles**
O3-Cu1-O4	88.9(5)	C3-N1-Cu1	125.6(13)
O3-Cu1-N2	158.3(5)	O1-N1-Cu1	124.9(11)
O4-Cu1-N2	89.8(6)	C10-N2-Cu1	129.8(15)
O3-Cu1-N1	90.1(6)	O2-N2-Cu1	118.0(11)
N1-Cu1-N2	99.7(7)	C5-O3-Cu1	130.1(12)
O4-Cu1-N1	156.0(6)	C12-O4-Cu1	129.2(12)

TABLE-3
HYDROGEN-BONDING INTERACTIONS (Å, °)

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠D-H···A	Symmetry code
C1-H1B···O3	0.97	2.58	3.46(4)	151	1/2-x, 1/2 + y, 1/2-z
C1-H1A···Cl1	0.97	2.85	3.45(3)	120	1/2-x, 1/2 + y, 1/2-z
C2-H2A···Br1	0.97	3.01	3.74(3)	137	1/2-x, 1/2 + y, 1/2-z

molecule links two neighboring molecules into an infinite 1D chain-like supramolecular structure along the b axis *via* intermolecular C1-H1B···O3, C1-H1A···Cl1 and C2-H2A···Br1 hydrogen-bonding interactions[10,11] (Fig. 3).

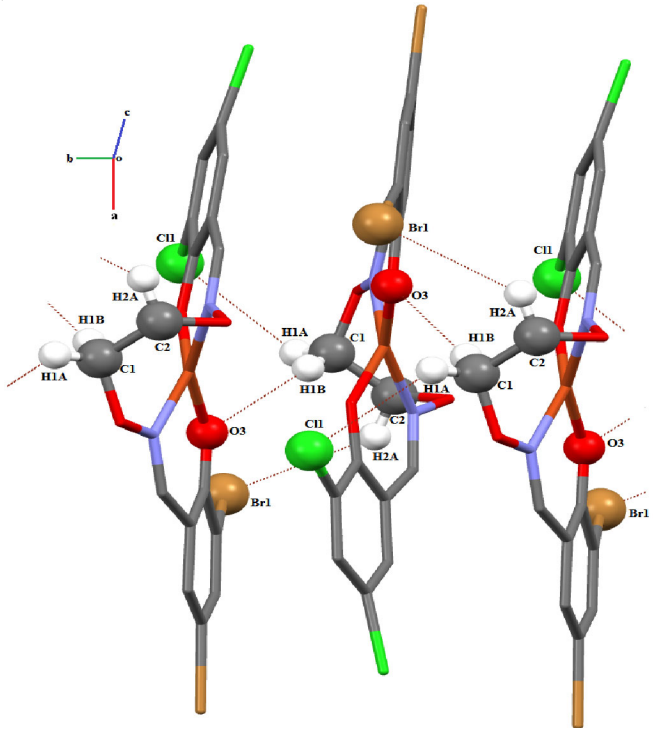

Fig. 3. (Colour online). View of 1D chain motif of Cu(II) complex units along the b-axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

ACKNOWLEDGEMENTS

This work was supported by the Scientific Research Fund of Gansu Provincial Education Department (20873), which is gratefully acknowledged.

REFERENCES

1. (a) A.K. Crane and M.J. MacLachlan, *Eur. J. Inorg. Chem.*, **2012**, 17 (2012); (b) A.D. Garnovskii, I.S. Vasichenko, D.A. Garnovskii and B.I. Kharisov, *J. Coord. Chem.*, **151**, 62 (2009); (c) A.W. Kleij, *Eur. J. Inorg. Chem.*, 193 (2009).
2. (a) E.M. McGarrigle and D.G. Gilheany, *Chem. Rev.*, **105**, 1563 (2005); (b) C. Mukherjee, T. Weyhermüller, E. Bothe and P. Chaudhuri, *Inorg. Chem.*, **47**, 11620 (2008).
3. (a) S. Akine, T. Taniguchi, W. Dong, S. Masubuchi and T. Nabeshima, *J. Org. Chem.*, **70**, 1704 (2005); (b) S. Akine, S. Kagiyama and T. Nabeshima, *Inorg. Chem.*, **46**, 9525 (2007); (c) S. Akine, S. Sunaga, T. Taniguchi, H. Miyazaki and T. Nabeshima, *Inorg. Chem.*, **46**, 2959 (2007); (d) S. Akine, T. Matsumoto, S. Sairenji and T. Nabeshima, *Supramol. Chem.*, **23**, 106 (2011).
4. R. Bagai and G. Christou, *Chem. Soc. Rev.*, **38**, 1011 (2009).
5. M.F. Summers, L.G. Marzilli, N. Bresciani-Pahor and L. Randaccio, *J. Am. Chem. Soc.*, **106**, 4478 (1984).
6. (a) A. Robertson and S. Shinkai, *Coord. Chem. Rev.*, **205**, 157 (2000); (b) P.D. Beer and E.J. Hayes, *Coord. Chem. Rev.*, **240**, 167 (2003).
7. L. Rigamonti, F. Demartin, A. Forni, S. Righetto and A. Pasini, *Inorg. Chem.*, **45**, 10976 (2006).
8. W.K. Dong, S.J. Xing, Y.X. Sun, L. Zhao, L.Q. Chai and X.H. Gao, *J. Coord. Chem.*, **65**, 1212 (2012).
9. S. Bunce, R.J. Cross, L.J. Farrugia, S. Kunchandy, L.L. Meason, K.W. Muir, M. O'Donnell, R.D. Peacock, D. Stirling and S.J. Teat, *Polyhedron*, **17**, 4179 (1998).
10. W.K. Dong, W. Du, X.Y. Zhang, G. Li and X.Y. Dong, *Spectrochim. Acta A*, **132**, 588 (2014).
11. W.K. Dong, G. Li, X. Li, C.J. Yang, M.M. Zhao and X.Y. Dong, *Chinese J. Inorg. Chem.*, **30**, 1911 (2014).