Synthesis and Crystal Structure of Dinuclear Copper(II) Complex with Salamo-Type Ligand

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An unexpected dinuclear Cu(II) complex, $[\text{Cu}_2(\text{L}^2)_2]$ ($\text{H}_2\text{L}^2 = 3\text{-methoxysalicylaldehyde-O-(2-hydroxyethyl)oxime}$) has been synthesized through the complexation of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ with an asymmetrical Salamo-type compound 6-ethyloxy-6'-methoxy-2,2'-[ethylenediylidioxibis(nitrilomethylidyne)]diphenol (H_2L^1). The catalysis of Cu(II) ions results in the unexpected cleavage of one of the N-O bonds in the ligand H_2L^1 , giving a novel dialkoxo-bridged dinuclear Cu(II) complex possessing a Cu-O-Cu-O four-membered ring core instead of the usually desired Salamo-type $\text{Cu-N}_2\text{O}_2$ mononuclear complex. In the crystal structure, two intermolecular hydrogen bonds, $\text{C2-H2B} \cdots \text{O3}$ and $\text{C2-H2B} \cdots \text{O4}$ linked the neighboring molecules into an infinite chain parallel to the a axis.

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

INTRODUCTION

Supramolecular chemistry has developed into one of the most exciting fields of chemistry¹. Coordination MOTIFS have been used constantly to construct all kinds of supramolecular structures². Salamo-type ligand which has a N_2O_2 cavity can easily form stable complexes with transition metals³⁻⁹. Research in the development of Salamo-type complexes for supramolecular applications in photophysical, molecular recognition and self-assembly have received much attention in recent years¹⁰⁻¹⁴. Especially as the host of molecular recognition, Salamo-type complex can identify small nitrogenous molecules and complicated molecular systems, such as sugars and DNA¹⁵. Therefore, this kind of compounds and their complexes are being pursued in present study.

Herein, we report the synthesis and crystal structure of a dinuclear Cu(II) complex $[\text{Cu}_2(\text{L}^2)_2]$ with the new ligand 3-methoxysalicylaldehyde-O-(2-hydroxyethyl)oxime (H_2L^2) which is formed in the course of complexation of an asymmetrical Salamo-type compound 6-ethyloxy-6'-methoxy-2,2'-[ethylenediylidioxibis(nitrilomethylidyne)]diphenol (H_2L^1) and Cu(II) acetate monohydrate. The obtained results show the cleavage of one of the N-O bonds of H_2L^1 in the complexation of the ligand H_2L^1 with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and give an unexpected dialkoxo-bridged dinuclear Cu(II) complex possessing a Cu-O-Cu-O four-membered ring core instead of the usually desired Salamo-type $\text{Cu-N}_2\text{O}_2$ complex.

EXPERIMENTAL

3-Methoxysalicylaldehyde and 3-ethoxysalicylaldehyde ($\geq 99\%$) were purchased from Alfa Aesar 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. 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_2L^1 : The major reaction steps involved in the synthesis of H_2L^1 are given in **Scheme-I**.

H_2L^1 was synthesized according to a similar method reported^{3,4}. Yield 75 %. m.p. 111-112 °C. Anal. calcd. for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_6$ (%): C, 60.95; H, 5.92; N, 7.48. Found: C, 61.22; H, 5.87; N, 7.52.

Synthesis of Cu(II) complex: A solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2.10 mg, 0.01 mmol) in methanol (2 mL) was added dropwise to a solution of H_2L^1 (3.60 mg, 0.01 mmol) in acetone (2 mL) at room temperature. The colour of the mixing solution turned to brown 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 two weeks, the solvent was partially evaporated and obtained brown prismatic single

Scheme-I: Synthetic route to the asymmetrical Salamo-type compound H_2L^1

crystals suitable for X-ray crystallographic analysis. Anal. calcd. for $C_{20}H_{22}N_2O_8Cu_2$ (%): C, 44.04; H, 4.07; N, 5.14; Cu, 23.30. Found: C, 43.89; H, 4.21; N, 5.01; Cu, 23.49.

X-Ray structure determination: The single crystal of the Cu(II) complex, with approximate dimensions of 0.43 mm $\times$ 0.10 mm $\times$ 0.06 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 ($\lambda = 0.71073$ 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. Details of the data collection and refinements of title compound are listed in Table-1.

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

Empirical formula	$C_{20}H_{22}N_2O_8Cu_2$
Formula weight	545.49
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Cell dimensions, (Å, deg)	$a = 5.1336(5)$, $b = 9.7178(8)$, $c = 12.2771(11)$, $\alpha = 106.151(2)$ $\beta = 99.4320(10)$, $\gamma = 103.7120(10)$
Volume (Å ³)	553.93(9)
Z	1
Density (calculated) (mg/m ³)	1.635
Absorption coefficient (mm ⁻¹)	1.968
$F(000)$	383
Index ranges	$-6 \leq h \leq 5$, $-7 \leq k \leq 11$, $-14 \leq l \leq 14$
Reflections collected	2749/1890 [R(int) = 0.0386]
Data/restraints/parameters	1890/0/147
Goodness of fit indicator	1.034
R [I > 2σ(I)]	$R_1 = 0.0637$, $wR_2 = 0.1863$
Largest diff. peak and hole (e Å ⁻³)	1.712 and -0.803

RESULTS AND DISCUSSION

Crystal structure of the Cu(II) complex: The synthesis of the Cu(II) complex $[Cu_2(L^2)_2]$, was conducted by slow evaporation at room temperature as same as the synthesis of the mononuclear complex³. However, it is worth noting that an unexpected dinuclear Cu(II) complex $[Cu_2(L^2)_2]$ was obtained, instead of the desired Salamo-type complex $[Cu(L^1)]$, obtained in the course of the complexation of H_2L^1 and $Cu(OAc)_2 \cdot H_2O$. The results show that because of the catalysis of Cu(II) ions^{16,17}, the complexation resulted in a cleavage of

one of the N-O bonds in H_2L^1 , giving a new O-N-O tridentate ligand H_2L^2 , which coordinates with Cu(II) ions forming a dialkoxo-bridged dinuclear Cu(II) complex^{18,19} with a Cu-O-Cu-O four-membered ring core instead of the expected Salamo-type Cu-N₂O₂ complex (**Scheme-II**).

(a) Complexation of the ligand H_2L^1 with $Cu(OAc)_2 \cdot H_2O$

(b) 3-methoxysalicylaldehyde-O-(2-hydroxyethyl)oxime (H_2L^2)

Scheme-II: Complexation of H_2L^1 with $Cu(OAc)_2 \cdot H_2O$ and chemical structure of H_2L^2

The molecular structure and crystallographic atom numbering of the Cu(II) complex $[Cu_2(L^2)_2]$ are given in Fig. 1. Selected bond lengths and bond angles are listed in Table-2.

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

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

Bond	Lengths	Bond	Lengths	Bond	Lengths
Cu1-O3	1.884(5)	Cu1-O1	1.917(4)	Cu1-O1 ^{#1}	1.923(5)
Cu1-N1	1.931(6)	Cu1-Cu1 ^{#1}	3.009(3)		
Bond	Angles	Bond	Angles	Bond	Angles
O3-Cu1-O1	171.2(2)	O1-Cu1-O1 ^{#1}	77.2(2)	O3-Cu1-N1	93.8(2)
O3-Cu1-O1 ^{#1}	94.2(1)	O1-Cu1-N1	94.9(2)	O3-Cu1-Cu1 ^{#1}	132.7(2)
O1-Cu1-Cu1 ^{#1}	38.7(2)	O1-Cu1-N1 ^{#1}	171.9(2)	O1-Cu1 ^{#1} -Cu1	38.5(2)
N1-Cu1-Cu1 ^{#1}	133.60(2)				

 Symmetry transformations used to generate equivalent atoms: ^{#1} -x, -y, -z

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

Single-crystal X-ray structure revealed that the Cu(II) complex is a neutral homobinuclear entity with crystallographic inversion symmetry. The ORTEP shows that two $[\text{Cu}(\text{L}^2)]$ moieties in the same molecule are bridged together through two alkoxo bridges, each of which obtained from the new ligand H_2L^2 . The whole complex sits on a center of inversion forming the μ -dialkoxo-bridged binuclear structure with both tetra-coordinated Cu(II) centers. Their geometry can be best described as slightly distorted square-planar with CuN_1O_3 coordination (one oxime N1 atom, one phenoxo O3 atom and two bridging alkoxo O1 and O1^{#1} atoms) (Fig. 2). Thus, a planar Cu_2O_2 core is formed by two Cu(II) ions and their bridging two alkoxo oxygen atoms with a $\text{Cu1}\cdots\text{Cu1}^{\#1}$ separation of 3.009(3) Å. The distance of $\text{Cu1}\cdots\text{Cu1}^{\#1}$ is relatively too long to be considered as intramolecular Cu-Cu bonding. The bridging Cu-O bonds are slightly asymmetric, one being short (Cu1-O1) with 1.917(4) Å and one long ($\text{Cu1-O1}^{\#1}$) is 1.923(5) Å. The bond lengths Cu1-O3 and Cu1-N1 are 1.884(5) and 1.931(6) Å, respectively. The four-membered ring $\text{Cu1-O1-Cu1}^{\#1}\text{-O1}^{\#1}$ is exactly planar as required by symmetry. The

angles $\text{Cu1-O1-Cu1}^{\#1}$ and $\text{O1-Cu1-O1}^{\#1}$ are 132.7(2)° and 38.5(2)°, respectively.

Intermolecular interactions of $[\text{Cu}_2(\text{L}^2)_2]$: The Cu(II) complex in the crystal self-assembles through two intermolecular hydrogen bonds. The hydrogen bond data are listed in Table-3. In the crystal structure, two intermolecular hydrogen bonds, $\text{C2-H2B}\cdots\text{O3}$ and $\text{C2-H2B}\cdots\text{O4}$, are formed between the methylene unit (C2-H2A) of the O-alkyl chain and the phenolic O3 and the alkoxy O4 atoms of the $(\text{L}^2)^2$ unit, linking the neighboring molecules into an infinite chain parallel to the a axis, as illustrated in Fig. 3²⁰⁻²².

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

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠ D-H...A
$\text{C2-H2B}\cdots\text{O4}$	0.97	2.62	3.25(3)	123
$\text{C2-H2B}\cdots\text{O3}$	0.97	2.67	3.57(3)	157

REFERENCES

1. J.M. Lehn, *Chem. Eur. J.*, **6**, 2097 (2000).
2. M. Yoshizawa, M. Tamura, M. Fujita, *Science*, **312**, 251 (2006).
3. (a) 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). (b) W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta*, **362**, 117 (2009). (c) W.K. Dong, Y.X. Sun, X.N. He, J.F. Tong and J.C. Wu, *Spectrochim. Acta A*, **76**, 476 (2010). (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, C.Y. Zhao, Y.X. Sun, X.L. Tang and X.N. He, *Inorg. Chem. Commun.*, **12**, 234 (2009). (f) 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). (g) W.K. Dong, S.J. Xing, Y.X. Sun, L. Zhao, L.Q. Chai

 Fig. 2. Coordination configuration of the Cu(II) complex $[\text{Cu}_2(\text{L}^2)_2]$

- and X.H. Gao, *J. Coord. Chem.*, **65**, 1212 (2012). (h) W.K. Dong, Y.X. Sun, S.J. Xing, Y. Wang and X.H. Gao, *Z. Naturforsch.* **67b**, 197 (2012). (i) W.K. Dong, Y.X. Sun, C.Y. Zhao, X.Y. Dong and L. Xu, *Polyhedron*, **29**, 2087 (2010).
4. S. Akine, T. Taniguchi, W.K. Dong, S. Masubuchi and T. Nabeshima, *J. Org. Chem.*, **70**, 1704 (2005).
 5. M.J. Samide and D.G. Peters, *J. Electroanal. Chem.*, **443**, 95 (1998).
 6. J. Losada, I. del Peso and L. Beyer, *Inorg. Chim. Acta.*, **321**, 107 (2001).
 7. M. Inouye, K. Takahashi and H. Nakazumi, *J. Am. Chem. Soc.*, **121**, 341 (1999).
 8. M. Mazik, H. Bandmann and W. Sicking, *Angew. Chem. Int. Ed. Engl.*, **39**, 551 (2000).
 9. D.J. Gravert and J.H. Griffin, *Met. Ions. Biol. Syst.*, **33**, 515 (1996).
 10. S.J. Wezenberg and A.W. Kleij, *Angew. Chem. Int. Ed.*, **47**, 2354 (2008).
 11. S. Akine, S. Kagiya and T. Nabeshima, *Inorg. Chem.*, **46**, 9525 (2007).
 12. M. Kuil, P.E. Goudriaan, A.W. Kleij, D.M. Tooke, A.L. Spek, P.W.N.M. van Leeuwen and J.N.H. Reek, *Dalton Trans.*, **15**, 2311 (2007).
 13. A.W. Kleij, M. Kuil, D.M. Tooke, M. Lutz, A.L. Spek, J.N.H. Reek, *Chem. Eur. J.*, **11**, 4743 (2005).
 14. A.W. Kleij, J.N.H. Reek, *Chem. Eur. J.*, **12**, 4218 (2006).
 15. T.K. Ronson, H. Adams and M.D. Ward, *Inorg. Chim. Acta*, **358**, 1943 (2005).
 16. X.R. Bu, X.Z. You and Q.J. Meng, *Comments Inorg. Chem.*, **9**, 221 (1990).
 17. Q.J. Meng, X.R. Bu and S.H. Sun, *Chinese J. Inorg. Chem.*, **6**, 124 (1990).
 18. J. Madarasz, P. Bombicz, M. Czugler and G. Pokol, *Polyhedron*, **19**, 457 (2000).
 19. A. Karadag, V.T. Yilmaz and C. Thoene, *Polyhedron*, **20**, 635 (2001).
 20. H.L. Wu, F. Jia, F. Kou, B. Liu, J.K. Yuan and Y. Bai, *Transition Met. Chem.*, **36**, 847 (2011).
 21. X.Q. Song, J.R. Zheng, W.S. Liu and Z.H. Ju, *Spectrochim. Acta A*, **69**, 49 (2008).
 22. X.Q. Song, W.S. Liu, W. Dou, Y.W. Wang, J.R. Zheng and Z.P. Zang, *Eur. J. Inorg. Chem.*, 1901 (2008).