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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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### Study on Synthesis and Crystal Structure of an Unexpected Dialkoxo-Bridged Dinuclear Cu(II) Complex

Wen-Kui Dong<sup>a</sup>, Shou-Ting Zhang<sup>a</sup>, Yin-Xia Sun<sup>a</sup>, Yuan Wang<sup>a</sup> & Li Wang<sup>a</sup> <sup>a</sup> School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu, P. R. China Accepted author version posted online: 14 Mar 2012.Published online: 01 May 2012.

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### Study on Synthesis and Crystal Structure of an Unexpected Dialkoxo-Bridged Dinuclear Cu(II) Complex

Wen-Kui Dong, Shou-Ting Zhang, Yin-Xia Sun, Yuan Wang, and Li Wang

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

An unprecedented dinuclear copper(II) complex,  $[Cu_2(L^2)_2]$  $(H_2L^2 = 3$ -Methoxysalicylaldehyde O-(2-hydroxyethyl)oxime), has been synthesized via the complexation of copper(II) acetate monohydrate with unsymmetrical Salen-type ligand  $H_2L^1$  ( $H_2L^1 =$ 3-Methoxy-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol). The crystal structure of the copper(II) complex has been determined by single-crystal X-ray diffraction method. The catalysis of copper(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 copper(II) complex possessing a Cu=O-Cu=O fourmembered ring core instead of the usually desired Salen-type bisoxime Cu=N\_2O\_2 mononuclear complex.

Keywords complexation behavior, copper(II) complex, crystal structure, synthesis, unsymmetrical Salen-type ligand

### INTRODUCTION

Salen-type compounds and their metallosalen complexes have been of considerable present interest due to their ubiquitous use in a variety of catalytic chemical transformations. Examples where Salen complexes offer both high reactivity and selectivity include epoxidation of olefins, asymmetric ring opening of epoxides, olefin aziridination, olefin cyclopropanation, and formation of cyclic and linear polycarbonates.<sup>[1]</sup> And can be used to obtain non-linear optical materials,<sup>[2]</sup> biological systems,<sup>[3]</sup> interesting magnetic properties,<sup>[4]</sup> and building blocks for cyclic supramolecular structures.<sup>[5]</sup> Thus, new materials can be produced by using these compounds, which seem to be suitable candidates for further chemical modifications.<sup>[6]</sup>

Recently, a preferable class of Salen-type bisoxime ligands was reported, using an O-alkyloxime unit [-CH=N-O-(CH<sub>2</sub>)<sub>n</sub>-O-N=CH-] instead of the

 $[-CH=N-(CH_2)_n-N=CH-]$  group, the large electronegativity of oxygen atoms is expected to affect strongly the electronic properties of the N<sub>2</sub>O<sub>2</sub> coordination sphere, which can lead to different and novel properties and structures of the resulting complexes.<sup>[7-10]</sup> The reported copper(II) complexes with symmetrical Salen-type bisoxime ligands show structures of 1:1,<sup>[11-13]</sup> 2:2,<sup>[14]</sup> 3:2,<sup>[12,15]</sup> and 4:2(Cu:L).<sup>[16]</sup> Although the studies of Salen-type bisoxime complexes have made great progress,<sup>[17-19]</sup> it has not been found the cleavage of N–O bonds of unsymmetrical Salen-type bisoxime ligands when the ligands are allowed to react with metal salt, consequently, gained a unexpected complex with the new ligands.

In this article, we report the synthesis and structural characterization of a copper(II) complex with new ligand,  $H_2L^2$  ( $H_2L^2 = 3$ -methoxysalicylaldehyde *O*-(2-hydroxyethyl)oxime), which is formed in course of the complexation of an unsymmetrical Salen-type bisoxime ligand,  $H_2L^1$  {3-Methoxy-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol}, and copper(II) acetate monohydrate. The obtained results show cleavage of one of the N–O bonds in  $H_2L^1$  in the complexation of unsymmetrical Salen-type ligand  $H_2L^1$  with copper(II) acetate monohydrate, and giving an unexpected dialkoxo-bridged dinuclear copper(II) complex possessing a Cu–O–Cu–O four-membered ring core instead of the usually desired Salen-type bisoxime Cu–N<sub>2</sub>O<sub>2</sub> complex.

### EXPERIMENTAL

#### Materials and Instruments

All chemicals were of analytical reagent grade and were used without further purification. C, H, and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. Elemental analysis for Cu was detected by an IRIS ER/S·WP–1 ICP atomic emission spectrometer. IR spectra were recorded on a Bruker VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (500–4000 cm<sup>-1</sup>) and CsI (100–500 cm<sup>-1</sup>) pellets. Electrolytic conductance measurement was made with a DDS–11D type conductivity bridge using a 1.0  $\times 10^{-3}$  mol·L<sup>-1</sup> solution in DMF at room temperature. <sup>1</sup>H NMR spectra were determined by German Bruker AVANCE DRX-400 spectroscopy (Madison, WI, USA). X-ray single-crystal

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Address correspondence to Wen-Kui Dong, School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, 730070, P. R. China. E-mail: dongwk@126.com



SCH. 1. Synthetic route of 3-Methoxy-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol (H<sub>2</sub>L<sup>1</sup>).

structure determination was carried out on a Bruker Smart Apex CCD diffractometer. Melting points were obtained by use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company (P. R. China) and were uncorrected.

### Syntheses of H<sub>2</sub>L<sup>1</sup>

The major reaction steps involved in the synthesis of the unsymmetrical Salen-type chelate ligand  $H_2L^1$  {3-Methoxy-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol} are given in Scheme 1.

1,2-Bis(phthalimidoxy)ethane was prepared according to the literature.<sup>[8,9]</sup> Yield 95.6%. m.p. 250°C.

1,2-Bis(aminooxy)ethane was synthesized according to an analogous method reported previously.<sup>[10,12]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, d, ppm): 3.79 (s, 4H), 5.52 (s, 4H).

Monooxime compound was synthesized according to an analogous method reported previously in the literature.[18-20] To an ethanol solution (4 mL) of 1,2-bis(aminooxy)ethane (97.7 mg, 1.06 mmol) was added dropwise the ethanol solution (6 mL) of 2-hydroxy-3-methoxybenzaldehyde (80.7 mg, 0.53 mmol). The mixture solution was heated at 50–55°C for 2 h, and the solution was concentrated in vacuo and yielding 94.2 mg white needle-like crystals after recrystallization (chloroform/hexane). Yield 78.6%. m.p. 96–97°C, Anal. Calcd. for C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>: C, 53.09; H, 6.24; N, 12.38; Found: C, 52.90; H, 6.26; N, 12.27. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.91 (s, 3H), 3.97 (t, J = 4.4 Hz, 2H), 4.37 (t, J = 4.4 Hz, 2H), 5.52 (brs, 2H), 6.81 (dd, J = 7.7, 1.6 Hz, 1H), 6.86 (t, J = 7.7 Hz, 1H), 6.91 (dd, J = 7.7, 1.6 Hz, 1H), 8.23 (s, 1H), 9.87 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 56.0 (CH<sub>3</sub>), 72.5 (CH<sub>2</sub>), 73.6 (CH<sub>2</sub>), 113.2 (CH), 116.4 (C), 119.3 (CH), 122.1 (CH), 146.9 (C), 148.0 (C), 151.3 (CH=N).

For 3-Methoxy-2,2'-[ethylenedioxybis(nitrilomethylidyne)] diphenol (H<sub>2</sub>L<sup>1</sup>), to an ethanol solution (10 mL) of monooxime compound (113.1 mg, 0.50 mmol), the ethanol solution (10 mL) of 2-hydroxybenzaldehyde (61.0 mg, 0.50 mmol) was added dropwise, and the color of the mixture turned into pale yellow.

The mixture solution was heated at 55–60°C for 5 h, and the solution was concentrated *in vacuo*, yielding 99.1 mg white needle-like crystals after recrystallization (chloroform/hexane). Yield 60%. m.p. 80.5~81.5°C. Anal. Calcd. for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>5</sub> (%): C, 61.81; H, 5.49; N, 8.48;. Found: C, 61.65; H, 5.40; N, 8.63. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.90 (s, 3H), 4.50 (s, 4H), 6.81 (dd, J = 7.6, 1.8 Hz, 1H), 6.87 (t, J = 7.6 Hz, 1H), 6.91 (t, J = 7.9 Hz, 1H), 6.93 (dd, J = 7.6, 1.6 Hz, 1H), 6.99 (d, J = 7.8 Hz, 1H), 7.17 (dd, J = 7.8, 1.6 Hz, 1H), 7.29 (t, J = 7.8 Hz, 1H), 8.24 (s, 1H), 8.26 (s, 1H), 9.76 (s, 1H), 9.78 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  56.4 (CH<sub>3</sub>), 72.7 (CH<sub>2</sub>), 73.0 (CH<sub>2</sub>), 113.4 (CH), 116.2 (C), 116.5 (C), 116.8 (CH), 119.5 (CH), 119.7 (CH), 122.5 (CH), 130.9 (CH), 131.2 (CH), 147.1 (C), 148.0 (C), 151.9 (CH=N), 152.5 (CH=N), 157.7 (C).

### Synthesis of [Cu<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>]

A solution of copper(II) acetate monohydrate (3.49 mg, 0.018 mmol) in ethanol (3 mL) was added dropwise to a solution of  $H_2L^1$  (4.01 mg, 0.012 mmol) in hot ethanol (3 mL). The color of the mixing solution turned to brown immediately, and then stirring was continued for 2 h at room temperature. The mixture was filtered and the filtrate was allowed to stand at room temperature for about three weeks, the solvent was partially evaporated and obtained pale-brown block-like single crystals suitable for X-ray crystallographic analysis. Anal. Calcd. for  $C_{20}H_{22}Cu_2N_2O_8$  [ $Cu_2(L^2)_2$ ] (%): C, 44.04; H, 4.07; N, 5.14; Cu, 23.30. Found: C, 44.01; H, 4.09; N, 5.24; Cu, 23.28.

## Data Collection, Structure Determination, and Refinement

X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer at  $(294 \pm 2)$  K using graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54187$  Å). Unit cell parameters were determined by least-squares analysis. The LP factor and semiempirical absorption corrections were applied to the intensity data. The structure was solved by the direct method (SHELXS-97) and subsequent difference-Fourier map revealed

Empirical formula	$C_{20}H_{22}Cu_{2}N_{2}O_{8} \\$	Absorption correction	Semiempirical from equivalents	
Formula weight	545.48	F (000)	278	
Т / К	294(2)	Crystal size / mm	$0.20 \times 0.16 \times 0.04$	
Wavelength / Å	1.54187	$\theta$ Range for data collection /(°)	2.125 to 35.995	
Crystal system	Triclinic	Index ranges	$-5 \le h \le 4, -11 \le k \le 11, -13 \le l \le 13$	
Space group	$P\overline{1}$	Completeness to $\theta = 33.875 \ (\%)$	96.4	
a / (Å)	5.0370(7)	Reflections collected	7798	
<i>b /</i> (Å)	9.759(1)	Independent reflections	1897 [ $R(int) = 0.0429$ ]	
c / (Å)	10.973(1)	Refinement method	Full-matrix least-squares on $F^2$	
α/(°)	106.222(9)	Data / restraints /parameters	1897/0/146	
β / (°)	98.070(9)	Goodness-of-fit on $F^2$	1.158	
γ / (°)	92.150(8)	Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0525, wR_2 = 0.1509$	
V / Å <sup>3</sup>	511.1(1)	<i>R</i> indices (all data)	$R_1 = 0.0529, wR_2 = 0.1511$	
Ζ	1	$(\Delta \rho)_{\rm max}/({\rm e}\cdot{\rm \AA}^{-3})$	0.456	
$D_c / (\mathrm{Mg} \cdot \mathrm{m}^{-3})$	1.772	$(\Delta \rho)_{\min}/(e\cdot \mathrm{\AA}^{-3})$	-0.437	

TABLE 1Crystal data and structure refinement for complex  $[Cu_2(L^2)_2]$ 

the positions of the remaining atoms, and all hydrogen atoms were added theoretically. All non-hydrogen atoms were refined anisotropically using a full-matrix least-squares procedure on  $F^2$  with SHELXL-97. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. The crystallographic data and structural refinements for the complex are listed in Table 1.

### **RESULTS AND DISCUSSION**

By the condensation of the monooxime compound with 2hydroxybenzaldehyde, it can give rise to a unsymmetrical Salentype ligand, which was easily identified by its IR spectrum, where replacement of the carbonyl by the imine group results in lowering of the energy of the  $v_{(C=O)}$  stretch. The unsymmetrical Salen-type ligand prepared in this way is formed in nearly quantitative yield and is of high purity. The results of the elemental analyses are in accord with the composition suggested for the unsymmetrical Salen-type ligand and the Cu(II) complex.

### **Molar Conductances**

Complex  $[Cu_2(L^2)_2]$  is soluble in DMF and DMSO, slightly soluble in CHCl<sub>3</sub>, but not soluble in EtOH, MeOH, MeCN, THF, acetone, and ethyl acetate. The complex displays good stability in air at room temperature. Meanwhile, the ligand H<sub>2</sub>L<sup>1</sup> is soluble in aforementioned solvents. Molar conductance values of complex  $[Cu_2(L^2)_2]$  at 18°C of 1.0 × 10<sup>-3</sup> mol·L<sup>-1</sup> DMF solutions are 3.8 S·cm<sup>2</sup>·mol<sup>-1</sup>, indicating the complex is nonelectrolyte. This implies that the two Cu(II) ions in complex  $[Cu_2(L^2)_2]$  are firmly held in the coordination sphere in solution.

### **IR Spectra Analyses**

The FT-IR spectra of  $H_2L^1$  and complex  $[Cu_2(L^2)_2]$  exhibit various bands in the 500–4000 cm<sup>-1</sup> region. Some important IR absorption bands are listed in Table 2. The O–H stretching frequency of the Salen-type ligands is expected in the 3300–3800 cm<sup>-1</sup> region, however, this frequency is generally displaced to *ca*. 3431 cm<sup>-1</sup> due to the internal hydrogen bond OH–N=C.<sup>[21]</sup> Thus, each unit of the polymeric ligands behaves as a dibasic tetradentate ONNO donor. As the hydrogen bond becomes stronger, the bandwidth increases, and this band sometimes is not detected. Electron-donating groups on the phenolic ring increase the electron density on the hydroxyl oxygen making the H–O bond stronger, the absorption usually appears as a broad band in the FT-IR spectrum. For the Cu(II) complex, the disappearance of this band is expected due to the substitution of hydrogen for the Cu(II) ion when the complex formed.<sup>[22]</sup>

The free ligand  $H_2L^1$  exhibits characteristic C=N stretching band at 1619 cm<sup>-1</sup>, while the C=N of the Cu(II) complex is

TABLE 2 The most important FT-IR bands for the ligands and complex  $[Cu_2(L^2)_2]$  (cm<sup>-1</sup>)

Compound	V(О-Н)	$v_{(C=N)}$	V <sub>(Ar-O)</sub>	V <sub>(Cu-N)</sub>	V <sub>(Cu-O)</sub>	$\nu_{(C-C)}$ benzene ring skeleton
$\overline{H_2L^1}$	3477	1619	1235	-	-	1537, 1472, 1406
$[\operatorname{Cu}_2(\mathrm{L}^2)_2]$	-	1608	1248	475	433	1575, 1504, 1408

observed in the 1608 cm<sup>-1</sup>. The C=N stretching frequency is shifted to lower frequency by *ca*. 11 cm<sup>-1</sup> upon complexation, indicating a decrease in the C=N bond order due to the coordination bonds of the Cu(II) ion with the oxime nitrogen lone pair.<sup>[23]</sup> In the 1403–1608 cm<sup>-1</sup> region, the observed bands are attributed to aromatic C-C vibrations. Upon coordination these bands shift to lower frequencies for the Cu(II) complexes.<sup>[24]</sup>

The Ar–O stretching frequency appears as a strong band within the 1263–1213 cm<sup>-1</sup> as reported for similar ligands.<sup>[22]</sup> This band occurs at 1235 cm<sup>-1</sup> for the ligand H<sub>2</sub>L<sup>1</sup>, and at 1248 cm<sup>-1</sup> for the Cu(II) complex. The Ar–O stretching frequency is shifted to a higher frequency, indicating that the Cu–O bond is formed between the Cu(II) ion and oxygen atoms of phenolic group.<sup>[23,24]</sup>

The far-infrared spectrum of complex  $[Cu_2(L^2)_2]$  is also obtained in the region of 500–100 cm<sup>-1</sup> in order to identify frequencies due to the Cu–O and Cu–N bonds. The band at 433 cm<sup>-1</sup> in Cu(II) complex is assigned to  $\nu$ (Cu–O), while band at 475 cm<sup>-1</sup> is assigned to  $\nu$ (Cu–N). These bands are observed as new peaks for complex  $[Cu_2(L^2)_2]$  and are not present in the spectrum of the free ligand H<sub>2</sub>L<sup>1</sup>. As pointed out by Percy and Thornton,<sup>[25]</sup> the metal–oxygen and metal–nitrogen frequency assignments are at times very difficult.

### **Description of Crystal Structure**

The synthesis of copper(II) complex was used the same synthetic route for the mononuclear complex according to our previous work.<sup>[12,13]</sup> However, it is remarkable that it did not form the desired unsymmetrical Salen-type bisoxime complex  $[Cu(L^1)]$ , but obtained a unexpected copper(II) complex  $[Cu_2(L^2)_2]$ , which was formed in the course of the complexation of  $H_2L^1$  and copper(II) acetate monohydrate. The results indicate the complexation of the ligand  $H_2L^1$  with copper(II) acetate monohydrate resulted in cleavage of one of the N–O bonds in  $H_2L^1$ ,<sup>[26,27]</sup> giving a new O–N–O tridentate ligand  $H_2L^2$ , which coordinates to Cu(II) ions forming an dialkoxo-bridged dinuclear Cu(II) complex with a Cu–O–Cu–O four-membered ring core instead of the usually desired Salen-type bisoxime Cu–N<sub>2</sub>O<sub>2</sub> complex (Figure 1).<sup>[11–14]</sup>

The crystal structure and atom numbering of complex  $[Cu_2(L^2)_2]$  are shown in Figure 2. Selected bond lengths and bond angles are listed in Table 3.



### (a) Complexation of the ligand $H_2L^1$ with copper(II) acetate.



(b) 3-Methoxysalicylaldehyde O-(2-hydroxyethyl)oxime (H<sub>2</sub>L<sup>2</sup>).

FIG. 1. Complexation of the ligand  $H_2L^1$  with copper(II) acetate and chemical structure of  $H_2L^2$ .



FIG. 2. Molecular structure and atom numbering of complex  $[Cu_2(L^2)_2]$ .

Single-crystal X-ray structure reveals the complex is a centrosymmetric neutral homobinuclear entity. Because of the catalysis of copper(II) ions,<sup>[27]</sup> the complexation of the ligand  $H_2L^1$  with copper(II) acetate monohydrate resulted in the unexpected cleavage of one of the N–O bonds in the ligand  $H_2L^1$ , giving a novel dialkoxo-bridged dinuclear copper(II) complex possessing a Cu–O–Cu–O four-membered ring core instead of the usually desired Salen-type bisoxime Cu–N<sub>2</sub>O<sub>2</sub> complex.

ORTEP illustration of the complex shows that two  $[Cu(L^2)]$  moieties in a same molecule are bridged together via two alkoxo

bridges, each of which comes from the individual new ligand  $H_2L^2$ . The whole complex sits on a crystallographically inverse center forming the  $\mu$ -dialkoxo-bridged binuclear structure with both tetra-coordinated Cu(II) centers. The local coordination environment is exactly identical for both centers, which can be best described as a slightly distorted square plane with CuN<sub>1</sub>O<sub>3</sub> (one oxime nitrogen atom N1, one phenoxo oxygen atom O2, and two bridging alkoxo oxygen atoms O<sub>3</sub> and O<sub>3</sub><sup>-1</sup>), as evidenced from Figure 2. Thus, a planar Cu<sub>2</sub>O<sub>2</sub> core is formed by two divalent copper(II) ions and their bridging two alkoxo



FIG. 3. Crystal structure of complex  $[Cu_2(L^2)_2]$  showing the polymeric array. (Color figure available online).

TABLE 3 Selected bond distances (Å) and bond angles (°) for complex  $[Cu_2(L^2)_2]$ 

Bond	Dist.	Bond	Dist.
Cu(1)-O(1)	1.875(3)	Cu(1)-O(3)	1.906(3)
$Cu(1)-O(3)^{\#1}$	1.922(3)	Cu(1)-N(1)	1.939(3)
$Cu(1)-Cu(1)^{\#1}$	2.9995(1)	O(1)-C(1)	1.320(5)
O(2)-N(1)	1.412(4)	O(2)-C(8)	1.443(5)
O(3)-C(9)	1.405(5)	O(3)-Cu(1) <sup>#1</sup>	1.922(3)
O(4)-C(6)	1.338(6)	O(4)-C(10)	1.422(7)
N(1)-C(7)	1.290(6)	C(1)-C(2)	1.404(6)
C(1)-C(6)	1.424(6)	C(2)-C(3)	1.423(6)
C(2)-C(7)	1.425(6)	C(3)-C(4)	1.347(8)
C(4)-C(5)	1.383(8)	C(5)-C(6)	1.386(7)
C(8)-C(9)	1.502(6)		
Bond	Angle	Bond	Angle
O(1)-Cu(1)-O(3)	170.9(1)	O(1)-Cu(1)-O(3) <sup>#1</sup>	94.3(1)
O(3)-Cu(1)-O(3) <sup>#1</sup>	76.7(1)	O(1)-Cu(1)-N(1)	93.8(1)
O(3)-Cu(1)-N(1)	93.8(1)	$O(3)^{\#1}$ -Cu(1)-N(1)	171.7(1)
$O(1)-Cu(1)-Cu(1)^{\#1}$	132.46(9)	$O(3)-Cu(1)-Cu(1)^{\#1}$	38.59(8)
$O(3)^{\#1}-Cu(1)-Cu(1)^{\#1}$	38.22(8)	$N(1)-Cu(1)-Cu(1)^{\#1}$	133.7(1)
C(1)-O(1)-Cu(1)	127.1(3)	N(1)-O(2)-C(8)	110.3(3)
C(9)-O(3)-Cu(1)	125.9(2)	C(9)-O(3)-Cu(1) <sup>#1</sup>	129.9(3)
Cu(1)-O(3)-Cu(1) <sup>#1</sup>	103.2(1)	C(6)-O(4)-C(10)	117.4(5)
C(7)-N(1)-O(2)	111.9(3)	C(7)-N(1)-Cu(1)	125.5(3)
O(2)-N(1)-Cu(1)	122.3(2)	O(1)-C(1)-C(2)	124.9(4)
O(1)-C(1)-C(6)	118.0(4)	C(2)-C(1)-C(6)	117.1(4)
C(1)-C(2)-C(3)	120.2(4)	C(1)-C(2)-C(7)	122.8(4)
C(3)-C(2)-C(7)	117.0(4)	C(4)-C(3)-C(2)	120.9(5)
C(3)-C(4)-C(5)	120.2(5)	C(4)-C(5)-C(6)	120.7(5)
C(4)-C(6)-C(5)	124.2(4)	O(4)-C(6)-C(1)	114.9(4)
C(5)-C(6)-C(1)	120.8(4)	N(1)-C(7)-C(2)	125.6(4)
O(2)-C(8)-C(9)	112.1(4)	O(3)-C(9)-C(8)	111.4(3)

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

oxygen atoms with a Cu—Cu separation of 2.9995 Å. The distance of Cu1–Cu1<sup>#1</sup> is relatively too long to be considered as intramolecular Cu—Cu bonding.

The bridging Cu–O bonds are slightly asymmetric with one being short, Cu1–O3 = 1.906 Å and one long Cu1–O3<sup>#1</sup> = 1.922 Å. The bond distance of Cu1–O1 and Cu1–N1 are 1.875 Å and 1.939 Å, respectively. The two planes O3–Cu1–O3<sup>#1</sup> and O3–Cu1<sup>#1</sup>–O3<sup>#1</sup> are parallel to each other, indicating Cu1, Cu1<sup>#1</sup>, O2, and O2<sup>#1</sup> are coplanar exactly. The angles of Cu1–O3–Cu1<sup>#1</sup> and O3–Cu1–O3<sup>#1</sup> are 103.3° and 76.7°, respectively. The dihedral angle of two planes O3–Cu1–O3<sup>#1</sup> and O1–Cu1–N1 is 2.86°, and the Cu1 atom deviates by 0.004 Å from the mean plane defined by the atoms O3, O3<sup>#1</sup>, O1, N1.

The polymeric array of complex  $[Cu_2(L^2)_2]$  is given in Figure 3, which is formed by the packing of the complex molecules.

The complex is stabilized by two pairs of C8–H8A···O1 and C8–H8A···O4 hydrogen bonds linking both molecules into a 1D infinite chain parallel to the *a* axis. The –C8H8A groups are hydrogen-bonded to the phenoxo oxygen (O1) atom and the oxygen (O4) atom of the methoxy group of the  $(L^2)^{2-}$  unit, respectively (Table 4).

TABLE 4Hydrogen-bonding (Å,  $^{\circ}$ ) of complex [Cu<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>]

D—H…A	d(D-H)	d(H···A)	DHA	d(D····A)
C8—H8A…O1	0.970	2.576	156.45	3.486
C8—H8A…O4	0.970	2.617	156.30	3.200

### **CONCLUSION**

In a summary, an unprecedented dinuclear copper(II) complex,  $[Cu_2(L^2)_2]$ , bearing a 2:2 ligand:metal stoichiometry, have been synthesized from ligand  $H_2L^1$  by the reaction with  $Cu(OAc)_2 \cdot H_2O$  in moderate yields. It is interesting that each copper(II) ion in the complex is tetra-coordinated by two monooxime  $(L^2)^{2-}$  units. The catalysis of copper(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 copper(II) complex possessing a Cu-O-Cu-O four-membered ring core instead of the usually desired Salen-type bisoxime Cu $-N_2O_2$  complex.

### SUPPLEMENTARY MATERIALS

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, No. CCDC 832646 for the complex. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Telephone: (44) 01223 762910; Fax: +44–1223-336033; E-mail: deposit@ccdc.cam.ac.uk). These data can be also obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.htm

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