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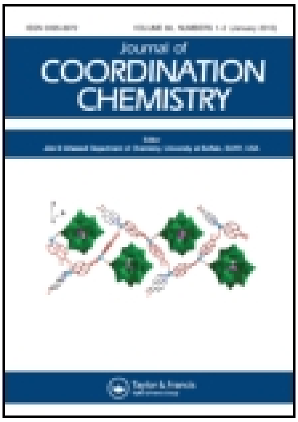

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, crystal structure, and fluorescence of an unexpected dialkoxo-bridged dinuclear copper(II) complex with bis(salen)-type tetraoxime

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Published online: 05 Apr 2012.

To cite this article: Lan-Qin Chai , Gang Wang , Yin-Xia Sun , Wen-Kui Dong , Li Zhao & Xiong-Hou Gao (2012) Synthesis, crystal structure, and fluorescence of an unexpected dialkoxo-bridged dinuclear copper(II) complex with bis(salen)-type tetraoxime, Journal of Coordination Chemistry, 65:9, 1621-1631, DOI: 10.1080/00958972.2012.677836

To link to this article: http://dx.doi.org/10.1080/00958972.2012.677836

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Journal of Coordination Chemistry
Vol. 65, No. 9, 10 May 2012, 1621–1631

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Synthesis, crystal structure, and fluorescence of an unexpected dialkoxo-bridged dinuclear copper(II) complex with bis(salen)-type tetraoxime

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(*Received 27 December 2011; in final form 28 February 2012*)

An unexpected dinuclear Cu(II) complex, $[Cu_2(L^2)_2]$ (H_2L^2 = 3-methoxysalicylaldehyde O-(2-hydroxyethyl)oxime), has been synthesized *via* complexation of Cu(II) acetate monohydrate with H_4L^1. Catalysis by Cu(II) results in unexpected cleavage of two N–O bonds in H_4L^1, giving a dialkoxo-bridged dinuclear Cu(II) complex possessing a Cu–O–Cu–O four-membered ring core instead of the usual bis(salen)-type tetraoxime Cu_3–N_4O_4 complex. Every complex links six other molecules into an infinite-layered supramolecular structure *via* 12 intermolecular C–H ⋯ O hydrogen bonds. Furthermore, Cu(II) complex exhibits purple emission with maximum emission wavelength $\lambda_{max} = 417$ nm when excited with 312 nm.

Keywords: Bis(salen)-type tetraoxime ligand; Cu(II) complex; Synthesis; Crystal structure; Fluorescence behavior

1. Introduction

Macrocyclic ligands play an important role in selective strong binding with metal ions in coordination chemistry. The difference between acyclic and cyclic ligands during coordination mainly arises from preorganization of the coordinating atoms for the metal ions (macrocyclic effect) [1]. Complexes of transition and non-transition metals with Schiff bases have been investigated because the complexes have many applications [2–6]. Salen-type N_2O_2 ligands coordinate tetradentate to various transition-metal ions to produce stable complexes [7–9]. Some of these complexes serve as catalysts of organic reactions [10], models of the catalytic centers of metalloenzymes [11], nonlinear optical materials [12], and metallomesogens [13]. Salen complexes are also used as a building block of supramolecular structures [14] or sensing of chiral organic molecules [15]. A molecule containing two or more salen moieties may have cooperation of several

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.677836

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metal centers. Studies of Cu(II) complexes with salen-type ligands have made great progress [16–20], but cleavage of two N–O bonds of bis(salen)-type tetroximes has not been observed when the ligands react with metal salts.

In this article, we report the synthesis, structural characterization, and fluorescence of a dinuclear Cu(II) complex with H_2L^2 which is formed in the course of complexation of H_4L^1 at Cu(II) acetate monohydrate, $[Cu_2(L^2)_2]$. The product is an unexpected dialkoxo-bridged dinuclear Cu(II) complex possessing a Cu–O–Cu–O four-membered ring core instead of the bis(salen)-type tetraoxime $Cu_3–N_4O_4$ complex. Fluorescence of the Cu(II) complex in DMF is also discussed.

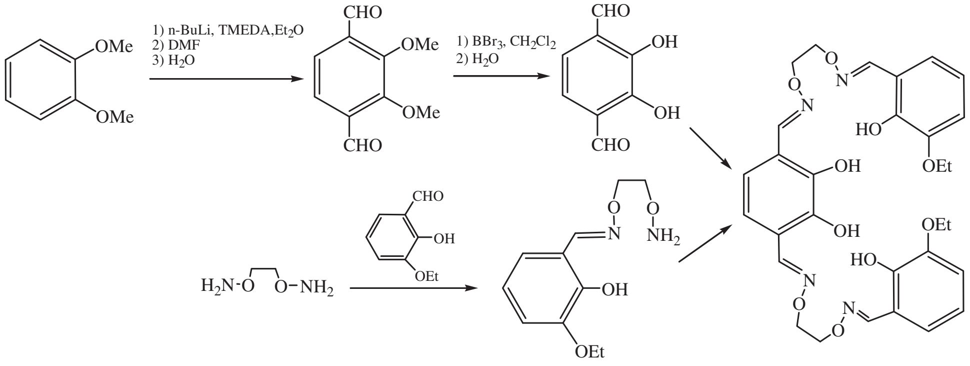
2. Experimental

2.1. *Materials and physical measurements*

All chemicals were of analytical reagent grade and used without purification. C, H, and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. Elemental analysis for Cu was determined by an IRIS ER/S · WP–1 ICP atomic emission spectrometer. UV-Vis absorption and fluorescence spectra were recorded on a Shimadzu UV-2550 spectrometer and Perkin-Elmer LS-55 spectrometer, respectively. Electrolytic conductance measurement was made with a DDS–11D type conductivity bridge using a $1.0 \times 10^{-3}\,mol\,L^{-1}$ solution in DMF at room temperature. ^1H NMR spectra were determined on a German Bruker AVANCE DRX-400 spectrometer. Single-crystal X-ray 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 by Beijing Taike Instrument Limited Company and are uncorrected.

2.2. *Preparation of H_4L and its complex*

2.2.1. Preparation of bis(salen)-type tetraoxime ligand (H_4L^1). The synthetic route of bis(salen)-type tetraoxime (H_4L^1) is shown in scheme 1.



Scheme 1. Synthetic route of tetraoxime H_4L^1.

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2,3-Dimethoxybenzene-1,4-dicarbaldehyde was synthesized from 1,2-dimethoxybenzene (0.166 g, 1 mmol), *N*,*N*,*N*′,*N*′-tetramethylenediamine (0.67 mL, 5 mmol) and *n*-butyllithium (2.66 mol L^{-1} hexane solution, 1.88 mL, 5 mmol) in 32.2% yield as pale yellow crystals [16]; m.p. 100–101°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.06 (s, 6H), 7.65 (s, 2H), 10.46 (s, 2H). Anal. Calcd for $C_{10}H_{10}O_4$ (Mw 194.18) (%): C, 61.85; H, 5.19. Found (%): C, 61.96; H, 5.05.

2,3-Dihydroxybenzene-1,4-dicarbaldehyde was synthesized from 2,3-dimethoxybenzene-1,4-dicarbaldehyde (0.398 g, 2 mmol) and boron tribromide (0.78 mL, 8.2 mmol) in 90% yield as yellow crystals after recrystallization (chloroform/hexane) [21]; m.p. 140.5–142.5°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 2H), 10.00 (s, 2H), 10.88 (s, 2H). Anal. Calcd for $C_8H_6O_4$ (Mw 166.13) (%): C, 57.84; H, 3.64. Found (%): C, 57.58; H, 3.76.

1,2-Bis(aminooxy)ethane was synthesized according to a method reported earlier [22, 23]. Yield, 75.2%. Anal. Calcd for $C_2H_8N_2O_2$ (Mw 92.1) (%): C, 26.08; H, 8.76; N, 30.42. Found (%): C, 25.98; H, 8.90; N, 30.38. ^{1}H NMR (400 MHz, $CDCl_3$): 3.79 (s, 4H), 5.52 (s, 4H).

Monooxime compound was synthesized from 2-hydroxy-3-ethoxybenzaldehyde (0.166 g, 1.0 mmol) and 1,2-bis(aminooxy)ethane (0.0921 g, 1.0 mmol) in 52.3% yield. The sample was purified by column chromatography (SiO_2, chloroform/ethyl acetate, 50 : 1) to give colorless crystals [24]; m.p. 168–169°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 3.98 (t, $J = 4.4$ Hz, 2H), 4.13 (t, $J = 4.4$ Hz, 2H), 4.36 (t, $J = 4.4$ Hz, 2H), 5.51 (brs, 2H), 6.82 (dd, $J = 7.7$, 1.6 Hz, 1H), 6.87 (t, $J = 7.7$ Hz, 1H), 6.92 (dd, $J = 7.7$, 1.6 Hz, 1H), 8.24 (s, 1H), 9.88 (s, 1H). Anal. Calcd for $C_{11}H_{16}N_2O_4$ (Mw 240.26) (%): C, 54.99; H, 6.71; N, 11.66. Found (%): C, 55.30; H, 6.56; N, 12.47.

H_4L^1 was synthesized from an ethanol solution (75 mL) of 2,3-dihydroxybenzene1, 4-dicarbaldehyde (0.0632 g, 2.21 mmol) and monooxime (0.25 g, 4.64 mmol) at 60°C, and the solution was stirred for 6 h at the same temperature. After the solution was allowed to stand overnight at room temperature, precipitates were collected on a suction filter to afford H_4L^1 (0.21 g, 83%) as yellow crystals; m.p. 128–129°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 6H), 4.46–4.53 (m, 8H), 4.63 (dt, $J = 5.4$, 1.5 Hz, 4H), 6.77 (s, 2H), 6.78–6.86 (m, 4H), 6.93 (dd, $J = 7.2$, 2.2 Hz, 2H), 8.25 (s, 2H), 8.28 (s, 2H), 9.60 (s, 2H), 9.69 (s, 2H). Anal. Calcd for $C_{30}H_{34}N_4O_{10}$ (Mw 610.61) (%): C, 59.01; H, 5.61; N, 9.18. Found (%): C, 59.15; H, 5.57; N, 8.96.

2.2.2. Preparation of $[Cu_2(L^2)_2]$. A solution of Cu(II) acetate monohydrate (0.00323 g, 0.016 mmol) in ethanol (3 mL) was added dropwise to a solution of H_4L^1 (0.00303 g, 0.005 mmol) in acetone (1 mL). The mixture turned brown immediately. Stirring was continued for 2 h at room temperature. The mixture was filtered and the filtrate was allowed to stand at room temperature for 3 weeks. The solvent was partially evaporated and yellowish-brown needle-like single crystals (yield: 36%) suitable for X-ray crystallographic analysis were obtained. Anal. Calcd for $C_{22}H_{26}Cu_2N_2O_8$ $[Cu_2(L^2)_2]$ (Mw 573.53) (%): 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.

2.3. *X-ray structure determination of $[Cu_2(L^2)_2]$*

The single crystal of $[Cu_2(L^2)_2]$ with approximate dimensions of 0.30 × 0.11 × 0.03 mm^3 was selected on a Bruker Smart Apex CCD area detector. The reflections were collected

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Table 1. Crystallographic data and data collection parameters for $[Cu_2(L^2)_2]$.

Empirical formula	$C_{22}H_{26}Cu_2N_2O_8$
Formula weight	573.53
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	12.571(1)
b	17.963(2)
c	5.1349(5)
β	95.595(1)
Volume (Å^3), Z	1154.0(2), 2
Calculated density (Mg m^{-3})	1.651
Absorption coefficient (mm^{-1})	1.894
$F(000)$	588
Crystal size (mm^3)	0.30 × 0.11 × 0.03
θ range for data collection (°)	2.79–25.02
Index ranges	$-14 \le h \le 14$; $-15 \le k \le 21$; $-6 \le l \le 6$
Reflections collected	5984
Independent reflection	2029 [R(int) = 0.0924]
Completeness to $\theta = 25.02$ (%)	99.6
Data/restraints/parameters	2029/0/155
Goodness-of-fit on F^2	1.029
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0513$, $wR_2 = 0.0860$
R indices (all data)	$R_1 = 0.0910$, $wR_2 = 0.0939$
Largest difference peak and hole (e Å^{-3})	0.604 and −0.404

using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. Data reduction and cell refinement were performed using SAINT [25]. The structure was solved by the direct method (SHELXS-97) and subsequent difference-Fourier map revealed 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 [26, 27]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. Crystallographic data and structural refinements for the Cu(II) complex are listed in table 1.

3. Results and discussion

3.1. *Crystal structure of* $[Cu_2(L^2)_2]$

The desired bis(salen)-type tetraoxime complex $[Cu_3(L^1)]$ was not formed, but an unexpected complex $[Cu_2(L^2)_2]$ was obtained which was formed in the course of complexation of H_4L^1 by Cu(II) acetate monohydrate. Because of the catalysis of copper(II) [28], complexation resulted in cleavage of two N–O bonds in H_4L^1, giving a new O–N–O tridentate ligand H_2L^2, which coordinates to Cu(II) forming a dialkoxo-bridged dinuclear Cu(II) complex with a Cu–O–Cu–O four-membered ring core instead of the desired bis(salen)-type tetraoxime Cu_3–N_4O_4 complex [29, 30] (figure 1).

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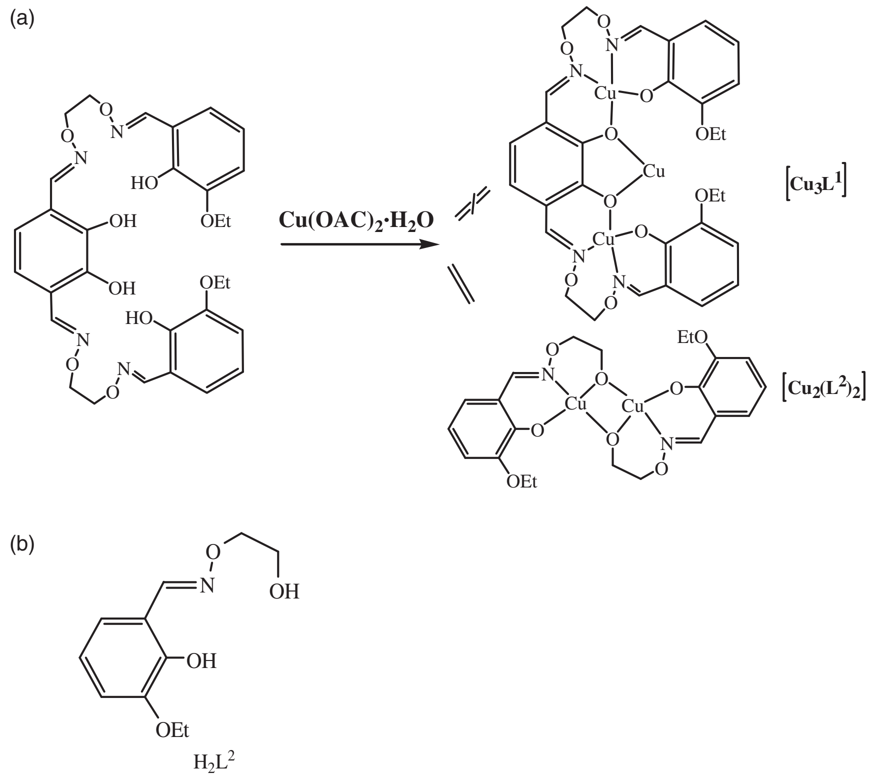

Figure 1. (a) Complexation of H_4L^1 with Cu(II) acetate and (b) chemical structure of H_2L^2.

The crystal structure and atom numbering of the Cu(II) complex are shown in figure 2. Selected bond lengths and angles are listed in table 2.

Single-crystal X-ray structure analysis reveals that the Cu(II) complex is a centrosymmetric neutral homobinuclear entity, $[Cu(L^2)]_2$, crystallizing in the monoclinic space group $P2_1/c$. The ORTEP shows that two $[Cu(L^2)]$ moieties are linked *via* two alkoxy bridges, each of which comes from H_2L^2. The whole complex resides on a crystallographic center of inversion and has two four-coordinate Cu(II) centers. Their geometry can be best described as slightly distorted square-planar with CuN_1O_3 coordination (one oxime nitrogen N1, one phenolic oxygen O3, and two bridging alkoxy oxygen atoms O2 and $O2^{\#1}$) as shown in figure 2. Thus, a planar Cu_2O_2 core is formed by two divalent coppers and two bridging alkoxy oxygen atoms with a Cu–Cu separation of 2.9916(1) Å which is too long to represent intramolecular Cu–Cu bonding. The bridging Cu–O bonds are slightly asymmetric with one being short, Cu1–O1 = 1.906(3) Å, and one long at Cu1–$O1^{\#1}$ = 1.914(3) Å. The bond lengths Cu1–O3 and Cu1–N1 are 1.875(3) and 1.930(4) Å, respectively. The two planes O1–Cu1–$O1^{\#1}$ and O1–$Cu1^{\#1}$–$O1^{\#1}$ are parallel to each other, indicating that Cu1, $Cu1^{\#1}$, O1, and $O1^{\#1}$ are exactly coplanar. The angles Cu1–O1–$Cu1^{\#1}$ and O1–Cu1–$O1^{\#1}$ are 103.08° and 76.92°, respectively. The dihedral angle of the two planes O1–Cu1–$O1^{\#1}$ and O3–Cu1–N1 is 2.51°. Cu1 deviates by 0.004 Å from the mean plane defined by O1, $O1^{\#1}$, O3, and N1.

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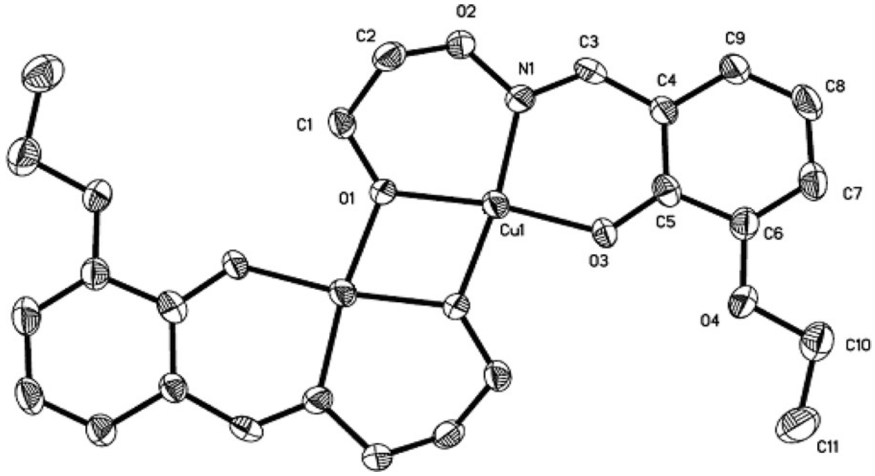

Figure 2. Molecular structure and atom numbering of the Cu(II) complex.

Table 2. Selected bond distances (Å) and angles (°) for the Cu(II) complex.

Cu1–O3	1.875(3)	Cu1–N1	1.930(4)
Cu1–O1	1.906(3)	Cu1–Cu1$^{\#1}$	2.9916(1)
Cu1–O1$^{\#1}$	1.914(3)		
O3–Cu1–O1	171.5(1)	C3–N1–Cu1	125.5(3)
O3–Cu1–O1$^{\#1}$	94.8(1)	O2–N1–Cu1	122.3(3)
O1–Cu1–O1$^{\#1}$	76.9(1)	C1–O1–Cu1	126.4(3)
O3–Cu1–N1	93.1(2)	C1–O1–Cu1$^{\#1}$	130.0(3)
O1–Cu1–N1	95.2(2)	Cu1–O1–Cu1$^{\#1}$	103.1(1)
O1$^{\#1}$–Cu1–N1	171.9(2)		

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

The Cu(II) complex is stabilized by four pairs of intermolecular hydrogen bonds, C2–H2B $\cdots$ O3 and C2–H2B $\cdots$ O4, linking both molecules into a 1-D infinite chain parallel to the *c*-axis (figure 3). The molecules are further linked by four intermolecular C3–H3 $\cdots$ O2 hydrogen bonds between the –C3H3 unit of the oxime and oxygen (O2) of the oxime to form a 2-D infinite planar motif (figure 4). Every complex molecule links six other molecules into an infinite-layered supramolecular structure *via* 12 intermolecular C–H $\cdots$ O hydrogen bonds (table 3, figure 5).

3.2. *Molar conductance*

$[Cu_2(L^2)_2]$ is soluble in DMF and DMSO, slightly soluble in $CHCl_3$ but not soluble in EtOH, MeOH, MeCN, THF, acetone, and ethyl acetate. The complex displays good stability in air at room temperature. H_4L^1 is soluble in the aforementioned solvents. Molar conductance values of $[Cu_2(L^2)_2]$ of $1.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ DMF solution are $3.4\,\mathrm{S\,cm^2\,mol^{-1}}$, indicating a non-electrolyte.

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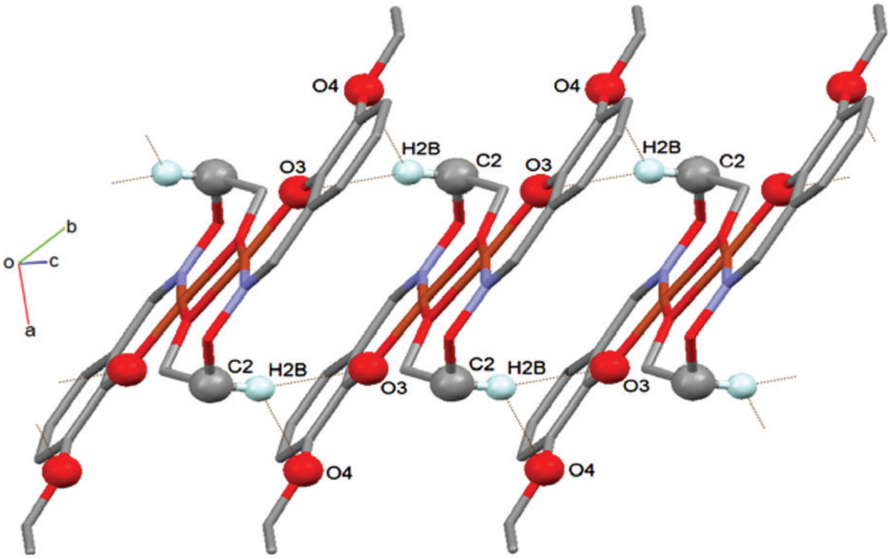

Figure 3. View of the 1-D chain motif of Cu(II) complexes along the *c*-axis (hydrogen atoms except those forming hydrogen bonds are omitted for clarity).

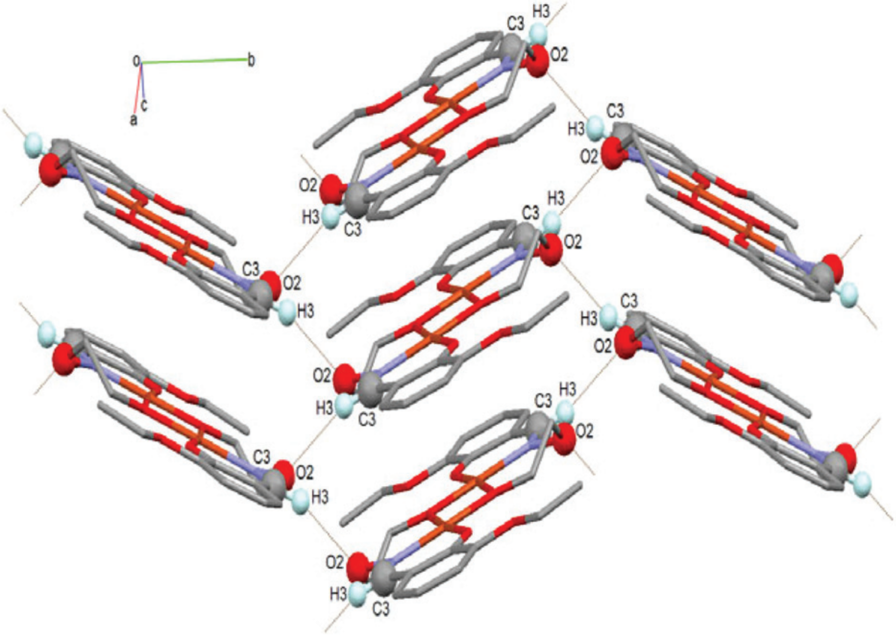

Figure 4. View of the 2-D layered motif of the Cu(II) complexes (hydrogen atoms except those forming hydrogen bonds are omitted for clarity).

Table 3. Hydrogen-bonding distances (Å) and angles (°) for the Cu(II) complex.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠D–H···A
C2–H2B···O3	0.97	2.60	3.514(3)	156
C2–H2B···O4	0.97	2.59	3.240(3)	125
C3–H3···O2	0.93	2.56	3.415(3)	154

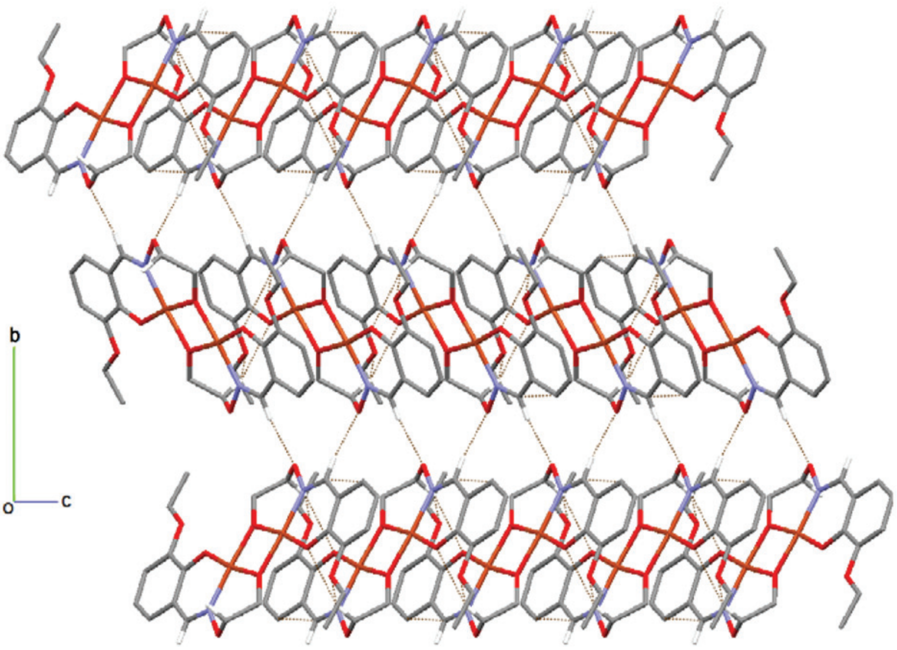

Figure 5. View of the 2-D supramolecular structure of the Cu(II) complex (hydrogen atoms except those forming hydrogen bonds are omitted for clarity).

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3.3. *UV-Vis absorption spectra*

UV-Vis absorption spectra of H_4L^1 and the complex were determined in $5 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ DMF solution. Absorptions of Cu(II) complex are obviously different from those of H_4L^1 (figure 6). Compared with the Cu(II) complex, an important feature of the absorption spectrum of H_4L^1 is that two absorptions are observed at 273 nm and 310 nm, respectively. The former is absent in the spectrum of Cu(II) complex. The other absorption at 310 nm of H_4L^1 shifts to 315 nm in Cu(II) complex, and a new absorption peak at 439 nm was observed in Cu(II) complex, indicating coordination of Cu.

3.4. *Fluorescence spectra*

The emission spectrum of the Cu(II) complex in dilute DMF at room temperature is shown in figure 7. The shape of excitation spectrum of the Cu(II) complex strongly

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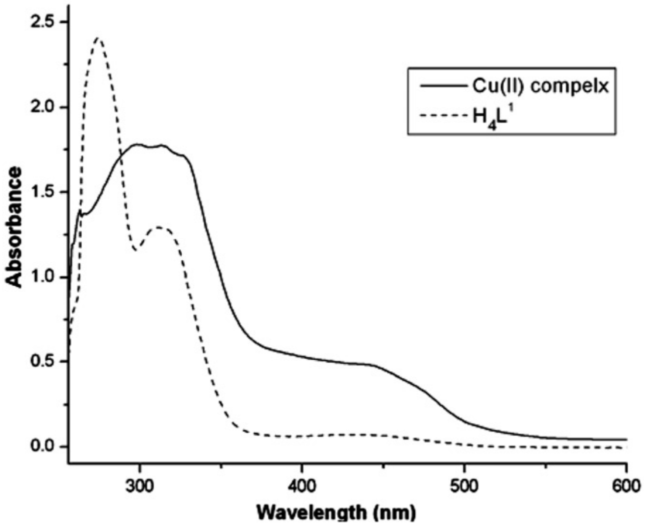

Figure 6. UV-Vis absorption spectra: H_4L^1 (- - -) and the Cu(II) complex (—) in DMF (5×10^{-5} mol L^{-1}).

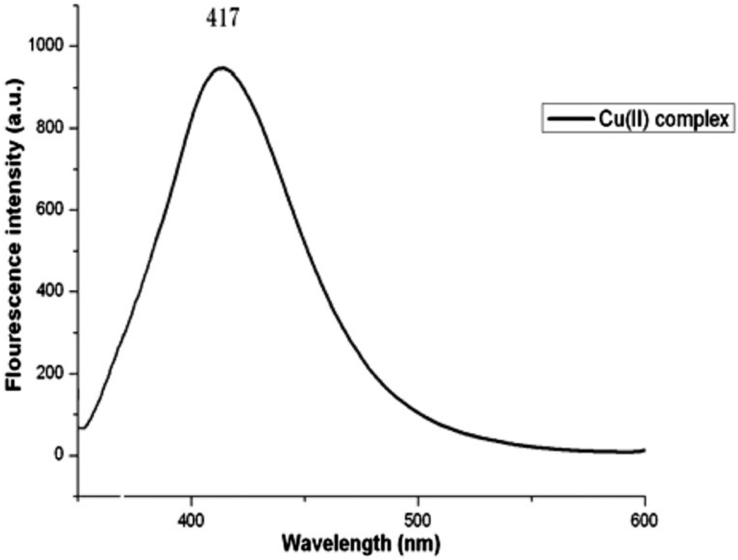

Figure 7. Emission spectrum of the Cu(II) complex in dilute DMF at room temperature ($c = 5 \times 10^{-5}$ mol L^{-1}, $\lambda_{em} = 417$ nm).

resembles that of UV-Vis absorption spectrum and intense excitation peak is observed at 312 nm. The emission peak of Cu(II) complex appears at 417 nm. The Stokes shift between the maximum wavelength of the fluorescence emission and the fluorescence excitation spectrum is 105 nm. This red-shift might be related to the head-to-tail dimeric structure, which make the conjugated system larger, and also indicates it may be a purple device.

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4. Conclusion

An unexpected dinuclear Cu(II) complex, $[Cu_2(L^2)_2]$, bearing a 2 : 2 ligand : metal stoichiometry, was synthesized from H_4L^1 in moderate yield. Cu(II) is four coordinate by two monooxime $(L^2)^{2-}$ units. Cu(II) caused an unexpected cleavage of two N–O bonds, giving a dialkoxo-bridged Cu(II) complex possessing a Cu–O–Cu–O four-membered ring core instead of the expected bis(salen)-type tetraoxime Cu_3–N_4O_4 complex. The molecules are linked to six other molecules in an infinite-layered supramolecular network *via* 12 intermolecular C–H $\cdots$ O hydrogen bonds. Meanwhile, Cu(II) exhibits purple emission with maximum emission wavelength $\lambda_{em} = 417$ nm when excited at $\lambda_{ex} = 312$ nm.

Supplementary material

Further details of the crystal structure investigation(s) may be obtained from the Cambridge Crystallographic Data Centre, Postal address: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk on quoting the depository number CCDC 852419.

Acknowledgments

This work was supported by the "Jing Lan" Talent Engineering Funds of Lanzhou Jiaotong University, which are gratefully acknowledged.

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