A Dinuclear Copper(II) Complex Based On the Bisoxime Ligand 5,5′-Dimethoxy-2,2′-[(ethylene)dioxybis(nitrilomethylidyne)]diphenol: Synthesis, Crystal Structure and Spectral Properties

Wen-Kui Dong[a], Guo-Hua Liu[a], Yin-Xia Sun[a], Xiu-Yan Dong[a], and Xiong-Hou Gao[b]

[a] School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu 730070, P. R. China
[b] Lanzhou Petrochemical Research Center, PetroChina, Lanzhou 730060, P. R. China

Reprint requests to Prof. Wen-Kui Dong. E-mail: dongwk@126.com

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A dinuclear Cu(II) complex, $[Cu_2(L^2)_2]$ (H_2L^2 = 4-methoxysalicylaldehyde *O*-(2-hydroxyethyl)-oxime), has been synthesized through the complexation of Cu(II) acetate monohydrate with the ligand H_2L^1 (H_2L^1 = 5,5′-dimethoxy-2,2′-[(ethylene)dioxybis(nitrilomethylidyne)]diphenol), and characterized by elemental analyses, IR, UV/Vis and emission spectra. The crystal structure of the Cu(II) complex has been determined by single-crystal X-ray diffraction. The catalysis by Cu(II) ions results in the unexpected cleavage 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 expected salen-type bisoxime Cu-N_2O_2 complex.

Key words: Bisoxime Ligand, Cu(II) Complex, Synthesis, Crystal Structure

Introduction

Oxime-type ligands and their complexes have been playing an important role in the development of coordination chemistry [1 – 4]. The development of new metal-organic complexes can provide new topologies for functional materials, in which coordination forms and functionality are important variables [5, 6]. Polynuclear complexes in which the metal centers are bridged through organic ligands are of much current interest, because of their enormous variety of structural topologies as well as their potential applications in optoelectronics and catalysis [7 – 14]. This subject is currently being pursued in our research, including the use of functional oxime groups and a study of the magnetic, photoelectric and catalytic properties of such complexes.

In this paper, we report the synthesis, structural characterization and spectral properties of an unexpected dinuclear Cu(II) complex with the new ligand H_2L^2 (H_2L^2 = 4-methoxysalicylaldehyde *O*-(2-hydroxyethyl)oxime) which is formed in the course of the complexation of H_2L^1 at Cu(II) acetate monohydrate. The product is a dialkoxo-bridged dinuclear Cu(II) complex possessing a Cu-O-Cu-O four-membered ring core instead of the usually expected salen-type complex [15, 16].

Experimental Section

Materials and physical measurements

4-Methoxy-2-hydroxybenzaldehyde ($\geq$ 98 %) from Alfa Aesar was used without further purification. The other reagents and solvents were of analytical grade from Tianjin Chemical Reagent Factory. IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (500 – 4000 cm^{-1}) and CsI (100 – 500 cm^{-1}) pellets. Fluorescence spectra were obtained from a 970CRT spectrofluoro-photometer. ^1H NMR spectra were recorded on a Bruker DRX 400 spectrometer in $CDCl_3$ solution with TMS as internal standard. Melting points were measured by the use of a $\times 10$ microscopic melting point apparatus made by Beijing Taike Instrument Limited Company, and are uncorrected.

Preparation of H_2L^1

5,5′-Dimethoxy-2,2′-[(ethylene)dioxybis(nitrilomethylidyne)]diphenol (H_2L^1) was synthesized according to an analogous method reported earlier [17 – 19]. To an ethanol solution (5 mL) of 4-methoxysalicylaldehyde (393.7 mg, 2.59 mmol) was added an ethanol solution (3 mL) of 1,2-bis(aminooxy)ethane (118.0 mg, 1.28 mmol). The mixture was stirred at 55 °C for 5 h. After cooling to r. t., the precipitate was filtered and washed successively with ethanol and ethanol-hexane (1 : 4). The product was dried *in vacuo*, and 355.3 mg of a colorless flocculent crystalline solid was ob-

Table 1. Crystal data and numbers pertinent to data collection and structure refinement for $[Cu_2(L^2)_2]$.

Molecular formula	$C_{20}H_{22}Cu_2N_2O_8$
M_r	545.48
Color, habit	brown, needle-like
Crystal size, mm^3	$0.40 \times 0.11 \times 0.08$
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	5.2380(4)
b, Å	15.3909(15)
c, Å	13.0131(12)
β, deg	100.210(1)
V, Å^3	1032.47(16)
Z	2
D_{calcd}, g cm^{-3}	1.76
T, K	298(2)
μ(MoK_α), mm^{-1}	2.1
$F(000)$, e	556
hkl range	$-6 \le h \le 6, -18 \le k \le 16, -10 \le l \le 15$
θ range for data collection, deg	2.65 – 25.02
Reflections collected / unique / R_{int}	5341 / 1819 / 0.0367
Data / restraints / parameters	1809 / 0 / 146
Final R_1 / wR_2 $[I \ge 2\sigma(I)]$[a]	0.0306 / 0.0816
Final R_1 / wR_2 (all data)[b]	0.0374 / 0.0853
Goodness-of-fit (F^2)[c]	1.010
Largest diff. peak / hole, e Å^{-3}	0.346 / -0.218

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(F_o2 - F_c2)^2/\Sigma w(F_o2)^2]^{1/2}$, $w = [\sigma^2(F_o2) + (0.0499P)^2 + 0.2789P]^{-1}$, where $P = (\mathrm{Max}(F_o2,0) + 2F_c2)/3$; [c] GoF $= [\Sigma w(F_o2 - F_c2)^2/(n_{obs} - n_{param})]^{1/2}$.

tained. Yield 78.9 %. M. p. 97 – 98 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.79 (s, 6H), 4.41 (s, 4H), 6.46 (d, J = 2.8 Hz, 2H), 6.49 (d, J = 2.4 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 8.17 (s, 2H), 9.94 (s, 2H). – $C_{18}H_{20}N_2O_6$ (360.36): calcd. C 59.99, H 5.59, N 7.77; found C 59.89, H 5.75, N 7.60.

Preparation of $[Cu_2(L^2)_2]$

A solution of Cu(II) acetate monohydrate (3.99 mg, 0.02 mmol) in ethanol (2 mL) was added dropwise to a solution of H_2L^1 (7.20 mg, 0.02 mmol) in dichloromethane (4 mL) at r. t. The color of the mixture turned to dark brown immediately. Stirring was continued for 1 h at r. t. The mixture was filtered, and the filtrate was allowed to stand at r. t. for about one week. The solvent was partially evaporated, and single crystals suitable for X-ray crystallographic analysis were obtained. Yield 25.6 %. – $C_{20}H_{22}Cu_2N_2O_8$ (545.49): calcd. C 44.04, H 4.07, N 5.14, Cu 23.30; found C 44.08, H 4.10, N 5.17, Cu 23.35.

X-Ray crystallography of $[Cu_2(L^2)_2]$

A suitable single crystal of $[Cu_2(L^2)_2]$ with approximate dimensions of $0.40 \times 0.11 \times 0.08$ mm^3 was placed on a Bruker Smart Apex CCD diffractometer. The reflections were collected using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 298(2) K. The structure was solved using the program SHELXS-97 and Fourier difference techniques, and refined by the full-matrix least-squares method on F^2 with SHELXL-97. All hydrogen atoms were added in calculated positions. Crystal data and numbers pertinent to data collection and structure refinement are given in Table 1.

Table 2. Selected bond lengths (Å) and angles (deg) for $[Cu_2(L^2)_2]$ with estimated standard deviations in parentheses[a].

Distances			
Cu1–O3	1.882(2)	Cu1–O2	1.913(2)
Cu1–O2$^{\#1}$	1.9258(19)	Cu1–N1	1.943(2)
O2–Cu1$^{\#1}$	1.9258(19)		
Angles			
O2–Cu1–O2$^{\#1}$	76.63(8)	Cu1–O2–Cu1$^{\#1}$	103.37(9)
O3–Cu1–O2	170.70(8)	O3–Cu1–O2$^{\#1}$	94.37(8)
O2–Cu1–O2$^{\#1}$	76.63(9)	O3–Cu1–N1	93.64(9)
O2–Cu1–N1	95.45(9)	O2$^{\#1}$–Cu1–N1	171.70(9)
C3–N1–Cu1	125.9(2)	O1–N1–Cu1	122.29(17)
C2–O2–Cu1	125.81(17)	C2–O2–Cu1$^{\#1}$	129.96(18)
C5–O3–Cu1	128.39(18)		

[a] Symmetry transformation used to generate equivalent atoms: $^{\#1}$ $1-x$, $1-y$, $1-z$.

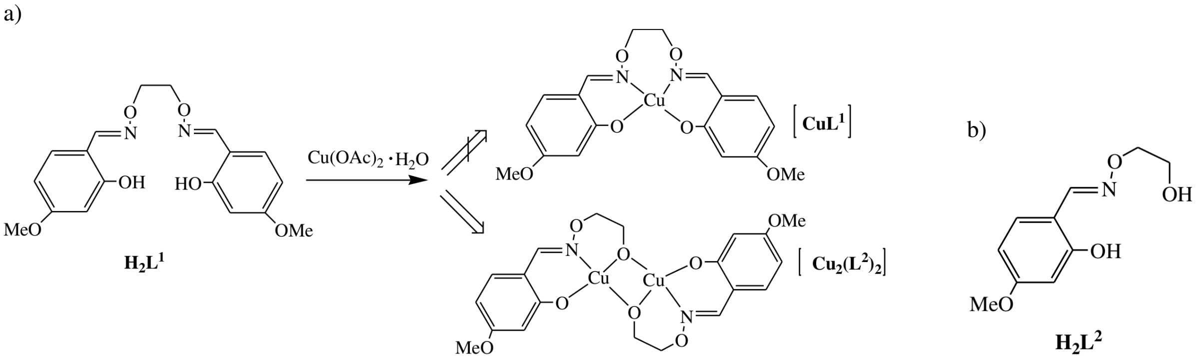
CCDC 832645 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The crystal structure of $[Cu_2(L^2)_2]$

For the synthesis of the copper(II) complex, the same synthetic route was used as for the mono-nuclear complex $[Cu(H_2L)]\cdot 2H_2O$ according to our previous work [17]. However, it is remarkable that the desired salen-type bisoxime complex $[Cu(L^1)]$ was not formed, but an unexpected dinuclear copper(II) complex $[Cu_2(L^2)_2]$ was obtained which was formed in the course of the complexation of H_2L^1 by copper(II) acetate. The results show that because of the catalysis of copper(II) ions [20, 21], 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 Cu(II) ions forming a dialkoxo-bridged dinuclear Cu(II) complex [22, 23] with a Cu-O-Cu-O four-membered ring core instead of the expected salen-type bisoxime Cu-N_2O_2 complex (Scheme 1).

The molecular structure and crystallographic atom numbering of the complex $[Cu_2(L^2)_2]$ are shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 2. The structure determination revealed that



Scheme 1. (a, left) Reaction of the ligand [H_2L^1] with Cu(II) acetate monohydrate, (b, right) chemical formula of H_2L^2 (4-methoxysalicylaldehyde *O*-(2-hydroxyethyl)oxime).

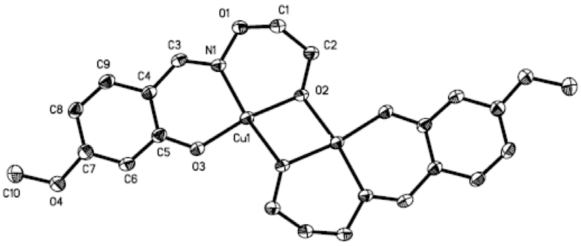


Fig. 1. ORTEP-style drawing of the title complex [$Cu_2(L^2)_2$].

the complex is a neutral homobinuclear entity with crystallographic inversion symmetry. Two [$Cu(L^2)$] moieties are linked *via* two alkoxo bridges, each of which comes from the individual new ligand [L^2]$^{2-}$. The whole complex resides on a center of inversion and has two tetra-coordinated Cu(II) centers. Their geometry can be best described as slightly distorted squareplanar with CuN_1O_3 coordination (one oxime nitrogen atom N1, one phenoxo oxygen atom O3 and two bridging alkoxo oxygen atoms O2 and O2$^{\#1}$) as shown in Fig. 1. Thus, a planar Cu_2O_2 core is formed by two divalent copper(II) ions and their bridging two alkoxo oxygen atoms with a Cu···Cu separation of 3.0118(6) Å which is too long to be considered as representing intramolecular Cu–Cu bonding.

The bridging Cu–O bonds are slightly asymmetric, one (Cu1–O2) with 1.913(2) Å, while the other (Cu1–O2$^{\#1}$) is 1.9258(19) Å. The bond lengths Cu1–O3 and Cu1–N1 are 1.882(2) and 1.943(2) Å, respectively. The four-membered ring Cu1–O2–Cu1$^{\#1}$–O2$^{\#1}$ is exactly planar as required by symmetry. The angles Cu1–O2–Cu1$^{\#1}$ and O2–Cu1–O2$^{\#1}$ are 103.37(9)° and 73.63(8)°, respectively. The dihedral angle of the two planes O2–Cu1–O2$^{\#1}$ and O3–Cu1$^{\#1}$–N1 is 3.32°, and the Cu1 atom deviates by 0.002 Å from the mean plane defined by the atoms O2, O2$^{\#1}$ O3, N1.

Intermolecular interactions of [$Cu_2(L^2)_2$]

Of special interest is the self-assembly of the Cu(II) complex in the crystal by twelve intermolecular hydrogen bonds. The hydrogen bond data are summarized in Table 3.

In the crystal structure, four intermolecular hydrogen bonds, C1–H1A···O3, are formed between the methylene unit (C1–H1A) of the O-alkyl chain and the phenolic oxygen atom (O3) of the (L^2)$^{2-}$ unit, which link the neighboring molecules into an infinite chain parallel to the *a* axis (Fig. 2).

Furthermore, the complex molecules are stabilized in their position by four pairs of hydrogen bonds, C3–H3···O4 and C10–H10B···O1, leading to an infinite 2D layer structure along the crystallographic *ac* plane (Fig. 3). The C3–H3···O4 hydrogen bonds are formed between the -C3H3 unit of the oxime groups and the oxygen atom (O4) of the methoxy group, while the hydrogen bonds C10–H10B···O1 are formed between a -C10H10B unit of the methoxy group and the oxygen atom (O1) of the oxime groups. Thus, each complex is linked to ten other molecules into an infinite 3D supramolecular network *via* intermolecular C–H···O hydrogen bonds.

IR spectra of H_2L^1 and [$Cu_2(L^2)_2$]

The neutral free ligand H_2L^1 exhibits characteristic C=N stretching bands at 1635 cm^{-1}, while the C=N bond of the Cu(II) complex was observed at 1614 cm^{-1}. Thus, the C=N stretching frequency is shifted to lower frequency by *ca.* 21 cm^{-1} upon

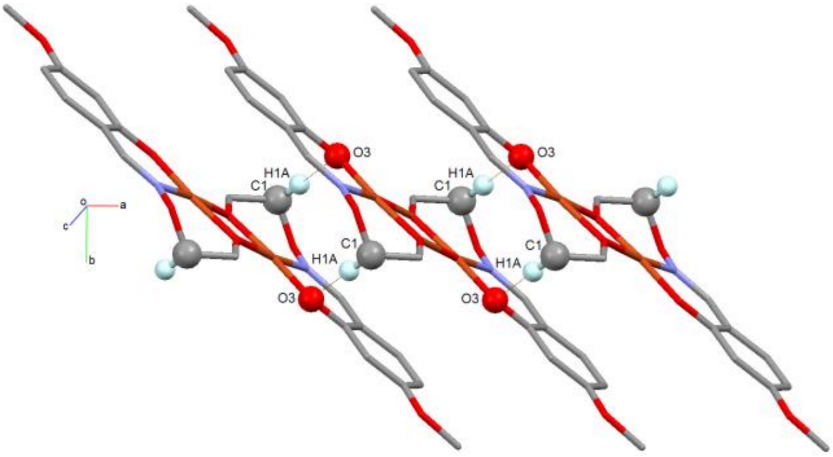


Fig. 2 (color online). View of the 1D chain motif of the complex units along the *a* axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

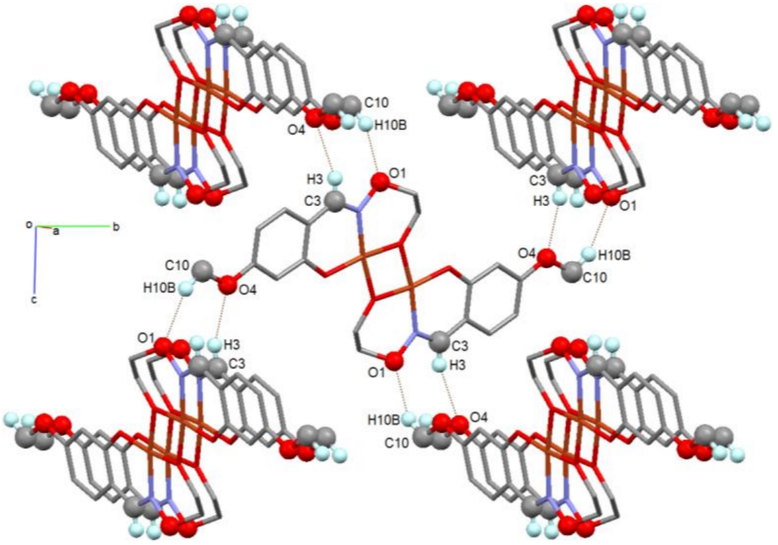


Fig. 3 (color online). View of the 2D layer motif along the *ac* plane (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

complexation, indicating a decrease in the C=N bond order due to the coordination of the Cu(II) ion to the oxime nitrogen lone pair [24 – 27]. In the 143 – 1519 cm^{-1} region, the observed bands were attributed to aromatic C=C vibrations. Upon coordination these bands are shifted to lower frequencies for the Cu(II) complex [28].

Ar-O stretching vibrations appear as strong bands in the range 1263 – 1213 cm^{-1} as reported for similar ligands [29]. This vibration occurs at 1231 cm^{-1} for the free ligand H_2L^1, and at 1238 cm^{-1} for the Cu(II) complex. Thus the Ar-O stretching vibration is shifted to a higher frequency upon complexation. This shift clearly results from the metal-phenolic oxygen interaction upon complexation and is similar to that reported for M(II) complexes with N_2O_2 chelate ligands [30, 31].

The far-infrared spectrum of the Cu(II) complex was obtained in the region 500 – 100 cm^{-1} in order to identify frequencies due to the Cu–O and Cu–N vibrations. $\nu_{(\text{Cu-N})}$ and $\nu_{(\text{Cu-O})}$ vibrations were found at 472 cm^{-1} and 431 cm^{-1}, respectively. As pointed out by Percy and Thornton [32], the metal-oxygen and metal-nitrogen frequency assignments are at times very difficult.

Emission spectrum of $[Cu_2(L^2)_2]$

The emission spectrum of the Cu(II) complex in dilute DMF solution at r. t. is shown in Fig. 4. An intense

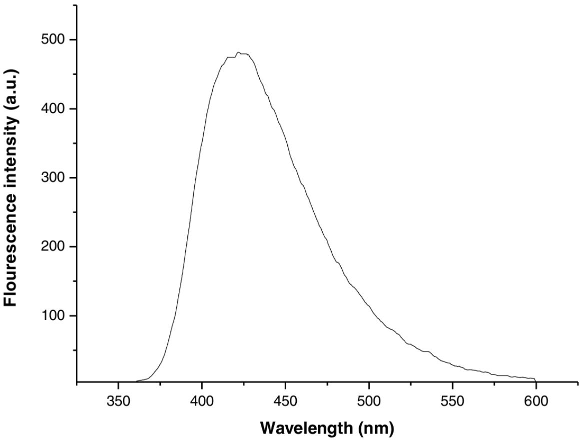


Fig. 4. Emission spectrum of the Cu(II) complex in dilute DMF solution at room temperature ($c = 5 \times 10^{-5}$ mol L^{-1}, λ_{ex} = 340 nm, λ_{em} = 441 nm).

excitation peak is observed at 340 nm. The emission peak appears at around 441 nm. The Stokes shift between the maximum wavelength of the fluorescence emission and the fluorescence excitation is 101 nm. This red-shift might be related to the coordination of the Cu(II) atom to the ligand and a head-to-tail dimeric structure, which make the conjugated system larger.

Conclusion

We have reported the synthesis and structural characterization of a new dinuclear Cu(II) complex. In this complex the Cu(II) ions are tetra-coordinated by two monooxime $[L^2]^{2-}$ units. In a catalysis by the Cu(II) ions an unexpected cleavage of the N–O bonds in the ligand H_2L^1 occurs, giving a dialkoxo-bridged Cu(II) complex possessing a Cu-O-Cu-O four-membered ring core instead of the usually expected salen-type bisoxime Cu-N_2O_2 complex. The molecules are linked to ten other molecules into an infinite supramolecular network *via* intermolecular C–H$\cdots$O hydrogen bonds. The Cu(II) complex exhibits blue emission with the maximum emission wavelength λ_{em} = 441 nm when excited at λ_{ex} = 340 nm.

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