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双烷氧桥联的双核铜(Ⅱ)Schiff 碱配合物的合成及配合行为

董文魁* 陈 晓 孙银霞 何雪妮 吕忠武 焉海波 唐晓璐 赵春宇
(兰州交通大学化学与生物工程学院,兰州 730070)

摘要:通过 Salen 型双肟配体 H_2L^1(H_2L^1=5,5′-二(*N*,*N*′-二乙胺)-2,2′-[乙二氧双(氮次甲基)]二酚)与乙酸铜反应,合成了一种双核铜(Ⅱ)配合物[$Cu_2(L^2)_2$](H_2L^2=4-(*N*,*N*′-二乙胺)水杨醛 O-(2-羟乙基)肟),并对其进行了 X-射线衍射单晶结构分析。在形成配合物时,铜(Ⅱ)离子的催化作用导致 Salen 型双肟配体的 1 个 N-O 键发生了断裂,意外地得到了一种新颖的含有 Cu-O-Cu-O 四元环中心的烷氧基氧桥联的双核铜(Ⅱ)配合物,而不是预期的 Salen 型双肟 Cu-N_2O_2 配合物。

关键词:Schiff 碱;铜(Ⅱ)配合物;合成;晶体结构;配合行为
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Synthesis and Complexation Behavior of a Dialkoxo-bridged Dinuclear Copper(Ⅱ) Complex with Schiff Base Ligand

DONG Wen-Kui* CHEN Xiao SUN Yin-Xia HE Xue-Ni
LÜ Zhong-Wu YAN Hai-Bo TANG Xiao-Lu ZHAO Chun-Yu
(*School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou* 730070)

Abstract: A unprecedented dinuclear copper(Ⅱ) complex, [$Cu_2(L^2)_2$] (H_2L^2=4-(*N*,*N*′-diethylamino)salicylaldehyde O-(2-hydroxyethyl)oxime), has been synthesized through the complexation of copper(Ⅱ) acetate monohydrate with ligand H_2L^1 (H_2L^1=5,5′-di(*N*,*N*′-diethylamino)-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 complex possessing a Cu-O-Cu-O four-membered ring core instead of the usually desired Salen-type bisoxime Cu-N_2O_2 complex. CCDC: 670381.

Key words: Schiff base; copper(Ⅱ) complex; synthesis; crystal structure; complexation behavior

The Schiff base ligands and theirs complexes have been playing an important part in the development of coordination chemistry[1]. And during the past several decades, a great number of Schiff base complexes have been studied extensively for their facile synthesis and easily tunable steric, electronic, and catalytic properties, such as catalysts for various organic reactions[2], models of reaction centers of metalloenzymes[3], outstanding magnetic properties[4], excellent biological activity[5], and nonlinear optical materials[6]. Although the studies of Schiff base complexes have made great progress[7~10], it has not been found the cleavage of N-O bonds of Schiff base ligands when the ligands are allowed to react with metal salt, consequently, gained a unexpected complex with the new ligands. In this paper, we report the synthesis and structural characterization of a copper(Ⅱ) complex with new ligand H_2L^2 which is formed in the course of the complexation of

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*通讯联系人。E-mail:dongwk@mail.lzjtu.cn
第一作者:董文魁,男,44 岁,教授,研究方向:功能配合物、超分子化学与材料。

H_2L^1 and copper(Ⅱ) acetate, $[Cu_2(L^2)_2]$ (H_2L^2=4-(*N*,*N*′-diethylamino)salicylaldehyde O-(2-hydroxyethyl)oxime). The obtained results show cleavage of one of the N-O bonds in H_2L^1 in the complexation of the ligand H_2L^1 with copper (Ⅱ) acetate, and giving an unexpected dialkoxo-bridged dinuclear complex possessing a Cu-O-Cu-O four-membered ring core instead of the usually desired Salen-type bisoxime Cu-N_2O_2 complex. It has not been reported up to now.

1 Experimental

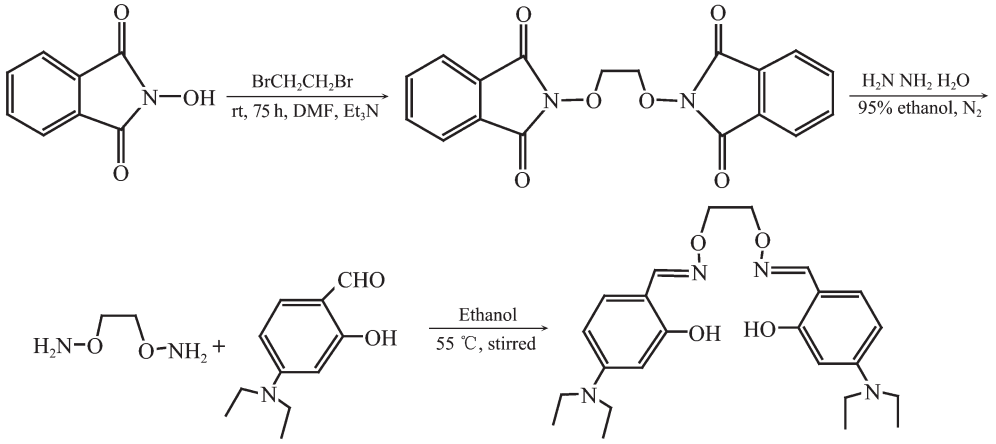
1.1 Materials and instruments

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 VERTEX70 FTIR spectrophotometer, with samples prepared as KBr (500~4 000 cm^{-1}) and CsI (100~500 cm^{-1}) pellets. ^1H NMR spectra were determined by German Bruker AVANCE DRX-400 spectroscopy, single crystal 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 and were uncorrected.

1.2 Synthesis of copper(Ⅱ) complex

1.2.1 Synthesis of H_2L^1

5,5′-Di(*N*,*N*′-diethylamino)-2,2′-[ethylenedioxybis(nitrilomethylidyne)]diphenol (H_2L^1) was synthesized according to our previously reported work[11]. The synthetic route is shown in Scheme 1. Yield, 68.6%. m.p. 125~126 ℃. Anal. Calcd. for $C_{24}H_{34}N_4O_4$ (%): C 65.14; H 7.74; N 12.66. Found: C 65.10; H 7.65; N 12.68. ^1H NMR (400 MHz, $CDCl_3$): 1.17 (t, *J*=7.6 Hz, 12H), 3.35 (dd, *J*=6.8 Hz, 8H), 4.38 (s, 4H), 6.20 (d, *J*=2.8 Hz, 2H), 6.22 (t, *J*=2.4 Hz, 2H), 6.94(d, *J*=8.8 Hz, 2H), 8.11 (s, 2H), 9.80 (s, 2H).



Scheme 1 Synthetic route of 5,5′-di(*N*,*N*′-diethylamino)-2,2′-[ethylenedioxybis(nitrilomethylidyne)]diphenol (H_2L^1)

1.2.2 Synthesis of $[Cu_2(L^2)_2]$

A solution of copper(Ⅱ) acetate monohydrate (20.0 mg, 0.1 mmol) in methanol (15 mL) was added dropwise to a solution of H_2L^1 (44.3 mg, 0.1 mmol) in acetone (15 mL) at room temperature. The color of the mixing solution turned to brown immediately, and then continuing stirring for 2 h at room temperature. The mixture was filtered and the filtrate was allowed to stand at room temperature for about several weeks, the solvent was partially evaporated and obtained dark-brown prismatic single crystals suitable for X-ray crystal structure analysis. Anal. Calcd. For $C_{26}H_{36}Cu_2N_4O_6$ $[Cu_2(L^2)_2]$ (%): C, 49.75; H, 5.78; N, 8.93; Cu, 20.25. Found (%): C, 49.79; H, 5.80; N, 8.91; Cu, 20.22.

1.3 Crystal structure determination

X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer at (298±2) K using graphite monochromatized Mo *Kα* radiation (λ=0.071 073 nm). The Lp factor and Semi-empirical absorption corrections were applied to the intensity data. The structure was solved by the direct method and subsequent difference-Fourier syntheses with SHELXS-97

program, 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 program. The crystallographic data and structural refinement parameters for the complex are listed in Table 1.

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

Empirical formula	$C_{26}H_{36}Cu_2N_4O_6$	μ (Mo $K\alpha$) / mm^{-1}	1.611
Formula weight	627.67	F(000)	326
T / K	298(2)	Crystal size / mm	0.53 × 0.40 × 0.23
Wavelength / nm	0.071 073	θ range for data collection / (°)	1.51~25.00
Crystal system	Triclinic	Index ranges	$-6 \leqslant h \leqslant 5, -8 \leqslant k \leqslant 11, -15 \leqslant l \leqslant 16$
Space group	$P\bar{1}$	Completeness to θ=25.01° / %	97.9
a / nm	0.526 60(8)	Reflections collected	3 502
b / nm	0.978 00(10)	Independent reflections	2 343 (R_{int}=0.0734)
c / nm	1.368 00(14)	Reflections with [$I>2\sigma(I)$]	2 001
α / (°)	92.460(2)	Data / restraints / parameters	2 343 / 0 / 175
β / (°)	97.860(2)	Goodness-of-fit on F^2	1.039
γ / (°)	102.340(3)	Final R indices [$I>2\sigma(I)$]	R_1=0.067 6, wR_2=0.173 7
V / nm^3	0.679 90(14)	R indices (all data)	R_1=0.07 62, wR_2=0.182 9
Z	1	Largest diff. peak and hole / (e·nm^{-3})	996 and −1 029
D_c / (Mg·m^{-3})	1.533		

2　Results and discussion

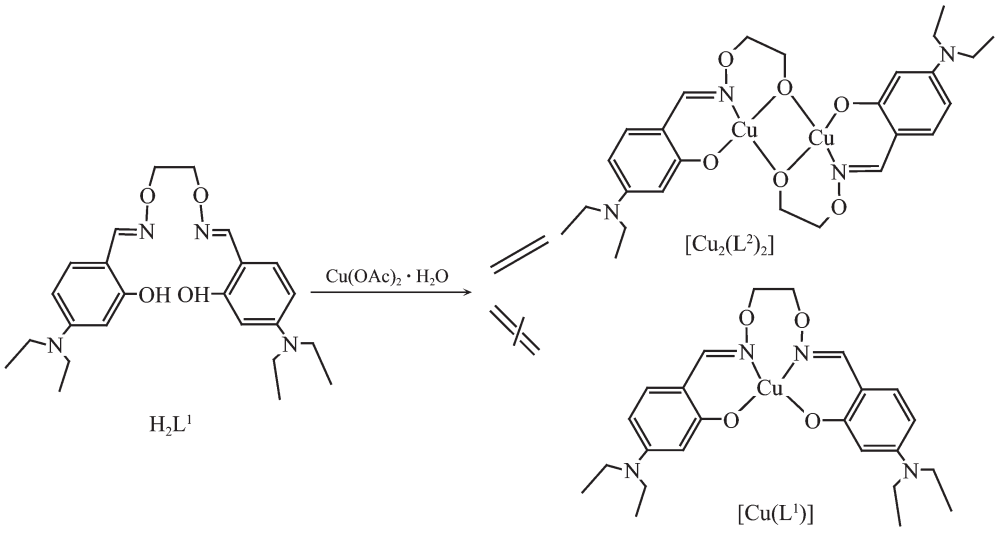
2.1　Crystal structure

The synthesis of copper(Ⅱ) complex was used the same synthetic route for the tri-nickel cluster {[NiL]$_2$(OAc)$_2$Ni} according to our previous work[11]. However, it is remarkable that it did not form the desired 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. The results show the complexation of the ligand H_2L^1 with copper(Ⅱ) acetate resulted in cleavage of one of the N-O bonds in H_2L^1, giving a new O-N-O tridentate ligand H_2L^2, which coordinate 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_2O_2 complex (Fig.1).

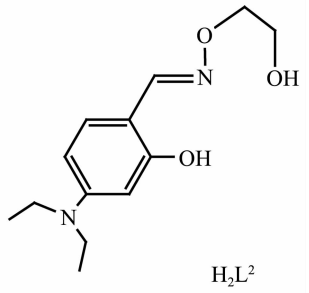
The crystal structure and atom numbering and packing diagram of complex [$Cu_2(L^2)_2$] are shown in Fig. 2 and Fig.3, respectively. Selected bond lengths and bond angles are listed in Table 2.

Single crystal structure reveals the complex is a centrosymmetric neutral homobinuclear entity. Because of the catalysis of copper(Ⅱ) ions[12,13], the complexation of the ligand H_2L^1 with copper(Ⅱ) acetate resulted in the unexpected cleavage of one of the N-O bonds in the ligand H_2L^1, giving a novel dialkoxo-bridged dinuclear complex possessing a Cu-O-Cu-O four-membered ring core instead of the usually desired Salen-type bisoxime Cu-N_2O_2 complex.

ORTEP illustration of the complex shows that two [Cu(L^2)] moieties in a same molecule are bridged together through two alkoxo bridges, each of which comes from the individual new ligand H_2L^2. The whole complex sits on a crystallographically inverse centre forming the μ-dialkoxo bridged binuclear structure with both tetra-coordinated Cu(Ⅱ) centres. The local coordination environment is exactly identical for both centres which can be best described as a slightly distorted square plane with CuN_1O_3 (one oxime nitrogen atom N1, one phenoxo oxygen atom O3 and two bridging alkoxo oxygen atoms O2 and O2#) as evidenced from Fig.2. 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 0.301 4 nm.



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



(b) 4-(*N*,*N*′-diethylamino)salicylaldehyde *O*-(2-hydroxyethyl)oxime (H_2L^2)

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

The distance of Cu1-Cu1# is relatively too long to be considered as intramolecular Cu-Cu bonding.

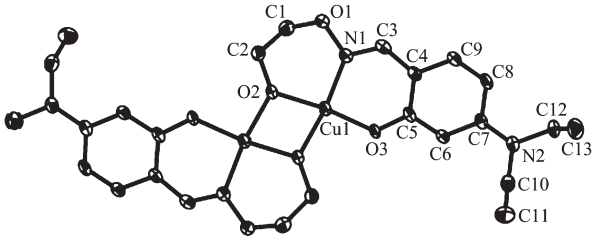


Fig.2 Structure and atom numbering of complex $[Cu_2(L^2)_2]$

The bridging Cu-O bonds are slightly asymmetric with one being short, Cu1-O2 0.192 6 nm and one long Cu1-O2# 0.193 4 nm. The bond distance of Cu1-O3 and Cu1-N1 are 0.190 8 nm and 0.194 5 nm, respectively. The two planes O2-Cu1-O2# and O2-Cu1#-O2# are parallel to each other, indicating Cu1, Cu1#, O2, and O2# are coplanar exactly. The angles of Cu1-O2-Cu1# and O2-Cu1-O2# are 102.67° and 77.33°, respectively. The dihedral angle of two planes O2-Cu1-O2# and O3-Cu1#-N1 is 8.92°, and the Cu1 atom deviates by 0.005 2 nm from the mean plane defined by the atoms O2, O2#, O3, N1. The unit cell packing of complex $[Cu_2(L^2)_2]$ is given in Fig.3, which is formed by the packing of the complex molecules. A detailed bonding study does not reveal any trace of intermolecular weak or hydrogen bonding interactions

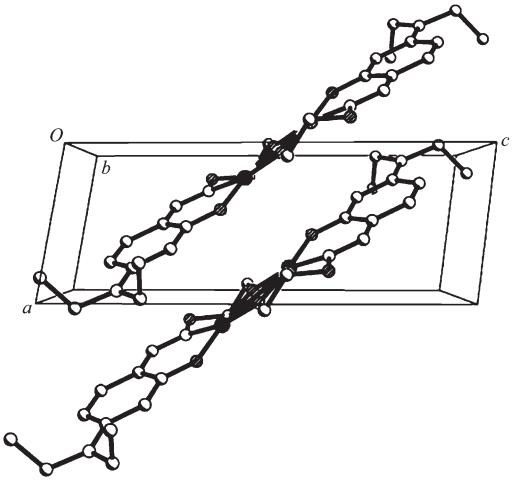


Fig.3 Packing diagram of complex $[Cu_2(L^2)_2]$ along *b* axis

Table 2　Selected bond distances (nm) and angles (°) for complex [Cu(L²)]

Cu(1)-O(3)	1.908(3)	Cu(1)-O(2)	1.926(3)	Cu(1)-O(2)#	1.934(3)
Cu(1)-N(1)	1.945(4)	Cu(1)-Cu(1)#	3.013 6(10)	O(2)-Cu(1)#	1.934(3)
O(3)-Cu(1)-O(2)	172.42(13)	O(3)-Cu(1)-O(2)#	95.61(14)	O(2)-Cu(1)-O(2)#	77.33(15)
O(3)-Cu(1)-N(1)	93.47(15)	O(2)-Cu(1)-N(1)	93.92(15)	O(2)#-Cu(1)-N(1)	167.77(16)
O(3)-Cu(1)-Cu(1)#	134.12(10)	O(2)-Cu(1)-Cu(1)#	38.76(10)	O(2)#-Cu(1)-Cu(1)#	38.57(10)
N(1)-Cu(1)-Cu(1)#	132.13(12)	C(3)-N(1)-Cu(1)	124.3(3)	O(1)-N(1)-Cu(1)	123.8(3)
C(2)-O(2)-Cu(1)	126.3(3)	C(2)-O(2)-Cu(1)#	131.0(3)	Cu(1)-O(2)-Cu(1)#	102.67(15)
C(5)-O(3)-Cu(1)	127.9(3)				

Symmetry transformations used to generate equivalent atoms: #: $-x+2$, $-y+1$, $-z+1$.

within the system.

2.2　FTIR spectra

The FTIR spectra of H_2L^1 and complex $[Cu_2(L^2)_2]$ exhibit various bands in the 500~4 000 cm^{-1} region. The O-H stretching frequency of the Salen-type ligand is expected in the 3 300~3 800 cm^{-1} region, however, this frequency is generally displaced to *ca.* 3 431 cm^{-1} due to the internal hydrogen bond OH···N=C[14]. 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 FTIR 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[15].

The free ligand H_2L^1 exhibits characteristic C=N stretching band at 1 634 cm^{-1}, while the C=N of the Cu(Ⅱ) complex is observed in the 1 612 cm^{-1}. The C=N stretching frequency is shifted to lower frequency by ca. 22 cm^{-1} 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[16]. In the 1 483~1 597 cm^{-1} region, the observed bands are attributed to aromatic C=C vibrations. Upon coordination these bands shift to lower frequencies for the Cu(Ⅱ) complexes[17].

The Ar-O stretching frequency appears as a strong band within the 1 263~1 213 cm^{-1} as reported for similar ligands[15]. This band occurs at 1 231 cm^{-1} for the ligand H_2L^1, and at 1 244 cm^{-1} 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[16,17].

The far-infrared spectrum of complex $[Cu_2(L^2)_2]$ is also obtained in the region 500~100 cm^{-1} in order to identify frequencies due to the Cu-O and Cu-N bonds. The band at 431 cm^{-1} in Cu(Ⅱ) complex is assigned to ν(Cu-O), while band at 474 cm^{-1} is assigned to ν(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_2L^1. As pointed out by Percy and Thornton[18], the metal-oxygen and metal-nitrogen frequency assignments are at times very difficult.

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