一维链状铜(Ⅱ)配合物的合成、晶体结构及热稳定性研究

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摘要：通过一种新的肟类配体 HL(HL=1-(4-{[(E)-3-乙氧基-2-羟苯亚甲基]氨基}苯乙酮肟)与一水合乙酸铜反应,合成了一种铜(Ⅱ)配合物[Cu(L)₂]·CH₃OH。X 射线单晶结构分析表明该配合物是一种单核配合物,其中铜(Ⅱ)原子以四配位的形式分别与 2 个单肟配体的酚氧原子和亚胺氮原子结合,形成稍微扭曲的平面四边形几何构型。O 和 N 配位原子互为反式,所形成的 Cu1N2O2 平面和 Cu1N4O5 平面的二面角为 23.33(3)°。在这个晶体结构中,每 1 个配合物分子分别与近邻的 2 个配合物分子通过 O-H⋯O 氢键连接,沿 b 轴形成了 1 个一维的无限延伸的链状结构。

关键词：肟类配体；铜(Ⅱ)配合物；合成；晶体结构；热性质
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Synthesis, Crystal Structure and Thermal Property of a 1D Chain-Like Copper(Ⅱ) Complex

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Abstract: A Cu(Ⅱ) complex, [Cu(L)₂]·CH₃OH, has been synthesized via the complexation of copper(Ⅱ) acetate monohydrate with a new oxime-type ligand　(HL=1-(4-{[(E)-3-ethoxyl-2-hydroxybenzylidene]amino}phenyl)ethanone oxime). X-ray crystal structure determination of the Cu(Ⅱ) complex shows that is a mononuclear complex. The Cu(Ⅱ) atom is four-coordinated by the phenolate O atoms and imine N atoms from two deprotonated oxime-type ligands, in a slightly distorted square-planar geometry. The O- and N-donor atoms are mutually trans and the dihedral angle between the two coordination planes (Cu1N2O2 and Cu1N4O5) is 23.33(3). In the crystal structure, each complex molecule links two other adjacent complex molecules into an infinite one-dimensional structure along the b axis through intermolecular O−H⋯O hydrogen bonds. CCDC: 871832.

Key words: oxime-type ligand; Cu(Ⅱ) complex; synthesis; crystal structure; thermal property

　　Oxime-type compounds are known to be versatile ligands. A large number of complexes with oxime-type ligands have been reported because of their interesting structures and potential applications[1]. Copper(Ⅱ) complexes with oxime-type ligands have been widely investigated in coordination chemistry and biological chemistry[2-5]. In the last few years there has been a burgeoning effort to identify the biological activities of copper, primarily through techniques associated with the interface of biology/biochemistry/coordination chemistry[6-8]. It appears that the biological role of copper is primarily in redox reactions and as a biological catalyst, although much remains to be understood[9]. An extensive effort has been made to prepare and characterize a variety of Cu(Ⅱ) coordination complexes in an attempt to model the physical and chemical behavior of copper-containing enzymes[10]. The peculiarity of copper lies in its ability

to form complexes with coordination number four, five or six[11-13]. As an extension of the work on the structural characterization of such complexes[14-19], the crystal structure of a new Cu(II) complex, [Cu(L)$_2$]·CH$_3$OH, is reported in this paper.

1 Experimental

1.1 Materials and instruments

3-Ethoxyl-2-hydroxybenzylidene was purchased from Alfa Aesar and used without further purification. 4-Aminophenylethanone oxime was synthesized according to an analogous method reported earlier[14-15]. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory.

Elemental analyses for Cu was detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (500~4 000 cm^{-1}) and CsI (100~500 cm^{-1}) pellets. TG-DTA analyses were carried out at a heating rate of 5 ℃·min^{-1} on a ZRY-1P thermoanalyzer. Electrolytic conductance measurement was made with a DDS-11D type conductivity bridge using a 1.0 mmol·L^{-1} solution in DMF at room temperature. X-ray single crystal structure was determined on a Bruker Smart 1000 CCD area detector. Melting points were obtained by use of an X4 microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and were uncorrected.

1.2 Preparation of the Cu(II) complex

1.2.1 Synthesis of HL

HL (1-(4-{[(E)-3-ethoxyl-2-hydroxybenzylidene] amino}phenyl)ethanone oxime) was synthesized by modification of the reported method[14-15]. To an ethanol solution of 2-hydroxy-3-ethoxybenzaldehyde (332.3 mg, 2.00 mmol) was added an ethanol solution of 4-aminophenylethanone oxime (300.4 mg, 2.00 mmol). The mixture solution was stirred at 328 K for 5 h. After cooling to room temperature, the precipitate was filtered, and washed successively with ethanol and n-hexane, respectively. The product was dried under vacuum, and obtained orange red microcrystal. Yield, 75.1%. m.p. 436~437 K. Anal. Calcd. for C$_{17}$H$_{18}$N$_2$O$_3$ (%): C 68.44; H 6.08; N 9.39. Found(%): C, 68.30; H, 6.02; N, 9.52.

1.2.2 Synthesis of the complex [Cu(L)$_2$]·CH$_3$OH

A solution of copper(II) acetate monohydrate (2.4 mg, 0.012 mmol) in methanol (2 mL) was added dropwise to a solution of HL (7.2 mg, 0.024 mmol) in methanol (5 mL) at room temperature. The color of the mixing solution turned brown immediately, and then continued to stirring for 4 h at room temperature. The mixture solution was filtered and the filtrate was allowed to stand at room temperature for about four weeks, the solvent was partially evaporated and obtained several green block-like single crystals suitable for X-ray crystallographic analysis. Anal. Calcd. for C$_{35}$H$_{38}$CuN$_4$O$_7$ ([Cu(L)$_2$]·CH$_3$OH)(%): C 60.52; H 5.46; N 8.35; Cu 9.41. Found(%): C 60.85; H 5.51; N 8.11; Cu 9.29.

1.3 Crystal structure determination

The X-ray diffraction measurement for the complex was performed on Bruker Smart 1000 CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ =0.071 073 nm) at 298(2) K. Empirical absorption correction was applied to the data using SADABS program. The structure was solved by direct methods and refined by full-matrix least-squares method on F^2 using the SHELXL program[20]. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. Details of the crystal parameters, data collection and refinements for the complex are summarized in Table 1.

CCDC: 871832.

2 Results and discussion

2.1 Crystal structure of [Cu(L)$_2$]·CH$_3$OH

X-ray crystallographic analysis of [Cu (L)$_2$]· CH$_3$OH reveals formation of a mononuclear structure. The Cu(II) complex crystallizes in the monoclinic system, space group $P2_1$, and Z =2. The complex consists of one Cu(II) atom, two deprotonated L$^-$ units and one crystallizing methanol molecule, as expected

Table 1　Crystal data and structure refinement for the title complex

Empirical formula	$C_{35}H_{38}CuN_4O_7$	Absorption correction	Multi-scan
Formula weight	690.23	Crystal size / mm	0.98×0.82×2.05
T / K	298(2)	θ range for data collection / (°)	2.37 to 25.02
Wavelength / nm	0.071 073	Index ranges	$-11 \leqslant h \leqslant 11, -9 \leqslant k \leqslant 9, -15 \leqslant l \leqslant 24$
Crystal system	Monoclinic	Completeness to θ=25.01° / %	99.60
Space group	$P2_1$	Reflections collected	8 256
a / nm	0.977 7(1)	Independent reflections	5 375 (R_{int}=0.038 0)
b / nm	0.821 6(1)	Reflections observed ($I>2\sigma(I)$)	3 761
c / nm	2.045 1(2)	Refinement method	Full-matrix least-squares on F^2
β / (°)	93.454(1)	Data / restraints / parameters	5 375 / 1 / 429
V / nm^3	1.639 8(2)	Goodness-of-fit on F^2	1.013
Z	2	Final R indices ($I>2\sigma(I)$)	R_1=0.047 3, wR_2=0.088 6
D_c / (g·cm^{-3})	1.398	R indices (all data)	R_1=0.080 1, wR_2=0.102 6
μ(Mo $K\alpha$) / mm^{-1}	0.721	Absolute structure parameter	−0.018(15)
$F(000)$	722	$(\Delta\rho)_{max}$ / $(\Delta\rho)_{min}$ / (e·nm^{-3})	369 / −258

Table 2　Selected bond distances (nm) and bond angles (°) for the title complex

Cu1-O5	0.189 4(3)	Cu1-O2	0.188 6(3)	Cu1-N2	0.198 1(4)
Cu1-N4	0.201 9(4)				
O5-Cu1-O2	168.6(2)	O5-Cu1-N2	90.0(1)	O2-Cu1-N2	93.0(1)
O5-Cu1-N4	88.8(2)	O2-Cu1-N4	91.3(2)	N2-Cu1-N4	159.4(2)
C9-N2-Cu1	122.4(3)	C6-N2-Cu1	120.6(3)	C26-N4-Cu1	119.4(3)
C23-N4-Cu1	120.9(3)	C11-O2-Cu1	127.8(3)	C28-O5-Cu1	125.1(3)

from the analytical data. The molecular structure of the Cu(Ⅱ) complex is shown in Fig.1, selected bond distances and angles are listed in Table 2. In asymmetric molecule unit of the Cu(Ⅱ) complex, the Cu(Ⅱ) center is tetra-coordinated by the phenolate O atoms and imine N atoms from two deprotonated oxime-type ligands, in a slightly distorted square-planar geometry. The coordinate bond lengths and
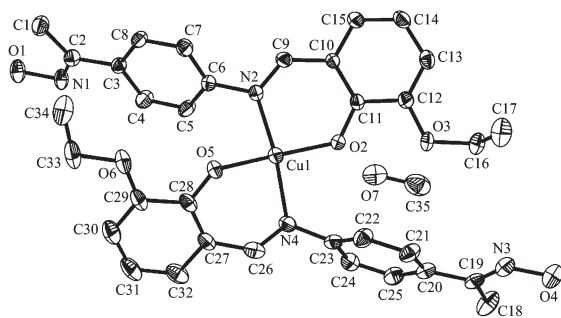
Thermal ellipsoids are plotted at 30% probability level; Hydrogen atoms are omitted for clarity

Fig.1　Crystal structure of the Cu(Ⅱ) complex with the atom numbering

angles around the Cu atom　(Table 1) are typical and comparable to the corresponding values observed in other Cu(Ⅱ) complexes with oxime-type ligands[21]. The two deprotonated oxime-type ligands are coordinated in a trans fashion. The dihedral angle between the coordination plane of O2-Cu1-N2 and that of O5-Cu1-N4 is 23.33(3)°, while another dihedral angle between the coordination plane of N2-Cu1-O5 and that of O2-Cu1-N4 is 23.27(3)°, indicating slight distortion toward tetrahedral geometry from the square planar structure[22-23].

The introduction of one crystallizing methanol molecule in the Cu(Ⅱ) complex successfully leads to the assembly of these monomeric units by intermolecular hydrogen bonds. As illustrated in Fig. 2, The phenolate O2 and ethoxyl O3 atoms of one ligand molecule, respectively, and the O7 atom of the crystallizing methanol molecule is bonded to the hydroxyl -O4H4 group of the other ligand unit of the Cu(Ⅱ) complex. Simultaneous, the phenolate O5 and ethoxyl O6 atoms of the ligand unit in the Cu(Ⅱ)

Table 3 Intermolecular hydrogen bonds for the Cu(II) complex

D–H···A	d(D-H) / nm	d(H···A) / nm	d(D···A) / nm	∠DHA / (°)
O1–H1···O5[i]	0.082	0.202	0.273 1(3)	145
O1–H1···O6[i]	0.082	0.263	0.329 8(3)	140
O4–H4···O7[ii]	0.082	0.194	0.271 8(3)	159
O7–H7···O2	0.082	0.239	0.315 7(3)	157
O7–H7···O3	0.082	0.251	0.315 1(3)	136

Symmetry codes: [i] x, $y-1$, z; [ii] x, $y+1$, z.
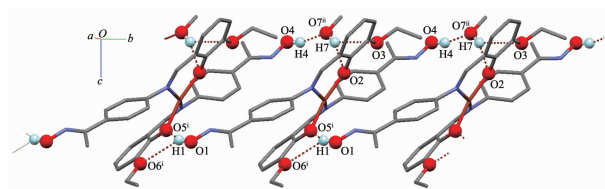
Symmetry codes: [i] x, $y-1$, z; [ii] x, $y+1$, z

Fig.2 Intermolecular hydrogen bonds of the Cu(II) complex

complex are hydrogen-bonded to the -O1H1 group of another adjacent Cu(II) complex unit, respectively. Thus, each molecule links two other adjacent molecules into an infinite one-dimensional chain supramolecular structure through six intermolecular O–H···O hydrogen bonds.

2.2 FTIR spectra

The FTIR spectra of HL and its corresponding Cu(II) complex in the 400~4 000 cm^{-1} region is given in Table 4. The free ligand HL exhibits characteristic C=N stretching band at 1 615 cm^{-1}, while the C=N of the Cu(II) complex was observed in the 1610 cm^{-1}. The C=N stretching frequency is shifted to lower frequency by $ca.$ 5 cm^{-1} upon complexation, indicating the behavior between the free ligand and the corresponding Cu(II) atom resulting in weakening the force constant of C=N bond[24-25]. The Ar-O stretching frequency appear as a strong band in the 1 253 cm^{-1} in the free ligand, and the toward lower wavenumber of the Ar-O absorption shift $ca.$ 18 cm^{-1} indicating that Cu-O bonds are formed between the Cu(II) atom and the oxygen atoms of the phenolic groups[26].

The N-O stretching frequencies of the oxime

group in free ligand and the Cu(II) complex all appear as a strong band in the 919 cm^{-1} indicating that the oxime N atoms do not involve in coordination. In the 1460~ 1591 cm^{-1} region, the observed bands were attributed to aromatic C =C vibrations. Upon coordination these bands shift to lower frequencies for the Cu(II) complex. In addition, the O-H stretching frequency of the free HL ligand appears at 3 289 and 3 241 cm^{-1}. The out-of-plane bending vibration of phenolic alcohol in HL at 1 277 cm^{-1}, which disappears in the complex, indicating the oxygen in the phenolic alcohol of the Cu(II) complex has been deprotoned and coordinated to the Cu(II) atom. Meanwhile, infrared spectrum of the Cu(II) complex shows the expected strong absorption band due to ν(O-H) at ca. 3 248 cm^{-1}, which is the evidence for the existence of methanol molecule.

The far-infrared spectrum of the Cu(II) complex was also obtained in the region 100~500 cm^{-1} in order to identify frequencies due to the Cu-O and Cu-N bonds. The FT-IR spectrum of the complex showed ν(Cu-N) and ν(Cu-O) vibration absorption frequencies at 515 and 440 cm^{-1}, respectively[16].

2.3 UV-Vis absorption spectra

The UV-Vis absorption spectra of HL and its Cu(II) complex in diluted chloroform solution are shown in Table 5. It can be seen that the absorption peaks of the Cu(II) complex are obviously different from those of the HL upon complexation. Compared with the Cu(II) complex, an important feature of the absorption spectrum of HL is shown that an

Table 4 Main IR bands for the ligand HL and the complex

(cm^{-1})

Compound	ν(O-H)	ν(C=N)	ν(Ar-O)	ν(Cu-N)	ν(Cu-O)	ν(C=C) benzene ring skeleton
HL	32, 893, 241	1 615	1 253	—	—	1 591, 1 490, 1 460
Complex	3 248	1 610	1 235	515	440	1 588, 1 462, 1 445

Table 5 UV-Vis data for the ligand HL and its Cu(Ⅱ) complex

Compound	Concentration / ($\mu mol \cdot L^{-1}$)	λ_{max} / nm	ε_{max} / ($L \cdot mol^{-1} \cdot cm^{-1}$)	Assignment
HL	25.12	235	4 612	π-π*
		301	4 861	π-π*
Complex	27.4	240	5 248	π-π*
		280	5 624	π-π*
		328	5 925	π-π*

absorption peak is observed at 301 nm, which is absent in the spectrum of the Cu(Ⅱ) complex. The other feature is that the absorption peak at 235 nm in HL is shifted to 240 nm in the Cu(Ⅱ) complex, and two new absorption peaks at 280 and 328 nm are observed in the Cu(Ⅱ) complex, indicating that the coordination of the Cu(Ⅱ) atom with HL.

2.4　Molar conductance of [Cu(L)$_2$]·CH$_3$OH

　　The Cu(Ⅱ) complex is soluble in ethanol, methanol, acetonitrile, acetone, THF, DMF, DMSO, but not soluble in diethyl ether and n-hexane. Molar conductance value of the Cu(Ⅱ) complex at 25 ℃ of 1 mmol·dm^{-3} DMF solutions is 2.8 $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$, indicating that the Cu(Ⅱ) complex is non-electrolyte. This implies that all the L$^-$ units in the Cu(Ⅱ) complex are always held in the coordination sphere in solution or solid state.

2.5　Thermal property of [Cu(L)$_2$]·CH$_3$OH

　　The thermal decomposition of the Cu(Ⅱ) complex can be mainly divided into two stages. First, the initial weight loss occurs in the range of 49.0 to 67.2 ℃, corresponding to an endothermic peak, and the TG curve shows that the weight loss corresponding to this temperature range is 4.3% that roughly coincides with the value of 4.6%, calculated for the loss of one crystalling methanol molecule; The Cu(Ⅱ) complex has no melting point. The Cu(Ⅱ) complex is more thermally stable than its ligand HL. Its second weight loss starts at around 265.6 ℃. Subsequently, continuous mass loss was observed up to 650 ℃. At this temperature, CuO is formed. The total mass loss found (86.7%) was approximately consistent with that calculated (88.5%).

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