Synthesis, Characterization and Crystal Structure of 1-(4-[(*E*)-4-Methoxyl-2-hydroxybenzylidene]amino}phenyl)ethanone Oxime and Its Copper(II) Complex

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A new Cu(II) complex, [Cu(L)₂], has been synthesized *via* the complexation of copper(II) acetate monohydrate with a new oxime-type ligand (HL = 1-(4-[(*E*)-4-methoxyl-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 Cu1O2N2) is 36.49 (3)°. In the crystal structure, each molecule links two other adjacent molecules into an infinite one-dimensional supramolecular structure along the *b* axis through intermolecular O1-H1...O2 hydrogen bonds and C16-H16B...O1 hydrogen bonds.

Keywords: Oxime-type ligand, Cu(II) complex, Synthesis, Crystal structure, Thermal property.

INTRODUCTION

Oxime-type compounds are known to be versatile ligands in coordination chemistry. A large number of complexes with oxime-type ligands have been reported because of their interesting structures and potential applications¹. Copper(II) complexes with oxime-type ligands have been widely investigated in coordination chemistry and biological chemistry²⁻⁵. 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 chemistry⁶⁻⁸. It appears that the biological role of copper is primarily in redox reactions and as a biological catalyst, although much remains to be understood⁹. 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 behaviour of copper-containing enzymes¹⁰. The peculiarity of copper lies in its ability to form complexes with coordination number four, five or six¹¹⁻¹³. As an extension of the work on the structural characterization of such complexes¹⁴⁻¹⁹, the crystal structure of a new Cu(II) complex, [Cu(L)₂], is reported in this paper.

EXPERIMENTAL

4-Methoxyl-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. The others are the same as literature¹⁶⁻¹⁹.

Synthesis of the ligand HL: HL (1-(4-[(*E*)-4-methoxyl-2-hydroxybenzylidene]-amino}phenyl)ethanone oxime) was synthesized by modification of the reported method^{14,15}. To an ethanolic solution of 2-hydroxy-4-methoxybenzaldehyde (304.3 mg, 2 mmol) was added an ethanol solution of 4-aminophenylethanone oxime (300.4 mg, 2 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. 438-440 K. Anal. Calcd. for C₁₆H₁₆N₂O₃ (%): C 63.10; H 5.26; N 9.20. Found(%): C, 63.35; H, 5.29; N, 9.47.

Synthesis of the Cu(II) complex: A solution of copper(II) acetate monohydrate (2.4 mg, 0.012 mmol) in ethanol (2 mL) was added dropwise to a solution of HL (7.3 mg, 0.024 mmol) in ethanol (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 two weeks, the solvent was partially evaporated and obtained several green block-like single crystals suitable for X-ray crystallographic analysis. Anal. Calcd. for C₃₂H₃₀N₄O₆Cu {[Cu(L)₂]}(%): C 64.21; H 5.02; N 9.36; Cu 9.36. Found: C64.52; H 5.11; N 9.14; Cu 9.29.

X-ray structure determination: The X-ray diffraction measurement for the Cu(II) complex was performed on Bruker Smart 1000 CCD diffractometer with graphite monochromated MoK α radiation ($\gamma = 0.071073$ 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. 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 Cu(II) complex are summarized in Table-1. CCDC: 871832.

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR THE Cu(II) COMPLEX

Empirical formula	C ₂₂ H ₃₀ N ₄ O ₆ Cu
Formula weight	630.14
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
Cell dimensions, (Å, °)	a = 10.3561(9), b = 17.3002(16), c = 8.3000(6), β = 101.399(2)
Volume (Å ³)	1457.7(2)
Z	2
Density (calculated) (mg/m ³)	1.436
Absorption coefficient (mm ⁻¹)	0.801
$F(000)$	654
Crystal size (mm)	0.45 × 0.43 × 0.40
Index ranges	-12 ≤ h ≤ 11, -20 ≤ k ≤ 19, -8 ≤ l ≤ 9
Reflections collected	7335 ($R_{\text{int}} = 0.0380$)
Independent reflections	5375
Reflections observed [$I > 2\sigma(I)$]	3761
Data/restraints/parameters	2568/0/198
Goodness of fit indicator	1.054
$R [I > 2\sigma(I)]$	$R_1 = 0.0454$, $wR_2 = 0.0853$
Largest diff. peak and hole (e Å ⁻³)	526, -256

RESULTS AND DISCUSSION

Molar conductance: 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 °C of 10⁻³ mol dm⁻³ DMF solutions is 3.1 Ω^{-1} cm² 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.

FT-IR spectra: The FT-IR spectra of HL and its corresponding Cu(II) complex in the 4000-400 cm⁻¹ region is given in Table-2. The free ligand HL exhibits characteristic (C=N) stretching band at 1615 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 about 5 cm⁻¹ upon complexation, indicating the behaviour between the free ligand and the corresponding Cu(II) atom resulting in weakening the force constant of (C=N) bond. The Ar-O stretching frequency appear as a strong band in the 1253 cm⁻¹ in the free ligand and the toward lower wavenumber of the Ar-O absorption shift

TABLE-2
MAIN IR BANDS FOR THE LIGAND
HL AND ITS Cu(II) COMPLEX (cm⁻¹)

Comp.	$\nu_{(\text{O-H})}$	$\nu_{(\text{C=N})}$	$\nu_{(\text{Ar-O})}$	$\nu_{(\text{Cu-N})}$	$\nu_{(\text{Cu-O})}$	$\nu_{(\text{C=C})}$ benzene ring skeleton
HL	3391	1623	1296	—	—	1594, 1541, 1459
Complex	—	1615	1206	565	467	1591, 1532, 1442

about 18 cm⁻¹ indicating that (Cu-O) bonds are formed between the Cu(II) atom and the oxygen atoms of the phenolic groups^{20,21}.

In the 1594-1459 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 3391 cm⁻¹, which disappears in the Cu(II) complex.

The far-infrared spectrum of the Cu(II) complex was also obtained in the region 500-100 cm⁻¹ in order to identify frequencies due to the Cu-O and Cu-N bonds. The FT-IR spectrum of the Cu(II) complex showed $\nu(\text{Cu-N})$ and $\nu(\text{Cu-O})$ vibration absorption frequencies at 565 and 467 cm⁻¹, respectively¹⁶.

UV-visible absorption spectra: The UV-visible absorption spectra of HL and its Cu(II) complex in DMF solution are shown in Table-3. 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 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.

TABLE-3
UV-VISIBLE SPECTRAL DATA FOR THE LIGAND
HL AND ITS Cu(II) COMPLEX

Comp.	Concentration (×10 ⁻⁵ mol L ⁻¹)	λ_{max} (nm)	λ_{max} (L mol ⁻¹ cm ⁻¹)	Assignment
HL	5.00	286	12200	$\pi-\pi^*$
		354	15800	$\pi-\pi^*$
Complex	5.00	304	24600	$\pi-\pi^*$
		378	15200	$\pi-\pi^*$

Crystal structure of the Cu(II) complex: X-ray crystallographic analysis of [Cu(L)₂] reveals formation of a mononuclear structure. The Cu(II) complex crystallizes in the monoclinic system, space group P2(1)/c and Z = 2. The Cu(II) complex consists of one Cu(II) atom, two deprotonated L⁻ units, as expected 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-4.

In symmetric 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 L⁻, in a slightly distorted square-planar geometry. The coordinate bond lengths and angles around the Cu atom (Table-4) are typical and comparable to the corresponding values

TABLE-4
SELECTED BOND DIATANCES (Å) AND
ANGLES (°) FOR THE Cu(II) COMPLEX

Bond	Lengths	Bond	Lengths	Bond	Lengths
Cu1-O2 ^{#1}	0.1873(2)	Cu1-O2	0.1873(2)	Cu1-N2 ^{#1}	0.1993(3)
Cu1-N2	0.1993(3)				
Bond	Angles	Bond	Angles	Bond	Angles
O2 ^{#1} -Cu1-O2	180.0	O2 ^{#1} -Cu1-N2 ^{#1}	91.31(9)	O2-Cu1-N2 ^{#1}	88.69(9)
O2 ^{#1} -Cu1-N2	88.69(9)	O2-Cu1-N2	91.31(9)	N2 ^{#1} -Cu1-N2	180.0
C9-N2-Cu1	122.8(2)	C6-N2-Cu1	118.8(2)	C11-O2-Cu1	126.3(2)

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

Fig. 1. Crystal structure of the Cu(II) complex with the atom numbering. Thermal ellipsoids are plotted at 30 % probability level. Symmetry code: ^{#1} -x + 1, -y + 1, -z + 1; H atoms are omitted for clarity

observed in other Cu(II) complexes with oxime-type ligands²². The two deprotonated oxime-type ligands L⁻ are coordinated in a *trans* fashion. The dihedral angle between the coordination plane of O2^{#1}-Cu1-N2^{#1} and that of N2-Cu1-O2 is 36.49 (3)°, while another dihedral angle between the coordination plane of N2^{#1}-Cu1-O2 and that of O2^{#1}-Cu1-N2 is 43.76 (3)°, indicating slight distortion toward tetrahedral geometry from the square planar structure.

Intermolecular interactions of the Cu(II) complex: 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 of one ligand molecule is bonded to the hydroxyl -O1H41 group of the other ligand unit of the Cu(II) complex (Table-5). Simultaneous, the oxime O1 of the ligand unit in the Cu(II) complex are hydrogen-

TABLE-5
HYDROGEN-BONDING
INTERACTIONS (Å, °) FOR THE Cu(II) COMPLEX

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠D-H...A
O1-H1...O2	0.82	1.95	164	2.748(3)
C16-H16B...O1	0.96	2.38	151	3.253(4)

Fig. 2. Intermolecular hydrogen bonds of the Cu(II) complex. Hydrogen atoms are omitted for clarity

bonded to the -C16H16B group of another adjacent Cu(II) complex unit. Thus, each molecule links two other adjacent molecules into an infinite one-dimensional chain supramolecular structure through intermolecular O1-H1...O2 hydrogen bonds and C16H18...O1 hydrogen bonds. As illustrated in Fig. 3.

Fig. 3. One-dimensional chain supramolecular structure of the Cu(II) complex

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