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CRYSTAL STRUCTURE AND ACTIVITY OF A NEW Cu(II) COMPLEX WITH O...Cu WEAK INTERACTION© 2011 W. Wang¹, X. Zhou¹, Y.-S. Ma², Z.-C. Zhang³, R.-X. Yuan², B.-G. Zhao³, L. Xu*^{1,4}¹College of Science, Nanjing Forestry University, Nanjing, China, 2 10037²Department of Chemistry and Materials Engineering, Changsu Institute of Technology, Changsu, China³College of Forest Resources and Environment, Nanjing Forestry University, Nanjing, China⁴State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, China

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A new CuL₂ (HL = α -hydroxyacetophenone) complex is synthesized and investigated by elemental analysis, IR, UV-Vis, and X-ray diffraction. The complex crystallizes in the orthorhombic space group *Pbca*, $a = 14.595(3)$, $b = 12.517(3)$, $c = 15.474(3)$ Å, $V = 2826.88(1)$ Å³, $Z = 4$. The title complex has a square-planar geometry around the central Cu²⁺ ion. Two molecules form a dimer via a weak Cu1...O3 interaction, and the neighboring dimers of molecules are connected into a 2D structure through two very weak C—H...O interactions. The title complexes has high activity of killing pine wood nematodes.

Key words: Cu(II) complex, structure, square-planar geometry, dimer.

The Schiff base ligands and their metal complexes have been extensively studied for many years [1—4]. These complexes play an important role in the development of coordination chemistry [5, 6]. Especially, Schiff base complexes containing amino acids have attracted an increasing amount of attention due to their anticancer, antiviral, and antibacterial activities [7, 8]. Taurine (2-aminosulfonic acid), a β -amino acid with the sulfo group (—SO₃H), is indispensable to human beings and plays an important role in physiological functions. During the synthesis of the taurine Schiff base complex, the title complex was obtained. The new complex has been investigated by X-ray diffraction.

EXPERIMENTAL

Materials and instrumentation. All commercially available chemicals were of analytical grade and used without further purification. Elemental analyses for C, H, N were performed on a Perkin-Elmer 240C Instrument. Infrared spectra were recorded in the 400—4000 cm⁻¹ range on a infrared spectra were recorded in 400—4000 cm⁻¹ range on a Bruker VETERX-70 spectrometer, and ultraviolet spectra was recorded on a SHIMADZU UV-2450 spectrometer.

Synthesis of the title complex. Method 1: After a mixture of α -hydroxyacetophenone (1 mmol) and taurine (1 mmol) in MeOH (5 ml), and KOH (1 mmol) in H₂O (2 ml) was refluxed for 2 h, Cu(AcO)₂·H₂O (0.5 mmol), 1 mmol *p*-phthalic acid, and 2 mmol KOH were added, and the reaction was refluxed for another 8 h. The green solid was collected by filtration and washed with cool MeOH. Single crystals suitable for X-ray diffraction were obtained by evaporation of the filtrate. Anal. Calcd for C₃₂H₂₈Cu₂O₈ (%): C 57.57, H 4.23. Found: C 57.62, H 4.19; UV-Vis (CH₃OH) data: λ_{\max}/nm ($\log(\epsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1})$): 202 (3.592), 269 (3.289), 300 (2.924), 364 (3.087), 402 (3.127).

Method 2: After a mixture of α -hydroxyacetophenone (1 mmol) and Cu(AcO)₂·H₂O (0.5 mmol) in MeOH (5 ml) was refluxed for 2 h, a dark green solution was obtained. Green solid was collected

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by filtration and washing with ethyl ether after evaporating part of solvent. Anal. Calcd for $C_{32}H_{28}Cu_2O_8$ (%): C 57.57, H 4.23. Found: C 57.52, H 4.28.

Crystallographic studies. Single crystal X-ray diffraction data were collected on a pale green block crystal of the title complex with the use of graphite monochromatic MoK radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K on a Bruker XSCANS diffractometer with the program SMART [9]. Cell refinement and data reduction were carried out with the use of the SAINT program [9], and the structure was solved and refined using the SHELXTL V6.14 software package [10].

The structure was solved by direct methods and difference Fourier maps. Full matrix least-squares refinements were carried out with anisotropy thermal parameters for all nonhydrogen atoms. Hydrogen atoms were placed in the calculated positions with C—H distances of 0.93–0.96 Å with isotropic thermal parameters and were included in the refinement in riding motion approximation with $U_{iso} = 1.2U_{eqI}$ or $U_{iso} = 1.5U_{eqI}$, where C is a parent C atom to which the H atom is attached.

Crystal data and refinement parameters: $C_{32}H_{28}Cu_2O_8$ ($M = 667.62$), orthorhombic, $Pbca$ space group, $a = 14.595(3) \text{ \AA}$, $b = 12.517(3) \text{ \AA}$, $c = 15.474(3) \text{ \AA}$, $V = 2826.88(100) \text{ \AA}^3$, $Z = 4$, $\mu(\text{MoK}\alpha) = 1.557 \text{ mm}^{-1}$, $d_x = 1.569 \text{ g/cm}^3$. Final R indices: $R = 0.0423$ and $wR2 = 0.0997$ for 2705 observed reflections with intensities higher than 2σ (refinement on F^2), 192 parameters, 0 restraints; $R = 0.053$ and $wR2 = 0.104$ for all 3237 reflections collected; GOOF = 1.227.

A CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 734398, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif

RESULTS AND DISCUSSION

Molecular and crystal structure. The structure of the title complex is shown in Fig. 1. The selected bond distances and angles are given in Table 1. Fig. 2 shows the packing of the title complex in the unit cell.

The title complex has a square-planar geometry around the central Cu^{2+} ion that is coordinated by two α -hydroxyacetophenone ligands (Fig. 1). Two acyl O atoms are in a *trans* configuration. The CuO_4 moiety has approximate local C_i symmetry. The whole molecule includes two planes. O1/O2/Cu1/C1/C2/C3/C4/C5/C6/C7/C8 and O3/O4/Cu1/C9/C10/C11/C12/C13/C14/C15/C16 are

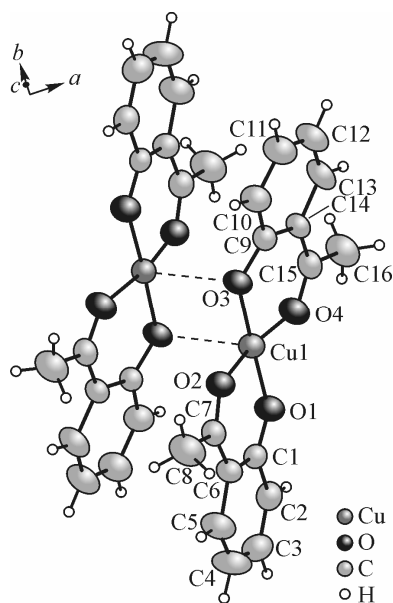


Fig. 1. Dimer structure of the title copper complex with a Cu...O weak interaction

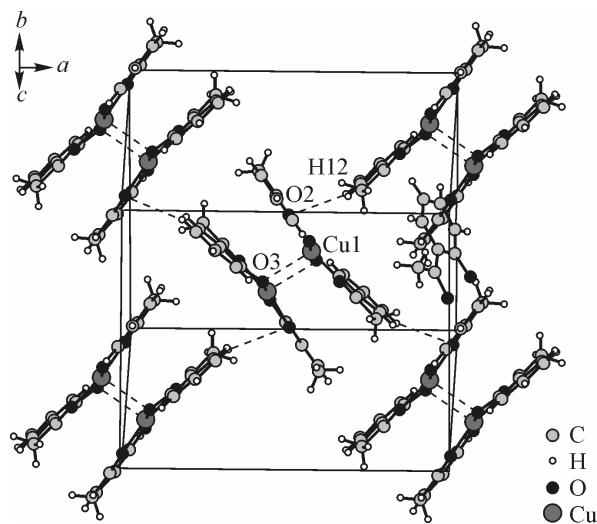


Fig. 2. Packing of the title complex in the unit cell, showing very weak hydrogen bonds as dashed lines

Table 1

Selected Bond Distances (Å) and bond angles (deg.)

Cu1—O1	1.868(2)	Cu1—O3	1.889(2)	O1—Cu1—O3	176.98(9)	O1—Cu1—O4	86.28(9)
Cu1—O4	1.940(2)	Cu1—O2	1.9431(19)	O3—Cu1—O4	91.40(9)	O1—Cu1—O2	92.23(9)
O2—C7	1.253(3)	O4—C15	1.237(4)	O3—Cu1—O2	89.71(8)	O4—Cu1—O2	169.59(9)
O1—C1	1.300(4)	C9—O3	1.313(3)	C7—O2—Cu1	128.3(2)	C15—O4—Cu1	129.7(2)
				C1—O1—Cu1	127.9(2)	C9—O3—Cu1	126.46(18)

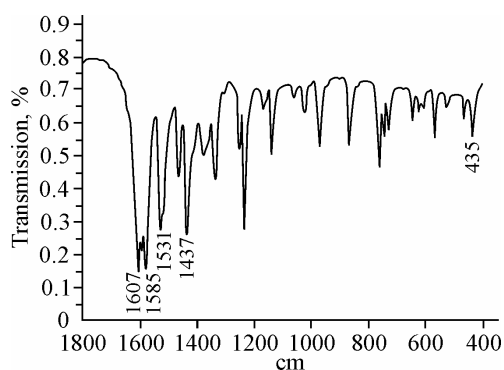


Table 2

Hydrogen bonding geometry (Å, deg.)

D—H...A	D—H	H...A	D...A	D—H...A
C12—H12...O2 ⁱ	0.930	3.005	3.620(5)	125.06(27)

Symmetry codes: (i) 0.5+x, 1.5-y, 1-z.

Fig. 3. Infrared spectrum of the title complex

planar with an average deviation of 0.0349 and 0.0763 Å respectively. The dihedral angle between the two planes is 13.23(9)°.

The average Cu—O bond distance of 1.910 Å is comparable with those found in other complexes with a CuO₄ core, e.g. bis(2-oxopyridinato N-oxide-K2O,O')copper(II) (1.919 (3) Å) [11]; bis(1,2-dimethyl-3-hydroxypyridin-4-one-O,O')copper(II) (1.920 (2) Å) [12], and bis(1,2-diethyl-3-hydroxypyridin-4-one-O,O')copper(II) (1.918 (2) Å) [12].

Dimers are formed by Cu1...O3ⁱ weak interactions [symmetry code: (i) -x, 2-y, 1-z] (Fig. 1). The Cu1...O3ⁱ distance is 2.593(2) Å, which is much longer than the average Cu—O bond distance (1.910 Å) within the molecule, but less than the sum of van der Waals radii of copper and oxygen (2.92 Å) [13–15]. Similarly, on account of the weak Cu...O interactions, one-dimensional chains are formed in a Cu^{II} (4,5-diazafluoren-9-one)-capped Keggin derivative with a Cu...O distance of 2.852 Å [16].

There are no intermolecular π—π interactions because the distance between two phenyl ring centers is too long (4.040(1) Å). Fig. 2 and Table 2 show that the neighboring dimers of the molecule are connected to form a 2D structure through other two weak C—H...O interactions [C12—H12...O2].

Infrared spectral characteristics. In the infrared spectrum (Fig. 3), a strong peak at ca. 1607 cm⁻¹ is attributable to the acyl group. There is a band at 435 cm⁻¹ from Cu—O bonds [17], which suggests that the α-hydroxyacetophenone ligand is coordinated to the copper atom via phenolic oxygen atoms. Medium to strong bands in the 1585 ~ 1437 cm⁻¹ range seem to be due to vibrations associated with the aromatic C=C fragments of the ligands. The new complex has high activity of killing pine wood nematodes.

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