研究简报

N-邻羟苄亚基苯胺 Schiff 碱铜配合物的合成、结构和性能表征

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Synthesis, Structure and Properties of Copper(Ⅱ) Complex with Schiff Base Ligand N-Salicylidene-aniline: [Cu($C_{13}H_{10}NO)_2$]

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The structure of the title compound has been determined by X-ray crystallography. Each copper atom is chelated by two N-salicylidene-aniline anion ligands with Cu-O and Cu-N distances of 0.187 6(3) and 0.200 1(4) nm, respectively. The central copper(Ⅱ) is four-coordinated and in distorted square-planar environment. The phenyl rings with salicylidene moieties form a dihedral angle of 65.40°. There are C–H$\cdots\pi$ supramolecular interactions in the crystal structure. The title compound is also examined by elemental analysis, FT-IR, UV spectra and TG-DSC analysis. CCDC: 222315.

Keywords: **Schiff base** **copper(Ⅱ) complex** **TG** **crystal structure**

0 Introduction

Currently there is considerable interest in the coordination chemistry of transition metals with the Schiff base family of ligands[1,2]. We selected the salicylidene Schiff base as a ligand because it could promote chelation and provide extra stability to the metal center. Also, copper(Ⅱ) complex of N-substituted salicylideneaminates may be used as an active catalyst for cyclopropanation of tetramethylethylene to produce alkylchrysanthemate[3] and as inhibitor in the oxidation of polyethylene glycols in solution[4]. In this paper, we report the crystal structure of the Schiff base of N-salicylaldene-aniline copper (Ⅱ) complex. Also, the structure of this compound has been characterized by TA, FT-IR, UV spectra and TG-DSC analysis.

1 Experimental

1.1 Synthesis of Schiff Base N-salicylaldene-aniline

All chemicals were of analytical grade and used directly without further purification. A solution of salicylaldehyde (2.72 g, 20.0 mmol) in anhydrous ethanol (100 mL) was added dropwisely to a solution of aniline (1.86 g, 20.0 mmol) in 100 mL of anhydrous

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ethanol. The reaction mixture was stirred for 1 h at room temperature, and yielded a yellow precipitation. The yellow product was filtrated and recrystallized with ethanol. The yellow crystals were obtained, yielding 90%.

1.2 Synthesis of bis(N-salicylaldene-aniline) Schiff Base Copper(Ⅱ) Complex

Copper(Ⅱ) benzoate (0.15 g, 0.5 mmol) was added to a hot solution of N-salicylaldene-aniline (0.20 g, 1.0 mmol) in EtOH (40 mL) and refluxed for 2 h. The reaction lasted until the yellow color completely disappeared and a brown solid precipitated. The precipitation was filtrated and dissolved in EtOH, and the solution was evaporated at room temperature. Brown rhombohedra crystals were obtained. The C, H and N content was determined by elemental analysis (Anal. Cald.(%) for $C_{26}H_{20}CuN_2O_2$: C 68.48, H 4.42, N 6.14; Found(%) C 68.62, H 4.25, N 6.09).

1.3 Physics Measurement

Elemental analysis for carbon, hydrogen and nitrogen was measured with a Perkin-Elmer 1400C analyzer. IR spectra (4 000~400 cm^{-1}), as KBr pellets, were recorded on a Nicolet FT-IR 170X spectrophotometer. Electronic spectra, as water solvent, were taken on a UV-Vis-NIR 756 spectrophotometer. Thermal gravity (TG) and differential scanning calorimetry (DSC) were recorded on an SDT 2980 simultaneously for the samples of *ca.* 10 mg under a nitrogen atmosphere (150 mL·min^{-1}) at a heating rate of 10 ℃·min^{-1}.

1.4 Crystallographic Data Collection and Structure Determination

X-ray diffraction data were collected on a Siemens P4 diffractometer for a brown rhombohedral crystal, using graphite monochromated Mo$K\alpha$ radiation (λ=0.071 073 nm). The technique used was ω-scan with θ limits of 2.03°<θ<24.91°. The structure of the title compound was solved by direct methods and refined by least squares on F^2 by using the SHELXTL[5] software package. All non-H atoms were anisotropically refined. All hydrogen atoms were included in calculated position. The final residual factors are $R(F)$=0.045 0 and wR (F^2)=0.108 0 for 1 151 reflections with $I>2\sigma(I)$ and weighting scheme, $w=1/[\sigma^2(F^2)+(0.059\ 0P)^2]$, where $P=(F^2+2F_c^2)/3$, S=0.994.

CCDC: 222315.

2 Results and Discussion

2.1 Crystal and Molecular Structure of the Title Compound

Fig.1 shows the molecular structure of the title compound. Fig.2 shows the crystal packing in the unit cell of the title compound. A summary of the key crystallographic information is given in Table 1. Selected bond lengths and bond angles are presented in Table 2. The crystal structure has a center of symmetry at the copper atom. The copper(Ⅱ) ion is in a coordination sphere of a slightly distorted *trans* square-planar configuration with two equivalent Cu-N and Cu-O bonds. The Schiff base loses a proton from the hydroxyl group and acts as a single charged bidentate ligand coordinating to copper(Ⅱ) through the hydroxyl O and amino N atoms. The six-membered chelated rings are fairly co-planar, the deviation of copper atom

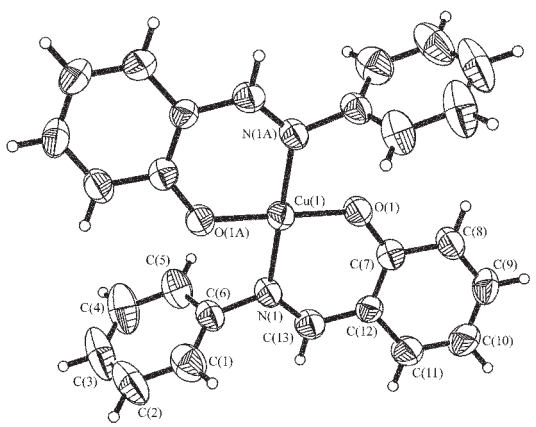

Fig.1 Structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme

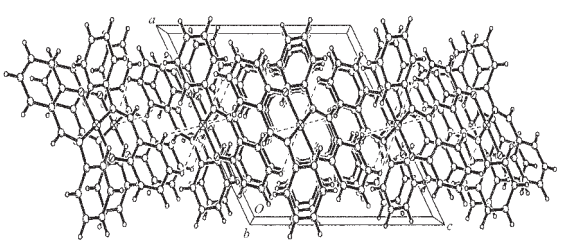

Fig.2 A view of the crystal packing down the *b* axis for the title compound

Table 1　Crystal Data and Structure Refinement for the Title Compound

empirical formula	$C_{26}H_{20}CuN_2O_2$
formula weight	455.98
temperature / K	293(2)
crystal system	monoclinic
space group	$P2_1/c$
a / nm	1.195 6(2)
b / nm	0.797 99(16)
c / nm	1.343 1(5)
β / (°)	122.843(18)
volume / nm^3	1.076 6(5)
Z	2
calculated density / (Mg·m^{-3})	1.407
absorption coefficient / mm^{-1}	1.040
F(000)	470
crystal size / mm	0.31 × 0.24 × 0.20
θ range for data collection / (°)	2.03 to 24.91
limiting indices	$0 \leqslant h \leqslant 15$, $-10 \leqslant k \leqslant 10$, $-16 \leqslant l \leqslant 14$
reflections collected / unique	2914 / 1787 [R(int)=0.033 2]
completeness to θ=24.91	98.0%
data / restraints / parameters	1 787 / 0 / 143
goodness-of-fit on F^2	0.994
final R indices [$I>2\sigma$]	R_1=0.045 0, wR_2=0.108 0
R indices (all data)	R_1=0.103 0, wR_2=0.118 3
largest diff. peak and hole / (e·nm^{-3})	289 and −430

Table 2　Bond Lengths (nm) and Angles (°) for the Title Compound

Cu(1)-O(1)	0.187 6(3)	Cu(1)-N(1)	0.200 1(4)
O(1)-C(7)	0.131 0(5)	N(1)-C(13)	0.128 9(5)
N(1)-C(6)	0.145 8(5)	C(12)-C(13)	0.143 2(6)
O(1)-Cu(1)-N(1)	91.42(13)	O(1)-Cu(1)-N(1)#1	88.58(13)
C(13)-N(1)-C(6)	116.4(4)	N(1)-C(13)-C(12)	125.7(4)
C(11)-C(12)-C(13)	117.1(4)		

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

from the least squares plane through the ring atoms is 0.001 5 nm. The copper atom is located in the center of the coordination plane defined by O(1), N(1), C(7), C(12), C(13) and O(1A), N(1A), C(7A), C(12A), C(13A). This plane is nearly parallel to that of salicylaldene plane. The dihedral angle between them is only 7.30(2)°. The planes of phenyl ring and the salicylidene group form a dihedral angle of 65.40(2)°. The bond distances of Cu-O(1) and Cu-N(1) are 0.187 6(3) and 0.200 1(4) nm, respectively. All these parameters are in close agreement with those reported for square-planar copper(Ⅱ) compounds[6~8]. The C-C, C-O and C-N bond lengths of the title compound are in normal range.

There are C–H$\cdots\pi$ supramolecular interactions[9] in the lattice (See Table 3). The feature of intermolecular interaction is due to the two types of C–H$\cdots\pi$ supramolecule interactions between C-H and salicylidene rings in the crystal lattice. The distances between C(4)-H(4A) to salicylidene ring and C(13)-H(13A) to salicylidene ring are 0.374 2(3) and 0.395 6(2) nm, respectively. The crystal structure was stabilized by hydrogen bonds which connected molecule to form hydrogen bonds networks. The intermolecular interaction distances of the title compound are listed in Table 3.

2.2　IR and UV Spectra

In the IR spectrum, there are strong and broad absorption bands at around 3 450 cm^{-1}, which may be the absorption for unsaturated C-H bond stretching vibration of aniline ring and salicylidene ring[10]. The three absorptions bands at 1 609, 1 592 and 1 535 cm^{-1} are attributed to $\nu_{C=N}$[11]. The absorption bands at 1 329 cm^{-1} attribute to phenolic C-O stretching vibration. The bands at around 1 450~1 535 cm^{-1} attribute to C=C of the phenyl ring. A broad medium band at about 3 100 cm^{-1} due to ν_{O-H} of salicylidene in the free ligand disappears in the IR spectra of the Cu(Ⅱ) complex, this suggests that the coordination of copper(Ⅱ) through deprotonated phenolic oxygen.

The UV spectra of the title complex show one strong band at about 267 nm. The band is assigned to the π-π^* transition of C=N or C=C bands. There is a medium bond at about 343 nm which attribute to ligand to metal charge transfer (LMCT). In addition, there is a wide bond at about 700 nm, which is assigned to the d-d transition of copper ion.

Table 3 Intermolecular Interaction Distances (nm) of the Title Compound

D H A	symm	D-H	H···A	D···A	D–H···A
C(4)–H(4A)···C_g(sal)	1–*x*, 1–*y*, –*z*	0.093 00	0.294 0	0.374 2	145.32
C(13)–H(13A)···C_g(sal)	1–*x*,1/2+*y*,1/2–*z*	0.093 00	0.304 4	0.395 6	167.37

C_g(I)=Plane number Ⅰ

2.3 Thermal Analysis

Differential scanning calorimetry (DSC) of the title compound reveals that there are one intense exothermic peak and two weak exothermic peaks. There is one weak peak at 99.4 ℃ but no weight loss, which suggests that the title compound melts. At 220 ℃, decomposition occurs. The first process of the weight loss corresponds to the loss of four phenyl rings (found 65.08% calc. 67.19%) with one intense endothermic peak at 236.2 ℃ and one weak exothermic peak at 296.5 ℃, and residue may be $Cu(CN)_2O_2$. The second process of the weight loss is attributed to the cracks of Cu-O bond and corresponds to the loss of two oxygen atoms (found 7.88% calc. 7.01%). The final weight of the residue suggests existence of $Cu(CN)_2$ (found 25.00% calc. 25.35%).

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