研究简报

呋喃甲醛缩二乙撑三胺希夫碱铜配合物的合成及结构

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Synthesis and Structure of a New Copper(Ⅱ) Complex with Schiff Base Derived from Furaldehyde and Diethylenetriamine

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Abstract: A novel copper(Ⅱ) complex $CuL(NO_3)_2$ (where L=*N*,*N*′-bis(furaldehyde)-diethylenetriamine) was synthesized and characterized by X-ray crystallography analysis. The crystal belongs to monoclinic, space group *C*2/*c* with cell parameters *a*=1.924 0(6) nm, *b*=0.792 8(3) nm, *c*=2.504 1(8) nm, *β*=111.163(5)°, and *Z*=8. The coordination geometry around Cu(Ⅱ) is a distorted trigonal-bipyramid, and one-dimensional chain is formed through intermolecular hydrogen bonds. CCDC: 255629.

Key words: furaldehyde; Schiff base; copper(Ⅱ) complex; crystal structure

0 Introduction

Schiff base ligands have played an important role in the development of coordination chemistry since the late 19th century. The finding that metal complexes of these ligands are ubiquitous is a reflection of their facile synthesis, wide application and the accessibility of diverse structural modifications[1]. Schiff base complexes are of great interests especially for inorganic and bioinorganic chemistry. To the best of our knowledge, in the past two decade years, Schiff base complexes derived from furaldehyde have been less reported[2]. In a recent paper[3], we have reported the synthesis, crystal structure of the complex ZnL_1Cl_2 (L_1=*N*, *N*′-bis(2-furaldehyde)ethylenediamine. From a chemical point of view, Schiff base *N*,*N*′-bis(furaldehyde)-diethylenetriamine is considered to be a good type of chelating ligand, which can coordinate to transition metals as a tridentate, tetradentate or pentadentate ligand, with consequent variable chemical properties. In this paper, we report the synthesis and crystal structure of a new copper (Ⅱ) complex $CuL(NO_3)_2$ (L =*N*,*N*′ -bis (furaldehyde)-diethylenetriamine).

1 Experimental

1.1 Materials and instruments

All reagents were of analytical grade from commercial sources and used without further purification. Elemental analyses were performed on a Vario EL-Ⅲ instrument. Infrared spectra were recorded on an E-

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quinox55 spectrophotometer in the 4 000~400 cm^{-1} regions using a powdered sample on a KBr plate. Electronic spectrum was recorded on a CARY 300 Bio spectrophotometer.

1.2 Synthesis of the complex $CuL(NO_3)_2$

To a solution of diethylenetriamine (0.109 mL, 1.0 mmol) in 30 mL of dichloromethane was added furaldehyde (0.167 mL, 2.0 mmol). The mixture was stirred for 30 min at 25 ℃ in the presence of anhydrous sodium sulfate as a drying agent. The resultant bright yellow solution was filtered and the filtrate was concentrated under reduced pressure, leaving a yellow oil (L), which was dissolved in 20 mL of methanol and $Cu(NO_3)_2 \cdot 3H_2O$ (0.241 6 g, 1.0 mmol) was added. After stirring for 30 min at 25 ℃ the solution turned to dark blue, which was filtered off. The blue single crystal suitable for X-ray analysis was obtained by slow evaporation of the filtrate at room temperature. Yield: 0.350 g (81%). Anal.calcd for $C_{14}H_{17}N_5O_8Cu$ (%): C 37.58, H 3.80, N 15.65. Found (%): C 37.51, H 3.64, N 15.49. IR (KBr) ν: 1 643, 1 279, 1 332, 1 427, 3 421, 3 128.

1.3 X-ray crystallography

The diffraction data were collected on a Brucker Smart Apex CCD diffractometer employing graphite monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) with φ-ω scan mode. The structure was solved by direct method[4] and least-squares refinement was performed with the program SHEXTL-97[5]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically. The Crystallographic data, conditions used for the intensity collections, and some features of the structure refinement are listed in Table 1.

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Table 1　Crystal data and structure refinement

Chemical formula	$C_{14}H_{17}N_5O_8Cu$	F(000)	1 832
Formula weight	446.87	Crystal size / mm	0.45 × 0.41 × 0.14
Temperature / K	298(2)	θ range for data collection / (°)	1.74 to 25.03
Wavelength / nm	0.071 073	Limiting indices	$-22 \leqslant h \leqslant 22, 8 \leqslant k \leqslant 9, -29 \leqslant l \leqslant 20$
Crystal system	Monoclinic	Completeness to θ=25.03°	100%
Space group	$C2/c$	Reflections collected / unique	9 122 / 3 156 [R_{int}=0.048 7]
a / nm	1.924 0(6)	Absorption correction	ψ-scan
b / nm	0.792 8(3)	Refinement method	Full-matrix least-squares on F^2
c / nm	2.504 1(8)	Data / restraints / parameters	3 156 / 6 /253
β / (°)	111.163(5)	Goodness-of-fit on F^2	0.994
Volume / nm^3	3.561 8(19)	Final R indices [$I>2\sigma(I)$]	R_1=0.042 2, wR_2=0.074 6
Z	8	R indices (all data)	R_1=0.077 6, wR_2=0.080 7
Calculated density / ($g \cdot cm^{-3}$)	1.667	Largest diff. peak and hole / ($e \cdot nm^{-3}$)	528 and −278
Absorption coefficient / mm^{-1}	1.282		

2 Results and discussion

2.1 IR and UV-Vis spectra of the complex

The IR spectrum of the title complex displays a characteristic strong absorption at 1 643 cm^{-1} assigned to the $\nu_{C=N}$ of the Schiff base moiety owing to the imino group[6,7]. The three strong absorption at 1 279, 1 332 and 1 375 cm^{-1} are attributed to $\nu_{C=C}$ for the furaldehyde ring. Other bands, could be assigned: 3 128 cm^{-1} ($\nu_{C=H}$); 3 421 cm^{-1} (ν_{N-H}). The UV-Vis spectrum has a absorption band at 291 nm which is assigned to the transfers of $\pi \rightarrow \pi^*$. Comparing with the free N,N'-bis (furaldehyde)-diethylenetriamine ligand (271 nm) the absorption band is slightly red-shifed.

2.2 Structure description

The coordination unit and packing view of the title complex are shown in Fig.1 and 2, respectively. The selected bond lengths and angles are listed in Table 2. In the title complex, the two furaldehyde moieties are almost coplanar, but are oriented differently (torsion angle is 5.6°). Each copper(Ⅱ) ion is in five-coordinated environment, which is best described as a distorted trigonal-bipyramid .The metal is bounded to three nitrogen atoms N(1), N(2), N(3) from the

ligand *N*,*N*′-bis (furaldehyde)-diethylenetriamine and two oxygen atoms O(3), O(6) of two NO_3^- anions. The O(3), O(6) and N(2) occupy the equatorial plane, while the N(1) and N(3) atoms occupy the apical positions. The Cu(1)-N(1), Cu(1)-N(2), and Cu(1)-N(3) bond distances are 0.196 5(3), 0.200 1(3), and 0.197 3(3) nm, respectively, which is similar to the typical of Cu-dien (dien=diethyllenetriamine) bond distances reported for the complexes $[Cu(nic)(NO_3)(dien)(H_2O)]\cdot H_2O$ (nic = nicotinate), (average 0.202 31 nm)[8] and $[Cu(Hbz)_2(dien)]$ (H_2bz =5-phenylsulfonamide-1,3,4-thiadiazole-2-sulfonamide), (average 0.202 2 nm)[9]. But these values are slightly shorter than Cu-dien bond distances found in the complex $[Cu(dien)(OAC)]\cdot(ClO_4)$ (average 0.212 6 nm)[10].

Table 2 Selected bond lengths (nm) and angles (°)

Cu(1)-N(1)	0.196 5(3)	Cu(1)-O(3)	0.205 4(2)
Cu(1)-N(3)	0.197 3(3)	Cu(1)-O(6)	0.226 3(3)
Cu(1)-N(2)	0.200 1(3)		
N(1)-Cu(1)-N(3)	168.42(13)	N(2)-Cu(1)-O(3)	149.32(12)
N(1)-Cu(1)-N(2)	83.80(12)	N(1)-Cu(1)-O(6)	92.86(11)
N(3)-Cu(1)-N(2)	84.78(12)	N(3)-Cu(1)-O(6)	94.78(11)
N(1)-Cu(1)-O(3)	93.91(10)	N(2)-Cu(1)-O(6)	121.63(11)
N(3)-Cu(1)-O(3)	94.91(10)	O(3)-Cu(1)-O(6)	89.00(10)

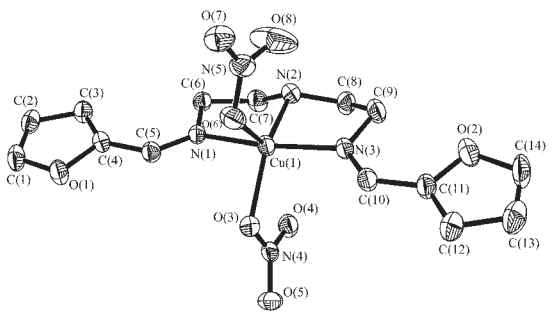

Fig.1 ORTEP view of $CuL(NO_3)_2$
(Hydrogen atoms are not shown for the sake of clarity)

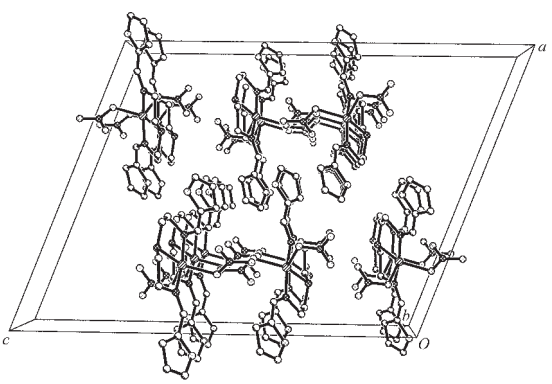

Fig.2 Packing view of $CuL(NO_3)_2$
(Hydrogen atoms are omitted for clarity)

As indicated from the sum of the equatorial angles (359.95°) around the Cu atom [O(3)-Cu(1)-O(6), 89°, O (6)-Cu (1)-N (2), 121.63°, N (2)-Cu (1)-O (3), 149.32°], the distortion of the coordination environment of $CuL(NO_3)_2$ is best illustrated by the deviation of the equatorial angles from 120°. The axial angle N(1)-Cu(1)-N(3) is 168.42°, and much smaller than the ideal value of 180°. Hydrogen bonds are formed by hydrogen atoms of the secondary amines of the ligand L with the O atoms of the coordination NO_3^- anions of another molecule [N(2)–H(2)⋯O(7) 0.305 3 nm, 137.46° (symmetry code i: $-x+1/2$, $y+1/2$, $-z+1/2$)]. Therefore, through the above interaction, a novel one-dimensional chain is formed.

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