

铜的喹哪啶配合物 $[\text{Cu}(\text{Me-quin})_2\text{H}_2\text{O}]$ 的合成、表征及晶体结构

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本文合成了铜的喹哪啶配合物 $[\text{Cu}(\text{Me-quin})_2\text{H}_2\text{O}]$, 并得到蓝色柱状晶体。晶体属正交晶系, 空间群为 $Pbcn$, 晶胞参数 $a = 0.7538(8)\text{nm}$, $b = 0.9109(1)\text{nm}$, $c = 2.4851(5)\text{nm}$, $\alpha = \beta = \gamma = 90^\circ$ 。配合物内每个Cu原子与两个2-甲基-8-羟基喹啉配体中的2个N、2个O和1个水分子中的O原子配位, 形成扭曲的四方锥体, 其中水分子中的O位于锥顶。配合物通过 $\text{O}(2w) - \text{H}\cdots\text{O}(1)$ 形成一维氢键网络, 对结构起到稳定作用。

关键词: 铜配合物 2-甲基-8-羟基喹啉 晶体结构 氢键网状结构 四方锥
分类号: O641.121 O766.3

The Crystal Structure and Spectral Studies of (2-Methyl-8-Quinolinolato) Copper (II) Complex, $[\text{Cu}(\text{Me-quin})_2\text{H}_2\text{O}]$

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The title compound has been prepared and characterized by elemental analysis, IR, UV and EPR spectra and X-ray diffraction single crystal analysis. The crystal belongs to orthorhombic, space group $Pbcn$ with $a = 0.7538(8)\text{nm}$, $b = 0.9109(1)\text{nm}$, $c = 2.4851(5)\text{nm}$, $\alpha = \beta = \gamma = 90^\circ$, and $Z = 4$. In the molecule, the coordination geometry of the central Cu atom is square pyramidal with two N atoms and two O atoms from two 2-methyl-8-quinolinolato ligands in the basal position and one O atom from H_2O in the apical position. The molecules form a one-dimensional hydrogen bond network through $\text{O}(w) - \text{H}\cdots\text{O}$ intermolecular hydrogen bonds, which stabilize the structure of the complex.

Keywords: copper complex 2-methyl-8-quinolinolato-N, O crystal structure
hydrogen bond network square pyramidal

0 Introduction

8-Quinolinol and its substituted analogues have been widely used as an extracting agent for transition metals and in the fluorescence analysis of 3A group elements, as well as in the preparation

收稿日期: 2000-11-10。收修改稿日期: 2000-12-25。

江苏省自然科学基金(No. BK99072)。

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of non-linear optical materials with second harmonic generation at high intensity and stability at room temperature^[1-3]. Its complexes with transition metals have also been found extensive applications. For example, bis(8-quinolinolato-N, O) nickel (II) [Ni(Quin)₂] has been used as a free-resistant additive for olefin polymers and as a fungicide for leather^[4], and tri(8-quinolinolato) cobalt (III) has been synthesized and used to assist in the metal-ligand assignments^[5]. Tris(8-quinolinolato) aluminum has excellent properties as an emitting material for use in organic electroluminescent devices^[6-8]. In this paper, the characteristic results of IR, UV and EPR spectra and the crystal structure for this title complex are reported.

1 Experimental

1.1 Physical measurements

Elemental analyses were performed on a Perkin Elmer 240C analytical instrument. The IR spectra were recorded in the 4000 ~ 400cm⁻¹ region using KBr pellets on a Bruker VECTOR 22 FTIR spectrometer. UV-vis solution spectra were recorded on a Rui Li UV-1100 spectrophotometer at the room temperature. Magnetic measurements on powder samples were performed in the 75 ~ 300K temperature range by means of a Faraday-type magnetometer. The powder EPR spectra were recorded on a Bruker 2000-SRC spectrometer.

1.2 Synthesis

All chemicals were obtained from a commercial source and used without further purification. To a warm solution of excess (8-quinolinolato-N, O) (1.00g, 6.29mmol) in EtOH(80mL), the Cu(Ac)₂ (0.387g, 3.145mmol) was added with stirring, and then for the mixed solution a reflux operation was carried out for 20 minutes. The deep blue solution obtained was filtered and the filtrate was left to stand undisturbedly. Upon slow evaporation at room temperature, a blue crystalline solid appeared after three weeks and was isolated by filtration. Single crystals suitable for X-ray analysis were obtained by recrystallization from EtOH solution. The C, H and N contents were determined by elemental analysis (Found: C, 60.12; H, 4.54; N, 7.05%. Calcd. for C₂₀H₁₈CuN₂O₃: C, 60.30; H, 4.52; N, 7.04%)

1.3 X-ray structure determination

A summary of the key crystallographic information is given in Table 1. Selected bond distances and angles are listed in Table 2. The selected crystal of the title compound was mounted on a SMART CCD diffractometer. Reflection data were measured at 20°C using graphite monochromated Mo K α ($\lambda = 0.071073\text{nm}$) radiation with a detector distance of 4cm and swing angle of -35° . The

Table 1 Summary of Crystallographic Results for [Cu(Me-quin)₂H₂O]

formula	C ₂₀ H ₁₈ CuN ₂ O ₃	formula weight	397.90	color/shape	blue/prism
crystal system	orthorhombic	space group	<i>Pbcn</i>	crystal size/mm	0.34 × 0.16 × 0.06
<i>a</i> /nm	0.7538(8)	<i>b</i> /nm	0.9109(1)	<i>c</i> /nm	2.4851(5)
cell volume/nm ³	1.7066(0)	<i>Z</i>	4	<i>D</i> (calcd.)/(g · cm ⁻³)	1.320
abs coeff./mm ⁻¹	1.303	GOF	1.055	<i>F</i> (000)	816
θ range/(°)	1.64 to 28.36	<i>T</i> _{max} and <i>T</i> _{min}	0.9259, 0.6658	reflections collected	11076
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0900, <i>w R</i> ₂ = 0.2159	independent reflections	2106[<i>R</i> (int) = 0.1325]		
<i>R</i> (all data)	<i>R</i> ₁ = 0.1411, <i>w R</i> ₂ = 0.2411	largest diff. peak and hole	1942 and -1923e ⁻ · nm ⁻³		

Table 2 Selected Bond Distances(nm) and Bond Angles (°) of the Title Compound

Cu-O(1)	0.1994(3)	Cu-N(1)	0.2017(4)	Cu-O(1A)	0.1994(3)
Cu-N(1A)	0.2017(4)	Cu-O(2)	0.2836(6)	O(1)-C(2)	0.1329(6)
N(1)-C(9)	0.1338(7)	N(1)-C(1)	0.1380(7)		
N(1)-Cu-N(1A)	176.0(2)	O(1)-Cu-O(1A)	135.1(2)	C(1)-N(1)-Cu	110.3(3)
N(1)-Cu-O(2)	88.02(12)	O(1)-Cu-N(1)	83.15(16)	O(1)-C(2)-C(1)	118.2(5)
O(1)-Cu-O(2)	112.47(1)	O(1A)-Cu-N(1)	98.37(15)	O(1)-C(2)-C(3)	123.8(5)

Symmetry transformations used to generate equivalent atoms: $-x$, $-y$, $-z+1/2$

collected data were reduced by using the program SAINT^[10] and empirical absorption correction was done by using the SADABS^[11] ($T_{\min} = 0.6658$, $T_{\max} = 0.9259$) program. Reflections with $3.28 \leq 2\theta \leq 56.72^\circ$ were used for structure refinement. The structure was solved by direct methods and refined by full-matrix least-squares method on F_{obs}^2 by using the SHELXTL^[12] software package. All non-H atoms were anisotropically refined. The hydrogen atoms were geometrically located and allowed to ride on parent atoms to which they attached. The final conventional representation is $R_1 = 0.0900$, $wR_2 = 0.2159$ for 1279 reflections with $I > 2\sigma(I)$, and the weighting scheme is $w = 1/[2(F_o^2) + (0.1387P)^2]$ in which $P = (F_o^2 + 2F_c^2)/3$. The molecular graphics were created by using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-Ray Crystallography^[13].

2 Results and discussion

2.1 Description of the structure

The crystal structure of the complex $[\text{Cu}(\text{Me-quin})_2\text{H}_2\text{O}]$ is built up by some discrete monomeric molecules. Fig. 1 shows a perspective view of the monomeric unit with the atomic numbering scheme of the title compound, and Fig. 2 shows a perspective view of the molecular packing in the unit cell.

In the molecule, the geometry of the pentacoordinated copper (II) atom is distorted square pyramidal. The basal coordination positions are occupied by the O and N atoms of bidentate ligands, and the apical position is occupied by the O atom from the water molecule, while the copper (II) atom is located in the center of the square pyramid. The Cu-O(1) [0.1994(3) nm] and Cu-N(1) [0.2017(4) nm] distances fall within the normal range, compared with corresponding bond lengths in other five coordinative Cu complexes [Cu-O 0.1910(9) ~ 0.1997(8) nm^[14]; Cu-N 0.1979(2) ~ 0.2029(2) nm^[15]; Cu-O 0.201(1) nm, Cu-N 0.195 ~ 0.201 nm^[16]; Cu-O 0.1942 ~ 0.1958 nm, Cu-N 0.2016 ~ 0.2019 nm^[17]]; The axial Cu-O(2) [0.2283(6) nm] bond length, however, is significantly longer than the equatorial Cu-O(1) bond, which is normal coordination bond length and is agreement with that found in similar Cu-O1w bond compound^[15]. The five-member chelate ring [Cu, O(1), N(1), C(1) and C(2)] and

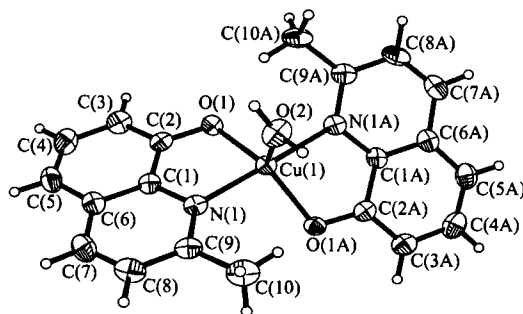


Fig. 1 Molecular structure for the title compound with the atomic numbering scheme

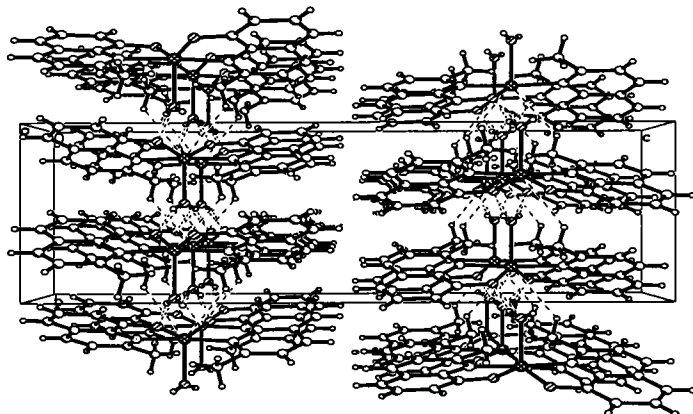


Fig. 2 A view of the crystal packing down the axis for the title compound

2-methyl-8-quinolinolate ligand are coplanar, with maximum deviation of atoms is 0.0039(4) nm. The dihedral angle between the two quinolinolate ligand planes is 48.4(1)°. The structure of CuO₂N₂ is obviously distorted towards a square pyramidal. The coordination plane composed of Cu, O(1), O(1A) and O(2) has a dihedral angle of 81.7(1)° with the Cu, N(1), N(1A) and O(2) plane. They form the dihedral angle 84.0(1)° and 65.9(1)° with chelate ring plane, respectively.

There is a intermolecular hydrogen bond between O(1) and O(2w) [$-1/2 - x, 1/2 - y, 1 - z$], with separation of 0.2744(4) nm. This means that a strong hydrogen bond exist in there. This complex forms a one-dimensional network through O(2w) – H···O(1) hydrogen bonds (See Fig. 2).

2.2 Spectroscopic Studies

The IR data of the complex is given in Table 3. In the IR Spectrum of the complex a wide absorption band at 3159.7cm⁻¹ may be attributed to OH stretching modes of coordinated water. The band at 748cm⁻¹ is attributed to the 8-quinolato ligand ring breathing, and the bands at 1378, 1429, 1463, 1506, 1568cm⁻¹, belonging to ligand ring stretching. Also, the compound shows a characteristic absorption peak at 510cm⁻¹ for 8-quinolinolato metal chelates but not for the free 8-hydroxyquinoline^[18], and two non-ligand bands are observed in the 466cm⁻¹ and 428cm⁻¹ regions, which may be assigned to $\nu_{(\text{Cu-O})}$ and $\nu_{(\text{Cu-N})}$ modes, respectively.

Table 3 IR Spectral Data for the Complexes(KBr Pellets)

compound	$\nu(\text{Cu-N})$	$\nu(\text{Cu-O})$	$\nu(-\text{OH})$
Cu(C ₁₀ H ₈ NO) ₂ H ₂ O	428cm ⁻¹	466cm ⁻¹	3159.7cm ⁻¹

The spectral data of the solution electronic spectra of the title compound in EtOH at room temperature are summarized in Table 4. The broad band around 384nm is assigned to ligand → copper (II) charge-transfer transitions. The strong sharp bands at 208nm and 264nm belong to the intraligand $n \rightarrow \pi^*$ transitions of the 2-methyl-8-quinolinolato.

Table 4 UV Spectral Data for the Complexes (EtOH Reference)

compound	M → L	$n \rightarrow \pi^*$	
Cu(C ₁₀ H ₈ NO) ₂ H ₂ O	384nm	208nm	264nm

The EPR spectrum was measured for a polycrystalline powder at room temperature and is shown

in Fig. 3. EPR Spectra of polycrystalline copper (II) complexes, exhibiting two types of g values, $g_{\parallel}$ and $g_{\perp}$, have been used^[19-22] to distinguish unambiguously between $d_{x^2-y^2}$ and d_{z^2} ground states for which $g_{\parallel} > g_{\perp}$ and $g_{\perp} > g_{\parallel} \approx 2.00$, respectively. The parameters of the title complex obtained from the room temperature spectrum ($g_{\parallel} = 2.2683$, $g_{\perp} = 2.1128$, and $g_{\parallel} > g_{\perp}$) confirms a square-based pyramidal geometry with a $d_{x^2-y^2}$ ground state^[21, 23].

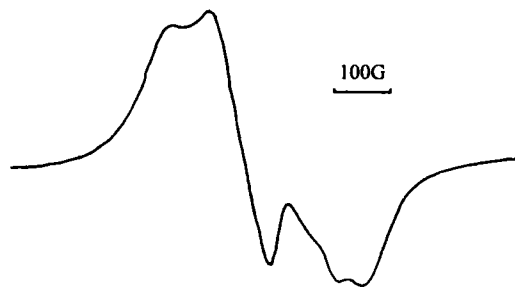


Fig. 3 Room-temperature EPR spectra of the title compound

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