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含 NO_4 五齿配体的一维铜配位聚合物的合成、晶体结构与生物活性

罗飞华[1,2] 胡宗球*[,2] 杨 莉[1] 张 萍[1] 刘 丹[1]
([1]四川文理学院化学与化学工程系,达州 635000)
([2]华中师范大学化学学院,武汉 430079)

摘要:利用邻氧乙酸苯甲醛与水杨酰肼合成了五齿配体 Schiff 碱 H_2L 及其一维链状聚合物$[(CuL)DMSO]_n$。产物经元素分析、红外、差热–热重分析及 X-射线单晶结构分析等表征。在配位聚合物中 Cu(Ⅱ)与配体的羰基氧、亚胺基氮、醚氧基氧及羧基氧配位形成一个 O_2N_2 平面,进一步被另一个配体的羧基氧桥联而形成一维配位聚合物。选取 6 种真菌对配体及其 Cu(Ⅱ)配合物进行了抗真菌活性测试,测试结果表明配体及配合物均表现出了一定抗真菌活性。

关键词:铜配合物;晶体结构;五齿配体配合物;抗菌活性
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Synthesis, Biological Activity and Crystal Structure of a Novel One-Dimensional Copper(Ⅱ) Polymer of a Pentadentate NO_4 Ligand

LUO Fei-Hua[1,2] HU Zong-Qiu*[,2] YANG Li[1] ZHANG Ping[1] LIU Dan[1]
([1]*Department of Chemistry And Chemical Engineering, Sichuan University of Arts and Science, Dazhou, Sichuan* 635000)
([2]*College of chemistry, Central China Normal University, Wuhan* 430079)

Abstract: The Schiff base H_2L formed by condensation of 2-(2-formylphenoxy)acetic acid with Salicyloylhydrazine behaves as a pentadentate ligand, forming a one-dimensional Cu(Ⅱ) polymer of empirical formal $[(CuL)DMSO]_n$. Element analysis, IR, TGA, X-Ray crystallography were used for the characterization of the complex. In the complex, the enolate-O, the imine-N, the aether-O, and the deprotonated carboxyl-O form an O_2N_2 square-plane around the Cu(Ⅱ) ion, and coordinated by carboxylate oxygen atom from another ligand to from one-dimensional polymer. The schiff base and its Cu(Ⅱ) complex were tested against six pathogenic fungi to assess their antimicrobial properties. Both the ligind and compound exhibit mild antifungal activities. CCDC: 710884.

Key words: copper complex; crystal structures; pentadentate ligand complex; antimicrobial properties

0 Introduction

Hydrazone compleses have been the subject of a big number of studies for many years due to their antimicrobial and antitumor properties[1-3]. Cu(Ⅱ) carboxylates, especially those with nitrogen donor ligands, have been the subject of numerous investigations[4]. Some carboxylic acids and their derivatives also play an important role in biological processes[5-11]. Different coordination modes of carboxylate groups can also form mononuclear and polynuclear structures. Hydrazone with carboxylate groups can also form mononuclear and polynuclear structures in different condictions[12].

In this work, we present a synthesis, element

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*通讯联系人。E-mail:zqhu@mail.ccnu.edu.cn
第一作者:罗飞华,男,26 岁,讲师;研究方向:配位化学。

analysis, spectra of a new hydrazone ligind with carboxyl, and the X-ray single-crystal analysis of an one-dimensional Cu(Ⅱ) polymer of the ligind, together with the biological activities. Both the ligind and compond exhibit mild bilogical activites.

1 Experimental

1.1 Reagents and physical measurements

Salicyloylhydrazine and 2-(2-formylphenoxy)acetic acid were synthesized according to the literature method[13], The other materials and solvents for synthesis were purchased from Shanghai Chemical Reagent Company without further purification.

The IR spectra were recorded on a Perkin-Elmer 983 infrared spectrophotometer using KBr discs in 4 000~400 cm^{-1} region. Element analyses for C, H and N were carried out with a Perkin-Elmer 2400 analyzer. ^1H NMR analyses were carried out on a Mercury-400 spectrometer in DMSO-d_6 withTMS as the internal standard. Mass spectrum was recorded on a Thermofinnigan HP5988A automated GC-MS. Differential thermal analyses were carried out using a NETZS-CHSTA Differential thermal analyzer 409PC.

1.2 X-ray crystallography

A green single crystal with dimensions of 0.10 mm ×0.10 mm ×0.20 mm was selected for X ray structure analysis. The data were collected on a Bruker Smart APEX CCD-based diffractometer using a graphite -monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) at 293(2) K. A total of 11 904 reflections were collected in the range of 1.60° ≤θ≤26.00° by using an ω-2θ scan mode, of which 3 785 were unique. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 program[14-15]. All of the non-hydrogen atoms were refined for 3 085 observed reflections with $I>2\sigma$ (I) to give the final R=0.054 7, wR=0.137 0 (w=1/[$\sigma^2(F_o^2)$+(0.076 2P)^2+1.844 4P], where P=(F_o^2+2F_c^2)/3, s=1.030. Positional parameters of all the H atomswere calculated geometrically and were allowed to ride on their respective parent atoms, with U_{iso}(H)=1.2U_{eq}(C) or U_{iso}(H)=1.5U_{eq}(O). The highest peak and deepest hole in the final difference Fourier map are 936 and −650 e·nm^{-3}, respectively. Crystal data are given in Table 1, together with refinement details.

CCDC: 710884.

Table 1　Crystallographic data for compelx

Compound	Complex	ρ(calculated) / (Mg·m^{-3})	1.563
Empirical formula	$C_{18}H_{18}CuN_2O_6S$	μ / mm^{-1}	1.278
Formula weight	453.94	Reflections collected	11 904
Crystal system	Monoclinic	Unique reflections	3 785
Space group	$P2_1/c$	Range of h, k, l	−13≤h≤16,−10≤k≤10, −21≤l≤21
Temperature / K	293(2)	F(000)	932
a / nm	1.350 70(10)	Min / max θ range / (°)	1.60~26.00
b / nm	0.857 26(6)	Data / restraints / parameters	3 785 / 0 / 297
c / nm	1.766 63(12)	R_1, wR_2 [$I>2\sigma(I)$]	0.054 7, 0.137 0
β / (°)	109.405 0(10)	R_1, wR_2 [all date]	0.068 2, 0.145 2
V / nm^3	1.929 4(2)	Goodness-of-fit on F^2	1.030
Z	4	Largest diff. peak and hole / (e·nm^{-3})	936, −650

1.3 Synthesis of the ligand and complex

Ligand was prepared by dissolving an equimolar mixture of 2-(2-formylphenoxy)acetic acid and salicyloylhydrazine in methanol, and the solvent was heated at 80 ℃ for 8 h. Then a white solid was obtained, washed with methanol and dried under reduced pressure. Yield: 90% . Anal. Calcd for $C_{16}H_{14}N_2O_5$(%): C,61.14; H,4.49; N,8.91. Found(%): C, 61.11; H,4.52; N,8.96; ^1H NMR:11.77(1H, d, -COOH), 11.95(1H, d, NH), 6.86~7.90(8H, m, PhH), 8.41(1H, d, -N=CH-), 3.43, 3.45 (2H, d, -O-CH_2-), 4.76 (2H, s, -OH); Ms m/z (%): 314.9 (3.34), 314.1 (M^+,4.78), 126.9 ($C_7H_4N_2O^+$, 100), 120($C_7H_4O_2^+$, 72.8), 194.3($C_9H_7O_3N_2^-$, 33.5).

The complex was prepared by dissolving the appropriate $Cu(NO_3)_2 \cdot 6H_2O$(1 mmol) in ethanol(15 mL) and adding to a solution of the ligand (0.5 mmol) in DMSO (3 mL). The resulting mixture was stirred at room temperature for 2 h, Then the mixture was filtrated to remove any impurities, the filtrate was kept for slow evaporation in air. After two weeks the complex was precipitated as DMSO solvent in the form of deep green crystallinc material. This was collected by filtration, washed with cold entanol and dried in air. Anal. Calcd for $C_{18}H_{18}CuN_2O_6S$ (%): C,47.62; H,3.99; N,6.17. Found (%): C,47.60; H,3.96; N,6.16.

1.4 Qualitative antimicrobial assay

Six pathogenic fungi were use to test the biological activity potentials of the hydrazone and its Cu (Ⅱ) complex. These were Fusarium oxysporium, Rhizoctonia solani, Botrytis cinereapers, Gibberella zeae, Apple Physalospora, Cotton anthrax. Antimicrobial actibity of the extracts was determined qualitatively by a midified dis duffusion method[16]. A lawn of microorganisms was prepared by pipetting and evenly spreading 10 μL of inoculun onto agar set in petri dishes, using potato dextrose agar (PDA) for the fungi. The culture media was poured into sterile plates and microorganisms were introduced on the surface of the agar plates individually. The blank sterile discs, were soaked in a known concentration of the test compounds. Then the soaked discs were implanted on the surface of the plates. A blank disc was soaked in the solvent (DMF) and implanted as a negative control on each plate along with the standard drugs. The plates were incubated at 27 ℃ (48 h) for fungal strains. The inhibition zones were measured and compared with standard drugs. The zone of inhibition values are given in Table 4.

2 Results and discussion

2.1 FTIR studies

The important IR date for the ligind and its complex are list in Table 2, A strong band at 3 415 cm^{-1} in the free ligand assigned to ν(OHCOOH) disappears in its complex, indicating that the carboxyls of the ligand have bond to Cu(Ⅱ)[17]. The ν(C=OCOOH) vibtation for the free ligind at 1 722 cm^{-1} disappears in its complex, but exhibits two new bands at 1 402 and 1 363 cm^{-1} assigned to ν_{as} and $\nu_a(CO_2^-)$ incomparison with IR spectra of free ligind. The strong bands for ν(NH) and δ(NHN-CONHN=) at 3 284 and 1 553 cm^{-1} in the free ligind disappear in its complex, due to enolization of the -CONHN= group followed by the formation of the complex through deprotonation[18]. This is further comfired by the shift of ν(C=O) and ν(C=N) vibration from 1 600 and 1 454 cm^{-1} in the free ligind to 1 516 and 1 494 cm^{-1} in the complex, indicating that ν(C=O) and ν(C-N) bonds become close to ν(C-O) and ν(C=N). Two week bands at 598 and 418 cm^{-1} assigned to ν(M-O) and ν(M-N), which are absent in the free ligind indicate that N and O of the ligind have bonded to the metal ion Cu(Ⅱ), in agreement with the conclusion given from X-ray analyse.

Table 2 Important characteristic IR data for the ligand and its complex

Comp.	$\nu_{OH(COOH)}$	N-H	C=N	C=O	asCOOH	sCOOH	M-O	M-N
H_2L	3 415	3 284	1 454	1 600	1 722	1 454	—	—
Complex	—	—	1 494	1 516	1 402	1 363	598	418

2.2 Description of the structure

The molecular structure of complex is depicted in Fig.1. The selected bond parameters associated with the metal ions are listed in Table 3. The complex molecule consists of the pentadentate ligand L^{2-} and Cu(Ⅱ) ion in a 1∶1 ratio. One disordered DMF molecule involved is free from co-ordination and captured in the lattice. In the complex, the dinegative ligand L^{2-} coordinates to the metal ion Cu(Ⅱ) via the the enolate-O, the imine-N, the aether-O, and the deprotonated carboxyl-O forming O_2N_2 square-plane around the Copper(Ⅱ) ion, the fifth site is satisfied by the oxygen atom of the deprotonated carboxy of other L^{2-} and finally formed a disordered Pyramid. Each Cu(Ⅱ) centre in compound is a five-coordinated tetragonal pyramid coordination sphere, and each L^{2-} acts as a pentadentate ligand coordinating

Table 3　Selected bond lengths (nm) and angles (°) for complex

Cu(1)-N(2)	0.190 9(3)	Cu(1)-O(2)	0.192 4(2)	Cu(1)-O(5)(A)	0.225 3(3)
Cu(1)-O(3)	0.201 4(2)	Cu(1)-O(4)	0.190 4(3)		
N(2)-Cu(1)-O(3)	91.61(11)	O(4)-Cu(1)-O(3)	83.64(10)	O(4)-Cu(1)-O(5)(A)	100.34(11)
O(4)-Cu(1)-N(2)	166.54(12)	O(2)-Cu(1)-O(3)	171.77(10)	N(2)-Cu(1)-O(5)(A)	91.70(11)
O(4)-Cu(1)-O(2)	100.40(11)	O(2)-Cu(1)-O(5)(A)	101.61(11)	O(3)-Cu(1)-O(5)(A)	84.57(10)
N(2)-Cu(1)-O(2)	82.85(11)				

Symmetry code: (A) $-x$, $y-1/2$, $-z+1/2$.

to two metal ions (Fig.1). The Cu-O and Cu-N distances in the basal plane agree well with those found in other square-plane Cu(Ⅱ) complexes[19-20], but the Cu(Ⅱ) ion deviating from the plane (0.016 nm) which is shorter then similar Cu(Ⅱ) complexes[21]. The bond length of C16-O4 (0.126 8 nm) and C16-O5 (0.123 9 nm) were near the same as the carboxylate group delocalized and the Cu(Ⅱ) ions are sequentially bridged by carboxylate groups to form an infinite linear one-dimensional polymeric chain extened along the crystallographic *b*-axis (Fig.2). Each polymeric chain is linked to other ones by strong π-π interactions with a shortest

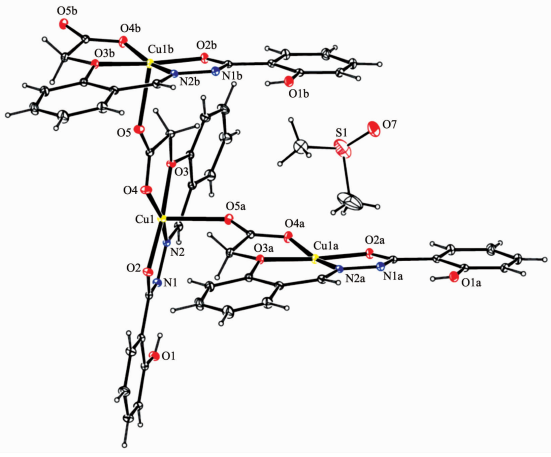

Fig.1　ORTEP diagram of complex

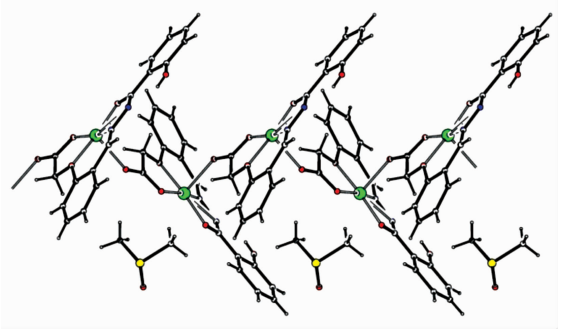

Fig.2　One-dimensional (1D) chains structure of complex

interplanar distance of 0.383 7 nm, futher stabilized by weak hydrogen bonds C(3)–H(3)⋯O(5) (x, $1/2-y$, $z-1/2$) [C(3)–O(5) 0.347 1(5) nm; H(3)⋯O(5) 0.257 nm; C(3)–H(3)⋯O(5) 163.9°] rmation of a 2D sheet structure (Fig.3a,b).

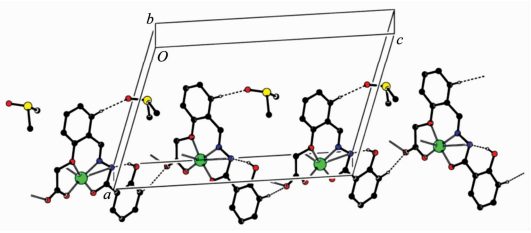

Fig.3a　One-dimensional (1D) chains structure linked by hydrogen bonds between two molecuers, the H atoms which do not form hydrogen bond

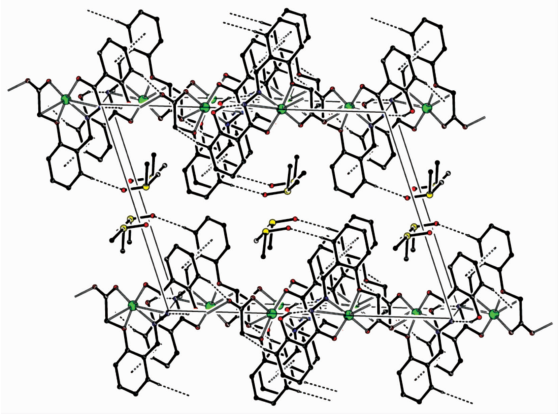

Fig.3b　Crystal packing of complex, omitted omitted the H atoms which do not form hydrogen bond

2.3　Thermal analysis

The TGA and DTA analysis of $[(CuL)DMSO]_n$ was investigated under inert atmosphere. Thermal analysis shows the weight lost under a nitrogen atmosphere between 15 and 125 ℃ is about 4.77%, which is nearly water solvent in the complex, at 209 ℃ the melting peak point can be observed easily. Between 160 and 240 ℃ there is the lose of the DMSO solvent molecuer

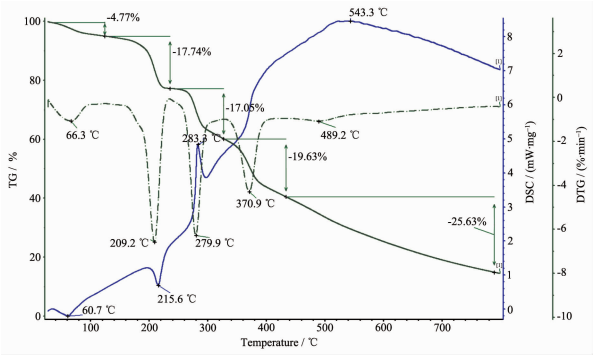

Fig.4 TG-DSC curve of complex

and between 260 and 440 ℃ is the decompose of the ligand(Fig.4).

2.4 Antifungal activity

The free ligand of H_2L showed little activity against six Fungies while the complex of $[(CuL)DMSO]_n$ show better antifungal activity. This was confirmed by Similar complexes[22]. Both H_2L and $[(CuL)DMSO]_n$ show selective against six Fungies. $[(CuL)DMSO]_n$ were found to be active against Botrytis cinereapers and Apple Physalospora positive (Table 4).

Table 4 Antimicrobial activity of test H_2L and complex

Compound	Fusarium oxysporium	Rhizoctonia solani	Botrytis cinereapers	Gibberella zeae	Apple physalospora	Cotton anthrax
H_2L	36.84	10.26	43.48	3.70	35.85	22.73
Complex **1**	28.57	43.53	77.14	42.42	63.64	21.05

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