

含取代芳酰肼和单齿 *N*-杂环分子铜(II)配合物的合成、结构及荧光性质

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摘要: 合成了 1 个含有取代芳酰肼和单齿 *N*-杂环分子的三元铜配合物[Cu(L)(ampy)]($H_2L=5$ -溴水杨醛苯甲酰肼, ampy=2-氨基吡啶), 并通过 IR、UV、荧光光谱和循环伏安进行了性质研究。[Cu(L)(ampy)]的晶体结构分析表明, 中心金属通过酰肼配体的酚基氧原子、亚胺基氮原子、去质子酰胺氧原子以及中性杂环分子的氮原子形成平面四方形的 N_2O_2 配位环境。配合物通过 N-H \cdots O 和 N-H \cdots N 氢键作用形成一维链状结构。

关键词: 铜(II)配合物; 晶体结构; 取代芳酰肼; 荧光

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Synthesis, Structure and Fluorescence of Copper(II) Complex with Substituted Aroylhydrazone and Monodentate *N*-heterocycle

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Abstract: A ternary copper(II) complex, [Cu(L)(ampy)], with a substituted aroylhydrazone, 5-bromosalicylaldehyde benzoylhydrazone (H_2L) and monodentate *N*-heterocycle, 2-aminopyridine (ampy), has been synthesized and characterized by IR spectra, UV spectra, fluorescence spectra and cyclic voltammetry. The single crystal structure of [Cu(L)(ampy)] reveals that the Cu(II) is in a square-planar N_2O_2 coordination environment formed by the phenolate-O, the imine-N and the deprotonated amide-O atoms of L^{2-} , and the N atom of ampy. In the crystal, the complex is involved in N-H \cdots O and N-H \cdots N hydrogen bonds, leading to a 1D chain arrangement. CCDC: 635866.

Key words: copper(II) complex; crystal structure; substituted aroylhydrazone; fluorescence

0 Introduction

The coordination chemistry of substituted hydrazones has received much attention due to their chelating capability and potential pharmacological application^[1-3]. Recently, Das et al. have reported four copper (II) complexes, [Cu(bhac)(hc)], with a Schiff base, acetylacetonone benzoylhydrazone (H_2bhac), and monodentate neutral *N*-donor heterocycles, 3,5-dimethylpyrazole, pyrazole, imidazole, and pyridine^[4,5]. Interestingly, the

nature and the directionality of the intermolecular weak interactions and the ensuing supramolecular structures differ drastically in these apparently very similar complexes^[4]. Several structure studies have been carried out on Cu(II) and Ni(II) complexes with substituted salicylaldehyde acylhydrazone^[6-13], showing this type of diprotic ligand typically acts as a tridentate planar chelating agent coordinating through the phenolic and amide oxygen as well as imine nitrogen atoms^[6-13]. Herein, we report the synthesis and structure of a new copper(II)

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complex, [Cu(L)(ampy)], with 5-bromosalicylaldehyde benzoylhydrazone (H₂L) and monodentate *N*-heterocycle, 2-aminopyridine(ampy). Its spectroscopic properties and electrochemical properties are also studied.

1 Experimental

1.1 Materials and instrumentation

Elemental analyses (C, N and H) were carried out with a Varian EL elemental analyzer. IR spectra were recorded on a Bruker Tensor27 FTIR spectrophotometer as KBr pellets. UV spectra were recorded on a Shimadzu UV-2501PC spectrometer. Fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer. Cyclic voltammetry measurements were performed on a LK98 Microcomputer-based electrochemical analyzer with a glassy carbon as a working electrode, a platinum wire as a counter electrode and Ag-AgCl (1 mol·dm⁻³ KCl) as a reference electrode.

1.2 Synthesis of complex

5-bromosalicylaldehyde benzoylhydrazone (H₂L) was prepared according to the literature method^[14]. To a mixed solution of MeOH (40 mL) and DMF (10 mL) of

H₂L (0.32 g, 1 mmol) and 2-aminopyridine (0.47 g, 5 mmol), a methanol solution (20 mL) of Cu(O₂CCH₃)₂·H₂O (0.19 g, 1 mmol) was added gradually with stirring. The resulting green solution was further stirred for 2 h. The volume of the reaction mixture was then reduced to 25 mL on a steam bath, cooled to room temperature and filtered. The greenish brown crystals separated after about 3 days were collected with yield of about 40%. Anal. Calc. for C₁₉H₁₅BrCuN₄O₂ (%): C, 48.06; N, 11.80; H, 3.19. Found (%): C, 47.86; N, 10.98; H, 3.42.

1.3 Crystal structure determination

Diffraction data for single crystal of [Cu(L)(ampy)] were collected on Bruker Smart-1000 CCD diffractometer with a graphite-monochromatized Mo K α radiation ($\lambda=0.071\ 073$ nm) at 298(2) K. The structure was solved by direct method and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all nonhydrogen atoms. All the hydrogen atoms were located geometrically and refined isotropically. The data collection and refinement details are summarized in Table 1.

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Table 1 Crystal data and structural refinements for [Cu(L)(ampy)]

Formula	C ₁₉ H ₁₅ BrCuN ₄ O ₂	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.689
Formula weight	474.80	$F(000)$	474
Crystal system	Triclinic	$\mu(\text{Mo } K\alpha) / \text{mm}^{-1}$	3.331
Space group	$P\bar{1}$	Crystal size / mm	0.16 × 0.11 × 0.05
a / nm	0.850 5(2)	θ range / (°)	1.62 to 25.00
b / nm	0.906 1(3)	Limiting indices	$-9 < h < 10, -9 < k < 10, -15 < l < 15$
c / nm	1.346 6(3)	Reflections collected / unique	4 549 / 3 163 ($R_{\text{int}}=0.058\ 0$)
$\alpha / (^\circ)$	109.112(2)	Data / restraints / parameters	3 163 / 12 / 244
$\beta / (^\circ)$	93.674(3)	Goodness-of-fit on F^2	1.003
$\gamma / (^\circ)$	105.112(3)	$R_1, wR_2 [I > 2\sigma(I)]$	0.079 7, 0.181 7
V / nm^3	0.933 8(5)	R_1, wR_2 (all data)	0.147 0, 0.217 4
Z	4		

2 Results and discussion

2.1 IR spectra

IR spectra of [Cu(L)(ampy)] do not display the C=O stretch of the amide functionality observed for the free H₂L at 1 646 cm⁻¹. This observation is consistent with the deprotonation and the enolate form of the

amide functionality in complex^[4,5,11,13]. A strong band at 1 629 cm⁻¹ are attributed to the conjugated C=N-N=C fragment and the peak at 1 636 cm⁻¹ corresponding to $\nu(\text{C}=\text{N})$ of free H₂L shifts to 1 610 cm⁻¹ indicating azomethine nitrogen coordination^[4-9].

2.2 Crystal structure

The molecular structure of [Cu(L)(ampy)] is illus-

trated in Fig.1. The selected bond lengths and angles are listed in Table 2. The copper(II) centre is in a square-planar N_2O_2 coordination environment formed by the phenolate-O, the imine-N and the deprotonated amide-O atoms of L^{2-} , and the N atom of the neutral heterocycle.

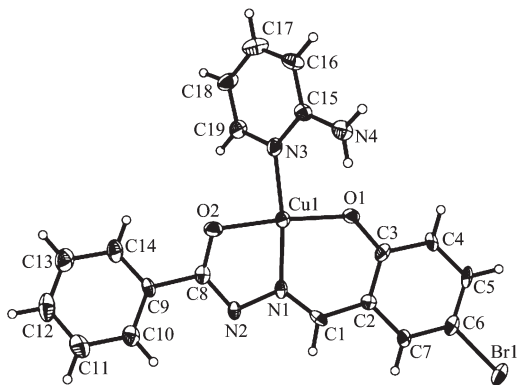


Fig.1 Molecular structure of $[Cu(L)(ampy)]$, showing 40% probability displacement ellipsoids

The Cu-O(amide) distance (0.192 2(7) nm) is shorter than the distances (0.197 6(2)~0.206 3(2) nm) found in copper(II) complexes in which the O-coordinating amide functionality is protonated^[15,16] and comparable with the distances (0.1914(4)~0.1989(5) nm) observed for complexes in which the copper(II) is coordinated to deprotonated amide-O^[4-9]. The Cu-O(phenolate) (0.189 0(7) nm) and Cu-N(imine) (0.192 9(8) nm) bond lengths are comparable to the bond lengths observed in copper(II) complexes having the same coordinating atoms^[4-9]. The Cu-N(heterocycle) bond length (0.200 7(8) nm) is comparable to the value reported previously^[6-9]. The C8-O2 (0.128 7(11) nm) and C8-N2 (0.132 1(12) nm) distances are consistent with the enolate form of the amide functionality^[4-9]. The ligand forms a satisfactory N_2O_2 square-plane (mean deviation are in the range

0.000 36~0.002 57 nm) around the metal ion. However, the complex molecule as a whole is non-planar. The dihedral angle between the phenyl ring plane and the plane constituted by O1, O2, N1, N2, C1-C8 atoms (mean deviations are in the range 0.000 90~0.005 44 nm) is 14.52(42)°. The dihedral angle between the heterocycle plane and the plane containing O1, O2, N1, N2, C1-C8 atoms is 41.97(26)°.

In the crystal, $[Cu(L)(ampy)]$ participates in two hydrogen bonds and the chain arrangement is formed (Fig.2). The N-H group of 2-aminopyridine moiety is intrahydrogen bonded with phenolate-O atom with the $N\cdots O$ distance and $N-H\cdots O$ angle of 0.288 0 nm and 129.46°, respectively. In addition, the same 2-aminopyridine moiety is also involved in interhydrogen bond with uncoordinated and deprotonated amide-N atom of L^{2-} . The $N\cdots N$ distance and $N-H\cdots N$ angle are 0.339 6 nm and 155.53°, respectively.

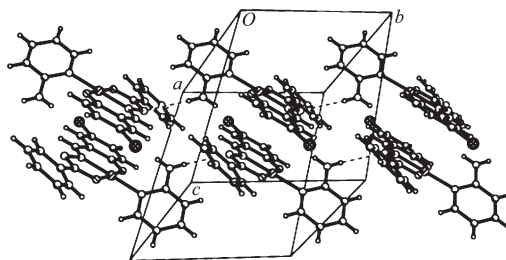


Fig.2 1D chain structure of $[Cu(L)(ampy)]$ in crystal

2.3 Electronic spectra and Fluorescence spectra

The electronic spectra of $[Cu(L)(ampy)]$ in DMF show three bands at 304, 317 and 334 nm, which are attributed to $L^{2-} \pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The band at 400 nm may be assigned to the ligand to metal charge-transfer transition^[17].

Fig.3 shows the fluorescence spectra of $[Cu(L)$

Table 2 Selected bond distances (nm) and angles (°) for $[Cu(L)(ampy)]$

Cu1-O1	0.189 0(7)	Cu1-N3	0.200 7(8)	N2-C8	0.132 1(12)
Cu1-O2	0.192 2(7)	N1-C1	0.130 1(12)	O2-C8	0.128 7(11)
Cu1-N1	0.192 9(8)	N1-N2	0.141 3(10)		
O1-Cu1-O2	174.8(3)	O2-Cu1-N3	91.6(3)	N2-N1-Cu1	115.6(6)
O1-Cu1-N1	94.2(3)	N1-Cu1-N3	172.1(3)	C8-N2-N1	106.8(8)
O2-Cu1-N1	80.8(3)	C1-N1-N2	118.2(8)	C3-O1-Cu1	128.0(6)
O1-Cu1-N3	93.5(3)	C1-N1-Cu1	126.1(7)	C8-O2-Cu1	111.3(6)

(ampy)] in DMF, indicating that the complex exhibits intense fluorescence emission with the maximum emission peaks at 351 nm when excited at 298 nm. Whereas free ligand H₂L does not give the convincing fluorescence spectra. This behavior may be attributed to the enolate form of the amide functionality in complex, which effectively increase the rigidity of the molecular skeleton^[18,19]. Another, the ampy NH₂-group may also play important role in improving the fluorescence intensity.

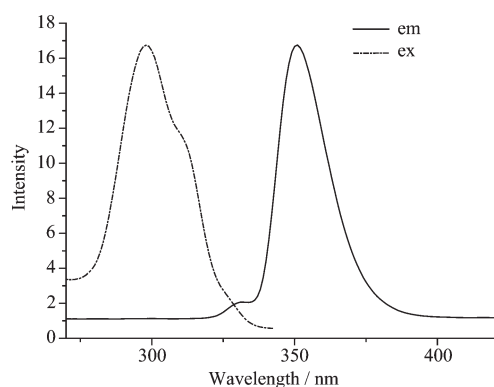


Fig.3 Fluorescence spectra of [Cu(L)(ampy)]

2.4 Cyclic voltammetry

Cyclic voltammogram of [Cu(L)(ampy)] was measured in DMF with 0.1 mol·dm⁻³ (n-Bu)₄NClO₄ (TBAP) as a supporting electrolyte in the potential range of -0.2 to -1.8 V (Fig.4). The complex exhibits an irreversible reduction wave at the potential of -0.9 V (vs Ag-AgCl). On the anodic side no anodic wave occurs. The similar results have previously been reported for copper (II) complexes with Schiff base ligand^[20-22]. Thus the reduction observed for complex may be assigned to Cu(II) to Cu(I) reduction.

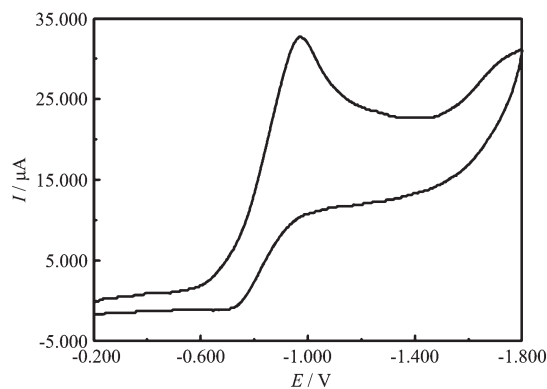


Fig.4 Cyclic voltammetry of [Cu(L)(ampy)]

References:

- [1] Chan C, Koh L L, Leung P H, et al. *Inorg. Chim. Acta*, **1995**, **236**:101~108
- [2] Carcell M, Mazza P, Pelizzi C, et al. *J. Inorg. Biochem.*, **1995**, **57**:43~62
- [3] Satyanarayan P, Samudranil P. *J. Chem. Soc., Dalton Trans.*, **2002**:2102~2108
- [4] Das S, Muthukumaragopal G P, Pal S, et al. *New J. Chem.*, **2003**, **27**:1102~1107
- [5] Das S, Pal S. *J. Mol. Struct.*, **2005**, **741**:183~192
- [6] LU Wen-Guan(卢文贯), FENG Xiao-Long(冯小龙), LIU Hong-Wen(刘宏文), et al. *Wuji Huaxue Xuebao(Chinese J. Inorg. Chem.)*, **2003**, **19**(2):206~210
- [7] LU Wen-Guan(卢文贯), LIU Hong-Wen(刘宏文), FENG Xiao-Long(冯小龙). *Wuji Huaxue Xuebao(Chinese J. Inorg. Chem.)*, **2004**, **20**(12):1493~1496
- [8] LU Wen-Guan(卢文贯), LIU Hong-Wen(刘宏文). *Jiegou Huaxue(Chinese J. Struct. Chem.)*, **2005**, **24**(9):1078~1082
- [9] CHEN Xiao-Hua(陈小华), LIU Shi-Xiong(刘世雄). *Wuji Huaxue Xuebao(Chinese J. Inorg. Chem.)*, **2004**, **20**(6):668~670
- [10] DING Yu(丁瑜), ZHANG Zhong-Hai(张忠海), HU Zong-Qiu(胡宗球), et al. *Wuji Huaxue Xuebao(Chinese J. Inorg. Chem.)*, **2006**, **22**(7):1187~1190
- [11] DING Yu(丁瑜), HU Zong-Qiu(胡宗球), ZHANG Zhong-Hai(张忠海). *Jiegou Huaxue(Chinese J. Struct. Chem.)*, **2006**, **25**(4):439~442
- [12] HU Zong-Qiu(胡宗球), WU Yu(吴宇), JIA Bing(加兵), et al. *Wuji Huaxue Xuebao(Chinese J. Inorg. Chem.)*, **2005**, **21**(11):1715~1718
- [13] HU Zong-Qiu(胡宗球), DING Yu(丁瑜), ZHU Xin-De(祝心德), et al. *Wuji Huaxue Xuebao(Chinese J. Inorg. Chem.)*, **2005**, **21**(1):78~82
- [14] Liu H Y, Wang H Y, Gao F, et al. *Acta Cryst.*, **2006**, **E62**:o4495~o4496
- [15] Sangeetha N R, Pal S N, Anson C, et al. *Inorg. Chem. Commun.*, **2000**, **3**:415~419
- [16] Sangeetha N R, Pal S. *J. Chem. Crystallogr.*, **1999**, **29**:287~293
- [17] WUYu(吴宇), CHENG Cui-Xia(程翠霞), SHI Shao-Min(施少敏), et al. *Huazhong Shifan Daxue Xuebao(J. Centra China Normal University)*, **2006**, **40**(1):55~57
- [18] LIN Yan-Yong(林龔勇), CHEN Zi-Yun(程梓云), YU Xiao-Lan(余小岚), et al. *Wuji Huaxue Xuebao(Chinese J. Inorg. Chem.)*, **2006**, **22**(8):1467~1472
- [19] HE Jin-Run(何锦润), WANG Yu-Ling(王玉玲), BI Wen-Hua(毕文华), et al. *Wuji Huaxue Xuebao(Chinese J. Inorg. Chem.)*, **2006**, **22**(8):1380~1386
- [20] Liu H Y, Wang H Y, Niu D Z. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **2005**, **35**(6):429~432
- [21] Zolezzi S, Spodine E, Decinti A. *Polyhedron*, **2002**, **21**(1):55~59
- [22] Bharathi K S, Rahiman A K, Rajesh K, et al. *Polyhedron*, **2006**, **25**(15):2859~2868