PMBP 缩 4-甲基水杨酰肼铜、锌配合物：合成、结构及锌配合物的荧光性质

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摘要：合成并通过单晶衍射、元素分析、红外光谱表征了配合物[(Cu)(L)(Cl)]·0.5EtOH·1.5H$_2$O (**1**)和{[Zn(L)(NO$_3$)]·2CH$_3$CN}$_n$ (**2**)的结构(HL 为 PMBP 缩 4-甲基水杨酰肼; PMBP=1-phenyl-3-methyl-4-benzoyl-5-pyrazolone)。单晶衍射结果表明，配合物 **1** 中，Cu(II)离子与来自烯醇化脱质子配体 L$^-$的 2 个 O 原子和 1 个 N 原子，及 1 个氯离子配位，采取扭曲的平面正方形配位构型。而配合物 **2** 中，Zn(II)离子采取扭曲的三角双锥配位构型，与来自 L$^-$的 NO$_2$ 电子供体，1 个单齿配位的硝酸根和相邻配体吡唑啉酮 N 原子配位，形成沿 b 轴方向的一维链状结构。在 310 nm 紫外光激发下，配合物 **2** 在 434 和 459 nm 处有很强的荧光发射，而配体的荧光发射峰在 521 nm，强度明显弱于配合物。此外，固态配体和配合物 **2** 的荧光寿命分别为 7.352 8 和 7.755 6 μs。

关键词：酰腙；Zn(II)配合物；Cu(II)配合物；荧光；晶体结构
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Cu(II) and Zn(II) Complexes with an Acylhydrazone Derived from 4-Methyl Salicylic Hydrazide and PMBP: Crystal Structures and Fluorescence Property of Zn(II) Complex

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Abstract: Two complexes [(Cu)(L)(Cl)]·0.5EtOH·1.5H$_2$O and {[Zn(L)(NO$_3$)]·2CH$_3$CN}$_n$ (HL is the acylhydrazone ligand derived from 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) and 4-methyl salicylic hydrazide) have been synthesized and characterized by single-crystal X-ray diffraction, elemental analysis and IR spectroscopy. X-ray diffraction analysis results show that the coordination geometry of the Cu(II) ion in **1** is a distorted square planar geometry with nitrogen and two oxygen atoms provided by the enolizated ligand L^{-1} and one chloride anion. However, in complex **2**, the Zn(II) ion with a distorted trigonal biyramid coordination geometry is five-coordinated, involving one nitrate anion, one NO$_2$ donor set of an enolizated ligand L$^-$ and one pyrazoline nitrogen atom from another adjacent acylhydrazone ligand, thus forming one dimension chain-like framework along b axis. When excited at 310 nm, complex **2** exhibits two strong emissions at 434 and 459 nm, while the ligand shows relatively weak emission at 521 nm. In addition, luminescent decay data show that the mean lifetime <τ> are 7.352 8 and 7.755 6 μs for HL and complex **2**, respectively. CCDC: 1058420, HL·0.5EtOH; 1058421, **1**; 1058422, **2**.

Key words: hydrazone; Zn(II) complex; Cu(II) complex; fluorescence; crystal structure

It is well known that Schiff bases are an important class of ligands in coordination chemistry and have been found extensive application in different fields[1-5]. Among them, the Schiff base derivatives of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) and their metal complexes have been widely investigated due to their high biological and pharmaceutical activities, such as antibacterial, antitumor, antivirus enzyme-inhibitor[6-8]. Although some PMBP Schiff bases have been reported to show excellent photochromic and fluorescence properties[9-10], studies on the fluorescence properties of the metal complexes with such series of ligands are relatively few.

Generally, zinc ion is closely related to biochemistry, clinical diagnostics as well as environmental pollution[11-15]. Furthermore, a large amount of Zn(II) acylhydrazones have been reported for their fluorescence properties[11,14-15]. Therefore, in this paper, Cu(II) and Zn(II) complexes with an acylhydrazone ligand derived from PMBP and 4-methyl salicylic hydrazide have been synthesized and structural determined by single-crystal X-ray diffraction. In addition, the fluorescence properties of the ligand and its Zn(II) complex were discussed in detail.

1 Experimental

1.1 Materials and measurements

Solvents and starting materials for synthesis were purchased commercially and used as received. Elemental analysis was carried out on an Elemental Vario EL analyzer. The IR spectra (ν=4 000~400 cm^{-1}) were determined by the KBr pressed disc method on a Bruker V70 FTIR spectrophotometer. ^{1}H NMR spectra of HL was acquired with Bruker AV400 NMR instrument in DMSO-d$_6$ solution with TMS as internal standard. Fluorescence spectra were determined on an Edinburgh FLS980 spectrophotometer.

1.2 Preparations of the ligand and complexes

As shown in Scheme 1, the ligand HL was prepared by condensation of PMBP (2.78 g, 10 mmol) and 4-methyl salicylic hydrazide (1.66 g, 10 mmol) in ethanol solution (30 mL) under reflux condition for 5 h. The yellow solid was filtered and washed three times with ethanol. Crystals of HL·0.5EtOH suitable for X-ray diffraction analysis were obtained by recrystallization of HL from ethanol solution. Yield: 3.02g (71%). m.p. 138~142 ℃. Elemental analysis Calcd. for HL (C$_{25}$H$_{22}$N$_4$O$_3$)(%): C: 70.41; H: 5.20; N: 13.14; Found: C: 70.34; H: 5.21; N: 13.24. FTIR (cm^{-1}): ν(O-H) 3 404, ν(O=C pyrazolone) 1 634, ν(O=C acylhydrazone) 1 596, ν(C =C) 1 580, ν(C =N pyrazolone) 1 536. ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 6.798~6.833 (2H), 7.278~7.750 (10H), 8.022~8.046 (1H) for Ar-H, 2.302 (3H, s, CH$_3$ of benzene ring), 1.276 (3H, s, -CH$_3$ of pyrazolone ring).

The complex **1** and **2** were generated by reaction of HL (5mmol) with equal molar of CuCl$_2$·2H$_2$O in ethanol and Zn (NO$_3$)$_2$·6H$_2$O (1:1 molar ratio) in acetonitrile solution, respectively. Crystals of **1** and **2** suitable for X-ray diffraction analysis were obtained by evaporating the reaction solutions at room temperature.

1: green needles. Anal. Calcd. for C$_{26}$H$_{27}$N$_4$O$_5$CuCl (%): C: 54.36; H: 4.74; N: 9.75. Found (%): C: 54.18; H: 4.42; N: 10.13. FTIR (cm^{-1}): ν(O-H) 3415, ν(O=C-N pyrazolone) 1 613, ν(C=C) 1 571, ν(C=N pyrazolone)1 531, ν(C=N)1 486.

2: colorless blocks. Anal. Calcd. for C$_{29}$H$_{27}$N$_7$O$_6$Zn (%): C: 54.86; H: 4.29; N: 15.44. Found (%): C: 54.81; H: 4.18; N: 15.52. FTIR (cm^{-1}): ν(O-H) 3 405,
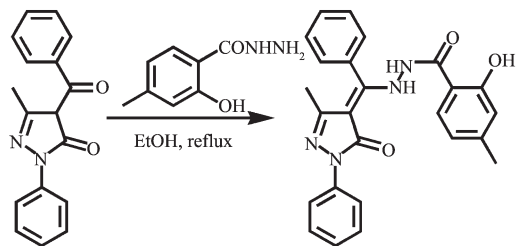
Scheme 1   Reaction scheme for the synthesis of HL

ν(O=C-N pyrazolone) 1 618, ν(C=C)1 586, ν(C=N pyrazolone)1 548, ν(C=N) 1 489.

1.3.1　X-ray crystallography

The X-ray diffraction measurement for HL · 0.5EtOH, complexes **1** and **2** was performed on a Bruker SMART APEX Ⅱ CCD diffractometer equipped with a graphite monochromatized Mo-$K\alpha$ radiation (λ=0.071 073 nm) by using φ-ω scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program[16]. The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-97 program [17]. All non-hydrogen atoms were refined anisotropically. All H atoms were positioned geometrically and refined using a riding model. SQUEEZE procedure was applied to deal with the crystal solvent molecules of complexes **1** and **2**. Details of the crystal parameters, data collection and refinements for three compounds are summarized in Table 1.

CCDC: 1058420, HL ·0.5EtOH; 1058421, **1**; 1058422, **2**.

2　Results and discussion

2.1　Crystal structures description

Selected bond distances and angles of three

Table 1　Crystal data and structure refinement for the HL·0.5EtOH, 1 and 2

	HL·0.5EtOH	1	2
Empirical formula	$C_{26}H_{25}N_4O_{3.50}$	$C_{26}H_{27}ClCuN_4O_5$	$C_{29}H_{27}N_7O_6Zn$
Formula weight	449.50	574.51	634.95
T / K	296(2)	296(2)	293(2)
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$
a / nm	0.749 13(3)	0.962 5(7)	2.523 8(4)
b / nm	1.082 99(5)	1.495 4(13)	1.108 39(19)
c / nm	1.399 85(5)	1.882 8(15)	2.389 7(4)
α / (°)	97.179(3)	95.41(4)	90
β / (°)	90.156(3)	94.63(3)	119.300(3)
γ / (°)	92.455(3)	103.575(16)	90
V / nm³	1.125 72(8)	2.608(4)	5.829 6(17)
Z	2	4	8
D_c / (g·cm⁻³)	1.326	1.463	1.447
Absorption coefficient / mm⁻¹	0.090	0.984	0.898
Crystal size / mm	0.16×0.14×0.12	0.25×0.10×0.08	0.15×0.12×0.10
F(000)	474	1 188	2 624
θ range for data collection / (°)	1.47~27.94	2.51~25.15	1.85~25.00
Index ranges (h, k, l)	$-9 \leqslant h \leqslant 9$	$-11 \leqslant h \leqslant 11$	$-30 \leqslant h \leqslant 22$
	$-14 \leqslant k \leqslant 14$	$-17 \leqslant k \leqslant 17$	$-13 \leqslant k \leqslant 12$
	$-18 \leqslant l \leqslant 18$	$-22 \leqslant l \leqslant 22$	$-26 \leqslant l \leqslant 28$
Reflections collected	18 538	22 978	14 337
Unique (R_{int})	5 360 (0.062 3)	9 318 (0.159 5)	5 142 (0.053 8)
Data/restraints/parameters	5 360 / 19 / 319	9 318 / 3 / 642	5 142 / 15 / 334
Goodness-of-fit (GOF) on F^2	1.001	1.051	1.033
Final R indices [$I>2\sigma(I)$]	R_1=0.055 4	R_1=0.087 9	R_1=0.054 2
	wR_2=0.134 6	wR_2=0.212 1	wR_2=0.131 5
R indices (all data)	R_1=0.122 1	R_1=0.141 3	R_1=0.085 5
	wR_2=0.166 1	wR_2=0.249 3	wR_2=0.143 7
Largest peak and hole / (e·nm⁻³)	216 and −178	633 and −460	521 and −671

compounds are listed in Table 2. As shown in Fig.1a, HL in the crystal structure of HL·0.5EtOH is in a ketone form, in which the bond lengths of carbonyl C7-O1 (0.126 4(2) nm) and C18-O2 (0.125 1(2) nm) are comparable to those of some reported Schiff base ligands derived from PMBP[9].

Once coordinated with metal ion, the acylhydrazone ligand HL is deprotonated. In addition, the distances of the enolized C-O and imine C-N bands in both complexes are intermediate between single and double bond, suggesting an extended conjugation in anionic ligand after complexation. The structural analysis reveals that the asymmetric unit of **1** (Fig.1b) is build of two similar neutral mononuclear complex units, a half crystal ethanol and a half crystal water. Each copper(Ⅱ) center with distorted square planar geometry is four-coordinated as [Cu(OON)Cl], with one nitrogen and two oxygen atoms provided by the enolizated ligand L⁻ and one chloride anion. The coordination bond lengths around both Cu(Ⅱ) center are in the normal range, with Cu-O being 0.189 6(5)~ 0.197 5(5) nm, Cu-N being 0.196 6(6) and 0.197 7(7) nm, Cu-Cl being 0.221 5(3) and 0.222 7(3) nm, respectively.
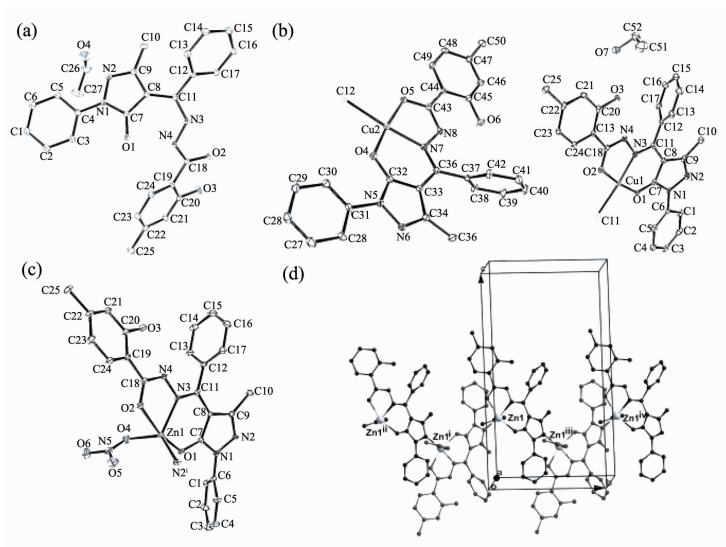
H atoms are ommited for clarity; Symmetry code: ^{i} 0.5−x, −0.5+y, 0.5−z; ^{ii} x, −1+y, z; ^{iii} 0.5−x, 0.5+y, 0.5−z; ^{iv} x, 1+y, z

Fig.1   ORTEP drawing of HL·0.5EtOH (a), **1** (b) and **2** (c) with 10% thermal ellipsoids; (d) Chain-like structure along b axis in complex **2**

However, the zinc(Ⅱ) center in **2** (Fig.1 (c)) is surrounded by one nitrate anion, one NO₂ donor set of an enolizated ligand L⁻ and one pyrazoline nitrogen atom from another adjacent acylhydrazone ligand, thus forming one dimension chain-like framework along b axis (Fig.1(d)). According to the Addison rule[18], the geometric index τ is 0.526 2, indicating that the coordination geometry of Zn(Ⅱ) ion is best described as a distorted trigonal biyramid rather than tetragonal pyramid. The equatorial plane of the trigonal biyramid is made up of N2^{i}, N3 and O4 atoms (Symmetry code: ^{i} 0.5 −x, −0.5 +y, 0.5 −z), while O1 and O2 atoms occupy the axial positions in trans manner.

2.2   IR spectra

The IR spectra for both complexes are more or less similar due to the similarity in coordination modes of the ligands with the metal centre. ν (O=C pyrazolone) vibrations of the free ligand is at 1 634 cm⁻¹, it shifts to 1 613 and 1 618 cm⁻¹ in complexes **1** and **2**, respectively, showing the pyrazolone O=C bond participates in the coordination in each complex. The O=C-N characteristic stretching vibration absorption of the acylhydrazone group in the free ligand is at 1 597 cm⁻¹, while it is absent in both complexes. Meanwhile, new (N =C-O) stretching vibration absorption are observed at 1 486 and 1 489 cm⁻¹ in complexes **1** and

Table 2　Selected bond lengths (nm) and angles (°) in HL·0.5EtOH, 1 and 2

		HL·0.5EtOH			
O1-C7	0. 126 4(2)	O2-C18	0.125 1(2)	N1-N2	0.139 9(2)
C7-C8	0. 143 5(3)	C8-C11	0.141 3(3)	N3-C11	0.132 8(2)
N3-N4	0.137 0(2)	N4-C18	0.134 0(2)	N2-C9	0.130 6(3)
		1			
Cu1-O1	0.189 6(5)	Cu1-O2	0.197 1(5)	Cu1-N3	0.197 7(7)
Cu1-Cl1	0.221 5(3)	Cu2-O4	0.191 7(5)	Cu2-N7	0.196 6(6)
Cu2-O5	0.197 5(5)	Cu2-Cl2	0.222 7(3)		
O1-Cu1-O2	173.1(2)	O1-Cu1-N3	91.9(2)	O2-Cu1-N3	81.2(2)
O1-Cu1-Cl1	93.02(19)	O2-Cu1-Cl1	93.84(17)	N3-Cu1-Cl1	175.01(18)
O4-Cu2-N7	93.0(2)	O4-Cu2-O5	173.8(2)	N7-Cu2-O5	81.4(2)
O4-Cu2-Cl2	93.83(16)	N7-Cu2-Cl2	173.14(17)	O5-Cu2-Cl2	91.82(15)
		2			
Zn1-N2^i	0.202 8(3)	Zn1-O1	0.204 9(3)	Zn1-O4	0.208 0(4)
Zn1-N3	0.211 0(3)	Zn1-O2	0.213 3(3)		
N3-Zn1-O2	76.16(11)	N2^i-Zn1-O1	94.84(13)	N2i-Zn1-O4	128.99(15)
O1-Zn1-O4	87.77(14)	N2^i-Zn1-N3	125.25(13)	O1-Zn1-N3	86.22(12)
O4-Zn1-N3	105.76(15)	N2i-Zn1-O2	101.97(12)	O1-Zn1-O2	160.56(11)
O4-Zn1-O2	89.15(13)				

Symmetry code: ^{i} 0.5−x, −0.5+y, 0.5−z

Table 3　Luminescent decay data of HL and complex 2 in the solid state

	$\tau1$ / μs	B1 / %	$\tau2$ / μs	B2 / %	$<\tau>$ / μs
HL	0.661 2	58.42	8.118 5	41.58	7.352 8
Complex **2**	0.738 6	63.62	8.787 1	36.38	7.755 6

2, respectively, which revealing that in both complexes the acylhydrazone C=O in O=C-N moiety has enolized and the oxygen atom coordinates to the central metal ion[8]. The peak at 1 536 cm^{-1} should be assigned to the ν (C=N pyrazolone) vibration, it appears at 1 531 and 1 548 cm^{-1} in complexes **1** and **2**, respectively, clearly indicating that the nitrogen atom of pyrazolone ring takes part in the coordination with Zn(Ⅱ) ion in complex **2**, while does not in complex **1**. It is in accordance with the X-ray diffraction analysis result.

2.3　Fluorescence spectra

In the solid state, the fluorescence intensity of **1** is much too weak, thus is not discussed in this work. Fig.2 shows the excitation and emission spectra of the acylhydrazone ligand and **2** in solid state. When

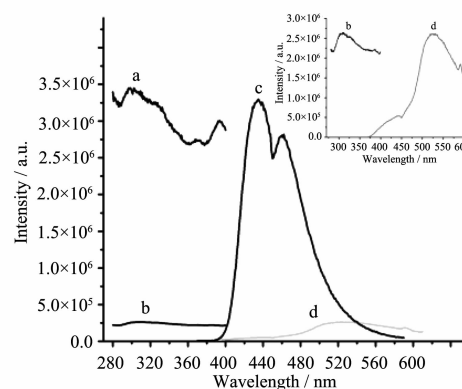excited at 310 nm, complex **2** exhibits two strong emissions at 434 and 459 nm, while the ligand shows

Fig.2　Fluorescence excitation spectra of complex **2** (a) and free ligand HL (b); emission spectra of complex **2** (c) and free ligand HL (d) in the solid state at room temperature

relatively weak emission at 521 nm. This is probably due to the energy transferring from the ligand to the Zn(II) ion[19]. The behavior of Zn^{2+} coordinated to the ligand is regarded as that of emissive species resulted in a CHEF effect (chelation enhancement of the fluorescence emission)[20]. Luminescent decay data of HL and complex **2** in solid state are shown in Table 3, where τ_1 and τ_2 are short- and long-decay components, separately. The lifetime values (μs) are determined to be 0.661 2 and 8.118 5 for HL, while 0.738 6 and 8.787 1 for the complex **2**. The mean lifetimes $<\tau>$ are 7.352 8 μs for HL and 7.7556 μs for the complex **2** calculated by the following equation[21]: $<\tau>=(B_1\tau_1^2+B_2\tau_2^2)/(B_1\tau_1+B_2\tau_2)$, where B_1 and B_2 are weight factors.

References：

[1] HUANG Chao(黄超), WU Juan(吴娟), CHEN Dong-Mei (陈冬梅), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2015,31**:109-113

[2] CHEN Yan-Min(陈延民), XIE Qin-Fan(解庆范), LIU Jin-Hua(刘金花), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2015,31**:74-80

[3] CHEN Yan-Min(陈延民), CHU Zhao-Hua(储召华), HAO Gui-Xia(郝桂霞), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2015,31**:317-322

[4] ZHUO Xin(卓馨), PAN Zhao-Rui (潘兆瑞), WANG Zuo-Wei (王作为), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2006,22**:1847-1851

[5] LI Shi-Xiong (李石雄), LIAO Bei-Ling(廖蓓玲), LUO Pei (罗培), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2015,31**:291-296

[6] Yang Z Y, Yang R D, Li F S, et al. *Polyhedron*, **2000,19**: 2599-2604

[7] Yang Z Y, Wang B D, Li Y H. *J. Organomet. Chem.*, **2006, 691**:4159-4166

[8] Wang Y, Yang Z Y. *Transition Met. Chem.*, **2005,30**:902-906

[9] Wang Y, Yang Z Y. *J. Lumin.*, **2008,128**:373-376

[10]ZHANG Shu-Ming (张姝明), LI Pei-Fan(李培凡), YU Ming (郁铭), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2004,20**:439-443

[11]Zhou X Y, Li P X, Shi Z H, et al. *Inorg. Chem.*, **2012,51**: 9226-9231

[12]Wu Z K, Chen Q Q, Yang G Q, et al. *Sens. Actuators B.*, **2004,99**:511-515

[13]Zhang G Q, Yang G Q, Zhu L N, et al. *Sens. Actuators B.*, **2006,114**:995-1000

[14]Sali S, Grabchev I, Chovelon J M, et al. *Spectrochim. Acta A*, **2006,65**:591-597

[15]Kulatilleke C P, Silva S A, Eliav Y. *Polyhedron*, **2006,25**: 2593-2596

[16]Sheldrick G M. *SADABS, University of Göttingen, Germany*, **1996**.

[17]Sheldrick G M. *SHELX*-97, *Program for the Solution and the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[18]Addison A W, Rao T N. *J. Chem. Soc. Dalton Trans.*, **1984**,1349-1356

[19]CHENG Mei-Ling (程美令), CAO Xiang-Qian (曹向前), WANG Chun-Lan(王春兰), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2006,22**:1222-1226

[20]Vicente M, Bastida R, Lodeiro C, et al. *Inorg. Chem.*, **2003,42**:6768-6779

[21]Buddhudu S, Morita M, Murakami S, et al. *J. Lumin.*, **1999**,83-84:199-203