

## 3-甲基吡唑-5-甲酸基 Zn(II)配合物的合成、晶体结构及荧光性质

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## Synthesis, Crystal Structure of 3-Methylpyrazole-5-carboxylate Based Zinc(II) Complex and its Fluorescent Property

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**Abstract:** A transition metal complex  $\text{Zn}(\text{mpc})_2(\text{H}_2\text{O})_2$  ( $\text{Hmpc}$ =3-methylpyrazole-5-carboxylic acid) has been synthesized by the reaction of  $\text{Hmpc}$  with  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  using hydrothermal method, which was characterized by IR spectra, elemental analysis and single-crystal X-ray structure analysis. The structure reveals that the complex crystallizes in the trigonal space group  $R\bar{3}c$  with the  $\text{Zn}^{\text{II}}$  atom on a threefold axis, composed of one  $\text{Zn}^{\text{II}}$  atom, two independent  $\text{mpc}^-$  ligands and two coordinated water. Hydrogen bonds link the molecules into a three-dimensional supramolecular architecture. Fluorescent analysis in the dilute EtOH solution shows that the title complex exhibits a broad fluorescent band at 471 nm upon photoexcitation at 280 nm and has a bathochromic shift of the emission energy compared with the free ligand, possibly due to metal-to-ligand charge transfer (MLCT). CCDC: 682402.

**Key words:** zinc(II) complex; pyrazole-carboxylate; crystal structure; fluorescent property

$\text{Zn}^{2+}$  ions play an important role in the gene expression, metalloenzyme regulation, neural signal transmission and other biological processes<sup>[1-3]</sup>. The syntheses of Zn(II) complexes have been stimulated to obtain specific molecular probes<sup>[4]</sup> or provide models for the coordination environment of the active site in metalloenzyme<sup>[5]</sup>. It is well-known that the N, O ligands

such as imidazole-carboxylic acid, pyridine-carboxylic acid and amino acid have often been employed in coordination complexes<sup>[6-8]</sup>. Considering the introduction of a hydrophilic moiety to obtain soluble and stable complexes under physiological conditions<sup>[9]</sup>, 3-methylpyrazole-5-carboxylic acid ( $\text{Hmpc}$ ) seems to be a suitable ligand for candidate. As part of initial investigations

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into the transition metal coordination chemistry of this new ligand, the 3-methylpyrazole-5-carboxylate based zinc(II) complex,  $\text{Zn}(\text{mpc})_2(\text{H}_2\text{O})_2$ , has been synthesized and characterized by IR spectra, elemental analysis and single-crystal X-ray structure analysis in this paper.

## 1 Experimental

### 1.1 Reagent and instruments

All chemicals were of analytical grade and used without further purification. The hydrothermal reaction was performed in a 25 mL Teflon-lined stainless steel autoclave under autogenous pressure. The elemental analysis was carried out on a Perkin-Elmer 240C. Infrared spectra were recorded from KBr discs in the range of 4000~400  $\text{cm}^{-1}$  on a VECTOR-22 spectrometer.

### 1.2 Synthesis of the title complex

An mixture solution of Hmpc (126 mg, 1 mmol),  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (149 mg, 0.5 mmol) and 8 mL  $\text{H}_2\text{O}$  was adjusted to pH 7 with 1 mol  $\cdot \text{L}^{-1}$  NaOH solution and then heated at 140  $^{\circ}\text{C}$  for 3 days. After filtration, the filtrate was cooled slowly to room temperature, the colorless crystals were obtained and air-dried ca. 65% yield based on Zn.

Anal. calcd (%) for  $\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_6\text{Zn}$ : C 34.16; N 15.93; H 4.01; Found (%): C 34.20; N 15.95; H 3.97. IR (KBr discs,  $\nu_{\text{max}}$  /  $\text{cm}^{-1}$ ): 3 408(vs), 3 161(s), 2 985(s),

1 595(vs), 1 493(m), 1 464(s), 1 433(m), 1 352(vs), 1 311(vs), 1 213(m), 1 101(w), 1 016(s), 916(w), 876(w), 837(m), 785(s), 683(w), 656(w), 627(w), 586(m), 519(m).

### 1.3 Analysis of the crystal structure

The crystal structure data collection was done on a BRUKER SMART APEX CCD diffractometer using graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071\,073\,\text{nm}$ ) at 295(2) K. The collected data were reduced using SAINT<sup>[10]</sup>. Out of the total 11 219 reflections collected in the range of  $2.02^{\circ} \leq \theta \leq 27.5^{\circ}$ , 1 574 were independent with  $R_{\text{int}}=0.086\,6$ , of which 1 506 were considered as observed [ $I > 2\sigma(I)$ ] and used in the structure solution and refinement. The crystal structure was solved by direct methods using SHELXS-97 program<sup>[11]</sup>. All non-hydrogen atoms were refined anisotropically using the full-matrix least-squares techniques with SHELXL-97 program<sup>[11]</sup>. The hydrogen atoms were generated geometrically and refined isotropically. The final  $R=0.039\,5$ ,  $wR_2=0.149\,9$  ( $w=1/[\sigma^2(F_o^2)+(0.126\,2P)^2]$  where  $P=(F_o^2+2F_c^2)/3$ ,  $S=1.063$ ,  $(\Delta/\sigma)_{\text{max}}=0.000$ ,  $(\Delta\rho)_{\text{max}}=543\,\text{e} \cdot \text{nm}^{-3}$  and  $(\Delta\rho)_{\text{min}}=835\,\text{e} \cdot \text{nm}^{-3}$ . The crystal data and structure refinement results of the title complex are given in Table 1. Selected bond lengths and angles are listed in Table 2.

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Table 1 Crystal data and structure refinement parameters

Formula	$\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_6\text{Zn}$	Crystal size / mm	0.40×0.50×0.60
Formula weight	351.62	$T / \text{K}$	295(2)
Crystal system	Trigonal	$\lambda(\text{Mo } K\alpha) / \text{nm}$	0.071 073
Space group	$R\bar{3}c$ (No.167)	$\theta_{\text{min}}, \theta_{\text{max}} / (^{\circ})$	2.02, 27.5
$a / \text{nm}$	1.484 3(3)	Tot., uniq. data ( $R_{\text{int}}$ )	11 219, 1 574 (0.087)
$c / \text{nm}$	3.232 7(9)	Observed data [ $I > 2\sigma(I)$ ]	1 506
$V / \text{nm}^3$	6.168(2)	Nref, Npar	1 574, 96
$Z$	18	$R, wR_2$	0.0395, 0.1499
$\rho_{\text{calc}} / (\text{g} \cdot \text{cm}^{-3})$	1.704	$S$	1.063
$\mu / \text{mm}^{-1}$	1.826	$(\Delta/\sigma)_{\text{max}}$	0
$F(000)$	3 240	$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	543, -835

Table 2 Selected bond lengths (nm) and bond angles ( $^{\circ}$ ) for the title complex

Zn1-O1	0.214 2(2)	C1-O1	0.125 7(3)	C3-C4	0.138 3(4)
Zn1-O3	0.209 7(2)	C1-C2	0.149 8(3)	C4-N1	0.134 3(3)
Zn1-N2	0.212 3(2)	C2-N2	0.133 4(3)	C4-C5	0.149 1(4)
C1-O2	0.124 6(3)	C2-C3	0.140 0(3)	N1-N2	0.134 5(3)

Continued Table 2

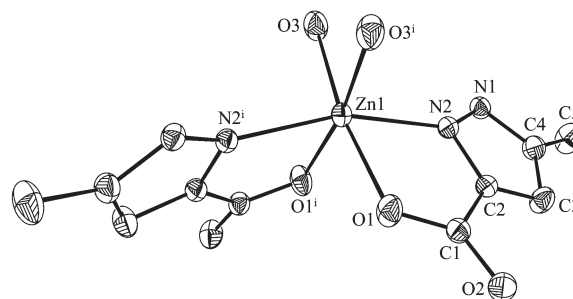
O3i-Zn1-O3	87.8(1)	O3i-Zn1-O1	88.6(1)	N2-Zn1-O1	77.3(1)
O3i-Zn1-N2	97.8(1)	O1-Zn1-O1i	95.9(1)	N2i-Zn1-O1	90.3(1)
O3-Zn1-N2	95.4(1)	O3-Zn1-O1	171.4(1)	N2-Zn1-N2i	161.6(1)

## 2 Results and discussion

### 2.1 Description of the structure

The title complex crystallizes in the centrosymmetric space group  $R\bar{3}c$ , composed of one  $Zn^{II}$  atom, two independent  $mpc^-$  ligands and two coordinated water. The  $Zn^{II}$  atom is located on a threefold axis in a distorted octahedral construction (Fig.1) and coordinated to two pyrazole N atoms (N2, N2<sup>i</sup>), two carboxyl O atoms (O1, O1<sup>i</sup>) from two  $mpc^-$  ligands and two water ligands. The Zn1-O1 bond length (0.214 2(2) nm) is significantly longer than the Zn1-O3 bond length (0.209 7(2) nm) and slightly longer than the Zn1-N2 bond length (0.212 3(2) nm). The angles around the  $Zn^{II}$  atom are in the range of 77.3(1)° to 171.4(1)°. Both the bonds and angles around the  $Zn^{II}$  atom correspond to those in the reported 3,5-pyrazoledicarboxylate based Zn(II) complexes<sup>[12-14]</sup>. As a bidentate ligand, the  $mpc^-$  anion chelate one  $Zn^{II}$  atom with pyrazole N atom and carboxyl O atom to form a five membered ring of Zn1-O1-C1-C2-N2. As expected, the pyrazole ring C2~C4/N1~N2 is nearly planar with the mean deviation from this plane being 0.000 30 nm. The methyl group in the terminal position (C5) and the carboxyl C (C1) are both bonded to the pyrazole ring with the deviation from the pyrazole ring plane being 0.006 77 nm. The dihedral angles between the carboxylate group and the plane of correspondingly linked pyrazolyl rings is 12.2°. The C1-O1 bond length of the coordinated O atom nearly equals to the C1-O2 bond length of the noncoordinated O atom. Both of the C1-C2 0.149 8(3) nm and C4-C5 0.149 1(4) nm bonds fall in the normal

single-bond range, as observed in the reported structures<sup>[15,16]</sup>. The bond lengths in the pyrazole ring are N1-N2 0.134 5(3) nm, C2-N2 0.133 4(3) nm, C4-N1 0.134 3(3) nm, C2-C3 0.140 0(3) nm and C3-C4 0.138 3(4) nm, respectively, in line with the known values<sup>[17,18]</sup>.



Symmetry code: <sup>i</sup>  $y+1/3, x-1/3, z+1/6$

Fig.1 Molecular structure of the title complex, shown with 30% probability displacement ellipsoids; Hydrogen atoms are omitted for clarity

Additionally, there are three intermolecular hydrogen bonds observed in the crystal lattice, associated with the noncoordinated carboxyl O atom (O2), the noncoordinated pyrazole N atom (N1) and the coordinated water (O3). One is with atom O3 acting as donor to atom O2<sup>ii</sup> [symmetry code: <sup>ii</sup>  $x-1/3, x-y+1/3, z-1/6$ ] as acceptor, another one is with atom O3 acting as donor to atom O2<sup>iii</sup> [symmetry code: <sup>iii</sup>  $y+5/3, x+4/3, z-1/6$ ] as acceptor, the third one is with atom N1 as donor to atom O2<sup>ii</sup> as acceptor. All the hydrogen bonds are normal since distances are 0.271 6(3)~0.289 9(3) nm and bond angles 152°~162°. Obviously, the molecules are linked through these hydrogen bonds to generate a three-dimensional supramolecular architecture.

Table 3 Hydrogen bonding geometry in the title complex

Doner-H...Acceptor	D-H / nm	H...A / nm	D...A / nm	D-H...A / (°)
N1-H1...O2 <sup>ii</sup>	0.086	0.207	0.289 9(3)	161
O3-H3A...O2 <sup>iii</sup>	0.091	0.184	0.271 6(3)	162
O3-H3C...O2 <sup>ii</sup>	0.090	0.205	0.288 4(3)	152

Symmetry codes: <sup>ii</sup>  $x-1/3, x-y+1/3, z-1/6$ ; <sup>iii</sup>  $y+5/3, x+4/3, z-1/6$ .

### 2.2 Spectroscopic properties of the title complex

The IR spectrum exhibits a strong broad band at

3 408  $cm^{-1}$ , which can be assigned to  $\nu(OH)$  of the coordination water and  $\nu(NH)$ . The band at 3 161 and 2 985

$\text{cm}^{-1}$  are attributed to  $\nu(\text{CH})$  of the pyrazole ring and  $\nu(\text{CH}_3)$ , respectively. It is known that a band active in IR spectra appears around  $1700\text{ cm}^{-1}$  [ $\nu(\text{C}=\text{O})$ ] when the carbonyl is hydrogen-bonded but not dimerized. No band was observed around  $1700\text{ cm}^{-1}$  to confirm no hydrogen atom located on the carboxyl group. The band at  $1352$  and  $1311\text{ cm}^{-1}$  may be attributed to two different vibrations of  $\nu(\text{C}-\text{O})$ . The band at  $586$  and  $519\text{ cm}^{-1}$  may be assigned to the metal-nitrogen and metal-oxygen stretching<sup>[19]</sup>.

Fig.2 shows the fluorescence spectra of free ligand (a) and the title complex (b) in EtOH at ambient temperature. Upon photoexcitation at  $280\text{ nm}$ , the ligand molecule emits at  $448\text{ nm}$ , while the title complex exhibits a broad fluorescent band at  $471\text{ nm}$ . Compared with that of the ligand, the emission spectrum of the title complex is obviously red-shift, possibly attributed to the lowering of the energy gap between  $\pi$  and  $\pi^*$  with the formation of N-Zn and O-Zn bonds. The electrons in the full d-orbitals of the  $\text{Zn}^{2+}$  ion are accessible for back bonding to  $\pi$ -acceptor L, which can result in emissions assigned to the metal-to-ligand band<sup>[20]</sup>. Additionally, the emission intensity of the title complex is weaker than that of the ligand may owing to the fact that the coordination of a water molecule can quench luminescence<sup>[21]</sup>.

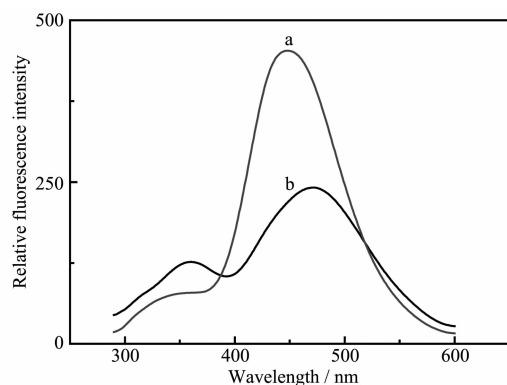


Fig.2 Fluorescence emission ( $\lambda=280\text{ nm}$ ) spectra of (a) free ligand ( $8\times 10^{-4}\text{ mol}\cdot\text{L}^{-1}$ ) (b) the title complex ( $4\times 10^{-4}\text{ mol}\cdot\text{L}^{-1}$ ) in EtOH solution at room temperature

### 3 Conclusion

A Zn(II) complex based on 3-methylpyrazole-5-carboxylate was successfully synthesized and characterized. The complex consists of one  $\text{Zn}^{\text{II}}$  atom, two

independent  $\text{mpc}^-$  ligands and two coordinated water. As a bidentate ligand, the  $\text{mpc}^-$  ion chelate the  $\text{Zn}^{\text{II}}$  atom with the pyrazole N atom and carboxyl O atom. Hydrogen bonds stabilize the crystal structure and link the molecules into a three dimensional supramolecular architecture. The complex in the dilute EtOH solution emits in violet region and has a bathochromic shift of the emission energy compared with the free ligand, possibly due to metal-to-ligand charge transfer (MLCT).

### References:

- [1] Assaf S Y, Chung S H. *Nature*, **1984**,**308**:734~736
- [2] Clarke N D, Berg J M. *Science*, **1998**,**282**:2018~2022
- [3] Vahrenkamp H. *Dalton Trans.*, **2007**, (42):4751~4759
- [4] Burdette S C, Lippard S J. *Coord. Chem. Rev.*, **2001**,**216**~**217**: 333~361
- [5] Meyer F. *Eur. J. Inorg. Chem.*, **2006**, (19):3789~3800
- [6] Shimizu E, Kondo M, Fuwa Y, et al. *Inorg. Chem. Comm.*, **2004**, (7):1191~1194
- [7] Wu W P, Wang Y Y, Wu Y P, et al. *Cryst. Eng. Comm.*, **2007**, **9**:753~757
- [8] Nagy L, Szorcsik A. *J. Inorg. Biochem.*, **2002**,**89**:1~12
- [9] Santini C, Pellei M, Lobbia G G, et al. *J. Inorg. Biochem.*, **2003**,**94**:348~354
- [10] Bruker SMART and SAINT, Bruker AXS Inc., Madison, Wisconsin, USA, **2000**.
- [11] Sheldrick G M. *SHELXS-97 and SHELXTL-97*, University of Göttingen, Germany, **1997**.
- [12] Pons J, March R, Rius J, et al. *Inorg. Chim. Acta*, **2004**,**357**: 3789~3792
- [13] King P, Clerac R, Anson C E, et al. *Dalton Trans.*, **2004**, (6): 852~861
- [14] Pan L, Ching N, Huang X Y, et al. *Chem. Eur. J.*, **2001**,**7**: 4431~4437
- [15] Xie H D, Xie C Z, Wang X Q, et al. *Acta Crystallogr.*, **2006**, **E62**:m3119~m3121
- [16] Bandoli G, Dolmella A, Lobbia G G, et al. *Inorg. Chim. Acta*, **2006**,**359**:4036~4042
- [17] Hammes Brian S, Luo X M, Carrano M W, et al. *Inorg. Chim. Acta*, **2002**,**341**:33~38
- [18] Crane J D, Fox O D, Sinn E. *Dalton Trans.*, **1999**, (9):1461~1466
- [19] Peica N, Kostova I, Kiefer W. *Chem. Phys.*, **2006**,**325**:411~421
- [20] Zheng S L, Zheng J P, Chen X M, et al. *Chem. Eur. J.*, **2003**, **9**:3888~3896
- [21] Yang X P, Su C Y, Kang B S, et al. *Dalton Trans.*, **2000**, (19): 3253~3260