

以 3,5-二甲基-1-羧甲基-4-吡唑甲酸为配体的两个锌的配合物的合成、晶体结构和荧光性能

刘秀秀¹ 程美令¹ 任艳秋¹ 夏庆洪¹ 韩伟¹ 刘琦^{*,1,2}

(¹常州大学石油化工学院,江苏省绿色催化材料和技术重点实验室,常州 213164)

(²南京大学配位化学国家重点实验室,南京 210093)

摘要: 以 3,5-二甲基-1-羧甲基-4-吡唑甲酸和 4,4'-联吡啶为配体,合成了 1 个单核锌(II)配合物 $[\text{Zn}(4,4'\text{-bpy})(\text{Hcmdpca})_2(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ (**1**) 和 1 个锌(II)的一维配位聚合物 $[\text{Zn}(4,4'\text{-bpy})(\text{Hcmdpca})_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ (**2**) (H_2cmdpca =3,5-二甲基-1-羧甲基-4-吡唑甲酸; 4,4'-bpy=4,4'-联吡啶),并用元素分析、红外光谱、X-射线单晶衍射结构分析、热重分析等对其进行了表征。配合物 **1** 和 **2** 都属于单斜晶系,空间群为 $P2_1/c$ 。配合物 **1** 的锌离子都位于一个畸变的八面体构型中。配合物 **1** 中的独立结构单元间通过分子间氢键作用构成一个三维的超分子结构。而在 **2** 中,锌离子位于一个畸变的四方锥构型中,每个 4,4'-联吡啶分子桥联 2 个相邻的锌(II)离子,形成一个一维链;这些一维链和水分子通过分子间氢键进一步形成一个三维的结构。此外还考察了 **1** 和 **2** 的热稳定性和固体荧光性质。

关键词: 锌; 3,5-二甲基-1-羧甲基-4-吡唑甲酸; 4,4'-联吡啶; 晶体结构; 荧光

中图分类号: O614.24¹

文献标识码: A

文章编号: 1001-4861(2015)03-0611-08

DOI: 10.11862/CJIC.2015.098

Two Zinc Complexes Based on 1-Carboxymethyl-3,5-dimethyl-1H-pyrazole-4-carboxylic Acid: Syntheses, Structures, and Luminescent Properties

LIU Xiu-Xiu¹ CHENG Mei-Ling¹ REN Yan-Qiu¹ XIA Qing-Hong¹ HAN Wei¹ LIU Qi^{*,1,2}

(¹School of Petrochemical Engineering and Jiangsu Key Laboratory of Advanced

Catalytic Materials and Technology, Changzhou University, Changzhou, Jiangsu 213164, China)

(²State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China)

Abstract: One monomeric complex $[\text{Zn}(4,4'\text{-bpy})(\text{Hcmdpca})_2(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ (**1**) and one 1D coordination polymer $[\text{Zn}(4,4'\text{-bpy})(\text{Hcmdpca})_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ (**2**) (H_2cmdpca =1-carboxymethyl-3,5-dimethyl-1H-pyrazole-4-carboxylic acid, 4,4'-bpy=4,4'-bipyridine) have been synthesized and characterized by elemental analysis, IR spectra, single crystal X-ray diffraction, thermogravimetric analysis. Complexes **1** and **2** all crystallize in the monoclinic system, space group $P2_1/c$. In **1**, Zn(II) ion is located in distorted octahedral coordination geometry, discrete mononucleate units and water molecules are assembled into a 3D network. In **2**, each Zn(II) ion is located in distorted square-pyramid geometry. Each 4,4'-bpy ligand bridges two adjacent Zn(II) ions, forming a 1D chain. These chains and water molecules are connected by hydrogen bonds, forming a 3D supramolecular network. The thermal stability and luminescent properties of the complexes are also investigated. CCDC: 963357, **1**; 979480, **2**.

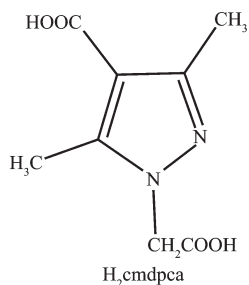
Key words: zinc(II); 1-carboxymethyl-3,5-dimethyl-1H-pyrazole-4-carboxylic acid; 4,4'-bipyridine; crystal structure; photoluminescence

收稿日期: 2014-11-02。收修改稿日期: 2014-12-31。

国家自然科学基金(No.20971060、21101018),南京大学配位化学国家重点实验室开放课题资助项目。

*通讯联系人。E-mail: liuqi62@163.com, Tel: 0519-86330185; 会员登记号: S060018987P。

Supramolecular frameworks/coordination polymers assembled by coordinate bond and hydrogen bond have attracted increasing research interest not only because of their appealing structural and topological novelty but also owing to their tremendous potential applications in gas storage^[1-3], separation^[4-5], magnetic and optical materials^[6-8], catalysis^[9-11] and lithium-ion batteries^[12-14]. Generally speaking, the structural diversity of such crystalline materials is dependent on many factors, such as the metal ion, the templating agents, the metal-ligand ratio, the pH value, the counteranion and the number of coordination sites provided by organic ligands^[15-16]. Among the strategies, the rational selection of organic ligands or coligands according to their length, rigidity and functional groups is important for the assembly of structural controllable supramolecular frameworks, and a great deal of significant works have been done by using this strategy^[17]. Pyrazole carboxylic acid type ligand, as a multidentate ligand, not only can provide multi-coordination sites involving nitrogen atoms on pyrazole ring and carboxylate oxygen atoms^[18-24], but also act as a donor and/or acceptor in hydrogen bond interactions. They have proven to be considerable advantageous ligands for the self-assembly of supramolecular frameworks^[25-26]. Recently, we have synthesized some luminescent complexes containing pyrazole carboxylic acids, such as 3,4-pyrazoledicarboxylic acid^[18-19], and 5-methyl-1*H*-pyrazole-3-carboxylic acid^[20-24] etc. In order to expand the study in this field, we designed and synthesized a new ligand 1-carboxymethyl-3,5-dimethyl-1*H*-pyrazole-4-carboxylic acid ($H_2cmdpca$) (Scheme 1). Compared to 3,5-dimethyl-1*H*-pyrazole-4-carboxylic acid with rigid structure, due to the flexible carboxymethyl group addition, $H_2cmdpca$ has become



Scheme 1 Molecular structure of $H_2cmdpca$

a semi-rigid ligand and has more potential coordination sites. Besides, two carboxyl groups of $H_2cmdpca$ can be partially or fully deprotonated to generate $Hcmdpca^-$ and $cmdpca^{2-}$ at different pH values, which is useful to synthesize new functional complexes. On the other hand, 4,4'-bipyridine (4,4'-bpy) is a good candidate for molecular building blocks. Many coordination polymers based on 4,4'-bpy have been reported^[12,27]. As the continuation of our research, and motivated by our interest in functional metal complexes, we carried out the reactions of $H_2cmdpca$, 4,4'-bpy and $Zn(NO_3)_2 \cdot 6H_2O$, and obtained two new complexes with uncoordinated carbonyl groups, namely, $[Zn(4,4'-bpy)(Hcmdpca)_2(H_2O)_3] \cdot 2H_2O$ (**1**), and $[Zn(4,4'-bpy)(Hcmdpca)_2(H_2O)] \cdot 3H_2O$ (**2**). Moreover, thermal stability and fluorescence properties of the complexes have also been studied. To the best of our knowledge, this is the first report on the metal complexes based on $H_2cmdpca$.

1 Experimental

1.1 Materials and instruments

All reagents and solvents were used as received from the commercial source without further purification. The ligand 1-carboxymethyl-3,5-dimethyl-1*H*-pyrazole-4-carboxylic acid ($H_2cmdpca$) was prepared according to similar method reported in literature^[28]. The single-crystal X-ray determination measurement of **1** and **2** was performed on a Bruker SMART CCD diffractometer at 293(2) K. The elemental analysis (C, H and N) was performed with a Perkin-Elmer 2400 Series II element analyzer. FIIR spectra were recorded on a Nicolet 460 spectrometer using KBr pellets in the range of 4 000~400 cm^{-1} . The luminescent spectra of the solid samples were recorded with a Varian Cary Eclipse spectrometer. Thermogravimetric analysis (TGA) experiments were carried out on a DuPont thermal analyzer from room temperature to 800 $^{\circ}C$ under N_2 atmosphere at a heating rate of 10 $^{\circ}C \cdot min^{-1}$.

1.2 Synthesis

1.2.1 Synthesis of complex $[Zn(4,4'-bpy)(Hcmdpca)_2(H_2O)_3] \cdot 2H_2O$ (**1**)

A solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 mmol, 0.029 7 g)

in distilled water (2 mL) was slowly added to a solution of H_2cmdpca (0.2 mmol, 0.039 6 g) and 4,4'-bpy (0.05 mmol, 0.009 9 g) in DMF (4 mL) to obtain a colorless solution. The resulting solution was allowed to stand at ambient temperature for some days, giving colorless crystals in 33.8% yield based on Zn. Anal. Calcd. For $\text{C}_{26}\text{H}_{36}\text{N}_6\text{O}_{13}\text{Zn}(\%)$: C, 44.23; H, 5.14; N, 11.88. Found(%): C, 44.21; H, 5.13; N, 11.85. IR (KBr pellet, cm^{-1}): 3 395 (s), 3 156 (m), 2 674 (m), 2 592 (m), 1 957 (w), 1 637 (vs), 1 597 (w), 1 547 (w), 1 497 (s), 1 430 (w), 1 388 (vs), 1 310 (s), 1 289 (s), 1 127 (vs), 1 102 (w), 1 070 (s), 943 (m), 924 (w), 877 (m), 853 (w).

1.2.2 Synthesis of complex $[\text{Zn}(4,4'\text{-bpy})(\text{Hcmdpca})_2(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ (**2**)

Synthesis of **2** was similar to that of **1**, but the molar ratio of $n_{\text{Zn}^{2+}}:n_{\text{H}_2\text{cmdpca}}:n_{4,4'\text{-bpy}}$ is 1:2:1. The resulting solution was allowed to stand at ambient temperature for some days, yielding colorless crystals in 24.67% yield based on Zn. Anal. Calcd. For $\text{C}_{26}\text{H}_{34}\text{ZnN}_6\text{O}_{12}(\%)$: C, 45.35; H, 4.94; N, 12.21. Found (%): C, 45.38; H, 4.99; N, 12.20. IR (KBr pellet, cm^{-1}): 3 450 (m), 2 993 (s), 2 782 (s), 2 423 (m), 1 667 (m), 1 571 (s), 1 386 (vs), 1 290 (w), 1 201 (m), 1 141 (m), 1 043 (m), 885 (w), 807 (s), 762 (w).

1.3 X-ray analysis

Single-crystal X-ray diffraction measurements were carried out with a Bruker Smart Apex CCD area detector at 293(2) K. Intensity reflections were measured adopting graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071\ 073\ \text{nm}$) with the φ - ω scan mode. The structure were solved by direct methods and refined by full-matrix least-squares methods on F^2 employing the SHELXTL-97 program^[29]. Anisotropic thermal factors were assigned to all the non-hydrogen atoms, H atoms attached to C were placed geometrically and allowed to ride during subsequent refinement with an isotropic displacement parameter fixed at 1.2 times U_{eq} of the parent atoms. H atoms attached to O atoms from the water molecules were first located in difference Fourier maps and then placed in the calculated sites and included in the refinement. Structure crystallographic data and experimental details for the two compounds are summarized in Table 1. The selected bond lengths and bond angles are given in Table 2, and the hydrogen bond distances and angles are presented in Table 3.

CCDC: 963357, **1**; 979480, **2**.

Table 1 Crystal data and structure refinement parameters for **1** and **2**

Compound	1	2
Empirical formula	$\text{C}_{26}\text{H}_{36}\text{ZnN}_6\text{O}_{13}$	$\text{C}_{26}\text{H}_{34}\text{ZnN}_6\text{O}_{12}$
Formula weight	705.98	687.96
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / nm	1.743 5(7)	1.598 05(16)
b / nm	0.768 1(3)	1.182 69(12)
c / nm	2.490 4(9)	2.220 26(16)
$\beta / (^\circ)$	114.85(2)	133.585(4)
V / nm^3	3.026(2)	3.039 6(5)
Z	4	4
$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.549	1.503
μ / mm^{-1}	0.890	0.890
$F(000)$	1 572	1 432
Crystal size / mm	0.26×0.20×0.20	0.24×0.22×0.21
θ range for data collection / $(^\circ)$	1.70~26.3	1.76~25.5
Index ranges (h, k, l)	$-21 \leq h \leq 15, -9 \leq k \leq 7, -30 \leq l \leq 30$	$-19 \leq h \leq 18, -14 \leq k \leq 14, -20 \leq l \leq 27$
Reflections collected	17 702	17 495
Independent reflection (R_{int})	6 059 (0.165 6)	5 901 (0.034 2)

Continued Table 1

Data / restraints / parameters	6 064 / 3 / 408	5 901 / 10 / 407
Goodness-of-fit on F^2	1.026	1.018
R_1, wR_2 ($I > 2\sigma(I)$)	0.075 2, 0.183 2	0.056 8, 0.162 8
R_1, wR_2 (all data)	0.159 1, 0.219 7	0.066 7, 0.168 5
Largest diff. peak and hole / ($e \cdot nm^{-3}$)	1 025 and -1 649	987 and -818

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for complexes 1 and 2

Complex 1					
Zn1-O11	0.210 8(4)	Zn1-O5	0.203 2(4)	Zn1-O9	0.214 2(6)
Zn1-O1	0.205 2(4)	Zn1-N5	0.215 2(6)	Zn1-O10	0.209 6(5)
O5-Zn1-N5	87.71(17)	O5-Zn1-O1	175.6(18)	O1-Zn1-N5	89.64(17)
O5-Zn1-O10	93.09(18)	O10-Zn1-N5	91.4(2)	O1-Zn1-O10	90.45(18)
O11-Zn1-N5	179.8(2)	O5-Zn1-O11	92.23(16)	O9-Zn1-N5	91.7(2)
O1-Zn1-O11	90.43(16)	O11-Zn1-O9	88.5(2)	O10-Zn1-O11	88.45(18)
O10-Zn1-O9	176.12(16)	O5-Zn1-O9	89.53(18)	O1-Zn1-O9	87.08(18)
Complex 2					
Zn1-N6 ⁱⁱ	0.230 0(4)	N5-Zn1	0.228 6(6)	O5-Zn1	0.231 2(46)
N6-Zn1 ⁱ	0.230 0(4)	O9-Zn1	0.234 9(6)	O1-Zn1	0.230 1(7)
N5-Zn1-O1	94.3(2)	N6 ⁱⁱ -Zn1-O5	88.55(16)	N5-Zn1-N6 ⁱⁱ	165.38(18)
N5-Zn1-O9	89.1(2)	O1-Zn1-N6 ⁱⁱ	90.82(18)	O1-Zn1-O9	80.28(16)
N5-Zn1-O5	91.1(2)	N6 ⁱⁱ -Zn1-O9	105.29(17)	O1-Zn1-O5	160.60(17)
O5-Zn1-O9	81.3(2)				

Symmetry codes: ⁱ $x-1, -y+1/2, z-1/2$; ⁱⁱ $x+1, -y+1/2, z+1/2$ Table 3 Hydrogen bond distances (nm) and angles ($^\circ$) for compounds 1 and 2

D-H \cdots A	$d(D-H)$	$d(H\cdots A)$	$d(D\cdots A)$	$\angle D-H\cdots A$
Complex 1				
O(9)-H(9X) \cdots O(12) ⁱ	0.082	0.221	0.272 0(7)	120
O(11)-H(11X) \cdots O(6)	0.082	0.211	0.270 1(6)	129
O(11)-H(11Y) \cdots O(2)	0.082	0.211	0.268 2(6)	127
O(12)-H(12X) \cdots N(3) ⁱⁱ	0.082	0.210	0.291 7(7)	175
O(13)-H(13Y) \cdots O(2) ⁱⁱⁱ	0.083	0.191	0.267 6(7)	154
C(1)-H(1B) \cdots O(4)	0.096	0.235	0.300 8(10)	126
C(9)-H(9A) \cdots O(8)	0.096	0.252	0.329 3(9)	138
C(17)-H(17) \cdots O(1)	0.093	0.244	0.303 2(11)	121
C(21)-H(21) \cdots O(5)	0.093	0.231	0.290 7(8)	122
Complex 2				
O(7)-H(7) \cdots O(10) ⁱ	0.082	0.178	0.258 6(7)	161
O(9)-H(9X) \cdots O(3) ⁱ	0.082	0.243	0.273 1(15)	102
O(10)-H(10X) \cdots O(6)	0.082	0.220	0.277 6(10)	128
O(11)-H(11X) \cdots O(10) ⁱ	0.082	0.238	0.318 2(19)	169
O(11)-H(11X) \cdots O(8)	0.082	0.254	0.288 8(14)	107
O(11)-H(11Y) \cdots O(8)	0.082	0.219	0.288 8(14)	144
O(12)-H(12X) \cdots O(1)	0.082	0.206	0.278 3(13)	148

Continued Table 1

O(4)–H(4)···N(3) ⁱⁱ	0.082	0.188	0.267 0(8)	162
C(1)–H(1B)···O(3)	0.096	0.257	0.305 9(13)	112
C(6)–H(6B)···O(4)	0.096	0.241	0.300 9(9)	120
C(9)–H(9B)···O(7)	0.096	0.259	0.292 6(12)	101

Symmetry codes: ⁱ $x, -1+y, z$; ⁱⁱ $x, 1+y, z$; ⁱⁱⁱ $-1+x, y, z$ for **1**; ⁱ $x, 1+y, z$; ⁱⁱ $x, -1+y, z$ for **2**

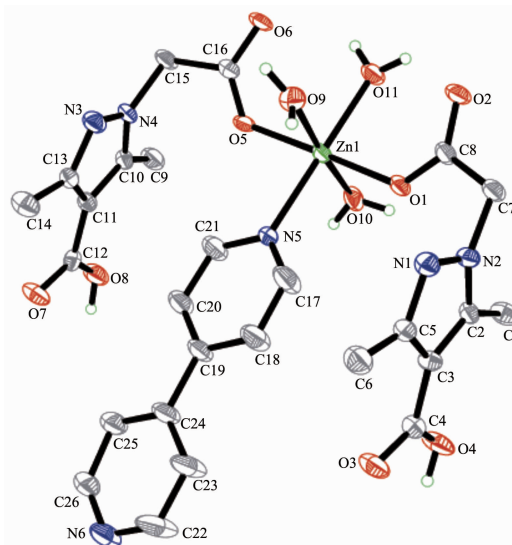
2 Results and discussion

2.1 Syntheses and infrared spectra

Complex **1** can be obtained by slow evaporation of a mixed solution of DMF and deionized water of Zn(II) and ligands with molar ratio of 1:2:0.5 ($n_{\text{Zn}^{2+}}:n_{\text{H}_2\text{cmdpca}}:n_{4,4'\text{-bpy}}$). When the molar ratio changed into 1:2:1, complex **2** was obtained. This fact shows that the outcome is molar-ratio-dependent. For complexes **1** and **2**, they have similar IR spectra (see supporting information, Fig.S1). The strong and broad peaks around 3 000~3 500 cm^{-1} are assigned to $\nu(\text{OH})$ of the water molecules. The strong peaks at 1 637 cm^{-1} (**1**), 1 667 cm^{-1} (**2**), and 1 388 cm^{-1} (**1**), 1 386 cm^{-1} (**2**), are assigned to the $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ stretching vibration of Hcmdpca^- [30]. Those assignments are supported by the X-ray crystal structure analysis.

2.2 Crystal structures of complexes 1 and 2

Complex **1** possesses mononuclear structure and crystallizes in the monoclinic space group $P2_1/c$. As shown in Fig.1, in **1**, the coordination sphere is defined by two oxygen atoms (O1, O5) from two carboxyl groups of two Hcmdpca^- anions ligands, three oxygen atoms (O9, O10, O11) from three coordinated water molecules respectively, and a nitrogen atom (N5) from one 4,4'-bpy, leading to a distorted octahedron geometry. Four oxygen atoms (O1, O5, O9, O10) form the equatorial plane of the octahedron, one nitrogen atom (N5) and one oxygen (O11) occupy the apical position. The bond distances of Zn1–O are in the range of 0.205 2~0.214 8 nm and Zn1–N bond length is 0.215 2 nm (Table 2), which are close to those observed in zinc complexes based pyrazole derivative ligands [28]. The degree of distortion from the ideal octahedral geometry is reflected in cisoid ($87.08(18)^\circ \sim 93.09(18)^\circ$) and transoid angles ($175.6(18)^\circ \sim 179.8(2)^\circ$).

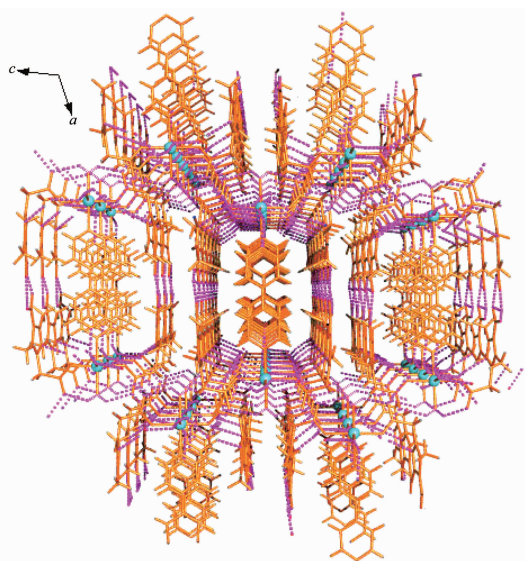


Only hydrogen atoms on oxygen atoms are drawn, and others are omitted for clarity

Fig.1 Molecular structure of the complex **1** with thermal ellipsoid at 30% probability level

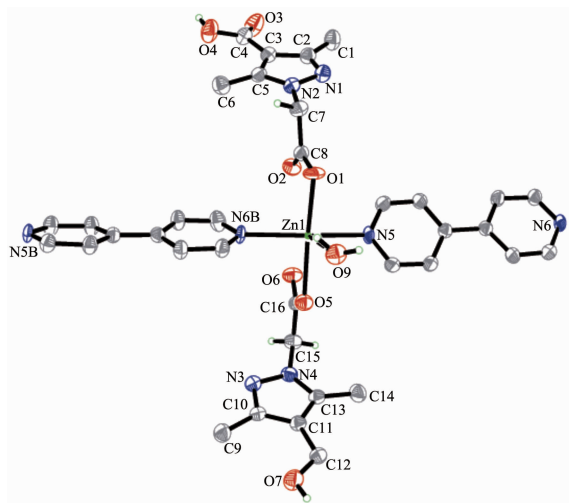
In addition, independent components $[\text{Zn}(4,4'\text{-bpy})(\text{Hcmdpca})_2(\text{H}_2\text{O})_3]$ and H_2O are linked by three kinds of hydrogen bonds ($\text{N}-\text{H}\cdots\text{O}$, $\text{O}-\text{H}\cdots\text{O}$, $\text{C}-\text{H}\cdots\text{O}$) (Table 3), as shown in Fig.2, resulting in the formation of a three dimensional supramolecular architecture; while the intermolecular $\pi-\pi$ interactions between pyrazolyl rings and between 4,4'-bpy molecules (centroid-centroid distances are in the range of 0.359 6~0.365 5 nm) further increase the stability of the structure.

Complex **2** also crystallizes in monoclinic system and space group $P2_1/c$. The asymmetric unit of **2** contains one Zn(II) ion, two Hcmdpca^- anion ligands, one 4,4'-bpy molecule, and one coordinated water molecule. As shown in Fig.3, the Zn(II) ion is five-coordinated and surrounded by two oxygen atoms (O1, O5) from two carboxylate groups of two Hcmdpca^- anion ligands, one oxygen atoms (O9) from a coordinated water molecule, and two nitrogen atoms



Only hydrogen atoms involved in the hydrogen bonds are shown; dash lines represent hydrogen bonds

Fig.2 3D network of complex 1



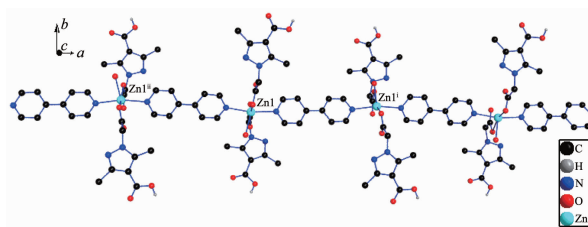
Only hydrogen atoms on oxygen atoms are drawn, and others are omitted for clarity; Symmetry code: $^{\text{ii}}x+1, -y+1/2, z+1/2$

Fig.3 A view of the coordination environment around the Zn(II) ions in **2** with thermal ellipsoid at 30% probability level

(N5, N6ⁱⁱ) from two 4,4'-bpy, leading to a distorted square-pyramidal coordination geometry. Two nitrogen atoms and two oxygen atoms (N6ⁱⁱ, N5, O1, and O5) form the base plane of the square-pyramidal structure, one oxygen atom (O9) occupy the apical position. N6ⁱⁱ, N5, O1 and O5, and Zn(II) deviate 0.033 1 and 0.004 84 nm from the the base plane, respectively. The bond distances of Zn1-O and Zn1-N are in the range of 0.230 1~0.230 0 nm and 0.228 6~0.230 0 nm respec-

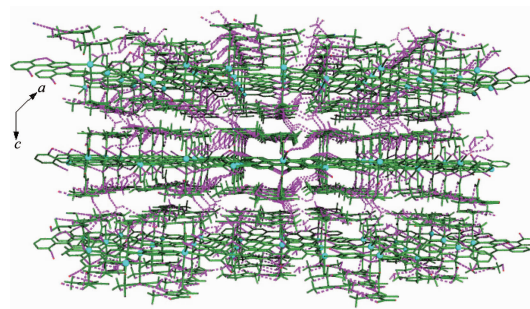
tively (Table 2), which are slight larger than the values observed in the complex **1**. The bond angles of N5A-Zn1-N6, N6-Zn1-O9, N5A-Zn1-O9 are 165.38(18)°, 105.29(17)° and 89.1(2)° respectively.

The adjacent Zn(II) ions are linked together by one 4,4'-bpy ligand to form a one-dimensional chain structure, as shown in Fig.4. The distance between two Zn(II) ions is 1.160 4 nm. These 1D chains, free water molecules are linked by multiple hydrogen bonds (N-H...O, O-H...O, C-H...O)(Table 3), as shown in Fig.5, resulting in the formation of a three dimensional supramolecular architecture with micropore. PLATON shows that the effective volume for the inclusion is about 0.259 9 nm³ per unit cell, comprising 8.6% of the crystal volume of **2**.



Only hydrogen atoms on oxygen atoms are drawn, and others are omitted for clarity; Symmetry code: $^{\text{i}}x-1, -y+1/2, z-1/2$; $^{\text{ii}}x+1, -y+1/2, z+1/2$

Fig.4 1D chain structure of complex **2** along the *a* axis



Dash lines represent hydrogen bonds

Fig.5 3D network of complex **2**

The considerable interesting observation is that complex **2** contains uncoordinated carboxyl groups (free carboxylic acids) and nitrogen atoms from Hcmdpca⁻, while **1** not only keeps uncoordinated carboxyl groups but also uncoordinated nitrogen atoms from 4,4'-bpy molecules and Hcmdpca⁻. These uncoordinated carboxyl groups/nitrogen atoms might serve as Lewis acid/base sites in catalytic and acid-

base reactions^[28,31]. On the other hand, the metal complexes with uncoordinated carboxyl groups could be further modified using a variety of organic and inorganic reactions to afford new metal complexes with different properties. The relative research is under way in our group.

2.3 Thermal analysis

For detecting the thermal stabilities of complexes **1** and **2**, thermal gravimetric (TG) analyses were carried out from the room temperature to 850 °C in a nitrogen atmosphere (see Fig.S2, supporting information). For complex **1**, the initial weight loss of 12.84% occurs from 55 to 169 °C, corresponding to the loss of five water molecules (Calcd. 12.76%). Above 169 °C, the remaining material decomposes gradually. For complex **2**, the first weight loss of 12.84% which occurred from 50 to 166 °C corresponds to the release of five water molecules (10.46%). Above 166 °C, the remaining part begins to decompose gradually.

2.4 Luminescent properties

Luminescent compounds are currently of great interest because of their various applications in chemical sensors, photochemistry, and electroluminescent display. The photoluminescent behaviors of complexes **1** and **2** as well as free ligand H₂cmdpca are studied in the solid state at room temperature. As illustrated in Fig.6, the blue emission for H₂cmdpca and complexes **1** and **2** can be observed, where their maximum emission wavelengths are all at about 425 nm. Apparently, the main emission speaks of all of the complexes **1** and **2** are similar to that of the ligand

H₂cmdpca in terms of the position and the band shape, indicating that the emission bands of **1** and **2** may be attributed to the emission of intraligand π - π^* transition^[28,31].

3 Conclusions

In this work, two zinc complexes with uncoordinated carbonyl groups have been successfully synthesized by the self-assembly of Zn(NO₃)₂·6H₂O, H₂cmdpca, and 4,4'-bpy in different molar ratio. Complex **1** is a mononuclear structure, and **2** shows a 1D structure. The coordination modes of Hcmdpca⁻ with metal atoms are the same in the two complexes. The intermolecular weak interactions play important roles in the formation of three-dimension supramolecular architectures of **1** and **2**. Complexes **1** and **2** all display blue fluorescence in the solid state.

Supporting Information: Supporting information is available at <http://www.wjhxsb.cn>

References:

- [1] O'Keeffe M, Yaghi O M. *Chem. Rev.*, **2012**, *112*(2):675-702
- [2] Rosi N L, Eckert J, Eddaoudi M, et al. *Science*, **2003**, *300*: 1127-1129
- [3] Choi H J, Dinc M, Long J R, et al. *J. Am. Chem. Soc.*, **2008**, *130*(25):7848-7850
- [4] Wang B, Côté A P, Furukawa H, et al. *Nature*, **2008**, *453*:207-211
- [5] Li J R, Sculley J, Zhou H C, et al. *Chem. Rev.*, **2012**, *112*(2): 869-932
- [6] Kreno L E, Leong K, Farha O K, et al. *Chem. Rev.*, **2012**, *112*(2):1105-1125
- [7] Yao M X, Zheng Q, Cai X M, et al. *Inorg. Chem.*, **2012**, *51* (4):2140-2149
- [8] Y Li, X L, Wang T W, et al. *Inorg. Chem.*, **2010**, *49*(3):1266-1270
- [9] Ohara K, Kawano M, Inokuma Y, et al. *J. Am. Chem. Soc.*, **2010**, *132*(1):30-31
- [10] Hasegawa S, Horike S, Matsuda R, et al. *J. Am. Chem. Soc.*, **2007**, *129*(9):2607-2614
- [11] Yoon M, Srirambalaji R, Kim K, et al. *Chem. Rev.*, **2012**, *112*(2):1196-1231
- [12] Liu Q, Yu L L, Wang Y, et al. *Inorg. Chem.*, **2013**, *52*(6): 2817-2822

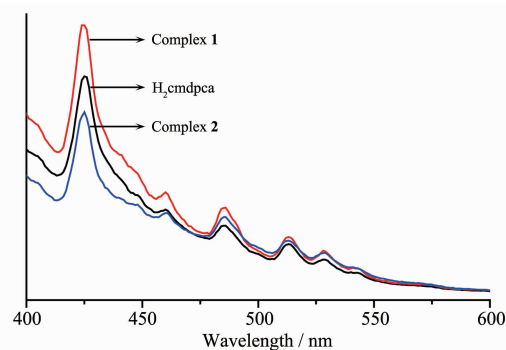


Fig.6 Solid-state emission spectra for compounds H₂cmdpca, **1** and **2** (excitation wavelength= 370 nm) at room temperature

- [13]Férey G, Millange F, Morcrette M, et al. *Angew. Chem. Int. Ed.*, **2007**,**46**(18):3259-3263
- [14]Nagarathinam M, Saravanan K, Phua E J H, et al. *Angew. Chem.*, **2012**,**124**(24):5968-5972
- [15]Zhou J M, Shi W, Xu N, Cheng P, *Inorg. Chem.*, **2013**,**52**(14):8082-8090
- [16]GUO Li-Fang(郭利芳), WANG Zhao-Xi(王兆喜), LI Ming-Xing(李明星). *Chinese J. Inorg. Chem.*(无机化学学报), **2013**,**29**(9):1921-1927
- [17]Zhang M D, Qin L, Yang H T, et al. *Cryst. Growth Des.*, **2013**,**13**(5):1961-1969
- [18]Chen L T, Tao F, Wang L D, et al. *Z. Anorg. Allg. Chem.*, **2013**,**639**(3/4):552-557
- [19]Wang L D, Tao F, Cheng M L, et al. *J. Coord. Chem.*, **2012**, **65**(6):923-933
- [20]HAN Wei(韩伟), CHENG Mei-Ling(程美令), LIU Qi(刘琦), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2012**,**28**(9):1997-2004
- [21]BAO Jin-Ting(包金婷), CHENG Mei-Ling(程美令), LIU Qi(刘琦), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2013**, **29**(7):1504-1512
- [23]Cheng M L, Han W, Liu Q, et al. *J. Coord. Chem.*, **2014**,**67**(2):215-226
- [24]REN Yan-Qiu(任艳秋), HAN Wei(韩伟), CHENG Mei-Ling(程美令), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2014**,**30**(11):2635-2644
- [25]Zhou X H, Du X D, Li G N, et al. *Cryst. Growth Des.*, **2009**,**9**(10):4487-4496
- [26]Lincke J, Lssig D, Kobalz M, et al. *Inorg. Chem.*, **2012**,**51**(14):7579-7586
- [27]Li M, Xu Z, You X Z, et al. *Polyhedron*, **1993**,**12**(8):921-924
- [28]Su S, Cheng M L, Ren Y, et al. *Transition Met. Chem.*, **2014**,**39**(5):559-566
- [29]Sheldrick G M. *SHELXTL-97, Program for X-ray Crystal Structure Determination*, University of Göttingen, Göttingen, Germany, **1997**.
- [30]Hong J, Cheng M L, Liu Q, et al. *Transition Met. Chem.*, **2013**,**38**(4):385-39
- [31]Gadzikwa T, Farha O K, Mulfort K L, et al. *Chem. Commun.*, **2009**:3720-3722