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以樟脑酸及咪唑基化合物为配体的锌配合物的合成、晶体结构及荧光性质

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摘要:以硝酸锌、樟脑酸(H_2CAM)和 1,2-二咪唑基二甲苯(obix)或 4,4′-二咪唑基二甲联苯(bimb)为原料,在水热条件下得到 2 个结构不同的配位聚合物$[Zn(obix)(CAM)]_n$ (**1**)和$[Zn(bimb)(CAM)]_n$ (**2**)。对它们进行了元素分析、红外光谱和热重等分析,并利用 X-射线衍射测定了它们的单晶结构。配合物 **1** 中 2 个锌离子通过 2 个 obix 配体桥连成一个 24 元大环,它再通过 CAM 配体连接成一维管状结构,而配合物 **2** 中锌离子通过两种配体桥连成二维层状结构。结果说明了辅助配体在配合物组装过程中起着非常重要的作用。此外还研究了它们的荧光性质。

关键词:锌配合物;樟脑酸;晶体结构;荧光
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Syntheses, Crystal Structures and Fluorescent Properties of Zinc Coordination Polymers Based on Camphor Acid and Imidazole Ligand

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Abstract: Two zinc coordination polymers: $[Zn(obix)(CAM)]_n$ (**1**) and $[Zn(bimb)(CAM)]_n$ (**2**) (H_2CAM=camphor acid, obix=1,2-bis (imidazol-1-ylmethyl)benzene and bimb=4,4′-bis (imidazol-1-ylmethyl)biphenyl) have been synthesized under hydrothermal conditions and characterized by elemental analysis, IR spectroscopy, TGA and single-crystal X-ray diffraction. The crystal structures show that complex **1** crystallizes in triclinic, space group $P\bar{1}$ with a=0.973 4(3) nm, b=1.113 18(12) nm, c=1.210 3(2) nm, α=101.548(3)°, β=101.257(2)°, γ=103.373(2)°, V=1.209 3(4) nm^3, Z=2, D_c=1.378 g·cm^{-3}, F(000)=524, μ=1.052 cm^{-1}, the final R_1=0.051 3, wR_2=0.108 3. While complex **2** crystallizes in monoclinic, space group $P2_1/c$ with a=1.111 1(4) nm, b=1.409 6(6) nm, c=1.770 0(7) nm, β=92.366(5)°, V=2.769 8(19) nm^3, Z=4, D_c=1.386 g·cm^{-3}, F(000)=1 208, μ=0.929 cm^{-1}, the final R_1=0.058 2, wR_2=0.116 7. The bis(imidazole) ligands with different spacer lengths exhibit conformational flexibility and lead to the generation of diversified architectures. Complex **1** consists of 24-membered $\{Zn_2(obix)_2\}$ rings that are further bridged by CAM anions into a one-dimensional tubular structure. Complex **2** shows a two-dimensional (2D) lattice network with (4,4) topology. Moreover, their luminescent properties have been investigated in the solid state. CCDC: 796695, **1**; 796696, **2**.

Key words: Zn(Ⅱ) complex; camphor acid; crystal structure; fluorescence

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0 Introduction

Over the last two decades, there has been much interest in the area of crystal engineering of metal-organic frameworks (MOFs) in view of their potential applications in adsorption, the photochemical area, and catalysis, as well as their variety of intriguing architectures[1-6]. To attain novel structures, much effort has been devoted to modifying the building blocks and to controlling the assembled motifs for required products via selecting different organic ligands[7-8]. Besides that, several important factors also influence the construction of molecular structures, such as metal ions, pH, temperature, and solvent. So far, more attention has been paid to the flexible ligands[9-10]. As we know, the flexible ligands have been used widely in the construction of MOFs with interesting topologies and attractive properties, because the flexible ligands have variable coordination modes and can adopt a variety of conformations according to the restrictions imposed by the coordination geometry of the metal ion to meet the coordination requirement of the metal ions, which can result in more topological structures than for the rigid ligand[11-13].

On the other hand, among the N-donor bridging ligands, bis(imidazole) ligands, as an important family of flexible N-donor ligands, have attracted great interest[14-16]. In our previous work[17-18], we have reported a series of fascinating archetypal structures based on the 1,2-bis(imidazol-1-ylmethyl)benzene (obix) or 4,4′-bis (imidazol-1-ylmethyl)biphenyl (bimb) ligands. On careful inspection of the reported cases, we found that the flexible nature of the alkyl (-CH_2-) spacer allows the ligands to bend and rotate freely so as to conform to the coordination geometries of central metal atoms. Compared with the linear bpy ligand, the bidentate obix and bimb ligands can feature various coordination modes, such as *cis*- and *trans*-conformations, during the assembly with the metal ions. Taking these into consideration, our synthetic strategy is to select camphor acid (H_2CAM) as the main ligand, in the presence of neutral obix or bimb as co-ligands and metal salts to construct complexes. As expected, we successfully isolated two new coordination polymers $[Zn(obix)(CAM)]_n$ (**1**) and $[Zn(bimb)(CAM)]_n$ (**2**). Herein, we report their syntheses, crystal structures and luminescent properties.

1 Experimental

1.1 Materials and general methods

All the reagents and solvents for syntheses and analyses were commercially available and employed as received without further purification. The ligands obix and bimb were prepared according to the reported method[19]. Elemental analyses (C, H and N) were performed on a Vario EL Ⅲ elemental analyzer. Infrared spectra were performed on a Nicolet AVATAR-360 spectrophotometer with KBr pellets in the 400~4 000 cm^{-1} region. The luminescent spectra for the powder solid samples were measured at room temperature on a Hitachi F-4500 fluorescence spectrophotometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5 nm. All the measurements were carried out under the same experimental conditions. Thermal gravimetric analyses (TGA) were performed on a Netzsch STA-409PC instrument in flowing N_2 with a heating rate of 10 ℃·min^{-1}.

1.2 Synthesis of $[Zn(obix)(CAM)]_n$ (1)

A mixture of H_2CAM (0.1 mmol, 20.0 mg), obix (0.1 mmol, 23.8 mg), $Zn(NO_3)_2·6H_2O$ (0.1 mmol, 29.8 mg), NaOH (0.2 mmol, 8.0 mg) and H_2O (15 mL) was stirred for 30 min. The mixture was transferred to a 25 mL Teflon-lined stainless steel vessel and heated at 140 ℃ for 3 d. Then the reaction system was cooled to room temperature, and colorless block crystals of **1** were obtained. Yield: 62% (based on Zn). Anal. calcd. for $C_{24}H_{28}N_4O_4Zn$(%): C, 57.43; H, 5.62; N, 11.16. Found (%): C, 57.29; H, 5.66; N, 11.13. IR spectrum: 3 461, 2 959, 1 519, 1 409, 1 385, 1 293, 815, 754, 659 and 439 cm^{-1}.

1.3 Synthesis of $[Zn(bimb)(CAM)]_n$ (2)

Complex **2** was prepared by a method similar to **1** except for using bimb instead of obix. Yield: 57% (based on Zn). Anal. calcd. for $C_{30}H_{32}N_4O_4Zn$(%): C, 62.34; H, 5.58; N, 9.69. Found(%): C, 62.28; H, 5.62;

N, 9.65. IR spectrum: 3 415, 3 141, 2 928, 1 587, 1 522, 1 449, 1 367, 1 321, 1 256, 1 127, 1 071, 10 33, 1 004, 946, 901, 794, 723 and 651 cm^{-1}.

1.4 X-ray crystallography

The single crystals of complexes **1** and **2** with approximate dimensions of 0.28 mm×0.24 mm×0.22 mm and 0.30 mm×0.24 mm×0.22 mm were placed on a Bruker Smart Apex Ⅱ CCD diffractometer. The diffraction data were collected using a graphite monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm) at 291(2) K. The Lp factor and semi-empirical adsorption corrections were applied to the intensity data. The structure was solved by the direct method using SHELXS-97[20] and refined by full-matrix least squares on F^2 using SHELXL-97[21]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added according to the theoretical model. Atoms (C24 in **1** and C29 in **2**) disordered into two positions with the site occupancy factors of 0.5. The details of the crystal parameters, data collection and refinement for two complexes are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are listed in Table 2.

CCDC: 796695, **1**; 796696, **2**.

Table 1　Crystal data and structure refinement for 1 and 2

Complex	**1**	**2**
Formula	$C_{24}H_{28}N_4O_4Zn$	$C_{30}H_{32}N_4O_4Zn$
Formula weight	501.87	577.97
Temperature / K	291(2)	291(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a / nm	0.973 4(3)	1.111 1(4)
b / nm	1.113 18(12)	1.409 6(6)
c / nm	1.210 3(2)	1.770 0(7)
α / (°)	101.548(3)	
β / (°)	101.257(2)	92.366(5)
γ / (°)	103.373(2)	
V / nm^3	1.209 3(4)	2.769 8(19)
Z	2	4
D_c / ($g\cdot cm^{-3}$)	1.378	1.386
Absorption coefficient / mm	1.052	0.929
θ range / (°)	1.78~26.00	1.83~26.00
Limiting indices	$-11 \leqslant h \leqslant 11, -13 \leqslant k \leqslant 13, -14 \leqslant l \leqslant 14$	$-13 \leqslant h \leqslant 13, -17 \leqslant k \leqslant 17, -21 \leqslant l \leqslant 21$
F(000)	524	1 208
Reflections collected	8 947	19 881
Independent reflections (R_{int})	4 550 (0.036 2)	5 353 (0.070 4)
Reflections observed ($I>2\sigma(I)$)	3 367	3 629
Data / restraints / parameters	4 550 / 0 / 311	5 353 / 0 / 353
Goodness-of-fit on F^2	1.053	1.055
R_1, wR_2 ($I>2\sigma(I)$)	0.051 3, 0.108 3	0.058 2, 0.116 7
R_1, wR_2 (all data)	0.071 8, 0.112 8	0.091 6, 0.124 4
$(\Delta\rho)_{max}$ / ($e\cdot nm^{-3}$)	684	402
$(\Delta\rho)_{min}$ / ($e\cdot nm^{-3}$)	−481	−441

Table 2　Selected bond lengths (nm) and angles (°) for 1 and 2

1					
Zn(1)-N(2)	0.228 1(3)	Zn(1)-N(4)^{i}	0.228 5(3)	Zn(1)-O(1)	0.233 0(3)
Zn(1)-O(3)^{ii}	0.231 2(3)	Zn(1)-O(2)	0.235 1(3)	Zn(1)-O(4)^{ii}	0.242 6(2)

Continued Table 2

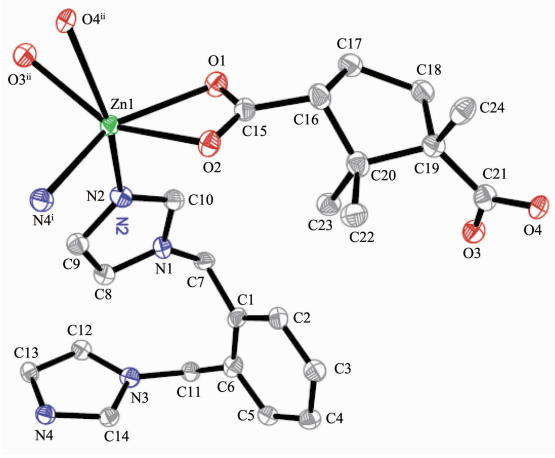
N(2)-Zn(1)-N(4)^{i}	94.07(11)	O(3)^{ii}-Zn(1)-O(2)	148.78(9)	N(2)-Zn(1)-O(3)^{ii}	103.29(10)
O(1)-Zn(1)-O(2)	54.84(9)	N(4)^{i}-Zn(1)-O(3)^{ii}	97.56(11)	N(2)-Zn(1)-O(4)^{ii}	156.45(10)
N(2)-Zn(1)-O(1)	89.59(10)	N(4)^{i}-Zn(1)-O(4)^{ii}	93.32(10)	N(4)^{i}-Zn(1)-O(1)	147.31(11)
O(3)^{ii}-Zn(1)-O(4)^{ii}	53.52(9)	O(3)^{ii}-Zn(1)-O(1)	113.18(9)	O(1)-Zn(1)-O(4)^{ii}	96.13(9)
N(2)-Zn(1)-O(2)	105.15(10)	O(2)-Zn(1)-O(4)^{ii}	96.74(9)	N(4)^{i}-Zn(1)-O(2)	93.03(10)
		2			
Zn(1)-N(1)	0.209 4(3)	Zn(1)-N(4)^{iii}	0.205 8(3)	Zn(1)-O(1)	0.197 3(3)
Zn(1)-O(4)^{iv}	0.213 0(3)				
O(1)-Zn(1)-N(4)^{iii}	119.14(13)	O(1)-Zn(1)-O(4)^{iv}	106.52(12)	O(1)-Zn(1)-N(1)	115.70(13)
N(4)^{iii}-Zn(1)-O(4)^{iv}	123.14(14)	N(4)^{iii}-Zn(1)-N(1)	97.07(13)	N(1)-Zn(1)-O(4)^{iv}	91.49(13)

Symmetry code: **1**: ^{i} $-x+1, -y+1, -z+2$; ^{ii} $x+1, y, z$; **2**: ^{iii} $x+1, -y+3/2, z-1/2$; ^{iv} $x, -y+3/2, z-1/2$.

2 Results and discussion

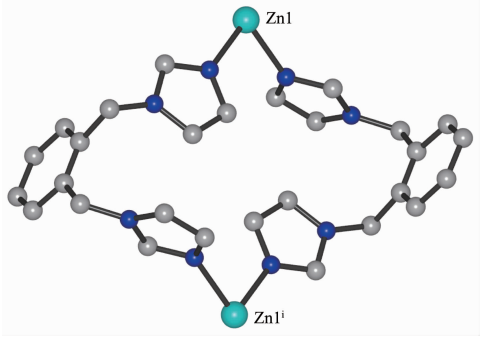
2.1 Crystal structure

The crystallographic analysis reveals that **1** is a one-dimensional tubular structure. As shown in Fig.1, the asymmetric unit contains one Zn(Ⅱ) ion, one CAM anion, and one obix ligand. Each Zn(Ⅱ) ion is six-coordinated by four oxygen atoms from two different carboxylate groups, and two nitrogen atoms from two obix ligands to form a distorted octahedral geometry and its equatorial plane is occupied by three oxygen atoms, O2, O3 and O3^{ii}, and one nitrogen atom, N4^{i}, while the apical position is occupied by one oxygen atom, O4^{ii}, and one nitrogen atom, N2. The Zn-O bond lengths are in the range of 0.231 2 (3)~0.242 6 (2) nm, the Zn-N bond lengths are 0.228 1(3)~0.228 5(3) nm. Two Zn(Ⅱ) ions are linked by a couple of obix ligands to form 24-membered $\{Zn_2(obix)_2\}$ ring and the distance of neighboring Zn(Ⅱ) ions is about 0.891 3 nm as presented in Fig.2. The obix ligand adopts a cis-conformation with the dihedral angle between the two imidazole rings of 83.86°. Two carboxylate groups of CAM^{2-} ligand adopt bidentate chelating coordination mode and link to the neighboring $\{Zn_2(obix)_2\}$ rings, giving a one-dimensional tubular structure. The separation of neighboring Zn(Ⅱ) ions is about 0.973 4 nm as illustrated in Fig.3. The packing structure of **1** shows a three-dimensional



Symmetry code: ^{i} $-x+1, -y+1, -z+2$; ^{ii} $x+1, y, z$, Hydrogen atoms are omitted for clarity

Fig.1 ORTEP drawing of **1** showing the labeling of atoms with thermal ellipsoids at 30% probability



Symmetry code: ^{i} $x, y-1$, **z**

Fig.2 View of 24-membered $\{Zn_2(obix)_2\}$ ring in complex **1**

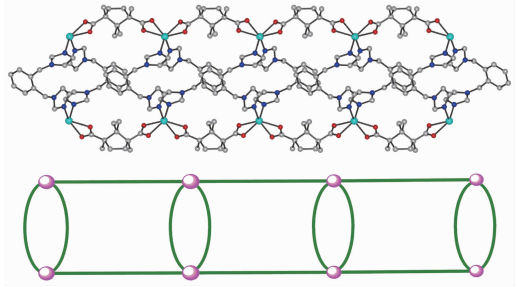
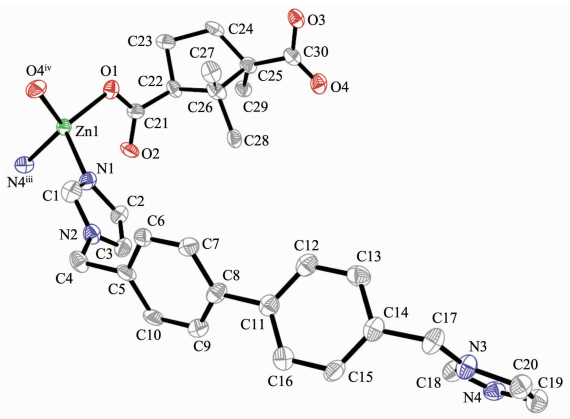


Fig.3 Schematic representation of the 1D tubular structure in complex **1**

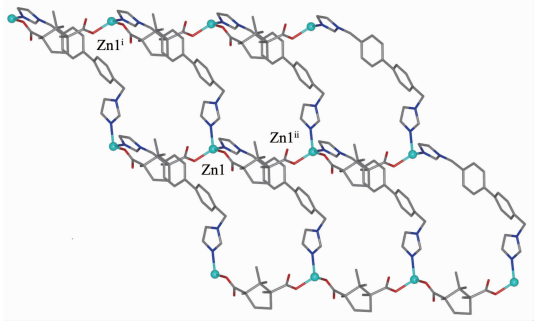
supramolecular network derived from chains formed via intermolecular C–H···O hydrogen bonds and weak $\pi\cdots\pi$ stacking interactions.

When bimb was reacted with $Zn(NO_3)_2$ and H_2CAM using a preparation procedure similar to that of **1**, complex **2** was isolated. As shown in Fig.4, the structure of **2** contains one Zn(Ⅱ) ion, one CAM anion, and one bimb ligand. The Zn(Ⅱ) ion adopts a tetrahedral coordination geometry, coordinating to two carboxylate O atoms from two CAM anions (Zn1-O1 0.197 3(3) nm and Zn1-O4^{iv} 0.213 0(3) nm) and two N atoms from two bimb ligands (Zn1-N1 0.209 4(3) nm and Zn1-N4^{iii} 0.205 8(3) nm). The bimb ligand adopts a *cis*-conformation with a dihedral angle between the two imidazole rings of 46.34°. Zn(Ⅱ) ions are linked by bimb ligands to form a one-dimensional chain and the distance of neighboring Zn(Ⅱ) ions is about 1.476 9(4) nm as illustrated in Fig.5. The neighboring chains are bridged



Symmetry code: ^{iii} $x+1, -y+3/2, z-1/2$; ^{iv} $x, -y+3/2, z-1/2$, Hydrogen atoms are omitted for clarity

Fig.4　ORTEP drawing of **2** showing the labeling of atoms with thermal ellipsoids at 30% probability



Symmetry code: ^{i} $x+1, -y+3/2, z-1/2$; ^{ii} $x, -y+3/2, z-1/2$

Fig.5　View of two dimensional layer constructed from $[Zn_4(CAM)_2(bimb)_2]$ units

by CAM anions to afford a 2D sheet with (4,4) topology (Fig.5). Two carboxylate groups of CAM anions adopt bis (monodentate) coordination mode and the Zn···Zn distances separated by CAM anion are 0.930 3(3) nm. The resulting layers are packed in a parallel fashion and stacked along the *b* axis.

2.2　IR spectra

The IR spectral data show the features attributable to the carboxylate stretching vibrations of two complexes. The absence of bands in the range of 1 760~1 680 cm^{-1} indicates the complete deprotonation of the H_2CAM ligand. The characteristic bands of the carboxylate groups appear in the range 1 550~1 620 cm^{-1} for the asymmetric stretching and 1 380~1 480 cm^{-1} for the symmetric stretching, and the value of $\Delta[\nu_{as}(COO^-)-\nu_s(COO^-)]$ reveals that the carboxylate groups are coordinated in two different coordination fashions, which is consistent with the results of the X-ray analysis. The IR spectra of two complexes show the C=N stretching vibration of imidazolyl group at about 1 520 cm^{-1}[22].

2.3　Thermogravimetric analyses

Thermal gravimetric analyses (TGA) were carried out to examine the thermal stability of two complexes. The samples were heated up in flowing N_2 with a heating rate of 10 ℃·min^{-1}. Both the complexes exhibit similar thermal behaviors. They are stable up to ca. 290 ℃. The remaining weights correspond to ZnO (obsd. 17.09%, calcd. 16.22% for **1**; obsd. 15.53%, calcd. 14.08% for **2**, respectively).

2.4　Luminescent properties

Luminescent complexes are currently of great interest because of their various applications in chemical sensors, photochemistry, and electroluminescent display[23-24]. The luminescent properties of Zn and Cd carboxylate compounds have been investigated[25]. The photoluminescent spectra of complexes **1** and **2** and free neutral ligands obix and bimb were measured at room temperature. As illustrated in Fig.6, the intense emission bands at 415 nm (λ_{ex}=354 nm) for **1** and 409 nm (λ_{ex}=346 nm) for **2** are observed, respectively. The free obix and bimb exhibit fluorescent emission bands at 465 nm (λ_{ex}=371 nm) and 427 nm (λ_{ex}=348 nm),

respectively. In order to understand the nature of the emission band, the photoluminescence properties of the H_2CAM ligand were analyzed. A weak emission (λ_{max}= 561 nm) could be observed. In comparison to the free ligands, the emission maximums of complexes **1** and **2** have changed. This may be caused by a change in the HOMO and LUMO energy levels of deprotonated CAM anions and neutral ligands coordinating to metal centers, a charge-transfer transition between ligands and metal centers, and a joint contribution of the intraligand transitions or charge-transfer transitions between the coordinated ligands and the metal centers[26-29]. These observations indicate that they may be excellent candidates for potential photoactive materials.

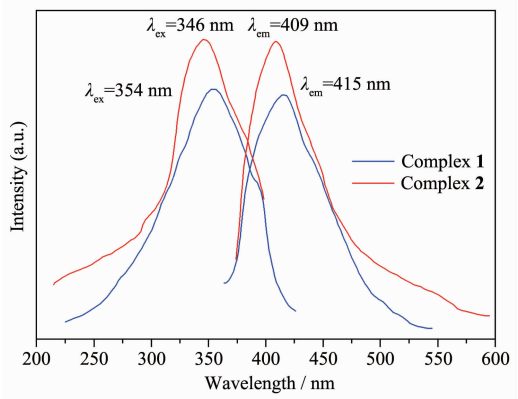


Fig.6 Solid-state photoluminescent spectra of **1** and **2** at room temperature

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