

一个新颖的二维锌配位聚合物 $[\text{Zn}(\text{L})(1,4\text{-BDC})]_n$ 的合成、结构和表征

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Synthesis, Structure and Characterization of a Novel Two-Dimensional Zn(II) Coordination Polymer: $[\text{Zn}(\text{L})(1,4\text{-BDC})]_n$

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Abstract: The title coordination polymer, $[\text{Zn}(\text{L})(1,4\text{-BDC})]_n$ (**1**) (L =2-(4-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline and 1,4- H_2BDC =1,4-benzenedicarboxylic acid) has been synthesized by hydrothermal method and characterized by elemental analysis, IR and single-crystal X-ray diffraction. It crystallizes in triclinic, space group $P\bar{1}$ with $a=0.970\ 85(16)$ nm, $b=1.076\ 98(18)$ nm, $c=1.203\ 6(2)$ nm, $\alpha=63.894(2)^\circ$, $\beta=69.051(2)^\circ$, $\gamma=80.427(2)^\circ$, $V=1.055\ 4(3)$ nm³, $Z=2$, $\text{C}_{27}\text{H}_{15}\text{FN}_4\text{O}_4\text{Zn}$, $M_r=543.80$, $D_c=1.711$ g·cm⁻³, $F(000)=552$, $\mu(\text{Mo } K\alpha)=1.220$ mm⁻¹, $R=0.037\ 2$ and $wR=0.084\ 4$. The 1,4-BDC ligands linked the Zn(II) atoms to form a two-dimensional layer structure. The π - π stacking interactions between L ligands extended the adjacent layers into a three-dimensional supramolecular network. Finally, the N-H \cdots O hydrogen bonds further stabilizes the structure of **1**. CCDC: 779676.

Key words: coordination polymer; crystal structure; 1,10-phenanthroline derivative; 1,4-benzenedicarboxylic acid

The design and synthesis of discrete and polymeric metal-organic complexes is currently attracting considerable attention in view of their interesting structural topologies and properties^[1-9]. In this regard, the preparation of ordered functional crystalline solids, which display a variety of well-defined supramolecular architectures mediated by supramolecular interactions, is currently of great interest and importance^[10]. So far, several rational synthetic strategies have been proposed to achieve the metal-organic supramolecular arrays, and one of the most effective approaches is to employ appropriate

aromatic N-donor chelating ligands capable of forming π - π interactions^[11-13]. Up to now, 1,10-phenanthroline (phen) has been widely used to build supramolecular architectures because of its excellent coordinating ability and large conjugated system that can easily form π - π interactions^[14]. However, to the best of our knowledge, coordination polymer based on its derivative 2-(4-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (L), has not been reported^[15-16]. Here, we selected 1,4-benzenedicarboxylate dianion (1,4-BDC) as an organic linker and L as a N-donor chelating ligand, generating a new two-dimensional coordination polymer, $[\text{Zn}(\text{L})(1,4\text{-BDC})]_n$.

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BDC)]_n **1**, which will be reported.

1 Experimental

1.1 Generals

The L ligand was synthesized according to the reported method^[15] and all other materials were analytical reagent grade and used as received without further purification. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer; IR spectra were obtained on a Perkin-Elmer 2400LS II spectrometer.

1.2 Synthesis and crystal growth

The pH value of a mixture of ZnCl₂·2H₂O (0.5 mmol), 1,4-H₂BDC (0.5 mmol) and L (0.5 mmol) in 12 mL distilled water was adjusted to between 5 and 6 by addition of triethylamine. The resultant solution was heated at 458 K in a Teflon-lined stainless steel autoclave for four days. The reaction system was then slowly cooled to room temperature. Pale yellow crystals of **1** suitable for single crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water and dried in air at ambient temperature. Yield 47% based on Zn(II). IR (KBr, cm⁻¹): 3 041w, 1 610s, 1 581m, 1 538 m, 1 462m, 1 344m, 841m, 733w, 620w. Anal. Calcd. for C₂₇H₁₅FN₄O₄Zn(%): C, 59.58; H, 2.76; N, 10.30. Found(%): C, 59.71; H, 2.69; N, 10.01.

1.3 X-ray structure determination

A single crystal with dimensions of 0.31 mm×0.27 mm×0.17 mm was selected and mounted on a Bruker Smart Apex CCD diffractometer equipped with a graphite-monochromatized Mo K α (λ =0.071 073 nm) radiation by using an φ - ω scanning method at a temperature of (20±2) °C. Out of the total 5 938 reflections

collected in the 1.99° ≤ θ ≤ 26.05° range, 4 048 were independent with R_{int} =0.017 8, of which 3 474 were considered to be observed ($I > 2\sigma(I)$) and used in the succeeding refinement. The structure was solved by Direct Method with SHELXS-97 program^[17] and refined with SHELXL 97^[18] by full-matrix least-squares techniques on F^2 . All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The H atoms of water molecule were not located from difference Fourier map. The final R =0.037 2 and wR =0.084 4 ($w=1/[\sigma^2(F_o^2)+(0.037\ 7P)^2+0.28P]$, where $P=(F_o^2+2F_c^2)/3$). S =1.054, ($\Delta\rho$)_{max}=0.387, ($\Delta\rho$)_{min}=-0.346 e·nm⁻³ and (Δ/σ)_{max}=0.001.

CCDC: 779676.

2 Results and discussion

2.1 IR analysis

In the IR spectrum, the asymmetric and symmetric stretching vibrations of the carboxylate groups have bands at 1 538 and 1 382 cm⁻¹. Peaks at 1 610, 1 581 and 1 462 cm⁻¹ could be attributed to $\nu(\text{C}=\text{C})$ vibration of aromatic ring. The peak at 1 344 cm⁻¹ is ascribed to the $\nu(\text{C}=\text{N})$ vibration of L.

2.2 Description of crystal structure

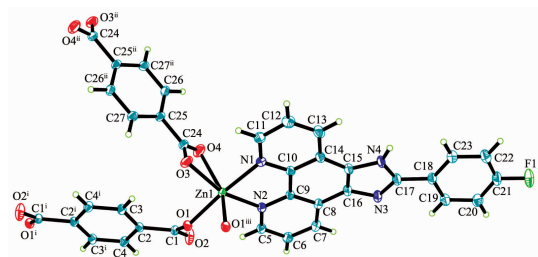
The selected bond distances and angles are listed in Table 1. The asymmetric unit of **1** consists of one Zn(II) atom, one L molecule, and two half 1,4-BDC ligands (Fig.1). The 1,4-BDC ligand is at an inversion center. The coordination geometry of each Zn(II) centre is distorted octahedral, with two N atoms from one L, and four O atoms from three different 1,4-BDC ligands (Fig.1). Notably, there exist tetra-bridging and bis-chelating 1,4-BDC ligands in **1**. The two carboxylates of

Table 1 Selected bond distances (nm) and angles (°)

Zn(1)-N(1)	0.214 8(2)	Zn(1)-O(3)	0.211 3(2)	Zn(1)-N(2)	0.211 5(2)
Zn(1)-O(4)	0.235 0(2)	Zn(1)-O(1)	0.206 49(17)	Zn(1)-O(1) ⁱⁱⁱ	0.212 78(17)
O(1)-Zn(1)-O(3)	91.21(8)	N(2)-Zn(1)-N(1)	77.81(8)	O(1)-Zn(1)-N(2)	102.33(8)
O(1)#1-Zn(1)-N(1)	92.67(7)	O(3)-Zn(1)-N(2)	160.92(8)	O(1)-Zn(1)-O(4)	93.97(7)
O(1)-Zn(1)-O(1) ⁱⁱⁱ	80.33(7)	O(3)-Zn(1)-O(4)	58.60(8)	O(3)-Zn(1)-O(1) ⁱⁱⁱ	94.93(8)
N(2)-Zn(1)-O(4)	106.50(8)	N(2)-Zn(1)-O(1) ⁱⁱⁱ	100.51(8)	O(1) ⁱⁱⁱ -Zn(1)-O(4)	153.00(8)
O(1)-Zn(1)-N(1)	172.93(7)	N(1)-Zn(1)-O(4)	92.75(8)	O(3)-Zn(1)-N(1)	90.42(8)

Symmetry codes: ⁱⁱⁱ 1- x , - y , 2- z .

tetra-bridging 1,4-BDC ligand connect two neighboring Zn(II) atoms to form a dimeric Zn(II) unit. The dimeric Zn(II) units are bridged by the backbones of the tetra-bridging 1,4-BDC ligands to form an one-dimensional chain structure. The chains are further linked by another type of 1,4-BDC ligands in bis-chelating modes to generate a two-dimensional layer (Fig.2). The L ligands from neighboring layers are well matched, allowing the formation of the aromatic π - π stacking interactions. The π - π stacking interactions between the pyridine ring [C(10)-C(14)/N1] of L ligand and the benzene ring [C(18)-C(23) at $(-x, 1-y, 1-z)$] of the L ligand (centroid-to-centroid distance of 0.365 3(5) nm, face-to-face distance of 0.328 5(5) nm, and dihedral angle of $3.425(4)^\circ$), extended the adjacent layers into a three-dimensional supramolecular network (Fig.3). Obviously, the strong aromatic π - π stacking interactions play an important role in stabilizing the supramolecular architecture of **1**. Finally, the N-H \cdots O hydrogen bond (N(4)-H(4A)=0.086 nm, H(4A) \cdots (4)^{iv}=0.232 nm, N(4) \cdots O(4)^{iv}=0.303 4(3) nm, \angle N(4)-H(4A) \cdots O(4)^{iv}=140.7 $^\circ$, symmetric codes: ^{iv} $x-1, y, z$) further stabilizes the structure of **1**. So far, although several coordination compounds constructed by metal(II) ions, dicarboxylate ligands and phen derivatives have been reported, most



Symmetry code: ⁱ $2-x, -y, 2-z$; ⁱⁱ $2-x, -y, 1-z$; ⁱⁱⁱ $1-x, -y, 2-z$
Displacement ellipsoids at the 30% probability level

Fig.1 Coordination environment of Zn(II) atom in complex **1**

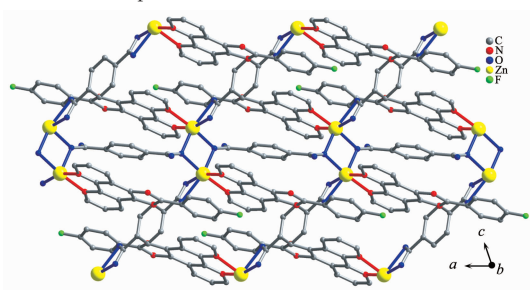


Fig.2 View of the layer structure of complex **1**

of these reported compounds show discrete or one-dimensional chain structures^[15-16]. However, the present two-dimensional layer structure based on L ligand has not been observed.

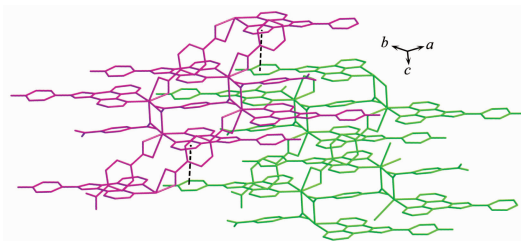


Fig.3 View of the three-dimensional supramolecular architecture of **1** constructed through interlayer π - π interactions

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