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以邻菲咯啉衍生物及 1,3-间苯二甲酸为配体的一维链状 Cd(Ⅱ)配位聚合物的合成及结构

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摘要:在水热条件下,我们利用邻菲咯啉衍生物配体(L=2-(3-fluorophenyl)-1*H*-imidazo[4,5-f][1,10]phenanthroline)和 1,3-间苯二甲酸(1,3-H_2BDC)反应得到了一维配位聚合物 $[Cd_2(L)_2(1,3\text{-}BDC)_2]_n$,并对该化合物进行了元素分析、红外和单晶 X-射线表征。该化合物属于三斜晶系,空间群 $P\bar{1}$,晶胞参数 a=1.080 8(4) nm,b=1.149 5(4) nm,c=1.924 8(7) nm,α=106.482(5)°,β=99.436(6)°,γ=93.093(6)°,V=2 249.2(14) nm^3,Z=4,$C_{27}H_{15}CdFN_4O_4$,M_r=590.83,D_c=1.745 g·cm^{-3},F(000)=1 176,μ(Mo $K\alpha$)=1.024 mm^{-1},R=0.044 5 和 wR=0.111 7。该化合物为一维链状结构,链与链之间又进一步地通过 CH-π 相互作用形成二维层状超分子结构。

关键词:配位聚合物;晶体结构;邻菲咯啉衍生物;1,3-苯二甲酸

中图分类号:O614.24+2 **文献标识码**:A **文章编号**:1001-4861(2012)04-0851-05

Synthesis and Crystal Structure of a One-Dimensional Cd(Ⅱ) Coordination Polymer Based on 1,10-Phenanthroline Derivative and 1,3-Benzenedicarboxylic Acid

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Abstract: A new 1D chain coordination polymer, $[Cd_2(L)_2(1,3\text{-}BDC)_2]_n$ **1** (L=2-(3-fluorophenyl)-1*H*-imidazo[4,5-f][1,10]phenanthroline and 1,3-H_2BDC =1,3-benzenedicarboxylic acid) has been hydrothermally synthesized and characterized by elemental analysis, IR and single-crystal X-ray diffraction. It crystallizes in triclinic, space group $P\bar{1}$ with a=1.080 8(4) nm, b=1.149 5(4) nm, c=1.924 8(7) nm, α=106.482(5)°, β=99.436(6)°, γ=93.093(6)°, V=2.249 2(14) nm^3, Z=4, $C_{27}H_{15}CdFN_4O_4$, M_r=590.83, D_c=1.745 g·cm^{-3}, F(000)=1 176, μ(Mo $K\alpha$)=1.024 mm^{-1}, R=0.044 5 and wR=0.111 7. In compound **1**, the 1,3-BDC ligands linked the adjacent Cd(Ⅱ) atoms to generate a one-dimensional chain structure. The CH-π interactions between L and 1,3-BDC extended the adjacent chains into a two-dimensional supramolecular layer. The N−H···O hydrogen bond further stabilizes the structure of **1**. CCDC: 859146.

Key words: coordination polymer; crystal structure; 1,10-phenanthroline derivative; 1,3-benzenedicarboxylic acid

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0 Introduction

Metal-organic coordination polymers have received considerable interest in coordination chemistry and material science due to their intriguing structural diversities and potential applications in functional materials, nanotechnology, and biological recognition[1-3]. Up to now, lots of coordination polymers with interesting structures and topologies have been investigated and reported[4]. However, their controllable syntheses are still a great challenge because many factors play important roles in their self-assemblies, such as the chemical structures of the ligands, the metal, the anions, reaction temperature and pH value[5]. In this regard, the selection of ligand is a vital subject in the construction of the coordination polymers[6].

Usually, coordination-bonded interactions for the construction of coordination polymers are the most effective force. Moreover, noncovalent interactions, such as π-π stacking interactions and hydrogen bonding interactions, which are described as supramolecular glues, are often used as structural directing tools in generating a number of novel supramolecular structures with promising properties[7-9]. Therefore, versatile functional organic ligands (such as N- or O-containing ligands) which have strong coordination ability as well as providing the π-conjugated systems and hydrogen bond acceptors/donors are often employed in the construction of novel supramolecular framework[10]. So far, N-containing ligands, such as 1,10-phenanthroline (phen), pyrazine, 2,2′-bipyridine, 4,4′-bipyridine and bis (imidazole) have been employed widely in the construction of coordination polymers[11-12]. Among the N-containing ligand, (2-(3-fluorophenyl)-1*H*-imidazo[4,5-f][1,10]phenanthroline (L) is an excellent N-donor chelating ligand for the construction of coordination polymers[13]. In this work, we selected 1,3-benzenedicarboxylate (1,3-BDC) as an organic linker and L as a N-donor chelating ligand, generating a new one-dimensional coordination polymer, $[Cd_2(L)_2(1,3\text{-BDC})_2]_n$ (**1**).

1 Experimental

1.1 Generals

The L ligand was synthesized according to the reported method[13] 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

A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.5 mmol), 1,3-H_2BDC (0.5 mmol) and L (0.5 mmol) was dissolved in 8 mL distilled water. The pH value of the mixture was adjusted to between 5 and 6 by addition of triethylamine. The resultant solution was heated at 455 K in a Teflon-lined stainless steel autoclave for seven 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: 32% based on Cd(Ⅱ). IR (KBr, cm^{-1}): 1 621s, 1 612m, 1 580m, 1 544m, 1 460m, 1 377w, 1 340m, 1 127w, 865m, 736w, 629w. Anal. Calcd. for $C_{20}H_{20}CdFN_4O_{10}$ (%): C, 39.52; H, 3.32; N, 9.22. Found (%): C, 39.72; H, 3.25; N, 9.30.

1.3 X-ray structure determination

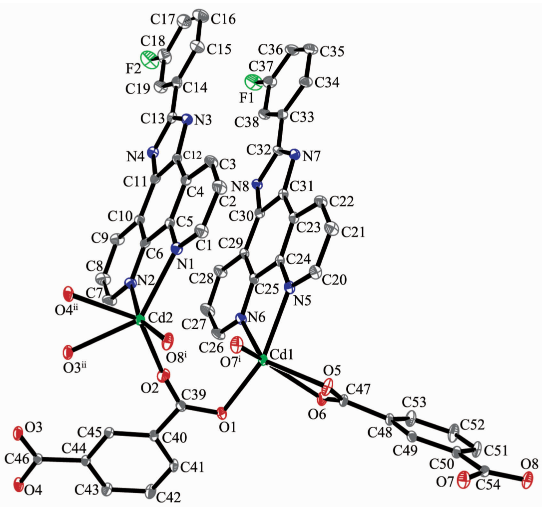
A single crystal with dimensions of 0.20 mm×0.15 mm×0.12 mm was selected and mounted on a Bruker Smart Apex CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ (λ=0.071 073 nm) radiation by using an ω-2θ scanning method at a temperature of (20±2) ℃. Out of the total 10 842 reflections collected in the 1.86° $\le\theta\le$ 25.0° range, 7 690 were independent with R_{int}=0.020 9, of which 6 106 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[14] and refined with SHELXL 97[15] by full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The flurophenyl unit is disordered over two sites in a 1∶1 ratio. The final R=0.044 5 and wR=0.111 7 ($w=1/[\sigma^2(F_o^2)+(0.054\,6P)^2+6.753\,7P]$, where $P=(F_o^2+2F_c^2)/3$). S=1.062, $(\Delta\rho)_{max}$=0.979 e·nm^{-3}, $(\Delta\rho)_{min}$=−0.598 e·nm^{-3} and $(\Delta/\sigma)_{max}$=0.000.

CCDC: 859146.

2 Results and discussion

2.1 Description of crystal structure

The selected bond distances and angles are listed in Table 1. The asymmetric unit of **1** contains two crystallographically independent Cd(Ⅱ) atoms (Cd1 and Cd2), two kinds of L ligands, and two kinds of 1,3-BDC anions. As shown in Fig.1, each Cd(Ⅱ) atom is coordinated by two nitrogen atoms from one L ligand and four carboxylate oxygen atoms from three different 1,3-BDC anions, exhibiting a distorted CdN_2O_4 octahedral coordination geometry. The Cd-O distances range from 0.234 3(4) to 0.284 8(5) nm. Notably, the two carboxylates of each 1,3-BDC show different coordination modes: one carboxylate chelates one Cd(Ⅱ) atom, while the other bridges two Cd(Ⅱ) atoms (Fig.1). The bridging carboxylate group of the 1,4-bdc anion connects two Cd(Ⅱ) atoms to form a dimer with the Cd⋯Cd distance of 0.336 7(4) nm (Fig.2). The dinuclear units are bridged by the backbones of the 1,4-bdc ligands to form a chain structure (Fig.2). The ligands L are attached to both sides of the layers, allowing the formation of CH-π interactions (0.342 nm), and connect the adjacent chains to a two-dimensional supramolecular architecture (Fig.3). Obviously, the strong CH-π stacking interactions play an important role in stabilizing the supramolecular architecture of **1**. Moreover, the N−H⋯O hydrogen bonds (N(3)−H(3A) 0.088 nm, H(3A)⋯O(6)^{iii} 0.205 nm, N(3)⋯O(6)^{iii} 0.289 2(6) nm, N(3)−H(3A)⋯O(6)^{iii}=158.5° (symmetry code: ^{iii} x, y−1, z); N(8)-H(8A) 0.088 nm, H(8A)⋯O(4)^{iv} 0.198 nm, N(8)⋯O(4)^{iv} 0.279 3(6) nm, N(8)−H(8A)⋯O(4)^{iv}=152.5° (symmetry code: ^{iv} 2−x, 2−y, 1−z)) further stabilizes the structure of **1**. Notably, when a similar phen derivative pyrazino [2,3-f][1,10]phenanthroline (L′) was used to react with Cd(Ⅱ) atoms in the presence of 1,4-naphthalenedicarboxylate (1,4-NDC), a structurally-different three-dimensional α-polonium structure



Symmetry codes: ^{i} 1−x, 2−y, −z; ^{ii} 1−x, 2−y, 1−z

Fig.1 Coordination environments of Cd(Ⅱ) atoms in complex **1** with displacement ellipsoids at 30% probability level

Table 1 Selected bond distances (nm) and angles (°) fro the title complex

Cd(1)-N(5)	0.234 9(5)	Cd(1)-N(6)	0.239 4(5)	Cd(1)-O(1)	0.220 3(4)
Cd(1)-O(5)	0.235 6(4)	Cd(1)-O(6)	0.243 4(4)	Cd(1)-O(7)^{i}	0.226 8(4)
Cd(2)-N(1)	0.237 8(5)	Cd(2)-N(2)	0.234 9(5)	Cd(2)-O(8)^{i}	0.222 1(4)
Cd(2)-O(3)^{ii}	0.237 9(4)	Cd(2)-O(4)^{ii}	0.238 7(4)	Cd(2)-O(2)	0.223 5(4)
O(1)-Cd(1)-O(7)^{i}	105.07(16)	O(1)-Cd(1)-N(5)	157.16(15)	O(7)^{i}-Cd(1)-N(5)	82.83(16)
O(1)-Cd(1)-O(5)	111.55(16)	O(7)^{i}-Cd(1)-O(5)	84.35(15)	N(5)-Cd(1)-O(5)	90.32(16)
O(1)-Cd(1)-N(6)	88.59(16)	O(7)^{i}-Cd(1)-N(6)	122.06(16)	N(5)-Cd(1)-N(6)	69.39(15)
O(5)-Cd(1)-N(6)	142.31(16)	O(1)-Cd(1)-O(6)	85.51(14)	O(7)^{i}-Cd(1)-O(6)	137.90(14)
N(5)-Cd(1)-O(6)	103.12(15)	O(5)-Cd(1)-O(6)	54.36(13)	N(6)-Cd(1)-O(6)	98.39(15)
O(8)^{i}-Cd(2)-O(2)	99.29(18)	O(8)^{i}-Cd(2)-N(2)	162.29(16)	O(2)-Cd(2)-N(2)	85.53(18)
O(8)^{i}-Cd(2)-O(3)^{ii}	110.65(16)	O(2)-Cd(2)-O(3)^{ii}	83.36(15)	N(2)-Cd(2)-O(3)^{ii}	86.76(16)
O(8)^{i}-Cd(2)-N(1)	93.84(16)	O(2)-Cd(2)-N(1)	122.73(17)	N(2)-Cd(2)-N(1)	69.51(15)
O(3)^{ii}-Cd(2)-N(1)	141.40(15)	O(8)^{i}-Cd(2)-O(4)^{ii}	92.44(14)	O(2)-Cd(2)-O(4)^{ii}	137.66(15)
N(2)-Cd(2)-O(4)^{ii}	95.37(16)	O(3)^{ii}-Cd(2)-O(4)^{ii}	54.54(14)	N(1)-Cd(2)-O(4)^{ii}	96.59(15)

Symmetry codes: ^{i} 1−x, 2−y, −z; ^{ii} 1−x, 2−y, 1−z.

[Cd(1,4-NDC)(L′)]$_n$ was reported[8]. Clearly, the topological difference between **1** and the reported one is mainly attributed to the structural difference of the dicarboxylates.

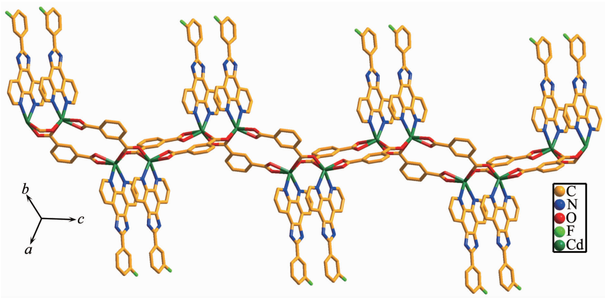


Fig.2 View of the chain structure of complex **1**

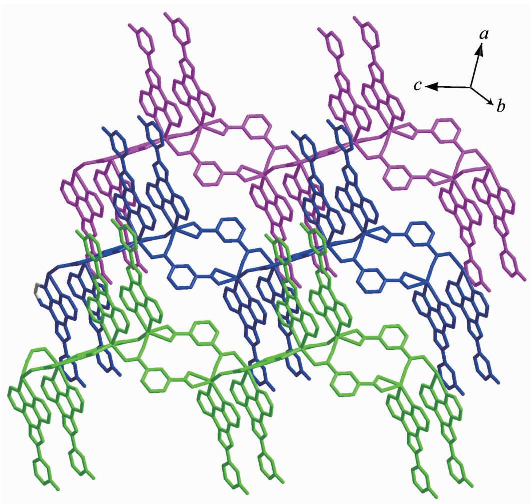


Fig.3 View of the 2D supramolecular layer architecture of **1** constructed through interchain CH-π interactions

2.2 IR analysis

The infrared spectrum of the compound 1 has a strong peak at about 1 621 cm^{-1} corresponding to the stretching vibration of imino C=N bonds of the L ligand. Asymmetric and symmetric stretching of the carboxylate group of the 1,3-BDC appear at 1 612, 1 580 cm^{-1} (ν(OCO)$_{assym}$) and 1 340, 1 377 cm^{-1} (ν(OCO)$_{sym}$), respectively. The absence of characteristic bands at about 1 700 cm^{-1} in the compound **1** indicates the complete deprotonation of 1,3-BDC ligand upon reaction with Cd(Ⅱ) atoms.

2.3 Thermal analysis

Thermogravimetric analysis was carried out for compound **1** in order to characterize the compound more fully in terms of thermal stability. The experiment was performed under N_2 atmosphere with a heating rate of 10 ℃·min^{-1} in temperatures ranging from room temperature to 800 ℃. As shown in Fig.4, the anhydrous compound **1** is thermally stable up to around 395 ℃. The first weight loss corresponds to the release of 1,3-BDC ligand in the temperature range of 395~450 ℃ (obsd. 25.9%, calcd. 27.3%). The second weight loss from 450 to 630 ℃ can be attributed to the decomposition of L ligand (obsd. 49.2%, calcd. 51.7%). This result is in good accordance with the composition of the complex.

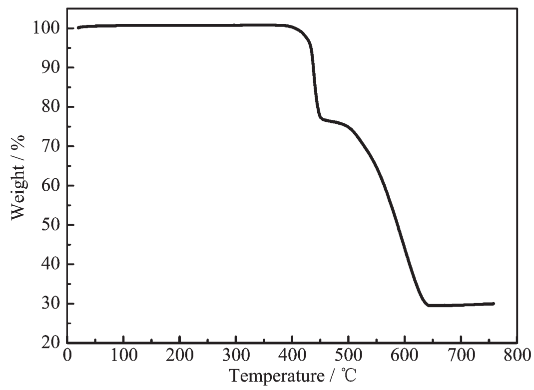


Fig.4 TGA curve of compound **1**

2.4 Luminescent property

The luminescent properties of compound **1**, free ligands L and 1,3-H_2BDC have been studied at room temperature (Fig.5). The photoluminescent spectra of L and 1,3-H_2BDC show the emissions maxima at 545 (λ_{ex}=325 nm) and 385 nm (λ_{ex}=325 nm), respectively. These emissions may be assigned to π*-n or π*-π transitions of the intraligands. Compound **1** shows a maximum emission at 403 nm (λ_{ex}=325 nm). In comparison with the 1,3-H_2BDC ligand, the emission maximum of

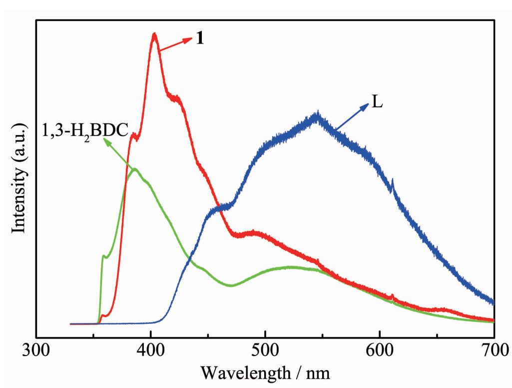


Fig.5 Emission spectra of compound **1**, free ligands L and 1,3-H_2BDC

compound **1** has slightly changed and show a little red shift. Therefore, the origin of the emission for compound **1** might be attributed to the intraligand transition of 1,3-H_2BDC anion[12].

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