6,6′-二硫二烟酸构筑的锌配位聚合物的合成、晶体结构和荧光性能

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摘要: 本文以 6,6′-二硫二烟酸为主配体,通过水热法合成了新的配合物{[Zn(cpds)(dpa)]·H$_2$O}$_n$ (**1**)(H$_2$cpds=6,6′-dithiodinicotinic acid,dpa=dipyridin-2-ylamine)。用 X-射线单晶衍射分析确定了配合物为三斜晶系,$P\bar{1}$ 空间群,其晶体学参数为 a=0.846 7(2),b=1.167 4(3),c=1.226 5(3) nm,α=73.605(3)°,β=78.656(3)°,γ=81.484(3)°,V=1.134 7(5) nm³,D_c=1.850 g·cm⁻³,Z=2。结构分析表明配合物 **1** 为一维链状结构,相邻一维链之间堆积形成三维超分子网络结构。本文还研究了配合物的热稳定性和荧光性质。

关键词: 晶体工程;配位聚合物;6,6′-二硫二烟酸;荧光

Synthesis, Crystal Structure and Luminescent Property of Zn(II) Polymer Coordination Based on 6,6′-Dithiodinicotinic Acid

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Abstract: A novel zinc coordination polymer {[Zn(cpds)(dpa)]·H$_2$O}$_n$ (**1**) (H$_2$cpds=6,6′-dithiodinicotinic acid, dpa= dipyridin-2-ylamine) has been hydrothermally synthesized and structurally characterized by single-crystal. Complex **1** crystallizes in the triclinic system, space group $P\bar{1}$ with a=0.846 7(2), b=1.167 4(3), c=1.226 5(3) nm, α=73.605(3)°, β=78.656(3)°, γ=81.484(3)°, V=1.134 7(5) nm³, D_c=1.850 g·cm⁻³, Z=2. Single-crystal X-ray analysis reveal that compound **1** contains an infinite 1D chain structure, and the 1D chain was stacked together to form a 3D supramolecular network. Additionally, the fluorescent property and TG analysis for compound **1** were also measured and discussed. CCDC: 931127.

Key words: crystal engineering; coordination polymer; 6,6′-dithiodinicotinic acid; fluerescence

The currently progressive impetus for the design and fabrication of novel metal-organic frameworks (MOFs) is rooted not only in their fascinating topological structures but also from their promising properties and great potential applications in the fields of gas storage, magnetism, and optical properties, and so on[1-7]. It has been observed that organic ligands play crucial roles for the designed synthesis of some interesting coordination networks, such as the donating type, the flexibility, and the geometry of the organic ligands[8]. Among various organic ligands, polycarboxyl compounds have been extensively used as multifunctional tectons[9-10]. However, in contrast to rigid carboxylates, the coordination networks constructed from flexible carboxylates are relatively underdeveloped[11]. It is difficult to predict either the composition or the network topology constructed from a flexible carboxylate due to the

conformational freedom in the assembly process. However, the special conformation and coordination functionality of the flexible ligand might generate some unprecedented coordination frameworks[12]. In this regard, flexible disulfide derivatives bearing -S-S- spacers have attracted considerable interest, because they can afford more rich structure information compared with rigid ligands[13]. Nevertheless, it is still a challenge to predict and control the ligand reactions toward our target products, and more knowledge of this field is needed[14]. In this report, we focused our attention on utilizing flexible disulfide derivative of carboxylate ligand, 6,6′-dithiodinicotinic acid (H$_2$cpds), adopting a twist conformation with a C-S-S-C torsion angle of *ca.* 90° which can show the axial chirality with the M- and P- forms of the enantiomers to construct interesting coordination frameworks. Moreover, H$_2$cpds not only has hard-only (carboxylate-O) but also has soft-only (pyridine-N) donor sets presenting versatile coordination modes to connect metal ions into higher-dimensional structures[15].

For resolving the poor solubility of reactants, the hydrothermal reaction can offer a good synthetic route to prepare polymeric solids with better-quality crystals than traditional solution techniques such as diffusion, evaporation, and cooling. Accordingly, we choose employing H$_2$cpds and Zn(Ⅱ) ion to construct extended polymer networks through a hydrothermal technique, with the help of N-donor coligand dipyridin-2-ylamine (dpa), a new complex {[Zn(cpds)(dpa)]·H$_2$O}$_n$ (**1**) was obtained. The results show that these ligands exhibit the special ability to formulate complex and play an important role in directing the final structures. In addition, the fluorescent property and TG analysis of compound **1** have been discussed.

1　Experimental

1.1　Materials and physical measurements

The reagents were used directly as supplied commercially without further purification. Elemental analyses (C, H, N) were determined with a Perkin-Elmer model 240C automatic instrument. Infrared spectra on KBr pellets were recorded on a Bruker Equinox-55 spectrometer in the range of 4 000~400 cm^{-1}. Luminescence spectra for the solid samples were investigated with a Hitachi F-4500 fluorescence spectrophotometer. The X-ray powder diffraction pattern was recorded with a Pigaku D/Max 3III diffractometer. Thermal analysis was determined with a Netzsch STA 449C microanalyzer under flowing N$_2$ atmosphere at a heating rate of 10 ℃·min^{-1}.

1.2　Synthesis of {[Zn(cpds)(dpa)]·H$_2$O}$_n$ (1)

Compound **1** was obtained by the reaction of ZnNO$_3$ (0.1 mmol), dpa (0.1 mmol) and H$_2$cpds (0.1 mmol) in molar ratio of 1∶1∶1 mixed with 15 mL of aqua and 1mL of triethylamine under hydrothermal conditions (at 150 ℃ for 6 d and cooled to room temperature with a 5 ℃·h^{-1} rate). Then the pH value of the resulting solution was adjusted to 7. Colorless crystal of **1** was collected in 55% yield. Anal. Calcd. for C$_{22}$H$_{16}$ZnN$_5$O$_5$S$_2$ (%): C, 47.19; H, 2.88; N,12.51. Found(%): C, 48.04; H, 3.01; N, 12.36. IR (KBr, cm^{-1}): 3 441(w), 3 278(w), 2 450(w), 1 706(s), 1 664(s), 1 608(s), 1 544(w), 1 487(m), 1 360(s), 1 230(m), 1 132(w), 1 069 (m), 828(m), 767(m), 650(m), 547(m).

1.3　Crystal structure determination

Diffraction experiment for **1** was carried out with Mo *K*α radiation using a BRUKER SMART APEX CCD diffractometer at 293(2) K. A summary of the crystallography data and structure refinement is given in Table 1, and selected bond lengths and angles of compound is listed in Table 2. Possible hydrogen bond geometries of complex is listed in Table 3. Structure was solved by direct methods and refined with the full-matrix leastsquares technique on F^2 using the SHELXS-97[16] and SHELXL-97[17] program. All non-hydrogen atoms were refined anisotropically. All solvent hydrogen atoms were located in successive different Fourier Maps and the other hydrogen atoms were treated as riding method.

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2　Results and discussion

2.1　Description of the structure {[Zn(cpds)(dpa)] ·H$_2$O}$_n$

Single-crystal X-ray diffraction analysis of **1**

Table 1　Selected crystallographic data for compound 1

Empirical formula	$C_{22}H_{16}ZnN_5O_5S_2$	V / nm³	1.134 7(5)
Formula mass	559.89	Z	2
Crystal system	Triclinic	D_c / (g·cm⁻³)	1.850
Space group	$P\bar{1}$	μ / mm⁻¹	1.313
a / nm	0.846 7(2)	$F(000)$	570
b / nm	1.167 4(3)	θ / (°)	1.83~25.10
c / nm	1.226 5(3)	Reflections collected / unique	5 730 / 3 956 (R_{int}=0.021 0)
α / (°)	73.605(3)	Completeness to θ=25.10° / %	98.2
β / (°)	78.656(3)	Goodness-of-fit on F^2	1.069
γ / (°)	81.484(3)	Final R indices ($I>2\sigma(I)$)	R_1=0.045 2, wR_2=0.109 6

$R_1=\sum (|F_o|-|F_c|)/\sum|F_o|$; $wR_2=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

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

Zn(1)-O(3)ᵃ	0.197 7(2)	Zn(1)-O(2)	0.200 7(3)	Zn(1)-O(1)	0.266 4(3)
Zn(1)-O(4)ᵃ	0.252 3(5)	Zn(1)-N(1)	0.204 2(4)	Zn(1)-N(3)	0.204 4(3)
O(3)ᵃ-Zn(1)-O(2)	113.58(13)	O(3)a-Zn(1)-N(1)	100.32(15)	O(3)ᵃ-Zn(1)-N(3)	137.51(14)
O(2)-Zn(1)-N(1)	118.19(13)	N(1)-Zn(1)-N(3)	89.70(14)	O(2)-Zn(1)-N(3)	96.80(12)
O(2)-Zn(1)-O(1)	53.76(10)	O(1)-Zn(1)-O(3)ᵃ	83.55(13)	O(2)-Zn(1)-O(4)ᵃ	99.79(12)
O(1)-Zn(1)-O(4)ᵃ	119.38(13)	O(3)ᵃ-Zn(1)-O(4)ᵃ	56.46(14)	O(1)-Zn(1)-N(1)	82.80(13)
O(1)-Zn(1)-N(3)	138.19(13)	O(4)ᵃ-Zn(1)-N(1)	141.68(14)	O(4)ᵃ-Zn(1)-N(3)	90.81(13)

Symmetry code: ᵃ x+1, y−1, z.

Table 3　Hydrogen-bonding geometries for compound 1

| D–H⋯A	d(D-H) / nm	d(H⋯A) / nm	d(D⋯A) / nm	∠DHA / (°)
O(5)−H(5A)⋯N(2)ᵃ	0.086	0.196	0.282 4(5)	179
O(5)−H(5B)⋯N(5)ᵇ	0.086	0.196	0.282 1(5)	179

Symmetry codes: ᵃ 1−x, 1−y, 1−z, ᵇ 1+x, y, z.

reveals that the crystal is of triclinic, space group $P\bar{1}$ with Z=2. The symmetric unit of **1** consists of one Zn(Ⅱ) atom, one cpds²⁻, one dpa ligand and a lattice water molecule (Fig.1). The charge neutrality is achieved by the two deprotonated carboxylate groups of the cpds²⁻ molecule. The Zn(Ⅱ) atom adopts a distorted squared pyramidal geometry, bonding two nitrogen atoms from one dpa ligand and four oxygen atoms from two cpds²⁻ ligands. The Zn-O and Zn-N bond distances are in the range 0.197 7(2)~0.264 4(3) and 0.204 2(4)~0.204 4(3) nm, respectively, which are in agreement with those reported for Zn(Ⅱ) complexes[18].

The carboxylate group of cpds²⁻ ligand coordinates to Zn(Ⅱ) ion with a bridging chelating mode to produce an infinite 1D chain along b axis (Fig.2). On the other hand, the chelating N-donor ligand (dpa) can

constrain the prolongation of the framework and result in the formation of lower dimensionality. Furthermore,
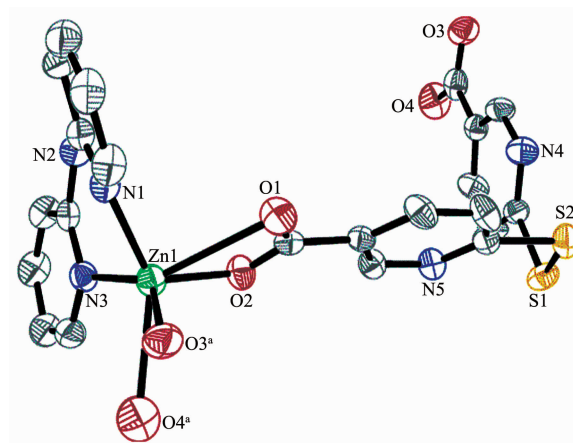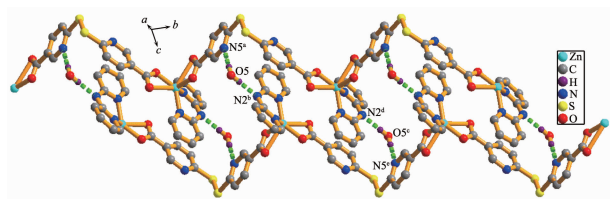

Symmetry code: ᵃ x+1, y−1, z

Fig.1　Asymmetric unit and coordination environment of Zn(Ⅱ) in **1**

the adjacent 1D chains are further linked by the hydrogen bonding between N and O atoms from cpds^{2-}, dpa ligands and lattice waters （O5···N2 0.282 4(5) nm, O5···N5 0.282 1(5) nm）(Fig.3), forming a larger infinite 1D wave-like chain. But the hydrogen bonding interaction can not connect the 1D wave-like chains to form a 2D framework. Finally, the 1D wave-like chains stack together in the 3D crystal packing diagram, which is shown in Fig.4.
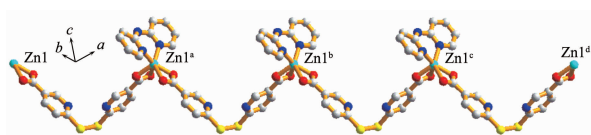
Symmetry codes: [a] 1+x, −1+y, z; [b] 2+x, −2+y, z; [c] 3+x, −3+y, z; [d] 4+x, −4+y, z

Fig.2　1D chain constructed via Zn(Ⅱ) atoms and cpds^{2-} ligands

Hydrogen bonds are shown as dashed lines; Symmetry codes: [a] 1+x, y, z; [b] 1−x, 1−y, 1−z; [c] 1−x, 2−y, 1−z; [d] x, 1+y, z; [e] −x, 2−y, 1−z

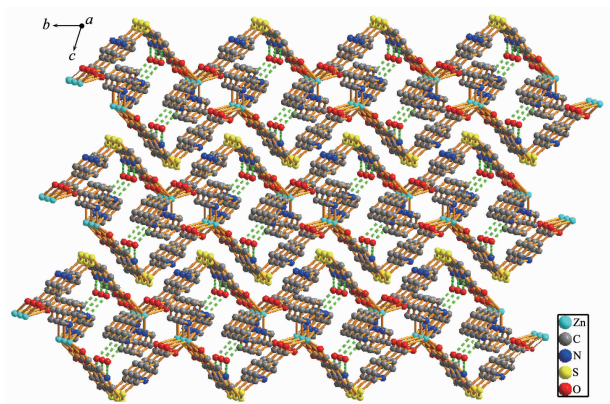Fig.3　Adjacent 1D chain connected through hydrogen bonding in **1**

Fig.4　3D packing diagram in **1**

2.2　TGA analysis and solid-state fluorescent property

To identify the thermal stability of compound **1**, The TGA measurement was carried out （Fig.5). In **1**, the result shows that a first major weight loss equal to 4.06% before 200 ℃ ascribed to the release of all free water molecules （Calcd. 3.22%). Accordingly, the framework is stable up to 200 ℃, at which point the remove of organic ligands can ensue. Finally, the residual weight of 15.82% may be attributed to the percentage (expected 14.54%) of ZnO.
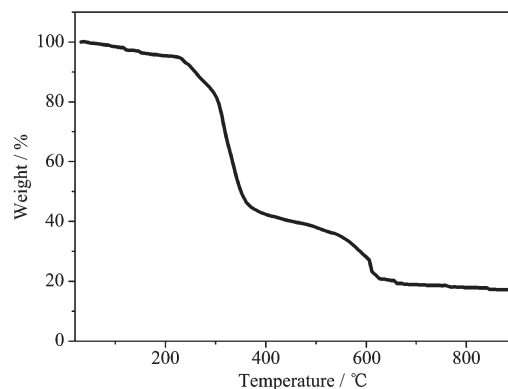

Fig.5　TG curve of compound **1**

The photoluminescent feature of complex **1** in the solid-state is depicted in Fig.6. Intense emission bands are observed at 395 and 450 nm （λ_{ex}=280 nm) for H$_2$cpds, which can be assigned to the ligand-centered electronic transition, that is $\pi^*\rightarrow n$ or $\pi^*\rightarrow\pi$ electronic transitions[19-24]. Compound **1** shows one main peak at 370 nm upon excitation at 280 nm. According to the literature, the luminescent properties of **1** can be attributed to ligand-to-metal charge transfer[25-26]. Generally speaking, the weak luminescences based on Zn(Ⅱ)-cpds coordination polymer is always observed, and more work is needed to elucidate to the real nature of emission.
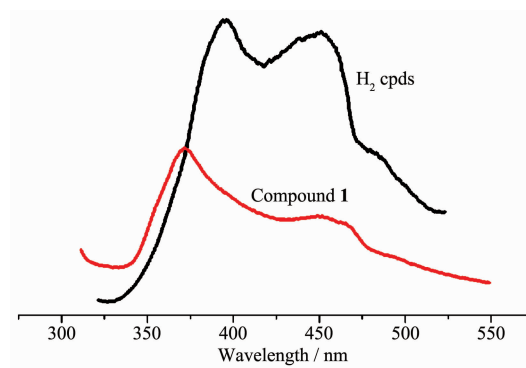

Fig.6　Solid-state photoluminescent spectrum of complex **1** and the free ligand (H$_2$cpds)

3　Conclusions

This research focuses on the synthesis, structural

characterization, and properties of a Zn-containing coordination polymer based on 6,6′-dithiodinicotinic acid (H$_2$cpds) and dipyridin-2-ylamine (dpa). The complex exhibits an infinite 1D hydrogen bonding chain by hydrogen bonding interactions and the 1D chain stack together to form a 3D supramolecular network, in which hydrogen bonds play important roles in formation of the resulting structures. Additionally, fluorescent properties and TG analysis for compound **1** were also measured and discussed. Subsequent works will be focused on the structures and properties of a series of coordination polymers constructed by 6,6′-dithiodinicotinic acid with more auxiliary ligands and metal ions.

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