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镉(Ⅱ)磺基水杨酸配合物的合成、结构和荧光性质

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摘要：配体 2,2′-联吡啶(bipy)、磺基水杨酸(H_2hssal)和镉盐反应合成了配合物[Cd(hssal)(bipy)(H_2O)$_2$]·H_2O (**1**),用单晶 X-射线和元素分析对生成的晶体进行了表征,结构研究发现该晶体属于单斜晶系 $P2_1/c$ 空间群。Cd(Ⅱ)采取八面体配位几何构型,磺基水杨酸作为二齿桥联配体连结不同的 Cd(Ⅱ)原子形成一维链结构,一维链被 O–H…O 氢键连接形成二维层,再进一步由 O–H…O 氢键将二维层联结在一起形成三维结构。研究了配合物 **1** 的荧光性质。CCDC:772715。

关键词：Cd(Ⅱ)配合物；2,2′-联吡啶；磺基水杨酸；荧光性质

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Synthesis, Structure and Luminescent Property of Cadmium(Ⅱ) Complex of Sulphosalicylic Acid

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Abstract: A new complex, [Cd(hssal)(bipy)(H_2O)$_2$]·H_2O (**1**) (H_2hssal: sulphosalicylic acid, bipy: 2,2′-bipyridine), is a metal-carboxylate coordination polymer prepared by hydrothermal synthesis techniques and characterized by single crystal X-ray diffraction and elemental analysis. Complex **1** crystallizes in monoclinic space group $P2_1/c$ and has 1D chain-like architecture. The crystal structure reveals that Cd(Ⅱ) centre adopts a pseudo octahedral geometry. Ligand 2,2′-bipyridine chelates with Cd(Ⅱ) atom. $Hssal^{2-}$ acts as a bridge coordinating to two different Cd(Ⅱ) centers to give rise to a 1D infinite stepped chain polymer. 1D chains of **1** are connected together to form 3D structure through O–H…O hydrogen bond. The luminescent property of complex **1** was also studied. CCDC: 772715.

Key words: Cd(Ⅱ) complex; 2,2-bipyridine; sulphosalicylic acid; luminescent property

The self-assembly of metal-organic coordination polymers attracted great attention because of their potential as functional materials[1-7], and much effort in this area has been devoted to the preparation of polymeric solids with specific network topologies as well as potentially interesting properties[8-10], such as catalysis, porosity, magnetism, luminescence, conductivity, sensing, chirality, nonlinear optics (NLO), and optical limiting capability[11-19]. In metal-organic crystal engineering, the strategy using metals and organic ligands which have coordinating ability to each others is usually employed to synthesis new coordination polymers. The design and synthesis of metal-organic frameworks based on the selection of ligands and metal ions as linker and node to constructure two-dimensional (2D) and three-

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dimensional (3D) topological structure has become a very attractive research field and payed much attention. Therefore, in the recently, contrasting to 2D and 3D frameworks in abundance, the one-dimensional chain-like polymeric solids have been less extensively reported to date[20-21]. However, even for these 1D simple chain-like polymers, there are still many fascinating diversities and interesting structural features[22]. On the other hand, Cd(Ⅱ)-containing coordination compounds have received considerable interest recently because of their ability to form bonds with different donors, their large radius, their various coordination modes, and potential applications of complexes in catalysis, luminescent materials, and nonlinear optics (NLO) materials[23-25]. Herein, we report the synthesis and structural characterization of one-dimensional (1D) coordination polymer, $[Cd(hssal)(bipy)(H_2O)_2]\cdot H_2O$ (**1**), and luminescent property of complex **1** was investigated.

1 Experimental

1.1 Reagents and physical measurements

All reagents commercially available were of reagent grade and used without further purification. Solvents were purified according to the standard methodes. C, H, N and S elements analyses were carried out on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Vector22 FTIR spectrophotometer by using KBr pellet in the range of 4 000~400 cm^{-1}. The luminescent spectra for the solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrophotometer with a xenon arc lamp as the light source. In the measurements of the emission and excitation spectra, the pass width is 5.0 nm.

1.2 Synthesis of complex

The mixture of 5-sulfosalicylic acid dihydrate 76.3 mg (0.6 mmol) and $CdCO_3$ 43.1 mg (0.25 mmol) in 5 mL distilled water was stirred for 10 h at room temperature, and 46.5 mg (0.3 mmol) 2,2-bipy was added. Then 5 mL CH_3OH was added to the clear solution and sealed in a 25 mL Teflon-lined stainless steel container, which was heated at 140 ℃ for 69 h. After the sample was cooled to room temperature, yellow prism crystals were produced (75.2 mg). Anal. Calcd. for $C_{17}H_{18}N_2O_9SCd$ (%): C, 37.90; H, 3.37; S, 5.95; N, 5.20. Found(%): C, 37.85; H, 3.33; S, 5.83; N, 5.29. FTIR spectrum was run as KBr pellets on a Vector 22 FTIR spectrophotometer (KBr pellet, cm^{-1}): 3 435(bs), 1 647(s), 1 587(s), 1 467(s), 1 429(m), 1 355(m), 1 290(s), 1 241(m), 1 151(s), 1 126(m), 1 093(m), 1 028(m), 909(m), 843(m), 828(m), 811(m), 755(m).

1.3 Crystal structure determination

A crystal with dimensions of 0.12 mm×0.08 mm×0.06 mm was put on a Bruker Smart Apex Ⅱ CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation (λ=0.071 073 nm) by using an ω-2θ scan mode at 293(2) K. Out of the total 17 158 reflections collected in the range of $1.79° \leqslant \theta \leqslant 27.47°$, 4 673 were independent with R_{int}=0.023 5, of which 3 924 were considered to be observed ($I>2\sigma(I)$) and used in the succeeding refinement. The crystal structure was solved by direct methods using SHELXS-97 program. Corrections for Lp factors and empirical adsorption were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97. The crystal parameters, data collection and refinement results for the complex are listed in Table 1. The selected bond lengths and bond angles are listed in Table 2.

CCDC: 772715.

Table 1　Crystallographic data for complex 1

Empirical formula	$C_{17}H_{18}N_2O_9SCd$	b / nm	1.586 28(18)
Formula weight	538.79	c / nm	1.645 64(19)
Crystal system	Monoclinic	β / (°)	99.459(2)
Space group	$P2_1/c$	V / nm^3	2.046 8(4)
a / nm	0.794 90(9)	Z	4

Continued Table 1

Temperature / K	293(2)	Goodness of fit	1.064
Crystal color	Yellow	Reflections collected	17 158
D_c / (g·cm^{-3})	1.748	Independent reflns. (R_{int})	4 673
μ / mm^{-1}	1.221	Obsd. reflns. ($I>2\sigma(I)$)	3 924
Crystal dimension / mm	0.12×0.08×0.06	Parameters refined	295
θ range / (°)	1.79~27.47	R, wR ($I>2\sigma(I)$)	0.029 6, 0.060 3
F(000)	1 080	R, wR (all reflections)	0.038 9, 0.063 2

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

Cd(1)-O(2)	0.224 58(18)	Cd(1)-O(6)	0.225 9(2)	Cd(1)-O(5)#1	0.233 03(19)
Cd(1)-O(7)	0.235 0(2)	Cd(1)-N(1)	0.230 2(2)	Cd(1)-N(2)	0.232 3(2)
Cd(1)-O(5)#2	0.233 03(19)				
O(2)-Cd(1)-N(1)	99.47(8)	O(6)-Cd(1)-N(1)	167.68(9)	O(2)-Cd(1)-N(2)	171.01(8)
O(6)-Cd(1)-N(2)	96.42(9)	N(1)-Cd(1)-N(2)	71.73(9)	O(2)-Cd(1)-O(5)#1	86.72(7)
O(6)-Cd(1)-O(5)#1	85.41(7)	N(1)-Cd(1)-O(5)#1	98.19(8)	N(2)-Cd(1)-O(5)#1	92.65(7)
O(2)-Cd(1)-O(7)	85.74(8)	O(6)-Cd(1)-O(7)	91.28(9)	N(1)-Cd(1)-O(7)	86.65(9)
Cd(1)-N(2)-O(7)	95.37(8)	O(5)-Cd(1)-O(7)#1	171.63(8)	O(2)-Cd(1)-O(6)	92.47(8)

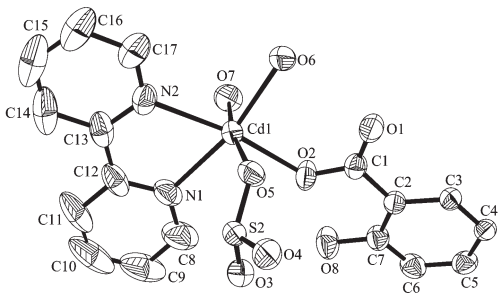
Symmetry codes: #1: $-x+2$, $y-1/2$, $-z+1/2$; #2: $-x+2$, $y+1/2$, $-z+1/2$.

2 Results and discussion

2.1 Crystal structure of the complex 1

The strong and broad absorption bands in the range of 3 000~3 700 cm^{-1} for **1** is assigned as the characteristic peaks of OH vibration. The strong vibrations around 1 647 and 1 587 cm^{-1} for **1** correspond to the asymmetric and symmetric stretching vibrations of carboxylate group, respectively. The absence of strong bands ranging from 1 690 to 1 730 cm^{-1} indicates the deprotonation of ligand H_2hssal, which agrees with the structural results.

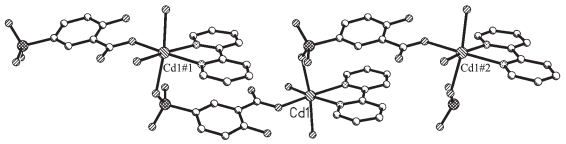
Complex **1** crystallizes in the monoclinic space group $P2_1/c$. ORTEP diagram of the complex **1** with atom numbering scheme is shown in Fig.1. The coordination diagram displays that Cd1 atom is coordinated to N1, N2, O2, O5, O6, O7 atoms, in which N1 and N2 atoms are from a chelate ligand 2,2′-bipy, O6, O7 atoms from two water molecules, O2, O5 from two different hssal^{2-} anions. The Cd-O bond distances range from 0.224 58(18) to 0.235 0(2) nm, and the average is 0.229 6 nm. The lengthes of Cd1-N1, Cd1-N2 bonds are 0.230 2(2) and 0.232 3(2) nm, respectively. The distances of Cd-O, Cd-N are quite similar to those of normal Cd-O and Cd-N bonds[26-27]. The bond angles around the cadmium center range from 71.73(9)° to 171.63(8)°. The data from Table 2 indicate that Cd1 atom lies in a distorted octahedral geometry (Fig.1).



Hydrogen atoms and uncoordinated water molecule omitted for clarity

Fig.1 Coordination environment around the Cd(Ⅱ) atom of **1** with 50% probability displacement

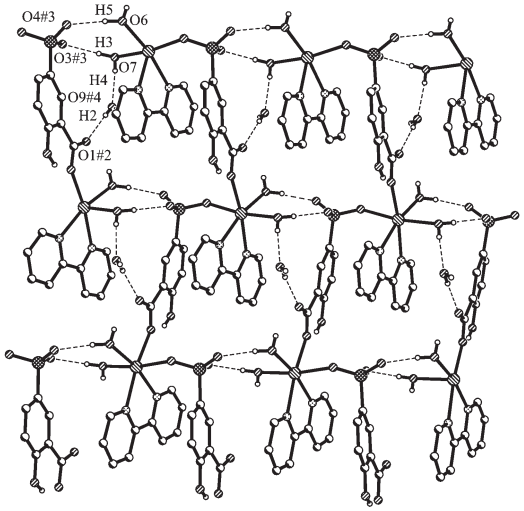
Fig.2 displays that hssal^{2-} is a bidentate ligand and acts as a bridge coordinating to two different Cd(Ⅱ) ions with a Cd-Cd separation of about 0.936 nm, resulting in a one-dimensional stepped coordination chain (Fig.2). In ligand hssal^{2-}, among the three oxygen atoms in sulfonate group, only an oxygen atom coordinates to Cd(Ⅱ) ion. Similar to sulfonate group, in the carboxylate group, only an oxygen atom participate in coordinating with Cd(Ⅱ). The hydroxyl group of ligand hssal^{2-} does



Symmetry codes: #1: $-x+2$, $y-1$, $-z+1$; #2: $-x+2$, $y+1/2$, $-z+1/2$; Hydrogen atoms omitted for clarity

Fig.2　1D chain structure in **1**

not participate in the coordination with Cd(Ⅱ). Close up view of the hydrogen bonding interaction and packing diagram various H-bonding interaction viewed down *c* axis for **1** in the formation of extended H-bonded network is depicted in Fig.3. The two uncoordinated sulfonate group end oxygen atoms (O3 and O4) acts as a strong acceptor for O–H···O hydrogen bonding interactions with the H atoms of coordinated water molecule. In addition, the uncoordinated water molecules (O9) with coordinated water molecules (O7), uncoordinated oxygen atoms (O1) of carboxylate group form O–H···O hydrogen bonds. All these O–H···O hydrogen bonds connect the adjacent chains to generate two-dimensional networks (Fig.3). There is hydrogen bonding interaction between uncoordinated water molecule with hydroxyl group and carboxylate group of $hssal^{2-}$ anion, which link two-dimensional networks to generate three-dimensional structure. The various H-bonding parameters with symmetry code are given in Table 3.



Symmetry codes: #2: $1-x$, $1/2+y$, $1/2-z$; #3: $1-x$, $-1/2+y$, $1/2-z$; #4: x, $-1+y$, z

Fig.3　Crystal packing diagram, hydrogen bonds indicated by dashed lines

Table 3　Hydrogen bonds for complex 1

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠(DHA) / (°)
O(9)–H(1)···O(8)#1	0.077(5)	0.216(5)	0.293 1(4)	177
O(9)–H(2)···O(1)#2	0.075(5)	0.203(5)	0.278 0(4)	172
O(7)–H(3)···O(3)#3	0.083(4)	0.195(4)	0.277 8(3)	179
O(7)–H(4)···O(9)#4	0.073(3)	0.201(3)	0.273 8(4)	174
O(6)–H(5)···O(4)#3	0.084(4)	0.187(3)	0.270 2(3)	172
O(6)–H(7)···O(1)	0.078(5)	0.201(5)	0.273 9(3)	156
O(8)–H(8B)···O(2)	0.082	0.175	0.248 6(3)	148

Symmetry transformations are used to generate equivalent atoms: #1: $1-x$, $1-y$, $-z$; #2: $1-x$, $1/2+y$, $1/2-z$; #3: $1-x$, $-1/2+y$, $1/2-z$; #4: x, $-1+y$, z.

2.2　Luminescence properties of complex 1

Fluorescent transition-metal complexes containing rigid multichromophoric ligands with a π-conjugation system have been studied intensively because of their potential use. On the other hand, to extend the π-conjugation only by synthesis and modification of organic composition may be difficult and tedious. Synthesis of inorganic/organic coordination complexes by using functional ligands gained from simplified synthetic approaches, some coligands, and transition-metal centers can be a useful method to obtain new photoluminescent materials. The luminescent properties of the free ligand H_2hssal, 2,2′-bipy and complex **1** were investigated at room temperature in the solid state, and the emission spectrum of **1** is indicated in Fig.4. Complex **1** exhibits photoluminescence with emissions at 411 nm upon excitation at 336 nm. But in the some conditions, free ligand H_2hssal, 2,2′-bipy were not observed evident emission. It can be assigned to the ligand-to-metal charge transfer (LMCT)[28].

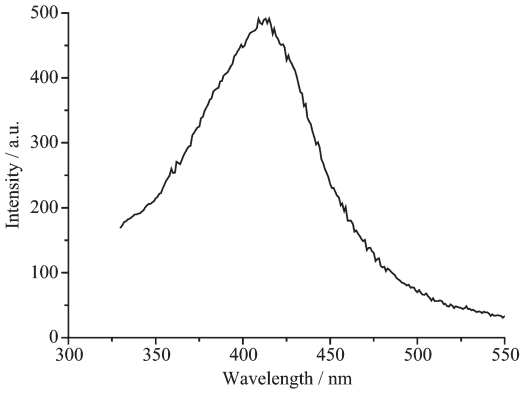


Fig.4 Emission spectrum of complex **1** in the solid state at room temperature

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