

一种新的配位聚合物 $[\text{Cd}(\text{SCN})_2(\text{POM})_2]_n$ 的合成和晶体结构

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Synthesis and Crystal Structure of a Novel Coordination Polymer of $[\text{Cd}(\text{SCN})_2(\text{POM})_2]_n$

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The one-dimensional chain self-assembled coordination polymer, $[\text{Cd}(\text{SCN})_2(\text{POM})_2]_n$ (where POM is 3-methyl-4-nitropyridine-*N*-oxide), was synthesized and characterized. The crystal data for the title coordination polymer: monoclinic, space group $P2_1/c$, $a = 1.182\ 3(1)$ nm, $b = 0.591\ 1(1)$ nm, $c = 1.419\ 2(1)$ nm, $\beta = 102.875(1)^\circ$, $Z=2$, $\mu = 1.391\ \text{mm}^{-1}$, final $R_1 = 0.062\ 8$, $wR_2 = 0.145\ 2$. The coordination polymer exhibits a strong fluorescent emission band at ca. 518 nm. CCDC: 211506.

Keywords: self-assembled coordination polymer solid state fluorescence POM

0 Introduction

Formation of self-assembled coordination polymers, hydrogen-bonded networks and $\pi \cdots \pi$ stacking structures has attracted considerable interest at present^[1,2]. One aspect is the fascinating structural diversity and potential applications as functional materials in selective separation and catalysis^[3,4]. Much attention has been given to the synthesis of one-, two-, and three-dimensional extended materials involving cadmi-

um^[5-8]. Rigid bridged ligands are frequently employed to construct these materials^[9]. The low-dimensional coordination of cadmium-thiocyanate exhibits some interesting properties such as nonlinear optical behavior^[10] and photoluminescent properties. So we expect to get the coordination polymer with fluorescence property by selecting thiocyanate as a rigid bridged ligand and POM as little conjugate ligand.

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1 Experimental

1.1 Materials

All solvents were dried and purified by usual methods. POM was synthesized through 3-methylpyridine according to literature method^[11] and purified in acetone three times. Elemental analyses were performed with a Perkin-Elmer 240 instrument. IR spectra were recorded with a Nicolet NEXUS 870 instrument in the 4 000~400 cm^{-1} region. Luminescence spectra and TGA were performed with Perkin-Elmer LS-55 instrument and Perkin-Elmer Pyris-1 DMDA-V1, respectively.

1.2 Synthesis of the $[\text{Cd}(\text{SCN})_2(\text{POM})_2]_n$

POM (1.52 g, 0.01 mol) and cadmium-thiocyanate (1.15 g, 0.005 mol) were added into 25 mL dry methanol. The mixture was stirred for 4 h then filtered. The filtrate was left to evaporate slowly and yellow crystals were obtained 2 days later. Yield (86%). Anal. Calc. for $[\text{Cd}(\text{SCN})_2(\text{POM})_2]_n$: C, 31.33; H, 2.22; N, 15.69. Found: C, 31.32; H, 2.25; N, 15.66%. IR (KBr pellet, cm^{-1}): 3 039(m), 2 105(vs), 1 607(s), 1 579(s), 1 521(s), 1 457(s), 1 342(s).

1.3 X-ray Data Collection

A single crystal with dimensions 0.46 mm \times 0.18 mm \times 0.08 mm of the title compound was selected and sealed in a capillary containing the mother liquor. Intensity data were measured using a Siemens SMART-CCD area detector diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.071\ 073\text{nm}$) with a ω -scan mode. The structure was solved by direct method and refined on F^2 using full-matrix least-squares method using SHELXTL^[12]. The hydrogen atom positions were geometrically idealized and allowed to ride on their parent atoms and fixed displacement parameters. The crystal data and refinement details are listed in Table 1, selected bond lengths, angles in Table 2.

CCDC: 211506.

2 Results and Discussion

Fig.1 shows the coordinatin environment of the

Table 1 Crystallographic Data for Complex (I)

empirical formula	$\text{C}_{14}\text{H}_{12}\text{CdN}_6\text{O}_6\text{S}_2$
formula weight	536.82
temperature / K	293(2)
crystal system	monoclinic
space group	$P2_1/c$
a / nm	1.182 3(1)
b / nm	0.591 1(1)
c / nm	1.419 2(1)
β / ($^\circ$)	102.875(1)
volume / nm^3	0.966 92(11)
Z	2
calculated density / ($\text{Mg}\cdot\text{m}^{-3}$)	1.844
absorption coefficient / mm^{-1}	1.391
$F(000)$	532
crystal size/ mm	$0.46 \times 0.18 \times 0.08$
reflection collected	5 825
independent reflections	2 360
number of parameters	134
goodness of fit on $F^2(\text{s})$	1.175
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.062\ 8, wR_2 = 0.145\ 2$
R indices (all data)	$R_1 = 0.074\ 6, wR_2 = 0.150\ 4$

Table 2 Selected Bond Lengths (nm) and Angles ($^\circ$) for Complex (I)

Cd(1)-N(3)#1	0.226 2(5)
Cd(1)-O(1)	0.233 4(4)
Cd(1)-S(1)	0.272 57(17)
Cd(1)-S(1)#3	0.272 57(17)
S(1)-C(7)	0.165 3(6)
C(7)-N(3)	0.113 9(7)
N(3)#1-Cd(1)-O(1)	89.40(19)
O(1)#3-Cd(1)-O(1)	180.000(1)
N(3)#1-Cd(1)-S(1)	89.68(14)
N(3)#2-Cd(1)-S(1)	90.32(14)
O(1)#3-Cd(1)-S(1)	90.50(15)
O(1)-Cd(1)-S(1)	89.50(15)
S(1)-Cd(1)-S(1)#3	180.0

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

cadmium in the polymer and packing diagram of the polymer is given in Fig.2. The local coordination environment of the cadmium(II) ion can be described as a distorted octahedron completed by two oxygen atoms

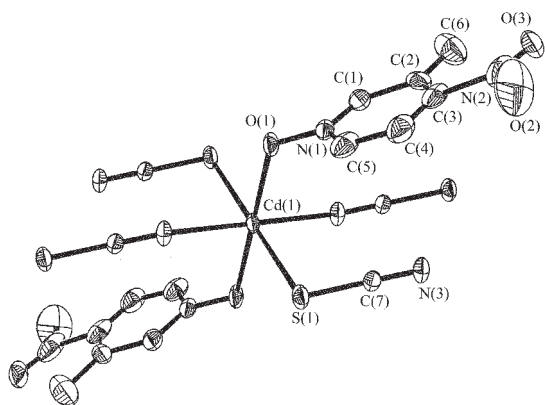


Fig.1 Coordination environment of the cadmium in the polymer

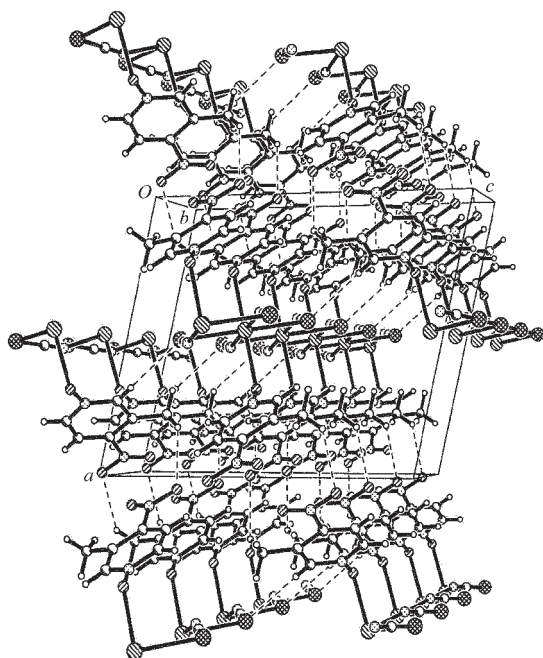


Fig.2 Packing diagram of the polymer (hydrogen bonds are indicated by dashed lines)

from POM, two sulfur atoms and two nitrogen atoms from thiocyanate ions. Adjacent cadmium atoms are linked by two bridging SCN^- ligand, forming $[\text{Cd}(\text{SCN})_2(\text{POM})_2]_n$ zigzag polymeric chain, which is shown in Fig.3. The distance of Cd-Cd is 0.5911 nm. The average S-C and C-N distances of 0.165 nm and 0.114 nm, respectively. In the complex indicate partial π delocalization along the metal-thiocyanate chains. This observation is consistent with the fact that the SCN^- ligand is easily polarizable ($\text{S}-\text{C} \equiv \text{N} \leftrightarrow \text{S}=\text{C}=\text{N}^-$). The

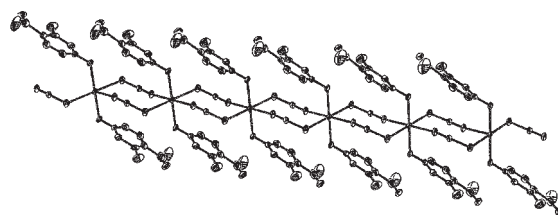


Fig.3 One-dimension chain structure of the coordination polymer $[\text{Cd}(\text{SCN})_2(\text{POM})_2]_n$

non-bridging POM ligand is bonded to Cd atoms through its oxygen atom attached to nitrogen of pyridine ring. The pyridine rings of the POM ligands on the opposite side of the polymer chains are parallel. It is also found that there is a kind of hydrogen bonding interactions between the polymer chains. The details of the hydrogen bond are C(1)-H(1A) 0.093 nm, H(1A) \cdots S(1) 0.2864 nm, C(1) \cdots S(1) 0.3759 nm, C(1)-H(1A) \cdots S(1) 161.9° (symmetry code: $x, 1/2-y, -1/2+z$).

It is well known that rigid π -conjugate plane structure exhibit luminescence. At the same experimental condition, it is found that $\text{Cd}(\text{SCN})_2$ and ligand (POM) show no luminescence. But the complex exhibits luminescence. The fluorescent spectrum of solid state of the polymer at room temperature shows that maximal emission peak occurred at 518.3 nm, which suggest that the polymer is a potential fluorescent-emitted material. It may be that $\text{Cd}(\text{SCN})_2$ coming into rigid chains and a great many parallel ligands on chains make metal-to-ligand, Cd-centered emission, ligand-centered emission and interligand charge transfer possible^[10]. The TGA of the coordination polymer reveals that its decomposing temperature point is at 472 K and it keeps solid until decomposing. That is to say, as a material the complex is thermostable.

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