

以异烟酰胺吡啶基异酞酸为配体的二维钕配合物的合成、晶体结构和荧光性质

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摘要: 标题化合物 $[\text{Eu}(\text{L})(\text{HL})] \cdot 2\text{H}_2\text{O}$ 是由 $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、5-异烟酰胺吡啶基异酞酸(H_2L)、经水热反应得到。采用元素分析、IR 及 X-射线衍射法对该配合物进行了表征。晶体结构测试表明: 晶体属于单斜晶系, 空间群 $P2_1/c$, 晶胞参数为: $a=1.344\ 02(18)\ \text{nm}$, $b=1.377\ 50(18)\ \text{nm}$, $c=1.623\ 07(15)\ \text{nm}$, $\beta=115.820(8)^\circ$, $V=2.704\ 9(6)\ \text{nm}^3$, $Z=4$, $M_r=757.45$, $D_c=1.860\ \text{g} \cdot \text{cm}^{-3}$, $\mu=2.396\ \text{mm}^{-1}$, $F(000)=1\ 504$, $R_{\text{int}}=0.051\ 4$, $R_1=0.032\ 2$, $wR_2=0.089\ 1$ 。配合物的中心钕离子是八配位稍变形的双帽三棱柱结构, 5-异烟酰胺吡啶基异酞酸将配合物桥联成二维双层结构。

关键词: 钕配合物; 晶体结构; 5-异烟酰胺吡啶基异酞酸; 水热合成

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Hydrothermal Synthesis, Crystal Structure and Luminescence Property of a 2D Eu(III) Complex Based on 5-(Isonicotinamido)isophthalic Acid

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Abstract: The title complex, $[\text{Eu}(\text{L})(\text{HL})] \cdot 2\text{H}_2\text{O}$ **1**, where H_2L =5-(isonicotinamido)isophthalic acid, was synthesized and its crystal structure was determined by X-ray diffraction analysis. The crystal is of monoclinic, space group $P2_1/c$ with $a=1.344\ 02(18)\ \text{nm}$, $b=1.377\ 50(18)\ \text{nm}$, $c=1.623\ 07(15)\ \text{nm}$, $\beta=115.820(8)^\circ$, $V=2.704\ 9(6)\ \text{nm}^3$, $Z=4$, $M_r=757.45$, $D_c=1.860\ \text{g} \cdot \text{cm}^{-3}$, $\mu=2.396\ \text{mm}^{-1}$, $F(000)=1\ 504$, $R_{\text{int}}=0.051\ 4$, $R_1=0.032\ 2$, $wR_2=0.089\ 1$. In the complex, the central Eu(III) atom is eight-coordinated by eight carboxylate oxygen atoms, completing a distorted bicapped trigonal prismatic geometry. The molecules are connected to form a 2D bilayer structure bridged by 5-(isonicotinamido)isophthalic acid. CCDC: 826595.

Key words: Eu(III) complex; crystal structure; 5-(isonicotinamido)isophthalic acid; hydrothermal synthesis

In recent years, the chemistry of metal-organic coordination polymers exploiting non-covalent interaction such as coordination bonds, hydrogen bonding etc^[1-3], has received much attention due to enormous variety of intriguing structural topologies and the potential application in catalysis, adsorption and photoelectronics^[4-8]. In construction of metalorganic

frameworks, plentiful bridging ligands especially multidentate ones are used. And the design and construction of aromatic carboxylate complex is one of the most active areas in the materials researches. However, much less work has been carried out to investigate coordination polymers of 5-(isonicotinamido)isophthalic acid^[9-12]. The introduction of one amide-

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pyridine group to isophthalic acid will contribute to rich hydrogen bonds and construct the architecture of supramolecular structure. Compared with the transition metal coordination polymers, lanthanide coordination polymers were less investigated.

In order to continue our studies on the lanthanide complexes, we have chosen 5-(isonicotinamido) isophthalic acid as ligand and investigated its reaction with $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. We report herein the synthesis, crystal structure and property of the novel 2D bilayer $\text{Eu}(\text{III})$ complex, $[\text{Eu}(\text{L})(\text{HL}) \cdot 2\text{H}_2\text{O}]_n$ (**1**).

1 Experimental

1.1 Materials and instruments

All the reagents and solvents were used as commercial sources without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. The IR spectra were recorded on Shimadzu FTIR-8700 spectrophotometer using KBr discs. Powder X-ray diffraction (PXRD) patterns were obtained on a Shimadzu XRD-6000 X-ray diffractometer with $\text{Cu } K\alpha$ ($\lambda=0.15418 \text{ nm}$) radiation at room temperature. The luminescent spectra for the solid powdered samples were recorded at room temperature on an Aminco Bowman Series 2 spectrophotometer with xenon arc lamp as the light source. In the measurements of the emission and excitation spectra, the pass width was 4.0 nm. All the measurements were carried out under the same conditions.

1.2 Synthesis of the title complex

The complex was hydrothermal synthesized under

autogenous pressure. A mixture of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.225 g, 0.5 mmol), 5-(isonicotinamido)isophthalic (0.286 g, 1.0 mmol), NaOH (0.041 g, 1.0 mmol) and $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (10 mL, 2:1) was heated in a 25 mL capacity Teflon-lined reaction vessel at 140 °C for 3 d, the reaction mixture was cooled to room temperature over a period of 24 h. The product was collected by filtration, washed with H_2O and air-dried, yield 32%. Molecular formula is $\text{C}_{28}\text{H}_{21}\text{EuN}_4\text{O}_{12}$. Elemental analysis calc(%): C, 44.36; H, 2.77; N, 7.39. Found(%): C, 44.39; H, 2.75; N, 7.32. Main IR bands (cm^{-1}): 3 393 (s), 1 675 (s), 1 606 (m), 1 556 (m), 1 528 (m), 1 499 (w), 1 425 (m), 1 383 (s), 1 324 (m), 1 068 (m), 790 (m), 674 (w), 594 (w).

1.3 X-ray crystallography

A colorless block crystal with dimension of 0.20 mm×0.14 mm×0.10 mm was selected for the measurement. The diffraction data were collected at 296(2) K on a Bruker Smart Apex II CCD diffractometer equipped with a graphite-monochromatized $\text{Mo } K\alpha$ radiation ($\lambda=0.071073 \text{ nm}$). A total of 13 767 reflections were collected in the range of $1.68^\circ \leq \theta \leq 25.49^\circ$ by using an ω -scan mode, of which 5 016 were unique and used in the succeeding structure calculations. The structure was solved by direct methods and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. All calculations were performed with SHELXTL-2000 package. Crystal data and structure refinement parameters are listed in Table 1.

CCDC: 826595.

Table 1 Crystal data and structure parameters for the title complex

Empirical formula	$\text{C}_{28}\text{H}_{21}\text{N}_4\text{EuO}_{12}$	Z	4
Formula weight	757.45	Absorption coefficient / mm^{-1}	2.396
Temperature / K	296(2)	$F(000)$	1 504
Crystal system	Monoclinic	Crystal size / mm	0.20×0.14×0.10
Space group	$P2_1/c$	$\theta / (^\circ)$	1.68 to 25.49
a / nm	1.344 02(18)	Limiting indices	$-16 \leq h \leq 15, -16 \leq k \leq 16, -19 \leq l \leq 16$
b / nm	1.377 50(18)	Reflections collected / unique (R_{int})	13 767 (0.051 4)
c / nm	1.623 07(15)	Data / restraints / parameters	5 016 / 0 / 406
$\beta / (^\circ)$	115.820(8)	Goodness of fit on F^2	1.044
V / nm^3	2.704 9(6)	final R indices ($I > 2\sigma(I)$)	$R_1=0.032 2, wR_2=0.089 1$
$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.86	Largest diff. peak and hole / ($\text{e}\cdot\text{nm}^{-3}$)	1 220 and -679

Finally, the 2D bilayers packed together through N-H \cdots O and O-H \cdots O hydrogen bonding interactions (Table 3) to generate 3D framework, and these hydrogen

bonds also exist in the crystal packing diagram, which further consolidate the structure.

Table 3 Parameters of hydrogen bonds for the complex 1

D-H \cdots A	$d(\text{D-H}) / \text{nm}$	$d(\text{H-A}) / \text{nm}$	$d(\text{D-A}) / \text{nm}$	$\angle \text{D-H-A} / (^\circ)$
N(1)-H(1) \cdots O(1W) ^D	0.086	0.206	0.284 6(5)	151
O(1W)-H(1WA) \cdots O(9) ^E	0.085	0.188	0.273 3(4)	177
N(2)-H(2) \cdots O(2) ^F	0.089	0.185	0.272 4(4)	171
O(1W)-H(1WB) \cdots O(10) ^F	0.085	0.200	0.284 3(4)	171
O(2W)-H(2WA) \cdots O(10) ^G	0.085	0.251	0.312 3(5)	129
O(2W)-H(2WA) \cdots O(4) ^H	0.085	0.236	0.292 3(5)	125
N(3)-H(3A) \cdots O(2W) ^I	0.086	0.215	0.295 3(5)	156
O(2W)-H(2WB) \cdots O(1) ^J	0.085	0.210	0.295 5(4)	178

Symmetry code: ^D $x, 1/2-y, 1/2+z$; ^E $-1+x, y, -1+z$; ^F $-1+x, 1/2-y, -1/2+z$; ^G $-1+x, 1+y, z$; ^H $1-x, 1/2+y, 3/2-z$;

^I $2-x, -1/2+y, 3/2-z$; ^J $-x, 1-y, 1-z$.

2.2 Powder X-ray diffraction, thermogravimetric analyses and photoluminescent property

PXRD was used to check the purity of **1**. The results show that all the peaks displayed in the measured patterns at room temperature closely match those in the simulated patterns generated from single-crystal diffraction data, indicating single phases of **1** is formed, as shown in Fig.3.

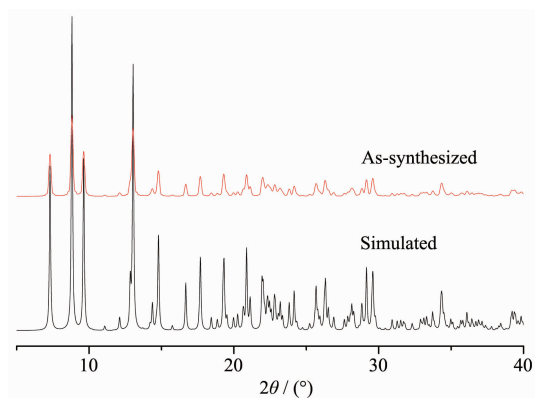


Fig.3 XRD patterns of complex 1

The results of thermogravimetric (TG) analyses indicate that complex **1** loses its noncoordinated water molecules in the 20~160 °C temperature range. The weight loss (found) of 4.65% is consistent with that calculated (4.75%). After the loss of the H₂O molecules, the 2D network is stable up to 335 °C, followed by another weight loss after that temperature.

On the other hand, complex **1** emits strong red

fluorescence under ultraviolet light, therefore, the solid-state visible luminescent property of **1** was investigated at room temperature. Complex **1** displays red luminescence (Fig.4) upon excitation at 362 nm, the emissions at 595, 614, 650 and 692 nm are attributed to the characteristic emissions of $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ transitions of the Eu(III) ion [13-14]. The $^5D_0 \rightarrow ^7F_1$ transition is a magnetic dipole transition, and its intensity varies with the crystal field strength acting on Eu(III) ions. Moreover, the $^5D_0 \rightarrow ^7F_2$ transition is an electric dipole transition and is extremely sensitive to chemical bonds in the vicinity of Eu(III) ion. The intensity ratio $I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)$ is equal to *ca.* 5.2, which also suggests the noncentrosymmetric coordination environment of the Eu(III) ions in **1** [15-16].

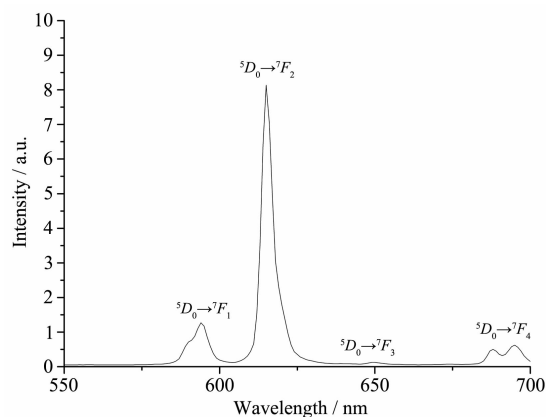


Fig.4 Photoluminescence spectra of complex 1 in the solid state at room temperature

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