

## 5-异烟酰胺基异酞酸构筑的钕化合物的合成、晶体结构和荧光性质

陈满生 许金生\* 邓奕芳 张春华\* 邝代治 聂 雪

(功能金属有机材料湖南省普通高等学校重点实验室, 衡阳师范学院化学与材料科学系, 衡阳 421008)

**摘要:** 由水热法合成了钕化合物 $[\text{Nd}(\text{HINAIP})(\text{INAIP})(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$  (**1**), ( $\text{H}_2\text{INAIP}$ =5-异烟酰胺基异酞酸), 并进行了元素分析、IR、TG 及 X-射线衍射法表征。晶体结构表明: 配合物 **1** 属于三斜晶系,  $P\bar{1}$  空间群。配合物 **1** 是由桥联配体 5-异烟酰胺基异酞酸的羧基氧连接成二维层, 此二维结构被氢键拓展成三维超分子结构。荧光光谱测试结果表明配合物 **1** 具有典型稀土钕的近红外荧光特征。

**关键词:** 5-异烟酰胺基异酞酸; 晶体结构; 水热合成; 荧光

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## Hydrothermal Synthesis, Crystal Structure and Photoluminescent Property of Nd(III) Complex Constructed from 5-(Isonicotinamido)-isophthalic Acid

CHEN Man-Sheng XU Jin-Sheng\* DENG Yi-Fang ZHANG Chun-Hua\* KUANG Dai-Zhi NIE Xue

(Key Laboratory of Functional Organometallic Materials of Hengyang Normal University,

College of Hunan Province, Department of chemistry and Materials Science, Hengyang, Hunan 421008, China)

**Abstract:** The complex  $[\text{Nd}(\text{HINAIP})(\text{INAIP})(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$  was obtained by hydrothermal assembly of Nd(III) salt with a 5-(isonicotinamido)isophthalic acid ( $\text{H}_2\text{INAIP}$ ) and its crystal structure was determined by X-ray single-crystal diffraction. It is of triclinic,  $P\bar{1}$  space group. Single-crystal X-ray diffraction analysis revealed that the  $\text{HINAIP}^-$  and  $\text{INAIP}^{2-}$  ligands connect Nd(III)-carboxylate chains to form 2D layers in complex **1**. Finally, It was extended to 3D supramolecular structures by H-bonding interactions. The complex was characterized by TG, IR, UV and near IR fluorescence spectra. CCDC: 958122.

**Key words:** 5-(isonicotinamido)isophthalic acid; crystal structure; hydrothermal synthesis; photoluminescence

## 0 Introduction

Coordination polymers using carboxylic acids as ligands have been widely studied in the past decades<sup>[1-3]</sup> because of carboxylates' diverse coordination styles as well as the carboxylic acids based coordination polymers' rigid structures. In recent years, much attention has been drawn on the construction of

lanthanide coordination polymers due to their unique optical, magnetic and catalytic applications<sup>[4-8]</sup>. As we known, lanthanide ions tend to coordinate with O-donor ligands in high and flexible coordination numbers (CNs), which can usually vary from eight to twelve. However, many factors can influence the synthesis of lanthanide coordination polymers, such as the character of ligand, the coordination geometry of

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\*通讯联系人。E-mail: hynuxjs@163.com, zhangchunhua668@163.com; 会员登记号: S06N7223M1009。

lanthanide ions, and the reaction conditions.

Of all these factors, the choice of ligands is mostly important for constructing the structures<sup>[9-10]</sup>. According to the above considerations, we have recently designed and synthesized a novel ligand: 5-(isonicotinamido)isophthalic acid namely, (H<sub>2</sub>INAIP)<sup>[11-15]</sup>. In order to further investigate the influence of organic ligands on the coordination architectures and related properties, reactions of with 5-(isonicotinamido)isophthalic acid as well as lanthanide (Nd) were carried out. Herein, we report the syntheses, crystal structures and properties of the coordination polymers, namely [Nd(HINAIP)(INAIP)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>·nH<sub>2</sub>O (**1**).

## 1 Experimental

### 1.1 Materials and instruments

The reagents were used as commercial sources without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were recorded on Bruker Vector22 FT-IR spectrophotometer using KBr discs. Thermogravimetric analyses (TGA) were performed on a TGA V5.1A Dupont 2100 instrument heating from room temperature to 700 °C under N<sub>2</sub> with a heating rate of 20 °C·min<sup>-1</sup>. Luminescence spectra and lifetime were recorded at 77 K on an Edinburgh FLS920 phosphorimeter. UV-Vis spectra were recorded at room temperature on a Shimadzu UV-160A spectrophotometer in barium sulfate based paint.

### 1.2 Synthesis of the complex 1

The compound was hydrothermal synthesized

under autogenous pressure. A mixture of Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.221 g, 0.5 mmol), 5-(isonicotinamido)isophthalic (0.287 g, 1.0 mmol), NaOH (0.021 g, 0.5 mmol) and H<sub>2</sub>O/DMF (9 mL, 2:1) was heated in a 16 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<sub>2</sub>O and air-dried, Yields 34% . Molecular formula is C<sub>28</sub>H<sub>23</sub>NdN<sub>4</sub>O<sub>13</sub>. Elemental Analysis, Calcd.(%): C, 43.76; H, 2.99; N, 7.29. Found (%): C, 43.79; H, 2.95; N, 7.32. Main IR bands (cm<sup>-1</sup>): 3 393 (s), 1 695 (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

The X-ray diffraction measurement for **1** were performed on the Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$ =0.071 073 nm) at 293(2) K. The data were integrated by using the SAINT program<sup>[16]</sup>, which also did the intensity corrections for Lorentz and polarization effect. An empirical absorption correction was applied using the SADABS program<sup>[17]</sup>. The structures were solved by direct methods using the program SHELXS-97 and all the non-hydrogen atoms were refined anisotropically on  $F^2$  by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package<sup>[18-19]</sup>. Crystal data and structure refinement parameters are listed in Table 1. The selected bond lengths and bond angles are given in Table 2.

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Table 1 Crystal data and structure parameters for complex 1

Empirical formula	C <sub>28</sub> H <sub>23</sub> N <sub>4</sub> NdO <sub>13</sub>	$V / \text{nm}^3$	1.439 45(18)
Formula weight	767.74	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.771
Temperature / K	293(2)	$Z$	2
Crystal system	Triclinic	Absorption coefficient / mm <sup>-1</sup>	1.881
Space group	$P\bar{1}$	$F(000)$	766
$a / \text{nm}$	0.967 27(5)	$\theta / (^\circ)$	2.36 to 25.03
$b / \text{nm}$	1.064 51(7)	Reflections collected / unique	7 227 ( $R_{\text{int}}$ =0.093 7)
$c / \text{nm}$	1.583 32(15)	Data / restraints / parameters	5 000 / 1 / 409
$\alpha / (^\circ)$	81.783(2)	Goodness of fit on $F^2$	1.023
$\beta / (^\circ)$	78.757 0(10)	final $R$ indices ( $I > 2\sigma(I)$ )	$R_1$ =0.043 2, $wR_2$ =0.118 4
$\gamma / (^\circ)$	64.450(2)	Largest diff. peak and hole / ( $\text{e} \cdot \text{nm}^{-3}$ )	1 707 and -1 605

**Table 2** Selected bond lengths (nm) and bond angle ( $^{\circ}$ )

Nd(1)-O(2)	0.248 3(3)	Nd(1)-O(4A)	0.251 0(3)	Nd(1)-O(1W)	0.259 5(3)
Nd(1)-O(7D)	0.247 6(3)	Nd(1)-O(6)	0.252 5(3)	Nd(1)-O(3C)	0.260 3(3)
Nd(1)-O(1B)	0.248 2(3)	Nd(1)-O(2W)	0.256 9(4)	Nd(1)-O(4C)	0.289 8(3)
O(1B)-Nd(1)-O(1W)	66.28(11)	O(1B)-Nd(1)-O(4C)	139.90(10)	O(4A)-Nd(1)-O(4C)	80.04(11)
O(4A)-Nd(1)-O(1W)	81.76(11)	O(6)-Nd(1)-O(3C)	103.67(11)	O(1B)-Nd(1)-O(4C)	139.90(10)
O(2W)-Nd(1)-O(1W)	124.88(13)	O(4A)-Nd(1)-O(3C)	117.36(11)	O(2)-Nd(1)-O(4C)	116.73(10)
O(7D)-Nd(1)-O(3C)	71.84(14)	O(4C)-Nd(1)-O(3C)	46.48(10)	O(4C)-Nd(1)-O(7D)	82.12(10)
O(2)-Nd(1)-O(3C)	70.91(10)	O(4C)-Nd(1)-O(1W)	150.05(10)	O(1B)-Nd(1)-O(3C)	126.96(12)
O(1B)-Nd(1)-O(3C)	142.71(12)	O(4C)-Nd(1)-O(2W)	83.18(12)	O(2W)-Nd(1)-O(3C)	71.14(15)

A:  $1+x, -1+y, z$ ; B:  $-x, 1-y, -z$ ; C:  $-x, 2-y, -z$ ; D:  $1-x, 1-y, -z$ .

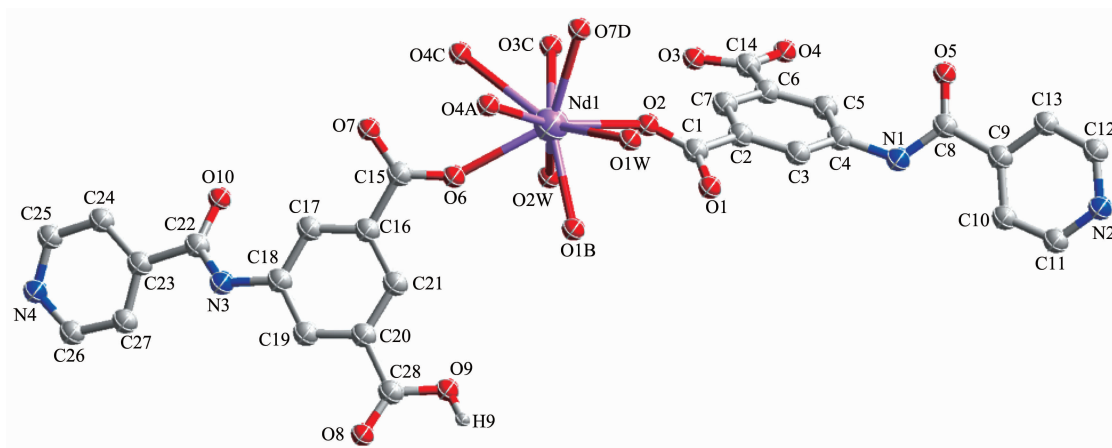
## 2 Results and discussion

### 2.1 Structure description

The results of structural analysis revealed that complex **1** has a 2D layer structure. It is noticed that in contrast to the complete deprotonation of carboxylate groups of H<sub>2</sub>INAIP to give INAIP<sup>2-</sup>, the ligand H<sub>2</sub>INAIP is only partial deprotonated in **1** to HINAIP<sup>-</sup> as confirmed by crystallographic and IR spectral data (a strong IR band from -COOH appeared at 1 695 cm<sup>-1</sup>, see experimental section). The asymmetric unit of **1** contains one Nd(III) atom, one INAIP<sup>2-</sup> ligand, one HINAIP<sup>-</sup> ligand, two coordinated and one non-coordinated water molecules. As shown in Fig.1, the Nd(III) ion is nine-coordinated and surrounded by five oxygen atoms from four INAIP<sup>2-</sup> ligands, two oxygen atoms from two HINAIP<sup>-</sup> ligands, and two terminal oxygen atoms from two aqua ligands to form a distorted tricapped trigonal prism. The coordination

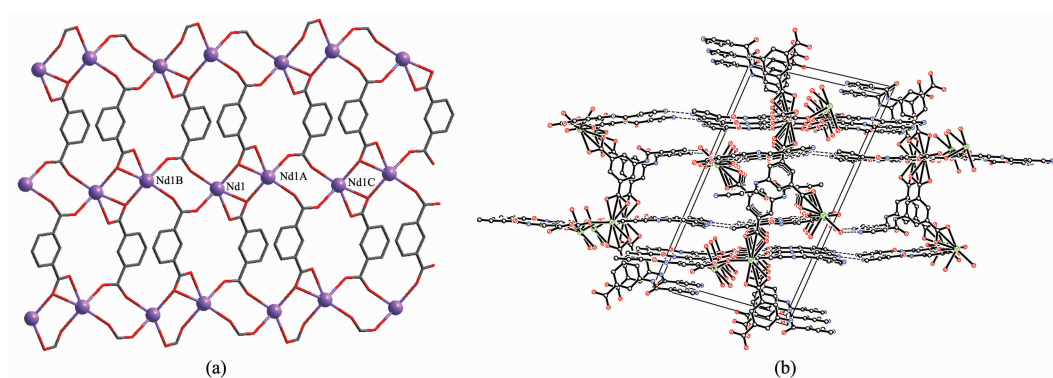
environment of Nd(III) in complex **1** is different from that of  $[\{\text{Eu}(\text{L})(\text{HL})\} \cdot 2\text{H}_2\text{O}]_n^{[20]}$ , in which the Eu<sup>3+</sup> ions have eight coordination with distorted bicapped trigonal prismatic geometry. In **1**, the Nd-O (carboxylate) bond distances range from 0.248 2(3) to 0.289 8(3) nm, and those of Nd-O(aqua) bonds are 0.256 9(4) and 0.259 5(3) nm. In complex **1**, the HINAIP<sup>-</sup> anions adopt  $\mu_2\text{-}\eta^1\text{:}\eta^1$  bridging coordination mode, while two carboxylate groups of each INAIP<sup>2-</sup> ligand have different coordination modes, one is  $\mu_2\text{-}\eta^1\text{:}\eta^1$  bridging and the other one acts as  $\mu_2\text{-}\eta^2\text{:}\eta^1$ -bridging coordination mode. Such connectivity repeats infinitely to give the 2D layer network as depicted in Fig.2.

On the other hand, the uncoordinated isonicotinamido groups nitrogen atoms and carboxylate oxygen atoms provide the hydrogen-bonding donor and acceptor, respectively, resulting in the complex being extended into a 3D architecture through supramole-



All water molecules are omitted for clarity; Symmetry code: A:  $1+x, -1+y, z$ ; B:  $-x, 1-y, -z$ ; C:  $-x, 2-y, -z$ ; D:  $1-x, 1-y, -z$

Fig.1 Molecular structure of complex **1**



Symmetry code: A:  $1+x, -1+y, z$ ; B:  $-x, 1-y, -z$ ; C:  $-x, 2-y, -z$

Fig.2 (a) 2D-Nd layer structure linked by  $\text{INAIP}^{2-}$  and (b) 3D packing structure of **1**

Table 3 Parameters of hydrogen bonds for the complex **1**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
N(1)-H(1)...O(3)E	0.086	0.249	0.332 0(6)	164
O(1W)-H(1WA)...O(3W)F	0.085	0.209	0.274 5(7)	134
N(3)-H(3A)...O(8)G	0.086	0.214	0.296 6(7)	162
O(2W)-H(2WA)...N(4)H	0.085	0.192	0.269 8(6)	152
O(3W)-H(3WA)...O(5)I	0.085	0.198	0.283 3(10)	175
O(3W)-H(3WB)...O(10)H	0.085	0.195	0.227 67(9)	161
O(9)-H(9)...N(2)J	0.085	0.178	0.259 4(8)	159

Symmetry code: E:  $-1-x, 1+y, z$ ; F:  $x, y, -1+z$ ; G:  $1-x, -y, 1-z$ ; H:  $1-x, 1-y, 1-z$ ; I:  $1+x, -1+y, 1+z$ ; J:  $-1-x, 1-y, -z$ .

cular interactions (Fig.2). The detailed data of hydrogen bonds for complex **1** are shown in Table 3.

## 2.2 IR and thermal gravimetric analyses

The infrared spectrum of the complex has been recorded and some important assignments are shown above. No strong IR band from  $-\text{COOH}$  appeared at nearly  $1\,700\text{ cm}^{-1}$  ( $1\,695\text{ cm}^{-1}$ ), indicating that the coordinated carboxylate groups are not all deprotonated, and the band at  $3\,415\text{ cm}^{-1}$ , due to the  $\nu(\text{O-H})$  absorptions of water molecules. The characteristic bands at  $1\,606$  and  $1\,556\text{ cm}^{-1}$  should be assigned to the asymmetric and symmetric vibration of carboxylate groups of the ligand, respectively. These IR results are coincident with the crystallographic structural analyses. On the other hand, thermal gravimetric analyses (TGA) were performed to verify the thermal stability of the complexes. Complex **1** lost a weight of 7.11% was observed in the temperature range of  $25\sim 165\text{ }^\circ\text{C}$ , which corresponds to the release of two coordinated water molecules and one free water molecule (Calcd. 7.03%), and then the residue decomposed upon

further heating at about  $305\text{ }^\circ\text{C}$ . Therefore, the results indicate that the complex has high stability (Fig.3).

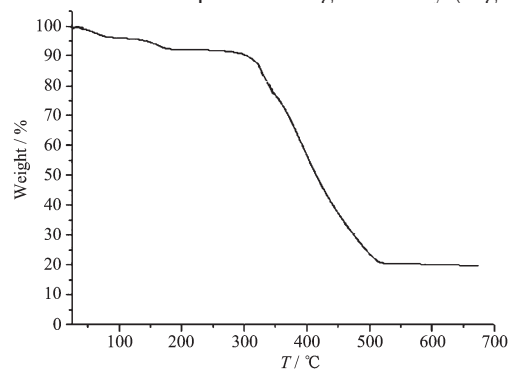


Fig.3 TGA curve of complex **1**

## 2.3 Luminescent property and UV-Vis spectra

The fluorescence spectrum with solid sample for the complex was determined in near-infrared (NIR) region with the excitation of UV-rays at 77 K, the emission spectra was shown in Fig.4. The emission bands of **1** at around 890 nm are tentatively assigned to be  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ , at around 1 062 nm to be  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  and at 1 330 nm to be  ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$  transitions (Fig.4). Some crystal-field fine structures can be observed,

which indicated that the  $\text{Nd}^{3+}$  ions occupied the well-defined crystallographic sites in the compound. Among the three emission bands of the Nd complex, the transition band at 1 062 nm has the strongest emission intensity, which is potentially applicable for laser emission. On the other hand, the UV-Vis absorption spectra of complex **1** were investigated in the solid state. As shown in Fig.5, it could be found that the B band of  $\text{INAIP}^{2-}$  ligand which is attributed to the  $\pi-\pi^*$  transition in 235 nm. The most intense absorption at 265 nm could be assigned to the K band between the  $\text{INAIP}^{2-}$  ligands and the central  $\text{Nd}^{3+}$  ions<sup>[21]</sup>.

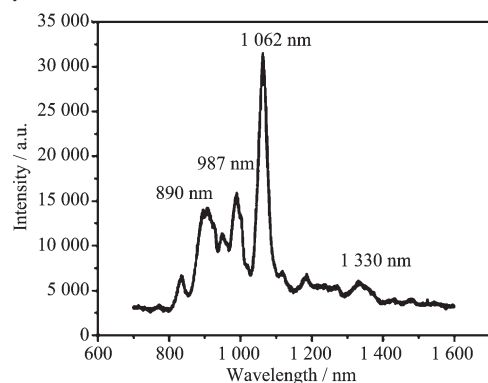


Fig.4 Emission spectrum of the complex with the excitation at 315 nm at 77 K

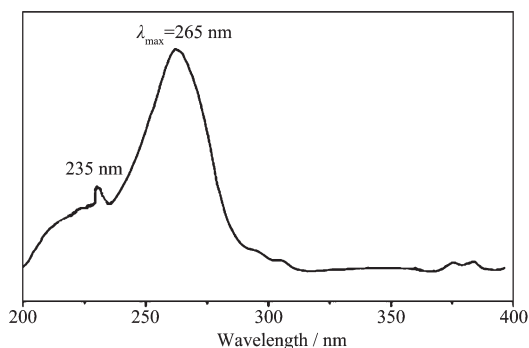


Fig.5 UV-Vis absorption spectroscopy of **1** in solid state

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