

稀土-异烟酰肼席夫碱配合物的设计、合成与结构

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摘要: 由异烟酰肼和 2-吡啶甲醛合成了席夫碱配体 HL, 并和稀土离子合成组装得一系列稀土配合物。用 X-射线单晶衍射对配合物的结构进行了测定。通过荧光测试发现 La 配合物有荧光, 而 Eu, Dy 则使配体的荧光淬灭。

关键词: 稀土; 荧光; 席夫碱; 双功能配体

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Lanthanide-isonicotinic Carboxhydrazone Schiff Base Complex: Design, Synthesis and Luminescent Property

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Abstract: A series of the lanthanide complexes were synthesized by the reaction of Ln^{3+} ($\text{Ln}=\text{La}$, Eu and Dy) with the Schiff base HL which was prepared by the reaction of isonicotinic carboxhydrazone with 2-carboxyaldhyde pyridine. The complexes were structurally characterized by X-ray diffraction single-crystal structure analyses. The luminescence of the ligand and the lanthanide complexes were also determined. CCDC: 683448, **1**; 683449, **2**; 683450, **3**.

Key words: lanthanide; luminescence; schiff base; bi-function ligand

0 Introduction

The design and syntheses of lanthanide complexes with predictable structures are of great interesting in supramolecular chemistry and materials chemistry due to their unique properties such as luminescence and catalysis^[1-3]. But the Ln ions' tendency toward high and variable coordination numbers with low stereochemical preference makes the Ln ions' selective introduction into a highly ordered structure more difficult^[4-7]. For example, the assembly of extended hetero-Ln-TM metal-organic frameworks (MOFs) structures is still a challenge^[8-10]. Usually the construction of Ln-TM hete-

ronuclear supramolecular complexes was achieved by one-step self-assembly method or started from a TM-containing metalloligand. However, this often resulted in the low ordered structures^[11,12].

On the other hand, isonicotinic acid (HIN) was usually chosen as the multifunctional bridging ligand, because of: (1) It is a rigid ligand with oxygen and nitrogen donors on opposite sides, enabling the IN ligand to act as a linear bridge; (2) The carboxyl group may induce the oxophilic lanthanide ions to undergo hydroxo lanthanide cluster aggregation, the nitrogen atoms can coordinate to TM ions, and thus extended solids containing hydroxo lanthanide cluster cores and

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TM ions might be obtained^[13]. Here we reported a series of lanthanide-based metalloligands building from the isonicotinic acid derivatives, which comprise of a tridentate chelating site that can limit the number and orientation of the ligands coordinating to the lanthanide center, so that the topology of the final complex can be controlled, and a N-donor coordinating sites, leaving as a possible binding group to combine the TM ions. This isonicotinic carboxyhydrazone Schiff base ligand is a promising bifunctional building block to construct high ordered Lanthanide based metal-organic frameworks with interesting function. The luminescent properties of these complexes are also investigated.

1 Experimental

1.1 Materials and instrumentation

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Elemental analyses (C, H and N) were carried out with a Perkin-Elmer 2400 Analyzer. IR spectra were recorded on a VECTOR 22 Bruker spectrophotometer with KBr pellets in the range of 4 000~400 cm^{-1} . ^1H NMR spectra were performed on DRX500 Bruker spectrometer at 298 K with TMS as an internal reference. Fluorescence emission spectra were obtained using AB-series2 luminescence spectrometer.

1.2 Synthesis of the ligand HL

5 drops of acetic acid were added to a methanol (25 mL) solution of 2-pyridinecarboxaldehyde (0.21 g, 2 mmol) with isonicotinic carboxyhydrazide (0.27 g, 2 mmol). After refluxed for 3 h, a pale yellow precipitate was collected by filtration, washed with methanol-ether, and dried in vacuo. Yield: 0.726 g, 72.6%. ^1H NMR (in d^6 -DMSO): 12.27 (s, 1H, -NH), 8.88 (d, 1H, py), 8.80(d, 2H, py1), 8.63(d, 1H, py2), 8.51(s, 1H, -CH=N), 8.18(t, 1H, py2), 7.82 (d, 2H, py1), 7.51 (t, 1H, py2). Element analysis of $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}$ (226.16): Calc.(%): C 63.71, H 4.46, N 24.76; Found(%): C, 63.55; H, 4.63; N, 24.70.

1.3 Synthesis of the complex 1~3

1.3.1 Preparation of compound $\text{LaL}_2(\text{OH})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ (1)

The solution of $\text{LaCl}_3 \cdot \text{H}_2\text{O}$ (0.035 g, 0.1 mmol) in 15 mL methanol was added to a suspension of HL

(0.045 g, 0.2 mmol) in 10 mL methanol. The mixture was stirred at room temperature for 20 mins to get a clear solution. After standing at room temperature several days, the yellow block crystals suitable for X-ray diffraction were obtained (0.042 g, 52.5%). IR (solid KBr pellet, cm^{-1}): 3 415.27(m), 2 364.20(m), 1 626.97(s), 1 551.55 (s), 1 311.44 (s), 1 083.93 (m), 694.16(w). Element analysis of $\text{La}(\text{C}_{12}\text{H}_9\text{N}_4\text{O})_2(\text{OH})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ (696.45): Calc.(%): C 41.39, H 4.20, N 16.09; Found(%): C, 41.13; H, 4.17; N, 16.27.

1.3.2 Preparation of compound $\text{EuL}_2(\text{OH})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ (2)

The compound was obtained by the same above procedure by displace $\text{LaCl}_3 \cdot \text{H}_2\text{O}$ by $\text{EuCl}_3 \cdot \text{H}_2\text{O}$. IR (solid KBr pellet, cm^{-1}): 3 417.75 (m), 2 362.73(m), 1 595.24(m), 1 506.40(s), 1 375.86(s), 1 050.08(s), 703.75 (w). Element analysis of $\text{Eu}(\text{C}_{12}\text{H}_9\text{N}_4\text{O})_2(\text{OH})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ (691.49): Calc.(%): C 41.69, H 3.94, N 16.21; Found(%): C 41.56, H 3.79, N 16.48.

1.3.3 Preparation of compound $\text{DyL}_2(\text{OH})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ (3)

The compound was obtained by the same above procedure by displace $\text{LaCl}_3 \cdot \text{H}_2\text{O}$ by $\text{DyCl}_3 \cdot \text{H}_2\text{O}$. IR (solid KBr pellet, cm^{-1}): 3 405.76 (m), 2 841.78(m), 1 624.82(s), 1 368.26(s), 1 047.92(m), 1 083.93(m), 701.97 (w). Element analysis of $\text{Dy}(\text{C}_{12}\text{H}_9\text{N}_4\text{O})_2(\text{OH})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ (665.99): Calc.(%): C 41.06, H 3.88, N 15.96; Found(%): C 40.82, H 3.80, N 16.12.

1.4 Crystal structure determination

Suitable crystals were selected for single-crystal X-ray diffraction structural analysis and the data were collected on a Siemens SMART APEX CCD diffractometer with graphite-monochromatized $\text{Mo K}\alpha$ radiation ($\lambda=0.071\,073\,\text{nm}$), using the SMART and SAINT programs^[14]. 45 frames of data were collected at 298 K with an oscillation range of 1 deg/frame and an exposure time of 10 s/frame. Indexing and unit cell refinement were based on all observed reflections from those 45 frames. The structures were solved by direct method and refined on F^2 by full-matrix least-squares methods with SHELXTL version 5.1^[15]. Anisotropic thermal parameters were refined for non-hydrogen atoms. Hydrogen atoms were localized in their calculation positions and

refined by using the riding model. Crystallographic data and parameters for data collection and refinement of the

compounds are summarized in Table 1.

CCDC: 683448, **1**; 683449, **2**; 683450, **3**.

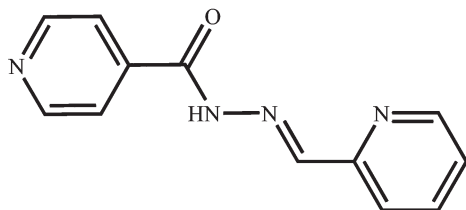
Table 1 Crystallography data of complex **1**, **2** and **3**

Compound	1	2	3
Molecular formula	C ₂₄ H ₂₉ LaN ₈ O ₈	C ₂₄ H ₂₇ EuN ₈ O ₇	C ₂₄ H ₂₇ DyN ₈ O ₇
<i>M_r</i>	696.46	691.5	702.04
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	<i>P2₁/n</i>	<i>Pbcn</i>	<i>Pbcn</i>
<i>a</i> / nm	1.105 3(2)	2.553 6(2)	2.535 0(2)
<i>b</i> / nm	2.070 5(3)	1.365 3(1)	1.369 8(1)
<i>c</i> / nm	1.543 4(2)	1.797 1(2)	1.789 7(2)
β / (°)	99.936(2)		
<i>V</i> / nm ³	3.479 0(8)	6.265 1(9)	6.214 5(9)
<i>Z</i>	4	8	8
<i>T</i> / K	291(2)	291(2)	291(2)
<i>D</i> _{calcd} / (Mg·m ⁻³)	1.33	1.466	1.501
μ / mm ⁻¹	1.277	2.053	2.456
<i>F</i> (000)	1 400	2 768	2 792
No. refs measured	18 378	32 144	33 563
No. unique refs (<i>R</i> _{int})	6 805 (0.041 5)	6 153 (0.071 0)	6 113 (0.076 5)
No. observed. refs [<i>I</i> ≥ 2σ(<i>I</i>)]	4 821	4 184	4 152
<i>R</i> ₁	0.049 1	0.059 7	0.050 9
<i>wR</i> ₂	0.111 5	0.126 0	0.099 9
Goodness of fit	1.091	1.085	1.083

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

2 Results and discussion

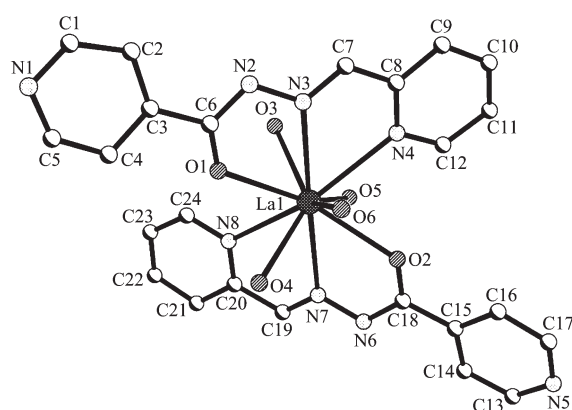
The Schiff base HL (Scheme 1) was prepared by the reaction of isonicotinic carboxhydrazide with 2-carboxydehyde pyridine. It can, in principle exhibit enamine-ketone or imine-enol tautomerism, since it contains a -NH-C=O functional group. ¹H NMR shows the signal on 12.27 ppm, revealing enamine-ketone form in the solution. Such chelating site with carbonyl oxygen atoms, pyridine and imine nitrogen atoms was employed successfully to assemble a series of lanthanide-based octahedral cages [16]. It is illustrated that the better control of the lanthanide ions assembling



Scheme 1 Ligand HL

into ordered architecture can be achieved through the use of highly predisposed ligands.

Slowly evaporating the methanol solution of HL mixing with LnCl₃ (Ln=La, Eu and Dy, respectively) offered the crystals suitable for X-ray structure analysis. Single crystal analysis reveals the formation of complex LaL₂(OH)(H₂O)_n·H₂O (*n*=3 for La, *n*=2 for Eu and Dy) (Fig.1,2). The La complex crystallized in the monoclinic space group *P2₁/n* with one coordination specie and two solvent water molecules in the asymmetry unit. The La atom is coordinated with two ligands, three water molecules and one hydroxyl ion. The metal centre comprises its ten-coordinated configuration by the carbonyl oxygen atoms, pyridine nitrogen atoms, and imine nitrogen atoms from two ligand species in a chelating fashion, in addition to four oxygen atoms from three water molecules and one hydroxyl speices. Both of the ligands are almost planar and coordinated to the La centre in a mer configuration with the dihedral angle of



Hydrogen atoms and lattice solvent molecule H_2O are omitted for clarity; Selected bond lengths (nm) and angles ($^\circ$):

La(1)-O(5) 0.255 7(3),	La(1)-O(1) 0.255 9(3),
La(1)-O(4) 0.257 2(3),	La(1)-O(6) 0.257 7(3),
La(1)-O(3) 0.259 1(3),	La(1)-O(2) 0.260 3(4),
La(1)-N(7) 0.272 3(4),	La(1)-N(3) 0.272 8(3),
La(1)-N(4) 0.275 6(3),	La(1)-N(8) 0.280 8(3)
N(7)-La(1)-N(3) 177.5(2),	N(7)-La(1)-N(4) 120.9(2),
N(3)-La(1)-N(4) 57.9(2),	N(7)-La(1)-N(8) 59.0(2),
N(3)-La(1)-N(8) 123.3(1),	N(4)-La(1)-N(8) 148.8(1)

Fig.1 ORTEP drawing of molecular structure of $\text{LaL}_2(\text{OH})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ with the atomic partially numbering scheme

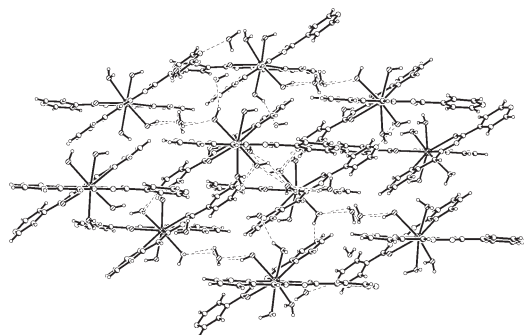
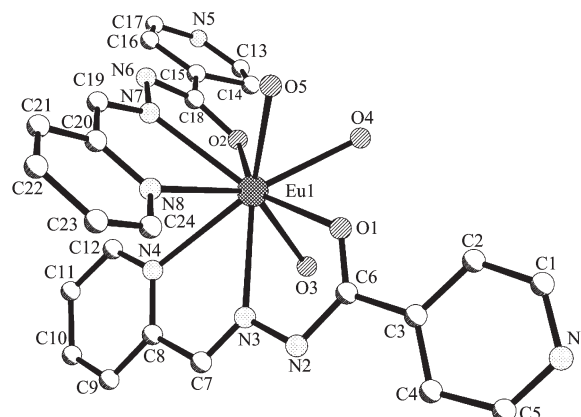


Fig.2 Packing diagram of complex **1** (viewed down the b axis) two coordination plane being 45° . The La-N and La-O distances were in the range of 0.273~0.281 nm and 0.256~0.260 nm, respectively. The C-O (0.124 nm) and C-N (0.132 nm) bond distances of the acylhydrazone groups are intermediate between formal single and double bonds, indicating the loss of the amide protons. The interesting hydrogen bond between coordinated water molecule and the solvent water link the monoclear structure to stack in a 3D network pattern. The Eu and Dy complexes were isomorphous (Fig.3, 4), both crystallized in the orthorhombic space group $Pbcn$ with one coordination specie and two

solvent water molecules in the asymmetry unit. The metal centre is coordinated with two ligands, two water molecules and one hydroxyl ion, comprising a nine-coordinated configuration. There are also interlinked hydrogen bonds between the water molecules, resulting in the formation of a 3D network structure. The N atoms of the pyridine groups in these structures are remained, and are promising to combine the transition metal



Hydrogen atoms and lattice solvent molecule H_2O are omitted for clarity; Selected bond lengths (nm) and angles ($^\circ$):

Eu(1)-O(1) 0.234 8(5),	Eu(1)-O(2) 0.238 1(5),
Eu(1)-O(4) 0.243 4(5),	Eu(1)-O(3) 0.244 3(6),
Eu(1)-O(5) 0.247 0(5),	Eu(1)-N(7) 0.252 7(6),
Eu(1)-N(3) 0.254 8(5),	Eu(1)-N(8) 0.263 5(5),
Eu(1)-N(4) 0.265 7(5)	
N(7)-Eu(1)-N(3) 124.0(2),	N(7)-Eu(1)-N(8) 61.8(2),
N(3)-Eu(1)-N(8) 72.9(2),	N(7)-Eu(1)-N(4) 74.3(2),
N(3)-Eu(1)-N(4) 62.3(2),	N(8)-Eu(1)-N(4) 73.8(2)

Fig.3 ORTEP drawing of molecular structure of $\text{EuL}_2(\text{OH})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$ with the atomic partially numbering scheme

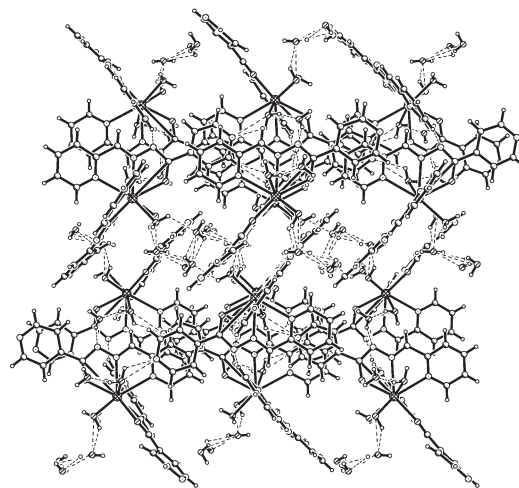
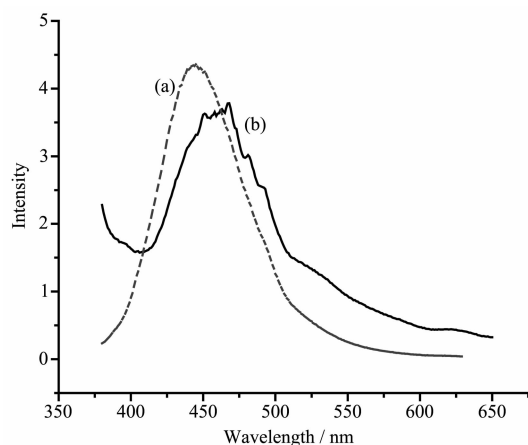


Fig.4 Packing diagram of complex **2** (viewed down the b axis) ions to form ordered coordination framework.

The luminescent properties of the ligand and the lanthanide complexes were also investigated. Solid fluorescent determination showed that the ligand itself exhibited an emission band near 450 nm when exciting at 350 nm. The emission was kept when the ligand coordinated to the La ions and quenched by the Eu and Dy ions, that is probably due to the single electron existing in the latter two ions (Fig.5).



(a) Spectra of ligand HL was recorded at 450 nm with excitation on 350 nm; (b) Spectra of complex **1** was recorded at 450 nm with excitation on 355 nm

Fig.5 Luminescences of ligand HL and complex **1**

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