

吡啶-2,5-二羧酸钐(III)、镝(III)配合物的合成、结构及性质

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摘要: 以 $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、 $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、吡啶-2,5-二羧酸(H_2pydc)为原料,用水热合成法合成了 2 个新的稀土金属配合物 $[\text{Ln}(\text{pydc})_2(\text{H}_2\text{O})_5] \cdot 4\text{H}_2\text{O}$ ($\text{Ln}=\text{Sm}$ (**1**), Dy (**2**)), 单晶结构经 X 单晶衍射仪分析确定,两种配合物的晶系均为单斜晶系, $C2/c$ 空间群。对晶体的性质进行元素分析、热重、红外光谱、荧光等分析。结果表明,配合物 **1** 和 **2** 在常温下表现出稀土离子相应的特征荧光发射。另外,本文对两种配合物进行了热稳定性及动力学分析。

关键词: 稀土; 配合物; 羧酸; 水热合成; 荧光性质

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Synthesis, Structure and Properties of Sm(III) and Dy(III) Complexes with Pyridine-2,5-dicarboxylic Acid

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Abstract: Two new Lanthanide complexes $[\text{Ln}(\text{pydc})_2(\text{H}_2\text{O})_5] \cdot 4\text{H}_2\text{O}$ ($\text{Ln}=\text{Sm}$ (**1**), Dy (**2**)) were obtained by the hydrothermal reactions of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, pyridine-2,5-dicarboxylic acid (H_2pydc) with 1:1 mole ratio. Single-crystal X-ray diffraction analysis reveals that both the crystals belong to monoclinic, space group $C2/c$. The structure and property of complexes have been characterized by elemental analysis, thermal analyses, IR spectra and Fluorescence. The single crystal structures show that the two complexes are isomorphic and have zero-dimensional structures and hydrogen bonds result in three-dimensional supramolecular structures. the coordination number of central ion $\text{Ln}(\text{III})$ is nine. The complex **1** and **2** exhibit intense luminescence in the liquid state at room temperature. CCDC: 869044, **1**; 874032, **2**.

Key words: lanthanide; coordination complex; carboxylic acid; thermal synthesis; fluorescence

At present, because of their unique properties in physical and chemical, Rare earth coordination polymers have shown a wide application prospect in magnetic, catalysis, fluorescence, adsorption and separation application, etc^[1-9]. Therefore, in the process of the design and synthesis of these complexes, the

selection of metal and ligand will have greatly affected to their structure and properties. In the choice of metal, we found that the rare earth elements contribute to the synthesis of novel coordination polymers. In the choice of ligand, because of flexible coordination mode and strong coordination ability,

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some mixed ligands which contain O atoms or N atoms, especially multi-carboxylic acid ligands are often used to synthesize rare earth coordination polymers^[10-13]. Consequently, in the experiment, we choose pyridine-2,5-dicarboxylic acid as ligand, design and assembled two new complexes: [Sm(pydc)₂(H₂O)₅]·4H₂O and [Dy(pydc)₂(H₂O)₅]·4H₂O. Their structure have been measured by single crystal diffraction instrument, physical and chemical properties have been characterized by elemental analysis, thermal analyses, IR spectra and Fluorescence. The experimental results show that the complex **1** and **2** show the corresponding characteristic emission of the rare earth ions at room temperature. In addition, we analyze thermal stability and dynamics of two complexes and get pyrolysis kinetic parameters.

1 Experimental

1.1 General materials and methods

All starting materials in the experiments were obtained from commercial sources and used without further purification. The crystal was determined on a Bruker Smart Apex II CCD diffractometer by using graphite monochromatized Mo K α radiation (λ =0.071 073 nm). Elemental analysis (C, H, N) was performed on a Perkin-Elmer 240C type elemental analyzer. Thermogravimetric analyses data was carried out on a Sweden's TGA/SDTA851^e thermogravimetric analyzer, with a heating rate of 10 °C·min⁻¹ from 25~800 °C in nitrogen atmosphere. The infrared spectra were recorded on a FTTR-8400 spectrometer using KBr pellets. The emission spectra were recorded on an America SLM-48000DSCF spectrometer.

1.2 Syntheses

A mixture of Ln(NO₃)₃·6H₂O (0.2 mmol, 0.044 4 g), glutaric acid (0.2 mmol, 0.013 1 g) and pyridine-2,5-dicarboxylic acid (0.2 mmol, 0.016 6 mg) in 12 mL distilled water was moved in a 25 mL poly (tetrafluoroethylene)-lined stainless steel autoclave, sealed and heated at 180 °C for 5 d under autogenous pressure, then cooled to room temperature at a rate of 5 °C·h⁻¹, light-yellow block crystals for **1** and colourless block crystals for **2** were yielded. Yield is 0.033 g

(52%) and 0.045 g (69%) respectively. Anal. Calcd. (%) for C₁₄H₁₄N₂O₁₇Sm (**1**): C, 26.14; H, 2.18; N, 4.36. Found (%): C, 26.10; H, 2.19; N, 4.34. IR (KBr disc, cm⁻¹): 3 384s, 1 719m, 1 639s, 1 575s, 1 483w, 1 391s, 1 374s, 1 290m, 1 121w, 1 035w, 848w, 793m, 749m, 691m, 569m, 519m. Anal. Calcd.(%) for C₁₄H₁₄N₂O₁₇Dy (**2**): C, 25.65; H, 2.14; N, 4.28. Found(%): C, 25.63; H, 2.16; N, 4.29. IR (KBr disc, cm⁻¹): 3 385s, 1 718m, 1 637s, 1 575s, 1 482w, 1 393s, 1 375s, 1 291m, 1 122 w, 1032w, 846w, 795m, 748m, 692m, 567m, 518m.

1.3 Crystal structure determination

Two single crystals for the complex **1** (0.30 mm×0.25 mm×0.12 mm) and **2** (0.20 mm×0.15 mm×0.15 mm) were used for X-ray diffraction analysis. Data collection was carried out at 293 K on a Bruker Smart Apex II CCD diffractometer by using graphite monochromatized Mo K α radiation (λ =0.071 073 nm) in phi and omega scans mode. The structure was solved by direct method and difference Fourier syntheses. Refinement of the structures was done by full-matrix least-squares methods based on F^2 . The H atoms were positioned geometrically and allowed to ride on the parent atoms. All calculations were carried out with SHELXTL program^[14]. The data and structure refinement for the complexes are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are listed in Table 2.

CCDC: 869044, **1**; 874032, **2**.

2 Results and discussion

2.1 Crystal structure of the complex

Both the complex **1** and **2** are isostructural and crystallize in the monoclinic $C2/c$ space group. Only structure **1** is described in detail. A coordination environment view of complex **1** with the labelling scheme is given in Fig.1(a).

In complex **1**, the central Sm³⁺ atoms are coordinated by two N atoms and seven O atoms in which two are from two H₂pydc ligands and five from coordinated water molecules. coordination polyhedron of Sm(III) ion is given in Fig.1(b), Sm(III) ion present a distorted three cap tri-prism coordination geometry, N1, O5W, N2, O6W, O7W and O9W is the vertexs. O8W, O8

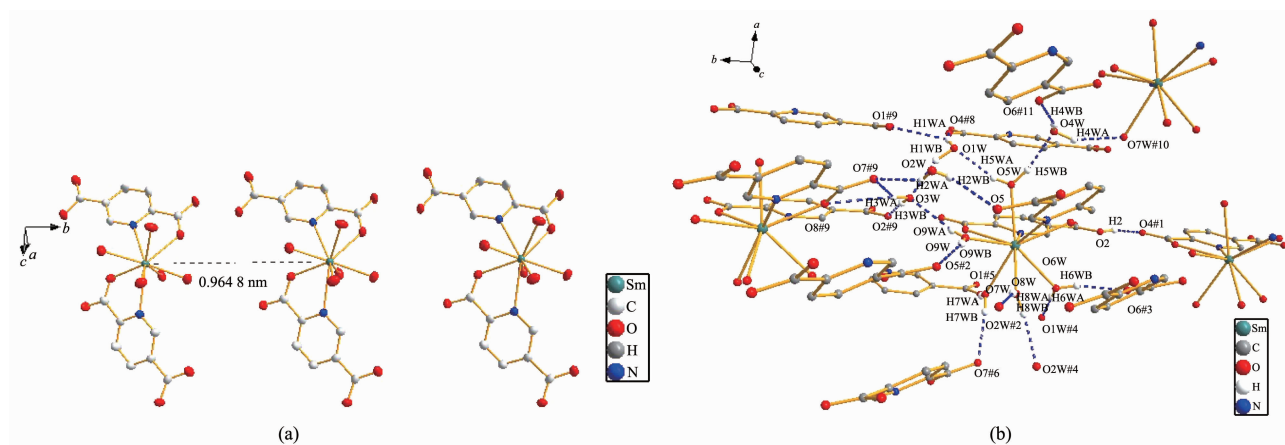
Table 1 Crystal data collection and structure refinement details for the complex 1 and 2

Formula	C ₁₄ H ₂₅ N ₂ O ₁₇ Sm (1)	C ₁₄ H ₂₅ N ₂ O ₁₇ Dy (2)
Formula weight	643.71	655.86
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> / nm	1.392 83(10)	1.379 25(8)
<i>b</i> / nm	0.964 77(7)	0.963 02(6)
<i>c</i> / nm	3.307 64(2)	3.285 8(2)
β / (°)	93.490(10)	93.218 0(10)
<i>V</i> / nm ³	4.436 4(5)	4.357 5(5)
<i>Z</i>	8	8
<i>D_c</i> / (g·cm ⁻³)	1.928	1.999
<i>F</i> (000)	2 568	2 600
Abs. coeff. / mm ⁻¹	2.735	3.519
Goodness of fit on <i>F</i> ²	1.035	1.062
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> >2σ(<i>I</i>))	0.037 6; 0.106 2	0.041 5; 0.083 4
Reflns. collected	11 997	14 524
Unique reflns. (<i>R</i> _{int})	3 862; 0.034 1	3 793; 0.025 6
Observed reflections (<i>I</i> >2σ(<i>I</i>))	3 565	3 637
Parameters refined	362	308

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

Complex 1					
Sm1-N1	0.263 3(4)	Sm1-O8	0.240 3(4)	Sm1-O7W	0.250 7(4)
Sm1-N2	0.266 0(5)	Sm1-O5W	0.241 6(4)	Sm1-O8W	0.248 7(4)
Sm1-O3	0.246 5(4)	Sm1-O6W	0.249 7(4)	Sm1-O9W	0.239 0(4)
O9W-Sm1-O8	137.65(14)	O5W-Sm1-O6W	136.38(14)	O3-Sm1-N1	62.95(12)
O9W-Sm1-O5W	81.54(14)	O3-Sm1-O6W	125.99(14)	O8W-Sm1-N1	144.17(14)
O8-Sm1-O5W	71.37(14)	O8W-Sm1-O6W	71.72(15)	O6W-Sm1-N1	78.02(14)
O9W-Sm1-O3	67.58(13)	O9W-Sm1-O7W	86.62(15)	O7W-Sm1-N1	80.67(13)
O8-Sm1-O3	128.06(13)	O8-Sm1-O7W	134.90(15)	O8-Sm1-N2	63.34(13)
O5W-Sm1-O3	70.67(14)	O5W-Sm1-O7W	138.39(14)	O9W-Sm1-N2	78.13(14)
O9W-Sm1-O8W	71.10(14)	O3-Sm1-O7W	67.93(14)	O5W-Sm1-N2	73.04(14)
O8-Sm1-O8W	109.45(15)	O8W-Sm1-O7W	71.47(14)	O3-Sm1-N2	132.75(14)
O5W-Sm1-O8W	138.56(15)	O6W-Sm1-O7W	70.25(15)	O8W-Sm1-N2	71.34(14)
O3-Sm1-O8W	122.48(14)	O8-Sm1-N1	75.09(13)	O6W-Sm1-N2	101.16(14)
O9W-Sm1-O6W	140.84(14)	O9W-Sm1-N1	130.16(13)	O7W-Sm1-N2	142.63(13)
O8-Sm1-O6W	67.87(14)	O5W-Sm1-N1	77.17(14)	N1-Sm1-N2	134.56(13)
Complex 2					
Dy1-N1	0.262 2(3)	Dy1-O8	0.239 5(3)	Dy1-O7W	0.249 4(3)
Dy1-N2	0.263 6(3)	Dy1-O5W	0.239 4(3)	Dy1-O8W	0.245 7(3)
Dy1-O3	0.244 9(3)	Dy1-O6W	0.247 9(3)	Dy1-O9W	0.236 7(3)
O9W-Dy1-O8	138.19(10)	O5W-Dy1-O6W	136.69(10)	O3-Dy1-N1	63.29(9)
O9W-Dy1-O5W	81.76(10)	O3-Dy1-O6W	126.11(10)	O8W-Dy1-N1	144.22(11)
O8-Dy1-O5W	71.44(10)	O8W-Dy1-O6W	71.53(9)	O6W-Dy1-N1	78.06(10)

Pyrolysis kinetic parameters of two compounds are obtained based on the pyrolysis curves and similar. Pyrolysis kinetic parameters comprise the



Symmetry codes: #1: $x, y-1, z$; #2: $-x+1, -y+1, -z+1$; #3: $-x+1, -y, -z+1$; #4: $x-1/2, y-1/2, z$; #5: $-x+1/2, y+1/2, -z+1/2$; #6: $x-1/2, y+1/2, z$; #7: $-x+1, y+1, -z+1/2$; #8: $-x+1, y, -z+1/2$; #9: $x, y+1, z$; #10: $x+1/2, y-1/2, z$; #11: $-x+3/2, -y+1/2, -z+1$

Fig.2 Distance between the Sm^{3+} atom along b axis for complex **1** (a) and the 3D supramolecular structure through the hydrogen bonds (b)

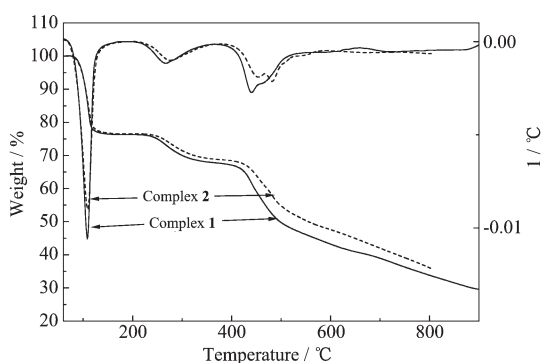
Table 3 Hydrogen bonds distances and angle for the complex **1** and **2**

D-H $\cdots$ A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^{\circ})$
Complex 1				
O2-H2 $\cdots$ O4#1	0.082 0	0.172 1	0.252 9	168.32
O9W-H9WB $\cdots$ O3W	0.085 0	0.191 8	0.274 6	164.41
O9W-H9WA $\cdots$ O5#2	0.084 7	0.181 2	0.263 7	163.88
O5W-H5WB $\cdots$ O4W	0.084 4	0.185 9	0.270 1	174.70
O5W-H5WA $\cdots$ O1W	0.084 4	0.185 4	0.268 4	166.95
O6W-H6WB $\cdots$ O6#3	0.085 0	0.200 1	0.284 0	168.82
O6W-H6WA $\cdots$ O1W#4	0.085 0	0.196 4	0.281 3	178.79
O8W-H8WB $\cdots$ O2W#2	0.083 1	0.209 9	0.291 4	166.90
O8W-H8WA $\cdots$ O2W#4	0.084 5	0.195 4	0.278 4	167.10
O7W-H7WA $\cdots$ O1#5	0.084 9	0.196 1	0.279 8	168.49
O7W-H7WB $\cdots$ O7#6	0.084 9	0.200 3	0.283 8	167.78
O1W-H1WA $\cdots$ O1#7	0.084 9	0.248 0	0.291 2	112.44
O1W-H1WA $\cdots$ O4#8	0.084 9	0.226 1	0.304 9	154.35
O1W-H1WB $\cdots$ O3W	0.085 0	0.191 3	0.272 7	160.24
O2W-H2WA $\cdots$ O7#9	0.077 7	0.222 4	0.284 1	136.79
O2W-H2WB $\cdots$ O5	0.104 0	0.171 9	0.269 7	154.96
O3W-H3WB $\cdots$ O2#9	0.084 5	0.206 0	0.289 7	170.86
O3W-H3WA $\cdots$ O7#9	0.084 9	0.196 9	0.272 8	148.31
O3W-H3WA $\cdots$ O8#9	0.084 9	0.262 7	0.340 2	152.43
O4W-H4WA $\cdots$ O7W#10	0.084 7	0.233 7	0.308 2	146.89
O4W-H4WB $\cdots$ O6#11	0.084 8	0.191 6	0.275 8	172.30
Complex 2				
O2-H2 $\cdots$ O4#1	0.082 0	0.169 5	0.250 2	167.40
O9W-H9WA $\cdots$ O3W	0.082 2	0.192 1	0.273 9	173.03
O9W-H9WB $\cdots$ O5#2	0.084 3	0.179 7	0.263 7	174.30
O5W-H5WA $\cdots$ O4W	0.082 3	0.186 4	0.268 2	172.56
O5W-H5WB $\cdots$ O1W	0.085 0	0.182 9	0.267 7	174.70

Continued Table 3

O6W-H6WA...O6#3	0.072 8	0.210 7	0.282 8	171.17
O6W-H6WB...O1W#4	0.085 5	0.191 5	0.276 8	175.47
O8W-H8WB...O2W#2	0.082 9	0.197 3	0.275 2	156.12
O8W-H8WA...O2W#4	0.083 7	0.204 7	0.288 2	174.80
O7W-H7WB...O1#5	0.079 0	0.199 5	0.277 8	171.39
O7W-H7WA...O7#6	0.074 5	0.208 0	0.281 0	166.49
O1W-H1WB...O1#7	0.067 3	0.246 0	0.290 4	125.59
O1W-H1WB...O4#8	0.067 3	0.242 2	0.303 8	153.25
O1W-H1WA...O3W	0.075 4	0.197 2	0.270 2	163.16
O2W-H2WA...O7#9	0.082 5	0.203 6	0.280 5	154.98
O2W-H2WB...O5	0.065 3	0.205 9	0.268 8	162.26
O3W-H3WB...O2#9	0.080 9	0.209 4	0.285 0	155.49
O3W-H3WA...O7#9	0.082 5	0.203 6	0.280 5	154.98
O4W-H4WA...O7W#10	0.071 7	0.238 4	0.308 2	150.16
O4W-H4WB...O6#11	0.083 2	0.192 0	0.273 9	16793

Symmetry transformations used to generate equivalent atoms: #1: $x, y-1, z$; #2: $-x+1, -y+1, -z+1$; #3: $-x+1, -y, -z+1$; #4: $x-1/2, y-1/2, z$; #5: $-x+1/2, y+1/2, -z+1/2$; #6: $x-1/2, y+1/2, z$; #7: $-x+1, y+1, -z+1/2$; #8: $-x+1, y, -z+1/2$; #9: $x, y+1, z$; #10: $x+1/2, y-1/2, z$; #11: $-x+3/2, -y+1/2, -z+1$.

Fig.3 TGA and DTG curves of the complex **1** and **2**

activation energy E_a , the most probable mechanism function $G(\alpha)$ and pre-exponential A. Pyrolysis kinetic parameters of three steps are shown in Table 4. The iterative iso-conversional methods (Flym-Wall-Ozawa method and KAS method) are applied to calculate E_a

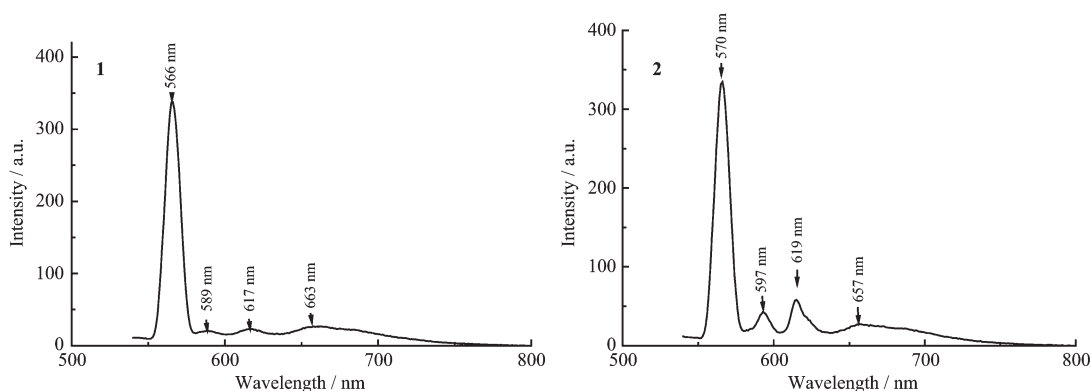
and $G(\alpha)$ is determined by means of the master plots method^[17-19].

2.3 Fluorescence properties

The fluorescence spectra of the complexes are determined in Fig.4. In order to study the fluorescence of these complexes, we measured the fluorescence of the solvent (DMF), the ligand and the two compounds ($c = 1.0 \mu\text{mol} \cdot \text{L}^{-1}$). Experimentally determined results show that two complexes have characteristic fluorescence respectively at room temperature. For **1**, under excitation of 309 and 333 nm, it has four metal centered emission bands: 566 nm ($^5D_0 \rightarrow ^7F_1$), 589 nm ($^5D_0 \rightarrow ^7F_2$), 617 nm ($^5D_0 \rightarrow ^7F_3$), 663 nm ($^5D_0 \rightarrow ^7F_4$). For **2**, under excitation of 309 and 332 nm, it has four metal centered emission bands:

Table 4 Pyrolysis kinetic parameters of the complex **1** and **2**

Step	$E_a / (\text{kJ} \cdot \text{mol}^{-1})$	$G(\alpha)$	$\ln(A / \text{s}^{-1})$
Complex 1			
1	111.345	$[-\ln(1-x)]^{0.806}$	$10.706 \pm 0.028 8$
2	166.461	$[-\ln(1-x)]^{2.564}$	$9.723 \pm 0.027 5$
3	231.207	$[-\ln(1-x)]^{2.415}$	$9.962 \pm 0.020 2$
Complex 2			
1	111.264	$[-\ln(1-x)]^{0.799}$	$10.777 \pm 0.032 8$
2	166.392	$[-\ln(1-x)]^{2.556}$	$9.742 \pm 0.022 4$
3	231.135	$[-\ln(1-x)]^{2.407}$	$9.933 \pm 0.025 6$

Fig.4 Emission spectra curves of the complex **1** and **2**

570 nm ($^5D_0 \rightarrow ^7F_1$), 597 nm ($^5D_0 \rightarrow ^7F_2$), 619 nm ($^5D_0 \rightarrow ^7F_3$), 657 nm ($^5D_0 \rightarrow ^7F_4$)^[11,20].

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