

二苯基喹啉氧基乙酰胺的 La、Ce 同构配合物的合成、表征及荧光性质

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摘要: 合成了并通过单晶衍射表征了 2 个同构稀土配合物 $[\text{LnL}_2(\text{NO}_3)_3]$ ($\text{L}=\text{N}, \text{N}$ -二苯基-2-(8-喹啉氧基)乙酰胺, $\text{Ln}=\text{La}(\text{III}), \text{Ce}(\text{III})$, **1**); $\text{Ce}(\text{III})$, **2**)。在每个配合物中, 十二配位的稀土离子采取扭曲的二十面体配位构型, 分别与来自 2 个配体的 4 个氧原子和 2 个氮原子及来自 3 个双齿配位硝酸根的 6 个氧原子配位。乙腈溶液中, 配合物发射强荧光。

关键词: 酰胺配体; 稀土配合物; 荧光; 晶体结构

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Isostructural Lanthanide Complexes (La, Ce) of Diphenyl-quinolinyloxy Acetamide Ligand: Syntheses, Structures and Fluorescent Properties

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Abstract: Two isostructural lanthanide complexes, $[\text{LnL}_2(\text{NO}_3)_3]$ ($\text{L}=\text{N}, \text{N}$ -diphenyl-2-(quinolin-8-yloxy)acetamide, $\text{Ln}=\text{La}(\text{III}), \text{Ce}(\text{III})$, **1**; $\text{Ce}(\text{III})$, **2**) were synthesized and characterized by X-ray diffraction. In each complex, center metal ion is coordinated to four oxygen and two nitrogen atoms from two independent acetamide ligands and also to six oxygen atoms from three nitrate anions, possessing a coordination geometry closer to a distorted icosahedron. In CH_3CN solution, both complexes exhibit strong fluorescence emission. CCDC: 941145, **1**; 941146, **2**.

Key words: amide type ligand; lanthanide complex; fluorescence; crystal structure

0 Introduction

Owing to their good luminescent properties, such as the large Stokes shifts, narrow emission profiles, long lifetimes and so on^[1-2], the lanthanide complexes are attracting more and more attention and have been widely used in many aspects, such as light-emitting diode (LED), laser materials, optical signal amplification and fluoroimmunoassay^[3-6]. The amide type ligands have often been chosen as an sensitizer to enhance the fluorescence emission intensity of the lanthanide complexes, because they are flexible in structure and

would shield the encapsulated lanthanide ion from interaction with the surroundings effectively^[1-2]. In our previous work, we have reported the synthesis and possible structures of six lanthanide complexes (lanthanide ions = La, Sm, Eu, Gd, Tb, Dy) with the ligand L, including the fluorescence properties of Eu (III) complex. However, the crystal structures of such complexes are still not confirmed. Therefore, in this paper, two isostructural lanthanide (La(III) and Ce(III)) complexes of the ligand L were synthesized and characterized by X-ray diffraction. Furthermore, the fluorescence spectra of the complexes in CH_3CN

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solution were investigated.

1 Experimental

1.1 Materials and measurements

Solvents and starting materials for synthesis were purchased commercially and used as received. Elemental analysis was carried out on an Elemental Vario EL analyzer. The IR spectra ($\nu=4\ 000\sim 400\ \text{cm}^{-1}$) were determined by the KBr pressed disc method on a Bruker V70 FT-IR spectrophotometer. All conductivity measurements were performed in acetone with a DDS-11A conductometer at room temperature. The UV spectra were recorded on a Purkinje General TU-1901 spectrophotometer. Fluorescence spectra were determined on a Varian CARY Eclipse spectrophotometer.

1.2 Preparations of the complexes

The ligand L^[7] (0.070 4 g, 2 mmol) and $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (0.043 3 g, 1 mmol) were dissolved in acetone (20 mL). After stirring for 1 h, the mixture was filtered

and set aside to crystallize at room temperature. The product **1**, which was collected by filtration, washed with Et_2O and dried in air. Some of the obtained crystals were suitable for a single crystal X-ray analysis. The synthesis of **2** is similar to that of **1**, while $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ instead of $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$.

1: Colorless blocks. Yield 41%. Anal. Calcd. for $\text{C}_{46}\text{H}_{36}\text{N}_7\text{O}_{13}\text{La}$ (%): C, 53.45; H, 3.51; N, 9.48. Found (%): C, 53.54; H, 3.23; N, 9.17. IR (KBr, cm^{-1}): $\nu(\text{C}=\text{O})$ 1 667, $\nu(\text{C}=\text{N})$ 1 593, $\nu(\text{Ar}-\text{O}-\text{C})$ 1258, $\nu_4(\text{NO}_3)$ 1 493, $\nu_1(\text{NO}_3)$ 1 318. Λ_{m} ($\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$): 3.95.

2: Colorless blocks. Yield 57%. Anal. Calcd. for $\text{C}_{46}\text{H}_{36}\text{N}_7\text{O}_{13}\text{Ce}$ (%): C, 53.38; H, 3.51; N, 9.47. Found (%): C, 53.49; H, 3.82; N, 9.21. IR (KBr, cm^{-1}): $\nu(\text{C}=\text{O})$ 1 667, $\nu(\text{C}=\text{N})$ 1 594, $\nu(\text{Ar}-\text{O}-\text{C})$ 1 256, $\nu_4(\text{NO}_3)$ 1 494, $\nu_1(\text{NO}_3)$ 1 319. Λ_{m} ($\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$): 4.83.

1.3.1 X-ray crystallography

The X-ray diffraction measurements for two complexes were performed on a Bruker SMART APEX

Table 1 Crystal data and structure refinement for the complexes

	1	2
Empirical formula	$\text{C}_{46}\text{H}_{36}\text{N}_7\text{O}_{13}\text{La}$	$\text{C}_{46}\text{H}_{36}\text{N}_7\text{O}_{13}\text{Ce}$
Formula weight	1 033.73	1 034.94
Temperature / K	296(2)	296(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
Z	4	4
a / nm	2.620 87(19)	2.621 51(14)
b / nm	1.155 04(9)	1.154 85(6)
c / nm	1.824 42(13)	1.824 37(10)
β / ($^\circ$)	128.551(1)	128.553(1)
V / nm^3	4.319 2(6)	4.319 3(4)
D_{c} / ($\text{g}\cdot\text{cm}^{-3}$)	1.590	1.592
μ / mm^{-1}	1.066	1.131
$F(000)$	2 088	2 092
Crystal size / mm	0.32×0.26×0.23	0.23×0.21×0.20
θ range for data collection / ($^\circ$)	1.99 to 27.85	1.99 to 28.32
Reflections collected	13 423	13 685
Independent reflections (R_{int})	5 002 (0.026 7)	5 212 (0.017 6)
Observed reflections ($I>2\sigma(I)$)	4 552	4 883
Final GooF	1.026	1.016
R_1, wR_2 ($I>2\sigma(I)$)	$R_1=0.025\ 0, wR_2=0.063\ 1$	$R_1=0.020\ 8, wR_2=0.055\ 2$
R_1, wR_2 (all data)	$R_1=0.028\ 7, wR_2=0.065\ 2$	$R_1=0.023\ 1, wR_2=0.056\ 7$

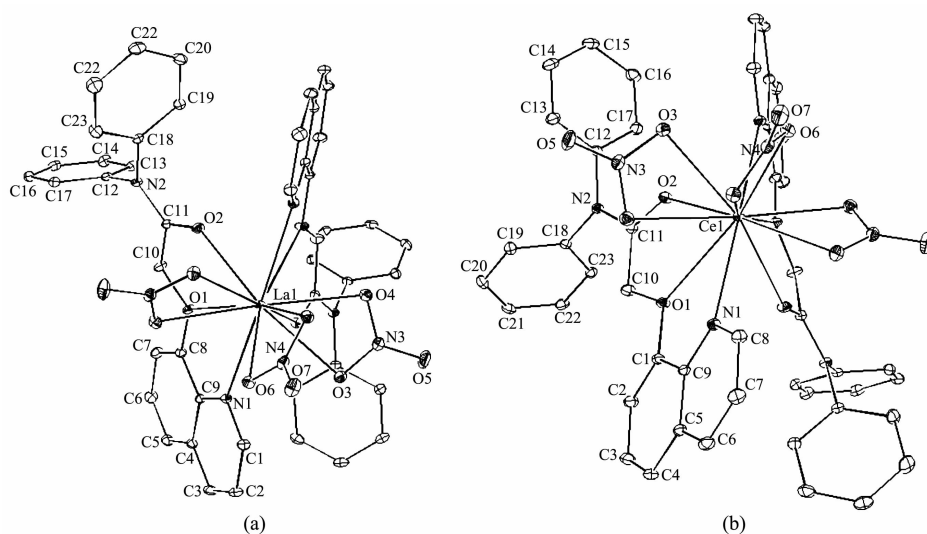
II CCD diffractometer equipped with a graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) by using φ - ω scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program^[8]. The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-97 program^[9]. All non-hydrogen atoms were refined anisotropically. All H atoms were generated geometrically and refined isotropically using the riding mode. Details of the crystal parameters, data collection and refinements for **1** and **2** are summarized in Table 1.

CCDC: 941145, **1**; 941146, **2**.

2 Results and discussion

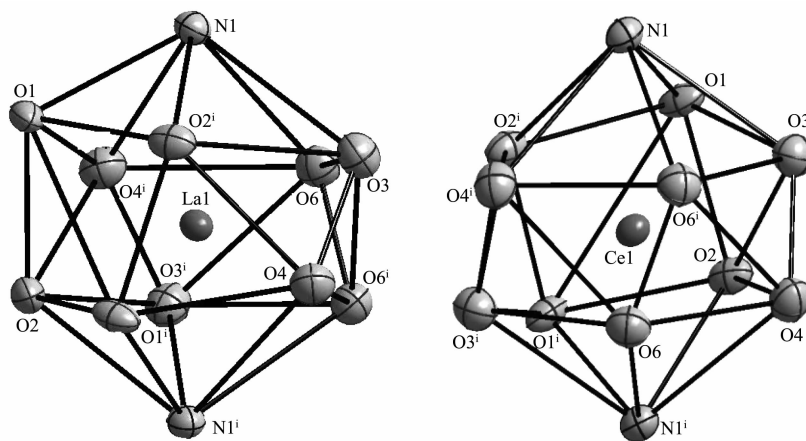
2.1 Crystal structure of the complexes

As show in Fig.1a, the asymmetric unit of the complex **1** contains a half of the molecule with N4 and O7 atoms from one nitrate anion lying on the two fold rotational axis. In complex **1**, the twelve-coordinated La atom is in a distorted icosahedron geometry (Fig. 2a) with the donor centers of four oxygen and two nitrogen atoms from two independent acetamide ligands, and six oxygen atoms from three nitrate anions. Selected bond lengths and angles are summarized in Table 2. The La-N and La-O bond lengths are



Unlabelled atoms are related with the labelled ones by symmetry operation $(-x, y, -z+1/2)$

Fig.1 Molecular structures of the complex **1** (a) and **2** (b) shown with 10% probability displacement ellipsoids



Symmetry code $i: -x, y, -z+1/2$

Fig.2 Coordination geometries of the center lanthanide ions shown with 30% probability displacement ellipsoids in the complex **1** (a) and **2** (b)

Table 2 Selected bond lengths (nm) and angles ($^{\circ}$) in the complexes

1					
La1-O1	0.285 94(14)	La1-O2	0.257 53(13)	La1-O3	0.267 39(15)
La1-O4	0.265 76(17)	La1-O6	0.265 67(15)	La1-N1	0.278 98(17)
O2i-La1-O2	97.86(7)	O2-La1-O6	130.11(5)	O2-La1-O6 ⁱ	123.85(5)
O6-La1-O6 ⁱ	47.81(7)	O2-La1-O4	120.76(5)	O6-La1-O4	102.24(5)
O6 ⁱ -La1-O4	69.67(5)	O2-La1-O4 ⁱ	65.54(5)	O4-La1-O4 ⁱ	171.51(7)
O2-La1-O3 ⁱ	67.55(5)	O4 ⁱ -La1-O3	127.55(5)	O2-La1-O3	163.69(5)
O6-La1-O3	66.13(5)	O6i-La1-O3	66.44(5)	O4-La1-O3	47.58(5)
O3 ⁱ -La1-O3	127.81(7)	O2-La1-N1 ⁱ	65.23(5)	O6-La1-N1 ⁱ	114.43(5)
O4-La1-N1 ⁱ	69.42(5)	O3-La1-N1 ⁱ	112.03(5)	O2-La1-N1	111.12(5)
O6-La1-N1	70.61(5)	O4-La1-N1	110.98(5)	O3-La1-N1	70.38(5)
N1 ⁱ -La1-N1	174.89(7)	O2-La1-O1 ⁱ	62.62(5)	O2-La1-O1	56.66(4)
O6-La1-O1	116.76(4)	O6 ⁱ -La1-O1	162.67(5)	O4-La1-O1	126.46(5)
O4 ⁱ -La1-O1	61.28(5)	O3 ⁱ -La1-O1	101.96(4)	O3-La1-O1	117.94(4)
N1 ⁱ -La1-O1	118.67(4)	N1-La1-O1	56.74(4)	O1 ⁱ -La1-O1	79.59(6)
2					
Ce1-O1	0.284 80(11)	Ce1-O2	0.255 97(11)	Ce1-O3	0.263 16(14)
Ce1-O4	0.265 81(13)	Ce1-O6	0.264 06(12)	Ce1-N1	0.277 73(14)
O2-Ce1-O2 ⁱ	98.25(6)	O3-Ce1-O4	47.93(4)	N1-Ce1-N1 ⁱ	175.40(5)
O2-Ce1-O3	65.73(4)	O6 ⁱ -Ce1-O4	66.43(4)	O2-Ce1-O1	56.84(3)
O2-Ce1-O3 ⁱ	120.52(4)	O6-Ce1-O4	66.24(4)	O2 ⁱ -Ce1-O1	62.58(4)
O3-Ce1-O3 ⁱ	171.52(6)	O4 ⁱ -Ce1-O4	127.85(6)	O3-Ce1-O1	61.28(4)
O2-Ce1-O6 ⁱ	129.85(4)	O2-Ce1-N1	111.50(4)	O3 ⁱ -Ce1-O1	126.47(4)
O3-Ce1-O6 ⁱ	69.39(4)	O3-Ce1-N1	69.12(4)	O6 ⁱ -Ce1-O1	116.71(4)
O2-Ce1-O6	123.67(4)	O6-Ce1-N1	114.26(4)	O6-Ce1-O1	162.98(4)
O3-Ce1-O6	102.53(4)	O4-Ce1-N1	112.05(4)	O4 ⁱ -Ce1-O1	117.84(4)
O6 ⁱ -Ce1-O6	48.12(6)	O2-Ce1-N1 ⁱ	65.23(4)	O4-Ce1-O1	102.10(4)
O2-Ce1-O4 ⁱ	163.84(4)	O3-Ce1-N1 ⁱ	111.24(4)	N1-Ce1-O1	57.05(4)
O3-Ce1-O4 ⁱ	127.23(4)	O6-Ce1-N1 ⁱ	70.27(4)	N1 ⁱ -Ce1-O1	118.82(4)
O2-Ce1-O4	67.35(4)	O4-Ce1-N1 ⁱ	70.12(4)	O1-Ce1-O1 ⁱ	79.34(5)

Symmetry codes: ⁱ $-x, y, -z+1/2$.

0.278 98(17) and 0.257 53(13)~0.285 94(14) nm, respectively, comparable to the La complexes with similar donor sets^[10]. In complex **1**, mostly bond angles are highly deviated from those of ideal icosahedron geometry. It is obvious that the crystal structure of **1** is different from its suggested structure in our previous work^[2], in which the coordination number for La atom is 8, and there is a free nitrate group.

Complex **2** (Fig.1b and 2b) is isostructural to **1**. The bond lengths of Ce-N (0.277 73(14) nm) and Ce-O (0.255 97(11)~0.284 80(11) nm) are shorter than

that of La-N and La-O bonds in complex **1**, which may be due to lanthanide contraction^[3]. As expected, there are no classic hydrogen bonds in both complexes.

2.2 Molar conductivities and IR spectra

The molar conductivity values of the complexes in acetone are 3.95 and 4.83 S·cm²·mol⁻¹, respectively, indicating that both complexes are non-electrolytes^[11]. In our previous work^[2], the molar conductivity was determined in DMF, the different results are probably due to the coordination ability of DMF, in which the complexes may be not stable enough.

The IR spectra of L show strong band at 1 679 cm^{-1} , which are attributable to stretch vibrations of the carbonyl group of amide ($\nu(\text{C}=\text{O})$). The peak at 1 618 cm^{-1} should be assigned to the $\nu(\text{C}=\text{N})$ ^[2]. Upon coordination with Ln(III) ion, $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ shift about 13 and 25 cm^{-1} in both complexes; indicating that carboxyl oxygen atom and quinoline nitrogen atom take part in coordination to the Ln(III) ion^[1-2,12-13]. The similar bands of $\nu(\text{Ar-O-C})$ at about 1 258 cm^{-1} in the acetamide ligand^[2] and the complexes are mainly due to the fact that the ligands have large sterically hindered effect, which prevents ethereal oxygen atom from tight coordinating Ln(III) ion^[12]. In addition, the two intense absorption bands in the spectra of both complexes associated with the asymmetric stretching appear at around 1 318 cm^{-1} (ν_4) and 1 493 cm^{-1} (ν_1), clearly establishing that there are some coordinated NO_3 groups (C_2). The differences between the two bands lie at 175 cm^{-1} , suggesting that the coordinated nitrate groups are bidentate^[12]. It is in accordance with the result of the crystal structure study.

2.3 UV spectra

The UV spectra of L, **1** and **2** in CH_3CN solution (concentration: $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) were measured at room temperature (Fig.3). The spectra of L feature three main bands located around 203 (ϵ : 96 696 $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 239 (ϵ : 53 091 $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and 294 nm (ϵ : 1 856 $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), respectively. The bands could be assigned to characteristic $\pi-\pi^*$ transitions

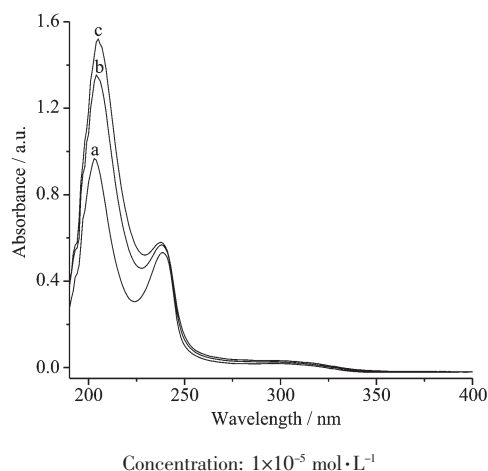


Fig.3 UV spectra of L (a), **1** (b) and **2** (c) in CH_3CN solution at room temperature

centered on benzene ring, quinoline ring and the acetamide unit, respectively^[13]. The spectra of **1** and **2** are quite similar as that of L. The ϵ values of the corresponding bands in complex **1** and **2** are 13 542, 5 679, 2 613 and 152 065, 57 925, 3 256 $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, respectively. However, the hyperchromicities indicate that the ligand L takes part in the coordination in both complexes.

2.4 Fluorescence spectra

The fluorescence spectra of L, **1** and **2** in CH_3CN solution (concentration: $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) was measured at room temperature. The excitation and emission wavelengths of three compounds are at 300 and 389 nm, respectively (Fig.4). It also can be seen that the emission intensity of the complexes are much higher than that of L, which may be explained from two aspects: first, in the complexes the molar ratios of the ligand and Ln ion are 2:1; second, the coordination of Ln ion may enhance the $\pi \rightarrow \pi^*$ electron transition of the acetamide ligand^[5].

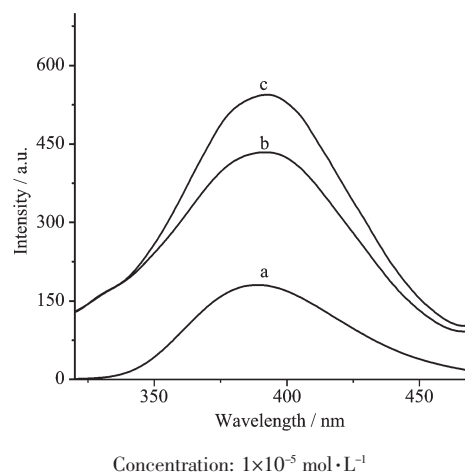


Fig.4 Fluorescence emission spectra of L (a), **1** (b) and **2** (c) in CH_3CN solution at room temperature

References:

- [1] Song X Q, Wen X G, Liu W S, et al. *J. Solid State Chem.*, **2010**,**183**:1-9
- [2] Wu W N, Tang N, Yan L. *J. Fluoresc.*, **2008**,**18**:101-107
- [3] LIU Mei-Juan(刘美娟), CAO Deng-Ke(曹登科), HUANG Jian(黄建), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2012**,**28**:2017-2024
- [4] LIU Jian-Fen(刘建凤), CHEN Ji-Fei(陈吉妃), ZHAO Guo

- Liang (赵国良), *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2011**,**27**:100-106
- [5] LI Li (李丽), CHEN Ya-Shao(陈亚苟), ZHAO Li-Fang(赵丽芳), *Chem. J. Chinese Universities(Gaodeng Xuexiao Huaxue Xuebao)*, **2006**,**27**:199-203
- [6] Liu D Y, Kou Z Q, Li Y F, et al. *Inorg. Chem. Commun.*, **2009**,**12**:461-464
- [7] Wen Y H, Zhang S S, Li M J, et al. *Acta Cryst. E*, **2005**,**61**: o1807-o1809
- [8] Sheldrick G M. *SADABS*, University of Göttingen, Germany, **1996**.
- [9] Sheldrick G M. *SHELX-97, Program for the Solution and the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.
- [10] LIU Ru(刘茹), ZHU Wen-Xiang(朱文祥), ZHANG Yong-An(张永安), et al. *Acta Chim. Sin.(Huaxue Xuebao)*, **2001**,**59**: 533-537
- [11] Geary W. *J. Coord. Chem. Rev.*, **1971**,**7**:81-121
- [12] Wu W N, Cheng F X, Yan L, et al. *J. Coord. Chem.*, **2008**, **61**:2207-2215
- [13] Song X Q, Zang Z P, Liu W S, et al. *J. Solid State Chem.*, **2009**,**182**:841-848