

两个喹啉氧基乙酰胺的镧系(La、Pr)配合物的合成、表征及荧光性质

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摘要: 合成并通过单晶衍射表征了 2 个稀土配合物 $[\text{LnL}_2(\text{NO}_3)(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ ($\text{L}=\text{N}$ -苯基-2-(8-喹啉氧基)乙酰胺, $\text{Ln}=\text{La}(\text{III})$, $n=0, 1$; $\text{Pr}(\text{III})$, $n=1, 2$)。在每个配合物中, 十配位的稀土离子采取扭曲的双帽四方反棱柱配位构型, 分别与来自 2 个配体的 4 个氧原子和 2 个氮原子, 来自 1 个双齿配位硝酸根的 2 个氧原子及来自 2 个配位水分子的 2 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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Two Lanthanide Complexes (La, Pr) of Quinolinyloxy Acetamide Ligand: Syntheses, Structures and Fluorescent Properties

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Abstract: Two lanthanide complexes, $[\text{LnL}_2(\text{NO}_3)(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ ($\text{L}=\text{N}$ -phenyl-2-(quinolin-8-yloxy)acetamide, $\text{Ln}=\text{La}(\text{III})$, $n=0, 1$; $\text{Pr}(\text{III})$, $n=1, 2$) 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, two oxygen atoms from one nitrate anion, and also to two oxygen atoms from two water molecules, possessing a coordination geometry closer to a distorted bicapped square antiprism geometry. In CH_3CN solution, both complexes exhibit strong fluorescence emission. CCDC: 998228, **1**; 998229, **2**.

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

The lanthanide complexes have been paid more and more attention due to their good luminescent properties^[1-6]. Since the $f-f$ transitions are spin- and parity-forbidden, to enhance their fluorescence emission intensity, it is necessary to design suitable ligand which can encapsulate the lanthanide ion and also transfer energy to the excited state of the lanthanide ion^[2]. Therefore, owing to their good

coordination abilities and terminal-group effects, a great deal of open-chain acetamide ligands have been chosen as sensitizer ligands^[1-3,5]. In our previous work, we have reported the synthesis and possible structures of four lanthanide complexes (lanthanide ions=La, Sm, Eu, Gd) with quinolinyloxy acetamide ligand **L**, including the fluorescence properties of Eu (III) complex^[2]. However, the crystal structures of such

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complexes are still not confirmed. Thus, in this paper, two lanthanide [La(Ⅲ) and Pr(Ⅲ)] complexes of the ligand **L** were synthesized and characterized by X-ray diffraction. Furthermore, the fluorescence spectra of the complexes in CH₃CN 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 ($\nu=4\,000\sim400\text{ cm}^{-1}$) were determined by the KBr pressed disc method on a Bruker V70 FTIR spectrophotometer. The UV spectra were recorded on a Purkinje General TU-1800 spectrophotometer. Fluorescence spectra were determined on a Varian CARY Eclipse spectrophotometer.

1.2 Preparations of the complexes

The ligand **L**^[2] (0.055 6 g, 2 mmol) and La(NO₃)₃·6H₂O (0.043 3 g, 1 mmol) were dissolved in acetonitrile (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 Et₂O 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 Pr(NO₃)₃·6H₂O instead of La(NO₃)₃·6H₂O.

1: Colorless blocks. Yield 57%. Anal. Calcd. for

C₃₄H₃₂N₇O₁₅La (%): C, 44.51; H, 3.52; N, 10.69. Found (%): C, 44.48; H, 3.31; N, 10.87. IR (KBr, cm⁻¹): $\nu(\text{O-H})$ 3 398, $\nu(\text{C=O})$ 1 661, $\nu(\text{C=N})$ 1 573, $\nu(\text{Ar-O-C})$ 1 256, $\nu_4(\text{NO}_3)$ 1 477, $\nu_0(\text{NO}_3)$ 1 384, $\nu_1(\text{NO}_3)$ 1 316, $\rho(\text{O-H})$ 915.

2: Colorless blocks. Yield 62%. Anal. Calcd. for C₃₄H₃₄N₇O₁₆Pr (%): C, 43.56; H, 3.66; N, 10.46. Found (%): C, 43.58; H, 3.48; N, 10.22. IR (KBr, cm⁻¹): $\nu(\text{O-H})$ 3 375, $\nu(\text{C=O})$ 1 659, $\nu(\text{C=N})$ 1 569, $\nu(\text{Ar-O-C})$ 1 258, $\nu_4(\text{NO}_3)$ 1 473, $\nu_0(\text{NO}_3)$ 1 384, $\nu_1(\text{NO}_3)$ 1 314, $\rho(\text{O-H})$ 912.

1.3.1 X-ray crystallography

The X-ray diffraction measurements for two complexes were performed on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatized Mo *K*α 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^[7]. The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-97 program^[8]. All non-hydrogen atoms were refined anisotropically. H atoms for water molecules are located from difference Fourier map and refined with restraints in bond length and thermal parameters. All the other H atoms were positioned geometrically and refined using a riding model. Details of the crystal parameters, data collection and refinements for **1** and **2** are summarized in Table 1.

CCDC: 998228, **1** 998229, **2**.

Table 1 Crystal data and structure refinement for the complexes

	1	2
Empirical formula	C ₃₄ H ₃₂ N ₇ O ₁₅ La	C ₃₄ H ₃₄ N ₇ O ₁₆ Pr
Formula weight	917.58	937.59
Temperature / K	296(2)	296(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system	Monoclinic	Triclinic
Space group	<i>C2/c</i>	<i>P</i> $\bar{1}$
<i>Z</i>	4	2
<i>a</i> / nm	2.86 373(15)	1.044 20(13)
<i>b</i> / nm	0.930 40(5)	1.117 80(14)
<i>c</i> / nm	2.024 90(11)	1.743 9(2)
α / (°)	90	90.514(2)
β / (°)	123.776 0(10)	94.782(2)

Continued Table 1

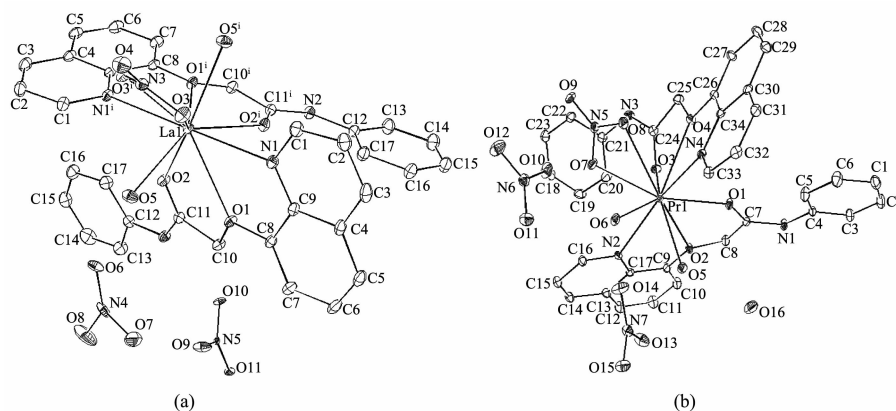
$\gamma / (^{\circ})$	90	113.765(2)
V / nm^3	4.484 6(4)	1.854 4(4)
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.359	1.679
μ / mm^{-1}	1.02	1.399
$F(000)$	1 848	948
Crystal size / mm	0.23×0.22×0.18	0.19×0.18×0.15
θ range for data collection / $(^{\circ})$	1.71 to 27.93	1.17 to 25.01
Reflections collected	13 815	9 827
Independent reflections (Rint)	5 250(0.025 1)	6 494(0.033 4)
Observed reflections ($I > 2\sigma(I)$)	4 617	5 303
Final GooF	1.066	1.053
$R_1, wR_2(I > 2\sigma(I))$	$R_1=0.050\ 7, wR_2=0.150\ 0$	$R_1=0.040\ 8, wR_2=0.080\ 0$
$R_1, wR_2(\text{all data})$	$R_1=0.057\ 1, wR_2=0.157\ 3$	$R_1=0.055\ 8, wR_2=0.086\ 5$

2 Result and discussion

2.1 Crystal structure of the complexes

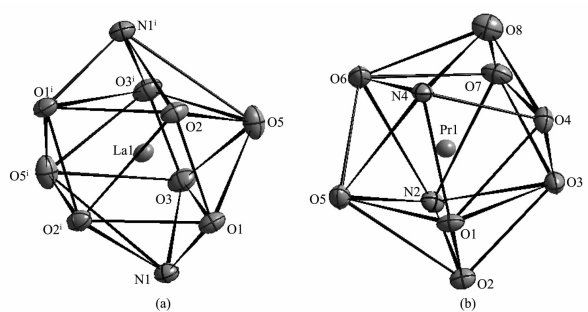
As show in Fig.1a, the asymmetric unit of the complex **1** contains a half of the molecule with N3 and O4 atoms from one nitrate anion lying on the two fold rotational axis. In complex **1**, the ten-coordinated La atom is in distorted bicapped square antiprism geometry (Fig.2a) with the donor centers of four oxygen and two nitrogen atoms from two independent acetamide ligands, two oxygen atoms from one nitrate anion, and two oxygen atoms from two water molecules. However, in our previous work [2], the suggested structure of the lanthanide complexes with ligand L is $[\text{Ln}(\text{L})_2(\text{NO}_3)_2]\text{NO}_3$, in which the lanthanide

atom coordinates with two bidentate nitrates, and there is a free nitrate group. Selected bond lengths and angles are summarized in Table 2. The La-N and La-O bond lengths are 0.271 5 (4) and 0.249 3 (3)~0.278 8 (3) nm, respectively, which are shorter than that of $[\text{LaL}_2(\text{NO}_3)_3]$ ($\text{L}^1 = N,N$ -diphenyl-2-(quinolin-8-ylloxy)acetamide)^[3]. As shown in Fig.3 and Table 3, in the crystal, intermolecular O-H...O hydrogen bonds between the coordination water molecules and free nitrate O atoms link the complex molecules into chains along the b axis. Intramolecular O-H...O hydrogen bond between the coordinated water molecular and free nitrate O atom, and N-H...O hydrogen bond between the ligand L and free nitrate O atom are also present.



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

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

Symmetry code: $i -x, y, -z+1/2$ for **1**Fig.2 Coordination geometries of the center lanthanide ions shown with 30% probability displacement ellipsoids in the complexes **1** (a) and **2** (b)**Table 2** Selected bond lengths (nm) and angles ($^{\circ}$) in the complexes

1					
La1-O1	0.278 8(3)	La1-O2	0.249 3(3)	La1-O3	0.263 8(3)
La1-O5	0.251 1(3)	La1-N1	0.271 5(4)		
O2 ⁱ -La1-O2	81.35(15)	O3 ⁱ -La1-O3	47.56(14)	O2 ⁱ -La1-O1	66.90 (10)
O2-La1-O5	73.55(11)	O2-La1-N1 ⁱ	67.48(10)	O2-La1-O1	58.35 (9)
O2-La1-O5 ⁱ	138.02(11)	O5-La1-N1 ⁱ	85.03(13)	O5-La1-O1	71.32 (10)
O5-La1-O5 ⁱ	144.67(15)	O3-La1-N1 ⁱ	111.39 (10)	O5 ⁱ -La1-O1	133.42 (11)
O2-La1-O3 ⁱ	124.82(10)	O2-La1-N1	115.74 (10)	O3 ⁱ -La1-O1	144.65 (10)
O2-La1-O3	144.79(11)	O5-La1-N1	93.79(12)	O3-La1-O1	106.91 (9)
O5-La1-O3	71.33(11)	O3-La1-N1	64.75(10)	N1 ⁱ -La1-O1	124.86 (10)
O5 ⁱ -La1-O3	76.40(11)	N1 ⁱ -La1-N1	176.13(14)	N1-La1-O1	57.95 (10)
O1-La1-O1 ⁱ	105.60(12)				
2					
Pr1-O3	0.243 9(3)	Pr1-O7	0.262 2(3)	Pr1-O8	0.266 6(3)
Pr1-O5	0.245 2(3)	Pr1-N4	0.263 1(4)	Pr1-O4	0.268 0(3)
Pr1-O1	0.247 0(3)	Pr1-N2	0.264 3(4)	Pr1-O2	0.275 6(3)
Pr1-O6	0.248 5(3)				
O3-Pr1-O5	138.28(11)	O3-Pr1-N2	76.60(11)	O1-Pr1-O4	68.58(10)
O3-Pr1-O1	87.80(10)	O5-Pr1-N2	80.42(11)	O6-Pr1-O4	128.85(10)
O5-Pr1-O1	71.76(10)	O1-Pr1-N2	116.07(10)	O7-Pr1-O4	89.15(10)
O3-Pr1-O6	140.19(11)	O6-Pr1-N2	82.40(11)	N4-Pr1-O4	60.56(10)
O5-Pr1-O6	68.28(10)	O7-Pr1-N2	70.51(11)	N2-Pr1-O4	136.42(10)
O1-Pr1-O6	131.97(10)	N4-Pr1-N2	163.02(11)	O8-Pr1-O4	61.98(10)
O3-Pr1-O7	68.53(11)	O3-Pr1-O8	88.70(11)	O3-Pr1-O2	64.39(10)
O5-Pr1-O7	133.71(11)	O5-Pr1-O8	132.92(11)	O5-Pr1-O2	73.95(10)
O1-Pr1-O7	153.79(11)	O1-Pr1-O8	124.35(10)	O1-Pr1-O2	58.29(9)
O6-Pr1-O7	72.71(11)	O6-Pr1-O8	71.21(11)	O6-Pr1-O2	129.63(10)
O3-Pr1-N4	120.33(11)	O7-Pr1-O8	47.38(10)	O7-Pr1-O2	116.39(10)
O5-Pr1-N4	85.00(11)	N4-Pr1-O8	67.84(11)	N4-Pr1-O2	124.71(9)
O1-Pr1-N4	66.68(10)	N2-Pr1-O8	116.91(11)	N2-Pr1-O2	59.08(10)
O6-Pr1-N4	84.17(11)	O3-Pr1-O4	59.98(10)	O8-Pr1-O2	153.09(10)
O7-Pr1-N4	115.05 (11)	O5-Pr1-O4	135.08(10)	O4-Pr1-O2	101.42(9)

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

Table 3 Selected hydrogen bonding parameters in **1** and **2**

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
1				
O5-H5B...O6	0.087	0.186	0.272 5(7)	172
O5-H5A...O10 ⁱⁱ	0.070	0.210	0.274 4(5)	153
N2-H2A...O10	0.084 4(10)	0.216(4)	0.283 0(6)	136(5)
2				
O5-H5A...O16	0.082	0.188	0.265 7(5)	157
O5-H5C...O13	0.084 2(10)	0.200 1(10)	0.284 1(4)	175(3)
O6-H6A...O14	0.082	0.210	0.281 6(5)	147
O6-H6C...O10	0.084 0(10)	0.188 5(9)	0.268 9(5)	160(2)
O16-H16C...O12 ⁱⁱⁱ	0.085 6(10)	0.193 8(18)	0.277 1(6)	164(6)
O16-H16B...O9 ⁱⁱⁱ	0.085 0(10)	0.216(4)	0.293 9(5)	151(7)
N1-H1A...O15 ^{iv}	0.086	0.211	0.295 0(5)	166
N3-H3A...O15 ^v	0.086	0.248	0.307 2(5)	127

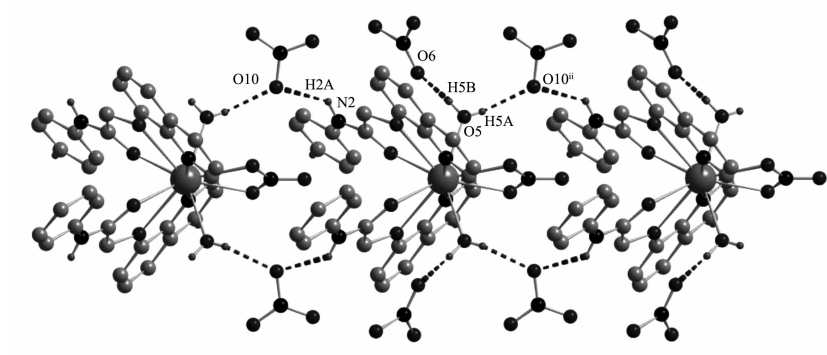
Symmetry codes: ⁱⁱ *x*, *y*+1, *z* for **1**; ⁱⁱⁱ *x*+1, *y*, *z*; ^{iv} *x*, *y*-1, *z*; ^v *x*-1, *y*-1, *z* for **2**

Because of an additional crystal water molecular, complex **2** (Fig.1b and 2b) has different crystal system from complex **1**. However, the coordination behavior of the center metal ion in both complexes are similar. The bond lengths of Pr-N (2.631(4) and 2.643(4) nm) and Pr-O (2.439(3)~2.666(3) nm) are shorter than that of La-N and La-O bonds in complex **1**, which may be due to lanthanide contraction [4]. In the crystal, abundant O-H...O and N-H...O hydrogen bonds are helpful to consolidate an extended structure paralleling to (110) plane (Fig.4 and Table 3).

2.2 IR spectra

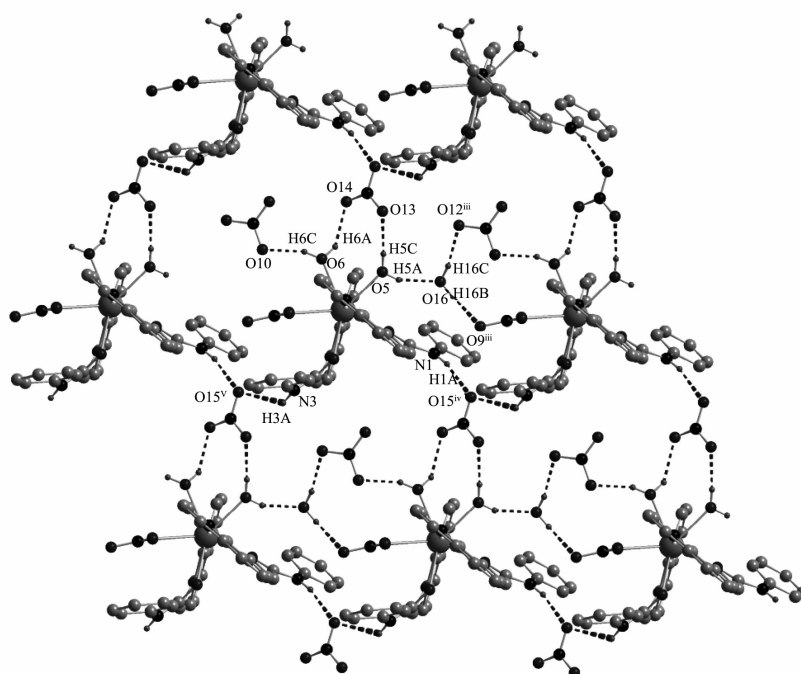
The IR spectra of **L** show strong band at 1 699 cm⁻¹, which are attributable to stretch vibrations

of the carbonyl group of amide ($\nu(\text{C=O})$). The peak at 1 618 cm⁻¹ should be assigned to the $\nu(\text{C=N})$ and the peak at 1 247 cm⁻¹ to $\nu(\text{Ar-O-C})$ [2]. Upon coordination with Ln(III) ion, $\nu(\text{C=O})$, $\nu(\text{C=N})$ and $\nu(\text{Ar-O-C})$ shift about 40, 35 and 11 cm⁻¹, respectively; indicating that carboxyl oxygen atom and quinoline nitrogen atom take part in the coordination in both complexes [1-2,9-10]. In addition, the two intense absorption bands in the spectra of both complexes associated with the asymmetric stretching appear at around 1 315 (ν_4) and 1 475 cm⁻¹ (ν_1), clearly establishing that there are some coordinated NO₃ groups (*C_{2v}*). The differences between the two bands lie at about 160 cm⁻¹, suggesting that the coordinated nitrate groups are



Symmetry code: ⁱⁱ *x*, *y*+1, *z*

Fig.3 Chain-like structure along the *b* axis formed by hydrogen bonds (dashed line) in complex **1**



Symmetry code: ⁱⁱⁱ $x+1, y, z$; ^{iv} $x, y-1, z$; ^v $x-1, y-1, z$.

Fig.4 Extended structure paralleling to [110] plane formed by hydrogen bonds (dashed line) in complex **2**

bidentate^[9-10]. The aqueous $\nu(\text{O-H})$ bands at about 3 380 cm^{-1} and the medium intensity bands at about 915 cm^{-1} show that there are some coordinative water molecules in both complexes^[2]. 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

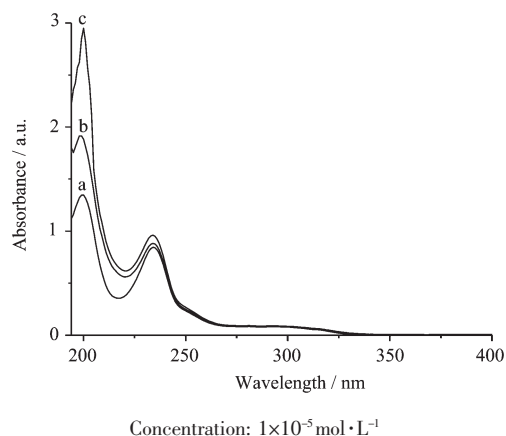


Fig.3 UV spectra of L (a), **1** (b) and **2** (c) in CH_3CN solution at room temperature

main bands located around 200 ($\epsilon/(\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})$, 134 700), 234 ($\epsilon/(\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})$, 84 400) and 292 nm ($\epsilon/(\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})$, 8 200), respectively. The bands could be assigned to characteristic $\pi-\pi^*$ transitions centered on benzene ring, quinoline ring and the acetamide unit, respectively^[10]. The spectra of **1** and **2** are quite similar as that of L. The ϵ values ($\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) of the corresponding bands in complexes **1** and **2** are 191 500, 88 200, 8 900 and 294 700, 96 100, 8 300, 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 around 238 and 382 nm, respectively (Fig.4). It also can be seen that the emission intensity of the complexes are lower than that of L, this is probably due to the coordination of $\text{Ln}(\text{III})$ ion influencing the fluorescence emission of the ligand L^[5].

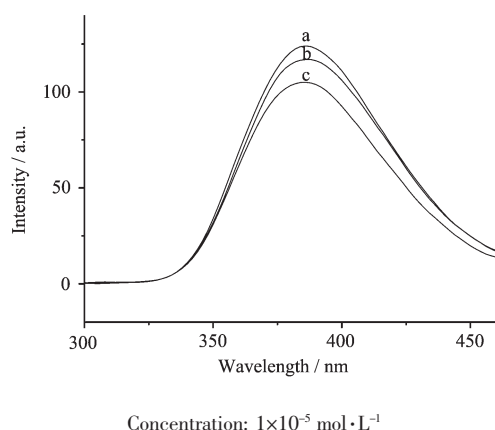


Fig.4 Fluorescence emission spectra of L (a), **1** (b) and **2** (c) in CH₃CN solution at room temperature

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