三个喹啉氧基乙酰胺镧系(Eu、Gd、Er)配合物的合成、结构及 Eu 配合物的荧光性质

毛盼东　　陈　亮*　　吴伟娜*　　贾　磊　　王　元

(河南理工大学物理化学学院，焦作　454000)

摘要： 合成并通过单晶衍射表征了 3 个稀土配合物 Ln(L)(NO₃)₃(H₂O)(L=N-苯基-2-(5-氯-8-喹啉氧基)乙酰胺，Ln=Eu (**1**)，Gd (**2**)，Er (**3**))，结构与拥有相同有机配体的 Pr，Nd 和 Sm 配合物同构。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 1 个配体 L 的 2 个氧原子和 1 个氮原子，3 个双齿配位硝酸根和 1 个水分子配位。配合物 **1** 能够发射 Eu(Ⅲ)离子特征荧光，荧光寿命为 437 μs。

关键词： 酰胺配体；喹啉；稀土配合物；荧光；晶体结构
中图分类号： O614.33⁺8；O614.33⁺9；O614.344　　　**文献标识码：** A　　　**文章编号：** 1001-4861(2016)05-0336-07
DOI： 10.11862/CJIC.2016.050

Three Lanthanide (Eu, Gd, Er) Complexes with Quinolinyloxy Acetamide Ligand: Syntheses, Crystal Structures and Fluorescence Property of Eu Complex

MAO Pan-Dong　　CHEN Liang*　　WU Wei-Na*　　JIA Lei　　WANG Yuan

(*Department of Physics and Chemistry, Henan Polytechnic University, Jiaozuo, Henan 454000, China*)

Abstract: Three lanthanide(Ⅲ) complexes Ln(L)(NO₃)₃(H₂O) based on L (Ln=Eu (**1**), Gd (**2**), Er (**3**); L=N-phenyl-2-(5-chloro-quinolin-8-yloxy) acetamide) have been synthesized and characterized by elemental analyses, IR spectra and X-ray diffraction analyses. The results reveal that all three complexes are isostructral with those of the Pr, Nd and Sm complexes bearing same ligand. The Ln(Ⅲ) ion in each complex is surrounded by one tridentate L with NO₂ donor set, three bidentate nitrate anions and one water molecule, thus giving bicapped square antiprism coordination geometry. In addition, complex **1** could exhibit characteristic fluorescent emissions of the Eu(Ⅲ) ion in the visible region with the average lifetime being 437 μs. CCDC: 1419225, **1**; 1419226, **2**; 1419227, **3**.

Keywords: amide type ligand; quinolone; lanthanide complex; fluorescence; crystal structure

　　Eu(Ⅲ) and Tb(Ⅲ) complexes have been paid much attention due to their good luminescent properties, such as the large stokes shifts, narrow emission profiles, long lifetimes and so on[1-2]. Generally, direct excitation of Eu(Ⅲ) or Tb(Ⅲ) ion is not efficient because of its inherently small absorption cross section[2]. In particular, an organic chromophore, which serves as an antenna or sensitizer, absorbing the excitation light and transferring the energy from its lowest triplet state energy level (T) to the resonance level of Eu(Ⅲ) and Tb(Ⅲ) ions, is highly desired[1-8].

　　In fact, our previous work has proved that the Sm(Ⅲ) complex with N-phenyl-2-(5-chloro-quinolin-8-yloxl) acetamide exhibit the characteristic emission of

the Sm(Ⅲ) ion[9]. As a continuation of our research, we report here the structures of the ligand′s another three Ln(Ⅲ) complexes (Ln=Eu, Gd and Er), together with the fluorescence property of the Eu complex.

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 (ν=4 000~400 cm^{-1}) were determined by the KBr pressed disc method on a Bruker V70 FT-IR spectrophotometer. Fluorescent emission spectra were determined on an Edinburgh FLS980 spectrophotometer.

1.2 Preparations of complexes 1~3

The Ln(Ⅲ) (Ln=Eu, **1**; Gd, **2**; Er, **3**) complexes have been synthesized according to the literature method[9].

1: Colorless blocks. Anal. Calcd. for $C_{17}H_{14}ClN_5O_{12}Eu$(%): C, 30.58; H, 2.11; N, 10.49. Found(%): C, 30.62; H, 2.00; N, 10.55. FT IR (cm^{-1}): ν(O-H) 3 410, ν(C=O) 1 661, ν(C=N) 1 575, ν(Ar-O-C) 1 170, ν_1(NO$_3$) 1 502, ν_4(NO$_3$) 1 293, ρ(O-H) 882.

2: Colorless blocks. Anal. Calcd. for $C_{17}H_{14}ClN_5O_{12}Gd$(%): C, 30.34; H, 2.10; N, 10.41. Found(%): C, 30.23; H, 2.21; N, 10.49. FT IR (cm^{-1}): ν(O-H) 3 400, ν(C=O) 1 663, ν(C=N) 1 570, ν(Ar-O-C) 1 169, ν_1(NO$_3$) 1 506, ν_4(NO$_3$) 1 290, ρ(O-H) 876.

3: Colorless blocks. Anal. Calcd. for $C_{17}H_{14}ClN_5O_{12}Er$(%): C, 29.89; H, 2.07; N, 10.25. Found(%): C, 30.12; H, 1.94; N, 10.33. FT IR (cm^{-1}): ν(O-H) 3 404, ν(C=O) 1 661, ν(C=N) 1 575, ν(Ar-O-C) 1 169, ν_1(NO$_3$) 1 502, ν_4(NO$_3$) 1 287, ρ(O-H) 878.

1.3 X-ray crystallography

The X-ray diffraction measurement for complexes **1**~**3** were performed on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) by using φ-ω scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program[10]. The structures were solved by direct methods and refined by fullmatrixleast-square on F^2 using the SHELXTL-97 program[11]. All non-hydrogen atoms were refined anisotropically. The 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 complexes **1**~**3** are summarized in Table 1.

CCDC: 1419225, **1**; 1419226, **2**; 1419227, **3**.

Table 1　Selected crystallographic data for complexes 1~3

	1	**2**	**3**
Empirical formula	$C_{17}H_{14}ClN_5O_{12}Eu$	$C_{17}H_{14}ClN_5O_{12}Gd$	$C_{17}H_{14}ClN_5O_{12}Er$
Formula weight	668.75	674.04	684.05
T / K	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / nm	1.101 8(3)	1.101 10(5)	1.099 41(4)
b / nm	0.888 1(2)	0.886 09(4)	0.878 13(4)
c / nm	2.494 6(6)	2.491 02(10)	2.465 82(9)
β / (°)	111.353(9)	111.275(2)	110.626(2)
V / nm^3	2.273 4(10)	2.264 79(17)	2.227 97(15)
Z	4	4	4
D_c / (g·cm^{-3})	1.954	1.977	2.039
Unique reflection	3 996	3 982	3 926
R_{int}	0.021 1	0.020 5	0.023 1

Continued Table 1

GOF on F^2	1.052	1.063	1.044
R indices [$I>2\sigma(I)$]	R_1=0.020 4, wR_2=0.046 1	R_1=0.019 6, wR_2=0.046 9	R_1=0.020 1, wR_2=0.048 7
R indices (all data)	R_1=0.024 4, wR_2=0.047 8	R_1=0.023 2, wR_2=0.048 6	R_1=0.024 3, wR_2=0.050 8
Largest peak and hole / (e·nm^{-3})	378 and −459	562 and −725	516 and −547

2　Results and discussion

2.1　Crystal structures of the complexes

Selected bond distances, hydrogen bonds information for complexes **1**~**3** are summarized in Table 2

and 3, respectively. As shown in Fig.1a~c, complexes **1**~**3**, namely Ln(L)(NO$_3$)$_3$(H$_2$O) (Ln=Eu (**1**), Gd (**2**), Er (**3**)) are isostructural and crystallize in the monoclinic, space group $P2_1/c$, same as the reported Pr, Nd and Sm complexes with same ligand[9]. The Ln(Ⅲ) ion in

Table 2　Selected bond lengths (nm) and bond angles (°) in complexes 1~3

1					
Eu1-O12	0.237 1(2)	Eu1-O6	0.249 2(2)	Eu1-O4	0.253 4(2)
Eu1-O2	0.237 94(19)	Eu1-O11	0.251 6(3)	Eu1-O3	0.254 0(2)
Eu1-O9	0.246 4(3)	Eu1-O8	0.251 9(2)	Eu1-N1	0.257 8(2)
Eu1-O1	0.260 11(19)				
O12-Eu1-O2	142.45(7)	O12-Eu1-O4	70.38(6)	O9-Eu1-N1	158.99(9)
O12-Eu1-O9	79.76(9)	O2-Eu1-O4	138.83(7)	O6-Eu1-N1	69.65(8)
O2-Eu1-O9	78.36(8)	O9-Eu1-O4	89.17(8)	O11-Eu1-N1	133.01(8)
O12-Eu1-O6	85.69(8)	O6-Eu1-O4	139.99(7)	O8-Eu1-N1	113.86(7)
O2-Eu1-O6	78.43(8)	O11-Eu1-O4	72.13(8)	O4-Eu1-N1	75.36(7)
O9-Eu1-O6	118.33(9)	O8-Eu1-O4	136.75(6)	O3-Eu1-N1	68.84(7)
O12-Eu1-O11	116.84(9)	O12-Eu1-O3	117.89(7)	O12-Eu1-O1	140.95(7)
O2-Eu1-O11	69.61(8)	O2-Eu1-O3	98.55(7)	O2-Eu1-O1	61.92(6)
O9-Eu1-O11	50.84(9)	O9-Eu1-O3	111.95(9)	O9-Eu1-O1	137.98(8)
O6-Eu1-O11	147.64(8)	O6-Eu1-O3	127.55(7)	O6-Eu1-O1	68.56(7)
O12-Eu1-O8	69.60(7)	O11-Eu1-O3	64.35(8)	O11-Eu1-O1	99.55(8)
O2-Eu1-O8	74.06(7)	O8-Eu1-O3	172.51(6)	O8-Eu1-O1	109.98(6)
O9-Eu1-O8	68.26(9)	O4-Eu1-O3	50.18(6)	O4-Eu1-O1	111.23(6)
O6-Eu1-O8	50.58(7)	O12-Eu1-N1	81.66(8)	O3-Eu1-O1	64.53(6)
O11-Eu1-O8	113.09(8)	O2-Eu1-N1	122.63(7)	N1-Eu1-O1	62.41(7)
2					
Gd1-O12	0.235 6(2)	Gd1-O6	0.248 2(2)	Gd1-O4	0.251 64(19)
Gd1-O2	0.236 85(19)	Gd1-O11	0.251 4(2)	Gd1-O3	0.253 38(19)
Gd1-O9	0.245 4(2)	Gd1-O8	0.251 49(19)	Gd1-N1	0.257 2(2)
Gd1-O1	0.258 84(19)				
O12-Gd1-O2	142.08(7)	O12-Gd1-O4	70.30(6)	O9-Gd1-N1	158.48(9)
O12-Gd1-O9	79.55(9)	O2-Gd1-O4	139.03(7)	O6-Gd1-N1	69.79(7)
O2-Gd1-O9	78.55(8)	O9-Gd1-O4	88.46(8)	O11-Gd1-N1	132.96(8)
O12-Gd1-O6	85.72(7)	O6-Gd1-O4	140.25(7)	O8-Gd1-N1	114.08(7)
O2-Gd1-O6	78.20(8)	O11-Gd1-O4	72.08(7)	O4-Gd1-N1	75.52(7)
O9-Gd1-O6	118.60(8)	O8-Gd1-O4	136.39(6)	O3-Gd1-N1	68.75(7)
O12-Gd1-O11	117.04(8)	O12-Gd1-O3	117.87(6)	O12-Gd1-O1	141.16(7)

Continued Table 2

O2-Gd1-O11	69.59(8)	O2-Gd1-O3	98.95(6)	O2-Gd1-O1	62.04(6)
O9-Gd1-O11	50.88(9)	O9-Gd1-O3	111.80(8)	O9-Gd1-O1	138.08(8)
O6-Gd1-O11	147.43(8)	O6-Gd1-O3	127.51(7)	O6-Gd1-O1	68.71(7)
O12-Gd1-O8	69.52(7)	O11-Gd1-O3	64.38(7)	O11-Gd1-O1	99.16(8)
O2-Gd1-O8	73.73(7)	O8-Gd1-O3	172.61(6)	O8-Gd1-O1	110.26(6)
O9-Gd1-O8	68.29(8)	O4-Gd1-O3	50.38(6)	O4-Gd1-O1	111.48(6)
O6-Gd1-O8	50.79(7)	O12-Gd1-N1	81.53(8)	O3-Gd1-O1	64.41(6)
O11-Gd1-O8	112.92(8)	O2-Gd1-N1	122.95(7)	N1-Gd1-O1	62.72(7)

3

Er1-O12	0.230 3(2)	Er1-O6	0.242 4(2)	Er1-O3	0.249 6(2)
Er1-O2	0.232 0(2)	Er1-O4	0.246 9(2)	Er1-O11	0.250 8(2)
Er1-O9	0.239 9(2)	Er1-O8	0.248 8(2)	Er1-N1	0.252 1(3)
Er1-O1	0.253 9(2)				

O12-Er1-O2	140.99(8)	O12-Er1-O3	118.53(7)	O9-Er1-N1	156.55(9)
O12-Er1-O9	78.58(9)	O2-Er1-O3	99.15(7)	O6-Er1-N1	69.99(8)
O2-Er1-O9	78.55(9)	O9-Er1-O3	111.38(8)	O4-Er1-N1	75.89(8)
O12-Er1-O6	85.28(8)	O6-Er1-O3	127.40(8)	O8-Er1-N1	114.96(8)
O2-Er1-O6	79.03(8)	O4-Er1-O3	51.33(7)	O3-Er1-N1	68.91(8)
O9-Er1-O6	119.40(8)	O8-Er1-O3	171.96(7)	O11-Er1-N1	132.40(8)
O12-Er1-O4	70.28(7)	O12-Er1-O11	117.73(9)	O12-Er1-O1	141.43(8)
O2-Er1-O4	138.55(7)	O2-Er1-O11	68.76(8)	O2-Er1-O1	63.03(7)
O9-Er1-O4	86.31(8)	O9-Er1-O11	51.63(9)	O9-Er1-O1	138.87(8)
O6-Er1-O4	140.60(8)	O6-Er1-O11	147.60(9)	O6-Er1-O1	68.92(8)
O12-Er1-O8	69.46(7)	O4-Er1-O11	71.57(8)	O4-Er1-O1	112.44(7)
O2-Er1-O8	72.83(7)	O8-Er1-O11	112.62(8)	O8-Er1-O1	110.54(7)
O9-Er1-O8	68.15(9)	O3-Er1-O11	63.71(8)	O3-Er1-O1	64.16(7)
O6-Er1-O8	51.54(8)	O12-Er1-N1	81.08(9)	O11-Er1-O1	98.29(9)
O4-Er1-O8	135.60(7)	O2-Er1-N1	124.89(8)	N1-Er1-O1	63.65(8)

Table 3　Hydrogen bond information in complexes 1~3

D–H···A	d(D-H) / nm	d(H···A) / nm	d(D···A) / nm	$\angle$DHA / (°)
1				
O12–H12A···O4[i]	0.085 2(10)	0.202 8(13)	0.286 4(3)	167(3)
O12–H12B···O8[ii]	0.085 2(10)	0.188 4(11)	0.273 5(3)	176(4)
N2–H2A···O3[iii]	0.092	0.201	0.287 5(3)	156.3
2				
O12–H12A···O4[i]	0.085 1(10)	0.204 5(14)	0.287 4(3)	164(3)
O12–H12B···O8[ii]	0.085 0(10)	0.189 1(11)	0.273 8(3)	175(3)
N2–H2A···O3[iii]	0.091	0.201	0.287 1(3)	156.0
3				
O12–H12A···O4[i]	0.084 9(10)	0.204 2(13)	0.287 5(3)	166(3)
O12–H12B···O8[ii]	0.085 3(10)	0.189 8(11)	0.275 0(3)	177(4)
N2–H2A···O3[iii]	0.089	0.203	0.286 6(3)	155.2

Symmetry code: [i] $-x+1$, $y+1/2$, $-z+1/2$; [ii] $-x+1$, $y-1/2$, $-z+1/2$; [iii] $-x+1$, $-y$, $-z$
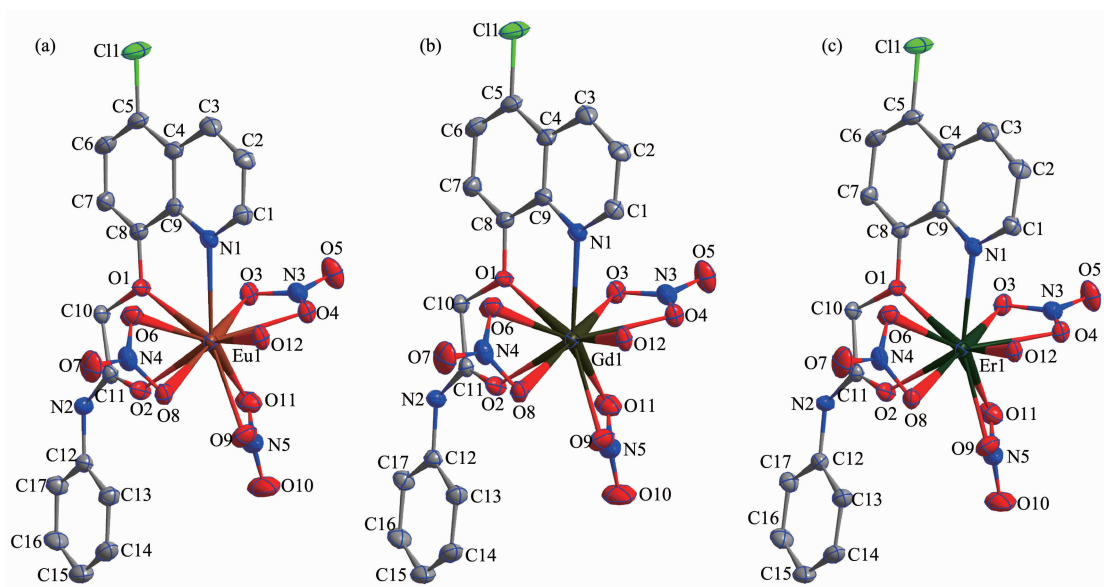
Fig.1 Molecular structures of complexes **1** (a), **2** (b) and **3** (c) shown with 30% probability displacement ellipsoids

each complex is surrounded by one tridentate L with NO_2 donor set, three bidentate nitrate anions and one water molecule, thus giving bicapped square antiprism coordination geometry. The Ln-O/N bond length decreases gradually with the increase of the atomic number of Ln(Ⅲ) ions, which is consistent with the effect of lanthanide contraction. Similarly, in the crystal of each complex, intermolecular O –H ··· O (O12–H12A···O4[i] and O12–H12B···O8[ii]) and N–H··· O (N2–H2A···O3[iii]) hydrogen bonds link the complexes into a 2D supramolecular network (Symmetry code: [i] $-x+1$, $y+1/2$, $-z+1/2$; [ii] $-x+1$, $y-1/2$, $-z+1/2$; [iii] $-x+1$, $-y$, $-z$).

2.2 IR spectra

The spectral regions for all the complexes are more or less similar due to the similarity in coordination modes of the ligand with the metal centre. The free ligand L exhibit three absorption bands at 1 682, 1 598 and 1 241 cm^{-1}, assigned to $\nu(C=O)$, $\nu(C=N)$ and $\nu(C\text{-}O\text{-}C)$, respectively[5-9]. However, in the complexes, three absorption bands assigned to $\nu(C=O)$, $\nu(C=N)$ and $\nu(C\text{-}O\text{-}C)$ in free ligand shift evidently to lower frequency, indicating that the oxygen atoms of the carbonyl group, quinoline nitrogen atoms and ethereal oxygen atoms take part in coordination to the central Ln(Ⅲ) ion. Additionally, for all complexes, the characteristic absorptions of bidentate coordinated

nitrate anions and coordinative water molecule could be observed[9]. It is in accordance with the result of the crystal structure study.

2.3 Fluorescence spectra

As shown in Fig.2, emission transitions from $^5D_0$ to ^7F_J (J=1, 2, 3) of Eu(Ⅲ) ion are clearly observed in the spectrum of Eu(Ⅲ) complex **1** (excited at 338 nm)[4-8]. It is found that the intensity of $^5D_0 \rightarrow {^7F_2}$ transition is higher than that of $^5D_0 \rightarrow {^7F_1}$ transition, and the intensity ratio is equal to 5.39, showing that the line-like emission spectrum results from intra-4f transitions of predominantly electric dipole character. Thus, Eu(Ⅲ) lies in a non-centrosymmetric ligand field[5-8], which is in agreement with the result of the X-ray crystal structure analysis. By contrast, the emission intensity of the literature complex [Eu (L[1])$_2$ (NO$_3$)$_2$]NO$_3$ (L[1] =N-(phenyl)-2-(quinolin-8-yloxy)acetamide) [8] (excited at 332 nm) is much less than that of complex **1**. In addition, complex **1** exhibits almost none of the free ligand emission band, indicating an efficiently intermolecular energy transfer from the ligand L to the Eu(Ⅲ) ion[12-13]. The luminescence decay of complexes **1** and [Eu(L[1])$_2$(NO$_3$)$_2$]NO$_3$ were measured in solid state at room temperature (Fig.3). The lifetime of complex **1** and [Eu(L[1])$_2$(NO$_3$)$_2$]NO$_3$ is fitted to be 437 and 325 μs, respectively, which is moderate compared with some reported Eu(Ⅲ) β-diketonate complexes[12].
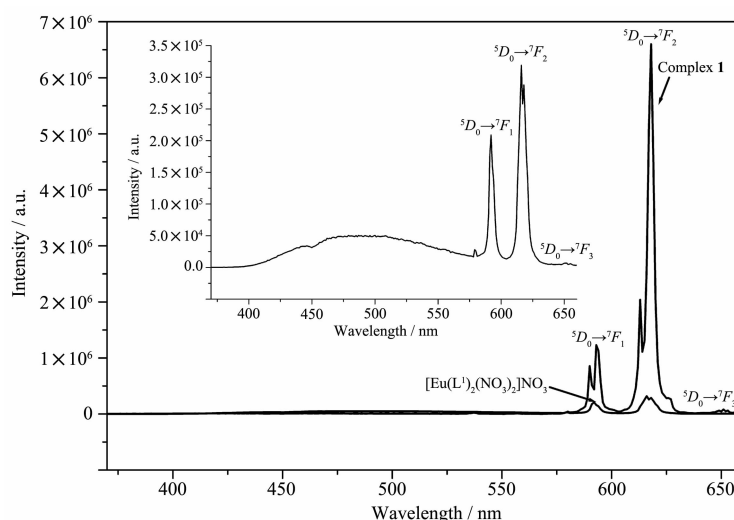
Inset: enlarge view of the emission spectra of $[Eu(L^1)_2(NO_3)_2]NO_3$

Fig.2　Fluorescence emission spectra of complex **1** (excited at 338 nm) and $[Eu(L^1)_2(NO_3)_2]NO_3$ (excited at 332 nm) in solid state at room temperature
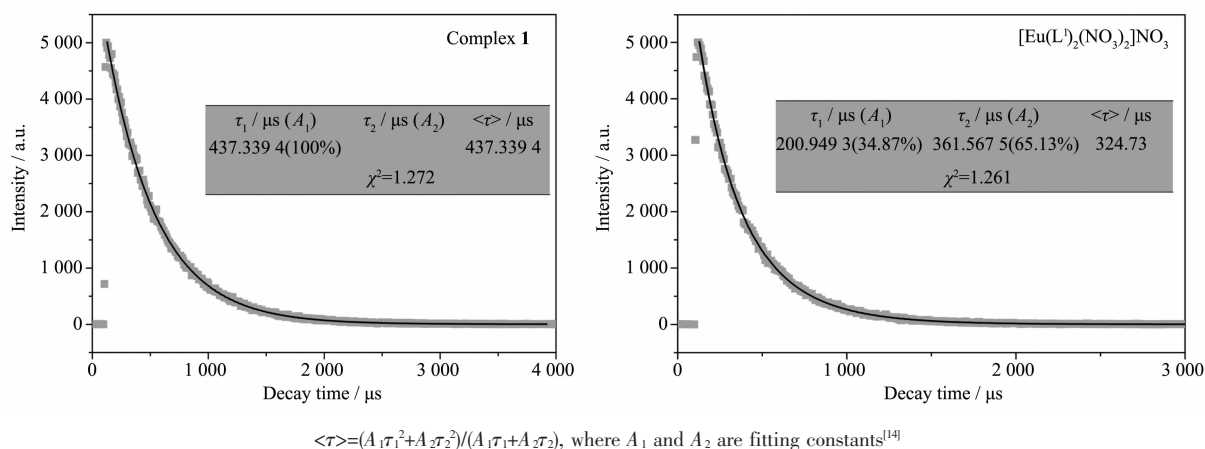
$<\tau>=(A_1\tau_1^2+A_2\tau_2^2)/(A_1\tau_1+A_2\tau_2)$, where A_1 and A_2 are fitting constants[14]

Fig.3 Fluorescence decay dots and fitted curves of complex **1** and $[Eu(L^1)_2(NO_3)_2]NO_3$

To fully understand the energy transfer processes between the Eu(Ⅲ) ion and the organic ligand L, phosphorescence spectrum of the Gd complex **2** was recorded. At 77 K in a solution of methanol-ethanol (1∶1, *V/V*), complex **2** display only one weak phosphorescent emission band at 473 nm, which can be assumed to be the 0-0 transition[4-8]. The triplet state energy level *T* of the ligand L, which was calculated from the shortest wavelength phosphorescence band of the corresponding Gd(Ⅲ) complex **2**[4-8], is 21 142 cm⁻¹, while that of L^1 is 22 831 cm⁻¹ (438 nm) as reported[8]. The energy level *T* of the ligand L is above the lowest excited resonance level $^5D_1$ of Eu(Ⅲ) (19 020 cm⁻¹), indicating that the absorbed energy could be trans-ferred from ligand to the Eu ion. Furthermore, it is demonstrated that the intramolecular transfer efficiency depends mainly on two energy transfer processes: one is from the lowest triplet level of ligand to the resonance level of Ln(Ⅲ) by resonant exchange interaction; the other is just an inverse energy transfer by the thermal de-excitation mechanism. Both energy transfer rate constants are dependent on the energy difference $(\Delta E_{T-^5D_1})$[15-16]. It has been noted that the well suitable ΔE in the range of 1 000~2 000 cm⁻¹ is associated with the strong fluorescence emission of Eu(Ⅲ) complex[16]. According to this, the strong luminescence of complex **1** should be due to the optimal $\Delta E_{T-^5D_1}$ (2 122 cm⁻¹), thus confirming that the

ligand L possesses higher energy transfer efficiency to the Eu(Ⅲ) ion than the reported ligand L^1 (3 811 cm^{-1}). Comparing the structures of both ligands, it can be roughly concluded that the high emission intensity of complex **1** may be attributed to the additional electron -accepting chloro-substitute on the quinoline ring in the ligand L. Based on these studies, some new aryl amide type ligands could be synthesized to optimize the fluorescence properties of Eu(Ⅲ).

References:

[1] Binnemans K. *Coord. Chem. Rev*., **2015**,**295**:1-45

[2] Bünzli J C G. *Coord. Chem. Rev*., **2015**,**293**-**294**:19-47

[3] Yan Z Z, Hou N, Wang C M. *Spectrochim. Acta A*, **2015**, **137**:1265-1269

[4] Song X Q, Xing D Y, Lei Y K, et al. *Inorg. Chim. Acta*, **2013**,**404**:113-122

[5] Wu W N, Tang N, Yan L. *Spectrochim. Acta A*, **2008**,**71**: 1461-1465

[6] Wu W N, Cheng F X, Yan L, et al. *J. Coord. Chem.*, **2008**, **61**:2207-2215

[7] Wu W N, Tang N, Yan L. *J. Fluoresc.*, **2008**,**18**:101-107

[8] Wu W N, Yuan W B, Tang N, et al. *Spectrochim. Acta A*, **2006**,**65**:912-918

[9] CAI Hong-Xin(蔡红新). *Thesis for the Master of Henan Polytechnic University*(河南理工大学硕士论文). **2014**.

[10]Sheldrick G M. *SADABS*, University of Göttingen, Germany, **1996**.

[11]Sheldrick G M. *SHELX*-97, *Program for the Solution and the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[12]Li J, Li H, Yan P, et al. *Inorg. Chem.*, **2012**,**51**:5050-5057

[13]Li L, Zhao X, Xiao N, et al. *Inorg. Chim. Acta*, **2015**,**426**: 107-112

[14]Buddhudu S, Morita M, Murakami S, et al. *J. Lumin.*, **1999**, **83**-**84**:199-203

[15]Chai W J, Li W X, Sun X J, et al. *J. Lumin.*, **2011**,**131**:225-230

[16]Sato S, Wada M. *Bull. Chem. Soc. Jpn.*, **1970**,**43**:1955-1962