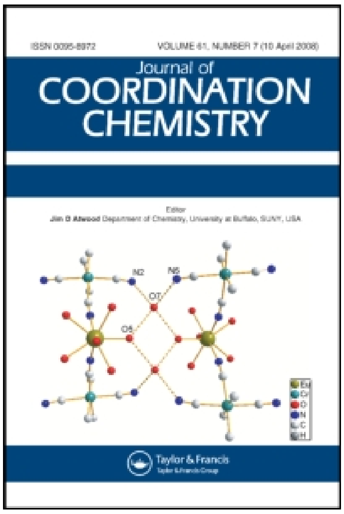

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and fluorescent properties of lanthanide complexes with two aryl amide ligands

Wei-Na Wu[a]; Fei-Xiang Cheng[a]; Lan Yan[a]; Ning Tang[a]
[a] College of Chemistry and Chemical Engineering and State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P.R. China

To cite this Article Wu, Wei-Na , Cheng, Fei-Xiang , Yan, Lan and Tang, Ning(2008) 'Synthesis, characterization and fluorescent properties of lanthanide complexes with two aryl amide ligands', Journal of Coordination Chemistry, 61: 14, 2207 — 2215

To link to this Article: DOI: 10.1080/00958970801901329

URL: http://dx.doi.org/10.1080/00958970801901329

Journal of Coordination Chemistry
Vol. 61, No. 14, 20 July 2008, 2207–2215

Taylor & Francis
Taylor & Francis Group

Synthesis, characterization and fluorescent properties of lanthanide complexes with two aryl amide ligands

WEI-NA WU, FEI-XIANG CHENG, LAN YAN and NING TANG*

College of Chemistry and Chemical Engineering and State Key Laboratory of Applied
Organic Chemistry, Lanzhou University, Lanzhou 730000, P.R. China

(*Received 26 August 2007; in final form 3 October 2007*)

Two aryl amide ligands, *N*-(p-tolyl)-2-(quinolin-8-yloxy)acetamide (**L^1**) and *N*-(4-chlorophenyl)-2-(quinolin-8-yloxy)acetamide (**L^2**), were synthesized. With these ligands, two series of lanthanide(III) complexes were prepared, $Ln(L^n)_2(NO_3)_3$ ($n = 1, 2$; Ln = La, Sm, Eu, Gd, Dy), and characterized by the elemental analyses, molar conductivity, ^{1}H NMR spectra, IR spectra and TG-DTA. The fluorescence properties of the complexes and the triplet state energies of the ligands were studied in detail. In addition, the quantum yields of both Eu(III) complexes and $Eu(L^0)_2(NO_3)_3$ [where **L^0** is N-(phenyl)-2-(quinolin-8-yloxy)acetamide] [1] were calculated. The results indicate that among the lowest triplet energies (T) of the three ligands, that of **L^2** is most suitable to the resonance level ($^5D_1$) of Eu(III) ion. Furthermore, $Eu(L^2)_2(NO_3)_3$ has the highest fluorescence intensity and quantum yield of the three Eu(III) complexes.

Keywords: Lanthanide complexes; Aryl amide; Synthesis; Fluorescence properties; Triplet state energy

1. Introduction

Europium(III) is the most extensively studied of various luminescent materials largely due to its long-lived, millisecond lifetime, narrow-width emission bands and hypersensitivity to coordination environment [2–6]. However, direct excitation of Eu(III) is not efficient because of its small absorption cross section. To overcome this problem, 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) ion, is desired [7, 8]. Such energy transfer is one of the most important processes determining the fluorescence properties of Eu(III) complexes.

The inherent nature of amide-based, open-chain ligands, such as ring-like coordination structure and terminal group effects [9–11], enables them to shield the encapsulated ion effectively from interaction with the surroundings and has strong antenna effect to Eu(III) ion [12, 13]. Therefore, two amide-based open-chain ligands were selected as "antennae" in this work; the lowest triplet energy levels of the ligands (T) and the fluorescence quantum yields of their Eu(III) complexes were studied in detail.

---

*Corresponding author. Email: tangn@lzu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970801901329

2. Experimental

2.1. *Materials*

The lanthanide(III) nitrates were prepared from their oxides, acquired from Yue Long (P. R. C). All other chemicals used were of analytical grade. Absolute chloroform and N,N′-dimethylformamide (DMF) were obtained after distillation by standard methods.

2.2. *Physical measurements*

The melting points of the ligands were determined on a XT4-100x microscopic melting point apparatus (made in Beijing, China). Elemental analyses were carried out on an Elemental Vario EL analyzer. The metal contents of the complexes were determined by titration with EDTA. The infrared spectra (IR, $\nu = 4000$–$400\,\mathrm{cm^{-1}}$) were determined by the KBr pressed disc method on a Nicolet-170SX FT-IR spectrophotometer. The 200 MHz ^{1}H NMR spectra were recorded on a Bruker DRX-200 spectrometer in CD_3COCD_3 solutions with TMS as internal standard. All conductivity measurements were carried out with a DDS-11A conductometer bridge (made in China) using $1.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ solution in acetonitrile at 25°C. Thermal behavior was monitored on a PCT-2 differential thermal analyzer and α-Al_2O_3 was used as a reference in static air. The mass spectrum was obtained on a HP-5988 EI mass spectrometer. Absorption spectra were measured on a Shimadzu UV-240 spectrophotometer. Fluorescence emission and excitation spectra were determined on a Hitachi F-4 500 FL spectrophotometer. Phosphorescence spectra at 77 K were taken on the same spectrophotometer equipped with phosphorescence measurement apparatus. All the complexes were dried at 100°C to constant weight before these measurements.

2.3. *Synthesis of ligands*

The synthesis is shown in figure 1. Compounds **1** [2-chloro-*N*-(4-R-phenyl)acetamide] (figure 1) and $\mathbf{L}^n$ were prepared according to literature methods [1]. $\mathbf{L^1}$: yield 36%, m.p. 128–130°C; EI-MS, *m*/*z*: 292 (M^+) $\mathbf{L^2}$: yield 42%. m.p. 146–147°C; EI-MS, *m*/*z*: 312 (M^+)

The ^{1}H NMR chemical shifts δ (ppm/TMS) for $\mathbf{L^1}$ and $\mathbf{L^2}$ in CD_3COCD_3 are listed in table 2.

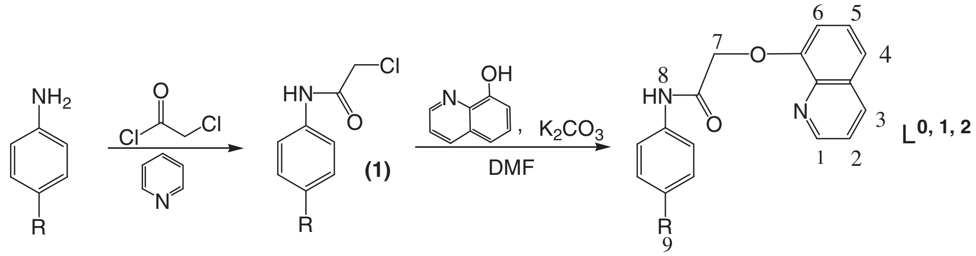

Figure 1. Synthesis of the ligands ($\mathbf{L^0}$: R = H; $\mathbf{L^1}$: R = CH_3; $\mathbf{L^2}$: R = Cl).

2.4. *Synthesis of the complexes*

The ligand ($\mathbf{L}^n$) (0.1 mmol) was dissolved in ethyl acetate (2 mL) and then was added dropwise to an ethyl acetate solution (2 mL) containing $Ln(NO_3)_3 \cdot nH_2O$ (0.05 mmol). After stirring for 4 h at room temperature, the precipitate was separated from the solution by suction filtration, purified by washing several times with ethyl acetate, and dried for 24 h in a vacuum. The yields were in the 50–60% range.

3. Results and discussion

3.1. *Properties of the complexes*

The elemental analyses (table 1) show that the complexes are $Ln(\mathbf{L}^n)_2(NO_3)_3$ ($n = 1, 2$), white powders, soluble in DMF, DMSO, acetone, methanol, acetonitrile and ethanol, slightly soluble in ethyl acetate and insoluble in water and ether. The molar conductivity values of the complexes in acetonitrile are in the range 58–73 $s\,cm^2 \cdot mol^{-1}$, indicating non-electrolytes [14].

3.2. *^1H NMR spectra*

The ^1H NMR spectra of the free ligands and their La(III) complexes were measured in CD_3COCD_3 at room temperature (table 2). For $\mathbf{L^1}$, the signals of H_1, H_2–H_5

Table 1. Analytical and molar conductance data for the complexes.

Complexes	C% found (Calc)	H% found (Calc)	N% found (Calc)	Ln% found (Calc)	Λ_m $(s \cdot cm^2 \cdot mol^{-1})$
$La(\mathbf{L^1})_2(NO_3)_3$	47.49(47.54)	3.52(3.55)	10.68(10.78)	15.7(15.3)	67.5
$Sm(\mathbf{L^1})_2(NO_3)_3$	47.12(46.95)	3.37(3.50)	10.29(10.65)	16.5(16.3)	58.3
$Eu(\mathbf{L^1})_2(NO_3)_3$	46.53(46.86)	3.42(3.50)	10.36(10.63)	16.9(16.5)	60.5
$Gd(\mathbf{L^1})_2(NO_3)_3$	46.87(46.60)	3.29(3.48)	10.76(10.57)	17.2(17.0)	70.0
$Dy(\mathbf{L^1})_2(NO_3)_3$	46.50(46.33)	3.62(3.46)	10.35(10.51)	17.2(17.4)	65.4
$La(\mathbf{L^2})_2(NO_3)_3$	43.14(42.97)	2.58(2.76)	10.59(10.32)	14.1(14.6)	72.5
$Sm(\mathbf{L^2})_2(NO_3)_3$	42.16(42.45)	2.91(2.72)	10.37(10.19)	16.1(15.6)	64.4
$Eu(\mathbf{L^2})_2(NO_3)_3$	42.77(42.38)	2.45(2.72)	10.41(10.18)	15.6(15.8)	62.0
$Gd(\mathbf{L^2})_2(NO_3)_3$	41.96(42.15)	2.87(2.71)	9.93(10.12)	16.4(16.2)	68.5
$Dy(\mathbf{L^2})_2(NO_3)_3$	42.24(41.93)	2.53(2.69)	10.30(10.07)	16.4(16.7)	71.3

Table 2. The ^1H NMR data of free ligands and their complexes in CD_3COCD_3 (ppm).

Compounds	H_1	$H_2 \sim H_5$ and $C_6H_5^a$-protons	H_6	H_7	H_8	H_9
$\mathbf{L^1}$	9.11–9.13d	7.15–7.73mt	8.40–8.45d	4.91s	10.88s	2.30s
$La(\mathbf{L^1})_2(NO_3)_3$	9.13–9.16d	7.15–7.81mt	8.52–8.56d	5.24s	10.71s	2.31s
$\mathbf{L^2}$	9.12–9.14d	7.36–7.90mt	8.41–8.45d	4.93s	11.17s	
$La(\mathbf{L^2})_2(NO_3)_3$	9.14–9.16d	7.34–7.74mt	8.52–8.56d	5.17s	10.91s	

[a] The phenyl of $\mathbf{L^1}$ and $\mathbf{L^2}$.

*s = singlet; d = doublet; mt = multiplet.

(and C_6H_5–protons), H_6, H_7, H_8 and H_9 are at 9.11–9.13, 7.15–7.73, 8.40–8.45, 4.91, 10.88 and 2.30 ppm, respectively. Upon coordination, the signals shift to 9.13–9.16, 7.15–7.81, 8.52–8.56, 5.24, 10.71 and 2.31 ppm, respectively. For $\mathbf{L^2}$, the signals of H_1, H_2–H_5 (and C_6H_5-protons), H_6, H_7 and H_8 shift by 0.02, 0.02–0.16, 0.11, 0.24 and 0.26 ppm in the La(III) complex, respectively. The signals of H_2–H_5 (and C_6H_5–protons) move to higher field, probably due to: (1) reduction of the conjugation in the ring of benzene and quinoline, (2) the flexibility in conformation of the ligand in the complex [15, 16]. It can be concluded that the oxygen of the carbonyl group, ether oxygen and quinoline nitrogen take part in coordination in $La(\mathbf{L^1})_2(NO_3)_3$ and $La(\mathbf{L^2})_2(NO_3)_3$ [15–17]. Furthermore, the larger shifts for H_8 and H_6 than for H_1 indicate that the Ln–O(C=O) and Ln–O(C–O–C) bonds are stronger than the Ln–N(C=N) bond [18].

3.3. *IR spectra*

On the basis of similar IR spectra of the complexes (table 3), similar coordination structures may be assumed. The IR spectra of the free ligands show strong bands at 1673–1677 cm^{-1}, attributable to stretch of the carbonyl group of amide (ν(C=O)). Absorptions at 1540–1549 cm^{-1} can be assigned to ν(C–N) of amide, the peak at 1603–1604 cm^{-1} to ν(C=N) and the peak at 1244–1245 cm^{-1} to ν(Ar–O–C). In the IR spectra of the lanthanide(III) complexes, the ν(C=O), ν(C–N), ν(C=N) and ν(Ar–O–C) shift by 13–35, 10–29, 8–24 and 24–35 cm^{-1}, respectively, indicating coordination by carbonyl oxygen, ether oxygen and quinoline nitrogen [19–22]. In addition, the smaller shift of 8 cm^{-1} in ν(C=N) of the $\mathbf{L^1}$ complexes is possibly due to a large steric effect, preventing the quinoline nitrogen from tight coordination with lanthanide [23]. The IR data are in accord with assumptions made on the basis of ^1H NMR spectra.

For all complexes, two intense absorption bands in the spectra associated with NO_3^- asymmetric stretching appear in the range 1312–1317 cm^{-1} (ν_4) and 1493–1511 cm^{-1} (ν_1), clearly establishing coordination [24]. The differences between the two bands are 178–195 cm^{-1}, suggesting bidentate NO_3^- groups [25].

Table 3. Major IR data of the free ligands and their complexes (cm^{-1}).

Compounds	ν(C=O)	ν(C=N)	ν(C–N)	ν(Ar–O–C)	$\nu_1(NO_3)$	$\nu_4(NO_3)$	ν_1–$\nu_4(NO_3)$
$\mathbf{L^1}$	1673	1603	1540	1245			
$La(\mathbf{L^1})_2(NO_3)_3$	1660	1612	1559	1211	1510	1315	195
$Sm(\mathbf{L^1})_2(NO_3)_3$	1649	1612	1567	1211	1510	1317	193
$Eu(\mathbf{L^1})_2(NO_3)_3$	1646	1612	1567	1213	1511	1316	195
$Gd(\mathbf{L^1})_2(NO_3)_3$	1645	1612	1568	1215	1511	1317	194
$Dy(\mathbf{L^1})_2(NO_3)_3$	1645	1611	1569	1215	1511	1317	194
$\mathbf{L^2}$	1677	1604	1549	1244			
$La(\mathbf{L^2})_2(NO_3)_3$	1661	1620	1559	1209	1493	1315	178
$Sm(\mathbf{L^2})_2(NO_3)_3$	1650	1626	1562	1216	1493	1315	178
$Eu(\mathbf{L^2})_2(NO_3)_3$	1651	1626	1562	1215	1493	1315	178
$Gd(\mathbf{L^2})_2(NO_3)_3$	1646	1627	1563	1217	1493	1315	178
$Dy(\mathbf{L^2})_2(NO_3)_3$	1642	1628	1562	1220	1493	1312	181

3.4. *TG-DTA analysis*

All complexes were dried at 100°C to constant weight before analysis. The DTA curves of free ligands have endothermic peaks at 128°C (**L^1**) and 147°C (**L^2**), respectively. But there is no weight loss on the corresponding TG curve, showing that this is a phase transition process. For complexes, there are no endothermic peaks and weight losses on the corresponding TG curves before 220°C, indicating no water in the complexes, in accord with infrared spectra and elemental analyses. For all complexes, three or four exothermic peaks appear around 223–555°C. The final products were found to be Ln_2O_3 when the temperature was above 850°C, and the weight losses of the complexes are close to the calculated values (table 4).

According to the elemental analyses, molar conductivity, ^{1}H NMR spectra, IR spectra and TG-DTA, composition of the two series of complexes are $[Ln(\mathbf{L}^n)_2(NO_3)_3]$ ($n = 1$, 2), and the coordination number for the complexes is 12. Possible molecular structures of the complexes are shown in figure 2.

Table 4. Thermal analyses of the compounds.

Compounds	T_{endo} (°C)	T_{exo} (°C) t_1	t_2	t_3	t_4	Residue (Calcd*)%
L^1	128	321	533			
$La(\mathbf{L}^1)_2(NO_3)_3$		262	336	474	483	18.21(17.92)
$Sm(\mathbf{L}^1)_2(NO_3)_3$		286	357	474	485	18.36(18.94)
$Eu(\mathbf{L}^1)_2(NO_3)_3$		285	379	468		19.53(19.09)
$Gd(\mathbf{L}^1)_2(NO_3)_3$		289	354	471	490	19.99(19.55)
$Dy(\mathbf{L}^1)_2(NO_3)_3$		286	350	407	485	20.45(20.00)
L^2	147	228	317	552		
$La(\mathbf{L}^2)_2(NO_3)_3$		275	338	437	513	17.70(17.15)
$Sm(\mathbf{L}^2)_2(NO_3)_3$		223	342	459	537	17.66(18.13)
$Eu(\mathbf{L}^2)_2(NO_3)_3$		229	338	440	518	18.85(18.27)
$Gd(\mathbf{L}^2)_2(NO_3)_3$		236	354	467	555	19.15(18.72)
$Dy(\mathbf{L}^2)_2(NO_3)_3$		272	459	541		18.64(19.15)

*The calculated value is the mass ratio of Ln_2O_3 with the corresponding $Ln(\mathbf{L}^n)_2(NO_3)_3$.

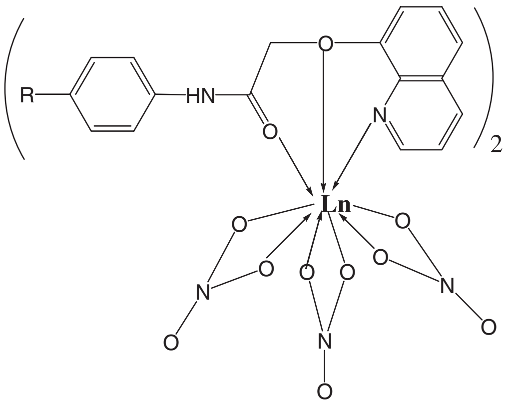

Figure 2. Possible molecular structures of the complexes (**L^1**: R = CH_3; **L^2**: R = Cl).

3.5. *Spectral properties of the complexes*

3.5.1. Fluorescence. The emission spectra of the Eu(III) complexes in solid state are shown in figure 3 **(solid)**. From the fluorescence spectral data of the Eu(III) and Sm(III) complex of each ligand in solid state (table 5), it is found that the emission intensity of the Eu(III) complex is stronger than that of the Sm(III) complex, indicating that intermolecular energy transfer from each ligand to the Eu(III) is more efficient than to Sm(III). Furthermore, the order of the emission intensity for the three Eu(III) complexes is $Eu(\mathbf{L}^2)_2(NO_3)_3 > Eu(\mathbf{L}^0)_2(NO_3)_3$ [1] $> Eu(\mathbf{L}^1)_2(NO_3)_3$. From comparison of $\mathbf{L}^{1,2}$ with $\mathbf{L}^0$, ligand $\mathbf{L}^2$ containing the electron-accepting group(−Cl) enhances the emission intensity, while the ligand $\mathbf{L}^1$ containing the electron-donating group($-CH_3$) weakens the emission intensity slightly, suggesting that the emission intensity can be strengthened by introduction of the proper conjugate terminal group. In addition, La(III), Gd(III) and Dy(III) complexes exhibit free ligand band emission.

Due to strong emission intensity, the fluorescence spectra of $Eu(L^2)_2(NO_3)_3$ in different solutions were measured. Figure 3 **(solution)** shows that in acetonitrile solution the $Eu(\mathbf{L}^2)_2(NO_3)_3$ has the strongest luminescence, and then in acetone, tetrahydrofuran, 1,4-dioxane, ethanol and methanol. This is due to coordinating effects of solvents, namely solvate effect [26]. Together with increasing coordination abilities of acetonitrile, acetone, tetrahydrofuran, 1,4-dioxane, ethanol and methanol for the lanthanide ions, the oscillatory motions of the entering molecules consume more energy which the ligand triplet level transfers to the emitting level of the lanthanide ion. Thus, the energy transfer could not be carried out perfectly.

3.5.2. Fluorescence quantum yields. The fluorescence quantum yield for each Eu(III) complex was measured using the ratio method, $[Ru(bpy)_3]Cl_2$ in degassed acetonitrile

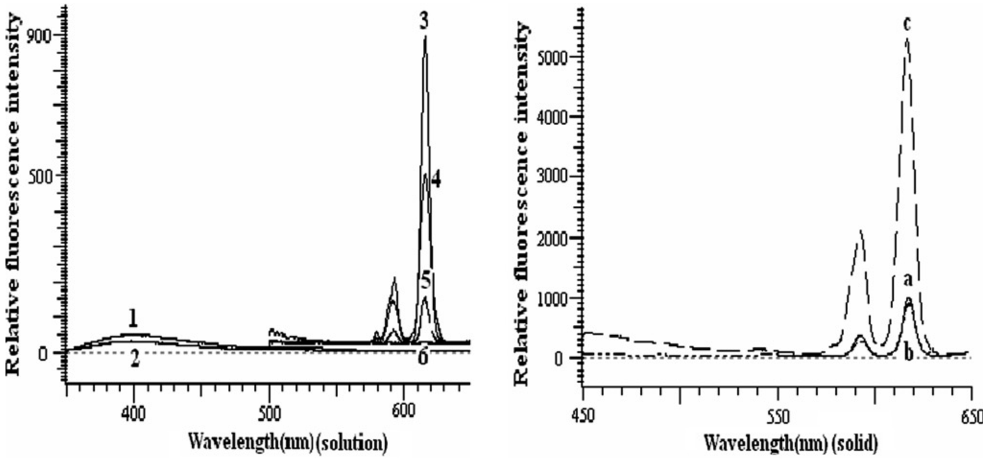

Figure 3. **(solution)**. The emission spectra of $Eu(\mathbf{L}^2)_2(NO_3)_3$ in different solutions (5×10^{-4} mol L^{-1}) at room temperature: (1) ethanol; (2) methanol; (3) acetonitrile; (4) acetone; (5) tetrahydrofuran; (6) 1,4-dioxane: the emission slit is 5 nm.**(solid)**. The fluorescence emission spectra of Eu(III) complexes in solid state at room temperature: (a) $Eu(\mathbf{L}^0)_2(NO_3)_3$ $\lambda_{Ex} = 332$ nm [1]; (b) $Eu(\mathbf{L}^1)_2(NO_3)_3$ $\lambda_{Ex} = 321$ nm; (c) $Eu(\mathbf{L}^2)_2(NO_3)_3$ $\lambda_{Ex} = 340$ nm.

solution as a standard, $\Phi_s = 0.062$ [27]. All the samples were also dissolved in acetonitrile. Each solution was excited at λ_{max} (table 5) on a Hitachi F-4500 FL spectrophotometer. The equation (1) used for determining the quantum yield, Φ_c, of the Eu(III) complex was [28]:

$$\Phi_c = \frac{F_c \Phi_s A_s}{F_s A_c} \tag{1}$$

where F denotes the integrated area under the emission spectrum; A is the absorbance at the exciting wavelength.

From the fluorescence quantum yield of each sample (table 5), the order of the quantum yield is in agreement with that of the fluorescence emission intensity for Eu(III) complexes.

3.5.3. Phosphorescence. Phosphorescence spectra for methanol-ethanol (1 : 1) solutions (1×10^{-5} mol L^{-1}) of gadolinium(III) complexes with $\mathbf{L^1}$ and $\mathbf{L^2}$ were measured at 77 K. The lowest triplet-state energies of the ligands (T) were determined by the shortest wavelength transition in the phosphorescence spectra, 22,883 cm^{-1} (437 nm) for $\mathbf{L^1}$ and 21,277 cm^{-1} (470 nm) for $\mathbf{L^2}$ [29], while the triplet-state energy of $\mathbf{L^0}$ is 22,831 cm^{-1} (438 nm) (table 6) [1].

Since the triplet states of the ligands are above the resonance levels of Eu(III), the energy can be transferred from the excited ligands to Eu(III). The intramolecular transfer efficiency depends on two energy transfer processes, one from the lowest triplet level (T) of ligand to the resonance level of Eu(III) ($^5D_1$) by resonant exchange interaction, and the other an inverse energy transfer by thermal de-excitation [30].

Table 5. Fluorescence spectrum data (nm) and fluorescence quantum yield of the complexes at room temperature.

Compounds	Ex slit	Em slit	λ_{Ex}	λ_{Em}	Emission intensity	Transition	Quantum yield Φ
Eu($\mathbf{L^0}$)$_2$(NO$_3$)$_3$*	5	5	332	557	24	$^5D_1 \rightarrow {}^7F_2$	0.0388
				593	364	$^5D_0 \rightarrow {}^7F_1$	
				618	1007	$^5D_0 \rightarrow {}^7F_2$	
Eu($\mathbf{L^1}$)$_2$(NO$_3$)$_3$	5	5	321	464	60	$^5D_2 \rightarrow {}^7F_1$	0.0374
				492	45	$^5D_1 \rightarrow {}^7F_1$	
				546	53	$^5D_1 \rightarrow {}^7F_2$	
				593	282	$^5D_0 \rightarrow {}^7F_1$	
				618	896	$^5D_0 \rightarrow {}^7F_2$	
Eu($\mathbf{L^2}$)$_2$(NO$_3$)$_3$	5	5	340	543	141	$^5D_1 \rightarrow {}^7F_2$	0.1781
				593	2097	$^5D_0 \rightarrow {}^7F_1$	
				617	5322	$^5D_0 \rightarrow {}^7F_2$	
Sm($\mathbf{L^1}$)$_2$(NO$_3$)$_3$	5	5	362	563	50	$^4G_{5/2} \rightarrow {}^6H_{5/2}$	
				597	55	$^4G_{5/2} \rightarrow {}^6H_{7/2}$	
				643	18	$^4G_{5/2} \rightarrow {}^6H_{9/2}$	
Sm($\mathbf{L^2}$)$_2$(NO$_3$)$_3$	5	5	370	562	50	$^4G_{5/2} \rightarrow {}^6H_{5/2}$	
				593	39	$^4G_{5/2} \rightarrow {}^6H_{7/2}$	
				615	79	$^4G_{5/2} \rightarrow {}^6H_{7/2}$	
				643	10	$^4G_{5/2} \rightarrow {}^6H_{9/2}$	

The values for all compounds are at room temperature.
* The complex of the reference [1].

Table 6. Triplet state energies of the Gd(III) complexes and ΔE (T–$^5D_1$) for the ligands.

Complexes	λ_{Ex} (nm)	0–0 transition (nm)	Triplet state energy level (cm^{-1})	ΔE(T–$^5D_1$^{a}) (cm^{-1})
Gd($\mathbf{L^0}$)$_2$(NO$_3$)$_3$^{b}	280	438	22,831	3811
Gd($\mathbf{L^1}$)$_2$(NO$_3$)$_3$	280	437	22,883	3863
Gd($\mathbf{L^2}$)$_2$(NO$_3$)$_3$	302	470	21,277	2257

[a] $^5D_1$: 19,020 cm^{-1} [the resonance levels of Eu(III) ion] [31].
[b] The complex of the reference [1].

Both energy transfer rate constants are dependent on the energy gap (ΔE) between T and $^5D_1$.

Sato and Wada [30] have estimated that when ΔE is in the range 1000–2000 cm^{-1}, the fluorescence quantum yield of Eu(III) complex is very high at room temperature. According to the discussions of optimal ΔE, the strong fluorescence of the Eu(III) complex with $\mathbf{L^2}$ as well as the order of the emission intensity for three Eu(III) complexes can be reasonably explained.

4. Conclusions

According to the data and discussion above, it is obvious that the ligands formed complexes with lanthanide(III). The europium(III) complexes exhibit the characteristic fluorescence and comparisons of the fluorescence spectra and quantum yield show that the emission intensity order for the Eu(III) complexes is Eu($\mathbf{L^2}$)$_2$(NO$_3$)$_3$ > Eu($\mathbf{L^0}$)$_2$(NO$_3$)$_3$ > Eu($\mathbf{L^1}$)$_2$(NO$_3$)$_3$, in accord with the triplet energy level studies. The triplet energy level of the ligand is the chief factor, dominating the emission intensity of Eu(III) complex. Comparing the structure of the ligands, we conclude that high emission intensity may be attributed to the electron-accepting group of the ligand. Based on those studies, some new aryl amide type ligands could be synthesized to optimize the fluorescence properties of europium(III).

Acknowledgements

This work is supported by the National Science Foundation of China (20431010). The authors are also grateful to the Instrumental Analysis and Research Center of Lanzhou University and State Key Laboratory of Applied Organic Chemistry for providing instrumentation facilities.

References

[1] W.N. Wu, W.B. Yuan, N. Tang, R.D. Yang, L. Yan, Z.H. Xu. *Spectrochim. Acta A*, **65**, 912 (2006).
[2] B.S. Panigrahi. *Spectrochim. Acta A*, **56**, 1337 (2000).
[3] F.S. Richardson. *Chem. Rev.*, **82**, 541 (1982).
[4] X.Y. Li, Y.Q. Zhang, Z.C. Liu, F. Liu. *Chin. J. Anal. Chem.*, **33**, 54 (2005).

[5] E.S. Voropai, M.P. Samtsov, V.N. Chalov, É.A. Zhavrid. *J. Appl. Spectrosc.*, **68**, 468 (2001).

[6] Y.M. Dang, X.Q. Guo, Y.B. Zhao. *Chem. J. Chinese Universities*, **25**, 1245 (2004).

[7] (a) G.F. de Sá, O.L. Malta, C. de Mello Donegá, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. da Silva Jr. *Coord. Chem. Rev.*, **196**, 165 (2000), (b) C. Bazzicalupi, A. Bencini, A. Bianchi, C. Giorgi, A. Masotti, B. Valtancoli, V. Fusi, A. Roque, F. Pina. *Chem. Commun.*, **7**, 561 (2000).

[8] (a) W. Dawson, J. Kropp, M. Windsor. *J. Chem. Phys.*, **45**, 2410 (1966), (b) M. Latva, H. Takalob, V.M. Mukkala, C. Matachescuc, J.C. Rodriguez-Ubisd, J. Kankarea. *J. Lumin.*, **75**, 149 (1997), (c) F. Gutierrez, C. Tedeschi, L. Maron, J.P. Daudey, R. Poteau, J. Azema, P. Tisnès, C. Picard. *J. Chem. Soc., Dalton Trans.*, **9**, 1334 (2004).

[9] Y.S. Yang, S.H. Cai. *Hua Xue Shi Ji.*, **6**, 133 (1984).

[10] Y.Z. Ding, J.Z. Lu, Y.S. Yang. *Hua Xue Shi Ji.*, **8**, 201 (1986).

[11] Y.H. Wen, Z. Qin, W.S. Liu. *J. Radioanal. Nucl. Chem.*, **250**, 285 (2001).

[12] B. Tümmler, G. Maass, F. Vêgtle. *J. Am. Chem. Soc.*, **101**, 2588 (1979).

[13] Zh.H. Cai, M.Y. Tan. *J. Rare Earths*, **20**, 382 (2002).

[14] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).

[15] M. Xu, Zh.P. Ji, W.J. Xiao. *Acta Chim. Sinica*, **49**, 36 (1991).

[16] B.D. Gou, W.X. Zhu. *J. Beijing Normal University (Natural Science)*, **35**, 242 (1999).

[17] Z.J. Guo, M.Y. Tan. *J. Nuclear and Radiochemistry*, **25**, 177 (2003).

[18] K.Z. Tang, J. Zhang, Y. Tang, W.S. Liu, M.Y. Tan, Y.X. Sun. *Inorg. Chim. Acta*, **359**, 1207 (2006).

[19] X.L. Hu, L.Y. Fan, L. Yan, R.D. Yang. *Chin. J. Appl. Chem.*, **19**, 727 (2002).

[20] H.M. Randall, R.G. Fowler, N. Fuson and J.R. Dangl. *Infra-red Determination of Organic Structure*, Van Nostrand, New York (1949).

[21] Y.H. Jiang, R.D. Yang, L. Yan, X.L. Hu, W.B. Yuan. *J. Chin. Rare Earth Soc.*, **20**, 474 (2002).

[22] Y.P. Zhou, Z.Y. Yang, H.J. Yu, R.D. Yang. *Chin. J. Appl. Chem.*, **16**, 37 (1999).

[23] Y.L. Zhang, W.S. Liu, W. Dou, W.W. Qin. *Spectrochim. Acta A*, **60**, 1707 (2004).

[24] W. Carnall, S. Siegel, J. Ferrano, B. Tani, E. Gebert. *Inorg. Chem.*, **12**, 560 (1973).

[25] Y.L. Zhang, W.S. Liu, W. Dou, W.W. Qin. *Spectrochim. Acta A*, **60**, 1707 (2004).

[26] H.Q. Liu, T.C. Cheung, C.M. Che. *Chem. Commun.*, **9**, 1039 (1996).

[27] J.V. Caspar, T.J. Meyer. *J. Am. Chem. Soc.*, **105**, 5583 (1983).

[28] J.W. Owens. *Inorg. Chim. Acta*, **279**, 226 (1998).

[29] S.L. Wu, Y.L. Wu, Y.S. Yang. *J. Alloys Comp.*, **180**, 399 (1992).

[30] S. Sato, M. Wada. *Bull. Chem. Soc. Jpn.*, **43**, 1955 (1970).

[31] E.V. Sayre, S. Freed. *J. Chem. Phys.*, **24**, 1213 (1956).