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# Synthesis and fluorescence properties of lanthanide(III) complexes of a novel bis(pyrazolyl-carboxyl)pyridine-based ligand

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ABSTRACT

A novel bis-pyrazolyl-carboxyl ligand, 2,6-bis(5-methyl-3-carboxypyrazol-1-ylmethyl)pyridine (**L**), was designed and synthesized and its several lanthanide(III) complexes Eu(III), Tb(III), Sm(III) and Gd(III) were successfully prepared and characterized in detail based on elemental analysis, infrared, mass, proton nuclear magnetic resonance spectroscopy and TG–DTA studies. Analysis of the IR spectra suggested that each of the lanthanide metal ions coordinated to the ligand via the carbonyl oxygen atoms and the nitrogen atom of the pyridine ring and pyrazole rings. The fluorescence spectra exhibits that the Tb(III) complex and the Eu(III) complex display characteristic metal-centered fluorescence in solid state while ligand fluorescence is completely quenched. However, the Tb(III) complex displays more effective fluorescence than the other complexes, which is attributed to especial effectivity in transferring energy from the lowest triplet energy level of the ligand (**L**) onto the excited state ($^5D_4$) of Tb(III).

## 1. Introduction

In recent years there has been an increasing interest in luminescent lanthanide (Ln) complexes because of their attractive emission properties such as long lifetime, large stokes shift, and line-like emission [1–3]. The f–f transitions in lanthanide, Ln, ions lead to interesting light-emission properties. These ions have been widely studied for a number of applications such as luminescent materials [4,5], chemosensors [6,7], fluorescence labels [8], and as photoluminescence devices[9,10] for their photophysical properties arising from f–f transitions. However, since the f–f transitions are forbidden by spin and parity selection rules, the emission occurs through sensitization with coordinated ligands, which function as antennas [11]. The ligands range from simple aromatic acids, such as the widely utilized dipicolinic acid, to more complicated multidentate ligand architectures capable of selectively binding different lanthanide ions [12].

It is known that, although free lanthanide metal ions are inefficient at absorbing and emitting light, many lanthanide complex compounds containing organic ligands are highly capable of emitting strong and characteristic fluorescence [13]. In the lanthanide complexes, the organic ligands that have lonepair and/or π-electrons can efficiently serve as the light absorbing chromophores. If the excited state of the antenna organic ligands is energetically high enough, and the gathered energy is transferred to the lanthanide metal ions held nearby, the characteristic fluorescence would be emitted. For effective excitation of Ln ions, organic chromophore, so-called “antenna”, is usually attached to Ln complex [14–16]. In these systems, the photoexcited antenna successfully transfers its energy to the adjacent Ln ion (energy transfer (ET) process), forming excited-state Ln. For practical application of luminescent Ln ions for analytical purpose, these must be encapsulated within suitable ligand groups that can stabilize the ions kinetically and thermodynamically [17].

In the present paper we report the synthesis and fluorescence study of lanthanide ions [Eu(III), Tb(III), Sm(III) and Gd(III)] complexes of a novel ligand 2,6-bis(5-methyl-3-carboxypyrazol-1-ylmethyl)pyridine (**L**, Scheme 1). The ligand contain amine functionalities which known for its capability to bind lanthanide ions via interaction with C=O oxygen atoms and amine nitrogen atoms [18].

Our interest in the properties of metal complexes, and especially in a good aqueous stability, led us to investigate the preparation of structures containing both subunits, pyrazolyl-carboxyl. Besides, the geometry of the five-membered pyrazole ring was expected to provide interesting spectral properties to its metal complexes. To this end the both subunits pyrazolyl-carboxyl of the ligand were exploited as organic antennae.

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## 2. Experimental

### 2.1. Reagents and instruments

Methyl β-acetylpyruvate **1** [19] and 2,6-bis(methoxycarbonyl)pyridine **3** [20] was prepared according to the literature methods. Pyridine-2,6-dicarboxylic acid and other regents used were purchased and used as analytical grade. Rare earth chlorides were prepared according to the literature method [21].

Contents of carbon, hydrogen and nitrogen were determined using an Elementar vario EL elemental analyzer. Content of Ln(III) was determined by EDTA titration. Infrared spectra (4000–400 $cm^{-1}$) were recorded with samples as KBr discs using a Nicolet NEXUS 670 FTIR spectrophotometer. $^1$H-NMR was measured with a Bruker-400 MHz nuclear magnetic resonance spectrometer with $CDCl_3$ or DMSO as solvent and TMS as internal reference. Mass spectrum was measured using a ZAB-HS analyzer. Fluorescence measurements were made on a Hitich F-4500 spectrometer.

### 2.2. Synthesis of the ligand

#### 2.2.1. Synthesis of methyl 5-methyl-1H-pyrazole-3-carboxylate (*2*)

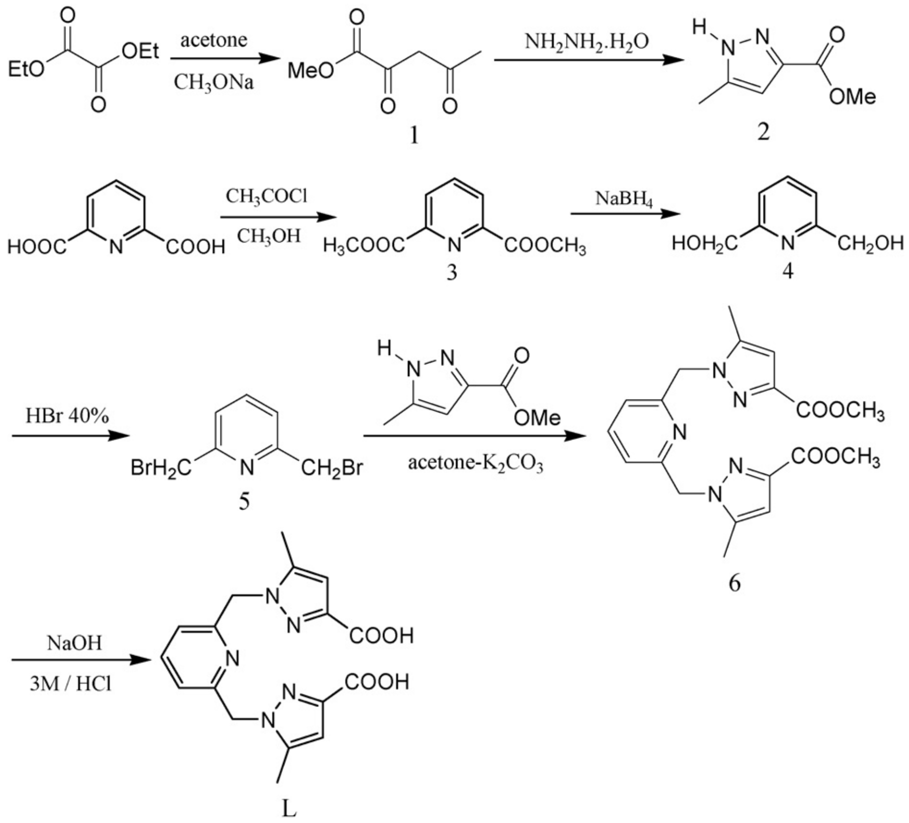
To 50 mL of anhydrous MeOH was added 5.00 g of methyl β-acetylpyruvate **1** (34.7 mmol), after stirring for 10 min, 2.39 g of $NH_2NH_2{\cdot}H_2O$ (80%, 38.2 mmol) in anhydrous MeOH (15 mL) at 0 °C was treated dropwise within 30 min. The mixture was stirred at room temperature for a further 30 min and then concentrated under reduced pressure. The residue was dissolved in EtOAc, washed with water, dried ($Na_2SO_4$), evaporated and the crude products was purified by recrystallization from EtOAc, to give **2** (4.11 g, 84.4%): mp 77–79 °C, $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 2.37 (s, 3H, $CH_3$), 3.89 (s, 3H, $CH_3O$), 6.69 (s, 1H, Pz–H). EI MS: *m/z* 140 ($M^+$), 109 ($M^+$–OMe) and 81 ($M^+$–OCOMe). Anal. calcd. for $C_6H_8N_2O_2$: C, 51.42; H, 5.75; N, 19.99; found: C, 51.36; H, 5.88; N, 20.08, respectively.

#### 2.2.2. Synthesis of pyridine-2,6-dimethanol (*4*)

To pyridine-2,6-dicarboxylic acid dimethyl ester **3** 5.00 g (25.6 mmol) in THF (50 mL) was slowly added $NaBH_4$ 4.21 g (110.5 mmol), and the solution was then stirred at room temperature for 12 h. After evaporation of the solvent, the residue was dissolved in 30 mL water, adjusted to pH 3 with 2 M HCl, and then adjusted to pH 9 with saturated aqueous $Na_2CO_3$ solution. Evaporation of the solvent, the residue was extracted with $CHCl_3$ (300 mL) by continuous liquid–liquid extraction for 10 h. After evaporation of the solvent, the white product was washed with $Et_2O$ and dried in vacuo to give compound **4** (3.1 g, 85.2% yield): mp 111–113 °C (Ref. [22] 112–114 °C). $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 3.64 (bs, 2H), 4.34 (s, 4H), 6.94 (d, 2H, $J$ = 7.8 Hz) and 7.35 (t, 1H, $J$ = 7.8 Hz). Anal. calcd. for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07; found: C, 60.33; H, 6.58; N, 10.14.

#### 2.2.3. Synthesis of 2,6-bis(bromomethyl)pyridine (*5*)

To a mixture of bromhydric and acetic acid (150 mL), 1.20 g (8.6 mmol) of pyridine-2,6-dimethanol **4** were added and the solution refluxed for 48 h. Upon cooling at 0 °C, a white precipitate formed, which was recovered by filtration, dissolved in $CH_2Cl_2$ (40 mL) and washed with an aqueous solution (100 mL) of $NaHCO_3$ (2.4 g). The crude product was then extracted from the aqueous phase with 5 mL× 20 mL portions of $CH_2Cl_2$. The organic phases were combined, dried over $MgSO_4$, and evaporated to dryness in vacuo, affording 0.98 g of analytically pure compound in 43% yield.



**Scheme 1.** Synthesis of the ligand (**L**).

**Table 1**
Elemental analytical data for the complexes.

| Complex | M (%) found (calc.) | C (%) found (calc.) | H (%) found (calc.) | N (%) found (calc.) |
|---|---|---|---|---|
| $Na_2TbLCl_3{\cdot}9H_2O$ | 19.21(19.22) | 24.73(24.70) | 3.98(4.02) | 8.45(8.47) |
| $Na_2EuLCl_3{\cdot}7H_2O$ | 19.42(19.39) | 26.09(26.05) | 3.76(3.73) | 8.91(8.94) |
| $Na_2SmLCl_3{\cdot}6H_2O$ | 19.65(19.68) | 26.76(26.72) | 3.51(3.56) | 9.15(9.17) |
| $Na_2GdLCl_3{\cdot}7H_2O$ | 19.91(19.93) | 25.92(25.88) | 3.67(3.70) | 2.85(8.88) |

**Table 2**
Characteristic IR bands ($cm^{-1}$) of the ligand and its complexes.

| | L | $Na_2TbLCl_3{\cdot}9H_2O$ | $Na_2EuLCl_3{\cdot}7H_2O$ | $Na_2SmLCl_3{\cdot}6H_2O$ | $Na_2GdLCl_3{\cdot}7H_2O$ |
|---|---|---|---|---|---|
| $\nu$(OH) | | 3397 | 3390 | 3393 | 3408 |
| $\nu$(C=O) | 1727 | | | | |
| $\nu_{as}(COO^-)$ | | 1597 | 1596 | 1596 | 1597 |
| $\nu_s(COO^-)$ | | 1381 | 1379 | 1381 | 1380 |
| $\nu_{py}$(C=N) | 1578 | 1506 | 1509 | 1506 | 1505 |
| $\nu_{pz}$(C=N) | 1390 | 1314 | 1316 | 1314 | 1314 |
| $\rho_{\gamma}$(H2O) | | 849 | 844 | 845 | 850 |
| $\rho_{\omega}$(H2O) | | 644 | 645 | 643 | 647 |
| $\delta$(Ln–N) | | 570 | 575 | 570 | 573 |
| $\delta$(Ln–O) | | 454 | 464 | 453 | 453 |

The product is light sensitive and was stored in a dark brown bottle. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta_H$ 4.50 (s, 4H, $CH_2$), 7.40 (d, 2H, ArH), 7.70 (t, 1H, ArH). EI MS: *m*/*z* 266 ($M+H^+$). Anal. calcd. for $C_7H_7NBr_2$: C, 31.73; H, 2.66; N, 5.29; found: C, 32.03; H, 2.57; N, 5.23.

### 2.2.4. Synthesis of 2,6-bis(5-methyl-3-methoxycarbonyl-pyrazol-1-ylmethyl) pyridine (*6*)

A mixture of 2,6-bis(bromomethyl)pyridine **5** 1.00 g (3.79 mmol) and 5-methyl-1H-pyrazole-3-carboxylate **2** (1.06 g, 7.58 mmol) in acetone (40 mL), anhydrous $K_2CO_3$ 0.63 g (4.49 mmol) was refluxed for 24 h. The organic layer was then separated, and evaporated in vacuo. The crude product was washed with water (40 mL) and chromatographed on silica gel, eluting with EtOAc/$CH_2Cl_2$ (1:1), followed by crystallization from EtOAc, to give **6** (849 mg, 58.5% yield): mp 136–138 °C. $^1H$ NMR (400 MHz, $CDCl_3$): 2.14 (s, 6H, $CH_3$) 3.84 (s, 6H, $CH_3O$), 5.37 (s, 4H, $CH_2$), 6.56 (s, 2H, Pz (**4**) H), 6.76 (d, 2H, ArH) and 7.51 (t, 1H, ArH). EI MS: *m*/*z* 383 ($M^+$). Anal. calcd. for $C_{19}H_{21}N_5O_4$: C, 59.52; H, 5.52; N, 18.27; found: C, 59.45; H, 5.65; N, 18.38.

### 2.2.5. Synthesis of 2,6-bis(5-methyl-3-carboxypyrazol-1-ylmethyl)pyridine (*L*)

A mixture of 50 mL ethanol, 0.8 g KOH, 2 mL $H_2O$, and 1.00 g 2,6-bis(5-methyl-3-methoxycarbonyl-pyrazol-1-ylmethyl) pyridine **6** (2.61 mmol) was refluxed with stirring for 5 h. After the solvent was evaporated, the residue was dissolved in 30 mL water, and the solution was filtered. To the solution was added dropwise 3 M HCl to adjust the pH to 1, and the solution was stirred for 3 h at room temperature. The precipitate was collected by filtration and washed with 1% aqueous HCl. After drying, the product was added to 50 mL of acetonitrile, and the mixture was refluxed 1 h with stirring. The precipitate was filtered and dried to give compound **L** (0.75 g, 80.9% yield): mp 294 °C (decomp.). $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta_H$ 2.18 (s, 6H, $CH_3$), 5.41 (s, 4H, $CH_2$), 6.51 (s, 4H, Pz (**4**) H), 7.03 (d, 2H, ArH), 7.77 (t, 1H, ArH) and 12.54 (s, 2H, COOH). EI MS: *m*/*z* 355 ($M^+$). Anal. calcd. for $C_{17}H_{17}N_5O_4$: C, 57.46; H, 4.82; N, 19.71; found: C, 57.41; H, 4.91; N, 19.76.

**Table 3**
Fluorescence data for the complexes.

| Complex | $\lambda_{ex}$ (nm) | $\lambda_{em}$ (nm) | RFI[a] | Assignment |
|---|---|---|---|---|
| $Na_2TbLCl_3{\cdot}9H_2O$ | 259 | 490 | 3553 | $^5D_4$–$^7F_6$ |
| | | 543 | 9574 | $^5D_4$–$^7F_5$ |
| | | 583 | 786 | $^5D_4$–$^7F_4$ |
| | | 619 | 287 | $^5D_4$–$^7F_3$ |
| $Na_2EuLCl_3{\cdot}7H_2O$ | 256 | 590 | 3416 | $^5D_0$–$^7F_1$ |
| | | 616 | 9776 | $^5D_0$–$^7F_2$ |
| | | 648 | 171 | $^5D_0$–$^7F_3$ |
| | | 694 | 241 | $^5D_0$–$^7F_4$ |
| $Na_2SmLCl_3{\cdot}6H_2O$ | 298 | 372 | 9220 | |
| $Na_2GdLCl_3{\cdot}7H_2O$ | 363 | 443 | 9739 | |

[a] The width of emission slit and excitation slit of the Tb(III) complex was 2.5 nm and other complexes were 5.0 nm, the voltage of photomultiplier tube was 700 V.

### 2.3. Synthesis of the complexes

An solution of $LnCl_3{\cdot}6H_2O$ (Ln = Eu, Tb, Sm and Gd) (0.2 mmol) in ethanol (5 mL)was added dropwise to a solution of the ligand (0.6 mmol) in ethanol and the mixture stirred at 60 °C for 3 h. The resulting precipitate was collected by filtration, washed three times each with ethanol, chloroform and dried in vacuo to give a flake solid (typically about 80% yield).

## 3. Result and discussion

### 3.1. Properties of the complexes

The results of elemental analysis (see Table 1) indicated that the composition of the complexes conforms to be $Na_2TbLCl_3{\cdot}9H_2O$, $Na_2EuLCl_3{\cdot}7H_2O$, $Na_2SmLCl_3{\cdot}6H_2O$ and $Na_2GdLCl_3{\cdot}7H_2O$. All complexes were found to be soluble in $H_2O$, DMF, DMSO, slightly soluble in ethanol and acetone, and insoluble in benzene, diethyl ether and tetrahydrofuran.

### 3.2. IR spectra of the complexes

The IR spectra of all four complexes are similar, indicating that they are structurally alike. Table 2 summarises the characteristic bands observed for the ligand and its metal complexes. The IR spectrum of the free ligand shows bands at 1727, 1578 and 1390 $cm^{-1}$, which can be assigned as $\nu$(C=O), $\nu_{py}$ (C=N) of pyridine ring and $\nu_{pz}$ (C=N) of pyrazole ring respectively. In the complexes, these bands are shifted upfield by 69–73 $cm^{-1}$ for $\nu_{py}$ (C=N) and upfield by 74–76 $cm^{-1}$ for $\nu_{pz}$ (C=N). The bands (C=O) in free ligands disappear and the new bands appear at 1596–1597 $cm^{-1}$ and 1379–1381 $cm^{-1}$ assignable to [$\nu_{as}$ ($COO^-$) +$\nu_s$ ($COO^-$)]. In each

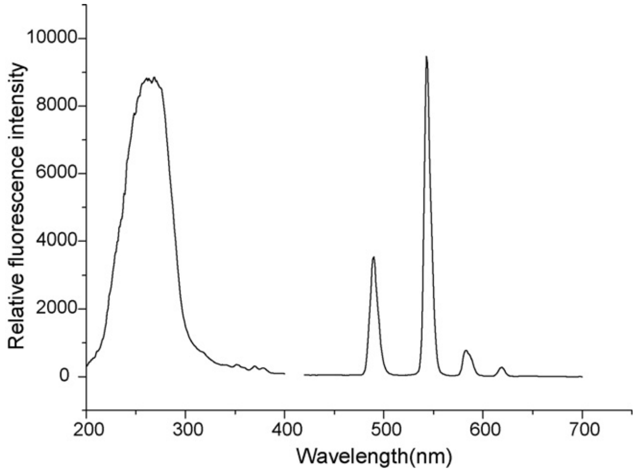


**Fig. 1.** The excitation and emission spectrum of the Tb(III) complex. The excitation and emission slit widths were 2.5 nm in solid state and the drive voltage was 700 V.

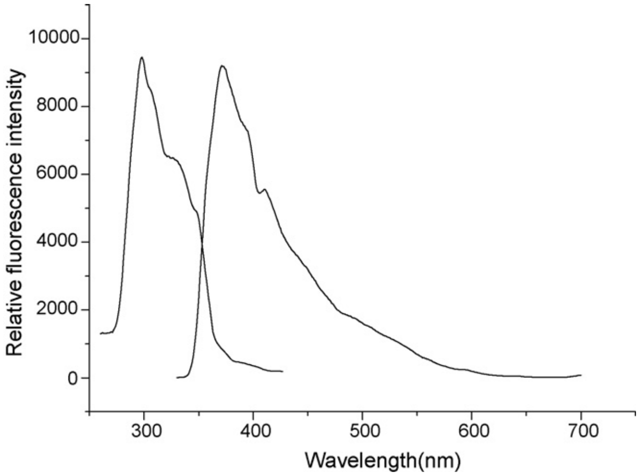


**Fig. 3.** The excitation and emission spectrum of the Sm(III) complex. The excitation and emission slit widths were 5.0 nm in solid state and the drive voltage was 700 V.

case, the shifts suggested that the relevant oxygen and nitrogen atoms of the ligand were involved in coordination to the metal centre. The bands centered at about 3400 cm$^{-1}$ and characteristic of $\nu$(OH) vibrations are always relatively intense and can be attributed to crystal water and combined water molecules. The absorption bands assigned to the Ln–O and Ln–N stretching frequencies of the complexes were observed at 453–464 and 470–475 cm$^{-1}$, respectively. The appearance of the $\rho_\gamma$($H_2O$) and $\rho_\omega$($H_2O$) bands in the spectra of the complexes at approximately 850 and 645 cm$^{-1}$, respectively, indicates the presence of coordinated water [23].

### 3.3. Fluorescence studies

The fluorescence data for each of the complexes in the solid state was listed in Table 3. The maximum excitation wavelengths ($\lambda_{ex}$) of the Tb(III), Eu(III), Sm(III) and Gd(III) complexes were 259, 256, 298 and 363 nm, respectively (Table 3).

Fluorescent spectra for the Eu(III), Sm(III) and Gd(III) complexes were measured at two different slit widths, 2.5 nm (Fig. 1) and 5.0 nm (Figs. 2–4). At 2.5 nm, the fluorescent intensity observed from Eu(III), Sm(III) and Gd(III) complexes were very weak, while very strong from the Tb(III) complex (Fig. 1) under the same experimental conditions. It appears that the energy-transfer from the organic ligand (**L**) to the central Tb(III) ions is much more effective compared to other Ln(III) ions we have studied. It is thought that the strong emission observed is due to the $^5D_4$–$^7F_5$ transitions of the 4f electrons of the Tb(III) ions [24].

The emission spectrum of solid Tb(III) complex consists of four main lines at 490 nm ($^5D_4\rightarrow{}^7F_6$), 543 nm ($^5D_4\rightarrow{}^7F_5$), 583 nm ($^5D_4\rightarrow{}^7F_4$) and 619 nm ($^5D_4\rightarrow{}^7F_3$) (Fig. 1). Due to the presence of a scattering signal at 490 nm, and the $^5D_4\rightarrow{}^7F_5$ emission is a magnetic dipole transition, which is less affected by the ligand field, so the peak height at 543 nm for terbium was used to measure the fluorescence intensities. We can see that the emission band ($^5D_4\rightarrow{}^7F_5$) is obviously stronger than the other emission bands ($^5D_4\rightarrow{}^7F_6$, $^5D_4\rightarrow{}^7F_4$, $^5D_4\rightarrow{}^7F_3$) from Fig. 1. The typical narrow emission bands of Tb(III) ions can be detected upon excitation of the ligand-centered absorption band, indicating that the ligand is a comparative good organic chelator to absorb energy and transfer them to Tb(III) ion.

The fluorescence spectrum of solid Eu(III) complex exhibits four sharp characteristic emission peaks at 590 nm ($^5D_0\rightarrow{}^7F_1$), 616 nm ($^5D_0\rightarrow{}^7F_2$), 648 nm ($^5D_0\rightarrow{}^7F_3$) and 694 nm ($^5D_0\rightarrow{}^7F_4$) (Fig. 2)

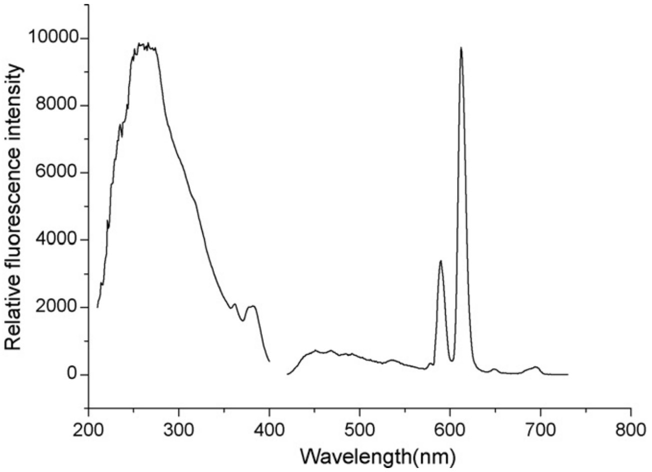


**Fig. 2.** The excitation and emission spectrum of the Eu(III) complex. The excitation and emission slit widths were 5.0 nm in solid state and the drive voltage was 700 V.

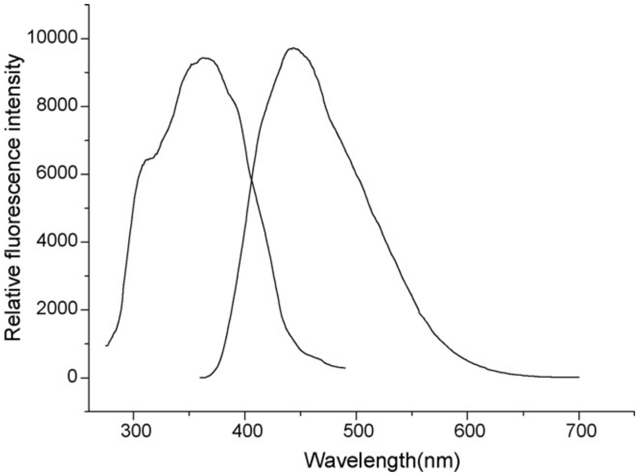


**Fig. 4.** The excitation and emission spectrum of the Gd(III) complex. The excitation and emission slit widths were 5.0 nm in solid state and the drive voltage was 700 V.

**Table 4**
TG–DTA date of the ligand and the complexes.

| Complex | $T_{endo}$ (°C) | | $H_2O$ loss (calcd.) (%) | $T_{exo}$ (°C) | | Total weight loss (calcd.) (%) |
|---|---|---|---|---|---|---|
| | t1 | t2 | | t1 | t2 | |
| $Na_2TbLCl_3 \cdot 9H_2O$ | 48 | 261 | 20.05(20.23) | 356 | 599 | 59.28(59.03) |
| $Na_2EuLCl_3 \cdot 7H_2O$ | 50 | 274 | 15.14(14.89) | 352 | 601 | 71.04(70.25) |
| $Na_2SmLCl_3 \cdot 6H_2O$ | 49 | 265 | 18.77(18.56) | 358 | 603 | 66.98(65.55) |
| $Na_2GdLCl_3 \cdot 7H_2O$ | 52 | 270 | 17.11(17.25) | 354 | 605 | 62.39(61.47) |

corresponding to the $^5D_0$–$^7F_J$ ($J$ = 1–4) transition of Eu(III) ion, respectively. The hypersensitive $^5D_0$–$^7F_2$ transition of Eu(III) complex is observed at 616 nm as the most prominently single peak without splitting which indicates that the energy collected by the "antenna" effect of the ligand can be effectively transferred to the central Eu(III) ion.

The excitation and emission maximum wavelengths are 298 and 372 nm for Sm(III) complex is shown in Fig. 3. A broad excitation band (280–360 nm) centered at 298 nm was observed on the excitation spectrum for solid Sm(III) complex, and the emission spectrum for the solid Sm(III) complex showed a wide fluorescence emission band-centered at 372 nm at room temperature, which was attributed to the free ligand emission.

The excitation and emission maximum wavelengths are 363 and 443 nm for Gd(III) complex is shown in Fig. 4. A broad excitation band (300–420 nm) centered at 363 nm was observed on the excitation spectrum for solid Gd(III) complex, and the emission spectrum for the solid Gd(III) complex showed a wide fluorescence emission band-centered at 443 nm at room temperature, which was attributed to the free ligand emission.

The fluorescence of Ln(III) complexes is related to the efficiency of the intra-molecular energy transfer between the triplet energy states of the ligand and the emitting energy states of the metal ions. One factor that can contribute to the observed fluorescence intensity of the Tb(III) complex at 545 nm was much stronger than that of the Eu(III), Sm(III) and Gd(III) complexes, it can be inferred that the energy difference between the ligand triplet states and the emitting energy state of Tb(III) is more favorable for energy transfer than those of the other three rare earth ions.

### 3.4. Thermal analysis

In order to examine the thermal stability of the complexes, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 30 and 750 °C in the static atmosphere of air (Figs. 5–8). The heating rate is 10 °C/min and the TG–DTA curves

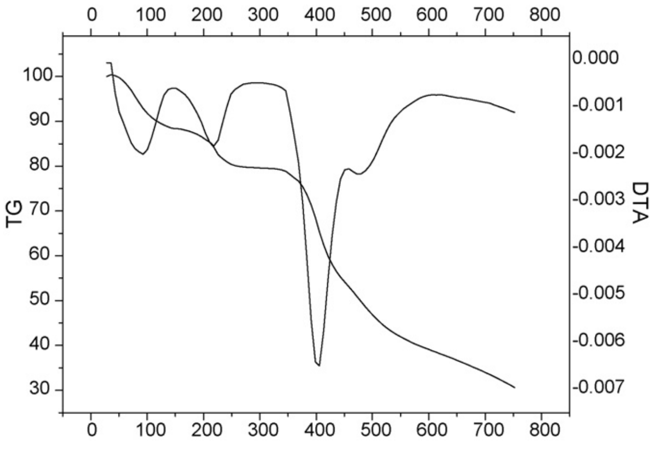


**Fig. 5.** TG and DTA curves for original Tb(III) complex.

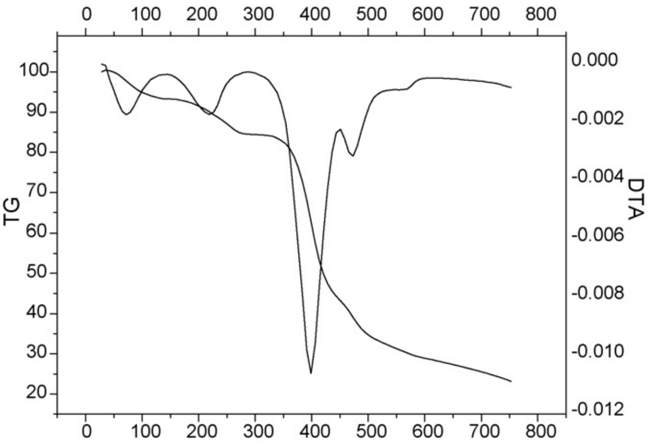


**Fig. 6.** TG and DTA curves for original Eu(III) complex.

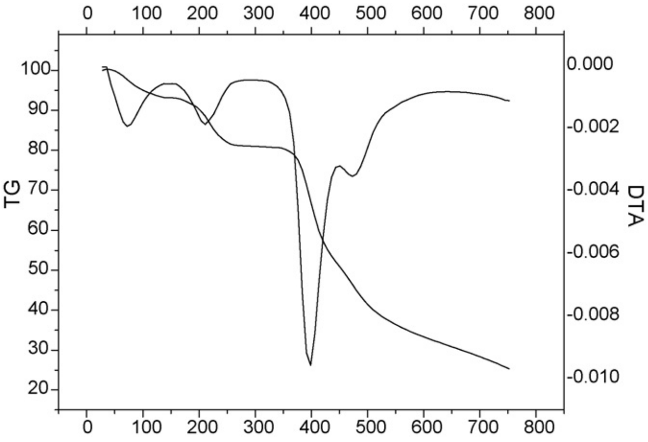


**Fig. 7.** TG and DTA curves for original Sm(III) complex.

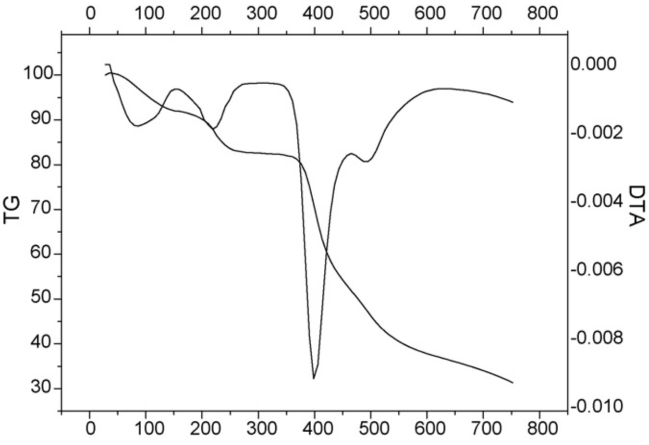


**Fig. 8.** TG and DTA curves for original Gd(III) complex.

showing the weight loses gradually as the increase of temperature. Some data of TG–DTA spectra are listed in Table 4. The thermal behavior of La(III) ion complexes is interesting. The TG–DTA curves show two mass loss, each coinciding with one kind of water molecule which shows clear the presence of crystal and coordinated water; this is also confirmed by IR spectroscopy. The TG curves of Tb(III), Eu(III), Sm(III) and Gd(III) ion complexes show the first mass loss between 48–147, 50–142, 49–140 and 52–150 °C, respectively, which corresponds to the release of crystal water content. The relatively high temperature of mass loss between 162–261, 166–274, 156–265 and 164–270 °C shows that this is coordinated water hold. The third mass loss stage of the La(III) ion complexes in region of 350–600 °C is attributed to elimination and/or decomposition of free ligand. The initial temperature of decomposition is over 350 °C, which indicates that the thermal stability of the complexes is higher than that of the free ligand (294 °C decomp.) showing that there may be large conjugation in the chelate ring in the complexes [25].

## 4. Conclusions

We have successfully synthesized a novel bis-pyrazolyl-carboxyl containing ligand and shown that it can form stable complexes with Eu(III), Tb(III), Sm(III) and Gd(III) ions. The complexes have suitable conjugated $\pi$-electron system to efficiently sensitize Ln(III) ion fluorescence. The fluorescence spectra show that Tb(III) and Eu(III) complex all display characteristic metal-centered fluorescence while ligand fluorescence is completely quenched showing that efficient ligand-to-metal energy transfer (antenna effect) occurred.

The complexes each exhibited fluorescence, with the Tb(III) complex being an excellent green luminescent material and exhibit stronger fluorescence than that of Eu(III), Sm(III) and Gd(III) complexes and can be hopefully used in photoluminescence and luminescent materials. Based on our results, a series of novel bis-pyrazolyl-carboxyl containing ligand could be synthesized and screened to optimize the luminescent properties of these lanthanide ions complexes.

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