

# Preparation, Crystal Structures and Luminescent Properties of Terbium and Europium Complexes with a New Amino-Alkenone Type Ligand

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**Abstract** Solid complexes of terbium and europium nitrates with an amino-alkenone type ligand, 1-[2-(6-methylpyridin-2-ylamino)-5,6-dihydro-4H-pyran-3-yl]ethanone (L) have been prepared and characterized by elemental analysis, conductivity measurements, and IR spectra. The crystal and molecular structures of the complexes  $[\text{TbL}_2(\text{NO}_3)_3(\text{H}_2\text{O})]\cdot\text{CHCl}_3$  (1) and  $[\text{EuL}_2(\text{NO}_3)_3(\text{H}_2\text{O})]\cdot\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$  (2) have been determined by single crystal X-ray diffraction. And the coordination spheres of the complexes are similar. At the same time, the luminescent properties of the  $\text{Tb}^{3+}$  complex in solid state and in solvents were investigated at room temperature. Under the excitation of UV light, Tb(III) complex exhibited characteristic emissions but not for the Eu(III) complex. The lowest triplet state energy level of the ligand in the complex matches better to the resonance level of Tb(III) than Eu(III) ion.

**Keywords** Terbium · Europium · Amino-alkenone type ligand · Luminescent properties · Crystal structures

## Introduction

Lanthanide ions have sharp and intense emission bands based on their f-f electronic transitions and a wide range of luminescence lifetimes, suitable for various applications such as chemosensors [1, 2], and as probes and labels in a variety of biological and chemical devices [3, 4]. However,

the application of lanthanide-based luminescence suffers from two serious drawbacks: (1) the low absorption coefficients because of the f-f electronic transitions which are forbidden and (2) the efficient non-radiative deactivation of their excited states by O-H oscillators such as water [5].

In order to avoid these obvious problems for the application of lanthanides, a strategy has been developed that involves the so-called antenna effect. In this approach, the lanthanide ion is linked via complexation with a ligand, an organic chromophore which serves as an antenna or sensitizer. In the subsequent process, this chromophore can absorb the excitation light energy and transfer the energy from its lowest triplet state energy level ( $T_1$ ) to the resonance level of lanthanides [6]. Furthermore, the complexation with a ligand provides lanthanides with a certain degree of protection from the solvent molecules, hence, increasing their luminescence quantum yields. And the ligands which have simple preparation process and can provide some of proper conjugate absorption groups suitable for energy transfer to lanthanide ion are easy for applications in devices. Among the lanthanide complexes, the europium and terbium complexes have received many attentions due to the unique photophysical properties of these ions, such as their large Stokes shift and narrow emission profiles [7, 8].

In the present work, we prepared a new amino-alkenone type ligand, 1-[2-(6-methylpyridin-2-ylamino)-5,6-dihydro-4H-pyran-3-yl]ethanone (L) with simple and flexible structure and perfect yield to synthesize. The lowest triplet state energy level of the ligand which was calculated from the phosphorescence spectrum of the  $\text{Gd}^{3+}$  complex at 77 K indicates that the triplet state energy level of the ligand matches better to the resonance level of  $\text{Tb}^{3+}$ . Owing to their tuneable nature, we believe that the lanthanide

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complexes with this amino-alkenone type ligand have potential to modify and functionalize the surface of the inorganic matrices and allow construction of functional materials with various optical properties.

## Experimental section

### Materials

Lanthanide nitrates were prepared according to the literature [9]. N-[6-(2-methylpyridinyl)]-ketoacetamide (3) was prepared by the reaction of 2-amino-4-picoline (1) with ethyl acetoacetate (2), as described previously [10]. The other commercially available chemicals were of A.R. grade and were used without further purification.

### Methods

Carbon, nitrogen and hydrogen were determined using an Elementar Vario EL (see Table 1). The IR spectra were recorded in the 4,000–400  $\text{cm}^{-1}$  region using KBr pellets and a Nicolet Nexus 670 FTIR spectrometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured on a Varian Mercury 300 spectrometer in  $\text{CDCl}_3$  solutions, with TMS as internal standard. Luminescence and phosphorescence spectra were obtained on a Hitachi F-4500 fluorescence spectrophotometer. The quantum yield of the terbium sample was determined by an absolute method using an integrating sphere (150 mm diameter,  $\text{BaSO}_4$  coating) from Edinburgh Instruments FLS920. The lifetime measurement was measured on an Edinburgh Instruments FLS920 Fluorescence Spectrometer with Nd pumped OPOlette laser as the excitation source.

### Crystal structure determination

Suitable single crystal of the terbium and europium nitrate complexes were carefully selected under an optical microscope and mounted in a fine-focus sealed tube. Crystallographic data for the compound was collected with graphite-monochromatic  $\text{Mo-K}\alpha$  radiation on a Bruker APEX area-detector diffractometer by the phi and omega scans technique. Unit cell dimensions were obtained with least-squares refinements, and all structures were solved by direct methods. The program SMART [11] was used to collect the intensity data, SAINT for integration of the

intensity [11] and SHELXTL [12] for structure solution and refinements on  $F^2$ . All the H atoms were positioned geometrically and refined using a riding model. The final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters assigned for all the non-hydrogen atoms. CCDC-758552 and CCDC-758553 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

### Preparation of the ligand L

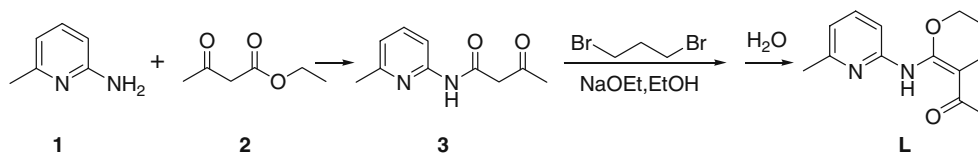
The synthetic route for the ligand 1-[2-(6-methylpyridin-2-ylamino)-5,6-dihydro-4H-pyran-3-yl]ethanone (L) is shown in Scheme 1. Sodium metal (0.069 g, 3.0 mmol) was dissolved in ethanol (10 mL), then N-[6-(2-methylpyridinyl)]-ketoacetamide (3, 0.534 g, 3.0 mmol) which had been dissolved in ethanol was added. The mixture was stirred continuously for 1 h. Then, 3.0 mmol (0.606 g) of 1,3-dibromopropane was added dropwise into the solution with stirring. The mixture was heated to reflux at 78  $^\circ\text{C}$  for 24 h. After cooling down, 5 mL  $\text{H}_2\text{O}$  was added to the solution to cause precipitation. Subsequently, the solution was filtered, and a yellow powder was obtained. The above yellow precipitation was washed with ethyl acetate three times. Finally, a pure yellow powder was obtained and dried in a vacuum. Yield: 71%. m.p.: 138–141  $^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm)  $\delta$ =1.97–2.02 (m, 2H,  $\text{CH}_2$ ), 2.15 (s, 3H,  $\text{CH}_3\text{C}=\text{O}$ ), 2.44 (s, 3H,  $\text{CH}_3\text{-Py}$ ), 2.45–2.51 (t, 2H,  $\text{CH}_2$ ), 4.25–4.28 (t, 2H,  $\text{CH}_2\text{-O}$ ), 6.75–6.76 (d, 1H,  $\text{Py-H}$ ), 7.18–7.20 (d, 1H,  $\text{Py-H}$ ), 7.41–7.45 (t, 1H,  $\text{Py-H}$ ), 13.00 (s, 1H, NH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ =22.04 ( $\text{CH}_2\text{-C}$ ), 22.16 ( $\text{CH}_2\text{-C}$ ), 24.15 ( $\text{CH}_3\text{-Py}$ ), 27.12 ( $\text{CH}_3\text{C}=\text{O}$ ), 67.89 ( $\text{OCH}_2$ ), 86.92 ( $\text{C}=\text{C}=\text{O}$ ), 111.51 (Py (CH)), 117.61 (Py (CH)), 137.62 (Py (CH)), 151.10 (Py (C=N)), 157.48 (Py (C=N)), 160.37 ( $\text{C}=\text{C}=\text{O}$ ), 195.20 (C=O). IR (KBr pellet,  $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{O})$  1,620 (s),  $\nu(\text{C}=\text{N})$  1,573 (s),  $\nu(\text{N-H})$  3,426 (s), and  $\nu(\text{C-O})$  1,228 (s).

### Preparation of the complexes

The solution of 0.3 mmol ligand (L) in chloroform (2 mL) was added dropwise to a solution of 0.1 mmol lanthanide nitrates ( $\text{Ln} = \text{Tb}, \text{Eu}$ ) in ethyl acetate (2 mL). Then the

**Table 1** Analytical and molar conductance data of the solid complexes (calculated values in parentheses)

Complexes	%C (Calc.)	%H (Calc.)	%N (Calc.)	$A_m(\text{cm}^2\Omega^{-1}\text{mol}^{-1})$
$[\text{TbL}_2(\text{NO}_3)_3\cdot\text{H}_2\text{O}]\cdot\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	38.99(39.35)	4.503(4.62)	10.54(10.71)	11.8
$[\text{EuL}_2(\text{NO}_3)_3\cdot\text{H}_2\text{O}]\cdot\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	39.23(39.65)	4.531(4.66)	10.72(10.79)	10.9

**Scheme 1** The synthetic route for the ligand L

mixture was stirred at room temperature for 4 h. And the precipitated solid complex was filtered, washed with mixed solvent of chloroform and ethyl acetate (v:v=1:1), dried in vacuo over  $\text{P}_4\text{O}_{10}$  for 48 h and submitted for elemental analysis. All the complexes were obtained as yellow powders. Yield: 60–70%. Single crystals of the terbium and europium complexes were grown from ethyl acetate and chloroform (v:v=1:1) mixed solution with slow evaporation at room temperature. After approximately 1 month, transparent yellow crystals were formed from the solution.

## Results and discussion

The analytical data for the newly synthesized complexes, listed in Table 1, indicate that the two complexes conform to a 1:2 metal-to-ligand stoichiometry. All the complexes are soluble in DMF, DMSO, methanol, ethanol, acetone, acetonitrile, THF, but slightly soluble in chloroform and

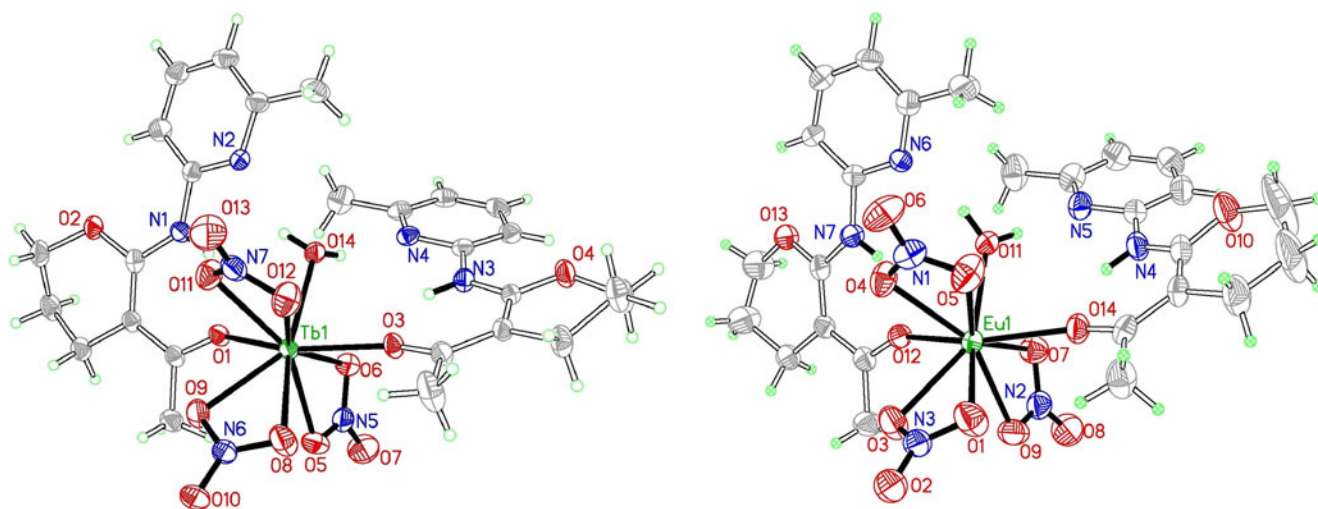
ethyl ether. The molar conductances of the complexes in acetone (see Table 1) reveal that the two complexes act as non-electrolytes [13], implying that all nitrate groups are in the coordination sphere.

## Description of the crystal structures

Single-crystal X-ray diffraction investigation reveal that the two complexes all crystallize in monoclinic with space group  $P2(1)/c$  and the results of the structure analysis of the complexes  $[\text{TbL}_2(\text{NO}_3)_3(\text{H}_2\text{O})] \cdot \text{CHCl}_3$  (1) and  $[\text{EuL}_2(\text{NO}_3)_3(\text{H}_2\text{O})] \cdot \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$  (2) show that they have the similar coordination sphere, thus only the structure of the terbium complex is described here as an example. Selected crystallographic data are shown in Table 2. X-ray crystal structures of the Tb complex and Eu complex with atom numbering scheme are presented as ORTEP figures in Fig. 1 and the crystal packing diagrams of the Tb complex and Eu complex are shown in Fig. 2. The experimental parameters of the single-crystal X-ray analysis of the Tb

**Table 2** Crystal data and structure refinement for the Tb and Eu complexes

Empirical formula	$\text{C}_{27}\text{H}_{35}\text{Cl}_3\text{N}_7\text{O}_{14}\text{Tb}$	$\text{C}_{34}\text{H}_{34}\text{N}_7\text{O}_{14}\text{Eu}$
Formula weight	946.49	916.64
Temperature (K)	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$
$a, b, c / \text{\AA}$	19.165(3), 10.6459(14), 18.475(2)	19.500(2), 14.0762(15), 14.3967(2)
$\beta / ^\circ$	97.914(2)	99.107(2)
$V (\text{\AA}^3)$	3734.8(8)	3901.9(7)
$Z$	4	4
$D_{\text{calc}} / \text{g}\cdot\text{cm}^{-3}$	1.684	1.560
$\mu (\text{Mo K}\alpha) (\text{mm}^{-1})$	2.180	1.682
Crystal size /mm	0.53 × 0.40 × 0.38	0.20 × 0.18 × 0.15
Range /deg	2.15 to 25.00	1.79 to 28.38
$F(000)$	1896	1848
Index ranges	$-22 \leq h \leq 22$ ; $-12 \leq k \leq 11$ ; $-19 \leq l \leq 21$	$-25 \leq h \leq 24$ ; $-18 \leq k \leq 10$ ; $-18 \leq l \leq 19$
Measured reflections	18377	23165
Independent reflections	6560 [R(int)=0.0292]	9346 [R(int)=0.0480]
Refinement method	semi-empirical from equivalents	semi-empirical from equivalents
Data/restraints/parameters	6560/0/489	9346/3/493
Goodness-of-fit on $F^2$	1.040	1.005
Final R indices [ $I > 2\sigma(I)$ ]	0.0257, 0.0687	0.0490, 0.1076
R indices (all data)	0.0369, 0.0687	0.1133, 0.1373



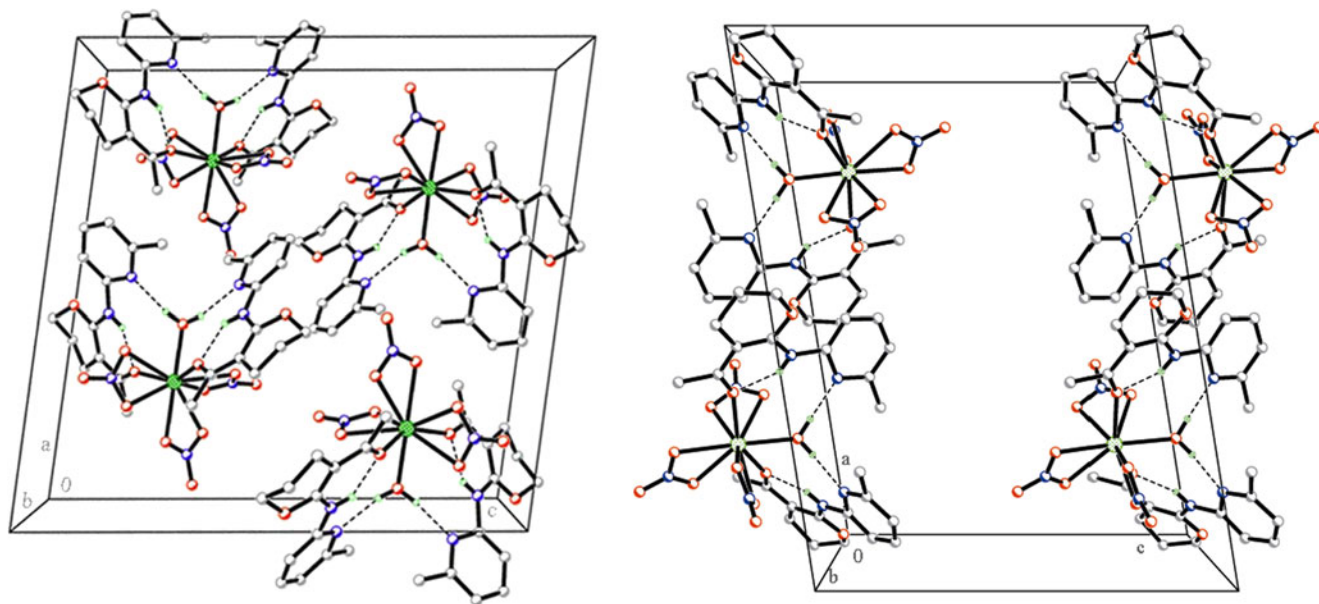
**Fig. 1** Structures of  $[\text{TbL}_2(\text{NO}_3)_3(\text{H}_2\text{O})]\cdot\text{CHCl}_3$  and  $[\text{EuL}_2(\text{NO}_3)_3(\text{H}_2\text{O})]\cdot\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$  showing the coordination sphere of  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  along with atom labeling schemes. Solvent molecules are omitted for clarity

complex indicate that the mononuclear Tb atom is surrounded by nine coordinated oxygen donor atoms. Six of them belong to the three bidentate nitrate groups, two belong to the carbonyl oxygen atoms of the ligands and one belongs to the coordinated water molecule (with all the Tb–O bond lengths range from 2.309(2) Å to 2.534(3) Å and the O–Tb–O angles range from 50.34(9) to 155.86(10)°). The Tb–O bond distances (2.309(2)–2.323(2) Å) are similar to those found for the terbium complex with carbonyl type ligand [14–16]. The coordination polyhedra around  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  are both distorted tricapped trigonal prisms, which are shown in Fig. 3.

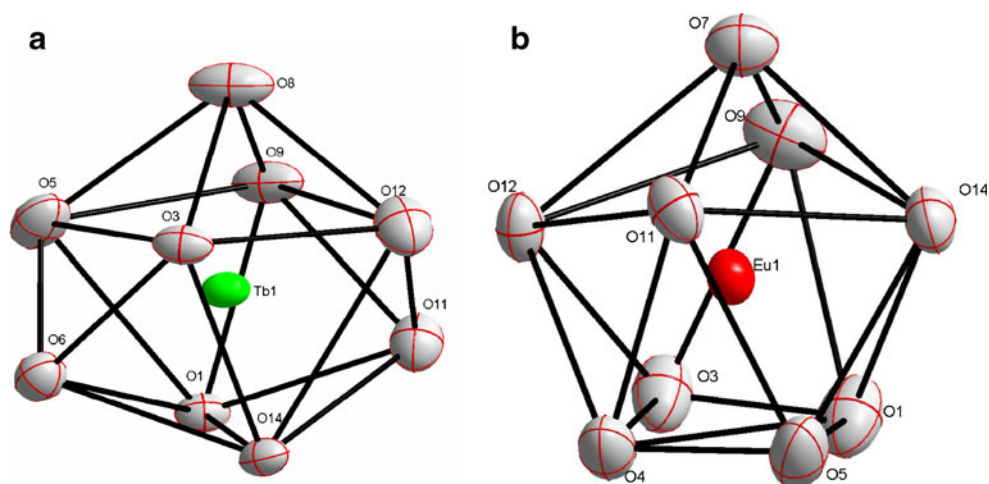
The mononuclear Tb complex is stabilized by two different kind of intramolecular hydrogen bonds (N–H...O and O–H...O). All of the relevant hydrogen-bonding values are listed in Table 3.

#### Infrared spectra

The complexes have similar IR spectra, of which the characteristic bands have similar shifts, suggesting that they have a similar coordination structure. The infrared spectrum of the free ligand shows strong bands at about 1,620  $\text{cm}^{-1}$  and 1,228  $\text{cm}^{-1}$  which are assigned to  $\nu(\text{C}=\text{O})$



**Fig. 2** View of the packing diagrams of the Tb and Eu complex (the solvent molecules and some of the hydrogen atoms are omitted)

**Fig. 3** Coordination polyhedra of Tb1 **a** and Eu1 **b** ions

and  $\nu(\text{C}-\text{O}-\text{C})$ , respectively. In the nitrate complexes, the low-energy band remains unchanged, but the high-energy band red shifts to about  $1,615 \text{ cm}^{-1}$  ( $\Delta\nu=5 \text{ cm}^{-1}$ ) compared with its counterpart for the ligand. The red shift is due to the following two effects. First, the oxygen atom of the ligand takes part in the coordination to the lanthanide ion decreasing the  $\pi$ -bond character. Second, the conjugating effect of  $\text{C}=\text{C}$  remains the  $\pi$ -bond character in the  $\text{C}=\text{O}$  bond.

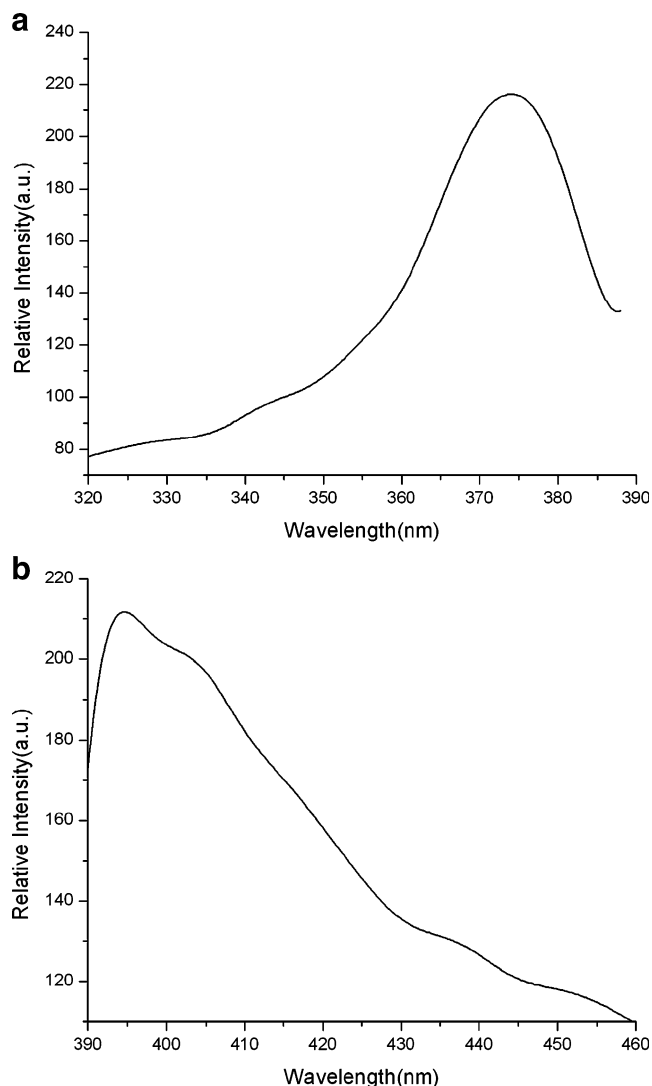
The characteristic frequencies of the coordinating nitrate groups ( $\text{C}_{2v}$ ) appear at ca.  $1,463 \text{ cm}^{-1}$  ( $\nu_1$ ),  $1,303 \text{ cm}^{-1}$  ( $\nu_4$ ),  $1,026 \text{ cm}^{-1}$  ( $\nu_2$ ) and  $797 \text{ cm}^{-1}$  ( $\nu_3$ ) [17], and the difference between two strongest absorptions ( $\nu_1$  and  $\nu_4$ ) of the nitrate groups is about  $150\text{--}160 \text{ cm}^{-1}$ , clearly establishing that the  $\text{NO}_3^-$  groups in the solid complexes coordinate to the lanthanide ion as bidentate ligands [18]. Additionally, no bands at  $1,380$ ,  $820$  and  $720 \text{ cm}^{-1}$  in the spectra of complexes indicates that free nitrate groups ( $\text{D}_{3h}$ ) are absent. In addition, broad bands at ca.  $3,422 \text{ cm}^{-1}$  could be attributed to the O-H stretching vibrations of  $\text{H}_2\text{O}$  molecules, which is in agreement with the results of the elemental analysis.

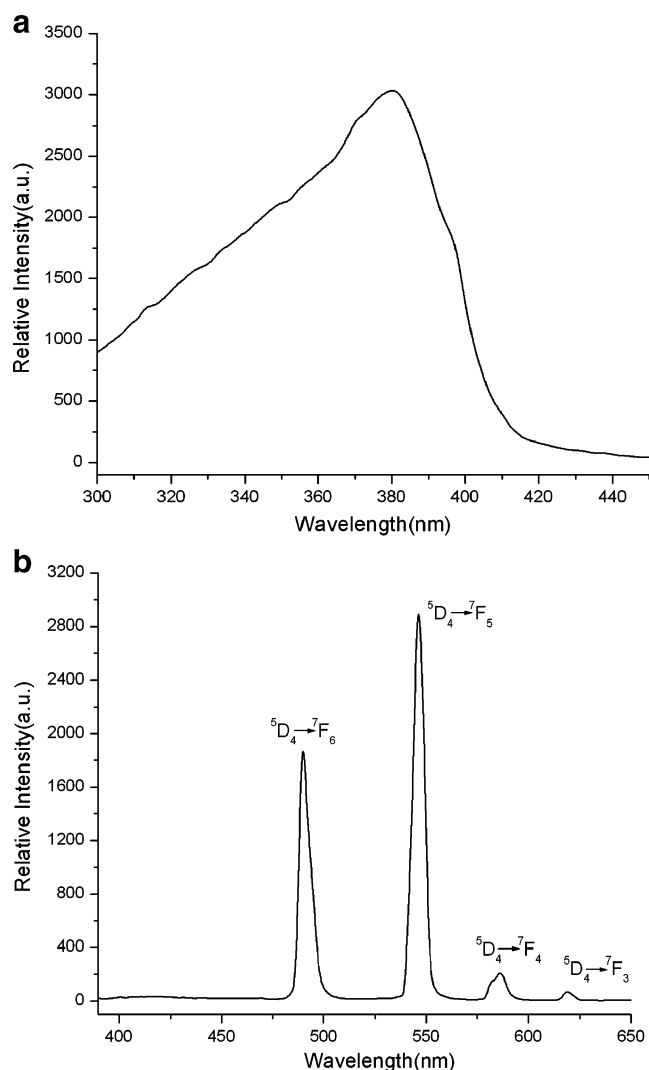
#### Luminescent properties of the complex

The ability to transfer energy from ligand-centered to metal-centered is important in the design of lanthanide(III)

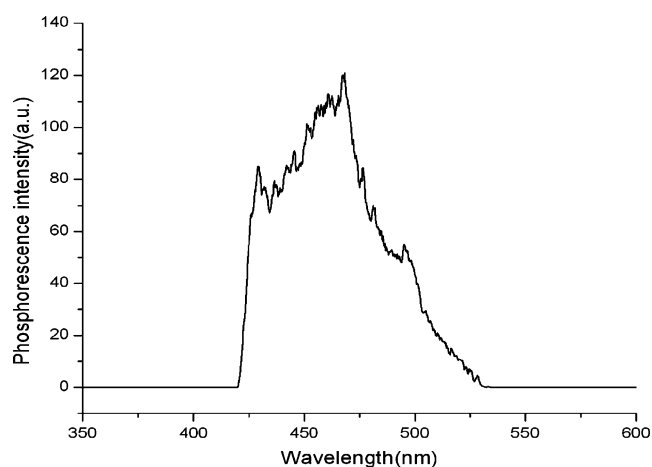
**Table 3** Main intramolecular hydrogen bonds data for the  $\text{Tb}^{3+}$  complex ( $\text{\AA}$ ,  $^\circ$ )

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
O14-H14b...N2	0.850	1.994	2.779	153.12
O14-H14c...N4	0.850	1.965	2.767	156.92
N1-H1...O1	0.860	1.914	2.608	136.85
N3-H3...O3	0.860	1.878	2.591	139.16

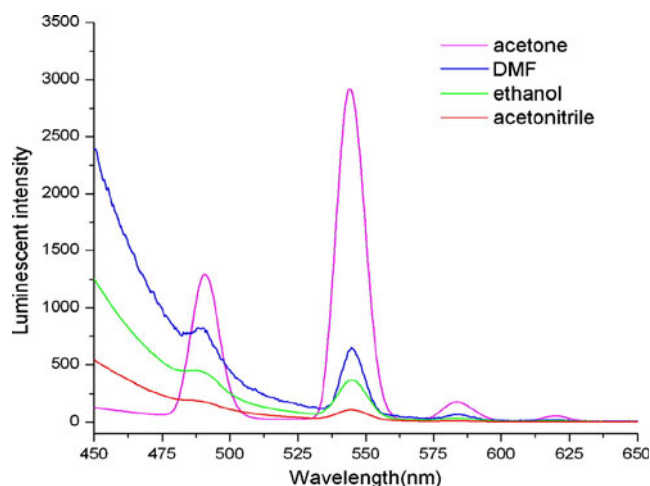
**Fig. 4** Excitation spectrum **a** and emission spectrum **b** of the ligand in solid state (excited at  $374 \text{ nm}$ )



**Fig. 5** Excitation spectrum **a** and emission spectrum **b** (excited at 380 nm) of Tb complex in solid state



**Fig. 6** The phosphorescence spectra of the Gd nitrate complex



**Fig. 7** Emission spectra of the Tb complex in different solutions at room temperature

photonic devices [19, 20]. The luminescence spectra of the ligand and its  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  complexes in solid state were recorded at room temperature. Among the complexes, luminescence of the complex of  $\text{Tb}^{3+}$  nitrate was observed but not for the  $\text{Eu}^{3+}$  complex. Excited by the absorption band at 374 nm (Fig. 4a), the ligand exhibits a wide emission peak ( $\lambda_{\text{max}}=395$  nm) in solid state as shown in Fig. 4b. The luminescence excitation and emission spectra

**Table 4** Luminescence data for the Tb complex in solid state and in different solutions at room temperature

Solvent	$\lambda_{\text{Ex}}$ (nm)	$\lambda_{\text{Em}}$ (nm)	RFI [a]	Assignments
Solid state	380	489.8	1,866	$^5\text{D}_4 \rightarrow ^7\text{F}_6$
		546.2	2,888	$^5\text{D}_4 \rightarrow ^7\text{F}_5$
		586.2	208.1	$^5\text{D}_4 \rightarrow ^7\text{F}_4$
		619.0	67.64	$^5\text{D}_4 \rightarrow ^7\text{F}_3$
Acetone	380	490.8	1,295	$^5\text{D}_4 \rightarrow ^7\text{F}_6$
		543.8	2,919	$^5\text{D}_4 \rightarrow ^7\text{F}_5$
		583.8	178.3	$^5\text{D}_4 \rightarrow ^7\text{F}_4$
		620.2	53.64	$^5\text{D}_4 \rightarrow ^7\text{F}_3$
DMF	358	490.2	825.1	$^5\text{D}_4 \rightarrow ^7\text{F}_6$
		544.6	646.6	$^5\text{D}_4 \rightarrow ^7\text{F}_5$
		582.6	68.61	$^5\text{D}_4 \rightarrow ^7\text{F}_4$
		619.6	21.18	$^5\text{D}_4 \rightarrow ^7\text{F}_3$
Ethanol	362	487.0	449.0	$^5\text{D}_4 \rightarrow ^7\text{F}_6$
		544.8	361.6	$^5\text{D}_4 \rightarrow ^7\text{F}_5$
		583.6	33.93	$^5\text{D}_4 \rightarrow ^7\text{F}_4$
		618.4	11.64	$^5\text{D}_4 \rightarrow ^7\text{F}_3$
Acetonitrile	356	488.2	188.5	$^5\text{D}_4 \rightarrow ^7\text{F}_6$
		544.2	108.2	$^5\text{D}_4 \rightarrow ^7\text{F}_5$
		584.4	10.74	$^5\text{D}_4 \rightarrow ^7\text{F}_4$

of the terbium complex in solid state (the excitation and emission slit widths were 2.5 and 1.0 nm respectively, Fig. 5) were recorded at room temperature. Ligand-based excitation at 380 nm causes the characteristic f-f transition emissions of the terbium complex while the ligand fluorescence is completely quenched. This indicates that the ligand is a comparative good organic chelator to absorb energy and transfer it to Tb ion. An intramolecular energy transfer from the triplet state of the ligand to the resonance level of the Ln(III) ion is one of the most important processes having influence on the Ln(III) luminescent properties of Ln(III) complexes [21].

The fluorescence quantum yield  $\Phi$  of the terbium nitrate complex in solid state was found to be  $13.16 \pm 0.1\%$ . And the Tb(III) complex luminescence decay is best described by a single-exponential process with significantly longer lifetime of  $\tau = 1.106 \pm 0.001$  ms, indicating the presence of one distinct emitting species. The relatively long luminescence lifetime is an indication that the ligand provides a significant level of protection from non-radiative deactivation of the lanthanide cations which is consistent with the single crystal analysis.

In order to acquire the triplet excited state  $T_1$  of the ligand, the phosphorescence spectrum of the Gd(III) complex was measured at 77 K in a methanol–ethanol mixture (v:v=1:1), as shown in Fig. 6. And the triplet state energy level  $T_1$  of the ligand, which was calculated from the shortest-wavelength phosphorescence band [22], is  $23,310 \text{ cm}^{-1}$ . This energy level is above the lowest excited resonance level  $^5D_0$  of Eu(III) ( $17,300 \text{ cm}^{-1}$ ) and  $^5D_4$  of Tb(III) ( $20,500 \text{ cm}^{-1}$ ). Thus, the absorbed energy may be transferred from ligand to the Eu or Tb ions. And we may deduce that the triplet state energy level  $T_1$  of this ligand matches better to the lowest resonance level of Tb(III) ( $\Delta\nu = 2,810 \text{ cm}^{-1}$ ) than to Eu(III) ( $\Delta\nu = 6,010 \text{ cm}^{-1}$ ) ions, because such large  $\Delta\nu(T_1 - ^5D_0)$  could result in the non-radiative deactivation of the lanthanide emitting state and quench the luminescence of the complex [21, 23].

The luminescence emission spectra of the Tb complex in acetone, DMF, ethanol and acetonitrile solutions (concentration:  $1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ , the excitation and emission slit widths were 10.0 nm, Fig. 7) were recorded at room temperature. It could be seen from Fig. 7 that in acetone solution the Tb complex has the strongest luminescence, and then in DMF, ethanol and acetonitrile solution (Table 4). The result may be due to the coordinating effects of solvents, so-called solvate effect [24]. Together with the raising coordination abilities of acetone, DMF, ethanol to acetonitrile for the lanthanide ions, the oscillatory motions of the entering molecules consume more energy, which the ligand triple level transfers to the emitting level of the lanthanide ion. Thus, the energy transfer could not be carried on perfectly.

## Conclusions

In summary, two new lanthanide nitrate complexes  $[\text{LnL}_2(\text{NO}_3)_3(\text{H}_2\text{O})]$  (Ln = Tb, Eu) of the amino-alkenone type ligand, 1-[2-(6-methylpyridin-2-ylamino)-5,6-dihydro-4H-pyran-3-yl]ethanone (L) were obtained and structurally characterized. The lanthanide ion of each crystal is coordinated toward nine donor atoms. The coordination environment around the Tb and Eu centers both can be described as distorted tricapped tripisms although they have slight differences. Meanwhile, the luminescent properties of the Tb(III) complex in solid state and different solutions were investigated. In addition, the lowest triplet state energy level of the ligand indicates that the triplet state energy level of the ligand matches better to the resonance level of Tb(III). Under the excitation of UV light, the complex exhibited characteristic emission of the central Tb(III) ion rather than Eu(III). And the Tb complex does possess comparatively long luminescence lifetime. To sum up, we have designed a new ligand which can strongly bind Ln(III) ions and effectively sensitize Tb(III) luminescence emission. In particular, the results presented here should help to design useful agents exploiting luminescent properties of lanthanide complexes rationally. Owing to their tunable nature, we believe that the lanthanide complexes with this amino-alkenone type ligand have potential to modify and functionalize the surface of the inorganic matrices and allow construction of functional materials with various optical properties.

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