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# Synthesis, structure and spectroscopic properties of rare earth complexes with a new aryl amide 2,2'-bipydine derivative

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## Abstract

Solid complexes of rare earth nitrates and picrates with a new aryl amide ligand 3.3'-bis(benzylamido)-2,2'-bipyridine (**L**) were synthesized and characterized by elemental analysis, IR and molar conductivity measurements. The molecular structures of the complex [TbL<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>H<sub>2</sub>O]·2H<sub>2</sub>O have been determined by single-crystal X-ray diffraction. The fluorescent properties of the Eu(III) and Tb(III) nitrates and picrates complexes in solid state were also investigated in detail. Under the excitation, these complexes exhibited characteristic emissions of europium and terbium ions. It is worth noting that the nature of the anion has a great effect upon the composition of the complexes as well as emission properties of them.

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Keywords: Bipyridine; Amide ligand; Rare earth complex; Fluorescence properties

## 1. Introduction

The specific spectroscopic and magnetic properties of rare earth ions have made them one of the essential components in the preparation of new materials and ideal as probes in studies of biological systems [1]. Among these studies, much attention has been paid to the fluorescent rare earth complexes that are found and used as labels and sensors for natural and medical science [2,3], mainly due to their large Stokes shifts, narrow emission profiles [4]. More and more chemists are attracted to design the organized molecular architectures containing trivalent rare earth ions (Eu<sup>3+</sup>, Tb<sup>3+</sup>) working as efficient light conversion devices [5,6].

The emission originates from 4f–4f intra-atomic electronic and magnetic dipole transitions that are parity-forbidden. As such, the absorption cross sections for directly exciting trivalent rare earth ions are small and the use of ligands to excite trivalent rare earth ions through an energy-transfer process is, in general, therefore much more effective [7]. In order to obtain strongly fluorescent complexes, the chromophoric ligands which coordi-

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nate to rare earth metals should be able to absorb energy and transfer it efficiently to the central metal [8].

Our group is interested in the supramolecular coordination chemistry of rare earth ions with amide type ligands which have strong coordination capability to the rare earth ions and enhanced luminescence of rare earth complexes by providing some of proper conjugate absorption groups suitable for energy transfer [9–11]. The chelate ligands 2,2-bipyridine (bpy), 1,10-phenanthroline (phen), and their substituted derivatives have played an important role in the development of coordination chemistry [12,13]. Studies have also shown that rare earth luminescence enhancement can be facilitated in complexes possessing an aromatic ring that has a nitrogen atom, such as 1,10-phenanthroline or bipyridine [14–16]. In the present work, we designed and synthesized a new amide type bridged ligand with a 3,3'-disubstituted-2,2'pyridine antenna effect, 3,3'-bis(benzylamido)-2,2'-bipyridine (L) (Scheme 1) with two relatively long "arms", and studied the crystal structure and luminescent properties of rare earth complexes with this new ligand. The crystal structure of the complex [TbL<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>H<sub>2</sub>O]·2H<sub>2</sub>O shows that only one arm of each ligand bind one Tb atom. The fluorescent properties of the solid complexes of europium(III) and terbium(III) ions with this new ligand were also studied in detail. And the results indicated that counter anion notably

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Scheme 1. The synthesis route of the ligand L.

affected the fluorescence characteristics of europium and terbium ions.

# 2. Experimental

## 2.1. Materials

The rare earth nitrates [17] and picrates [18] were prepared according to literature method. Pyridine was dried according to literature procedures. Other commercially available chemicals were of reagent grade and were used without further purification.

## 2.2. Methods

The metal ions were determined by EDTA titration using xylenol orange as indicator. Carbon, Nitrogen and Hydrogen analyses were performed using an EL elemental analyzer. Infrared spectra (4000–400 cm<sup>-1</sup>) were obtained with KBr discs on a Therrno Mattson FTIR spectrometer. <sup>1</sup>H NMR spectra were recorded on a Brucker DRX 200 spectrometer in D<sub>2</sub>O or CDCl<sub>3</sub> solution with TMS as internal standard. Electronic spectra were recorded with a Varian Cary 100 spectrophotometer in ethyl acetate solution. Fluorescence measurements were made on a Hitachi F-4500 spectrophotometer and a shimadzu RF-540 spectro-fluorophotometer equipped with quartz curettes of 1 cm path length. The excitation and emission slit widths were 5 and 2.5 nm, respectively. The molar conductance values measurements were carried out on a model DDS-307 type conductivity bridge using  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> solutions in acetone at 25 °C.

2.3. Synthesis of the ligand

2,2'-Binicotinic acid was prepared according to the literature [19]. <sup>1</sup>H NMR (D<sub>2</sub>O) 8.67 (dd, 2H), 8.57 (dd, 2H), 7.75 (t, 2H).

## 2.3.1. Preparation of

# 3,3'-bis(chlorocarbonyl)-2,2'-bipyridine and

#### 3,3'-bis-(benzylamido)-2,2'-bipyridine (L)

2,2'-Binicotinic acid (1.07 g, 4.4 mmol) was directly dissolved in 20 ml of SOCl<sub>2</sub> and refluxed until the white powder disappeared completely. And the residue SOCl<sub>2</sub> was removed away completely under reduced pressure. The resulting 3,3'bis(chlorocarbonyl)-2,2'-bipyridine was dissolved in 20 ml of dry pyridine immediately. Then the pyridine solution of benzylamine (1.07 g, 10 mmol) was dropwise added into the 3,3'-bis(chlorocarbonyl)-2,2'-bipyridine solution under stirring in the ice bath. Continuous stirring at room temperature for 10 h. Distilled water (10 ml) and methanol (5 ml) were added, after 4 days a pale flocculent solid was obtained. Recrystallization in ethyl acetate afforded a white flocculent solid. Yield: 1.52 g (78%) L: <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.39 (dd, 2H), 7.85 (dd, 2H), 7.67 (t, 2H), 7.26–6.98 (m, 10H, ArH), 4.34 (dd, 4H).

#### 2.4. Synthesis of the complexes

A solution of 0.1 mmol rare earth nitrate in 5 ml of ethyl acetate was added dropwise to the solution of 0.2 mmol L in 10 ml of ethyl acetate. The mixture was stirred at room temperature for 8 h. The precipitated solid complex was filtered, washed with ethyl acetate three times and dried in vacuo over  $P_4O_{10}$  for 48 h. All the nitrate complexes were obtained as white powders which are stable in air, yield: 40%. Single crystals of nitrate complex were grown from ethyl acetate and acetone (*V*:*V*=3:1) mixed solution with slow evaporation at room temperature. After ca. 3 weeks, transparent colorless crystals were formed from the solution which is suitable for X-ray diffraction analysis.

An ethyl acetate solution  $(5 \text{ cm}^3)$  of rare earth picrate (0.1 mmol) was added dropwise to a solution of 0.1 mmol ligand L in the  $(5 \text{ cm}^3)$  ethyl acetate. The mixture was stirred at room temperature for 8 h. And then the precipitated solid complex was filtered, washed with ethyl acetate, dried in vacuo over P<sub>4</sub>O<sub>10</sub> for 48 h and submitted for elemental analysis, yield: 70%.

# 3. Results and discussion

#### 3.1. Properties of the discussion

Analytical data for the newly synthesized complexes, listed in Table 1, conform to a 1:2 metal-to-L stoichiometry for nitrate complex and 1:1 for picrate complex. All complexes are soluble in DMF, DMSO, acetone, ethanol and methanol, but slightly soluble in ethyl acetate and hexane. The molar conductance of the complexes in acetone (see Table 1) indicates that all complexes act as non-electrolytes.

# 3.2. IR spectra

Tables 4 and 5 show the characteristic bands of the ligand and its complexes. The IR spectrum of the free ligand shows bands at 1628 and 1553 cm<sup>-1</sup>, which may be attributed to stretch vibration of the carbonyl group of amide (C=O) and(C=N) of bipyridine, respectively. In the nitrate complexes, the bands for one of (C=O) is shifted by about 24 (from 1628 to 1604) indicate that one of the carbonyl of the ligand take part in coordination.

2	1	· · · · · · · · · · · · · · · · · · ·	,		
Complex	Analysis (%)	$\Lambda m (\Omega^{-1}  cm^2  mol^{-1})$			
	С	Н	Ν	Ln	
$\overline{[La(NO_3)_3L_2\cdot H_2O]\cdot 2H_2O}$	51.36(51.03)	4.18(4.12)	12.69(12.59)	11.08(11.35)	53.6
$[Eu(NO_3)_3L_2\cdot H_2O]\cdot 2H_2O$	50.84(50.49)	4.20(4.07)	12.58(12.46)	12.09(12.28)	54.3
$[Gd(NO_3)_3L_2\cdot H_2O]\cdot 2H_2O$	50.54(50.28)	4.18(4.06)	12.28(12.40)	12.41(12.66)	55.2
$[Tb(NO_3)_3L_2 \cdot H_2O] \cdot 2H_2O$	50.38(50.21)	4.15(4.05)	12.49(12.39)	12.46(12.78)	54.9
$[Er(NO_3)_3L_2\cdot H_2O]\cdot 2H_2O$	50.13(49.87)	4.10(4.02)	12.23(12.30)	13.20(13.66)	47.8
La(Pic) <sub>3</sub> L	42.68(42.43)	2.14(2.27)	14.72(14.62)	10.95(11.15)	50.3
Eu(Pic) <sub>3</sub> L	42.13(41.99)	2.13(2.24)	14.68(14.47)	11.88(12.07)	64.5
Gd(Pic) <sub>3</sub> L	42.01(41.81)	2.15(2.23)	14.63(14.41)	12.25(12.44)	58.6
Tb(Pic) <sub>3</sub> L	41.90(41.75)	2.09(2.23)	14.45(14.39)	12.31(12.56)	60.8
Er(Pic) <sub>3</sub> L	41.50(41.28)	2.21(2.22)	14.38(14.29)	12.97(13.13)	61.5

 Table 1

 Analytical and molar conductance data for the complexes (calculated values in parentheses)

Notably, the vibration  $\nu$  (C=N) of pyridine ring at 1553 cm<sup>-1</sup> is shifted towards higher frequency in the complexes as compared to counterpart for the free ligand. This may be due to coordination of the oxygen atoms of **L** to trivalent rare earth ion which causes the fixing of **L** conformation. The fact that the amide terminal group (benzylamine) has large sterically hindered effect, which prevents both of carbonyl oxygen atoms of one ligand from coordinating to lanthanide ion could account for these changes.

The absorption bands assigned to the coordinated nitrates were observed as two group bands at about 1492 ( $\nu_1$ ) and 1290 ( $\nu_5$ ) cm<sup>-1</sup> for the complexes. The differences between the strongest absorption band  $\nu_1$  and  $\nu_5$  of nitrate group lie in 194–206 cm<sup>-1</sup>, indicating that coordinated nitrate groups in the complexes are bidentate ligands [20], the  $\nu_3$  of free nitrate group disappears in the spectra of the complexes in agreement with the results of the conductivity experiment. Additionally, strong and broad bands at 3340 cm<sup>-1</sup> indicate that H<sub>2</sub>O is existent in the complexes, the N–H stretch vibration were also observed at 3422, 3217 and 3064 cm<sup>-1</sup>, confirming the elemental analysis.

In the picrate complexes, after forming the complex, the characteristic frequency of the free ligand  $\nu$ (C=O) at 1628 cm<sup>-1</sup>shifts ca. 13 cm<sup>-1</sup> towards lower wave numbers, indicating that the oxygen atom of C=O take part in coordination to the metal ion. The OH out-of-plane bending vibration of the free HPic at 1151 cm<sup>-1</sup> disappears in the spectra of the complexes, indicating that the H-atom of the OH group is replaced by rare earth ions. The free HPic has  $\nu_{as}$ (–NO<sub>2</sub>) and  $\nu_{s}$ (–NO<sub>2</sub>) at 1555 and 1342 cm<sup>-1</sup>, respectively, which split into two bands at ca. 1577, 1543 cm<sup>-1</sup> and ca. 1364, 1333 cm<sup>-1</sup>. This indicates that some of the nitryl O atoms take part in coordination [21].

#### 3.3. Crystal structure of $[TbL_2(NO_3)_3H_2O] \cdot 2H_2O$

A summary of crystallographic data and details of the structure refinements are listed in Table 2. The selected bond lengths and bond angles are given in Table 3. The single-crystal Xray analysis of the complex  $[TbL_2(NO_3)_3H_2O]\cdot 2H_2O$  exhibits a distorted monocapped square antiprism. L functions as monodentate ligand as shown in Fig. 1. The ninth coordination site is occupied by the O atom (O8) of water molecular. Due to the space obstacle, the two pyridine rings provide a non-coplanarity arrangement with the dihedral angle of  $70.09^{\circ}$  which is in agreement with IR spectra.

## 3.4. Electronic spectra

The spectral profiles of the nitrate rare earth complexes are very similar. Absorption spectra of L and  $[TbL_2(NO_3)_3H_2O] \cdot 2H_2O$  are presented in Fig. 2. The electronic spectrum of the free ligand L in ethyl acetate displays only one strong absorption band with maximum at 258 nm which attributed to  $\pi - \pi^*$  transitions centered on the 2,2'-bipyridine group is different from wavelengths compared to those of the free 2,2'-bipyridine (232 and 279 nm), which exists in a trans

Table 2

	Crv	ystal	data	and	structure	refinement	for	the	nitrate	com	pley
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5	1
CCDC	636943
Empirical formula	$C_{52}H_{50}N_{11}O_{16}Tb$
Formula weight	1261.67
Temperature	294(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2(1)/ <i>m</i>
Unit cell dimensions	a = 10.0575(5) Å
	$b = 20.7418(11)$ Å, $\beta = 96.9640(10)$
	c = 14.0835(7)  Å
Volume	2916.3(3) Å <sup>3</sup>
Ζ	2
Density (calculated)	1.417 Mg/m <sup>3</sup>
Absorption coefficient	$1.287  \mathrm{mm}^{-1}$
<i>F</i> (000)	1264
Crystal size	$0.31\text{mm}\times0.17\text{mm}\times0.06\text{mm}$
Theta range for data collection	1.76–23.93°
Index ranges	-11 <= h <= 11, -19 <= k <= 23,
	-15 <= l <= 16
Reflections collected	13430
Independent reflections	4629 [ <i>R</i> (int) = 0.0729]
Completeness to theta $= 23.93$	98.7%
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	4629/190/472
Goodness-of-fit on $F^2$	1.017
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0639, wR2 = 0.1578
R indices (all data)	R1 = 0.0788, wR2 = 0.1646
Largest diff. peak and hole	$1.023$ and $-0.987 e^{-3}$

Table 3
Selected bond lengths (Å) and angles (°) for the complex $[TbL_2(NO_3)_3H_2O] \cdot 2H_2O$

Tb(1)-O(9) 2.310(6)	Tb(1)–O(9)#1 2.310(6)	Tb(1)–O(8) 2.430(8)	Tb(1)–O(2) 2.434(9)
Tb(1)-O(2)#1 2.434(9)	Tb(1)–O(5) 2.441(10)	Tb(1)–O(4) 2.447(7)	Tb(1)–O(4)#1 2.447(7)
Tb(1)-O(6) 2.459(10)			
O(9)-Tb(1)-O(9)#1 148.9(3)	O(9)–Tb(1)–O(8) 80	0.50(2)	O(9)#1-Tb(1)-O(8) 80.50(2)
O(9)-Tb(1)-O(2) 76.4(3)	O(9)#1-Tb(1)-O(2)	128.8(3)	O(8)-Tb(1)-O(2) 148.9(3)
O(9)-Tb(1)-O(2)#1 128.8(3)	O(9)#1-Tb(1)-O(2)	#1 76.4(3)	O(8)-Tb(1)-O(2)#1 148.9(3)
O(2)-Tb(1)-O(2)#1 53.2(6)	O(9)-Tb(1)-O(5) 86	5.84(2)	O(9)#1-Tb(1)-O(5) 86.84(2)
O(8)-Tb(1)-O(5) 130.2(4)	O(2)-Tb(1)-O(5) 69	9.2(4)	O(2)#1-Tb(1)-O(5) 69.2(4)
O(9)-Tb(1)-O(4) 74.5(3)	O(9)#1-Tb(1)-O(4)	124.7(2)	O(8)-Tb(1)-O(4) 78.1(3)
O(2)-Tb(1)-O(4) 75.9(3)	O(2)#1-Tb(1)-O(4)	98.4(4)	O(5)-Tb(1)-O(4) 143.4(3)
O(9)-Tb(1)-O(4)#1 124.7(2)	O(9)#1-Tb(1)-O(4)	#1 74.5(3)	O(8)-Tb(1)-O(4)#1 78.1(3)
O(2)-Tb(1)-O(4)#1 98.4(4)	O(2)#1-Tb(1)-O(4)	#1 75.9(3)	O(5)-Tb(1)-O(4)#1 143.4(3)
O(4)-Tb(1)-O(4)#1 51.5(4)	O(9)-Tb(1)-O(6) 76	5.29(16)	O(9)#1-Tb#1-Tb(1)-O(6) 76.29(16)
O(8)-Tb(1)-O(6) 80.0(3)	O(2)-Tb(1)-O(6) 11	3.7(4)	O(2)#1-Tb(1)-O(6) 113.7(4)
O(5)-Tb(1)-O(6) 50.2(4)	O(4)-Tb(1)-O(6) 14	45.9(3)	O(4)#1-Tb(1)-O(6) 145.9(3)



 $Fig. \ 1. \ ORTEP \ diagram \ (30\% \ probability \ ellipsoids) \ showing \ the \ coordination \ sphere \ of \ TbL_2(NO_3)_3 \cdot 2H_2O.$ 



Fig. 2. Absorption spectra in ethyl acetate of L (left) and Tb complex (right).

Table 4 The most important IR bands for the rare earth nitrate complexes(cm<sup>-1</sup>)

Compound	ν (C=O)	ν (C=N)	$V_1 (NO_3^-)$	$V_4 (NO_3^-)$	$V_2 (NO_3^-)$	$V_3 (NO_3^-)$	$ V_1 - V_4 $
L	1628	1553	_	_	_	_	_
$[La(NO_3)_3L_2\cdot H_2O]\cdot 2H_2O$	1624, 1604	1578	1492	1298	1031	818	194
$[Eu(NO_3)_3L_2\cdot H_2O]\cdot 2H_2O$	1623, 1606	1578	1494	1307	1027	818	187
$[Gd(NO_3)_3L_2\cdot H_2O]\cdot 2H_2O$	1626, 1606	1579	1494	1289	1026	817	205
$[Tb(NO_3)_3L_2 \cdot H_2O] \cdot 2H_2O$	1624, 1605	1578	1491	1308	1027	817	183
$[Er(NO_3)_3L_2\cdot H_2O]\cdot 2H_2O$	1625, 1604	1578	1493	1287	1030	817	206

conformation [22]. It is interesting to note that complexation with rare earth ions resulted in almost no shift of the maximum. The ligand includes a bipyridine chromophore and a benzyl chromophore, however, it is the bipyridine that sensitizes the metal centred emission. not for the Tb picrate complex. Under identical experimental conditions, the fluorescence characteristic emissions in solid state are listed in Table 6. The emission spectra of the ligand and complexes are shown in Fig. 3.

## 3.5. Fluorescence studies

The fluorescence characteristics of the ligand, europium and terbium complexes in solid state were measured at room temperature. Among these four complexes, fluorescence of the complexes of Eu, Tb nitrates and Eu picrate were observed but Excited at 318 nm, the "free" ligand exhibits broad emission bands ( $\lambda_{max} = 417$  nm) in solid state. The efficient energy transfer from ligand to centre ions (antenna effect) is one of key factors to achieve rare earth characteristic fluorescence. It is shown in Fig. 3 that the complexes show the characteristic emissions of Eu<sup>3+</sup> or Tb<sup>3+</sup>. This indicates that the ligand L is a good organic chromophore to absorb and transfer energy to metal ions.



Fig. 3. (a) Emission spectrum of L in solid state, (b) emission spectrum of  $[Eu(NO_3)_3L_2 \cdot H_2O] \cdot 2H_2O$  in solid state, (c) emission spectrum of  $[Tb(NO_3)_3L_2 \cdot H_2O] \cdot 2H_2O$  in solid state and (d) emission spectrum of  $Eu(Pic)_3L$  in solid state.

Table 5
The most important IR bands of the rare earth picrate complexes (cm <sup>-1</sup> )

Compound	ν (C=O)	ν (C=N)	V (C-O)	$V_{\rm as}$ (-NO <sub>2</sub> )	$V_{\rm s}$ (-NO <sub>2</sub> )
L	1628	1553	-	-	-
HPic	_	_	1265	1555	1342
La(Pic) <sub>3</sub> L	1616	1578	1274	1578, 1543	1363, 1332
Eu(Pic) <sub>3</sub> L	1616	1578	1273	1578, 1542	1364, 1333
Gd(Pic) <sub>3</sub> L	1615	1578	1273	1578, 1543	1364, 1333
Tb(Pic) <sub>3</sub> L	1616	1578	1274	1578, 1543	1364, 1333
Er(Pic) <sub>3</sub> L	1616	1578	1274	1578, 1543	1364, 1333

Table 6

Fluorescence data for the ligand and Eu and Tb complexes

	Slit(nm)	$\lambda_{ex}$ (nm)	$\lambda_{em}$ (nm)	RFI	Assignment
L	5	318	417	390.9	
$[Eu(NO_3)_3L_2\cdot H_2O]\cdot 2H_2O$	5	397	593	38.57	${}^{5}\mathrm{D}_{0} \rightarrow {}^{7}\mathrm{F}_{1}$
			616	104.9	${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$
			581	29.18	${}^5\mathrm{D_0} \rightarrow {}^7\mathrm{F_0}$
Eu(Pic) <sub>3</sub> L	2.5	449	592	177.6	${}^{5}\mathrm{D}_{0} \rightarrow {}^{7}\mathrm{F}_{1}$
			617	1502	${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$
			492	909.1	${}^{5}\text{D}_{4} \rightarrow {}^{7}\text{F}_{6}$
$[Tb(NO_3)_3L_2{\cdot}H_2O]{\cdot}2H_2O$	5	318	546	2134	$^5D_4 \rightarrow {}^7F_5$
			586	132.4	$^5D_4 \! \rightarrow {}^7F_4$

It is noted that the intensity ratio of the  ${}^{5}D_{0}-{}^{7}F_{2}$  transition to the  ${}^{5}D_{0}-{}^{7}F_{1}$  transition is widely used as a measure of the coordination state and the site symmetry of the europium ion, since the  ${}^{5}D_{0}-{}^{7}F_{1}$  emission is independent of the ligand environment, and primarily magnetic dipole in character, while the  ${}^{5}D_{0}-{}^{7}F_{2}$ emission is essentially purely electric dipole in character, and its intensity is very sensitive to the crystal field symmetry. In the two spectrums of Eu(III) complexes, the transition  ${}^{5}D_{0}-{}^{7}F_{2}$  is the strongest in the transitions with about three or eight times the strength of the transition of  ${}^{5}D_{0}-{}^{7}F_{1}$ . The results show that Eu(III) has the lower symmetric coordination environment [23].

Intramolecular energy transfer from the triplet state of the ligand to the resonance level of the rare earth ion is one of the most important processes influencing the fluorescence quantum yields of rare earth complexes [24]. The energy difference between the triplet state energy level of the ligand and the lowest excited state level of rare earth cannot be too large or too small. In order to acquire the triplet excited state  $T_1$  of the ligand L, the phosphorescence spectra of the Gd(III) nitrate complexes were measured at 77 K in a methanol solution. The triplet state energy levels  $T_1$  of the ligand L in the nitrate and picrate complexes, which were calculated from the shortest wavelength phosphorescence bands [25] of the corresponding Gd(III) complexes, are 23,585 and 21,245 cm<sup>-1</sup>, respectively. We deduced that the electrostatic factors in the ligand-metal bonding, which may be affected by the different counter anion in these two series complexes, influenced the triplet state energy level of the ligand L [26] and made this  $T_1$  energy be lowered in the picrate complexes. These energy levels are both above the lowest excited resonance level  ${}^{5}D_{0}$  of Eu(III)  $(17,300 \text{ cm}^{-1})$  and  ${}^{5}\text{D}_{4}$   $(20,500 \text{ cm}^{-1})$  of Tb(III). Thus, the absorbed energy could be transferred from ligand to the Eu

or Tb ions. And we may deduce that the triplet state energy level T<sub>1</sub> of this ligand L in the nitrate complexes matches better to the lowest resonance level of Tb(III) ( $\nu = 3085 \text{ cm}^{-1}$ ) than Eu(III) ( $_\nu = 6285 \text{ cm}^{-1}$ ) ion, because such big  $\nu (T_1 - {}^5D_0)$  could result in the non-radioactive deactivation of the europium emitting state and quench the fluorescence of the Eu nitrate complex [26]. Comparing the emission spectra of these two nitrate complexes, we could find that the fluorescence intensity of terbium nitrate complex is much stronger than that of Eu(III) complexes. And the triplet state energy level  $T_1$  of this ligand L in the picrate complexes matches better to the lowest resonance level of Eu(III)  $(v = 3945 \text{ cm}^{-1})$  than Tb(III)  $(v = 745 \text{ cm}^{-1})$  ion, because such small  $\nu(T_1-^5D_4)$  could result in the non-radioactive deactivation of the terbium emitting state via a back-energy transfer process  $(T_1 \leftarrow Tb({}^5D_4))$  and quench the luminescence of the Tb picrate complex [26]. Actually we do not observe the fluorescence of the Tb picrate complex at room temperature.

# 4. Conclusions

According to the data and discussion above, the new aryl amide ligand 3,3'-dibenzylamido)-2,2'-bipydine can form stable solid complexes with rare earth nitrates and picrates. When the ligand formed the rare earth complexes, obvious changes in IR spectra were observed. In the complexes, rare earth ions were coordinated to the C=O oxygen atoms of the ligand **L**. The fluorescent properties of the Eu and Tb complexes in solid state were investigated. Under the excitation, the complexes exhibited characteristic fluorescence of europium and terbium ions. And the lowest triplet state energy levels of the ligand in the nitrate and picrate complexes indicate that the counter anion of the complexes is very essential in determining both the composition and the fluorescent properties of the rare earth complexes by influencing the electrostatic factors in the ligand–metal bonding.

## 5. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No.636943. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mails: linstead@ccdc.cam.ac.uk; deposit@ccdc.cam.ac.uk, direct line: +44 1223 762910; Tel: +44 1223 336408; fax: +44 1223 336033).

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at .

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