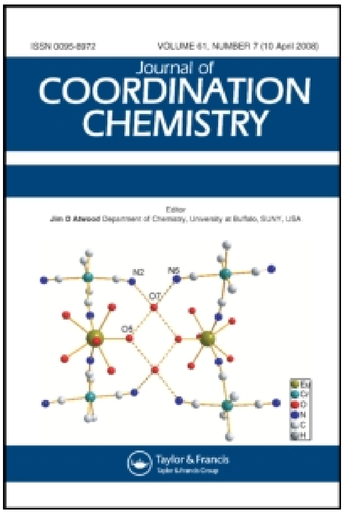

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Crystal Structure and Luminescence of a Europium Nitrate Complex with Furancarboxylic Acid and 2,2'-Bipyridine

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CRYSTAL STRUCTURE AND LUMINESCENCE OF A EUROPIUM NITRATE COMPLEX WITH FURANCARBOXYLIC ACID AND 2,2′-BIPYRIDINE

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A quaternary mixed ligand europium complex, $[Eu(FA)_2NO_3bipy]_2$, has been synthesized, where FA = α-furancarboxylic acid anion and bipy = 2,2′-bipyridine. The europium complex crystallizes in the triclinic system, space group $P\bar{1}$. Its structure was determined by X-ray diffraction methods. The two europium ions in the dimer are held together by four carboxylate groups of furancarboxylic acid and each europium ion is further bonded to one chelated bidentate nitrate and one 2,2′-bipyridine molecule. The coordination modes of the four carboxylate groups are divided into two types, bidentate bridging and tridentate bridging, making a coordination number of 9. Excitation and luminescence spectra observed at 77 K show that the europium ion site in the crystal has low symmetry and emission $^5D_1 \rightarrow {}^7F_J$ of the Eu^{3+} ion disappears after 20 μs.

Keywords: Europium; mixed ligand complex; crystal structure; luminescence

INTRODUCTION

Crystal structures and luminescence of ternary lanthanide complexes with organic acids and 2,2′-bipyridine or 1,10-phenanthroline have been extensively studied.[1–11] This is largely a consequence of their interesting structures

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and intense fluorescence characteristics, and X-ray diffraction analysis combined with site-selective excitation spectroscopy provides more information on molecular structures and metal ion sites. However, few quaternary mixed anion complexes of lanthanides have been reported.[12–14] Zhu *et al.* reported structures of $[La(CH_2ClCOO)_2(NO_3)(phen)(H_2O)]_n$ and $[Ce(CH_3COO)_2(NO_3)(phen)]_2$, where phen = 1,10-phenanthroline.[15,16] In comparison with lanthanide complexes with phen, 2,2'-bipyridine (bipy) is difficult to coordinate to lanthanide elements because free bipy is in the *trans*-form while bipy coordinated with lanthanide elements is in the *cis*-form. As part of our study of lanthanide complexes containing unsaturated carboxylic acids and bipy, we report here crystal structure and luminescence of $[Eu(FA)_2NO_3bipy]_2$.

EXPERIMENTAL

Preparation

Some 1.5 mmol of α-furancarboxylic acid was dissolved in 15 cm^3 of 95% C_2H_5OH to which 1 mmol of 2,2'-bipyridine dissolved in 10 cm^3 of 95% C_2H_5OH was added and the pH of the mixed solution was controlled in a range 6–7 with 1 M NaOH solution. A $Eu(NO_3)_3$ solution (0.5 mmol of $Eu(NO_3)_3 \cdot 6H_2O$ dissolved in 10 cm^3 of H_2O) was added to the solution. The mixture was heated under reflux with stirring for 4 h. A precipitate formed. Single crystals were obtained from the mother liquor after one week at room temperature.

X-ray Structure Determination

Crystal Data

$Eu_2C_{40}H_{28}N_6O_{18}$, $M = 1184.61$, triclinic, space group $P\bar{1}$, $a = 10.230(1)$, $b = 11.069(3)$, $c = 9.962(3)$ Å, $\alpha = 104.19(2)$, $\beta = 110.02(1)$, $\gamma = 85.50(2)°$, $V = 1027.6(4)$ Å^3, $Z = 1$, $Dc = 1.914$ g cm^{-3}, $\lambda(MoK\alpha) = 0.71069$ Å, $\mu = 31.05$ cm^{-1}, $F(000) = 580$.

A colourless prismatic crystal with dimensions 0.20 × 0.20 × 0.30 mm was mounted on a glass fibre. Intensity data were measured on a Rigaku AFC7R diffractomer at 20.0°C using the ω–2θ scan technique to a maximum 2θ value of 50.0°. Data were corrected for Lorentz and polarization effects. Empirical absorption corrections were used. Of the 3842 reflections collected, 3621 were unique ($Rint = 0.037$).

The structure was solved by the Patterson method and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Reliability factors are defined as $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2\}^{1/2}$ where $w = 4F_o^2/\sigma^2(F_o^2)$. All calculations were performed using the TEXSAN crystallographic software package.[17] The final R and R_w values were 0.025 and 0.034, respectively. Details of X-ray data collection, structure solution and refinement, complete F_c and F_o tables, thermal parameters, H atom positions and full lists of bond lengths and angles are available from Linpei Jin upon request.

Excitation and Luminescence Measurements

Excitation and luminescence spectra were recorded as described previously.[18]

RESULTS AND DISCUSSION

Structure of $[Eu(FA)_2NO_3bipy]_2$

The structure of (2,2′-bipyridine)bis(furancarboxylato)europium(III) nitrate is shown in Figure 1. The structure is composed of centrosymmetric dimers

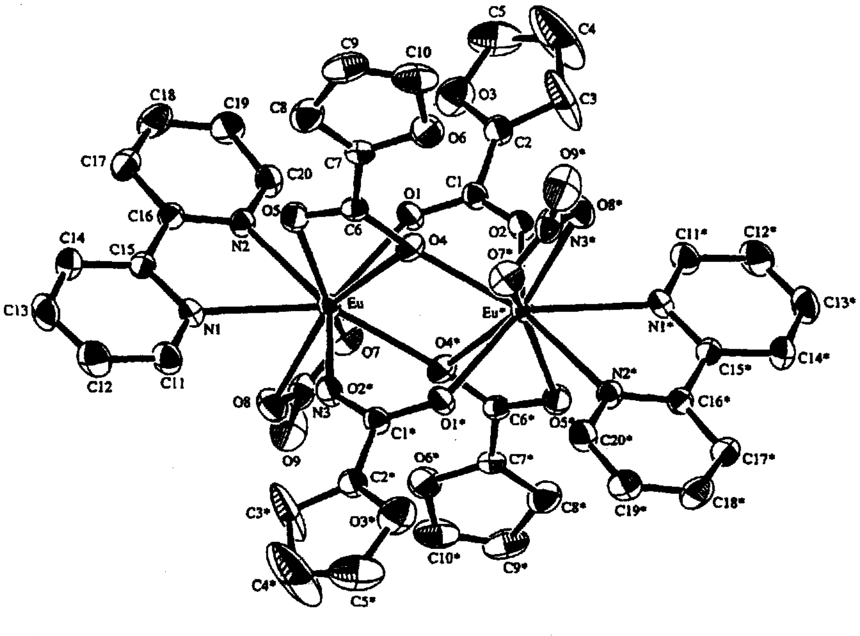

FIGURE 1 Molecular structure of the complex.

in which the two europium ions are connected by four carboxylate groups. The carboxylato groups of the four molecules of furancarboxylic acid are bidentate bridging and tridentate, chelating-bridging. Two of the four carboxylate groups simultaneously bridge two europium ions and the other two carboxylato groups chelate one europium ion and at the same time bridge two europium ions. Each europium ion is further bonded to one bidentate-chelating nitrate ion and one 2,2′-bipyridine molecule to form a nine-coordinate europium complex. Final atomic coordinates for non-hydrogen atoms and equivalent thermal parameters are given in Table I, and bond lengths and angles in Tables II and III, respectively.

Eu–$O_{carboxyl}$ distances in $Eu(FA)_2NO_3bipy$ range from 2.685(3) to 2.346(3) Å with a mean value of 2.439(3) Å. In comparison to an average

TABLE I Fractional atomic coordinates and equivalent thermal parameters

Atom	x/a	y/b	z/c	B_{eq} (Å^2)
Eu	−0.00586(2)	−0.16156(2)	−0.14511(2)	1.939(5)
O(1)	0.1468(3)	−0.1679(3)	0.0942(3)	2.64(6)
O(2)	0.1374(3)	0.0083(3)	0.2597(3)	2.98(6)
O(3)	0.3446(4)	−0.2617(4)	0.3104(4)	5.02(10)
O(4)	0.1320(3)	0.0547(3)	−0.0050(3)	2.73(6)
O(5)	0.1925(3)	−0.0789(3)	−0.1766(3)	3.22(7)
O(6)	0.3786(3)	0.1856(3)	0.0758(4)	3.99(8)
O(7)	−0.1058(4)	−0.3335(3)	−0.0797(4)	3.75(8)
O(8)	−0.2102(3)	−0.2979(3)	−0.2930(3)	3.73(8)
O(9)	−0.2898(4)	−0.4418(3)	−0.2277(5)	5.5(1)
N(1)	0.0004(4)	−0.2415(3)	−0.4110(3)	2.49(7)
N(2)	0.1355(4)	−0.3606(3)	−0.1963(4)	2.43(7)
N(3)	−0.2045(4)	−0.3607(4)	−0.1998(5)	3.47(9)
C(1)	0.1843(4)	−0.0977(4)	0.2211(4)	2.41(9)
C(2)	0.2932(5)	−0.1450(4)	0.3363(5)	3.4(1)
C(3)	0.346(1)	−0.0894(6)	0.4750(6)	9.8(2)
C(4)	0.450(1)	−0.174(1)	0.5378(10)	13.4(3)
C(5)	0.4425(7)	−0.2755(7)	0.4423(9)	7.0(2)
C(6)	0.2137(4)	0.0198(4)	−0.0788(4)	2.26(8)
C(7)	0.3353(4)	0.0957(4)	−0.0503(5)	2.48(9)
C(8)	0.4185(5)	0.0927(5)	−0.1304(6)	4.0(1)
C(9)	0.5207(5)	0.1885(6)	−0.0470(7)	4.7(1)
C(10)	0.4929(5)	0.2392(5)	0.0729(7)	4.7(1)
C(11)	−0.0688(5)	−0.1816(4)	−0.5157(5)	3.4(1)
C(12)	−0.0589(6)	−0.2134(5)	−0.6549(5)	4.2(1)
C(13)	0.0244(6)	−0.3102(5)	−0.6879(5)	4.0(1)
C(14)	0.0970(5)	−0.3724(5)	−0.5815(5)	3.4(1)
C(15)	0.0841(4)	−0.3360(4)	−0.4429(4)	2.40(8)
C(16)	0.1592(4)	−0.4006(4)	−0.3243(4)	2.43(8)
C(17)	0.2482(5)	−0.4998(4)	−0.3452(5)	3.5(1)
C(18)	0.3118(6)	−0.5584(5)	−0.2325(6)	4.1(1)
C(19)	0.2871(5)	−0.5186(4)	−0.1021(5)	3.6(1)
C(20)	0.1977(5)	−0.4202(4)	−0.0890(5)	3.08(10)

TABLE II Bond lengths (Å) for the complex

Atom	*Atom*	*Distance*	*Atom*	*Atom*	*Distance*
Eu	O(1)	2.376(3)	N(1)	C(15)	1.346(5)
Eu	O(2)*	2.352(3)	N(2)	C(16)	1.342(5)
Eu	O(4)	2.685(3)	N(2)	C(20)	1.341(5)
Eu	O(4)*	2.348(3)	C(1)	C(2)	1.470(6)
Eu	O(5)	2.433(3)	C(2)	C(3)	1.306(7)
Eu	O(7)	2.542(3)	C(3)	C(4)	1.44(1)
Eu	O(8)	2.473(3)	C(4)	C(5)	1.27(1)
Eu	N(1)	2.600(3)	C(6)	C(7)	1.463(6)
Eu	N(2)	2.580(3)	C(7)	C(8)	1.345(6)
O(1)	C(1)	1.258(5)	C(8)	C(9)	1.434(8)
O(2)	C(1)	1.254(5)	C(9)	C(10)	1.304(8)
O(3)	C(2)	1.355(6)	C(11)	C(12)	1.382(7)
O(3)	C(5)	1.388(8)	C(12)	C(13)	1.363(7)
O(4)	C(6)	1.272(5)	C(13)	C(14)	1.374(7)
O(5)	C(6)	1.249(5)	C(14)	C(15)	1.389(6)
O(6)	C(7)	1.356(5)	C(15)	C(16)	1.485(6)
O(6)	C(10)	1.364(6)	C(16)	C(17)	1.393(6)
O(7)	N(3)	1.259(5)	C(17)	C(18)	1.376(7)
O(8)	N(3)	1.274(5)	C(18)	C(19)	1.368(7)
O(9)	N(3)	1.216(5)	C(19)	C(20)	1.377(6)
N(1)	C(11)	1.337(5)			

of La–$O_{carboxyl}$ distances (2.573(4) Å) in La(FA)$_3$(H$_2$O)$_2$,[19] the average Eu–$O_{carboxyl}$ distance for the title complex is shorter. This may be attributed to the larger steric effects of the three furancarboxylate groups of the La(FA)$_3$(H$_2$O)$_2$ complex, the larger radius of the La^{3+} ion (0.02 Å greater than Eu^{3+}) and close packing for the mixed ligands in the Eu(FA)$_2$NO$_3$bipy complex. It is reasonable that the average Eu–O distance for the bidentate bridging carboxyl, 2.364(3) Å, is shorter than that for the terdentate bridging carboxylate group, 2.488(3) Å.

Calculated least-squares planes show that all the furyl rings involved in the dimer are planar with a maximum deviation of 0.05(2) Å, and the two pyridyl rings of the 2,2′-bipyridine molecule are planar with a maximum deviation of 0.007(5) Å. The dihedral angle between the two pyridyl rings is 2.43°. Regular packing for the pyridyl rings and furyl rings is found in the complex. For instance, the dihedral angle between the C2–C5, O4 plane and the C11–C15, N1 plane is 33.33° and the angle between the C2–C5, O4 plane and the C16–C20, N2 plane is 35.43°. The dihedral angle between the C7–C10, O6 plane and the C11–C51, N1 plane is 91.24°, and the angle between the C7–C10, O6 plane and the C16–C20, N2 plane is 89.73°. This phenomenon is similar to packing effects of aromatic rings found in Cu(II) complexes with aromatic amino acids.[20]

TABLE III Bond angles (°) for the complex

Atom	*Atom*	*Atom*	*Angle*	*Atom*	*Atom*	*Atom*	*Angle*
O(1)	Eu	O(2)*	136.16(9)	Eu	O(4)	Eu*	104.7(1)
O(1)	Eu	O(4)	68.14(9)	Eu	O(4)	C(6)	87.7(2)
O(1)	Eu	O(4)*	77.5(1)	Eu	O(4)*	C(6)*	167.4(3)
O(1)	Eu	O(5)	85.8(1)	Eu	O(5)	C(6)	100.1(3)
O(1)	Eu	O(7)	75.9(1)	C(7)	O(6)	C(10)	106.0(4)
O(1)	Eu	O(8)	126.5(1)	Eu	O(7)	N(3)	95.3(2)
O(1)	Eu	N(1)	135.8(1)	Eu	O(8)	N(3)	98.3(3)
O(1)	Eu	N(2)	77.84(10)	Eu	N(1)	C(11)	120.6(3)
O(2)	Eu	O(4)	73.56(10)	Eu	N(1)	C(15)	120.8(3)
O(2)	Eu	O(4)*	72.8(1)	C(11)	N(1)	C(15)	118.3(4)
O(2)	Eu	O(5)	86.1(1)	Eu	N(2)	C(16)	121.6(3)
O(2)	Eu	O(7)	125.1(1)	Eu	N(2)	C(20)	119.9(3)
O(2)	Eu	O(8)	85.0(1)	C(16)	N(2)	C(20)	118.2(4)
O(2)	Eu	N(1)	78.7(1)	O(7)	N(3)	O(8)	115.8(4)
O(2)	Eu	N(2)	141.5(1)	O(7)	N(3)	O(9)	123.2(5)
O(4)	Eu	O(4)*	75.3(1)	O(8)	N(3)	O(9)	121.1(5)
O(4)	Eu	O(5)	50.59(9)	O(1)	C(1)	O(2)	126.6(4)
O(4)	Eu	O(7)	137.7(1)	O(1)	C(1)	C(2)	116.8(4)
O(4)	Eu	O(8)	156.4(1)	O(2)	C(1)	C(2)	116.6(4)
O(4)	Eu	N(1)	112.8(1)	O(3)	C(2)	C(1)	122.0(4)
O(4)	Eu	N(2)	118.53(10)	O(3)	C(2)	C(3)	110.6(4)
O(4)	Eu	O(5)	125.7(1)	C(1)	C(2)	C(3)	127.3(5)
O(4)	Eu	O(7)	75.9(1)	C(2)	C(3)	C(4)	104.8(6)
O(4)	Eu	O(8)	89.3(1)	C(3)	C(4)	C(5)	109.2(6)
O(4)	Eu	N(1)	146.7(1)	C(3)	C(5)	C(4)	108.4(6)
O(4)	Eu	N(2)	143.8(1)	O(4)	C(6)	O(5)	121.4(4)
O(5)	Eu	O(7)	148.1(1)	O(4)	C(6)	C(7)	120.1(4)
O(5)	Eu	O(8)	138.9(1)	O(5)	C(6)	C(7)	118.5(4)
O(5)	Eu	N(1)	67.8(1)	O(6)	C(7)	C(6)	119.1(4)
O(5)	Eu	N(2)	78.2(1)	O(6)	C(7)	C(8)	110.3(4)
O(7)	Eu	O(8)	50.6(1)	C(6)	C(7)	C(8)	130.6(4)
O(7)	Eu	N(1)	108.4(1)	C(7)	C(8)	C(9)	105.6(5)
O(7)	Eu	N(2)	72.6(1)	C(8)	C(9)	C(10)	106.8(5)
O(8)	Eu	N(1)	71.1(1)	O(6)	C(10)	C(9)	111.3(5)
O(8)	Eu	N(2)	84.4(1)	N(1)	C(11)	C(12)	122.8(4)
N(1)	Eu	N(2)	62.8(1)	C(11)	C(12)	C(13)	118.9(5)
Eu	O(1)	C(1)	138.3(3)	C(12)	C(13)	C(14)	119.1(4)
Eu	O(2)*	C(1)*	137.3(3)	C(13)	C(14)	C(15)	119.6(5)
C(2)	O(3)	C(5)	106.5(5)	N(1)	C(15)	C(14)	121.2(4)
N(1)	C(15)	C(16)	116.9(3)	C(16)	C(17)	C(18)	119.2(4)
C(14)	C(15)	C(16)	121.8(4)	C(17)	C(18)	C(19)	119.8(4)
N(2)	C(16)	C(15)	116.9(4)	C(18)	C(19)	C(20)	118.0(4)
N(2)	C(16)	C(17)	121.3(4)	N(2)	C(20)	C(19)	123.5(4)
C(15)	C(16)	C(17)	121.8(4)				

Luminescence Studies

Luminescence for $^5D_0 \rightarrow {}^7F_{0-4}$ transitions of the Eu^{3+} ion in $Eu(FA)_2NO_3$-bipy excited with 337.1 nm N_2 laser energy at 77 K is shown in Figure 2. It can be seen that $2J+1$ components and O–O transitions are observed, implying that the Eu^{3+} ion site must be of low symmetry. This is in

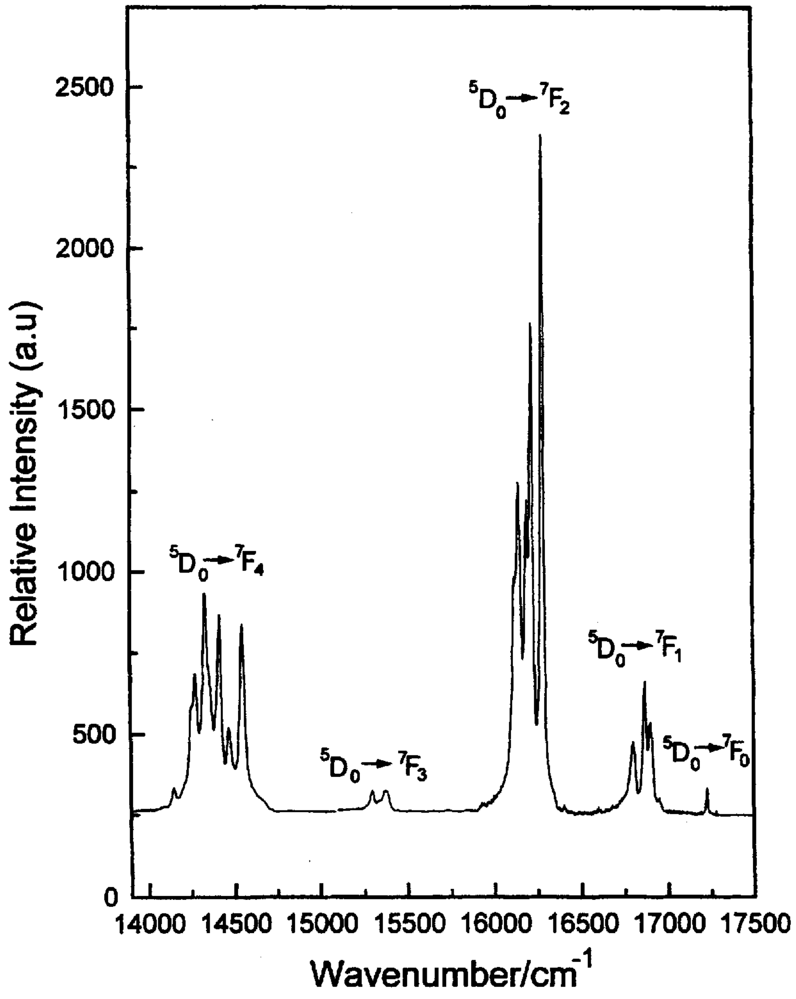

FIGURE 2 Fluorescence spectrum of the complex, $\lambda_{exc} = 337.1$ nm, 77 K.

agreement with the results of the X-ray analysis. Emission bands arising from $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions are centred at 17225; 16896, 16866 and 16800; 16277, 16218, 16189, 16145 and 16118 cm^{-1}, respectively. Single emission band with full width at half-maximum height (FWHM) of 0.41 nm obtained from O–O transition is due to a single Eu^{3+} ion site in the Eu(FA)$_2$NO$_3$bipy complex.[21] This is unlike the ternary complexes Eu(*p*-MBA)$_3$bipy[4], Eu(*p*-MOBA)$_3$bipy[10] and Eu(BA)$_3$dmbpy[11] in which the Eu^{3+} ions are in slightly different chemical environments due to the conformation of the bipyridyl ligand. However, in the title complex the bipyridyl ligand is rigid because of matched stacking for the different ligands in the crystal.

The time resolved spectra are shown in Figure 3. Emission bands of $^5D_1 \rightarrow {}^7F_J$ ($J = 1-3$) transitions were observed when the delay time was 2 μs. However, $^5D_1 \rightarrow {}^7F_J$ transition bands disappear after 20 μs delay while

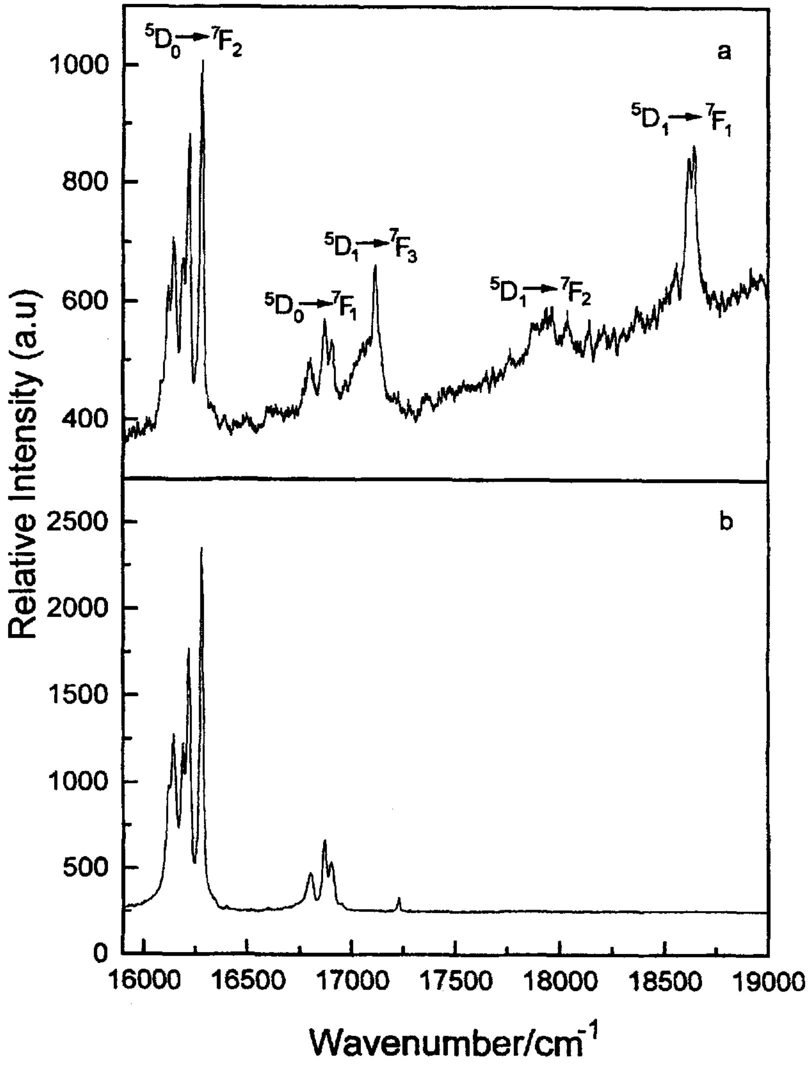

FIGURE 3 Time resolved spectra of the complex, a: 2 μs delay; b: 20 μs delay.

emission band intensity of the $^5D_0 \rightarrow {}^7F_J$ transition increases. This indicates that the lowest triplet state of the ligand is higher than the emission level $^5D_1$ of the Eu^{3+} ion and the lifetime of the $^5D_1$ state is much shorter than that of the $^5D_0$ state of the Eu^{3+} ion. Results also show energy transfer from the triplet state of the ligand to $^5D_1$ level of the Eu^{3+} ion when the title complex is excited at 337.1 nm, when the $^5D_1 \rightarrow {}^7F_J$ transition occurs. Simultaneously, energy transfers from the $^5D_1$ level of the Eu^{3+} ion to the $^5D_0$ level of the Eu^{3+} ion although it is possible that energy directly transfers from the triplet level of the ligand to the $^5D_0$ level of the Eu^{3+} ion, and then the $^5D_0 \rightarrow {}^7F_J$ transition takes place.

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