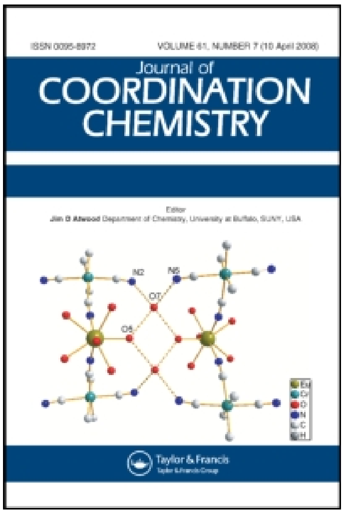

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Structure and fluorescence properties of a europium complex with *N*-ethyl-2-{2'-[(ethylphenylcarbamoyl) methoxy]-[1,1']binaphthalenyl-2-yloxy}-*N*-phenylacetamide

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Structure and fluorescence properties of a europium complex with *N*-ethyl-2-{2′-[(ethylphenylcarbamoyl) methoxy]-[1,1′]binaphthalenyl-2-yloxy}-*N*-phenylacetamide

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A binaphthylamide complex derived from 1,1′-2,2′-binaphthol (BINOL) and europium picrate has been formed with a wave-like coordination structure through π–π interactions. The molecular structure of [Eu(pic)$_3$L] (L = *N*-ethyl-2-{2′-[(ethylphenylcarbamoyl)methoxy]-[1,1′]binaphthalenyl-2-yloxy}-*N*-phenylacetamide; pic = picrate) shows that the Eu(III) ion is nine-coordinate with four oxygen atoms from L and five from two bidentate and one unidentate picrates. The structure of the complex was investigated in solution by ^{1}H NMR, and its fluorescence properties in the solid state and in solution were studied.

Keywords: Europium picrate; Complex; π–π stack; Wave-like supramolecular structure; Fluorescence properties

1. Introduction

Binaphthyl-containing ligands have been widely used in both coordination and organometallic chemistry [1, 2]. Some binaphthyl-containing ligands that were synthesized from 1,1′-2,2′-binaphthol (BINOL) have been used for chiral recognition and catalysis [3–8]. Much less attention has been paid to amide-type binaphthyl-containing ligands [9], and few structures of such complexes have been determined by X-ray measurements. Recently we reported a new BINOL ligand, *N*-ethyl-2-{2′-[(ethylphenylcarbamoyl)methoxy]-[1,1′]binaphthalenyl-2-yloxy}-*N*-phenylacetamide (L), and the crystal

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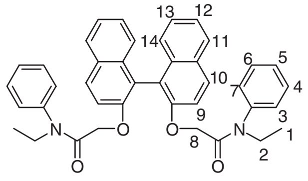

L

structure of its complex [Tb(pic)$_3$L] [10]. The ligand, with a chiral and conjugated group, is predicted to form luminescence rare earth complexes, which are potential structural probes. As part of our systematic investigation into the structure and fluorescence properties of such rare earth complexes, we report here the crystal structure and fluorescence of a europium complex. The europium complex has strong, characteristic luminescence, very different from the terbium complex, which has no luminescence.

Unlike their pure organic analogs, supramolecular systems assembled by metal–ligand bonds present a number of advantages [11]. Among these, aryl–aryl (π-stacking) noncovalent interactions might offer an alterative means of controlling the assembly of photoactive metal centers [12]. In this work, the single-crystal X-ray analysis of the europium complex reveals that the naphthalene ring and the picrate form a π–π stacking structure, and through this interaction the complex forms a 1D supramolecular structure. Although the structures of the Eu(III) and Tb(III) complexes are similar, their fluorescence properties are very different.

2. Experimental

2.1. *Chemical and physical measurements*

The metal ions were determined by EDTA titration using xylenal orange as indicator. C, N and H were determined using an Elementar Vario EL instrument. Conductivity measurements were carried out with a DDS-307 conductivity bridge using $10^{-3}\,\mathrm{mol\,dm^{-3}}$ solutions in acetone at 25°C. IR spectra were recorded on a Nicolet Avatar 360 FTIR instrument using KBr disks in the 400–4000 cm^{-1} region. ^{1}H NMR spectra were measured on a Varian Mercury plus 300BB spectrometer in CDCl$_3$ solution with TMS as internal standard. Luminescence spectra were obtained with a Hitachi F-4500 spectrophotometer. Time-resolved fluorescence measurements were performed at 77 K using a Nd-YAG pumped dye laser with RG 10 dye as the excitation source and a Spex 1403 double grating monochromator.

2.2. *Materials*

Europium picrate was prepared according to a literature method [13]. L as the enantiomer was synthesized from BINOL by a method reported previously [14]. All commercially available chemicals were reagent grade and were used without further purification.

2.3. *General preparation of the complex*

The method of preparation of the europium complex was similar to that of the terbium complex [10].

Table 1. Crystal data and structure refinement for the complex Eu(pic)$_3$L.

Empirical formula	C58H42EuN11O25
Temperature (K)	295(2)
Crystal color	Yellow
Crystal size (mm)	$0.56 \times 0.38 \times 0.36$
Formula weight	1444.99
Crystal system	Monoclinic
Space group	$P2(1)/c$
a (Å)	20.705(4)
b (Å)	36.611(9)
c (Å)	16.399(3)
β (°)	106.33(1)
V (Å^3)	11 929(4)
Z	8
Density (calculated) (mg m^{-3})	1.609
$F(000)$	5840
Radiation, graphite-monochromatized, λ (Å)	0.71073
Reflections collections	22 917
Independent reflection	21 002
θ range for data collection (°)	1.51–25.01
Index range	$-24 \leq h \leq 23$, $-43 \leq k \leq 0$, $0 \leq l \leq 19$
Goodness-of-fit on F^2	0.851
R [$I > 2\sigma(I)$]	$R = 0.0432$, $wR = 0.0715$
R (all data)	$R = 0.1009$, $wR = 0.0824$
Largest difference peak and hole (e Å^{-3})	0.593, −0.731

Table 2. Analytical and molar conductance data for the complex Eu(pic)$_3$L (calculated values in parentheses).

Analysis (%)				
C	H	N	Eu	Λ_m (ohm^{-1} cm^2 mol^{-1})
47.82 (48.19)	3.28 (2.91)	10.75 (10.66)	10.46 (10.52)	28.1

2.4. *X-ray crystallography*

For the europium complex, X-ray measurements were performed on a P4 four-circle diffractometer with graphite-monochromatized Mo Kα radiation at 295(2) K, using the $\omega/2\theta$ scan mode. Lorentz and polarization corrections were applied, and empirical absorption correction was performed. Crystallographic data and details of the structure refinement are presented in table 1. The structure was solved by direct methods and refined by full-matrix least-squares techniques with all nonhydrogen atoms treated anisotropically. All calculations were performed on an Eclipse S/140 computer with the program package SHELXTL [15] version 5.10.

3. Results and discussion

Analytical data for the complex (table 2) conform to a 1 : 3 : 1 metal : picrate : L stoichiometry [Eu(pic)$_3$L]. The complex is soluble in DMF, DMSO, CH$_3$CO$_2$Et, acetone and CHCl$_3$, and slightly soluble in ethanol and methanol. The molar

Table 3. The most important IR bands (cm^{-1}).

Compound	ν(C=O)	ν(C–O–C)	ν(C–O)	ν_{as}(–NO$_2$)	ν_s(–NO$_2$)
Hpic	–	–	1265	1555	1342
L	1676	1104	–	–	–
Eu(pic)$_3$L	1617	1081	1276	1584 1545	1362 1331

conductance of the complex in acetone (see table 2) indicates that the complex is a nonelectrolyte, implying that all of the picrate groups are in the coordination sphere.

3.1. *IR spectra*

The most important IR data are listed in table 3. The IR spectrum of L shows a strong band at 1676 cm^{-1}, attributable to stretching of the amide carbonyl group [ν(C=O)]. Two peaks at 1274 and 1223 cm^{-1} can be assigned to ν(=C–O–C), and the peak at 1104 cm^{-1} to ν(C–O–C). The peaks at 1591 and 1499 cm^{-1} are assigned to the C=C stretches of naphthalene and phenyl rings, those at 1444 and 1414 cm^{-1} are assigned to the bending vibration of –CH$_2$–CO–, and those at 750 and 700 cm^{-1} are assigned to the stretch of the phenyl ring.

In the IR spectra of the europium complex, ν(C=O) and ν(C–O–C) shift by ca 59 and 23 cm^{-1} to lower wavenumbers, respectively, indicating that all the C=O and the ether O atoms take part in coordination to the metal ion. The larger shift ν(C=O) in the spectra of the complexes suggests that the carbonyl Ln–O bond is stronger than the ether Ln–O bond. The OH out-of-plane bending vibration of free Hpic at 1151 cm^{-1} disappears in the spectrum of the complex, indicating that the H atom of the OH group is replaced by Eu(III). The ν(C–O) vibration at 1265 cm^{-1} is shifted to higher frequency by 11 cm^{-1} in the complex. This can be explained by two effects. First, the hydrogen atom of the OH group is replaced by Eu(III), increasing the π-bond character in the C–O bond. Second, coordination of the oxygen atom of L to Eu(III) causes the π-character to be weakened. The free Hpic has ν_{as}(NO$_2$) and ν_s(NO$_2$) at 1555 and 1342 cm^{-1}, respectively, which splits into two bands at 1584, 1545 cm^{-1} and 1362, 1331 cm^{-1} in the complex, indicating that some of the nitryl O atoms take part in coordination [16].

3.2. *NMR studies*

The ^{1}H NMR spectra of the free ligand L and its europium complex were determined in CDCl$_3$. The ^{1}H NMR spectra of the complex display 10 different signals for the aromatic protons in the range 4.6–10.5 ppm and the methyl and methylene protons in the range -0.6 to 2.4 ppm. A large shift accompanied by slight line broadening, as expected for a paramagnetic ion, is observed for [Eu(pic)$_3$L], for which the assignment of the NMR signals has been confirmed by a two-dimensional homonuclear COSY correlation spectrum (see figure 1). The assignments of the ^{1}H NMR signals are given in table 4.

Upon coordination, the proton signals of –N–CH$_2$– and –O–CH$_2$– split into two singlets at 0.17, 0.62 ppm and 2.38, 1.05 ppm, indicating that in solution no symmetry axis exists. The proton signal of –C$_6$H$_5$ splits into three singlets at 4.57, 6.60 and 6.96 ppm, which are shifted upfield. The proton signal of C$_{20}$H$_{12}$– splits into five

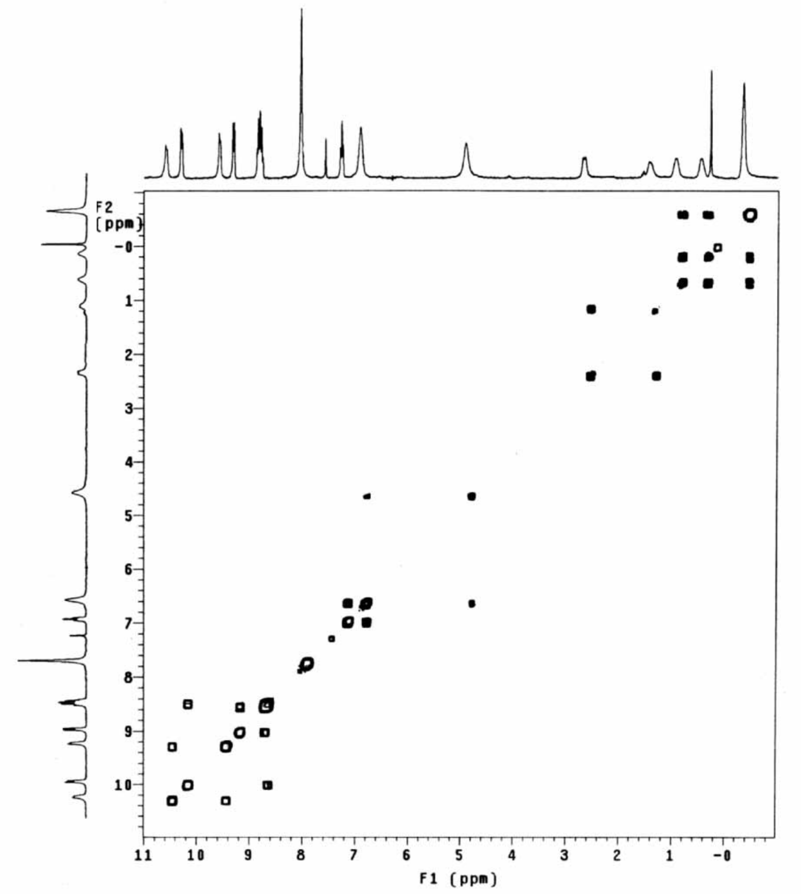

Figure 1. 300-MHz two-dimensional homonuclear COSY ^{1}H NMR correlation spectrum of [Eu(pic)$_3$L] in CDCl$_3$.

Table 4. ^{1}H NMR shifts (with respect to TMS) for the ligand L and complex [Eu(pic)$_3$L] in CDCl$_3$.

Compound	$H_{3,7}$	$H_{4,6}$	H_5	CH_3–	–N–CH_2–	–O–CH_2–	H_9	H_{10}	H_{11}	$H_{12,13}$	H_{14}
L		7.18–6.80		0.96–1.00	3.59–3.62	4.11	7.81–7.88			2.23–2.32	
[Eu(pic)$_3$L]	4.57	6.60	6.96	−0.63	0.17, 0.62	2.38, 1.05	9.29	10.15	9.91	8.49	8.99

singlets at 8.49, 8.99, 9.29, 9.91 and 10.15 ppm, which are shifted to low field. The singlet at 7.73 ppm is assigned to pic$^-$.

3.3. *X-ray crystal structure*

There are two enantiomers in the crystal structure of [Eu(pic)$_3$L]. Figure 2 shows the structure and the atom-numbering schemes for the europium complex. Figure 3 shows the wave-like supramolecular structure along the *z*-axis in the unit cell. Selected bond lengths and angles are given in table 5.

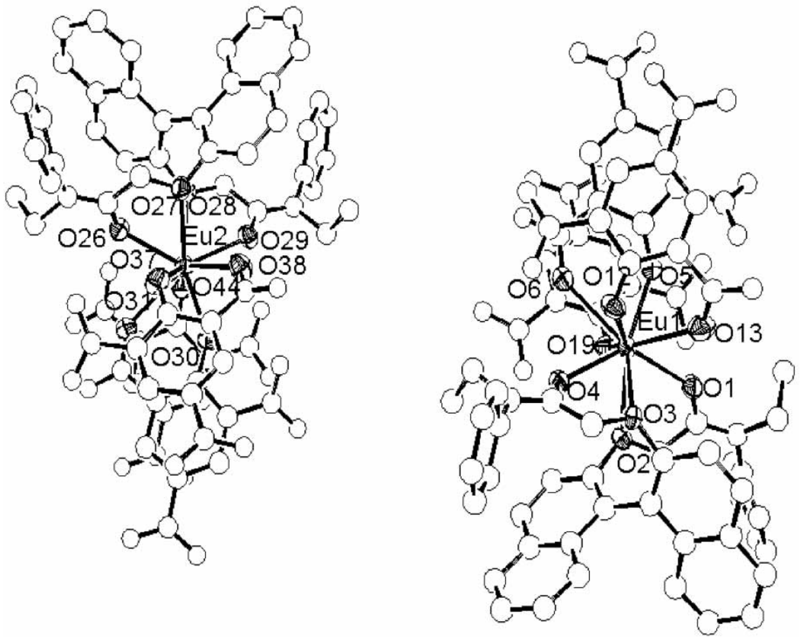

Figure 2. ORTEP drawing of molecular structure of [Eu(pic)$_3$L].

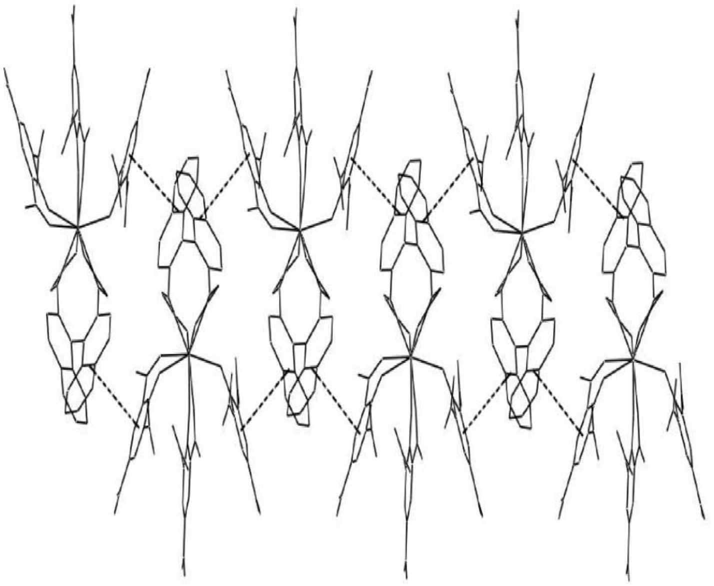

Figure 3. The wave-like structure of [Eu(pic)$_3$L] linked by π–π stacks in the unit cell. All the *N*-ethylanilines are omitted for clarity.

Table 5. Selected bond lengths (Å) and angles (°) for Eu(pic)$_3$L.

Eu(1)–O(1)	2.308(3)	Eu(2)–O(26)	2.341(3)
Eu(1)–O(2)	2.662(3)	Eu(2)–O(27)	2.544(3)
Eu(1)–O(3)	2.599(3)	Eu(2)–O(28)	2.691(3)
Eu(1)–O(4)	2.312(3)	Eu(2)–O(29)	2.342(3)
Eu(1)–O(5)	2.282(3)	Eu(2)–O(30)	2.287(3)
Eu(1)–O(6)	2.644(3)	Eu(2)–O(31)	2.607(3)
Eu(1)–O(12)	2.353(3)	Eu(2)–O(37)	2.358(3)
Eu(1)–O(13)	2.671(3)	Eu(2)–O(38)	2.652(4)
Eu(1)–O(19)	2.305(3)	Eu(2)–O(44)	2.286(3)
O(1)–Eu(1)–O(2)	60.92(10)	O(26)–Eu(2)–O(27)	63.86(10)
O(1)–Eu(1)–O(3)	80.54(11)	O(26)–Eu(2)–O(28)	71.80(10)
O(1)–Eu(1)–O(5)	93.71(11)	O(26)–Eu(2)–O(31)	71.02(11)
O(1)–Eu(1)–O(13)	65.42(11)	O(26)–Eu(2)–O(37)	74.76(11)
O(1)–Eu(1)–O(19)	85.46(12)	O(26)–Eu(2)–O(44)	98.40(11)
O(2)–Eu(1)–O(3)	68.18(9)	O(27)–Eu(2)–O(28)	66.47(11)
O(2)–Eu(1)–O(4)	72.87(10)	O(27)–Eu(2)–O(29)	81.69(11)
O(2)–Eu(1)–O(19)	67.66(10)	O(27)–Eu(2)–O(37)	72.07(11)
O(3)–Eu(1)–O(4)	63.35(10)	O(27)–Eu(2)–O(38)	70.86(11)
O(3)–Eu(1)–O(12)	72.38(11)	O(28)–Eu(2)–O(29)	60.65(10)
O(3)–Eu(1)–O(13)	71.28(10)	O(28)–Eu(2)–O(44)	70.42(10)
O(4)–Eu(1)–O(6)	71.69(10)	O(29)–Eu(2)–O(30)	94.18(11)
O(4)–Eu(1)–O(12)	75.56(11)	O(29)–Eu(2)–O(38)	67.20(11)
O(4)–Eu(1)–O(19)	95.69(12)	O(29)–Eu(2)–O(44)	81.65(11)
O(5)–Eu(1)–O(6)	65.32(10)	O(30)–Eu(2)–O(31)	65.78(11)
O(5)–Eu(1)–O(12)	83.46(11)	O(30)–Eu(2)–O(37)	82.30(12)
O(5)–Eu(1)–O(13)	73.66(11)	O(30)–Eu(2)–O(38)	72.54(11)
O(5)–Eu(1)–O(19)	79.45(11)	O(30)–Eu(2)–O(44)	79.24(11)
O(6)–Eu(1)–O(12)	70.63(11)	O(31)–Eu(2)–O(37)	70.50(12)
O(6)–Eu(1)–O(19)	73.52(12)	O(31)–Eu(2)–O(44)	74.53(12)
O(12)–Eu(1)–O(13)	63.31(11)	O(37)–Eu(2)–O(38)	63.97(11)

The Eu(III) ion is nine-coordinate with four oxygen atoms from the ligand L, five from two bidentate and one unidentate picrates. The coordination polyhedron is a tricapped trigonal prism. Because of the space restrictions, the two naphthalene rings in the molecule are almost perpendicular to each other, with a mean angle of 79.8° between the two rings. The two naphthalene rings of one complex are almost parallel to the two adjacent molecules. The corresponding dihedral angle is 0.0°. The L molecule wraps around the metal ion with its oxygen atoms and forms a ring-like coordination structure together with the europium atom. A naphthalene ring of one complex and a unidentate picrate of the adjacent complex form a π–π stack; the dihedral angle is 17.2° and the shortest and the longest distances of the atom-to-centroid are 3.2922 and 4.1112 Å, respectively. There is a wave-like structure in the unit cell, which is from metal to naphthalene to picrate (the unit revolves three times), through π–π interactions between naphthalene and picrate.

The average Eu–O (C=O) distance (2.460 Å) is shorter than that of Eu–O (C–O–C) (2.456 Å), suggesting that the former is stronger than the latter, in agreement with the IR spectral data.

3.4. *Luminescence study in the solid state at 77 K*

The emission spectrum at 77 K for the solid complex is shown in figure 4. The most intense transition is $^5D_0 \rightarrow {}^7F_2$ at 613 nm when excitation is at 420 nm. The $^5D_0 \rightarrow {}^7F_1$

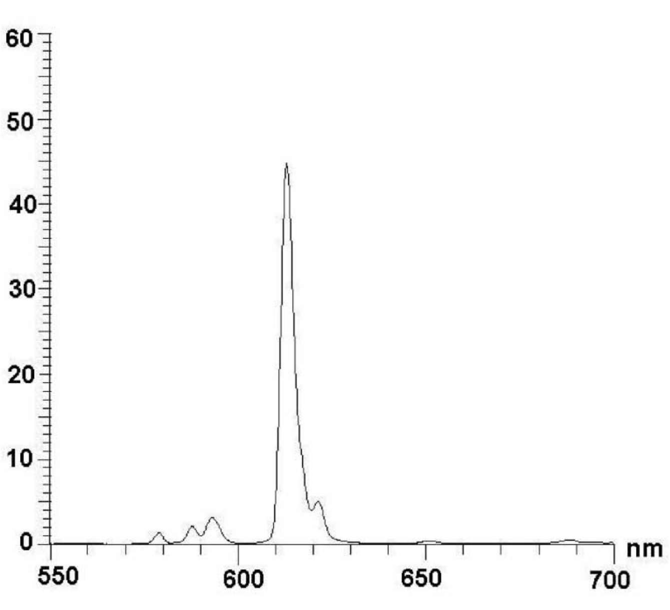

Figure 4. Emission spectrum at 77 K for the solid complex [Eu(pic)$_3$L].

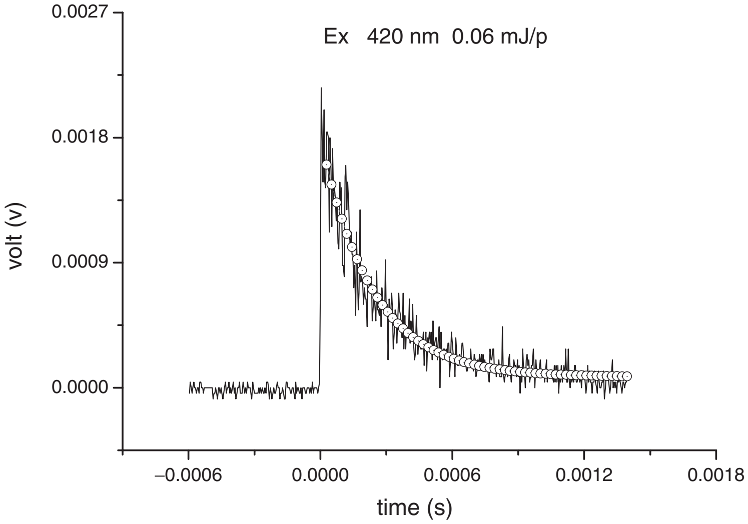

Figure 5. Time-resolved fluorescence spectroscopy of the europium complex at 77 K.

transition consists of three peaks at 579, 588 and 593 nm, and the $^5D_0 \rightarrow {}^7F_2$ transition consists of two peaks at 613 and 621 nm. The value of the intensity ratio η [$^5D_0 \rightarrow {}^7F_2$ (613 nm)/$^5D_0 \rightarrow {}^7F_1$ (593 nm)] is about 11.0, indicating a low symmetry for the electrostatic field surrounding Eu^{3+} [17], in accord with the crystal structure of the complex.

The results of luminescence lifetime studies by time-resolved laser-induced fluorescence spectroscopy of the europium complex at 77 K are shown in figure 5. The lifetime

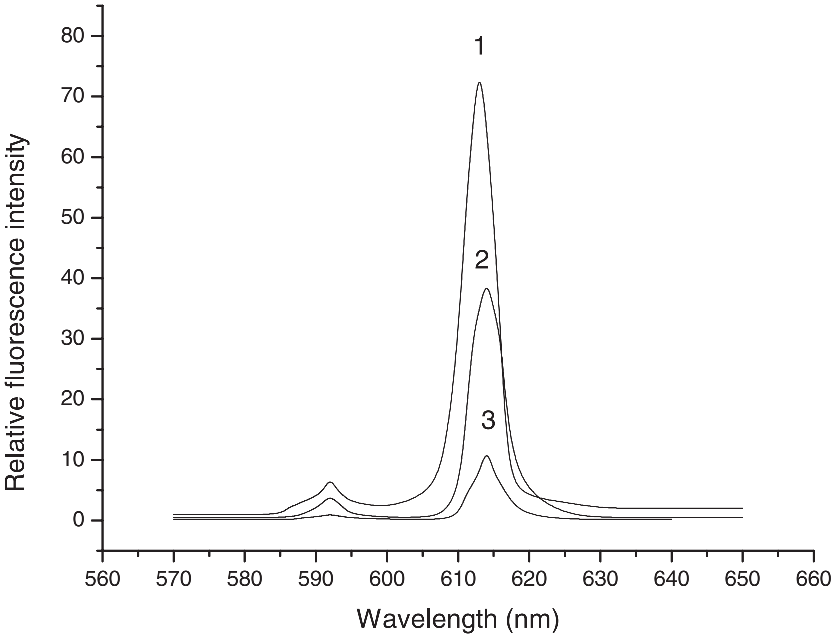

Figure 6. Emission spectra of the europium complex in (1) $CHCl_3$, (2) CH_3COOEt and (3) acetone solution.

Table 6. Fluorescence data for the europium complex $[Eu(pic)_3L]$.

Solvent	λ_{ex} (nm)	λ_{em} (nm)	Relative Flourescence Intensity	Assignment
Solid state	425	592	4000	$^5D_0 \rightarrow {}^7F_1$
		614	28 000	$^5D_0 \rightarrow {}^7F_2$
CH_3Cl	460	592	7	$^5D_0 \rightarrow {}^7F_1$
		614	76	$^5D_0 \rightarrow {}^7F_2$
Acetone	465	592	1	$^5D_0 \rightarrow {}^7F_1$
		614	12	$^5D_0 \rightarrow {}^7F_2$
AcOEt	455	592	4	$^5D_0 \rightarrow {}^7F_1$
		614	40	$^5D_0 \rightarrow {}^7F_2$
DMF	–	–	–	–

of the $^5D_0$ level of the Eu^{3+} ion in the complex obtained from the delayed curve is 0.24 ms.

3.5. *Luminescence study in the solid state and in solution at room temperature*

The emission spectra of $[Eu(pic)_3L]$ at room temperature in the solid state and in solution (figure 6) are similar to each other and show characteristic emission bands of the Eu(III) ion at about 592 and 614 nm, corresponding to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, respectively. The fluorescence intensities at 614 nm are stronger than those at 592 nm, so the peak height at 614 nm was used to measure the fluorescence intensities of the Eu(III) complex. Fluorescence characteristics of the europium complex in the solid state and in $CHCl_3$, AcOEt and DMF solutions (1.0×10^{-3} mol L^{-1}) are listed in table 6. In DMF solution the fluorescence of europium was quenched, which is attributed to the decomposition of the complex in this solvent. In the other three solvents the complex has similar excitation and emission wavelengths and intensity and the fluorescence intensity of the europium complex is about 400 times lower than that in the solid state. We consider this to be due to the coordinating effects of solvents.

Unlike the Eu^{3+} complex, no fluorescence of the Tb^{3+} complex was observed, either in the solid state or in solution. The luminescence of Ln^{3+} chelates is related to the efficiency of the intramolecular energy transfer between the triplet level of the ligand and the emitting level of the ions, which depends on the energy gap between the two levels. In this work, the energy gap between the triplet levels of the ligand and the picrates and the emitting level of the europium favor the energy transfer process.

4. Conclusion

According to the data and discussion above, the ligand L forms a stable complex with europium picrate. From ^1H NMR and IR spectra, the europium ion was shown to be coordinated to the C=O oxygen atoms and C–O–C oxygen atoms, showing high coordination ability, which could be useful for catalysis in organic reactions. The europium complex exhibits characteristic fluorescence, and could be used in biological systems as a luminescent probe. Further studies of the ligand are under way.

Supplementary data

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 220535. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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