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Synthesis, characterization of the luminescent lanthanide complexes with (*Z*)-4-(4-methoxyphenoxy)-4-oxobut-2-enoic acid

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Abstract

(*Z*)-4-(4-Methoxyphenoxy)-4-oxobut-2-enoic acid and its solid rare earth complexes $LnL_3{\cdot}2H_2O$ (Ln = La, Eu, Tb) were synthesized and characterized by means of MS, elemental analysis, FTIR, ^{13}C NMR and TG–DTA. The IR and ^{13}C NMR results show that the carboxylic groups in the complexes coordinated to the rare earth ions in the form of a bidentate ligand, but the ester carboxylic groups have not taken part in the coordination. The luminescence spectra of Eu(III) and Tb(III) complexes in solid state were also studied. The strong luminescence emitting peaks at 616 nm for Eu(III) and 547 nm for Tb(III) can be observed, which could be attributed to the ligand has an enhanced effect to the luminescence intensity of the Eu and Tb.

Keywords: (*Z*)-4-(4-Methoxyphenoxy)-4-oxobut-2-enoic acid; Synthesis; Complexes; Luminescence properties

1. Introduction

Derivatives of 2-butenedioic acid, such as its alkyl esters [1–3], possess a conjugated structure and have been widely applied as potential catalysts, semiconductors, photoresist devices, and can improve the stability of polymers. Some 2-butenedioic acid monoalkyl esters form quite strong coordination bonds with alkali and alkaline earth metals, such as Li^+, Ca^{2+} and Mg^{2+}, etc., giving excellent antibacterial and a static action. And luminescent lanthanide complexes [4–6] have attracted intense research interest from both material and biological science [7] mainly due to their strong fluorescence emission, large stokes' shifts, narrow emission profiles and long fluorescence lifetime [8], they have been widely used in many aspects, such as fluorescence mark, fluorescence analysis, environmental sciences, and cell biology [9–12]. Their use has opened up a lot of opportunities in growing fields of large social and economical impact. As part of our continuing investigation into the preparation of lanthanide and actinide compounds with the derivatives of 2-butenedioic acid, we report here the synthesis and spectroscopic study of the (*Z*)-4-(4-methoxyphenoxy)-4-oxobut-2-enoic acid and its complexes with La(III), Eu(III), Tb(III). The results indicate that the carboxlic group acting as a bidentate chelate coordinated to the lanthanide ions, and the Eu(III) and Tb(III) complexes exhibit characteristic luminescence with comparatively high brightness and good monochromatic.

2. Experimental

2.1. Materials

All commercially available chemicals were of A.R. grade and all solvents used were purified by standard methods.

2.2. Methods

The metal ions were determined by EDTA titration using xylenol orange as an indicator. Nitrogen, carbon and hydrogen analyses were determined using a Vario EL elemental analyzer. IR spectra were recorded on a Nicolet Avatar 360 FTIR instrument using KBr discs in the 400–4000 cm^{-1} region. Thermal analysis (TG–DTA) was carried out on a PCT-2A thermal balance; ^{13}C NMR spectra were measured on a Varian Mercury-400BB NMR spectrometer. MS were performed on a HP-5988A spectrometer (EI at 70 eV). Luminescence measurements were made on a Hitachi F-4500 spectrophotometer equipped with quartz curettes of 1 cm path length at room

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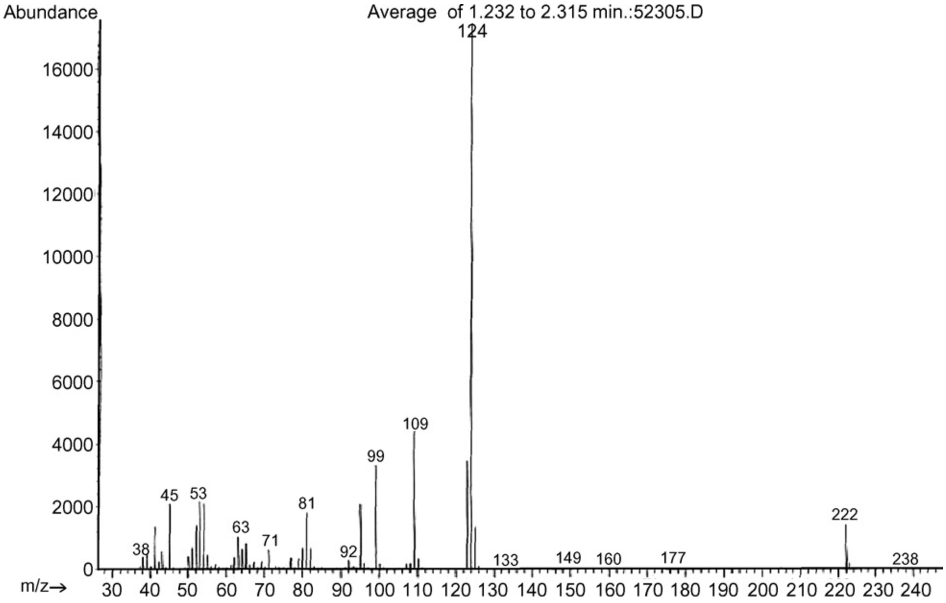

Fig. 1. The MS spectrum of HL.

temperature. The excitation and emission slit widths were 2.5 nm.

2.3. Synthesis of the ligand

Maleic anhydride 2.94 g (30 mmol) and *p*-hydroxyanisole 3.72 g (30 mmol) was added to a three-neck flask equipped with a condenser, heated it to 95 °C, then anhydrous pyridine (0.4 ml) was added dropwise to the mixture under stirring, 0.2 ml pyridine was added in the same way after 15 min again. The reaction mixture was stirred at the temperature of 95–100 °C for 1.5 h. After cooling to the room temperature, the crude product was chromatographed on silia gel [5:1, v:v petroleum ether/ethyl acetate] to afford ligand as a white solid, yield: 45%. MS (EI, 70ev): *m*/*z* (%) 222 (M^+, 8.99), 124 (100), 109 (27.41), 99 (19.74), 81 (10.50), 45 (15.25), as in Fig. 1. And the structure is shown in Fig. 2.

2.4. Synthesis of the complexes

The solution of the ligand (1.5 mmol) in the acetone (15.0 ml) was adjusted with the solution of NaOH (3.0 ml) to neutralize all of the carboxylic groups, this is solution a. A solution (7.0 ml) containing $Ln(NO_3)_3·6H_2O$ (Ln = La, Eu, Tb) (0.5 mmol) was added dropwise to the solution a. The mixture was stirred for 2 days and white precipitate formed. The precipitate was collected and washed three times with the mixture of acetone/water (v:v, 2:1). Further drying in a vacuum afforded a pale white powder, yield: 70–80%.

Table 1
Elemental analyses of the ligand and complexes

Complexes	C (%)	H (%)	RE (%)
HL	59.42 (59.46)	4.511 (4.505)	0
$LaL_3·2H_2O$	47.62 (47.26)	3.453 (3.699)	16.66 (16.59)
$EuL_3·2H_2O$	46.41 (46.53)	3.536 (3.642)	18.09 (17.86)
$TbL_3·2H_2O$	45.73 (46.15)	3.606 (3.613)	18.63 (18.53)

3. Results and discussion

3.1. Properties of the complexes

Analytical data for the complexes are listed in Table 1. The results show that the formulas of the complexes are $LnL_3·2H_2O$. All complexes are soluble in DMSO and DMF.

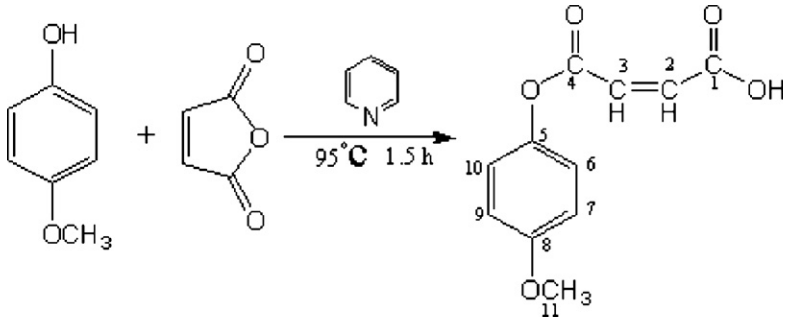

Fig. 2. Scheme of the synthesis of the ligand.

Table 2
IR spectra data of the free ligand and its complexes (cm^{-1})

Complexes	*V* O–H	*V* COO$^-$		*Vs* CH$_3$	*Vas* C–O–C	*Vs* C–O–C	*Vas* COO$^-$	*Vs* COO$^-$	Δ*Vas-s*	*V* Ln–O
HL	3440	1743	1685	2838	1235	1143				
NaL	3448	1737		2836	1251	1144	1596	1400	196	
$LaL_3 \cdot 2H_2O$	3438	1734		2837	1248	1147	1555	1430	125	455
$EuL_3 \cdot 2H_2O$	3420	1736		2837	1248	1147	1548	1435	113	457
$TbL_3 \cdot 2H_2O$	3422	1737		2834	1249	1148	1547	1440	107	456

3.2. *IR spectra*

The IR spectra of the complexes are obviously different from the ligand, but they resemble with each other. The characteristic bands of the ligand and complexes are listed in Table 2.

The infrared spectrum of ligand shows strong bands at 1743 cm^{-1} and 1685 cm^{-1}, which are assigned to ν(C=O) of ester carbonyl group and carboxylic group, respectively. In the complexes, the band for ν(C=O) of ester carbonyl group is shifted by 6–9 cm^{-1} towards lower wave numbers, compared with NaL, it is clear that the ester carbonyl group does not take part in coordination. At the same time, the band for ν(C=O) of carboxylic group is disappeared completely, thus indicates that all the carboxylic groups take part in coordination. This is corresponding with the results of ^{13}C NMR. The peaks at *ca.* 2837 cm^{-1} and 1248 cm^{-1} are assigned to the $\nu_{as}(CH_3)$ and ν(C–O–C) [13], the two bands indicated that there has Ar–O–CH_3 group in the ligand and complexes. Two strong absorption bands lying at 1430–1440 cm^{-1} and 1547–1555 cm^{-1} were observed in complexes, which were attributed to the symmetric vibration absorption υ_s (COO^-) and asymmetric vibration absorption υ_{as} (COO^-) of the carboxylic groups. The determined Δ*Vas-s* for the Ln(III) complexes is far smaller than that of NaL (196 cm^{-1}), which shows that the symmetry of the carboxylic group in the complexes is C_{2v}, the same to the free ion. This state clearly that the carboxlic group acting as a bidentate chelate coordinated to the lanthanide ions in the complexes [14,15]. The two absorption approximately at 788 and 560 cm^{-1} are assigned to in-plane and out-of-plane bending vibration of coordination water, respectively [16]. The broad continuous absorption (*ca.* 3400 cm^{-1}) indicates that crystal water is simultaneously present [16,17].

3.3. *^{13}C NMR spectra*

The ^{13}C NMR of free ligand and the La(III) complex were measured in CD_3COCD_3, CD_3SOCD_3 at room temperature, respectively. The ^{13}C NMR data were shown in Table 3, and Fig. 3 is the ^{13}C NMR spectra of the HL and the La(III) complex.

There are two resonance peaks at 165.928 and 164.399 ppm, which can be assigned to C1 and C4, respectively. It is worthy of note that chemical shift of C1 undergo about 5.965 ppm downfield shift in the complex, but the change of C4 is not significant, these results indicate that the oxygen atom attached to C1 takes part in coordination, and the oxygen atom attached to C4 does not.

From the results of ^{13}C NMR of ligand and La(III) complex. We can see that the change of chemical shifts of C2 and C3 are obvious. This is because C2 and C3 were affected by C1 and C4 at the same time in the ligand, so the chemical surroundings of C2 and C3 are similar with each other, and the chemical shifts are similar, too. In the La(III) complex, the oxygen atom attached to C1 was coordinated with La(III), so C2 and C3 were affected by C4 only, so the chemical shifts of C2 and C3 undergo about 7.620 and 6.292 ppm downfield and upfield shifts, respectively.

For the La(III) complex, the ^{13}C chemical shifts for C5–C11 are all found at rather normal positions, which are similar to those observed in ligand. These results indicate that all oxygen atoms attached to these carbons do not take part in the coordination.

On the basis of above evidence and analyses, the possible structure of the complexes is shown in Fig. 4.

3.4. *TG–DTA analysis*

Thermal behaviors of the ligand and the La(III) complexes have been studied. Samples of about 10 mg were placed in a crucible, and heated up to 800 °C at the rate of 10 °C/min in an air atmosphere at ambient pressure, using α-Al_2O_3 as reference material.

The DTA curve of free ligand has an endothermic peak at 153 °C, but there is no weight loss on the corresponding TG curve, showing that this is a phase transition process, which is the same as the melting point of the ligand (148 °C). In the range of 273–285 °C, the free ligand has an obvious weight loss, exceeded 85%, but there has a small endothermic peak on the DTA curve, this is because it has a decomposition process in the range of the temperature, and a large part of produces of decomposition have volatilized in a form of gas. There is an endothermic

Table 3
^{13}C NMR (100 MHz) data of HL and $LaL_3 \cdot 2H_2O$

	1	2	3	4	5	6, 10	7, 9	8	11
HL(CD_3COCD_3)	165.928	135.992	133.448	164.399	144.855	123.104	115.171	158.475	55.836
$LaL_3 \cdot 2H_2O(CD_3SOCD_3)$	171.893	143.612	127.156	164.772	143.675	122.421	114.378	156.91	55.374
Δδ[a]	−5.965	−7.620	6.292	−0.373	1.180	0.683	0.793	1.565	0.462

[a] $\Delta\delta = \delta HL - \delta LaL_3 \cdot 2H_2O$.

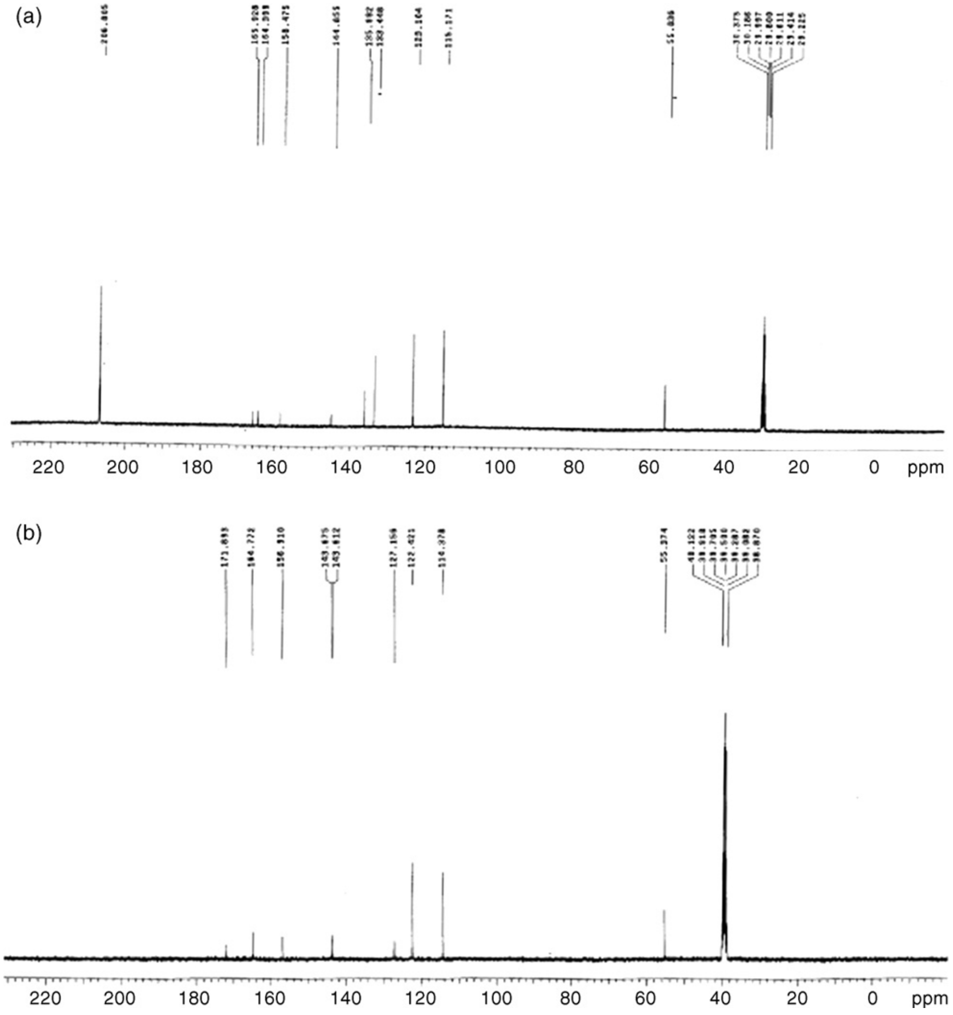

Fig. 3. ^{13}C NMR of HL and lanthanum complex ((a) HL and (b) La(III) complex).

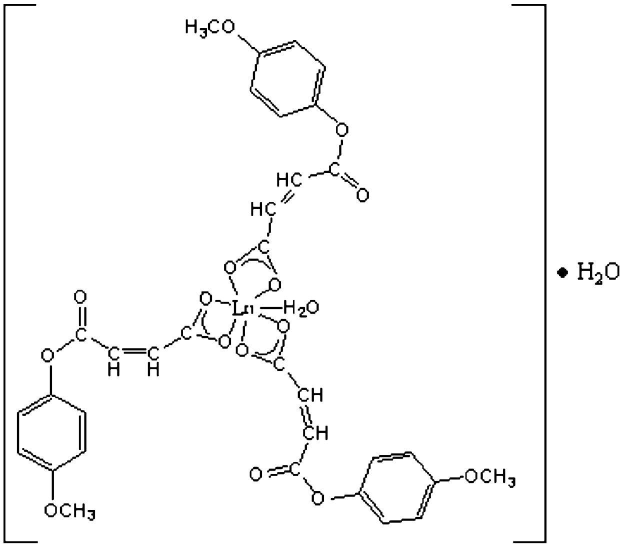

Fig. 4. Suggest structure of the complexes.

peak at 170–189 °C for the La(III) complex, the corresponding TG curve shows that the weight loss is equal to two water molecules, it indicates that the presence of two coordinating water molecules in the La(III) complex. The result is accord with the elemental analyses study. Two strong exothermic peaks on DTA curve can be observed in the range of 338–420 °C. Although the discontinuous changes on TG curves indicate that the decomposition have taken place in steps, but the changes are so nearly to deduce the detailed decomposition processes.

3.5. Luminescence studies

The excitation and emission spectra, as well as the luminescence intensity, were measured on dried and finely powdered samples at room temperature. The major luminescence spectral data are summarized in Table 4. Fig. 5 is the luminescence spectral of the complexes of Eu(III) and Tb(III).

The europium and terbium complexes exhibited strong characteristic luminescence of europium and terbium ions. The emission spectrum of the europium complex is shown in Fig. 5a. Two visible bright emission peaks, which centered at 592.0 nm and 615.6 nm were observed [18] and assigned to $^5D_0 \rightarrow {}^7F_1$ and

Table 4
Fluorescence data of the solid complexes

Complexes	Slit (nm)	λ_{ex} (nm)	λ_{em} (nm)	RFI[a]	Assignment
$EuL_3 \cdot 2H_2O$	2.5	466.0	592.0	678	$^5D_0 \rightarrow {}^7F_1$
			615.6	1365	$^5D_0 \rightarrow {}^7F_2$
$TbL_3 \cdot 2H_2O$	2.5	370.0	492.4	242	$^5D_4 \rightarrow {}^7F_6$
			546.6	6790	$^5D_4 \rightarrow {}^7F_5$
			585.2	499	$^5D_4 \rightarrow {}^7F_4$
			621.0	189	$^5D_4 \rightarrow {}^7F_3$

[a] RFI: relative fluorescence intensity.

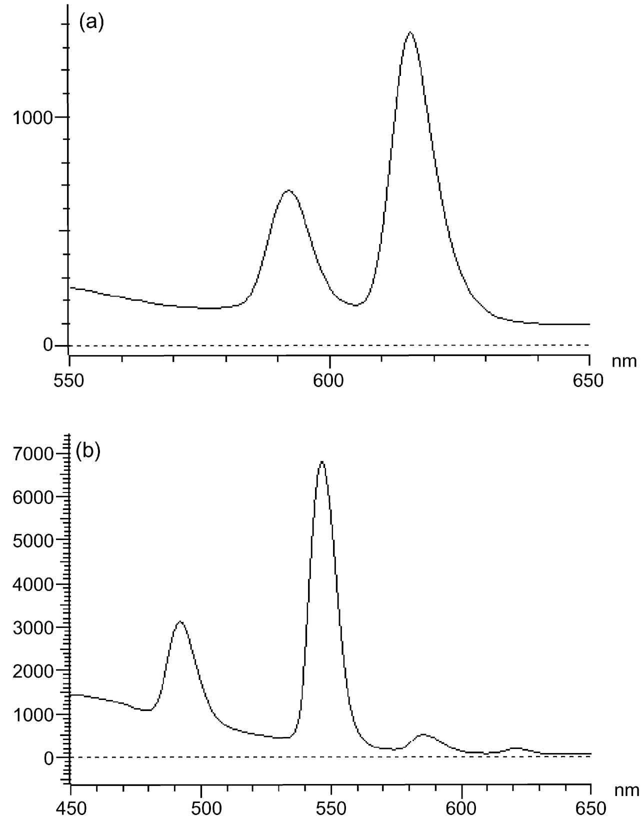

Fig. 5. The emission spectrum of the complexes ((a) Eu(III) complex and (b) Tb(III) complex).

$^5D_0 \rightarrow {}^7F_2$, respectively. And the intensity of $^5D_0 \rightarrow {}^7F_2$ transition is far stronger than that of $^5D_0 \rightarrow {}^7F_1$, the intensity ratio value ($^5D_0 \rightarrow {}^7F_2 / {}^5D_0 \rightarrow {}^7F_1$) is 2.0, indicating a low symmetry for the electrostatic field surrounding Eu(III) [19]. From Fig. 5b, it can be seen that four characteristic emission peaks were observed in terbium complex [18]. These peaks were corresponding to the $^5D_4 \rightarrow {}^7F_J$ transition [20]. As we know luminescence intensity of solid Ln (Ln = Eu, Tb) nitrate is quite weak, but from the date of Table 4 we know that the luminescence intensity of Ln (Ln = Eu, Tb) complex is far stronger than that of Ln (Ln = Eu, Tb) nitrate, respectively. So we can say that the ligand has an enhanced effect to the luminescence intensity of the Eu and Tb. Further work has to be undertaken in order to investigate the effect.

4. Conclusion

According to the data and discussions above, it is obvious that the ligand form complexes with lanthanide(III) ions. The Eu(III) and Tb(III) complexes exhibited characteristic luminescence of Eu(III) and Tb(III) ions. Obvious changes in IR spectra and ^{13}C NMR were observed when the ligand formed the lanthanide complexes, these results indicate that the Eu(III) and Tb(III) ions were coordinated to the oxygen atoms of the carboxylic group.

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