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Fluorescence of complexes of Eu Ⅲ with aromatic carboxylic acid-1, 10-phenanthroline①

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[Abstract] The 1, 10-phenanthroline-aromatic carboxylic acid (benzoic acid and *o*-phthalic acid) binary and ternary complexes of europium were synthesized. The fluorescence and FT-IR spectroscopy, elemental analysis, UV spectroscopic studies on these complexes were also performed. These complexes can emit strong red fluorescence of Eu Ⅲ excited by UV light. At the same excited wavelength, the fluorescence spectra of the complexes were also studied. The results indicated that the fluorescence intensities of ternary complexes are stronger than that of binary complexes. The reason is that phenanthroline has higher electron density and higher orbit scope in the conjugated system and consequently an easier energy transfer to the europium ion, which makes the fluorescence intensity of ternary complexes be stronger than that of binary complexes.

[Key words] complexes of europium; *o*-phthalic acid; benzoic acid; 1, 10-phenanthroline; fluorescence spectra
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1 INTRODUCTION

Luminescent complexes of rare earth are of important fluorescent materials for industries, for example, fluorescent paint and inks, interior displays and light conversion agents[1~3]. They have good characteristic fluorescence and high fluorescent intensity. Gradually, these properties have attracted many researchers to study. At large, the excited spectra of rare earth ions come from their f-f electronic transition and their specific emission appears in narrow banded line. This is one of the reasons why the rare earth ions have low luminescent efficiency. However, the excited spectra of organic molecules are almost broad bands and situated in blue and violet regions. Furthermore, the rare earth ions can easily coordinated to the organic molecules containing O groups, such as carboxylic acid, aromatic carboxylic acid. This coordination can sensitize the rare earth ions and enhance the fluorescent efficiency. Rare earth complexes with aromatic carboxylic acid are kinds of luminescent materials with good properties[4~11]. In this paper, we synthesized the binary, ternary complexes of aromatic carboxylic acid and 1, 10-phenanthroline with Eu(Ⅲ) and studied the luminescent properties of the solid powders.

2 EXPERIMENTAL

2.1 Materials

The purity of europium oxide was of 99.9%, potassium biphthalate (HKL_1), sodium benzoate (NaL_2), 1, 10-phenanthroline (phen) and others were pure chemicals.

Europium chloride stock solution was obtained by dissolving europium oxide in HCl, evaporating the excess acid and then diluting to the designed volume with deionized water, and was adjusted to pH 4 by NaOH.

The synthesis of europium-benzoic acid (or *o*-phthalic acid) binary complexes was performed as following process. The aqueous $EuCl_3$ solution was slowly added to the sodium benzoate ($Eu^{3+} : L_2 = 1:3$) or potassium biphthalate ($Eu^{3+} : L_1 = 2:3$) solution. The mixture was adjusted to pH = 5.5~6.5, thus, a white precipitate was obtained and then separated by filtration, washed with deionized water, and then dried at 90 ℃ for 4 h.

The synthesis of europium-benzoic acid (or phthalic acid)-phen ternary complexes was similar to that of binary complexes. But the ratios were different ($Eu^{3+} : L_1 : \text{phen} = 2:3:2$, $Eu^{3+} : L_2 : \text{phen} = 1:3:1$). Phen was dissolved in ethanol solution (ethanol : water = 1 : 1).

2.2 Measurement technique

UV-VIS absorption spectra of free ligands and complexes in ethanol solution were observed by UV-754 double spectrophotometer. IR spectra was measured on Nicolrt Magnal R-750 spectrophotometer, using KBr pellet. The excited and luminescent spectra were obtained by using RF-540 Fluorolog spectrofluorometer. The method was that adding about 0.1 g solid sample which was attrited to powder, to a round plastic cell (the diameter is 10 mm, the thickness is 3 mm), leveling the surface with a glass panel, then measuring their fluorescence spectra.

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3 RESULTS AND DISCUSSION

3.1 Composition of complexes

Using xvlenol orange as denote agent, the europium contents in complexes were determined by EDTA capacity methods. The element analysis of C, H, N was performed according to the ordinary methods. The results are shown in Table 1.

Table 1 Results of element analysis (%)

Complex	Eu	C	H	N
$Eu(C_6H_5COO)_3$ phen	21.31 (21.65)	56.98 (56.34)	3.01 (3.51)	4.03 (3.80)
$Eu(C_6H_5COO)_3$	28.99 (29.51)	48.54 (48.93)	2.43 (2.91)	
$Eu[C_6H_4(COO)_2]_{3/2}$ phen	25.63 (25.92)	48.87 (49.11)	2.41 (2.64)	4.83 (4.77)
$Eu[C_6H_4(COO)_2]_{3/2}$	38.01 (38.17)	35.94 (36.16)	1.49 (1.51)	

From Table 1, it can be seen that the results of element analysis are the same as the results of calculation according to the formula.

3.2 UV-VIS absorption spectra

The UV absorption peaks of free ligands and complexes in ethanol solution are shown in Table 2. The UV spectra of some complexes are shown in Fig. 1. From Table 2 and Fig. 1, it can be seen that the absorption bands of binary complexes of europium do not show significant difference in comparison with those of their corresponding free ligand molecules except that the absorption peak shifted lightly to a longer wavelength. The energy absorption of the complexes mostly comes from that of ligands. In the UV spectra of ternary complexes of Eu-L_1-phen, there are typical absorptions of phthalic acid and phenanthroline. In Eu-L_2-phen, there are almost energy absorptions of benzoic acid and phen. The energy absorption of ternary complexes also lies on that of the ligands which have intense absorption in the region of 200 ~ 400 nm. The region is wider than that of binary complexes. The UV spectra prove the coordination.

Table 2 UV peaks of complexing agent and complexes

Complex	Wavelength/nm		
	λ_1	λ_2	λ_3
Phen·H_2O	200	230	268
Benzoic acid	239	260	
o-phthatic acid	227	256	280
Eu-L_1	259	282	
Eu-L_2	256	260	
Eu-L_1-phen	230	260	280
Eu-L_2-phen	210 ~ 280		

3.3 Fluorescence spectra

The fluorescence spectra of Eu-L_1, Eu-L_2, Eu-L_1-phen, Eu-L_2-phen were studied by exciting the solid samples at 295 nm in order to find how the ligands, different kinds and different configuration complexes influence the fluorescence intensity. Table 3 shows the assignment and relative intensity of fluorescence spectra of Eu(Ⅲ) complexes. Fig. 2 and Fig. 3 show the fluorescent spectra of Eu-L_2 and Eu-L_2-phen. The experiment proves that the excited and emission wavelength of complexes are basically stable. The ligands absorb the energy and the energy was transferred to Eu(Ⅲ) ions, then the Eu(Ⅲ) emits typically red fluorescence. The fluorescence intensity has much difference with the species and configurations of complexes. At large, the intensity of ternary complexes is higher than that of binary complexes,

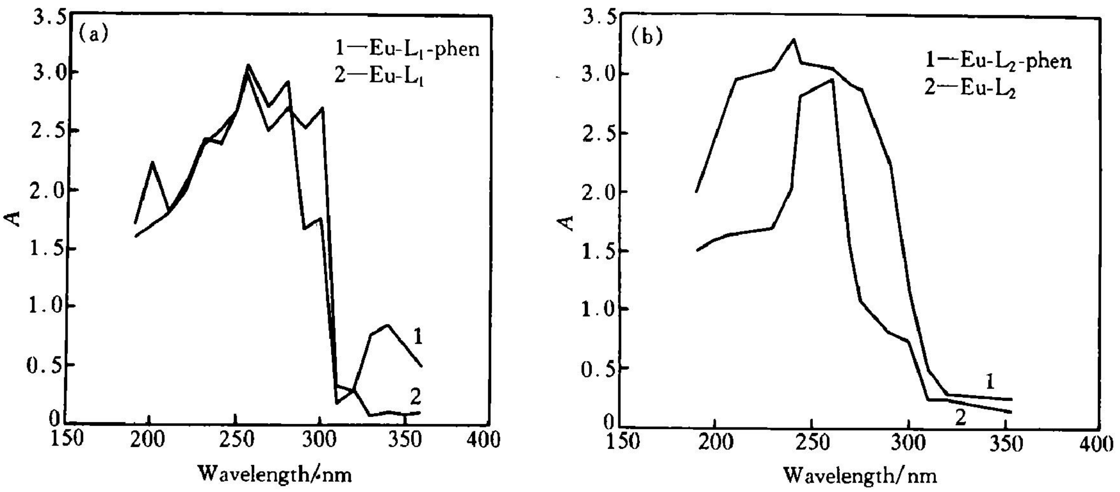

Fig. 1 UV spectra of complexes of Eu(Ⅲ)

Table 3 Assignment and relative intensity of fluorescence spectra of Eu(Ⅲ) complexes

Complex	$^5D_2$-$^7F_0$/nm	$^5D_0$-$^7F_1$/nm	$^5D_0$-$^7F_2$/nm
Eu-L_1	467.4(10.12)	593.2(5.50)	617.9(6.71)
Eu-L_2	464.4(5.40)	593.6(4.55)	617.3(7.25)
Eu-L_1-phen		595.6(59.11)	619.7(71.90)
Eu-L_2-phen		594.0(66.50)	615.7(88.5)

The numbers in brackets are relative intensities

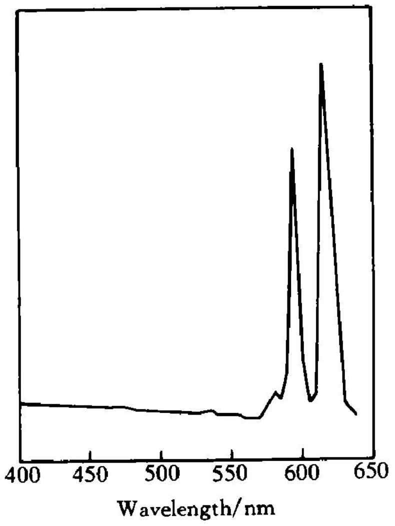

Fig.2 Fluorescent spectrum of Eu-L_2(× 64)

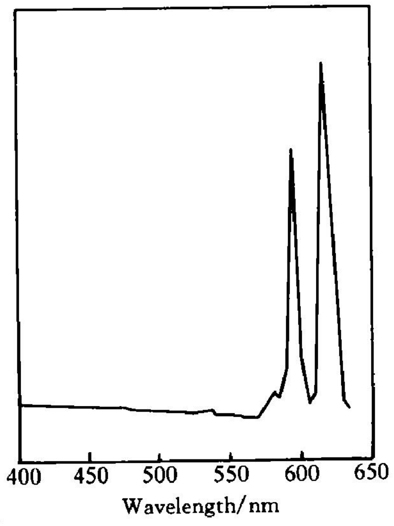

Fig.3 Fluorescent spectrum of Eu-L_2-phen(× 8)

such as Eu-L_1-phen > Eu-L_1. The reason is that adding the second ligand to the complexes, the conjugated system can be enlarged and it benefits energy transfer to rare earth ions. When aromatic carboxylic acid and phen are coordinated with Eu(Ⅲ), the complexes of Eu(Ⅲ) form π electron conjugated system and increase the rigidity of the configuration. This stable configuration benefits to energy transfer. The lowest triplet state of phen is situated at 22 123 cm^{-1}, it is higher than the excited level $^5D_0$(17 250 cm^{-1}) and $^5D_1$(19 020 cm^{-1}) of Eu(Ⅲ) ion. It satisfies the conditions that the triplet state of energy transfer ligand is higher than the excited level of rare earth ions. As the second ligand, phen can enhance the typically fluorescence intensity of Eu(Ⅲ).

3.4 IR spectra

The infrared (IR) spectra of the samples in KBr pellet were recorded in the region of 4 000 ~ 400 cm^{-1}. The IR spectra of complexes have much changed in comparison with the ligands. In binary complexes of potassium biphthalate coordinated to Eu(Ⅲ), the asymmetric stretching vibration $\upsilon_{as}(COO^-)$ and symmetric stretching vibration $\upsilon_s(COO^-)$ have changed. The $\upsilon_{as}(COO^-)$ changes from 1 558 ~ 1 586 cm^{-1} to 1 529 ~ 1 583 cm^{-1}, $\upsilon_s(COO^-)$ from 1 265 ~ 1 383 cm^{-1} to 1 384 ~ 1 432 cm^{-1}. In binary complexes of Eu-L_2, the $\upsilon_s(COO^-)$ changes from 1 415 cm^{-1} to 1 403 ~ 1 409 cm^{-1}, $\upsilon_{as}(COO^-)$ from 1 552 cm^{-1} to 1 525 ~ 1 533 cm^{-1}. So it was suggested that the coordinate bond was formed between —COO^- groups and Eu(Ⅲ) ions in these compounds. In ternary complexes, the υ(COOH)(1 677 cm^{-1}), υ(C—OH) (1 287 cm^{-1}) and υ(OH)(2 500 ~ 2 900 cm^{-1}) absorption peaks disappeared. It shows that the hydrogen of hydroxy was replaced and the complexes have been synthesized. In IR spectra of phenanthroline and the complexes, the $\upsilon(C-C+C=N)$ changes from 1 561 cm^{-1} to 1 518 cm^{-1}, δ_{C-H} changes from 856 cm^{-1} and 742 cm^{-1} to 847 cm^{-1} and 730 cm^{-1}. It proves the N of phen takes part in the coordination.

4 CONCLUSIONS

Four complexes of Eu(Ⅲ) which coordinated with potassium biphathalate, sodium benzoate and phen as ligands were obtained. The four complexes can emit red fluorescence by excited at 365 nm UV light. Their UV-VIS, IR and fluorescent spectra were studied.

The IR spectra give good evidences that Eu(Ⅲ) is coordinated with the ligands via C=O and C=N groups. The coordination is also confirmed by UV-VIS spectra which also shows the complexes have strong absorption in the region of 200 ~ 400 nm. The fluorescence spectra show that all of the complexes can emit typically red fluorescence of europium. Moreover, the fluorescence intensity of ternary complexes is higher than that of binary complexes. Enhancing the intensity by adding the second ligand is a good way. All of the complexes have good fluorescent properties. The following study on them will open up new possibilities for the development and application of new and cheaper luminescent materials.

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