

Syntheses, characteristics and fluorescence properties of complexes of terbium with benzoic acid and its derivatives^①

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Abstract: The binary complexes of terbium with benzoic acid and its derivatives (phthalic acid, *isophthalic* acid, *o*-aminobenzoic acid, salicylic acid, sulfosalicylic acid) were synthesized and their compositions were identified by elemental analyses. UV, IR of the complexes were investigated. The UV spectra indicate that the complexes' ultraviolet absorption is mainly the ligands' absorption, but the location of peak drifts. The IR spectra show that the IR spectra of complexes are different from those of free ligands, and the band at 400 - 500 cm⁻¹, due to the stretching vibration of Tb-O, is absent for free ligands. The fluorescence properties were investigated by using luminescence spectroscopy, the results show that all the six complexes of terbium exhibit excellent luminescence, due to the transition from the lowest excited state ⁵D₄ to ⁷F ground state manifold, the complexes of terbium with sulfosalicylic acid have the strongest fluorescence intensity, and is stronger than *o*-aminobenzoic acid-terbium, whose fluorescence intensity is regarded as the strongest one in the literature, and even stronger than some phosphor of terbium.

Key words: rare earth; terbium; benzoic acid; fluorescence; complexes

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1 INTRODUCTION

Rare earth complexes with aromatic carboxylic acids are a kind of luminescent materials with good properties^[1, 2]. Much attention has been paid to the fluorescence properties of these complexes. There are some reports about fluorescence properties of the complexes of a part of rare earth with phthalic acid and terbium with benzoic acid and salicylic acid^[3-9]. However, no report on systemic study of the fluorescence properties concerning rare earth complexes with different aromatic carboxylic acids has been published. For this purpose, we have synthesized fourteen complexes of Sm, Eu, Tb, Dy with benzoic acid derivatives^[10-14], such as RC₆H₄COOH (R = *o*-NH₂, H, *p*-NH₂, *o*-OH, *m*-Cl, *o*-COOH, *m*-COOH, *p*-COOH, *p*-OH, *m*-NO₂, 3, 5-Dinitro, *p*-Br, *o*-I, 2-OH-5-SO₃H) and it is found that the complexes of Sm and Dy with these aromatic acids show little fluorescence, and Eu and Tb with some of these aromatic acids show strong fluorescence in the excitation of UV, and that the complexes of terbium with sulfosalicylic acid had the strongest fluorescence intensity, and was stronger than that of *o*-aminobenzoic acid-terbium, whose fluorescence in-

tensity was regarded as the strongest one in the literature, and even stronger than some phosphor of terbium. In this paper, terbium complexes with aromatic acids are synthesized and their fluorescence properties were investigated.

2 EXPERIMENTAL

2.1 Materials

The purity of terbium oxides was 99.99%, *p*-phthalic acid was chemical pure and *isophthalic* acid, *o*-aminobenzoic acid, salicylic acid, sulfosalicylic acid, sodium benzoate were analytical reagents.

2.2 Synthesis

Terbium chloride stock solution was obtained by dissolving terbium oxides in hydrochloric acid, evaporating excess acid and then diluting to predetermined concentration. The stock solution of sodium benzoate was prepared by dissolving the sodium benzoate to water, and the stock solution of phthalic acid, *isophthalic* acid, *o*-aminobenzoic acid, salicylic acid, sulfosalicylic acid was prepared by dissolving them respectively to 95% ethanol.

The aqueous TbCl₃ solution was slowly added

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to ligand solution according to the molar ratio of Tb^{3+} to ligand 1: 3 or 2: 3 (phthalic acid, isophthalic acid) at 80 °C under stirring. The pH of the mixture was adjusted to 6.0–6.5 by addition of sodium hydroxide solution. Thus, white precipitates of the complexes came into being. After another 2 h, stop stirring, the mixture was cooled to room temperature. The white precipitates of the complexes were filtered, washed with deionized water and ethanol till no chloridion could be found, then dried at 85 °C under vacuum for 4 h.

2.3 Measurements

Infrared spectra were recorded using KBr pellets on NEXUS-470 Fourier Transform infrared spectrophotometer (Nicolet Co. USA). Elementary analyses were carried out on Perkin Elmer-240 elementary analysis instrument. UV-visible absorption spectra were recorded on UV-754 spectrophotometers. The luminescence spectra were measured on Hitachi F-2500 fluorospectrophotometers. The method was as follows: finely powered sample was added to a cylindrical plastic sample cell, debulked and leveled the surface of the sample with a glass panel, then the fluorescence spectra was measured in a solid sample bracket.

3 RESULTS AND DISCUSSION

3.1 Composition of complexes

Using xylene orange as denote agent, the terbium 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 Elementary analysis of complexes

Complexes	Mass fraction/ %			
	C	H	N	Tb
$Tb(BA)_3$	48.22 (48.28)	2.92 (2.87)		30.27 (30.46)
$Tb(\sigma\text{-amino})_3$	44.61 (44.44)	3.28 (3.17)	7.47 (7.40)	28.00 (28.04)
$Tb(Sal)_3$	44.31 (44.21)	2.64 (2.63)		27.96 (27.89)
$Tb_2(Ssal)_3$	26.11 (26.09)	1.18 (1.24)		32.78 (32.92)
$Tb_2(Phth)_3 \cdot 4H_2O$	35.68 (35.56)	1.64 (1.48)		39.30 (39.26)
$Tb_2(iso\text{-}Phth)_3 \cdot 4H_2O$	35.66 (35.56)	1.60 (1.48)		39.28 (39.26)

Values in parentheses are calculated ones.

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

3.2 IR spectra

The infrared spectra of the samples in KBr pellets were recorded in the region of 4 000–400 cm^{-1} . Special attention was paid to their IR around 1 700–1 200 cm^{-1} . The IR spectra of complexes have changed much in comparison with the uncomplexed ligands. Compared with sodium carboxylate, the symmetric stretching vibration of carboxyl (ν_{s, COO^-}) is shifted from 1 260–1 283 cm^{-1} to 1 384–1 430 cm^{-1} and the asymmetric stretching vibration of carboxyl (ν_{as, COO^-}) is shifted from 1 558–1 582 cm^{-1} to 1 529–1 600 cm^{-1} and the absorption becomes weak. The changes of stretching vibration of carboxyl suggests that carboxyl are indeed bound to the $Tb(III)$ ion. Moreover, the band at 400–500 cm^{-1} , due to the stretching vibration of $Tb-O$, is absent for uncomplexed ligands.

The IR spectra of $Tb(\sigma\text{-amino})_3$ and $Tb_2(Ssal)_3$ are shown in Figs. 1 and 2. It is clearly seen from Fig. 1 that, in comparison with σ -aminobenzoic acid, the symmetric stretching vibration of amino-group (ν_{s, NH_2}) is shifted from 3 239.26 to 3 311.64 cm^{-1} and the asymmetric stretching vibration of amino-group (ν_{as, NH_2}) is shifted from 3 322.19 to 3 367.22 cm^{-1} ; and that the symmetric stretching vibration of carboxyl (ν_{s, COO^-}) is shifted from 1 484.10 to 1 454.55 cm^{-1} and the asymmetric stretching vibration of carboxyl (ν_{as, COO^-}) is shifted from 1 666.40 to 1 617.69 cm^{-1} ; and that the wide band at 2 564 cm^{-1} in the free ligand disappear after forming complexes. All these changes suggest that complexes have been synthesized.

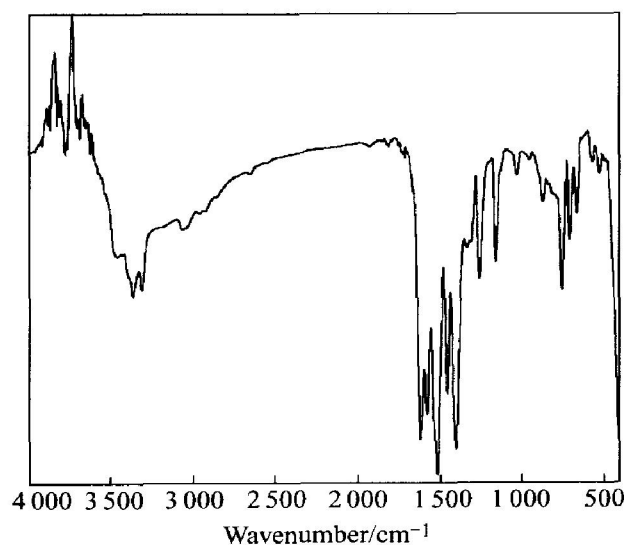


Fig. 1 IR spectrum of $Tb(\sigma\text{-amino})_3$

In the IR spectrum of $Tb_2(Ssal)_3$ (Fig. 2), the IR spectrum of the complexes is apparently different from the ligand. The stretching vibration of carboxyl of ligand at 1 686 cm^{-1} disappears and the symmetric stretching vibration and asymmetric stretching vibration of carboxyl at 1 601 and 1 489

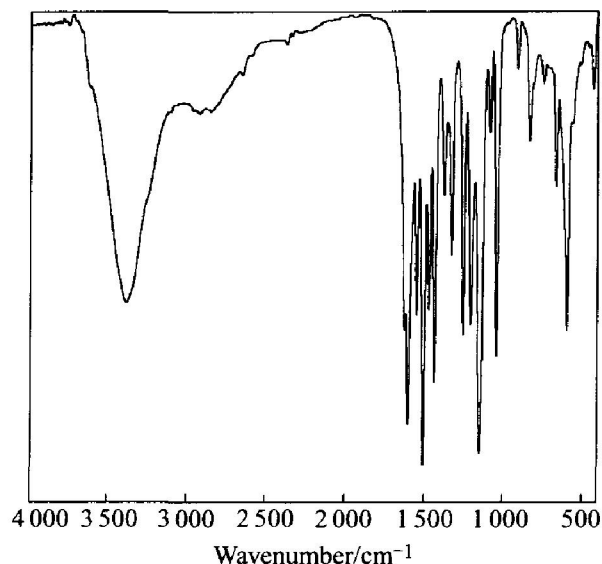


Fig. 2 IR spectrum of $\text{Tb}_2(\text{Ssal})_3$

cm^{-1} appears. The stretching vibration of $\text{Ar}-\text{OH}$ is shifted from 1282 to 1225 cm^{-1} , which overlay the characteristic peak of sulfonic acid group at 1230 cm^{-1} forming an wide band. Additionally, the characteristic peak of the stretching vibration of $\text{Tb}-\text{O}$ is at 448 cm^{-1} . From the analyses we can conclude that the carboxyl and phenol take part in coordination.

3.3 UV-visible absorption spectra

Table 2 illustrates the UV absorption of ligands and their complexes in ethanol solution. It is clearly seen that the absorption of complexes are characterized by the high intensity bands of the corresponding ligands, which have intense absorption than rare earth ion in the region of $200-400\text{ nm}$, and whose absorption energy can transfer to terbium ion after forming complexes.

Table 2 UV absorption peaks of ligands and their complexes

Complexes	$\lambda_{\text{max}}/\text{nm}$	
Benzoic acid (BA)	230	270
$\text{Tb}(\text{BA})_3$	290	
σ Aminobenzoic acid (σ Amino)	220	264
$\text{Tb}(\sigma\text{ amino})_3$	262.0	334
Salicylic acid (sal)	227	297
$\text{Tb}(\text{Sal})_3$	300	351
Suflosalicylic acid (Ssal)	240	272
$\text{Tb}_2(\text{Ssal})_3$	272.3	
Phthalic acid (Phth)	282.8	290.3
$\text{Tb}_2(\text{Phth})_3 \cdot 4\text{H}_2\text{O}$	287.5	
<i>m</i> -Phthalic acid (<i>p</i> -Phth)	282.8	290.3
$\text{Tb}_2(\text{is}\sigma\text{ Phth}) \cdot 4\text{H}_2\text{O}$	272.3	

3.4 Fluorescence properties

3.4.1 Excitation spectra

The excitation spectra were measured when the emission wavelength was fixed at 545 nm and the excitation spectra of complexes are shown in Fig. 3.

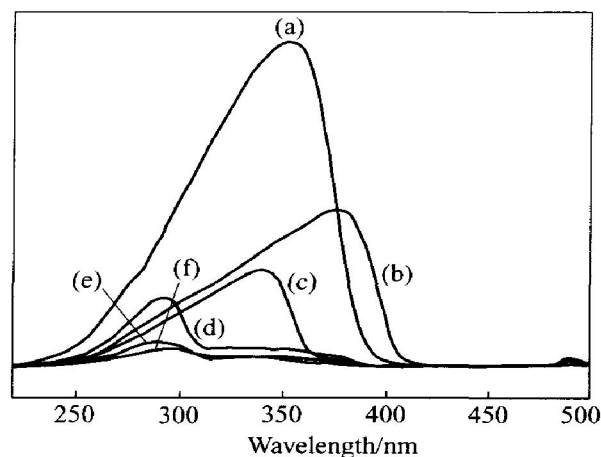


Fig. 3 Fluorescence excitation spectra of $\text{Tb}_2(\text{Ssal})_3$ (a), $\text{Tb}(\sigma\text{ amino})_3$ (b), $\text{Tb}(\text{Sal})_3$ (c), $\text{Tb}(\text{BA})_3$ (d), $\text{Tb}_2(\text{Phth}) \cdot 4\text{H}_2\text{O}$ (e) and $\text{Tb}_2(\text{is}\sigma\text{ Phth}) \cdot 4\text{H}_2\text{O}$ (f)

Fig. 3 shows that all complexes give a wide band from 250 to 400 nm but the peak differ greatly. The excitation intensity of complexes decreases in the following order: $\text{Tb}_2(\text{Ssal})_3 > \text{Tb}(\sigma\text{ amino})_3 > \text{Tb}(\text{Sal})_3 > \text{Tb}(\text{BA})_3 > \text{Tb}_2(\text{Phth}) \cdot 4\text{H}_2\text{O} > \text{Tb}_2(\text{is}\sigma\text{ Phth}) \cdot 4\text{H}_2\text{O}$ and the strongest excitation peak in turn is $353, 376, 340, 292, 290, 295\text{ nm}$. Regarding the UV absorption of free ligands which have a strong absorption in the region of $250-380\text{ nm}$, we know that the excitation spectra of complexes are due to the $\pi \rightarrow \pi^*$ transition of ligands.

3.4.2 Emission spectra

Under the excitation of UV, the six complexes are strongly luminescent, due to the transition from the lowest excited state $^5\text{D}_4$ to ^7F ground state manifold, that is $^5\text{D}_4 \rightarrow ^7\text{F}_6$ (491 nm), $^5\text{D}_4 \rightarrow ^7\text{F}_5$ (545 nm), $^5\text{D}_4 \rightarrow ^7\text{F}_4$ (586 nm), $^5\text{D}_4 \rightarrow ^7\text{F}_3$ (622 nm) etc. This suggests that the lowest triplet state energy level of these ligands and $\text{Tb}(\text{III})$ matches very much^[15]. Take $\text{Tb}(\sigma\text{ amino})_3$ as example, the relative intensity of the emission peak is $2411:5326:384.6:173.7$.

Table 3 shows the assignment and relative intensity of fluorescence emission spectra of complexes. Fig. 4 shows the fluorescence emission spectra of complexes.

From Table 3 and Fig. 4, it is obvious that, according to the changes of substituting group of benzene ring, the fluorescence intensity of complexes decreases in the following order as: $\text{Tb}_2(\text{Ssal})_3 > \text{Tb}(\sigma\text{ amino})_3 > \text{Tb}(\text{Sal})_3 > \text{Tb}(\text{BA})_3 > \text{Tb}_2(\text{is}\sigma\text{ Phth}) \cdot 4\text{H}_2\text{O} > \text{Tb}_2(\text{Phth}) \cdot 4\text{H}_2\text{O}$, and of which $\text{Tb}_2(\text{Ssal})_3$ has the strongest fluorescence

Table 3 Fluorescence emission peak positions and their relative intensities and assignments

Complexes	$^5D_4 \rightarrow ^7F_6$			$^5D_4 \rightarrow ^7F_5$		$^5D_4 \rightarrow ^7F_4$		$^5D_4 \rightarrow ^7F_3$	
	λ_{ex}/nm	λ_{em}/nm	$I/(a.u)$	λ_{em}/nm	$I/(a.u)$	λ_{em}/nm	$I/(a.u)$	λ_{em}/nm	$I/(a.u)$
Tb(BA) ₃	292	490	863.3	545	1 958	588	4 085	624	52.41
Tb(σ amino) ₃	376	489	2 411	550	5 436	584	384.6	626	173.7
Tb(Sal) ₃	340	490	1 410	550	2 993	58	165.2	624	78.06
Tb ₂ (Ssal) ₃	353	490	4 666	544	> 10 000	586	611.0	623	250.5
Tb ₂ (<i>m</i> -Phth) · 4H ₂ O	290	492	305.1	549	772.0	585	30.21	625	19.72
Tb ₂ (σ Phth) ₃ · 4H ₂ O	295	492	267.9	551	565.3	588	19.64	625	16.04

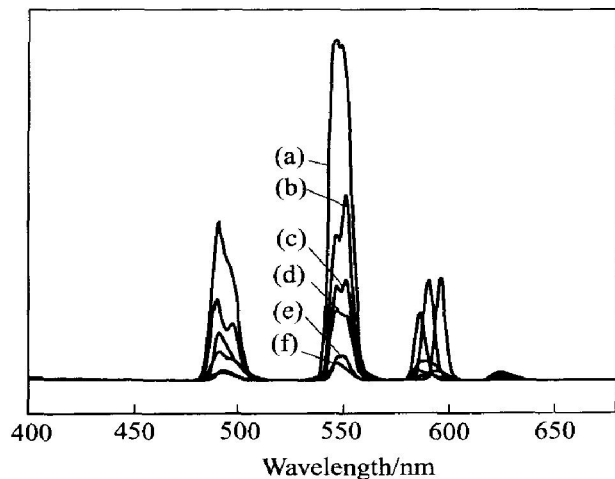


Fig. 4 Fluorescence emission spectra of Tb₂(Ssal)₃ (a), Tb(σ amino)₃ (b), Tb(Sal)₃ (c), Tb(BA)₃ (d), Tb₂(*iso*-Phth) · 4H₂O (e) and Tb₂(Phth) · 4H₂O (f)

intensity, and is stronger than σ -aminobenzoic acid-terbium, whose fluorescence intensity is regarded as the strongest one in the literature^[9], and even stronger than some phosphor of terbium.

4 CONCLUSIONS

1) The binary complexes of terbium with benzoic acid and its derivatives (phthalic acid, isophthalic acid, σ -aminobenzoic acid, salicylic acid, sulfosalicylic acid) are synthesized.

2) The UV spectra indicated that the complexes' ultraviolet absorption is mainly the ligands' ultraviolet absorption, but the location of peak drifts. The IR spectra of complexes are different from those of free ligands and suggests that coordination bonds form between ligands and terbium ion.

3) All the six complexes of terbium exhibit excellent luminescence, according to the changes of substituting group of benzene ring, the fluorescence intensity of complexes decreases in the following order as: Tb₂(Ssal)₃ > Tb(σ amino)₃ >

Tb(Sal)₃ > Tb(BA)₃ > Tb₂(*iso*-Phth) · 4H₂O > Tb₂(Phth) · 4H₂O.

4) Tb₂(Ssal)₃ is firstly synthesized which has the strongest fluorescence intensity, and is stronger than σ -aminobenzoic acid-terbium, whose fluorescence intensity is regarded as the strongest one in the literature^[9], and even stronger than some phosphor of terbium.

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