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Synthesis and Characterization of Quaternary Complexes of Light Rare Earth Perchlorate with Diphenyl Sulfoxide, Benzoic Acid and Studies on Fluorescence of Eu^{3+} Complex

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Abstract Four solid quaternary complexes of light rare earth perchlorate with diphenyl sulfoxide (L) and benzoic acid (L') have been synthesized and characterized. By elemental analysis, TGA-DTA and the molar conductivities in acetone solution studies, the composition of the complexes were suggested as $[\text{REL}_5\text{L}'(\text{CD}_4)](\text{CD}_4)$ ($RE = \text{La}, \text{Pr}, \text{Nd}, \text{Eu}$; $L = \text{C}_6\text{H}_5\text{SO}_2\text{C}_6\text{H}_5$, $L' = \text{C}_6\text{H}_5\text{COO}^-$). As shown in IR spectra, the absorption band associated with the $\text{S}=\text{O}$ stretching modes in the first ligand diphenyl sulfoxide appears at 1037 cm^{-1} , while the absorption bands in the complexes appear between 987 cm^{-1} and 989 cm^{-1} . A shift of the $\text{S}=\text{O}$ stretching frequency towards lower wave number by about 50 cm^{-1} suggests that rare earth ions are bonded with an oxygen atom in sulfoxyl group. In the second ligand benzoate, the absorption band associated with $\nu_{\text{as}(\text{COO}^-)}$ appears at 1550 cm^{-1} , $\nu_{\text{s}(\text{COO}^-)}$ appears at 1416 cm^{-1} . The value of $\Delta n[\nu_{\text{as}(\text{COO}^-)} - \nu_{\text{s}(\text{COO}^-)}]$ is 134 cm^{-1} . A shift of $\nu_{\text{as}(\text{COO}^-)}$ frequency in complexes towards higher wave number, while a shift of $\nu_{\text{s}(\text{COO}^-)}$ frequency in complexes towards lower wave number. What's more, the value of $\Delta n[\nu_{\text{as}(\text{COO}^-)} - \nu_{\text{s}(\text{COO}^-)}]$ in complexes is higher than that of $\Delta n[\nu_{\text{as}(\text{COO}^-)} - \nu_{\text{s}(\text{COO}^-)}]$ in sodium benzoate. This showed that benzoate (L') bonded with RE^{3+} ions by one oxygen atom in carboxyl group which coordinate as an unidentate group. One of two perchlorates (CD_4^-) is coordinated with RE^{3+} while another is not. Fluorescent spectra of Eu^{3+} complex showed that quaternary complexes have stronger fluorescence than the binary one whose ligand is diphenyl sulfoxide (the fluorescence intensity of Eu^{3+} complex increased by 469%). Phosphorescent spectra of two ligands showed that the lower limit of the triplet state with benzoic acid was overlapped by the upper limit with diphenyl sulfoxide, the energy level range of triplet state was extended. As a result, matching extent of triplet state of ligands with excited state of the rare earths have been increased by coordination of the second ligand benzoic acid, the transmit efficiency also have been increased. Attributed to the addition of the second ligand, the symmetry of the complexes always have been decreased, as a result, the fluorescence intensity was increased.

Key words light rare earth quaternary complexes, diphenyl sulfoxide, benzoic acid, fluorescence, phosphorescent spectra

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1 Introduction

The complexes of rare earth ions with carboxylic acids have optimal fluorescence^[1~3], but the solu-

bility of the complexes is not ideal. To some extent, this limited the applications of the complexes. While the rare earth ions such as Sm^{3+} , Eu^{3+} , Tb^{3+} , Dy^{3+} with sulfoxides not only have fine luminescence but

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also have good solubility^[4-7]. Whether a complexes have both advantages of the complexes with sulfoxide as ligand and advantages of the complexes with carboxyl acid as ligand, when it contains sulfoxide and carboxyl acid as ligands? In order to get rare earth complexes having strong luminescence, high thermodynamic stability and good solubility, we have synthesized four solid quaternary complexes of rare earth perchlorate with diphenyl sulfoxide as the first ligand and benzoic acid as the second ligand. We have investigated the fluorescence of complexes and the effects of fluorescence. The researches in this article have theoretical significance and application value of organic rare earth materials having excellent luminescent performance.

2 Experimental Section

2.1 Materials and Instrumentation

Rare earth oxides ($\geq 99.99\%$); benzoic acid A.R. ($\geq 99.5\%$); other chemicals were analytical reagent grade. Element analysis of carbon hydrogen was obtained on PE-2400 elemental analyzer. The rare earth ion content was determined by the standard EDTA complexometric titration. IR spectra were recorded with a Nicolet NEXUS 670 FT-IR spectrometer using KBr plates in the range of $400\sim 4000\text{ cm}^{-1}$.

The molar conductivities were measured by DDS-11D detector at room temperature. The solvent was acetone and the concentration of the solution was $1.0 \times 10^{-3}\text{ mol}\cdot\text{L}^{-1}$. The solid state fluorescent emission spectra and excitation spectra were recorded

Table 1 Composition analysis(%), molar conductivities($\text{s}\cdot\text{cm}^2\cdot\text{mol}^{-1}$), m. p ($^{\circ}\text{C}$) and decomposing point($^{\circ}\text{C}$) of the rare earth complexes(25°C).

Complex	C	H	RE	λ_m	m. p	decomposing point
$[\text{La}_5\text{L}'(\text{CD}_4)](\text{CD}_4)$	54.46 (54.73)	3.79 (3.74)	9.12 (9.46)	126.7	164.5~167	
215.7 $[\text{Pr}_5\text{L}'(\text{CD}_4)](\text{CD}_4)$	54.38 (54.66)	3.77 (3.74)	9.70 (9.58)	127.2	176~179	
217.8 $[\text{Nd}_5\text{L}'(\text{CD}_4)](\text{CD}_4)$	54.21 (54.54)	3.75 (3.73)	9.24 (9.78)	126.8	188~191	
220.1 $[\text{Eu}_5\text{L}'(\text{CD}_4)](\text{CD}_4)$	53.92 (54.25)	3.69 (3.71)	9.92 (10.26)	134.1	178.5~180	218.3

(Theoretical data are in the bracket)

3.2 The Analysis of TGA-DTA

TGA-DTA curve (as shown in Fig. 1) of La^{3+}

by Hitachi F-3010 fluorospectrophotometry at room temperature. The slit width was 3 nm (L-42 filter was used). Phosphorescent spectra were recorded with SPEX 1934D phosphorimeter at room temperature. TGA-DTA curve was drawn on SDT2960 differential thermal and gravimetric analyzer.

2.2 The Synthesis of Quaternary Complexes

0.7 mmol sulfoxide ($\text{C}_6\text{H}_5\text{SOC}_6\text{H}_5$) was weighed and dissolved in the ethanol, then the ethanol solution of rare earth perchlorate (0.1 mmol) was added slowly in the ethanol solution of ligand to give the complex as a precipitate. After refluxed half an hour, ethanol was added to dissolve the precipitate. Then the solution of benzoic acid weighed 0.1 mmol was added, controlling pH to be 6 using ammonia, after reaction for 10 h, cooled, the complex was extracted, washed with anhydrous ethanol and dried in vacuo. The yield of product was 70% ~ 75%.

3 Results and Discussion

3.1 Composition Analysis of Complexes and the Molar Conductivity

Composition analysis data of the complexes were shown in Table 1. It showed that the complexes have the general formula $[\text{REL}_5\text{L}'(\text{CD}_4)](\text{CD}_4)$, ($\text{RE} = \text{La, Pr, Nd, Eu}$; $\text{L} = \text{C}_6\text{H}_5\text{SOC}_6\text{H}_5$, $\text{L}' = \text{C}_6\text{H}_5\text{COO}^-$). The range of molar conductivities is from 126.7 to 134.1 $\text{s}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, according to the literature^[8], this indicated that complexes were 1:1 type electrolytes. One of two inorganic anions CD_4^- was coordinated and the other was not.

complex was drawn in N_2 and the heating rate was $10^{\circ}\text{C}/\text{min}$. According to TGA curve of La^{3+} complex,

at 166.31 °C there is an endothermic peak area accordance with the m. p of the complex (showed in Table 1). La^{3+} complex began to lose weight at 215.61 °C and weight loss was 41.47%. And on the DTA curve of La^{3+} complex, there is an endothermic peak area at 267.65 °C which was caused by the decomposition of La^{3+} complex, the percentage of the weight loss was in good accordance with the theoretical data 41.25% when the complex lose three ligands ($\text{C}_6\text{H}_5\text{SOC}_6\text{H}_5$). The La^{3+} complex began to lose weight at 292.61 °C again, the weight loss was 44.37%. what's more on the DTA curve of La^{3+} complex, there is an exothermic peak area at 409.94 °C caused by the oxidized decomposition of complex, the percentage of the weight loss was in good accordance with the theoretical data 44.65% when the complex lose weight to become $\text{La}_2\text{O}(\text{CO}_3)_2$. The complex began to lose weight between 557.64 °C and 793.78 °C for the third time. The percentage of the lose weight was 2.849%, it was in accordance with the theoretical data 2.995% when the complex lose carbon dioxide. Until 1 000 °C, the complex didn't lose weight, the composition of complex had the formula La_2O_3 .

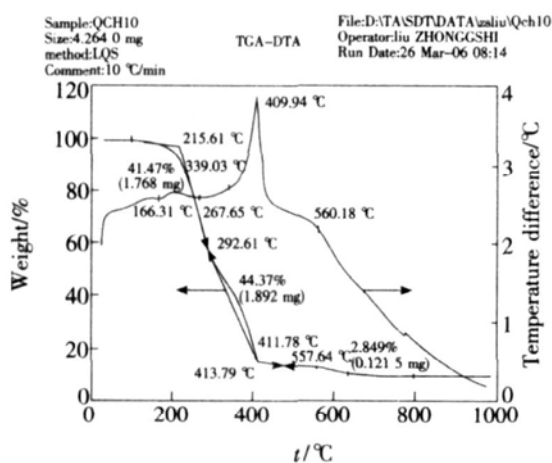


Fig 1 TGA-DTA data of $[\text{LaL}_5\text{L}'(\text{CD}_4)](\text{CD}_4)$.

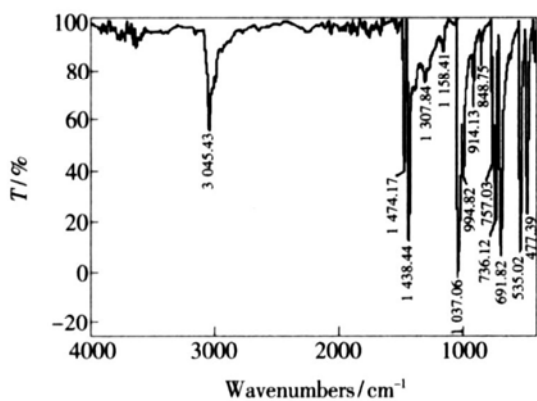
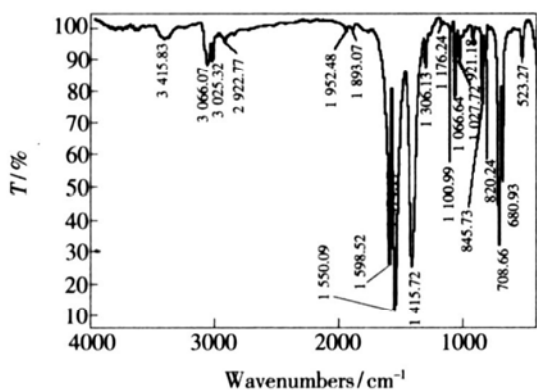
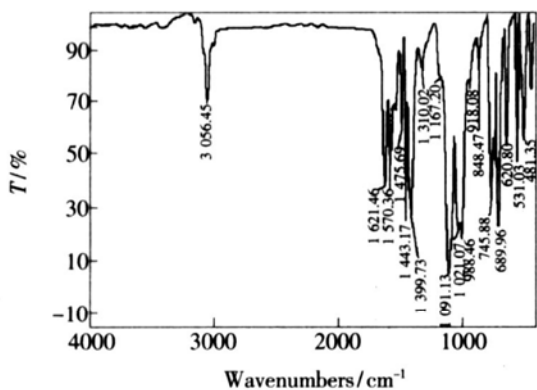
3.3 The Properties of Complexes

The quaternary complexes have the higher solubility. All the complexes can be dissolved in water (5 g/100 mL), ethanol (10 g/100 mL) and acetone (23 g/100 mL). The complexes also have good solubility in chloroform, DMSO and DMF. The decomposition temperature of the complexes is high, so they are thermostable, as shown in Table 1, the de-

composing point of the complexes is very high.

3.4 IR Spectra

The IR spectra of diphenyl sulfoxide, sodium benzoate and quaternary complexes were recorded (shown in Fig 2, Fig 3, Fig 4). The absorption band associated with the $\text{S}=\text{O}$ stretching modes in the diphenyl sulfoxide ligand appears at $1\,037\text{ cm}^{-1}$, while the absorption bands in the complexes appear between 987 cm^{-1} and 989 cm^{-1} . A shift of the $\text{S}=\text{O}$ stretching frequency towards lower wave number by about 50 cm^{-1} suggests that rare earth ions are bonded with an oxygen atom in sulfoxyl group. In the benzoate, the absorption band $\nu_{\text{as}(\text{COO}^-)}$ appears at $1\,550\text{ cm}^{-1}$, and $\nu_{\text{s}(\text{COO}^-)}$ appears at $1\,416\text{ cm}^{-1}$. The value of $\Delta\nu[\nu_{\text{as}(\text{COO}^-)} - \nu_{\text{s}(\text{COO}^-)}]$ is 134 cm^{-1} . The absorption band $\nu_{\text{as}(\text{COO}^-)}$ in the complexes splits into two bands, one appears from $1\,570$ to $1\,575\text{ cm}^{-1}$ and the other appears from $1\,621$ to $1\,623\text{ cm}^{-1}$. The absorption band $\nu_{\text{s}(\text{COO}^-)}$ appears from $1\,398$ to $1\,400\text{ cm}^{-1}$. The value of $\Delta\nu[\nu_{\text{as}(\text{COO}^-)} - \nu_{\text{s}(\text{COO}^-)}]$ is from 170 to 177 cm^{-1} and from 221 to 225 cm^{-1} . A shift of $\nu_{\text{as}(\text{COO}^-)}$ frequency in complexes towards higher wave number, while a shift of $\nu_{\text{s}(\text{COO}^-)}$ frequency in complexes towards lower wave number. What's more, the value of $\Delta\nu[\nu_{\text{as}(\text{COO}^-)} - \nu_{\text{s}(\text{COO}^-)}]$ in complexes is higher than that of $\Delta\nu[\nu_{\text{as}(\text{COO}^-)} - \nu_{\text{s}(\text{COO}^-)}]$ in sodium benzoate. This showed that benzoate (L') bonded with RE^{3+} ions by one oxygen atom in carboxyl group which coordinate as an unidentate group^[9]. In the IR spectra of the complexes, the absorption bands of perchlorate ions appear at $1\,091\sim 1\,092\text{ cm}^{-1}$, $1\,163\sim 1\,170\text{ cm}^{-1}$, $1\,014\text{ cm}^{-1}$ and 621 cm^{-1} . According to the literatures^[10,11], when CD_4^- isn't coordinated, it has T_d symmetry and there are two absorption bands. When CD_4^- is coordinated as an unidentate group, it has C_{3v} symmetry and there are five absorption bands. In the IR spectra of the complexes, four absorption bands can be seen clearly. So CD_4^- isn't all with the T_d symmetry and some of them should have C_{3v} symmetry. In terms with the molar conductivities, it can be induced that one of two perchlorates (CD_4^-) is coordinated with RE^{3+} while another is


 Fig. 2 IR spectrum of $\text{C}_6\text{H}_5\text{SOC}_6\text{H}_5$.

 Fig. 3 IR spectrum of $\text{C}_6\text{H}_5\text{COONa}$.

 Fig. 4 IR spectrum of $[\text{EuL}_5\text{L}'(\text{ClO}_4)](\text{ClO}_4)$.

not Above data showed that the coordination number of quaternary complexes is 7.

3.5 Phosphorescence Spectra

The phosphorescence spectra of diphenyl sulfoxide and benzoic acid were recorded (shown in Fig 5, Fig 6). The energy level range of triplet state of diphenyl sulfoxide and benzoic acid were from $21\,459\text{ cm}^{-1}$ to $16\,863\text{ cm}^{-1}$ ($466\sim 593\text{ nm}$) and from $30\,120\text{ cm}^{-1}$ to $20\,964\text{ cm}^{-1}$ ($332\sim 477\text{ nm}$) respectively. (The energy level range of triplet state was calculated by half-peak width of the relative intensity). The energy level of $^5\text{D}_0$ of Eu is

$17\,360\text{ cm}^{-1}$. The energy levels of triplet state of the two ligands were a little higher than that of the excited state $^5\text{D}_0$, which can emit fluorescence of the rare earths, so the energy can transmit from the triplet state of the two ligands to the $^5\text{D}_0$ excited state. What's more, the lower limit of the triplet state with benzoic acid was overlapped by the upper limit with diphenyl sulfoxide, the energy level range of triplet state was extended (As shown in Fig 7). As a result, matching extent of triplet state of ligands with excited state of the rare earths have been increased, the transmit efficiency also have been increased.

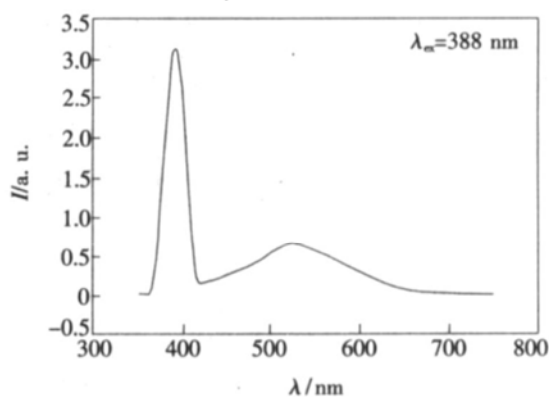
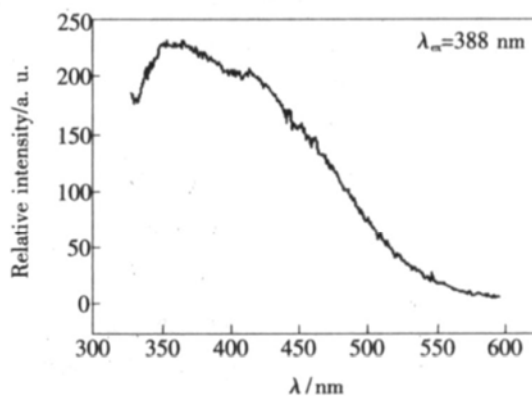
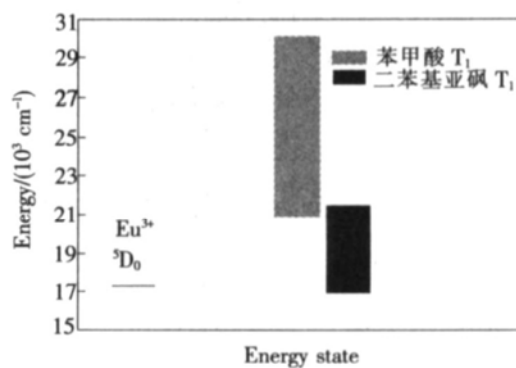

 Fig. 5 Phosphorescence spectrum of $\text{C}_6\text{H}_5\text{SOC}_6\text{H}_5$.

 Fig. 6 Phosphorescence spectrum of $\text{C}_6\text{H}_5\text{COOH}$.


Fig. 7 Energy level scheme of triplet state of ligands and excited state of the rare earths.

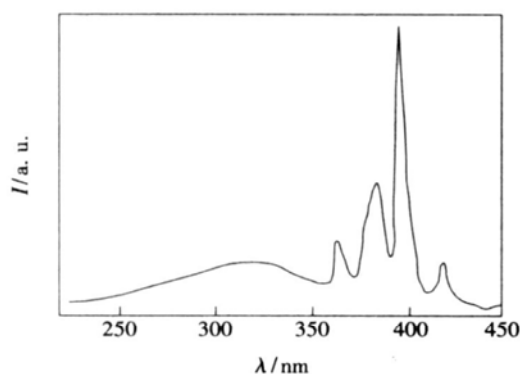


Fig. 8 Fluorescent excitation spectrum of $[EuL_5L'(ClO_4)]-(ClO_4)$.

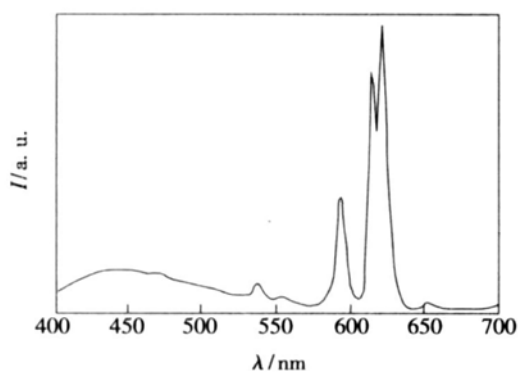


Fig. 9 Fluorescent emission spectrum of $[EuL_5L'(ClO_4)]-(ClO_4)$.

3 6 Fluorescence Spectra

3 6 1 The Fluorescent Excitation and Emission Spectra

The fluorescence excitation and emission spectra of Eu^{3+} complex were shown in Fig 8, Fig 9.

The most suitable excitation wavelength of Eu^{3+} complex is 336 nm. The excitation peak of Eu^{3+} complex is wide band. According to the literature^[12], if we use the light whose wavelength is between 280 nm and 350 nm to excite the rare earth complexes, the excitation have taken place in ligands not rare earth ions, but the character emission of rare earth appeared in the emission spectra of the complexes, this contributed to the energy transfer from ligands to rare earth ions. The excitation spectra of Eu^{3+} quaternary complex in this article belong to this kind.

3 6 2 Symmetry of Complexes

In the emission spectra of Eu^{3+} complex, the emission intensity of ${}^5D_0 \rightarrow {}^7F_2$ is stronger than that of ${}^5D_0 \rightarrow {}^7F_1$. The ratio is 5:2. It can be had seen that the symmetry of the complexes is not good.

There was no symmetry center in the complexes, that is, the ions didn't lie in the symmetry center of crystal lattice.

3 6 3 Comparison of Fluorescence Intensity between Binary Complexes and Quaternary Ones

In order to investigate the effect of benzoic acid as the second ligand to the fluorescence intensity of complexes, in this article, we compared the fluorescent emission spectra data^[13-15] of binary to that of quaternary complexes which were recorded at the same condition (The 3 nm width of the slit, room temperature, particle size and the test conditions of instrumentation). The data were shown in table 3.

After formed quaternary complexes, the location of emission band of rare earth didn't changed. But the fluorescence intensity increased by 469%.

There are two factors affected the fluorescence intensity:

(1) matching extent of triplet state of ligands with excited state of the rare earths.

The energy level of the triplet state of diphenyl sulfoxide was from $21\,459\text{ cm}^{-1}$ to $16\,863\text{ cm}^{-1}$, it was a little higher than that of the excited state of Eu^{3+} which can emit fluorescence, so the energy can transfer from the triplet state to the excited state. The phosphorescence spectra of diphenyl sulfoxide was wide peak, the phosphorescence spectra of benzoic acid was wide too, the energy level is from $30\,120\text{ cm}^{-1}$ to $20\,964\text{ cm}^{-1}$, so the lower limit of the triplet state of benzoic acid was overlapped by the upper limit of the triplet state of diphenyl sulfoxide, the energy level range of triplet state was extended (as shown in Fig 7). This indicated that the matching extent of triplet state of ligands with excited state of the rare earths was increased.

(2) The symmetry of complexes.

When the rare earth ions are not lie in the symmetry center of the crystalline field, the exclusion of f-f transition was released. That is, the lower the symmetry of complexes is, the stronger the fluorescence intensity is. Attributed to the addition of the second ligand, the symmetry^[16] of the complexes was always decreased, as a result, the fluorescence intensity was increased.

Table 3 Comparison of fluorescent emission spectra data of binary and quaternary complexes

Complexes	λ_{ex} (nm)	λ_{em} (nm)	I (a.u)	Transition
EuL ₇ (CD ₄) ₃	395	595.2	36.21	⁵ D ₀ → ⁷ F ₁
		617.4	70.62	⁵ D ₀ → ⁷ F ₂
[EuL ₅ L'(CD ₄)](CD ₄)	395	594.0	133.4	⁵ D ₀ → ⁷ F ₁
		616.2	275.4	⁵ D ₀ → ⁷ F ₂
		623.2	331	⁵ D ₀ → ⁷ F ₂

4 Conclusion

Four solid quaternary complexes of rare earth perchlorate with diphenyl sulfoxide (*L*) and benzoic acid (*L'*) have been synthesized. The composition of the complexes were suggested as [REL₅L'(CD₄)]-

(CD₄) (*RE* = La, Pr, Nd, Eu, *L* = C₆H₅SOC₆H₅, *L'* = C₆H₅COO⁻). Fluorescent spectra of Eu³⁺ complex showed that quaternary complex has the stronger fluorescence than that of binary complex. All the quaternary complexes have higher solubility.

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二苯基亚砷、苯甲酸与轻稀土高氯酸四元配合物的合成表征及光致发光

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摘要: 合成并表征了高氯酸稀土与二苯基亚砷、苯甲酸的四种四元配合物。经元素分析、稀土络合滴定、摩尔电导率及差热-热重分析, 表明四元配合物组成为 $[REL_3L'(CD_4)](CD_4)$ ($RE = La, Pr, Nd, Eu, L = C_6H_5SO_2C_6H_5, L' = C_6H_5COO^-$)。在红外光谱中, 第一配体二苯基亚砷的 ν_{S-O} 的特征吸收峰出现在 1037 cm^{-1} 处, 而各稀土配合物的 ν_{S-O} 向低波数移动到 $984\sim 989\text{ cm}^{-1}$, 红移 50 cm^{-1} 左右, 表明稀土离子与亚砷基团的氧原子之间发生配位作用。第二配体苯甲酸钠的反对称伸缩振动吸收峰 $\nu_{as(COO^-)}$ 出现在 1550 cm^{-1} , 对称伸缩振动吸收峰 $\nu_{s(COO^-)}$ 出现在 1416 cm^{-1} 处, 羧基伸缩振动吸收频率差 $\Delta n[\nu_{as(COO^-)} - \nu_{s(COO^-)}]$ 值为 134 cm^{-1} ; 在所有配合物的红外光谱图中 $\nu_{as(COO^-)}$ 向高波数方向发生了位移, 而 $\nu_{s(COO^-)}$ 向低波数方向发生了位移, 并且 Δn 值均大于钠盐的 Δn 值, 由此可以认为配合物中羧基是通过单齿方式与稀土离子配位。测定了配合物在丙酮溶液中的摩尔电导率, 根据配合物在常见有机溶剂中的摩尔电导率与正负离子的关系结合配合物的红外光谱中高氯酸根离子的四条特征吸收带, 表明配合物为 1:1 型电解质, 两个 CD_4^- 无机抗衡阴离子, 其中一个在外界, 一个进入内界与稀土离子配位。配合物的荧光发射光谱表明, 四元配合物的荧光强度比二苯基亚砷高氯酸稀土二元配合物的荧光强度提高 469%。磷光光谱表明苯甲酸三重态能级的下限和二苯基亚砷三重态能级的上限重叠, 导致三重态能级范围扩大, 由此可见第二配体的加入提高了配体的三重态能级与 Eu^{3+} 离子 5D_0 能级的匹配程度。同时在配合物的荧光发射光谱中还可以看到铈离子的电偶极跃迁强度大于磁偶极跃迁, 表明稀土离子不处于晶体场的对称中心。在四元配合物中, 由于第二配体的加入, 往往会降低配合物的对称性, 从而增强稀土离子的荧光强度。本文合成的稀土配合物具有良好的荧光性能, 而且在室温下稳定, 溶解性好, 分解温度较高。

关键词: 二苯基亚砷; 苯甲酸; 轻稀土四元配合物; 磷光光谱; 发光

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