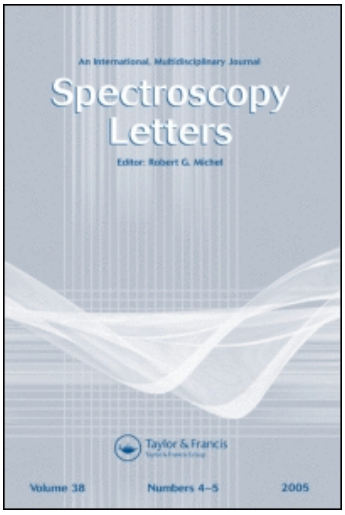

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PHOTOACOUSTIC SPECTROSCOPY STUDY ON EU(III) & TB(III) TERNARY COMPLEXES

Key words: PA spectra,rare earth, ternary complex

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ABSTRACT

The photoacoustic spectra(PAS) of ternary complexes $EuPhen_2Sal_3$ and $TbPhen_2Sal_3$ are reported. Compared with the PA spectra of binary complexes ,the change of PA relative intensities of salicylic acid(Sal) in ternary complexes indicates the different probabilities of nonradiative transitions and different relaxation processes . Combined with emission spectra , the relaxation and energy transfer processes ,especially the interaction between two ligands are discussed.

INTRODUCTION

The luminescence of rare earth complexes has always attracted a great interest since they may be used for laser materials and luminescent probes in

fluoroimmunoassay[1]. According to antenna effect[2], the ligands which have strong and wide absorption band in the UV-visible region may transfer the absorbed energy to central ion(Ln^{3+}) and sensitize the luminescence of Ln^{3+}.Many kinds of binary complexes with organic ligands(such as hydroxyl acids and β-diketones) have been studied[3]. In order to enhance the luminescence efficiency, the study of rare earth ternary complexes is necessary and important.

Photoacoustic spectroscopy (PAS) can be used to study optical absorption property and intermolecular energy transfer of nontransparent or highly scattering solids including naturally occurring biological materials,semi-conductor powders, and metals. Much attention has been paid to the study of the PA spectra of some inorgnic compounds[4,5] and binary organic complexes[6].However, the PA technique has not been used in rare earth ternary complexes. In this paper, the ternary complexes of Eu(III) & Tb(III) with phenanthroline(Phen) and salicylic acid(Sal) were synthesized, the photoacoustic spectra are interpreted and the energy transfer processes in ternary complexes are discussed.

EXPERIMENTAL

(I) Preparation of the Complexes:$TbPhen_2Sal_3$ and $EuPhen_2Sal_3$:

Eu_2O_3(or Tb_4O_7) was converted to the chloride $LnCl_3.6H_2O$(Ln=Eu or Tb) by treatment with concentrated HCl.

3mmol Sal was dissolved in 10ml of ethanol. The pH value of this solution was adjusted to 7 with 20% KOH ethanolic solution.

2mmol of Phen and 1mmol of $EuCl_3.6H_2O$($TbCl_3.6H_2O$) were dissolved into 10ml ethanol respectively and mixed. The solution was heated on a water bath at 70 ℃.The solution of Sal was added in drops under stirring. The mixed solution was cooled down on the water bath and then kept in drier for one week.The white microcrystalline were filtered, washed with ethanol and dried in vacuum drier under 30 ℃.

The elemental analyses were corresponding to their molecular structures.

(II) IR spectra

Infrared spectra were measured as KBr pellets on MAGNA IR-750 spectrometer. The IR spectra of the title complexes are indicative of their structure formulae (Table 1). The IR spectra of $LnPhen_2Sal_3$ show that the carboxyl stretching frequencies are observed at 1580cm^{-1} (ν_{as}^{COO-}) and 1445cm^{-1} (ν_{a}^{COO-}). Compared with free salicylic acid(Sal) , the absorption bands observed at 1685cm^{-1} (ν^{COO-}) and 927cm^{-1} (δ_{OH}) disappear. These facts imply that Ln^{3+} is coordinated with -COO$^-$ and -OH of Sal . The IR spectra also show that the stretching frequencies of phenanthroline(Phen) are observed at 1515cm^{-1} ($\nu_{C=N}$) ,843cm^{-1} (δ_{C-C}) and 727cm^{-1} (δ_{C-H}). Compared with isolated Phen ,these absorptions all have some red shifts. It indicates that Ln^{3+} is coordinated with N atom of Phen .

(III) Spectroscopic Measurements

The PA spectra were measured on a single-beam PA spectrometer constructed in our lab[7]. A 500W Xenon lamp, a CT-30F monochromator and a PA cell with an ERM 10 electret microphone were used.The chopper frequency was 12Hz. After preamplification , output signal was fed into a lock-in-amplifier (LI-574A).The output signal was normalized using a carbon-black reference. The PA spectra of $LnPhen_2Sal_3$(Ln=Eu or Tb) microcrystalline samples were recorded at room temperature in the range of 300-700nm.

The absorption spectra were recorded in ethanolic solution by the Shimadzu UV-240 UV-Vis spectrophotometer.

The fluorescence spectra of $LnPhen_2Sal_3$ microcrystalline samples were taken with the Shimadzu RF-540 spectrofluorophotometer.

RESULTS AND DISCUSSION

(I) Photoacoustic Spectra

The photoacoustic signal is obtained by detecting the heat generated through the nonradiative relaxation released by the sample after absorbing the

TABLE 1

Ligands and chelate stretching frequencies (cm^{-1})

ligand or chelate	ν_{as}^{COO-}	ν_{s}^{COO-}	δ_{OH}	$\nu_{C=N}$	δ_{C-C}	δ_{C-H}
Sal	1685		927			
Phen				1558	852	737
$LnPhen_2Sal_3$	1580	1446		1515	843	727

modulated incident light. It appears in the location of absorption but it does not necessarily coincide with the absorption spectrum. It reveals the absorption and relaxation information of a sample.

The PA spectra of $EuPhen_2Sal_3$ and $EuSal_3.H_2O$ in the range of 300-700nm are shown in Fig.1a. For $EuPhen_2Sal_3$,there exist two moderately strong and broad absorption at 314nm and 343nm respectively. For $EuSal_3.H_2O$,there is only one band at 343nm. It is clear that the 314nm band is due to the π-π^* transition of Phen and the band at 343nm may be assigned as the π-π^* transition of Sal.The PA relative intensities of Sal in $EuPhen_2Sal_3$ is weaker than that in $EuSal_3.H_2O$. The PA spectra of $TbPhen_2Sal_3$ and $TbSal_3.H_2O$ in the range of 300-700nm are shown in Fig.1b. For $TbPhen_2Sal_3$,it displays a very strong absorption peak at 314nm and a weak shoulder peak at 343nm.. However, $TbSal_3.H_2O$ shows one weak band at343nm. The PA absorption of $TbPhen_2Sal_3$ is stronger than $TbSal_3.H_2O$ at 343nm .Compared with ligands, the absorption of Ln^{3+} is too weak to be observed in the range of 300-700nm.

(II) The PAS Study on The Relaxation Process

It is known that after excitation , there are two relaxation processes : radiative and nonraditive. The PA signal(A) is only respond to the nonradiative process and it can be given by[18]:

$$A = k \cdot P_{abs} \cdot \gamma \qquad (1)$$

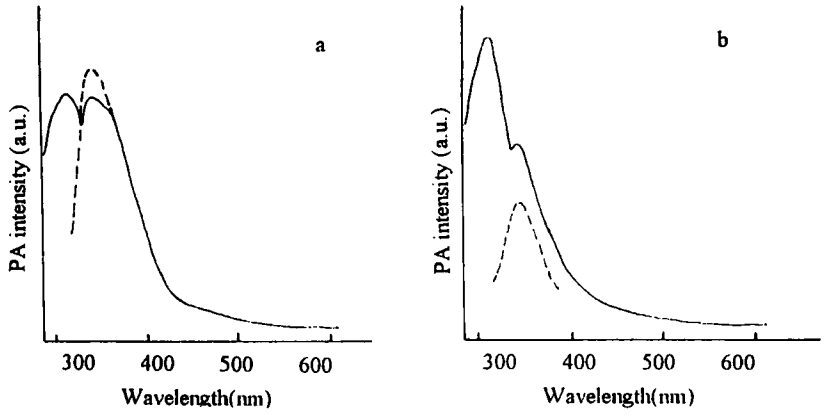

FIG.1 a. PA spectra of $EuPhen_2Sal_3$ (solid line) and $EuSal_3.H_2O$(dashed line)
b. PA spectra of $TbPhen_2Sal_3$ (solid line) and $TbSal_3.H_2O$(dashed line)

here P_{abs} is the absorbency of the sample , γ is the probability for nonradiative transitions after excitation and k is a constant determined by the thermal transfer characteristics of the sample and by the instrumental arrangement employed. Because the PA spectrum only gives response to the nonradiative relaxation process, the PA signal of what relax by radiative process partly will be relatively weak[19].

For $EuPhen_2Sal_3$,the PA relative intensities of Sal decrease when another ligand Phen added. It indicates that Phen reduces the probability for nonradiative transition of Sal in ternary complex . The radiative part of Sal must increase while the nonradiative part decreased . In another word , more energy absorbed by Sal is converted into fluorescence when Phen is added .It shows that Phen is of advantage for Sal sensitizing the fluorescence of Eu^{3+}. As is shown in Fig.1a.

In Fig.1b ,the opposite phenomenon appears. The PA absorption of $TbPhen_2Sal_3$ is stronger than $TbSal_3.H_2O$ in the location of Sal absorption . Phen may increases the probability for nonradiative transition of Sal .With Phen added, the fluorescence of Tb^{3+} sensitized by Sal decreases.

In conclusion, with the second ligand added,the relaxation process of the first ligand will be affected. For different central ions , the inflence may be different.

(III) Fluorescence Property

As is known, lanthanide ions show very small absorption coefficients in the UV-visible region and the fluorescence of Ln^{3+} ions may be weak . This drawback can be overcome by using organic ligand which has strong absorption in the UV-visible region. Ligands can transfer the absorbed energy from triplet state to the excited states of Ln^{3+} to sensitize the luminescence of Ln^{3+} .

Fig.2a,b is the emission spectra of $EuPhen_2Sal_3$ and $EuSal_3.H_2O$(a), $TbPhen_2Sal_3$ and $TbSal_3.H_2O$(b) with the excited wavelength fixed in the region of Sal absorption(λ_{ex}=343nm) . It is clear that the luminescence of Eu^{3+} in $EuPhen_2Sal_3$ is much stronger than in $EuSal_3.H_2O$ while that of Tb^{3+} in $TbPhen_2Sal_3$ much weaker than in $TbSal_3.H_2O$. These facts imply that Phen can increase the sensitized luminescence of Eu^{3+} by Sal but weaken the luminescence of Tb^{3+} .The results of fluorescence spectra coincide with the PA spectra.

(IV) Energy Transfer Processes in Ternary Complexes

In binary complexes , the suitability of the energy gap between the excited triplet energy level of ligands(T*) and the lower energy leved of Ln^{3+}(I*) is a critical factor for sensitized luminescence of the central Ln^{3+} ions[10] . For ternary complexes , another important factor that shoud be considerd is the interaction of the ligands.

The resonance levels of Eu^{3+} and Tb^{3+} ions and the triplet states of Sal and Phen are shown in Fig3. Since the intramolecular energy transfer is of a spin-forbidden type[11] , the energy is transferred by the resonant exchange interaction. According to Dexter's theory[12] , the energy transfer rate constant P_{sa} is given by:

$$P_{sa} = (\frac{2\pi Z^2}{h}) \int F_s(E) \cdot \xi_a(E) \cdot dE \qquad (2)$$

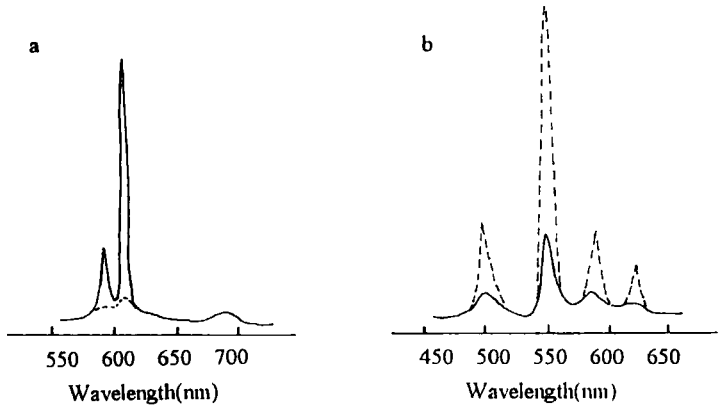

FIG.2 a.Emission spectra of $EuPhen_2Sal_3$ (solid line) and $EuSal_3.H_2O$(dashed line)
b.Emission spectra of $TbPhen_2Sal_3$ (solid line) and $TbSal_3.H_2O$(dashed line)

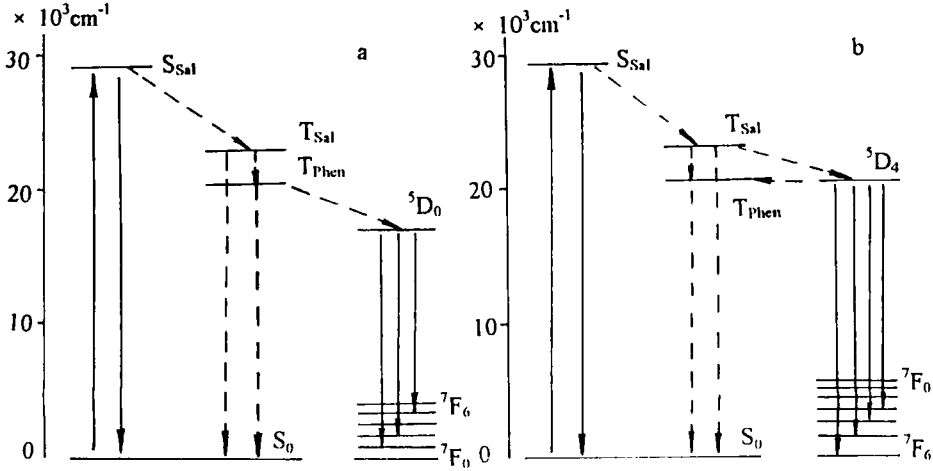

FIG.3 Energy transfer and relaxation processes of $EuPhen_2Sal_3$ (a)
and $TbEuPhen_2Sal_3$ (b)
Radiative(solid line) Nonradiative(dashed line)

TABLE 2

$\Delta E_{T\text{-}Ln(III)}$ between the triplet state of Sal and Phen and the resonant level of the rare earth ion

	Sal	Phen
$\Delta E_{T\text{-}Eu(III)}$ ($^5D_0$)	6300cm^{-1}	3600cm^{-1}
$\Delta E_{T\text{-}Tb(III)}$ ($^5D_4$)	3300cm^{-1}	300cm^{-1}

where $F_s(E)$ represents the observed shape of the emission band of the triplet state of ligand(donor) ; $\xi_a(E)$ is the shape of the absorption band of the excited state of central ion(acceptor). Therefore , P_{sa} is decided by the overlap between the triplet state of ligand and the resonance level of Ln^{3+}.If the energy gap is too large , the energy transfer rate constant will decrease due to the diminution in the overlap between donor and acceptor.

On the other hand, the thermal deexcitation rate constant $R(T)$ is given as follows[13]:

$$R(T) = A \cdot \exp(\frac{-\Delta E_{T-Ln^{3+}}}{RT}) \qquad (3)$$

Where ΔE is the energy gap between the ligand triplet state and the resonance level of rare earth ion . If the energy gap is too small , the efficiency of energy transfer will decrease because of the thermal deexcitivation process. So the suitability of the energy gap between the excited triplet energy level of ligands and the resonance energy level of rare earth ions is critical for efficient energy transfer.

For $EuSal_3.H_2O$, the energy gap between Sal and Eu^{3+} is too large to transfer energy from Sal to Eu^{3+} ion efficientlly. For $EuPhen_2Sal_3$, because the energy gap between Eu^{3+} and Phen is suitabe for energy transfer, some energy absorbed by Sal may be transfered to Phen firstly ,then transfered to Eu^{3+}. So the

luminescence of Eu^{3+} in $EuPhen_2Sal_3$ is stronger than in $EuSal_3.H_2O$ .The very strong luminescence of Tb^{3+} in $TbSal_3.H_2O$ is due to the suitabe energy gap between Tb^{3+} and Sal . But in $TbPhen_2Sal_3$, the energy gap between Tb^{3+} and Phen is so small that the thermally activated Tb-to-ligand(Phen) back-transfer mecanism is taking place . The energy transfered from Sal to Tb^{3+} deexcitated after being transfered to Phen . So the luminescence of Tb^{3+} in $TbPhen_2Sal_3$ is weak. The energy transfer and relaxation processes of $EuPhen_2Sal_3$ and $TbEuPhen_2Sal_3$ are shown in Fig. 3.

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