

# Synthesis, Characterization, and Photophysical Properties of Rare Earth Complexes of N-Phenyl-2-aminobenzoic Acid and 1,10-Phenanthroline

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**Summary.** Some novel binary and ternary complexes of rare earth ions (Gd, Eu, Tb) with N-phenyl-2-aminobenzoic acid and 1,10-phenanthroline were synthesized by homogenous precipitation and characterized by elemental analysis, IR spectra, UV/Vis spectra, and thermal analysis. The phosphorescence spectra and lifetimes of gadolinium complexes were measured, and the triplet state energies of N-phenyl-2-aminobenzoic acid and 1,10-phenanthroline as well as the energy transfer efficiencies between N-phenyl-2-aminobenzoic acid and 1,10-phenanthroline were determined. The photophysical properties such as luminescence and intramolecular energy transfer between the rare earth center ions and the ligands and between ligands are discussed.

**Keywords.** Complexes of Gd<sup>3+</sup>, Eu<sup>3+</sup>, and Tb<sup>3+</sup>; Synthesis; Characterization; Photophysical properties; N-Phenyl-2-aminobenzoic acid; 1,10-Phenanthroline.

## Synthese, Charakterisierung und photophysikalische Eigenschaften von Seltenerdkomplexen der N-Phenylanthranilsäure und des 1,10-Phenanthrolins

**Zusammenfassung.** Einige neue binäre und ternäre Komplexe von Seltenerdionen (Gd, Eu, Tb) mit N-Phenylanthranilsäure und 1,10-Phenanthrolin wurden durch homogene Fällung synthetisiert und durch Elementaranalyse, IR- und UV/Vis-Spektren und thermische Analyse charakterisiert. Die Phosphoreszenzspektren und Lebensdauern der Gadoliniumkomplexe wurden gemessen, und die Triplettenergien der N-Phenylanthranilsäure und des 1,10-Phenanthrolins sowie die Energietransfereffizienz zwischen den beiden wurden abgeleitet. Die photophysikalischen Eigenschaften wie Lumineszenz und intramolekularer Energietransfer zwischen Seltenerdion und Liganden sowie zwischen den Liganden werden diskutiert.

## Introduction

In recent years, there has been a growing interest in the potential application of europium and terbium coordination compounds as luminescent materials and luminescent probes for a variety of chemical and biological studies [1, 2]. Con-

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siderable investigations focused on the luminescence properties, energy match, and energy transfer of rare earth chelates with  $\beta$ -diketones [3–5]. However, little attention has been paid to luminescent rare earth complexes with aromatic carboxylic acids [6]. Compared to the rare earth chelates with  $\beta$ -diketones, complexes with aromatic carboxylic acids offer the advantage of stability of the luminescent properties owing to their infinite chain structure [7, 8]. In this paper, a series of novel binary and ternary complexes of  $Gd^{3+}$ ,  $Eu^{3+}$ , and  $Tb^{3+}$  with N-phenyl-2-aminobenzoic acid and 1,10-phenanthroline were synthesized by homogenous precipitation and characterized by elemental analysis, IR spectra, thermal analysis, and UV/Vis spectra. Gadolinium complexes were used as model complexes, and the triplet state energies of N-phenyl-2-aminobenzoic acid and 1,10-phenanthroline were determined. From the energy match assumption, the luminescence properties of the corresponding complexes of europium and terbium were studied. The intramolecular energy migration processes between the acid and  $Ln^{3+}$  and from N-phenyl-2-aminobenzoic acid to 1,10-phenanthroline are discussed.

## Results and Discussion

The compositions of the complexes were confirmed on the basis of elemental analyses; the corresponding data are summarized in Table 1.

The IR spectra of the binary and ternary complexes differ from those of the free ligands (Table 2). In the rare earth complexes, the following bands present in the spectra of the free ligand are missing:  $\nu(C=O)$  at  $1657\text{ cm}^{-1}$  and  $\nu(OH)$  at  $2863.3$ ,

**Table 1.** Compositions of the complexes (N-HPA: N-phenyl-2-aminobenzoic acid; *phen*: 1,10-phenanthroline; *RE* = rare earth)

	Found (%)				Calculated (%)			
	C	H	N	RE	C	H	N	RE
Gd(N-PA) <sub>3</sub> ·4H <sub>2</sub> O	53.98	4.11	5.08	18.36	54.06	4.39	4.85	18.17
Eu(N-PA) <sub>3</sub> ·4H <sub>2</sub> O	54.07	4.20	5.10	17.93	54.38	4.42	4.88	17.68
Tb(N-PA) <sub>3</sub> ·4H <sub>2</sub> O	53.64	4.09	5.04	18.04	53.95	4.38	4.84	18.32
Gd(N-PA) <sub>3</sub> · <i>phen</i> ·2H <sub>2</sub> O	60.13	3.94	6.68	15.17	60.60	4.16	6.93	15.57
Eu(N-PA) <sub>3</sub> · <i>phen</i> ·2H <sub>2</sub> O	60.41	4.01	6.74	15.00	60.92	4.18	6.98	15.13
Tb(N-PA) <sub>3</sub> · <i>phen</i> ·2H <sub>2</sub> O	60.13	3.99	6.74	15.47	60.50	4.15	6.92	15.71

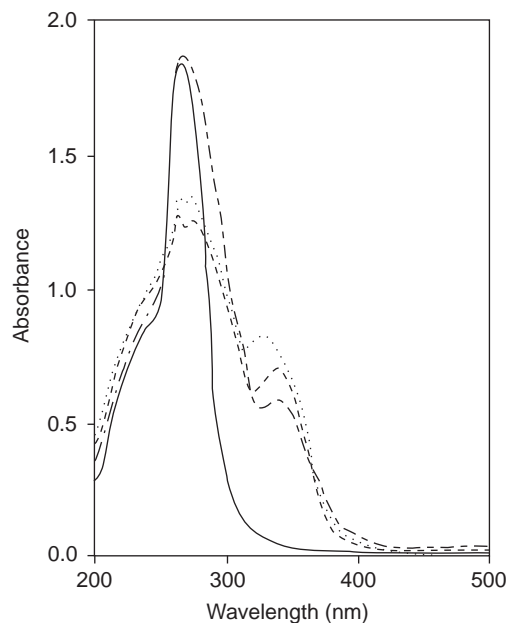
**Table 2.** IR spectroscopic data

	Absorption bands/cm <sup>-1</sup>					
	$\nu_s(NH)$	$\nu_s(C-H)$	$\nu_s(COO^-)$	$\nu_{as}(COO^-)$	$\Delta\nu(COO^-)$	$\nu(C-N-C)$
N-PA	3333.6 m		1657.9 w	1409.7 s		1324.6 w
Na(N-PA)	3322.0 m	3039.7 w	1610.8 w	1386.0 s	224.8	1317.6 w
Eu(N-PA) <sub>3</sub> ·4H <sub>2</sub> O	3308.9 m	3042.1 w	1609.0 w	1398.5 s	211.4	1318.3 w
Eu(N-PA) <sub>3</sub> · <i>phen</i> ·2H <sub>2</sub> O	3309.4 m	3042.4 w	1612.1 w	1396.7 s	215.4	1316.2 w
Tb(N-PA) <sub>3</sub> ·4H <sub>2</sub> O	3318.9 m	3041.9 w	1610.9 w	1397.1 s	213.8	1316.2 w
Tb(N-PA) <sub>3</sub> · <i>phen</i> ·2H <sub>2</sub> O	3305.7 m	3040.5 w	1612.2 w	1398.5 s	213.7	1315.2 w
Band assignment	$\nu_s(NH)$	$\nu_s(C-H)$	$\nu_s(COO^-)$	$\nu_{as}(COO^-)$	$\Delta\nu(COO^-)$	$\nu(C-N-C)$

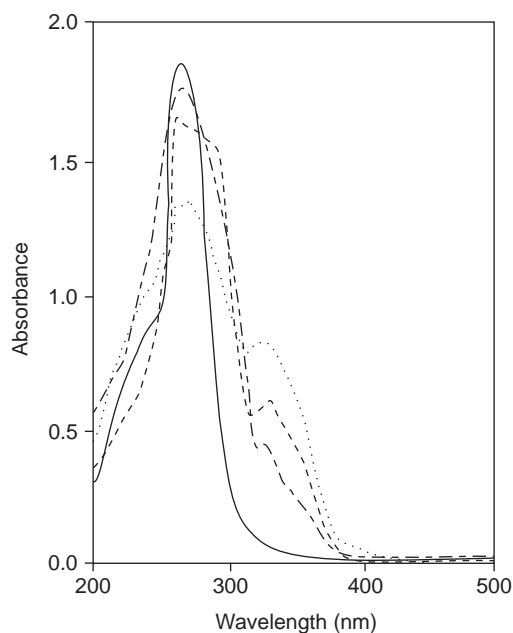
2732.6, 2640.2, and 2567.9  $\text{cm}^{-1}$ . The characteristic absorption band of NH appears both in complexes and ligand, indicating that the coordination of the rare earth ions with N-HPA proceeds *via* the oxygen atom of carboxyl group and not *via* the nitrogen atom of the amino group. Besides, the  $\Delta\nu$  ( $\nu_s - \nu_{as}$ ) value of  $\text{COO}^-$  of rare earth complexes is lower than that of the sodium salt of N-HPA (211.4, 215.4, 213.8, and 213.7  $\text{cm}^{-1}$  vs. 224.8  $\text{cm}^{-1}$ ). This implies that to bidentate coordination takes place [8]. From the IR spectra of the ternary complexes, it can also be seen that the vibration frequency of 1650  $\text{cm}^{-1}$  belonging to the phenyl ring of 1,10-phenanthroline becomes weaker than that of free *phen*. The out-of-plane bending vibrations of the hydrogen atoms on the phenyl ring of *phen* decrease from 855 and 740  $\text{cm}^{-1}$  to 844 and 724  $\text{cm}^{-1}$ , indicating that *phen* participates in the coordination.

When heated in air, the TG-DTA curves of Gd(III), Eu(III), and Tb(III) with N-HPA show two steps: The first one corresponds to the loss of crystal water and yields the anhydrous salts, accompanied by an endothermic effect; the second refers to the decomposition of the anhydrous complexes to the oxides  $\text{Gd}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\text{Tb}_4\text{O}_7$  and is accompanied by a strong exothermic effect. The oxides are stable in the temperature range of 1163–1273 K.

Figures 1 and 2 show the UV/Vis spectra of  $\text{NaN-PA}$ ,  $\text{Eu}(\text{phen})_2 \cdot \text{Cl}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{Eu}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{Eu}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$  and  $\text{NaN-PA}$ ,  $\text{Tb}(\text{phen})_2 \cdot \text{Cl}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{Tb}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{Tb}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$ , respectively. The absorption peaks in the spectra of the complexes show a slight red shift, the shape and intensity of the peaks being basically similar to that for the free ligands. This implies that the absorption depends mainly on the ligand. Besides, in the spectra of  $\text{Eu}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$  and  $\text{Tb}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$  the characteristic absorption of N-PA



**Fig. 1.** UV/Vis spectra of  $\text{NaN-PA}$  ( $\cdots$ ),  $\text{Eu}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$  ( $- -$ ),  $\text{Eu}(\text{phen})_2 \cdot \text{Cl}_3 \cdot 2\text{H}_2\text{O}$  ( $-$ ), and  $\text{Eu}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$  ( $- \cdot -$ )



**Fig. 2.** UV/Vis spectra of NaN-PA ( $\cdots$ ), Tb(N-PA) $_3$ ·4H $_2$ O ( $-\ -$ ), Tb(phen) $_2$ ·Cl $_3$ ·2H $_2$ O ( $—$ ), and Tb(N-PA) $_3$ ·phen·2H $_2$ O ( $- \cdot -$ )

**Table 3.** Low temperature phosphorescence spectra and phosphorescence lifetimes ( $\pm 10\%$ )

	Gd(N-PA) $_3$ ·4H $_2$ O	Gd(N-PA) $_3$ ·phen·2H $_2$ O
Lowest triplet state energies (cm $^{-1}$ )	24330	—
$\Delta E(T-^5D_0)$ (cm $^{-1}$ )	7066	—
$\Delta E(T-^5D_4)$ (cm $^{-1}$ )	3830	—
Phosphorescence lifetimes (s)	3.0	2.1
Energy transfer efficiency (%)	—	30

(337 nm) can only be observed as a small peak overlapping with the spectrum of *phen*. Nevertheless, the characteristic absorption peak of *phen* (265 nm) is present. These phenomena suggest that for the differences in the absorption wavelengths and molecular absorption coefficients the energy transfer process from ligand to rare earth ion has to be accounted. In the binary complexes Eu(N-PA) $_3$ ·4H $_2$ O and Tb(N-PA) $_3$ ·4H $_2$ O, N-PA absorbs energy and transfers it to Eu $^{3+}$  and Tb $^{3+}$ , whereas in the ternary complexes Eu(N-PA) $_3$ ·phen·2H $_2$ O and Tb(N-PA) $_3$ ·phen·2H $_2$ O, *phen* absorbs energy and transfers it to the rare earth ion; the amount of energy absorbed by N-PA is very low in this case.

Gd $^{3+}$  complexes were selected as model complexes for the determination of the triplet state energies of the organic ligands owing to their high phosphorescence-fluorescence ratios compared to those of other Ln $^{3+}$  complexes. The phosphorescence spectra of Gd(N-PA) $_3$ ·4H $_2$ O and Gd(N-PA) $_3$ ·phen·2H $_2$ O were measured at 77 K in ethanol. The lowest triplet state energy was determined assigning the shortest wavelength of the phosphorescence band to the 0–0 transition. The energy differences between the triplet state of the ligands and the resonance energy levels of Eu $^{3+}$  ( $^5D_0$ ) and Tb $^{3+}$  ( $^5D_4$ ) ions were calculated. The results are summarized in

Table 3. From the energy differences ( $\Delta E(\text{Tr}-^5\text{D}_j)$ ,  $j = 0$  or  $4$ ) it can be seen that N-HPA can sensitize europium and terbium ions effectively. The lowest triplet energy position of N-HPA is more suitable for the excited energy level of  $\text{Tb}^{3+}$ ; therefore it can be predicted that the fluorescence intensity of  $\text{Tb}^{3+}$  complexes would be stronger. According to the luminescence principle of rare earth complexes with organic ligands [4], the intramolecular energy transfer efficiency depends chiefly on two energy transfer processes [5]: the first one leads from the lowest triplet level of the ligands to the emissive energy level of the  $\text{Ln}^{3+}$  ion by Dexter's resonant exchange interaction; the second one is just an inverse energy transfer by a thermal deactivation mechanism. Both energy transfer rate constants depend on the energy difference between the lowest triplet level energy of the ligands and the resonant emissive energy of  $\text{Ln}^{3+}$ .

Intramolecular energy transfer in rare earth complexes conforms to Dexter's exchange energy transfer theory [9, 13]:

$$k_{\text{ET}} = (2\pi Z^2/R) \exp(-2r/l) \int F_{\text{d}}(E)F_{\text{a}}(E)dE \quad (1)$$

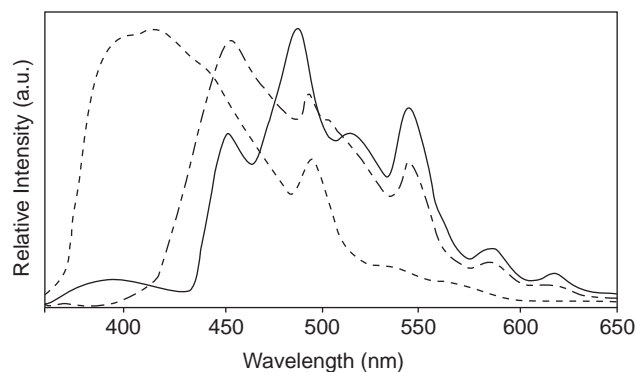
$k_{\text{ET}}$  is the rate constant of energy transfer,  $r$  is the intermolecular distance between the energy donor and acceptor atoms,  $l$  is the *van der Waals* radius, the integral represents the overlap between the luminescence spectrum of the ligands and the absorption spectrum of  $\text{Ln}^{3+}$  ( $F_{\text{d}}(E)$ : the luminescence spectrum of energy donor (ligand),  $F_{\text{a}}(E)$ : absorption spectrum of energy acceptor ( $\text{Ln}^{3+}$ ), and  $2\pi Z^2/R$  is a constant relating to the mutual distance between  $\text{Ln}^{3+}$  and coordinated atom.  $r$  and  $l$  are both considered to be constant for intramolecular energy transfer processes.

From Eq. (1),  $k_{\text{ET}}$  increases with decreasing energy difference  $\Delta E(\text{Tr}-\text{Ln}^{3+})$  between the triplet state energy of ligands and the resonance emission energy of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ . Thus, ligands with a larger energy difference cannot sensitize rare earth ions effectively. On the other hand, there exists an inverse energy transfer process which affects luminescence intensity by temperature [10, 13] ( $k(T)$ : rate constant of inverse energy transfer process (thermal deactivation process),  $A$ : preexponential factor):

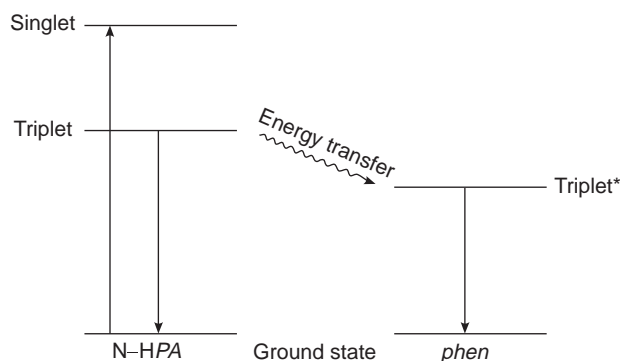
$$k(T) = A \exp(-\Delta E(\text{Tr} - \text{Ln}^{3+})/RT) \quad (2)$$

It can be seen that in the inverse energy transfer process the activation energy is approximately equal to  $\Delta E(\text{Tr}-\text{Ln}^{3+})$ ; therefore, a decreasing energy difference increases  $k(T)$ . Based on this evidence the conclusion can be drawn that  $\Delta E(\text{Tr}-\text{Ln}^{3+})$  is of opposite influence on the two energy transfer processes and an optimal value can be assumed to exist.

Many reports have indicated that the luminescence properties of ternary complexes of rare earth with carboxylic acids and *phen* change dramatically in contrast to those of the binary complexes [11]. Therefore we can guess that in ternary complexes systems *phen* will influence the luminescence intensity considerably. Figure 3 shows the phosphorescence spectra of  $\text{Gd}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{Gd}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$ , and  $\text{Gd}(\text{phen})_2 \cdot \text{Cl}_3 \cdot 2\text{H}_2\text{O}$ , respectively. The phosphorescence spectrum of the ternary complex  $\text{Gd}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$  is similar to that of the binary complex  $\text{Gd}(\text{phen})_2 \cdot \text{Cl}_3 \cdot 2\text{H}_2\text{O}$  but different from that of corresponding binary complex of N-HPA. Obviously, in  $\text{Gd}^{3+}$  ternary complexes *phen* is



**Fig. 3.** Low temperature phosphorescence spectra of  $\text{Gd}(\text{phen})_2 \cdot \text{Cl}_3 \cdot 2\text{H}_2\text{O}$  (—;  $\lambda_{\text{ex}} = 302.0 \text{ nm}$ ),  $\text{Gd}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$  (- -;  $\lambda_{\text{ex}} = 318.7 \text{ nm}$ ), and  $\text{Gd}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$  (- · -;  $\lambda_{\text{ex}} = 307.6 \text{ nm}$ ) in  $5 \cdot 10^{-4} \text{ mol/l}$  ethanol:DMF = 4:1 at 77 K



**Fig. 4.** Intramolecular energy transfer process from N-phenyl-2-aminobenzoic acid to 1,10-phenanthroline

main energy donor and predominantly sensitizes the  $\text{Ln}^{3+}$  ions luminescence. Besides, there exists an intramolecular energy migration from N-HPA to *phen*. In order to verify this assumption, the low temperature phosphorescence lifetimes of the complexes were determined, and the intramolecular energy transfer efficiency between aromatic carboxylic acid and *phen* were calculated (Table 3). The intramolecular energy transfer process can be described as sketched in Fig. 4 [12–14]. The energy transfer rate equation and the energy transfer efficiency equation can be represented as follows:

$$k_{\text{ET}}^* = \tau_0^{-1} - \tau_1^{-1} \quad (3)$$

$$\eta_{\text{ET}} = k_{\text{ET}}^* (k_{\text{ET}}^* + k_1)^{-1} \quad (4)$$

$k_{\text{ET}}^*$  is the rate constant of energy transfer from N-PA to *phen*,  $k_1$  is the rate constant of phosphorescence of the  $\text{Gd}^{3+}$  complex with N-PA,  $\tau_0$  and  $\tau_1$  are the phosphorescence lifetimes of the binary and ternary complex, respectively, and  $\eta_{\text{ET}}$  is the energy transfer efficiency from N-PA to *phen*. From the data it is obvious that the intramolecular energy transfer efficiency from N-PA to *phen* is rather large.

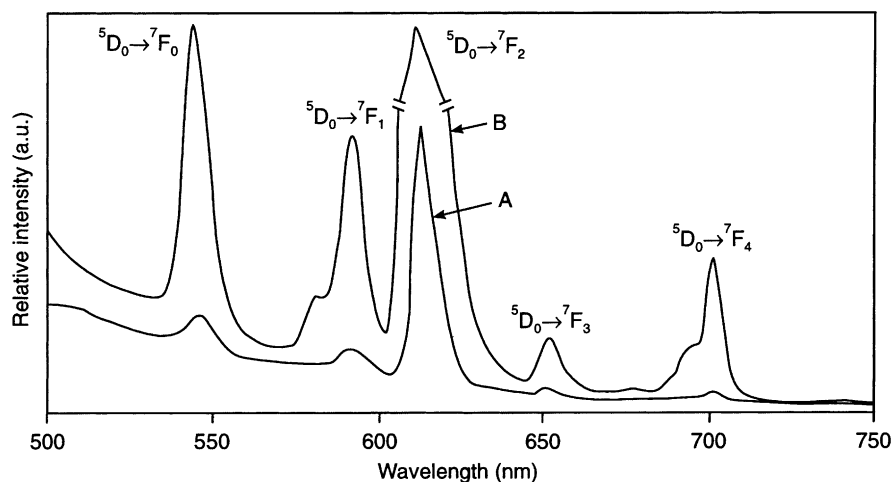


Fig. 5. Luminescence spectra of  $\text{Eu}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$  (A) and  $\text{Eu}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$  (B)

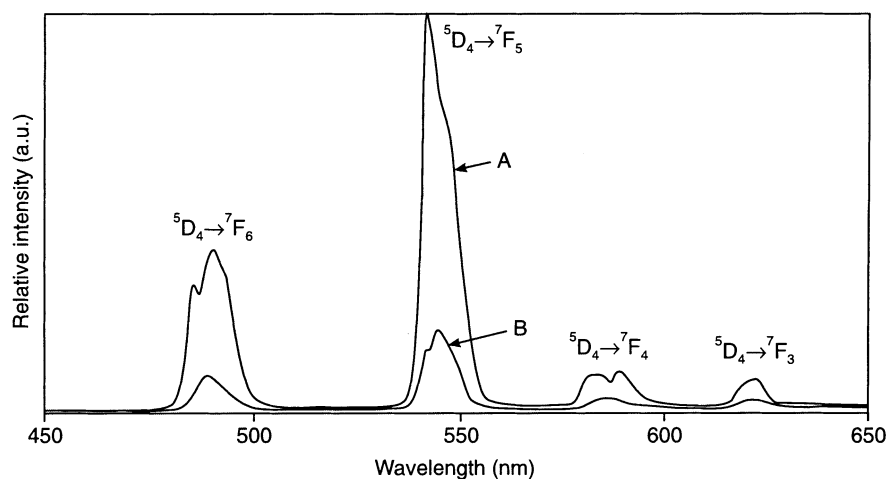


Fig. 6. Luminescence spectra of  $\text{Tb}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$  (A) and  $\text{Tb}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$  (B)

Therefore, in the ternary complexes the energy match between *phen* and  $\text{Ln}^{3+}$  has to be considered as the most important factor determining the luminescence properties of the complexes.

In order to confirm the prediction resulting from the energy difference between the triplet state of the ligands and the excited energy level of the rare earth ions, fluorescence spectra of binary and ternary complexes of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  were measured. The luminescence spectra of all rare earth complexes are similar owing to the characteristic emission of the rare earth center ions. Different organic ligands only change the emission intensity; the emission position hardly varies. Figs. 5 and 6 show the fluorescence spectra of  $\text{Eu}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{Eu}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$ ,  $\text{Tb}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$ , and  $\text{Tb}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$ . In Fig. 5, the emissions of  $\text{Eu}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$  and  $\text{Eu}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$  are similar, but the intensity of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition is higher for the former complex.

**Table 4.** Luminescence properties of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  complexes

	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm)	Luminescence lifetimes ( $\mu\text{s}$ )	Relative intensities (a.u.)
$\text{Eu}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$	322	613	361	0.7 <sup>1</sup>
$\text{Tb}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$	370	543	587	54.6 <sup>1</sup>
$\text{Eu}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$	327	614	404	7.4 <sup>2</sup>
$\text{Tb}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$	397	544	116	11.0 <sup>2</sup>

<sup>1</sup> Excitation and emission slit width: 3 nm; <sup>2</sup> excitation and emission slit width: 0.5 nm

$\text{PA})_3 \cdot 4\text{H}_2\text{O}$  at 545.5, 583 (595), 614, 652, and 702 nm originate from  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ ,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ , and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  transitions; the corresponding values for  $\text{Eu}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$  are 546, 591, 613.5, 684 (655), and 702 nm. Among these transitions,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  is the strongest. In Fig. 6, the analogous situation for the couple  $\text{Tb}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$  (486 (491), 542.6, 583 (589), and 621.3 nm;  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$ ,  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ ,  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$ , and  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_3$ ) and  $\text{Tb}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$  (489, 545.4, 583, and 622 nm) is shown,  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$  transition being the strongest among these transitions. Table 4 gives the relative luminescence intensities of  $\text{Eu}^{3+}$  complexes for  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  and of  $\text{Tb}^{3+}$  complexes for  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ . The data indicate that the emission intensities of  $\text{Tb}^{3+}$  complexes are stronger than those of the  $\text{Eu}^{3+}$  ones. This results from the more convenient energy difference between the triplet state energy of ligands and central ions. The results also show that the luminescence intensities of ternary complexes are higher than those of binary complexes in the case of  $\text{Eu}^{3+}$ , whereas the opposite holds for  $\text{Tb}^{3+}$  complexes. This can be well explained on the basis of relative energies: if intramolecular energy transfer takes place from N-PA to *phen*, the difference in energy leads to a mismatch between the lowest triplet state of *phen* and the first excited state of europium. Table 4 also gives the luminescence lifetimes of the above complexes, and from these data, it can be concluded that the lifetime of  $\text{Eu}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$  is longer than that of  $\text{Eu}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$ , whereas the lifetime of  $\text{Tb}(\text{N-PA})_3 \cdot \text{phen} \cdot 2\text{H}_2\text{O}$  is less than that of  $\text{Tb}(\text{N-PA})_3 \cdot 4\text{H}_2\text{O}$ . This can be interpreted in a way that *phen* is used as an additional ligand to modify the luminescence properties of corresponding complexes. Binary and ternary terbium complexes with N-phenyl-2-aminobenzoic acid and 1,10-phenanthroline have excellent luminescence properties and, their further study could lead to the development of a luminescent material of great potential.

## Experimental

### Preparation of rare earth complexes

The rare earth oxides ( $\text{Gd}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Tb}_4\text{O}_7$ ) (99.99%) were converted to their chlorides by treatment with concentrated hydrochloric acid. The rare earth complexes with N-phenylanthranilic acid were prepared by homogeneous precipitation. An aqueous solution of rare earth chloride was added to an aqueous alcoholic solution of N-phenyl-2-aminobenzoic acid whose *pH* value was adjusted to 6.0–7.0 by addition of aqueous sodium hydrate with stirring (molar ratio of



$LnCl_3 \cdot 6H_2O$ :N-phenyl-2-aminobenzoic acid: 1:3). The precipitate was filtered off, washed with water and ethanol, dried, and stored over silica gel.

The ternary complexes were prepared in the following way: The ethanolic solution of 1,10-phenanthroline was added to the solutions of the binary complexes synthesized as above (molar ratio of binary rare earth complex to 1,10-phenanthroline: 1:1) and refluxed several hours at 343 K in a water bath. The precipitates were filtered off, washed with water and ethanol, dried, and stored over silica gel.

#### *Measurement of the properties of rare earth complexes*

Elemental analyses were carried out with a Carlo-Erba 1106 elemental analyzer. The rare earth ion contents were determined by titration with *EDTA* using xylenol orange as indicator and hexamethylene tetramine as buffer. Infrared spectra in the region of  $4000\text{--}400\text{ cm}^{-1}$  were recorded on a Biorad infrared spectrophotometer (Model FTS-7) employing the KBr pellet technique. The TG and DTA curves were recorded on an Thermoflex DTA derivatograph at a heating rate of  $10\text{ K}\cdot\text{min}^{-1}$  in air (sensitivities: TG: 10 mg, DTA:  $\pm 50\text{ }\mu\text{V}$ ). UV/Vis spectra were measured with a UV-300 spectrophotometer. Phosphorescence spectra and phosphorescence lifetimes of gadolinium complexes were determined with a SPEX 1934D spectrophotometer at liquid nitrogen temperature in a mixed solution ( $5 \cdot 10^{-4}\text{ mol/l}$ ) of absolute ethanol and *DMF* (4:1) using a 450 W pulse xenon lamp as excitation source. Fluorescence lifetimes were obtained with the same spectrophotometer at room temperature. Fluorescence spectra were recorded on a SPEX FL-2T2 spectrofluorometer.

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