

# Ytterbium (III) Luminescence in *m*-Methylbenzoic Acid-Containing Compounds

I. V. Kalinovskaya · A. N. Zadorozhnaya

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**Abstract** Complex compounds of ytterbium(III) with *m*-methylbenzoic acid and nitrogen-containing ligands luminescent in near infrared range have been synthesized. Spectral luminescence characteristics of heteroligand compounds of ytterbium(III) have been investigated. It has been established that ytterbium (III) *m*-methylbenzoate with 1,10-phenanthroline is characterized by the highest luminescence intensity.

**Keywords** Lantanides · Luminescence · Luminescent markers · Immunofluorescent analysis · Heteroligand compounds of ytterbium (III)

## Introduction

For many years methods of immunochemical analysis are among most important methods of biochemical studies. They are often used for diagnosing infectious, tumorous, autoimmune endocrine diseases as well as in drug screening, sanitary-hygienic and ecological monitoring. Among various methods of immunoassay with different detection principles immunofluorescent method has wide range of applications. It has great variety of stable for a long time tracers. Application of fluorescent tracers is not limited only to

immunofluorescence analysis. Many fluorescent dyes are known in literature as molecular probes. The application of fluorescent probes and markers in various fields of research is enormous. The most urgent task is to find modern new high-sensitivity markers, including the lanthanide chelates, and increase the sensitivity of the existing ones.

Recently, complex compounds of ytterbium (III) have been attracted a substantial attention in view of their application as transformers of the ultraviolet radiation into that in the near infrared range, which is rather important in solving some biomedical problems [1]. These transformers are extensively applied as luminescent markers in the immunofluorescent analysis and could find further application to increase the sensitivity of silicon photodetectors in the ultraviolet range (their sensitivity maximum is in the near infrared range). At present, IR luminophors are applied in optoelectronics and laser engineering. Aside from the applications, a substantial interest is concerned with fundamental studies of luminescent characteristics of compounds of ytterbium (III) with carbonic acids. Information on synthesis and physical-chemical properties of ytterbium (III) compounds with carbonic acids is rather limited [2, 3].

The ytterbium (III) ion is characterized by the presence of one excited level  $^2F_{5/2}$ , whose energy is equal to  $\approx 10000\text{ cm}^{-1}$  that is significantly lower than that of triplet levels of the used *m*-methylbenzoic acid and neutral ligands. According to the available data, the ytterbium ion is characterized by high probability of the radiative transition, far higher than that for the europium (III) ion, which has an intensive luminescence in compounds with carbonic acids [2]. Luminescence properties of complex ytterbium (III) compounds with monocarboxylic acids have not yet been a subject of systematic studies.

The objective of the present work was to study spectral-luminescence properties of heteroligand compounds

I. V. Kalinovskaya (✉)  
Russian Academy of Sciences, Institute of Chemistry, Far-Eastern Branch, 159, Prosp. 100-letya Vladivostoka, Vladivostok 690022, Russia  
e-mail: kalinovskaya@ich.dvo.ru

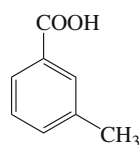
A. N. Zadorozhnaya  
Pacific State University of Medicine, 2a, Prosp. Ostryakova, Vladivostok 690002, Russia

of compositions  $[\text{Yb}(\text{m-MBA})_3 2\text{H}_2\text{O}]_n$ ,  $[\text{Yb}(\text{m-MBA})_3 n\text{D}]_2 \cdot x\text{H}_2\text{O}$ , where m-MBA – the m-methylbenzoic acid ion; D – 1, 10-phenanthroline (phen), 2,2'-dipyridyl (dipy) ( $n=1$ ,  $x=0$ ), dimethylformamide (DMFA) ( $n=1$ ,  $x=2$ ), and  $[\text{Yb}(\text{m-MBA})_3]_2 \cdot 2\text{D}$ , where D – diphenylguanidine (DPHG).

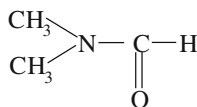
## Experimental

### Materials

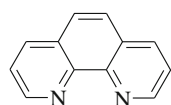
For synthesis of the compounds the following reagents were used:



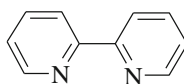
**m-HMBA**  
m-methylbenzoic acid



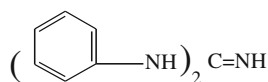
**DMFA**  
dimethylformamide



**phen**  
1,10-phenanthroline



**dipy**  
2,2'-dipyridil



**DPHG**  
diphenylguanidine

### Synthesis

Mixed-ligand compounds with m-methylbenzoic acids were prepared by interaction of a ytterbium salt, sodium salt of the acid, and a neutral ligand (in the molar ratio 1 : 3 : 2). The method was described in detail in [4]. The synthesized compounds were recrystallized from ethanol. The obtained compounds purity was controlled using the chemical element analysis, X-ray diffraction, UV and IR spectroscopy.

### Luminescence Measurements

The luminescence spectra were recorded on a SDL-1 spectrometer with a FEU-62 photomultiplier in the range 900–1100 nm. Luminescence was excited by xenon (DXSh-130)

and mercury (DRSh-250) lamps in a broad spectral range (350–650 nm) filtered by optical filters SZS-23 and SZS-26. The samples were recorded at room temperatures in Pyrex cuvettes.

### UV-Visible Measurements

The absorption spectra were registered on a UV-2550 UV-spectrophotometer Shimadzu in ethanol at concentrations of  $10^{-4}$  mol/L.

### XRD-Visible Measurements

XRD-diffractograms of the compounds were recorded with DRON-2,0 in  $\text{CuK}_\alpha$ .

**Table 1** The composition of rare complexes by elemental analysis

Complex	Found (%)				Calculated (%)			
	C	H	N	RE	C	H	N	RE
$[\text{Yb}(\text{m-MBA})_3 2\text{H}_2\text{O}]_n$	47,45	4,40	–	28,7	46,90	4,10	–	28,2
$[\text{Yb}(\text{m-MBA})_3 \text{phen}]_2$	57,32	4,97	3,83	23,14	56,99	4,88	3,69	22,82
$[\text{Yb}(\text{m-MBA})_3 \text{dipy}]_2$	55,74	4,05	3,97	23,83	55,59	3,95	3,81	23,57
$[\text{Yb}(\text{m-MBA})_3 \text{DMFA}]_2 \cdot 2\text{H}_2\text{O}$	48,83	4,37	2,00	25,46	48,43	4,18	2,09	25,86
$[\text{Yb}(\text{m-MBA})_3]_2 \cdot 2\text{DPHG}$	56,67	4,48	5,02	21,83	56,27	4,06	5,32	21,93

**Table 2** X-ray diffraction data for compounds of ytterbium (III) with m-methylbenzoic acid and neutral ligands

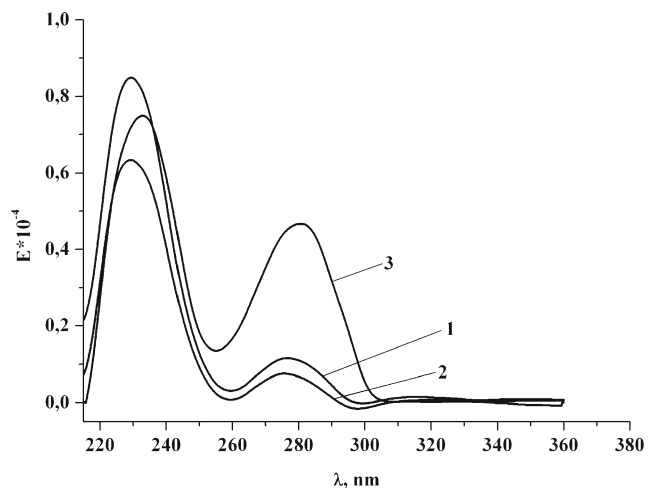
[Eu (m-MBA) <sub>3</sub> phen] <sub>2</sub>		[Yb (m-MBA) <sub>3</sub> phen] <sub>2</sub>		[Yb (m-MBA) <sub>3</sub> dipy] <sub>2</sub>	
d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>	d, Å	I/I <sub>0</sub>
11,78	73,3	11,71	73,0	11,05	100,0
10,65	73,3	10,76	73,1	10,11	37,8
9,93	100,0	9,84	100,0	9,78	43,0
9,27	56,7	9,24	56,4	9,30	31,1
8,81	33,3	8,78	33,5	8,10	72,2
6,92	30,0	6,90	30,4	6,32	17,0
5,69	20,0	5,60	20,1	7,87	74,4
6,19	33,3	6,22	33,5	7,66	15,6
5,75	20,0	5,71	20,5	7,02	10,0
6,19	33,3	6,17	33,4	5,64	43,4
5,29	20,3	5,41	20,5	5,50	52,2
5,53	33,3	5,59	33,7	5,35	8,9
5,29	23,3	5,25	23,0	5,18	32,2
4,69	33,3	4,72	33,6	5,02	10,1
4,55	30,3	4,55	30,6		
4,43	36,7	4,51	36,8		

### Chemical Elemental Analysis

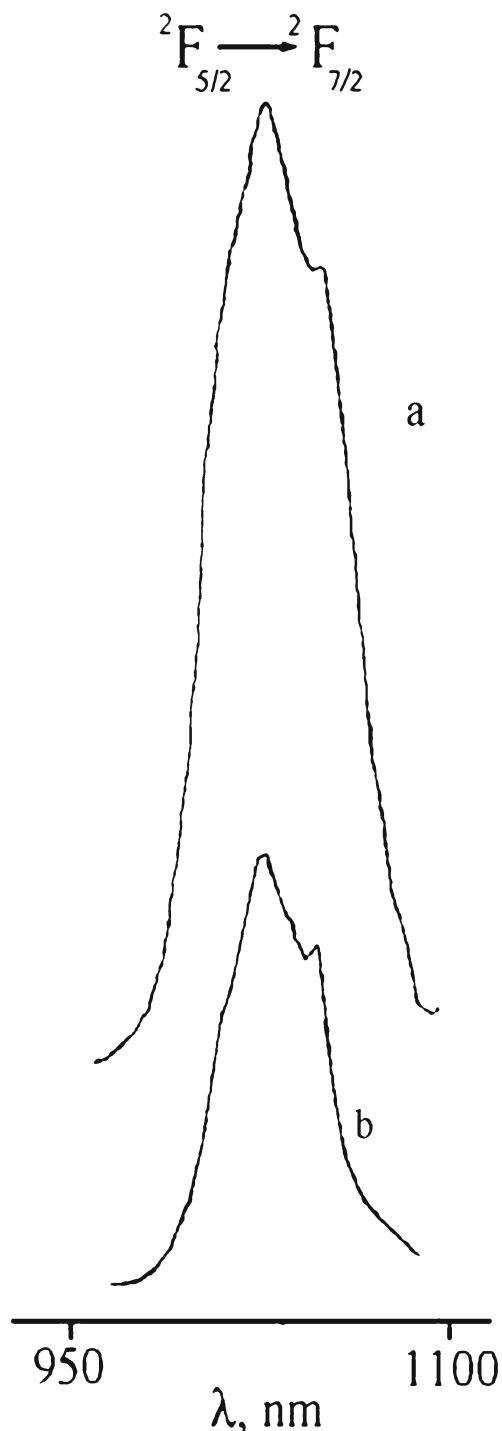
The elemental contents of complexes were measured with EURO EA 3000.

### Results and Discussion

The results of elemental chemical analysis of our compounds are given in Table 1. X-ray diffraction studies of the synthesized heteroligand compounds of ytterbium (III) with nitrogen-



**Fig. 1** Electron absorption spectra in ethanol ( $10^{-4}$  M): 1 – HMBA, 2 – [Yb (m-MBA)<sub>3</sub>·2H<sub>2</sub>O]<sub>n</sub>, 3 – [Yb (m-MBA)<sub>3</sub>·dipy]<sub>2</sub>



**Fig. 2** Luminescence spectra of ytterbium (III) compounds with m-methylbenzoic acid at 293 K: 1 – [Yb (m-MBA)<sub>3</sub>·dipy]<sub>2</sub>, 2 – [Yb (m-MBA)<sub>3</sub>·phen]<sub>2</sub>

containing neutral ligands performed using the powder technique corroborated their individuality (Table 2).

The phase analysis indicates to the absence of lines of initial substances and possible impurities. The obtained complex compounds are stable in air. XRD studies of complex compounds indicates to the isostructural character of ytterbium

(III) and europium (III) compounds. According to the literature data and XRD results, complex compounds of lanthanides (III) with neutral ligands have a dimer structure [5, 6].

The absorption compounds of ytterbium (III) compounds with *m*-methylbenzoic acid in ethanol are shown in Fig. 1. Juxtaposition of the obtained absorption spectra of ytterbium (III) compounds with that of *m*-methylbenzoic acid demonstrates that they absorb in the wavelength range 210–310 nm. In the absorption spectra of complexes [Yb (*m*-MBA)<sub>3</sub>:nD]<sub>2</sub> one observes additional bands corresponding to  $\pi$ - $\pi^*$  transitions of adduct-forming nitrogen-containing molecules: 1, 10-phenanthroline, 2,2'-dipyridyl, diphenylguanidine (Fig. 1). For example, in the absorption spectrum of [Eu (*m*-MBA)<sub>3</sub>:dipy]<sub>2</sub> the maximum of a broad band with  $\lambda_{\text{max}}=260$ –300 nm is somewhat shifted to longer wavelength range relatively to this band maximum for the pure *m*-methylbenzoic acid spectrum. The broad band shape differs from that of the band observed in the absorption spectrum of the polymer [Yb (*m*-MBA)<sub>3</sub> 2H<sub>2</sub>O]<sub>n</sub>. Thus, overlapping of neutral ligand and *m*-methylbenzoic acid ( $\lambda=280$  nm) bands must be observed. Along with increase of the complex compounds solutions concentrations, in the absorption spectra one observes narrow bands characteristics for the ytterbium (III) ion around 900 nm.

Different positions of resonance levels of europium (III), neodymium (III), and ytterbium (III) ions could cause some specific differences in optical characteristics of their complex compounds. We have established that the synthesized ytterbium (III)  $\beta$ -diketonates have more intensive luminescence in near IR range than similar neodymium (III) diketonates [7].

The luminescence spectra of the synthesized complex compounds of ytterbium (III) in the crystalline state were recorded at room temperature. 4f-luminescence of ytterbium (III) ions in the synthesized compounds was observed in the range 920–1120 nm (near IR range) with a maximum at 980 nm (excitation in the range 500–600 nm). Figure 2 shows the luminescence spectra of the synthesized heteroligand compounds of ytterbium (III) with *m*-methylbenzoic acid, nitrogen-containing neutral ligands. The fluorescence spectra of ytterbium (III) compounds with *m*-methylbenzoic acid comprise intensive

bands of the  $^2F_{5/2}$ - $^2F_{7/2}$  transition with the centroid around 1000 nm. We juxtaposed the intensities of the  $^2F_{5/2}$ - $^2F_{7/2}$  transition bands for the synthesized ytterbium (III) complex compounds (Table 3).

The synthesized heteroligand compounds of ytterbium (III) with *m*-methylbenzoic acid have more intensive luminescence than similar complex compounds of neodymium (III) (2–3-fold) and exceed by about an order of magnitude the intensity of the initial ytterbium (III) nitrate [8]. Substitution of neutral molecules in the obtained ytterbium (III) carboxylates (1,10-phenanthroline, 2,2'-dipyridyl, diphenylguanidine) results in changes of the luminescence intensity. Among the ytterbium (III) complex compounds with *m*-methylbenzoic acid, the ytterbium (III) compound with 1,10-phenanthroline has the most intensive luminescence.

The luminescence intensity for the latter compound is 1.5-fold higher than that of heteroligand ytterbium (III) compounds with other neutral ligands (Fig. 2) and is comparable to the intensity of highly luminescent  $\beta$ -diketonates – ytterbium hexafluoroacetylacetonatoeuropiates and dibenzoylmethanates with phosphorus-containing neutral ligands [7]. We have revealed that the relative intensity of fluorescence of ytterbium (III) *m*-methylbenzoate with 1, 10-phenanthroline is 2 times higher than that of earlier described ytterbium (III) thenoyltrifluoroacetate with 1, 10-phenanthroline (for the crystalline state) [8]. For *m*-methylbenzoate having the dimer structure, the maximum luminescence value is characteristic for europium complexes with 1,10-phenanthroline and 2,2'-dipyridyl, which is caused by the presence of more developed  $\pi$ -conjugated system of neutral molecules and the absence of water molecules in the complex coordination sphere. According to the XRD data, in europium *m*-methylbenzoate with 1,10-phenanthroline (isostructural to ytterbium (III) *m*-methylbenzoate with 1,10-phenanthroline) the europium atom coordinates two nitrogen atoms of the 1,10-phenanthroline molecule [6]. In [Eu (*m*-MBA)<sub>3</sub>]<sub>2</sub>2DPHG the diphenylguanidine molecule is not directly coordinated by the central europium (III) ion [5]. The presence of the diphenylguanidine molecule, which is not included into the lanthanide ion coordination, in the complex compound structure deteriorates the efficiency of the energy transfer

**Table 3** Relative integral luminescence of the bands of  $^2F_{5/2}$ - $^2F_{7/2}$  transition of ytterbium (III) compounds with *m*-methylbenzoic acid, nitrogen-containing neutral ligands

Compound	$I_{\text{rel}}(^2F_{5/2}-^2F_{7/2})$ %	Compound	$I_{\text{rel}}(^2F_{5/2}-^2F_{7/2})$ %
[Yb ( <i>m</i> -MBA) <sub>3</sub> 2H <sub>2</sub> O] <sub>n</sub>	50,0	[Yb ( <i>m</i> -MBA) <sub>3</sub> ] <sub>2</sub> 2DHPG	20,0
[Yb ( <i>m</i> -MBA) <sub>3</sub> dipy] <sub>2</sub>	78,0	[Yb ( <i>m</i> -MBA) <sub>3</sub> DMFA] <sub>2</sub> 2H <sub>2</sub> O	32,0
[Yb ( <i>m</i> -MBA) <sub>3</sub> phen] <sub>2</sub>	100,0	Yb (NO <sub>3</sub> ) <sub>3</sub> 2phen	8,0
Yb (TTA) <sub>3</sub> 2phen	65,0		

to the luminescence center and yields the luminescence quenching.

## Conclusion

A series complex compounds of ytterbium (III) with *m*-methylbenzoic acid and nitrogen-containing ligands luminescent in near infrared range have been synthesized. The performed studies of luminescence properties of ytterbium (III) heteroligand complex compounds with *m*-methylbenzoic acid demonstrated that among the synthesized compounds the ytterbium (III) complex compounds with 1,10-phenanthroline and 2,2'-dipyridyl of a dimer structure had the most intensive luminescence in the IR range. Near-infrared – emissive heteroligand complexes have several advantages over common luminescent probes; therefore, the proposed lanthanide heteroligand complexes have potential analytical applications in proteomics, metabolics, food science, astrobiology, medicine, and related technologies.

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**Conflict of Interest** The authors declare that they have no conflict of interest.

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