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Luminescence of Ytterbium(III) Cinnamate Compounds

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Abstract—The spectral luminescent characteristics of mixed-ligand compounds of ytterbium (III) with cinnamic acid, nitrogen- and phosphorus-containing neutral ligands were studied by the methods of fluorescent spectroscopy. The luminescence intensity of the obtained compounds was measured and it was found that the highest intensity of luminescence has the polymeric ytterbium(III) cinnamate.

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The ytterbium(III) complex compounds attract now considerable attention due to their use as converters of radiation from the ultraviolet into the near-infrared region, which is important in solving biomedical problems [1]. Such converters are widely used as fluorescent labels in immunofluorescence analysis, and can also be used to increase the sensitivity in the UV region of the silicon detectors, which have a maximum spectral sensitivity in the near infrared region. The IR luminophores are used in optoelectronics and laser technology. Besides the practical importance, of considerable interest is to study the fundamental characteristics of the ytterbium(III) fluorescent compounds with carboxylic acids. The data on the synthesis and physicochemical properties of compounds with REE phenylcarboxylic acids are limited [2, 3].

The ytterbium(III) ion is characterized by the presence of one excited $^2F_{5/2}$ level with the energy ~10000 cm^{-1}, which is much less than the energy of the lower triplet levels of the used cinnamic acid and neutral ligands. There is evidence that the ytterbium(III) ion is characterized by a high probability of radiative transition, which is much greater than that of europium(III) ion; the latter fluoresces intensely in compounds with carboxylic acids [2]. Luminescent properties of the ytterbium(III) complexes in the compounds with carboxylic acids have not been studied systematically.

The aim of this work was to study the spectral-luminescent properties of the mixed-ligand compounds of composition $[Yb(C_9N_7O_2)_3]n$ and $Yb(C_9N_7O_2)_3 \cdot 2D \cdot nH_2O$, where $C_9N_7O_2$ is the cinnamate anion and D denotes a ligand of the series 1,10-phenanthroline ($C_{12}H_8N_2$), triphenylphosphine oxide ($C_{18}N_{15}P$), 2,2'-dipyridyl ($C_{10}H_8N_2$), and diphenylguanidine $[(C_6H_5NH)_2C{=}NH]$.

The XRD investigation of powders of the synthesized mixed-ligand ytterbium(III) compounds with nitrogen- and phosphorus-containing neutral ligands confirmed that they are individual compounds (see the table). Phase analysis indicated the absence of lines of source materials and possible impurities. The resulting complexes are stable in air.

The X-ray study indicated that the ytterbium(III) complex compounds are isostructural with those of europium(III). According to the XRD analysis, anhydrous europium cinnamate has a polymeric structure [4, 5].

The absorption spectra of compounds of ytterbium(III) with cinnamic acid in ethanol are shown in Fig. 1. The comparison of the absorption spectra of the studied ytterbium(III) cinnamates shows that the ytterbium(III) complex compounds absorb in the wavelength range 190-310 nm. The absorption spectra of complexes of $Yb(C_9N_7O_2)_3 \cdot nD \cdot xH_2O$ contain additional bands corresponding to the π– π* transitions of the adduct-forming neutral molecules of 1,10-phenanthroline and 2,2'-dipyridyl. Thus, in the absorption spectrum of $Eu(C_9N_7O_2)_3 \cdot 2C_{12}H_8N_2 \cdot H_2O$ the maximum of the broad band λ = 264 nm is shifted somewhat to the shorter wavelengths relative the maximum of the same band in the spectrum of free cinnamic acid. The broad band differs in the shape from the band observed in the absorption spectrum of $[Yb(C_9N_7O_2)_3]_n$. Apparently, there is overlapping of the bands of phenanthroline and cinnamic acid (λ = 264 nm). Also a redistribution of the intensity of the absorption bands of cinnamic acid is observed: The band at λ = 202 nm decreases in intensity while the band at λ = 223 nm increases.

The luminescence spectra of the synthesized ytterbium(III) complexes in the crystalline state were registered at room temperature. The 4*f* luminescence of ytterbium(III) in the synthesized compounds is observed in the region 920–1120 nm. Figure 2 shows the luminescence spectra of the mixed-ligand compounds of ytterbium(III) with cinnamic acid, nitrogen- and phosphorus-containing neutral ligands. The spectra contain a diffuse band consisting of two to three components with the center of gravity at about 1000 nm.

The synthesized mixed-ligand compounds of ytterbium(III) with cinnamic acid have a stronger luminescence than similar complexes of neodymium(III) (two to three times) and almost an order of magnitude more intense than that of the initial Yb(III) nitrate [6]. Among the compounds with cinnamic acid the most intense luminescence shows the anhydrous polymeric ytterbium(III) cinnamate. The luminescence intensity of this complex compound is twice higher than that of the mixed-ligand compounds of ytterbium(III) with cinnamic acid and neutral ligands (Fig. 2) and is comparable with the luminescence intensity of the luminescent β-diketonates, the europium hexafluoroacetylacetonate and ytterbium(III) dibenzoylmethanate with phosphorus-containing neutral ligands [7]. We found that the relative fluorescence intensity of polymeric ytterbium(III) cinnamate is twice higher than that of the earlier described ytterbium(III) thenoyltrifluoroacetonate with 1,10-phenanthroline (in the crystalline state) [8]. The observed high intensity of the ytterbium(III) luminescence in the obtained compounds can be apparently explained by the presence of polymer structure and the effect of the π-stacking between the cinnamic acid anions [4, 5]. Overlapping of the bands of cinnamic acid and neutral ligands in the absorption spectra, as well as the superposition of a number of bands of the *n*–π* transition of cinnamic acid with the bands of *n*–π* transitions of the neutral ligands in the luminescence excitation spectra of mixed-ligand europium(III) cinnamates with nitrogen- and phosphorus-containing neutral ligands isostructural with the ytterbium compounds seems to indicate that the bulk of the energy absorbed by the cinnamic acid is lost nonradiatively. The observed effect is also due to both structural features of the cinnamic acid structure and the location of its energy levels: the *trans*-cinnamic acid is known to be a complex system consisting of an electron-donor styrene group and electron-acceptor carboxy group [9].

X-ray analysis data of ytterbium(III) with cinnamic acid and neutral ligands

$[Eu(C_9H_7O_2)_3]_n$		$[Yb(C_9H_7O_2)_3]_n$		$Yb(C_9H_7O_2)_3{\cdot}2C_{12}H_8N_2$	
d, Å	*I*/*I*$_0$	*d*, Å	*I*/*I*$_0$	*d*, Å	*I*/*I*$_0$
11.05	100.0	11.00	100.0	9.00	100.0
6.39	24.8	6.76	25.0	5.86	19.2
5.54	54.0	5.54	53.0	4.82	20.0
4.37	4.8	4.49	4.4	4.74	22.0
4.10	29.2	4.10	29.5	4.50	12.1
3.83	3.8	3.90	3.4	4.12	11.0
3.72	12.0	3.50	12.1	3.97	9.5
3.55	2.0	3.27	2.5	3.82	9.2
3.49	2.8	3.07	3.0	3.56	9.0
3.23	5.2	2.97	5.4	3.27	10.3
3.11	11.6	2.81	11.2	3.05	20.9
2.94	3.6	2.79	4.0	2.93	26.1
2.90	2.8	2.65	3.0	2.80	25.1
2.81	4.4	2.75	4.0	2.64	7.1
2.65	1.6	2.55	1.6		
2.57	8.4	2.51	8.0		

According to published data [10], the triplet level of cinnamic acid (20100 cm^{-1}) is located below the triplet levels of 1,10-phenanthroline (22075 cm^{-1}) and 2,2'-dipyridyl (22900 cm^{-1}). It is known [11, 12] that the luminescence of the mixed-ligand rare-earth carboxylates is defined by the position of the triplet levels of the acid and the neutral ligands. The process of energy transfer between the ligands (carboxylic acid and a neutral ligand) is commonly possible when the position of the triplet level of the acid is located above the triplet level of the neutral ligand [13]. The energy transfer on the levels of the lanthanide ions in the

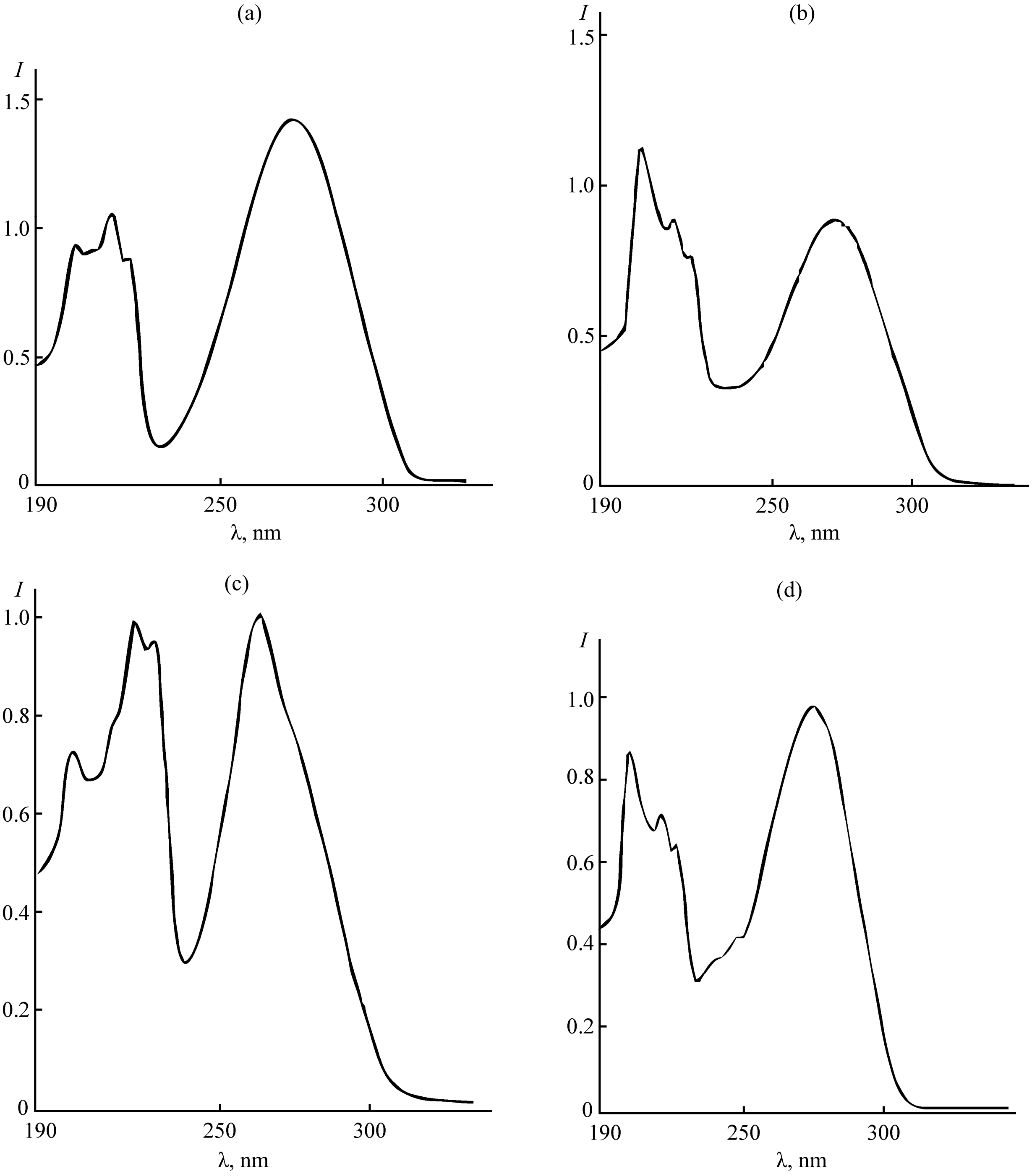

Fig. 1. Electron absorption spectra of solutions in ethanol (10^{-4} M): (a) cinnamic acid, (b) $[Yb(C_9H_7O_2)_3]_n$, (c) $Yb(C_9H_7O_2)_3\cdot 2C_{12}H_8N_2H_2O$, and (d) $Yb(C_9H_7O_2)_3\cdot 2C_{10}H_8N_2H_2O$.

mixed-ligand cinnamates occurs to a greater extent from the triplet levels of the neutral ligand than from the levels of cinnamic acid. This, apparently, explains the weak luminescence of the investigated mixed-ligand ytterbium(III) compounds with cinnamic acid.

Thus, our study of luminescent properties of the mixed-ligand ytterbium(III) compounds with cinnamic acid showed that among the synthesized ytterbium(III) compounds the strongest luminescence in the IR region shows polymeric ytterbium(III) cinnamate.

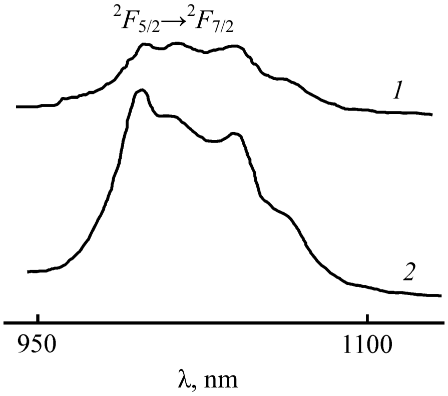

Fig. 2. The luminescence spectra of ytterbium cinnamates at 293 K.

EXPERIMENTAL

Synthesis of mixed-ligand ytterbium(III) complexes with cinnamic acid was carried out according to the described procedures [6]. The synthesized compounds were recrystallized from ethanol. The purity of the compounds was monitored by chemical elemental analysis, X-ray diffraction analysis, UV and IR spectroscopy. The luminescence spectra were recorded on a SDL-1 spectrometer with a photomultiplier FEU-62 in the range 900-1100 nm. The luminescence was excited by xenon (DKsSh-130) and mercury (DRSh-250) lamps with a broad band in the spectral range 350–650 nm separated by optical filters SZS-23 and SZS-26. The samples were taken at room temperature in Pyrex cells. The absorption spectra of the compounds were recorded on an SF-256 UV-Vis spectrophotometer in ethanol at concentrations of 10^{-5} M.

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