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LETTERS
TO THE EDITOR

Synthesis and Luminescence of Complexes of Europium(III) and Terbium(III) with Pyridinedicarboxylic Acids

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Complex compounds of lanthanides with carboxyl-containing ligands are among the most promising classes of materials for the creation of electroluminescent devices [1–3]. The luminescence intensity of lanthanide coordination compounds depends on the degree of absorption of electrical or electromagnetic energy by the organic ligand and its transmission to the lanthanide ion. Thus, the molecular design of promising luminescent lanthanide compounds is reduced to the selection of ligands that can effectively absorb and transfer the energy to the lanthanide ion. We have previously produced the efficiently luminescent compounds of Tb^{3+} and Eu^{3+} with aminocarbonylphenoxyacetic [4, 5], dimethoxybenzoic [6, 7], and 1,10-phenanthroline-2,9-dicarboxylic acids [8]. It was interesting to synthesize and study the fluorescent properties of complexes of terbium(III) and europium(III) with pyridinedicarboxylic acids. As is known [9], coordination compounds of europium(III) and terbium(III) with pyridine-2,6-dicarboxylic (dipicolinic acid) have a high efficiency of luminescence in the visible region. However, there are no data on the luminescent properties of Eu^{3+} and Tb^{3+} complexes with the other pyridinedicarboxylic acid. Therefore, the aim of this work was synthesis and study of the luminescence of coordination compounds of europium(III) and terbium(III) with 2,4-pyridinedicarboxylic (lutidinic, Hlutid), 3,4-dicarboxylic (cinchomeronic, Hcinch), and pyridine-3,5-dicarboxylic (dinicotinic, Hdinic) acids.

According to the elemental and thermogravimetric analyzes, the resulting compounds have the following composition: $Tb_2lutid_3 \cdot 9H_2O$, $Eu_2lutid_3 \cdot 12H_2O$, $K_3Tbcinch_3 \cdot 5H_2O$, $K_3Eucinch \cdot 6H_2O$, $Tb_2dinic_3 \cdot 9H_2O$, $Eu_2dinic_3 \cdot 12H_2O$. According to thermogravimetric analysis, in the temperature range 80–185°C the complexes with lutidinic and dinicotinic acids lose the mass due to dehydration; in the range of 185–290°C there is a thermostability region; at the temperatures above 290°C the thermal decomposition of the complexes was observed. For complexes with cinchomeronic acid the dehydration takes place in the range of 110–170°C; in the range of 170–300°C there is the thermostability region; the heating above 300°C causes the thermal decomposition of the complexes.

The IR spectra of the complexes contain the absorption bands of the symmetric and asymmetric vibrations of the ionized carboxy groups COO^- at 1390–1420 and 1570–1610 cm^{-1}, respectively, and no absorption bands of the stretching vibrations of the C=O bonds of non-ionized carboxy groups in the range of 1700–1720 cm^{-1}.

The difference between the frequencies of the asymmetric and symmetric stretching vibrations of the ionized carboxy group of the synthesized compounds with lutidinic, dinicotinic and cinchomeronic acids is 204, 187, and 182 cm^{-1}, respectively. It allows a conclusion on the bidentate coordination of the carboxy groups with the lanthanides ions [10, 11].

According to the excitation spectra [λ 546 nm for europium(III) compounds, λ 616 nm for terbium(III) compounds], coordination compounds of lanthanides have the most intensive luminescence when excited by the radiation of a wavelength of 290 nm.

According to the luminescence spectra (λ 290 nm), the integral luminescence intensity of complexes of europium(III) and terbium(III) with cinchomeronic and

lutidinic acids is 1.4 and 1.9 times higher, respectively, compared with trisbenzoates of the corresponding lanthanides. The integral intensity of the luminescence of lanthanide complexes with dinicotinic acid does not significantly differ from the corresponding lanthanides trisbenzoates. The highest intensity of the luminescence is observed for $K_3Eu(cinch)_3 \cdot 6H_2O$ and $K_3Tb(cinch)_3 \cdot 5H_2O$, which allows us to recommend them as promising luminescent materials.

In this work the following reagents were used: pyridine-2,4-dicarboxylic, pyridine-3,4-dicarboxylic, pyridine-3,5-dicarboxylic acids (Merck, ≥ 97%) recrystallized from bidistilled water, $TbCl_3 \cdot 6H_2O$ (chemically pure), $EuCl_3 \cdot 6H_2O$ (chemically pure), KOH (chemically pure).

Tris(pyridine-2,4-dicarboxylato) diterbium(III) nonahydrate. To a solution of 0.5 g (0.606 mmol) of 2,4-pyridinedicarboxylic acid in 5 ml of water was added 1 N aqueous potassium hydroxide solution to pH 5.5. To the resulting mixture was added a solution of lanthanide chloride (0.202 mmol). The resulting clear reaction mixture was evaporated at 70°C until precipitate formation. The latter was filtered off and dried in a desiccator until the constant weight. Yield 85%. Found, %: C 25.94; H 2.87; N 4.49; Tb 31.56. $C_7H_{21}NO_{13}Tb_2$. Calculated, %: C 25.86; H 2.79; N 4.31; Tb 32.59.

Other complex compounds were synthesized similarly.

The IR spectra were recorded on a Infralum FT-02 instrument with a resolution of 2 cm^{-1} from KBr discs. Thermogravimetric analysis was performed on a Netzch STA instrument in the range of 30–1000°C in air atmosphere, heating rate 10°C min^{-1}. The luminescence spectra and luminescence excitation spectra were recorded on a Fluorat-02-Panorama spectrofluorimeter at 297 K. Lanthanide content was defined by complexometric titration of the solution obtained after burning of the complex sample and dissolving the formed lanthanide oxide in hydrochloric acid. Carbon and hydrogen content was determined on a Vario EL III CHN-analyzer.

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