
LETTERS
TO THE EDITOR

Lanthanide Complexes with 2,4-Dimethoxybenzoic Acid

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Lanthanide complexes have fluorescent properties, which are used in biological fluorescent labels [1], lasers [2], and for other purposes [3]. Therefore, the synthesis and study of photophysical properties of lanthanide complexes with dimethoxybenzoic acids is an important task.

In this connection, we carried out synthesis of the lanthanides complex compounds with 2,4-dimethoxybenzoic acid (**HL**) $[\text{LnL}_3(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$, where $\text{Ln} = \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}$. The complex compounds were synthesized by the reaction of water–alcohol solution of the corresponding lanthanide chloride and the ligand ammonium salt in a 1:5 molar ratio at $\text{pH} \approx 6.5$. The resulting precipitate was filtered off, washed with alcohol, water and dried in air.

In the IR spectra of the complexes the absorption bands of the non-ionized carboxyl group disappear while appear the absorption bands of ionized carboxyl group: $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ at 1610 and 1392 cm^{-1} , respectively, indicating the bidentate coordination of carboxyl group with lanthanide ions, as is known for all complex compounds: $\Delta(\text{COO}^-) = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-) = 218\text{--}227 \text{ cm}^{-1}$ [4].

The triplet energy level equal to 21300 cm^{-1} was determined for the 2,4-dimethoxybenzoic acid anion from the phosphorescence spectrum of its gadolinium complex (the shortest phosphorescence band of the Gd complex compound is assumed to correspond to the triplet energy level [5]).

Based on the mechanism [5] and experimental luminescence spectra, the complex compound $[\text{TbL}_3(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ was found to have the most intense luminescence. The phosphorescence of the organic ligand is absent, and the observed emission bands of terbium ion **III** is intensive, suggesting good energy

redistribution in the lanthanide ion. Based on this data, we can conclude that 2,4-dimethoxybenzoic acid is a promising ligand for the synthesis of lanthanide-containing luminophores.

Synthesis of terbium 2,4-dimethoxybenzoate. To a solution of 0.91 g (5 mmol) of 2,4-dimethoxybenzoic acid in 25 ml of rectified ethyl alcohol was added an aqueous solution of 1 mmol of terbium chloride. To the warm reaction mixture was cautiously added a diluted aqueous ammonia solution to $\text{pH} \approx 6.5$ at the vigorous stirring. Then the mixture was stirred at room temperature for 3 h. The resulting precipitate was filtered off, washed with alcohol and then with water. The resulting complex compounds was dried in air to constant weight. Yield 65%.

The IR spectra were recorded on a Infracum FT-02 Fourier spectrometer in the range of 350–4000 cm^{-1} . The samples were prepared by the pellets pressing under vacuum (2 mm Hg), the content is 1 mg of the complex per 100 mg of KBr. The luminescence spectra of the solid samples were recorded on a SPEX Ramalog spectrometer; photoexcitation source is a LGI-21 nitrogen laser (λ 337 nm).

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