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LETTERS TO THE EDITOR

Synthesis and Luminescent Properties of Europium(III), Terbium(III), and Gadolinium(III) Complex Compounds with Ethoxybenzoic Acids

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Lanthanide complexes are widely used in organic diodes, cathodoluminescence screens, lasers, and lamps due to the fact that their photoluminescence is characterized by a high quantum efficiency and very narrow spectral bands [1-3]. The majority of works on the luminescent complexes of lanthanides with organic ligands concerns β-diketonates of lanthanides [3], whose essential drawbacks are low photo- and thermal stability. In this respect coordination compounds of lanthanides with aromatic carboxylic acids offer noticeable advantages, as they have absorbing properties and photo- and thermal stability exceeding those of β-diketonates. However the majority of these compounds are poorly soluble in organic solvents impeding further operations with them.

The introduction of an alkyl substituent into a benzene ring should lead to an increased solubility of complexes. The synthesis and luminescent properties of europium(III) and terbium(III) complex compounds with metoxybenzoic acids were described in [4]. We have not found published data on the synthesis and luminescent properties of lanthanide complexes with ethoxybenzoic acids.

We have prepared and studied spectral luminescent properties of europium(III), terbium(III), and gadolinium(III) complex compounds with *p*-(HL^1) and *o*-ethoxybenzoic (HL^2) acids $LnL_3^{1,2}\cdot 3H_2O$ ($Ln = Eu^{3+}$, Gd^{3+}, Tb^{3+}).

According to the IR-spectroscopy data, it has been found that *p*- and *o*-ethoxybenzoic acids are coordinated through carboxy groups in the bidentate mode, as the difference between stretching asymmetric and symmetric vibrations of carboxy groups for all synthesized complexes is in the range of 185–210 cm^{-1} [5]. Oxygen of the ester group does not participate in the coordination, as the absorption band of the stretching vibration of the C–O bond at 1030 cm^{-1} is not essentially displaced.

The energies of the triplet excited level of ligands (T_1) 24625 (L^1) and 22812 (L^2) cm^{-1} were determined from the maxima of emission bands in the phosphorescence spectra of gadolinium(III) complexes at 77 K. The efficiency of luminescence of lanthanides complex compounds is defined by the probability of the intramolecular energy transfer from a ligand molecule to a lanthanide ion, and, more precisely, by the value of the energy gap between the excited triplet ligand level (T_1) and radiating level of a lanthanide(III) ion [$^5D_0$ for europium(III) and $^5D_4$ for terbium(III)] [1–3]. The difference in energies of 2500–4000 cm^{-1} is necessary for the effective luminescence of Tb^{3+} coordination compounds, and that of 2500–3500 cm^{-1}, for Eu^{3+}. The energy gap value for both complexes does not fit in this range, however, according to experimental data, integrated luminescence intensities of the compounds $TbL_3^1\cdot 3H_2O$, $TbL_3^2\cdot 3H_2O$, and terbium(III) benzoate (taken as the standard) are in the ratio 5.26 : 0.78 : 1.00.

Among europium(III) complexes, only the $T_1 \rightarrow {}^5D_2$ transition in the $EuL_3^1\cdot 3H_2O$ falls within the range of effective luminescence, for which the luminescence is

expected. It is confirmed by the experimental data: integrated intensity of luminescence of compounds $EuL^1_3 \cdot 3H_2O$ and europium(III) benzoate are in the ratio 1.23 : 1.00, and we failed to detect the luminescence of the complex $EuL^2_3 \cdot 3H_2O$ at room temperature.

Terbium(III) 4-ethoxybenzobenzoate trihydrate. To a solution of *p*-ethoxybenzoic acid (3 mmol in 25 mL of the 1 : 1 ethanol–water mixture) an ammonia solution was added dropwise up to reaching pH = 6. Then a lanthanide chloride solution (1 mmol in 5 mL of the 1 : 1 ethanol–water mixture) was added dropwise with intensive stirring. The precipitated complex compound was filtered off, washed several times by distilled water, then by ethanol, and dried up in a vacuum oven to a constant weight. Yield 62.3%, white fine-crystalline powder. IR spectrum (KBr), ν, cm^{-1}: 3400 (O–H), 1608 [ν_{as}(COO)], 1425 [ν_s(COO)], 1044 (C–O). Found, %: C 48.35; H 3.78; Tb 24.92. $C_{27}H_{27}O_9Tb$. Calculated, %: C 49.55; H 4.16; Tb 24.88.

The IR spectra were taken on a Bruker Fourier spectrometer in KBr tablets in the range of 4000–400 cm^{-1}. The C and H elemental analysis was carried out on a Vario EL III (Elementar) analyzer, the analysis for terbium(III), by complexometric titration. Luminescence spectra were recorded on a Flyuorat-02-Panorama spectrofluorimeter.

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