Synthesis, crystal structure, and photoluminescence of lanthanide fumarates (Ln = Sm, Eu, Nd, Er).

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Streszczenie

The complexation of trivalent lanthanides with fumaric acid was studied. Monocrystals of $Ln_2(C_4O_4H_2)_3{\cdot}8H_2O$ (Ln = Sm, Eu, Nd) and $Er_2(C_4O_4H_2)_3{\cdot}12H_2O$ were formed during the slow evaporation of appropriate aqueous solutions. The spectroscopic investigations were performed for samarium(III) fumarate, and the crystal structures were solved for the samarium(III) (**1**), europium(III) (**2**), neodymium(III) (**3**), and erbium(III) (**4**) complexes. It was found that the Nd, Eu, and Sm fumarates were isostructural (space group

), but the Er compound was different (space group$P2_1/c$). In the three former crystals, there is one symmetry-independent Ln(III) cation, which adopts a 9-coordinate geometry with six oxygen atoms from the carboxylate groups and three oxygen atoms from water molecules. In the Er(III) complex, the metal ion is eight-coordinated (six atoms from the fumarate carboxyl groups and two water molecules). In all four crystals, 3-dimensional polymeric structures are formed. For Sm(III) fumarate, electronic (absorption and emission) spectra were recorded at room and low temperatures. In the emission spectra at 293 K and 77 K, peaks correspond to four J levels of the ^6H_J term (J = 5/2, 7/2, 9/2, 11/2), and these transitions split at 77 K indicating the low symmetry of the Sm^{3+} ion. The most intense transition in UV–Vis is the hypersensitive $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition, and the $I(^4G_{5/2} \rightarrow {}^6H_{9/2})/I(^4G_{5/2} \rightarrow {}^6H_{5/2})$ (η_{Sm}) ratio was calculated.

The nephelauxetic ratio β and Sinha's parameter σ, calculated on the basis of the absorption spectra, suggested the decrease in the "degree of covalency" of the Sm–O bond from Sm maleate to Sm fumarate.

Słowa kluczowe

samarium, fumarate complexes, crystal structure, UV-Vis spectroscopy, covalency

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