

Crystal structures of new lanthanide hydroxybenzoates and different roles of LMCT state in the excitation energy transfer to Eu^{3+} ions.

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Streszczenie

A series of europium and terbium hydroxybenzoates [$\text{Eu}(\text{2-OH-Benz})_3(\text{H}_2\text{O})$] (**1**), [$\text{Eu}(\text{3-OH-Benz})_3(\text{H}_2\text{O})_3$] $\cdot 2\text{H}_2\text{O}$ (**2**), $\text{TbNa}_3(\text{2-OH-Benz})_3\cdot 3\text{H}_2\text{O}$ (**3**), [$\text{Tb}_2(\text{3-OH-Benz})_6(\text{H}_2\text{O})_4$] $\cdot 2\text{H}_2\text{O}\cdot 0.5(\text{3-OH-HBenz})$ (**4**), [$\text{Tb}(\text{4-OH-Benz})_3$] $\cdot \text{H}_2\text{O}$ (**5**) has been prepared and investigated using X-ray diffraction and luminescence spectroscopy. Two methoxysalicylates $\text{Ln}_2(\text{2-OH-5-OCH}_3\text{-Benz})_3\cdot 6\text{H}_2\text{O}$ ($\text{Ln}=\text{Eu, Tb}$) are also under consideration. A dimeric crystal structure of **2** and polymeric structures of **4** and **5** were first determined by single crystal X-ray analysis. Low-energy ligand-metal charge transfer (LMCT) states caused by a particular binding of the ligands with Ln^{3+} ion were identified in the europium compounds. Different roles of the LMCT states located under and above the lowest triplet state of the ligand in the excitation energy transfer in europium hydroxybenzoates are discussed. The lifetimes of $^5\text{D}_0$ (Eu^{3+}) and $^5\text{D}_4$ (Tb^{3+}) states at 77 K are consistent with the number of water molecules and other quenchers containing in the compounds. A qualitative correlation is observed between the luminescence brightness of hydroxybenzoates and an efficiency of nonradiative processes caused by the LMCT state and directly the multiphonon relaxation. Nonradiative processes due to the LMCT state are the most efficient at the location of this state lower the lowest triplet of 2-hydroxybenzoate ligand in complex **1**.

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