Structures and manifestation of *ortho*-,*meta*-, and *para*-NH_2-substitution in the optical spectra of europium and terbium aminobenzoates.

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Streszczenie

Four pairs of isostructural europium and terbium *ortho*-, *meta*, and *para*-aminobenzoates ([Ln(2-ABenz)$_3$(H$_2$O)], [Ln(3-ABenz)$_3$(H$_2$O)$_3$], [Ln(3-ABenz)$_3$(H$_2$O)$_3$]·3H$_2$O, [Ln(4-ABenz)$_3$(H$_2$O)], (Ln = Eu, Tb; ABenz – aminobenzoate anion)) were investigated using X-ray diffraction and optical spectroscopy (luminescence and luminescence excitation spectra, as well as vibrational IR and Raman spectra). The crystal structures of [Tb(2-ABenz)$_3$(H$_2$O)], [Eu(3-ABenz)$_3$(H$_2$O)$_3$], [Eu(3-ABenz)$_3$(H$_2$O)$_3$]·3H$_2$O, and [Eu(4-ABenz)$_3$(H$_2$O)] were determined by single crystal X-ray analysis. The [Eu(3-ABenz)$_3$(H$_2$O)$_3$] structure constitutes a new type of lanthanide *m*-aminobenzoate in the *R*3 space group. The Ln^{3+} coordination polyhedron formed by three bidentate chelate carboxylic groups and three terminal water molecules in both structures of *m*-aminobenzoate can be described as a distorted three-capped trigonal prism. The influence of the incorporation of three solvate outer-sphere H$_2$O molecules in the crystal lattice of *m*-aminobenzoate on the Eu^{3+} luminescence center was analyzed. Restructuring of the LnO_9 coordination polyhedron results in a decrease in the distortions of the crystal field that appears as a loss of extra splitting of the Ln^{3+} electronic levels in [Ln(3-ABenz)$_3$(H$_2$O)$_3$]·3H$_2$O. The effect of the electron-donating NH$_2$ group located in different positions on the benzene ring on process of the excitation energy transfer to Ln^{3+} ion is examined. The hypsochromic shift of an intense interligand charge transfer (ILCT) band in the Tb^{3+} excitation spectra of the sequence of *o*-, *m*-, and *p*-NH$_2$-substituted compounds is observed. This shift is the consequence of the different electron density distribution depending on the NH$_2$ position in the ligands. The predominant role of low-energy ligand–metal charge transfer (LMCT) states in the quenching of the luminescence of the europium *o*- and *p*-aminobenzoates in contrast with the europium *m*-aminobenzoates is discussed. Compounds including a supplementary Cl substituent on the benzene ring [Ln(2-A-5-Cl-Benz)$_3$(H$_2$O)$_n$] (Ln = Eu, Tb) and [Eu(4-A-2-Cl-Benz)$_3$(H$_2$O)$_n$] are also under consideration.

Słowa kluczowe

Eu3+, Tb3+, aminobenzoate, luminescence, X-ray crystal structure, LMCT state

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