

## Spectroscopy and structure of Ln<sup>III</sup> complexes with sulfonylamidophosphate-type ligands as sensitizers of visible and near-infrared luminescence.

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### Streszczenie

Lanthanide complexes with sulfonylamidophosphate-type ligands: dibenzyl(phenylsulfonyl)amidophosphate (**HSB**) and di(4-methylphenyl)-phenylsulfonyl-amidophosphate (**HSK**) have been synthesized and show promise as new sensitizers of visible and near-infrared luminescence. They constitute a new part of coordination chemistry for this type of ligand, creating simultaneously a new class of lanthanide complexes with  $\pi$ -conjugated ligands possessing the structural fragment SO<sub>2</sub>NHP(O). Two series of stable lanthanide complexes Na[Ln(**SB**)<sub>4</sub>] (**1Ln**) and Na[Ln(**SK**)<sub>4</sub>] (**2Ln**), where Ln=Nd<sup>III</sup>, Eu<sup>III</sup>, Gd<sup>III</sup>, Tb<sup>III</sup>, Er<sup>III</sup>, Yb<sup>III</sup>, were characterized by X-ray structure analysis. The IR, absorption, emission, and excitation spectra at 293, 77, and 4 K, as well as luminescence decay times and emission quantum yields were used to characterize the complexes in the solid state. The relation between the crystal structure and its spectroscopic properties is also discussed. The influence of the  $\pi$ - $\pi$  stacking interactions and a ligand-to-metal charge transfer state on ligand-to-metal energy transfer efficiency was demonstrated and discussed. Crystal-field lines determined from absorption and fluorescence spectra of **2Nd** were used in computational analysis employing free-ion operators, one-electron crystal-field operators, and two-particle correlation crystal-field operators. The performed analysis enabled the determination of the Hamiltonian parameters and an unambiguous assignment of 85 crystal-field levels of Nd<sup>III</sup> ion with a mean error of 12.0 cm<sup>-1</sup>.

### Słowa kluczowe

Crystal field, parameters, lanthanides, luminescence,  $\pi$ - $\pi$ stacking interactions, sulphonylamidophosphates, X-ray diffraction

Adres publiczny

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