Synthesis, Crystal Structures, and Optical and Magnetic Properties of Samarium, Terbium, and Erbium Coordination Entities Containing Mono-Substituted Imine Silsesquioxane Ligands

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Streszczenie

Mono-substituted cage-like silsesquioxanes of the T_8-type can play the role of potential ligands in the coordination chemistry. In this paper, we report on imine derivatives as ligands for samarium, terbium, and erbium cations and discuss their efficient synthesis, crystal structures, and magnetic and optical properties. X-ray analysis of the lanthanide coordination entities $[MCl_3(POSS)_3]\cdot 2THF$ [M = Er^{3+} (**3**), Tb^{3+} (**4**), Sm^{3+} (**5**)] showed that all three compounds crystallize in the same space group with similar lattice parameters. All compounds contain an octahedrally coordinated metal atom, and additionally, **3** and **5** structures are strictly isomorphous. However, surprisingly, there are two different molecules in the crystal structure of the terbium coordination entity **4**, monomer (sof 65%) and dimer (sof 35%), with one and two metal centers. Absorption measurements of the investigated materials recorded at 300 K showed that regardless of the lanthanide involved, their energy band gap equals 2.7 eV. Moreover, the analogues containing Tb^{3+} and Sm^{3+} exhibit luminescence typical of these rare earth ions in the visible and infrared spectral range, while the compound with Er^{3+} does not generate any emission. Direct current variable-temperature magnetic susceptibility measurements on polycrystalline samples of **3–5** were performed between 1.8 and 300 K. The magnetic properties of **3** and **4** are dominated by the crystal field effect on the Er^{3+} and Tb^{3+} ions, respectively, hiding the magnetic influence between the magnetic cations of adjacent molecules. Complex **5** exhibits a nature typical for the paramagnetism of the samarium(III) cation.

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https://www.acs.org/content/acs/en.html