

Crystal field splitting of the ground state of terbium(III) and dysprosium(III) complexes with a triimidazolyl tripod ligand and an acetate determined by magnetic analysis and luminescence.

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Streszczenie

Terbium(III) and dysprosium(III) complexes with a tripodal N₇ ligand containing three imidazoles (H₃L) and a bidentate acetate ion (OAc⁻), [Ln^{III}(H₃L)(OAc)](ClO₄)₂·MeOH·H₂O (Ln = Tb, **1**; Ln = Dy, **2**), were synthesized and studied, where H₃L = tris[2-(((imidazol-4-yl)methylidene)amino)ethyl]amine. The Tb^{III} and Dy^{III} complexes have an isomorphous structure, and each Tb^{III} or Dy^{III} ion is coordinated by the tripodal N₇ and the bidentate acetate ligands, resulting in a nonacoordinated capped-square-antiprismatic geometry. The magnetic data, including temperature dependence of the magnetic susceptibilities and field dependence of the magnetization, were analyzed by a spin Hamiltonian, including the crystal field effect on the Tb^{III} ion (4f⁸, *J* = 6, *S* = 3, *L* = 3, *g_J* = 3/2, ⁷F₆) and the Dy^{III} ion (4f⁹, *J* = 15/2, *S* = 5/2, *L* = 5, *g_J* = 4/3, ⁶H_{15/2}). The Stark splittings of the ground states ⁷F₆ of the Tb^{III} ion and ⁶H_{15/2} of the Dy^{III} ion were evaluated from the magnetic analyses, and the energy diagram patterns indicated an easy axis (Ising type) anisotropy for both complexes, which is more pronounced for **2**. The solid-state emission spectra of both complexes displayed sharp bands corresponding to the f–f transitions, and the fine structures assignable to the ⁵D₄ → ⁷F₆ transition for **1** and the ⁶F_{9/2} → ⁶H_{15/2} transition for **2** were related to the energy diagram patterns from the magnetic analyses. **1** and **2** showed an out-of-phase signal with frequency dependence in alternating current (ac) susceptibility under a dc bias field of 1000 Oe, indicative of a field-induced SIM.

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