New Dy$^{III}$ and Tb$^{III}$ complexes with tripodal ligands
$2,2'\-\[(2$-pyridinylmethyl)imino\]di(methylene)\]-bis(4-methyl-phenol). Syntheses, structures and luminescence properties

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New rare earth complexes, $[\text{Tb}_2\text{L}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (I), $[\text{Dy}_2\text{L}_2(\text{NO}_3)_2(\text{MeOH})_2]$ (II) and $[\text{Tb}_2\text{L}_2(\text{NO}_3)_2(\text{DMF})_2].0.5\text{DMF}.0.5(\text{C}_2\text{H}_5)_2\text{O}$ (III), $\text{L} = 2,2'-\[(2$-pyridinylmethyl)-imino\]-di(methylene)\]-bis(4-methyl-phenol), were synthesized by a Mannich type reaction with 2-(methylamino)-pyridine and p-cresol. The single crystal X-ray diffraction data show that in each complex (I) to (III) the lanthanide ions are eight coordinated with the coordination sphere completed by one pyridyl and one amine nitrogen atoms, three phenoxo oxygens, one solvate oxygen (water for (I), methanol for (II) and N,N’-dimethylformamide for (III)) and a bidentate nitrate. The optical properties of the complexes were studied by diffuse reflectance, luminescence and decay curve measurements. The studied compounds exhibit slight different luminescence properties under excitation at ligand energy levels, indicating that varying the solvent the characteristic emissions of Tb$^{III}$ and Dy$^{III}$ ions are not substantially affected. The luminescence intensity ratios Y/B (Dy$^{III}$) and G/B (Tb$^{III}$) were calculated and are close to 1.3 and 1.2 respectively, indicating a more covalent character of the bonding between the lanthanide ions and surrounding ligands. The decay curves of Tb$^{III}$ samples exhibit a double exponential behavior, with a long lifetime up to 1.11 ms, whereas a single exponential behavior was observed for Dy$^{III}$ samples, with very small lifetimes ∼0.011 ms. These results are consistent with the relatively small energy gap between the $^4\text{F}_{9/2}$ and $^4\text{F}_{1/2}$ Dy$^{III}$ levels, $\Delta E \approx 7600 \text{ cm}^{-1}$, in comparison with the large energy gaps between $^5\text{D}_4$ and $^5\text{F}_0$ energy states of Tb$^{III}$, $\Delta E \approx 14820 \text{ cm}^{-1}$, showing that the values of lifetimes increase with increasing of $\Delta E$ values, i.e., Ln$^{III}$ ions with smaller $\Delta E$ quench the luminescence more efficiently than those Ln$^{III}$ ions with large $\Delta E$. The CIE coordinates were calculated for all complexes from their emission spectra in order to find out the color emission characteristics of the reported complexes. The results indicate that the Tb$^{III}$ and Dy$^{III}$ compounds could be used in solid state-lighting.

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