Novel dipivaloylmethanate compounds of trivalent lanthanide ions: synthesis, structure and energy transfer

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This work reports on the synthesis, characterization and investigation of photoluminescence properties of novel $[Ln(dpm)(NO_3)_2(thpo)_2]$ complexes (where THPO : trihexylphosphine oxide and Ln : Tb, Gd or Eu). The compounds were characterized by elemental analysis of CHN, vibrational spectroscopy in the infrared region, thermogravimetric analysis and their spectroscopic properties were investigated by molecular diffuse reflectance, excitation and emission as well as decay times of emitting states. Single-crystal X-ray diffraction analyses reveal that $[Ln(dpm)(NO_3)_2(thpo)_2]$ complexes crystallize in the monoclinic space group P21/n with parameters cell: a =17.1926(2), b = 18.1226(2) c = 18.2508(2) Å; $\alpha = 90°$; $\beta = 108.908°$ e $\gamma = 90°$. Interestingly, the phosphine oxide ligands are located in opposite positions, in contrast to that observed for similar complexes presenting dbm (dibenzoylmethanate) and hmpa (hexamethylphosphoramide) ligands (Figure 1). These results reflect differences in the luminescence properties of the Ln-mono(diketonate) complexes. The presence of metal ligand charge transfer state (TCLM) of low energy in the Eu^{3+} compounds was also investigated. According with the experimental data, ligand to metal charge transfer state (TCLM) for the $[Eu(dpm)(NO_3)_2(thpo)_2]$ system is located in higher energy than for dimeric complex of formula $[Eu_2(DPM)_6]$.[1]

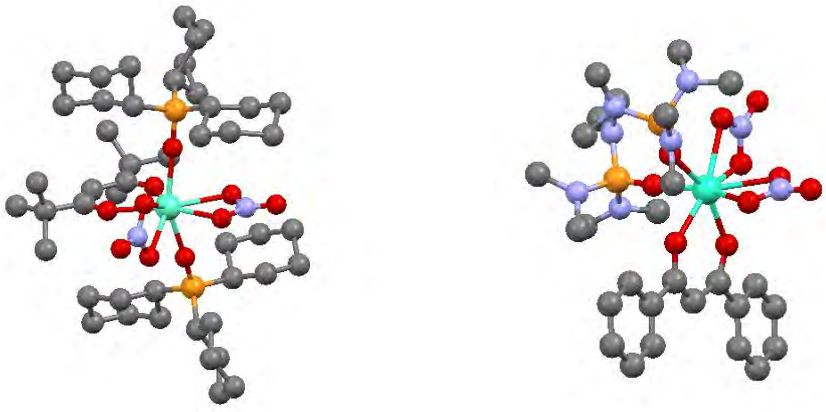

Figure 1. X-ray diffraction structure of $[Eu(dpm)(NO_3)_2(thpo)_2]$ (a) and $[Ln(dbm)(NO_3)_2(tppo)_2]$ (b) complexes.

Keywords: Lanthanide, β-diketonate complexes, Luminescence, charge transfer state.

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References

[1] Y. C. Miranda, L. L. A. L. Pereira, J. H. P. Barbosa, H. F. Brito, M. C. F. C. Felinto, O. L. Malta, W. M. Faustino, E. E. S. Teotonio. Eur. J. Inorg. Chem. 2015, 3019, 2015