ABSTRACT

Synthesis, Structural and Spectroscopic Characterization of Novel Lanthanide Dinuclear Macrocyclic Schiff Base Complexes.

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The first crystal structure of novel dinuclear lanthanide complexes synthesized by template condensation of 2,6-diformyl-p-cresol and 3,6-dioxo-octanediamine in the presence of lanthanide (La-Dy) nitrates is reported. The solution of the structure of the digadolinium complex confirms encapsulation of a pair of cation in the macrocycle at ≈ 4Å apart. X-ray diffraction and crystal morphology studies confirm that the homo- and heterodinuclear complexes are isostructural.

Intense sensitized luminescence of Eu^{3+} (lifetime - 860 ± 10 μs) and Tb^{3+} (lifetime - 1618 ± 20 μs) ions at 77 K is revealed; Tb^{3+} ions showing strong, efficient emission even at RT, when present only as an impurity ion in 99.999% pure gadolinium nitrate.

Pr^{3+}-Pr^{3+} interaction is suggested by magnetic susceptibility data whereas other metal-metal

interactions are revealed in photophysical studies e.g. Eu^{3+}-Sm^{3+} (Eu^{3+} lifetime = 94 ± 1 μs). High resolution Eu^{3+} luminescence spectroscopic studies show unusual multiplicities of the $^7F_1$ and $^5D_1$ states which are attributed to metal-metal interactions.

Very unusually broad ^{13}C resonances without the normal paramagnetic shifts were observed in the Cross Polarization Magic Angle Spin Nuclear Magnetic Resonance of polycrystalline samples at constant and variable temperatures.