ABSTRACT

Synthesis, Structural and Spectroscopic Characterization of Novel Lanthanide Dinuclear Macroyclic 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 \( \approx 4\AA \) apart. X-ray diffraction and crystal morphology studies confirm that the homo- and heterodinuclear complexes are isostructural.

Intense sensitized luminescence of Eu\(^{3+}\) (lifetime \(-860 \pm 10 \mu s\)) and Tb\(^{3+}\) (lifetime \(-1618 \pm 20 \mu s\)) 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.