Novel luminescent tetrakis lanthanide β-diketonate complexes showing luminescence in Vis and NIR region and temperature sensing

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Synthesis of homonuclear complexes

Scheme 1. Graphical presentation of the synthesis results

The single crystals were obtained by slow evaporation of a solution of the complex from methanol.

The tetrakis TFAA Ln complexes crystallize in the orthorhombic non-centrosymmetric space group P2₁2₁2. The lanthanide ion is coordinated with eight oxygen atoms from β-diketonate ligands and with one sodium cation as counter ion.

Crystal structures

Fig. 1. Structure of the tetrakis TFAA Ln complex

Fig. 2. Crystal packing of the tetrakis TFAA Ln complex 3D polymeric chains growing along the c-axis, viewed down the b-axis

The tetrakis TFAA Ln complexes crystallize in the monoclinic centrosymmetric space group P2₁/n. The lanthanide ion is coordinated with six oxygen atoms from β-diketonate ligands and with two oxygen atoms from water molecules.

Fig. 3. Structure of the tetrakis TFAA Ln (Pr, Nd) complex

Synthesis of heteronuclear complex

The synthesis of the heteronuclear complex of [Eu₄⁺/Tb⁺⁺(TFAA)₈]Na⁺ was synthesized by adding the Eu³⁺ TFAA complex and the Tb³⁺ TFAA complex to a methanol solution in a 1:1 ratio and left to stir for 24h. Afterwards the solution was left to crystallize by slow evaporation in order to obtain single crystals.

Fig. 4. Structure of the heteronuclear [Eu₄⁺/Tb⁺⁺(TFAA)₈]Na⁺ complex

Fig. 5. Crystal packing of the [Eu₄⁺/Tb⁺⁺(TFAA)₈]Na⁺/heteronuclear complex 1D polymeric chains growing along the b-axis, viewed down the c-axis

Temperature-dependent luminescence

Fig. 13. Emission spectra in a temperature range from 10 K to 355 K [Eu₄⁺/Tb⁺⁺(TFAA)₈]Na⁺

Fig. 14. Plot showing relative sensitivity values at different temperatures (10-355 K) for [Eu₄⁺/Tb⁺⁺(TFAA)₈]Na⁺

Fig. 15. Emission spectra in a temperature range from 280 K to 380 K [Dy⁺⁺(TFAA)₈]Na⁺

Fig. 16. Plot showing relative sensitivity values at different temperatures (280-380 K) for [Dy⁺⁺(TFAA)₈]Na⁺

Conclusion

We have obtained several new crystal structures with a well-known β-diketonate ligand throughout the series of lanthanide ions. With the synthetic procedure that was used we obtained both the homonuclear complexes as well as heteronuclear complexes. Both types of complexes show luminescence properties in solution and solid state. The Eu³⁺, Tb³⁺ mixed complex as well as Dy³⁺ complex show good temperature-sensing properties in a wide temperature range.