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**Title: Mono- and Dinuclear Lanthanide Complexes of Trifluoroacetylacetone and Heterocyclic Amines. Syntheses, NMR, 4f-4f Absorption and Photoluminescence**

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## Abstract

Lanthanide(III)  $\beta$ -diketonates are among the most studied lanthanide coordination complexes because of their potential applications ranging from luminescent probes in biology, to NMR shift reagents, electroluminescent materials and lasers. The essence of electronic spectroscopy of  $\text{Ln}^{3+}$  ions is associated with their characteristic narrow emission bands (UV to NIR regions 380 – 2500 nm) arising from the intraconfigurational  $4f-4f$  transitions and long lifetimes, which make these ions very interesting and demanding for such purpose. This Ph.D. work describe in this thesis deals with the design and synthesis of mono- and di- lanthanide complexes which are thermally stable and excellent candidate for the use in fabrication of luminescent display devices. The visible light photoluminescence,  $4f-4f$  absorption and hypersensitivity of these complexes are studied in different environments. For this purpose, 1,1,1-trifluoro-2,4-pentanedione (tfaa), a fluorinated  $\beta$ -diketonate and 1,10-phenanthroline (phen), 2,2'-bipyridyl (bpy) and 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) ligands for mononuclear and bridging 2,2'-bipyrimidine (bpm) and pyrazine (pyz) ligands for the synthesis of dinuclear complexes were chosen. The work is distributed over seven chapters.

In first the strategy (**Chapter 2**), two series of the lanthanide complexes of the type  $[\text{Ln}(\text{tfaa})_3\text{L}]$  ( $\text{Ln} = \text{La}-\text{Lu}$ , except Ce, Pm and Gd and  $\text{L} = \text{phen}$  or bpy) are synthesized by an improved *one pot-one step* method. The <sup>1</sup>H NMR spectra of  $[\text{Ln}(\text{tfaa})_3\text{L}]$  (where  $\text{L} = \text{phen}$  or bpy) complexes display only one set of signals for the aromatic as well as  $\beta$ -diketone protons which substantiates presence of only one species in the solution. The spectra of the complexes show huge downfield or upfield shifts, with the exception of Sm complexes where small upfield shifts are noted and the spectra are comparable with the respective diamagnetic analogue. All the complexes with the exception of  $[\text{Nd}(\text{tfaa})_3\text{bpy}]$  where signal due to H(2) could not be observed, display six resonances; four due to the bpy or phen and two due to the methine and methyl of the tfaa, coordinated to Ln, in the intensity ratio of 2:2:2:2:3:9 (indicating that  $\beta$ -diketone to bpy or phen ratio, in the complexes, is 3:1). It reflects the presence of one bpy or phen unit in the complexes, besides three units of tfaa and the complexes are eight-coordinate.

In the third strategy (**Chapter 3**), the  $4f-4f$  absorption spectra of  $[\text{Ln}(\text{tfaa})_3\text{phen}]$  and  $[\text{Ln}(\text{tfaa})_3\text{bpy}]$  (where  $\text{Ln} = \text{Pr}$ , Nd, Ho and Er) complexes in chloroform and dichloromethane are studied and analyzed. The band shape of hypersensitive transition  ${}^4\text{G}_{5/2}, {}^2\text{G}_{7/2} \leftarrow {}^4\text{I}_{9/2}$  of  $[\text{Nd}(\text{tfaa})_3\text{H}_2\text{O}]$  is different than to the  $[\text{Nd}(\text{tfaa})_3\text{phen}]$  and  $[\text{Nd}(\text{tfaa})_3\text{bpy}]$  and resembles well with the band shape of the typical seven-coordinate neodymium  $\beta$ -diketonate complexes. The band shape of this transition of bpy and phen complexes is similar to the typical eight-coordinate  $[\text{Nd}(\beta\text{-diket})_3\text{NN}]$ . Thus, it is concluded that the hydrated complex is seven-coordinate while the bpy and phen complexes are eight-coordinate. Among the Ho(III) transitions examined in this study the absorption intensity of  ${}^5\text{G}_6 \leftarrow {}^5\text{I}_8$  (Ho-V) exhibits the greatest sensitivity to the ligand (solvent) environment. The oscillator strength of this transition increases almost 11.94-, 11.28- and 9.90- fold on going from Ho(III) aqua-system to the  $[\text{Ho}(\text{tfaa})_3\text{H}_2\text{O}]$ ,  $[\text{Ho}(\text{tfaa})_3\text{bpy}]$  and  $[\text{Ho}(\text{tfaa})_3\text{phen}]$  complexes, respectively in chloroform.

In the fourth strategy (**Chapter 4**), the photoluminescence properties of the complexes:  $[\text{Ln}(\text{tfaa})_3\text{phen}]$  and  $[\text{Ln}(\text{tfaa})_3\text{bpy}]$  [where  $\text{Ln} = \text{Pr(III)}$ , Sm(III), Eu(III), Tb(III), Dy(III) and Tm(III)] in chloroform is studied. The effect of changing the environment (ancillary ligands) around the metal ions on the luminescence intensity and band shape of hypersensitive emission transitions of the complexes are explored and discussed. The complexes of Pr(III), Sm(III), Eu(III), Tb(III), Dy(III) and Tm(III), respectively, emits characteristic red, pink, intense red, green, yellow and blue luminescence. The energy difference between ligand (i.e. tfaa, phen or bpy) centered triplet state and emitting levels of Eu(III) and Tb(III) suggests that ligand-to-metal energy transfer is very efficient in these complexes. The luminescence decay curves of the  ${}^1\text{D}_2, {}^4\text{G}_{5/2}, {}^5\text{D}_0, {}^5\text{D}_4, {}^4\text{F}_{9/2}$  and  ${}^1\text{G}_4$  emitting levels for Pr(III), Sm(III), Eu(III), Tb(III), Dy(III) and Tm(III) complexes in chloroform at room temperature were monitored for the  ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4, {}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}, {}^5\text{D}_0 \rightarrow {}^7\text{F}_2, {}^5\text{D}_4 \rightarrow {}^7\text{F}_5, {}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$  and  ${}^1\text{G}_4 \rightarrow {}^3\text{H}_4$  transitions. The lifetime ( $\tau_{\text{obs}}$ ) of the  ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4, {}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}, {}^5\text{D}_0 \rightarrow {}^7\text{F}_2, {}^5\text{D}_4 \rightarrow {}^7\text{F}_5, {}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$  and  ${}^1\text{G}_4 \rightarrow {}^3\text{H}_4$  transitions of Pr(III), Sm(III), Eu(III), Tb(III), Dy(III) and Tm(III) complexes, respectively, were determined from the mono-exponential fitting of the decay curve and are consistent with the presence of one major luminescent species in the complexes. The fluorescence lifetime of the

hydrated complexes of Sm(III), Eu(III) and Tb(III) are relatively lower than the anhydrous phen and bpy complexes. The lower value of the lifetime of hydrated complexes could be due to dominant non-radiative decay channels associated with vibronic coupling due to the presence of the coordinated H<sub>2</sub>O molecule present in the first coordination sphere of these complexes.

In the fifth strategy (**Chapter 5**), the synthesis of nine-coordinate complexes of the type [Ln(tfaa)<sub>3</sub>tptz] (where Ln = La, Pr-Er) by a modified in situ method is described. The absorption spectra of the [Nd(tfaa)<sub>3</sub>tptz] complex are studied in a series of non-aqueous solvents. The band shape of the hypersensitive transition  ${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$  of the complex is distinctively different from those reported for typical eight- and ten-coordinate neodymium  $\beta$ -diketonate complexes. The band shape of the hypersensitive transition in DMSO is different from the band shape of this transition arising in any of the solvents studied and is similar to eight-coordinate neodymium  $\beta$ -diketonate complexes. The DMSO invades the complex and replaces the tptz from the inner-coordination sphere. Two DMSO molecules coordinate and the complex acquires eight-coordinate structure, [Nd(tfaa)<sub>3</sub>(DMSO)<sub>2</sub>] in this solvent. The praseodymium, samarium, europium and terbium complexes emit red, pink, brilliant red and green luminescence.

In sixth strategy (**Chapter 6**), 2,2'-bipyrimidine and the fluorinated and non-fluorinated pentanediones i.e. trifluoroacetylacetone and acetylacetone is being presented. The effect of fluorine substitution on the physical and chemical properties of the complexes is discussed and analyzed. The complexes synthesized are [(tfaa)<sub>3</sub>Ln( $\mu$ -bpm)Ln(tfaa)<sub>3</sub>] and [(acac)<sub>3</sub>Ln( $\mu$ -bpm)Ln(acac)<sub>3</sub>] where Ln stands for all lanthanides (except Ce, Pm and Gd) in the case of trifluoroacetylacetone and La, Pr, Nd, Sm, Eu, Tb, Dy, Ho and Er in the case acetylacetone. The single crystal X-ray structure analysis of [(tfaa)<sub>3</sub>Tb( $\mu$ -bpm)Tb(tfaa)<sub>3</sub>] indicates that it crystallizes without solvent in the lattice in the monoclinic space group P2<sub>1</sub>/n. The coordination geometry around Tb(III) ion is described as distorted square antiprism. Apart from the crystal structure the presence of two lanthanide centers, in these complexes, is reflected by their elemental analysis, <sup>1</sup>H NMR. The two fold higher oscillator strength of the hypersensitive transition  ${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$  of dinuclear complexes (tfaa complex = 101.43 x 10<sup>-6</sup> and acac complex = 87.0 x 10<sup>-6</sup>) than their mononuclear analogues (tfaa complex = 53.00 x 10<sup>-6</sup> and acac complex = 43.43 x 10<sup>-6</sup>), also manifests the presence of two neodymium centers in the dinuclear complexes. The Sm(III), Eu(III) and Tb(III) complexes under UV excitation emit characteristic pink, red and green luminescences. The luminescent study demonstrates that changing acetylacetone (non-fluorinated) by (fluorinated) trifluoroacetylacetone results in enhancement of <sup>5</sup>D<sub>0</sub> lifetime from 360 to 810  $\mu$ s. The intrinsic quantum yield ( $\Phi_{Ln}$ ) of [(tfaa)<sub>3</sub>Eu( $\mu$ -bpm)Eu(tfaa)<sub>3</sub>] is higher than [(acac)<sub>3</sub>Eu( $\mu$ -bpm)Eu(acac)<sub>3</sub>] while the  $\Phi_{Ln}$  is higher for [(acac)<sub>3</sub>Tb( $\mu$ -bpm)Tb(acac)<sub>3</sub>] than [(tfaa)<sub>3</sub>Tb( $\mu$ -bpm)Tb(tfaa)<sub>3</sub>]. These results suggest that tfaa sensitized Eu(III) emission efficiently than acac while acac sensitizes the Tb(III) luminescence more efficiently than tfaa.

In seventh strategy (**Chapter 7**), a simple non-chelating pyrazine ligand was used to synthesize low-symmetry dinuclear complexes of the type [(tfaa)<sub>3</sub>Ln( $\mu$ -pyz)Ln(tfaa)<sub>3</sub>] (where Ln = La, Nd, Sm, Eu, Tb, Ho and Er). The complexes are moisture sensitive and quickly pick up moisture from the atmosphere. The NMR spectra of the Ln-Ln complexes display one sharp resonance for the coordinated pyrazine which confirms the symmetric bridging of pyrazine to two Ln(tfaa)<sub>3</sub> units. The 4f – 4f absorption spectra of the [(tfaa)<sub>3</sub>Nd( $\mu$ -pyz)Nd(tfaa)<sub>3</sub>] complex are recorded in chloroform (non-coordinating) and ethanol (coordinating) to see the effect of coordinating and non-coordinating solvents on the oscillator strength and band shape of the hypersensitive transition  ${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$ . The oscillator strength of the hypersensitive transition,  ${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$  of the [(tfaa)<sub>3</sub>Nd( $\mu$ -pyz)Nd(tfaa)<sub>3</sub>] is two fold higher than the mononuclear [Nd(tfaa)<sub>3</sub>.H<sub>2</sub>O] and the band shape is similar to typical seven-coordinate  $\beta$ -diketonate complexes. One ethanol molecule coordinates and changes the geometry from seven- to eight-coordinate. The band shape of the hypersensitive transition in ethanol is distinctively different from the band shape in chloroform. The change in the band shape is accompanied by a decrease in the oscillator strength (104.66 x 10<sup>-6</sup>) of the hypersensitive transition. The higher value of the oscillator strength in chloroform (109.42 x 10<sup>-6</sup>) is consistent with the low molecular symmetry of the seven-coordinate structure, suggesting the premise that the oscillator strength of the hypersensitive transition depends upon the asymmetry of the field on the ion and the oscillator strength increase with an increase in asymmetry around the lanthanide ion. The samarium, europium and terbium complexes emit pink, brilliant red and green luminescence. The experimental intensity ( $\eta$ ) parameter of the Sm(III), Eu(III) and Tb(III) are 3.49, 10.89 and 2.62, respectively, which implies that these complexes have structure with no imposed symmetry.