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Supervisor	:	Prof. K. Iftikhar
Title of the PhD thesis	:	*Lanthanide Complexes of Hexafluoroacetylacetone and Heterocyclic Amines. Synthesis, Photoluminescence, 4f-4f Absorption, Hypersensitivity and NMR Studies*

Abstract

The Ph.D. work described in this thesis deals with the design and synthesis of new volatile lanthanide complexes which are thermally stable and are excellent candidates for the use in fabrication of luminescent display devices. For this purpose, lanthanide complexes are synthesized based on a fluorinated β-diketone, 1,1,1,5,5,5-hexaflouroacetylacetone (Hhfaa) and different ancillary ligands, 1,10-phenanthroline (phen), 2,2′-bipyridine (bpy), 2,4,6-tripyridyl-1,3,5-triazine (tptz), 1*H*-indazole (*H*ind) and 1*H*-pyrazole (pz).

Chapter 1 is the literature overview of lanthanide β-diketonate complexes, NMR, 4f-4f absorption and hypersensitivity and luminescence. In chapter 2, a series of lanthanide complexes of the type $[Ln(hfaa)_3(phen)_2]$ (Ln = La, Pr and Nd) and $[Ln(hfaa)_3phen]$ (Ln = Nd- Lu, except Gd) is synthesized. These complexes are synthesized in high yields by an *in situ* method. In Chapter 3, the effect of environment (solvent/ligand) on 4*f*-4*f* absorption properties of the complexes of Pr(III), Nd(III), Ho(III) and Er(III) in chloroform and dichloromethane is presented. The distinctively different band shapes of the hypersensitive transition, $^4G_{5/2},^2G_{7/2} \leftarrow {}^4I_{9/2}$ for the two neodymium complexes (eight- and ten-coordinate) indicate different environment around the Nd(III) ion (Fig. 1).

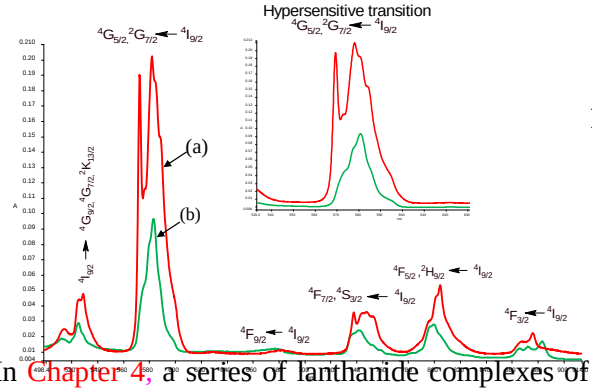
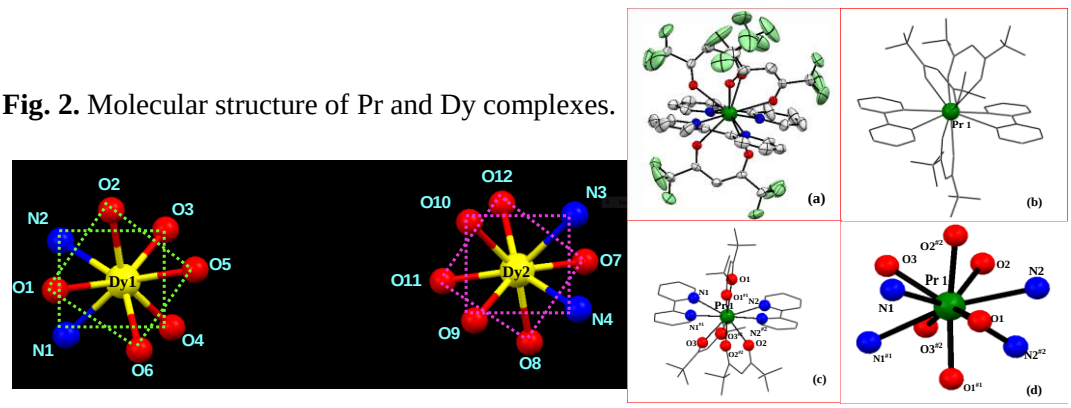


Fig. 1. 4f-4f absorption spectra of (a) eight- coordinate $[Nd(hfaa)_3(phen)]$(red) and (b) ten- coordinate $[Nd(hfaa)_3(phen)_2]$(green) in chloroform. Inset: hypersensitive transition $^4G_{5/2},^2G_{7/2} \leftarrow {}^4I_{9/2}$.

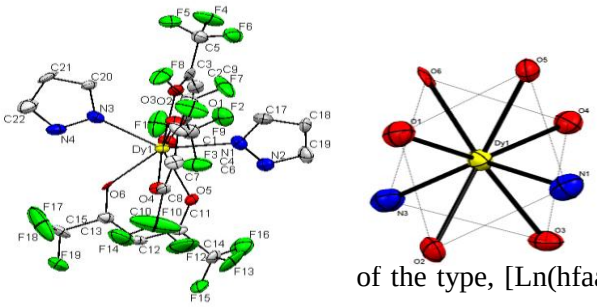
In Chapter 4, a series of lanthanide complexes of the type $[Ln(hfaa)_3(bpy)]$ (Ln = Nd- Lu, except Gd) and $[Ln(hfaa)_3(bpy)_2]$ (Ln = La, Pr, Nd and Sm) is synthesized and characterized by elemental analysis, IR, ESI-MS^+, 4*f*-4*f* absorption, NMR and Single-crystal X-ray crystallography (Fig. 2).

Fig. 2. Molecular structure of Pr and Dy complexes.



In Chapter 5, the 4*f*-4*f* absorption spectra of the complexes (syntheses are given in chapter 4) of Pr, Nd, Ho and Er are studied and analyzed in chloroform and dichloromethane. The eight- and ten-coordinate neodymium complexes display distinctively different band shape. In Chapter 6, a series of eight-coordinate air and moisture stable lanthanide complexes of the type $[Ln(hfaa)_3(pz)_2]$ (Ln= La, Pr-Yb, except Pm and Gd) have been synthesised and characterized by elemental analysis, IR, ESI-MS^+, 4*f*-4*f* absorption, NMR studies and Single-crystal X-ray crystallography. The complexes are highly volatile in nature.

Fig. 6. (a) Molecular structure of $[Dy(hfaa)_3(pz)_2]$.



In Chapter 7, a synthesis of nine-coordin of the type, $[Ln(hfaa)_3(tptz)]$ (Ln = La, Pr-Lu, except Pm) is described and characterized by elemental analysis, IR, ESI-MS and NMR. The band shape of hypersensitive $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ transition is distinctively different from the band shape of known typical eight- and ten-coordinate neodymium β-diketonates complexes (Fig. 7).

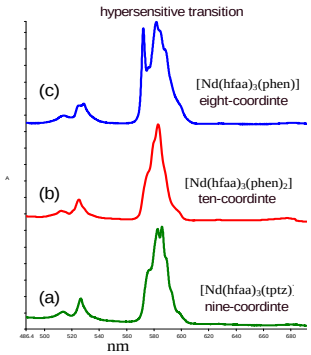


Fig.7. $^4G_{5/2}$, $^2G_{7/2}$ hypersensitive transition of (a) nine-coordinate, $[Nd(hfaa)_3(tptz)]$ (green) ; (b) ten- coordinate, $[Nd(hfaa)_3(phen)_2]$ (red) and (c) eight-coordinate, $[Nd(hfaa)_3(phen)]$ (blue) in chloroform.

In Chapter 8, the photoluminescence, 4*f*-4*f* absorption and NMR studies of nine- coordinate complexes of the type $[Ln(hfaa)_3(Hind)_3]$ (Ln = La, Pr, Nd and Sm) are described. These complexes are synthesized in a single pot and characterized by elemental analysis, IR, ESI-MS^+ and NMR studies. The low molecular symmetry of the complexes leads to intense luminescence with prominent stark splitting of the bands. The band shape of the $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ transition of neodymium is similar to that of nine-coordinate tptz complex described in chapter 7.

Fig. 8. Emission spectra of $[Sm(hfaa)_3(Hind)_3]$ in Different solvents at room temperature.