International Journal of Enhanced Research in Educational Development (IJERED)
ISSN: 2320-8708, Vol. 12 Issue 1, Jan.-Feb., 2024, Impact Factor: 8.376

Luminescence Studies of Dy (III) Complex with Acetylacetonate and a Novel Tridentate Phosphine Oxide Co-Ligand

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ABSTRACT

The present work comprises the synthesis, structural characterization and photophysical studies of a ternary Dy(III)-β-diketonate complex [Dy(acac)3PO_3)]. The primary ligand used for complexation is acetylacetone (acac), which acts as the antenna ligand. The secondary ligand used is novel chelate phosphine oxide derivative [(phenylphosphoryl)bis(methylene) bis (diphenylphosphinoxide)] which is conveniently represented as DPMPO or (PO_3) The Dy(III) complexes were structurally authenticated by EA, IR and TG analysis. The luminescence study demonstrated that the PO_3 can serve as an effective ancillary ligand for generating high luminescence performance in Dy(III)-tris(β -diketonate) complex. Thus, it can be concluded that the new complex developed during this study may find potential application in many photonic devices.

Keywords: Quantum yield, life-time, sensitization, radiative-emission, Antenna molecule, trichromic light.

INTRODUCTION

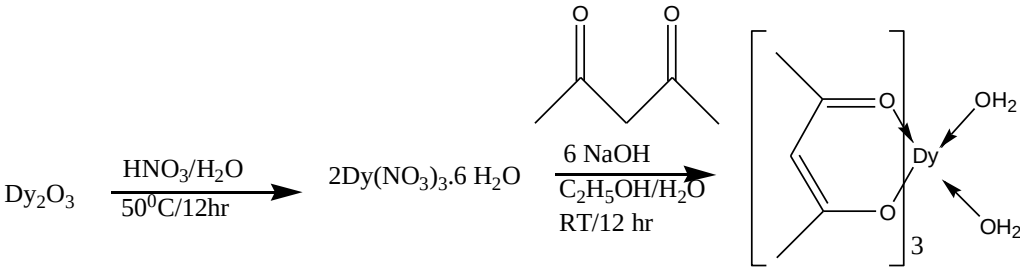
Stable complexes of trivalent lanthanide ions (Ln(III)) with wide variety of organic ligands are reported.[1] Due to their interesting magnetic and spectroscopic properties these complexes are used in many fields. It is their long lived luminescence lifetimes which increased their significance. Ln(III) ions have wide applications based on their luminescent properties. High purity inorganic materials which can emit light when exposed to excitation sources are called luminescent materials.[2] They consist of a host lattice doped with small amount of lanthanide ions which activate the luminescent host.[3] Due to the distinctive colour purity Ln ions are cited to have good photophysical properties. Dy(III), Tm(III), Sm(III) etc. doped with $GdVO_4$ crystal is a promising laser materials having strong and broad absorption band and are hence recognised as excellent materials in high power LD solid-state lasers.[4,5] Ln(III) ions are preferable candidates for developing single-molecule-magnets (SMM) with significant magnetic behaviour of which Dy(III) ions are the most studied ones.[6] The lanthanides have long excited-state lifetimes and high chromaticity and hence used in solid-state materials technologies. Therefore Ln-based materials are well suited for the production of trichromic light emissions by mixing different lanthanide ions because of the purity of the Eu(III), Tb(III), and Tm(III) red, green and blue characteristic emissions and hence are used in fluorescent tubes, multicolour displays and organic light emitting diodes (OLEDs).[7]

MATERIALS AND METHODS

Synthesis of Dy(III) complexes

1. $Dy(acac)_3(H_2O)_2]$

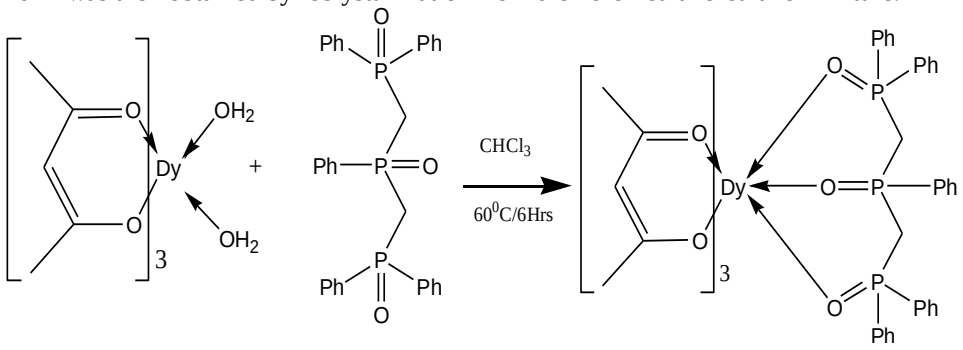
The Dy(III) complex $[Dy(acac)_3(H_2O)_2]$ was synthesised by means of the following general procedure.[8] 1 mmol of Dy_2O_3 is first converted to $[Dy(NO_3)_3.6H_2O]$ by treating it with HNO_3/H_2O (1:1) mixture at 50^0C. The excess solvent was removed by evaporation and $[Dy(NO_3)_3.H_2O]$ is dissolved in 2 ml of ethanol and was added to a solution of 6 mmol of the acetylacetone and 6 mmol of NaOH in 50 ml of ethanol along with 50 ml of water. The reaction mixture was stirred at room temperature for 12 hours. The precipitate thus obtained was filtered off, washed with water and dried in vacuo. Then, it was purified by recrystallizing from ethanol/dichloromethane (1:1) mixture. The colourless crystalline solid thus obtained was used for further analysis as well as for the photo physical studies.



Scheme 1. Synthetic procedure for the compound $[Dy(acac)_3(H_2O)_2]$

2. $Dy(acac)_3(PO_3)$

The synthetic route of the complex $[Dy(acac)3PO_3]$ is shown in scheme 2. Equimolar solutions of $[Dy(acac)_3(H_2O)_2]$ and PO_3 were stirred in $CHCl_3$ for 6 hours at 600C to yield $[Dy(acac)_3PO_3]$. The solvent was then evaporated and the product in pure form was then obtained by recrystallization from dichloromethane-ethanol mixture.[9, 10]



Scheme 2. Synthetic procedure for the complex $[Dy(acac)_3(PO_3)]$

Methods

IR spectral data were recorded on KBr (neat) disks with a Perkin-Elmer Spectrum One FT IR spectrometer. The thermogravimetric analysis were performed on a STA 6000 instrument (Perkin-Elmer).[11] It is a method of thermal analysis in which mass of the substance is measured as a function of temperature, while it is subjected to controlled temperature program.[12] Photoluminescence spectra were recorded on a Fluorolog FL 3-22 spectrometer from Horiba-Jobin Y von-Spex equipped for both visible and NIR measurements and were recorded for instrumental function.[13] Lifetime measurements were carried out at room temperature, using a Spex 1040 D phosphorimeter.[14]

RESULTS AND DISCUSSION

1.Physical nature and Structure of Complexes

Both the binary $[Dy(acac)_3(H_2O)_2]$ and ternary $[Dy(acac)_3(PO_3)]$ complexes of Dysprosium were isolated as powder. The binary complex was white in colour, whereas the ternary complex is slightly yellowish. Both the complexes were readily soluble in dichloromethane and chloroform. Molecular structures of the Dy(III) complexes are studied.

2. IR- spectroscopy

IR Spectra shows the carbonyl stretching frequency of the free ligand acetylacetone appears at νs(C=O) =1710, 1729 cm^{-1} and the value shifts to lower values 1519- 1590 cm^{-1} in the complex.[15] This variation indicates the coordination of carbonyl oxygen to the Dy(III) in the complex. The IR carbonyl stretching frequency of the free ligand acetylacetone appears at νs(C=O) =1710, 1729 cm^{-1} and the value shifts to lower values 1519- 1590 cm^{-1} in the complex. This variation indicates the coordination of carbonyl oxygen to the Dy(III) in the complex.[16]

3. Thermogravimetric Analysis

The thermal behaviour of the new Dy(III) complex $[Dy(acac)_3(PO_3)]$ was examined by means of thermogravimetric analysis (TGA). The typical thermogram of the ternary complex $[Dy(acac)_3(PO_3)]$ is explained. Thermal decomposition temperature is found to be higher than 250^0C. Subsequent thermal decomposition of the complex consist of two major steps. $[Dy(acac)_3(PO_3)]$ have higher thermal stablility and the organic matter last till 750^0C leaving a residual weight of approximately 29% of the initial mass and corresponds to the formation of Dy_2O_3.[17]

Optical Properties of the Complex

1.Excitation Studies

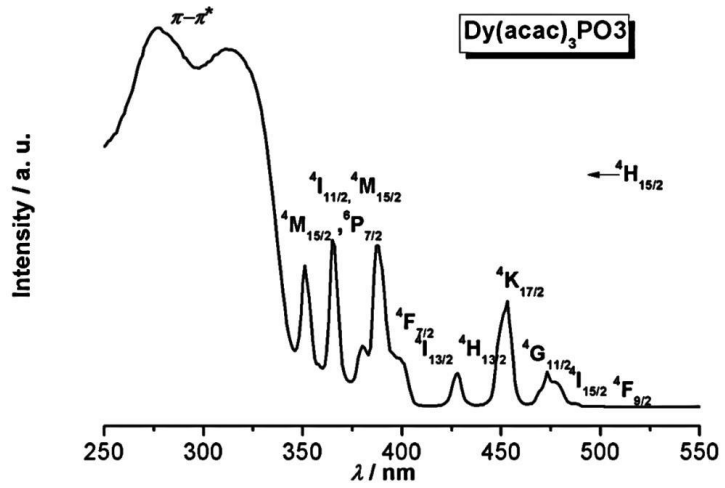


Figure. 1. Solid-state excitation spectra for the complex [Dy(acac)$_3$(PO$_3$)] with emission monitored around 576nm at 298K

The excitation spectra of Dy(III) complexes at 298K in $CHCl_3$ (c=2×10^{-5} M) is monitored around the intense $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition of Dy(III) ion emission wavelength at 576nm is shown in the figure.1 The excitation spectra consist of a broad band extending between 250 and 350 nm and a few weak lines characteristic of Dy(III) energy level structures is also seen. These transitions are weaker than the absorption of organic ligands which indicates that the luminescence sensitisation via excitation of the ligand is more efficient than the direct excitation of the Dy(III) ion absorption level. The high intensity spectrum obtained suggest the high sensitisation effect toward Dy(III) attributed by the PO_3 co-ligand.[18]

2. Emission Studies

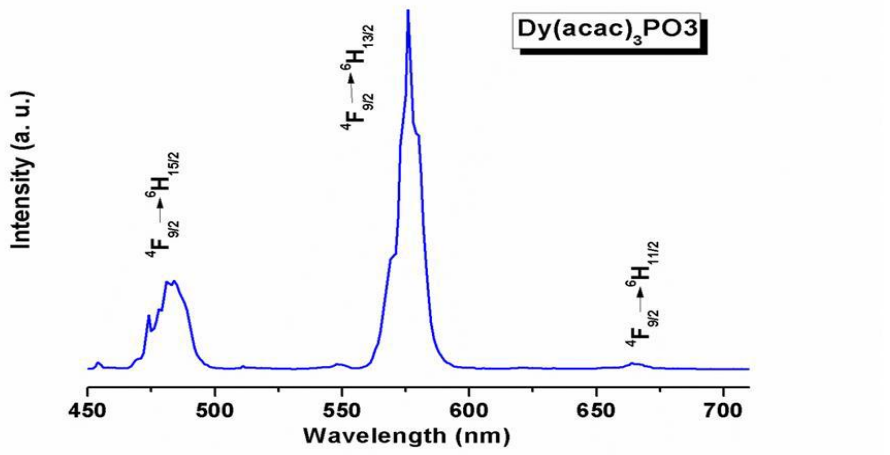


Figure. 2. Solid-state emission spectra for complex [Dy(acac)$_3$PO$_3$] at 298K (*λ*ex =315nm)

The emission spectra of Dy(III) complex in $CHCl_3$ (c=2×10^{-5} M) at room temperature under the excitation wavelength of 375nm that maximise the Dy(III) emission intensity are shown in the figure.2. The emission spectra of the complex display a characteristic sharp peak in the 475-675 nm region associated with the $^4F_{9/2} \rightarrow$6HJ transitions of the Dy(III) ion. All expected peaks for the $^4F_{9/2} \rightarrow$6HJ (where J=15/2, 13/2, 11/2) transitions are well resolved and the hypersensitive $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition is very intense, pointing to highly polarizable chemical environment around the Dy(III) ion.[19]

3. Excited State Lifetime Measurements

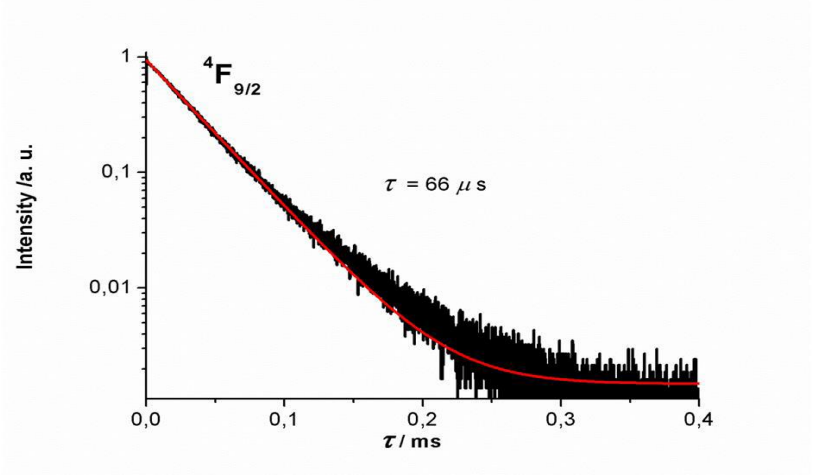


Figure.3. $^4F_{9/2}$ decay profiles in the complex [Dy(acac)PO_3] at 298K (λex=315nm and emission monitored at 576nm)

The lifetime value (τobs) of the ^{4}F9/2 level were determined by the luminescent decay profile for the complex [Dy(acac)(PO_3)] at 298K temperature by fitting with a mono-exponential curve showed a value of τobs=66 μs.[20] Typical decay profile of the complex is shown in the figure 4.6. The relatively shorter lifetime obtained for the complex may be due to dominant non-radiative decay channels associated with vibronic coupling due to the presence of solvent molecules and that is well documented for many of the hydrated Ln(III)-β-diketonate complexes. The substitution of water molecules by phosphinoxide ligand greatly enhances the lifetime of the complex.

CONCLUSION

A new Dy(III)-β-diketonate complex with a novel chelate phosphinoxide, [(phenylphosphoryl) bis(methylene) bis (diphenylphosphinoxide)] (PO_3) as co-ligand have been synthesized, characterized and investigated their photophysical properties are promising in laser materials having strong and broad absorption band and are hence recognised as excellent materials in high power LD solid-state lasers . The Dy(III) complexes were structurally authenticated by EA, IR and TG analysis. The luminescence study demonstrated that the PO_3 can serve as an effective ancillary ligand for generating high luminescence performance in Dy(III)-tris(β-diketonate) complex. Thus, it can be concluded that the new complex developed during this study may find potential application in many photonic devices.

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