

SYNTHESIS AND LUMINESCENCE PROPERTIES OF TERBIUM COMPLEX: $Tb(BMPD)_3(H_2O)_2$

¹Manju Bala, ²Satish Kumar, ³Vinod Bala Taxak, ⁴S.P. Khatkar*

¹⁻²Research Scholar, ³⁻⁴Professor

Department of Chemistry

Maharshi Dayanand University, Rohtak, Haryana 124001, India

ABSTRACT:

New luminescent terbium complex was synthesized by using β -diketonate 1,3-[bis(4-methoxyphenyl)]propane-1,3-dionato (BMPD) ligand. The formation of BMPD and its terbium complex was confirmed with the help of various techniques such as CHN elemental analysis, IR, NMR. The organic ligand absorbed the energy and transferred it to the central metal ion in an efficient manner through sensitization process which was supported by the UV-visible and photoluminescence spectroscopy. The luminescence behavior of the complex was examined in detail. The characteristic bands corresponding to $^5D_4 \rightarrow ^7F_j$ transitions of terbium ion observed in the emission spectrum of complex. Among the transitions, the most intense electric dipole transition was appeared at 545 nm which was assigned to the $^5D_4 \rightarrow ^7F_5$ transition. This prominent peak was responsible for the green color of the terbium complex. This fact further supported by color coordinates which were also located in the green region of the chromaticity diagram. These results indicated that the complex can be used as emitting material in display devices.

Keywords: IR, UV-visible, terbium ion, luminescence properties.

1. INTRODUCTION

Nowadays, the rare earth complexes are of great interest to scientist mainly due to their attractive photophysical properties which encouraged numerous applications such as luminescence materials [1], electroluminescence devices [2], luminescent probes for development of fluoroimmuno-assays [3], organic light emitting devices (OLEDs) [4] and labels in biological system [5]. The absorption of directly excited terbium ion is small, therefore, terbium ion requires coordination with suitable organic chromophore which behaves as antenna [6]. The organic ligand absorbs the excitation energy and transfers it to the emitting levels of terbium ion via sensitization mechanism. Infact, the photoluminescence intensity of complexes is controlled by the efficiency of energy transfer mechanism from ligand to central metal ion. The bidentate β -diketone ligand possesses strong absorption over a long range of wavelength and has the ability to encapsulate the terbium ion, conferring stability to complex [7]. These characteristics make the β -diketone ligand a good class of organic chromophore which meets all the requirements as described above to sensitize the luminescence of terbium ion.

In this communication, to obtain highly luminescent complex, a β -diketonate 1,3-[bis(4-methoxyphenyl)]propane-1,3-dionato ligand has been employed. The synthesized complex was characterized by various techniques. A detailed investigation of excitation and emission spectra, CIE color coordinates and decay curve has been done in order to explore the luminescence properties.

2. Experimental

High purity terbium nitrate [$Tb(NO_3)_3 \cdot 5H_2O$; 99.9%] was obtained from Sigma Aldrich. The other chemicals such as 4-methoxyacetophenone, 4-methoxybenzoyl chloride and potassium carbonate were purchased from commercial source and used as received. The ligand BMPD was synthesized adopting ecofriendly microwave approach and then recrystallized three times with DMSO to obtain ligand of high purity. Double distilled water was used through the experiments.

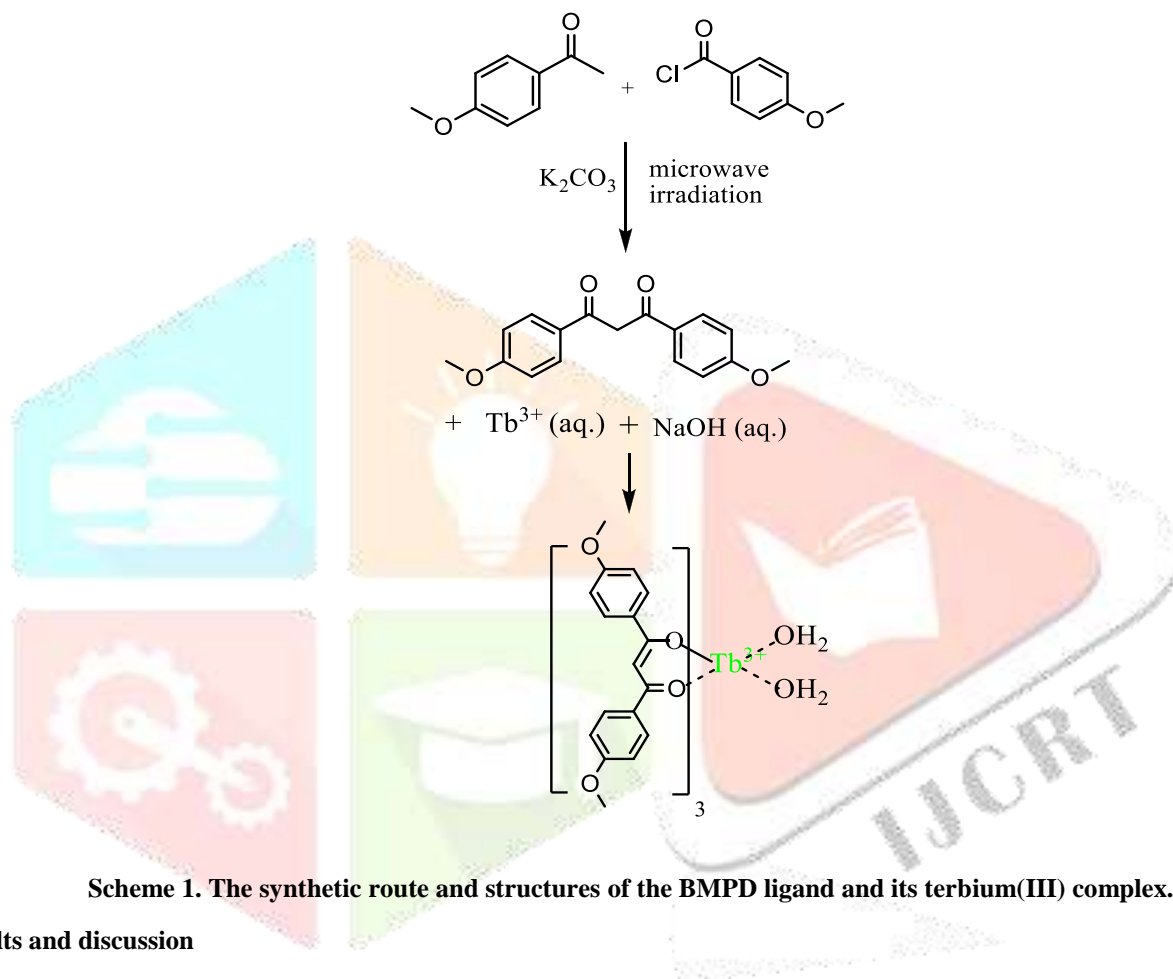
2.1 Synthesis of HBMPD ligand

A few drops of water were added in a mixture of 4-methoxyacetophenone (0.75 g, 5 mmol), 4-methoxybenzoyl chloride (0.68 mL, 5 mmol) and potassium carbonate (1.38 g, 10 mmol) to make homogenous mixture. Then, the resulting mixture was irradiated with microwave radiation for 40 s. The progress of the reaction was examined by TLC (thin layer chromatography). The crushed ice was added to the mixture and acidified with concentrated hydrochloric acid. The solid was separated out and recrystallized three times with DMSO solvent [8]. The HBMPD was obtained as yellow crystalline solid in 90% yield with 112°C melting point. IR (KBr): cm^{-1} 3480 (b), 3045 (w), 2949 (w), 1680 (s), 1597 (s), 1490 (s), 1446 (s), 1307 (s), 1251 (s), 1024 (s), 837 (s), 783 (s), 509 (m); 1H -NMR (400MHz): δ 12.07 (s, 1H, enolic OH), 7.93-6.91 (m, 8H, Ar-H), 6.83 (s, 1H, enol CH), 4.80 (s, 2H, keto- CH_2), 4.62 (s, 6H, OCH_3) ppm. Anal. Calcd for: C, 71.83, H, 5.63; found: C, 71.62; H, 5.58.

2.2 Synthesis of terbium(III) complex

An ethanolic solution of BMPD ligand (0.909 g, 3.2 mmol) was slowly mixed with the aqueous solution of terbium nitrate pentahydrate (0.43 g, 1.0 mmol). The resulting reaction mixture was stirred for 3 h at 50-60°C temperature. The pH of the mixture was adjusted to 6.0-6.5 with 0.05M aqueous NaOH solution. The slow evaporation formed yellow precipitates of terbium complex which were filtered, washed and dried in hot air oven [9].

Tb(BMPD)₃(H₂O)₂ (C1): yellow solid, yield 75%; IR (KBr): cm⁻¹ 3412 (b), 3067 (s), 3000 (s), 2934 (s), 1602 (s), 1492 (s), 1462 (s), 1426 (s), 1379 (s), 1302 (s), 1257 (s), 1226 (s), 1183 (s), 1126 (s), 1018 (s), 937 (s), 848 (s), 791 (s), 467 (m); ¹H-NMR (400MHz): δ 8.85-7.15 (m, 24H, Ar-H), 4.65 (s, 18H, -OCH₃), 3.62 (s, 3H, enol CH). Anal. Calcd for TbC₅₁H₄₅O₁₂: C, 58.62; H, 4.69; Tb, 15.22; found: C, 58.32; H, 4.48; Tb, 15.08.



Scheme 1. The synthetic route and structures of the BMPD ligand and its terbium(III) complex.

3. Results and discussion

3.1. Elemental analysis

The observed elemental analytical data of HBMPD ligand and terbium(III) complex for the carbon, hydrogen and nitrogen elements are closely approaching to calculated values, suggesting that the composition of the complex is conformed to Tb(BMPD)₃(H₂O)₂.

3.2 FT- IR and NMR spectral analysis

The binding nature of ligands to the terbium(III) ion is assessed by a comparative study of spectra of ligand and complex. In the spectrum of ligand, a broad absorption band of enolic -OH proton at 3480 cm⁻¹ noticed, which was found to be absent in the spectrum of complex, proposing the involvement of enolic -OH of ligand in coordination to the Tb(III) ion. The strong absorption band of >CO stretch at 1680 cm⁻¹ in spectrum of ligand exhibited a noticeable decrease in the >CO frequency in spectrum of complex, suggesting the coordination of ligand to the metal through >CO group of ligand [10]. This fact is further affirmed by visualizing a medium intense band of Tb-O vibration in 467 cm⁻¹ range. Similarly, in spectrum of complex the enolic C=C stretching vibrations were red shifted relative to spectrum of ligand, indicating the extension of π-conjugation in complex.

In ¹H-NMR spectra, the singlet peaks were noticed in spectrum of ligand at 12.07 ppm and 4.80 ppm, ascertaining to enolic -OH and ketonic -CH₂ protons, respectively. These signals disappeared in the spectrum of complex, suggesting that the ligand in enolic

form coordinates with the Tb(III) ion. The signal of enolic =CH proton at 6.83 ppm in the spectrum of ligand shifts to high upfield in the spectrum of complex, intends the paramagnetism of terbium ion.

3.3 UV-visible absorption spectra

Figure 1 displays the UV-visible absorption spectra of BMPD ligand and terbium(III) complex in DMSO solution (1×10^{-5} mol/L) at room temperature [11]. The UV-absorption profile of terbium complex was almost similar to the BMPD ligand absorption profile, proposing that the coordination of terbium metal ion does not affect the singlet excited level of ligand in a significant way. The maximum absorption at 360 nm was associated with the π - π^* transition of organic ligands as the terbium ion shows negligible absorption in this range.

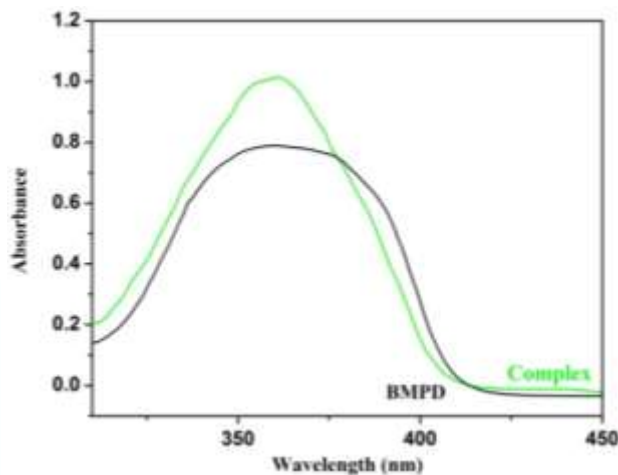


Fig. 1. The UV-visible absorption spectra of BMPD ligand and terbium complex in DMSO solvent.

3.4 Luminescence properties

The solid state photoluminescence excitation spectrum of terbium(III) complex measured at 545 nm wavelength corresponds to $^5D_4 \rightarrow ^7F_5$ intense emission transition of terbium(III) ion as depicted in Fig. 2. It consists of a broad excitation band in 280-450 nm region in which the maxima observed at 362 nm assigned to the π - π^* transitions of ligands. The strong band in 300-400 nm region reveals that the ligands are favourable for absorption of energy and transfer to the terbium(III) ion, resulting into characteristic emission bands of Tb(III) ion.

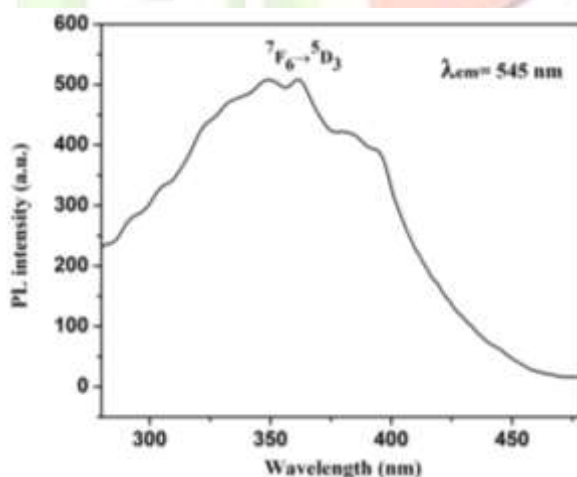


Fig. 2. The solid state excitation spectrum terbium(III) complex monitored at 545 nm.

Upon excitation at 362 nm, the photoluminescence emission spectrum of terbium(III) complex comprise of discrete bands predominantly located in 400-600 nm region corresponding to the transitions from $^5D_{3,4}$ excited levels to $^7F_{4-6}$ levels of terbium ion. Figure 3 shows three main characteristic bands at 448 nm, 490 nm and 545 nm attributed to $^5D_3 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_6$ (magnetic dipole) and $^5D_4 \rightarrow ^7F_5$ (electric dipole) transitions respectively. The peak of $^5D_3 \rightarrow ^7F_4$ transition is forbidden in both electric and in magnetic dipole field. The peak of electric dipole transition is highly sensitive to the chemical environment around the terbium ion and directs the green luminescent color of the complex. While, the peak of magnetic dipole transition is non-sensitive to the coordination

environment of terbium ion. The intensity of these transitions is controlled by local symmetry and crystal field of terbium ion. Therefore, a prominent electric dipole transition in the spectra suggests that the terbium(III) ion is located in the asymmetric coordination site of the complex.

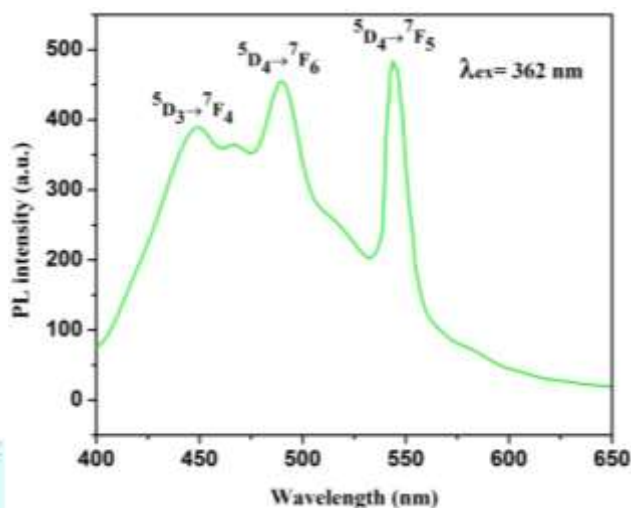


Fig. 3. The solid state luminescence emission spectrum of terbium(III) complex excited at 362 nm.

Figure 4 shows the CIE (Commission Internationale de Eclairage) chromaticity color coordinates (x and y) of terbium(III) complex estimated from the emission spectra excited at 362 nm which are located in green region of chromaticity diagram. The value of CIE coordinates are calculated as $x = 0.1932$; $y = 0.3941$ for the complex.

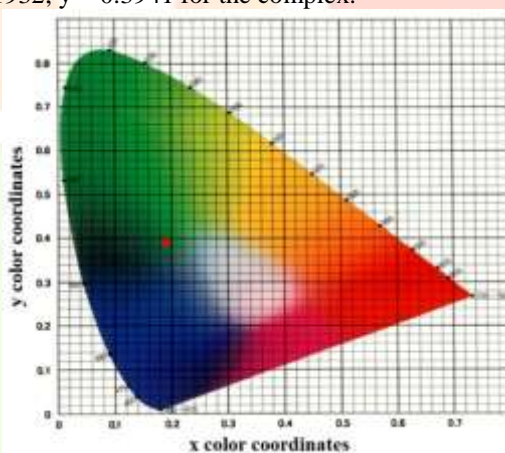


Fig. 4. The CIE color coordinates of terbium(III) complex.

In order to explore the coordination environment around central terbium(III) ion in complex, the decay curves of terbium(III) complex are obtained as depicted in Fig. 5. The luminescence decay time of 5D_4 excited level of Tb^{3+} ion in complex was recorded from the decay curves by monitoring the most intense emission peak ($^5D_4 \rightarrow ^7F_5$) at 545 nm in solid state. The decay profile of $^5D_4 \rightarrow ^7F_5$ transition obey single exponential function as $I = I_0 \exp(-t/\tau)$ where τ is the radiative decay time, I and I_0 are the luminescence intensities at time t and 0, respectively. The results of the decay curves proposed that the terbium ion is present in single chemical environment in complex.

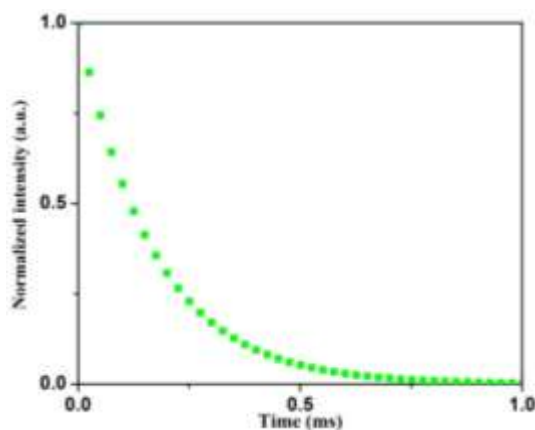


Fig. 5. The photoluminescence decay curve terbium(III) complex.

Acknowledgement

The authors are grateful for the financial support from the CSIR (Council of Scientific Industrial Research) in the form of SRF fellowship.

References

1. Parker, D., Senanayake, P.K. and Williams, J.A.G. 1998. Luminescent sensors for pH, pO₂, halide and hydroxide ions using phenanthridine as a photosensitizer in macrocyclic europium and terbium complexes. *Journal of Chemical Society Perkin Transactions 2*: 2129-2140.
2. Fu, Y.J., Wong, T.K.S., Yan, Y.K. and Hu, X. 2003. Syntheses, structures and luminescent properties of Sm(III) and Eu(III) chelates for organic electroluminescent device applications. *Journal of Alloys Compounds*, 358(1-2): 235-244.
3. Robinson, M.R., Regan, M.B. O and Bazan, G.C. 2000. Synthesis, morphology and optoelectronic properties of tris[(N-ethylcarbazolyl)(3',5'-hexyloxybenzoyl)methane](phenanthroline)europium. *Chemical Communications*, 4: 1645-1646.
4. Sheats, J.R., Antoniadis, H., Hueschen, M., Leonard, W., Miller, J., Moon, R., Roitman, D. and Stocking, A. 1996. *Organic Electroluminescent Devices*. Science, 273 (5277):884-8.
5. Li, Y. and Yang, Z.Y. 2010. Rare Earth Complexes with 3-Carbaldehyde Chromone-(Benzoyl) Hydrazone: Synthesis, Characterization, DNA Binding Studies and Antioxidant Activity. *Journal of Fluorescence*, 20(1): 329-342.
6. Niyama, E., Brito, H.F. and Cremona, M. 2005. Synthesis and spectroscopic behavior of highly luminescent Eu³⁺-dibenzoylmethanate (DBM) complexes with sulfoxide ligands. *Spectrochimica Acta, Part A*, 61 (11-12): 2643-2649.
7. Luo, Y.M., Li, J., Xiao, L.X., Tang, R.R. and Tang, X.C. 2009. Synthesis, characterization and fluorescence properties of Eu(III) and Tb(III) complexes with novel mono-substituted β -diketone ligands and 1,10-phenanthroline. *Spectrochimica Acta, Part A* 72(4): 703-708.
8. Bala, M., Kumar, S., Taxak, V.B., Boora, P. and Khatkar, S.P. 2016. Optical Features of Efficient Europium(III) Complexes with β -diketonato and Auxiliary Ligands and Mechanistic Investigation of Energy Transfer Process. *Journal of Fluorescence*, 26: 1813-1823.
9. Bala, M., Kumar, S., Taxak, V.B., Boora, P. and Khatkar, S.P. 2016. Terbium(III) complexes sensitized with β -diketone and ancillary ligands: Synthesis, elucidation of photoluminescence properties and mechanism. *Journal of Material Science: Materials in Electronics*, 27: 9306-9313.
10. Sareen, V. and Gupta, R. 1996. Studies in fluorinated 1,3-diketones and related compounds. Part XVIII. Synthesis of some new tris(1,3-diketonato)lanthanide complexes. *Journal of Fluorine Chemistry*, 76(2):149-150.
11. Biju, S., Ambili Raj, D.B., Reddy, M.L.P. and Kariuki, B.M. 2006. Synthesis, Crystal Structure, and Luminescent Properties of Novel Eu³⁺+Heterocyclic β -Diketone Complexes with Bidentate Nitrogen Donors. *Inorganic Chemistry*, 45(26) 10651-10660.