Preparation and photoluminescence enhancement in terbium(III) ternary complexes with β-diketone and monodentate auxiliary ligands

Devender Singh1*, Kapoor Singh1§, Shri Bhagwan1§, Raman Kumar Saini1, Ritu Srivastava2 and Ishwar Singh1*

Abstract: A series of new solid ternary complexes of terbium(III) ion based on β-diketone ligand acetylacetone (acac) and monodentate auxiliary ligands (aqua/urea/triphenylphosphineoxide/pyridine-N-oxide) had been prepared. The structural characterizations of synthesized ternary compounds were studied by means of elemental analysis, infrared (IR), and proton nuclear magnetic resonance (NMR) spectral techniques. The optical characteristics were investigated with absorption as well as photoluminescence spectroscopy. Thermal behavior of compounds was examined by TGA/DTA analysis and all metal complexes were found to have good thermal stability. The luminescence decay time of complexes were also calculated by monitoring at emission wavelength corresponding to \(^{5}D_{4} \rightarrow ^{7}F_{5}\) transition. A comparative inspection of the luminescent behavior of prepared ternary compounds was performed in order to determine the function of auxiliary ligands in the enhancement of luminescence intensity produced by central terbium(III) ion. The color coordinates values suggested that compounds showed bright green emission in visible region in electromagnetic spectrum. Complexes producing green light could play a significant role in the fabrication of efficient light conversion molecular devices for display purposes and lightning systems.

Subjects: Engineering & Technology; Material Science; Physical Sciences

Keywords: ternary terbium(III) complexes; acetylacetone; auxiliary ligands; photoluminescence

ABOUT THE AUTHORS

Devender Singh is presently working as an assistant professor (Stage-III) of Chemistry, Maharshi Dayanand University, Rohtak, Haryana. He has completed his MSc (2001) and PhD(2005) in inorganic chemistry under the supervision of Ishwar Singh and Sang Do Han (KIER, S. Korea) from the Maharshi Dayanand University, Rohtak, India. His current research interest focuses on light-emitting materials and their fabrication for optoelectronic display applications. He has published more 55 research papers in well-reputed international journals. Presently, he is a principal investigator for the major research project funded by the University Grant Commission, New Delhi.

PUBLIC INTEREST STATEMENT

Terbium complexes prepared with diketones and neutral ancillary ligands have attracted interest due to their enhanced optoelectronic characteristics. These Tb-complexes have proficient emission of green light under the UV excitation source. Commonly all the key colors are essential for the making of the full color. These synthesized complexes of terbium emit bright green luminescence (543–544 nm) that could be efficiently used for the generation of light for the various electronic display devices.

© 2016 The Author(s). This open access article is distributed under a Creative Commons Attribution (CC-BY) 4.0 license.
1. Introduction
Lanthanide ions, particularly Eu³⁺ and Tb³⁺, are potential candidates among more conventional used organic fluorophores, because of their sharp emission upon irradiation with ultraviolet light, long fluorescence lifetime, and large Stoke’s shift (Binnemans, 2009; Bunzli & Piguet, 2005; Kido & Okamoto, 2002). All of these unique photophysical properties of Ln³⁺ ions arise due to intra-configurational 4f transitions. In current years, extensive attention has been paid on the examination of the optical characteristics of Ln³⁺ complexes due to their wide-ranging applications as in efficient light conversion molecular devices (LCMDs) (Pavithran et al., 2006), optical signal amplification (Kuriki, Koike, & Okamoto, 2002), luminescent sensors (dos Santos, Harte, Quinn, & Gunnlaugsson, 2008) luminescent probes (Hemmila & Laitala, 2005), etc. However, Laporte-forbidden f-f electronic transitions make direct excitation of electron in lanthanide ion inefficient due to its intrinsically low absorption cross-section resulting in weak luminescence. In order to conquer this problem, design of highly efficient lanthanide complexes with organic ligand (Armelao et al., 2010; Bazzicalupi, Bencini, & Bianchi, 2000) which serves not only as an antenna or sensitizer but also shielding the lanthanide(III) ion from vibrational coupling and increasing the amount of light absorption referred to as “antenna effect” (Driesen, Deun, Gorller-Walrand, & Binnemans, 2004; Sabatini, Guardigli, & Lehn, 1993) is highly preferred. The main ligands include macrocyclic ligands (Beeby, Dickins, Faulkner, Parker, & Williams, 1997; Sabatini et al., 1995), carboxylic acid derivatives (An, Gong, Li, Zhang, & Cheng, 2005; Xi, Gu, Chen, He, & Huang, 2007), heterobiaryl ligands (Mikola, Takkalo, & Hemmila, 1995; Sa, Nunes, & Choppin, 1993), β-diketones (Shi et al., 2013), pyridines (Song, Zheng, Liu, & Ju, 2008; Yip, Wen, Song, & Wong, 2012), 1,10-phenanthroline (Liu, Hu, Wang, & Su, 2009; Lv, Zhang, Cao, & Fu, 2009) etc. Among all of these, β-diketone ligands have strong absorption within a large UV range for their π-π* transition, high luminescence quantum efficiency (Melby, Rose, Abramson, & Caris, 1964; Yang, Srdanov, Robinson, Bazan, & Heeger, 2002), and also proved to be one of the significant “antennas” which successfully transmit the energy intra-molecularly from the coordinated ligands to the metal ion through radiative process.

Indeed, conventional synthesis usually yields bis (hydrated)tris(β-diketonates). When O–H groups are coordinated to Ln³⁺ ion, efficient nonradiative decay takes place by high frequency vibrational modes of O–H oscillator, leads to weak absorption. In addition, emission intensities and luminescence lifetime of complexes are enhanced, when an additional neutral ancillary ligand in place of aqua ligand coordinates with the coordinatively unsaturated central metal cation (Ahmed & Iftikhar, 2010; Irfanullah & Iftikhar, 2009; Zucchi et al., 2010). Additionally, to our knowledge, reports describing the luminescent behavior of lanthanide β-diketonates using monodentate auxiliary heterocyclic ligands are still rare.

Therefore, to bridge gap, in this communication, we have prepared ternary terbium(III) compounds of acetylacetone (acac) with heteroaromatic monodentate auxiliary ligands having oxygen (O) as donor atoms. Ln³⁺ ions being hard Lewis acids, preferred to bind with O-donors atom which makes them best for the design of efficient light-emitting materials because of high bond-valence contribution of the oxygen donor atom towards 4f orbital mixing.

2. Experimental section
2.1. Materials and methods
The following available chemicals were used without any additional refinement: acetylacetone, ≥99% (Aldrich); terbium(III) chloride hexahydrate, 99.9% (Aldrich); urea, 98% (Aldrich); triphenylphosphineoxide, 99% (Acros Organics); pyridine N-oxide, 95% (Acros Organics). All other chemicals used were of analytical reagent (AR) grade. The elemental analysis of carbon, hydrogen, and nitrogen were detected on Elemental Analyzer Perkin Elmer 2400 CHN. A Bruker Avance 400 MHz nuclear magnetic resonance (NMR) spectrometer used to record proton NMR spectrum in CDCl₃, solvent, showed the peaks at the different chemical shift (δ) values with respect to tetramethylsilane as an internal standard. Perkin Elmer 5700 FTIR spectrometer was used to obtain the IR spectrum in KBr pellet to obtain infrared spectral data in the range of 4,000–400 cm⁻¹. Thermal analyses TGA/DTA
were carried out using STA 7300 Hitachi Thermal Analyzer. Absorbances of ternary terbium(III) complexes in tetrahydrofuran (THF) were recorded with a UV-vis spectrophotometer Shimazdu UV-2450.Photoluminescence spectra were measured using spectrophotometer Horiba Jobin YVON Fluorolog Model FL-3-11 equipped with Xenon lamp (450 W) as the source of excitation. The decay time values of the complexes were calculated in solid powder form.

2.2. Synthesis of Tb(acac)₃·(H₂O)₂
An aqueous solution of TbCl₃·6H₂O (0.187 g, 0.5 mmol) was added dropwise to a solution of ammonium salt of acetylacetone (0.150 g, 1.5 mmol). Complexation took place instantly, and the mixture was stirring continuous on magnetic stirrer for 12 h at room temperature as shown in Scheme 1. The reaction mixture was maintained at pH 6 throughout the progress of the reaction. The crystalline precipitate, thus formed was filtered and washed several times with deionized water to remove excess free ligand and stored in desiccator containing P₄O₁₀. The crude product was then purified by recrystallization. The recrystallized product dried in vacuum over P₄O₁₀ for several days.

Scheme 1. Synthetic route of tris(acetylacetone)diaqua terbium(III) complex.

Scheme 2. Synthetic route for complexes 2–4.
2.3. Synthesis of complexes 2–4

Synthetic route of complexes (2–4) is shown in Scheme 2. All ternary compounds were synthesized by the same procedure as stated in the synthesis of complex 1. Furthermore, a solution of \([\text{Tb}(acac)_3(H_2O)_2]\) (1.1 mmol) in acetone was refluxed with a solution of monodentate ancillary ligands such as urea (4.0 mmol)/ triphenylphosphine oxide (4.0 mmol)/pyridine-N-oxide (4.0 mmol) in acetone for 20 min with continuous stirring. The solution was cooled and refrigerated for 16 h. The white powder was filtered off and dried in vacuo. The prepared ternary complexes were characterized with useful analytical techniques such as elemental analysis, FTIR, NMR and the absorption as well as photoluminescence spectra.

3. Results and discussion

3.1. Elemental analysis and \(^1\)H NMR

The analytical contents of carbon, hydrogen, nitrogen, and values of \(^1\)H NMR chemical shifts in ppm (\(\delta\)) of all prepared (1–4) compounds are listed in Table 1. The outcome of elemental analysis clearly indicated satisfactory agreement between calculated and experimental CHN values for all the prepared complexes and observed values also implied the exclusion of water molecules from complexes (2–4). The \(^1\)H-NMR spectra of complexes exhibits a strong sharp resonance at 1.78–1.86 ppm (\(\delta\)) which integrates for 18 protons and has been assigned to the methyl (–CH\(_3\)) group of the acetylacetone (acac) ligand moieties. The multiplet signal of aromatic protons in ancillary ligands is shifted down field in the spectra of complexes. A strong singlet at 3.39–3.47 ppm (\(\delta\)) integrating for methine (–CH) protons which is shifted to upfield in complexes, indicates the large paramagnetic magnetic nature of lanthanide ion (Wang, Zheng, Fan, Zheng, & Wei, 2012).

3.2. FTIR spectra

The important IR characteristics frequencies of complexes (1–4) are listed in Table 2 which showed detailed absorption frequencies for the synthesized metal complexes. The IR spectral data of

| Table 1. \(^1\)H NMR and elemental analysis of ternary Tb(III) complexes |
|---|---|---|---|---|
| S. No. | Molecular formula | Experimental values | Calculated values | NMR data |
| 1 | Tris(acetylacetonato) diaqua terbium(III) \([\text{Tb}(acac)_3(H_2O)_2]\) | TbC\(_{15}\)H\(_{25}\)O\(_8\) | C = 34.99; H = 3.97 | 1.86 (s, 18H), 3.42(s, 3H). |
| 2 | Tris(acetylacetonato) diurea terbium(III) \([\text{Tb}(acac)_3{(NH_2)2CO)]_2\) | TbC\(_{17}\)H\(_{29}\)F\(_9\)O\(_8\)N\(_4\) | C = 34.16; H = 4.32; N = 8.27 | 1.83 (s, 18H), 3.39(s, 3H), 4.23(d, 8H). |
| 3 | Tris(acetylacetonato) bis(triphenylphosphine oxide) terbium(III) \([\text{Tb}(acac)_3{(C_6H_5)3PO}]_2\) | TbC\(_{51}\)H\(_{51}\)F\(_9\)O\(_8\)P\(_2\) | C = 58.83; H = 4.92 | 1.86 (s, 18H), 3.42 (s, 3H), 7.45 (d, 6H), 7.17 (t, 6H), 7.18 (t, 3H). |
| 4 | Tris(acetylacetonato) bis(pyridine-N-oxide) terbium(III) \([\text{Tb}(acac)_3{(C_5H_5NO}]_2\) | TbC\(_{25}\)H\(_{31}\)O\(_8\)N\(_2\) | C = 45.56; H = 4.58; N = 4.29 | 1.83 (s, 18H), 3.39 (s, 3H), 7.49 (d, 4H), 6.84 (t, 4H), 6.61 (t, 2H). |

| Table 2. Important characteristics IR bands (cm\(^{-1}\)) of the ternary terbium(III) complexes 1–4 |
|---|---|---|---|---|---|---|
| Complexes | \(v(O\text{–H})\) | \(v(CH_3)\text{ sym.}\) | \(v(CH_3)\text{ asym.}\) | \(v(C=O)\) | \(v(Tb-O)\) | Other peaks |
| 1 | 3,451 (b) | 2,960 (s) | 2,872 (s) | 1,612 (s) | 483 (m) | – |
| 2 | – | 2,962 (s) | 2,872 (s) | 1,605 (s) | 485 (w) | 3350 (s) |
| 3 | – | 2,963 (s) | 2,874 (s) | 1,606 (s) | 487 (m) | 1,169 (s) |
| 4 | – | 2,961 (s) | 2,873(s) | 1,610 (s) | 491 (m) | 3,087 (s) |

Notes: (b) = broad, (s) = strong, (m) = medium, (w) = weak.
complex 1 shows a broad absorption band at 3,451 cm\(^{-1}\), representing the presence of water molecules in the complex. However, the absence of the broad band for complexes (2–4) suggests that water molecules had been replaced by the monodentate ancillary ligands. Two strong absorption bands at ~2,960 cm\(^{-1}\) and ~2,872 cm\(^{-1}\) indicated asymmetric and symmetric stretching of –CH\(_3\) group. There were no marked changes in the C–H stretching of methyl group in the spectra of complexes, indicating that –CH\(_3\) group was not involved in the coordination with central ion. Two absorption bands due to C–H in plane bending vibrations also appeared at 1,460 and 1,380 cm\(^{-1}\). The shift in stretching frequency of >C=O (carbonyl) group from 1,720 to 1,612–1,605 cm\(^{-1}\) confirmed the coordination between and Tb(III) ion carbonyl oxygen. A sharp broad band at 3,350 cm\(^{-1}\) and peak at 1,670 cm\(^{-1}\) was due to N–H and C–O bond stretching of urea. A sharp peak at 1,169 cm\(^{-1}\) is due to P–O stretching of triphenylphosphine oxide. The absorption at 3,087 cm\(^{-1}\) stretching vibration was consistent with C–H stretching vibration of pyridine ring. The absorption in the range of 491–485 cm\(^{-1}\) corresponds to Tb–O stretching vibrations in the spectra of complexes.

The prepared complexes reveal an analogous thermal behavior which is consistent with one-step weight loss that reflects the whole evaporation of the complexes without dissociation. The thermogram of complex 3 as representative complex as shown in Figure 1, a minor weight loss (1.37%) between 105 and 214°C, indicates elimination of enduring wetness present in the complex. Also, shows a major weight loss (85.96%) up to 458°C.

The differential scanning calorimetry of the complexes shows three endothermic peaks, a small peak at lower temperature around ~64°C indicating loss of moisture, a broad peak at ~135°C corresponds to melting point of the complex followed by a third another small peak at higher temperature (211°C) reliable with complete evaporation of the compounds. The volatile nature and very high thermal stability of these complexes makes them valuable precursors for their use in the fabrication efficient functional display devices.

### 3.4. UV–visible and photoluminescence spectra

A comparative study of the excitation absorption bands and characteristics emission peak of all prepared ternary terbium(III) complexes is summarized in Table 3 and shown in Figures 2 and 3, respectively. The UV–visible absorption spectra of tris(acetylacetonato) diaqua terbium(III) complex and the complexes (2–4) with different auxiliary oxide ligands were recorded in THF (1 × 10\(^{-5}\) mol/L) solvent at room temperature.
The synthesized metal complexes showed absorption peaks principally due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions. Under excitation of these wavelengths metal complexes show bright green luminescence in the visible region. Appearance of a broad intense band in absorption spectra indicated an efficient transfer of energy from ligand to metal, thereby indicating the transition was...
ligand-centered excited states. The change of excitation wavelength and its intensity cannot much influence the position of characteristics strong emission band due to \( ^{5}D_{4} \rightarrow ^{7}F_{j} \) transition of \( \text{Tb}^{3+} \) ion, but it would influence relative intensity of emitted light. The solid ternary \( \text{Tb(III)} \) complexes (1–4) upon excitation with energized \( \pi-\pi^{*} \) ultraviolet radiation exhibit the characteristics line emission. Luminescence in metal complexes was generated by the transfer of excitation energy through the triplet energy level of ligands to metal ion in the excited state. Also, no emission from the ligands in the prepared complexes was observed, indicating that photon captured by the \( \beta \)-diketone ligand was proficiently transferred to terbium(III) ion, so that ternary complexes showed intense and characteristic emission peaks corresponding to \( (^{5}D_{4} \rightarrow ^{7}F_j, j = 3–6) \) transitions.

The emission band corresponding to \( ^{5}D_{4} \rightarrow ^{7}F_{5} \) transition of terbium(III) complexes is markedly highly intense than the other transition. The luminescence decay profile of \( ^{5}D_{4} \) level of metal ion corresponding to (1–4) complexes as shown in Figure 4 was investigated by monitoring emission wavelength corresponding to \( ^{5}D_{4} \rightarrow ^{7}F_{5} \) transition. The decay time values of all prepared complexes were calculated in powder form, tabulated in Table 3. The decay graph for these compounds obey a first-order exponential decay which can be represented as \( I = I_{0} \exp(-t/\tau) \), where \( I_{0} \) and \( I \) are the luminescence intensities at time 0 and \( t \), respectively, and \( \tau \) is the radiative decay time, suggesting that only uniform chemical environment around the terbium(III) ion.

The Commission Internationale d’Eclairage color coordinates value of terbium(III) complexes were at \( x = 0.45, y = 0.24 \) for complex (1), \( x = 0.48, y = 0.22 \) (2), \( x = 0.54, y = 0.29 \) (3), and \( x = 0.57, y = 0.25 \) (4), as shown in Figure 5 which clearly revealed that the coordinates for all prepared Tb complexes were found in pure green region. These results revealed the emission of bright green light with high luminescence quantum yield.

The optical band gap was calculated from excitation spectrum and shown in Figure 6. The optical band gap energy for different complexes of terbium(III) was found to be \(~3.88 \text{ eV}\). These above results helps that the synthesized metal complexes can be properly used as light-emitting material for optoelectronic applications.

### 3.5. Density functional theory calculations

The optimization of molecular structures and the computation of electron density distribution in terms of their frontier molecular orbitals (FMOs) were performed by B3LYP correlational functional and 6-31G (d,p) basis set. All of the calculations were carried out with the Gaussian package. The
FMOs are principally dominated by the orbitals originating from those of the ligand in the complex and contribution from the lanthanide ion appears to be very small. The minimal energy three-dimensional structures, selected MOs such as HOMO – 1, HOMO, LUMO, LUMO + 1, and the numerical values of energies of all selected FMOs in eV are shown in Figure 7. The finding of optical band gap was supported by the density functional theory (DFT) calculation of the FMOs and the HOMO–LUMO gap at DFT/B3LYP/6-31G (d,p) studies.

4. Conclusions
In detail, a series of ternary terbium(III) complexes had been synthesized and were spectroscopically characterized. The room temperature photoluminescence spectral measurement indicated that β-diketone could successfully sensitize the lanthanide ion. Luminescence studies of these complexes also indicated that binding of the “antenna” ligands to lanthanide ion developed a strong absorption of the ligand in the UV region and an efficient energy transfer from the ligands to the central Tb(III) ion. In all the prepared complexes of terbium(III), the complexes prepared with pyridine-N-oxide showed highest photoluminescence intensity. Sublimed synthesized metal complex gave bright green light under the UV source which could be efficiently used for various potential applications and could play a significant role in the design of high-performance LCMDs.
Figure 7. Optimized 3D molecular geometry, molecular orbital surfaces (0.05 e au⁻³) and energies (in parenthesis, eV) of the selected FMOs of ternary terbium(III) complexes.

| Complex          | LUMO+1     | LUMO       | HOMO       | HOMO-1     |
|------------------|------------|------------|------------|------------|
| Tb(acac)₃·(H₂O)₂ | (-1.59 eV) | (-2.87 eV) | (-4.89 eV) | (-5.41 eV) |
| Tb(acac)₃·(H₂NCONH₂)₂ | (-1.61 eV) | (-2.90 eV) | (-5.03 eV) | (-5.59 eV) |
| Tb(acac)₃·{(C₆H₅)₃PO}₂ | (-1.78 eV) | (-2.94 eV) | (-5.13 eV) | (-5.84 eV) |
| Tb(acac)₃·(C₅H₅NO)₂ | (-1.89 eV) | (-3.02 eV) | (-5.24 eV) | (-5.98 eV) |

Acknowledgment
The authors are thankful to the Maharshi Dayanand University, Rohtak, for providing them necessary facility for carrying out this research work.

Funding
The authors received no direct funding for this research.

Author details
Devender Singh¹
E-mail: devjakhar@gmail.com
ORCID ID: http://orcid.org/0000-0002-2180-5049
Kapoor Singh¹
E-mail: kchahar1962@yahoo.com
Shri Bhagwan¹
E-mail: chmshris25@gmail.com
Raman Kumar Saini¹
E-mail: ramsansain07@gmail.com
Ritu Srivastava²
E-mail: ritu@mail.nplindia.org
Ishwar Singh¹
E-mail: ishsingh@rediffmail.com

¹ Department of Chemistry, Maharshi Dayanand University, Rohtak 124001, Haryana, India.
² Center for Organic Electronics, OLED Lab, National Physical Laboratory, New Delhi 110012, India.

These two authors contributed equally to this work.

Citation information
Cite this article as: Preparation and photoluminescence enhancement in terbium(III) ternary complexes with β-diketone and monodentate auxiliary ligands, Devender Singh, Kapoor Singh, Shri Bhagwan, Raman Kumar Saini, Ritu Srivastava & Ishwar Singh, Cogent Chemistry (2016), 2: 1134993.

References
Ahmed, Z., & Ifikhar, K. (2010). Solution studies of lanthanide (III) complexes based on 1,1,1,5,5,5-hexafluoro-2,4-pentanedione and 1,10-phenanthroline Part-I: Synthesis, ¹H NMR, 4f-4f absorption and photoluminescence.
