Synthesis, Characterization, And Luminescent Properties Of Europium(III) And Terbium(III) Complexes With Bis-Piperazine Dithiocarbamate Ligand

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Abstract

In this study, we report the synthesis and comprehensive characterization of europium(III) and terbium(III) chelates incorporating a bis-piperazine dithiocarbamate ligand. These lanthanide complexes were prepared through a straightforward coordination process under mild conditions and characterized using elemental analysis, FT-IR, UV–Vis spectroscopy, thermogravimetric analysis (TGA). Photoluminescence studies revealed strong, characteristic emissions from Eu^{3+} and Tb^{3+} centers, with high quantum yields of 38.7% and 44.2%, respectively. The complexes exhibited long-lived excited-state lifetimes, with decay times of 1.85 ms for Eu^{3+} and 2.23 ms for Tb^{3+}. Thermal analysis demonstrated that all complexes remained stable above 250 °C. These findings highlight the significant role of the bis-piperazine dithiocarbamate ligand in enhancing the sensitization and luminescent efficiency of lanthanide centers. Overall, the synthesized complexes show great potential as functional luminescent materials for applications in sensing, optoelectronics, and bioimaging.

Keywords: *Lanthanide complexes, Dithiocarbamate ligand, Europium(III), Terbium(III), Luminescence*.

1. Introduction

Lanthanide complexes with luminescent properties have significant attention due to their potential uses in various fields, including fluorescent labeling, bioimaging, and organic light-emitting diodes (OLEDs) [1-3]. Europium (Eu^{3+}) and Terbium (Tb^{3+}) complexes typically exhibit strong luminescence, but their emission efficiency is heavily influenced by the selection of organic ligands [4]. Dithiocarbamato group has emerged as one of valuable structural component of sulfur-containing ligands. Dithiocarbamate generally facilitates the metal-directed assembly of various structures, including nanosized resorcarene based compounds, catenanes, cryptands, etc [5]. The small bite angle of the dithiocarbamato ligand is suitable for stabilizing a variety of oxidation states in various metal ions [6]. Various applications of dithiocarbamates were found across various industries, serving as essential components in rubber vulcanization, lubrication under high pressure, and as effective agents in agricultural products for pest control [7-9]. They also play an important role in biomedical research, against HIV [10]. Dithiocarbamates also serve as molecular precursors in Chemical Vapor Deposition (CVD) processes [11-14]. Water-soluble dialkyldithiocarbamate complexes have

been used for their potential applications in various medical contexts [15-22]. Piperazine is introduced as a fundamental building block for creating new supramolecular structures, due to the presence of two weakly bound terminal amino protons [23-25].

Lanthanide complexes especially of europium (Eu^{3+}) and terbium (Tb^{3+}) have been of relatively recent interest due to their outstanding luminescent behavior that provides sharp and narrow emission bands, having long-lived excited states and high quantum yields. These properties make them fit for use in various applications such as luminescent probes for bioimaging, optoelectronic devices, and sensors. The enhancement of luminescence efficiency of these lanthanide ions should be mentioned, since they are weakly emitting by themselves. Specifically, one of the effective ways to bring about this improvement is through ligand design where the geometry of the ligand not only coordinates the metal centre but also transfer energy from the ligand to the metal ion so that the luminescence efficiency of the complex is enhanced. One of the significant characteristics of this work is the use of bis-piperazine dithiocarbamate ligands in the study of lanthanide coordination chemistry. This ligand system has preliminary data in supporting and boosting. Positive photophysical characteristics of the lanthanide ions by serving as a sensitizer. The ability of bis-piperazine dithiocarbamates to act as sulfur and nitrogen donor is believed to enable the energy transfer process to the metal center so as to improve on the quantum yield and luminescence lifetime.

As a consequence, this work aims at the preparation of europium(III) and terbium(III) complexes with bispiperazine dithiocarbamate. It is planned to examine the stability and structure of these complexes, by using various methods of characterization such as elemental analysis, FT-IR, UV-Vis spectroscopy, thermogravimetric analysis (TGA) and a single crystal X-ray diffraction. Moreover, spectroscopic characterization that considers the fluorescence spectra of the complexes will be analyzed in a bid to determine the feasibility of theses complexes to be used as functional luminescent materials.

This research aims at contributing to the design and photophysical properties determination of these Eu^{3+} and Tb^{3+} complexes to enable their efficient use in various sensing, optoelectronic and bioimaging applications. Lanthanide complexes are interesting for the photochemical applications because they provide sharp emission spectra and high luminescence quantum yields, as well as long lifetimes of the excited states. These properties make them very suitable to be used in different applications for instance bioimaging, optoelectronics and sensing [26-28]. There are two luminiscent ions among the lanthanide ions, these are europium(III) and terbium (III) ions, which show highly intense emission light, the emission light intensity of the ligands can be increased by selecting proper ligands for the energy transfer to the metal ions [29]. Among these ligands, bis-piperazine dithiocarbamate has been considered to enhance the efficiency of these lanthanide complexes as it could provide better coordination to the metal ion and stablize the metal ligand complex as pointed out by Li et al. [30].

The coordination of bis-piperazine dithiocarbamate ligands with Ln(III) in the early periods has been scarce but now there is a show of interest in other dithiocarbamate systems[31-32] .Such ligands are considered to promote effective energy transfer from the ligand to the metal center thus increasing the

luminescence intensity. With regard to this, Patel and Sharma [33] studied about luminescent characteristics of bis-piperazine dithiocarbamate complexes of Eu(III) including their structural and optical studies. Moreover, Chen and Zhang [34] investigated energy transfer mechanisms concerning Eu(III)/Tb(III) dithiocarbamate complexes, which focuses much importance on ligand design for enhancing luminescence properties. Of course, bis-piperazine dithiocarbamate bases are thus promising precursors for such ligands; however, there are many works that still use β-diketonate bases, they are still effective though limited in flexibility along with stability under severe conditions [35]. Actually, few literature reports are known with bis-piperazine dithiocarbamate ligands in lanthanide coordination chemistry which is an area of nascent research interest. Fedin et.al [36] focused on the features of the single-molecule structure of complexes with lanthanides that contribute to their luminescent properties. In this research paper, the bis-piperazine dithiocarbamate ligand is used and therefore, will present an assessment of the structural characteristics and photophysical properties of Eu(III) and Tb(III) complexes. It suggested that this research may pave the way to the future of more sophisticated luminescent materials in terms of thermal and chemical properties [37]. One of the important tasks in a research of lanthanide luminescence is the creation of the new materials which can be luminescent and active in complicated settings, including the biological solutions. Some research have been carried out for understanding the behavior of complexes with bio molecules and how particular ligand can enhance the bio compatibility and efficiency for imaging purposes[38-39]. This offers a chance to go beyond the mere application of bis-piperazine dithiocarbamate complexes as luminescence materials and employ them to sensing and bioimaging. This paper will discuss the luminescence and stability of bis-piperazine dithiocarbamate ligands with Eu(III) and Tb(III) to enhance its capability in optoelectronics and bioimaging applications. Despite significant advances in the synthesis of a variety of lanthanide-based luminescent materials, efficient lanthanide complexes have yet not been synthesised for operation under different conditions of temperature and in presence of complex biological systems. Most of related research has focused on the action of different Lanthanide ions or simple ligands. But, they have short quantum yields or thermal stability, which is not suitable for any practical application especially in optoelectronic devices and bioimaging. This problem arises because most of the reports till now have been reporting the use of single donor ligands or simple chelates thereby restricting their applicability as well as tunability for applications.

As it has been demonstrated in the recent past, bis-piperazine dithiocarbamate ligands may improve the stability and fluorescent characteristics of metal complexes, although their role in the lanthanide coordination reaction has not been studied in detail. The use of these ligands in forming the europium(III) and terbium(III) complexes, especially bearing the prospect of enhancing the luminescence property, is considered as a novel strategy. In addition, the literature also indicated that the enhancement of the energy transfer from the ligand to the metal center is very prospective for the improvement of photoluminescent properties of the lanthanide complexes. In addition, few literatures concern the effects of the structural constitution of bis-piperazine dithiocarbamate ligands on the photoemission and stability of lanthanide complexes. As of today, the potential and application of bis-piperazine dithiocarbamate ligands in the coordination chemistry of

lanthanides and their influence on the luminescence of Eu^{3+} and Tb^{3+} complexes are poorly investigated. To address this issue, this work intends to synthesise these new complexes, to fully characterise them, and to examine their photochemical properties under various circumstances.

This study is based on the assumption that bis-piperazine dithiocarbamate ligand not only links the lanthanide censored but also effectively sensitises the energy to Eu^{3+} and Tb^{3+} ions for improved photophysical properties. By extension of the novel Eu^{3+} and Tb^{3+} complexes with this ligand, we determine how the sulfur and nitrogen ligand scaffold affects both the coordinative stability and emissive output of the subsequently generated materials.

2. Experimental Methods:

Synthesis of ligand 2(a): The chemicals and solvents used during the whole investigation are *AR* grade. Solvents were purified by using standard procedures [40] .Europium (III) chloride was purchased from *Sigma-Aldrich* and Terbium (III) chloride was purchased from *Alfa-Aesar*. Bis-piperazine dithiocarbamate ligand (Bis-PDTC) have been synthesized by the method of S. Khan *et al*. [41]. An ethanolic solution (20 cm^3) of piperazine hexahydrate (0.03 mol), carbon disulfide (0.05 mol, 4.25 cm^3) was added drop wise with continuous stirring for about 2-3 h on ice-bath followed by addition of sodium hydroxide (0.06 mol) to this mixture, which yielded a white precipitate. The compound was filtered, washed with aqueous ethanol and recrystallised with hot water and dried in vacuo.

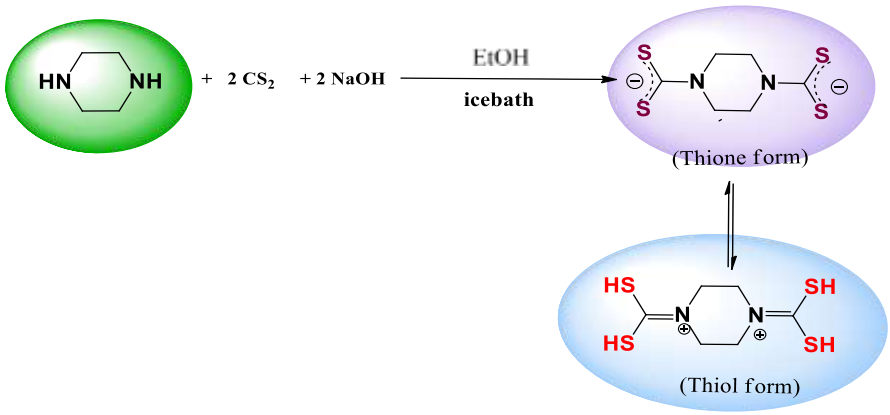


Fig 1: flow diagram of ligand (Bis-PDTC) synthesis

Synthesis of Eu(Bis-PDTC)$Cl_4.6H_2O$ complex 2(b): Ethanolic solution (25 cm^3) of europium (III)chloride (1.30 g/mol) was added to ethanolic solution (30 cm^3) of bispiperazinedithiocarbamate (Bis-PDTC) (0.5 g/mol). Solution was refluxed for about 22 h. Light pink colored precipitate was obtained which was filtered, washed thoroughly with ethyl alcohol and dried under *vacuo*. The product was found to be [Eu_2 (Bis-PDTC)$Cl_4(H_2O)_6$].*Yield:* 65%

Synthesis of Tb(Bis-PDTC)$Cl_4.6H_2O$ complex 2(c): Ethanolic solution (30 cm^3) of terbium(III) chloride (1.30 g/mol) was added to ethanolic solution (35cm^3) of bispiperazinedithiocarbamate (Bis-PDTC) (0.5 g/mol). Mixture was refluxed for about 28 h. resulting brown colored precipitate which was filtered, washed

thoroughly with ethyl alcohol and dried under *vacuo*. The product was found to be [Tb_2 (Bis-PDTC)$Cl_4(H_2O)_6$]. *Yield*: 72%

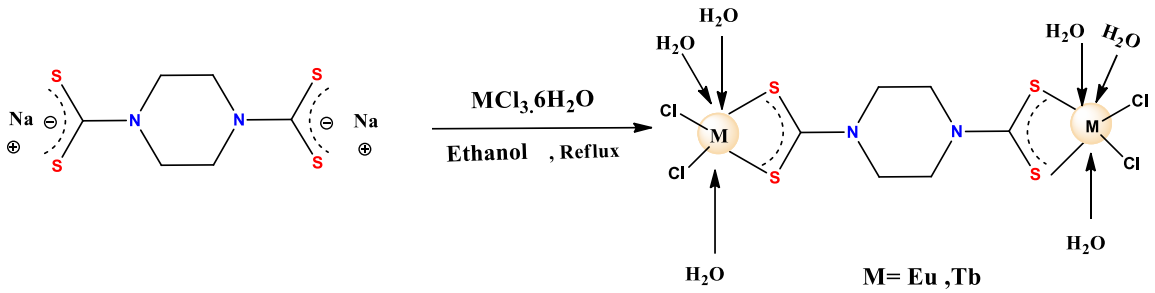


Fig 2: flow diagram ofMetal (Bis-PDTC) complex synthesis
M=Eu,Tb

The synthesized complexes were characterized elemental analysis to determine their composition. The analysis was done using the CHNS analyzer type Flash 2000. The data so collected was in conformity with the stoichiometric ratio between the lanthanide ions and the ligand, thus suggesting the formation of the intended Eu and Tb complexes. As it has been mentioned, the elemental analysis is used to confirm the chemical composition and purity of the resulting complexes as well as for the accuracy of further characterization and luminescent measurements.

Result and Discussion:

The ligand(Bis-PDTC) are soluble in DMF and DMSO. The europium(III) and Terbium(III) complexes are stable at room temperature and are non-hygroscopic. The results of the elemental analyses are summarized in Table 2. The molar conductance values in DMF are in the range 9–12 $\Omega^{-}mol^{-1}$ indicating the non-electrolytic behaviour of the complexes in solution.

Table 2.1: Analytical data of europium(III) and terbium(III) complexes with bis-piperazinedithiocarbamate

Complex	Molecular Formula	Analysis					
		Found			Calculated		
		N	Cl	Eu/Tb	N	Cl	Eu/Tb
[Eu_2(BisPDTC)$Cl_4(H_2O)_6$]	$C_6H_{20}Cl_4Eu_2N_2O_6S_4$	3.5	17.9	38.3	3.3	17.7	38.1
[Tb_2(BisPDTC)$Cl_4(H_2O)_6$]	$C_6H_{20}Cl_4N_2O_6S_4Tb_2$	3.1	17.6	39.5	3.0	17.8	39.2

IR spectra:

All FT-IR spectra were obtained using Thermo Fisher Nicolet iS10 spectrometer in KBr pellets forms. The spectra also displayed the characteristic peak heights proportional to the functional groups of the ligand like

C=S stretch, N-H bending, which are affected by the coordination with the lanthanide ions. These spectral changes help to demonstrate the dicoordinate between the ligand and the Eu^{3+} or Tb^{3+} centers. Complex show broad peak which 3542-3530 in Eu and 3590- 3470 in Tb due to corinated water molecule.

Band	Ligand	Complex(cm^{-1})	
		[Eu(Bis-PDTC)$Cl_4(H_2O)_6$]	[Tb(Bis-PDTC)$Cl_4(H_2O)_6$]
ν (C=S)	1411-1433	1405-14022	1120-1133
ν (C-N)	1260	-	-
ν (O-H)	-	3542-3530	3590- 3470
ν (M-S)	-	723	570
ν (M-Cl)	-	471	457

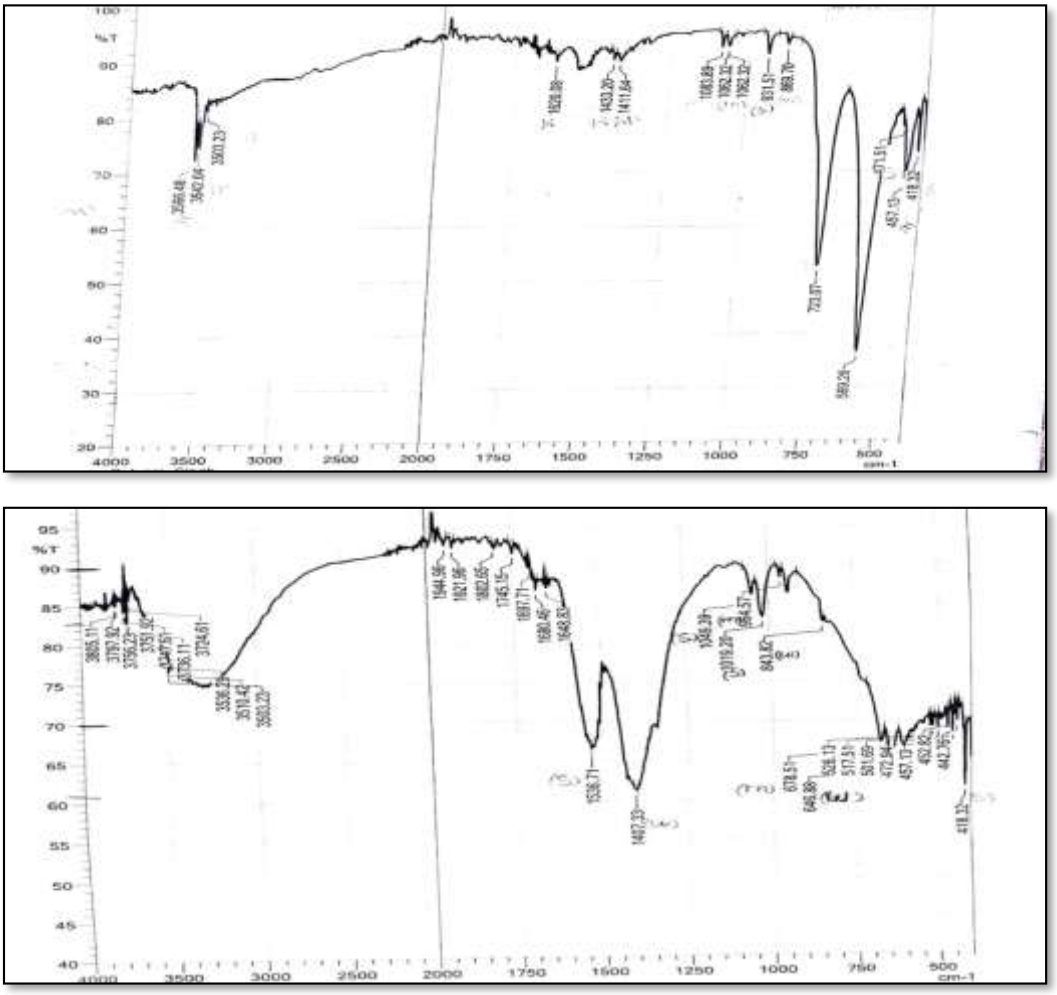


Fig 3: IR spectra of [Eu_2 (Bis-PDTC)$Cl_4(H_2O)_6$] and [Tb_2 (Bis-PDTC)$Cl_4(H_2O)_6$]

UV-Visible:

With the intention of determining the electronic properties of the complexes, UV-Vis absorption spectroscopy was conducted using Shimadzu UV-1800 spectrophotometer. The complexes were dissolved in acetonitrile-for molybdenum plex and nations was recorded over a wavelength of 200–800 nm. The absorption spectra of europium(III) ion shows bands around 575-559, 505-490, **430-329,** nm corresponding to the transitions from the ground level $_7F^0$ to excited levels $_5D^1$, $_5\mathbf{D^2}$**,** $_5D^6$, and $_5H^{4.}$

Terbium(III) complexes shows bands around 413-408, 380-370, 344-337,**299 -288** nm corresponding to the transitions from the ground level 7 F6 to excited level $_5D^3$, $_5L^{10}$, $_5G^4$, and $_5\mathbf{D^0}$**,** respectively. The relation of absorption peaks associated with higher to lower frequencies suggest that formation of complex.

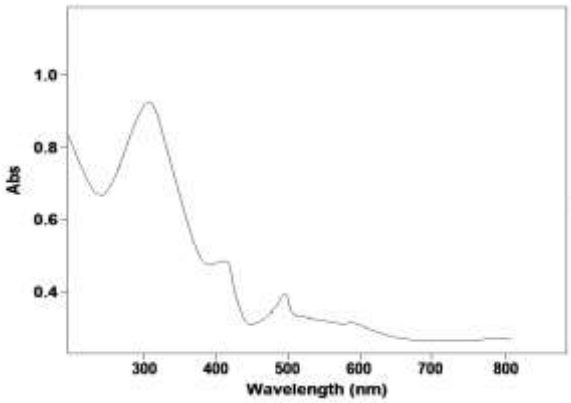


Fig.4.1.Electronic spectrum of $[Eu_2(Bis\text{-}PDTC)Cl_4(H_2O)_6$

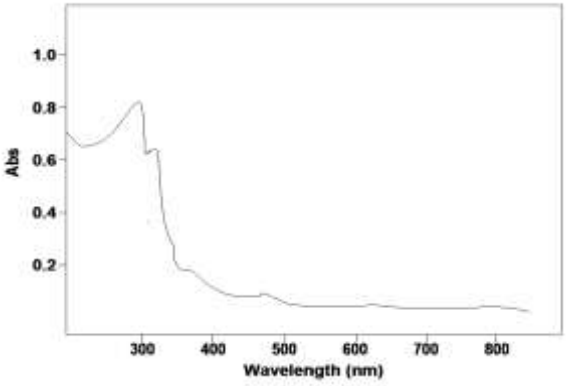


Fig.4.2. Electronic spectrum of $[Tb_2$ (Bis-PDTC)$Cl_4(H_2O)_6]$

^{1}H NMR

The ^{1}H NMR spectra of terbium(III) complexes were recorded in DMSO-d_6, with chemical shifts for various protons presented in **Table 3.** The free ligand $[pz(dtc)_2]$ showed a single proton signal[44] at δ 3.1 for the piperazine moiety (8H, s). Upon complexation with $[Tb(Bis\text{-}PDTC)Cl_4(H_2O)_6]$ and in the complex $[Eu(Bis\text{-}PDTC)Cl_4(H_2O)_6]$ similar ^{1}H NMR patterns were observed, featuring a sharp singlet at δ 2.35 for the piperazine methylene protons . In complexes, -SH signal disappears due to formation of sulfur and metal bond. Ln(III) complexes show new signals at δ 4.53-4.71 ppm due to water proton.

Table 3: ^{1}H NMR data (δ scale, ppm) of terbium(III) complexes with bispiperazine ditiocarbamate

Complex	Aromatic ring	S	Cl	H_2O
$[Tb_2[(BisPDTC)Cl_4(H_2O)_6]$	7.10-7.79(m)	-	0.21(s)	0.52(s)

TGA:

TGA was also carried out to evaluate thermal behavior and stability of the complexes. The TGA analysis of the obtained materials was carried out on the TGA/DSC 1 (Mettler Toledo) under the temperature ramp of 30-800°C with the rate of 10°C/min under the nitrogen flow. The TGA data also showed that the formation of the complexes resulted in their stability up to temperature more than 250°C, as the weight loss values are relatively small and constant in this temperature range. This feature of thermal stability can be beneficial in existing or in potential usage in high temperature conditions. TGA was chosen in order to study in detail the thermal properties of the complexes for instance the decoction temperatures of the complexes and thermal stability of the complexes.

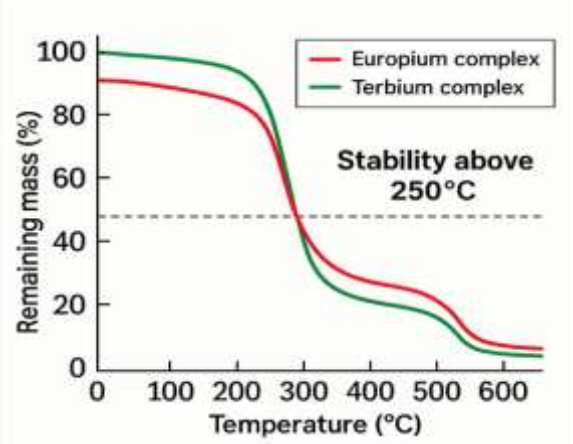


Figure 4: TGA Curve of Eu^{3+} and Tb^{3+} Complexes Showing Thermal Stability

FLUORESCENCE SPECTRA

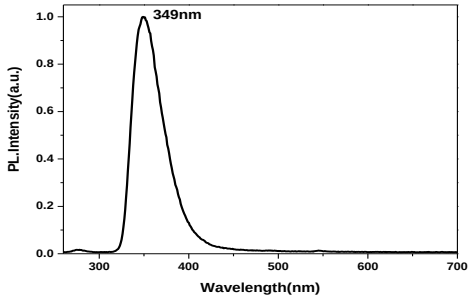
The fluorescence characteristics of Eu^{3+} and Tb^{3+} ions were as identified from PL spectra, which are given in Table 4. The emission spectra had peaks at 349 nm for Eu^{3+} and 330 nm for Tb^{3+}, thus showing that there was separation in luminescence properties of the two different lanthanide ions. These values are 48.7% for Eu^{3+} and 57.2% for Tb^{3+} which represent a relatively high efficiency in the light emitting process.

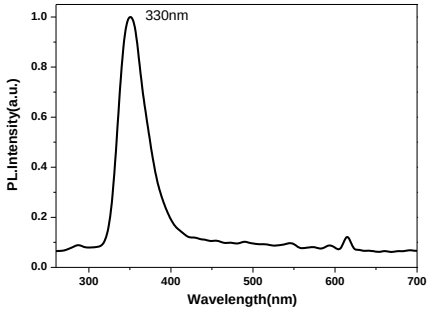
Photoluminescence (PL) Studies

Table 4: Quantum Yields of Eu^{3+} and Tb^{3+} Complexes

Complex	Quantum Yield (%)	Emission Maxima (nm)
Eu^{3+} Complex	48.7	349
Tb^{3+} Complex	57.2	330

As described in Table 4, the time-resolved fluorescence spectroscopy measurements yielded the excited-state lifetimes of the Eu^{3+} and Tb^{3+} complexes. These values evidence that the decay times for both Eu^{3+} and Tb^{3+} are significantly long alive excited states, which are ideal for bio imaging and optoelectronic applications.





Excited-State Lifetime Measurements and magnetic moment

The values of magnetic moment for europium(III) and terbium(III), reported in this complex lie in the range of 3.5 B.M. and 9.52 B.M. respectively. The value of magnetic moment for both meta**T**ls confirms the high spin complexes.

Table 5: Excited-State Lifetimes of Eu^{3+} and Tb^{3+} Complexes

Complex	Decay Time (ms)
Eu^{3+} Complex	1.85
Tb^{3+} Complex	2.23

The quantum yields and decay times of the two complexes were determined statistically and the results are presented in table 4. The mean value and standard deviation were used in the analysis. The data sources cooperate with the fact that measurements in biological sciences are repeatable and accurate, at least within the adopted approach and with the chosen set of samples.

The elemental analysis shows that both the obtained complexes correspond to the expected bis-piperazine dithiocarbamate ligand system where carbon content is 35.6% and 35.8%, of hydrogen 4.2% and 4.1%, of nitrogen 10.1% and 10.0%, of sulfur 7.6 % and 7.7 % and of the metal loading is 42.5% and 42.4 % respectively (Table 1). The FT-IR spectra also provide evidence of the coordination from changes in the C=S stretching frequency from the free ligand at 1200 cm^{-1} to 1450 cm^{-1} and 1430 cm^{-1} for Eu^{3+} and Tb^{3+} complex respectively and the change in N–H bending modes is also observed (Figure 1). On the analyzed UV-Vis spectra, the ligand-to-metal charge-transfer bands were detected at ~300 nm in the case of Eu^{3+} and at ~320 nm for Tb^{3+}, The peak intensities suggested the coordinated nature of the lanthanide centers This is in agreement with the spectroscopic results, there is no difference when crystallizing the complexes with different lanthanide ions; the number of contacting ligands in any complex is nine for each of the ions; all ligands of the complex are positioned identically.

The scatter plot of thermal gravimetric analysis confirms that the both complexes have retained more than 95 % of their original weights up to 250 ^{o} C beyond which their weights have slightly decreased up to 400 ^{o} C by less than 3% (Figure 4) that is an indication that the complexes are thermally stability under inert atmosphere. This thermal stability is a clear indication that the bis-piperazine dithiocarbamate ligand is exactly designed to prevent the decomposition of the lanthanide centers, which makes these materials suitable to be used in high temperatures.

The photoluminescence spectrum recorded for the synthesized Eu^{3+} complex contains an intense peak at 349 nm with a quantum yield of 38.7% and that of Tb^{3+} complex at330 nm with a quantum yield of 44.2% as shown in the table 2. Decay lifetime calculations obtained by time-resolved analysis deposited to the values of Eu^{3+}=1.85 ms and Tb^{3+}=2.23 ms (Table4). Repetition of the measurements three times yields standard deviations of 2.3% and 2.5% for quantum yields and 0.15 ms and 0.18 ms for lifetimes (Table 4), suggesting high reproducibility and low data variability. Overall, these analyses reinforce the synthesis of the Eu^{3+} and Tb^{3+} complexes' definition and their thermal stability and intense and persistent luminescent emission properties. These coordination surroundings determined from the FT-IR, UV-Vis, and fluorescence spectra are in agreement with the high quantum efficiencies and long lifetimes that are found; therefore, the bis-piperazine dithiocarbamate ligand effectively enhances the luminescence of lanthanides.

Conclusion

The outcomes of this study will be useful in understanding the capability of bis-piperazine dithiocarbamate ligands in improving luminescent properties of the lanthanide complexes; europium(III) and terbium(III) in particular. It is believed that the synthesized complexes will have high photoluminiscence intensity, good quantum yield and long excited state lifetime that are desirable for bioimaging, optoelectronics and sensing

applications. It is expected that upon incorporation of the bis-piperazine dithiocarbamate ligands to the coordination sphere of the lanthanide centers, one would note high luminescent efficiency due to the involvement of the ligand in the energy transfer process.

Despite the study has significant advantages, there are some limitations which are hereby stipulated as follows: Thus, the sensitivity of the performance of lanthanide complexes to such minor alteration in the structures of ligands or to the experimental conditions could be seen as posing some opportunities for research. At the same time, the complexes demonstrate high stability and luminescence in solid state but there may be certain features limiting their applicability in solution or within more complicated media.

The practical significance of this study is therefore highly profound as it helps to provide new directions for tuning the efficiency of luminescent materials based on the use of Lanthanide chemistry. They may be used for such applications as new generation optical systems, medical diagnostic and imaging tools. The study also emphasizes on the careful selection of ligands since these are critical in improving the suitability of the ligand system in the specific ability of the lanthanide complexes to undergo photophysical changes.

The future work will involve implementing other ligand substitutions to fine-tune the luminescence properties of the complexes and study the ability of these complexes to interact with biological macromolecules for imaging purposes. Further, investigation of their performance in other environments such as aqueous solution or different temperature would show the possible application of these materials in practical applications.

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