Synthesis, Characterization and luminescent studies of Europium (III) and Terbium (III) complexes with 1,2,4-Triazole and1,3-diphenylpropane-1,3-dione Derived Schiff Base ligand

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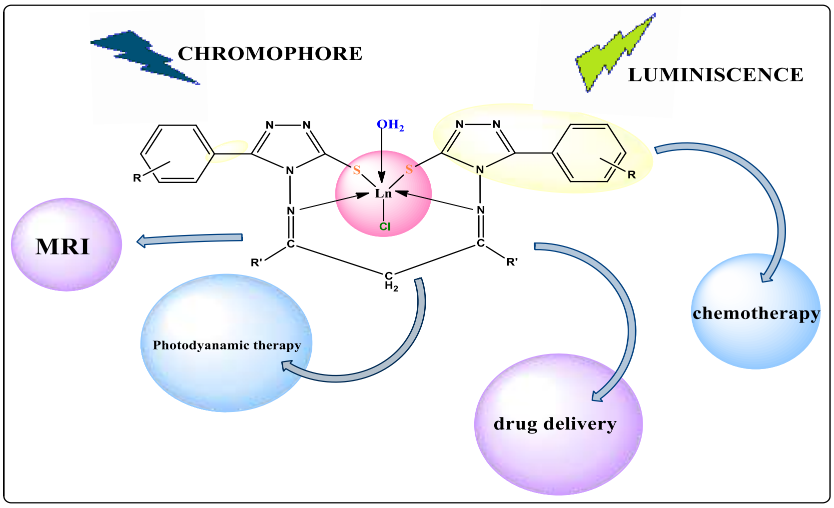
ABSTRACT

Europium (III) and Terbium (III) complexes of types [Eu(L)Cl(H_2O)] and [Tb(L)Cl(H_2O)] (H_2L =Schiff base derived from condensation of 3-(phenyl/substituted phenyl)-4-amino-5-mercapto-1,2,4-triazole with 1,3-diphenylpropane-1,3-dione have been synthesized by the reactions of anhydrous europium (III) chloride and anhydrous terbium (III) chloride with Schiff bases in ethanol. The obtained complexes were characterized on the basis of elemental analysis, spectroscopic measurement including elemental analysis, electronic spectroscopy, IR spectra, 1H-NMR, magnetic moment, electrical conductance. The photoluminescence properties of europium (III) and terbium (III) complexes have also been studied. Europium (III) and Terbium (III) complexes show very strong characteristic emission in red and green regions, respectively.

GRAPHICAL ABSTRACT



KEYWORDS 1,2,4-triazole, photoluminescence, Europium, Terbium IR.

INTRODUCTION

The luminescence properties of rare earth complexes, particularly Ln(III) complexes with organic ligands, have been widely explored for their potential uses in diagnostics, photonics, and renewable energy[1-5]**.** Lanthanide ions need suitable "antenna" ligands to sensitize energy transfer, enabling efficient excitation and luminescence. These ligands also shield the metal center from solvents, minimizing non-radiative decay. Careful ligand design is essential to optimize photophysical properties for specific applications[6-9]**.** Lanthanide ions exhibit exceptional optical properties, including high fluorescent monochromaticity, long lifetimes, and large Stokes shifts, due to their distinctive 4f electronic configuration and 4f-4f or 4f-5d transitions[10,11]. Lanthanide ions, especially Eu(III), have garnered significant research interest due to their unique properties. However, their f-f transitions result in low absorption coefficients[12-14] and weak fluorescence. To address this limitation, researchers design organic ligands with high absorption coefficients and suitable excitation energies, enabling efficient energy transfer and enhanced luminescence through the antenna effect. The choice of ligand is crucial for optimizing energy transfer and fluorescence properties[15, 16]. Schiff-base ligands play a significant role in rare earth coordination due to their ease of preparation, strong coordination properties, and ability to donate electrons[17,18] . These ligands exhibit strong binding affinity for lanthanide ions and significantly enhance their fluorescence properties[19,20]. Reported Schiff-base ligands successfully sensitize lanthanides but lack desirable standalone properties, limiting their utility[21]. Developing ligands with improved characteristics and coordination abilities is essential for progressing rare earth coordination chemistry and materials science.

In this work, we developed a series of 3-(phenyl/substituted phenyl)-4-amino-5-mercapto-1,2,4-triazole with 1,3-diphenylpropane-1,3-dione Schiff-base derivatives ,which characterized by 1 H NMR,UV-visble , and IR. Their corresponding Eu(III) and Tb(III) complexes were synthesized and characterized by molar conductivity, 1H-NMR,UV–vis spectra and FT-IR spectra. Furthermore, The photo luminescence property, of Eu(III) and TB(III) complexes were investigated.

MATERIALS AND METHODS

The chemicals and solvents used during the whole investigation are “Analytical Reagent” grade. Solvents were purified by using standard procedures[22]. Europium (III) oxide was purchased from Sigma-Aldrich and converted into Europium (III) chloride by reported method[23] and Terbium (III) chloride was purchased from Alfa-Aesar.

SYNTHESIS OF LIGAND AND Eu(III)/Tb(III) COMPLEX

The ligands were prepared according to the reported method[24]. A mixture of 3-(phenyl / substituted phenyl)-4-amino-5-mercapto-1,2,4-triazoles and 1,3diphenylpropane-1,3-dione in molar ratio 2:1, respectively was refluxed in aqueous ethanol (50%, 50 cm^3) for 6 h under acidic condition. The crystals were separated out which was washed with aqueous ethanol and recrystallized from methanol.

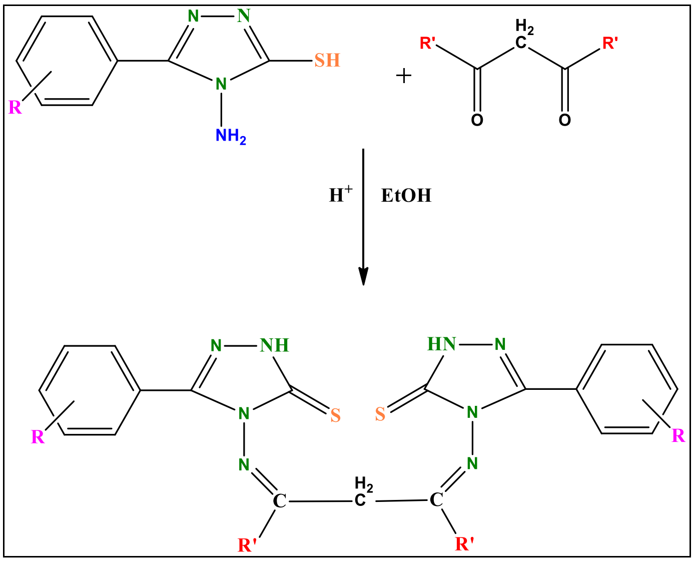


Fig1: 1,2,4-triazoles Schiff base ligand
(Where-R=H, NO_2, Cl:, $R' = C_6H_5$)

The reactions of europium(III) chloride and terbium(III) chloride with Schiff base ligands (LH_2) derived from 3-(phenyl/substituted phenyl)-4-amino-5-mercapto-1,2,4-triazoles and 1,3-diphenylpropane -1,3-dione have been carried out in ethanol in 1:1 molar ratio. The complexes are obtained according to the following equations.

$$EuCl_3 + LH_2 \xrightarrow[\text{Reflux}]{\text{ethanol}} [Eu(L)Cl(H_2O)] + 2HCl$$

$$TbCl_3 + LH_2 \xrightarrow[\text{Reflux}]{\text{ethanol}} [Tb(L)Cl(H_2O)] + 2HCl$$

RESULT AND DISSCUSSION

The analytical data and physical properties of the europium(III) and terbium(III) complexes are given in **(Tables 1 and 2)**. All the newly synthesized complexes are colored solid, soluble in DMF, DMSO, chloroform. The analytical data are in good agreement with the proposed stoichiometry of the complexes. The electrical conductance measurements in ethanol indicate that the complexes are non-electrolytic in nature.

Reactant	**Product**	**Color**	**Yield (%)**	**Decomp. temp. (˚C)**
$EuCl_3 + LH_2$	$Eu(L)Cl(H_2O)$	Yellow	82	197
$TbCl_3 + LH_2$	$Tb(L)Cl(H_2O)$	Brown	78	168

Table 1: physical properties of the europium(III) and terbium(III) complexes

Complex	Molecular formula	Analysis (%)									
		Found					Calculated				
		C	H	N	Cl	Eu/ Tb	C	H	N	Cl	Eu/Tb
Eu(L)Cl(H_2O)	$C_{31}H_{24}N_8S_2OClEu$	47.8	3.1	14.4	4.7	19.5	47.4	3.0	13.5	4.3	19.2
Tb(L)Cl(H_2O)	$C_{31}H_{24}N_8S_2OClTb$	44.5	3.1	13.3	8.4	19.0	44.7	3.3	13.5	8.6	19.1

Table 2:Analytical data of europium(III) and terbium(III) complexes with Schiff bases derived from 3-phenyl-4-amino- 5 -mercapto-1,2,4-triazoles and 1,3-diphenylpropane-1,3-dione.

MAGNETIC MOMENT The europium(III) and terbium(III) complexes exhibit magnetic moments of 3.35-3.58 B.M. and 9.47-9.57 B.M., respectively, with minor variations from the van Vleck values.

UV-VISIBLE SPECTRAL ANALYSIS

The UV–Vis absorption spectra of ligand , and Eu(III)/Tb(III)complexes were obtained in ethanol t at suitable temperature with the concentration of 15 μM. Europium(III) complexes exhibit absorption bands corresponding to transitions from the $^7F_0$ level to excited levels: 17,355-17,960 cm^{-1} ($^5D_0$), 23,110-23,535 cm^{-1} ($^5D_6$ is likely a typo and might refer to $^5D_1$ or another level, as $^5D_6$ is not a common transition for Eu(III)), 26,445-27,310 cm^{-1} ($^5L_{10}$), and 30,855-31,240 cm^{-1} ($^5H_4$).Terbium(III) complexes exhibit absorption bands corresponding to transitions from the $^7F_6$ level to excited levels: 20,810-21,720 cm^{-1} ($^5D_4$), 28,545-29,405 cm^{-1} ($^5G_4$ or possibly $^5L_8$ or another nearby level, as $^5G_4$ might not be the exact assignment), and 31,720-34,225 cm^{-1} might correspond to several possible transitions, given the high energy.

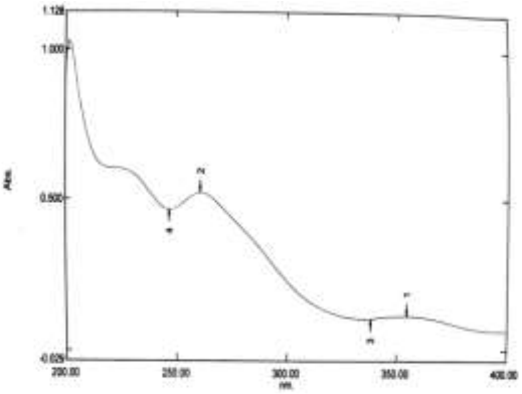
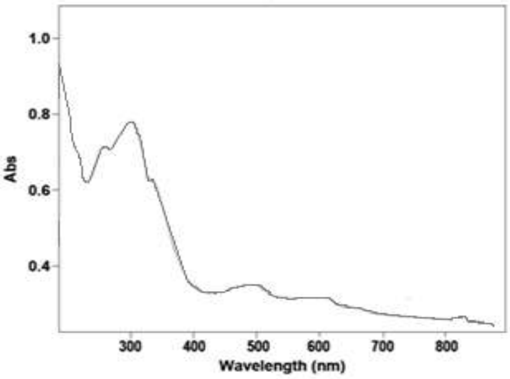


Fig 1: Electronic spectrum of [Eu(PAMTD)Cl(H_2O)]

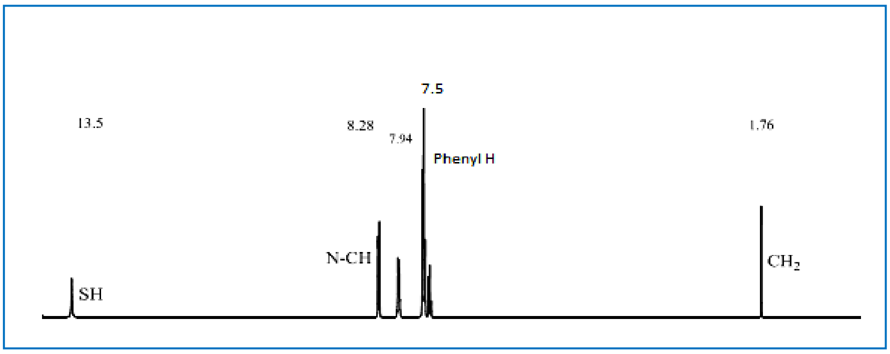


2. Electronic spectrum of [Tb(PAMTD)Cl(H_2O)]

PROTON MAGNETIC RESONANCE SPECTRA

1H NMR spectra of europium(III) and terbium(III) complexes were obtained in DMSO-d_6, yielding chemical shifts for protons in defferent chemical environments in **Table3**. The Schiff bases exhibit a signal at approximately δ13.58 ppm in the NMR spectrum, corresponding to the –SH proton. This indicates that the ligands predominantly exist in the thiol form in solution. The disappearance of the –SH signal in the complexes suggest that coordination between the Eu and Tb metal and sulfur. Schiff bases and their complexes show chemical shifts between δ 7.51-7.94 ppm for aromatic protons. The methyl protons in the Schiff base (PAMTD) appear at δ 1.37 as a singlet and shift upfield upon complexation with Eu/Tb(III). These complexes show new signal at ca. δ8.28 ppm due to water protons. ^{1}H-NMR spectrum of one representative complex is shown in **fig:3.**

Complex	**Aromatic ring**	**-CH_3**	**C=NH**	**H_2O**
L(PAMTD)	7.42-7.50(m)	1.76(s)	-	-
[Eu(NPAMTD) Cl(H_2O)]	7.30-8.20(m)	1. 72(s)	3.70(s)	8.52(s)
[Tb(CPAMTD)Cl(H_2O)]	7.45-8.45(m)	1.76(s)	3.98 (s)	8.26(S)



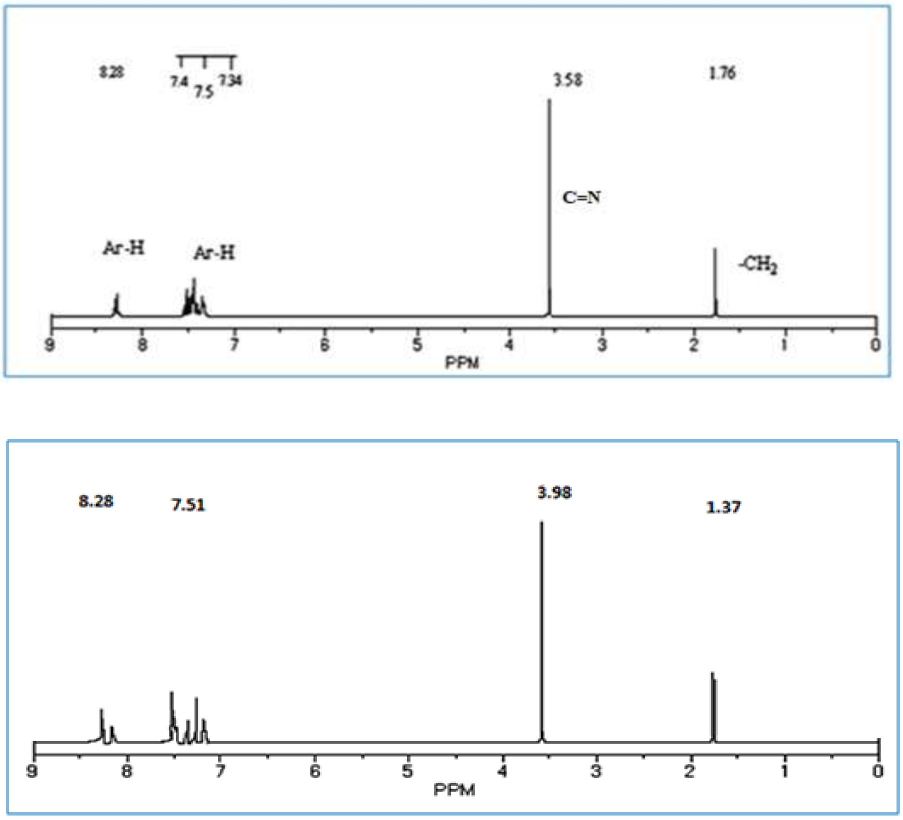


Fig 3: ^{1}H NMR data of ligand (PAMTD) and europium (III) and terbium(III) complex

IR STUDIES

Sulfur-containing compounds, like thiols, similar to the structure of oxygen-containing compounds (alcohols and ethers) but with sulfur instead of oxygen. Their IR spectra typically display weak C-S and C-S-H stretching bands, and the frequencies are lower than those of oxygen analogues due to sulfur's greater mass[25]. The Schiff bases posses a weak infrared band at 2775-2650 cm^{-1}, attributed to ν(S-H), which vanishes in the complexes. This disappearance suggests deprotonation of the thiol group and subsequent metal-sulfur bond formation. This is confirmed by appearance of new bands in complexes at ca. 460-550 cm^{-1} assignable to ν(Ln-S). The ligands exhibit strong band at ca. 1645-1630 cm^{-1} of ν(C=N) but this band shifts to lower frequency at ca. 1520-1635 cm^{-1} in the complexes, indicating the participation of azomethine nitrogen in bond formation with Ln(III) ion[26]. The band due to ν(C=N) (triazole ring) appears at ca. 1580 cm^{-1} in the ligands which remains almost at the same position in the complexes indicating non-coordination of ring azomethine nitrogen in bond formation. The new bands in Ln(III) complexes at ca. 425-385 cm^{-1} are assignable to ν(Ln-N) vibrations. The bands appears at ca. 3500-2850 cm^{-1} indicating the presence of ν(Ar-H). The broad bands appear at ca. 3455-3205 cm^{-1} indicating the presence of coordinated water molecule in the complexes. IR spectra of [Eu(PAMTD)Cl(H_2O)] and [Tb(PAMTD)Cl(H_2O)] complexes are shown in **Fig. 3 & 4.**

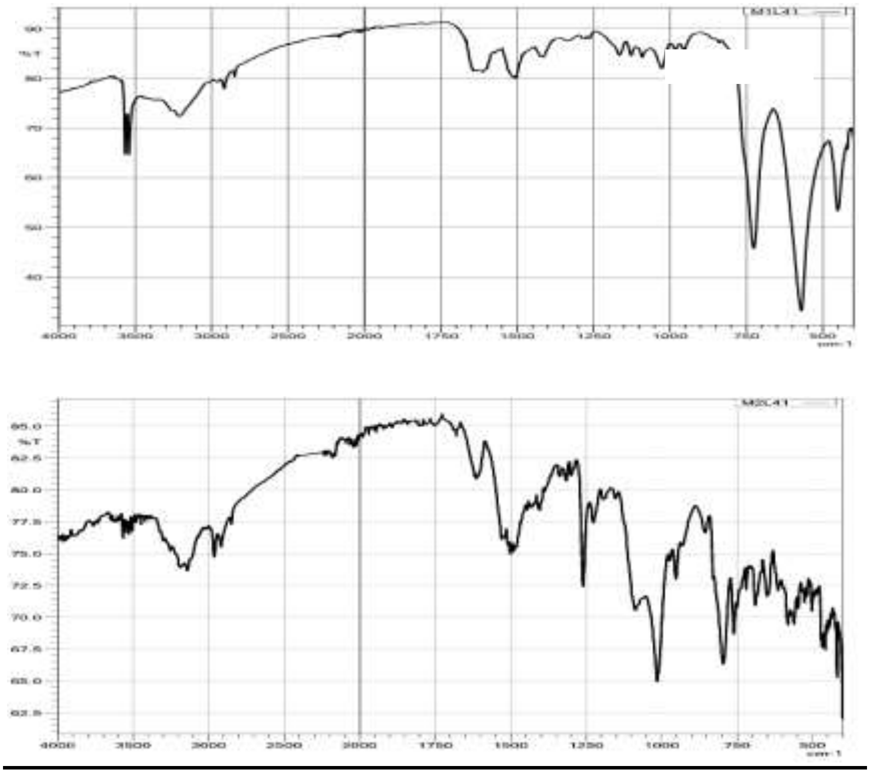
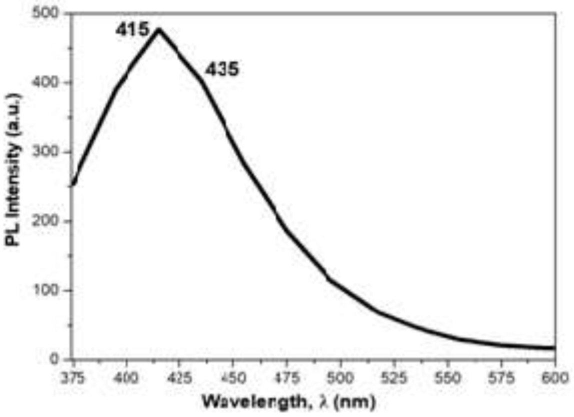
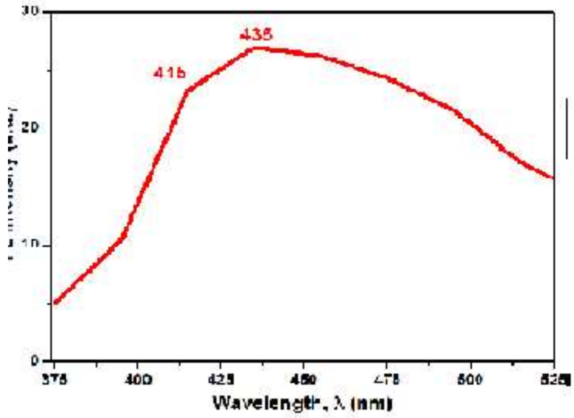


Fig:3,4: IR data of [Eu(PAMTD)Cl(H_2O)]and [Tb(PAMTD)Cl(H_2O)] complex

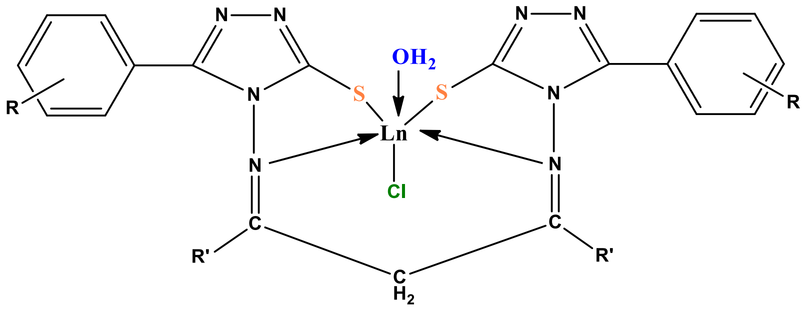
FLUORESCENCE PROPERTIES

The importance of energy transfer from the excited state of the organic ligand to the lanthanide(III) ion within a complex is widely recognized [27.] The emission spectra of newly synthesized Eu(III) and Tb(III) complexes were measured in dichloromethane at room temperature There are two emission peak found at 365 nm excitation wavelength for both Eu(III) complex and for Tb(III) complex. Two emission peaks of Eu(III) complexes are at 415 nm, 435 nm, exhibits 5D3→7F1, and 5D0→7F2 transitions, respectively. Two emission peaks of Tb(III) complexes are, 435 nm, 455 nm, assignable 5D3→7F4, 5D4→7F5, transitions, respectively. Difference in the position of the peak is due to environmental difference around the metals. The characteristic peaks of Eu(III) and Tb(III) exhibit the strong red and green emission found at 618 and 550 nm corresponding to 5D0→7F2and 5D4→7F5 transitions, respectively which are electrical dipole allowed transitions. The peak at 435 nm is strongest for the Eu(III) complex and the peak at 455 nm is strongest for the Tb(III) complex. Nonetheless, the peak at 415 nm of Eu(III) complex and peak at 435 nm of Tb(III) complex are slightly stronger, which imitates the modification of the transition prospect and effect of diverse coordination spheres. Figure 5 fluorescence spectra of (a) complex and (b) complex .





Thus, on the basis of above spectral analyses and data, the following structure is tentatively proposed for the complexes.



Where- Ln;Eu(III),Tb(III)

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