

Spectral Characterization and Photoluminescence Properties of Europium(III) Complexes Derived from Hydrazino-Triazole and o-Hydroxyacetophenone

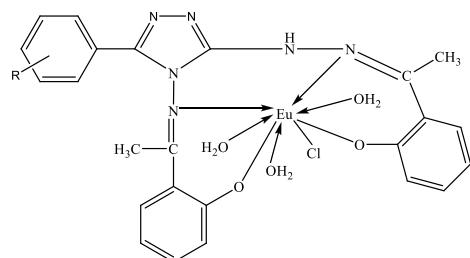
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Abstract-

Novel europium(III) complexes were successfully synthesized via the reaction of europium(III) chloride with Schiff bases, which were produced by the condensation of 3-(phenyl or phenyl-substituted)-4-amino-5-hydrazino-1,2,4-triazole and o-hydroxyacetophenone in ethanol. The resulting complexes were comprehensively characterized using elemental analysis, various spectroscopic methods, magnetic susceptibility measurements, electrical conductance studies, and X-ray diffraction analysis. Additionally, the photoluminescence behaviour of the synthesized Eu(III) complexes was investigated, demonstrating intense and characteristic red emission associated with europium centres.

Graphical Abstract-



Keywords: Europium(III) complexes, Schiff bases, hydrazine-triazole, o-hydroxyacetophenone, infrared spectroscopy (IR), photoluminescence, spectral characterization

Introduction

Schiff bases containing the triazole ring system have gained significant importance in coordination and medicinal chemistry because of their diverse biological potential. These ligands are capable of forming stable metal complexes that resemble biologically active system and display a variety of pharmacological actions, including anti-inflammatory, anticonvulsant, antibacterial, anticancer, and antifungal effects¹⁻⁹. Among them, the 1,2,4-triazole heterocyclic nucleus contributes notably to antimicrobial activity¹⁰⁻¹⁷. Hydrazino Schiff bases bearing the

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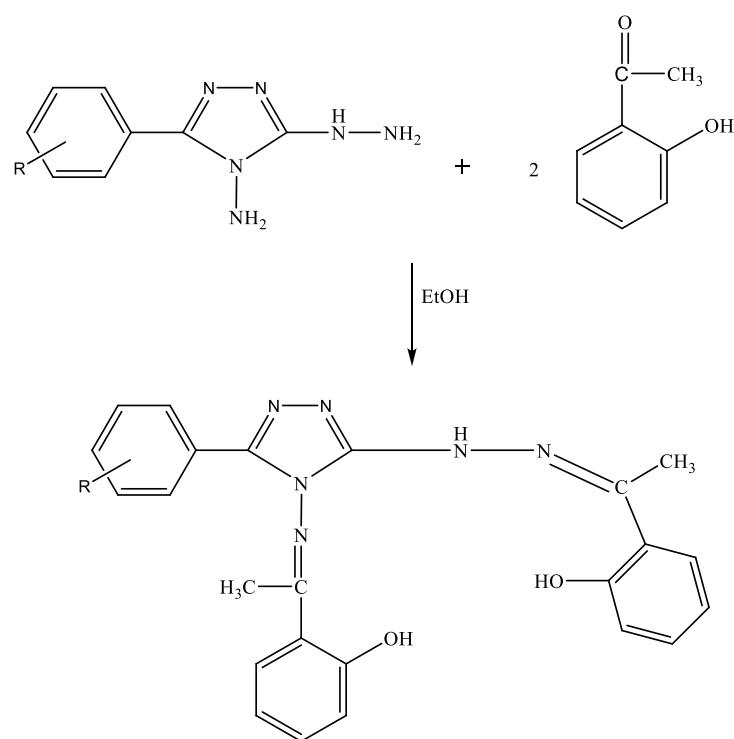
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1,2,4-triazole moiety have attracted special attention because they are easy to synthesize, possess flexible coordination sites, and exhibit a wide spectrum of biological, photochemical, and analytical applications¹⁸⁻²³. In view of these features, the present investigation focuses on the synthesis and characterization of novel europium(III) complexes containing Schiff base ligands derived from o-hydroxyacetophenone. This study also aims to explore their structural behaviour and potential photo-physical characteristics.

Experimental

1.1. Materials and methods

All reagents and solvents used in this study were of analytical grade and utilized without further purification. Europium(III) chloride was procured from Sigma-Aldrich. The Schiff base ligands were synthesized following a procedure reported in the literature²⁴. In a typical synthesis, 3-(phenyl or phenyl-substituted)-4-amino-5-hydrazino-1,2,4-triazole was refluxed with o-hydroxyacetophenone in a 1:2 molar ratio in ethanol, in the presence of a few drops of acid, for approximately 7-8 hours. The resulting solid product was separated by filtration, thoroughly washed, and recrystallized to obtain the purified ligand.



Where, R= H (L₁), p-NO₂ (L₂), o-Cl (L₃), p-Cl (L₄)

Figure 1. Methodology of Schiff bases ligand

1.2. Methodology of complexes

The synthesized Schiff bases were reacted with europium(III) chloride in ethanol using a 1:1 molar ratio. The reaction mixture was refluxed for approximately 11-13 hours to ensure complete complexation. After completion, the resulting crystalline product was separated,

filtered, thoroughly washed with ethanol, and dried under vacuum. The physical properties and analytical data of the prepared complexes are summarized in Table 1 and 2, respectively.

Table 1. Physical characteristics of Europium(III) complexes

S.N.	Reactants (molar ratio)	Refluxing time	Product	Yield (%)	Molecular formula	Color
1	EuCl ₃ + L ₁	15	[Eu(L ₁)Cl(H ₂ O) ₃]	68	C ₂₄ H ₂₆ N ₆ O ₅ ClEu	Green
2	EuCl ₃ + L ₂	14	[Eu(L ₂)Cl(H ₂ O) ₃]	66	C ₂₄ H ₂₅ N ₇ O ₇ ClEu	Brown
3	EuCl ₃ + L ₃	14	[Eu(L ₃)Cl(H ₂ O) ₃]	72	C ₂₄ H ₂₅ N ₆ O ₅ Cl ₂ Eu	Green
4	EuCl ₃ + L ₄	14	[Eu(L ₄)Cl(H ₂ O) ₃]	70	C ₂₄ H ₂₅ N ₆ O ₅ Cl ₂ Eu	Green

Table 2. Analytical data of Europium(III) complexes.

Complex	Analysis (%)									
	Found					Calcd.				
	C	H	N	Cl	Eu/ Tb	C	H	N	Cl	Eu/ Tb
[Eu(L ₁)Cl(H ₂ O) ₃]]	43.0 4	3.4 5	12.1 7	5.21 4.76	22.5 8	43.2 7	3.9 0	12.6 2	5.33 4.90	22.8 3
[Eu(L ₂)Cl(H ₂ O) ₃]]	39.4 5	3.1 4	15.1 3	10.0 1	20.7 4	39.7 5	3.4 5	15.4 5	10.1 4	20.9 7
[Eu(L ₃)Cl(H ₂ O) ₃]]	40.8 4	3.1 6	11.7 4	10.0 4	21.3 5	41.1 4	3.5 7	12.0 0	10.1 4	21.7 0
[Eu(L ₄)Cl(H ₂ O) ₃]]	40.9 5	3.2 0	11.5 6		21.4 4	41.1 4	3.5 7	12.0 0		21.7 0

3. RESULTS AND DISCUSSION

The synthesized europium(III) complexes were found to be soluble in ethyl alcohol, methyl alcohol, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and chloroform, and remained stable at room temperature. The measured molar conductance values of the complexes ranged from 09-12 $\Omega^{-1} \text{cm}^2 \text{ mol}^{-1}$, suggesting their non-electrolytic nature.

3.1. Electronic spectra

The absorption spectra of the europium (III) complexes exhibit characteristic bands in the ultraviolet and visible regions, which corresponds to electronic transitions from the ground

state 7F_0 to various excited states of the 4f configuration. The observed absorption bands appear around 581-571 nm, 425-416 nm, 380-370 nm, and 350-340 nm, which can be assigned to the $^7F_0 \rightarrow ^5D_0$, $^7F_0 \rightarrow ^5D_6$, $^7F_0 \rightarrow ^5L_8$ and $^7F_0 \rightarrow ^5L_{10}$ transitions, respectively. From the obtained spectral data, the nephelauxetic ratio (β), Sinha's covalency parameter (δ) and bonding parameter ($b^{1/2}$) were calculated as presented in **Table 3**.

Parameters of synthesized europium(III) complexes

Complex	β	δ	$b^{1/2}$
[Eu(L ₁)Cl(H ₂ O) ₃]	0.9929	0.7150	0.0595
[Eu(L ₂)Cl(H ₂ O) ₃]	0.9930	0.7049	0.0591
[Eu(L ₃)Cl(H ₂ O) ₃]	0.9921	0.7962	0.0628
[Eu(L ₄)Cl(H ₂ O) ₃]	0.9908	0.9285	0.0678

3.2. Infrared spectra

Table 4 presents the infrared spectral data of the synthesised europium(III) complexes. The IR spectra provide valuable information regarding the functional groups involved in metal coordination. The spectra of the free Schiff bases display a band at 3225-3180 cm^{-1} corresponding to the $\nu(\text{N-H})$ vibration, which remains almost unchanged in the complexes, indicating that the NH group does not participate in coordination. A strong band²⁵ observed around 1635-1620 cm^{-1} attributed to the $\nu(\text{C=N})$ stretching of the azomethine group, shows a negative shift upon complexation, suggesting the coordination of the azomethine nitrogen atom to the metal ion²⁶⁻²⁸. The absorption bands appearing near 3115-3055 cm^{-1} are assigned to aromatic C-H stretching vibrations, while those around 1545 cm^{-1} correspond to the stretching of the $-\text{NO}_2$ group. The bands observed in the range of 780-765 cm^{-1} ascribed to C-Cl stretching modes. Additional weak bands in the region of 440-430 cm^{-1} and 465-460 cm^{-1} are attributed to $\nu(\text{Ln-N})$ and $\nu(\text{Ln-O})$ vibrations, respectively, confirming metal-nitrogen and metal-oxygen bonding. Moreover, a broad band appearing near 3450-3435 cm^{-1} indicates the presence of coordinated water molecules within the complexes.

3.3. ^1H NMR spectra

The ^1H NMR spectra of the europium(III) complexes were recorded in deuterated dimethyl sulfoxide (DMSO-d₆). The spectra displayed signals in the region of δ 7.11–8.30 ppm, which are attributed to the aromatic protons present in both the Schiff bases and their corresponding metal complexes. The free ligands derived from o-hydroxyacetophenone showed a singlet near δ 10.3 ppm, corresponding to the $-\text{OH}$ proton. In the europium(III) complexes, this $-\text{OH}$ signal disappeared, suggesting that the hydroxyl groups underwent deprotonation and participated in coordination with the metal ion.

Additionally, the Schiff bases exhibited singlets around δ 12.2 ppm and δ 8.14 ppm due to the $-\text{NH}$ and azomethine ($-\text{CH}=\text{N}-$) protons, respectively. In the complexes, the $-\text{NH}$ signal

remained nearly unchanged, whereas the azomethine proton signal shifted downfield, indicating coordination of the azomethine nitrogen atom to the europium(III) centre. Both the Schiff bases and their europium(III) complexes displayed a signal near δ 1.79 ppm corresponding to the methyl protons. A new signal observed at approximately δ 5.6 ppm in the europium(III) complexes was assigned to coordinated water molecules.

3.4. X-ray powder diffraction pattern

X-ray powder diffraction (XRD) is an analytical method used to determine the crystalline nature of materials through the constructive interference of monochromatic X-rays with a crystalline sample²⁹⁻³⁰. The diffraction peaks obtained in the XRD pattern confirm the crystalline structure of the synthesized europium(III) complexes. The average crystallite size of the complexes was calculated using the Debye–Scherrer equation, which is expressed as:

$$D = 0.94 \lambda / \beta \cos \theta$$

Where,

D = average particle size,

λ = wavelength of the X-ray used,

β = full width at half maximum (FWHM) of the diffraction peak, and

θ = Bragg's diffraction angle.

The calculated particle size of the europium(III) complexes was found to be in the range of 14–29 nm, confirming their nanocrystalline nature.

Photoluminescence properties

The emission spectra of the synthesized europium(III) complexes were recorded in DMF at room temperature. A dominant emission band was observed at 614 nm ($^5D_0 \rightarrow ^7F_2$) corresponding to the electric dipole (hypersensitive) transition, while a comparatively weaker peak appeared near 440 nm ($^5D_3 \rightarrow ^7F_3$), attributed to the transition. The prominent peak at 614 nm indicates the characteristic red emission of europium(III) ions (Figure 2). The quantum yield and emission lifetime of the Eu(III) complexes were also evaluated, with quantum yield values ranging between 0.55 and 0.57, and lifetimes measured in the range of 9.08–10.54 μ s (Figure 3, Table 4).

Table 4. Luminescence parameters of europium(III) complexes

Complex	Excitation (nm)	Emission (nm)	QY (ϕ)	Lifetime (μ s)
[Eu(L ₁)Cl(H ₂ O) ₃]	315	618	0.55	9.08
[Eu(L ₂)Cl(H ₂ O) ₃]	310	614	0.57	10.54
[Eu(L ₃)Cl(H ₂ O) ₃]	310	608	0.56	9.94
[Eu(L ₄)Cl(H ₂ O) ₃]	315	620	0.56	9.25

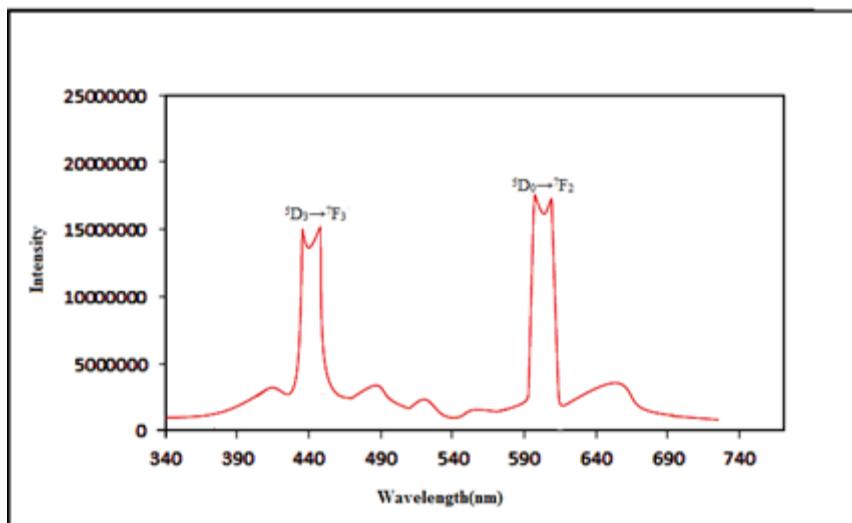


Figure 2. Emission spectrum of $[\text{Eu}(\text{L}_2)\text{Cl}(\text{H}_2\text{O})_3]$

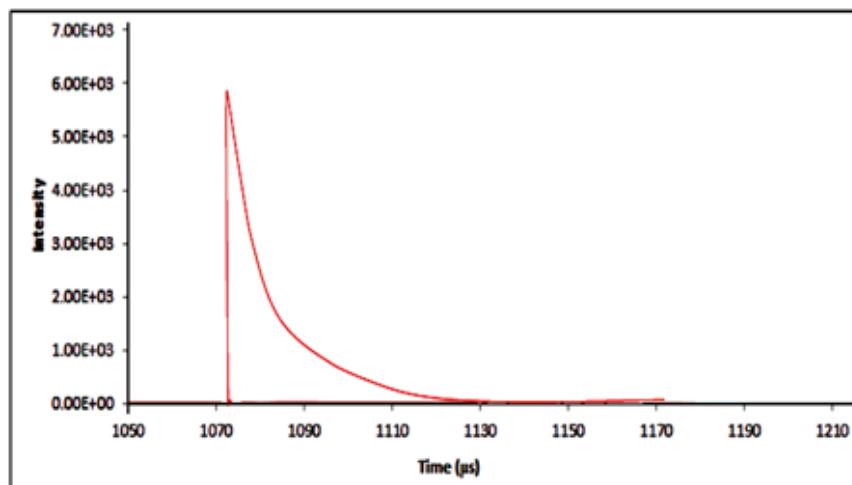


Figure 3. Emission lifetime spectrum of $[\text{Eu}(\text{L}_2)\text{Cl}(\text{H}_2\text{O})_3]$

Based on the results obtained from analytical and spectroscopic studies, the following structural arrangement of the europium(III) complexes has been proposed (Figure 4).

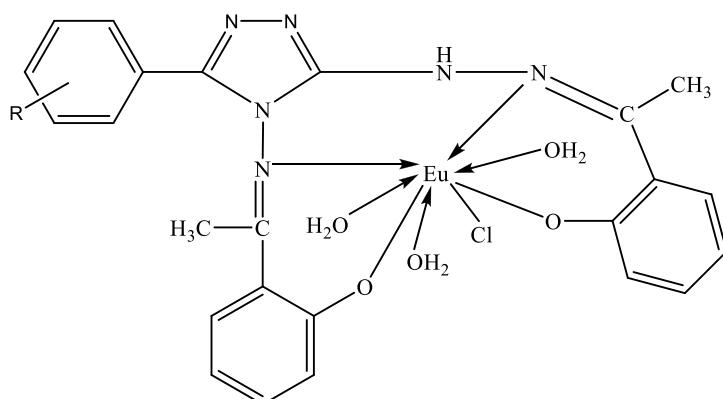


Figure 4. Structural arrangement of Eu(III) complexes

CONCLUSIONS

In conclusion, novel europium(III) complexes were successfully synthesized and thoroughly characterized through elemental and spectral analyses. The study confirms that the europium(III) ion coordinates with two oxygen and two azomethine nitrogen donor atoms of the Schiff base ligand, forming stable chelated structures. The photoluminescence investigation revealed strong and characteristic red emission, attributed to the transition of the europium(III) ion. These findings highlight the potential applicability of the synthesized complexes in luminescent and optoelectronic materials.

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