



Research Article

Synthesis, Structural Characterization and Coordination Behaviour of a Tris(2-aminoethyl)amine-Based Tripodal Schiff Base Ligand and Its Europium(III) Complex

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ABSTRACT

A chlorinated tripodal Schiff base ligand (H_3L) was synthesized by the condensation of tris(2-aminoethyl)amine (tren) with 3,5-dichlorosalicylaldehyde and subsequently employed in the preparation of its Eu(III) complex. The ligand and complex were comprehensively characterized by elemental analysis, FTIR, UV-Visible spectroscopy, high-resolution mass spectrometry (HRMS), and single-crystal X-ray diffraction (SCXRD). Coordination of Eu(III) was confirmed by the shift of the azomethine stretching vibration from 1635 cm^{-1} in the free ligand to 1604 cm^{-1} in the complex, accompanied by changes in the phenolic C–O stretching frequency. Electronic absorption spectroscopy revealed two characteristic bands for H_3L at 263 and 335 nm, assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, whereas the Eu(III) complex exhibited absorption bands at 259, 321, and 412 nm, the latter indicating ligand-to-metal charge transfer following coordination. High-resolution mass spectrometry further confirmed the proposed compositions, with the ligand displaying a sodium adduct peak at m/z 684.9870 ($[M + Na]^+$; calculated. 684.9877) and the Eu(III) complex exhibiting a molecular ion peak at m/z 812.2216 ($[M+H]^+$; calculated 812.9035). Single-crystal X-ray diffraction analysis of H_3L established the molecular structure and confirmed the formation of the anticipated chlorinated tripodal Schiff base ligand. The ligand crystallized in the trigonal $R3$ space group and adopted a rigid tripodal conformation stabilized by intramolecular O–H $\cdots$ N hydrogen bonding. The crystallographic analysis revealed a preorganized N_4O_3 donor environment and an ordered three-dimensional packing arrangement, providing structural evidence for its suitability as a heptadentate ligand. Collectively, the spectroscopic and crystallographic findings demonstrate that H_3L serves as an effective coordination platform for Eu(III), providing a structurally robust framework for the development of functional lanthanide complexes and future investigations of their photophysical, catalytic, and sensing properties.

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1.0 INTRODUCTION

Lanthanide coordination compounds continue to attract considerable research interest owing to their unique electronic structures and the wide range of physicochemical properties arising from their partially filled 4f orbitals (Aggarwal *et al.*, 2026; Fernández-Fariña, Kotova, Donohoe *et al.*, 2025; Reddy, Bejoymohandas, & Divya, 2022). Among the lanthanide ions, europium(III) has received particular attention because of its favourable coordination chemistry and its potential applications in luminescent materials, optical sensing, molecular imaging, photonic devices, and advanced functional materials (Lewandowski *et al.*, 2024; Li *et al.*, 2024; Redhu *et al.*, 2025). Unlike transition metal ions, the electronic transitions of Eu(III) are largely shielded by the outer 5s and 5p orbitals, making the coordination environment imposed by the ligand an important factor in determining the stability and physicochemical behaviour of the resulting complexes (Binnemans, 2015; Ferreira da Rosa *et al.*, 2021; Kitagawa *et al.*, 2024). Consequently, the rational design of suitable ligands capable of providing rigid and well-defined coordination environments remains a central objective in lanthanide coordination chemistry.

Tripodal ligands derived from tris(2-aminoethyl)amine (tren) constitute an important class of multidentate chelating agents because of their three-dimensional architecture and ability to simultaneously coordinate metal ions through multiple donor atoms (Baral *et al.*, 2016; Brewer, 2020). The tripodal framework provides a preorganized binding cavity that enhances complex stability while reducing conformational flexibility, thereby facilitating the formation of structurally well-defined coordination compounds (Singh *et al.*, 2024; Vostrikova, 2023). The synthetic versatility of tren further allows facile functionalization through condensation reactions with aldehydes or ketones, producing Schiff base ligands with tunable steric and electronic properties. Such structural flexibility has led to extensive investigations of tren-derived ligands in coordination chemistry, catalysis, supramolecular chemistry, molecular recognition, and metal ion sequestration (Debuyck *et al.*, 2025; Malav & Ray, 2025).

Schiff base ligands remain among the most widely investigated ligand systems in coordination chemistry because of their ease of synthesis, structural diversity, and strong affinity toward both transition and rare-earth metal ions. Salicylaldehyde-derived Schiff bases provide a versatile N,O-donor coordination environment through azomethine nitrogen and phenolic oxygen atoms, enabling the formation of stable metal complexes with diverse geometries (Abd-El-Aziz *et al.*, 2025; Abdel-Rhman *et al.*, 2023; Sridevi & Madheswari, 2025). Incorporation of salicylaldehyde moieties into a tripodal tren framework generates ligands possessing multiple coordination sites, enhanced rigidity, and favourable chelating ability, characteristics that are particularly attractive for lanthanide coordination (Alimi *et al.*, 2024; Kanesato *et al.*, 2001; Sharma *et al.*, 2023). Furthermore, the phenolic groups contribute to intramolecular hydrogen bonding and increased structural stability, while the conjugated imine framework offers opportunities for fine-tuning the electronic environment surrounding the metal centre (Falco *et al.*, 2022; Popa & Mădălan, 2022; Sarkar *et al.*, 2021).

The performance of lanthanide complexes is strongly influenced by ligand design. The ligand not only determines the coordination geometry and thermodynamic stability of the complex but also governs the electronic interactions between the ligand and the metal ion (Lucaccini *et al.*, 2017). For europium(III), appropriately designed Schiff base ligands can provide rigid coordination environments capable of minimizing non-radiative vibrational relaxation pathways while facilitating ligand-to-metal energy transfer through the well-established antenna effect (Chen *et al.*, 2002; Lionetti *et al.*, 2017). Although the photophysical behaviour of such systems ultimately requires experimental investigation, structural features such as ligand rigidity, donor atom arrangement, and coordination geometry are widely recognized as important parameters influencing the optical properties of Eu(III) complexes. Consequently, the synthesis and detailed characterization of new europium coordination compounds remain essential for the development of future lanthanide-based functional materials (Craze *et al.*, 2017; Kanesato *et al.*, 2011; Kuppusamy *et al.*, 2023).

Despite the considerable number of Schiff base complexes reported in the literature, comparatively fewer studies have focused on tripodal tren-derived salicylaldehyde ligands coordinated to europium(III) (Molloy *et al.*, 2018; Popa *et al.*, 2023). In many cases, emphasis has been placed primarily on photophysical investigations, while comprehensive physicochemical characterization and coordination behaviour have received comparatively less attention. Establishing reliable spectroscopic, analytical, and thermal evidence for complex formation is essential for understanding the coordination chemistry of these systems and for providing a foundation for subsequent investigations of their functional properties.

In this work, a tripodal Schiff base ligand was synthesized through the condensation of tris(2-aminoethyl)amine with salicylaldehyde, followed by complexation with europium(III). The ligand and its Eu(III) complex were comprehensively characterized using Fourier-transform infrared (FTIR) spectroscopy, ultraviolet-visible (UV-Vis) spectroscopy, ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectrometry (HRMS), CHN elemental analysis, and thermogravimetric analysis (TGA). The coordination behaviour of the ligand toward Eu(III) is discussed based on complementary spectroscopic and analytical evidence, while the structural characteristics of the complex are considered in relation to their potential significance for the future design of functional lanthanide coordination compounds. Although the ligand has been previously reported by our group, together with its biological evaluation (Waziri *et al.*, 2026), its coordination chemistry with Eu(III) has not previously been investigated. Therefore, the novelty of the present study lies in the synthesis and characterization of the Eu(III) complex and the investigation of its coordination behaviour, providing a structural and

spectroscopic basis for future evaluation of its photophysical properties.

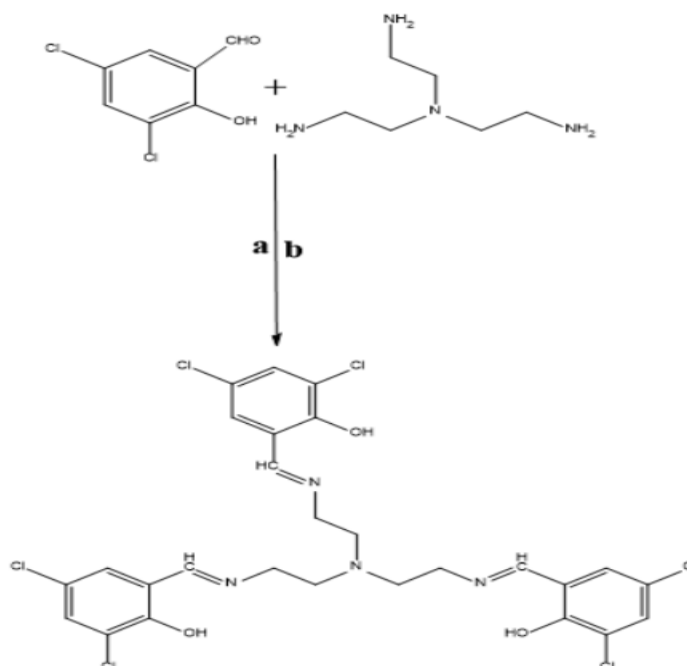
EXPERIMENTAL

Materials and reagents

All chemicals and solvents employed throughout this work were of analytical reagent grade and were obtained from Sigma-Aldrich. Unless otherwise specified, the reagents were used directly without additional purification. Tris(2-aminoethyl)amine (tren) and 3,5-chlorosalicylaldehyde served as the starting materials for ligand synthesis. Methanol and dichloromethane were used as the reaction solvents, while formic acid was added to facilitate the condensation reaction. Following synthesis, the crude products were washed and purified using diethyl ether to remove residual impurities.

Synthesis of the tren-based ligand: H_3L

The tripodal Schiff base ligand (H_3L) was synthesized via a condensation reaction between tris(2-aminoethyl)amine (tren) and 3,5-dichlorosalicylaldehyde in a 1:3 molar ratio, following a modified literature procedure (Buch *et al.*, 2020; Waziri *et al.*, 2026). Briefly, 3,5-dichlorosalicylaldehyde (0.97 g, 5.1 mmol, 3 equiv.) was dissolved in absolute ethanol (30 mL) and stirred at room temperature. A solution of tris(2-aminoethyl)amine (0.25 g, 1.7 mmol, 1 equiv.) in absolute ethanol (20 mL) was then added dropwise to the aldehyde solution under continuous stirring. Three drops of formic acid were subsequently added to catalyse the condensation reaction. The reaction mixture was stirred at room temperature for 3 h, and the progress of the reaction was monitored by thin-layer chromatography (TLC). Upon completion, the yellow precipitate formed was collected by gravity filtration, washed with diethyl ether, and dried under ambient conditions to afford the desired ligand. The purified product was subsequently characterized using the appropriate spectroscopic and analytical techniques. The synthetic route is illustrated in **Scheme 1**, while the corresponding characterization data are presented below.



Scheme 1: Synthetic route for the preparation of ligand H₃L via the condensation of 3,5-dichlorosalicylaldehyde and tris(2-aminoethyl)amine. Reagents and conditions: (a) ethanol, catalytic formic acid; (b) room temperature, 3 h.

Extracted spectral data of the (H₃L)

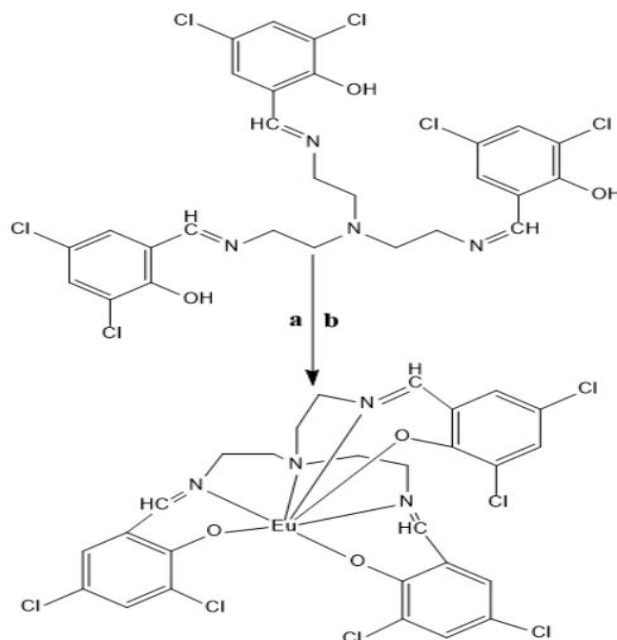
Orange solid; yield: 0.86 g (76.1%); m.p.: 181–183 °C (melted); FTIR (ATR, cm⁻¹): 3100 (O–H), 1635 (C=N), 1442 (C–O), 1157 (C–O), 732 (C–Cl); UV-vis (DMSO, 10⁻³ M): 263 (π→π*), 335 (n→π*); ¹H NMR (500 MHz, DMSO-*d*₆): δ_c (ppm): 14.32 (s, 3H, OH), 8.30 (s, 3H, HC=N), 7.42 (d, 3H, *J* = 2.5 Hz, Ar–H), 6.99 (d, 3H, *J* = 3.0 Hz, Ar–H), 3.66 (t, 6H, *J* = 5.0 Hz, (–C=N–CH₂)₃), 2.88 (t, 6H, *J* = 5.0 Hz, (–N–CH₂)₃); ¹³C NMR (125 MHz, DMSO-*d*₆): δ (ppm): 165.4 (C=N), 163.4 (C–O), 116.3, 116.7, 124.4, 129.8, 132.6 (Ar–C), 53.6 (3C, C=N–CH₂), 51.9 (3C, –N–CH₂); anal. calc. For C₂₇H₂₄Cl₆N₄O₃; C, 48.75, H, 3.64, N, 8.42, found: C, 48.45, H, 3.60, N, 8.38; ESI (DMSO) *m/z* [M + Na], [found (calc.)]: 684.9870 (684.9877).

Synthesis of the Eu(III) Complex (EuL)

The europium(III) complex (EuL) was synthesized using a 1:1 molar ratio of ligand to metal salt in a dichloromethane/methanol solvent system following a modified literature procedure (Buch *et al.*, 2020; Molloy *et al.*, 2018). Briefly, the ligand H₃L (0.20 g, 0.30 mmol, 1 equiv.) was dissolved in dichloromethane (20 mL) under

continuous stirring at room temperature. A solution of sodium acetate (0.04 g, 0.45 mmol, 1.5 equiv.) in methanol (5 mL) was then added to promote deprotonation of the phenolic hydroxyl groups, and the resulting mixture was stirred at 65 °C for 1 h. Subsequently, a methanolic solution (10 mL) of europium(III) nitrate pentahydrate, Eu(NO₃)₃·5H₂O (0.13 g, 0.30 mmol, 1 equiv.), was added dropwise to the reaction mixture. The reaction was maintained at 65 °C with continuous stirring for an additional 4 h to ensure complete complexation.

Upon completion of the reaction, the resulting precipitate was collected by gravity filtration, washed several times with cold methanol to remove any residual unreacted ligand and inorganic impurities, and dried in a desiccator over fused calcium chloride. The isolated Eu(III) complex was subsequently characterized using appropriate spectroscopic and physicochemical techniques to confirm its composition and coordination environment. The proposed synthetic route is presented in **Scheme 2**, while the corresponding characterization data are provided in the following section.



Scheme 2: Synthetic route for the preparation of the Eu(III) complex (EuL) from ligand H₃L. Reagents and conditions: (a) CH₃COONa; (b) Eu(NO₃)₃·5H₂O, CH₂Cl₂/CH₃OH, 65 °C, 5 h.

Extracted spectral data of the (EuL)

Yellow solid, yield: 0.21 g (65%); m.p.: 322–326 °C(decomposed); FTIR (ATR, cm⁻¹): 1604 (C=N), 1458 (C–O), 1280 (C–O), 763 (C–Cl); UV-vis (DMSO, 10⁻³M): 259 (π→π*), 321 (n→π*), 412 (LCT); Anal. calc. For C₂₇H₂₁Cl₆EuN₄O₃; C, 39.83, H, 2.60, N, 6.88, found: C, 39.78, H, 2.55, N, 6.84; ESI (DMSO) *m/z* [M+H]⁺, [found (calc.)]: 812.2216 (812.9035).

Measurement and instrumentation

The synthesized Schiff base ligand (H₃L) and its Eu(III) complex (EuL) were characterized using various analytical and spectroscopic techniques such as: The elemental compositions (carbon, hydrogen, and nitrogen) of these compounds were determined using a VarioElementar III microbe CHNS analyzer. Infrared spectra were recorded using a Tensor 27 Bruker and PerkinElmer FT-IR spectrometer BX, covering the range of 4000–400 cm⁻¹. Electronic absorption spectra were obtained using a Shimadzu UV-Vis 1800 spectrophotometer in DMSO at room temperature, spanning the range of 800–200 nm. The ¹H and ¹³C NMR spectra for the free ligand were acquired on a Bruker 500 MHz and 125 MHz spectrometer, respectively, at

room temperature. Chemical shifts are reported in parts per million (ppm), relative to tetramethylsilane as the internal standard for both ¹H and ¹³C NMR. Mass spectra were acquired using a Waters Acquity UPLC Synapt G2 HD mass spectrometer.

RESULTS AND DISCUSSION

Synthesis

The chloro-substituted tren-based tripodal Schiff base ligand (H₃L) was synthesized via a condensation reaction between 3,5-dichlorosalicylaldehyde and tris(2-aminoethyl)amine (tren) using a 3:1 molar ratio of aldehyde to amine in methanol, with a catalytic amount of formic acid to facilitate the dehydration step (Scheme 1). The resulting ligand was subsequently reacted with Eu(NO₃)₃·5H₂O in a 1:1 molar ratio in a dichloromethane/methanol solvent mixture to afford the corresponding europium(III) complex (EuL) (Scheme 2).

The ligand was isolated as an orange solid, whereas the europium(III) complex was obtained as a yellow solid, with moderate isolated yields ranging from 65 to 76%. The observed colour change upon complexation is consistent with coordination of the ligand to the Eu(III) ion,

which alters the electronic environment of the ligand. Although Eu(III) ions exhibit characteristic $f-f$ electronic transitions, these transitions are Laporte-forbidden and therefore contribute only weakly to the observed colour of the complex (Langyan, 2025; Thor *et al.*, 2024). Both the ligand and the complex were stable under ambient conditions. The ligand was readily soluble in chloroform, dichloromethane, hot methanol, ethanol, dimethyl sulfoxide (DMSO), and dimethylformamide (DMF), whereas the Eu(III) complex was soluble only in DMSO and DMF. This reduction in solubility following complexation is consistent with changes in the physicochemical properties of the ligand upon coordination to the metal centre, including altered molecular polarity and intermolecular interactions.

Furthermore, the Eu(III) complex exhibited a higher melting point than the free ligand, suggesting increased thermal stability following metal coordination. This behaviour is commonly observed for coordination compounds and is attributed to the formation of a more rigid and thermally stable coordination framework.

The preliminary physicochemical properties, including colour, solubility, and melting point, provide initial evidence for successful ligand synthesis and complex formation. To further confirm their structures and coordination behaviour, comprehensive spectroscopic and analytical characterization was carried out. The results obtained from these techniques are presented and discussed in the following sections.

Spectroscopic Characterization

Nuclear magnetic resonance

The formation of the ligand was confirmed by ^1H and ^{13}C NMR spectroscopy recorded in $\text{DMSO-}d_6$ at 500 and 125 MHz, respectively. NMR characterization could not be extended to the Eu(III) complex because of the paramagnetic nature of Eu(III), arising from its $4f^6$ electronic

configuration, which results in significant signal broadening and paramagnetic shifts. The spectrum of the ligand exhibited characteristic features of a salicylidene-based Schiff base.

The ^1H NMR spectrum (Figure 1a) displayed a strongly deshielded singlet at δ 14.33 ppm, assigned to the phenolic hydroxyl proton involved in intramolecular $\text{O-H}\cdots\text{N}$ hydrogen bonding. The azomethine (HC=N) proton appeared as a singlet at δ 8.30 ppm, confirming successful Schiff base formation through the disappearance of the aldehydic and amino proton resonances of the starting materials (Hasnaoui *et al.*, 2026; van Dyk, Jacobs, Kroon, Makhaola, & Brink, 2023). Aromatic proton resonances were observed in the range of δ 6.99–7.42 ppm. These signals exhibited weak splitting due to long-range meta coupling within the 3,5-dichloro-substituted aromatic ring, with small coupling constants typically in the range of $^4J \approx 1\text{--}3$ Hz. The methylene protons of the tris(2-aminoethyl)amine backbone resonated as multiplets between δ 2.88 and 3.67 ppm, corresponding to the chemically distinct $-\text{CH}_2-$ groups of the tripodal framework. Their splitting patterns are consistent with vicinal 3J coupling constants of approximately 5–7 Hz, characteristic of coupled ethylene linkages (Baral *et al.*, 2016; Mandal *et al.*, 2012).

The ^{13}C NMR spectrum (Figure 1b) further substantiated the proposed structure of the ligand. The resonance at δ 165.4 ppm was assigned to the azomethine (C=N) carbon, while the phenolic C-O carbon resonated at δ 163.4 ppm. The aromatic carbon resonances appeared mainly within δ 116–132 ppm, whereas the methylene carbons of the tripodal backbone were observed at δ 51.9 and 53.6 ppm, corresponding to the $-\text{CH}_2-\text{C=N}$ and $-\text{N-CH}_2-$ carbon atoms, respectively. The ^1H and ^{13}C NMR data confirm the successful synthesis of the tripodal Schiff base ligand.



Figure 1: (a) ¹H NMR (500 MHz, DMSO-*d*₆) and (b) ¹³C NMR (125 MHz, DMSO-*d*₆) spectra of the tripodal Schiff base ligand H₃L synthesized from tris(2-aminoethyl)amine and 3,5-dichlorosalicylaldehyde. The resonance assignments are indicated using the lettering scheme shown in the inset molecular structures. Owing to the molecular symmetry, only one of the three chemically equivalent salicylidene arms is labelled.

Infrared spectroscopy

The FTIR spectra of the free ligand (H₃L) and its europium(III) complex (EuL) are presented in Figure 2. Comparison of the two spectra provides clear evidence for coordination of the tripodal Schiff base ligand to the Eu(III) centre.

The spectrum of H₃L exhibits a broad absorption band centred at approximately 3100 cm⁻¹, assigned to the phenolic O–H stretching vibration involved in intramolecular O–H⋯N hydrogen bonding (Keypour *et al.*, 2002). Upon complexation, this band disappears completely in the spectrum of EuL, indicating deprotonation of the phenolic groups and subsequent coordination of the resulting phenolate oxygen atoms to the Eu(III) ion. This observation is characteristic of salicylidene-derived Schiff base complexes and confirms the involvement of the phenolic oxygen atoms in metal binding.

The azomethine stretching vibration, ν(C=N), observed at approximately 1635 cm⁻¹ for H₃L shifts to a lower wavenumber (1604 cm⁻¹), in the EuL spectrum. This shift reflects a reduction in the C=N bond order resulting from donation of

the azomethine nitrogen lone pair to the europium centre, providing strong evidence for coordination through the imine nitrogen atoms. Likewise, the phenolic ν(C–O) stretching vibration also shifts after complex formation, consistent with increased electron delocalization following deprotonation and coordination of the phenolate oxygen atoms. A slight shift of the ν(C–N) vibration is also observed, suggesting participation of the tertiary amine nitrogen of the tris(2-aminoethyl)amine backbone in coordination (Fanna *et al.*, 2015).

Further evidence for complex formation is provided by the appearance of new low-frequency absorption bands in the EuL spectrum at approximately 550–500 cm⁻¹ and 480–430 cm⁻¹, which are assigned to ν(Eu–O) and ν(Eu–N) stretching vibrations, respectively. These bands are absent in the spectrum of the free ligand and therefore confirm the formation of europium–oxygen and europium–nitrogen coordination bonds (Buch *et al.*, 2020).

Collectively, the FTIR spectral changes demonstrate that H₃L undergoes complete

deprotonation upon complexation and coordinates to the Eu(III) ion through the three phenolate oxygen atoms, the three azomethine nitrogen atoms, and the central tertiary amine nitrogen atom. The ligand therefore behaves as a heptadentate N_4O_3 donor, furnishing a seven-

coordinate coordination environment around the europium(III) centre. This coordination mode is consistent with the well-established behaviour of tris(2-aminoethyl)amine-derived tripodal Schiff base ligands reported for lanthanide complexes.

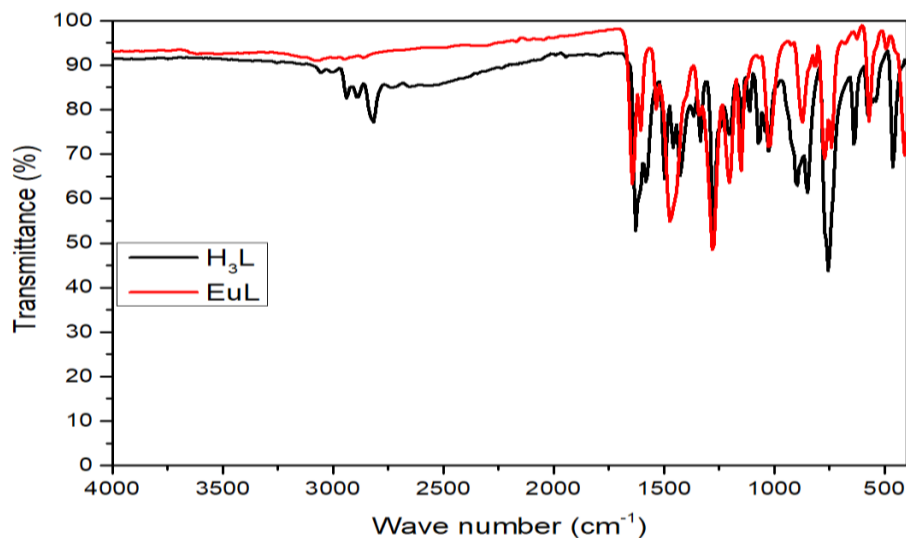


Figure 2: Comparative FTIR spectra of the tripodal Schiff base ligand H_3L and its europium(III) complex (EuL), illustrating the coordination-induced spectral changes, including the disappearance of the phenolic O–H stretching vibration, shifts in the azomethine $\nu(C=N)$, phenolic $\nu(C-O)$, and $\nu(C-N)$ bands, and the appearance of Eu–O and Eu–N stretching vibrations, consistent with the proposed heptadentate N_4O_3 coordination mode of the ligand.

UV-Vis spectroscopy

The electronic absorption spectra of the free ligand (H_3L) and the europium(III) complex (EuL) recorded in DMSO are presented in Figure 3. The free ligand exhibits two prominent absorption bands centred at 263 and 335 nm. The high-energy band at 263 nm is assigned to the ligand-centred $\pi \rightarrow \pi^*$ transition associated with the aromatic rings and azomethine chromophore, while the lower-energy band at 335 nm is attributed to an $n \rightarrow \pi^*$ transition involving the lone-pair electrons of the azomethine nitrogen atoms.

Upon coordination with Eu(III), the electronic spectrum undergoes noticeable changes. The $\pi \rightarrow \pi^*$ transition undergoes a slight hypsochromic shift from 263 to 259 nm, whereas the $n \rightarrow \pi^*$ transition shifts from 335 to 321 nm. These spectral changes reflect modification of the ligand's electronic environment following coordination. In particular, the shift of the $n \rightarrow \pi^*$ transition is attributed to coordination of the azomethine nitrogen atoms to the Eu(III) centre,

which reduces the availability of the nitrogen lone-pair electrons involved in the electronic transition (Martins *et al.*, 2021).

A new broad absorption band appears at approximately 412 nm in the spectrum of EuL . This band is assigned to a ligand-to-metal charge transfer (LMCT) transition arising from electron donation from the coordinated phenolate oxygen atoms to the Eu(III) centre. The appearance of this band provides additional evidence for successful complex formation and supports coordination through the deprotonated phenolic oxygen atoms. Similar charge-transfer bands have been reported for lanthanide complexes containing phenolate-based Schiff base ligands.

It is noteworthy that characteristic Eu(III) intra-4f electronic transitions are not clearly observed in the absorption spectrum. This is expected because the 4f–4f transitions of Eu(III) are Laporte-forbidden and possess very low molar absorptivity, rendering them considerably weaker than the ligand-centred and charge-transfer transitions. Consequently, the electronic spectra

are dominated by transitions originating from the Schiff base ligand.

The observed spectral shifts together with the emergence of the LMCT band provide spectroscopic evidence for coordination of H_3L to $Eu(III)$. These findings are consistent with the

FTIR results and support the proposed heptadentate N_4O_3 coordination mode, in which the ligand binds through the three phenolate oxygen atoms, three azomethine nitrogen atoms, and the central tertiary amine nitrogen atom (Tyagi *et al.*, 2020)

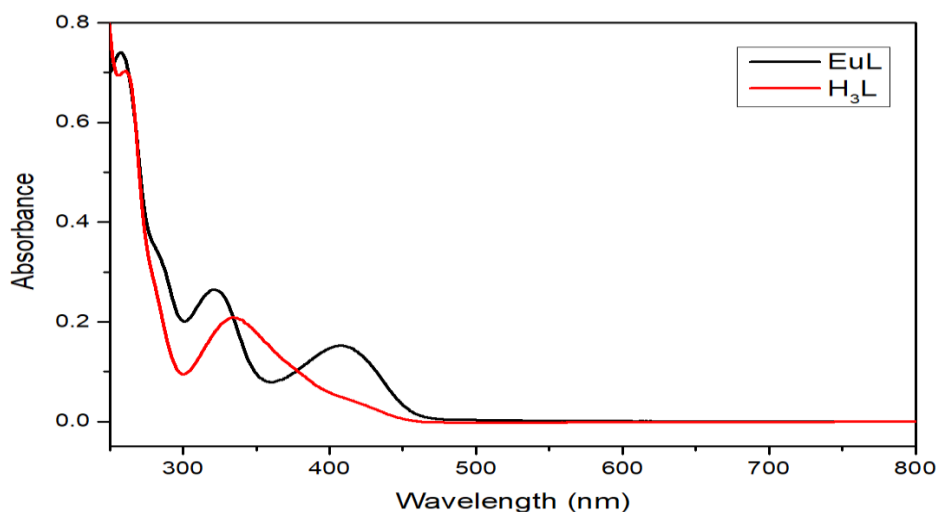


Figure 3: UV–Visible absorption spectra of the tripodal Schiff base ligand H_3L and its europium(III) complex (EuL) recorded in DMSO, illustrating the coordination-induced changes in the ligand-centred electronic transitions and the appearance of a ligand-to-metal charge-transfer band upon complex formation.

Thermogravimetric Analysis (TGA)

The thermal stability of the free ligand (H_3L) and its europium(III) complex (EuL) was investigated by thermogravimetric analysis, and the corresponding thermograms are presented in Figure 4.

The free ligand (H_3L) exhibits a multistep decomposition pattern. The thermogram remains essentially unchanged up to approximately 180–190 °C, indicating the absence of lattice or coordinated solvent molecules and confirming the good thermal stability of the ligand at lower temperatures. A major decomposition step occurs between approximately 190 and 270 °C, corresponding to a weight loss of about 40%, which is attributed to cleavage of the salicylidene-imine framework and decomposition of the organic ligand skeleton. Beyond this temperature, gradual mass loss continues up to 800 °C, arising from further degradation and carbonization of the remaining organic fragments. At the end of the analysis, the ligand exhibits a total mass loss of approximately 63.41%, leaving a carbonaceous residue.

In contrast, the europium(III) complex (EuL) displays a distinctly different decomposition profile, reflecting the influence of metal coordination on the thermal behaviour of the ligand. A small initial weight loss of approximately 5.34% is observed below 300 °C, which may be attributed to the removal of weakly bound solvent molecules or adsorbed moisture. The principal decomposition stage occurs between approximately 300 and 420 °C, accounting for a mass loss of about 40.57%. This process is assigned to decomposition of the coordinated Schiff base framework and cleavage of the metal-bound organic moieties. Above 420 °C, the complex undergoes a more gradual decomposition up to 800 °C, ultimately leaving a significantly higher residual mass than the free ligand. The larger residue is attributed to the formation of thermally stable europium-containing inorganic species, most likely europium oxide (Eu_2O_3), together with a small amount of residual carbon (Lai *et al.*, 2019).

Comparison of the two thermograms demonstrates that coordination to $Eu(III)$ significantly alters the thermal decomposition

pathway of the tripodal Schiff base ligand. While the free ligand begins its principal decomposition at lower temperatures, the major decomposition of EuL is shifted to higher temperatures, indicating enhanced thermal stability arising from coordination. The increased thermal resistance can be attributed to the formation of strong Eu–O and Eu–N coordination bonds within the rigid heptadentate N_4O_3 coordination framework, which increases the energy required to disrupt the coordinated structure. Furthermore,

the higher residual mass observed for EuL is consistent with the presence of the non-volatile europium centre and provides additional evidence for successful complex formation.

The TGA results complement the spectroscopic characterization and support the proposed coordination of H_3L as a heptadentate N_4O_3 ligand toward Eu(III), demonstrating that metal coordination enhances the thermal robustness of the ligand framework.

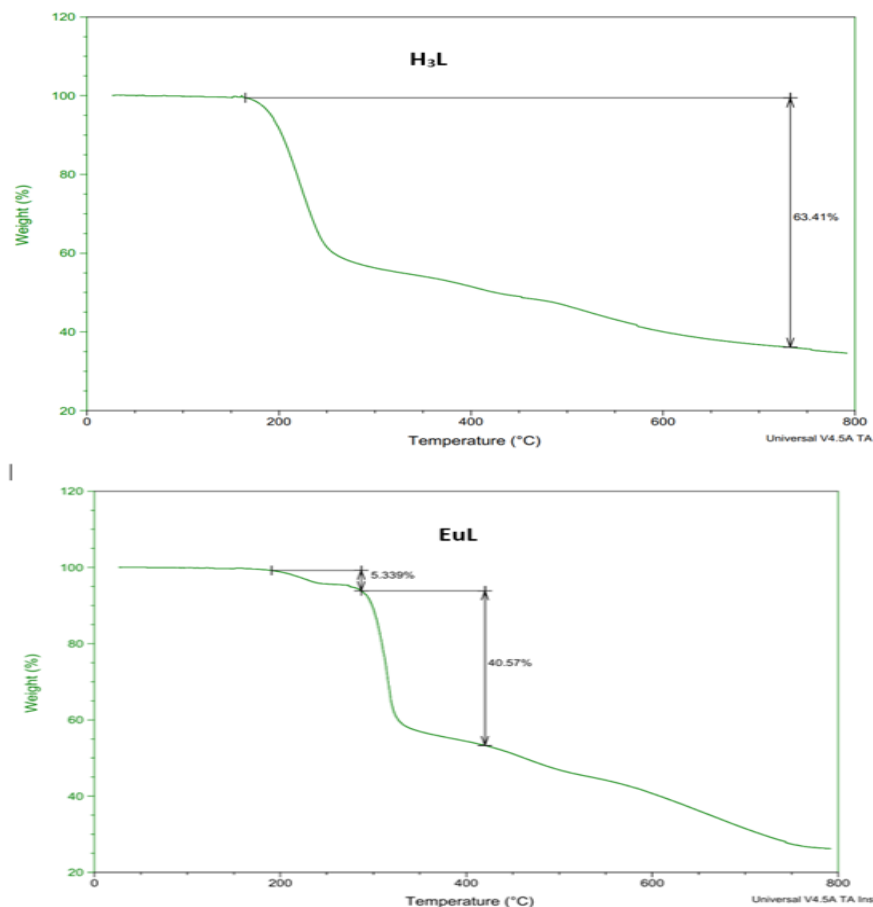


Figure 4: Thermogravimetric (TGA) curves of the tripodal Schiff base ligand H_3L and its europium(III) complex (EuL) recorded under a nitrogen atmosphere, illustrating the effect of Eu(III) coordination on the thermal decomposition behaviour and stability of the ligand.

Mass spectral study

The high-resolution mass spectra of H_3L and EuL are presented in Figure 5 and provide further evidence for the successful synthesis of the ligand and its europium(III) complex. The spectrum of H_3L exhibits a prominent molecular ion peak at m/z 684.9870, which is assigned to the sodium adduct $[M + Na]^+$. This value is in excellent

agreement with the calculated mass of 684.9877, confirming the molecular composition of the tripodal Schiff base ligand.

Following coordination, the mass spectrum of EuL displays a molecular ion peak at m/z 812.2216, calculated as 812.9035, assigned to the molecular ion $[M+H]^+$. The appearance of this higher-mass ion is consistent with formation of

the europium(III) complex and confirms incorporation of the metal centre into the ligand framework. The absence of a significant peak corresponding to the free ligand further supports successful complexation under the reaction conditions employed.

Together, the HRMS results corroborate the proposed molecular formulations of H₃L and EuL and complement the spectroscopic and thermal characterization, providing additional evidence for the successful synthesis and coordination of the tripodal Schiff base ligand to the europium(III) ion.

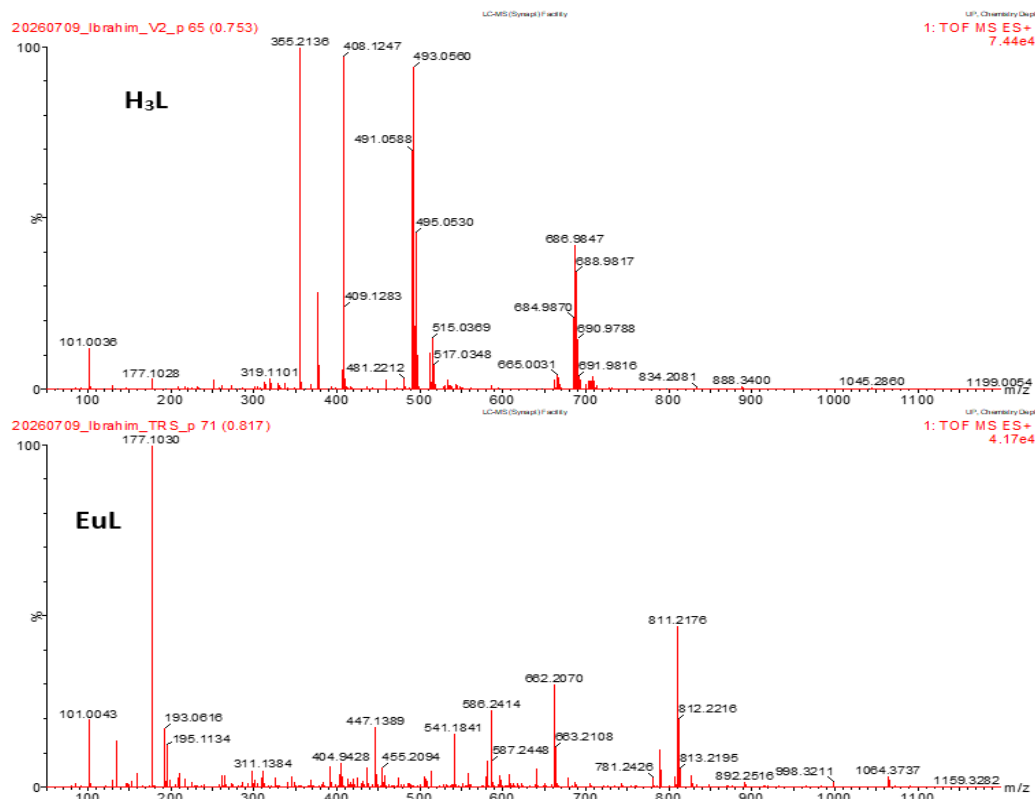


Figure 5: High-resolution TOF mass spectra of the tripodal Schiff base ligand H₃L and its europium(III) complex (EuL), showing the characteristic molecular ion peaks corresponding to $[M+Na]^+$ for H₃L and $[M+H]^+$ for EuL

Scanning Electron Microscopy (SEM)

The surface morphologies of the free ligand (H₃L) and the europium(III) complex (EuL) were examined by scanning electron microscopy, and the corresponding micrographs are shown in Figure 6.

The free ligand (H₃L) exhibits a well-defined rod-like morphology composed of elongated, randomly oriented crystallites with relatively smooth surfaces (Figure 6a). This morphology is characteristic of an ordered crystalline material and is attributed to the efficient molecular packing of the tripodal Schiff base molecules through intermolecular interactions, including π -

π stacking and hydrogen bonding involving the phenolic groups.

In contrast, the Eu(III) complex (EuL) displays a markedly different surface morphology (Figure 6b), consisting of densely packed, irregular granular particles with considerably smaller particle sizes than those observed for the free ligand. The disappearance of the rod-like crystallites and the formation of agglomerated granular domains indicate that coordination of the ligand to Eu(III) substantially modifies the crystal growth process and the packing arrangement of the molecules (Quan *et al.*, 2026).

The observed morphological transformation can be attributed to the formation of the three-dimensional coordination structure around the Eu(III) centre. Coordination through the heptadentate N_4O_3 donor set restricts the molecular flexibility of the ligand and alters the intermolecular interactions that govern nucleation and crystal growth. Furthermore, deprotonation of the phenolic groups and formation of Eu–O and Eu–N coordination bonds disrupt the hydrogen-bonding network present in the free ligand, leading to a different crystallization pathway and ultimately producing

the compact granular morphology observed for EuL (Arauzo *et al.*, 2025).

The increased particle aggregation observed for the complex is typical of many lanthanide Schiff base complexes and is likely associated with stronger intermolecular interactions between neighbouring coordination units during crystallization. These morphological changes are consistent with successful complex formation and complement the spectroscopic, thermal, and crystallographic characterization, providing further evidence that coordination to Eu(III) significantly modifies the structural organization of the tripodal Schiff base ligand.

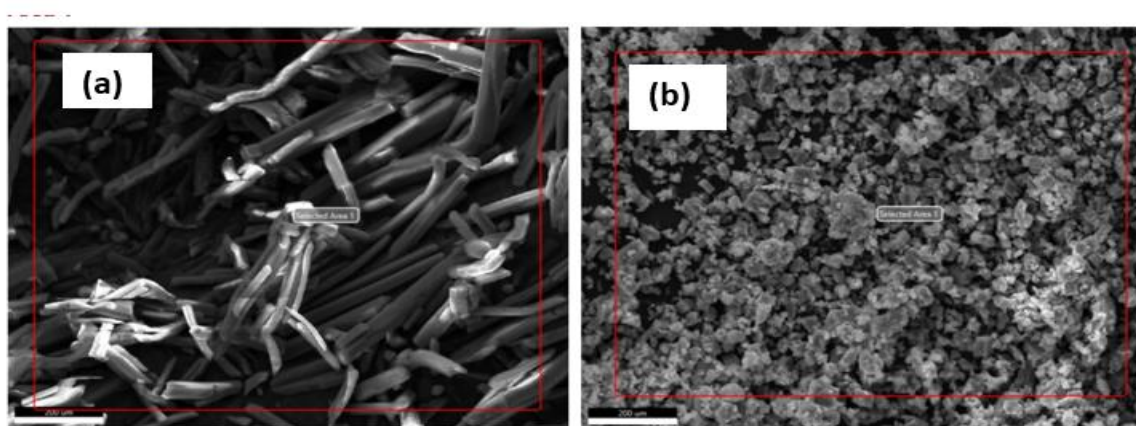


Figure 6: Scanning electron microscopy images of (a) the tripodal Schiff base ligand H_3L and (b) its europium(III) complex (EuL), illustrating the coordination-induced transformation from rod-like crystallites to densely packed granular particles.

X-ray Crystal Structure Analysis

Several attempts were made to obtain single crystals suitable for single-crystal X-ray diffraction (SCXRD) analysis of the synthesized compounds. Although the Eu(III) complexes were successfully synthesized, repeated crystallization attempts did not yield crystals of sufficient quality for structural determination. Consequently, only the free ligand H_3L afforded suitable single crystals for SCXRD analysis. The crystals were obtained by slow evaporation of a methanolic solution at room temperature over 24 h.

The molecular structure of H_3L was determined by SCXRD, and the thermal ellipsoid representation is shown in Figure 7. The ligand crystallized in the trigonal $R\bar{3}$ space group. The crystal structure unequivocally confirms the

successful formation of the chlorinated tripodal Schiff base ligand and reveals a well-defined molecular geometry without significant structural disorder. The crystallographic analysis also provides valuable insight into the ligand framework and the donor atom arrangement responsible for coordination with the Eu(III) ion. Selected bond lengths and bond angles are summarized in Table 1.

The molecular structure exhibits the characteristic features expected for a salicylaldehyde-derived tripodal Schiff base. The C–Cl bond length of 1.747(7) Å lies within the normal range reported for aryl C–Cl bonds, reflecting the larger covalent radius of chlorine compared with carbon. This observation is consistent with previously reported

crystallographic studies of chlorinated aromatic Schiff base ligands (Maliha *et al.*, 2025).

The imine functionality is clearly established by the C=N bond length of 1.271(9) Å, confirming successful Schiff base formation and the expected partial double-bond character arising from π -conjugation. Likewise, the adjacent C–N single bond length of 1.460(9) Å is in good agreement with values reported for structurally related tripodal Schiff base ligands.

Furthermore, the crystal structure reveals the presence of a strong intramolecular O–H $\cdots$ N

hydrogen bond, with an H $\cdots$ N separation of 1.883 Å. This interaction stabilizes the molecular conformation through the formation of a six-membered pseudo-chelate ring, a structural feature commonly observed in salicylaldehyde-derived Schiff base ligands (Teixeira *et al.*, 2025). The resulting rigid and preorganized ligand framework are expected to favour coordination through the three-imine nitrogen and three phenolate oxygen donor atoms, thereby facilitating the formation of the corresponding Eu(III) complexes.

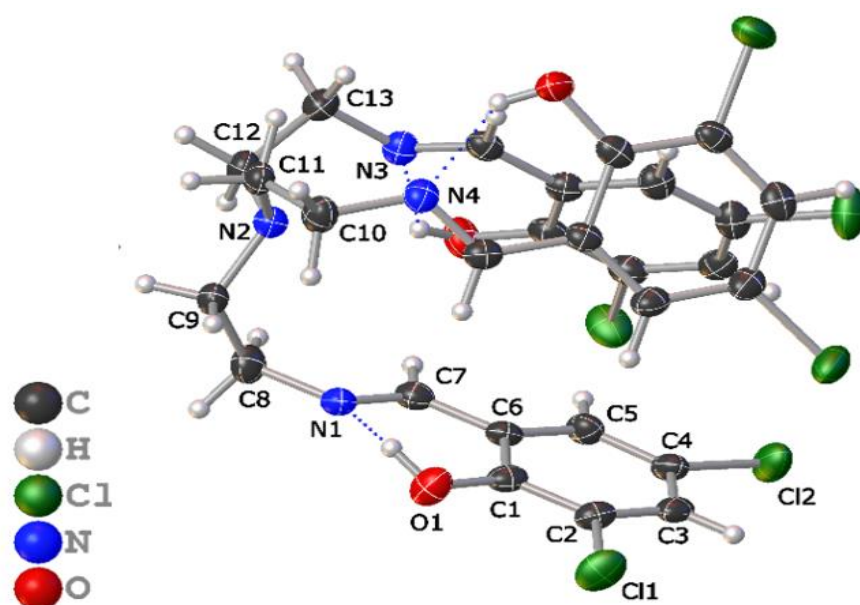


Figure 7. ORTEP representation of the molecular structure of H₃L. Thermal ellipsoids is shown at the 50% probability level, while hydrogen atoms are depicted as spheres of arbitrary radius.

Bond angle analysis further supports the molecular geometry of H₃L. The N–C–C bond angle of 122.6(6)° is consistent with the trigonal planar geometry of the imine carbon atom and reflects the conjugated nature of the azomethine functionality. Likewise, the C–C–Cl bond angle of 119.8(5)° falls within the expected range for chlorinated aromatic systems, indicating that chlorine substitution does not significantly perturb the aromatic framework. These geometric parameters agree well with those reported for structurally related salicylaldehyde-derived tripodal Schiff base ligands (Teixeira *et al.*, 2025).

The refined crystal structure, characterized by low residual factors and the absence of significant structural disorder, confirms the reliability of the molecular model. The ligand adopts the anticipated tripodal conformation, in which the three salicylidene arms are arranged around the central tertiary amine nitrogen to generate a preorganized coordination cavity. This spatial arrangement positions the three imine nitrogen atoms and three phenolic oxygen atoms in a favourable orientation for hexadentate coordination, thereby providing an ideal ligand framework for complexation with Eu(III) ions.

Table 1: Selected mean crystallographic structural parameters for H₃L

Parameters	H ₃ L1 ^a
Selected bond lengths (Å)	
C–Cl	1.747 (7)
C–N	1.460 (9)
C–N _{imine}	1.271 (9)
C–O	1.329 (9)
N...H	1.883
Selected bond angles (°)	
N–C–C	122.6 (6)
C–N–C	121.4 (6)
C–C–Cl	119.8 (5)

Note: A parenthesis indicates standard deviation on the last significant figure.

Crystallographic Packing Analysis

The crystal packing diagram of H₃L is shown in Figure 8. The molecules adopt a well-ordered three-dimensional arrangement within the crystal lattice, exhibiting a regular repeating packing motif without noticeable structural disorder. The packing is governed by the rigid tripodal framework of the ligand, which promotes efficient molecular organization in the solid state. The molecular conformation is well preserved throughout the crystal lattice, with the three salicylidene arms maintaining their orientation around the central tertiary amine nitrogen. Consequently, the spatial arrangement of the

three-imine nitrogen and three phenolic oxygen donor atoms remain essentially unchanged from one molecule to another, demonstrating the inherent rigidity of the ligand framework (Demaision *et al.*, 2003).

The packing analysis further indicates that the chlorine substituents do not induce significant distortion of the molecular geometry. Instead, the ligand retains its preorganized N₄O₃ donor cavity while accommodating efficient crystal packing. This structural rigidity is advantageous for subsequent coordination to Eu(III), as only minimal conformational rearrangement is expected during complex formation.

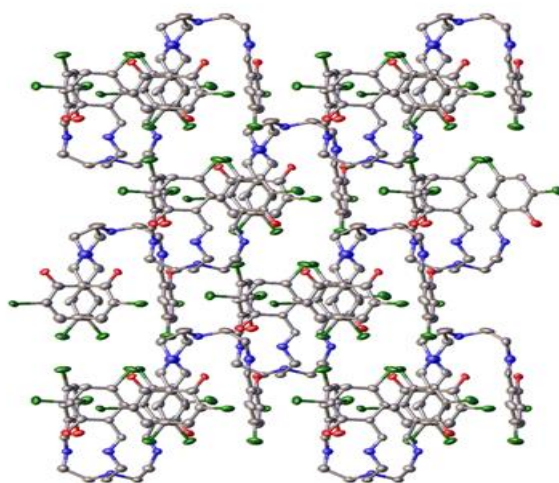


Figure 8: Crystal packing diagram of H₃L viewed along the [001] axis, showing the ordered three-dimensional arrangement of the molecules within the crystal lattice.

Localised Disorder and Packing-Induced Flexibility

Localised positional disorder is observed in the crystal structure of the compound (Figure 9) and is confined primarily to the peripheral chlorine-substituted region of the molecule. The disorder was successfully modelled over split positions and does not extend into the donor environment. Importantly, the donor nitrogen atoms and linker geometries remain well-defined despite localised positional flexibility.

The disorder's restricted nature indicates that the observed flexibility is mainly due to peripheral substituent motion rather than large-scale deformation of the molecular scaffold. This interpretation is further supported by the strong overlap observed between the chloro molecular conformations, confirming that the donor arrangement remains conserved despite local packing adjustments (Demaision *et al.*, 2003).

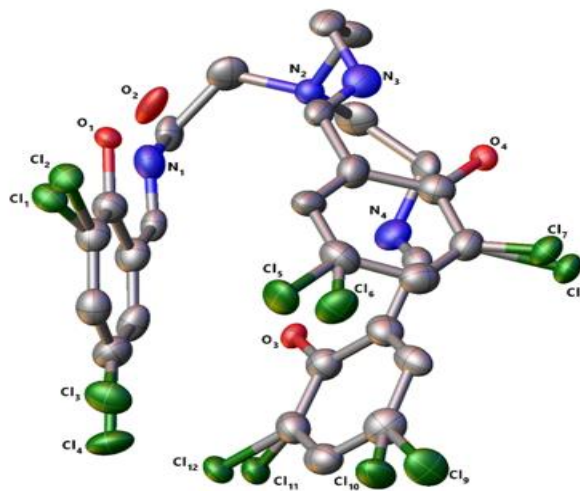


Figure 9: Localised positional disorder observed in the compound. This disorder is confined to the peripheral region bearing chlorine substituents and is associated with weak local Cl $\cdots$ O contacts. Hydrogen atoms have been omitted for clarity.

CONCLUSION

The successful synthesis of H₃L and its Eu(III) complex demonstrates that chlorinated salicylidene-based tripodal ligands derived from tris(2-aminoethyl)amine provide an effective platform for lanthanide coordination. The complementary spectroscopic analyses confirmed ligand formation and metal coordination, while single-crystal X-ray diffraction of the free ligand unequivocally established its molecular architecture and revealed a rigid, preorganized N₄O₃ donor environment ideally suited for heptadentate metal binding.

Although suitable single crystals of the Eu(III) complex could not be obtained, the crystallographic characterization of H₃L provides valuable insight into the structural features governing its coordination behaviour. The ligand adopts a well-defined tripodal conformation

stabilized by intramolecular O–H $\cdots$ N hydrogen bonding and an ordered crystal packing arrangement, features that preserve the orientation of the donor atoms and are expected to minimize conformational reorganization upon coordination. These structural characteristics account for the efficient chelation of Eu(III) observed from the spectroscopic investigations. The successful incorporation of Eu(III) into the tripodal ligand framework demonstrates the versatility of this ligand architecture for lanthanide coordination chemistry. The combination of a rigid heptadentate donor set, favourable coordination geometry, and excellent structural integrity makes this system a promising scaffold for the development of functional lanthanide complexes with potential applications in luminescent materials, molecular sensing, catalysis, and related areas of advanced coordination chemistry.

This study provides a comprehensive structural and spectroscopic foundation for the rational design of tripodal lanthanide complexes. The findings not only expand the chemistry of tren-derived Schiff base ligands but also establish a reliable platform for the development of new rare-earth coordination compounds with tailored structural and functional properties.

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Author Contributions

All authors contributed equally to the conception and design of the study, experimental work, data acquisition, data analysis, and manuscript preparation. All authors reviewed, revised, and approved the final version of the manuscript.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Data availability statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request. Crystallographic data for H₃L have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under deposition number 2558230 and can be obtained free of charge from the CCDC.

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