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Prepared and characterized complexes formed by imine from 2,2,6,6-tetramethyl-3,5-heptanedione, involving samarium and zinc as the metal centers

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ABSTRACT

A Schiff base ligand was prepared by reacting 2,2,6,6-tetramethyl-3,5-heptanedione (a diketone) with primary amines in both aliphatic and aromatic forms. The process employed was microwave-assisted, which is considered environmentally friendly because it eliminates the needed for solvents, lowers chemical hazards, and greatly accelerates reaction times compared to conventional methods. The resulting compounds were characterized using a comprehensive set of nuclear magnetic resonance (NMR) techniques, including ^{1}H-NMR, ^{13}C-NMR, HSQC, and COSY experiments. These spectroscopic methods were crucial due to the structural ambiguity caused by tautomerism. The detailed analysis confirmed the successful formation of the imine (–C=N–) group, verified the ligand structures, and established a solid basis for their further use in coordination chemistry and potential biological activity testing. Overall, the results indicated that microwave-assisted synthesis provides a simple, energy-efficient, and environmentally friendly approach for preparing Schiff base ligands derived from diketones. This method can be extended to design a wide range of Schiff bases with tailored properties for use in catalysis, materials, and pharmaceutical applications

Key words : Samarium metal, Zinc metal, NMR, β-Diketone, Imine compound, Complex.

Introduction

In simply the β-dicarbonyl compounds containing at least one α-hydrogen atom that can reversibly switch between two enolic forms through keto–enol tautomerism. In the cis-enolic forms, the molecule's [1] spatial arrangement allows the hydrogen of the hydroxyl group to be positioned at an optimal distance and in a favorable orientation, enabling the formation of an intramolecular hydrogen bond (IHB). This interaction stabilizes the cis-enolic form of β-dicarbonyl compounds[2].The functional groups involved hydroxyl, carbonyl, and alkene participate in both enolic forms within a six-membered ring, facilitating π-electronic conjugation[3], which results in a cyclic chelated ring. Many β-dicarbonyl compounds mainly exist in the enolic form, both pure and in solution. The study of TMHD (2, 2, 6,6-tetramethyl-3,5-heptanedione), also known as dipivaloyl methane, is particularly interesting because[4] it contains two bulky tert-butyl groups with strong electron-donating properties at both β-positions. The steric bulk and electron-donating effects of these substituents are expected to enhance[5] the intramolecular hydrogen bond (IHB). In this context, Mahajan et al. reported the synthesis of thieno (2,3) quinoline-2-carboxylic acid derivatives (flavonoid-like) and pyrazole-type compounds[6], demonstrating antioxidant and anti-inflammatory activities through ultrasonic catalysis starting from asymmetric β-diketone. Regarding the biocatalytic synthesis of 1,3-diketones[7], a straightforward method was first described in 2010 by Müller and colleagues, utilizing a recombinant enzyme (YpYerE, a thiamine diphosphate (ThDP)-dependent ldolase from Yersinia pseudotuberculosis O: VI). This enzyme catalyzes the cross-aldol condensation[8] between aldehyde (formed via in situ decarboxylation of pyruvate) and ketones, producing chiral α-acyl tertiary alcohols. The biocatalyst displays broad substrate tolerance, accepting cyclic and open-chain ketones, diketones, and α- and β-ketoesters[9] as acceptor substrates. Therefore, when this acceptor is an α-diketone, the final product is a β-diketone with two substituents (alkyl and hydroxyl) on the central methylene[10]. Schiff bases are an important group of biologically active compounds, commonly called imines, characterized by the presence of the azomethine group (C=N bond). The discoveries of Hugo Schiff marked[11] a pivotal moment in chemistry, as their influence continues to grow across many fields, especially in coordination chemistry[12]. Schiff bases are frequently used as ligands in coordination complexes because of their ability to bind metal ions through the nitrogen atom. In 1889, Alphonse Combes reported the creation of the first metal complex[13] of Schiff bases, where a copper complex was formed by reacting ethylene diamine with two equivalents of acetylacetone, marking the earliest use of Schiff bases as ligands in coordination chemistry. Since then, many applications[14] of metal–Schiff base complexes have been identified, and these complexes have played a vital role in various scientific and technological fields[15]. Microwave-assisted synthesis (MW) has played a significant role in organic synthesis over the past decade. In certain study [16], reported that microwave-assisted reactions are up to eighty times faster than traditional heating and are more energy-efficient[17]. Microwave heating provides better thermal efficiency faster reaction rates, energy savings, and improved product quality, making it highly valuable in organic synthesis[18]. The synthesis of aminothiazole derivatives under microwave conditions is particularly important[19]. The preparation of 2-(N-substituted) aminothiazole derivatives from α-bromoketones using microwave irradiation has been reported [20]. In addition, the synthesis of 2-amino-4-phenylthiazole under microwave conditions has been described [21]. This work aims to prepare Schiff base ligands through the reaction of 2,2,6,6-tetramethyl-3,5-heptanedione (TMHD) with primary amines using microwave-assisted synthesis, a fast, efficient, and environmentally friendly method.The prepared ligands are characterized with comprehensive NMR techniques (^{1}H, ^{13}C, HSQC, COSY) to confirm their structures and resolve tautomeric ambiguities. The study also aims to establish a reliable method for preparing well-defined ligands with potential uses in coordination chemistry, catalysis, materials science, and pharmaceutical research.

MATERIAL AND METHODS

Chemicals

In this study, chemicals was prepared by several used companies, as shown in Table 1:

Table 1. Reagents and materials.

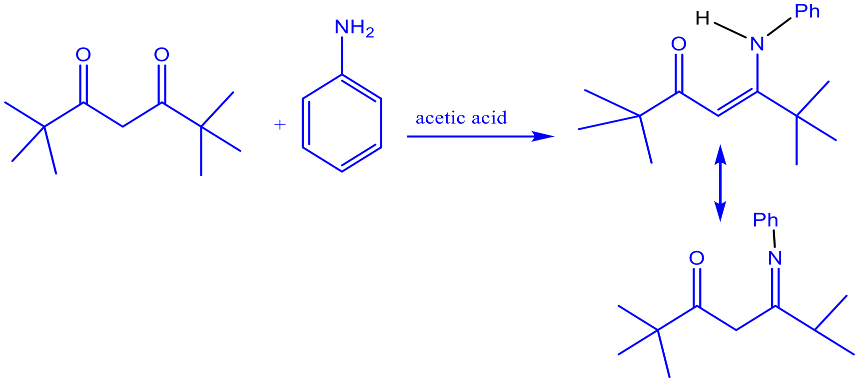
Chemicals	Formula	Company Supply
2,2,6,6-Tetramethyl-3,5-Heptan Dione (TMHD)	$C_{11}H_{20}O_2$	Shanghai Macklin Biochemical Co., Ltd
Aniline	$C_6H_5NH_2$	LOBA CHEMIE PVT.LTD
Acetic acid	CH_3COOH	Merck
Methanol	CH_3OH	Chem-LAB
n-Hexane	C_6H_{14}	Alph Chemika
Ethanol	C_2H_5OH	Honey Well
Zinc Acetate	$Zn(CH_3COO)_2.2H_2O$	Scharlaus

Samarium Chloride	$SmCl_3 \cdot 6H_2O$	Leyan Biotechnology Co., Ltd

Preparation.

1. Preparation of the Schiff bases.

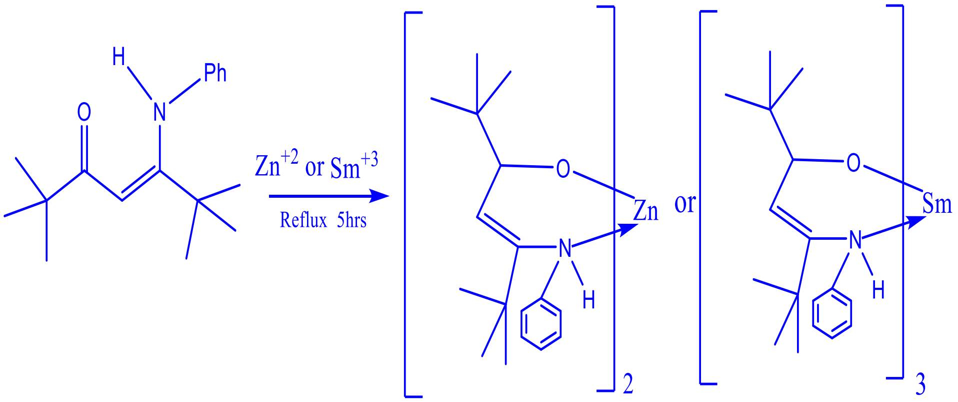
Preparation of the Enamine Compound was done from the Condensation of Primary Amine Aniline with β-Diketone 2,2,6,6-Tetramethyl-3,5-Heptanedione. Based on a previous study [22] with some modifications, 0.41 mL of TMHD, the β-diketone compound, was added to a small volumetric flask, followed by 1 mL of acetic acid. The mixture was placed on a mixing device, and then 0.18 mL of aniline was added. The mixture was stirred for 10 minutes. It was then transferred to a microwave (MW) for 7 seconds, rested for 1 minute, microwaved for 8 seconds, and rested again for 1 minute. Next, it was microwaved for 15 seconds, followed by a 1-minute rest, and this cycle was repeated 11 times. The product was analyzed by TLC using an eluent mixture of 0.2 mL methanol and 3 mL hexane, and finally purified by column chromatography with the same eluent Scheme (1).



Scheme1. The preparation of Schiff Base Ligands.

2. Complexes Preparation

Non-nano zinc and samarium complexes were prepared through the reaction of the THMD reaction with Zn and Sm metals, as displayed in scheme 2. Involved mixing 1 mmol (0.0766 g) of $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved in 4 mL of methanol with a ligand prepared in the first step, using 0.2 mL (1 mmol) dissolved in 4 mL of ethanol, at a ratio of 1:2. Similarly, 0.0848 g (1 mmol) of $SmCl_3 \cdot 6H_2O$ was dissolved in 6 mL of ethanol and mixed with the ligand prepared in the first step, 0.2 mL (1 mmol), dissolved in 2 mL of ethanol, in a ratio of 1:3. The mixtures were refluxed at 64 °C for 3 hours and 78 °C for 4 hours, respectively. Each mixture was stirred using a magnetic stirrer for 15 minutes and allowed to stand for 10 minutes. The resulting precipitates were filtered, dried in an oven at 45 °C, and finally purified by washing with 50% ethanol[23].



Scheme 2. Synthesis of Zinc and Samarium Complex.

RESULTS AND DISCUSSION

The ligand is prepared by reacting 2,2,6,6-tetramethyl-3,5-heptanedione with aniline to produce an imine compound in the form of an enol, which is identified by NMR spectra, including ^{1}H NMR, ^{13}C NMR, COSY, and HSQC techniques. The compound is well confirmed because it exists as an enol, and the nitrogen atom is bonded to a hydrogen atom, confirming it as an imine. This is observed in the spectra in Figures(1-4), which show a signal at 9.981 ppm. The confirmation that this signal is due to a proton attached to nitrogen is the absence of any spot in the two-dimensional NMR spectrum in Figure 1, indicating the hydrogen atom is bonded to nitrogen rather than carbon. Another key observation is the vinylic proton signal, appearing at 6.800 ppm. The aromatic protons show three signals: two are doublets, and the third appears as a triplet at 7.048 ppm. This pattern confirms that the apparent pairing corresponds to an ortho arrangement, causing the two middle protons on the ring—sharing the same chemical environment—to appear as a single signal. In contrast, the outer protons form an ortho pair, resulting in the triplet in the spectrum [24]. The reaction of the prepared ligand with zinc metal forms a tetrahedral complex with sp^3 hybridization. This is indicated by the absence of magnetism in the magnetic susceptibility results, whereas the samarium complex with the ligand shows a magnetic moment, suggesting that the complex exhibits d^2sp^3 hybridization Infrared spectrum: A significant change in the shape of the spectrum and the positions of the bands is observed in the spectra of complex. A strong absorption band was recorded at 1571 and 1504 cm^{-1}, attributed to C=C stretching vibrations in aromatic rings. A characteristic band also appeared at 1045 cm^{-1}, which can be assigned to M–O–C or M–N–C vibrational modes, thereby strengthening the evidence for a direct interaction between the metal and the donor sites in the ligand. Meanwhile, the low-frequency region of the spectrum exhibited clear bands at 472 and 412 cm^{-1}, corresponding to the stretching vibrations of the Zn–O and Zn–N bonds, which are considered definitive spectroscopic indicators of the formation of genuine coordination bonds between the zinc ion and the oxygen and nitrogen atoms of the ligand Figures 5, A broad absorption band is observed at 3444 cm^{-1}, which is attributed to the stretching vibrations of the N–H group overlapped with the symmetric stretching of the O–H bond of a water molecule. An absorption band at 2953 cm^{-1} is assigned to the aliphatic C–H stretching vibrations of the vinyl group. Bands appearing in the range 1400 - 1384 cm^{-1} are attributed to C–N and C–O stretching vibrations, while the bands at 867, 759, and 734 cm^{-1} are assigned to out-of-plane C–H bending vibrations of the aromatic ring, indicating the presence of an aromatic moiety in the ligand. Furthermore, bands observed at 601 and 476 cm^{-1} are attributed to Sm–O and Sm–N vibrations, respectively, confirming the formation of coordination bonds between the samarium ion and the oxygen and nitrogen atoms in the ligand Figure 6 [25]. The molar conductivity (Λm) measurements of the complex [Sm(L)$_3$] showed relatively low values of 20 µS·, respectively. These low values clearly indicate that both complexes behave as non-electrolytes (non-ionic) in the employed solvent. This behaviour can be attributed to the absence of dissociation of the complexes into free ions upon dissolution, which suggests that the ligands are strongly coordinated to the samarium ion within the coordination sphere, with no counter ions present outside the complex. Table (2) [26].

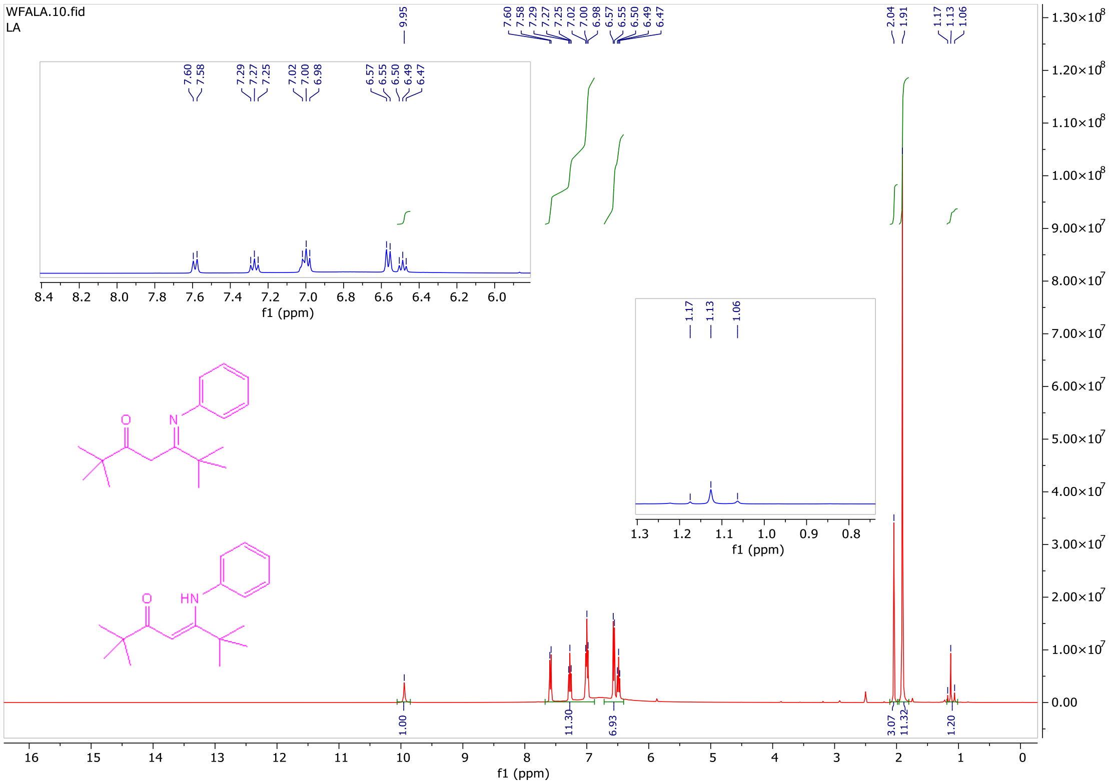


Figure 1. The proton nuclear magnetic resonance spectrum (^{1}H NMR) of the compound LA.

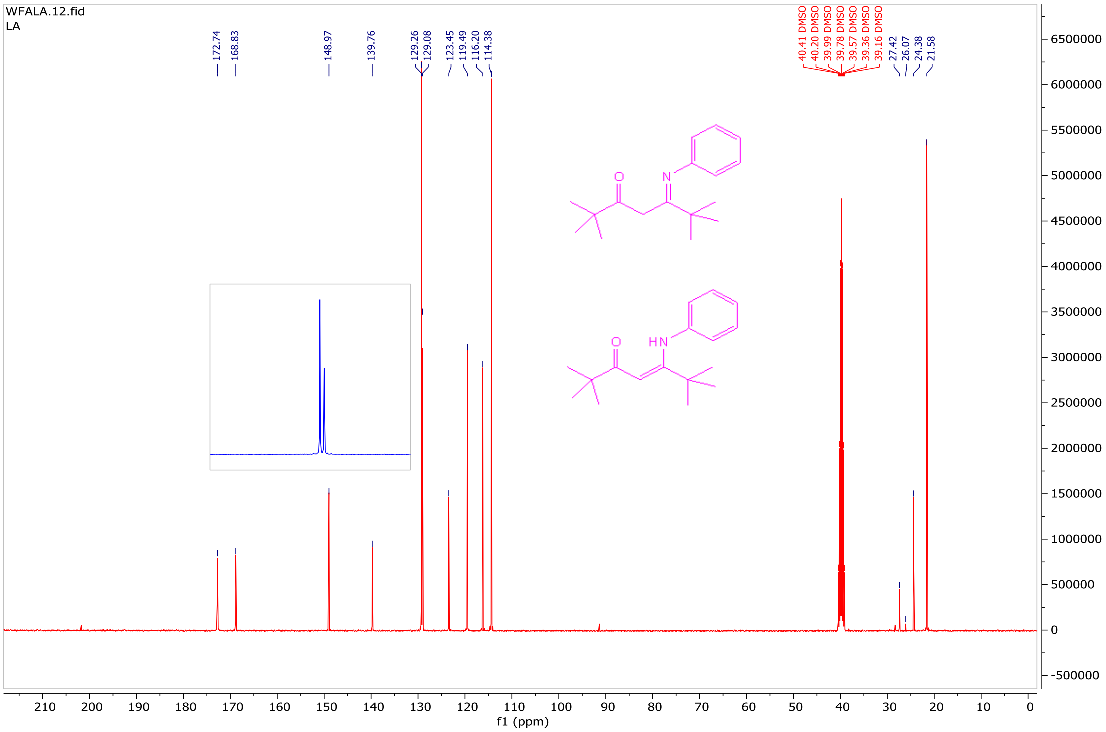


Figure 2. The ^{13}C nuclear magnetic resonance spectrum (^{13}C NMR) of compound LA.

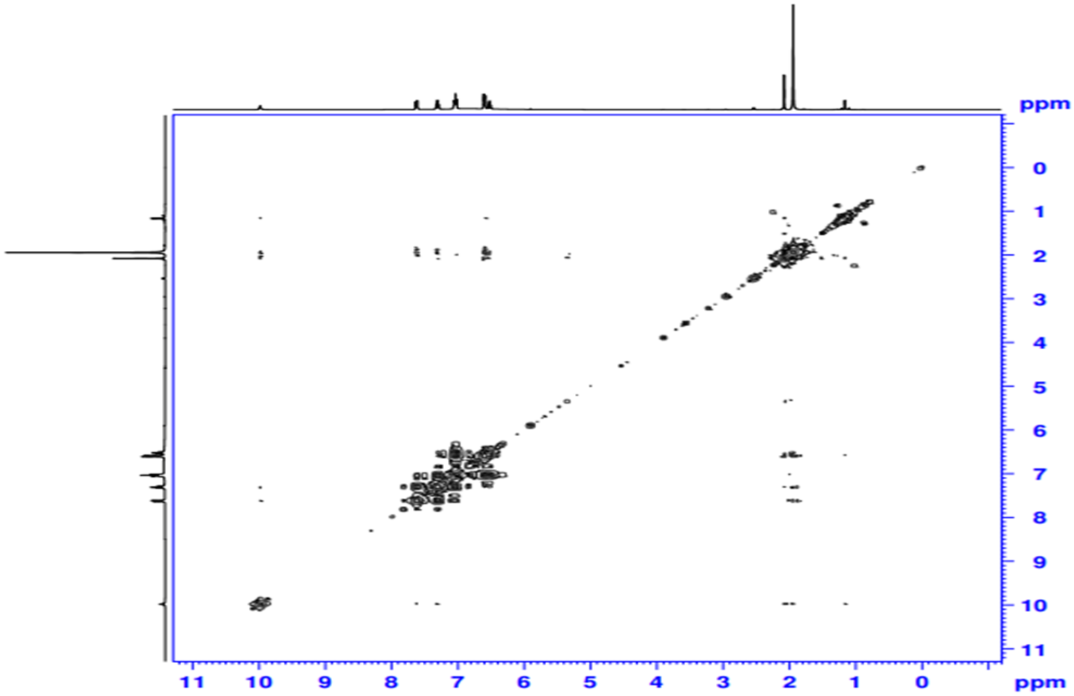


Figure 3. Two-dimensional ^{1}H NMR COSY spectrum of compound LA.

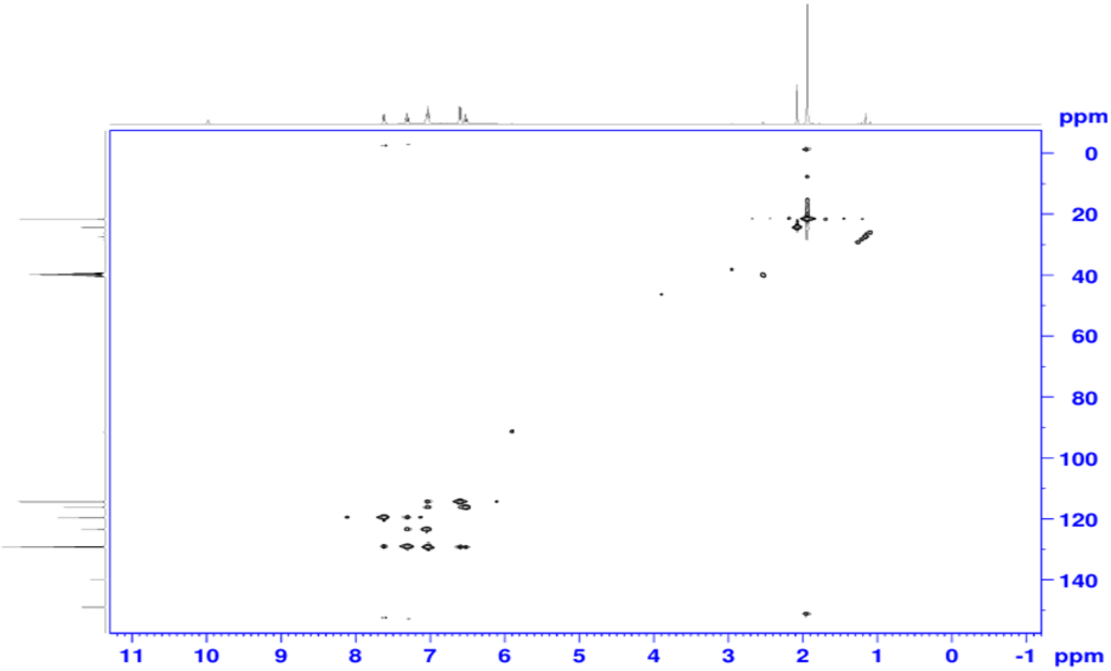


Figure 4. Two-dimensional ^{1}H, ^{13}C HSQC NMR spectrum of compound LA.

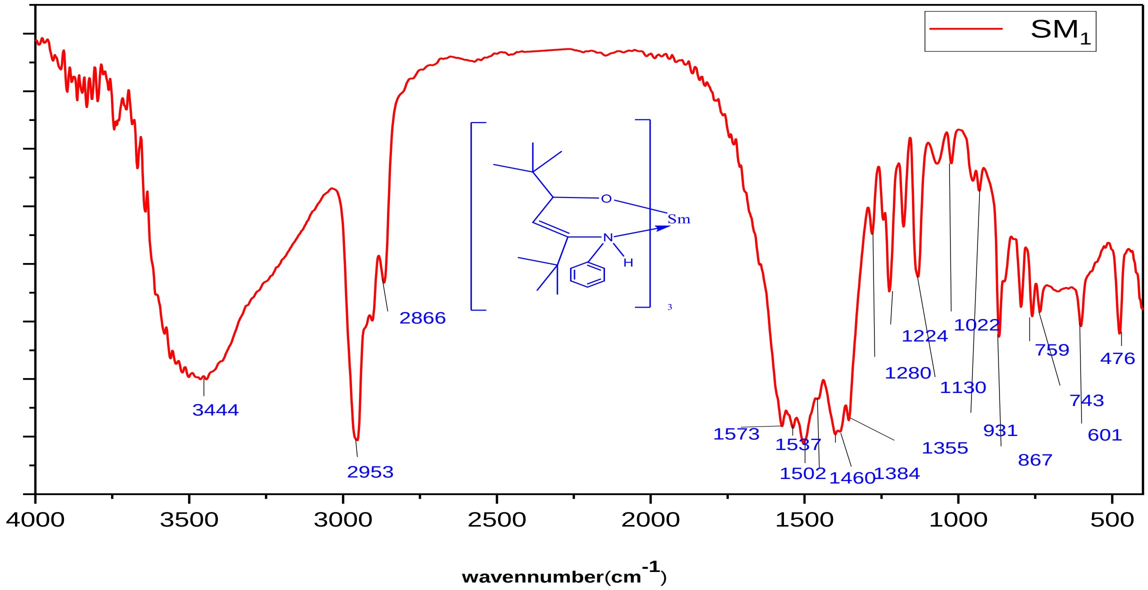


Figure 5. The FT-IR spectrum of the Samarium complex.

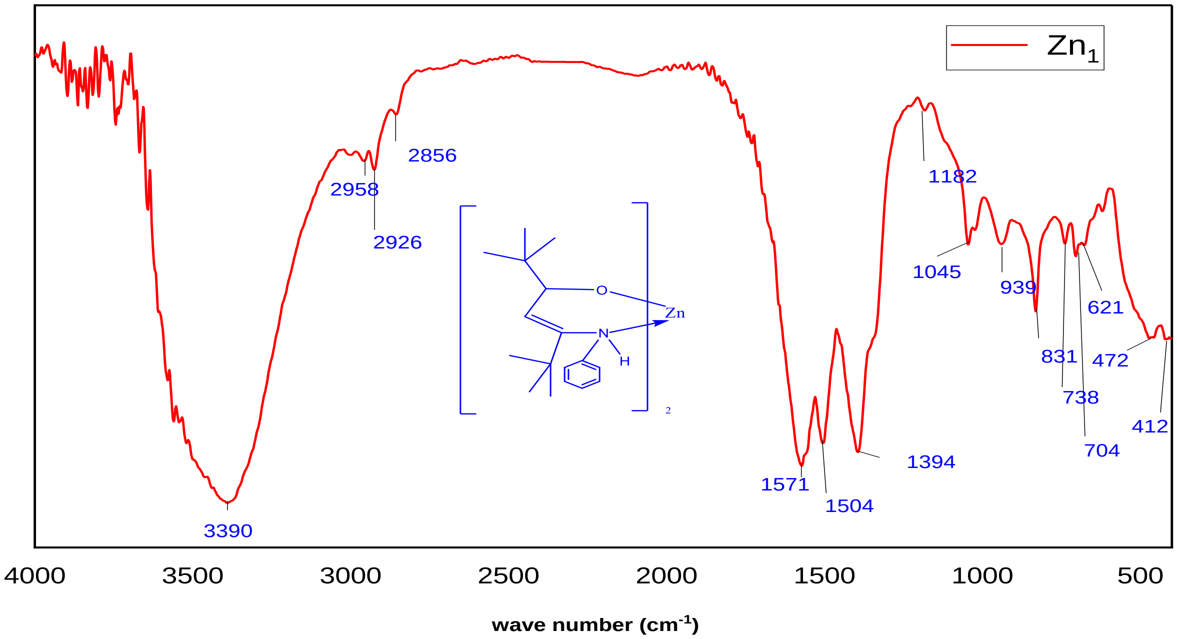


Figure 6. FT-IR spectrum of the Zn1 complex.

The molar conductivity measurements were carried out in ethanol at a concentration of 1×10^{-3} M and at room temperature (25 ^{o}C).

Table 1. Molar conductivity values of the synthesized complexes measured in μs

No	Complex	Λ_m/ μs	The ionic ratio
1	$[Sm(L)_3]$ Nano	5	Non-ionic
2	$[Sm(L)_3]$	20	Non-ionic

Table2. Magnetic susceptibility data of the synthesized compound

Hybrids	**Effective magnetic moment** ***(μeff)/ B.M***	**Atomic sensitivity** **$XA \times 10^{-6}$**	**Correction factor** ***$D \times 10^{-6}$***	**molar sensitivity** ***$X_M \times 10^{-6}$***	**Gram sensitivity** ***$X_g \times 10^{-6}$***	**Complexes**
SP^3	0.00	0.00	0.00	0.00	0.00	**$[Zn(L_1)_3]$**
d^2SP^3	0.8161	284.27×10^{-6}	-275×10^{-6}	9.27×10^{-6}	0.027×10^{-4}	**$[Sm(L_2)_3]$**

Conclusions

The compound (Z)-6,6,2,2-tetramethyl-5-(phenylamine)hept-4-en-3-one was prepared via the reaction of the parent compound 6,6,2,2-tetramethyl-5,3-heptadione with aniline, yielding the product in its enol form in solution through the formation of a C=N bond. Subsequently, metal complexes were prepared by reacting the imine with zinc (Zn^{2+}) and samarium (Sm^{3+}), resulting in a tetrahedral complex with sp^3 hybridisation around zinc and an octahedral complex with d^2sp^3 hybridisation around samarium. The imine was characterised by infrared (IR) spectroscopy and ^1H- and ^{13}C-NMR spectroscopy to confirm its functional groups and stereochemistry, while the metal complexes were analyzed using magnetic susceptibility measurements and molar conductivity to investigate their electronic configuration and electrolytic nature.

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