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Annu Devi
 Department of Chemistry,
 Kurukshetra University,
 Kurukshetra, Haryana, India

Mamta
 Department of Chemistry,
 Kurukshetra University,
 Kurukshetra, Haryana, India

Anita Phor
 Department of Chemistry, Hindu
 College Sonapat, Sonapat,
 Haryana, India

JS Phor
 Department of Physics, CRA
 College, Sonapat, Haryana, India

Ashu Chaudhary
 Department of Chemistry,
 Kurukshetra University,
 Kurukshetra, Haryana, India

Corresponding Author:
Ashu Chaudhary
 Department of Chemistry,
 Kurukshetra University,
 Kurukshetra, Haryana, India

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Synthesis, characterization and remarkable pharmacological applications of lanthanide complexes with Schiff base moiety

Annu Devi, Mamta, Anita Phor, JS Phor and Ashu Chaudhary

Abstract

The lanthanide ions are distinguished from those of the d-transition metal ions by their propensity to exhibit enhanced coordination numbers by the lanthanide complexes. Complexes of lanthanides range in coordination number from 6 to 12. Lanthanides, often known as rare earth elements, are a group of 15 different elements. One of the many parts of rare earths, coordination compounds, is crucial for the diagnosis and treatment of a wide range of illnesses. These substances can also be used as antimicrobial, antibacterial, and antiviral agents, as well as pharmacological agents in the diagnosis of cancer. Because of their paramagnetic properties, lanthanides and their complexes are often used in medicine as contrast agents for magnetic resonance imaging. They aid in the treatment of neoplastic diseases as well. Lanthanide (III) ions can be used to successfully create Schiff base compounds. The anticancer, antibacterial, antiviral, and antifungal activity of Schiff base compounds can be markedly improved by coordination to a metal ion, according to recent studies, which has sparked more interest in these substances. The synthesis and biological functions of Schiff-based lanthanide compounds will be summarised in this review.

Keywords: Schiff base ligands, lanthanides, antimicrobial, antibacterial and anticancer

Introduction

In recent years, lanthanides' coordination chemistry has grown significantly. The high charge and compact size requirements for high coordination are all met by lanthanides. "The ions of lanthanides can achieve coordination numbers between 6 and 12, with 6 being the most common. Lanthanides are widely recognized for their extensive coordination chemistry. The investigation of lanthanide complexes has increased over the last few years. Because of their stability, biological activity, and possible uses in fields like oxidation catalysis, electrochemistry, etc., metal complexes of Schiff bases containing nitrogen and other donors have received a lot of interest during the past two decades [1]. Due to their wide range of biological activities, which include pharmacological anticancer, fungicidal, bactericidal, anti-inflammatory, and antiviral activities [2], the synthesis of transition metal complexes with Schiff bases of nitrogen and oxygen donor has sparked interest. Schiff bases are often ligands that can form very stable complexes with transition metals, such as bidentate (1), tridentate (3), tetradentate (3), or polydentate (4) ligands. They can only operate as coordinating ligands if they include a functional group, often the hydroxyl, close enough to the condensation site to allow for the formation of a five- or six-membered ring in response to a metal ion. Numerous areas, including biological, inorganic, and analytical chemistry, use schiff bases produced from aromatic amines and aromatic aldehydes [3-4]. Over a century of research has not diminished interest in Schiff bases and their metal complexes [5]. Bases have a chelating structure, are easy to produce, mild electron donors, and have easily controllable electronic and steric effects, making them useful. The active component of a nematocidal composition is a Schiff base metal complex with ONO and ONS donor sites⁶. Due to its coordinative [7], pharmacological, and analytical chemistry applications as metal extraction agents [8], hydrazine derivatives have been the subject of extensive research in the last ten years. Coordination chemistry has greatly benefited by the development of Schiff base metal complexes. The relevance of N and O donor ligands in both industry and biology has generated a lot of interest in metal complexes containing these ligands [9]. According to their chemical makeup, some Schiff bases were investigated for fungicidal action.

Numerous of these substances have a variety of therapeutic benefits, including activity against leprosy, bacterial and viral infections, as well as leprosy, TB, and other diseases. O, N donor chemicals have gained significant momentum in recent years, presumably as a result of their extraordinary potential to block ribonucleotide reductase, a necessary enzyme in DNA synthesis [10]. They can be used as fungicidal, antibacterial, and drug-like substances. The chelating abilities of Schiff bases made from 2-hydroxy aldehydes and ketones have a wide range of uses in industry, agriculture, and medicine. A variety of enzymatic processes involving the interaction of an enzyme's amino group, often a lysine residue, with a substance's carbonyl group appears to involve the use of Schiff bases as crucial intermediates. A charge transfer between these groups and the oxygen atoms of the Schiff bases can occur when they are formed between methylal and the amino group of the lysine side chains of proteins, according to stereo chemical research using molecular models. Schiff bases made from pyridoxal (the active form of vitamin B₆) and amino acids are regarded as very important ligands from biology. Non-enzymatic

glycosylations involve the use of Schiff bases as intermediates. Numerous physiologically significant Schiff bases have been documented in the literature to exhibit antifungal, anti-inflammatory, anticonvulsant, anticancer, and anti-HIV activities [11]. The chemistry of vision involves an interaction between the amino group of the protein (OPSIN) [12] and the aldehyde function of the 11-cis retinal. Due to their synthetic versatility, selectivity, and sensitivity to a range of metal atoms, Schiff bases' metal complexes are intensively researched. They are discovered to be helpful in catalysis, in medical as antibiotics and anti-inflammatory agents, in industry as antibiotics and anti-inflammatory agents, and in industry as anticorrosion. Due to their intriguing and significant characteristics, such as their capacity to catalyse the hydrogenation of olefins and the transfer of an amino group, a vast variety of Schiff bases and their complexes have been researched [13]. Preparing their solid complexes makes use of the Schiff bases' strong chelation affinity for transition metal ions." In Figure 1, we list the uses for Schiff base ligands and their complexes.

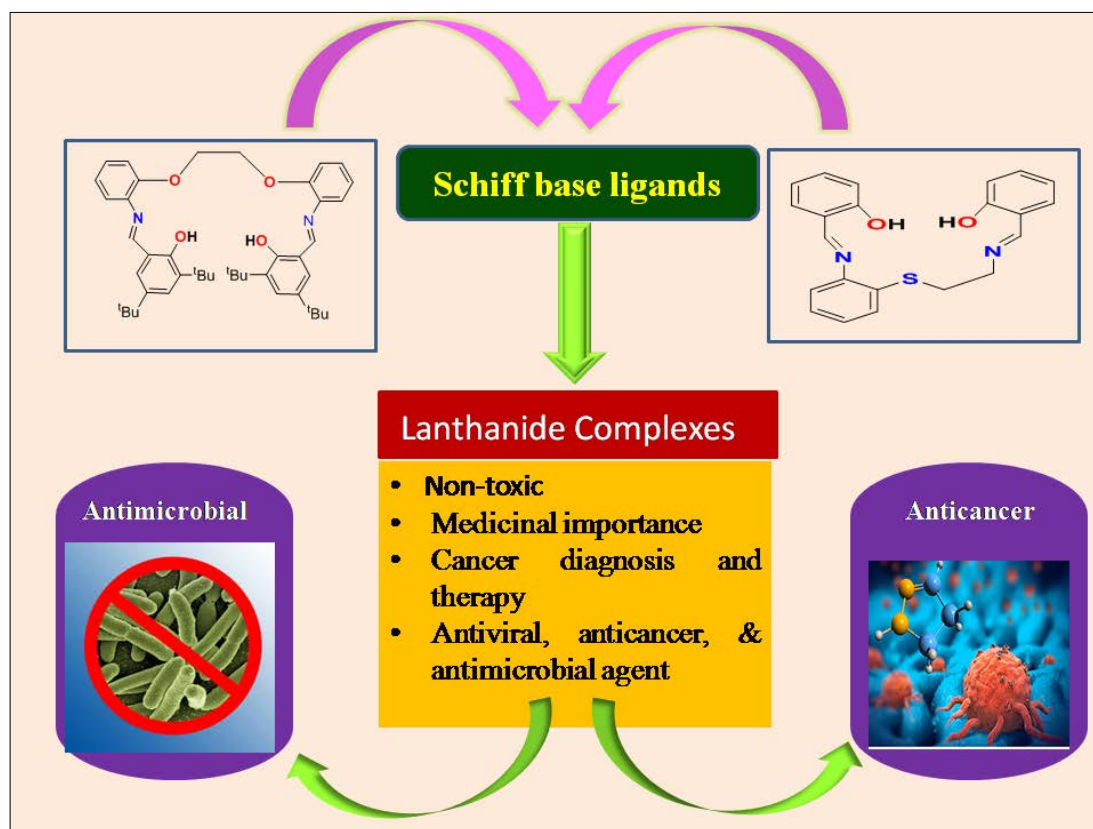
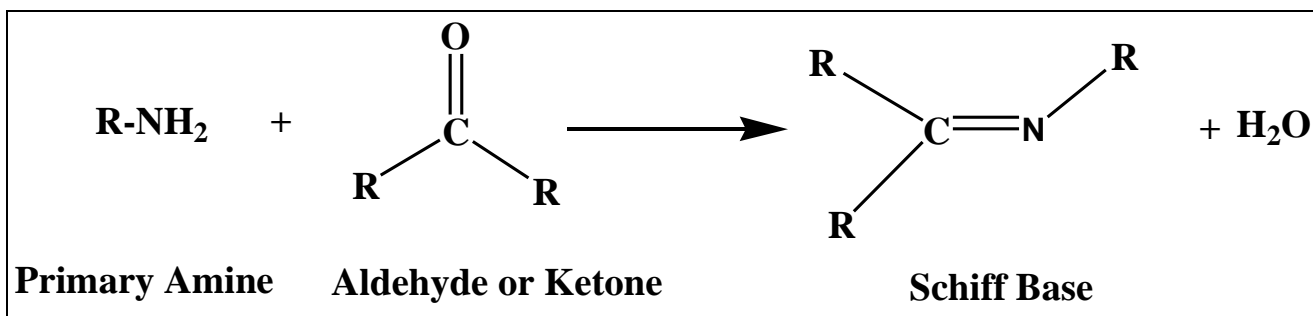


Fig 1: Schiff base derivatives of Lanthanides

Schiff Base Ligands

The growth of coordination chemistry has been significantly influenced by Schiff bases. "These ligands' metal complexes have undergone substantial research due to their appealing chemical and physical characteristics and wide range of potential applications in several scientific fields. Such complexes have undergone considerable exploration in recent years, and numerous papers and reviews have been written about them. The literature on lanthanide Schiff base metal complexes which covers a very broad range of organometallic compounds and numerous facets of bioinorganic chemistry, is difficult to cover in this chapter. The introduction section is therefore constrained to a brief review of Schiff bases, their metal complexes, and broad uses of these Schiff bases with

lanthanide metal complexes. Applications of biological modelling, the construction of molecular magnets for catalysis, and material chemistry [14] has all sparked research in this field. Coordination chemistry has made significant progress thanks to the contributions of Schiff base complexes with transition metals [15]. In 1864, Schiff published the first report on the condensation products of primary amines with carbonyl compounds, which are frequently referred to as Schiff bases [16]. A Schiff base is an aldehyde or ketone that has a C=N-R group in place of the > C=O group as the nitrogen analogue." It is usually formed by condensation of an aldehyde or ketone with primary amine according to the following scheme-1.

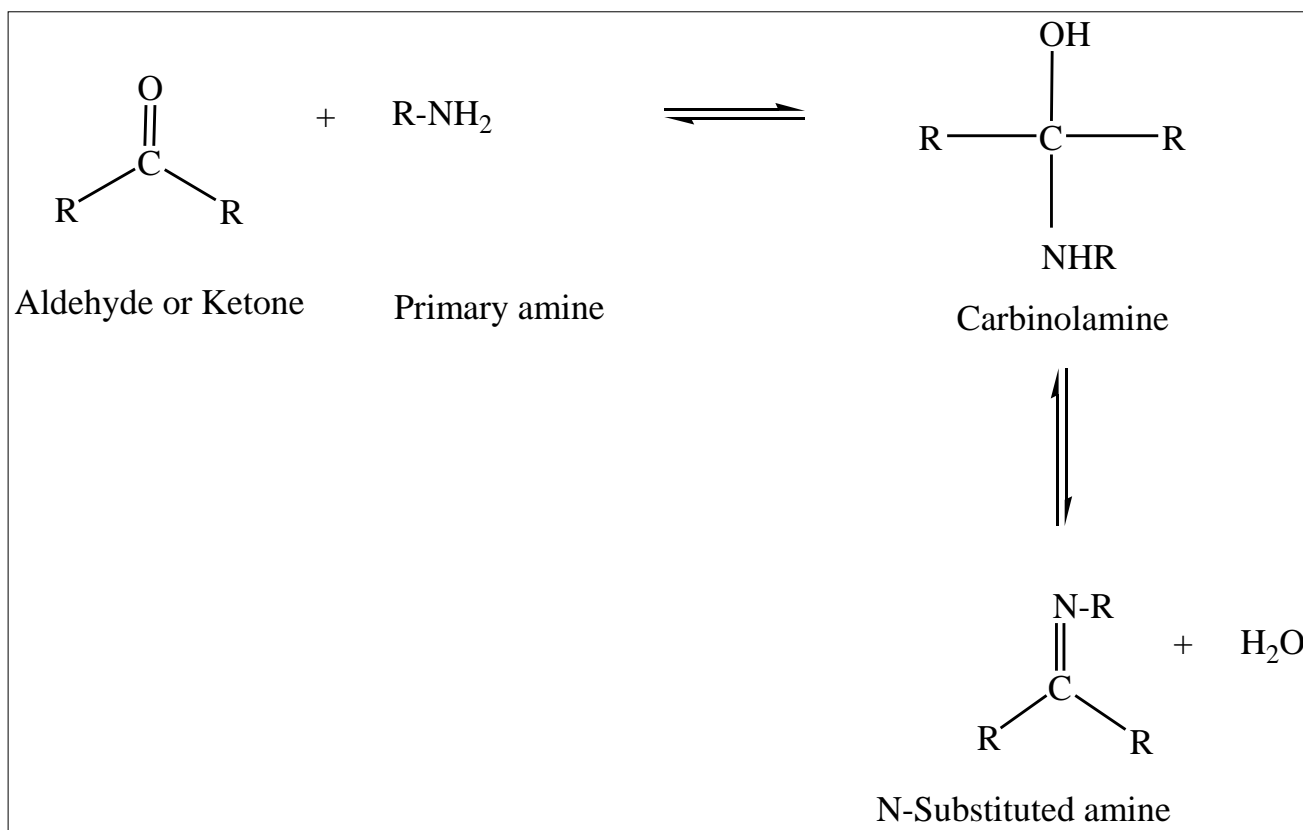


Scheme 1: Preparation of Schiff Bases

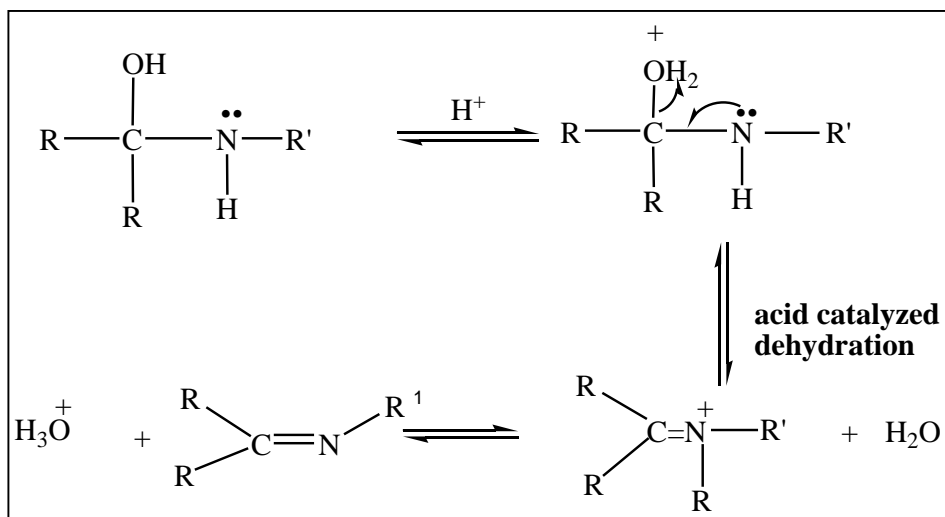
Where R = may be an alkyl or an aryl group. "Aryl Schiff bases are significantly more stable and easier to synthesize than their alkyl counterparts, which are more prone to instability. Aliphatic aldehyde Schiff bases are highly unstable and easily polymerize, whereas aromatic aldehydes with efficient conjugation have more durable Schiff bases. Aldehydes or ketones can be converted into Schiff bases in a reversible process that often occurs when an acid or base catalyzes the reaction or when the substance is heated. In most cases, the product is separated from the formation, the water is removed, or both are done. Aqueous acid or base has the ability to hydrolyze many Schiff bases back to their original aldehyde, ketones, and amines. The process of forming a Schiff base is an additional application of the nucleophilic addition to the carbonyl group. The amine is the nucleophile in this situation. The amine interacts with the aldehyde or ketone in the first step of the process to produce carbinolamine, an unstable addition product. By bases or

acids catalyzing the process, the carbinolamine loses water". The dehydration of the carbinolamine (Schemes 2 and 3) is acid catalysed because it is an alcohol.

Usually, the rate-determining step in the creation of a Schiff base is the dehydration of the carbinolamine, which is why acids are used to catalyse the reaction. Yet because amines are basic chemicals, the acid concentration cannot be allowed to be excessive. The synthesis of carbinolamine is prevented by equilibrium being pulled to the left if the amine is protonated and turns non-nucleophilic. Therefore, a little acidic pH is ideal for carrying out the syntheses of several Schiff bases. Base also acts as a catalyst for the dehydration of carbinolamines. With the exception of the fact that it is not a concerted reaction, this reaction is comparable to the E2 elimination of alkyl halides. It goes through an anionic intermediate in two phases. In reality, the Schiff base creation involves two different sorts of reactions: Addition followed by elimination^[17].



Scheme-2: Formation of carbinolamine and N-substituted amine

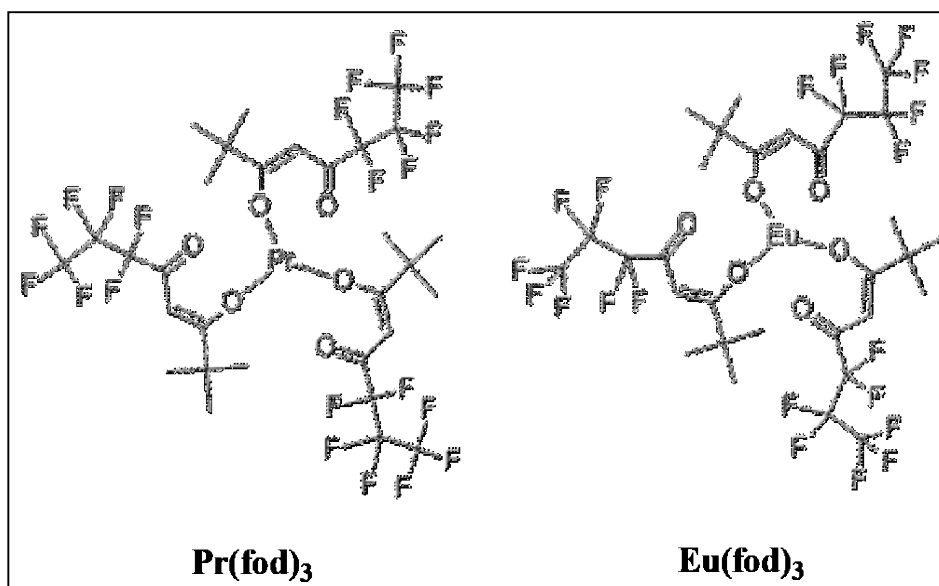


Scheme-3: Acid catalyzed dehydration of carbylamines

Schiff Base Complexes of Lanthanides

The greatest examples of these are tris(-diketonato) lanthanide (III) complexes, [Pr(fod)₃] and [Eu(fod)₃] (fod = anion of 6, 6,

7, 7, 8, 8, 8-heptafluoro-2,2-dimethyl-3, 5-octanedione), which are also commonly used as shift reagents in NMR spectroscopy.



The ability of organic molecules with free electron pairs to form adducts with the tris-diketonate complexes of paramagnetic and magnetically anisotropic lanthanide (III) ions is a factor in the shift of the proton resonances. These Lewis bases are one type of organic molecule that can do this. Because the metal ion in these complexes only has a coordination number of six, whereas lanthanide ions prefer to be connected to eight or nine donor atoms, the coordination sphere of the lanthanide ion in a tris (-diketonato) lanthanide (III) complex is unsaturated. By creating adducts with neutral compounds that have oxygen- or nitrogen-donor atoms, the lanthanide ion in the tris-diketonate complexes can widen the range of its coordination. Tris (-diketonato) lanthanide (III) complexes are quickly converted into bis (hydrates) by the presence of such a molecule, which is water. However, water can be swapped out for polydentate ligands (such 1, 10-phenanthroline) in the first coordination sphere, and the resulting lanthanide complexes frequently exhibit a strong photoluminescence.

The “compound [Eu-(tfa)₃ (phen)] (tfa = anion of thenoyltrifluoroacetone, phen = 1,10-phenanthroline)¹⁸ is a classic illustration of a luminous lanthanide complex. Organic

light-emitting diodes (OLEDs)^[19] can use these luminescent complexes. Lewis-base adducts of tris (-diketonato) lanthanide (III) complexes can be doped into a nematic liquid-crystal mixture to produce luminous liquid crystals, as demonstrated by Binnemans and Moors^[20]. By doping cholesterylalkanoate adducts of [Eu(tta)₃] into a cholesteric liquid crystal, Hapiot and colleagues achieved comparable results. Naturally, rather than relying on host-guest systems, it would be intriguing to construct lanthanide -diketonate complexes that have a liquid-crystalline phase themselves. Early attempts to construct liquid-crystalline lanthanide compounds with -diketonate ligands failed²¹, but more recently, two novel, independent techniques produced interesting outcomes. Starting from mesomorphic -diketonel ligands^[22], Galyametdinov and associates synthesised monotropic liquid crystalline lanthanide complexes. A monotropicsmectic was described by Binnemans and Lodewyckx in a communication. A mesophase in [Ln(dbm)₃] complexes with salicylaldimine Schiff bases (DBM = dibenzoylmethane anion)^[23]. However, the resultant bisadducts are liquid crystalline even though neither the Schiff base nor the tris (-diketonato) lanthanide

(III) complex show a mesophase in these compounds. It should be mentioned that the Schiff bases used in this study are the same ones that were previously employed to create liquid crystalline lanthanide complexes with Schiff-base ligands. Three diketonate anions in each highly coordinated complex neutralise the charge of the Eu^{3+} cation and further bind a neutral substrate. Three diketonate ligands are arranged geometrically in the lanthanide coordination sphere under the strong influence of the extra coordination. Because of this, a suitable lanthanide centre and original ligand combination can precisely regulate the highly coordinated complexation with a particular substrate".

The characteristics of the coordination ligand, lanthanide centre, competitive solvent, and other surroundings are primarily what give the lanthanide complexes their high coordination numbers and distinctive geometry. "The majority of trivalent lanthanide cations develop OCTA or nano coordination complexes, which are where the mechanical distortions necessary to accommodate steric interactions typically take place. These steric restrictions have a profound impact on the structure and stability of the lanthanide complex since the lanthanide coordination has little to no directionality. Elements with a quickly expanding relevance are lanthanides. They belong to the same family as scandium, yttrium, and lanthanum, which is the rare earth family. Lanthanides' use in chemistry and other applications is made easier by their accessibility at relatively low costs. Recent years have seen significant advancements in the investigation and synthesis of novel materials using lanthanide-based reagents or catalysts, as well as in the coordination chemistry of lanthanides [24]. In recent years, the chemistry of coordination molecules containing physiologically active ligands has drawn a lot of interest. As a result of the distinctive magnetic and photo-physical characteristics of their compounds, trivalent lanthanide coordination chemistry has seen an increase in interest over the past few decades. The vast range of uses for these compounds in areas as diverse as catalytic processes serves as the driving force behind the coordination chemistry of lanthanides, which is a promising research subject. In bioinorganic and coordination chemistry, lanthanide ions are a topic of growing interest [25]. We know that a change in the quantity of 4f electrons results in significantly diverse biological features based on the limited data that is currently available. Interest has been sparked by the discovery of the lanthanide shift reagent and the coordination chemistry of lanthanides in biological systems. The best ions for forming stable, highly coordinated complexes are lanthanide (III) ions due to their size and charge. There are lanthanide coordination compounds that show coordination numbers 6 to 10 for the lanthanide ions. The bonding with ligands of tripositive lanthanide ions is primarily electrostatic, with just a small amount of effect from their own d or f orbital. From this, it has been explained by others that in the case of lanthanide complexes, the idea of coordination saturation is equivalent to that of steric saturation. When studied across the lanthanide series, a wide range of physicochemical features of lanthanide complexes might therefore change gradually until, at a given limit, a sudden difference is observed. This occurrence can be attributed to the lanthanide metal's ionic radius gradually shrinking until the metal environment becomes so congested that one or more ligand atoms are forced out of the primary co-ordination sphere. The assembly of lanthanide complexes with novel structures and specific properties presents both great challenges and opportunities in terms of controlling their

shape and dimensionality [26]. This is due to the peculiar properties of lanthanide ions, such as their large radius, high and variable coordination numbers, and existence of multi-single electrons".

There have been many reports of three-dimensional lanthanide polymeric complexes with multi-carboxylate ligands, proving that careful organic ligand selection in combination with lanthanide ions can result in the development of novel complexes with intriguing structures and distinctive characteristics. One of the most prevalent neurological illnesses, epilepsy, affects around 4% of people throughout their lifetime and is a significant public health concern. Recent research showed that when given intraperitoneally to mice, certain aryl semicarbazones exhibited anticonvulsant activity in the maximum electroshock (MES) and subcutaneous pentylenetetrazole (scPTZ) screens. Thiosemicarbazones and aryl and heteroarylsemicarbazones have recently become known as structurally new anticonvulsants [27]. Additionally, good anticonvulsant action of aryl semicarbazides has been discovered in mice and rats. The FDA has approved several new medications in the last ten years, including rufinamide, retigabine, and pregabalin. Antiepileptic drug therapy still has several limits, despite advancements in the drug treatment of epilepsy. So, the search for novel anticonvulsant medications remains a focus of research in medicinal chemistry. Thiosemicarbazones can be used to create electrodes because certain metals easily form compounds with them. According to the study, benzyl bis-thiosemicarbazones have been employed to make electrodes. The copper bis (thiosemicarbazone) complexes have demonstrated particular potential as radiopharmaceuticals in a different investigation, as demonstrated by a per fusion imaging agent [28].

According to current research, there is a structural class that has anti-pox viral function. Isatin derivatives have been suggested to be chemoprophylactic for smallpox, such as methisazone (marboran), the -thiosemicarbazone of N-methyl isatin. When administered to susceptible contacts, methisazone lowers morbidity and mortality but has no direct therapeutic benefit against variola and is no longer produced as a pharmacological material. According to reports, thiosemicarbazones have antituberculosis properties. In addition, 1, 3, 4-thiadiazoles, 1, 3-thiazoles, and their derivatives demonstrate a wide range of biological actions, including, but not limited to, antituberculosis, antibacterial, anti-inflammatory, antiviral, anticonvulsant, antihypertensive, local anaesthetic, anticancer, hypoglycemic, and cytotoxic activity. Due to its bioactivity, which includes certain actions that regulate plant growth as well as antibacterial activity, 1, 3, 4-thiadiazole and related compounds are of great interest to chemists. Thiadiazoles having aromatic cycles linked to them via the methyleneoxy group have also been found to have antitubercular properties, and compounds of this type have demonstrated inhibition of both cyclooxygenase and 5-lipoxygenase activities.

Some thiodiazoles with antihelminthic properties have been synthesised by Lee and colleagues. More recently, it has been revealed that 1, 3, 4-thiadiazole sulfonamide derivatives act as a modulator of anticancer therapy when combined with some cytotoxic substances. Due to their intriguing and potentially useful chemotherapeutic properties, metal complexes of Schiff bases produced from S-alkyldithiocarbazates have generated a great deal of study attention. Dithiocarbazoic acid's S-alkyl and aryl esters frequently function as adaptable chelating agents and show promise bioactivities in Schiff

bases. According to stoichiometry, Singh *et al.* [29] synthesised the lanthanide (III) complexes with the bibasic tridentate azomethine ligands S-methyl dithiocarbazate and S-benzyl

dithiocarbazate in various molar ratios (1:1, 1:2, and 2:3). Figure 2 depicts the structure of the synthesised ligands (a) and metal complexes (b).

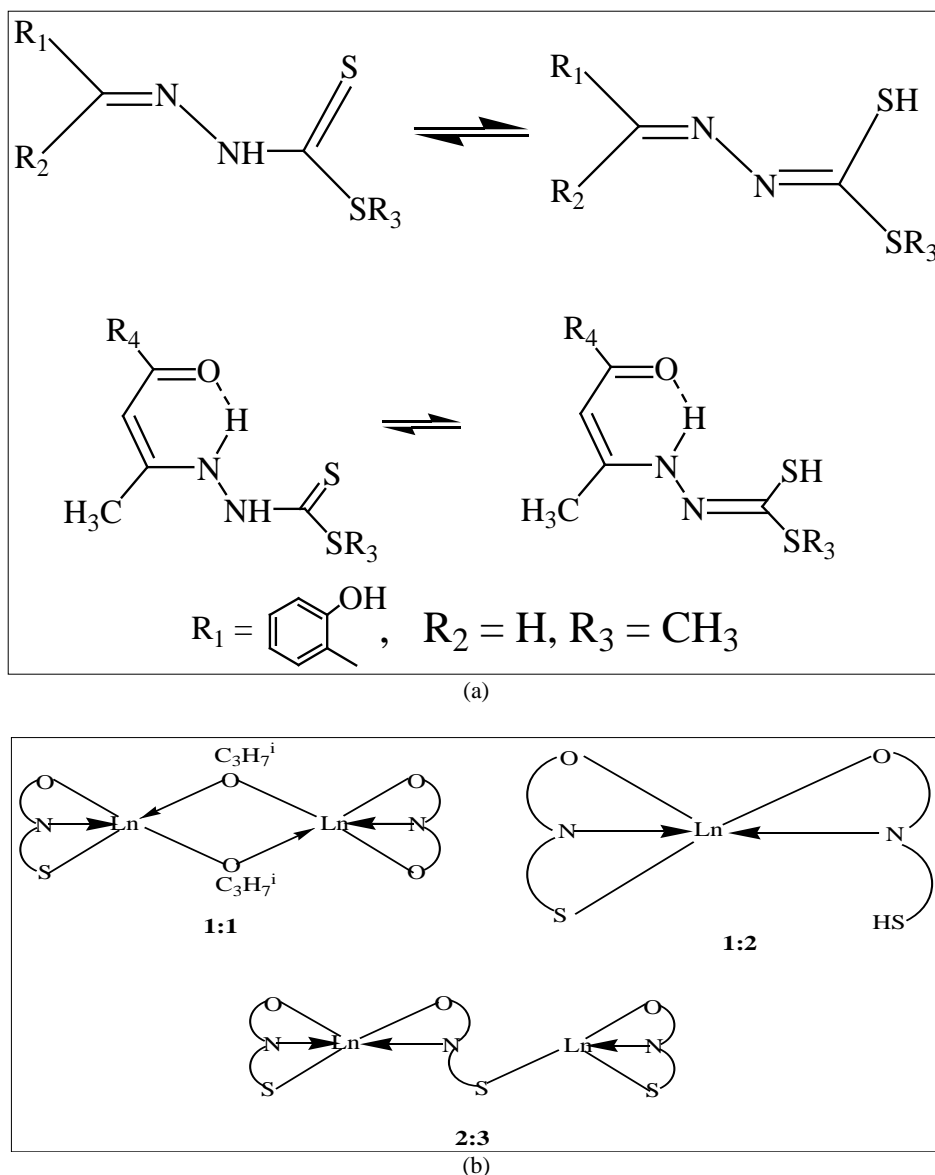
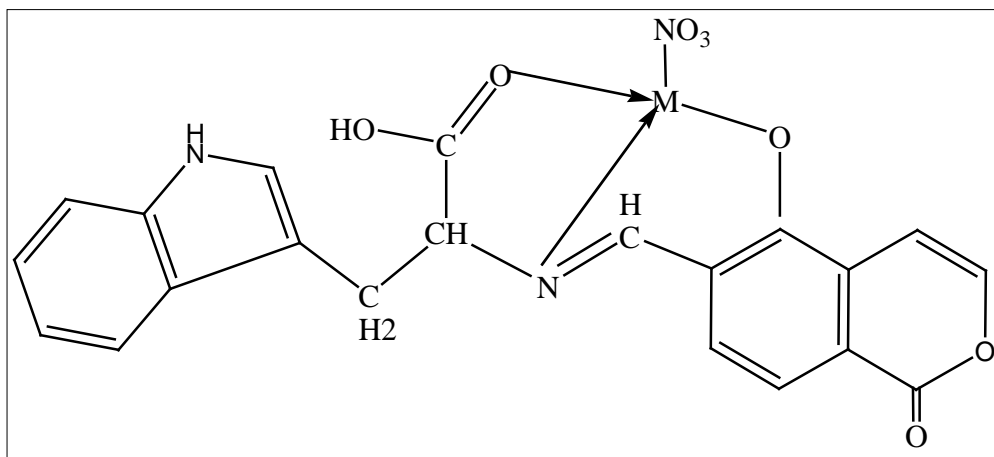


Fig 2: Proposed structures of the ligands (a) and metal complexes (b)

“Due to the variety of the ligand system and the quantity of metals that have been found to form complexes with semicarbazones, the coordination chemistry of these compounds has been found to be quite intriguing. The discovery of the preferred coordination geometries of metal complexes has been greatly aided by ligands produced from substituted semicarbazones. In particular, those involving higher valent metal ions were of interest since they exhibit unexpected chemical variety in both the coordination geometry and the ligand's subtler alterations. The biological functions of semicarbazones have been extensively reported. They have been utilised as anticonvulsants, antiprotozoa agents, radioprotectors, or radiopharmaceuticals. They are also widely known for their antileukemia activity in mice, antibacterial properties, and pesticide effects. Therefore, it is crucial to create substituted semicarbazones and characterise their metal complexes. The lanthanide (III) complexes with 4-methyl-7-hydroxy coumarin have been created by Kostova, *et*

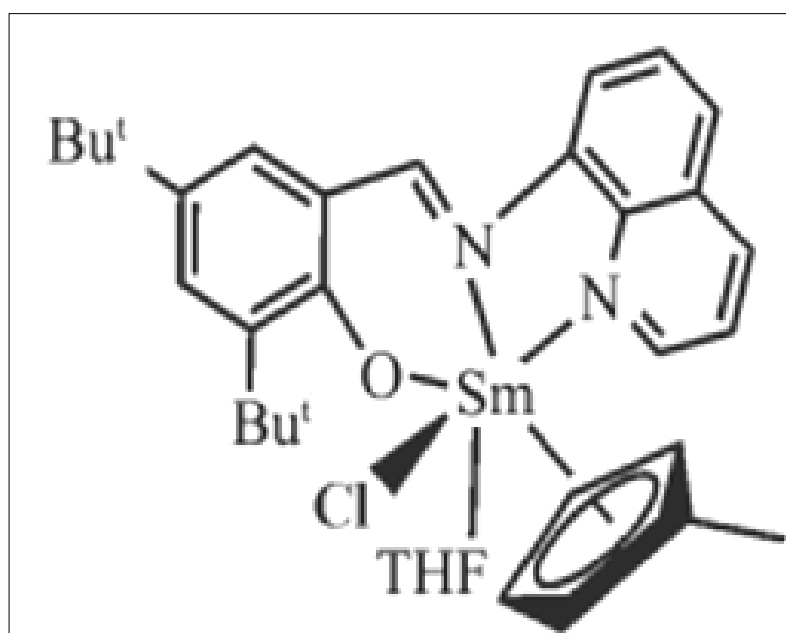
al. The production and physicochemical characteristics of various lanthanide (III) complexes with 2-(3-comaryl) imidazole pyridine have been reported by TR. Goudar *et al.* in article [31]. After chelation, ligands have more biological activity. The optical characteristics of coumarins been improved through chelation with lanthanides. Kostova has described coumarins with carboxylic acid groups that are lanthanide complexes that also have antiproliferative properties. 4-hydroxycoumarin complexes with neodymium (III) have shown anticoagulant properties. La (III), Ce(III), and Pr(III) Schiff base complexes with 2-((7-hydroxy-2-oxo-2H-chromen-8-yl) methyl-eneamino)-3-(1H-indol-3-yl) propanoic acid have been reported by Rishipal Singh *et al.* [32] (Figure 3)”.

The crystal structure of the bulky tridentate [N, N, O] Schiff base ligand 3, 5-But²-2-(OH) C₆H₂CH=N-8-C₉H₆N Sm (III) complex has been described by Bangyu *et al.* [33] (Figure 4).

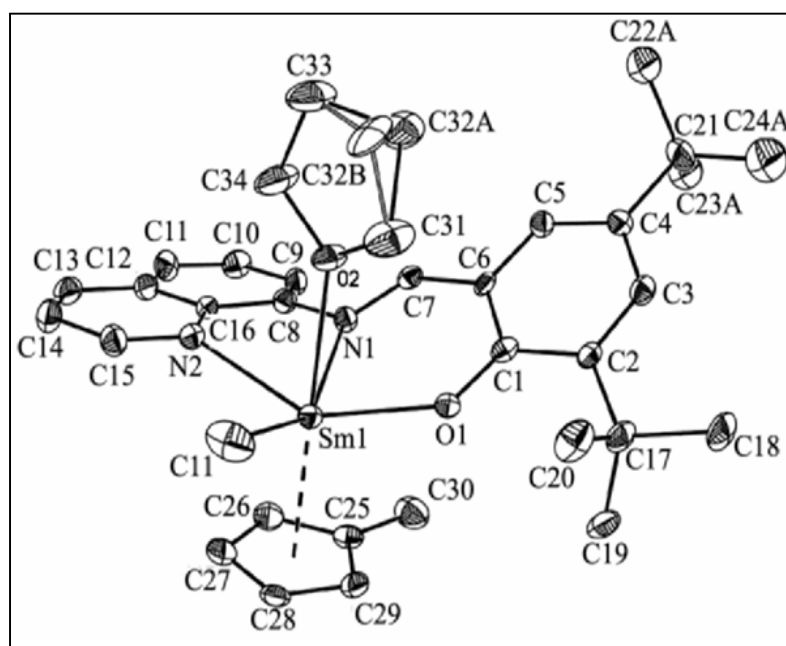


Where M= La(III), Ce (III) and Pr (III)
Ln= La,Sm,Dy, Yb and Nd

Fig 3: Structure of metal complex



(a)



(b)

Fig 4: ORTEP diagram of complex SmL(CH₃C₅H₄)Cl(THF)

Due to their pharmacological attributes and distinctive conjugated molecular architecture, 4-hydroxycoumarins (2H-1-benzopyran-2-ones) have generated a lot of interest. "Many of them exhibit significant pharmacological effects, such as analgesic, anti-arthritis, anti-inflammatory, anti-pyretic, anti-bacterial, anti-viral, and anti-cancer activities. Treatment of illnesses characterised by excessive or unwelcome clotting, such as thrombophlebitis, pulmonary embolism, and several cardiac problems, has been successfully accomplished with the use of 4-hydroxycoumarin and its derivatives as anticoagulants [34]. Numerous comparative pharmacological studies on the 4-hydroxycoumarin derivatives have demonstrated strong anticoagulant efficacy together with few side effects and minimal toxicity [35]. In the fields of bioinorganic and coordination chemistry, 4-hydroxycoumarin derivatives show a propensity to combine with transition and rare earth derivatives of hydroxycoumarin. Trivalent lanthanide complexes have found use as contrast agents for Nuclear Magnetic Resonance (NMR) imaging, stains for fluorescence imaging, responsive luminescent systems, catalysts for specific cleavage of RNA hydrolysis, or active agents in radiotherapy for cancer [36]. Lanthanide (III) complexes of coumarin-based ligands are the subject of this study, which also examines their synthesis, characterisation, and biological evaluation. The biological assessment of the complexes has been emphasised. The recent finding shows that the ferrocenyl moiety increases the antibiotic action of penicillins and cephalosporins [37] has sparked interest in ligands that contain the ferrocenyl group. The potential uses of ferrocenyl compounds in catalysis, electrical, magnetic, and luminous materials have been investigated. Electron transfer between the organometallic and coordination sites may result through mutual contact between metal sites with various surroundings and oxidation states. These interactions might also bring about a brand-new kind of reactivity towards substrates. The structures of several of the recently synthesised Schiff bases of ferrocene derivatives and their metal complexes with lanthanide and transition metal ions have been characterized" [38].

Conclusion

Extensive research has been conducted on lanthanides and their compounds due to their significant roles in the human body. Lanthanide (III) compounds have proven useful as radiopharmaceuticals and contrast agents for magnetic resonance imaging (MRI). Surprisingly, these lanthanide complexes have demonstrated remarkable biological activities, including antiviral, antibacterial, and antifungal properties. However, researchers still face challenges in designing and synthesizing novel compounds with optimal relaxation properties for use as contrast agents. One interesting phenomenon observed is the "antenna effect", where complexes formed by lanthanide (III) ions enhance their luminescence properties. The ability of lanthanide (III) ions to substitute calcium ions and to bind water molecules makes them very desirable for medicinal purposes. In-depth research has been done on the utilisation of lanthanide (III) ions complexes as contrast agents and antibacterial agents. Presently, additional study into the applications of lanthanides as new generation pharmaceuticals for the treatment of neoplastic illnesses appears to be wholly justified. This is especially true when combined with biologically active substances like ligands.

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