REVIEW

Lanthanide(III) complexes of 4-aminoantipyrine Schiff base derivatives and their antimicrobial applications: A review

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Abstract

Lanthanides, also known as lanthanoids (inner transition elements), constitute an interesting group of fifteen elements which are predominantly trivalent and exhibit similar physicochemical properties. These elements occupy the 4f inner transition series (lanthanides) in the periodic table. Over the years, the investigation of lanthanide(III) complexes has generated increased interest due to their interesting biological, photo-physical and magnetic properties. Lanthanide(III) complexes of Schiff bases of 4-aminontipyrine derivatives constitute another class of compounds that show fascinating coordination and bio-inorganic chemistry. 4-Aminoantipyrine and its derivatives have formed stable complexes with many lanthanide metal ions. This literature review examines the lanthanide(III) complexes of 4-aminoantipyrine derivatives which were synthesized and characterized using various spectro-analytical techniques from which various structures were proposed. Antimicrobial applications of some of these lanthanide(III) complexes synthesized over the years have been reported. This review serves as a guide for the development of new lanthanide(III) complexes of 4-aminoantipyrine derivatives as potential antibacterial and antifungal agents as well as other applications.

Keywords: 4-Aminoantipyrine, antimicrobial application, coordination chemistry, lanthanides(III) complexes, Schiff bases, metal complexes

Introduction

Coordination chemistry is a fascinating branch of chemistry. Lanthanide(III) complexes are garnering heightened interest in bio-inorganic and coordination chemistry. The lanthanides comprise fifteen elements, with atomic numbers spanning from 57 (lanthanum) to 71 (lutetium). They are silvery-white metals, chemically reactive, and belong to the 4f inner transition series. The lanthanides predominantly occur in the +3 oxidation state. The oxidation states of +2 and +4 are recognized. However, they exhibit instability in aqueous conditions. The electrons in the 4f orbitals of lanthanide(III) ions are effectively shielded by the 5s and 5p orbitals, resulting in minimal environmental influence on the 4f electrons. The severity of f-f transitions is diminished because of their Laporte forbidden nature (Purohit & Bhojak, 2013). The structure of lanthanide complexes is determined by the interplay of several factors: maintaining spherical symmetry for the central metal ion, minimizing ligand-ligand and metal-metal repulsion, and the steric demands of the ligand (Arora & Burman, 2009). The filling of the 4f shell in the lanthanides results in a progressive reduction in the size of atoms and ions, referred to as lanthanide contraction. This results from the inadequate shielding of one 4f electron by another. The lanthanide ions possess higher coordination numbers, resulting in diverse coordination modes of complexes (Tang et al., 2013). Lanthanide complexes exhibit great bioinorganic and coordination chemistry. Research has revealed that ligands featuring nitrogen and oxygen donor atoms serve as effective precursors for the synthesis of several lanthanide coordination compounds. The distinctive magnetic, luminescent, and spectroscopic characteristics of lanthanide(III) ions are the primary factors contributing to the significance of these complexes in the industrial, chemical, biological, and medical fields. They are attractive for organic synthesis because of their low toxicity and availability. Numerous interesting and important properties of lanthanide(III) complexes are being investigated. In addition to their bonding interactions and structural variations, the extensive uses of lanthanide(III) complexes render them an interesting subject within coordination chemistry (Singh et al., 2010).

Recently, lanthanide compounds have garnered interest due to their characteristics and significant potential in many applications, including catalysis, magnetism, optoelectronic devices, medicinal separation, and ion recognition (Lama et al., 2010). Reviews on the various applications of lanthanides have been made by various researchers in the areas of electroluminescence ((Døssing, 2005: Werts, 2005: Jing & Zhang, 2013; Wei et al., 2018, Wang et al., 2019), biological applications (Cârâc, 2017; Prajapati et al., 2018, Tamanna and Mutreja, 2022; Evans, 1990; Cotton & Harrowfield, 2012; Misra, et al. 2004; Cotruvo, 2019; Xian et al., 2023), antimicrobial (Kaczmarek et al., 2018), anticancer (Kaczmarek, et al., 2018; Kostovo, 2005; Toe et al., 2016;; Chundawat et al., 2021; Patyal et al., 2023, Madanhire et al., 2024, Wang et al., 2024), biomedical imaging application (Faulkner et al., 2005; Bünzil, 2010; Chan & Wong, 2014; Bünzli & Eliseeva, 2013; Eliseeva & Bünzli, 2010; Monteiro, 2020), therapeutic application (Jastrzab et al., 2019; Bao, 2020; Woods et al., 2002; Thompson & Orvig, 2006; Zhang et al., 2011), lanthanum based materials as target (Jadhav et al., 2025) (Table 1), green synthesis of lanthanide based organic compounds and its applications (Chaturvedi et al., 2022).

Table 1. Reviews on biological applications of lanthanides.

Biological applications	Title	References
Antimicrobial and Anticancer agents	Lanthanides: Schiff Base Complexes, Applications in Cancer Diagnosis, Therapy, and Antibacterial Activity.	Kaczmarek et al., (2018)
Anticancer agents	Lanthanides: Applications in Cancer Diagnosis and Therapy	Toe et al., (2016)
	Lanthanides as Anticancer Agents.	Kostovo (2005)
	Lanthanide Complexes as Anticancer agents: A Review	Chundawat et al., (2021)
	Innovative Lanthanide Complexes: Shaping the Future of Cancer/Tumor Chemotherapy	Patyal et al.,(2023)
	Lanthanides and Their Complexes/Nanoparticles: A Review of Cancer Diagnosis, Therapeutics, Toxicity Considerations, and Clinical Trials.	Madanhire et al., (2024)
	Current Development of Lanthanide Complexes for Biomedical Applications	Wang et al., (2024)
Therapeutic agents	Targeted Complexes of Lanthanide(III) Ions as Therapeutic and Diagnostic Pharmaceuticals.	Woods et al., (2002)
	Editorial: Lanthanide Compounds for Therapeutic and Diagnostic Applications.	Thompson & Orvig (2006)
	Recent Progress in Therapeutic and Diagnostic Applications of Lanthanides	Zhang et al., (2011)
	Lanthanide Complexes for Drug Delivery and Therapeutics.	Bao (2020)
	DNA as a Target for Lanthanide(III) Complexes Influence.	Jastrząb et al., (2019)
Lanthanum based materials as target	A Critical Review of Lanthanum and Lanthanum-Based Materials: Synthesis, Applications, and Challenges.	Jadhav et al., (2025)
General biological applications	Biological and Biomedical Applications of the Lanthanide Compounds. A Mini Review.	Cârâc (2017)
	A Review: Lanthanide Complexes and Their Biological Importance.	Prajapati et al., (2018)
	Biomedical Applications of Lanthanide Complexes.	Tamanna & Mutreja (2022)
	Past, Present, and Possible Future Clinical Applications of the Lanthanides. In: Biochemistry of the Lanthanides.	Evans (1990)
	Lanthanides: Biological Activity and Medical Applications.	Cotton & Harrowfield (2012)
	Biological and Clinical Aspects of Lanthanide Coordination Compounds.	Misra et al., (2004)
	The Chemistry of Lanthanides in Biology: Recent Discoveries, Emerging Principles, and Technological Applications.	Cotruvo (2019)
	Functionalization of Luminescent Lanthanide Complexes for Biomedical Applications	Xian et al., (2023)
Bioimaging application	Lanthanide Complexes for Luminescence Imaging Applications.	Faulkner et al., (2005)

Biological applications	Title	References
	Lanthanide Luminescence for Biomedical Analyses and Imaging.	Bünzil (2010)
	Recent Development in Lanthanide Coordination Compounds for Biomedical Imaging Applications.	Chan & Wong (2014)
	Intriguing Aspects of Lanthanide Luminescence.	Bünzli & Eliseeva (2013)
	Lanthanide Luminescence for Functional Materials and Bio-sciences	Eliseeva & Bünzli (2010)
	Recent Advances in Luminescence Imaging of Biological Systems Using Lanthanide(III) Luminescent Complexes.	Jorge & Monteiro (2020)

Schiff bases play a significant role as ligands in metal coordination chemistry (Aydoğan et al., 2001). Their metal complexes have garnered significant attention over the past decades and have greatly contributed to the advancement of coordination chemistry. These contributions have resulted in several publications, encompassing both pure synthetic research and contemporary physicochemical and biochemically pertinent studies of metal complexes (Ribeiro Da Silva et al., 1997). Specifically, owing to their facile synthesis (Mukhtar et al., 2021), extensive applications (Ghosh et al., 2021), availability of various structural modifications, and their roles in biological modeling (Al-Zoubi, 2013), catalysis (Lacopetta et al., 2023), molecular ferromagnetic design, material chemistry, and electroluminescence (Zhao et al., 2005; Wu & Tsai, 2006;, Li et al., 2025).

4-Aminoantipyrine (4-amino-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one) is a heterocyclic compound (Figure 1) that possesses the pyrazolone ring which comprises two nitrogen atoms and one carbonyl group. The presence of hetero atoms affects electron redistribution, hence demonstrating an aromatic character, referred to as the hetero atom effect (Matczak & Domagala, 2017), which contributes to reactivity, chelation, and other properties.

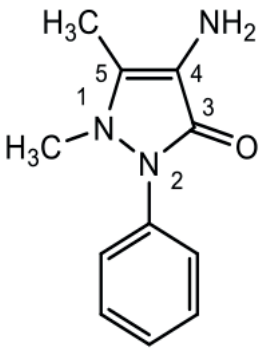


Figure 1. 4-Amino-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one.

4-Aminoantipyrine has reacted with aldehydes, ketones, thiosemicarbazides and semicarbazides etc. to give new Schiff ligands whose coordination properties have been modified (Agarwal et al., 1997; Raman et al., 2007, Raman et al.,2007). Schiff bases derived from 4-aminoantipyrine have been synthesized from diverse compounds including aromatic aldehydes, thiosemicarbazides, semicarbazones, furfuraldehyde, aminothiazole, 2-hydroxy-1-naphthalaniline, isatin, triazole rings,

amino acids, and pyrazolones (Dong-Dong et al., 2007; Piotr & Bogumit, 2002; Miao et al., 2003). 4-Aminoantipyrine and its derivatives have formed stable complexes with many transition and lanthanide metal ions which have played many important roles in organic and inorganic chemistry. Coordination chemists, medicinal chemists, and analytical chemists have conducted substantial research on 4-aminoantipyrine. The Schiff base metal complexes of 4-aminoantipyrine and its derivatives possess various applications in biological, clinical, analytical, and pharmaceutical areas (Donia & El-Saied, 1988; Maurya et al., 1992; Joseph et al., 1995; Chorpra et al., 2000, Agarwal & Singh, 2003). The increase in antibiotic resistance in our environment has become a serious health problem. The search for new and effective antimicrobial agents that would improve the effectiveness of the current therapeutic drugs is a challenge to scientists (Cota et al. 2019, Cotruvo, 2019; Herlan & Bräse, 2020). This review serves as a useful guide for the development of lanthanide(III) complexes of 4-aminoantipyrine derivatives that possess different biological activities, which can be a promising approach towards reducing the threat of antibiotic resistant infections.

There have been review works on the transition metals complexes of antipyrine (Madhu et al., 2003), 4-aminoantipyrine derivatives (Raman et al., 2009), and its biological applications (Krishnan et al., 2022; Sakthivel et al., 2020; Marchetti et al., 2019, Deshmukh et al., 2015), transition and lanthanide metal complexes of Schiff bases derived from salicylidene-4-aminoantipyrine and its biological applications (Ebosie et al., 2021) (Table 2). Agarwal et al. (2012, 2013) reviewed all their research work on lanthanide(III) complexes formed with Schiff bases derived from 4-aminoantipyrine and their properties. The present review constitutes the various lanthanide(III) complexes of 4-aminoantipyrine Schiff base derivatives synthesized over the years and some of their antimicrobial applications.

Table 2. Reviews on biological applications of Schiff bases derived from 4-aminoantipyrine and its derivatives.

Biological applications	Title	References
Antibacterial and antifugal agents	Transition Metal Complexes of 4-Aminoantipyrine Derivatives and Their Antimicrobial Applications.	Krishnan et al., (2022)
Antibacterial, antifungal, anticancer. DNA binding and cleavage agents	Biological and Analytical Applications of Schiff Base Metal Complexes Derived from Salicylidene-4-aminoantipyrine and Its Derivatives: A Review.	Ebosie et al., (2021)
General biological application	Recent Advances in Schiff Base Metals Complexes Derived from 4-Aminoantipyrine Derivatives and Their Potential Applications	Sakthivel et al., (2020)
General biological application	4-Aminoantipyrine: A Significant Tool for the Synthesis of Biologically Active Schiff Bases and Metal Complexes	Deshmukh et al., (2015)
Antibacterial, antifungal, anticancer agents	Coordination Chemistry of Pyrazolone-Based Ligands and Applications of Their Metal Complexes	Marchetti et al., (2019)

Lanthanide(III) complexes of 4-aminoantipyrine

This review reveals that both the amino nitrogen atom and the carbonyl oxygen of 4-aminoantipyrine are susceptible to certain reactions, allowing for the synthesis of diverse derivatives by the introduction of appropriate functional groups at that site. 4-Aminoantipyrine functions as either a uni dentate or bidentate ligand by coordinating through the amino nitrogen atom, the carbonyl oxygen atom, or both. The derivatives of 4-aminoantipyrine encompass uni dentate and multidentate ligands. The lanthanides can form stable and characterizable complexes with 4-aminoantipyrine and

its derivatives, and numerous such complexes are known. This section presents several derivatives of 4-aminantipyrine Schiff bases and its lanthanide(III) complexes (Table 3).

Novel compounds of lanthanide(III) perchlorates, nitrates and thiocyanates of 4-aminoantipyrine (AAP) were obtained and characterized by Chacko et al. (1975,1976), Nair and Chacko (1978). The general formula $[Ln(AAP)_6](ClO_4)_3$, $[Ln(AAP)_3(NO_3)_3]$ and $[Ln(AAP)_3(SCN)_3].4H_2O$ were assigned to the nitrate and perchlorate complexes respectively where Ln represents La, Pr, Nd, Sm, Gd, Dy or Y. 4-Aminoantipyrine acted as a unidentate ligand by coordinating to the lanthanide ions through the carbonyl oxygen only.

John and Radhakrishnan (1978) prepared yttrium and lanthanide(III) iodide complexes of 4-aminoantipyrine (AAP). They were characterized using spectroscopic methods. The synthesized complexes exhibited the general composition $[Ln(AAP)_4I_2]I$, with Ln representing La, Pr, Sm, Nd, and Gd, and $[Ln(AAP)_4I_3]$ where Ln can be Y or Dy. The ligand, 4-aminoantipyrine (AAP), is described as a neutral monodentate ligand coordinating via the carbonyl oxygen atom. In the complexes of La, Pr, Nd, Sm, and Gd. Only one of the iodides was uncoordinated and acted as an outer sphere ligand. Thermal analyses were conducted to determine the stability of the complexes.

Agarwal (1978) reported the synthesis and characterization of lanthanide(III) chloride complexes of 4-[(*N*-benzoyl)aminoantipyrine]. The ligand, coordinated bidentately to the metal ion via the oxygen atoms. The lanthanide ions were assigned a coordination number of seven. Agarwal et al. (1978) also investigated the lanthanide(III) iodide complexes of 4[*N*-(benzalidene)amine]antipyrine. Similarly, Agarwal (1978, 1991, 1992) prepared and characterized lanthanide(III) nitrates, thiocyanates, and perchlorate complexes of 4-(*N*-acetyl)aminoantipyrine using various spectral and analytical techniques.

Shankar et al. (1986) synthesized lanthanide(III) nitrate complexes of acetylacetone-4-aminoantipyrine (AAP), derived from acetylacetone and 4-aminoantipyrine. The resultant Schiff base ligand and its lanthanide(III) complexes were analysed with several spectro-analytical techniques. The complexes possess a general formula of $[Ln(AAP)_2](NO_3)_3$ where Ln may be Pr, Nd, Sm, Gd, Dy, or Y. The ligand AAP functions as a neutral tridentate ligand, coordinating via the azomethine nitrogen atom, carbonyl oxygen atom, and hydroxyl oxygen atom. The nitrate ions did not coordinate with the metal ion but remained ionic. The lanthanide ion in the complexes was assigned a coordination number of six

Sarivastava et al. (1989) synthesized and characterized a series of lanthanide(III) chlorides and bromides of 4-(*N*-acetyl)aminoantipyrine (NAAA). The ligand, 4-(*N*-acetyl)aminoantipyrine, was synthesized through the acetylation of 4-aminoantipyrine. It functioned as a bidentate ligand, coordinating to the lanthanide(III) ion via the oxygen atoms, thus creating a seven-membered chelate ring. The complexes possessed the general formula, $Ln(NAAA)_2X_3$, where Ln represented La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, or Yb, and X denoted Cl^- or Br^-. The lanthanide(III) ions were assigned a coordination number of seven.

Radhakrishnan and Indrasenan (1989) synthesized eighteen novel complexes of lanthanide(III) perchlorates and nitrates with the Schiff base, 4-(pyridine-3′-carboxalidene)aminoantipyrine (P3CAAP) (Figure 2), which was derived from pyridine-3′-carboxaldehyde and 4-aminoantipyrine. The complexes have the usual formulas, $[Ln(P3CAAP)_4](ClO_4)_3$ and $[Ln(P3CAAP)_2(NO_3)_3]$ where Ln represented La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, or Y. They were characterized through various spectro-analytical techniques. The Schiff base, P3CAAP, functioned as a terdentate ligand with potential coordination sites at the azomethine nitrogen atom, carbonyl oxygen atom, and pyridine nitrogen

atom. The perchlorate ion was not coordinated to the metal ion but remains ionic, while the nitrate ion was coordinated to the metal ion in a unidentate manner. The metal ions of the nitrate and perchlorate complexes were assigned coordination numbers of seven and eight, respectively.

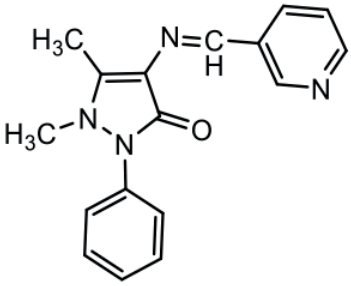


Figure 2. Structure of 4-(pyridine-3′-carboxalidene)aminoantipyrine.

Lanthanide(III) nitrate and perchlorate complexes of the Schiff base, 4-(pyridine-2′-carboxalidene) aminoantipyrine (P2CAAP) synthesized from pyridine-2′-carboxaldehyde and 4-aminoanti pyrine were reported by Radhakrishnan and Indrasenan (1990). The complexes were reported to possess the general formulas, $[Ln(P2CAAP)_3](ClO_4)_3$ and $[Ln(P2CAAP)_2(NO_3)_3]$ with Ln representing La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, or Y. The ligand, 4-(pyridine-2′-carboxalidene)aminoantipyrine (P2CAAP), was reported to function as a bidentate ligand, cordinating to the metal ion via the azomethine nitrogen atom and the carbonyl oxygen atom of the pyrazolone moiety. The perchlorate ions retained their ionic nature, but the nitrate ions were coordinated in a unidentate fashion. The metal ions were assigned a coordination number of nine.

Rajendran and Sreeletha (2001) investigated the coordination behavior of the Schiff base, 4-(pyridine-2′-carboxalidene)aminoantipyrine (P2CAAP), in the presence of oxygen donor ligands such as dimethylsulphoxide (DMSO). The complexes were determined to have the composition $[Ln(P2CAAP)(DMSO)](NO_3)_3]$, where Ln represented La, Pr, Nd, Sm, Gd, or Dy. In these complexes, the principal ligand, P2CAAP, functioned as a neutral bidentate ligand coordinating through the carbonyl oxygen, azomethine nitrogen, and pyridine nitrogen, while the secondary ligands, DMSO and the monovalent nitrate anion, coordinated in a uni dentate fashion to produce adduct compounds.

Agarwal and Agarwal (1995) prepared a series of lanthanide(III) nitrate, isothiocyanate, and perchlorate complexes of the Schiff base, 4[(*N*-cinnamalidene)amino]antipyrine (CAAP), derived from the reaction of cinnamaldehyde with 4-aminoantipyrine (Figure 3). The lanthanide(III) complexes were analyzed via physicochemical methods. The complexes exhibited a general composition of $Ln(CAAP)_2(NO_3)_3$, $Ln(CAAP)_n(NCS)_3$ and $Ln(CAAP)_4(ClO_4)_3$. The Schiff base, 4[(*N*-cinnamalidene)amino]antipyrine (CAAP), functioned as a bidentate (N, O) ligand by coordinating via the carbonyl oxygen and azomethine nitrogen. The nitrate ions possessed a non-ionic character and are located within the coordination sphere. It exhibited a bidentate character with a coordination number of ten (Figure 4). The non-electrolytic characteristic of the isothiocyanato indicated that its ions were coordinated to the lanthanide ion. Nd, Sm, Gd, Tb, and Dy and a coordination number of nine was assigned to them (Figure 5A), whereas La and Pr were allocated a coordination number of seven (Figure 5B). This was due to the increase in the ionic potential of the lanthanide during the period which results in a stronger attraction of ligands by the heavier lanthanides. All three perchlorate ions were located outside the coordination sphere. All its complexes were assigned a coordination number of eight (Figure 6).

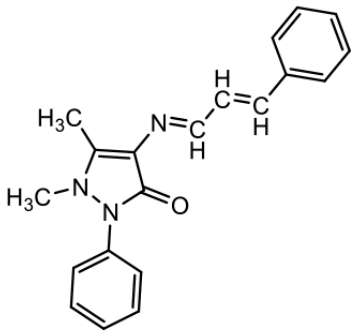


Figure 3. Structure of 4[(*N*-cinnamalidene)-amino]antipyrine (CAAP).

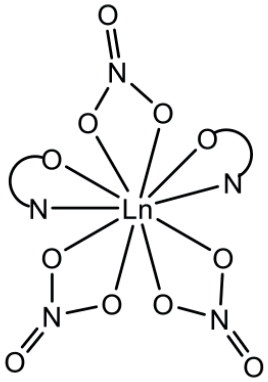


Figure 4. Proposed structure of $Ln(CAAP)_2(NO_3)_3$.

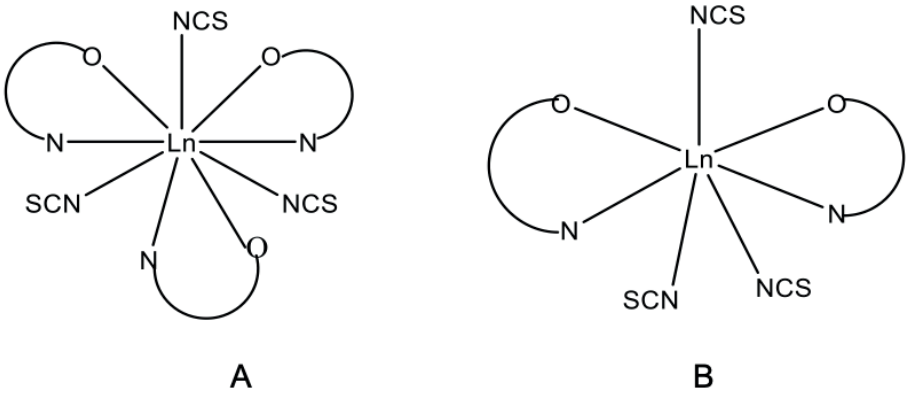


Figure 5. Structure of the isothiocyanate complexes, $Ln(CAAP)_n(NCS)_3$ for Nd, Sm, Gd, Tb or Dy (A) and for La and Pr (B).

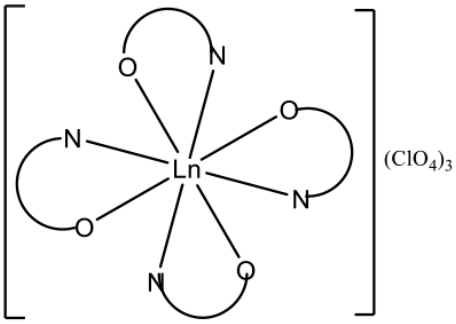


Figure 6. Structure of perchlorate complexes, $Ln(CAAP)_4(ClO_4)_3$.

Seven novel lanthanide(III) nitrate complexes of the Schiff base, 4-[*N*-(2-methoxybenzylimine) formyl]-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (2MBFA) derived from 2-methoxybenzylamine and antipyrine-4-carboxaldehyde (Figure 7), were prepared by Rijulal and Indrasenan (1995). The prepared compounds were characterized by spectroscopic and analytical techniques. The Schiff base, 2MBFA, acted as a neutral bidentate ligand, coordinating to the metal ions via the carbonyl oxygen and azomethine nitrogen in the complexes. The lanthanide(III) complexes were assigned a coordination number of seven. The lanthanide(III) complexes have a monocapped octahedral geometry and general formula, $[Ln(2MBFA)_2(NO_3)_3]$, where Ln may represent La, Pr, Nd, Sm, Gd, Dy, or Y. The nitrate ions in these complexes are coordinated in a uni dentate manner to the lanthanide ions (Figure 8).

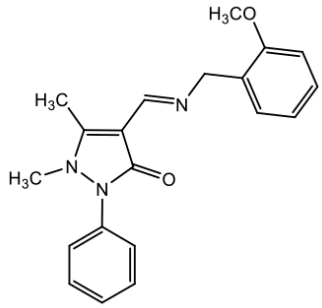


Figure 7. Structure of the Schiff base ligand, 4-[*N*-(2-methoxybenzylimine)formyl]-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (2MBFA).

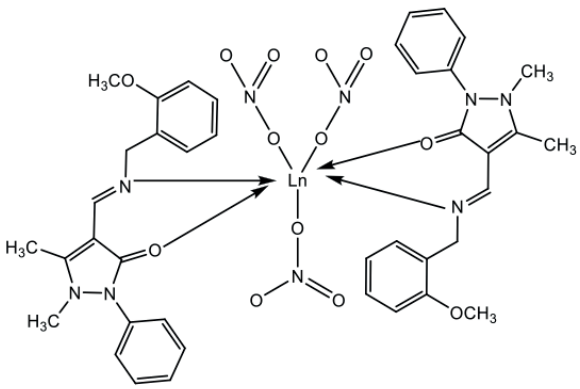


Figure 8. Proposed structure of the lanthanide(III) nitrate complexes.

Abid (2013) prepared the Schiff base, 4-*tert*-but-2,6-diformylphenolbis(4-aminoantipyrine) (HIL), by reacting 2,6-diformyl-4-*ter*-butylphenol with 4-aminoantipyrine (Figure 9), along with its La(III), Ce(III), and Gd(III) complexes (Figure 10). The complexes were analyzed using spectro-analytical techniques. The complexes were designated a coordination number of seven. The Schiff base acted as a pentadentate donor ligand, coordinating two chloride ions to the lanthanide ion. The complexes had a general formula of $[LnL^{/}Cl_2]$.

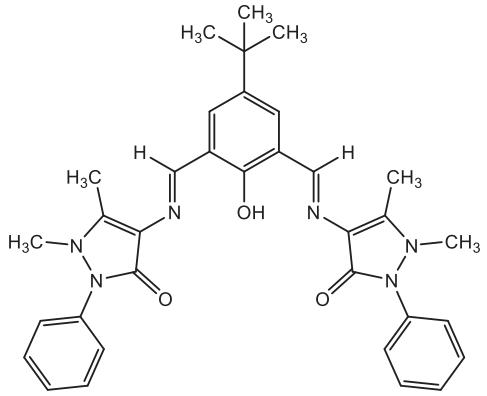


Figure 9. Structure of the ligand, $L^{/}H$.

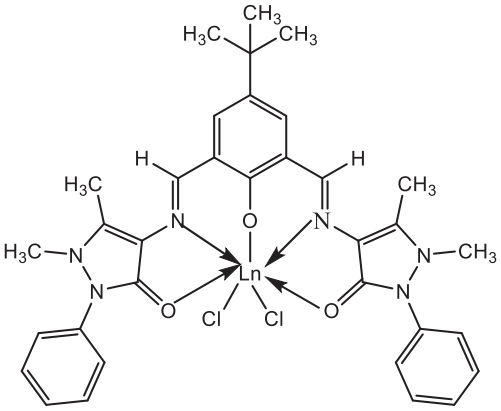


Figure 10. Structure of lanthanide(III) complexes, $[LnL^{/}Cl_2]$, where Ln can be La, Ce or Gd.

A novel series of yttrium and lanthanide(III) iodide, perchlorate, and nitrate complexes of the Schiff base, 1,2-(diimino-4$^{/}$-antipyrinyl)ethane (GA) (Figure 11), derived from glyoxal and 4-aminoantipyrine, were synthesized and characterized by Nair and Radhakrishnan (1995, 1995, 1996). The complexes were assigned a general formula of $[Ln(GA)_2(ClO_4)](ClO_4)_2$ and $[Ln(GA)_2(NO_3)_3]$ respectively, where Ln could be Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, and Er. The Schiff base, GA, acted as a neutral tetradentate ligand, coordinating through the carbonyl oxygen atoms and both azomethine nitrogen atoms, leading to the formation of a five-membered ring that significantly enhances the stability of the complexes. The iodide and perchlorate complexes were allocated a coordination number of nine, but the nitrate complexes had a coordination number of eleven.

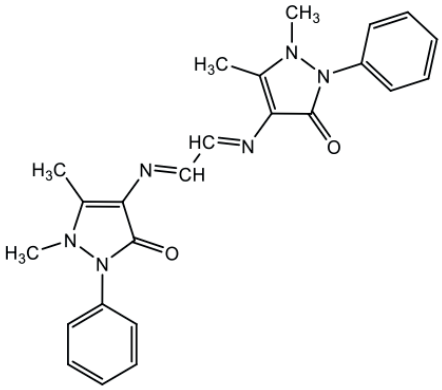


Figure 11. Structure of 1,2-(diimino-4′-antipyrinyl)ethane (GA).

Yu et al. (2002) reported six new lanthanide(III) nitrate complexes of Schiff bases synthesized from 2,6-diformylpyridine-N-oxide and 4-aminoantipyrine. The complexes possessed a general formula of $LnL(NO_3)_3$, where Ln may represent La, Pr, Eu, Tb, Er, or Y.

Harraf et al. (2024) prepared and characterized promethium(III), samarium(III), gadolinium(III), dysprosium(III), and holmium(III) complexes of the Schiff base, (L) derived from 4-aminoantipyrine and 5-bromosalicylaldehyde. The x-ray analysis revealed that all the crystals exhibited isomorphism. All synthesized compounds were nine-coordinated. Their geometries were classified as distorted tricapped trigonal prisms. The emission spectra indicated that the peak intensities vary. The emission spectrum alters as the lanthanide ions change.

Table 3. Lanthanide(III) complexes of 4-aminoantipyrine and its derivatives.

Schiff Base	Constituents	Anion	Lanthanides	CN	Formula	Ref.
4-aminoantipyrine		perchlorates, nitrates and thiocyanates	La, Pr, Nd, Sm, Gd, Dy, Y		$[Ln(AAP)_6(ClO_4)_3$ $[Ln(AAP)_3(NO_3)_3]$ $n(AAP)_3(SCN)_3].4H_2O$	Chako et al. (1975, 1976), Nair & Chako (1978)
4-aminoantipyrine		iodide	La, Pr, Sm, Nd, Gd, Y, Dy		$[Ln(AAP)_4I_2]I$ $[Ln(AAP)_4I_3]$	John & adhakrishnan (1978)
4-[(N-benzoyl)amino-antipyrine.		chloride		7		Agarwal (1978)
4-[(N-benzalidene) amine] antipyrine.		iodide				Agarwal et al. (1978)
4-(N-acetyl)aminoan-tipyrine		nitrate, thio-cyanates, perchlorate				Agarwal (1978, 1991, 1992)
Acetylacetone-4-aminoantipyrine (AAP)	4-aminoantipyrine and acetylacetone	nitrate	Pr, Nd, Sm, Gd, Dy, Y	6	$[Ln(AAP)_2](NO_3)_3$	Shankar et al. (1986)
4-(N-acetyl)aminoan-tipyrine (NAAA)		perchlorates, nitrates	La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y	7,8	$Ln(NAAA)_2X_3$	Radhakrishnan & Indrasenan (1986)
4-(pyridine-3′-carbox-alidene) aminoanti-pyrine (P3CAAP)	4-aminoantipyrine and pyridine-3′-car boxaldehyde,	chloride, bro-mide	La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Yb	7	$[Ln(P3CAAP)_4](ClO_4)_3$ $[Ln(P3CAAP)_2(NO_3)_3]$	Sarivastava et al. (1986)

Schiff Base	Constituents	Anion	Lanthanides	CN	Formula	Ref.
4-(pyridine-2′-carboxalidene) aminoantipyrine (P2CAAP)	4-aminoantipyrine and pyridine-2′-carboxaldehyde	nitrate, perchlorate	La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y	9	$Ln(P2CAAP)_3](ClO_4)_3$ $[Ln(P2CAAP)_2(NO_3)_3$	Radhakrishnan & Indrasenan (1990)
4-(pyridine-2′-carboxalidene) aminoantipyrine (P2CAAP) with dimethylsulphoxide (DMSO)	4-aminoantipyrine, pyridine-2′-carbox aldehyde and dimethylsulphoxide	nitrate	La, Pr, Nd, Sm, Gd, Dy		$Ln(P2CAAP)(DMSO)](NO_3)_3$	Rajendran & Sreeletha (2001)
4[(N-cinnamalidene)-amino] antipyrine (CAAP)	4-aminoantipyrine and cinnamaldehyde	nitrate, isothiocyanates and perchlorate	Nd, Sm, Gd, Tb, Dy	10, 7, 9, 8	$Ln(CAAP)_2(NO_3)_3$ $Ln(CAAP)_n(NCS)_3$ $Ln(CAAP)_4(ClO_4)_3$.	Agarwal & Agarwal (1995)
4-[N-(2-methoxybenzylimine) formyl]-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (2MBFA)	2-methoxybenzyl-ami ne and anti-pyrine-4- carboxaldehyde	nitrate	La, Pr, Nd, Sm, Gd, Dy, Y	7	$Ln(2MFA)_2(NO_3)_3$	Rijulal & Indrasenan (1995)
4-tert-but-2,6-di-formylphenolbis (4-aminoantipyrine) (HIL)	4-aminoantipyrine and 2,6-diformyl-4-ter-butylphenol	chloride	La, Ce, Gd	7	$LnL'Cl_2$	Abid (2013)
1,2-(diimino-4′-antipyrinyl)ethane (GA)	4-aminoantipyrine and glyoxal	iodide, perchlorate and nitrate	Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er,	9, 11	$Ln(GA)_2I]I_2$, $[Ln(GA)_2(ClO_4)](ClO_4)_2$ and $[Ln(GA)_2(NO_3)_3]$	Nair & Radhakrishnan (1995, 1995, 1996)
2,6-diformylpyridine-N-oxide with 4-aminoantipyrine	4-aminoantipyrine and 2,6-diformylpyridine-N-oxide	nitrate	La, Pr, Eu, Tb, Er , Y		$LnL(NO_3)_3$	Yu et al. (2002)

Lanthanide(III) complexes of 4-N-(2′-furfurylidene) aminoantipyrine and its derivatives

The Schiff base ligand, 4-*N*-(2′-furfurylidene)aminoantipyrine (FAA) was derived from 4-aminoantipyrine and furfural. It forms mixed Schiff base ligand with benzaldehyde (Teran et al., 2019), 2-aminobenzo thiazole (Leelavathy and Anthony, 2013) and o-phenylenediamine (Suresh and Prakash, 2011). FAA coordinates to metal ions to form stable complexes. There are few reports on the lanthanide(III) complexes of the Schiff base, FAA (Table 4).

Vinodkumar and Radkrishnan (1997) developed and characterized yttrium and lanthanide(III) perchlorate complexes of 4-*N*-(2′-furfurylidene)aminoantipyrine (FAA), derived from furfural and 4-aminoantipyrine (Figure 12). The complexes possessed the general formula, $[Ln(FAA)_3(ClO_4)_2]ClO_4$, where Ln could be Y, La, Pr, Nd, Sm, Gd, Eu, Dy, Ho, or Er. The ligand, FAA, acted as a neutral tridentate ligand by coordinating through the carbonyl oxygen atom, the azomethine nitrogen atom, and the oxygen atom of the furan ring. Two perchlorate ions coordinated with the metal ion in a unidentate fashion, while the third ion remained ionic (Figure 13). The metal ion in these complexes was assigned a coordination number of eleven, enabling it to adopt the geometry of an octadecahedron or its distorted form determined by steric requirements. The thermal analysis indicated that the complexes remained stable up to 150°C and underwent decomposition in two phases prior to the formation of the corresponding metal chlorides.

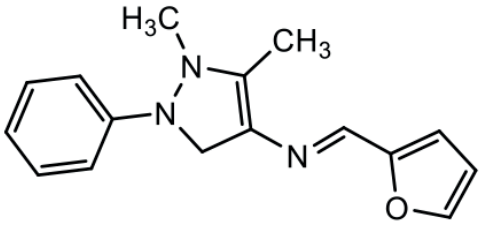


Figure 12. Structure of the ligand, 4-*N*-(2′-furfurylidene)aminoantipyrine (FAA).

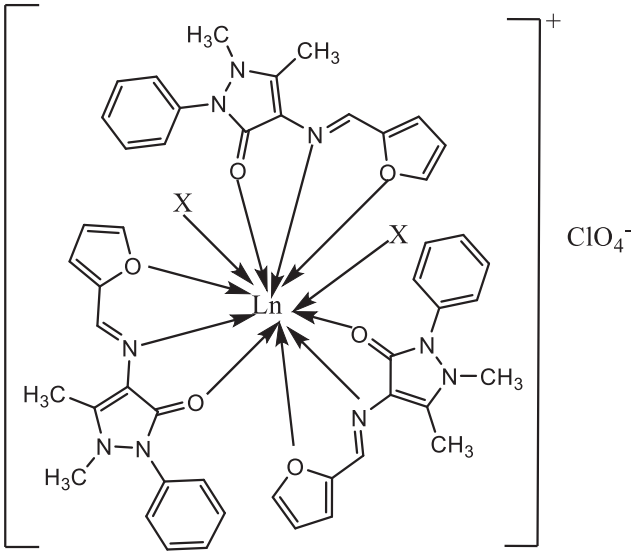


Figure 13. Structure of the complexes where Ln can be Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho and Er.

Vinodkumar et al. (2000) elucidated the mechanism and kinetics of thermal decomposition of lanthanide(III) nitrate complexes of the Schiff base, 4-*N*-(2′-furfurylidene)aminoantipyrine (FAA), employing thermogravimetric and derivative thermogravimetric techniques. The synthesized complexes were characterized by spectroanalytical techniques. The complexes were assigned the general formula $[Ln(FAA)(NO_3)_2]NO_3$, where Ln represented La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, and Er. The metal ions in the complexes were assigned a coordination number of seven. The kinetic parameters and mechanism of the thermal decomposition were derived using the Coats-Redfern equation. The activation energy suggested that the metal-ligand bond was notably weak, while the negative entropy of activation indicated that the activated complex possessed a more ordered structure than the corresponding reactants. No definite trend was observed in the values of activation energy and activation entropy.

A collection of lanthanide nitrate, perchlorate, and isothiocyanate complexes of 4-[(*N*-furfural) amino] antipyrine (FFAP), synthesized through the reaction of furfural with 4-aminoantipyrine (Figure 14), were prepared and characterized by Agarwal et al. (1996); Agarwal and Agarwal (2001). The complexes exhibited a general composition of $Ln(FFAP)_nX_3$, where Ln represented La, Pr, Nd, Sm, Gd, Tb, or Dy, and X could be NO_3^-, n = 2; NCS^-, n = 2 or 3; X = ClO_4^-, n = 4. The ligand, FFAP acted as a bidentate ligand. A coordination number of ten was proposed for all lanthanide ions in the nitrate complexes,

[Ln(FFAP)$_2$(NO$_3$)$_3$], (Figure 15) suggestive of a decahedron or bicapped square antiprism geometry for each of the compounds. For the isothiocyanate complexes, [Ln(FFAP)$_3$(NCS)$_3$], a coordination number of seven was proposed for La and Pr (Figure 16), indicative of pentagonal bipyramidal, capped trigonal prism, or capped octahedral geometry, while a coordination number of nine was assigned to Nd, Sm, Gd, Tb, or Dy (Figure 17), indicative of nonadecahedral or tricapped trigonal prism geometry. For the perchlorate complexes, [Ln(FFAP)$_4$](ClO$_4$)$_3$ (Figure 18), a coordination number of eight was proposed indicating square antiprism, dodecahedral, or cubic geometry.

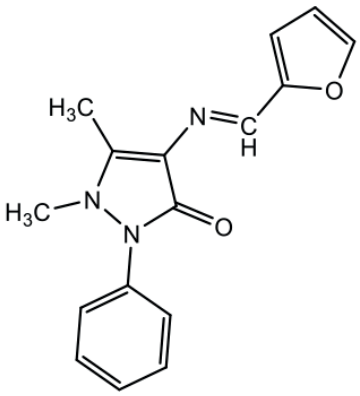


Figure 14. Structure of the ligand 4-[(*N*-furfural)amino]antipyrine, FFAP.

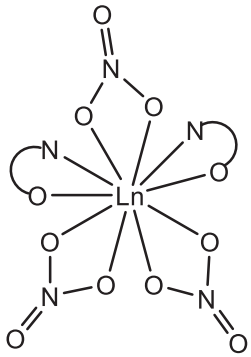


Figure 15. Lanthanide(III) nitrato complexes of FFAP, [Ln(FFAP)$_2$(NO$_3$)$_3$] where Ln could be La, Pr, Nd, Sm, Gd, Tb or Dy.

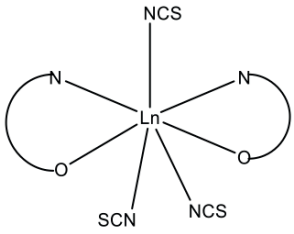


Figure 16. Lanthanide(III) isothiocyanato complexes of FFAP [Ln(FFAP)$_2$(NCS)$_3$] where Ln can be La or Pr.

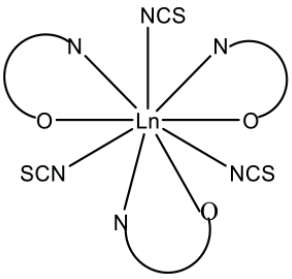


Figure 17. Lanthanide(III) isothiocyanato complexes of FFAP, [Ln(FFAP)$_3$(NCS)$_3$] where Ln can be Nd, Sm, Gd, Tb or Dy.

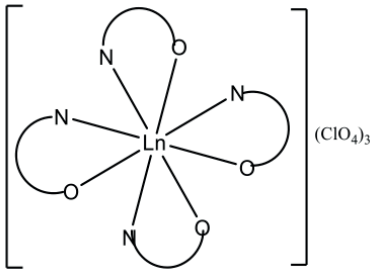


Figure 18. Lanthanide(III) perchlorate complexes of FFAP, [Ln(FFAP)$_4$](ClO$_4$)$_3$ where Ln can be La, Pr, Nd, Sm, Gd, Tb or Dy.

Agarwal et al. (2004) obtained and characterized the lanthanide(III) chloride complexes of the Schiff base, 4[*N*-(furfural)amino]antipyrine (FDPPO). The ligand FDPPO functioned as a bidentate ligand, coordinating through the azomethine nitrogen atom and carbonyl oxygen to form a five-membered chelate ring. It had a composition of [Ln(FDPPO)$_2$Cl$_3$], where Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho (Figure 19). The chloride ions were ionic in nature and placed within the inner coordination sphere. The complexes were assigned a coordination number of seven.

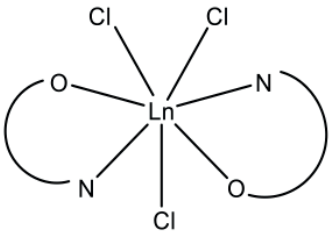


Figure 19. Proposed structure of [Ln(FDPPO)$_2$Cl$_3$] where Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy or Ho.

Lanthanide(III) complexes of 4-*N*-(2′-thienylideneaminoantipyrine) and its derivatives

4-*N*-(2′-thienylideneaminoantipyrine) (TAA) is a Schiff base prepared from the condensation reaction of 4-aminoantipyrine and thiophene-2-carboxaldehyde. 4-*N*-(2′-thienylideneaminoantipyrine (TAA) coordinates to metal ions using its sulphur, oxygen and nitrogen atoms thereby forming stable

complexes with interesting physicochemical properties and biological activity (Rahim et al, 2015). Very few lanthanide(III) complexes of the Schiff base, TAA, are known (Table 5).

Vinodkumar and Radhakrishnan (1996,1997) documented the synthesis and characterization of lanthanide(III) perchlorate complexes of the Schiff base, 4-*N*-(2′-thienylideneaminoantipyrine) (TAA) derived from thiophene-2-carboxaldehyde and 4-aminoantipyrine (Figure 20), using spectroanalytical techniques. The proposed formula for the complexes was $[Ln(TAA)_3(ClO_4)](ClO_4)_2$ where Ln may be Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, or Er (Figure 21). The ligand, 4-*N*-(2′-thienylideneaminoantipyrine) (TAA) functioned as a neutral tridentate ligand by coordinating through the carbonyl oxygen, azomethine nitrogen, and the sulfur of the thiophene ring. Two perchlorate ions were ionic, while the third coordinated monodentately to the metal center. The metal ion in these complexes was assigned a coordination number of ten. The compounds exhibited stability up to 180°C and underwent decomposition in two phases, yielding the corresponding metal halide.

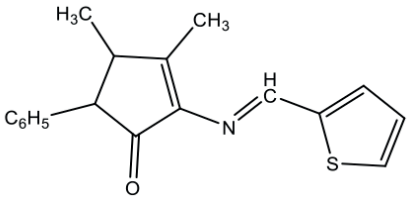


Figure 20. Structure of the Schiff base, 4-*N*-(2′-thienylideneaminoantipyrine) (TAA).

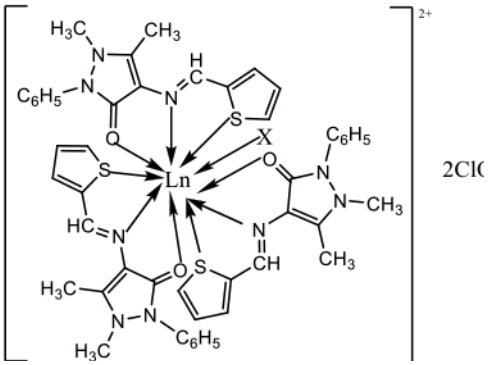


Figure 21. Tentative structure of the complexes where X is ClO_4^- and Ln could be Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho or Er.

They also went further to develop and characterize lanthanide and yttrium perchlorate complexes of the Schiff base, 4-*N*-(5′-nitro-2′-thienylidene)aminoantipyrine (NTAAP), derived from 5-nitrothiophene-2-carboxaldehyde and 4-aminoantipyrine using spectroscopic methods (Figure 22) (Vinodkumar and Radhakrishnan, 1997). The complexes possessed the composition $[Ln(NTAAP)_2(ClO_4)_2]ClO_4$, where Ln may be Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, or Er (Figure 23). The Schiff base, 4-*N*-(5′-nitro-2′-thienylidene)aminoantipyrine (NTAAP) acted as a neutral tridentate ligand coordinating through the azomethine nitrogen atom, carbonyl oxygen atom, and sulphur atom of the thiophene ring. Two perchlorate ions coordinate with the metal ion in a monodentate manner, while the third is ionic. The compounds exhibited thermal stability up to 110 °C and underwent decomposition in two phases. The metal ions in the complexes were assigned a coordination number of eight.

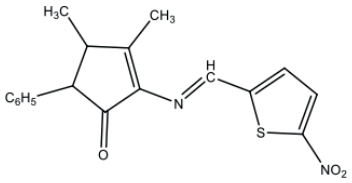


Figure 22. Structure of the Schiff base, 4-*N*-(5′-nitro-2′-thienylidene)amino-antipyrine (NTAAP).

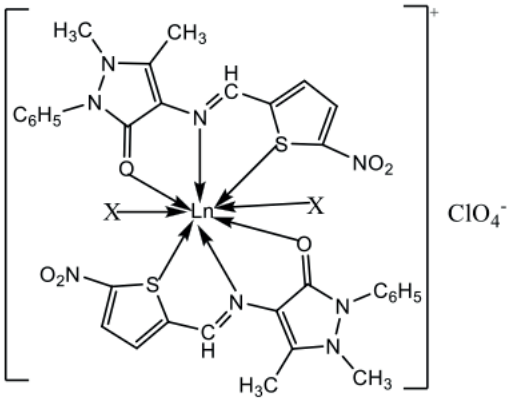


Figure 23. Tentative structure of the complexes where X is ClO_4^- and Ln could be Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho or Er.

Table 4. Lanthanide(III) complexes of 4-N-(2′-furfurylidene)aminoantipyrine and its derivatives.

Schiff Base	Constituents	Anion	Lanthanides	CN	Formula	Ref.
4-N-(2′-furfurylidene) amino antipyrine (FAA)	4-aminoantipyrine and furan-2-carboxaldehyde	perchlorate	Y, La, Pr, Nd, Sm, Gd, Eu, Dy, Ho, Er	11	$[Ln(FAA)_3(ClO_4)_2]ClO_4$	Vinokumar and Radhakrishnan (1997)
4-N-(2′-furfurylidene) amino antipyrine (FAA)	4-aminoantipyrine and furan-2-carboxaldehyde	nitrate	La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er	7	$[Ln(FAA)(NO_3)_2]NO_3$	Vinokumar et al. (2000)
4-[(N-furfural)amino] antipyrine (FFAP)	4-aminoantipyrine and furfural	nitrate, per-chlorate and isothiocyanate	La, Pr, Nd, Sm, Gd, Tb, Dy	10, 7, 9	$[Ln(FFAP)_2(NO_3)_3]$ $[Ln(FFAP)_3(NCS)_3]$ $[Ln(FFAP)_4](ClO_4)_3$	Agarwal (1978), Agarwal & Agarwal (2001)
4[N-(furfural)amino] antipyrine (FDPPO)	4-aminoantipyrine and furfural	chloride	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho	7	$[Ln(FDPPO)_2Cl_3]$	Agarwal et al. (2004)

Table 5. Lanthanide(III) complexes of 4-*N*-(2′-thienylidene)aminoantipyrine and its derivatives.

Schiff Base	Constituents	Anion	Lanthanides	CN	Formula	Ref.
4-N-(2′-thienylidene) amino antipyrine (TAA)	4-aminoantipyrine and thiophene-2-carboxalde hyde	perchlorate	Y, La, Pr, Nd, Sm, Gd, Eu, Dy, Ho, Er	10	$[Ln(TAA)_3(ClO_4)](ClO_4)_2$	Vinokumar and Radhakrishnan (1996, 1997)
4-N-(5′-nitro-2′-thienylidene) aminoantipyrine (NTAAP)	4-aminoantipyrine and 5-nitrothiophene-2-carbox aldehyde	perchlorate	Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er	8	$[Ln(NTAAP)_2(ClO_4)_2]ClO_4$	Vinokumar and Radhakrishnan (1997)

Lanthanide(III) complexes of 4-N-(4′-antipyrylmethylidene) aminoantipyrine and its derivatives

4-*N*-(4′-antipyrylmethylidene)aminoantipyrine (AA) is a Schiff base derived from 4-aminoantipyrine and 4-antipyrinecarboxaldehyde (4-formylantipyrine). The structure of AA consists of two pyrazolone rings, carbonyl oxygen donor atoms and imine nitrogen donor atom. AA forms stable complexes with lanthanides (Table 6). There should be further studies on its biomedical potential.

Radhakrishna (1992) prepared lanthanide(III) nitrate complexes of the Schiff base, 4-*N*-(4′-antipyrylmethylidene)aminoantipyrine (AA) The synthesized compounds were analyzed using spectroscopic techniques. The ligand, 4-*N*-(4′-antipyrylmethylidene)aminoantipyrine (AA) acts as a neutral tridentate ligand in all complexes, coordinating via the oxygen of both carbonyl groups and the nitrogen of the azomethine group. Two nitrate ions were reported to coordinate in a monodentate fashion, while the remaining nitrate remained uncoordinated. The lanthanide ion in the complexes was assigned a coordination number of eight. Yttrium and lanthanide(III) nitrate complexes of the Schiff base, 4-*N*-(4′-antipyrylmethylidene)aminoantipyrine (AA), derived from 4-antipyrinecarboxyaldehyde and 4-amino antipyrine, were characterized by Muraleedharan Nair and Radhakrishnan (1993). The complexes possess the composition, $[Ln(AA)_2(NO_3)_2]NO_3$, where Ln could be Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, or Er. The Schiff base, AA, acted as a tridentate ligand by coordinating through the oxygen of the carbonyl groups and the azomethine nitrogen. Only two nitrate ions were coordinated to the central metal ion in a monodentate fashion, while the third remained uncoordinated. The thermal analysis indicated that the complexes can maintain stabiity up to 220 °C. The coordination number of $[Nd(AA)_2(NO_3)_2]NO_3$ was designated as eight.

Muraleedharan Nair and Radhakrishnan (1995) obtained and characterized twenty novel chloride and bromide complexes of yttrium and lanthanides of the Schiff base, 4-*N*-(4′-antipyrylmethylidene) aminoantipyrine (AA) The complexes possessed the general formulae $[Ln(AA)_2Cl_3]$ and $[Ln(AA)_2Br_2]$ Br, where Ln represented Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, and Er. The Schiff base acted as a terdentate ligand, coordinating via the oxygen atom of the carbonyl groups and the azomethine nitrogen.

Muraleedharan Nair and Radhakrishnan (1995) synthesized yttrium and lanthanide(III) iodide complexes of the Schiff base, 4-*N*-(4′-antipyrylmethylidene)aminoantipyrine (AA) obtained from 4-aminoantipyrine and 4-antipyrinecarboxyaldehyde (Figure 24) They were characterized using spectroscopic techniques. The complexes possessed the general formula $[Ln(AA)_2I]I_2$, where Ln may be Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, or Er. The Schiff base, 4-*N*-(4′-antipyrylmethylidene) aminoantipyrine (AA), acted as a neutral tridentate ligand, coordinating via the oxygen atoms of the carbonyl groups and the azomethine nitrogen atom. Only one iodide ion coordinated with the metal ion, while the other two remained ionic. The metal ion was assigned a coordination number of seven.

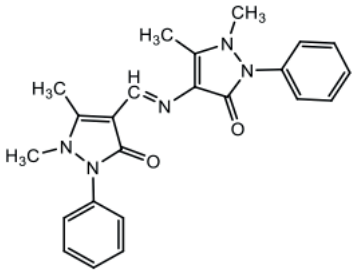


Figure 24. Structure of the ligand, 4-*N*-(4′-antipyrylmethylidene)aminoantipyrine (AA).

Muraleedharan Nair and Radhakrishnan (1996) obtained and characterized rare earth perchlorate complexes of the Schiff base, 4-*N*-(4′-antipyrylmethylidene)aminoantipyrine (AA), by spectroscopic and analytical techniques. The perchlorate complexes exhibited a general formula of $[Ln(AA)_2ClO_4](ClO_4)_2$, where Ln represented La, Pr, Nd, Sm, or Eu, and $[Ln(AA)_3](ClO_4)_3$, where Ln denoted Gd, Dy, Ho, Er, or Y. Perchlorate ions were observed to coordinate in a monodentate fashion solely in the light rare earths, whi[e remaining uncoordinated outside the coordination sphere in the heavy rare earth. The ligand, AA, functioned as a neutral terdentate ligand coordinating through the azomethine nitrogen and carbonyl oxygen atoms, leading to the formation of two chelate rings: one five-membered and one six-membered, which provided additional stability to the complexes. The light lanthanides, comprising of La, Pr, Nd, Sm, and Eu, were assigned a coordination number of seven, while the heavy lanthanide complexes, including Gd, Dy, Ho, Er, and Y, were assigned a coordination number of nine.

Muraleedharan Nair and Radhakrishnan (1997) subsequently studied the thermal decomposition, mechanism and kinetics of lanthanide(III) perchlorate complexes of the Schiff base, 4-*N*-(4′-antipyrylmethyl idene)aminoantipyrine (AA). The complexes were previously characterized by analytical and spectroscopic methods. They exhibited the general formula $[Ln(AA)_2(ClO_4)](ClO_4)_2$ where Ln represented La, Pr, Nd, Sm, or Eu, and, $[Ln(AA)_3](ClO_4)_3$ where Ln denoted Gd, Dy, Ho, or Er. The perchlorate complexes of light lanthanides, namely La, Pr, Nd, Sm, and Eu exhibited greater thermal stability than the corresponding heavy lanthanides, specifically Gd, Dy, Ho, and Er. This phenomenon can be ascribed to steric strain due to the presence of three bulky ligand molecules in the heavy lanthanides and two ligand molecules in the light lanthanides. The presence of the steric strain led to lesser thermal stability in the heavy lanthanides.

They also went further to study the thermal decomposition of lanthanum complexes with perchlorate, nitrate, chloride, bromide, and iodide of the Schiff base 4-*N*-(4′-antipyrylmethylidene)amino antipyrine (AA) using TG and DTG techniques (Muraleedharan Nair & Radhakrishnan, 1995). The complexes were analyzed via spectroscopic techniques. The complexes possessed the following formulas: $[La(AA)_2(ClO_4)](ClO_4)_2$, $[La(AA)_2(NO_3)_2](NO_3)$, $[La(AA)_2Cl_3]$, $[La(AA)_2Br_2]Br$ and $[La(AA)_2I]I_2$. The Schiff base, 4-*N*-(4′-antipyrylmethylidene)aminoantipyrine (AA), acted as a neutral terdentate ligand, coordinating via both the carbonyl oxygen and the azomethine nitrogen, resulting in the formation of two ring systems (a five-membered ring and a six-membered ring). Thermal analysis revealed that the breakdown characteristics depends on the anion present. The halide complexes exhibited lesser thermal stability compared to perchlorate and nitrate complexes. The order of reduction, increase

in the size of the halide ions and steric strain on the central atom followed the sequence: chloride > bromide > iodide. The thermal stability of the lanthanum complexes was as follows: perchlorate ≈ nitrate > chloride > bromide > iodide.

Lanthanide(III) complexes of 4-N-(2′-hydroxy-1′-naphthylidene) aminoantipyrine and its derivatives

4-*N*-(2′-hydroxy-1′-naphthylidene)aminoantipyrine (HNAAP) is a Schiff base derived from the reaction of 4-aminoantipyrine with 2-hydroxy-1-naphthaldehyde. The Schiff base ligand, HNAAP consists of pyrazolone ring, naphthalene ring, hydroxyl group and azomethine group. Its reaction with metal ions gave rise to complexes with enhanced biological properties (Table 7), Studies have shown that HNAAP exhibited significant antibacterial and antifungal activity (Guo et al.,2007; Al-labban et al., 2019).

Radhakrishnan (1985) obtained a series of lanthanide(III) nitrate complexes of 4-*N*-(2′-hydroxy-1′-naphthylidene)aminoantipyrine (HNAAP). These complexes were analyzed by spectroscopic techniques. The complexes possessed the general formula $[Ln(HNAAP)_2(NO_3)_3]$, with Ln representing La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, or Y. The Schiff base, 4-*N*-(2′-hydroxy-1′-naphthylidene) aminoantipyrine (HNAAP) acted as a bidentate neutral ligand coordinating to the metal ion via the carbonyl oxygen and azomethine nitrogen, while the nitrate group coordinated in a monodentate fashion. The complexes had a coordination number of seven. The thermal stabilities of the complexes were examined.

Radhakrishnan (1986) reported the synthesis and characterisation of rare earth iodide complexes with the ligand, 4-*N*-(2′-hydroxy-1′-naphthylidene)aminoantipyrine (HNAAP,HL). The complexes exhibited a general composition of $[LnL_2I]$ where Ln represented Nd, Sm, Gd, Tb, Dy, Ho, or Y. The synthesized compounds were characterized by spectroanalytical techniques. The Schiff base, HNAAP, acts as a monovalent terdentate ligand with coordination numbers of seven in La and Pr complexes, and a neutral bidentate ligand with coordination number of nine in Nd, Sm, Gd, Tb, Dy, Ho, or Y complexes. Thermal analysis was conducted on the synthesized complexes.

Radhakrishnan (1986) prepared and characterized lanthanide(III) perchlorate complexes of 4-*N*-(2′-hydroxy-1′-naphthylidene)aminoantipyrine [HNAAP(HL)]. The complexes possessed the general formula, $[Ln(L)_2ClO_4]$ where Ln may be La, Pr, Nd, or Sm, and $[Ln(HL)_4](ClO_4)_3$ where Ln may be Gd, Tb, Dy, Ho, or Y. The ligand, 4-*N*-(2′-hydroxy-1′-naphthylidene)aminoantipyrine (HNAAP) acted as a monovalent terdentate ligand in the perchlorate complexes of the heavier lanthanides.

Agarwal et al. (1993) developed and characterized a variety of lanthanide(III) bromo and perchlorate complexes of 4-*N*-(2′-hydroxy-1′-naphthylidene)aminoantipyrine (HNAAP). The complexes had a general formula of $[Ln(HNAAP)_nX_3]$, where X could be Br^-, n = 2 or ClO_4^-, n = 3 and Ln could be La, Pr, Nd, Sm, Gd, Tb or Dy. The Schiff base ligand (HNAAP) acts as a bidentate ligand, coordinating via the carbonyl oxygen and azomethine nitrogen. The lanthanide ions were assigned coordination numbers of six and seven in the bromo and perchlorate complexes, respectively.

Radhakrishnan and Radhakrishnan (1998) obtained five complexes of La, Nd, Gd, Ho and Er bromides with the Schiff base, 4-*N*-(2′-hydroxy-1′-naphthylidene)aminoantipyrine (HNAAP) (Figure 25). They were characterized using spectral and analytical methods. The complexes had a general composition of $[M(HNAAP)_2Br_2]Br$ (Figure 26). The Schiff base, HNAAP, acted as a neutral tridentate ligand coordinating to the lanthanide ions through the azomethine nitrogen

atom, carbonyl oxygen atom and hydroxyl oxygen atom. Two of the bromide ions coordinated to the lanthanide ions in a uni dentate manner while the remaining one was ionic. A coordination number of eight was assigned to the lanthanide ion. Thermal analysis was also carried out to determine the kinetic parameter.

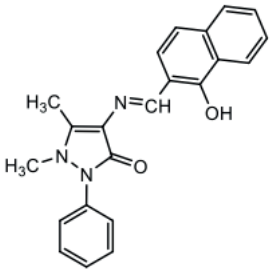


Figure 25. Structure of 4-*N*-(2′-hydroxy-1′-naphthylidene)aminoantipyrine (HNAAP).

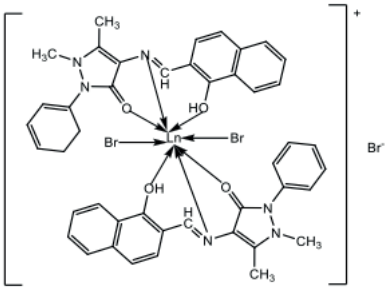


Figure 26. Tentative structure of the complexes.

Table 6. Lanthanide(III) complexes of 4-*N*-(4′-antipyrylmethylidene)aminoantipyrine and its derivatives.

Schiff Base	Constituents	Anion	Lanthanides	CN	Formula	Ref.
4-N-(4′-antipyrylmethylidene) aminoantipyrine (AA)	4-aminoantipyrine and 4-antipyrinecarboxyaldehyde	nitrate	Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er.	8	$[Ln(AA)_2(NO_3)_2]NO_3$	Radhakrishnan (1992); Nair & Radhakrishnan (1993)
4-N-(4′-antipyrylmethylidene) aminoantipyrine (AA)	4-aminoantipyrine and 4-antipyrinecarboxyaldehyde	chloride and bromide	Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er.		$[Ln(AA)_2Cl_3]$, $[Ln(AA)_2Br_2]Br$	Nair & Radhakrishnan (1995)
4-N-(4′-antipyrylmethylidene) aminoantipyrine (AA)	4-aminoantipyrine and 4-antipyrinecarboxyaldehyde	iodide	Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er.	7	$[Ln(AA)_2I]I_2$	Nair & Radhakrishnan (1996)
4-N-(4′-antipyrylmethylidene) aminoantipyrine (AA)	4-aminoantipyrine and 4-antipyrinecarboxyaldehyde	perchlorate	La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er.	7,9	$[Ln(AA)_2(ClO_4)](ClO_4)_2$	Nair & Radhakrishnan (1996)

Table 7. Lanthanide(III) complexes of 4-N-(2′-hydroxy-1′-naphthylidene)aminoantipyrine and its derivatives.

Schiff Base	Constituents	Anion	Lanthanides	CN	Formula	Ref.
4-N-(2′-hydroxy-1′-naphthylidene) aminoantipyrine	4-aminoantipyrine and 2-hydroxynaphthaldehyde	nitrate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Y	7	$[Ln(HNAAP)_2(NO_3)_3]$	Radhakrishnan (1985)
4-N-(2′-hydroxy-1′-naphthylidene) aminoantipyrine	4-aminoantipyrine and 2-hydroxynaphthaldehyde	iodide	Nd, Sm, Gd, Tb, Dy, Ho, Y	7,9	$[LnL_2I]$	Radhakrishnan (1986)
4-N-(2′-hydroxy-1′-naphthylidene) aminoantipyrine	4-aminoantipyrine and 2-hydroxynaphthaldehyde	perchlorate	La, Pr, Nd, Sm , Gd, Tb, Dy, Ho, Y		$[Ln(L)_2ClO_4]$ $[Ln(HL)_4](ClO_4)_3$	Radhakrishnan (1986)
4-N-(2′-hydroxy-1′-naphthylidene) aminoantipyrine	4-aminoantipyrine and 2-hydroxynaphthaldehyde	bromide and perchlorate	La, Pr, Nd, Sm, Gd, Tb, Dy	6,7	$[Ln(HNAAP)_nX_3]$	Agarwal et al. (1993)
4-N-(2′-hydroxy-1′-naphthylidene) aminoantipyrine	4-aminoantipyrine and 2-hydroxynaphthaldehyde	bromides	La, Nd, Gd, Ho, Er	8	$[M(HNAAP)_2Br_2]Br$	Radhakrishnan & Radhakrishnan (1998)

Lanthanide(III) complexes of benzylidene-4-aminoantipyrine and its derivatives

A lot of Schiff bases derived from the reaction of 4-aminoantipyrine with benzaldehyde or substituted benzaldehydes and their metal complexes have been synthesized over the years. Their bioactivities have been reported (Erbaş et al., 2025; Salah et al., (2021). But less research work has been conducted on the bioactivity of its lanthanide(III) complexes. In this section, various lanthanide(III) complexes of benzylidene-4-aminoantipyrine and its derivatives synthesized over the years are presented (Table 8).

Agarwal and Sarin (1993) reported the synthesis and characterization of lanthanide(III) nitrates and isothiocyanate complexes of 4-[(*N*-4-methoxybenzalidene)amino]antipyrine (MBAAP) using spectroanalytical techniques. The general compositions were $[Ln(MBAAP)_2(NO_3)_3]$ and $[Ln(MBAAP)_n(NCS)_3]$, where n is 2, Ln could be La or Pr; n is 3, Ln can be Nd, Sm, Gd, Tb, or Dy. The ligand acted as a bidentate ligand, coordinating via the carbonyl oxygen and the azomethine nitrogen atom. The coordination numbers of seven, nine, and ten were allocated to the complexes based on their anion.

Lanthanide(III) perchlorate complexes of the Schiff base ligand, 4-[(*N*-4-methoxybenzylidene) amino] antipyrine (MBAAP) and 4-[(*N*-4-hydroxy-3-methoxybenzylidene)amino]antipyrine (HMBAAP) derived from 4-aminoantipyrine and 4-methoxybenezaldehyde/4-hydroxy-3-methoxybenzaldehyde were prepared and characterized. These complexes were reported to have a general formula of $[Ln(MBAAP)_4](ClO)_{4.3}$ or $[Ln(HMBAAP)_4](ClO)_4)_3$, where Ln could be La, Pr, Nd, Sm, Gd, Tb or Dy. Both ligands acted in a bidentate manner, coordinating through the carbonyl oxygen and azomethine nitrogen. The perchlorate complexes were ionic with a coordination number of eight assigned to the metal ions (Agarwal & Sarin,1993).

Agarwal and Sarin (1994) obtained lanthanide(III) nitrate and isothiocyanate complexes of a Schiff base, 4-[(*N*-4-hydroxy-3-methoxybenzalidene)amino]antipyrine (HMBAAP) derived from 4-hydroxy-3-methoxybenzaldehyde and 4-aminoantipyrine. The synthesized compounds were characterized by spectroscopic techniques. The complexes exhibited a general formula of $[Ln(HMBAAP)_2(NO_3)_3]$, where Ln could be La, Pr, Nd, Sm, Gd, Tb, or Dy, and $[Ln(HMBAAP)_n(NCS)_3]$, where n is 2 for La

or Pr, and n is 3 for Nd, Sm, Gd, Tb, or Dy. The spectral data indicated that the ligand coordinated at a molar ratio of either 3:1 or 2:1. The complexes acted as non-electrolytes in nitrobenzene and exhibited greater thermal stability than the ligand.

Chaudhary (2016) developed and characterized the Schiff base, 4[*N*-4-ethoxybenzalidene) aminoantipyrine (EBAAP) (Figure 27) and its isothiocyanate complexes. The complexes were represented by the formula [Ln(EBAAP)n$(NCS)_3$], where n is 2, Ln could be La or Pr; n is 3, Ln can be Nd, Sm, Gd, Tb, or Dy. The carbonyl group and the azomethine group participated in chelation with the lanthanide ion. The coordination number of seven was designated for La and Pr, while a coordination number of nine was designated for Nd, Sm, Gd, Tb, and Dy.

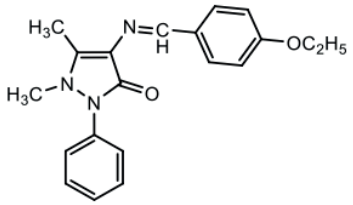


Figure 27. Structure of 4[*N*-4-ethoxybenzalidene)aminoantipyrine (EBAAP).

Agarwal et al. (1994) examined the lanthanide(III) iodide complexes of 4[*N*-(p dimethylaminobenzalidene) amino] antipyrine (DABAAP). Agarwal et al. (1992) reported the synthesis and characterization of many lanthanide(III) nitrate and isothiocyanate complexes of 4[*N*-(4-dimethylaminobenzylidene)amino] antipyrine (DABAAP), derived from p-dimethylaminobenzaldehyde and 4-aminoantipyrine (Figure 28). The synthesized compounds were characterized by spectroscopic and physicochemical methods. The complexes exhibited a general formula of [Ln$(DABAAP)_2(NO_3)_3$], with Ln represented as La, Pr, Nd, Sm, Gd, Tb, or Dy, and [Ln$(DABAAP)_n(SCN)_3$], where n is 2 with Ln as La or Pr, and n is 3 with Ln as Nd, Sm, Gd, or Dy. The Schiff base, DABAAP, acted as a bidentate ligand by coordinating through the carbonyl oxygen and azomethine nitrogen atoms. In the isothiocyanate complex, a coordination number of seven was designated for La and Pr (Figure 29A), while a coordination number of nine was assigned to Nd, Sm, Gd, Tb, or Dy (Figure 29B). The nitrate complexes were given a coordination number of ten (Figure 29C). The varying coordination numbers occurred as a result of a reduction in the size of lanthanide ions across the period. The impact of this effect ultimately leads to a decrease in the coordination number for the heavier lanthanides. Furthermore, the heavier lanthanides attracted a larger number of ligands owing to the increase in ionic potential across the period from La to Lu. The second factor was more prominent than the first factor.

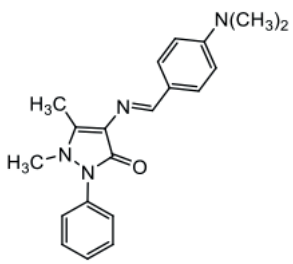


Figure 28. Structure of the Schiff base ligand, 4[*N*-(4-dimethylamin-obenzylidene)amino]antipyrine, DABAAP.

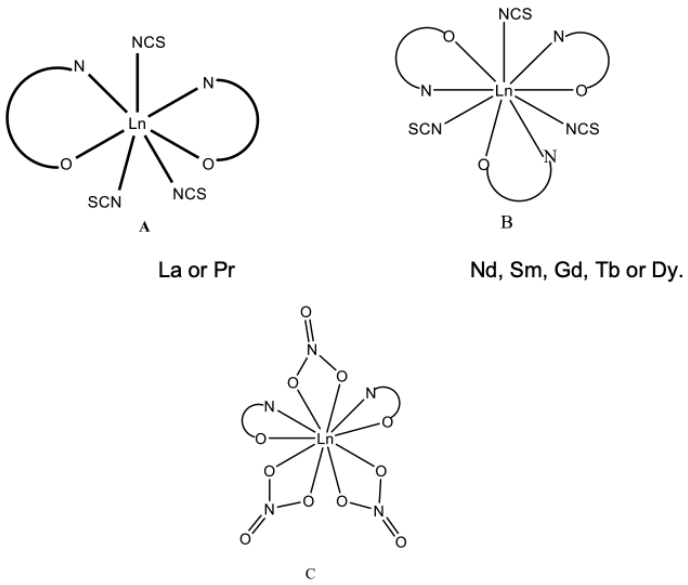


Figure 29. Tentative structures of the lanthanide(III) nitrate and isothiocyanate complexes.

Agarwal and Sarin (1994) prepared and characterized lanthanide(III) perchlorate complexes of the Schiff base, 4-[(*N*-4-dimethylaminobenzalidene)amino]antipyrine (DABAAP), using spectrochemical techniques. The complexes had a composition of $[Ln(DABAAP)_4](ClO_4)_3$, where Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, or Yb (Figure 30). All complexes were assigned a coordination number of eight. The three perchlorate ions were located outside the coordination sphere. Their thermal analysis was also studied.

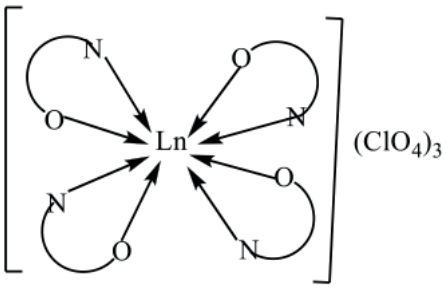


Figure 30. Structure of the complexes.

Lanthanide(III) halides complexes of the Schiff base, 4-[*N*-(p-dimethylaminobenzylidene) amino]antipyrine (DABAAP) were reported and characterized by Agarwal et al. (1995). The metal ion in these complexes was assigned a coordination number of seven. The compounds were structured as $[Ln(DABAAP)_2X_3]$, with Ln representing La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, or Yb, and X denoting Cl^- or Br^-.

Chaudhary (2012) reported the synthesis of the Schiff base ligand, 4 [(*N*-4-diethylamino-2-methylbenzalidene) amino]antipyrine (DAMBAAP), derived from 2-methyl-4-*N,N*-diethylaminobenz aldehyde and 4-aminoantipyrine and its lanthanide(III) nitrate complexes. The complexes possesed the general formula $Ln(DAMBAAP)_2(NO_3)_3$ where Ln could be La, Pr, Nd, Sm, Gd, Tb, or Dy. A coordination number of eight or nine was proposed for the metal ion in the complexes.

Wang et al. (2001) developed a series of lanthanide(III) nitrate complexes using the Schiff base, 4-(5-bromosalicylidenemine)-2,3-dimethyl-1-phenyl-3-pyrazolone (5-BSALADPPH), derived from the reaction of bromosalicylaldehyde with 4-aminoantipyrine. Its characterization was carried out using spectral and analytical methods. The complexes were formulated as $[Ln(5\text{-}BSALADPPH)_2(NO_3)_3]$, where Ln represented La, Eu, or Gd. The Schiff base functioned as a bidentate ligand, coordinating via the carbonyl oxygen and the azomethine nitrogen.

Table 8. Lanthanide(III) complexes of benzylidene-4-aminoantipyrine and its derivatives.

Schiff Base	Constituents	Anion	Lanthanides	CN	Formula	Ref.
4-[(*N*-4-methoxybenzalidene) amino]antipyrine (MBAAP)	4-aminoantipyrine and 4-methoxybenzaldehyde	nitrates and isothiocyanate	La, Pr, Nd, Sm, Gd, Tb, Dy	7,9,10	$[Ln(MBAAP)_2(NO_3)_3]$ and $[Ln(MBAAP)n(NCS)_3]$	Agarwal and Sarin (1993)
4-[(*N*-4-methoxybenzylidene) amino]antipyrine (MBAAP) and 4-[(*N*-4-hydroxy-3-meth oxybenzylidene)amino] antipyrine (HMBAAP)	4-aminoantipyrine and 4-methoxybenezaldehyde/ 4-hydroxy-3-methoxybenz aldehyde	perchlorate	La, Pr, Nd, Sm, Gd, Tb, Dy	8	$[Ln(MBAAP)_4](ClO)_4)_3$. $[Ln(HMBAAP)_4](ClO)_4)_3$,	Agarwal and Sarin (1993)
4[*N*-4-ethoxybenzalidene) aminoantipyrine (EBAAP)	4-aminoantipyrine and 4-ethoxybenezaldehyde	isothiocyanate	La, Pr, Nd, Sm, Gd, Tb, Dy	7,9	$[Ln(EBAAP)_n(NCS)_3]$	Chaudhary (2016)
4[*N*-(4-dimethylaminobenzylidene)amino]antipyrine (DABAAP)	4-aminoantipyrine and p-dimethylaminobenzaldehyde	iodide				Agarwal et al. (1994)
4[*N*-(p-dimethylaminobenzalidene)amino]antipyrine (DABAAP)	4-aminoantipyrine and p-dimethylaminobenzaldehyde	nitrate and isothiocyanate	La, Pr, Nd, Sm, Gd, Tb, Dy	7,9,10	$[Ln(DABAAP)_2(NO_3)_3]$ $[Ln(DABAAP)n(SCN)_3]$	Agarwal et al. (1992)
4-[(*N*-4-dimethylaminobenzalidene)amino]antipyrine (DABAAP)	4-aminoantipyrine and p-dimethylaminobenzaldehyde	perchlorate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Yb	8	$[Ln(DABAAP)_4]$-$(ClO_4)_3$	Agarwal and Sarin (1994)
4-[*N*-(p-dimethylaminobenzylidene)amino]antipyrine (DABAAP)	4-aminoantipyrine and p-dimethylaminobenzaldehyde	halides	La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho	7	$[Ln(DABAAP)_2X_3]$	Agarwal et al. (1995)
4[(*N*-4-diethylamino-2-methyl benzalidene) amino]antipyrine (DAMBAAP)	4-aminoantipyrine and 2-methyl-4-*N*,*N*-diethylamino benzaldehyde	nitrate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Yb	8,9	$Ln(DAMBAAP)_2(NO_3)_3$	Chaudhary (2012)
4-[(*N*-4-hydroxy-3-methoxy benzalidene) amino]antipyrine (HMBAAP)	4-aminoantipyrine and 4-hydroxy-3-methoxybenz aldehye	nitrate and isothiocyanate	La, Pr, Nd, Sm, Gd, Tb, Dy		$[Ln(HMBAAP)_2(NO_3)_3]$	Agarwal and Sarin (1994)
4-(5-bromosalicylidenemine)-2,3-dimethyl-1-phenyl-3-pyrazolone;(5-BSALADPPH)	4-aminoantipyrine and bromosalicylaldehyde	nitrate	La, Eu, Gd		$[Ln(5\text{-}bsaladpph)_2(NO_3)_3]$	Wang et al. (2001)

Lanthanide(III) complexes of 4-aminoantipyrine semicarbazone derivatives

Semicarbazones of 4-aminoantipyrine and its derivatives were obtained by the condensation reaction between the carbonyl group of 4-aminoantipyrine and a semicarbazide. Semicarbazide exhibits chelating ligand behavior forming transition metal and lanthanide complexes with biological potentials (Dhabale et al., 2022; Mir et al., 2023). This section of the review presents lanthanide(III) complexes of various 4-aminoantipyrine semicarbazone derivatives (Table 9).

Agarwal et al. (1996) reported a series of lanthanide(III) nitrate complexes of 4[*N*-(benzylidene) amino]antipyrine semicarbazone (BAAPS), synthesized from 4-aminoantipyrine, benzaldehyde and semicarbazide hydrochloride (Figure 31). They were characterized by spectral and analytical methods. The Schiff base, BAAPS, acted as a tridentate ligand by coordinating through the carbonyl oxygen atom, hydrazine nitrogen atom, and azomethine nitrogen atom, while the nitrate ion exhibited bidentate characteristics. The lanthanide(III) complexes had a general composition of $[Ln(BAAPS)(NO_3)_3]$ where Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy and Ho (Figure 32). The complexes were allocated a coordination number of nine. Thermal studies were also carried out.

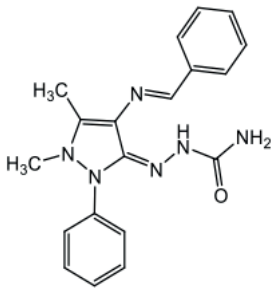


Figure 31. Structure of 4[*N*-(benzylidene)amino)antipyrine semicarbazone (BAAPS).

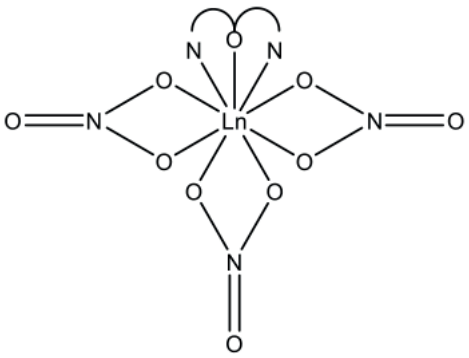


Figure 32. Structure of $[Ln(BAAPS)(NO_3)_3]$ where Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy and Ho.

Chakraborthy et al. (2002) investigated the influence of chloride and perchlorate ions on lanthanide(III) coordination compounds of 4[*N*-(benzalidene)amino]antipyrine semicarbazone (BAAPS). The isolated compounds possessed the compositions, $Ln(BAAPS)_2Cl_3$ and $Ln(BAAPS)_2(ClO_4)_3$, where Ln

represented La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho. The compounds were analyzed using spectroscopic techniques. The coordination number of the central metal ion was either six or nine, indicating octahedral or nonahedral geometry based on the type of anion present. The thermal characteristics of these compounds were also examined.

Agarwal et al. (2001) documented the synthesis of chloro and thioisocyanate lanthanide(III) complexes of 4[*N*-(p-dimethylaminobenzalidene)amino]antipyrine semicarbazone (DABAAPS), derived from 4-aminoantipyrine, p-dimethylaminobenzaldehyde and semicarbazide hydrochloride. The synthesized complexes were characterized by physicochemical techniques. The lanthanide exhibited a general formula of $[Ln(DABAAPS)_2X_3]_1$, where Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho, and X denoted Cl^- or NCS^-. The Schiff base, DABAAPS, acted as a tridentate (N,N,O) ligand by coordinating via two nitrogen atoms and one oxygen atom. The metal ion in the complexes was assigned a coordination number of nine. The thermal stabilities of these compounds were examined.

Chakraborti and Goel (2003) synthesized and characterized lanthanide(III) perchlorate and nitrate complexes of 4[*N*-(4′-dimethylaminobenzalidene)amino]antipyrine semicarbazone (DABAAPS) (Figure 33). The complexes possess a general formula of $Ln(DABAAPS)_nX_3$ where X could be ClO_4^- if n is 2, or NO_3^- if n is 1, and Ln is La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho. They had a general formula of $Ln(DABAAPS)_2(ClO_4)_3$ and $Ln(DABAAPS)(NO_3)_3$. The Schiff base, DABAAPS, acted as a tridentate (N,N,O) ligand by coordinating via the carbonyl oxygen atom, hydrazinic nitrogen atom, and azomethine nitrogen atom. The spectral data suggested a bidentate nitrate coordination. The nitrate ions were located within the coordination sphere with coordination of nine assigned to the complexes while the perchlorate groups were located outside the coordination sphere with a coordination number of six existing in their complexes. This confirmed their ionic character.

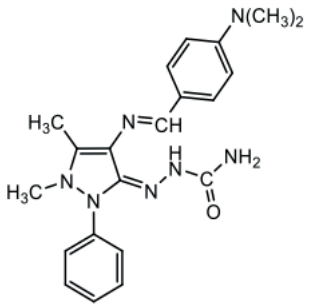


Figure 33. Structure of 4[*N*-(4′-dimethylaminobenzalidene)amino]antipyrine semicarbazone.

The lanthanide(III) chloro complexes of the Schiff bases, 4[*N*-(4′-hydroxy-3′-methoxybenzalidene) amino]antipyrine semicarbazone (HMBAAPS) (Figure 34) and 4[*N*-(3′, 4′, 5′-trimethoxy benzalidene) amino]antipyrine semicarbazone (TMBAAPS) (Figure 35) were developed by Agarwal et al. (2004). The synthesized compounds were characterized by spectro-analytical methods and exhibited a general composition of $[Ln(L)_2Cl_3]$, where Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho (Figure 36), and L could be (HMBAAPS) or (TMBAAPS). The Schiff bases, (HMBAAPS) and (TMBAAPS), exhibited tridentate characteristics. The complexes were assigned a coordination number of nine. Their thermal properties were studied.

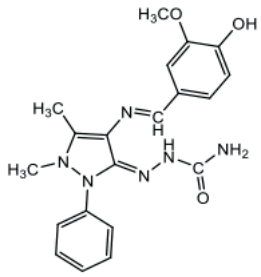


Figure 34. Structure of 4[*N*-(4′-hydroxy-3′-methoxybenzalidene)amino]antipyrine semicarbazone (HMBAAPS).

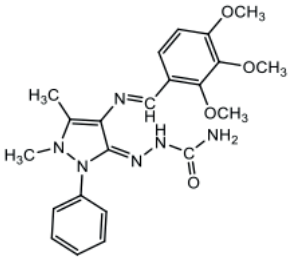


Figure 35. Structure of 4[*N*-(3′,4′,5′-trimethoxybenzalidene)amino] antipyrine semicarbazone (TMBAAPS).

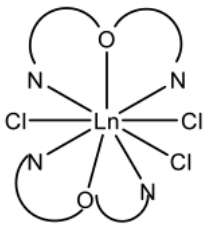


Figure 36. Structure of the complexes, $Ln(L)_2Cl_3$ where Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy or Ho. L could be HMBAAPS or TMBAAPS.

Agarwal et al. (2006) reported the synthesis and characterization of lanthanide(III) nitrate, perchlorate, and thioisocyanate complexes of 4[*N*-2′-hydroxy-1′-naphthalidene)amino]antipyrine semicarbazone (HNAAPS) using spectroscopic techniques. The ligand, HNAAPS acted as a neutral tridentate (N,N,O) ligand. The general formula was $Ln(HNAAPS)_nX_3$, where X could be NO_3^-, n is 1, or NCS^- or ClO_4^-, n is 2, and Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho. The Schiff base, 4[*N*-2′-hydroxy-1′-naphthalidene)amino]antipyrine semicarbazone, behaved as a neutral tridentate N,N,O ligand. The nitrate and isothiocyanate complexes were assigned a coordination number of nine, while the perchlorate complexes were assigned a coordination number of six. The thermal analysis verified the absence of both coordinated and uncoordinated water molecules in the complexes.

Agarwal et al. (2007) prepared a Schiff base from 4[*N* - (cinnamalidene) amino] antipyrine semicarbazone (CAAPS), and diphenyl sulfoxide (DPSO) along with its nitrate, thiocyanate, and perchlorate lanthanide(III) complexes (Figure 37). The synthesized compounds were characterized

using spectrochemical techniques. The general formula was $LnX_3.n(CAAPS).DPSO$, where Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho; X could be NCS^- or ClO_4^- if n is 2 and X could be NO_3^- if n is 1. The two prominent vibrations in the $[Ln(CAAPS)(NO_3)_3DPSO]$ complex were attributed to covalently bonded nitrate groups, indicating that the nitrate groups resided within the coordination spheres. The nitrate groups in these compounds exhibited bidentate characteristics. In the $[Ln(CAAPS)_2(NCS)_3DPSO]$ complex, the C-N and C-S stretching frequencies indicated that the thiocyanate group was bound through a nitrogen atom. All the NCS^- ions were coordinated to the metal ion. In the thiocyanate and nitrate complexes, the CAAPS acted as a neutral tridentate (N, N, O-donor), while the DPSO coordinated via its lone oxygen atom. A coordination number of seven and ten were assigned to these complexes, as illustrated in the figs. 38A and 38B. The observation of two prominent bands in the spectra of the perchlorate complexes, $[Ln(CAAPS)_2DPSO](ClO_4)_3$, indicated that the perchlorate group resided outside the coordination sphere and confirmed the tetrahedral geometry of the perchlorate ion, which was unbound to the Ln^{3+} ion (Figure 38C).

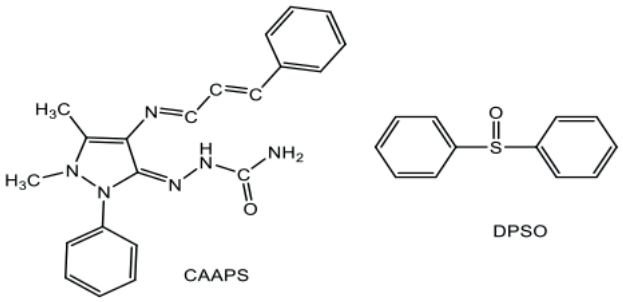


Figure 37. Structure of the Schiff base, 4[*N*-(cinnamalidene)amino] antipyrine semicarbazone (CAAPS) and diphenyl sulfoxide (DPSO).

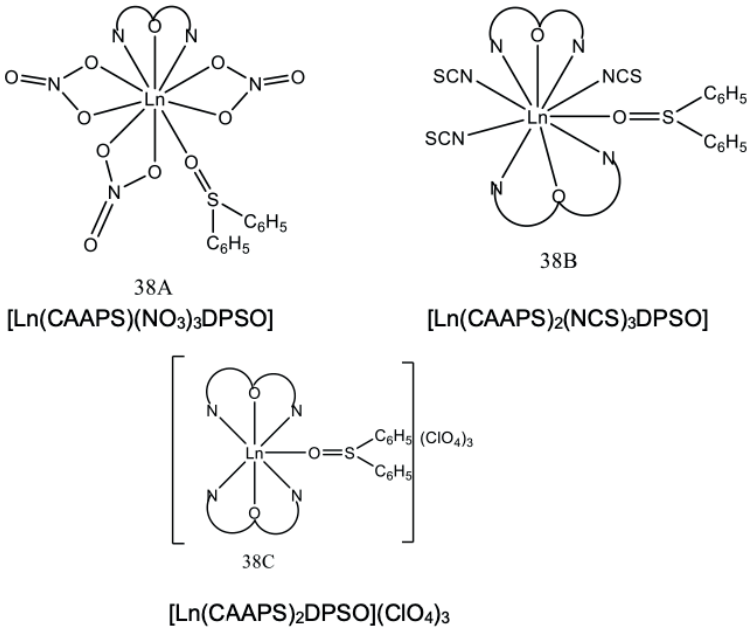


Figure 38. Structures of the complexes.

The lanthanide(III) perchlorate complexes of 4- [*N*-(4′-ethylbenzalideneamino) antipyrine semicarbazone (EBAAPS) as primary ligand and pyridine (py) as secondary ligand (Figure 39) were investigated by Kaushik (2017). The complexes were analyzed using spectroanalytical techniques. The general formula of the complex was $[Ln(EBAAPS)_2py](ClO_4)_3$, where Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy or Ho. The primary ligand, (EBAAPS), acted as a neutral tridentate (O, N, N) ligand, while the secondary ligand, pyridine (py), acted as a uni dentate nitrogen donor, coordinating to the metal ion via its hetero-nitrogen atom. These complexes were assigned a coordination number of seven. The thermal stabilities of the synthesized compounds were examined using thermogravimetric analysis.

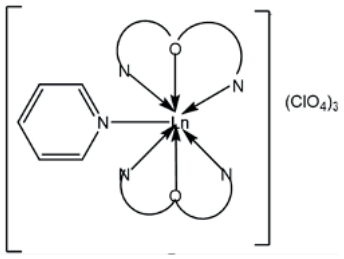


Figure 39. The structure of the complex, $[Ln(EBAAPS)_2py](ClO_4)_3$, where Ln is La, Pr, Nd, Sm, Gd, Tb, Dy or Ho.

Lanthanide(III) complexes of 4-aminoantipyrine thiosemicarbazone derivatives

Structurally, thiosemicarbazide was obtained by replacing the oxygen atom in a semicarbazide with a sulphur atom. Thiosemicarbazones of 4-aminoantipyrine derivatives are derived by reacting the carbonyl group of 4-aminoantipyrine with a thiosemicarbazide. The lanthanide(III) ions cordinate to the Schiff base ligands in a tridentate (N, N, S) form. Metal complexes of thiosemicarbazones have garnered a lot of interest due to their diverse biological applications (Zahra et al., 2024, Veg et al., 2025). Meanwhile, the various lanthanide(III) complexes of thiosemicarbazone of 4-aminoantipyrine derivatives are being reviewed (Table 10).

Singh et al. (1999) reported the synthesis and characterization of a new series of sixteen lanthanide(III) complexes of 4-[*N*-(benzalidene)amino]antipyrine thiosemicarbazone (BAAPTS) with the general composition, $Ln(BAAPTS)_nX_3$ where X is Cl^- and NO_3^-, n is 2 and 1 respectively, Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho. The Schiff base ligand, BAAPTS, acted as a neutral tridentate (N,N,S) ligand, coordinating via the nitrogen atoms and the sulphur atoms. The nitrate ions are coordinated in a bidentate fashion. The metal ions in these complexes were assigned a coordination number of nine.

Singh et al. (1999) went further to prepare lanthanide(III) perchlorate and thioisocyanate complexes of 4[*N*-(p-dimethylaminobenzylidene)amino]antipyrine thiosemicarbazone (3′-NO_2BAAPTS). The lanthanide(III) complexes were characterized by several spectroscopic and analytical methods. The compounds exhibited a general formula of $Ln(DABAAPTS)_2X_3$, where Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho, and X could be ClO_4^- or NCS^-. The ligand acted as a neutral tridentate (N,N,S) ligand.

Lanthanide(III) nitrate complexes of the Schiff base, 4[*N*-(4-(methoxybenzylidene)amino]antipyrine thiosemicarbazone (MBAAPTS) were developed by Agarwal et al. (2001). The complexes possessed a general formula of $[Ln(MBAAPTS)_2(NO_3)_3]$, where Ln represented La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho. The ligand, MBAAPTS, acted as a tridentate (N,N,S) ligand, while the nitrate ions exhibited bidentate nature. Thermal properties of the complexes were also examined. Agarwal et al. (2002) also documented the synthesis and characterization of the perchlorate complexes of the lanthanides of the same Schiff base, MBAAPTS.

Chakraborti (2003) obtained a series of trivalent lanthanide(III) perchlorate coordination compounds of the Schiff base ligand, 4[*N*-(3′-nitrobenzalidene)amino]antipyrine thiosemicarbazone (3′-NO_2BAAPTS) characterized by the general formula, $[Ln(3'\text{-}NO_2BAAPTS)_2](ClO_4)_3$ where Ln represented La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho. The spectroscopic study indicated that the three perchlorate ions were located outside the coordination sphere. The ligand, 3′-NO_2BAAPTS, functioned as a neutral tridentate (N,N,S) ligand. The complexes were assigned a coordination number of six. The conductance values in nitrobenzene indicated that the complexes are ionic, with all three perchlorate ions located outside the coordination sphere.

Chakraborti (2003) also developed and characterized a series of eight new nine-coordinated lanthanide(III) nitrate complexes of the composition $[Ln(L)(NO_3)_3]$ where Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy or Ho and L is 4[*N*-(3′-nitrobenzalidene)amino]antipyrine thiosemicarbazones (3′-NO_2BAAPTS). A coordination number of nine was assigned to the lanthanide ions in the complex. The thermal properties of the compounds were also studied. Possible structures of these complexes were proposed.

Lanthanide(III) chloride and thiocyanate complexes of 4[*N*-(3′-nitrobenzalidene)amino]antipyrine thiosemicarbazones (3′-NO_2BAAPTS) were obtained and reported by Chakraborti (2003). Their general formula was $[Ln(3'\text{-}NO_2BAAPTS)_2X_3]$, where Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho, and X could be Cl^- and NCS^-. The ligand, 4[*N*-(3′-nitrobenzalidene)amino]antipyrine thiosemicarbazones, functioned as a neutral tridentate ligand.

Chakraborti (2003) reportedly prepared and characterized nine-coordinated lanthanide(III) complexes with 4[*N*-(p-methoxybenzalidene)amino]antipyrine thiosemicarbazone (MBAAPTS). The complexes possessed the general formula $Ln(MBAAPTS)_2X_3$, where Ln represented La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho, and X denoted Cl^- or NCS^-. The metal ions of the complex were assigned a coordination number of nine. The thermal stability of the complexes was examined.

Agarwal et al. (2009) prepared and characterized a series of lanthanide(III) chloro complexes of a Schiff base, 4-[*N*-(4′-nitrobenzalidene)amino]antipyrine thiosemicarbazone (4′-NO_2BAAPTS) as the primary ligand and pyridine (py) as the secondary ligand. The overall composition was Ln(4/NO2BAAPTS)2Cl3.py] and Ln was La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho (Figure 41). The thiosemicarbazone (4′-NO_2BAAPTS) acted as a tridentate (N,N,S) ligand, while the pyridine coordinated to the central metal ion via its hetero nitrogen atom. A coordination number of ten was proposed for the complexes. The thermal analysis was also investigated.

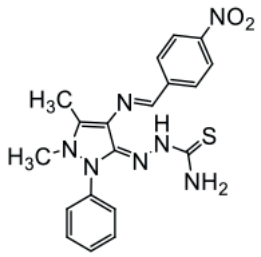


Figure 40. The structure of the Schiff base, 4-[*N*-(4′-nitrobenzalidene) amino]antipyrine thiosemicarbazone (4′-NO_2BAAPTS).

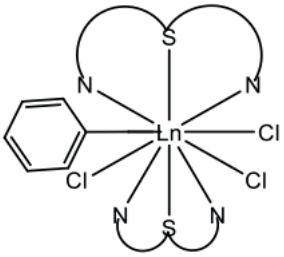


Figure 41. The structure of [Ln(4′-NO_2BAAPTS)$_2$(py)Cl_3], where Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy or Ho.

Trivalent lanthanide(III) nitrate, thioisocyanate, and perchlorate complexes of 4-[*N*-(2′-hydroxy-1′-naphthylidene)amino]antipyrine thiosemicarbazone (HNAAPTS) (Figure 42) were synthesized by Agarwal et al. (2005). The synthesized complexes were characterized by spectroanalytical techniques. The complexes possessed a general formula of Ln(HNAAPTS)$_n$$X_3$, where X could be NO_3^- if n is 1, X could be NCS^- or ClO_4^- if n is 2 and Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy or Ho. The spectrum data indicated that HNAAPTS acted as a neutral tridentate (N,N,S) ligand. The coordination number of these complexes depended on the characteristics of the anionic ligand. The nitrate and isothiocyanate complexes were assigned a coordination number of nine, while the perchlorate complexes were assigned a coordination number of six.

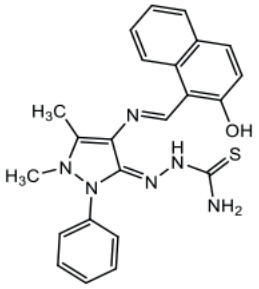
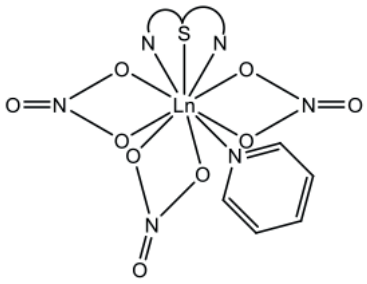


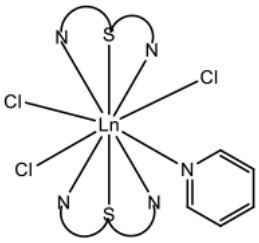
Figure 42. Structure of the Schiff base, 4-[*N*-(2′-hydroxy-1′-naphthylidene)amino]antipyrine thiosemicarbazone (HNAAPTS).

On the other hand, Agarwal and Kumar (2010) investigated the influence of pyridine on the stereochemistry of lanthanide(III) nitrate, chloride, isothiocyanate, and perchlorate complexes of

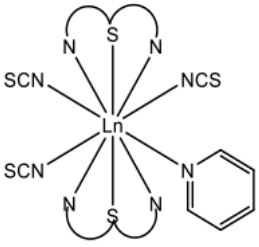
4[*N*-(2′-hydroxy-1′-naphthalidene)amino]antipyrine thiosemicarbazone (HNAAPTS). The Schiff base, 4[*N*-(2′-hydroxy-1′-naphthalidene)amino]antipyrine thiosemicarbazone (HNAAPTS) acted as the primary ligand, while pyridine acted as the secondary ligand. The general composition of the complexes was determined to be $Ln(HNAAPTS)_nX_3.py$ where Ln was La, Pr, Nd, Sm, Gd, Tb, Dy or Ho while X was NO_3^- if n was 1 and Cl^-, NCS^- or ClO_4^- if n was 2, py was pyridine (Figure 43-46). All complexes were characterized using spectroscopic techniques. The HNAAPTS acted as a neutral tridentate (N,N,S) ligand, while the pyridine coordinated via its heteroatom. Each nitrate ion exhibited a bidentate nature. All nitrate, chloro, and thiocyanate groups except perchlorate ions were coordinated to the lanthanide ion, resulting in a coordination number of ten. Perchlorate ions exhibited a coordination number of seven.



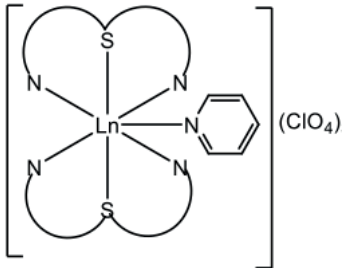
| **Figure 43.** The structure of the complex, $[Ln(HNAAPTS)(NO_3)_3.py]$.



| **Figure 44.** The structure of the complex, $[Ln(HNAAPTS)Cl_3.py]$.



| **Figure 45.** The structure of the complex, $[Ln(HNAAPTS)(NCS)_3.py]$.



| **Figure 46.** The structure of the complex, [Ln(HNAAPTS).py]$(ClO_4)_3$.

Table 9. Lanthanide(III) complexes of 4-aminoantipyrine semicarbazone derivatives.

Schiff Base	Constituents	Anion	Lanthanides	CN	Formula	Ref.
4[*N*-(benzylidene) amino] antipyrine semicarbazone (BAAPS)	4-aminoantipyrine, benzaldehyde and semicarbazide hydrochloride	nitrate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho	9	$Ln(BAAPS)(NO_3)_3$	Agarwal et al. (1996)
4[*N*-(benzalidene) amino] antipyrine semicarbazone, (BAAPS).	4-aminoantipyrine, benzaldehyde and semicarbazide hydrochloride	chloride and perchlorate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho.	6,9	$Ln(BAAPS)_2Cl_3$ $Ln(BAAPS)_2(ClO_4)_3$	Chakraborti et al. (2002)
4[*N*-(p-dimethylaminobenzalidene)amino]antipyrine semicarbazone (DABAAPS)	4-aminoantipyrine, p-dimethylaminobenzaldehyde and semicarbazide hydrochloride.	chloride and isothiocyanate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho,	9	$[Ln(DABAAPS)_2X_3]$	Agarwal et al. (2001)
4[*N*-(4′-dimethylaminobenzalidene)amino]antipyrine semicarbazone (DABAAPS)	.4-aminoantipyrine, p-dimethylaminobenzaldehyde and semicarbazide hydrochloride	perchlorate and nitrate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho	9,6	$Ln(DABAAPS)_2(ClO_4)_3$ $Ln(DABAAPS)(NO_3)_3$	Chakraborti and Goel (2003)
4[*N*-(4′-hydroxy-3′-methoxy benzalidene)amino] antipyrine semicarbazone HMBAAPS) and 4[*N*-(3′,4′,5′-trimethoxy benzalidene)amino] antipyrine semicarbazone (TMBAAPS)	4-aminoantipyrine, 4-hydroxy-3-methoxybenzaldehye, 3/,4/,5/-trimethoxybenzaldehyde and semicarbazide hydrochloride.	chloro	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho	9	$[Ln(L)_2Cl_3]$	Agarwal et al. (2004)
4[*N*-2′-hydroxy-1′-naphtha lidene) amino]antipyrine semi carbazone (HNAAPS)	4-aminoantipyrine, 2-hydroxy naphthaldehyde and semicarbazide hydrochloride.	nitrate, perchlorate and thioisocyanate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho.	9,6	$Ln(HNAAPS)nX_3$	Agarwal et al. (2006)

Schiff Base	Constituents	Anion	Lanthanides	CN	Formula	Ref.
4[*N*-(cinnamalidene) amino] antipyrine semicarbazone (CAAPS) and diphenyl sulfoxide (DPSO)	4-aminoantipyrine, cinnamaldehyde, and semicarbazide hydrochloride	nitrate, thiocyanate and perchlorate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho	7, 10	$Ln(CAAPS)_nX_3DPSO$ $Ln(CAAPS)(NO_3)_3DPSO$ $Ln.(CAAPS)_2(NCS)_3DPSO]$ $Ln(CAAPS)_2DPSO](ClO_4)$	Agarwal et al. (2007)
4-[*N*-(4′-ethylbenzalidene amino)antipyrine semicarba zone (ebaaps) with pyridine (py)	4-aminoantipyrine, 4-ethylbenzaldehyde, and semicarbazide hydrochloride	perchlorate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho.	7	$[Ln(ebaaps)_2py](ClO_4)_3$	Kaushik (2017)

Table 10. Lanthanide(III) complexes of 4-aminoantipyrine thiosemicarbazone derivatives.

Schiff Base	Constituents	Anion	Lanthanides	CN	Formula	Ref.
4-[*N*-(benzalidene) amino] antipyrine thiosemicarbazone (BAAPTS)	4-aminoantipyrine, benzaldehyde, and thiosemicarbazide	chloride, nitrate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho	9	$Ln(BAAPTS)_nX_3$	Singh et al. (1999)
4[*N*-(p-dimethylamino benzylidine) amino]antipyrine thiosemicarbazone (DABAAPTS)	4-aminoantipyrine, p-dimethyl aminobenzaldehyde and thiosemicarbazide	perchlorate and thioisocyanate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho		$Ln(DABAAPTS)_2X_3$	Singh et al. (1999)
4[*N*-(4-(methoxybenzylidene)amino]antipyrine thiosemicarbazone (MBAAPTS)	4-aminoantipyrine, 4-methoxybenzaldehyde, and thiosemicarbazide	nitrate,	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho		$Ln(MBAAPTS)_2(NO_3)_3$	Agarwal et al. (2001)
4[*N*-(3′-nitrobenzalidene) amino]antipyrine thiosemicarbazone (3′-NO_2BAAPTS)	4-aminoantipyrine, 3-nitrobenzaldehyde and thiosemicarbazide	perchlorate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho	6	$Ln(3'\text{-}NO_2BAAPTS)_2]$ $(ClO_4)_3$	Chakraborti (2003)
4[*N*-(3′-nitrobenzalidene) amino]antipyrine thiosemicarbazone (3′-NO_2BAAPTS)	4-aminoantipyrine, 3-nitrobenzaldehyde and thiosemicarbazide	nitrate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho	9	$[Ln(L)(NO_3)_3]$	Chakraborti (2003)
4[*N*-(3′-nitrobenzalidene) amino]antipyrine thiosemicarbazones (3′-NO_2BAAPTS)	4-aminoantipyrine, 3-nitrobenzaldehyde and thiosemicarbazide	chloride and thiocyanate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho		$[Ln(3'\text{-}NO_2BAAPTS)_2X_3]$	Chakraborti (2003)
4[*N*-(p-methoxybenzalidene)amino]antipyrine thiosemicarbazone (MBAAPTS).	4-aminoantipyrine, 4-methoxybenzaldehyde and thiosemicarbazide	chloride and thioisocyanate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho	9	$Ln(MBAAPTS)_2X_3$	Chakraborti (2003)

Schiff Base	Constituents	Anion	Lanthanides	CN	Formula	Ref.
4-[*N*-(4′-nitrobenzalidene) amino]anti-pyrine thiosemi-carbazone (4′-NO_2BAAPTS) with pyridine (py)	4-aminoantipyrine, 4-nitrobenzaldehyde, thiosemicarbazide and pyridine	chloride	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho	10	$[Ln(4'NO_2BAAPTS)_2Py]$ Cl3,	Agarwal et al. (2009)
4-[*N*-(2′-hydroxy-1′-naphth ylidene) amino]antipyrine thiosemicarba-zone (HNAAPTS)	4-aminoantipyrine, 2-hydroxynaphthal-dehyde and thiosemicarbazide	nitrate, thioiso-cyanate and perchlorate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho.	9,6	LnX_3.n(HNAAPTS)	Agarwal et al. (2005)
4[*N*-(2′-hydroxy-1′-naphtha lidene) amino]antipyrine thiosemicarba-zone (HNAAPTS) with pyridine	4-aminoantipyrine, 2-hydroxynaph-thaldehyde, thiosemicarbazide and pyridine	nitrate, chlo-ride, isothio-cyanate and perchlorate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho	9,6	LnX_3.n(HBAAPS).py	Agarwal & Kumar (2010)

Lanthanide(III) complexes of diazotized 4-aminoantipyrine derivatives/hydrazo derivatives of 4-aminoantipyrine

Diazotization of 4-aminoantipyrine involves the conversion of the primary amine group of 4-aminoantipyrine into a diazonium salt using $NaNO_2$/HCl at 0 – 5 °C. The diazonium intermediate reacts with aromatic compounds such as naphthols, phenols, anilines etc. to give azo-Schiff derivatives. Due to the emerging antimicrobial resistance, new therapeutic drugs are being synthesized to solve the menace. Diazotized 4-aminoantipyrine is being considered a promising candidate/product due to its antimicrobial properties (Mishra et al., 2024). Some of its lanthanide(III) complexes are being reported (Table 11).

Radhakrishnan (1995) prepared lanthanide(III) nitrate complexes of the Schiff base ligand, 4-(2/,4/-dihydro xyphenylazo)antipyrine (DPAAP) derived from diazotized 4-aminoantipyrine and resorcinol in an alkaline medium. The general composition was $[Ln(DPAAP)2(NO_3)_3]$, where Ln was La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, or Y. They were characterized by spectroscopic and analytical techniques. These methods were employed to ascertain their proposed structural types. DPAAP cordinated as a neutral bidentate ligand, coordinating via the carbonyl oxygen and one azo nitrogen atom, thereby creating a five-membered ring. The nitrate group was coordinated in a monodentate manner.

Rare earth perchlorate complexes of 4-(2′,4′-dihydroxyphenylazo)antipyrine.(H-RAP) have been reported by Abraham and Radhakrishnan (1990). The perchlorate group remained uncoordinated.

Alaudeen and Radhakrishnan (1990) described the synthesis of rare earth nitrates of 4-(2′-hydroxynaphthylazo)antipyrine (H-NAP) derived from diazotized 4-aminoantipyrine and 2-naphthol (Figure 47). The complexes possessed a general formula of $[Ln(NAP)_2NO_3]$, where Ln was La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, or Y. In these compounds, the NAP acted as a tridentate ligand, coordinating via the carbonyl oxygen, phenolic oxygen, and one nitrogen of the azo group. The nitrate ions cordinated to the metal ion in a bidentate fashion. The synthesized complexes exhibited thermal stability up to ~ 280°C. Rare earth perchlorate complexes of 4-(2′,4′-dihydroxyphenylazo)antipyrine (H-RAP) have been reported by Abraham and Radhakrishnan (1990). The perchlorate group remains uncoordinated.

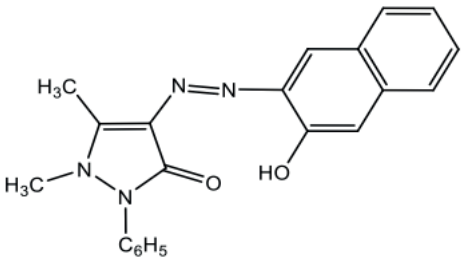


Figure 47. The structure of the Schiff base, 4-(2′-hydroxynaphthylazo)antipyrine (H-NAP).

Thomas et al. (1995) have synthesized rare earth iodide complexes (Figure 48) of 4-(2′,4′-dihydroxyphenylazo)antipyrine (H-RAP) obtained from diazotized 4-aminoantipyrine (Figure 49). The complexes were characterized via spectroanalytical methods. The complexes possessed a general formula of $[Ln(H\text{-}RAP)_2I_2]I$, where Ln represented Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, or Er. The diazotized compound, H-RAP, acted as a neutral bidentate ligand, coordinating via the carbonyl oxygen and one of the azo nitrogens. Two iodide ions were coordinated, while the third ion is positioned outside the coordination sphere. Thermogravimetric analyses indicated that the complexes were stable up to 440 K, and subsequently underwent complete breakdown between 440 and 1110 K, which led to the formation of the respective metal iodides.

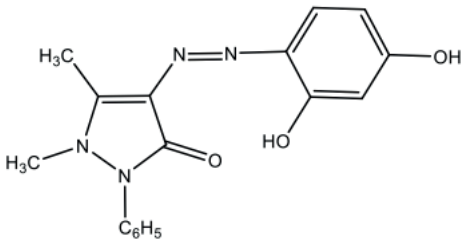


Figure 48. The structure of the Schiff base, 4-(2′,4′-dihydroxyphenylazo)antipyrine (H-RAP).

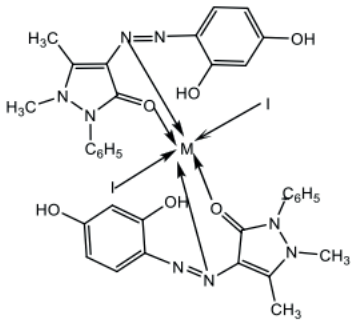


Figure 49. The tentative structure of the complexes, M can be Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho or Er.

Mohanan et al. (2009) designed and characterized hydrazone derivative of 4-aminoantipyrine, 3-{[2-(*N*-1-phenyl-2,3-dimethylpyrazol-3-in-5-on-4-yl)]hydrazone}pent-2,3,4-trione (HAAP), derived by coupling diazotized 4-aminoantipyrine with acetylacetone (Figure 50). The La(III), Ce(III), Pr(III), Nd(III), Sm(III), and Gd(III) complexes of the heterocyclic ligand were represented by the formula, $[Ln(HAAP)_2(NO_3)_3]$. The ligand and lanthanide(III) complexes were characterized by spectrochemical techniques. The spectrum results revealed that the ligand was present in the hydrazo form rather than the azo-enol form, and this structure persisted in the metal complexes. The ligand coordinated to the metal ion in a neutral tridentate fashion via the carbonyl oxygen of the pyrazolone ring, the hydrazo nitrogen, and the carbonyl oxygen of the acetylacetone moiety, without deprotonation, while the nitrate ions coordinated in a bidentate manner. A coordination number of twelve was suggested for the lanthanide(III) nitrate complexes. The thermal analyses demonstrated that the lanthanide(III) complexes displayed higher stability relative to the ligand.

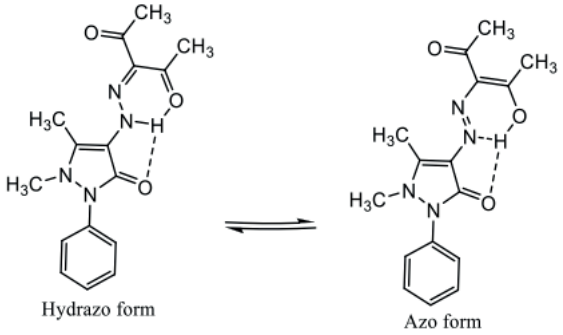


Figure 50. Tautomeric structure of the ligand, 3-{[2-(*N*-1-phenyl-2,3-dimethylpyrazol-3-in-5-on-4-yl)]hydrazone}pent-2,3,4-trione (HAAP).

Table 11. Lanthanide(III) complexes of diazotized 4-aminoantipyrine derivatives/hydrazo derivatives of 4-aminoantipyrine.

Schiff Base	Constituents	Anion	Lanthanides	CN	Formular	Ref.
4-(2′,4′-dihydroxyphenylazo) antipyrine (DPAAP)	diazotized 4-aminoantipyrine and resorcinol	Nitrate	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Y		$[Ln(DPAAP)_2(NO_3)_3]$	Radhakrishnan (1995)
4-(2′-hydroxynaphthylazo) antipyrine (H-NAP)	diazotized 4-aminoantipyrine and. 2-naphthol	nitrates	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Y		$[Ln(NAP)_2NO_3]$	Alaudeen & Radhakrishnan (1990)
4-(2′,4′-dihydroxyphenylazo) antipyrine. (H-RAP)	diazotized 4-aminoantipyrine	perchlorate				Abraham & Radhakrishnan (1990)
4-(2′,4′-dihydroxyphenylazo) antipyrine(H-RAP)	diazotized 4-aminoantipyrine	Iodide	Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho or Er.		$[Ln(H\text{-}RAP)_2I_2]I$	Thomas et al. (1995)
3-{[2-(*N*-1-phenyl-2,3-dimethylpyrazol-3-in-5-on-4-yl)]hydrazone} pent-2,3,4-trione (HAAP)	diazotized 4-aminoantipyrine with acetylacetone	Nitrate	La, Ce, Pr, Nd, Sm and Gd	12	$[Ln(HAAP)_2(NO_3)_3]$	Mohanan et al. (2009)

Antimicrobial activities of lanthanide(III) complexes of some Schiff bases derived from 4-aminoantipyrine

In recent years, a lot of 4-aminoantipyrine Schiff bases and their metals complexes have been synthesized. Their spectroscopic and structural properties were studied inorder to understand their chemical and biological activity (Cunha et al., 2005, Alam and Lee, 2021, Aguilar-Llanos et al., 2023). They were found to exhibit antimalarial, anticancer, antimicrobial, anticonvulsant, anti-inflammatory, antiviral, antiprotozoal activity etc. The antimicrobial activity has been the most encountered. Less research studies have been carried out on the antimicrobial activity of lanthanide(III) complexes of Schiff bases derived from 4-aminoantipyrine. This section of the review enlisted some of them (Table 12).

Agarwal et al. (1992) prepared and characterized lanthanide(III) iodide complexes of the Schiff base, 4-[*N*-(m-methoxybenzilidene)amino]antipyrine (MBAAP), obtained from 4-methoxybenzaldehyde and 4-aminoantipyrine. The complexes were reported to have the composition $[Ln(MBAAP)_2I_3]$, with Ln represented as La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, or Ho. The ligand (MBAAP) acts as a bidentate ligand in the complexes coordinating through the carbonyl oxygen and azomethine nitrogen. A coordination number of seven was assigned to the metal ions inside these complexes. Their thermal stabilities were also studied. The antibacterial activity of the ligand and its lanthanide(III) complexes was investigated.

Alaudeen et al. (1995) obtained and reported rare earth perchlorate complexes of 4-(2′-hydroxynaphthylazo)antipyrine (H-NAP) with the formula, $[Ln(NAP)_2]ClO_4$ where Ln represented La, Pr, Nd, Sm, Gd, Dy, or Y. The ligand, H-NAP, acted as a monovalent tridentate ligand coordinating through the carbonyl oxygen, phenolic oxygen, and one nitrogen of the azo group, thereby creating two chelate rings: a five-membered ring and a six-membered ring, while the perchlorate ion remained uncoordinated and ionic. The metal ions were assigned a coordination number of six. The antibacterial activity was examined against the microorganism, *Staphylococcus aureus* (strain-H), using a turbidimetric assay method. The synthesized compounds were shown to exhibit antibacterial activity at a concentration of 0.05 mg/ml. The sequence of the activity was established as follows: Y > Dy > Gd > Pr > La > Nd > Sm. The complexes exhibited more activity than the Schiff base ligand, H-NAP, but were less active compared to 4-aminoantipyrine.

Rajendran and Sreeletha (2002) synthesized and characterized some mixed ligand complexes of lanthanide(III) ions with the Schiff base, pyridine-2′-carboxaldehyde-4-aminoantipyrine (P2CAAP) and different anions such as acetate, chloride, nitrate and thioisocyanate using various spectroscopic methods. The composition of the complexes was found to be $[Ln(P2CA4AAP)_2(an)_3]$ where Ln could be La, Pr, Nd, Sm, Gd, Dy and a could be acetate, chloride, nitrate and thiocyanate ions. In these complexes, the primary ligand acted as a neutral tridentate ligand while the secondary ligands, namely the monovalent acetate, chloride, nitrate and thiocyanate anions were unidentate. Antimicrobial analysis was conducted using the agar diffusion method against the following bacteria: *Staphylococcus aureus*, *Escherichia coli, Klebsiella pneumonia* and *Pseudomonas aeuruginosa*. It was observed that the activity of the synthesized compounds depended on the nature of the substitutents. The chloro group increased its antibacterial activity while the nitro group decreased its activity. The lanthanide(III) complexes exhibited greater activity than the ligand.

Agarwal and Prakash (2005) investigated the influence of diphenyl sulphoxide (DPSO) on the stereochemistry of lanthanide(III) complexes of the Schiff base, 4-[N-(2′-hydroxy-1′-naphthylidene)

amino] antipyrine semicarbazone (HNAAPS) (Figure 51) using spectral and analytical techniques. The complexes were determined to have the composition $Ln(HNAAPS)_nX_3.DPSO$, where Ln represented La, Pr, Nd, Sm, Gd, Tb, Dy or Ho; X could be NO_3^- when n is 1 and X could be NCS^- or ClO_4^- when n is 2 (Figs. 52-54). The infrared analysis revealed that HNAAPS acted as a neutral tridentate (N,N,O) ligand, while DPSO coordinated to the metal ion through its lone oxygen atom. The nitrate ions coordinated in a bidentate fashion, while the thiocyanate coordinated via the strong nitrogen atom. The perchlorate ions were outside the coordination sphere. The nitrato groups and isothiocyanate complexes were assigned a coordination number of ten, whilst the perchlorate complexes were assigned a coordination number of seven. Antibacterial studies and thermal analysis were also carried out.

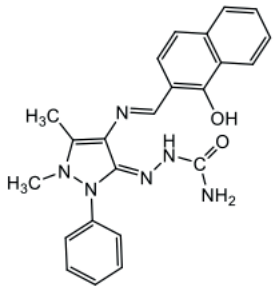


Figure 51. Structure of 4-[*N*-(2′-hydroxy-1′-naphthylidene)amino]antipyrine semicarbazone HNAAPS).

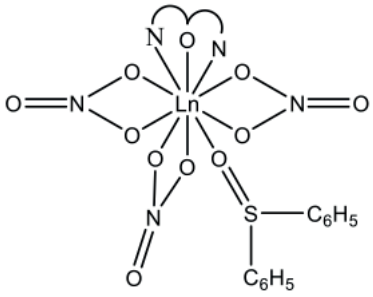


Figure 52. Structure of $[Ln(L)(NO_3)_3DPSO]$.

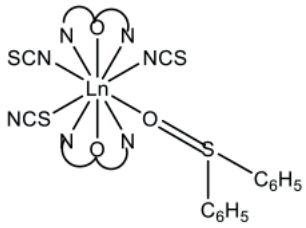


Figure 53. Structure of $[Ln(L)_2(NO_3)_3DPSO]$.

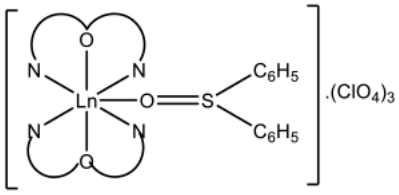


Figure 54. Structure of $[Ln(L)_2DPSO](ClO_4)_3$.

The synthesis of cerium(III) mixed ligand complexes of 2,3-dimethyl-1-phenyl-4-salicylidene-3-

pyrazolin-5-one (L) with oxalic acid (Ox) (Figure 55), 8-hydroxyquinoline (8-OHqu) (Figure 56), and 2-aminopyridine (2-ampy) using a deprotonating agent, LiOH was reported by Abd El-Wahab et al. (2005). The mixed ligand cerium(III) complex exhibited an octahedral geometry. The ligands were coordinated to the central metal ion as either a monoanionic tridentate (O,N,O) or a monoanionic tetradentate (O,N,O,N) ligand. The binuclear cerium(III) complex was synthesized pyrolytically by the thermal conversion of the mononuclear complex. The complexes and their respective thermal products were separated and characterized by physical and spectroscopic methods. The antimicrobial activity was examined against the bacterial species; *Staphylococcus aureus*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, *Escherichia col*i, and the fungal species; *Aspergillus fumigatus, Penicillium italicum*, *Syncephalastrum racemosum*, *Alternaria alternata*, and *Candida albicans*. Chloramphenicol and Terbinafin were used as reference drugs for antibacterial and antifungal activity, respectively. The cerium(III) complex exhibited reduced activity against *Bacillus subtilis*, *Escherichia coli*, and *Candida albicans* in comparison to the Schiff base. The binary cerium (III) complex exhibited diminished antifungal efficacy against *Syncephalastrum racemosum* and showed no activity against *alternaria alternata*. The Schiff base ligand and its metal complexes exhibited higher antimicrobial efficacy compared to some of the reference drugs.

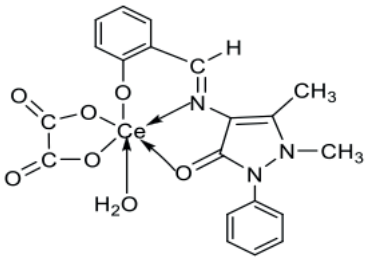


Figure 55. Proposed structure of the octahedral configuration of Ce(III) mixed ligand complex containing 2,3-dimethyl-1-phenyl-4-salicylidene-3-pyrazolin-5-one and oxalic acid.

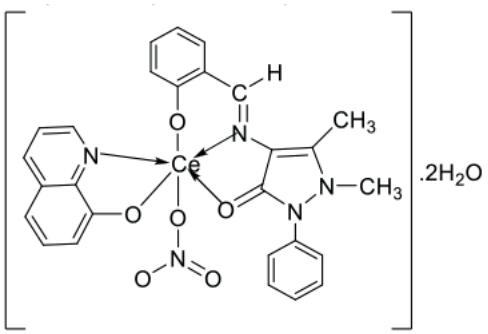


Figure 56. Proposed structure of the Ce(III) mixed ligand complexes containing 2,3-dimethyl-1-phenyl-4-salicylidene-3-pyrazolin-5-one and 8-hydroxyquinoline.

The Schiff base, 1-(4-aminoantipyrine)-3-tosylurea (H_2L) synthesized from 4-aminoantipyrine with ethyl-N-(3-tossulfonyl)carbamate and its lanthanide(III) nitrate complexes, $M(H_2L)_3.3NO_3$ where M = Nd(III), Sm(III) and Eu(III) were reported by Xi et al. (2009). The antioxidant activity and DNA binding studies were investigated. The complexes were found to possess potent antioxidant activity

and DNA binding affinity. The findings portray the potentials of the lanthanides for biomedical applications.

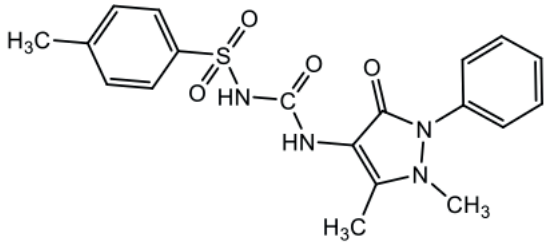


Figure 57. Structure of 1-(4-aminoantipyrine)-3-tosylurea (H_2L).

Agarwal et al. (2011) investigated the influence of α, β, and γ picolines on the stereochemistry of lanthanide(III) nitrate complexes of 4[*N*-(furfural)amino]antipyrine semicarbazone (FFAAPS), derived from 4-aminoantipyrine, furfural, and semicarbazone hydrochloride (Figure 58). The FFAAPS acted as the primary ligand, and α, β, and γ picolines acted as secondary ligands. The synthesized compounds were characterized by spectroscopic techniques. The complexes exhibited a general composition of [Ln(FFAAPS$(NO_3)_3$Pic] with Ln represented as La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho. The ligand, FFAAPS, functioned as a neutral tridentate ligand, while the NO_3^- coordinated in a bidentate fashion, and the α, β, and γ picolines coordinated via their heterocyclic nitrogen atoms. The lanthanide(III) ion was designated a coordination number of ten. The antibacterial efficacy of the selected lanthanide(III) complexes was evaluated against the gram-positive bacterial species, *Bacillus subtilis* and *Staphylococcus aureus,* as well as the gram-negative species, *Escherichia coli* and *Salmonella typhi*, utilising the agar-cup method. The reference drug used was tetracycline. The Schiff base ligand, FFAAPS, and α-picoline demonstrated moderate antibacterial activity, but was less active compared to the reference drug.

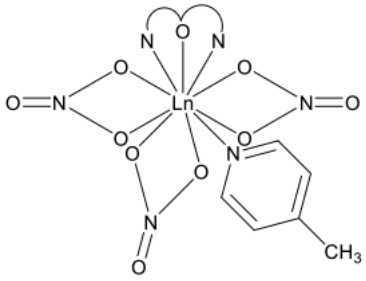


Figure 58. Proposed structure of [Ln(FFAAPS)$(NO_3)_3$Pic], where Ln is La, Pr, Nd, Sm, Gd, Tb, Dy or Ho.

Agarwal and Kumar (2011) prepared and characterized ten and seven coordinate complexes of trivalent lanthanide(III) with 4[*N*-(4′-dimethylaminobenzalidene)amino]antipyrine thiosemicarbazone (DMBAAPTS) (Figure 59). DMBAAPTS and pyridine acted as the primary and secondary ligands, respectively. The general molecular formula was Ln(DMABAAPTS)nX_3.py expressed as Ln$L(NO_3)_3$.py, Ln.$L_2(NCS)_3$.py and Ln$L(ClO_4)_3$.2py, where Ln denoted La, Pr, Nd, Sm, Gd, Dy or Ho; X is NO_3- if n = 1; X may be NCS^- or ClO_4^- if n = 2, with pyridine. The ligand, DMBAAPTS, functioned as a neutral tridentate (N,N,S) ligand, coordinating via the nitrogen atoms of the two azomethine groups and the

sulphur atom of the thioketo group, while the pyridine was coordinated with the metal by its lone pair nitrogen atom. The thermal analysis and antimicrobial activity were also examined.

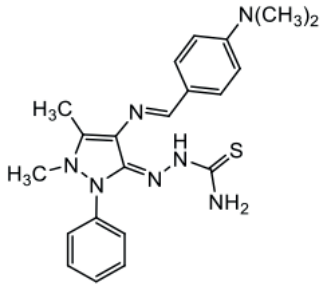


Figure 59. The structure of the Schiff base, 4[*N*-(4′-dimethylamin-obenzalidene)amino]antipyrine thiosemicarbazone (DMBAAPTS).

Prasad et al. (2011) documented the synthesis of mixed ligand complexes comprising lanthanide(III) nitrate, thioisocyanate, and perchlorate of 4[*N*-(furfuralamino)antipyrine semicarbazone (FFAAPS) as the primary ligand and diphenyl sulfoxide (DPSO) as the secondary ligand. The complexes exhibited a general composition of Ln(FFAAPS)X_3.nDPSO, where X could be NO_3^- if n is 1; X could be NCS^- or ClO_4^- if n is 2 and Ln could be La, Pr, Nd, Sm, Gd, Tb, Dy or Ho. The synthesized complexes were characterized by spectroscopic techniques. The ligand, FFAAPS, functioned as a neutral (N,N,O) tridentate donor, whereas diphenylsulfoxide (DPSO) served as a unidentate oxygen donor, and the NO_3^- displayed bidentate characteristics. The coordinating anion determines the coordination number of lanthanide(III) complexes. The coordination number assigned to the nitrate and thiocyanate complex was ten while that of the perchlorate complexes was seven. The antimicrobial activity was examined on five bacterial species: *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis, Streptococcus pneumonia*, and *Pseudomonas aeruginosa,* and two fungal species, *Aspergillus niger* and *Penicillium notatum* using the cup-plate method. The results of the antibacterial and antifungal activity of the synthesized compounds demonstrated inhibitory effects against all examined species. This was attributed to the variation of the conjugated system of the Schiff base resulting from the coordination of the lanthanide ions. The thermal analysis was also carried out.

Aghav et al. (2011) designed and characterized cerium(III) complexes of the Schiff base, 2,3-dimethyl-1-phenyl-4-salicylidene-3-pyrazolin-5-one (AAP) and several amino acids (L), namely L-tryptophan, L-tyrosine, L-cysteine, L-leucine, and L-serine (Figure 60). The Schiff base, 2,3-dimethyl-1-phenyl-4-salicylidene-3-pyrazolin-5-one (AAP) served as the primary ligand, while the amino acids (L) functioned as secondary ligands, coordinating via the carboxylate oxygen and amino nitrogen. The antibacterial activity was examined against the following bacteria: *Staphylococcus aureus*, *Corynebacterium diphtheriae*, *Pseudomonas aeruginosa*, and *Escherichia coli*. The antibacterial efficacy was assessed via the agar cup method with tetracycline as the reference drug. The results demonstrated that the cerium(III) complexes displayed a better inhibitory effect compared to each of the Schiff base ligands.

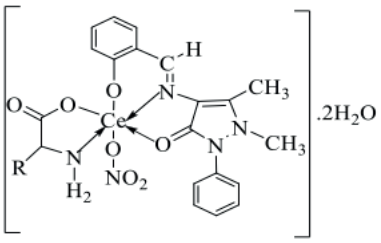


Figure 60. Structure of [Ce(L)(AAP)] complex where L can tryptophan, tyrosine, cysteine, leucine or serine.

Aghav and Lokhande (2016) further elucidated and characterized lanthanum(III) complexes of the Schiff base, 2,3-dimethyl-1-phenyl-4-salicylidene-3-pyrazolin-5-one (HL) and various amino acids, namely L-tryptophan, L-phenylalanine, L-isoleucine, L-proline, and L-serine (Figure 61,62). The complexes were assigned a coordination number of six. The antibacterial efficacy was examined against the following bacteria: *Staphylococcus aureus*, *Corynebacterium diphtheriae*, *Pseudomonas aeruginosa,* and *Escherichia coli*. The antibacterial efficacy was assessed via the agar cup method, with tetracycline as the control agent. The lanthanum(III) complexes demonstrated better antibacterial activity compared to the Schiff base ligands. This is attributed to the presence of the azomethine group present on the structure of the ligand. The presence of nitrogen and oxygen atoms tend to inhibit enzyme production. Enzymes tends to be deactivated by chelation to metal ions.

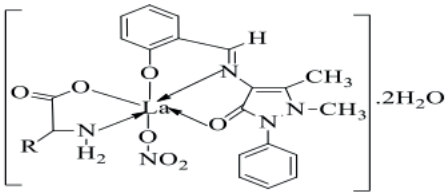


Figure 61. Proposed structure of $[La(L)(AAP)NO_3].2H_2O$ complex where L could be tryptophan, phenylalanine, isoleucine, proline or serine.

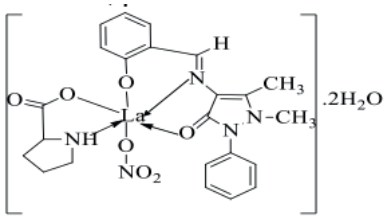


Figure 62. Proposed structure of $[La(Pro)(AAP)NO_3]\cdot 2H_2O$ complex where L was proline.

Abbas (2015) synthesized lanthanium(III), cerium(III), neodymium(III), europium(III), and gadolinum(III) complexes of the azo Schiff base ligand, 2-(4-aminoantipyren)-L-tryptophan (AAT), derived from diazotized 4-aminoantipyrine and L-tryptophan. The ligand and its metal complexes were analyzed utilizing spectral and physicochemical techniques. The formula of the complexes was proposed as

$[Ln(AAT)_2Cl_3]$. The ligand acted as a neutral bidentate ligand. The complex had a pentagonal bipyramidal structure. The stability constant (K) and Gibbs free energy (ΔG) were determined. The synthesized Schiff base, AAT, and its lanthanide(III) complexes were evaluated against the bacterial species; *Escherichia coli* and *Staphylococcus aureus*, as well as the fungal species; *Candida albicans* and *Aspergillus niger,* using diffusion technique. The lanthanide(III) complexes showed better biological activity against the examined bacteria and fungi compared to the Schiff base, AAT. This enhanced activity can be attributed to chelation in which the metal ion adsorbed on the cell wall of the microorganism blocks the protein synthesis. This is regarded as an important factor in the growth of microorganisms.

Philip et al. (2018) developed a novel heterocyclic ligand via the Knoevenagel method. The ligand, 1,2-dihydro-1,5-dimethyl-4-[(1-2-oxo-2*H*-1-benzopyran-3-yl)ethylidene]amino]-2-phenyl-3*H*-pyrazol-3-one (ACAP) was prepared through the reaction of aminoantipyrine with 3-acetylcoumarin (Figure 63), along with its La(III), Pr(III), Sm(III), Ga(III), and Dy(III) complexes (Figure 64). The ligand and the lanthanide(III) complexes were analyzed using several physicochemical and spectroscopic techniques. The complexes possessed the general formula, $[Ln(ACAP)(H_2O)_3Cl_3]$. The spectral data demonstrated that the Schiff base acted as a bidentate ligand, coordinating to the central metal ions via the azomethine nitrogen and the oxygen atom of the pyrazolone ring. The α-amylase inhibitory activity of the synthesized compounds was assessed using the Apostolidis method, while the antioxidant property was evaluated using the DPPH assay. The metal complexes exhibited greater inhibitory and antioxidant activity than the ligand, respectively. The α-amylase inhibitory activity was enhanced due to its complexation with metal ions. The antioxidant activity provides useful information for the study of lanthanide(III) complexes as therapeutic agents based on their ability to mitigate oxidative damage induced by free radicals in the body. Free radicals assault cellular structures, leading to ailments including aging, cancer, and cardiovascular and neurological illnesses.

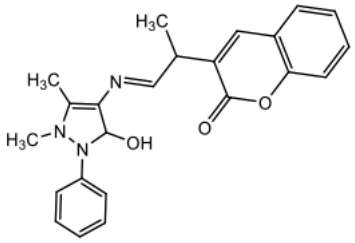


Figure 63. Structure of the ligand, 1,2-dihydro-1,5-dimethyl-4-[(1-2-oxo-2*H*-1-benzopyran-3-yl)ethylidene]amino]-2-phenyl-3*H*-pyrazol-3-one (ACAP).

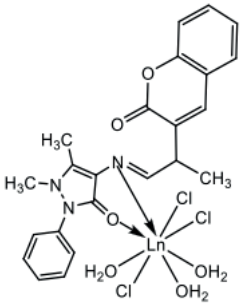


Figure 64. Structure of the lanthanide complex, $[Ln(ACAP)(H_2O)_3Cl_3]$.

Hua et al. (2020) obtained and characterized a hexanuclear Nd(III) complex of the Schiff base, dihydroxybenzaldehyde-4-aminoantipyrine. The complex was of the formula, $\{[Nd_6(HL)_2L_2X_2(NO_3)_8(EtOH)_6].(EtOH)(H_2O)_3\}$, where H_2L was 2,3-dihydroxybenzaldehyde-4-aminoantipyrine and H_2X was 2,3-dihydroxybenzaldehyde. The single crystal diffraction studies indicated that the Nd(III) complex formed a trinuclear cluster structure which further forms a hexanuclear monomer through two bridging ligands, L_2. The monomers had π-π interactions and a lot of intramolecular hydrogen bonds. The Nd(III) complex exhibited significant antifungal activity against *Candida albicans* with an inhibitory zone of 26mm. The IC_{50} value of the Nd(III) complex had ranges from 4.02 to 4.85 µM, which was much smaller than that of the control drug, gemcitabin and free ligand (H_2L).

Hussein and Shaalan (2022) studied the lanthanum(III), neodymium(III), europium(III), gadoliium(III), and dysprosium(III) complexes of the Schiff base, (L) synthesized from 4-aminoantipyrine and dimedone (Figure 65). The ligand showed greater activity against gram-negative bacteria, *Escherichia coli* and *Pseudomonas aeruginosa* than gram-positive bacteria, *Staphylococcus aureus* and *Streptococcous pyogenes*. The sequence of activity is as follows: $Nd^{3+} > La^{3+} > Eu^{3+} > Gd^{3+} > Dy^{3+}$. Dy^{3+} had no inhibitory activity against the examined bacterial species.

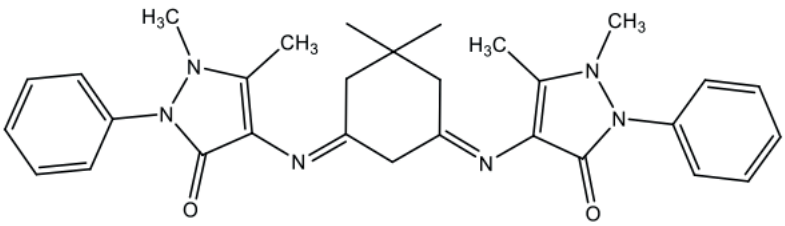


Figure 65. Structure of Schiff base derived from 4-aminoantipyrine and dimedone.

Hussein et al. (2023) synthesized and characterized a Schiff base, L from the condensation reaction of 4-antipyrinecarboxaldehyde and ethylenediamine (Figure 66) and its lanthanide(III) complexes with the formula, $[M_2L_2(NO_3)_6].6H_2O$ where Ln could be La, Nd, Er, Gd and Dy. The bioactivity of the synthesized compound was examined against the following bacteria: *Staphylococcus aureus, Bacillius subtilis, Escherichia coli, Klebsilla pneumonia* using agar well diffusion method. The complexes showed higher antibacterial activity against *Staphylococcus aureus* and *Bacillius subtilis* compared to the Schiff base ligand.

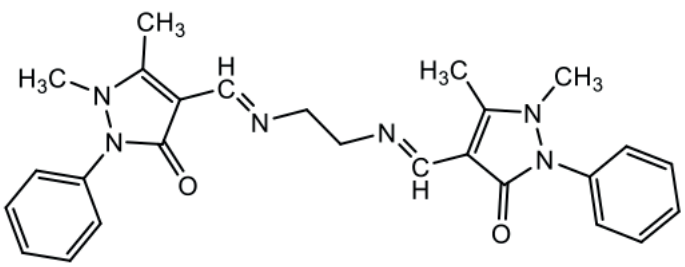


Figure 66. Structure of Schiff base, L from 4-antipyrinecarboxaldehyde and and ethylenediamine.

Rijulal et. al. (2024) evaluated the biological activity of fourteen lanthanide(III) nitrate complexes of the Schiff base, 4-[*N*-(3-methoxyphenylmethanamine)formyl]-2,3-dimethyl-1-phenyl-3-pyazolin-5-one (3MPMAFA) and 4-[*N*-(4-methoxyphenylmethanamine)formyl]-2,3-dimethyl-1-phenyl-3-pyazolin-5-one (4MPMAFA) (Figure 67) derived from the condensation reaction of 3-methoxybenzylamine/4-methoxybenzylamine with antipyrine-4-carboxaldehyde. The lanthanide(III) complexes (Figure 68) had a general formula of $[ML_2(NO_3)_3]$ where M could be La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Yb(III) and L was 3MPMAFA or 4MPMAFA. According to the spectral data, the Schiff bases; 3MPMAFA and 4MPMAFA acted as neutral bidentate ligand coordinating through the carbonyl oxygen and azomethine nitrogen. The compounds had a monocapped octahedral geometry with a coordination number of seven. The antimicrobial screening was performed using the disc diffusion technique against the bacteria species; *Escherichia coli*, *Staphylococcus aureus, Bacillius subtilis* and fungi; *Aspergillus niger* and *Penicillium notatum.* The biological analysis revealed that the lanthanide(III) complexes exhibited a higher antimicrobial activity than the respective Schiff base ligands. This was attributed to the characteistics of the metal ions which was being adsorbed on the cell wall of the microorganisms thereby blocking the protein synthesis which is important for the further growth of these organisms.

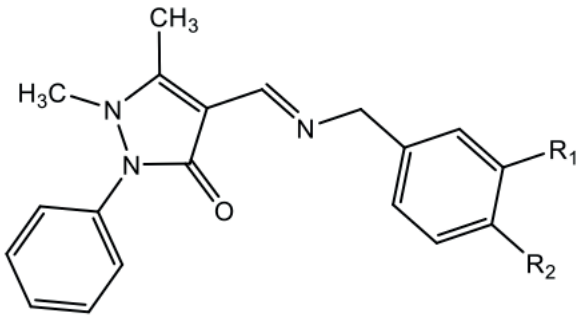


Figure 67. Structure of 3MPMAFA where R_1 = OCH_3, R_2 = H and 4MPMAFA where R_1 = H, R_2 = OCH_3.

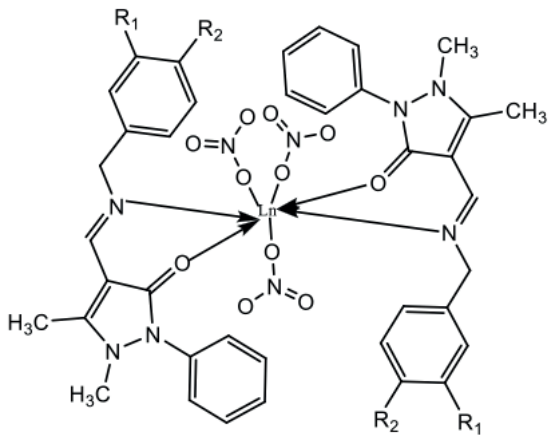


Figure 68. Structure of the lanthanide(III) nitrate complexes where Ln = La, Pr, Nd, Sm, Gd, Dy and Y, R_1 = OCH_3, R_2 = H for 3MPMAFA and R_1 = H, R_2 = OCH_3 for 4MPMAFA.

Hussein et al. (2024) prepared a Schiff base, 4,4'-(((2*E*,5*E*)-hexane-2,5-diylidene)bis(azaneylylidene))bis(1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one) from 4-antipyrinecarboxaldehyde and aceto nylacetone (Figure 69) and its lanthanide(III) nitate salts, $[Ln(L)_2(NO_3)].nH_2O$ where Ln could be La, Nd, Er, Gd and Dy. The synthesized compounds were tested on the following organisms; *S. aureus, E. coli, K. pneumonia* and *S. mutans*. The results of the antibacterial analysis revealed that the synthesized compounds were less active on *E. coli* compared to other tested organisms.

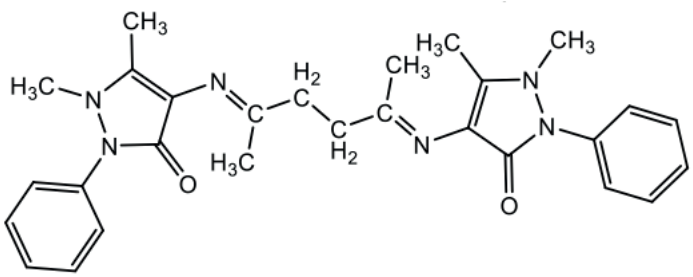


Figure 69. Structure of the Schiff base ligand, 4,4'-(((2E,5E)-hexane-2,5-diylidene)bis(azaneylylidene))bis(1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one).

Lanthanide(III) nitrate complexes of the Schiff base, L obtained from the condensation reaction of 4-antipyrinecarboxaldehyde and 2-aminobenzothiazole (Figure 70) were reported by Hussein et al. (2024). The general formula of the complexes was $[Ln_2(L)_2(NO_3)_6].6H_2O$ where Ln could be La, Nd, Er, Gd, Dy. Antimicrobial analysis was examined on four strains of bacteria, namely *Staphylococcus aureus, Bacillius subtilis, Escherichia coli, Klebsilla pneumonia* and three fungi strains, namely; *Candida albicans, tropical fungi* and *Scandal fungi* using the diffusion method. It was observed that the metal complexes showed higher activity in *Klebsilla pneumonia* and *Candida albicans*.

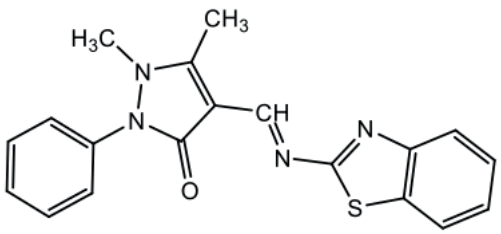


Figure 70. Structure of the Schiff base from 4-antipyrinecarboxaldehyde and 2-aminobenzothiazole.

Muraleedharan and Viswanathan (2025) reported the synthesis and characterization of lanthanide(III) chloride complexes of the Schiff base (L) derived from 4-antipyrinecarboxaldehyde and 2-aminophenol (Figure 71) using a microwave irradiation method. The complexes had a general formula $[Ln(L_1)_2Cl_2]$

Cl.4H_2O where Ln could be La, Sm, Eu Dy (Figure 72). Antimicrobial properties of the synthesized compounds were assessed against the following bacteria species: *E. coli*, *S. aureus, A. hydrophilia, K. pneumoniae, V. chloerae*, *B. subtilis* and fungi species; *A. fumigatus*, *A. flavus* and *C. albicans* using disc diffusion method. Streptomycin and amphotericin were used as reference drugs for their antibacterial and antifungal activity, respectively. The complexes showed higher activity against *E. coli* with an IZD of 24 – 33 mm, while only La and Eu showed activity against *A. fumigatus* and *A. flavus* with an IZD of 11 - 14 mm. Generally, the complexes exhibited increased bioactivity compared to the Schiff base. This is attributed to chelation, which raises the lipophilic nature of the central metal ion.

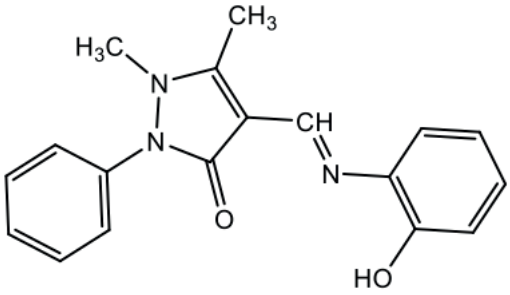


Figure 71. Structure of the Schiff base from 4-antipyrinecarboxaldehyde and 2-aminophenol.

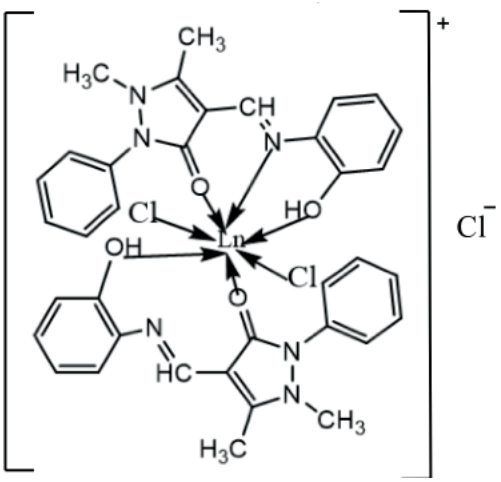


Figure 72. Proposed Structure of the lanthanide(III) complex of the Schiff base, L.

Table 12. Antimicrobial activities of lanthanide(III) complexes of some Schiff bases derived from 4-aminoantipyrine.

Constituents	Lanthanides	Formula	Micro-organisms (Bacterial and fungi)	Antimicrobial Activity (MIC or IZD)	Method	Reference drug	Ref.
4-aminoantipyrine and 4-methoxybenzaldehyde	La, Ce, Pr, Nd, Sm, Gd, Tb, Dy or Ho.	$[Ln(MBAAP)_2I_3]$					Agarwal et al. (1992)
Diazotized 4-aminoanti pyrine and 2-naphthol	La, Pr, Nd, Sm, Gd, Dy or Y	$[Ln(NAP)_2]ClO_4$,	*Staphylococcus aureus*	MIC= 0.05mg/ml	turbidimetric assay method		Alaudeen et al. (1995)
4-aminoantipyrine and pyridine-2/-carboxaldehyde.	La, Pr, Nd, Sm, Gd, Dy	$Ln(P2CA4AAP)_2(an)_3$	*Staphylococcus aureus, Escherichia coli, Klebsiella pneumonia, Pseudomonas aeuruginoas*		Agar diffusion method	.	Rajendra & Sreeletha (2002)
4-aminoantipyrine, 2-hydroxynaphthaldehyde, semicarbazide hydrochloride and diphenyl sulphoxide	La, Pr, Nd, Sm, Gd, Tb, Dy or Ho	$Ln(HNAAPS)_nX_3.DPSO$	*Staphylococcus aureus, Klebsiella pneumonia, Escherichia coli Pseudomonas aeruginosa*				Agarwal & Prakash (2005)
4-aminoantipyrine, 2-hydroxybenzaldehyde, oxalic acid, 8-hydroxyquinoline and 2-aminopyridine	Ce		*Staphylococcus aureus, Bacillus subtilis, Pseudomonas aeruginosa, Escherichia coli, Aspergillus fumigatus, Penicillium italicum, Syncephalastrum racemosum, Alternaria alternata, Candida albicans.*		diffusion	chloramphenicol and terbinafin	Abd El-Wahabi et al. (2005)
4-aminoantipyrine, furfural semicarbazide hydrochloride and α, β and γ picolines	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho.	$[Ln(FFAAPS(NO_3)_3Pic]$	*Bacillus subtilis, Staphylococcus aureus, Escherichia coli, Salmonella typhi*	MIC = 50µg/ml	agar-cup diffusion	tetracycline.	Agarwal et al. (2011)
4-aminoantipyrine, p-methylaminobenzalde hyde, thiosemicarbazide and pyridine	La, Pr, Nd Sm, Gd, Dy, Ho	$LnL(NO_3)_3.py$, $LnL_2(NCS)_3.py$ and $LnL_2(ClO_4)_3.py$	*Staphylococcus aureus, Corynebacterium diphtheriae, Salmonella typhi, Pseudomonas aeruginosa*				Agarwal & Kumar (2011)
4-aminoantipyrine, furfural and semicarbazide hydrochloride	La, Pr, Nd, Sm, Gd, Tb, Dy, Ho	$Ln(FFAAPS)_nX_3DPSO$	*Escherichia coli, Staphylococcus aureus, Bacillus subtilis, S. pneumonia, Pseudomonas aeruginosa, Aspergillus niger Penicillium notatum*		cup-plate		Prasad et al. (2011)

Constituents	Lanthanides	Formula	Micro-organisms (Bacterial and fungi)	Antimicrobial Activity (MIC or IZD)	Method	Reference drug	Ref.
4-amino-antipyrine, 2-hydroxybenz-aldehyde and L-tryptophan, L-tyros ine, L-cysteine, L-leucine or L-serin	Ce	[Ce(L)(AAP)]	*Staphylococcus aureus, Corynebacterium diphtheriae, Pseudomonas aeruginosa, and Escherichia coli.*	MIC (*µg/cm3*) = 300-350 (*s.aureus*), 400 – 500) (*c.diphtheriae*), 400 – 500 (*p. aeruginosa*), 250 – 300 (*e. coli*) IZD (mm) = 13 - 14 (*s.aureus*), 11 – 12 (*c. diphtheriae*), 12 – 13 (*p. aeruginosa*), 16 – 15 (*e. coli*)	agar cup, Tube dilution	tetracy-cline	Aghav et al. (2011)
4-amino-antipyrine, 2-hydroxybenz-aldehyde and L-tryptophan, L-phenyl alanine, L-isoleucine, L-prol ine or L-serine	La	[La(L)(AAP)]	*Staphylococcus aureus, Corynebacterium diphtheriae, Pseudomonas aeruginosa, and Escherichia coli.*	MIC (µg/cm3) = 300-350 (*s.aureus*), 400 - 500 (*c. diphtheriae*), 400 – 500 (*p. aeruginosa*), 250 – 300 (*e. coli*) IZD (mm) = 13 - 14 (*s.aureus*),11 – 13 (*c. diphtheriae*), 11 – 13 (*p. aeruginosa*), 15 – 16 (*E. coli*)	agar cup, Tube dilution	tetracy-cline	Aghav & Lokhande (2016)
Diazotized 4-aminoanti pyrine and L-tryptophan.	La, Ce, Nd, Eu, Gd	$[Ln(AAT)_2Cl_3]$	*Escherichia coli Staphylococcus aureus, Candida albicans, Aspergillus niger*	MIC = 1 mg/ml	diffusion tech-nique		Abbas (2015)
4-aminoan-tipyrine and 2,3-dihydroxy-benzaldehyde	Nd	$\{[Nd_6(HL)_2L_2X_2(NO_3)_8(EtOH)_6]. (EtOH)(H_2O)_3\}$	*Candida albicans*	IZD = 26 mm		gemcit-abine	Hua et al. (2020)
4-aminoanti-pyrine and dim-edone	Nd, La, Eu, Gd, Dy	$[Ln_2(L)_2(NO_3)_6]. 6H_2O$	*Escherichia coli and Pseudomonas aeruginosa Staphylococcus aureus, Streptococcous pyogenes.*	IZD (mm) = 1 - 10 (*E. coli*), 1 – 10 (*S. aureus*), 6 - 10 (*p. aeruginosa*), 6 – 10 (*s. pyogenes*)			Hussein & Shaalan (2022)
4-antipyrinecar-boxaldehyde and and ethylenedi-amine	La, Nd, Er, Gd and Dy	$[M_2L_2(NO_3)_6].6H_2O$	*Staphylococcus aureus, Bacillius subtilis, Escherichia coli, Klebsilla pneu-monia*	IZD (mm) =24 – 35 (*S. aureus*), 24 – 32 (*B. subtilis*), 18 - 28 (*E. coli*), 18 – 28 (*K. pneumoniae*),	agar well diffusion		Hussein et al. (2023)
4-antipyrinecar-boxaldehyde and 3-methoxy-benzylamine /4-methoxyben-zylamine	La, Pr, Nd, Sm, Gd, Dy, Yb	$[ML_2(NO_3)_3]$	*Escherichia coli, Staphylococcus aureus, Bacillius subtilis and Aspergillus niger and Penicillium notatum*		disc diffusion		Rijulal et. al. (2024)

Constituents	Lanthanides	Formula	Micro-organisms (Bacterial and fungi)	Antimicrobial Activity (MIC or IZD)	Method	Reference drug	Ref.
4-antipyrinecarboxaldehyde and acetonylacetone	La, Nd, Er, Gd and Dy	$[Ln(L)_2(NO_3)]\cdot nH_2O$	*S.aureus, E. coli, K. pneumonia and S. mutans*	IZD (mm) = 6 (*E. coli*), 12 - 24 (*S. aureus*), 7-12 (*K. pneumonia*), 13 – 22 (*S. mutans*)	diffusion method		Hussein et al. (2024)
4-antipyrinecarboxaldehyde and 2-aminobenzothiazole	La, Nd, Er, Gd and Dy	$[Ln_2(L)_2(NO_3)_6].6H_2O$	*Staphylococcus aureus, Bacillius subtilis, Escherichia coli, Klebsilla pneumonia, Candida albicans, tropical fungi and Scandal fungi*	IZD (mm) = 20 – 33 (*S. aureus*), 20 – 30 (*B. subtilis*), 18 - 25 (*E. coli*), 27 – 34 (*K. pneumon iae*), C. tropical (*10 – 12*), C. scandal (*9 -13*), C. albicans (*10 -15*)	diffusion method		Hussein et al. (2024)
4-antipyrinecarboxaldehyde and 2-aminophenol	La, Sm, Eu, Dy	$[Ln(L_1)_2Cl_2]Cl.4H_2O$	*Escherichia coli, Staphylococcus aureus, A. hydrophilia, K. pneumoniae, V. chloerae B. subtilis, A. fumigatus, Candida albicans, Aspergillus flavus*	IZD (mm) = 24 - 33 (*E. coli*), 8 – 10 (*K. pneum on iae*), 15 – 34 (*V. chloerae*), 10 – 30 (*A. hydroph ilia*), 8 – 15 (*S. aureus*), 9 – 15 (*B. subtilis*), 19 – 26 (*C. albicans*), 14 (*A. flavus*), 11 (*A. fumigatus*)	Diffusion	streptomycin and amphotericin	Muraleedharan and Viswanathan (2025)

Conclusion

Lanthanide(III) complexes of 4-aminoantipyrine-derived Schiff bases represent a compelling class of coordination compounds due to their structural diversity and versatile bonding characteristics. Their broad functional potential underscores their significance within coordination chemistry and highlights the need for continued investigation. Future studies should focus on obtaining single crystals of these ligands, their derivatives, and corresponding lanthanide(III) complexes to enable detailed structural elucidation via single-crystal X-ray crystallography. In parallel, comprehensive evaluation of their biological activities—including antioxidant, antibacterial, antifungal, anti-inflammatory, antimalarial, and anticancer properties—remains essential. Computational analyses will further support structure–activity relationship insights, while investigations into their catalytic, surfactant, electrochemical, and anticorrosive behaviors may reveal additional functional applications. Moreover, the application of these Schiff base ligands in solvent extraction processes for various metal ions, as well as their incorporation into nanoparticle systems, offers promising avenues for advanced material design. Equally important is the development of green and environmentally sustainable synthetic approaches to minimize the release of hazardous substances. Collectively, these research directions are expected to significantly expand the applicability and scientific relevance of 4-aminoantipyrine Schiff base derivatives and their lanthanide(III) complexes across multiple disciplines.

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Conflict of interest

No conflict of interest.

Data availability statement

It is not required.

Ethics committee approval

Ethics committee approval is not required for this study.

Authors'contribution statement

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Abbreviations

Ln Lanthanide, La Lanthanum, Ce Cerium, Pr Praseodymium, Nd Neodymium, Gd Gadolinium, Sm Samarium, Ho Holmium, Dy Dysprosium,Tb Terbium,Yb Ytterbium, Er Erbium, Y Yttrium, Eu Europium, TG Thermogravimetry, DTG Derivative thermogravimetry, CN Coordination Number, Abb Abbreviation.

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