CHAPTER 1

Introduction to coordination chemistry of Inner transition metal complexes, acylpyrazolone ligands and brief literature review.

1.1 Introduction

1.1.1 Progress of coordination chemistry

Studies on the Prussian blue substance employed as a pigment by artists began in the early 18th century. Coordination chemistry has advanced significantly since its inception in the 18th century. With an example of $[Co(NH_3)_6]Cl_3$, Werner laid the foundation of coordination chemistry in 1913 [1]. He introduced concepts like coordination numbers, laying the foundation for modern understanding. Following that, research into coordination compound isomerism began [2]. Progress continued through the 20th century with the development of inorganic techniques, the exploration of various ligands, and applications in industry, catalysis, and materials science. Then, models for the composition and bonding of spatial structural arrangement of complexes are suggested. Bioinorganic chemistry emerged, focusing on the role of metal ions in biology, while green chemistry initiatives integrated coordination compounds into environmentally friendly processes. Coordination chemistry also contributes to nanotechnology and relies on computational methods to understand complex behaviours. Multidisciplinary collaboration is now common, making it a thriving and diverse field. Figure 1.1 emphasises further development in these areas [3]. The trajectory of coordination chemistry's progression has been accelerated by advances in organometallic, transition metal catalysis, optical, and bioinorganic chemistry.

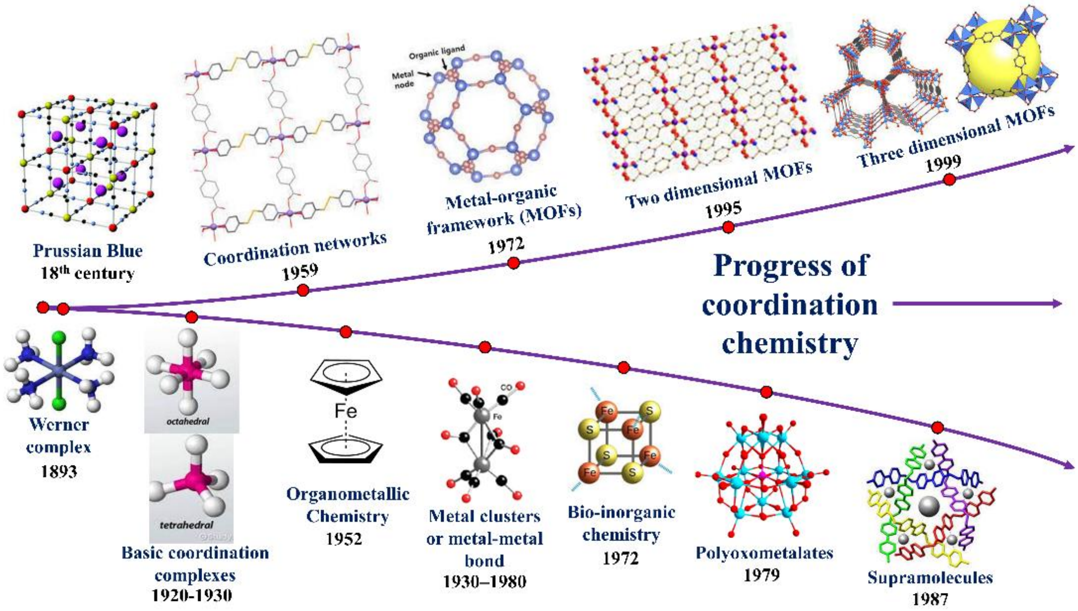


Figure 1.1 Progress of coordination chemistry.

1.1.2 Progress in Inner Transition Metal Coordination Chemistry

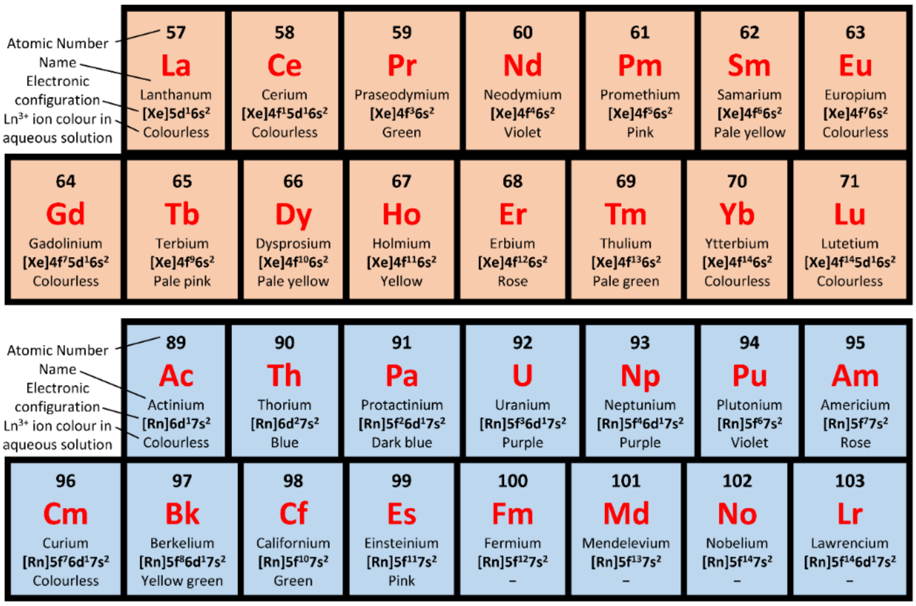
The elements in the periodic table from Ce to Lu and Th to Lr are known as the inner transition metals or f-block elements. Inner transition metal coordination chemistry has seen significant advancement since the 20th century. The unique electronic configurations and properties of lanthanides and actinides have driven this progress. Researchers have focused on isolating and characterizing these elements [4–6], leading to their integration into coordination chemistry. Notably, lanthanides exhibit distinctive magnetic and luminescent properties [7], making their complexes valuable in catalysis [8], luminescent materials [9], and medical imaging contrast agents [10]. On the other hand, the versatile coordination chemistry of actinides has critical applications in nuclear energy, environmental science, and nuclear waste management [11]. Ligand design, advanced spectroscopic techniques, and computational methods have all played essential roles in furthering our understanding of inner transition metal complexes. Research in inner transition series is a key, with applications spanning various scientific fields, including chemistry, physics, materials science, and environmental science [12–14].

1.2 Characteristics of Inner Transition Metals

Inner transition metal ions, specifically the lanthanides and actinides, possess distinctive characteristics (Figure 1.2). The filling of f-orbitals characterizes their electronic configuration. The general pattern for lanthanides (atomic numbers 58 to 71) is $[Xe]4f^n5d^16s^2$, with n representing the number of f-electrons. Actinides (atomic numbers 90 to 103) generally have a more complex configuration $[Rn]5f^n6d^17s^2$. These distinctive electronic configurations contribute to these elements' unique chemical and physical properties. They often exhibit magnetic behaviour and complex electronic spectra and form stable complexes with ligands [15,16]. Additionally, some actinides are radioactive and have crucial roles in nuclear applications [17]. Lanthanides have a regular 4f-orbital filling and unique magnetic properties [16]. The chemical reactivity of these ions varies depending on the specific element and oxidation state. These ions can exhibit varying degrees of ionic character in their chemical interactions. The ionic character of inner transition metal ions is influenced by factors such as their oxidation state, electron localization, and their ability to form stable complexes with ligands [18–

20]. Their versatile nature allows them to display both ionic and covalent characteristics in different chemical applications.

These elements can exhibit a broad spectrum of colours in their compounds, and this colouration is often particularly pronounced in coordination complexes [21,22]. The colour of inner transition elements varies significantly depending on the specific element, its oxidation state, the ligands present, and the electronic transitions involving their f-electrons. Factors like concentration and the chemical environment can also influence the observed colours, making these elements valuable in chemistry for identification and quantification [23,24]. Overall, inner transition metal ions have unique properties due to their electronic structure and high atomic numbers, making them important in various scientific and technological applications.



Atomic Number Name Electronic configuration Ln^{3+} ion colour in aqueous solution	57 **La** Lanthanum [Xe]$5d^{1}6s^{2}$ Colourless	58 **Ce** Cerium [Xe]$4f^{1}5d^{1}6s^{2}$ Colourless	59 **Pr** Praseodymium [Xe]$4f^{3}6s^{2}$ Green	60 **Nd** Neodymium [Xe]$4f^{4}6s^{2}$ Violet	61 **Pm** Promethium [Xe]$4f^{5}6s^{2}$ Pink	62 **Sm** Samarium [Xe]$4f^{6}6s^{2}$ Pale yellow	63 **Eu** Europium [Xe]$4f^{7}6s^{2}$ Colourless
64 **Gd** Gadolinium [Xe]$4f^{7}5d^{1}6s^{2}$ Colourless	65 **Tb** Terbium [Xe]$4f^{9}6s^{2}$ Pale pink	66 **Dy** Dysprosium [Xe]$4f^{10}6s^{2}$ Pale yellow	67 **Ho** Holmium [Xe]$4f^{11}6s^{2}$ Yellow	68 **Er** Erbium [Xe]$4f^{12}6s^{2}$ Rose	69 **Tm** Thulium [Xe]$4f^{13}6s^{2}$ Pale green	70 **Yb** Ytterbium [Xe]$4f^{14}6s^{2}$ Colourless	71 **Lu** Lutetium [Xe]$4f^{14}5d^{1}6s^{2}$ Colourless

Atomic Number Name Electronic configuration Ln^{3+} ion colour in aqueous solution	89 **Ac** Actinium [Rn]$6d^{1}7s^{2}$ Colourless	90 **Th** Thorium [Rn]$6d^{2}7s^{2}$ Blue	91 **Pa** Protactinium [Rn]$5f^{2}6d^{1}7s^{2}$ Dark blue	92 **U** Uranium [Rn]$5f^{3}6d^{1}7s^{2}$ Purple	93 **Np** Neptunium [Rn]$5f^{4}6d^{1}7s^{2}$ Purple	94 **Pu** Plutonium [Rn]$5f^{6}7s^{2}$ Violet	95 **Am** Americium [Rn]$5f^{7}7s^{2}$ Rose
96 **Cm** Curium [Rn]$5f^{7}6d^{1}7s^{2}$ Colourless	97 **Bk** Berkelium [Rn]$5f^{8}6d^{1}7s^{2}$ Yellow green	98 **Cf** Californium [Rn]$5f^{10}7s^{2}$ Green	99 **Es** Einsteinium [Rn]$5f^{11}7s^{2}$ Pink	100 **Fm** Fermium [Rn]$5f^{12}7s^{2}$ –	101 **Md** Mendelevium [Rn]$5f^{13}7s^{2}$ –	102 **No** Nobelium [Rn]$5f^{14}7s^{2}$ –	103 **Lr** Lawrencium [Rn]$5f^{14}6d^{1}7s^{2}$ –

Figure 1.2 Inner transition elements.

1.2.1 Complex forming ability of Inner transition metals

Inner transition metals are recognized for their strong capacity to form complexes. This ability is rooted in their electronic structure and atomic characteristics. These ions have partially filled f-orbitals, high atomic numbers, and strongly localized f-electrons. Their cubic set of f-orbitals is characterized by its unique three-dimensional, cloverleaf or dumbbell-shaped structure. These orbitals, labelled as 4f orbitals, consist of seven different orbital types (f_x^3, f_y^3, f_z^3, $f_{x(z^2-y^2)}$, $f_{z(x^2-y^2)}$, $f_{y(z^2-x^2)}$, f_{xyz}) with specific lobe orientations along the x, y, and z axes. These f-orbitals are integral to the distinctive properties of lanthanides, including their complex forming ability, luminescence, and magnetic behaviour [16,25]. Their distinct lobe orientation contributes to the complex electronic spectra and behaviour observed in compounds containing lanthanide elements. These metals can form complexes with higher coordination numbers due to several key factors [26–31]. These elements have large ionic radii, accommodating more ligands. They also possess numerous unpaired electrons in their partially filled f-orbitals, enabling bonding with a greater number of ligands. High positive charge density and variable oxidation states further contribute to their ability to form complexes with varying coordination numbers [26–31]. Additionally, their complex electronic structure and lack of steric hindrance facilitate the arrangement of ligands around the metal ion. This versatility in coordination chemistry is a distinctive characteristic of inner transition metals.

Research on complexes of inner transition elements covers a wide range of applications [32–36]. This field delves into coordination chemistry, luminescent materials, catalysis, actinide chemistry for nuclear applications, environmental and analytical chemistry for understanding their environmental behaviour, magnetic materials for electronics, medicinal applications in cancer treatment and imaging, and material science for the development of advanced materials [32–36]. This interdisciplinary research area is crucial for technological advancements, addressing environmental concerns, and gaining insights into fundamental chemical processes.

1.2.2 Absorption and Emission Characteristics

Inner transition metal complexes have distinctive absorption and emission properties due to their partially filled f-orbitals. These properties are influenced by the electronic structure of the metal ion, ligand interactions, and crystal field effects [37]. Their absorption spectra exhibit sharp and well-defined bands in the UV and visible regions due to distinct energy levels of f-electrons. These 4f electrons in lanthanides generate either sharp internal 4f-4f transitions that defy Laporte selection rules or broad f-d transitions that adhere to Laporte's allowed transitions [37]. While the Laporte ($\Delta L=\pm1$) and Spin ($\Delta S=0$) rules traditionally impose restrictions on 4f-4f transitions, a subset of spectral transitions, known as hypersensitive transitions, deviate from these limitations and exhibit significantly higher intensities [38,39]. These hypersensitive transitions are particularly remarkable due to their exceptional sensitivity to the specific environment of the ligands, thereby having a profound impact on covalency [40].

Ligands around the metal ion create energy level differences, affecting absorption wavelengths. Mishra's findings indicate that the enhancement of the hypersensitive band often correlates with a reduction in the coordination number and increased participation of the metal's 4f orbitals in bonding with the ligating atom [38–40].

Numerous theories have been proposed to elucidate the concept of hypersensitivity. The Judd-Ofelt theory has been employed to comprehend lanthanide intensities using three phenomenological parameters: Ω_2, Ω_4 and Ω_6 [41,42]. The oscillator strength of hypersensitive transitions arises from the coulombic correlation between the transition-induced electric dipole of the ligand and the quadrupole of the f electrons of the metal ion. This correlation provides a quantitative description of the intensities of hypersensitive transitions in the spectra of lanthanide complexes. The alterations in oscillator strength of hypersensitive transitions serve to ascertain the symmetries of complex species in a solution and offer insights into their coordination number and molecular structure [43].

The focus and enthusiasm for luminescent inner transition complexes stem from the distinctive photophysical characteristics of inner transition ions, which are well-suited for 'organic' lasers, offering high colour purity and optical amplifiers [36,44]. The optical properties of Ln(III) ions are distinguished by the contribution of the 4f electrons [36]. These ions display distinct excitation and emission profiles due to the unperturbed nature of the 4f electrons. The inner 4f orbitals are shielded by the outer $5s^25p^6$ subshells, resulting in minimal vibronic coupling. Another characteristic is the extended lifetime of lanthanide ion emissions. As electric dipole transitions necessitate opposite parity configurations, the shift between 4f orbitals is Laporte-forbidden. This results in lanthanide compounds having emissions with a notably longer duration (typically ms–μs range) compared to organic compounds and transition metal complexes. Since the molar coefficients of f-f transitions are less, an organic chromophore is introduced to the Ln(III) ions [45]. The main ideas about the emission process of lanthanide ions can be explained using the Antenna effect energy diagram (Figure 1.3), which illustrates how energy is absorbed by the organic ligand, known as the ‘central ligand’. The central β-diketonate ligand absorbs energy and is excited to its singlet state, through intersystem crossing, then transits to its triplet state, and the energy is intramolecularly transferred to the energy levels of the Ln ion. [44]. In addition to the negatively charged β-diketonate ligand, Ln ion also needs a zero-charged ligand (generally H_2O, EtOH, etc.), called 'neutral ligand', to coordinate for structural stability.

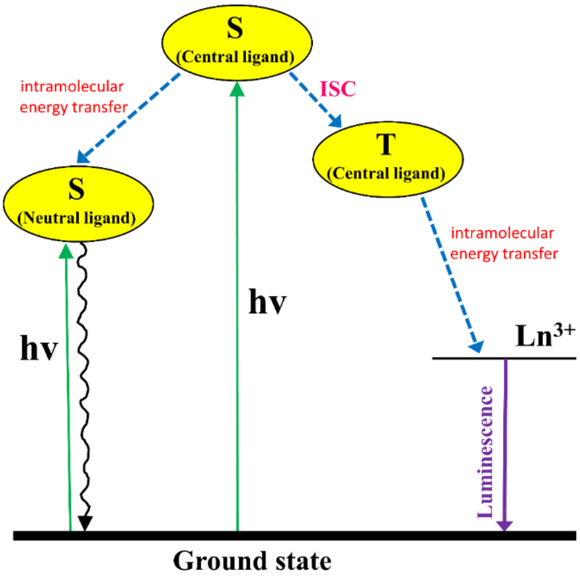


Figure 1.3 General diagram of "Antenna effect".

1.2.3 Covalency in inner transition metal complexes

Covalency in inner transition metal complexes refers to the extent of electron sharing between the central metal atom and the surrounding ligands. It is influenced by factors such as the nature of ligands, the oxidation state of the metal ion, orbital overlap, crystal field effects, bonding geometry, and steric hindrance [46,47]. Covalency in lanthanides is more extensively studied than in actinides due to their greater accessibility, lower cost, and partially filled 4f orbitals [46,47]. This covalent character can impact the reactivity and magnetic properties of these complexes. Oscillator strength and Judd-Ofelt parameters are important tools for assessing the covalent character of inner transition metal complexes [43,48]. Oscillator strength measures the intensity of electronic transitions and is higher in complexes with stronger metal-ligand interactions, indicating a greater degree of covalency [48]. The Judd-Ofelt parameters (Ω_2, Ω_4 and Ω_6) are highly sensitive to covalency and are used to predict spectroscopic properties [43,49]. Additional parameters such as the Nephelauxetic ratio, bonding parameter, Sinha parameter, and angular overlap parameter can be employed to evaluate and establish relationships regarding the covalent characteristics of inner transition metal complexes [49]. Understanding these parameters is crucial for designing materials and optimizing their properties for lighting, laser, and sensor applications.

1.3 Acylpyrazolone: Special class of β-diketone ligands

1.3.1 β-diketone ligands

β-diketone ligands are organic compounds featuring two ketones (C=O) groups attached to a central carbon atom (See Figure 1.4). They are significant in coordination chemistry because of their chelating capability, allows them to form multiple coordination bonds with metal ions [50]. These ligands play a crucial role in catalysis and can be structurally modified to achieve desired properties in coordination complexes, contributing to various chemical processes and applications [51,52]. Research on β-diketone ligands encompasses their synthesis, coordination chemistry, and catalytic applications [52]. Study of their structures, metal-ligand bonding, and reactivity are often employed in materials science and biomedical fields, where they form metal complexes for various chemical reactions [53,54]. Computational chemistry aids in understanding their electronic properties [55]. Researchers examine these compound's environmental and health implications, exploring variations in ligand structures and their involvement in supramolecular chemistry [56]. This research field is dynamic and continually evolving with new ligands and applications.

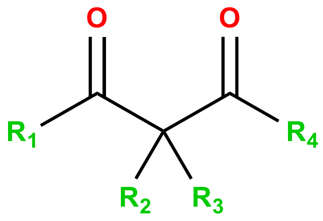


Figure 1.4 Common structure of β-diketone ligands.

1.3.2 4-acyl 5-pyrazolones

4-acyl-5-pyrazolones constitute a fascinating group of β-diketones in which a pyrazole is fused to a chelating moiety. They are organic compounds with a pyrazolone ring featuring an acyl group at the fourth carbon position (C-4). They are versatile in organic chemistry and have applications in pharmaceuticals, dyes, and coordination chemistry [57–59]. These compounds are notable for their involvement in various chemical reactions and unique structural characteristics, making them important in medicinal and synthetic chemistry.

Jensen described a direct one-step synthesis method [60], which involves acylation at the C-4 position of the pyrazole ring in a basic dioxane solution containing calcium hydroxide at reflux temperature. This calcium complex was stable under alkaline conditions, which prevented unwanted further reactions. Subsequent treatment with an acid aqueous solution yielded the acylpyrazolone (AP) in a high yield as a solid powder that was insoluble in water. Figure 1.5 illustrates the typical synthesis pathway for 4-acyl-5-pyrazolone. This enables the creation of chelating ligands customized for effective coordination with a specific metal ion. This approach was successfully employed for the preparation of various 4-acyl substituted pyrazolones [60].

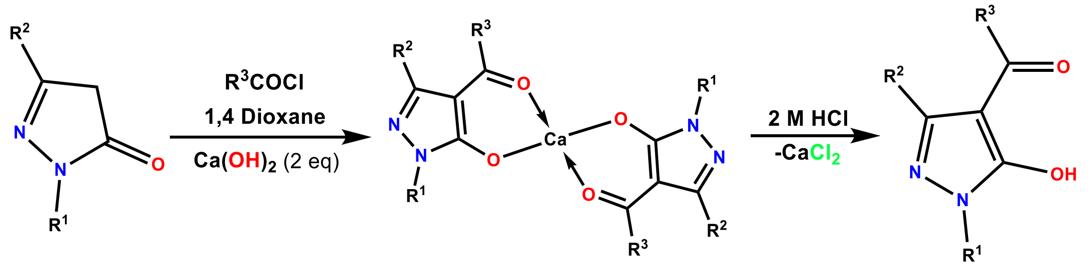


Figure 1.5 One-step synthesis route for 4-acyl-5-pyrazolone.

1.3.3 Expansibility of 4-acyl-5-pyrazolones

One common reactivity of 4-acyl-5-pyrazolones involves the creation of Schiff bases that incorporate extended conjugated systems. These extended systems enhance the denticity of these ligands. Numerous recent studies have focused on pyrazolones, particularly those that feature hydrazone, semicarbazone, and thiosemicarbazone functional groups [59]. The versatility of 4-acyl-5-pyrazolones is primarily achieved through condensing a ketone group within pyrazolones with substituted hydrazine via a Schiff base reaction [61]. Various categories of ligands, ranging from class I to VI [59], can be encompassed under the general category of 'expanded pyrazolone-based ligands.' This expansion typically involves strategically utilising a 5-pyrazolone synthon, as described in Figure 1.6. Thus far, many bidentate, tridentate, tetradentate, hexadentate, bis-, tris-, and tetrakis-5-pyrazolones have been synthesized, and their coordination chemistry has been extensively investigated [59].

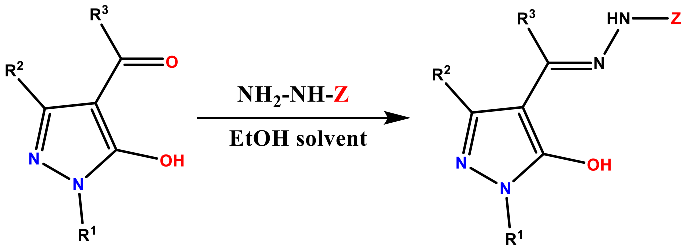


Figure 1.6 Expansion of 4-acyl-5-pyrazolones via Schiff base reaction.

1.4 Brief literature review on inner transition metal complexes

1.4.1 Recent research work on inner transition metal complexes

Recent progress addresses neglected effects like zero-field splitting and magnetic susceptibility anisotropy, enhancing the theory of paramagnetic chemical shift and relaxation enhancement [62]. As per the review by Chundawat et al. in 2021 [63], recent progress has focused on lanthanide-based coordination complexes, characterized by diverse ligands (Figure 1.7), showing promise for expanded antitumor efficacy. These complexes hold notable potential in radioimmunotherapy and photodynamic therapy, along with the attraction of therapeutic radioisotopes.

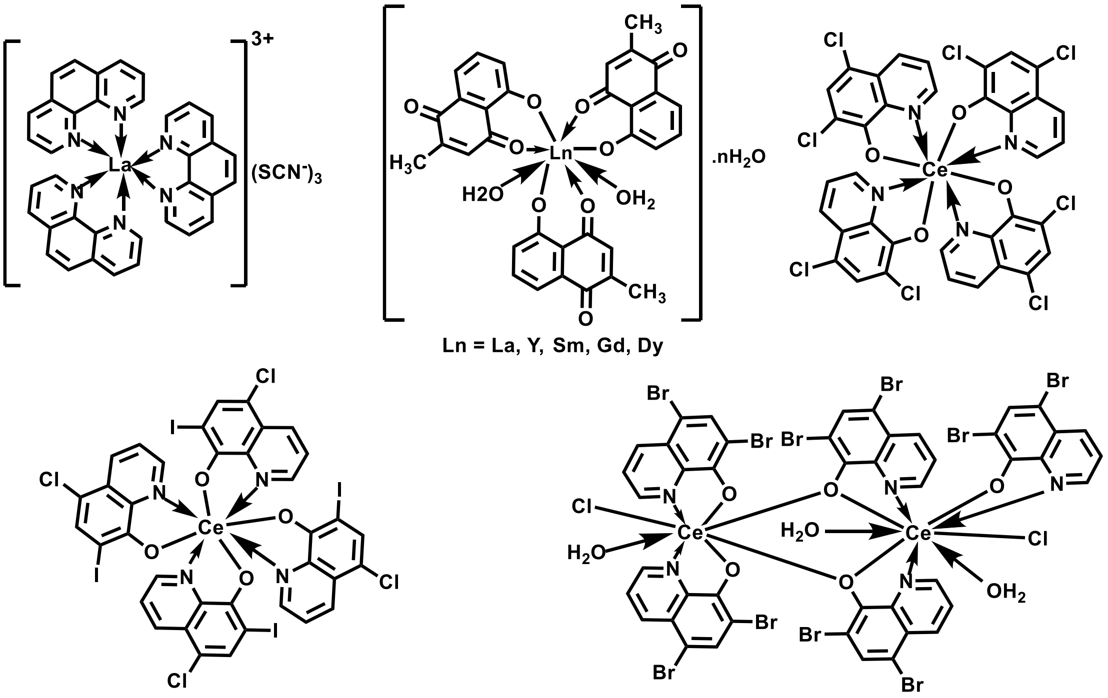


Figure 1.7 lanthanide-based coordination complexes, characterized by diverse ligands as per the review by Chundawat et al. [63].

A collection of [Ln^{III}(phen)(sal)$_3$] complexes (where Ln represents Nd, Eu, Tb, Dy, Er, Yb, Sm) has been synthesized by Dragancea et al., revealing unique luminescent features [64]. With their determined single crystal structures, these complexes exhibit characteristic emissions typical of europium and samarium, alongside near-infrared luminescence observed in the ytterbium and neodymium derivatives. The unique feature of neodymium, dysprosium, and terbium metal complexes among all lanthanides lies in their distinct magnetic and luminescent properties, making them particularly valuable for applications in technologies such as magnetic materials, sensors, and optoelectronic devices. Nawrocki and Sorensen's research highlights the significance of understanding the solution chemistry of neodymium(III), which is crucial in various applications such as green energy production and electric propulsion, necessitating the development of predictive structure-property relationships [65]. Chebyshev et al. reported on the solid-state and sol-gel synthesis of neodymium molybdate $Nd_5Mo_3O_{16+\delta}$ [66]. Their method enables the direct production of a single-phase neodymium molybdate through the decomposition of the organic precursor, consequently reducing the synthesis temperature by 200 K. Llanos' research team suggests that the wide chemical diversity observed in chiroptical active lanthanide systems is valuable for attempting a systematic classification to elucidate general structural trends linked with their fundamental properties [67]. You et al.'s review highlights the appealing features of lanthanide coordination polymers, demonstrating their potential as effective and recyclable heterogeneous catalysts in various organic transformations [68]. Nd(III) complexes have been recognized as turn-on fluorescence sensors for the highly sensitive detection of 6-mercaptopurine, as demonstrated in the research conducted by Rajpal et al [69]. Balashova et al. identified first neodymium and dysprosium perylene complexes (See Figure 1.8) with distinct structures, leading to variations in their luminescent characteristics [70].

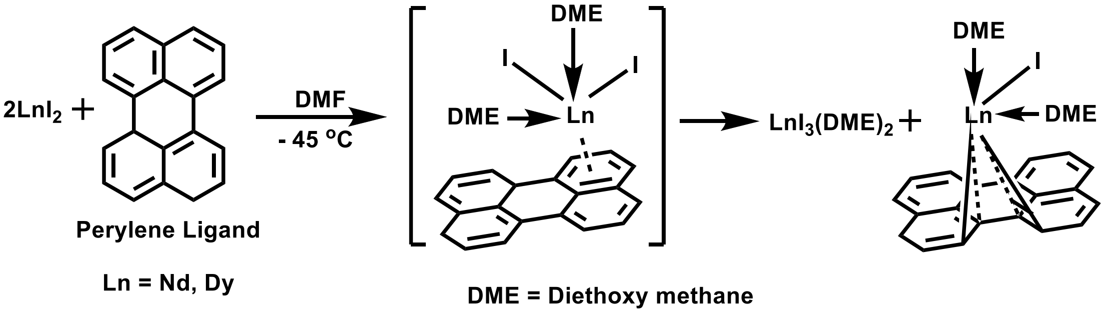


Figure 1.8 The formation of mononuclear $[LnI(Per)(DME)_2]$and $LnI_3(DME)_2$ Perylene complexes of Neodymium and Dysprosium [70].

The photoluminescent evaluation of binary and ternary Tb(III) complexes (given in Figure 1.9) unveiled vivid green emission attributed to the $^5D_4 \rightarrow ^7F_5$ transition under UV irradiation, showing enhanced emission upon secondary sensitizer inclusion, higher quantum yields in ternary complexes, and superior luminescence performance, as reported by Khatri et al. in 2022 [71].

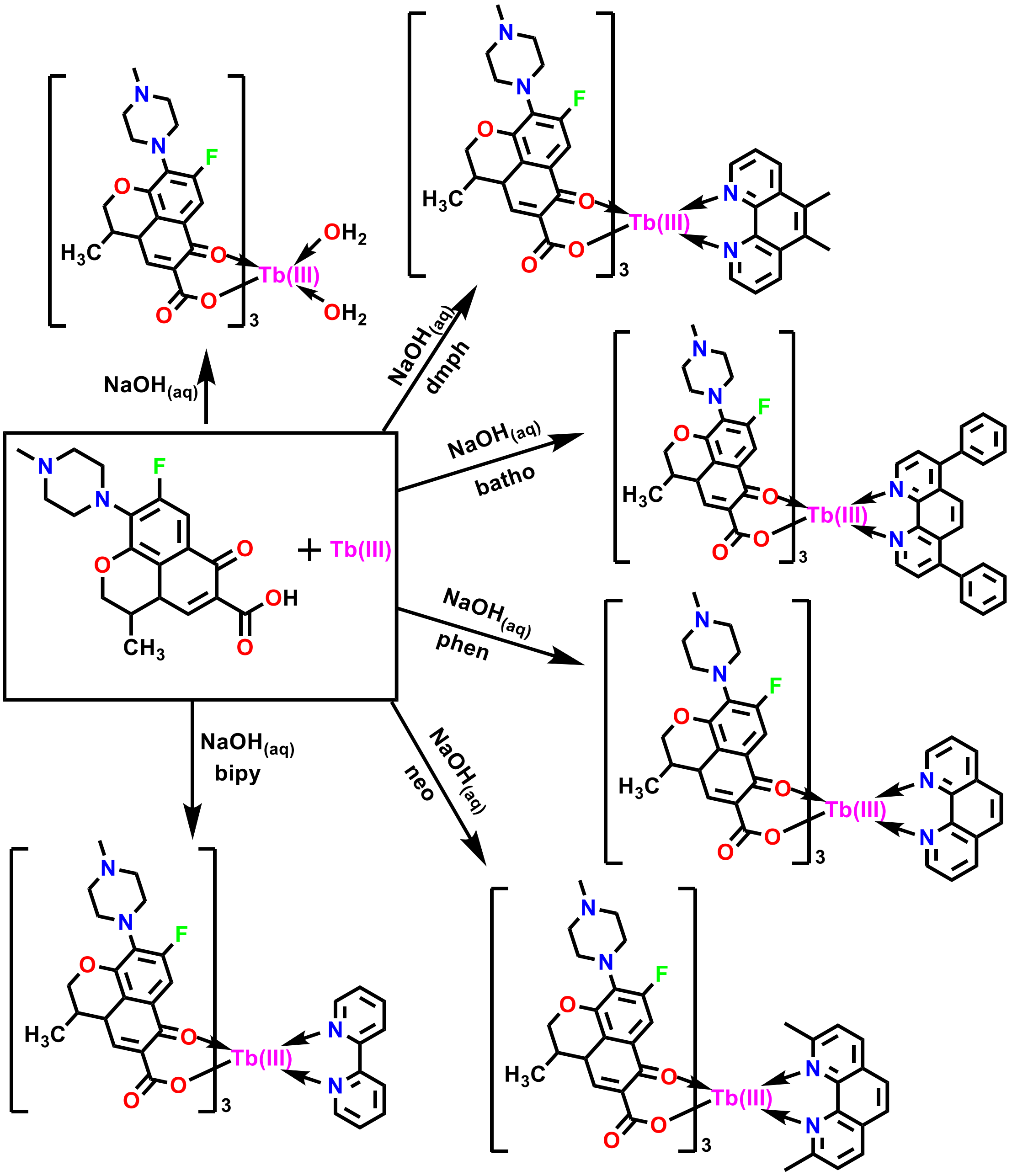


Figure 1.9 Structure and synthetic path of Tb(III) complexes proposed by Khatri and research group [71].

Vijayalakshmi's research group has documented the production of cool white light and adjustable multicolour emission in Tb^{3+}/Dy^{3+} co-activated glasses under various excitations, offering potential applications in WLEDs [72]. Aggarwal et al. conducted an in-depth study on ternary dysprosium complexes for white light emission, elucidating their semiconductor properties and optimal deactivation lifetimes, suggesting their applicability in diverse fields such as basic research, security printing, sensors, detectors, and OLEDs [73].

In the actinide series, thorium and uranium show characteristic chemical properties, including variable oxidation states and complex coordination chemistry. As Tutson and Gorden's review outlined, thorium can form complexes with coordination numbers spanning from 5 to 12, offering utility as catalysts or actinide sequestering agents [74]. The advancements made in organo-f-element chemistry throughout 2015 are outlined in the review authored by Frank T. Edelmann [75]. Atoini and colleagues investigated seven uranyl ion complexes with polycarboxylates, employing 1,1′-Dimethyl-4,4′-bipyridinium ("paraquat") as a structure-directing counterion in solvo-hydrothermal synthesis [76]. This approach led to the discovery of novel arrangements and facilitated an analysis of the weak interactions implicated. In January 2024, Banerjee's research team conducted quantum chemical calculations to explore the electronic structures and complexation behavior of methyl-substituted phosphonic acids with uranyl (VI) nitrate [77]. Eralie et al. reported on 8-coordinated thorium pyrasal complexes (Figure 1.10), highlighting their photometric properties and elucidating how the electron-withdrawing effects of the pyrazine ring induce changes in the thorium coordination environment, resulting in a secondary solid-state extended structure that minimizes pi-pi stacking [78].

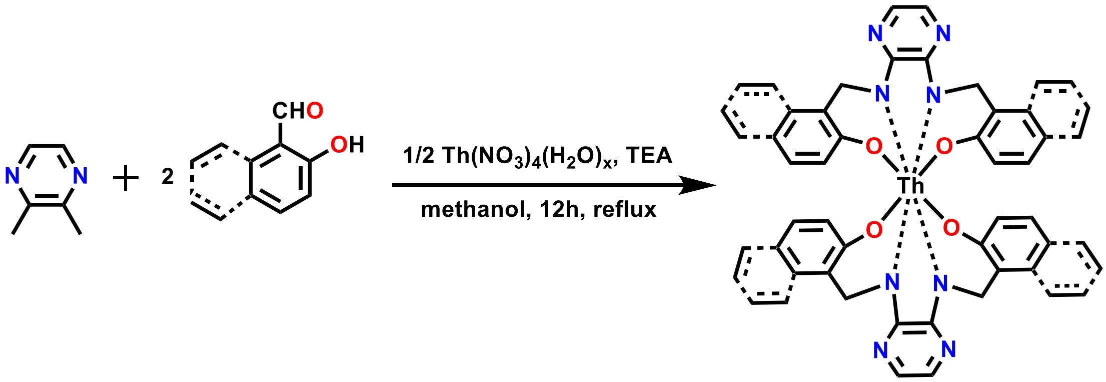


Figure 1.10 Structure of thorium pyrasal complexes reported by Eralie et al. [78].

Jin et al. explored the solvent extraction behaviours across various systems, examining the complexation mechanism of phenanthroline amide with U(VI), Th(IV), and Sc(III) [79]. Similarly, Selva et al. have revealed that azo dyes, Schiff bases derived from hydrazides, and organo-phosphine oxides serve as prominent molecular sensors for recognising Th^{4+} [80].

1.4.2 Complexes of inner transition metals with acylpyrazolones

One of the primary benefits of Acylpyrazolone ligands is their capability to create enduring complexes with a wide range of elements, including main group, transition metals, lanthanides, and actinides [81], which can be utilized for various purposes. Acylpyrazolone has been used in inorganic chemistry to separate and determine rare earth elements and actinides [82]. Research on acylpyrazolone complexes with inner transition metals is an area of active study in chemistry. These complexes are known for their unique properties and applications.

As per findings of Taydakov and colleagues (given in Figure 1.11), complexes involving Gd(III), Yb(III), and Lu(III) with 1,10-phenanthroline and 1,3-bis(1,3-dimethyl-1H-pyrazol-4-yl)propane-1,3-dionate demonstrate efficient light absorption properties, acting as effective antennas for sensitizing Yb^{3+} near-infrared (NIR) luminescence at 980 nm [83]. Additionally, Taydakov and colleagues investigated the interaction between 1-phenyl-3-methyl-4-cyclohexylcarbonyl-pyrazol-5-one (HQCY) and europium and gadolinium nitrates in the presence of alkalis (MOH = LiOH-CsOH) in different proportions [84]. Nine-coordinated complexes featuring a tricapped trigonal prismatic geometry have been documented along with computational analysis [85].

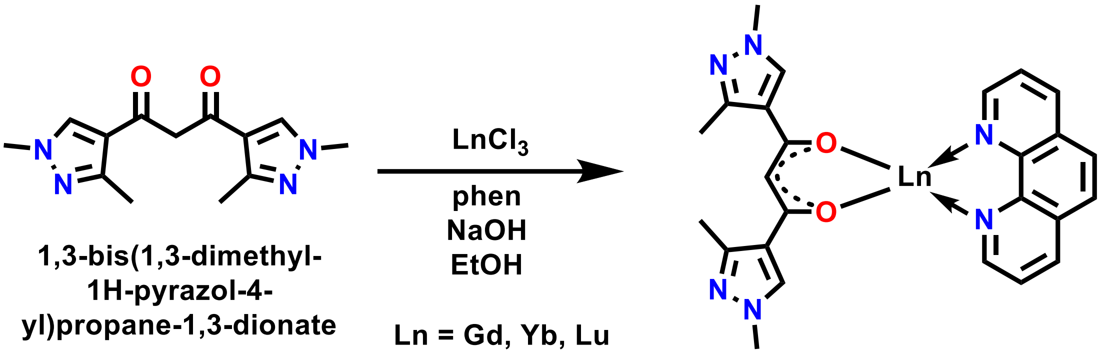


Figure 1.11 complexes involving Gd(III), Yb(III), and Lu(III) with 1,10-phenanthroline and 1,3-bis(1,3-dimethyl-1H-pyrazol-4-yl)propane-1,3-dionate [83].

Drawing from the existing literature, we synthesized and characterized diverse derivatives of acyl pyrazolone, including their Schiff bases and subsequent complexes with inner transition f-block elements such as U, Nd, Dy, Tb, Th, among others. These compounds were thoroughly characterized using spectroscopic techniques, including single crystal x-ray diffraction. Additionally, we employed computational methods like DFT and Hirshfeld analysis to gain deeper insights into the structural aspects of these complexes. Our research aims to explore various aspects such as the nature and extent of covalency, extraction potential, Antenna effect energy diagrams, oscillator strength, Judd-Ofelt parameters, covalency parameters, etc., derived from the electronic and solid-state emission spectra of these complexes.

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