Chapter I

General Introduction

The revelation of the close connection between biology and inorganic chemistry gave birth to a distinct discipline called bioinorganic chemistry. The employment of superior spectroscopic tools and revolutionary high-resolution image-processing instruments flourished in this field. New and fascinating interdisciplinary research are being done since then. Especially, the role of metal ions in this field is undeniable. Metal ions are essential for the nourishment of life and can be considered as the protagonist in various biochemical reactions, playing structural and functional roles. The specificity of any metal ion for a particular biological process depends upon factors like valency, redox property, coordination plasticity, ligand affinity, etc. Metal ions having tunable redox properties like Fe, Co, Mn, Ni, Cu, and redox inactive ones like Zn, Ca, Mg, Na, and K are commonly employed in biological systems. For example, metalloprotein in photosynthesis[1], respiration[2], oxygen transport both in vertebrates[3] and invertebrates[4], and biocatalysts like nitric oxide reductases[5], hydrogenase[6], nitrogenase[7,8], superoxide dismutase[9,10], and many other engage metals to carry out their respective functionality.

In addition, Metal complexes constitute a significant category of compounds with diverse applications across multiple fields. The scientific literature on this topic is vast and constantly growing to uncover new applications and properties of these fascinating compounds. Their incorporation in different ailments ranging from microbial infections to cancer treatment is noteworthy.[11-16] However, the journey from their discovery to commercialization is a time-consuming process and goes through a series of regulatory hurdles to get government approval. Therefore, the judicious designing of metallo-therapeutics remains a challenging task for bioinorganic chemists. Literature survey suggests that the ability of metal complexes to activate and stabilize reactive intermediates makes them a perfect candidate for catalysis in numerous organic reactions.[17-23] One of the most interesting features of metal complexes is their inherent flexibility which brings about the formation of a variety of structures. This property has gathered the attention of part of the modern scientific community to employ them in designing various functional materials.[24] Their implementation in the field of developing magnetic materials [25,26], sensors [27] and switches [28], energy storage [29,30], gas storage [31], luminescent materials for optoelectronics [32], solar cells [33], electronic devices [34], semiconductors [35] and light-emitting materials [36]

is elevating human civilization to the next level. Moreover, they are delivering a positive impact on sustaining our environment through pollution control, soil remediation [37], and water purification.[38-41]

Overall, metal complexes represent a significant category of compounds that have a wide range of applications across different domains. The scientific literature on this topic is vast and constantly growing as new applications for metal complexes are discovered.

I.1. Ligands and Chelators

The term "ligand" was introduced by Alfred Stock in 1916 in the domain of silicon chemistry. He derived it from the Latin word "ligare" which means "to tie or bind". The phrase was later used by R.J.P. Williams and H. Irving in their paper published in Nature, where they described what is now known as the Irving-Williams series.[42] This was the first known usage of the term in a British journal.

Ligands and chelators are both types of molecules that can bind to metal ions.

Ligands are a class of chemical entities that bind to metal ions through coordination bonds. These types of bonds are formed between a metal ion and a molecule that can be a neutral or an ion that attaches to the central atom through the donation of electron pairs via one or more atoms. The metal ion can coordinate with these electrons, forming a stable complex. Ligands can be organic or inorganic molecules, and they can vary in size and shape. These can be classified into various categories e.g.,

- monodentate ligand
- polydentate ligand (bi, tri, tetra, penta and hexadentate)
- ambidentate ligands
- bridging ligand

based on denticity

- cyclic or ring ligand
- strong field ligand
- weak field ligand

based on ligand field theory

- σ-donor ligand
- π-donor ligand
- π-acceptor ligand

based on frontier orbitals

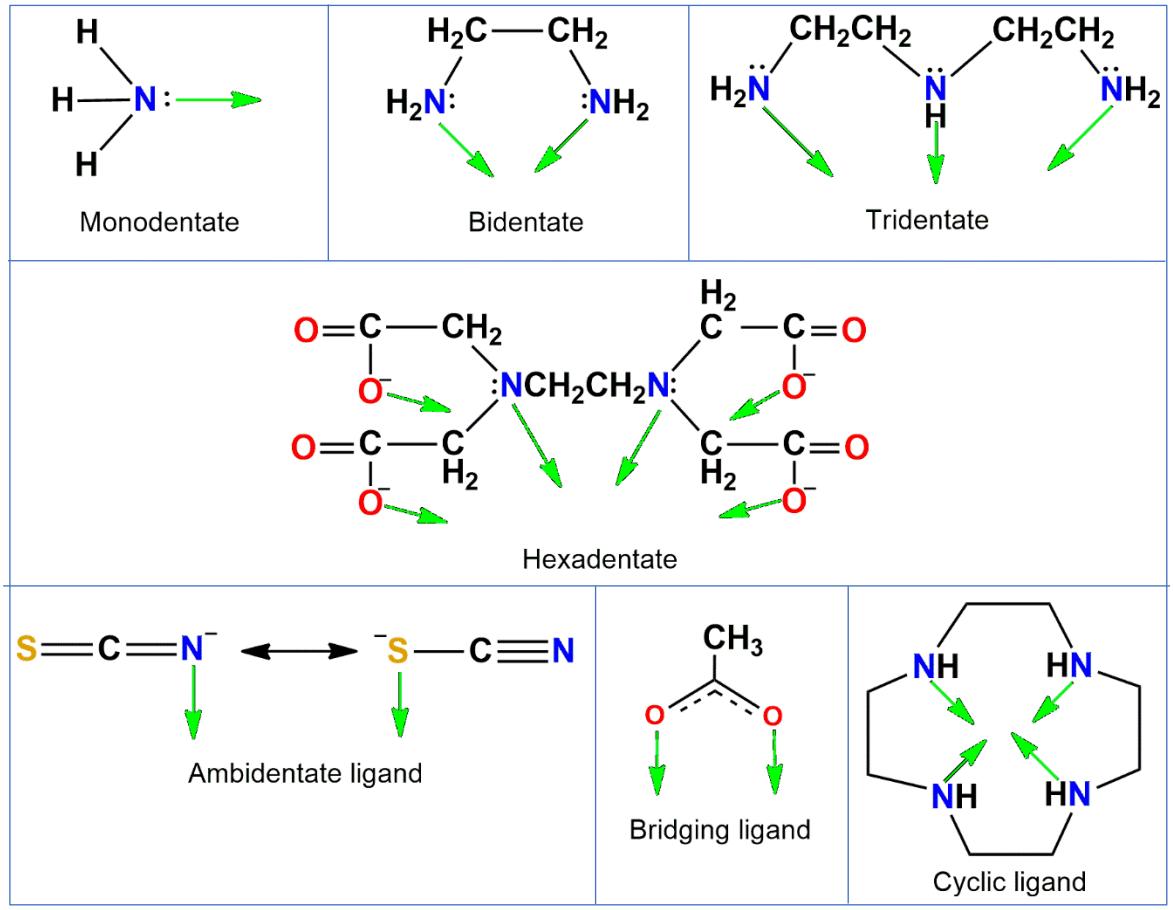


Fig I.1 Different types of ligands

Chelators are a specific type of ligand that can bind to a metal ion with multiple coordination bonds. The term "chelator" comes from the Greek word "chelē," which means claw. Chelators have multiple binding sites that can coordinate with the same metal ion, forming a ring-like structure around the metal ion. This ring structure is known as a chelate.

The term "denticity" originates from the Greek word "dentis," which translates to tooth. Essentially, denticity refers to the number of ligand bites or bonds to the central atom. It is noteworthy that the words chelator and chelating ligand are also general terms used to refer to these kinds of ligands. The preliminary idea of chelation is based on pure coordination chemistry. The term “chelate” was first coined by Morgan and Drew (1920) who depicted it as groups resembling calipers, which act as two connecting units and attach to the central atom, resulting in the formation of heterocyclic rings.[43]

While there are various methods to classify ligands, our attention was directed toward the classification based on their generation. On this basis, they can be classified mainly in two ways e.g., synthetic ligands and commercial ligands.

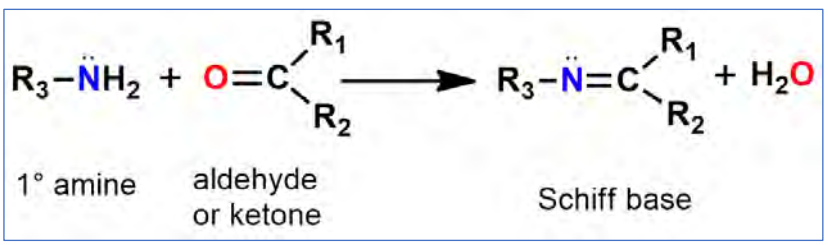
Commercial ligands are ligands that are available for purchase from chemical suppliers e.g., EDTA, Phenanthroline, Bipyridine, Dipicolinic acid, Nitrilotriacetic acid, etc. These ligands are less specialized than synthetic ligands and are used in a variety of settings, such as in catalysis, separation technologies, and industrial-scale chemical synthesis.

While Synthetic ligands are ligands that are designed and synthesized by chemists in standard laboratory settings. These ligands are typically used in academic research to unfold their multi-directional application. These kinds of ligands are designed in such a way that they can specifically bind to a particular receptor or target molecule. This generally takes place via different donor sites of ligands e.g., O-donor, N-donor, S-donor, and so on.[44]

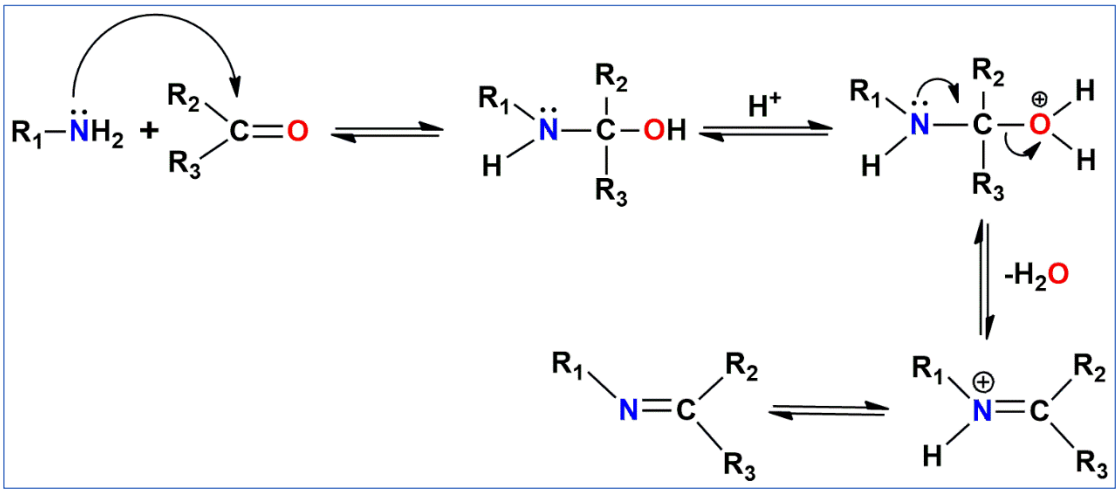
In order to maintain coherence with the subject matter explored in this thesis, I concentrated on the ligands containing (N, N) and (N, O)-donor sites specifically Schiff base ligands and some commercially available ones e.g., bipyridine, phenanthroline.

I.2. Schiff base ligands

These ligands are commonly referred to as privileged ligands as their preparation involves simple condensation. Although for the latter case, a few more steps are added. Schiff bases were first reported by a German chemist, Hugo Schiff (1834 – 1915), and are compounds carrying imine or azomethine (–HC=N–) linkage [45], which can be conveniently tailored to bind with different metal ions having varying coordination numbers and oxidation states. $R_2C=NR'$ ($R' \neq H$) is typically the formula of Schiff base. Azomethine Group (R-CH=NR' where $R' \neq H$) is determined by the blend of a carbonyl group and amino group. The simple process of synthesis and utility value pave the way for an extensive and important role in modern chemistry. These coordinate with metals which results in the suppression or development of chemical activity by forming metal complexes. Metal complex is a subject of extensive interest, being researched not just by inorganic chemists but also by organic and physical chemists, biochemists, molecular biologists, pharmacologists, and environmentalists.



Scheme I.1 Preparative route of Schiff base synthesis



Scheme I.2 Mechanistic route of Schiff base formation

The Schiff base generally contains a carbon-nitrogen double bond.[46] The nitrogen atom in the imine group has a lone pair of electrons and they are utilized in the bonding. Dative bonds to metal ions are framed and result in Schiff metal complexes. These bases having nitrogen or sulphur atoms are utilized as medications. Different metal ions can organize with them to make six-member chelate rings. Schiff bases including alkyl substituents can be set up in basic methodology and have more continuance.[47] This isn't the situation with Schiff bases comprising aliphatic aldehydes, as they are unstable. Polymerization happens immediately when contrasted with aromatic aldehyde Schiff bases. A protic solvent is required for the development of Schiff bases from the carbonyl compounds. It is basic that the imine bond ought to be kept from hydrolysis and subsequently should be dry.

I.3. Application of Schiff base metal complexes

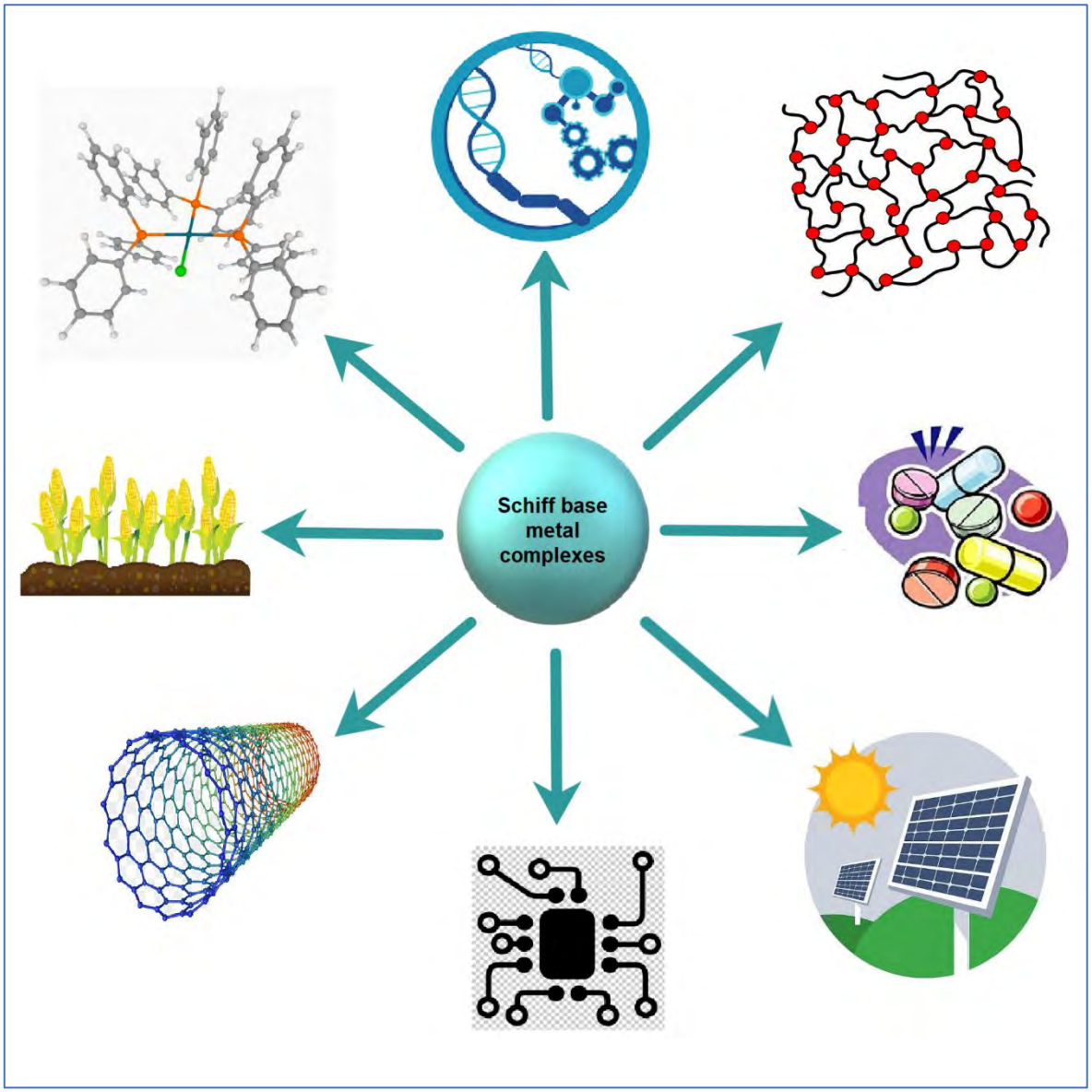


Fig I.2 Versatile applications of Schiff base metal complexes

I.3.1. Application in Biology

Schiff base metal complexes have been discovered to have significant roles in biological systems, including catalysis of enzymatic reactions, transport of metal ions across cell membranes, and regulation of gene expression. Numerous Schiff base ligands and the corresponding complexes were studied due to their remarkable and significant characteristics, including mimicking bio enzymes, reversible oxygen binding, and their

ability to bind with certain harmful metals. In addition, some Schiff base complexes exhibit promising potential in biological activity and modeling.[48]

Numerous enzymes rely on metal ions to facilitate their catalytic activity. Metalloenzymes, which are enzymes containing metals, act as natural factories that exhibit both chemo- and stereo-selectivity, allowing them to catalyze a wide range of reactions. Many researchers have investigated the mechanism and function of natural metalloenzymes. The design of artificial enzymes involves considering several crucial factors, with the structure of the ligand being one of them. Various organic compounds, including Schiff base, porphyrins, oxamido, guanidinium, crown ether, imidazole, aza-crown ethers, macrocyclic polyamine, and bipyridine, have been developed and utilized as ligands to create artificial enzymes. Typically, these ligands contain nitrogen atoms that serve as the coordination atoms in the metal complexes. Among these compounds, Schiff base ligands are of particular significance.

❖ Oxygen is crucial for living beings yet it can generate harmful metabolites known as reactive oxygen species like hydrogen peroxide and superoxide anion. These oxidants can damage cells' structure and function by attacking tissues and membranes. To prevent this damage, two essential metalloenzymes-superoxide dismutases and catalase - work within cells to decompose hydrogen peroxide and superoxide.

Kensler *et.al.* initiated the synthesis of a low molecular weight copper coordination complex having SOD mimetics properties.[49] Darr et. al., Faulkner et. al., Riley et. al. also synthesized a few manganese base complexes showing such activities.[50, 51, 52] Later Mn-salen and Mn-cyclic salen-crown ether complexes synthesized by Baundry and co-workers proved to be more stable than the previously reported ones.[53, 54] Vecchio et al. further modified the Mn-salen complexes for enhanced stability in the aqueous medium.[55, 56] Schiff base complex having SOD-like activity was presented by a group of Yao-Xin Li and Yu-Li Zhang where they prepared cobalt(III) and Ni(II) complexes respectively. [57,58] Gonul et. al. synthesized a set of Schiff base complexes containing Ni(II), Co(II), and Cu(II) metals, which were then subjected to DPPH radical scavenging, cupric reducing antioxidant capacity (CUPRAC), and SOD activity assays. The IC_{50} values of the compounds in the DPPH radical scavenging assay were compared to vitamin C, and the ligand had a similar IC_{50} value to vitamin C in terms of antioxidant activity. The Schiff base ligands as well as their metal complexes demonstrated noteworthy antioxidant activity compared to the reference compound Trolox.[59]

Group of R. C. Maurya synthesized a Fe-complex containing glucosamine-based Schiff base. This complex shows great potential as a superoxide dismutase, with an IC_{50} value of 69 μM.[60] Zhang et. al. synthesized a series of Mn(III), Fe(III), and Co(III) complexes with Schiff base ligands and studied their Superoxide dismutase activity in which Mn-complex outperformed such activity.[61]

Similarly, Hong Liang and co-workers synthesized a few water-soluble chiral Schiff base ligands along with their Mn(III), Ni(II), and Cu(II) complexes and studied SOD activity. The results of their experiments suggested that the Mn(III) complexes exhibit the highest level of activity, while the Ni(II) complexes show the lowest activity. Upon binding with BSA, the Mn-complex showed enhanced SOD activity. The researchers inferred that the BSA molecule could have a favorable impact on the SOD activity of certain complexes and there is quite a lot of room for the development of synthetic metalloenzymes as therapeutic agents by utilizing BSA.[62] The primary emphasis of SOD and catalase model research has been on manganese salen derivatives. However, the activity of salen complexes consisting of different transition metals, such as Cu [63, 64], Fe [65], and V [66], has also been examined for their SOD and catalase-mimicking properties. Jacob et al. discovered that some Cu salen complexes are capable of breaking down H_2O_2 at rates that are similar to those of natural enzymes when they are enclosed within zeolites.[67]

❖ In plant cell vacuoles and cytoplasm, Catechol exists in low amounts. However, when plant tissues are damaged by bacterial or fungal diseases, Catechol is released and transformed into ortho-quinone by the action of catecholase. This natural antiseptic plays a vital role in the plant's defense mechanisms. Catecholase activity is operated by a protein namely catechol oxidase, with an active site of type III that contains two copper atoms and is capable of catalyzing the oxidation of various o-diphenols, also known as catechols, to produce o-quinones. In vitro, biomimetic copper complexes have been utilized to simulate this enzymatic activity, employing atmospheric oxygen as a naturally available oxidizing agent. This holds significant value in terms of environmental and economic factors.

Anbu et. al. synthesized a Schiff base type copper(II) compound that is inexpensive, easy to prepare, and non-toxic has been developed, and it demonstrates effective oxidation of catechol in aqueous methanol.[68] Mondal and colleagues synthesized copper complexes using a Schiff base ligand with (N, N, O) donor atoms. One of these complexes exhibited exceptional activity as a catecholase.[69]

Das et. al. prepared two new Cu(II) Schiff base complexes consisting of a flexible piperazinyl moiety, both of which exhibited activity in the oxidation of catechol.[70] Group of D. Das designed three distinct Mn(II) complexes using a compartment ligand. All three complexes were tested as potential candidates for catechol oxidation activity. Further, they proved that the oxidation of catechol catalyzed by these Mn(II) complexes is caused by the production of ligand-bound radicals rather than metal-centered redox participation with the help of EPR and CV studies. Extensive DFT calculations on catechol oxidation demonstrated that imine-bound radicals, rather than phenoxo radicals, are formed during the oxidation process.[71] Keshavarzian et. al. prepared a hetero-dinuclear Cu-Gd (3d-4f) Schiff base complex derived from o-vanillin in a two-step process which shows excellent catechol oxidation activity.[72] A new Schiff base was used by a team led by B. Dede to synthesize two complexes of Mn(II) and Cu(II). Surprisingly, the Mn-complex exhibited higher catalytic activity than the Cu-complex in the oxidation reaction of 3,5-di-tert-butylcatechol under aerobic conditions.[73]

❖ The biosynthesis of actinomycin D involves several steps, and the final step is catalyzed by the enzyme phenoxazinone synthase. Also, the oxidative conversion of 2-aminophenol to the phenoxazinone chromophore, a key component of actinomycin D, requires this specific enzyme. The phenoxazinone chromophore is an important component of actinomycin D because of its ability to intercalate into DNA and inhibit RNA synthesis. Without the phenoxazinone chromophore, actinomycin D would not be able to function as an antibiotic and anticancer agent. In recent decades, the use of transition-metal complex catalysts to mediate oxidations of organic substrates with molecular dioxygen has garnered significant interest among researchers, particularly in the development of reactions that aim to mimic the bio functions of metalloenzymes.[74, 75, 76]

Chatterjee et. al. developed one polymeric and one dinuclear Fe(III)-Schiff base complex containing (O, N, N, O) donor atoms. These complexes exhibit remarkable catalytic activity in the oxidation of 2-aminophenol, indicating their potential as functional models for the phenoxazinone synthase enzyme.[77] Garai et al. synthesized tetranuclear zinc(II)-Schiff base complex and investigated its catalytic activity towards the oxidation of 2-aminophenol (2-AP) in ethanol. The complex showed good phenoxazinone synthase-like activity with a turnover number (k_{cat}) of 6.19×10^2 per hour under aerobic conditions. The reaction mechanism was proposed to involve the formation of an adduct between the substrate and catalyst, followed by the generation of radicals that drive the oxidative coupling of 2-AP.[78]

A novel dinuclear copper(II) Schiff base complex was synthesized by Mudi et al. The efficiency of this Cu(II) compound in mimicking biological processes was evaluated by studying its catalytic activity towards 2-aminophenol (2-AP) as a model substrate in an acetonitrile medium. The results indicated that the Cu(II) complex catalyzed the oxidative coupling of 2-AP to aminophenoxazinone species with a remarkable turnover number of 78.14 h^{-1}.[79] Mandal and co-workers synthesized three mononuclear copper(II) Schiff base complexes supported by N3 donor ligands with varying donor moieties. The researchers investigated the phenoxazinone synthase mimicking activities for all of the prepared complexes by studying the oxidation of 2-aminophenol to 2-amino-phenoxazine-3-one in a methanol-water solvent. Their study established a relationship between the structure of the complexes and their catalytic reactivity. Notably, they observed valence tautomerism in the complex-substrate adduct and the generation of a reactive Cu^{I}-intermediate species, which was accountable for activating molecular dioxygen. This finding has significant implications for understanding the mechanism of the catalytic reaction.[80] Mudi et. al. prepared two copper(II) Schiff base complexes that are structurally alike. Moreover, the study also examined the effect of auxiliary ligands, such as chloride and nitrate, on the catalytic efficiency of the phenoxazinone synthase biomimetics. Their study revealed that the complex with coordinated nitrate demonstrated higher catalytic efficiency than the one with chloride, as the former creates steric repulsion in the square plane, which makes the complex more unstable and enables the entrance of 2-AP to the Cu(II) center.[81]

Interestingly, Ghosh and colleagues successfully developed two trinuclear heterometallic complexes by utilizing a previously prepared copper complex as a metalloligand which shows both catecholase and phenoxazinone synthase-like activity. The complexes were then evaluated for their catalytic abilities in mimicking biomimetic oxidase processes. The results revealed that only the complex containing a loosely coordinated water molecule at the Mn(II) center exhibited exceptionally high catalytic activity in catecholase reactions, surpassing all other synthetic complexes reported thus far. Furthermore, this particular complex demonstrated the highest phenoxazinone synthase-like activity. During the catalytic conversions, catecholase activity led to the formation of H_2O_2, while phenoxazinone synthase-like activity resulted in the production of H_2O. [82]

I.3.2. Application in Catalysis

Attaching various substituents to the ligand in Schiff base metal complexes can alter the coordination center's environment and provide valuable scopes for the enrichment of electronic and steric properties. Naturally, structural fine-tuning becomes a necessity to achieve such properties. The metal complexes formed by Schiff bases involving p-block and d-block metals can serve as efficient catalysts in various syntheses and other beneficial reactions.[83-85] The ease of synthesis and resistance to heat exhibited by Schiff base metal complexes in organic synthesis have made them promising candidates for use in catalysis.[86]

❖ Chen et. al. synthesized a few mononuclear asymmetric Cu(II) Schiff base complexes with the help of various salicylaldehyde derivatives. Metal-coordinated polymerization of methyl methacrylate is catalyzed by these complexes for the formation of polymethyl methacrylates (PMMAs) in the presence of AIBN. Surprisingly they noticed the chain growth of the obtained PMMAs influences the presence of substituent in the ligand.[87] A Zn-Schiff base complex was designed and synthesized by Lihui et al. for initiating the ring-opening polymerization of L-lactide. The polymerization process was well-controlled, resulting in the production of polylactide with benzyl ester and hydroxyl groups at the ends. The study suggested that the catalytic activity of the complex was affected by the structure of the ancillary ligands. Specifically, the introduction of an electron-rich methoxy group at the ortho phenoxy substituent led to a reduction in the polymerization rate. [88] During the synthesis of a heterometallic Schiff base, Bao and colleagues noticed that the incorporation of rare ions resulted in a minor reduction in catalytic activity during the ROP of l-lactide, as well as an increase in the molecular weights (M_w or M_n) of the resulting polymer and enhanced polymerization controllability.[89] With the assistance of lanthanide Schiff base complexes synthesized by Ni et al., successful ring opening polymerization (ROP) of ε-caprolactone (Cl) was achieved as a result of using these complexes as catalysts. The neodymium complex, in particular, resulted in a controlled ROP of Cl synthesized a series of five- and six-membered-ring Al complexes bearing Schiff base ligand and studied their CL polymerization.[90] They observed that the five-membered-ring Al complexes revealed an appreciably higher (2−3-fold) polymerization rate than the six-membered-ring Al complexes in the CL polymerization. The reported new strategy can be used to design Al complexes bearing Schiff base ligands with high catalytic activity for CL polymerization.[91] The use of alkaline-earth metal complexes of Schiff bases in the ring-opening polymerization (ROP) of cyclic esters has shown great potential as a catalyst. These metals

are not only abundant in the earth's crust but also have low toxicity, making them a promising option for biocompatible applications.[92] Lu et. al. synthesized a group of NNO-tridentate Schiff base ligands coordinated with lithium and the catalytic activity of these complexes was also evaluated for the ring-opening polymerization of L-lactide. The Li complex with two tert-butyl groups was found to have the most effective catalytic activity and excellent controllability.[93]

❖ Among the essential chemical reactions in organic chemistry, oxidation reactions hold a prominent position. Selective catalytic oxidations are particularly challenging for organic chemists because they require the oxidation of a specific functional group or site within a molecule while leaving other functional groups or sites untouched.

A few Ruthenium-Schiff base metal complexes were synthesized by Norouzi and colleagues, which were discovered to be successful in oxidizing alcohols and sulfides at room temperature with the aid of NMO as an oxidant. This approach presented a universal technique for oxidizing various types of alcohols under gentle conditions. Primary and secondary benzylic alcohols were transformed into products with excellent yields, while aliphatic and cyclic alcohols produced carbonyl compounds with moderate yields.[94] The group of Maurya studied four dioxidomolybdenum(VI) complexes that have been used as catalysts for the homogeneous oxidation of secondary alcohols, using 30% H_2O_2 as an oxidant. The optimized reaction conditions resulted in the production of the corresponding ketones with high yields from secondary alcohols.[95] An oxovanadium(IV) Schiff base complex was synthesized by Menati et. al. which demonstrated exceptional catalytic activity for converting various sulfides to their corresponding sulfones without the need for a solvent. The utilization of H_2O_2 as an oxidizing agent and the exclusion of a solvent make these reactions particularly noteworthy in terms of their positive impact on the environment and economics.[96] Mohebbi and co-workers synthesized a novel catalyst composed of Schiff base complexes of transition metal ions, which were supported on magnetic cobalt nanoparticles coated with silica. This heterogeneous catalyst exhibited remarkable selectivity and achieved high yields in converting alcohols to their corresponding aldehydes. The catalyst showed exceptional catalytic performance, demonstrating the selective conversion of alcohols both with and without solvents.[97] Fe(II) and VO(II) based Schiff base complexes synthesized by Godhani et al. were employed as heterogeneous catalysts for the oxidation of cyclohexene in the liquid phase. Remarkably, these catalysts were able to maintain their activity even after being recovered and reused up to three times.[98] A new

Schiff base Mn(II) complex was synthesized by Azar et. al. and then covalently attached to silica-coated magnetic cobalt nanoparticles as support. The resulting catalyst exhibited remarkable catalytic activity in converting alcohols and sulfides into their respective aldehydes and sulfoxides through oxidation.[99] A green catalyst for the solvent-free aerobic oxidation of amines was synthesized by Jain et al. using a Fe(III) Schiff base complex. The Schiff base was prepared using an amino acid-derived ionic liquid and subsequently treated with salicylaldehyde. This resulted in the production of an efficient, reusable, and green Schiff base complex supported by an amino acid-derived ionic liquid. The complex was successfully used in the aerobic oxidation of various benzylamines, aliphatic amines, and secondary amines to produce the corresponding nitriles and imines.[100]

❖ Carbon-carbon coupling reactions are of great importance in organic chemistry as they enable the formation of C-C bonds, which are essential for the synthesis of complex organic molecules. These reactions have revolutionized the field of organic synthesis and have found widespread applications in a variety of fields.

In this context, Schiff base metal complexes have also been used in other carbon-carbon coupling reactions, such as the Suzuki reaction, the Sonogashira reaction, and the Hiyama coupling reaction.

Tamizh and coworkers synthesized some new Ni(II) and Pd(II) complexes incorporating a tridentate Schiff base with ONS donor and triethylphosphite. One of the Ni(II) complexes was identified as a proficient catalyst for Kumada-Tamao-Corriu cross-coupling reaction, while the Pd(II) complex with a salicylaldimine ligand demonstrated high efficiency as a catalyst for Suzuki–Miyaura cross-coupling reaction. The complexes are air and thermally stable, and their key advantage lies in enabling carbon-carbon coupling reactions to synthesize biaryls under aerobic conditions.[101] Two palladium(II) Schiff base complexes were synthesized by Sedighipoor et al. These complexes were employed in the Suzuki reaction of aryl halides, and the findings revealed that both Pd complexes exhibited exceptional conversion rates. The optimized conditions involved utilizing KOH as the base in ethanol at a temperature of 70°C for the Suzuki reaction of aryl halides.[102] B.R. Bhat and colleagues documented the synthesis of a cobalt Schiff base complex that exhibited air stability. They investigated its effectiveness as a catalyst in the Suzuki-Miyaura cross-coupling reaction of aryl halides, employing K_2CO_3 as a base and toluene as the solvent.[103] Saroja et. al. devised a straightforward and efficient method for creating a diverse catalyst by securely attaching a cobalt Schiff base complex to the surface of graphene oxide

functionalized with amino groups. This catalyst was employed in the cross-coupling of aryl boronic acids and aryl halides. Through catalytic experimentation using gas chromatography, it was verified that the Suzuki cross-coupling achieved a remarkable product yield of up to 96.5%.[104] Group of Zaim synthesized a collection of bidentate Schiff bases by condensing aromatic amines with pyridoxal-5'-phosphate that coordinates with palladium ions. These complexes were designed to enhance the stability of palladium ions. The researchers then examined the catalytic performance of the chosen palladium complexes in the Suzuki cross-coupling reaction involving various boronic acids and aryl halides in a mixture of water and ethanol.[105] Two novel Schiff base complexes with tetradentate ONNO ligands were synthesized by Kargar and colleagues, one containing palladium(II) and the other containing nickel(II). The Pd complex was found to be a remarkably efficient homogeneous catalyst for the Suzuki-Miyaura cross-coupling reaction.[106]

I.3.3. Biomedical application

The discovery of the antitumor behavior of cisplatin made by Rosenberg *et. al.* during the 1960s opened up new opportunities for the bio-inorganic chemist to bridge physiology and inorganic chemistry.[107] Gradually, the metal complex began to play a key role in featuring antibacterial, antiviral, antioxidant, and anticancer properties. Schiff bases exhibit chelation properties with donors of O, N, and S, enabling their complexes with metals to possess diverse biological activities against various pathogens and tumors. The imine group present in these compounds is primarily responsible for their numerous biological properties.[108,109]

❖ Due to pathogenic contamination, a significant portion of the population is at risk. The need for a potent therapeutic approach is a contributing factor to this issue. To address this concern, there is a strong push to develop a new generation of antimicrobial drugs with a modified mechanism.[110] One potential solution lies in metal complexes with their ligands, which have shown promising results as antipathogenic agents.

Abid et al. synthesized a few Zr(II), Pd(II), VO(II), Cd(II), V(III), and Rh(III) Schiff base metal complexes and demonstrated remarkable antibacterial activity against both Gram-positive and Gram-negative strains. These findings highlight the potential of these complexes due to their chelating properties.[111]

Similarly, the group of Faeq synthesized metal complexes Cr(III), Cu(II), Fe(III), Ni(II), and Co(II)these metal complexes showed better antibacterial activity than the free ligand. The main reason for this was the complexation of ligands with metals.[112] Abdel-Rahman and

colleagues produced Fe(II) and Cu(II) Schiff base complexes in the nano-scale size range. The antimicrobial activity of these synthesized complexes was evaluated against M. luteus, E. coli, B. subtilis, A. niger, S. cerevisiae, and C. glabrata. The results indicated that the complexes exhibited stronger antimicrobial effects compared to the unbound ligands.[113] Group of Saleem prepared a few Schiff base complexes using Co(II), Fe(III), UO_2(II), and Ni(II) derived from 2-thiophene carboxaldehyde and 2-aminobenzoic acid. These complexes were found to be effective in inhibiting bacterial strains like P. aeruginosa, E coli, and S. pyogenes, indicating their potential use in treating infections caused by these bacteria.[114] Xu et al. conducted a fascinating study in which they utilized Schiff base to imbue cellulose fibers with excellent antibacterial properties. To achieve this, they formed a complex by chelating copper ions with the Schiff base. The resulting complex significantly enhanced the antibacterial efficacy of the cellulose fibers. The antibacterial tests revealed that the cellulose-based Schiff base Cu(II) complex had an inhibition zone width that was 472% and 823% higher than the Schiff base ligand when tested against E. coli and S. aureus, respectively. The remarkable improvement in antibacterial properties could be attributed to the incorporation of copper ions (II) into the complex.[115] A polymeric Cu-Schiff base complex was synthesized by Batool and colleagues, exhibiting distorted cis-octahedral (CuN_2O_4) geometry. The complex displayed noteworthy activity against E. coli.[116] A novel dinuclear copper(II) Schiff base complex was synthesized by Behzad and colleagues. They investigated the antibacterial properties of the complex against human pathogenic bacteria, including Salmonella (sp), Proteus (sp), E. coli, S. aureus, and K. pneumonia. The complex exhibited moderate antibacterial activity against both Gram-positive and Gram-negative bacteria, with the most significant activity observed against K. pneumonia and E. coli.[117] Jai Devi et al. synthesized two Schiff bases and evaluated their organotin and organosilicon complexes for antibacterial activity against K. pneumonia, P. aeruginosa, S. hominis, and S. epidermidis. Several compounds exhibited superior antibacterial activity compared to the standard drug ciprofloxacin.[118]

❖ Schiff base metal complexes have been investigated for their potential use as anticancer and antitumor agents. The mode of activity of Schiff base metal complexes arises from their ability to interact with cellular biomolecules, such as DNA, proteins, and enzymes. These complexes can induce apoptosis, inhibit cell proliferation, and interfere with cell signaling pathways, leading to cancer cell death.

A Cu-Schiff base compound was synthesized by the group of Hajrezaie, which shows promise as a potential candidate for developing novel chemotherapeutic agents derived from metal-based compounds for in vivo and clinical colon cancer studies. The group administered the prepared complex on HT-29 colon cancer cells and noticed a powerful antiproliferative effect on that cell line, with an IC_{50} value of 2.87 µg/mL after 72 hours of treatment.[119]

The antitumor effects of a Schiff base copper coordinated compound synthesized by Xia et. al. was investigated in two gastric cancer cell lines (BGC-823 and SGC-7901) and a mouse model of gastric cancer. The researchers found that the compound caused cancer cell death by inhibiting NF-κB, producing ROS, and inducing autophagy. Notably, the SBCCC demonstrated a lower IC_{50} compared to cisplatin, suggesting its potential as a treatment option with fewer side effects for clinical use.[120]

AM Abu-Dief et al. synthesized Ag(I), Pd(II), VO(II)-Schiff base complex which was analyzed for high cytotoxicity towards various carcinoma cell lines, including HepG-2, MCF-7, and HCT-116.[121] Azam and colleagues prepared a mononuclear Pt(II) Schiff base complex, which was found to possess chemotherapeutic properties against human SW620 and HT-29 cancer cell lines. The real-time cell monitoring xCELLigence system and MTT assay demonstrated that the complex effectively suppressed cell viability and proliferation in a concentration-dependent manner.[122]

Revathi et al. reported the synthesis of Co(II), Cu(II), Zn(II), and Ni(II)-Schiff base complexes using a pyrimidine-based azomethine ligand. The MTT method was used to evaluate the anticancer activity of these complexes against HEp2, NHDF, HeLa, and MCF-7 cell lines. The results indicated that complexes Cu and Co exhibited a modest level of activity against the cancer cell lines compared to the ligand and Ni and Zn complexes.[123]

Li et al. synthesized an array of water-soluble platinum(II) complexes employing amino acid Schiff bases that had been reduced to explore their viability as anticancer agents. They evaluated the interaction of these compounds with salmon sperm DNA and their efficacy in inhibiting cancer cell growth in vitro by performing MTT assays on BGC-823, Bel-7402, KB, and HL-60 cell lines. One of the complexes exhibited superior cytotoxicity compared to cisplatin against HL-60 and BGC-823 cell lines and demonstrated similar cytotoxicity against the Bel-7402 cell line.[124]

A group of researchers, led by Patterson, synthesized 12 novel Pt-Schiff base complexes using various amines and salicylaldehyde. The complexes were then tested for in vitro cytotoxicity against three different human glioma cell lines (Hs683, LN405, and LN18). The

findings indicated that there was a positive correlation between cytotoxicity in all cell lines and the presence of new aromatic rings in the complexes as well as the length of the aliphatic group. The team believes that these organometallic complexes have the potential to serve as the promising onset for the fabrication of new therapeutic strategies for treating brain tumors.[125] Tan et al. synthesized and characterized multiple azomethine Sn(IV) complexes containing substituted salicylaldehydeo-aminophenol azomethine ligands. These compounds were then tested for their anticancer activity against NCIeH460, Hela, MCF7, Colo205, and HepG2 cancer cells. Interestingly, the organotin complexes displayed remarkable anticancer activity, surpassing that of carboplatin, while the ligand alone did not exhibit such effects.[126] Three novel manganese and copper Schiff base complexes were synthesized by Chang et al. and were found to exhibit significant cytotoxicity against cancer cell lines (MDA-MB231, A549, and HepG2) in vitro. The level of cytotoxicity observed was even greater than that of cisplatin.[127]

❖ Metal-based antioxidants have emerged as promising contenders in safeguarding living cells against oxidative stress due to their superior efficacy. Synthetic antioxidants have surpassed their natural counterparts in popularity due to their greater productivity and affordability. Extensive research has been conducted on various Schiff bases metal complexes, demonstrating their effectiveness as efficient scavengers of reactive oxygen species (ROS).

Reddy et al. reported on the antioxidant properties of bi-metallic Schiff base complexes containing Co(II), Zn(II), Cu(II), U(IV), and Ni(II). The study investigated the in vitro effects of these compounds using various assays, including NO DPPH, reducing power, and hydroxyl radical scavenging.[128] Akila et al. successfully prepared Schiff base complexes of VO(II), Cu(II), and Ni(II) through synthesis. These metal complexes were subjected to DPPH activity testing, and the results indicated their notable effectiveness. Moreover, the experiments revealed that the complexes displayed significant efficacy in inhibiting the formation of DPPH radicals, as evidenced by their lower IC_{50} values in antioxidant assays. These findings highlight the complexes' distinctive and selective ability to scavenge radicals, suggesting their potential as drug candidates for radical removal.[129] Gulcan and colleagues provided a description of the unique characteristics exhibited by six coordination M(II) Schiff base complexes. These complexes were assessed for their antioxidant properties, including activities such as reducing power, chelation of ferrous ions, and scavenging of DPPH free radicals, in comparison to Trolox and ascorbic acid. The experimental findings

revealed that the scavenging effect is concentration-dependent, with a higher concentration leading to a greater proportion of radical scavenging.[130] Tadavi et al. conducted the synthesis of several metal complexes with Schiff bases and evaluated their antioxidant properties compared to ascorbic acid. Compared to the unbound ligand, the metal complexes exhibited greater scavenging activity.[131]

I.3.4. Application in Optoelectronics and energy materials

Schiff base metal complexes have been extensively studied for their potential applications in optoelectronics and energy materials. These complexes exhibit interesting electronic and optical properties, which renders them attractive for a variety of optoelectronic applications, such as solar cells, light-emitting diodes (LEDs), and sensors.

❖ Organic Light Emitting Diodes (OLEDs) are energy-saving displays and light sources, as they do not require a backlight for displays and contribute significantly towards energy conservation. The emission properties of Schiff base metal complexes can be tuned by varying the metal center and the substituents on the ligand, which makes them attractive for use in OLEDs. The complexes can also be designed to have high thermal stability and good solubility in organic solvents, which are important properties for their use in device fabrication.

Schiff base complexes of Pt(II) are well recognized as effective dopants due to their excellent environmental durability.[132] Zhou et. al. prepared a few complexes of Pt(II) Schiff base that are sterically hindered. One of these complexes displays red emission, having a high quantum yield of 0.29. This complex was utilized in making organic light-emitting diodes and achieved high current efficiency at high brightness.[133] These complexes exhibit yellow to red light emissions, with the most efficient one having a quantum yield of 8.6%.[134] Zhang et. al. successfully synthesized and characterized a group of Pt(II)-Schiff base complexes. The emission of light from these complexes in the solid state varies from green to orange, depending on the electron-donating or -withdrawing groups that are present. The authors were able to construct OLEDs that emit light from blue to orange with moderate efficiency values.[135]

Additionally, Schiff base complexes of zinc and nickel with conjugated polymers have emerged as promising active materials for OLED fabrication.[136,137]

Gusev et al. prepared a structurally rigid Zn-Schiff base complex which showed blue emission with a quantum yield of 70.4%.[138]

Comparably, Gondia et al. created a complex of Zn-Schiff base that possesses the ability to function as an active material with a wide band gap, thereby facilitating the production of violet OLEDs with increased device efficiency.[139] A polymetallic Mn(III)-Fe(III) Schiff base complex was synthesized by Donmez and colleagues. The complex displayed a cyan-blue hue and has the potential for application as a functional material in OLEDs.[140] The team of Chan and colleagues introduced a tungsten (W) Schiff base complex that functions as a thermally activated delayed fluorescence (TADF) emitter. This TADF emitter was utilized in a green OLED and demonstrated a remarkable Quantum Yield of up to 84%.[141]

❖ One of the most promising applications of Schiff base metal complexes is in organic solar cells. These complexes can be used as electron donors or acceptors in organic solar cells, due to their high molar absorptivity and good charge transport properties. Additionally, they can be easily synthesized and modified to improve their photovoltaic properties. They found that when [M(Schiff)], a Schiff base ligand coordinated with a metal ion, is used as a sensitizer, the excited state of the complex can rapidly transfer electrons to the band zone of TiO_2 (titanium dioxide) rather than reacting with oxygen. This efficient electron transfer process can potentially be utilized in the design of new photoelectrochemical devices for solar energy conversion.[142] Nine new complexes of transition metals (M = Zn, Cd, and Hg) were created by Dong et al. Among these complexes, the Zn3/N719 device demonstrated a superior J_{sc} of 16.59% mA cm^{-2}, resulting in an overall conversion efficiency of 6.94%. This efficiency was approximately 36% higher than that of devices sensitized with single N719/TiO_2. These findings suggest that the developed complexes have significant potential for use in DSSC applications.[143] Babadi and colleagues synthesized a new Schiff base cobalt complex and also demonstrated its novel application as a redox mediator system in dye-sensitized solar cells. The complex's high redox potentials make it highly promising for increasing the voltage of solar cells.[144] Tian et al. utilized several Schiff base metal complexes as secondary electron acceptors for dye sensitizers in dye-sensitized solar cells (DSSCs) to assess their impact on photovoltaic performance. They measured the power conversion efficiency (PCE) and short-circuit photocurrent density (Jsc) of these complexes. The Jsc and PCE values of the four polymeric metal complexes exhibited a decreasing trend. This phenomenon can be attributed to two factors: the varying strength of the coordination

bond formed between the metal ion and ligand, influenced by the metal ion's charge number and radius, and the superior electron-donating capability of BDTT.[145]

Overall, synthetic ligands are important tools in chemistry for understanding the properties and functions of molecules and developing new materials and drugs. Overall, synthetic ligands are powerful tools in the field of chemistry that allow scientists to selectively target specific molecules, opening up a world of possibilities for the development of new drugs, materials, and technologies.

I.4. Commercial Ligand

Bipyridines and Phenanthrolines belong to a typical class with nitrogen donor-based chelating ligands. They are used as ligands in coordination chemistry, where they can bind to metal ions to form coordination complexes. Their binding process with metals is entropically favored for these chelators.

Bipyridine (or 2,2'-bipyridine) has a molecular formula of $C_{10}H_8N_2$ and consists of two pyridine rings that are linked together by a carbon-carbon bond. Bipyridine is a colorless solid that readily dissolves in organic solvents.

Phenanthroline (or 1,10-phenanthroline) has a molecular formula of $C_{12}H_8N_2$ and consists of two fused benzene rings that are linked together by two nitrogen atoms. Phenanthroline is a yellow crystalline solid that is soluble in organic solvents. Both bipyridine and phenanthroline have similar structures and properties and are often used interchangeably as ligands in coordination chemistry. However, there are some differences in their reactivity and selectivity towards certain metal ions, which can make them better suited for specific applications. These kinds of ligands are advantageous in terms of Convenience as they provide a convenient option for researchers to eliminate the need for time-consuming synthesis and purification processes. Also, they offer greater reproducibility compared to individually synthesized ligands.

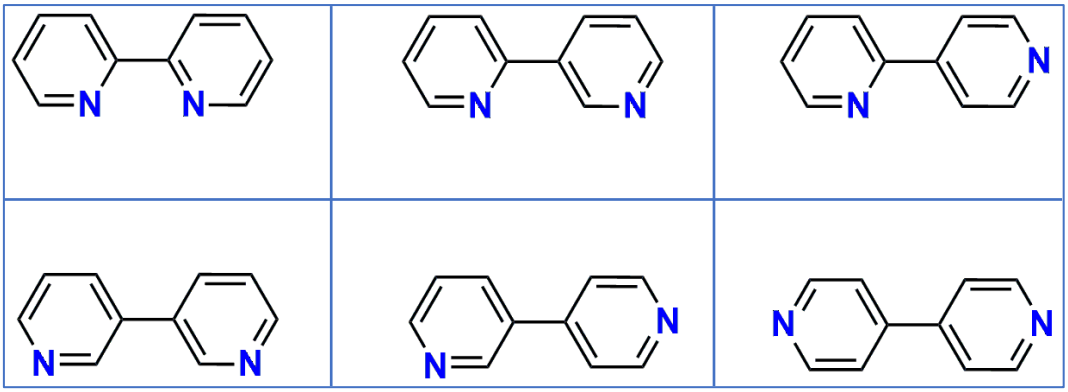


Fig I.3 Different isomers of bipyridine

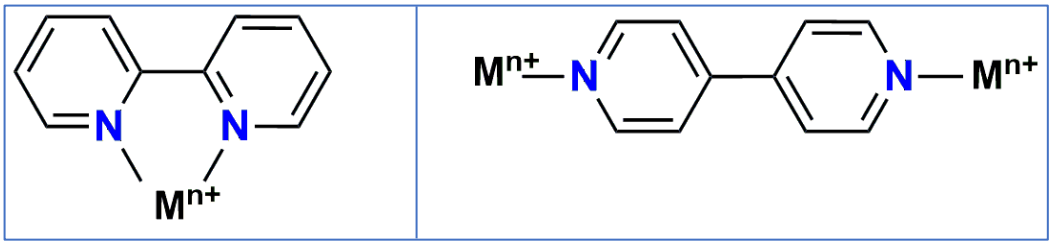


Fig I.4 Most probable binding motifs of bipyridine

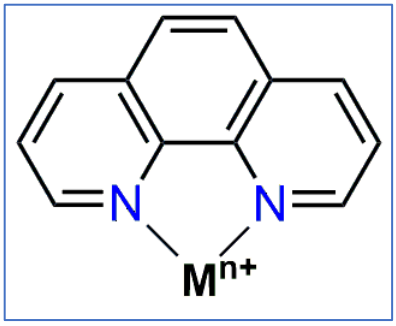
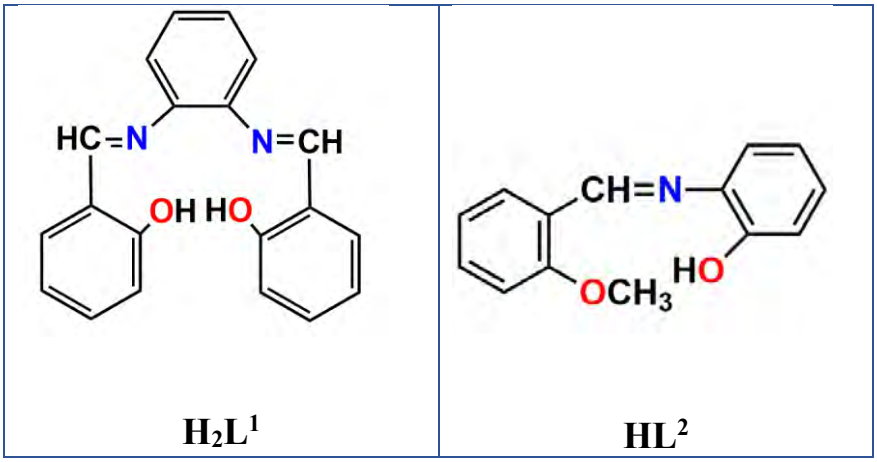


Fig I.5 Binding mode of phenanthroline with metals

In this context, A range of hybrid d-f block type metal complex salts has been developed by us with the incorporation of (N, N)-donor ligands e.g., bipyridine and phenanthroline as commercially available ligand which shows excellent charge transport properties.

We also synthesized and characterized a few Cu, Zn, and Pd complexes with (N, O) donor-based synthetic Schiff base ligands, namely, 2,2'-((1,2-phenylenebis(azanylylidene))bis(methanylylidene))diphenol [$\mathbf{H_2L^1}$], 2-(2-methoxybenzylideneamino)phenol [$\mathbf{HL^2}$].



Scheme I.3 Schematic presentation of the prepared ligands

I.5. Scope and objective of the present study

The primary focus of this study is to devise, synthesize, and employment of spectroscopic analysis of various novel coordination assemblies. Additionally, the research explores their properties and potential applications in several catalytic transformations. The dissertation's central theme can be summarized as follows:

(i) Employing a rational approach to design and synthesize ligands and novel coordination compounds.

(ii) Thoroughly characterizing these compounds using diverse analytical techniques.

(iii) Utilizing X-ray structures to examine the synthetic compounds and their supramolecular frameworks, thereby revealing the primary and secondary coordination zones as well as non-covalent interactions.

(iv) Utilizing spectroscopic findings and computational calculations to elucidate the stereochemical, geometrical, and electronic structures of these previously unknown compounds.

(v) Investigating various bio-inspired oxidation reactions, such as Phenoxazinone Synthase, and Catechol Dioxygenase Activity.

(vi) Assessing the catalytic activity of both the newly formulated and previously reported coordination compounds through comparison.

(vii) Examining the potential antimicrobial effects on a range of detrimental pathogens.

The references in my Ph.D. thesis are organized in the following format:

author names, abbreviated journal name (in italics), year, volume number (bold), and page/article number. e.g.,

S. Mahato, N. Meheta, M. Kotakonda, M. Joshi, M. Shit, A. R. Choudhury and B. Biswas, *Polyhedron*, 2021, **194**, 114933.

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