Chapter I

General Introduction

The divulgence of the close connection between biology and inorganic chemistry made a distinct discipline called bioinorganic chemistry. The application of superior spectroscopic tools and revolutionary high-resolution image-processing instruments has flourished in this field. New and exciting interdisciplinary research has been done since then. Specifically, the role of metal ions in this field is irrefutable. Metal ions are indispensable for nourishing life and can be considered the protagonists 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 applied 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.

Again, Metal complexes are an essential class of compounds with a wide range of applications in various fields. The scientific literature on this topic is vast and constantly growing to unearth new applications and properties of these fascinating compounds. Their incorporation in ailments ranging from microbial infections to cancer treatment is significant.[11-16] However, the journey from their invention to commercialization is time-consuming and goes through a series of regulatory obstacles to get government approval. Therefore, the prudent designing of metallo-therapeutics remains difficult for bioinorganic chemists. A literature survey suggests that the ability of metal complexes to activate and stabilize reactive intermediates makes them an impeccable candidate for catalysis in various organic reactions.[17-23] One of the most fascinating features of metal complexes is their underlying flexibility, which forms multiple structures. This property has drawn the attention of part of the modern scientific community to apply it in designing various functional materials.[24] Their application 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 escalating human civilization to the next level. Moreover, they are positively impacting our environment through pollution control, soil remediation [37], and water purification.[38-41]

Finally, metal complexes are an essential class of compounds with various applications in various fields. The scientific literature on this topic is vast and constantly growing as new applications for metal complexes are discovered.

1.1 Ligands and Chelators

In 1916, Alfred Stock first coined the term "ligand" in the context of silicon chemistry, deriving it from the Latin word "ligare," meaning "to bind or tie." The term was later used by H. Irving and R.J.P. Williams in their paper published in Nature, describing 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 chemical entity that binds to metal ions through coordination bonds. Coordination bonds are formed between a metal ion and a molecule that can be a neutral or an ion that attaches to the central atom by donating 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, varying in size and shape. These can be classified into different 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

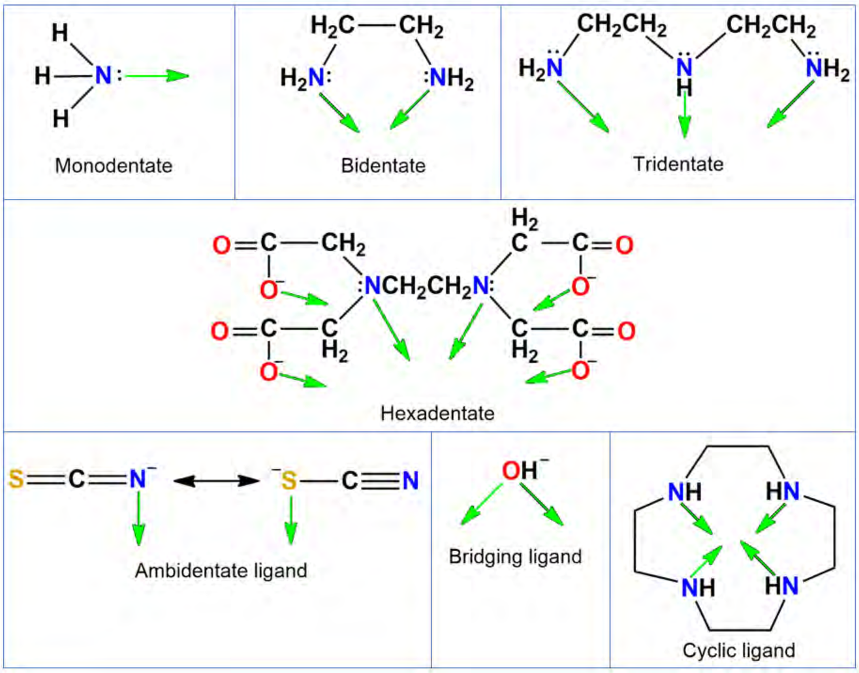


Fig 1.1 Different types of ligands

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

Denticity originates from the Greek word “dentis,” meaning tooth. So, the number of bites/bonds from the ligand to the central atom is known as its denticity. Notably, the words chelator and chelating ligand are general terms used to refer to these ligands. The primary concept of chelation is based on pure coordination chemistry. The term chelate was first used by Morgan and Drew in 1920. They depicted it as “caliper-like groups which function as two associating units and fasten to the central atom to produce heterocyclic rings.”[43]

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

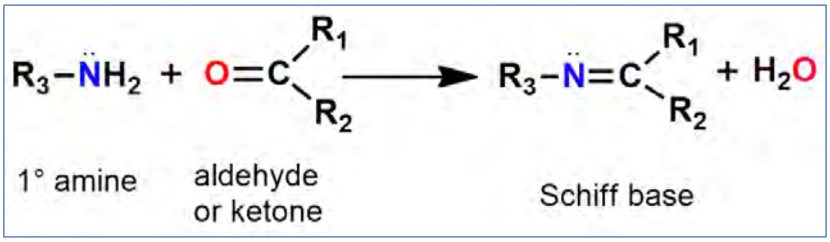
Commercial ligands are available for purchase from chemical suppliers e.g., EDTA, Phenanthroline, Bipyridine, Dipicolinic acid, Nitrilotriacetic acid, etc. These ligands are less specialized than synthetic ones and are used in various settings, such as in catalysis, separation technologies, and industrial-scale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

Synthetic ligands are designed and synthesized by chemists in standard laboratory settings. These ligands are typically used in academic research to explore 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 occurs via different donor sites of ligands, e.g., O-donor, N-donor, S-donor, and so on.[44]

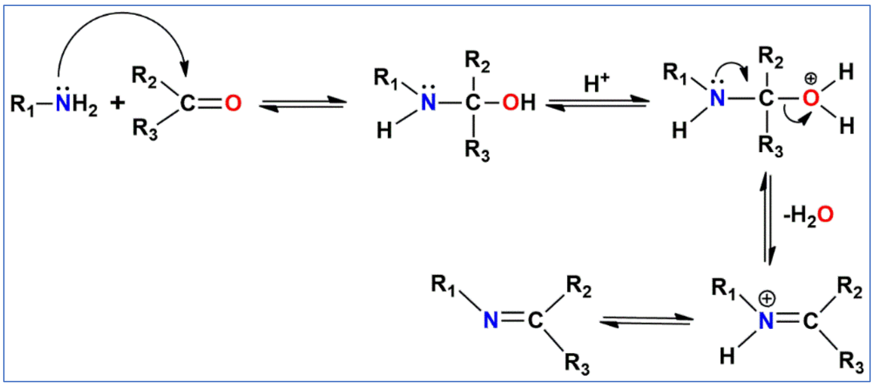
In order to maintain coherence with the subject matter explored in this thesis, I focussed on the ligands having (N, O) and (N, N)-donor sites, specifically Schiff base ligands and some commercially available ones, e.g., bipyridine, phenanthroline.

1.2 Schiff base ligands

These ligands are considered privileged ligands as their preparation involves simple condensation. However, 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 efficiently designed to coordinate different metal ions in a variety of oxidation states and coordination numbers. $R_2C=NR'$ ($R' \neq H$) is typically the formula of Schiff base. Azomethine Group ($R-CH=NR'$ where $R' \neq H$) is determined by the carbonyl group and amino group mixture. The simple synthesis and utility value process pave the way for an extensive and vital 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 of widespread interest. It is studied by inorganic chemists, physical and organic chemists, biochemists, pharmacologists, molecular biologists, and environmentalists.



Scheme 1.1 Preparative route of Schiff base synthesis



Scheme 1.2 Mechanistic route of Schiff base formation

A carbon-nitrogen double bond is found in the bases.[46] The nitrogen atom in the imine group has a lone pair of electrons 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 used as medications. Different metal ions can organize with them to form 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 to develop Schiff bases from the carbonyl group. It is essential that the imine bond ought to be kept from hydrolysis and subsequently should be dry.

I.3 Application of Schiff base metal complexes

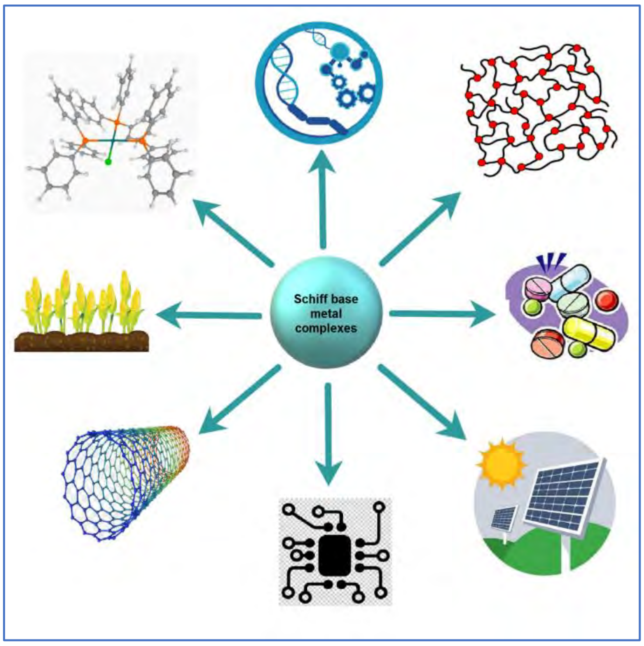


Fig 1.2 Versatile applications of Schiff base metal complexes

1.3.1 Application in Biology

Schiff base metal complexes have been found to play paramount roles in biology, including catalysis of enzymatic reactions, transport of metal ions across cell membranes, and regulation of gene expression. Numerous Schiff base ligands and their complexes were studied due to their remarkable and significant characteristics, including mimicking bio enzymes, reversible oxygen binding, and their ability to bind with certain toxic 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 having metals, act as natural factories that exhibit both chemo- and stereo-selectivity, allowing them to catalyse 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 produce harmful metabolites known as reactive oxygen species (ROS), like superoxide anion and hydrogen peroxide. 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 mimetic properties.[49] Darr et al., Faulkner et al., and Riley et al. also synthesized a few manganese base complexes showing such activities.[50, 51, 52] Later, Mn-sales and Mn-cyclic salen-crown ether complexes synthesized by Baundry and co-workers proved 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 Co(II), Ni(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 and 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 of dehydroacetic acid. This complex shows excellent potential as a superoxide dismutase, with an IC_{50} value of 69 μM.[60] Zhang et al. synthesized a series of Mn(III)/Co(III)/Fe(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)/Cu(II)/Ni(II) complexes and studied SOD activity. The results of their experiments suggested that the Mn(III) complexes exhibit the highest activity level, while the Ni(II) complexes show the lowest activity. Upon binding with BSA, the SOD activity of the Mn-complex was enhanced. The researchers inferred that the BSA molecule could have a favorable impact on the SOD activity of specific complexes. There is much room for developing 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 other transition metals, such as Cu [63, 64], Fe [65], and V [66], has also been examined for their SOD and catalase-like properties. Jacob et al. discovered that some Cu salen complexes can break down H2O2 at rates similar to those of natural enzymes when enclosed within zeolites.[67]

- In plant cell vacuoles and cytoplasm, Catechol exists in low amounts. However, when bacterial or fungal diseases damage plant tissues, Catechol is released and transformed into ortho-quinone by catecholase. This natural antiseptic plays a vital role in the plant's defense mechanisms. Catecholase activity is operated by a catechol oxidase protein, with an active site of type III that contains two copper atoms and can catalyze the oxidation of various o-diphenols, also known as catechols, to produce o-quinones. This enzymatic activity has also been modeled in vitro with several biomimetic copper complexes and iron complexes using aerial oxygen as a naturally viable oxidant, which is immensely important in economic and environmental issues.

Anbu et al. synthesized A Schiff base type copper(II) compound that is cheap, 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 tridentate Schiff base ligand with (N, N, O) donor atoms derived from pyridoxal. One of these complexes exhibited exceptional activity as a catecholase.[69]

Das et al. prepared two new Cu(II) complexes of a Schiff base ligand containing a flexible piperazinyl moiety exhibiting catechol oxidation activity.[70] Group of D. Das designed three distinct mononuclear Mn(II) complexes using an "end-off" 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) complex with di-compartmental Schiff base ligand 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 to 3,5-di-tert-butylquinone under aerobic conditions.[73]

❖ The biosynthesis of actinomycin D involves several steps, and the enzyme phenoxazinone synthase catalyzes the final step. Also, this enzyme is responsible for the oxidative coupling of 2-aminophenol to the phenoxazinone chromophore, which is a crucial component of actinomycin D. The phenoxazinone chromophore is an essential component of actinomycin D because of its ability to intercalate into DNA and inhibit RNA synthesis. Without the phenoxazinone chromophore, actinomycin D could not 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 developing reactions that aim to mimic the bio functions of metalloenzymes.[74, 75, 76]

Chatterjee et. al. developed one polymeric and one dinuclear Fe(III) complex using an (O, N, N, O) donor Schiff base ligand. These complexes exhibit remarkable catalytic activity in oxidizing 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) complexes supported by Schiff base N3 donor ligands with varying donor moieties. The researchers investigated the phenoxazinone synthase-like activities of all three complexes by studying the oxidation of 2-aminophenol (H_2AP) to 2-amino-phenoxazine-3-one (APX) in a methanol-water (pH 8.6) 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-(substrate radical)" intermediate responsible 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. Further, the impact of ancillary ligands, namely chloride and nitrate, on the catalytic activity of the bio-mimics of phenoxazinone synthase was also investigated. 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) centre.[81] Interestingly, Ghosh and colleagues successfully developed two trinuclear heterometallic complexes by utilizing a previously prepared copper complex as a metal ligand 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) centre 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 action resulted in the production of H_2O. [82]

I.3.2 Application in catalysis

Attaching different substituents to the ligand in Schiff base metal complexes can alter the coordination centre's environment and give a valuable range of steric and electronic properties. This fine-tuning of structure and reactivity is crucial. The metal complexes formed by Schiff bases involving p-block and d-block metals can act as effective catalysts in various syntheses and other valuable 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 series of mononuclear asymmetric Cu(II) Schiff base complexes with the help of five salicylaldehyde derivatives. These complexes catalyse metal-coordinative polymerization of methyl methacrylate to form synbio-enriched PMMAs (poly(methyl methacrylates) in the presence of AIBN. Astonishingly, 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 (ROP) of L-lactide (L-LA). The polymerization process was well-controlled, producing 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 using these complexes as catalysts. The neodymium complex 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] Using alkaline-earth metal complexes of Schiff bases in the ring-opening polymerization (ROP) of cyclic esters has shown great potency as a catalyst. These metals are abundant in the earth's crust and 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. These complexes were also tested as catalysts 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 magnificent controllability.[93]

❖ In organic chemistry, oxidation reactions are some of the most significant ones. 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 areas 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 results.[94] The group of Maurya studied four dioxide molybdenum(VI) complexes that have been used as catalysts for the homogeneous oxidation of secondary alcohols, using 30% H_2O_2 as an oxidant. Under the optimized reaction conditions, secondary alcohols gave high yields of the respective ketones.[95] An oxovanadium (IV) Schiff base complex was synthesized by Manatí et al., demonstrating exceptional catalytic activity for converting various sulfides to their corresponding sulfones without needing a solvent. Utilizing H_2O_2 as an oxidizing agent and excluding a solvent make these reactions particularly noteworthy regarding their positive impact on the environment and economics.[96] A new type of catalyst consisting of Schiff base complexes of transition metal ions supported on silica-coated magnetic cobalt nanoparticles was synthesized by the Mohebbi group. 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 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 liquid-phase oxidation of cyclohexene. Remarkably, these catalysts could maintain their activity even after being recovered and reused thrice.[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 treated with salicylaldehyde, producing 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 benzylamines, aliphatic amines, and secondary amines to produce the corresponding nitriles and imines.[100]

- Carbon-carbon coupling reactions are important in organic chemistry as they enable the formation of C-C bonds, which are essential for synthesizing complex organic molecules. These reactions have revolutionized the field of organic synthesis and have found widespread applications in various areas.

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

Tamizh and co-workers synthesized some new Ni(II) and Pd(II) complexes incorporating a tridentate Schiff base with ONS donor and triethylphosphite. One Ni(II) complex was identified as a proficient catalyst for the Kumada-Tamao-Corriu cross-coupling reaction. In contrast, the Pd(II) complex with a salicylaldimine ligand demonstrated high efficiency as a catalyst for the Suzuki–Miyaura cross-coupling reaction. The complexes are air and thermally stable, and their crucial 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 applied 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 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 efficacy 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 cross-coupling aryl halides and aryl boronic acids. Catalytic experimentation using gas chromatography verified that the Suzuki cross-coupling achieved a notable 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 aryl halides and boronic acids in a mixture of water and ethanol (H_2O/EtOH).[105] Two novel Schiff base complexes with tetradentate ONNO ligands were synthesized by Kargar and colleagues, one containing palladium(II) and the other nickel(II). The Pd complex was a highly effective homogeneous catalyst for the Suzuki-Miyaura cross-coupling reaction.[106]

1.3.3 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 started to play a vital 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 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 contributes to this issue. There is a strong push to develop a new generation of antimicrobial drugs with a modified mechanism to address this concern.[110] One potential solution lies in metal complexes with their ligands, which have shown promising results as antipathogenic agents.

Zr(II), VO(II), Pd(II), V(III), Cd(II), and Rh(III) Schiff base metal complexes were synthesized by Abid et al. 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), Ni(II), Fe(III), and Co(II). These metal complexes showed better antibacterial activity than the free ligand. The leading cause for this was the complexation of ligands with metals.[112] Abdel-Rahman and colleagues produced Cu(II) and Fe(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 more substantial antimicrobial effects than the unbound ligands.[113] Group of Saleem prepared a few Schiff base complexes using Fe(III), Co(II), Ni(II), and UO_2(II) derived from 2-thiophene carboxaldehyde and 2-aminobenzoic acid. These complexes were effective in inhibiting bacterial strains like Escherichia coli, Pseudomonas aeruginosa, and Staphylococcus 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. They formed a complex by chelating copper ions with the Schiff base to achieve this. The resulting complex significantly enhanced the antibacterial efficacy of the cellulose fibres. The antibacterial tests revealed that the cellulose-based Schiff base-Cu(II) complex had an inhibition zone width of 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 incorporating 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 new 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 Escherichia coli, Klebsiella pneumonia, Salmonella (sp), Proteus (sp), and Staphylococcus aureus. The complex exhibited moderate antibacterial activity against 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 signalling 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. were investigated in two gastric cancer cell lines (SGC-7901 and BGC-823) 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 IC50 than 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 HCT-116, MCF-7, and HepG-2.[121] Azam and colleagues prepared a mononuclear Pt(II) Schiff base complex, which was found to possess chemotherapeutic properties against human HT-29 and SW620 colorectal cancer cell lines. The MTT assay and real-time cell monitoring xCELLigence system demonstrated that the complex effectively suppressed cell viability and proliferation concentration-dependent.[122]

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

Li et al. prepared a range of water-soluble platinum(II) complexes using reduced amino acid Schiff bases to investigate their potential 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 HL-60, KB, BGC-823, and Bel-7402 cell lines. One of the complexes exhibited superior cytotoxicity compared to cisplatin against BGC-823 and HL-60 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 tested for in vitro cytotoxicity against three human glioma cell lines (Hs683, LN405, and LN18). The results revealed that the presence of new aromatic rings in the complexes and the length of the aliphatic group were positively correlated with cytotoxicity in all cell lines. The team believes that these organometallic complexes have the potential to serve as promising starting points for the development of new therapeutic strategies for treating brain tumors.[125] Tan et al. synthesized and characterized multiple azomethine Sn(IV) complexes containing substituted salicylaldehyde-aminophenol azomethine ligands. These compounds were 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 three cancer cell lines (HepG2, MDA-MB231, and A549) 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 and their metal complexes, demonstrating their effectiveness as efficient reactive oxygen species (ROS) scavengers.

Reddy et al. reported on the antioxidant properties of bi-metallic Schiff base complexes containing Zn(II), Co(II), Cu(II), Ni(II), and U(IV). 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 described 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, compared to Trolox and ascorbic acid. The experimental findings revealed that the scavenging effect is concentration-dependent, with a higher concentration leading to a more significant proportion of radical scavenging.[130] Tadavi et al. synthesized several metal complexes with Schiff bases and evaluated their antioxidant properties compared to ascorbic acid. The metal complexes demonstrated higher scavenging activity in comparison to the unbound ligand.[131]

1.3.4 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 make them promising candidates for various optoelectronic devices 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 centre 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 essential 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 increased 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. In the solid state, these complexes emit light ranging from green to orange, depending on the electron-withdrawing or -donating groups 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 Zn-Schiff base complex that can 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 could be applied as a functional material in OLEDs.[140] The team of Chan and colleagues introduced a tungsten (W) complex containing a Schiff base 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 Schiff base metal complexes' most promising applications is organic solar cells. Due to their high molar absorptivity and good charge transport properties, these complexes can be used as electron donors or acceptors in organic solar cells. 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 designing 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 devices sensitized with single N719/TiO_2. These findings suggest that the developed complexes have significant potential for DSSC applications.[143] A new Schiff base cobalt complex was synthesized by Babadi and colleagues, who 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 auxiliary electron acceptors for dye sensitizers in dye-sensitized solar cells (DSSCs) to assess their impact on photovoltaic performance. They measured these complexes' short-circuit photocurrent density (Jsc) and power conversion efficiency (PCE). 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 essential tools in chemistry for understanding the properties and functions of molecules and developing new materials and drugs. Overall, synthetic ligands are potent tools in chemistry that allow scientists to selectively target specific molecules, opening up a world of possibilities for developing new drugs, materials, and technologies.

1.4 Synthetic and commercial ligand

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

Bipyridine (or 2,2'-bipyridine) has a molecular formula of $C_{10}H_8N_2$ and consists of two pyridine rings linked together by a carbon-carbon bond. Bipyridine is a colorless solid that is soluble 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 linked 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, some differences in their reactivity and selectivity towards certain metal ions can make them better suited for specific applications. These ligands are advantageous because they provide a convenient option for researchers to eliminate the need for time-consuming synthesis and purification processes. Also, they offer more excellent reproducibility compared to individually synthesized ligands.

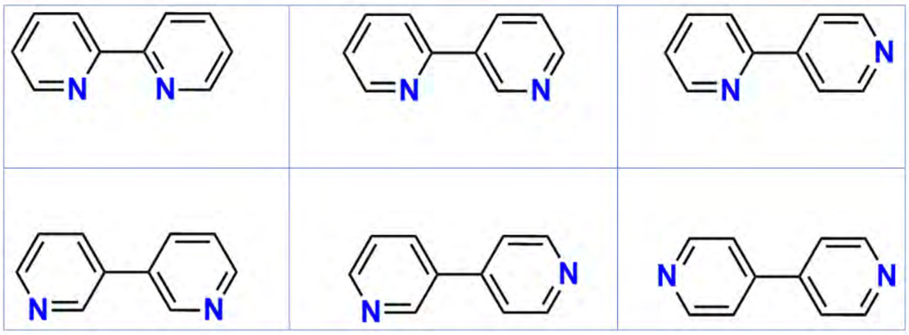


Fig 1.3. Different isomers of bipyridine

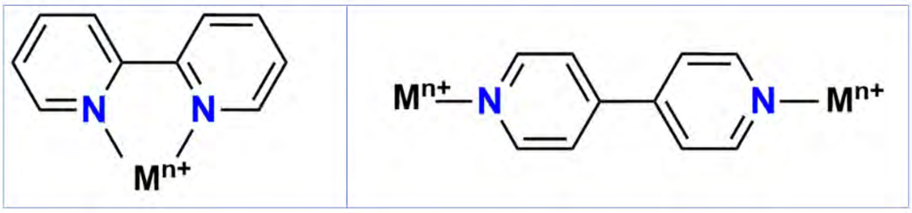


Fig 1.4 Most probable binding motifs of bipyridine

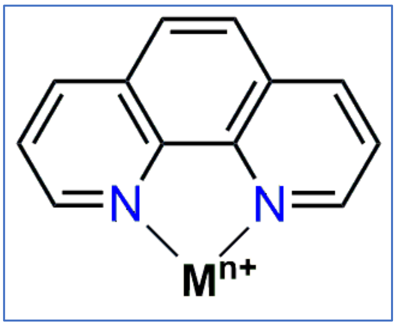
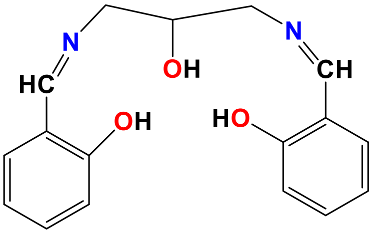


Fig 1.5 Binding mode of phenanthroline with metals

In this context, we have developed a series of metal complex salts of the novel hybrid d-f block type, incorporating (N, N)-donor ligands e.g., bipyridine and phenanthroline as commercially available ligands, which show excellent charge transport properties.

We also synthesized and characterized a few Fe, Zn and Pb complexes with a (N, O) donor-based synthetic Schiff base ligand, namely, 2,2'-((1Z,1'Z)-((2-hydroxypropane-1,3-diyl)bis(azaneylylidene))bis(methaneylylidene))diphenol [$\mathbf{H_2L^1}$], including 1,10-phenanthroline, and 2,2’-bipyridine.



Scheme 1.3 Schematic presentation of the prepared ligand

I.5 Scope and objective of the present study

The primary focus of this study is to devise, synthesize, and apply 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 and non-covalent interactions.

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

(v) Investigating various bio-inspired oxidation reactions, such as Phosphatase, and Catecholase Activity.

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

The references in my PhD 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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