Chapter I

General Introduction

In bioinorganic chemistry, one of the most fascinating areas is the interaction of metal ions with biological molecules.[1-3] Most of the periodic table metals are capable of the development of smart coordination compounds with functional promiscuities. Typically, a metal ion or central metal ion binds with suitable ligands (molecules or anions) to produce a new chemical entity with specific geometry.[4] The coordination compounds play a crucial role in natural processes and living systems.[5-7] Some bio-metal ions are essential to maintain human homeostasis and also play key roles in different natural processes by acting as cofactors in the proteins' function thereby resulting in the stabilization, regulation and completion courses of cellular functions.[8-11] Chlorophyll, heme proteins, carbonic anhydrase, nitrogenase, vitamin B_{12} etc. are some of the important examples to understand their indispensable role in the living world.[12-18] Therefore, the design and development of bio-inspired coordination compounds gain a huge interest in the scientific community.[19-21]

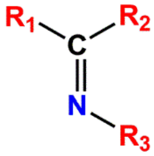
Further, metal complexes are considered an intriguing class of metallo-therapeutics for the treatment and diagnosis of simple to complex diseases. [22-24] Therefore, the design of metallo-therapeutics remains one of the challenging issues in inorganic medicinal chemistry. Literature survey suggests that the metal complexes show crucial molecular and biological properties.[25-28] Nevertheless, metal complexes exhibit a wide range of reactivities, structural flexibility and various applications like in the development of powerful magnets, optoelectronics, smart catalysts, emerging energy harvesting materials, potential therapeutics etc.[29-33] These properties of coordination compounds led to the recent development of functional materials of scientific and industrial significance. It is well documented that commercially available and synthetic ligands play a pivotal role in the synthesis of smart coordination compounds.[34-36] Among the different classes of ligands, Schiff base marks a distinctive impact on the scientific community.

1.1. Schiff bases

Schiff base was first prepared by the German Chemist, Hugo Schiff in 1864 and it was named so.[37] Schiff bases are polydentate chelators having azomethine (–C=N–) functional group with a wide range of important applications in many disciplines in science including medicinal science, biological sciences, optical sciences, physical sciences, material sciences and so on.[38]

1.2. Structure and physicochemical properties of Schiff base

Schiff base contains an azomethine chromophore which exhibits an interesting structural feature towards metal ions.[39] **Scheme 1.1** presents the structural backbone of a substituted Schiff base.

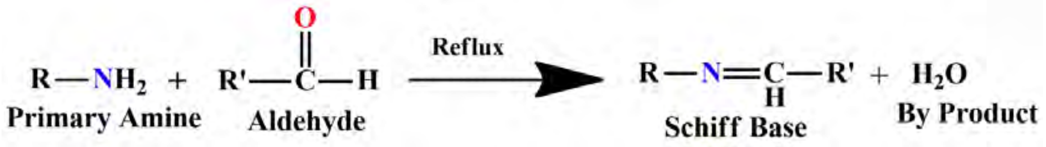


Scheme 1.1. Structural backbone of Schiff base

(R_1, R_2 and R_3 are the substituents)

Schiff bases are weak bases and are simply hydrolysed by dilute mineral acids, but not by aqueous alkali. They also form insoluble salts with strong acids through the coordination of the electrons on the nitrogen atom of the azomethine group.[40] Typically, π-conjugated aromatic aldehydes form highly stable Schiff bases, while aliphatic aldehyde mediated Schiff bases are found to be less stable. Aliphatic Schiff bases tend to polymerize and are difficult to isolate.[41] Generally, aldehydes effortlessly form Schiff base ligands than the ketones as the former exists in sterically less hindered geometry, in contrast, the later contributes more electron density causing less electrophilicity to the azomethine carbon.[42]

Hugo Schiff reported the preparation of Schiff base through the condensation of primary amines and active carbonyl groups under azeotropic distillation [43] followed by the removal of water, thus formed in using molecular sieves.[44] In the 1990s, dehydrating solvents like tetramethyl orthosilicate or trimethyl orthoformate were used to eliminate water.[45,46] In 2004, Chakraborti *et al.* reported the design of Schiff base compounds by the use of highly electrophilic carbonyl compounds and strongly nucleophilic amines. They also reported the Lewis acids or Bronsted-Lowry acid catalysed-condensation of the carbonyl groups and amines, followed by the elimination of water in the final step.[47] In the past decades, many innovations and new techniques have been reported to prepare the Schiff base including solvent-free irradiation.[48-51] **Scheme 1.2** shows the general method for the synthesis of Schiff bases.

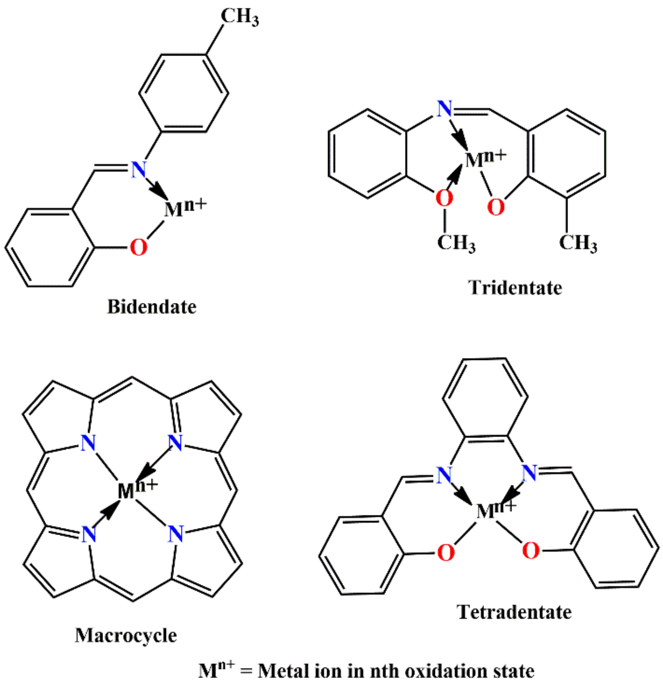


Scheme 1.2. Synthesis of Schiff base

Mechanistically, two steps are involved for the synthesis of the Schiff base (**Scheme I.3**). In the first step, the azomethine nitrogen makes a nucleophilic attack to the carbonyl-C. In the second step, the secondary nitrogen of carbinolamine gets deprotonated, with the release of water and simultaneously the formation of an azomethine group, –C=N– bond is developed.[52-54]

Scheme 1.3. Mechanistic route of Schiff base formation

Scientific studies reveal that the physicochemical properties of the Schiff base arise due to the presence of a lone pair of electrons in the sp^2 hybridized orbital of the nitrogen atom of the azomethine group. Ease of preparation, synthetic flexibility and the special property of –C=N– group makes Schiff base an outstanding chelating agent.[55] The Schiff bases with functional groups like (–OH), (–SH), ($-NO_2$), (–COOH), ($-OCH_3$) are considered as useful chelating agents. Schiff bases are insoluble in water and some of them are readily hydrolysed back to amine and aldehyde under certain circumstances.[56] Schiff bases can act as bidentate, tridentate, tetradentate or polydentate ligands (Scheme 4).[57-59] Nevertheless, Schiff base macrocycles are formed by the self-condensation reaction of suitable carbonyl and primary amine precursors that have fundamental applications in biochemistry and supramolecular chemistry.[60]



Scheme 1.4. Examples of bidentate, tridentate, tetradentate and macrocyclic chelants

1.3. Application of Schiff base and their coordination compounds

Schiff bases and heterocyclic Schiff base scaffolds mainly sulphur, nitrogen and oxygen atoms bear great importance in many areas like biological, medicinal, analytical and pharmaceutical fields.[61] Schiff base derived coordination compounds possess a wide range of activities in materials, biological and pharmaceutical sciences.

Schiff base is a unique class of molecules in coordination chemistry that has become a frequently used chelator in the formation of metal complexes. Owing to their unique physicochemical properties, Schiff bases are employed to develop efficient catalysts of scientific and industrial importance, smart magnetic materials, therapeutics, opto-electronic gadgets, bio-mimetic and bio-inspired models, and so on. The newly designed Schiff bases and their coordination compounds hold a great deal of promise for the scientific community.

A large number of scientists across the globe are engrossed in the development of suitable Schiff bases and their coordination compounds.[62-66] One of the pioneers in this field is Prof. Ashutosh Ghosh, University of Calcutta, West Bengal, India. Prof. Ghosh and co-workers introduced the synthetic approach for the design and development of d-, d-f- and f-block metal complexes of varied nuecleartities based on tailor-made synthetic Schiff base ligands. For example, the research group has been successfully controlled the nuclearity of antiferromagnetic Cu (II)-Mn (II) coordination compounds employing an asymmetric Schiff base.[67] Prof. Ghosh also showed the synthetic ease of an isomeric d-f-metal complex based on Schiff base ligand with an interesting observation of field-induced slow relaxation of magnetisation applicable to the Gd (III) ion.[68] They also cited the synthesis of hetero-metallic trinuclear complexes with Schiff base ligand, The compounds were evaluated as bio-inspired oxidative catalysts.[69] Prof. Debasis Das of Dept. of Chemistry, University of Calcutta, is another distinguished scientist who made a significant effort in the design and application of Schiff bases and their metal complexes. His group explored the synthesis and applications of d-block metal complexes based on Schiff base ligands. Like, they designed a suitable Schiff base which turned out to be an effective chemosensor for Hg^{2+} ion in a matrix of ions.[70] The research group further developed a series of bio-inspired catechol oxidase metallo-enzyme analogues with zinc ions and Schiff base complexes and exhibited catalytic oxidation through ligand-centred radical pathways.[71]

Prof. Chittaranjan Sinha and co-workers of the department of Chemistry, Jadavpur University, developed various synthetic Schiff bases for selective detection of metal ions.[72] They also made a significant effort to synthesise Schiff base mediated coordination polymers.[73]

Prof. Shouvik Chattopadhyay of Jadavpur University is another promising scientist who engaged in the design and synthesis of different Schiff base and their reduced forms and explored the ligational motifs towards metal ions in the absence and presence of co-ligands.[74] His group also developed the trinuclear hetero nickel/ lead metal-based Schiff base complexes and explored the application of electrical properties of these heteronuclear Schiff base metal complexes.[75]

Prof. Barindra Kumar Ghosh, ex-Professor of the department of chemistry, University of Burdwan is one of the renowned scientists who made his distinct mark in the field of coordination and Schiff base chemistry. Prof. Ghosh and co-workers have been successfully designing the Schiff base ligand and synthesising various coordinated d-block metal complexes. This group exhibited the diversified coordination abilities of the Schiff base ligands towards the development of interesting nuclearities and dimensionalities of the coordination compounds.[76]

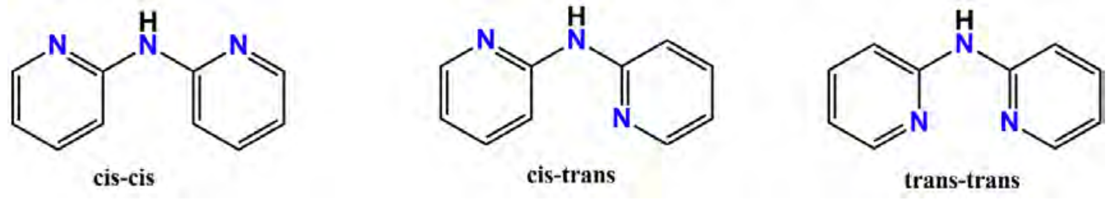
Dr. Anangamohan Panja of Panskura Banamali College showed the suitability of the Schiff base-metal complexes as promising candidates for bioinspired oxidation catalysts.[77]

Different scientific groups across the globe have also been engaged in the synthesis of smart coordination compunds based on Schiff bases with various applications in the different branches of science.[78,79] Melanie Pilkington of Brock University, Canada and the co-workers were synthesised 2,2′-bipyridyl functionalized quarterpyridine ligand and their metal complexes showing their catalytic utilities in rearrangement reactions.[80] Pof. Rui-Qing Fan and Yu-Lin Yang of Harbin Institute of Technology, China developed substituted Schiff bases and their coordination compounds containing 3d^{10}-, 4d^{10}-, 5d^{10}- metal ions. They also explored the metal complexes as the sensitizers in the solar cell devices.[81] Qiubin Kan of Jilin University, China and his group were designed various 3d-metal complexes with Schiff base ligands and the compounds were immobilized onto graphene oxide to investigate the epoxidation of different alkene groups.[82] Yingming Yao of Soochow University, China, also designed and synthesized the f-block metal complexes having pentadentate Schiff base ligands and studied the catalytic aspects towards the heteroselective polymerization of rac-lactide.[83] Prof. Kusum K. Bania and co-workers designed the chiral nickel(II)-Schiff base complexes and investigated their heterogeneous adduct with zeolite-Y as a chiral catalyst for asymmetric Henri reaction.[84] Wen-Jing Xiao and coworkers also engaged in the synthesis of chiral sulfoxide–Schiff base ligands and their copper complexes for the catalytic application for asymmetric Henri reaction.[85] The Japan Scientist Takashiro Akitsu and co-workers were developed modified salen type chiral Schiff bases and these complexations with various divalent 3d-metal ions with chiral Schiff bases.[86] Furthermore, Zahra Besharati and coworkers were synthesised the palladium nanoparticles (PdNPs) supported halloysite functionalised Schiff base composites and explored their catalytic efficiency in Sonogashira reaction.[87] Further, Yuping Dong and group developed diethylaminophenol functionalised Schiff base and studied its application for security printing and data storage based on the opto-electronic properties.[88] Hadis Afshar Hezarkhani and co-workers were successfully developed copper-(II) Schiff base complex functionalised boehmite nano particles. His group also exhibited the application of catalysts for the oxidation of sulfides and thiol.[89] The scientist Mohamed Habila and co-workers were synthesised fabrication Schiff base functionalised porous carbons materials. His group was studies the water treatment application for removing hazardous metal ions from wastewater.[90]

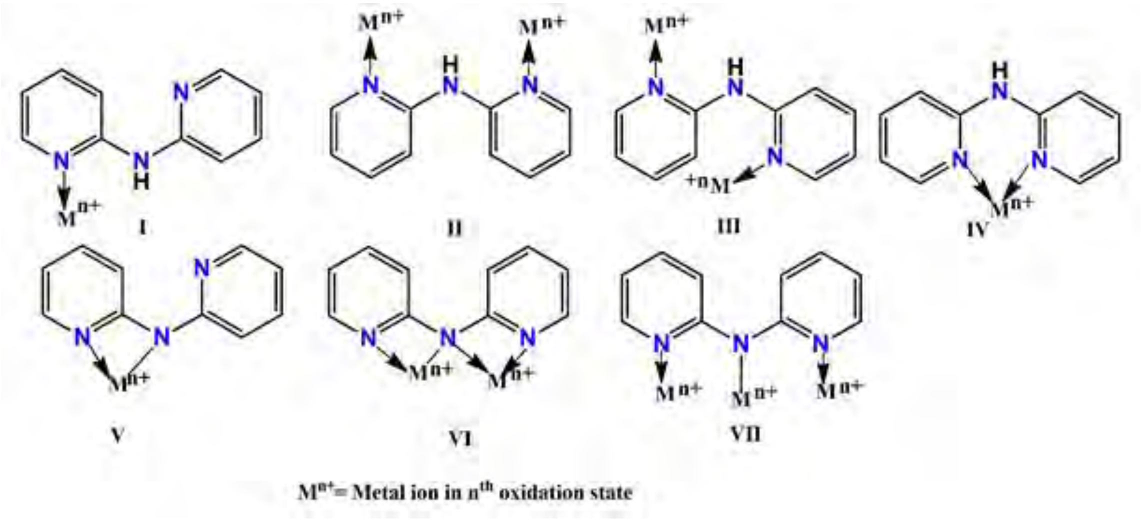
Nevertheless, during the last few years, we are also engaged in the design of new Schiff base ligands and their modified form. We also explored the coordination ability of the synthetic Schiff bases towards different d- and f- block metal ions. It is also observed that few Schiff bases underwent zwitterionic form during their coordination with metal ions at a certain reaction condition.[91] Sometimes the Schiff bases did not offer all the donor centres for metal ions during chelation.[92] Therefore, the Schiff base may turn out to be a flexidentate ligand and a congregation in the development of coordination compounds. We also evaluated the Schiff base as an effective and selective ions sensor in the solution phase.[93] We also synthesised and explored various bioinspired coordination compounds containing (N, N), (N, O), (N, N, O)-donor Schiff base ligands.[94] It is further evident that the Schiff base may be considered as an important building block for developing nano dimensional molecular aggregates with light-harvesting properties.[95]

Scientifically, it is proven that polypyridyl compounds are considered effective chelators.[96-100] 2,2′-bipyridine, 1,10-phenanthroline, 2,2′-dipyridylamine and their substituted forms are widely used chelating agents in the formation of metal complexes with various metal ions. Like, 2,2′-dipyridylamine, a commercially available ligand, is a neutral (N, N)-donor chelating ligand, which exhibits the existence of different conformations during interactions with metal ions.[101, 102]

Setifi et al. discovered three conformations for 2,2′-dipyridylamine (dpa): cis–cis, cis–trans, and trans–trans (**Scheme 1.5**); The cis and trans conformations refer to the orientation of the pyridyl-N to the secondary amine-N.[103] Several bonding modes are possible involving just the pyridyl nitrogen atoms (**Scheme 1.6**). Although, the dpa ligand may show its existence in different conformations or binding modes I to VII, but II and IV forms are the most common conformations we observed during its chelation with transition metals. However, additional binding modes are possible for anionic dpa.

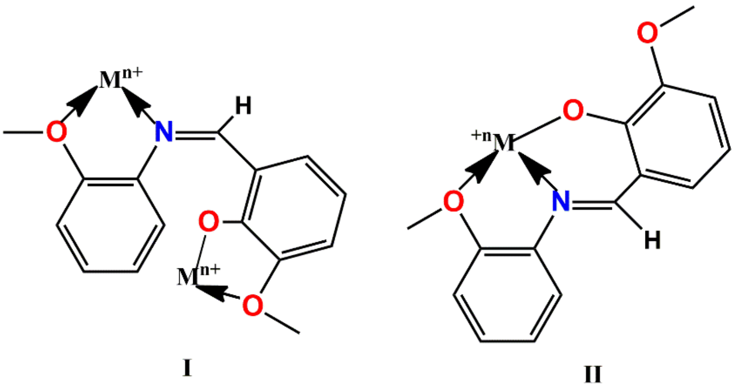


Scheme 1.5. Different conformers of 2,2′-dipyridylamine



Scheme 1.6. Various binding modes of 2,2′-dipyridylamine

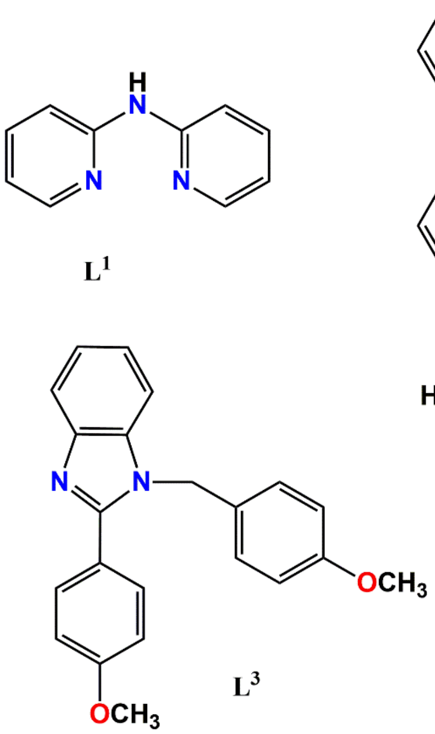
We also surveyed the ligational motifs for a few synthetic Schiff base ligands. For example, (Z)-2-methoxy-6-(((2-methoxyphenyl)imino) methyl)phenol ligand may be easily synthesised by refluxing o-anisidine and o-vanillin in ethanol medium. Virtually, this synthetic ligand adopts four donor centres and may be able to bind a metal ion through its tetradentate binding sites. However, it behaved as a tridentate chelator towards a divalent copper ion. The binding conformation of the ligand is shown in **Scheme 1.7.**



M^{n+}= Metal ion in n^{th} oxidation state

Scheme 1.7. Different binding modes of 2-methoxy-6-(((2-methoxyphenyl)imino) methyl)phenol ligand

In this context, I have designed and synthesized a few mono- and dinuclear metal complexes of cobalt, nickel, copper, and zinc with different (N,N) and (N,O) donor organic blockers viz. 2,2′-dipyridylamine (**L**^{1}), 1,2-bis(phenyl(pyridin-2-yl)methylene)hydrazine (**L**^{2}), 1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1Hbenzo[d]imidazole (**L**^{3}) and 2-methoxy-6-(((2-methoxyphenyl)imino) methyl)phenol (**L**^{4}).



Scheme 1.8. Schematic presentation of polydentate ligands

1.4. Scope and objectives of the present study

This work focuses on the design, synthesis and spectroscopic characterization of different new coordination assemblies and investigates their properties as well as their potential application for several catalytic transformations.[104-107] The theme of this dissertation is summarized below:

(i) Rational design and synthesis of ligands and new coordination compounds;

(ii) Through characterization them through different analytical techniques;

(iii) X-ray structures of the synthetic compounds and their supramolecular frameworks to reveal the primary and secondary zone of coordination and non-covalent interactions;

(iv) Elucidation of stereochemical, geometrical and electronic structure of these hitherto unknown compounds using spectroscopic results and computational calculations;

(v) Investigatation of different bio-inspired oxidation reactions like Phenoxazinone Synthase, Phosphatase activity; and Catechol Dioxygenase Activity;

(vi) Comparison of the catalytic activity between the reported and newly developed coordination compounds.

In my PhD thesis, the references are arranged according to following format….
name of authors, abbreviated journal name in italic, year, volume in bold, page/article number….

P. K. Mudi, L. Singla, A. Chamuah, S. Bhattacharya, A. R. Choudhury and B. Biswas, *Cryst. Engg. Commun*., 2022, **24**, 2418-2428.

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