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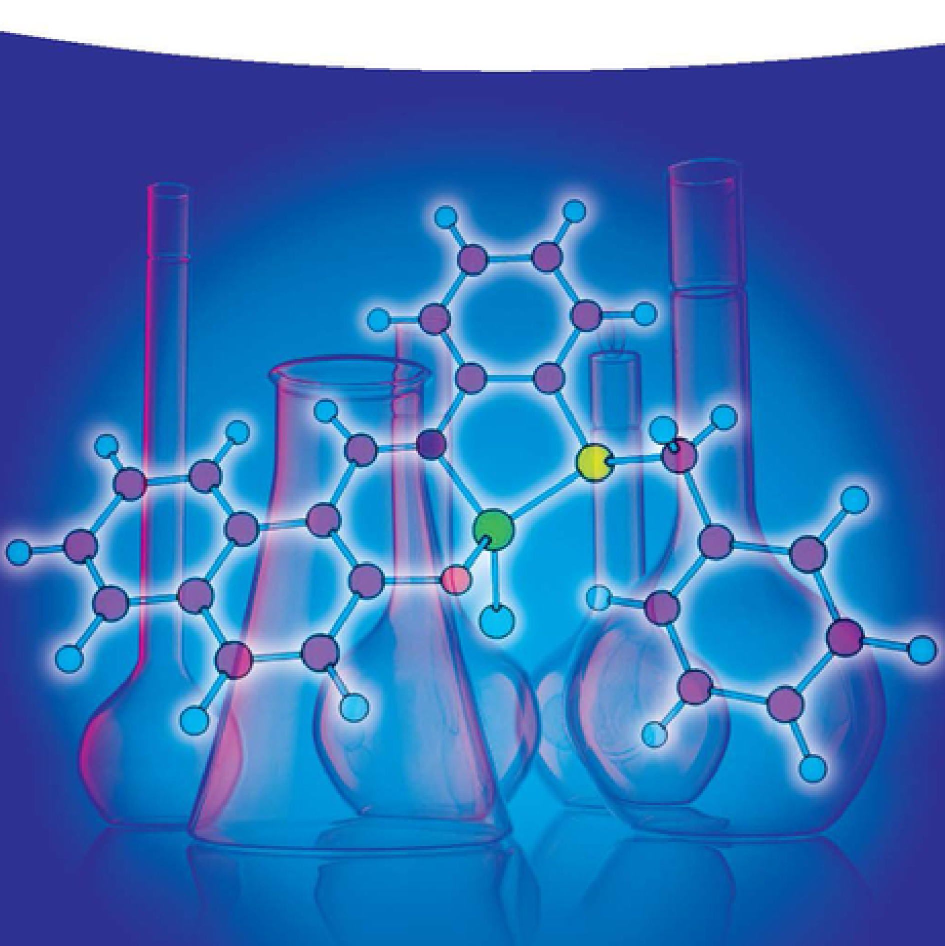
Synthesis and Applications



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Preface

Schiff bases (SBs) are extensively used as organic compounds that coordinate with metal ions through imine or azomethine nitrogen (C=N) and are subjected to subsidizing an ample spectrum of biological behaviors to these azomethinic compounds. SBs have wide applications in various fields including organic and inorganic chemistry, analytical, catalysis, pharmaceutical, biological, food and dye industry, pharmacological such as anti-inflammatory, antitumor, anticonvulsant, antifungal, analgesic, antibacterial, antimalarial, antiviral, anthelmintic, anti-oxidant, and so forth. SB effortlessly forms stable complexes with main group elements, transition metals, lanthanides, and actinides as they easily retain tenability of their stereo-electronic structures, which is why it is also regarded as "privileged ligand."

Many coordination complexes have been used in medicine contain metals such as platinum (as cisplatin, anticancer chemotherapy drug); gold (as auranofin, used for rheumatoid arthritis); technetium and rhenium (as radiopharmaceuticals used in imaging and radiotherapy); manganese and gadolinium (used in magnetic resonance imaging); ruthenium (as an anticancer drug); lithium (as Li_2CO_3 to treat prophylaxis of manic-depression behavior); bismuth (bismuth salicylate used as an antacid); iron, vanadium, and titanium (used to treat cancer as they react with DNA specifically in tumor cells); lanthanum (lanthanum carbonate used as a phosphate binder in patients suffering from chronic kidney disease); gold, silver, and copper (as anticancer drugs); gallium; lutetium.

Over the past decade, substantial emphasis has concentrated on the evolution of SB metal complexes owing to their DNA-binding properties, catalytic activities, electroluminescent properties, sensors, organic photovoltaic materials, fluorescence properties, energy materials, synthesis of polymeric materials, and biological activities. This area has been the subject of numerous reviews due to its distinct and peculiar structural properties, particularly its distinguished catalytic activity, selectivity, and stability, along with various physicochemical properties. The coordination of both essential and nonessential elements with these versatile ligands can lead to alterations in their physiochemical and biological properties, which depicts them as competent contenders to use judiciously in various fields.

This book is a collection of the experiences assembled during the experiments performed in the laboratory. Since the author has more than fifteen years of experimental and theoretical experience on this topic as well as published more than 50 research articles in reputed journals. So, all the information, as well as the experience gathered from the students and research scholars, is going to be highlighted in detail.

- This book covers up-to-date information and discussion based on the authors' experiences and references. The difficulties and technicalities faced by students and research scholars in the laboratory can be solved through this book.
- The authors express the data and information concisely, systematically, and orderly so that the readers will get benefitted in all aspects related to SBs and their metal complexes.
- The book is written for undergraduates, Ph.D. students, postdocs, and researchers in academia and industry.
- This book highlights the SB metal complexes and includes synthesis and applications of SBs and their metal complexes.
- This book also covers the biological applications and stereochemistry-related information of SBs and their metal complexes.
- The methodologies discussed in this book are uncomplicated, easy, and unconventional. We have discussed green methodologies like a solid support system, microwave synthesis, and solvent-free methodology for the synthesis of SBs and their metal complexes.
- This book also discusses various applications, such as DNA binding and fluorescence, of SBs and their metal complexes. This book highlights computational or theoretical studies on the reactivity of the SBs and their metal complexes depending on the steric effect, electronic effect, and field effect. This book also focuses on some of the tips or drawbacks of the methods and applications so far, so that research scholars as well as industry people can do more work in the near future.

Silchar, October 2022

Pranjit Barman
Anmol Singh

Part I

Introduction

1

Historical Background

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1.1 Introduction

Over the past few decades, chemistry of coordination compounds has expanded and diversified considerably. Coordination chemistry accomplished a significant interdisciplinary place at the interface of numerous fields, which serves as a connecting link between the different classes of chemical, physical, and biological sciences. The precise date that the first coordination compound was prepared is challenging to ascertain. Johann Jacob Diesbach, a color manufacturer, discovered the blue pigment known as Prussian blue in the seventeenth century, which is the beginning of coordination complex chemistry [1]. Chromium was discovered in 1798 by the German researchers Lowitz and Klaproth separately in a sample of a heavy black rock located near north of the Beres of Mines. The chromium in the same mineral from a small deposit in the Var region of South-eastern France was discovered by another German chemist Tassaert in 1799. He identified this mineral as the Cr–Fe spinel, also known as chromite ($FeO{\cdot}Cr_2O_3$) [2].

Alfred Werner's findings marked the beginning of an insight into coordination compounds and their varied properties. Werner's coordination theory in 1893 was the first effort which focused on the quantity and type of groups connected to the central metal ion to characterize the bonding and interpretation of coordination complexes. In 1913, Werner's idea and meticulous work over the ensuing 20 years earned him the Noble Prize in Chemistry. Due to the development of sophisticated physicochemical techniques of high accuracy and precision, his fundamental theories regarding the stereochemistry of metal complexes, mechanisms of isomerization, and racemization, etc. prevail indisputable even now despite all the advancements that have occurred since his time and through the last 50 years [3, 4]. These have greatly improved our knowledge of the attributes of metal–ligand connection, the configuration and stereochemistry of metal complexes, and their stabilities, liabilities, and other characteristics [5, 6]. Werner's theory became a key component of "The Electronic Theory of Valency" proposed by G.N. Lewis (1916) and extensively related to coordination compounds by N.V. Sidgwick (1927),

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replacing the majority of the earlier concepts presented by Berzelius (1819), Grohen (1837), Claus (1856), Blomstr (1869), and Jorgenson (1894).

Coordination chemistry has expanded in three dimensions, taking into consideration its breadth, depth, and applications. The five Noble awards that significantly impact the topic reflect the sustained respect for the emerging science (A. Werner, 1913; M. Eigen, 1967; Wilkinson and Fischer, 1973; H. Taube, 1983; Cram, Lehn and Pedersen, 1987). In the list, Werner and Cram, Lehn & Pedersen acknowledged the ancient and new domains of coordination chemistry [7].

A coordination compound, also known as a metal complex, comprises an ensemble of bonded ions or molecules, regarded as ligands, and a central ion or atom called a coordination center, which is typically a metal ion. There are reasonably profound changes in the properties of a metal ion on the complex formation, which reflects in structures, stereochemistry, stability, and many other properties. It is necessary to understand the properties of bond between the metal ion and ligand to interpret the design of complex.

1.2 Theories of Coordinate Bond

1.2.1 Valence Bond Theory

According to Lewis and Sidgwick theory, ligands donate an electron pair to a metal ion to establish a coordinate bond [8, 9]. In 1931, L. Pauling expanded this theory to comprehend and predict various coordination complex traits, including magnetic behavior, stereochemistry, kinetics, and other physical and other chemical characteristics [10]. This hypothesis states that a coordinate bond between the metal and ligand leads to the complex formation of the duo. It describes how s, p, or d orbitals, as well as hybridized orbitals, i.e. sp^3, d^2sp^3 or sp^3d^2, or dsp [2], etc. generate strong bonds. Tetrahedral, octahedral, and square planar stereochemistry, each dealt by coordinate covalent bonds, formed by metal atoms having sp^3, d^2sp^3/sp^3d^2, or dsp [2] hybrid orbitals with the ligand orbitals. Through semi-quantitative calculations, Pauling and Gould elucidated the stability of complexes and concluded that the formation of sigma bonds among ligand and metal from electron donation occurs in carbonyl and nitrosyl compounds [10]. Back donation, i.e. $d\pi$–$p\pi$ linkage amid metal and ligand, justifies the stability of carbonyl and nitrosyl compounds.

1.2.2 Crystal Field Theory

The splitting of d or f orbitals is explained by crystal field theory (Figure 1.1). Degeneracies of electron orbital states are typically brought on by a static electric field induced by the distribution of charges nearby. Hans Bethe and John Hasbrouck van Vleck, two scientists, proposed a theory that describes several spectroscopies of transition metal coordination complexes, specifically optical spectra (colors) [11, 12]. Although it makes an effort to characterize and explain bonding, crystal field theory (CFT) is effective in defining colors, magnetic characteristics, and hydration enthalpies of transition metal complexes. The attraction among the positively charged metal cation and ligands leads to the interaction between a

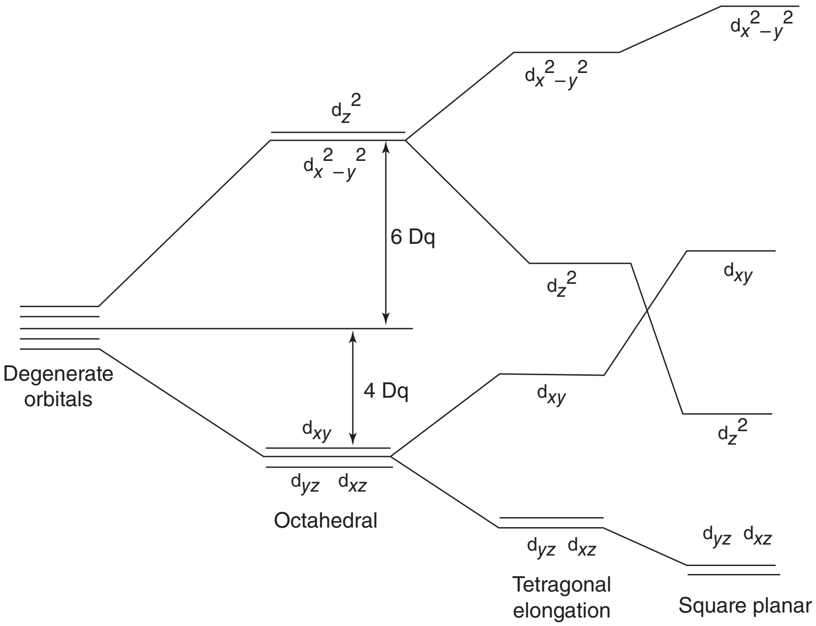

Figure 1.1 Crystal field splitting in tetragonally elongated, octahedral, and square planar filled.

transition metal and ligands. Owing to the attraction between like charges, the electrons in the ligand's d-orbital resist one another, splitting the energy of the d-orbital. The following factors have an impact on this splitting:

1. Concerning the spherical field, the distribution of ligands encircling metal, the coordination number of the metal ion, such as tetrahedral or octahedral, and the type of ligands, a greater oxidation state of the metal causes considerable splitting.
2. Tetrahedral symmetry hinders the ligand electrons from approaching d-orbitals directly. The higher energy orbitals are $d_z{}^2$ and $d_x{}^2{}_{-y}$ [2], while lower energy orbitals are d_{xy}, d_{yz}, d_{xz}. The energy splitting will be less than in an octahedral field. CFT can also be used to explain complex geometry.

1.2.3 Molecular Orbital Theory

The electronic structure of molecules is described using quantum mechanisms. The electrons are not allocated to specific atom-to-atom linkage; instead, they are regarded as moving under the influence of the nuclei in the entire molecule. In 1935, molecular orbital theory (MOT) stated that molecular orbitals were formed by linear combinations of atomic orbitals. Atomic orbitals must overlap within space and cannot form molecular orbitals if they are too apart. The electrons in an atom may be either waves or particles; therefore, electrons can be considered as accommodating an atomic orbital or a wave function ψ, which is a solution of Schrodinger wave equation. The overlapping atomic orbitals must have nearly the same energy; maximum overlapping must have symmetry concerning the molecular bonding axis [13, 14].

1.2.4 Ligand Field Theory

The orbital configuration, bonding, and other properties of coordinating complexes are explained by ligand field theory (Figure 1.2). To formulate the more extensive and realistic ligand field theory, which describes the process of chemical bonding in transition metal complexes, the MOT and CFT were later integrated. This theory which elucidates the loss of degeneracy of metal d-orbitals in transition metal complexes was developed by incorporating the tenets of CFT and MOT. Ligand field theory originated in the 1930s by John Hasbrouck Van Vleck and Orgel to explain the results using CFT and visible spectra of transition metal complexes [12, 15–18]. The vacant d-orbitals of transition metals facilitate bonding, which affects the colors they absorb in solution. Depending on the intensity of the surrounding ligands, the various d-orbitals are influenced differentially and have their energy raised or diminished. The symmetry orbitals of the ligands in octahedral complexes generate bonding and antibonding combinations through the d_{z^2} and $d_{x^2-y^2}$ orbitals as a result of approaching along the x-, y-, and z-axes. In contrast, the d_{xy}, d_{xz}, and d_{yz} orbitals remain nonbonded [19, 20].

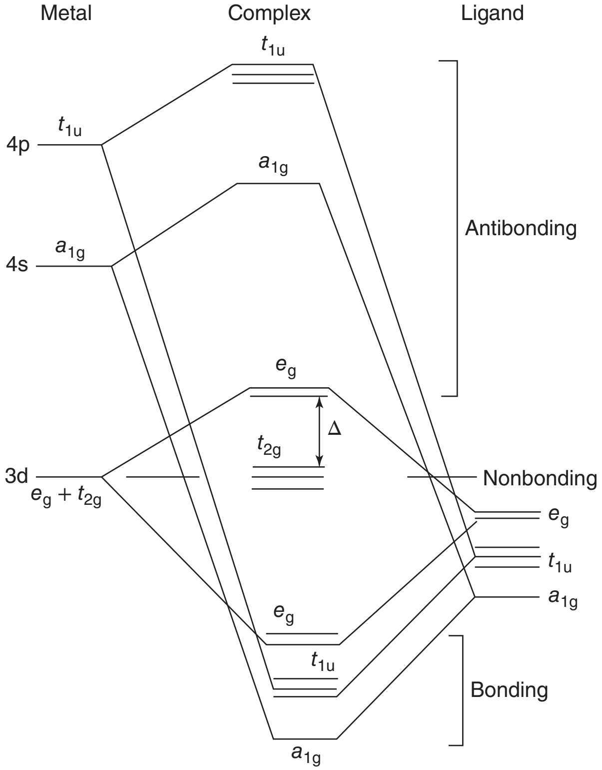

Figure 1.2 Molecular orbital energy-level diagram of an octahedral complex.

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