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TITRE

Course : Basic Concepts in Metal Complexes

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*********** Preface************

This course material is intended primarily for second-year undergraduate students in Chemistry (Licence 2, Faculty of Sciences). It is also designed to be useful for Master's students**,** particularly those enrolled in Environmental Chemistry and Analytical Chemistry programs**,** as well as for students in pharmacy, biology, and related disciplines who wish to acquire a solid foundation in coordination chemistry.

The content is organized into six chapters and covers the basic concepts of metal complexes, including their formation, structure, bonding theories, properties, and applications. The aim is to provide students with a clear and accessible introduction to the fundamental principles of coordination chemistry, which is essential for understanding more advanced topics in inorganic, bioinorganic, and analytical chemistry. I hope this manual serves as a helpful guide and reference for students throughout their academic journey.

*********** SUMMARY ************

CHAPTER 1 : General Information on Metal complexes

CHAPTER II : Nomenclature of Coordination Compounds

CHAPTER III : Geometries of Complexes

CHAPTER IV : Isomerism in Metal Complexes

CHAPTER V : Stability of Coordination Complexes and Equilibria

CHAPTER VI : Theories of Metal Complexes

*********** General Introduction************

Coordination chemistry is a fundamental branch of inorganic chemistry that plays a crucial role in many areas of science and technology, including catalysis, materials science, environmental chemistry, bioinorganic chemistry, and analytical chemistry. The study of metal complexes is essential for understanding the behavior of transition metals, their interactions with ligands, and their applications in both industrial and biological systems.

This course material has been developed in the context of undergraduate and graduate chemistry education, with the aim of providing students with a structured and progressive introduction to the principles of coordination chemistry. It is intended primarily for second-year undergraduate students in Chemistry (Licence 2) and also serves as a reference for Master's students, particularly those specializing in Environmental Chemistry and Analytical Chemistry, as well as for students from related disciplines.

The main pedagogical objectives of this document are to:

- introduce the fundamental concepts of coordination chemistry;
- explain the formation, structure, and bonding of metal complexes using appropriate theoretical models;
- develop students' ability to understand and predict the properties and reactivity of coordination compounds;
- provide a solid foundation for more advanced courses in inorganic, bioinorganic, environmental, and analytical chemistry.

The content is organized into six chapters, progressing from basic definitions to more advanced concepts, with an emphasis on clarity and conceptual understanding. This manual is intended to support students in their learning process and to serve as a useful reference throughout their academic studies.

Chapter I

GENERAL INFORMATION ON METAL COMPLEXES

I.1. Definitions

I.1.1 Definition of metal complexe

A metal complex (or coordination compound) is a chemical species formed by the combination of a central metal atom or ion and one or more molecules or ions, called ligands, that are bonded to it through coordinate covalent bonds. In such bonds, both electrons in the shared pair originate from the ligand. The resulting structure can be neutral, cationic, or anionic depending on the charges of the metal and the ligands involved.

I.1.2 What is a metal for the chemist?

From a chemist's point of view, a metal is an element that tends to lose electrons to form positive ions (cations) and that can participate in metallic or coordinate bonding. Metals are typically good conductors of heat and electricity, possess a shiny appearance, and are malleable and ductile in their solid form. Chemically, they are characterized by their ability to form complex compounds with a variety of ligands.

It is important to note that most elements in the periodic table are metals. They occupy the left and center blocks (s, d, and f blocks) (Fig. 1), including the alkali metals, alkaline earth metals, transition metals, lanthanides, and actinides. Out of the 118 known elements, over 90 are classified as metals. This abundance reflects their fundamental role in the structure of matter and in numerous chemical processes, including the formation of coordination compounds.

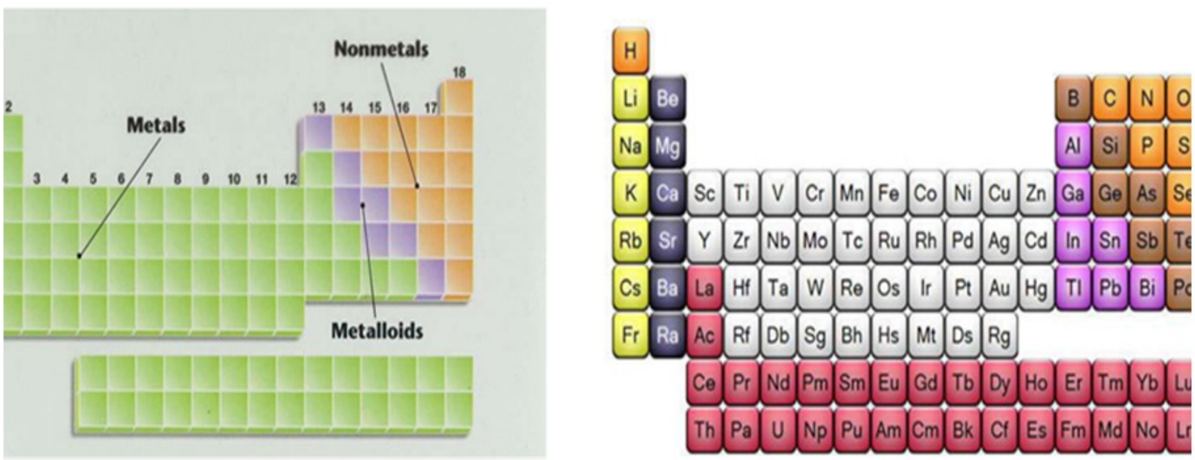


Figure 1. Location of metallic elements in the periodic table

I.1.3 Coordinate covalent bond

A coordinate covalent bond, also known as a dative bond, is a type of chemical bond in which both electrons in the shared pair originate from the same atom. This bonding interaction typically occurs when a Lewis base, which has a lone pair of electrons, donates that pair to a Lewis acid, which has an empty orbital capable of accepting electrons. Despite its unique origin, once formed, a coordinate covalent bond is indistinguishable from a regular covalent bond in terms of strength and properties. These bonds are commonly found in coordination complexes, where metal ions (acting as Lewis acids) bind with ligands (acting as Lewis bases). For example, in the complex $[Cu(NH_3)_4]^{2+}$, each ammonia molecule donates a lone pair of electrons to the copper(II) ion, forming four coordinate covalent bonds (Fig. 2). This type of bonding plays a crucial role in coordination chemistry, catalysis, and bioinorganic systems such as metalloproteins and enzyme active sites.

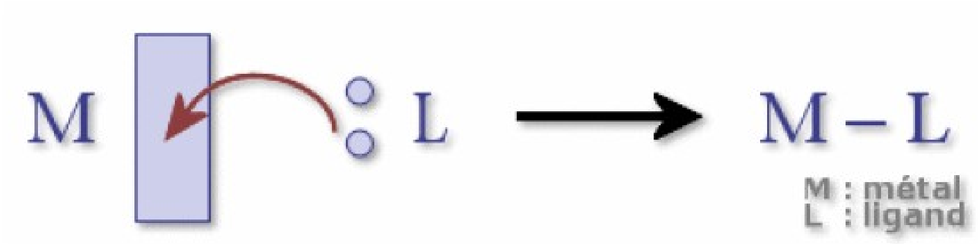


Figure 2. Formation of a coordinate covalent bond via lone pair donation

I.1.4 General characteristics of metal complexes

Metal complexes, also known as coordination compounds, are formed when central metal ions bind to surrounding molecules or ions called ligands through coordinate covalent bonds. These complexes exhibit several general characteristics:

- Geometry: Depending on the metal ion and its coordination number, metal complexes can adopt various geometries such as octahedral, tetrahedral, or square planar.
- Coordination number: This refers to the number of ligand donor atoms bonded to the central metal ion, typically ranging from 2 to 8.
- Oxidation state and charge: The metal ion’s oxidation state and the nature of the ligands determine the overall charge of the complex.
- Color: Most metal complexes are colored due to d–d electronic transitions or charge transfer, which are influenced by the metal and ligand types.

- Magnetic properties: Depending on the number of unpaired electrons in the metal ion, complexes may be paramagnetic or diamagnetic.
- Stability: The stability of metal complexes depends on factors such as the metal-ligand bond strength, ligand type, chelation, and the presence of competing ions.

These characteristics make metal complexes important in fields such as catalysis, bioinorganic chemistry, medicine, and environmental science.

I.2. Historical background

I.2.1 Early developments in coordination chemistry

The origins of coordination chemistry trace back to the late 18th and early 19th centuries, when chemists began observing unusual properties in certain metal-containing compounds that could not be explained by classical valence theories. One of the earliest breakthroughs came in 1798 when French chemist Claude-Louis Berthollet studied Prussian blue, a complex iron-cyanide compound, highlighting the need for a new understanding of metal-ligand interactions. However, coordination chemistry truly began to take form in the 19th century with the discovery of a variety of colored metal salts that displayed different reactivities and solubilities despite having the same empirical formula. This led to confusion and debate among chemists regarding the structure and composition of such compounds. The most significant early advancement was made by Alfred Werner in 1893, who proposed the coordination theory to explain the bonding in metal complexes. He introduced the concept of primary and secondary valences and demonstrated that metals like cobalt could form stable coordination compounds with ammonia and other ligands. Werner's work laid the foundation for modern coordination chemistry and earned him the Nobel Prize in Chemistry in 1913. His octahedral model of coordination around central metal atoms was revolutionary and provided a consistent explanation for the isomerism observed in many metal complexes.

I.2.2 Alfred Werner's coordination theory (Nobel Prize 1913)

Alfred Werner (Fig. 3), awarded the Nobel Prize in Chemistry in 1913, is renowned for his groundbreaking coordination theory, which revolutionized the understanding of the structures of coordination compounds. Before Werner's work, the bonding in metal complexes was poorly understood and often explained by the outdated chain theory. Werner proposed that metal atoms could form coordination bonds with a specific number of surrounding ligands, giving rise to well-defined geometric structures such as octahedral, tetrahedral, and square planar arrangements. He introduced the concepts of primary valence (corresponding to the oxidation state of the metal) and secondary valence (the number of ligands bound to the metal), laying the foundation for modern coordination chemistry. His theory successfully explained the existence of isomers in metal complexes, such as the different forms of $[Co(NH_3)_4Cl_2]Cl$, which could not be accounted for by earlier models. Werner's ideas opened new avenues in inorganic chemistry, influencing fields ranging from bioinorganic chemistry to materials science, and remain fundamental to the design and understanding of metal-ligand complexes today.

Figure 3. Alfred Werner (1866–1919), founder of modern coordination chemistry and Nobel Laureate in Chemistry (1913)

I.2.3 Evolution of coordination concepts in the 20th century

The 20th century witnessed a remarkable evolution in coordination chemistry, building upon Alfred Werner's foundational theory. As experimental techniques such as X-ray crystallography, UV-visible spectroscopy, and NMR advanced, chemists were able to explore the structure and reactivity of coordination compounds in greater detail. The concept of ligand field theory emerged, refining earlier crystal field theory by incorporating molecular orbital theory to explain electronic structures and spectroscopic properties of complexes. This period also saw the classification of ligands according to their denticity, electronic effects, and ability to form chelates, which led to a deeper understanding of complex stability. The introduction of macrocyclic and supramolecular chemistry further expanded the field, enabling the design of highly selective and functional metal-ligand systems. Coordination chemistry also became essential in understanding biological processes, such as the role of metalloproteins and enzyme cofactors. By the late 20th century, the development of organometallic and bioinorganic coordination compounds opened new frontiers in catalysis, medicine, and materials science, firmly establishing coordination chemistry as a cornerstone of modern inorganic chemistry.

I.3. Importance of metal complexes

Metal complexes are of great importance in both theoretical and applied chemistry. They serve as fundamental models for understanding coordination interactions, metal-ligand bonding, and molecular geometry. Their versatility arises from the ability of metal ions to adopt various oxidation states and to coordinate with a wide range of ligands, forming stable and diverse structures. This property makes metal complexes essential in fields such as catalysis, environmental remediation, medicine, and materials science. In biological systems, many vital functions depend on metal complexes, including oxygen transport, electron transfer, and enzymatic activity. Furthermore, their unique optical, magnetic, and electronic properties make them valuable in developing sensors, electronic devices, and pharmaceutical compounds. The study of metal complexes thus bridges inorganic chemistry with industrial, biomedical, and environmental applications.

I.3.1 Role in chemical bonding and structure

Metal complexes play a central role in shaping our understanding of chemical bonding and molecular structure. When metal ions bind to ligands, they form coordination compounds with well-defined geometries, such as octahedral, tetrahedral, and square planar—depending on factors like coordination number, ligand type, and electronic configuration of the metal. The development of crystal field theory and ligand field theory provided essential tools for explaining these geometries and predicting key properties such as magnetism, color, and reactivity. The spatial arrangement of ligands around the metal center influences not only the compound’s stability but also its chemical behavior. Chelating ligands, for example, form highly stable ring structures with metal ions, enhancing both selectivity and structural rigidity. These principles are not only crucial for fundamental chemistry but also for designing catalysts, drugs, and functional materials based on metal-ligand interactions.

I.3.2 Importance in biological systems (metalloenzymes, metalloproteins)

Metal complexes are essential in many biological functions. Their roles can be summarized as follows:

- Structural and functional components of biomolecules:
  - Metalloproteins contain metal ions that stabilize structure or assist in biochemical activity.
  - Metalloenzymes use metal ions in their active sites to catalyze vital reactions.
- Examples of biological roles:
  - Hemoglobin (Fe^{2+}): Iron binds and transports oxygen in the blood.
  - Chlorophyll (Mg^{2+}): Magnesium enables the absorption of light during photosynthesis (Fig. 4).
  - Carbonic anhydrase (Zn^{2+}): Catalyzes the conversion of CO_2 and water into bicarbonate.
  - Cytochrome c oxidase (Fe, Cu): Involved in electron transport during cellular respiration.
- Chemical functions of the metal ion:
  - Acts as a Lewis acid to activate substrates.
  - Participates in redox reactions (electron transfer).
  - Influences the geometry and reactivity of the enzyme.

Understanding these natural metal complexes provides valuable insight for biochemistry, medicine, and the design of biomimetic catalysts.

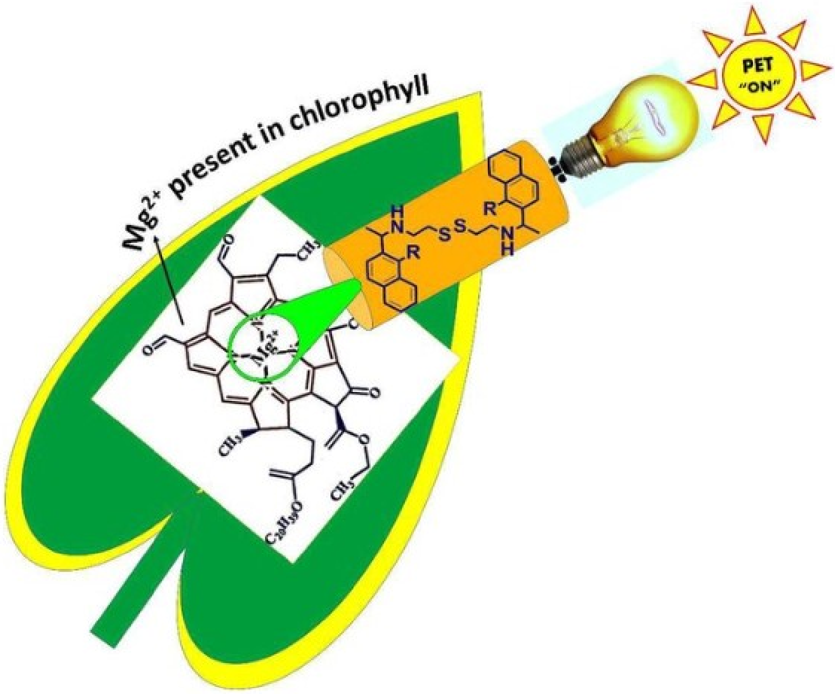


Figure 4. Schematic diagram of metal ion sensing: interaction of compound LH_2 with Mg^{2+} in a chlorophyll-like context

I.3.3 Relevance to industrial and environmental chemistry

Metal complexes play a pivotal role in both industrial processes and environmental applications due to their unique coordination properties, redox behavior, and catalytic activity. In industry, transition metal complexes are widely used as homogeneous and heterogeneous catalysts in reactions such as hydrogenation, polymerization, oxidation, and carbon–carbon coupling. For example, palladium and platinum complexes are central to catalytic converters in automotive exhaust systems, reducing harmful emissions by converting carbon monoxide (CO), nitrogen oxides (NO_x), and unburnt hydrocarbons into less toxic substances like CO_2, N_2, and H_2O.

In the field of environmental chemistry, metal complexes contribute to pollution control, wastewater treatment, and heavy metal sequestration. Chelating agents, often based on organic ligands, form stable complexes with toxic metal ions such as Pb^{2+}, Cd^{2+}, and Hg^{2+}, facilitating their removal from contaminated water sources. Additionally, synthetic and biomimetic metal complexes are being developed for photocatalytic degradation of organic pollutants, including dyes and pharmaceuticals, using sunlight or visible light.

Furthermore, metal complexes are at the heart of green chemistry innovations, aiming to design more sustainable processes. For instance, iron or copper-based catalysts are explored as safer alternatives to rare and toxic metals, contributing to environmentally benign synthesis routes.

The understanding and design of metal complexes are therefore essential not only for advancing industrial efficiency but also for addressing pressing environmental challenges such as water purification, atmospheric pollution, and the development of clean energy systems.

I.4. Applications of Metal Complexes

Metal complexes have a broad range of applications across various scientific and technological fields, owing to their structural diversity and versatile chemical properties. Their ability to interact selectively with biomolecules, catalyze reactions, bind pollutants, or form stable colored compounds makes them indispensable in biology, medicine, industry, environmental science, and analytical chemistry. This section highlights some of the most significant and practical uses of metal complexes in both natural systems and engineered processes.

I.4.1 Biological and medicinal applications

Metal complexes play a fundamental role in numerous biological processes and have become increasingly important in medicinal chemistry. In biological systems, metal ions are essential for the structure and function of many biomolecules. For instance, hemoglobin, a heme-containing protein, uses iron (Fe^{2+}) at its core to reversibly bind and transport oxygen in the bloodstream. Similarly, vitamin B_{12} contains a cobalt (Co^{3+}) ion at the center of a corrin ring, essential for DNA synthesis and nervous system function.

In medicine, metal complexes are exploited for their therapeutic and diagnostic properties. One of the most well-known examples is cisplatin (carboplatin), a platinum-based complex used as a chemotherapeutic agent to treat various cancers by binding to DNA and interfering with cell division. Other metal complexes, such as gold-based compounds, have been explored for their anti-inflammatory or antimicrobial properties, while technetium complexes are commonly used in nuclear medicine imaging due to their favorable radioactive properties (Fig. 5).

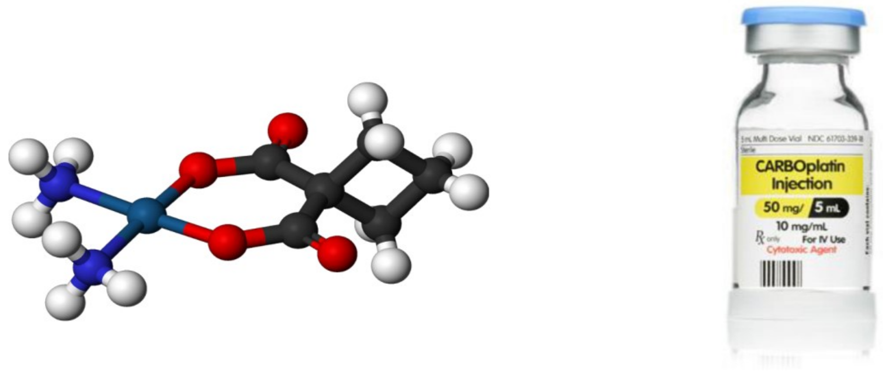


Figure 5. Molecular structure and pharmaceutical form of carboplatin, a platinum complex used in oncology

Moreover, metalloenzymes, which contain metal ions at their active sites, serve as natural catalysts in vital metabolic pathways. Understanding their mechanisms has inspired the design of biomimetic metal complexes that can mimic enzyme function or selectively target specific biomolecules in therapeutic applications.

Thus, metal complexes are not only integral to life but also offer powerful tools for advancing medical diagnosis, treatment, and biochemical understanding.

I.4.2 Industrial applications

- Catalysis
  - Metal complexes are essential in industrial catalysis, particularly those involving transition metals like palladium (Pd), platinum (Pt), rhodium (Rh), and ruthenium (Ru).
  - They serve as catalysts in key transformations such as:
    - Hydrogenation reactions, used to convert alkenes and alkynes into alkanes in the food and petrochemical industries.
    - Carbon–carbon coupling reactions (e.g., Suzuki, Heck, and Sonogashira reactions), widely used in the synthesis of pharmaceuticals, agrochemicals, and organic materials.
    - Catalytic reforming in petroleum refining, where platinum-based complexes are used to improve fuel quality by rearranging hydrocarbon structures.
  - Their selectivity and efficiency reduce energy consumption and waste, aligning with the goals of green chemistry.

 Dyes and Pigments

- Metal-containing dyes are known for their vibrant and stable colors. Examples include:
  - Phthalocyanines with metals like copper or cobalt, used in textile dyeing, printing inks, and automotive paints.
  - Azo-metal complexes, in which a metal ion stabilizes the azo (-N=N-) chromophore, enhancing lightfastness and thermal stability.
- These complexes allow fine control over hue and color properties by modifying the metal center or surrounding ligands.

 Advanced Functional Materials

- Metal complexes are increasingly used in high-tech applications such as:
  - OLEDs (organic light-emitting diodes) for flexible displays and lighting, where complexes of iridium or europium provide efficient and tunable luminescence.
  - Solar cells, especially dye-sensitized solar cells (DSSCs), which use ruthenium complexes to absorb sunlight and convert it into electricity.
  - Conductive polymers, where metal complexes act as dopants to enhance electrical conductivity.
- Their electronic and photophysical properties make them ideal for use in next-generation technologies.

 Industrial Significance

- The versatility of metal complexes helps to streamline production processes, reduce costs, and minimize environmental impact.
- Their ability to function under mild conditions and with high specificity is vital for the development of sustainable industrial chemistry.

I.4.3 Environmental applications

 Water Treatment and Purification

- Metal complexes are increasingly used in the removal of pollutants from water, especially heavy metals such as lead (Pb^{2+}), cadmium (Cd^{2+}), mercury (Hg^{2+}), and copper (Cu^{2+}).

- Certain ligands can form stable complexes with these metal ions, allowing their precipitation, extraction, or adsorption.
- Example: Schiff base ligands and EDTA (ethylenediaminetetraacetic acid) form chelate complexes with toxic metals, making them easier to remove from contaminated water sources.

 Heavy Metal Chelation and Detoxification

- In environmental remediation, metal-binding agents (chelators) are used to immobilize or extract heavy metals from soil and industrial effluents.
- Chelating agents can be natural (e.g., phytochelatins, siderophores) or synthetic (e.g., DTPA, EDTA, thiosemicarbazones).
- These complexes reduce the bioavailability and toxicity of metals in ecosystems.

 Pollution Control and Emission Reduction

- Metal complexes are also used in technologies that limit atmospheric pollution, such as:
  - Selective catalytic reduction (SCR) systems that use vanadium or titanium complexes to reduce NO_x emissions in exhaust gases.
  - Catalytic converters in vehicles, which use platinum, rhodium, and palladium complexes to convert toxic CO, NO_x, and hydrocarbons into less harmful gases.

 Environmental Sensors and Monitoring

- Some metal complexes are used in the development of chemical sensors that detect environmental pollutants (e.g., cyanide, fluoride, or heavy metals).
- These sensors often rely on colorimetric or fluorescent changes upon binding with target species, enabling real-time detection.

 Green Chemistry and Sustainable Processes

- The use of metal complexes in catalysis contributes to greener industrial processes, reducing the need for harsh conditions or toxic reagents.
- Example: Iron- or copper-based catalysts for oxidative degradation of organic pollutants in wastewater.

I.4.4 Analytical chemistry

 Complexometric Titrations

- One of the most important applications of metal complexes in analytical chemistry is complexometric titration, especially using EDTA (ethylenediaminetetraacetic acid) (Fig. 6).
- EDTA forms strong 1:1 chelate complexes with most metal ions (e.g., Ca^{2+}, Mg^{2+}, Zn^{2+}, Fe^{3+}), making it ideal for quantitative analysis of metal concentrations in water, food, pharmaceuticals, and industrial samples.

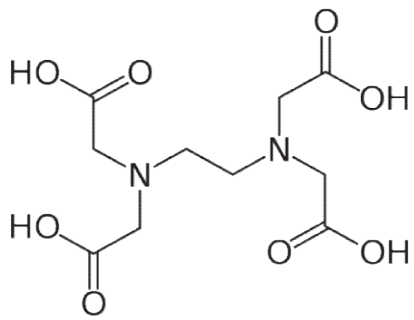


Figure 6. Molecular structure of EDTA (ethylenediaminetetraacetic acid)

 Indicators and Detection

Specialized metal ion indicators (e.g., Eriochrome Black T, Calmagite) are used in titrations. These indicators form weak complexes with metal ions and change color when displaced by a stronger ligand like EDTA. This color change indicates the endpoint of the titration, providing precise and visible detection.

 Spectrophotometric Methods

Metal complexes often have distinctive absorption spectra in the UV-visible region due to d–d transitions or ligand-to-metal charge transfer (LMCT). These properties allow for the quantitative determination of metal ions using UV–Vis spectrophotometry, even at very low concentrations.

 Electroanalytical Techniques

- In voltammetry or potentiometry, metal complexes are used as:
    - Redox-active species to probe electron transfer reactions
    - Electrochemical sensors for detecting specific analytes in environmental or biological samples

- For example, complexes of copper or cobalt are used in biosensors for glucose or metal ion detection.

 Separation and Preconcentration

- Chelating agents form complexes that can be selectively extracted from mixtures, aiding in the separation or preconcentration of trace metals before analysis.
- Techniques such as liquid–liquid extraction, solid-phase extraction, or ion exchange often rely on metal–ligand complexation.

Chapter II

NOMENCLATURE
OF
COORDINATION
COMPOUNDS

II.1. Introduction

The nomenclature of coordination compounds is a systematic method used to describe the composition, structure, and charge of a complex in a clear and internationally standardized way. The name of a coordination compound conveys essential information such as the identity of the central metal atom, its oxidation state, the nature, number, and charge of the ligands, and the overall charge of the complex (whether it is a neutral molecule, a cation, or an anion).

Correct nomenclature provides not only a linguistic description but also structural insight, such as potential geometry, coordination number, and type of bonding. Mastering this system is essential for interpreting chemical literature, drawing molecular structures, and ensuring accurate scientific communication across disciplines.

II.2. General Rules for Naming Coordination Compounds

A coordination compound's name must accurately reflect its composition and structure. To ensure clarity and consistency, the IUPAC provides a systematic set of rules, summarized and explained as follows:

II.2.1 Order of naming (ligands before metal)

In the name of a coordination compound, ligands are always named before the central metal atom or ion. The ligands are listed in alphabetical order, not by their charge, denticity, or the number of times they appear.

- Prefixes such as *di*-, *tri*-, *tetra*- are used to indicate the number of each type of ligand. These prefixes are not considered when determining alphabetical order.
- For complex ligands (e.g., ethylenediamine, bipyridine), special multiplicative prefixes such as *bis*-, *tris*-, *tetrakis*- are used, and the ligand name is placed in parentheses.

Example:
$[Co(NH_3)_4Cl_2]^+$ → tetraamminedichloridocobalt(III) ion
(ammine comes before chloro alphabetically, despite Cl^- being an anion).

II.2.2 Coordination Sphere Notation

The coordination sphere consists of the central metal and all ligands directly bonded to it. This entire structure is enclosed in square brackets [ ].

- If the complex is part of a salt or has a counterion, the square brackets help distinguish the coordination part from spectator ions.
- The species outside the brackets are written separately, typically after the complex, without brackets.

Examples:

- Neutral complex:[$Ni(CO)_4$] → tetracarbonylnickel(0)
- Ionic complex: $[Cr(H_2O)_6]Cl_3$ → hexaaquachromium(III) chloride

II.2.3 Charge and Oxidation State Indications

The oxidation state of the central metal is written in Roman numerals in parentheses, immediately after the metal's name, with no space between them.

- The oxidation state is determined by considering the formal charges of all ligands and the overall charge of the complex.
- If the complex is anionic, the metal name is modified with the suffix "-ate", often using the Latin name of the metal (e.g., *ferrate*, *cuprate*).

Examples:

- $[Fe(CN)_6]^{4-}$ → hexacyanoferrate(II) ion
- $[Cu(NH_3)_4]^{2+}$ → tetraamminecopper(II) ion

II.2.4 Use of Parentheses and Brackets

To avoid ambiguity and maintain clarity:

- Square brackets [ ] enclose the coordination complex.
- Round parentheses ( ) are used to:
  - Enclose oxidation states of the metal.
  - Enclose ligand names when they are complex or contain prefixes, especially when using *bis*-, *tris*-, etc.

Examples:

- $[Ni(en)_3]^{2+}$ → tris(ethylenediamine)nickel(II) ion
- $[Co(NH_3)_4(H_2O)Cl]^{2+}$ → tetraammineaquachloridocobalt(III) ion

These general rules form the foundation for naming more complex coordination species. They allow chemists to deduce the structure, charge, and bonding features of a compound simply by analyzing its name.

II.3. Naming Ligands

In coordination chemistry, ligands are named before the central metal atom in the complex's systematic name. The naming of ligands depends on their charge (neutral, anionic, or cationic), their structure (monodentate or polydentate), and the number of identical ligands present in the coordination sphere.

Neutral ligands usually retain their common names, but some have special names in coordination nomenclature: for instance, water becomes aqua, ammonia becomes ammine, carbon monoxide becomes carbonyl, and nitric oxide becomes nitrosyl.

Anionic ligands are named by replacing the ending of the anion with -o. For example, Cl^- becomes chloro, CN^- becomes cyano, OH^- becomes hydroxo, and $C_2O_4^{2-}$ becomes oxalato.

Polydentate ligands, which can coordinate to the metal through two or more donor atoms, are named according to their standard names, such as ethylenediamine (en), diethylenetriamine (dien), and ethylenediaminetetraacetate (EDTA).

When multiple identical ligands are present, prefixes are used to indicate their number: di-, tri-, tetra-, etc., for simple ligands. However, if the ligand's name already includes a prefix or is a complex name (e.g., ethylenediamine), the prefixes bis-, tris-, tetrakis- are used, and the ligand name is placed in parentheses (e.g., bis(ethylenediamine)).

Ligands are listed in alphabetical order in the full name of the complex, ignoring any multiplicative prefixes. This naming convention ensures clarity, consistency, and universal understanding in chemical communication, especially for complex coordination compounds.

Tableau 1. Naming conventions for common ligands

Ligand	Nom	Ligand	Nom	Ligand	Nom
H^-	hydrure	OCN^-	cyanato	SO_3^{2-}	sulfito
O^{2-}	oxo	SCN^-	thiocyanato	$S_2O_3^{2-}$	thiosulfato
OH^-	hydroxo	NH_2^-	amido	ClO_3^-	chlorato
S^{2-}	thio	N_3^-	azido ou azoturo	ClO_2^-	chlorito
I^-	iodo	$NHOH^-$	hydroxylamido	O_2^{2-}	peroxo
Br^-	bromo	NO_3^-	nitrato	H_2O	aqua
Cl^-	chloro	NO_2^-	nitrito	NH_3	ammine
F^-	Fluoro	SO_4^{2-}	sulfato	CO	carbonyl
CO_3^{2-}	carbonato	NO	nitrosyl	CN^-	cyano
PO_4^{3-}	phosphato	en	éthylènediamine	CH_3COO^-	acétato
$C_2O_4^{2-}$	oxalato	$C_6H_4(COO)_2^{2-}$	phtalato	$C_6H_4(OH)(COO)_2^-$	salicylato

II.4. Naming the central metal atom/ion

In the nomenclature of coordination compounds, the central metal atom or ion is named after the ligands. The way the metal is named depends on the overall charge of the complex.

When the coordination complex is neutral or cationic, the name of the metal remains unchanged. For example, in the complex $[Co(NH_3)_6]^{3+}$, the metal is named cobalt, and the full name becomes hexaamminecobalt(III).

However, when the coordination complex is an anion, the name of the central metal typically ends in « **ate** », and often uses a Latin-derived name. This change distinguishes anionic complexes from neutral or cationic ones. For example:

- $[Fe(CN)_6]^{3-}$ is named hexacyanoferrate(III) (not “iron”)
- $[CuCl_4]^{2-}$ becomes tetrachlorocuprate(II)
- $[Au(CN)_2]^-$ is dicyanoaurate(I)

These modified names are derived from Latin roots of the element’s name, especially for older or classical transition metals. Common Latin-based names include:

- Iron → ferrate (from *ferrum*)
- Copper → cuprate (from *cuprum*)
- Silver → argentate (from *argentum*)
- Tin → stannate (from *stannum*)

- Gold → aurate (from *aurum*)
- Lead → plumbate (from *plumbum*)

These adaptations are essential for correctly distinguishing the type and charge of a complex and are a key part of IUPAC coordination compound nomenclature.

II.5. Common errors and clarifications

II.5.1 Typical student mistakes

Despite the standardized rules for naming coordination compounds, students often encounter difficulties due to the complexity and specificity of the nomenclature system.

 One of the most common mistakes is the misuse of neutral ligand names**:**
– For example, using “ammonia” instead of the correct term “ammine”, or using “water” instead of “aqua”.

 Students often forget the rule of alphabetical ordering of ligands**,**
– Ligands must be listed alphabetically by their names, not by multiplicative prefixes (e.g., di-, tri-, bis-).

 Improper use of multiplicative prefixes is another common issue:
– Use di-, tri-, tetra- for simple ligands (e.g., chloro, ammine).
– Use bis-, tris-, tetrakis**-** for complex or polydentate ligands (e.g., ethylenediamine, EDTA), and enclose the ligand name in parentheses (e.g., bis(ethylenediamine)).

 Students may also omit or misplace the oxidation state of the metal:
– The oxidation state must appear in Roman numerals, in parentheses, immediately after the metal name.
– Example: hexaamminecobalt(III), not just "hexaamminecobalt".

II.5.2 Differences between english and french usage

Another point of confusion arises when switching between English and French nomenclature systems. Although both systems follow IUPAC rules, certain conventions differ slightly. For instance, in English, the name “hexaaquacobalt(III) chloride” is used, whereas in French, the same compound might appear as “chlorure de hexaaquacobalt(III)”, following a reversed order and different grammar. The placement of oxidation states, use of commas or hyphens, and grammar rules may vary, so care must be taken when translating or switching contexts.

II.5.3 Tips for consistent naming

To avoid such mistakes and ensure consistent and accurate naming, students are advised to follow a step-by-step approach:

- ✓ Identify and correctly name each ligand based on its charge and denticity.
- ✓ Determine the correct oxidation state of the metal based on the overall charge of the complex.
- ✓ Apply proper multiplicative prefixes, especially for polydentate ligands.
- ✓ Respect the alphabetical order of ligands.
- ✓ For anionic complexes, ensure that the metal name is modified to its Latin-derived form with the suffix « ate ».

By following these conventions carefully, students can master the systematic naming of coordination compounds and avoid the most common pitfalls.

II.6. Application examples

Name the following coordination complexes and determine the oxidation state of the central atom :

$[Fe(CN)_6]^{4-}$, $K_3[AlF_6]$, $[Ir(NO)Cl_2(PPh_3)_2]$, $[Co(NCS)(NH_3)_5]^{2+}$, $[Cr(H_2O)_6]Cl_3$, $[(CO)_5Mn\text{-}Mn(CO)_5]$, $K[PtCl_3(\eta^2\text{-}C_2H_4)]$, $[Co(ONO)(NH_3)_5]^{2+}$, $Na_3[Co(NO_2)_6]$, $[Fe(NH_3)_5H_2O]^{2+}$, $K[Au(OH)_4]$, Cis$[PtCl_2(NH_3)_2]$, $Na_3[Ag(S_2O_3)_2]$, $[Co(ONO)(NH_3)_5]SO_4$, $K_3[Cr(C_2O_4)_3]H_2O$, $K[PtCl_3(C_2H_5)]$, $K[CrF_4O]$

Solution :

$[Fe(CN)_6]^{4-}$ Hexacyanoferrate(II) ion

$K_3[AlF_6]$ Potassium hexafluoroaluminate(III)

$[Ir(NO)Cl_2(PPh_3)_2]$ Dichloronitrosylbis(triphenylphosphine)iridium(I)

$[Co(NCS)(NH_3)_5]^{2+}$ Pentaammineisothiocyanatocobalt(III) ion

$[Cr(H_2O)_6]Cl_3$ Hexaaquachromium(III) chloride

$[(CO)_5Mn\text{-}Mn(CO)_5]$ Decacarbonyldimanganese(0)

$K[PtCl_3(\eta^2\text{-}C_2H_4)]$ Potassium trichloro(ethene)platinate(II)

$[Co(ONO)(NH_3)_5]^{2+}$ Pentaamminenitritocobalt(III) ion

$Na_3[Co(NO_2)_6]$ Sodium hexanitrocobaltate(III)

$[Fe(NH_3)_5H_2O]^{2+}$ Pentaammineaquairon(II) ion

$K[Au(OH)_4]$ Potassium tetrahydroxyaurate(III)

Cis$[PtCl_2(NH_3)_2]$ Cis-diamminedichloroplatinum(II)

$Na_3[Ag(S_2O_3)_2]$ Sodium bis(thiosulfato)argentate(I)

$[Co(ONO)(NH_3)_5]SO_4$ Pentaamminenitritocobalt(III) sulfate

$K_3[Cr(C_2O_4)_3]H_2O$ Potassium tris(oxalato)chromate(III) monohydrate

$K[PtCl_3(C_2H_5)]$ Potassium trichloro(ethyl)platinate(II)

$K[CrF_4O]$ Potassium tetrafluorooxochromate(V)

Chapter III

Geometries of Complexes

III.1. Introduction

The geometry of coordination complexes plays a crucial role in determining their physical, chemical, and biological properties. The spatial arrangement of ligands around a central metal ion influences several fundamental characteristics, including:

- *Reactivity:* The geometry affects how substrates or reactants can approach and interact with the metal center, thereby modulating catalytic activity and reaction mechanisms.
- *Spectroscopic Properties:* Geometrical differences lead to variations in electronic transitions, which can be observed in UV-Visible and IR spectra. These differences are key to identifying and characterizing complexes.
- *Magnetic Behavior:* The arrangement of ligands influences the electronic configuration of the metal ion, particularly the splitting of d-orbitals. This, in turn, affects the number of unpaired electrons and thus the magnetic properties (paramagnetism, diamagnetism).
- *Stability:* Certain geometries are more stable for specific metals and ligand types due to electronic and steric factors, influencing the overall thermodynamic and kinetic stability of the complex.

Understanding and predicting the geometry of a complex is therefore essential in coordination chemistry, not only for structural identification but also for applications in catalysis, materials science, bioinorganic chemistry, and environmental remediation.

III.2. Factors influencing the geometry of complexes

The geometry adopted by a coordination complex is not arbitrary; rather, it is the result of a delicate balance between various electronic and steric factors. These factors determine the most stable spatial arrangement of ligands around the central metal ion. Understanding these influences is essential for predicting the structure and behavior of metal complexes in different chemical environments, such as in catalysis, biological systems, and materials science.

III.2.1 Nature of the central metal ion

The central metal ion plays a fundamental role in determining the geometry of a coordination complex. Several intrinsic characteristics of the metal influence how ligands are arranged around it. The most significant of these include:

a) ***Ionic radius (size of the metal ion)***

The size of the metal ion dictates how many ligands can be accommodated in its coordination sphere. Larger metal ions can support higher coordination numbers and geometries that require more spatial room, such as octahedral (6 ligands), pentagonal bipyramidal (7 ligands), or square antiprismatic (8 ligands) geometries. In contrast, smaller metal ions tend to favor lower coordination numbers, such as tetrahedral or square planar, to minimize steric crowding.

b) Oxidation State of the Metal

The oxidation state affects the effective nuclear charge experienced by the ligands. A higher oxidation state typically leads to stronger metal-ligand electrostatic attraction, potentially pulling ligands closer and affecting bond angles and lengths. This can favor more compact geometries and influence ligand field splitting patterns, which are crucial in determining electronic configuration and magnetic properties.

c) Electronic Configuration and d-Orbital Occupancy

The electronic configuration of the metal, particularly the number of d-electrons, is a key determinant of geometry. Transition metals exhibit a wide variety of geometries due to the involvement of their d-orbitals in bonding. For example:

d^8 metals (like Ni^{2+}, Pd^{2+}, Pt^{2+}) often form square planar complexes due to ligand field stabilization in that geometry.

d^0 or d^{10} metals (like Zn^{2+} or Ti^{4+}) typically form tetrahedral complexes because there is no ligand field stabilization energy favoring other geometries.

d) ***Preference for Specific Coordination Numbers***

Each metal has a preferred range of coordination numbers, depending on its size and electron count. For example:

Fe(II) commonly forms octahedral complexes (coordination number 6).

Cu(I) often forms linear (coordination number 2) or tetrahedral (coordination number 4) complexes.

Lanthanides *and* ***actinides***, due to their large radii, tend to form complexes with high coordination numbers (8–10).

e) ***Relativistic Effects and Special Cases***

In heavier elements (especially 4d and 5d transition metals), relativistic effects can alter orbital energies and lead to different geometric preferences compared to their 3d counterparts. For instance, platinum(II) often favors square planar geometry due to these effects, unlike nickel(II), which may form either tetrahedral or square planar complexes depending on the ligand.

III.2.2 Coordination Number (Number of Ligands)

The coordination number refers to the number of ligand donor atoms that are directly bonded to the central metal ion in a coordination complex. This number is one of the most important factors influencing the geometry of the complex, as it largely determines the spatial arrangement of the ligands around the metal center. Each coordination number is typically associated with one or more preferred geometrical arrangements. The most common coordination numbers and their typical geometries are: 2, 4 and 6.

These geometries arise from the need to minimize electronic repulsion between ligands while maximizing the stability of the metal-ligand interactions. The coordination number is influenced by several factors such as the size and electronic configuration of the metal, as well as the steric and electronic properties of the ligands. A clear understanding of coordination numbers provides a foundation for predicting and rationalizing the structures and behaviors of coordination compounds.

III.2.3 Nature and stereo-electronic properties of ligands

Ligands play a crucial role in determining the geometry of coordination complexes. Their steric and electronic characteristics can either stabilize or distort certain geometries, depending on how they interact with the central metal ion and with each other. These ligand properties can influence the coordination number, bond angles, and overall symmetry of the complex.

a) ***Steric Effects (Size and Bulkiness of Ligands)***

Bulky ligands can impose significant steric hindrance, limiting the number of ligands that can coordinate to the metal center. When steric repulsion between ligands becomes important, the complex may adopt geometries that reduce crowding, sometimes favoring lower coordination numbers or distorted shapes. For example, a tetrahedral geometry might be favored over an octahedral one if the ligands are too bulky to allow six of them around the metal center.

b) ***Denticity and Chelation***

The denticity of a ligand or the number of donor atoms it uses to bind to the metal also affects geometry. Monodentate ligands contribute to flexible geometries, while bidentate or polydentate ligands (chelating agents) often enforce specific spatial arrangements due to the fixed distance between their donor atoms. Chelation can stabilize certain geometries and even reduce the number of possible isomers.

c) ***Electronic Effects***

The donor ability of a ligand (σ-donor, π-donor, or π-acceptor) impacts the metal–ligand bonding and can influence geometry. Strong σ-donor ligands tend to increase electron density at the metal center, while π-acceptor ligands can withdraw electron density, stabilizing low oxidation states. These electronic interactions affect the crystal field splitting of the d-orbitals, which is key in determining the preferred geometry, especially for transition metal complexes.

d) ***Ligand Field Strength***

According to Crystal Field Theory, the strength of the ligand field (as ranked in the spectrochemical series) influences whether a complex adopts a high-spin or low-spin configuration, which in turn can favor certain geometries over others. Strong-field ligands may favor geometries that maximize ligand–metal orbital overlap and ligand field stabilization energy.

Together, these factors govern the three-dimensional arrangement of atoms in coordination compounds and are essential for predicting and rationalizing complex behavior in various chemical environments.

III.3. Geometries of complexes according to coordination number

The geometry of a coordination complex is closely linked to its coordination number, which defines the number of ligand donor atoms directly bonded to the central metal ion. For each coordination number, certain spatial arrangements are more favorable due to factors such as electronic configuration, ligand-ligand repulsion, and orbital hybridization. This section presents the most common geometries observed for coordination numbers ranging from 2 to 9, highlighting their structural features and stability.

III.3.1 Complexes with coordination number 2

Coordination number 2 corresponds to complexes in which the central metal ion is directly bonded to two ligand donor atoms. This situation is relatively rare and typically observed in metal ions with a low oxidation state, a filled d-shell (especially d^{10}), or in systems with strong spatial constraints. Two types of geometries may be observed:

a) Linear Geometry

In most cases, coordination number 2 leads to a linear geometry, where the two ligands are positioned 180° apart from each other around the central metal. This arrangement minimizes electronic repulsion between the ligands and is favored when the central metal uses sp hybrid orbitals or when d-orbitals are fully occupied, resulting in no preference for angular distortion.

Example**:**

- $[Ag(NH_3)]^{2+}$: A classic example of a linear d^{10} complex.
- $[AuCl_2]^-$: A linear complex formed by gold(I), with a d^{10} configuration.

This geometry is typical for metal ions such as Ag^+**,** Au^+**,** and Cu^+.

b) Bent Geometry (Exceptional Cases)

In rare and exceptional situations, bent (nonlinear) geometries may appear in coordination number 2 complexes. These deviations from linearity are usually caused by:

- Lone pairs on the metal center that repel bonding pairs (similar to VSEPR effects),
- Ligand–ligand repulsion in bulky systems,
- Constraints imposed by chelating ligands, especially in ring structures,
- Hybridization preferences that do not favor linearity.

Example**:**

- $[SnCl_2]$ (in the gas phase): Although it has two ligands, the presence of a lone pair on Sn(II) leads to a bent geometry, similar to the shape of H_2O.

Bent geometries are more common in main group element complexes or when the central atom has non-bonding electron pairs that influence the spatial arrangement.

III.3.2 Complexes with coordination number 3

Complexes with a coordination number of 3 involve three ligand donor atoms directly bonded to the central metal ion. Although less common than higher coordination numbers, several stable geometries can arise depending on the nature of the metal and the ligands. The two primary geometries observed are:

a) Trigonal Planar Geometry

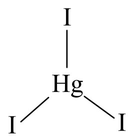
In the trigonal planar geometry, the three ligands lie in the same plane, arranged at 120° angles around the central metal ion. This geometry is typically favored when:

- The central metal ion has a d^8 or d^{10} electronic configuration,
- There is minimal steric hindrance from the ligands,
- The bonding involves sp^2 hybridization.

This geometry is often observed in complexes of transition metals in low oxidation states or in main group elements like boron and aluminum.

Exemple :

$[HgI_3]^-$ Triiodomercurate(II) ion



b) Trigonal Pyramidal Geometry

The trigonal pyramidal geometry occurs when the three ligands form a base of a pyramid, with the metal at the apex. This arrangement arises when the metal center possesses a lone pair of electrons that occupies one position of a hypothetical tetrahedron, causing the remaining three ligands to adopt a pyramidal shape. This is conceptually similar to the geometry of ammonia (NH_3).

Trigonal pyramidal geometry is more common for main group elements or early transition metals with low coordination numbers and nonbonding electron pairs.

Exemple :

$[SnCl_3]^-$ Trichlorostannate(II) ion

Complexes with coordination number 3 can adopt either a flat trigonal planar geometry or a distorted trigonal pyramidal structure, depending on the electronic configuration of the metal and the presence of lone pairs. Both geometries have important implications for reactivity and molecular symmetry.

III.3.3 Complexes with coordination number 4

Coordination number 4 is one of the most common in coordination chemistry and can lead to two distinct and well-known geometries: tetrahedral and square planar. The geometry adopted by a complex depends primarily on the nature of the central metal ion (particularly its electronic configuration) and the properties of the ligands involved.

a) Tetrahedral Geometry

In tetrahedral geometry, the four ligands are arranged around the central metal ion at the corners of a tetrahedron, with bond angles of approximately 109.5°. This geometry is typically observed when:

- The metal center is from the main group or first-row transition metals (especially with a d^0, d^5 high-spin, or d^{10} configuration),
- The ligands are small or cause minimal steric hindrance,
- Electronic repulsion between ligands favors spatial separation.

Tetrahedral geometry is common due to its minimal ligand-ligand repulsion and simple orbital hybridization (sp^3).

Exemples :

$[FeCl_4]^-$ Tétrachloroferrate(III) ion d^5

$[Zn(NH_3)_4]^{2+}$ Tétraamminezinc(II) ion d^{10}

b) Square Planar Geometry

In square planar geometry, the four ligands lie in the same plane, arranged at 90° angles around the central metal ion. This geometry is particularly common for:

- d^8 metal ions, especially second- and third-row transition metals (e.g., Pt(II), Pd(II), Ni(II)),
- Complexes with strong-field ligands, as predicted by Crystal Field Theory,

- Systems where ligand-ligand repulsion is significant, and a planar arrangement minimizes crowding.

Square planar geometry typically arises from dsp^2 hybridization and is especially stabilized in low-spin d^8 systems.

Exemples :
$[Pt(NH_3)_4]^{2+}$ Tétraammineplatinum(II) ion d^8
$[Ni(CN)_4]^{2-}$ Tétracyanonickelate(II) ion d^8

Tableau 1. Comparison between tetrahedral and square planar geometries

Criterion	**Tetrahedral**	**Square Planar**
Common for	Main group elements, 1st-row transition metals	2nd and 3rd-row transition metals (d^8)
Typical d-electron config	d^0, d^5 high-spin, d^{10}	d^8 low-spin
Ligand type	Weak-field, small, neutral ligands	Strong-field, bulky or π-acceptor ligands
Bond angles	~109.5°	90°
Hybridization	sp^3	dsp^2

The choice between tetrahedral and square planar geometries depends on a delicate balance between electronic configuration, ligand field strength, and steric factors. Understanding this balance is crucial for predicting the structure and reactivity of four-coordinate complexes.

III.3.4 Complexes with coordination number 5

Complexes with a coordination number of 5 are relatively less common but can adopt two primary geometries: trigonal bipyramidal and square pyramidal. These geometries are close in energy, and the actual structure adopted often depends on subtle electronic and steric factors.

a) Trigonal Bipyramidal Geometry

In this geometry, three ligands occupy positions in a horizontal plane (the equatorial plane), separated by 120°, while the remaining two ligands are positioned above and below this plane (the axial positions), forming a bipyramid.

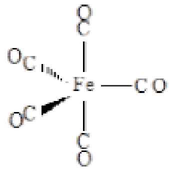
This geometry is typically observed when:

- The ligands are small and electronically similar**,**
- There is minimal steric hindrance between equatorial and axial positions,
- The system favors dsp^3 hybridization.

Trigonal bipyramidal geometry is common in p-block compounds and in some transition metal complexes, especially when the ligand field does not strongly favor square planar or octahedral arrangements.

Exemple

$[Fe(CO)_5]$ pentacarbonylfer d^8



b) Square Pyramidal Geometry

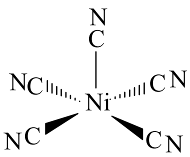
In the square pyramidal geometry, four ligands occupy the corners of a square plane, and the fifth ligand is positioned above the center of the square, forming a pyramid. This structure is often observed when:

- There is strong ligand–metal bonding in the square plane,
- One ligand is significantly different in size, charge, or donor strength (often occupying the axial site),
- The metal has an electronic configuration that disfavors equal distribution of ligands (e.g., in Jahn–Teller distorted systems).

Square pyramidal geometry can also appear as an intermediate in ligand substitution reactions or fluxional processes**.**

Exemple

$[Ni(CN)_5]^{3-}$ Penatacyanonickelate(II) ion d^8



c) Dynamic Behavior

Five-coordinate complexes can exhibit fluxional behavior, where the ligands rapidly interconvert between different positions (especially in trigonal bipyramidal geometries). This dynamic rearrangement often complicates structural determination unless studied at very low temperatures or in the solid state.

III.3.5 Complexes with coordination number 6

Coordination number 6 is the most common in transition metal chemistry and typically leads to an octahedral geometry. This highly symmetrical structure provides optimal spatial distribution for six ligands around a central metal ion. However, depending on the metal's electronic configuration and the nature of the ligands, distortions from the ideal octahedral shape may occur, such as tetragonal elongation or tetragonal compression.

a) Octahedral Geometry

In the ideal octahedral geometry, six ligands are positioned at the corners of an octahedron, forming 90° bond angles. This arrangement is energetically favorable due to:

- Maximum separation between ligands (minimizing repulsion),
- Suitability for a wide range of metal ions and ligand types,
- Favorable orbital overlap, typically involving d^2sp^3 hybridization**.**

This geometry is common for transition metals in oxidation states +2, +3, or higher and for a wide variety of ligand types, including monodentate and multidentate ligands.

Exemples :

$[Fe(CN)_6]^{3-}$ Hexacyanoferrate(III) ion d^5

$[Fe(H_2O)_6]^{2+}$ Hexaaquafer(II) ion d^6

$[Ni(NH_3)_6]^{2+}$ Hexaamminenickel(II) ion d^8

b) Tetragonal Distortions

While many six-coordinate complexes are perfectly octahedral, deviations can occur due to electronic effects (especially Jahn–Teller distortions) or ligand field asymmetry**.** The two most common distortions are:

- *Tetragonal Elongation:* The two axial bonds (along the z-axis) are longer than the four equatorial bonds. This distortion often occurs in d^9 systems (e.g., Cu(II) complexes), where degeneracy in the eg orbitals is lifted to lower the overall energy.
- *Tetragonal Compression*: The axial bonds are shorter than the equatorial ones. This distortion is less common but can appear in certain low-spin d^6 systems or due to strong axial ligand interactions.

These distortions affect the electronic spectra, magnetic properties, and reactivity of the complexes and are significant in interpreting experimental data (e.g., in EPR or UV-vis spectroscopy).

III.3.6 Complexes with coordination number (7, 8, 9…)

While coordination numbers 2 to 6 are the most common in coordination chemistry, higher coordination numbers such as 7, 8, or 9 are also observed, particularly for large metal ions, such as lanthanides, actinides, and early transition metals. These complexes often involve bulky ligands or polydentate chelators and typically adopt less regular geometries due to steric and electronic constraints.

a) Coordination Number 7

Seven-coordinate complexes exhibit several possible geometries, the most common being:

- *Pentagonal bipyramidal geometry:* five ligands lie in an equatorial pentagonal plane, and two occupy axial positions above and below the plane. This geometry is often seen in complexes of lanthanides and actinides.
- *Capped octahedron or monocapped trigonal prism:* alternative arrangements with slight distortions based on ligand flexibility or electronic preferences.

b) Coordination Number 8

Eight-coordinate complexes are more typical of large metal ions (e.g., Ce^{4+}, Zr^{4+}) and often adopt:

- *Square antiprismatic geometry:* two parallel squares are staggered and connected by ligands, forming an antiprism. This structure minimizes repulsions in crowded coordination environments.
- *Dodecahedral geometry:* less common but observed in some lanthanide complexes, where eight ligands form the corners of a snub cube-like structure.

- *Cubic geometry*: sometimes idealized in highly symmetrical systems, though rarely achieved perfectly in practice.

c) Coordination Number 9 and Above

Coordination numbers of 9 or higher are rare and generally limited to very large metal centers with small, monodentate ligands like water or halides. The geometries become increasingly complex and less well-defined, with possible arrangements such as:

- Tricapped trigonal prism (for CN = 9),
- Hexagonal bipyramidal (for CN = 8 or 9),
- Irregular polyhedra or distorted caps due to crowding.

d) Factors Favoring High Coordination Numbers

- Large ionic radius of the metal ion, allowing accommodation of many ligands,
- Small ligand size, reducing steric hindrance,
- Chelating ligands, which may wrap around the metal and force higher coordination,
- Solvent effects, particularly in aqueous or polar environments.

Higher coordination numbers lead to a variety of geometries that are often less symmetrical and more dependent on ligand and metal size. While geometrically more complex, these high-coordinate complexes are important in lanthanide/actinide chemistry, bioinorganic systems, and materials science, and they illustrate the flexibility and diversity of coordination compounds beyond the classic models.

III.4. Experimental techniques for determining complex geometry

The geometry of coordination complexes can be determined or inferred using various experimental techniques. Each method provides specific types of information about the spatial arrangement of atoms, electronic structure, or magnetic behavior. The most commonly used techniques include:

a) X-ray Diffraction (XRD)

X-ray crystallography is the most direct and accurate method for determining the three-dimensional structure of a complex. It provides:

- Precise atomic positions in the crystal,
- Bond lengths and bond angles,
- Clear visualization of the coordination geometry.

However, it requires high-quality single crystals**,** and results represent the solid-state structure, which may differ from the structure in solution.

b) Spectroscopic Methods

Several spectroscopic techniques offer indirect evidence of geometry based on electronic transitions, vibrational modes, or nuclear environments:

- *Infrared (IR) spectroscopy**:*** can reveal information about the symmetry of a complex. Certain vibrational bands (e.g., M–L stretches) may appear or split depending on the coordination geometry.
- *UV-Visible spectroscopy**:*** provides insight into d–d transitions and ligand-to-metal charge transfer (LMCT)**.** The number, position, and intensity of absorption bands can help distinguish between different geometries (e.g., tetrahedral vs. octahedral).
- *Nuclear Magnetic Resonance (NMR)* spectroscopy: useful for diamagnetic complexes, it reflects the chemical environment of ligands. Symmetry in the NMR spectrum can indicate the type of geometry (e.g., equivalence of ligand environments in square planar or tetrahedral complexes).

c) Magnetic Data

The magnetic behavior of a complex particularly the number of unpaired electrons can provide valuable clues about its geometry:

- For example, tetrahedral and square planar geometries may differ in spin states even for the same metal ion and oxidation state.
- Magnetic susceptibility measurements and Evans method (NMR-based) can help estimate the number of unpaired electrons and therefore infer likely geometries, especially when combined with ligand field theory.

By combining structural, spectroscopic, and magnetic data, chemists can reliably determine or predict the geometry of coordination complexes both in the solid state and in solution. These techniques are essential tools in coordination and bioinorganic chemistry.

III.4. The Importance of Geometry in Understanding the Properties of Metal Complexes

The geometry of coordination complexes is a key factor in understanding their chemical behavior and physicochemical properties. The spatial arrangement of ligands around a central metal ion such as octahedral, tetrahedral, square planar, or trigonal bipyramidal directly influences the electronic distribution, stability, and reactivity of the complex. For example, the geometry determines the crystal field splitting pattern, which affects magnetic properties, electronic spectra, and the strength of metal–ligand interactions. Moreover, the geometry plays a critical role in stereoisomerism (such as cis-trans or fac-mer isomers), which can significantly influence the biological activity and catalytic performance of complexes. In bioinorganic systems, geometric preferences also govern how metal centers interact with biomolecules. Therefore, a thorough understanding of coordination geometry is essential for predicting the structure–function relationship of metal complexes and for rational design in areas such as catalysis, materials science, and medicinal chemistry.

Chapter IV

ISOMERISM IN METAL COMPLEXES

IV.1. Introduction

Isomerism is a fundamental concept in coordination chemistry, referring to the existence of two or more compounds with the same chemical formula but different arrangements of atoms or ligands. In metal complexes, isomerism plays a crucial role in determining physical properties, chemical reactivity, biological activity, and overall stability. The three-dimensional nature of coordination compounds, along with the variety of possible ligand types and coordination numbers, leads to a rich diversity of isomeric forms.

Isomers in coordination chemistry are generally classified into two main types: structural (or constitutional) isomers**,** which differ in the connectivity of atoms, and stereoisomers**,** which have the same atom-to-atom connections but differ in the spatial arrangement of ligands around the metal center. Each type of isomerism provides insight into the geometry, bonding, and function of metal complexes. Understanding these isomeric forms is essential for interpreting experimental data, designing metal-based drugs, and developing catalytic systems in both industrial and biological settings.

This chapter explores the various types of isomerism found in metal complexes, illustrates their structural characteristics through representative examples, and discusses their importance in practical applications.

IV.2. Structural isomerism (constitutional isomerism)

Structural isomerism, also known as constitutional isomerism, occurs when coordination compounds have the same molecular formula but differ in the connectivity or arrangement of atoms within the molecule. This means that the composition of the coordination sphere or the nature of the attached ligands and counter-ions varies from one isomer to another. These differences lead to distinct chemical and physical properties, even though the overall stoichiometry remains the same. Structural isomerism in coordination compounds can be categorized into several types, including ionization isomerism, hydration isomerism, coordination isomerism, and linkage isomerism.

IV.2.1 Ionization isomerism

i. ***Definition and Principle***

Ionization isomerism occurs in coordination compounds that yield different ions in solution, even though they have the same overall composition. This phenomenon arises when a ligand inside the coordination sphere exchanges places with an ion of opposite charge located outside the sphere (typically a counter-ion). As a result, the isomers produce different ions upon dissolution in water, which can be detected by standard analytical methods such as precipitation reactions or conductivity measurements.

This type of isomerism highlights the fact that the chemical behavior of a complex is not solely dependent on its formula, but also on the specific connectivity and distribution of ions and ligands.

ii. ***General Characteristics***

- The metal center remains the same.
- The total number and type of ligands are identical, but their positions (inside or outside the coordination sphere) are different.
- The isomers dissociate differently in aqueous solution.
- They often show distinct colors and reactivities due to the different environments of the ligands.

Example:
A classic example is provided by the two cobalt(III) complexes:

- $[Co(NH_3)_5Br]SO_4$
- $[Co(NH_3)_5SO_4]Br$

Both compounds have the same empirical formula: $Co(NH_3)_5BrSO_4$. However, in the first isomer, the bromide ion is coordinated to the cobalt center, and the sulfate ion acts as a counter-ion. In the second isomer, the sulfate is coordinated, and bromide is outside the coordination sphere. When dissolved in water:

- $[Co(NH_3)_5Br]SO_4$ dissociates into $[Co(NH_3)_5Br]^{2+}$ and SO_4^{2-}
- $[Co(NH_3)_5SO_4]Br$ dissociates into $[Co(NH_3)_5SO_4]^{+}$ and Br^{-}

These two species can be distinguished by:

- Precipitation tests (e.g., adding $BaCl_2$ to test for free SO_4^{2-})
- Conductivity measurements (since they produce different numbers of ions)
- UV-visible spectroscopy (due to differences in ligand field strength and d-d transitions)

iii. **Significance**

Ionization isomerism is important in analytical chemistry and coordination chemistry, as it demonstrates how small changes in ligand positioning can significantly affect the chemical and physical behavior of coordination complexes. It is also relevant in pharmaceutical and industrial applications, where the bioavailability or reactivity of a metal complex may vary depending on its isomeric form.

IV.2.2 Hydration isomerism

i. ***Definition and Principle***

Hydration isomerism, also known as solvation isomerism, arises when water molecules (or other solvent molecules) occupy different positions in a coordination compound either inside the coordination sphere as ligands directly bonded to the metal center, or outside the sphere as free (or lattice) solvent molecules. Although the overall chemical composition remains the same, the location of the water molecules changes the structure and properties of the complex.

This form of isomerism is especially common in transition metal aqua complexes, where coordination numbers and hydration environments are easily altered without modifying the stoichiometry.

ii. ***General Characteristics***

- The complexes have the same empirical formula and overall composition.
- The number of coordinated versus free water molecules differs.
- The isomers often exhibit differences in color, solubility, and reactivity.
- They show different behavior in dehydration or thermogravimetric analysis (TGA).
- Their conductivity may also vary depending on the number of ions released into solution.

Example:

A well-known set of hydration isomers involves chromium(III) chloride in its hydrated forms:

1. $[Cr(H_2O)_6]Cl_3$
2. $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$
3. $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

These three isomers share the overall molecular formula $CrCl_3 \cdot 6H_2O$, but differ in the placement of the water molecules and chloride ions:

- In $[Cr(H_2O)_6]Cl_3$, all six water molecules are directly bonded to the chromium ion. The three chloride ions are free in solution.
- In $[Cr(H_2O)_5Cl]Cl_2{\cdot}H_2O$, one Cl^- replaces a water molecule in the inner coordination sphere, and one H_2O is found outside the sphere.
- In $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$, two Cl^- ions are coordinated to Cr^{3+}, and two water molecules are present as free solvates.

iii. ***Behavior in Aqueous Solution***

These isomers can be differentiated by:

- Conductivity tests**:** due to differing numbers of free ions in solution.
- Chloride ion precipitation**:** using $AgNO_3$ to test for free Cl^-.
- Infrared and UV-Vis spectroscopy**:** as changes in the ligand field affect electronic transitions.
- Color**:** each isomer may have a different hue depending on the ligand field strength and symmetry.

iv. ***Significanc***

Hydration isomerism is a key concept in coordination chemistry, illustrating the lability and versatility of solvent molecules in metal complexes. It has implications in the design of materials with specific hydration properties, in crystal engineering, and even in biological systems where hydration shells play a crucial role in metalloprotein function. Moreover, understanding these isomers is essential for proper characterization of coordination compounds in both academic and industrial laboratories.

IV.2.3 Coordination isomerism

i. ***Definition and Principle***

Coordination isomerism arises in compounds that contain more than one metal center, typically in the form of both a cationic and an anionic complex within the same compound. This type of isomerism occurs when there is an exchange of ligands between the two metal ions, leading to different distributions of ligands without altering the overall chemical formula. The total number and types of ligands remain constant, but they are coordinated to different metal centers in each isomer.

This isomerism is only possible in bimetallic complexes where at least two coordination centers are present usually one forming a positively charged complex (cation) and the other forming a negatively charged complex (anion).

ii. ***General Characteristics***

- Involves compounds with two different coordination complexes: one cationic, one anionic.
- The ligands are redistributed between the two metal centers.
- The isomers have the same molecular formula and oxidation states but differ in ligand-metal assignments.
- They often exhibit differences in color, solubility, magnetic properties, and reactivity.

Example**:**

A classical example is found in the pair of coordination compounds:

- $[Co(NH_3)_6][Cr(CN)_6]$
- $[Cr(NH_3)_6][Co(CN)_6]$

Both have the same overall formula: $CoCr(NH_3)_6(CN)_6$, but the coordination of ligands is inverted:

- In the first isomer, the cobalt(III) ion is coordinated to six ammonia ligands, forming the cation $[Co(NH_3)_6]^{3+}$, while the chromium(III) ion is coordinated to six cyanide ligands, forming the anion $[Cr(CN)_6]^{3-}$.
- In the second isomer, the roles are reversed: chromium(III) binds six NH_3 molecules, and cobalt(III) binds six CN^- ligands.

These isomers differ in:

- Spectroscopic properties**,** as NH_3 and CN^- are very different ligands in terms of field strength.
- Magnetic behavior**,** since CN^- is a strong field ligand and may cause low-spin configurations, while NH_3 is a weaker field ligand.
- Reactivity**,** especially toward substitution or redox reactions, which depends on the specific metal-ligand environment.

iii. ***Significance***

Coordination isomerism is particularly important in the field of coordination chemistry and materials science**,** as the properties of the complex can drastically change depending on which metal is coordinated to which ligand. This concept is essential for the rational design of functional materials, catalysts, and coordination polymers. It also illustrates the concept of metal-ligand specificity**,** which is crucial in biological systems and catalysis.

Understanding coordination isomers allows chemists to explore the subtle differences in reactivity and behavior that result purely from the spatial and electronic redistribution of ligands despite having the same overall formula.

IV.2.4 Linkage isomerism

i. ***Definition and Principle***

Linkage isomerism occurs in coordination compounds that contain ambidentate ligands ligands capable of coordinating to the central metal atom or ion through two (or more) different atoms, but only one at a time. These ligands possess multiple donor atoms, but they can bind through only one donor atom in a given complex, leading to different possible modes of coordination. The resulting isomers, known as linkage isomers**,** have identical chemical compositions but differ in the identity of the donor atom bonded to the metal center.

This isomerism provides clear evidence of the directional nature of coordinate bonds and of the electronic and steric effects that influence ligand-metal interactions.

ii. General Characteristics

- The ligand remains the same in terms of molecular formula, but its coordination mode differs.
- The coordination sphere is unchanged in terms of the number of ligands and overall charge.
- The isomers differ in physical properties such as color, dipole moment, and spectral behavior.
- Often detected and confirmed through IR spectroscopy, UV-Vis spectroscopy, and X-ray crystallography.

iii. Ambidentate Ligands Capable of Linkage Isomerism

- NO_2^- (nitrite ion)**:** can bind via nitrogen (**NO_2**, nitro) or via oxygen (**ONO**, nitrito).
- SCN^- (thiocyanate ion)**:** can bind via sulfur (**SCN**, thiocyanato-S) or via nitrogen (NCS, thiocyanato-N).
- CN^- (cyanide ion)**:** can bind via carbon (**–C≡N**, cyano) or nitrogen (**–N≡C**, isocyano).
- $S_2O_3^{2-}$ (thiosulfate)**:** can bind through sulfur or oxygen atoms.

Example:

One of the most well-known examples involves the nitrite ion:

- $[Co(NH_3)_5(NO_2)]^{2+}$
- $[Co(NH_3)_5(ONO)]^{2+}$

In the first isomer, the NO_2^- ligand is coordinated to the cobalt(III) center via the nitrogen atom ($–NO_2$), forming the nitro isomer.
In the second isomer, the same ligand is coordinated through an oxygen atom (–ONO), forming the nitrito isomer.

These two isomers can be distinguished by:

- Infrared (IR) spectroscopy: The $–NO_2$ and –ONO groups have distinct vibrational frequencies.
- UV-visible spectroscopy: Due to different ligand field effects and charge transfer bands.
- Color: The two isomers often exhibit different colors. For example, the nitro isomer is typically yellow, while the nitrito isomer is red.

iv. ***Significance***

Linkage isomerism plays an important role in both fundamental coordination chemistry and in applied fields such as catalysis, bioinorganic chemistry, and materials science. In biological systems, certain metalloenzymes exhibit selectivity for specific donor atoms of ambidentate ligands, which can influence enzymatic activity or metal transport.

In industrial catalysis, the coordination mode of ambidentate ligands can significantly affect catalytic performance, selectivity, and stability. Therefore, understanding and controlling linkage isomerism is vital for the rational design of coordination compounds with tailored properties.

IV.3. Stereoisomerism

Two main types of stereoisomerism are encountered in coordination chemistry: geometrical isomerism and optical isomerism. Each type arises from specific spatial arrangements of ligands around the metal center and plays a fundamental role in determining the physicochemical and biological behavior of metal complexes.

IV.3.1 Geometrical isomerism (cis/trans or fac/mer)

i. ***Definition and Principle***

Geometrical isomerism is a type of stereoisomerism that arises in coordination compounds when the spatial arrangement of ligands around the central metal ion differs, even though the coordination formula remains the same. This phenomenon is commonly observed in square planar and octahedral complexes, where ligands can occupy different relative positions leading to distinct isomers, usually referred to as cis and trans, or facial (fac) and meridional (mer) isomers.

These isomers have different chemical and physical properties, such as color, solubility, dipole moment, and reactivity. In biological or pharmaceutical contexts, geometrical isomers may also display different levels of activity or toxicity.

A. cis/trans Isomerism

This type is typically found in:

- Square planar complexes with the general formula $[MA_2B_2]$, especially for d^8 metal ions like Pt(II), Pd(II), or Ni(II).
- Octahedral complexes with the general formula $[MA_4B_2]$, where A and B are monodentate ligands.

Example 1 – Square Planar Complex:

- $[Pt(NH_3)_2Cl_2]$

  This complex exists in two geometrical isomers:
- cis-$[Pt(NH_3)_2Cl_2]$, where the two chloride ligands are adjacent.
- trans-$[Pt(NH_3)_2Cl_2]$, where the two chloride ligands are opposite.

The cis-isomer of this complex is medically important it corresponds to cisplatin, a widely used anticancer drug, while the trans-isomer is biologically inactive.

Example 2 – Octahedral Complex:

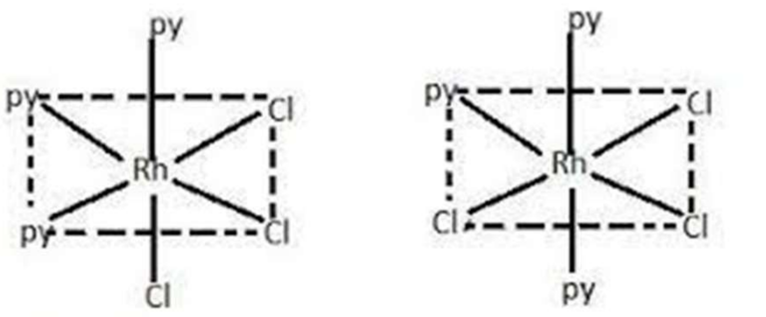
- $[Co(NH_3)_4Cl_2]^+$

  In the cis-isomer, the two chloride ligands are next to each other.
  In the trans-isomer, they are on opposite sides of the octahedron.

B. fac/mer Isomerism

This form of geometrical isomerism is specific to octahedral complexes of the type $[MA_3B_3]$, where three identical ligands occupy coordination positions.

- facial (fac) isomer**:** The three identical ligands (e.g., A) occupy positions at the corners of one face of the octahedron, forming a triangle all are 90° apart.
- meridional (mer) isomer**:** The three identical ligands occupy a meridian plane through the metal center two ligands are trans (180° apart), and the third is cis (90°) to each.



Cis - or fac-isomer　　trans - or mer-isomer

Example:

- $[Co(NH_3)_3(NO_2)_3]$

  This complex exhibits two geometrical isomers:
- fac-$[Co(NH_3)_3(NO_2)_3]$**,** where the NO_2^- groups are on the same face.
- mer-$[Co(NH_3)_3(NO_2)_3]$**,** where the NO_2^- groups form a meridional plane.

These isomers can be distinguished using infrared spectroscopy**,** UV-visible spectroscopy**,** or X-ray crystallography**.**

ii. ***Significance***

Geometrical isomerism significantly influences the reactivity, stability, and biological activity of coordination compounds. For example:

- In drug design (like cisplatin), the biological activity depends on the specific geometry.
- In catalysis, different isomers can exhibit markedly different efficiencies or selectivities.
- In optical and magnetic materials, geometrical arrangements affect electronic transitions and magnetic behavior.

Understanding geometrical isomerism is essential in coordination chemistry as it helps predict and interpret the structural diversity and functional behavior of metal complexes.

IV.3.2 Optical isomerism

i. *Definition and Principle*

Optical isomerism is a type of stereoisomerism observed in certain coordination compounds that lack a plane or center of symmetry. These compounds can exist as two non-superimposable mirror images, known as enantiomers, much like a pair of human hands. Despite having identical chemical compositions and connectivity, these isomers differ in the way they interact with plane-polarized light: one enantiomer rotates it to the right (dextrorotatory, +), and the other to the left (levorotatory, –).

This property of rotating the plane of polarized light is called optical activity, and it arises from the chirality of the complex. A complex is said to be chiral when it cannot be superimposed on its mirror image.

ii. *Characteristics of Optical Isomers*

- Same physical and chemical properties in achiral environments.
- Different behavior in chiral environments, including biological systems (e.g., enzymes, receptors).
- Cannot be interconverted without breaking coordination bonds.
- Separation of enantiomers (called resolution) requires chiral agents or chromatographic techniques.
- Identified and studied using polarimetry, circular dichroism (CD), and X-ray crystallography.

iii. *Conditions for Optical Isomerism in Coordination Complexes*

- The complex must be chiral, i.e., it must lack symmetry elements like a mirror plane or inversion center.
- Most commonly observed in octahedral complexes, especially with bidentate ligands that form chelate rings.
- Also possible in tetrahedral complexes, particularly when four different ligands are attached to the metal center (analogous to a chiral carbon in organic chemistry).

Examples

1. *Octahedral Complexes with Bidentate Ligands:*

Example:

- $[Co(en)_3]^{3+}$

  (en = ethylenediamine)

  This complex contains three bidentate ligands (en), forming three chelate rings around the cobalt ion. It exists in two optically active forms:

- Λ-isomer (lambda): left-handed twist.
- Δ-isomer (delta): right-handed twist.

  These are mirror images that cannot be superimposed. They rotate plane-polarized light in opposite directions and have different interactions with chiral biological molecules.

2. *Mixed-Ligand Octahedral Complexes:*

Example:

- $[Cr(ox)_2(H_2O)_2]^-$

  (ox = oxalate, a bidentate ligand)

  This complex is also chiral and exhibits optical isomerism due to the arrangement of the two oxalate ligands, which form non-superimposable mirror images.

iv. ***Tetrahedral Complexes***

Although less common, tetrahedral complexes can also show optical isomerism if all four ligands are different, much like the case of a chiral carbon atom in organic compounds.

Example:

- [M(ABCD)]

  Where A, B, C, and D are four different monodentate ligands.

v. ***Biological and Practical Importance***

- Bioinorganic Chemistry: Many metal-containing biomolecules are chiral. Only one enantiomer of a drug may be biologically active, while the other could be inactive or even harmful.
- Asymmetric Catalysis: Chiral metal complexes are used as catalysts to induce the formation of specific enantiomers in organic synthesis (important in pharmaceuticals).

- <u>Materials Science:</u> Optical isomers may have different optical or electronic properties, useful in molecular devices.
- Optical isomerism highlights the importance of three-dimensional structure in coordination chemistry. The existence of chiral metal complexes and their unique interactions with light and biological systems make this type of isomerism especially significant in both theoretical and applied chemistry. Mastery of this concept is essential for chemists working in fields such as stereochemistry, drug design, and catalysis.

IV.4. Applications and importance of isomerism in coordination compounds

Isomerism in coordination compounds plays a fundamental role in determining their chemical behavior, biological activity, and industrial applications. The different spatial arrangements of ligands around the central metal atom can significantly influence reactivity, selectivity, and function. Below are some key areas where isomerism is particularly important:

1. Medicinal Chemistry

Isomerism can drastically affect the pharmacological properties of metal-based drugs. A well-known example is cisplatin and transplatin**,** two geometric isomers of the platinum(II) complex $[PtCl_2(NH_3)_2]$.

- ***Cisplatin*** (cis-$[PtCl_2(NH_3)_2]$) is one of the most effective chemotherapy agents, particularly against testicular, ovarian, and bladder cancers. Its activity is due to its ability to form cross-links with DNA, disrupting replication and transcription.
- ***Transplatin*** (trans-$[PtCl_2(NH_3)_2]$), however, is biologically inactive. The difference arises from the geometric arrangement of ligands, which affects the drug's ability to interact with DNA and cellular targets.

This example illustrates how geometrical isomerism directly influences biological efficacy and therapeutic application.

2. Catalysis

In asymmetric catalysis, optical isomerism (chirality) in coordination complexes is crucial for inducing enantioselectivity in chemical reactions.

- Chiral metal complexes are used as homogeneous catalysts to produce enantiomerically pure products, especially in the pharmaceutical industry.
- For instance, chiral Rh and Ru complexes have been used in asymmetric hydrogenation, enabling the selective formation of one enantiomer over another.
- The specific configuration of the isomeric form of the catalyst determines the stereochemistry of the product.

Thus, isomerism, particularly stereoisomerism**,** is a key tool in the development of highly selective and efficient catalytic systems.

3. Bioinorganic Chemistry and Metal-Based Drugs

In biological systems, metal complexes often exhibit structural isomerism and linkage isomerism, which can influence how they interact with biomolecules like proteins, enzymes, or DNA.

- Many metalloenzymes rely on the specific coordination geometry of metal centers for their function, and slight changes in isomeric form can lead to loss or alteration of activity.
- Linkage isomers, such as those involving nitrite ligands binding through nitrogen (nitro) or oxygen (nitrito), can display different reactivities and biological behaviors.
- In the development of metal-based drugs**,** understanding isomerism helps in optimizing activity, reducing toxicity, and improving stability.

These applications highlight the importance of coordination geometry and ligand orientation in drug design and biochemical interactions.

IV.5. Review Exercises

Application 1:

Consider the complex $[PtBrClI(NH_3)_2]^{2+}$

1. Determine the geometry around the platinum atom.
2. Identify all possible isomers of this complex.

Solution

1. Geometry:

The platinum(II) ion in this complex is coordinated to five monodentate ligands: Br^-, Cl^-, I^-, and two NH_3 molecules. With a coordination number of 5, the most likely geometry is trigonal bipyramidal.

2. Possible isomers:

- Geometrical isomers (cis and trans arrangements of ligands, e.g., NH_3 groups being 90° or 180° apart): 2

Thus, this complex exhibits:

- 2 geometrical isomers

Application 2:

Consider the complex $[Cr(CN)_3(NH_3)_3]$

1. Determine the geometry around the chromium atom.
2. Identify all possible isomers of this complex.

Solution

1. Geometry: Octahedral.
2. Isomers: Geometrical isomers: 2 (fac and mer).

Chapter V

STABILITY OF COORDINATION COMPLEXES AND EQUILIBRIA

V.1. Introduction

The stability of coordination complexes is a central concept in coordination chemistry, as it governs the formation, existence, reactivity, and practical applications of metal–ligand systems. When a metal ion interacts with one or more ligands to form a complex, the extent to which this process proceeds and the persistence of the resulting complex depends on its stability**.**

Stability can be considered from two complementary perspectives: *thermodynamic stability*, which refers to the energetics and equilibrium position of complex formation, and *kinetic stability*, which relates to the rate at which a complex forms or breaks apart. A complex may be thermodynamically stable (favorable to form) but kinetically labile (easily dissociates), or vice versa. Distinguishing between these types of stability is essential for understanding both the behavior of metal complexes in solution and their roles in chemical and biological systems.

Thermodynamic stability is quantitatively described by stability constants**,** which measure the tendency of a metal ion to form complexes with specific ligands. These constants allow chemists to predict whether complexation will occur, and to what extent, under given conditions. The magnitude of the stability constant depends on various factors, such as the nature of the metal ion, the type of ligand, and the surrounding medium (e.g., solvent, pH, ionic strength).

Understanding coordination equilibria is also crucial in a wide range of applications:

- In *analytical chemistry***,** complexation reactions are the basis for titrations (e.g., EDTA complexometric titration).
- In *bioinorganic chemistry***,** metal–ligand interactions are fundamental to the structure and function of metalloproteins and metal-based drugs.
- In *environmental chemistry*, stability governs metal speciation, mobility, and toxicity in natural waters.

This chapter will explore the principles that govern complex stability, distinguish between kinetic and thermodynamic aspects, examine the factors influencing equilibrium, and present the quantitative tools used to describe and calculate stability. Through both theoretical concepts and practical examples, students will gain a comprehensive understanding of how and why metal–ligand complexes form, persist, or dissociate in chemical systems.

V.2. Types of stability

Coordination complexes can be described in terms of two fundamental types of stability: thermodynamic stability and kinetic stability. While both concepts refer to the persistence or behavior of a complex, they are fundamentally different in their meaning and implications. A complete understanding of metal–ligand systems requires the distinction and appreciation of both.

V.2.1 Thermodynamic stability

i. Definition

Thermodynamic stability refers to the energetic favorability of complex formation at equilibrium. It is a measure of how likely a complex is to form and remain intact under equilibrium conditions. A complex is said to be thermodynamically stable if it has a low free energy and is strongly favored over the dissociated metal ion and free ligands.

This type of stability is quantified by stability constants (also called formation constants), which are equilibrium constants for the reaction between a metal ion and one or more ligands.

Stepwise Stability Constants (K_1, K_2, K_3, ...)

The formation of a complex often occurs in a stepwise fashion, where ligands bind one at a time to the metal ion. Each step has its own equilibrium constant:

$$M^{n+} + L \rightleftharpoons [ML]^{n+} \quad K_1$$

$$[ML]^{n+} + L \rightleftharpoons [ML2]^{n+} \quad K_2$$

$$[ML2]^{n+} + L \rightleftharpoons [ML3]^{n+} \quad K_3$$

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- K_1, K_2, K_3,… are the stepwise stability constants, and they typically decrease in magnitude with each successive ligand addition, due to increasing electrostatic repulsion or steric hindrance.

ii. ***Overall stability Constant (βn)***

The overall formation constant, denoted by $\boldsymbol{\beta_n}$, describes the formation of a complex in a single step:

$$Mn^{+} + nL \rightleftharpoons [MLn]^{n+}$$

$$\beta n = K_1 \cdot K_2 \cdots\cdots K_n$$

- Larger values of β_n indicate greater thermodynamic stability.
- In practice, log β values are often used for convenience.

V.2.2 Kinetic stability

i. ***Definition***

Kinetic stability refers to the rate at which a complex reacts particularly how fast it undergoes ligand substitution or dissociation. A kinetically stable (or inert) complex resists ligand exchange reactions, even if it is thermodynamically unstable. Conversely, a labile complex undergoes ligand substitution rapidly, regardless of its thermodynamic stability.

This concept is independent of equilibrium constants and instead relates to reaction kinetics and activation energy.

ii. ***Labile vs. inert complexes***

According to the IUPAC classification (based on substitution half-lives at room temperature):

- ***Labile complexes****:* React quickly (half-life < 1 minute)
  - Example: $[Ni(H_2O)_6]^{2+}$
- ***Inert complexes****:* React slowly (half-life > 1 hour)
  - Example: $[Cr(NH_3)_6]^{3+}$

It is possible for a complex to be:

- *Thermodynamically stable but kinetically labile*
- *Thermodynamically unstable but kinetically inert*

iii. ***Factors affecting substitution rates***

Several factors influence the kinetic behavior of metal complexes:

- *Oxidation state of the metal:* Higher oxidation states often lead to more inert complexes.
- *Electronic configuration:* d^3, d^6 low-spin, and d^8 square planar complexes are often inert.
- *Ligand field effects:* Strong field ligands may stabilize inert configurations.
- *Steric hindrance:* Bulky ligands can slow down substitution.
- *Solvent and temperature:* These can alter activation energies for substitution reactions.

V.3. Formation equilibria of complexes

The formation of coordination complexes in solution is governed by chemical equilibria. These equilibria are described using formation constants, which quantify the affinity between a metal ion and ligands. Understanding these constants allows chemists to predict the extent of complexation under given conditions.

V.3.1 Stepwise formation reactions

i. General equation

The formation of a complex usually proceeds step by step, with ligands coordinating one at a time to the central metal ion. Each individual step is an equilibrium process described by a stepwise formation constant Ki:

$$M^{n+} + L \rightleftharpoons [ML]^{n+} \quad K_1$$

$$[ML]^{n+} + L \rightleftharpoons [ML2]^{n+} \quad K_2$$

$$[ML2]^{n+} + L \rightleftharpoons [ML3]^{n+} \quad K_3$$

Where:

- M = metal ion
- L = ligand
- $K_1, K_2, K_3,\ldots$ are the stepwise formation constants.

These constants reflect the ease with which each successive ligand binds. Typically:

$K_1 > K_2 > K_3$ (due to decreasing availability of coordination sites and increasing repulsion).

ii. Examples with numerical values

Formation of $[Cu(NH_3)_4]^{2+}$

Copper(II) ions react with ammonia in a stepwise fashion to form a tetraammine complex:

$Cu^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)]^{2+}$ $K_1=10^{4.3}$

$[Cu(NH3)]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2]^{2+}$ $K_2=10^{3.9}$

$[Cu(NH_3)_2]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3]^{2+}$ $K_3=10^{3.2}$

$[Cu(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$ $K_4=10^{2.6}$

Here we see the typical trend: each additional NH_3 binds less strongly than the previous one.

V.3.2 Overall formation constants (β)

i. Definition and relation to stepwise constants

The overall formation constant βn describes the equilibrium for the complete formation of a complex with *n* ligands in a single step:

$$Mn^{+} + nL \rightleftharpoons [MLn]^{n+}$$

$$Bn = [ML_n]/[M^{n+}][L]^n$$

The overall constant is the product of the individual stepwise constants:

$$Bn = K_1 \cdot K_2 \cdot K_3 \cdots K_n$$

This cumulative constant reflects the total affinity of the metal ion for all ligands in the final complex.

ii. Logarithmic Notation

Because stability constants often span many orders of magnitude, their logarithms (base 10) are commonly used:

$$\text{Log } \beta n = \log K_1 + \log K_2 + \cdots + \log K_n$$

This simplifies data handling and comparison between different systems.

Example: $[Cu(NH_3)_4]^{2+}$ (continued)

From the earlier example:

$$K_1 = 104.3$$

$$K_2 = 103.9$$

$$K_3 = 103.2$$

$$K_4 = 102.6$$

$$\beta_4 = K_1 \cdot K_2 \cdot K_3 \cdot K_4 = 10^{4.3+3.9+3.2+2.6} = 10^{14.0}$$

Thus:

$$\text{Log } \beta_4 = 14.0$$

A high log β value indicates a highly stable complex under equilibrium condition.

V.4. Factors influencing stability

The stability of coordination complexes depends on several interrelated factors, both intrinsic (such as the nature of the metal ion) and extrinsic (such as the type of ligands). These factors influence the extent to which a metal ion can bind to ligands and maintain a stable complex under equilibrium conditions.

V.4.1 Nature of the metal ion

i. Charge, Size, and Electronic Configuration

- Charge**:** Higher positive charge on the metal ion increases electrostatic attraction to negatively charged or neutral electron-donating ligands, enhancing complex stability.
  - Example: Fe^{3+} forms more stable complexes than Fe^{2+} due to its higher charge.
- Ionic Radius**:** Smaller metal ions have higher charge density, resulting in stronger electrostatic attraction.
  - Example: Al^{3+} (small and highly charged) forms highly stable complexes with ligands like fluoride or EDTA.
- Electronic Configuration**:** The d-electron configuration influences the ligand field stabilization energy (LFSE), which contributes to the stability of the complex.
  - d^3 and low-spin d^6 configurations are generally associated with inert and stable complexes.

ii. Irving–Williams Series

This empirical trend ranks the stability of complexes of first-row transition metals with a given ligand (e.g., NH_3, EDTA):

$$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$$

- The increasing trend is due to increasing nuclear charge and ligand field stabilization.

- Cu^{2+} often shows abnormally high stability due to the Jahn–Teller distortion**.**
- The order of stability is the inverse order of the size of the cations. To be convinced of this, just take a look at the position of these metals in the periodic table (Fig. 7).

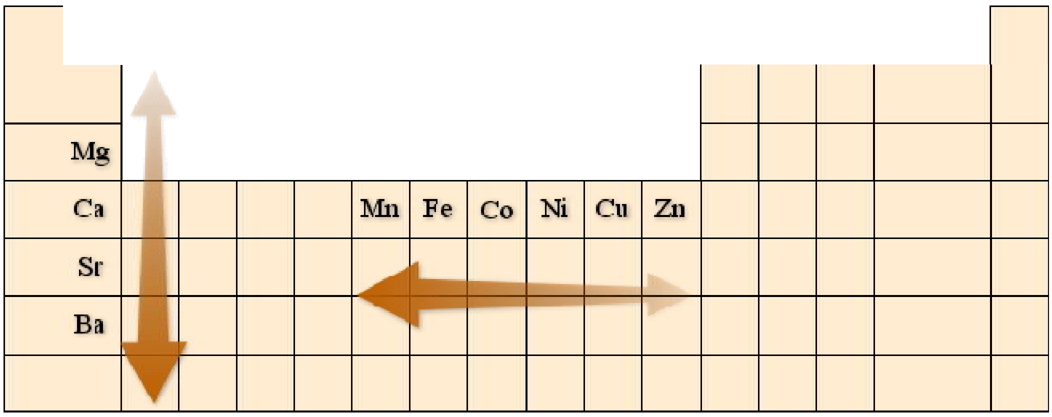
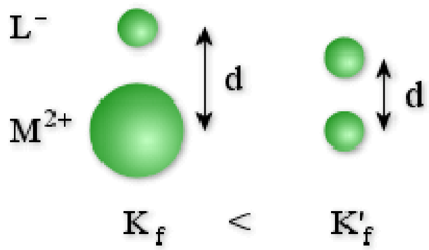


Figure 7. Position of some metals in the periodic table

This order has two origins:

Electrostatic: larger ions have lower constants: the metal-ligand charges are far apart; the electrostatic interaction energy (inversely proportional to the distance d between the metal and the ligand) is low.



Between and, the ESCC increases in absolute value if the ion is in its high-spin state (in this context, the P electron pairing energy was not taken into account):

This increase in ESCC is accompanied by a stabilization of the complex as a whole.

V.4.2 Nature of the ligand

i. Denticity and Chelation

- *Monodentate ligands* coordinate through a single donor atom (e.g., Cl^-, NH_3).
- *Polydentate ligands* (chelating agents) coordinate through multiple donor atoms.
    - Example: Ethylenediamine (en) is a bidentate ligand.

- Complexes formed with chelating ligands are more stable due to the chelate effect

ii. ***HSAB Theory (Hard and Soft Acids and Bases)***

The Hard and Soft Acids and Bases (HSAB) theory helps predict the strength of metal–ligand interactions:

- Hard acids (e.g., Al^{3+}, Fe^{3+}) prefer hard bases (e.g., F^-, OH^-).
- Soft acids (e.g., Pt^{2+}, Hg^{2+}) prefer soft bases (e.g., CN^-, S^{2-}).

iii. ***Compatibility increases stability.***

- Example: Pt^{2+} forms a stable complex with SCN^- (both soft).
- Fe^{3+} forms a stable complex with F^- (both hard).

V.4.3 Chelate Effect

The chelate effect refers to the enhanced stability observed when a metal ion binds to a ligand containing multiple donor sites (chelating ligand) compared to an equivalent number of monodentate ligands.

i. Thermodynamic Origin

The increased stability arises from:

- Enthalpic contributions: multiple bonds between metal and ligand.
- Entropy gain: replacement of multiple free ligands by a single chelating ligand increases the disorder of the system.

ii. Entropy Considerations

Consider the reaction:

$$M^{2+} + 3en \rightleftharpoons [M(en)_3]^{2+}$$

vs.

$$M^{2+} + 6NH_3 \rightleftharpoons [M(NH_3)_6]^{2+}$$

In the first case, 4 species become 1, a net loss of 3 particles. In the second, 7 become 1, a net loss of 6 particles greater decrease in entropy, thus less favorable**.**

Hence, chelation is entropically favored due to fewer molecules being consumed during complex formation.

<u>*Comparison Between Monodentate and Polydentate Ligands*</u>

Ligand Type	Example	Stability of Complex
Monodentate	NH_3, Cl^-	Moderate
Bidentate	Ethylenediamine	Higher
Hexadentate	EDTA	Very High

V.4.4 Macrocyclic and cryptate effects

i. Preorganization concept

Macrocyclic ligands, such as crown ethers or porphyrins, are preorganized**:** their donor atoms are arranged in a rigid cyclic structure, ideally positioned to bind a metal ion.

This preorganization reduces the entropic and enthalpic cost of complex formation, resulting in greater stability than with open-chain analogs.

ii. ***Enhanced stability of macrocyclic ligands***

- Known as the macrocyclic effect**.**
- Macrocyclic ligands form more stable complexes than comparable acyclic chelators.
  - Example: 18-crown-6 forms a very stable complex with K^+.
  - $[K(18\text{-crown-6})]^+$ is more stable than a K^+ complex with six individual ether molecules.

iii. ***Cryptate Effect***

- Cryptands are three-dimensional polycyclic ligands that encapsulate the metal ion inside a "cage".
- This cryptate effect leads to exceptional stability due to full coordination and shielding of the metal ion.

Example:

$$[Na(2.2.2\text{-crypt})]^+ \gg [Na(18\text{-crown-6})]^+$$

Cryptate complexes are especially useful in selective ion recognition and phase-transfer catalysis.

V.5. Competition reactions

Competition reactions are a powerful tool in coordination chemistry for understanding the relative stability of metal–ligand complexes. They involve two or more competing processes either between different ligands for the same metal ion or between different metal ions for the same ligand. These reactions are often used to deduce or compare stability constants under equilibrium conditions.

V.5.1 Ligand exchange equilibria

Ligand exchange reactions involve the replacement of one ligand by another at the coordination site of a metal complex.

General reaction:

$$[ML_n] + L' \rightleftharpoons [ML'L_{n-1}] + L$$

Where:

- L is the original ligand,
- L′ is the incoming ligand,
- ML_n is the initial complex,
- $ML'L_{n-1}$ is the new complex after substitution.

Purpose and Significance:

- Used to compare the relative affinity of different ligands for a metal ion.
- Helps determine which ligand forms a more stable complex**.**

Example:

Let's consider the exchange between NH_3 and en (ethylenediamine) with a Cu^{2+} ion:

$$[Cu(NH_3)_4]^{2+} + en \rightleftharpoons [Cu(en)(NH_3)_2]^{2+} + 2NH_3$$

Here, en (a bidentate ligand) replaces two monodentate NH_3 molecules. This equilibrium tends to favor the formation of the chelated complex due to the chelate effect**.**

V.5.2 Metal displacement reactions

In metal displacement reactions, two different metal ions compete for binding to the same ligand. These reactions are governed by the relative stability constants (β) of the respective metal–ligand complexes.

General reaction:

$$[M_1L_n] + M_2^{z+} \rightleftharpoons [M_2L_n] + M_1^{z+}$$

Where:

- M_1 and M_2 are metal ions,
- L is a ligand,
- M_2 displaces M_1 if its complex with L is more stable.

Example:

Let's consider EDTA (a hexadentate ligand) and the metals Zn^{2+} and Cu^{2+}:

$$[Zn(EDTA)]^{2-} + Cu^{2+} \rightleftharpoons [Cu(EDTA)]^{2-} + Zn^{2+}$$

The stability constant of Cu–EDTA is higher than that of Zn–EDTA:

- log β(Cu–EDTA) ≈ 18.8
- log β(Zn–EDTA) ≈ 16.5

Thus, the reaction proceeds to the right, and Cu^{2+} displaces Zn^{2+} from the EDTA complex.

Applications:

- Used in metal purification and selective extraction.
- Important in bioinorganic systems, where metal replacement can affect enzymatic activity (e.g., displacement of Zn^{2+} by toxic Cd^{2+}).

V.5.3 Use of competition to determine stability constants

When the direct determination of a stability constant is difficult (e.g., due to very high or very low values), competition methods are used.

Method Overview:

A known complex is allowed to react with a competing ligand or metal, and the position of equilibrium is measured. From this, the unknown stability constant can be calculated using known values.

Types of Competitive Methods:

- Ligand Competition: Competing ligands for one metal ion.
- Metal Competition: Competing metal ions for one ligand.

- Spectrophotometric or potentiometric titrations are often used to monitor the equilibrium position.

Example:
Suppose we want to determine the stability constant for the complex $[Fe(EDTA)]^-$, but it cannot be directly measured. Instead, we use a reference complex, such as $[Zn(EDTA)]^{2-}$ with a known stability constant.

$$[Zn(EDTA)]^{2-} + Fe^{3+} \rightleftharpoons [Fe(EDTA)]^{-} + Zn^{2+}$$

By measuring the equilibrium concentrations of Fe^{3+}, Zn^{2+}, and the complexes, and knowing β for Zn–EDTA, the β for Fe–EDTA can be calculated.

Why Use Competition?

- Ideal for very strong complexes where direct measurement isn't feasible.
- Applicable in biochemical and environmental systems where multiple ligands or metals coexist.

V.6. Conditional (effective) stability constants

In real-world chemical systems, especially those in aqueous solutions or biological environments, the formation of metal complexes is often influenced by variables such as pH, competing equilibria, and ionic strength**.** To account for these factors, chemists use conditional (or effective) stability constants, which provide a more realistic measure of complex stability under specific experimental conditions.

V.6.1 Influence of pH

The pH of the solution significantly affects the availability of both metal ions and ligands for complexation. Many ligands, particularly those containing acidic or basic functional groups (e.g., $-COOH$, $-NH_2$, $-OH$), can exist in protonated or deprotonated forms, depending on the pH.

Effect on Ligands:
For a ligand L that must be deprotonated to bind a metal ion M:

$$HL \rightleftharpoons H^+ + L^-$$

The formation of the complex:

$$Mn^{+} + L^{-} \rightleftharpoons [ML]^{(n-1)+}$$

Thus, the true stability of the complex depends not only on the metal–ligand interaction but also on the protonation state of the ligand, which is governed by the pH.

Example: EDTA and pH Dependence

EDTA (ethylenediaminetetraacetic acid) has four carboxylic acid groups and two amine groups. Its ability to bind metals strongly depends on the deprotonation of its acidic groups. The fully deprotonated form, Y^{4-}, is the active chelating species.

At low pH, most of the EDTA is protonated and less effective at forming complexes. As pH increases, more Y^{4-} is available, and complexation becomes more favorable.

V.6.2 Complexes in aqueous media

In aqueous systems, additional equilibria must be considered:

- Hydrolysis of metal ions
- Protonation/deprotonation of ligands
- Competition with water or hydroxide ions

These factors complicate the use of "true" stability constants ($\log \beta$), which are determined under idealized conditions.

Definition of Conditional Stability Constant (K'):

The conditional stability constant refers to the apparent equilibrium constant for complex formation under fixed pH and ionic strength. It is denoted as K′ and is specific to a given set of conditions.

$$K' = [ML]/[M][L_{free}]$$

Where:

- [ML] is the concentration of the complex
- [M] is the free metal ion concentration
- $[L_{(protected)}]$ accounts for the effective free ligand concentration, considering its protonation state

Application Example:

Let's consider Cu^{2+} with glycine (H_2Gly), a simple amino acid. At pH ~7, glycine exists largely as the zwitterion ($^+H_3NCH_2COO^-$), and only the deprotonated $–NH_2/–COO^-$ forms can chelate Cu^{2+}.

Thus, the observed stability constant for Cu–glycine complex at pH 7 is a conditional constant, reflecting the actual amount of reactive ligand present at that pH.

V.6.3 Application in speciation studies

Speciation refers to the distribution of an element among various chemical forms (free ions, complexes, precipitates) in a system. Conditional stability constants are crucial for predicting and modeling speciation in:

- *Environmental chemistry* (e.g., metal transport in water bodies).
- *Biological systems* (e.g., drug–metal interactions).
- *Industrial processes* (e.g., water treatment).

Example: Lead Speciation in Natural Water

In a natural aqueous system, Pb^{2+} may exist in various forms:

- Free Pb^{2+} ion
- Complexed with carbonate: $[Pb(CO_3)]$
- Complexed with humic substances
- Precipitated as $Pb(OH)_2$ or $PbCO_3$

The conditional stability constants of each complex depend on pH, ionic strength, and ligand concentrations. Modeling software (e.g., Visual MINTEQ, PHREEQC) uses these conditional constants to simulate the speciation.

V.7. Applications of stability concepts

The concept of complex stability, whether thermodynamic or kinetic, is fundamental across several fields of chemistry. Understanding how strongly a metal ion binds to a ligand (and under what conditions) allows chemists to design analytical techniques, develop pharmaceuticals, and predict or control the fate of metals in the environment. This section highlights three major areas where stability concepts are crucial: analytical chemistry, medicine, and environmental chemistry.

V.7.1 In analytical chemistry: EDTA titrations

One of the most widespread applications of stability constants is in complexometric titrations, particularly using EDTA (ethylenediaminetetraacetic acid), a powerful hexadentate chelating agent.

Principle:

EDTA forms very stable 1:1 complexes with most metal ions in aqueous solution:

$$Mn^{+} + Y^{4-} \rightleftharpoons [MY]^{(n-4)}$$

- Y^{4-} is the fully deprotonated form of EDTA.
- The equilibrium constant (log β) is high, indicating strong complexation.

Application in Titration:

In a typical titration:

- A known amount of metal ion solution is titrated with an EDTA solution.
- An appropriate metal ion indicator (e.g., Eriochrome Black T for Mg^{2+}) is used.
- The endpoint is reached when all free metal ions are complexed by EDTA.

Importance of Conditional Stability Constant:

Since EDTA has multiple acidic protons, its effective chelating ability depends on pH**.** Therefore, titrations are often carried out in buffered media to maintain a constant pH (e.g., pH 10 for Ca^{2+} and Mg^{2+} titrations).

Example:

Determination of water hardness involves titrating Ca^{2+} and Mg^{2+} ions with EDTA at pH 10 using Eriochrome Black T as an indicator.

V.7.2 In medicine: metal–ligand interactions in drugs

In medicinal chemistry, the stability of metal–ligand complexes plays a central role in drug design, diagnosis, and therapy. Metal ions can serve as:

- Therapeutic agents (e.g., cisplatin),
- Carriers for active drugs,
- Imaging agents in diagnostics.

A. Metal-Based Drugs:

- Cisplatin $[Pt(NH_3)_2Cl_2]$ is a classic example. Its square planar structure and controlled ligand substitution kinetics are essential for its anticancer activity.
- Inside the cell, chloride ions are replaced by water (aquation), enabling the Pt center to bind to DNA nitrogen bases, leading to cell apoptosis.

B. Chelation Therapy:

Certain drugs act as chelating agents to remove toxic metals from the body.

- Deferoxamine is used to chelate excess Fe^{3+} in iron overload.
- Dimercaprol (BAL) is used for arsenic and lead poisoning.

The selectivity and stability constants of these ligands are crucial to ensure they bind toxic metals without disturbing essential metal ions like Zn^{2+} or Mg^{2+}.

C. Imaging Agents:

Gadolinium (Gd^{3+}) complexes with DTPA or DOTA are used in MRI contrast agents. Free Gd^{3+} is toxic, so the ligand must form a very stable complex ($\log \beta > 20$) to prevent its release in vivo.

V.7.3 In environmental chemistry: metal transport and speciation

The mobility, bioavailability, and toxicity of metal ions in natural systems are strongly influenced by their complexation behavior with ligands found in soil and water (e.g., humic acids, carbonate, phosphate).

A. Speciation and Stability:

Speciation studies help predict how a metal is distributed among its free ionic form and various complexes. This is essential for:

- Understanding metal cycling in aquatic systems,
- Predicting bioavailability to organisms,
- Designing remediation strategies for polluted sites.

Example:

In groundwater:

$$Cu^{2+} + CO_3^{2-} \rightleftharpoons [CuCO_3]$$

$$Cu^{2+} + \text{humic acid} \rightleftharpoons [\text{Cu–humic}]$$

The relative stabilities of these complexes (reflected in their log β values) determine how copper behaves, whether it is soluble, adsorbed onto solids, or bioavailable.

B. Toxic Metal Removal:

Chelating agents are also used in wastewater treatment to sequester toxic metals like Pb^{2+}, Cd^{2+}, and Hg^{2+}. The selection of a suitable ligand depends on:

- The stability constant for metal binding,
- The pH and ionic strength of the water,
- The kinetic lability of the metal complex.

Chapter VI

THEORIES OF METAL COMPLEXES

VI.1. Introduction

The study of coordination compounds has significantly evolved since the early 20th century, thanks to various theoretical models that have deepened our understanding of metal-ligand interactions. Coordination complexes exhibit a wide range of structural, magnetic, and electronic properties, which cannot be explained by classical valence theories alone. To address these complexities, several theories have been developed over time, each contributing key insights into the nature of bonding and structure in metal complexes.

The earliest systematic approach was proposed by Alfred Werner, whose coordination theory laid the foundation for modern coordination chemistry. Later, the Valence Bond Theory (VBT) introduced the concept of hybridization to describe the geometries of metal complexes. However, VBT fell short in explaining important features such as color and magnetic behavior.

This gap was partially filled by the Crystal Field Theory (CFT), which treats the metal-ligand interaction as a purely electrostatic phenomenon. Although CFT successfully accounts for many electronic properties of transition metal complexes, it neglects covalent bonding aspects. To overcome these limitations, more advanced models such as Ligand Field Theory (LFT) and Molecular Orbital Theory (MOT) have been developed, integrating concepts from quantum chemistry and molecular orbital interactions.

This chapter presents a comprehensive overview of the major bonding theories in coordination chemistry, comparing their assumptions, applications, and limitations. Understanding these theoretical frameworks is essential for predicting the structure, reactivity, magnetic properties, and electronic spectra of coordination compounds.

VI.2. Werner's coordination theory

Alfred Werner, a Swiss chemist, is considered the father of coordination chemistry. In 1893, he proposed a revolutionary theory to explain the structures and properties of metal complexes that could not be interpreted by classical valence theories. His work was based on experimental observations of the number of ions produced in solution and the ability of complexes to form different isomers.

VI.2.1 Primary and secondary valencies

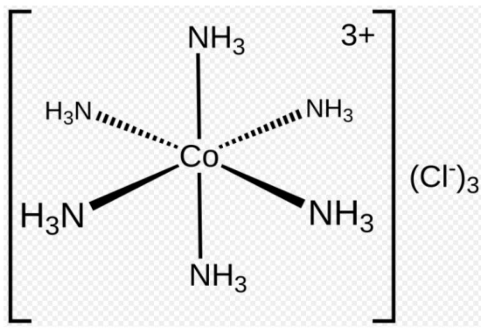
Werner introduced the concept of two types of valencies in coordination compounds:

- Primary Valency (Ionizable Valency):
  Corresponds to the oxidation state of the central metal ion. These valencies are satisfied by anions and are ionizable in solution.
- Secondary Valency (Coordination Valency):
  Refers to the number of ligands directly bonded to the central metal ion. These are non-ionizable and correspond to the coordination number.

Example:

In the complex $[Co(NH_3)_6]Cl_3$

- Primary valency = +3 (satisfied by 3 Cl^-, ionizable in water)
- Secondary valency = 6 (satisfied by 6 NH_3 ligands)



Werner observed that metal ions tend to bind with a fixed number of ligands, called the coordination number (CN), which determines the geometry of the complex.

- Common Coordination Numbers:
  - CN = 2 → Linear geometry (e.g.,$[Ag(NH_3)]^{2+}$)
  - CN = 4 → Tetrahedral (e.g., $[ZnCl_4]^{2-}$) or Square Planar (e.g., $[PtCl_4]^{2-}$)
  - CN = 6 → Octahedral (e.g., $[Cr(H_2O)_6]^{3+}$)

VI.2.2 Limitations of werner's theory

Although Werner's theory was groundbreaking, it had several limitations:

- It did not explain the nature of the metal-ligand bond (whether ionic or covalent).
- It provided no insight into the magnetic or spectral properti**es** of complexes.
- It could not predict high-spin or low-spin behavior.
- It did not consider electronic structure or orbital interactions.

These limitations led to the development of more advanced theories like Valence Bond Theory (VBT) and Crystal Field Theory (CFT), which provided electronic explanations for bonding and properties.

VI.3. Valence bond theory (VBT)

Valence Bond Theory (VBT) is one of the earliest approaches used to explain the bonding in coordination complexes. It describes how atomic orbitals of a central metal atom/ion hybridize to form bonding orbitals, which then overlap with the orbitals of ligands.

VI.3.1 Basic Concepts and Hybridization

In coordination chemistry, VBT assumes that the metal ion provides vacant orbitals to accommodate the electron pairs donated by ligands (via coordinate covalent bonds).

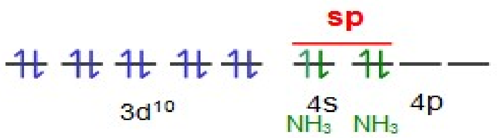
These vacant orbitals hybridize to form a set of equivalent orbitals with specific geometry.

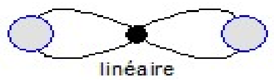
The type of hybridization depends on the coordination number and the geometry of the complex.

Coordination Number	Geometry	Hybridization
4	Tetrahedral	sp^3
4	Square planar	dsp^2
6	Octahedral	d^2sp^3 or sp^3d^2

Examples:

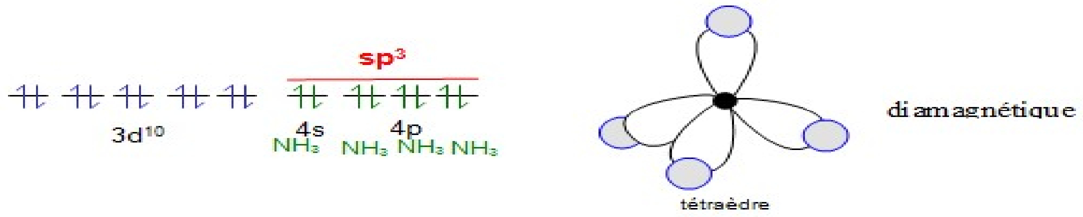
$[Cu(NH_3)_2]^+$
$Cu^+ : [Ar]\ 3d^{10}4s^0 4p^0 4d^0$





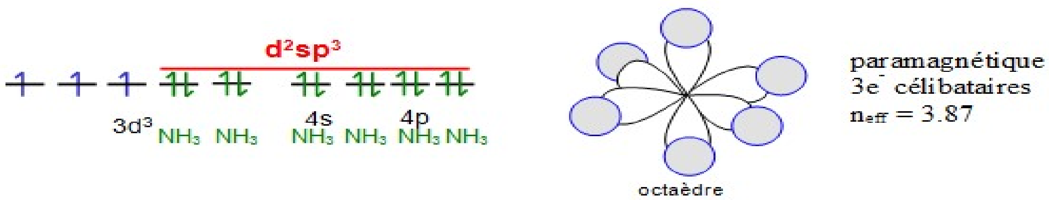
diamagnétique

$[Zn(NH_3)_4]^{2+}$
$Zn^{2+} : [Ar]\ 3d^{10}4s^0 4p^0 4d^0$



CN^- $[Ni(CN)_4]^{2-}$
Ni^{2+} : [Ar] $3d^8 4s^0 4p^0 4d^0$

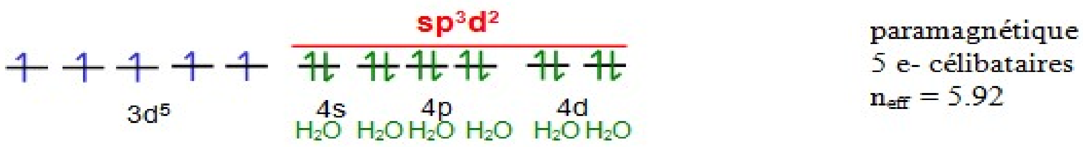
$[Cr(NH_3)_6]^{3+}$
Cr^{3+} : [Ar] $3d^3 4s^0 4p^0 4d^0$



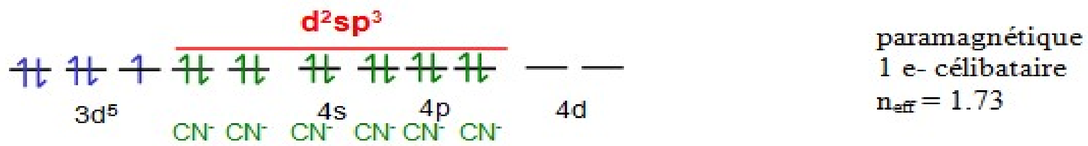
In some cases, it must be assumed that the hybrid atomic orbital involves 4d atomic orbitals to respect the geometry and observed magnetic moment.

The Fe^{3+} ($3d^5$) ion exhibits both types of hybridization:

$[Fe(H_2O)_6]^{3+}$ use of 4d orbitals



$[Fe(CN)_6]^{3-}$ use of 3d orbitals



VI.3.2 Explanation of magnetic properties

VBT explains the magnetic behavior of complexes based on the number of unpaired electrons after hybridization.

- Paramagnetic = has unpaired electrons → attracted by a magnetic field.
- Diamagnetic = all electrons are paired → repelled by a magnetic field.

Example 1: $[Fe(H_2O)_6]^{2+}$

- $Fe^{2+} = 3d^6$
- H_2O is a weak field ligand → no pairing → high spin
- Hybridization: sp^3d^2 → Octahedral
- Four unpaired electrons → Paramagnetic

Example 2: $[Fe(CN)_6]^{4-}$

- $Fe^{2+} = 3d^6$
- CN^- is a strong field ligand → electrons pair up
- Hybridization: d^2sp^3 → Octahedral
- No unpaired electrons → Diamagnetic

VI.3.3 Limitations of VBT

Despite its usefulness, VBT has several limitations:

1. Does not explain color
   - VBT cannot account for the absorption of light in the visible region due to d–d transitions.
2. Cannot predict spectra
   - It gives no information about the electronic spectra of complexes.
3. Fails to explain thermodynamic stability
   - The theory does not predict the stability constants of complexes.
4. Inadequate for weak vs. strong field ligands
   - No quantitative basis for distinguishing between high spin and low spin complexes.
5. No concept of crystal field splitting
   - Unlike Crystal Field Theory (CFT), VBT does not explain the splitting of d-orbitals in various fields.

VI.4. Crystal field theory (CFT)

Crystal Field Theory (CFT) is a model used to describe the electronic structure of coordination compounds. It explains how the energy levels of d-orbitals of a metal ion are affected by the presence of ligands. CFT treats the interaction between metal ions and ligands as purely electrostatic, focusing on the repulsion between electron-rich ligands and the d-electrons of the metal ion.

VI.4.1 Fundamentals of crystal field theory

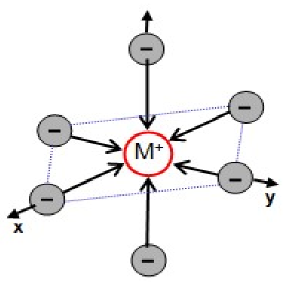
Electrostatic Nature of Metal-Ligand Interactions

- Ligands are considered negative point charges (in the case of anions like Cl^-) or dipoles (as in neutral ligands like NH_3 or H_2O).
- These ligands approach the metal ion and cause electrostatic repulsion with its d-electrons.
- The metal-ligand bond is considered ionic in nature in CFT (no covalent character is assumed).

Assumptions

- Ligands are point charges or dipoles: No orbital overlap is considered.
- **No** covalent bonding: The theory ignores metal-ligand orbital interactions.
- Static field: The ligands generate a fixed field that influences d-orbital energies.

Example:
In $[Fe(H_2O)_6]^{3+}$, H_2O molecules are treated as point dipoles. Their negative ends face the Fe^{3+} ion and repel the d-electrons, causing a splitting in the d-orbitals.



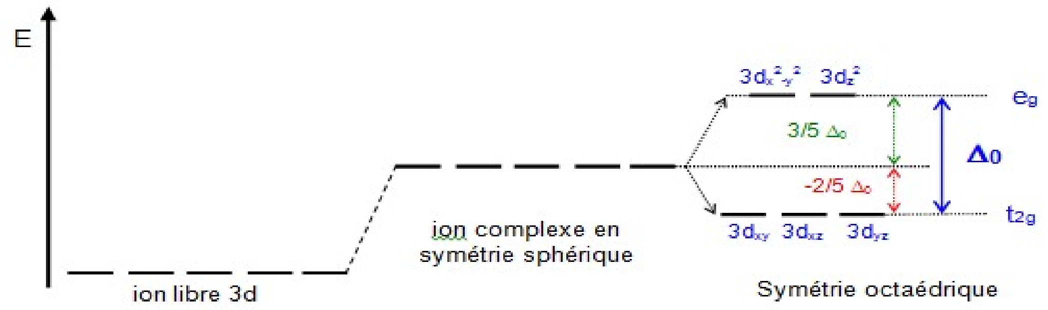
VI.4.2 Crystal field splitting

Free Metal Ion

In a free metal ion, the five d-orbitals (d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, dz^2) are degenerate (equal in energy).

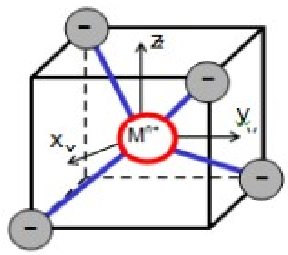
Octahedral Field (common in 6-coordinate complexes)

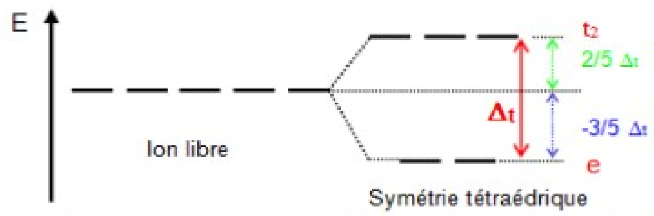
- Ligands approach along the axes (x, y, z).
- d-orbitals split into two groups:
  - t_2g (lower energy): d_{xy}, d_{yz}, d_{xz}
  - e_ng (higher energy): $d_{x^2-y^2}$, dz^2
- The energy gap between these is denoted **Δ_0** (octahedral splitting energy).



Tetrahedral Field (4-coordinate complexes)

- Ligands approach between the axes.
- Reverse of octahedral:
  - e (lower energy): $d_{x^2-y^2}$, dz^2
  - t_2 (higher energy): d_{xy}, d_{yz}, d_{xz}
- Splitting energy is smaller, denoted **Δ_t**, and typically $\Delta_t \approx 4/9\ \Delta_0$.



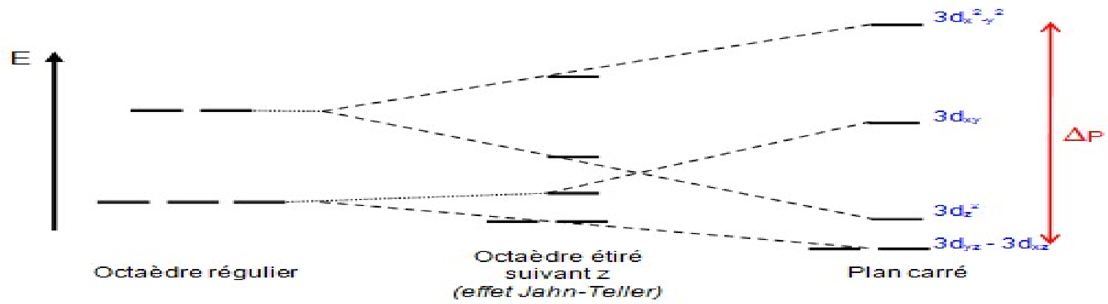


Dédoublement des orbitales d dans un champ tétraédrique

Square Planar Field (especially for d^8 metals like Ni^{2+}, Pt^{2+})

- Ligands lie in the x–y plane.
- Splitting is more complex, and $d_{x^2-y^2}$ is the highest in energy due to direct ligand approach.

- Order:
  $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz} \approx d_{yz}$



VI.4.3 Crystal field stabilization energy (CFSE)

CFSE is the net energy stabilization due to the preferential filling of lower-energy d-orbitals.

Calculation

- For octahedral:
  CFSE = (number of e^- in t_2g) × ($-0.4\Delta_0$) + (number of e^- in e_ng) × ($+0.6\Delta_0$)

High-spin vs Low-spin Complexes

- Weak field ligands (e.g., H_2O, F^-): small Δ_0 → electrons stay unpaired (high-spin).
- Strong field ligands (e.g., CN^-, CO): large Δ_0 → electrons pair in t_2g orbitals (low-spin).

Examples:

1. $[Fe(H_2O)_6]^{2+}$ → $Fe^{2+} = d^6$, weak field → high-spin → CFSE = $(4\times-0.4 + 2\times0.6)\Delta_0 = -0.4\Delta_0$
2. $[Fe(CN)_6]^{4-}$ → $Fe^{2+} = d^6$, strong field → low-spin → all 6 e^- in t_2g → CFSE = $6\times(-0.4\Delta_0) = -2.4\Delta_0$

Influence of Metal and Ligand

- Higher oxidation states → greater attraction → larger Δ
- Strong-field ligands (based on the spectrochemical series) → larger Δ

VI.4.4 Factors Affecting Crystal Field Splitting Energy (Δ)

1. ***Nature of the Metal Ion***

- Higher oxidation state → larger Δ (e.g., $Cr^{3+} > Cr^{2+}$)
- Smaller ionic radius → ligands closer → stronger interaction

2. ***Type of Ligand: Spectrochemical Series***

   Order (from weak to strong field ligands):

   $I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 <$ en $< NO_2^- < CN^- < CO$

3. ***Geometry of the Complex***
   - Δ_o (octahedral) > Δ_t (tetrahedral)
   - Square planar splitting is largest (especially in d^8 systems)

VI.4.5 Magnetic properties

Pairing Energy (P) vs. Splitting Energy (Δ)

- If Δ > P → pairing occurs → low-spin
- If Δ < P → no pairing → high-spin

Prediction of magnetic behavior

- Use the number of unpaired electrons:
  - Paramagnetic → unpaired electrons
  - Diamagnetic → all electrons paired

Magnetic moment (μ_eff)

- Calculated by:

  μeff=n(n+2) BM\mu_{\text{eff}} = \sqrt{n(n+2)} \ \text{BM}μeff=n(n+2) BM

  where **n** = number of unpaired electrons

Examples

- $[CoF_6]^{3-}$: $Co^{3+} = d^6$, F^- is weak field → high-spin → 4 unpaired e^- → μ_eff ≈ 4.9 BM
- $[Co(CN)_6]^{3-}$: $Co^{3+} = d^6$, CN^- strong field → low-spin → no unpaired e^- → μ_eff = 0 BM

VI.4.6 Electronic transitions and color

d–d Transitions

- When light is absorbed, an electron may jump from a lower-energy d-orbital (e.g., t_2g) to a higher-energy orbital (e.g., e_ng).
- This corresponds to a specific wavelength (color) of light.

Laporte Rule

- Forbidden in centrosymmetric complexes (octahedral), but allowed via vibronic coupling.
- Tetrahedral complexes often show stronger color because they are non-centrosymmetric.

Relation between Δ and Absorption

- Larger Δ → absorbs higher-energy light → appears blue or violet
- Smaller Δ → absorbs lower-energy light → appears red or yellow

Examples:

- $[Ti(H_2O)_6]^{3+}$: $Ti^{3+} = d^1$ → one d–d transition → purple color
- $[Cu(H_2O)_6]^{2+}$: d^9 → blue color due to d–d transition

VI.4.7 Limitations of crystal field theory

Crystal Field Theory (CFT), despite its usefulness in explaining the electronic structure and magnetic properties of coordination complexes, has several important limitations. First, it assumes that metal-ligand interactions are purely ionic, providing no explanation for covalent bonding or orbital overlap, which are often significant in real complexes. Second, CFT fails to account for π-bonding interactions such as π-backbonding, which occur with ligands like carbonyl (CO) that can accept electron density from metal d-orbitals, this crucial aspect is entirely neglected in the model. Third, the theory is an oversimplification and cannot reliably predict thermodynamic stability, reactivity, or the detailed features of electronic spectra. Finally, to overcome these shortcomings, more advanced models like Ligand Field Theory (LFT) or Molecular Orbital Theory (MOT) are necessary, as they incorporate both the covalent character of bonding and the mixing of metal and ligand orbitals, offering a more comprehensive and accurate description of coordination compounds.

VI.5. Ligand Field Theory (LFT)

Ligand Field Theory (LFT) is a more refined approach to understanding metal-ligand bonding in coordination complexes. It merges ideas from Crystal Field Theory (CFT) and Molecular Orbital Theory (MOT) to explain not only the electronic structure and geometry of complexes but also their spectroscopic and magnetic properties.

VI.5.1 Integration of CFT with Molecular Orbital Theory

Crystal Field Theory considers the interaction between the central metal ion and the ligands as a purely electrostatic (ionic) phenomenon, which explains d-orbital splitting in various geometries (octahedral, tetrahedral, square planar, etc.). However, CFT does not account for covalency in bonding.

Ligand Field Theory improves upon this by integrating *Molecular Orbital Theory*, which considers both electrostatic and covalent aspects of bonding. In LFT:

- The metal d, s, and p orbitals interact with ligand orbitals (usually lone pairs on atoms like N, O, or Cl) to form molecular orbitals.
- These interactions result in bonding, antibonding, and nonbonding molecular orbitals.

Example: Octahedral Complex $[Co(NH_3)_6]^{3+}$

- The six NH_3 ligands donate lone pairs from their nitrogen atoms (σ-donors).
- These interact with the metal's 3d, 4s, and 4p orbitals.
- The ligand orbitals combine with metal orbitals of appropriate symmetry to form:
  - σ-bonding orbitals (strong overlap with ligand orbitals)
  - Nonbonding t_2g orbitals (mainly metal dxy, dxz, dyz)
  - Antibonding e^*g orbitals ($dx^2–y^2$ and dz^2)

This leads to an energy diagram similar to CFT but with molecular orbital justification for the splitting.

VI.5.2 Metal-Ligand bonding and overlap

In LFT, bonding depends on the type of overlap between metal orbitals and ligand orbitals:

- *σ-overlap:* Involves ligand orbitals pointing directly toward the metal (e.g., NH_3, H_2O).
- *π-donor overlap:* Occurs when ligands with filled π orbitals (e.g., Cl^-, OH^-) donate electron density to metal d-orbitals.
- *π-acceptor overlap:* Involves ligands like CO, CN^- that have empty π* orbitals that can accept electron density from filled metal d-orbitals (backbonding).

These interactions influence the energy and occupancy of molecular orbitals, thus affecting:

- The color of the complex (due to d-d transitions).
- Magnetic properties (number of unpaired electrons).
- Stability and reactivity (ligand field stabilization energy, LFSE).

Example: $[Fe(CN)_6]^{4-}$ vs. $[Fe(H_2O)_6]^{2+}$

- $[Fe(CN)_6]^{4-}$: CN^- is a strong field ligand and a π-acceptor → large Δ_0 → low-spin complex.
- $[Fe(H_2O)_6]^{2+}$: H_2O is a weak field ligand and a σ-donor → small Δ_0 → high-spin complex.

VI.5.3 Comparison with VBT and CFT

Feature	**Valence Bond Theory (VBT)**	**Crystal Field Theory (CFT)**	**Ligand Field Theory (LFT)**
Nature of Bonding	Localized, covalent (hybridization-based)	Purely electrostatic (ionic model)	Covalent and electrostatic (molecular orbitals)
Geometry Explanation	Uses hybrid orbitals (e.g., dsp^2, d^2sp^3)	Based on ligand repulsion and orbital splitting	Based on symmetry-adapted orbital interactions
Orbital Overlap Considered?	Yes	No	Yes
Spectral Predictions	Limited	Good (color, d-d transitions)	Excellent (UV-Vis, charge transfer, d-d transitions)
Magnetic Properties	Explains some cases (high-spin/low-spin)	Predicts spin states	bonding effects
Limitation	Too simplistic; neglects delocalization	Ignores covalent aspects of bonding	Requires knowledge of group theory and MO diagrams

Ligand Field Theory offers a comprehensive model that accounts for both electrostatic and covalent interactions between metals and ligands. By incorporating orbital overlap and symmetry considerations, LFT provides a more accurate understanding of the geometry, magnetism, and electronic spectra of coordination compounds.

VI.6. Molecular orbital theory (MOT) applied to complexes

Molecular Orbital Theory (MOT) provides a quantum mechanical model of bonding in coordination complexes by treating electrons as delocalized over the entire molecule. It allows for a more accurate description of metal-ligand interactions than simple ionic or localized models. MOT explains bonding, antibonding interactions, and accounts for σ and π contributions, which in turn affect a complex's geometry, magnetism, and color.

VI.6.1 Construction of MO diagrams for octahedral complexes

To construct a Molecular Orbital diagram for an octahedral complex, follow these steps:

1. Identify symmetry and coordinate system:
    - Assume the metal is at the center, with ligands placed along the Cartesian axes (x, y, z).
    - Octahedral complexes follow the *Oh* point group.
2. Determine atomic orbitals of the metal:
    - Metal valence orbitals:
        - s orbital: spherical symmetry
        - p orbitals (px, py, pz): directional, suitable for bonding
        - d orbitals: classified based on symmetry as:
            - eg → d_z^2, $d_x^2{-}_y^2$
            - t2g → d_{xy}, d_{xz}, d_{yz}
3. Combine with ligand orbitals:
    - Ligands donate lone pairs through σ-orbitals (one orbital per ligand).
    - Use symmetry-adapted linear combinations (SALCs) of ligand orbitals to match the symmetry of metal orbitals.
4. Form molecular orbitals:
    - Bonding orbitals: strong overlap, lower in energy.
    - Antibonding orbitals: poor overlap, higher in energy.
    - Nonbonding orbitals: no symmetry match; remain at original energy levels.

Example: $[Co(NH_3)_6]^{3+}$

- Metal: Co^{3+} ($3d^6$)

- NH_3 donates σ lone pairs.
- MO diagram shows:
  - Bonding orbitals (σ-type) mostly ligand in character.
  - t_2g orbitals (nonbonding, mostly metal d-character).
  - eg orbitals (antibonding, contain d and ligand character).

VI.6.2 Bonding and antibonding orbitals

In a typical octahedral MO diagram:

- Bonding orbitals (lowest energy):
  - Arise from the constructive overlap of ligand σ-orbitals with metal s, p, and d orbitals.
  - These orbitals are usually ligand-dominated in character.
- Nonbonding orbitals (middle energy):
  - Typically the t_2g set of d orbitals (dxy, dxz, dyz) in σ-only bonding situations.
  - Do not interact significantly with ligand orbitals if there's no π bonding.
- Antibonding orbitals (highest energy):
  - The eg* set ($dx^2–y^2$, dz^2), which strongly overlap with ligand σ-orbitals.
  - These are mostly metal-dominated and critical for electronic transitions.

VI.6.3 π-Acceptor and π-donor ligands

MOT can accommodate π interactions that modify the MO diagram:

- ***π-Donor Ligands***:
  - Have filled π orbitals (e.g., $Cl^−$, $OH^−$, H_2O).
  - These can interact with the metal t_2g orbitals (back donation from ligand to metal).
  - Result: t_2g orbitals become more antibonding (↑ in energy), decreasing Δ_0.
- ***π-Acceptor Ligands***:
  - Have empty π* orbitals (e.g., CO, $CN^−$).
  - Can accept electron density from filled metal t_2g orbitals (backbonding).
  - Result: t_2g orbitals are stabilized (↓ in energy), increasing Δ_0.

Examples:

- $[Fe(CN)_6]^{4−}$: Strong π-acceptor → large splitting → low-spin
- $[Fe(H_2O)_6]^{2+}$: Weak σ-donor → small splitting → high-spin
- $[FeCl_6]^{3−}$: $Cl^−$ is a π-donor → destabilizes t_2g → smaller splitting → high-spin

VI.6.4 Predicting magnetic and spectral properties

MOT allows precise predictions of a complex's:

(a) Magnetic Properties

- Determined by the number of unpaired electrons in molecular orbitals.
- Low-spin vs. high-spin configurations arise from Δ_0 relative to pairing energy.

Example:

- $[Fe(CN)_6]^{4-}$ (d^6): All 6 electrons fill bonding and t_2g MOs → low-spin → diamagnetic.
- $[FeF_6]^{3-}$ (d^6): t_2g and eg* occupied → high-spin → paramagnetic.

(b) Spectral Properties

- Electronic transitions occur from t_2g to eg* (d-d transitions).
- The energy gap (Δ_0) corresponds to the wavelength of light absorbed.

Example:

- $[Ti(H_2O)_6]^{3+}$ (d^1): One electron in t_2g → t_2g → eg* transition possible → violet color.
- $[Cr(NH_3)_6]^{3+}$ (d^3): All electrons in t_2g → d-d transitions possible → absorbs green → appears red.

MOT also explains charge-transfer bands:

- Ligand-to-metal charge transfer (LMCT): electron transfer from ligand to metal.
- Metal-to-ligand charge transfer (MLCT): common with π-acceptor ligands.

Molecular Orbital Theory applied to coordination complexes allows a deep understanding of bonding by incorporating both σ and π interactions. Through MO diagrams, we can rationalize the origin of magnetic properties, spectroscopic transitions, and stability trends far beyond what CFT or VBT can offer. It provides a quantum mechanical basis for ligand field effects and is essential in modern inorganic chemistry.

VI.7. Comparison of Theories

Coordination chemistry has evolved through successive theoretical models to explain the structure, bonding, magnetism, and reactivity of metal complexes. Each theory, VBT, CFT, and MOT provides different levels of approximation and insight. Understanding their strengths, limitations, and domains of applicability is essential for choosing the right model depending on the system studied.

VI.7.1 Strengths and weaknesses

1. Valence Bond Theory (VBT)

Strengths:

- Simple and intuitive.
- Explains geometry using hybridization (e.g., dsp^2, d^2sp^3).
- Accounts for magnetic properties (number of unpaired electrons).

Weaknesses:

- Cannot explain spectral (color) properties or the electronic structure in detail.
- Ignores delocalization and π-bonding.
- Fails for complexes with ambiguous geometries or strong field ligands.

Example:

- Explains square planar geometry of $[Ni(CN)_4]^{2-}$ as dsp^2 hybridization.
- Cannot explain why $[NiCl_4]^{2-}$ is tetrahedral while $[Ni(CN)_4]^{2-}$ is square planar.

2. Crystal Field Theory (CFT)

Strengths:

- Introduces d-orbital splitting based on geometry (octahedral, tetrahedral, etc.).
- Explains color (d–d transitions) and magnetic behavior.
- Accounts for high-spin vs. low-spin configurations using Δ and pairing energy.

Weaknesses:

- Treats bonding as purely electrostatic (ignores covalency).
- Does not account for orbital overlap or π-bonding.
- Inaccurate for complexes involving soft ligands or backbonding.

Example:

- Predicts that $[Fe(H_2O)_6]^{2+}$ is high-spin and $[Fe(CN)_6]^{4-}$ is low-spin due to Δ_0 values.
- Cannot explain why π-acceptor ligands increase Δ_0.

3. Molecular orbital theory (MOT) / ligand field theory (LFT)

Strengths:

- Most complete and accurate.

- Explains both σ and π bonding.
- Accurately predicts geometry, magnetic properties, and spectra.
- Handles delocalized bonding and back-donation.

Weaknesses:

- Mathematically complex.
- Requires knowledge of group theory and orbital symmetry.
- Less intuitive than VBT or CFT for beginners.

Example:

- Explains π-backbonding in $[Fe(CO)_5]$ and strong field behavior of CN^- in $[Fe(CN)_6]^{4-}$.
- Can rationalize why t_2g orbitals are stabilized by π-acceptor ligands.

VI.7.2 Applicability to different types of complexes

The applicability of bonding theories in coordination chemistry depends largely on the nature of the metal center, the type of ligands, and the complexity of the bonding involved. Valence Bond Theory (VBT) is most appropriate for simple coordination compounds, particularly those involving first-row transition metals with predominantly σ-donor ligands, such as water or ammonia. It provides a qualitative understanding of geometry and magnetic properties using hybridization concepts, but it fails to account for spectral properties and π-interactions. Crystal Field Theory (CFT)**,** on the other hand, is better suited for explaining the behavior of complexes where the metal-ligand interaction is primarily ionic or electrostatic, as in many 3d metal complexes with halide or neutral ligands. CFT is widely used to predict magnetic behavior and electronic transitions, making it especially useful for interpreting UV-Visible spectra. However, it oversimplifies bonding and does not include covalency or orbital overlap. In contrast, Molecular Orbital Theory (MOT) and its extension, Ligand Field Theory (LFT) is the most versatile and accurate model. It is applicable to a broad range of coordination complexes, including those with significant covalent character, π-donor or π-acceptor ligands, and organometallic species. MOT successfully explains complex bonding scenarios, such as synergic backbonding in metal carbonyls, and provides quantitative insight into the electronic structure, color, reactivity, and stability of metal complexes. Thus, while VBT and CFT are useful for introductory or qualitative analysis, MOT is indispensable for advanced or precise interpretation, especially in complexes involving π-interactions or low-symmetry environments.

Theory	Best Suited For	Limitations
VBT	First-row transition metals with simple geometries and σ-bonding only.	Inaccurate for explaining color, charge transfer, or π-bonding.
CFT	Transition metal complexes with regular geometries and limited covalency.	Fails for covalent or π-interacting ligands; ignores orbital overlap.
MOT/LFT	Complexes with covalent bonding, π-donation or π-acceptance; organometallics.	Requires advanced tools; not ideal for rapid qualitative predictions.

Examples:

- VBT is sufficient for $[Cr(H_2O)_6]^{3+}$ to explain paramagnetism.
- CFT is effective for interpreting the UV-Vis spectrum of $[Ti(H_2O)_6]^{3+}$.
- MOT is required to explain the synergic bonding in $[Fe(CO)_5]$ and dπ–pπ backbonding in $[Mn(CO)_6]^+$.

VI.7.3 Summary table

Feature / Theory	Valence Bond Theory (VBT)	Crystal Field Theory (CFT)	Molecular Orbital Theory (MOT)
Nature of Bonding	Covalent (localized)	Electrostatic (ionic)	Covalent + electrostatic (delocalized)
Geometry Explanation	Yes (via hybridization)	Yes (from ligand repulsion)	Yes (MO symmetry and overlap)
Magnetic Properties	Limited prediction	Good (Δ vs pairing energy)	Excellent (based on orbital filling)
Color / Spectra Prediction	No	Yes (d–d transitions)	Excellent (d–d, CT transitions)
π-Bonding	No	No	Yes (π-donation & π-

			backbonding)
Orbital Overlap Considered	Yes (simplified)	No	Yes (σ and π overlap)
Applicable Complexes	Simple 3d complexes	Ionic and symmetrical complexes	All complexes, including organometallics
Mathematical Complexity	Low	Moderate	High
Examples it explains well	$[Ni(CN)_4]^{2-}$ hybridization	$[Fe(H_2O)_6]^{3+}$ high spin, color	$[Fe(CO)_5]$, $[Mn(CO)_6]^+$, π-backbonding cases

Each theory in coordination chemistry has its place and utility.

- **VBT** provides simple, fast predictions of geometry and spin.
- **CFT** introduces useful energy level splitting and LFSE.
- **MOT/LFT** offers a complete quantum mechanical view that explains all types of bonding interactions σ, π, and backbonding.

A modern chemist often uses these models together: VBT or CFT for quick analysis, and MOT for detailed electronic interpretation.

VI.8. Applications of coordination theories

Coordination theories such as Valence Bond Theory (VBT), Crystal Field Theory (CFT), and Molecular Orbital Theory (MOT) are not just theoretical tools. They have practical applications in understanding the behavior of coordination compounds. These theories allow chemists to interpret experimental data, predict chemical reactivity, and even design new ligands for applications in medicine, catalysis, and environmental remediation**.**

VI.8.1 Interpretation of spectral data (UV-Vis, magnetic susceptibility)

(a) UV-Visible Spectroscopy

Coordination theories help interpret the electronic absorption spectra of transition metal complexes:

- *Crystal Field Theory (CFT)* explains how d-orbital splitting (Δ) results in d–d transitions, where an electron is promoted from a lower energy set (e.g., t_2g) to a higher one (e.g., e_g*).
- The energy of the transition (Δ) corresponds to a specific wavelength of visible light, which determines the observed color of the complex.

Example:

- $[Ti(H_2O)_6]^{3+}$ (d^1):
  One electron in the t_2g orbital. A single d–d transition from $t_2g \rightarrow e_g$* occurs, absorbing green light and giving a violet appearance.
- $[Cr(NH_3)_6]^{3+}$ (d^3):
  Three electrons fill the t_2g orbitals; the complex absorbs light corresponding to the transition $t_2g \rightarrow e_g$*, leading to red or purple color depending on the ligands.

(b) Magnetic Susceptibility

- *Number of unpaired electrons* determines magnetic behavior.
- *Paramagnetic***:** Unpaired electrons present; attracted to a magnetic field.
- *Diamagnetic***:** All electrons paired; repelled by a magnetic field.

CFT and MOT allow accurate predictions of high-spin vs low-spin configurations by comparing ligand field strength (Δ) and pairing energy (P)**.**

Example:

- $[Fe(H_2O)_6]^{2+}$ (d^6, weak field): High-spin → 4 unpaired electrons → strongly paramagnetic.
- $[Fe(CN)_6]^{4-}$ (d^6, strong field): Low-spin → all electrons paired in t_2g → diamagnetic.

These properties can be confirmed experimentally using magnetic susceptibility measurements (e.g., Gouy balance or Evans method).

VI.8.2 Stability and reactivity of complexes

(a) Thermodynamic Stability

- CFT introduces *Ligand Field Stabilization Energy (LFSE)***,** which helps quantify how much stabilization a complex gains from d-orbital splitting.
- *Greater LFSE* usually implies greater thermodynamic stability**.**

Example:

- $[Co(NH_3)_6]^{3+}$ is more stable than $[CoF_6]^{3-}$ because NH_3 is a stronger field ligand, leading to greater LFSE.

(b) Kinetic Reactivity

- The geometry and electron configuration of a complex (predicted by CFT/MOT) influence how easily it undergoes substitution or redox reactions.
- Octahedral d^3 and low-spin d^6 complexes are often inert due to fully filled t_2g orbitals.
- High-spin d^5 complexes (e.g., $[Mn(H_2O)_6]^{2+}$) are typically labile due to minimal LFSE.

Example:

- $[Cr(NH_3)_6]^{3+}$ (d^3): Inert; substitution is slow.
- $[Cu(H_2O)_6]^{2+}$ (d^9): Labile; substitution is fast due to Jahn-Teller distortion.

(c) Chelate and Macrocyclic Effects

- Ligand design (e.g., chelating ligands like EDTA) enhances complex stability via the chelate effect**.**
- Theories explain how multiple coordination points increase entropy and enthalpic stabilization.

VI.8.3 Design of ligands in medicinal and environmental chemistry

(a) Medicinal Applications

Coordination theories guide the design of metal-based drugs and therapeutic ligands:

- Anticancer agents like cisplatin ($[PtCl_2(NH_3)_2]$) work by binding DNA bases. Its square planar geometry (predicted by VBT/MOT) is essential for activity.
- Ligands with strong π-acceptor properties can stabilize metal centers in oxidation states useful in redox-active drugs.

Example:

- $[Ru(bipy)_3]^{2+}$ (bipy = bipyridine): A luminescent complex used in bioimaging and potential anticancer applications.

(b) Environmental Applications

- Ligand field theory is used in designing ligands for heavy metal removal (e.g., Pb^{2+}, Cd^{2+}, Cu^{2+}) from contaminated water.
- Ligands are tailored to bind selectively and strongly to metal ions through donor atoms (N, O, S) and optimized geometry.

Example:

- Thiosemicarbazone ligands chelating Cu^{2+} through N and S donors to form stable square planar complexes.
- EDTA used in wastewater treatment forms stable hexadentate complexes with multiple heavy metals.

(c) Catalysis and Sensors

- Understanding the electronic structure through MOT allows for rational design of homogeneous catalysts (e.g., Wilkinson's catalyst) and metal-based sensors.
- Theories help fine-tune redox potentials, ligand exchange rates, and electronic transitions.

Coordination theories are essential in interpreting experimental data (spectroscopy, magnetism), predicting chemical behavior, and designing ligands for advanced applications. Their relevance spans academic research and real-world problems in health, industry, and environmental protection.

VI.9. Evolution of Theories Towards More Accurate Models

The development of coordination chemistry theories reflects the ongoing evolution of scientific understanding, moving from descriptive models toward more accurate, predictive frameworks. Werner's theory laid the foundation by distinguishing between coordination and ionic valencies, offering a structural basis for complex formation, yet it lacked an explanation for bonding mechanisms. Valence Bond Theory (VBT) advanced the field by introducing orbital hybridization and providing a qualitative understanding of geometry and magnetism. However, it did not adequately address electronic transitions or ligand effects. Crystal Field Theory (CFT) introduced a more physical, electrostatic approach that explained color, magnetism, and spectral properties based on d-orbital splitting, but it still treated ligands as point charges and ignored covalency. Ligand Field Theory (LFT), as an extension of CFT, began integrating molecular orbital concepts, acknowledging metal-ligand orbital overlap and partial covalency. Molecular Orbital Theory (MOT) further refined these ideas by constructing energy-level diagrams and predicting bonding, antibonding interactions, and electronic properties with greater precision.

The gradual integration of quantum chemistry into coordination theory has allowed for a more nuanced and accurate description of complex systems. Modern models no longer rely solely on electrostatics or localized bonds, but rather consider the delocalized nature of electrons, π-backbonding, and orbital symmetry. As a result, these theories have become essential tools not only for interpreting experimental data but also for designing novel complexes with tailored properties in catalysis, medicine, and materials science. The evolution of these theories marks a transition from observation to rational design, highlighting the dynamic nature of inorganic chemistry.

VI.10. Review Exercise

The following octahedral complexes are characterized by the intensity of the crystal field created by each type of ligand:

Complex	**ΔE (cm^{-1})**
$[Fe(H_2O)_6]^{2+}$	10,400
$[Fe(CN)_6]^{3-}$	35,000

ΔE is the crystal field splitting energy, representing the energy gap between the two sets of d orbitals in the complex.

The pairing energy (P) for two d electrons is approximately 17,600 cm^{-1} for Fe^{2+} and 29,875 cm^{-1} for Fe^{3+}.

a) Indicate the oxidation state of Fe in each complex.

b) Draw the electronic configuration of each complex by representing the d-orbital energy diagram according to the Crystal Field Theory model.

c) Calculate the Crystal Field Stabilization Energy (CFSE) for each complex.

d) Deduce the magnetic properties of both complexes (Fe: Z = 26).

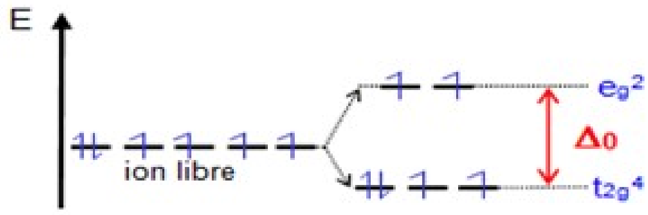
Solution

a)

- $[Fe(H_2O)_6]^{2+}$ → Oxidation state of Fe = +II
- $[Fe(CN)_6]^{3-}$ → Oxidation state of Fe = +III

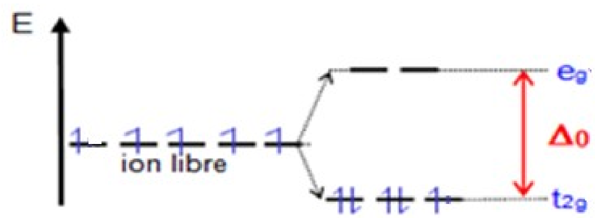
b) $[Fe(H_2O)_6]^{2+}$

- Electronic configuration: d^6, weak field → high-spin (4 unpaired electrons)
- CFSE(1) = $4(-2/5\Delta_o) + 2(+3/5\Delta_o) + 1P$
- CFSE(1) = $-13440\ cm^{-1}$



$[Fe(CN)_6]^{3-}$

- Electronic configuration: d^5, strong field → low-spin (1 unpaired electron)
- CFSE(2) = $5(-2/5\Delta_o) + 1P$
- CFSE(2) = $-10250\ cm^{-1}$



d) Both complexes are paramagnetic**.**

*********** General Conclusion************

This course has provided a comprehensive introduction to the fundamental principles of coordination chemistry. Through the study of metal complexes, their formation, structures, bonding theories, properties, and applications, students have acquired the essential knowledge required to understand the behavior of coordination compounds in various chemical contexts.

By the end of this course, students are expected to have developed a solid understanding of the key concepts of coordination chemistry, including coordination numbers, geometries, ligand types, electronic structure, and stability of metal complexes. These concepts constitute an essential foundation for further studies in inorganic chemistry and related fields such as bioinorganic chemistry, environmental chemistry, and analytical chemistry.

The knowledge gained in this course enables students to analyze coordination compounds encountered in academic research, industrial applications, and environmental systems. Moreover, it prepares them for more advanced topics, including reaction mechanisms of metal complexes, catalysis, metal-based materials, and the role of coordination compounds in biological and environmental processes.

In conclusion, this course aims not only to convey theoretical knowledge but also to develop students' analytical and conceptual skills, which are crucial for their academic and professional development. The principles of coordination chemistry introduced in this manual will serve as a valuable foundation for future learning and specialization in chemistry and related scientific disciplines.

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