INORGANIC CHEMISTRY

M.Sc., First Year,
Semester-II, Paper-II

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FOREWORD

Since its establishment in 1976, Acharya Nagarjuna University has been forging ahead in the path of progress and dynamism, offering a variety of courses and research contributions. I am extremely happy that by gaining 'A+' grade from the NAAC in the year 2024, Acharya Nagarjuna University is offering educational opportunities at the UG, PG levels apart from research degrees to students from over 221 affiliated colleges spread over the two districts of Guntur and Prakasam.

The University has also started the Centre for Distance Education in 2003-04 with the aim of taking higher education to the door step of all the sectors of the society. The centre will be a great help to those who cannot join in colleges, those who cannot afford the exorbitant fees as regular students, and even to housewives desirous of pursuing higher studies. Acharya Nagarjuna University has started offering B.Sc., B.A., B.B.A., and B.Com courses at the Degree level and M.A., M.Com., M.Sc., M.B.A., and L.L.M., courses at the PG level from the academic year 2003-2004 onwards.

To facilitate easier understanding by students studying through the distance mode, these self-instruction materials have been prepared by eminent and experienced teachers. The lessons have been drafted with great care and expertise in the stipulated time by these teachers. Constructive ideas and scholarly suggestions are welcome from students and teachers involved respectively. Such ideas will be incorporated for the greater efficacy of this distance mode of education. For clarification of doubts and feedback, weekly classes and contact classes will be arranged at the UG and PG levels respectively.

It is my aim that students getting higher education through the Centre for Distance Education should improve their qualification, have better employment opportunities and in turn be part of country's progress. It is my fond desire that in the years to come, the Centre for Distance Education will go from strength to strength in the form of new courses and by catering to larger number of people. My congratulations to all the Directors, Academic Coordinators, Editors and Lesson-writers of the Centre who have helped in these endeavors.

Prof. K. Gangadhara Rao
M.Tech., Ph.D.,
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M.Sc. Chemistry
FIRST YEAR, SEMESTER – II
204CH242 INORGANIC CHEMISTRY-II
SYLLABUS

Learning Objectives:
To know the classification and Applications of Metal clusters.
To know the reactions of organo metallic compounds.
To know the Anation Reactions and Trans effects.
To know the Selection rules, corelation diagrams and orgel diagrams. To know the Cotton effect and Faraday effect, structures of Haemoglobin and Myoglobin, vitamin B_{12}, Photo Chemical Laws.

UNIT-I

Metal clusters classification: LNCs and HNCs, Isoelectronic and Iso lobal relationships, electron counting rules: Wade's and Lauher's rules. M-M multiple bonding; Preparation, structure and bonding in di nuclear $[Re_2cl_8]^{2}$, tri nuclear $[Re_3cl_9]$, tetra nuclear $[W_4OR_{16}]$ and hexa nuclear $[Mo_6cl_8]^{4+}$; $Nb_6uCl_{12}]^{2+}$ cluster molecules and ions.
Poly atomic Zintle ions and chevrel phases. Applications of clusters
Metal π-Complexes Preparation, structure and bonding in Nitrosyl, Dinitrogen and Dioxygen complexes.

UNIT-II

Organometallic complexes of transition Metals: classification Metallocenes with four, five, six, seven and eight (η^4 - η^8) membered rings. Synthesis, structure and bonding of Ferrocene. cyclopenta dienyr, Arene, cyclohepta triene Tropylium complexes of transition metals.
Reactions of organometallic compounds-oxidative addition, reductive elimination, insertion and elimination.
Applications of organometallic compounds-catalytic hydrogenation, Hydroformylation and polymerization of olefin using Zeigler- Nutta catalyst.

UNIT- III

Reaction Mechanism in Transition Metal Complexes: Kinetics of octahedral substitution, acid hydrolysis, base hydrolysis-conjugate base (CB) mechanism. Direct and indirect evidences in favour of CB mechanism.
Anation Reactions: Reactions without metal-ligand bond cleavage. Factors affecting the substitution reactions in octahedral complexes. Trans effect on substitution reactions in square planar complexes.
Mechanism of redox reactions, outer sphere mechanism, cross reactions and Marcus -Hush equation, inner sphere mechanism, complementary and non - complementary reactions.

UNIT-IV

Electronic Spectra of Transition Metal Complexes: Electronic configurations of metal ions and Spectroscopic terms. Selection rules, Breakdown of selection rules, Slator - Condon repulsion parameters, Racah parameters, Term separation energies for d^n electronic configurations.

Correlation diagrams and Orgel diagrams. Tanabe-sugano diagrams for configurations from d^1 to $d^{9\ \text{octahedral}}$ and tetrahedral transition metal complexes of 3d series.

Calculations of Dq, B and β parameters. Charge transfer spectra.

UNIT – V

Magnetic Properties of Transition Complexes: Types of magnetism, anomalous magnetic moments - Orbital and spin contribution, spin - orbit coupling and magnetic moments. Chiroptical properties, Cotton effect and Faraday effect.

Biochemical Aspects of Iron and Cobalt: Binding, storage and transport of dioxygen by Hemoglobin and Myoglobin, Vitamin Brz and its importance.

Photo Inorganic Chemistry: Introduction, Photochemical laws, photo redox reactions and photo anation reactions. Photo chemical decomposition of water.

Reference Books:

l) Inorganic Chemistry, Huheey. Harper and Row.
2) Concise Inorganic Chemistry, J. D. Lee, ELBS.
3) Inorganic chemistry, K.F. Purcell and J.c. Kotz, Holt Saunders intemational 4) organometallic chemistry, R.c. Mehrotra and A. Singh. New Age Intemational.
5) Advancedlnorganic Chemistry, Cotton and Wilkinson, Wiley Eastem
6) Inorganic Reaction Mechanism, Basolo and pearson, Wiley Eastem
7) Bioinorganic Chemistry, K. Hussan Reddy
8) Biological Aspects of inorganic chemistry, A. W. Addiso, W. R. Cullen, D. Dorphin and G. J. James. Weliey Interscience.
9) Photochemistry of coordinationcompounds, V.Balzaniand V.Carassiti. Academic Press.

Learning Outcomes:

- ✓ The student will understand the various metal clusters and metal **π** complexes.
- ✓ Understanding the reactions of organo metallic compounds and its applications
- ✓ The students are able to understanding the reaction mechanism in transition metal complexes, anation reactions, and complementary reactions.
- ✓ The students are able to understand the orgel diagrams and electronic spectra of transition metal complexes.
- ✓ The study of magnetic properties and anamolous magnetic moments of transition complexes.
- ✓ The students are able to understanding structure and functions of haemoglobin, myoglobin and vitamin Bl2, photochemical laws.

(204CH24)

M.Sc. DEGREE EXAMINATION, MODEL QUESTION PAPER
SECOND SEMESTER
PAPER-IV: INORGANIC CHEMISTRY-II

Time: Three hours **Maximum: 70 marks**

UNIT-I

1. (a) Explain Isoelectronic and Iso Lobal relationships. [4 Marks]

(OR)

(b) Write about Zintle ions.

2. (a) Discuss the Wade's rule and Lauher's rule. [10 Marks]

(OR)

(b) Explain the preparation, structure and bonding in Nitrosyl.

UNIT-II

3. (a) Write the Nephelauxetic effect. [4 Marks]

(OR)

(b) Write note on applications of CFT.

4. (a) Discuss the Jahn Teller Effect in detail. [10 Marks]

(OR)

(b) Write the splitting of d-orbitals in Tetrahedral and square pyramidal Geometries.

UNIT-III

5. (a) Explain the Π donor & Π acceptor ligands on Δ_o. [4 Marks]

(OR)

(b) Write the short notes on Bent rule.

6. (a) Draw the MO diagram of Octahedral complexes with examples.

[10 Marks]

(OR)

(b) What is resonance and discuss the resonance in homo and hetero atomic molecules.

UNIT-IV

7. (a) Write a note on trends in stepwise stability constant. [4 Marks]

(OR)

(b) Explain Job's Method and their limitations.

8. (a) Discuss the Bjerrum method in detail. [10 Marks]

(OR)

(b) Write a brief note on HSAP

UNIT-V

9. (a) Write the preparation and structure of higher boranes. [4 Marks]

(OR)

(b) Explain the Isopoly and Hetero poly salts and acids

10. (a) Write a note on Cage compounds of P-O & P-S. [10 Marks]

(OR)

(b) Explain the P-N cyclic compounds with examples

CONTENTS

LESSON-1

METAL CLUSTERS

1.0 OBJECTIVES:

After studying this lesson, you should be able to:

- To know the classification and identification of metal clusters.
- To study about the of structure and bonding of M-M multiple bonding.
- To study about application of metal clusters.

STRUCTURE:

1.1 INTRODUCTION

Metal Cluster

In inorganic chemistry, **clusters** are compounds containing three or more metal atoms bonded together, often forming triangular or larger structures. **Metal clusters** are a specific type of cluster where metal-metal bonds are the primary feature, and they can be homonuclear (all the same metal) or heteronuclear (multiple different metals).

Metal-metal bond is a bond between two metal centers, particularly between two transition metal atoms, which ranges from a single to a quadruple bond. The existence of metal-metal bond in transition metals is mainly due to the of presence of (n+1)s , (n+1)p and nd orbitals as valence shell electronic configuration. The transition metals can form three general types of bonds such as covalent bonds, dative bonds and weak metal-metal symmetry interactions where covalent bonds being the strongest and symmetry interactions are the weakest. The compounds containing a large number of metal-metal bonds forming triangular and larger structures are called cluster compounds, however these also include linear M-M bonds. The metal clusters can also be defined as any entity that contains a metal-metal bond.

Metal clusters are **chemical species that contain two or more metal atoms directly bonded to each other**, often stabilized by surrounding ligands such as carbonyls (CO), halides (Cl^-, Br^-), phosphines (PR_3), or hydrides (H^-). These ligands help prevent aggregation and decomposition of the metal atoms.

In simple terms, a **metal cluster** is an intermediate structure between a **mononuclear complex** (single metal center) and **bulk metal** (infinite array of metal atoms). Thus, clusters serve as a bridge between **molecular chemistry** and **solid-state metallic bonding**.

General Representation

$M_n L_x$ where,

- **M** = metal atom,
- **n** = number of metal atoms (≥ 2),
- **L** = ligands coordinated to metal center.

1.2 CLASSIFICATION OF METAL CLUSTERS

Metal clusters can be classified in several ways depending on composition, metal–metal bonding, and ligand type.

1.2.1 Based on Composition:

- **Homonuclear clusters**: Composed of atoms of a single metal.
- **Heteronuclear clusters**: Contain two or more different types of metal atoms.
- **Ligand-stabilized clusters**: Surrounded by ligands, which can include carbonyls, halides, or other organic/inorganic groups.
- **Naked clusters**: Clusters of metal atoms that are not stabilized by ligands.

1.2.2 Based on type of Ligands:

- Polynuclear carbonyls, nitrosyls and related compounds
- Halide and oxide clusters.

Polynuclear carbonyls, nitrosyls and related compounds

In these complexes, metal atoms are in low formal oxidation states +1, 0 -1. These are formed by transition metals on the right side of the periodic table. (Eg. Fe, Co, No, Ru, Pd, Os, Ir and Pt) of the d-block elements.

Halide and oxide clusters

In these complexes metal atoms are in higher formal oxidation states +2 and +3. The transition metals on the left side I and III row transition metals form this type of clusters.

1.2.3 Based on the Number of Metal Atoms (Nuclearity)

(a) Low-Nuclearity Clusters (LNCs)

- Contain two or three metal atoms.
- Usually have well-defined M–M bonds and simple geometries.
- **Examples:**
  - $Mn_2(CO)_{10}$ (binuclear)
  - $Fe_3(CO)_{12}$ (trinuclear)

(b) High-Nuclearity Clusters (HMCs)

- Contain four or more metal atoms.
- Exhibit complex, often 3D frameworks such as tetrahedral, octahedral, or cubane-type geometries.
- **Examples:**
  - $Co_4(CO)_{12}$ (tetranuclear)
  - $Ru_6(CO)_{18}$ (hexanuclear)

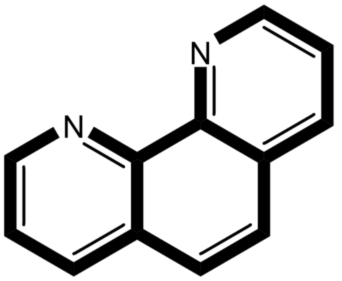
1.3 STRUCTURAL PATTERN OF LNC AND HNC

LNC and HNC in the context of metal cluster refer to Low Nuclear Carbonyl Clusters and High Nuclear Carbonyl Clusters, respectively. They are classifications based on the number of metal atoms present in the cluster's core, and are not specific ligands themselves. Metal carbonyl clusters are compounds containing two or more metal atoms linked by metal-metal bonds, with carbon monoxide (CO) groups serving as the primary ligands. These are categorized by their "nuclearity" (the number of metal centers):

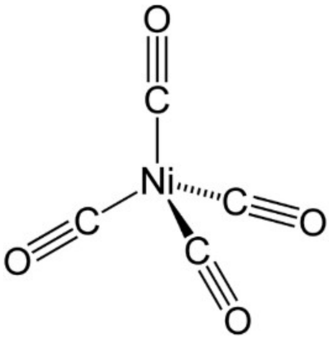
1.3.1 Low Nuclearity Carbonyl Clusters (LNCC or LNC): These clusters typically contain a smaller number of metal centers, generally in the range of **2 to 4** metal atoms.

Examples: $Ni(CO)_4$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Mn_2(CO)_{10}$, $Ru_3(CO)_{12}$ and $Rh_4(CO)_{12}$.

The electron diffraction studies shows that the configuration of tetrahedral (sp^3hybridization) and the Ni-C-O group is linear. Ni-C bond distance is 182 pm and that of C-O is 115 pm. When alcoholic solution shows that the carbonyl is treated with ortho-phenanthroline and $Ni(CO)_2$ then phenanthroline was formed. This reaction conforms that the two C≡O groups of $Ni(CO)_4$ are replaced by one molecule of phenanthroline.

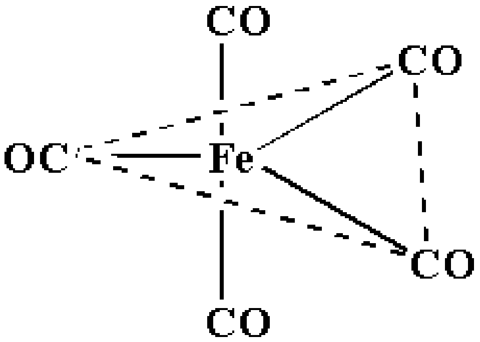


Phenanthroline



Example: $Fe(CO)_5$

Electron diffraction and x-ray studies revels that the configuration of $Fe(CO)_5$ is regular trigonal bipyramid (SP^3d) and the molecule is diamagnetic nature.



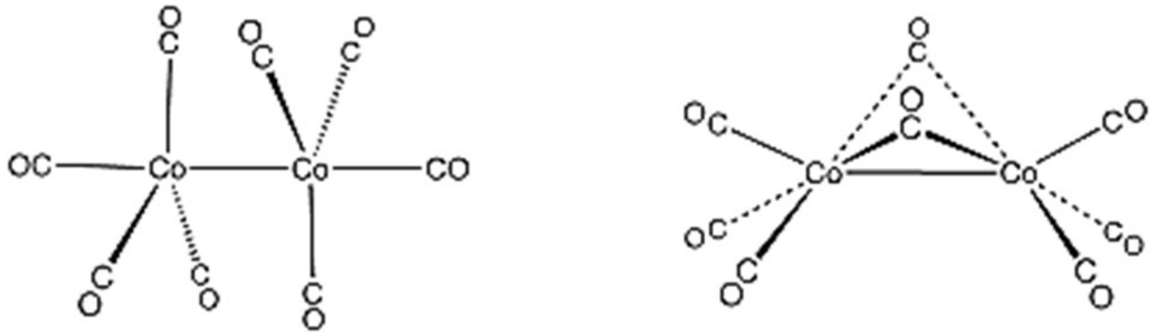
1.3.2 High Nuclearity Carbonyl Clusters (HNCC or HNC): These clusters possess a larger number of metal centers, generally **5 or more** metal atoms.

Examples: $[Rh_{13}(CO)_{24}H_3]^{2-}$ and $[Pt_{3n}(CO)_{6n}]^{2-}$ where n=26.

The poly nuclear compounds with M-M bonds Eg. $Mn_2(CO)_{10}$ supplemented in some cases with bridging carbonyl groups.

Example: $Co_2(CO)_8$

In the case of poly nuclear carbonyls, 18-electron rule suggest that two arrangements are equally liked for hypothetical $Co_2(CO)_8$. In figure (a) the two metals each with terminal Co-ligands bonded to each other or in figure (b) the two metals share two ligands as bridging groups in addition to M-M bond. For $CO_2(CO)_8$ adopts both of these configurations the farmers in solution and later in solid state.

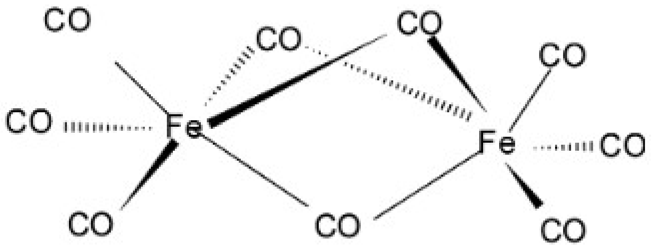


Liquid State **Solid State**

$Co_2(CO)_8$

Mononuclear metal carbonyls can combine to form **polynuclear complexes** by **loss of CO ligands**, leading to the formation of **metal–metal (M–M) bonds**. These bonds may occur **with or without bridging CO ligands** between the metal centers.

A well-known example is **diiron nonacarbonyl, $Fe_2(CO)_9$**. This compound can satisfy the **18-electron rule** and exists in two possible structural forms. Among these, the structure containing **three bridging CO ligands and one Fe–Fe bond** is considered **stable and possible**, whereas the alternative form with **only one bridging CO ligand and one Fe–Fe bond** is **not feasible**.



$Fe_2(CO)_9$ Structure

1.4 SUMMARY

- To know the classification and identification of metal clusters.
- To study about the of structure and bonding of M-M multiple bonding.
- To study about application of metal clusters.

1.5 TECHNICAL TERMS

Metal Clusters, Ligand, HNC, LNC, Nuclearity

1.6 SELF ASSESSMENT QUESTIONS:

1. Define Metal Clusters
2. Explain the types of Metal clusters.
3. Write short note on classification of metal clusters.
4. Explain the high nuclear carbonyl clusters.
5. Describe the low nuclear carbonyl clusters.

1.7 REFERENCE BOOKS:

1. Inorganic Chemistry Huheey, Harper and Row.
2. Physical methods in Inorganic Chemistry, R.S. Drago. Affiliated East-West Pvt. Ltd.
3. Concise Inorganic Chemistry, J. D. Lee, ELBS.
4. Modern Inorganic Chemistry, W. L. Jolly, McGrawHill.
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8. Quantum Chemistry, R. K. Prasad.
9. Inorganic Chemistry, Atkins, ELBS.
10. Advanced Inorganic Chemistry, Cotton and Wilkinson, Wiley Eastern.
11. Quantum Chemistry, R. K. Prasad.
12. Concise Coordination Chemistry, R.Gopalan and V.Ramalingam.

Dr. K. Krishnadevi

LESSON-2

ELECTRON COUNTING RULE

2.0 OBJECTIVES:

After studying this lesson, you should be able to:

- To know the Isoelectronic and Iso lobal relationships.
- To study about the electron counting rules.
- To know about Wade's and Lauher's rules.
- To study about the calculation of valency electrons.

STRUCTURE:

2.1 INTRODUCTION

2.1.1 ISOELECTRONIC SPECIES

Two or more species (atoms, ions, or molecules) are said to be **isoelectronic** if they have the **same number of total electrons** and often **similar electronic structures**.

Isoelectronic species ⇒ Same total number of electrons and similar bonding pattern. **Examples:**

Species	**Total electrons**	**Remarks**
N_2, CO	14	Both are diatomic molecules with triple bonds
CN^-, NO^+	14	Isoelectronic with CO
O_2, S_2	16	Similar bonding (π^* orbitals partially filled)
$[Fe(CO)_4]^{2-}$ and $Ni(CO)_4$	36	Isoelectronic metal carbonyls

- Isoelectronic species often exhibit **similar geometries, bond lengths, and properties**.
- However, differences in **nuclear charge (Z)** can slightly alter their bond strength and polarity.

2.1.2 ISOLOBAL CONCEPT

Isolobal analogy is a strategy used in organo metallic chemistry to relate the structure of organic and inorganic molecular fragments in order to predict the bonding properties of organometallic compounds.

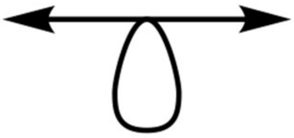
The concept of **isolobal analogy** was introduced by **Roald Hoffmann (1976)** to relate **fragments of organometallic compounds** to organic molecular fragments. It extends the idea of **isoelectronicity** to **molecular fragments** that have **similar frontier orbitals** (number, symmetry, and energy).

Two molecular fragments are said to be **isolobal** if their **frontier orbitals** (orbitals that participate in bonding) are:

- Similar in **number**
- Similar in **symmetry**
- Similar in **energy** and **shape**

Isolobal fragments behave similarly in bonding and reactivity.

Isolobal species are indicated with an isolobal arrow symbol, a double headed arrow with half and orbital.

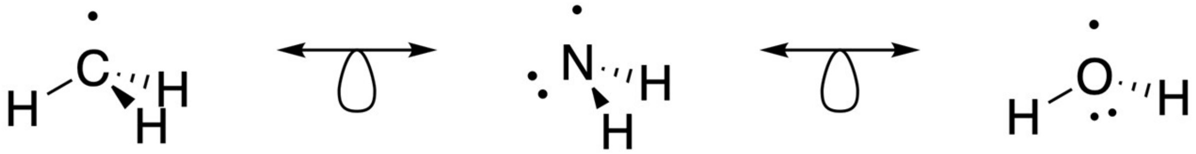


2.1.2.1 Isolobal Fragments of main group elements

There is a simple means to determine if fragments are isolobal. In main group chemistry the octet rule is a very helpful guide, especially for the period 2 elements (B, C, N, O, F) for which the octet rule holds fairly strictly. The difference between the number "8" and the number of valence electrons (VE) of the molecular fragment is equal to the number of frontier orbitals and the number of electrons in it.

of frontier orbitals = of electrons in frontier orbitals = 8 – VE

Thus, **when two fragments (of main group elements) have the same number of valence electrons, they can be considered isolobal.** For example, the CH_3 fragment created by homolytic cleavage of a C-H bond from CH_4 is shown in Figure. This CH_3 fragment has 7 VE on the carbon, and therefore it has one frontier orbital with one electron it (Figure). The same is true for the NH_2 (7 VE) and OH (7 VE) fragments. All of these fragments have 7 VE and one frontier orbital (Figure).



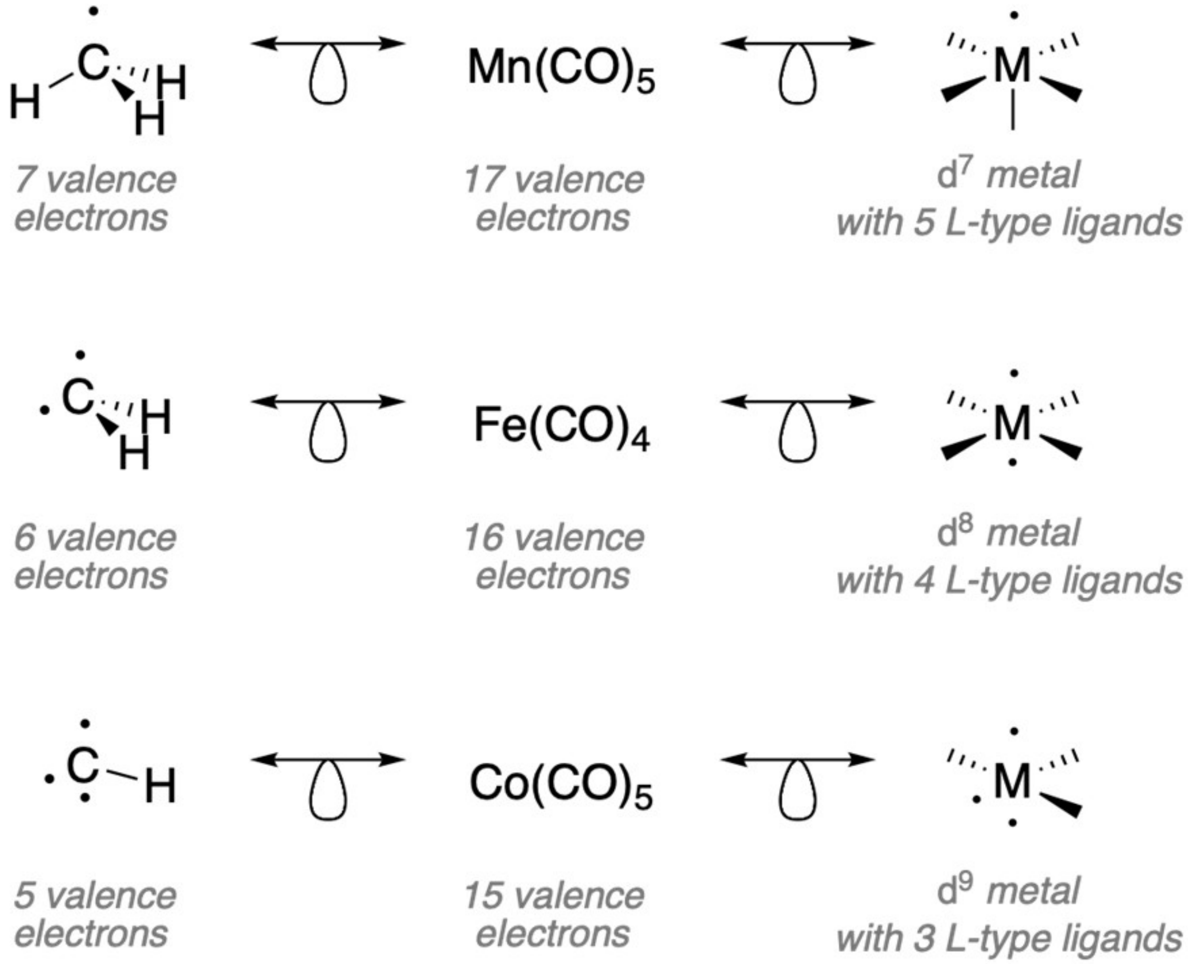
(All have 7 valence electrons around the central atom, thus they each have one frontier orbital.)

2.1.2.2 Isolobal fragments of transition elements

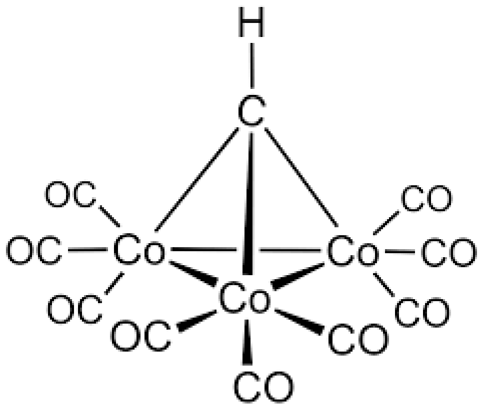
In the way the octet rule can help to predict the number of frontier orbitals and the electrons in them for main group element fragments, the 18 electron rule can be used to predict the number of frontier orbitals and electrons for organometallic fragments, including carbonyl fragments. The number of frontier orbitals and the number of electrons in them is 18 minus the number of valence electrons the organometallic fragment has:

frontier orbitals = of electrons in frontier orbitals = 18 – VE

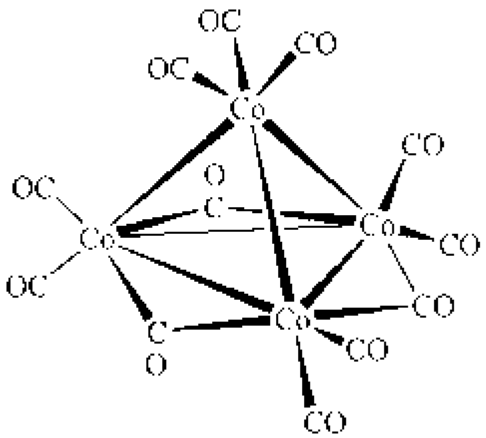
For example, a metal complex with a count of 17 electrons, such as $Mn(CO)_5$, there is one frontier orbital with one electron. This implies that a 17 VE carbonyl fragment is isolobal to a 7 VE organic fragment such as CH_3. For a 16 VE fragment such as $Fe(CO)_4$ there are two frontier orbitals with one electron in each of them, and for a 15 VE fragment such as $(CO)_3Co$ there are three frontier orbitals with overall three valence electrons (Figure). Similarly, a 16 VE metal carbonyl fragment is isolobal to a 6 VE fragment such as CH_2, and a 15 VE fragment is isolobal to a 5 VE fragment such as CH (Figure).



Ex: $Co_3(CO)_9$ (CH) and $Co_4(CO)_{12}$ both of which can be regarded as triangular $Co_3(CO)_9$ or by CH. The CH and $Co(CO)_3$ groups are isolobal because each one has 3-orbiytals and 3 e^- available for participation in frame work bonding.



$Co_3(CO)_9$ (CH) Structure



$Co_4(CO)_{12}$ Structure

2.1.3 Applications of the Isolobal Concept

1. Prediction of Cluster Structures:
   Helps understand and predict structures of metal clusters by relating them to known fragments.
2. Understanding Reactivity:
   Fragments that are isolobal often react similarly, even if their compositions differ.
3. Design of Organometallic Compounds:
   Guides the synthesis of new complexes by substituting isolobal fragments.
4. Bridge between Organic and Organometallic Chemistry:
   Explains similarities in bonding and reactivity patterns between organic radicals and metal carbonyl fragments.

2.2 ELECTRN COUNTING

Electron counting is a fundamental concept in **organometallic and coordination chemistry** used to determine the **total number of valence electrons** associated with a metal center in a complex. It helps predict the **stability, bonding, and reactivity** of metal complexes, especially **metal carbonyls** and **clusters**. A stable **transition metal complex** generally tends to achieve a **noble gas configuration** in its valence shell — i.e., **18 valence electrons** (analogous to krypton configuration).

This is known as the **18-Electron Rule**.

$\text{Stable complex: Total valence electrons} = 18$**2.2.1 Basis of the 18-Electron Rule:** Transition metals have **nine valence orbitals** available for bonding:

- **One s orbital (2 electrons)**
- **Three p orbitals (6 electrons)**
- **Five d orbitals (10 electrons)**
  → Total = 18 electrons

Thus, when all these orbitals are filled, the complex achieves maximum stability.

2.2.2 Methods of Electron Counting

Two common methods are used to determine the total electron count in a metal complex:

(a) Neutral Atom Method (Covalent Method)

- Count the **valence electrons of the neutral metal atom**.
- Add electrons donated by **ligands** (according to their donor type).
- Add or subtract electrons for **overall charge** of the complex.

$\text{Total } e^- = \text{Metal valence } e^- + \text{Ligand } e^- \pm \text{Charge}$**(b) Oxidation State Method (Ionic Method)**

- Determine the **oxidation state** of the metal.
- Use the **metal's d-electron count** after oxidation.
- Add the **donor electrons** from each ligand.

$$\text{Total } e^{-} = (\text{Metal d-electrons}) + (\text{Ligand contributions})$$

2.2.3. Common Ligand Electron Donor Numbers

Ligand	Type	Electrons Donated
CO	Neutral (π-acceptor)	2
PPh_3, PR_3	Neutral	2
NH_3	Neutral	2
H_2O	Neutral	2
Cl^-, Br^-	Anionic	2
H^-	Anionic	2
$C_5H_5^-$ (η^5-Cp)	Anionic	6
η^6–C_6H_6	Neutral	6
NO (linear)	Neutral	3
NO (bent)	Neutral	1

Example 1: $Ni(CO)_4$

- Metal: Ni (group 10 → 10 valence e^-)
- Ligands: 4 CO (each 2 e^- × 4 = 8 e^-)

$$\text{Total} = 10 + 8 = 18\,e^{-¿\backslash(\text{Stable complex}\backslash)¿}$$

Example 2: $Fe(CO)_5$

- Metal: Fe (group 8 → 8 e^-)
- Ligands: 5 CO (5 × 2 = 10 e^-)

$$\text{Total} = 8 + 10 = 18\,e^{-¿\backslash(\text{Stable complex}\backslash)¿}$$

Example 3: $Fe_2(CO)_9$

Each Fe contributes 8 valence e^-
→ 2 × 8 = 16 e^-

Total CO = 9 × 2 = 18 e^-
→ 16 + 18 = 34 e^- total in molecule

→ Per Fe = 17 e^-

One **Fe–Fe bond** contributes **1 electron to each Fe**,
thus each Fe achieves **18 e^-**, satisfying the rule.

Hence, **$Fe_2(CO)_9$** follows the 18-electron rule.

2.2.4 Exceptions to the 18-Electron Rule

Some complexes are **stable even if they do not have 18 electrons**, especially for:

- **Early transition metals (Groups 3–7):** often 16 e^- or fewer due to large size and weak π-backbonding.
- **Square planar d^8 complexes (e.g., Pt(II), Pd(II)):** stable with 16 e^-.
- **Steric hindrance** or **π-donor ligands** may reduce electron count.

2.2.5 Applications

- Predicting **stability** of metal complexes.
- Understanding **bonding and reactivity** patterns.
- Explaining **structure and magnetic properties**.
- Designing **catalysts** and **organometallic compounds**.

2.3 WADE'S RULE

Wade's Rules (proposed by Kenneth Wade in 1971) are empirical guidelines used to predict the shapes and structures of boranes, carboranes, and metal clusters based on electron count. They correlate the number of skeletal electron pairs (SEP) with the geometry (polyhedral structure) of the cluster. Originally developed for boranes (B_nH_{n+4}, B_nH_{n+6}, etc.), the rules were later extended to transition metal carbonyl clusters and Zintl ions.

Each cluster consists of a skeletal framework formed by n atoms bonded together. The total number of skeletal bonding electron pairs (SEP) determines the type of polyhedron the cluster adopts.

Classification According to Skeletal Electron Pairs

Type of Cluster	General Formula	No. of SEPs	Geometry / Structure
Closo	$B_nH_n^{2-}$	n + 1	Closed deltahedral (e.g., octahedral, icosahedral)
Nido	B_nH_{n+4}	n + 2	One vertex missing from closo structure
Arachno	B_nH_{n+6}	n + 3	Two vertices missing
Hypho	B_nH_{n+8}	n + 4	Three vertices missing
Klado	B_nH_{n+10}	n + 5	Four vertices missing

Step-by-Step Application of Wade's Rules

Step 1: Determine the total number of valence electrons.

- Each boron (B) contributes 3 electrons.
- Each hydrogen (H) contributes 1 electron.
- Add or subtract electrons depending on charge.

Step 2: Subtract 2 electrons per B–H terminal bond (since they are localized σ-bonds).

Step 3: Divide the remaining electrons by 2 → gives the number of skeletal electron pairs (SEP).

Step 4: Compare the SEP with Wade's table to identify the type of cluster (closo, nido, etc.) and its geometry.

Examples

(a) $B_6H_6^{2-}$

- Total valence electrons = (6 × 3) + (6 × 1) + 2 = 26
- Terminal B–H bonds = 6 × 2 = 12 electrons
- Remaining = 26 − 12 = 14 electrons
- Skeletal pairs = 14 ÷ 2 = 7
  → For n = 6, SEP = n + 1 = 7 → Closo type
  Structure: Octahedral

(b) B_5H_9

- Total valence electrons = (5 × 3) + (9 × 1) = 24
- Terminal B–H bonds = 9 × 2 = 18 electrons
- Remaining = 24 − 18 = 6 electrons
- Skeletal pairs = 6 ÷ 2 = 3
  → For n = 5, SEP = n + 2 = 7 pairs → Nido type
  Structure: Trigonal bipyramid with one vertex missing

(c) B_4H_{10}

- Total valence electrons = (4 × 3) + (10 × 1) = 22
- Terminal B–H bonds = 10 × 2 = 20 electrons
- Remaining = 2 electrons
- Skeletal pairs = 1
  → For n = 4, SEP = n + 3 = 7 pairs → Arachno type
  Structure: Tetrahedral with two vertices missing

2.3.1 Extension to Metal Clusters

Wade's rules can also be applied to transition metal carbonyl clusters, where the metal atoms form the skeletal framework.

In this case:

- Each metal atom contributes its valence (d + s) electrons.
- Each terminal CO ligand contributes 2 electrons.
- Bridging CO or metal–metal bonds are accounted for in skeletal electron counting.

Cluster	SEP	Type	Structure
$Fe_3(CO)_{12}$	7	Closo	Triangular
$Co_4(CO)_{12}$	8	Nido	Tetrahedral
$Ru_6(CO)_{18}$	9	Closo	Octahedral

Geometrical Correlation Table

Type	SEP	Polyhedral Geometry	Example
Closo	n + 1	Complete deltahedron	$[B_6H_6]^{2-}$
Nido	n + 2	One vertex missing	B_5H_9
Arachno	n + 3	Two vertices missing	B_4H_{10}
Hypho	n + 4	Three vertices missing	B_3H_{11}
Klado	n + 5	Four vertices missing	—

2.3.2 Significance of Wade's Rules

- Predicts structure and geometry of boranes and metal clusters.
- Helps in understanding bonding and delocalization in cluster compounds.
- Extends the concept of molecular orbitals to polyhedral frameworks.
- Serves as a foundation for the polyhedral skeletal electron pair theory (PSEPT).

2.4 LAUER'S RULE:

Lauher's Rule (also known as the **Lauher–Hoffmann Rule**) is an **extension of Wade's Rules** used to explain and predict the **structures of transition metal carbonyl clusters**. While **Wade's rules** work well for **boranes** and simple **main group clusters**, **Lauher's rule** helps to describe **metal–metal bonded clusters**, where **d-orbitals** of metals play a crucial role in bonding. The rule was developed by **John Lauher and Roald Hoffmann (1976)** through **molecular orbital (MO) analysis** of transition metal clusters.

"The stability and structure of metal clusters depend on the **number of bonding and antibonding metal–metal molecular orbitals**, which arise from the overlap of the metal's d orbitals." In other words, **metal–metal bonding molecular orbitals** (derived mainly from d orbitals) determine the **shape and electron count** of the cluster. Thus, the **total valence electron count (TVEC)** of the cluster helps predict whether all bonding orbitals are filled (stable structure) or if antibonding orbitals are partially occupied (less stable).

2.4.1 Relation to Wade's Rule

Aspect	Wade's Rule	Lauher's Rule
Applicable to	Main group clusters (boranes, carboranes)	Transition metal clusters
Basis	Skeletal electron pairs (SEP)	Molecular orbital (MO) filling of M–M bonds
Key Orbitals	s and p orbitals	Mainly d orbitals
Geometry Prediction	Closo, Nido, Arachno	Metal carbonyl cluster geometry and stability

Hence, **Lauher's rule generalizes Wade's concept** to **transition metal clusters** using **d orbital symmetry considerations**.

Fundamental Concept

- In metal carbonyl clusters, **each metal atom** contributes its **valence electrons (s + d)**.
- These orbitals combine to form **metal–metal bonding MOs**, similar to skeletal orbitals in boranes.
- The **filled bonding orbitals** determine the **cluster framework** (closo, nido, etc.).
- When **antibonding orbitals** begin to fill, the structure tends to **distort or fragment**, leading to **lower nuclearity clusters**.

2.4.2 Electron Counting Under Lauher's Rule

Lauher and Hoffmann related the **metal–metal framework bonding** to the **total electron count (TEC)**, where the stable clusters satisfy:

$$\text{Bonding MOs filled} \Rightarrow \text{Stable cluster} \text{Antibonding MOs occupied} \Rightarrow \text{Unstable or distorted cluster}$$
T
ypically, for **octahedral (closo-type)** metal clusters, **60 cluster valence electrons (CVE)** correspond to a **closed-shell (stable)** configuration.

For instance:

Type of Cluster	No. of Metal Atoms	Typical Stable Electron Count	Example
Triangular (M_3)	3	48 CVE	$Fe_3(CO)_{12}$
Tetrahedral (M_4)	4	60 CVE	$Co_4(CO)_{12}$
Octahedral (M_6)	6	86 CVE	$Ru_6(CO)_{18}$

Thus, **Lauher's rule** helps predict the **stability and bonding** in such clusters.

Example: $Co_4(CO)_{12}$

- Each Co atom = 9 valence electrons → 4 × 9 = 36 e^-

- Each CO ligand = 2 e^- → 12 × 2 = 24 e^-
- Total = 36 + 24 = 60 electrons

→ Matches the **60-electron rule**, corresponding to a **tetrahedral closo-type structure**. Stable, consistent with **Lauher's Rule**.

2.4.3 Significance of Lauher's Rule

- Explains **why certain cluster geometries** (triangular, tetrahedral, octahedral) are stable for specific electron counts.
- Extends **Wade–Mingos theory** to **transition metal systems**.
- Helps interpret **metal–metal bonding** using **molecular orbital theory**.
- Useful in understanding **metal carbonyl clusters**, **Zintl ions**, and **intermetallic compounds**.

Summary Table

Concept	Applies To	Governing Orbitals	Stability Criterion
Wade's Rule	Boranes / Main group clusters	s, p orbitals	n + 1, n + 2, n + 3 skeletal pairs
Lauher's Rule	Transition metal clusters	d orbitals	Bonding MOs filled (60e, 86e rules)

2.5 SUMMARY

- To know the Isoelectronic and Iso lobal relationships.
- To study about the electron counting rules.
- To know about Wade's and Lauher's rules.
- To study about the calculation of valency electrons.

2.6 TECHNICAL TERMS

Electron Counting, Wade's, Lauher's rules, Iso Lobal, Iso electronic

2.7 SELF ASSESSMENT QUESTIONS:

1. Write short notes on Iso electronic and Iso lobal relationships.
2. Write short notes on Electron Counting rule.
3. Define Wade's Rule.
4. Explain Lauher's Rule.
5. Calculate the valency electrons for carbonyl compounds.

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Dr.K.Krishnadevi

LESSON-3

METAL-METAL MULTIPLE BONDING

3.0 OBJECTIVES:

After studying this lesson, you should be able to:

- To know the M-M multiple bonding.
- To study about the Di nuclear cluster of $[Re_2Cl_8]^{2-}$.
- To know about the tri and hexa nuclear clusters.

STRUCTURE:

3.1 INTRODUCTION

Metal–metal (M–M) multiple bonding refers to the direct bonding interactions between two metal atoms through the overlap of their d-orbitals. Such bonds can range from single (σ) to quadruple (σ + 2π + δ) bonds, depending on how many orbitals overlap. These types of bonds are found mainly in transition metal complexes, particularly those with low oxidation states and vacant coordination sites that allow d–d orbital overlap.

Origin of M–M Bonds

Transition metals possess five d orbitals, which can participate in metal–metal bonding through:

- End-on overlap of d_{z^2} orbitals → σ bond
- Sidewise overlap of d_{xz} and d_{yz} orbitals → π bonds
- Face-to-face overlap of d_{xy} orbitals → δ bond

Hence, two metal atoms can form up to four bonds (σ, 2π, δ), giving rise to quadruple bonds in certain cases.

3.2 PREPARATION, STRUCTURE, AND BONDING OF THE DINUCLEAR COMPLEX $[Re_2Cl_8]^{2-}$

The **octachlorodirhenate(III) ion**, **$[Re_2Cl_8]^{2-}$**, is one of the **most famous examples of a metal–metal multiple bonded complexes**. It contains a **rhenium–rhenium (Re–Re) quadruple bond**, which was the **first experimentally confirmed metal–metal quadruple bond**. It demonstrates the presence of **σ, two π, and one δ bond** between the two rhenium atoms.

3.2.1 Preparation

$[Re_2Cl_8]^{2-}$ is generally prepared from **rhenium(III) chloride ($ReCl_3$)** or **rhenium(V) chloride ($ReCl_5$)** through reduction. Usually carried out in the presence of **HCl** or a **reducing agent** like **ethanol** or **$SnCl_2$**, followed by crystallization with a counterion such as **K^+, $(NBu_4)^+$, or Cs^+** to form salt like: $K_2[Re_2Cl_8]$

$$ReCl_3 + 2Cl^- \longrightarrow [Re_2Cl_8]^{2-}$$

Each rhenium atom in the complex is in the **+3-oxidation state**.

$[Re_2Cl_8]^{2-} \rightarrow 2x + 8(-1) = -2 \rightarrow x = +3$

So each **Re^{3+}** ion has a **$5d^4$** configuration.

Re: $[Xe]\ 4f^{14}\ 5d^5\ 6s^2 \rightarrow Re^{3+}: 5d^4$

Thus, two Re^{3+} centers together contribute **8 d-electrons** to the metal–metal bond.

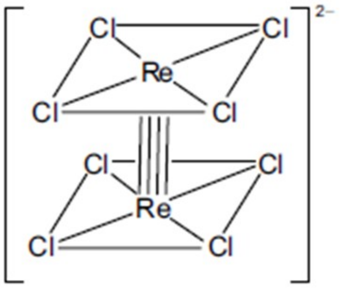
3.2.2 Structure of $[Re_2Cl_8]^{2-}$

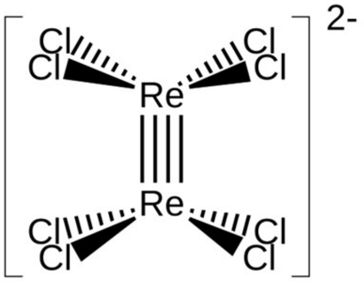
The structure of this complex possesses two unusual features.

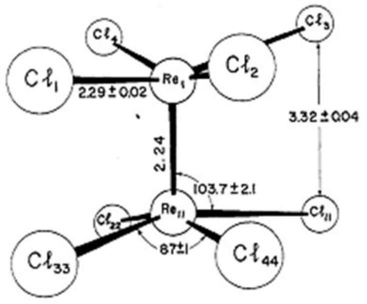
(a). Re-Re distance is found to be extremely short (about 224 pm) when compared to Re-Re distance in Rhenium metal (275 pm).

(b). The chloride atoms are in eclipsed configuration. These two unusual features wer explained by *Cotton et.al* through a quadrupole bond.

The complex consists of two **$ReCl_4$ units** joined by a **direct Re–Re bond**. Each **Re atom** is **octahedrally coordinated**, surrounded by four **equatorial bridging Cl^- ligands** and two **terminal Cl^- ligands** (one on each Re). The **Re_2Cl_4 core** lies along the molecular axis, and the four bridging chlorides form a **rectangular plane** between the two Re atoms.







Re–Re bond distance: 2.24 Å (very short, indicative of a quadruple bond) **Symmetry:** D_{4h}, **Color:** Red-violet (intense due to metal–metal transitions), **Magnetic nature: Diamagnetic**, since all bonding orbitals are filled.

3.2.3 Bonding of $[Re_2Cl_8]^{2-}$

Total d-electrons:

Each $Re^{3+} = 5d^4$
Total d-electrons = 4 + 4 = **8 d-electrons**

These 8 electrons participate in metal–metal bonding.

The d orbitals of the two Re atoms overlap to form the following molecular orbitals (MOs):

Type of Bond	Orbitals Involved	Number of Bonds	Contribution
σ bond	Head-on overlap of d_z^2 orbitals	1	Strongest bond
π bonds (2)	Sidewise overlap of d_xz and d_yz orbitals	2	Intermediate strength
δ bond	Face-to-face overlap of d_xy orbitals	1	Weakest bond but unique to metals

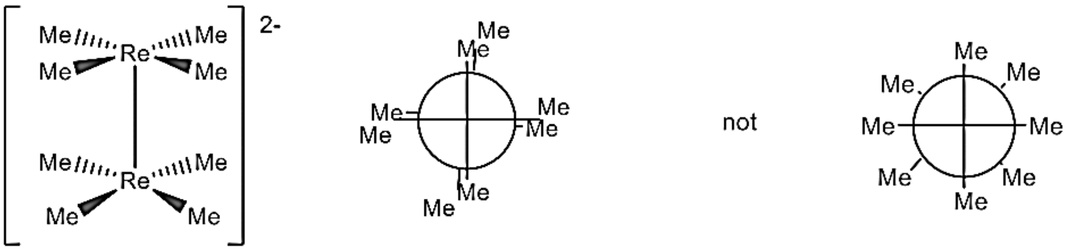
Thus, total = **1σ + 2π + 1δ = 4 bonds**

Hence, the **bond order = 4**, confirming a **quadruple Re–Re bond**.

The Re-Cl bonds are formed by overlapping of dsp^2 hybrid orbitals of each Re with P_z orbitals of chloride. The $d_z{}^2$ and $_{dz}{}^2$ orbitals of each Re lie along the bond axis (z-axis) and undergoes hybridization resulting in the formation of two $d_z{}^2$ hybrid orbitals. Out of these two, one hybrid orbital is directed towards the other Re and can overlaps along the axis resulting in the formation of a σ bond. The remaining hybrid orbitals are directed in opposite direction and forms an approximately non-bonding orbital.

The d_{yz} and d_{zx} orbitals of each Re are directed towards their counter parts on the other Re and can overlap to form two Π bonds one in zx plane and other in yz plane is as follows. The fourth bond is formed by sideways overlap of the remaining two d_{xy} orbitals on each Re resulting in the formation of δ bond. The overlap of d_{xy}-d_{xy} orbitals can only occur of the chlorine atoms are staggered the two d_{xy} orbitals be staggered with resulting zero overlap is as follows.

The fourth bond is formed by sideways overlap of the remaining two d_{xy} orbitals on each Re resulting in the formation of δ bond. The overlap of d_{xy}-d_{xy} orbitals can only occur of the chlorine atoms are in eclipsed. If the chlorine atoms are staggered the two dxy orbitals be staggered with resulting zero overlap is as follows.



eclipsed conformation not staggered conformation

Property	Observation	Explanation
Magnetic moment	0 BM (diamagnetic)	All bonding orbitals filled
Color	Deep red or violet	d–d and metal–metal transitions
Re–Re bond length	2.24 Å	Very short, consistent with a quadruple bond
IR spectra	Bridging and terminal Cl bands	Confirm μ_2-Cl bridges

First complex to confirm the presence of a **metal–metal quadruple bond**. Demonstrates **d–d orbital overlap** leading to **σ, π, and δ bonds**. Serves as a **prototype** for understanding **metal–metal interactions** in transition metal chemistry. Important in **cluster chemistry**, **catalysis**, and **metallic bonding theory**.

Feature	$[Re_2Cl_8]^{2-}$
Metal oxidation state	+3

Feature	$[Re_2Cl_8]^{2-}$
d-electron configuration	d^4–d^4
Re–Re bond type	$\sigma + 2\pi + \delta$ (quadruple)
Bond order	4
Geometry	D_4h (two octahedral $ReCl_4$ units)
Magnetic property	Diamagnetic
Re–Re bond length	2.24 Å
Preparation	Reduction of $ReCl_3$ or $ReCl_5$
Color	Red-violet
Example of	M–M multiple bonding (quadruple bond)

3.3 PREPARATION, STRUCTURE, AND BONDING OF THE TRINUCLEAR COMPLEX $[Re_3Cl_9]$

The complex **$[Re_3Cl_9]$** is a **trinuclear rhenium chloride cluster**, notable for its **metal–metal bonding**. It contains a **triangular array of three rhenium atoms**, each surrounded by **six chloride ligands** (a mix of bridging and terminal). This compound demonstrates how **metal–metal bonds** can extend beyond dinuclear systems (like $[Re_2Cl_8]^{2-}$) into **trinuclear cluster frameworks**.

3.3.1 Preparation of $[Re_3Cl_9]$

$[Re_3Cl_9]$ can be prepared by several methods, most commonly through **thermal decomposition** or **controlled oxidation–reduction** reactions of lower chlorides of rhenium. Heating **rhenium(III) chloride** in an inert atmosphere (N_2 or Ar) leads to trimerization and formation of **Re–Re bonds**. In both routes, **Re(III)** is the oxidation state in the product.

$$3ReCl_3 \xrightarrow{\Delta} Re_3Cl_9$$

$$3[Re_2Cl_8]^{2-} + \text{Oxidant} \longrightarrow 2[Re_3Cl_9] + Cl^-$$

Let the oxidation state of Re be **x** in $[Re_3Cl_9]$:

$3x + 9(-1) = 0,\ x = +3$

Thus, each **rhenium atom is in the +3 oxidation state**.

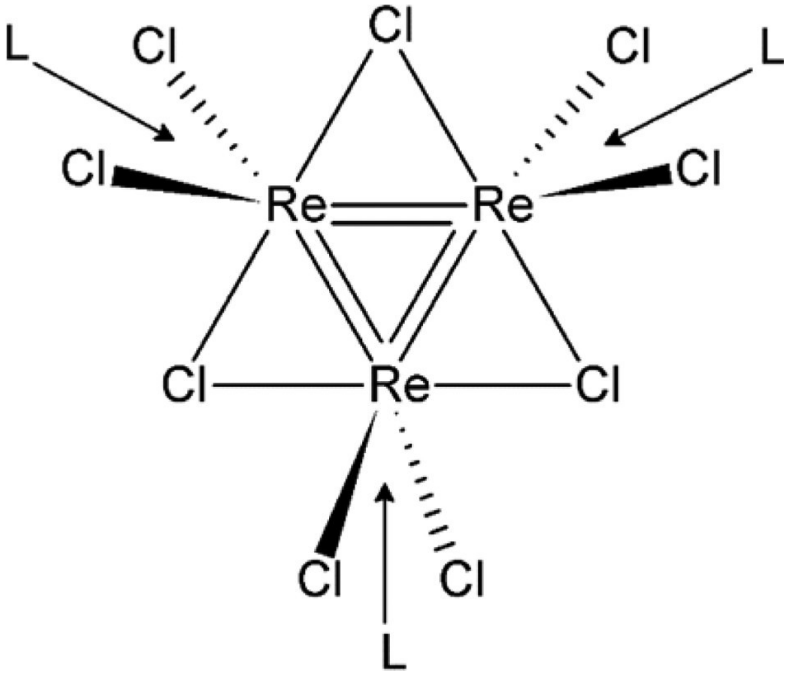
Re: $[Xe]4f^{14}\,5d^5\,6s^2 \rightarrow Re^{3+} \rightarrow 5d^4$

Each rhenium has a **d^4 configuration**, meaning a total of **12 d-electrons** (3 × 4) are available for **metal–metal bonding**.

3.3.2 Structure of [Re_3Cl_9]

Metal–Metal Bonds, The three rhenium atoms form an **equilateral triangle** connected by **three Re–Re single bonds**. The **Re–Re bond length** ≈ **2.48 Å**, consistent with a **single M–M bond**. **Bonding in [Re_3Cl_9]. Metal–Ligand Bonding,** Each Re(III) center is surrounded by: Two **terminal Cl ligands** (σ-donors), Two **bridging Cl ligands** shared with neighboring Re atoms. **Metal–Metal Bonding,** Each Re has a **d^4 configuration**, contributing electrons for metal–metal interactions. Total valence d-electrons = $3 \times 4 = 12\ e^-$. Each Re–Re edge utilizes **two electrons**, forming **three Re–Re single bonds**. **Bond Type is** Each Re–Re bond is primarily a **σ-type d–d overlap**. Delocalization across the Re_3 triangle also gives rise to **3-center–2-electron bonding**, stabilizing the triangular cluster.

3.3.3 Bonding of [Re_3Cl_9]



Feature	Description
Formula	[Re_3Cl_9]
Oxidation state of Re	+3
Electronic configuration	d^4 for each Re
Geometry	Triangular Re_3 cluster
Coordination number (per Re)	6 (octahedral)
Ligand types	2 terminal + 2 bridging Cl per Re
Metal–metal bonds	3 Re–Re single bonds forming Re_3 triangle

Feature	Description
Bond order per Re–Re link	1
Symmetry	D_3h

3.4 PREPARATION, STRUCTURE, AND BONDING OF TETRANUCLEAR TUNGSTEN OXO CLUSTER – $[W_4O_{16}]$

$[W_4O_{16}]$ is a **tetranuclear metal-oxo cluster** containing **four tungsten atoms** linked together by **bridging oxide ligands (μ-O)**. It is a well-known example of a **tetranuclear metal cluster** with **W–W metal–metal interactions** mediated by oxo bridges. **Chemical formula:** $[W_4O_{16}]$, **Metal oxidation state:** +6 for each W, **Ligands:** All **oxide ions (O^{2-})** — terminal and bridging.

Total charge = 4(+6) + 16(-2) = -8 →$[W_4O_{16}]^{8-}$, Hence, the anionic species is **$[W_4O_{16}]^{8-}$**.

3.4.1 Preparation of $[W_4O_{16}]$

(a) From Tungstate Salts (Condensation Route): This occurs under **acidic conditions**, where four **$[WO_4]^{2-}$ tetrahedra** condense by **elimination of water** to form the **tetranuclear cluster**. **(b) From Tungsten(VI) Chloride (Hydrolysis Route):** Controlled hydrolysis of WCl_6 or $W(OEt)_6$ can yield **W_4O_{16}** or its solvated derivatives.

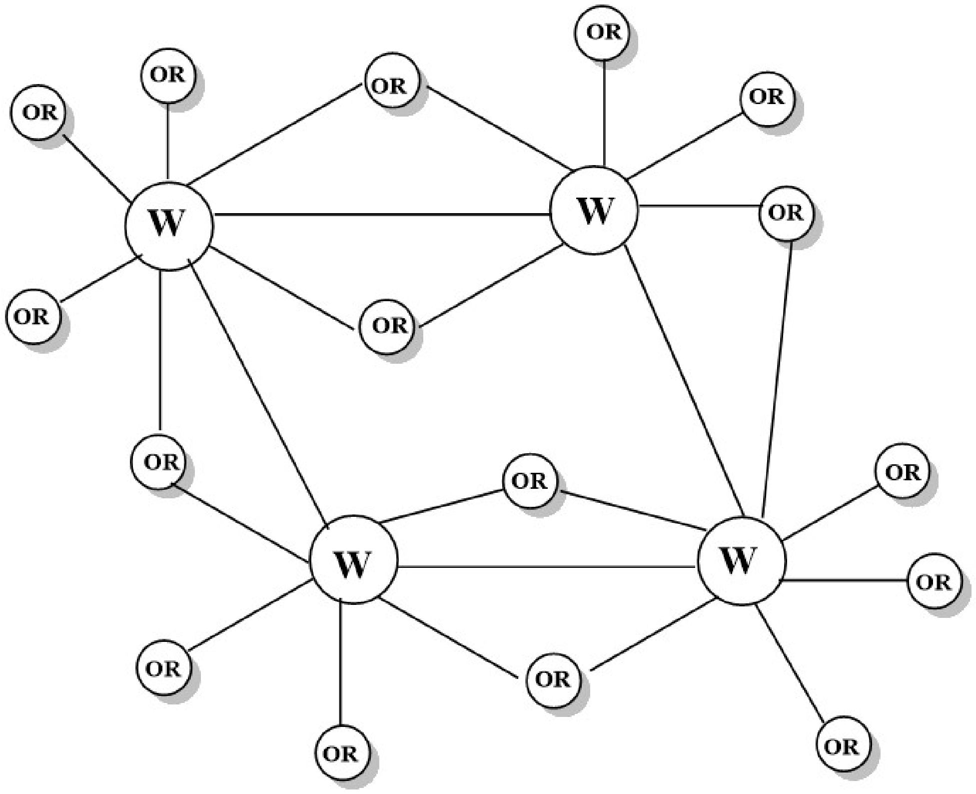
$$\text{(a)}\quad 4[WO_4]^{2-} + 2H^+ \longrightarrow [W_4O_{16}]^{8-} + H_2O$$

$$\text{(b)}\quad 4WCl_6 + 8H_2O \longrightarrow [W_4O_{16}] + 24HCl$$

3.4.2 Structure of $[W_4O_{16}]$

The four tungsten atoms form a **tetrahedral arrangement** (W_4 core). The cluster has **μ_2-oxo bridges** (each oxygen bridges two tungsten atoms). No terminal oxo ligands are present in the idealized $[W_4O_{16}]^{8-}$ anion — every oxygen acts as a **bridging ligand**. Each W atom is **octahedrally coordinated** by oxygen atoms: Four oxygens are **bridging (μ_2-O)**, shared with adjacent W atoms. Two oxygens are **terminal (W=O)** in some formulations. The resulting structure may be described as a **face-sharing array of WO_6 octahedra**, forming a **W_4O_{16} cage-like framework**. The cluster possesses **T_d (tetrahedral)** or **D_2d** symmetry depending on crystallization and ligand distribution.

3.4.3 Bonding of $[W_4O_{16}]$



Metal–Oxygen Bonding, Bridging μ_2-O ligands form **W–O–W linkages**, delocalizing electron density across the cluster. **W=O bonds** (terminal) are short and strong (~1.7 Å), while **W–O(μ)** are slightly longer (~1.9–2.0 Å). The bonding involves **π donation from O 2p orbitals to empty W 5d orbitals** (π-backbonding minimal since W(VI) is d^0). There are **no direct W–W bonds** (each W(VI) is d^0 → no d–d overlap possible). However, **indirect metal–metal interactions** occur through the **bridging oxygens**, giving the cluster a **delocalized 3-center–2-electron (3c–2e)** bonding network. Each W(VI) center is **d^0**, so the cluster is stabilized purely by **W–O σ and π bonding** with the oxide ligands.

Feature	Description
Formula	$[W_4O_{16}]^{8-}$
Oxidation state (W)	+6
Electronic configuration (W^{6+})	d^0
Core geometry	Tetrahedral (W_4 core)
Coordination	Each W is octahedral (WO_6)
Ligand type	Oxide (μ_2-O bridges + possible terminal O)
Metal–metal bonding	Indirect via μ-O bridges (no direct W–W)
Symmetry	T_d or D_2d
Magnetism	Diamagnetic (all d^0)
Color	White to pale yellow
Bonding type	Delocalized W–O network (3c–2e bonds)

3.5 PREPARATION, STRUCTURE, BONDING, AND PROPERTIES OF HEXANUCLEAR CLUSTER $[Mo_6Cl_8]^{4+}$,

The **$[Mo_6Cl_8]^{4+}$** ion is one of the most well-known **octahedral metal cluster compounds**, consisting of **six molybdenum atoms** surrounded by **eight bridging chloride ligands**. It is the **parent cluster ion** for a large family of **molybdenum halide and chalcogenide clusters** and serves as a **prototype** for understanding **metal–metal bonding** in **high-nuclearity transition-metal clusters**.

Component	Quantity	Role
Mo atoms	6	Form the metal core
Cl ligands	8	Form μ_3-bridges between metal atoms
Charge	+4	Cluster cation $[Mo_6Cl_8]^{4+}$

Each Mo atom is octahedrally coordinated by **4 other Mo atoms** and **4 Cl atoms**.

Let the oxidation state of Mo = x

$6x + 8(-1) = +4 \rightarrow 6x = +12 \rightarrow x = +2$

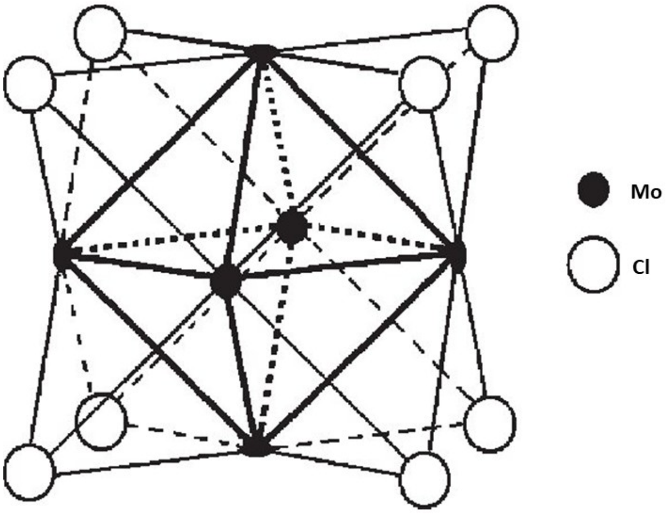
So, each **Mo atom is in the +2 oxidation state.** Atomic number of Mo = 42, Electronic configuration of Mo: $[Kr]4d^5 5s^1$, For $Mo^{2+} \rightarrow [Kr]4d^4$. Each Mo^{2+} contributes **4 d-electrons**, hence the cluster has: 6 x 4 = 24 d-electrons. These 24 electrons are responsible for **metal–metal bonding** within the Mo_6 octahedron.

3.5.1 Preparation of $[Mo_6Cl_8]^{4+}$

$[Mo_6Cl_8]^{4+}$ cluster cations are generally obtained from **reduction of molybdenum(V) chlorides** under high temperature. **Reducing agent:** $SnCl_2$ (reduces Mo^{5+} to Mo^{2+}), **Product:** $[Mo_6Cl_8]Cl_4$ (which contains the $[Mo_6Cl_8]^{4+}$ cation)

$$6MoCl_5 + 4SnCl_2 \xrightarrow{\Delta} [Mo_6Cl_8]Cl_4 + 4SnCl_2$$

3.5.2 Structure of $[Mo_6Cl_8]^{4+}$



Metal Core, The six Mo atoms form an **octahedral cluster (Mo_6 core)**. Each Mo is bonded to **four neighboring Mo atoms** (M–M bonding) and to **four μ_3-Cl ligands**. **Ligand Arrangement.** The eight Cl atoms occupy the **corners of a cube**, which **encloses the Mo_6 octahedron**. Each Cl bridges **three Mo atoms (μ_3-Cl)**. The complex has **O_h symmetry**.

3.5.3 Bonding of $[Mo_6Cl_8]^{4+}$

Metal–Metal Bonding, Each Mo^{2+} (d^4) participates in **delocalized metal–metal bonding** within the Mo_6 octahedron. The 24 cluster valence electrons occupy **molecular orbitals derived from Mo–Mo interactions**. **Molecular Orbital (MO) Scheme,** For an **octahedral M_6 cluster**, metal–metal bonding MOs are classified as:

Type	Symmetry	Degeneracy	Bonding Character
a_1g	Non-degenerate	1	σ bonding
t_1u	Triply degenerate	3	π bonding
e_g	Doubly degenerate	2	δ bonding

Total of **6 bonding orbitals**, which can hold **12 electron pairs (24 e^-)**. Since $[Mo_6Cl_8]^{4+}$ has **24 cluster electrons**, all these orbitals are **completely filled**, giving **maximum bonding stability**.

Parameter	Description
Core geometry	Octahedral (Mo_6)
Ligand geometry	Cubic (Cl_8)
Overall symmetry	O_h
Mo–Mo distance	~2.60 Å (short, indicative of bonding)
Mo oxidation state	+2
Mo coordination	8-coordinate (4 Mo + 4 Cl)
Bridging type	μ_3-Cl (each Cl bridges 3 Mo)

Parameter	Description
Color	Green to orange (depends on ligand environment)
Magnetic property	Diamagnetic (all bonding MOs filled)

3.6 SUMMARY

- To know the M-M multiple bonding.
- To study about the Di nuclear cluster of $[Re_2Cl_8]^{2-}$.
- To know about the tri and hexa nuclear clusters.

3.7 TECHNICAL TERMS

Metal-Metal bonding, Di nuclear, Tri nuclear, Tetra nuclear, Hexa nuclear

3.8 SELF ASSESSMENT QUESTIONS:

1. Write short notes on M-M multiple Bonding.
2. Explain the preparation, structure and properties of di nuclear clusters.
3. Write the preparation, structure and properties of Tetra nuclear clusters.
4. Write the preparation, structure and properties of Hexa nuclear clusters.

3.9 REFERENCE BOOKS:

1. Inorganic Chemistry Huheey, Harper and Row.
2. Physical methods in Inorganic Chemistry, R.S. Drago. Affiliated East-West Pvt. Ltd.
3. Concise Inorganic Chemistry, J. D. Lee, ELBS.
4. Modern Inorganic Chemistry, W. L. Jolly, McGrawHill.
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10. Advanced Inorganic Chemistry, Cotton and Wilkinson, Wiley Eastern.
11. Quantum Chemistry, R. K. Prasad.
12. Concise Coordination Chemistry, R.Gopalan and V.Ramalingam.

Dr. K. Krishnadevi

LESSON-4

METAL Π COMPLEXES

4.0 OBJECTIVES:

After studying this lesson, you should be able to :

- To know the Zintle and Chevrel phase.
- To study about the Nitrosyl complexes.
- To know about the Dinitrogen complexes.
- To know about the Dioxygen complexes.

STRUCTURE:

4.1 INTRODUCTION

4.1.1 ZINTLE PHASE

Zintle phases are ionic compounds formed from an electropositive metal and a main group anionic component, resulting in polyanionic or polycationic clusters. Homo polyatomic (Zintle) ions are devoid of ligands and they are sometimes referred to as naked clusters.

Earlier it was known that the most transition metals dissolve in liquid NH_3 in the presence of alkali metals to give highly coloured ions. In the 1930's polyatomic anions such as Sn_9^{-4}, Pb_7^{4-}, Pb_9^{4-}, Sb_7^{3-} and Bi_3^{3-} were identified but not structurally characterized because crystals were decomposed in solution. So, it is difficult to isolate and characterized. Later, it overcomes at 1975, the crystals were stabilized by the cation of the salt as a cryptate. Eg. $[Na(crypt)_2Pb_5]$ and $[Na(crypt)_4Sn_9]$. This reduces the tendency of the salt to convert to a metal alloy, structure of ions is as follows. Salts of Zintle cations such as Bi_9^{3+} and Tl_6^{4+} are obtained from metals and stabilized by large weakly basic anions such as $AlCl_4$.

$$\mathbf{Bi + BiCl_3 + AlCl_3\ (excess) \longrightarrow Bi_5(AlCl_4)_3}$$

In general, there is good correlation between electronic structure and geometry as predicted by wade's rule for these clusters though some exceptions are known for Bi_9^{5+} and Sn_9^{4+} are iso electronic but they have different structures.

4.1.2 CHEVREL PHASE

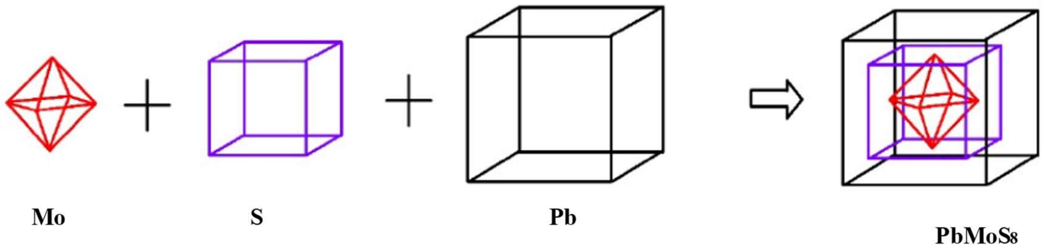
A class of ternary metal chalcogenide clusters with a general formula of MX_6Y_8), where M is a metal, X is a chalcogen (like S, Se), and Y is an anion (like S). chevrel phase have both unusual structures and interesting electrical and magnetic properties and those compounds often called as chevrel phase. **Chevrel phases** are **solid-state cluster compounds** composed of **transition metal chalcogenides** with a general formula: Named after **R. Chevrel**, who first discovered these compounds in the early 1970s.

$$\mathbf{M_xMo_6X_8}$$

where

- **M** = metal cation (Cu, Ag, Pb, Sn, etc.)
- **Mo** = molybdenum
- **X** = chalcogen (S, Se, Te)

Eg. $PbMo_6S_8$, which is a super conductor at temperature below 13.3 K. The structure may be thought of as an octahedral cluster of Mo atoms surrounded by a cubic cluster of sulphur atoms, which in turn is surrounded by a cubic lattice of lead atoms. The super conductivity is thought to be dependent upon the overlap of the d-orbitals on Mo and this property is tuneable by appropriate choice of metals.



4.2 APPLICATIONS OF CLUSTERS IN CATALYSIS

Metal clusters = compounds with **two or more metal atoms** bonded together. They act as **catalysts** because: They have **many active metal centers**. Can **activate molecules like H_2, CO, N_2** easily. Behave like **mini-models of metal surfaces**. Clusters are good catalyst because. **Many metal atoms** → cooperate during reactions. **Flexible oxidation states** → help in redox reactions. **Delocalized electrons** → easy bond breaking/forming. **Ligands** (like CO, phosphines) stabilize the active site.

4.2.1 Important Cluster Catalysts and Their Uses

Cluster Catalyst	Reaction Catalyzed	Product / Use
$[H_4Ru_4(CO)_{12}]$	Hydrogenation	Converts alkenes → alkanes
$Rh_6(CO)_{16}$	Hydroformylation	Alkene + CO + H_2 → Aldehyde
$Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$	Fischer–Tropsch	$CO + H_2 \rightarrow$ Hydrocarbons
$Fe_3(CO)_{12}$	Water–gas shift	$CO + H_2O \rightarrow CO_2 + H_2$
$MoFe_3S_4$ (Nitrogenase model)	Nitrogen fixation	$N_2 \rightarrow NH_3$
Mo_6S_8 (Chevrel phase)	Hydrodesulfurization	Removes sulfur from fuels

4.2.2 Types of Cluster Catalysts

1. **Homogeneous clusters:** soluble in reaction medium. → e.g. $[H_4Ru_4(CO)_{12}]$, $Rh_6(CO)_{16}$.
2. **Supported clusters:** attached to solid support (SiO_2, Al_2O_3). → More stable, reusable.
3. **Heterogeneous clusters:** solid catalysts; model for metal surfaces.

4.2.3 Advantages

- Work under mild conditions. High **selectivity and efficiency**. Act as **models** for understanding real metal surface catalysis.

4.3 METAL π-COMPLEXES:

Metal Nitrosyls: Metal nitrosyls are co-ordination compounds in which nitric oxide (NO) molecule is attached as NO^+ ion to metal atom (or) ion, in these compounds the attachment of NO^+ (Nitrosonium) to the metal atom takes place through 'N' atom. (or) The Co-ordination compounds of transition metals containing NO^+ as ligand are called metal nitrosyls.

4.3.1 CLASSIFICATION:

4.3.1.1. Linear nitrosyl ligand complexes: If the nitrosyl ligand is attached to metal in a linear manner are called as linear ligand complexes.

$$M\text{-}N^+\equiv O$$

Preparation: These are prepared by the action of NO^+ on metal at 95°C.

$$Fe(CO)_5 + 2\ NO \rightarrow Fe(CO)_2(NO)_2 + 3\ CO$$

$$Co_2(CO)_8 + 2\ NO \rightarrow 2\ Co(CO)_3(NO)_2 + 2\ CO$$

4.3.1.2. Bent nitrosyl ligand complexes:

If the nitrosyl ligand is attached to the metal in a bent manner are called bent nitrosyl ligand complexes.

Preparation:

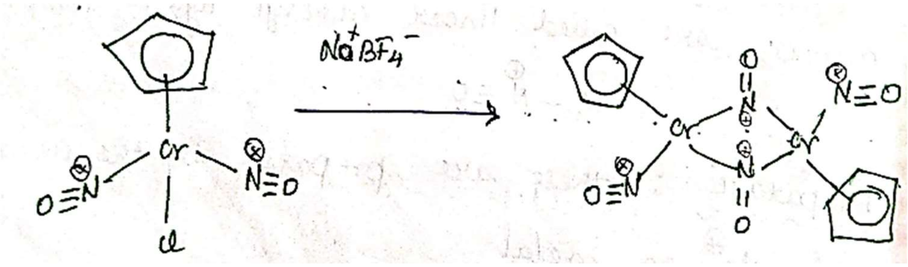
These are prepared from Vaska's complex

$$[IrCl(CO)(PPh_3)_2] + NO^+BF_4^- \rightarrow [IrCl(CO)(NO)(PPh_3)_2]$$

4.3.1.3. Bridging Nitrosyl ligand complexes:

If the nitrosyl nligand acts as a bridge between two metal atoms and ions are called bridging nitrosyl ligand complexes.

Preparation:



4.4 PROPERTIES OF NITROSYL COMPLEXES:

Substitution Reaction: When the metal carbonyls and nitrosyls are treated with ligands like PR_3, CNR etc., only 'CO' groups are replaced by these ligands. Because NO^+ ions are firmly attached with metal ion than 'CO' groups.

$$Fe(CO)_2(NO)_2] + 2\,L\ (L = PR_3,\ CNR) \rightarrow Fe(L)_2(NO)_2 + 2\,CO$$

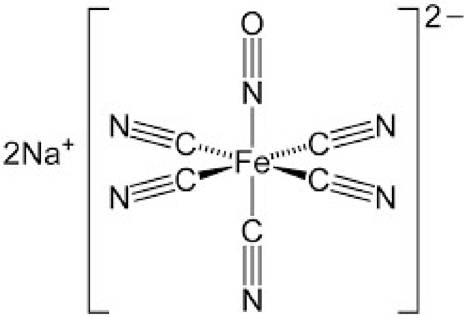
$$Fe(CO)_2(NO)_2] + Phen \rightarrow Fe(Phen)(NO)_2 + 2\,CO$$

Actions of halogens: Metal carbonyls and nitrosyls gives metal nitrosyl halides on treatment with halogens

$$2\,[Fe(CO)_2(NO)_2] + I_2 \rightarrow [Fe(NO)_2I]_2 + 4\,CO$$

Examples for metal nitrosyls: Some important examples are sodium nitroprusside $Na_2[Fe^{2+(}CN)_5(NO^+)]$ and nitroso sulphate $[Fe^+(NO^+)]SO_4$.

$Na_2[Fe(CN)_5(NO)]$ Sodium nitro pruside:



1. Action of $NaNO_2$ on sodium ferrocyanide:

$Na[Fe^{(}CN)_6] + NaNO_2 + H_2O \rightarrow$ **$Na_2[Fe(CN)_5(NO)] + 2\,NaOH +$**

2. By passing nitric oxide (NO) into 2 NaCN and acidified solution of $Na_4[Fe(CN)_6]$.

$Na_4[Fe(CN)_6] + H_2SO_4 + 3\ NO \rightarrow 2\ Na_2[Fe(NO)(CN)_5] + 2\ NaCN + \frac{1}{2}\ H_2 + H_2O$

4.4.1 Properties of Nitrosyl Complexes:

- When freshly prepared sodium nitro preside is added to a solution containing sulphide ion i.e., Na_2S, a purple (or) violet colour is produced. It is due to formation of $Na_4[Fe(CN)_5(NO)S]$.

  $Na_2S + Na_2[Fe(CN)_5(NO)] \rightarrow Na_4[Fe(CN)_5(NO)S]$ Violet/Purple colour

  This test is used to confirm the presence of S^{2-} ion in a given mixture.

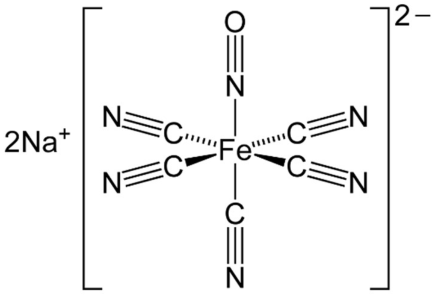
- Alkali sulphates give a rose red colour due to formation of $Na_4[Fe(CN)_5(NO)SO_3]$.

  $Na_2SO_3 + Na_2[Fe(CN)_5(NO)] \rightarrow Na_4[Fe(CN)_5(NO)SO_3]$

  This test is used to distinguish sulphides $(SO_3)^{2-}$ from thiosulphates $(SO_4)^{2-}$

- $[Fe(CN)_5(NO)]^{2-}$ ion has diamagnetic character. It confirms that 'NO' is present as NO^+ ion in the complex ion.

4.4.2 Structure of Nitrosyl Complexes: $[Fe(CN)_5(NO)]^{2-}$ ion has octahedral structure with Fe+2 ion located at the centre of octahedron. The 'NO' groups acquire one positive charge and gets co-ordinated to GFe_{2+} ion as NO^+ radical. This view is supported by the fact that $Na_2[Fe(CN)_5NO]^{-2}$ is diamagnetic, where as $K_3[Fe(CN)_6]$ is paramagnetic. Thus in $[Fe(CN)_5NO]^{-2}$ there are total 3 positive charges (Fe = +2, NO = +1) and 5 negative charges (CN^-).



Uses: It is used as a reagent in qualitative analysis for the detection of sulphites, aldehyde and ketones.

4.5 Di-Nitrogen Complexes:

Molecular nitrogen 'N_2' is isoelectronic with both CO and NO^+ formed many years it proved to be impossible to form complexes of dinitrogen. This difference in behavior was usually due to the lack of polarity of N_2 and resultant inability to behave as a π-acceptor.

Dinitrogen complexes are co-ordination compounds in which N_2 molecule is attached to the metal atom or ion.

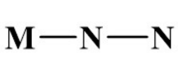
$$RuCl_3 \cdot xH_2O \xrightarrow[Zn/Hg]{NH_3} [Ru(NH_3)_5H_2O]^{2+} \xrightarrow[N_2, 0\text{–}5^\circ C]{} [Ru(NH_3)_5N_2]^{3+}$$

Due to strong nucleophilicity of N_2 shown by its displacement of water in above reaction bridged complexes are formed.

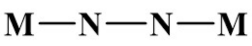
$$[Ru(NH_3)_5N_2]^{3+} + [Ru(NH_3)_5H_2O]^{3+} \rightarrow [Ru(NH_3)_5N_2Ru(NH_3)_5]^{4+}\ H_2O$$

4.5.1 Structure and bonding:

The structural possibilities are

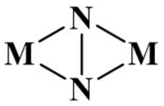


End-on-terminal



End-on bridging

Side-on terminal

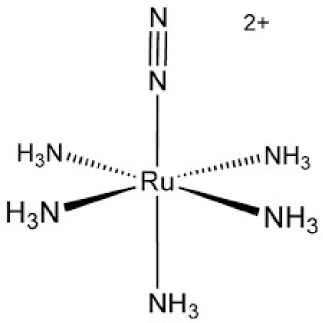


Side-on bridging

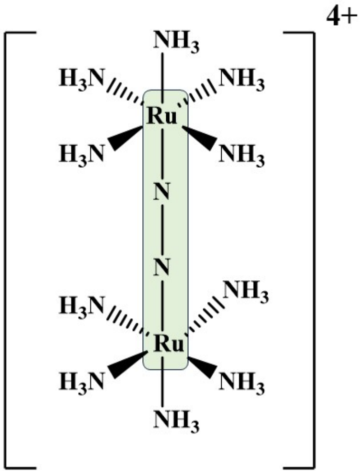
Ex: **For end-on terminal**

X-ray study of original ruthenium dinitrogen complex indicates that the nature of the Ru-N-N linkage was “end-on terminal”.

The Raman spectroscopy frequency for N-N bond in $[Ru(NH_3)_5N_2]Cl_2$ appears at 2105 cm^{-1}.



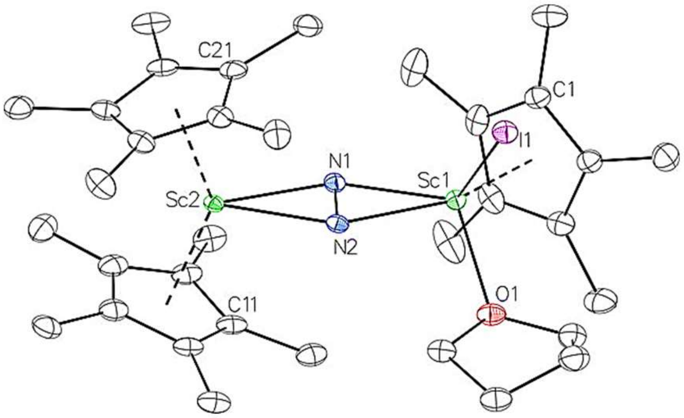
For end-on bridging: When dinitrogen function as a bridging ligand, it usually exhibits end-on co-ordination Ex: Diruthenium complex $[Ru(NH_3)_5N_2Ru(NH_3)_5]^{4+}$.



For Side-on bridging: Sm(η^5-C_5Me_5)$_2N_2$ in this Samarium complex, the two 'Sm' atom and the two nitrogen atoms are in a planar arrangement. The Sm-N bond distance suggest the presence of Sm(II) implying a reduced N-N bond.

The N-N bond distance in free nitrogen (109.8 pm). Its indicates that nitrogen group is in side-on bridging arrangement with two Sm atoms.

Structure:



4.6 Di-oxygen complexes:

The compound which is capable of adding molecular oxygen and giving it up reversibly is called as oxygen carrying compound.

$$\text{Compound} + O_2 \leftrightarrow \text{Compound } O_2$$

Ex: Hemoglobin, Hemocyanin, Hemorythrin

4.6.1 Preparation of Di-oxygen complexes:

1. From Vaska's complex: $[Ir(PPh_3)_2COCl] + O_2 \leftrightarrow [Ir\ COCl\ O_2\ (PPh_3)_2]$

2. From metal complex: $[Pt(PPh_3)_4] + 2\ O_2 \leftrightarrow [Pt(O_2)(PPh_3)_2] + 2\ Ph_3PO$

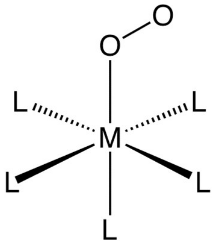
3. From H_2O_2: $CrO_4^{2-} + H_2O_2 + OH^- \leftrightarrow [Cr(O_2)_4^{]3-}$

4. Hb-Hemoglobin $Hb + 4\ O_2 \leftrightarrow Hb(O_2)_4$

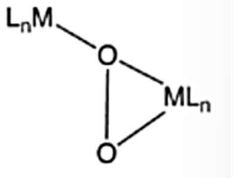
4.6.2 Structure of Di-oxygen complexes:

There are 5 structural types of dioxygen ligands they are

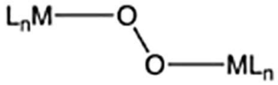
(1:1) End-on terminal (Superoxo)



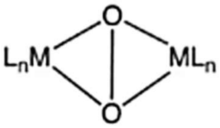
(1:1) Side-on terminal (Peroxo)



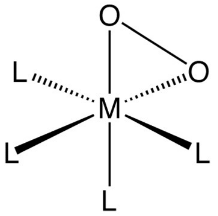
(2:1) End-on bridging (Peroxo)



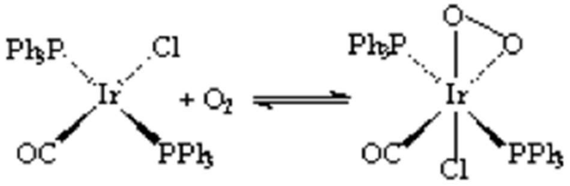
(2:1) Side-on bridging



(4:1)



Ex: For Side-on complexes can be formed from Vaska's complex



4.6.3 Reactions of Dioxygen complexes: (Oxo Heme)

If free Heme in aqueous solution is exposed to dioxygen it is convert immediately into a μ-oxo dimer known known as "Hematin" (here Heme group is symbolized by the circle about on iron atom)

Step 1:

$$Fe^{II} + O_2 \rightarrow Fe^{II}\text{--}O{=}{=}O$$

Step 2: The bound dioxygen can now co-ordinate to a second Heme, forming a μ-peroxo complex.

$$Fe^{II}\text{--}O{=}{=}O + Fe^{II} \rightarrow \underset{\mu\text{-peroxo complex}}{Fe^{II}\text{--}O{=}{=}O\text{--}\ Fe^{II}}$$

Step 3: The peroxo complex will be cleared into two molecules of ferryl complex with the iron in +4 oxidation state.

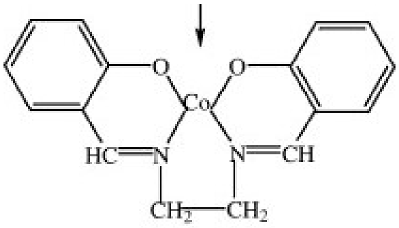
$$Fe^{II}—O—O—Fe^{II} \rightarrow 2\ Fe^{IV}{=}O$$

Step 4: The ferryl complex attarcks on another Heme results in the formation of Hematin.

$$Fe^{IV}{=}O + Fe^{II} \rightarrow Fe^{III}—O—\ Fe^{III}$$

It is clear that, living system have found a way to prevent above reactions otherwise all of the Heme would be precipitated as Hematin rather that carrying di-oxygen molecules in oxyhemoglobin. The globin part of the molecule prevents one oxoheme from attacking another.

Structure of some other dioxygen complexes:



4.7 SUMMARY

- To know the Zintle and Chevrel phase.
- To study about the Nitrosyl complexes.
- To know about the Dinitrogen complexes.
- To know about the Dioxygen complexes.

4.8 TECHNICAL TERMS

Zintle, Chevrel phase, Nitrosyl, Dinitrogen, Dioxygen,

4.9 SELF ASSESSMENT QUESTIONS:

1. Explain the Zintle and Chevrel phase in detail.
2. Explain the preparation, structure and properties of Nitrosyl complexes.
3. Write the preparation, structure and properties of Dinitrogen complexes.
4. Write the preparation, structure and properties of Dioxygen complexes.

4.10 REFERENCE BOOKS:

1. Inorganic Chemistry Huheey, Harper and Row.
2. Physical methods in Inorganic Chemistry, R.S. Drago. Affiliated East-West Pvt. Ltd.
3. Concise Inorganic Chemistry, J. D. Lee, ELBS.
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LESSON - 5

ORGANOMETALIC COMPLEXES OF TRANSITION METALS

5.0 OBJECTIVES

After studying this lesson, you should be able to:

- To know able to the Classification Organometallic complexes
- To study about Electron counting rules ($18e^-$ rules)
- To study about Metallocenes with Five Membered Rings

STRUCTURE

5.1 CLASSIFICATION ORGANOMETALLIC COMPLEXES:

Organometallic complexes containing at least one chemical bond between a carbon atom of an organic molecules and a metal including alkali, alkali earth and transition metals.

Organometallic compounds containing a covalent bond between a carbon atom and a metal.

Classification

1. Organo metallic compounds
2. Organo metalloids
3. Fluxional organometallic compounds
4. Metallocene’s and sandwich compounds.

1. Organo metallic compounds

These are the substance in which a metal π chemical bond to carbon by a linkage which may be either ionic or covalent. In reversal, the more active metal and more reactive organometallic compound derived from it. Since the more active metals are inclined to be cationic where as carbon strongly prefers covalence.

Ex: C_2H_5Li, C_2H_5Mg, $(CH_3)Al$

2. Organo metalloids:

These are alkyl (or) aryl derivatives of silicones, boranes and other elements which are not true metals but which form organic derivative and their contain formal resemblance to organometallic compounds.

Ex: CH_3SiCl_3, $(CH_3)_2SiCl_2$, $C_6H_5SnBr_3$

3. Fluxional organometallic compounds

In these compounds, the actual chemical bond, which cannot be classified as ionic or covalent or as any mixture of the two. The electrons are frequently delocalized. So that we can no longer think of individual metal- carbon bonds.

4. Metallocene's and sandwich compounds.

The metal atoms are sandwiched in between flat hydrocarbon rings in which the entire ring is bonded centro symmetrically to the metal atom by sharing of a cloud of π-electrons and they are named as metallocene's.

Ex: $(C_5H_5)_2Fe$, $(C_6H_6)_2Cr$, $(C_6H_6)_2V$ etc.

Further Classifications are three types.

1. Based on hapticity.
2. Based on composition.
3. Based on position of metal in the periodic table.

I. based on hapticity (η):

The number of carbon atoms of an organic ligand which are directly attached to the metal in an organometallic compound based on their hapticity.

a. Monohapto (η^1) ligands:

Only one carbon atom is directly attached to the metal atom. Ex: alkyl(R), aryl (Ar), -CO.

b. Dihapto (η^2) ligands:

Two carbon atoms are directly attached to the metal atom. Ex: $[PtCl_4C_2H_4]$ K (Zeises salt).

c. Trihapto (η^3) ligands:

Three carbon atoms are closely associated with the metal atom. Ex: $(CO)_4 MnC_3H_5$.

d. Tetrahapto (η^4) ligands:

Four carbon atoms are closely associated with the metal atom. Ex: $C_4H_8Fe\ (CO)_3$.

e. Pentahapto (η^5) ligands:

Five carbon atoms are closely associated with the metal atom. Ex: $Fe\ (\eta^5 C_5H_5)_2$

f. Hexahapto(η^6) ligands:

Six carbon atoms are closely associated with the metal atom. Ex: $Cr(\eta^6 C_6H_6)_2$.

g. Heptahapto (η^7) ligands:

Seven carbon atoms are closely associated with the metal atom.

Ex: $[C_7H_{14}[(CO)_3Mo]]^+\ BF_4^-$

h. Octahapto (η^8) ligands:

Eight carbon atoms are closely associated with the metal atom.

Example: $U\ (\eta^8 C_8H_8)_2$.

II. Based on composition: These are two types.

a. Simple organometallic compound:

Which have only hydrocarbon radical (or) hydrogen atom attached to the metal atom are called simple organometallic compound. Ex:- $(CH_3)_3SnH$.

These are two types: 1. Symmetrical -Ex: $(CH_3)_2Cd$,

2. Unsymmetrical -- Ex: $CH_3ZnCH_2CH_3$

b. Mixed organometallic compound:

In which groups other than hydrocarbon radicals (or) hydrogen atom are also directly attached to the metal atom are called mixed organometallic compounds.

Ex: CH_3MgBr, $(CH_3)_2Sncl_2$.

III. Based on position of metal in the periodic table:

These are two types.

a. Main group organometallic compounds:

The organometallic compounds formed by S-Block & P-block elements are called main group organometallic compounds. Ex:CH_3Li, CH_3MgBr.

b. d- and f-block organometallic compounds:

The organometallic compounds formed by d- and f-block elements are called d- and f block organometallic compounds. Ex: $Fe(\eta^5C_5H_5)_2$, $U(\eta^8C_8H_8)_2$.

5.2. ELECTRON COUNTING RULES (18E$^-$ RULES):

Sidgwick explained the nature of bonding in transition metal complex based on electron count concept. Ligand act as Lewis base and metal ion act as Lewis acid.

Effective Atomic Number (EAN): The sum of the electrons on the central metal atom (or) ion and the electrons donated from the ligands is called the effective atomic number (EAN) of the metal atom and it is equal to the atomic number of noble gases viz 18 (Ar), 36 (Kr),54 (Xe), 86(Rn).

E.A.N = No. of electrons in central metal atom + No. of electron donated by the Ligands +/- charge = Nearest inert gas atomic numbers.

Examples:

1. **$Fe(CO)_5$**

No. of electrons in central metal (Free metal) = 8 ($[Ar]4S^23d^6$)

No. of electron donated by the ligands = 5*2 (10)

Total = 18 [Ar]

2. **$Fe_2(CO)_9$**

No. of electrons in central metal (Free metal) = 8*2 = 16 e$^-$ ($[Ar]4S^23d^6$)

No. of electron donated by the ligands = 9*2 = 18 e$^-$

No. of Fe- Fe bonds are one = 1*2 = 2 e$^-$

Total = 36 [Kr]

$Fe(CO)_5$ and $Fe_2(CO)_9$these complexes are followed $18e^{\theta}$ rules**.** Hence these complexes are stable**.**

3. $Mn_2(CO)_{10}$

No. of electrons in central metal (Free metal) = 7*2 = 14 e^- ([Ar]$4S^2 3d^5$)

No. of electron donated by the ligands = 10*2 = 20 e^-

No. of Mn-Mn bonds are one = 1*2 = 2 e^-

Total = 36 [Kr]

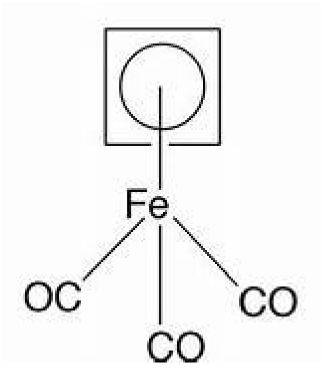
5.3 METALLOCENES WITH FIVE MEMBERED RINGS

Metallocenes are the complexes which contains cyclic π-dinars in which the metal atom is bound between two parallel carboxylic rings. Metallocenes participated in the like that of aromatic molecules. Many of the metallocene complexes obey 18 electron rules.

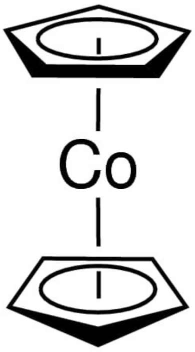
Ex: η^4, η5, η6, η^7 & η^8

1. Cyclobutadienyl complexes (η^4)

Cyclobutadiene is antiaromatic and unstable in free states but it can be stabilize by bonding to a metal atom with suitable electron configuration.



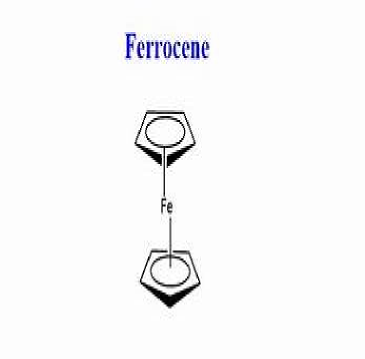
(C_4H_4)Fe(CO_3)

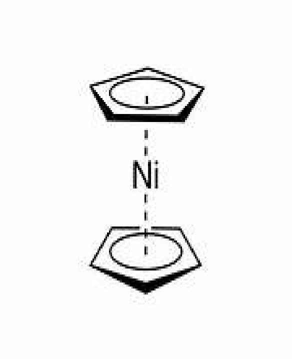


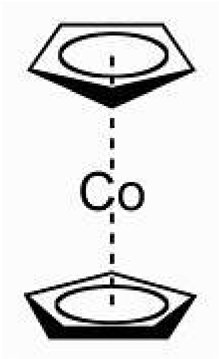
(C_4H_4)Co(C_5H_5)

2. Cyclopentadienyl Complex [$(C_5H_5)_2M$] (η^5)

This complex is the most important in organometallic chemistry. The reaction b/w cyclopenta dienyl anion and suitable derivatives of the transition metals are called metallocene.







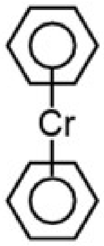
$Fe(\eta^5C_5H_5)_2$, $Ni(\eta^5C_5H_5)_2$, $Co(\eta^5C_5H_5)_2$.

Ferrocene Nickelocene Cobaltocene

Cyclopentadienyl group can act as monohapto (η^1) trihapto (η^3) & pentahapt o(η^5)ligand.

3. Arene complex (or) diazo benzene chromium $[Cr(\eta^6C_6H_6)_2]$:

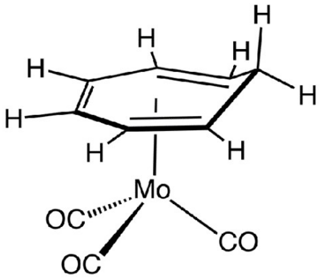
Bis benzene metal complexes are generally called as arene complexes. Benzene and substituted benzenes normally acts as six electron donors.



Dibenzene Chromium

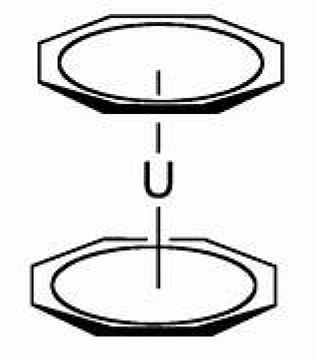
4. Metallocenes with seven membered rings – Cycloheptatriene (η^7):

Cycloheptatrienyl triene is a six-electron donor that can form complexes similar to that of benzene but differ in localization of π- electrons in C_3H_7.



5. Metallocenes with eight membered rings - Cyclooctatetraene: (η⁸)

The best example for this complex is Uranocene. It is a sandwich molecule. In which all C-C bond lengths are equal the bonding in uranocene sis similar to that of ferrocene except that it involves 'f' orbitals of Uranium.



5.4 SUMMARY

- To know about classifications Organometallic complexes
- To study about classification Based on hapticity, based on composition, Based on position of metal in the periodic table.
- To study about Electron counting rules ($18e^-$ rules) for various complexes
- Metallocenes with Five, Six and Seven Membered Rings

5.5 SELF-ASSESSMENT QUESTIONS

1. Write about electronic count rules for $Fe(CO)_5$ and $Mn_2(CO)_{10}$ complexes.
2. Explain the classification of Organometallic complexes.
3. Write the various metallocene's complexes.

5.6 REFERENCE BOOKS

1. Inorganic Chemistry, Huheey. Harper and Row.
2. Concise Inorganic Chemistry, J. D. Lee, ELBS.
3. Inorganic chemistry, K.F. Purcell and J.C. Kotz, Holt Saunders international
4. Organometallic chemistry, R.C. Mehrotra and A. Singh. New Age International

Prof. K. Rambabu

LESSON - 6

SYNTHESIS, STRUCTURE AND BONDING OF FERROCENE, CYCLOPENTA DIENYL, ARENE, CYCLOHEPTA TRIENE AND TROPYLIUM COMPLEXES OF TRANSITION METALS

6.0 OBJECTIVES

- To know about ferrocene, the synthesis of ferrocene.
- To Knowledge on the structure and bonding in ferrocene.
- Apply the 18-electron rule for Ferrocene and properties and stability of ferrocene.
- To study about Arene complex (or) diazo benzene chromium $[Cr(\eta^6C_6H_6)_2$ complexes
- To knowledge about on Metallocenes with seven membered rings – Cycloheptatriene.
- To know about Tropylium cation complex structure**.**

STRUCTURE

6.1 CYCLOPENTA DIENYL COMPLEXES OF TRANSITION METAL COMPLEXES

Ferrocene ($Fe(\eta^5C_5H_5)_2$)

Ferrocene is the most important metallocene. It is highly stable and decomposes above 500 °C.

Preparation (or) Synthesis:

1. Metal halides on treatment with sodium cyclopentadiene then formed product is cyclopentadieny1 complex [ferrocene].
2. Metal halides on treatment with Grignard reagent.

Structure:

In ferrocen molecule, iron atom is present b/w two paraiiei and planer cyclopentadinyl rings.The following two important conformers of ferrocen.

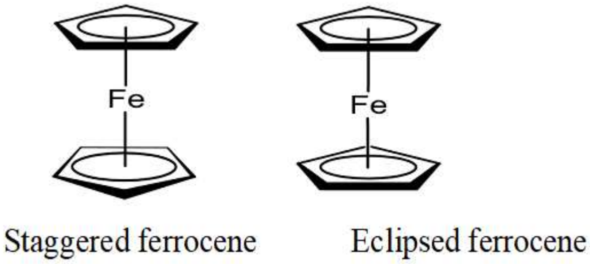
1. Staggered ferrocene
2. Eclipsed ferrocene

Staggered – Ferrocene:

It is crystalline substance X-ray diffraction method explained by this structure. Two cyclopentadieny1 rings are staggered conformation. Point group is D_5d (**Figure 6.1**).

Eclipsed – Ferrocene:

It is gas phase structure. Electro diffraction method explained by this structure. Two cyclopentadieny1 rings are eclipsed conformation. Point group is D_5h (**Figure 5.1**).



Staggered ferrocene Eclipsed ferrocene

Figure 6.1: Staggered and Eclipsed forms of Ferrocene

Bonding:

Each carbon atom of the cyclic & planar C_5H_5 group is sp^2 hybridisation. Valency electronic configuration of 'C' atom in C_5H_5 ring is $2S^1$, $2P_x^1$, $2P_y^1$ and $2P_z^1$. Hybridised orbitals are S, P_x and P_y and P_z is unhybridized. Each carbon atom forms three sigma bonds, one with H atom and two with adjacent c atom [These three bonds only [S, P_x, P_y] hybridised orbital]. Unhybridized singly occupied $2P_z$ atomic orbital remains unused on each carbon atom which is perpendicular to the plane C_5H_5 ring i.e. XY-plane. This five singly occupied and parallel $2P_z$ atomic orbital of the cyclopentadienyl (C_5H_5) ring take part in linear combination producing five π MO's as following ψ_1, ψ_2, ψ_3, ψ_4, ψ_5 (**Figure 6.2**).

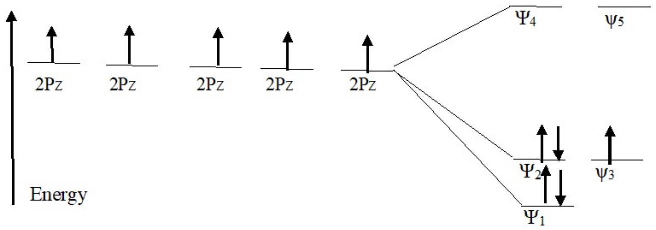


Figure 6.2: Electron distribution of C_5H_5

ψ_1 is the lowest energy that has no nodal plane and this MO is designated as “a” & strongly BMO’s. ψ_2 and ψ_3 are the slightly high energy than ψ_1 and it has one nodal plane and this BMO is designated as ‘e^1’& weakly bonding MO’s. ψ_4 and ψ_5 are the two nodal plane and high energy than ψ_1, ψ_2 and ψ_3 and this anti bonding MO’s designated as ‘e^2’ (**Figure 6.3**).

The five π MO’s of one cyclopentadienyl ring interact with five π MO’s of the other cyclopentadienyl ring of ferrocene molecule to produced 10 ligand group orbitals (LGO’s). based upon LGO’s these combinations are divided into two labelled gerade & ungerade.

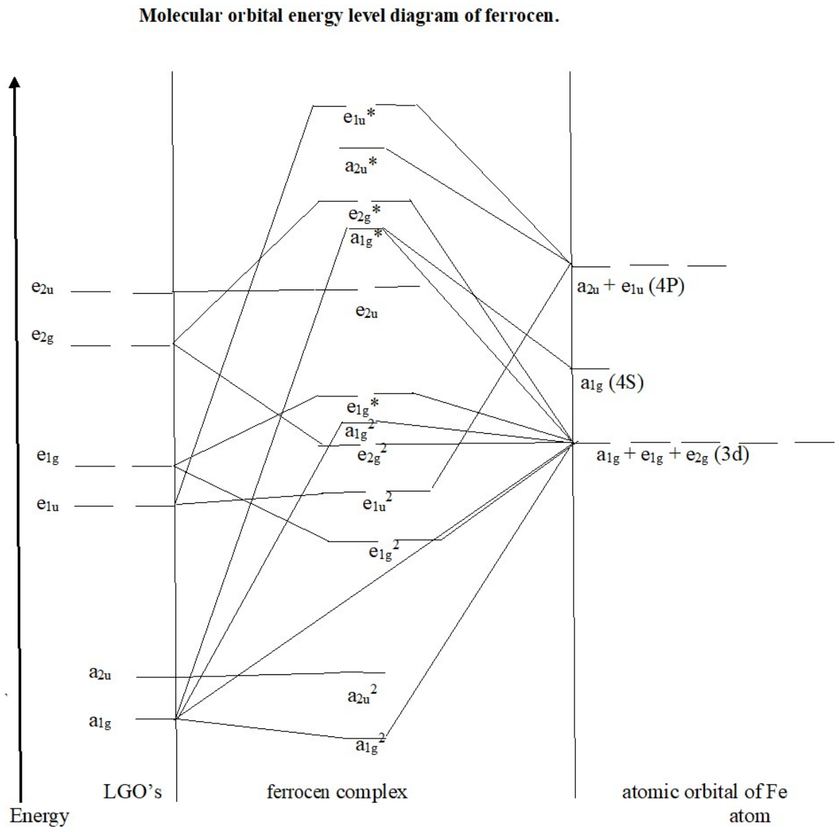


Figure 6.3: Energy level diagram of Ferrocene

Gerade LGO’s having centre of symmetry (i). Ungerade LGO’s having no centre of symmetry.

Let us take ψ_1 (or) a, this orbital has no nodal plane & perpendicular to the ring. It the wave function of this orbital on ring number one& on ring number two are written with the same sign. To produce LGO “a_{1g}”. If the wave functions are written with opposite signs to produce LGO a_{24}. Hence ψ_1(a) splitting in to a_{2u} and a_{1g}. Similarly, other LGO’s are produced following manner. ψ_2 and ψ_3(e_1) splitting in to e_{1g} and e_{1u}. ψ_4 and ψ_5 (e_1) splitting in to e_{2g} and e_{2u}.The LGO’s of two cyclopentadienyl (C_5H_5) rings and the AO’s of the iron atom with matching symmetry for ferrocene are given below. Valence orbitals of iron atom 4S, 4P, 3d. This orbital splitting terms are following.4S = a_{1g};$4P_z = a_{2u}$;$4P_x = 4P_z = e_{1u}$;$3d_{xy} = 3d_{x^2-y^2} = e_{2g}$; $3d_{xz} = 3d_{yz} = e_{1g}$. So, MO diagram explains bond b/w Fe atom and LGO's of two cyclopentadienyl (C_5H_5) rings.

Ferrocene followed 18 electron rule.

No of electrons present on two C_5H_5 rings = 2 x 5 = 10
No of electrons present on Fe atom = 8
Total = 18.

6.2 ARENE COMPLEX (OR) DIAZO BENZENE CHROMIUM [$Cr(\eta^6C_6H_6)_2$]:

Preparation (or) Synthesis:

The condensation of vapour of a metal in the presence of benzene produces η^6-arene complex.

$$M(s) \rightarrow M(g) + C_6H_6 \rightarrow [M(\eta^6C_6H_6)_2] \text{ [where M = Cr, Mo \& W]}$$

Structure

The various diffraction methods such as X-diffraction, Neutron diffraction, Electron diffraction studies on η^6-arene complex. Suggest that Cr atom is sandwiched b/w two planar and parallel benzene rings which are eclipsed conformation **(Figure 6.4)**. Point group exits as D_{6h}.Cr-C distance = 2.15A^0, C-H distance = 1.11 A^0, C-C distance = 1.39 A^0, interring distance = 3.23A^o.

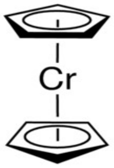


Figure 6.4: Diazo benzene chromium [$Cr(\eta^6C_6H_6)_2$]

Bonding:

Each carbon atom of the cyclic & planar C_6H_6 group is sp^2 hybridisation. Valency electron configuration of 'c' atom in C_6H_6 ring is $2S^1$,$2P_x^1$,$2P_y^1$and $2P_z^1$. Hybridised orbitals are S, Px and Py, P_z is unhybridized. Each carbon atom form three sigma bonds, one with H atom and two with adjacent c atom [These three bonds only [S, Px, Py] hybridised orbital]. Unhybridized singly occupied $2P_z$ atomic orbital remains unused on each carbon atom which is perpendicular to the plane C_6H_6 ring i.e. XY-plane. This six singly occupied and parallel $2P_z$ atomic orbital of the arene (C_6H_6) ring take part in linear combination producing six π MO's as following ψ_1, ψ_2, ψ_3, ψ_4, ψ_5 & ψ_6 **(Figure 6.5)**.

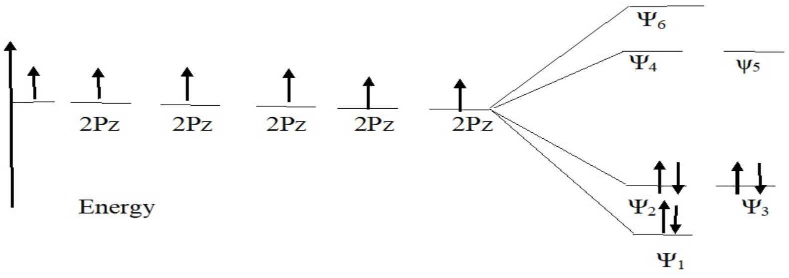


Figure 6.5: Electron distribution of C_6H_6

Six π MO's of one C_6H_6 interact with six π MOs of another C_6H_6 ring producing 12 ligand group orbitals (LGO's). These LGO's are labelled g and u depending upon whether they contain centre of symmetry (i) (or) not. The LGO's are produced by addition and subtraction of wave functions of π BMOs and π ABMO's of two C_6H_6 in the same as in the case of ferrocene. ψ_1(a) splitting in to a_{2u} and a_{1g}. ψ_2 and $\psi_3(e_1)$ splitting in to e_{1g} and e_{1u}. ψ_4 and $\psi_5(e_1)$ splitting in to e_{2g} and e_{2u}. ψ_6(b) splitting in to b_{2g} and a_{1u}. Valence orbitals of chromium atom 4s, 4p, 3d. This orbital splitting terms are following. $4S = a_{1g}$; $4P_z = a_{2u}$; $4P_x = 4P_z = e_{1u}$; $3d_{xy} = 3d_{x^2-y^2} = e_{2g}$; $3d_{xz} = 3d_{yz} = e_{1g}$. So, MO diagram explains bond b/w Cr atom and LGO's of two arene (C_6H_6) rings (**Figure 6.6**).

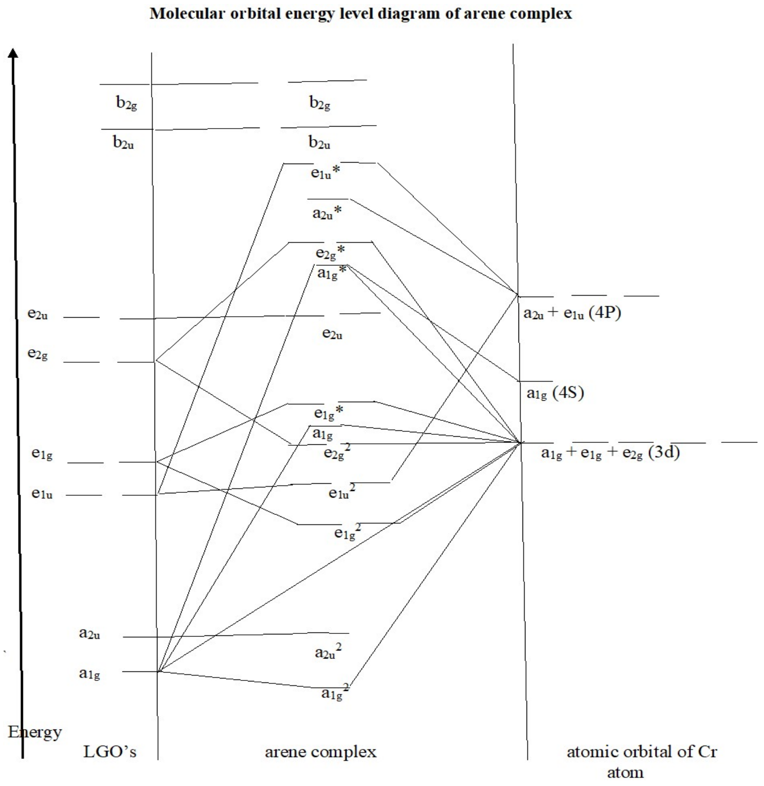


Figure 6.6: MO diagram of $[Cr(\eta^6C_6H_6)_2]$

η^6-arene complex followed 18 electron rules:

No of electrons present on two C_6H_6 rings = 2 x 6 = 12

No of electrons present on Cr atom = 6

Total No of electrons present η^6-arene complex = 18.

6.3 METALLOCENES WITH SEVEN MEMBERED RINGS - CYCLOHEPTATRIENE:

This complex contains cycloheptatriene(C_7H_8) act as ligand. This, type of complex knows as cycloheptatriene complexes. Cycloheptatriene is a six electron's donor that can form complexes like benzene but differs in the delocalisation of π e's. Ex:- [$C_7H_8Mo(CO)_3$]

Preparation:

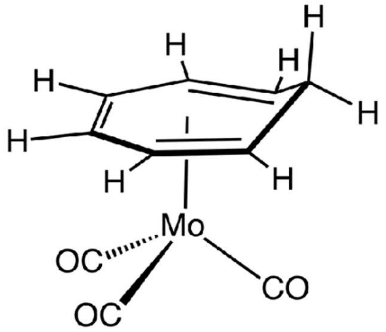
An octahedral complex is treated with cycloheptatriene to form cycloheptatriene complex.

$$Mo(CO)_6 + C_7H_8 \rightarrow C_7H_8\,Mo(CO)_3 + 3CO$$

Cycloheptatriene

Structure:

The bond b/w metal and the cycloheptatriene rings is formed by overlapping of d-orbitals of metals and delocalisation of π e's in C_7H_8 rings. The delocalisation of π e's is limited up to 6 carbon atoms. 7th carbon atom contains two hydrogens. So cycloheptatriene is a $6e^{\theta}$ donor and it is a η^6-ligand. In these Structure the double bond lying trans to the carbonyl group.

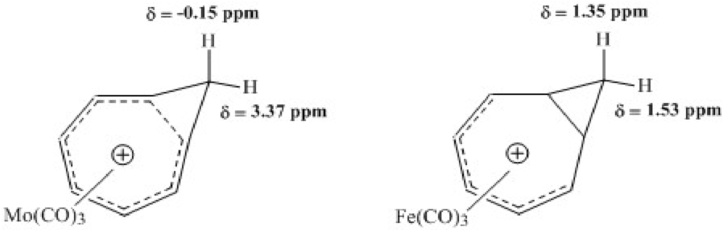


6.4 TROPYLIUM CATION COMPLEX

These complexes containing tropylium cation act as ligand. So, this complex is known as tropylium cation complex.

$$C_7H_8Mo(CO)_3 + Ph_3C^{(+)} BF_4^- \rightarrow [\eta^7\text{- }C_7H_7\ Mo(CO)_3]^+ BF_4^-$$

Structure:



In this structure the double bonds are trans to the carbonyl group. The tropylium cation ($C_7H_7^+$) is a cyclic and planar species with equal C-C distance like benzene and the cyclopentadienide ion, the tropylium cation is an aromatic and $6e^{\theta}$ donor ligand.

$$[V(CO)_4(\eta^5\text{-}C_5H_5)] + C_7H_8 \rightarrow [V\ (\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_7H_{87}) + 4CO + ½\ H_2$$

V-C distance (five membered ring) = 2.23A^0, V-C distance (seven membered ring) = 2.25A^0, V- five membered ring distance (cantered) = 1.90A°, V- Seven membered ring distance (cantered) = 1.90A° = 1.50. The bonding appears to be like that in (η^5- C_5H_5) & (η^6-C_6H_6) complex. The cycloheptatrienyle complexes are formed by early transition metals V, Cr, M$_O$, Mn etc in [V(η^5- C_5H_5)(η^7-C_7H_7)] the rings are in the eclipsed conformation. Theη^7-C_7H_7 ring is closer than η^5- C_5H_5 ring to the vanadium atom (**Figure 6.7**).

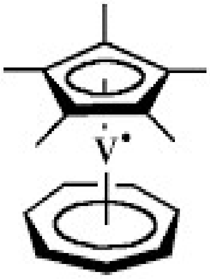


Figure 6.7: V(η^5- C_5H_5)(η^7-C_7H_7)

6.5 SUMMARY

- To know about ferrocene, the synthesis of ferrocene.
- To Knowledge on the structure and bonding in ferrocene.
- Apply the 18-electron rule for Ferrocene and properties and stability of ferrocene.
- To study about Arene complex (or) diazo benzene chromium [Cr($\eta^6C_6H_6$)$_2$ complexes

- To knowledge about on Metallocenes with seven membered rings – Cycloheptatriene.
- To know about Tropylium cation complex structure.

6.6 SELF-ASSESSMENT QUESTIONS

1. Explain the synthesis, bonding and structure of ferrocene.
2. Discuss about structure and synthesis of $[Cr(\eta^6C_6H_6)_2$ complexes.
3. Write the synthesis and bonding involved in Tropylium cation complex.
4. Discuss the synthesis and bonding involving in – Cycloheptatriene.

6.7 REFERENCE BOOKS

1. Inorganic Chemistry, Huheey. Harper and Row.

2. Concise Inorganic Chemistry, J. D. Lee, ELBS.

3. Inorganic chemistry, K.F. Purcell and J.C. Kotz, Holt Saunders international

4. Organometallic chemistry, R.C. Mehrotra and A. Singh. New Age International.

5. Advanced Inorganic Chemistry, Cotton and Wilkinson, Wiley Eastern

Prof. K. Rambabu

LESSON – 7

REACTIONS OF ORGANOMETALLIC COMPOUNDS

7.0 OBJECTIVES

After studying this lesson, you should be able to:

- To know about various types of Reaction of organometallic compounds
- To study on Oxidative addition reactions
- To know about Reductive elimination reactions
- To knowledge on Insertion reactions
- To knowledge on Elimination reactions

STRUCTURE

7.1 TYPES OF REACTION OF ORGANOMETALLIC COMPOUNDS

These are four types

1. Oxidative addition reactions
2. Reductive elimination reactions
3. Insertion reaction
4. Elimination reaction

7.1.1. Oxidative-addition reaction

Electronically and coordinatively unsaturated transition metal complex (LYM) reacts with a molecule AB [i.e. H_2, HCl, CH_3, etc.] to produce a product. which product electron count, co-ordination number & oxidation number of central metal atom increase by two units is called an oxidative-addition reactions.

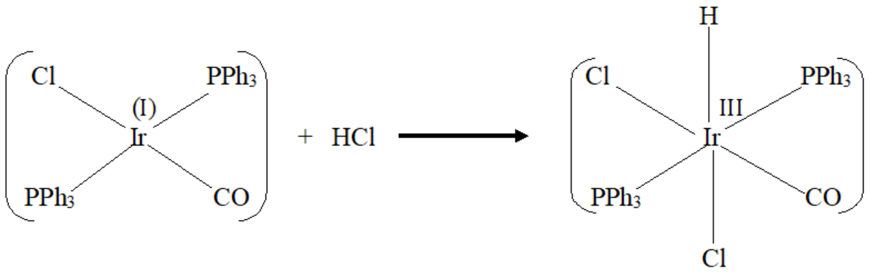
$$LyM^{+n} + A\text{-}B \rightarrow LyM^{+(n+2)}(A)(B)$$

Y = Co-ordination number   Y+2 = Co-ordination number

+n = Oxidation number   +(n+2) = Oxidation number

$16e^{\theta}$ = Electron count $18e^{\theta}$ = Electron count

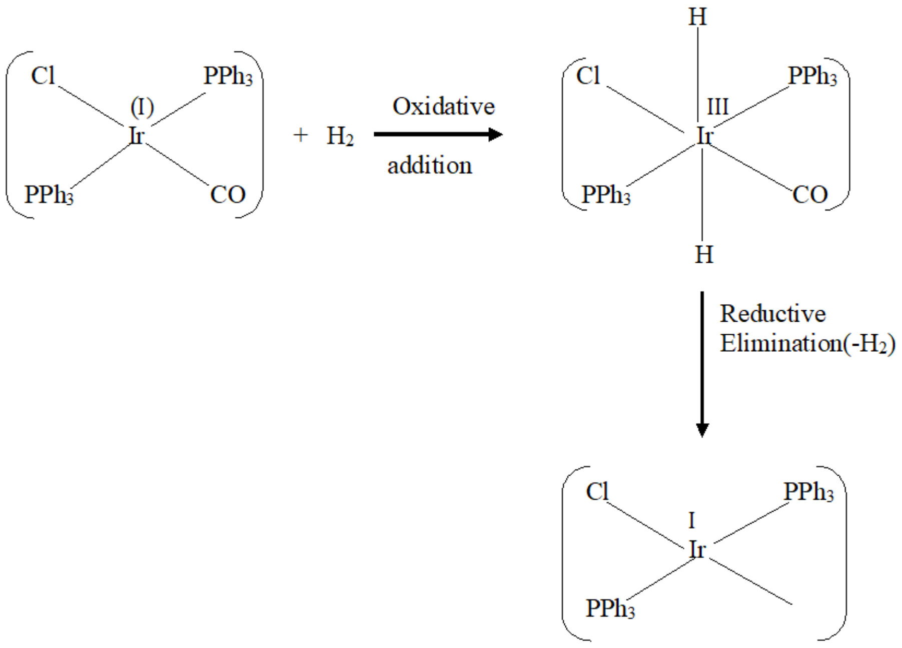
Let us take example.



Co-ordination no = 4	Co-ordination no = 6
Oxidation no = +1	oxidation no = +3
Electron count = $16e^{\theta}$	Electron count = $18e^{\theta}$

7.1. 2. Reductive elimination

The chemical reaction in which the co-ordination numbers, Oxidation number and electron count of the central metal atom all decrease by two units is called a reductive elimination. It is just reverse of the oxidative-addition reactions. This roll is applicable by $18e^{-}$ complex molecule. This elimination is effect for the intermediate oxidation state such as the d^{8} system [Ni^{II}, Pd^{II}, Au^{III}] & d^{6} system [N^{IV}, Pd^{IV}, $Ir^{(III)}$& $Rh^{(III)}$].



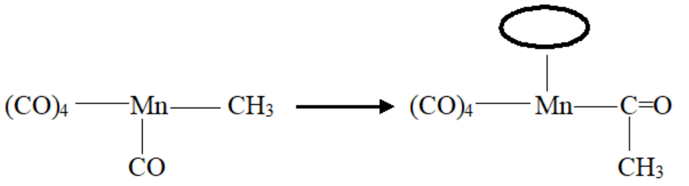
The reductive-elimination reactions are involved in many catalytic processes. A reductive – elimination is often the last step in a catalytic cycle.

7.1.3. Insertion reaction

The chemical reaction in which an atom (or) group of atoms is inserted b/w two atoms which are initially bound together is called an “insertion” reaction (or) migration at reaction.

$$\text{Ln M-X} + \text{AB} \rightarrow \text{Ln M} - \text{(AB)-X}$$

During an insertion reaction a co-ordinated $2e^{\theta}$ donor ligand AB, inserts itself into the M-X bond [X is one electron donor] to give M–(AB)–X where ABX is a new le donor ligand in which a bond has been formed b/w AB and both M and X.



Electron count = $18e^{\theta}$
Oxidation number = +1

Electron count = $16e^{\theta}$
Oxidation number = 0

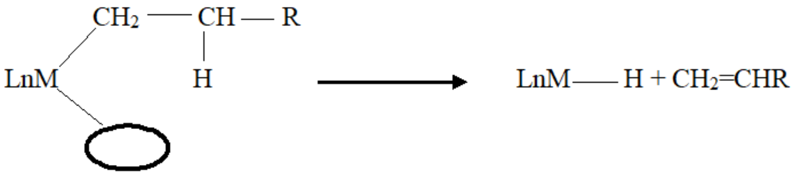
7.1.4 Deinsertion (or) limination reaction:

The reverse of insertion is called deinsertion (or) elimination reaction.

$$\text{Ln(M)-AB-X} \rightarrow \text{Ln(M)-X} + \text{AB}$$

Ex 1: Beta elimination

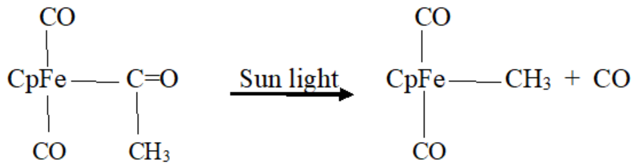
The reverse of alkene insertion is called beta elimination.It is the most important pathway for the decomposition of transition metal alkyl complexes.



Vacant Co ordinate site

Ex 2: Decarbonylation

Many acyl complex undergo decarbonylation on heating with sun light.



7.2 SUMMARY

- To know about various types of Reaction of organometallic compounds
- To study on Oxidative addition reactions
- To know about Reductive elimination reactions
- To knowledge on Insertion reactions
- To knowledge on Elimination reactions

7.3 SELF-ASSESSMENT QUESTIONS

1. Discuss the various types of reactions involved in organometallic compounds.
2. Write the Oxidative addition reactions and Reductive elimination reactions.
3. What are the reactions involved in Insertion reactions.
4. Write about Insertion reactions and Elimination reactions.

7.4 REFERENCES BOOKS

1. Inorganic Chemistry, Huheey. Harper and Row.
2. Inorganic chemistry, K.F. Purcell and J.C. Kotz, Holt Saunders international.
3. Organometallic chemistry, R.C. Mehrotra and A. Singh. New Age International.
4. Inorganic Reaction Mechanism, Basolo and Pearson, Wiley Eastern.

Prof. K. Rambabu

LESSON - 8

APPLICATIONS OF ORGANOMETALLIC COMPOUNDS

8.0 OBJECTIVES

After studying this lesson, you should be able to:

- To know about catalysts with homogeneous and heterogeneous catalyst.
- To study the importance of Catalytic hydrogenation(or) Hydrogenation of alkenes with Wilkinson's catalyst
- To know about the Hydro carbonylation of olefins
- To knowledge on Ziegler – Natta catalyst for the polymerization of olefins

STRUCTURE

8.1 CATALYSTS

Catalysts are two types.

1.Homogeneous catalyst 2.Heterogeneous catalyst.

1. Homogeneous catalyst:

The catalyst which constituents a single phase with the reactants is called a homogeneous catalyst.

$$H_2O_2(aq) \xrightarrow{Fe^{++}} H_2O(l) + O_2(g)$$

2. Heterogeneous catalyst:

If the catalyst and the reactants constitute different phases.It is called a heterogeneous.

$$H_2O_2(aq) \xrightarrow{pt} H_2O(l) + \frac{1}{2} O_2(g)$$

8.2 CATALYTIC HYDROGENATION(OR) HYDROGENATION OF ALKENE:

The conversion of alkene in to an alkane on treatment with hydrogen is called hydrogenation of alkene.

$$CH_2{=}CH_2(g) + H_2(g) \rightarrow CH_3CH_3$$

Most of the heterogeneous catalytic processes for the hydrogenation of alkene require very high pressure and temperature.

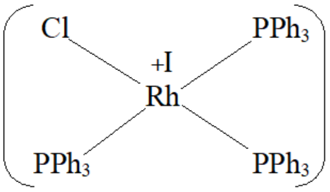
$$CH_2{=}CH_2(g) + H_2(g) \xrightarrow{Ni} CH_3\ CH_3$$

Homogeneous catalytic process for the hydrogenation of alkene and alkyne in the presence of Wilkinson's catalyst $[Rhcl(PPh_3)_2]$, can be carried out at 1atm and room temperature. Only Homogeneous catalytic process is major.

$$CH_2{=}CH_2(g) + H_2(g) \xrightarrow[1atm\ and\ 25^{\circ}c]{[Rhcl(pph_3)_2]} CH_3\ CH_3$$

Wilkinson's catalyst:

This catalyst is a square-planar complex compound having three bulky triphenylphosphine ligands. The oxidation number of Rh is in Wilkinson's catalyst and thus it is a $16e^{\theta}$ complex.



Valence of Rh is 9, oxidation state is +1.

Hence total electron count = $9+8-1= 16e^{\theta}$.

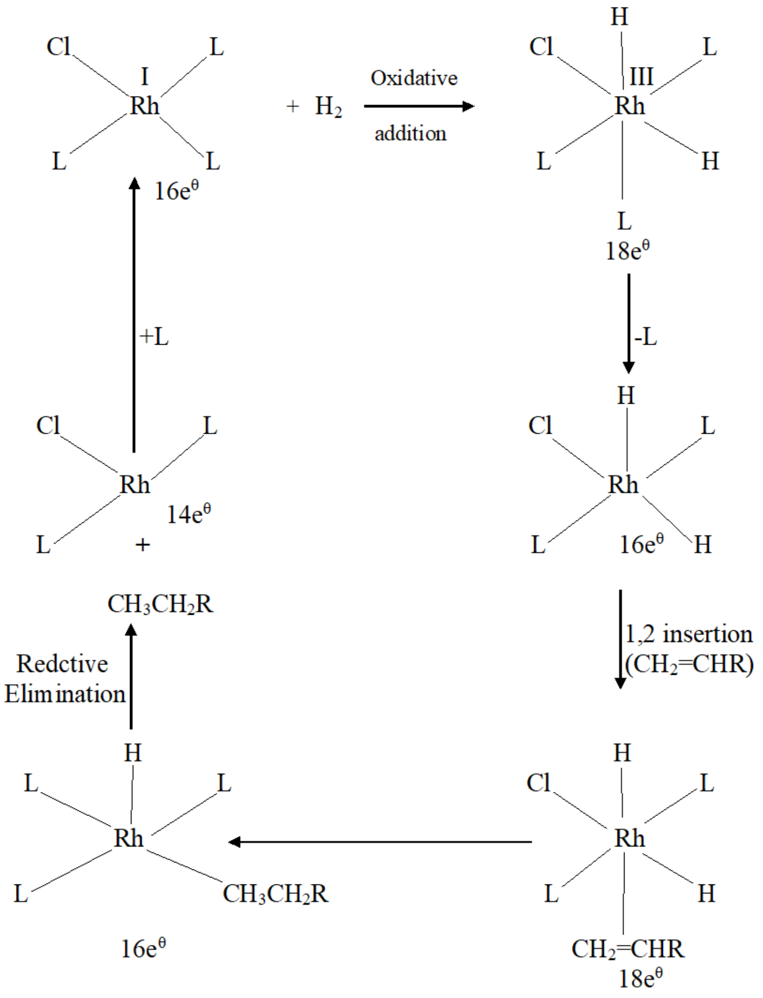
The homogeneous catalytic process for the hydrogenation of alkene and alkyne in the presence of Wilkinson's catalyst $[Rhcl(PPh_3)_2]$, can be carried out at 1atm and room temperature.

$$CH_2{=}CH_2(g) + H_2(g) \xrightarrow[1atm\ and\ 25^{\circ}c]{[Rhcl(pph_3)_2]} CH_3\ CH_3$$

This reaction proceeds through the following steps:

1. Wilkinson's catalyst undergoes oxidative–addition reaction with H_2 molecule producing a cis-dihydride complex. The oxidation number of Rh increases from +I to +III and its co-ordination number increase 4 to 6. At the same time, a $16e^-$ species transforms into an $18e^-$ complex.
2. The hexacoordinated Rh (III) complex losses on bulky PPh_3 ligand forming a 5 co-ordinated $16e^-$ complex.
3. The alkene molecule gets coordinated to Rh (III) through the vacant co-ordinate site.
4. The coordinate alkene molecule is inserted in to Rh-H bond [1,2 Insertion].
5. Alkyl derivative of Rh (III) undergoes reductive-elimination of alkane. It regenerates Rh(I) species which is tri coordinated.
6. The tri coordinated Rh(I) species accepts a PPh_3 ligand and thus the catalytic cycle is completed.
7. This catalyst only hydrogenation of double bond & triple bond only but C=O, CN, NO_2, COOR are unaffected.

Mechanism:



8.3 HYDRO CARBONYLATION OF OLEFINS:

1. The reaction b/w alkene & carbon monoxide (CO) + hydrogen gas (H_2) in presence of cobalt (Co) or rhodium (Rh) complexes as catalyst produces an aldehyde. In this reaction number of one carbon increase in the product.

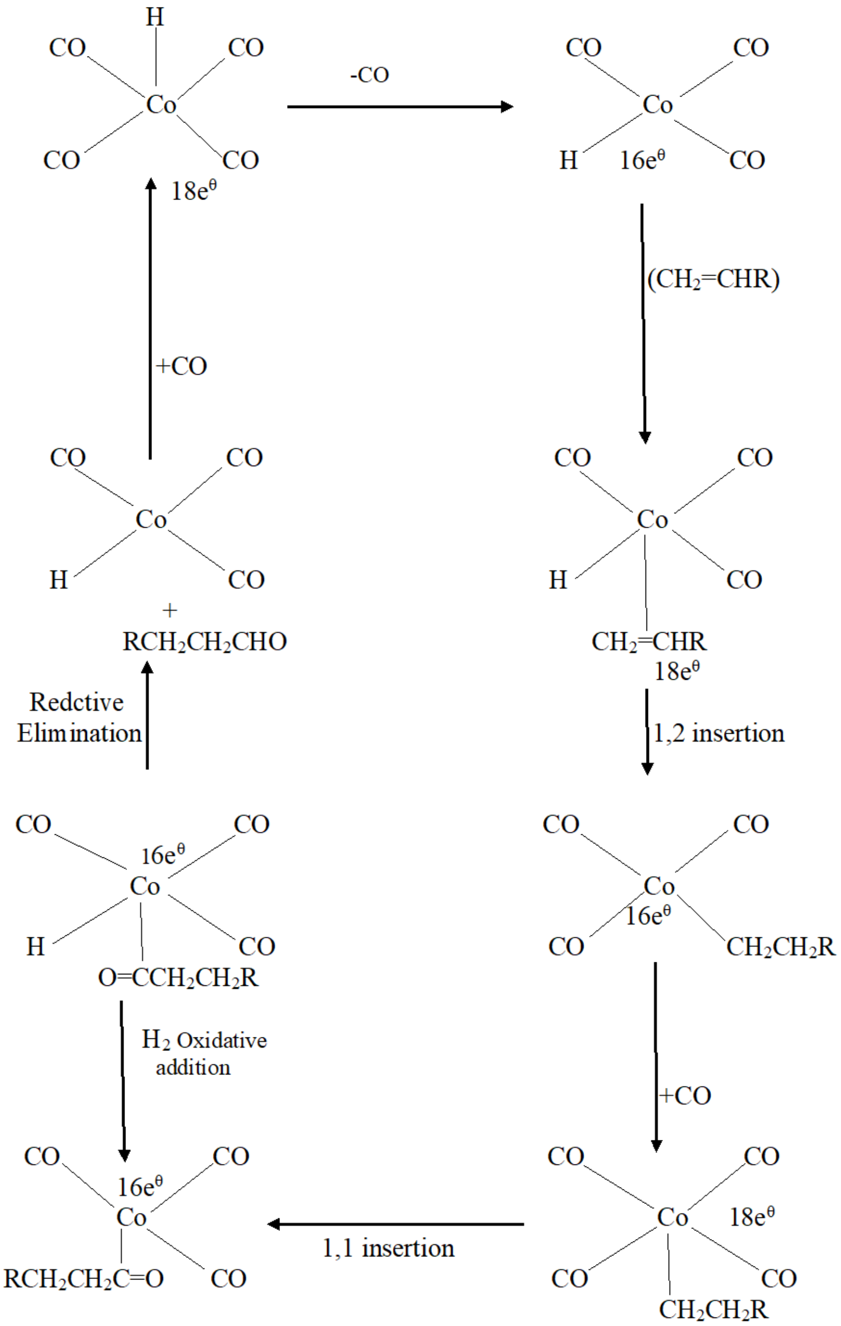
$$RCH{=}CH_2(g) + (H_2{+}CO) \xrightarrow{\text{catalyst}} RCH_2\,CHO$$

2. In this reaction involves the addition of hydrogen(H) atom and formyl (CHO) group derived from H_2 and CO on C-C bond. Therefore it is known as hydroformylation (or)hydro carbonylation reaction. It is also known as oxo-process because it introduces oxygen atom into the hydrocarbon.
3. The classical hydroformylation reaction involved the use of $CO_2(CO)_8$ as a catalyst, temperature range 150 ^{0}C to 180 ^{0}Cand pressure of 200 to 400 atm. Under this condition the $Co_2(CO)_8$ is converted into $HCo(CO)_4$.Which is the active catalyst.

$$H_2 + Co_2(CO)_8 \xrightarrow{\text{High temp| High pressure}} 2HCo(CO)_4$$

Reaction proceeding through following steps.

1. $HCo(CO)_4$ [$18e^{\theta}$ complex] loses one CO molecule forming $HCo(CO)_3$ [$16e^{\theta}$ complex] and creating a vacant co-ordination site.
2. Alkene molecule is coordinated to Co through the vacant coordination site recreating $18e^{\theta}$ complex.
3. The coordinated alkene undergoes migratory insertion into Co-H bond creating a $16e^{\theta}$ transition metal alkyl and another vacant coordination site.
4. A CO molecule is coordinated to Co through a vacant co-ordinate site. Producing an $18e^{\theta}$ complex.
5. One ‘CO’ ligand of $RCH_2CH_2Co(CO)_4$ is inserted into Co–alkyl bond producing a transition metal acyl, $RCH_2CH_2(C{=}O)Co(CO)_3$ ($16e^{\theta}$ species).
6. $RCH_2CH_2(C{=}O)Co(CO)_3$undergoes oxidative addition with H_2 to form a cis-dihydro complex.
7. Above cis-dihydro complex under goes reductive-elimination reaction. Producing aldehyde & regenerating $HCo(CO)_3$.
8. $HCo(CO)_3$ picks up one CO forming $HCo(CO)_4$ and thus the catalytic cycle is completed.



8.4 ZIEGLER – NATTA CATALYST FOR THE POLYMERISATION OF OLEFINS:

This catalyst is prepared in situ the treatment of titanium tetrachloride ($TiCl_4$) with triethyl aluminium [$Al(C_2H_5)_3$] in a hydrocarbon solvent such as n-heptane.

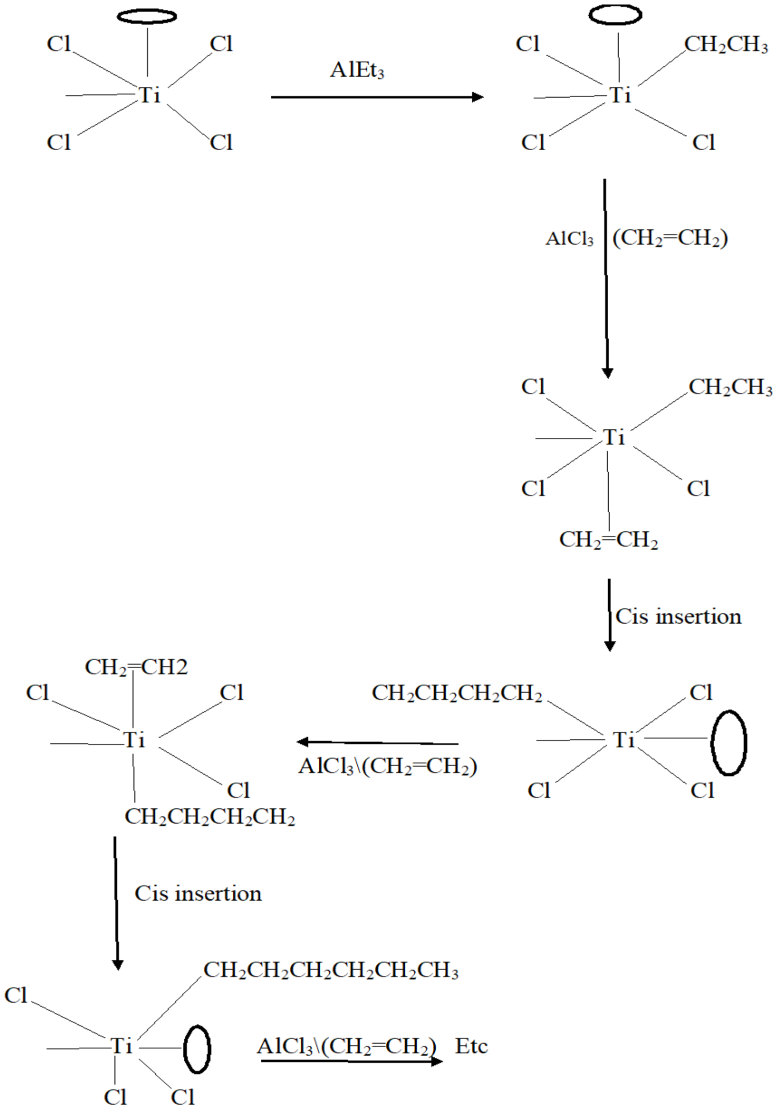
$Ticl_4$ and $AlEt_3$ react together to give polymeric insoluble and fibrous form of $Ticl_4$ which is used in the form of fine powder. This catalyst is a heterogeneous catalyst. This catalyst treated with n moles of ethylene molecule under the conditions 25^0C, 1 atm & n-heptane used as a solvent.

$$n\ CH_2{=}CH_2 \xrightarrow[25^0C,\ 1\ atm\ \&\ n\text{-}hep]{(Ticl4\ and\ AlEt_3)} \underset{\text{Polyethane}}{(-CH_2\ CH_2-)_2}$$

The Ziegler – Natta polymerisation of ethane proceeds through the following steps.

This mechanism was proposed by Cossee and Arlman and hence it is called Cossee and Arlman mechanism.

1. One of the Cl atoms coordinated to a titanium atom is replaced by and ethyl group from $AlEt_3$.
2. The Ti atom on the surface of solid catalyst has a vacant coordination site. A molecule of ethylene is coordinated to Ti atom through this vacant coordination site.
3. The coordinated ethylene molecule is inserted into the Ti-C via four centered transition state. This process is known as cis-insertion.
4. The result of the above cis-insertion is that a vacant coordination site is regenerated on Ti atom and it can be occupied by other molecule of ethene and steps II & III are repeated several times. The resulting substance is a straight chain polymer.



8.5 SUMMARY

- To know about catalysts with homogeneous and heterogeneous catalyst.
- To study the importance of Catalytic hydrogenation(or) Hydrogenation of alkenes with Wilkinson's catalyst.
- To know about the Hydro carbonylation of olefins.
- To knowledge on Ziegler – Natta catalyst for the polymerization of olefins.

8.6 SELF-ASSESSMENT QUESTIONS

1. Explain the applications of organometallic compounds.

2. Discuss about the Hydrogenation of alkenes with Wilkinson's catalyst.

3. Write the Hydro carbonylation of olefins.

4. Write the Ziegler – Natta catalyst for the polymerization of olefins.

8.7 REFERENCE BOOKS

1. Inorganic Chemistry, Huheey. Harper and Row.
2. Inorganic chemistry, K.F. Purcell and J.C. Kotz, Holt Saunders international.
3. Organometallic chemistry, R.C. Mehrotra and A. Singh. New Age International.
4. Inorganic Reaction Mechanism, Basolo and Pearson, Wiley Eastern.

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LESSON – 9

INORGANIC REACTION MECHANISM IN TRANSITION METAL COMPLEXES

9.0 OBJECTIVES

After studying this lesson, you should be able to:

- To know able to the Acid hydrolysis in octahedral complexes with their Factors.
- To study about Base hydrolysis for octahedral complexes with their Factors.
- To study about SN^1 (Conjugate Base) Mechanism.
- To knowledge about on their Direct and indirect evidences in favour of conjugate mechanism.

STRUCTURE

9.1 INTRODUCTION

Most of the reactions in inorganic chemistry are ionic in nature. As such as they take place almost instaneously and hence no mechanism is involved in their occurrence. Reactions of coordination compounds are slow and proceeds through definite path ways.

Rate of reaction gives misinterpretation of the mechanism of the reaction. But, substitution reactions in aqueous solution is found to be accelerated by the presence of an acid or base.

The pH of the Solution is the deciding factor for nature of the product in the hydrolysis reactions; the water containing complex is obtained in acidic solution while the hydroxo (HO-) complex is obtained in basic Solution.

9.2 ACID HYDROLYSIS OF OCTAHEDRAL COMPLEX

The reaction in which a water molecule replaces a coordinated ligand from the complex species in an aqueous medium is termed as aquation reaction or acid hydrolysis.

The rates of hydrolysis of the reaction of the type

$$[Co(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{3+} + Cl^-$$

This reaction have been studied and found to be first order in the complex hence

$$-d/dt[Co(NH_3)_5Cl]^{2+} = k_A[Co(NH_3)_5Cl]^{2+}$$

The rate of the reaction would be dependent only on the concentration of the complex. The rate law alone does not indicate whether these reactions proceed by an SN^1 dissociation followed by addition of H_2O or by an SN^2 displacement of Cl^- by H_2O. The nature of mechanism depends on the following factors.

Factors affecting acid hydrolysis

1. **Charge on the complex**: An increase in the positive charge on the complex species decreases its rate of acid hydrolysis. The decrease in reaction rate is observed as the charge of the complex increases, a dissociative nucleophilic substitution SN^1 process seems to be operative. Hence, for example, the acid hydrolysis (i.e. replacement of one Cl^- ion by H_2O) of the $[Co(NH_3)4Cl_2]$+complex occurs in two steps

$$[Co(NH_3)_4Cl_2]^{+} + H_2O \xrightarrow{\text{Fast}} [Co(NH_3)_4(Cl)(H_2O)]^{2+} + Cl^-$$

$$\downarrow \text{Slow } H_2O$$

$$[Co(NH_3)_4(H_2O)_2]^{3+} + Cl^-$$

The increase of charge on the complex would make the breaking of the M-Cl bond more difficult hence the rate of reaction is decrease. However, if it takes place through SN^2 mechanism the rate of reaction should practically unchanged with any change in the charge on the substrate.

2. **Effect of chelation:** An increase in the steric crowding around the metal ion preferably favours a dissociative nucleophilic substitution SN^1 mechanism. For example, when we

consider the $[Co(NH_3)5Cl]^{2+}$ complex, the NH_3 molecule in $[Co(NH_3)5Cl]^{2+}$ complex ion are replaced by ethylenediaamine (en) the rate of acid hydrolysis of the complex is decreases.

$$[Co(NH_3)_5Cl]^{2+} + H_2O \xrightarrow{\text{Fast}} [Co(NH_3)_5H_2O]^{3+} + Cl^-$$

$$[Co(en)_2(NH_3)Cl]^{2+} + H_2O \xrightarrow{\text{slow}} [Co(en)_2(NH_3)(H_2O)]^{3+} + Cl^-$$

It has been observed that the chelation shorten Co-N bond distance and hence transfer more charge to the metal ion, this should be enhance the rate of acid hydrolysis. However, according to the solvation theory the relative rates of acid hydrolysis of the chelated complexes decreases because the hydration of any species decreases its energy and thus stabilizes it. The higher the charge and smaller the size of the complex species, results higher extent of hydration and consequentially its stabilization for examples.

$$[Co(NH_3)_5Cl]^{2+}_{\text{hydrated}} \xrightarrow[-Cl^-]{\text{fast}} \underset{\text{Intermediate}}{[Co(NH_3)_5]^{3+}_{\text{hydrated}}} \xrightarrow{+H_2O} [Co(NH_3)_5(H_2O)]^{3+}_{\text{hydrated}}$$

$$\begin{array}{ccc}
[Co(en)_2(NH_3)Cl]^{2+}_{\text{hydrated}} & \xrightarrow[-Cl^-]{\text{Slow}} & [Co(NH_3)(en)_2]^{3+}_{\text{hydrated}} \\
 & & \text{Intermediate} \\
 & & \Big\downarrow {+H_2O} \\
 & & [Co(en)_2(NH_3)(H_2O)]^{3+}_{\text{hydrated}}
\end{array}$$

The intermediate $[Co(en)_2(NH_3)]^{3+}$ of the chelated complex is bigger in size than the intermediate $[Co(NH_3)_5]^{3+}$ of non-chelated complex. Hence, the rate determining step of the chelated complex $[Co(en)(NH_3)3Cl]^{2+}$ would be slower than that in the non-chelated complex $[Co(NH_3)Cl]^{2+}$. it is evident that the chelation factor can be explained with the help of dissociative SN^1 mechanism.

3. **Effect of leaving group:** The rate of acid hydrolysis of $[Co(NH_3)5Cl]^{2+}$ complex during the replacement of Cl^- with H_2O molecule depends on the nature of leaving group because the rate determine step would be the bond breaking step. It has been observed

that the reactivity of leaving group decreases in the order of

$$HCO_3^- > NO_3^- > I^- > Br^- > Cl^- > SO_4^{2-} > F^- > CH_3COO^- > SCN^- > NO_2^-$$

Since, the strength of the M-L bond is directly proportional to the basicity of the leaving group, the rate of acid hydrolysis decreases with the increase in the strength of M-X bond i.e. with the increase of basicity of the leaving group. This indicates that the rate determining step in the acid hydrolysis involve the dissociation (i.e. SN^1 mechanism).

9.3 BASE HYDROLYSIS FOR OCTAHEDRAL COMPLEX

Hydrolysis of octahedral complexes in the presence of hydroxyl (HO^-) ions is known as the base hydrolysis. It is observed that rate of hydrolysis of complex in the basic medium is faster as compared to the acidic medium. Base hydrolysis is an overall second order reaction being first order with respect to the complex ion and with respect to hydroxyl (HO^-) ion. The rate is represented as

$$r = k[\text{substrate}][HO-]$$

Ammine complex of Co(III) has been studied very well with respect to base hydrolysis for example

$$[Co(NH_3)_5Cl]^{2+} + HO^- \longrightarrow [Co(NH_3)_5OH]^{2+} + Cl^-$$

This can be proceeded by any of the following two mechanisms

SN^2 Mechanism

Accordingly the rate of hydrolysis (r) is represented as

$$r = k[\text{Complex}][HO-]$$

$$\begin{tikzcd}
{[Co(NH_3)_5Cl]^{2+} + HO^-} \arrow[r, "\text{slow}"] & {[Co(NH_3)_5Cl(OH)]^+} \arrow[d, "\text{fast} \\ Cl^-"] \\
& {[Co(NH_3)_5OH]^{2+}}
\end{tikzcd}$$

It has been observed that the above mechanism fails to explain some of the experimental evidence

1. At very high concentration of hydroxyl [HO$^-$] ion the reaction rate becomes almost independent of hydroxyl [HO$^-$] ion and seems to be first order with respect to [complex] only. This can’t be explained by a assuming SN^2 mechanism.

2. In the SN^2 mechanism the rate of base hydrolysis directly depend on the strength of the nucleophilicity of the attacking ligand. The concentration of NCS$^-$, NO$_2^-$, N$_3^-$ do not affect the rate of hydrolysis of the ammine complex, even though, it has been observed that these are equally strong nucleophiles like HO$^-$ ion. It is also evident that the rate of hydrolysis of ammine complexes is dependent only on the concentration of the complex ion. The SN^2 mechanism unable to explain the cause of effect of rate of base hydrolysis alone by HO- and no other strong nucleophilic should influence.

9.4 SN^1 (CONJUGATE BASE) MECHANISM:

The complex $[Co(NH_3)_5Cl]^{2+}$ acts as a Bronsted acid is converted into its conjugate base (CB), $[Co(NH_3)_4(NH_2)Cl]^+$. The CB is obtained by removal of a proton (H$^+$) from ammine group (NH$_3$) coordinated with the complex. CB is an amido complex since it contains an amido group (H$_2$N$^-$). HO$^-$ ion acts as a base and is converted into its conjugate acid, H$_2$O.

$$[Co(NH_3)_5Cl]^{2+} + {}^-OH \overset{\text{fast}}{\rightleftharpoons} \underset{\text{(CB)}}{[Co(NH_3)_4(NH_2)Cl]^+} + H_2O$$

$$K = [CB][H_2O]/[Co(NH_3)_5Cl]^{2+}\,[HO^-]$$

It has been observed that the CB $[Co(NH_3)_4(NH_2)Cl]^+$ is more labile than the complex $[Co(NH_3)_5Cl]^{2+}$. Hence, it undergoes SN^1 dissociation mechanism by a slow step to lose Cl$^-$ ion and form a 5-Coordinated intermediate species.

$$[Co(NH_3)_4(NH_2)Cl]^+ \underset{S_N1}{\overset{\text{slow}}{\rightleftharpoons}} [Co(NH_3)_4(NH_2)]^{2+} + Cl^-$$

The five coordinated intermediate $[Co(NH_3)_4(NH_2)]^{2+}$ after reaction with H$_2$O to form the final product of hydration

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \rightleftharpoons [Co(NH_3)_5OH]^{2+}$$

9.5 DIRECT AND INDIRECT EVIDENCES IN FAVOUR OF CONJUGATE MECHANISM

The above CB mechanism can be experimentally verified by following explanations

1. It has been observed that the 2nd order kinetics can fallow SN^1(CB) mechanism because the equilibrium constant of reaction (ii) is obtained very fast and the conjugate base (CB) present at equilibrium is of small i.e. K is small since the reaction (ii) involves the dissociation of Cl- from the conjugate base it is slower than (i) and (iii) thus it is rate determining step

   $r = k[Co(NH_3)_4(NH_2)Cl]^+$

   From reaction (i)

   $K = [Co(NH_3)_4(NH_2)Cl]^+ / [Co(NH_3)_5Cl]^+ [HO^-]$

   so, $[Co(NH_3)_4(NH_2)Cl]^+ = K[Co(NH_3)_5Cl]^{2+} [HO^-]$

   $r = kK[Co(NH_3)_5Cl]^{2+} [HO^-]$

   $= K'[Co(NH_3)_5Cl]^+ [HO^-]$

2. At very high $[HO^-]$, the rate of base hydrolysis tends to be almost independent of $[HO^-]$, this observation can be explained by SN^1(CB) mechanism. If the amount of HO^- ion added is very large, there would be very little differences in the concentration of HO^- after adding acid HO- can be taken as constant so that the rate of hydrolysis as given above in (i) becomes

$$r = k'[Co(NH_3)_5Cl]^{2+}[\text{constant}]$$

3. The ligands such as NO_2^-, NCS^-, N_3^- etc are as strong nucleophile as HO^- but they do not influence the rate of hydrolysis of ammine complexes. This is explained as strong nucleophile such as NO_2^-, NCS^-, N_3^- are not as strong babe as the HO^- and hence unable to extract a proton from the ammine group of complex to yield a conjugate base (CB) of the complex by the reaction (i). So hydrolysis cannot proceed through SN^1(CB) mechanism for these ligands.

4. It has been also observed that for the reactions proceeding through SN^2 mechanistic path, HO_2^- is better nucleophile than HO^-. The HO_2^- ion can be generated by the action of H_2O_2 on HO^-.

$$H_2O_2 + HO^- \rightleftharpoons H_2O + HO_2^-$$

Therefore, it assumes that the rate of base hydrolysis increases with the addition of H_2O_2 on SN^2 mechanism, because H_2O_2 coverts HO_2^- as a better nucleophile. However, it is noted down that the rate of base hydrolysis decreases with addition of H_2O_2 because the concentration of HO^- decreases which is necessary for the production of CB.

Experimentally, it has been observed that the addition of H_2O_2 actually deceases the rate of base hydrolysis of ammine complex of Co(III) which then strongly favors SN^1(CB) mechanism.

5. The isotopic exchange studies on base hydrolysis using ^{18}OH supports the SN^1(CB) mechanism for base hydrolysis of CO(III) ammine complex

It has been evident from the above explanation that the rate of base hydrolysis is million-fold faster than acid hydrolysis provided –OH ion is used as base. The reason of faster rate for base hydrolysis over acid hydrolysis is proton abstraction from coordinated ammonia in the reacting complex which forms a conjugate base (CB) and $[Co(NH_3)_4(NH_2)Cl]^+$ acts as driving force for Cl^- dissociation.

9.6 SUMMARY

After studying this lesson, you should be able to:

- To know able to the Acid hydrolysis in octahedral complexes with their Factors.
- To study about Base hydrolysis for octahedral complexes with their Factors.
- To study about SN^1 (Conjugate Base) Mechanism.
- To knowledge about on their Direct and indirect evidences in favour of conjugate mechanism.

9.7 SELF-ASSESSMENT QUESTIONS

1. Write the acid hydrolysis in octahedral complexes.
2. Discuss about base hydrolysis for octahedral complexes.
3. Discuss the about the SN^1 (Conjugate Base) Mechanism in reactions.
4. write about the Direct and indirect evidences in favour of conjugate mechanism.

9.8 REFERENCES BOOKS

1. Inorganic Chemistry, Huheey. Harper and Row.
2. Concise Inorganic Chemistry, J. D. Lee, ELBS.
3. Inorganic chemistry, K.F. Purcell and J.C. Kotz, Holt Saunders international.
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LESSON – 10

ANATION REACTIONS- REACTIONS WITHOUT METAL-LIGAND BOND CLEAVAGE. FACTORS AFFECTING THE SUBSTITUTION REACTIONS IN OCTAHEDRAL COMPLEXES

10.0 OBJECTIVES

After studying this lesson, you should be able to:

- To study about Anation Reactions.
- To study about Substitution Reactions.
- To knowledge about on their Metal - Ligand Substitution reactions in octahedral complexes and their factors.

STRUCTURE

10.1 Anation Reactions
10.2 Substitution Reactions
10.3 Metal - Ligand Substitution reactions in octahedral complexes
10.4 Factors effecting octahedral substitution reactions
10.5 Summary
10.6 Self-Assessment Questions
10.7 Reference Books

10.1 ANATION REACTIONS

The replacement of water from aqua complex by an anionic group is called Anation reaction”

Or

The reversal of acid hydrolysis (aquation) reactions is called anation reactions”

$$[Co(NH_3)_5 H_2O]^{3+} + X- \rightarrow [Co(NH_3)_5 X]^{2+} + H_2O$$

The kinetic studies of anation reactions in aqua solutions shows that there are bimolecular reactions with a rate which depends on the concentration of complex and X^-. however, this information alone not difficult to prove that, there reactions are bimolecular, because the same second order kinetics has been observed for a unimolecular reaction line

$$\underset{\text{Aqua complex}}{[Co(NH_3)_5\,H_2O]_3^{+}} \underset{\text{Fast}\ +H_2O}{\overset{\text{Slow}\ -H_2O}{\rightleftharpoons}} \underset{\text{Penta co-ordinated intermediate}}{[Co(NH_3)_5]^{3+}} \xrightarrow[X^-]{\text{Fast}} [Co(NH_3)_5X]^{2+} + H_2O$$

the above reactions can be generally represented as

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$$

$$B + C \xrightarrow{K_3} D$$

The rate of formation of 'B' can be given as

$$\frac{d}{dt}[B] = K_1[A] - K_2[B] - K_3[B][C]$$

Since, 'B' is very reactive intermediate, the steady state approximations assumes that is concentration remains small.

$$\frac{d}{dt}[B] = 0$$

$$0 = K_1[A] - K_2[B] - K_3[B][C]$$

$$[B] = \frac{K_1[A]}{K_2 + K_3[C]}$$

The rate of formation of final product is 'D'

$$\frac{d}{dt}[D] = K_3[B][C]$$

$$\frac{d}{dt}[D] = \frac{K_1K_3[A][C]}{K_2 + K_3[C]}$$

Case i) if $K_2 >> K_3$ [C] then

$$\frac{d}{dt}[D] = \frac{K_1K_3}{K_2}[A][C]$$

Hence, it is second order reaction.

Where, A = $[Co(NH_3)_5 H_2O]^{3+}$ and C = X^-

Case ii) K_3 [C] >> K_2

$$\frac{d}{dt}[D] = \frac{K_1K_3[A][C]}{K_3[C]}$$

$$\frac{d}{dt}[D] = K_1 [A]$$

Hence, it is first order reaction, which is independent of concentration & depends only on [A].

10.2 SUBSTITUTION REACTIONS

Substitution reactions are divided into two broad classes a) Nucleophilic substitutions (S_N) and b) Electrophilic substitutions (S_E.)

a). Replacement of one ligand by the other is called a Nucleophilic substitution reaction or (S_N) type reaction

$$ML_6 + L^1 \rightarrow ML_5L^1 + L$$

$$\text{For example : } [Co(H_2O)_6]^{2+} + Cl^- \rightarrow [Co(H_2O)_5Cl]^+ + H_2O$$

b). Replacement of one metal ion by the other is called an electrophilic substitution reaction or (S_E) type reaction.

$$ML_6 + M' \rightarrow M'L_6 + M$$

$$\text{For example}: [Co(NH_3)_5Cl]^{2+} + Hg^{2+} \rightarrow [Hg(NH_3)_5Cl] + Co^{2+}$$

The nucleophilic substitution reaction is a special type of general acid- base process in which the metal ion functions as a Lewis acid (electron – pair acceptor) and the replacing ligand as a Lewis base (Electron-pair donor). Hughes and Ingold classified S_N reactions into:

SN^1 substitution nucleophilic unimolecular and SN^2 substitution nucleophilic bimolecular. But they are rarely used today because a) they are too inflexible to deal with subtle variations in real mechanisms and b) they tend to suggest relationships between observed rate laws and mechanisms that are often erroneous. Hence an alternate classification which takes away undue emphasis on the molecularity of reaction has been proposed by Langford and Gray as

1. a dissociative process (denoted by D) involving a detectable intermediate in which the central atom has a lower coordination number.

2. an associative process (denoted by A) in which the central atom of a detectable intermediate has higher coordination number than it has in the reactant.

3. an interchange mechanism (denoted by I), a one step process in which no evidence from intermediate exists. Here the activated complex contains the substrate and the ligand.

10.3 METAL - LIGAND SUBSTITUTION REACTIONS IN OCTAHEDRAL COMPLEXES

a) Dissociative Mechanism: In the dissociative path the leaving group is lost in the first step or rate determining step, thus producing an intermediate of reduced coordination number.

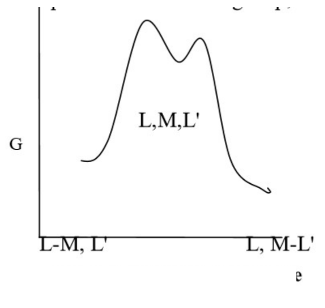

Figure 10.1: Reaction coordiantes for dissociative mechanism

$$ML_6 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ML_5 + L$$

$$ML_5 + L' \xrightarrow{K_2} ML_5L'$$

The intermediate is assumed to live long enough to be able to discriminate between potential ligands in its vicinity including the one just lost L, the new ligand L^1 and also the solvent molecules. By employing the well-known steady state approximation for $[ML_5]$, the above mechanism leads to the rate law.

$$\text{Rate}= \frac{k_1k_2[ML_6][L']}{k_{-1}[L]+k_2[L']}$$

The rate clearly depends in general on [L'] as well as on [ML6]. But when [L'] becomes very large, k_{-1} becomes negligible compared to $k_2[L']$ and the rate law reduces to:

$$\text{Rate}= k_1[ML_6]$$

For example :

$$W(CO)_6 \rightarrow W(CO)_5 + CO$$
$$W(CO)_5 + PPh_3 \rightarrow W(CO)_5PPh_3$$

Under laboratory conditions the intermediate $[W(CO)_5]$is rapidly captured by an ether solvent, such as THF(tetrahydrofuran) $[W(CO)_5(THF)]$ which in turn is converted to the phosphane product, presumably by a second dissociative process. The reaction profile is shown in **Figure 10.1**.

b) Interchange mechanism

This is concerted path in which the leaving ligand moves from inner to the outer coordination sphere as the entering ligand moves from outer to the inner. There is no intermediate of modified coordination number. The interchange mechanism is shown by reactions of the six Coordinate d^8 complex, $[Ni(H_2O)_6]^{2+}$. The reaction profile for interchange mechanism is given in **Figure 10.2**. Two types of interchange mechanisms are recognized:

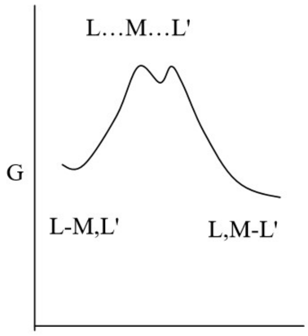

Figure 10.2: Reaction coordinates for interchange mechanism

Id Mechanism (Dissociative interchange mechanism):

This is the dissociative interchange mechanism. The transition state involves considerable extension of an M-L bond (but not its complete rupture), together with some incipient interaction with the incoming ligand L'. We may represent this by the scheme;

$$ML_6 + L' \xrightarrow{K} ML_6, L' \xrightarrow{k} [L_5M....L, L']^{\neq} \rightarrow ML_5L' + L$$

The species ML_6, L' is called an outer-sphere complex or, if ML_6 is a cation and L' an anion, an ion-pair.

Ia mechanism (Associative interchange mechanism):

This is the associative interchange mechanism. Again, there is interchange of ligands between the inner and the next nearest coordination sphere; but here the interaction between M and L' is much more advanced in the transition state; M…… L' bonding is important in defining the activated complex.

c. Associative mechanism:

In the associative pathway the entering group adds on in the first step or rate determining step, producing an intermediate of increased coordination number. This mechanism is suspected for many reactions of square planar Pt(II), Pd(II) and Ir(I) complexes. The exchange of $^{14}CN^-$ with the ligands in the square planar complex $[Ni(CN)_4]^{2-}$ appears to be associative and in the reaction the coordination number of Ni^{+2} is increased to form a transient species.

$$[Ni(CN)_4]^{2-} + {}^{14}CN^- \longrightarrow [Ni(CN)_4({}^{14}CN)]^{3-}$$

$$[Ni(CN)_4({}^{14}CN)]^{3-} \longrightarrow [Ni(CN)_3({}^{14}CN)]^{2-} + CN^-$$

The radioactivity of Carbon-14 (^{14}C) provides a means of monitoring this reaction. In the presence of excess CN^- ions, the proposed intermediate $[Ni(CN)_5]^{-3}$ can be isolated from solution and it can also be detected spectroscopically in solution. The important features of dissociative and associative mechanisms are bond-breaking and bond making respectively. Whereas in an interchange process both are of similar status.

10.4 FACTORS EFFECTING OCTAHEDRAL SUBSTITUTION REACTIONS

The effect of sizes and charges of the central metal ion, the entering group, the leaving group and the passive ligands are tabulated in **Table 10.1**.

The various factors that influence the substitution reactions in complexes arises from usual factors such as temperature, catalyst etc., are

1. Nature of central metal ion
2. Nature of leaving ligand
3. Nature of entering ligand
4. Nature of other ligands attached to the metal atom
5. Charge on the complex
6. Nature of the solvent

Table 10.1: effect of sizes and charges on rates of dissociative and associative reactions

Changes made	Dissociative rate	Interexchange rate	Associative rate
Increase positive charge of central atom	Decrease	Opposite effects	Increase
Increase size of the central metal atom	Increase	Increase	Increase
Increase negative charge of entering group	No Effect	Increase	Increase
Increase size of entering group	No Effect	Decrease	Decrease
Increased size of leaving group	Decrease	Decrease	Decrease
Increased negative charge of leaving group	Increase	Opposite effects	Decrease
Increased negative charge for non-labile ligands	Increase	Opposite effects	Decrease
Increased size of non-labile ligands	Increase	Opposite effects	Decrease

Assuming other factors remain constant:

1. **Increasing the charge on central atom** will increase the strength of the metal-ligand bond and hinder a dissociative mechanism of charge separation; but will favor an associative process by aiding new bond formation with an entering group.

2. **Increasing size of the central metal atom** is expected to weaken the metal-ligand bond and also facilitate the accommodation of an entering group, hence an increase of rate is predicted irrespective of mechanism.

3. **Changes in charge or size of the entering nucleophile** have no effect on the rate of dissociative process.

4. **In an associative process, increased charge of the substitute** will increase the rate by promoting new bond formation; but increased size will impede bond formation

5. **Increase in (negative) charge of the leaving group** will reduce the rate of substitution; bond breaking and also bond formation are rendered more difficult due to the smaller effective positive charge on the central metal.

6. **An increase in size of the leaving group** will make the rupture of the metal-ligand bond easier and assist a dissociative process; but the rate of reaction via an associative mechanism will be reduced due to difficulty in expanding coordination number.

7. **A greater negative charge on the non-labile ligands** will help a dissociative process by repelling the reactive group but, since bond formation is made more difficult, will decrease the rate of an associative process.

8**. Steric strain resulting from increasing the size of the non-reactive ligands** will assist a dissociative process but by hindering the expansion of coordination number, will decrease the rate via an associative mechanism.

10.5 SUMMARY

- To study about Anation Reactions.
- To study about Substitution Reactions.
- To knowledge about on their Metal - Ligand Substitution reactions in octahedral complexes and their factors

10.6 SELF-ASSESSMENT QUESTIONS

1. Define anation reactions with suitable examples.
2. Write about Substitution Reactions.
3. discuss about Metal - Ligand Substitution reactions and their factors influencing octahedral substitution reactions.
4. write the factors influencing octahedral substitution reactions.

10.7 REFERENCE BOOKS

1. Organometallic chemistry, R.C. Mehrotra and A. Singh. New Age International.
2. Advanced Inorganic Chemistry, Cotton and Wilkinson, Wiley Eastern.
3. Inorganic Reaction Mechanism, Basolo and Pearson, Wiley Eastern
4. Inorganic Chemistry, Huheey. Harper and Row.
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6. Inorganic chemistry, K.F. Purcell and J.C. Kotz, Holt Saunders international.

Prof. K. Rambabu

LESSON – 11

TRANS EFFECT ON SUBSTITUTION REACTIONS IN SQUARE PLANAR COMPLEXES

11.0 OBJECTIVES

After studying this lesson, you should be able to:

- To study about Ligand substitution reactions in square planar complexes.
- To study about Factors effecting rate of substitution in square planar complexes.
- To knowledge about on their Trans effect involved in other groups in the complex.

STRUCTURE

11.1 LIGAND SUBSTITUTION REACTIONS IN SQUARE PLANAR COMPLEXES

Square complexes are formed by d^8 metal ions of Pt(II), Pd(II), Ni(II), Au(III), Rh(I) & Ir(I)

1) Nickel forms both square-planar and tetrahedral complexes while Pt and Pd from only square planar complexes.

2) Ni(II) compounds undergo substitution reactions at rates 106 times faster than Pt(II) complexes.

3) Pt(II) is more stable to oxidation than Rh(I) or Ir(I) In view of these observations, the ligand substitution reactions of Pt(II) complexes are studied in detail.

For example : $[Pt(NH_3)_3Cl]^+ + Y^- \rightarrow [Pt(NH_3)_3Y]^+ + Cl^-$

The kinetics corresponds to a two term rate law;

$$\text{Rate}= -\frac{d_{[Complex]}}{dt} = k_s[complex] + k_Y[complex][Y^-]$$

where, s is for solvent which indicates that the reaction proceeds through two parallel paths, Solvent path:

$$[\mathrm{Pt(NH_3)_3}Cl]^+ + \mathrm{H_2O} \xrightleftharpoons{\text{slow, k}_\text{s}} [\mathrm{Pt(NH_3)_3}H_2O]^{2+} + \mathrm{Cl}^-$$

$$[\mathrm{Pt(NH_3)_3}H_2O]^{2+} + \mathrm{Y}^- \rightarrow [\mathrm{Pt(NH_3)_3}Y]^+ + H_2O$$

a). Direct replacement of ligand by incoming nucleophile

$$[Pt(NH_3)_3Cl]^+ + Y^- ===== [(NH_3)_3Pt\!<^{\mathrm{Y}}_{\mathrm{Cl}}] \xrightarrow{fast} [Pt(NH_3)_3Y]^+ + Cl^-$$

$$\text{So, rate}= -\frac{d[complex]}{dt} = k_s[complex] + k_Y[complex][Y^-]$$

$$= \{\mathrm{k_s} + \mathrm{k_Y}[Y^-]\}[complex]$$

This rate law shows that the substitution in square planar complexes proceeds by associative mechanism.

11.1.1 Evidences in favor of Associative Mechanism

(i) Variation of charge:

This has only a slight effect on the rate, contrary to the reaction of octahedral complexes were variation of charge effects rates drastically. Insensitivity of rate to charge on the complex is a characteristic feature of Associative process. **Table 11.1** Rate data (at 25 ºC and μ = 0.32 M) for aquathon and chloride exchange of amminechloroplatinum (II) complexes.

Table 11.1: Insensitivity of rate of Associative process

Complex	$10^5 k_{H_2O}, s^{-1}$	$10^5 k_{Cl^{-1}}, M^{-1}s^{-1}$
$[PtCl_4]^{2-}$	3.9	< 3
$[Pt(NH_3)Cl_3]^-$	5.6	< 3
Trans-$[Pt(NH_3)_2Cl_2]$	9.8	> 8
$[Pt(NH_3)_3Cl\ ]^+$	2.6	7

In Associative process bond making and bond breaking are of equal importance.

In Associative process bond making and bond breaking are of equal importance.

ii) Increase in Steric Hindrance

Increase in steric hindrance normally increases the rate of dissociative processes. But in these reactions with increase in steric strain, there is a decrease in reactivity.

Ex: Reactions of a series of cis & trans [Pt (Pet)$_3$ RCl] complexes with pyridine in ethanol medium are considered. As R is varied from Phenyl to tolyl to mesityl the relative rate of cis and trans isomers is 100,000:200:1 and 30:6:1 respectively. Hence, the decrease in reactivity is an indication of an associative mechanism.

11.2 FACTORS EFFECTING RATE OF SUBSTITUTION IN SQUARE PLANAR COMPLEXES

1) Nature of entering group

2) Other groups in the complex, a. Ligands trans to the leaving group

b. Ligands cis to the leaving group

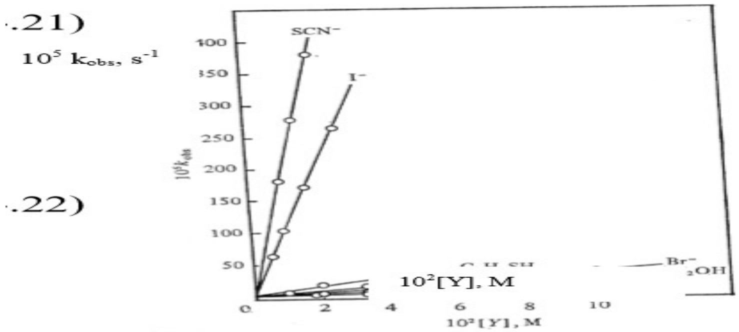
3) Nature of the leaving group

4) Effect of Central Metal ion.

11.2.1 Nature of entering group:

The entering group has a definite effect on rate of substitution in square planar complexes because they proceed by associative mechanism.

Ex: The rates of substitution reactions of trans-[Pt(Py)$_2$Cl$_2$] with various nucleophiles (Y) confirms to the expression **(Figure 11.1**)



trans [(PtPy)$_2$Cl$_2$] in methanol a
30°C as a function of the
concentrations of different
nucleophiles

Figure 11.1: trans-[Pt(Py)$_2$Cl$_2$] in methanol at 30 ^{o}C as a function of the concentrations of different nucleophiles

$$\text{Rate}= k_s\,[Pt(Py)_2Cl_2] + k_Y\,[Pt(Py)_2Cl_2][Y^-]$$
$$= \{k_s + k_Y\,[Y^-]\}[Pt(Py)_2Cl_2]$$

under high concentration of Y, the observed rate constant is defined as

kobs = ks + k_Y [Y^-]. A plot of kobs Vs [Y^-] gives a common intercept equal to sk and the slopes of lines give ky value for the particular nucleophile (Y).

Same type of plots is obtained for reactions of $[Pt(dien)Cl]^-$ with I^- Br^- Cl^- OH^- and $[Pt(dien)Br]^+$ with $SC(NH_2)_2$, SCN^-, I^-, N^{3-}, NO^{2-} Py, Cl^-, OH^-.

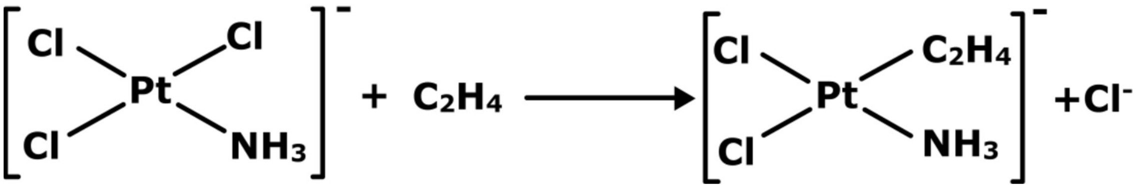
Therefore, to explain the reactivity Pearson's theory of hard acids and bases is considered. Accordingly soft acids and bases are easily polarized while hard acids and bases are not and hard acids prefer to co-ordinate with hard bases and soft acids with soft bases. Pt(II) is a soft acid and reacts rapidly with soft bases. From SCN^- to NO^{2-} the softness of the bases decreases and so k decreases.

11.2.2 Other groups in the complex:

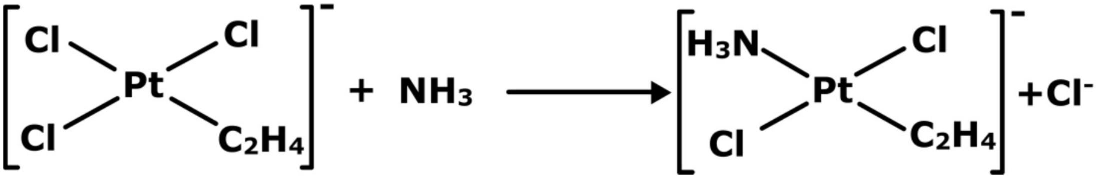
a) Ligand trans to leaving group-Trans effect :

The ligand present trans to the leaving group has considerable effect on the rate of substitution in square planar complexes. This is called trans effect and is purely kinetic one.

The trans effect gives the relationship between the reaction rate and the nature of the ligand trans to the leaving group. This effect was studies by Chernuyae (1926) to understand the kinetic behavior of a planner complex. The ability of a group to direct substitution into its opposite position (i.e. trans) is called the trans effect for ex.



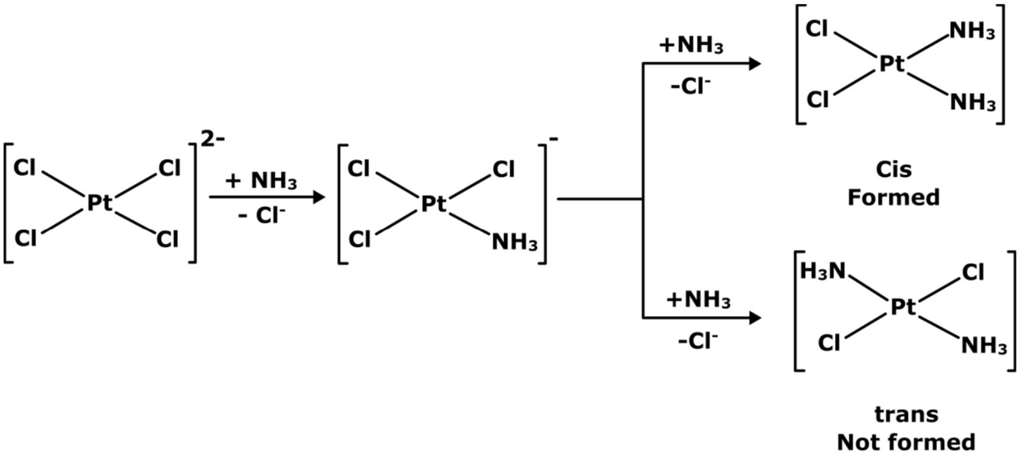
Since Cl^- has greater Trans effect than NH_3, hence Cl^- opposite to NH_3 do not replaced.



Since C_2H-has greater Trans effect than Cl^-, hence Cl^- opposite to C_2H_4 is replaced.

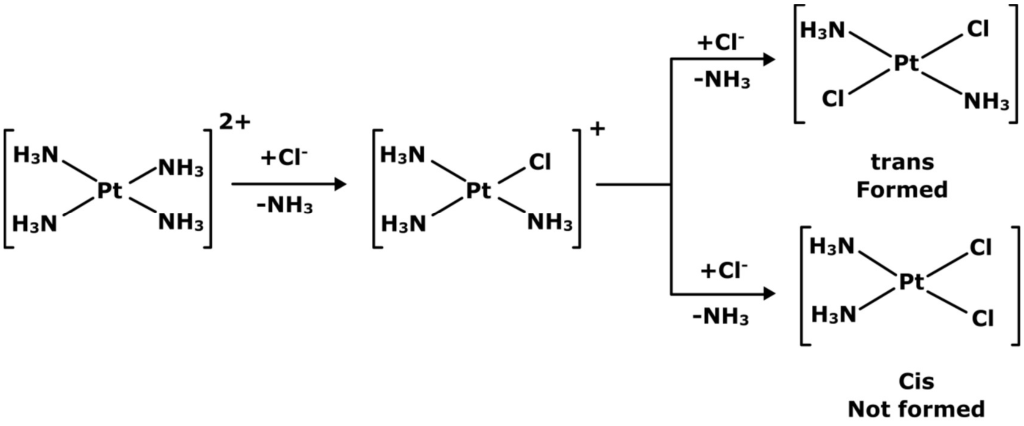
The Trans effect can easily determine the formation of products of fallowing reactions.

(a) Substitution of Cl^- ions from $[PtCl_4]_2$- by NH_3



Since all the four ligands (Cl^-) are identical hence one Cl^- ion will replace by one NH_3 molecule. In the next step trans effect of Cl^- is higher than NH_3, hence only one Cl^- will replace by NH_3; resulting the formation of cis-$[Pt(NH_3)_2Cl_2]$.

(b) Substitution of NH_3 from $[Pt(NH_3)_4]^{2+}$ by Cl^-



Since all the four ligands (NH_3) are identical hence one NH_3 will replace by one Cl^- ion.

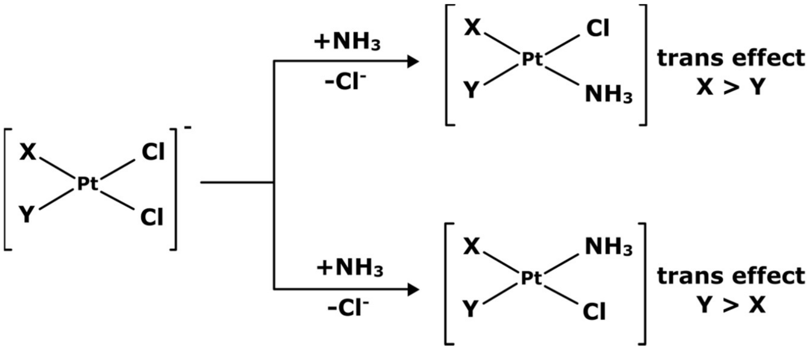
In the next step trans effect of Cl^- is higher than NH_3, hence only one NH_3 (i.e. trans to Cl^-) will replace by Cl^-; resulting the formation of trans-$[Pt(NH_3)_2Cl_2]$.

The formation of these products are governed by the substitution of ligands in the square planner complex trans to Cl^- ions; are called as trans effect. The group that directs the substitution trans to it, called as trans directing group.

The trans directing series

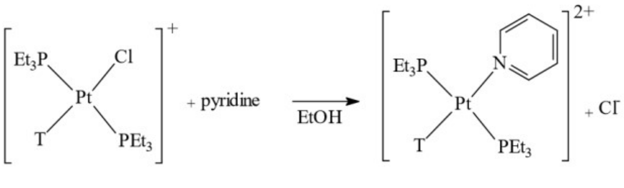
Langford and Gray find out a series of lignads for trans directing ability. The series is given as below

$CN^- \sim C_2H_4 \sim CO \sim NO > SC(NH_2)_2 \sim SR_2 \sim PR_3 \sim SO_3H^- \sim NO^-_2 \sim I^- \sim CNS^- > Br^- > Cl^- >$ Py $RNH_2 \sim NH_3 > OH^- > H_2O$.



It has been observed that the Trans directing ability of ligands such as CO, CN^-, NO etc. are higher because of presence of vacant π or π* orbital for accepting electron from filled metal orbital to form d_π-d_π or d_π-p_π type of metal-ligand bond. The π-bonding ability is directly effects the ability of trans effects; more will be π-bonding ability of ligands, higher will be the trans effect. However, the ligands such as H_2O, NH_3, Cl^- etc.; due to lack of π-bonding ability their trans directing ability is govern by the polarisability. Higher will be polarisability, more will be ability to trans effect.

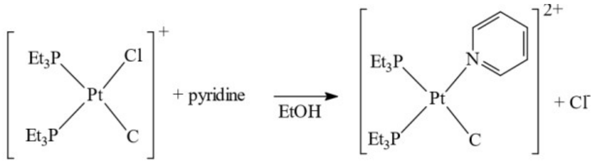
b. Ligands cis to leaving group: The cis effect is less marked compared to trans effect.



The relative ordering of trans labializing effects measured against T = Cl as the standard case T = $H^{-} > CH_3^{-} > C_6H_5^{-} > Cl^{-}$.

$$\frac{k_{(Y)}(T)}{k_{(Y)}(Cl^{-})} = > 10^4 \quad 1700 \quad 400 \quad 1.0$$

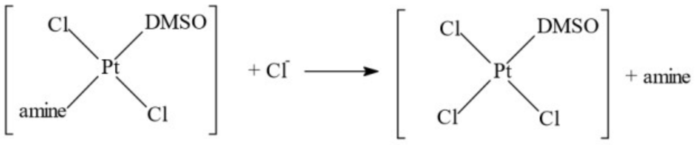
In contrast, the cis effect of these same ligands is in the same order but is considerably less.



C = $CH_3^{-} > C_6H_5^{-} > Cl^{-}$

$$\frac{k_Y(C)}{k_Y(Cl)} = 3.6 \quad 2.3 \quad 1.0$$

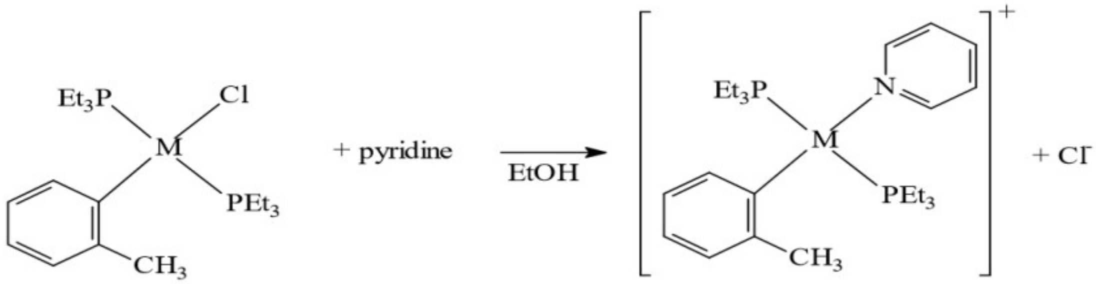
11.2.3 Nature of leaving group: The nature of the leaving group can effect the rate of substitution reaction.



The displacement of a wide variety of amines was found to proceed by both k_Y and ks paths. Here the rate of substitution depends on the basicity of amine group. As the basicity of amine increases the strength of the bond increases and the rate of substitution decreases. So, there is an excellent correlation between the pKa of the leaving group and log ks. This implies that bond breaking is important in the rate-determining step.

11.2.4 Effect of central metal ion

The rates of substitution of trans-$[M(PEt_3)_2(O\text{-tolyl})Cl]$ where M = Ni, Pd and Pt with pyridine follow the order Ni(II) > Pd(II) > Pt(II). This order of reactivity is in the same order as the tendency to form five-coordinated complexes. More ready formation of a five coordinate intermediate complex leads to stabilization of transition state and to rate enhancement.



for M = Ni, $k_y = 33\ M^{-1}s^{-1}$

for M = Pd, $k_y = 0.58\ M^{-1}s^{-1}$

for M = Pt, $k_y = 6.7 \times 10^{-6}\ M^{-1}s^{-1}$

11.3 SUMMARY

- To study about Ligand substitution reactions in square planar complexes.
- To study about Factors effecting rate of substitution in square planar complexes.
- To knowledge about on their Trans effect involved in other groups in the complex.

11.4 SELF-ASSESSMENT QUESTIONS

1. Define Trans effect on substitution reactions in square planar complexes.

2. Explain the ligand substitution reactions in square planar complexes.

3. discuss the importance of effect of central metal ion in complexes.

11.5 REFERENCES BOOKS

1. Organometallic chemistry, R.C. Mehrotra and A. Singh. New Age International.

2. Advanced Inorganic Chemistry, Cotton and Wilkinson, Wiley Eastern.

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LESSON - 12

REDOX REACTIONS: ELECTRON TRANSFER REACTIONS; OUTER SPHERE MECHANISM, CROSS REACTIONS AND MARCUS –HUSH EQUATION, INNER SPHERE MECHANISM, COMPLEMENTARY AND NON - COMPLEMENTARY REACTIONS

12.0 OBJECTIVES

After studying this lesson, you should be able to:

- To study about redox reactions in transition metal complexes.
- To study about Inner sphere and Outer sphere Mechanism involved in transition metal complexes.
- To knowledge about on cross over reactions.
- To understand about Marcus-Cross-Relation reactions.
- To know about the differentiation of Complementary and Non - Complementary Reactions

STRUCTURE

12.1 INTRODUCTION

The redox reactions are basically electron transfer reactions can be chemically defined as '*It is the study and manipulation of valence electrons of atoms or molecules*'. In principle, redox reactions are considered as electron-transfer reactions however mechanistic studies have demonstrated that in some of the redox reactions transfer of atoms or ions also takes place. Redox Reactions needs straightforward transfer of electrons such as a) electron transfer takes place from one metal to another in electrochemical cell, b) transfer of group of ligands along with their electrons that can efficiently oxidize or reduce a metal centre. Prior to define the concept, one must understand the meaning of oxidation and reduction. Redox reaction literally visualizes the transfer of following species between two redox partners:

i) electron(s), ii) hydrogen atom, iii) hydride ion, iv) oxygen atom, v) chlorine atom etc.

12.2 REDOX REACTIONS IN TRANSITION METAL COMPLEXES

The reactions in which the electron transfer reactions takes place from one atom to another metal atom is known as electron transfer reactions. These are two types

1. one e^- transfer reactions, 2 . Two e^- transfer reactions

1. One e^- transfer reactions

The reactions in which two e^θ s are transferred from one metal atom to another metal atom are known as two e^θ transfer reactions.

a. Inner sphere mechanism (or) Bridged (or) Group transfer mechanism
b. Outer sphere (or) direct e^θ transfer mechanism.

2. Two e^- transfer reactions

The reactions in which two e^θ s are transferred from one metal atom to another metal atom are known as two e^θ transfer reactions.

a. Complementary Reactions
b. Non Complementary Reactions

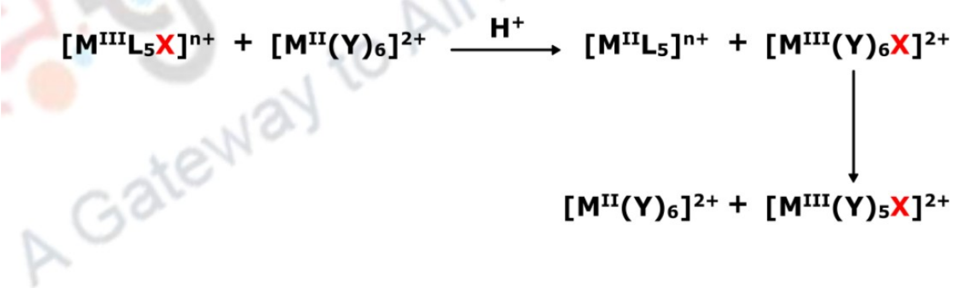
Under two main headings, a total of four sets of redox reactions are recognized i.e. outer sphere electron transfer reactions (direct electron transfer) and inner sphere electron transfer reactions (atom/group/ion transfer); including (1) Inorganic oxidant and inorganic substrate, (2) Inorganic oxidant and organic substrate, (iii) Organic oxidant and organic substrate and, (iv) Organic oxidant and inorganic substrate. The redox reactions concerning metal ions can be categorized on the basis of species transfer; whether the electron transfer incorporates ionic sphere or it involves coordination sphere of the metal complex. An example of metal complex based redox reaction is given below:

12.3 INNER SPHERE MECHANISM (OR) BRIDGED (OR) GROUP TRANSFER MECHANISM

The inner sphere reactions are those which incorporate “sharing/bridging” of at least one ligand for electron transfer and the reactants undergo change in complementary oxidation state. The reactants join together to result a single primary bond system through adopting ligand bridging pathway. There are two significant points for inner sphere reactions to take place; 1) The complex having at least one ligand with secondary binding site that is sterically favorable to the second metal ion is desirable (not compulsory) condition for inner sphere reactions; 2) Complex receiving the ligand must be labile in terms of expanding its coordination number at the time of electron transfer. Therefore, such reactions can be considered to be mediated by bridging ligand. Unlike to that for outer sphere mechanism, the coordination sphere of the complex participates in the inner sphere mechanism and atom/group/ion transfer occurs.

The redox process can plausibly be accomplished through various routes for polyatomic bridging ligands while incoming metal binds with just one of the diverse bridging ligands available. Reaction between $[(NH_3)^5Co(-NC_6H_4CONH_2)]^{3+}$ and $[Cr(H_2O)_6]^{2+}$ possesses two probable remote binding sites. The activated complex has been structurally authenticated that incorporates bonding of $[Cr(H_2O)_6]^{2+}$ with the remote carbonyl moiety. A major deliberation deals with the atomic geometry upon chelation with the activated complex in due course of reaction.

The general representation of inner sphere reactions as follows:



$$[M^{III}L_5X]^{n+} + [M^{II}(Y)_6]^{2+} \xrightarrow{H^+} [M^{II}L_5]^{n+} + [M^{III}(Y)_6X]^{2+}$$

$$\downarrow$$

$$[M^{II}(Y)_6]^{2+} + [M^{III}(Y)_5X]^{2+}$$

L = Ligand (generally NH_3); X = bridging ligand; Y = Ligand (generally H_2O)

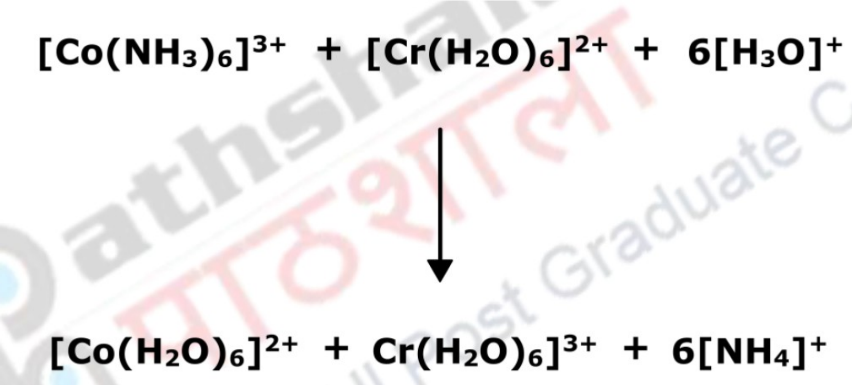
A representative reaction is given below:

$$[Co(NH_3)_5{}^*Cl]^{2+} + [Cr(H_2O)_6]^{2+} + 5[H_3O]^+$$

$$\downarrow$$

$$[Co(H_2O)_6]^{2+} + [Cr(H_2O)_5{}^*Cl]^{2+} + 5[NH_4]^+$$

The above reaction which involves inner sphere path proceeds with appreciably high rate (k = 6 x 105 $M^{-1}sec^{-1}$). However if we replace the Cl^- by NH_3 from Co(III) complex such as:



$$[Co(NH_3)_6]^{3+} + [Cr(H_2O)_6]^{2+} + 6[H_3O]^+ \longrightarrow [Co(H_2O)_6]^{2+} + Cr(H_2O)_6]^{3+} + 6[NH_4]^+$$

This reaction proceeds through outer sphere path with considerable slower rate ($k = 10^{-3}$ $M^{-1}sec^{-1}$).

The comparative inner sphere and outer sphere reaction pathways strongly recommend the presence of a bridging ligand in one of the metal complex reactants to precede the reaction through inner sphere pathway.

The bridging ligands are usually negatively charges monodentate ligands. i.e.: Cl-, Br-, I-, OH-, NCS- or SCN-, N3-, CN- etc.

Mechanism of inner sphere redox reaction

General considerations of inner sphere redox reaction mechanism are:

These reactions usually proceed in three significant steps:

1. Both the metal complexes should connect with a bridging ligand during the course of substitution. One of the reacting species should have a ligand that can form a bridge between both the metal complexes. The bridging ligand formation is basically intermediate therefore it is occasionally called a ligand-bridged mechanism. For instance, H_2O and NH_3 are monodentate ligands but these cannot serve as bridging ligands, whereas Cl^- and CN^- can act as bridging ligand.

2. The transfer of electron as well as sometimes transfer of ligand occurs depending upon the groups or ligands attached with the reactants. However, inner-sphere redox reactions are slower relative to that of outer-sphere reactions.

3. Eventually, the products are separated to form inert complexes.

The common reaction mechanism is:

$$\underset{\text{Ox}}{L_5M^{III}X} + \underset{\text{Red}}{M'^{II}Y_6} \underset{K_{-a}}{\overset{K_a}{\rightleftharpoons}} \left\{L_5M^{III}—X—M'^{II}Y_5\right\} + Y$$

$$\left\{L_5M^{III}—X—M'^{II}Y_5\right\} \xrightarrow{K_{ET}} \left\{L_5M^{II}—X—M'^{III}Y_5\right\}$$

$$Y + \left\{L_5M^{II}—X—M'^{III}Y_5\right\} \xrightarrow{K_d} L_5M^{II}Y + XM'^{III}Y_5$$

Or

$$Y + \left\{L_5M^{II}—X—M'^{III}Y_5\right\} \xrightarrow{K_d} L_5M^{II}X + M'^{III}Y_6$$

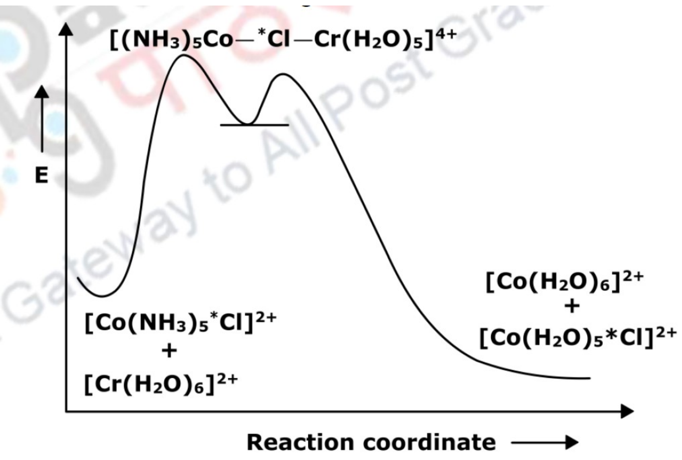
The bridging/sharing ligand mediates inner sphere electron transfer process. It is evident from the above depicted general mechanism that-

i) A ligand is shared/bridged between oxidant and reductant both in the precursor and successor complexes.

ii) The electron transfer takes place between both the metals only after activation through bridging of the ligand.

iii) The transfer of ligand may also occur between metal complexes however it is not a essential requirement**.**

The slowest step is the electron transfer process which is the rate determining step. However, in general, rate determining step may be electron transfer step or bridge-breaking step or bridge-forming step. Majority of the inner-sphere redox reactions exhibits second order kinetics. The energetic of abovementioned reaction is given below:



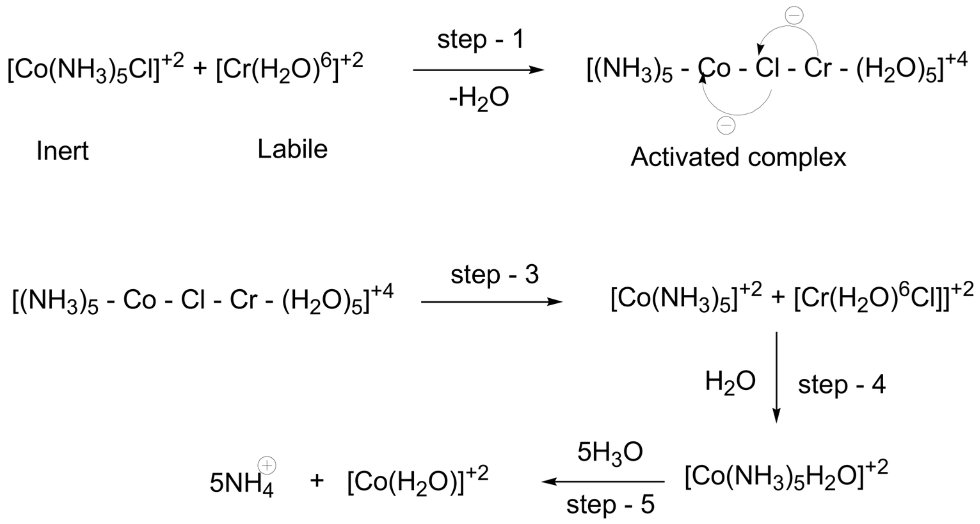
These are the e^{θ} transfer reactions in which e^{θ} transfer & ligand transfer occurs. The transfer of these two things is only possible by an intimate contact b/w the oxidant and Reductant. This requirement is fulfilled by an activated bridge b/w the two complexes. The activated bridge contains one ligand which is common to the coordination sphere of both the complexes and this ligand forms a bridge b/w them.

For Example: The Redox reaction of C_O (III) amine complex and aqua chromium complex in acidic media is as follows.

$$[Co(NH_3)_5Cl]^{+2} + [Cr(H_2O)_6]^{+2} + 5H_3O^+ \rightarrow [Co(H_2O)_6]^{+2} + [Cr(H_2O)_5Cl]^{+2} + 5NH^+_4$$

Oxidant	Reductant	Reduced product	Oxidized Product
Inert, low spin	Labile, high spin	Labile	Inert

Mechanism



The above reaction proceeds through the following steps.

Step–I The labile nature of $[Cr(H_2O)_6]^{+2}$ allows this complex to lose a molecule of water to form an activated bridged intermediate b/w C_O^{+3} & Cr^{+2} ion which are linked together through chloride ion. The bridged chloride ion in activated bridge complex is from the inert reactant $[C_O(NH_3)_5Cl]^{+2}$. This can be proved by taking labelled chloride ion (i.e $^{36}Cl^{\theta}$). If $[C_O(NH_3)_5Cl]^{+2}$ containing Cr^{+2}, it is found that after the reaction the product $[Cr(H_20)_5Cl]^{+2}$ is found to contain labeled chloride ion. Hence it indicate that the chloride ion is supplied $[C_O(NH_3)_5Cl]^{+2}$ Only.

Step–II : In the step – II there is a transfer of an e^{θ} from Cr^{+2} to Co^{+3} through the bridging chloride ion to convert Cr^{+2} to Cr^{+3} & Co^{+3} to Co^{+2}.

Step–III : The Cr^{+3} ion attracts chloride ion more strongly the Co^{+2}. Now chloride ion becomes a part of the Cr^{+3} complex. The activated bridge intermediate decomposes into Hexa Co-Ordinated chromium complex & Penta Coordinate cobalt amine complex.

<u>Step–IV:</u> As the cobalt amine complex (Penta Coordinated) being labile, if gets aquatic and transformed into hydrated complex to form $[Co(NH_3)_5H_2o]^{+2}$.

Step–V: The formed Hexa Co-Ordinate cobalt complex in acid media hydrolyzed to form a complete hydrated complex. Here the labile $[Co\,(H_2O)]^{+2}$ is converted into an inert $[Cr(H_2O)_5Cl]^{+2}$ to substitution and the inert $[Co(NH_3)_5Cl]^{+2}$ becomes labile $[Co(H_2O)_6]^{+3}$. The rate of the reaction is found to depend up on the concentrations of both the complexes.

$$\text{Rate} = K\ [\text{ oxidant}]\ \ [\text{reductant}]$$

$$\text{Rate} = K\ \ [Co(NH_3)_5Cl]^{+2}\ \ [Cr(H_2O)_5Cl]^{+2}$$

12.4 OUTER SPHERE MECHANISM (OR) DIRECT E^{Θ} TRANSFER REACTION

The metal complexes which do not go through substitution reaction involve outer sphere electron transfer reaction. It means none of the bonds are broken or formed in either of the metal complex reactants. In other words, these reactions include complementary change in the oxidation state of both the metals through a pathway where the ligand does not undergo "bridging" mode in the coordination sphere of the complexes. Therefore, coordination spheres of the metal complex reactants in an *outer-sphere reaction* stay intact. The favourable factor for an outer sphere reaction is the inertness of the complexes towards substitution over the time needed for a redox reaction to occur.

$$\underset{\textbf{oxidant}}{M^{(a+1)+}L_X} + \underset{\textbf{reductant}}{M^{b+}L_y} \rightleftharpoons \underset{\textbf{reduced}}{M^{a}L_X} + \underset{\textbf{oxidized}}{M^{(b+1)+}L_y}$$

Examples of outer sphere reaction:

$$[Fe^{II}(CN)_6]^{4-} + [Ir^{IV}Cl_6]^{2-} \longrightarrow [Fe^{III}(CN)_6]^{3-} + [Ir^{III}Cl_6]^{3-}$$

These reactions are genuinely quite fast and before Lx or Ly exchange or bridging occurs, redox process takes place.

The coordination sphere of the complex remains intact because reactants do not interact significantly with each other during the electron transfer; i.e. through space, diffusion control.

Mechanism

The mechanism of outer sphere redox reactions initiates with the formation of precursor complex which further undergo rearrangement route to become suitable for electron transfer process.

In these reactions, one of the reacting species utilizes the second coordination sphere or outer sphere of other reacting species. Both the reactants involved must be inert towards substitution to prefer outer sphere mechanism over that of inner sphere mechanism.

General mechanism:

$$[\mathrm{Ox}] + [\mathrm{Red}] \overset{K_A}{\rightleftharpoons} \{\mathrm{Ox} \| \mathrm{Red}\}$$

$$\{\mathrm{Ox} \| \mathrm{Red}\} \overset{K_{ET}}{\rightleftharpoons} \{\mathrm{Ox}^- \| \mathrm{Red}^+\}$$

$$\{\mathrm{Ox}^- \| \mathrm{Red}^+\} \overset{K_{diss}}{\rightleftharpoons} [\mathrm{Ox}^-] + [\mathrm{Red}^+]$$

$$K_{OBS} = K_A K_{EL}$$

In the complex form, it can be depicted as:

1. Precursor complex formation is basically that where both the reactants are weakly interacting to each other without changing their oxidation state and indeed in equilibrium.

$$M^{(a+1)+}L_X + M^{b+}L_y \overset{K_{eq}}{\rightleftharpoons} [M^{(a+1)+}L_X \text{----} M^{b+}L_y] \text{ Precursor complex}$$

2. Reorganization of the precursor complex to become suitable for electron transfer followed by relaxation of the successor complex.

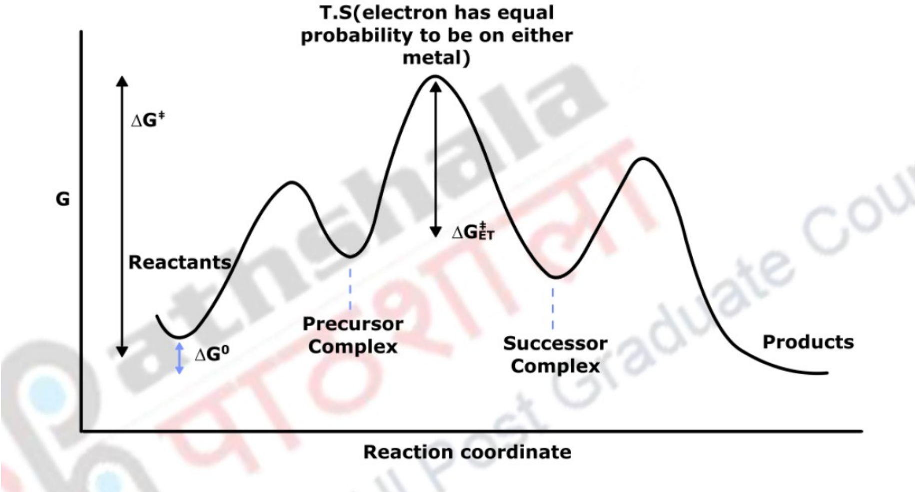
$$[M^{(a+1)+}L_X \text{-----} M^{b+}L_y] \xrightarrow{K_{ET}} [M^{a+}L_X \text{----} M^{(b+1)+}L_y] \text{ Successor complex}$$

3. Dissociation of the successor complex eventually leads to the formation of ultimate products where both the complexes have changed their oxidation state by one.

$$[M^{a+}L_x\text{-----}M^{(b+1)+}L_y] \xrightarrow{K_{diss}} [M^{a+}L_x] + [M^{(b+1)+}L_y]$$

The rate of reaction can be determined from step 2 which is the slowest step of the reaction whereas formation of precursor complex as well as dissociation of the successor complex is quite rapid.

The thermodynamic energy profile diagram for outer sphere reaction is given below:



$\Delta G^{\#} = \Delta Gt^{\#}$ (energy required to bring reactants together) + $\Delta G0^{\#}$ (energy required for solvent recombination) + $\Delta Gi^{\#}$ (energy needed for change in bond lengths by bringing orbitals in same energy level).

The outer sphere mechanism will operate in a system where both oxidizing agent & reducing agent are insert for substitution. Here the e^{θ} transfer occurs without any chemical change at a rapid rate than substitution. In the outer sphere mechanism ,the e^{θ} transfer will occur directly from one species to the other species and the ligands acts as conducting media.

Step –I The oxidant & Reductant combine to form a pre curser complex. But there is no bond b/w these two complexes.

Oxidant + Reductant // Oxidant / Reductant percussed complex

Step –II : Chemical activity of precursor complex loses by e^{θ} transfer and it relaxes to succussed complex i.e. formation of successor complex.

Eg:- Oxidant // Reductant // Oxidant$^-$ // Reductant$^+$

Eg: $[Fe^*(CN)_6]^{-4} + [Fe^*(CN)]^{-3} \rightarrow [Fe^*(CN)_6]^{-3} + [Fe(CN)]^{-4}$

Oxidant	+ Reductant	→ Reduced product	+ Oxidized Product
Inert, low spin	Inert, low spin	Inert, low spin	Inert, low spin
Fe-C bond	Fe-C bond	Fe-C bond	Fe-C bond
Length is high	Length is low	Length is low	Length is high

The rate of the above reaction can be studied by labelling either o the complexes with a radioactive isotope of "Fe" atom. As both the above reactants are inert for substitution, the close approach of these two complexes is impossible & hence the e^{θ} transfer takes place by outer sphere mechanism (or) tunneling mechanism". In the above reaction the normal Fe-C bond length in $[Fe(CN)_6]^{-3}$ is shorts than the Fe-C bond length in $[Fe^*(CN)_6]^{-4}$. After the transfer the Fe-C bond length in $[Fe(CN)_6]^{-3}$ is longer than the Fe-C bond length in $[Fe^*(CN)_6]^{-4}$. The rate of this reaction can be determined basing on π^* (or) σ^* nature of electron donor molecular orbitals of reductant and electron acceptor molecular orbitals of oxidant.

Mechanism

Step:1 $[Fe^*(CN)_6]^{-4} + [Fe^*(CN)]^{-3} \rightarrow [Fe^*(CN)_6]^{-3} // [Fe(CN)]^{-4}$

Precursor complex

Step:2 $[Fe^*(CN)_6]^{-3} // [Fe^*(CN)]^{-4} \rightarrow [Fe^*(CN)_6]^{-3} // [Fe(CN)]^{-4}$

Step:3 $[Fe^*(CN)_6]^{-3} // [Fe^*(CN)]^{-4} \rightarrow [Fe^*(CN)_6]^{-3} + [Fe(CN)]^{-4}$

In the above reaction electron transfer takes place rapidly. The slowness of the reaction is due to the large difference in the Co-N bond length in both complexes. Another important reason for the slowness of the reaction is the wide difference in electronic configurations of the two complexes i.e. one is low spin ($t_{2g}^6\ e_g^0$) and other is high spin (t_{2g}^5, e_g^2). Hence the transfer of e^{θ} is will result in the formation of high spin complexes into a low spin & low spin complexes into a high spin which requires high activation energy & so the reaction occurs at a slow rate.

12.5 CROSS REACTIONS

Unlike to the outer sphere and inner sphere redox reactions, cross reactions demand the reacting partners which are different to each other by more than the oxidation states. The very common example chosen from numerous known reactions of this kind is reduction of MnO_4^- by I^- to afford I_2 and again $MnO4_2^-$. As far as cross reactions in metal complexes are concerned, it requires one of the reacting complexes to be relatively inert with respect to the other complex. It is deeply associated with self-exchange reactions with the distinction that cross reaction involves two different metals. The general schematic representation is given below:

$$[ML_n]^{x+} + [M'L_n]^{y+} \rightleftharpoons [ML_n]^{y+} + [M'L_n]^{x+}$$

Moreover, the complex which is relatively inert in nature should not have a binding site (non-bonding electron pair should be absent), otherwise it will react with the labile partner. The reaction provided below represents cross reaction:

$$\underset{\text{Labile}}{[Cr(H_2O)_6]^{2+}} + [Ru(NH_3)_6]^{3+} \xrightarrow{K_{21} = 2 \times 10^2\ M^{-1}\ s^{-1}} [Cr(H_2O)_6]^{3+} + [Ru(NH_3)_6]^{2+}$$

Although, replacing Cr(II) by V(II) from above reaction another cross reaction is obtained where $[V(H_2O)_6]^{2+}$ is not that labile like $[Cr(H_2O)_6]^{2+}$.

$$[V(H_2O)_6]^{2+} + [Ru(NH_3)_6]^{3+} \xrightarrow{K = 1.3 \times 10^{3}\ M^{-1}\ s^{-1}} [V(H_2O)_6]^{3+} + [Ru(NH_3)_6]^{2+}$$

$$[V(H_2O)_6]^{3+/2+}\ E^0 = -\ 0.255V$$

Some other cross reactions are also given below:

$$[Os(bipy)_3]^{2+} + [Mo(CN)_8]^{3-} \longrightarrow [Os(bipy)_3]^{3+} + [Mo(CN)_8]^{4-}$$

$$[Fe(phen)_3]^{3+} + [Fe(CN)_4]^{4-} \longrightarrow [Fe(phen)_3]^{2+} + [Fe(CN)_6]^{3-}$$

$$[IrCl_6]^{2-} + [Fe(CN)_6]^{4-} \longrightarrow [IrCl_6]^{3-} + [Fe(CN)_6]^{3-}$$

The thermodynamic and kinetic data for a couple of self-exchange reactions are compared with cross-reaction data by Marcus-Hush theory. The data for cross reaction lie between the two self-exchange counterparts. Determination whether the reaction proceeds through an outer sphere mechanism is also done on the basis of this theory.

The equilibrium constants for self-exchange type reactions are given as k_{11}, K_{22} etc and for cross reactions equilibrium constants are given as k_{12}, K_{21} etc. Likewise, standard Gibbs energy of cross reactions is denoted as $\Delta G°_{12}$, $\Delta G°_{21}$ etc.

For self-exchange reactions $\Delta G° = 0$ whereas for cross reactions $\Delta G° \neq 0$.

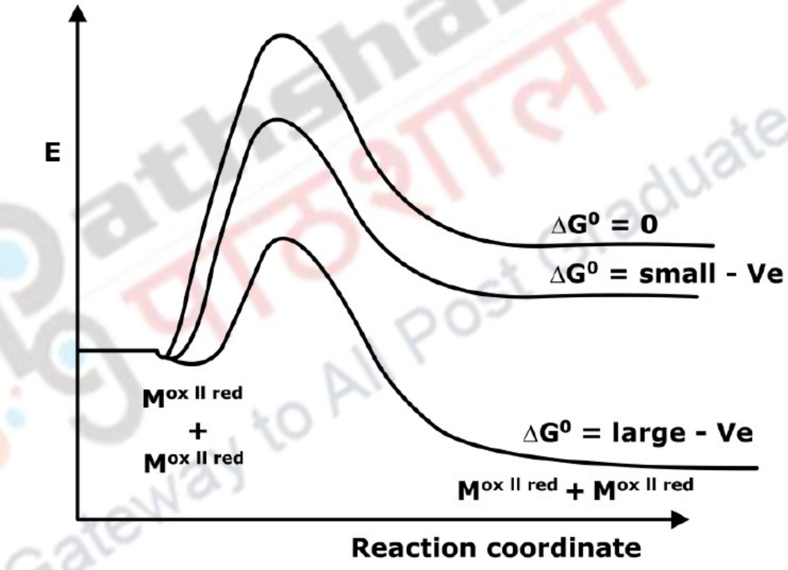
Gibbs free energy of activation ($\Delta G^{\#}$) is symbolized by the equation given below:

$$\Delta G^{\#} = \Delta_w G^{\#} + \Delta_s G^{\#} + \Delta_0 G^{\#} + RT \ln (k'T/hZ)$$

- $\Delta_w G^{\#}$ = Energy related to repulsion of ion in bringing the oxidant and reductant partners close together
- $\Delta_0 G^{\#}$ = Energy related to the change in M-L bond distances
- $\Delta_S \Delta G^{‡}$= Energy related to the solvent rearrangements

T = Temperature (K)
R = Gas constant
K’ = Boltzman’s constant
h = Planck’s constant
Z = effective collision frequency in solution ~ 10^{11} dm^3 mol^{-1} s^{-1}

ln (k’T/hZ) = accounts for the energy lost in the formation of the encounter complex.



12.6 MARCUS-CROSS-RELATION

An equation was illustrated by Rudolph A. Marcus pertaining to the electron transfer as well as for the calculation of associated rate constant. The basic hypothesis behind deriving this equation is the solvation additivity and the vibration barrier of reacting couples: Marcus equation which generally expresses the rates of outer sphere electron transfer relating to free energy change is given by:

$$K_{12} = \sqrt{k_{11} \times k_{22} \times K_{12} \times f_{12}}$$

(K = equilibrium constant, k = rate constants, for the self-exchange reactions, f = correction term for the free enthalpy differences between two educts. k_{11}, k_{22}, k_{12} and K_{12} can be acquired experimentally. Alternatively, k_{11} and k_{22} can be obtained theoretically as:

$$k = \kappa Z\, e^{-\Delta G^{\#}} /RT$$

$$K_{12}\ \text{experimental} \cdot E_{\text{cell}}$$

Parameter f is generally close to 1 and is given by:

$$\log f = \frac{(\log k_{12})^2}{4\log \frac{k_1 k_2}{z^2}}$$

Wherein z is collision frequency

Most significant equation for one electron transfer process at RT (25 °C),

$$\text{Log } k_{12} = 0.5\ (\log k_{11} + \log k_{22} + \frac{\Delta E^0}{0.059} + \log f\,)$$

For such cross reactions, one order magnitude to the rate is contributed if ΔE_0 increases by 0.12V.

The cross-reaction deviates from outer-sphere mechanism and may signify other than outer-sphere mechanism if calculated k_{12} value obtained from the abovementioned equation corroborates with experimental value of k_{12}.

The electron transfer barrier comprises two parts; i) the thermodynamic part ($G_{12}°$) and ii) the intrinsic contribution. The following equation represents activation of free energy for electron transfer ($G_{12}^{\#}$):

$$\Delta G^{\ddagger}_{12} = \frac{(\Delta G^{\ddagger}_{1} + \Delta G^{\ddagger}_{2})}{2} + \frac{\Delta G_{12}}{2}$$

Intrinsic thermodynamic contribution

As from the previous modules, it is evident that a bridging ligand that can serve as Lewis base is the one most essential condition for inner sphere mechanism. However, employing ambident ligands instead of normal Lewis base ligand one can differentiate whether ligand attack is proximity or remote. Therefore, two separate mechanisms are known for electron transfer through bridging/sharing ligands.

1) One step mechanism: it involves redox reaction between the redox couples only);

2) Two step mechanism: It involves bridging/sharing ligand in the redox or electron transfer reaction.

The activation of electron transfer reactions can be achieved either thermally wherein lower energy complex is preferred or photochemically wherein higher energy complex is preferred).

Given below is the example how to calculate the rate constant for cross reactions:

$$\underset{Ox}{MnO_4^-} + \underset{Red}{[Fe(CN)_6]^{4-}} \xrightarrow{K_{12} = ?} MnO_4^{2-} + [Fe(CN)_6]^{3-}$$

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-} \quad E^0 = 0.56V$$

$$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-} \quad E^0 = 0.36V$$

$$MnO_4^- + MnO_4^{2-} \xrightarrow{K_{11}} MnO_4^{2-} + MnO_4^- \quad k_{11} = 3600\ M^{-1}s^{-1}$$

$$[Fe(CN)_6]^{3-} + [Fe(CN)_6]^{4-} \xrightarrow{K_{22}} [Fe(CN)_6]^{4-} + [Fe(CN)_6]^{3-} \quad k_{22} = 300\ M^{-1}s^{-1}$$

Remeber,

$$\Delta G^{o} = -RT\ln K$$

also, $\Delta G^{o} = -nF\Delta E^{o}$

Therefore,

$$-RT\ln K = -nF\Delta E^{o}, \qquad K = e^{\left(\frac{-nF\Delta E^{o}}{RT}\right)}$$

$$K_{12} = e^{\{38.94(\overset{ox}{0.56} - \overset{red}{0.36})\}} = 2.4 \times 10^{3}$$

$$k_{12} = (3600 \times 300 \times 2.4 \times 10^{3})^{1/2} = 5.1 \times 10^{4}\ M^{-1}s^{-1}$$

$$k_{exp} = 1.3 \times 10^{4}\ M^{-1}s^{-1}$$

12.7 COMPLEMENTARY AND NON - COMPLEMENTARY REACTIONS

Complementary Reaction:

If the oxidation states of reactants change by same number of units, then the reactions are called as “Complementary Reactions”. (or)

The Oxidation states of the reactants change by equal amount and the stoichiometries are 1:1 such reaction are called as “Complementary Reactions”.

A Consequence of such reactions is that only one molecule of each reactant is required to react.

Example:

Oxidant + Reductant → Oxidized product + Reduced Product

1. $Sn^{+2} + Tl^{+3} \rightarrow Sn^{+4} + Tl^{+}$
2. $Sn^{+2} + Hg^{+2} \rightarrow Sn^{+4} + Hg$

Non-Complementary Reactions: -

The Oxidation states of the reactants change by equal amount and the stoichiometries are not 1: 1 such reaction is called as “Non-Complementary Reactions”.

Example:

1. $2Fe^{+2}(aq) + Tl^{+3}(aq) \rightarrow 2Fe^{+3}(aq) + Tl^{+}(aq)$.

12.8 SUMMARY

- To study about redox reactions in transition metal complexes.
- To study about Inner sphere and Outer sphere Mechanism involved in transition metal complexes.

- To knowledge about on cross over reactions.
- To understand about Marcus-Cross-Relation reactions.
- To know about the differentiation of Complementary and Non - Complementary Reactions

12.9 SELF-ASSESSMENT QUESTIONS

1. Discuss about cross over reactions.
2. Write about Marcus-Cross-Relation reactions.
3. Differentiate Complementary and Non - Complementary Reactions.
4. Write the mechanism involved in Inner sphere and Outer sphere in transition metal complexes.
5. Explain Complementary and Non - Complementary Reactions.

12.10 REFERENCE BOOKS

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LESSON - 13

ELECTRONIC SPECTRA OF TRANSITION METAL COMPLEXES

13.0 OBJECTIVES :

After studying this lesson, you should be able to:

- To know the types of Electronic Spectra.
- To study about Selection Rules for Electronic Spectra.
- To study about Breakdown of selection rules
- To study about Term separation energy of d^n configuration

STRUCTURE

13.1 INTRODUCTION

Electronic spectra of complexes are useful in explaining and predicting the modern bonding theories. The spectra are also used to understand the nature of the electronic structure and bonding of coordination compounds. The vibrational and rotational levels are very close in energy. Hence it is very difficult to resolve them into separate absorption bands. But considerable broadening of the electronic absorption bands in d-d spectra takes place. Band widths are generally of the order of 1000-300 cm^{-1}. The spectrum of a colored solution is easily measured using a spectrophotometer.

13.2 TYPES OF ELECTRONIC SPECTRA

1) d-d or ligand field (LF) spectra

These spectra arise due to transitions between the split d levels of the central atom. These transitions range from 1000 to 3000 cm^{-1}.

2) Ligand to metal charge transfer (LMCT) spectra

These spectra These spectra arise due to transitions from MO’s, primarily located on the ligands to nonbonding or anti bonding MO’s primarily located on the metal atom.

3) Metal to ligand charge transfer (MLCT) spectra

These spectra arise due to transitions of electrons excited from nonbonding or anti bonding orbitals primarily located on the metal atom to anti bonding orbitals primary located on the ligands.

The intra ligand (IL) transitions

These occur due to the electronic transitions involving the electrons of one ligand orbital excited into another ligand orbital.

Ex: For SCN^- ligand, these occur in UV region. The above-mentioned transitions are theoretically possible, but not all of them are observed. A set of selection rules distinguish between the allowed and forbidden transitions. If at all the forbidden transition occurs, it takes place much less frequently, with a much lower intensity.

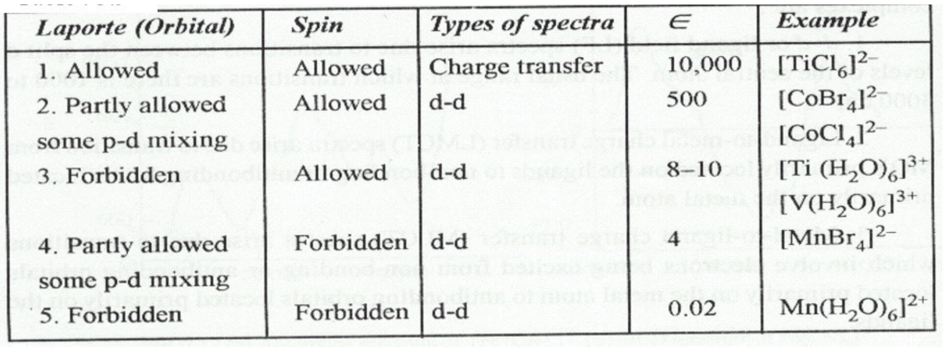
13.3 SELECTION RULES FOR ELECTRONIC SPECTRA

1. Laporte ‘orbital’ selection rule

Transitions which involve a change in the subsidiary quantum number, $\Delta_l = \pm 1$, are Laporte allowed transitions. Therefore, they have a high absorbance. Thus, for Ca, $s^2 \rightarrow s^1\ p^1$, +l changes by +1 and the molar absorption coefficient is 5000-10000 liters per mole per centimeter. Transitions within a given set of p-orbitals or transitions within a given set of d-orbitals involve only redistribution of electrons in the given sub shell. Hence, they are forbidden. If the molecule or ion has center of symmetry, the transitions between two g states or two u states are forbidden. The d-d transitions are Laporte forbidden as $\Delta_l = 0$. Therefore, spectra of much lower absorbance are observed ($\varepsilon_{\iota} = 510\ l/mol^{-1}/\ cm^{-1}$) because of slight relaxation in the Laporte rule. When a transition metal ion forms a complex, it is surrounded by ligands. Some mixing of d and p orbitals occurs. As the transition is no longer of pure d-d nature, spectra of lower absorbance are observed. Split d-d transitions are allowed due to some mixing of d and p orbitals and they do not possess a center of symmetry (**Table 13.1**).

Thus tetrahedral complexes like $[MnBr_4]^{2-}$or asymmetrically substituted octahedral complexes like $[Co(NH_3)_5Cl]^{2+}$ are colored.

Table 13.1: Molar absorption coefficient for different types of transition



Laporte (Orbital)	*Spin*	*Types of spectra*	$\in$	*Example*
1. Allowed	Allowed	Charge transfer	10,000	$[TiCl_6]^{2-}$
2. Partly allowed some p-d mixing	Allowed	d-d	500	$[CoBr_4]^{2-}$ $[CoCl_4]^{2-}$
3. Forbidden	Allowed	d-d	8–10	$[Ti(H_2O)_6]^{3+}$ $[V(H_2O)_6]^{3+}$
4. Partly allowed some p-d mixing	Forbidden	d-d	4	$[MnBr_4]^{2-}$
5. Forbidden	Forbidden	d-d	0.02	$Mn(H_2O)_6]^{2+}$

The intemnsity of laporte allowed transistions is given by

$$-\log I/I_o = \varepsilon cl$$

Where I, I_0 are intensities of incident and transimitted light.

ε = molar extension co-efficient

C = concentration

l = path length

2. Spin selection rule

If $\Delta s = 0$, Transitions are allowed. Transitions are forbidden between states of different multiplicity ($\Delta s \neq 0$) . It means that the number of unpaired electrons should not be changed. The transition $s^2 \rightarrow s^1p^1$ is spin allowed only when the two electrons in the s1p1have the spins +1/2 or –1/2 (singlet state), But transitions to triplet state are not allowed. For the spin selection rule, there are fewer exceptions than for the Laporte selection rule.

For example, in $[Mn(H_2O)_6]^{3+}$, the d-d transitions are forbidden because each of the d orbitals are singly occupied. Thus, many Mn^{2+} compounds are white or pale pink. As the spin forbidden transitions are very weak, in the analysis of spectra of transition metal complexes, we consider only those excited states which have the same multiplicity as the ground state.

13.4 BREAKDOWN OF SELECTION RULES

1. spin forbidden rule:

Spin forbidden transitions take place due to spin orbit coupling because of spin orbit ccoupling changes will occur in the energies of different states because of slight mixing of two states (i.e. If singlet is mixed with triplet state). The ground state becomes 99 %, singlet & 1%

triplet and the excited state become 99 % triplet and 1 % singlet.

Hence the transitions may takes place between singlet and single, triplet & triplet due to spin orbit coupling. The breakdown of spin selection rule by spin-orbit coupling is called as heavy atom effect.

$^1T_1 \rightarrow {}^3T_2$ Allowed

$^1T_1 \rightarrow {}^3T_1$ Forbidden

$^3T_1 \rightarrow {}^1A_2$ Forbidden

2. Laporte forbidden rule

The breakdown of Laporte selection rule occurs due to mixing of orbitals on the metal in (or) due to vibrational electronic coupling.

If ‘d & p’ orbitals are mixed

$$\psi^1 = \psi\,(3d) + \alpha\psi\,(4p)$$

Where α = co-efficient of mixing

The center of symmetry will be removed as a result of vibronic coupling and hence the transitions are highly in active.

13.5 DETERMINATION OF TERM SYMBOLS AND GROUND STATE

The following procedure can be employed to determine the term symbols of the various energy states and for the ground state. The procedure shall be explained by taking some

Example 1: Filled subshells contribute nothing to L or S, because the sum of the s and ml values for a filled subshell is zero. Since S and L values are zero, the term symbol for such system is $^1S_0$. This is true for s^2, p^6 and d^{10} configurations.

Example 2: For incompletely filled subshells, the procedure is to write different possible ways in which the electrons can be arranged in the orbitals, represented by pigeon hole diagram. For example, for a p^2 system like carbon, the pigeon hole diagram can be represented as follows in **Table 13.2.**

Table 13.2: pigeon hole diagram for 2P system

M_L	**+2**	**+1**	**0**	**0**	**-1**	**-2**	**+1**	**0**	**-1**
-1			↓		↓	↓↑		↑	↑
0		↓		↓↑	↑		↑		↑
+1	↓↑	↑	↑				↑	↑	
S=	0	0	0	0	0	0	1	1	1

The rules for constructing such a pigeon hole diagram are:

1. Use one horizontal row for each value of m,
2. In each column, place the first electron with spin up,
3. The other electrons in each column are placed in rows above that of the first electron,
4. In subsequent columns, systematically place the electrons in higher rows until all possibilities have been exhausted;
5. The Pauli exclusion principle must be obeyed. The resultant mL values, which represent the sum of the m values, is indicated in the top row and total spin in the bottom row. In the above example, the mL values are +2, +1, 0, -1, -2 and 0 for S=0. Similarly, m_L values are +1, 0, -1 for S=1. The corresponding term symbols are D S P 1 1 3, and the ground state of an atom can be chosen, from various possible states.

By applying the following rules:

1. Of the Russel-Saunders states arising from a given electron configuration, and allowed by the Pauli's principle, the state with the lowest energy will be the one with the greatest multiplicity.
2. Of the terms with a given value of S, the one with the largest value of L lies the lowest in energy.
3. Of the states with given L and S values in a configuration consisting of less than half the electrons in a subshell, the state with the smallest value of J is of the lowest energy. For a configuration of more than half the electrons in a subshell, the state with the largest J is of the lowest energy.

According to the first rule, the p^2 system should have ^3P as the ground state. For this state the J values corresponding to L=1 and S=1 is 2, 1 and 0 and the term symbols are $^3P_2$, $^3P_1$ and $^3P_0$ Application of the third rule, infers that $^3P_0$ is the term symbol for the ground state. Thus, there are five microstates (^1S ^1D $^3P_2$, $^3P_1$ and $^3P_0$) for the p^2 system. The splitting of these microstates is shown in **Figure. 13.1**.

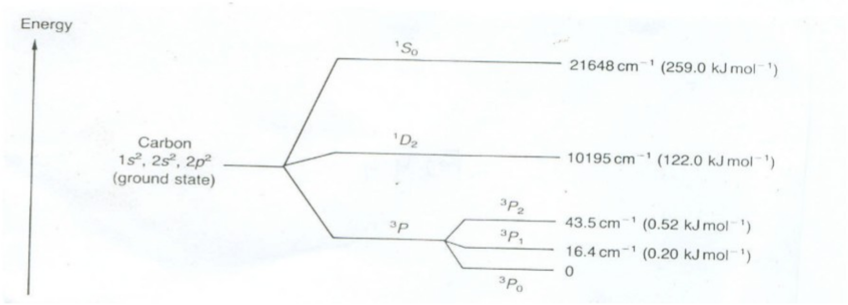
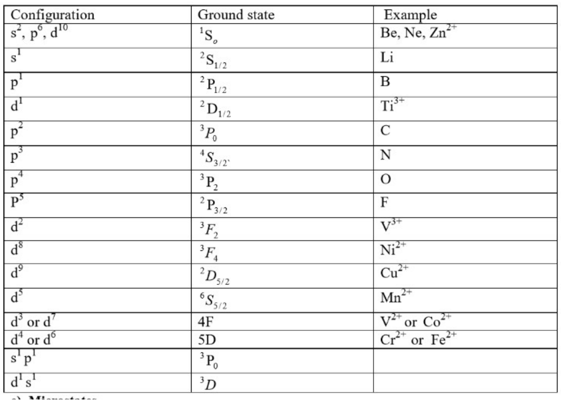


Figure 13.1: the five micirostates for the $1s^2$ $2s^2$ $2p^2$ configuration of carbon.

Hole Formalism

When a subshell is more than half full, it is convenient to work out the terms by considering the 'holes'- that is the vacancies in the various orbitals. The terms derived in this way for the ground state of oxygen, which has a p^4 configuration and hence two' holes' are the same as for carbon with a p^2 configurations, that is ^1S ^1D and ^3P. However, oxygen has a more than half filled subshell, and hence when Hund's third rule is applied, the ground state becomes 2 ^3P. In a similar way, by considering' holes', the terms which arise for pairs of atoms with p^n and p^{6-n} arrangements, and d^n and d^{10-n} give rise to identical terms (**Table 13.3**).

Table 13.3: The ground state term symbols for various electronic configurations



Configuration	Ground state	Example
s^2, p^6, d^{10}	^1S_o	Be, Ne, Zn^{2+}
s^1	$^2S_{1/2}$	Li
p^1	$^2P_{1/2}$	B
d^1	$^2D_{1/2}$	Ti^{3+}
p^2	$^3P_0$	C
p^3	$^4S_{3/2}$	N
p^4	$^3P_2$	O
P^5	$^2P_{3/2}$	F
d^2	$^3F_2$	V^{3+}
d^8	$^3F_4$	Ni^{2+}
d^9	$^2D_{5/2}$	Cu^{2+}
d^5	$^6S_{5/2}$	Mn^{2+}
d^3 or d^7	4F	V^{2+} or Co^{2+}
d^4 or d^6	5D	Cr^{2+} or Fe^{2+}
s^1p^1	$^3P_0$	
d^1s^1	^3D	

13.6 TERM SEPARATION ENERGY OF D^N CONFIGURATION:-

The term separation energies of d^n configuration can be explained by two types of parameters.

1. Inter electronic repulsion parameters.

2. Spin – orbit coupling parameters.

1. Inter electronic repulsion parameters:

The Inter electronic repulsion parameters are two types.

a) Slatter–condon parameter [F_0, F_2, F_4]

b) Racah parameters [A, B, C]

a) Slatter–Condon parameters:

Slatter–Condon parameters are also called as "Inter electronic repulsion parameters". A term is separated from the other term by certain energy due to inter electronic repulsion of the configuration. So it necessary to develop a theory of inter electronic repulsion the configuration.

$$A = F_0 - 49\ F_4$$

$$B = F2 - 5\ F_4$$

$$C = 35\ F_4$$

b) Racah parameter:

The Inter electronic repulsion which causes the bonding of spectral lines is expressed by the "Racah–parameters". The racah parameters are [A,B,C]. Racah parameters are used in the energy separation of term by the linear combination. But they are usually obtained for different metals the value of "B" is as follows.

Metal	**M^{+2}**	**M^{+3}**
Ti	695 cm^{-1}	-
V	755 cm^{-1}	81.6 cm^{-1}
Cr	810 cm^{-1}	918 cm^{-1}
Mn	860 cm^{-1}	965 cm^{-1}
Fe	917 cm^{-1}	1015 cm^{-1}

13.7 SUMMARY

- To know the various types of Electronic Spectra
- To study about the of selection rules and Breakdown of selection rules in electronic spectra.
- Knowing about Term separation energy of d^n configuration To study about application of metal clusters.

13.8 SELF-ASSESSMENT QUESTIONS

1. Write the various types of Electronic Spectra.
2. Discuss selection rules in electronic spectra.
3. Write about Breakdown of selection rules
4. Explain Term separation energy of d^n configuration.
5. Write about Racah parameters.

13.9 REFERENCE BOOKS:

1. Inorganic Chemistry Huheey, Harper and Row.
2. Modern Inorganic Chemistry, W. L. Jolly, McGrawHill.
3. Concise Inorganic Chemistry, J. D. Lee, ELBS.
4. Physical methods in Inorganic Chemistry, R.S. Drago. Affiliated East-West Pvt. Ltd.

Dr. K. Bala Murali Krishna

LESSON -14

LIGAND SPECTRA (d-d Transitions)

14.0 OBJECTIVES:

After studying this lesson, you should be able to:

- To know the Ligand field spectra (d-d transitions).
- To study about electronic spectra's for d^1, d^2, d^3 to d^9 complexes

STRUCTURE

14.1 Introduction to Ligand field spectra (d-d transitions)
14.2 Spectra of $d^1$and d^9 ions
14.3 Spectra of d^2 and d^8 ions
14.4 Summary
14.5 Self-Assessment Questions
14.6 Reference Books

14.1 INTRODUCTION TO LIGAND FIELD SPECTRA (D-D TRANSITIONS)

Cis-complexes of the type MA_4 B_2 and tetrahedral complexes do not have center of symmetry. So, d-d transitions in these complexes take place and strong absorption bands are observed. Similar is the case of tetrahedral complexes. Intensity of d-d transitions increases as octahedral complexes are changed to tetrahedral complexes.

For example, when excess of conc. hydrochloric acid is added to an aqueous solution of Co(II) salt, the colour changes from pale red of $[Co(H_2O)_6]^{2+}$ to blue of $[CoCl_4]^{2-}$

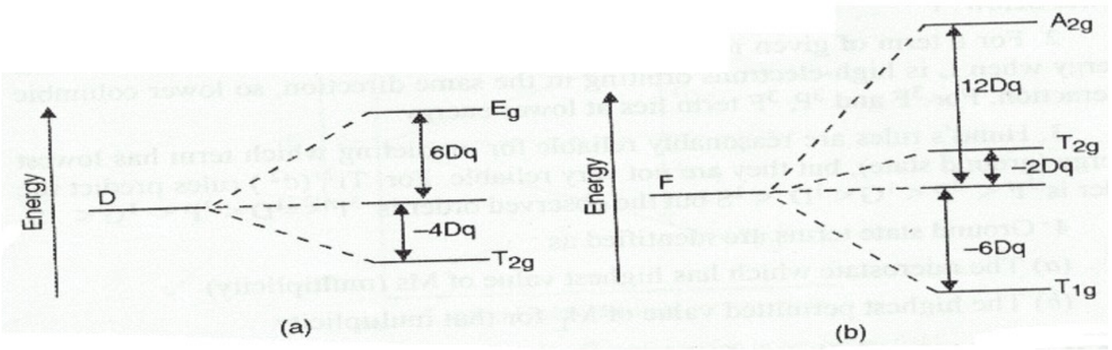


Figure 14.1: Ground and spectroscopic state of a) d^1 configuration, b) d^2 configuration

In the above **Figure 14.1 (a)** for a d^1 configuration, the ground state is a ^2D state. The t_{2g}

and e_g levels correspond to the T_{2g} and Eg spectroscopic states. In the **Figure 14.1 (b)** for a d^2 configuration, the ground state is a ^3F state and it is split into a triply degenerate T_{1g} state and a triply degenerate T_{2g} level and a single A_{2g} state.

14.2 SPECTRA OF D^{1}AND D^9 IONS

The spectra of the complexes of the ions of the two configurations are quite related. For a d^1 octahedral complex, only one transition from t_{2g} to eg is possible. A single absorption band corresponding to the process $t_{2g}{}^1eg^o \rightarrow t_{2g}{}^oe_g{}^1$ is observed. The absorption spectrum of $[Ti(H_2O)_6]^{3+}$ shows only one band with a peak at 20, 300 cm^{-1}. The magnitude of splitting Δ_o, depends upon the ligand.

For example, for $[Ti(H_2O)_6]^{3+}$ the peak occurs at 13000 cm^{-1}, for $[Ti F_6]^{3-}$ at 18900 cm^{-1}and for $[Ti(CN)_6]^{3-}$ at 22300 cm^{-1}.

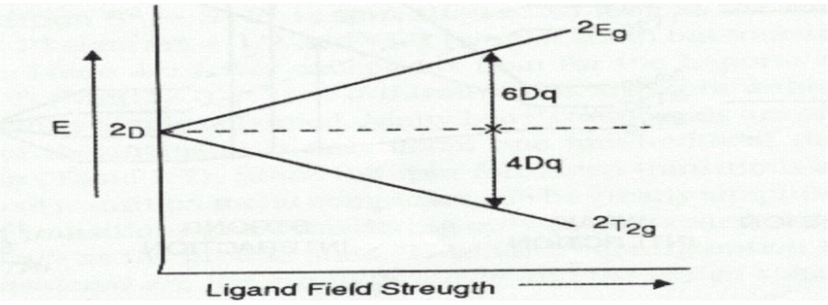


Figure 14.2: Splitting of energy levels for d^1 configuration in octahedral field

In the above **Figure 14.2**, the term symbol ^2D is the ground state term for a free ion with a d^1 configuration. Under the influence of an octahedral ligand field these splits into two states ^2Eg and $^2T_{2g}$. The two stats would be separated more as the ligand field strength increases.

Octahedral complexes of ions with d^9 configuration like $[Cu(H_2O)_6]^{2+}$ can be treated as the octahedral complexes of ions with d1 configuration, like Ti^{+3} complexes. In the d^1 case, the single electron is in the lower t_{2g} level. But in the d^9 case, a single hole is in the upper e_g level. The transition in d1case is promoting an electron from the t_{2g} level to the e_g level. But in the d^9 case, the promotion of one electron can be taken as the transfer of a hole from eg to t_{2g}. Thus, the energy diagram of the d^9 case is inverse to that of the d^1 case (**Figure 14.3**).

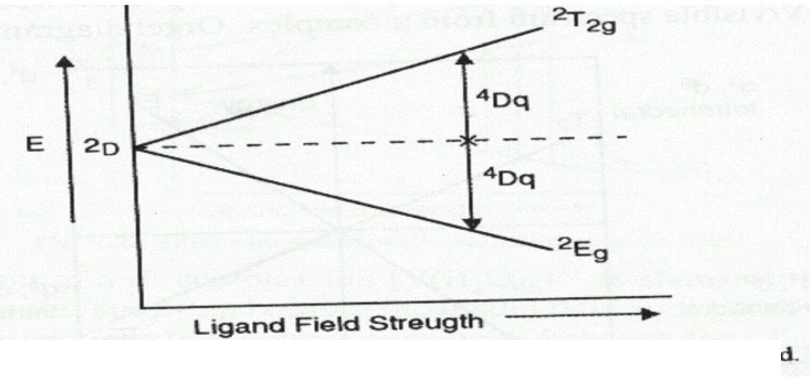


Figure 14.3: Splitting of energy levels for d^9 configuration in octahedral field

The energy level diagram of d^1 complexes in tetrahedral field is the inverse of the diagram of octahedral field. Similar is the d^9 octahedral case. But the amount of splitting in a tetrahedral field is only about 4/9 Δ_o.

For d^1 tetrahedral complex the electronic transition is $^2E \rightarrow {}^2T_2$ and for d^9, it is $^2T_2 \rightarrow {}^2E$. As there is a no center of symmetry in tetrahedral complexes, no g or u designation is necessary. In d^5 metal ion, each d orbital, has one electron and the metal ion is spherically symmetrical similar to d^0 ion or d^{10} ion.

Removal of one d electron from such complex results in a weak field d^4 complex. This is analogous to removal of a d electron from a d^{10} metal ion complex. Addition of a d-electron results in a weak d^6 complex. This addition is analogous to addition of an electron to a d^0 complex (**Figure 14.4**).

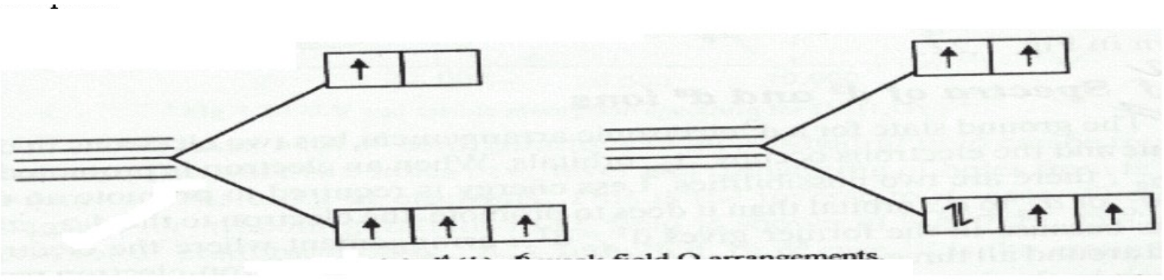


Figure 14.4: Splitting energy levels for d^4 and d^6 configuration weak field in octahedral arrangements

The transitions involving reversal of electron spin are forbidden transitions. They give extremely weak bands. For d^6 weak field complexes, the paired electron in t_{2g} level whose spin is opposed to the spin of all the other electrons undergoes the only permitted transition to the e_g

level. The energy level diagram is same as that of d^1 case. The energy level diagram for d^4 is same as the d^9 case. Similar is the spectral behavior of d^4 and d^6 tetrahedral complexes.

14.3 SPECTRA OF D^2 AND D^8 IONS

The d^2 electronic arrangement in ground state has two electrons in different t_{2g} orbitals. There are two possibilities for the promotion of one electron $t_{2g}{}^2 \rightarrow eg^1\ t_{2g}{}^1$. To promote an electron from d_{xy} or d_{yz} to dz^2 orbital less energy is required. But to promote the electron to the d_{x2-y2} orbital more energy is required. In the first possibility, $d^1_{xy}\ d^1_{z2}$, the electrons are spread around all the three directions x, y and z. This results in the decrease of electron-electron repulsion. But in the second possibility, d^1_{xy}, d^1_{x2-y2} arrangement, the electrons are confined to xy plane only. If both electrons are promoted, another high energy state is formed.

For d^2 configuration, the ground state term is ^3F and excited state terms are ^3P (parallel spins) and ^1G,^1D,^1S (opposite spins). The transitions from the ground state to the three states, ^1G,^1D,^1S are spin-forbidden. They are very weak and can be ignored, The two remaining ^3F and ^3P have spin permitted transitions. In octahedral field, ^3P is transferred to $^3T_{1g}$ state and ^3F is split into $^3A_{2g} + {}^3T_{1g} + {}^3T_{2g}$. The energy level diagram is represented in **Figure 14.5**.

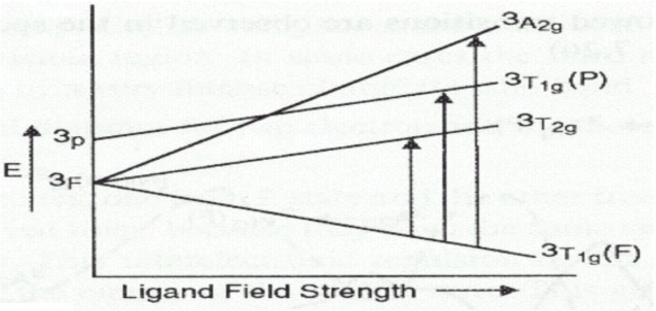


Figure 14.5: Energy diagram for d^2 configuration

Three transitions are possible from the ground state $^3T_{1g}$ (F) to $^3T_{2g}$, $^3T_{1g}$ (P) and $^3A_{2g}$ respectively. Therefore, three peaks appear in the spectrum.

In the spectra of a d^2 complex ion, $[V(H_2O)_6]^{3+}$, only two peaks occur. The ligand field strength of water results in very close transitions and they do not cross over the point between the $^3T_{1g}$(P) and $^3A_{2g}$ levels. Therefore, these two transitions are not resolved into two separate peaks. V^{3+} ion complexed with a different ligand would show the three peaks **(Figure 14.6)**.

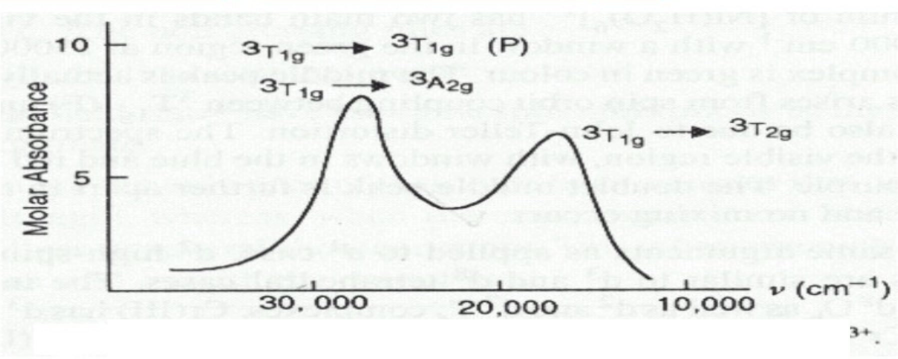
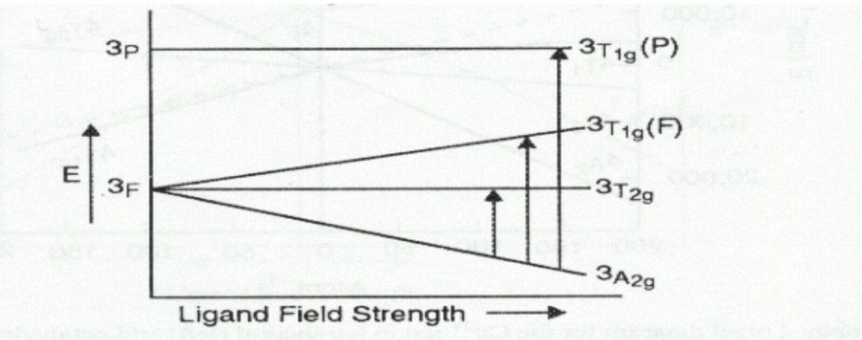


Figure 14.6: UV-Visible absorption spectrum of $[V(H_2O)_6]^{3+}$

Ni^{2+} complexes with d^8 configurations in an octahedral field can be treated in a similar way. Transferring of the two holes in the e_g level to t_{2g} level is equivalent to transferring of electrons This is the inverse d^2 case (**Figure 14.7**).



Energy level diagram for d^8 in O_h field (Triplet state only included).

Fig : 3.16

Figure 14.7: Energy level diagram for d^2 configuration in Octahedral (Triplet state only included)

The ground state term of d^8 configuration is $^3A_{2g}$. In both d^2 and d^8 cases ^3F is the ground state. Three spin allowed transitions are observed in the spectra of $[Ni(H_2O)_6]^{2+}$ and $[Ni\ (en)_3]^{2+}$ are in **Figure 14.8.**

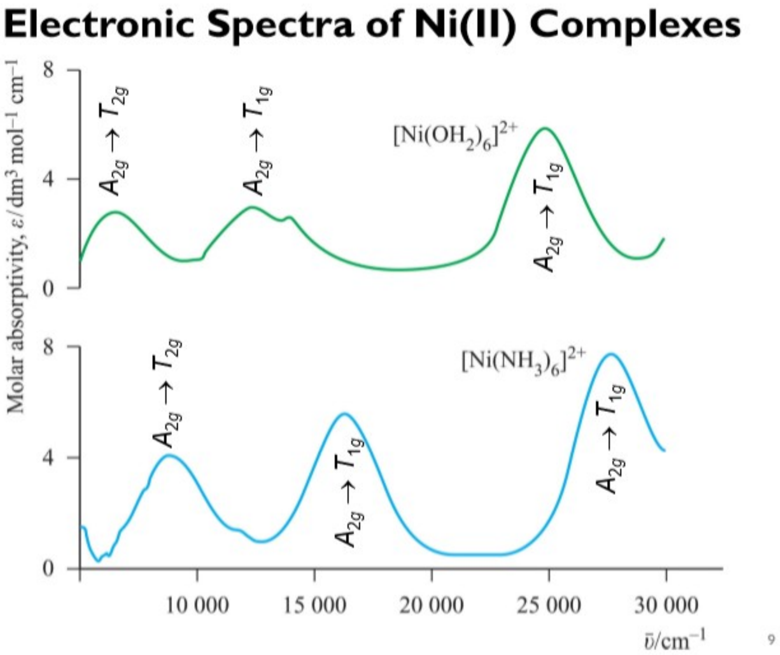


Figure 14.8: UV-Visible absorption spectrum for $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$

The spectrum has three bands as expected for a d^8 configuration. The main bands of the spectrum of $[Ni(H_2O)_6]^{2+}$ are in the visible region at 9000 cm^{-1} and 14000cm^{-1}. A window in the green region is at 25000cm^{-1} (~5500A°). Hence this complex is green in colour. The middle peak of the spectrum is a doublet. This may arise from the spin orbit coupling between $^3T_{1g}$ (F) and a nearby ^1E_g. This may also be due to Jahn-Teller distortion.

The spectrum of $[Ni(en)_3]^{2+}$ has one band in the visible region. It has two windows in the blue and red regions. Hence the complex is coloured purple. The middle peak of this spectrum is also a doublet. In strong field ethylenediamine, this is further apart and no mixing takes place. It can be found that d^2 high spin and d^7 octahedral energy diagrams are similar to d^3 and d^8 tetrahedral cases. The inverse diagram applies to d^3 and d^8 Oh as well as d^2 and d^7 Td complexes.

As Cr(III) has d^3 configuration, the spectra of Cr(III) complexes also has d^3 configuration. For the spectra of Cr(III) complexes, the ground state ^3F shows three absorption bands due to the transitions, $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{2g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{2g}$ (P). Cr(III) complexes show at least two well defined absorption peaks in the visible region. In some cases, a third band is also seen. But it is often hidden by the very intense charge transfer band.

14.4 SUMMARY

- To know the charge transfer spectra (d-d transitions).
- How to assign energy levels of electronic spectra's for d^1, d^2, d^3 to d^9 ions in octahedral and tetrahedral complexes.

14.5 SELF-ASSESSMENT QUESTIONS

1. Explain the charge transfer spectra involved in d^n configuration.
2. How to draw energy level diagram for d^1 and d^9 configuration in octahedral and tetrahedral complexes.
3. How to draw energy level diagram for d^2 and d^8 configuration in octahedral and tetrahedral complexes.

14.6 REFERENCE BOOKS:

1. Inorganic Chemistry Huheey, Harper and Row.
2. Modern Inorganic Chemistry, W. L. Jolly, McGrawHill.
3. Advanced Inorganic Chemistry, Cotton and Wilkinson, Wiley Eastern
4. Inorganic Reaction Mechanism, Basolo and Pearson, Wiley Eastern

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LESSON – 15

CORRELATION DIAGRAMS (OR) ORGEL DIAGRAMS (OR) ENERGY LEVEL DIAGRAMS

15.0 OBJECTIVES:

After studying this lesson, you should be able to:

- To know about the Orgel diagrams.
- To study about how to draw orgel diagrams for d^1, d^2, d^3 to d^9 configurations in octahedral and tetrahedral complexes.
- To lean about Orgel diagram for d^5 configuration in Octahedral and Tetrahedral complexes.

STRUCTURE

15.1 INTRODUCTION TO ORGEL DIAGRAMS

The Orgel diagrams depict the energies of states as a function of field strength Δ_0, the ground and excited states of the same multiplicity of a particular configuration is also represented with Orgel diagrams.

In these diagrams, excited states of multiplicities different from ground state are omitted. Only weak field or high spin are included. Hence the diagrams are quite simple. Orgel diagrams help to predict the number of spin-allowed absorption bands that can be expected in a UV-Vis spectrum of a complex.

15.2 SPECTROSCOPIC TERMS FOR ELECTRONIC CONFIGURATION

Configuration	**Ground state terms**	**Other terms**
d^1, d^9	^2D	-
d^2, d^8	^3F, ^3P	^1G, ^1D, ^3F, ^1S
d^3, d^7	^4F, ^4P	^2G, ^2D, ^2F, ^2P, ^2H
d^4, d^6	^5D	^3G, ^3P, ^3F, ^3H, ^1I, ^1F
d^5	^6S	^4G, ^4P, ^4D, ^4F,

15.3 MULLIKAN'S STATES FOR THE TERMS

Term	**Mullikan's states**
S	**A_{1g}**
P	**T_{1g}**
D	**$T_{2g} + E_g$**
F	**$A_{2g} + T_{1g} + T_{2g}$**
G	**$T_{1g} + T_{2g} + E_g$**
H	**$E_g + T_{1g} + T_{1g} + T_{2g}$**
I	**$A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$**

15.4 CORRELATION DIAGRAMS (OR) ORGEL DIAGRAMS (OR) ENERGY LEVEL DIAGRAMS

Postulates of Orgel Diagram

1. Orgel diagrams include two sets of graphs which include all the high spin cases of octahedral and tetrahedral complexes.

2. Orgel diagrams cover only the high spin cases.

3. Orgel diagrams are only for the quantative purpose

4. The following relationships are valid for the Orgel diagrams.

   * dn and dn+5 have the same diagram for octahedral field.

   * dn and dn+5 have the same diagram for tetrahedral field.

   * dn and dn+5 in an octahedral field is reverse to that of dn and * dn+5 for a tetrahedral field.

   * dn of octahedral field is same as that of d10-n of the tetrahedral field

   * dn of the tetrahedral field is same as that of d10-n of the octahedral field.

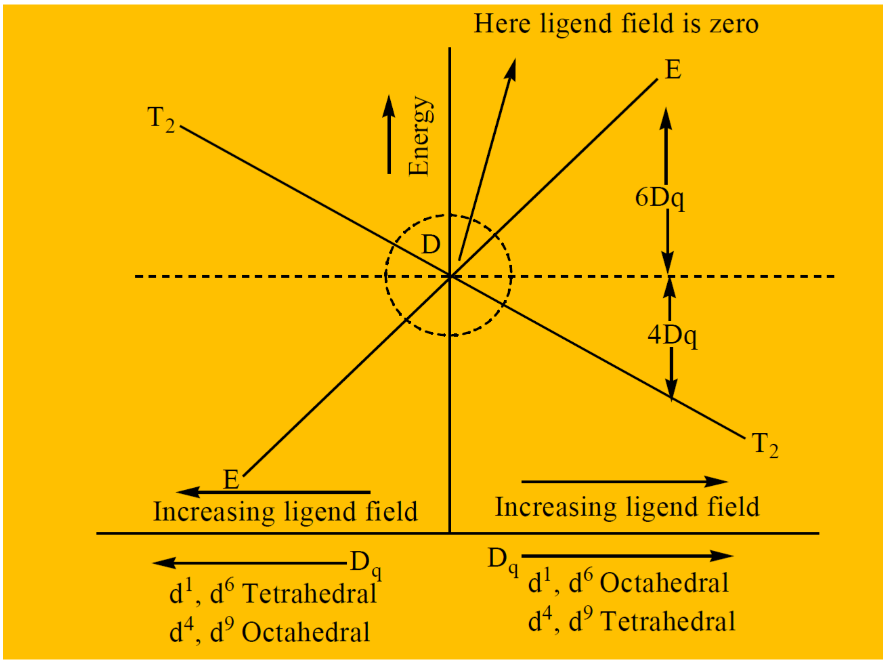
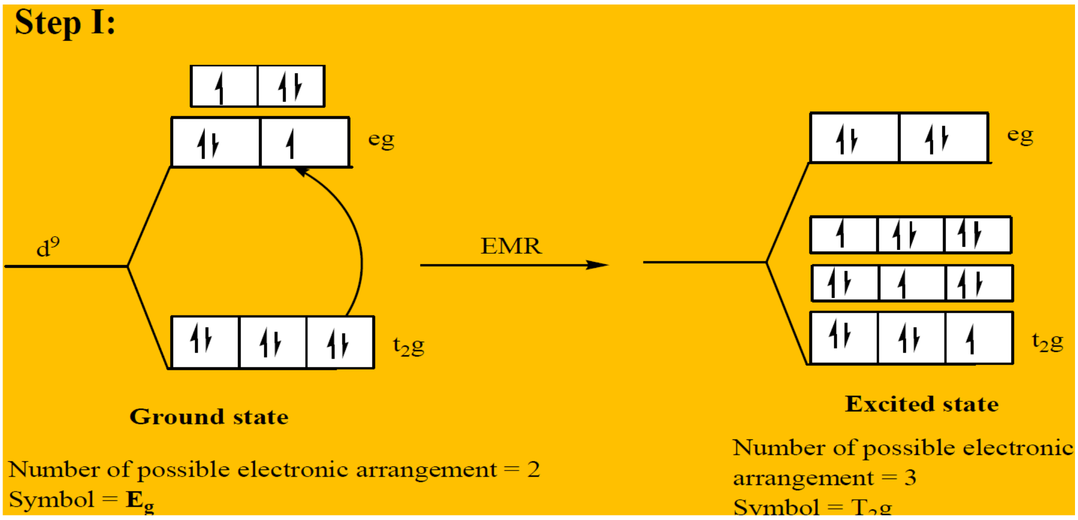


Figure 15.1: General representation of an Orgel diagram

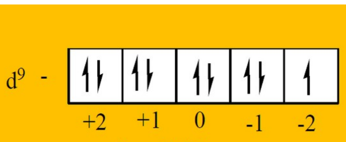
1. Orgel energy level diagram for the d^9 octahedral complexes:

Orgel energy level diagram for the d1 configuration containing

tetrahedral complexes can be explained in the three different steps, which are given below:



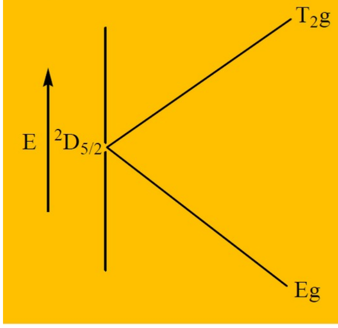
Step II:

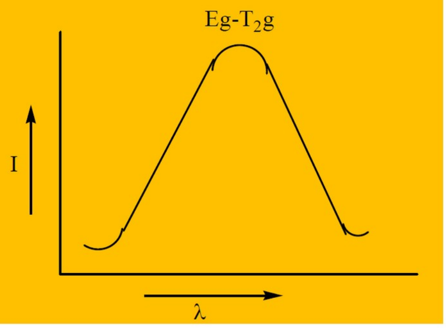


L = 2 (D)
S = 1/2
J = 5/2
M = 2

So term symbol for d^9 configuration = $^2\mathbf{D}_{5/2}$

Step III:

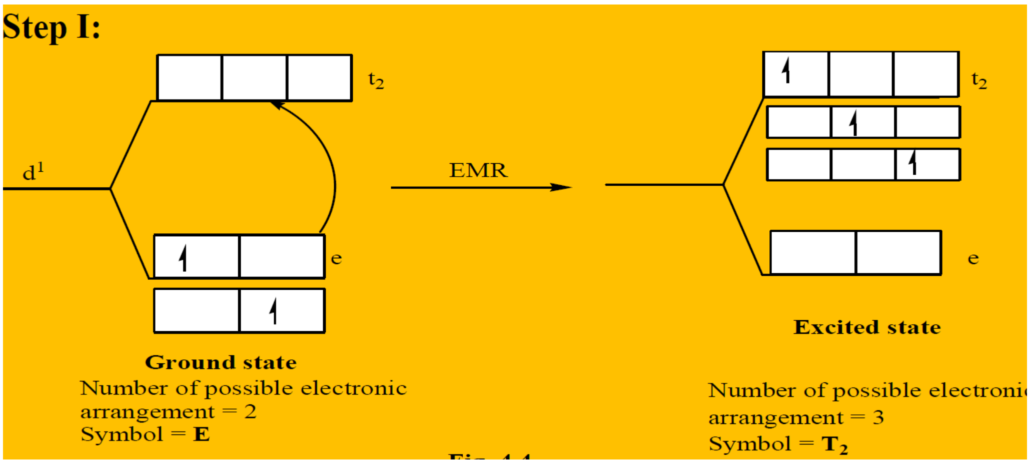




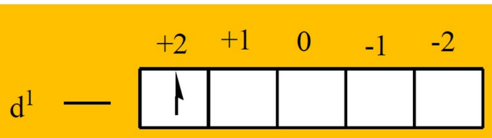
2. Orgel energy level diagram for d^1 Tetrahedral complexes

Orgel energy level diagram for the d^1 configuration containing tetrahedral complexes can be explained in the three different steps, which are given below:

Step I:



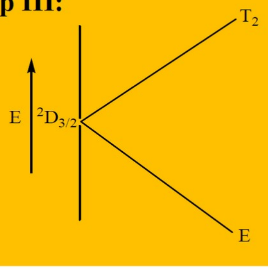
Step II:

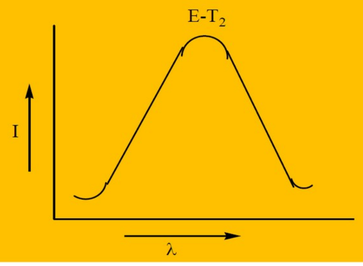


L = 2 (D)
S = 1/2
J = 3/2
M = 2

So term symbol for d^9 configuration = $^2\mathbf{D}_{3/2}$

Step III:

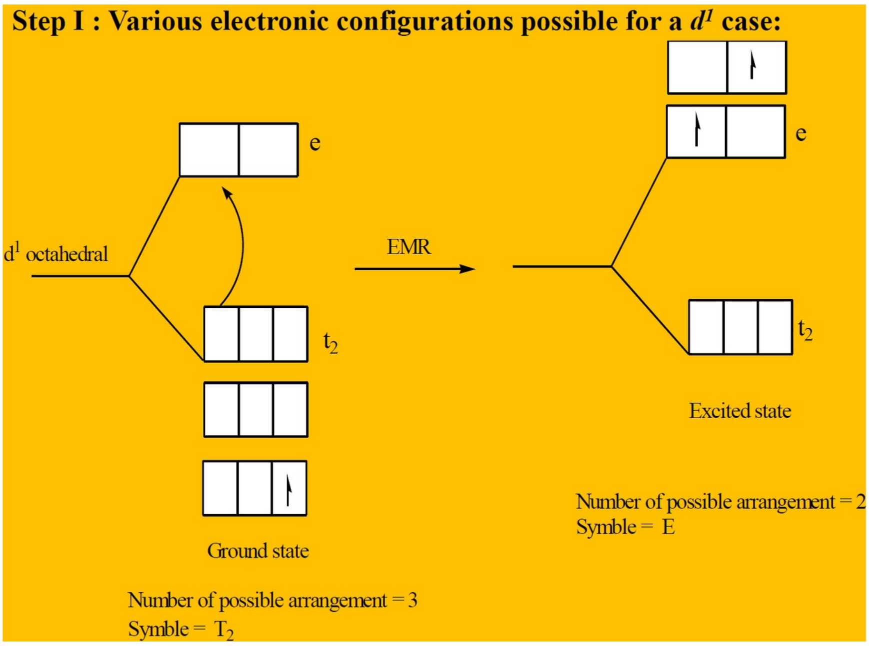




3. Orgel Diagram for the d^1 Octahedral Case

If we consider d^1 configuration, as in the case of the complex $[Ti(H_2O)_6]^{3+}$, the crystal field splitting will lead to lifting of degeneracy of the five d orbitals and thus lower t_{2g} level will now be occupied. It can be represented as t_{2g1} e_{g0}. when absorption of light occurs, the d electrons lying in the low t_{2g} levels get promoted to the higher e_g level leading to a configurational change to t_{2g0} e_{g1}. This change has been represented below in figure given below

Step I : Various electronic configurations possible for a d^1 case:



Number of possible arrangement = 3
Symble = T_2

Number of possible arrangement = 2
Symble = E

Step II: **Various electronic configurations possible for a *d*^{1} case**

The ground state free ion term for this configuration can be calculated as follows.

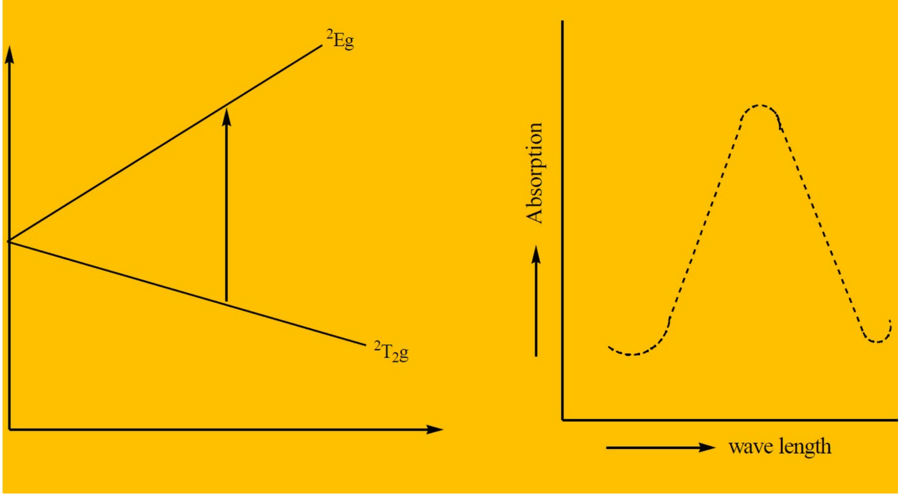
Total orbital angular momentum value = $L = (m + l) = 2$

Total spin angular momentum value = $S = \Sigma ms = 1/2$

Spin multiplicity = $(2S+1) = (2(1/2)+1) = 2$

Thus the free ion ground state term for **d^1** configuration comes out to be 2D.

Step III:



4. Orgel energy level diagram for d^2 octahedral complexes:

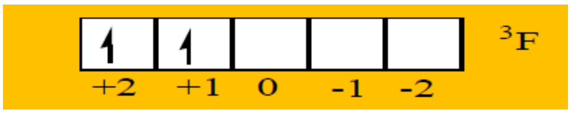
When the spectra of d^2 configuration containing octahedral complexes

like $[V(H_2O)_6]^{+3}$ was studied then it was observed that there occur two peaks in the range of 1700 cm & 2100 cm -1 which indicate that the d^2 configuration containing octahedral complexes can exhibit two types of the electronic transition which are can be defined as:

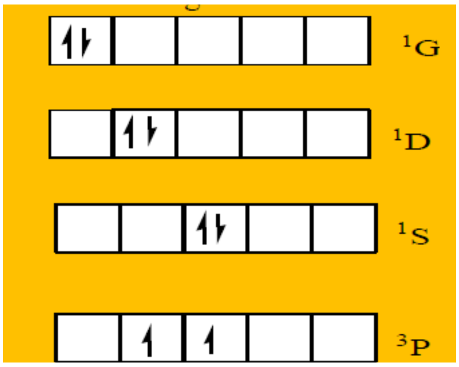
According to orgel the d^2 configuration having ground that term symbol ^{3}F & various exited state term symbol like ^{1}S, ^{1}D, ^{1}G, ^{3}P. Out of which only ^{3}P term symbol is used during the electronic transition because the electronic transition from ground state to this excited state being allowed while the electron transition from ground state to other excited states like ^{1}S, ^{1}G and ^{1}D being forbidden

Now the orgel energy level diagram/spectra corresponding to this allowed transition in the d^2 configuration containing octahedral complexes can be given below.

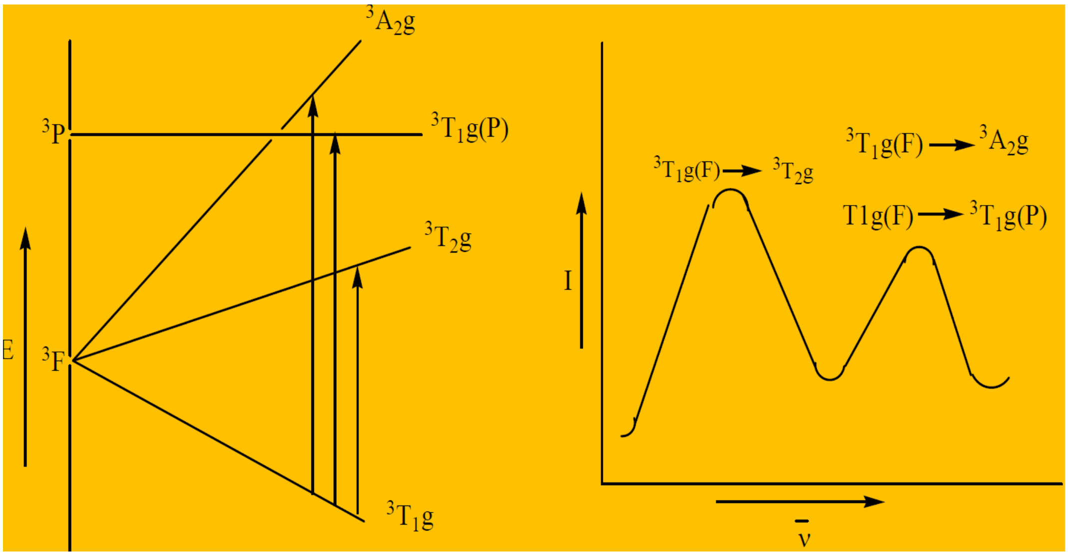
Ground state electronic arrangement for d^2 octahedral complexes.



Exited state electronic arrangement for d^2



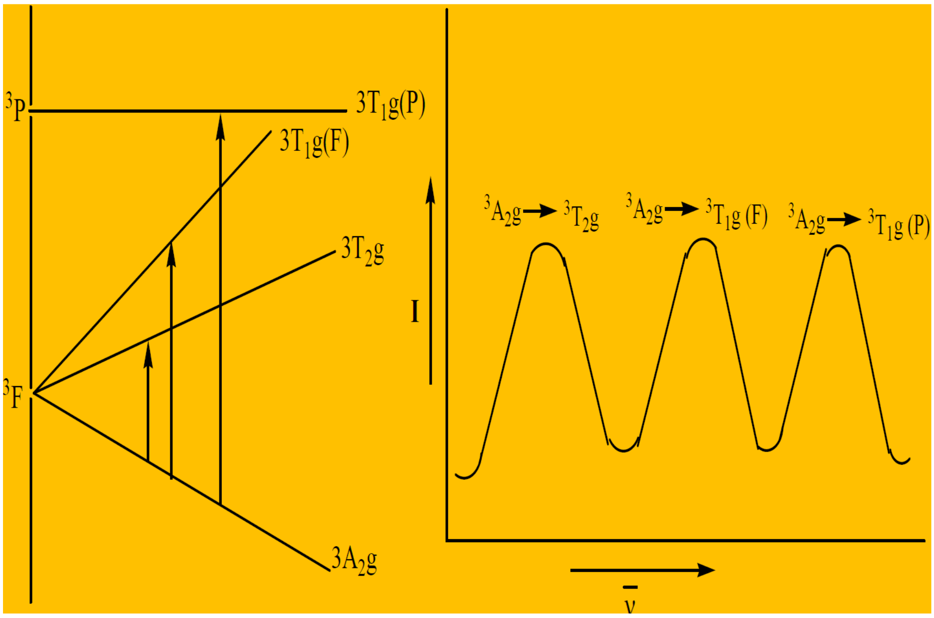
Thus according to the above ground state electronic arrangement and excited state electronic arrangement the Orgel energy level diagram as well as spectra for d2 configuration containing octahedral complexes can be represented as:



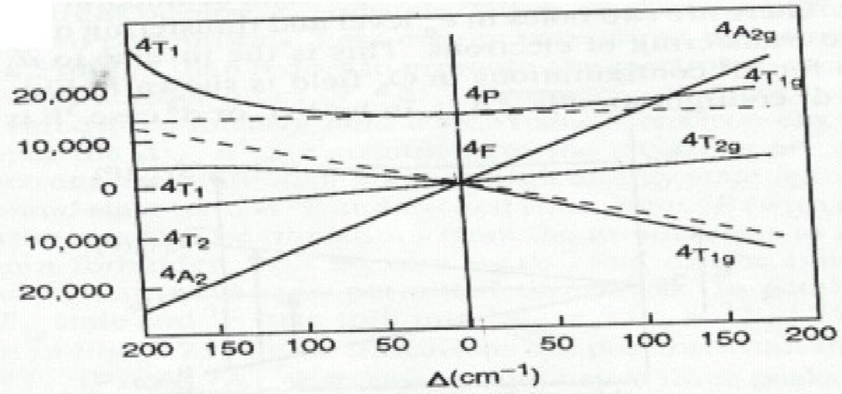
5. Orgel energy level diagram for d^8 octahedral complexes:

When the spectra of d^8 configuration containing octahedral complex was studding then it was observed that the spectra containing there different peaks which indicate that the spectra of d^8 configuration containing octahedral complexes like $[Ni(H_2O)_6]^{+2}$ will have their different types of the transitions, which can be defined as:

According to the orgel ground state form symbol for the d^8 configuration will be ^3F and excited state term symbol will be ^3P. According the Orgel energy level diagram as well as spectra for d^8 configuration containing octahedral complex will be as:



The combined Orgel diagram for two electron and two-hole configurations is given below in **Figure 15.2.**



Combined orgel diagram for the Co^{2+} ion in tetrahedral (left) and octahedral (right) fields. The dashed lines represent terms before mixing.

Fig : 3.19

Figure 15.2: Combined orgel diagram for the Co^{2+} ion in Tetrahedral (Left side) and octahedral fields (Right side) the dashed lines represent terms before mixing

In this diagram, we find two T_{1g} states. One is from the ‘P’ state and the other is from the F state. Both the states have the same symmetry and therefore the two T_{1g} states are slightly curved lines, They interact with one another. This inter electronic repulsion lowers the energy of the lower state and rises the energy of the higher state. This effect is more marked on the left of the diagram because the two levels are close in energy. If the lines had been straight, they would cross each other. This implies that at the cross-over point, the two electrons of the same atom have the same symmetry and same energy. This is impossible and hence it is prohibited by the non-crossing rule. The non-crossing rule states that the states of symmetry cannot cross each other. The mixing or inter-electronic repulsion causes the bending of the lines and it is expressed by Recah parameters B and C.

6.Orgel diagram for d^5 configuration in Octahedral and Tetrahedral:

Ex: $[Mn(H_2O)_6]^{2+}$

It contains ‘5’ unpaired electrons with parallel spins. The ground state term symbol for d^5 configuration is ^{6}s. This ground state term does not split and gives the Mullikan state $^6A_{1g}$. For d^5 configuration the exited state term symbols with multiplicity “4” are ^{4}G, ^{4}P, ^{4}D and ^{4}F. The energy order of these terms is $^6S < {}^4G < {}^4P < {}^4D < {}^4F$. The above terms can split and gives the below Mullikan state.

$^6S \rightarrow {}^6A_{1g}$,

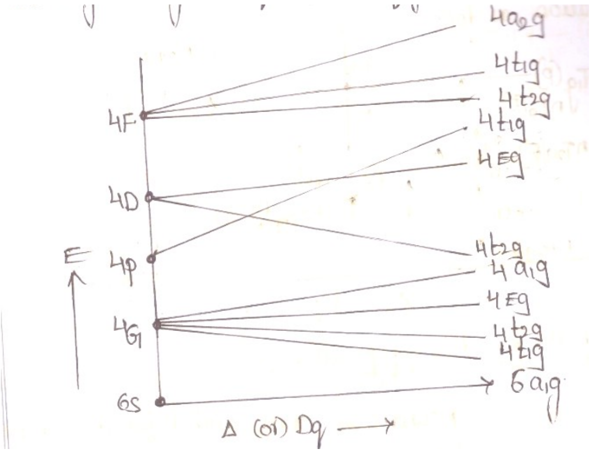
$^4G \rightarrow {}^4E_g + {}^4A_{1g} + {}^4T_{1g} + {}^4T_{2g}$,

$^4P \rightarrow {}^4T_{1g}$,

$^4D \rightarrow {}^4T_{2g} + {}^4Eg$,

$^4F \rightarrow {}^4T_{1g} + {}^4T_{2g} + {}^4A_{2g}$

Orgel diagram for d^5 configuration is as follows



In this diagram 4Eg(D), ${}^4A_{1g}$ (G), ^{4}Eg (D) and ${}^4A_{2g}$ (F) are horizontal lines, the transitions from ground state (${}^6A_{1g}$) to there 4 states give sharp peaks.

The possible transitions are

${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G)

${}^6A_{1g} \rightarrow {}^4T_{2g}$ (G)

${}^6A_{1g} \rightarrow {}^4E_g$ (G), $\rightarrow {}^4A_{1g}$ (G)

${}^6A_{1g} \rightarrow {}^4T_{2g}$ (D)

The same diagram is for d5 (Tetrahedral), but the subscript ‘g’ must be removed the curvatures of =the lines in the diagram is due to inter electronic repulsions between the states of same symmetry.

The curvatures of the lines in the diagram is due to inter electronic repulsions between the Mullikan states. If same symmetry. This is called as configurational interaction (or) Non–crossing rule.

Uses of orgel diagrams:

1. By using orgel diagrams it is very easy to explain the no. of transitions which are more intense and which are less intense.
2. The nature of electronic transitions that occur in b/w which two states in the absorption spectra of complexes can be explained by using orgel diagrams.

Limitations:

1. There are only applicable for weak field complexes.
2. There are only useful for spin allowed transitions.

15.5 SUMMARY

- To know about the Orgel diagrams.
- To study about how to draw orgel diagrams for d^1, d^2, d^3 to d^9 configurations in octahedral and tetrahedral complexes.
- To lean about Orgel diagram for d^5 configuration in Octahedral and Tetrahedral complexes.

15.6 SELF-ASSESSMENT QUESTIONS

1. Draw the orgel diagram for d^2 configuration in octahedral complexes.
2. Draw the orgel diagram for d^5 configuration in octahedral and Tetrahedral complexes.

3. Write the orgel diagram for d^3 configuration in octahedral complexes.

15.7 REFERENCE BOOKS

1) Inorganic Chemistry, Huheey. Harper and Row.

2) Concise Inorganic Chemistry, J. D. Lee, ELBS.

3) Inorganic chemistry, K.F. Purcell and J.C. Kotz, Holt Saunders international

4) Organometallic chemistry, R.C. Mehrotra and A. Singh. New Age International.

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Dr. K. Bala Murali Krishna

LESSON – 16

TANABE-SUGANO DIAGRAMS

16.0 OBJECTIVES:

After studying this lesson, you should be able to:

- To know about the Tanabe – Sugano diagrams (T–S diagram)
- To study about how to draw Tanabe – Sugano diagrams for from d^1 to d^9 configurations in octahedral and tetrahedral complexes.
- To lean about Difference b/w orgel diagrams and T–S diagrams.
- To know calculation of of Dq, B and β parameters.
- To know about Charge transfer spectra (CT)-MLCT and LMCT**.**

STRUCTURE

16.1 TANABE – SUGANO DIAGRAMS (T–S DIAGRAM):

The main drawback of orgel diagram is, they are for only weak field complexes and failed to interpret the spectrum in proper manner. Hence the more comprehensiveness of the spectra can be achieved by the T–S diagrams. The T–S diagrams includes both weak field and strong fields. Low spin states are also included. i.e. the spin multiplicity lower than the ground state are also included. The ground state is always taken as a horizontal axis. It can provide a constant reference point. The other energy states are plotted relative to this line. The T–S diagrams are plotted by taking E/B values along y–axis, △/B (or) Dg/B along x-axis here B = Inter. Electronic repulsion parameter (or) racah parameter.

16.2 T–S DIAGRAM FOR D^2 CONFIGURATION:

In d^2 configuration there is no fundamental difference. b/w strong filed and weak filed. In this diagram the ground state term ^3F is taken as (Horizontal axis).

For example: $[V(H_2O)_6]^{3+}$

For d^2 configuration the ground state and exited state terms are ^3F, ^1D, ^3P, ^1G, ^1S.

The energy order of these terms is $^3F<^1D<^3P<^1G<^1S$. Due to ligand field (or) inter electronic repulsions these terms can split into Mullikan states,

$^3F \rightarrow {}^3T_{1g} + {}^3T_{2g} + {}^3A_{2g}$

$^1D \rightarrow {}^1T_{2g} + {}^1Eg$,

$^3P \rightarrow {}^3T_{1g}$,

$^1G \rightarrow {}^1E_g + {}^1A_{1g} + {}^1T_{1g} + {}^1T_{2g}$,

$^1S \rightarrow {}^1A_{1g}$

In d^2 system there is no fundamental difference between strong field and weak fields. They are for octahedral complexes $^3T_{1g}(F)$ is a lower energy state and it is taken as horizontal axis. The T–S diagram for d^2 configuration is as shown in **Figure 16.1**.

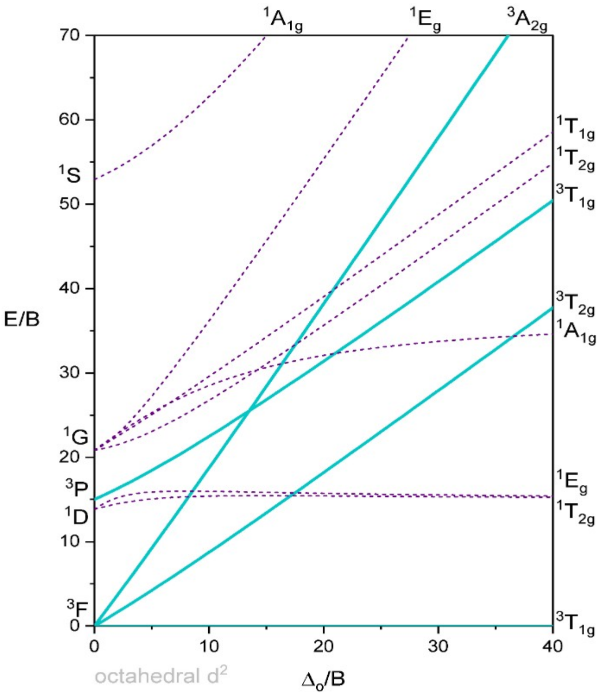


Figure 16.1: splitting of free ions terms for d^2 complexes in octahedral complexes

16.3 T–S DIAGRAM FOR D^3 CONFIGURATION:

Ex: $[Cr(NH_3)_6]^{3+}$ Hexaminochromium (III)

For d^3 configuration the terms are ^4F, ^4P, ^2G, ^2D, ^2F, ^2P, ^2H.

for simplicity we have to take the high multiplicity terms ^4F, ^4P and exited state terms ^2F, ^2G only due to ligand field (or) inter electronic repulsions.

$^4F \rightarrow {}^4T_{1g} + {}^4T_{2g} + {}^4A_{2g}$

$^4P \rightarrow {}^4T_{1g}$,

$^2G \rightarrow {}^2T_{1g} + {}^2T_{2g} + {}^2E_g + {}^2A_{1g}$

$^2F \rightarrow {}^2T_{1g} + {}^2T_{2g} + {}^2A_{2g}$

The absorption spectrum of this complex contains two bands and a very weak band. The weak band having lower electron and it is explained by the transition from $^4A_{2g} \rightarrow {}^2E_g$. First band occurs at 28,500 cm^{-1}, which can be explained by a transition from $^4A_{2g} \rightarrow {}^4T_{1g}$.

Second band occurs at 21,550 cm^{-1} and it is explained by the transition from $^4A_{2g} \rightarrow {}^4T_{2g}$ can be shown in **Figure 16.2.**

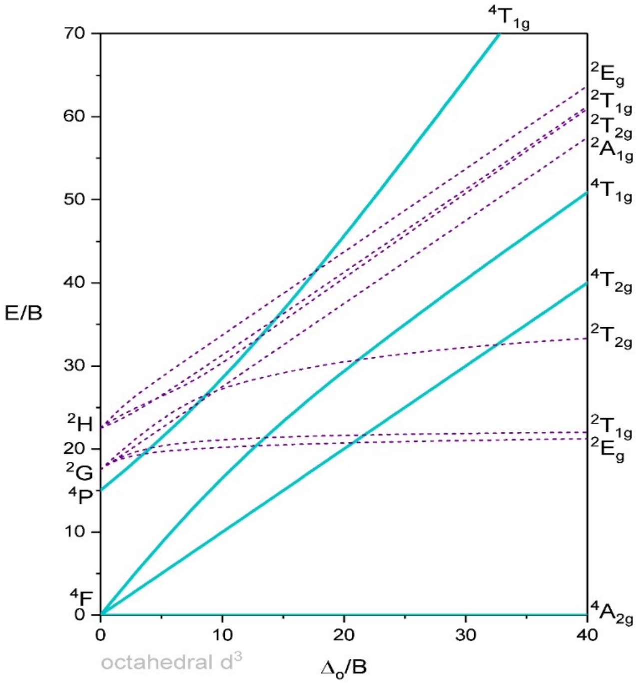


Figure 16.2: Tanabe-Sugano Diagram for octahedral metal complex with d^3 system

16.4 T–S DIAGRAM FOR D^4 CONFIGURATION:

Now let us look at the Tanabe-Sugano diagram of a d^4 octahedral complex (**Figure 16.3**). You can see that this diagram is separated into two parts separated by a vertical line. The line indicates the ligand field strength at which the complex changes from a high spin complex to a low spin complex. At lower ligand field strengths, the ground term is a ^5E_g term (solid turquoise line). At higher field strength the ground term is a $^3T_{1g}$ term (dashed purple line).

$^5D \rightarrow {}^5T_{2g} + {}^5E_g$

$^3H \rightarrow {}^3T_{1g} + {}^3T_{2g} + {}^3E_g$

$^1I \rightarrow {}^1A_{1g}$

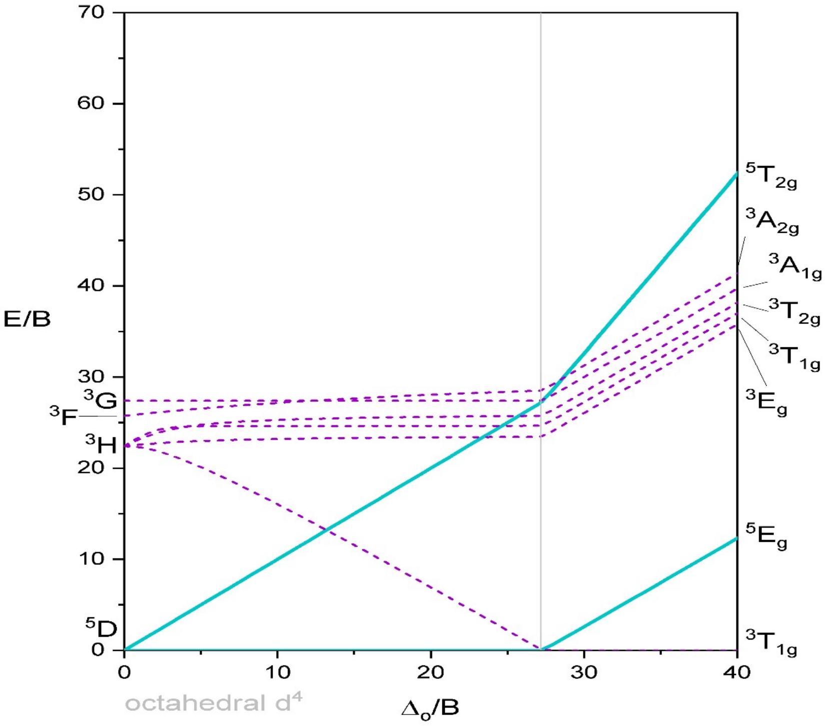


Figure 16.3: Tanabe-Sugano Diagram for octahedral metal complex with d^4 electrons.

16.5 T–S DIAGRAM FOR D^5 CONFIGURATION:

The Tanabe-Sugano diagram of a d^5 octahedral complex is also divided into two parts separated by a vertical line (**Figure 16.4**). The left part reflects the high spin and the right part the low spin complex.

A T–S diagram for a d5 configuration has a distinct shape for high-spin and low-spin complexes due to the difference in the ground state spin multiplicity.

For high-spin complexes, the ground state is a sextet (6A$_1$g), and there are no spin-allowed transitions, so these complexes are colorless or very pale. For low-spin complexes, the ground state is a doublet ($^2T_{2g}$) and the diagram shows spin-allowed transitions to other doublet states, resulting in colored complexes with absorption bands.

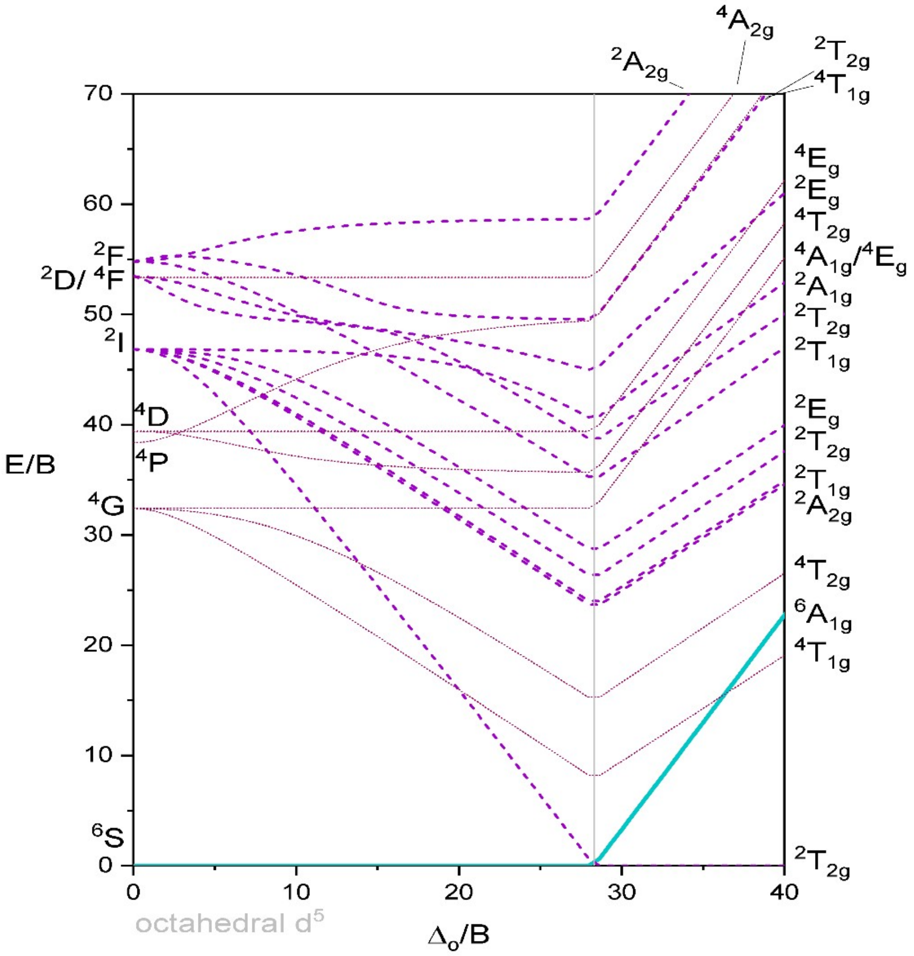


Figure 16.4 Tanabe-Sugano Diagram for octahedral metal complex with ^{5}d electrons

16.6 T–S DIAGRAM FOR D^6 CONFIGURATION:

For d^6 configuration the terms are ^{5}D, ^{3}H, ^{3}F, ^{3}G, ^{3}P, ^{1}I,^{1}G, ^{1}F for simplicity the singlet's ^{1}I, ^{1}G, ^{1}F and ^{5}D terms are shown in the **Figure 16.5** for d^6 configuration the ground state term is ^{5}D. This split by an octahedral field into ^{5}Eg + ^{5}T2g + ^{5}T2g is a ground state symbol and ^{5}Eg is an exited state symbol. Thus $^5T_{2g}$ is taken as horizontal axis. The ^{1}I, ^{1}G states are of higher energy than ^{5}D state and split by the octahedral field to give different states. They are $^1A_{2g}$ + ^{1}Eg + $^1T_{2g}$ + $^1T_{1g}$ + $^1A_{1g}$. Among those five states $^1A_{1g}$ is most important. The higher energy state term is ^{1}F. It split into $^1T_{2g}$ + $^1T_{1g}$ + $^1A_{1g}$. For simplicity the splitting states T_{1g}, T_{2g} of ^{1}F are neglected.

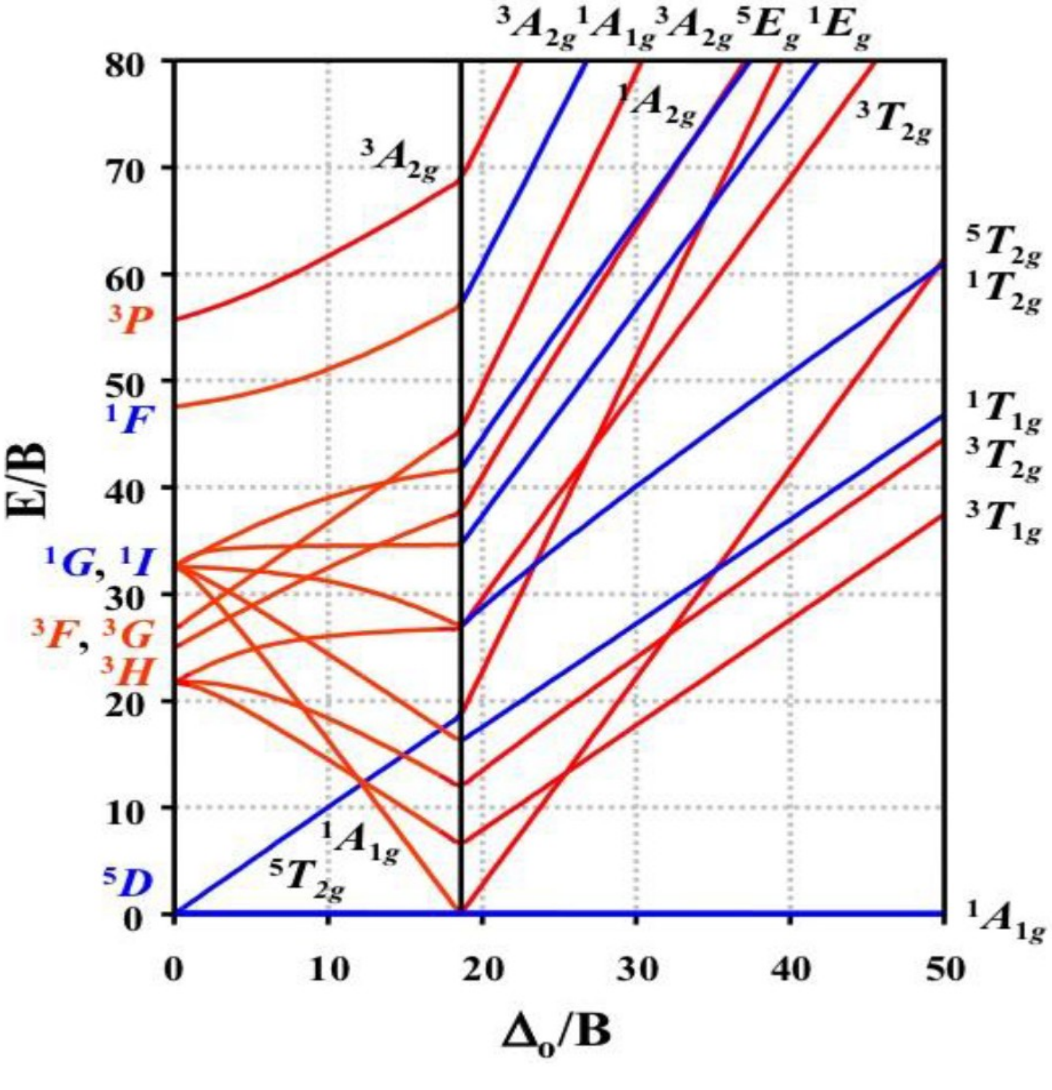


Figure 16.5: Tanabe-Sugano diagram of the d^6 octahedral complex

16.7 T–S DIAGRAM FOR D^7 CONFIGURATION:

The terms for d7 metal ion is ^4F, ^4P, ^2G, ^2F

$^4F \rightarrow {}^4T_{1g} + {}^4T_{2g} + {}^4A_{2g}$

$^4P \rightarrow {}^4T_{1g}$,

$^2G \rightarrow {}^2T_{1g} + {}^2T_{2g} + {}^2E_g + {}^2A_{1g}$

$^2F \rightarrow {}^2T_{1g} + {}^2T_{2g} + {}^2A_{2g}$

Metal complexes with d^7 configuration have ^4F ground state. The ground state term symbol becomes $^4T_{1g}$ in weak field and ^2E_g in strong field ligand for octahedral complexes **(Figure 16.6).**

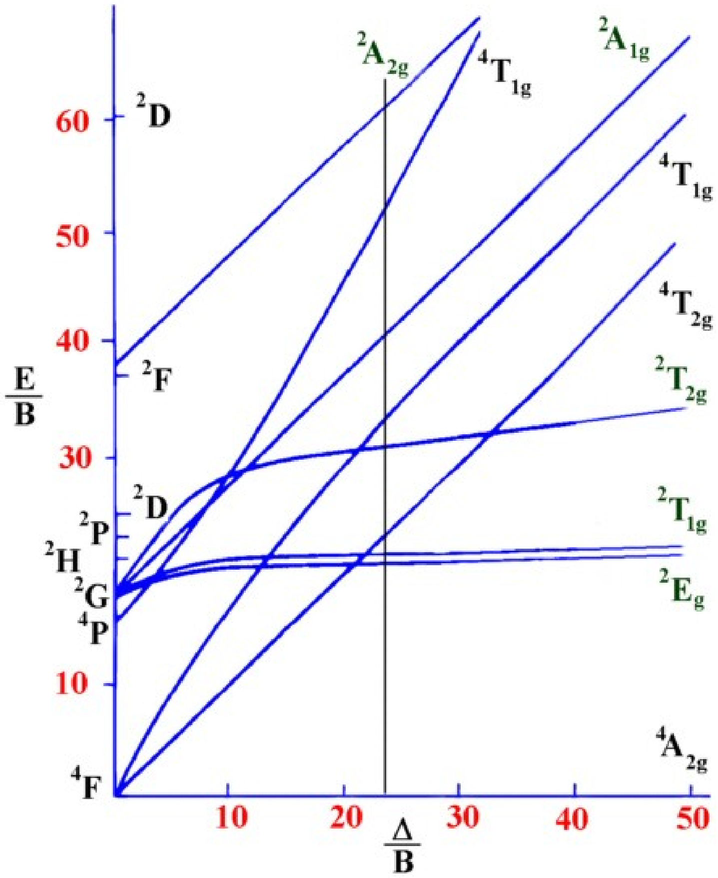


Figure 16.6: Tanabe-Sugano diagram of the d^7 complex

16.8 T–S DIAGRAM FOR D^8 CONFIGURATION:

The Tanabe-Sugano diagram for a d^8 configuration in an octahedral complex shows that the ground state is always the $^3A_{2g}$ term, regardless of ligand field strength, which is represented on the y-axis as E/B (**Figure 16.7**). There are three spin-allowed electronic transitions from this ground state to the $^3T_{2g}$,$^3T_{1g}$ (F), and $^3T_{1g}(P)$ excited states. The x-axis represents the ligand field strength as $\Delta o/B$, where Δ_o is the octahedral crystal field splitting energy and B is the Racah parameter.

Ground state: The ground state is always the $^3A_{2g}$ term for octahedral d^8 complexes

*Spin-allowed transitions***:** Three spin-allowed electronic transitions are possible from the $^3A_{2g}$ ground state to higher energy states:

$^3T_{2g} \leftarrow {}^3A_{2g}$

$^3T_{1g}(F) \leftarrow {}^3A_{2g}$

$^3T_{1g}(P) \leftarrow {}^3A_{2g}$

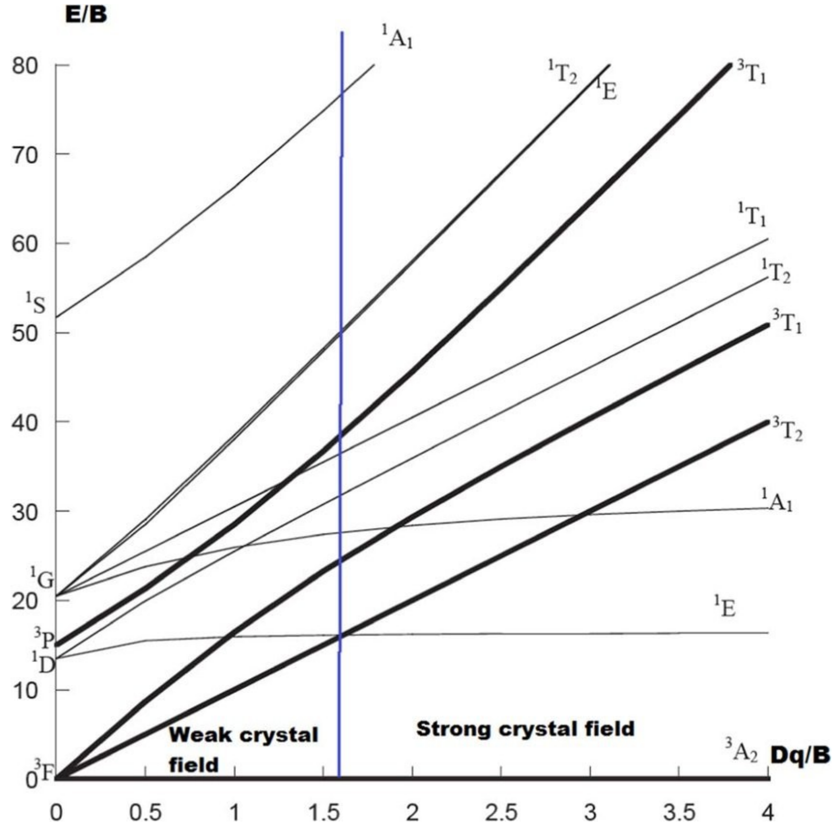


Figure 16.7: Tanabe-Sugano diagram of the d^8 complex

16.9 DIFFERENCE B/W ORGEL DIAGRAMS AND T–S DIAGRAMS:

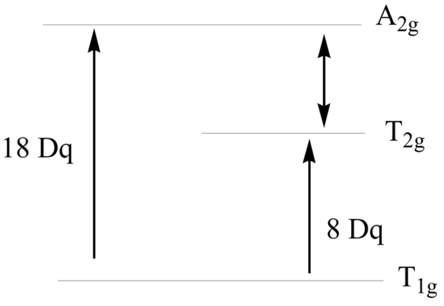
T–S diagram	Orgel diagrams
1. T–S diagram are used to interpret the spectrum of both weak and strong ligand fields.	1. In case of orgel diagrams these are for only weak field complexes.
2. In T–S diagrams E/B takes along Y – axis plotted against Dg / B (or) △/B taken on X-axis.	2. In orgel diagrams the energy's "E" of different states taken on Y–axis plotted directly against ligand field strength △ (or) Dg
3. There is a break at some critical field strength in T–S diagram.	3. There is no break at any field strength.
4. T–S diagrams consider ground state terms as well as exited state terms.	4. Orgel diagrams considers only ground state terms.
5. The energy of ground state is fixed "O" in T–S diagrams.	5. There is some energy for the lowest energy state in orgel diagram.

16.10 CALCULATIONS OF DQ, B AND B PARAMETERS.

1**. The calculation of Dq, B and β for the complex CaF_6^-**

The '3' absorption band in Ca^{+2} (d^7) surrounded octahedrally by $6F^-$ ions due to transitions are B = 9 + 1

1. $^4T_{1g} \rightarrow {}^4T_{2g} \rightarrow \upsilon_1 = 7150\ cm^{-1}$
2. $^4T_{1g} \rightarrow {}^4A_{2g} \rightarrow \upsilon_2 = 15{,}200\ cm^{-1}$.
3. $^4T_{1g} \rightarrow {}^4T_g(p) \rightarrow \upsilon_3 = 19{,}300\ cm^{-1}$



Solution

$\upsilon_2 - \upsilon_1 = 10\ Dq$

15,200-7150 = 10 Dq

10 Dq = 8050

Dq = 805 cm^{-1}

Racah parameter ‘B’ is calculated as follows

$$15\ B' = \upsilon_3 + \upsilon_{2\text{-}}3\gamma_1$$

$$15\ B' = 19{,}300 + 15{,}200 - 3(7150)$$

$$B' = \frac{19{,}300 + 15{,}200 - 3(7150)}{15}$$

$$B' = 870\ \text{cm}^{-1}$$

$$\beta = \frac{B`}{B}$$

$$\beta = \frac{870}{971}$$

$$B = 0.89$$

2. Calculate Dq, B and β parameters for V^{2+}, (d^8 ion in octahedral complex) & spectral data.

$\upsilon_1 = 9000\ \text{cm}^{-1}$, $\upsilon_3 = 25{,}000\ \text{cm}^{-1}$

$\upsilon_2 = 14{,}000\ \text{cm}^{-1}$, $B = 1030\ \text{cm}^{-1}$

Solution

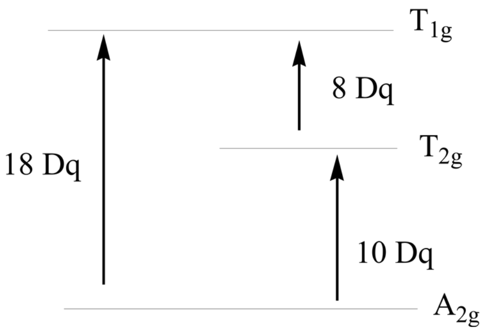
$$10\ Dq = \upsilon_1$$

$$10\ Dq = 9000$$

$$Dq = 900$$

$$15\ B` = \upsilon_1 + \upsilon_2 - 3\upsilon_1$$

$$B` = \frac{25{,}000 + 14{,}000 - 3(9000)}{15}$$



$$B` = 800\ \text{cm}^{-1}$$

$$\beta = \frac{B`}{B}$$

$$\beta = \frac{870}{1030}$$

$$B = 0.776$$

16.11 CHARGE TRANSFER SPECTRA (CT)

If an electron is transferred from one atom or group in the molecule to another, it is called charge transfer transition. This transition occurs between MO's which are essentially centered on different atoms. Very intense bands with molar absorptivity's of 104 L/mol^{-1}/cm^{-1} are the result of a charge transfer. The charge transfer spectra are also called redox spectra. The charge transfer transition is often demonstrated by 'Solvatochromism', the variation of transition energy with changes in solvent permittivity. These are thus distinguished from $\pi \rightarrow \pi^*$ transitions on ligands. In C-T transitions a large change in molecular dipole is observed.

There are two types of charge transfer.

1.Ligand to metal charge transfer (LMCT) transitions

2. Metal to ligand charge transfer (MLCT) transitions

1. Ligand to metal charge transfer (LMCT) transitions

The ligands of the complexes should have electrons in their π orbitals for this type of transfer to occur. An energy level diagram for a complex of this type is given below.

Ligands possess σ, σ*, π, π* and nonbonding (n) molecular orbitals. If the ligand molecular orbitals are full, charge transfer may occur from the ligand molecular orbitals to the empty or partially filled metal d-orbitals. The absorptions that arise from this process are called ligand-to-metal charge-transfer (LMCT) bands (**Figure 16.8**). LMCT transitions result in intense bands. Forbidden d-d transitions may also take place giving rise to weak absorptions. Ligand to metal charge transfer results in the reduction of the metal.

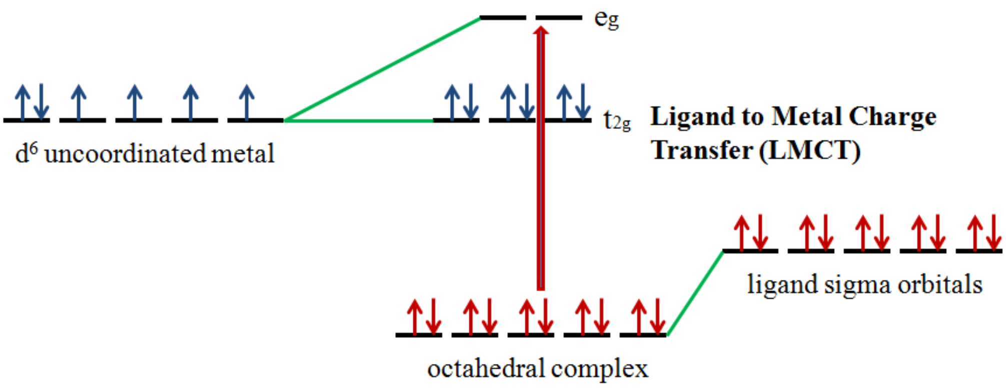


Figure 16.8: Ligand to Metal Charge Transfer (LMCT) involving an octahedral complex.

2. Metal to ligand charge transfer (MLCT) transition

If the metal is in a low oxidation state (electron rich) and the ligand possesses low-lying empty orbitals (e.g., CO or CN^-) then a metal-to-ligand charge transfer (MLCT) transition may occur. MLCT transitions are common for coordination compounds having π-acceptor ligands. Upon the absorption of light, electrons in the metal orbitals are excited to the ligand orbitals. **Figure 16.9** illustrates the metal to ligand charge transfer in a d^5 octahedral complex. MLCT transitions result in intense bands. Forbidden d–d transitions may also occur. This transition results in the oxidation of the metal.

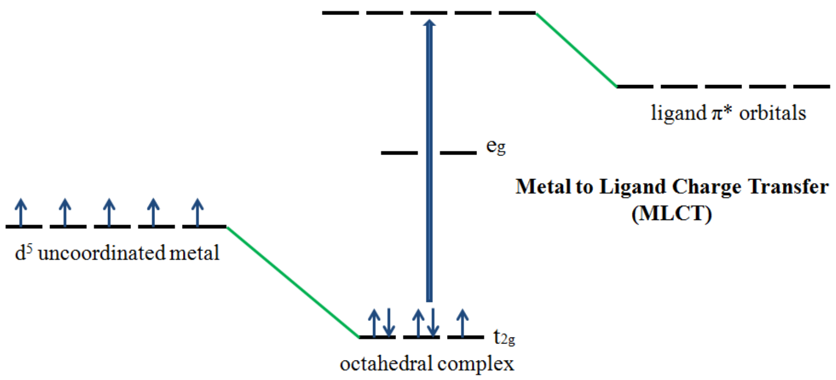


Figure 16.9: Metal to Ligand Charge Transfer (MLCT) involving an octahedral d^5 complex.

Effect of Solvent Polarity on CT Spectra

The position of the CT band is reported as a transition energy and depends on the solvating ability of the solvent. A shift to lower wavelength (higher frequency) is observed when the solvent has high solvating ability.

Polar solvent molecules align their dipole moments maximally or perpendicularly with the ground state or excited state dipoles. If the ground state or excited state is polar an interaction will occur that will lower the energy of the ground state or excited state by solvation.

16.12 SUMMARY

- To know about the Tanabe – Sugano diagrams (T–S diagram)
- To study about how to draw Tanabe – Sugano diagrams for from d^1 to d^9 configurations in octahedral and tetrahedral complexes.
- To lean about Difference b/w orgel diagrams and T–S diagrams.
- To know calculation of of Dq, B and β parameters.
- To know about Charge transfer spectra (CT)-MLCT and LMCT.

16.13 SELF-ASSESSMENT QUESTIONS

1. Draw and explain Tanabe-Sugano diagram for d^3 and d^6 electronic configuration.
2. Write a note on charge transfer spectra.
3. Draw T-S diagram for d^2 configuration in octahedral complexes.
4. Differentiate orgel diagrams and T–S diagrams.

16.14 REFERENCE BOOKS

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LESSON – 17

MAGNETIC AND CHIROPTICAL PROPERTIES OF TRANSITION METAL COMPLEXES

17.0 OBJECTIVES:

After studying this lesson, the student will be able to:

1. **Understand the origin and types of magnetism** in transition metal complexes.
2. **Differentiate diamagnetic and paramagnetic behaviour** based on electronic configuration.
3. **Interpret magnetic moments** using spin-only and orbital contributions.
4. **Explain the effects of spin–orbit coupling and anomalous magnetic moments**.
5. **Relate magnetic properties to electronic structure, geometry, and ligand field strength**.

STRUCTURE

17.1 INTRODUCTION

Transition metal complexes exhibit rich **magnetic and chiroptical behaviour** due to the presence of **partially filled *d*-orbitals** and, in many cases, **asymmetric or chiral ligand environments**. These properties are not merely descriptive; rather, they serve as **powerful experimental probes** for understanding the **oxidation state, electronic configuration, ligand field strength, geometry, metal–ligand bonding, and stereochemistry** of the metal centre. Consequently, magnetic and chiroptical studies occupy a central position in advanced coordination chemistry.

17.2 MAGNETIC PROPERTIES OF TRANSITION METAL COMPLEXES

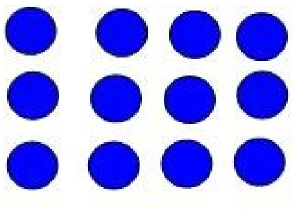
17.2.1 Origin of Magnetism

The magnetic behaviour of transition metal complexes arises primarily from the **presence or absence of unpaired electrons in the *d*-orbitals** of the central metal ion. When a complex is placed in an **external magnetic field**, the spins and, in some cases, the orbital motion of electrons interact with the field, producing characteristic magnetic responses.

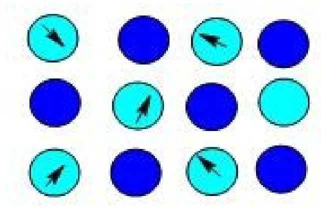
Magnetic measurements are extremely valuable because they help in:

- Determining the **number of unpaired electrons** and hence the electronic configuration
- Distinguishing between **high-spin and low-spin complexes**, especially in octahedral fields
- Assessing **ligand field strength** and metal–ligand interactions
- Probing **metal–metal interactions and magnetic exchange** in polynuclear or cluster complexes

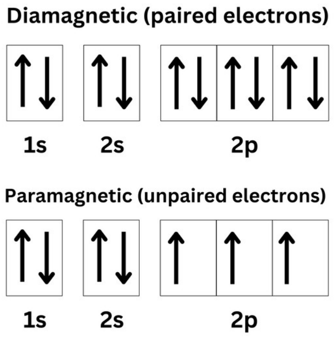
17.3 TYPES OF MAGNETISM IN COMPLEXES



Diamagnetism

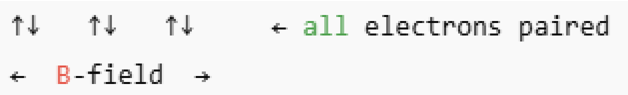


Paramagnetism



(i) Diamagnetism

Diamagnetism is observed when **all the electrons in a complex are paired**. In an applied magnetic field, the motion of paired electrons induces tiny circulating currents in the electron cloud. According to **Lenz's law**, the induced magnetic field opposes the applied field, resulting in weak repulsion.



```
↑↓    ↑↓    ↑↓      ← all electrons paired
←  B-field  →
```

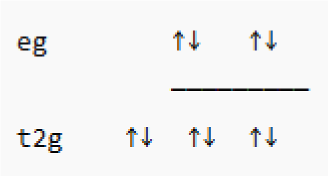
Characteristics

- Substances are **weakly repelled** by a magnetic field
- Magnetic susceptibility (χ) is **small, negative, and temperature-independent**
- Diamagnetism is a **universal property** of matter but becomes evident only when no unpaired electrons are present

Examples

Diamagnetism is typical of:

- d^{10} systems such as Zn^{2+}, Cd^{2+} and Cu^{+}
- Many **low-spin** $\boldsymbol{d^6}$ **octahedral complexes** with strong-field ligands



```
eg          ↑↓    ↑↓
            ──────────

t2g      ↑↓    ↑↓    ↑↓
```

A classic example is: $[Co(NH_3)_6]^{3+}$

In this complex, ammonia acts as a **strong-field ligand**, producing a large octahedral crystal field splitting (Δ_o). All six *d*-electrons pair in the lower-energy t_{2g} orbitals, leaving the e_g orbitals empty. As no unpaired electrons are present, the complex is **diamagnetic**.

(ii) Paramagnetism

Paramagnetism arises from the presence of **one or more unpaired electrons**. Each unpaired electron possesses a spin magnetic moment. In the absence of a magnetic field, these moments are randomly oriented and cancel on average. When a magnetic field is applied, partial alignment of spins occurs, and the substance is attracted toward the field.

```
↑     ↑     ↑       ← unpaired electrons
←  B-field  →
```

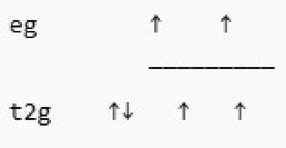
Characteristics

- Magnetic susceptibility (χ) is **positive**
- The magnitude of paramagnetism **increases with the number of unpaired electrons**
- Paramagnetism is generally **temperature-dependent**, decreasing as temperature increases

Examples

Most complexes of first-row transition metal ions such as Mn^{2+}, Fe^{2+}/Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} are paramagnetic.

A representative example is the high-spin d^6 complex: $[CoF_6]^{3-}$



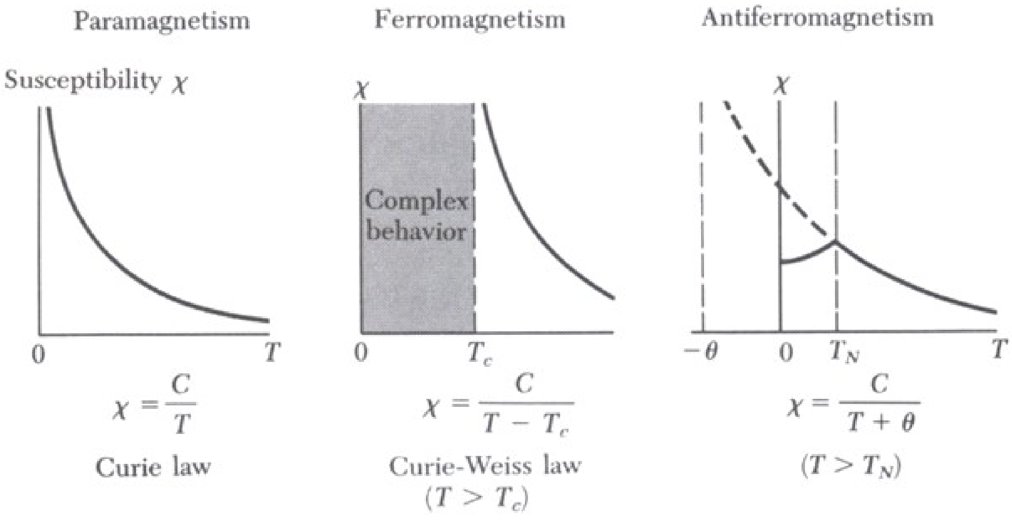
Here, fluoride (F^-) is a **weak-field ligand**, resulting in a small crystal field splitting. Electrons occupy both t_{2g} and e_g orbitals according to Hund's rule, leading to **four unpaired electrons** and hence strong paramagnetism.

(iii) Temperature-Dependent Paramagnetism

For many **first-row transition metal complexes**, paramagnetism approximately follows **Curie's law**, and the magnetic moment can be described satisfactorily by the **spin-only formula**, assuming that orbital angular momentum is quenched by the ligand field.

However, for **second- and third-row transition metal complexes**, significant deviations are observed due to **strong spin–orbit coupling**:

- Orbital angular momentum is **not completely quenched**
- Magnetic moments become **strongly temperature-dependent**
- The behaviour often follows the **Curie–Weiss law** rather than ideal Curie behavior



$\chi = \frac{C}{T}$ Curie law

$\chi = \frac{C}{T - T_c}$ Curie-Weiss law ($T > T_c$)

$\chi = \frac{C}{T + \theta}$ ($T > T_N$)

Figure: Magnetic susceptibility curves

These effects are more pronounced in heavier transition metals because of their **larger atomic numbers and stronger relativistic effects**.

(iv) Cooperative Magnetism (Brief Note)

In extended solids and polynuclear complexes, individual magnetic moments can interact with one another:

- **Ferromagnetism** – parallel alignment of spins, giving a large net moment
- **Antiferromagnetism** – antiparallel alignment with equal magnitude, leading to cancellation of the net moment
- **Ferrimagnetism** – antiparallel alignment with unequal spins, resulting in partial cancellation

In coordination chemistry, **weak antiferromagnetic coupling** is frequently observed in polynuclear complexes and is often detected through deviations in the temperature dependence of the magnetic moment.

17.4 MAGNETIC MOMENT AND ITS CONTRIBUTIONS

The **magnetic moment (μ)** of a transition metal complex is a **quantitative measure of its response to an external magnetic field**. It reflects the intrinsic magnetic properties of the electrons associated with the metal ion and provides direct information about the **electronic structure and bonding environment**.

The total magnetic moment arises from two fundamental contributions:

- **Spin angular momentum (S)** of unpaired electrons
- **Orbital angular momentum (L)** associated with the motion of electrons in degenerate orbitals

Magnetic moments are expressed in **Bohr magnetons (BM)** and are measured experimentally using techniques such as the **Gouy method, Evans method, SQUID magnetometry, and Vibrating Sample Magnetometry (VSM)**. By comparing experimental values with theoretical predictions, one can determine the **number of unpaired electrons, spin state, coordination geometry, and presence of magnetic interactions**.

17.4.1 Spin-Only Magnetic Moment

In many coordination complexes—especially those of **first-row transition metals**—the ligand field removes orbital degeneracy and **quenches orbital angular momentum**. Under such conditions, magnetism arises solely from electron spin.

Spin-Only Formula,

$$\mu_{so} = \sqrt{n(n+2)}\ \mathrm{BM}$$

Where, n = **number of unpaired electrons**

$n = 1 \rightarrow \mu \approx 1.73$ BM,

$n = 2 \rightarrow \mu \approx 2.83$ BM,

$n = 3 \rightarrow \mu \approx 3.87$ BM,

$n = 4 \rightarrow \mu \approx 4.90$ BM,

$n = 5 \rightarrow \mu \approx 5.92$ BM.

Applicability

- Works well for many **first-row octahedral complexes**
- Particularly accurate for **high-spin d^5 systems**
- Assumes negligible orbital contribution

Examples

- **Mn^{2+} (high-spin d^5)** → 5 unpaired electrons
- **Fe^{3+} (high-spin d^5)** → 5 unpaired electrons

For these ions, the observed magnetic moments are very close to the spin-only value (~5.9 BM).

Importance

This approximation is extremely useful in practice: **simply measuring μ often directly reveals the number of unpaired electrons**, making it a powerful diagnostic tool in coordination chemistry.

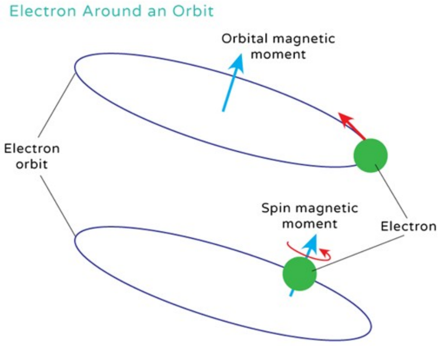


Figure: Orbital and spin magnetic moments of an electron

17.4.2 Orbital Contribution and Anomalous Magnetic Moments

Orbital Contribution

In some complexes, **orbital angular momentum is not fully quenched**. This occurs particularly when the ground electronic term is **orbitally degenerate** (T terms), allowing electrons to move between equivalent orbitals.

Origin

- Degenerate *d*-orbitals such as d_{xy},d_{yz},d_{xz} electrons can circulate among these orbitals
- This circulation produces an additional **orbital magnetic moment**

Result

$$\mu_{obs} > \mu_{so}$$

That is, the **observed magnetic moment exceeds the spin-only value**.

Typical Cases

- **Octahedral high-spin Co^{2+} (d^7)**
- **Tetrahedral Ni^{2+} (d^8)**

Such deviations from spin-only predictions are known as **anomalous magnetic moments**.

17.4.3 Spin–Orbit Coupling

Definition

Spin–orbit coupling is the interaction between an electron's **spin magnetic moment** and the **magnetic field generated by its orbital motion** around the nucleus.

Key Features

- Lifts degeneracy of electronic energy levels
- Mixes spin and orbital states
- Alters ground-state energy and magnetic properties
- Becomes increasingly important for **4d and 5d transition metals** due to higher nuclear charge

Consequences

- Spin-only formula becomes **inadequate**

- Magnetic moment becomes **temperature-dependent**
- **Magnetic anisotropy** (direction-dependent magnetism) may arise
- Fine structure appears in electronic spectra

Spin–orbit coupling is therefore essential for understanding the magnetic behaviour of **heavier transition metal complexes**.

17.5 ANOMALOUS MAGNETIC MOMENTS

An **anomalous magnetic moment** is one that deviates significantly from values predicted by simple **spin-only** or **spin + orbital** models. These anomalies are not experimental errors; instead, they provide **deep insight into electronic structure and metal–metal interactions**.

(i) Spin Crossover

Some complexes lie close to the energetic boundary between **high-spin and low-spin states**.

- Thermal energy can shift the equilibrium between spin states
- Magnetic moment changes with temperature
- Results in **intermediate or variable μ values**

Spin crossover is commonly observed in d^4–d^7 octahedral complexes of Fe^{2+} and Fe^{3+}.

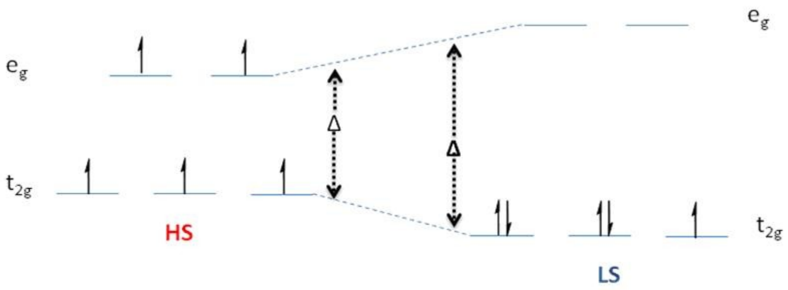


Figure: High-spin and low-spin octahedral crystal-field splitting diagram

(ii) Antiferromagnetic Coupling

In **polynuclear or cluster complexes**, magnetic exchange interactions may occur between adjacent metal centres.

- Spins align **antiparallel**
- Partial or complete cancellation of magnetic moments occurs

- Observed μ is **lower than expected** for isolated metal ions

This behaviour is characteristic of metal–metal bridged systems and magnetic clusters.

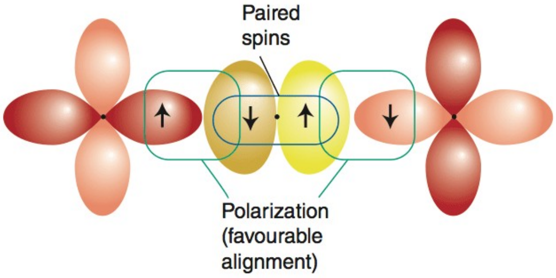


Figure: Spin pairing due to exchange interaction (antiferromagnetic coupling)

17.6 SUMMARY:

1) **Magnetic properties of transition metal complexes arise from unpaired electrons** in d-orbitals.
2) **Diamagnetic complexes** contain only paired electrons and are weakly repelled by magnetic fields.
3) **Paramagnetic complexes** contain unpaired electrons and are attracted to magnetic fields.
4) The magnitude of paramagnetism depends on the **number of unpaired electrons**.
5) **Temperature-dependent paramagnetism** often follows **Curie or Curie–Weiss laws**.
6) **Cooperative magnetism** includes **ferromagnetism, antiferromagnetism, and ferrimagnetism**.
7) The **magnetic moment (μ)** arises from **spin and orbital angular momentum**.
8) The **spin-only formula** successfully predicts magnetic moments for many first-row transition metal complexes.
9) **Orbital contribution** leads to **anomalous magnetic moments**, especially in orbitally degenerate systems.
10) **Spin–orbit coupling** becomes significant in heavier transition metals, affecting μ and spectral properties.
11) **Spin crossover** and **antiferromagnetic coupling** cause deviations from expected magnetic behaviour.
12) Magnetic studies provide valuable information about **electronic structure, spin state, and metal–metal interactions**.

17.7 SELF-ASSESSMENT QUESTIONS

A. Short Answer Questions

1) What is the origin of magnetism in transition metal complexes?
2) Define diamagnetism and paramagnetism.
3) What is magnetic susceptibility?

4) What is the spin-only magnetic moment?
5) Why is orbital angular momentum often quenched?
6) What is spin–orbit coupling?
7) What is meant by anomalous magnetic moment?
8) Define spin crossover.
9) What is antiferromagnetic coupling?
10) Name any two experimental methods for measuring magnetic moments.

B. Long Answer Questions

1) Explain the origin of magnetic properties in transition metal complexes.
2) Distinguish between diamagnetism and paramagnetism with examples.
3) Discuss the spin-only magnetic moment and its applicability.
4) Explain orbital contribution to magnetic moment with suitable examples.
5) Describe spin–orbit coupling and its consequences.
6) Discuss anomalous magnetic moments with reference to spin crossover and antiferromagnetic coupling.
7) Explain how magnetic measurements help in determining electronic structure.

17.8 TECHNICAL TERMS:

1) **Magnetism** – Response of a substance to an external magnetic field.
2) **Diamagnetism** – Weak repulsion shown by substances with all electrons paired.
3) **Paramagnetism** – Attraction shown by substances containing unpaired electrons.
4) **Magnetic susceptibility (χ)** – Measure of the degree of magnetization of a material.
5) **Magnetic moment (μ)** – Quantitative measure of magnetic strength of a complex.
6) **Spin angular momentum** – Magnetic contribution due to electron spin.
7) **Orbital angular momentum** – Magnetic contribution due to electron motion in orbitals.
8) **Spin-only magnetic moment** – Magnetic moment arising solely from electron spin.
9) **Orbital contribution** – Additional magnetic moment due to unquenched orbital motion.
10) **Spin–orbit coupling** – Interaction between electron spin and orbital motion.
11) **Anomalous magnetic moment** – Magnetic moment deviating from spin-only prediction.
12) **Spin crossover** – Temperature-induced transition between high-spin and low-spin states.
13) **Antiferromagnetism** – Magnetic ordering with antiparallel spin alignment.
14) **Ferromagnetism** – Magnetic ordering with parallel spin alignment.
15) **Ferrimagnetism** – Antiparallel alignment with unequal spins.

17.9 REFERENCE TEXTBOOKS :

1) **J. E. Huheey, E. A. Keiter & R. L. Keiter**, *Inorganic Chemistry: Principles of Structure and Reactivity*, Harper Collins.
2) **D. F. Shriver, P. W. Atkins & C. H. Langford**, *Inorganic Chemistry*, Oxford University Press.
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Dr. P. Bharath

LESSON – 18

CHIROPTICAL AND MAGNETO-OPTICAL PROPERTIES OF COORDINATION COMPOUNDS

18.0 OBJECTIVES:

After studying this lesson, the student will be able to:

1) **Understand optical isomerism and chirality** in coordination complexes.
2) **Explain optical activity, enantiomerism, and structural requirements** for chirality.
3) **Describe the Cotton effect, ORD, and CD** as chiroptical tools.
4) **Assign Δ and Λ configurations** of octahedral complexes.
5) **Understand the Faraday effect and Magnetic Circular Dichroism (MCD)**.

STRUCTURE

18.1 CHIROPTICAL PROPERTIES (OPTICAL ISOMERISM)

Chiroptical properties describe how *chiral* molecules interact with **plane-polarized light**. In coordination chemistry, this interaction is most clearly expressed through **optical isomerism**, a form of stereoisomerism in which a coordination complex is *asymmetric* and therefore **non-superimposable on its mirror image**. Such complexes exist as pairs of mirror-image isomers and exhibit optical activity.

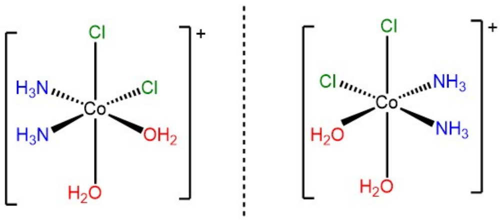
18.1.1 Nature of Optical Activity

Enantiomers

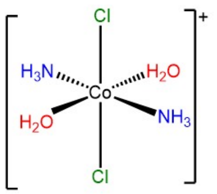
Asymmetric coordination complexes occur as pairs of isomers known as **enantiomers**. These two forms are identical in composition, connectivity, and most physical properties, but differ in their spatial arrangement in a mirror-image manner.

- One enantiomer rotates the plane of polarized light **clockwise** and is designated **d** (dextro, +).
- The other rotates it **counter-clockwise** and is designated **l** (laevo, −).

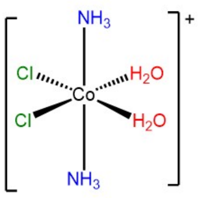
The two together constitute an **enantiomorphic pair**. Importantly, enantiomers have identical chemical behavior in *achiral* environments but can be distinguished using chiroptical techniques such as optical rotation measurements or circular dichroism spectroscopy.



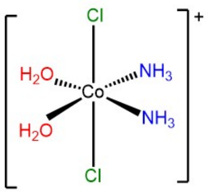
enantiomers of -*cis* NH_3, *cis*-Cl_2, *cis*-H_2O



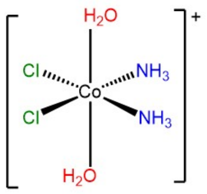
all trans



trans NH_3, *cis*-Cl_2, *cis*-H_2O



cis NH_3, *trans*-Cl_2, *cis*-H_2O



is NH_3, *cis*-Cl_2, *trans*-H_2O

The Phenomenon of Optical Rotation

The rotation of plane-polarized light arises because chiral molecules interact differently with left- and right-circularly polarized components of light. This differential interaction is the fundamental basis of optical activity and provides direct evidence of molecular chirality.

18.2.2 Structural Requirements for Optical Isomerism

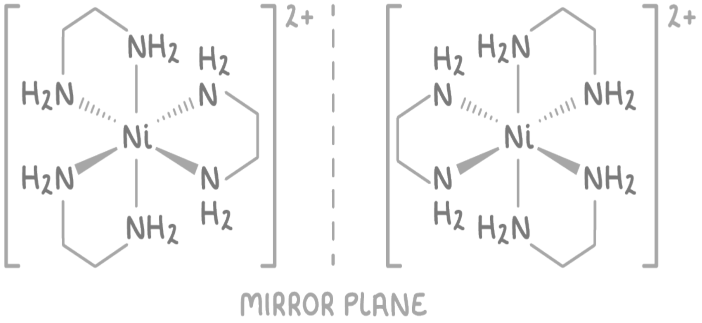
Optical isomerism in coordination compounds requires the **absence of symmetry elements** such as a plane of symmetry (σ), a center of symmetry (i), or an improper rotation axis (S_n). It is particularly common in **octahedral complexes** containing **bidentate (chelating)**

ligands, which bind the metal ion through two donor atoms and form stable five- or six-membered rings.

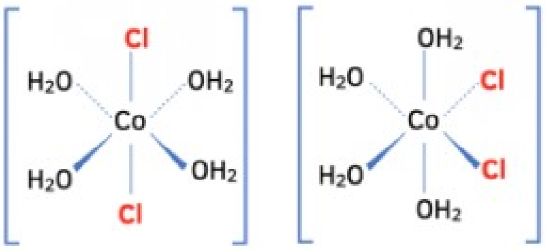
Illustrative Example: [Co(*en*)$_2$Cl$_2$]$^+$

Here, *en* denotes **ethylenediamine ($H_2N–CH_2–CH_2–NH_2$)**, a neutral bidentate ligand.

- **Cis-isomer**
  - The two chloride ligands occupy adjacent positions.
  - The overall geometry lacks a mirror plane or center of symmetry.
  - As a result, the cis form exists as two optically active enantiomers: **d-cis** and **l-cis**.
  - These forms rotate plane-polarized light in equal magnitude but opposite directions.



- **Trans-isomer**
  - The two chloride ligands are positioned opposite to each other.
  - This arrangement introduces a plane of symmetry.
  - Consequently, the trans form is **optically inactive**, despite having the same formula and coordination number.



This classic example clearly demonstrates how **ligand arrangement and molecular symmetry**, rather than mere composition, determine optical activity.

18.2.3 Optical Activity in Polynuclear Complexes

Optical isomerism is not restricted to mononuclear complexes; it can also occur in **polynuclear complexes** containing two or more metal centers linked by bridging ligands.

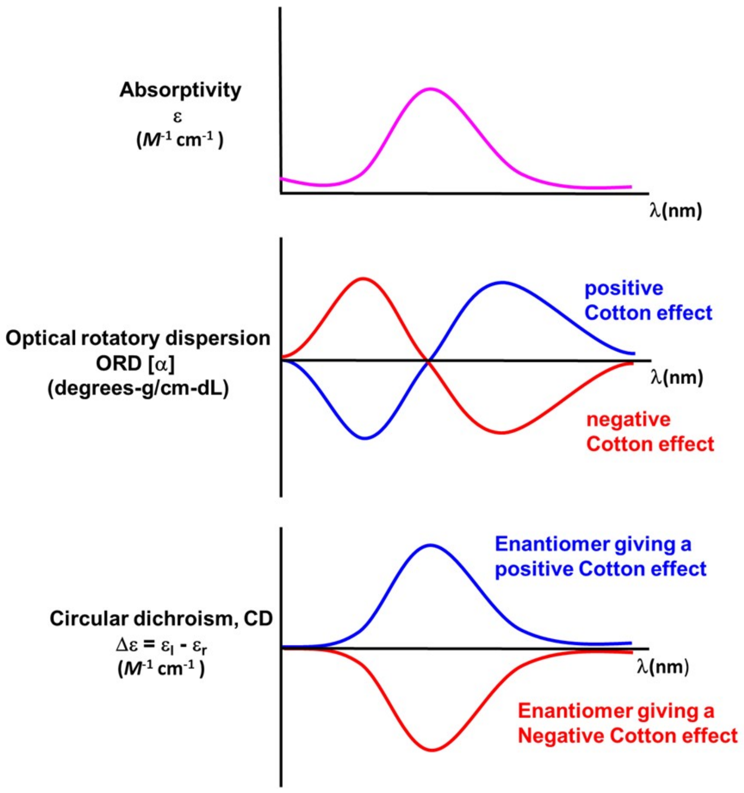
- Such complexes may exist as **optically active d and l forms**, provided the overall structure is chiral.
- In some cases, a special stereoisomer known as a **meso form** is observed.

Meso Form

A meso compound contains multiple stereogenic elements but is **optically inactive** due to **internal compensation**. Although individual parts of the molecule are chiral, the overall structure possesses an internal plane of symmetry that causes the optical rotations from different regions to cancel each other.

18.3 THE COTTON EFFECT

The **Cotton Effect** is a hallmark chiroptical phenomenon observed in **chiral molecules** when their **optical activity is measured in the vicinity of an electronic absorption band**. It represents the characteristic behavior of both **Optical Rotatory Dispersion (ORD)** and **Circular Dichroism (CD)** as the wavelength of light passes through an absorption transition.



18.3.1 Circular Dichroism (CD)

Circular Dichroism refers to the **differential absorption** of **left- (LCP)** and **right-circularly polarized (RCP)** light by a chiral molecule.

$$\Delta\varepsilon = \varepsilon_L - \varepsilon_R$$

- A **non-zero Δε** is direct evidence of molecular chirality.
- CD signals appear as **positive or negative peaks** corresponding to electronic transitions such as **d–d**, **charge-transfer**, or ligand-centered transitions.
- CD is especially sensitive to **coordination geometry and absolute stereochemistry**.

18.3.2 Optical Rotatory Dispersion (ORD)

Optical Rotatory Dispersion describes the **variation of optical rotation (α)** with **wavelength (λ)**.

- Far from absorption bands, α changes smoothly with wavelength.
- Near an absorption band, α changes rapidly and anomalously, giving rise to the Cotton effect.

18.3.3 Characteristic Cotton Effect Curve

In the region of an electronic absorption (for example, a **d–d transition** in a transition-metal complex):

- Optical rotation **increases sharply** to a **maximum**
- Then **decreases rapidly**, passing through **zero** at or near the absorption maximum
- Followed by a **minimum** of opposite sign

This produces a distinctive **S-shaped ORD curve**, while the corresponding CD spectrum shows a **positive or negative peak**.

18.3.4 Significance and Applications

- The **sign** (positive or negative) and **magnitude** of the Cotton effect are characteristic of the **three-dimensional arrangement of ligands**.
- It is extensively used to determine the **absolute configuration** of chiral coordination complexes, especially octahedral complexes with chelating ligands.

Example:
For complexes such as $[M(en)_3]^{n+}$:

Positive Cotton effect → Δ (right-handed helix)

Negative Cotton effect → Λ (left-handed helix)

Thus, the Cotton effect provides a **direct spectroscopic link between optical activity and molecular geometry**.

18.4 THE FARADAY EFFECT (MAGNETO-OPTICAL ROTATION)

In contrast to the Cotton effect, which is an **intrinsic property of chiral molecules**, the **Faraday Effect** is an **induced optical activity** produced by an external magnetic field.

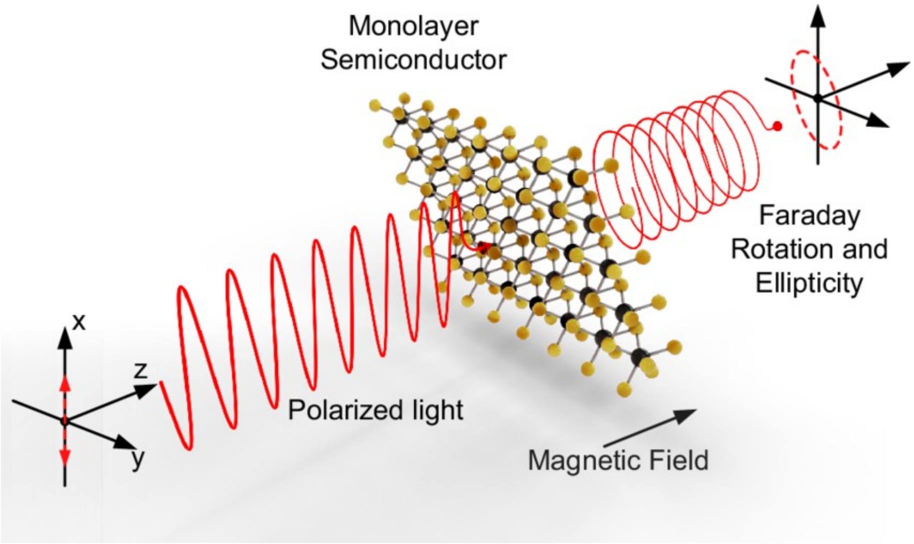


Figure: Faraday Effect (Magneto-optical rotation and ellipticity)

18.4.1 Phenomenon

When any substance—**chiral or achiral**—is placed in a **strong magnetic field** parallel to the direction of light propagation:

- The plane of polarized light is **rotated**
- The direction of rotation depends on the **direction of the magnetic field**, not on molecular chirality

This phenomenon is known as **magneto-optical rotation** or the **Faraday Effect**.

18.4.2 Mechanism

- The applied magnetic field **perturbs the electronic energy levels** of the molecule (Zeeman splitting).

- This induces a difference in the **refractive indices** for left- and right-circularly polarized light.
- As a result, unequal phase velocities lead to rotation of the plane of polarization.

Unlike optical rotation due to chirality, **Faraday rotation does not reverse sign** when the light path is reversed.

18.4.3 Magnetic Circular Dichroism (MCD)

The Faraday effect forms the theoretical basis of **Magnetic Circular Dichroism (MCD) spectroscopy**, which measures the differential absorption of circularly polarized light in the presence of a magnetic field.

Why MCD is important:

- Particularly powerful for **transition-metal complexes**
- Highly sensitive to:
  - Degenerate or near-degenerate ground states
  - Spin-allowed and spin-forbidden transitions
  - Metal-centered electronic structure
- Complements **UV–Visible spectroscopy**, especially when conventional spectra are weak, broad, or overlapping
-

18.5 SUMMARY:

1) **Chiroptical properties** arise from the interaction of **chiral coordination complexes with plane-polarized light**.
2) **Optical isomerism** occurs when a complex lacks symmetry element and exists as **d- and l- enantiomers**.
3) **Octahedral complexes with bidentate ligands** commonly exhibit optical activity.
4) The **Cotton effect** is the anomalous optical rotation near an electronic absorption band.
5) **Circular Dichroism (CD)** and **Optical Rotatory Dispersion (ORD)** are key techniques for studying chirality.
6) The **sign of the Cotton effect** is used to assign **Δ and Λ configurations**.
7) The **Faraday effect** is magnetically induced optical rotation, independent of molecular chirality.
8) **Magnetic Circular Dichroism (MCD)** is a powerful spectroscopic method for transition-metal complexes.

18.6 SELF-ASSESSMENT QUESTIONS:

A. Short Answer Questions

1) What are chiroptical properties?
2) Define optical isomerism.
3) What are enantiomers?
4) What is optical rotation?
5) State the structural requirements for optical isomerism.
6) Why is cis-$[Co(en)_2Cl_2]^+$ optically active?
7) What is a meso form?

8) Define the Cotton effect.
9) What is Circular Dichroism?
10) What is the Faraday effect?

B. Long Answer Questions

1) Explain optical isomerism in coordination complexes with suitable examples.
2) Discuss the origin of optical activity in chiral coordination compounds.
3) Describe the Cotton effect and its significance in coordination chemistry.
4) Explain ORD and CD techniques and their relationship.
5) Discuss optical activity in polynuclear complexes and meso forms.
6) Explain the Faraday effect and its distinction from optical rotation.
7) Describe Magnetic Circular Dichroism and its applications.

18.7 TECHNICAL TERMS:

1) **Chirality** – Property of a molecule that makes it non-superimposable on its mirror image.
2) **Optical isomerism** – Stereoisomerism due to molecular asymmetry causing optical activity.
3) **Enantiomers** – Mirror-image isomers rotating plane-polarized light in opposite directions.
4) **Optical rotation** – Rotation of plane-polarized light by a chiral molecule.
5) **Circular Dichroism (CD)** – Differential absorption of left- and right-circularly polarized light.
6) **Optical Rotatory Dispersion (ORD)** – Variation of optical rotation with wavelength.
7) **Cotton effect** – Anomalous optical rotation near an absorption band.
8) **Δ and Λ configuration** – Right- and left-handed helical arrangements in octahedral complexes.
9) **Meso form** – Optically inactive stereoisomer with internal compensation.
10) **Faraday effect** – Magnetically induced rotation of plane-polarized light.
11) **Zeeman splitting** – Splitting of electronic energy levels in a magnetic field.
12) **Magnetic Circular Dichroism (MCD)** – Differential absorption of circularly polarized light in a magnetic field.

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LESSON - 19

BIOCHEMICAL ASPECTS OF IRON AND COBALT

19.0 OBJECTIVES:

After studying this lesson, the student will be able to:

1. **Understand the role of iron and cobalt in biological systems** from a bio-inorganic perspective.
2. **Explain the structure and function of the heme group** in oxygen binding.
3. **Describe oxygen transport by hemoglobin** and storage by myoglobin.
4. **Understand cooperative binding and the Bohr effect** in hemoglobin.
5. **Explain iron storage and transport** through ferritin and transferrin.
6. **Describe the structure and biological importance of vitamin B_{12}**.
7. **Recognize the importance of coordination chemistry in life processes**.

STRUCTURE

19.1 INTRODUCTION

Bio-inorganic chemistry is a specialised branch of chemistry that focuses on the role of **metal ions and coordination compounds in biological systems**. Many essential life processes depend on the unique chemical properties of **transition metals**, particularly their ability to exist in **multiple oxidation states**, form **stable coordination complexes**, and interact selectively with **biological ligands** such as proteins and nucleic acids. Among biologically important metals, **iron (Fe)** and **cobalt (Co)** occupy a central position. **Iron** is indispensable for **oxygen transport, oxygen storage, and electron-transfer processes**, whereas **cobalt** plays a highly specialised role through its presence in **vitamin B_{12}**. Together, these metals demonstrate how **coordination**

chemistry underlies vital life processes such as **respiration, metabolism, growth, and neurological function**.

19.2 IRON IN BIOLOGICAL SYSTEMS

Iron is an **essential trace element** widely distributed in plants, animals, and microorganisms. In biological systems, iron mainly exists in the **ferrous (Fe^{2+})** and **ferric (Fe^{3+})** oxidation states. This ability to undergo **reversible redox reactions** makes iron ideally suited for **oxygen binding and electron transfer**. However, **free iron ions are toxic** because they can catalyse the formation of **reactive oxygen species**. Therefore, living organisms strictly regulate iron by binding it to **specific proteins**, ensuring **controlled reactivity and physiological availability**.

One of the most important biological roles of iron is its participation in **oxygen transport and storage**, which is carried out by **heme proteins**, notably **hemoglobin** and **myoglobin**.

19.3 HEME GROUP AND OXYGEN BINDING

The key structural feature common to hemoglobin and myoglobin is the **heme group**, an **iron–porphyrin coordination complex** derived from **protoporphyrin IX**. At the centre of the porphyrin macrocycle lies an **Fe^{2+} ion** coordinated to **four nitrogen atoms** in a planar arrangement. A **fifth coordination site** is occupied by a **histidine nitrogen** from the surrounding **globin protein**, while the **sixth coordination site** remains available for **reversible oxygen binding**. This precisely tuned coordination environment allows iron to bind oxygen **efficiently and reversibly** without undergoing **irreversible oxidation**.

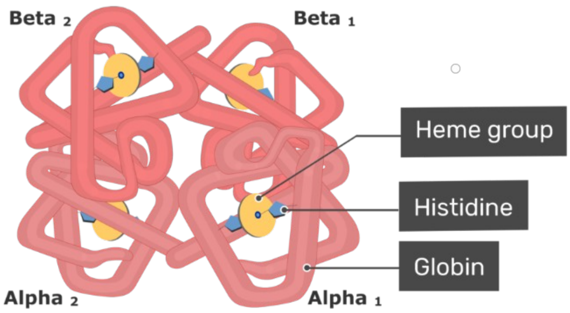

Figure: Quaternary structure of hemoglobin ($\alpha_2\beta_2$)

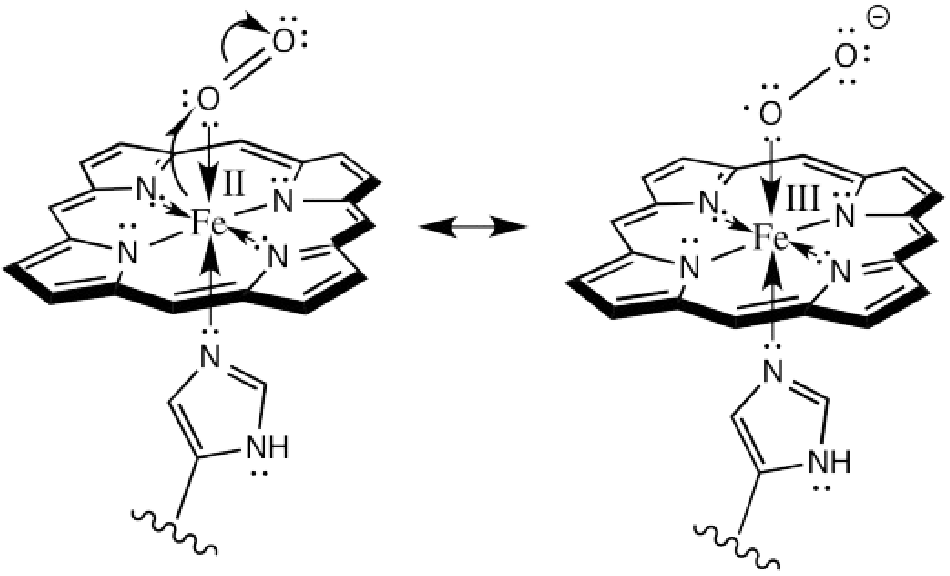

Figure: Resonance structures of oxyhemoglobin (Fe–O_2 bonding)

19.4 HEMOGLOBIN: TRANSPORT OF OXYGEN

Hemoglobin is the **red respiratory pigment** present in **red blood cells (RBCs)** and is responsible for **transporting oxygen from the lungs to tissues**. It is a **tetrameric globular protein** with a molecular weight of about **65,000**, consisting of **four polypeptide subunits**, each containing a **heme group**. Thus, one hemoglobin molecule can bind **four molecules of oxygen**.

In the absence of oxygen, hemoglobin exists as **deoxyhemoglobin**, in which **Fe^{2+}** is **five-coordinate**, **high-spin**, and **paramagnetic**, with a **water molecule** weakly bound at the sixth position. When oxygen is available in the lungs, the water molecule is displaced and **oxyhemoglobin** is formed. In this state, iron remains in the **Fe^{2+} oxidation state**, but the complex becomes **six-coordinate**, **low-spin**, and **diamagnetic**. This reversible interconversion enables hemoglobin to function as an **efficient oxygen carrier**.

A unique feature of hemoglobin is its **cooperative oxygen binding**. Binding of the first oxygen molecule induces a **conformational change** from the **tense (T) state** to the **relaxed (R) state**, increasing the oxygen affinity of the remaining subunits. As a result, hemoglobin exhibits a **sigmoidal oxygen dissociation curve**, ideal for oxygen uptake in the lungs and release in tissues.

The oxygen-binding affinity of hemoglobin is also influenced by **pH and carbon dioxide concentration**. A decrease in pH or an increase in CO_2 lowers oxygen affinity, promoting oxygen release in actively respiring tissues. This phenomenon is known as the **Bohr effect**. Hemoglobin also indirectly assists in **carbon dioxide transport** by binding **protons**, facilitating CO_2 removal.

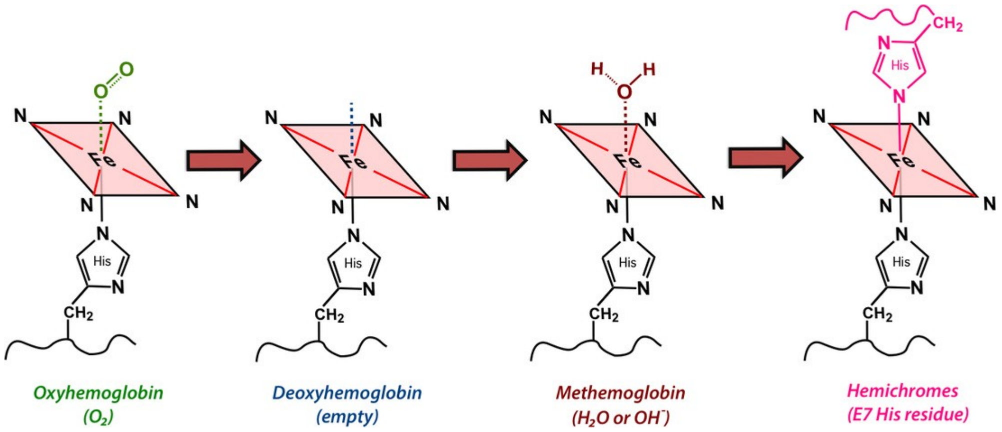

Figure: Different forms of hemoglobin based on axial ligand coordination

19.5 MYOGLOBIN: STORAGE OF OXYGEN

Myoglobin is a **heme protein** found mainly in **skeletal and cardiac muscles**. Structurally, it resembles a **single subunit of hemoglobin** and contains **one polypeptide chain** with **one heme group**, having a molecular weight of approximately **17,000**. Unlike hemoglobin, myoglobin does not exhibit cooperative binding and shows a **hyperbolic oxygen dissociation curve**.

Myoglobin has a **higher affinity for oxygen** than hemoglobin, enabling it to accept oxygen from hemoglobin and **store it within muscle cells**. During **vigorous exercise**, when oxygen demand increases and partial pressure of oxygen decreases, myoglobin releases its stored oxygen. Hence, myoglobin acts as an **intracellular oxygen reservoir**, ensuring continuous **aerobic respiration**.

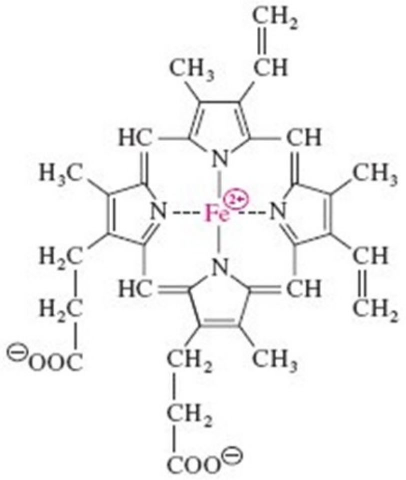

Figure: Chemical Structure of the Fe(II) Protoporphyrin IX heme group in myoglobin and hemoglobin

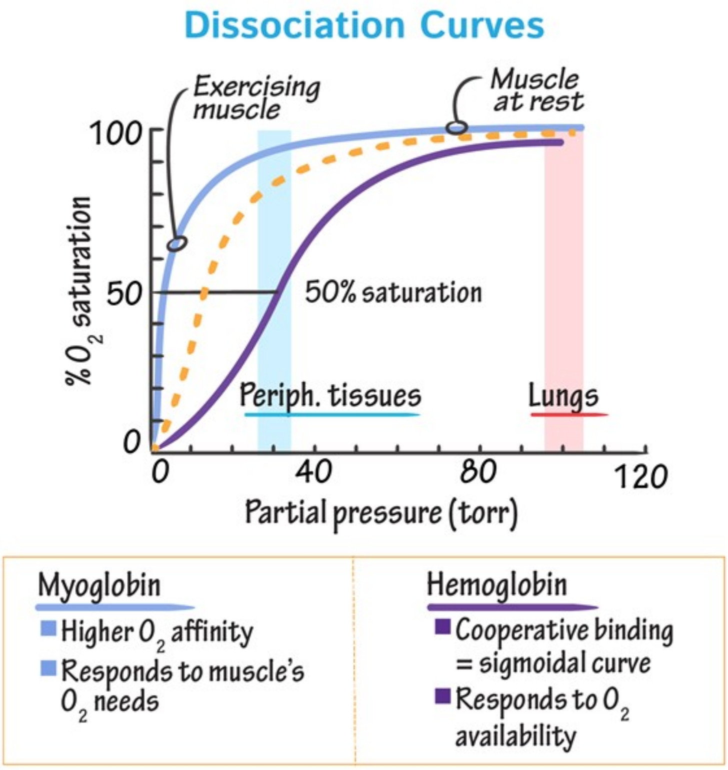

Figure: Oxygen dissociation curves of hemoglobin and myoglobin

19.6 STORAGE AND TRANSPORT OF IRON

Iron homeostasis in the body is maintained by specialised proteins. **Ferritin** is the major **iron storage protein**, capable of storing thousands of iron atoms in the **Fe^{3+} state** within a hollow protein shell, thereby preventing **oxidative damage**. **Transferrin** is a **plasma glycoprotein** responsible for **transporting Fe^{3+} ions** through the bloodstream and delivering iron safely to tissues via **receptor-mediated uptake**.

19.7 COBALT IN BIOLOGICAL SYSTEMS

In contrast to iron, **cobalt** has a **highly specialised biological role**, almost exclusively through its presence in **vitamin B_{12} (cobalamin)**. Vitamin B_{12} was identified as the **anti-pernicious anaemia factor** and is essential for **normal growth, blood formation, and nervous system function**.

19.7.1 Structure of Vitamin B_{12}

Vitamin B_{12} contains a central **cobalt ion in the +3 oxidation state (Co^{3+})** coordinated within a macrocyclic ligand called the **corrin ring**. The corrin ring resembles porphyrin but is **less rigid**, **partially saturated**, and lacks one methine bridge. The cobalt ion is coordinated to **four corrin nitrogen atoms**, axially bonded to a **dimethylbenzimidazole nitrogen**, and a **variable upper axial ligand** such as **CN^-, CH_3, or adenosyl group**. A remarkable feature of vitamin B_{12} is the presence of a **stable cobalt–carbon (Co–C) bond**, which is **extremely rare in biological systems**.

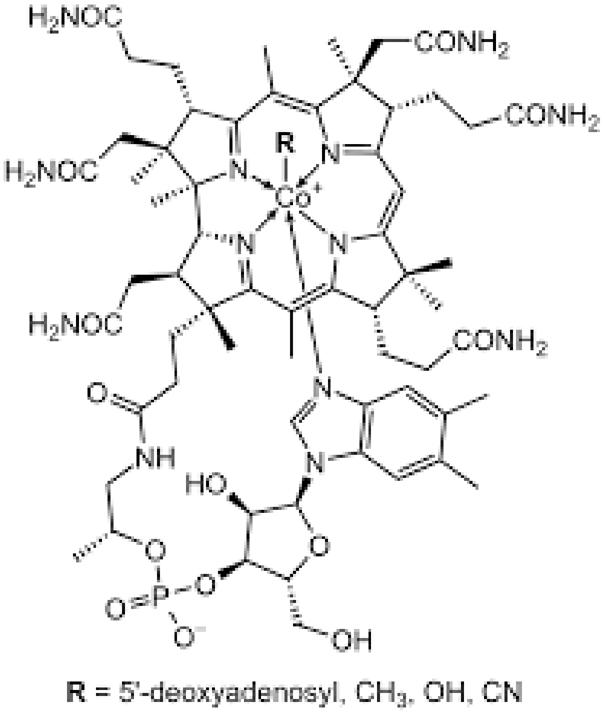

Figure: Vitamin B_{12} (Cobalamin)

19.7.2 Biochemical Functions and Importance of Vitamin B_{12}

Vitamin B_{12} acts as an essential **coenzyme** in several metabolic reactions. It plays a vital role in **DNA synthesis**, **methyl-group transfer reactions**, and **red blood cell formation**, particularly in the conversion of **homocysteine to methionine**. It is also involved in **molecular rearrangement reactions**, such as the conversion of **methylmalonyl-CoA to succinyl-CoA**, linking fatty-acid and amino-acid metabolism to the **citric acid cycle**.

Deficiency of vitamin B_{12} results in **pernicious (megaloblastic) anaemia** and is frequently accompanied by **neurological disorders**, including **numbness, memory loss, and cognitive impairment**.

19.7.3 Conclusion

The biochemical roles of **iron and cobalt** highlight the **fundamental importance of coordination chemistry in living systems**. **Iron**, through **hemoglobin and myoglobin**, enables **oxygen transport, storage, and aerobic respiration**, while **cobalt**, through **vitamin B_{12}**, supports **essential metabolic pathways, DNA synthesis, and nervous system function**. These metal-based systems clearly demonstrate that **metal–ligand interactions are central to life, health, and energy production**.

19.8 SUMMARY:

1) **Bio-inorganic chemistry** explains the role of **metal ions in biological systems**.
2) **Iron** plays a key role in **oxygen transport, storage, and electron transfer**.
3) **Hemoglobin** is a **tetrameric heme protein** that transports oxygen and shows **cooperative binding**.
4) **Deoxyhemoglobin** is **paramagnetic**, while **oxyhemoglobin** is **diamagnetic**, with iron remaining as **Fe^{2+}**.
5) The **Bohr effect** facilitates oxygen release in metabolically active tissues.
6) **Myoglobin** is a **monomeric protein** that stores oxygen in muscles.
7) **Ferritin** stores iron safely, and **transferrin** transports iron in blood.
8) **Cobalt** is biologically important as **vitamin B_{12}**, which contains a **corrin ring and a Co–C bond**.
9) **Vitamin B_{12}** functions as a **coenzyme in DNA synthesis and metabolism**, and its deficiency causes **pernicious anaemia**.
10) **Iron and cobalt demonstrate the essential role of coordination chemistry in life processes**.

19.9 SELF-ASSESSMENT QUESTIONS

A. Short Answer Questions

1) What is bio-inorganic chemistry?
2) Why is free iron toxic in biological systems?
3) What is the heme group?
4) Define deoxyhemoglobin and oxyhemoglobin.
5) What is the Bohr effect?
6) Why does myoglobin have a higher oxygen affinity than hemoglobin?
7) What is the biological role of ferritin?
8) Name the oxidation state of cobalt in vitamin B_{12}.
9) What is the corrin ring?
10) Mention one function of vitamin B_{12}.

B. Long Answer Questions

1) Describe the structure and oxygen-binding mechanism of hemoglobin.
2) Explain cooperative oxygen binding in hemoglobin with reference to the dissociation curve.

3) Compare hemoglobin and myoglobin in structure and function.
4) Discuss the storage and transport of iron in biological systems.
5) Describe the structure and biochemical functions of vitamin B_{12}.
6) Explain the biological importance of iron and cobalt with suitable examples.

19.10 TECHNICAL TERMS:

1) **Bio-inorganic chemistry**: Study of the role of metal ions and coordination compounds in biological systems.
2) **Heme group**: An iron–porphyrin complex responsible for oxygen binding.
3) **Porphyrin**: A macrocyclic ligand containing four nitrogen donor atoms.
4) **Deoxyhemoglobin**: Hemoglobin without bound oxygen; high-spin and paramagnetic.
5) **Oxyhemoglobin**: Oxygen-bound hemoglobin; low-spin and diamagnetic.
6) **Cooperative binding**: Increase in oxygen affinity after binding of the first O_2 molecule.
7) **Bohr effect**: Decrease in oxygen affinity of hemoglobin at low pH or high CO_2.
8) **Myoglobin**: Monomeric heme protein that stores oxygen in muscles.
9) **Ferritin**: Iron storage protein that stores iron as Fe^{3+}.
10) **Transferrin**: Plasma protein that transports iron in blood.
11) **Cobalamin**: Chemical name for vitamin B_{12}.
12) **Corrin ring**: Macrocyclic ligand in vitamin B_{12} similar to porphyrin but less rigid.
13) **Co–C bond**: Rare cobalt–carbon bond present in vitamin B_{12}.
14) **Pernicious anaemia**: Anaemia caused by vitamin B_{12} deficiency.

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LESSON – 20

PHOTO-INORGANIC CHEMISTRY

20.0 OBJECTIVES:

After studying this lesson, the student will be able to:

1) **Understand the fundamentals of photo-inorganic chemistry** and the role of light in inorganic reactions.
2) **Differentiate between thermal and photochemical reactions** based on excited-state behaviour.
3) **Explain electronic excitation processes** such as d–d, MLCT, and LMCT transitions.
4) **Describe the photochemical laws** governing light-induced reactions.
5) **Understand the concept of quantum yield** and factors affecting photochemical efficiency.
6) **Explain the principles and mechanisms of photo-redox reactions**.
7) **Describe photo-anation reactions** and their mechanistic features.
8) **Understand photochemical water splitting** as an application of photo-inorganic chemistry.
9) **Recognize the technological applications** of photo-inorganic processes in energy, environment, and medicine.

STRUCTURE

20.1 INTRODUCTION

Photo-inorganic chemistry investigates how the interaction of **light (UV, visible, or near-IR radiation)** with inorganic and coordination complexes induces chemical transformations. Unlike thermal reactions, which proceed through **ground-state collisions and thermal activation (Arrhenius behaviour)**, photochemical reactions operate on **excited-state potential energy surfaces**. The fundamental shift occurs when absorption of a photon promotes an electron to a higher energy level, **instantaneously altering the geometry, bond strengths, and redox potential** of the complex.

These electronically excited states are typically **short-lived (femtoseconds to microseconds)** but exhibit dramatically different chemical behaviour. For example, **metal-to-ligand charge-transfer (MLCT)** excited states can convert a stable species into a **powerful reductant**, whereas **ligand-to-metal charge-transfer (LMCT)** states can generate **highly oxidizing systems**. Such transient reactivity enables chemical transformations that are **inaccessible under purely thermal conditions**.

20.1.1 Key Mechanisms and Features

The reactivity in photo-inorganic chemistry is governed by distinct **electronic excitation pathways** and quantitative efficiency parameters. **d–d transitions**, which are metal-centred, often induce structural distortion or labilization of metal–ligand bonds. In contrast, **charge-transfer (CT) transitions** dominate photochemical reactivity. In **MLCT excitation**, electron density is shifted from the metal to ligand π^* orbitals, facilitating reduction or ligand dissociation. **LMCT excitation** transfers electron density from ligand to metal, creating strongly oxidizing ligand radicals.

The efficiency of a photochemical reaction is measured by the **quantum yield (Φ)**, defined as the number of molecules reacting per photon absorbed. While thermal reactions are intrinsically limited, **photochemical chain reactions and photoredox cycles may exhibit $\Phi > 1$**, reflecting catalytic turnover. A unique advantage of photochemistry is **precision control**:

reactions can be initiated instantaneously, confined spatially to illuminated regions, and selectively driven by tuning the wavelength and intensity of light.

20.1.2 Excited-State Dynamics

The photochemical event follows a well-defined sequence governed by fundamental photochemical laws. Upon **absorption of light**, in accordance with the **Grotthuss–Draper law**, the system undergoes a vertical transition to a **Franck–Condon excited state**. Rapid vibrational relaxation follows, often accompanied by **intersystem crossing (ISC)** from singlet to triplet states, a process enhanced by the **heavy-atom effect** of metal centres.

According to the **Stark–Einstein law of photochemical equivalence**, one photon activates one molecule in the primary step. The resulting long-lived triplet excited state can then participate in **electron transfer, ligand dissociation, or energy transfer**, ultimately leading to chemical transformation or return to the ground state.

20.1.3 Transformative Applications

Photo-inorganic chemistry bridges **fundamental photophysics with advanced technological applications**. In **solar energy conversion and artificial photosynthesis**, coordination complexes act as light harvesters in dye-sensitized solar cells and water-splitting systems that generate **hydrogen fuel**. In **photoredox catalysis**, visible light drives single-electron transfer reactions for organic synthesis, including C–H functionalization and cross-coupling, with increasing use of **earth-abundant metals such as copper and nickel**.

In **environmental remediation**, photocatalysts such as **TiO_2** promote the degradation of organic pollutants and pesticides under sunlight. In **medicine**, photoactivatable **Pt(IV) and Ru(II) complexes** remain biologically inert until irradiated at target sites, where they release cytotoxic species, thereby minimizing systemic toxicity in **photoactivated chemotherapy and photodynamic therapy**.

20.2 PHOTOCHEMICAL LAWS

Photochemical reactions differ fundamentally from thermal reactions because they are initiated by the **absorption of radiant energy** rather than heat. The theoretical framework governing such reactions is provided by two classical laws of photochemistry: the **Grotthuss–Draper Law** and the **Stark–Einstein Law of Photochemical Equivalence**. Together, these laws define **when light can induce a chemical reaction and how efficiently absorbed light is converted into chemical change**.

20.2.1 Grotthuss–Draper Law (First Law of Photochemistry)

The **Grotthuss–Draper law** states that **only light that is absorbed by a substance can produce a photochemical change**. Radiation that is transmitted through a system or reflected from it has no chemical effect. Thus, **absorption of light is a necessary condition for any photochemical reaction**.

From a molecular perspective, photochemical reactions begin only when a molecule absorbs a photon and is promoted to an **excited electronic state**. If the incident radiation does not correspond to an allowed electronic transition of the molecule, no excitation occurs and, consequently, no chemical transformation takes place. This principle explains why many substances are photochemically inert under certain wavelengths but highly reactive under others.

Implications in Photo-Inorganic Chemistry

In photo-inorganic chemistry, this law emphasizes the importance of the **electronic absorption spectra of metal complexes**. Only radiation matching **d–d transitions** or **charge-transfer bands**—such as **metal-to-ligand charge transfer (MLCT)** or **ligand-to-metal charge transfer (LMCT)**—can initiate photochemical processes. For example, complexes that absorb strongly in the visible region can be activated by sunlight, whereas those absorbing only in the far UV remain inactive under ambient conditions.

Thus, the Grotthuss–Draper law establishes that **spectral overlap between the light source and the absorption band of the complex is essential** for photochemical reactivity.

20.2.2 Stark–Einstein Law of Photochemical Equivalence (Second Law)

The **Stark–Einstein law** states that **each absorbed photon activates one molecule in the primary photochemical step**. In other words, the absorption of one quantum of light (hv) results in the excitation of **one and only one molecule**, producing at most one chemically activated species.

The energy of the absorbed photon is given by: $E = h\nu$

and on a molar basis,

$$E = N_A h\nu$$

Were
$h$is Planck's constant,
$\nu$is the frequency of radiation, and
$N_A$is Avogadro's number.

This law applies strictly to the **primary photochemical event**, i.e., the formation of an excited molecule. Subsequent chemical changes may involve multiple steps, but the initial excitation always follows a **one-photon–one-molecule relationship**.

20.2.2.1 Quantum Yield and Deviations from Unity

The Stark–Einstein law leads directly to the concept of **quantum yield (Φ)**, which measures the efficiency of a photochemical reaction:

$$\Phi = \frac{\text{Number of molecules reacting}}{\text{Number of photons absorbed}}$$

In an ideal photochemical reaction, **Φ = 1**, indicating that every absorbed photon results in one chemical transformation. However, real systems often deviate from this ideal behaviour.

- **Φ > 1** occurs in **photochemical chain reactions**, where a single photon initiates a sequence of thermal reactions, leading to multiple product molecules.
- **Φ < 1** is observed when excited molecules lose energy through **non-reactive pathways**, such as **fluorescence, phosphorescence, internal conversion, or collisional deactivation**.

Thus, while the Stark–Einstein law governs the primary step, the observed quantum yield reflects the **balance between productive and non-productive excited-state processes**.

20.2.3 Combined Significance of the Two Laws

Together, the two photochemical laws provide a complete conceptual foundation for photochemistry:

- The **Grotthuss–Draper law** establishes **absorption as a prerequisite** for photochemical change.
- The **Stark–Einstein law** defines the **stoichiometric relationship between light and molecular excitation**.

These laws distinguish photochemical reactions from thermal reactions and are essential for understanding **photo-redox processes, photo-anation reactions, actinometry, excited-state kinetics, and energy conversion in photo-inorganic chemistry**.

20.2.4 Conclusion

The photochemical laws reveal that light is not merely a source of energy but a **quantized reagent** that controls chemical reactivity at the electronic level. By dictating the conditions for excitation and the efficiency of light-induced processes, the **Grotthuss–Draper and Stark–Einstein laws** form the theoretical backbone of **photo-inorganic chemistry**, enabling rational design of photochemical systems for **solar energy conversion, catalysis, and environmental and medicinal applications**.

20.3 PHOTO-REDOX REACTIONS

20.3.1 Introduction and Fundamental Concept

Photo-redox reactions are oxidation–reduction processes that are **initiated by light absorption** and proceed through **electronically excited states** of inorganic or coordination compounds. Many such reactions are **thermodynamically or kinetically inaccessible under thermal conditions**, but become feasible when light supplies energy directly to the electronic structure of a molecule.

When a metal complex absorbs radiation in the UV–visible region, it is promoted from the **ground state to an excited electronic state**, commonly a **metal-to-ligand charge-transfer (MLCT)** state, **ligand-to-metal charge-transfer (LMCT)** state, or an excited **d–d state**. These excited states possess **dramatically altered redox potentials**, making them **much stronger oxidants or reductants** than their ground-state counterparts.

20.3.2 Change in Redox Behaviour upon Excitation

Electronic excitation fundamentally reshapes redox chemistry. In the excited state, electron density is redistributed between the metal centre and ligands:

- In **MLCT excitation**, electron density is transferred from the metal to ligand π* orbitals, generating a **reduced ligand and oxidized metal centre**, often producing a **powerful excited-state reductant**.
- In **LMCT excitation**, electron density flows from ligand to metal, leaving behind **ligand-based radicals** and creating **strongly oxidizing excited states**.
- **d–d excited states**, though often short-lived, can weaken metal–ligand bonds and facilitate electron transfer or substitution.

As a result, an excited complex can **donate an electron to an acceptor** or **accept an electron from a donor**, thereby converting **light energy into chemical redox energy**.

20.3.3 General Reaction Scheme

The basic sequence of a photo-redox process is:

Excitation

$$M + hv \rightarrow M^{¿}$$

where $M^{¿}$ is the excited metal complex.

Electron-Transfer Pathways

Oxidative quenching (excited complex donates an electron):

$$M^{\text{¿}} + A \rightarrow M^{+\text{¿}+A^{-\text{¿¿}}\text{¿}}$$

Reductive quenching (excited complex accepts an electron):

$$M^{\text{¿}} + D \rightarrow M^{-\text{¿}+D^{+\text{¿¿}}\text{¿}}$$

Where, A = electron acceptor; D = electron donor

These steps illustrate how light absorption enables **single-electron transfer reactions** that are central to photo redox chemistry.

Neat Mechanism: MLCT-Based Photo-Redox Reaction

Example: Ru(II) Polypyridyl Complex

Step 1: Light absorption (MLCT excitation)

$$\text{¿}$$

The MLCT state involves transfer of electron density from Ru(II) to the bipyridine ligands.

Step 2: Excited-state electron transfer

$$\text{¿}$$

The excited complex acts as a **strong reductant**, donating an electron.

Step 3: Catalyst regeneration

$$\text{¿}$$

Thus, the Ru(II) complex functions as a **photoredox catalyst**, undergoing repeated light-driven redox cycles.

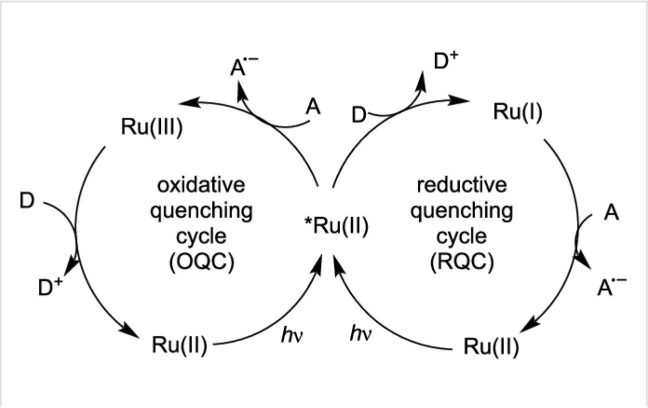

Figure: Photoredox catalysis mechanism

20.3.4 Representative Inorganic Examples

A classic inorganic example is **Fe(III) photochemistry**, where irradiation of complexes such as ¿or $FeCl_4^{-¿¿}$leads to **reduction of Fe(III) to Fe(II)** accompanied by **oxidation of coordinated ligands**. This reaction demonstrates light-induced redox change within the coordination sphere itself.

Ru(II) polypyridyl complexes represent the most widely studied photoredox systems. Their long-lived triplet MLCT states make them exceptionally efficient in mediating **single-electron transfer reactions**, forming the foundation of modern **photoredox catalysis**.

20.3.5 Significance and Applications

Photo-redox reactions form the chemical basis of several important technologies:

- **Photoredox catalysis**, enabling mild and selective redox reactions in inorganic and organic synthesis
- **Solar-energy conversion**, where light energy is stored as chemical redox energy
- **Artificial photosynthesis**, involving light-driven water splitting and CO_2 reduction
- **Environmental photochemistry**, including degradation of pollutants

These reactions vividly illustrate how **electronic excitation transforms redox behaviour**, establishing light as a **true chemical reagent rather than a mere energy source**.

20.3.6 Conclusion

Photo-redox reactions exemplify the power of photo-inorganic chemistry to **unlock new redox pathways** by exploiting excited-state electronic structure. Through MLCT, LMCT, and related excited states, metal complexes acquire extraordinary oxidizing or reducing ability, enabling **light-driven redox cycles central to catalysis, energy conversion, and sustainable chemistry**.

20.4 PHOTO-ANATION REACTIONS

20.4.1 Definition and Fundamental Concept

Photo-anation reactions are a special class of **photochemical ligand-substitution reactions** in which a **neutral ligand, most commonly water (H_2O), is replaced by an anionic ligand (X^-)** in the coordination sphere of a metal complex under the influence of light. These reactions are typically observed in coordination compounds that are **thermally inert**, but become reactive upon electronic excitation.

Upon absorption of light, the metal complex is promoted to an **excited electronic state**, often involving **ligand-to-metal charge transfer (LMCT)** or population of **metal–ligand antibonding orbitals**. This excitation weakens the metal–ligand bond, generating a **labile excited state** that readily undergoes substitution by an entering anion.

20.4.2 General Reaction Scheme

$$¿$$

where
$X^{-¿=Cl^{-¿,Br^{-¿,SCN^{-¿¿}¿}¿}¿}$, etc.

This reaction clearly illustrates that **light acts as the activating reagent**, enabling substitution without the need for high temperature or strong nucleophiles.

20.4.3 Mechanism of Photo-Anation

The mechanism of photo-anation involves three key steps:

i. Electronic Excitation

Absorption of light promotes an electron into an **antibonding orbital** (such as $e_g^{¿}$in octahedral complexes) or into a **charge-transfer excited state (LMCT)**:

$$¿$$

ii. Labilization of the Metal–Ligand Bond

Population of antibonding orbitals **reduces the metal–ligand bond order**, particularly the M–OH_2 bond. This converts an otherwise inert complex into a **highly reactive, labile excited state**.

iii. Ligand Substitution

The weakened neutral ligand dissociates, allowing **nucleophilic attack by an anionic ligand**:

¿

Representative Example

A classic example involves chromium(III), which is **kinetically inert under thermal conditions**:

¿

This reaction does not occur appreciably in the dark, but proceeds readily upon irradiation, clearly demonstrating **photo-induced ligand substitution**.

Relation to Photoaquation

Photo-anation is closely related to **photoaquation**, which is the **reverse process**:

- **Photoaquation**: replacement of a coordinated ligand by water upon irradiation
- **Photo-anation**: replacement of coordinated water by an anionic ligand upon irradiation

Together, these reactions show that **light can reversibly control ligand substitution pathways**.

20.4.4 Significance and Applications

Photo-anation reactions are significant because they demonstrate how **light can control coordination geometry, ligand environment, and substitution kinetics** with high spatial and temporal precision. They are particularly important for:

- Understanding **photochemical reactivity of inert metal complexes** (e.g., Cr(III), Co(III))
- Designing **photoactivatable metal complexes**, including Ru and Pt systems used in **photoactivated chemotherapy**
- Achieving **ligand substitution under mild conditions**, without heat or aggressive reagents

These reactions exemplify how **electronic excitation transforms coordination chemistry**, allowing selective and controllable reactivity.

20.4.5 Conclusion

Photo-anation reactions illustrate the power of light to **induce ligand substitution by generating labile excited states** in otherwise inert coordination complexes. Through excitation into antibonding or charge-transfer orbitals, metal–ligand bonds are weakened, enabling substitution by anionic ligands. As such, photo-anation represents a key mechanism in **photo-inorganic chemistry**, bridging excited-state electronic structure with controlled chemical reactivity.

20.5 PHOTOCHEMICAL DECOMPOSITION OF WATER (WATER SPLITTING)

20.5.1 Introduction and Basic Concept

The **photochemical decomposition of water**, also known as **photolysis or water splitting**, is one of the most important applications of **photo-inorganic chemistry**. In this process, **light energy is converted into chemical energy** by splitting water molecules into **hydrogen and oxygen**, thereby storing solar energy in chemical bonds. Because hydrogen is a clean, high-energy fuel, this reaction is regarded as a cornerstone of **solar-fuel and renewable-energy research**.

The overall reaction is:

$$2H_2O \overset{\square}{\rightarrow} 2H_2+O_2(\Delta G^{\circ}>0)$$

This reaction is **thermodynamically uphill (endergonic)** and does not proceed spontaneously. It therefore requires **photocatalysts**, typically **transition-metal complexes, metal oxides, or inorganic semiconductors**, to harness light energy and drive the reaction.

20.5.2 Role of Photocatalysts

Photocatalysts absorb light and generate **electron–hole pairs or excited electronic states** capable of driving redox reactions. A complete photocatalytic system generally contains:

- A **light-harvesting unit** (semiconductor or metal complex)
- A **water-oxidation catalyst** (often Ru, Ir, Co, Mn complexes or metal oxides)
- A **proton-reduction catalyst** (Pt, Ni, Co complexes or related materials)

In **natural photosynthesis**, metal centres play a crucial role in water oxidation. **Artificial systems** aim to mimic this process using inorganic catalysts.

Neat Mechanism: Semiconductor-Assisted Water Splitting

Step 1: Light Absorption and Charge Generation

A semiconductor (e.g., TiO₂) absorbs a photon with energy greater than its band gap:

$$\text{Catalyst}+hv \rightarrow e_{CB}^{-¿+h_{VB}^{+¿¿}¿}$$

An electron is promoted to the **conduction band (CB)**, leaving a positive **hole (h⁺)** in the **valence band (VB)**.

Step 2: Oxidation of Water (at the Hole Site)

$$2H_2O+4h^{+¿\rightarrow O_2+4H^{+¿¿}¿}$$

The photogenerated holes oxidize water to molecular oxygen.

Step 3: Reduction of Protons (at the Electron Site)

$$4H^{+¿+4e^{-¿\rightarrow 2H_2¿}¿}$$

The conduction-band electrons reduce protons to hydrogen gas.

Overall Half-Reactions

Water oxidation (4-electron process):

$$2H_2O \rightarrow O_2+4H^{+¿+4e^{-¿¿}¿}$$

Proton reduction:

$$4H^{+¿+4e^{-¿\rightarrow 2H_2¿}¿}$$

Efficient coupling of these half-reactions results in complete water splitting.

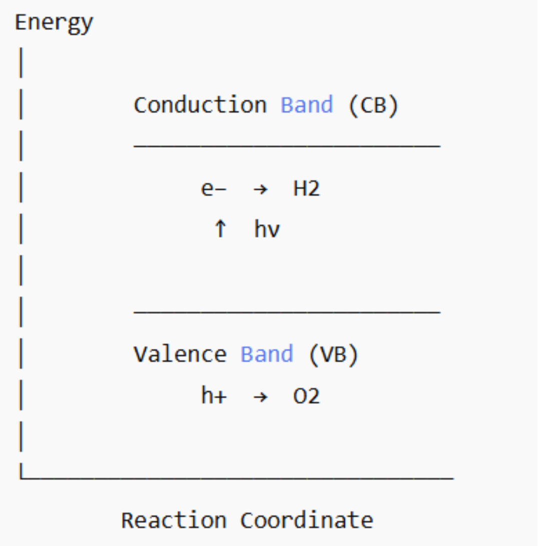

Figure: Energy-Level (Band) Diagram

Absorption of light promotes an electron from the **valence band** to the **conduction band**, generating an **electron–hole pair**. The excited electrons drive **proton reduction to hydrogen**, while the holes oxidize **water to oxygen**, resulting in overall photochemical decomposition of water.

20.5.3 Challenges in Photochemical Water Splitting

Despite its promise, several challenges limit efficiency:

- **Charge recombination**: electrons and holes recombine, releasing heat instead of driving chemistry
- **Back reaction**: generated H_2 and O_2 can recombine to form water
- **Band-gap limitation**: materials like TiO_2 absorb only UV light (~4% of solar spectrum)
- **Catalyst stability and overpotential** issues

Current research focuses on **doping, heterojunctions, and transition-metal co-catalysts** to overcome these limitations.

20.5.4 Significance

Photochemical decomposition of water is of immense importance because it:

- Converts **solar energy into chemical fuel**
- Provides a **clean, renewable source of hydrogen**
- Mimics natural photosynthesis using inorganic systems
- Forms the foundation of **solar-fuel chemistry and artificial photosynthesis**

20.5.5 Conclusion

The photochemical decomposition of water demonstrates the power of **photo-inorganic chemistry** to harness light for large-scale chemical transformations. By using light-absorbing catalysts to generate reactive electrons and holes, water can be split into hydrogen and oxygen, offering a sustainable pathway toward **renewable energy and a hydrogen-based economy**.

20.6 SUMMARY:

1) **Photo-inorganic chemistry** deals with chemical reactions initiated by **absorption of light** by inorganic and coordination compounds.
2) Light absorption promotes molecules to **excited electronic states**, which exhibit altered **geometry, bonding, and redox properties**.
3) **Charge-transfer transitions (MLCT and LMCT)** dominate photochemical reactivity in metal complexes.
4) **Excited-state dynamics** involve Franck–Condon transitions, vibrational relaxation, and intersystem crossing.
5) The **Grotthuss–Draper law** states that only absorbed light can produce a photochemical change.
6) The **Stark–Einstein law** states that one absorbed photon activates one molecule in the primary step.
7) **Quantum yield (Φ)** measures the efficiency of photochemical reactions and may be greater or less than unity.
8) **Photo-redox reactions** involve light-induced oxidation–reduction via excited metal complexes.
9) **Photo-anation reactions** are light-induced ligand substitution reactions involving replacement of neutral ligands by anions.

10) **Photochemical decomposition of water** converts solar energy into chemical energy, producing hydrogen and oxygen.
11) Photo-inorganic chemistry forms the basis of **solar-energy conversion, photoredox catalysis, environmental remediation, and photomedicine**.

20.7 SELF-ASSESSMENT QUESTIONS:

A. Short Answer Questions

1) What is photo-inorganic chemistry?
2) Why are photochemical reactions different from thermal reactions?
3) Define MLCT and LMCT transitions.
4) State the Grotthuss–Draper law of photochemistry.
5) State the Stark–Einstein law of photochemical equivalence.
6) What is quantum yield?
7) What is a photo-redox reaction?
8) Define photo-anation reaction.
9) What is photochemical water splitting?
10) Mention one application of photo-inorganic chemistry.

B. Long Answer Questions

1) Explain the fundamental principles of photo-inorganic chemistry.
2) Describe the Grotthuss–Draper and Stark–Einstein laws and their significance.
3) Discuss excited-state dynamics in coordination compounds.
4) Explain the mechanism of photo-redox reactions with suitable examples.
5) Describe photo-anation reactions and compare them with photo-aquation.
6) Discuss the photochemical decomposition of water and its significance.
7) Explain the applications of photo-inorganic chemistry in energy and environmental science.

20.8 TECHNICAL TERMS:

1) **Photo-inorganic chemistry** – Study of light-induced reactions in inorganic and coordination compounds.
2) **Excited state** – A higher-energy electronic state formed after photon absorption.
3) **d–d transition** – Electronic transition between d-orbitals of a metal ion.
4) **MLCT** – Metal-to-ligand charge-transfer transition.
5) **LMCT** – Ligand-to-metal charge-transfer transition.
6) **Quantum yield (Φ)** – Number of molecules reacting per photon absorbed.
7) **Grotthuss–Draper law** – Only absorbed light causes photochemical change.
8) **Stark–Einstein law** – One photon activates one molecule in the primary step.
9) **Intersystem crossing** – Transition between electronic states of different spin multiplicity.
10) **Photo-redox reaction** – Light-induced oxidation–reduction reaction.
11) **Photo-anation** – Light-induced substitution of a neutral ligand by an anionic ligand.

12) **Photocatalyst** – A substance that absorbs light and promotes chemical reactions.
13) **Water splitting** – Photochemical decomposition of water into hydrogen and oxygen.
14) **Artificial photosynthesis** – Mimicking natural photosynthesis using inorganic systems.

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