



GOVERNMENT ARTS AND SCIENCE COLLEGE
(Affiliated to Manonmaniam Sundaranar University)
KANAYAKUMARI-629401

STUDY MATERIAL FOR B.Sc. CHEMISTRY
INORGANIC CHEMISTRY- III
VI – SEMESTER



ACADEMIC YEAR 2022 - 2023
PREPARED BY
DEPARTMENT OF CHEMISTRY

STUDY MATERIAL FOR B.Sc. CHEMISTRY
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Objectives

- To study the theories in coordination chemistry.
- To study the chemistry of metal carbonyls
- To understand the role of metal ions in biological systems
- To study the basic principles of photo inorganic chemistry

UNIT - I Coordination Chemistry - I

Introduction: IUPAC nomenclature, Ligands- monodentate, bidentate, and polydentate ligands; coordination sphere; coordination number; nomenclature of mononuclear and dinuclear complexes. Structural and stereoisomerism in tetrahedral, square planar and octahedral complexes. Valence Bond theory – applications of valence bond theory to tetrahedral, square planar and octahedral complexes- Merits and limitations of VB theory.

UNIT – II Coordination Chemistry - II

Crystal field theory - splitting of d-orbitals in octahedral and tetrahedral complexes - factors affecting the magnitude of crystal field splitting - effects of crystal field splitting - spectrochemical series - applications of CFT - magnetic properties and spectra of transition metal complexes - crystal field stabilization energy and their uses - limitations of CFT - effective atomic number rule - stability of complexes - step-wise and overall stability constants - factors affecting the stability of complexes - determination of stability constants.

UNIT – III Coordination Chemistry - III

Labile and inert complexes - ligand substitution reactions in octahedral complexes: aquation, base hydrolysis and anation reactions - substitution reactions in square planar complexes - Trans effect - theories of trans effect - mechanism of substitution reactions - redox reactions: inner-sphere and outer-sphere electron transfer reactions.

UNIT - IV Organometallic Chemistry

Introduction–History, Nomenclature of organometallic compounds, EAN rule and

18 electron rule. Structure and nature of M-L bond in metal carbonyls - metal nitrosyls. Preparation of organo metallic compounds of Mg, Zn, Li, Cu, P, B, Ti, Fe and Co

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Wilkinson's catalyst and alkene hydrogenation, hydro formylation, Monsanto acetic acid process, Ziegler – Natta catalyst and polymerization of olefins.

UNIT – V Inorganic photochemistry

Electronic transitions in metal complexes: selection rules - metal-centered and charge-transfer transitions - properties of excited states - bimolecular quenching and energy transfer - photochemical pathways: substitution, reduction-oxidation and isomerization processes – photo substitution reactions of Cr(III) complexes - Adamson's rules - photo redox reactions of Co(III) complexes - photoisomerisation in Pt(II) complexes. Photochemical conversion and storage of solar energy : photolytic cleavage of water into H₂ and O₂ - photo electrochemical devices : photogalvanic cells and semiconductor based photovoltaic cells.

Reference books :

J.D. Lee, Concise Inorganic Chemistry 5th Ed., Blackwell Science Ltd.,

James E. Huheey, Elien A. Keiter and Richard L. Keiter, Inorganic Chemistry : Principles Structure and Reactivity, 4th Ed., Harper College Publisher.

F. Albert Cotton, Geoffrey Wilkinson, Carlos A. Marilo and Manfred Bochman, Advanced Inorganic Chemistry, 6th Ed., Wiley Interscience Publication.

Fred Basolo and Ralph G. Pearson, Mechanisms of Inorganic Reactions : A study of metal complexes in solution, 2nd Ed., John wiley and sons, Inc.,

David E. Fenton, Biocoordination Chemistry, 1st Ed., Oxford Science Publications.

Ivano Bertini, Harry B Gray, Stephen J Lippard, Joan Selverstone Valentine, Bioinorganic Chemistry, 1st Ed., Viva Books Pvt. Ltd.,

J.K. Rohatgi - Mukherjee, Fundamentals of Photochemistry - Wiley Eastern Revised Ed.,

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UNIT - I

COORDINATION CHEMISTRY-I

Introduction to Naming of Co-ordination Compounds

Just like nomenclature of organic compounds, nomenclature is important in Coordination Chemistry also. Naming of coordination compounds is needed for providing an unambiguous method for representing and describing formulas and names of coordination compounds systematically. The nomenclature becomes even more important when dealing with the isomers of the same coordination compound.

The formulas and names which are used for coordination compounds are based on the rules of the International Union of Pure and Applied Chemistry (IUPAC).

Before we learn how to write name of any coordination compounds, lets first learn how to write the formula of any coordination compound

The formula of a coordination compound is a tool which is used for providing basic information regarding the constitution of the coordination compound in a brief, convenient and meaningful manner.

In Coordination Compounds

- * Within the coordination entities the central atom/ion is listed first followed by the ligands
- * The ligands are then listed after the central metal atom/ion in alphabetical order.
- * The formula of coordination entity, is written in square brackets.
- * Ligand abbreviations are also written in parentheses.
- * There should be no space between the ligands and the metal within a coordination sphere.
- * The charge on the cation(s) is balanced by the charge of the anion(s).

Let's have a look at these IUPAC rules for nomenclature of organic compounds one by one.

Rule 1:

While naming a coordination compound, cation is always named before the anion irrespective of the fact that whether the complex is cation or anion.

For example:

$\text{Na}[\text{Co}(\text{NH}_4)(\text{Cl})_2] \rightarrow$ Na is to be named first followed by $[\text{Co}(\text{NH}_4)(\text{Cl})_2]$ Sodium

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tetraamminedichlorocobaltate(I)

$[\text{Co}(\text{NH}_4 (\text{Cl})_2)\text{SO}_4 \rightarrow [\text{Co}(\text{NH}_4 (\text{Cl})_2]$ is to be named first followed by SO_4
Tetraamminedichlorocobalt(0) sulphate.

Rule 2:

If there are more than one type of ligands present in any coordination compound, the name of the ligands is to be done in alphabetic order followed by the name of central metal atom/ion.

Name of the anionic ligands, ends with 'o'. For example,

Chloride \rightarrow Chlorido, Nitrate \rightarrow Nitrito

For neutral ligands, their common name are used as such e.g. $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \rightarrow$
ethylenediamine

$\text{H}_2\text{O} \rightarrow$ aqua,

$\text{NH}_3 \rightarrow$ ammine,

$\text{CO} \rightarrow$ carbonyl

$\text{N}_2 \rightarrow$ dinitrogen|

$\text{O}_2 \rightarrow$ dioxygen.

Rule 3:

If the names of the ligands already contains a numerical prefix, then the terms, bis, tris, tetrakis are used and the ligand to which they refer being placed in parentheses. For example,

$[\text{NiCl}_2(\text{PPh}_3)_2]$ is named as dichloridobis(triphenylphosphine)nickel(II)

Rule 4:

After naming the ligand in alphabetic order, name the central metal atom/ion is written.

- * If the complex ion is a cation, metal is named same as the element.
- * If the complex is an anion, the name of metal ends with the suffix -ate for Latin name.

Rule 5:

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The oxidation state of the metal in the complex is given as a roman numeral in parentheses.

Rule 6:

The neutral complex molecule is named similar to that of the complex cation.

Rule 7:

These are some ligands which may be attached to the central metal atom/ion through different atoms. For example NO₂, CN etc..

Thus

M-NO₂ → nitroM-ONO → nitrito.

M-SCN → thiocyanato

M-NCS → isothiocyanato

Bonding theories in coordination complexes

In the previous lectures, we were talking about old theories in bonding of coordination complexes which are chain theory and Werner theory. In this part of lectures we will talk about of remaining theories such as VBT, CFT, and MOT. These theories have been proposed to explain the nature of metal-ligand bonding in complexes and also explain the color, geometry and magnetic properties of the complexes compounds.

Valence Bond theory (VBT)

This theory is mainly due to (Pauling and J.L.Slater, 1935). It deals with the electronic structure of the central metal ion in its ground state, kind of bonding, geometry and magnetic properties of the complexes.

Assumption of VBT

The central metal atom or ion makes available a number of empty s, p and d atomic orbital equal to its coordination number. These vacant orbital hybrid together to form hybrid orbitals which are the same in number as the atomic orbitals hybridizing together. These hybrid orbitals are vacant, equivalent in energy and have definite geometry. Important types of hybridization occurring in the first row transition metal (3d metals) complexes and the geometry of the complexes are given in table (8).

The ligands have a last one σ -orbital containing lone pair of electron.

Vacant orbital hybrid of the metal atom or ion overlap with the filled (containing lone pair

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of electrons) σ -orbital of the ligands to form ligand-- metal σ -bond. This bond which is generally known as coordination bond is a special type of covalent bond and shows the characteristics of both the overlapping orbitals. However, it also possesses a considerable amount of polarity because of the mode of its formation.

The non- bonding electrons of the metal atom or ion are often then arrangement in the metal orbitals which do not participate in forming the hybrid orbitals. The rearrangement of non-bonding electrons takes place according to Hund's

Table Important types of hybridization occurring in the first row transition metal (3d metals) complexes and the geometry of the complexes.

Coordination number of metal atom / ion	Type of hybridization	Geometry of complexes	Example
2	$sp(4s, 4p_x)$	linear	$[CuCl_2]^-$, $[Cu(NH_3)_2]^+$
3	$sp^2(4s, 4p_x, 4p_y)$	Trigonal planar	$[Cu(S \begin{array}{c} \diagup \\ N \\ \diagdown \\ N \\ \diagup \\ H \end{array})_3]^+$
4	$sp^3(4s, 4p_x, 4p_y, 4p_z)$	Tetrahedral	$[FeBr_4]^{2-}$, $Ni(CO)_4$
4	$dsp^2(3d_{x^2-y^2}, 4s, 4p_x, 4p_y)$	Square planar	$[Ni(CN)_4]^{2-}$
5	$sp^3d(4s, 4p_x, 4p_y, 4p_z, 3d_{z^2})$	Trigonal bipyramidal	$[CuCl_5]^{3-}$
5	$dsp^3(4s, 4p_x, 4p_y, 4p_z, 3d_{x^2-y^2})$	Square-based pyramidal	$[Ni(CN)_5]^{3-}$
6	$sp^3d^2(4s, 4p_x, 4p_y, 4p_z, 4d_{z^2}, 4d_{x^2-y^2})$	outer-orbital , Octahedral	$[Co(H_2O)_6]^{+2}$
6	$d^2sp^3(3d_{z^2}, 3d_{x^2-y^2}, 4s, 4p_x, 4p_y, 4p_z)$	Inner-orbital , Octahedral	$[Co(NO_2)_6]^{-3}$

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7	$sp^3d^3(4s, 4p_x, 4p_y, 4p_z, 3d_{xy}, 3d_{x^2-y^2}, 3d_{z^2})$	Pentagonal bipyramidal	$[NiF_7]^{-5}$
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Geometry of 6-coordinate complex ions

The coordination number in these complexes is six and hence these complexes have octahedral geometry. This octahedral geometry arises due to sp^3d^2 or d^2sp^3 hybridization of the central metal atom or ion. These types of two hybridizations depend on the number of unpaired or paired electrons present in the complex ion.

Octahedral complexes in which the central atom is sp^3d^2 hybridized are called outer orbital octahedral complexes while the octahedral complexes in which the central atom is d^2sp^3 hybridized are called inner orbital octahedral complexes.

sp^3d^2 hybridization in outer orbital octahedral complexes

This type of hybridization takes place in those octahedral complex ions which contain weak ligands. Weak ligands are those which cannot force the electrons of d^2 and d - orbitals. In this hybridization, $(n-1)d^2$ and $(n-1)d$ - orbitals are not available for hybridization. In place of these orbitals, we use nd^2 and nd - orbitals (these d -orbitals belong to the outer shell) and hence sp^3d^2 hybridization can be represented as $ns, np_x, np_y, np_z, nd_{z^2}, nd_{x^2-y^2}$. The octahedral complexes resulting from sp^3d^2 hybridization are called **outer orbital octahedral complexes** and also

called **high spin** or **spin free octahedral complexes**.
 d^2sp^3 hybridization in inner orbital octahedral complexes

$z \quad x^2 y^2$

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This type of hybridization take place in octahedral complex ions which contain strong ligands. Strong ligands are those which force the electrons of (n-1)d orbital's in this hybridization. In the formation of six d^2sp^3 hybrid orbitals, two (n-1) d orbitals [(n-1) d_z^2 and (n-1) $d_{x^2-y^2}$ orbitals], one ns and three np (np_x , np_y and np_z) orbitals combine together and form six d^2sp^3 hybrid orbitals.

(n-1) d_z^2 and (n-1)d - orbitals are available and used for hybridization, (these d- orbitals belong to the inner shell) and hence d^2sp^3 hybridization can be represent (n-1) dz^2 , (n-1) dx^2-y^2 , ns, np_x , np_y , np_z . The octahedral complexes resulted from d^2sp^3 hybridization are called **inner orbital octahedral complexes** and also called **low spin** or **spin paired octahedral complexes**.

The inner orbital octahedral complexes have comparatively lesser number of unpaired electrons than the outer orbital octahedral complexes.

LIMITATIONS OF VALENCE BOND THEORY

Valence Bond Theory (VBT) is a hybridization based theory proposed by the Pauling. According to them, metal- ligand bonding in a complex compound is of 100% covalent nature but there are certain limitations related to this theory which can be given as:

VBT cannot give the idea about the relative stabilities for different shapes and different coordination numbers in transition metal complexes, e.g. it cannot explain satisfactorily as to why Co^{+2} (d^7 configuration) forms both tetrahedral and octahedral complexes while Ni^{+2} (d^8 configuration) rarely form tetrahedral complexes.

VBT cannot explain why Cu^{+2} forms only distorted octahedral complexes even when all the six ligands are identical.

VBT cannot give the idea about the colour of the complexes.

VBT was failed to explain the strength of the ligands i.e. it cannot explain that which of the ligands will be called as stronger or weaker ligand.

According to the VBT magnetic moment of the complexes can determined by the following equation:

$$\mu_s = B.M.$$

But the actual value of magnetic moment is found to be slightly greater than as calculated by the above equation, which cannot be explained by VBT. In other word, we can say that VBT cannot give the idea about the orbital contribution in the magnetic moment of complexes.

This theory does not predict the magnetic behaviours of complexes. This theory only predicts the number of unpaired electrons and their correlation with stereochemistry is misleading. For example it was assumed that all the square planar complexes of Ni^{+2} (d^8 configuration) formed by dsp^2 hybridization, were diamagnetic in nature, while all tetrahedral complexes of Ni^{+2} formed

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by sp^3 hybridization were paramagnetic due to the presence of two unpaired electrons. By the X-ray analysis, it was observed that Ni^{+2} complexes have shown that one and the same complex can be obtained in both, paramagnetic form and diamagnetic form. VBT has no explanation for it.

According to VBT, inner orbital octahedral complexes with d^2sp^3 hybridization are covalent in nature and outer orbital octahedral complexes with sp^3d^2 hybridization are ionic in nature but there are certain complexes which have covalent character according to VBT but exhibit ionic property, which cannot be explained by VBT.

VBT cannot give any explanation for the order of reactivities of the inner orbital inert complexes of d^3 , d^4 , d^5 & d^6 ions and of the observed differences in the energies of activation in a series of similar complexes.

VBT was failed to explain the kinetics of the complexes.

UNIT – II

CO-ORDINATION CHEMISTRY II

Crystal field theory considers the bonding in the complexes to be entirely electrostatic

Postulates of Crystal Field Theory:

- * Crystal field theory considers a complex as a combination of a central metal ion surrounded by ligands.
- * Ligands are considered as point charges or point dipoles.
- * The bonding between the metal cation and ligands arises due to the "electrostatic attraction" between the nucleus of the metal cation and the partial negative charge present on the ligands.
- * Thus the bond between the metal and the ligand is purely (100%) ionic.
- * The interaction between the electrons of the cation and those of the ligands is entirely repulsive. These repulsive forces are responsible for the splitting of the „d“ orbitals of the metal cation. The splitting of the d orbitals is different for different geometries.
- * This theory does not consider the overlapping between the metal orbitals and ligand orbitals.

Splitting of ‘d’ orbitals in octahedral complexes

In an octahedral complex, the ligands approach the central metal ion along the three Cartesian axes, x, y and z. Since the lobes of two axial ($d_{x^2-y^2}$, d_{z^2}) orbitals (e_g) point directly at the path of the approaching ligands, the electrons in these orbitals experience greater repulsion from the ligand. The non-axial orbitals (d_{xy} , d_{yz} , d_{zx}) experience less repulsion. Hence the energy of the e_g orbitals are increased and the energy of the t_{2g} orbitals are decreased. Thus the five „d“ orbitals which have same energy (degenerate) in the metal ion are split into two levels t_{2g} and e_g in the metal complex. This splitting is called "crystal field splitting". The energy difference between e_g and t_{2g} levels is denoted by Δ_0 or $10Dq$ and is called the crystal field splitting energy in octahedral geometry.

High spin or spin free complexes:

Under the influence of weak field ligands such as I⁻, Br⁻ etc., the energy difference between the t_{2g} and e_g orbitals will be smaller. Therefore the distribution of d electrons in t_{2g} and e_g orbitals take place according to Hund's rule. So such complexes possess maximum number of unpaired electrons and are known as high spin or spin free complexes.

Example: [CoF₆]³⁻, [CoBr₆]³⁻, [Mn(H₂O)₆]²⁺ etc.

- * [CoF₆]³⁻: F⁻ is a weak field ligand. Therefore Δ_o is smaller and the distribution of dⁿ electrons takes place according to Hund's rule. Hence the complex [CoF₆]³⁻ is paramagnetic (4 unpaired electrons) and a high spin complex.
- * [Mn (H₂O)₆]²⁺: Water is a weak field ligand. Therefore Δ_o is smaller and the distribution of dⁿ electrons takes place according to Hund's rule. Hence the complex [Mn (H₂O)₆]²⁺ is paramagnetic (5 unpaired electrons) and a high spin complex.

Low spin or spin paired complexes:

Low spin or spin paired complexes are those which are formed by strong field. Under the influence of strong field ligands such as NO₂⁻, CN⁻, CO etc., the energy difference between the t_{2g} and e_g orbitals will be larger. Therefore the distribution of dⁿ electrons in t_{2g} and e_g orbitals take place against Hund's rule. So pairing of electrons takes place in the t_{2g} level. Such complexes are known as low spin or spin paired complexes.

Example: [Co (NH₃)₆]³⁺, [Fe (CN)₆]⁴⁻ etc.

- * [Co (NH₃)₆]³⁺: NH₃ is a strong field ligand. Therefore Δ_o is large and the distribution of dⁿ electrons take place against Hund's rule. Hence the complex [Co (NH₃)₆]³⁺ is diamagnetic and low spin or spin paired complex.
- * [Fe (CN)₆]⁴⁻: CN⁻ is a strong field ligand. Therefore Δ_o is large and the distribution of dⁿ electrons take place against Hund's rule. Hence the complex [Fe (CN)₆]⁴⁻ is diamagnetic and low spin or spin paired complex.

Splitting of 'd' orbitals in tetrahedral complexes

In the case of tetrahedral complexes, none of the five 'd' orbitals is directly pointing to the ligands. The angle between the eg orbitals and the ligand is $54^{\circ}44'$ and the angle between the t_{2g} orbitals and the ligand is $35^{\circ}16'$. Thus the d_{xy}, d_{xz} and d_{yz} orbitals (t_{2g}) are nearer to the ligands. Therefore they experience greater repulsion with the ligand orbitals in a tetrahedral complex. The energy of the t_{2g} orbitals is increased and the energy of eg orbitals is decreased. The mode of splitting of 'd' orbitals in a tetrahedral complex is just reverse of octahedral complex. The magnitude of crystal field splitting energy of tetrahedral geometry is less than that in octahedral fields. There are two reasons for this

- * There are only four ligands in a tetrahedral complex. But there are six ligands in an octahedral complex. So the ligand field splitting in a tetrahedral field is only $2/3$ ligand field splitting in an octahedral field.
- * (ii) In the tetrahedral complex, the direction of the orbitals does not coincide with the direction of the ligands. This reduces the ligand field splitting by further $2/3$.

FACTORS AFFECTING THE MAGNITUDE OF CRYSTAL FIELD SPLITTING

1. Nature of the ligands

The greater the ease with which the ligands can approach the central ion, the greater is the crystal field splitting caused by it. Therefore, the ligands with large negative charge, small size and having good sigma donor and pi acceptor powers will give large crystal field splitting as they can approach the central ion closely.

2. Oxidation state of the metal ion

The metal ion with higher oxidation state causes larger crystal field splitting than is done by the ion with lower oxidation state. For example, the crystal field splitting energy for [Co(H₂O)₆]³⁺ complex in which the oxidation state of cobalt is +3, is 18,600 cm⁻¹ whereas for the complex [Co(H₂O)₆]²⁺ in which the oxidation state of Co is +2, is 9,300 cm⁻¹. Similarly, for the crystal field splitting energy is 13,700 cm⁻¹ and 10,400 cm⁻¹ respectively.

3. Size of 'd' orbitals (Transition series)

The extent of crystal field splitting for similar complexes of a metal in the same oxidation state increases on going from 3d series (First transition series) to 4d series (Second transition series) and on going from 4d series (Second transition series) to 5d series (Third transition series). 4d orbitals in comparison to 3d orbitals are bigger in size and extend farther into space. As a result, the electrons in 4d orbitals can interact more strongly with the electrons in the ligand orbitals and, therefore, the crystal field splitting is more. Similarly, 5d orbitals are bigger than 4d

orbitals and hence the crystal field splitting for complexes of the elements of the Third transition series is more than that for Second transition series.

4. Geometry of the complex:

The crystal field splitting energy of tetrahedral complexes (Δ_t) is nearly half the value for octahedral complexes ($\Delta_t = 4/9 \Delta_0$). As a result, the splitting energy for tetrahedral complexes is small as compared to the pairing energy P. The tetrahedral complexes are, therefore, mostly high spin complexes.

EFFECTS OF CRYSTAL FIELD SPLITTING

- i. The colour of transition metal complexes can be easily explained using CFT. Example: $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4$ is blue and $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ is deep blue.
- ii. This theory explains clearly the number of unpaired electrons and magnetic properties of coordination complexes.
- iii. This theory can be used to predict the most favorable geometry of complex. Example: Cu^{2+} prefers square planar rather than tetrahedral.
- iv. It accounts for the fact that certain four coordinate complexes are square planar whereas others are tetrahedral.
- v. Example: $[\text{NiCl}_4]^{2-}$ is tetrahedral. $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar.
- vi. It explains the formation of inner and outer orbital complexes by the concepts of low spin and high spin complexes.
- vii. It explains the stabilization of oxidation state of metal ion by the concept of crystal field stabilization energy.
- viii. CFT explains the variation in the heat of hydration of divalent ions of first row transition elements.
- ix. This theory helps to predict the site selection in spinel and antispinel structures.

SPECTROCHEMICAL SERIES

A spectro chemical series is a list of ligands ordered on ligand strength and a list of metal ions based on oxidation number, group and its identity.

Spectrochemical series of ligands:



Ligands arranged on the left end of this spectrochemical series are generally regarded as weaker ligands and cannot cause forcible pairing of electrons within 3d level and thus form outer

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orbital octahedral complexes. On the other hand ligands lying at the right end are stronger ligands and form inner orbital octahedral complexes after forcible pairing of electrons within 3d level.

Spectrochemical series of metals:

The metal ions can also be arranged in order of increasing Δ and this order is largely independent of the identity of the ligand.



Δ increases with increasing oxidation number and increases down a group.

APPLICATIONS OF CRYSTAL FIELD THEORY

1. Colour and spectra of complexes:

Most of the complexes of transition metals give absorption bands in the visible region. According to crystal field theory, the colour is due to d-d transitions between the t_{2g} and e_g electrons. The energy difference between the t_{2g} and e_g is so small that absorption of even low radiation in the visible light causes excitation from the lower to the higher 'd' level. $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ absorbs green light in the visible region and hence it is purple in colour. An aqueous solution of copper sulphate absorbs radiation in the orange region and appears blue.

2. Magnetic properties:

The number of unpaired electrons (n) in a complex can be calculated using the value of magnetic moment. Once the number of unpaired electrons is known, crystal field theory may be applied to study the complex.

Example: i) The observed magnetic moment of the fluoro complex of cobalt (III), $[\text{CoF}_6]^{3-}$ is

5.3 B.M while the ammine complex of cobalt (III), $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic.

CRYSTAL FIELD STABILIZATION ENERGY AND THEIR USES

The separation of five d orbitals of the metal ion into two sets (t_{2g} and e_g) having different energies is called crystal field splitting. The energy gap between t_{2g} and e_g sets is denoted by Δ_0 or $10 Dq$ where 0 in Δ_0 indicates octahedral arrangement of the ligand around the central metal ion. This energy difference which arises because of the difference in electrostatic field exerted by the ligands on t_{2g} and e_g sets of orbitals of the central metal cation is called crystal field splitting energy. With the help of simple geometry it can be shown that the energy of t_{2g} orbital is Δ_0 ($4Dq$) less than the hypothetical degenerate d-orbitals and that of e_g orbitals is $0.6 \Delta_0$ ($6Dq$) above that of the hypothetical degenerate d-orbitals.

Uses

- * CFSE values explain why certain oxidation states are preferentially stabilized by coordinating with certain ligands. E.g. H₂O a weak ligand stabilizes Co²⁺ ion and not Co³⁺ ion. NH₃ a strong ligand stabilizes Co³⁺ ion and not Co²⁺ ion
- * CFSE values are used to calculate heat of hydration of divalent ions of first row transition elements:

LIMITATIONS OF CFT

- * CFT considers only metal 'd' orbitals and not the metal 'p' orbitals.
- * It cannot explain the difference in the splitting power of ligands.
- * It considers (M -L) bonding as 100% ionic. But actually (M- L) bonding has some covalent character as proved by NMR and ESR spectra.
- * It cannot explain the Π -bond formation in metal complexes.

EFFECTIVE ATOMIC NUMBER (EAN)

In the formation of a complex, each ligand is considered to be donating one electron pair to the central metal ion. The total number of electrons which the central metal ion appears to possess in the complex including those gained by it in bonding is called the effective atomic number of the central metal ion. It was found that in many cases ligands are added until the central metal ion gets the same number of electrons as are present in the next noble gas. Accordingly, the effective atomic number in a complex should be equal to 36 (electrons in krypton), 54 (electrons in xenon) or 86 (electrons in radon).

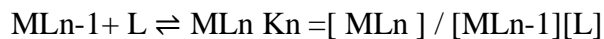
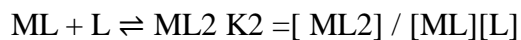
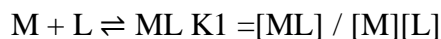
Example: Consider the complex ion, [Co(NH₃)₆]³⁺. The atomic number of cobalt is 27. The number of electrons in Co³⁺ ion is 24. Each of the six ammonia molecules donates a pair of electrons so that EAN becomes $24 + 2 \times 6 = 36$. This is the same as the atomic number of krypton. However, many stable complexes are known in which the EAN is a few units above or below the number of electrons in the next noble gas.

STABILITY OF COMPLEXES

Step-wise and overall stability constants: According to J Bjerrum (1941) the formation of a complex in solution proceeds by the stepwise addition of the ligands to the metal ion. Thus the formation of the complex ML_n (M = central metal cation, L = monodentate ligand and n = maximum coordination number of the metal ion M for the ligand L. n varies from one ligand to another for the same metal ion) may be supposed to take place by the following n consecutive steps

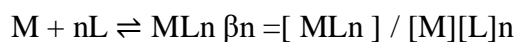
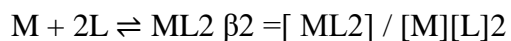
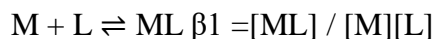
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and equilibrium constants



The equilibrium constants K_1, K_2, \dots, K_n are called stepwise formation constants or stepwise stability constants.

The formation of the complex ML_n may also be expressed by the following steps and equilibrium constants



The equilibrium constants $\beta_1, \beta_2, \dots, \beta_n$ are called overall (or cumulative) formation constants or overall (or cumulative) stability constants. β_n is termed as nth overall (or cumulative) formation constant or overall (or cumulative) stability constant.

The overall stability constant is the product of stepwise stability constants i.e. $\beta_n = K_1 \cdot K_2 \cdot K_3 \cdot \dots \cdot K_n$

The higher the value of the stability constant for a complex ion, the greater will be its stability.

Factors affecting the stability of complexes:

i) Charge on the metal ion

The effect of this factor on stability of complexes can be explained on the basis of crystal field theory. For a given ligand, greater the charge on the metal ion greater is the magnitude of crystal field splitting which ultimately affects the stability of the complex.

Example:

Ions	Ligands	CFSE (Δ_o in cm^{-1})
V^{2+}	6H ₂ O	12600
V^{3+}	6H ₂ O	17700

ii) Principal quantum number

Even though the metal ions have same charge, if the principal quantum numbers are different, then the magnitude of CFSE will be different and hence stability will be different.

iii) Nature of ligands

Properties of ligands like size, charge, dipole moment, polarizability and π -bonding capacity will affect the CFSE and stability of complexes. Smaller the size of the ligand, greater is the approach of the ligand with the metal ion and greater is the crystal field splitting. Larger the charge on the anion, greater the polarizability and greater is the magnitude of crystal field splitting.

iv) Chelation

Chelation increases stability. This is because the entropy factor is favourable in case of chelate complexes. For example $[\text{Cd}(\text{en})_2]^{2+}$ is more stable than $[\text{Cd}(\text{MeNH}_2)_4]^{2+}$ since in the former there is chelation.

v) Macro cyclic ligands

The increased stability of complexes due to macro cyclic ligands is termed as “macro cyclic effect”. The reason for this effect is mainly entropy and enthalpy factors. The macro cyclic ligands have cavities of particular size and hence selectively form strong complexes with metal ions of corresponding sizes.

vi) Hardness and softness

Stability of complexes depends also on hardness and softness of the metal and the ligands. As per HSAB theory, hard acids prefer hard bases and soft acids prefer soft bases. For example, Ni^{2+} is a hard acid and hence it forms stable complex with NH_3 and not with soft ligand PH_3 . But Pd^{2+} being soft acid forms stable complex with PH_3 rather than with NH_3 .

vii) Surrounding conditions

Even though the above factors outline the stability of complexes, many complexes which are stable under particular conditions may not be stable under some other conditions. For example $[\text{Co}(\text{NH}_3)_6]^{3+}$ is unstable in an acidic solution but is stable in water under neutral conditions.
 $[\text{Co}(\text{NH}_3)_6]^{3+} + 6\text{H}_3\text{O}^+ \rightarrow [\text{Co}(\text{H}_2\text{O})_6]^{3+} + 6\text{NH}_4^+$

The conditions may be heat, light, acidity or basicity.

Methods of determination of stability constants

a) Spectrophotometric method:

This method is based on Beer's law. Consider the following reaction: $\text{Fe}^{3+} + \text{NCS}^- \rightleftharpoons [\text{Fe}(\text{NCS})]^{2+}$

The stability constant is given by

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$$k = \frac{[Fe(NCS)]_2 + Fe^{3+} + [NCS^-]}{[Fe^{3+}][NCS^-]^2}$$

The complex is bright red with λ_{max} 450 nm. The concentration of the complex can be estimated by measuring its absorbance in the visible region using spectrophotometer. The stability constant K can be determined by mixing a known concentration of Fe^{3+} i.e. $[Fe^{3+}]_0$ with a solution of NCS- of known concentration $[NCS^-]_0$. The mixture is allowed to attain equilibrium. When the complex is formed the absorbance A at 450 nm is measured.

Since $A = \epsilon l [Fe(NCS)_2^+]$ (Beer's law) $[Fe(NCS)_2^+] = A / \epsilon l$

$$[Fe^{3+}] = [Fe^{3+}]_0 - [Fe(NCS)_2^+] \text{ and } [NCS^-] = [NCS^-]_0 - [Fe(NCS)_2^+]$$

Hence K can be calculated by substituting the values. Thus the stability constant of the complex is determined.

b) Bjerrum method:

According to Bjerrum, the formation of a complex solution proceeds by the stepwise addition of ligands to metal ion. The different steps involved in the formation of a complex are represented here.

$$M + L \rightleftharpoons ML \quad K_1 = \frac{[ML]}{[M][L]} \text{ -----(1)}$$

$$ML + L \rightleftharpoons ML_2 \quad K_2 = \frac{[ML_2]}{[ML][L]} \text{ ----- (2)}$$

$$ML_{n-1} + L \rightleftharpoons ML_n \quad K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \text{ -----(3)}$$

Eqn (1), (2) and (3) may be written as $[ML] = K_1 [M][L]$ (4)

$$[ML_2] = K_2 [ML][L] = K_1 K_2 [M][L]^2 \text{ -----(5)}$$

The average number of ligand molecule bound per mole of metal,

$$n = \frac{[ML] + 2[ML_2] + \dots + n[ML_n]}{[M] + [ML] + [ML_2] + \dots + [ML_n]} \text{ ----- (7)}$$

$$\text{i.e. } n = \frac{K_1 [M][L] + 2K_1 K_2 [M][L]^2 + \dots + n K_1 K_2 \dots K_n [M][L]^n}{[M] + K_1 [M][L] + K_1 K_2 [M][L]^2 + \dots + K_1 K_2 \dots K_n [M][L]^n}$$

$$[L]^2 + \dots + K_1 K_2 \dots K_n [M][L]^n$$

$$n = \frac{K_1 [L] + 2K_1 K_2 [L]^2 + \dots + n K_1 K_2 \dots K_n [L]^n}{1 + K_1 [L] + K_1 K_2 [L]^2 + \dots + K_1 K_2 \dots K_n [L]^n} \text{ ----- (8)}$$

Eqn (8) is called Bjerrum formation function

The concentration of uncomplexed ligand [L] can be calculated experimentally. n can be calculated

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from the equation

$$n = \frac{[L]_0 - [L]}{[M]_0 - [M]} \quad [L]_0 = \text{Total concentration of ligand} \quad [M]_0 = \text{Total concentration of metal}$$

Solutions of equation (8) for known values of n and corresponding $[L]$ values give the stability constants K_1, K_2 etc.

UNIT – III

CO-ORDINATION CHEMISTRY III

LABILE AND INERT COMPLEXES

On the basis of the difference in rates of replacement of one ligand by the other, complexes are classified into two classes:

- * The complexes in which substitution takes place slowly are called inert complexes.
- * The complexes in which the ligands are rapidly replaced by others are called labile or non-inert complexes.

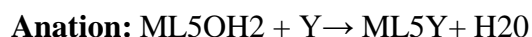
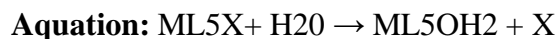
According to valence bond theory, if one or more inner „d“ orbitals are empty then labile complexes are formed. If no inner „d“ orbitals are available (even though they are singly occupied) then inert complexes are formed. According to molecular orbital terminology those complexes with vacant orbitals will be labile if one of the t_{2g} orbitals is empty and inert if all the t_{2g} orbitals are occupied. Most inert complexes are those of Co (III) and Cr (III). In general the octahedral complexes of transitional metals of periods V and VI are more inert as compared to IV period metals. Moreover Mo (III), W (III), Rh (III) and Ir (III) form particularly inert octahedral complexes. Nevertheless the complexes of Cr (III) with low energy 3d-orbitals half-filled and the spin paired complexes of Co (III) with low energy 3d-orbitals fully occupied are much more important.

LIGAND SUBSTITUTION REACTIONS IN OCTAHEDRAL COMPLEXES

Aquation (Acid Hydrolysis) and Anation reactions

One of the most common types of reactions that complexes like [Co (NH₃)₅Cl]²⁺ involves is

- * Replacement of the Cl⁻ (X⁻) by H₂O, a process known as aquation or acid hydrolysis followed by
- * Displacement of H₂O by an entering ligand (Y) a process known as anation. A general reaction may be formulated as

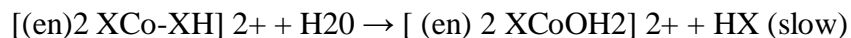
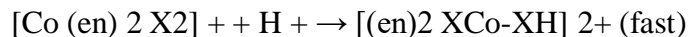


(where M = Co³⁺ or Cr³⁺ etc.)

For example, the acid hydrolysis (or aquation) of pentammine chlorocobalt ion is [Co (NH₃)₅Cl]²⁺ + H₂O → [Co (NH₃)₅H₂O]³⁺ + Cl⁻

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Acid Hydrolysis: Acid catalysed hydrolysis also occurs in certain coordination compounds. Ligands that are strongly basic or those which form hydrogen bond (e.g. CO₃²⁻, NO₂⁻ etc.,) are hydrolysed in acid solutions. The mechanism postulated is

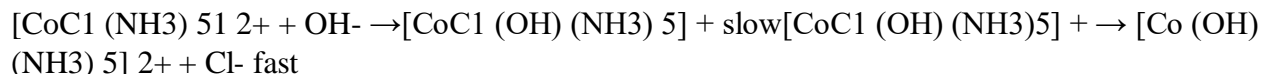


where X = F⁻, N₃⁻, NO₂⁻ etc.

Base Hydrolysis:

The rate of base hydrolysis is commonly a million times faster than that of acid hydrolysis. The reaction of base hydrolysis is of second order (first order in complex and first order in OH⁻). The OH⁻ ion reacts rapidly than other ligands and is unique in its reaction in water because it can be easily transferred to an adjacent suitable oriented H₂O molecule into OH⁻ ion.

Example:



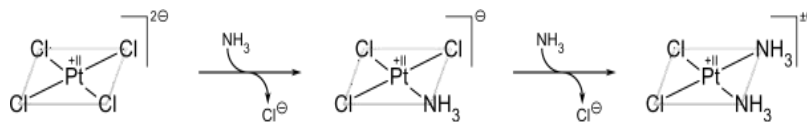
SUBSTITUTION REACTIONS IN SQUARE PLANAR COMPLEXES

Trans Effect

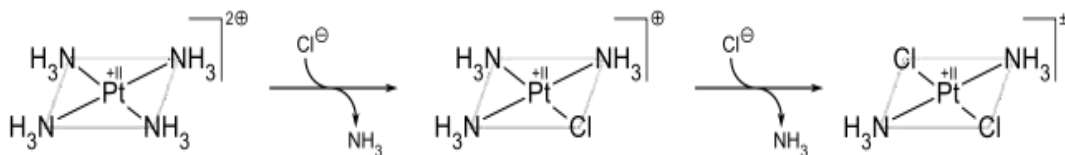
The ability of an attached group to direct substitution into a position trans (i.e. opposite) itself is called the trans effect. Such a group has a marked influence on the rate of a reaction. The trans effect is a kinetic phenomenon affecting the magnitude of activation energy of a reaction. Most important feature of square planar substitution is the trans effect. The intensity of the trans effect (as measured by the increase in rate of substitution of the trans ligand) follows this sequence:

F⁻, H₂O, OH⁻ < NH₃ < py < Cl⁻ < Br⁻ < I⁻, SCN⁻, NO₂⁻, SC(NH₂)₂, Ph⁻ < SO₃²⁻ < PR₃, AsR₃, SR₂, CH₃⁻ < H⁻, NO, CO, CN⁻, C₂H₄

The classic example of the trans effect is the synthesis of cisplatin. Starting from PtCl₄²⁻, the first NH₃ ligand is added to any of the four equivalent positions at random. However since Cl⁻ has a larger trans effect than NH₃, the second NH₃ is added trans to a Cl⁻ and therefore cis to the first NH₃.



If, on the other hand, one starts from $\text{Pt}(\text{NH}_3)_4^{2+}$, the trans product is obtained instead:



The trans effect in square complexes can be explained in terms of an addition/elimination mechanism that goes through a trigonal bipyramidal intermediate. Ligands with a high trans effect are in general those with high π acidity which prefer the more π -basic equatorial sites in the intermediate. The second equatorial position is occupied by the incoming ligand the departing ligand must also leave from an equatorial position. The third and final equatorial site is occupied by the trans ligand, so the net result is that the kinetically favored product is the one in which the ligand trans to the one with the largest trans effect is eliminated.

Theories of trans effect

1) Polarisation Theory:

Let us consider a square planar complex MX_4 . If Y is highly polarisable ligand enters into MX_4 complex than it distorts the induced dipole in planar complex. The mutual polarisation of M and Y results in diminished positive charge of the central ion directly opposite to Y. Substitution might be more likely in this position. Thus the polarization theory offers a simple but effective model to explain the trans effect.

To support this theory it is found that the order of increasing trans effect for the halide ions is in the same order of increasing polarisability of halide ions ($\text{Cl}^- < \text{Br}^- < \text{I}^-$)

2) π Bonding Theory:

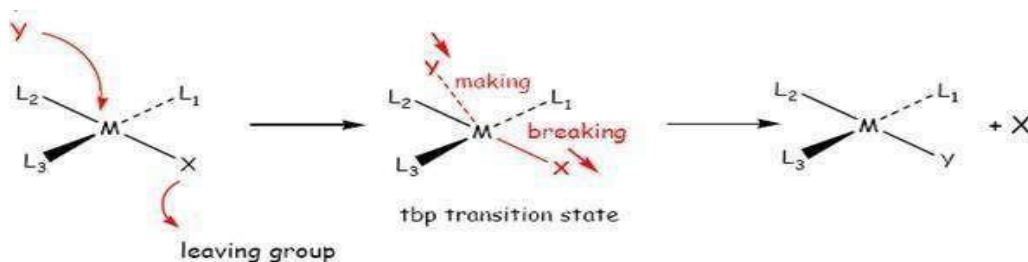
Covalent π bonding is one of the most important factors for the increased stability of transition state in bimolecular displacement reactions. Ligands like CN^- , CO and C_2H_4 possess high trans effect indicate clearly like that trans effect is due to π bond formation between metal and ligand. Ligands like CN^- , CO and C_2H_4 have vacant orbital for d-p- π bonding using filled d- orbital of the metal. The formation of π bond increases the electron density in the direction of group opposite to Y. The entering ligand (X') should approach from the direction of lower electron density, resulting in the displacement of X.

MECHANISM OF SUBSTITUTION REACTIONS

Substitution reaction in Pt(II) square-planar complexes proceed by bimolecular displacement ($\text{S}_\text{N}2$) mechanism involving either the solvent or the entering ligand as the

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nucleophilic agent. Experimental evidence in favor of SN2 mechanism has been presented. Because of steric and electronic reasons the coordination number of the metal is increased to include the entering ligand. The metal is exposed for attack above and below the plane. Furthermore Pt(II) which is a d8 system has a vacant pz- orbital of relatively low energy which accepts the pair of electrons donated by the entering ligand. Substitution reactions of cis- and trans- PtA2LX with Y to yield PtA2LY have been explained on the basis of nucleophilic attack of Y through trigonal bipyramidal structure. The process is entirely stereospecific: cis- PtA2LX yields cis product and trans give trans.



Martin and his students have shown that the rates of hydrolysis reaction of the four complexes viz. $[PtCl_4]^{2-}$, $[Pt(NH_3)Cl_3]$, $[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_3Cl]^+$ vary only by a factor of two (quite a small effect), although the charge on the reactant Pt(II) complex changes from -2 to +1. This variation in rate is remarkably small. The breaking of a Pt-Cl bond should become much more difficult in this series of four complexes as the charge on the complex becomes more positive. However, the formation of a new bond (i.e. the attraction of Pt for a nucleophile) should increase in the same order. Since there is small effect of change of charge on the complex on the rate of the reaction, both Pt-Cl bond breaking and Pt...OH₂ bond making are of comparable importance. This is a strong evidence in favour of SN2 mechanism.

For the substitution reaction of square planar complex, $[PtA_3X]^{n+}$ with Y^- to yield $[PtA_3Y]^{n+}$ in water involves a complication, since the solvent water also behaves as a potential ligand. For this reaction a two-term rate law is given by the expression:

$$\text{Rate} = k_1[PtA_3X]^{n+} + k_2[PtA_3Y]^{n+} [Y^-]$$

Here

k_1 = first-order rate constant for solvent-controlled reaction,

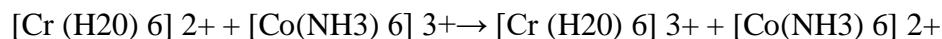
k_2 = second-order rate constant for reaction with Y^- .

Thus reaction of ligand displacement may proceed by two paths. Of course both supporting associative(SN2) mechanism, the first path involves solvent, the second involves entering ligand group Y .

REDOX REACTIONS (OXIDATION-REDUCTION REACTIONS):

Electron transfer reactions:

Consider the reaction



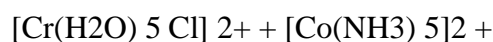
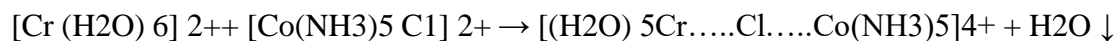
In this reaction, the chromium complex gets oxidised and the cobalt complex gets reduced. This is a simple redox reaction in which an electron is transferred from chromium complex to the cobalt complex. For such reactions two types of mechanisms are proposed.

a) Outer-sphere mechanism:

In this mechanism the electron jumps from the reductant to the oxidant. $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ - Reductant $[\text{Co}(\text{NH}_3)_6]^{3+}$ - Oxidant

- * During the reaction the coordination sphere remains unaffected.
- * The electron is set to tunnel through the medium from the reductant to the oxidant.
- * Since there is no movement of ligand, the Frank-Condon activation barrier for this reaction is small.
- * The reaction is first order in each reactant. The over-all order is two.

b) Inner-sphere mechanism:



- * In this mechanism, there will be a bridge between the reductant and oxidant.
- * The bridge helps the transfer of electron from reductant to the oxidant.
- * The reactant molecules should orient in a proper position. Therefore activation is necessary.
- * There should be at least one ligand capable of binding the two metals.
- * The intermediate formed in this reaction is bimolecular.
- * The rate-determining step is the electron transfer step.



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UNIT – IV

CO-ORDINATION CHEMISTRY IV

METAL CARBONYLS

Metal carbonyls are compounds formed by transition metals with carbon monoxide as ligand.

18-electron rule

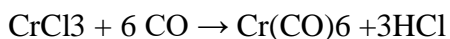
The **18-electron rule** is a rule used primarily for predicting and rationalizing formulae for stable metal complexes, especially organometallic compounds. The rule is based on the fact that the valence shells of transition metals consist of nine valence orbitals (one s orbital, three p orbitals and five d orbitals), which collectively can accommodate 18 electrons as either bonding or nonbonding electron pairs. This means that, the combination of these nine atomic orbitals with ligand orbitals creates nine molecular orbitals that are either metal ligand bonding or non-bonding. When a metal complex has 18 valence electrons, it is said to have achieved the same electron configuration as the noble gas in the period. The 18 electron rule enables us to decide whether a d-block organometallic complex is likely to be stable. The rule states that the sum of the d-electrons possessed by the metal plus those donated by the ligands (2 per $C\equiv O$) must total eighteen.

Carbonyls of Chromium

Chromium hexacarbonyl, $Cr(CO)_6$

Preparation

- * $Cr(CO)_6$ may be prepared by carbonylating $CrCl_3$ with CO in the presence of $LiAlH_4$ at 175 °C and 70 atm pressure.



- * It can also be prepared when a chromic salt dissolved in ether is treated with CO and $Al(C_2H_5)_3$ at high temperature and pressure

Properties

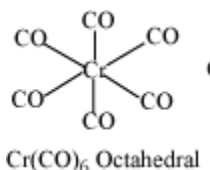
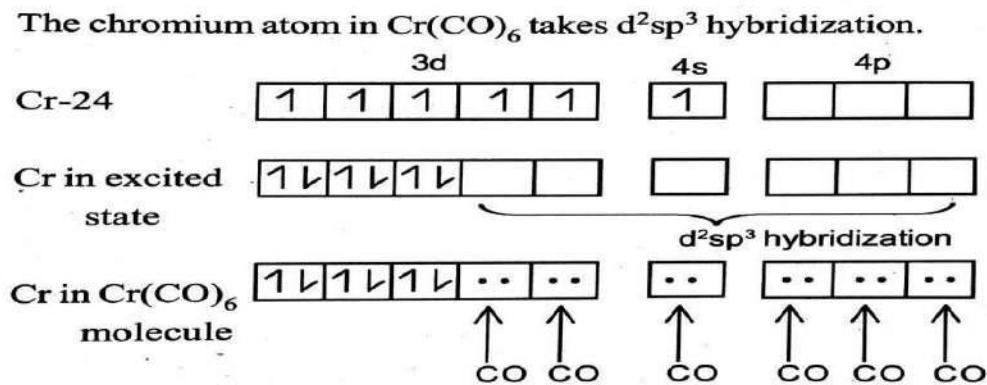
- * It is a white solid and resistant to chemical attack.
- * It is decomposed by F_2 at $-75^\circ C$ to give $CrF_6 \cdot Cr(CO)_6 + 3F_2 \rightarrow CrF_6 + 6CO$

Structure

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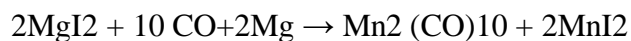
IR, Raman, Electron diffraction and X-ray measurements of chromium hexacarbonyl are in agreement with a perfectly octahedral structure. Cr exhibits d^2sp^3 hybridisation. Three hybrid orbitals are half filled and three hybrid orbitals are empty.

Each of the six CO groups are linked to the metal atom by a σ bond and three are linked by π Bonds



Carbonyls of Manganese Dimanganesedecacarbonyl, $\text{Mn}_2(\text{CO})_{10}$ Preparation

It is prepared by treating manganese iodide and magnesium with CO in ether under a high pressure of 200atms.

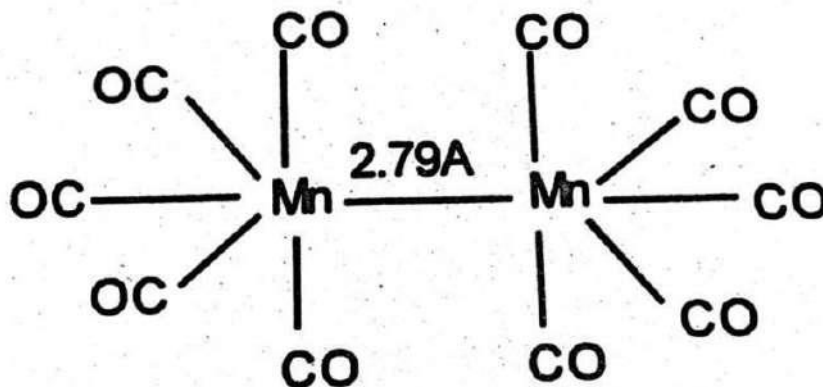
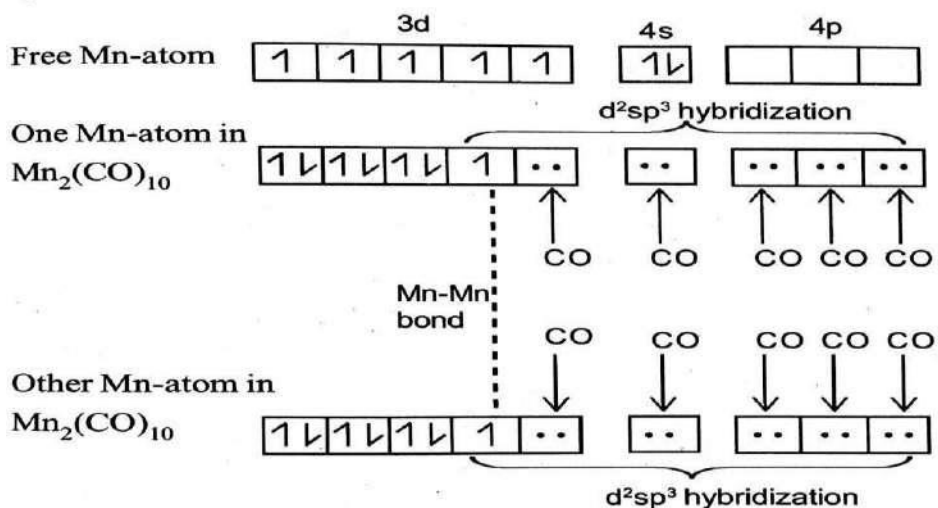


Properties

- * With H_2 , it forms carbonyl hydride.
- * $\text{Mn}_2(\text{CO})_{10} + \text{H}_2 \rightarrow 2\text{HMn}(\text{CO})_5$
- * With halogen, it forms carbonyl halides.
- * $\text{Mn}_2(\text{CO})_{10} + \text{X}_2 \rightarrow 2\text{Mn}(\text{CO})_5\text{X}$
- * It undergoes substitution reaction with PR_3 . $\text{Mn}_2(\text{CO})_{10} + 2\text{PR}_3 \rightarrow 2\text{Mn}(\text{CO})_4\text{PR}_3 + 2\text{CO}$
- * $\text{Mn}_2(\text{CO})_{10}$ is diamagnetic. This shows that there is a Mn-Mn covalent bond.

Structure of Mn₂(CO)₁₀

Mn₂(CO)₁₀ is a simple binuclear carbonyl formed by joining two square pyramidal Mn(CO)₅ through Mn- Mn bond. X-ray diffraction studies show that each manganese atom contains 5 terminal CO groups. The Mn-Mn bond is slightly larger (2.79Å) than the expected single bond distance. This may be due to repulsion of adjacent CO groups. Each manganese atom takes d² sp³ hybridization.

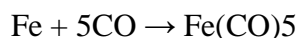


Carbonyls of Iron

Iron pentacarbonyl, Fe(CO)₅ Preparation

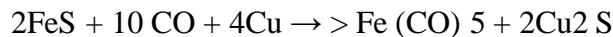
i) Direct synthesis:

Fe(CO)₅ is prepared by passing CO over finely powdered iron metal at 200°C and 200 atm pressure.



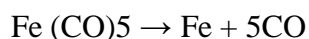
ii) Reductive carbonylation:

When ferrous sulphide (FeS) is reduced with copper in the presence of CO at high temperature and pressure, Fe(CO)₅ is formed.



Properties

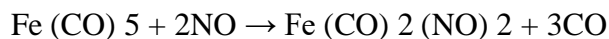
- i) It is a yellow liquid soluble in organic solvents like methanol, ether etc.
- ii) It decomposes on heating to 250° C.



iii) When a cooled solution of Fe(CO)₅ in glacial acetic acid is irradiated with UV-light, Fe₂(CO)₉ is formed.



iv) It reacts with nitric oxide to give carbonyl nitrosyl complex.



v) It reacts with halogen to give carbonyl halides. $\text{Fe(CO)}_5 + \text{X}_2 \rightarrow [\text{Fe(CO)}_4\text{X}_2] + \text{CO}$

Structure

Combined IR and Raman spectral measurements show that Fe(CO)₅ takes trigonal bipyramidal structure. It is further confirmed by single crystal X-ray studies. The iron atom in Fe(CO)₅ takes dsp³ hybridization.

Di-ironennacarbonyl, Fe₂(CO)₉

Preparation

When a cooled solution of Fe(CO)₅ in glacial acetic acid is irradiated with UV-light, Fe₂(CO)₉ is formed.
 $2\text{Fe(CO)}_5 \rightarrow \text{Fe}_2(\text{CO})_9 + \text{CO}$

Properties

- * It is a golden yellow crystalline solid.
- * It reacts with nitric oxide to give Fe(CO)₂(NO)₂, Fe(CO)₅ and Fe₃(CO)₁₂
 $3\text{Fe}_2(\text{CO})_9 + 4\text{NO} \rightarrow 2\text{Fe(CO)}_2(\text{NO})_2 + \text{Fe(CO)}_5 + \text{Fe}_3(\text{CO})_{12} + 6\text{CO}$
- * When heated to 500°C it gives higher carbonyl.
 $3\text{Fe}_2(\text{CO})_9 \rightarrow 3\text{Fe(CO)}_5 + \text{Fe}_3(\text{CO})_{12}$

Structure

X-ray studies show that Fe₂(CO)₉ contains six terminal carbonyl groups, three bridged carbonyl groups and one single bond between two Fe atoms. The iron atoms take d²sp³ hybridization.

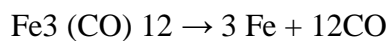
The Fe-Fe distance is 2.46\AA which shows that there is a single bond between the two Fe atoms. The diamagnetic nature of $\text{Fe}_2(\text{CO})_9$ also confirms Fe-Fe bond.

Iron dodecacarbonyl, $\text{Fe}_3(\text{CO})_{12}$ Preparation

It is prepared by heating $\text{Fe}_2(\text{CO})_9$ dissolved in toluene to 70°C .
 $3\text{Fe}_2(\text{CO})_9 \rightarrow \text{Fe}_3(\text{CO})_{12} + 3\text{Fe}(\text{CO})_5$

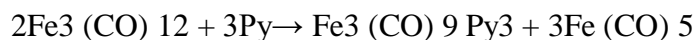
Properties

- i) It forms deep green crystals, soluble in organic solvents like toluene, alcohol.
- ii) When heated to 140°C , it decomposes to give Fe and CO.



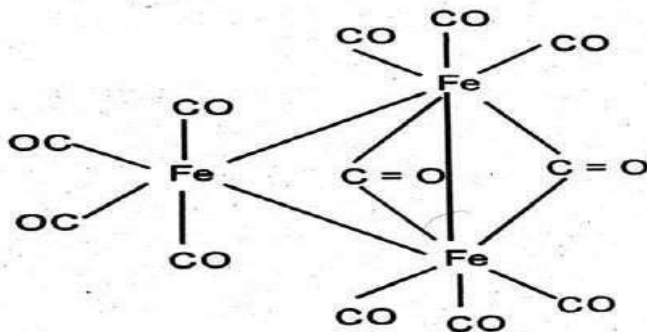
- iii) Reaction with sodium in liquid NH_3
 $\text{Fe}_3(\text{CO})_{12} + 6\text{Na} \rightarrow 3\text{Na}_2[\text{Fe}(\text{CO})_4]$

- iv) Reaction with pyridine



v) It reacts with NO giving carbonyl nitrosyl complex. $\text{Fe}_3(\text{CO})_{12} + 6\text{NO} \rightarrow 3\text{Fe}(\text{Co})_2(\text{NO})_2 + 6\text{CO}$ **Structure**

Spectral studies prove a cyclic structure for $\text{Fe}_3(\text{CO})_{12}$.



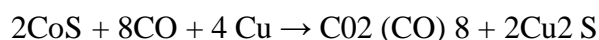
Carbonyls of Cobalt

Dicobaltoctacarbonyl, $\text{Co}_2(\text{CO})_8$ Preparation

i) Direct synthesis:

It is prepared by passing CO powdered cobalt at 200°C and 100 atm pressure. $2\text{Co} + 8\text{CO} \rightarrow \text{Co}_2(\text{CO})_8$

ii) It is also prepared by the reduction of cobaltous sulphide with copper in the presence of CO at high temperature and pressure.

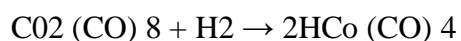


Properties

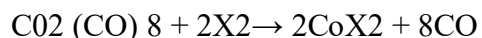
i) $\text{Co}_2(\text{CO})_8$ forms orange crystals with melting point 51°C .

ii) When heated to about 60°C , it forms higher poly nuclear carbonyl. $2\text{Co}_2(\text{CO})_8 \rightarrow \text{Co}_4(\text{CO})_{12} + 4\text{CO}$

iii) It reacts with hydrogen to give carbonyl hydride.



iv) With halogens, it forms cobaltous halide.

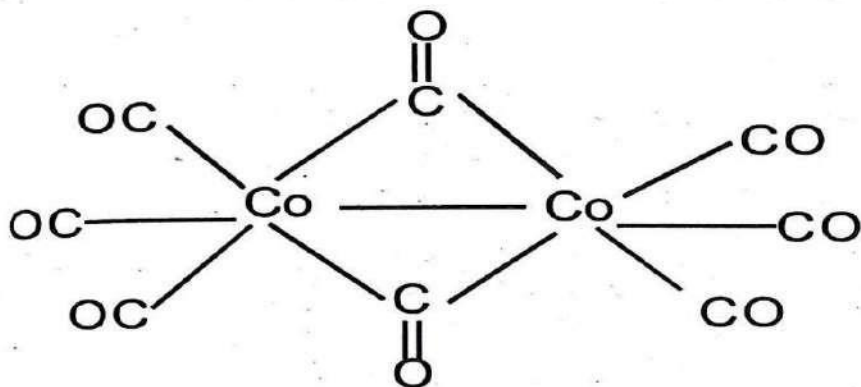
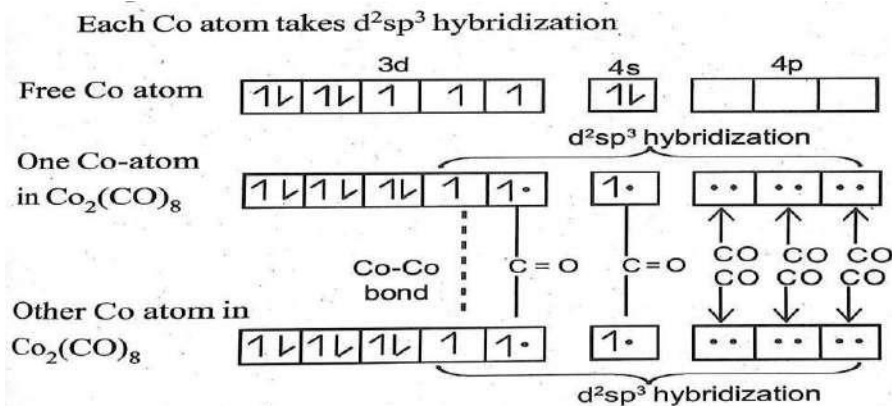


Structure of $\text{Co}_2(\text{CO})_8$

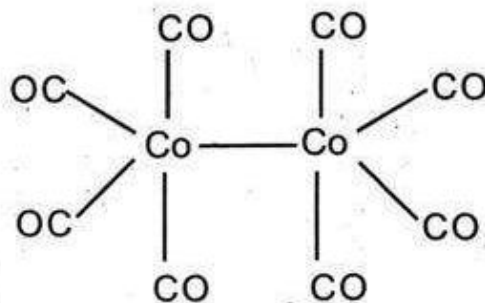
In dicobaltoctacarbonyl, each cobalt atom takes d^2sp^3 hybridization and contains three terminal carbonyl groups. The remaining two carbonyl groups act as bridging groups between the two

cobalt atoms. There is Co-Co bond supported by diamagnetic nature of $\text{Co}(\text{CO})_8$. A non-bridged structure is also proposed. Both bridged (a) and non-bridged (b) structures are present in equal proportions at room temperature.

Bonding in bridged carbonyl



Bridged Structure



UNIT – V

INORGANIC PHOTOCHEMISTRY

PHOTOCHEMISTRY OF CHROMIUM (III) COMPLEXES

Chromium(III) is the best known oxidation state of the element, forming a very large number of hexacoordinate complexes of moderate kinetic stability. In the absence of light, ligand exchange reactions of these complexes-aquation, ligand substitution, isomerization, and racemization-all require activation energies of 15-27 kcal/mole and have half-lives of several hours at 25°. These processes are thus convenient for study, and considerable work has been done on the mechanism of thermal ligand exchange processes of chromium(III) complexes. Excellent reviews of this subject are available. Reactions (4)-(7) are illustrative examples of ligand-exchange reactions of chromium(III) complexes

Semiconductor based photo voltaic cells

Solar cells convert light energy into electrical energy either indirectly by first converting it into heat, or through a direct process known as the **photovoltaic effect**. The most common types of solar cells are based on the photovoltaic effect, which occurs when light falling on a two-layer semiconductor material produces a potential difference, or voltage, between the two layers. The voltage produced in the cell is capable of driving a current through an external electrical circuit that can be utilized to power electrical devices. This tutorial explores the basic concepts behind solar cell operation.

The most common photovoltaic cells employ several layers of doped silicon, the same semiconductor material used to make computer chips. Their function depends upon the movement of charge-carrying entities between successive silicon layers. In pure silicon, when sufficient energy is added (for example, by heating), some electrons in the silicon atoms can break free from their bonds in the crystal, leaving behind a **hole** in an atom's electronic structure. These freed electrons move about randomly through the solid material searching for another hole with which to combine and release their excess energy. Functioning as free carriers, the electrons are capable of producing an electrical current, although in pure silicon there are so few of them that current levels would be insignificant. However, silicon can be modified by adding specific impurities that will either increase the number of free electrons (**n**-silicon), or the number of holes (missing electrons; also referred to as **p**-silicon). Because both holes and electrons are mobile within the fixed silicon crystalline lattice, they can combine to neutralize each other under the influence of an electrical potential. Silicon that has been doped in this manner has sufficient photosensitivity to be useful in photovoltaic applications

Solar Cell Operation

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The tutorial initializes at an arbitrarily set "medium" photon intensity level, with photons randomly impacting the surface of the solar cell to generate free electrons. The released electrons complete a simple circuit containing two light bulbs that become illuminated when current flows through. In order to increase or decrease the photon flux, use the **Photon Intensity** slider to adjust the number of photons incident on the surface.

Today, the most common photovoltaic cells employ several layers of doped silicon, the same semiconductor material used to make computer chips. Their function depends upon the movement of charge-carrying entities between successive silicon layers. In pure silicon, when sufficient energy is added (for example, by heating), some electrons in the silicon atoms can break free from their bonds in the crystal, leaving behind a **hole** in an atom's electronic structure. These freed electrons move about randomly through the solid material searching for another hole with which to combine and release their excess energy. Functioning as free carriers, the electrons are capable of producing an electrical current, although in pure silicon there are so few of them that current levels would be insignificant. However, silicon can be modified by adding specific impurities that will either increase the number of free electrons (**n**-silicon), or the number of holes (missing electrons; also referred to as **p**-silicon). Because both holes and electrons are mobile within the fixed silicon crystalline lattice, they can combine to neutralize each other under the influence of an electrical potential. Silicon that has been doped in this manner has sufficient photosensitivity to be useful in photovoltaic applications.

STUDY MATERIAL FOR B.Sc. CHEMISTRY
INORGANIC CHEMISTRY- III
VI - SEMESTER, ACADEMIC YEAR 2022-2023

In a typical photovoltaic cell, two layers of doped silicon semiconductor are tightly bonded together (illustrated in Figure 1). One layer is modified to have excess free electrons (termed an **n-layer**), while the other layer is treated to have an excess of electron holes or vacancies (a **p-layer**). When the two dissimilar semiconductor layers are joined at a common boundary, the free electrons in the n-layer cross into the p-layer in an attempt to fill the electron holes. The combining of electrons and holes at the p-n junction creates a barrier that makes it increasingly difficult for additional electrons to cross. As the electrical imbalance reaches an equilibrium condition, a fixed electric field results across the boundary separating the two sides.

When light of an appropriate wavelength (and energy) strikes the layered cell and is absorbed, electrons are freed to travel randomly. Electrons close to the boundary (the p-n junction) can be swept across the junction by the fixed field. Because the electrons can easily cross the boundary, but cannot return in the other direction (against the field gradient), a charge imbalance results between the two semiconductor regions. Electrons being swept into the n-layer by the localized effects of the fixed field have a natural tendency to leave the layer in order to correct the charge imbalance. Towards this end, the electrons will follow another path if one is available. By providing an external circuit by which the electrons can return to the other layer, a current flow is produced that will continue as long as light strikes the solar cell. In the construction of a photovoltaic cell, metal contact layers are applied to the outer faces of the two semiconductor layers, and provide a path to the external circuit that connects the two layers. The final result is production of electrical power derived directly from the energy of light.