

Biyani's Think Tank
Concept based notes
Inorganic Chemistry
(B.Sc. III)

Dr. Rajyashree
Deptt. of Science
Biyani Girls College, Jaipur



Published by :

Think Tanks

Biyani Group of Colleges

Concept & Copyright :

©Biyani Shikshan Samiti

Sector-3, Vidhyadhar Nagar,

Jaipur-302 023 (Rajasthan)

Ph : 0141-2338371, 2338591-95 • Fax : 0141-2338007

E-mail : acad@biyanicolleges.org

Website : www.gurukpo.com; www.biyanicolleges.org

First Edition : 2009

While every effort is taken to avoid errors or omissions in this Publication, any mistake or omission that may have crept in is not intentional. It may be taken note of that neither the publisher nor the author will be responsible for any damage or loss of any kind arising to anyone in any manner on account of such errors and omissions.

Leaser Type Setted by :

Biyani College Printing Department

Preface

I am glad to present this book, especially designed to serve the needs of the students. The book has been written keeping in mind the general weakness in understanding the fundamental concepts of the topics. The book is self-explanatory and adopts the “Teach Yourself” style. It is based on question-answer pattern. The language of book is quite easy and understandable based on scientific approach.

This book covers basic concepts related to the microbial understandings about diversity, structure, economic aspects, bacterial and viral reproduction etc.

Any further improvement in the contents of the book by making corrections, omission and inclusion is keen to be achieved based on suggestions from the readers for which the author shall be obliged.

I acknowledge special thanks to Mr. Rajeev Biyani, *Chairman* & Dr. Sanjay Biyani, *Director (Acad.)* Biyani Group of Colleges, who are the backbones and main concept provider and also have been constant source of motivation throughout this Endeavour. They played an active role in coordinating the various stages of this Endeavour and spearheaded the publishing work.

I look forward to receiving valuable suggestions from professors of various educational institutions, other faculty members and students for improvement of the quality of the book. The reader may feel free to send in their comments and suggestions to the under mentioned address.

Author

INORGANIC CHEMISTRY

(B.Sc. III-I)

INDEX

Contents
Page No.

Chapter - I

1. Unit I - Hard and Soft Acids and Bases
2. Unit II
Chapter II - Metal-Ligand Bonding in Transition Metal Complexes
Chapter III - Magnetic Properties of Transition Metal Complexes
3. Unit III
Chapter IV - Electron spectra of Transition
Metal Complexes
Chapter V - Thermodynamic And Kinetic Aspects of
Metal Complexes
4. Unit IV
Chapter VI - Organometallic Chemistry
5. Unit V
Chapter VII - Bioinorganic Chemistry
Chapter VIII - Silicones and Phosphazenes

Unit - I**Hard and Soft Acids and Bases (HSAB) :**

Classification of acids and bases as hard and soft. Pearson's HSAB concept acid-base strength and hardness and softness. Symbiosis, theoretical basis of hardness and softness, electronegativity and hardness and softness.

Unit - II**Metal-Ligand Bonding in Transition Metal complexes :**

Limitations of valence bond theory, an elementary idea of crystal field theory, crystal field splitting in octahedral, tetrahedral and square planar complexes, factors affecting the crystal-field parameters.

Magnetic Properties of Transition Metal Complexes :

Types of magnetic behavior, methods of determining magnetic susceptibility, spin-only formula. L-S coupling, correlation of μ values, orbital contribution to magnetic moments, application of magnetic moment data for 3d metal complexes.

Unit - III**Electron Spectra of Transition Metal Complexes :**

Types of electronic transitions, selection rules for d-d transitions, spectroscopic ground states, spectrochemical series, Orgel-energy level diagram for d1 and d9 states, discussion of the electronic spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex.

Thermodynamic and Kinetic Aspects of Metal Complexes :

A brief outline of thermodynamic stability of metal complexes and factors affecting the stability, substitution reactions of square planar complexes.

Unit - IV**Organometallic Chemistry :**

Definition, nomenclature and classification of organometallic compounds. Preparation, properties, bonding and applications of alkyl and aryls of Li, Al, Hg, Sn and Ti, a brief account of metal ethylenic complexes and homogeneous hydrogenation, mononuclear carbonyls and the nature of bonding in metal carbonyls.

Unit - V**Bioinorganic Chemistry :**

Essential and trace elements to Biological processes, metalloporphyrins with special reference to haemoglobin and myoglobin. Biological role of alkali and alkaline earth metal ions with special reference to Ca^{2+} Nitrogen fixation.

Silicones and Phosphazenes :

Silicones and phosphazene as examples of inorganic polymers, nature of bonding in triphosphazenes.

Unit - I

Chapter - 1

Hard And Soft Acids and Bases (HSAB)

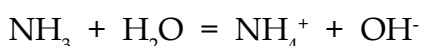
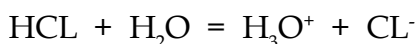
Q.1. Give the basic concept of acids and bases according to

(i) Bronsted-Lowry

(ii) Lewis concept

Ans. Bronsted-Lowry Concept of Acids And Bases :

An **acid** is a substance which can give a proton and **base** is a substance which can accept a proton.



A substance which can act both as an acid as well as base in different reaction is called **amphoteric**.

Bronsted-Lowry Acids and Bases

Type	Acid	Base
Molecular	HCL, HBr, HClO ₄ , H ₂ SO ₄ , H ₃ PO ₄ , H ₂ O	NH ₃ , N ₂ H ₄ , amines, H ₂ O
Cationic	NH ₄ ⁺ , [Fe(H ₂ O) ₆] ⁺³	[Fe(H ₂ O) ₅ OH] ⁺²
Anionic	HS ⁻ , HCO ₃ ⁻ , HSO ₄ ⁻	Cl ⁻ , Br ⁻ , OH ⁻

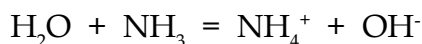
Bronsted-Lowry gave the concept of Conjugate acids and Bases Conjugate acids and bases - An acid-base pair which differs by a proton is called conjugate acid-base pair.



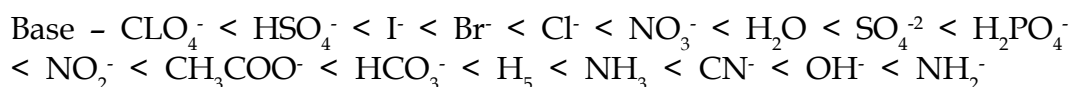
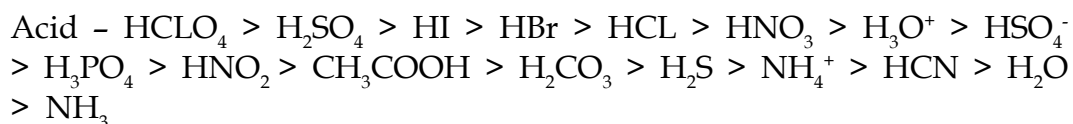
Conjugate pair I

Conjugate pair II





From Bronsted-Lowry concept, it can be proved that a strong acid has a weak conjugate base and vice-versa.



Lewis Concept of Acids and Bases :

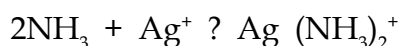
Lewis Acid - is an electron pair acceptor.

Lewis acids can be classified in three classes :

- (i) All the cations are Lewis acids as they can combine with electron pairs, e.g., Ag^+ , Fe^{+2} , Co^{+2} etc.
- (ii) Electron deficient compounds e.g. GaCl_3 , BCl_3 , BF_3 etc.
- (iii) Molecules in which central atom has one or more multiple bonds e.g. SO_2 , CO_2 in which a slight charge separation takes place.

Lewis Base is an electron pair donor.

Neutralization involves the formation of a new coordinate covalent bond between electron donor and acceptor.



Electron Donor Electron acceptor

Q.2.(a) Define HSAB. Give the main point of differences.

Ans. In 1963 R.G. Pearson suggested a very simple concept regarding the relative stability of acid-base reactions. This is known as Hard and Soft Acid and Base (HSAB) concept.

Metal ion may be classified into two types depending on the stability of their complexes with certain ligands. Based upon this preferential bonding metals and ligands have been classified as

Class (a) metals**Class (b) metals**

= (alkali and alkaline earth metal ions etc)(heavier metal ions, on the ions in low O.S. e.g. Ag^+ , Cu^+)

Tendency of donor atoms to complex with class (a) metal ions Tendency to complex with class (b) metal ions

$\text{N} > \text{P} > \text{As} > \text{Sb} > \text{O} > \text{S} > \text{Se} > \text{Te} > \text{F} > \text{Cl} > \text{Br} > \text{I} > \text{N} < \text{P} < \text{As} < \text{Sb} < \text{O} < \text{S} < \text{Se} < \text{Te} < \text{F} < \text{Cl} < \text{Br} < \text{I}$

Pearson suggested that terms hard and soft can be used for class (a) and class (b) respectively.

According to him,

“Hard acids prefer to bind with hard bases and soft acids prefer to bind with soft bases.” Thus the complex A:B is stable when both A and B are either hard or soft.

A + B ? A : B

Hard Acid Hard Base Stable Complex

Thus we can say that

Hard Acid**Soft Acid****Hard Base****Soft Base**

Are lewis acids with no d-electrons, small in size and not so easily polarisable.

Are lewis acids with nearly full electrons, larger in size and easily polarisable.

Are those lewis bases in which the donor atom have low polarisibilities and high electro negativity Are those bases in which the donor atoms are easily polarised and have low electronegativity.

e.g. H^+ , Li^+ , Na^+ , K^+ , Be^{+2}
 Po_4^{3-}

Cu^+ , Ag^+ Au^+ , $\text{Te}^+\text{H}_2\text{O}$, OH^- , F^- , CH_3COO^- ,
 R_2S , RSH , CN^-

Q.2 (b) Give the application of HSAB Concept.

Ans. 1. Hard acid will prefer to combine with hard base whereas soft acid

prefer to coordinate with soft bases.



Soft acid Soft base Stable complex



Soft acid Hard base Unstable complex

2. $(\text{CoF}_6)^{3-}$ (hard acid + hard base) is more stable than $(\text{CoI}_6)^{3-}$ (hard acid + soft base)

3. Hard acids such as Mg^{+2} , Ca^{+2} , and Al^{+3} occur in nature as MgCO_3 , CaCO_3 and Al_2O_3 respectively. This is because the acid cations and anions (CO_3^{2-} and O^{2-}) all are hard.

4. Soft acids such as Cu^+ , Ag^+ and Hg^{+2} occur as sulphides.

5. The border line acids, Ni^{+2} , Cu^{+2} and Pb^{+2} occur in nature both as sulphides and carbonates.

Unit - II

Chapter - II - Metal Ligand Bonding in Transition Metal Complexes

Q.3. What is crystal field theory? Give a representation of splitting of d-orbitals in various types of complexes.

Ans. Crystal Field Theory was given by Brethe and Van Vleck in 1932. According to this theory

(1) The interaction between the metal ion (nucleus) and ligands is purely electrostatic one in a complex species. Ligands are considered as point charges or as point dipoles.

(2) The interaction between the electrons of metal cation and ligand is entirely repulsive. These repulsive forces are responsible for splitting of d-orbitals of metal ion.

(3) The metal ion and the ligands do not mix their orbitals or share electrons i.e., it doesn't consider any orbital overlap.

The separation of five d-orbitals of the metal ion into two sets having different energies is called **crystal field splitting**. This concept of crystal field splitting makes the basis of CFT.

The energy gap between t_{2g} and e_g sets is denoted by $10 Dq$ or Δ_o (For octahedral complexes) and $4/9 \Delta_o$ for tetrahedral complexes. $10 Dq$ is called crystal field splitting energy.

Diagram

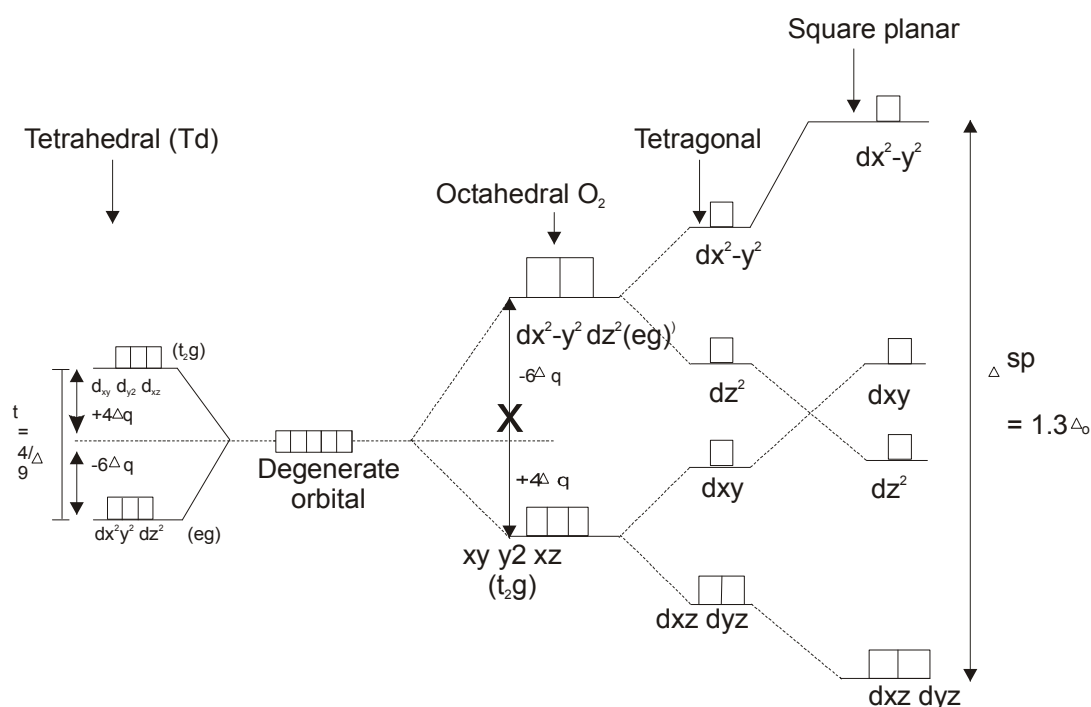
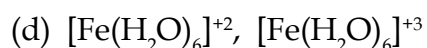
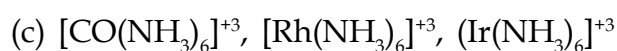
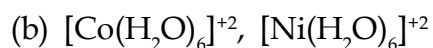
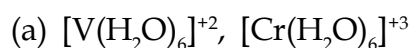


Fig: crystal splitting of de-orlinitats of metal ions of various compleas.

Fig. Crystal field splitting of d-orbitals of metal ions of various complexes.

Q.4. (i) What are the various factors influencing the magnitude of crystal field splitting energy?

(ii) Arrange the following complexes on the basis of increasing CFSE



Ans. (i) Factors influencing the magnitude of CFSE :

A. Nature of Metal Ions :

1. Different charges on the cation of the same metal i.e., charge $\times 10^4 \Delta_o$
2. Different charges on the cations of different metals i.e, charge $\times 10^4 \Delta_o$
3. Same charges on the cation but the no. of d electrons are different. $10^4 \Delta_o$ decreases with the increase of no. of d-electrons.
4. Quantum number of d-orbitals of the central metal ion - $10^4 \Delta_o$ increases about 30% to 50% from $3d^n$ to $4d^n$ and by about the same amount again from $4d^n$ to $5d^n$ complexes.

B. Nature of Ligand

Value of $10^4 \Delta_o$ is high for stronger ligands and value of $10^4 \Delta_o$ is low for weak ligands, spectrochemical series : $\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{N}_3^- < \text{F}^- < \text{Urea}, \text{O}^- < \text{OH}^- < \text{Ox}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{Py}, \text{NH}_3 < \text{en} < \text{bpy}, \text{phen} < \text{NO}_2^- < \text{C}_6\text{H}_5 < \text{Ph}^- < \text{C}_6\text{H}_5 < \text{CO}$

C. Geometry of the complex

$\Delta_{\text{sp}} > \Delta_{\text{o}} > \Delta_{\text{t}}$ and $\Delta_{\text{o}} = 9/4 \Delta_{\text{t}}$

(ii) (a) $[\text{V}(\text{H}_2\text{O})_6]^{+2}$? $3d^3$ system ? $12,400 \text{ cm}^{-1}$ (CFSE)

$[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$? $3d^3$ system ? $17,400 \text{ cm}^{-1}$ (CFSE)

Though both are d^3 system but greater the oxidation state greater is splitting for different metals.

b. $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$? d^7 system ? 9300 cm^{-1} (CFSE)

$[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$? d^8 system ? 8500 cm^{-1} (CFSE)

Both metal ion are of same transition series : CFSE decreases with increase of number of d-electrons.

c. $[\text{Co}(\text{NH}_3)_6]^{+3}$? $3d^6$ system ? $23,000 \text{ cm}^{-1}$ = (CFSE)

$[\text{Rh}(\text{NH}_3)_6]^{+3}$? $4d^6$ system ? $34,000 \text{ cm}^{-1}$ = (CFSE)

$[\text{Ir}(\text{NH}_3)_6]^{+3}$? $5d^6$ system ? $41,000 \text{ cm}^{-1}$ = (CFSE)

Thus CFSE increase from Co^{+3} to Rh^{+3} to Ir^{+3} as expected increase from 3 d to 4d to 5 d series respectively.

d. $[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$? $10,400 \text{ cm}^{-1}$ = (CFSE)

$[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$? $13,700 \text{ cm}^{-1}$ = (CFSE)

Greater is the charge, greater is the splitting.

Q.5. Calculate CFSE for following configuration in octahedral and tetrahedral complexes d^1 , d^4 , d^6 and d^8

Ans. Octahedral field (Complexes) Tetrahedral Complexes

D^n configuration	Weak field electronic configuration	Unpaired electron and CFSE	Strong Field	Unpaired And CFSE	Unpaired	Weak field electronic configuration	and CFSE
D^1	$t_{2g}^1 e_g^0$	1 CFSE = $-0.4 \Delta_o$	$t_{2g}^1 e_g^0$	1 $-0.4 \Delta_o$	1	$t_{2g}^0 e_g^1$	1 $-0.6 \Delta_q$
D^4	$t_{2g}^1 e_g^3$	3 $-1.2 \Delta_o$	$t_{2g}^4 e_g^0$	2 $-0.6 \Delta_q$	4	$t_{2g}^2 e_g^2$	$-0.4 \Delta_q$
D^6	$t_{2g}^4 e_g^2$	4 $-0.4 \Delta_o$	$t_{2g}^6 e_g^0$	0 $-2.4 \Delta_o + 3P$	4	$t_{2g}^3 e_g^3$	$-0.4 \Delta_q + P$
D^8	$t_{2g}^6 e_g^2$	2 $-1.2 \Delta_o + 3P$	$t_{2g}^6 e_g^2$	2 $-1.2 \Delta_o + 3P$	2	$t_{2g}^4 e_g^4$	$-0.8 \Delta_q + 3P$

Fig. Distribution of d-electrons in t_{2g} and e_g orbitals in Octahedral complexes.

Note : -

1. Low spin tetrahedral complexes are extremely rare and possibly non-existent.

2. No high spin square planar complexes have been observed as yet.

Q.6. Give application of CFT (Crystal field Theory)

Ans. CFT is able to explain the various properties of Transition Metal Complexes.

(i) No. of unpaired electrons and explanation of magnetic properties - Using this theory, number of unpaired electron can be calculated and we can determine magnetic moment of given complex.

$U = n(n + 2)$ B.M. where

n = no. of unpaired electron

Since magnetic moment generated by orbital motion of electrons is quenched by ligand due to their closer approach.

(ii) Explanation of geometry of complexes - On the basis of various favourable condition for formation of octahedral, tetrahedral and square planar complexes suitable geometry can be suggested.

(iii) Explanation of colours of complexes - Following two process are responsible for colour generation in complexes.

A. d-d electronic transition.

B. Charge transfer spectra.

Colour intensity for charge transfer complexes is greater than that of d-d transition.

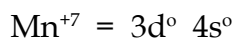
(iv) Explanation of distorted complexes with the help of Jahn Teller Distortion Theorem which results in release of Jahn Teller Stabilisation energy.

Q.7. Explain Why?

(i) KMnO_4 has deep purple colour.

(ii) Colour of Iodine is violet in CCl_4 but change to brown in benzene.

Ans. (i) In KMnO_4 , Mn has the oxidation state of +7 i.e. $\text{Mn} = 3d^5 4s^2$



Since it has no unpaired electron in d-orbital, how the complex is coloured.

It is explained on the basis of charge Transfer spectra. Ligand to Metal charge transfer transition is responsible for deep purple colour of K MnO_4

(ii) Iodine in CCl_4 ? Violet in colour.

Iodine in benzene ? Brown in colour

This is due to charge transfer process from benzene to iodine.

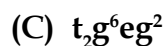
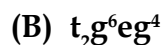
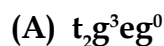
Diagram

Q.8. The CFSE will be maximum for which complex, CoF_6^{-3} , $[\text{Co}(\text{NH}_3)_6]^{+3}$, $[\text{Mn}(\text{H}_2\text{O})_6]^{+2}$, $[\text{Co}(\text{CN})_4]^{-2}$

Ans. First step is to calculate CFSE,

Complex	Electronic Cont.	State	Distribution of electron	CFSE
CoF_6^{-3}	d^6	High spin octahedral	$t_{2g}^4 e_g^2$	$-0.4 \Delta_o$
$[\text{Co}(\text{NH}_3)_6]^{+3}$	d^6	Low spin octahedral	$t_{2g}^6 e_g^0$	$-2.4 \Delta_o$
$(\text{Mn}(\text{H}_2\text{O})_6]^{+2}$	d^4	High spin octahedral	$t_{2g}^3 e_g^1$	$-0.6 \Delta_o$
$[\text{Co}(\text{CNS})_4]^{-2}$	Tetrahedral and $\Delta_o > \Delta_t$			

Q.9. Low spin octahedral complexes are maximum distorted in which state?



(D) $t_2g^5eg^0$

Ans. eg unsym i.e., contain 1, 2 or 3 electron in low spin complex lead to strong distortion leading to tetragonal or square planar complexes.

: $t_2g^6eg^2$ is the maximum distorted one.

Q.10. Calculation of magnetic moment for following complexes.

$K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$

Ans. $K_4[Fe(CN)_6]$

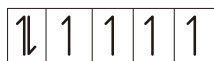
Oxidation state of Fe $\rightarrow 4 + x - 6 = 0$

$$x = +2 \text{ i.e., } Fe^{+2}$$

Now

Fe - $3d^64s^2$

Fe^{+2} - $3d^64s^0$



= 4 unpaired electron are present.

Magnetic moment

$$\mu = \sqrt{n(n+2)}$$

$$\mu = \sqrt{4(4+2)} = \sqrt{4 \times 6} = \sqrt{24} = 4.89 B.M$$

where n is no. of unpaired electron

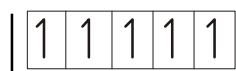
$K_3[Fe(CN)_6]$

Oxidation state of Fe ? $3 + X - 6 = 0$

$$X = 3 \text{ i.e., } Fe^{+3}$$

Now Fe ? $3d^64s^2$

Fe^{+3} ? $3d^54s^0$



= 5 unpaired electron are present.

Magnetic moment,

$$\mu = \sqrt{n(n+2)}$$

$$\mu = \sqrt{5 \times 7} = 5.913$$

Q.11. What is Orbital quenching?

Give an account for L-S coupling.

Ans. For proper identification of an electron, three quantum numbers are required and they help in calculating contribution towards magnetic moment.

(i) Spin angular Momentum (S) - Individual spin moment of each electron couples, $s_i s_i$; $s_i s_j$ or $s_j s_j$ and results in net spin contribution i.e., S value.

(ii) Orbital angular momentum (L) - Individual orbital contribution by each electron and their coupling i.e., $l_i l_i$, $l_i l_j$ or $l_j l_j$ results in net orbital contribution i.e., L value.

(iii) L-S coupling (Resultant angular Momentum (J)) - Atomic no. < 20 ? For atoms, having number of electrons less than 20, only spin contribution is calculated for contribution towards magnetic moment.

Atomic no. > 20 ? But for atoms having atomic no. more than 20, their orbital contribution can not be neglected. They have an appreciable L value.

The resultant angular momentum (J) for such species results from

(i) L + S value (For shells half filled/more than half filled)

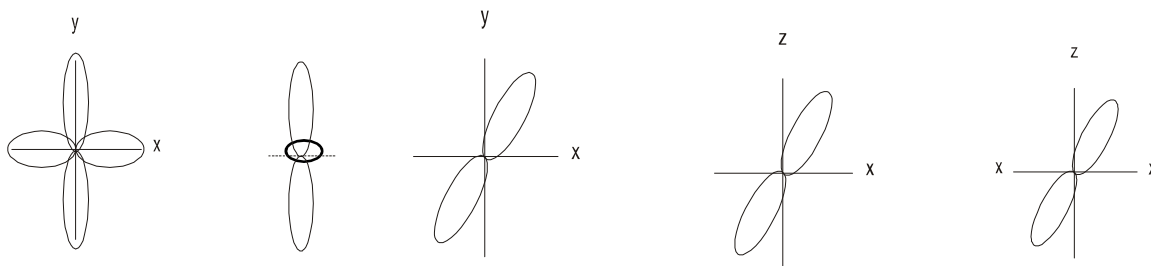
(ii) L - S value (for shells less than half filled)

This is known as L-S coupling or R-S coupling (Russell-Saunders)

Coupling).

Orbital Quenching :

There are five d orbitals according to their orientation in space.



$d_{x^2-y^2}$
 d_{xz}

d_{z^2}
 d_{y^2}

d_{xy}

When the interaction of d orbitals of Metal atom, in the presence of ligand. The contribution of $d_{x^2-y^2} = \pm 2 h/2Z$ units of angular momentum.

The contribution of d_{xz} , $d_{xy} = \pm 1 h/2r$ units of angular momentum.

The contribution of $d_{z^2} = 0$ to angular momentum.

The net contribution towards total angular magnetic moment is reduced. Moreover, when there is S or P mixing with d orbitals then again there is reduction in magnetic moment.

Thus total angular magnetic momentum that we should get if the d-orbitals were pure is reduced when there is interaction of Metal d-orbitals with ligand as per CFT. This is known as **orbital Quenching**.

Q.12. Calculation of Term Symbol or Spectroscopic Ground state for following configuration of ions.

Ti^{+3} , V^{+3} , Mn^{+2}

Ans.

Ion	Electronic Configuration	No. of unpaired electron (n)	S = n/2	Spin multiplicity 2S + 1	L = E Me	L + S/ L - S	Term Symbol or Ground State Spectroscopic
Ti ⁺³	3d ¹ 4s ⁰	1	1/2	2	2	3/2	2D _{3/2}
V ⁺³	3d ² 4s ⁰	2	1	3	3	2	3F ₂
Mn ⁺²	3d ⁵ 4s ⁰	5	5/2	6	0	5/2	6S _{5/2}

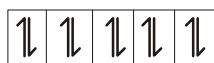
Q.13. Why some salts of zinc as ZnCl₂ are colourless and some as CuCl₂ are colour.

Ans. Transition metals are coloured because of the presence of unpaired electrons. If they have no unpaired electron, electronic transition can't occur and they are colourless.

(i) In ZnCl₂, Zn has oxidation state + 2

Zn ? 3d¹⁰4s²

Zn⁺² ? 3d¹⁰4s⁰

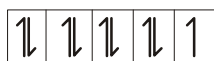


unpaired electron absent.

(ii) In CuCl₂, Cu is in + 2 oxidation State

Cu ? 3d¹⁰4s¹

Cu⁺² ? 3d⁹4s⁰



number of unpaired e = 1

Therefore, electronic transition possible and salt is coloured.

Q.14. Arrange the following ions in increasing or decreasing order of their magnetic moment.

Cu^{+2} ,

Mn^{+2} ,

Fe^{+2} , Ni^{+2} , Co^{+2}

Ans. First step is to calculate number of unpaired electron, since

Number of unpaired electron \times Magnetic Moment

$\text{Cu}^{+2} ? 3d^4 4s^0$ $\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow} \rightarrow 1$ unpaired electron.

$\text{Mn}^{+2} ? 3d^5 4s^0$ $\boxed{\uparrow} \boxed{\uparrow} \boxed{\uparrow} \boxed{\uparrow} \boxed{\uparrow} \rightarrow 5$ unpaired electron.

$\text{Co}^{+2} ? 3d^7 4s^0$ $\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \rightarrow 3$ unpaired electron.

$\text{Fe}^{+2} ? 3d^6 4s^0$ $\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \rightarrow 4$ unpaired electron.

$\text{Ni}^{+2} ? 3d^8 4s^0$ $\boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \boxed{\uparrow\downarrow} \rightarrow 2$ unpaired electron.

$\therefore \text{Mn}^{+2} > \text{Fe}^{+2} > \text{Co}^{+2} > \text{Ni}^{+2} > \text{Cu}^{+2}$

Unit - II Chapter - III

Magnetic Properties of Transition Metal Complexes

Q.15. Give various types of magnetic behaviour.

Ans. Types of Magnetic Behaviour

1. Diamagnetism - (1) Substances which are feebly repelled by magnets are called diamagnetic (2) Substance do not attract lines of force.

(3) When any substance is placed in an external magnetic field, there is an induced circulation of electrons producing a net magnetic moment aligned in opposition to the applied field.

(4) Substances possessing inert gas (8-electron) pseudo-inert gas (15 electrons) and pseudo inert gas +2 (18+2 electrons) are always diamagnetic.

Type : Inert Gas Type

Similarity with inert gas

Li^+ , Be^{+2} , B^{+3} , C^{+4} , N^{+5}

Helium

Na^+ , Mg^{+2} , Al^{+3}

Neon

K^+ , Ca^{+2} , Ti^{+4} , U^{+5}

Argon

Pseudo-inert gas type

Cu^+ , Zn^{+2} , Ga^{+3}

3d10

Ag^+ , Cd^{+2}

4d10

Au^+ , Hg^{+2}

5d10

Pseudo-inert gas type + 2 electrons

Ga^+ , Ge^{+2} , As^{+3}

(5) Diamagnetism is independent of temperature.

2. Paramagnetism

- (1) Paramagnetism is produced by unpaired electrons present in a sample.
- (2) The spin and orbital motions of these electrons give rise to permanent molecule magnetic moments that tend to align themselves with an applied field.
- (3) Paramagnetism is shown by substances when the magnetic effect of individual electrons are not cancelled.
- (4) Paramagnetism is shown by many ions of d-8 and block elements containing odd no. of electrons.
- (5) Paramagnetism is temperature dependent. it decrease in magnitude as the temperature is increased.

3. Ferromagnetism

- (1) Ferromagnetic materials are special case of paramagnetism in which the moments of individual atoms become aligned and all point in same direction.
- (2) Magnetic susceptibility is greatly enhanced.
- (3) Ferromagnetic substances may become permanently magnetised.
- (4) Fe, Co, Ni exhibit ferromagnetism.

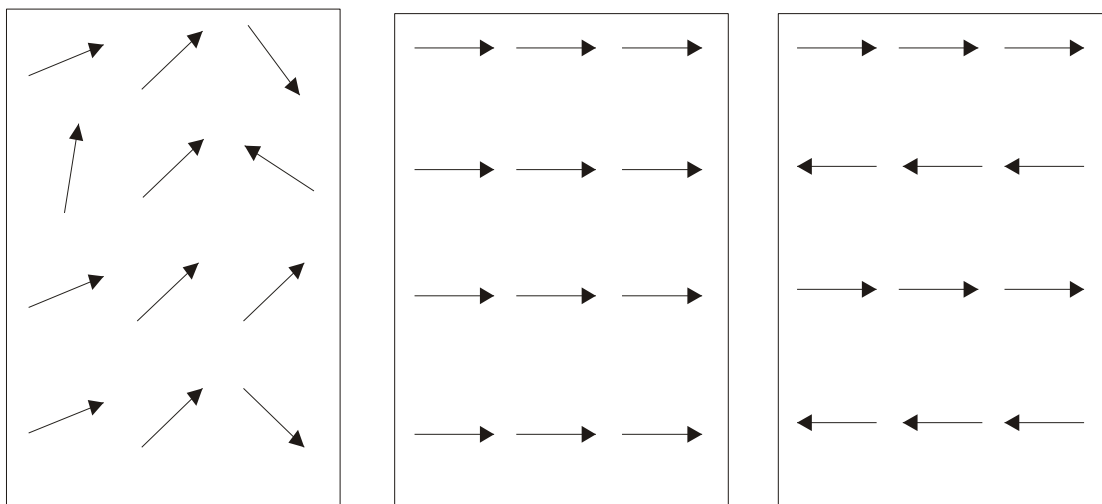
4 Antiferromagnetism

- (1) Antiferromagnetism is achieved by pairing the moments on adjacent atoms which points in opposite direction.
- (2) No resultant magnetic moment.
- (3) In this case thermal motion upto a certain temp. (neel temperature) results in an increased susceptibility, above this temperature, when normal paramagnetism replaces antiferromagnetism, the susceptibility with further rise in temperature.
- (4) Typical paramagnetic substances are MnO, and NiF₃

5. Ferrimagnetism

(1) In Fe_3O_4 an inverse spinel, half the Fe^{3+} ions occupy tetrahedral holes and half occupy octahedral holes. The interaction between spin in different sites is usually cancel.

compounds which are ferromagnetic owing to incomplete canceling of coupled spins are known as ferromagnetic.



paramagnetism

Ferromagnetism

Antiferromagnetism

Q.16 What are the various methods for determination of magnetic susceptibility describe Gouy method.

Ans. Determination of magnetic susceptibility:

Two methods which are very common for measurement of magnetic susceptibility are

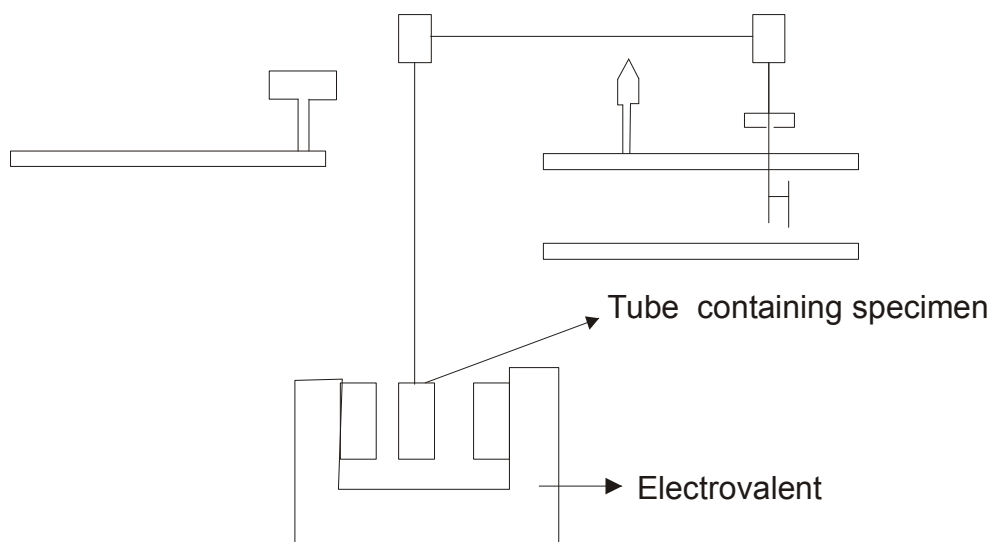
Govy Method**Faraday Method**

1. Sample size –comparitively larger. Govy technique requires approx. 1 gm.
 1. Sample size – is very small. Requires several milligram of material.
2. Gives volume susceptibility which must be converted to specific susceptibility.
 2. Gives specific susceptibility directly.

Inspite of its disadvantages, Govy method is more often used.

Govy's Method :

Experimental requirement – Sample is present as a long rod of material, a solution, or a glass tube packed with powder. One end of the sample is placed in a uniform magnetic field and the other end in a very low or zero field.



If g is the acceleration due to gravity the force F acting on a sample is given by

$$F = \Delta \text{ m.g.} \quad - (1)$$

If χ_1 is the volume susceptibility of the sample

χ_2 is the volume susceptibility of air.

$$F = \frac{1}{2} (\chi_1 - \chi_2) a. \mu_0 H^2 \quad - (2)$$

Combining (1) and (2)

$$\Delta \text{ m.g.} = \frac{1}{2} (\chi_1 - \chi_2) a. \mu_0 H^2$$

$$\text{hence } \chi_1 = \chi_2 + 2 \Delta \text{ m.g.} / a. \mu_0 H^2 \quad - (3)$$

Q.17. How will you find out magnetic moments from magnetic susceptibilities?

Ans. When a substance is subjected to magnetic field H , and a magnetization I is induced. The ratio I/H is called the volume susceptibility K and can be measured by a number of techniques as Gouy's Method. The volume susceptibility is related to the gram susceptibility X and the molar susceptibility X_m .

$$X = K/d \quad X_m = KM/d \quad - (1)$$

Where d and M are the density and mol. cut. of the substance. For a paramagnetic substance K , X and X_m are the positive quantities. The effective magnetic moment M_{eff} is calculated from the relation.

$$M_{\text{eff}} = 2.83 \sqrt{XMT} \quad - (2)$$

Where T is the absolute temperature and the constant 2.83 is obtained from quantum mechanical calculations

$$X_{\text{para}} = N_A M_{\text{eff}}^2 / 3KT$$

N_A = Avogadro number, K = Boltzmann constant. On substituting the values we get the equation (2).

Magnetic susceptibility would be independent of the strength of the

external field applied. However, magnetic susceptibility would depend on temperature since the thermal agitation would tend to randomise the atomic or molecular magnetic dipoles which get aligned in the direction of the magnetic applied field. The variation of X_{para} with temperature is expressed in the form of Curiew law as

Curie's Law

Pierre Curie established that paramagnetic susceptibility is inversely proportional to the absolute temperature,

$$X_m = C/T$$

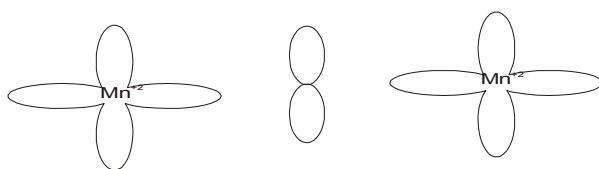
This is known as Curies law in which C is a characteristic of the substances and is known as Curie Constant where $C = N\mu^2/3R$

Where N is Anogadro's number and R is gas molar constant.

The Curie law is followed by great accuracy by some systems as $[\text{FeF}_6]^{3-}$. However, many paramagnetic material deviate slightly from the ideal behaviour and obey Curie- Weiss law

$X_{\text{para}} = C/(T-Q)$ where Q = Weiss constant with units of temperature.

In materials that are not magnetically dilute, unpaired spins on neighbouring atoms may couple with each other called as **magnetic exchange**. Such materials obey Curie-Weiss laws. In certain cases, there will be some temperature below which magnetic exchange dominates. This temperature is called the **Curie temperature** (T_c) if the type of exchange displayed is ferromagnetic and the Neel temperature (T_N) if it is antiferromagnetic, the change in susceptibility as the temperature is decreased below either T_c or T_N may be quite high.



Magnetic exchange

Magnetic exchange

Antiferromagnetism is very much temperature dependent. For antiferromagnetic substances there is a characteristic temperature known as Neel temperature or Neel point above which the antiferromagnetic substances behave as a normal paramagnetic substances.

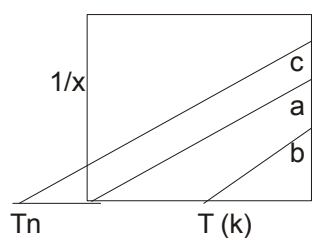


Fig. Plot of $1/x$ vs temperature for three magnetic behaviours :

(a) the Curie law

(b) the Curie-Weiss law for a ferromagnetic substance with Curie temperature, T_c .

(c) the Curie-Weiss law for an antiferromagnetic substance with Neel temperature, T_N .

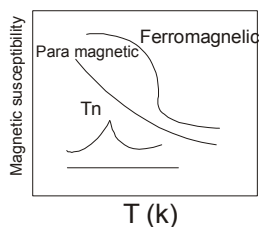


Fig. Variation of magnetic susceptibility with temperature for diamagnetic, paramagnetic, ferromagnetic and antiferromagnetic substances.

Unit III

Chapter - IV

Electron Spectra of Transition Metal Complexes

Q.18. (a) Give the rules for determining the order of energy for different terms.

(b) What is microstate? Calculate number of microstate for an electronic configuration.

(c) Describe selection rules for electronic spectra.

Ans. (a) The rules are as under -

1. The terms are arranged depending upon their spin multiplicities, e.g., their S- Values. The most stable state has the highest S-value and stability decreases as the value of S decreases. This means that the most stable state (ground state) has maximum unpaired electron because this gives the minimum electrostatic repulsion. This is in accordance with Hund's rule.

2. For a given value of S, the state with the highest value of L is most stable. This means if two or more terms have same value of S (same spin multiplicity), the state with highest value of L will have the lowest energy.

3. For a given value of S and L, the terms with smallest J value is most stable if the subshell is less than half filled and the term with maximum J is most stable if subshell is more than half filled.

(b) Each different arrangement of electrons in a set of orbitals exhibit slightly different energy and is called a **microstate**. The number of microstates can be calculated from the number of orbitals and number of electrons by using formula : $(n/r) = n/r/n-r$

where n is double the number of orbitals.

R is number of electrons.

Example : Calculate number of microstates for a d^2 system. Since there are five orbitals so $n = 10$, and two electrons so $r = 2$. Hence

$$(10/2) = 10/2/10-2 = 10/2/8 = 10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1 / 2 \times 1 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1$$

= 45 microstates

(c) The main selection rules for electronic spectra are :

1. *Transition in which number of unpaired electrons changes is going from a lower to higher energy state are referred to as **spin or multiplicity forbidden**.*

This means that transitions to only those excited states are considered which have the same spin multiplicity as the ground state i.e., transitions in which $\Delta S = 0$.

For e.g., for a d^2 configuration, the only transitions which are seen, are from 3F (G.S.) to 3P (E.S.) because both 3F and 3P have same spin multiplicity 3. The transitions in which $\Delta S = 0$ are forbidden or very weak.

2. *Transition which do not involve a change in the subsidiary quantum number ($\Delta l = 0$) are forbidden if molecule has centre of symmetry.* These forbidden transitions are called **Laporte forbidden transitions**. The transitions which involve a change in the subsidiary quantum Number (i.e., $\Delta l = \pm 1$) are Laporte allowed transitions and have a high absorbance. This rule suggests that transitions from one d-level to another d-level (i.e., d-d transitions) in transition metal complexes are not allowed (Laporte forbidden transition) because the change in $l = 0$ but spectra of much lower absorbance are observed ($\epsilon = 5$ to $10 \text{ l mol}^{-1} \text{ cm}^{-1}$) because of slight relaxation in Laporte rule.

Q.19. What is an Orgel diagram? Draw Orgel diagrams for d^1 , d^9 Octahedral system.

Ans. Orgel diagram : It describes in a qualitative way the effect of electron configurations with one electron, one electron more than a half filled level, one electron less than a full shell, and one electron less than a half filled shell. In a Orgel diagram quantum mechanically calculated energy of term level (as ordinate) is plotted against an increasing value of Δ , ligand field splitting parameter (as abscissa).

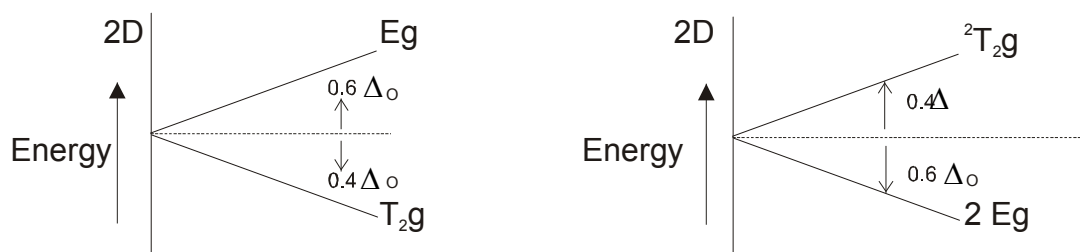


Fig. Splitting of energy levels for d^1 and d^9 configuration in Octahedral field.

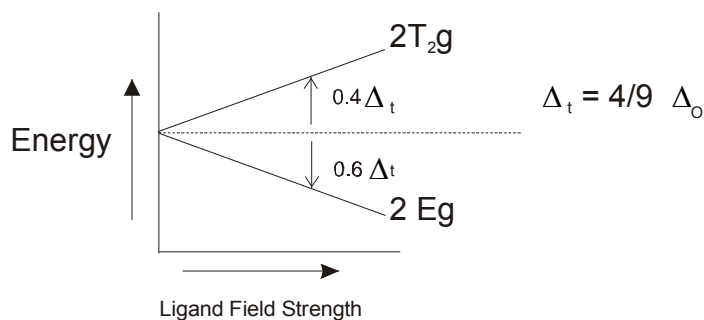


Fig. Splitting of energy levels for d^1 configuration in tetrahedral field.

Chapter - V

Thermodynamic And Kinetic Aspects of Metal Complexes

Q.20. Derive stepwise and overall formation constant. How are they related?

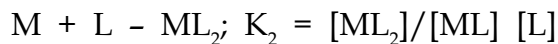
Ans. Stepwise formation Constant :

It deals with stability of formation of complexes in aqueous solution in each step

$$K_1$$

For e.g., $M + L \rightleftharpoons ML$; $K_1 = \frac{[ML]}{[M][L]}$

$$K_2$$

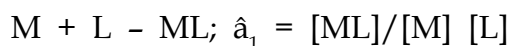


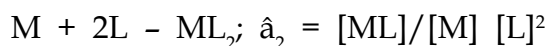
$$K_n$$


So that $K_n = [ML_n]/[ML_{n-1}][L]$

and K_n is known as stepwise formation constant. Generally $K_1 > K_2 > K_3 > K_4 \dots$

Overall formation constant :

$$\hat{K}_1$$


$$\hat{K}_2$$


and $M + nL \rightleftharpoons ML_n$

$\therefore \hat{K}_n = [ML_n]/[M][L]^n$

The relationship between stepwise and overall formation constant is as

$\hat{K}_n = K_1 \cdot K_2 \cdot K_3 \dots K_n$

Q.21. What is Thermodynamic and Kinetic stability. On what basis complexes can be categorised as stable and unstable complexes, Labile and Inert complexes. Give suitable energy profile diagram.

Ans. The stability of a complex depends on the reaction energy (ΔH) while the lability depends on the activation energy.

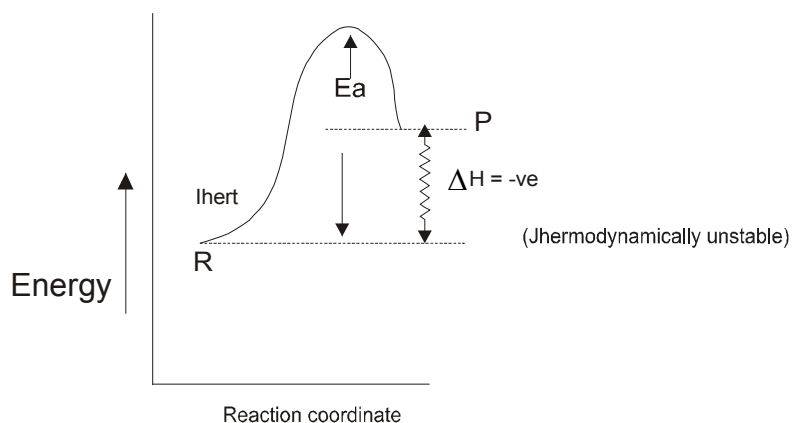
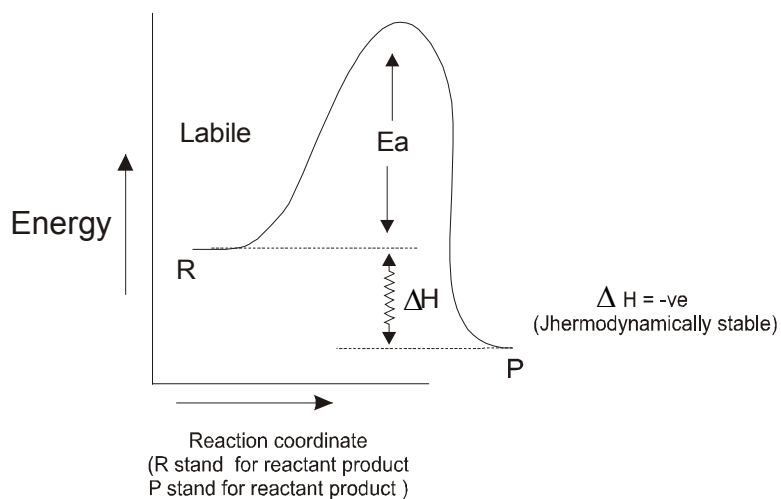
Thus, Heat of reaction (ΔH) deals with thermodynamic stability and Activation energy (E_a) deals with kinetic stability.

Depending upon -

(i) Thermodynamic Stability : Complexes are of two types - Stable and Unstable complexes.

(ii) Kinetic Stability : Complexes are of two types - Labile and Inert complexes.

The complexes in which the ligands are rapidly replaced by others are called labile while those in which substitution occurs slowly are termed inert complexes.



Energy Profile Diagram for Stable and Unstable, Labile and Inert Complexes.

Q.22. What are the various factors affecting the lability and stability of a complex.

Ans. Factor affecting Liability of a complexes

- (1) Change of the central Metal ion \times 1/Liability
- (2) Radius of the central Metal ion \times Liability.

(3) Charge to radius ratio $\times 1/\text{Liability}$.

(4) Geometry of the complex :

Tetrahedral complexes are more labile as compared to octahedral.

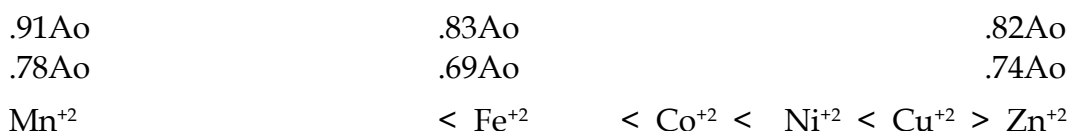
Factors affecting the stability of complexes

(A) Properties of Central Metal ion :

Stability increasing factors - High charge, Small size

Consider the series :

Natural order of Stability :



Reason - Charge/Radius Ratio

(B) Properties of Ligand : Chelate effect, size and charge of ligand, steric effects, chelate ring size basic character of ligand.

Q.23. Describe John Teller Distortion Theorem.

Ans. According to this theorem, for a non linear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy and lower the energy.

We can determine which octahedral complexes will be subjected to John Teller distortion by considering ground state degeneries.

Configuration for which John Teller distortions are expected in ML_6 complexes.

$D^1 \ d^2$	d^4	d^5
$d^6 \ d^7$	d^9	
Both H.S. and L.S. H.S. and L.S.	L.S.	H.S.

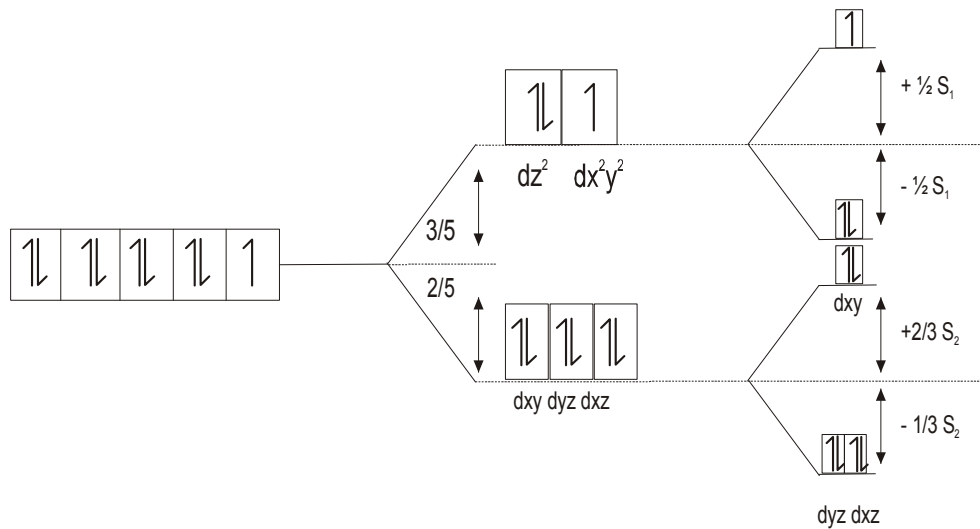
Generally strong distortion occur in following cases.

(A) $d^4 ? t_{2g}^3 e_g^1$

(B) $d^9 ? t_{2g}^6 e_g^3$

(C) $d^8 ? t_{2g}^6 e_g^2$

Calculation of John Teller stabilisation energy for d^9 system (Cu^{+2} ion)



Contribution from t_{2g} electron

$$= 4 \times (-1/3 \ddot{a}_2) + 2 \times (2/3 \ddot{a}_2) = 0$$

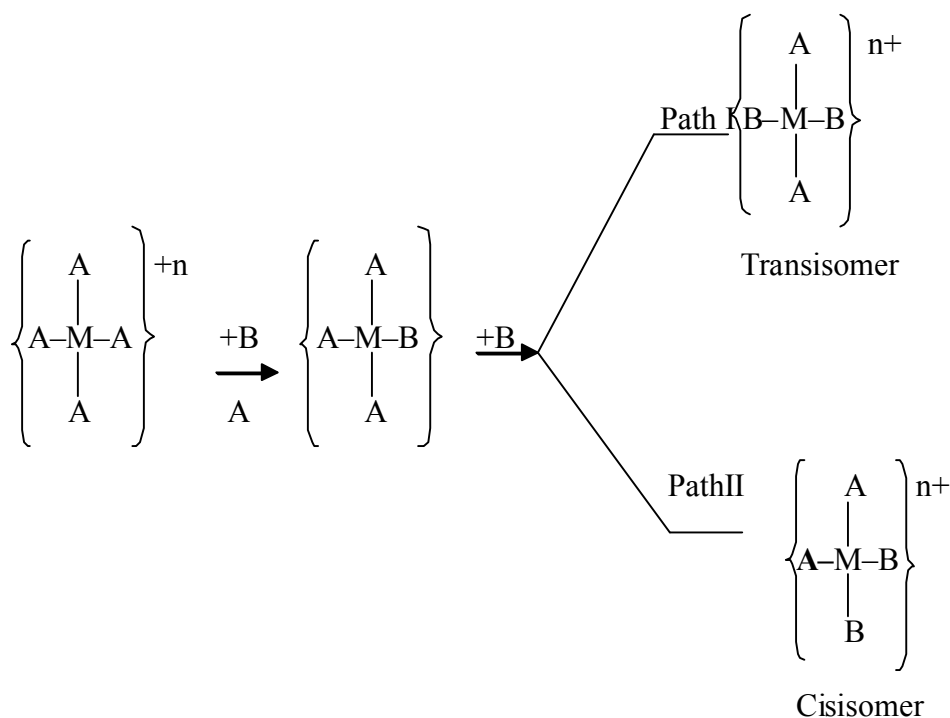
Contribution from e_g electron

$$= 1 \times (+1/2 \ddot{a}_1) + 2 \times (-1/2 \ddot{a}_1) = -1/2 \ddot{a}_1$$

It means, the net lowering of the electronic energy in case of e_g level is $\ddot{a}/2$. This net energy equal to $-\ddot{a}_1/2$, might be called the John Teller Stabilisation energy and provides the driving force for distribution.

Q.24. Give an account of Reactions in Square Planar complexes describing Trans Effect.

Ans. Consider a reaction



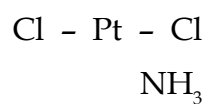
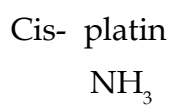
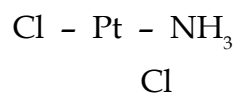
When the trans directing effect of Ligand B is greater than A, path I occurs and trans product is formed. But path II is followed when trans effect of A is greater than B.

Trans effect series : This is arranged on the basis of increasing polarisability.

$\text{C}\equiv\text{N} > \text{CO}, \text{C}_2\text{H}_4, \text{NO} > \text{PR}_3, \text{H}^- > \text{OH}^-, \text{NH}_2^- > \text{S} > \text{C} > \text{NH}_2, \text{Ph}, \text{NO}_2^-, \text{I}^- > \text{Br}^-, \text{Cl}^- > \text{Py} > \text{NH}_3 > \text{H}_2\text{O}$

Q.25. What is application of Trans effect. How can they be synthesized.

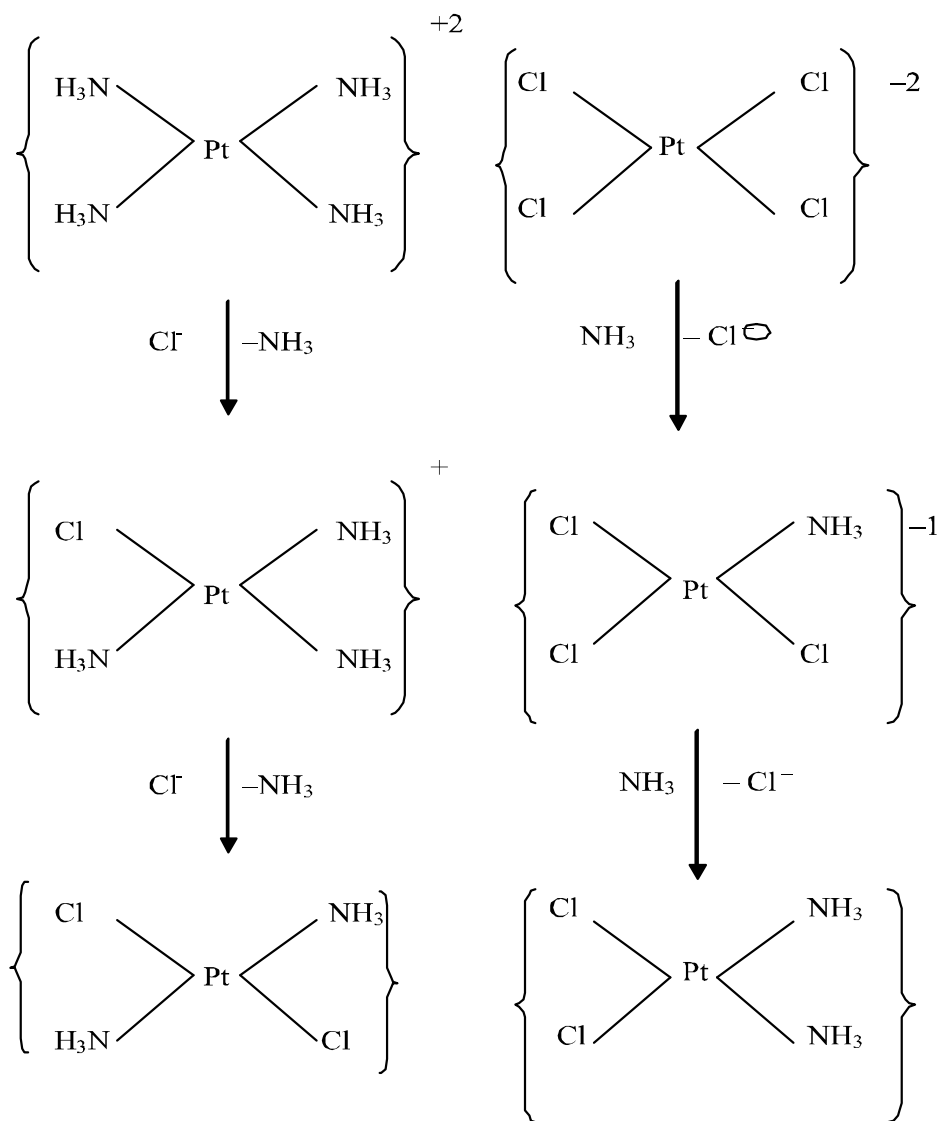
Ans. Using trans effect series, various geometrical isomers of desired need can be prepared.



Trans-platin

Cis platin has biological importance as it is an important drug for eradication of tumours while its trans isomers is not.

Synthesis of Cis trans $[\text{Pt} (\text{NH}_3)_2 \text{Cl}_2]$



Trans product

Cis Product

Unit-IV**Chapter-VI****Organometallic Chemistry**

Q.26. What are organometallic compounds. Give its classification.

Ans. The term 'organometallic' denotes compounds in which organic groups are linked directly to the metal through at least one carbon atom.

Those compounds which doesn't have M-C bond are not included in organo metallics as C_2H_5ONa , $Ti(OCH_3)_4$ etc. As well as those having M-C bond but not organic group attached to the metal are not included in organometallics as $K_4[Fe(CN)_6]$, CaC_2 etc.

Some organometallic compounds are :

Diethyl zinc, $(C_2H_5)_2 Zn$

Trimethyl aluminium, $(CH_3)_3 Al$

Nickle carbonyl, $Ni (CO)_4$

Although metal cyanides, carbides and carbonyls contain M-C bonds but only carbonyls are included as others chemistry is more related to inorganic rather than organometallic chemistry.

Classification of Organometallic Compounds

A. On the basis of bond type of the metal-carbon bonding present.

1. Ionic compounds
2. Covalent compounds
3. Delocalieed-electron bond or A-bond compounds

Ionic Compounds : Strong electropositive elements having electronegativity less than 1.2 form ionic organometallic compounds. The ionic compound formation is favoured when the hydrocarbon anion (e.g., cyclopenta dienyl radical, C_5H_5) is stabilised by accepting an electron to form a aromatic system e.g. $(C_5H_5)_2 Mg^{+2}$

Covalent Compounds :

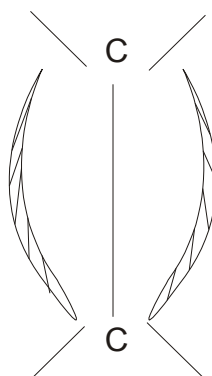
Metals having electronegativities between 1.5 and 2.0 and non-metals leaving lower electro negating than carbon e.g. Li, Be, Al, Zn, B etc. Such

organometallic compounds have definite structure.

Hybridization	Geometry	Compounds
Sp	Linear	$(C_2H_5)_2Zn$
Sp ²	Trigonal	$(CH_3)_3 B$
Sp ³	Tetrahedral	$(CH_3)_4 Si$
Dsp ²	Square planar	$(C_6H_5)_2 Pt (PR_2)_2$
Dsp ³	Trigonal bipyramid	$(CH_3)_3 NbCl_2$

Delocalised π -electron-bond compounds

This type of bond have appreciable double bond character.



(i) Olefinic and acetylene compounds.

(ii) Sandwich compounds, e.g. $(C_6H_6)_2 Cr$, $(C_5H_5)_2 Fe$

B. On the basis of type of alkyl group (R) linked with metal

Organometallic Compounds

Simple Compounds (RM_n) Mixed Compound (RMX)

Eg : $(\text{CH}_3)_3 \text{SnCl}$

$(\text{CH}_3)_2 \text{SnCl}_2$

Symmetrical (R group will remain same)

Asymmetrical (Different R groups)

Eg : $(\text{C}_2\text{H}_5)_2 \text{Fe}$

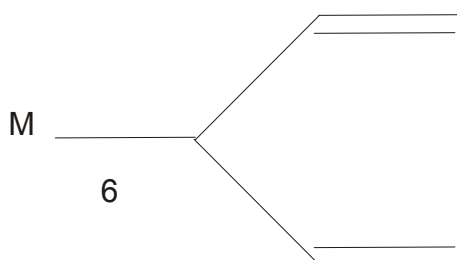
Eg : $\text{C}_2\text{H}_5 \text{Mg C}_4\text{H}_9$

$(\text{C}_2\text{H}_5)_2 \text{Zn}$

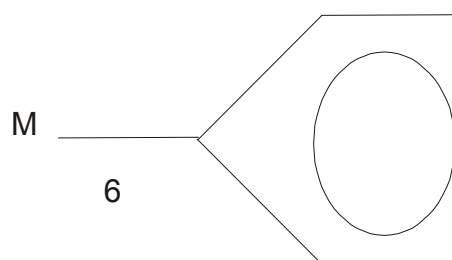
$\text{CH}_3\text{MgC}_6\text{H}_5$

C. On the basis of Hapticity of Organic Group

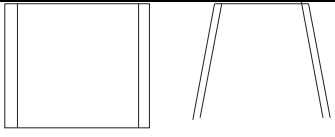
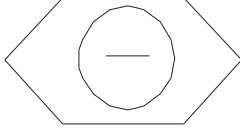
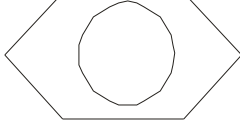
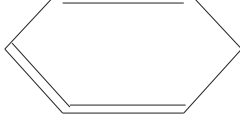
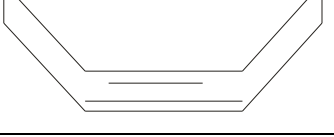
The number of attached C atoms is called hapticity of the organic group. On this criteria organometallic ligands are classified according to the number of carbon atoms of a group attached to a metal. For e.g.



Mono-Hapts (n^1)



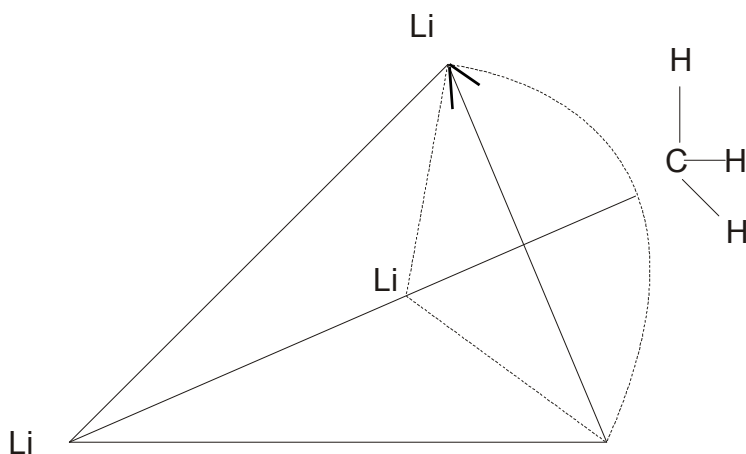
Penta --Hapts (n^5)

S.No.	Hapticity	Examples	Formula
1	N1 (monohapto)	Alkyl, aryl, CO etc	R - , Ar-, CO
2	N2 (dihapto)	Alkene, alkyne	CH ₂ = CH ₂ , CH = CH
3	N3 (trihapto)	Allyl	CH ₂ = CH - C-H ₂
4	N4 (tetrahapto)	Cyclobutadiene, butadiene	
5	N5 (pentahapto)	Cyclopentadienyl	
6	N6 (hexahapto)	Benzene and its derivatives	
7	N7 (Septahapto)	Cycloheptatriene	
8	N8 (Octahapto)	Cyclooctatetraene	

Q.27. Give the structure of important organometallic compounds.

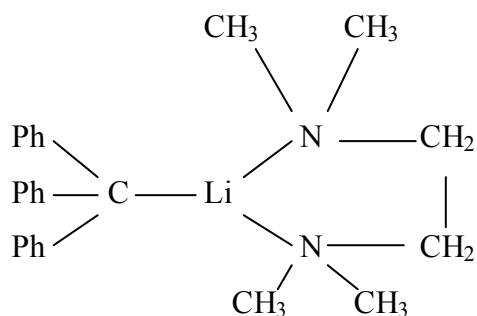
1. Methyllithium (CH_3Li)₄
2. Triphenyl methyl lithium tetramethyl ethylenediamine
3. Trimethyl aluminium
4. Dialkyls and Diaryls of Mercury
5. Diethyltin
6. Methyltin fluoride

Ans. 1. Structure of methyl lithium (CH_3Li)₄



The 4 Li atoms of $(\text{CH}_3\text{Li})_4$ are on the corners of the tetrahedron. The C atom of each methyl group is above the face of the tetrahedron. Each C atom is bonded to three hydrogen atoms ($-\text{CH}_3$) and three Li atoms (multicentered bonds); thus the coordination numbers of carbon is six.

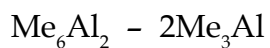
2. Structure of $[\text{Li C Ph}_3 \text{ TME}]$



TME Δ = Tetramethyl ethylene diamine

3. Structure of trimethyl aluminium

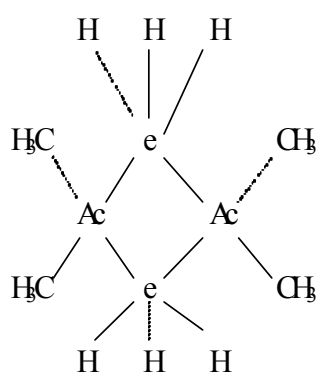
It is dimeric in benzene solution and monomer dimer equilibrium established in vapour phase.



Dimer

Monomer

The structure of dimer, $(\text{Me}_3\text{Al})_2$



Q.28. Give the application of Organometallic Chemistry.

Or

Why organometallics are in demand of research scientists.

Ans. First organometallic compound isolated was tetramethyl-diarsine $[(CH_3)_4]As_2$ by de-Glaussicourt.

Edward Franplanar, synthesized first organo zinc compound $[(C_5H_5)_2Zn]$, known as Frankland reagent and led the foundation of organometallic chemistry and extended his studies to other elements as Hg, Cd, Sn, Pb and Si.

The discovery of Gregnard Reagent (RMg X) contributed a lot, synthesis of ferrocene $(X-C_5H_5)_2Fe$ in 1951 opened a new area of research in organometallics.

Application

I. Organometallic Compounds of Lithium :

1. Simple organolithium compounds e.g., butyl lithum are used as polymerisation catalysts.
2. Lithum acetylide is used in production of Vitamin A, tranquilizer.
3. Phenyl lithum is used to introduce phenyl group in organic synthesis.

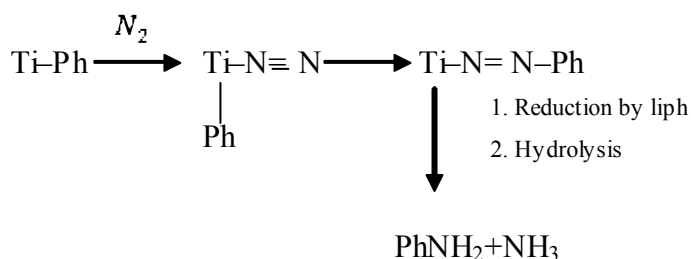
II. Organometallic Compounds of Aluminium

1. Trialkyl aluminium is widely used as reducing agent in reduction of metal halides, chloral to trichloroethanol, aldehyde and ketones to alcohols, cyanides to amines and alkenes to alkanes.
2. Trialkyl aluminium are used as alkylating agents.

Organometallic compounds of Titanium

1. Some organotitanium compounds are used to catalyse the fixation of nitrogen.

The reaction involves the insertion of N_2 molecule between Ti-Ph bond.



2. Polymerisation by Titanium compounds (Ziegler-Natta Catalyst)

The Ziegler-Natta catalyst is a heterogeneous catalyst and the active metal species is fibrous form of TiCl_3 formed in situ from TiCl_4 and AlEt_3 but performed TiCl_3 can be used. Polymers produced are stereospecific polymers.

Diagram

Q.29. Explain the hydrogenation in organometallic compounds.

Or

Write a short note on Wilkinson catalyst.

Ans. The first rapid and practical system for the homogeneous reduction of alkenes, alkynes and other unsaturated substances at 25°C and 1 atm pressure used the complex $\text{RhCl}(\text{PPh}_3)_3$ known as Wilkinson catalyst. It dissociates to only a small extent at 25°C .



Coordinately saturated Coordinately unsaturated

Mechanism :

Diagram

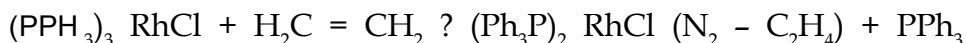
Under hydrogen $\text{RhCl}(\text{PPh}_3)_3$ solution becomes yellow and an octahedral dihydride is first formed but due to strong trans effect of H, this rapidly dissociates at room temperature to give a fluxional five-coordinate rhodium (III) species.

The species then coordinates alkene.

Diagram

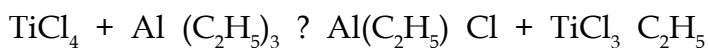
Fig : Simplified Catalytic Cycle for hydrogenation of $>C=C<$ bonds

The process is very slow because of the formation of stable rhodium ethylene complex, which doesn't readily reacts with hydrogen.



Q.30. What is the basis of Ziegler-Natta polymerization? Is Ziegler-Natta system homogeneous?

Ans. Ziegler-Natta Polymerization - The polymerization of defines by catalysts of the Ziegler-Natta type represents a most important polymerization reaction. The Ziegler catalyst is formed from $TiCl_4$ and aluminium alkyl.



In the inert hydrocarbon solvents used an insoluble mixed halide-alkyl complex of aluminium and titanium is formed of variable composition. This material is the active catalyst for the polymerization of ethylene, acting as a heterogeneous catalyst. The Ziegler-Natta system is heterogeneous and the active metal species is fibrous form of $TiCl_3$ formed in situ from $TiCl_4$ and $AlEt_3$ but performed $TiCl_3$ can be used.

[See the mechanism in Q.28]

The function of aluminium alkyl are mainly :

- (i) The formation of active metal species $TiCl_3$.
- (ii) The replacement of one of the chloride ions in a Ti^{+3} ion at the surface by an alkyl radical derived from it.

Unit - V

Chapter - VII - Bio Inorganic Chemistry

Q.31. What is Bioinorganic Chemistry?

Ans. Bioinorganic chemistry is a specialized field that spans the chemistry of metal-containing molecules within biological systems. This field is

concerned with the control and use of metal ions in biochemical processes. Although bioinorganic chemistry includes the study of artificially introduced metals (e.g. medicinally), many natural occurring biological processes (such as respiration) depend upon molecules containing inorganic elements, such as metalloproteins, and these natural processes are also studied by bioinorganic chemistry. Bioinorganic chemistry has developed from the continuing research in inorganic chemistry and its important associations in biological chemistry.

It is a discipline which is focused on :

- the study of elements and inorganic compounds in biological systems and the study of inorganic models that could imitate the chemical behaviour in those biological systems.
- the study of non-essential elements with an application in the diagnosis and therapeutic field.

As a mix of biochemistry and inorganic chemistry, bioinorganic chemistry is important in realizing the implications of electron-transfer proteins, substrate bindings and activation, atom and group transfer chemistry as well as metal properties in biological chemistry.

History

Paul Ehrlich used organoarsenic ("arsenicals") for the treatment of syphilis, demonstrating the relevance of metals, or at least metalloids, to medicine, that blossomed with Rosenberg's discovery of the anti-cancer activity of cisplatin ($\text{cis-PtCl}_2(\text{NH}_3)_2$). The first protein ever crystallized (see James B. Sumner) was urease, later shown to contain nickel at its active site. Vitamin B₁₂, the cure for pernicious anemia was shown crystallographically by Dorothy Crowfoot Hodgkin to consist of a cobalt in a corrin macrocycle. The Watson-Crick structure for DNA demonstrated the key structural role played by phosphate-containing polymers.

Q.32. Give the various applications of Bioinorganic Chemistry?

Ans. There are several distinct systems of interest in bioinorganic chemistry. These areas include metal ion transport and storage, metallohydrolase enzymes, metal-containing electron transfer proteins, oxygen transport and activation proteins, bioorganometallic systems such as hydrogenases

and alkyltransferases, and enzymes involved in nitrogen metabolism pathways.

1. Metal ion transport and storage covers a diverse collection of ion channels, ion pumps (e.g. NaKATPase), vacuoles, siderophores, and other proteins and small molecules whose aim is to carefully control the concentration of metal ions in the cell (sometimes referred to as metallohome).

2. Hydrolase enzymes include a diverse collection of proteins that interact with water and substrates. Examples of this class of metalloproteins and carbonic anhydrase, metallophosphatases, and metalloproteinases.

Metal-containing electron transfer proteins are organized into three major classes :

- ion-sulfur proteins such as rubredoxins, ferredoxins, and Rieske proteins
- blue copper proteins
- Cytochromes

These electron transport proteins are complementary to the non-metal electron transporters nicotinamide adenine dinucleotide (NAD) and flavin adenine dinucleotide (FAD).

3. Oxygen transport and activation proteins make extensive use of metals such as iron, copper, and manganese. Heme is utilized by red blood cells in the form of hemoglobin for oxygen transport and is perhaps the most recognized metal system in biology. Other oxygen transport systems include myoglobin, hemocyanin, and hemerythrin. Oxidases and oxygenases are metal systems found throughout nature that take advantage of oxygen to carry out important reactions such as energy generation in cytochrome c oxidase or small molecule oxidation in cytochrome P450 oxidases or methane monooxygenase. Some metalloproteins are designed to protect a biological system from the potentially harmful effects of oxygen and other reactive oxygen-containing molecules such as hydrogen peroxide. These systems include peroxidases, catalases, and superoxide dismutases. A complementary metalloprotein to those that react with oxygen is the oxygen evolving complex present in plants. This system

is part of the complex protein machinery that produces oxygen as plants perform photosynthesis.

4. Bioorganometallic systems such as hydrogenases and methylcobalamin are biological examples of organometallic chemistry.

5. The nitrogen metabolism pathways make extensive use of metals. Nitrogenase is one of the more famous metalloproteins associated with nitrogen metabolism. More recently, the cardiovascular and neuronal importance of nitric oxide has been examined, including the enzyme nitric oxide synthase. (See also: nitrogen assimilation).

6. Metals in medicine is the study of the design and mechanism of action of metal-containing pharmaceuticals, and compounds that interact with endogenous metal ions in enzyme active sites. This diverse field includes the platinum and ruthenium anti-cancer drugs, chelating agents, gold drug chaperones, and gadolinium contrast agents.

Q.33. Discuss the role of calcium in human body.

Ans. Calcium is an essential element in living organism. It plays an important role in the metabolism of nitrogen in some plants where a deficiency of calcium leads to poor absorption of nitrogen. Lack of calcium in plant nutrition leads to a reduction in the number and size of the chloroplasts.

Calcium is the most abundant inorganic element in the higher animals and is located principally in the bones and teeth as apatite, a calcium phosphate mineral. Blood is also a huge reservoir of calcium in animals. Calcium is distributed throughout all tissues where it has special roles in controlling nerve impulse transmission, muscle action, blood action, blood clotting and cell permeability.

Calcium deficiency is exhibited by the onset of rickets, failure of the blood-clotting mechanism, nervous disorder and convulsive muscular contractions. Vitamin D greatly improves the absorbability of calcium ion and the value of this vitamin in treating rickets is based in part on this effect.

Large intakes of calcium lead to excessive calcification and kidney stones.

Q.34. Discuss Biological Role of Magnesium

Ans. Fersman (1934) commented on the relatively unimportant role of magnesium in biochemical processes. The comparatively limited radius of its ions, the stability and relative insolubility of its compounds prevent its taking an active part in the reactions of living matter. On the other hand, we have the statement of Vernadskii that in the plankton film of the ocean, in the ordinary accumulations and more massive growths, the amount of magnesium-containing chlorophyll must reach the order of 10^{-4} per cent by weight, if not higher, so that a small quantity of magnesium, entering into the composition of the chlorophyll-complex of the plankton, ultimately regulates the main part of the oxygenating function of living matter, the creation of free atmospheric oxygen. The material summarized by us likewise affords evidence of the importance of the role of magnesium in biological processes.

All this, however, does not justify sharp differentiation between the biological role of magnesium and its role in biochemical processes. In all probability these processes are conditional to each other, although they are not identical processes.

It is important to note the established and incontestable role of magnesium in many enzymatic processes in both the plant and animals kingdoms.

The antagonistic action between magnesium and calcium, resulting from artificial changes in the ratios of these elements in soil, plants, and animals, can hardly occur under natural conditions, and, conversely, it must be assumed that a liable equilibrium between these elements is always maintained.

The depressing action of magnesium ions on the central nervous system acquires considerable biological significance, since this permits the assumption that these ions in the animal organism may facilitate inhibitory processes in the nerve cell and insure the normal course of catabolic and anabolic processes.

The narcotic and cholinolytic effects of magnesium constitute the basis for the wide therapeutic use of magnesium salts in medical practice.

Q.35. Discuss role of Zinc in Human body.

Ans. Zinc

Biological role

Zinc is an essential element, necessary for sustaining all life. It is estimated that 3000 of the hundreds of thousands of proteins in the human body contain zinc.

Zinc Deficiency

Zinc deficiency in humans is often a result of inadequate intake of zinc, or inadequate absorption of zinc into the body. Signs of Zinc deficiency includes hair loss, skin lesions, diarrhea, wasting of body tissues, and, eventually, death. Eyesight, taste, smell and memory are also connected with zinc and a deficiency in zinc can cause malfunctions of these organs and functions.

Obtaining a sufficient zinc intake during pregnancy and in young children is a very real problem, especially among those who cannot afford a good supply of met and a varied diet. Brain development is stunted by zinc insufficiency in utero and in youth.

There is zinc in semen. As much as half a milligram of zinc will be found in 1 mL of seminal fluid, which explains why males require a higher intake of zinc than do females. Zinc deficiency in males can lead to reduced sperm count and sex drive, but this is probably just a by-product of the general malaise of advanced malnutrition. There is no evidence that zinc supplements enhance male sexuality in males who have adequate general nutrition.

Zinc Toxicity

Even though zinc is almost an essential requirement for a healthy body, too much zinc can be harmful to the human body. Excessive absorption of zinc into the human body can lead to reduced iron function, and impair the immune system. Experiments have also been conducted where the excessive intake of zinc led to nausea and vomiting within 30 minutes of ingestion.

Immune System

According to some sources, taking zinc tablets may provide some immunity against *colds* and flu, although this is disputed. The biological basis of this is that it has been established that the immune system is

impaired by zinc deficiency and so will respond to zinc supplements. The direct effect of zinc (as in lozenges) on bacteria and viruses is also well-established, and has been used since at least 2000 BC, from when zinc salts in palliative salves are documented. However, exactly how to deliver zinc salts against pathogens (germs) without injuring one's own tissues is still being investigated.

Psoriasis

Since Zinc deficiency can cause hair loss, many naturopathic health products and topical creams used to treat psoriasis contain zinc as one of the ingredients.

Q.What is Nitrogen fixation? Describe the process of biological nitrogen fixation and chemical nitrogen fixation.

Ans. Nitrogen fixation is the process by which nitrogen is taken from its relatively inert molecular form (N_2) in the atmosphere and converted into nitrogen compounds (such as ammonia, nitrate and nitrogen dioxide).

Nitrogen fixation is performed naturally by a number of different prokaryotes, including bacteria, actinobacteria, and certain types of anaerobic bacteria. Microorganisms that fix nitrogen are called diazotrophs. Some higher plants, and some animals (termites), have formed associations with diazotrophs. Recently, the role of certain Archaea, particularly some mesophilic Crenarcheota, in nitrogen fixing has been under investigation; some researchers believe these microbes may have a much larger role in the global nitrogen cycle than previously thought.

Nitrogen fixation also occurs as a result of non-biological processes. These include lightning, industrially through the Haber-Bosch Process, and combustion.

Biological nitrogen fixation was discovered by the Dutch microbiologist Martinus Beijerinck.

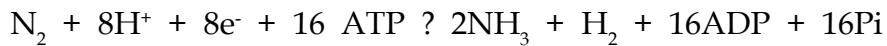
Biological nitrogen fixation

Diagram

Schematic representation of the nitrogen cycle.

Biological Nitrogen Fixation (**BNF**) occurs when atmospheric nitrogen is

converted to ammonia by a pair of bacterial enzymes called nitrogenase. The formula for BNF is :



Although ammonia (NH_3) is the direct product of this reaction, it is quickly protonated into ammonium (NH_4^+). In free-living diazotrophs, the nitrogenase-generated ammonium is assimilated into glutamate through the glutamine synthetase/glutamate synthase pathway.

In most bacteria, the nitrogenase enzymes are very susceptible to destruction by oxygen (and many bacteria cease production of the enzyme in the presence of oxygen). Low oxygen tension is achieved by different bacteria by: living in anaerobic conditions, respiring to draw down oxygen levels, or binding the oxygen with a protein such as Leghemoglobin (also spelt leghaemoglobin).

The best-known plants which contribute to nitrogen fixation in nature, are in the legume family-Fabaceae, which includes such taxa as clover, beans, alfalfa, lupines and peanuts. They contain symbiotic bacteria called rhizobia within nodules in their root systems, producing nitrogen compounds that help the plant to grow and compete with other plants. When the plant dies, the fixed nitrogen is released, making it available to other plants and this helps to fertilize the soil. The great majority of legumes have this association, but a few genera (e.g. *Styphnolobium*) do not. In many traditional and organic farming practices, fields are rotated through various types of crops, which usually includes one consisting mainly or entirely of clover or buck wheat (family Polygonaceae), which were often referred to as "green manure", since the other natural way of adding nitrogen to the soil is via animal waste products. The entire plant is often ploughed back into the field, thus not only adding more nitrogen, but also improving the soil's organic content and volume.

[edit] Non-leguminous nitrogen-fixation plants

Diagram

A sectioned Alder tree root nodule.

A whole Alder tree root nodule.

Although by far the majority of nitrogen-fixing plants are in the legume

family *Fabaceae*, there are a few non-leguminous plants that can also fix nitrogen. These plants, referred to as “actinorhizal plants”, consist of 22 genera of woody shrubs or trees scattered in 8 plant families. The ability to fix nitrogen is not universally present in these families. For instance, of 122 genera in the *Rosaceae*, only 4 genera are capable of fixing nitrogen.

Chemical nitrogen fixation

Nitrogen can also be artificially fixed for use in fertilizer, explosives, or in other products. The most popular method is by the Haber process. This artificial fertilizer production has achieved such scale that it is now the largest source of fixed nitrogen in the Earth’s ecosystem.

The Haber process requires high pressures and very high temperatures and active research is committed to the development of catalyst systems that convert nitrogen to ammonia at ambient temperatures. Many compounds can react with atmospheric nitrogen under ambient conditions (e.g. lithium makes lithium nitride if left exposed), but the products of such reactions are not easily converted into biologically accessible nitrogen sources. After the first dinitrogen complex was discovered in 1965 based on ammonia coordinated to ruthenium ($[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$), research in chemical fixation focused on transition metal complexes. Since that time a large number of transition metal compounds that contain dinitrogen as ligand have been discovered. The dinitrogen ligand can be bound either to a single metal or bridge two (or more) metals. The coordination chemistry of dinitrogen is rich and under intense study. This research may lead to new ways of using dinitrogen in synthesis and on an industrial scale.

The first example of homolytic cleavage of dinitrogen under mild conditions was published in 1995. Two equivalents of a molybdenum complex reacted with one equivalent of dinitrogen, creating a triple bonded MoN complex. Since this triple bonded complex has been used to make nitriles. The first catalytic system converting nitrogen to ammonia at room temperature and 1 atmosphere was discovered in 2003 and is based on another molybdenum compound, a proton source and a strong reducing agent. Unfortunately, the catalytic reduction only undergoes a few turnovers before the catalyst dies.

Diagram

In contrast to the graphic shown above, the major product of this reaction is ammonia (NH_3) and not an ammonium salt ($[\text{NH}_4][\text{X}]$). In fact, approximately 75% of the ammonia produced can be distilled away from the reaction vessel (suggesting the ammonia is not protonated) into a vessel containing HCl as a trap. This method of trapping the NH_3 was doubtlessly chosen because it makes the product easier to handle. Also, note that because only 1 equiv of Cl⁻ anion is available under catalytic conditions (via reduction of the precatalyst molybdenum chloride, shown) therefore it is unlikely that the product ammonium salt would always have this counterion.

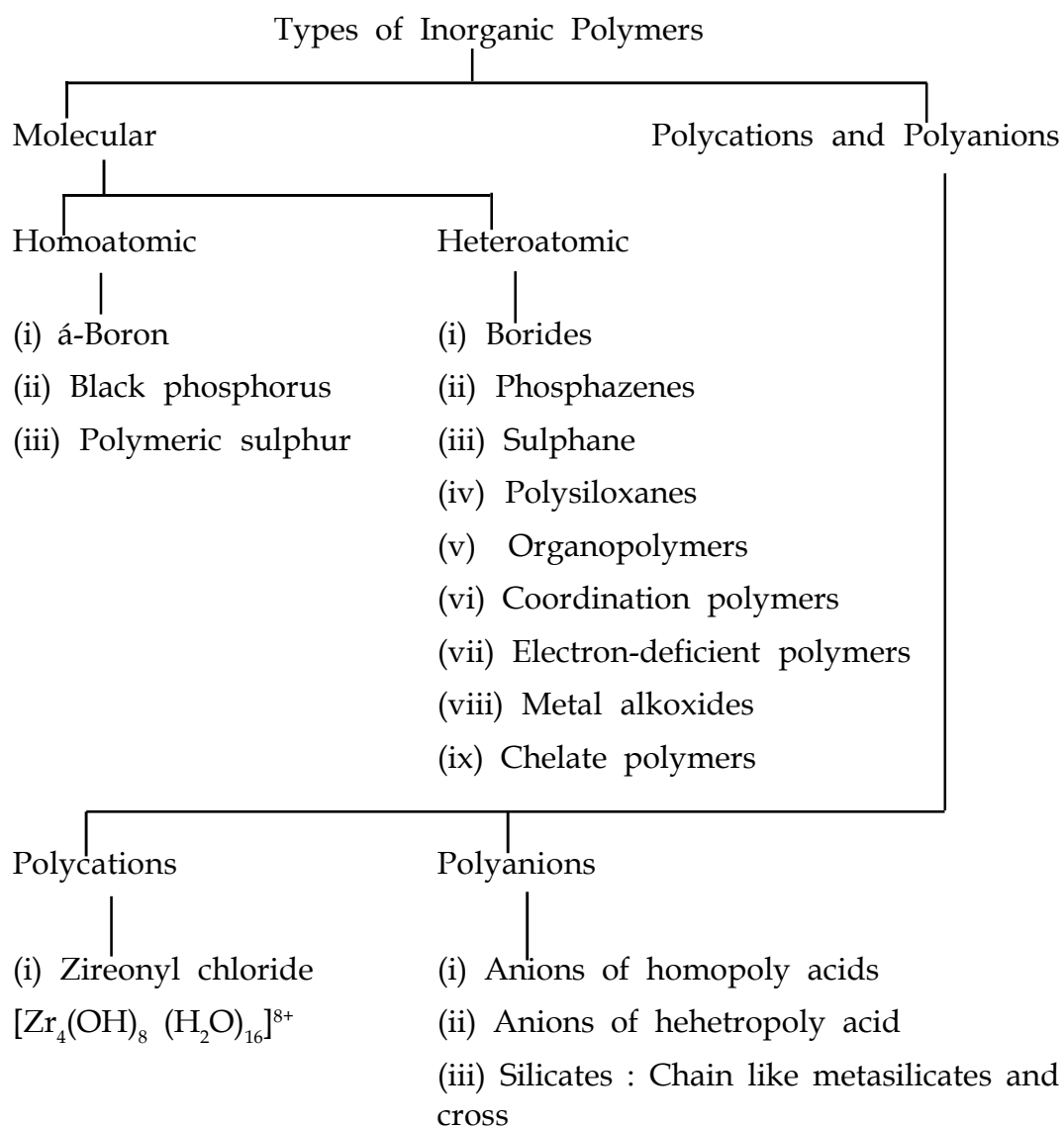
Note also that although the dinitrogen complex is shown in brackets this species can be isolated and characterized. Here the brackets do not indicate that the intermediate is not observed.

Chapter VIII

Silicones and Phosphorenes

Q.38. What are inorganic polymers? Give its classification.

Ans.



linked.

(iv) Feldspars and Zeolites

(v) Borates

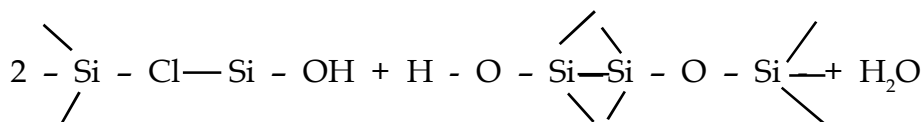
(vi) Condensed phosphates

Inorganic Polymers - The polymeric compound characterized by the presence of a repeating structural unit in the molecule. When such units contain elements other than carbon, joining together to form long chain or ring compounds, then such polymeric compounds are called inorganic polymers.

In this chapter we are concerned with silicones and phosphazenes.

Q. What are silicones? Describe briefly preparation of silicones.

Ans. These are organo-silicon polymers containing Si-O-si linkages, and each silicon atom is attached its one or two organic groups. These are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their polymerisation.



Chlorosilane

Silanol

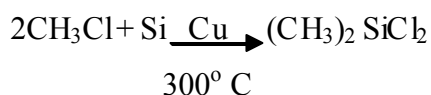
Siloxane

(Hydroxy intermediates)

Preparation of Silicones :

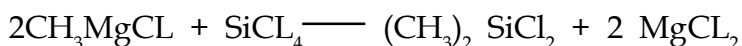
(a) Preparation of alkyl chlorositanes

Raw how's Direct Silicone Process - Methylchlorosilanes are prepared which are of great commercial value.

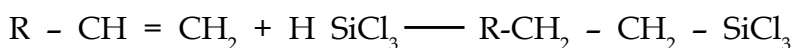


Grignard Method

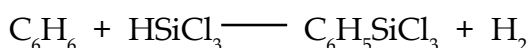
The nature of the product depends upon ratio of Grignard Reagent and SiCl_4 used.



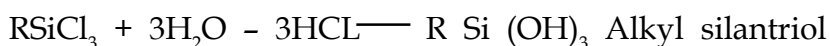
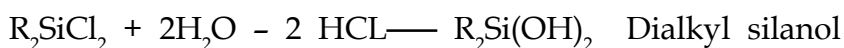
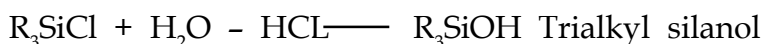
Hydrosilylation of olefins



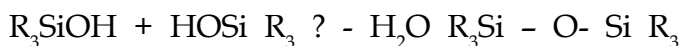
Aromatic Silylation - Preparation of arylsilicon halides are prepared.

**(b) Hydrolysis of Alkylchlorosilanes**

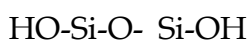
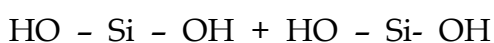
Hydrolysis of alkyl chlorosilanes yield corresponding silanols.

**(c) Condensation of silanols**

Condensation of trialkyl silanol - Gives Dimer



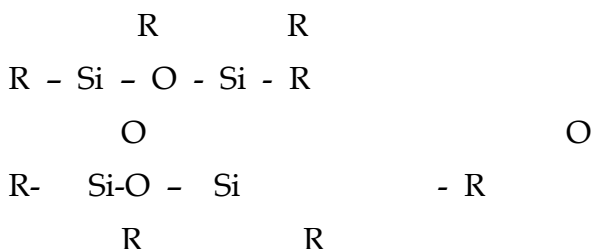
Condensation of dialkyl silandiol - Linear thermoplastic polymer



Condensation of dialkyl silane chlorides under controlled conditions -
Cyclic Polymers

Diagram

Tris cyclo dialkylsilonane



Tetrakisyclo dialkylsiloxane

Q.39. Draw the structure for**(i) Ladder Polymers****(ii) Tri and tetra phosphonitrilic chloride****(iii) Tetraphenyl dichlorotriphosphazene**

(i) "Ladder Polymers" - When Ph SiCl_3 is hydrolysed, the product is a ladder type, cycloliner, stereo regular polymer.

Diagram**(ii) $(\text{NPCL}_2)_3$ Triand tetra phosphonitrilic chloride****Diagram****(iii) Diagram**

Tetraphenyl dichlorotriphosphazene

Q.40. Short Note on Phosphazenes/Phosphonitric Compounds.

Ans. Phosphazenes - Nitrogen and Phosphorus exhibit only a slight tendency to calinate themselves. But together, N and P may bond together to form a large number of long chain cyclic and linear polymers, called phosphazenes or phosphonitrilic compounds.

The phosphazenes are the group of compounds of the composition $(\text{NPX}_2)_n$ where $X = \text{Cl, F, Br, SCN}$ etc. All these compounds are polymeric. Out of these best known are chlorides, $(\text{NPCL}_2)_n$. following homologous

are well known.

Triphosphonitrilic chloride, $(\text{NPCL}_2)_3$

Tetraphosphonitrilic chloride, $(\text{NPCL}_2)_4$

Pentaphosphonitrilic chloride, $(\text{NPCL}_2)_5$

Hexaphosphonitrilic chloride, $(\text{NPCL}_2)_6$

Heptaphosphonitrilic chloride, $(\text{NPCL}_2)_7$

They have interesting properties as :

- (i) Thermally stable and resistant to chemical attack.
- (ii) On heating, they give rubber-like products.
- (iii) It undergoes both electrophilic and nucleophilic substitution.
- (iv) Cyclic tri-phosphonitric compounds have aromatic character.

The End

PPP